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Electronic and Vibronic Spectra of Transition Metal Complexes II

Volume Editor: H. Yersin

With contributions by
T. Azumi, H. B. Gray, W. Humbs,
H. Miki, V. M. Miskowski, H. H. Patterson,
T. Schönherr, J. Strasser, H. Yersin



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Preface

The properties of transition metal compounds have fascinated physicists and chemists for a long time. These compounds have an enormous potential for future applications of solar energy conversion, information storage systems, chemical or biochemical sensors, lowdimensional semiconductors, supramolecular systems, chemical synthesis, etc. Most of these applications are related to the characteristics of the low-lying electronic and vibronic states. In the present volume as well as in its companion volume¹ leading researchers – physicists and chemists – present theoretical as well as experimental approaches towards a deeper understanding of these compounds. Both volumes build a bridge between physicists and chemists by showing how controlled chemical variations can be applied to tune physical properties in a defined way and vice versa, by demonstrating how detailed spectroscopical and quantum mechanical investigations allow the chemical characterization of ground and excited states.

In particular in this volume, an introduction into properties of spin sublevels of metal centered (MC), ligand centered (LC) and metal-to-ligand-charge-transfer (MLCT) states is given by T. Azumi and H. Miki. Further, a modern ligand field theory based on the Angular Overlap Model is presented by T. Schönherr. In the contribution by V. M. Miskowski and H. B. Gray it is shown how to characterize bi-nuclear Os(III) complexes from polarized single-crystal electronic spectra and magnetic susceptibility measurements. In experimental case studies H. H. Patterson discusses selected d-electron systems in a variety of environments such as neat and mixed crystals as well as on surfaces. On the basis of highly frequency-resolved and time-resolved spectra, H. Yersin, W. Humbs, and J. Strasser investigate and characterize a series of metal bipyridine compounds. Consequences of adjustable metal d-orbital involvement, which leads to variable spin-orbit coupling, zero-field splittings, and spin-lattice relaxation processes in the time domain, are treated. Further, several specific effects such as magnetic-field induced tunability of Herzberg-Teller to Franck-Condon activity, chromophore-matrix interactions, and spectroscopic fingerprints of localization/delocalization processes in the excited states are also studied.

A series of compounds is investigated in detail, for example $[\text{Rh}(\text{phen})_3]^{3+}$, *cis*- $[\text{Rh}(\text{CN})_2(\text{phen})_2]^+$, $[\text{Pt}(\text{bpy})_2]^{2+}$, $[\text{Ru}(\text{bpy})_3]^{2+}$, $[\text{Ru}(\text{i-biq})_2(\text{bpy})]^{2+}$, $[\text{Os}(\text{bpy})_3]^{2+}$,

¹ The first volume, *Topics in Current Chemistry 171 Electronic and Vibronic Spectra of Transitions Metal Complexes I* (ed H. Yersin), appeared in 1994.

$[\text{Cr}(\text{bpy})_3]^{3+}$, $[\text{Cr}(\text{urea})_6]^{3+}$, $[\text{Cr}(\text{acac})_3]$, Cr(III) and Cr(IV) doped oxide lattices, $[\text{MnF}_6]^{2-}$, $[\text{ReBr}_6]^{2-}$, $[\text{OsCl}_6]^{2-}$, bi-nuclear Os(III) complexes, Mo(II) chloride clusters, and two-dimensional layers of $[\text{Au}(\text{CN})_2]^-$ complexes.

I hope that the contributions in the present volume will not only stimulate the interaction between the different fields of basic research in chemistry and physics but will also open pathways for new applications.

Regensburg, May 1997

Hartmut Yersin

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Spectroscopy of the Spin Sublevels of Transition Metal Complexes

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The theoretical and experimental aspects of the spin sublevels of transition metal complexes are briefly reviewed. First, the complexes with organic ligands are discussed. For metal-localized dd states and metal-to-ligand charge transfer $d\pi^*$ states, the splitting among spin sublevels is mainly governed by the spin-orbit coupling, and the magnitude of the splitting is of the order of $10-100\text{ cm}^{-1}$. For ligand-localized triplet $\pi\pi^*$ states, the splitting is mainly governed by the spin-spin coupling, and the magnitude of the splitting is of the order of 0.1 cm^{-1} . Theoretical evaluation of the radiative rate constants for the individual spin sublevels is discussed, and is compared with experimental data. Finally, the spin sublevels of metal clusters are discussed.

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1

Introduction

When an eigenstate of the electronic Hamiltonian of a molecular system is split into several states by a perturbation involving spin, the set of split levels are called spin sublevels. In this paper we focus attention on spin sublevels in the zero external magnetic field. Thus, the splitting of a level by the Zeeman effect is not considered.

For atoms, spin sublevels have been well studied. One of the typical examples is the splitting of sodium D line, the emission from the $3p$ state to the $2s$ state. In the $3p$ state, the orbital part is three-fold degenerate and the spin part is doubly degenerate, and thus the total degeneracy is six. This six-fold degeneracy is partially lifted by spin-orbit interaction. The state is split into two sublevels one corresponding to $j = 3/2$ and the other corresponding to $j = 1/2$. This type of the splitting of atomic levels is well discussed in standard textbooks [1] of atomic spectroscopy and of quantum chemistry, and thus there is nothing to discuss here any further.

The spin sublevels for organic molecules in their triplet excited states have been well studied by ESR and ODMR (optical detection of magnetic resonance) spectroscopy.

However, for metal complexes, research on spin sublevels is rather scarce. In this paper we try to review the spectroscopy of the spin sublevels for metal complexes.

2

Experimental Methods to Obtain Energies and Other Spectroscopic Properties of the Spin Sublevels

We briefly summarize various experimental methods to determine the sublevel properties.

2.1

Direct Spectroscopic Observation

In atomic spectroscopy, to experimentally observe the spin-sublevel structures is quite easy. However, for large organic molecules and for metal complexes, to detect the splitting directly in the luminescence is difficult because of a number of reasons.

In order for the sublevel luminescence to be observed, the population of the individual sublevels should be sufficiently large. Thus, the energy separation among sublevels should be of the order of kT or less. However, even if the temperature is of the order of kT , the inhomogeneous broadening still may prevent the resolution of the spectrum, and thus the bands from different sublevels are

hard to detect separately. An ingenious way to avoid this inhomogeneous broadening is the site-selection spectroscopy using narrow band laser excitation. In this method only a few sites are selected by narrow band excitation. The method is schematically illustrated in Fig. 1. In the case of a triplet state, three sites are excited. If the relaxation among the sublevels is suppressed, we would observe only one emission line. If, on the other hand, the relaxation among the sublevels exists, each excited site emits three lines, and thus we should observe total of $3 \times 3 = 9$ lines, among which three lines are at the same energy. Thus, we have 7 lines. The sublevel properties such as energies and relative radiative rate constants can be obtained by analyzing the observed spectrum. Various modifications of this spectroscopy have been made, and they are discussed in a number of review articles [2–6].

2.2

Microwave Resonance in Zero Magnetic Field

If the separation among the sublevels is in the range of microwave frequency, sublevel properties can be obtained by observing the effect of microwave resonance on the emission from this state. The zero-field splitting is of the order of microwave frequency for most of $^3\pi\pi^*$ states. Thus, the sublevel properties can be obtained by analyzing the effect of microwave resonance on the phosphorescence intensity. The method is called phosphorescence-microwave double resonance (PMDR) or optical detection of magnetic resonance (ODMR).

The information that can be obtained from this method is as follows: a) zero-field splitting, b) decay rate constants for individual sublevels, c) relative radia-

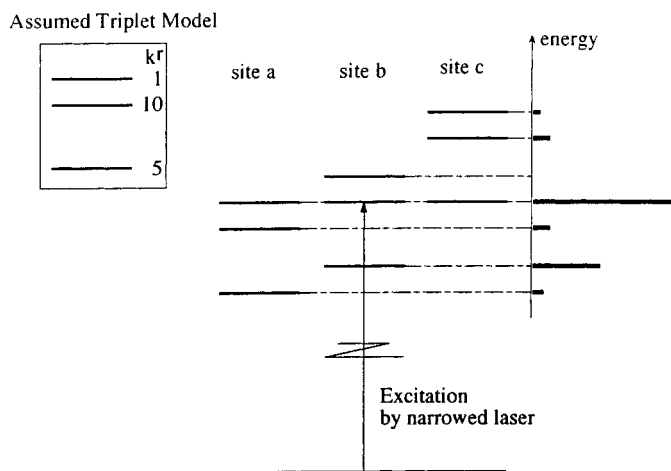


Fig. 1. Schematic illustration of the direct observation of the sublevel phosphorescence in a zero external magnetic field. In this example, the relative radiative rate constants of the sublevels are set 1:10:5. Three different sites are excited by a narrow laser band, and total of nine bands (of which there appear at the same location) are observed in the manner illustrated in the figure

tive rate constants for individual sublevels, and d) relative populating rate constants for individual sublevels, and e) the phosphorescence spectra for individual sublevels [7–8].

The method has been discussed in a number of textbooks and review articles [9–13], and therefore we are not going to discuss it here any further.

2.3

ESR Spectroscopy

The sublevel properties of triple excited states of organic molecules have been studied extensively also by ESR spectroscopy. In addition to the ordinary steady-state ESR spectroscopy, time-resolved ESR and optical-detection ESR spectroscopy have also been applied.

The information that can be obtained by the ESR spectroscopy is as follows: a) zero-field splitting, and b) relative populating rate constants for individual sublevels.

Since ESR spectroscopy has been repeatedly discussed in a number of textbooks [14–16], we are not going to discuss it here any further.

2.4

Temperature Dependence of Lifetime and Intensity of Luminescence

If the zero-field splitting is larger than the microwave frequency in such cases as ^3dd and $^3d\pi^*$ excited states of transition metal complexes (vide supra), microwave resonance method cannot be applied. For example, if the separation among sublevels is of the order of 10 to 100 cm^{-1} , it is practically impossible to find electromagnetic radiation sources that can continuously cover such an energy region. In this case, one can obtain the sublevel properties indirectly by observing the temperature dependence of the lifetime and of the intensity of the luminescence.

This method can be applied when all the sublevels are in thermal equilibrium. In this case the apparent decay rate constant k of the luminescence is expressed as follows:

$$k = \frac{\sum_i g_i k_i \exp\left(-\frac{E_i}{kT}\right)}{\sum_i g_i \exp\left(-\frac{E_i}{kT}\right)} \quad (1)$$

Where E_i and g_i are the energy and the degeneracy of the i -th sublevel, and k_i is the rate constant associated with the i -th sublevel. Similarly, the intensity I of the luminescence is expressed as follows:

$$I = \frac{\sum_i g_i k_i \exp\left(-\frac{E_i}{kT}\right)}{\sum_i g_i \exp\left(-\frac{E_i}{kT}\right)} \quad (2)$$

where k_i' is the radiative rate constant for the i -th sublevel. Therefore, if the lifetime and the intensity of the luminescence are experimentally obtained at various temperatures, one can simulate the experimental data in terms of Eq. (1) and (2) and determine a) sublevel energies (E_i), b) decay rate constants (k_i) for individual sublevels, c) relative radiative rate constants (k_i') for individual sublevels, and e) degeneracy (g_i) of the sublevels. Thus, the information one can obtain is quite similar to the information obtained by the ODMR method; however, one must note the possibility that a completely erroneous set of parameters may lead to similar results in the simulation.

3

Theory and Experimental Results

In the following, we discuss the theory to obtain the sublevels and briefly review the relevant experimental results for some selected classes of transition metal complexes. We first discuss the transition metal complexes having organic ligands. We then extend the discussion to some metal clusters.

The excited states of transition metal complex having organic ligands are classified into three classes: 1) metal-localized dd states, 2) ligand-localized $\pi\pi^*$ states, and 3) metal-to-ligand charge-transfer $d\pi^*$ states. The features of the spin sublevels are vastly different depending on the class of the states, and therefore, we will discuss spin sublevels for these classes of excited states separately.

As will be discussed in detail below, the Hamiltonian that is responsible for the splitting is either the spin-orbit interaction or the spin-spin interaction. When the state in question involves degenerate p or d atomic orbitals, the spin-orbit interaction plays a major role in determining the splitting. If the state in question does not involve any orbitally degenerate p or d atomic orbitals, the spin-orbit interaction is effective only in the second order, and hence, the spin-spin interaction may be equally important depending on the kind of metals and on the energy difference among orbitals.

In the case of metal clusters, the d or p atomic orbitals of various metal ions are delocalized over the whole clusters, and therefore, we need to apply an entirely different theory.

3.1

Spin Sublevels of dd States

We first discuss the dd states that are localized on the central metal ion. Since the electronic wavefunctions are localized on the central metal ion, the wavefunctions and energies may be obtained in a manner essentially identical to the atomic case. However, the following differences should be noted. First, because of the loss of the central symmetric nature, quantum numbers such as l and j are no longer good quantum numbers. Therefore, characterization of states in terms of these quantum numbers is no longer possible. For example, in an atomic case, sublevels are very simply described in terms of the quantum number j , and the energy separation is governed by the Lande interval rule [1]; however, such a rule does not exist for metal-localized states of transition metal complexes.

Second, due to the crystal field the five-fold degeneracy of the d atomic orbital is partially lifted, and this symmetry breakdown results in a rather large effect in the splitting of the levels.

Even though the quantum numbers l and j lose their meaning in the case of the metal complex, symmetry properties based on group theory can be used to classify the states and to simplify the theory. Theoretical treatment of dd states may be slightly different depending on the symmetry and the number of d -electrons. In the following, we restrict ourselves to the symmetry of O. We will illustrate the theories for systems of one d -electron and of six d -electrons.

3.1.1

Spin Sublevels of a System of a Single d Electron in a Cubic Field

We start by illustrating a very simple system of one d -electron [17–18]. In the atomic case, the d -electron state is split into two states, one corresponding to $j = 5/2$ and the other corresponding to $j = 3/2$, the energy separation being $3/2 \xi_{nd}$. If the electron is in the cubic field, the manner of the splitting is quite different as discussed below.

The total Hamiltonian is expressed as follows:

$$H = H_0 + V_C + H_{SO} \quad (3)$$

where V_C is the crystal field potential, and H_{SO} is the spin-orbit interaction defined as follows:

$$\begin{aligned} H_{SO} &= \xi(r) \ell \cdot S \\ &= \xi(r) \left[\ell_z S_z + \frac{1}{2} \ell_+ S_- + \frac{1}{2} \ell_- S_+ \right] \end{aligned} \quad (4)$$

where

$$\xi(r) = \frac{1}{4\pi\epsilon_0} \frac{Ze^2}{2m^2c^2} \frac{1}{r^3} \quad (5)$$

The energies and eigenstates of the Hamiltonian (3) are obtained by diagonalizing the Hamiltonian with respect to a set of basis functions. As the basis function, one could use the eigenfunction of $H_0 + V_C$, or alternately, one could use the eigenfunction of $H_0 + H_{SO}$. As long as calculations are carried out properly, the final results should be independent of the choice of the basis function. Therefore, we here adopt the former choice.

The energies and wavefunctions of $H_0 + V_C$ are expressed as follows:

T_2 states: (Energy = 0)

$$\xi = d_{yz} = \sqrt{\frac{1}{2}} i(d_1 + d_{-1}) \quad (6a)$$

$$\eta = d_{zx} = -\sqrt{\frac{1}{2}} (d_1 - d_{-1}) \quad (6b)$$

$$\xi = d_{xy} = \sqrt{\frac{1}{2}} i(d_2 - d_{-2}) \quad (6c)$$

E states: (Energy = Δ)

$$\theta = d_{z^2} = d_0 \quad (7a)$$

$$\varepsilon = d_{x^2-y^2} = -\sqrt{\frac{1}{2}}(d_{+2} - d_{-2}) \quad (7b)$$

where d_2, d_1, d_0, d_{-1} , and d_{-2} are the atomic d functions defined as

$$d_m = R_{n2} Y_{2m}(\theta, \phi) \quad (m = 2, 1, 0, -1, -2) \quad (8)$$

The expression of d -orbitals by the notations of $\xi, \eta, \zeta, \varepsilon$, and θ is due to Sugano et al. [18]. In the point group of O, the E state is located at $\Delta = 10 Dq$ above the T_2 state. We set the T_2 state as the origin of the energy scale.

The matrix elements of the Hamiltonian with respect to the above basis functions are expressed as follows:

$$H = \frac{\zeta_{nd}}{2} \begin{bmatrix} \xi\alpha & \xi\beta & \eta\alpha & \eta\beta & \zeta\alpha & \zeta\beta & \theta\alpha & \theta\beta & \varepsilon\alpha & \varepsilon\beta \\ \begin{bmatrix} 0 & 0 & i & 0 & 0 & -1 & 0 & -\sqrt{3}i & 0 & -i \\ 0 & 0 & 0 & -i & 1 & 0 & -\sqrt{3}i & 0 & -i & 0 \\ -i & 0 & 0 & 0 & 0 & i & 0 & \sqrt{3} & 0 & -1 \\ 0 & i & 0 & 0 & i & 0 & -\sqrt{3} & 0 & 1 & 0 \\ 0 & 1 & 0 & -i & 0 & 0 & 0 & 0 & 2i & 0 \\ -1 & 0 & -i & 0 & 0 & 0 & 0 & 0 & 0 & -2i \\ 0 & \sqrt{3}i & 0 & -\sqrt{3} & 0 & 0 & \Delta' & 0 & 0 & 0 \\ \sqrt{3}i & 0 & \sqrt{3} & 0 & 0 & 0 & 0 & \Delta' & 0 & 0 \\ 0 & i & 0 & 1 & -2i & 0 & 0 & 0 & \Delta' & 0 \\ i & 0 & -1 & 0 & 0 & 2i & 0 & 0 & 0 & \Delta' \end{bmatrix} \end{bmatrix} \quad (9)$$

where

$$\Delta' = \frac{\Delta}{\left(\frac{\zeta_{nd}}{2}\right)} \quad (10)$$

and ζ_{nd} is the spin-orbit coupling parameter for the nd state defined as follows:

$$\begin{aligned} \zeta_{nd} &= \hbar^2 \langle R_{n2}(r) | \xi(r) | R_{n2}(r) \rangle \\ &= \hbar^2 \int_0^\infty R_{n2}(r) \xi(r) R_{n2}(r) r^2 dr \\ &= \frac{\hbar^2}{4\pi\epsilon_0} \frac{Ze^2}{2m_e^2 c^2} \int_0^\infty R_{n2}(r) \frac{1}{r^3} R_{n2}(r) r^2 dr \end{aligned} \quad (11)$$

How can one diagonalize the ten-dimensional matrix shown in Eq. (9)? It appears formidable to analytically diagonalize the matrix. One could, of course, numerically diagonalize the matrix after substituting the specific Δ value. By numerical diagonalization, however, the physical meaning of the results is less clear, and if possible we wish to obtain analytical solutions. We want to emphasize that the whole matrix can be analytically diagonalized perfectly by using group theory. Before making the complete treatment, we will qualitatively analyze the problem. Since we are going to discuss problems involving spin, we need to use the double group instead of the ordinary single-valued group. The double group for O is denoted as O'. The character table for O' is shown in Table 1. A variety of notations for the representations exist [17, 19, 20]. In Table 1, three different versions of the notations are shown. In the following we will use the notations adopted by Herzberg [19].

We first obtain the representations of the ten basis functions. The spatial part of the wavefunctions is of course either T_2 or E . The spin wavefunctions α and β belong to the degenerate representation $E_{1/2}$. Thus the total (space $\times$ spin) wavefunctions for the T_2 states are

$$T_2 \times E_{1/2} = E_{5/2} + G_{3/2} \quad (12)$$

and those for the E states are

$$E \times E_{1/2} = G_{3/2} \quad (13)$$

Therefore, the states should be expressed schematically in a manner shown in Fig. 2. In this figure, the energy order of $E_{5/2}$ and $G_{3/2}$ coming from T_2 is unknown from the group theory alone. As is shown in Fig. 2, ten basis functions are classified into two four-fold degenerate $G_{3/2}$ representations and one doubly degenerate $E_{5/2}$ representation. Once we know the representations, the next step we should take is to determine the wavefunctions that are the bases of the irreducible representation of the O' double group. This can be easily done by applying the projection operator to any one of the basis functions. To do so, we need

Table 1. Character table for the O' double group

Representation			E	R	$4C_3$	$4C_3^2$	$3C_2$	$6C_2'$	$3C_4$	$3C_4^3$
					$4C_3^2R$	$4C_3R$	$3C_2R$	$6C_2R$	$3C_4^3R$	$3C_4R$
(a)	(b)	(c)								
A_1	A_1	A'_1	1	1	1	1	1	1	1	1
A_2	A_2	A'_2	1	1	1	1	1	-1	-1	-1
E	E	E'_1	2	2	-1	-1	2	0	0	0
T_1	T_1	T'_1	3	3	0	0	-1	-1	1	1
T_2	T_2	T'_2	3	3	0	0	-1	1	-1	-1
$E_{1/2}$	E'	E'_2	2	-2	1	-1	0	0	$\sqrt{2}$	$-\sqrt{2}$
$E_{5/2}$	E''	E'_3	2	-2	1	-1	0	0	$-\sqrt{2}$	$\sqrt{2}$
$G_{3/2}$	U'	G'	4	-4	-1	1	0	0	0	0

Representations adopted by (a) Herzberg [19], (b) Griffith [20], (c) Ballhausen [17].

to know the effect of the symmetry operations on the spatial wavefunctions ξ , η , ζ , θ and ε , and on the spin wavefunctions α and β .

The effect of symmetry operations on the spatial wavefunctions can be obtained without any difficulty. To manipulate the effect of the symmetry operations on the spin wavefunctions, on the other hand, requires rather tedious procedures. The spin functions α and β are transformed by rotation through an angle ϕ around an axis whose direction cosines are λ , μ and ν in the following manner [21]:

$$C_\phi(\lambda\mu\nu)[\alpha\beta] = [\alpha\beta] \begin{bmatrix} \cos \frac{\phi}{2} - i\nu \sin \frac{\phi}{2} & -\mu \sin \frac{\phi}{2} - i\lambda \sin \frac{\phi}{2} \\ \mu \sin \frac{\phi}{2} - i\lambda \sin \frac{\phi}{2} & \cos \frac{\phi}{2} - i\nu \sin \frac{\phi}{2} \end{bmatrix} \quad (14)$$

Even though the equation is of a simple form, to obtain the transformation properties of α and β for all the 48 symmetry operations is quite tedious. In Table 2 we summarize the transformation properties of α and β together with those of ξ , η , and ζ . In this table $C_3(1\bar{1}1)$, for example, is the rotation by $2\pi/3$ around the axis connecting between the points (0, 0, 0) and (1, -1, 1).

Once the transformation properties are given, one can easily determine the wavefunctions that are the bases of the irreducible representations of the O' group by the use of the projection operator method.

The wavefunctions of the $E_{5/2}$ representation are as follows:

$$\begin{aligned} \varphi_1(E_{5/2}) &= -\sqrt{\frac{1}{3}} (\xi\alpha - i\eta\alpha - \xi\beta) \\ \varphi_2(E_{5/2}) &= -\sqrt{\frac{1}{3}} (\xi\beta - i\eta\beta - \xi\alpha) \end{aligned} \quad (15)$$

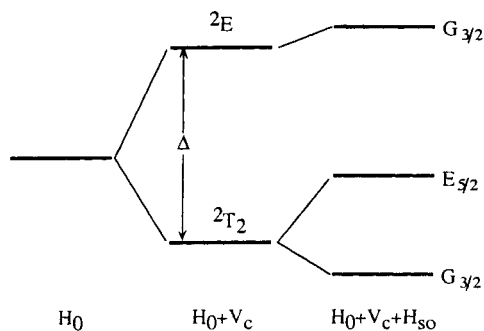


Fig. 2. Schematic representation of the splitting of the energy levels for a system of one d -electron in the point group of O'

Table 2. Transformation of ξ , η , and ζ d -orbitals and α and β spin functions in the O' point group. See the text for the notations for symmetry operations

G	$G\xi$	$G\eta$	$G\zeta$	$G\alpha$	$G\beta$
E	ξ	η	ζ	α	β
R	ξ	η	ζ	$-\alpha$	$-\beta$
$C_3(111)$	η	ζ	ξ	$\frac{1-i}{2}\alpha + \frac{1-i}{2}\beta$	$-\frac{1+i}{2}\alpha + \frac{1+i}{2}\beta$
$C_3(111)^2R$	ζ	ξ	η	$\frac{1+i}{2}\alpha - \frac{1-i}{2}\beta$	$\frac{1+i}{2}\alpha + \frac{1-i}{2}\beta$
$C_3(111)^2$	ζ	ξ	η	$-\frac{1+i}{2}\alpha + \frac{1-i}{2}\beta$	$-\frac{1+i}{2}\alpha - \frac{1-i}{2}\beta$
$C_3(111)R$	η	ζ	ξ	$-\frac{1-i}{2}\alpha - \frac{1-i}{2}\beta$	$-\frac{1+i}{2}\alpha - \frac{1+i}{2}\beta$
$C_3(11\bar{1})R$	$-\zeta$	ξ	$-\eta$	$\frac{1+i}{2}\alpha + \frac{1-i}{2}\beta$	$-\frac{1+i}{2}\alpha + \frac{1-i}{2}\beta$
$C_3(11\bar{1})^2R$	η	$-\zeta$	$-\xi$	$\frac{1-i}{2}\alpha - \frac{1-i}{2}\beta$	$\frac{1+i}{2}\alpha + \frac{1+i}{2}\beta$
$C_3(11\bar{1})^2$	η	$-\zeta$	$-\xi$	$-\frac{1-i}{2}\alpha + \frac{1-i}{2}\beta$	$-\frac{1+i}{2}\alpha - \frac{1+i}{2}\beta$
$C_3(11\bar{1})R$	$-\zeta$	ξ	$-\eta$	$-\frac{1+i}{2}\alpha - \frac{1-i}{2}\beta$	$\frac{1+i}{2}\alpha - \frac{1-i}{2}\beta$
$C_3(1\bar{1}1)$	ζ	$-\xi$	$-\eta$	$\frac{1-i}{2}\alpha - \frac{1+i}{2}\beta$	$\frac{1-i}{2}\alpha + \frac{1+i}{2}\beta$
$C_3(1\bar{1}1)^2R$	$-\eta$	$-\zeta$	ξ	$\frac{1+i}{2}\alpha + \frac{1+i}{2}\beta$	$-\frac{1-i}{2}\alpha + \frac{1-i}{2}\beta$
$C_3(1\bar{1}1)^2$	$-\eta$	$-\zeta$	ξ	$-\frac{1+i}{2}\alpha - \frac{1+i}{2}\beta$	$\frac{1-i}{2}\alpha - \frac{1-i}{2}\beta$
$C_3(1\bar{1}1)R$	ζ	$-\xi$	$-\eta$	$-\frac{1-i}{2}\alpha + \frac{1+i}{2}\beta$	$-\frac{1-i}{2}\alpha - \frac{1+i}{2}\beta$
$C_3(\bar{1}11)$	$-\zeta$	$-\xi$	η	$\frac{1-i}{2}\alpha + \frac{1+i}{2}\beta$	$-\frac{1-i}{2}\alpha + \frac{1+i}{2}\beta$
$C_3(\bar{1}11)^2R$	$-\eta$	ζ	$-\xi$	$\frac{1+i}{2}\alpha - \frac{1+i}{2}\beta$	$\frac{1-i}{2}\alpha + \frac{1-i}{2}\beta$
$C_3(\bar{1}11)^2$	$-\eta$	ζ	$-\xi$	$-\frac{1+i}{2}\alpha + \frac{1+i}{2}\beta$	$-\frac{1-i}{2}\alpha - \frac{1-i}{2}\beta$
$C_3(\bar{1}11)R$	$-\zeta$	$-\xi$	η	$-\frac{1-i}{2}\alpha - \frac{1+i}{2}\beta$	$-\frac{1+i}{2}\alpha - \frac{1+i}{2}\beta$
$C_2(x)$	ξ	$-\eta$	$-\zeta$	$-i\beta$	$-i\alpha$
$C_2(x)R$	ξ	$-\eta$	$-\zeta$	$i\beta$	$i\alpha$
$C_2(y)$	$-\xi$	η	$-\zeta$	β	$-\alpha$
$C_2(y)R$	$-\xi$	η	$-\zeta$	$-\beta$	α
$C_2(z)$	$-\xi$	$-\eta$	ζ	$-i\alpha$	$i\beta$
$C_2(z)R$	$-\xi$	$-\eta$	ζ	$i\alpha$	$-i\beta$
$C_2'(011)$	ξ	$-\zeta$	$-\eta$	$-\sqrt{\frac{1}{2}}i\alpha + \sqrt{\frac{1}{2}}\beta$	$-\sqrt{\frac{1}{2}}\alpha + \sqrt{\frac{1}{2}}i\beta$
$C_2''(011)R$	ξ	$-\zeta$	$-\eta$	$\sqrt{\frac{1}{2}}i\alpha - \sqrt{\frac{1}{2}}\beta$	$\sqrt{\frac{1}{2}}\alpha - \sqrt{\frac{1}{2}}i\beta$

Table 2. (continued)

G	$G\xi$	$G\eta$	$G\zeta$	$G\alpha$	$G\beta$
$C'_2(01\bar{1})$	ξ	ζ	η	$\sqrt{\frac{1}{2}}i\alpha + \sqrt{\frac{1}{2}}\beta$	$-\sqrt{\frac{1}{2}}\alpha - \sqrt{\frac{1}{2}}i\beta$
$C'_2(01\bar{1})R$	ξ	ζ	η	$-\sqrt{\frac{1}{2}}i\alpha - \sqrt{\frac{1}{2}}\beta$	$\sqrt{\frac{1}{2}}i\alpha + \sqrt{\frac{1}{2}}i\beta$
$C'_2((101)$	$-\zeta$	η	$-\xi$	$-\sqrt{\frac{1}{2}}i\alpha - \sqrt{\frac{1}{2}}i\beta$	$-\sqrt{\frac{1}{2}}i\alpha + \sqrt{\frac{1}{2}}i\beta$
$C'_2(101)R$	$-\zeta$	η	$-\xi$	$\sqrt{\frac{1}{2}}i\alpha + \sqrt{\frac{1}{2}}i\beta$	$\sqrt{\frac{1}{2}}i\alpha - \sqrt{\frac{1}{2}}i\beta$
$C'_2(10\bar{1})$	ζ	η	ξ	$\sqrt{\frac{1}{2}}i\alpha - \sqrt{\frac{1}{2}}i\beta$	$-\sqrt{\frac{1}{2}}i\alpha - \sqrt{\frac{1}{2}}i\beta$
$C'_2(10\bar{1})R$	ζ	η	ξ	$-\sqrt{\frac{1}{2}}i\alpha + \sqrt{\frac{1}{2}}i\beta$	$\sqrt{\frac{1}{2}}i\alpha + \sqrt{\frac{1}{2}}i\beta$
$C'_2(110)$	$-\eta$	$-\xi$	ζ	$\sqrt{\frac{1}{2}}(1-i)\beta$	$-\sqrt{\frac{1}{2}}(1+i)\alpha$
$C'_2(110)R$	$-\eta$	$-\xi$	ζ	$-\sqrt{\frac{1}{2}}(1-i)\beta$	$\sqrt{\frac{1}{2}}(1+i)\alpha$
$C'_2(1\bar{1}0)$	η	ξ	ζ	$\sqrt{\frac{1}{2}}(1+i)\beta$	$-\sqrt{\frac{1}{2}}(1-i)\alpha$
$C'_2(1\bar{1}0)R$	η	ξ	ζ	$-\sqrt{\frac{1}{2}}(1+i)\beta$	$\sqrt{\frac{1}{2}}(1-i)\alpha$
$C_4(x)$	$-\xi$	ζ	$-\eta$	$\sqrt{\frac{1}{2}}\alpha - \sqrt{\frac{1}{2}}i\beta$	$-\sqrt{\frac{1}{2}}i\alpha + \sqrt{\frac{1}{2}}\beta$
$C_4^3(x)R$	$-\xi$	$-\zeta$	$-\eta$	$\sqrt{\frac{1}{2}}\alpha + \sqrt{\frac{1}{2}}i\beta$	$\sqrt{\frac{1}{2}}i\alpha + \sqrt{\frac{1}{2}}\beta$
$C_4^3(x)$	ξ	$-\eta$	$-\eta$	$-\sqrt{\frac{1}{2}}\alpha - \sqrt{\frac{1}{2}}i\beta$	$-\sqrt{\frac{1}{2}}i\alpha - \sqrt{\frac{1}{2}}\beta$
$C_4(x)R$	$-\xi$	$-\eta$	$-\eta$	$-\sqrt{\frac{1}{2}}\alpha + \sqrt{\frac{1}{2}}i\beta$	$\sqrt{\frac{1}{2}}i\alpha - \sqrt{\frac{1}{2}}\beta$
$C_4(y)$	$-\xi$	$-\eta$	$-\xi$	$\sqrt{\frac{1}{2}}\alpha + \sqrt{\frac{1}{2}}\beta$	$-\sqrt{\frac{1}{2}}\alpha + \sqrt{\frac{1}{2}}\beta$
$C_4^3(y)R$	ξ	$-\eta$	ξ	$\sqrt{\frac{1}{2}}\alpha - \sqrt{\frac{1}{2}}\beta$	$\sqrt{\frac{1}{2}}\alpha + \sqrt{\frac{1}{2}}\beta$
$C_4^3(y)$	ξ	$-\zeta$	ξ	$-\sqrt{\frac{1}{2}}\alpha + \sqrt{\frac{1}{2}}\beta$	$-\sqrt{\frac{1}{2}}\alpha - \sqrt{\frac{1}{2}}\beta$
$C_4(y)R$	ξ	$-\zeta$	$-\xi$	$-\sqrt{\frac{1}{2}}\alpha - \sqrt{\frac{1}{2}}\beta$	$\sqrt{\frac{1}{2}}\alpha - \sqrt{\frac{1}{2}}\beta$

Table 2. (continued)

G	$G\xi$	$G\eta$	$G\zeta$	$G\alpha$	$G\beta$
$C_4(z)$	$-\eta$	ξ	$-\zeta$	$\sqrt{\frac{1}{2}}(1-i)\alpha$	$\sqrt{\frac{1}{2}}(1+i)\beta$
$C_4^3(y)R$	η	$-\xi$	$-\zeta$	$\sqrt{\frac{1}{2}}(1+i)\alpha$	$\sqrt{\frac{1}{2}}(1-i)\beta$
$C_4^3(z)$	η	$-\xi$	$-\zeta$	$-\sqrt{\frac{1}{2}}(1+i)\alpha$	$-\sqrt{\frac{1}{2}}(1-i)\beta$
$C_4(z)R$	η	ξ	$-\zeta$	$-\sqrt{\frac{1}{2}}(1-i)\alpha$	$-\sqrt{\frac{1}{2}}(1+i)\beta$

The two wavefunctions shown above are orthonormal to each other. They are further diagonal with respect to the total Hamiltonian (3). Thus, the energy of the double degenerate $E_{5/2}$ state is

$$E(E_{5/2}) = \xi_{nd} \quad (16)$$

As for the wavefunctions of the $G_{3/2}$ representation, there are two sets of 4-fold degenerate wavefunctions corresponding to the spatial wavefunctions of ${}^2T_2$ and ${}^2E$. The wavefunctions that correspond to the ${}^2E$ spatial wavefunctions are as follows:

$$\begin{aligned}
 \varphi_1(G_{3/2}) &= \sqrt{\frac{1}{2}}(\xi\alpha + i\eta\alpha) \\
 \varphi_2(G_{3/2}) &= \sqrt{\frac{1}{6}}(\xi\alpha + i\eta\alpha + 2\xi\beta) \\
 \varphi_3(G_{3/2}) &= \sqrt{\frac{1}{2}}(\xi\beta - i\eta\beta) \\
 \varphi_4(G_{3/2}) &= \sqrt{\frac{1}{6}}(\xi\beta + i\eta\beta - 2\xi\alpha)
 \end{aligned} \quad (17)$$

The wavefunctions that correspond to ${}^2T_2$ are as follows:

$$\begin{aligned}
 \varphi_5(G_{3/2}) &= \theta\beta \\
 \varphi_6(G_{3/2}) &= \varepsilon\beta \\
 \varphi_7(G_{3/2}) &= \theta\alpha \\
 \varphi_8(G_{3/2}) &= \varepsilon\alpha
 \end{aligned} \quad (18)$$

In terms of these eight basis functions, shown in Eqs. (17) and (18), the matrix elements with respect to the total Hamiltonian are expressed as follows:

$$H = \frac{\zeta_{nd}}{2} \begin{bmatrix} \varphi_1 & \varphi_2 & \varphi_3 & \varphi_4 & \varphi_5 & \varphi_6 & \varphi_7 & \varphi_8 \\ \begin{matrix} -1 & -\sqrt{6}i & 0 & 0 & 0 & 0 & 0 & 0 \\ +\sqrt{6}i & \Delta' & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & -1 & -\sqrt{6}i & 0 & 0 & 0 & 0 \\ 0 & 0 & +\sqrt{6}i & \Delta' & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & -1 & -\sqrt{6}i & 0 & 0 \\ 0 & 0 & 0 & 0 & +\sqrt{6}i & \Delta' & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & -1 & -\sqrt{6}i \\ 0 & 0 & 0 & 0 & 0 & 0 & +\sqrt{6}i & \Delta' \end{matrix} \end{bmatrix} \quad (19)$$

The above results is quite amazing. The eight-dimensional matrix can now be blocked into four identical two-dimensional matrices, which are quite easily diagonalized.

The energies for the two four-fold degenerate $G_{3/2}$ states are thus obtained as follows:

$$E(G_{3/2}) = \frac{\Delta}{2} \frac{\zeta_{nd}}{4} \pm \frac{1}{2} \sqrt{\Delta^2 + \zeta_{nd}\Delta + \frac{25}{4} \zeta_{nd}^2} \quad (20)$$

In the limit of $\Delta \gg \zeta_{nd}$, the energies expressed in Eq. (20) converge to Δ and $-\frac{1}{2} \zeta_{nd}$. On the otherhand, in the limit of $\Delta \ll \zeta_{nd}$, the energies converge to ζ_{nd} and $-\frac{1}{2} \zeta_{nd}$, identical to the atomic case. The energy levels are schematically shown in Fig. 3 for various values of ζ_{nd}/Δ .

As is shown in Fig. 3, the spin-orbit coupling induces the splitting of the ${}^2T_2$ state into the $E_{5/2}$ state and the $G_{3/2}$ state. As is understood in Fig. 3, the splitting is of the order of the spin-orbit coupling parameter, ζ_{nd} , of the metal ion. Typi-

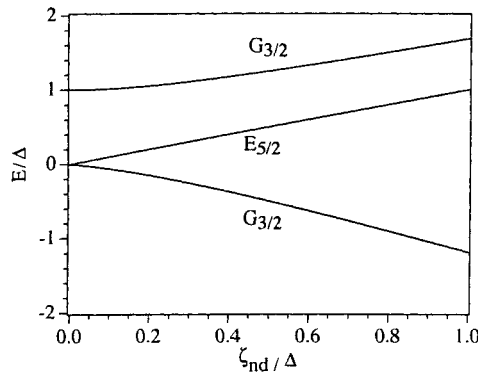


Fig. 3. Splitting of the energy levels of a system of a single d -electron in the point group of O' as a function of $\zeta_{nd}/\Delta = 10Dq$ is the ligand field strength

Table 3. The spin-orbit coupling parameter ζ_{nd} (in cm^{-1}) for some of the transition metal ions^a

Charge	Cr	Mn	Fe	Co	Mo	Ru	Rh
0	790	720	806	798	553	878	968
1	710	873	869	878	672	887	1212
2	830	960	1056	1115	–	990	1235
3	1030	1140			817		

^a J.S. Griffith [20].

cal ζ_{nd} values for the transition metal ions are shown in Table 3. (Various modification of ζ_{nd} values have been proposed and Table 3 is only intended to show approximate values.) Thus, for any complexes of any transition metal ions, the splitting would be of the order of 10^2 to 10^3 cm^{-1} . The very large splitting is a characteristic property of the dd excited states.

3.1.2

Spin Sublevels of a System of Six d Electrons

As the second example of the dd state we now consider the excited states of a system of six d electrons. For a system having more than one electron, electron repulsion should be taken into consideration. This point is well discussed in standard textbooks, and there is nothing to further discuss here. Difficulty exists again in diagonalization. The matrix to be diagonalized is much more complicated as compared with the single electron system. However, we again wish to emphasize that the proper use of the group theory makes a seemingly formidable task quite easy. As, in the previous section, we shall discuss the problem in the crystal field of O.

In the ground state, all the six electrons are in the t_2 orbital, and because of the closed shell structure the ground electronic state is not split further. If an electron in the t_2 orbital is promoted to the e orbital, the resultant spatial wavefunctions are $^1T_1$, $^1T_2$, $^3T_1$, and $^3T_2$. If electron repulsion is taken into consideration, these four excited states are not degenerate any more, and the energies are expressed in the following manner:

$$\begin{aligned}
 E(^1T_2) &= \Delta + 15A - 14B + 14C \\
 E(^1T_1) &= \Delta + 15A - 30B + 14C \\
 E(^3T_2) &= \Delta + 15A - 22B + 12C \\
 E(^3T_1) &= \Delta + 15A - 30B + 12C
 \end{aligned} \tag{21}$$

where A , B , and C are the Racah parameters [17]. Since $C \gg B$, the energy order of the spatial wavefunctions should be $^1T_2 > ^1T_1 > ^3T_2 > ^3T_1$. Thus, the lowest excited state should be $^3T_1$. All these excited states are split into several spin sublevels by the spin-orbit interaction. However, we here focus attention on the spin sublevels associated with the lowest excited state, $^3T_1$. The three

triplet spin functions belong to the T_1 representation in the point group of O. Since

$$T_1 \times T_1 = A_1 + E + T_1 + T_2 \quad (22)$$

there are four spin sublevels whose space $\times$ spin symmetries are A_1, E, T_1 and T_2 . In the following, we try to determine the energies and wavefunctions associated with these spin sublevels.

The method of constructing the wavefunctions as a linear combination of the Slater determinants is discussed in standard textbooks [18]. The spatial wavefunctions are constructed in such a way that they transform exactly identical to the x, y , and z vectors in the O group. Following Sugano, Tanabe, and Kamimura [18], the wavefunctions so constructed are labeled as α, β , and γ . Usually, the wavefunctions are further constructed by taking a linear combination of these in such a manner that they are the eigenfunctions of the spin operator S_z . In the case of the triplet state, the M_s values (i.e. eigenvalues for the spin operator $S_z/\hbar$) should be $+1, 0$, or -1 . Thus, we should have $3 \times 3 = 9$ wavefunctions. The nine wavefunctions thus constructed are as follows:

$$\begin{aligned} |\alpha 1\rangle &= -\frac{\sqrt{3}}{2} |\xi \eta \bar{\eta} \zeta \bar{\zeta} \theta| - \frac{1}{2} |\zeta \eta \bar{\eta} \zeta \bar{\zeta} \epsilon| \\ |\beta 1\rangle &= -\frac{\sqrt{3}}{2} |\xi \bar{\xi} \eta \zeta \bar{\zeta} \theta| - \frac{1}{2} |\xi \bar{\xi} \eta \zeta \bar{\zeta} \epsilon| \\ |\gamma 1\rangle &= |\xi \bar{\xi} \eta \bar{\eta} \zeta \epsilon| \\ |\alpha 0\rangle &= -\frac{1}{2\sqrt{2}} \left\{ -\sqrt{3} |\xi \eta \bar{\eta} \zeta \bar{\zeta} \theta| - \sqrt{3} |\xi \bar{\xi} \eta \zeta \bar{\zeta} \theta| - |\xi \eta \bar{\eta} \zeta \bar{\zeta} \epsilon| - |\xi \bar{\xi} \eta \zeta \bar{\zeta} \epsilon| \right\} \\ |\beta 0\rangle &= -\frac{1}{2\sqrt{2}} \left\{ -\sqrt{3} |\xi \bar{\xi} \eta \zeta \bar{\zeta} \theta| + \sqrt{3} |\xi \bar{\xi} \eta \zeta \bar{\zeta} \theta| - |\xi \bar{\xi} \eta \zeta \bar{\zeta} \epsilon| - |\xi \bar{\xi} \eta \zeta \bar{\zeta} \epsilon| \right\} \\ |\gamma 0\rangle &= -\frac{1}{\sqrt{2}} \left\{ |\xi \bar{\xi} \eta \bar{\eta} \zeta \epsilon| + |\xi \bar{\xi} \eta \bar{\eta} \zeta \epsilon| \right\} \\ |\alpha -1\rangle &= -\frac{\sqrt{3}}{2} \left\{ |\xi \eta \bar{\eta} \zeta \bar{\zeta} \theta| - \frac{1}{2} |\xi \bar{\xi} \eta \zeta \bar{\zeta} \epsilon| \right\} \\ |\beta -1\rangle &= -\frac{\sqrt{3}}{2} \left\{ |\xi \bar{\xi} \eta \zeta \bar{\zeta} \theta| - \frac{1}{2} |\xi \bar{\xi} \eta \zeta \bar{\zeta} \epsilon| \right\} \\ |\gamma -1\rangle &= |\xi \bar{\xi} \eta \bar{\eta} \zeta \epsilon| \end{aligned} \quad (23)$$

Where, the first argument, α, β , or γ , specifies the transformation property of the spatial wavefunction, and the second argument denotes the M_s values.

These wavefunctions are, of course, diagonal with respect to $H_0 + V_C$, and the diagonal term is $E(^3T_1)$ expressed in Eq. (21). In the following, we take the $E(^3T_1)$ as the origin of the energy. Then, the matrix elements of the total Hamiltonian with respect to these nine basis functions are expressed as follows:

$$H = \frac{\xi_{nd}}{4\sqrt{2}} \begin{bmatrix} \alpha 1 & \beta 1 & \gamma 1 & \alpha 0 & \beta 0 & \gamma 0 & \alpha - 1 & \beta - 1 & \gamma - 1 \\ 0 & +\sqrt{2}i & 0 & 0 & 0 & -1 & 0 & 0 & 0 \\ -\sqrt{2}i & 0 & 0 & -3i/2 & 0 & +i & 0 & 0 & 0 \\ 0 & 0 & 0 & +1 & -i & 0 & 0 & 0 & 0 \\ 0 & 3i/2 & +1 & 0 & 0 & 0 & 0 & 0 & 1 \\ 0 & 0 & +i & 0 & 0 & 0 & 0 & 0 & i \\ -1 & -i & 0 & 0 & 0 & 0 & -1 & -i & 0 \\ 0 & 0 & 0 & 0 & 0 & -1 & 0 & -\sqrt{2}i & 0 \\ 0 & 0 & 0 & 0 & 0 & +i & +\sqrt{2}i & 0 & 0 \\ 0 & 0 & 0 & +1 & -i & 0 & 0 & 0 & 0 \end{bmatrix} \quad (24)$$

The diagonalization of the matrix in an analytical form appears quite difficult, if not impossible. In order to obtain analytical solutions, we must devise a new approach.

As pointed out above, the spin sublevels must belong to A_1 , E , T_1 , and T_{2b} . We should therefore construct all nine wavefunctions so as to be the bases of these irreducible representations. For this purpose, we think of the conventional method of constructing the wavefunction in terms of the transformation properties. However, different from the single electron system discussed in the previous section, the transformation properties become very complicated in the present case. For example, let us examine the operation $C_3(111)$. Under this operation, the spatial orbitals and spin functions transform as follows:

$$\begin{aligned} \xi &\rightarrow \eta \\ \eta &\rightarrow \zeta \\ \zeta &\rightarrow \xi \\ \theta &\rightarrow -\frac{1}{2}\theta + \frac{\sqrt{3}}{2}\varepsilon \\ \varepsilon &\rightarrow -\frac{\sqrt{3}}{2}\theta - \frac{1}{2}\varepsilon \\ \alpha &\rightarrow \frac{1}{2}(1-i)\alpha + \frac{1}{2}(1-i)\beta \\ \beta &\rightarrow \frac{1}{2}(1+i)\alpha + \frac{1}{2}(1+i)\beta \end{aligned} \quad (25)$$

In term of these transformation properties, we must calculate how, for example, the Slater determinant $|\xi\eta\bar{\eta}\zeta\bar{\zeta}\theta|$ transforms. This is extremely tedious even for one symmetry operation. If we employ this procedure for all the 48 symmetry

operations, the work becomes extremely lengthy and tedious. Is there no way of avoiding this?

An important point is the choice of the spin functions. Usually, the wavefunctions are chosen so that they are the eigenfunctions of S_z . As long as S_z commutes with the total Hamiltonian, this choice of wavefunctions is meaningful. However, if, as in the present case, S_z does not commute with the total Hamiltonian, such choice of the spin functions is meaningless. We should rather choose the spin functions so that they are the bases of the irreducible representations of the point group.

Without giving the details, we show the three spin functions that are the bases of the T_1 representation of the O' point group.

$$\begin{aligned}\tau_x &= \sqrt{\frac{1}{2}}(\beta_1\beta_2 - \alpha_1\alpha_2) \\ \tau_y &= \sqrt{\frac{1}{2}}i(\beta_1\beta_2 - \alpha_1\alpha_2) \\ \tau_z &= \sqrt{\frac{1}{2}}(\alpha_1\beta_2 - \beta_1\alpha_2)\end{aligned}\tag{26}$$

Furthermore, τ_x , τ_y , and τ_z transform identically with the x , y , and z functions for all the 48 symmetry operations in the O' group (This can be checked in terms of the transformation properties shown in Table 2).

As stated above, the spatial wavefunctions denoted by α , β , and γ transform in exactly the same way as x , y , and z . We have just shown that the spin functions denoted by τ_x , τ_y , and τ_z also transform exactly as x , y , and z . Therefore, with the help of the Clebsh-Gordan coefficients [18], we are able to construct wavefunctions that are the bases of the irreducible representations of the group. The final results are given below.

$$A_1(e) = -\sqrt{\frac{1}{3}}(\alpha\tau_x + \beta\tau_y + \gamma\tau_z)$$

$$E(\theta) = +\sqrt{\frac{1}{6}}(\alpha\tau_x + \beta\tau_y - 2\gamma\tau_z)$$

$$E(\epsilon) = +\sqrt{\frac{1}{2}}(-\alpha\tau_x + \beta\tau_y)$$

$$T_1(\alpha) = +\sqrt{\frac{1}{2}}(-\beta\tau_z + \gamma\tau_y)$$

$$T_1(\beta) = +\sqrt{\frac{1}{2}}(\alpha\tau_z - \gamma\tau_x)$$

$$T_1(\gamma) = +\sqrt{\frac{1}{2}}(\alpha\tau_y - \beta\tau_x)$$

$$\begin{aligned}
T_2(\xi) &= + \sqrt{\frac{1}{2}} (-\beta\tau_z - \gamma\tau_y) \\
T_2(\eta) &= + \sqrt{\frac{1}{2}} (-\alpha\tau_z - \gamma\tau_x) \\
T_2(\gamma) &= + \sqrt{\frac{1}{2}} (-\alpha\tau_y - \beta\tau_x)
\end{aligned} \tag{27}$$

The notations shown in the parentheses after the group theoretical notations denote the transformation properties. For example, $E(\theta)$ and $E(\varepsilon)$ transform in exactly the same way as the θ and ε d -orbitals, respectively. In terms of the wavefunctions shown in Eqs. (23) and (26), the individual terms on the righthand sides of Eq. (27) are expressed as follows:

$$\begin{aligned}
\alpha\tau_x &= \sqrt{\frac{1}{2}} (|\alpha-1\rangle - |\alpha1\rangle) \\
\alpha\tau_y &= \sqrt{\frac{1}{2}} i(|\alpha-1\rangle + |\alpha1\rangle) \\
\alpha\tau_z &= |\alpha0\rangle \\
\beta\tau_x &= \sqrt{\frac{1}{2}} (|\beta-1\rangle - |\beta1\rangle) \\
\beta\tau_y &= \sqrt{\frac{1}{2}} i(|\beta-1\rangle + |\beta1\rangle) \\
\beta\tau_z &= |\beta0\rangle \\
\gamma\tau_x &= \sqrt{\frac{1}{2}} (|\gamma-1\rangle - |\gamma1\rangle) \\
\gamma\tau_y &= \sqrt{\frac{1}{2}} i(|\gamma-1\rangle + |\gamma1\rangle) \\
\gamma\tau_z &= |\gamma0\rangle
\end{aligned} \tag{28}$$

The results expressed in Eq. (27) are very important. All the wavefunctions are the bases of the irreducible representations in the point group of O' . We have one A wavefunction, two E wavefunctions, three T_1 wavefunctions, and three T_2 wavefunctions. Thus, we do not have to diagonalize the nine-dimensional matrix; we may diagonalize one one-dimensional matrix, one two-dimensional matrix, and two three-dimensional matrices.

Since there is only one wavefunction of A_1 symmetry, the basis function $A_1(e)$ is itself the eigenfunction. The energy is

$$E(A_1) = 2 \frac{\zeta_{nd}}{4} \tag{29}$$

The matrix for E representation is

$$H = \frac{\zeta_{nd}}{4} \begin{bmatrix} -1 & 0 \\ 0 & -1 \end{bmatrix} \quad (30)$$

The matrix for the T_1 representation is

$$H = \frac{\zeta_{nd}}{4} \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \quad (31)$$

Finally, the matrix for the T_2 representation is

$$H = \frac{\zeta_{nd}}{4} \begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{bmatrix} \quad (32)$$

These matrices are really amazing. All of them are already diagonalized. We are thus able to obtain complete solutions without any diagonalization procedures. The energies are summarized as follows:

$$\begin{aligned} A_1: & \Delta + 15A - 30B + 12C + \frac{\zeta_{nd}}{2} \\ T_1: & \Delta + 15A - 30B + 12C + \frac{\zeta_{nd}}{4} \\ E: & \Delta + 15A - 30B + 12C - \frac{\zeta_{nd}}{4} \\ T_2: & \Delta + 15A - 30B + 12C - \frac{\zeta_{nd}}{4} \end{aligned} \quad (33)$$

where the energies are scaled from the ground state. The energy levels are schematically shown in Fig. 4.

As in the one d -electron system discussed in Sect. 3.1.1, the splittings are again of the order of the atomic spin-orbit coupling parameter ζ_{nd} for the d -orbital. This point may be generalized to any dd excited states.

The sublevels properties for the d^6 system were experimentally studied for $\text{Co}(\text{CN})_6$ by Hipps and Crosby [22]. The energies and the lifetimes of the individual sublevels determined by these authors are shown in Fig. 5. The sublevels structures shown in this figure are quite analogous to the theoretical prediction shown in Fig. 4. Theoretically, only the emission from the T_1 sublevel is optically allowed. That the lifetime of the T_{1g} sublevel is the shortest is in agreement with this theoretical prediction. (The fact that the g states emit at all is probably due either to the vibronic coupling with a vibration of the u symmetry or to the loss of the center of inversion by the symmetry breakdown). Theoretically, the lowest two sublevels are degenerate; however, experimentally the two levels are split. This is probably due to the second order spin-orbit coupling. As Fig. 4

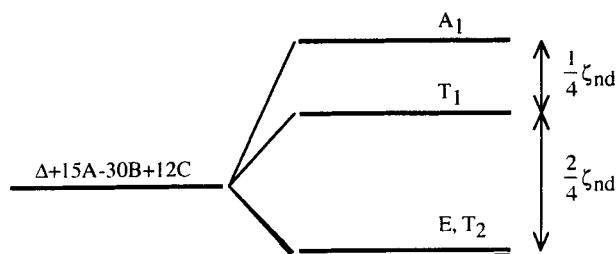


Fig. 4. Sublevels of the lowest triplet state ${}^3T_1$ for a system of six d -electrons in O' point group

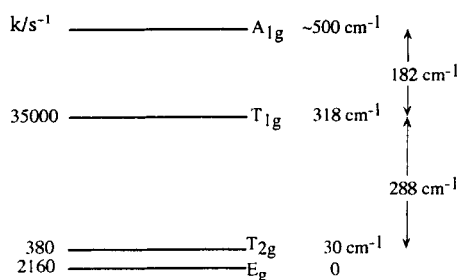


Fig. 5. The experimentally derived energies and the total decay rate constants of the four lowest spin sublevels of $\text{Co}(\text{CN})_6$ after Hipps and Crosby [22]

shows, the $T_{1g} - E_g$ energy gap is expected to be twice that of the $A_{1g} - T_{1g}$ gap, but this theoretical prediction is not satisfied exactly in the experimental observation. If we assume the $A_{1g} - T_{1g}$ energy gap to be $\frac{1}{4} \zeta_{nd}$, the ζ_{nd} value should be 728 cm^{-1} . If on the other hand, the $T_{1g} - T_{2g}$ energy gap is equated to $\frac{1}{2} \zeta_{nd}$, then $\zeta_{nd} = 576 \text{ cm}^{-1}$. It appears that the $T_{1g} - E_g$ energy gap is more trustworthy because the location of the quite forbidden A_{1g} state is difficult to ascertain experimentally and it was determined [22] by theoretical calculation.

3.2

Spin Sublevels of the Ligand-Localized ${}^3\pi\pi^*$ State

The spin sublevel properties of the ligand-localized ${}^3\pi\pi^*$ states are very much different from the dd states discussed above. Since π molecular orbitals are constructed from nondegenerate p atomic orbitals, any ${}^3\pi\pi^*$ state is not diagonal with respect to the spin-orbit coupling. Hence, the spin-orbit coupling can be effective only on the second order. For most organic ligand molecules, the spin-spin coupling is more effective than the spin-orbit coupling. In the following, we first discuss the first order correction of the spin-spin coupling.

3.2.1

Spin-Spin Interaction

The Hamiltonian for the spin dipole-spin dipole interaction is expressed as follows

$$H = \frac{\mu_0}{4\pi} \left\{ \frac{\mathbf{m}_1 \mathbf{m}_2}{r_{12}^3} - \frac{3(\mathbf{m}_1 \mathbf{r})(\mathbf{m}_2 \mathbf{r})}{r_{12}^5} \right\} \quad (34)$$

where μ_0 is the vacuum permeability. The magnetic moment $\mathbf{m}$ is expressed as

$$\mathbf{m} = g \mu_B \mathbf{S} \quad (35)$$

where $\mathbf{S}$ is the spin operator and μ_B is Bohr magneton. Thus, the Hamiltonian is expressed as

$$H = \frac{\gamma_0}{4\pi} g^2 \mu_B^2 \left\{ \frac{\mathbf{S}_1 \mathbf{S}_2}{r_{12}^3} - \frac{3(\mathbf{S}_2 \mathbf{r})(\mathbf{S}_1 \mathbf{r})}{r_{12}^5} \right\} \quad (36)$$

This Hamiltonian can be further reduced to

$$H = \sum_{p,q} \Lambda_{pq} S_{1p} S_{2q} \quad (p, q = x, y, z) \quad (37)$$

where

$$\Lambda_{pp} = \frac{\mu_0}{4\pi} \mu_B^2 \frac{r_{12}^2 - 3p_{12}^2}{r_{12}^5} \quad (38)$$

$$\Lambda_{pp} = \frac{\mu_0}{4\pi} \mu_B^2 \frac{p_{12} - q_{12}}{r_{12}^5} \quad (p \neq q) \quad (39)$$

Since the electronic states are separated considerably more than the spin states, we can consider the effect of H only diagonal with respect to the electronic state, ψ_i . Thus, the effective Hamiltonian for the spin-spin coupling is expressed as

$$\begin{aligned} H_{ss} &= \sum_{p,q} \langle \psi_i | \Lambda_{pq} | \psi_i \rangle S_{1p} S_{2q} \\ &= \sum_{p,q} \Omega_{pq} S_{1p} S_{2q} \end{aligned} \quad (40)$$

where

$$\Omega_{pq} = \langle \psi_i | \Lambda_{pq} | \psi_i \rangle \quad (41)$$

One can diagonalize Ω_{pq} by the appropriate choice of the coordinates x, y , and z . Thus, the effective Hamiltonian is now expressed as

$$H_{ss} = \Omega_{xx} S_{1x} S_{2x} + \Omega_{yy} S_{1y} S_{2y} + \Omega_{zz} S_{1z} S_{2z} \quad (42)$$

Since

$$x_{12}^2 + y_{12}^2 + z_{12}^2 = r_{12}^2 \quad (43)$$

we have

$$\Omega_{xx} + \Omega_{yy} + \Omega_{zz} = 0 \quad (44)$$

We further try to express Eq. (42) in a somewhat simpler manner. Since

$$\begin{aligned} S_{1x}S_{2x} &= \frac{1}{2}(S_x^2 - S_{1x}^2 - S_{2x}^2) \\ S_{1y}S_{2y} &= \frac{1}{2}(S_y^2 - S_{1y}^2 - S_{2y}^2) \\ S_{1z}S_{2z} &= \frac{1}{2}(S_z^2 - S_{1z}^2 - S_{2z}^2) \end{aligned} \quad (45)$$

Further since

$$S_{1x}^2 = S_{2x}^2 = S_{1y}^2 = S_{2y}^2 = S_{1z}^2 = S_{2z}^2 = \frac{1}{4}\hbar^2 \quad (46)$$

the Hamiltonian is expressed as

$$H = \sum_p \Omega_{pp} \left(\frac{1}{2} S_p^2 - \frac{1}{4} \hbar^2 \right) \quad (47)$$

We define new parameters X , Y , and Z as follows

$$\begin{aligned} X &= -\frac{1}{2} \Omega_{xx} \\ Y &= -\frac{1}{2} \Omega_{yy} \\ Z &= -\frac{1}{2} \Omega_{zz} \end{aligned} \quad (48)$$

From Eq. (44)

$$X + Y + Z = 0 \quad (49)$$

The effective Hamiltonian for the spin-spin interaction is now reduced to

$$H_{ss} = -(XS_x^2 + YS_y^2 + ZS_z^2) \quad (50)$$

We take the triplet spin functions τ_x , τ_y , and τ_z defined in Eq. (26). In terms of these spin functions, the Hamiltonian (50) is expressed as follows

$$H_{ss} = \begin{bmatrix} X & 0 & 0 \\ 0 & Y & 0 \\ 0 & 0 & Z \end{bmatrix} \quad (51)$$

That is, the Hamiltonian (50) is diagonal, and the zero-field energies are X , Y , and Z .

As discussed above, X , Y , and Z are roughly the expectation values of $1/r^3$. Therefore, the energy should be less stabilized if the electron cloud is more extended. The order of the zero-order states are thus simply estimated from the shape of the molecule. They are schematically shown in Fig. 6.

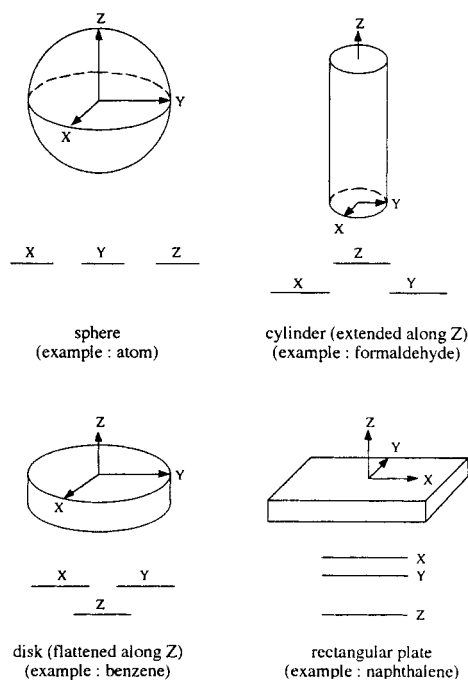


Fig. 6. Schematic illustration of the energies of the triplet sublevels for various molecular shapes

The zero-field splitting for ${}^3\pi\pi^*$ states has been determined for a number of molecules, and the data are compiled in a number of places [16, 23]. Zero-field energies for some organic ligands [24–26] are summarized in Fig. 7. As is seen in these examples, the splitting is of the order of 0.1 cm^{-1} for ${}^3\pi\pi^*$ states or organic molecules. Thus, the splitting is four to five orders of magnitude smaller than those of dd states.

3.2.2

Spin-Orbit Coupling

In the case of organic molecules, the zero-field splitting is mainly governed by the spin-spin coupling. In some cases, the spin-orbit coupling may affect the splitting. Since the ${}^3\pi\pi^*$ state is not diagonal with respect to H_{SO} , the spin-orbit coupling may be effective only in the second order. In the following, we discuss the effect of the second order spin-orbit coupling to the triplet state of the ${}^3\phi_a\phi_b$ configuration (i.e., a configuration arising from the electron-promotion from the ϕ_a orbital to the ϕ_b orbital). The wavefunctions for the three triplet sublevels T_x , T_y , and T_z are expressed as follows.

$$T_x(\phi_a, \phi_b) = \sqrt{\frac{1}{2}} \{ |\bar{\phi}_a\bar{\phi}_b| - |\phi_a\phi_b| \} \quad (52)$$

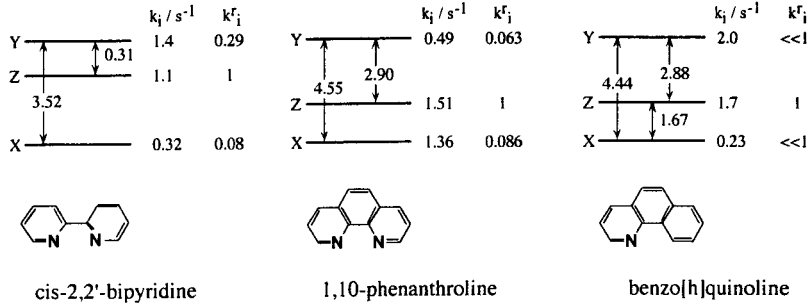


Fig. 7. Zero-field splitting (in units of GHz), total decay rate constants for individual sublevels, and the relative radiative rate constants for 2,2'-bipyridine (bpy) [24], 1,10-phenanthroline (phen) [25], and benzo[h]quinoline (bhqH) (26). For all the ligand molecules listed here the lowest triplet state is $^3\pi\pi^*$. For bpy the decay rate constants have not been determined. The axis system is common for the three compounds: x-axis is normal to the molecular plane, and x- and y-axes are the short and the long axes, respectively, in the molecular plane

$$T_y(\phi_a, \phi_b) = \sqrt{\frac{1}{2}} i \{ |\bar{\phi}_a \bar{\phi}_b| + |\phi_a \phi_b| \}$$

$$T_z(\phi_a, \phi_b) = \sqrt{\frac{1}{2}} \{ |\phi_a \bar{\phi}_b| + |\bar{\phi}_a \phi_b| \} \quad (\text{zu } 52)$$

We first discuss the spin-orbit coupling between the above triplet sublevels and the singlet states. The spin-orbit coupling is nonvanishing only between the configurations in which one electron occupies the same orbital and the other electron occupies a different orbital. Thus, the singlet state which may spin-orbit couple with $^3\phi_a\phi_b$ is of the form $^1\phi_a\phi_c$, where ϕ_b should not be equal to ϕ_c . The wavefunction of this singlet state is expressed as

$$S(\phi_a, \phi_b) = \sqrt{\frac{1}{2}} \{ |\phi_a \bar{\phi}_b| - |\bar{\phi}_a \phi_b| \} \quad (53)$$

The spin-orbit coupling between the triplet states [Eq. (52)] and the singlet state [Eq. (53)] are expressed as follows:

$$\begin{aligned} \langle T_x(\phi_a, \phi_b) | H_{SO} | S(\phi_a, \phi_c) \rangle &= - \langle S(\phi_a, \phi_c) | H_{SO} | T_x(\phi_a, \phi_b) \rangle \\ &= - \frac{\hbar}{2} \langle \phi_b | \xi(r) \ell_x | \phi_c \rangle \\ \langle T_y(\phi_a, \phi_b) | H_{SO} | S(\phi_a, \phi_c) \rangle &= - \langle S(\phi_a, \phi_c) | H_{SO} | T_y(\phi_a, \phi_b) \rangle \\ &= - \frac{\hbar}{2} \langle \phi_b | \xi(r) \ell_y | \phi_c \rangle \\ \langle T_z(\phi_a, \phi_b) | H_{SO} | S(\phi_a, \phi_c) \rangle &= - \langle S(\phi_a, \phi_c) | H_{SO} | T_z(\phi_a, \phi_b) \rangle \\ &= - \frac{\hbar}{2} \langle \phi_b | \xi(r) \ell_z | \phi_c \rangle \end{aligned} \quad (54)$$

We next discuss the spin-orbit coupling between triplet states. The spin-orbit coupling between a sublevels ${}^3\phi_a\phi_b$ and a sublevel of ${}^3\phi_a\phi_c$ is nonvanishing only in the following pairs.

$$\begin{aligned}
 \langle T_x(\phi_a, \phi_b) | H_{SO} | T_y(\phi_a, \phi_c) \rangle &= \langle T_y(\phi_a, \phi_c) | H_{SO} | T_x(\phi_a, \phi_b) \rangle \\
 &= -\frac{1}{2} i\hbar \langle \phi_b | \xi(r) \ell_z | \phi_c \rangle \\
 \langle T_y(\phi_a, \phi_b) | H_{SO} | T_z(\phi_a, \phi_c) \rangle &= \langle T_z(\phi_a, \phi_c) | H_{SO} | T_y(\phi_a, \phi_b) \rangle \\
 &= -\frac{1}{2} i\hbar \langle \phi_b | \xi(r) \ell_x | \phi_c \rangle \\
 \langle T_z(\phi_a, \phi_b) | H_{SO} | T_x(\phi_a, \phi_c) \rangle &= \langle T_x(\phi_a, \phi_c) | H_{SO} | T_z(\phi_a, \phi_b) \rangle \\
 &= -\frac{1}{2} i\hbar \langle \phi_b | \psi(r) \ell_z | \phi_c \rangle
 \end{aligned} \tag{55}$$

As is seen above, all the spin-orbit matrix elements are reduced to the integral of the type $\langle \phi_b | \xi(r) \ell_u | \phi_c \rangle$ where u is one of x, y , and z . We shall analyze this type of integral in the following two types of interaction. First, we discuss the spin-orbit coupling between two $\pi\pi^*$ states. Let $\phi_b = \pi$ and $\phi_c = \pi'$. Then, $\langle \pi | \xi(r) \ell_x | \pi' \rangle = 0$ and $\langle \pi | \xi(r) \ell_y | \pi' \rangle = 0$ by symmetry. (We here assume that the π orbitals have a node in the xy plane.) On the other hand $\langle \pi | \xi(r) \ell_z | \pi' \rangle$ is nonzero; however, it contains only the three center integrals. (See page 227 of Ref. 16 for detailed discussion.) Thus, the spin-orbit coupling between two $\pi\pi^*$ states is practically negligibly small. Second, we discuss the spin-orbit coupling between $\pi\pi^*$ and $n\pi^*$ states. In this case let $\phi_b = \pi$ and $\phi_c = n$. (Here we assume that the n -orbital is extended along the x -axis.) Then $\langle \pi | \xi(r) \ell_x | n \rangle = 0$ and $\langle \pi | \xi(r) \ell_z | n \rangle = 0$ by symmetry, and $\langle \pi | \xi(r) \ell_y | n \rangle$ has one-center spin-orbit coupling. Thus, the zero-field sublevel energies of a ${}^3n\pi^*$ state are affected by the spin-orbit coupling with either ${}^1n\pi^*$ or ${}^3n\pi^*$ states that are located in the proximity. The stabilization of sublevels by the spin-orbit coupling with upper singlet or triplet states is schematically shown in Fig. 8.

3.2.3

Experimental Results on Some Ligand-Localized ${}^3\pi\pi^*$ States and Their Interpretation

One of the well-studied examples of luminescence from the ligand-localized ${}^3\pi\pi^*$ state is the complex of Rh(III) with a variety of imines. Triplet sublevel properties have been investigated in detail for Rh(bpy) $_3^{3+}$ [27], Rh(phen) $_3^{3+}$ [27, 28], Rh(CN) $_2$ (phen) $_2^+$ [28], Rh(thpy)(phpy)(bpy) $^+$ [29], and Rh(phpy) $_2$ (bpy) $^+$ [29]. For all of these complexes, the phosphorescence is similar to that of a free ligand in its spectral location and vibrational structures, and for this reason the lowest triplet state of the complex has been assigned as the ligand-localized ${}^3\pi\pi^*$ state. However, the lifetime is significantly shorter than that of the free ligand. Examples are shown in Fig. 10, where the zero-field splitting, the total decay rate con-

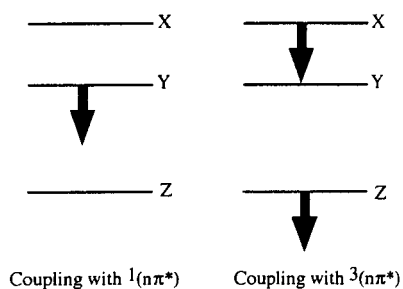


Fig. 8. Stabilization of the sublevels of the ${}^3\pi\pi^*$ state by the spin orbit coupling with upper ${}^1n\pi^*$ or ${}^3n\pi^*$ states. We assume that the n orbitals are extended along the z -axis and the n -orbital expended along x -axis. The sublevels indicated by downward arrows are stabilized

stants, the relative radiative rate constants, and the lifetime (measured at 77 K) are compared with those of phen. The most remarkable observation is the significant shortening of the lifetime by coordination to the metal. This means that even in the state so far assigned as the ligand-localized ${}^3\pi\pi^*$ state, there is a significant participation of metal orbitals.

Komada et al. [27] have treated the metal orbital participation by the spin-orbit coupling with ${}^1d\pi^*$ MLCT states. The proposed mixing scheme is schematically shown in Fig. 9a. Frei et al. [30] have also adopted this mechanism in trying to interpret their polarized absorption spectrum of $\text{Rh}(\text{phpy})_2(\text{bpy})^+$. This mechanism, however, encounters several difficulties. First, the spin-orbit coupling between ${}^3\pi\pi^*$ and ${}^1d\pi^*$ involves only the two-center integrals on Rh. The two-center integral is usually quite small, and does not appear to be responsible for the large effect introduced by the metal. In fact, Miki et al. [28] calculated the magnitude of this spin-orbit coupling. The exact magnitude is slightly dependent on the choice of the orbital exponent of atomic orbitals. However, whatever the values of the orbital exponent are chosen, the total spin-orbit coupling matrix element $\langle {}^3\pi\pi^* | H_{\text{SO}} | {}^1d\pi^* \rangle$ is smaller than the matrix element $\langle {}^3\pi\pi^* | H_{\text{SO}} | {}^1\sigma\pi^* \rangle$ or $\langle {}^3\pi\pi^* | H_{\text{SO}} | {}^1n\pi^* \rangle$ that is responsible for the lifetime of the free ligand. Thus, two-center spin-orbit coupling is never able to account for the significant effect introduced by metal. The mechanism proposed by Komada et al. has difficulty also in the tipole transition, because the dipole transition between ${}^1d\pi^*$ and the ground state has only two-center terms, and is almost forbidden. (That the transition to a ${}^1d\pi^*$ state is often strongly observed is due to the configuration interaction between the ${}^1d\pi^*$ and ${}^1\pi\pi^*$ states.) This further supports our idea that the configuration interaction should be included.) Thus, in this mechanism, the additional radiative character introduced by metal is negligibly small as compared with the original radiative character of the free ligand.

In order to overcome the difficulties outlined above, Miki et al. [28] proposed an entirely new mechanism. (See Fig. 9b). In this mechanism, ${}^3\pi\pi^*$ state is mixed with ${}^3dd$ and ${}^3d\pi^*$ states by the configurational interaction. Likewise, ${}^1\pi\pi^*$ and ${}^1\sigma\pi^*$ states are configurationally mixed with ${}^1dd$ and ${}^1d\pi^*$ states. The spin-orbit coupling is effective between ${}^3d\pi^*$ and ${}^1d\pi^*$ states and also between

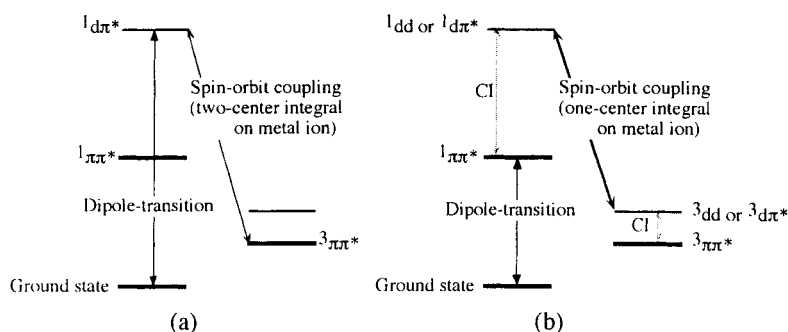


Fig. 9 a, b. Schematic illustration of metal d -orbital participation in the ligand localized $3\pi\pi^*$ state. **a** Mechanism proposed by Komada et al. [27], **b** Mechanism proposed by Miki et al. [28]

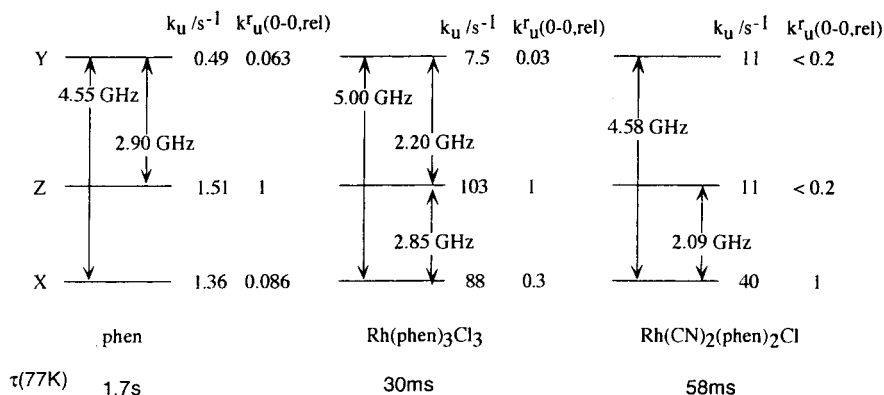


Fig. 10. Zero-field splittings, relative radiative rate constants, and the total decay rate constants of individual sublevels and the 77 K lifetimes for phen, *cis*-Rh(CN)₂(phen)₂Cl, and Rh(phen)₃Cl₃. From Miki et al. [28]

^3dd and ^1dd states. In this case, the spin-orbit coupling has a one-center term on Rh. Since one-center spin-orbit coupling constant ζ_{nd} is significantly larger than the one-center term on carbon, the significant effect introduced by Rh is well explained.

A similar approach has also been given by Giesbergen and Glasbeek [29]. Different from the valence bond theory adopted by Miki et al., these authors approached the problem via molecular orbital theory. The modified molecular orbital is expressed as the combination of π orbitals of the ligand and d orbitals of Rh. Thus, the participation of the metal d -orbital appears as the one-center spin-orbit coupling on Rh.

As outlined above, a significant increase in radiativity introduced by coordination to metals has been interpreted by two entirely different mechanisms. In one mechanism the increase of the radiative character induced by metal is ascribed to two-center spin-orbit coupling in which the metal orbital is partially involved. In the other mechanism, the increase in radiative character is ascribed

to one-center spin-orbit coupling on the metal. We here emphasize that the latter mechanism can account for most of the sublevel properties quite satisfactorily. In what follows we try to illustrate how well the proposed mechanism can interpret the radiative characteristics of the individual sublevels.

The manner in which the spin-forbidden triplet-singlet transition acquires radiative properties by spin-orbit coupling is expressed in terms of the first order perturbation theory. The dipole transition moment for the transition between the u sublevel of the lowest triplet state (T_{1u}) and the ground state (S_0) is expressed as follows:

$$\langle T_{1u} | e\mathbf{r} | S_0 \rangle = \sum_i \frac{\langle T_{1u} | H_{SO} | S_i \rangle \langle S_i | e\mathbf{r} | S_0 \rangle}{E(S_i) - E(T_{1u})} \quad (56)$$

Thus, the transition moment can be estimated by a) spin-orbit coupling, b) the transition dipole moment in the singlet manifold, and c) the energy denominator. If either the spin-orbit coupling or the transition dipole moment in the singlet manifold is forbidden, the total singlet-triplet transition moment should be considered as forbidden. If none of the matrix elements is zero, then the spin-orbit coupling plays by far the most important role.

Before discussing the radiative properties of the Rh complexes, let us examine those of the free phen in terms of Eq. (56).

The mechanisms of radiative transitions are schematically shown in Table 4 and in Fig. 11. Table 4 summarizes the perturbing singlet state and relevant matrix elements of the spin-orbit coupling and dipole transition. The y -emission is group-theoretically forbidden in the C_{2v} -point group. Thus, if the radiative rate constant is not exactly zero, it should be due to the breakdown of the C_{2v} point group. Anyway, the radiative rate constant should be very small for the y -emission. In the x -emission, the spin-orbit coupling has only three-center terms and therefore emissivity should be very small. On the other hand, the z -emission is associated with the one-center spin-orbit coupling. These considerations lead us to expect that $k_x^r \gg k_y^r, k_z^r$. This expectation is indeed what is observed experimentally.

Having established a plausible radiative mechanism for phen, we turn next to an analysis of $\text{Rh}(\text{phen})_3^{3+}$. A significant increase of the decay rate constant is noted for the z - and x -emissions. As outlined above, the emitting state is considered as the configurational mixing of $^3\pi\pi^*$ and $^3d\pi^*$ and ^3dd states. Namely, the lowest triplet state T_1 is expressed as

$$T_1 = c_1^3\pi\pi^* + c_2^3d\pi^* + c_3^3dd \quad (57)$$

where $c_1 > c_2, c_3$.

The radiative mechanisms for $\text{Rh}(\text{phen})_3^{3+}$ are shown in Table 5 and Fig. 12. In this Table, the mixing coefficients in the configurationally mixed states are all omitted for simplicity. The y -emission is still group-theoretically forbidden as long as the complex retains its C_{2v} symmetry. Both the x - and z -emissions are associated with the one-center spin-orbit coupling on Rh. The large value of the spin-orbit coupling parameter ζ_{4d} of Rh thus accounts for the significant increase of the radiativity of the x - and z -emissions.

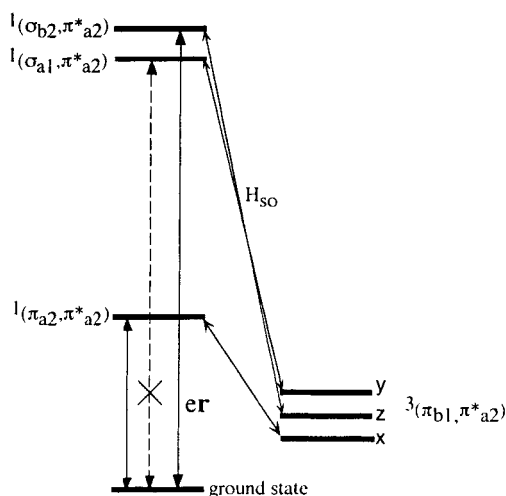


Fig. 11. Schematic representation of the radiative mechanisms of the triplet sublevels of phen. Only the lowest triplet state and the singlet manifolds that may mix with the lowest triplet state are shown

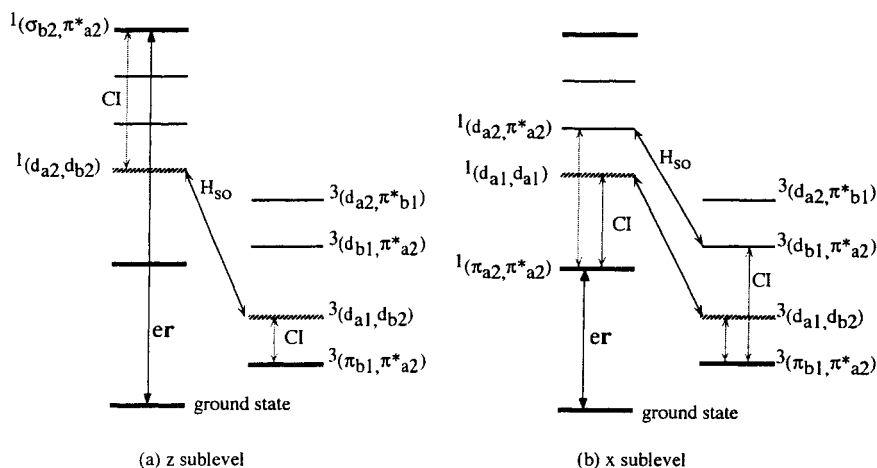
Table 4. Mechanism of radiative transitions for the triplet sublevels of phen

T_1	sublevel	perturbing singlet S_i	spin-orbit coupling	dipole transition $S_i - S_0$
B_2 (π_{b1}, π_{a2}^*)	y	$1A_2(\sigma_{a1}, \pi_{a2}^*)$	$\langle 3\pi_{b1}\pi_{a2}^* H_{SO} 1\sigma_{a1}\pi_{a2}^* \rangle$ one-center on C	group theoretically forbidden
	z	$1B_1(\sigma_{b2}, \pi_{a2}^*)$	$\langle 3\pi_{b1}\pi_{a2}^* H_{SO} 1\sigma_{b2}\pi_{a2}^* \rangle$ one-center on C	$\langle \sigma_{b2}\pi_{a2}^* er S_0 \rangle$
	x	$1A_1(\pi_{a2}, \pi_{a2}^*)$	$\langle 3\pi_{b1}\pi_{a2}^* H_{SO} 1\pi_{a2}\pi_{a2}^* \rangle$ three center	$\langle \pi_{a2}\pi_{a2}^* er S_0 \rangle$

We next turn to discuss $\text{Rh}(\text{CN})_2(\text{phen})_2^+$. When one of the phen ligands is replaced by two CN^- ligands of much stronger ligand field, the location of the ^3dd state should shift to a higher energy state. Therefore, the configurational mixing of the ^3dd state into the $^3\pi\pi^*$ state should significantly decrease. The radiative mechanisms are shown in Table 6 and Fig. 13, assuming that c_3 in Eq. (57) is zero. In this case, the one-center spin-orbit coupling term in the mechanism of the z-emission is only on the C atom and not on the Rh atom, and therefore, the effect of the metal should not exist. The complete absence of the $3dd$ contribution is somewhat over-exaggerated; however, a significant decrease

Table 5. Mechanisms of radiative transitions for the triplet sublevels of Rh(phen)_3^{3+}

T_1	sublevel	perturbing singlet S_i	spin-orbit coupling	dipole transition $S_i - S_0$
B_2 (π_{b1}, π_{a2}^*) + (d_{b1}, π_{a2}^*) + (d_{a1}, d_{b2}^*)	y	$^1A_2(\sigma_{a1}, \pi_{a2}^*)$ + (d_{b1}, d_{b2})	$\langle {}^3d_{a1}d_{b2} H_{SO} {}^1d_{b1}d_{b2} \rangle$ one-center on Rh	group theoretically forbidden
	z	$^1B_1(\sigma_{b2}, \pi_{a2}^*)$ + (d_{a2}, d_{b2})	$\langle {}^3d_{a1}d_{b2} H_{SO} {}^1d_{a2}d_{b2} \rangle$ one-center on Rh	$\langle \sigma_{b2}\pi_{a2}^* er S_0 \rangle$
	x	$^1A_1(\pi_{a2}, \pi_{a2}^*)$ + (d_{a2}, π_{a2}^*) + (d_{a1}, d_{a1})	$\langle {}^3d_{b1}\pi_{a2}^* H_{SO} {}^1d_{a2}\pi_{a2}^* \rangle$ $\langle {}^3d_{a1}d_{b2} H_{SO} {}^1d_{a1}d_{a1} \rangle$ one-center on Rh	$\langle \pi_{a2}\pi_{a2}^* er S_0 \rangle$

**Fig. 12.** Schematic representation of the radiative mechanisms for the allowed transitions from the x- and z-triplet sublevels of Rh(phen)_3^{3+} **Table 6.** Mechanisms of radiative transitions for the triplet sublevels of $\text{Rh(CN)}_2(\text{phen})_2^+$

T_1	sublevel	perturbing singlet S_i	spin-orbit coupling	dipole transition $S_i - S_0$
B_2 (π_{b1}, π_{a2}^*) + (d_{b1}, π_{a2}^*)	y	$^1A_2(\sigma_{a1}, \pi_{a2}^*)$ + (d_{a1}, π_{a2}^*)	$\langle {}^3d_{b1}\pi_{a2}^* H_{SO} {}^1d_{a1}\pi_{a2}^* \rangle$ one-center on Rh	group theoretically forbidden
	z	$^1B_1(\sigma_{b2}, \pi_{a2}^*)$	$\langle {}^3\pi_{b1}\pi_{a2}^* H_{SO} {}^1\sigma_{b2}\pi_{a2}^* \rangle$ one-center on C	$\langle \sigma_{b2}\pi_{a2}^* er S_0 \rangle$
	x	$^1A_1(\pi_{a2}, \pi_{a2}^*)$ + (d_{a2}, π_{a2}^*)	$\langle {}^3d_{b1}\pi_{a2}^* H_{SO} {}^1d_{a2}\pi_{a2}^* \rangle$ one-center on Rh	$\langle \pi_{a2}\pi_{a2}^* er S_0 \rangle$

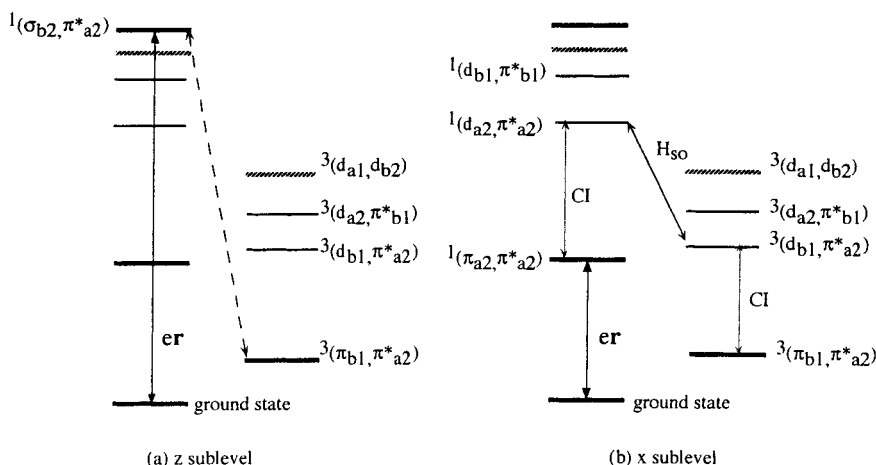


Fig. 13. Schematic representation of the radiative mechanisms for the allowed transitions from the x- and z-triplet sublevels of $\text{Rh}(\text{CN})_2(\text{phen})_2^+$

of the radiativity for the z-sublevel from $\text{Rh}(\text{phen})_3^{3+}$ to $\text{Rh}(\text{CN})_2(\text{phen})^+$ is expected. The experimental findings shown in Fig. 13 are indeed in accord with this expectation.

The mechanism discussed above can also account for various complexes of Rh with a variety of ligands of different ligand field strength, including ortho-metalating ligands such as bhq. Thus, the mechanism involving the configurational mixing of $^3d\pi^*$ and ^3dd into $^3\pi\pi^*$ can quite satisfactorily account for the radiative characteristics of all the sublevels in a variety of Rh complexes.

3.3

Spin Sublevels of a Metal-to-Ligand Charge-Transfer Triplet State

The behavior of sublevels of $^3d\pi^*$ states is similar to that of dd states. The energies of sublevels can be obtained by diagonalization of the whole matrix with respect to the total Hamiltonian. As is illustrated below, the spin-orbit coupling plays an important role, as in the case of the dd states discussed in Sect. 3.1. Therefore, the spin-orbit coupling needs not to be considered.

As is discussed in Sect. 3.2, the spin-orbit coupling is non-vanishing between the configurations in which one electron occupies the same orbital and the other electron occupies a different orbital. Thus, non-vanishing matrix elements among $^3d\pi^*$ states are classified into the following two types: a) Coupling between $^3d\pi_1^*$ and $^3d\pi_2^*$ where π_1^* should be different from π_2^* , b) Coupling between $^3d_1\pi^*$ and $^3d_2\pi^*$ where d_1 should be different from d_2 . In the former case, the matrix element is reduced to integrals of the type $\langle \pi_1^* | \xi(r) \ell_u | \pi_2^* \rangle$. As is discussed above, this matrix element has only the three-center terms and is consequently negligibly small. The latter type of matrix element is reduced to integrals of the type $\langle d_1 | \xi(r) \ell_u | d_2 \rangle$. This integral has a one-center type and the

magnitude is of the order of ζ_{nd} . (For example, $\langle d_{z^2} | \xi(r) \ell_x | d_{x^2-y^2} \rangle = \sqrt{3}i \zeta_{nd}$, $\langle d_{xy} | \xi(r) \ell_x | d_{xz} \rangle = -i \zeta_{nd}$.) Because of the large magnitude of ζ_{nd} (see, for example, Table 3), the spin-orbit coupling mainly governs the magnitude of the splitting. The zero-field energies that can be obtained by diagonalizing the matrix discussed above may be somewhat different depending on whether the d -orbitals are degenerate or not. Of course the splitting is larger for the completely degenerate case. However, even if none of d -orbitals are degenerate as in the case of complexes of lower symmetry, the splitting is still of the order of ζ_{nd} .

Thus, the magnitude of the zero-field splitting is of the order of $100-1000 \text{ cm}^{-1}$ depending on the central metal ion. This is in the same order of magnitude as the splitting of the dd states.

As a typical example of $^3d\pi^*$ state, we shall briefly discuss $\text{Ru}(\text{bpy})_3^{2+}$. The luminescence of this complex has been assigned as the emission from $^3d\pi^*$ on the basis of the spectral location and lifetime ($\sim 10 \mu\text{s}$). For this type of complex, there have been a great number of debates, trying to understand whether the excitation is delocalized over the three ligands or is localized on one of ligands [31–38]. However, to review these contributions is not the main subject of this paper. We here simply try to illustrate a theoretical model to handle the sublevels of such complexes.

In the following, we briefly review the theory developed by Kober and Meyer [33] which is based on the localized model. In this localized model, we may consider only the central metal ion and one bpy ligand. The symmetry of the complex can therefore be treated as C_{2v} . In the C_{2v} point group, the occupied d -orbitals belong to be a_1 , b_2 , and a_2 representation, and the LUMO of the ligand belongs to the b_2 representation. Thus, we should consider three types of $d\pi^*$ states both in the singlet and the triplet states.

The d -orbitals are expressed as follows:

$$\begin{aligned} d_{a_1} &= d_{x^2-z^2} = \frac{\sqrt{3}}{2} d_0 - \frac{1}{2} (d_2 - d_{-2}) \\ d_{a_2} &= d_{xy} = -\sqrt{\frac{1}{2}} (d_2 - d_{-2}) \\ d_{b_2} &= d_{yz} = \sqrt{\frac{1}{2}} (d_1 - d_{-1}) \end{aligned} \quad (58)$$

The wavefunctions of the singlet states and the triplet sublevels associated with the above-stated $d\pi^*$ states are as follows, where the first representation, shown in the parentheses denotes the spatial part symmetry and the second representation refers to the space $\times$ spin total representation.

$$\begin{aligned} \psi(^1A_1; A_1) &= \sqrt{\frac{1}{2}} \{ |d_{a_2} \bar{d}_{a_2} d_{a_1} \bar{d}_{a_1} d_{b_2} \pi_{-b_2}| - |d_{a_2} \bar{d}_{a_2} d_{a_1} \bar{d}_{a_1} \pi_{b_2} b_2| \} \\ \psi(^3A_1; B_2) &= \sqrt{\frac{1}{2}} \{ |d_{a_2} \bar{d}_{a_2} d_{a_1} \bar{d}_{a_1} d_{b_2} \pi_{-b_2}| - |d_{a_2} \bar{d}_{a_2} d_{a_1} \bar{d}_{a_1} d_{b_2} \pi b_2| \} \end{aligned}$$

$$\begin{aligned}
\psi(^3A_1; B_1) &= \sqrt{\frac{1}{2}} i \{ |d_{a_2} \bar{d}_{a_2} d_{a_1} \bar{d}_{a_1} \bar{d} \bar{\pi}_{b_2}| + |d_{a_2} \bar{d}_{a_2} d_{a_1} \bar{d}_{a_1} d_{b_2} \pi b_2| \} \\
\psi(^3A_1; A_2) &= \sqrt{\frac{1}{2}} \{ |d_{a_2} \bar{d}_{a_2} d_{a_1} \bar{d}_{a_1} d_{a_2} \bar{\pi}_{b_2}| + |d_{a_2} \bar{d}_{a_2} d_{a_1} \bar{d}_{a_1} \bar{d}_{b_2} \pi b_2| \} \\
\psi(^1B_1; B_1) &= \sqrt{\frac{1}{2}} \{ |d_{b_2} \bar{d}_{b_2} d_{a_1} \bar{d}_{a_1} d_{a_2} \bar{\pi}_{b_2}| - |d_{b_2} \bar{d}_{b_2} d_{a_1} \bar{d}_{a_1} \bar{d}_{a_2} \pi b_2| \} \\
\psi(^3B_1; A_2) &= \sqrt{\frac{1}{2}} \{ |d_{b_2} \bar{d}_{b_2} d_{a_1} \bar{d}_{a_1} \bar{d}_{a_2} \bar{\pi}_{b_2}| - |d_{b_2} \bar{d}_{b_2} d_{a_1} \bar{d}_{a_1} d_{a_2} \pi b_2| \} \\
\psi(^3B_1; A_1) &= \sqrt{\frac{1}{2}} i \{ |d_{b_2} \bar{d}_{b_2} d_{a_1} \bar{d}_{a_1} \bar{d}_{a_2} \bar{\pi}_{b_2}| + |d_{b_2} \bar{d}_{b_2} d_{a_1} \bar{d}_{a_1} d_{a_2} \pi b_2| \} \\
\psi(^3B_1; B_2) &= \sqrt{\frac{1}{2}} \{ |d_{b_2} \bar{d}_{b_2} d_{a_1} \bar{d}_{a_1} d_{a_2} \bar{\pi}_{b_2}| + |d_{b_2} \bar{d}_{b_2} d_{a_1} \bar{d}_{a_1} \bar{d}_{a_2} \pi b_2| \} \\
\psi(^1B_2; B_2) &= \sqrt{\frac{1}{2}} \{ |d_{a_2} \bar{d}_{a_2} d_{b_1} \bar{d}_{b_2} d_{a_1} \bar{\pi}_{b_2}| - |d_{a_2} \bar{d}_{a_2} d_{b_2} \bar{d}_{b_1} \bar{d}_{a_1} \pi b_2| \} \\
\psi(^3B_2; A_1) &= \sqrt{\frac{1}{2}} \{ |d_{a_2} \bar{d}_{a_2} d_{b_2} \bar{d}_{b_2} \bar{d}_{a_1} \bar{\pi}_{b_2}| - |d_{a_2} \bar{d}_{a_2} d_{b_2} \bar{d}_{b_2} d_{a_1} \pi b_2| \} \\
\psi(^3B_2; A_2) &= \sqrt{\frac{1}{2}} i \{ |d_{a_2} \bar{d}_{a_2} d_{b_1} \bar{d}_{b_2} \bar{d}_{a_1} \bar{\pi}_{b_2}| + |d_{a_2} \bar{d}_{a_2} d_{b_2} \bar{d}_{b_1} d_{a_1} \pi b_2| \} \\
\psi(^3B_2; B_1) &= \sqrt{\frac{1}{2}} \{ |d_{a_2} \bar{d}_{a_2} d_{b_1} \bar{d}_{b_2} d_{a_1} \bar{\pi}_{b_2}| + |d_{a_2} \bar{d}_{a_2} d_{b_2} \bar{d}_{b_2} \bar{d}_{a_1} \pi b_2| \} \quad (59)
\end{aligned}$$

Thus, nine wavefunctions shown above are classified into three wavefunctions of A_1 symmetry, three wavefunctions of A_2 symmetry, three wavefunctions of B_1 symmetry, and three wavefunctions of B_2 symmetry. The energies of the sublevels are then obtained by diagonalizing the four three-dimensional matrices with respect to the total Hamiltonian including the spin-orbit coupling. One difficulty is that the energy separations (even the energy order) among the three occupied d -orbitals are unknown. Kober and Meyer [33] calculated the energies of the sublevels by parameterizing the unknown terms.

From these calculations, Kober and Meyer concluded that four sublevels exist in a lower energy region, and the energy separations among these levels are 10–100 cm^{-1} . The sublevel structures of $\text{Ru}(\text{bpy})_3^{2+}$ were obtained by Hager and Crosby [38] by analyzing the temperature dependence of the phosphorescence lifetime. The results are schematically shown in Fig. 14. The figure shows that three levels were determined. The three levels have also been measured directly in the emission spectrum by Yersin and Braun [39] as sharp lines. The energy separation to the second and the third electronic states are 9 and 61 cm^{-1} , respectively, in good agreement with the results of Hager and Crosby. If the experiment were extended to much higher temperature range, the fourth level

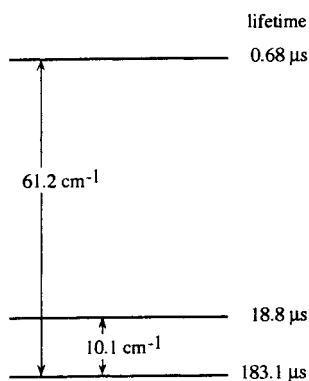


Fig. 14. The energies and the decay rate constants of $\text{Ru}(\text{bpy})_3^{2+}$ obtained by analyzing the temperature dependence of the phosphorescence lifetime after Hager and Crosby [38]. The lowest three levels have also been directly observed spectroscopically by Yersin and Braun [39]. The energy separation is quite in agreement with the results shown in the figure

predicted by Kober and Meyer might be experimentally detected. Thus, the theoretical prediction is not inconsistent with the experimental data.

3.4

Spin Sublevels of the Hexanuclear Molybdenum(II) Chloride Cluster

As an example of the spin sublevels of metal cluster, we here discuss the hexanuclear molybdenum(II) chloride cluster in, $[\text{Mo}_6\text{Cl}_{14}]^{2-}$. As is shown in Fig. 15, the cluster is composed of six (Mo(II) ions and the point group is O_h . Since the cluster has 48 d -electrons a theoretical treatment of the spin sublevels appears quite formidable. However, because of the high symmetry, the theoretical treatment can be simplified by the proper use of group theory. In the following, we briefly review the theory developed by Azumi and Saito [40] together with the experiments carried out by Saito et al. [41] and Miki et al. [42].

Molecular orbitals are constructed as a linear combination of the 48 d atomic orbitals of the six molybdenum(II) ions. The symmetry-adapted molecular orbitals are as follows:

$$\varphi(t_{1u}, \alpha) = \frac{1}{\sqrt{2}} (\theta_1 - \theta_4)$$

$$\varphi(t_{1u}, \beta) = \frac{1}{\sqrt{2}} (\theta_2 - \theta_5)$$

$$\varphi(t_{1u}, \gamma) = \frac{1}{\sqrt{2}} (\theta_3 - \theta_6)$$

$$\varphi(t_{2g}, \xi) = \frac{1}{2} (-\xi_3 + \xi_6 - \eta_{12} + \eta_{15})$$

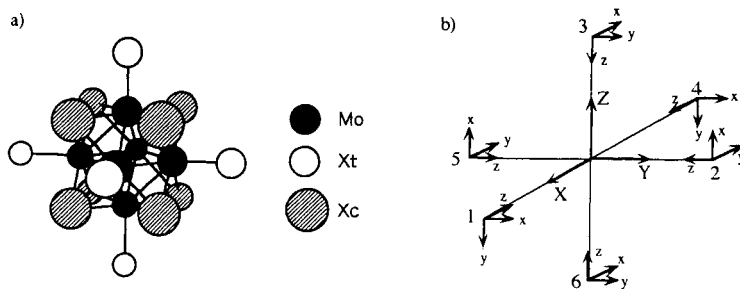


Fig. 15. a) Structure of $[\text{MoCl}_{14}]^{2-}$. Xt and Xc are, respectively, the terminal and cap Cl^- ligand. b) Coordinate system and numbering of Mo atoms

$$\varphi(t_{2g}, \eta) = \frac{1}{2} (\xi_1 - \xi_4 + \eta_3 + \eta_6)$$

$$\varphi(t_{2g}, \zeta) = \frac{1}{2} (\xi_2 - \xi_5 - \eta_1 + \eta_4)$$

$$\varphi(t_{2u}, \xi) = \frac{1}{\sqrt{2}} (\epsilon_1 - \epsilon_4)$$

$$\varphi(t_{2u}, \eta) = \frac{1}{\sqrt{2}} (\epsilon_2 - \epsilon_5)$$

$$\varphi(t_{2u}, \zeta) = \frac{1}{\sqrt{2}} (\epsilon_3 - \epsilon_6)$$

$$\varphi(e_g, \theta) = \frac{1}{2} (\epsilon_1 - \epsilon_2 + \epsilon_4 - \epsilon_5)$$

$$\varphi(e_g, \epsilon) = \frac{1}{\sqrt{12}} (\epsilon_1 + \epsilon_2 - 2\epsilon_3 + \epsilon_4 + \epsilon_5 - 2\epsilon_6) \quad (60)$$

Where the ξ_i etc. appearing on the right hand side are the d -orbitals of the i atom shown in Fig. 15. The second argument shown in the parentheses denotes the transformation properties. That is, α , β , and γ mean that they transform identically as x , y and z , respectively, in the point group O, ξ , η , ζ , θ , ϵ mean that they transform identically as these d atomic orbitals [Eq. (6) and (7)].

The HOMO is t_{2g} and the LUMO is t_{1u} . Promotion of one d -electron from the HOMO to LUMO produces four triplet states: ${}^3A_{2u}$, ${}^3E_u$, ${}^3T_{1u}$, and ${}^3T_{2u}$, of which ${}^3T_{2u}$ is the lowest.

We focus attention on the spin sublevels associated with the lowest triplet state. ${}^3T_{1u}$, because the sublevels of higher triplet states cannot be studied experimentally. In the point group of O, the three triplet spin functions belong to T_{1g} . Thus, as is clear from the direct product,

$$T_{1u} \times T_{1g} = A_{1u} + T_{1u} + E_u + T_{2u} \quad (61)$$

the lowest triplet state is split into four sublevels whose total (space $\times$ spin) symmetries are A_{1u} , T_{1u} , E_u , and T_{2u} . The wavefunctions of these sublevels are obtained as follows:

$$\begin{aligned}
 \Psi(A_{1u}, e) &= \frac{1}{\sqrt{12}} \left\{ \begin{array}{l} -|\xi\bar{\xi}\eta\bar{\eta}\zeta\bar{\beta}| - |\xi\bar{\xi}\zeta\bar{\zeta}\eta\bar{\gamma}| + |\xi\bar{\xi}\eta\bar{\eta}\zeta\beta| + |\xi\bar{\xi}\zeta\bar{\zeta}\eta\gamma| \\ -i|\xi\bar{\xi}\eta\bar{\eta}\zeta\bar{\alpha}| - i|\eta\bar{\eta}\zeta\bar{\zeta}\bar{\gamma}| - i|\xi\bar{\xi}\eta\bar{\eta}\zeta\alpha| - i|\eta\bar{\eta}\zeta\bar{\zeta}\xi\gamma| \\ -|\xi\bar{\xi}\zeta\bar{\zeta}\eta\alpha| - |\xi\bar{\xi}\zeta\bar{\zeta}\eta\alpha| - |\eta\bar{\eta}\zeta\bar{\zeta}\beta| - |\eta\bar{\eta}\zeta\bar{\zeta}\xi\beta| \end{array} \right\} \\
 \Psi(E_u, \theta) &= \frac{1}{\sqrt{24}} \left\{ \begin{array}{l} |\xi\bar{\xi}\eta\bar{\eta}\bar{\beta}| + |\xi\bar{\xi}\zeta\bar{\zeta}\eta\bar{\gamma}| - |\xi\bar{\xi}\eta\bar{\eta}\beta| - |\xi\bar{\xi}\zeta\bar{\zeta}\eta\gamma| \\ +i|\xi\bar{\xi}\eta\bar{\eta}\zeta\bar{\alpha}| + i|\eta\bar{\eta}\zeta\bar{\zeta}\bar{\gamma}| + i|\xi\bar{\xi}\eta\bar{\eta}\zeta\alpha| + i|\eta\bar{\eta}\zeta\bar{\zeta}\xi\gamma| \\ -2|\xi\bar{\xi}\zeta\bar{\zeta}\eta\alpha| - 2|\xi\bar{\xi}\zeta\bar{\zeta}\eta\alpha| - 2|\eta\bar{\eta}\zeta\bar{\zeta}\gamma| - 2|\eta\bar{\eta}\zeta\bar{\zeta}\xi\beta| \end{array} \right\} \\
 \Psi(E_u, \varepsilon) &= \frac{1}{\sqrt{8}} \left\{ \begin{array}{l} -|\xi\bar{\xi}\eta\bar{\eta}\zeta\bar{\beta}| - |\xi\bar{\xi}\zeta\bar{\zeta}\eta\bar{\gamma}| + |\xi\bar{\xi}\eta\bar{\eta}\zeta\beta| + |\xi\bar{\xi}\zeta\bar{\zeta}\eta\gamma| \\ +i|\xi\bar{\xi}\eta\bar{\eta}\zeta\bar{\alpha}| + i|\eta\bar{\eta}\zeta\bar{\zeta}\bar{\gamma}| + i|\xi\bar{\xi}\eta\bar{\eta}\zeta\alpha| + i|\eta\bar{\eta}\zeta\bar{\zeta}\xi\gamma| \end{array} \right\} \\
 \Psi(T_{1u}, \alpha) &= \frac{1}{\sqrt{8}} \left\{ \begin{array}{l} -|\xi\bar{\xi}\eta\bar{\eta}\zeta\bar{\alpha}| - |\xi\bar{\xi}\zeta\bar{\zeta}\eta\bar{\alpha}| - |\eta\bar{\eta}\zeta\bar{\zeta}\xi\gamma| - |\eta\bar{\eta}\zeta\bar{\zeta}\xi\bar{\gamma}| \\ +i|\xi\bar{\xi}\zeta\bar{\zeta}\eta\bar{\alpha}| + i|\eta\bar{\eta}\zeta\bar{\zeta}\xi\beta| + i|\xi\bar{\xi}\zeta\bar{\zeta}\alpha| + i|\eta\bar{\eta}\zeta\bar{\zeta}\xi\beta| \end{array} \right\} \\
 \Psi(T_{1u}, \beta) &= \frac{1}{\sqrt{8}} \left\{ \begin{array}{l} |\xi\bar{\xi}\eta\bar{\eta}\zeta\bar{\beta}| + |\xi\bar{\xi}\eta\bar{\eta}\zeta\bar{\beta}| + |\xi\bar{\xi}\zeta\bar{\zeta}\eta\gamma| + |\xi\bar{\xi}\zeta\bar{\zeta}\eta\bar{\gamma}| \\ -|\xi\bar{\xi}\zeta\bar{\zeta}\eta\bar{\alpha}| - |\eta\bar{\eta}\zeta\bar{\zeta}\bar{\beta}| + i|\xi\bar{\xi}\zeta\bar{\zeta}\eta\alpha| + |\eta\bar{\eta}\zeta\bar{\zeta}\xi\beta| \end{array} \right\} \\
 \Psi(T_{1u}, \gamma) &= \frac{1}{\sqrt{8}} \left\{ \begin{array}{l} |\xi\bar{\xi}\eta\bar{\eta}\zeta\bar{\alpha}| + |\eta\bar{\eta}\zeta\bar{\zeta}\bar{\gamma}| - |\xi\bar{\xi}\eta\bar{\eta}\zeta\alpha| - |\eta\bar{\eta}\zeta\bar{\zeta}\xi\gamma| \\ -|\xi\bar{\xi}\eta\bar{\eta}\zeta\bar{\beta}| - i|\xi\bar{\xi}\zeta\bar{\zeta}\eta\bar{\gamma}| + i|\xi\bar{\xi}\eta\bar{\eta}\zeta\beta| + i|\xi\bar{\xi}\zeta\bar{\zeta}\eta\gamma| \end{array} \right\} \\
 \Psi(T_{2u}, \xi) &= \frac{1}{\sqrt{8}} \left\{ \begin{array}{l} -|\xi\bar{\xi}\eta\bar{\eta}\zeta\bar{\alpha}| - |\xi\bar{\xi}\eta\bar{\eta}\xi\alpha| - |\eta\bar{\eta}\zeta\bar{\zeta}\xi\gamma| - |\eta\bar{\eta}\zeta\bar{\zeta}\xi\bar{\gamma}| \\ -i|\xi\bar{\xi}\zeta\bar{\zeta}\eta\bar{\alpha}| - i|\eta\bar{\eta}\zeta\bar{\zeta}\xi\bar{\beta}| - i|\xi\bar{\xi}\zeta\bar{\zeta}\eta\alpha| - i|\eta\bar{\eta}\zeta\bar{\zeta}\xi\beta| \end{array} \right\} \\
 \Psi(T_{2u}, \eta) &= \frac{1}{\sqrt{8}} \left\{ \begin{array}{l} -|\xi\bar{\xi}\eta\bar{\eta}\zeta\bar{\beta}| - |\xi\bar{\xi}\eta\bar{\eta}\zeta\bar{\beta}| - |\xi\bar{\xi}\zeta\bar{\zeta}\eta\gamma| - |\xi\bar{\xi}\zeta\bar{\zeta}\eta\bar{\gamma}| \\ -|\xi\bar{\xi}\zeta\bar{\zeta}\eta\bar{\alpha}| - i|\eta\bar{\eta}\zeta\bar{\zeta}\xi\bar{\beta}| + |\xi\bar{\xi}\zeta\bar{\zeta}\eta\alpha| + |\eta\bar{\eta}\zeta\bar{\zeta}\xi\beta| \end{array} \right\} \\
 \Psi(T_{2u}, \zeta) &= \frac{1}{\sqrt{8}} \left\{ \begin{array}{l} -|\xi\bar{\xi}\eta\bar{\eta}\zeta\bar{\alpha}| - |\eta\bar{\eta}\zeta\bar{\zeta}\bar{\gamma}| + |\xi\bar{\xi}\eta\bar{\eta}\zeta\alpha| + |\eta\bar{\eta}\zeta\bar{\zeta}\xi\gamma| \\ -i|\xi\bar{\xi}\eta\bar{\eta}\zeta\bar{\beta}| - i|\xi\bar{\xi}\zeta\bar{\zeta}\eta\bar{\gamma}| + i|\xi\bar{\xi}\eta\bar{\eta}\zeta\beta| + i|\xi\bar{\xi}\zeta\bar{\zeta}\eta\gamma| \end{array} \right\}
 \end{aligned} \tag{62}$$

These wavefunctions are constructed in such a way that they transform exactly identical to one of p or d atomic orbitals. The second argument in the parentheses denotes the transformation properties. This choice of wavefunction is discussed in Section 3.1.2 [see Eq. (27)], and is very important in diagonalization. Once the wavefunctions are constructed in such a way, all these wavefunctions are diagonal with respect to the spin orbit interaction. Thus, no more diagonalization is necessary.

The diagonal terms then are as follows:

$$\begin{aligned}
 \langle A_{1u} | H_{SO} | A_{1u} \rangle &= \zeta_{4d} \\
 \langle E_u | H_{SO} | E_u \rangle &= -\frac{1}{2} \zeta_{4d} \\
 \langle T_{1u} | H_{SO} | T_{1u} \rangle &= \frac{1}{2} \zeta_{4d} \\
 \langle T_{2u} | H_{SO} | T_{2u} \rangle &= \frac{1}{2} \zeta_{4d}
 \end{aligned} \tag{63}$$

where ζ_{4d} is the spin-orbit coupling parameter for the 4d electron of Mo. Thus, in the approximation of the first order spin-orbit coupling (that is, in the diagonalization among the sublevels derived from ${}^3T_{1u}$ state), the E_u and T_{2u} sublevels are degenerate.

In order to examine whether the degeneracy of E_u and T_{2u} is lifted, the second order spin-orbit coupling with the sublevels derived from the higher triplet states is examined. The relevant matrix elements are as follows:

$$\begin{aligned}
 \langle E_u({}^3T_{1u}) | H_{SO} | E_u({}^3T_{2u}) \rangle &= 0 \\
 \langle T_{2u}({}^3T_{1u}) | H_{SO} | T_{2u}({}^3T_{2u}) \rangle &= 0 \\
 \langle T_{2u}({}^3T_{1u}) | H_{SO} | T_{2u}({}^3A_{2u}) \rangle &= \frac{1}{4\sqrt{3}} \zeta_{4d} \\
 \langle T_{2u}({}^3T_{1u}) | H_{SO} | T_{2u}({}^3E_u) \rangle &= \frac{3}{\sqrt{6}} \zeta_{4d}
 \end{aligned} \tag{64}$$

where the parent triplet states are designated in parentheses. The E_u sublevel remains unchanged. The T_{1u} sublevel, on the other hand, interacts with sublevels associated with the third and the fourth triplet states. Thus, the T_{2u} sublevel in the lowest triplet state is somewhat stabilized by this interaction, and the degeneracy is lifted. The splitting is schematically shown in Fig. 16. The sublevels associated with ${}^3T_{1u}$ are (in order of increasing energy) T_{2u} , E_u , T_{1u} and A_{1u} . Since at this moment we do not know the energy separations between ${}^3T_{1u}$ and ${}^3A_{2u}$ and between ${}^3T_{1u}$ and ${}^3E_u$, the effect of the second-order spin-orbit coupling cannot be obtained quantitatively. We can only presume that the splitting between the lowest two sublevels is very small.

The sublevel structures have been determined experimentally by Saito et al. [41] and Miki et al. [42]. Since the splitting is expected to be of the order of ζ_{4d} of Mo, the ODMR method cannot be applied. These authors determined the zero-field splitting, the lifetime and the relative radiative rate constants for individual sublevels by analyzing the temperature dependence of the phosphorescence lifetime and the spectral distribution. The results are schematically shown in Fig. 17; they are strikingly in accord with the theoretical prediction. The lowest two sublevels are somewhat separated. The energy gap between T_{2u} and T_{1u} is observed as 710 cm^{-1} , and this value is quite close to the ζ_{4d} of Mo. We

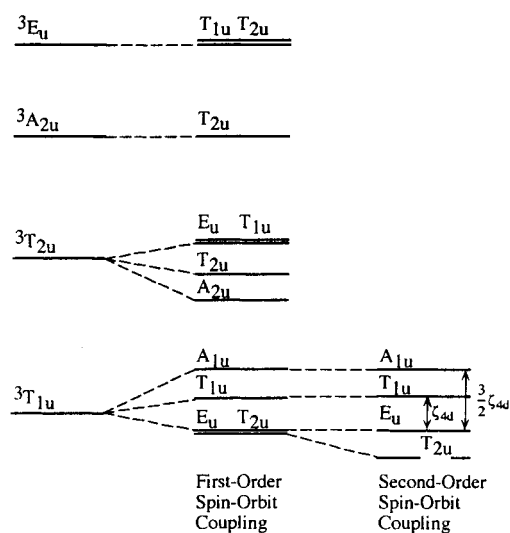


Fig. 16. Schematic representation of the spin sublevels associated with the lowest triplet state, $^3T_{1u}$, of the hexanuclear molybdenum cluster ion, $[\text{Mo}_6\text{Cl}_{14}]^{2-}$

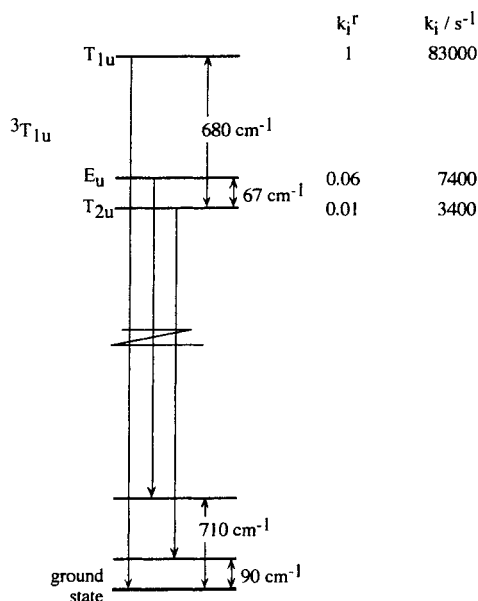


Fig. 17. Experimental results on the sublevel energies, relative radiative rate constants, total decay rate constants for the lower three spin sublevels associated with the lowest triplet state, $^3T_{1u}$. The phosphorescence from the E_u and T_{2u} sublevel is allowed by the vibronic coupling with nontotally symmetric vibrations of 710 cm^{-1} and 904 cm^{-1} , respectively

expert the A_{1u} state. However it is difficult, using the temperature dependence method, to locate a considerably lower emissive level above the emissive level.

Figure 17 also shows why the emission from E_u and T_{2u} should occur. The transitions are group-theoretically forbidden. The emissions from the E_u and T_{2u} sublevels gain radiative character by the vibronic coupling with non-totally symmetric vibrations of 710 cm^{-1} and 90 cm^{-1} , respectively.

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4

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Magnetic and Spectroscopic Properties of $\text{Os}_2(\text{O}_2\text{CR})_4\text{Cl}_2$. Evidence for a $^3(\delta^*\pi^*)$ Ground State*

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Variable temperature magnetic susceptibility measurements have been made for $\text{Os}_2\text{piv}_4\text{Cl}_2$ (piv is trimethylacetate). Electronic spectra of $\text{Os}_2(\text{O}_2\text{CR})_4\text{Cl}_2$ (O_2CR is piv, butyrate, acetate) in fluid solutions and CsCl pellets have been examined, and polarized single crystal spectra have been measured for $\text{Os}_2\text{piv}_4\text{Cl}_2$. The measurements have been extended to liquid helium temperature for solid samples. The temperature-dependent magnetic behavior and the presence of a $\delta \rightarrow \delta^*$ transition in the absorption spectrum near 850 nm (solution $\epsilon = 70 \text{ M}^{-1} \text{ cm}^{-1}$, z-polarized, structured in $\nu(\text{Os}_2) \sim 220 \text{ cm}^{-1}$) indicate that the ground state of these molecules is $^3E_u(\delta^*\pi^*)$. Tentative assignments have been made for the z-polarized bands at 1200 nm (solution $\epsilon = 14 \text{ M}^{-1} \text{ cm}^{-1}$, structured in $\nu(\text{Os}_2)$ at low temperature) and 394 nm (solution $\epsilon = 11,600 \text{ M}^{-1} \text{ cm}^{-1}$) as, respectively, spin-forbidden $\delta^* \rightarrow \pi^*$ and spin-allowed $\pi(\text{Cl}) \rightarrow \pi^*(\text{Os}_2)$ transitions. The latter assignment is supported by the observation of a large red-shift to 455 nm (solution $\epsilon = 12,600 \text{ M}^{-1} \text{ cm}^{-1}$) for the analogous band of $\text{Os}_2\text{piv}_4\text{Br}_2$.

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* Dedicated to the memory of Günter Gliemann.

1

Introduction

The first multiply bonded binuclear $\text{Os}_2(\text{III,III})$ complex to be structurally characterized was $\text{Os}_2\text{hp}_4\text{Cl}_2$ (hp is 2-hydroxypyridinate) [1], followed shortly by the carboxylate-bridged analogues [2], $\text{Os}_2(\text{O}_2\text{CR})_4\text{Cl}_2$. While these compounds all have Os_2 distances (2.30–2.36 Å) that are reasonably consistent with the Os–Os triple bonds that should formally result from their d-electron count [3, 4], they are unusual in that they are strongly paramagnetic [2b]. The expected ground state is a singlet, $(\delta^*)^2$, assuming the standard ordering ($\sigma^* > \pi^* > \delta^*$) of metal-metal antibonding orbitals [3]. Indeed, both the $\text{Re}_2\text{Cl}_4(\text{PMe}_3)_4$ [5] and $\text{Os}_2\text{X}_8^{2-}$ ($\text{X} = \text{Cl}, \text{Br}$) [6] complexes are diamagnetic, in accord with a $(\delta^*)^2$ ground state.

On the other hand, $\text{Ru}_2(\text{O}_2\text{CR})_4^+$ complexes have *quartet* $(\pi^*)^2\delta^*$ ground states [7]. On the basis of theoretical calculations [8], this high-spin ground state has been attributed to a near degeneracy of the π^* and δ^* orbitals, so that spin-pairing energies (two-electron terms) predominate over one-electron terms. The near degeneracy was specifically attributed to a π -donor interaction of the carboxylate HOMO, a filled, internally nonbonding π -symmetry level, with the δ^* metal-metal level. The δ^* level is thereby destabilized to an energy close to that of π^* . Support for this picture has come from experimental [9a] and theoretical [9b] studies of triazenate-bridged complexes such as $\text{Ru}_2(\text{di}(p\text{-tolyl})\text{-triazenate})_4$, which has a diamagnetic $(\pi^*)^4$ ground state. Since the triazenate ligands are much stronger electron donors than carboxylates, the δ^* level is about 1 eV higher than π^* [9].

The observed paramagnetism [2b] of the $\text{Os}_2(\text{III,III})$ carboxylates could indicate a triplet ground state with a $\pi^*\delta^*$ or $(\pi^*)^2$ configuration. However, the reported magnetic moments (1.6–2 B.M. at room temperature [2b, 10, 11] are considerably less than the triplet spin-only value, and decrease at lower temperature. In an attempt to understand this puzzling magnetic behavior, we have made extensive studies of both the magnetic and spectroscopic properties of $\text{Os}_2(\text{O}_2\text{CR})_4\text{Cl}_2$ complexes. Our work indicates that the ground state is $^3E_u(\delta^*\pi^*)$.

2

Experimental Section

The compounds $\text{Os}_2\text{ac}_4\text{Cl}_2$ and $\text{Os}_2\text{bu}_4\text{Cl}_2$ (ac is acetate; bu is butyrate) were prepared by the literature method [2b]. These and other compounds described below are air stable as solids. Samples of the butyrate complex are often contaminated with a deep-blue impurity. Pure (brown) samples were obtained in low yield by careful recrystallization from CH_2Cl_2 /hexane.

The compound $\text{Os}_2\text{piv}_4\text{Cl}_2$ (piv is trimethylacetate) was prepared as follows: $\text{Os}_2\text{ac}_4\text{Cl}_2$ was stirred in molten Hpiv in an open Ehrlenmeyer flask on a hot plate for 2 h. Heating was maintained such that the Hpiv refluxed gently on the sides of the flask. Prolonged heating is necessary to achieve complete elimination of acetic acid. After cooling and solidification of Hpiv, hexane was added, and

the slurry was filtered and washed with hexane to yield a microcrystalline greenish-brown solid. The solid was dissolved in CH_2Cl_2 , and Hpiv was added to the filtered solution to double the volume. Very slow evaporation over several days resulted in the formation of glistening black cubic crystals. When the Hpiv had finally solidified, hexane was added and the product was filtered and washed with hexane. *Calcd(fd)*: C, 28.07 (28.13); H, 4.24 (4.16). Highly crystalline material was also obtained from neat CH_2Cl_2 solution, but it rapidly lost solvent of crystallization (with loss of crystallinity) upon removal from the mother liquor.

The compound $\text{Ru}_2\text{piv}_4\text{Cl}$ was prepared from $\text{Ru}_2\text{ac}_4\text{Cl}$ and molten Hpiv as described above for the $\text{Os}_2(\text{III,III})$ derivative. The resulting brown powder was recrystallized from CH_2Cl_2 /hexane and vacuum-dried. *Calcd(fd)*: C, 37.41 (36.43); H, 5.65 (5.63).

Attempts to isolate $\text{Os}_2\text{piv}_4\text{Br}_2$ were not successful. However, adjustment of a 2×10^{-4} M solution of $\text{Os}_2\text{piv}_4\text{Cl}_2$ to 2×10^{-2} M in tetraethylammonium bromide resulted in rapid (< 5 min) and complete conversion to a complex with a spectrum attributable to the dibromo derivative. No attempt was made rigorously to exclude moisture in these experiments, and it is likely that the axial substitution reaction would otherwise be much slower [12]. On a longer time scale, > 15 min, an additional slow reaction became evident. As a similar reaction was observed in the presence of excess tetraethylammonium chloride, substitution of halide for bridging carboxylate probably takes place. A partially substituted compound of this type has been structurally characterized [13], and the $\text{Os}_2\text{X}_8^{2-}$ anions have been prepared from the acetate under forcing conditions [6].

Crystals of $\text{Os}_2\text{piv}_4\text{Cl}_2$ were examined by X-ray photographic methods. They were determined to be body-centered tetragonal, $4/m$ Laue symmetry, $a = b = 11.5$ Å and $c = 10.5$ Å, with systematic absences consistent with any of the three space groups $\text{I4}_1\bar{1}$, I4 , and $\text{I4}/m$. Isomorphism with the $\text{I4}/m$ structures of $\text{M}_2\text{piv}_4\text{Cl}_2$ ($\text{M} = \text{Re}, \text{Tc}$) [14] seems very probable in view of the close agreement in unit cell parameters. Since numerous $\text{Os}_2(\text{O}_2\text{CR})_4\text{Cl}_2$ structures are available [2, 11], we did not carry the X-ray analysis of $\text{Os}_2\text{piv}_4\text{Cl}_2$ any further.

Raman spectra were measured at the University of Texas, Austin, in the laboratory of W.H. Woodruff (current address: INC-14, Los Alamos National Laboratory, Los Alamos, NM 87545).

Room-temperature magnetic susceptibilities were determined for solid samples with a Faraday balance that was calibrated with $\text{HgCo}(\text{SCN})_4$. Variable temperature magnetic susceptibility measurements were performed at the University of Southern California SQUID Instrumentation Facility on a SHE Corporation 905 VTS SQUID susceptometer employing a magnetic field of 10 kG. Identical results were obtained for polycrystalline and finely ground samples of $\text{Os}_2\text{piv}_4\text{Cl}_2$. Magnetic moments were calculated from the susceptibility data using calculated [15b] diamagnetic susceptibilities of -239×10^{-6} ($\text{Os}_2\text{ac}_4\text{Cl}_2$), -334×10^{-6} ($\text{Os}_2\text{bu}_4\text{Cl}_2$), and -381×10^{-6} emu/mol ($\text{Os}_2\text{piv}_4\text{Cl}_2$).

Low-temperature electronic absorption spectra were measured as described previously [16]. Thin single crystals of $\text{Os}_2\text{piv}_4\text{Cl}_2$ suitable for polarized spectroscopy were obtained by polishing large crystals. Both axial (perpendicular to the c axis) and " σ/π " (containing the c axis) faces were obtained in this way.

3 Raman Spectra

Clark et al. [17] have reported extensive vibrational spectroscopic studies of $\text{Os}_2(\text{O}_2\text{Cr})_4\text{Cl}_2$ complexes. Our Raman spectrum of $\text{Os}_2\text{ac}_4\text{Cl}_2$ (room temperature, 457.9 nm (preresonant) excitation) shows a strong line at 229 cm^{-1} as well as weak features at 293 and 191 cm^{-1} . The strong line is in perfect agreement with Clark's report [17b], where evidence for assignment to $\nu(\text{Os}_2)$ was presented. (For comparison, $\text{Re}_2\text{ac}_4\text{Cl}_2$ has $\nu(\text{Re}_2)$ [18] at 289 cm^{-1} ; as expected from structural comparisons [14], $\nu(\text{M}_2)$ is higher for quadruply bonded $\text{Re}_2(\text{III},\text{III})$). The 293 cm^{-1} line is attributable to $\nu(\text{OsCl})$, while the 191 cm^{-1} feature is probably $\delta(\text{Os}_2\text{O})$. Clark [17a] also reported $\nu(\text{Os}_2) = 228\text{ cm}^{-1}$ for $\text{Os}_2\text{bu}_4\text{Cl}_2$.

We have measured the Raman spectrum of crystalline $\text{Os}_2\text{piv}_4\text{Cl}_2$ (457.9 nm excitation); it shows a strong line at 245 cm^{-1} , attributable to $\nu(\text{Os}_2)$, together with weak features at 323 and $\sim 200\text{ cm}^{-1}$. The value of $\nu(\text{Os}_2)$ is a little higher than the highest previously reported frequency for an $[\text{Os}(\text{III})]_2$ carboxylate complex (236 cm^{-1}) [17b]. The compound was sufficiently soluble in CH_2Cl_2 to allow measurement of the solution Raman spectrum; $\nu(\text{Os}_2)$, at 241 cm^{-1} , was found to be strongly polarized ($\rho = 0.4$), consistent with the assignment [17].

For comparison with $\text{Os}_2\text{piv}_4\text{Cl}_2$, we also determined the Raman spectrum of solid $\text{Ru}_2\text{piv}_4\text{Cl}$ (647.1 nm excitation). It shows a strong $\nu(\text{Ru}_2)$ line at 349 cm^{-1} along with weaker features at 465 ($\nu(\text{RuO})$), 210 ($\delta(\text{ORuO})$), 173 ($\delta(\text{Ru}_2\text{O})$), and 156 cm^{-1} ($\nu(\text{RuCl})$). The $\nu(\text{Ru}_2)$ value is the highest reported for a $\text{Ru}_2(\text{O}_2\text{Cr})_4\text{Cl}$ compound (the $\text{Ru}_2\text{ac}_4\text{Cl}$ frequency is 326 cm^{-1}) [19a]. The electronic absorption spectrum of $\text{Ru}_2\text{piv}_4\text{Cl}$ is entirely normal for a $^4B_{2u}(\pi^*)^2\delta^*$ ground state [19], with $\pi(\text{O}(\pi), d\pi) \rightarrow \pi^*$ at 450 nm and $\delta \rightarrow \delta^*$ at 1100 nm [20]. We therefore conclude that bridging pivalate ligands result in significantly higher (for a given metal ion and ground state) $\nu(\text{M}_2)$ values than acetate ligands. It is not clear whether this is an electronic effect (perhaps resulting from the strongly electron-donating nature of the *t*-butyl group), or a vibrational coupling effect (owing to a large rigid-body mass of *t*-butyl) [19a], or some combination thereof.

4 Magnetic Properties

Our measured value for the room-temperature (297 K) magnetic moment of a solid sample of $\text{Os}_2\text{ac}_4\text{Cl}_2$ (1.95 B.M.) is larger than the literature value (1.65 B.M. at 288 K) [2b, 10], but consistent with our room-temperature moment for $\text{Os}_2\text{piv}_4\text{Cl}_2$ (Fig. 1) and with the reported moment for $\text{Os}_2(2\text{-phenylbenzoate})_4\text{Cl}_2$ [11].

We have performed detailed studies of the temperature dependence of the magnetic susceptibility of $\text{Os}_2\text{piv}_4\text{Cl}_2$; the results (Fig. 1) are reasonably consistent with data reported for other derivatives [2b]. The temperature dependence of the moment is gently down to 40 K; below 40 K, the moment drops abruptly.

The data are not at all like those expected for a thermal equilibrium among discrete singlet and triplet states [11, 15, 21]; that is, they do not follow a simple

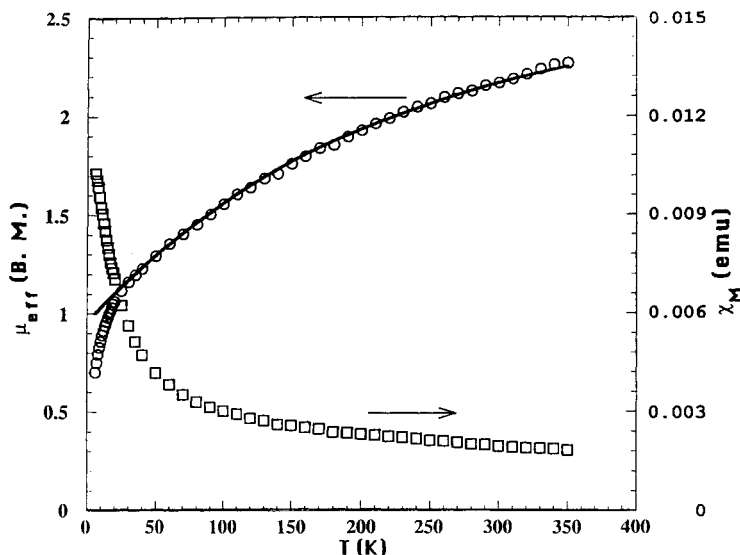


Fig. 1. Magnetic data (a diamagnetic correction has been applied) for solid $\text{Os}_2\text{pivCl}_2$: χ_M (□); μ_{eff} (○); Table 1. The solid line is a theoretical fit of the magnetic moment to Eq. (2). In this (nonlinear least-squares) fit, data below 20 K were weighted at 1% of the higher-temperature data

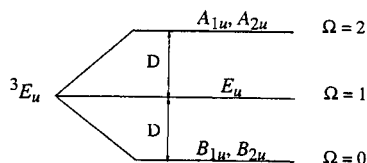
Boltzmann temperature dependence. What the data do resemble is the temperature dependence typical of strongly spin-orbit-split states [15], where second-order Zeeman terms yield [5, 22, 23] unusual temperature dependences, and, in particular, large χ_{TIP} terms because of mixing of the spin-orbit states by the magnetic field.

We now consider the possibility that the ground state may be a single, strongly spin-orbit-split state. There are two possible triplet ground states, $^3(\pi^*)^2$ and $^3(\pi^*\delta^*)$. First, consider the $^3A_{2g}(\pi^*)^2$ state. This state has no orbital degeneracy, so first-order spin-orbit coupling vanishes. Second-order spin-orbit coupling splits the state into A_{1g} ($S_z = 0$) and E_g ($S_z = \pm 1$) spin-orbit states, and the temperature dependence is predicted [23a] by Eq. 1; this equation has been shown to fit the data well for the compounds $\text{Os}_2(\text{di-}p\text{-toly-formamidine})_4\text{Cl}_2$ ($D = 1350 \text{ cm}^{-1}$, $g_{\text{eff}} = 1.802$) [23b] and $\text{Os}_2(\text{hp})_4\text{Cl}_2$ ($D = 1196 \text{ cm}^{-1}$, $g_{\text{eff}} = 1.922$) [11], as well as for $\text{Ru}_2(\text{II,II})$ compounds that have a $(\pi^*)^2(\delta^*)^2$ ground state [23a]:

$$\mu_{\text{eff}}^2 = 2(g_{\text{eff}})^2 \left[\frac{e^{-x} + (2/x)(1 - e^{-x})}{1 + 2e^{-x}} \right], \quad x = D/k_B T \quad (1)$$

Here, D is the zero-field splitting [24] $W(E_g) - W(A_{1g})$, k_B is the Boltzmann constant, and μ_{eff} is related to χ_M by a standard equation [15]. For positive D , Eq. (1) goes smoothly to $\mu_{\text{eff}} = 0 \text{ B.M.}$ at 0 K, while the low-temperature limit is 2.0 B.M. for negative D . In either case, agreement with the experimental data for $\text{Os}_2\text{piv}_4\text{Cl}_2$ is extremely poor for any reasonable parameter values, as was concluded by Cotton et al. [11] for (very similar) data obtained for the compound $\text{Os}_2(2\text{-phenylbenzoate})_4\text{Cl}_2$.

We therefore turn to the second triplet possibility, ${}^3E_u(\pi^*d^*)$. First-order spin-orbit coupling splits this orbitally degenerate state as sketched below. We include the D_{4h} symmetry labels and also values of the cylindrical quantum number Ω , which measures the total parallel angular momentum [22].



The sign of the zero-field splitting that is shown is the theoretical one [25, 26] for a less-than-half-filled π -symmetry orbital, and theory additionally predicts [25] $D = \zeta/2$; where ζ is the atomic spin-orbit coupling constant. The theoretical temperature dependence [22] of the magnetic moment is given by Eq. 2 [27].

$$\mu_{\text{eff}}^2 = (g_{\text{eff}})^2 \left[\frac{1 + e^{-x} + 9e^{-2x} + (8/x)(1 - e^{-2x})}{4(1 + e^{-x} + e^{-2x})} \right], \quad x = D/k_B T \quad (2)$$

Equation (2) our data well, as shown in Fig. 1, with $D = 331(9) \text{ cm}^{-1}$ and $g_{\text{eff}} = 1.91(1)$. Negative D does not fit the data, predicting a moment that does not drop below 3 B.M. (for $g_{\text{eff}} \approx 2$), and very little temperature dependence. The value of D is much smaller than expected from the theory, however, as ζ for Os is about 2500 cm^{-1} . We note that for D large with respect to $k_B T$, Eq. (2) reduces to Eq. (3).

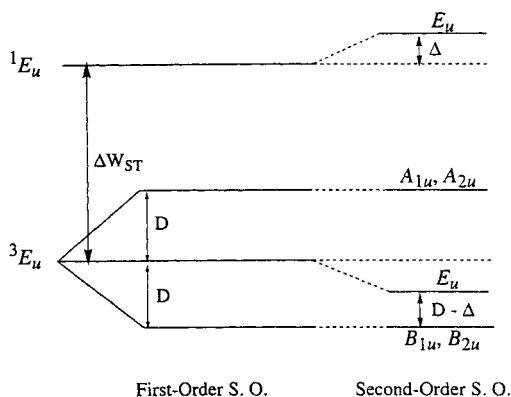
$$\mu_{\text{eff}}^2 = (g_{\text{eff}}/4)^2 [1 + 8/x] \quad (3)$$

Equation (3) is the sum of a weak Curie term (the spin angular momentum is partially cancelled by the orbital angular momentum in the $\Omega = 0$ levels) and χ_{TIP} term resulting from magnetic field mixing of the $\Omega = 0$ and $\Omega = 1$ levels. The actual fitted D is small enough for some thermal population of the E_u level (17% at room temperature), but Eq. (3) still fits the data quite well.

In actuality, 2nd-order spin-orbit coupling, neglected in Eq. (2), will lower the energy of the E_u spin-orbit component relative to the other components, because of interaction of $E_u({}^3E_u)$ with the ${}^1E_u$ state that also arises from the π^*d^* configuration, as sketched below. Additional off-diagonal couplings of ${}^3E_u$ spin-orbit states to $(\delta^*)^2$ and $(\pi^*)^2$ excited states are eliminated because these states are of gerade symmetry. The off-diagonal element connecting the two E_u states is substantial ($\zeta/2$) [25]. With ΔW_{ST} (the zero-order difference in the energy of the singlet and triplet E_u states) expected to be roughly 2000 cm^{-1} and ζ_{Os} about 2500 cm^{-1} , diagonalization of the 2×2 matrix for the E_u states (Eq. 4) yields an estimate of $\Delta \approx 600 \text{ cm}^{-1}$.

$$\Delta = ((\Delta W_{\text{ST}})^2 + D^2)^{1/2} - \Delta W_{\text{ST}} \quad (4)$$

The predicted value of the zero-field splitting, $D' = D = \Delta = 650 \text{ cm}^{-1}$, is in much better agreement with the experimental parameter from the magnetic measurements. Reduction of either ΔW_{ST} or ζ_{Os} (or both) by covalency effects from the values assumed in the calculation may account for the remaining discrepancy.



Moreover, the $3E_u$ state is in principle Jahn-Teller unstable, and any such distortion can lead to partial quenching of spin-orbit splittings [28].

We note that there is no point to introducing Δ as an adjustable parameter in the magnetic fits since Eq. (2) would not be parametrically changed unless there is substantial thermal population of the A_{1u}, A_{2u} levels, and this is precluded by the magnitude of D .

We wish to emphasize that this fit is plausible, and an improvement over the treatment of similar data for $\text{Os}_2(2\text{-phenylbenzoate})_4\text{Cl}_2$ [11]. The fit is not, however, conclusive, since the data could, as implied by Eq. (3), also be fit by a combination of a paramagnetic Curie-law "impurity" together with a temperature-independent intrinsic contribution to χ_M such as Eq. (1) gives in the limit $D \gg k_B T$. The amount of "impurity" that would be required appears to be implausibly large to us; for example, it is much larger than impurity contributions that have been required for fits to $3A_{2g}$ ground states of related molecules [11, 23].

The strict degeneracy of the B_{1u}, B_{2u} components of $3E_u$ holds only when second-order interactions with B_{1u} and B_{2u} states of other configurations are neglected. Moreover, if there is a Jahn-Teller distortion, the B_{1u} and B_{2u} states can undergo additional (low-symmetry) mixing with other states. Effects of this sort could possibly be involved in the low-temperature (< 40 K) magnetic behavior. Alternatively, there may be weak dimer-dimer antiferromagnetic coupling.

5 Solution Electronic Spectra

The electronic absorption spectrum of $\text{Os}_2\text{piv}_4\text{Cl}_2$ in CH_2Cl_2 solution is shown in Fig. 2. Our data for $\lambda < 500$ nm are in good agreement with those [2b, 17] for the acetate, propionate, and butyrate analogues; and $\text{Os}_2\text{bu}_4\text{Cl}_2$ and $\text{Os}_2\text{ac}_4\text{Cl}_2$ have previously unreported low-energy ($\lambda > 500$ nm) absorption bands virtually identical with those of $\text{Os}_2\text{piv}_4\text{Cl}_2$. We note that impure samples of these compounds exhibit increased absorption in the 550–700 nm region, leading to a stronger greenish to blue color. However, all of the absorptions of Fig. 2 appear reproducibly for fresh solutions of analytically pure material.

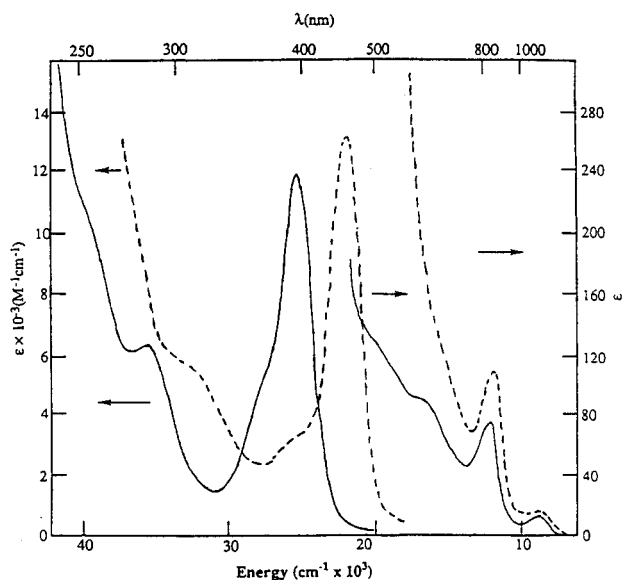


Fig. 2. Solution (CH_2Cl_2) electronic spectra of $\text{Os}_2\text{piv}_4\text{Cl}_2$ (—) and $\text{Os}_2\text{piv}_4\text{Br}_2$ (---) at room temperature

The spectrum of a freshly prepared, dry CH_3CN solution of $\text{Os}_2\text{piv}_4\text{Cl}_2$ is identical with that in CH_2Cl_2 . However, significant decomposition occurs within a few hours, whereas CH_2Cl_2 solutions are stable for days. The spectra of freshly prepared solutions in protic solvents such as CH_3OH are very different from those in CH_2Cl_2 and CH_3CN , showing much weaker absorption in the visible region.

The spectrum of a CH_3CN solution immediately after stoichiometric precipitation of Cl^- with AgBF_4 is similar to that in CH_3OH , showing a relatively weak ($\epsilon \sim 4000 \text{ M}^{-1} \text{ cm}^{-1}$) band at 365 nm [29]. Assuming that the initial product is the bis(solvent) axial adduct, then the intense ($\epsilon = 11,600 \text{ M}^{-1} \text{ cm}^{-1}$) band of $\text{Os}_2\text{piv}_4\text{Cl}_2$ at 394 nm is likely due to an axial chloride ligand-to-metal charge-transfer (LMCT) transition. Support for this assignment comes from the spectrum of $\text{Os}_2\text{piv}_4\text{Br}_2$ [30], in which the intense band is strongly red-shifted to 455 nm (Fig. 2). Other bands to higher energy of 455 nm that exhibit significant red-shifts also may be LMCT transitions ($\sigma, \pi(\text{X}^-) \rightarrow \delta^*, \pi^*$).

The two lowest energy bands in these spectra (~ 1100 and ~ 850 nm) are, in contrast, insensitive to axial ligand substitution. They are good candidates for Os_2 -localized transitions.

6

Solid-State Electronic Spectra

Room and low-temperature electronic absorption spectra for the (110) face of a $\text{Os}_2\text{piv}_4\text{Cl}_2$ crystal are shown in Figs. 3 and 4. No absorption attributable to electronic transitions could be found in the 1300–2000 nm region. Strong vibrational overtone absorption prevents extension of the measurements beyond

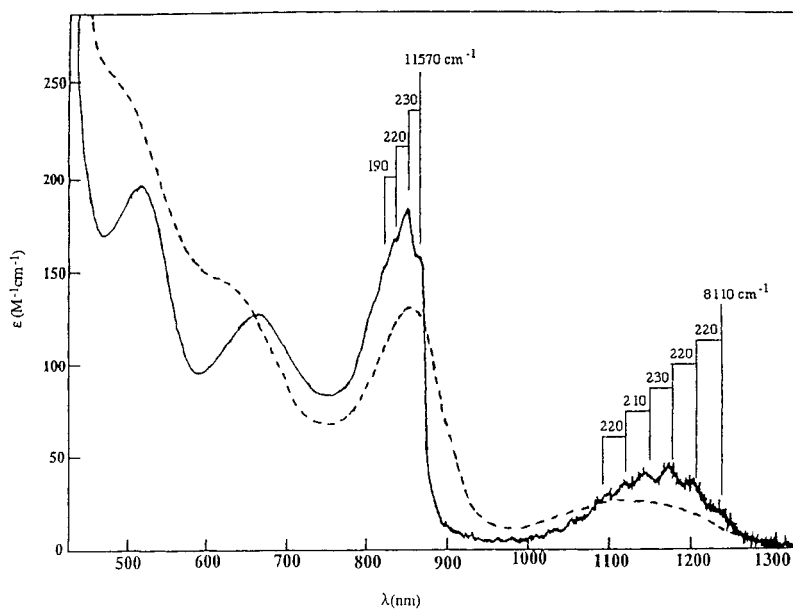


Fig. 3. Electronic spectra of the (110) face of a single crystal of $\text{Os}_2\text{piv}_4\text{Cl}_2$, $\parallel c(\parallel z)$ polarization, at 20 (—) and 295 K (---)

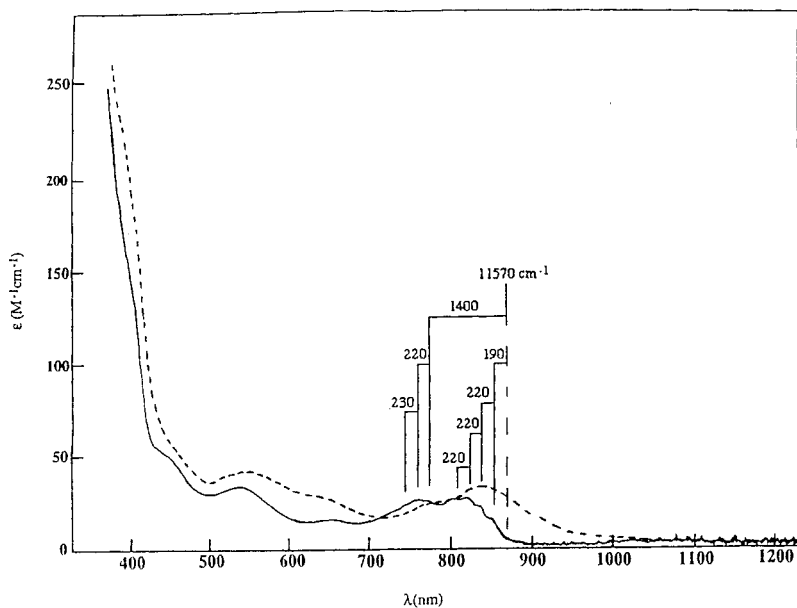


Fig. 4. Electronic spectra of the (110) face of a single crystal of $\text{Os}_2\text{piv}_4\text{Cl}_2$, $\perp c(\perp z)$ polarization, at 20 (—) and 295 K (---)

2000 nm. The spectrum for an axial (001) crystal face was identical with the $\parallel c$ spectrum of the (110) face, in accord with electric-dipole selection rules for tetragonal crystals. Assuming the structure to be isomorphous with those of $M_2\text{piv}_4\text{Cl}_2$ ($M = \text{Re}, \text{Tc}$) [14], the $\parallel c$ polarization of the (110) crystal face is composed of transitions polarized parallel to molecular z (the Os-Os axis), while the $\perp c$ polarization (and also the axial spectrum) is composed of molecular x, y -polarized transitions.

A key point is that no new bands are observed to grow in as the temperature increases. If there were a thermal equilibrium among several electronic states of different electronic configurations (as distinct from spin-orbit states of a single electronic configuration), larger thermal effects on the absorption spectrum would be expected, as the different electronic configurations should have different spectroscopic signatures. This observation is particularly important in the < 40 K range, where there is anomalous magnetic behavior.

The spectra are dominated by molecular z ($\parallel c$)-polarized absorption. The extremely intense 394 nm solution band is z -polarized, as indicated by the fact that we could scan well past 400 nm in $\perp c$ polarization. This conclusion is consistent with Clark's [17] determination of z -polarization for this band in solution via resonance Raman depolarization ratio measurements. Stealing intensity from this band is likely to be the dominant intensity-giving mechanism for the weak bands.

Most striking is that the two lowest-energy bands both show vibronic progressions in frequency intervals of $200\text{--}230\text{ cm}^{-1}$ at low temperature. The resolution is poor (like that of the $^1(\delta \rightarrow \delta^*)$ transition of isomorphous $\text{Re}_2\text{piv}_4\text{Cl}_2$) [31], but it is nonetheless clear, by comparison to the ground-state vibrational data (vide supra), that the structure is reasonably assigned to $\nu(\text{Os}_2)$ of the excited states. The z -polarization of the ~ 850 nm band exhibits narrowing and peak intensification as the temperature decreases, which is typical behavior for a dipole-allowed transition, while the weaker x, y -polarized intensity of this band decreases at low temperature, suggesting that it is vibronically induced. The even more strongly z -polarized ~ 1200 nm band appears to slightly *increase* its integrated intensity at low temperature.

Better resolution is obtained for CsCl pellets of $\text{Os}_2\text{ac}_4\text{Cl}_2$ and $\text{Os}_2\text{bu}_4\text{Cl}_2$ (Fig. 5 and 6), and the $\nu(\text{Os}_2)$ progressions are well defined, but considerable additional complexity is evident for the ~ 850 nm band [32] (Fig. 5). In addition to the $\nu(\text{Os}_2)$ progression built upon the electronic origin, we detect additional features at about $300, 600$, and 1430 cm^{-1} above the $0\text{--}0$ line, the last two of which serve as origins for $\nu(\text{Os}_2)$ progressions.

The polarized single-crystal spectra help to untangle this complexity. The origin line ($11,570\text{ cm}^{-1}$) is completely z -polarized, together with a $\nu(\text{Os}_2)$ progression built upon it. However, the $\sim 1400\text{ cm}^{-1}$ origin, together with a $\nu(\text{Os}_2)$ progression, appear strongly in x, y -polarization, suggesting that the 1400 cm^{-1} interval is a nontotally symmetric (e_g symmetry) vibration that is vibronically inducing x, y -intensity in the electronic transition. There is considerable precedent [19, 33, 34] for significant vibronically induced intensity components for weak metal-metal transitions. In particular, we have previously shown that the $\delta \rightarrow \delta^*$ transition of $\text{Ru}_2(\text{O}_2\text{CR})_4^+$ (~ 1100 nm) [19] has e_g x, y -intensity inducing

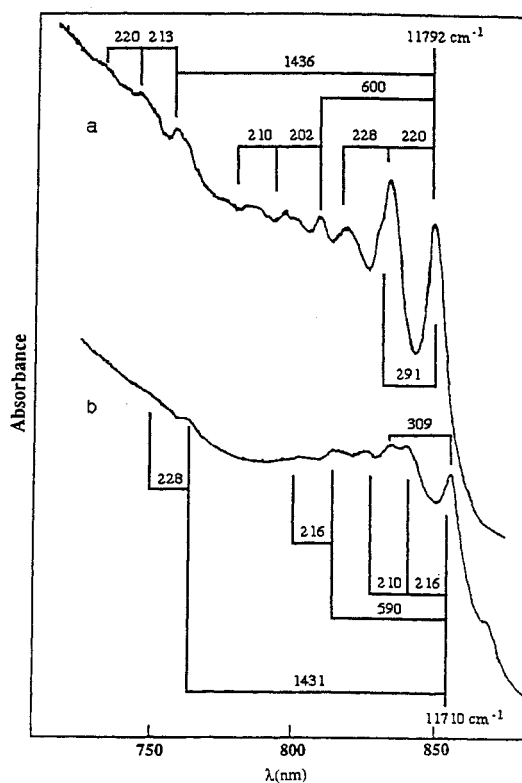


Fig. 5. Electronic spectra of (a) $\text{Os}_2\text{ac}_4\text{Cl}_2$ and (b) $\text{Os}_2\text{bu}_4\text{Cl}_2$ (CsCl pellets, 4.2 K, 700–900 nm)

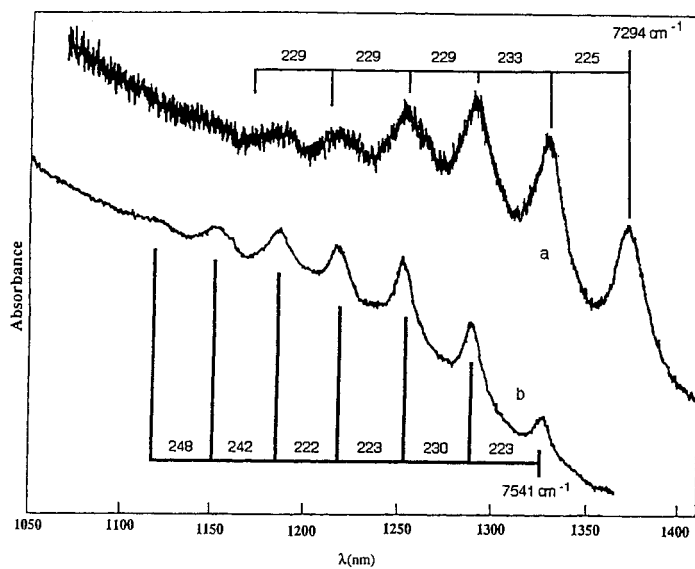


Fig. 6. Electronic spectra of (a) $\text{Os}_2\text{ac}_4\text{Cl}_2$ and (b) $\text{Os}_2\text{bu}_4\text{Cl}_2$ (CsCl pellets, 4.2 K, 1050–1450 nm)

modes at ~ 1450 (the asymmetric $\nu(\text{Co}_2)$ mode), ~ 300 , and $\sim 250 \text{ cm}^{-1}$. We assign the $\sim 1400 \text{ cm}^{-1}$ x, y -polarized origin of the $\text{Os}_2\text{piv}_4\text{Cl}_2$ spectrum to a similar mode.

All of our data are consistent with assignment of the $\sim 850 \text{ nm}$ band to the $\delta \rightarrow \delta^*$ transition. The energy ($\sim 11,500 \text{ cm}^{-1}$) and distortion along the metal-metal coordinate (maximum at one quantum of $\nu(\text{Os}_2)$) both fall between the parameters for $\text{Ru}_2(\text{O}_2\text{CR})_4^+$ ($\sim 9100 \text{ cm}^{-1}$, maximum at the electronic origin) [19] and quadruply bonded $\text{Mo}_2(\text{O}_2\text{CR})_4$ ($\sim 22,000 \text{ cm}^{-1}$, maximum at 2 quanta of $\nu(\text{Mo}_2)$) [33], as would be expected for the intermediate bond order. That the $\delta \rightarrow \delta^*$ transition energies of the $\text{Os}_2(\text{III,III})$ and $\text{Ru}_2(\text{II,III})$ complexes should both be much lower energy than that of the $\text{Mo}_2(\text{II,II})$ compounds is a consequence of the former species having a half-filled δ^* orbital, which results in there being a negligible two-electron contribution to the $\delta \rightarrow \delta^*$ transition energy [35]. In this regard, an additional excellent comparison is to the $\delta \rightarrow \delta^*$ transition of doublet (δ^*) ground-state $\text{Tc}_2\text{hp}_4\text{Cl}$ (electronic origin at $12,194 \text{ cm}^{-1}$, maximum between 1 and 2 quanta of $\nu(\text{Tc}_2)$) [34]. For a $^3(\pi^*)^2$ ground state, $\delta \rightarrow \delta^*$ would be expected at relatively high energy because of two-electron contributions to the transition energy [35], while for a $^1(\delta^*)^2$ ground state [36], no $\delta \rightarrow \delta^*$ transition exists. The zero-field splitting of the $\delta \rightarrow \delta^*$ excited state, $^3E_g [\delta(\delta^*)^2\pi^*]$, should have the same sign and magnitude as that of the ground state. The z -polarized $B_{1u}, B_{2u} \rightarrow B_{1g}, B_{2g}$ transitions will therefore be the lowest energy spin-orbit components of the transition. The x, y -polarized $B_{1u}, B_{2u} \rightarrow E_g$ transitions should lie above the z -polarized transitions by the excited-state value of the zero-field splitting $D - \Delta$, and may contribute to the x, y -polarized feature 630 cm^{-1} above the origin, in addition to the vibronically induced x, y -intensity mentioned above.

Assignment of the $\sim 1200 \text{ nm}$ band is less straightforward. It shows a long progression in $\nu(\text{Os}_2)$, maximizing between 2 and 3 quanta, which indicates a larger distortion along the metal-metal coordinate than for the $\delta \rightarrow \delta^*$ excited state. No other vibronic features are resolved, and the vibronic structure is quite different in appearance from that of the $\delta \rightarrow \delta^*$ transition. The only reasonable candidates for metal-metal electronic transitions at this relatively low energy (other than $\delta \rightarrow \delta^*$) are $\pi^* \rightarrow \delta^*$ and $\delta^* \rightarrow \pi^*$, and both of the latter excitations should show larger metal-metal distortions than $\delta \rightarrow \delta^*$ because of the large metal-metal antibonding character of π^* [3]. The excited-state $\nu(\text{Os}_2)$ would be expected to be, respectively, higher and lower than the ground-state value for these two excitations.

The excited-state $\nu(\text{Os}_2)$ actually appears to be similar to be ground-state value (within the rather large, $\pm 20 \text{ cm}^{-1}$, measurement uncertainty) for the $\sim 1200 \text{ nm}$ band, which is an ambiguous result. The band is similar in this regard to a (much weaker, $\epsilon \sim 2 \text{ M}^{-1} \text{ cm}^{-1}$) band observed at about 1400 nm for $\text{Ru}_2(\text{O}_2\text{CR})_4^+$ compounds [19] that was tentatively assigned to a spin-forbidden $\pi^* \rightarrow \delta^*$ excitation. It is likely that the broad progressions of these bands conceal vibronic complexity that may affect the apparent $\Delta\nu$.

Since the 1200 nm band exhibits dipole-allowed z -polarization, the excited state must be of B_{1g} or B_{2g} symmetry. There is then only one possible excited-state assignment among the $\pi^* \rightarrow \delta^*$ and $\delta^* \rightarrow \pi^*$ excitations, namely, $\delta^* \rightarrow \pi^*$

$[B_{1u}, B_{2u} (^3E_u) \rightarrow B_{1g}, B_{2g} (^1B_{1g}, ^1B_{2g})]$; mixing with the nearby $\delta \rightarrow \delta^*$ transitions of identical symmetry is likely. A problem with this assignment is that the spin- and dipole-allowed excitation $\delta^* \rightarrow \pi^* [B_{1u}, B_{2u}, (^3E_u) \rightarrow E_g(^3A_{2g})]$ ought to lie a few thousand wavenumbers to lower energy [23, 24], but this is not observed. The predicted energy of this latter transition is, however, close to the experimental limit that is set by intense vibrational overtone absorption at $\leq 5000 \text{ cm}^{-1}$. Moreover, the preponderant z-polarized intensity of the entire absorption spectrum suggests that formally allowed x,y-polarized absorption bands might be very weak. Examples of the intensity of weak metal-metal transitions being completely dominated by coupling to an intense higher-energy transition have been found [37]. In summary, we assign the 1200 nm band to a $\delta^* \rightarrow \pi^*$ excitation, but we recognize that there are several difficulties with this interpretation.

We next consider the unstructured weak between 400 and 700 nm. The temperature dependences of the z-polarized absorptions at ~ 500 and ~ 650 nm are obscured by overlapping absorptions to shorter and longer wavelengths, so it is not clear whether they are dipole-allowed transitions. The $\perp$ z-polarized intensity appears to be largely vibronically induced, as it decreases at lower temperature. A $\perp$ z band at ~ 650 nm could be a vibronic counterpart of the z-polarized band at the same wavelength, and the $\perp$ z shoulder at ~ 400 nm probably corresponds to the very intense z-polarized LMCT band at 394 nm; but the $\perp$ z-polarized bands at ~ 450 and ~ 550 nm both have absorption maxima at wavelengths that are significantly shifted from the z-polarized maximum at ~ 510 nm, so they appear to be different electronic transitions. Thus, at least 4 additional electronic transitions fall in this region.

There are many possible assignments, prominent among which are $\delta \rightarrow \pi^*$ and $\pi \rightarrow \delta^*$ excitations [5, 14, 20]. Both (formally) spin-forbidden and spin-allowed transitions may have observable intensity; the 450/510 and 550/650 nm pairs of absorption bands might, for example, represent singlet/triplet pairs of transitions. We do not, however, have sufficient information to make detailed assignments.

We finally consider the intense LMCT bands observed in the solution spectra. The 394 nm band of $\text{Os}_2\text{piv}_4\text{Cl}_2$ is found to be z-polarized, which indicates the assignments $\sigma(\text{Cl}) \rightarrow \sigma^*(\text{Os}_2)$ or $\pi(\text{Cl}) \rightarrow \pi^*(\text{Os}_2)$; the high intensity of this band demands, in addition to spin- and dipole-allowed character, bonding-to-antibonding character [19b]. We favor the $\pi \rightarrow \pi^*$ assignment because the transition in question is expected to lie at lower energy than the $\sigma(\text{Cl}) \rightarrow \sigma^*(\text{Os}_2)$ LMCT, and there are no obvious LMCT bands to lower energy of the 394 nm band. Clark also has argued for this assignment [17].

7

Structural Correlations

The temperature-dependent magnetic behavior, and both the energy and existence of the $\delta \rightarrow \delta^*$ transition, strongly support a ^3E_u ($\pi^*\delta^*$) ground state for the $\text{Os}_2(\text{O}_2\text{CR})_4\text{Cl}_2$ compounds. This ground state is fully consistent with structural information.

Table 1. Magnetic data for $\text{Os}_2(\text{piv})_4\text{Cl}_2$

T (K)	χ_M (emu)	$\mu_{2\text{ff}}$ (B. M.)
6	0.0099685	0.69163
7	0.0097596	0.73917
8	0.0095506	0.78170
9	0.0092521	0.81606
10	0.0089238	0.84480
11	0.0087248	0.87610
12	0.0084462	0.90033
13	0.0082074	0.92375
14	0.0079387	0.94280
15	0.0077098	0.96172
16	0.0074909	0.97906
17	0.0072422	0.99229
18	0.0070730	1.0091
19	0.0069437	1.0272
20	0.0067447	1.0387
25	0.0059486	1.0906
30	0.0053317	1.1310
35	0.0048342	1.1633
40	0.0044263	1.1899
50	0.0038790	1.2454
60	0.0035208	1.2998
70	0.0032123	1.3410
80	0.0029835	1.4283
100	0.0027148	1.4735
110	0.0026153	1.5168
120	0.0024860	1.5446
130	0.0024163	1.5850
140	0.0022969	1.6037
150	0.0022671	1.6491
160	0.0022074	1.6806
170	0.0021676	1.7167
180	0.0020680	1.7254
190	0.0020481	1.7642
200	0.0020083	1.7923
210	0.0019785	1.8229
220	0.0019387	1.8469
230	0.0019088	1.8738
240	0.0018690	1.8941
250	0.0018193	1.9072
260	0.0017994	1.9343
270	0.0017596	1.9492
280	0.0017098	1.9568
290	0.0016899	1.9798
300	0.0016501	1.9898
310	0.0016203	2.0043
320	0.0016004	2.0238
330	0.0015904	2.0488
340	0.0015705	2.0665
350	0.0015307	2.0700

It has been firmly established for the series [5c] $[\text{Re}_2\text{Cl}_4(\text{PMe}_2-(\text{C}_6\text{H}_5))_4]^{0,+ \cdot 2+}$ that population of the δ^* orbital has little effect upon metal-metal distance [3]. The $(\delta^*)^0$ and $(\delta^*)^2$ bond lengths in this series are 2.215 and 2.241 Å in various salts [6] is very similar, consistent with a $(\delta^*)^2$ ground state.

By contrast, the metal-metal bond lengths of the $\text{Os}_2(\text{O}_2\text{CR})_4\text{Cl}_2$ compounds (2.271–2.317 Å) [2b, c, 11] are 0.06–0.08 Å longer than those of $\text{Re}_2(\text{O}_2\text{CR})_4\text{Cl}_2$ [38]. The decrease in $\nu(\text{M}_2)$ is still more striking, as noted earlier. These large structural and vibrational effects suggest population of the π^* metal-metal orbital, as the metal-metal π bond is considerably stronger [3] than the δ bond.

The compound $\text{Os}_2\text{hp}_4\text{Cl}_2$ has been established to possess a $(\pi^*)^2$ ground state by magnetic measurements [11, 39]. The osmium-osmium distances are 2.344 and 2.357 Å in two X-ray structures [1, 2b], considerably longer than those of both the rhenium(III) and osmium(III) carbocylate derivatives. The large increase in metal-metal bond length for the $(\pi^*)^2$ configuration relative to the $(\delta^*)^2$ configuration is consistent with many related comparisons [3]. The metal-metal distance in $\text{Os}_2(\text{di-}p\text{-tolylformamidinate})_4\text{Cl}_2$, for which a $(\pi^*)^2$ ground state has been established [23b], is much longer at 2.467 Å. However, an accumulating body of structural data [3] suggests that the very strongly electron-donating diarylformamidinate bridging ligands (and also diaryltriazene [9] ligands) result in longer metal-metal distances (for a given ground state) than do carboxylates. There are many examples, on the other hand, of virtually identical metal-metal distances for corresponding carboxylate and hydroxypyridinate complexes [3]. The difference in $\text{Os}_2(\text{III,III})$ bond lengths for the hydroxypyridinate and carboxylate complexes is therefore significant.

The intermediate values of metal-metal distance for the $\text{Os}_2(\text{O}_2\text{CR})_4\text{Cl}_2$ compounds clearly accord with an intermediate ground state, namely $\pi^*\delta^*$. Such a ground state requires an “accidental” near-degeneracy of the π^* and δ^* orbitals. However, so does the $(\pi^*)^2\delta^*$ ground state of $\text{Ru}_2(\text{O}_2\text{CR})_4$ compounds [8], so there is precedent for this situation.

It is evident that the $\text{Os}_2(\text{III, III})$ carboxylates are close to a crossover of ground states between $\pi^*\delta^*$ and $(\pi^*)^2$ triplets. Just how close is not clear, because the available data on the carboxylates can be interpreted without invoking any significant thermal population of a $(\pi^*)^2$ triplet state.

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8

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26. Since the δ^* orbital carries no orbital angular momentum, the ordering of the ^3E_u levels according to Ω is the same as it would be for a $^3\Pi_u(D_{\infty h})$ diatomic state [25a] with the same number of π -symmetry electrons. However, the b_{1u} symmetry of δ^* in D_{4h} exchanges the D_{4h} symmetry labels A, B of the $\Omega = 0$ and $\Omega = 2$ spin-orbit levels relative to those expected by correlation to the diatomic triplet state [25a]: $\Delta > \Pi > \Sigma^+, \Sigma^- (D_{\infty h})$

- correlate to $B_1, B_2 > E > A_1, A_2$ by descent in symmetry. This rather odd result occurs because δ^* correlates to a degenerate (Δ symmetry) level in D_{4h} , and correlations to D_{4h} are scrambled; it has no effect on the theoretical magnetic behavior (Ω is not changed), but is an important consideration in determining electric-dipole selection rules
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 32. We believe that the weak absorption line of $\text{Os}_2\text{bu}_4\text{Cl}_2$ at $11,547 \text{ cm}^{-1}$ (Fig. 5) is due to an impurity, as no analogous feature is seen for the other compounds
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 34. Cotton FA, Fanwick PE, Gage LD (1980) *J Am Chem Soc* 102:1570
 35. Hopkins MD, Miskowski VM, Gray HB (1987) *Polyhedron* 6: 705
 36. The lowest energy absorption band ($\sim 750 \text{ nm}$) of $(\delta^*)^2 \text{Os}_2\text{X}_3^-$ ($\text{X}=\text{Cl}, \text{Br}, \text{I}$), assigned to $\delta \rightarrow \pi^*$, is reported to exhibit vibronic structure at low temperature: Preetz W, Hollman P, Thiele G, Hillebrecht HZ (1990) *Naturforsch* 45b:1416. However, this structure bears no resemblance to that seen in our study of $\text{Os}_2(\text{O}_2\text{CR})_4\text{Cl}_2$ complexes, as the progressions are extremely long, and the excited-state frequencies are $80-90 \text{ cm}^{-1}$ lower than the ground-state frequencies
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 39. In the course of this work, we also made magnetic measurements on $\text{Os}_2\text{hp}_4\text{Cl}_2$ that are in agreement with those reported in Ref. [11]

Luminescence and Absorption Studies of Transition Metal Ions in Host Crystals, Pure Crystals and Surface Environments

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In this review article vibronic spectra are presented for selected d^0 , d^3 , and d^{10} systems in a variety of environments such as pure crystals, mixed crystals and surfaces. In the d^0 example, vanadium oxide on a SiO_2 substrate, the relation between the vibronic structure and the $\text{V}=\text{O}$ bond length in the lowest excited electronic state and the reactivity toward CO is discussed. In the d^3 example, ReBr_6^{2-} and MnF_6^{2-} ions in single and mixed crystals, group theory selection rules are shown to be important for understanding the vibronic mechanism by which $d \rightarrow d$ transitions occur in an octahedral environment. In the final example, d^{10} $\text{Au}(\text{CN})_2^-$ and $\text{Ag}(\text{CN})_2^-$ ions in different pure crystals, the appearance of vibronic structure is related to the relative rates for radiative and non-radiative processes.

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1

Introduction

Room temperature optical absorption spectra of transition metal ions in solution or in the solid state mostly consist of broad bands from which little information can be obtained. Dorain, Patterson and others [1–4] reported more than twenty years ago that when complex ions such as ReCl_6^{2-} , with broad room temperature absorption bands, are doped as impurity ions into suitable host lattices and cooled to low temperatures the broad absorption bands are sometimes resolved into a series of sharp vibronic lines. In a classic study in 1966, Dorain and Wheeler reported the optical absorption spectra of mixed $\text{K}_2(\text{Re,Pt})\text{Cl}_6$ and $\text{Cs}_2(\text{Re,Zr})\text{Cl}_6$ single crystals at 4.2 K. In this case the $5d^3$ ReCl_6^{2-} ion is doped as a substitutional impurity into the K_2PtCl_6 and Cs_2ZrCl_6 host lattices. Information was obtained about the nature of the observed electronic transitions, the excited electronic state vibrational energies and the magnetic properties of the low-lying excited electronic states.

Patterson and coworkers [5–18] have reported detailed luminescence studies of selected transition metal complex ions in a variety of different environments such as in single crystals, in host crystals and on surfaces. For example, for vanadium oxide on a SiO_2 substrate the vanadium oxide (d^0) is present in low concentrations on the substrate and detailed information can be obtained from the luminescence spectra about the vanadium oxide system [5]. This is a case where charge transfer transitions are present. This d^0 system is the first example to be discussed in Sect. 3.

Materials of the type Cs_2MX_6 ($X = \text{F, Cl, Br}$) have the cubic antiferroite crystal structure in which the M ions occupy a face-centered cubic lattice and possess octahedral point group symmetry. A large number of high-resolution MX_6^{2-} octahedral impurity ion optical studies have been reported [19–22] in which the impurity ions are doped into host lattices such as Cs_2SiF_6 , Cs_2ZrCl_6 , and Cs_2ZrBr_6 which have an antiferroite crystal structure and are optically clear in the regions in which the impurity ions absorb or emit light. The experimental spectra are characterized by detailed vibronic structure. In an attempt to understand these data, comparisons have been made with Raman and infrared determined MX_6^{2-} vibrational mode energies. However, these are not the only vibrations that can participate in the electronic transitions and, in fact, there are generally more experimental vibronic peaks than predicted from a simple isolated-ion model [6]. In Sect. 4 of this review article selected d^3 systems are considered in which vibronic structure present in the luminescence spectra of the impurity ions are compared with the host density of states. It is shown that the observed vibronic structure can be correlated with a lattice dynamical model, based on 6 K inelastic neutron scattering measurements, for the host lattice. Here, $t_{2g}^3 \rightarrow t_{2g}^3$ transitions are considered.

In the final example in Sect. 5 of this review article we consider the vibronic spectra of two-dimensional layered d^{10} compounds [11–17] in which the observed transitions are charge-transfer in nature. In particular, the $M[Au(CN)_2]$ and $M[Ag(CN)_2]$ compounds (e.g. with $M = K^+, Cs^+, Tl^+, \frac{1}{3} Eu^{3+}, \frac{1}{3} Dy^{3+}$) have been the subject of increasing interest recently due to their unusual two-dimensional layered structures. The crystal structure consists of layers of $Au(CN)_2^-$ or $Ag(CN)_2^-$ linear ions alternating with layers of M^+ ions. When the cation is changed, the distance between gold or silver atoms within a layer changes. For example, for the potassium salt of gold dicyanide the nearest-neighbor Au-Au separation is 3.64 Å at room temperature but for the corresponding tetrabutylammonium salt the nearest-neighbor Au separation is 8.8 Å. In general, the optical absorption spectrum of the $Au(CN)_2^-$ ion in aqueous solution shows charge-transfer absorption bands at energies greater than 40 000 cm^{-1} , while the salts of $Au(CN)_2^-$ in the solid state have absorption bands shifted to lower energies by as much as 20 000 cm^{-1} . Therefore, a study of the different salts of $Au(CN)_2^-$ and $Ag(CN)_2^-$ in the solid state provides an opportunity to study how the optical properties of these layered compounds are related to the interactions between Au and Ag atoms within layers. Further, the unique properties of lanthanide ions such as Eu^{3+} and Dy^{3+} provide the opportunity for studying excited-state energy-transfer processes in these layered Au and Ag dicyanide systems [16,17].

The overall objective of this article is to indicate what information can be obtained from highly resolved vibronic spectra of transition metal complexes. Here, different types of transitions in different environments are discussed to demonstrate the importance of spectroscopic studies in understanding the electronic states, vibrational states, and electronic-vibrational coupling in interesting transition metal systems.

2 Theoretical Background

2.1 Franck-Condon Model

The probability, W , that a transition will occur from the initial state $|\chi_i\rangle$ to the final state $|\chi_f\rangle$ per unit time of exposure of a system to electromagnetic radiation of frequency ν_{if} is given by [23] Eq. (1)

$$W = \left(\frac{2\pi}{h} \right) \rho(\nu_{if}) M_{if}^2 \quad (1)$$

where $\rho(\nu_{if})$ is the density of states for the perturbation and M_{if} , the electric dipole transition moment, is given by Eq. (2)

$$M_{if} = \langle \chi_i | \mu | \chi_f \rangle \quad (2)$$

where μ is the electric dipole moment operator. The Born-Oppenheimer approximation allows one to express a vibronic wave function as the product of electronic and vibrational wave functions

$$\chi = \psi_e(r, Q) \phi_v(Q) \quad (3)$$

With this approximation the electronic wave function, ψ_e , is a function of the electronic coordinates r and the nuclear coordinates Q and the vibrational wave function ϕ is a function of only the nuclear coordinates Q .

The transition moment is represented by the equation:

$$\mu = \mu_e + \mu_{\text{nuc}} \quad (4)$$

Here, μ_e is the transition moment due to electrons and μ_{nuc} is the transition moment due to nuclei. However, it can be shown that the integrals involving the μ_{nuc} will vanish. Thus,

$$M_{if} = \langle \psi_i(r, Q) | \mu_e | \psi_f(r, Q) \rangle \langle \phi_v''(Q) | \phi_v'(Q) \rangle \quad (5)$$

and if we define the first integral as M_e then

$$M_{if} = M_e \langle \phi_v''(Q) | \phi_v'(Q) \rangle \quad (6)$$

To evaluate the Franck-Condon overlap integral in Eq. (6) the vibrational wave function for the ground and excited electronic states, $\phi_v''(Q)$ and $\phi_v'(Q)$, have to be expressed in terms of Hermite polynomials including displacement of the origin of the normal coordinates of the ground and excited electronic states. The ratio of an integral corresponding to $(v' = 0) \rightarrow (v'' = 1)$ to an integral corresponding to $(v' = 0) \rightarrow (v'' = 0)$ can be expressed as the following [19]

$$\frac{R(1,0)}{R(0,0)} = -\frac{2D}{(B^2+1)} \quad (7)$$

Here D is a parameter proportional to the difference in the internuclear equilibrium separation between the ground and excited electronic states [24] and B is the square root of the ratio of the frequency of the excited states to the ground electronic state [24]. The ratio of $R(n,0)$ to $R(0,0)$ can be determined from the following relationship for Hermite polynomials [24]:

$$\frac{R(n+1,0)}{R(n,0)} = -\frac{2D}{(B^2+1)(n+1)^{1/2}} + \frac{n^{1/2}}{n+1} \cdot \frac{(B^2-1)}{(B^2+1)} \cdot \frac{R(n-1,0)}{R(n,0)} \quad (8)$$

The Franck-Condon overlap integrals, R , are related to the relative intensities for the vibronic emission peaks by [24]:

$$\frac{\text{Intensity of transition for } (0 \rightarrow n)}{\text{Intensity of transition for } (0 \rightarrow 0)} = \frac{E(n,0)^4}{E(0,0)^4} \cdot \frac{R(n,0)^2}{R(0,0)^2} \quad (9)$$

where $E(n,0)$ refers to the energy of the vibronic peak corresponding to a transition from $v' = 0$ to $v'' = n$.

Equations (7-9) can be compared with the formulas given by Blasse (Eq. 4) and Schmidtke (Eqs. 36-40) in the first volume of this series [25].

2.2

Lattice-Dynamical Model for Vibronic Sidebands

Let us now consider the necessary conditions for the appearance of phonons in impurity-ion electronic spectra. The presence of a substitutional defect in an otherwise perfect crystal removes the translational symmetry of the system and reduces the symmetry group of the system from the crystal space group to the point group of the lattice site. Loudon [26] has provided a table for the reduction of the space group representations of a face-centered cubic lattice into a sum of cubic point-group representations. A portion of that table is shown in Table 1 here. Consider an impurity ion that undergoes a vibronic electric-dipole allowed transition, with Γ_i and Γ_f the irreducible representations of the initial and final electronic states. Since the electric dipole operator transforms as Γ_4^- in the cubic point group, O_h , the selection rule for participation of a phonon is that one of its site symmetry irreducible representations is contained in the direct product $\Gamma_i \times \Gamma_4^- \times \Gamma_f$.

If the impurity-ion interaction with the host-lattice vibrations is linear with the phonon normal coordinates, the probability W for a transition of the impurity ion from electronic state i to state f with creation of a phonon is given at low temperatures by [27])

$$W = (2\pi/\hbar) |\langle \chi_i | 0 | \chi_f \rangle|^2 g(\omega) \delta(E - \hbar\omega - E_f), \quad (10)$$

with $g(\omega)$ is the density of phonon states. Also,

$$\langle \chi_i | 0 | \chi_f \rangle = \sum_p \left(\frac{\hbar}{2\omega_{\vec{q}r}} \right)^{1/2} \left(\frac{\langle \psi_i | f_{\vec{q}r} | \psi_p \rangle \langle \psi_p | 0 | \psi_f \rangle}{E_i - (E_p + \hbar\omega_{\vec{q}r})} \right) + \left(\frac{\langle \psi_i | 0 | \psi_p \rangle \langle \psi_p | f_{\vec{q}r} | \psi_f \rangle}{(E_f + \hbar\omega_{\vec{q}r}) - E_p} \right). \quad (11)$$

with μ the electric dipole operator and $f_{\vec{q}r}$ is the part of the interaction Hamiltonian H^1

$$H^1 = \sum_{\vec{q}} f_{\vec{q}r} Q_{\vec{q}r} \quad (12)$$

which operates only on the impurity electronic states. $f_{\vec{q}r}$ is the derivative of the electron-nuclear part of the potential energy of the system with respect to a par-

Table 1. Reduction of Space-group Irreducible Representations to the Cubic Site Group Irreducible Representations for the Face-Centered Cubic Lattice (for X and L Irreducible Representations only [25])

$X_1^+ \rightarrow a_{1g} + e_g$	$X_4^- \rightarrow t_{1u}$
$X_2^+ \rightarrow a_{2g} + e_g$	$X_5^- \rightarrow t_{1u} + t_{2u}$
$X_3^+ \rightarrow t_{2g}$	$L_1^+ \rightarrow a_{1g} + t_{2g}$
$X_4^+ \rightarrow t_{1g}$	$L_2^+ \rightarrow a_{2g} + t_{1g}$
$X_5^+ \rightarrow t_{1g} + t_{2g}$	$L_3^+ \rightarrow e_g + t_{1g} + t_{2g}$
$X_1^- \rightarrow a_{1u} + e_u$	$L_1^- \rightarrow a_{1u} + t_{2u}$
$X_2^- \rightarrow a_{2u} + e_u$	$L_2^- \rightarrow a_{2u} + t_{1u}$
$X_3^- \rightarrow t_{2u}$	$L_3^- \rightarrow e_u + t_{1u} + t_{2u}$

ticular normal mode $Q_{\vec{q}_r}$ [28, 29]. For the initial state, $|\chi_i\rangle$, the phonon state belongs to the identity representation, and thus $|\chi_i\rangle$ transforms the same way as the initial electronic state $|\psi_i\rangle$; also, the final phonon state $|\chi_f\rangle$ involves the electronic state $|\psi_f\rangle$ and phonon with energy $\hbar W_{\vec{q}_r}$. From equations 10 and 11 we expect vibronic transitions to be observed at those phonon energies where the phonon density of states peaks. The relative strength of an individual vibronic transition will be governed by the selection rules for the phonons which contribute to the phonon density of states (PDS) peak and by the magnitude of the $\langle\chi_i|\mu|\chi_f\rangle$ matrix element. Thus, if a particular PDS peak involves phonons with only gerade symmetry, that peak will not appear in the experimental d-d vibronic spectrum. Also, if a PDS peak arises from phonons with the correct site symmetry, there is the additional requirement from Eq. (11) that these phonons provide a changing crystal field at the metal impurity site location. If this does not occur, then $\langle\chi_i|\mu|\chi_f\rangle=0$ and the PDS peak cannot appear in the impurity-ion vibronic spectrum.

3

d° Example

3.1

Background

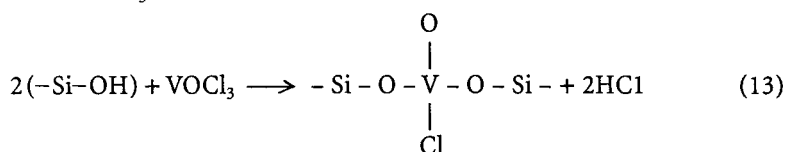
For an understanding of photocatalysis on the molecular level it is important to probe the excited states of the catalysts and their dynamics. Studies of the luminescence of catalysts can be very useful to clarify the excited states and the primary processes of photocatalysis. Many metal oxide catalysts exhibit luminescence in the visible region from a charge-transfer excited state of the catalyst [30–32]. Thus, luminescence is a convenient technique for the investigation of the structure and properties of the surface active sites on the supported catalysts. In this section a Franck-Condon analysis is presented of the well-resolved luminescence spectra at 77 K of vanadium oxide catalysts anchored onto SiO_2 with different vanadium concentrations. The results of the Franck-Condon analysis can be related to the different photoreactivities of these catalysts toward CO molecules.

Vanadium(V) oxide plays an important role as a catalyst. Vanadium(V) oxide anchored on silicon dioxide is a supported transition metal oxide. Its physical and chemical characteristics are seriously modified by the substrate, with the catalytic or photocatalytic properties dramatically changed from bulk vanadium oxide, resulting in increased activity and selectivity. For instance, it has been reported [33] that vanadium oxide can catalyze the synthesis of phenol from benzene. Only 0.2% of phenol was obtained when the reaction occurred with bulk V_2O_5 as the catalyst. Using 3.3 wt% V_2O_5 anchored on SiO_2 as the catalyst gave the phenol in 48% yield. Lower yields of phenols were obtained with an increased weight percentage of vanadium oxide as the catalyst. The catalysts with 4.2, 7.2 and 13.6 wt% V_2O_5 gave 32, 30 and 17% yields of phenol, respectively. Thus, there is a certain optimum weight percentage of vanadium oxide for the catalyst that gives the highest yield of the product.

3.2

Preparation of Anchored V/SiO₂ Catalysts

Anchored V/SiO₂ samples were made by M. Anpo from Japan [5]. The preparation was by the following method: VOCl₃ in benzene solution reacted with the surface OH groups of SiO₂ which had been degassed at 423 K for 20 hours, in anhydrous conditions at 350 K. The following reaction is involved in the anchoring reaction of VOCl₃ with the substrate:

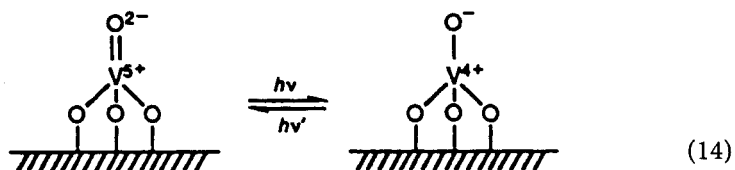


The samples were repeatedly washed with benzene, dried and then hydrolyzed with H₂O and dried again. Finally, these samples were calcined in O₂ at 773 K. The concentrations of the anchored vanadium oxide samples were determined to be 1.30 (for V/SiO₂-sample 1), 2.23 (for V/SiO₂-sample 2), and 3.07 (for V/SiO₂-sample 3) V wt %, respectively, by plasma emission spectrometry.

3.3

Luminescence Spectra of V/SiO₂

The lowest energy absorption and luminescence bands are attributed to charge transfer transitions for the surface vanadyl group (V=O) of the V/SiO₂ catalyst [34]. This involves an electron transfer from O²⁻ to V⁵⁺ and a reverse reaction, respectively:



In particular, the lowest energy absorption band corresponds to electron transfer from O²⁻ to V⁵⁺ while luminescence corresponds to the V⁴⁺ – O⁻ excited state going back to the V=O ground state.

Figure 1 shows the luminescence spectra at 77 K of three vanadium oxide catalysts [5], which are labeled anchored V/SiO₂-sample 1, V/SiO₂-sample 2 and V/SiO₂-sample 3. Among them, the V/SiO₂-2 has the strongest intensity for the luminescence, which means there are the most V=O double bonded species on the surface of anchored V/SiO₂-sample 2, since the luminescence is associated with the V=O double bond. Figure 2 shows the excitation spectra of the anchored vanadium oxides (5) corresponding to the luminescence spectra in Fig. 1. These luminescence and excitation spectra are in good agreement with those obtained with supported V/SiO₂ oxide catalysts prepared by a conventional impregnation method and with vanadium oxide catalysts anchored onto porous Vycor glass by a photochemical vapor deposition method [30].

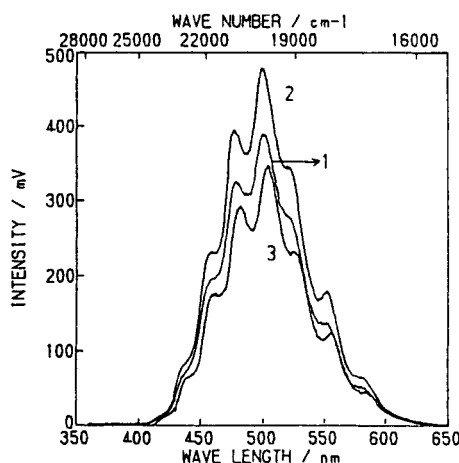


Fig. 1. Luminescence spectra of anchored V/SiO₂ catalysts at 77 K with excitation wavelength 280 nm, 5 nm slit width and concentrations of anchored vanadium oxide: 1:1.3; 2:2.23; 3: 3.07 V wt%, [5]

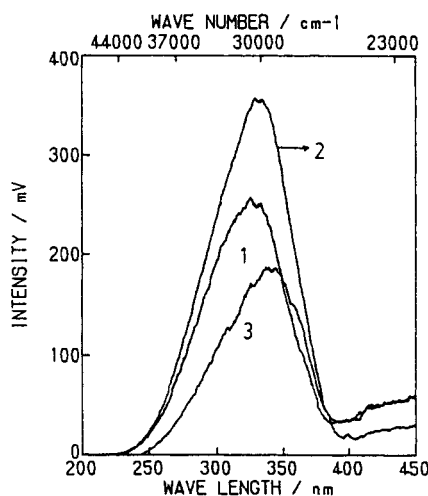


Fig. 2. Excitation spectra at 77 K of the phosphorescence of anchored V/SiO₂ catalysts corresponding to the spectra in Fig. 1 [5]. Emission monitored at 500 nm

The lifetimes of the luminescence of these catalysts has been measured [5]. The decay curve of the vanadium oxide catalysts gives a single-exponential for the V/SiO₂-sample 1 and V/SiO₂-sample 2 catalysts. The V/SiO₂-sample 3 with the highest vanadium content has two lifetimes. The lifetimes at 77 K of V/SiO₂-sample 1, V/SiO₂-sample 2 and V/SiO₂-sample 3 are 5.6, 5.6 and an average value of 5.0 ms, respectively. Thus, based on the lifetime values, the luminescence is assigned to a spin-forbidden process, that is, phosphorescence.

We are now able to reach the following conclusions from the above results. First, in the V/SiO₂-sample 3, some weak interaction among the V=O units arise because higher vanadium loading leads to additional radiationless pathways, which results in a shorter lifetime of the phosphorescence and some deviation from a single exponential decay of the phosphorescence of the catalyst. The presence of such interaction is also proved by the red shift in the excitation spectrum of V/SiO₂-sample 3 compared with V/SiO₂-sample 1 and V/SiO₂-sample 2 with lower vanadium concentration. Second, the V/SiO₂-sample 3 has at least two types of vanadium oxide on the silicon dioxide substrate, V=O units and V₂O₅ bulk. The V=O unit is located on the surface to produce the phosphorescence spectrum while the bulk V₂O₅ does not show any phosphorescence. If bulk V₂O₅ is on the surface, some energy transfer will occur to bulk to make the phosphorescence have a lower intensity and a shorter lifetime.

The energies of the luminescence spectra of the anchored V/SiO₂ catalysts at 77 K show that the lowest energy peaks in the luminescence spectrum are separated by about 1050 cm⁻¹, being attributed to the vanadyl V=O double bond [5]. Comparing this value with peaks in the Raman and IR spectra (5) shows there is good agreement between the energy separation of the lowest energy peaks of the phosphorescence and with the vibrational energy of the V=O group. This result indicates that the photon energy absorbed by the catalyst is mainly localized on the vandy groups, i.e., V=O surface bonds of the catalyst.

3.4

Photoreduction of Anchored Vanadium Oxide with CO

UV irradiation of anchored V-oxide catalysts at 280 K in the presence of CO leads to the formation of CO₂ molecules. Figure 3 shows the time profile of this photoinduced reaction for the anchored V/SiO₂ samples -1, -2, -3 catalysts [5]. After photoreduction of the anchored catalysts and further evacuation of excess CO, O₂ was admitted under 4.0 Torr at 280 K for a few minutes and then evacuated. After this treatment the photoreduction with CO proceeded with the same efficiency as before. This result indicates that the original state of the catalyst surface is completely restored at 280 K by contact with oxygen. As shown in Fig. 3, the yield of photoformed CO₂ is the highest with anchored V/SiO₂-sample 2 catalyst and then anchored V/Si-sample 1 and V/SiO₂-sample 3 catalysts yields follow.

3.5

Franck-Condon Analysis

A Franck-Condon analysis was used to analyze the difference in the lowest excited electronic state and the ground electronic state for samples of vanadium oxide anchored on silicon dioxide.

If the internuclear equilibrium distance of the excited electronic state (r'_e) is shifted by a value Δ from the internuclear equilibrium distance of the ground

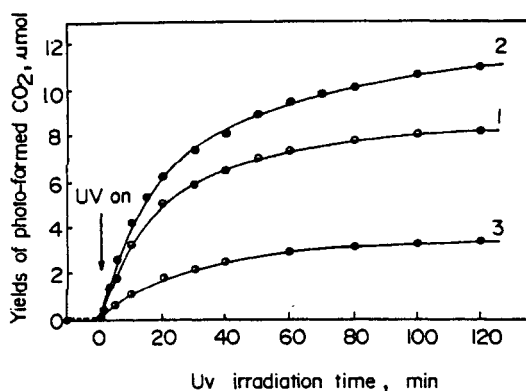


Fig. 3. Time profiles of the photoformation of CO_2 under UV irradiation of anchored V/SiO_2 -1, -2, and -3 catalysts in the presence of CO molecules at 4.0 Torr [5]. Here, 1 = anchored V/SiO_2 -1, 2 = anchored V/SiO_2 -2; 3 = anchored V/SiO_2 -3

state (r_e''), the Franck-Condon principle allows for transitions to a number of excited vibrational levels. The shapes of the harmonic potential also have an effect on the Franck-Condon integral. In the present case, the theoretical intensities have been calculated as a function of Δ and B . B is the square root of the ratio of the frequency of the excited electronic state to the ground electronic state [24]. The experimental frequencies and intensities were obtained from the experimental emission spectra of the anchored V/SiO_2 catalysts. The parameters B and Δ have been varied until the theoretical intensities match closest to the experimental intensities and the standard deviation is as small as possible [5]. In Fig. 4 (a, b, c), the fit of the progression obtained from the experimental photoluminescence spectra for the anchored V/SiO_2 catalysts and the theoretical Franck-Condon analysis are shown [5]. Here Fig. 4a (the top portion of the figure) corresponds to anchored V/SiO_2 -1, Fig. 4b corresponds to anchored V/SiO_2 -2 and Fig. 4c corresponds to V/SiO_2 -3.

Table 2 shows the values of Δ and B obtained from the Franck-Condon analysis for anchored V/SiO_2 -1, -2, and -3 samples [5]. The following two points should be emphasized from the results in table 2. First, the excited state potential is displaced from the ground state potential by $0.12 \text{ \AA}$, in agreement with the assignment of the electronic transition from O^{2-} to V^{+5} ions of surface ($\text{V}=\text{O}$) vanadyl groups. Secondly, the order of the photoreactivity of the anchored V/SiO_2 -1, -2, and -3 toward CO molecules is in good agreement with the values of Δ , with anchored V/SiO_2 -2 having the highest photoreactivity and the largest value of Δ .

Since the average vibrational energy of the progression for the phosphorescence is larger than 1000 cm^{-1} , we can assume that $v' = 0''$ vibrational level in the excited electronic state is populated to the greatest extent and the emission occurs from this level to the vibrational levels of the ground state in which the Franck-Condon integral is non-zero. If we assume that the observed structure in the luminescence spectrum is due to a progression for the electronic state with

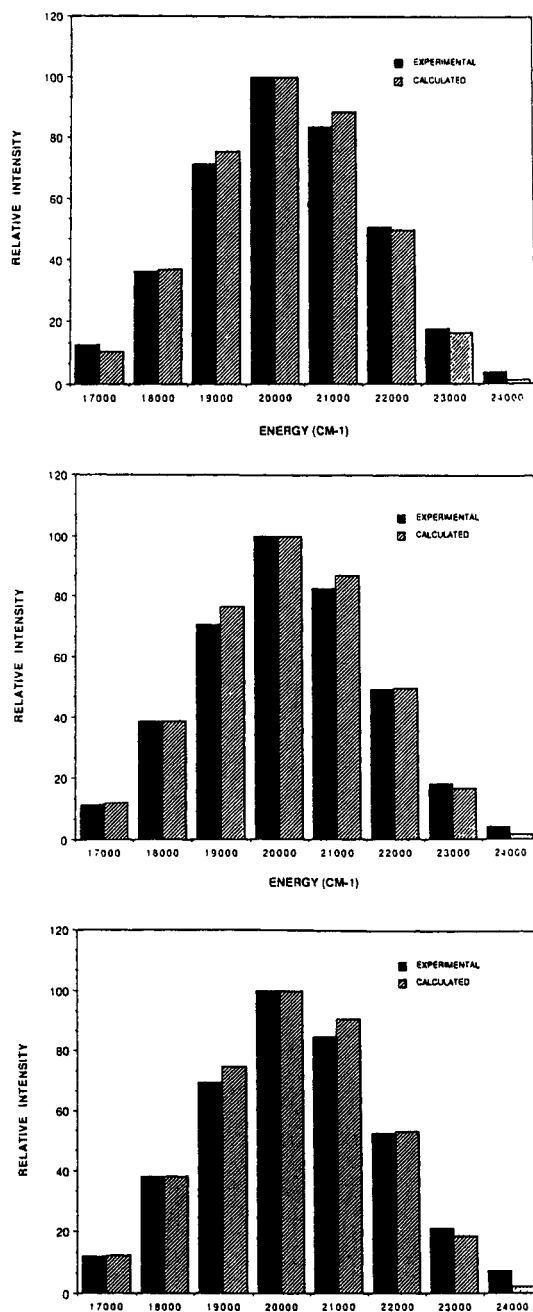


Fig. 4. Progression of the vibrational fine structure of the phosphorescence spectrum of anchored V/SiO₂-1, -2, and -3 catalysts at 77 K and fit of the theoretical Franck-Condon analysis [5]. Here, *top progression* corresponds to anchored V/SiO₂-1; *middle progression* corresponds to V/SiO₂-2; and *bottom progression* corresponds to V/SiO₂-3

Table 2. Franck-Condon Δ and B Values Determined for the Anchored V/SiO₂-1, -2, and -3 Catalysts at 77 K [5]. Δ is the amount in Å by which the internuclear equilibrium distance of the excited electronic state is shifted from the internuclear equilibrium distance of the ground state. B is the square root of the ratio of the frequency of the excited electronic state to the ground electronic state

Catalyst	Δ , Å	B
anchored V/SiO ₂ -1	0.1180	0.750
anchored V/SiO ₂ -2	0.1185	0.760
anchored V/SiO ₂ -3	0.1175	0.780

the energy of v vibrational quanta given by

$$E(v) = W_e(v + 1/2) - W_e X_e (V + 1/2)^2 \quad (15)$$

Since $E(v+1) - E(v) = W_e - 2W_e X_e(v+1)$, a plot of $E(v+1) - E(v)$ versus $(v+1)$ gives a linear relation with a value for $W_e X_e$ of about 6.8 cm^{-1} . This implies that only a small amount of anharmonicity is present in the ground-electronic state vanadyl group vibrational potential and a harmonic oscillator model is a good approximation to the potential surface. It is interesting to note that, due to anharmonicity, the intensity distribution in the Franck-Condon progression is slightly different for $r'_e > r''_e$ in comparison to $r'_e < r''_e$ because a steeper part of the potential is sampled in the latter case, giving a broader maximum in the progression intensity. Comparison of the experimental spectra with the calculated spectra indicates the experimental spectra are slightly sharper than the calculated spectra, implying that $r'_e > r''_e$.

4

d³ Example

4.1

ReBr₆²⁻: Cs₂ZrBr₆ Impurity Ion Spectra

Room temperature optical spectra of 4d and 5d configuration ions in solids or solutions generally consist of broad absorption bands. Here, we discuss sharp-line luminescence and absorption spectra for ReBr₆²⁻ doped as an impurity into single cubic crystals of Cs₂ZrBr₆ at 20 K. This system is of particular interest since Re⁴⁺ is isoelectronic with Cr³⁺. Also, in this case weak coupling exists between the impurity ion and the Cs₂ZrBr₆ host lattice. The luminescence for the ReBr₆²⁻ ion is sufficiently intense such that the absorption and luminescence were recorded simultaneously on photographic plates without phase-sensitive detection instrumentation.

Rhenium (+4) has a 5d³ electronic configuration. When the ion is placed in an octahedral field the following terms in order of increasing energy result within the t_{2g}³ configuration: ⁴A_{2g}, ²E_g, ²T_{1g} and ²T_{2g}. These terms are further split by spin-orbit interaction into states denoted in the Bethe notation as Γ_i ($i = 6, 7, 8$)

where Γ_i is the appropriate irreducible representation of the cubic group. The transition observed at about 13000 cm^{-1} has been assigned as $\Gamma_8^+(^4A_{2g}) - \Gamma_7^+(^2T_{2g})$ and this is our focus here [21].

To assign the vibronic structure associated with the 13000 cm^{-1} electronic transition shown in Fig. 5 we must consider the possible vibrational states. The normal modes of vibration for the ReBr_6^{2-} complex may be denoted as $\nu_1(a_{1g})$, $\nu_2(e_g)$, $\nu_3(t_{1u})$, $\nu_4(t_{1u})$, $\nu_5(t_{2g})$ and $\nu_6(t_{2u})$, where the expression in parenthesis gives the irreducible representation of the O_h point group according to how the mode transforms. Woodward and Ware [35] have measured the infrared spectrum of Cs_2ReBr_6 in mulls and the Raman spectrum of ReBr_6^{2-} in solution and found that $\nu_1 = 213\text{ cm}^{-1}$, $\nu_2 = 174\text{ cm}^{-1}$, $\nu_3 = 217\text{ cm}^{-1}$, $\nu_4 = 118\text{ cm}^{-1}$ and $\nu_5 = 104\text{ cm}^{-1}$. The ν_6 mode is inactive.

The ReBr_6^{2-} ion doped in the Cs_2ZrBr_6 host crystal possesses inversion site symmetry. Thus, a d-d electric dipole type transition is forbidden. Three mechanisms can account for the appearance of d-d type transitions: (1) magnetic dipole mechanism; (2) vibrational-electronic coupling to destroy the center of symmetry; and (3) destruction of inversion symmetry by static distortions.

For the spectrum shown in Fig. 5 [21] the emission and absorption portions form symmetrical mirror images of each other about line 0; therefore, line 0 can be assigned as the 0-0 no-phonon line unsplit by a static distortion. Since the magnetic dipole operator transforms as the Γ_4^+ irreducible representation of the O_h point group it follows that the no-phonon line is magnetic-dipole allowed. If the difference in energy between the B' , C' emission lines and line 0 are compared with the mode energies measured by Woodward and Ware then B' and C' can be assigned to the ν_4 and ν_3 modes of the $\Gamma_8^+(^4A_{2g})$ ground electronic state. Line A' can be assigned to the ν_6 mode on the basis of force-constant calcula-

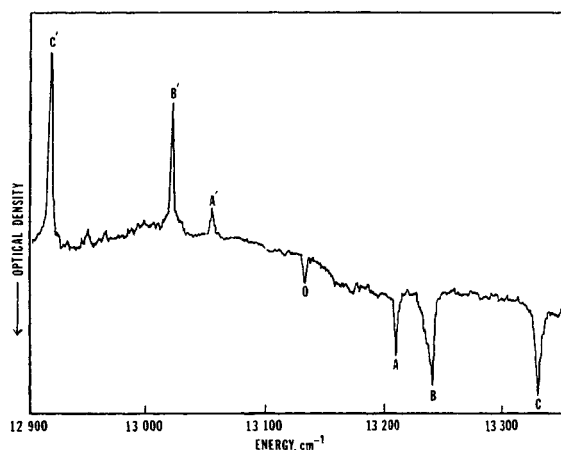


Fig. 5. Microphotometer tracing of the $\Gamma_8^+(^4A_{2g}) - \Gamma_7^+(^2T_{2g})$ absorption and luminescence spectrum for ReBr_6^{2-} doped in Cs_2ZrBr_6 at 20 K [21]. Optical density is defined as $\log_{10} I_0/I$ where I_0 is the intensity of a beam of radiation after it has passed through an unexposed portion of the emulsion of the photographic plate, and I is its intensity after being attenuated by the spectra on the photographic plate

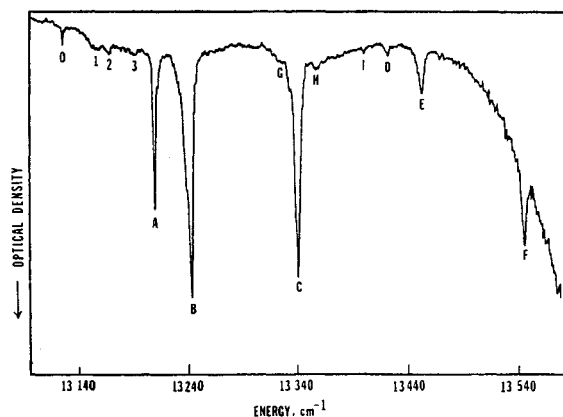


Fig. 6. Microphotometer tracing of the $\Gamma_8(^4A_{2g}) - \Gamma_7(^2T_{2g})$ absorption spectrum for ReBr_6^{2-} doped in Cs_2ZrBr_6 at 20 K showing the detailed vibronic structure [21]

tions by Krynaus and Pistorius [36]. A comparison of the vibrational mode energies for the $\Gamma_8(^4A_{2g})$ electronic state with the $\Gamma_7(^2T_{2g})$ state shows the excited electronic state odd mode energies to be about 5% smaller than the ground state odd mode energies.

In Fig. 6 the detailed structure in the complete absorption spectrum for the $\Gamma_8(^4A_{2g}) \rightarrow \Gamma_7(^2T_{2g})$ transition is shown [21]. In peaks D, E, and F the ν_6 , ν_4 and ν_3 odd modes appear coupled with the ν_1 symmetric mode, respectively. Also, for the weakly appearing peak I the ν_6 mode is coupled to the ν_2 mode and for the G, H peaks the ν_6 , ν_4 modes are coupled to the ν_5 mode, respectively. Peaks 1, 2, 3 are assigned to lattice vibrations of Cs_2ZrBr_6 coupling with the $\Gamma_7(^2T_{2g})$ ReBr_6^{2-} electronic state. It is interesting to note that the very same pattern of lattice peaks appears in both absorption and emission for the $\Gamma_1(^3T_{1g}) - \Gamma_1(^1A_{1g})$ transition observed for the d^4 OsBr_6^{2-} ion doped in the Cs_2ZrBr_6 host lattice at 20 K.

The results reported in this section should be compared with those reported by Flint et al. [37, 38] and Schmidtke et al. [39]. Also, it should be pointed out that detailed sharp-line absorption, luminescence and Raman studies have been reported for the 5d^3 hexafluororhenate(IV) ion in both pure and host crystal environments [40].

4.2

MnF_6^{2-} : Cs_2SiF_6 Impurity Ion Spectra

In this section, we consider how the optical spectra of an impurity ion mixed-crystal system can be understood in terms of a lattice-dynamical model [6]. In particular, we consider the d^3 manganese (IV) MnF_6^{2-} ion doped in a Cs_2SiF_6 lattice. The sharp lines and detailed vibronic structure of the absorption and emission spectra of the $^4A_{2g} - ^2E_g$ transition makes the Mn^{+4} ion in cubic symmetry an ideal system for study [7].

Patterson and Lynn [6] have reported a lattice dynamical study of the host lattice Cs_2SiF_6 based on neutron scattering, Raman, and infrared absorption measurements. Dispersion relations for phonons with energies less than 160 cm^{-1} have been determined along three symmetry directions by coherent inelastic neutron scattering experiments. In Fig. 7 the phonon dispersion results for Cs_2SiF_6 are shown [6] in which the experimental data are represented by circles. The solid lines correspond to dispersion curves calculated with a rigid-ion, lattice dynamical model.

Patterson et al. [7] have reported the detailed ${}^2\text{E}_g \rightarrow {}^4\text{A}_{2g}$ emission spectrum at liquid helium temperature for MnF_6^{2-} impurity ions in a Cs_2SiF_6 host lattice. In Fig. 8a is shown the emission spectrum recorded using a Spectra Physics model 375 tunable dye laser with Rh6G dye solution and pumped by an argon ion laser tuned to the ν_6 absorption peak at 16245 cm^{-1} . In Fig. 8b is also shown the excitation spectrum recorded by monitoring the intensity of the ν_6 vibronic emission at 15799 cm^{-1} as a function of the laser frequency. For both spectra the sample was cooled to 10 K so all vibrations are in the initial state.

The MnF_6^{2-} system has been the subject of a number of studies and the identity of the main features in the ${}^4\text{A}_{2g} - {}^2\text{E}_g$ vibronic band have been established (41, 42, 19). The zero-phonon line in Fig. 8 is located at 16028 cm^{-1} and the three strong lines displaced by 229, 333 and 625 cm^{-1} from the zero-phonon line are associated with the $\nu_6(t_{2u})$, $\nu_4(t_{1u})$ and $\nu_3(t_{1u})$ localized vibrations of the

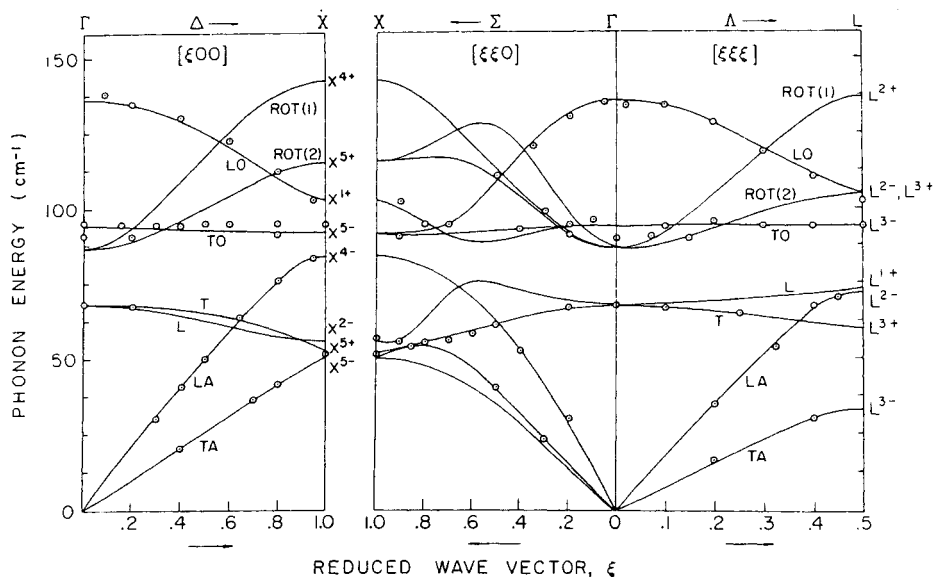


Fig. 7. Phonon dispersion results for Cs_2SiF_6 at 6 K in the Δ , λ , and Σ directions [6]. The Δ , λ , and Σ directions correspond to the $[\xi 00]$, $[\xi \xi \xi]$ and $[\xi \xi 0]$ reciprocal-lattice directions, respectively [6]. Experimental data represented by circles. The solid lines correspond to dispersion curves calculated from the O'Leary and Wheeler rigid-ion model with the lattice-dynamics parameter values in Table 3 of reference [6]

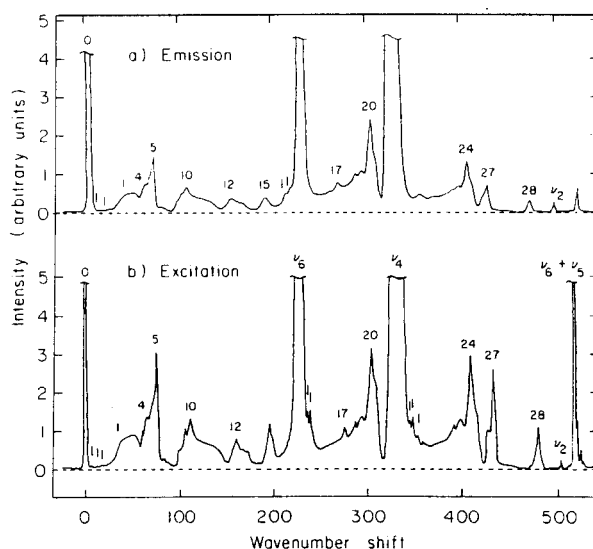


Fig. 8. The emission **a** and the excitation spectrum **b** associated with the ${}^4A_{2g} - {}^2E_g$ transition for MnF_6^{2-} doped in Cs_2SiF_6 with a crystal temperature of 10 K [7]. The spectrum of **a** the lower, and **b**, the higher energy side of the zero-phonon line at 16028 cm^{-1} , are displayed to facilitate the comparison. The vertical marks indicate very weak features considered to be associated with pair transitions

MnF_6^{2-} impurity ion, respectively. The zero-phonon transition is magnetic dipole in origin and the vibronic transitions are electric dipole induced by the odd parity vibrations. The intensity allowed by both of these mechanisms can be redistributed by an electronic-vibrational interaction to give features involving even parity vibrations. The $\nu_2(e_g)$ localized mode gives a weak feature at about 500 cm^{-1} and the $\nu_5(t_{2g})$ localized mode when coupled to the $\nu_6(t_{2u})$ mode gives the line at 517 cm^{-1} . These are all the features associated with the localized MnF_6^{2-} modes.

The lattice vibrations of Cs_2SiF_6 can be considered in two parts [79]. There are the high frequency modes involving the SiF_6^{2-} complex and, also, there are the low frequency modes where the SiF_6^{2-} complex moves with respect to the Cs^+ ions. As shown in Table 3 the features 17 and 28 are assigned to the $\nu_6(t_{2u})$ and $\nu_4(t_{1u})$ internal modes of the SiF_6^{2-} octahedra. Thus we find that the internal modes of the SiF_6^{2-} ion in the Cs_2SiF_6 host lattice, as well as the internal modes of the MnF_6^{2-} impurity ion, can couple with the $4A_{2g} - {}^2E_g$ transition to give observable peaks in the Fig. 8 luminescence spectrum.

The remaining features in the Fig. 8 spectrum are associated with the low frequency lattice modes in which the MnF_6^{2-} impurity ions moves with respect to the nearest neighbor Cs^+ ions. The low energy modes of the defect lattice should be very close in energy to those of the perfect lattice and an analysis of the vibronic features based on the lattice dynamical model of the perfect Cs_2SiF_6 lattice should be valid. Patterson and Lynn [6] reported for Cs_2SiF_6 at 6 K expe-

Table 3. Assignment of the Phonon Peaks Observed in the Luminescence Spectra (${}^2E_g - {}^4A_{2g}$) of $\text{Cs}_2\text{SiF}_6:\text{MnF}_6^{2-}$ [7]

Peak	Energy (cm^{-1})		Assignment	Calculated energy (cm^{-1})
	excitation	emission		
1	35	35	L_3^- (TA)	35
2	50	48	X_5^- (TA)	52
3	60	59		
4	64			
5	75	69	L_2^- (L cation)	75
6	81	78		
7	87		X_4^- (LA)	86
8	98	91	L_3^- (TO)	97
9	105	98	L_2^- (LO)	106
10	111	104	L_2^- LO)	106
11	141	128	Γ_4^-	139
12	161	151	151	
13	167			
14	172	164		
15	194	189		
16	198			
17	278	266	ν_6 (SiF_6^{2-})	265
18	290	286		
19	297	294		
20	305	304	ν_6 (MnF_6^{2-}) + L_1^+	306
21	310	306		
22	392	389		
23	400	398		
24	411	410	ν_4 (MnF_6^{2-}) + L_1^+	409
25	417	416		
26	423	420		
27	428	422	ν_4 (MnF_6^{2-}) + X_1^+	439
28	483	472	ν_4 (SiF_6^{2-})	470

rimental dispersion relations shown in Fig. 8 for normal modes of vibration along the $[\xi 00]$, $[\xi \xi \xi]$ and $[\xi \xi 0]$ symmetry directions. The maximum frequency of these lattice modes is 160 cm^{-1} . This means that if only one lattice vibrational quantum is involved we will only be able to account for features within 160 cm^{-1} of a parent transition.

The spectra have to be analyzed in terms of four separate regions. Within 160 cm^{-1} of the zero-phonon line, the first region, the transitions need only involve single quantum changes of the lattice modes. Similarly on the high energy side of the ν_6 and ν_4 features, but within 160 cm^{-1} of each, the transitions need only single quanta of the lattice modes in addition to the ν_6 or ν_4 modes. These are the second and third regions. This leaves a gap between the end of the first region at 160 cm^{-1} and the ν_6 localized mode peak at 229 cm^{-1} . This fourth region shows rather broad features with peaks 12–16 and are thought to involve two quanta of the lattice modes plus localized internal modes.

In region 1 immediately adjacent to the zero-phonon line (features 1–11) the integrated intensity of the vibronic band is considerably larger than the area of the zero-phonon line. Thus the band cannot arise through the coupling of the even parity vibrations as this coupling has been established to be weak. Rather the intensity must be induced by a distribution of odd parity vibrations. The odd parity vibrations involve the a_{2u} , e_u , t_{1u} and t_{2u} motions of the MnF_6^{2-} complex with respect to eight nearest neighbor Cs^+ ions. The vibrations produce at the central ion dynamic crystal fields and these are responsible for inducing the electric dipole transitions in the central MnF_6^{2-} ion. However, in the case of the a_{2u} and e_u vibrations the associated intensities will be weak. Thus, the intensity of the vibronic features in region 1 are therefore a consequence of the interaction with the vibrations of t_{1u} and t_{2u} symmetry.

The strongest peaks 5 and 10 correspond in energy to the longitudinal acoustic mode L_2^- and the longitudinal optical L_2^- . Table 1 shows that L_2^- reduces to t_{1u} and hence there is agreement with the above prediction. The longitudinal acoustic modes will also be responsible for peaks 3 and 4. However, there are no X or L zone boundary modes with the correct energies which contain t_{1u} or t_{2u} symmetry properties. These peaks are considered to arise from other high symmetry points in the Brillouin zone. As shown in Table 3, peak 7 can be assigned as arising from the longitudinal acoustic mode X^{4-} which contains t_{1u} symmetry but peak 6 must correspond to a high symmetry point other than X or L. The transverse acoustic modes give rise to the first broad maxima in the vibronic distribution and features 1 and 2 correspond well in energy to the L^{3-} and X^{5-} modes, respectively. Both, again contain t_{1u} and t_{2u} irreducible representations in the reduced symmetry and, therefore, satisfy the conditions for induced electric dipole transitions.

Above 100 cm^{-1} there is appreciable intensity and this appears to arise from the longitudinal vibrations rather than through the transverse vibrations. For example, there are no strong features associated with the very flat transverse optic mode at about 98 cm^{-1} even though it satisfies symmetry requirements at Γ , X and L. There is only the weak feature 8 which can be assigned to this mode. In contrast the longitudinal mode gives the strong peak 5 as well as feature 11 at the top of the branch corresponding to the t_{1u} zone center mode. The rotational modes are unlikely to give any intensity contribution and it is more likely that peak 9 corresponds to the longitudinal optical branch from a high symmetry point other than Γ , X or L.

In the second and third spectral regions above ν_6 and above ν_4 , respectively, the vibronic intensity arises from two quantum vibrations. A coupling of an even parity mode requires a difference in the potential surface between the ground and excited electronic states. For coupling of e_g or t_{2g} vibrations this requires a Jahn-Teller interaction whereas the coupling of an a_{1g} mode only requires a difference in internuclear distances. The a_{1g} mode is expected to be the dominant interaction and give a distribution of a_{1g} modes on the high energy side of both the ν_6 and ν_4 peaks. In the phonon dispersion curves the L^{1+} vibration at 76 cm^{-1} and X^{1+} at 105 cm^{-1} are two modes which reduce to give an a_{1g} irreducible representation. They give rise to the strongest lines in the spectrum. The vibration L^{1+}

is associated with peaks 20 and 24 and X^{1+} is associated with peak 27. The other peaks 18, 19, 21 and 26 are considered to arise from a_{1g} features from other symmetry points in the Brillouin zone. The peak assignments are summarized in Table 3.

In summary, upon comparing the detailed ${}^2E_g \rightarrow {}^4A_{2g}$ luminescence spectra for MnF_6^{2-} doped in Cs_2SiF_6 with dispersion curves for Cs_2SiF_6 the following model arises. Lattice modes with the proper symmetry and involving neighboring atom motions close to the impurity ion can couple to give observable peaks in the luminescence spectra. Even parity lattice modes of site symmetry a_{1g} can couple with MnF_6^{2-} ν_6 and ν_4 internal vibrational modes to give two-phonon peaks of moderate intensity. Finally, in this particular impurity ion system, lattice modes involving longitudinal motions exhibit more intensity than transverse motions. In a previous publication [43] this same effect was found for $OsCl_6^{2-}$ in Cs_2ZrCl_6 but for $OsCl_6^{2-}$ doped in K_2PtCl_6 transverse modes showed greater intensity.

It should be pointed out that comparisons between vibronic spectra and lattice dynamical models have been made for other M_2XY_6 systems. Chodos and Satten [44] calculated phonon dispersion curves for Cs_2UBr_6 and used these curves to interpret the vibronic structure of various electronic transitions for Cs_2UBr_6 . Durocher and Dorain [45] in a very similar fashion calculated the distributions of vibrations of different symmetry types for the optical analysis of $OsCl_6^{2-}$ doped in K_2PtCl_6 and of $ReCl_6^{2-}$ doped in K_2PtCl_6 . In contrast to these treatments by Chodos and Satten and Durocher and Dorain, the lattice dynamical model discussed here is based on dispersion curves fitted to experimental inelastic neutron scattering data. We are thus able to utilize very reliable Cs_2SiF_6 vibrational frequencies for analysis of the vibronic spectra of MnF_6^{2-} doped in the Cs_2SiF_6 host lattice.

5 d¹⁰ Example

5.1 KAu(CN)₂ System

$KAu(CN)_2$ has a layered structure for the gold atoms. The individual layers of gold are separated by 9.2 Å while the nearest neighbor gold distance in a layer is 3.64 Å [46]. When the cation is varied the distance between the gold atoms in the layers changes. This variation in nearest neighbor Au-Au separation with different cations provides an opportunity to study how the optical properties of two-dimensional layered systems are dependent on the interactions between Au atoms in layers. In this section we discuss luminescence results for $KAu(CN)_2$ in which only Au-Au interactions, and not cation-anion interactions, must be considered.

Figure 9 shows the luminescence spectra for a $KAu(CN)_2$ single crystal as a function of temperature (295, 140, 8 K) when excited with a pulsed N_2 laser at 337 nm [11]. The 295 K spectrum has a high-energy emission band at 390 nm and a low-energy band at 630 nm. As the crystal temperature is decreased, the

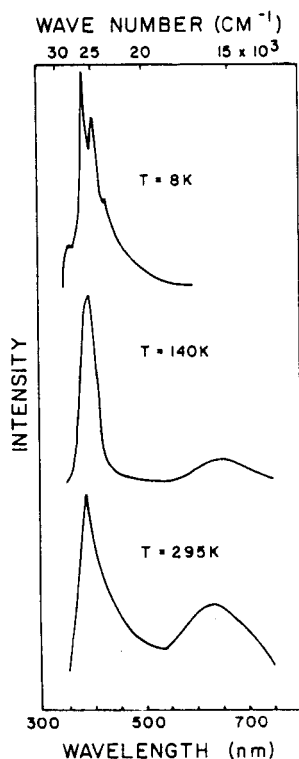


Fig. 9. Laser-excited luminescence spectra of a single crystal of $\text{KAu}(\text{CN})_2$ at temperatures of 8, 140 and 295 K with excitation wavelength of 337 nm [11]

low-energy band decreases in intensity and disappears below 120 K. At 8 K the high energy band has vibronic structure.

Both the high- and low-energy bands in the $\text{KAu}(\text{CN})_2$ single crystal luminescence spectra show a shift in position with a change in temperature. The data indicate that a temperature decrease from 300 K to 78 K results in a decrease of the emission maximum energy of the high-energy band by 1100 cm^{-1} and of the low-energy band by 400 cm^{-1} . X-ray measurements on $\text{KAu}(\text{CN})_2$ single crystals [11] between room temperature and 78 K indicate the nearest-neighbor Au-Au separation decreases from $3.64 \text{ \AA}$ at 278 K to $3.58 \text{ \AA}$ at 78 K. This temperature decrease also results in an increase of $0.06 \text{ \AA}$ between adjacent Au layers.

Polarized emission spectra were measured on a single $\text{KAu}(\text{CN})_2$ crystal oriented with the incident laser beam polarized parallel to the crystallographic *c* axis. The *c* axis in this case is the axis perpendicular to the in-plane Au-Au layers. Figure 10 shows a plot of the polarization *P* of the high-energy emission band as a function of temperature. *P* is defined by Eq. 16,

$$P = (I_{11} - I_1)/(I_{11} + I_1) \quad (16)$$

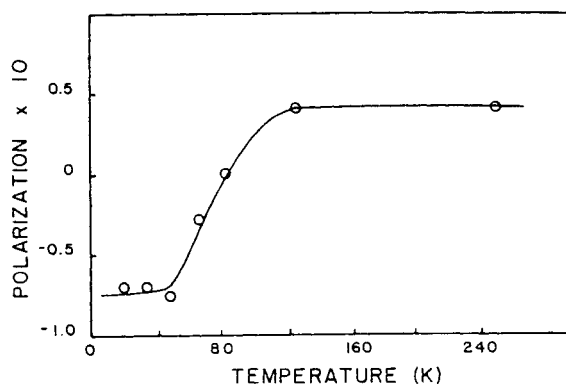


Fig. 10. Polarization of the high-energy emission band of a $\text{KAu}(\text{CN})_2$ single crystal as a function of temperature [11]. Polarization is defined by Eq. (16)

where I_{11} and $I_{\perp}$ are the intensities of the emitted beam polarized parallel and perpendicular, respectively, to the c axis.

At 8 K the single crystal high-energy emission band has peaks at 363, 388, 411, and 430 nm. Polarization measurements for the 388 and 411 nm peaks show [11] that they both have the same polarization. Lifetime measurements of the four peaks indicate [11] that the time dependence of the emission intensities at 8 K is best curve-fit by assuming emission occurs from two emitting states with less than 20 ns and 140 ns values with relative intensities of 0.8 and 0.2 respectively. At 78 K the 390 nm band has only a single lifetime value of 200 ns.

To assign the 390 nm luminescence band we have to consider the crystal structure of $\text{KAu}(\text{CN})_2$. The structure consists of layers of linear $\text{Au}(\text{CN})_2^-$ ions alternating with layers of K^+ ions [46]. In a given layer at room temperature, the $\text{Au}(\text{CN})_2^-$ linear ions are tilted 22° from the hexagonal c axis and the gold atoms lie in planes perpendicular to it. Every Au atom in a given layer has four nearest neighbors at 3.64 Å in a rectangular environment. The site symmetry of the gold atoms alone is D_{2h} which becomes C_{2h} in the presence of CN-ligands.

The high-energy luminescence band can be assigned on the basis of D_{2h} site symmetry considering nearest-neighbor Au-Au interactions. The decrease of the high energy emission energy with decreasing Au-Au separation within a layer suggests that the states involved in this luminescence correspond to metal orbitals with maximum overlap between nearest-neighbor gold atoms. There is evidence which suggests that for an isolated $\text{Au}(\text{CN})_2^-$ ion the HOMO has 6s and $5d_{z^2}$ composition and the LUMO has $6p_x$ and $6p_y$ composition. Extended Huckel molecular orbital calculations have been done [11] for five $\text{Au}(\text{CN})_2^-$ ions orientated as in Fig. 11. The luminescence results for the high-energy band of $\text{KAu}(\text{CN})_2$ may be interpreted on the basis of D_{2h} site symmetry considering nearest-neighbor Au-Au interactions. The resulting energy level diagram, also given in Fig. 11, indicates the HOMO has a_g symmetry while the LUMO has b_{3u} symmetry.

It is proposed [11] that the high-energy luminescence band can be assigned to a $a_g^1 b_{3u}^1 \rightarrow a_g^2$ electronic configuration change. The resulting excited states for

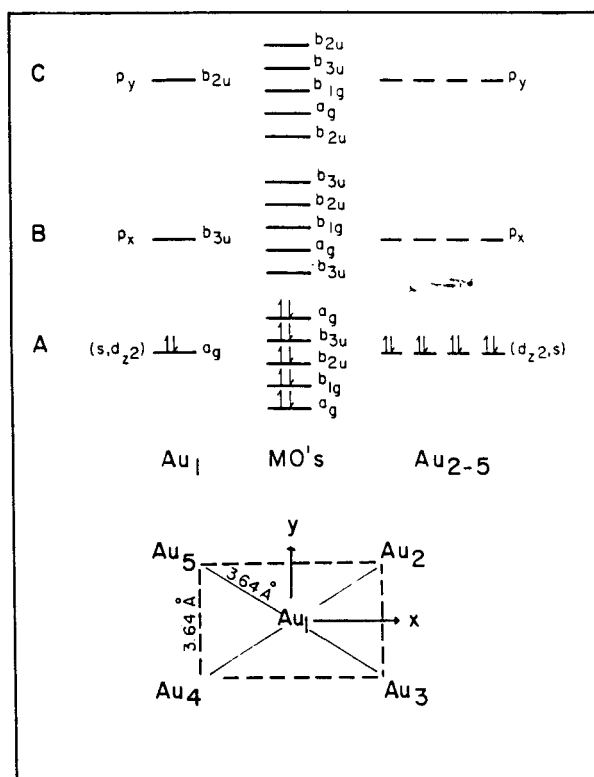


Fig. 11. Interaction of the valence atomic orbitals of neighboring Au atoms on a given layer of $\text{KAu}(\text{CN})_2$ to form molecular orbitals [11]. The definition of the axes for a layer of gold atoms in $\text{KAu}(\text{CN})_2$ is also shown [11]. The labels of the molecular orbitals have been assigned on the basis of D_{2h} site symmetry

the $a_g^1 b_{3u}^1$ configuration are a singlet ($^1B_{3u}$) and a triplet $^3B_{3u}$ with the triplet state lower in energy. In the presence of spin-orbit interaction, the $^3B_{3u}$ state splits into Γ_1^- (forbidden), Γ_2^- (z-polarized), and Γ_3^- (y-polarized). The primes are used to indicate the spin-orbit states in the Bethe notation and the selection rule results for an allowed electric dipole transition are given in parenthesis.

The 8 K lifetime results [11] for the high-energy emission band, with both less than 20 ns and 200 ns lifetime values, indicates that the emission occurs from both the $^1B_{3u} \rightarrow ^1A_{1g}$ (less than 20 ns) and $^3B_{3u} \rightarrow ^1A_{1g}$ (200 ns) transitions. At 78 K the presence of only a single lifetime (200 ns) indicates that at this higher temperature the intersystem radiationless process is quite effective and, thus, the $^3B_{3u} \rightarrow ^1A_{1g}$ transition is only observed.

The relative energies of the $^3B_{3u}$ three spin-orbit split states Γ_1^- , Γ_2^- , Γ_3^- can be determined from the plot of the polarization P of the emission versus temperature [11] in Fig. 10. The change in P from a (-) to a (+) value with changing temperature shows from the definition of P in Eq. (16) that I_{11} is greater than I_1 with

P(+) and implies that Γ_2^- with parallel polarization is becoming populated. We conclude from the P data versus temperature that $E(\Gamma_3^-) < E(\Gamma_2^-)$.

5.2

Exciton Model Predictions for Gold Dicyanide (I) Solids

The optical properties of the one-dimensional d^8 tetracyanoplatinate salts are very similar to those of the $\text{Au}(\text{CN})_2^-$ salts. For example, the $\text{Pt}(\text{CN})_4^{2-}$ ion in solution has no absorption bands below 35000 cm^{-1} but the solid salts are colored and show strong luminescence in the visible region. Yersin et al [47] have demonstrated that the emission and reflectivity energies vary linearly as R^{-3} . Day [48] has proposed that this behavior is characteristic of neutral Frenkel excitons. He has shown that the extrapolated energy of the transition at $R=\infty$ for the free ion should correspond to the solution transition energy case.

The optical luminescence data versus temperature for $\text{KAu}(\text{CN})_2$ have also been interpreted in terms of an exciton model in which the luminescence energy E is given by the relation [11]

$$E = E^0 - a/R^3 \quad (17)$$

where E^0 is the emission energy of an isolated $\text{Au}(\text{CN})_2^-$ ion and R is the Au-Au nearest-neighbor separation. An exciton results from an electron-hole pair, in the presence of a lattice, which varies in energy depending upon the Au-Au separation. Emission occurs when an electron and a hole recombine. For the $\text{KAu}(\text{CN})_2$ case, all of the $\text{Au}(\text{CN})_2^-$ ions are in approximately D_{2h} site symmetry with a nearest-neighbor room temperature separation of $3.64\text{ \AA}$. A plot of the $\text{KAu}(\text{CN})_2$ luminescence energy versus $1/R^3$ yielded a value of 43800 cm^{-1} for E^0 and 8.21×10^5 for the parameter a [11].

$\text{TlAu}(\text{CN})_2$ is a yellow-colored layered solid for which luminescence and neutron powder diffraction studies versus temperature have been reported [14, 15]. In $\text{TlAu}(\text{CN})_2$, Tl-Au interactions as well as Au-Au interactions are important in understanding the optical data. Further, there are three inequivalent $\text{Au}(\text{CN})_2^-$ ions in the unit cell unlike $\text{KAu}(\text{CN})_2$ where there is one equivalent $\text{Au}(\text{CN})_2^-$ ion in the unit cell [15].

For $\text{TlAu}(\text{CN})_2$ the observed luminescence has been assigned [14] to excitons localized along the Au(1) – Au(3) chain axis. When the emission energy is plotted [15] versus $1/R^3$, with R equal to the average Au–Au separation along the Au(1) – Au(3) chain axis, E^0 is calculated to be $(4.2 \pm 0.4) \times 10^4\text{ cm}^{-1}$ and the parameter a is equal to $(6 \pm 1) \times 10^5\text{ cm}^{-1}\text{ \AA}^3$. The experimental value for E^0 is estimated to be 42000 cm^{-1} from the tetra-*n*-butylammonium dicyanide (I) salt, where R is $8.04\text{ \AA}$ at room temperature (49). The calculated value of E^0 for $\text{TlAu}(\text{CN})_2$, like $\text{KAu}(\text{CN})_2$, is in very good agreement with the experimental value. This supports the assignment that, in $\text{TlAu}(\text{CN})_2$, the luminescence arises from excitons localized along the Au(1) – Au(3) chain axis in contrast to the $\text{KAu}(\text{CN})_2$ case where delocalization of the exciton occurs in Au layers.

5.3

Photoluminescence of Lanthanide Gold and Silver Dicyanides

Emission due to excited state energy transfer has been reported in layered low dimensional rare earth complexes such as uranyl phosphates [50], cryptates [51] and platinum tetracyanides [52, 53]. The luminescence properties of the low dimensional rare earth compounds of the type $\text{RE}[\text{M}(\text{CN})_2]_3$ where $\text{RE} = \text{Eu}^{3+}$, Dy^{3+} , Gd^{3+} and $\text{M} = \text{Au}, \text{Ag}$ are also interesting in this regard. We recently reported [16] that efficient excited state energy transfer from the $\text{Au}(\text{CN})_2^-$ and $\text{Ag}(\text{CN})_2^-$ ions to Eu^{3+} enhances the luminescence observed from the rare earth ion. A similar result is obtained from other rare earth salts [17]. In some cases vibronic structure appears in the luminescence spectrum.

Figure 12 shows the luminescence spectra [17] of $\text{Dy}[\text{Au}(\text{CN})_2]_3$ recorded using a nitrogen pulsed laser as the excitation source with the sample temperature at 10 K and 60 K. Three well resolved peaks are observed at 413.2, 424.9 and 456.5 nm. Two shoulders also appear at about 433 and 448 nm. The structure of this band appears to have a vibronic origin. Even though the spacings between the peaks are not uniform the average separation of the five peaks and shoulders is about 574 cm^{-1} . It is interesting to point out that for the corresponding $\text{Dy}[\text{Ag}(\text{CN})_2]_3$ silver solid [17] no luminescence at 10 and 60 K is observed in the high energy region (400–460 nm) of the spectrum unlike the Au case.

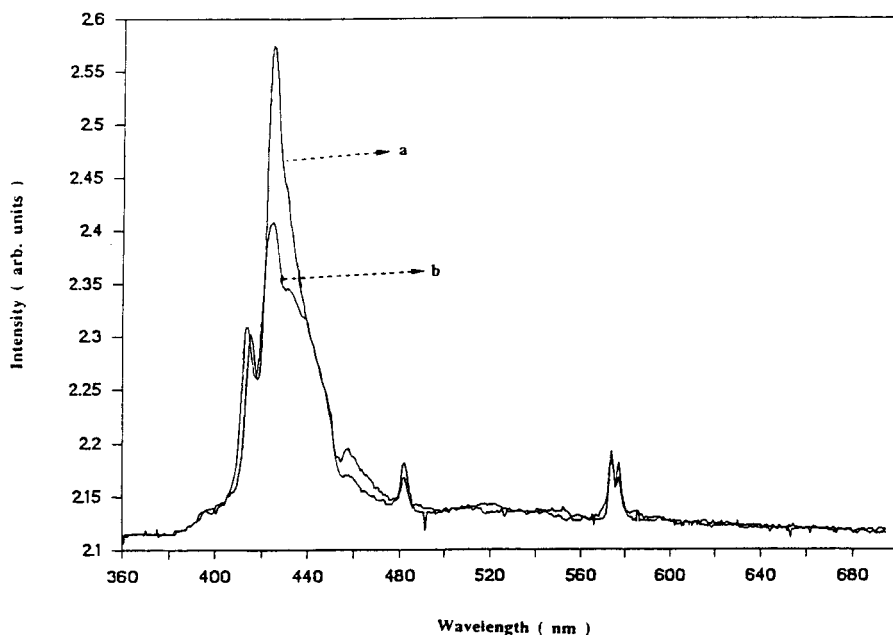


Fig. 12. Luminescence spectra of $\text{Dy}[\text{Au}(\text{CN})_2]_3$ recorded using a nitrogen pulsed laser as the excitation source: a 10 K; b 60 K [17]

The low temperature Raman spectrum of $\text{Dy}[\text{Au}(\text{CN})_2]_3$ is shown [17] in Fig. 13a. In order to facilitate the peak assignments, the spectra of the $\text{Eu}[\text{Au}(\text{CN})_2]_3$ and $\text{Gd}[\text{Au}(\text{CN})_2]_3$ systems are shown in Fig. 13b, c. The vibrational bands and their assignments are given in Table 4. The totally symmetric stretching mode (ν_1) for the CN appears at 2178 cm^{-1} . The peak at 470 cm^{-1} corresponds to the Au-C symmetric stretching mode and the Au-CN bending mode appears at 352 cm^{-1} . Two more weak Raman modes appear at 156 and 190 cm^{-1} and are assigned, respectively, to a lattice mode and a C-Au-C bending mode.

When the luminescence structure observed for the high energy region of $\text{Dy}[\text{Au}(\text{CN})_2]_3$ at low temperatures is compared with the low temperature Raman mode energies it is possible [17] to assign the vibronic structure. The results show the vibronic peaks for $\text{Dy}[\text{Au}(\text{CN})_2]_3$ are due to participation of the 470 , 190 and 156 modes. This is different from $\text{Dy}[\text{Ag}(\text{CN})_2]_3$ where no high energy luminescence appears because of efficient energy transfer from the $\text{Ag}(\text{CN})_2$ ion to the Dy^{3+} ion.

5.4

Energy Transfer for Lanthanide Gold and Silver Dicyanides

The luminescence spectrum of the $\text{Dy}[\text{Au}(\text{CN})_2]_3$ system shown in Fig. 12 is characterized by an intense high energy band and weak but sharp low energy bands.

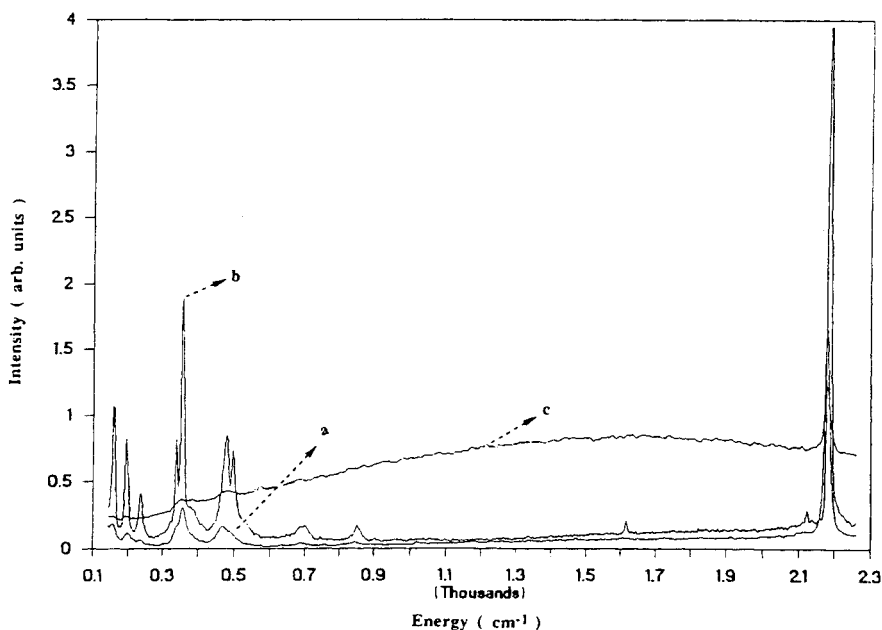


Fig. 13. Resonance Raman spectra recorded at 78 K using a Spectra Physics 2020 argon laser source [17]. The blue line at 456 nm was used as the excitation source: a $\text{Dy}[\text{Au}(\text{CN})_2]_3$; b $\text{Eu}[\text{Au}(\text{CN})_2]_3$; c $\text{Gd}[\text{Au}(\text{CN})_2]_3$

Table 4. Assignments of Resonance Raman Bands for the $\text{Dy}[\text{Au}(\text{CN})_2]_3$ Compound shown in Fig. 13 (a)^a [17]

Raman band (cm^{-1})	Assignment	Raman band (cm^{-1})	Assignment
156	lattice mode	470	Au–C str mode
190	C–Au–C bend mode	2178	CN str mode
352	Au–CN bend mode		

^a The 456 nm argon laser line was used as the excitation source. The spectra were collected at 78 K.

Assignment of the donor emission band in the $\text{Dy}[\text{Au}(\text{CN})_2]_3$ system is facilitated by comparison with the $\text{Gd}[\text{Au}(\text{CN})_2]_3$ system. In $\text{Gd}[\text{Au}(\text{CN})_2]_3$ the lowest excited state of the acceptor Gd^{3+} ion is at a much higher energy than for Dy^{3+} and the donor emission has been observed without any emission attributable to an f–f transition. The donor emission in the $\text{Gd}[\text{Au}(\text{CN})_2]_3$ system closely resembles that of the $\text{Dy}[\text{Au}(\text{CN})_2]_3$ system both in emission energy and temperature dependent behavior. This indicates that the broad high energy band in both systems originates from excitation of the donor $(\text{Au}(\text{CN})_2)^-$ ion.

The appearance of a high energy emission band in $\text{Dy}[\text{Au}(\text{CN})_2]_3$ is different from the luminescence observed for the $\text{Eu}[\text{Au}(\text{CN})_2]_3$ system [16]. In $\text{Eu}[\text{Au}(\text{CN})_2]_3$ excitation of the donor $\text{Au}(\text{CN})_2^-$ ion has resulted in the observation of only the sensitized emission from the Eu^{3+} ion at all temperatures. No emission assignable to the $\text{Au}(\text{CN})_2^-$ ion has been observed indicating very efficient energy transfer between the donor and the Eu^{3+} acceptor ions. In contrast, in the $\text{Dy}[\text{Au}(\text{CN})_2]_3$ system the Dy^{3+} ion is inefficient in quenching the donor emission significantly via energy transfer. For the $\text{Gd}[\text{Au}(\text{CN})_2]_3$ system the lowest excited state of the Gd^{3+} ion is at a much higher energy position than the donor state and, thus, energy transfer is not expected.

Finally, it should be pointed out that the luminescence spectrum of the $\text{Dy}[\text{Ag}(\text{CN})_2]_3$ compound is very different then in the $\text{Dy}[\text{Au}(\text{CN})_2]_3$ where, in the former case, no bands assignable to the donor $\text{Ag}(\text{CN})_2^-$ ion have been observed in the luminescence spectrum. The sensitized emission of the Dy^{3+} ion is strong in the $\text{Dy}[\text{Ag}(\text{CN})_2]_3$ system which is similar to the situation reported [16] for $\text{Eu}[\text{Ag}(\text{CN})_2]_3$. Finally, the Dy^{3+} ion emission intensity increases with an increase in temperature. Thus, energy transfer is efficient between the donor $\text{Ag}(\text{CN})_2^-$ ion layer and the Dy^{3+} ion layer in this unusual layered compound.

6 Summary

In this review article we have considered three examples in which vibronic structure provides valuable information. In the first example, that of the d^0 vanadium oxide on a SiO_2 substrate, Franck-Condon analysis of the luminescence spectrum indicates that an elongation of the internuclear distance between vanadium and oxygen ions in the excited states of the vanadyl groups may be

associated with the easier photoreduction of the catalyst with CO. In the second example, that of the d^3 ReBr_6^{2-} and MnF_6^{2-} impurity ions doped in a host lattice, the vibronic spectra allows us to deduce a model for the internal vibrations and lattice vibrations (phonons) which may appear in the vibronic spectra. For ReBr_6^{2-} , where the coupling of the impurity ion with the lattice is weak, internal vibrations dominate the vibronic spectra but in the MnF_6^{2-} case where the impurity ion coupling with the lattice is stronger a lattice dynamical model must be utilized. In the final example, that of the d^{10} $\text{Au}(\text{CN})_2^-$ and $\text{Ag}(\text{CN})_2^-$ ions in a layered structure, the appearance of vibronic structure for these anions can be explained by considering Au–Au and Ag–Ag interactions versus cation–anion interactions. In the $\text{TlAu}(\text{CN})_2$ case both Tl–Au and Au–Au covalent bonding are important. However, for the case where the cation is Eu^{3+} or Dy^{3+} the cation–anion interaction provides a pathway by which energy transfer from the anion to cation can occur.

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7

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Angular Overlap Model Applied to Transition Metal Complexes and d^N -Ions in Oxide Host Lattices

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The ability of the angular overlap model (AOM) to rationalize the d^N energy level scheme of an arbitrarily coordinated transition metal complex is shown. The underlying theory is summarized, including recent extensions such as s - d mixing, misdirected valency, and non-additive π -contributions (Orgel effect), which may be important when chelate ligands with conjugated π -electrons are present. Experimental data obtained from optical spectra in absorption and emission are used to derive AOM parameter values, which are still scarce for third-row transition metal ions. Special attention is paid to spectrum-structure correlations, in particular to the interrelation of d -level splittings with the angular geometry of the chromophore. Various examples are presented, in which angular distortions of the coordination sphere can be evaluated with high accuracy by means of the AOM. Further applications are given for some chromium-doped oxides for which particular metal-oxygen binding properties have to be considered.

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1

Introduction

Semiempirical methods have played and still play the major role in the elucidation of chemical bonding, the calculation of molecular geometries, and for the determination of other properties of larger molecules and extended systems. While ab-initio calculations have supplemented them for small and, increasingly, for medium-sized molecules, semiempirical methods still remain the better alternative even for relatively small molecules, when information on excited electronic states is demanded. This holds for open shell systems such as transition metal complexes, and, in particular, when heavier atoms are involved and/or spin-orbit coupling has to be considered.

In this field, the conventional ligand field theory (LFT), which was developed from Bethe's concept of crystal fields [1], represents an impressive example for a clear quantum-mechanical model that allows calculations on an enormous variety of compounds containing transition metal ions [2–4]. The exceptional value of the LFT approach for chemists, and physicists as well, lies in its easy and effective parametrization, when compared, for example, with NDO (neglect of differential overlap) methods [5]. When highly symmetric systems are considered, very few parameters are involved in the formalism; and low-symmetry complexes can often be effectively approximated by assuming a higher pseudo-symmetry. However, if more precise information is required, the actual low-symmetry potential must be rigorously applied. This leads to an uncomfortable increase of parameters [4], which tend to lose their intelligibility. This obstacle has thus far prevented the rigorous application of the LFT to systems with little or no symmetry, even though these represent the normal case of transition metal complexes.

On the other hand, a suitable technique for investigating low-symmetry complexes is available with the angular overlap model (AOM), which provides a parametrization independent of the molecular geometry [5–11]. Moreover, AOM parameters describe individual metal-ligand interactions of σ - and π -type that are better suited to chemical reasoning than the global (symmetry-adapted) quantities used within the LFT. Nevertheless, the more flexible AOM is still used only by a relatively small group of scientists, although this model was invented more than thirty years ago [12, 13] and worked out by numerous applications to d^N and f^N complexes (see Refs. [8, 11], for example). This situation is due to reasons of tradition and convenience that assume the conventional LFT to be *the* easy-to-handle approach for coordination compounds. Another argument arises from the universal applicability of the ingenious Tanabe-Sugano diagrams [14], although these are only valid for cubic symmetry (occasionally not recognized!).

This contribution, which presents some actual applications of the AOM, is organized as follows. Section 2 gives an illustration of the theoretical formalism including some modern extensions of the early model. To define the AOM parameters and to set up the perturbation matrix, the familiar tetragonally quantized d -orbitals will be used, which provide a natural basis for octahedral, tetragonal and orthorhombic complexes. On the other hand, for the exploration of *spectrum-structure correlations* in some spectroscopically well-investigated trischelated chromium(III) complexes, it is shown in more detail how to set up the related trigonal AOM matrix. The third section focuses on assignments of d - d transitions in chromium(III) and osmium(IV) complexes, which serve as suitable examples for the application of the AOM to other transition metal compounds. This part is structured according to the specific nature of the metal-ligand π -interaction, which can show isotropic, anisotropic or even more complicated behavior. Section 4 deals with chromium ions doped into oxide lattices, which have been found to provide excellent materials for tunable solid state lasers. Emphasis is placed on the question of how geometric distortions of the coordination sphere determine level splittings or, vice versa, how the coordination geometry can be derived by means of AOM calculations based on assignments of d - d transitions in optical spectra.

2

Angular Overlap Model

The underlying idea of the AOM is to consider local contributions to the ligand field potential, which arises from interactions of the metal d -orbitals with individual ligands. Parameters are defined, which describe the corresponding metal-ligand interactions of σ -, π -, and δ -type in a suitable geometric arrangement, the so-called *standard orientation*. To calculate the d -orbital energies, contributions from all ligands have to be summed up for setting up the (5×5) AOM perturbation matrix. The particular angular geometry is taken into account through a factorization of the integrals involved. This usually allows to use transferable bonding parameters for the calculations on d - d transitions in arbitrary complexes, even if low-symmetry arrangements of the ligating atoms are present within the coordination sphere(s) concerned.

In order to give a transparent illustration of the AOM formalism we begin with the most simple case of a diatomic M-L system considering only a single metal d -orbital that has finite overlap of σ -type with a valence orbital of the ligand. In a second step, the generalization is made to the full metal d -basis including further ligand orbitals also accounting for interactions of π - and δ -type. It is outlined then, how a general ligand field potential can be described in terms of the AOM parameters and relevant geometric variables. Finally, a brief description of Adamsky's computer program AOMX [15] is given, which has been used for most of our calculations.

2.1

Perturbation Energies

Starting within the one-electron approximation, the MO-LCAO wavefunction for a diatomic metal-ligand (M-L) model system is conveniently set up as

$$\psi^{MO} = c_M \varphi_M + c_L \varphi_L \quad (1)$$

where φ_M and φ_L denote a metal d -orbital and a valence orbital centered on the ligand, respectively. Within the Ritz variation procedure the orbital energy eigenvalues are obtained from the roots of the secular determinant

$$\begin{vmatrix} H_{MM} - E & H_{ML} - ES_{ML} \\ H_{ML} - ES_{ML} & H_{LL} - E \end{vmatrix} = 0 \quad (2)$$

the appropriate Hamiltonian involved being specified as described below. Absolute energies are not needed in order to describe d - d transitions, only their differences are relevant. We are concerned therefore only with the energy change of the metal d -orbital, ΔE_M , caused by the interaction, which is of σ -type for the present, with the coordinated ligand. Since the d -orbitals of the unperturbed metal ion are usually higher in energy than the occupied ligand orbitals, ΔE_M is obtained from the difference between the higher root of Eq. (2) and the d -orbital energy of the free ion (Fig. 1). The AOM assumes the interaction between the metal ion and the ligand to be relatively weak, i.e.

$$|H_{ML}| \ll |H_{MM} - H_{LL}| \quad (3)$$

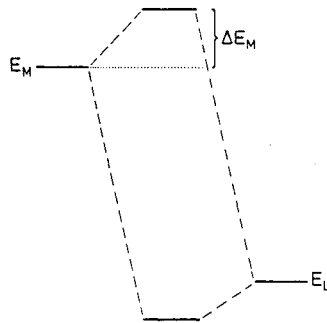


Fig. 1. MO diagram for one metal- d and one interacting ligand orbital

Eq. (3) is obviously correct for highly heteropolar *inorganic* compounds such as ammine, oxalate and halide complexes, where the transition metal ions are in their normal oxidation states. On the other hand, the AOM will be shown to be flexible enough to account also for many complexes with more covalent metal-ligand bonding by using a reasonable parametrization (see Sect. 3).

Using Eq. (3), the higher energy can be approximated by¹

$$E = H_{MM} + \frac{(H_{ML} - S_{ML}H_{LL})^2}{H_{MM} - H_{LL}} - \dots \quad (4)$$

The following formalism is simplified when the ligand wavefunction is taken orthogonal to the (real) metal d -orbital

$$\varphi_{L\perp} = \frac{1}{\sqrt{1 - S_{ML}^2}} (\varphi_L - S_{ML} \varphi_M), \text{ where } S_{ML} = \langle \varphi_M | \varphi_L \rangle \quad (5)$$

because of the vanishing overlap integral $S_{ML\perp}$ in the numerator of Eq. (4). The matrix elements H_{MM} , H_{ML} , H_{LL} contain an effective one-electron Hamiltonian, which can be separated into two parts due to the free metal ion and to the perturbation given by the ligand field potential

$$\mathfrak{H}^{\text{eff}} = \mathfrak{H}_M + \mathcal{V}_L \quad (6)$$

Notice that, according to the orbital approximation, d - d electron repulsion is not included into the formalism at this stage (see Sect. 2.5). The matrix element H_{MM} can be resolved now into

$$H_{MM} = \langle \varphi_M | \mathfrak{H}_M | \varphi_M \rangle + \langle \varphi_M | \mathcal{V}_L | \varphi_M \rangle \quad (7)$$

where $\langle \varphi_M | \mathfrak{H}_M | \varphi_M \rangle$ represents the d -orbital energy E_M in the free metal ion. The perturbation energy ΔE_M is then obtained as

$$\begin{aligned} \Delta E_M &= E - \langle \varphi_M | \mathfrak{H}_M | \varphi_M \rangle \\ &= \langle \varphi_M | \mathcal{V}_L | \varphi_M \rangle + \frac{H_{ML\perp}^2}{H_{MM} - H_{LL\perp}} \end{aligned} \quad (8)$$

The analogous decomposition of the $H_{ML\perp}$ integral results in

$$H_{ML\perp} = \langle \varphi_M | \mathfrak{H}_M | \varphi_{L\perp} \rangle + \langle \varphi_M | \mathcal{V}_L | \varphi_{L\perp} \rangle = \langle \varphi_M | \mathcal{V}_L | \varphi_{L\perp} \rangle \quad (9)$$

because the first term vanishes for the given set of orbitals, i.e.

$$\langle \varphi_M | \mathfrak{H}_M | \varphi_{L\perp} \rangle = \langle \mathfrak{H}_M \varphi_M | \varphi_{L\perp} \rangle = E_M S_{ML\perp} = 0 \quad (10)$$

In order to use further pure atomic orbitals as basis functions, the orthogonalized ligand orbitals $\varphi_{L\perp}$ are resubstituted by means of Eq. (5) leading, however, to rather complicated expressions in the numerator and denominator of Eq. (8). On the other hand, since the appearing integrals show different orders of magnitude, for example

$$\langle \varphi_M | \mathfrak{H}_M | \varphi_M \rangle > \langle \varphi_M | \mathfrak{H}_M | \varphi_L \rangle, S_{ML} > \langle \varphi_L | \mathfrak{H}_M | \varphi_L \rangle, S_{ML}^2 \quad (11)$$

¹ Making use of the expansion $(1 + q)^{1/2} = 1 + q/2 - q^2/8 + \dots$, if $q \ll 1$.

we can write the d -orbital perturbation energy in good approximation as

$$\Delta E_M = \langle \varphi_M | \mathcal{V}_L | \varphi_M \rangle + \frac{\langle \varphi_M | \mathcal{V}_L | \varphi_L \rangle^2}{E_M - E_L} \quad (12)$$

Though this may be a rather crude approximation, the AOM will take advantage of a flexible parametrization for calculating ΔE_M (see Sect 2.2). The first term in Eq. (12) represents the ionic part which describes the electrostatic interaction of the metal d -electron with the ligand field [2, 3]. The second term contains covalent contributions to ΔE_M , which are not considered within the framework of the conventional LFT². Although the LFT has been shown to be equivalent to the AOM on a certain stage of approximation [16], the explicit consideration of ligand orbitals may result in greatly different energy eigenvalues, when, for example, anisotropic M-L π -interaction is involved. In the third section we will discuss several complexes which show characteristic level splittings due to this effect.

Considering now all σ -interacting ligand orbitals of a ML_n complex, which are numerated by j , Eq. (12) expands to

$$\Delta E_M = \langle \varphi_M | \mathcal{V}_L | \varphi_M \rangle + \sum_j \frac{\langle \varphi_M | \mathcal{V}_L | \varphi_{Lj} \rangle^2}{E_M - E_{Lj}} \quad (13)$$

Another two approximations which are characteristic for the formalism of the AOM are introduced now into Eq. (13). At first, the potential of the entire ligand sphere is decomposed into a sum of contributions that are due to the individual ligators. This implies a simple *additive* ligand field potential

$$\mathcal{V}_L = \sum_l v_l \quad (14)$$

as being used in the framework of the conventional LFT, likewise. Consequently, the numerator of the second term in Eq. (13) will decompose into a sum of two-center and three-center integrals. The latter are expected to be relatively small and they will be neglected in the following, i.e.

$$\langle \varphi_M | v_{l \neq j} | \varphi_{Lj} \rangle = 0 \quad (15)$$

This relation is most important because these integrals cannot be factorized within spherical coordinates and this factorization is required in the AOM parametrization scheme (see Sect. 2.2.2). ΔE_M can be expressed now as a sum over l and we obtain

$$\Delta E_M = \sum_l \left\{ \langle \varphi_M | v_l | \varphi_M \rangle + \frac{\langle \varphi_M | v_l | \varphi_{Ll} \rangle^2}{E_M - E_{Ll}} \right\} = \sum_l \Delta E_{Ml} \quad (16)$$

² Some confusion has appeared in the literature due to various definitions on the AOM and LFT. Some authors definitely exclude the static (crystal field) terms from the AOM; others use static and dynamic contributions for defining a modern LFT.

³ The other basic formula (Eq. 42) results from the factorization of matrix elements into geometric and electronic components (see Sect. 2.2.2).

Eq. (16) can be regarded as the first master equation of the AOM.³ It shows that the energy of a single metal d -orbital is raised (or even lowered) by summing up individual contributions due to *all* ligands involved in the coordination sphere. In summary, we notice a significant energy difference between metal d -functions and ligand orbitals (Eq. 3), the additive ligand field (Eq. 14), and the neglect of three-center matrix elements (Eq. 15) as the three significant approximations within the AOM formalism.

In the next step one has to extend Eq. (16) in order to consider the complete basis of all five metal d -orbitals including further interactions with the relevant orbitals of each ligand, which may be of σ -, π - or δ -type. This procedure is rather lengthy but straightforward, leading to a (5×5) perturbation matrix which, in the normal case, has to be diagonalized. However, when a suitable set of wavefunctions is involved, by using, for example, the familiar tetragonally quantized set of orthogonalized d -orbitals interacting with properly adjusted ligand orbitals, symmetry arguments may reduce the number of non-vanishing off-diagonal matrix elements even down to zero. An illustrative example of this elementary case will be discussed in the next section.

2.2

Parametrization

2.2.1

Parameter definitions

The AOM parametrizes the individual (*local*) metal-ligand interactions that appear in Eq. (16). This strategy is in contrast to the earlier crystal field approach, for which symmetry-adapted (*global*) quantities like $\Delta (= 10Dq)$ are defined. For example, only this parameter is required to describe the contributions of all six ligands to the ligand field potential of an octahedrally coordinated d^N system. Therefore, the LFT parameters do not correlate with features of the non-symmetry molecular structure or with individual properties of the M-L bondings. This holds in particular when mixed-ligand complexes are considered that have low symmetry, or even no symmetry, and this, however, is the general case for transition metal complexes. The AOM, on the other hand, is especially designed to describe the interplay between energy levels (usually obtained from spectroscopic measurements) and structural properties of the chromophore by using parameters that are geometry-independent, giving also suggestions on the nature of the metal-ligand bondings involved. This approach leads to radial (anti)bonding AOM parameters e_λ , while the angular parts due to the complex geometry are extracted from the occurring matrix elements by means of the so-called angular-overlap factors (see Sect. 2.2.2). In order to derive a chemically reasonable parametrization, strong field metal wavefunctions are used [2, 3] and the orbitals to be considered are oriented as to give a maximum overlap integral at a given M-L distance. Figure 2 illustrates the related metal-to-ligand interactions that can be of σ -, π - or δ -type. This classification denotes to the number of nodal planes that contain the internuclear M-L axis: e_σ (no plane), e_π (one plane) and e_δ (two planes). e_σ is defined then by the interaction of the

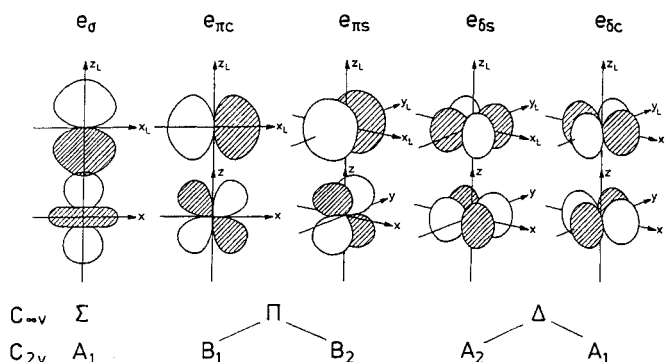


Fig. 2. AOM parametrization for the M-L system within the standard orientation, where the ligand is located on the z-axis

metal d_{z^2} with the p_z -orbital of the axial ligand (or a hybridized ligand valence orbital that is symmetric due to rotations around the z-axis), and, according to Eq. (12), we may write

$$e_\sigma = \langle d_{z^2} | v_L | d_{z^2} \rangle + \frac{\langle d_{z^2} | v_L | p_z \rangle^2}{E_{d_{z^2}} - E_{p_z}} = e_\sigma^{MM} + e_\sigma^{ML} \quad (17)$$

using the following abbreviations for the ionic and the covalent parts of the perturbation energy

$$e_\sigma^{MM} = \langle d_{z^2} | v_L | d_{z^2} \rangle \quad (18)$$

$$e_\sigma^{ML} = \frac{\langle d_{z^2} | v_L | p_z \rangle^2}{E_{d_{z^2}} - E_{p_z}} \quad (19)$$

Accordingly, the π -interaction via the ligand p_x -orbital is given by

$$e_{\pi c} = \langle d_{xz} | v_L | d_{xz} \rangle + \frac{\langle d_{xz} | v_L | p_x \rangle^2}{E_{d_{xz}} - E_{p_x}} = e_{\pi c}^{MM} + e_{\pi c}^{ML} \quad (20)$$

where ionic and covalent contributions can be summarized again into a single parameter $e_{\pi c}$, and similar equations define the other AOM parameters (see Fig. 2).

In view of the chemical feeling on the power of the respective (anti)bonding effects in transition metal compounds, the e_λ values should obey the relation

$$|e_\sigma| > |e_\pi| > |e_\delta| \quad (21)$$

This sequence is also established by comparing AOM parameters with the corresponding overlap integrals that are derived by substituting H_{ML} in Eq. (4) using the Wolfsberg-Helmholz approximation [17]

$$e_\lambda(M-L) \sim S_{ML}^2(\lambda) / \{H_{MM}(\lambda) - H_{LL}(\lambda)\} \quad (22)$$

Positive e_λ values characterize *donor* ligands which have $H_{MM} > H_{LL}$, while $e_\lambda < 0$ is associated with an *acceptor* behavior. e_σ is always positive, because the

interaction between a ligand lone-pair and a metal-centered d -orbital of σ -type always destabilized the d -orbital (cf. Fig. 1). π -parameters, on the other hand, can have positive or negative sign that depends on d_π -orbitals being destabilized (π -antibonding) or stabilized (π -bonding) by combination with occupied or with low-lying empty (π^*) ligand orbitals, respectively. Anisotropic π -bonding requires two π -parameters, $e_{\pi s}$ and $e_{\pi c}$, where the subscripts s and c reflect the *sine* and *cosine* dependencies of the φ -part of the respective metal d -wavefunction. For isotropic π -interaction, $e_{\pi s}$ equals $e_{\pi c}$, and the subscripts are omitted. Halogenide ions, for example, behave as isotropic π -donors, i.e. $e_{\pi s} = e_{\pi c} = e_\pi > 0$. A single (pseudoisotropic) π -parameter is occasionally used also for the HO^- and H_2O ligands, although a rotation around the metal-oxygen bond axis may influence certain energy levels considerably [18]. For ligated carboxylate ions, on the other hand, two nonequivalent parameters, $e_{\pi s} (= e_{\pi \perp})$ and $e_{\pi c} (= e_{\pi \parallel})$ must be involved in order to contribute to the rather different in-plane and out-of-plane π -interactions. The effect of π -anisotropy on the d^N energy level splittings will be illustrated for some chromium(III) and osmium(IV) complexes in Sect. 3.2.

Interactions of δ -type are small compared to σ and π due to small overlap integrals between the orbitals located on the central ion and on the ligating atoms.⁴ Although they may play a considerable role in polynuclear systems for describing metal-metal interactions, they are usually ignored. On the other hand, δ -interaction is implicitly involved in the formalism for eliminating radial contributions of the ligand field potential that are present in all of the e_λ parameters. This may be done by defining new quantities to

$$e'_\lambda = e_\lambda - e_\delta; \lambda = \sigma, \pi \quad (23)$$

However, unless δ -interaction is ever significant, this relation is not important and the superscripts will be omitted.

It is convenient to consider the local pseudo-symmetry for each type of metal-ligand bonding that is $C_{\infty v}$ for isotropic or C_{2v} for anisotropic π -interaction, respectively. Then, with the only exception of (negligible) σ - δ_c mixing, the AOM matrix is completely diagonal for the so-called *standard orientation*, because the three d -orbitals involved in σ - and π -bonding belong to different irreducible representations in the local symmetry group (cf. Fig. 2). Therefore, the AOM matrix relevant for the M-L system has the simple form

$$\begin{array}{ccc} d_{z^2} & d_{yz} & d_{xz} \\ \hline e_\sigma & 0 & 0 \\ 0 & e_{\pi s} & 0 \\ 0 & 0 & e_{\pi c} \end{array} \quad (24)$$

We will consider now, as an introductory example, an ML_6 complex of octahedral symmetry and evaluate the full AOM matrix by taking into account all

⁴ Cf. the article of H. B. Gray on δ -bonding effects (this volume).

terms that occur in Eq. (16). Other complexes of lower symmetry, showing even arbitrary positions of the ligating atoms in the coordination sphere, will be explored in the next section. Due to the parameter definitions given above, an octahedral arrangement is the most favorable case for calculating the perturbed orbital energies of an d^N system. This is because the tetragonally quantized (strong field) wavefunctions allow for an optimal arrangement due to maximum overlaps between the metal and all ligand valence orbitals (cf. Fig. 2) which is illustrated in Fig. 3 for axial (z) and equatorial (x, y) bonding of σ -type. Regarding now the σ -interactions via the valence orbitals of the ligands located on the z -axis, the energy of d_{z^2} is raised by $2e_\sigma$ according to Eq. (17). Further contributions come from the interactions with the σ -type orbitals of the four ligands which are located in the xy -plane (cf. Fig. 3a). From the particular angular shape of the d_{z^2} orbital that is entirely confined to $(3\cos^2\vartheta_d - 1)$ follows for any polar angle ϕ_d

$$d_{z^2}(\vartheta_d = 90, \phi_d)/d_{z^2}(\vartheta_d = 0, \phi_d) = -\frac{1}{2} \quad (25)$$

and, consequently, the equatorial matrix element which corresponds to Eq. (18) is given by

$$\langle d_{z^2} | v_{eq} | d_{z^2} \rangle = 1/4 e_\sigma^{MM} \quad (26)$$

The same fraction is obtained for the covalent part e_σ^{ML} , because the numerator in Eq. (19) exhibits the matrix element squared. We notice that for reasons of symmetry there are no other interactions possible with d_{z^2} . Hence the total perturbation energy of this orbital in an octahedrally coordinated ML_6 complex is obtained from the sum of all the individual contributions

$$\Delta E_{d_{z^2}} = 2 \cdot (e_\sigma^{MM} + e_\sigma^{ML}) + 4 \cdot \frac{1}{4} (e_\sigma^{MM} + e_\sigma^{ML}) = 3e_\sigma \quad (27)$$

The ionic and covalent terms accumulate into a single parameter e_σ that is efficient with respect to keeping the number of variables low. On the other hand, insight into the different contributions cannot be obtained at this stage, which would be of interest from the theoretical point of view.

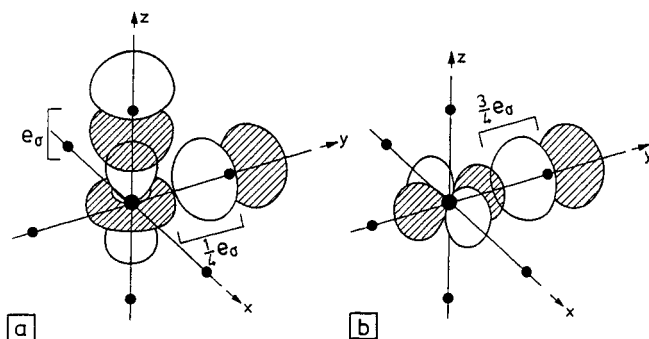


Fig. 3 a, b. Definitions for σ -antibonding AOM parameters. **a** Interactions with the d_{z^2} -orbital (cf. Eqs. 22, 26); **b** interaction with $d_{x^2-y^2}$ (cf. Eq. 29)

The angular structure of the $d_{x^2-y^2}$ -orbital yields the relationship

$$d_{x^2-y^2}(\vartheta_d = 0, \phi_d = 0)/d_{z^2}(\vartheta_d = 90, \phi_d) = \sqrt{\frac{3}{4}} \quad (28)$$

and determines now the strength of the σ -interaction with the other e_g -type orbital. As denoted in Fig. 3b, the corresponding matrix element becomes

$$\langle d_{x^2-y^2} | v_{eq} | d_{x^2-y^2} \rangle = \frac{3}{4} (e_{\sigma}^{MM} + e_{\sigma}^{ML}) = \frac{3}{4} e_{\sigma} \quad (29)$$

Due to the four lobes of $d_{x^2-y^2}$ a total perturbation energy of $3e_{\sigma}$ ($=\Delta E_{eg}$) is derived again (cf. Eq. 27) when the contributions of all four equatorial ligands are considered. Of course, the octahedral symmetry requires equal results for both e_g -orbitals.

Metal-ligand interactions of π -type can arise in an octahedral complex only with the three t_{2g} -orbitals d_{xy} , d_{xz} , d_{yz} (cf. Fig. 2). Since each of these metal orbitals interacts with four p_{π} ligand orbitals, the total perturbation energy equals $4e_{\pi}$ ($=\Delta E_{t_{2g}}$) assuming isotropic π -interaction ($e_{\pi s} = e_{\pi c}$). In summary, that the total perturbation energy of each d -orbital can be expressed by a sum of e_{λ} parameters, which are defined due to the specific metal-ligand interactions involved. In the case of octahedral symmetry this result reflects the well-known energy splitting of t_{2g} , e_g -orbitals which is depicted in Fig. 4. Hence, the LF parameter Δ_{Oh} is given by the difference between the total contributions of σ - and π -anti-bonding (or π -bonding, if $e_{\pi} < 0$)

$$O_h: \Delta_{Oh} = 10Dq_{Oh} = 3e_{\sigma} - 4e_{\pi} \quad (30)$$

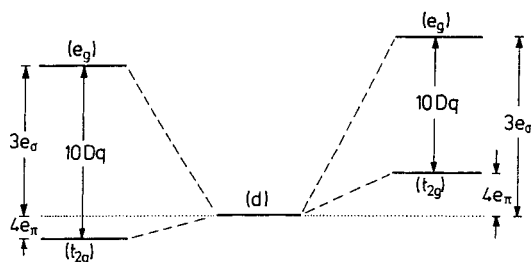


Fig. 4. d -orbital energies for π -donor (i.e. antibonding effect, right side) and π -acceptor ligands (i.e. bonding effect, left side) in an octahedral environment

The situation is a little more complicated for a tetrahedral surrounding, where σ - and π -contributions cannot be separated. However, by using angular overlap factors [9] (see next section) the following relation may be readily obtained

$$T_d: \Delta_{Td} = 10Dq_{Td} = -\frac{4}{9} (3e_{\sigma} - 4e_{\pi}) \quad (31)$$

Eq. (31) shows a reversed ordering of (t_2, e) -orbitals and a reduced energy splitting, when compared with the octahedral case. This is not unexpected due

to the smaller number of ligating atoms contributing to the ligand field potential, and to the fact that each d -orbital is influenced by σ - and π -interactions. It should be remarked that the LF parameter Dq can be derived from the two AOM parameters, but not *vice versa*. This holds also for relationships with other quantities used in the conventional LFT, e.g. when the tetragonal LF-parameters Ds and Dt are involved [16]. On the other hand, both parameters e_σ and e_π cannot be determined by spectroscopic investigation of a cubic system alone. Insight into bonding properties by means of the AOM therefore calls for an examination of complexes with lower (electronic) symmetry.

An example for such a complex is given by $trans-[Cr(py)_2(ox)_2]^-$, which is discussed in further detail in Sect. 3.2.2. Because we can expect pronounced *anisotropic* π -interactions here, $e_{\pi c}$ and $e_{\pi s}$ must be different for each ligand. Assuming an idealized geometry, i.e. a quasi-octahedral arrangement for the $[MN_2O_4]$ chromophore, the full AOM matrix takes the form

d_{xy}	d_{xz}	d_{yz}	$d_{x^2-y^2}$	d_{z^2}
$4e_{\pi c}(O)$	0	0	0	<u>0</u>
0	$2e_{\pi s}(O) + 2e_{\pi c}(N)$	<u>0</u>	0	0
0	<u>0</u>	$2e_{\pi s}(O) + 2e_{\pi c}(N)$	0	0
0	0	0	$3e_\sigma(O)$	0
<u>0</u>	0	0	0	$e_\sigma(O) + 2e_\sigma(N)$

(32)

so far as both pyridine ligands are orientated parallel to the xz -plane. Because of the axial π -anisotropy ($e_{\pi s}(N) \neq e_{\pi c}(N) \approx 0$, i.e. no π -interaction in the plane of the pyridine group), the d_{xy} - and d_{yz} -orbitals are no longer equivalent and the symmetry of the ligand field potential is reduced to D_{2h} . Lowering of the electronic symmetry has to be considered in any case when an extended π -electron system is involved, because in-plane and out-of-plane metal-ligand interactions should always be different. However, their effective contributions to the ligand field potential also depend upon the individual orientations of the respective ligand orbitals. This effect is accounted for by an angular variable ψ as described in the next section; examples for that will be given in Sect. 3.2. We notice that a staggered position for the pyridine ligands in $trans-[Cr(py)_2(ox)_2]^-$ implies a pseudo-isotropic axial π -bonding, and, consequently, the AOM matrix shows a pseudo- D_{4h} symmetry. Another point stresses the influence of geometric distortions, i.e. deviations from an orthoaxial surrounding, on the AOM matrix and on the d^N energy eigenvalues. When, for example the actual chelate bite angle ($\alpha < 90^\circ$) is taken into account,⁵ non-vanishing off-diagonals will occur at the positions underlined in the matrix (32). In the first volume of this series Hoggard [19] has thoroughly discussed the appearance of off-diagonals in the AOM matrix by considering tetragonal, orthorhombic and trigonal complexes

⁵ $\alpha(ox) \approx 82^\circ$ in many chromium(III) complexes.

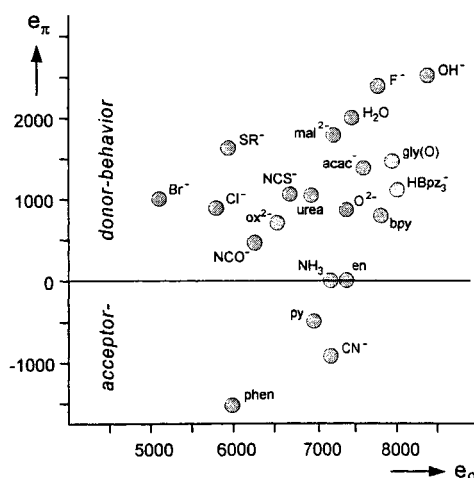


Fig. 5. Two-dimensional spectrochemical series for monodentate and chelate ligands in chromium(III) complexes showing σ - and π -binding properties in terms of the AOM parameterization. In cases of anisotropic π -interaction, the predominant contribution is considered. Ligand abbreviations: acac = acetylacetonate; bpy = 2,2'-bipyridine; en = ethylenediamine; gly = glycine; HBpz₃ = trispyrazolylborate; mal = malonate; ox = oxalate; phen = o-phenanthroline; py = pyridine

to which the reader is referred. The method of how to treat a ligand field potential having low or even no symmetry, which is the essential part in the framework of the AOM, is outlined in the following section.

In analogy to the spectrochemical series, in which ligands are arranged due to their potential in splitting the d -orbitals into t_{2g} - and e_g -orbitals, a *two-dimensional* spectrochemical series can be established on the basis of σ - and π -parameters. McClure first proposed such an arrangement in a two-dimensional plot when he characterized the electronic states of hexa-coordinated transition-metal ions by means of their σ - and π -bonding properties [20]. Figure 5 contains AOM parameter values for a series of familiar ligands that have been evaluated by fitting spectroscopic data of chromium(III) complexes. The ordering of e_σ and e_π parameters is similar for many other metal ions. The σ/π -ratio, otherwise, may vary considerably, especially when ions belonging to different rows of the periodic table are concerned.

2.2.2

Angular Dependencies of d -orbital Energies

This section describes the technique that allows the orbital energies to be calculated when the ligands are located at arbitrary angular positions. Obviously, the integrals involved in Eq. (16) reveal characteristic angular dependencies, from which this model has derived its name. Figure 6 shows a ligating atom, located in a general position. For a given internuclear distance, the geometry is completely determined by the two Eulerian angles ϑ_L and φ_L . In order to use the

AOM parameters as derived from an optimal alignment of metal and ligand orbitals, the standard set of d -orbitals is rotated by an orthogonal transformation $\mathcal{D}^{(d)}$ so that the standard orientation is obtained, in which the new d'_{z^2} orbital points directly towards the ligand (cf. Fig. 2).

$$\begin{pmatrix} d'_{z^2} \\ d'_{yz} \\ d'_{xz} \\ d'_{xy} \\ d'_{x^2-y^2} \end{pmatrix} = \mathcal{D}^{(d)} \begin{pmatrix} d_{z^2} \\ d_{yz} \\ d_{xz} \\ d_{xy} \\ d_{x^2-y^2} \end{pmatrix} \quad (33)$$

This basis transformation does not, of course, change energies, but it allows a factorization of the matrix elements. Using the conventional $F_{M\lambda}(\vartheta_L, \varphi_L)$ notation for the occurring geometrical factors, each of the matrix elements can be decomposed into

$$\langle \varphi_M | v_L | \varphi_M \rangle = \sum_{\lambda} F_{M\lambda}^2(\vartheta_L, \varphi_L) \langle \varphi_{M\lambda} | v_L | \varphi_{M\lambda} \rangle \quad (34)$$

$$\langle \varphi_M | v_L | \varphi_L \rangle = \sum_{\lambda} F_{M\lambda}(\vartheta_L, \varphi_L) \langle \varphi_{M\lambda} | v_L | \varphi_L \rangle \quad (35)$$

These are fundamental equations of the AOM and their utility for the calculations follows from the recognition that the $F_{M\lambda}$ are determined by the molecular structure with the angular positions of the ligands (ϑ_L, φ_L). They represent angular overlap factors that are fractions of the maximum overlap integrals $S_{ML}(\lambda)$ of σ -, π - or δ -type which result for the optimal orientations defined in Fig. 2. At a given metal-ligand distance these factors are determined for a particular molecular geometry only by the angular coordinates of each ligand, i.e., they are explicitly supplied with the rotation matrix $\mathcal{D}^{(d)}$. Indeed the name of the

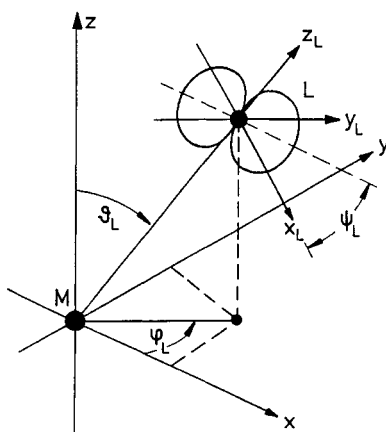


Fig. 6. Coordinate systems and structural angles for a ligand L located in an arbitrary position. The orientation of the ligand π -orbital with respect to the d -orbital considered is adjusted by the dihedral angle ψ (see text)

AOM follows from this, or, in other words, from the fact that the angular parts of the overlap integrals (cf. Eq. 4) transform identically to the angular parts of the respective d -orbitals

$$S_{M'L}(\lambda) = F_{M\lambda}(\vartheta_L, \varphi_L) S_{ML}(\lambda) \quad (36)$$

Note that the e_λ are related to the radial part of the overlap integral $S_{ML}(\lambda)$ given in Eq. (22).

When anisotropic π -interaction is involved, the dihedral angle ψ_L comes into play. The coordinate system of the ligand has then to be rotated further around z_L by the amount of ψ_L in order to orientate the ligand π -orbitals with the x_L -, y_L -axes. Thus, $\mathcal{D}^{(d)}$ generally depends on the three angles ϑ_L , φ_L and ψ_L ; its analytical form has been derived by Schmidtke [21] and Schäffer [6] by means of different mathematical methods. According to all possible e_λ contributions, the transformation matrix is arranged in five columns

$$\mathcal{D}^{(d)} = \mathcal{D}^{(\sigma)} \mathcal{D}^{(\pi s)} \mathcal{D}^{(\pi c)} \mathcal{D}^{(\delta s)} \mathcal{D}^{(\delta c)} \quad (37)$$

of which the ψ_L -independent σ -part is written as

$$\mathcal{D}^{(\sigma)} = \begin{pmatrix} (1 + 3 \cos 2\vartheta)/4 \\ (\sqrt{3/2}) \sin 2\vartheta \sin \varphi \\ (\sqrt{3/2}) \sin 2\vartheta \cos \varphi \\ (\sqrt{3/4}) (1 - \cos 2\vartheta) \sin 2\varphi \\ (\sqrt{3/4}) (1 - \cos 2\vartheta) \cos 2\varphi \end{pmatrix} \quad (38)$$

omitting the subscripts L. The complete matrix is given elsewhere [6, 21], some instructive sample calculations are presented in Ref. [11]. Then, according to Eq. (16), the complete AOM matrix of an ML_n complex, which summarizes the contributions of all ligands which may be in arbitrary positions, is given by

$$H_{ij}^{\text{AOM}} = \sum_l \left\{ \langle \varphi_{M_i} | v_l | \varphi_{M_j} \rangle + \frac{\langle \varphi_{M_i} | v_l | \varphi_{L_l} \rangle \langle \varphi_{L_l} | v_l | \varphi_{M_j} \rangle}{E_M - E_{L_l}} \right\} \quad (39)$$

i, j denoting the metal d -orbitals. According to Eqs. (34, 35), these integrals will be factorized by taking into account the geometrical position of each ligand. Hence, by using the abbreviations given in Eqs. (18, 19), we obtain the second master equation of the AOM formalism

$$H_{ij}^{\text{AOM}} = \sum_l \sum_\lambda F_{i\lambda}(\vartheta_l, \varphi_l) F_{j\lambda}(\vartheta_l, \varphi_l) e_{\lambda l} \quad (40)$$

which is valid for any geometry of arbitrary d^N systems! The sums run over the number of ligating atoms, $l = 1, 2, \dots, n$ and over $\lambda = \sigma, \pi, (\delta)$; the M-subscripts for the angular overlap factors are omitted here. The angular overlap factors $F_{i\lambda}$ equal one, if the ligands are located on special geometric positions. Then the d -orbital energies can be easily obtained from the respective AOM parameters e_λ as previously shown by the matrix (32). In the general case of lower symmetry, non-vanishing off-diagonals occur and the (5×5) -dimensional AOM matrix has to be diagonalized. However, the equations derived clearly demonstrate the

simplicity of the AOM formalism which allows *d*-electron orbital energies to be calculated by combining bonding parameters with geometric factors that are related to the explicit angular geometry of the chromophore.

2.2.3

Distance Dependencies of AOM Parameters

The integrals involved in the definitions of the (radial) e_λ parameters must depend upon the metal-ligand distance R . Consequently, this can lead to different parameters for describing the antibonding effect even within the same ML_n complex, when metal-ligand distances vary considerably. This situation appears, for example, with the $[\text{MnF}_6]^{3-}$ anion, where an enormous difference in equatorial and axial bond lengths occurs in the potassium salt [22]. The large multiplet splittings due to the strong tetragonal distortion can be calculated only if two different e_σ parameters are used, which are approximately related to each other by an R^{-5} dependency. The point charge approximation of the electrostatic model also assumes an inverse fifth power dependence of the cubic parameter $10Dq$ on the metal-ligand distance; however, additional terms will appear for potentials of lower symmetry [23]. Within the AOM, on the other hand, varying distances should affect the σ - and π -interactions in a different way, because for increasing metal-ligand distances the e_π parameters should decrease more rapidly than the e_σ parameters, parallel to the decrease of related overlap integrals. A theoretical approach to this problem has been given by Warren [24], who calculated e_λ distance dependencies by using the relationship

$$\partial e_\lambda / \partial R = (e_\lambda / S_\lambda^2) \cdot (\partial S_\lambda^2 / \partial R) \quad (41)$$

where S_λ is the appropriate diatomic overlap integral. The $\partial e_\lambda / \partial R$ terms have been evaluated for some fluoro- and chloro-complexes of the $3d$ series by using multiexponent SCF functions. These calculations indicate that the electrostatic model yields acceptable agreement only for the σ -interaction, whereas the decrease of the e_π parameters with increasing metal-ligand distances is substantially underestimated (see above).

However, the situation with the manganese(III) complex, which has an *Jahn-Teller* distorted ground state, is quite rare, since the M-L distances do not generally differ too much within the same molecule. This is the normal case also when different molecules are considered. For example, the Cr-NH₃ distances vary by less than two percent in most compounds which embody the $[\text{Cr}(\text{NH}_3)_5\text{X}]^{n+}$ anion, X = Cl⁻, NCO⁻, H₂O, reflecting also very small trans-effects on the Cr-N distances [25]. In general, metal-ligand distances do not deviate to an extent that would require a significantly different parametrization for the M-L group when incorporated in different complexes.⁶ This is rather important

⁶ The situation is different for d^N ions doped into host lattices, because in these systems the geometry of the substituted sites will predominantly determine the internuclear distances (cf. Sect. 4).

for the *transferability* of the e_λ parameters, which has been established over a wide range of related compounds. This property makes the AOM parametrization scheme a powerful tool, providing reasonable predictions to almost arbitrary molecules on the basis of given parameter sets for the individual contributions of σ - and π -interactions. Examples of this type of calculations will be given in Sect. 3.2.3.

Another factor that may come into play concerns the influence of outer coordination spheres, which can also contribute to the ligand field potential. In particular, if only a small number of ligator atoms form the first coordination sphere, as in a tetrahedron, the next-nearest ions or molecules may not be sufficiently shielded and can influence the d -orbital splitting considerably. Because of the very different distances to the central metal ion, the parameter values should dramatically decrease for those atoms further away. Since there is no direct way to determine the second sphere parameters, approximations using various R^{-n} laws have been proposed [23, 24]. However, for proving the necessity of higher sphere contributions, suitable compounds should be thoroughly investigated in order to obtain a more profound database that should also include pressure-induced band shifts or data on transition metal ions, doped in various host lattices of a similar type. In this field, however, sufficient and reliable spectroscopic information is not available up to now.

2.3

Extensions of the Angular Overlap Model

The AOM can be easily extended using guidelines given by the MO-LCAO theory. For example, the model is able to consider distinct π -effects that may occur when chelating ligands are involved which have an extended π -electron system. As already predicted by Orgel [26], phase relations of ligand frontier orbitals may cause an additional splitting of the metal d_π -orbitals. This idea has been introduced into the AOM by Ceulemans et al. [27], and a first application of their *phase-coupling* concept has been given by Atanasov et al. [28]. A detailed discussion on the respective AOM parametrization for complexes with conjugated bidentate ligands has appeared recently (Yamatera and Schäffer [29]). In the following we describe the formalism of the Orgel effect in some detail and discuss in Sect. 3.3 its influence on the d^N energies and geometries of tris-acetylacetonate complexes of trivalent first-row transition metal ions.

Another effect concerns σ - π mixing by introducing off-diagonals into the AOM matrix. In this case the “ σ -bonding” of the M-L group loses the rotational symmetry and, consequently, its pure σ -character. This peculiarity has been discussed for Schiff-base complexes by Gerloch et al. [30, 31], who proposed a misalignment of metal-ligand bonds in these chelate complexes. A brief description of their concept of *misdirected valency* is given in Sect. 2.3.2.

A further extension, which has been discussed for complexes having a small coordination number, considers interactions with unoccupied higher $(n+1)s$ or $(n+1)p$ metal orbitals. The inclusion of s - d (or p - d) *orbital mixing*, which implicitly enlarges the basis set of the five d -orbitals as well as the number of model parameters, is outlined in Sect. 2.3.3. However, one should recognize that no

more than four parameters are required for calculating the d -orbital splittings of arbitrary complexes. Therefore, the main subject for most extensions of the conventional AOM is to preserve the original parameter values and to account for special effects by a minimum of additional (*and physically reasonable!*) parameters. We notice that such quantities may also contribute to electronic properties of the molecule, which cannot be described within the first coordination sphere alone.

2.3.1

The Phase-Coupling Concept (Orgel Effect)

A profound extension of the AOM becomes important for chelate complexes having an extended π -electron system. An illustration is provided by a simple $[M(L-L)]$ system which consists of a metal ion and one symmetrical bidentate ligand. In the framework of the conventional (*additive*) AOM, the energy matrix for the π -orbitals is diagonal containing two antibonding parameters, which describe the π -interaction in the chelate plane by $e_{\pi c}$ (or $e_{\pi||}$) and perpendicular to it by $e_{\pi s}$ (or $e_{\pi\perp}$):

$$\mathcal{V}_{\pi} = \begin{array}{ccc} & \begin{array}{ccc} d_{yz} & d_{xz} & d_{xy} \end{array} \\ \begin{array}{c} e_{\pi s} \\ 0 \\ 0 \end{array} & \begin{array}{ccc} 0 & e_{\pi s} & 0 \end{array} \\ & \begin{array}{ccc} 0 & 0 & 2e_{\pi c} \end{array} \end{array} \quad (42)$$

This description of the ligand field potential is not valid when the chelating molecule has an extended π -electron system such as, for example, the acetylacetonate anion or 2,2'-bipyridine. In such cases the frontier molecular orbital of a symmetric chelate can be classified within C_{2v} symmetry as illustrated in Fig. 7; other properties of the chelate bridge will not be considered. The particular MO is either symmetric (χ -type) or antisymmetric (ψ -type) with respect to the $\tilde{C}_2$ -axis. Since combination with metal d -functions can take place only within the same subspace of symmetry, the tetragonally quantized t_{2g} -wavefunctions have to be transformed according to C_{2v} . This can easily be achieved by applying the transformation matrix

$$\mathfrak{T} = \begin{pmatrix} 1 & 1 & 0 \\ 1 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \quad (43)$$

on the t_{2g} basis set. The new wavefunctions d_{ψ} and d_{χ} are derived as linear combinations of the old basis functions, while the totally-symmetric in-plane d_{xy} -orbital is not changed

$$\begin{array}{l} b_1: d_{\psi} = \sqrt{1/2} (d_{xz} + d_{yz}) \\ a_2: d_{\chi} = \sqrt{1/2} (d_{xz} - d_{yz}) \\ a_1: d_{xy} \end{array} \quad (44)$$

Hence, two parameters are required to describe the out-of-plane interaction between ψ -type orbitals ($e_{\pi s}$) and χ -type orbitals ($e_{\pi s}'$), respectively. Using these

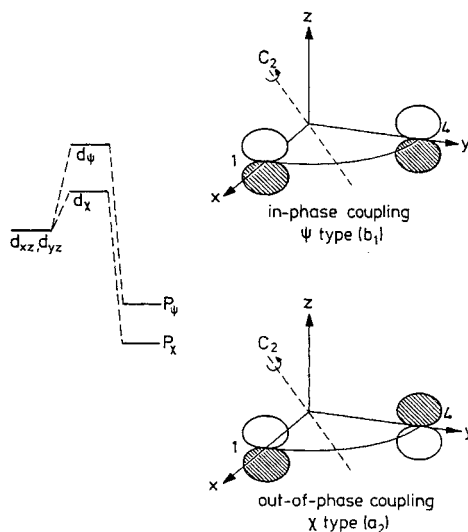


Fig. 7. Frontier π -orbitals of chelate ligands having an extended π -electron system in the local C_{2v} symmetry group

parameters, the symmetry-adapted AOM perturbation matrix, which considers phase coupling effects, takes the form

$$\mathcal{V}_{\pi}^{pc} = \begin{array}{ccc} \begin{array}{c} d_{\psi} \quad d_{\chi} \quad d_{xy} \\ e_{\pi s} \quad 0 \quad 0 \end{array} \\ \begin{array}{ccc} 0 & e'_{\pi s} & 0 \\ 0 & 0 & 2e_{\pi c} \end{array} \end{array} \quad (45)$$

These quantities will certainly depend on the respective MO energies of the free ligand, which are generally different for ψ -type and χ -type orbitals (cf. Fig. 7). The contribution of the HOMO (or the LUMO for acceptor ligands) can be expected to be the most important, because the smallest energy denominator is associated with this ligand orbital (cf. Eq. 24). This has been shown recently [28], when the Orgel effect was successfully applied to the unusual energy level scheme of $[\text{Cr}(\text{acac})_3]$ by taking into consideration only the HOMO of the acetylacetonate donor ligand. A more rigorous treatment, however, would require the consideration of all individual contributions of filled and empty ligand-orbitals, which has been investigated in a study of Zeeman splittings of the lowest doublet states of $[\text{Cr}(\text{bpy})_3]^{3+}$ [32].

A transformation back into the d -orbital basis set leads to

$$\mathcal{V}_{\pi} = \mathfrak{T}^{-1} \mathcal{V}_{\pi}^{pc} \mathfrak{T} = \begin{pmatrix} \frac{1}{2}(e_{\pi s} + e'_{\pi s}) & \frac{1}{2}(e_{\pi s} - e'_{\pi s}) & 0 \\ \frac{1}{2}(e_{\pi s} - e'_{\pi s}) & \frac{1}{2}(e_{\pi s} + e'_{\pi s}) & 0 \\ 0 & 0 & \frac{1}{2}(e_{\pi s}) \end{pmatrix} \quad (46)$$

Due to finite off-diagonal elements for $e_{\pi s} \neq e_{\pi s}'$ a three-center interaction via d_{xz} and d_{yz} is implicitly introduced, confining the strict additivity of the conventional AOM approach. In the case of $e_{\pi s} = e_{\pi s}'$ the matrix $\mathcal{V}_{\pi}^{pc}$ is converted into $\mathcal{V}_{\pi}$, preserving the validity of an additive ligand field.

2.3.2

Misdirected Valency

As argued in the preceding paragraphs, the local perturbation matrix is diagonal, strictly separating σ and π contributions of the metal-ligand bonding. However, when the local pseudosymmetry of the M-L bond is lower than C_{2v} due to misaligned ligand orbitals of σ - and/or π -type (bent bonds), off-diagonal matrix elements may appear in Matrix (24). Following an idea of Liehr [33] the concept of *misdirected valency* was introduced into the AOM formalism by Gerloch et al. [30, 31], who suggested that this effect is responsible for certain band splittings in planar cobalt(II) and trigonal-bipyramidal nickel(II) complexes. A non-ideal ligand alignment is reasonably explained by the rigidity of a chelate ligand and by considering the orientations of the related ligand orbitals, leading the maximum electron density to deviate from the M-L axis. Figure 8 illustrates this situation showing a ligand ' σ '-orbital that is disorientated by angles δ (in-plane) and ω (out-of-plane) from the internuclear axis. The fact that d_{xz} and d_{yz} orbitals can interact with the misaligned ' σ ' ligand orbitals results in contributions to $e_{\pi c}$ (in-plane) and $e_{\pi s}$ (out-of-plane). Reducing the C_{2v} (pseudo-)symmetry, which becomes now C_s or less, prevents the separation into pure σ - (a_1 -symmetry) and π -interactions (b_1 , b_2). Therefore, the AOM matrix for the M-L system in the standard orientation is no longer diagonal when σ - π mixing is included, taking the general form

$$\begin{array}{ccc}
 d_{z^2} & d_{yz} & d_{xz} \\
 \hline
 e_{\sigma} & e_{\sigma\pi s} & e_{\sigma\pi c} \\
 e_{\sigma\pi s} & e_{\sigma} & 0 \\
 e_{\sigma\pi c} & 0 & e_{\pi c}
 \end{array} \quad (47)$$

The corresponding AOM matrix for a ligating bidentate chelate is given elsewhere [34]. Two new off-diagonal parameters, $e_{\sigma\pi s}$ and $e_{\sigma\pi c}$, account for the

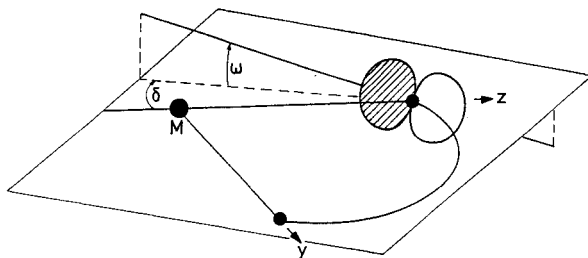


Fig. 8. General orientation of frontier orbitals for misdirected valency

mixing of d -orbitals due to misaligned ligand orbitals in the mean chelate plane and perpendicular to it, respectively. It is noticed that if the y -axis is oriented to the plane of the bent bond, $e_{\sigma ns}$ vanishes and only one additional parameter ($e_{\sigma n}$) is needed. As an example, peculiarities of the Ni–NCS bonding have been discussed by Duer et al. in their detailed paper on bent bonds [31]. Amazingly, the isothiocyanate ligand has been claimed to show donor behavior in $trans[Ni(NH_3)_4(NCS)_2]$ and marked acceptor behavior in $trans[Ni(en)_2(NCS)_2]$. However, considering the large deviation from a linear Ni–N–CS arrangement in the ethylenediamine complex, the effect of bent bonding or, alternatively, the lone-pair contribution due to *more* sp^2 hybridized ligand orbitals should result into a non-zero value for $e_{\sigma n}(NCS)$. And indeed, these authors showed that the recognition of misaligned bonds restores the π -donor property of NCS^- in the ethylenediamine complex. We finish here the discussion on effects due to misdirected valency, which, though likely, are not proved by this example; the interested reader is referred to the detailed theoretical and experimental investigation of Gerloch's group (cf. Ref. [31] and references therein).

2.3.3

s-d and p-d Orbital Mixing

When the symmetry of the complex is sufficiently low, $(n+1)s$ - and $(n+1)p$ -wavefunctions of the metal ion can mix with the metal d -orbitals of equal symmetry. Therefore, the odd-parity p -functions require the lack of an inversion center, whereas s -orbitals can exclusively mix with totally symmetric d -functions. Because of the higher p -orbital energies, p - d mixing is of minor importance, although it has been claimed to influence the electronic structures of some tetrahedrally coordinated complexes [8]. On the other hand, s -orbital mixing into d_{z^2} is certainly apparent in square-planar d^8 complexes [34, 35]. For considering this effect, the basis of metal d -orbitals is enlarged by the $(n+1)s$ -function. The effect on the d -orbital energies is derived then from a second order perturbation to give an additional term in Eq. (13) that includes s - d matrix elements of the effective ligand field Hamiltonian $\mathcal{V}_L$ (cf. Eqs. 6, 14). Separating the angular parts $F_{M\lambda}(\vartheta_L, \varphi_L)$ as in Eq. (34) and introducing new AOM parameters $e_{sd\lambda}$, the following matrix elements are obtained [36]

$$H_{ij}^{sd} = -(\sum_L F_{i\lambda}(\vartheta_L, \varphi_L)[e_{sd\lambda}(L)]^{1/2}) \times (\sum_L F_{j\lambda}(\vartheta_L, \varphi_L)[e_{sd\lambda}(L)]^{1/2}), \lambda = \sigma, \pi \quad (48)$$

However, since π -contributions must be much less important and require low symmetry and anisotropic metal-ligand bonding, they should not be considered. s - d mixing of σ -type, otherwise, is clearly established for square-planar d^8 and d^9 systems and some others having coordination numbers less than six. Generally the intermix of $(n+1)s$ with d_{z^2} is the leading term which provides for a stabilization of d_{z^2} (notice the negative sign in Eq. 48). In order to calculate d^N transition energies and g values, the mixing parameter e_{sd} has been

used, which is defined as

$$e_{sd} = \frac{\langle s | v_L | d_{z^2} \rangle^2}{|E_d - E_s|} \quad (49)$$

In practice, effects due to s - d orbital mixing are usually small and may be covered by a reasonable parametrization within the conventional formalism. On the other hand, when the nature of the axial coordination is largely different from the equatorial, as is the case in trigonal bipyramides or particularly in square-planar complexes, s - d mixing can affect the energy of the d_{z^2} orbital considerably. Matrix elements suitable for planar compounds $\text{tr}[\text{MA}_2\text{B}_2]$ of D_{2h} and C_{2h} symmetry have recently been worked out by Mink and Schmidtke [36]. These authors have shown for a paramagnetic (!) nickel(II) complex that in order to rationalize the triplet ground state and to keep reasonable e_σ , e_π parameter values, s - d mixing must be involved into the AOM calculations.

2.4

AOM Matrix for Trigonal $[\text{M}(\text{L-L})_3]$ Complexes

For octahedral, tetragonal and orthorhombic complexes, in fact we have a natural parametrization due to the shapes of the tetragonally quantized real d -orbitals. This results in a clear and transparent form of the AOM matrices considered. On the other hand, the situation with trigonal systems appears to be more complicated [37]. Since angular dependencies of several trigonally distorted complexes will be explicitly discussed in Sects. 3.2 and 3.3, we describe here how to set up the adequate trigonal AOM matrix in line with the procedure given elsewhere [28, 38] and present a parametrization scheme for various trigonally distorted systems.

Fig. 9 illustrates the angular geometry of a $[\text{M}(\text{L-L})_3]$ complex, where (L-L) represents a symmetrically coordinated bidentate ligand. For equal metal-ligand distances two types of distortions of the ML_6 octahedron are possible which maintain at least D_3 symmetry. Thus the coordination sphere can be definitely described by two quantities which are commonly given with the polar angle θ and the twist angle ϕ . The angle θ describes a compression ($\theta > \theta_{Oh}$) or elongation ($\theta < \theta_{Oh}$) of the octahedron along the three-fold axis from the octahedral value of $\theta_{Oh} = 54.74^\circ$. The other trigonal distortion involves a twist of opposite faces of the octahedron resulting in a deviation from $\phi_{Oh} = 60^\circ$. The often used chelate bite angle can be expressed in terms of θ and ϕ by

$$\cos(\alpha/2) = \sin\theta \cdot \cos(\phi/2) \quad (50)$$

When π -interactions are different for in-plane ($e_{\pi c}$) and out-of-plane ($e_{\pi s}$, $e_{\pi s}'$) orbitals the orientation of the ligand orbitals, which is given by the dihedral angle ψ , comes into play (cf. Sect. 2.2.2). Since ψ , being the angle between the L-M-L chelate plane and the plane containing the C_3 -axis and the M-L bond vector, is not independent of the other geometric variables, it can be derived for plane chelate ligands as $[\text{Cr}(\text{acac})_3]$, for example, from the relation

$$\cos\psi = \cos\theta \cdot \cos(\phi/2)/\sin(\alpha/2) \quad (51)$$

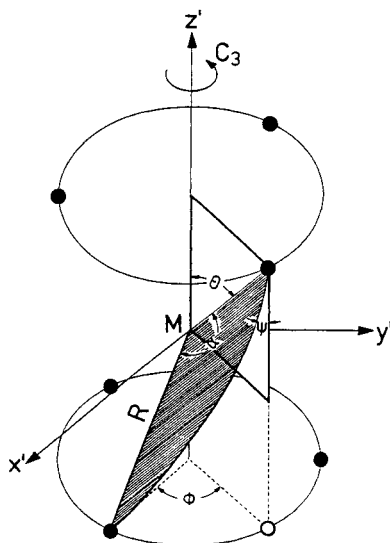


Fig. 9. Angular geometry of a trigonally coordinated tris-chelated complex $[M(L-L)_3]$ defined by the structural angles θ , ϕ and ψ (cf. Tables 1, 2)

In the trigonal oxalate complex $[\text{Cr}(\text{ox})_3]^{3-}$, on the other hand, ligands are not exactly planar but slightly twisted by an angle φ around the C-C [28]. In this case Eq. (51) is not valid, and for each oxalate both ligand atoms ψ depend now also on the position of the OCC plane. Relevant structural parameters for the chromium(III) complexes discussed in Sect. 3 are presented in Table 1.

Let us now consider the AOM matrix for general D_3 geometry, which can be easily obtained when starting from a reference position of the metal and one bidentate ligand as depicted in Fig. 10. Applying the common parameter definitions given in Fig. 2, the interaction with the $d_{x^2-y^2}$ orbital (that is of t_{2g} -type here, note the choice of x, y -coordinates) is readily seen to become $e_{\pi c}$ for a bite angle of $\alpha = 90^\circ$. A contribution that is purely of σ -type ($= 2 \cdot \frac{3}{4} e_\sigma$) would result if the ligand atoms coalesce at the same position ($a = 0^\circ$). The shape of the d_{z^2} orbital causes a matrix element independent of α . Accordingly, the complete matrix for this system, denoted $\mathcal{G}_{\text{AOM}}$, has the symmetric form

d_{z^2}	d_{yz}	d_{zx}	d_{xy}	$d_{x^2-y^2}$	
$\frac{1}{2} e_\sigma$	0	0	0	$\frac{\sqrt{3}}{2} \cos \alpha e_\sigma$	
	$2 \cos^2(\frac{\alpha}{2}) e_{\pi s}$	0	0	0	
		$2 \sin^2(\frac{\alpha}{2}) e_{\pi s}'$	0	0	(52)
			$\frac{3}{2} \sin^2 \alpha e_\sigma + 2 \cos^2 \alpha e_{\pi c}$	0	
				$\frac{3}{2} \cos^2 \alpha e_\sigma$	
				$+ 2 \sin^2 \alpha e_{\pi c}$	

In order to locate the ligand into its position in the trigonal complex (Fig. 10b), the AOM matrix derived has to be rotated by an angle γ around the y -axis

$$\mathcal{A}_{\text{AOM}} = D_y(\gamma) \cdot \mathcal{E}_{\text{AOM}} \cdot \tilde{D}_y(\gamma) \quad (53)$$

where γ is related to the other structural angles by

$$\cos \gamma = \tan(\varphi/2) / \tan(\alpha/2) = \cos \psi \cdot \tan \vartheta \cdot \tan(\varphi/2) \quad (54)$$

The complete AOM matrix for a trigonal $[\text{M}(\text{L-L})_3]$ chelate complex is derived then by two subsequent rotations of the ligand by angles of $\pm 120^\circ$ around the z -axis giving

$$\mathcal{A}_{\text{AOM}}^{\text{trig}} = \mathcal{A}_{\text{AOM}} + D_z(120^\circ) \mathcal{A}_{\text{AOM}} \tilde{D}_z(120^\circ) + D_z(-120^\circ) \mathcal{A}_{\text{AOM}} \tilde{D}_z(-120^\circ) \quad (55)$$

Further details including the matrices $D_y(\gamma)$ and $D_z(120^\circ)$ are given elsewhere [6, 38].

Finally, we will describe the full electronic and geometric parametrization required for octahedral and trigonally distorted complexes. Table 2 presents the occurring AOM parameters as well as the relevant structural variables for some representative examples. Not included are effects due to s - d (or p - d) mixing and misdirected valency which are negligible for hexa-coordinated d^N -systems. The number of independent electronic and geometric parameters varies from only one for the octahedrally coordinated hexa-ammine complex, where π -interaction can be excluded, to six in the case of the trigonally distorted oxalate and acetylacetonate complexes. $[\text{Cr}(\text{acac})_3]$, for example, exhibits anisotropic π -bonding and a pronounced phase-coupling effect due to the interaction of metal d -orbitals with the extended π -electron systems of the ligands. The examples marked by an asterisk in Table 2 will be discussed in Sect. 3 ($\text{M} = \text{Cr}$), exhibiting pseudo-octahedral geometries of the first coordination spheres for $[\text{Cr}\{\text{HB}(\text{pz})_3\}_2]^+$ and $[\text{Cr}(\text{acac})_3]$, and significantly distorted trigonal surroundings for the others ($[\text{Cr}(\text{urea})_3]^{3+}$, $[\text{Cr}(\text{ox})_3]^{3-}$, $[\text{Cr}(\text{bpy})_3]^{3+}$). Again, it should be remarked that because there are no more than four energy differences possible between the five d -orbitals, we may be confronted with an overparametrization, and all variables cannot be separately determined from spectroscopic measurements. Consequently, there may be some structural quantities (or ideas on it) necessary to determine the appearing AOM parameters, or, vice versa, geometric distortions may be evaluated by using AOM parameters known from related compounds as given, for example, in Fig. 5 with the two-dimensional spectro-

Table 1. Geometric parameters as defined in Fig. 4 for trigonal chromium(III) complexes, which are obtained from ^(a) AOM calculations and ^(b) X-ray data; ^(c) chelate bite-angle not defined. For ligand abbreviations see legend to Fig. 5

Angle	$[\text{Cr}(\text{urea})_6]^{3+ \text{ (a,c)}}$	$[\text{Cr}\{\text{HB}(\text{pz})_3\}_2]^+$	$[\text{Cr}(\text{ox})_3]^{3- \text{ (b)}}$	$[\text{Cr}(\text{acac})_3]^{(b)}$	$[\text{Cr}(\text{bpy})_3]^{3+ \text{ (b)}}$	O_h
θ	53	52	59	54.6	58	54.74
ϕ	60	60	48	61.5	49	60
ψ	70	2	41	45.8	41	45
α	–	–	83	91.1	79	90

Table 2. AOM parameters and angular variables for hexa-coordinated complexes where the first coordination spheres $[MA_6]$ ($A = N, O, Cl$) show an octahedral or trigonally distorted geometry. The lower symmetries may be induced, for example, by the chelate geometry or by impacts due to the crystal lattice. ^(a) The symmetry of the LF potential may be reduced if non-isotropic π -bonding is apparent. ^(b) The actual structure of the $[MA_6]$ entity is very near to an octahedron. ^(c) For planar chelates ψ is not independent from θ and ϕ (cf. Eq. 51). * Relevant (pseudo-)symmetries for the complexes investigated in this contribution

Complex	$O_h (\theta = 54.74^\circ, \phi = 60^\circ)^{(a)}$	$D_{3d} (\theta, \phi = 60^\circ)$	$D_3 (\theta, \phi)$
$[M(NH_3)_6]$	e_σ	e_σ, θ	e_σ, θ, ϕ
$[MCl_6]$	e_σ, e_π	e_σ, e_π, θ	$e_\sigma, e_\pi, \theta, \phi$
$[M(HBpz_3)_2]^{(b)}$	$e_\sigma, e_{\pi s}, \psi$	$e_\sigma, e_{\pi s}, \theta, \psi$	$e_\sigma, e_{\pi s}, \theta, \phi, \psi$
$[M(urea)_6]$	$e_\sigma, e_{\pi s}, e_{\pi c}, \psi$	* $e_\sigma, e_{\pi s}, e_{\pi c}, \theta, \psi$	$e_\sigma, e_{\pi s}, e_{\pi c}, \theta, \phi, \psi$
$[M(en)_3]$	e_σ	e_σ, θ	e_σ, θ, ϕ
$[M(ox)_3]$	$e_\sigma, e_{\pi s}, e_{\pi c}, \psi$	$e_\sigma, e_{\pi s}, e_{\pi c}, \theta, \psi$	* $e_\sigma, e_{\pi s}, e_{\pi c}, \theta, \phi, \psi$
$[M(bpy)_3]$	$e_\sigma, e_{\pi s}, e_{\pi s'} (\psi = 45)$	$e_\sigma, e_{\pi s}, e_{\pi s'}, e_{\pi c}, \theta, (\psi)^{(c)}$	* $e_\sigma, e_{\pi s}, e_{\pi s'}, \theta, \phi, (\psi)^{(c)}$
$[M(acac)_3]^{(b)}$	* $e_\sigma, e_{\pi s}, e_{\pi s'}, e_{\pi c} (\psi = 45)$	$e_\sigma, e_{\pi s}, e_{\pi s'}, e_{\pi c}, \theta, (\psi)^{(c)}$	* $e_\sigma, e_{\pi s}, e_{\pi s'}, e_{\pi c}, \theta, \phi, (\psi)^{(c)}$

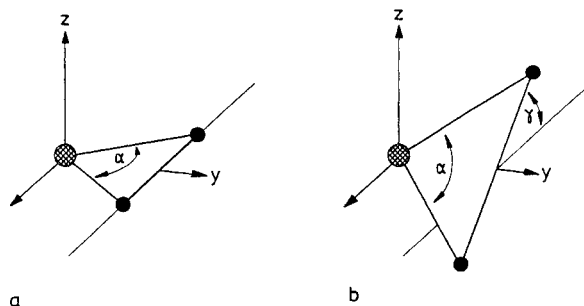


Fig. 10. a, b. Orientation of one chelate ligand in the reference position a, and in the trigonal complex b (see text)

chemical series for Cr(III) complexes. Such work will be presented by several examples described below.

2.5

The Program System AOMX

In this section we briefly describe how to calculate d -energy eigenvalues and wavefunctions for arbitrary transition metal complexes by means of the program system "AOMX". This versatile tool has been developed by Adamsky [15] on the basis of the FORTRAN program "AOM1" that was designed by Hoggard [11] for calculating energy levels of a d^3 -system. The underlying theory for describing many-electron d^N -systems is based on Slater's work on atoms and ions which is well described in several textbooks on the LFT, e.g. in Refs. [2–5,

39]. The unperturbed wavefunctions are set up as antisymmetrized determinants by using the tetragonally quantized d -orbitals of the strong-field approach, i.e. the familiar set of t_{2g} - and e_g -orbitals. A d^2 -system, for example, implies a total of $\binom{10}{2} = 45$ two-electron basis functions which can be written as $\psi_1 = |12|$, $\psi_2 = |13|$, $\psi_3 = |14|$, ..., $\psi_{44} = |\bar{3}\bar{5}|$, $\psi_{45} = |\bar{4}\bar{5}|$ by numbering the t_{2g} -(1, 2, 3) and e_g -orbitals (4, 5) with α or β (bar) spin. We notice that the choice of the basis functions is arbitrary, because the AOMX program performs full CI-calculations which include all interactions that originate from different states of the d^N -manifold. However, strong-field wavefunctions are more advantageous for describing effects of chemical bonding and they have also been used for defining the AOM parameters (cf. Figs. 2, 3).

In order to derive the electronic transition energies of a d^N -system, an effective many-electron Hamiltonian has to be diagonalized. H^{eff} is designed to the ligand field potential, the electron-electron repulsion ($N = 2, \dots, 8$), spin-orbit coupling, and further perturbations which have to be considered in special cases (see below).

$$H^{eff} = V_{LF} + H_{ee} + H_{so} + \dots \quad (56)$$

$V_{LF} (= \sum_i \mathcal{V}_L(i))$, where i numerates the metal d -electrons) delivers the AOM matrix for the various σ - and π -contributions of all ligands as outlined in the preceding paragraphs.

$$H_{ee} = \sum_{i < j} 1/r_{ij} \quad (57)$$

describes the two-electron Coulomb interactions which are commonly expressed by the spherical (!) Racah parameters B and C. A rigorous treatment of the interelectronic repulsion, which accounts for the real symmetry of the complex, would lead, however, to an inflation of parameters. On the other hand, a reasonable description of the electron-electron interaction in low-symmetry complexes can be derived by using orbital expansion coefficient(s). An application of this method, which avoids an overparametrization, is given in Sect. 3.2. with the elucidation of the unusually large doublet splittings in some pentaammine complexes of chromium(III).

The spin-orbit coupling energy is calculated by using the Hamiltonian

$$H_{so} = \sum_i \mathcal{H}_{so}(i) = \zeta \sum_i s_i \cdot \ell_i \quad (58)$$

where ℓ_i and s_i are the orbital and spin angular momentum operators, and ζ is the spin-orbit coupling constant for a d -electron. The resulting matrix elements of the one-electron operator $\mathcal{H}_{so}(i)$ are derived from weak field wavefunctions $|m_{\ell_i} m_{s_i}\rangle$. Transformation into the strong field basis set yields matrix elements of the form $\langle d_k | \zeta \cdot \ell \cdot s | d_l \rangle$ demanding for the parameter ζ in the calculation. If anisotropic spin-orbit coupling is apparent as found for some trigonally distorted chromium(III) complexes, Eq. (58) has to be replaced by Eq. (72) (Sect. 3.3.3).

Another correction, which is occasionally used in ligand field calculations, has been introduced by Trees [41] for fitting spectra of free ions. Then the Hamiltonian includes another term of the form

$$H_{Trees} = \alpha_T (\sum_i \ell_i^2 + 2 \sum_{i < j} \ell_i \cdot \ell_j) \quad (59)$$

which causes a change of the orbital angular momenta. Therefore Trees' correction will influence d^N -states by an orbital-orbital interaction in a different way depending upon the quantum number L of the respective parent states. Using non-zero values for α_T^7 can lead to considerable energy shifts that requires, however, a re-parametrization of the Racah parameters B and C.

An external magnetic field that causes Zeeman splittings of degenerate level is described by the one-electron operator

$$\begin{aligned} \mathcal{H}_{\text{mag}} = \beta H \{ & \sin \vartheta_{\text{mag}} \cos \varphi_{\text{mag}} (k_x \ell_x + 2s_x) \\ & + \sin \vartheta_{\text{mag}} \sin \varphi_{\text{mag}} (k_y \ell_y + 2s_y) + \cos \vartheta_{\text{mag}} (k_z \ell_z + 2s_z) \} \end{aligned} \quad (60)$$

where ϑ_{mag} , φ_{mag} refer to the orientation of the magnetic field H and β ($= 0.4668 \text{ cm}^{-1} \text{ Tesla}^{-1}$) represents Bohr's magneton. k_x , k_y and k_z are Stevens' orbital reduction factors which account for a magnetic anisotropy in transition metal complexes [39].

The energy level scheme and the many-electron wavefunctions of the d^N -systems investigated in this article were calculated with the AOMX program which diagonalizes the full $\binom{10}{n} \times \binom{10}{n}$ perturbation energy matrix taking into account all effects described above. Term symmetries can automatically be determined for cubic, tetragonal, trigonal and orthorhombic point groups from the characters of rotations C_4 , C_3 , C_2^x , etc., when applied to the respective eigenfunctions.

The AOMX program also contains an optimization routine that is based on Powells parallel subspace-algorithm [42]. This subroutine allows for fitting experimental data to a series of selected term energies. As far as computer capacity is concerned, we note that a full CI AOM calculation, which includes symmetry and time-consuming spin-orbit coupling, typically requires less than 10 s (100s) CPU time for evaluating the energy level scheme of a $d^3(d^4)$ complex when performed on a 486-DX2/66 personal computer. The optimization routines run almost equally fast when the term symmetries and spin-orbit coupling are not considered.

3 Transition Metal Complexes

Most applications of the AOM concern the interpretation of d - d spectra in inorganic transition metal complexes. In the following, we present several examples in order to show how d^N states can be calculated in terms of an adequate parametrization of the ligand field. Emphasis will be placed on the particular influence of the angular geometry of the chromophore on the energy level splittings, which often result in characteristic *spectrum-structure correlations*. This part is organized with respect to the different types of metal-ligand π -interaction. Starting in Sect. 3.1 with complexes where M-L bonding is *isotropic*, examples are

⁷ $\alpha_T = 80 \text{ cm}^{-1}$ was obtained for the free Cr^{3+} ion [8].

given for osmium(IV) and chromium(III) complexes with halide, pseudohalide (e.g. CN^-) and ammine ligands. We will also examine the particular role that electron repulsion may play in low-symmetry complexes. The next section (3.2) deals with the influence of *anisotropic* π -interaction on the electronic spectra of complexes containing monodentate and bidentate chelate ligands. It will be shown that the interrelation with geometric properties such as the chelate bite angle α (cf. Fig. 9) can be substantiated only if the different in-plane and out-of-plane π -interactions between metal and ligator atoms are adequately considered. Finally, the role of extended π -bonding for complexes with bidentate ligands that have an extended π -electron system, like acetylacetonate or 2,2'-bipyridin, is outlined in Sect. 3.3. Recent experimental data which include highly resolved Zeeman spectra of tris-acetylacetonate and tris-bipyridyl complexes of chromium(III) are reviewed in terms of an extended AOM that considers the so-called *phase coupling* of frontier orbitals. The directional impact of extended π -bonding on the molecular structure of trigonally distorted acetylacetonate complexes is shown for a series of trivalent first-row transition metal ions.

3.1

Complexes with Isotropic π -interaction

The first example in this series describes in more detail the analysis of intraconfigurational sharp-line transitions in $[\text{OsCl}_6]^{2-}$ that is slightly distorted from the symmetry of a regular octahedron when doped into the non-cubic K_2SnCl_6 host lattice. The question is addressed of how the actual geometry of the dopant correlates with the energy level splittings induced by the low-symmetry of the surrounding $[\text{SnCl}_6]^{2-}$ sites. The second part deals with σ - and π -bonding properties of some pseudohalide ligands in pentaammine complexes of Cr(III). Here special attention is paid on the unusually large ${}^2E_g(O_h)$ splittings which will be discussed in terms of orbital expansion coefficients that have been introduced into the interelectronic repulsion terms of the AOM recently.

3.1.1

$[\text{OsCl}_6]^{2-}$ Doped in K_2SnCl_6

Although there are only a few data available on the ligand fields in third-row transition metal complexes, the present series of examples starts with a doped compound containing $[\text{OsCl}_6]^{2-}$ anions. We have chosen this system for three properties making it to an almost ideal candidate for an AOM investigation: (i) only a single type of ligator atom showing isotropic π -behavior is involved reducing the number of AOM parameters to two; (ii) osmium(IV) complexes usually exhibit a series of well resolved *d-d* transitions within the (t_{2g}^4) subshell when doped into suitable host materials and when the temperature is sufficiently low, and (iii) the molecular geometry of the host material K_2SnCl_6 is known also at a low temperature. In recent years, a manifold of spin-orbit states of $[\text{OsCl}_6]^{2-}$ has been assigned from sharp-line absorption and emission spectra measured in the visible and near-infrared region with the peculiarity of multiple emission from several higher electronic levels [43–45]. Figure 11 shows the corresponding

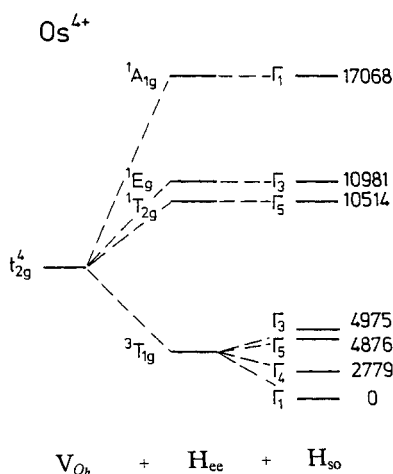


Fig. 11. Energy levels of $[\text{OsCl}_6]^{2-}$ resulting from the perturbed (t_{2g}^4) electron configuration in O_h symmetry [44, 45]

part of the energy level scheme for the parent cubic symmetry. However, the most detailed spectroscopic information has been obtained from low-symmetry systems. In the case of the host material K_2SnCl_6 , the cubic lattice of anti-fluorite type (denoted as phase III modification) is known to undergo two phase transitions at $T_1 = 261$ K and $T_2 = 255$ K. A closer inspection of the structural changes by a neutron powder investigation [46] has shown a tetragonal distortion of the $[\text{SnCl}_6]^{2-}$ octahedra in the intermediate phase II structure (space group $P_{4/mnc}$). Below T_2 an additional in-phase rotation around in cubic (110) axis takes place (phase I, $P_{21/n}$), and the molecular symmetry becomes C_i . The Sn sites are equivalent; that is a most useful property for getting definite band assignments in sharp-line spectra. The angular geometry of the $[\text{SnCl}_6]^{2-}$ entity in the low-temperature phase I is depicted in Fig. 12.

The spectroscopic data obtained by absorption, emission and MCD measurements, have been controversially discussed by Keiderling [43], Flint [44], and Schönherr [45] and coworkers. However, all assignments given so far were based on a pseudo-tetragonal distortion of the $[\text{OsCl}_6]^{2-}$ octahedra which may be present only in a small temperature interval, as induced by the tetragonal intermediate phase II structure of the the host crystal. The impacts of angular deviations from a rectangular surrounding that appear at temperatures lower than $T = 251$ K were not considered in either case. However, all degenerate states split when the symmetry is sufficiently lowered. Since our AOM calculations predict such splittings in the order of the experimentally expected resolution (see below), we have reinvestigated the optical transitions between the electronic states in question. Figure 13 shows, for example the low-temperature emission spectrum in the region $14000\text{--}14600\text{ cm}^{-1}$ that is due to $\Gamma_1(1A_{1g}) \rightarrow \Gamma_4(3T_{1g})$ transitions. The band shape can obviously be explained by the superposition of three similar sideband structures, each of them belonging to a different split component of

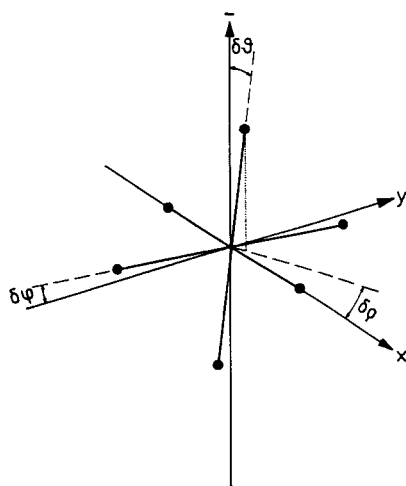


Fig. 12. Angular distortions of the SnCl_6 octahedra to C_{2v} -symmetry in the low-temperature phase I structure of $K_2[\text{SnCl}_6]$ as obtained from inelastic neutron scattering [46]

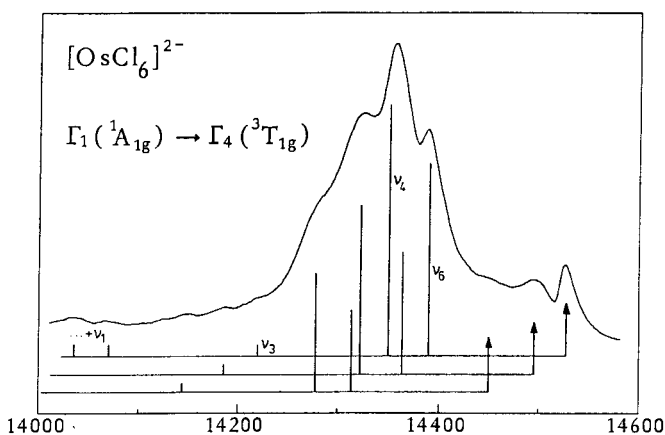


Fig. 13. Part of near-infrared emission spectrum of $K_2[\text{SnCl}_6]:[\text{OsCl}_6]^{2-}$ measured at $T = 2$ K showing three electronic origins due to the split levels of $\Gamma_4(3T_{1g})$ (arrows), each of them accompanied by a characteristic vibrational sideband structure (bars)

the triply degenerate Γ_1 state. The underlying zero-phonon transitions, which are electric-dipole parity-forbidden, are located at the high energy side of the spectrum at positions 14530 cm^{-1} , 14495 cm^{-1} , and 14465 cm^{-1} . The more intense vibrational sidebands, which are readily identified with the three odd vibrations of an octahedral ML_6 molecule, result from a vibronic coupling mechanism [47]. A band deconvolution shows these vibrational modes with frequencies of $\nu_6 = 140\text{ cm}^{-1}(t_{2u})$, $\nu_4 = 170\text{ cm}^{-1}(t_{1u})$, and $\nu_3 = 320\text{ cm}^{-1}(t_{1u})$, apart from each of the zero-phonon lines in accordance with the normal modes of the $[\text{OsCl}_6]^{2-}$ anion

[44, 48]. Another assignment problem is concerned with the three transitions of similar intensity which have maximum energies at 4965 cm^{-1} , 4983 cm^{-1} , and 5000 cm^{-1} on the low-energy side of the single-crystal absorption spectrum. Likewise, these bands can reasonably be assigned on the basis of three origins, which result from the $\Gamma_5(^3T_{1g})$ parent state when the phase I symmetry of the host lattice is considered. Less convincing is the earlier interpretation [43] that is based on two origins (reflecting a pseudo-tetragonal symmetry), particularly because it demands two different lattice modes to couple with either of these states. Accordingly, we conclude that the band splittings observed in the low-temperature spectra originate from a ligand field potential having a symmetry lower than tetragonal.

In order to study in which way the d -level splittings are influenced by the electronic and geometric factors, we have performed a series of AOM calculations by diagonalizing the full 210×210 secular determinant which arises from the perturbed d^4 system. A total of five electronic parameters occur: the Racah quantities B and C , the spin-orbit coupling parameter ζ , and the AOM parameters e_σ and e_π . Neglecting the small deviations in the metal-ligand distances, three angular parameters (cf. Fig. 12) may also be varied independently. Therefore, we are confronted with the problem of overparametrization which can lead to a good fit even for incorrect assignments. On the other hand, the parameters B , C , and ζ can be determined at first by fitting the energy levels of $[\text{OsCl}_6]^{2-}$ when located in cubic host lattices, e.g. by using doped $\text{Rb}_2[\text{SnCl}_6]$ crystals [45], where no geometric parameters appear as variables. In further calculations on the low-symmetry surroundings these parameters should be left unchanged.

It should be noted that our calculations on absolute transition energies did not yield as precise results as expected for similar first-row transition metal complexes due to several drawbacks: (i) the (large) nephelauxetic effect is poorly described by using only two Racah parameters, especially for complexes which contain highly charged heavier metal ions; (ii) interference with the lowest charge-transfer (CT) states may shift the energies of some ligand field states considerably; (iii) the ligand field strength, which yields a useful relationship for the e_σ and e_π parameters by Eq. (30), cannot be derived from *intra*-configurational transitions within the (t_{2g}^4) subshell; spectral features due to the higher *inter*-configurational transitions $(t_{2g}^4) \rightarrow (t_{2g}^4 e_g^1)$, however, are completely covered under intense CT bands. For these reasons we have used a wide range of parameter values for e_σ and e_π allowing e_σ/e_π ratios between 3 and 20. Although the inclusion of Trees' correction can somewhat improve the calculated transition energies, low-symmetry splittings considered here were found to be much less influenced by this extension. The spin-orbit coupling constant ζ , on the other hand, can be precisely obtained from the overall splitting of $^3T_{1g}(O_h)$, in good agreement with parameter values reported for related complexes [4].

In order to derive a plausible description for the low-symmetry environment of the Os^{4+} ions, we assume that the geometric distortions of doped ions will mainly be influenced by impacts due to the structural properties of the host material. Accordingly, the phase transitions which occur in K_2SnCl_6 will preferentially induce distortions of the substituting $[\text{OsCl}_6]^{2-}$ ions very similar to those of the host octahedra. Hence, for describing the angular part of the relevant

low-temperature structure (phase I) a distortion coordinate may be defined as

$$\delta Q = (0.24 \delta \varphi + 1.5 \delta \vartheta + 32 \delta \rho) \quad (61)$$

which summarizes the angular deviations with $\delta Q = 0$ giving the undistorted octahedral geometry, and $\delta Q = 1$ giving the low-temperature structure of the $[\text{SnCl}_6]^{2-}$ complex. The effect of slightly different metal-ligand distances, which are found to vary between 242 pm and 245 pm, was either neglected in the calculations or was involved by using the relation (see Sect. 2.2.3)

$$e_\lambda(R) = e_\lambda(R_0) \cdot \left(\frac{R_0}{R}\right)^n, n = 3, \dots, 6 \quad (62)$$

where R_0 denotes the averaged metal-ligand distance in the $[\text{SnCl}_6]^{2-}$ ion. By this procedure, informative energy level diagrams can be obtained by varying just one geometric parameter, δQ , changing the symmetry of the $[\text{OsCl}_6]^{2-}$ chromophore from O_h to C_i that is the relevant symmetry for comparing with data from low-temperature measurements. Figure 14 illustrates this geometric effect on the calculated splittings of spin-orbit levels resulting from the ${}^3T_{1g}$ parent state. Higher levels arising from the singlet states ${}^1T_{1g}$ and ${}^1E_g$ are not included since reliable assignments to individual split components have not yet been derived because of the very complicated band pattern in the near-infrared region. We found the calculated level splittings of the lower states in good agreement with the experimental results, if the angular geometry is assumed to be similar to the low-temperature structure of the host lattice. A least-squares fit yields $\delta Q \sim 0.9$, clearly showing the impacts of the phase transitions in the host material to be responsible for the geometric distortions of the $[\text{OsCl}_6]^{2-}$ moiety. In order to

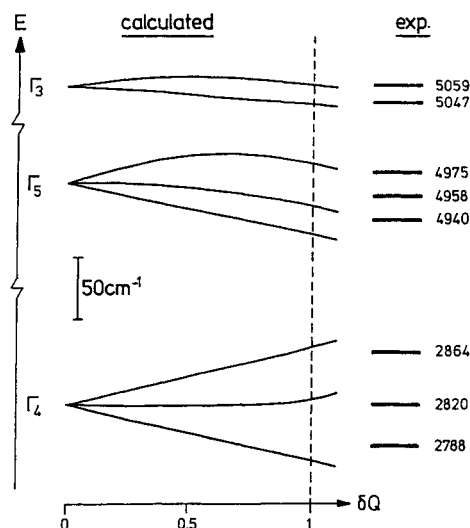


Fig. 14. Calculated energy level splittings of $\text{K}_2[\text{SnCl}_6]:\text{OsCl}_6^{2-}$ due to a phase I-type distortion as defined by Eq. (63). $e_\sigma = 9500$, $e_\pi = 1500$, $B = 400$, $C = 5B$, $\zeta = 2500$; in cm^{-1}

prove this result we allowed all the geometric and electronic parameters involved to vary independently. However, a geometry which is significantly different from the geometry of the $[\text{SnCl}_6]^{2-}$ ion could not be verified for any physically reasonable parameter set. This is not unexpected in view of the very similar ionic radii of the host and guest ions. In summary, our calculations clearly demonstrate the crucial influence of even small angular distortions on the observed level splittings. Consequently, the pseudo-tetragonal description of the ligand field used earlier is not valid for these systems. Moreover, we conclude from Fig. 14 that the AOM can provide valuable descriptions of $d-d$ transitions also for third-row transition metal complexes.

3.1.2

Doublet Splittings in Pentaammine Complexes of Chromium(III)

The electronic properties of acidopentaammine complexes have been thoroughly studied due to their interesting photochemical behavior. Schläfer was the first, who suggested the involvement of the lowest excited state, ${}^2E_g(O_h)$, in racemization and substitution reactions [49]. The elucidation of the underlying physical processes requires a profound knowledge of the energy level schemes, however, the unusually large splitting of ${}^2E_g$ observed in these complexes ($\approx 200 \text{ cm}^{-1}$) is not reproduced by conventional ligand field calculations [50]. In view of the fact that the LFT has been most successful in rationalizing the spectroscopic properties of chromium(III) compounds, and, particularly, because the pentaammine complexes are well-known textbook examples for illustrating that the ligand field description correctly predicts the quartet level splittings in tetragonal d^3 -systems [3, 4], this situation is quite amazing and has focused some attention on these molecules. Already twenty years ago, Flint has argued that the problem with the lowest doublets may be due to the shortcoming of using just two spherical Racah parameters B and C in the treatment of the interelectronic repulsion [51]. Following an idea of Atanasov, we pointed out recently that the inclusion of symmetry adapted π -orbital expansion factors (τ_i) into the electron repulsion part can provide an adequate description for the large ${}^2E_g$ splittings in acidopentaammine complexes of chromium(III) [40]. This approach is different from the earlier method of Jørgensen [52], who introduced particular nephelauxetic ratios for describing the *intra*- and *inter*-configurational transitions in optical spectra simultaneously. Such a parametrization would require several different B (and C) values in the energy matrix, which may account better for the manifold of different electron repulsion integrals appearing in a rigorous treatment even for high (octahedral) symmetry. However, the Jørgensen β_{ij} parameters, which are defined according to orbital occupations in cubic symmetry, cannot contribute to the low-symmetry effect which is responsible for the large splitting of ${}^2E_g$ in certain tetragonal ligand fields. For the present problem, our treatment of the interelectronic repulsion requires only one additional parameter, the orbital expansion factor τ that reduces the relevant matrix elements for the electron-electron interaction. This is for the following reasons: (i) we are concerned with pure spin-flip transitions within the (t_{2g}^3) electron configuration (see below); (ii) the axial ligands (NH_3) do not

contribute to π -interactions via t_{2g} -orbitals ($\tau_{xy} = 1$); (iii) in C_{4v} symmetry τ_{xz} equals τ_{yz} ($= \tau < 1$, subscripts can be omitted) when considering π -effects due to the delocalization of d_{xz}, d_{yz} electrons towards the axial heteroligand.

The Cr^{3+} ion has a d^3 system giving rise to three spin-allowed transitions from the ${}^4A_{2g}$ ground state into ${}^4T_{2g}$, ${}^4T_{1g}^a$ and ${}^4T_{1g}^b$ (in O_h notation). The excited states stem from a different electron configuration ($t_{2g}^2 e_g$) than the ground state (t_{2g}^3). Therefore they exhibit significantly different equilibrium geometries resulting in mostly unresolved broad bands for the corresponding optical transitions. The (t_{2g}^3) configuration also gives rise to the (lowest) doublet states ${}^2E_g$, ${}^2T_{1g}$ and ${}^2T_{2g}$. On the other hand, since these states have approximately the same bonding as ${}^4A_{2g}$ and thus almost the same equilibrium geometry, sharp-line spectra can be expected for the respective spin-forbidden transitions. Therefore, the most precise information on the electronic and structural parameters concerned can be obtained from an analysis of the highly resolved intra-configurational transitions. The pentaammine complexes investigated here contain the pseudohalide ligands NCO^- , NCS^- and CN^- , which are of special interest because of their potential ambidentate binding character. While the coordinated NCS^- group is well characterized in many compounds, much less is known on cyanate or isocyanate complexes. Since the crystal structures of $[\text{Cr}(\text{NH}_3)_5(\text{NCO})](\text{NO}_3)_2$ and $[\text{Cr}(\text{CN})(\text{NH}_3)_5]\text{Cl}(\text{ClO}_4)$ were solved recently [53, 54], we can combine geometric and spectroscopic data in order to characterize their chemical bonding to the central metal ion in terms of the AOM parametrization.

Figure 15 shows the vibrational fine structures in the intercombination band region of ${}^4A_{2g} \rightarrow {}^2E_g, {}^2T_{1g}$ transitions for the present pentaammine complexes. In each case the first two prominent bands represent the zero-phonon transitions into ${}^2E_g$, split by the tetragonal ligand field into ${}^2A_1$ and ${}^2B_1$ (or into the Kramers' doublets Γ_6, Γ_7 when spin-orbit coupling is taken into account).⁸ The spacings between both components of ${}^2E_g$ are found to be 200–240 cm^{-1} , similar to the values observed for the related acidopentaammines [40]. Detailed analyses of the vibronic transitions in the cyanate and cyanide complexes have been given recently by Schönherr [53] and Urushiyama et al. [54]. By a careful examination of the absorption profiles, these authors have identified all origins due to ${}^2T_{1g}$, which splits in C_{4v} symmetry into $\Gamma_6, \Gamma_7 ({}^2E)$ and $\Gamma_6 ({}^2A_2)$, respectively. The spectrum of the thiocyanate complex looks a little different showing a third prominent band centered at 15480 cm^{-1} that is slightly split by 10–15 wavenumbers. Although the spacings of these bands to the lower ${}^2E_g$ origins are not consistent with infrared frequencies, an assignment of these peaks to the zero-phonon components of ${}^2T_{1g}$ may be questioned.

The evaluation of the model parameters involved in the AOM calculations follows the guidelines given in the preceding section. Since the NH_3 ligand is known not to enter into π -interaction with metal ions, $e_\pi(\text{NH}_3)$ is reasonably set to zero. Hence, $e_o(\text{NH}_3)$ can be directly obtained from the position of the first quartet band ($= 10\text{Dq}$) in the related hexa-ammine complex, using $e_o(\text{NH}_3) =$

⁸ Using Bethe's Γ -notation for the underlying double group C_{4v}^* , that is isomorphous to D_4^* .

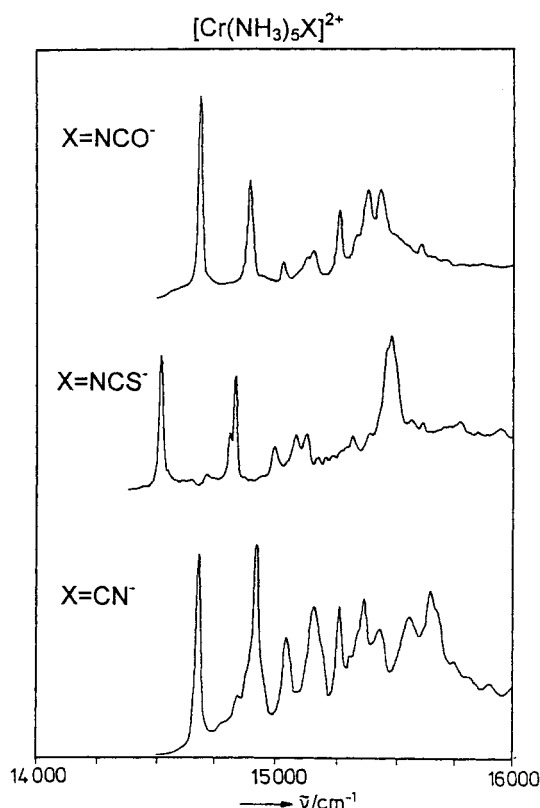


Fig. 15. ${}^4A_{2g} \rightarrow {}^2E_g, {}^2T_{1g}$ absorption spectra of pseudohalogenopentaammine complexes of chromium(III) measured as microcrystalline powders in a polyethylene matrix at $T = 15$ K

$10Dq/3 = 7200 \text{ cm}^{-1}$ (cf. Eq. 30). The AOM parameters for the hetero-ligands, which are not precisely known, were derived by fitting calculated energies to zero-phonon transitions identified in the spectral region of doublet transitions. As expected, the Racah parameters do actually not influence the low-symmetry level splittings considered here. In order to reduce the parameter space to a minimum, we could use therefore in first approximation parameter values which were obtained from the quartet band separation (${}^4T_{1g} - {}^4T_{2g} \approx 12B$), and from the energy position of the lowest doublet term (${}^2E_g - {}^4A_{2g} \approx 9B + 3C$). As pointed out above, large ${}^2E_g$ splittings ($>100 \text{ cm}^{-1}$) are calculated only if an adequate orbital reduction factor $\tau < 1$ is taken into account. This effect is illustrated by the energy diagram given in Fig. 16a showing the experimental splittings to be well reproduced at τ -values around 0.99. The AOM parameters of the pseudohalides NCO^- and CN^- were derived then from optimizing the calculated energies of the five spin-orbit components and of the quartet band splittings simultaneously [53, 54]. Relevant data on these complexes supplemented with our present results on the thiocyanate complex are collected in Table 3. We

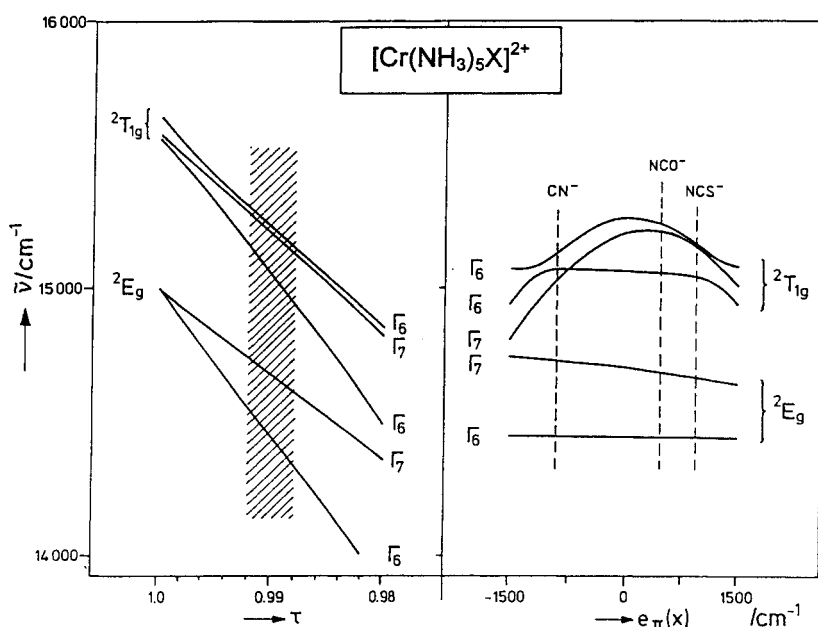


Fig. 16. Calculated doublet splittings in $[\text{Cr}(\text{NH}_3)_5\text{X}]^{2+}$ with respect to orbital expansion (τ) and π -bonding properties of the heteroligand. Parameters: $e_\sigma = 7000 \text{ cm}^{-1}$, $B = 700 \text{ cm}^{-1}$, $C = 5B$, $\zeta = 200 \text{ cm}^{-1}$, left side: $e_\pi(\text{X}) = 1000 \text{ cm}^{-1}$, right side: $\tau = 0.989$

Table 3. Experimental (calculated) energy level splittings and AOM parameters of pentaammine complexes with pseudohalide ligands as obtained from quartet and doublet transition energies (all in cm^{-1})

	$[\text{Cr}(\text{NH}_3)_5(\text{NCO})]^{2+}$	$[\text{Cr}(\text{NH}_3)_5(\text{NCS})]^{2+}$	$[\text{Cr}(\text{CN})(\text{NH}_3)_5]^{2+}$
${}^2E_g: \Gamma_7 - \Gamma_6$	213 (220)	322 (318)	-235 (-239)
${}^2T_{1g}: \Gamma_6 - \Gamma_6'$	168 (167)	- (234)	83 (67)
$\Gamma_7' - \Gamma_6'$	122 (141)	15 (32)	-34 (-46)
${}^4T_{2g}: {}^4B_2 - {}^4E$	1700 (1500)	1200 (1400)	-680 (-715)
${}^4T_{1g}: {}^4A_2 - {}^4E$	800 (400)	- (300)	-950 (-935)
e_σ	6060	6600	7060
e_π	420	950	-900

notice plausible trends for the NCX^- ligands ($\text{X} = \text{O}, \text{S}$), indicating smaller antibonding behavior for isocyanate due to the stronger electron-withdrawing property of the oxygen [49].

Of current interest is also the nature of the cyanide ligand, which is still not established although its unique position at the end of the spectrochemical series is well known. However, specific binding properties can clearly not be derived from the LF parameter $10Dq$ alone. On the other hand, π -acceptor behavior in chromium(III) complexes, ($e_\pi(\text{CN}) < 0$) has earlier been suggested by Van-

quickenborne [55] and Zinato [56]. According to Eq. (30), this property may explain the large value of $10Dq$ ($=26300\text{ cm}^{-1}$ [3]) as being confirmed by our recent analysis of the polarized quartet and more than 40 assigned (vibronic) doublet transitions in $[\text{Cr}(\text{CN})(\text{NH}_3)_5]\text{Cl}(\text{ClO}_4)$ [54]. In conclusion, the cyanide ligand exhibits, at least in chromium(III) complexes, a quite moderate σ -anti-bonding (*donor*) behavior that is comparable to that of ammonia. In fact, it is the strong π -acceptor property, which gives rise to the exceptionally high contribution of the CN^- ligands to the ligand field potential.

3.2

Anisotropic π -Interaction

If the metal-ligand bonding is not symmetric due to the M-L axis, two AOM parameters are generally required for describing the energy effect on the metal d -orbitals (cf. Sect. 2.2). The definitions for the corresponding quantities $e_{\pi c}$ and $e_{\pi s}$ are presented in Fig. 2, an example for the AOM perturbation matrix of a hexa-coordinated complex is given by Eq. (32). Anisotropic π -interaction generally occurs for non-linear ligands, for example, with the hydroxyl group or when chelate ligands are involved. In these cases, the π -contributions are properly described by parallel and perpendicular contributions with respect to a marked plane that is defined by the chelating molecule itself or by the atoms which contribute to the metal-ligand bonding concerned. An example of the latter type is given with the carboxyl group in amino acid complexes, where π -interaction is specified according to the plane that contains the $-\text{COO}^-$ group. Sometimes the equivalent parameters $e_{\pi \parallel}$ and $e_{\pi \perp}$ are used for describing in-plane ($e_{\pi c}$) and out-of-plane ($e_{\pi s}$) effects, respectively. For ligands such as pyridine, in-plane π -bonding ($e_{\pi c} = 0$) should be small and can reasonably be neglected. On the other hand, oxalate ligands will give rise to a considerable in-plane π -interaction ($e_{\pi c}$), as illustrated in Fig. 17. For this class of ligands, the parameter ratio $e_{\pi c}/e_{\pi s}$ can be estimated from geometrical relations between hybridized wavefunctions to have values near 0.6 in first-row transition metal complexes [57].

Here we present examples for the combined effect of anisotropic π -bonding and angular distortions on the d -level schemes of some chromium(III) and osmium(IV) complexes containing mono-, bi- and tri-dentate ligands. The thoroughly investigated acetylacetonate and bipyridine complexes, which also show pronounced anisotropic effects, require a more sophisticated theoretical treatment by considering interactions with the extended π -electron systems of the ligands for which the reader is referred to Sect. 3.3.

3.2.1

Level Splittings in Trigonal $[\text{Cr}(\text{urea})_6]^{3+}$ and $[\text{Cr}\{\text{HB}(\text{pz})_3\}_2]^+$

Previous interpretations of $d-d$ transitions in trigonal complexes performed in terms of the conventional LFT can generally not explain the physical origins of the observed level splittings. The reason for this is that several electronic and geometric sources exist that may independently contribute to the trigonal part of the ligand field potential:

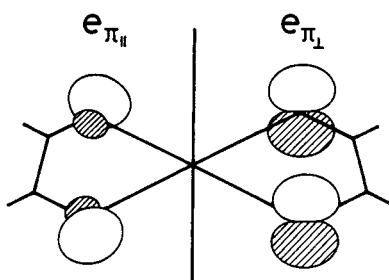


Fig. 17. AOM parametrization due to anisotropic π -interaction in the metal-oxalate group in the plane of the chelate ligand ($e_{\pi_{\parallel}} \triangleq e_{\pi_c}$) and perpendicular to this plane ($e_{\pi_{\perp}} \triangleq e_{\pi_s}$)

- (a) a trigonal compression or elongation (θ)
- (b) a twist of opposite triangles (ϕ)
- (c) anisotropic π -interaction ($e_{\pi_s} \neq e_{\pi_c}$)
- (d) extended π -bonding effects ($e_{\pi_s} \neq e_{\pi_s'}$)

All possible effects are summarized in only two symmetry-adapted trigonal LFT parameters (e.g. ν , ν' [2]), from which the complete physical information can clearly not be extracted. On the other hand, within the framework of the AOM parametrization, where the particular geometric and electronic effects are considered independently, the individual contributions (a) – (d) to the energy level splittings can be investigated in detail. They may be visualized by means of term diagrams which also provides an instructive way to get insight into spectrum-structure correlations. This is illustrated in Fig. 18 by four plots, which show quartet and doublet level splittings in trigonally coordinated chromium(III) complexes that depend on geometric and electronic effects. The two structural angles θ and ϕ , which are displayed in Fig. 9, adequately describe the angular geometry of a trigonal ML_6 moiety. The dihedral angle ψ that indicates the explicit orientations of the ligand frontier orbitals, accounts for different π -contributions for the in-plane (e_{π_c}) and the out-of-plane (e_{π_s}) interactions. From Fig. 18c it is apparent that $\psi = 45^\circ$ (or 135°) leads to a pseudo-isotropic π -interaction removing level splittings that are due to π -anisotropy. Further effects which may arise from extended π -electron structures on the ligands (d) are treated in Sect. 3.3.

The polarized absorption, emission and MCD spectra of the trigonal complexes $[Cr(urea)_6]^{3+}$ and $[Cr\{HB(pz)_3\}_2]^+$ exhibit significant band splittings in the region of quartet and doublet transitions [58, 59]. Figure 19 shows the polarized optical absorption spectrum of a single crystal of $[Cr(urea)_6](ClO_4)_3$, where $\sigma(\pi)$ defines the electric-dipole vector $\vec{E}$ to be perpendicular (parallel) to the molecular trigonal axis. The trigonal contribution to the ligand field is apparent from the highly anisotropic absorption observed for the spin-allowed transitions. Following selection rules for the actual D_3 symmetry, which are included in the energy level diagram given by Fig. 20, the σ -polarized quartet bands at 16100 cm^{-1} and 22600 cm^{-1} have been attributed by Yersin [60] to the electronic transitions $^4A_2 \rightarrow ^4E(^4T_{2g})$ and $^4A_2 \rightarrow ^4E(^4T_{1g})$, respectively. Since in π -polariza-

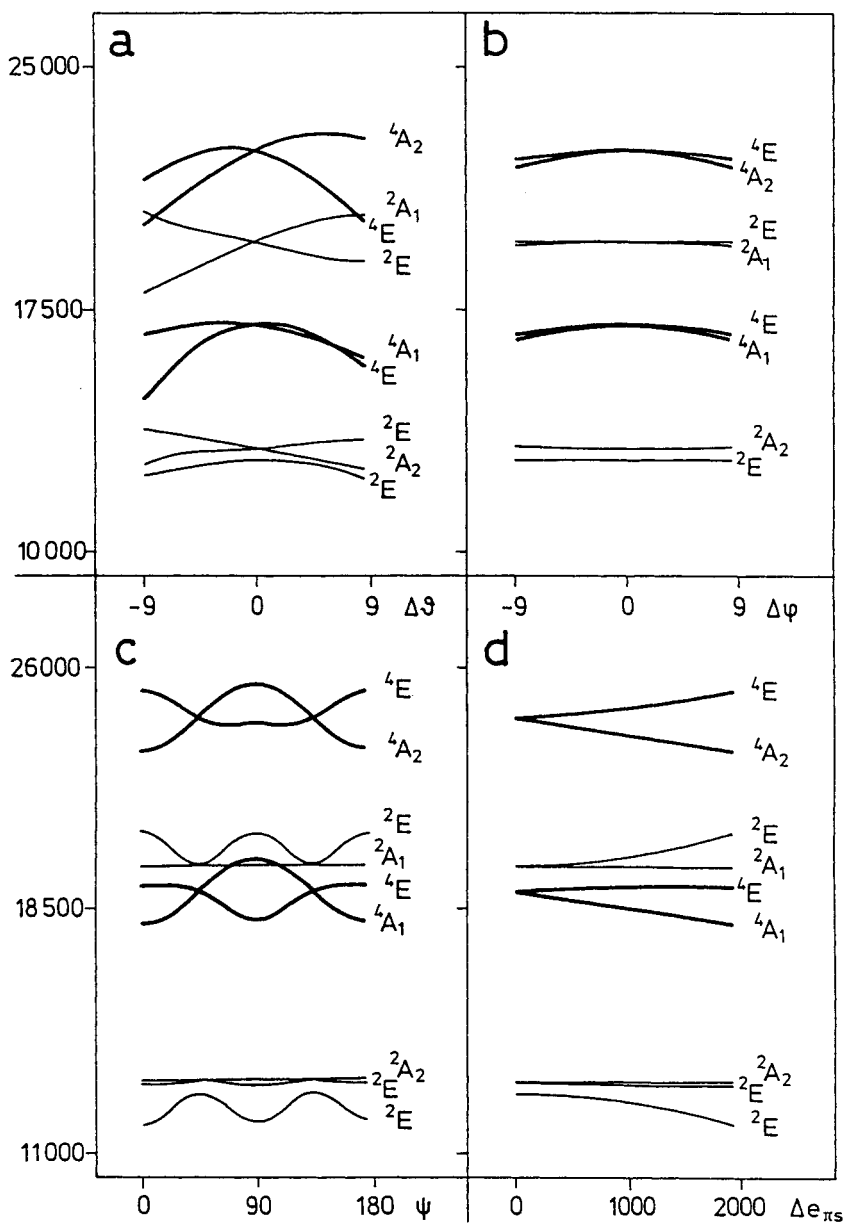


Fig. 18a-d. d^3 -energy level diagrams due to a trigonal compression or distortion (a), a trigonal twist (b), anisotropic π -bonding (c), and phase-coupling of π -orbitals (d). $e_o = 7000$, $e_\pi = 1000$, $B = 700$, $C = 3000$, $\zeta = 200$; (c): $e_{\pi s} = 1000$, $e_{\pi c} = 0$; (d): $\Delta e_{\pi s} = e_{\pi s} - e_{\pi s}'$, $e_{\pi c} = 0$ (all in cm^{-1})

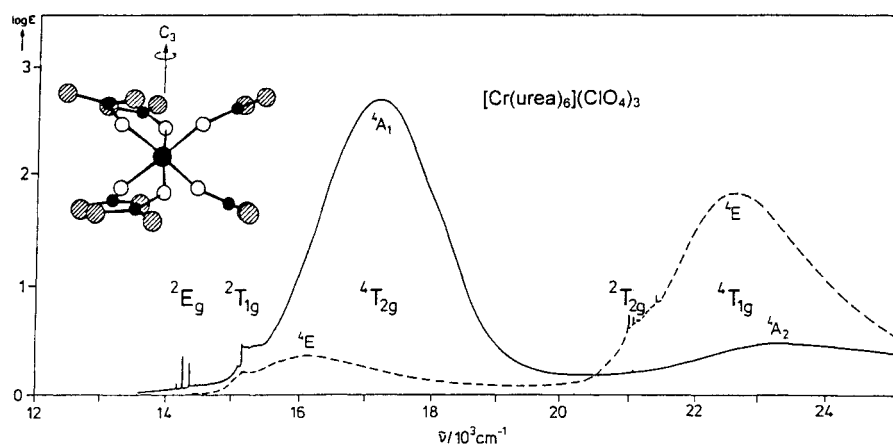


Fig. 19. $\vec{E} \parallel \vec{C}_3$ (—) and $E \perp C_3$ (---) polarized single-crystal absorption spectrum of trigonal $[\text{Cr}(\text{urea})_6](\text{ClO}_4)_3$ crystals measured at $T = 1.9$ K. (The author is grateful to Prof. H. Yersin for making the spectrum available prior to publication.)

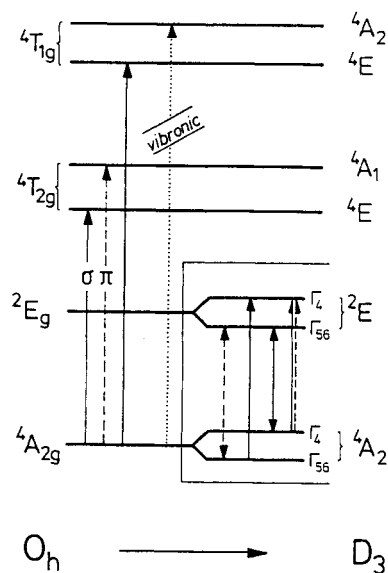


Fig. 20. Energy levels and selection rules for static (σ or π) electric-dipole transitions in hexacoordinated trigonal d^3 -complexes. The forbidden transition into ${}^4A_{2g}$ gains some intensity by a vibronic coupling mechanism

tion only the transitions ${}^4A_1({}^4T_{2g})$ is electric-dipole allowed (17000 cm^{-1}), the minor band at 23400 cm^{-1} probably arises from a vibronic coupling mechanism due to the transition ${}^4A_2 \rightarrow {}^4A_2({}^4T_{1g})$. Inspection of the energy diagrams displayed in Fig. 18a, b proves that the observed sequence of quartet split levels, i.e. ${}^4E < {}^4A_1 \leq {}^4E < {}^4A_2$, can by no means be reproduced by varying the structural angles θ and ϕ . This result is not changed when the AOM parameters involved are varied widely within physically reasonable values. However, by adjusting the dihedral angle ψ (cf. Fig. 18c) the correct level sequence is readily obtained resulting in an accurate fit for a ψ -value near 70° . This is a clear indication that anisotropic M-L π -interaction is apparent in the present complex. More quantitative results on the level splittings would require the knowledge of structural data, which are presently not available for hexaurea complexes of chromium(III). The X-ray analysis performed for the isomorphous titanium compound [61] yielded a small trigonal compression of the $[\text{TiO}_6]$ octahedron ($\theta = 53.6^\circ$, $\phi = 60^\circ$). However, such a small deviation from cubic symmetry cannot explain the relatively large quartet splittings observed in the optical absorption spectrum of $[\text{Cu}(\text{urea})_6](\text{ClO}_4)_3$.

Similar results are obtained for the rather different compound $\text{K}[\text{Cr}\{\text{HB}(\text{pz})_3\}_2]$ where the chromium ion is surrounded by six nitrogens of the pyrazolyl groups. The absorption spectrum, which is depicted in Fig. 21, shows unsymmetrical band shapes for both quartet transitions. A band deconvolution yields a considerable splitting of the ${}^4A_{2g} \rightarrow {}^4T_{2g}$ transition ($\sim 1700\text{ cm}^{-1}$), whereas the low-symmetry components of ${}^4T_{1g}$ are separated by about 700 cm^{-1} only. The lowest doublet states as derived from spin-forbidden transitions in emission, absorption and MCD spectra are also included in the figure. In a recent paper [59] we have shown by extensive AOM calculations that the sequence of d^3 -levels can be explained only if strong π -anisotropy and a relatively small trigonal deviation from the geometry of an octahedron is assumed. This may be either a compression or an elongation, in both cases, the deviation in the polar angle θ must be less than 5° . The dihedral angle ψ is expected to be not far from 0° predicting a highly symmetric arrangement with the pyrazolyl rings aligned in parallel direction to each other. These findings are similar to the known geometry of the isomorphous cobalt complex, which exhibits a slightly elongated chromophore with angles $\Delta\theta = \theta - \theta_{\text{cub}} = 3.5^\circ$, $\phi = 61^\circ$, $\psi = 3.7^\circ$ [62].

In summary, the observed trigonal band splittings in $[\text{Cr}(\text{urea})_6]^{3+}$ and $[\text{Cr}\{\text{HB}(\text{pz})_3\}_2]^+$ originate definitely from an unsymmetrical π -interaction that is due to the distinct orientations of the urea ligands or to steric properties of the coordinated tridentate chelate, respectively. From fitting the observed optical transitions we have obtained the following AOM parameters in cm^{-1}):

$$[\text{Cr}(\text{urea})_6](\text{ClO}_4)_3: e_\sigma = 6800, e_{\pi s} = 1200, e_{\pi c} = 720 \quad (63)$$

$$[\text{Cr}\{\text{HB}(\text{pz})_3\}_2](\text{ClO}_4)_3: e_\sigma = 8000, e_{\pi s} = 1100, e_{\pi c} = 0 \quad (64)$$

The structural parameters evaluated are summarized in Table 1 together with related data from other trigonal chromium(III) complexes.

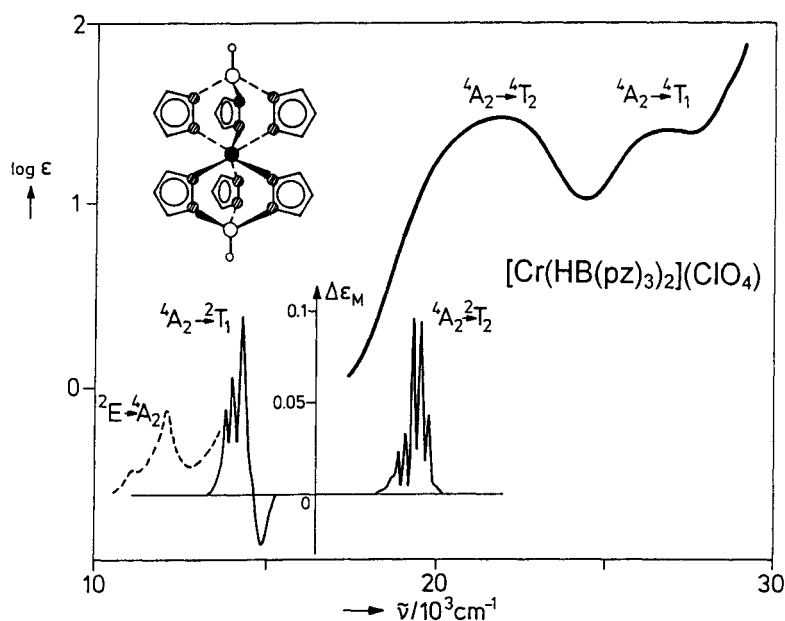


Fig. 21. Optical absorption (—), emission (---) and MCD (—) transitions in $[\text{Cr}\{\text{HB}(\text{pz})_3\}_2]^+$ measured at $T = 80 \text{ K}$ (absorption, emission) and $T = 295 \text{ K}$ (MCD) [59]

3.2.2

Angular Geometry of $[\text{Cr}(\text{ox})_3]^{3-}$ in $\text{NaMg}[\text{Al}(\text{ox})_3] \cdot 8\text{H}_2\text{O}$

The anion $[\text{Cr}(\text{ox})_3]^{3-}$ has been widely investigated both experimentally and theoretically and assignments of electronic transitions have already appeared in introductory articles [63]. Piper and Carlin [64] have given the first substantial interpretation of polarized spin-allowed transitions which could be satisfactorily explained by a trigonal ligand field acting on the CrO_6 octahedron. However, the low symmetry environment, to which the chromium ions are generally subjected in crystalline surroundings, provokes assignment problems which have led to controversial discussions, in particular concerning the identification of the lowest doublet states within the (t_{2g}^3) electron configuration. Coleman [65], for example, observed that the splitting of the emitting state, ${}^2E_g(\text{O}_h)$, varied by a factor of about 100 (!) for different host materials. Moreover, some confusion was appeared since doublet transitions are strongly influenced by the particular amount of crystalline water present in crystals such as $\text{NaMg}[\text{Al}(\text{ox})_3] \cdot n\text{H}_2\text{O}$ or $\text{K}_3[\text{Al}(\text{ox})_3] \cdot n\text{H}_2\text{O}$ [66, 67]. In order to rationalize the $d-d$ transition energies Zaric and Nicetic [68] have included outer sphere interactions, Trees' correction, orbital delocalization factors, and other effects into their extensive calculations on the $[\text{Cr}(\text{ox})_3]^{3-}$ anion. These authors concluded that the ligand field approach had failed by claiming that quartets and doublet transitions cannot be rationalized simultaneously by means of the AOM. However, a part of their experimental database, which was obtained from unpublished excitation spectra and by

averaging geometric parameters of related crystals, may be questioned. Additional assignment uncertainty arises from the appearance of non-equivalent chromium sites in most of the host materials investigated so far [68].

On the other hand, working with chromium(III) doped $\text{NaMg}[\text{Al}(\text{ox})_3] \cdot 8\text{H}_2\text{O}$ single crystals in our laboratory, we were able to rationalize the d^N level scheme of $[\text{Cr}(\text{ox})_3]^{3-}$. This salt is more favorable because the Cr^{3+} ions occupy equivalent sites, being located on the axis of trigonal symmetry [69]. The polarized zero-phonon bands in the region of ${}^4A_{2g} \rightarrow {}^2E_g$ transitions, which have been figured out in detail in Ref. [70], show comparable trigonal splittings into spin-orbit sublevels for ${}^2E_g$ (3.0 cm^{-1}) and ${}^4A_{2g}$ (1.55 cm^{-1}). The splitting of the ground state was found to be predominantly influenced by the trigonal compression or elongation rather than by other geometric distortions or distinct π -interactions [38]. This behavior is illustrated in Fig. 22a showing that a notable trigonal compression is required, i.e. $\theta \gg \theta_{\text{cub}} (= 54.74^\circ)$, to reproduce the relatively large splitting of the ${}^4A_{2g}$ ground state. This result is consistent with a ligand field analysis of the quartet transitions, where a relationship between LF parameters was used for an estimate of the polar angle θ to be around 61° [71]. However, such a large compression should produce a fairly wide separation of the ${}^2E_g$ split levels which is in contrast to the experimental findings. Hence, another geometric distortion could be responsible for the situation, with an unusually small splitting of ${}^2E_g$ in view of the considerable low-symmetry splittings of both quartet bands. It is noticed that in a symmetrically ligated tris-chelated complex, θ and ϕ are relat-

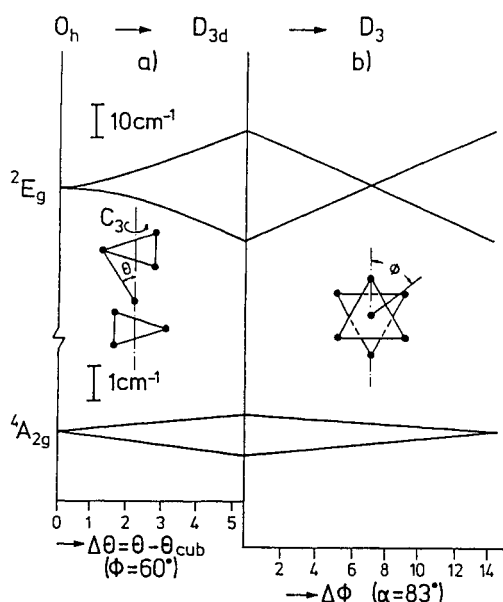


Fig. 22a, b. Calculated energy splittings for trigonal distortions of $[\text{Cr}(\text{ox})_3]^{3-}$ with respect to the polar angle θ (a) and the twist angle ϕ (b); $e_\sigma = 6750$, $e_\pi = 520$, $e_\pi = 0.6e_\pi$, $B = 700$, $\zeta = 200$ (in cm^{-1})

ed to the chelate bite angle α by Eq. (50) (cf. Fig. 9). Because it is plausible to assume that peculiarities of the MO_6 geometry will not lead to a dramatic change of this bite angle, α should be predominantly determined by the intrinsic electronic structure of the oxalate ligand. Hence, taking α fixed at a value of 83° , which is in accord with the oxalate bite in other compounds containing the $[\text{Cr}(\text{ox})_3]^{3-}$ anion as well as with the corresponding bite distance in the free anion, we calculated doublet and quartet level splittings in dependence of the trigonal twist around the $\vec{C}_3$ -axis. Figure 22b exhibits that the splitting of ${}^2E_g$ is strongly related to the twist angle ϕ , whereas the ground state splitting decreases moderately with $\Delta\phi (= 60^\circ - \phi, \text{ cf. Fig. 9})$, leading to calculated transition energies which are in accord with the experimental results.

In conclusion, we assume that the $d-d$ transitions in chromium(III) tris-oxalate compounds could be correctly described by means of the AOM, if the geometrical distortions of the CrO_6 entity are adequately considered. Table 4 summarizes our results on the observed and calculated quartet and doublet transitions in $\text{NaMg}[\text{Al}(\text{ox})_3] \cdot 8\text{H}_2\text{O}$. It should be emphasized that the anisotropic π -interaction, that is definitely apparent in oxalate complexes, is *not* the main source for the trigonal splittings, as has been claimed earlier [68]. This is because the dihedral angle ψ takes a value not far from 45° , resulting in a more or less pseudo-isotropic π -bonding (cf. Fig. 18c). In fact, the observed d^3 -level splittings originate predominantly from two independent geometrical distortions that are a trigonal twist and a trigonal compression of the CrO_6 chromophore. This explanation should hold also for the other $[\text{Cr}(\text{ox})_3]^{3-}$ compounds, provided reliable geometric and spectroscopic data are considered.

3.2.3

The Mixed Ligand Complexes $\text{trans-}[\text{Cr}(\text{py})_2(\text{ox})_2]^-$ and $[\text{OsCl}_4\text{ox}]^{2-}$

Since the AOM parameters have been found to be transferable to some extent, they can be used for predictions concerning spectra and structures of other

Table 4. Observed and calculated d -energy levels in $\text{NaMg}[\text{Al}(\text{ox})_3] \cdot \text{Cr}^{3+}$. Optimized parameter values: $e_\sigma = 7638$, $e_{\pi c} = 903$, $e_{\pi s} = 1505$, $\zeta = 250$, $B = 657$, $C = 3223$ (all in cm^{-1}); $\theta = 58.8^\circ$, $\phi = 46^\circ$, $\alpha = 82^\circ$ (cf. Fig. 9)

Assignment	Observed	Calculated	Deviation
${}^4A_{2g}$ -split	1.55	1.52	0.03
$\Gamma_4({}^2E_g)$	14489	14493	4
${}^2E_g$ -split	2.5	2.7	0.2
$\Gamma_4({}^2T_{1g})$	14809	14773	26
$\Gamma_{56}({}^2T_{1g})$	15261	15324	63
$\Gamma_4({}^2T_{1g})$	?	15351	–
${}^4A_1({}^4T_{2g})$	17750	17810	60
${}^4E({}^4T_{2g})$	18150	18050	100
${}^4A_2({}^4T_{1g})$	23800	23850	50
${}^4E({}^4T_{1g})$	25500	25510	10

transition metal complexes. An illustration of this type of study is given in our earlier investigation on *trans*-{bis(pyridine)-bis(oxalato)}chromate(III) [72]. This anion is of interest for several reasons: (i) informative optical spectra have been obtained; (ii) strong π -interactions are expected with pyridine and oxalate ligands; (iii) earlier SCF calculations [73] have figured out an unusual energy pattern for the d^3 states, which is at variance with the predictions of the ligand field approach.

Figure 23 shows the absorption spectrum, which exhibits the typical band pattern for octahedrally coordinated chromium(III) complexes. A qualitative description is already obtained by assuming a pseudo-tetragonal symmetry for the $[\text{CrO}_4\text{N}_2]$ entity. Considering only the diagonal elements of the tetragonal perturbation matrices in the strong field approach [74], the band splittings of ${}^4T_{2g}(\Delta E_1 = {}^4E_g - {}^4B_{2g})$ and ${}^4T_{1g}(\Delta E_2 = {}^4E_g - {}^4A_{2g})$ become

$$\Delta E_{1/2} = 2\delta\pi \mp 2\delta\sigma \quad (65)$$

using the abbreviations $\delta\lambda = e_\lambda(\text{ox}) - e_\lambda(\text{py})$, where $\lambda = \sigma, \pi$. Because of the relationship $e_\sigma \gg e_\pi$, these level splittings are usually determined by the differences in σ -bonding. However, the opposite π -contributions of oxalate (π -donor, i.e. $e_\pi > 0$) and pyridine (π -acceptor, i.e. $e_\pi < 0$) result here in a comparable contribution from the π -interaction, i.e. $\delta\pi \sim \delta\sigma > 0$. Using AOM parameters as derived from $[\text{Cr}(\text{ox})_3]^{3-}$ [70] and $[\text{Cr}(\text{py})_4\text{X}_2]^+$ [75] quartet band splittings around 500 cm^{-1} (${}^4T_{2g}$) and 3000 cm^{-1} (${}^4T_{1g}$) are expected. These values are reflected in the absorption spectrum by the different band shapes indicating a significant level splitting only for the second quartet transition. A band deconvolution

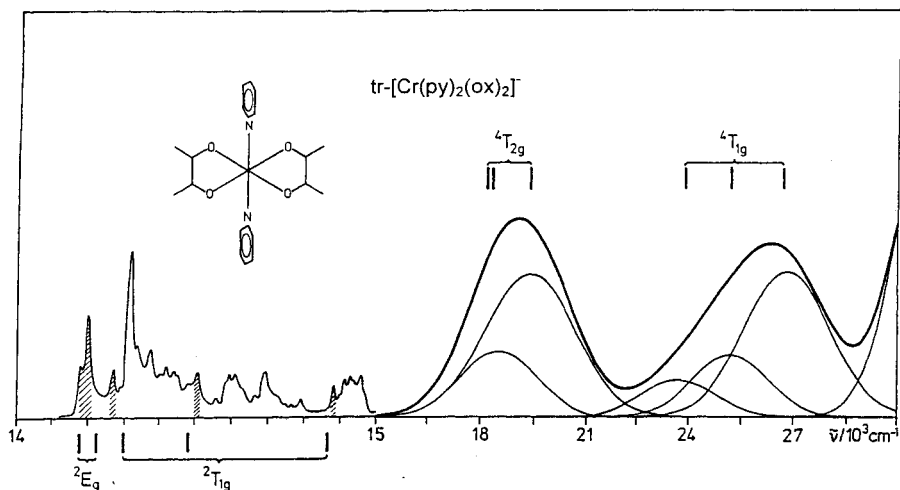


Fig. 23. Low-temperature ($T = 15\text{ K}$) absorption spectrum of $\text{K}[\text{Cr}(\text{py})_2(\text{ox})_2] \cdot 2\text{H}_2\text{O}$. A deconvolution is given for both quartet bands. The doublet region on the left side is enhanced by a factor of 10. Bars show term energies as calculated for an oxalate bite of 83° by using the parameters (in cm^{-1}): $e_\sigma(\text{py}) = 7000$, $e_\pi(\text{py}) = -500$, $B = 650$, $C = 3060$; other parameters as for Fig. 22

yields three maxima which are separated by 1500 cm^{-1} and 1600 cm^{-1} , respectively. The derived splitting of ${}^4T_{1g}$ into three components is caused by the actual symmetry of the chromophore, which is lower than tetragonal due to an oxalate bite angle α that deviates considerably from 90° . In the case of ${}^4T_{2g}$, reliable band positions for the three expected split levels cannot be obtained from fitting the band shape because of the definitely smaller energy separations between these sublevels. At the low-energy side of the absorption spectrum the weak sharp bands at 14176 and 14200 cm^{-1} represent the zero-phonon transitions into the sublevels of ${}^2E_g$. Towards higher energy the band pattern of spin-forbidden transitions can be almost completely interpreted in terms of a vibrational structure upon these origins showing a series of correspondences between the vibronic and infrared spectra (cf. Fig. 23). Three higher peaks, defying an assignment to vibrational sidebands of ${}^2E_g$, have been assigned to zero-phonon transitions into the split levels of ${}^2T_{1g}$ [72].

Two disparate effects are of particular interest in AOM calculations on the transition energies in *trans*-[Cr(py)₂(ox)₂]⁻: the variation of the oxalate bite angle α , and the π -behavior of the pyridine ligand. The combined influence of these properties on the energy level splittings can be visualized by a two-dimensional contour plot as illustrated in Fig. 24. Contour lines are depicted for the ${}^2E_g$ level splitting together with traces which correspond to the splittings of the second quartet band. This plot shows good agreement with the experimental results for an oxalate bite angle that is within the expected range between 81° and 85° . Moreover, the negative parameter value derived for $e_{\pi\perp}(\text{py})$ is in accord with earlier results of Schäffer's group [75]. In view of the pyridine MO's, low-lying LUMO's are considerably mixed with metal *d*-orbitals resulting in the net

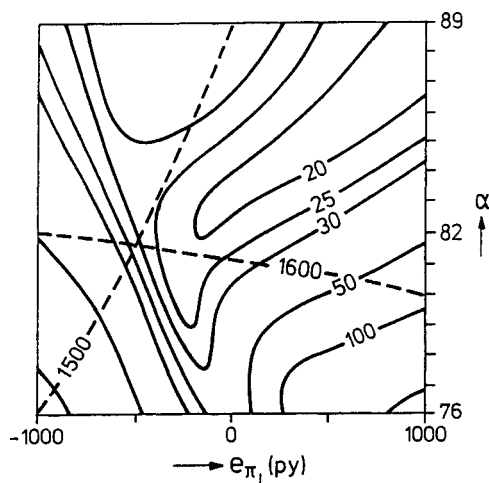


Fig. 24. Contour plot for the ${}^2E_g$ splitting in $\text{K}[\text{Cr}(\text{py})_2(\text{ox})_2] \cdot 2\text{H}_2\text{O}$ including isolines for the ${}^4T_{1g}$ splitting (---) which corresponds to the results of the band fit. Other parameters as given for Fig. 23

π -acceptor behavior ($e_{\pi\perp}(\text{py}) \approx -500 \text{ cm}^{-1}$). This property is supported by the appearance of internal pyridine vibrations as promoting and accepting modes in the region of spin-forbidden transitions [72]. In summary, our results show the validity of the AOM approach, which accounts for a reliable description of the d -energy level scheme by using parameters *transferred* from related complexes. The poor results obtained by the $X\alpha$ -calculation, on the other hand, demonstrate the obstacles that are met with when describing spectroscopic transitions within open-shell multiplets by means of SCF methods.

In the remainder of this section some of the preceding results will be used in order to provide an analysis of $d-d$ transitions in a mixed osmium(IV) complex. Homborg et al. [76] have reported well-resolved absorption bands for $[\text{OsCl}_4\text{ox}_2]^{2-}$ in the near-infrared region. The relevant energy level diagram for the parent octahedral symmetry is already given in Fig. 11 showing the ${}^3T_{1g}$ multiplet split by a considerable spin-orbit coupling into the totally symmetric Γ_1 ground state and the higher $\Gamma_4, \Gamma_5, \Gamma_3$ states. Because the molecular symmetry of the present mixed-ligand complex is reduced to at least C_{2v} , all degenerate states must split and a total of nine one-dimensional spin-orbit levels is obtained. ${}^3T_{1g}$. The differences in the axial and equatorial metal-ligand interactions will certainly contribute to these splittings; however, AOM calculations show that the most pronounced effect arises from the actual coordination geometry of the chelated oxalate. Although X-ray data are not available, geometrical considerations predict a strong deviation from an octahedral surrounding due to the rigidity of the oxalate anion. Using reasonable Os-O distances, a bite angle of about 74° may be expected.

We performed the calculations of the $d-d$ transition energies in $[\text{OsCl}_4\text{ox}_2]^{2-}$ by using the $e_o(\text{Os-Cl})$ and $e_{\pi}(\text{Os-Cl})$ parameter values derived in Sect. 3.1.1 from $[\text{OsCl}_6]^{2-}$. Accordingly, we estimated the oxalate parameters to be about twice as large as for chromium(III). As mentioned above, the variation of the oxalate bite α is of major importance for describing the observed transition energies, whereas minor contributions to the d -level scheme arise, for example, from the deviation of the opposite equatorial angle $\delta(\text{Cl-Os-Cl})$ from a rectangular arrangement. Figure 25 shows an energy diagram for the split levels of ${}^3T_{1g}$ together with the respective positions of measured absorption maxima. The near-infrared transition into $A_2(\Gamma_3)$ was not identified in the optical spectrum in accord with selection rules for C_{2v} symmetry. The fitting of the experimental term energies results in a most reasonable value for the bite angle ($\alpha = 79^\circ \pm 1^\circ$) reflecting the influence of a covalent M-L bonding ($\alpha > 74^\circ$) as well as rigidity of the chelate ligand ($\alpha \ll 90^\circ$). Again, this example illustrates that spectrum-structure correlations can be rather significant though easy to handle by means of the AOM.

3.3

Extended π -Interaction in Chelate Complexes

As has been described recently [27–29], *non-additive* contributions to the ligand field potential may occur in complexes with chelate ligands which have an extended π -electron system. Within the framework of the conventional

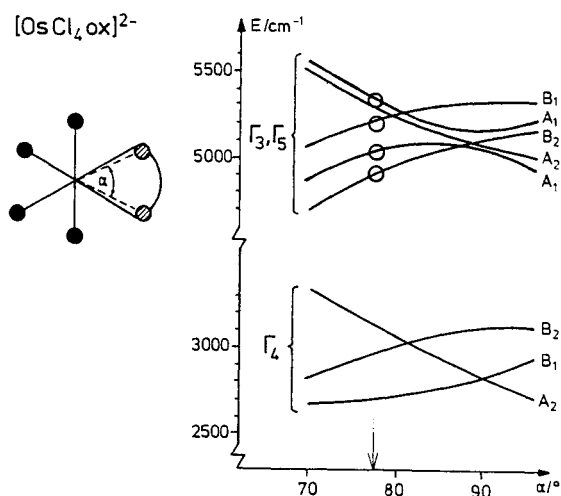


Fig. 25. Calculated (—) and experimental (○) spin-orbit sublevels of ${}^3T_{1g}(O_h)$. $e_\sigma(\text{Cl}) = 9500$, $e_\pi(\text{Cl}) = 1800$, $e_\sigma(\text{ox}) = 11000$, $e_\pi(\text{ox}) = 1200$ ($e_{\pi c} = 0.6 e_{\pi s}$), $B = 500$, $C = 5B$, $\zeta = 2650$ (in cm^{-1})

(additive) AOM, the energy matrix for the π -orbitals contains two antibonding parameters, which describe the interaction in the chelate plane by $e_{\pi c}$ (or $e_{\pi \parallel}$), and perpendicular to it by $e_{\pi s}$ (or $e_{\pi \perp}$). Following Orgel [26], this description is not valid when delocalized π -electrons are involved. Instructive examples are complexes with acetylacetonate and 2,2'-bipyridine ligands which will be discussed in the following paragraphs.

In Sect. 2.3.1 of the theoretical part we have outlined the concept for phase-coupled frontier orbitals and shown that the relevant molecular orbitals of the $M\bar{\zeta}_L^L$ entity can be classified with respect to the $\bar{C}_2$ -axis into symmetric (χ -type) or antisymmetric (ψ -type) MO's. Two different π -parameters are required to describe the specific $d_\pi^M - p_\pi^L$ out-of-plane interactions between in-phase ψ -type ($e_{\pi s}$) and out-of-phase χ -type ($e_{\pi c}$) orbitals, respectively. As indicated in Fig. 7, these quantities should largely depend on the respective MO energies of the free ligand which are generally different for ψ - and χ -type wavefunctions. The contribution of the HOMO (or the LUMO for acceptor ligands) is usually the most important because the smallest energy denominator in Eq. 16 is associated with this molecular orbital. However, consideration of the individual contributions of other filled and empty ligand orbitals may be required in some cases. In the following we deal with properties that are due to phase-coupled frontier orbitals in the trigonal complexes $[\text{Cr}(\text{acac})_3]$ and $[\text{Cr}(\text{bpy})_3]^{3+}$. Due to the different symmetries of the respective HOMO and LUMO ligand orbitals (the HOMO, for example, is of χ -type for acac and of ψ -type for bpy) we can expect opposite Orgel effects. However, since low-lying CT-states interfere with the d^N states, both complexes are still a challenge for semiempirical calculations.

The next section focuses on the relatively large level splittings observed in optical and EPR spectra of the acac complex, which cannot be explained within a conventional ligand field model, because the geometry of the CrO_6 entity is

very near to O_h (cf. Table 1). The results obtained will be applied then to other trivalent acetylacetonate complexes by showing how the various angular geometries of $[M(acac)_3]$ compounds can be elucidated by means of the Orgel effect. Finally, calculations on Zeeman level splittings in $[Cr(acac)_3]$ and $[Cr(bpy)_3]^{3+}$ are presented in Sect. 3.3.3.

3.3.1

Electronic States of $[Cr(acac)_3]$

As noted above, the polarized absorption spectrum indicates fairly large trigonal level splittings (e.g. 800 cm^{-1} for $^4T_{2g}$), although the coordinated oxygen atoms have an almost exact octahedral conformation [77]. Though the LFT is able to reproduce the energy level scheme [78], the parameters obtained have no physical meaning due to unreasonable radial parts of the d -wavefunctions. The conventional (additive) AOM can also not account for these level splittings because the anisotropic π -bonding is averaged by the orientation of the planar chelated ligands ($\psi \approx 45^\circ$), yielding a pseudo-isotropic behavior (cf. Fig. 18d). On the other hand, the observed sequence of the higher quartet split levels has been reasonably explained within the (non-additive) phase-coupling model [28]. Since acac is an oxygen donor ($e_\pi > 0$), it is the highest occupied MO which predominantly affects the metal- d orbitals. The HOMO of the free acac ligand (π_3) is of ψ -type and the related parameter $e_{\pi s}$ accounts for the interaction with metal- d orbitals via in-phase coupled frontier orbitals of the ligand (cf. Fig. 7). On the other hand, out-of-phase coupling is negligibly small ($e_{\pi s'} \approx 0$) because of the larger energy differences to the χ -type orbitals (π_2, π_4). Assuming a strong donor property ($e_{\pi s} \approx 1000\text{ cm}^{-1}$), the quartet level scheme is correctly rationalized not only with respect to the level ordering but also for the considerable low-symmetry splitting of $^4T_{2g}$.

Another assignment problem is concerned with the lowest ^2E_g sublevels due to the appearance of more than two prominent bands (R -lines) in the emission spectra of doped materials [38, 78–80]. However, by temperature-dependent and site-selective optical measurements, we could classify these peaks as belonging to different $[Cr(acac)_3]$ sites in the low-temperature phase of the respective crystal lattices [38, 78]. Figure 26 shows the single-crystal emission spectrum of $[Cr(acac)_3]$ doped into the isomorphous $[Ga(acac)_3]$ host lattice. Polarized bands in the region of zero-phonon transition are depicted in the inset, which shows four prominent peaks arising from nonequivalent crystallographic sites. They are optically resolved into two components separated from each other by 1.2 cm^{-1} . This value corresponds exactly to the zero-field splitting (zfs) of the $^4A_{2g}$ ground state as derived from EPR [81]. Since the sign of the zfs is known, leading to $\Gamma_{56}(\pm \frac{3}{2}) < \Gamma_4(\pm \frac{1}{2})$, the split levels of ^2E_g can be unambiguously assigned by the band polarizations. The emission spectrum shows the lower energy component of each zero-phonon line to be predominantly σ -polarized ($\vec{E} \perp \vec{C}_3$ -axis), whereas the higher energy transitions is π -polarized ($\vec{E} \parallel \vec{C}_3$ -axis). It follows from the electric-dipole selection rules given in Fig. 20 that the observed polarizations of the zero-phonon lines are only consistent with a Γ_{56} emitting state originating from ^2E_g . The additive AOM would predict the $\Gamma_4(^2E_g)$ to be

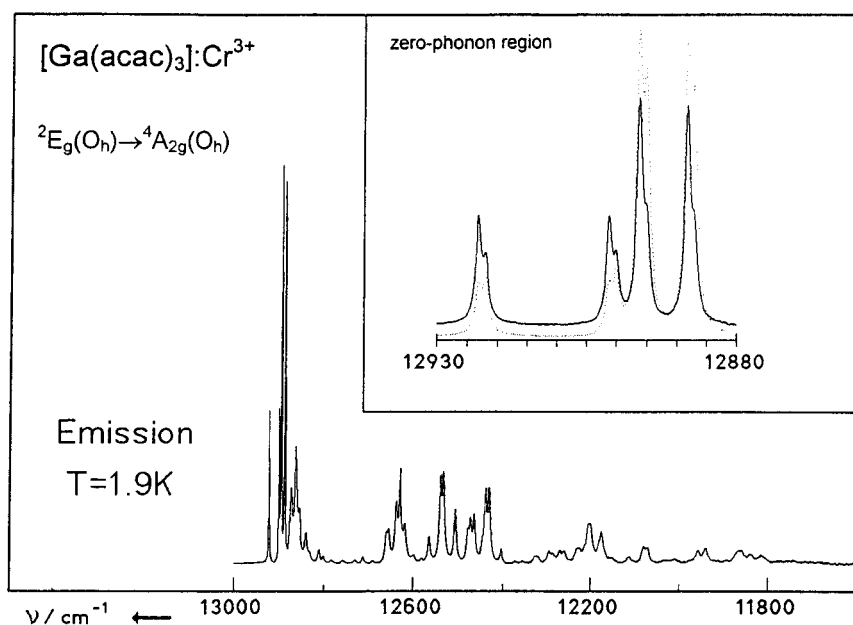


Fig. 26. High-resolution emission spectrum of $[\text{Ga}(\text{acac})_3]$ doped with 0.1% Cr^{3+} at $T = 1.9$ K. Polarized bands due to the electric vector orientated perpendicular (σ :) or parallel (π : —) to the crystallographic b -axis are depicted in the inset for the zero-phonon region

lowest in energy, i.e. different from the experimental results. The non-additive model, on the other hand, is consistent with the observed sequence and splittings of doublet and quartet excited states in view of the quasi-octahedral geometry of the CrO_6 entity [38]. Moreover, Zeeman band splittings in the emission spectrum due to $\Gamma_{56}(^2E_g) \rightarrow \Gamma_4, \Gamma_{56}(^4A_{2g})$ transitions are correctly reproduced by our calculations which will be presented in Sect. 3.3.3. In fact, $[\text{Cr}(\text{acac})_3]$ was the first complex, for which the Orgel effect could clearly be established.

3.3.2

Coordination Geometry of $[\text{M}(\text{acac})_3]$ Complexes

The phase-coupling model is able to elucidate geometric peculiarities also for other trivalent first-row transition acetylacetonates. Earlier attempts to correlate the O-O bite with the M-O distance or other geometric or electronic parameters failed [82, 83], and explanations based on Kepert's interligand repulsion model [84] did not lead to general rules for describing the individual geometric distortions. This shortcoming has led to the conclusion that "the structural details thus depend on complex factors, probably including the role played by unpaired d -electrons in the central metal ion" [85]. In the following, it is shown that the particular π -interaction, if properly accounted for by means of the non-additive AOM, determines the particular geometries of the MO_6 entities, which

may have octahedral, trigonally compressed ($\alpha < 90^\circ$) or trigonally elongated ($\alpha > 90^\circ$) surroundings.

The underlying idea in our investigation of the role played by the d -electrons was to consider closed-shell compounds as reference systems [86]. Due to their isotropic electron distribution, steric impacts should primarily arise from inter-ligand repulsion and the rigidity of the ligands. The latter effect explains the equal 'isotropic' bites of 271.7 pm ($= b^*$) observed for the acac complexes of Al(III) and Sc(III). In transition metal complexes, on the other hand, a deviation from this distance may be attributed to impacts of the d -electron system. Assuming b^* to be unchanged within the first transition series, a hypothetical bite angle α^* can be calculated for any $3d^N$ tris-acetylacetonate complex from the geometric relation

$$\sin(\alpha^*/2) = b^*/2R^* \quad (66)$$

where R^* denotes the metal-oxygen distance. A deviation of b^* from the experimental value may result from the actual bite angle ($\alpha \neq \alpha^*$) and/or from the actual internuclear distance ($R \neq R^*$). However, since the energy gradient is expected to be much steeper for R than for α , i. e.

$$\frac{\partial E(R, \alpha)}{\partial R} > \frac{\partial E(R, \alpha)}{\partial \alpha} \quad (67)$$

a change in R is of minor importance for a stabilizing geometric distortion of the chromophore. Therefore, R^* can be identified with the experimental R , and only changes of the bite angle from the hypothetical value, $\Delta\alpha = \alpha - \alpha^*$, have to be considered. The angular distortions, which are relevant in our model, can be derived by means of an α versus R plot (Fig. 27) in which the vertical differences from the line traced for a constant bite b^* are significant.

We shall now consider the antibonding d -contribution to the total energy of the electronic ground state. Using matrix elements $\langle d_i | \mathcal{V}_{\text{trig}} | d_j \rangle$ which explicitly depend on the bite angle α [81], and neglecting the off-diagonals $\langle t_{2g} | \mathcal{V}_{\text{trig}} | e_g \rangle$, a simple analytical expression was derived for a (t_{2g}^N) system

$$E(\alpha) \approx \frac{3}{2} e_\sigma \cos^2 \alpha + 2e_{\pi s} \cos^2(\alpha/2) + e_{\pi c} \sin^2 \alpha \quad (68)$$

which is valid for acac complexes where out-of-phase coupling is not operative ($e_{\pi s}' = 0$). Hence, the ground state energy becomes minimal with respect to a variation in α for

$$\cos \alpha = -e_{\pi s} / (3e_\sigma - 4e_{\pi c}) \quad (69)$$

Since the denominator must be positive ($e_\sigma \gg e_{\pi c}$) as is the case for $e_{\pi s}$ (donor ligand), we obtain $\alpha > 90^\circ$, reflecting the increase of the O-O bite in the d^N acetylacetonates compared to the closed shell compounds. The positive value that results for $\Delta\alpha$ represents a stretching with respect to the hypothetical bite angle α^* . Evidently, observed bite angles may be smaller than 90° for geometrical reasons (due to the actual metal-ligand distance); however, the corresponding bite distance b should always be larger than the isotropic bite b^* , in full agreement with the X-ray results presented in Fig. 27. A quantitative treatment, using AOM

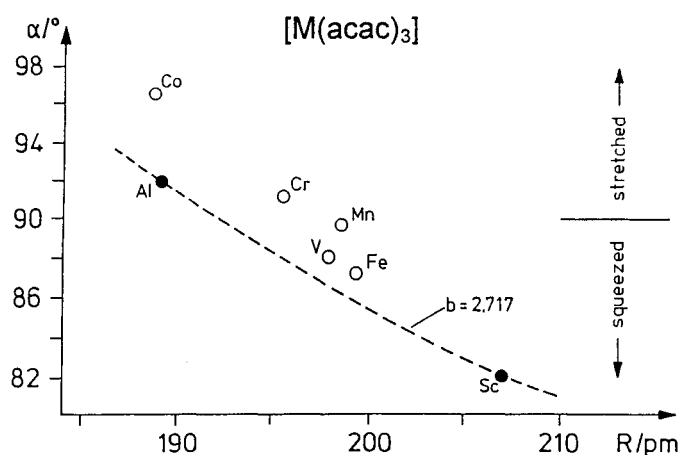


Fig. 27. Bite angle versus metal-ligand distance from X-ray data. The dashed line accounts for a constant O-O bite (*see text*)

parameters derived from band splittings in optical spectra, yielded a bite angle of 93.8° (93.9°) for the chromium (cobalt) complex that is equivalent to a correction of the hypothetical bite angle α^* of +3.2° (3.9°) [86]. This compares well with X-ray data showing $\Delta\alpha = +3.1^\circ$ (+4.6°). The other trisacetylacetonate complexes exhibit similar trends; however, quantitative results are not yet available because the lack of optically resolved band splittings has so far prevented the evaluation of reliable AOM parameters.

3.3.3

Zeeman Level Splittings in $[\text{Cr}(\text{acac})_3]$ and $[\text{Cr}(\text{bpy})_3]^{3+}$

There is considerable current interest in the nature of the lowest excited states in tris-acetylacetonate and 2,2'-bipyridine complexes because of their exceptional photochemical and photophysical properties. However, in the case of $[\text{Cr}(\text{bpy})_3]^{3+}$ the interference of *d-d* transitions with charge-transfer bands has so far prevented reliable assignments even for the familiar spin-allowed transitions. Information on the low-lying doublet states has been poor until Hauser et al. reported highly resolved optical spectra of $[\text{Cr}(\text{bpy})_3](\text{PF}_6)_3$ in neat and doped materials [88]. Their detailed Zeeman spectra provide further information for getting a better insight into the electronic properties of such compounds. Fields et al. [80] have reported level splittings induced by an external magnetic field for the ${}^2E_g \rightarrow {}^4A_{2g}$ transitions in $[\text{Cr}(\text{acac})_3]$. Thus the following discussion focuses on the lowest spin-forbidden transitions in these complexes.

The zero-field splitting of the states concerned are defined by

$$D({}^4A_{2g}) = \Gamma_{56(\pm 3/2)}({}^4A_{2g}) - \Gamma_{4(\pm 1/2)}({}^4A_{2g}) (=2D^9) \quad (70)$$

⁹ $2D$ is the zfs parameter commonly used in EPR.

$$D(^2E_g) = \Gamma_{56(\pm 1/2)}(^2E_g) - \Gamma_{4(\pm 1/2)}(^2E_g) \quad (71)$$

As described in Sect. 3.3.1, $D(^4A_{2g})$ has been determined for the acac complex by optical and EPR measurements of chromium-doped $[\text{Ga}(\text{acac})_3]$ to be $\sim 1.2 \text{ cm}^{-1}$ in agreement with the value obtained for the isomorphous system $[\text{Al}(\text{acac})_3] \cdot \text{Cr}^{3+}$ [80]. The corresponding splitting in $[\text{Cr}(\text{bpy})_3](\text{PF}_6)_3$ exhibits a value of $\sim 0.8 \text{ cm}^{-1}$ reflecting the same ordering $\Gamma_{56} < \Gamma_4$ for the ground state sub-levels. AOM calculations show $D(^4A_{2g})$ in a tris-chelated $[\text{Cr}(\text{L-L})_3]$ compound to be predominantly influenced by the trigonal deviation from the octahedral geometry rather than by a distinct π -interaction with either acceptor- or donor-type ligands. The calculated $^4A_{2g}$ level sequence $\Gamma_{56} < \Gamma_4$ ($\Gamma_4 < \Gamma_{56}$) was found to be strongly related to a trigonally compressed (elongated) geometry [38]. This is in accordance with the experimental data of the bipyridine complex showing a significant zfs together with the correct sequence of split levels corresponding to a trigonal compression of the CrN_6 octahedron by a considerable deviation of the polar angle $\theta (= 58^\circ)$ from the value for cubic symmetry (54.74°). In the case of $[\text{Cr}(\text{acac})_3]$, otherwise, the actually octahedral geometry of the CrO_6 entity does not allow the large experimental splitting of the $^4A_{2g}$ ground state to be reproduced without taking into account the anisotropic spin-orbit coupling that should be apparent in trigonally distorted complexes [38]. Anisotropic spin-orbit coupling is considered in the AOM calculations by using one-electron operators of the form (cf. Eq. 58)

$$\hat{H}_{\text{SO}} = \zeta \{ k \ell_z s_z + \ell_x s_x + \ell_y s_y \} \quad (72)$$

where $k (< 1)$ represents a Stevens' reduction factor [39]. Figure 28 illustrates the dependence of the ground state splitting on k for trigonal geometries varying from a slightly elongated ($\theta = 53^\circ$) to a strongly compressed ($\theta = 58^\circ$) octa-

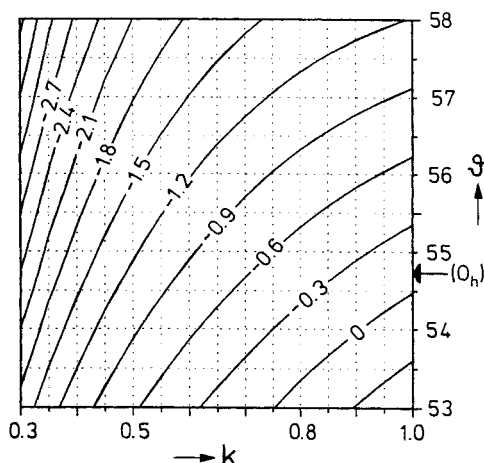


Fig. 28. Isolines for the zero field splitting of the $^4A_{2g}$ ground state ($\Gamma_{56} - \Gamma_4$) in $[\text{Cr}(\text{acac})_3]$ due to Steven's reduction (k) and trigonal distortion (θ); $e_\sigma = 7700$, $e_{\pi s}' = 1400$, $e_{\pi s} = 0$, $e_{\pi c} = 0.6e_{\pi s}'$, $B = 400$, $C = 6B$, $\zeta = 245$ (in cm^{-1})

hedron. This contour plot shows the experimental value reproduced for k taking values around 0.4, when the geometry of the neat $[\text{Cr}(\text{acac})_3]$ is considered ($\theta = 54.6^\circ$). This result is supported by our calculations of the Zeeman splittings of the emission lines which are discussed below.

Under the effect of an external magnetic field, the spin-orbit states of a d^3 system, which are at least twofold degenerate according to Kramers' theorem, split into components with opposite values of pseudo-spin M_s . The magnetic operator used is given with Eq. (60); the squared dipole oscillator strengths of the ${}^4A_{2g} \leftrightarrow {}^2E_g$ transitions for trigonal symmetry are presented in Table 5. A series of calculations on the respective Zeeman splittings shows that the experimental peak positions in $[\text{Al}(\text{acac})_3]:\text{Cr}^{3+}$ [80] can be reproduced only if k is significantly lowered. Good agreement with the spectroscopic results is obtained again for $k \approx 0.4$. This result is illustrated in Fig. 29 showing the zero-phonon emission lines of one Cr^{3+} -site without a magnetic field and with a field of $H_{\parallel} = 5.62$ tesla aligned parallel to the crystallographic b -axis which is orientated approximately parallel to the molecular trigonal axis. This figure reflects the ${}^4A_{2g}$ ground state splitting into four sublevels, where the calculated transition energies accurately fit the measured band positions. The energy shift of the lowest excited (emitting) state $\Gamma_{56(+1/2)} ({}^2E_g)$ is also correctly reproduced. The absorption profile is in accordance also with intensity relations which can be expected from the transition probabilities given in Table 5, exhibiting, for example, the highest intensity for the π -component in line with the zero-field polarizations, and only a marginal feature due to the forbidden transition into $\Gamma_{56(-3/2)} ({}^4A_{2g})$.

In the case of $[\text{Cr}(\text{bpy})_3](\text{PF}_6)_3$, the zfs of the lowest doublet state (cf. Eq. 71) has been determined to be $+19.5 \text{ cm}^{-1}$ [32], exhibiting a positive sign unlike the respective splitting in $[\text{Al}(\text{acac})_3]:\text{Cr}^{3+}$. The inverted level sequence was suggested as having originated from the different π -bonding in these complexes [27], since the HOMO (LUMO) of bpy is given by an out-of-phase (in-phase) combination of the ligator π -MO's, which is just opposite to the situation with the acetylacetonate ligand. This argument is supported by our AOM calculations, although strong trigonal distortions (bipyridine complex) also contribute to this splitting considerably.

The low energy part of the well-resolved polarized absorption bands of ${}^4A_{2g} \rightarrow {}^2E_g$ transitions measured with a magnetic field aligned parallel to the trigonal axis ($H_{\parallel} = 5 \text{ T}$) is depicted in Fig. 30. As shown by the coincidences with the calculated transition energies, all observed features can be properly explained as

Table 5. Electric-dipole probabilities for σ - and π -polarized ${}^4A_{2g} \leftrightarrow {}^2E_g$ transitions in trigonal d^3 -systems under the effect of an external magnetic field that is aligned parallel to the molecular trigonal axis (cf. Ref. [32])

${}^4A_{2g}/{}^2E_g$	$\Gamma_{4(+1/2)}$	$\Gamma_{4(-1/2)}$	$\Gamma_{56(+1/2)}$	$\Gamma_{56(-1/2)}$
$\Gamma_{4(+1/2)}$	$\sigma_0/6$	$\pi/6$	$\sigma_0/6$	$\sigma_1/12$
$\Gamma_{4(-1/2)}$	$\pi/6$	$\sigma_0/6$	$\sigma_1/12$	$\sigma_0/6$
$\Gamma_{56(+3/2)}$	$\sigma_1/4$	—	$\pi/2$	—
$\Gamma_{56(-3/2)}$	—	$\sigma_1/4$	—	$\pi/2$

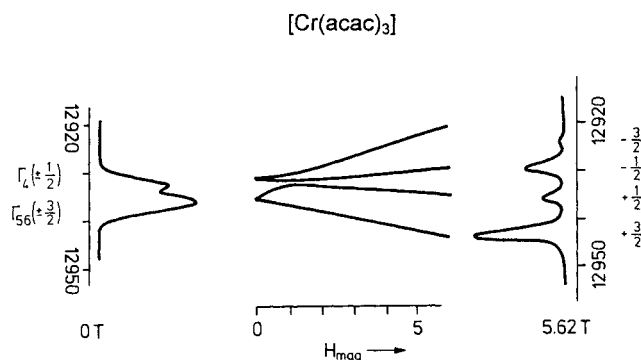


Fig. 29. Calculated Zeeman splittings for $\Gamma_{56(-3/2)}(^2E_g) \rightarrow \Gamma_4(^4A_{2g})$ transitions in $[\text{Al}(\text{acac})]:\text{Cr}^{3+}$. The experimental curves are taken from Ref. [80]

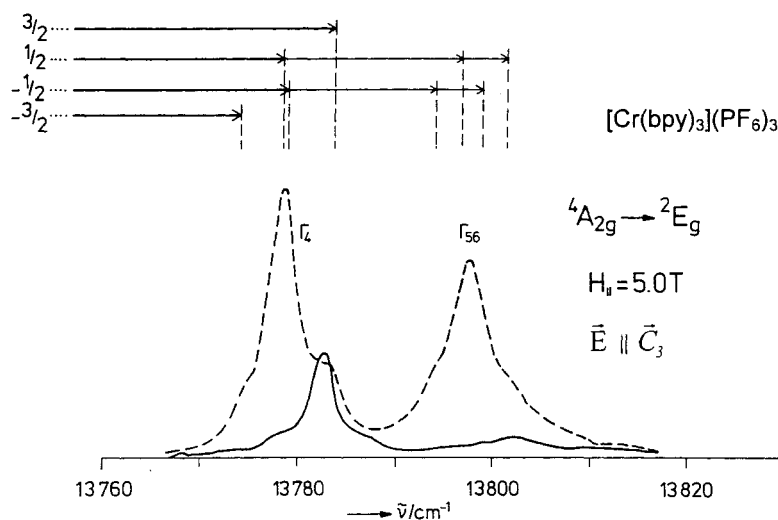


Fig. 30. $^4A_{2g} \rightarrow ^2E_g$ Zeeman transitions in $[\text{Cr}(\text{bpy})_3](\text{PF}_6)_3$ measured at temperatures $T = 1.6$ K (—) and $T = 12$ K (---) in σ -polarization (see text). Calculated energies (arrows) refer to Ref. [32]

being due to Zeeman level splittings of these states, and measured band intensities fit selection rules and Boltzmann populations [32]. For example, only one prominent absorption appears at $T = 1.4$ K, where only the lowest component of the ground state manifold, $\Gamma_{56(-3/2)}(^4A_{2g})$, is significantly populated. According to Table 5, the peak at 13783 cm^{-1} is identified as the transition into $\Gamma_{4(-1/2)}(^2E_g)$. The small features located at 13778 cm^{-1} and 13797 cm^{-1} , which grow rapidly with increasing temperature, are due to transitions from $\Gamma_{4(-1/2)}(^4A_{2g})$ into the $\Gamma_{4(-1/2)}$ and $\Gamma_{56(-1/2)}$ sublevels of ^2E_g . The spectral analysis yields similar splittings for both components of ^2E_g , i.e. 4.3 cm^{-1} for Γ_4 and 4.1 cm^{-1} for Γ_{56} , res-

pectively, and the corresponding values for $g_{\perp(\parallel)}$ are calculated from

$$g_{\perp(\parallel)} = \Delta E_{\perp(\parallel)} / \beta H_{\perp(\parallel)} \quad (73)$$

using $\beta = 0.4668 \text{ cm}^{-1} \text{ tesla}^{-1}$. The Zeeman splittings in the excited state for a magnetic field perpendicular to the trigonal axis are found to be very small and not resolved in the optical spectra. Consequently, the value for $g_{\perp}$ must be close to zero for both Kramers' doublets resulting from ${}^2E_g$. These findings are confirmed by the AOM, which describes the ground state splitting accurately, and calculates the much larger effect for a magnetic field that is aligned parallel to the trigonal axis. Moreover, the correct level sequence is derived for the Γ_4 , $\Gamma_{56}({}^2E_g)$ split components that can be distinguished by pseudo-spin values $-1/2, +1/2$. It should be mentioned that the calculated $g_{\parallel}$ values are significantly different for $\Gamma_4(g_{\parallel} = 3)$ and $\Gamma_{56}(g_{\parallel} = 0.9)$ unlike the similar values derived from the absorption spectrum (*see above*). On the other hand, the calculations on g -values can be improved when orbital reduction ($k \ll 1$) and/or Trees' correction ($\alpha_T \approx 200$) is taken into account. Both effects lower $g_{\parallel}(\Gamma_4)$ and increase $g_{\parallel}(\Gamma_{56})$ considerably, bringing these values close to the experimental ones [32]. Because Trees' correction shifts doublet and quartet levels in a different manner, the Racah parameters (B, C) have to be readjusted in such calculations.

In conclusion, the AOM also provides a useful description of the Zeeman band splittings measured in the emission spectra of the present complexes, where the particular π -bonding plays an important role. A quantitative explanation of the $g_{\parallel}$ -values of the lowest excited state ${}^2E_g$ requires at least one additional parameter in the calculations, either the orbital reduction factor k or the orbital coupling parameter α_T . This shows the necessity of using better wave functions than can be obtained by routine ligand field calculations in order to derive a more comprehensive understanding of the relatively small magnetic effects. It should be noted that the failure of earlier attempts to correlate the g -values of $[\text{Cr}(\text{acac})_3]$ and ruby ($\text{Al}_2\text{O}_3:\text{Cr}^{3+}$) [79] may be explained by the different Cr-O bonding properties that appear in these systems.

4

Chromium-Doped Oxide Lattices

There is a great deal of experimental work on the absorption and emission of transition metal ions doped in oxide crystals. These spectra have mostly been interpreted in terms of highly symmetric crystal fields (e.g. by means of Tanabe-Sugano diagrams), not considering the actual low-symmetry distortions of the coordination spheres. From the theoretical point of view, this may be due mainly to the lengthy treatment of non-symmetric potentials in terms of the conventional LFT. This shortcoming, however, has often prevented reliable assignments, which are required for deriving assignments of excited states with a view to understanding the underlying photophysical processes. On the other hand, chromium-doped materials in particular (minerals, glass ceramics) have gained in importance in the past decade for applications in laser physics [89] or as solar energy concentrators [90]. For example, the first tunable laser on the basis of a d^2 -ion was Cr^{4+} -doped forsterite (Mg_2SiO_4) developed by Petricevic

[91] in 1988. One year later, Shkadarevich and Zverev [92] reported the laser activity of Cr^{4+} in YAG, which is the most promising matrix for laser materials at present. Although considerable research is being done on this system, the complicated spectroscopic behavior, the geometry of the coordination sphere, and even the nature of the emitting states are by no means clear. In 1994, we reported the first AOM calculations of $d-d$ transitions in Cr^{4+} centers [93]; these are extended in Sect. 4.1. For the trigonally distorted Cr^{4+} sites of doped olivines, an AOM investigation has been given recently by Atanasov [94].

The alexandrite laser, on the other hand, has already achieved technical relevance [95], and a great deal of information is available on this Cr^{3+} -doped spinel. Precise data from X-ray investigations and optical measurements make this compound ideal for an investigation of spectrum-structure correlations in doped crystals, as discussed in Sect. 4.2. The goal of this work is not only to identify and calculate electronic states with respect to the geometric surroundings of the impurity ion, but also to elucidate the nature of the metal-ligand bonding in doped materials given in terms of the underlying AOM parametrization.

4.1

Cr^{4+} in the Garnet $\text{Y}_3\text{Al}_5\text{O}_{12}$ (YAG)

Garnets have the general formula $\text{A}_3\text{B}_2\text{C}_3\text{O}_{12}$, where A represents yttrium or a rare-earth ion (Gd, Nd, ...) in a dodecahedral position with coordination number eight; B and C are group III ions (Al, Sc, Ga, ...) at octahedral and tetrahedral sites, respectively. Transition metal ions can substitute both B^{3+} ions and Cr^{3+} ions, with a preference for sites that fit better to the ionic radii of the dopant. The yttrium-alumina-garnet (YAG) belongs to the cubic space group $\text{I}_{\text{a}3\text{d}}$ [96]. Figure 31 illustrates the crystal structure showing the different environments of both Al sites. Cr^{3+} and Cr^{4+} ions have been found to replace the B and the C positions, depending on their ionic charges. As expected, the trivalent chromium ion generally prefers the octahedral B-site. Cr^{4+} ions can be generated at these positions by mercury lamp (or gamma) irradiation of $\text{YAG}:\text{Cr}^{3+}$ crystals [96]. A more interesting case, however, concerns the substitution of the tetrahedral C-sites of YAG by laser-active Cr^{4+} ions. Suitable materials can be produced by growing crystals under oxidizing conditions, or by co-doping with divalent Ca or Mg ions for charge compensation [94]. Other oxide crystals containing d^2 -ions, such as Ti^{2+} , V^{3+} and Mn^{5+} , show also intense photoluminescence in the near-infrared. However no lasing action has been reported for these ions so far [97]. At present $\text{YAG}:\text{Cr}^{4+}$ appears as the best material for laser activity in the infrared region between 1.1 and 1.6 μm .

The electronic spectra of Cr, Ca-codoped YAG crystals have been attributed to transitions within tetrahedrally coordinated Cr^{4+} impurities [94, 98]. The d^2 electron configuration that represents the simplest non-Kramers system gives rise to three spin-allowed transitions from the $^3\text{A}_2$ ground state (electron configuration e_g^2), into $^3\text{T}_2(e_g t_{2g})$, $^3\text{T}_1^a(e_g t_{2g})$ and $^3\text{T}_1^b(t_{2g}^2)$. Each excitation causes a considerable shift in the equilibrium geometries, which usually results in broad unresolved bands. On the other hand, the lowest spin-forbidden transition $^3\text{A}_2 \rightarrow ^1\text{E}$ should exhibit sharp lines due to a pure spin-flip within the e_g^2 electron

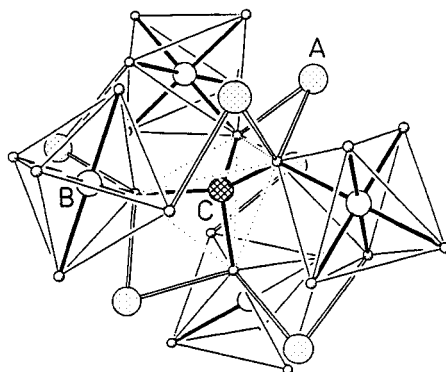
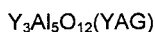


Fig. 31. Crystal structure of YAG showing octahedral (B) and tetrahedral (C) Al-sites [95]

configuration. The excitation spectrum, which was measured on the maximum of the near-infrared emission [99], is given in Fig. 32 together with a level diagram obtained from AOM calculations for the fourfold coordinated Cr^{4+} ion substituting C-positions of Al^{3+} in YAG. The model parameters involved can be obtained from fitting the band maxima by assuming tetrahedral symmetry. However, the symmetry of the Cr-substituted alumina sites is D_{2d} when the first coordination sphere, i.e. AlO_4 units, is considered. We have performed therefore energy level calculations by varying the related polar angle ϑ , $\Delta\vartheta > 0 (< 0)$, describing a compression (elongation) of the tetrahedron along the $\bar{S}_4$ -axis. Figure 32 shows that the approximation of a tetrahedral ligand field potential accounts only roughly for the electronic structure of Cr^{4+} in YAG, while distortion to a geometry near to that of the Al^{3+} -site (dashed line) is in accordance with the observed level splittings. Thus, the influence of the second coordination sphere, where also the charge-compensating bivalent counter ions (Ca^{2+}) may be located, should be small, giving rise only to marginal features in the optical spectra (see below).

At low temperatures, more complicated band structures are obtained and a partial mirror symmetry between absorption and emission is observed. Particularly the ${}^3A_2 \leftrightarrow {}^3T_2$, ${}^1E$ transitions in the near-infrared region exhibit a detailed fine structure, which is depicted in Fig. 33. The nature of the two prominent sharp lines located at 8975 cm^{-1} and 9279 cm^{-1} in the absorption spectrum has been controversially discussed [94, 98, 100]. Most likely, they belong to intraconfigurational spin-forbidden transitions into the split components of ${}^1E$, showing only very small changes between the equilibrium positions of the ground and excited states. This explains the sharpness of these bands as well as the fact that there is no clear indication of a pronounced vibrational progression upon these lines. Thus the situation resembles that of the spin-forbidden R -lines in Cr^{3+} doped alexandrite (see Sect. 4.2). The unexpected high intensity may arise from a mixing with close-lying spin-orbit components of ${}^3T_2$.

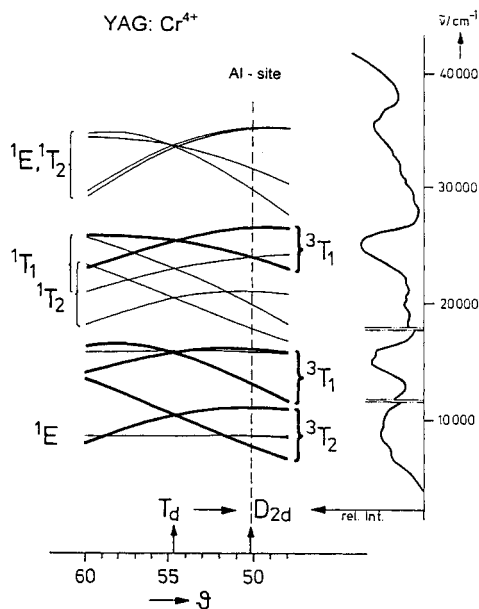


Fig. 32. Calculated level splittings for YAG:Cr⁴⁺ with corresponding transitions from the $^3A_2(T_d)$ ground state obtained from room temperature excitation spectra [93]. Model parameters: $e_\sigma = 8500$, $e_\pi = 700$, $B = 500$, $C = 6B$, $\zeta = 0$ (in cm^{-1})

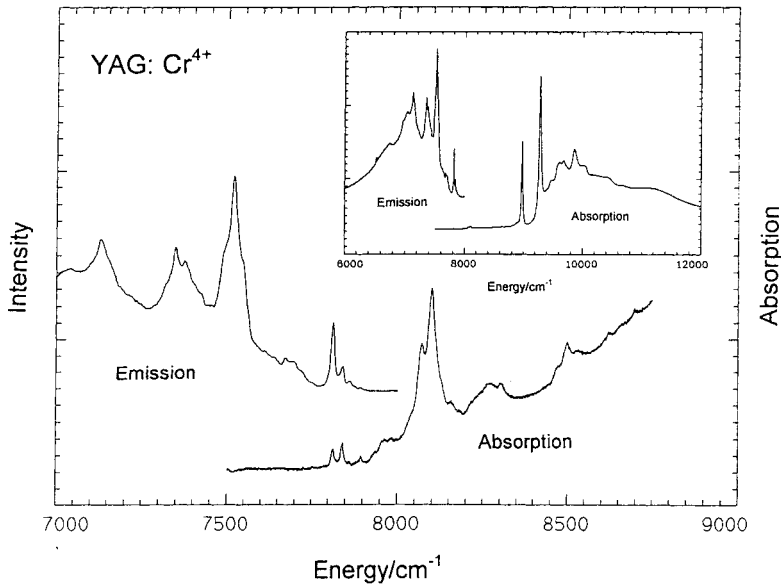


Fig. 33. High-resolution near-infrared absorption and emission bands of YAG:Cr⁴⁺ obtained at $T = 4.2$ K [93]

At the low-energy side of the absorption spectrum two weak bands appear at 7814 cm^{-1} and 7842 cm^{-1} which may be classified as the zero-phonon lines of the ${}^3B_1({}^3A_2) \rightarrow {}^3B_2({}^3T_2)$ transition. The zfs of the ground state, which was obtained from high-resolution Zeeman measurements to be 2 cm^{-1} [101], is optically not resolved, neither in absorption nor in emission. Thus, these two peaks are reasonably explained by an excited state splitting due to the effect of spin-orbit coupling. These lines have counterparts in the emission spectrum, separated by 28 cm^{-1} from each other and showing relative intensities in accord with Boltzmann populations. The band profile based on these origins exhibits a clear mirror symmetry, although the phonon energies are smaller in the absorption spectrum due to the weaker electron-phonon coupling in the excited state. The very weak lines located at 7864 cm^{-1} and 7893 cm^{-1} are probably due to a second Cr^{4+} center. Because the YAG host has to be co-doped with bivalent cations for charge compensation, other impurity sites (minorities) will appear and give rise to additional features in the optical spectra. On the other hand, the medium intense peaks located about 250 cm^{-1} higher in energy may be interpreted as vibronic sidebands due to promoting mode that makes ${}^3B_1(D_{2d}) \rightarrow {}^3B_2(D_{2d})$ transitions electric-dipole allowed. The broad band luminescence is assigned to ${}^3T_2(T_d) \rightarrow {}^3A_2(T_d)$ for the weak crystal field appearing in the Cr^{4+} -doped YAG lattices should give rise to broad band interconfigurational transitions.

Towards higher energy the absorption spectrum exhibits a strong band centered around 10000 cm^{-1} that shows some fine structure. The individual maxima are due to vibronic side-bands (accepting modes), which origin in the spectroscopically not identified zero-phonon lines of each component. From an analysis of the vibronic structure, the shift parameter Δ that describes the change in the excited state geometry with respect to the ground state is evaluated to be 2.4 which equals $S = 2.9$ for the respective Huang-Rhys factor [47]. This is a quite reasonable value according to the smaller geometry shifts in tetrahedrally coordinated systems, when compared, for example, with octahedral chromium(III) complexes which exhibit Δ values around 3 ($S = 4-5.5$) for interconfigurational transitions [47, 102]. The underlying accepting mode of 190 cm^{-1} has a clear counterpart in the Raman spectrum of Cr^{4+} -doped YAG crystals, where a broad band appears at 200 cm^{-1} [103]. Recently it was suggested on the basis of transition probabilities, polarization dependent measurements and piezospectroscopic results that this absorption band does not belong to ${}^3T_2$ but is a lower component of the ${}^3T_1$ state [98]. Following this assignment, the unresolved weaker band located around 12000 cm^{-1} must be attributed to the higher split-level of ${}^3T_2$ exhibiting a level crossing for the low symmetry components of ${}^3T_2$ and ${}^3T_1$. This is predicted also by our AOM calculations when a slightly more compressed CrO_4 tetrahedron is assumed (cf. Fig. 32). The other band assignments can also be rationalized by the AOM within a reasonable parametrization. Using $\zeta = 280\text{ cm}^{-1}$ and considering θ angles between 50° and 52° , the ground-state splitting, which is caused by the combined effects of low-symmetry and spin-orbit coupling, is calculated then to be in the range of $1-3\text{ wavenumbers}$ in accordance with the experimental value of 2 cm^{-1} (see above). The controversially discussed splitting of ${}^1E$ into Γ_1 and Γ_3 becomes about 250 cm^{-1} , and the spin-orbit components Γ_3 and Γ_5 of the emitting state ${}^3B_{1g}$ should be separated

by $30 - 50 \text{ cm}^{-1}$; both results are in remarkable good agreement with the experimental level splittings of 304 cm^{-1} and 28 cm^{-1} , respectively.

4.2

Cr^{3+} in the Spinel BeAl_2O_4 (Alexandrite)

The coordination behavior as well as the $d-d$ spectra of Cr^{3+} impurities are similar to those of chromium(III) complexes, where generally six nearest-neighbors (ligands) are the coordination sphere. This is due to the fact that sixfold coordination is favoured by the crystal field stabilization and the ionic radius of the Cr^{3+} ion. In the alexandrite lattice the chromium ions substitute the octahedrally coordinated alumina sites of chrysoberyl (undoped BeAl_2O_4). The space group is orthorhombic P_{nma} with four molecules per unit cell showing the Al^{3+} ions in the two non-equivalent sites that possess mirror (C_s) and inversion symmetry (C_i), respectively [104]. The chromium ions have been found to replace preferentially the alumina ions in the mirror sites (78%) and the rest going into the inversion sites [105]. We will briefly describe the detailed optical spectra which have been reported by Walling et al. [106, 107]. These authors observed that the spectral features are dominated by transitions associated with the mirror sites for two reasons: the inversion sites are less populated (see above), and the oscillator strengths of $d-d$ transitions should be much smaller for sites with inversion symmetry (parity rule). Their assignments of electronic origins are complicated, however, by the presence of the two non-equivalent sites. Moreover, highly doped crystals, which are needed for detecting weaker transitions in the C_i site chromium ions, exhibit additional lines due to exchanged coupled pairs of statistically neighbored Cr^{3+} ions. Therefore, a reliable analysis of the $d-d$ transitions in alexandrite is available only for the mirror-site chromium ions; the following discussion deals with this.

The polarized absorption spectra show both quartet bands due to $^4A_{2g} \rightarrow ^4T_{2g}$, $^4T_{1g}$ transitions split by about 1000 cm^{-1} . Intensity relations for different polarization directions are consistent with selection rules for C_s symmetry. The strong R lines, representing the zero-phonon transitions into the two Kramers' sublevels of ^2E_g , exhibit polarizations as expected for the mirror-site ions. The respective origins due to $^2T_{1g}$ have been identified by comparing the low-temperature emission spectrum with absorption spectra at different temperatures. The most intense sharp lines centered near 470 nm were associated with transitions into the split-levels of $^2T_{2g}$ that is the highest state with (t_{2g}^3) electron configuration. However, a more profound analysis due to the pronounced vibronic sideband structure has not been given so far.

Because of the comparable ionic radii of Cr^{3+} and Al^{3+} ions, a coordination geometry of the CrO_6 entity similar to the sixfold coordinated Al-sites is expected. Therefore, we can make use of structural data of the alumina polyhedra for the AOM calculations. Although we have not adopted the e_A parameters to the very different metal-oxygen distances, which vary between 183.5 pm and 198.9 pm at the mirror site [104], an acceptable fit of the spectroscopically determined transition energies could be obtained. Table 6 compares the experimental level scheme with the term energies calculated by using AOM parameters, which are

reasonable with respect to properties of the Cr-O bonding. However, the derived parameter set fails to reproduce the much larger splittings observed for $^4A_{2g}$ and ^2E_g in the slightly more distorted inversion-site Cr^{3+} ion. Alternative parameter sets, which better account for the splittings of the inversion-site ions, give poor results for the mirror-site ions. Neither by including additional parameters (by Trees' correction and/or orbital reduction) nor by considering distance-dependent AOM parameters was it possible to improve the calculations significantly. For example, an optimization of the radial e_λ parameters yields unreasonable R_{M-L} dependencies, e.g. $e_\sigma \sim R^{-1.2}$ for the Cr-O interaction (cf. Sect. 2.2.3).

On the other hand, a method to elucidate the d -electron energies is offered by the inspection of the geometric surroundings of the oxygen ligands. Fig. 34 illus-

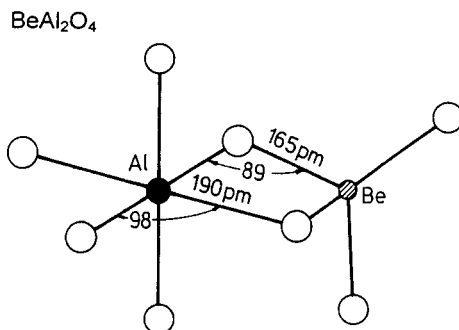


Fig. 34. Coordination geometry of surrounding oxygens in the alexandrite lattice for the Al(Cr) ion at the mirror site and for one neighboring Be ion

Table 6. Observed and calculated d -energy levels of Cr^{3+} in alexandrite (mirror site). Low symmetry split components are denoted by superscripts a, b, c. Optimized parameter values: $e_\sigma = 7205$, $e_\pi = 853$, $\zeta = 200$, $B = 660$, $C = 3270$; all data in cm^{-1} . ¹ From Refs. [105, 106]; ² uncertain assignment

Assignment	Observed ¹	Calculated	Deviation
$^4A_{2g}$ split	0.37	0.54	0.17
$^2E_g^a$	14734	14636	98
^2E_g split	34	36	2
$^2T_{1g}^a$	15324	15151	170
$^2T_{1g}^b - ^2T_{1g}^a$	147	115	32
$^2T_{1g}^c - ^2T_{1g}^b$	231	220	11
$^4T_{2g}^a$	16750	16900	150
$^4T_{2g}^b$	17600	17300	300
$^4T_{2g}^c$	17750	17550	200
$^2T_{2g}^a$	21234	21911	677
$^2T_{2g}^b - ^2T_{2g}^a$	166 ¹	240	74
$^2T_{2g}^c - ^2T_{2g}^a$	258 ²	484	226
$^4T_{1g}^a$	23700	23800	100
$^4T_{1g}^b$	23800	23900	100
$^4T_{1g}^c$	24200	24150	50

trates the relevant structural data showing an almost rectangular arrangement of the neighbored atoms Al(Cr)–O–Be. Within the picture of valence bond theory, the hybridization of the oxygen valence orbitals should result in a strong π -anisotropy of the Cr–O bonding. Extended Hückel MO calculations show these orbitals being misdirected from the Cr–O axis [108] as illustrated in Fig. 8, where the deviations from the M–L axis result from impacts due to the electronic structure of the metal-chelate entity. Thus we conclude that unsymmetrical π -interaction must be present in alexandrite (as in most other doped materials!), playing a crucial role in the calculations of sharp-line transitions. However, since the experimental data base is confined here to the splittings of $^4A_{2g}$ and ^2E_g , further conclusions cannot be drawn at present.

5 Perspectives

The examples given in this article show the angular overlap model to be a powerful tool for describing d^N -level splittings in transition metal complexes. This versatile model accounts not only for geometrical crystal field effects, but enables us also to characterize the metal-ligand bonding, as has been shown, for example, for anisotropic and/or extended π -interaction. There has been an animated discussion on corrections or extensions of this model as well as on the physical correctness of the transferability of AOM parameters. Limited experimental data, however, have often prevented more profound conclusions that might favor one approach. Likewise, although AOM parameters have been evaluated for a variety of complexes up to now, they were often not determined to an accuracy sufficient to reach clear-cut decisions in the controversies mentioned above. On the other hand, it must be recognized that there is at present no other approach available which accounts for d - d transitions like the AOM does. Moreover, the high accuracy of calculated level schemes is unique for a theoretical model that can treat such a wide variety of compounds. To the users we stress the point that reliable term energies can often be readily derived by applying geometric properties and reasonable (not fitted!) AOM parameters, and valuable spectrum-structure correlations can be demonstrated for the majority of assignment problems. Sometimes, values of e_λ have been estimated from molecular-orbital [32] or molecular-mechanics [109] calculations. However, a more sophisticated formalism is usually not required to calculate reasonable energy level schemes for widely different systems. By all means, an easily comprehensible underlying theory is an important premise for expanding the group of scientists who can make use of it. In this sense, a model that is too complicated is certainly not a good model.

Future applications of the AOM will include the analysis of the optical spectra and magnetic properties of transition metal ions located in polynuclear systems. Calculations on infinite structures (chains) have already been reported [110], and a parametrization scheme for the evaluation of orbital-exchange parameters in magnetically coupled dinuclear complexes was presented recently [111]. Another interesting aspect concerns the dynamic extension of the AOM which allows, for example, Jahn-Teller energies to be calculated [112, 113]. Finally, it should be

mentioned that this model has also been successfully applied to close-shell systems [114] and to f^N ions [9, 115, 116], which marked the beginning of the AOM story [12].

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Characterization of Excited Electronic and Vibronic States of Platinum Metal Compounds with Chelate Ligands by Highly Frequency-Resolved and Time-Resolved Spectra

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The lowest excited electronic states of triplet character and related vibronic properties are discussed in detail on the basis of highly frequency-resolved and time-resolved emission and excitation spectra of per-protonated, per-deuterated, and partially deuterated $[\text{Pt}(\text{bpy})_2]^{2+}$, $[\text{Rh}(\text{bpy})_3]^{3+}$, $[\text{Ru}(\text{bpy})_3]^{2+}$, and $[\text{Os}(\text{bpy})_3]^{2+}$. Emphasis is placed on the use of the enormous amount of information displayed in well-resolved vibrational satellite structures. For comparison, IR data and Raman spectra are also used. In addition, data are given for $[\text{Ru}(\text{bpz})_3]^{2+}$, $[\text{Ru}(\text{bpy})_2(\text{bpz})]^{2+}$, $[\text{Ru}(\text{bpdz})_3]^{2+}$, $[\text{Ru}(\text{bpy})_2(\text{bpdz})]^{2+}$, $[\text{Ru}(\text{i-biq})_2(\text{bpy})]^{2+}$, $\text{Pt}(\text{bhq})_2$, $\text{Pt}(\text{phpy})_2$, $\text{Pt}(\text{3-thpy})_2$, $\text{Pt}(\text{2-thpy})(\text{CO})(\text{Cl})$, $\text{Pt}(\text{2-thpy})_2$, $\text{Pt}(\text{qol})_2$, $\text{Pt}(\text{qtl})_2$. Trends and effects are also addressed, which are related to the amount of metal *d*-orbital mixing. In particular, we discuss the role of traps and sites in the context of high-resolution, site-selective, and line-narrowed spectra of chromophores doped into matrices; the interplay between states of ligand-centered $^3\pi\pi^*$ and $^3\text{MLCT}$ character; localization versus delocalization behavior; radiative decay properties; zero-field splittings; spin-lattice relaxations via direct and Orbach mechanisms; Arrhenius behavior after time delay; Franck-Condon activities and Huang-Rhys factors; Franck-Condon versus Herzberg Teller activities and tunability of these activities under high magnetic fields; isotope marking and deuteration effects; aggregate formation of $[\text{Ru}(\text{bpy})_3]^{2+}$; and radiationless energy transfer in neat $[\text{Ru}(\text{bpy})_3](\text{PF}_6)_2$. These effects are in part treated in detail, but the aim is to use easy-to-follow descriptions. In particular, it is emphasized throughout this review that chemical tunability opens fascinating possibilities for controlled variation of physical properties.

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1

Introduction

Compounds of the platinum metal group have been of interest for more than 100 years. They were used for analytical purposes and were impressive due to their deep colors and partly high-emission quantum yields [1–3]. More recently, within the last one or two decades, it has become apparent that these complexes exhibit an enormous potential for new applications due to their photophysical

and photochemical properties. For example, systems involving photo-redox processes for solar energy conversion [4–11], photovoltaic devices [12, 13], molecular photodiodes [14] or chemical synthesis [15], information storage systems [16], highly sensitive chemical sensors [17, 18] and biosensors [19–22], low-dimensional semiconductors with extreme tunabilities of optical transitions under high pressure [23, 24], and supramolecular systems with user-defined photophysical properties [25, 26] have already been explored or are under current investigation. All of these properties and possible applications are related to the characteristics of the lowest excited states. Therefore, many research groups concentrated their activities on the properties of these states (e.g., see [6, 9–11, 27–29] and references therein). However, in most cases, the information obtained, for example, from optical spectra, was not very detailed, since the spectra were relatively broad. Although one may often obtain a first insight into the system's properties using these broad spectra, it seems to be risky to use them to analyze a detailed behavior, like, changes in bonding properties or symmetries, charge redistributions, or a localization process upon excitation. Even an assignment to the HOMO-LUMO transition may be difficult. Moreover, at present, the current computational quantum chemical methods do not seem to be sufficiently powerful for a reliable computation of the lowest excited singlet and triplet states of platinum metal compounds. This is mainly due to the large number of electrons of the central metal ion and of the ligands involved. Fortunately, an experimental access based on spectroscopy may be very successful, if optical emission and absorption or excitation spectra are sufficiently detailed to resolve the regions of the electronic origins and the vibrational satellites. If this is achievable, variations of physical parameters like changes in temperature, external magnetic fields, high pressure, etc. will provide significant additional information. However, even these data may not be sufficient for a reliable understanding. Well-defined chemical alterations – in the sense of chemical tuning – can supply the information required to elucidate detailed electronic properties of the complexes.

It is the main subject of this review to investigate a series of complexes of the platinum metal group with protonated and deuterated 2,2'-bipyridine ligands. Figure 1 summarizes these compounds. For all selected compounds the efforts in obtaining highly resolved spectra were successful, due to the use of suitable matrices and the application of the powerful methods of laser and time-resolution spectroscopy.

In the scope of this study it is of special interest to analyze properties of the low-lying triplet states. These are largely ligand centered (LC) of $\pi\pi^*$ character with small metal d -orbital admixtures or, of metal-to-ligand charge transfer (MLCT) character, depending on their position in the sequence given in Fig. 1. In all cases the ground state is a singlet. Interestingly, the electronic transitions are always accompanied by very rich vibrational satellite structures. In particular, these structures carry important information about changes in binding properties or geometries in the excited states compared to the ground state. However, this information can only be extracted if the vibrational structures like Franck-Condon (FC) progressions are spectrally well resolved.

It is further intended to address a series of properties that are particularly related to the involvement of the central metal ion, e.g.,:

- Ligand-ligand coupling via the metal determines binding properties in the excited states and controls the interplay between localization and delocalization.
- Metal *d*-orbital contributions are important for radiative properties of the excited states and determine the zero-field splittings (zfs) of the triplets into sublevels via spin-orbit coupling (soc).
- A systematic analysis of the amount of zero-field splitting reveals relations between zfs and charge density distributions.
- The amount of zero-field splitting determines relaxation rates (spin-lattice relaxation, slr). These strongly affect the emission decay behavior.
- Different triplet sublevels of the same complex can be radiatively deactivated by different vibronic mechanisms, like Herzberg-Teller (HT) and/or Franck-Condon (FC) activity.

Moreover, a series of other interesting properties of importance for these compounds will also be analyzed, including:

- Formation of aggregates, which are observed for $[\text{Ru}(\text{bpy})_3]^{2+}$, if doped into a $[\text{Zn}(\text{bpy})_3](\text{ClO}_4)_2$ matrix, results in concentration-dependent spectroscopic features.
- Radiationless energy transfer between different crystallographic sites in $[\text{Ru}(\text{bpy})_3](\text{PF}_6)_2$ leads to specific emission decay properties.
- Effects of full and partial ligand deuteration are applied systematically to analyze electronic and vibrational properties, respectively, including IR and Raman activities, and are used for isotope marking.
- High magnetic fields may be applied for tuning of vibronic structures.
- Time-resolved emission spectroscopy allows access to the evolution in time of vibronic structures in emission.

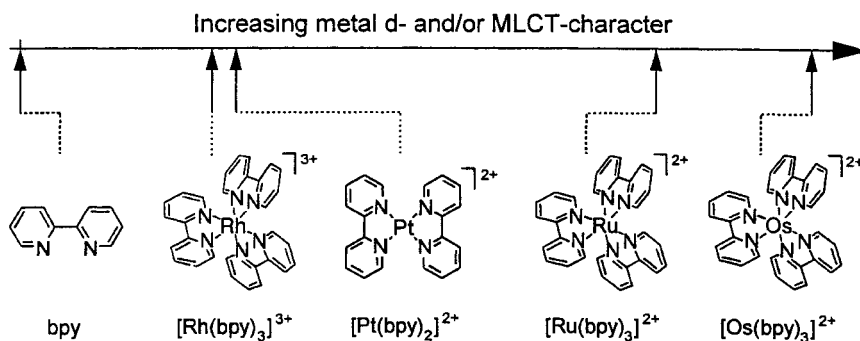


Fig. 1. The diagram symbolizes the increasing importance of metal *d*-orbital or metal-to-ligand charge transfer (MLCT) character in the lowest excited electronic triplet states. The transition metal complexes listed are investigated as per-protonated, per-deuterated, and partially deuterated compounds

As mentioned above, it is of utmost importance for all these detailed investigations to obtain highly resolved spectra. Often, this is possible at low temperature in crystalline materials. However, neat materials can present problems due to solid-state interactions like formation of energy bands or energy transfer and trapping combined with inhomogeneity effects. Thus, a doping of the chromophores into suitable inert host matrices at low concentration (to exclude a formation of pairs or clusters) can be very successful and thus has very often been applied (e.g., see [30–42]). Additionally, in suitable situations, low-energy traps of imperfect single crystals can be excited selectively by an exactly tuned laser. In this situation, it is also possible to investigate the properties of quasi-isolated chromophores (e.g., see [43, 44]).

2

[Pt(bpy)₂]²⁺

Planar Pt(II)-complexes have the tendency to crystallize in linear-chain structures with strong metal-metal interactions. Typical examples are the well-studied tetracyanoplatinates [23, 45–48] and compounds with α -diimine ligands, like Pt(bpy)Cl₂ [49–54], [Pt(bpy)₂][Pt(CN)₄] [52], and Pt(bpy)(CN)₂ [55]. On the other hand, structures are known in which the chromophores exhibit relatively small intermolecular interactions, like in [Pt(bpy)₂](ClO₄)₂ [56]. Therefore, this latter compound is a suitable candidate for studies in the sense of the present contribution.

Figure 2 shows the usual absorption and emission spectra of dissolved [Pt(bpy)₂]²⁺. These spectra correspond largely to those published elsewhere [56–59]. A comparison with the spectra of [Rh(bpy)₃]³⁺ (e.g., see [44, 60]) shows that both compounds exhibit a similar absorption. Thus, the observed transitions may be assigned similarly to singlet-singlet transitions of $\pi\pi^*$ character (cf. [56, 58] with [44]). A detailed analysis of the corresponding singlet states should certainly take into account a ligand-ligand interaction via a coupling of the very strong transition dipole moments, which may be described in a “Davydov” or a “molecular exciton” model [61]. Even if orbital overlap and admixture with *d*-orbitals of the metal ion are neglected, these dipole-dipole interactions are relatively strong for highly allowed electric dipole transitions (order of several 10² cm⁻¹ [62–65]). Consequently, the coupling results in singlet states belonging to the whole ligand system. For [Pt(bpy)₂]²⁺ this approach has not yet been carried out, but for the general procedures see [62–65].

The absorption spectrum of [Pt(bpy)₂]²⁺ shows a shoulder near 28000 cm⁻¹ ($\epsilon \approx 2-3 \cdot 10^3$ l mol⁻¹·cm⁻¹), which does not appear in the absorption of [Rh(bpy)₃]³⁺ (e.g., [44]). General considerations with respect to oxidation and reduction potentials [66], the energy of the corresponding transition, and the amount of allowedness of this shoulder (cf. also [51]) seem to allow one to assign it to a ¹MLCT transition.

The emitting state is assigned as a triplet due to the relatively long lifetime [58], but the orbital parentage has only very prudently been proposed as being of LC $\pi\pi^*$ character [56, 58, 67]. In this contribution it will be shown that this

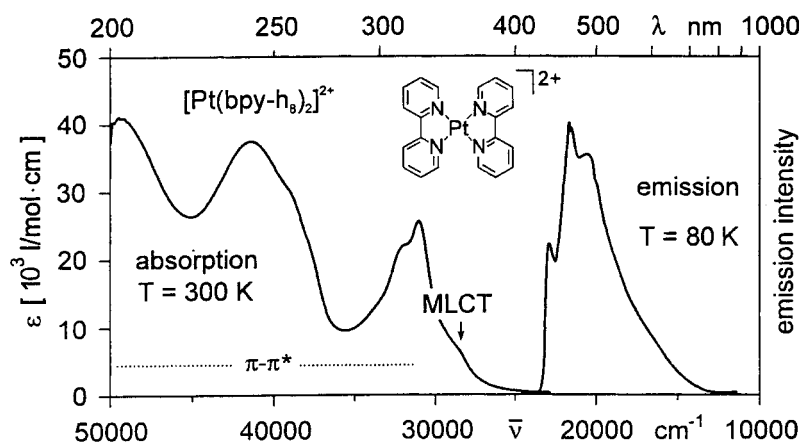


Fig. 2. Absorption and emission spectra of $[\text{Pt}(\text{bpy-h}_8)_2]^{2+}$ dissolved in DMF (excitation at 320 nm)

assignment is largely correct, though a small MLCT admixture is effective (see [44, 60], Sects. 2.2.1 and 2.2.2).

2.1

Suitable Matrices for $[\text{Pt}(\text{bpy})_2]^{2+}$

As outlined above, it is important to find an adequate matrix, if highly resolved spectra of a specific chromophore have to be registered. Hitherto, an inert matrix with a large free spectral range could not be found. However, in neat $[\text{Pt}(\text{bpy})_2](\text{ClO}_4)_2$ single crystals one finds defined $[\text{Pt}(\text{bpy})_2]^{2+}$ traps, which have their triplets several cm^{-1} below those of the majority of complexes and below the triplet exciton band. Such traps are often called X-traps. Thus, by exciting these traps selectively by an exactly tuned dye laser, one may obtain the desired emission spectrum. An important additional condition is that the sample temperature is low enough to prevent an energy migration, for example via thermally populated, energetically higher lying traps. Recently, a further matrix has been found [68] by applying a strategy that has already been well established for organic molecules (e.g., see [69–71]), but to our knowledge has not yet been used for transition metal complexes. This strategy is based on the fact that most deuterated compounds have higher transition energies than the corresponding protonated species. The reason for this important physical effect lies in different reductions of zero-point vibrational energies for the electronic ground state as compared to the excited state upon deuteration. One obtains a blue shift if the force constants are on average smaller in the electronically excited state (e.g., see [72–74]). Here, this effect is simply used to shift the lowest electronic transitions of the matrix to somewhat higher energy by applying $[\text{Pt}(\text{bpy-d}_8)_2](\text{ClO}_4)_2$ as a matrix for the $[\text{Pt}(\text{bpy-h}_8)_2]^{2+}$ chromophores. It is expected

that these chromophores replace matrix molecules without being strongly distorted.

Indeed, both procedures described above are successful. One obtains well-resolved emission spectra as shown in Fig. 3. However, both methods have the disadvantage of only relatively small free spectral ranges of $\approx 50 \text{ cm}^{-1}$ usable for excitation spectra. Moreover, the range of applicable sample temperatures is also restricted, since energy migration via thermally populated, higher lying traps may occur. This latter phenomenon is not discussed further in this contribution.

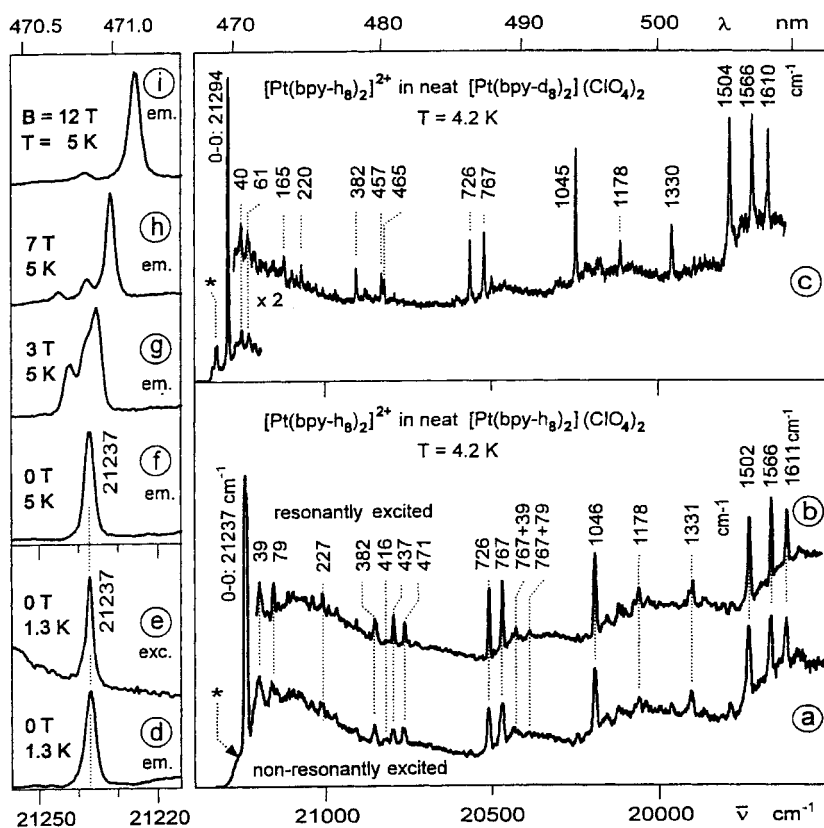


Fig. 3. *a, b* Emission spectra of $[\text{Pt}(\text{bpy-h}_8)_2]^{2+}$ in neat $[\text{Pt}(\text{bpy-h}_8)_2](\text{ClO}_4)_2$ at $T = 4.2 \text{ K}$ and *c* in neat $[\text{Pt}(\text{bpy-d}_8)_2](\text{ClO}_4)_2$. Concentration for *c* 1:200. Excitation at 457.9 nm ($\Delta 21840 \text{ cm}^{-1}$) for *a, c* and resonantly excited at the origin 21237 cm^{-1} for *b*. The energies of the vibrational satellites are specified relative to the respective electronic origin lines (0-0). The emission intensities for the different compounds are not comparable. The region of the electronic origins of $[\text{Pt}(\text{bpy-h}_8)_2]^{2+}$ in neat $[\text{Pt}(\text{bpy-h}_8)_2](\text{ClO}_4)_2$ is shown at an enlarged scale for $T = 1.3 \text{ K}$ and $B = 0 \text{ T}$ *d, e* and for $T = 5 \text{ K}$ for different magnetic fields (*f* to *i*). Excitation spectrum *e* is detected at $(21237 - 1611) \text{ cm}^{-1}$. The asterisks designate higher lying traps

2.2

Characterization of the Lowest Triplet of $[\text{Pt}(\text{bpy-h}_8)_2]^{2+}$

Figure 3 illustrates low-temperature emission and excitation spectra of $[\text{Pt}(\text{bpy-h}_8)_2]^{2+}$ in two different matrices [44, 68, 75]. These spectra are by a factor of about 300 better resolved than published to date (cf. [52, 58]; Fig. 2). The well-resolved electronic origins and the vibrational satellite structures reveal an enormous amount of information, which will be analyzed in the following sections.

2.2.1

Electronic Origin and Triplet Sublevels of $[\text{Pt}(\text{bpy-h}_8)_2]^{2+}$

The dominating line at $21\,237 \pm 1 \text{ cm}^{-1}$ in the emission spectrum of $[\text{Pt}(\text{bpy-h}_8)_2]^{2+}$ in neat $[\text{Pt}(\text{bpy-h}_8)_2](\text{ClO}_4)_2$ (Fig. 3 a) is assigned to the electronic origin of the singlet-triplet transition $S_0 \leftrightarrow T_1$ of the lowest trap observed. This transition can also be observed in absorption and excitation, where it lies exactly at the same energy (cf. Fig. 3 d with 3 e). This behavior is expected for an electronic origin. Moreover, this assignment as electronic origin is strongly supported by the vibrational satellite structure observed at the low energy side of this dominating line, since the vibrational energies fit only to this line (see Sect. 2.2.2).

The triplet state of $[\text{Pt}(\text{bpy})_2]^{2+}$ should exhibit a zero-field splitting (zfs) which, however, is not observable in the spectra registered with a spectral resolution of about 1 cm^{-1} . In principle, the resolution required is obtainable by methods of microwave double resonance, like ODMR spectroscopy. Such measurements were successfully accomplished, for example for $[\text{Rh}(\text{bpy})_3]^{3+}$ and related complexes, to resolve the zfs (e.g., see [76–80]), but these techniques have not yet been applied to $[\text{Pt}(\text{bpy})_2]^{2+}$. On the other hand, the three different triplet sublevels should display their individual properties in the time behavior of the emission at $T = 1.3 \text{ K}$. At this temperature, the relaxation processes between the triplet sublevels are usually very inefficient (for details see Sect. 3.4). Thus, one can observe the independent emissions from the three different sublevels $|I\rangle$, $|II\rangle$, and $|III\rangle$. The corresponding decay components observed at zero magnetic field and at $T = 1.3 \text{ K}$ are $\tau_I = 50 \pm 1 \mu\text{s}$, $\tau_{II} = 8 \pm 0.5 \mu\text{s}$, and $\tau_{III} = 3 \pm 0.3 \mu\text{s}$ (see Fig. 4; Table 1). The sequence of these levels, however, have not yet been determined. Presumably, the zfs is only of the order of 0.1 cm^{-1} ($\triangleq 3 \text{ GHz}$). For completeness it is mentioned that at higher temperature (e.g., at $T = 10 \text{ K}$) the individual decay components are no longer observable, since spin-lattice relaxation (slr) processes become very efficient with increasing temperature. This leads to an average value for the emission decay, τ_{av} , which can be calculated according to the expression given in Table 1. The corresponding mono-exponential emission decay time, τ_{exp} , could not be determined due to energy transfer processes at higher temperature for the $[\text{Pt}(\text{bpy})_2]^{2+}$ chromophores. However, for the corresponding $[\text{Rh}(\text{bpy})_3]^{3+}$, given in Table 1 for comparison, both values, τ_{av} and τ_{exp} , could be determined [60]. The very good agreement (within the experimental error of $\pm 10\%$), already obtained for $T \gtrsim 5 \text{ K}$, shows that the fast thermalization occurs at relatively low temperatures.

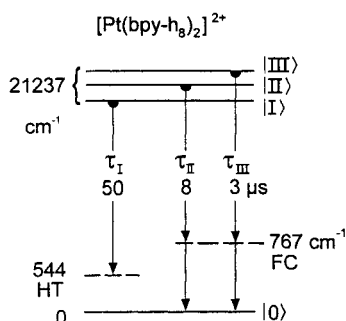


Fig. 4. Energy level scheme for the triplet sublevels and decay times for $T = 1.3$ K of $[\text{Pt}(\text{bpy-h}_8)_2]^{2+}$ in neat $[\text{Pt}(\text{bpy-h}_8)_2](\text{ClO}_4)_2$. The radiative deactivation from $|I\rangle$ is mainly vibronically induced by Herzberg-Teller (HT) active modes (e.g., 544 cm^{-1} vibration) [44], while the radiative deactivations from $|II\rangle$ and $|III\rangle$ to the ground state occur mainly at the electronic origins, which are accompanied by Franck-Condon (FC) active modes (e.g., 767 cm^{-1} mode). See also Table 2 and Section 2.2.2)

Table 1. Emission decay times (μs) of the lowest triplet states of $[\text{Pt}(\text{bpy})_2]^{2+}$ and $[\text{Rh}(\text{bpy})_3]^{3+}$ [60, 68]

Compounds	Emission decay components ^a				
	τ_I	τ_{II}	τ_{III}	τ_{av} ^b	τ_{exp} ^c
$[\text{Pt}(\text{bpy-h}_8)_2]^{2+}$ ^d	50	8	3	6.3	— ^f
$[\text{Pt}(\text{bpy-h}_8)(\text{bpy-d}_8)]^{2+}$ ^d	43	13	3	6.9	— ^f
$[\text{Pt}(\text{bpy-d}_8)_2]^{2+}$ ^d	50	8	2	4.7	— ^f
$[\text{Rh}(\text{bpy-h}_8)_3]^{3+}$ ^e	$4.5 \cdot 10^3$	$1.35 \cdot 10^3$	$0.65 \cdot 10^3$	$1.2 \cdot 10^3$	$1.4 \cdot 10^3$
$[\text{Rh}(\text{bpy-h}_8)_2(\text{bpy-d}_8)]^{3+}$ ^e	$6.3 \cdot 10^3$	$1.4 \cdot 10^3$	$0.65 \cdot 10^3$	$1.24 \cdot 10^3$	$1.4 \cdot 10^3$
$[\text{Rh}(\text{bpy-d}_8)_3]^{3+}$ ^e	$13.6 \cdot 10^3$	$1.55 \cdot 10^3$	$0.7 \cdot 10^3$	$1.4 \cdot 10^3$	$1.6 \cdot 10^3$

^a Emission decay of the lowest triplet sublevels $|I\rangle$, $|II\rangle$, and $|III\rangle$ at $T = 1.3$ K.

^b Calculated average decay time according to $\tau_{av} = 3(1/\tau_I + 1/\tau_{II} + 1/\tau_{III})^{-1}$ (cf. [60, 213, 216]).

^c Measured decay time at $T = 5$ K.

^d Investigated as traps in the respective $(\text{ClO}_4)^-$ salt.

^e Doped into $[\text{Zn}(\text{bpy-h}_8)_3](\text{ClO}_4)_2$.

^f Due to energy transfer processes at higher temperature ($T > 3$ K) between different traps, this value could not be determined.

The smallness of the zfs values reveals that the admixture of metal d -character to the triplet state(s) is very small. Otherwise, one would expect that the large spin-orbit coupling due to the $5d$ -orbitals of Pt(II) resulted in significantly larger values as found, for example, for $[\text{Ru}(\text{bpy})_3]^{2+}$ (Sect. 3.3.1) and $\text{Pt}(\text{2-thpy})_2$ (e.g., cf. [44, 81, 83]). Consequently, the smallness of zfs provides strong support for the assignment of T_1 as a ligand-centered transition being mainly of $\pi\pi^*$ character. Further support for this classification will result from an inspection of the vibrational satellite structures in the emission spectra, in

particular, since the vibrational satellites corresponding to *ligand* modes strongly dominate (see Sect. 2.2.2).

However, even the longest decay component of $\tau_f = 50 \mu\text{s}$ is relatively short compared to the decay times measured for the uncoordinated bpy (4 s, 0.77 s, and 0.38 s at $T = 1.2 \text{ K}$ [82]). From this behavior and the fact that the triplet can be directly exited, it is concluded that the triplet sublevels contain at least some admixture of higher lying singlet states, due to spin-orbit coupling induced by platinum. Further support for this result comes from an analysis of the vibrational satellite structures, in particular, from the weak occurrence of vibrational *metal-ligand* (M-L) satellites in the emission spectra (Sect. 2.3).

Furthermore, the three triplet sublevels manifest themselves by applying high magnetic fields, which lead to Zeeman splittings into three components (Fig. 3 f–i). For example, at $B = 7 \text{ T}$ the total splitting is $\approx 14 \text{ cm}^{-1}$. This value corresponds to a g -value of two, being typical for spin triplets. At $B = 12 \text{ T}$ (Fig. 3 i), the high energy Zeeman component is difficult to register, since at the temperature applied ($T = 5 \text{ K}$) this component is nearly frozen out. The Zeeman splitting is – as expected – linear in B for the high fields applied (e.g., cf. [32, 33]).

The electronic origin at $21\,237 \text{ cm}^{-1}$ corresponds to the lowest lying and well-resolvable X-trap of $[\text{Pt}(\text{bpy-h}_8)_2]^{2+}$ in $[\text{Pt}(\text{bpy-h}_8)_2](\text{ClO}_4)_2$. Note that a series of further traps are observed at $21\,266$, $21\,270$, $21\,278$, and $21\,289 \text{ cm}^{-1}$ (not all reproduced here, but see [68]).

In the per-deuterated $[\text{Pt}(\text{bpy-d}_8)_2](\text{ClO}_4)_2$ matrix, the electronic origin of the $S_0 \leftrightarrow T_1$ transition of doped $[\text{Pt}(\text{bpy-h}_8)_2]^{2+}$ is found at $(21\,294 \pm 1) \text{ cm}^{-1}$ (Fig. 3 c). In this matrix the electronic origin of the $[\text{Pt}(\text{bpy-h}_8)_2]^{2+}$ chromophore (representing a Y-trap) lies 48 cm^{-1} below the lowest trap of the neat per-deuterated material found at $21\,342 \text{ cm}^{-1}$. The vibrational structure observed supports the assignment of this origin (see below).

2.2.2

Vibrational and Phonon Satellite Structure of $[\text{Pt}(\text{bpy-h}_8)_2]^{2+}$

The very rich structure, which occurs as satellite pattern to the electronic origin in the emission spectrum, reveals a considerable amount of information about properties of the electronic states involved. Figure 3 a shows the nonselectively excited spectrum, while Fig. 3 b reproduces the resonantly excited one of the low-lying $[\text{Pt}(\text{bpy-h}_8)_2]^{2+}$ trap in neat $[\text{Pt}(\text{bpy-h}_8)_2](\text{ClO}_4)_2$. Due to the selective excitation, the spectrum in Fig. 3 b is line-narrowed and therefore better resolved than the one shown in Fig. 3 a.

The observed satellites are assigned to transitions into vibrational levels of the ground state. A comparison of these vibrational energies to Raman data shows excellent agreement and thus confirms further the assignment of the electronic origin given in Section 2.2.1 (Table 2; Fig. 5). The satellites, which appear in the low-energy range up to about 100 cm^{-1} relative to the electronic origin, are assigned to lattice modes or localized phonons, which may mix with low-energy vibrational modes of the complex (e.g., see [84]). A normal coordinate analysis is not yet available, nevertheless, a series of important assignments can still be given. The vibrational satellite structure is distinctly determined by ligand

Table 2. Vibrational satellites [cm^{-1}] in the emission from the lowest excited triplet state(s) of $[\text{Pt}(\text{bpy}-\text{h}_8)_2]^{2+}$ and $[\text{Pt}(\text{bpy}-\text{d}_8)_2]^{2+}$ as traps in neat perchlorate salts compared to Raman data

$[\text{Pt}(\text{bpy}-\text{h}_8)_2]^{2+}$		$[\text{Pt}(\text{bpy}-\text{d}_8)_2]^{2+}$		Assignments
Emission T = 4.2 K 0-0 ($T_1 \rightarrow S_0$) ^b : (21237 $\pm$ 1) cm^{-1}	Raman ^a T = 300 K	Emission T = 1.3 K 0-0 ($T_1 \rightarrow S_0$) ^b : (21787 $\pm$ 1) cm^{-1}	Raman ^a T = 300 K	
24		26		Lattice mode ^c
39		48		Lattice mode
59				Lattice mode
64				Lattice mode
79		72		Lattice mode
94		100		Lattice mode
121		114		
137				
		139		
165				
196		187		
227	226	216		
245				
267		256		
327		316		
382	382	368	368	L mode ^d
416		384		M-L mode ^e
437		432		M-L mode
471				M-L mode
544				HT ^f
565				HT
726	727	669		FC ^g , L mode
767	767	719	721	FC, L mode
		804		
806				767 + 39
848				767 + 79
		865		
994		972		
1046	1045	1030	1027	FC, L mode
1083				1046 + 39
1125		1103		
1163		1150		
1178				
1205				
1278	1275	1270		L mode
1331	1332	1329		FC, L mode
1370				1331 + 39
1425		1405		

^a Powder spectra, excitation at 1064 nm.^b Electronic origin corresponding to the three triplet sublevels |I>, |II>, and |III>.^c In this table, the lattice modes of the different compounds are not correlated.^d L mode: ligand mode.^e M-L: metal-ligand mode.^f HT: Herzberg-Teller active mode [44].^g FC: Franck-Condon active mode.

Table 2 (continued)

[Pt(bpy-h ₈) ₂] ²⁺		[Pt(bpy-d ₈) ₂] ²⁺		Assignments
Emission T = 4.2 K 0-0 (T ₁ → S ₀) ^b : (21237 ± 1) cm ⁻¹	Raman ^a T = 300 K	Emission T = 1.3 K 0-0 (T ₁ → S ₀) ^b : (21787 ± 1) cm ⁻¹	Raman ^a T = 300 K	
1451				2 × 726
1502	1503	1442	1441	FC, L mode
1535				2 × 767
1566	1566	1534	1534	FC, L mode
1611	1611	1576	1576	FC, L mode
1771				
1813				767 + 1046
		1897		865 + 1030
1945				767 + 1178
2004				726 + 1278
2088		2059		2 × 1046 2 × 1030
2226				1046 + 1178
2268		2163		767 + 1502 719 + 1442
2292				726 + 1566
2333		2254		767 + 1566 719 + 1536
2377		2296		767 + 1611 719 + 1578
		2307		867 + 1442
		2314		3 × 719
		2401		867 + 1536
		2442		867 + 1578
2547		2476		1046 + 1502 1030 + 1442
2610		2568		1046 + 1566 1030 + 1536
2656		2607		1046 + 1611 1030 + 1578
3000		2884		2 × 1502 2 × 1442
		2977		1442 + 1536
		3018		1442 + 1578
3132		3071		2 × 1566 2 × 1536
		3112		1536 + 1578
3221		3150		2 × 1611 2 × 1578

(L) modes beside, the weak phonon satellites and some weak vibrational satellites of metal-ligand (M-L) character. The M-L modes are clearly discernible from the L modes by comparing the spectra of partially deuterated [Pt(bpy-h₈)(bpy-d₈)]²⁺ with those of per-protonated and per-deuterated compounds (see Sect. 2.3). In particular, the satellites of [Pt(bpy-h₈)₂]²⁺ at 416, 437, and 471 cm⁻¹ are identified as M-L modes (Table 2). It is emphasized that their intensities relative to the intensities of other vibrational satellites are weak. This behavior displays the weak metal contribution of the wavefunctions of the electronic states involved in the corresponding transition (see also Sect. 5; [44, 60, 83, 85]).

Dominance of Radiative Deactivation by Franck-Condon Active Modes. The observed vibrational satellites can be induced by different mechanisms. In particular, they may result from Franck-Condon (FC) and Herzberg-Teller (HT)

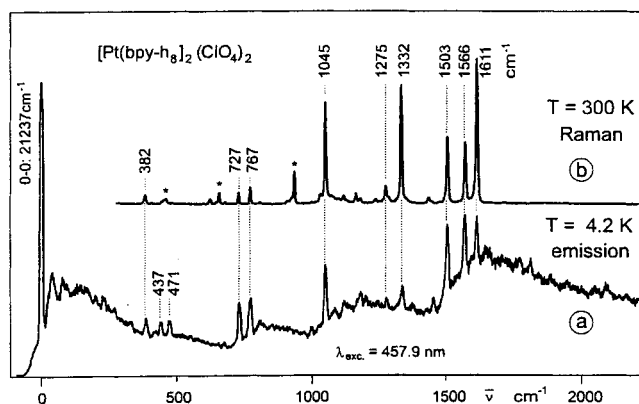


Fig. 5. a Emission spectrum at $T = 4.2$ K $[\text{Pt}(\text{bpy-h}_8)_2]^{2+}$ in neat $[\text{Pt}(\text{bpy-h}_8)_2](\text{ClO}_4)_2$ (excitation at 457.9 nm). The energies of the vibrational satellites are specified relative to the electronic origin line (0-0). b Raman spectrum at $T = 300$ K of $[\text{Pt}(\text{bpy-h}_8)_2](\text{ClO}_4)_2$ powder (excitation at 1064 nm). The asterisks mark $(\text{ClO}_4)^-$ Raman lines (cf. [109])

couplings (for theoretical background see, e.g., [86–91]; Sects. 4.1.3 and 4.1.4). It would be of great interest to obtain a detailed classification in this respect, since this would allow us to characterize the excited states further, as done, for example, for $[\text{Ru}(\text{bpy})_3]^{2+}$ (Sect. 3.3.2), $[\text{Os}(\text{bpy})_3]^{2+}$ (Sect. 4.1.3; [92]), and $\text{Pt}(\text{2-thpy})_2$ [93]. Although for $[\text{Pt}(\text{bpy-h}_8)_2]^{2+}$ such a detailed classification is not yet available, it could be shown by time-resolved emission spectroscopy that several vibrational modes may be assigned to be HT-active with respect to the long-lived state $|I\rangle$ (e.g., 544 and 565 cm^{-1} satellites; see Fig. 4; [44]). On the other hand, a series of FC modes is clearly observable in the emission spectrum. These modes are easily identified if one finds the 0–1 and 0–2 members of a vibrational progression. Indeed, this is the case, for example, for the 726, 767, 1046, 1331, 1502, 1566, and 1611 cm^{-1} satellites (see also Table 2). All these modes are also found as intense Raman lines (Fig. 5). This tells us that the main radiative deactivation occurs via the electronic origin and vibrational FC-active modes (Fig. 4). However, the emission spectrum clearly reveals that even the most prominent progressions may be regarded as relatively weak. (The corresponding energy range is not reproduced in Fig. 3, but see Fig. 9b in Section 2.5). This means that the Huang-Rhys factor S , which characterizes the strength of a progression, is small. This Huang-Rhys factor may be determined from the intensity distribution of the members of the progressions using the expression $S = \nu(I_\nu/I_{\nu-1})$, with I_ν being the intensity of one member of a specific progression and ν its vibrational quantum number [95–97]; (cf. also [94]). S is related to the Franck-Condon factor of the respective vibrational mode. The larger S is, the larger is the shift of the nuclear equilibrium positions of the potential hypersurfaces between ground and excited state for that specific vibrational mode. These progression-forming Franck-Condon modes are totally symmetric. For all progressions observed for $[\text{Pt}(\text{bpy-h}_8)_2]^{2+}$ one obtains $S \leq S_{\max} \approx 0.3$. The cor-

responding modes are characterized by FC in Table 2. Presumably, all other stronger satellites (see Fig. 3) also represent FC modes that, however, exhibit smaller S values. Nearly the same value of 0.3 has also been found for the uncoordinated bpy [83, 98]. Compared to the known range for S values of other compounds – values up to ten have been reported (e.g., see [94–97, 99, 100]) – it follows that a maximum value of 0.3 of the Huang-Rhys factor S must be regarded as small. This implies similar nuclear equilibrium positions of the triplet state(s) and the ground state for $[\text{Pt}(\text{bpy-h}_8)_2]^{2+}$.

All prominent vibrational satellites are accompanied by phonon satellites. For example, combinations of the 767 cm^{-1} mode with the 39 or 79 cm^{-1} lattice modes are clearly discernible for $[\text{Pt}(\text{bpy-h}_8)_2]^{2+}$ (Fig. 3b; Table 2). However, in most cases, these phonon satellites are smeared out to bands. These bands are in part responsible for the unresolved background observed in the emission spectra. As a consequence, one finds unusual structures when several vibrational satellites with their respective phonon side bands overlap (e.g., the range of the 1502 , 1566 , and 1611 cm^{-1} peaks in Fig. 3b). In low-resolution spectra, such a structure will appear as *one* dominating peak and might be taken as one member of a fictitious progression (e.g., see Fig. 2 and the examples given in [74, 101]).

Further, all clearly discernible peaks in the emission spectra at energies greater than about 1650 cm^{-1} are assigned to combinations of prominent vibrational modes or to higher members of very weak Franck-Condon progressions (Table 2). The occurrence of combinations with weak intensities in the vibrational satellite structures indicates small shifts along different normal coordinates (e.g., see [100]).

The vibrational satellite structure of $[\text{Pt}(\text{bpy-h}_8)_2]^{2+}$ doped into $[\text{Pt}(\text{bpy-d}_8)_2](\text{ClO}_4)_2$ (as Y-trap) is, as expected, similar to the structure of $[\text{Pt}(\text{bpy-h}_8)_2]^{2+}$ (as X-trap) in neat $[\text{Pt}(\text{bpy-h}_8)_2](\text{ClO}_4)_2$ apart from shifts of phonon energies and M-L modes (cf. Fig. 3b, c and Table 2). Thus, due to the perfect fits of the vibrational energies, one has direct confirmation for the assignment of the electronic origin of the Y-trap which lies at $21\,294\text{ cm}^{-1}$. Interestingly, a comparison of Fig. 3a with c shows that the intensities of the phonon satellites relative to those of the electronic origins or vibrational satellites are weaker for $[\text{Pt}(\text{bpy-h}_8)_2]^{2+}$ in the per-deuterated matrix compared to the per-protonated one. This indicates a lower coupling strength to lattice modes. Presumably, this effect can be used in future studies to obtain even better resolved emission spectra and may be of importance for the rates of spin-lattice relaxation between the three triplet sub-levels (e.g., see [84]; Sect. 3.4).

2.3

Emission Properties of $[\text{Pt}(\text{bpy-d}_8)_2]^{2+}$ and $[\text{Pt}(\text{bpy-h}_8)(\text{bpy-d}_8)]^{2+}$ Compared to $[\text{Pt}(\text{bpy-h}_8)_2]^{2+}$

The emission properties change in a characteristic way when the chromophores are deuterated. Moreover, if specific positions or spatial regions of the compound are isotopically designated, one may even obtain information about the spatial spread of the wave functions involved in the emission process. Similar investigations have already been carried out for organic molecules [74, 102, 103]

as well as for transition metal complexes [44, 60, 74, 85, 104]. Here, we focus on $[\text{Pt}(\text{bpy-d}_8)_2]^{2+}$ and $[\text{Pt}(\text{bpy-h}_8)(\text{bpy-d}_8)]^{2+}$. They are investigated as traps (X-traps) found in the neat ClO_4^- salts. Fortunately, it is also possible to obtain highly resolved spectra for the deuterated compounds, as shown in Fig. 6.

First, changes due to per-deuteration are discussed. The lowest triplet origin of $[\text{Pt}(\text{bpy-d}_8)_2]^{2+}$ is found at 21787 cm^{-1} (Fig. 6a). Usually, a deuteration leads to a shift of electronic transitions to higher energies, if the force constants of the excited state vibrational modes are on average lower than those of the ground state. This shift is connected to different reductions of the zero-point vibrational energies upon deuteration [72–74]. However, the value of the blue shift found for $[\text{Pt}(\text{bpy-d}_8)_2]^{2+}$ compared to $[\text{Pt}(\text{bpy-h}_8)_2]^{2+}$ of 550 cm^{-1} is much too large to be ascribed to such a deuteration effect, as can be concluded from a corresponding scale for transition metal complexes developed in ([74]; see also Table 12). For example, the value found for $[\text{Rh}(\text{bpy})_3]^{3+}$ [60] with similar emission properties is 61 cm^{-1} (cf. Fig. 9). Thus, one would expect to find a similar value also

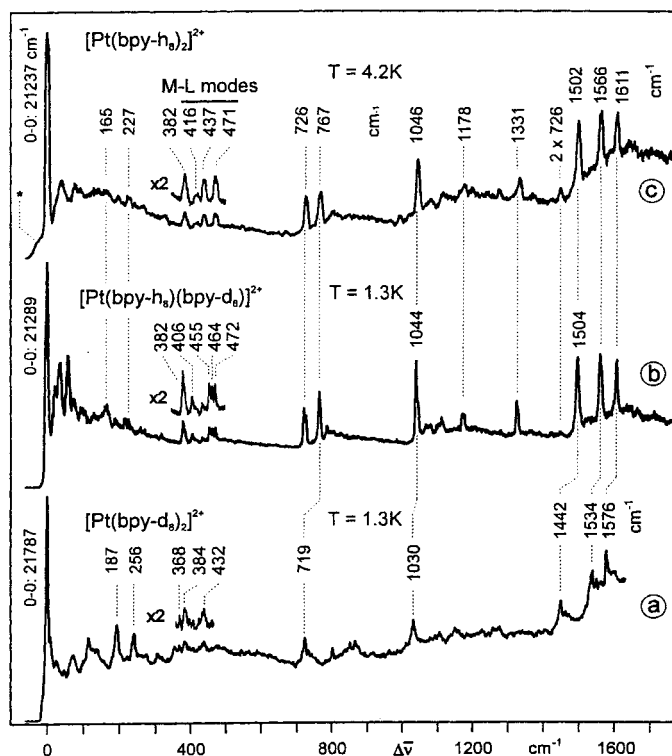


Fig. 6. Emission spectra of a $[\text{Pt}(\text{bpy-d}_8)_2]^{2+}$; b $[\text{Pt}(\text{bpy-h}_8)(\text{bpy-d}_8)]^{2+}$; c $[\text{Pt}(\text{bpy-h}_8)_2]^{2+}$ (a, b excitation at 457.9 nm ; c at 454.7 nm). a–c result from low-lying traps (X-traps) in the respective perchlorate salts. For a better comparison, the energies of the electronic origins are set to zero on a wavenumber scale. The energies of the vibrational satellites are specified relative to the respective electronic 0-0 lines (origins). The region of metal-ligand (M-L) vibrational modes is specified. The asterisk marks a higher lying trap

for $[\text{Pt}(\text{bpy})_2]^{2+}$. Indeed, there are indications that it lies near 50 cm^{-1} [68]. Therefore, the relatively large shift of the electronic origin displayed in Fig. 6 appears to be mainly a matrix/trap effect.

Beside the shift of the electronic transition energy, the emission properties of $[\text{Pt}(\text{bpy-d}_8)_2]^{2+}$ exhibit further changes with respect to $[\text{Pt}(\text{bpy-h}_8)_2]^{2+}$. Similar effects are well known and are usually observed upon deuteration of emitting centers (e.g., see [37, 44, 60, 74, 85, 102–107]). In particular, (1) all vibrational energies are red-shifted. A correlation of several vibrational modes of both compounds is carried out in Fig. 6 and Table 2 using in part the information worked out for $[\text{Rh}(\text{bpy})_3]^{3+}$, for example, to correlate the $719\text{ cm}^{-1}/767\text{ cm}^{-1}$ modes (cf. [60]). (2) The intensity distribution of the vibrational satellite structure is changed to some extent due to alterations of the forms (PEDs) of the normal coordinates (cf. [106]).

Interestingly, the emission spectrum of $[\text{Pt}(\text{bpy-h}_8)(\text{bpy-d}_8)]^{2+}$ (Fig. 6b) is nearly identical to that of the per-protonated complex (Fig. 6c), apart from some phonon satellites and M-L vibrational satellites. However, the spectrum is totally different if compared with that of the per-deuterated compound (Fig. 6a). None of the vibrational satellites observed in the emission spectrum of $[\text{Pt}(\text{bpy-d}_8)_2]^{2+}$ is found in the spectrum of the partially deuterated compound. This shows that the (bpy-d_8) ligand is *not* involved in the process of emission (for further details concerning this conclusion, see Sects. 3.5, 4.2.2; [44, 60, 85, 91, 104]). Consequently, in $[\text{Pt}(\text{bpy-h}_8)(\text{bpy-d}_8)]^{2+}$, the lowest excited state (of the specific trap studied) is clearly confined to the protonated ligand. This behavior fits well to the classification of the corresponding transition as being ligand-centered of $\pi\pi^*$ character as had already been proposed in [56, 58].

Vice versa, the *nonoccurrence* of any high-energy vibrational satellite ($\geq 600\text{ cm}^{-1}$) in the emission spectrum of $[\text{Pt}(\text{bpy-h}_8)(\text{bpy-d}_8)]^{2+}$ corresponding to internal-ligand modes of (bpy-d_8) character (Fig. 6b). Without allows us to rule out a remarkable coupling of these vibrations through space, for example, by the mechanism of dipole-dipole coupling [111] or via the heavy platinum metal. This behavior is in agreement with observations described for many other compounds [91, 106, 111–114]. However, the situation is different for the low-energy M-L vibrations, which exhibit a clearly observable vibrational coupling, since the movements of the metal are experienced by both ligands. Consequently, the energies of the M-L vibrational satellites are also distinctly altered with the exchange of a (bpy-h_8) to the heavier (bpy-d_8) ligand. It is stressed that such behavior is not observed in the energy range of the ligand modes. For these modes, the metal represents a heavy buffer (cf. Fig. 6b, c). Without having a normal coordinate analysis available, a more detailed assignment of these vibrations is not reasonable.

It is pointed out that the situation with respect to the appearance of vibrational satellites of the different ligands is distinctly *dissimilar* for the partially deuterated $[\text{Ru}(\text{bpy})_3]^{2+}$ [44, 85, 108] and $[\text{Os}(\text{bpy})_3]^{2+}$ [104] complexes, where the lowest excited states have to be classified in a delocalized description (details are discussed in Sects. 3.5 and 4.2.2).

For completeness, it is further added that the information available is not sufficient to decide whether the excitation in a *homoleptic* $[\text{Pt}(\text{bpy})_2]^{2+}$ complex is

also confined to a single ligand – as has been proposed for $[\text{Rh}(\text{bpy})_3]^{3+}$ on the basis of ODMR investigations [77, 110] – or whether both ligands are involved. This latter description would hold if the electronic interaction energy between the ligands were larger (for the triplet states studied) than any distortion energy experienced by one of the ligands at the specific matrix site (see also discussion in Sect. 3.8).

Raman Spectra. Raman spectra of the three neat materials are presented in Fig. 7. The main scattering intensities are found for vibrational ligand modes. It is immediately seen that the Raman spectrum of $[\text{Pt}(\text{bpy-h}_8)(\text{bpy-d}_8)]^{2+}$ (Fig. 7b), showing vibrational lines corresponding to both ligands, may be interpreted as a superposition of Raman spectra of the individual ligands. Interestingly, the Raman scattering intensities of the deuterated ligand are significantly higher than those of the protonated one. This phenomenon does not seem to be unusual (e.g., see [115]), but here it has been investigated for the first time in the same compound, where the intensities are intrinsically normalized.

It is further very instructive to compare the Raman and the emission spectra of $[\text{Pt}(\text{bpy-d}_8)(\text{bpy-h}_8)]^{2+}$ in the same diagram (Fig. 8). This comparison demonstrates clearly the different kinds of information carried in the two spectra. Interestingly, the M-L modes have (nearly) no Raman scattering intensities,

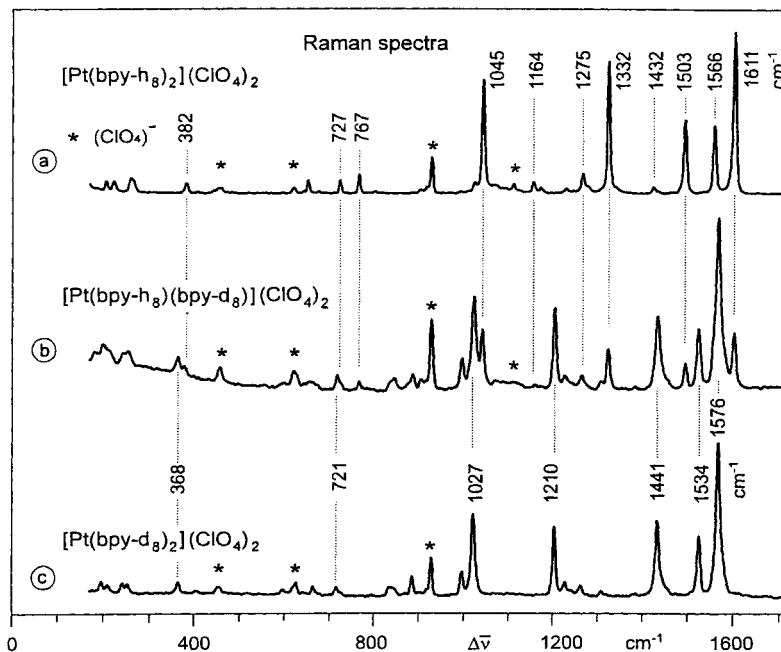


Fig. 7. Raman spectra at $T = 300$ K of a $[\text{Pt}(\text{bpy-h}_8)_2](\text{ClO}_4)_2$; b $[\text{Pt}(\text{bpy-h}_8)(\text{bpy-d}_8)](\text{ClO}_4)_2$; and c $[\text{Pt}(\text{bpy-d}_8)_2](\text{ClO}_4)_2$ powders (excitation at 1064 nm). The asterisks mark Raman active $(\text{ClO}_4)^-$ vibrations (cf. [109])

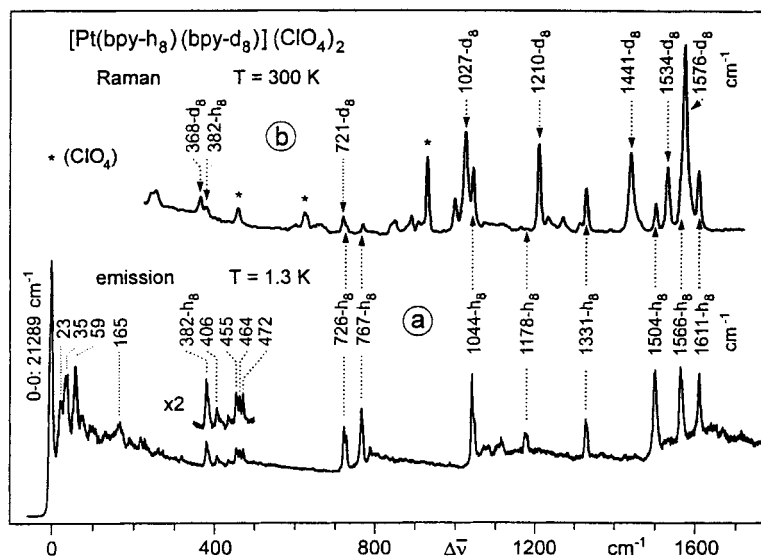


Fig. 8. **a** Emission spectrum at $T = 1.3$ K of $[\text{Pt}(\text{bpy-h}_8)(\text{bpy-d}_8)]^{2+}$ in neat $[\text{Pt}(\text{bpy-h}_8)(\text{bpy-d}_8)](\text{ClO}_4)_2$ (excitation at 457.9 nm). The energies of the vibrational satellites are specified relative to the electronic origin line (0-0) at $21\,289\text{ cm}^{-1}$. **b** Raman spectrum at $T = 300$ K of $[\text{Pt}(\text{bpy-h}_8)(\text{bpy-d}_8)](\text{ClO}_4)_2$ powder (excitation at 1064 nm). The asterisks mark Raman active $(\text{ClO}_4)^-$ vibrations (cf. [109]). h_8 and d_8 represent (bpy-h_8) and (bpy-d_8) vibrations, respectively

while they are clearly found as weak satellites in the emission spectrum. Moreover, Raman lines are observed for both ligands, while the emission spectrum is highly selective and displays the information about the emitting spatial region of the complex, which is the protonated ligand with a small metal admixture.

2.4

Dual Emission?

For heteroleptic complexes the question may arise whether an independent emission of the different ligands may occur. For example, several authors reported the occurrence of such a “dual emission”. Obviously, for $[\text{Pt}(\text{bpy-h}_8)(\text{bpy-d}_8)]^{2+}$ a dual emission does not appear. Apparently, the rate P_{D-A} of energy transfer from the deuterated ligand (donor D) to the protonated one (acceptor A) is much larger than the decay rate τ_{III}^{-1} of the fast decaying sublevel of the deuterated ligand. Thus, $P_{D-A} \gg \tau_{III}^{-1} \approx 5 \cdot 10^5\text{ s}^{-1}$ (from Table 1). This value, presenting a lower limit, is still very small for an intramolecular energy transfer and presumably, the effective rate is much larger. On the other hand, this estimate shows that already a very small transfer rate – for example, induced by the small coupling via the metal – will quench the emission of the (bpy-d_8) donor. Thus, an occurrence of a dual emission is prevented. Similar or related considerations have been applied to other heteroleptic complexes, for example, $[\text{Rh}(\text{bpy})_n(\text{phen})_{3-n}]^{3+}$

($n = 1, 2$; phen: 1,10-phenanthroline) [42], $[\text{Ir}(\text{bpy})_n(\text{phen})_{3-n}]^{3+}$ ($n = 1, 2$) [116], $[\text{Ir}(\text{bpy})(\text{phpy})_2]^+$ (phpy: 2-phenylpyridine) [42, 117], and $[\text{Rh}(\text{bpy}-\text{h}_8)_2(\text{bpy}-\text{d}_8)]^{3+}$ [60]. A dual emission could always be excluded (cf. also [118]). On the other hand, an occurrence of such a dual emission, e.g., for $[\text{Rh}(\text{bpy})_n(\text{phen})_{3-n}]^{3+}$ dissolved in glass-forming matrices [118–120], was reported. However, this observed behavior may be interpreted alternatively, as discussed by Henderson and Imbusch [97] for a related situation and by Güdel et al. [42] for the complexes mentioned above. According to these considerations, dual emission could result from superpositions of spectra resulting from the same chromophores, which, however, occupy different types of sites in the matrices investigated. For example, $[\text{Rh}(\text{bpy})_n(\text{phen})_{3-n}]^{3+}$ may lie on one specific site where the LC $\pi\pi^*$ transition of the phen ligands are the lowest in energy, while for other sites (other environments) the transitions of the bpy ligands may be lower. In such a situation, it is difficult to interpret the measured spectra correctly if they are not sufficiently resolved.

2.5

Emission Properties of $[\text{Pt}(\text{bpy})_2]^{2+}$ Compared to $[\text{Rh}(\text{bpy})_3]^{3+}$

The emission properties of these compounds are very similar, as demonstrated in Fig. 9. Both spectra are nearly identical when they are normalized to the energies of the electronic origins. (Obviously, the satellites resulting from lattice

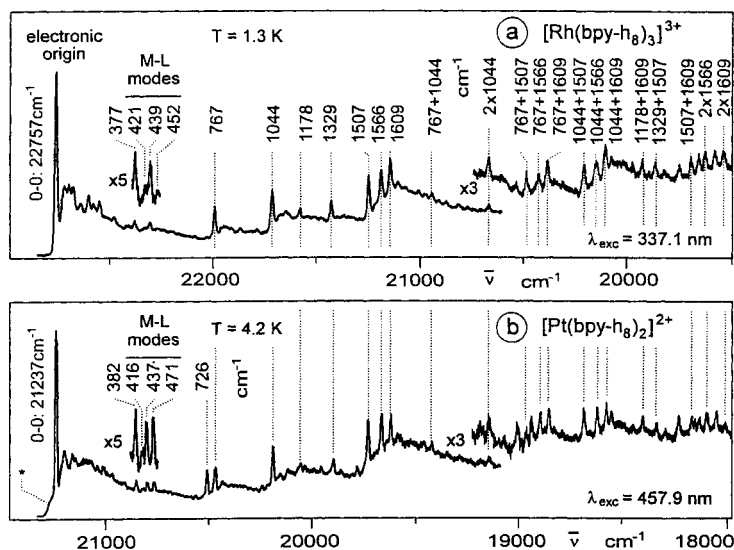


Fig. 9. Emission spectra of a $[\text{Rh}(\text{bpy}-\text{h}_8)_3]^{3+}$ doped into $[\text{Zn}(\text{bpy}-\text{h}_8)_3](\text{ClO}_4)_2$ (from [60]) (excitation at 337.1 nm) and b $[\text{Pt}(\text{bpy}-\text{h}_8)_2]^{2+}$ in $[\text{Pt}(\text{bpy}-\text{h}_8)_2](\text{ClO}_4)_2$ (from [68]) (excitation at 457.9 nm). *M-L* metal-ligand vibrational modes. The energies of the vibrational satellites are specified relative to the respective electronic origin lines (0-0). The asterisk in b marks a higher lying trap

modes have to be disregarded in this comparison, since the compounds are investigated in different matrices). In particular, the zero-field splittings are small for both compounds and the vibrational satellite structures (including progressions, Huang-Rhys factors, etc.) are very similar. This is also valid for the comparison of the partially deuterated compounds. Therefore, the arguments given in connection with the assignment of the lowest triplet state of $[\text{Rh}(\text{bpy})_3]^{3+}$ [44, 60] may be used largely to support the assignments given above for $[\text{Pt}(\text{bpy})_2]^{2+}$ [68]. Thus, in both compounds, the lowest triplet T_1 is classified as being ligand-centered of $^3\pi\pi^*$ character exhibiting some MLCT and/or $d-d$ metal character, which is slightly larger in $[\text{Pt}(\text{bpy})_2]^{2+}$ than in $[\text{Rh}(\text{bpy})_3]^{3+}$. This may be concluded from the larger intensities of the M-L vibrational satellites and is indicated by the much shorter emission lifetimes found for $[\text{Pt}(\text{bpy})_2]^{2+}$ (Table 1). A detailed and comparative discussion is presented in [44, 60].

3

$[\text{Ru}(\text{bpy})_3]^{2+}$

$[\text{Ru}(\text{bpy})_3]^{2+}$ has attracted the interest of many research groups, and one finds a very large number of related investigations in physical, chemical, biological, and medical research fields. It is not the aim of this section to discuss all these aspects (see reviews in [9, 27, 44, 83, 122–133]). Here, it is mainly focused on properties of the lower electronically excited states (and the ground state). However, in Section 3.1 it will become clear, using a group-theoretical procedure, that the number of lower lying excited states is very large and that a quantitative description is – compared to the level of experimental accuracy – far beyond today's computational possibilities. Therefore, the discussion is based primarily on experimental data stemming from highly resolved excitation and emission as well as from time-resolved emission measurements at low temperature, whereby the properties of the three lowest excited states are emphasized. In addition, a selected number of topics will be treated: (1) The matrices required to obtain highly resolved spectra exhibit some complications, e.g., the formation of clusters or aggregates, occurrence of various sites, etc. (Sect. 3.2.). (2) Energy transfer between nearest neighbors can influence the emission decay times (Sect. 3.6). (3) Even the emission of the “isolated” $[\text{Ru}(\text{bpy})_3]^{2+}$ complex decays bi-exponentially at low temperature (e.g., $T = 1.3$ K) with decay times, which span a range of over three orders of magnitude according to spin-lattice relaxation and usual radiative deactivation (Sect. 3.4). (4) Full and/or partial deuteration of the complex provides deep insight into the system properties and will be used to obtain information about the spatial spread of electron densities in the excited state(s) (Sect. 3.5). These results clearly display the delocalized situation of the excitation. (5) However, as shown in Section 3.7, a localization on a single (Ru-bpy) subunit can be achieved using $[\text{Ru}(\text{i-biq})_2(\text{bpy})]^{2+}$, for which clear changes are observed compared to the homoleptic $[\text{Ru}(\text{bpy})_3]^{2+}$. (6) Finally, the exciting problem of localization/delocalization, spectroscopic implications, and alternative views of other research groups are addressed in Section 3.8.

Figure 10 depicts room temperature absorption and 80 K emission spectra corresponding largely to the spectra published elsewhere (e.g., see [9]). The

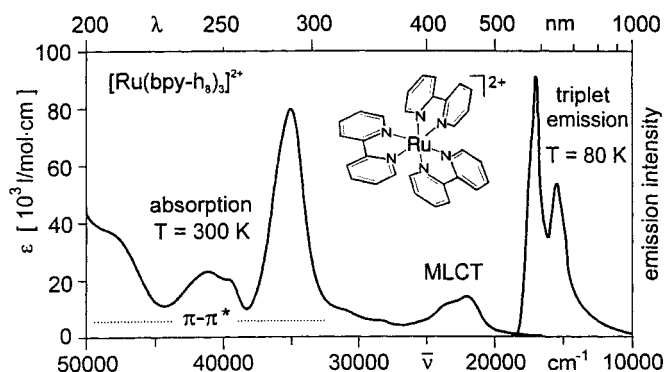


Fig. 10. Absorption and emission of $[\text{Ru}(\text{bpy})_3]^{2+}$ dissolved in H_2O and assignments to $\pi\pi^*$ and metal-to-ligand-charge transfer (MLCT) transitions

spectral features above $\approx 33\,000\text{ cm}^{-1}$ are usually assigned to singlet-singlet transitions of ligand $\pi\pi^*$ character. These strong transitions lead to a ligand-ligand coupling, even if one neglects the d -contributions, as discussed for $[\text{Pt}(\text{bpy})_2]^{2+}$ (Sect. 2; [61–65]). As a consequence, the corresponding excited singlet states have to be assigned to the whole ligand system. In the literature, the absorption structure near $22\,000\text{ cm}^{-1}$ is, in general agreement, assigned to result from $\text{Ru}4d\text{-bpy}\pi^* \rightarrow \text{MLCT}$ transitions, the ground state being a singlet [9, 27, 44, 83, 85, 122–156]. On the other hand, the emission at 80 K stems – also in general agreement – from a series of $^3\text{MLCT}$ states. At 300 K one can additionally detect a weak component of a singlet emission ($^1A_2$ in D_3) [145–148]. A more detailed discussion on the basis of the broad spectrum shown in Fig. 10 does not seem reasonable.

3.1

Molecular Orbitals, Covalency, and Manifold of Excited States

HOMO/LUMO. In the literature one finds a large number of valuable theoretical investigations, which all discuss the electronic structure of $[\text{Ru}(\text{bpy})_3]^{2+}$ [134–136, 138–141a, 149–156]. However, even if it is assumed that the molecule is rigid, it is for today's computational possibilities much too large for a description at the ab-initio level with experimental accuracy. The computational problems are particularly pronounced for an accurate description of the low-lying triplet sublevels, which are our main concern. The reason is that relativistic effects, in particular spin-orbit coupling, have to be taken into account. However, the theoretical investigations available may still be used to illuminate some important features of $[\text{Ru}(\text{bpy})_3]^{2+}$. In particular, general agreement seems to exist about the main features of the MO scheme in the HOMO/LUMO energy regions. Using these MOs, it is straightforward to determine the number and group-theoretical representations of the low-lying, many-electron states, including the triplet sublevels. This is briefly explained by using the one-electron MO scheme shown in Fig. 11 (cf. also [126, 134–136, 153, 154]). In D_3 parent group

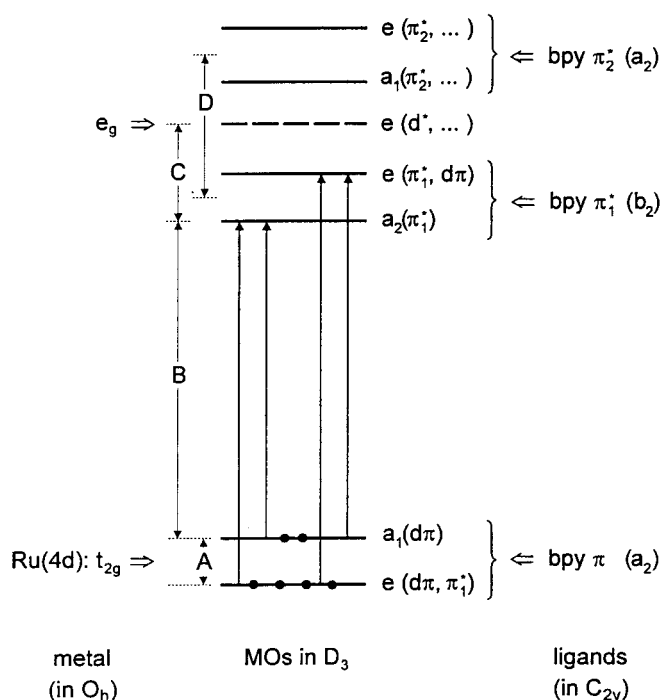


Fig. 11. Simplified MO scheme for [Ru(bpy)₃]²⁺. In several cases only the main contributions are given. The energy separations specified represent only first-order estimates. A 0.5–1.5 · 10³ cm⁻¹ [135, 136, 138, 139]; B 2 · 10⁴ cm⁻¹ (Fig. 10); C 2–3 · 10³ cm⁻¹ [158–160]; D 5–6 · 10³ cm⁻¹ [135, 136, 140]

symmetry, the metal t_{2g} orbitals (in O_h) split into a₁ and e. These orbitals will experience an admixture with ligand bpy π orbitals of the same representations. The resulting MOs are occupied with six electrons coming from the metal. These MOs represent the HOMO(s). Thus, the ground state configuration is e⁴a₁². The LUMO(s) a₂ and e result mainly from the lowest bpy π* orbitals of the three ligands.

It seems to be of importance for the properties of the complexes that both MOs of e character (from HOMO and LUMO) mix significantly. Therefore, we write e(dπ, π*) for the HOMO and e(π*₁, dπ) for the LUMO. This mixing results in an additional bonding (backbonding), since it stabilizes the HOMO e(dπ, π*) and destabilizes the corresponding LUMO. The significance of this effect has already been stressed by Orgel [134] and later, for example, by Ceulemans and Vanquickenborne [135], Daul et al. [138, 139], and Ferguson and Herren [153]. It is assumed that the energy separation between the e and the a₁ MOs (A in Fig. 11) is largely determined by this type of interaction. From [135, 138, 139, 153, 154], the corresponding value A is estimated to be of the order of 10³ cm⁻¹. Obviously, the larger this backbonding or orbital mixture is, the more covalent is the complex, and consequently, less net charge transfer occurs upon excitation. In this context we want to mention the early conclusion given by Orgel [134],

where he related already at that time the depression of the e orbital below the a_1 orbital with an extensive delocalization of metal electrons into the ligands. Obviously, this mixing is an important source of electronic ligand-ligand coupling induced by the metal.

States and Group-Theoretical Representations. The many-electron MLCT states of the complex can be determined from the orbital jumps between the one-electron MOs. Figure 11 shows four HOMO-LUMO jumps, leading in a first step to a series of singlet and triplet states. However, due to a relatively high spin-orbit coupling, these states can no longer be classified according to their spin quantum numbers or their spatial representations. Therefore, in a second step, one has to construct the spin-orbit (or double-group) states, which result from splittings of the triplets and mixings with other states of the same group-theoretical representation. This is illustrated by an example. The ground state configuration $e^4a_1^2$ represents an $^1A_1$ state, due to the closed-shell case. An electron jump from $e(d\pi; \pi_1^*)$ to $a_2(\pi_1^*)$ is signified by the configuration change $e^4a_1^2 \rightarrow e^3a_1^2a_2^1$. The corresponding many-electron state is obtained from the group-theoretical product $e \times a_2 = E$. An inclusion of the spins gives the states ^1E and ^3E . Further, in D_3 the spin singlet with $S = 0$ and the triplet with $S = 1$ transform as A_1 and $A_2 + E$, respectively (e.g., see [157]). Thus, the total symmetry labels for ^1E and ^3E are constructed by the group-theoretical products $A_1 \times E = E$ (for ^1E) and $(A_2 + E) \times E = E + A_1 + A_2 + E$ (for ^3E), respectively. In total, the orbital jump discussed above leads to three E terms of degenerate representations (one of these results from the singlet, while the other two come from the triplet) as well as to two nondegenerate states of A_1 and A_2 representation. The four excitations shown in Fig. 11 give rise to 24 MLCT terms (36 states: 6 A_1 , 6 A_2 , and 12 E). Under inclusion of spin-orbit coupling states with the same group-theoretical representation can mix. This leads to a loss of the strict singlet or triplet characters and to energy shifts (e.g., see [136, 153, 154]). It is of importance that this mixing of states by spin-orbit coupling represents a further source of an electronic, metal-induced ligand-ligand coupling.

The energy spread of these 24 terms has been determined by model calculations to span a range of about 5000 cm^{-1} [136, 140] to 6000 cm^{-1} [139]. Consequently, these states strongly overlap energetically with those stemming from the next higher lying MLCT transitions involving the π_2^* MOs, which are assumed to lie only about 6000 cm^{-1} above the π_1^* MOs ([135, 136, 140]; Fig. 11). Thus, one obtains 24 additional terms (6 A_1 , 6 A_2 , and 12 E). Moreover, the lowest $d \rightarrow d^*$ transitions were found to be only about 3000 cm^{-1} above the emitting states ([158, 159]; cf. also [160]) and thus they lie also in the energy range of the 24 ML(π_1^*) CT terms. In D_3 symmetry, the $d-d^*$ transitions give rise to further 4 A_1 , 4 A_2 , and 8 E terms. Although they do not carry high oscillator strengths for electric dipole transitions to the ground state, they will certainly be of importance for the properties of the emitting triplet sublevels (e.g., spin-orbit coupling, splittings, decay times, covalency, etc.).

This discussion clearly shows that model calculations based only on the four orbital jumps (Fig. 11) will certainly not successfully describe the experimental results. Moreover, the situation becomes still more complicated, if one takes into

account that the complex symmetry is reduced to C_2 (or even to lower symmetry), when $[\text{Ru}(\text{bpy})_3]^{2+}$ is doped into a low-symmetry matrix like $[\text{Zn}(\text{bpy})_3](\text{ClO}_4)_2$. Thus, all E terms will split and additional mixing routes are opened.

Here, we want to refer to some valuable experimental papers (including those with strong experimental reference) in which higher lying electronic states have been assigned group-theoretically, mainly on the basis of polarized absorption spectra [135–141, 145–148, 153–155, 161]. However, a generally accepted and sufficiently detailed group-theoretical classification has not yet emerged. This holds particularly for the lowest excited states (which are of our main concern) even though highly resolved spectra are available. There are several reasons why a straightforward experimental assignment is not easy. For example: (1) the spectroscopically relevant site symmetry of a dopant may be lower than expected from a structure determination, since a very slight lattice- or site-induced distortion of the chromophore can provide some oscillator strength to an originally strictly forbidden transition due to an admixture of a different state. In this case one would observe the polarization of the distorting term and thus might assign the state of interest incorrectly. Such a mixing has been demonstrated to dominate the low-temperature emission properties of $[\text{Os}(\text{bpy})_3]^{2+}$ (see [38, 92]; Sect. 4.1) and also seems to be of importance for $[\text{Ru}(\text{bpy})_3]^{2+}$. For completeness, note that highly allowed transitions are not very sensitive in this respect. (2) A very successful and often used matrix for investigations of $[\text{Ru}(\text{bpy})_3]^{2+}$ is $[\text{Zn}(\text{bpy})_3](\text{ClO}_4)_2$. However, in this matrix $[\text{Ru}(\text{bpy})_3]^{2+}$ has a great tendency to build aggregates (see [44]; Sect. 3.2.1). Without taking this property into account one might easily misinterpret experimental data (e.g., see [162, 163]; Sects. 3.5 and 3.8.1). (3) Time evolution of the low-temperature emission complicates the assignment further. Such effects have been ascribed to a symmetry change according to a localization process in the excited state [164] and, alternatively, to relatively slow spin-lattice relaxations between the lowest triplet sublevels of $[\text{Ru}(\text{bpy})_3]^{2+}$ (Sect. 3.4; [44, 129, 165, 166]).

In spite of these problems it has been possible to develop a relatively detailed description of important photophysical properties of the manifold of the three lowest excited states. In particular, this holds for $[\text{Ru}(\text{bpy})_3]^{2+}$ doped into $[\text{Zn}(\text{bpy})_3](\text{ClO}_4)_2$. However, a largely accepted group-theoretical assignment did not emerge.

3.2

Crystalline Matrices for $[\text{Ru}(\text{bpy})_3]^{2+}$ and High Spectral Resolution

The properties of the lowest excited states of $[\text{Ru}(\text{bpy})_3]^{2+}$ are not independent from the host material and the environment of the chromophore. Over the last 20 years, a large number of matrices have been investigated, but mostly only broad and unresolved spectra were found [9, 122, 137, 145–146, 161, 164, 168–174]. There are mainly two reasons for this result. (1) The inhomogeneous distribution of the chromophores is large, thus the electronic origins are spread over wide spectral ranges. (2) The coupling of phonons to electronic and vibronic

states is strong and distinct phonon progressions occur (large Huang-Rhys factor for the phonons, e.g., see [175]).

It is an important message that the described effects may be strongly influenced by chemical variation. For example, the electron-phonon coupling and/or the inhomogeneous distribution seem to depend on the crystal water content [174]. Thus, a water-free host material might be a good candidate. Our group began more than one decade ago with a systematic variation of compounds, in order to reduce the factors that are responsible for smearing out the spectra of $[\text{Ru}(\text{bpy})_3]^{2+}$. Indeed, this was successful for a number of neat materials [174–180]. Somewhat later, Hirota and coworkers [167] found that the crystalline $[\text{Zn}(\text{bpy})_3](\text{ClO}_4)_2$ matrix doped with $[\text{Ru}(\text{bpy})_3]^{2+}$ could also be successfully applied. In particular, the discovery of a matrix being inert in the spectral region of interest strongly stimulated the research.

Table 3 summarizes all matrices for which highly resolved spectra have been obtained, and gives a number of photophysical data found for the $[\text{Ru}(\text{bpy})_3]^{2+}$ chromophores (transition energies, zero-field splittings, emission lifetimes). Interestingly, the transition energy from the ground state to the lowest triplet sublevel $|I\rangle$ varies over more than 200 cm^{-1} , which may be used in the sense of “chemical tunability”.

Table 3. Matrices suitable for high-resolution spectroscopy with $[\text{Ru}(\text{bpy})_3]^{2+}$. The data refer to the three lowest electronic states

Matrices for $[\text{Ru}(\text{bpy})_3]^{2+}$	Lowest excited states Energies $[\text{cm}^{-1}]$, decay times $[\mu\text{s}]$			zero-field splittings $[\text{cm}^{-1}]$		References
	$ I\rangle$ (τ_I) ^c	$ II\rangle$	$ III\rangle$	ΔE_{I-II}	ΔE_{I-III}	
$[\text{Zn}(\text{bpy})_3]$ $(\text{ClO}_4)_2^a$	17684 (230)	17693	17745	8.7	61	[167, 44, 74] Structure: [144, 181, 182a, 182b]
$[\text{Ru}(\text{bpy})_3]$ $(\text{ClO}_4)_2^b$	17605	17613	17662	8.2	57	[126, 175, 183] Structure: [144]
$[\text{Ru}(\text{bpy})_3]$ $(\text{PF}_6)_2^b$	17809 ^d (250)	17816 ^d	17870	6.9	61	[176, 126, 180] Structure: [184]
$[\text{Ru}(\text{bpy})_3]$ $(\text{AsF}_6)_2^b$	17813 ^d (240)	17820 ^d	– ^e	7	– ^e	[126, 186]
$[\text{Ru}(\text{bpy})_3]$ $(\text{SbF}_6)_2^b$	17817 ^d (210)	17824 ^d	– ^e	7	– ^e	[126, 186]

^a Inert matrix.

^b Neat material.

^c Emission lifetimes at $T \leq 2\text{ K}$.

^d Energies of the lowest site A [185, 186].

^e Not yet known.

In the present investigation, results concerning two matrices will be discussed in detail: $[\text{Zn}(\text{bpy})_3](\text{ClO}_4)_2$. According to the closed-shell of Zn^{2+} , this compound does not exhibit any absorption in the visible energy range. Therefore, this matrix is suitable for doping of chromophores having their absorptions in the visible range. The highest site symmetry available for guest molecules that substitute $[\text{Zn}(\text{bpy})_3]^{2+}$ is C_2 ([144, 181, 182a, 182b]; but see also Sect. 3.2.2). Interestingly, it is possible for $[\text{Ru}(\text{bpy})_3]^{2+}$ and a series of other guest molecules (e.g., $[\text{Rh}(\text{bpy})_3]^{3+}$ and the compounds discussed in Sect. 3.7) to obtain highly resolved spectra with line widths of only a few wavenumbers, without applying the techniques of line narrowing. This indicates that the inhomogeneous broadening and the electron-phonon coupling strengths are relatively small. However, the $[\text{Ru}(\text{bpy})_3]^{2+}/[\text{Zn}(\text{bpy})_3](\text{ClO}_4)_2$ guest/host system has to be treated with care due to the tendency to form $[\text{Ru}(\text{bpy})_3]^{2+}$ aggregates (see below). $[\text{Ru}(\text{bpy})_3](\text{PF}_6)_2$. Despite the fact that this matrix represents a neat material one obtains highly resolved spectra of $[\text{Ru}(\text{bpy})_3]^{2+}$ complexes (e.g., see [175–180]). An advantage is that the chromophores lie on high-symmetry C_3 sites, where the molecular $\vec{\text{C}}_3$ axes lie parallel to the crystallographic $\vec{c}$ axis [184]. This is very convenient for measurements of polarized absorption spectra [145–148]. For emission measurements this matrix may cause some problems, if the occurrence of energy transfer processes between the three sites [184] in the unit cell (see [185]; Sect. 3.6) and/or via the lowest triplet exciton bands¹ is not taken into account. This problem is no longer valid for $[\text{Os}(\text{bpy})_3]^{2+}$ guests due to their much lower lying states. In this situation the occurrence of a high symmetry site is extremely useful for a detailed description of $[\text{Os}(\text{bpy})_3]^{2+}$ properties (see [38, 92]; Sect. 4.1).

3.2.1

Aggregates of $[\text{Ru}(\text{bpy})_3]^{2+}$ in $[\text{Zn}(\text{bpy})_3](\text{ClO}_4)_2$

The distribution of $[\text{Ru}(\text{bpy})_3]^{2+}$ guest molecules in the $[\text{Zn}(\text{bpy})_3](\text{ClO}_4)_2$ host material may cause problems. This can be seen visually by inspecting the doped crystals. Their central parts are often dark red, while the outer regions are nearly transparent. Moreover, the solutions, from which the crystals are grown, become more and more transparent with increasing precipitation of crystals. Crystals developed from very low concentrated solutions (e.g., $[\text{Ru}(\text{bpy})_3]^{2+}/[\text{Zn}(\text{bpy})_3]^{2+} < 0.03\%$) often exhibit a number of small red spots which are clearly seen under a microscope. This behavior strongly indicates that $[\text{Ru}(\text{bpy})_3]^{2+}$ is not built in statistically, but has the tendency to accumulate to aggregates in the $[\text{Zn}(\text{bpy})_3](\text{ClO}_4)_2$ host material.² Such behavior is not unusual (e.g., see [188,

¹ In [179] an upper limit for the bandwidth has been estimated to be of the order of a wave-number. However, in Section 3.6 and [185], it is shown that the energy transfer time between nearest neighbors in $[\text{Ru}(\text{bpy})_3](\text{PF}_6)_2$ is 60 ns, which would correspond to a bandwidth of $\approx 5 \cdot 10^{-4} \text{ cm}^{-1}$ for the lowest state.

² Clustering effects have also been observed for $[\text{Ru}(\text{bpy})_3]^{2+}$ in α -zirconium phosphates [187a] and for $[\text{Ru}(\text{phen})_3]^{2+}$ in solution [187b].

189)). It corresponds to an effective segregation coefficient k_{eff} that is significantly greater than 1. (k_{eff} is the ratio of guest concentration in the matrix relative to its concentration in solution). Values as large as $k_{eff} \approx 5$ were found for this guest/host system [190]. The fact that k_{eff} deviates significantly from 1 is already expected from a comparison of the structures of $[\text{Zn}(\text{bpy})_3](\text{ClO}_4)_2$ [144, 181, 182a, 182b] and $[\text{Ru}(\text{bpy})_3](\text{ClO}_4)_2$ [144, 181]. Although their space groups are identical, the cell parameters differ significantly. Independently, it has been shown [191] that both cations exhibit distinctly different electrostatic multipole potentials, implying different intermolecular interactions.

The situation with respect to the nonuniform colors of the doped crystals or $k_{eff} > 1$ is also found for many other dopants like partially and per-deuterated $[\text{Ru}(\text{bpy})_3]^{2+}$ and $[\text{Os}(\text{bpy})_3]^{2+}$ as well as for several mixed-ligand Ru(II) complexes.

The structures of the aggregates or clusters are not known. Presumably, the number of neighboring $[\text{Ru}(\text{bpy})_3]^{2+}$ guest complexes in the $[\text{Zn}(\text{bpy})_3](\text{ClO}_4)_2$ host is still relatively small, since otherwise one would expect to find the lowest excited states at energies of the $[\text{Ru}(\text{bpy})_3](\text{ClO}_4)_2$ bulk material, which is not the case (see Table 3).

3.2.2

Guest Site Symmetries and Environmental Interactions

The individual characteristics of guest sites are very important for the electronic and vibronic properties of the chromophores. For example: (1) the absolute transition energy depends on the host environment (Table 3). (2) The site symmetry determines electronic and vibronic coupling paths between different states, e.g., this has significant influence on the lowest states' properties of $[\text{Os}(\text{bpy})_3]^{2+}$ (Sects. 4.1 and 4.2; cf. also the detailed studies of $\text{Pt}(\text{2-thpy})_2$ [93]). (3) The formation of guest aggregates introduces a large number of different types of guest-guest and guest-host nearest neighbors. This situation, combined with distinct differences in electrostatic interactions between host and guest cations, can induce the occurrence of quite different guest sites.

Obviously, the whole situation is much too complex to make a clear prediction about the detailed structure and interaction energies experienced by the chromophore at an individual guest site. In particular, this is absolutely impossible just from an inspection of the crystal structure of the host material alone, as has recently been proposed (e.g., see [144, 162, 192]). The situation is still more difficult for partially deuterated complexes, if it is attempted to predict exact site symmetries and environments. Even such small chemical changes can have distinct structural consequences, which, however, are often underestimated. Earlier it had already been found that deuterated molecules exhibit smaller bond lengths than the protonated species (e.g., see [193, 194]). Even very small differences in some physical interactions (van-der-Waals bonding, hydrogen bonding, multipole interaction, electron-phonon coupling, etc.) can have important implications. Indeed, it is well known that deuterated matrices can provide distinctly different sites (number and spectroscopic properties) for

Table 4. Vibrational satellites [cm^{-1}] observed in time-integrated emission spectra (at $B = 0$ T and $B = 10$ T) compared to time-resolved data of $[\text{Ru}(\text{bpy}-\text{h}_8)_3]^{2+}$ doped into $[\text{Zn}(\text{bpy}-\text{h}_8)_3](\text{ClO}_4)_2$ (experimental error: $\pm 1 \text{ cm}^{-1}$)

Time-integrated emission	Time-integrated emission	Time-resolved emission ^a Delayed	Time-resolved emission ^b Fast	Assignments [74]
$B = 0$ T $T = 1.2$ K	$B = 10$ T $T = 1.5$ K	$t = 10 \mu\text{s}$; $\Delta t = 200 \mu\text{s}$ $T = 1.2$ K	$t = 0$ ns; $\Delta t = 300$ ns $T = 1.2$ K	
Origin I 17684 cm^{-1}	Origin I _B ^c 17681 cm^{-1}	Origin I 17684 cm^{-1}	Origin II 17693 cm^{-1}	
23	23			Lattice mode ^d
33	33			Lattice mode ^d
41	41			Lattice mode ^d
47	47			Lattice mode ^d
56	56			Lattice mode ^d
66	66			Lattice mode ^d
78	78			Lattice mode ^d
158	158		158	FC ^e
191	191		191	158 + 33
203		203		
236	236		236	158 + 78
296		296		M-L ^f , HT ^g
349		349		M-L, HT, IR 349 ^h
370		370		M-L, HT, IR 369 ^h
420		420		M-L, HT, IR 419 ^h
439		439		HT, IR 440 ^h
471				HT, IR 469 ^h
477		477		HT, IR 474 ^h
510		510		477 + 33
555		555		477 + 78
635		635		477 + 158
667	667		667	L ⁱ FC, RR, 668 ^j
767	767		767	FC, RR 767 ^j
1015		1015		HT, IR 1015 ^h
1029	1029		1029	FC, RR 1028 ^j
1048				1015 + 33
1062	1062		1062	1029 + 33
1174	1174		1174	FC, RR 1173 ^j
1275	1275		1275	FC, RR 1276 ^j
1325	1325		1325	FC, RR 1320 ^j
1358	1358		1358	1325 + 33
1403	1403		1403	1325 + 78
1495	1495		1495	FC, RR 1491 ^j
1528	1528		1528	1495 + 33
1559	1559			FC, RR 1558 ^j
1569		1569		HT, IR 1567 ^h
1573	1573		1573	1495 + 78
1607	1607		1607	FC, RR 1607 ^j
1651				158 + 1495
1971				477 + 1495

Table 4 (continued)

Time-integrated emission	Time-integrated emission	Time-resolved emission ^a Delayed	Time-resolved emission ^b Fast	Assignments [74]
B = 0 T T = 1.2 K	B = 10 T T = 1.5 K	$t = 10 \mu\text{s}$; $\Delta t = 200 \mu\text{s}$ T = 1.2 K	$t = 0 \text{ ns}$; $\Delta t = 300 \text{ ns}$ T = 1.2 K	
Origin I 17684 cm^{-1}	Origin I _B ^c 17681 cm^{-1}	Origin I 17684 cm^{-1}	Origin II 17693 cm^{-1}	
2349				1029 + 1325
2498				1174 + 1325
2520				1029 + 1495
2666				1174 + 1495
2814				1325 + 1495
2982				2 × 1495

^a Vibrational modes selectively observed in the delayed emission from state |I> (Fig. 16; [44]).

^b Vibrational modes dominating the fast emission from state |II> (Fig. 16; [44]).

^c Origin I_B, corresponding to the distorted state |I_B>, is slightly red-shifted due to the application of a high magnetic field. The modes summarized grow strongly in by applying a magnetic field.

^d Lattice modes detected in the same matrix doped with [Os(bpy)₃]²⁺ (Sect. 4.2; Fig. 30) and with [Rh(bpy)₃]³⁺ (33 and 47 cm^{-1} ; [60]), respectively.

^e FC: Franck-Condon active mode.

^f M-L: metal-ligand vibrational mode.

^g HT: Herzberg-Teller active mode.

^h IR-active mode of [Ru(bpy)₃](PF₆)₂ measured at 6 K [212].

ⁱ L: Ligand mode. Modes above $\approx 500 \text{ cm}^{-1}$ are assigned to ligand vibrations (e.g., see [106, 211]).

^j Resonance-enhanced Raman (RR) modes from [106, 211].

protonated guests in comparison to protonated matrices (e.g., see [68, 84, 195]; Sect. 3.5). Or vice versa, partially deuterated [Ru(bpy)₃]²⁺ and [Os(bpy)₃]²⁺ dopants are found on different sites in the [Zn(bpy)₃](ClO₄)₂ host material compared to the case observed for fully protonated or fully deuterated chromophores [44, 85, 98, 104]. The situation is even more distinct when heteroleptic Ru(II) complexes, like [Ru(bpy)₂(bpz)]²⁺ or [Ru(bpy)₂(bpdz)]²⁺ (with bpz = 2,2'-bipyrazine, bpdz = 3,3'-bipyridazine), are doped into the [Zn(bpy)₃](ClO₄)₂ matrix (Sect. 3.7). It is extremely improbable that all these different dopants are statistically built into this matrix and have exactly the same symmetry and environment as the substituted host cation. Such an assumption has been used as essential basis for a very detailed classification in [196, 197]. Again, and in contradiction to these assumptions, the occurrence of a number of different sites is also demonstrated for these heteroleptic guest chromophores [198].

Nevertheless, [Zn(bpy)₃](ClO₄)₂ can be used very successfully as a matrix for a number of different guest chromophores in order to obtain highly resolved spectra, as will be demonstrated below. However, one should be careful and avoid the use of oversimplified assumptions about the properties

(symmetries, environments, etc.) of individual guest sites, and one has to take into account that $[\text{Ru}(\text{bpy})_3]^{2+}$ as dopant is not statistically distributed in this matrix and that a formation of aggregates has to be considered. This is of particular importance if line-narrowed spectra with very high resolution are to be interpreted (see Sect. 3.5).

3.3

Highly Resolved Emission and Excitation Spectra of $[\text{Ru}(\text{bpy})_3]^{2+}$

Figure 12 shows non-line-narrowed, but already well-resolved emission and excitation spectra of $[\text{Ru}(\text{bpy})_3]^{2+}$ doped into $[\text{Zn}(\text{bpy})_3](\text{ClO}_4)_2$ with a resolution of about 3 cm^{-1} , which is clearly inhomogeneously determined. These spectra can be used well for a discussion of the properties of the chromophores and will allow us to elucidate important features of the electronic structure and of the vibronic coupling properties of the lowest excited states, although this guest/host system presents some intricacies which become distinctly apparent, when the spectral resolution is further increased (for details see Sect. 3.2.1 and Sect. 3.5).

3.3.1

Low-Energy Electronic Origins of $[\text{Ru}(\text{bpy})_3]^{2+}$

Figure 12a shows the time-integrated emission spectrum of $[\text{Ru}(\text{bpy}-\text{h}_8)_3]^{2+}$ doped into a $[\text{Zn}(\text{bpy}-\text{h}_8)_3](\text{ClO}_4)_2$ matrix measured at $T = 1.2 \text{ K}$. The dominating high-energy line at 17684 cm^{-1} is assigned as electronic origin for the transition from the lowest excited state $|I\rangle$ to the electronic ground state $|0\rangle$ (origin I). This assignment is supported by the good fit of vibrational energies exactly to this 0-0 transition (see Sect. 3.3.2; Table 4). A purely electronic transition should also be found in excitation or absorption spectra at exactly the same transition energy as in emission. However, the excitation spectrum in Fig. 12d does not show the corresponding peak, because the oscillator strength of the transition $|0\rangle \rightarrow |I\rangle$ is extremely small. This is also displayed, for example, in the long emission lifetime of $230 \mu\text{s}$ at $T = 1.2 \text{ K}$ (e.g., see [44]; Sect. 3.4).³ However, by applying a high magnetic field, the corresponding transition grows in and can be clearly detected in excitation. This behavior proves the assignment of the line at 17684 cm^{-1} as electronic origin⁴ [126, 178, 180, 199].

A second electronic origin is registered at 17693 cm^{-1} (origin II), which occurs in the excitation spectrum and as a weak peak at the same energy also in

³ For $[\text{Ru}(\text{bpy})_3]^{2+}$ in neat $[\text{Ru}(\text{bpy})_3](\text{PF}_6)_2$ the molar extinction coefficient $\epsilon(|0\rangle \rightarrow |I\rangle)$ has been determined to $\approx 0.02 \text{ l/mol cm}$ [126, 179].

⁴ This effect is well understood and described in detail in the references given. The magnetic field induces an admixture of the higher lying state $|II\rangle$, which has a larger radiative decay rate, and thus provides oscillator strength to the transition $|0\rangle \leftrightarrow |I\rangle$ (cf. Sect. 4.1.4).

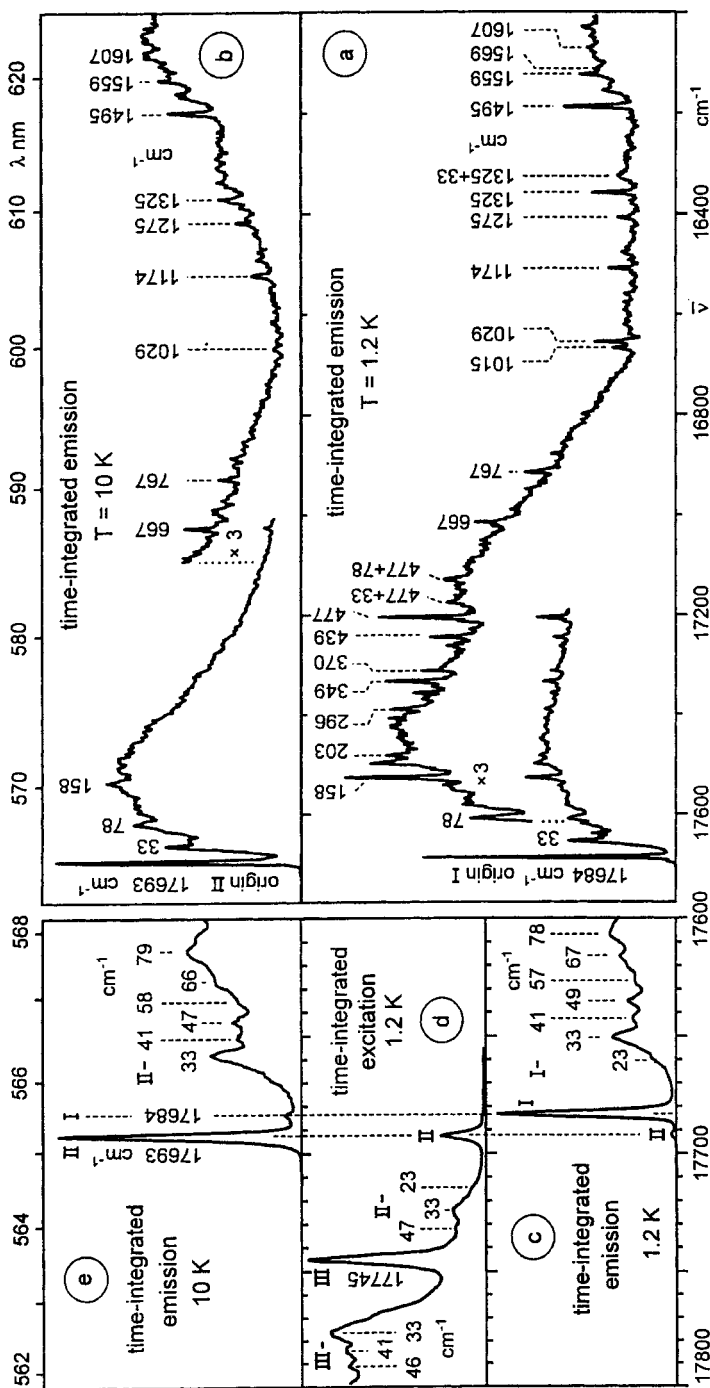


Fig. 12. Time-integrated emission and excitation spectra at $T = 1.2$ K and 10 K of $[\text{Ru}(\text{bpy-h}_8)_3]^{2+}$ in $[\text{Zn}(\text{bpy-h}_8)_3](\text{ClO}_4)_2$. The crystals were grown from water with a molar ratio in solution of Ru(II):Zn(II) of 0.5%. The emission spectra a, b, c, and e were obtained by exciting at 514.5 nm ($\Delta 19436 \text{ cm}^{-1}$), the excitation spectrum d was detected at 17207 cm^{-1} ($\Delta 477 \text{ cm}^{-1}$ satellite to origin I). The region of the electronic origins is reproduced at an enlarged scale. The energies of vibrational and phonon satellites are given relative to the respective electronic origins

the $T = 1.2$ K emission spectrum (Fig. 12c, d). With temperature increase to $T = 10$ K, origin line II strongly grows in and the emission spectrum, including the vibrational satellite structure, changes distinctly (cf. Fig. 12a, c to b, e). This effect is easily understood. The ratio of oscillator strengths of the transition $|0\rangle \rightarrow |II\rangle$ compared to $|0\rangle \rightarrow |I\rangle$ is roughly estimated to about 50 [186]. Therefore and according to the Boltzmann distribution, mainly state $|II\rangle$ (being 8.7 cm^{-1} above state $|I\rangle$) emits at $T = 10$ K. Again, the good fit of the vibrational satellites to line II (see Sect. 3.3.2; Table 4) and the magnetic field behavior mentioned above manifest the assignment of line II as a further electronic origin. The temperature dependence of the vibrational satellite structure is a consequence of differences in vibronic coupling properties, which is displayed in the emission spectra from the two states (for details see Sect. 3.3.2).

The spectra reveal a further interesting property. If the Boltzmann distribution were strictly valid, one would expect to find an emission intensity of origin II to be weaker by a factor of about 20 than that observed at $T = 1.2$ K (Fig. 12c). This is a first indication of a nonequilibrated emission from state $|II\rangle$. As shown in Section 3.4, this behavior can be ascribed to the quite general phenomenon of a relatively slow spin-lattice relaxation (slr) between states being separated by only small energy differences.

Finally, the excitation spectrum (Fig. 12d) displays a third electronic origin at 17745 cm^{-1} (origin III). An emission peak can also be observed at the same energy. However, the temperature has to be raised to $T \approx 20$ K, where the spectra are already largely smeared out [186].

Figure 13 shows the energy level diagram for the three lowest excited states, as discussed above. Beside the transition energies, the diagram also reproduces the (total) deactivation rates and emission lifetimes corresponding to the three different states. These values have been determined [186, 200] in analogy to the early investigations by Crosby and coworkers [141a, 171, 201] from the temperature dependence of the emission decay time between the three states (cf. also [142, 206]). The fitting procedure applied here provides more accurate data than published by Crosby's group, since the energy separations being essential in this fit are now exactly known from the highly resolved spectra.

Equivalent investigations have also been carried out for $[\text{Ru}(\text{bpy-d}_8)_3]^{2+}$ doped into $[\text{Zn}(\text{bpy-h}_8)_3](\text{ClO}_4)_2$. For completeness the energy levels and rates are also shown in Fig. 13. The typical deuteration-induced effects will be discussed in Section 3.5.

The three excited states are all of triplet character, as directly deduced from the relatively long emission lifetimes. In general agreement [9, 27, 44, 83, 122–148], the three lowest states are assigned as $^3\text{MLCT}$ sublevels. Presumably, they have largely the same orbital parentage. This is indicated by the fact that, though the absolute energies of these states experience matrix-induced shifts of $\approx 200\text{ cm}^{-1}$, the energy separations are only slightly altered (Table 3; [126]). This assignment is further supported (1) by high-pressure investigations, which show that the three states exhibit – within $\pm 0.7\text{ cm}^{-1}/\text{kbar}$ – the same red shifts of $13\text{ cm}^{-1}/\text{kbar}$ (at $T = 2\text{ K}$) [190, 202] and (2) by the fact that the three states exhibit a Zeeman interaction [178, 180, 203, 204]. (3) After per-deuteration the same energy separations between the three states are obtained. Consequently, the energy splittings

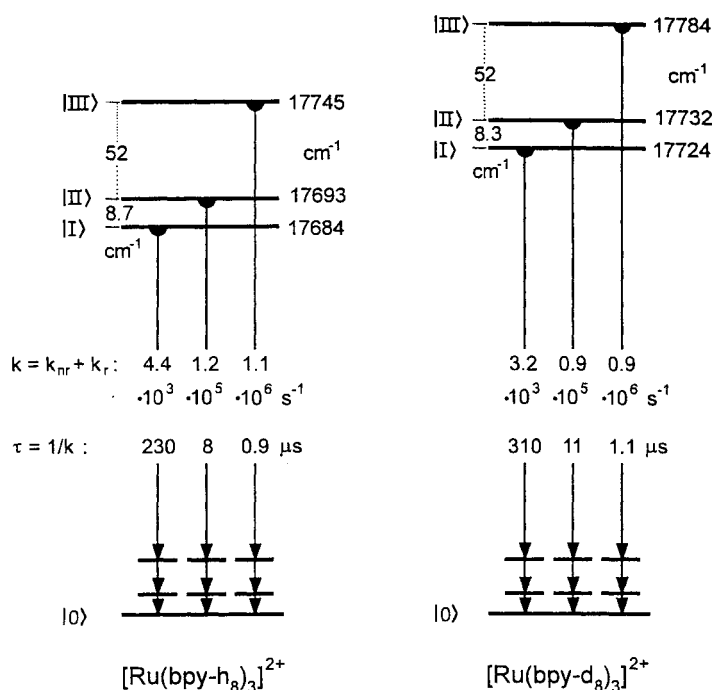


Fig. 13. Energy level diagrams for the three lowest excited states of $[\text{Ru}(\text{bpy}-h_8)_3]^{2+}$ and $[\text{Ru}(\text{bpy}-d_8)_3]^{2+}$ doped into $[\text{Zn}(\text{bpy}-h_8)_3](\text{ClO}_4)_2$. The emission decay times of the states |I> are measured at $T = 1.2$ K, while the times and rates k corresponding to the states |II> and |III> are determined from the temperature dependence of the average emission decay times (cf. [74, 126, 167, 186, 200]). k_r and k_{nr} are the radiative and non-radiative rates, respectively

between these states may be regarded as zero-field splittings (zfs) giving a relatively large value of $61 \pm 1 \text{ cm}^{-1}$ for the total zfs. This value displays the large Ru4d contribution in these states. Interestingly, the metal character is also manifested in the vibrational satellite structures (see Sect. 3.3.2; [44, 60, 83, 85]). A largely accepted group-theoretical assignment, however, has not been given yet. For the related, high-symmetry matrix $[\text{Ru}(\text{bpy})_3](\text{PF}_6)_2$ [184] the two lowest states are considered to belong to degenerate representations, but this assignment is still under debate (cf. [126, 139, 147, 203, 205] to [162, 163, 206–208]).

3.3.2

Vibrational Satellite Structures of $[\text{Ru}(\text{bpy})_3]^{2+}$

Connected with the electronic origins identified in the preceding section, the spectra shown in Fig. 12 for $[\text{Ru}(\text{bpy})_3]^{2+}$ doped into $[\text{Zn}(\text{bpy})_3](\text{ClO}_4)_2$ exhibit well-developed and informative satellite structures. Lines occurring below $\approx 100 \text{ cm}^{-1}$ (relative to the electronic origins) are largely determined by the matrix. This is supported by the fact that nearly the same values are found for

$[\text{Os}(\text{bpy})_3]^{2+}$ (see Table 9) and in part also for $[\text{Rh}(\text{bpy})_3]^{3+}$ [60], when doped into the same matrix. Such lattice modes or local phonons occur as sharp lines (e.g., at 23, 33, 41, 66, 78 cm^{-1} ; Table 4), but presumably also as multiphonon sidebands. (The Huang-Rhys factor for the phonons in other matrices could be roughly estimated in [175].)

Many vibrational satellites are observed in the energy range between ≈ 100 and $\approx 500 \text{ cm}^{-1}$ (e.g., lines at 296, 349, 370, 439 cm^{-1} ; Table 4). It has been shown that these modes represent metal-ligand (M-L) vibrations. Their intensities in vibronic spectra depend largely on the metal-*d*-orbital contribution to the involved electronic states. This intensity (relative to that of all vibrational satellites) may even be used to signify the importance of the metal character [44, 58, 60, 83, 85]. Thus, electronic LC- $\pi\pi^*$ transitions with relatively small metal contributions – as found for $[\text{Pt}(\text{bpy})_2]^{2+}$ and $[\text{Rh}(\text{bpy})_3]^{3+}$ (Sects. 2.2.2 and 2.5) – exhibit only very weak M-L satellites, while the emission spectra of $[\text{Os}(\text{bpy})_3]^{2+}$ show even more intense M-L satellites than found for $[\text{Ru}(\text{bpy})_3]^{2+}$ due to the greater metal involvement in the corresponding states of $[\text{Os}(\text{bpy})_3]^{2+}$ [44, 60, 83].

Vibrational modes of $[\text{Ru}(\text{bpy})_3]^{2+}$ with energies above $\approx 500 \text{ cm}^{-1}$ may be safely assigned to internal (bpy) ligand modes (L modes) (e.g., lines at 767, 1029, 1174, 1275, 1325, 1495, 1607 cm^{-1} ; see also Table 4). A detailed study of these vibrational modes is of interest. However, since a complete normal coordinate analysis is not yet available, we do not discuss these modes to a deeper extent. But we want to mention the analysis carried out by Kincaid and coworkers.⁵ ([106, 209]; cf. also to [211]).

Satellites occurring above $\approx 1650 \text{ cm}^{-1}$ are relatively weak. They are assigned to combinations and/or progressions. By carefully analyzing the spectra it is possible to find, beside the first, also the second member of a 1495 cm^{-1} Franck-Condon progression. (The respective spectral range is not reproduced in Fig. 12, but see Fig. 1 in [74]). The corresponding Huang-Rhys factor *S*, which is related to the Franck-Condon factor of that vibrational mode, is easily determined by using the expression given in Section 2.2.2. For this most prominent progression (of the 1495 cm^{-1} mode), one obtains a value of *S* ≈ 0.1 . This value is even smaller than the maximum Huang-Rhys factor determined for $[\text{Pt}(\text{bpy})_2]^{2+}$ and $[\text{Rh}(\text{bpy})_3]^{3+}$ (*S*_{max} ≈ 0.3 ; see Sect. 2.2.2; [60]). This small value implies that the ground $|0\rangle$ and the excited state $|I\rangle$ have nearly identical nuclear equilibrium positions. (For the theoretical background see e.g. [86–97, 99]). Equivalent arguments hold also for the second and the third excited state [74]. This result has an important consequence, since it implies that a localization of an excited electron on one ligand combined with a significant change in nuclear equilibrium positions (relative to those of the ground state $|0\rangle$) does not occur in any of the three excited states $|I\rangle$, $|II\rangle$, and $|III\rangle$. (For more details of this conclusion, see [129]; Sects. 3.5, 3.8, and 4.2).

⁵ It should be noted that the vibrational analysis by Kincaid and coworkers is carried out only with the restricted (Ru-bpy) model system. Nevertheless, their analysis seems to be well applicable for high-energy modes, since these do not exhibit any significant coupling through space or via the heavy central metal ([44, 60, 108, 112–114, 210]; see also Sect. 2.3).

The overall structure of the emission spectra (Fig. 12 a, b) is strongly smeared out, due to the coupling of phonons, not only to the electronic states but also to vibrational states. Many such combinations are observed, for example, at $(158 + 33)$, $(158 + 78)$, $(477 + 33)$, $(477 + 78)$, $(1325 + 33)$, and $(1495 + 78)$ cm^{-1} (Table 4). Combinations with multiphonon bands also seem to occur. All these effects are responsible for the pronounced background (cf. also to the situation described for $[\text{Pt}(\text{bpy})_2]^{2+}$ for the vibrational modes near 1500 cm^{-1} in Sect. 2.2.2 and Fig. 5a).

Herzberg-Teller Versus Franck-Condon Activity in $[\text{Ru}(\text{bpy})_3]^{2+}$. The vibrational satellite structure resolved in the emission from state $|I\rangle$ is clearly different to the emission structure connected with state $|II\rangle$. This is demonstrated in Fig. 12a, b (cf. also the time-resolved spectra shown in Fig. 16). Several vibrational satellites occur only in the spectrum from state $|I\rangle$ and are not resolved in the state $|II\rangle$ emission. Prominent modes with this behavior are found, for example, at 296, 349, 370, 439, 477, 1015, 1569 cm^{-1} (see Fig. 12a; Table 4). Most of these modes are IR active [212]. On the other hand, a number of dominant modes observed in the emission from state $|II\rangle$ (Fig. 12b) are also seen in the state $|I\rangle$ emission (e.g., 158, 667, 767, 1029, 1174, 1275, 1325, 1495 cm^{-1} ; see also Table 4). Nearly all of these vibrations exhibit a Raman activity with strong resonance enhancements, when exciting into the $^1\text{MLCT}$ states⁶ [106, 211].

The results clearly show that states $|I\rangle$ and $|II\rangle$ exhibit different vibronic coupling properties. Such a behavior is well known for organic molecules (e.g., see [91, 213–215]) and other transition metal complexes [38, 92, 93, 101, 216]. For example, the related $[\text{Os}(\text{bpy})_3]^{2+}$ doped into the $[\text{Ru}(\text{bpy})_3](\text{PF}_6)_2$ matrix displays this behavior much more distinctly. In particular, using this analogy (see Sects. 4.1.3 and 4.1.4), the properties of $[\text{Ru}(\text{bpy})_3]^{2+}$ in $[\text{Zn}(\text{bpy})_3](\text{ClO}_4)_2$ are more easily understood. Moreover, the following model considerations help to elucidate the properties described above.⁷

Due to the relatively strong forbiddenness of the purely electronic transition $|I\rangle \leftrightarrow |0\rangle$, for example, displayed in the long emission lifetime at $T = 1.2 \text{ K}$ of $\tau_I = 230 \mu\text{s}$, vibronic coupling (Herzberg-Teller, HT, coupling) becomes an important mechanism of radiative deactivation. This mechanism provides intensity to specific vibrational satellites by vibrationally induced admixtures of

⁶ An obvious explanation for this behavior simply on the basis of these emission spectra is not easily given, although time-resolved emission spectra (discussed in Sect. 3.4; [44]) show even more clearly that the vibrational modes may indeed be arranged into these two groups. Unfortunately, a group-theoretical classification of the electronic states is not yet available, since the symmetry of the chromophore is not known. Further, it is not totally clear whether or not the states $|I\rangle$ and $|II\rangle$ are degenerate (see Sect. 3.3.1). In the particular situation of degenerate E states (in the D_3 parent group), group-theoretical arguments would not help to explain the forbiddenness of an $E \rightarrow A_1$ (ground state) transition, which would be allowed formally with an $\vec{E} \perp \vec{C}_3$ polarization. Only a quantitative investigation could explain why the corresponding triplet sublevel, for example, would not exhibit a significant spin-orbit coupling to higher lying singlets of E representation.

⁷ For a theoretical background to these considerations see, for example, [86–92, 217–219].

higher lying electronic states to the electronic state $|I\rangle$. Since state $|I\rangle$ is a triplet sublevel, mixing with singlets that carry sufficient allowedness is required. Therefore, modes which are selectively observed in the emission from state $|I\rangle$, but not from state $|II\rangle$, are assigned to HT modes (Table 4).

On the other hand, the transition probability at the electronic origin II ($|II\rangle \leftrightarrow |0\rangle$) is significantly higher than that found for the purely electronic transition at origin I (factor of ≈ 50 ; Sect. 3.3.1). Obviously, state $|II\rangle$, representing also mainly a triplet sublevel, contains a relatively strong contribution from higher lying singlet(s). Such an admixture is usually induced by spin-orbit coupling (e.g., see [81, 86, 89, 90, 93, 217–219]). In this situation, the transition probability induced by vibronic HT coupling is probably too weak to compete significantly with the process induced by direct spin-orbit coupling. Those satellites that are observed in the emission from state $|II\rangle$ are preferentially assigned to Franck-Condon (FC) modes, as already discussed above for the 1495 cm^{-1} mode. The other intense satellites are also classified to FC modes, though with Huang-Rhys factors $S < 0.1$. Such small values allow us only to detect the fundamentals, but prevent the detection of the second members of the respective progressions. This assignment is strongly supported by resonance Raman investigations of Poizat and Sourisseau [211], who classified exactly these modes to totally symmetric FC vibrations (Table 4).

A further aspect is of high interest. It has been demonstrated that the wave functions of states $|I\rangle$ and $|II\rangle$ of $[\text{Ru}(\text{bpy})_3]^{2+}$ in $[\text{Zn}(\text{bpy})_3](\text{ClO}_4)_2$ strongly mix by applying a high magnetic field [178, 180]. However, a mixing to a certain extent seems to be present at already zero magnetic field and ambient pressure, as indicated by a comparison of $[\text{Ru}(\text{bpy})_3]^{2+}$ and $[\text{Os}(\text{bpy})_3]^{2+}$, investigated in the high-symmetry [184] $[\text{Ru}(\text{bpy})_3](\text{PF}_6)_2$ matrix [92, 178]. In this matrix the mixing between the two states is significantly lower for $[\text{Ru}(\text{bpy})_3]^{2+}$ and even nearly absent for $[\text{Os}(\text{bpy})_3]^{2+}$ (see also Sect. 4.1.2). Thus, it may be concluded that the occurrence of FC modes in the state $|I\rangle$ emission of $[\text{Ru}(\text{bpy})_3]^{2+}$ lying at sites of lower symmetry in $[\text{Zn}(\text{bpy})_3](\text{ClO}_4)_2$ is induced by this symmetry reduction. Vice versa, an unclear assignment of modes may be solved by applying high magnetic fields. Those satellites that grow in further in the spectrum of the (field-distorted) state $|I_B\rangle$ are most likely FC modes. This procedure is also used for the assignments given in Table 4 (cf. [92]; Sect. 4.1.4).

Blue-Shifts of Broadband Emission Spectra. The early measured broad and unresolved emission spectra clearly display the differences in vibronic coupling of the two lowest excited states of $[\text{Ru}(\text{bpy})_3]^{2+}$. This is manifested by the blue shift of the broad emission peaks by several hundred wavenumbers with temperature increase [141, 146, 201]. At low temperature mainly the lowest state $|I\rangle$ emits, while with a temperature increase state $|II\rangle$ is thermally populated and its emission with a different satellite structure becomes dominant. Similar shifts were observed by applying heat pulses at $T = 2\text{ K}$ [172], high magnetic fields [122, 178, 180, 199, 220, 221], and when comparing the time-delayed emission spectrum with the short-time spectrum (see Sect. 3.4; [129, 165, 166]).

3.4

Time-Resolved Emission and Spin-Lattice Relaxation in $[\text{Ru}(\text{bpy-h})_3]^{2+}$

At low temperature (e.g., $T = 1.2 \text{ K}$) $[\text{Ru}(\text{bpy})_3]^{2+}$ (doped into $[\text{Zn}(\text{bpy})_3](\text{ClO}_4)_2$) exhibits interesting emission decay properties. For example, when the emission is detected at the electronic origin II (at 17693 cm^{-1}), a fast decay of $220 \pm 10 \text{ ns}$ is observed, while measured at the origin I (17684 cm^{-1}), one obtains the usual and well-known long decay of $230 \pm 3 \mu\text{s}$ (see the insets in Fig. 15). If the spectra are not well-resolved, one always finds a bi-exponential decay, in particular when detecting in the range of the overlapping vibrational satellites. This behavior was found and ascribed already for more than half a decade ago by our group [129]⁸ to processes of spin-lattice relaxation (slr). Since these mechanisms have only rarely been discussed in connection with properties of transition metal complexes, it is useful to briefly introduce the main mechanisms before the properties of $[\text{Ru}(\text{bpy})_3]^{2+}$ are discussed in detail. The following summary is based on [97, 222–227].

Direct Processes of Spin-Lattice Relaxation (slr). Figure 14a shows two electronic states $|I\rangle$ and $|II\rangle$ with an energy separation ΔE of a molecule in a lattice environment. It is assumed that state $|II\rangle$ is populated either by a relaxation from

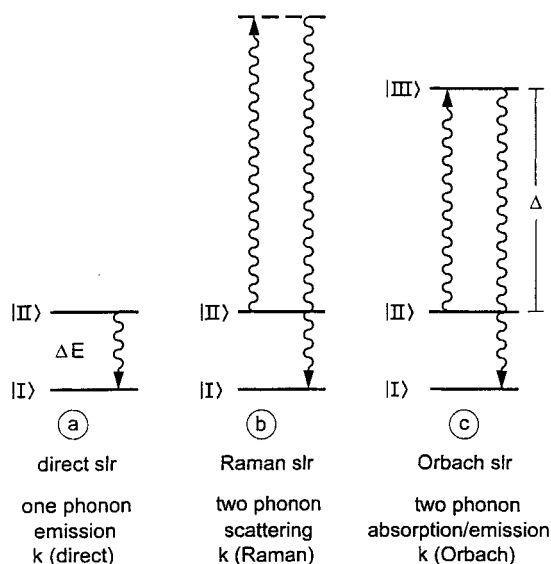


Fig. 14. Important mechanisms of spin-lattice relaxation (slr). $|I\rangle$, $|II\rangle$, and $|III\rangle$ represent electronic states of a molecule. k is the corresponding rate of slr

⁸ The value reported in [129] for the short decay time is slightly smaller than given here, since the time resolution of our early equipment was not sufficient.

a higher lying state, for example, by an intersystem crossing process or by an excitation of just that electronic state. A relaxation from state $|II\rangle$ to state $|I\rangle$ may occur by an emission of one phonon having the energy ΔE . This process is called *direct slr*. The corresponding rate $k(\text{direct})$ can be expressed as (e. g., see [97, 227]):

$$k(\text{direct}) = \text{const} \cdot (\Delta E)^3 \cdot v^{-5} \cdot |\langle II | \hat{H}_1 | I \rangle|^2 \cdot \coth(\Delta E/2k_B T),$$

where v is the mean velocity of sound in the lattice, k_B the Boltzmann constant; the matrix element describes the coupling of the two states by the electron-spin-phonon interaction operator $\hat{H}_1$. At low temperature with $\Delta E \gg k_B T$, $\coth(\Delta E/2k_B T)$ may be approximated by 1. Thus, one obtains the well-known $(\Delta E)^3$ dependence for $k(\text{direct})$. Indeed, in several experimental investigations [227–229], a corresponding dependence of the slr time $T_1(\text{direct}) = k^{-1}(\text{direct})$ on $(\Delta E)^3$ is found at low temperature ($T < 2$ K) and for ΔE values of the order of several cm^{-1} . For $[\text{Ru}(\text{bpy})_3]^{2+}$ discussed here, this process of direct slr is of great importance (see below, [129, 165, 166]). It should be mentioned that, for $\Delta E \leq k_B T$, $k(\text{direct})$ is roughly proportional to $(\Delta E)^2 \cdot T$ (according to the equation given above). Thus, it may be concluded that for compounds with zero-field splittings (zfs) of the triplet sublevels of the order of 0.1 cm^{-1} , the direct rate $k(\text{direct})$ is usually very small at low temperature (e. g., at $T = 1.3$ K) and may be neglected compared to radiative and nonradiative decay rates to the ground state. Consequently, the different sublevels emit independently ([76–82, 84, 101, 213, 216, 232–236]; see also Sect. 2.2.1).

Raman Process of Spin-Lattice Relaxation. In addition to the one-phonon process described above, a two-phonon scattering process according to Fig. 14 b can also occur. The temperature dependence of this Raman process of slr can be approximated (for the non-Kramers situation) at low temperature and for $\Delta E \ll$ phonon energies to $k(\text{Raman}) \sim T^7$ [97, 224, 227]. Also, this process has been observed experimentally [224, 227, 230, 231]. At very low temperature and in the presence of a fast direct process, Raman scattering can usually be neglected.

Orbach Process of Spin-Lattice Relaxation. When a real state $|III\rangle$ lies above the states $|I\rangle$ and $|II\rangle$ with an energy separation Δ above state $|II\rangle$, one phonon may be absorbed, while a second phonon can be emitted from this state $|III\rangle$ ⁹ (Fig. 14 c). This process of slr, called Orbach process, can be described by resonant upward and downward direct processes. The corresponding rate is roughly approximated to [97, 223, 224, 226, 227]:

$$k(\text{Orbach}) = \text{const} \cdot \Delta^3 v^{-5} \exp(-\Delta/k_B T).$$

The importance of the Orbach process has been often demonstrated [97, 223–227, 235, 236]. Recently, it could be shown that this process also governs the

⁹ Occasionally, this energy separation Δ has been approximated by a mean value from $|I\rangle$, $|II\rangle$ to $|III\rangle$ [97, 165].

slr in $[\text{Ru}(\text{bpy})_3]^{2+}$ for $T \gtrsim 6 \text{ K}$ [165, 166]. Note that, in general, all three processes have to be taken into account and may be of different importance in different temperature ranges.

Direct Process of Spin-Lattice Relaxation in $[\text{Ru}(\text{bpy})_3]^{2+}$ at $T = 1.2 \text{ K}$. The effects of slr on emission properties of $[\text{Ru}(\text{bpy})_3]^{2+}$ at $T = 1.2 \text{ K}$ are shown in Fig. 15. After an excitation, for example, into state $|III\rangle$, with a short pulse (e.g., of $\approx 10 \text{ ns}$), the states $|II\rangle$ and $|I\rangle$ are populated by direct processes of slr, which are expected to be very efficient due to the large ΔE values of 52 and 61 cm^{-1} , respectively, and the dependence of the corresponding rates on the third power of ΔE . The relaxation rates from state $|III\rangle$ to the states $|II\rangle$ and $|I\rangle$ have not yet been resolved. At a temperature of $T = 1.2 \text{ K}$ the other processes of slr discussed above are unimportant. On the other hand, due to the small energy separation between the states $|II\rangle$ and $|I\rangle$ of only 8.7 cm^{-1} , the relaxation from the occupied state $|II\rangle$ down to state $|I\rangle$ requires the relatively long spin-lattice relaxation time of $T_1 = 220 \text{ ns}$. At low temperature, this relaxation process $|II\rangle$ to $|I\rangle$ governs the population of state $|II\rangle$. Thus, during the corresponding time (order of T_1), one may register the emission resulting from state $|II\rangle$. Note that this time T_1 should not be confused with the emission lifetime of $8 \mu\text{s}$, which is governed by radiative and nonradiative decays from $|II\rangle$ into the ground state $|0\rangle$ (cf. Crosby et al., e.g., [122, 141]; see Fig. 13).

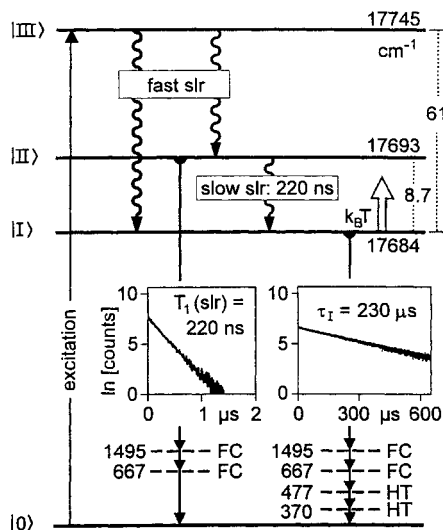


Fig. 15. Energy level diagram for the three lowest excited states of $[\text{Ru}(\text{bpy}-h_8)_3]^{2+}$ in $[\text{Zn}(\text{bpy}-h_8)_3](\text{ClO}_4)_2$. The spin-lattice relaxations (slr) from state $|III\rangle$ to the states $|II\rangle$ and $|I\rangle$ are very fast, but the relaxation from state $|II\rangle$ to $|I\rangle$ is hindered at $T = 1.2 \text{ K}$, due to a slow process of direct phonon emission. This leads to a decay time of $220 \pm 10 \text{ ns}$ [165, 166], while the emission from state $|I\rangle$ decays with the usual emission lifetime of $\tau_I = 230 \mu\text{s}$. Since the states $|II\rangle$ and $|I\rangle$ are deactivated differently by Franck-Condon (FC) and Herzberg-Teller (HT) vibrations, respectively, the emission spectra change distinctly with time (see Fig. 16). Similar properties are also observed for partially and per-deuterated $[\text{Ru}(\text{bpy})_3]^{2+}$ chromophores

Time-Resolved Spectra at $T = 1.2$ K. It is a very interesting behavior that during the time in which state $|II\rangle$ is occupied, given by the time T_1 of relaxation from $|II\rangle$ to $|I\rangle$, state $|II\rangle$ exhibits a well-measurable emission spectrum. This emission can be separated from the much more intense, long-lived component by registering the time-resolved *fast emission*. The spectrum recorded with no time delay with respect to the exciting laser pulse ($t = 0$ ns) and observed (integrated) over a time window of $\Delta t = 300$ ns is reproduced in Fig. 16a. As expected, this fast emission spectrum, resulting from state $|II\rangle$, is very similar to the time-integrated spectrum registered at $T = 10$ K (Fig. 12 b). At this temperature the emission from the thermally occupied state $|II\rangle$ dominates, due to the higher radiative rate from $|II\rangle$ to the ground state $|0\rangle$ compared to the rate from state $|I\rangle$ (Sect. 3.3.1).

After a sufficiently long delay time the initial population of state $|II\rangle$ is depleted, and one can only register the emission from state $|I\rangle$. Figure 16 b depicts the spectrum recorded with a delay time of $t = 10 \mu\text{s}$ and a time window of $\Delta t = 200 \mu\text{s}$. Obviously, this *delayed emission* spectrum is completely different compared to the *fast* one. Again, this is not unexpected since *different* states ($|I\rangle$ and $|II\rangle$) emit. Particularly drastic are the changes in the region of the electronic origins. While the *fast* spectrum shows (nearly) only the origin II line, the *delayed* spectrum exhibits solely the origin I line (Fig. 16 c, d). Moreover, the vibrational structure is very different; the *delayed* spectrum from state $|I\rangle$ (Fig. 16 b) shows many satellites that are not detectable in the *fast* spectrum from state $|II\rangle$. For example, prominent satellites lie at 349, 370, 439, 477, 1015, and 1569 cm^{-1} . These specific modes are indicated in Fig. 16 b and summarized in Table 4. In particular, this time behavior enables us to identify Herzberg-Teller active vibrations (see also Sect. 3.3.2).

One might expect that the *delayed* emission spectrum (Fig. 16 b, d) is similar to the time-integrated one registered at $T = 1.2$ K (Fig. 12 a, c). However, the comparison clearly reveals that the residual nonthermalized intensity from state $|II\rangle$ is present in the time-integrated spectrum. This implies that the usual, time-integrated emission represents a superposition of two spectra.

Orbach process of Spin-Lattice Relaxation in $[\text{Ru}(\text{bpy})_3]^{2+}$ Above $T = 6$ K. According to the very different temperature dependencies of mechanisms of spin-lattice relaxation (see above), it is possible [166] to determine the relevant mechanisms for $[\text{Ru}(\text{bpy})_3]^{2+}$ just from the temperature dependence of the rate of spin-lattice relaxation $k(\text{slr}) = T_1^{-1}$ from state $|II\rangle$ to state $|I\rangle$. T_1 is measured at the energy of the electronic origin II (see Fig. 15). Indeed, Fig. 17 shows that the experimental results (points) are well described by the direct process up to $T \approx 6$ K, while above this temperature the Orbach process strongly grows in. The fitting procedure leads to $\Delta E = (9 \pm 1) \text{ cm}^{-1}$ and $\Delta = (52 \pm 3) \text{ cm}^{-1}$, which are just the energy differences between the three states. The pre-factor to the coth-term of the equation shown in Fig. 17 represents the low-temperature value of T_1^{-1} . The pre-factor of the exponential is usually [165, 223–227] much larger, but a comparison to an independent observable of $[\text{Ru}(\text{bpy})_3]^{2+}$ in $[\text{Zn}(\text{bpy})_3](\text{ClO}_4)_2$ has not yet been discussed in the literature.

For completeness, it is mentioned that the two processes of slr, according to the direct and the Raman mechanism, do not fit the experimental data. Moreover, an

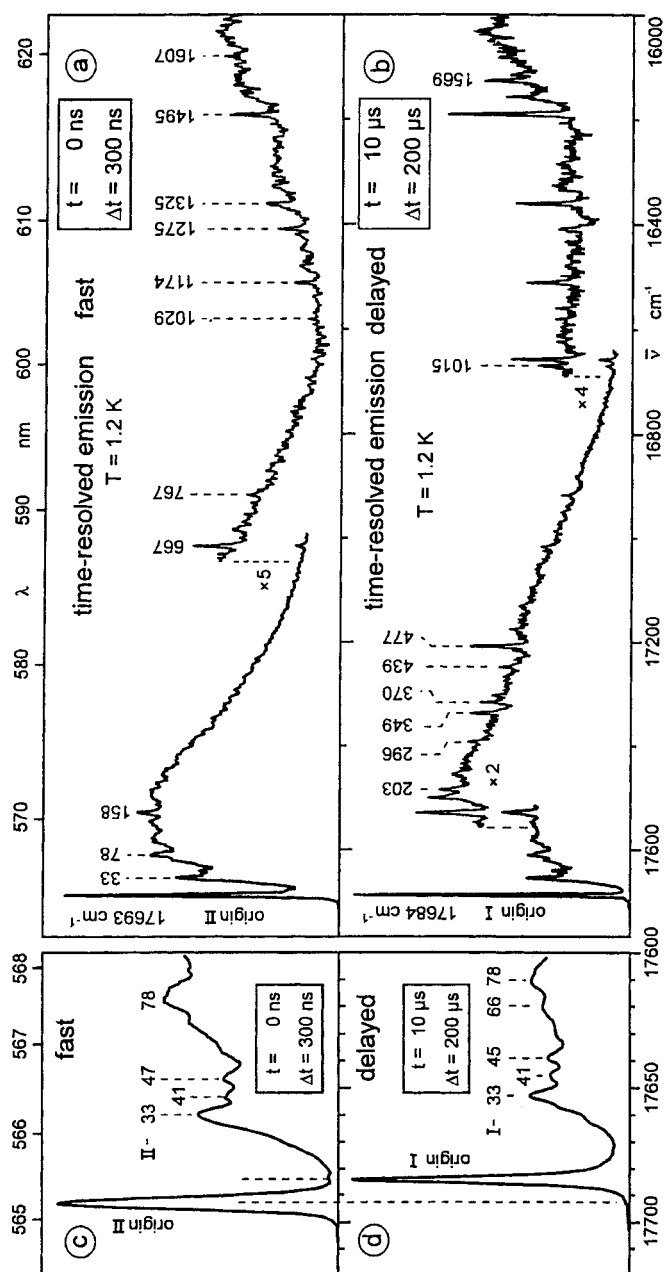


Fig. 16. Time resolved emission spectra of $[\text{Ru}(\text{bpy-h}_8)_3]^{2+}$ in $[\text{Zn}(\text{bpy-h}_8)_3](\text{ClO}_4)_2$ at $T = 1.2 \text{ K}$. a and c are recorded with zero time delay $t = 0 \text{ ns}$ with respect to the exciting laser pulse ($\bar{\nu}_{\text{exc}} = 17745 \text{ cm}^{-1}$, origin III) and integrated over a time window of $\Delta t = 300 \text{ ns}$. b and d are registered with a time delay of $t = 10 \mu\text{s}$ and a time window of $\Delta t = 200 \mu\text{s}$. The region of the two electronic origins is reproduced at an enlarged scale. The vibrational satellites marked in the delayed spectrum b from state |I> are assigned to Herzberg-Teller active vibrations, while all satellites resolved in the fast spectrum a are classified to fundamentals of Franck-Condon modes (see also Table 4)

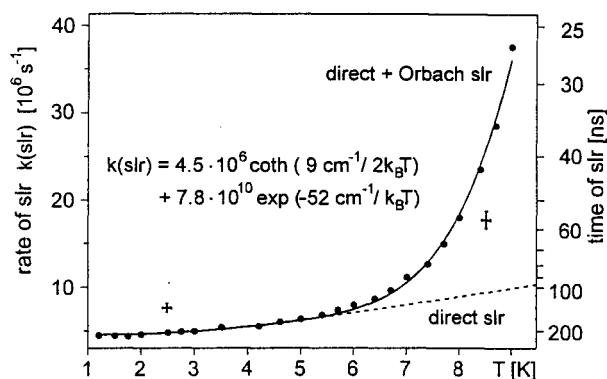


Fig. 17. Spin-lattice relaxation (slr) rate and time of $[\text{Ru}(\text{bpy-h}_8)_3]^{2+}$ in $[\text{Zn}(\text{bpy-h}_8)_3](\text{ClO}_4)_2$ versus temperature for the processes from state $|II\rangle$ to state $|I\rangle$. The experimental data (points) represent the fast emission decay times of state $|II\rangle$, and the solid curve represents the expression (best fit) shown in the diagram [166]. The broken line shows the dependence only according to the direct process of slr

inclusion of the Raman process as an additional third mechanism does not improve the fit. Therefore, it is concluded that the Raman process is not very important in the temperature range studied. Obviously, the occurrence of a real electronic state $|III\rangle$ in the energy vicinity of state $|II\rangle$ strongly favors the Orbach compared to the Raman process.

In summary, the results presented demonstrate that the behavior of the low temperature emission of $[\text{Ru}(\text{bpy})_3]^{2+}$ is dominated by processes of spin-lattice relaxation. In particular, slr is responsible for a spectral shift of the emission with time. This spectral shift with time has nothing to do with a localization of the excitation on one bpy ligand, as proposed in [164].

Arrhenius Plot and Time Resolution. The Boltzmann distribution is often applied to determine the relative population or the corresponding emission intensities of two states at a given temperature. However, this is only possible, if the thermal relaxations between the states are fast compared to other processes, like radiative deactivations (e.g., see [213, 237]). As discussed above, this is not the case for the two lowest excited states of $[\text{Ru}(\text{bpy})_3]^{2+}$ at low temperatures. Thus, it is interesting to see whether a usual Arrhenius plot will display these relatively slow relaxations between the two states. Therefore, in Fig. 18 the plot is carried out for the intensity ratio measured at the electronic origins II and I of the usual, time-integrated emission spectra. Indeed, a significant deviation from an ideal Arrhenius behavior is observable below $T \approx 2.2$ K. This effect is immediately explained by the fact that the emission from the higher lying state $|II\rangle$ cannot be frozen out (see Figs. 16a, c and 12c). Thus, the low-temperature value measured at $T = 1.2$ K is determined by the initial populations of the two states and not by $k_B T$ due to thermal equilibration.

On the other hand, after a certain delay, for example of $t = 10 \mu\text{s}$ (time window $\Delta t = 300 \mu\text{s}$), the states $|I\rangle$ and $|II\rangle$ are in thermal equilibrium, since the

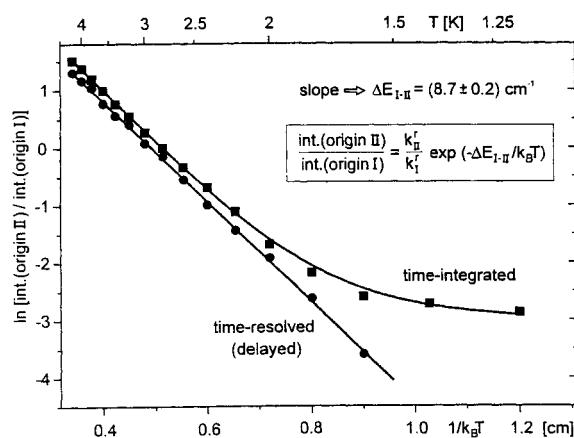


Fig. 18. Arrhenius plots for the emission intensities measured at the electronic origins II and I of $[\text{Ru}(\text{bpy-h}_8)_3]^{2+}$ in $[\text{Zn}(\text{bpy-h}_8)_3](\text{ClO}_4)_2$. The intensity ratio determined from usual, time-integrated emission spectra strongly deviates from a Boltzmann distribution below ≈ 2.2 K due to relatively slow thermalizations, while the intensity ratio determined from time-delayed spectra ($t = 10 \mu\text{s}$, $\Delta t = 300 \mu\text{s}$) follows strict Arrhenius behavior according to the expression given. k_{II}^r , k_{I}^r represent the radiative rates for the purely electronic (0-0) transitions (at the electronic origins). The error is smaller than the size of the experimental points. The curve shown for the time-integrated data is calculated from values known for decay rates, slr rates, and $\Delta E_{\text{I-II}}$.

processes of slr are fast compared to the deactivations into the ground state. One expects to observe strict Arrhenius behavior when the respective emission intensities are taken from time-resolved spectra like those shown in Fig. 16. Indeed, a straight line results, as is demonstrated in Fig. 18. The corresponding activation energy is $\Delta E = (8.7 \pm 0.2) \text{ cm}^{-1}$ and thus represents a value of the same accuracy as found from emission spectra registered with high resolution. Moreover, the Arrhenius plot taken from time-resolved spectra provides the ratio for the radiative rates $k^r(|\text{II}\rangle \leftrightarrow |0\rangle)/k^r(|\text{I}\rangle \leftrightarrow |0\rangle) \approx 50$.

The usual Arrhenius model, which assumes fast equilibration and neglects the relatively slow processes of slr, can be misleading at very low temperatures. However, if the temperature chosen is not too low (e.g., $T \gtrsim 4$ K) or the fraction of non-thermalized emission is relatively small, the simple models describe the situation with the correct tendency. Therefore, the early investigations may still be regarded as being very useful (e.g., see [122, 141, 146, 177, 199]).

Finally, an interesting aspect should be pointed out. Assuming a very fast electron transfer from an excited state of $[\text{Ru}(\text{bpy})_3]^{2+}$ to an acceptor molecule, it might be possible, even at room temperature, that such a process is faster than spin-lattice relaxation (cf. [238, 239]). In this case, a higher lying triplet sublevel might be more important for an electron transfer than the lowest excited state, which is often taken as the most probable candidate. In this situation the knowledge of specific properties of that individual state will help to elucidate the electron transfer process. Possibly, this aspect will further stimulate the investigation of the low-lying triplet sublevels.

3.5

Delocalized Situation in $[\text{Ru}(\text{bpy-h}_8)_2(\text{bpy-d}_8)]^{2+}$. Comparison to $[\text{Ru}(\text{bpy-h}_8)_3]^{2+}$ and $[\text{Ru}(\text{bpy-d}_8)_3]^{2+}$ ¹⁰

It has been demonstrated for $[\text{Pt}(\text{bpy})_2]^{2+}$ ([68]; Sect. 2.3), $[\text{Rh}(\text{bpy})_3]^{3+}$ [44, 60, 108], $[\text{Ru}(\text{bpy})_3]^{2+}$ [44, 85, 108], and $[\text{Os}(\text{bpy})_3]^{2+}$ [104] that isotope marking by deuteration of one or two ligands provides information about the spatial extension of excited states. This is achieved by analyzing the vibrational structures which are connected to the electronic states involved. The basis for this analysis is found in highly resolved, line-narrowed emission and excitation spectra. A localization on a single ligand – as often assumed – does not occur in the three lowest excited states of $[\text{Ru}(\text{bpy})_3]^{2+}$. Similar results are obtained for $[\text{Os}(\text{bpy})_3]^{2+}$ (see Sect. 4.2).

Vibrational Satellites in Emission Spectra. Figure 19 shows emission spectra of $[\text{Ru}(\text{bpy-h}_8)_3]^{2+}$, $[\text{Ru}(\text{bpy-h}_8)_2(\text{bpy-d}_8)]^{2+}$, and $[\text{Ru}(\text{bpy-d}_8)_3]^{2+}$. A comparison of the emission properties of the per-protonated to the per-deuterated complex shows that all effects, which usually occur upon deuteration (e.g., see Sects. 2.3, 4.2; [37, 44, 60, 74, 104]), can be observed, e.g.: (1) specific red shifts of *all* vibrational energies¹¹ (except phonons); (2) a distinct increase in the emission lifetime of state |I> from 230 to 310 μs (Fig. 13; [85]); and (3) a blue shift of the electronic origin I by 40 cm^{-1} [85, 74].

Of special interest are the emission properties of $[\text{Ru}(\text{bpy-h}_8)_2(\text{bpy-d}_8)]^{2+}$. While the homoleptic tris compounds were found to occupy one specific site in $[\text{Zn}(\text{bpy-h}_8)_3](\text{ClO}_4)_2$, partially deuterated complexes have the tendency to occupy different sites. This is expected, when taking the considerations in Section 3.2.2 into account. Thus, the spectrum of $[\text{Ru}(\text{bpy-h}_8)_2(\text{bpy-d}_8)]^{2+}$ (Fig. 19b) is registered for the site of lowest energy. Its electronic origin, lying at 17684 cm^{-1} , is identified similarly as described above (e.g., see Sect. 3.3.1). The transition energy is expected to be somewhat blue-shifted compared to that of the per-protonated compound due to the deuteration of one ligand, but this effect seems to be canceled by the interaction with the crystalline environment. As expected, partial deuteration leads to an increase in the emission decay time (at $T = 1.5 \text{ K}$) of state |I> to $\tau = (253 \pm 5) \mu\text{s}$ [85] compared to 230 μs for the per-protonated compound.

The satellite structure of $[\text{Ru}(\text{bpy-h}_8)_2(\text{bpy-d}_8)]^{2+}$ is assigned (1) to phonon satellites with the same energies as found for the tris compounds (e.g., 33, 47, 66, 78 cm^{-1}); (2) to metal-ligand (M-L) vibrations (most modes between ≈ 100 and $\approx 500 \text{ cm}^{-1}$); and (3) to ligand modes (above $\approx 500 \text{ cm}^{-1}$). The M-L modes cannot be directly correlated with those of the tris compounds, since this would require a complete normal coordinate analysis for each of the complexes, which, however, are not as yet available.

¹⁰ These compounds are investigated in a $[\text{Zn}(\text{bpy-h}_8)_3](\text{ClO}_4)_2$ matrix.

¹¹ For a comparison of the vibrational energies of $[\text{Ru}(\text{bpy-h}_8)_3]^{2+}$ to those of $[\text{Ru}(\text{bpy-d}_8)_3]^{2+}$ see [74, 106, 209, 211].

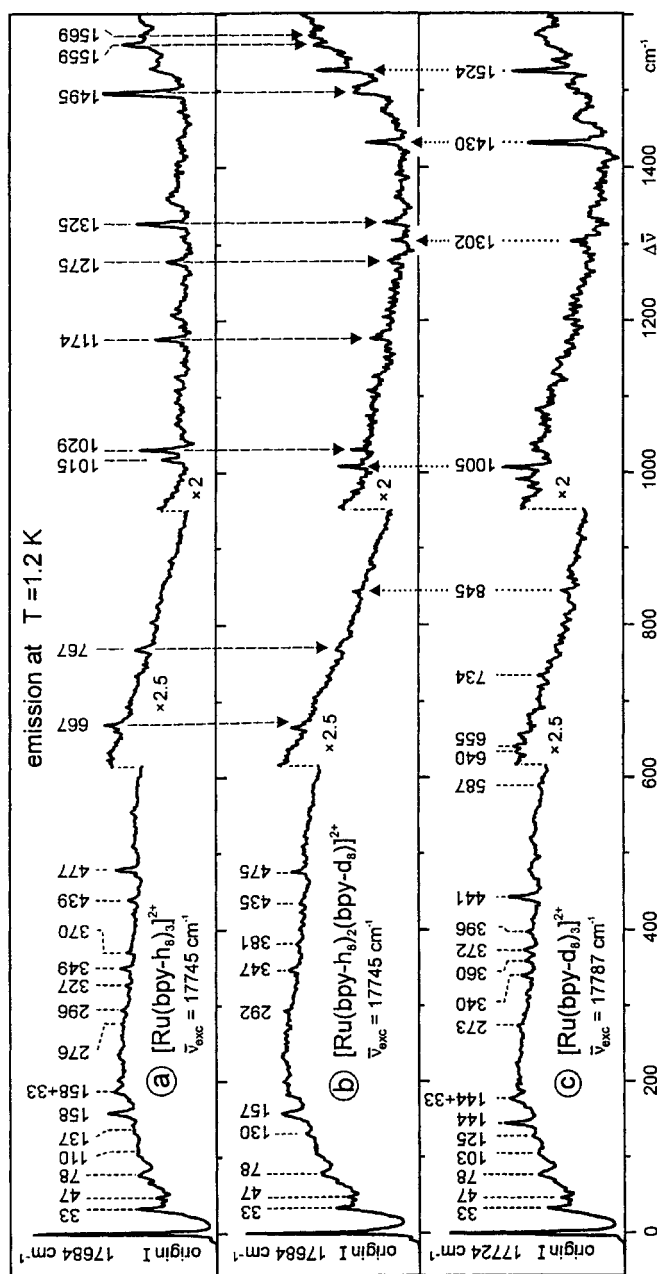


Fig. 19. Emission spectra of a $[\text{Ru}(\text{bpy}-h_8)_3]^{2+}$; b $[\text{Ru}(\text{bpy}-h_8)_2(\text{bpy}-d_8)]^{2+}$; and c $[\text{Ru}(\text{bpy}-d_8)_3]^{2+}$ in $[\text{Zn}(\text{bpy}-d_8)_3](\text{ClO}_4)_2$ at $T = 1.2$ K (cf. [85]). The spectra are selectively excited into the respective electronic origins III. The wavenumber scale gives the separation from the lowest electronic origin I. Note that $[\text{Ru}(\text{bpy}-h_8)_2(\text{bpy}-d_8)]^{2+}$ exhibits – in contrast to $[\text{Rh}(\text{bpy}-h_8)_2(\text{bpy}-d_8)]^{3+}$ [44, 60, 108] – vibrational satellites, which correspond to both types of ligands. This is very strong evidence for a delocalization in the lowest excited state(s). (Due to the better resolution of the spectra compared to those of [85] the vibrational energies given here deviate slightly)

Of extraordinary importance is the structure of satellites in the energy range of the ligand modes above $\approx 500 \text{ cm}^{-1}$ (Fig. 19b). One recognizes immediately that the observed modes are assignable to *both* protonated and deuterated ligands and that they belong to the same electronic origin I at 17684 cm^{-1} . Moreover, the corresponding satellites occur with nearly equal intensities, and no perceptible shifts of the vibrational energies are found compared to those of the tris compounds (Table 5; Fig. 19).¹²

This behavior is in contrast to the one found for $[\text{Pt}(\text{bpy-h}_8)(\text{bpy-d}_8)]^{2+}$ (Sect. 2.3; [68]) and for $[\text{Rh}(\text{bpy-h}_8)_2(\text{bpy-d}_8)]^{3+}$ [44, 60, 108]. The emission spectra of these compounds exhibit only vibrational satellites corresponding to the energetically lower lying protonated ligand(s), while satellites of internal-ligand modes of (bpy-d₈) character do not occur. This behavior allowed us to conclude in Section 2.3 on two important properties of the Pt(II) and Rh(III) complexes: (1) A significant *vibrational* coupling of high-energy vibrational modes via the heavy metal ions or through space (for example, by a multipole coupling, see

Table 5. Electronic origins, emission decay times, and vibrational satellites in the energy range of the ligand modes determined from the emission of the lowest excited state $|1\rangle$ of $[\text{Ru}(\text{bpy})_3]^{2+}$ doped into $[\text{Zn}(\text{bpy})_3](\text{ClO}_4)_2$ ($T = 1.3 \text{ K}$). Experimental errors: $\pm 2 \mu\text{s}$, $\pm 1 \text{ cm}^{-1}$ [83]

$[\text{Ru}(\text{bpy-h}_8)_3]^{2+}$	$[\text{Ru}(\text{bpy-h}_8)_2(\text{bpy-d}_8)]^{2+}$	$[\text{Ru}(\text{bpy-d}_8)_3]^{2+}$
Electronic origins $[\text{cm}^{-1}]$ ^a (Decay times $[\mu\text{s}]$) ^b		
III 17745	17743	17787
II 17693	17693	17732
I 17684 (230)	17684 (253)	17724 (310)
Vibrational satellites in emission $[\text{cm}^{-1}]$		
667	667	
	734	734
767	767	
	845	845
	1005	1005
1029	1029	
1174	1174	
1275	1275	
	1302	1302
1325	1325	
	1430	1430
1495	1495	
	1524	1524
1559	1559	

^a From [74, 83].

^b Emission decay time from [74, 98, 186].

¹² The larger number of vibrational satellites in $[\text{Ru}(\text{bpy-h}_8)_2(\text{bpy-d}_8)]^{2+}$ and the combinations of these with phonons result in a somewhat more pronounced background for the partially deuterated compound compared to the tris complexes.

also [111]) can be ignored (see also [112–114]). (2) An *electronic* ligand-ligand coupling is extremely small, which is in agreement with the ${}^3\pi\pi$ -LC character of the excited electronic states involved (Sects. 2.2, 2.5; [44, 60, 108]).

The situation of *vibrational* coupling (via the metal or through space) is expected to be nearly identical in $[\text{Ru}(\text{bpy-h}_8)_2(\text{bpy-d}_8)]^{2+}$ as in $[\text{Rh}(\text{bpy-h}_8)_2(\text{bpy-d}_8)]^{3+}$. Consequently, an occurrence of both types of vibrational internal-ligand satellites belonging to the same electronic origin in the emission of $[\text{Ru}(\text{bpy-h}_8)_2(\text{bpy-d}_8)]^{2+}$ (Fig. 19b; Table 5) forces one to conclude that the emitting, electronic state is spatially extended or delocalized over both (bpy-h₈) and (bpy-d₈) ligands. Obviously, the MLCT character induces an electronic coupling and thus the delocalization (cf. also Sect. 3.1). Similar conclusions with respect to the spatial extension of electronic states and the occurrence of vibrational satellites in vibronic spectra have been drawn for a long time for many other larger molecules (in particular see [91, 240, 241] and references therein; cf. also [83, 85, 104, 108]). For further considerations see below and Sects. 3.8 and 4.2.2.

Line-Narrowed Excitation Spectra and $[\text{Ru}(\text{bpy})_3]^{2+}$ Aggregates. It is also very instructive to discuss excitation spectra (Fig. 20). In the region of the electronic origins they can be well resolved by applying the technique of excitation line-narrowing. This is achieved if the detection energy is chosen to select only a small spectral range of the inhomogeneously broadened emission of line I. Figure 20a shows the line-narrowed excitation spectrum of $[\text{Ru}(\text{bpy-h}_8)_3]^{2+}$. The electronic origins II and III with line half-widths of $\approx 1.2 \text{ cm}^{-1}$ can be clearly observed. They occur together with a series of lattice mode satellites (see also Table 4). Both electronic origins are accompanied on their blue sides by spectrally broader features (half-widths $\approx 3.6 \text{ cm}^{-1}$), which cannot be assigned to phonon satellites due to their very small energy separations of $\approx 2.5 \text{ cm}^{-1}$ to the sharp origins. These broader features exhibit some peculiarities. (1) They disappear when detected at the high energy side of the inhomogeneously broadened origin line I, but the sharp lines can still be registered. (2) Their relative intensities vary at least by a factor of 2 according to the selected area of the crystal, depending on whether deeply or only slightly red colored sections are chosen, and on the concentration of the doped chromophores. The inset in Fig. 20a shows the corresponding features measured on the same crystal for the range of the electronic origin III. Similar behavior is found for the per-deuterated complex (Fig. 20c).

According to the discussion in Section 3.2.1, one has to take into account that the $[\text{Ru}(\text{bpy})_3]^{2+}$ complexes in the $[\text{Zn}(\text{bpy})_3](\text{ClO}_4)_2$ matrix are not statistically distributed. An accumulation of $[\text{Ru}(\text{bpy})_3]^{2+}$ to aggregates or nearest-neighbor arrangements occurs. Applying the line-narrowing technique, it is possible to select $[\text{Ru}(\text{bpy})_3]^{2+}$ species in the same environment, and one obtains the sharp origins. However, the selected species have nearest neighbors, which are inhomogeneously distributed. Thus, if these neighbors are excited and if they transfer their excitation energy to the species selected, one may observe inhomogeneously broadened features at the blue sides of the sharp origins. The relative intensities and half-widths of these broader features depend (1) on the detection energy, which lies within the inhomogeneous distribution of transition $|I\rangle \rightarrow |0\rangle$; (2) on the individual (and unknown) nearest-neighbor arrange-

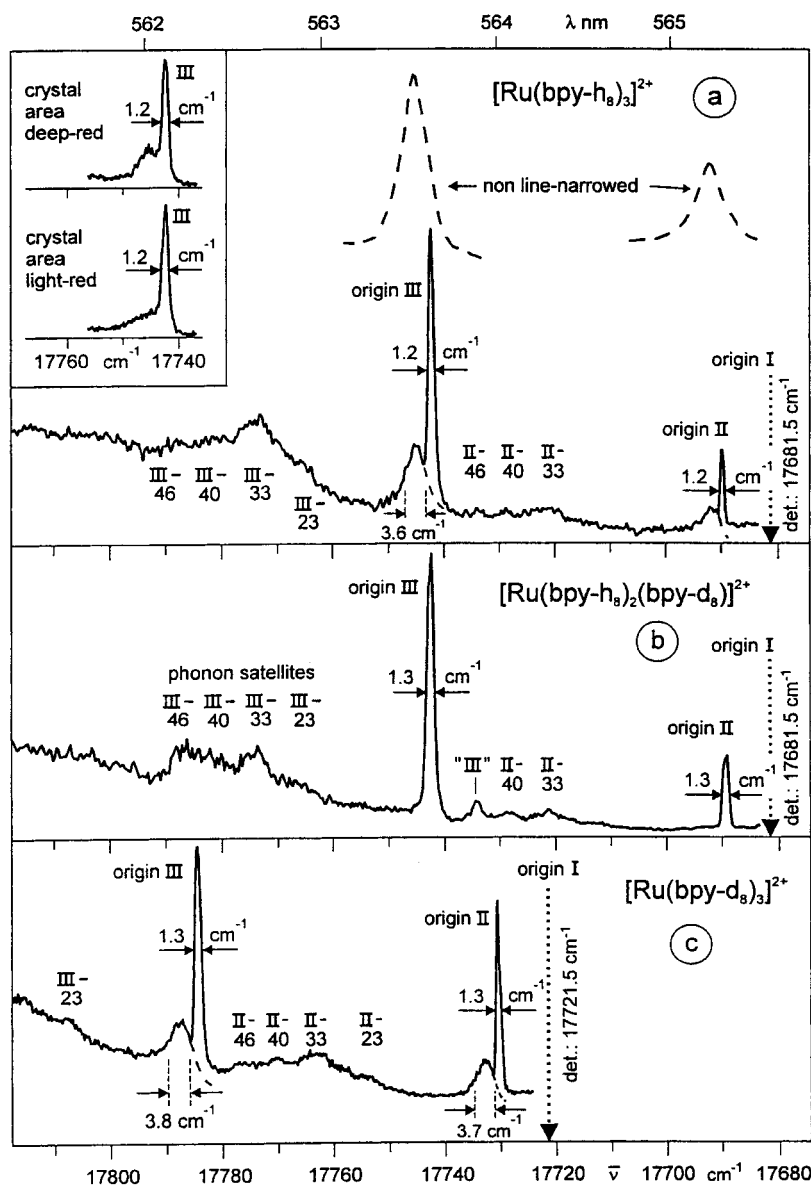


Fig. 20. Line-narrowed excitation spectra at $T = 1.2$ K of a $[\text{Ru}(\text{bpy-h}_8)_3]^{2+}$; b $[\text{Ru}(\text{bpy-h}_8)_2(\text{bpy-d}_8)]^{2+}$; and c $[\text{Ru}(\text{bpy-d}_8)_3]^{2+}$ in $[\text{Zn}(\text{bpy-h}_8)_3](\text{ClO}_4)_2$. The crystals were grown from aqueous solutions having molar ratios of $\text{Ru(II)}:\text{Zn(II)}$ in a, b: 0.5 %; c: 0.3 %; inset 0.03 %. The spectra show the electronic origins II and III and the corresponding phonon satellites. For detection the energy of the respective electronic origin I is chosen. Peak "III" represents an unavoidable artifact (see text). The inset shows the excitation structures of the electronic origin III (same cm^{-1} scale) measured at two positions of the same crystal. The spectral change displays the differences in clustering of the $[\text{Ru}(\text{bpy})_3]^{2+}$ chromophores (see Sect. 3.2.1)

ments; and (3) on the efficiencies of radiationless energy transfer to the species selected. In Section 3.6 the importance of an energy transfer between nearest neighbors will be demonstrated for different sites in $[\text{Ru}(\text{bpy-h}_8)_3](\text{PF}_6)_2$. The transfer process between non-resonant neighbors in this compound is governed by a 60 ns process [185]. Thus, emission decay and/or rise times in this order of magnitude for the nearest neighbors within the aggregates are also expected to be found. Indeed, such effects in a 20 ns time regime have been reported in [163] to occur for $[\text{Ru}(\text{bpy})_3]^{2+}$ in $[\text{Zn}(\text{bpy})_3](\text{ClO}_4)_2$. However, in [163] these effects are not ascribed to aggregates, but to a slow process of energy transfer between different ligands of the same complex. In such a model the broader features should exhibit fixed ratios relative to the sharp, line-narrowed electronic origins, but these ratios should neither depend on concentrations of the chromophores nor on the crystal area selected, contrary to the experimental results.

Manifold of Low-Lying Electronic States in $[\text{Ru}(\text{bpy-h}_8)_2(\text{bpy-d}_8)]^{2+}$. Figure 20b shows the line-narrowed excitation spectrum of $[\text{Ru}(\text{bpy-h}_8)_2(\text{bpy-d}_8)]^{2+}$. The emission is detected at origin I. One clearly finds the electronic origins of the two lowest excited states $|II\rangle$ and $|III\rangle$, but the broader features at the blue sides of the sharp peaks are not detected for the crystals investigated. This behavior indicates that the partially deuterated complexes are differently built into the $[\text{Zn}(\text{bpy})_3](\text{ClO}_4)_2$ matrix compared to the per-complexes; this is not unexpected according to Section 3.2.1.

It is emphasized that the excitation spectrum of $[\text{Ru}(\text{bpy-h}_8)_2(\text{bpy-d}_8)]^{2+}$ does not exhibit any additional electronic transition¹³ compared to the tris compounds. Note that the occurrence of two additional and distinct origins would be required to support the localized model proposed by Riesen and Krausz [162]. These authors investigated a spectral range (of line-narrowed excitation spectra) being too small to give support for their model. Moreover, they interpreted the overlapping phonon satellites to state $|III\rangle$ of 23, 33, 40, and 46 cm^{-1} as an additional electronic origin required by their model [162]. Thus, Fig. 20b shows directly that this model [162] breaks down (see also Sect. 3.8.1).

Intramolecular Excitation Hopping and Time Ranges – A Different Model? A hypothetical alternative model, in which we assume the occurrence of a localization due to some nuclear rearrangements on one of the three ligands of the

¹³ The occurrence of an additional peak, called “III” in Fig. 20b, might be surprising. It represents a peak resulting from an “artifact”, which is necessarily connected with the procedure of measuring line-narrowed excitation spectra, when the inhomogeneous line width is broader than the energy separation between lines I and II (8.7 cm^{-1} ; Fig. 15). This is the case for the partially deuterated complex doped into $[\text{Zn}(\text{bpy-h}_8)_3](\text{ClO}_4)_2$. By selecting the detection energy lying within the distribution of line I, some residual emission intensity of other complexes, having their emission line II just at that detection energy, cannot be avoided. Thus, the excitation peak “III” is connected to the emission due to line II, and appears exactly 8.7 cm^{-1} below line III. Indeed, the peak “III” displays the temperature and time behavior of the emission of state $|II\rangle$ (Sects. 3.3.1 and 3.4). Consequently, its appearance may be disregarded in the discussed context.

partially deuterated complex will now be discussed (see also Sect. 3.8). In particular, it is of interest to study what happens (at low temperature) when hopping, tunneling, or energy transfer processes occur from one ligand to another one. For this discussion it is appropriate to distinguish three time ranges, which depend on the relative magnitudes of the emission lifetime τ , the hopping, tunneling, or energy transfer time t_h , and the time t_n needed for a nuclear relaxation accompanying a localization process. t_n is of the order of 10^{-13} to 10^{-12} s (cf. [85, 104, 129]). (1) In the limit of $\tau \lesssim t_h$, the emission would preferentially occur from the (Ru-bpy- h_8) or (Ru-bpy- d_8) subunit, which is occupied in the first moment, presumably by a statistical distribution. Both subunits should manifest themselves by the occurrence of two electronic origins and two distinctly different emission lifetimes corresponding to the respective subunits. This behavior, however, is *not* found experimentally (Figs. 19b, 20b; Table 5). (2) For the time range $\tau \gg t_h \gg t_n$, a mono-exponential decay with a mean decay time is expected. However, the (Ru-bpy- h_8) and (Ru-bpy- d_8) subunits of $[\text{Ru}(\text{bpy-}h_8)_2(\text{bpy-}d_8)]^{2+}$ should possess different energy positions for their electronic origins due to the isotope-induced blue shift for the (Ru-bpy- d_8) subunit. Again, this behavior is not found experimentally. (3) A very fast hopping or tunneling with $t_h \ll t_n \approx 10^{-12}$ s is physically similar to a delocalized excitation because the nuclei cannot follow the electronic motions. For this situation one expects to find a mono-exponential emission decay and a single electronic origin. Such behavior is found experimentally for $[\text{Ru}(\text{bpy-}h_8)_2(\text{bpy-}d_8)]^{2+}$.

In summary, the experimental results show that the lowest excited state $|I\rangle$ of $[\text{Ru}(\text{bpy-}h_8)_2(\text{bpy-}d_8)]^{2+}$ in $[\text{Zn}(\text{bpy})_3](\text{ClO}_4)_2$ is delocalized over the different ligands and the metal. Thus, the lowest state will also be delocalized in the more symmetric per-complexes. These conclusions may also be extended to the second and the third excited state due to similar behavior with respect to the occurrence of vibrational ligand satellites in the emission of state $|II\rangle$ [98] and due to the same blue shifts found for all three electronic origins upon per-deuteration [74].

3.6

Radiationless Energy Transfer Between Different Sites in $[\text{Ru}(\text{bpy})_3](\text{PF}_6)_2$

The determination of the low-temperature structure of $[\text{Ru}(\text{bpy-}h_8)_3](\text{PF}_6)_2$ revealed the existence of three different crystallographic sites, where $[\text{Ru}(\text{bpy})_3]^{2+}$ sits on C_3 positions [184]. This crystallographic study confirms the spectroscopic investigations of $[\text{Os}(\text{bpy})_3]^{2+}$ doped into $[\text{Ru}(\text{bpy})_3](\text{PF}_6)_2$, where the guest molecules clearly display the occurrence of the three sites ([38, 92]; see also Sect. 4.1). However, for neat $[\text{Ru}(\text{bpy})_3](\text{PF}_6)_2$ only one spectroscopic site has been identified in earlier investigations (e.g., see [146, 180]). This site of lowest energy is designated as site A. Later, in [185], a second site B of $[\text{Ru}(\text{bpy})_3]^{2+}$ could also be detected spectroscopically. It is subject of this section to report on studies of energy transfer between the two sites.

Figure 21a shows the emission spectrum of $[\text{Ru}(\text{bpy})_3](\text{PF}_6)_2$ measured at $T = 1.3$ K. It is not well resolvable apart from the energy range, where the lowest

electronic origins occur.¹⁴ The broad bands result mainly from superpositions of vibrational satellites and their combinations with strongly coupled phonons. It has been shown that bands I and II stem mainly from the electronic states $|I\rangle$ and $|II\rangle$, respectively, with different vibronic coupling properties (Sect. 3.3.2). These two states are $6.9 \pm 0.2 \text{ cm}^{-1}$ apart. They lie about 125 cm^{-1} higher than the corresponding states of $[\text{Ru}(\text{bpy})_3]^{2+}$ doped into a $[\text{Zn}(\text{bpy})_3](\text{ClO}_4)_2$ matrix (see Table 3; [126, 178, 180, 199]).

The lowest electronic origins I and II of site B are found 19 and 18 cm^{-1} , respectively, above the corresponding origins of site A. The emission intensities at the origins of site B are by more than an order of magnitude smaller than those of site A. Moreover, the emission decay measured at origin I at 17828 cm^{-1} (site B) is mono-exponential over more than four lifetimes with $\tau(B, |I\rangle \rightarrow |0\rangle) = 60 \pm 10 \text{ ns}$ (Fig. 21 c). This value is by a factor of about 4000 smaller than the usual lifetime of state $|I\rangle$ at the same temperature of 1.2 K ($\tau(A, |I\rangle \rightarrow |0\rangle) = 250 \mu\text{s}$; Fig. 21 e). According to [185], this short emission lifetime τ_B is determined by a radiationless energy transfer from a $[\text{Ru}(\text{bpy})_3]^{2+}$ complex at site B to a neighboring one at site A. The corresponding transfer rate of $k(B \rightarrow A) \approx 1/\tau(B) = 1.7 \cdot 10^7 \text{ s}^{-1}$ between nearest neighbors is relatively small. This smallness may be ascribed to the very small spectral overlap (e.g., see [243, 244]) between donor emission (site B) and acceptor absorption (site A).

According to the identification of three crystallographic sites [184], one also expects the presence of a third spectroscopic site (site C) which should lie at higher energy than site B. Moreover, when $[\text{Os}(\text{bpy})_3]^{2+}$ is doped into $[\text{Ru}(\text{bpy})_3](\text{PF}_6)_2$ three spectroscopic sites of the probing guest molecules can be identified. The energy separation between sites A and B of $[\text{Os}(\text{bpy})_3]^{2+}$ is nearly equal to the separation between sites B and C (see Table 6; [38]; Sect. 4.1.2). Due to the similarity of $[\text{Os}(\text{bpy})_3]^{2+}$ and $[\text{Ru}(\text{bpy})_3]^{2+}$, this suggests that in neat $[\text{Ru}(\text{bpy})_3](\text{PF}_6)_2$ the origins of site C should lie approximately 20 cm^{-1} higher in energy than the origins of site B. However, the absorption in this spectral region, resulting from site A, is relatively high. Consequently, the spectral overlap integral and therefore the energy transfer probability [243, 244] from site C to site A is drastically increased compared to the transfer from site B to site A.

Table 6. Electronic origins [cm^{-1}] of the two lowest excited states $|I\rangle$ and $|II\rangle$ of $[\text{Ru}(\text{bpy})_3]^{2+}$ and $[\text{Os}(\text{bpy})_3]^{2+}$ in neat $[\text{Ru}(\text{bpy})_3](\text{PF}_6)_2$ [185]

Site	$[\text{Ru}(\text{bpy})_3]^{2+}$		$[\text{Os}(\text{bpy})_3]^{2+ \text{ a}}$	
	$ I\rangle$	$ II\rangle$	$ I\rangle$	$ II\rangle$
A	17809	17816	14423	14495
B	17828	17834	14460	14521
C	– ^b	– ^b	14496	14566

^a From [38], see also Section 4.1.1.

^b Not yet identified spectroscopically.

¹⁴ In ref [242] it is shown that a small number of vibrational satellites may be resolved.

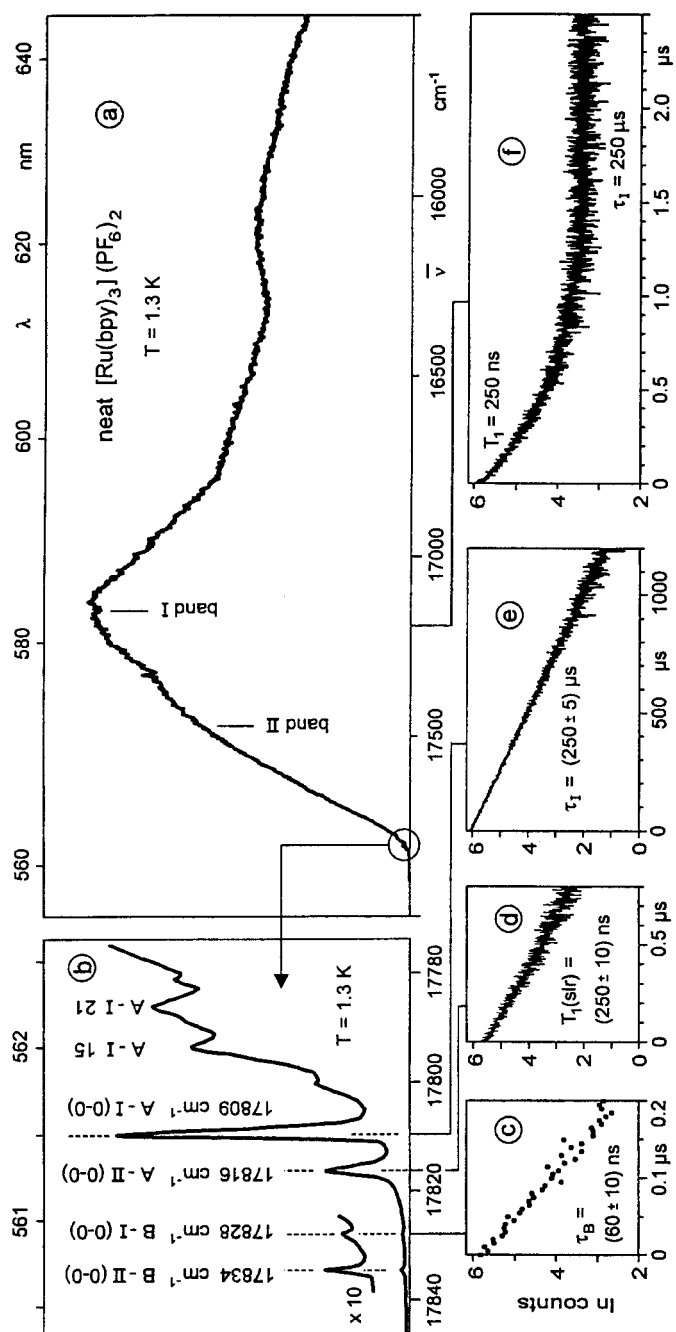


Fig. 21. Emission spectra and decay properties of neat $[\text{Ru}(\text{bpy})_3](\text{PF}_6)_2$, a survey of the broadband spectrum at $T = 1.3 \text{ K}$. Bands I and II correspond to the emission from state |I> and |II>, respectively. The bands are not resolved mainly due to overlapping vibrational and phonon satellites. b Spectral range of the electronic origins I and II at an enlarged scale. A and B represent different crystallographic sites. c Emission decay of the energetically higher lying site B. τ_B is determined by a radiationless energy transfer from site B to site A. d Emission decay of state |II> (site A) determined by spin-lattice (slr) relaxation due to the direct process of slr from state |I> and state |II>. e Usual emission decay from state |I>. f Two-component decay due to superimposed emissions from state |I> and state |II>

Additionally, an energy transfer from site C to site B is possible. Therefore, a very effective energy transfer totally quenches the *emission* of such a higher lying site. On the other hand, the *absorption* resulting from site A at the energy expected for the position of site C is too strong and thus the relatively weak origins of site C could not be detected in absorption or in excitation spectra [34, 126, 179].

Interestingly, at $T = 1.3$ K the emission of state $|I\rangle$ of site B is quenched more effectively by energy transfer than the emission of state $|II\rangle$ (cf. the intensity ratios of the origin lines in Fig. 21 b). This can be explained by the fact that the two donor states $|I\rangle$ and $|II\rangle$ are thermally not equilibrated according to the relatively slow spin-lattice relaxation (see Sect. 3.4). An equivalent behavior is induced by a fast radiationless energy transfer at low temperature from the $[\text{Ru}(\text{bpy})_3]^{2+}$ site A to an $[\text{Os}(\text{bpy})_3]^{2+}$ acceptor doped into $[\text{Ru}(\text{bpy})_3](\text{PF}_6)_2$ [35, 36].

Figure 21 also shows the emission decay measured at other spectral positions of the chromophores occupying site A. Though this behavior seems to be very complicated, an explanation is immediately given on the basis of the facts presented in Section 3.4. At 17816 cm^{-1} (origin II, site A), one observes the spin-lattice relaxation time from state $|II\rangle$ to state $|I\rangle$ according to a direct process. This relaxation of $T_1 = 250 \pm 10\text{ ns}$ at $T = 1.3\text{ K}$ (Fig. 21 d) is about 20% longer than that found for $[\text{Ru}(\text{bpy}-h_8)_3]^{2+}$ doped into $[\text{Zn}(\text{bpy}-h_8)_3](\text{ClO}_4)_2$. However, in this comparison, the T_1 values should scale according to the $(\Delta E)^3$ dependence by the factor $(8.7\text{ cm}^{-1}/6.9\text{ cm}^{-1})^3 = 2.0$. Thus, one would even expect a 100% longer slr time for $[\text{Ru}(\text{bpy})_3](\text{PF}_6)_2$. It is concluded that the slr is more effective in the neat material than in the doped matrix (see Sect. 3.4).

Finally, the decay time of $\tau_I = 250\text{ }\mu\text{s}$ measured at origin I of site A represents the usual emission decay of this triplet sublevel (Fig. 21 e). Due to the fact that in the spectral range of the unresolved satellite structures (e.g., at $\approx 17200\text{ cm}^{-1}$) emission components of states $|II\rangle$ and $|I\rangle$ are superimposed, one finds the expected bi-exponential decay (Fig. 21 f; cf. Fig. 15). There is no indication of processes which could be related to a localization in the excited states.

3.7

Localized Situation in $[\text{Ru}(\text{i-biq})_2(\text{bpy})_2]^{2+}$

In the preceding sections it was demonstrated that the lowest excited states of $[\text{Ru}(\text{bpy})_3]^{2+}$ doped into $[\text{Zn}(\text{bpy})_3](\text{ClO}_4)_2$ are delocalized. Confirmation is based on more *physical or spectroscopic* arguments. Thus, it is also highly attractive to present a case study, in which a localization on a (Ru-bpy) subunit is *chemically* induced. Such a situation is achievable with the very specific $[\text{Ru}(\text{i-biq})_2(\text{bpy})]^{2+}$ complex (with i-biq = 2,2'-bis-isoquinoline). This case study was already proposed more than a decade ago [245]. Based on emission and absorption data as well as on oxidation and reduction potentials measured for the whole series of $[\text{Ru}(\text{i-biq})_{3-n}(\text{bpy})_n]^{2+}$ compounds (with $n = 0-3$), the authors [245] came to the important conclusion that the lowest excited states are of $^3\text{MLCT}$ character and are confined to the (Ru-bpy) subunit, while the (i-biq) ligands may be regarded as "spectator ligands". This behavior is strongly sup-

ported by the fact that the lowest excited states of $[\text{Ru}(\text{i-biq})_3]^{2+}$ are of ^3LC character [246, 247].

The obvious question is whether both compounds, $[\text{Ru}(\text{bpy})_3]^{2+}$ and $[\text{Ru}(\text{i-biq})_2(\text{bpy})]^{2+}$, exhibit nearly the same spectroscopic properties, as is expected for a localized excitation in $[\text{Ru}(\text{bpy})_3]^{2+}$ or whether one observes a distinctly dissimilar behavior. Emission spectra measured above 80 K did not reveal any clear difference [245]. However, it cannot be excluded that crucial effects are smeared out at this relatively high temperature, where only broad bands can be recorded. Indeed, this is the case for the very characteristic values of zero-field splittings (zfs) into the low-lying triplet sublevels [248].

To illustrate how these values of zfs are determined by a chemical substitution, a series of homo- and heteroleptic compounds is studied. The data are summarized in Table 7. In particular, for $[\text{Ru}(\text{bpy})_2(\text{bpz})]^{2+}$ and $[\text{Ru}(\text{bpy})_2(\text{bpdz})]^{2+}$, the lowest excited states are – in general agreement [85, 196, 198, 210, 248–253] – localized on the (Ru-bpz) and the (Ru-bpdz) subunit, respectively. Interestingly, in these situations the values of zfs ΔE_{I-II} and ΔE_{I-III} are $\approx 100\%$ and $\approx 70\%$ larger, respectively, than those for the related tris compounds $[\text{Ru}(\text{bpz})_3]^{2+}$ and $[\text{Ru}(\text{bpdz})_3]^{2+}$.¹⁵ This behavior is easily understood if one takes into account that the amount of zfs into triplet sublevels is strongly dependent on spin-orbit coupling (soc) and that the soc constant is about two orders of magnitude larger for the $4d$ -orbitals of Ru^{2+} than for the π^* orbitals of the ligands (cf. [136, 254, 255] to [256, 257]). Effects resulting from these properties have already been studied on the basis of experimental data. In particular, it has been shown for a series of different transition metal complexes [44, 60, 83] that the importance of the d -orbital admixture can be directly correlated to the amount of zero-field splitting of $^3\text{MLCT}$ states. Thus, it may be concluded that the more ligands (with π^* orbitals) are involved in the wavefunctions of a $^3\text{MLCT}$ state, the smaller is the relative influence of the central metal ion. Thereby, the average influence of soc on the corresponding state is reduced. This implies that the values of zfs of a $^3\text{MLCT}$ state is reduced with an increasing number of organic ligands, which are electronically involv-

¹⁵ It is of interest to mention that the spatial confinement of the charge distribution in the lowest excited state(s) of $[\text{Ru}(\text{bpy})_2(\text{bpz})]^{2+}$ to the (Ru-bpz) subunit is also distinctly displayed in the vibrational satellite structure of the emission spectrum, if sufficiently well resolved. For example, for $[\text{Ru}(\text{bpy})_2(\text{bpz})]^{2+}$ in $[\text{Zn}(\text{bpy})_3](\text{ClO}_4)_2$, one clearly finds the vibrational bpz modes as satellites [248] at 798 (798), 1074 (1074), 1020 (1024), 1034 (1034), 1049 (1049), 1347 (1347), 1508 (1508), and 1568 (1568) cm^{-1} . The numbers in parentheses represent the values found for $[\text{Ru}(\text{bpz})_3]^{2+}$ in the same matrix ([248]; cf. also [210]). Of importance is the fact that *none* of the wellknown ligand satellites of $[\text{Ru}(\text{bpy})_3]^{2+}$ occurs in the spectrum of $[\text{Ru}(\text{bpy})_2(\text{bpz})]^{2+}$. In particular, this is confirmed for the vibrational satellites of highest intensity found at 767, 1015, 1029, 1174, 1275, 1325, 1495, and 1559 cm^{-1} (see Fig. 12; Table 4). This behavior demonstrates that the bpy ligands are not involved in the lowest excited states of $[\text{Ru}(\text{bpy})_2(\text{bpz})]^{2+}$. In ref [85] we came to the same conclusion. Unfortunately, the sample investigated at that time contained a very small amount of an impurity, which led to three additional peaks in the energy range of the ligand satellites (at 1544, 1563, and 1581 cm^{-1}) and which were erroneously also ascribed to bpz modes. Thus, these three lines should be disregarded in [85].

Table 7. Zero-field splittings (zfs) of the lowest $^3\text{MLCT}$ term of various homo- and heteroleptic Ru(II)-compounds

[Zn(bpy) ₃](ClO ₄) ₂ matrix	zfs of $^3\text{MLCT}$ [cm ⁻¹]		References and remarks
	ΔE_{I-II}	ΔE_{I-III}	
[Ru(bpy) ₂ (bpz)] ²⁺ ^a	18 ± 0.5	95 ± 1	[198, 85] Localized
[Ru(bpz) ₃] ²⁺	8.5 ± 0.3	54 ± 1	[248] ^b
[Ru(bpy) ₂ (bpdz)] ²⁺ ^a	15 ± 0.5	95 ± 1	[248, 196] Localized
[Ru(bpdz) ₃] ²⁺	8 ± 0.3	61 ± 1	[248, 196] ^b
[Ru(i-biq) ₂ (bpy)] ²⁺	15 ± 2	80 ± 3	[248] Localized ^c
[Ru(bpy) ₃] ²⁺	8.7 ± 0.2	61 ± 0.5	Fig. 13 Delocalized ^d

bpz = 2,2'-bipyrazine; bpdz = 3,3'-bipyridazine; i-biq = 2,2' bis-isoquinoline

^a Values given for the site of lowest energy.

^b Lowest excited states presumably delocalized.

^c See Section 3.7.

^d See Sections 3.5 and 3.8.

ed. In other words, an increasing spatial spread of the excited state wavefunction(s) into non-metal regions (of the type of ligands discussed here) reduces the amount of zero-field splittings.

The properties described imply an important message for [Ru(bpy)₃]²⁺, as is clearly displayed in the comparison of [Ru(bpy)₃]²⁺ with [Ru(i-biq)₂(bpy)]²⁺ (Table 7). The zfs ΔE_{I-II} and ΔE_{I-III} increase by more than 70 and 30 %, respectively, according to the reduced spatial spread of the wavefunctions to only one single ligand in the $^3\text{MLCT}$ state of [Ru(i-biq)₂(bpy)]²⁺ compared to the involvement of three ligands in [Ru(bpy)₃]²⁺. In the situation of a localization in both compounds one would not expect to observe any obvious difference. Therefore, the results described in this section and in [248] clearly demonstrate the delocalized situation in [Ru(bpy)₃]²⁺.

3.8

Localization Models and Their Spectroscopic Fingerprints – Alternative Views

The properties of the lowest excited states of [Ru(bpy)₃]²⁺ have been discussed in the context of three different models. Two of the models – though mutually excluding – favor a localization of the excitation on one ligand (Sects. 3.8.1 and 3.8.2), while the third one, strongly supported by the results presented in this review, is based on a delocalized description (in particular, see Sects. 3.5 and 3.7). It seems to be appropriate to sketch the basic ideas and physical consequences of the two localization models and to compare predictions of these models to the experimental situation.

3.8.1

Weak Ligand-Ligand Coupling and Localization by a Weak Distortion

It is suitable to discuss in a first step the situation of LC triplets of $\pi\pi^*$ character and to assume that a weak ligand-ligand interaction exists. If the different ligands are symmetry related (e.g., by a C_2 operation), the excited state wavefunctions can be described by symmetry-adapted linear combinations of wavefunctions of the individual ligands. The resulting wavefunctions correspond to a delocalized description (e.g., see [258]). In particular, one of the resulting electronic states of the coupled system is energetically stabilized by an energy called B with respect to the uncoupled situation. With the weak ligand-ligand coupling assumed it is expected that B is of the order of only one or a few cm^{-1} , similar to triplet exciton bandwidths in organic solid state compounds ([62c, 259–262]; see also discussion in [179]). In a second step, the effect of the transition metal is introduced by allowing an additional weak admixture of $^3\text{dd}^*$ or $^3\text{MLCT}$ states to the $^3\pi\pi^*$ states as well as weak spin-orbit coupling. This will lead to an increase in the effective ligand-ligand interaction and to an increase in the electronic stabilization energy B . However, environment-induced interactions (distortions), which may be different for the individual ligands of the same complex (inhomogeneity effects), can easily remove the equivalence of the ligands and lead to energy shifts, which may be significantly larger than the electronic stabilization energy B . As a consequence, a weak distortion may already decouple the ligands, and the electronic states will become confined to *different* ligands. This type of localization by a weak distortion describes well the situation of the ^3LC transitions of $[\text{Rh}(\text{bpy})_3]^{3+}$ and $[\text{Pt}(\text{bpy})_2]^{2+}$. In these compounds the *emission* results clearly from that ligand with the lower lying state(s) (cf. [77]). On the other hand, all ligands may be excited independently and show their specific *excitation* spectra. Details for $[\text{Pt}(\text{bpy})_2]^{2+}$ and $[\text{Rh}(\text{bpy})_3]^{3+}$ are discussed in Sections 2.2 to 2.5 (cf. also [60, 68, 108]).

In a series of recent publications by Riesen and Krausz, this type of localization is also favored to explain the properties of the lowest $^3\text{MLCT}$ states of $[\text{Ru}(\text{bpy})_3]^{2+}$ [144, 162, 163, 192, 196, 197, 204, 207, 208]. In this model $[\text{Ru}(\text{bpy})_3]^{2+}$ is regarded as consisting of largely independent (Ru-bpy) subunits, which all contain the same metal center.¹⁶ Every subunit yields three low-lying triplet sublevels of Ru4d bpy π^* -MLCT character. Further – according to this model – one of the three (Ru-bpy) subunits is environmentally distorted in the $[\text{Zn}(\text{bpy})_3](\text{ClO}_4)_2$ matrix used in these investigations, and this leads to a shift of the corresponding triplet sublevels of this specific subunit to higher energy, while the other two subunits, remaining equivalent, give three low-lying triplet sublevels for each subunit. Although these sublevels are deduced from $^3\text{MLCT}$ transitions involving the same pool of Ru4d electrons, it is assumed in this model that the interaction energy between identical MLCT states on different subunits is less than 0.1 cm^{-1} [162]. In this case one would easily obtain a localization due to a weak distortion, as discussed above.

¹⁶ More precisely, the authors discuss a model of (1/3 Ru-bpy) subunits (see Fig. 4 in [142]).

From the term splittings of the order of 10^3 cm^{-1} for $[\text{Ru}(\text{bpy})_3]^{2+}$ as discussed in Section 3.1 (Fig. 11) it is obvious that an interaction energy of less than 0.1 cm^{-1} is several orders of magnitude too small, and thus the model is certainly not applicable. Nevertheless, if we neglect this discrepancy for a moment, it is of interest to see whether predictions of that model fit the experimental situation. Some implications crucial for this model [162] are briefly addressed. (1) For $[\text{Ru}(\text{bpy-h}_8)_2(\text{bpy-d}_8)]^{2+}$, the model of [162] requires the occurrence of *two* sets of electronic origins, resulting from the different subunits (Ru-bpy-h_8) and (Ru-bpy-d_8), respectively. The corresponding transitions should be clearly observable in excitation spectra. Due to the fact that the transition $|0\rangle \rightarrow |1\rangle$ is strictly forbidden, one should observe the origins II-h and III-h of the subunit (Ru-bpy-h_8) as well as II-d and III-d of the subunit (Ru-bpy-d_8). However, the line-narrowed excitation spectrum (Fig. 20b) measured over a larger spectral range and better resolved than that reproduced in [162] shows that the predicted number of peaks does not occur. Presumably, the authors [162] misinterpreted phonon satellites at 33, 40, 46 cm^{-1} as electronic origins.¹⁷ (2) According to the model presented in [162], $[\text{Ru}(\text{bpy-h}_8)_2(\text{bpy-d}_8)]^{2+}$ should exhibit *only an emission* from one single (Ru-bpy-h_8) subunit due to its energetically lower lying states. However, Fig. 19b and Table 5 demonstrate that the lowest excited state clearly involves both protonated and deuterated ligands, as shown in the vibrational satellite structure (see Sect. 3.5). This discrepancy is seen by the authors [208] and is explained by introducing an additional electronic coupling between the ligands via the metal due to backbonding effects, though they excluded a significant electronic coupling as the most crucial condition for their model of isolated subunits. (3) The occurrence of spectrally broader features in the line-narrowed excitation spectra described in Section 3.5 and Fig. 20 has been interpreted [162, 208] as supporting the model of nearly uncoupled ligands. These features and the line-narrowed origin lines (being $\approx 2.5 \text{ cm}^{-1}$ apart) are, according to [162, 208], due to the crystallographically approximately equivalent positions of two uncorrelated (Ru-bpy) subunits of the same complex, whereby only one of these subunits gives line-narrowed spectra. Therefore, the intensities of line-narrowed origins to the broader features have to display a fixed ratio given by the number of subunits involved. For example, the model of [162] requires for $[\text{Ru}(\text{bpy-h}_8)_3]^{2+}$ a ratio of 1:1. However, the inset in Fig. 20a demonstrates that this ratio is strongly dependent on the concentration of the dopant, which is in contradiction to the model of [162]. Consequently, this behavior is better ascribed to combined effects of aggregation of $[\text{Ru}(\text{bpy})_3]^{2+}$ complexes and radiationless energy transfer in these aggregates (see also Sect. 3.2.1). Interestingly, it has been reported [163] that the related emission exhibits a fast decay of $\approx 20 \text{ ns}$. This time is of the right order of magnitude for a radiationless energy transfer between nearest neighbors, as discussed in Section 3.6 and [185], but it is much too long for an intramolecular energy transfer.

¹⁷ For completeness it is added that the excitation spectra of the related $[\text{Ru}(\text{bpy-h}_8)(\text{bpy-d}_8)_2]^{2+}$ are slightly more complicated due to the occurrence of two different, equally important sites (cf. [85, 186]; Sect. 3.2).

3.8.2

Strong Ligand-Ligand Coupling Via the Metal and Localization by a Strong Distortion

It is obvious that the simple model discussed above, regarding the ligands or the (Ru-bpy) subunits as separate molecular units, will no longer be applicable, if the electron orbitals of the metal and the ligands strongly overlap, as for $^3\text{MLCT}$ states. In this distinctly covalent situation, a determination of the energy states of the complex requires more sophisticated procedures than discussed above (e.g., see the approaches of [134–136, 138–140, 153–155]). In any case, one will obtain a significantly larger electronic stabilization (energy B) compared to noninteracting molecular subunits. A calculation of B for $[\text{Ru}(\text{bpy})_3]^{2+}$ has not yet been carried out, but a first estimate of a lower limit leads to the order of $B \approx 10^3 \text{ cm}^{-1}$ (Sect. 3.1; [134–136, 138, 139]). These considerations show that the electronic delocalization stabilizes the lowest excited states. This is a well-accepted phenomenon, which is similarly valid for conjugated organic molecules (e.g., see [258]). Nevertheless, a localization can still occur, if an intramolecular or environmentally induced distortion leads to a stabilization energy E_L with $E_L > B$. This means that one has to take into account that the distortion is relatively strong and exceeds about 10^3 cm^{-1} .

It is very interesting to discuss the situation including the spectroscopic implications, when the energy of distortion E_L is of about the same magnitude or only slightly larger than the purely electronic stabilization energy B (cf. discussion presented in [129]). One should keep in mind that a localization, which provides E_L , is connected to a deformation or a distinct nuclear relaxation process. Under the assumption of a symmetric ground state the localization of the excited electron may occur on every bpy ligand with equal probability. However, one has to consider an important additional physical property. In the case of an electronic interaction between neighboring ligands, the excited electronic charge distribution coupled to a certain deformation can still be delocalized. Or, in other words and in a slightly different model, a sufficiently large interaction of neighboring ligands induces a ligand to ligand movement or hopping of this deformation (e.g., see [263–266] and cf. [47, 48, 267]). The moving excitation takes the nuclear displacements (deformation) of “its” environment with it. It is “dressed” by the local polarization. This is in analogy with a moving polaron. However, in this situation, the electronic stabilization energy B_L is drastically reduced with respect to B . Now B_L describes the residual electronic coupling between the different ligands, which experience the nuclear deformation. B_L may be determined – mainly following Toyozawa [266] – by a product of the pure electronic energy B and a reduction factor due to the nuclear deformation. This reduction factor can be expressed by the square of an overlap integral of the wavefunctions of the distorted $\chi(Q - \Delta Q)$ and the undistorted $\chi(Q)$ zero-point vibrational states of harmonic oscillators. Further, it can be shown that this reduction factor $|\langle \chi(Q - \Delta Q) | \chi(Q) \rangle|^2$ is equal to e^{-S} in the low-temperature limit in which we are interested here. S is the Huang-Rhys factor for the active vibrational mode and can be determined from highly resolved spectra, as discussed in the preceding sections (see also [94–97, 99]). Thus, we obtain $B_L = B \cdot e^{-S}$. With the Heisenberg uncertainty principle, $\Delta E \cdot \Delta t \approx \hbar$ identifying ΔE

with B_L – and with $\Delta t \approx 10^{-12}$ s (being the time required during which the excited electron has to stay on one ligand to allow a complete nuclear relaxation), we obtain for the Huang-Rhys factor $S \approx \ln[B/\hbar \cdot 10^{12} \text{ s}]$.

It is very illustrative to apply this result to $[\text{Ru}(\text{bpy})_3]^{2+}$. Taking as lower limit for the electronic stabilization energy $B \approx 10^3 \text{ cm}^{-1}$, we obtain a Huang-Rhys factor of $S \approx 5$ as lower limit for a localized situation. This estimate implies that the shifts ΔQ of the nuclear positions of the (localized) excited state relative to those of the ground state have to be relatively large in order to lead to a localization. Such a large nuclear deformation is connected with a very distinct Franck-Condon progression, where the fifth ($S = 5$) vibrational member of the FC progression is the largest one. It would clearly be seen in highly resolved emission spectra. The experimental situation is obvious, the largest Huang-Rhys factor observed for $[\text{Ru}(\text{bpy})_3]^{2+}$ is ≈ 0.1 (see Sect. 3.3.2; [74].)

Before we come to a conclusion with respect to this model, we briefly address the question whether time-integrated or cw-emission experiments (usual spectra) would really display a localization if it occurred on a time scale of 10^{-12} s, while the emission lifetime of $[\text{Ru}(\text{bpy})_3]^{2+}$ (at $T = 1.2 \text{ K}$) is more than eight orders of magnitude longer. Thus, even a very small residual interaction energy (B_L), which couples the different ligands, would induce many hopping processes during the lifetime τ . For example, $B_L = 0.5 \text{ cm}^{-1}$ corresponds to $\Delta t \approx 10^{-11} \text{ s}$ and this implies $\approx 10^7$ hopping processes during τ . Thus, the deformation would not be confined to a specific ligand. However, in an usual cw-emission spectrum the hopping processes between completely relaxed positions would not be seen. The spectrum would clearly display the properties of the deformed (localized) excited state, since the time of the electronic transition itself is of the order of 10^{-15} s .

Thus, it can be summarized that a localization according to a strong distortion would be seen in emission spectra, but it is definitely excluded for the low-lying electronic state(s) of $[\text{Ru}(\text{bpy})_3]^{2+}$ doped into $[\text{Zn}(\text{bpy})_3](\text{ClO}_4)_2$.

The situation is possibly different at room temperature, when the complexes are dissolved in fluid and highly polar solutions. In [268–270, 209] it has been reported, using resonance Raman data of the excited state(s) of $[\text{Ru}(\text{bpy})_3]^{2+}$, that the vibrational energies are shifted relative to those of the electronic ground state. These shifts were interpreted in favor of a relatively strong distortion due to an electron localization in the lowest excited state(s). Polar solvent molecules may indeed lead to an asymmetrical distortion in the excited state(s) due to strong complex-solvent interactions, as proposed earlier [126, 146]. This might lead to an energy stabilization ($E_L > B$) at one ligand. However, a discussion of the whole system, metal complex and its nonrigid solvent cage, is beyond the scope of this contribution. It should be mentioned further that an alternative model might also explain the “frequency shifts” observed, simply by taking into account additional processes for the resonant Raman enhancements. This model is proposed in Section 4.3 in connection with the discussion of similar effects found for $[\text{Os}(\text{bpy})_3]^{2+}$.

It should be emphasized, however, that the two localization models discussed above in Sections 3.8.1 and 3.8.2 are based on drastically different electronic interaction energies (about four orders of magnitude). Thus, these models would display extremely different spectroscopic properties. Therefore, it is cer-

tainly not possible to use arguments that seem to support the weak coupling case to confirm the strong coupling situation as is sometimes presented in the literature.

4

[Os(bpy)₃]²⁺

[Os(bpy)₃]²⁺ or related Os(II)-compounds have been studied less frequently than [Ru(bpy)₃]²⁺, but there are a number of very interesting investigations in physical, chemical, and biological research fields [21, 271–277]. Moreover, Os(II)-bipyridine complexes represent suitable building blocks in connection with Ru(II)-polypyridine compounds for supramolecular systems [278, 279]. Recently, studies of interacting [Ru(bpy)₃]²⁺/[Os(bpy)₃]²⁺ or chemically modified systems have become attractive due to an efficient radiationless energy transfer from the [Ru(bpy)₃]²⁺ donor to the [Os(bpy)₃]²⁺ acceptor [280–283]. The importance of such processes was also emphasized more than a decade ago [35, 36, 126].

In this review our focus is mainly on properties of the lower lying excited states of the [Os(bpy)₃]²⁺ complex itself. These have been explored with regard to many interesting respects (e.g., see [123, 136, 153, 154, 161, 284–292]). However, reports on well-resolved spectra which display detailed information about the lowest excited states are only rarely found ([34–38, 83, 92, 98, 104, 126, 293] and [144, 192, 294, 295]). Results from these highly resolved spectra will be discussed and the low-lying electronic and vibronic states characterized.

With regard to the properties of [Os(bpy)₃]²⁺, it is suitable to present room temperature absorption and 80 K emission spectra (Fig. 22). Similar spectra have already been reported in part by other investigators (e.g., [161, 288, 290]). Like in [Ru(bpy)₃]²⁺ (see Fig. 10) the transitions above ca. 33 000 cm⁻¹ ($\approx$ 300 nm) are assigned to electronic transitions of ligand $\pi\pi^*$ character. Due to their very high transition probabilities, one has to take into account a significant coupling between the ligands due to dipole-dipole coupling (see also Sect. 2; [61–65, 69]). Thus, the ¹ $\pi\pi^*$ states are delocalized over the whole ligand system. This is even valid, if all *d*-orbital contributions are neglected. The absorption structures below $\approx$ 28 000 cm⁻¹ ($\approx$ 360 nm) down to $\approx$ 15 000 cm⁻¹ ($\approx$ 670 nm) are in general agreement assigned to Os5d-bpy π^* ¹MLCT and ³MLCT transitions from the singlet ground state [123, 126, 136, 153, 154, 161, 285–295]. The emission with its peak maximum near 14 000 cm⁻¹ ($\approx$ 715 nm) results – also in general agreement – from a number of low-lying states being largely of ³MLCT character [34–38, 123, 126, 136, 153, 154, 161, 285–295].

The manifold of the electronic states of [Os(bpy)₃]²⁺ can be similarly deduced as in the case of [Ru(bpy)₃]²⁺ in Section 3.1. In particular, the same orbital jumps have to be taken into account (see Fig. 11). However, compared to [Ru(bpy)₃]²⁺, the sequence of the resulting electronic states and their individual properties may be quite different, due to the much larger spin-orbit coupling (soc) in Os(II)-complexes (soc constant λ [Os(II)]: $\approx$ 3 · 10³ cm⁻¹; λ [Ru(II)]: $\approx$ 10³ cm⁻¹, see [123, 136, 153, 254, 255]). Moreover, the *d-d* states of the third-row transition

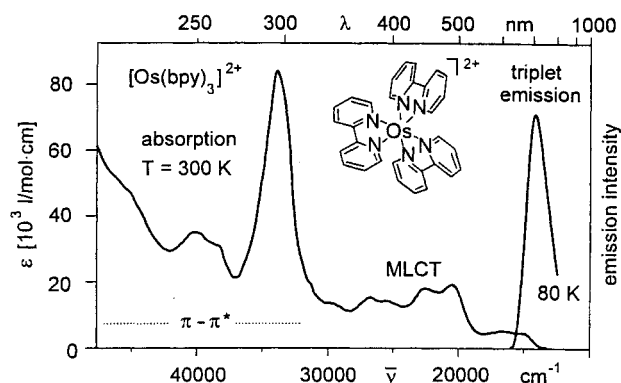


Fig. 22. Absorption and emission of $[\text{Os}(\text{bpy})_3]^{2+}$ dissolved in water and assignments to $\pi\pi^*$ and MLCT transitions

metal complexes lie significantly higher ($\approx 40\%$) than those of the corresponding second-row complexes (e.g., see [296]). Theoretical investigations of the electronic structure of $[\text{Os}(\text{bpy})_3]^{2+}$ have been carried out [136, 153, 154]. Although the studies provide interesting guidelines, they are still not realistic enough to be applicable for a characterization of the lowest triplet sublevels of $[\text{Os}(\text{bpy})_3]^{2+}$, as has been similarly exemplified for $[\text{Ru}(\text{bpy})_3]^{2+}$ in Section 3.1. Consequently, we want to use an experimental approach to characterize these states by applying the information displayed in highly resolved emission and absorption or excitation spectra.

None of the neat salts of $[\text{Os}(\text{bpy})_3]\text{X}_2$ investigated showed any fine structure. Fortunately, this is different when $[\text{Os}(\text{bpy})_3]^{2+}$ is doped into the matrices given in Table 8. Interestingly, the spectral resolution achievable is significantly better than found for $[\text{Ru}(\text{bpy})_3]^{2+}$. Table 8 summarizes further a series of properties of the lowest excited states of $[\text{Os}(\text{bpy})_3]^{2+}$ doped into these matrices. In Sections 4.1 and 4.2 we mainly discuss properties of this chromophore doped into $[\text{Ru}(\text{bpy})_3](\text{PF}_6)_2$ and $[\text{Zn}(\text{bpy})_3](\text{ClO}_4)_2$, respectively.

4.1

$[\text{Os}(\text{bpy})_3]^{2+}$ in $[\text{Ru}(\text{bpy})_3](\text{PF}_6)_2$

$[\text{Ru}(\text{bpy})_3](\text{PF}_6)_2$ represents a very interesting matrix for $[\text{Os}(\text{bpy})_3]^{2+}$. It is spectrally transparent below $\approx 17800\text{ cm}^{-1}$ and thus provides a spectral window of more than 3300 cm^{-1} above the lowest electronic state of $[\text{Os}(\text{bpy})_3]^{2+}$. As discussed in Section 3.6 (Table 6), $[\text{Os}(\text{bpy})_3]^{2+}$ can substitute all three crystallographic sites occurring in the low-temperature structure [184] of the $[\text{Ru}(\text{bpy})_3](\text{PF}_6)_2$ matrix [38, 92]. The dopants seem to replace the host molecules quite regularly. Thus, the positions of C_3 site symmetry provided by the matrix do not seem to be significantly distorted, as will be shown below. Mainly according to this situation, one can study the interesting effect of a dominance of vibronic (Herzberg-Teller) deactivations from the lowest excited state

Table 8. Suitable matrices for high-resolution spectroscopy of $[\text{Os}(\text{bpy})_3]^{2+}$; low-lying energy states and emission decay times ($T = 1.3 \text{ K}$)

Matrices for $[\text{Os}(\text{bpy})_3]^{2+}$	Electronic origins $[\text{cm}^{-1}]$				References, remarks
	I ^a	II ^a	III ^a	Γ, Δ ^b	
$[\text{Ru}(\text{bpy})_3](\text{PF}_6)_2$	14 423 ^c ($\tau_1 = 22 \mu\text{s}$)	14 495 ^c	14 640 ^{c, d}	14 432 ^c	[35, 38, 92, 185] C ₃ sites [184]
$[\text{Ru}(\text{bpy})_3](\text{AsF}_6)_2$	14 422 ^c ($\tau_1 = 22 \mu\text{s}$)	14 498 ^c		14 431 ^c	[38, 186]
$[\text{Ru}(\text{bpy})_3](\text{SbF}_6)_2$	14 425 ^c ($\tau_1 = 17 \mu\text{s}$)				[38, 186]
$[\text{Ru}(\text{bpy})_3](\text{ClO}_4)_2$	14 169 ($\tau_1 = 20 \mu\text{s}$)	14 230	14 380 ^e	14 245	[34, 37]
$[\text{Zn}(\text{bpy})_3](\text{ClO}_4)_2$	14 223 ($\tau_1 = 22 \mu\text{s}$)	14 286	14 444 ^e	14 297	[98, 104]

^a In a first-order approximation these states are assumed to result from a common parent term (same orbital jump), experimental errors: $\pm 1 \text{ cm}^{-1}$, $\pm 1 \mu\text{s}$, if not otherwise indicated.

^b Additional low-lying electronic state designated in the literature as Γ and Δ .

^c Energies given for the lowest site A. Two other crystallographic sites are identified at higher energies (see also Table 6).

^d Estimated energy position, error: $\pm 10 \text{ cm}^{-1}$.

^e Experimental error: $\pm 2 \text{ cm}^{-1}$.

|I> of $[\text{Os}(\text{bpy})_3]^{2+}$ (Sect. 4.1.3). Moreover, this specific vibronic coupling can be tuned to an extremely different situation, since one obtains totally different spectral features by applying high magnetic fields (Sect. 4.1.4).

Furthermore, it is of great interest that $[\text{Os}(\text{bpy})_3]^{2+}$ doped into $[\text{Ru}(\text{bpy})_3](\text{PF}_6)_2$ can be excited either directly or indirectly by first exciting the matrix molecules, which is then followed by a radiationless energy transfer to the dopant. Studies of donor (= matrix) emission decay and acceptor (= dopant) rise times at various temperatures, magnetic fields, and $[\text{Os}(\text{bpy})_3]^{2+}$ concentrations allowed us to elucidate the mechanisms of energy migration in the neat $[\text{Ru}(\text{bpy})_3](\text{PF}_6)_2$ material. Interestingly, these properties depend strongly on the electronic state of the matrix involved. In particular, the energy migration in the low-lying state(s) of the host material is relatively slow, while the final step of energy transfer from $[\text{Ru}(\text{bpy})_3]^{2+}$ to $[\text{Os}(\text{bpy})_3]^{2+}$ is fast and governed by a resonant transfer process. However, these results are not the subject of this investigation (see [35, 36, 297]).

4.1.1

Site-Selected Spectra of $[\text{Os}(\text{bpy})_3]^{2+}$ in $[\text{Ru}(\text{bpy})_3](\text{PF}_6)_2$

Figure 23a shows the non-selectively excited emission spectrum at $T = 2 \text{ K}$ of $[\text{Os}(\text{bpy})_3]^{2+}$ doped into $[\text{Ru}(\text{bpy})_3](\text{PF}_6)_2$. The spectrum is dominated by a triple structure, as reported earlier by our group [35, 38, 92, 126, 293]. It was proposed

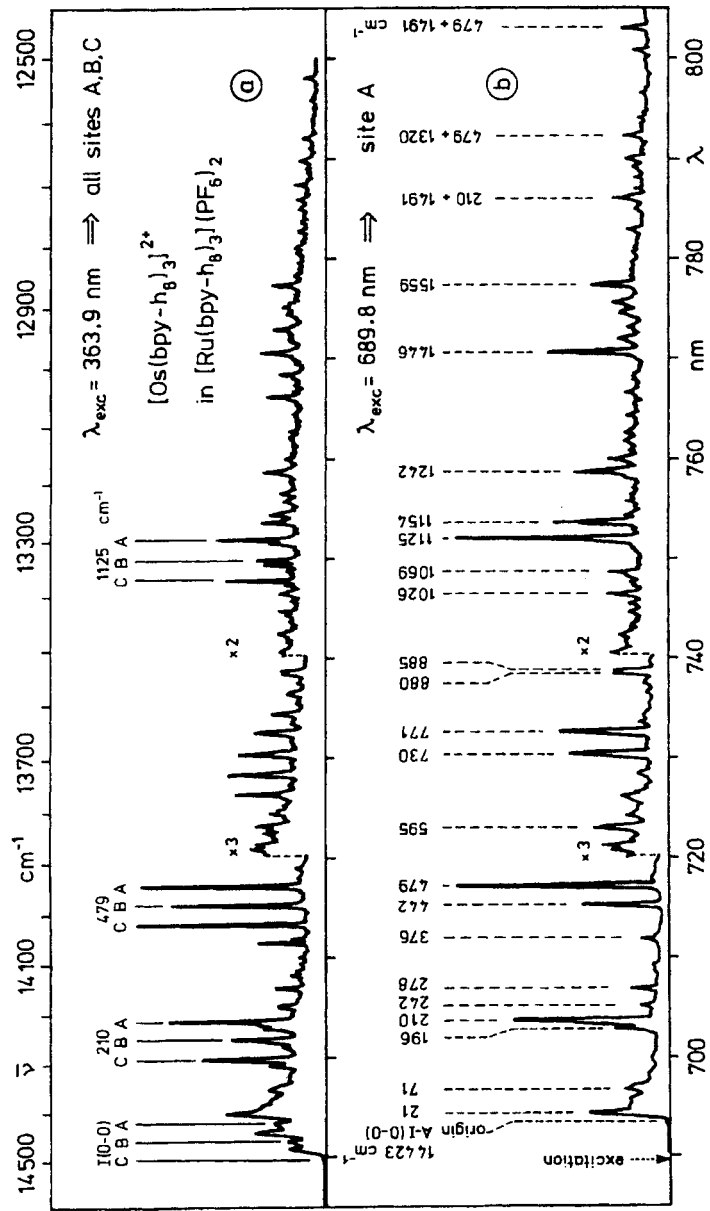


Fig. 23. Emission spectra at $T = 2 \text{ K}$ of $[\text{Os}(\text{bpy}-h_8)_3]^{2+}$ doped into $[\text{Ru}(\text{bpy}-h_8)_3](\text{PF}_6)_2$ [38]. a Non-selective excitation, three different sites A, B, and C are excited and emit. b Selective excitation of site A of transition $|0\rangle \rightarrow |II\rangle$ at $14,495 \text{ cm}^{-1}$. The energies of the vibrational satellites are specified relative to the very weak electronic origin I of site A at $14,423 \text{ cm}^{-1}$.

in [294] that this triple structure is due to a phonon progression. This explanation is certainly not applicable, as demonstrated in Fig. 23b. This spectrum results from a selective excitation at 689.9 nm ($\triangleq 14495\text{ cm}^{-1}$), which drastically simplifies the satellite structures. Obviously, the spectrum in Fig. 23a results from a superposition of three emitting sites (A, B, C), while the spectrum in Fig. 23b is obtained by exciting the lowest site A selectively. This behavior is expected from the knowledge of the low-temperature structure of $[\text{Ru}(\text{bpy})_3](\text{PF}_6)_2$ [184] which, however, was not yet available when the assignment to sites was given [35, 38, 92]. A similar behavior was found for $[\text{Os}(\text{bpy})_3]^{2+}$ doped into $[\text{Ru}(\text{bpy})_3](\text{AsF}_6)_2$ and $[\text{Ru}(\text{bpy})_3](\text{SbF}_6)_2$ [38, 186]. The energies and emission decay times of the low-lying electronic states are summarized in Table 8.

4.1.2

Electronic Origins

The assignment of the electronic origin I corresponding to the lowest state $|I\rangle$ of $[\text{Os}(\text{bpy})_3]^{2+}$ in the high-symmetry $[\text{Ru}(\text{bpy})_3](\text{PF}_6)_2$ matrix is not straightforward, since the transition between $|I\rangle$ and the electronic ground state $|0\rangle$ is strongly forbidden and thus is not observed in absorption or excitation spectra. Even in the emission spectrum at $T = 2\text{ K}$ it is so weak that one might not realize the existence of that small peak at $14423 \pm 1\text{ cm}^{-1}$ (Fig. 24a). However, the highly resolved vibrational satellite structure in emission strongly facilitates this assignment. Only for this energy position one does obtain a good fit of the satellites to vibrational energies determined independently by IR measurements (see Table 9; [38, 92]). A similar procedure of identifying or supporting the designation of electronic origins is described in Sections 2.2 and 3.3.2. The assignment of that small peak as electronic origin is further proven by spectral changes that are observed when a high magnetic field is applied. The field induces a mixing-in of higher lying state(s) to state $|I\rangle$. Thus, the originally forbidden transition at 14423 cm^{-1} becomes strongly allowed (see Fig. 24b, d; Sect. 4.1.4).

Figure 24c, d shows clearly that at $14495 \pm 1\text{ cm}^{-1}$, 72 cm^{-1} above origin I, a second electronic origin II occurs. The corresponding electronic transition has also been studied in absorption [38, 92]. A third state $|III\rangle$ seems to occur at $14640 \pm 10\text{ cm}^{-1}$. This value results from an excitation spectrum, which exhibits a relatively weak peak at that energy (not reproduced here). Moreover, the approximate position of this value is supported by data obtained for $[\text{Os}(\text{bpy})_3]^{2+}$ doped into $[\text{Ru}(\text{bpy})_3](\text{ClO}_4)_2$ and $[\text{Zn}(\text{bpy})_3](\text{ClO}_4)_2$, respectively (see also Fig. 25).

Similar to the situation in $[\text{Ru}(\text{bpy})_3]^{2+}$ (Sect. 3.3.1), $|I\rangle$, $|II\rangle$, and $|III\rangle$ represent zero-field split components, which result in their main contributions from the same orbital parentage or from one specific $^3\text{MLCT}$ state. This is indicated (1) by the fact that the splitting pattern does not strongly depend on the matrix, though the absolute energies are shifted over a range of more than 250 cm^{-1} , when the different matrices are compared (Table 8); (2) states $|I\rangle$ and $|II\rangle$ exhibit a strong Zeeman interaction (Sect. 4.1.4; [92]); and (3) both states are – within limits of experimental error of $< 1\text{ cm}^{-1}/\text{kbar}$ – equally shifted under

high-pressure application ($\sim 13 \text{ cm}^{-1}/\text{kbar}$ at $T = 2 \text{ K}$; [190, 202]). Furthermore, in a crude model it might be assumed that for $[\text{Ru}(\text{bpy})_3]^{2+}$ and $[\text{Os}(\text{bpy})_3]^{2+}$ the zero-field splittings of the corresponding $^3\text{MLCT}$ parent terms are mainly induced by spin-orbit coupling. In this situation the energy separations between states $|III\rangle$ and $|I\rangle$ of ≈ 60 and $\approx 220 \text{ cm}^{-1}$ for $[\text{Ru}(\text{bpy})_3]^{2+}$ (Fig. 13) and $[\text{Os}(\text{bpy})_3]^{2+}$ (Fig. 25), respectively, should relate to the constants of spin-orbit coupling for the two metal ions. Interestingly, the corresponding ratios deviate only by $\approx 20\%$, when largely accepted values like $\lambda(\text{Ru}^{2+}) \approx 10^3 \text{ cm}^{-1}$ and $\lambda(\text{Os}^{2+}) \approx 3 \cdot 10^3 \text{ cm}^{-1}$ [136, 153, 254, 255] are used for this comparison (cf. also [123]).

The excitation spectrum of site A (Fig. 24c) shows a further small peak Γ , which is considered as an additional electronic origin [38, 92, 98, 186]. Its intensity dependence on a magnetic field is totally different from that found for state $|I\rangle$ (cf. Fig. 24c to d). Moreover, there are indications that an additional peak, occurring in the $[\text{Ru}(\text{bpy})_3](\text{ClO}_4)_2$ and $[\text{Zn}(\text{bpy})_3](\text{ClO}_4)_2$ matrices, is related to this origin Γ (Table 8). If so, this electronic origin depends differently on the environment of $[\text{Os}(\text{bpy})_3]^{2+}$ than the origins $|I\rangle$, $|II\rangle$, and $|III\rangle$. Therefore, and in the context to the discussion above, it seems to be justified to assign this additional electronic origin to a different orbital parentage. With respect to the large number of low-lying states (see Sect. 3.1) this is not unexpected.

A generally accepted group-theoretical classification of the lowest excited states $|I\rangle$, $|II\rangle$, and $|III\rangle$ – being our main interest in this section – has not emerged yet. There is little doubt that state $|II\rangle$ may be assigned to a degenerate E representation in the C_3 point group symmetry.^{18a} This results from the selection rules for that group and the clear $\vec{E} \perp \vec{C}_3$ polarization ($\vec{E}$: electric field vector) for the $|0\rangle \rightarrow |II\rangle$ absorption. Due to the relatively high allowedness of this transition, a slight environmental distortion would not alter this distinct polarization (Fig. 24c, d; [92]). On the other hand, state $|I\rangle$ has also been assigned to a degenerate E representation due to the detection of ODMR signals [298]. In this case, however, we want to be cautious with this classification and wait for further support. It is added that even a distinct $\vec{E} \perp \vec{C}_3$ polarization for the transition $|I\rangle \rightarrow |0\rangle$ would possibly be misleading, since the extremely small transition probability at origin I may easily be induced by a weak distortion, whereby the distorting state may determine the effective polarization (cf. also Sect. 4.2).

4.1.3

Herzberg-Teller Activity

The emission spectrum at $T = 2 \text{ K}$ and $B = 0 \text{ T}$ exhibits a very weak electronic origin I at 14423 cm^{-1} combined with a very rich vibrational structure, which stems from the corresponding state $|I\rangle$. Obviously, the purely electronic tran-

^{18a} Formally, the point group C_3 has only one-dimensional irreducible representations. However, two of these are complex conjugate ones and are degenerate in situations with time-reversal symmetries.

sition is strictly forbidden, and state $|I\rangle$ is radiatively deactivated by paths involving vibrational modes. These match well to IR active vibrations (Table 9; [38, 92]). Thus, a Franck-Condon activity, according to totally symmetric modes, can be excluded as dominant process.^{18b} Therefore, it is concluded that vibronic coupling according to the Herzberg-Teller mechanism induces the vibrational satellite structure (e.g., see [86–93, 217]).

The forbiddenness of the purely electronic transition $|0\rangle \leftrightarrow |I\rangle$ seems to imply that direct spin-orbit coupling (soc) to state $|I\rangle$ is very small. Therefore, one has to consider such vibronic coupling mechanisms that provide singlet character to state $|I\rangle$. Two processes have been proposed [92], which may be responsible for a radiative deactivation of the lowest excited state of $[\text{Os}(\text{bpy})_3]^{2+}$. The theoretical background is discussed in [86–93].

1. *Spin-vibronic coupling* yields an interaction of wavefunctions of two electronic states by a vibration-induced change in soc. For organic compounds this mechanism is often regarded as unimportant due to the small value of the soc constant. However, for $[\text{Os}(\text{bpy})_3]^{2+}$, this mechanism cannot be neglected due to the very large soc constant carried by the $\text{Os}5d$ orbitals ($\lambda[\text{Os}^{2+}] \approx 3 \cdot 10^3 \text{ cm}^{-1}$; [123, 136]). In particular, such vibrations of the $\text{Os}(\text{II})$ -ion that induce changes in

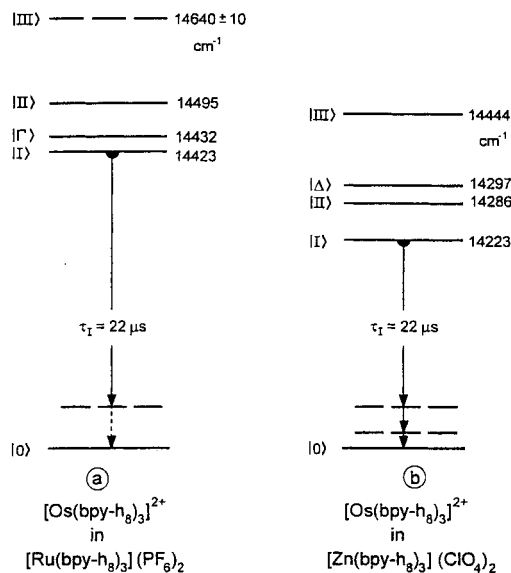


Fig. 25. a, b Low-lying electronic states of $[\text{Os}(\text{bpy}-h_8)_3]^{2+}$ doped into different matrices. They are given for $T = 1.3 \text{ K}$. The position of the electronic origin of state $|III\rangle$ in a is covered with a certain experimental uncertainty (see text)

^{18b} It is shown below that the maximum Huang-Rhys factor of Franck-Condon progressions for vibrations is less than $S = 0.08$.

Table 9. Vibrational satellites [cm^{-1}] observed in the emission of $[\text{Os}(\text{bpy}-\text{h}_8)_3]^{2+}$ doped into $[\text{Ru}(\text{bpy})_3](\text{PF}_6)_2$ (at $B = 0 \text{ T}$ and $B = 6 \text{ T}$) [92] compared to IR-active data and resonant Raman-enhanced modes of $[\text{Ru}(\text{bpy}-\text{h}_8)_3]^{2+}$ (experimental error: $\pm 1 \text{ cm}^{-1}$)

Emission $B = 0 \text{ T}$ $T = 1.2 \text{ K}$ origin I^a $14\,423 \text{ cm}^{-1}$	Emission $B = 6 \text{ T}$ $T = 1.5 \text{ K}$ origin $I_B^{a,b}$ $14\,423 \text{ cm}^{-1}$	IR-active vibra- tions c	Resonance Raman- enhanced d vibrations of $[\text{Ru}(\text{bpy})_3]^{2+}$	Assignments
15				Lattice mode
	16			Lattice mode
21				Lattice mode
	31			Lattice mode
38				Lattice mode
	40			Lattice mode
	45			Lattice mode
52				Lattice mode
	68			Lattice mode
71				Lattice mode
75				Lattice mode
	81			Lattice mode
	115			
	155			
	175			
196		195		HT e
210				HT
242		237		HT
	258			
278		277		HT
	296			
312		310/314		HT
325				210 + 115
376		374		HT
	383			
385				210 + 175
	417			
442		448		HT
479		481		HT
554				479 + 75
561		557		HT
595				479 + 115
617				442 + 175
653				479 + 175
	675		668	FC f , RR 667
730		730		HT
	766		767	FC, R g 766
771		773		HT
	791			
	849			
880		878		HT
885				210 + 675
1026		1026		HT
	1028		1028	FC, RR 1029 h
	1048			FC, RR 1048 h

Table 9 (continued)

Emission B = 0 T T = 1.2 K origin I ^a 14423 cm ⁻¹	Emission B = 6 T T = 1.5 K origin I _B ^{a,b} 14423 cm ⁻¹	IR-active vibra- tions ^c	Resonance Raman- enhanced ^d vibrations of [Ru(bpy) ₃] ²⁺	Assignments
1062				
1069		1068		HT
1110		1107		HT
1125		1123/1126		HT
1154				479 + 675
	1172		1173	FC, RR 1175 ^h
1242		1241		HT
	1263		1264	FC, RR 1268 ^h
1267		1264		HT
1314		1314		HT
	1320		1320	FC, RR 1322 ^h
1446		1447		HT
	1491		1491	FC, RR 1491 ^h
1513		1513		HT
1528				210 + 1320
	1552		1558	FC, RR 1558 ^h
1559		1560		HT
	1610		1607	FC, RR 1610 ^h
1650				479 + 1172
1699				210 + 1491
1764				442 + 1320
1801				479 + 1320
1937				442 + 1491
1969				479 + 1491

^a Site A of lowest energy is investigated.

^b These modes grow strongly in by applying a magnetic field. Origin I_B corresponds to the magnetic field perturbed state |I_B⟩.

^c IR-active vibrations of [Os(bpy-h₈)₃](PF₆)₂ measured at 6 K [212].

^d Resonance-enhanced Raman modes (Table 4; [106, 211, 268]).

^e HT-Herzberg-Teller active mode.

^f FC: Franck-Condon active mode.

^h Raman active mode.

electron density in the spatial region of the π^* ligand orbitals (with their very small soc constant [256, 257]) can also induce significant changes in the effective soc. The corresponding coupling process is described in first-order perturbation theory by the type of matrix element shown in Fig. 26a (e.g., see [86, 87, 89, 92]). $\hat{H}_{so}$ is the operator of soc, |I^o⟩ represents the unperturbed lowest excited state, while |S^o⟩ is a higher lying (unperturbed) singlet. Due to a vibration with the normal coordinate Q singlet character of |S^o⟩ is mixed into state |I^o⟩. This leads to the appearance of that specific vibronic satellite with the vibrational frequency $\bar{\nu}_Q$. Obviously, this mechanism of Herzberg-Teller activity can be effective for a large number of different vibrational modes.

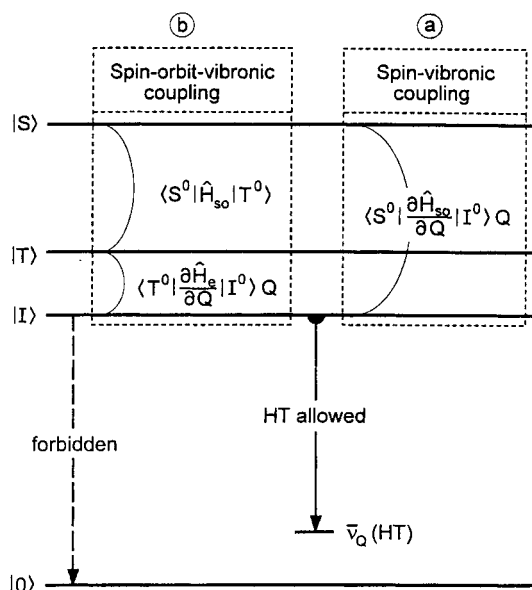


Fig. 26. Different mechanisms of vibronic coupling (Herzberg-Teller, HT, coupling) – symbolized by the matrix elements – open radiative deactivation paths from a triplet sublevel to a singlet ground state. This results in the occurrence of vibrational satellites $\bar{\nu}_Q$ (HT). These mechanisms become particularly obvious, when the purely electronic transition $|0\rangle \leftrightarrow |I\rangle$ is strongly forbidden like in $[\text{Os}(\text{bpy})_3]^{2+}$ doped into $[\text{Ru}(\text{bpy})_3](\text{PF}_6)_2$

2. *Vibronic coupling within the triplet manifold to a spin-orbit coupled state* may also provide allowedness for an originally forbidden radiative deactivation of $|I\rangle$ (e.g., [86, 87, 89, 92]). In this situation, state $|I^0\rangle$ obtains an admixture by usual vibronic coupling due to a change in the electronic Hamiltonian $\hat{H}_e$ with the vibration Q . Figure 26b shows this type of matrix element. $|T^0\rangle$ represents a triplet sublevel. Important is that this sublevel $|T^0\rangle$, from which state $|I^0\rangle$ borrows allowedness by vibronic coupling, experiences itself direct soc with a higher lying singlet $|S^0\rangle$ induced by the usual matrix element of soc $\langle S^0 | \hat{H}_{so} | I^0 \rangle$. For $[\text{Os}(\text{bpy})_3]^{2+}$ the higher lying triplet sublevel $|II\rangle$, lying 72 cm^{-1} above state $|I\rangle$, carries sufficient allowedness to represent a good candidate for this state $|T^0\rangle$. Also, this mechanism would provide Herzberg-Teller intensity for a series of vibrational satellites with energy separations $\bar{\nu}_Q$ from the electronic origin I .

In summary, all fundamentals observed as satellites in Fig. 24a (Table 9) seem to result from these vibronic (Herzberg-Teller) mechanisms discussed in (1) and (2) and shown in Fig. 26. It may be assumed that mechanism (1) might be more important for low-energy metal-ligand (M-L) vibrations than for high-energy internal ligand vibrations, since movements of the heavy metal, which carries the dominant soc, occur only for the M-L vibrational modes.

It is emphasized that a very weak Franck-Condon (FC) activity is also observed when comparing vibrational combinations of HT active modes with FC active ones (cf. Sect. 4.1.4; Table 9). In this case the HT satellite represents a

“false origin”. For example, one finds combination satellites at 1154 cm^{-1} [$\triangle 479\text{ cm}^{-1}$ (HT) + 675 cm^{-1} (FC)], 1650 cm^{-1} [$\triangle 479\text{ cm}^{-1}$ (HT) + 1172 cm^{-1} (FC)], and 1969 cm^{-1} [$\triangle 479\text{ cm}^{-1}$ (HT) + 1491 cm^{-1} (FC)] [92, 186]. In all cases, the Huang-Rhys factor S is smaller than 0.08. This implies that state $|I\rangle$ and the ground state $|0\rangle$ have nearly equal nuclear equilibrium positions.

4.1.4

Magnetic Field Effects and Field-Induced Tuning-In of Franck-Condon Activity

With application of a magnetic field the spectrum of $[\text{Os}(\text{bpy})_3]^{2+}$ doped into $[\text{Ru}(\text{bpy})_3](\text{PF}_6)_2$ changes drastically. Up to $B = 6\text{ T}$, the transition probability at the electronic origin I (of site A) increases by a factor of $\approx 10^3$, but the magnetic field-induced Zeeman shift is less than 1 cm^{-1} . Thus, origin I stays within experimental error at the same energy. The strong increase in allowedness makes it possible to observe electronic transitions also in excitation and absorption [92] spectra (Fig. 24d). This experiment gives strong support for the assignment of the very weak peak at 14423 cm^{-1} (Fig. 24a) as electronic origin I (cf. Sect. 4.1.2).

The mechanism of magnetic-field enhanced intensity can be described similarly as reported already a decade ago by our group for the case of neat $[\text{Ru}(\text{bpy})_3](\text{PF}_6)_2$ [178, 180]. By admixing the wavefunction of the higher lying state $|II\rangle$, being 72 cm^{-1} above state $|I\rangle$, to that of state $|I\rangle$ the resulting perturbed state $|I_B\rangle$ obtains properties of state $|II\rangle$ and thus gains the allowedness observed. Figure 27 symbolizes this perturbation mechanism. $\hat{H}_{\text{magn}} = \mu_B \cdot \vec{B} \cdot (\vec{L} + 2\vec{S})$ represents the corresponding Hamiltonian, where $\vec{L}$ and $\vec{S}$ are the orbital angular momentum and the spin operators, $\vec{B}$ the magnetic-field vector, and μ_B Bohr's magneton. In first-order perturbation theory the matrix element shown in Fig. 27 can be approximated to be proportional to the magnetic-field strength B . Perturbation theory predicts further a B^2 dependence of the radiative rate from state $|I_B\rangle$ [178, 180, 299]. To check whether this behavior is also valid for $[\text{Os}(\text{bpy})_3]^{2+}$, the magnetic-field dependence of the emission intensity of origin I normalized to the intensity at $B = 0\text{ T}$ is plotted in a log-log plot versus the magnetic field strength B . Indeed, Fig. 28 shows that the slope obtained is *two*, as expected. Interestingly, according to [300], it follows from this value that the nonradiative rates do not depend drastically on the magnetic-field strength.

It is a further highly interesting result that the magnetic-field-induced intensity increase at the electronic origin I is accompanied by the appearance of different vibrational satellites in the emission spectra. Many of these satellites correspond to resonance-enhanced Raman modes (Fig. 24b; Table 9). The corresponding vibrations are also observed as satellites in the zero-field emission spectrum from state $|II\rangle$ [98, 301]. Within the model presented, this behavior is easily explained. By the mixing-in of state $|II\rangle$ with its high radiative rate into state $|I\rangle$, not only the purely electronic transition $|I_B\rangle \rightarrow |0\rangle$ gains intensity at origin I but also the vibrational deactivation paths coupled to the transition $|II\rangle \rightarrow |0\rangle$ grow in. At $B = 6\text{ T}$ the emission structure from state $|I_B\rangle$ is dominated by the properties of state $|II\rangle$. For example, we use the 675 cm^{-1} vibrational satellite to check this model. Figure 29 shows that the intensity of this vibrational satellite increases also with B^2 as found for the perturbed purely electronic transition $|I_B\rangle \leftrightarrow |0\rangle$.

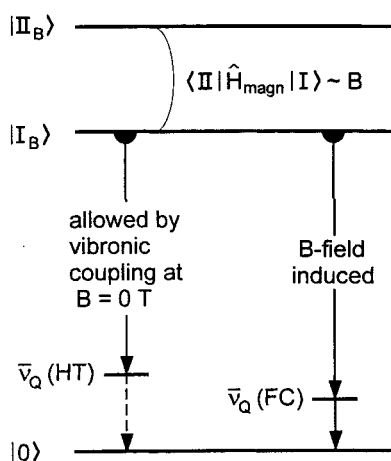


Fig. 27. By applying a magnetic field the wavefunctions of the states $|I\rangle$ and $|II\rangle$ mix. The matrix element shown symbolizes this mechanism, which provides allowedness to the transition from the perturbed state $|I_B\rangle$ to the ground state $|0\rangle$. Using this process it is possible to continuously tune the vibrational satellite structure in emission. At $B = 0$ T the spectrum is dominated by Herzberg-Teller (HT) induced satellites, while with increasing field strength the electronic origin and Franck-Condon (FC) satellites strongly grow in. This is seen in the spectra reproduced in Fig. 24

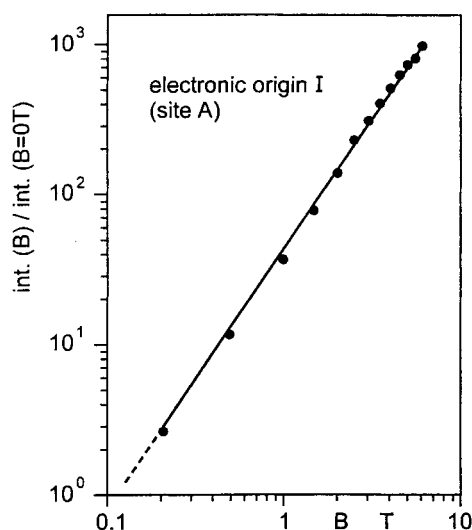


Fig. 28. Magnetic field-induced intensity enhancement at $T = 2$ K of the electronic origin I of $[\text{Os}(\text{bpy-h}_8)_3]^{2+}$ doped into $[\text{Ru}(\text{bpy-h}_8)_3](\text{PF}_6)_2$ with $\vec{B} \perp \vec{c}$ ($\vec{c}$ = crystallographic axis). The log-log plot is shown for the emission intensity at a field B relative to the one at $B = 0$ T [92, 186]. Note that the intensity of the electronic origin I increases by a factor of about 10^3 when a field of 6 T is applied

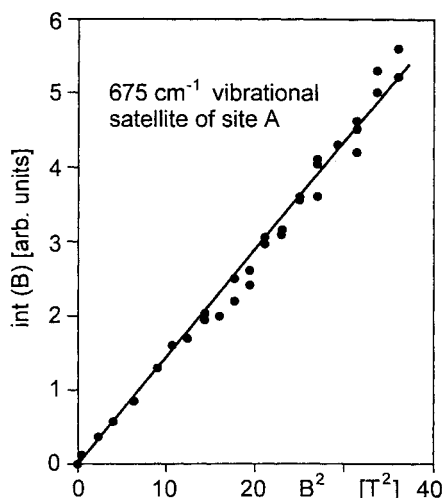


Fig. 29. Magnetic field dependence ($\vec{B} \perp \vec{c}$, $T = 2$ K) of the emission intensity of a typical Franck-Condon-induced vibrational satellite of $[\text{Os}(\text{bpy-h}_8)_3]^{2+}$ doped into $[\text{Ru}(\text{bpy-h}_8)_3](\text{PF}_6)_2$ [92]. This satellite grows in with the extent of admixture of state $|II\rangle$ into state $|I\rangle$ (see Figs. 27, 28). The good fit to a B^2 dependence indicates the applicability of first-order perturbation theory [180]

The vibrational modes that grow in with magnetic-field increase are summarized in Table 9. They are connected to the perturbing state $|II\rangle$, but are measured in the $T = 2$ K emission from the perturbed state $|I_B\rangle$. None of these modes is found to occur as a fundamental in the emission from the unperturbed state $|I\rangle$ (Sect. 4.1.3; Fig. 24a). It is expected that these B -field-induced modes represent Franck-Condon (FC) active modes. This is due to the fact that the transition $|0\rangle \rightarrow |II\rangle$ carries a relatively high oscillator strength due to direct spin-orbit coupling [92, 186] and that intensities of FC satellites are directly proportional to the allowedness of the corresponding origin (e.g., see [86–91, 94–97, 217]). Probably, HT activity does not grow in with the increasing field.¹⁹ Indeed, a very careful search for higher members of FC progressions reveals that the second member of the relatively strong 675 cm^{-1} fundamental occurs at 1350 cm^{-1} [186]. However, the related Huang-Rhys factor (cf. Sect. 2.2.2) is with $S \approx 0.08$ extremely small. Other progressions have not yet been found. Nevertheless most of these vibrational modes seem also to be assignable to FC modes, for which only the fundamentals are observed. The higher members of the corresponding progressions are hidden below the experimental noise level due to

¹⁹ A number of vibrational satellites, which are HT active with respect to the unperturbed state $|I\rangle$ (e.g., at 210 , 442 , and 479 cm^{-1}), are still relatively intense in the emission from the perturbed state $|I_B\rangle$ even at $B = 6$ T, while other HT satellites have strongly reduced intensities (e.g., 1242 and 1446 cm^{-1} ; Fig. 24). Possibly, the former modes are, besides their HT activity with respect to state $|I\rangle$, additionally FC-active with respect to state $|II\rangle$.

their small Huang-Rhys factors. This behavior implies that state $|I_B\rangle$ and thus the perturbing state $|II\rangle$ exhibit very similar nuclear equilibrium positions like the ground state $|0\rangle$. The same conclusion could be drawn for state $|I\rangle$ (Sect. 4.1.3).

Many of these modes that grow in under high magnetic fields are resonance Raman (RR)-enhanced (Table 9; see [302]). This behavior also supports the classification of these modes to FC active ones, if the RR enhancements result from a so-called Albrecht's *A*-Term scattering (FC-like) and if a *B*-term scattering (vibronic term) can be excluded for these ground state modes [104, 211, 303–308]. Interestingly, Poizat and Sourisseau [211] showed for a large number of vibrational modes of $[\text{Ru}(\text{bpy})_3]^{2+}$, which are RR-enhanced that these may be assigned to totally symmetric FC active modes (cf. Sect. 3.3.2). Due to the fact that the energies of these $[\text{Ru}(\text{bpy})_3]^{2+}$ modes fit exactly to those of $[\text{Os}(\text{bpy})_3]^{2+}$, the FC assignment is corroborated also for $[\text{Os}(\text{bpy})_3]^{2+}$ (Table 9).

In summary, it is emphasized that application of a magnetic field *B* opens a new deactivation path for the radiative transition from the lowest excited state. Applying a field of $B = 6$ T, the electronic origin line *I* grows in by about three orders of magnitude in emission, absorption, and excitation. Further, the vibronic coupling properties of the lowest excited state $|I\rangle$ of $[\text{Os}(\text{bpy})_3]^{2+}$ are *tunable* through magnetic fields. At $B = 0$ T, IR-active modes are involved, while with increasing magnetic-field strengths Raman-active modes grow in. The intensities of these latter satellites in the emission spectra may be taken as a measure of the distortion by a magnetic field and – as will be shown in the next section – of the extent of distortion of the site geometry.

4.2

$[\text{Os}(\text{bpy})_3]^{2+}$ in $[\text{Zn}(\text{bpy})_3](\text{ClO}_4)_2$

The highest site symmetry available for $[\text{Os}(\text{bpy})_3]^{2+}$ guest molecules in $[\text{Zn}(\text{bpy})_3](\text{ClO}_4)_2$ is a C_2 symmetry [144, 181, 182a, 182b]. In contrast to the $[\text{Ru}(\text{bpy})_3](\text{PF}_6)_2$ matrix with three crystallographic C_3 sites (Sect. 4.1.1), $[\text{Zn}(\text{bpy})_3](\text{ClO}_4)_2$ provides single-site spectra for the per-protonated and per-deuterated $[\text{Os}(\text{bpy})_3]^{2+}$ chromophores.²⁰ The matrix-induced symmetry reduction is clearly displayed in the properties of the lowest excited state(s) (Fig. 30). In particular, it can be estimated that the intensity of the purely electronic transition $|0\rangle \leftrightarrow |I\rangle$ (intensity of origin *I* normalized to the total intensity of all vibrational satellites) is at least by a factor of hundred stronger for $[\text{Os}(\text{bpy})_3]^{2+}$ doped into the $[\text{Zn}(\text{bpy})_3](\text{ClO}_4)_2$ matrix than origin *I* of $[\text{Os}(\text{bpy})_3]^{2+}$ (equally normalized) in the $[\text{Ru}(\text{bpy})_3](\text{PF}_6)_2$ matrix (cf. Figs. 30 and 24). Thus, this strong origin dominates the emission spectrum and can even be detected in an excitation spectrum (Fig. 30c).²¹

²⁰ $[\text{Os}(\text{bpy})_3]^{2+}$ also exhibits the tendency to aggregate in $[\text{Zn}(\text{bpy})_3](\text{ClO}_4)_2$. The spectroscopic consequences of this effect seem to be less distinct than found for $[\text{Ru}(\text{bpy})_3]^{2+}$ (Sects. 3.2.1 and 3.5) and probably therefore have not yet been discussed in the literature.

²¹ The identification of this origin at 14223 cm^{-1} has been carried out similarly as shown, for example, in Sections 2.2.1, 3.3.1, and 4.1.2.

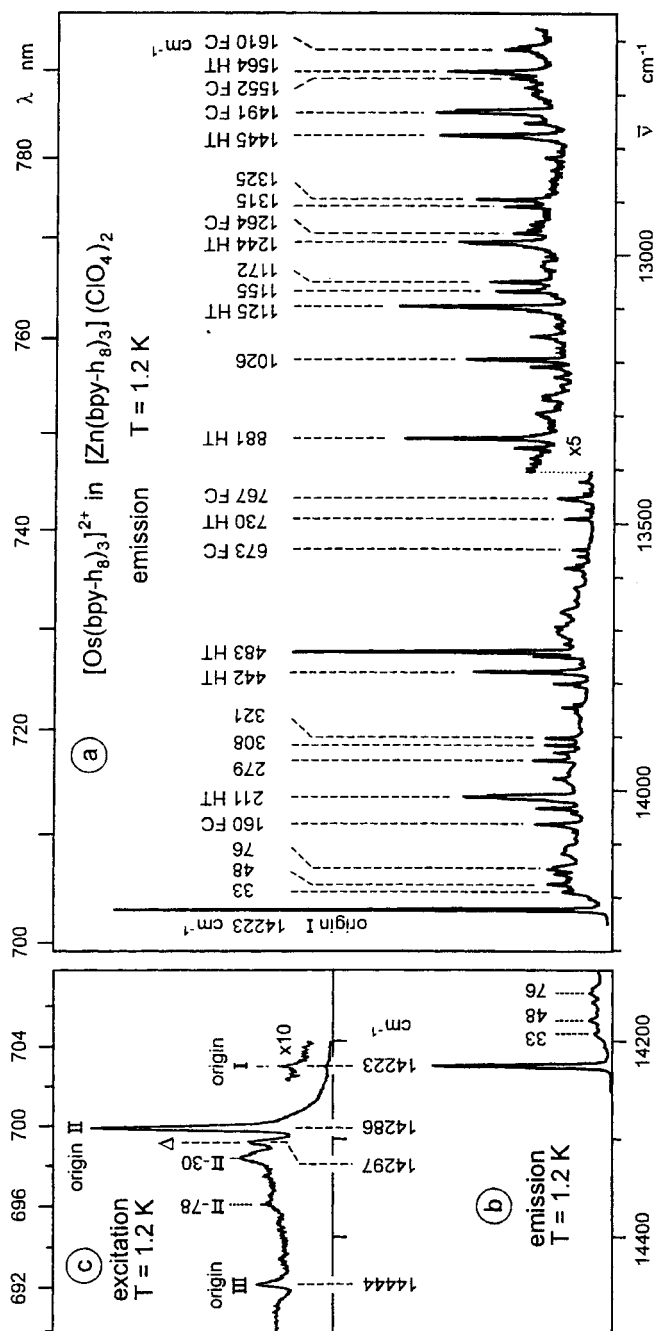


Fig. 30. a, b Emission and c excitation spectra at $T = 1.2 \text{ K}$ of $[\text{Os}(\text{bpy-h}_8)_3]^{2+}$ doped into $[\text{Zn}(\text{bpy-h}_8)_3](\text{ClO}_4)_2$; nominal concentration $\approx 0.2\%$. a, b Excitation at 514.5 nm ($\Delta 19436 \text{ cm}^{-1}$), c detection at 13740 cm^{-1} ($\Delta 483 \text{ cm}^{-1}$ satellite). Several satellites are assigned to Franck-Condon (FC) and Herzberg-Teller (HT) active modes, respectively. Most of the FC-active modes are also observed as excited state modes of states |II> and/or |III> with nearly the same energies as in the ground state (see Sect. 4.2.1)

In the context of the discussion presented in Section 4.1.4, it is obvious that this symmetry reduction leads to an admixture of state $|II\rangle$ into state $|I\rangle$ and thus provides allowedness to the transition $|0\rangle \leftrightarrow |I\rangle$. Indeed, this admixture is also displayed in the vibrational satellite structure observed in the emission from the lowest state $|I\rangle$. In Section 4.1.3 it was demonstrated that in the undistorted situation one finds only Herzberg-Teller (HT) active modes. However, Fig. 30a clearly shows that besides HT-active ones a large number of Franck-Condon (FC) satellites also appear. This FC activity stems from the mixing-in of state $|II\rangle$ character (cf. Sect. 4.1.4; Table 9). It cannot be excluded that a further, higher lying state can also provide such properties, but according to the energy proximity of state $|II\rangle$ and its high radiative rate it will certainly be the one of greatest importance.

The interpretation given implies that the intensities of the electronic origin I or of the FC satellites represent a measure of the amount of admixture of state $|II\rangle$ character into state $|I\rangle$. Thus, these intensities provide information about the importance of the geometrical distortions experienced by $[\text{Os}(\text{bpy})_3]^{2+}$ at that specific environment. Interestingly, under high-pressure application, the distortion can be further increased. This leads to a relative increase in the intensities of electronic origin I and vibrational satellites that are induced by FC-active modes (e.g., 1491 cm^{-1}) compared to HT-induced satellites (e.g., 1445 cm^{-1}).²²

4.2.1

Vibrational Energies of Excited States

In a very recent investigation [309] it has been possible to register an excitation spectrum of $[\text{Os}(\text{bpy})_3]^{2+}$ in $[\text{Zn}(\text{bpy})_3](\text{ClO}_4)_2$ up to about 2000 cm^{-1} above state $|I\rangle$ at $T = 1.3\text{ K}$. This spectrum (not reproduced) is relatively complicated, since vibrational satellite structures belonging to the excited states $|II\rangle$, $|III\rangle$ and presumably to two further electronic states superimpose. (State $|I\rangle$ is not of importance since it carries only a very weak allowedness). Nevertheless, a careful analysis of the vibrational structures reveals that a number of satellites of the respective excited electronic states can be identified. In particular, for the states $|II\rangle$ and/or $|III\rangle$ vibrational energies of 160 (160), 673 (673), 767 (767), 1263 (1264), 1491 (1491), 1554 (1552), and 1613 cm^{-1} (1610 cm^{-1}) can clearly be resolved. Ground state vibrational energies are given in brackets (Fig. 30a). (The experimental error for the excited state modes is $\pm 3\text{ cm}^{-1}$). Interestingly, at least for these modes, the vibrational energies of the excited states are nearly unchanged compared to those of the electronic ground state. This behavior is also indicated by the very small values of blue shifts of the energies of the electronic origins upon per-deuteration (see Table 10).²³

²² These experiments were carried out with $[\text{Os}(\text{bpy})_3]^{2+}$ doped into $[\text{Ru}(\text{bpy})_3](\text{ClO}_4)_2$ [186, 190, 200, 202, 292].

²³ Such blue shifts upon deuteration display an average reduction of vibrational force constants in the excited states compared to those of the ground state due to different reductions of the zero-point vibrational energies [37, 72–74, 104].

4.2.2

Isotope Marking and Evidence for Delocalized Low-Lying States

It is highly instructive to compare spectroscopic properties of $[\text{Os}(\text{bpy}-\text{h}_8)_2(\text{bpy}-\text{d}_8)]^{2+}$, $[\text{Os}(\text{bpy}-\text{h}_8)(\text{bpy}-\text{d}_8)_2]^{2+}$, and $[\text{Os}(\text{bpy}-\text{d}_8)_3]^{2+}$ to those of $[\text{Os}(\text{bpy}-\text{h}_8)_3]^{2+}$. All of these compounds can be doped into $[\text{Zn}(\text{bpy}-\text{h}_8)_3](\text{ClO}_4)_2$, and one always obtains highly resolved emission spectra²⁴ [98, 104]. Those of the two partially deuterated compounds represent superpositions of spectra of different sites if nonselectively excited. In [104] the occurrence of three sites A, B, and C for both complexes is reported, and it is shown that it is suitable to investigate sites B in more detail. These specific sites are easily singled out with the methods of site-selective spectroscopy. The spectra obtained are compared in Fig. 31 to those of the two per-complexes.

Deuteration of $[\text{Os}(\text{bpy})_3]^{2+}$ results in typical effects as discussed in the preceding Sections 2.3 and 3.5 as well as in [37, 44, 60, 68, 74, 85, 104, 108]. In particular, due to deuteration (1) the electronic origins are blue-shifted; (2) all vibrational energies are red-shifted (except phonons); (3) emission decay times become longer; and (4) the intensity distribution of the vibrational satellites changes in part. (Fig. 31; Table 10) However, of particular interest in the context of this section, is the vibrational satellite structure observed for the two partially deuterated compounds. This situation is very similar to the one found for partially deuterated $[\text{Ru}(\text{bpy})_3]^{2+}$ chromophores (Sect. 3.5), but the $[\text{Os}(\text{bpy})_3]^{2+}$ spectra are much better resolved due to weaker couplings to the lattice phonons (cf. Fig. 31 to 19; [104]).

Table 10. Low-lying electronic states and emission decay times of differently deuterated $[\text{Os}(\text{bpy})_3]^{2+}$ compounds at $T = 1.3 \text{ K}$ [83, 98, 104]

$[\text{Zn}(\text{bpy}-\text{h}_8)_3](\text{ClO}_4)_2$ matrix ^a	Lowest excited states $[\text{cm}^{-1}]$ ^c		Δ	III)
	I) ($\tau_1[\mu\text{s}]$) ^b	II)		
$[\text{Os}(\text{bpy}-\text{h}_8)_3]^{2+}$	14 223 (22)	14 286	14 297	14 444
$[\text{Os}(\text{bpy}-\text{h}_8)_2(\text{bpy}-\text{d}_8)]^{2+ \text{ d}}$	14 238 (26)	14 298	14 316	14 460
$[\text{Os}(\text{bpy}-\text{h}_8)(\text{bpy}-\text{d}_8)_2]^{2+ \text{ d}}$	14 233 (31)	14 290	14 308	14 454
$[\text{Os}(\text{bpy}-\text{d}_8)_3]^{2+}$	14 256 (46)	14 320	14 332	14 479

^a Nominal molar concentration in solution $\text{Os}:\text{Zn} \approx 0.002$.

^b The decay is strictly mono-exponential excitation at 337.1 nm.

^c Experimental error $\pm 1 \text{ cm}^{-1}$, $\pm 1 \mu\text{s}$.

^d The second highest site B is selected.

²⁴ The $[\text{Ru}(\text{bpy})_3](\text{PF}_6)_2$ matrix can also be used for doping of $[\text{Os}(\text{bpy})_3]^{2+}$. However, for partially deuterated compounds, one finds a relatively large number of sites in the matrix (for details see [98]).

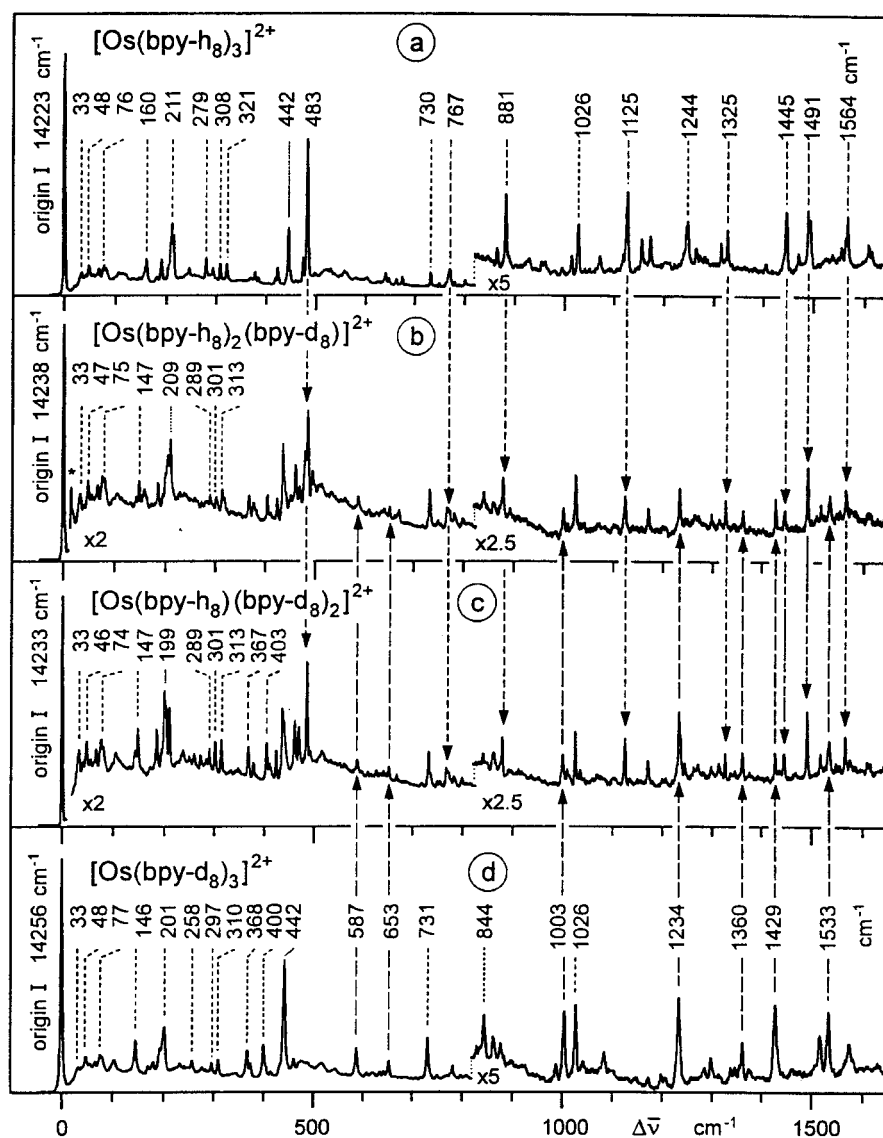


Fig. 31. Emission spectra at $T = 1.3$ K of $[\text{Os}(\text{bpy-h}_8)_n(\text{bpy-d}_8)_{3-n}]^{2+}$ in $[\text{Zn}(\text{bpy-h}_8)_3](\text{ClO}_4)_2$ with $n = 0$ to 3 [104]. The electronic origins are set to zero on a wavenumber scale. Their intensities are normalized. Nominal guest/host concentrations $\approx 0.2\%$. The spectra b, c represent site-selectively excited emission spectra of the second highest sites B. The asterisk in b designates the origin of a different site (site A), which could not be separated site-selectively. Note the important result: The partially deuterated compounds exhibit vibrational satellites in the energy range of internal ligand vibrations from (bpy-h₈) and (bpy-d₈) ligands. This is indicated by the arrows. Due to the fact that a vibrational ligand-ligand coupling may be neglected for these high-energy modes, this result allows us to conclude that an electronic coupling between the ligands occurs via the metal

The rich satellite structures seen in Fig. 31 are without doubt assigned to a single, excited electronic state in each case. For all compounds a mono-exponential emission decay is observed ([104]; Table 10). The low-energy satellites up to $\approx 100\text{ cm}^{-1}$ correspond to lattice modes and are determined by the matrix. Therefore, one finds the same energies also for $[\text{Ru}(\text{bpy})_3]^{2+}$ doped into this matrix (cf. Table 4). The satellites occurring between about 100 and 450 to 500 cm^{-1} are induced mainly by metal-ligand (M-L) vibrations. Obviously, such M-L modes cannot simply be assigned to specific ligands due to couplings via the moving metal. However, the situation changes with increasing energy or frequency, i.e., for high-energy ligand vibrations. In this case, the metal in the center serves as a buffer, which decouples the vibrations of the different ligands from each other, simply because the massive metal ion cannot follow the fast vibrations of the light atoms. This behavior is even more pronounced for the much heavier Os^{2+} than for Ru^{2+} [112–114]. Other coupling mechanisms, for example, through space by a multipole coupling [111], may also be disregarded in the limit of the spectral resolution of 1 cm^{-1} . In addition, the validity of these results is demonstrated experimentally by investigations with $[\text{Rh}(\text{bpy}-h_8)_2(\text{bpy}-d_8)]^{3+}$ and $[\text{Pt}(\text{bpy}-h_8)(\text{bpy}-d_8)]^{2+}$. For both compounds the emission spectra stem exclusively from the protonated ligand(s), and the spectra reveal definitely that no high-energy ligand satellite of (bpy- d_8) character occurs (see Sect. 2.3; [44, 60, 108]). Thus, it follows that the high-energy ligand vibrations may indeed be regarded as being confined to the individual ligands [cf. also Sect. 3.5).

Interestingly, a comparison of the four spectra reproduced in Fig. 31 shows clearly that both partially deuterated $[\text{Os}(\text{bpy})_3]^{2+}$ compounds exhibit vibrational satellites corresponding to the (bpy- h_8)- and to the (bpy- d_8)-ligands. Since a vibrational coupling is excluded, these modes can only occur as satellites to the respective electronic origin I for both compounds. This is only possible when the electronic charge distribution corresponding to state |I> is delocalized over the two different ligands. Only in this case the vibrations can manifest themselves by Herzberg-Teller and/or Franck-Condon activities. Or vice versa, if the electronic coupling between the ligands can be neglected, high-energy vibrations of isotopically differently marked ligands are not found in emission, as has been shown for partially deuterated $[\text{Rh}(\text{bpy})_3]^{3+}$ and $[\text{Pt}(\text{bpy})_2]^{2+}$ (Sect. 2.3; [44, 60, 108]). Further aspects with regard to the problem of localization/delocalization are discussed in connection with the properties of $[\text{Ru}(\text{bpy})_3]^{2+}$. These considerations are mostly also valid for $[\text{Os}(\text{bpy})_3]^{2+}$ (see Sects. 3.5, 3.7, and 3.8).

In conclusion, it has been shown by analyzing the series of $[\text{Os}(\text{bpy}-h_8)_n(\text{bpy}-d_8)_{3-n}]^{2+}$ compounds (with $n = 0$ to 3) with highly resolved and site-selectively excited emission spectra that the lowest excited state |I> for each of these compounds is delocalized over the different ligands and the metal. This is also valid if a high magnetic field of $B = 6\text{ T}$ is applied [83]. From this behavior it may be deduced that the second excited state is also delocalized.

Moreover, it is demonstrated that the equilibrium positions of the lowest excited state(s) and the ground state are even less shifted with respect to each other than in $[\text{Ru}(\text{bpy})_3]^{2+}$. This is displayed in the extremely small values of the Huang-Rhys factors, which characterize the distinctness of vibrational progres-

sions. Furthermore, it is strongly indicated that the vibrational energies of the excited states $|II\rangle$ and $|III\rangle$ and thus the vibrational force constants are nearly equal to those of the ground state. This has been directly demonstrated for several vibrational modes (see above) and may be independently deduced from the very small blue shifts of the electronic origins I, II and III upon deuteration (Table 10). Therefore, it may be concluded that the lowest $^3\text{MLCT}$ states of $[\text{Os}(\text{bpy})_3]^{2+}$ may be well described by a strongly covalent situation, in which the charge distribution is smeared out over the whole complex. Similar results have also been deduced for $[\text{Ru}(\text{bpy})_3]^{2+}$ (Sects. 3.5 and 3.8). Thus it follows that the simple picture of a transfer of one electron charge from the metal to the ligand(s) is not adequate to describe these states correctly. Presumably, the net amount of charge transfer from the metal to the ligands is very small, and thus the designation as “MLCT” states might be misleading if applied too literally.

4.3

Alternative Views

In the current literature one finds three models (each excluding the other) to describe the lowest excited states of $[\text{Os}(\text{bpy})_3]^{2+}$, similarly as for $[\text{Ru}(\text{bpy})_3]^{2+}$ (see Sect. 3.8). The present investigation strongly supports a delocalized and covalent characterization, while the other two models predict a localization due to a strong distortion [268, 302] and, in contrast, a delocalization due to a weak exciton coupling between (Os-bpy) subunits [310], respectively. These two models will be briefly compared to the experimental situation.

Strong Distortion in the Excited State(s). A strong distortion in the excited state(s) relative to the ground state may indeed lead to a localization. Obviously, such a process cannot occur without any changes, e.g., shifts of nuclear equilibrium positions and/or alterations of vibrational energies (see the detailed discussions in Sect. 3.8.2). However, as evidenced in the preceding section, $[\text{Os}(\text{bpy})_3]^{2+}$ doped into a rigid matrix does not exhibit such changes. In contrast, with respect to the nuclear equilibrium position and vibrational force constants, the three lowest excited states are very similar to the ground state.

On the other hand, distinct frequency shifts have been reported to occur in $^3\text{MLCT}$ state(s) of $[\text{Os}(\text{bpy})_3]^{2+}$. Table 11 summarizes the results from [268, 302]. The first column gives a number of ground state vibrational energies, while the second column shows values obtained by time-resolved resonance Raman scattering of largely saturated excited state(s). These values are significantly shifted to lower energies, if both columns are compared. These shifts are assigned to result from the localization of nearly one electron charge on one bpy-ligand. Thus, it is assumed in this model [268, 302] that these excited state vibrational energies should compare well to (bpy.)-vibrational energies. The values given in the third column are taken in refs [268, 302] as a confirmation of this model.

These experiments were carried out with $[\text{Os}(\text{bpy})_3]^{2+}$ dissolved in polar and fluid solutions at room temperature. Thus, a localization could possibly be induced by an asymmetrical complex-solvent interaction [104, 126, 146]. Such a process would not occur in a rigid matrix as used in our investigations (cf. Sect. 3.8.2).

Table 11. Comparison of energies of resonance-enhanced Raman modes (RR) of the electronic ground state of those to $^3\text{MLCT}$ state(s) of $[\text{Os}(\text{bpy})_3]^{2+}$ and of Libpy in solution [268, 302]. These values are set in relation to IR-active ground state modes of $[\text{Os}(\text{bpy})_3]^{2+}$

$[\text{Os}(\text{bpy})_3]^{2+}$		$(\text{bpy})^-$	$[\text{Os}(\text{bpy})_3]^{2+}$
RR ground state	RR $^3\text{MLCT}$	RR Libpy	IR ground state
1029	1023	992	1026
1048	1045	1019	1045
	1107		1107
1268	1220	1206	1220
1322	1288	1243	1285
1491	1429	1407	1421
1558	1512	1486	1513
1610	1558	1554	1560

However, an alternative explanation should not be disregarded. The fourth column of Table 11 displays a very interesting comparison. For each of the $^3\text{MLCT}$ modes (column 2), one finds an IR-active ground state mode (column 4), which fits in nearly all cases very well. This situation is not understandable in the model of localized $^3\text{MLCT}$ state(s), in which the excited state vibrational frequencies are shifted. However, it is not unexpected on the basis of a strongly covalent and delocalized description, where the charge densities are largely smeared out. In this description one even expects that the vibrational energies are not significantly altered due to the excitation (Sect. 4.2.1). However, at first sight, the occurrence of IR-active modes in resonance-enhanced Raman (RR) spectra seems to be unusual, since more commonly one finds a Franck-Condon type of RR scattering involving totally symmetric modes. Such a process is described by the so-called A-term scattering in Albrecht's formalism [303]. On the other hand, it is well known that a vibronic type of RR scattering (Albrecht's B term; [303]) may also very effectively enhance IR-active modes [304–308, 211]. Possibly, this vibronic mechanism of RR enhancement involving the electronic transitions within the manifold of different triplets of $[\text{Os}(\text{bpy})_3]^{2+}$ is dominating here.

In summary, the “shifts” of vibrational frequencies after excitation (cf. columns 1 and 2 of Table 11) might well result from changes in the mechanisms of RR scattering from Albrecht's A-term scattering of ground state modes to Albrecht's B-term scattering in the triplet states manifold. In particular, this is suggested by the data presented in Table 11. Consequently, before a conclusion on shifts of frequencies in the excited state(s) relative to those of the ground state can be drawn, one has to exclude the effectiveness of this scattering mechanism according to Albrecht's B term.

Weak Triplet Exciton Coupling. Recently, it has been proposed to describe the properties of $[\text{Os}(\text{bpy})_3]^{2+}$ by cutting the complex into (Os-bpy) subunits²⁵ and

²⁵ More accurately expressed, the authors [310] discuss a model of separated (1/3 Os-bpy) subunits, as proposed for Ru(II)-compounds in [142].

to introduce an exciton coupling for the triplets of these subunits [310]. A related model has been proposed by the same authors [162] also for $[\text{Ru}(\text{bpy})_3]^{2+}$ (see the discussion in Sects. 3.5 and 3.8.1). The basis of the model used in [310] is the Davydov exciton theory [62–65]. This theory provides in the limit of the dipole-dipole approximation and under the condition of zero wavefunction overlap a very simple expression for the energy splittings ΔE of states of interacting molecules. In this approximation one obtains [62–65] $\Delta E = \text{const} \cdot \alpha \cdot k^r$. α is a geometrical factor defined by the orientations and distances between interacting molecules, and k^r is the radiative rate ($\triangleq$ oscillator strength) corresponding to the excited state in the noninteracting situation. This model was briefly considered to describe a coupling of transition dipole moments of strong singlet-singlet $\pi\pi^*$ transitions of different ligands at the beginning of Sections 2 and 3. However, it is certainly not reasonable to use this simple approach to describe the triplet states of the strongly covalent $[\text{Os}(\text{bpy})_3]^{2+}$ complex.

Nevertheless, we want to apply this model for a moment. Due to [310], one hypothetical, low-lying excited state (near 14405 cm^{-1}) of each of two noninteracting (Os-bpy) subunits is assumed to split into two Davydov components by 158 cm^{-1} , when the interaction between the subunits (belonging to the same $[\text{Os}(\text{bpy})_3]^{2+}$ complex) is taken into account. These two components are then identified with the states $|II\rangle$ and $|III\rangle$ of our nomenclature (Fig. 25b). The same approach should hold according to [310] for other low-lying terms. Thus, states $|I\rangle$ and $|\Delta\rangle$ of our nomenclature, being separated by 74 cm^{-1} (Table 10; Fig. 25b), are assigned [310] to two Davydov components resulting from a second hypothetical state of the two noninteracting subunits. Due to the fact that the geometrical factor of the expression given above is equal for both situations, one can easily check whether both splitting values fit to each other. With the knowledge of the relative radiative rates for all four low-lying states of $[\text{Os}(\text{bpy})_3]^{2+}$ (see Fig. 30c), one can estimate²⁶ that the experimentally found value of 74 cm^{-1} is too large by a factor of at least four. The situation is even less favorable for the application of the Davydov model as proposed in [310], when data obtained under a high magnetic field are compared. In $[\text{Os}(\text{bpy})_3]^{2+}$ doped into $[\text{Ru}(\text{bpy})_3](\text{PF}_6)_2$ a magnetic field of $B = 6\text{ T}$ results in an increase in the radiative rate k^r of the lowest state by about a factor of 1000 (Fig. 28). In this case, the energies of the Davydov components should strongly depend on the magnetic field. A simple estimate shows that one should observe a more than two orders of magnitude larger Zeeman shift for the lower lying Davydov component than found for state $|I_B\rangle$ (cf. Sect. 4.1.4). In summary, it must be pointed out that the Davydov model, as it is applied in [310] to the triplet states of $[\text{Os}(\text{bpy})_3]^{2+}$, fails.

²⁶ In this estimate the geometrical factors are the same for the two situations and the relative radiative rates of the non-interacting hypothetical terms may be approximated using the sum rule of oscillator strengths (see [62c, Chap. 3.2.3]).

5

Conclusion and Outlook

The low-lying triplet states of the series of compounds investigated and shown in Table 12 differ strongly with respect to the metal d -orbital contributions. This amount governs all properties connected with these states. Relatively small contributions are found for $[\text{Rh}(\text{bpy})_3]^{3+}$ and $[\text{Pt}(\text{bpy})_2]^{2+}$. Thus, the lowest states are assigned to ligand-centered (LC) $^3\pi\pi^*$ states. However, if compared to the uncoordinated ligand [82], one finds relatively high probabilities of the $S_0 \rightarrow T_1$ transitions, a decrease in emission decay times by a factor of about 10^3 , and an occurrence of weak metal-ligand vibrational satellites. This behavior shows that at least a small admixture of metal character and an increased spin-orbit coupling to higher lying singlets are present. In this respect, the situation is more distinct for $[\text{Pt}(\text{bpy})_2]^{2+}$ than for $[\text{Rh}(\text{bpy})_3]^{3+}$. It is suitable to characterize the lowest triplet T_1 for these two systems schematically after soc is taken into account as (see also [81, 311]):

$$|T_1\rangle = a |^3\pi\pi^*\rangle + b |^3d\pi^*\rangle + c |^3dd^*\rangle + d (\text{singlet admixtures}) \text{ with } a \gg b, c, d.$$

The inclusion of dd^* states for $[\text{Rh}(\text{bpy})_3]^{3+}$ is reasonable, since it is expected that they lie only $\approx 2 \cdot 10^3 \text{ cm}^{-1}$ [312] higher than the emitting triplet, while for $[\text{Pt}(\text{bpy})_2]^{2+}$ an admixture of MLCT character seems to be more significant, due to its relatively low energy (Fig. 2; Sect. 2.1; [44, 60]).

The values of the mixing coefficients or the amount of an admixture of metal character to the lowest $^3\pi\pi^*$ states cannot be calculated as yet, but it is possible to develop a classification based on experimental results, allowing us to signify the importance of this admixture with respect to a series of physical properties. This can be achieved by a comparison with the uncoordinated bpy, on the one hand, and with $[\text{Ru}(\text{bpy})_3]^{2+}$ and $[\text{Os}(\text{bpy})_3]^{2+}$, on the other. Such results are summarized in Table 12, where the compounds are arranged according to increasing importance of metal character for the lowest excited and emitting states.

1. The first column shows that the transition energies are red-shifted with respect to the energy of the uncoordinated bpy. This stabilization results from the formation of the complex and from an increasing dd^* and/or MLCT admixture to the lowest ^3LC states of $[\text{Rh}(\text{bpy})_3]^{3+}$ [60] and $[\text{Pt}(\text{bpy})_2]^{2+}$ [44, 68], while for $[\text{Ru}(\text{bpy})_3]^{2+}$ and $[\text{Os}(\text{bpy})_3]^{2+}$ an MLCT character becomes dominant (e.g., see [134–156, 158–180]).

2. The second and third columns give the values of zero-field splittings (zfs). The total zfs for $[\text{Rh}(\text{bpy})_3]^{3+}$ [76–79] is nearly the same as that found for bpy [82]. This clearly illustrates the still relatively small dd^* or MLCT admixtures to the ^3LC states. The situation seems to be similar for $[\text{Pt}(\text{bpy})_2]^{2+}$. However, for $^3\text{MLCT}$ states, the zfs becomes very large (Figs. 13 and 25).

3. With increasing d -admixture and spin-orbit coupling the spin-selection rules are weakened. This leads to a significant increase in radiative rates or decrease in emission decay times of the lowest triplet sublevels. This tendency is well displayed in column (4) with the exception of the value found for $[\text{Pt}(\text{bpy})_2]^{2+}$. Possibly, in this planar compound nonradiative deactivation pro-

Table 12. Trends in spectroscopic properties of different metal compounds with 2,2'-bipyridine ligands^{a)}

Compounds	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)
	Triplet sublevels and zfs [cm ⁻¹]			Emission decay time ^d of 1> [μs]	Maximum Huang-Rhys factor S ^e	Deuteration-induced blue shift ^f [cm ⁻¹]	Characterization of electronic states ^g	References
	I> ^b	I>- II>	I>- III> ^c					
bpy in <i>n</i> -heptane	23 504	0.101 ± 3.03 GHz ^h 0.118 ± 3.52 GHz ^h		4 · 10 ⁶	0.3	86	³ ππ*	[82, 98]
[Rh(bpy) ₃] ³⁺ in [Zn(bpy) ₃](ClO ₄) ₂	22 757	0.077 ± 2.32 GHz ^h 0.116 ± 3.49 GHz ^h		4.5 · 10 ³ (13.6 · 10 ³) ⁱ	0.3	61	³ LC (ππ*) + small dd* admixtures	[60] Section 2.5
[Pt(bpy) ₂] ²⁺ in neat [Pt(bpy) ₂](ClO ₄) ₂	21 237	< 1	< 1	50	0.3	≈ 50	³ LC (ππ*) + small MLCT admixtures	[44, 68, 75] Section 2
[Ru(bpy) ₃] ²⁺ in [Zn(bpy) ₃](ClO ₄) ₂	17 684	8.7	61	230 (310) ⁱ	0.1	40	³ MLCT (dπ*) delocalized	[44, 74, 85] Section 3
[Os(bpy) ₃] ²⁺ in [Zn(bpy) ₃](ClO ₄) ₂	14 223	63	211	22 (46) ⁱ	0.08	32	³ MLCT (dπ*) delocalized	[104] Section 4

^a Data given for protonated compounds.^b Lowest electronic origin.^c Total zero-field splitting of the lowest triplet state.^d Longest emission decay component at T = 1.3 K.^e Largest Huang-Rhys factor observed.^f Blue shift of the electronic origin upon per-deuteration.^g For a more detailed classification of the lowest excited states see Section 5.^h Data from ODMR in investigations [78, 82].ⁱ Emission decay time for the per-deuterated chromophore.

cesses are more efficient. The increasing metal character in the series of bipyridine complexes discussed is also seen in the intensities of vibrational satellites of metal-ligand (M-L) character, if normalized to the total intensity of vibrational satellites. For example, a rough estimate shows that the relative intensity of M-L modes increases by more than two orders of magnitude, when $[\text{Rh}(\text{bpy})_3]^{3+}$ is compared to $[\text{Os}(\text{bpy})_3]^{2+}$. These values are not given in Table 12, but see [44, 60, 83].

4. Columns (5) and (6) allow us to come to a very important conclusion. The nuclear equilibrium positions of the ground state and of the triplet sublevels are similar for all compounds listed in Table 12. This is manifested by the small values of Huang-Rhys factors S (e.g., compare to [86–97, 99, 100]), which characterize the distinctness of Franck-Condon progressions, for example, in well-resolved emission spectra. Interestingly, this property does not depend very sensitively on small MLCT or dd^* admixtures, but for compounds with $^3\text{MLCT}$ states, the S values become distinctly *smaller*. This means that the equilibrium positions of ground and excited states of $[\text{Ru}(\text{bpy})_3]^{2+}$ and $[\text{Os}(\text{bpy})_3]^{2+}$ differ even less than those of $[\text{Rh}(\text{bpy})_3]^{3+}$ or $[\text{Pt}(\text{bpy})_2]^{2+}$ (see Sects. 2.2, 3.3.2, 4.2; [44, 60, 83]). Moreover, the values of deuteration-induced blue shifts of the lowest transitions become also distinctly smaller in the sequence given. Although such a shift represents only an average measure, it strongly indicates [74] that the vibrational force constants of ground and lowest excited states become increasingly similar for the compounds in the series presented. Indeed, it has been demonstrated for many excited state vibrational frequencies of $[\text{Os}(\text{bpy})_3]^{2+}$ that these are not altered compared to those of the ground state (Sect. 4.2.1). Column (7) summarizes the characterizations given in the preceding sections.

Interestingly, even a very small d -admixture provides enough electronic coupling between the different ligands in the partially deuterated Rh(III) - and Pt(II) -complexes to accomplish an efficient interligand energy transfer from the deuterated to the protonated ligand(s). Thus, one observes *only* an emission from the energetically lower lying protonated ligand(s). A dual emission does not occur (Sects. 2.4 and 2.5; [60]). However, this coupling between the triplets on different ligands seems to be far too small to delocalize the excited-state wavefunctions in the sense of a “molecular excitation”. Presumably, the coupling energy is much smaller than the inhomogeneous energy shifts experienced by the different ligands.

The situation is completely different for $[\text{Ru}(\text{bpy})_3]^{2+}$ and $[\text{Os}(\text{bpy})_3]^{2+}$. In these compounds the metal orbital admixtures induce relatively strong ligand-ligand couplings and lead to delocalized $^3\text{MLCT}$ states. Evidence for a delocalization has been given on the basis of several independent investigations:

- Isotope marking shows that different ligands are *electronically* involved in the excited states of $[\text{Ru}(\text{bpy})_3]^{2+}$ and $[\text{Os}(\text{bpy})_3]^{2+}$. This is most clearly illustrated by the drastic differences (1) in the patterns of vibrational satellites and (2) in the structure of low-lying electronic transitions of $[\text{Ru}(\text{bpy-}h_8)_2(\text{bpy-d}_8)]^{2+}$ and $[\text{Os}(\text{bpy-}h_8)_2(\text{bpy-d}_8)]^{2+}$ compared to $[\text{Rh}(\text{bpy-}h_8)_2(\text{bpy-d}_8)]^{2+}$. In particular, this comparison shows that a vibrational ligand-ligand coupling of high-energy modes can be neglected and that the occurrence of $(\text{bpy-}h_8)$ and

(bpy- d_8) satellites in partially deuterated Ru(II) and Os(II) complexes must be ascribed to an efficient electronic coupling (Sects. 3.5, 4.2; [44, 60, 85, 104, 108]).

- Chemically induced localization in $[\text{Ru}(\text{i-biq})_2(\text{bpy})]^{2+}$ with characteristically larger values of zero-field splittings than for $[\text{Ru}(\text{bpy})_3]^{2+}$ displays obviously the differences between localization and delocalization. This result is further strongly supported by a comparison of zfs values of $[\text{Ru}(\text{bpz})_3]^{2+}$ to $[\text{Ru}(\text{bpy})_2(\text{bpz})]^{2+}$, and of $[\text{Ru}(\text{bpdz})_3]^{2+}$ to $[\text{Ru}(\text{bpy})_2(\text{bpdz})]^{2+}$ (Sect. 3.7; Table 7; [248]).
- A comparison to alternative views, which favor different but localized descriptions, shows that reported contradictions to the delocalized characterization can be removed (Sects. 3.5, 3.8, and 4.3).

Interestingly, these delocalized excited states have nearly the same potential hypersurfaces like the ground state with respect to force constants and equilibrium positions. Consequently, these states have to be described by largely spread out electron charge densities in ground and excited states. An excitation into the investigated $^3\text{MLCT}$ states does not lead to a significant charge rearrangement. Therefore, one must be careful not to use this term of “metal-to-ligand charge-transfer” too literally.

This review presents further a number of highly interesting, but not yet well known properties. Most of these are associated with metal d -orbital contributions to the lowest excited states and therefore, they can be adjusted chemically, for example:

- The metal d -orbital contribution controls – besides radiative rates and emission lifetimes – the zero-field splittings (zfs) of the triplets mainly via spin-orbit coupling. The extent of these zfs determines the rates of spin-lattice relaxations (slr). For zfs values of several cm^{-1} , like in $[\text{Ru}(\text{bpy})_3]^{2+}$, one finds relatively long slr times (220 ns at $T = 1.2 \text{ K}$) according to a direct process of slr that is not very efficient. At higher temperature ($T \gtrsim 6 \text{ K}$) the Orbach mechanism grows in strongly (Sect. 3.4).
- In most cases, like in $[\text{Rh}(\text{bpy})_3]^{3+}$, $[\text{Pt}(\text{bpy})_2]^{2+}$, and $[\text{Ru}(\text{bpy})_3]^{2+}$, the low-temperature emission spectra represent superpositions of spectra of different triplet sublevels. It was possible to separate these spectra by time-resolution methods (Sects. 3.4, 2.2.2, [44]). In $[\text{Os}(\text{bpy})_3]^{2+}$ the slr from state $|II\rangle$ to state $|I\rangle$ is too fast to show such effects for the time resolution available.
- Due to the relatively slow equilibration between the two lowest excited states of $[\text{Ru}(\text{bpy})_3]^{2+}$, the Boltzmann distribution is not attained at low temperature ($T \lesssim 2.2 \text{ K}$). However, in the long-time regime, the emission decay components obey a perfect Arrhenius plot (Sect. 3.4).
- The radiative deactivation from the lowest excited state $|I\rangle$ of $[\text{Os}(\text{bpy})_3]^{2+}$ in a high-symmetry environment occurs exclusively by Herzberg-Teller mechanisms. Thus, the emission spectra are dominated by vibrational satellites, while the intensity at the electronic origin nearly vanishes. The vibrational modes can be well correlated to IR-active modes. These satellites represent so-called false origins. There are strong indications that radiative deactivations are in part induced by the still not well-studied processes of spin-orbit-

vibronic and spin-vibronic couplings. In particular, metal-ligand vibrations with a moving O s^{2+} ion, which carries a very large spin-orbit coupling compared to the organic ligands, seem to be important (Sect. 4.1.3). Similar effects, but slightly less distinct, are also found for $[\text{Ru}(\text{bpy})_3]^{2+}$ (Sect. 3.3.2) and presumably for $[\text{Pt}(\text{bpy})_2]^{2+}$ (Sect. 2.3).

- By applying magnetic field, the low-temperature emission spectra are strongly tunable. As discussed above, at zero field the satellite structure is governed by IR-active modes due to radiative Herzberg-Teller deactivation. At high fields (e. g., at $B = 6$ T) the spectrum is completely different. In this case it is dominated by totally symmetric Franck-Condon active modes. This effect is very distinct for $[\text{Os}(\text{bpy})_3]^{2+}$ doped into $[\text{Ru}(\text{bpy})_3](\text{PF}_6)_2$ (Sect. 4.1.4) and it is also observed but less pronounced for $[\text{Ru}(\text{bpy})_3]^{2+}$ in $[\text{Zn}(\text{bpy})_3](\text{ClO}_4)_2$ (Sect. 3.3.2; Table 4). This behavior results from a B-field-induced mixing of the two lowest excited states, which exhibit different vibronic coupling properties. Thus, at high field the emission from the lowest excited state displays mainly properties of state $|II\rangle$ (Sect. 4.1.4).
- Aggregate formation, for example of $[\text{Ru}(\text{bpy})_3]^{2+}$ in $[\text{Zn}(\text{bpy})_3](\text{ClO}_4)_2$, has to be taken into account, as demonstrated in Sections 3.2.1 and 3.5.
- Raman spectra, for example of $[\text{Pt}(\text{bpy-h}_8)(\text{bpy-d}_8)](\text{ClO}_4)_2$, show vibrational lines of both ligands. Interestingly, the scattering intensities of the deuterated ligand are significantly higher than those of the protonated one (Sect. 2.3).
- Results from resonance Raman scattering experiments reported in the literature for the lowest excited $^3\text{MLCT}$ states of $[\text{Os}(\text{bpy})_3]^{2+}$ [268, 302] and taken as evidence for strong frequency shifts in the excited state(s) compared to those of the ground state and, hence, for localization are presumably alternatively explained. It is found that the resonance-enhanced Raman modes given in [268, 302] fit much better to IR-active ground state modes than to $(\text{bpy})^-$ -ones. This behavior might be explained by the effectiveness of a mechanism of resonance Raman scattering which is usually neglected. The mechanism is based on vibronic scattering according to Albrecht's B-term scattering, while mostly only the A-term scattering due to totally symmetric modes is taken into account. The alternative interpretation given here requires further that the vibrational frequencies of ground and excited $^3\text{MLCT}$ states are nearly equal. However, this is strongly indicated as discussed in Sects 4.2.1 and 4.3.

The aspect of a chemical tunability of physical properties in this class of metal-bipyridine compounds opens fascinating possibilities. Thus, it is highly attractive to explore this concept further and to apply it as a guideline for studies of a number of related compounds. For example, one can analyze how effectively the properties of Pt(II)-complexes may be tuned chemically by changing the ligands. This discussion, based on Table 13, may be regarded as an outlook for future detailed studies [313].

The sequence of compounds given in Table 13 shows that the lowest triplet state can be tuned chemically over an energy range of more than 8000 cm^{-1} . For the orthometalated compounds this shift is related to an increase in MLCT character to the lowest state $|I\rangle$ compared to $[\text{Pt}(\text{bpy})_2]^{2+}$. This state, however, is still largely of LC character, as shown in [83, 84, 93, 101, 216, 313–316]. Moreover, the

Table 13. Trends in spectroscopic properties of Pt(II) compounds with different ligands

Compounds ^a	(1) Triplet sublevels and zfs [cm ⁻¹]	(2)	(3)	(4) Emission decay time ^d of $ I\rangle$ [μ s]	(5) Maximum Huang-Rhys factor S^e	(7) Characterization of the lowest electronic states	(8) References
	$ I\rangle^b$	$ I\rangle - II\rangle$	$ I\rangle - III\rangle^c$				
$[Pt(bpy)_2]^{2+}$ in neat $[Pt(bpy)_2](ClO_4)_2$	21237	< 1	< 1	50	0.3	$^3LC(\pi\pi^*)$ + small MLCT admixtures	[44, 60, 68, 75] Section 2
$Pt(bhq)_2$ in <i>n</i> -decane	20814	12	40	48	< 0.1	$^3LC + MLCT$ admixtures	[316]
$Pt(phpy)_2$	19571	6.6	32	72		$^3LC + MLCT$ admixtures	[314]
$Pt(3-thpy)_2$	18020	13	22	108		$^3LC + MLCT$ admixtures	[314]
$Pt(2-thpy)(CO)(Cl)$	18012	< 1	3.8	120	0.25	$^3LC + MLCT$ admixtures	[317]
$Pt(2-thpy)_2$	17156	7	16	110	0.1	$^3LC + MLCT$ admixtures	[93]
$Pt(qol)_2$	15426	< 1	< 1	60	0.2	^3ILCT	[195, 315, 318]
$Pt(qtl)_2$	13158	< 1	< 1	7	0.5	^3ILCT	[315, 318]

Ligands: bpy: 2,2'-bipyridine; bhq⁻: benzo[h]quinolate; phpy⁻: 2-phenylpyridinate; 3-thpy⁻: 2-(3-thienyl)pyridinate; 2-thpy⁻: 2-(2-thienyl)pyridinate; qol⁻: 8-quinolate, qtl⁻: 8-quinolineethiolate.

^a The chromophores are investigated in an *n*-octane Shpol'skii matrix, if not otherwise indicated.

^b Lowest electronic origin of triplet character for the lowest site.

^c Total zero-field splitting of the lowest triplet state.

^d Longest emission decay component at $T = 1.3$ K.

^e Largest Huang-Rhys factor observed.

MLCT admixture determines the zero-field splittings. Vice versa, the amount of zfs may be used to characterize the importance of an admixture of metal character. This property is highly attractive, since the series of compounds of Table 13 provides a quasi-continuous range of splitting patterns and metal admixtures. Thus, this series fills the gap of zfs values between $[\text{Pt}(\text{bpy})_2]^{2+}$ and $[\text{Ru}(\text{bpy})_3]^{2+}$ of Table 12 [166, 313]. This will give access to an enlarged range of different efficiencies and time ranges of spin-lattice relaxation [165, 166]. For example, it allows us to study effects of spin polarization in more detail, to influence the interplay between direct, Raman, and Orbach processes of spin-lattice relaxation, and possibly to generate a crossover situation from a ligand-confined excitation, for example found for $[\text{Pt}(\text{bpy})_2]^{2+}$, to a clearly delocalized situation as in $[\text{Ru}(\text{bpy})_3]^{2+}$ due to a chemically induced increase in electronic coupling between the different ligands.

It is briefly mentioned that the situation for Pt(II) complexes with qol^- and qtl^- ligands is different, since in these compounds the lowest excited states result from intraligand-charge transfer transitions ($^3\text{ILCT}$) with very small metal admixtures [195, 315, 318, 319]. This class of compounds exhibits highly efficient red to infrared emissions. It is noted that these Pt(II) compounds are related to systems like $\text{Al}(\text{qol})_3$ [315, 318, 319], which are of great interest for light-emitting electroluminescent devices for flat panel display systems [320, 321].

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