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Spectroscopy with Lasers

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I. Introduction

The development and technical improvement of many different laser systems during recent years has greatly enlarged the scope of possible laser applications in various fields of physics and chemistry. Laser oscillations have so far been obtained at several thousand different wavelengths, covering the range from submillimeter waves to the ultraviolet region, thus lasers have proved especially useful for spectroscopic investigations. Here they may solve problems where conventional light sources fail, and experiments which can hardly be done with spectral lamps often turn out to be much easier when a laser is used as the light source.

Some of these spectroscopic applications of lasers will be discussed in this review article, the experiments described exemplifying the laser's potential as a tool for spectroscopists.

It will be shown that the laser not only exceeds spontaneous light sources in intensity and spectral resolution, but, thanks to its special characteristics, makes possible investigations of a new and fundamental kind.

The first section explains the characteristics of the laser which are important for spectroscopic investigations and the differences as compared to spontaneous light sources.

The next section, which is the most extensive, deals with the various kinds of spectroscopic experiments which have been done or can be done with lasers as external light sources, where "external" means that the probe under investigation is placed outside the laser resonator. Together with a brief description of the experiments and a summary of the results, there is a discussion of the main qualities of the laser which made these special investigations possible.

Section IV explains a new approach to high resolution spectroscopy based on various kinds of saturation effects. Some of the experiments are performed inside the laser resonator, which implies the presence of coupling phenomena between the absorbing molecules under investigation and the laser oscillation itself. These feedback effects can be used for high-precision frequency stabilization and to measure frequency shifts and line profiles with an accuracy never previously obtained. By illuminating basic problems of the interaction of optical radiation with matter, these measurements may therefore serve as a check on theoretical approximations in this field.

The last section reports the results of some experiments with spectroscopy of the various laser media. This field is, of course, closely related to the understanding of the laser action itself, for instance, the elucidation of excitation mechanisms in different laser types, term assignments for various laser transitions or investigations of competing collision processes. Spectroscopy of laser media has therefore been performed by numerous laboratories; it is shown here that our knowledge of the spectroscopic properties of gaseous, liquid and solid-state media, especially in the infrared region, has been increased considerably by taking advantage of the laser characteristics described in Section II.

Especially interesting for chemists is the investigation of chemical lasers, where chemical energy from exothermic reactions is converted into light.

Since the field of spectroscopic laser applications is so vast and the number of published papers exceedingly large, this review cannot be complete. However, the author has tried to give a reasonable survey of what has been done and to offer some ideas about what can be done in modern spectroscopy1) with such an interesting and stimulating invention as the laser (Light Amplification by Stimulated Emission of Radiation).

II. Characteristic Features of Lasers as Spectroscopic Light Sources

There are five main qualities which make the laser an attractive spectroscopic light source [2]:

1. Its comparatively high output power on a single transition.
2. The spatial coherence of the induced emission which renders it possible to focus the laser output into a nearly parallel light beam.
3. Its temporal coherence, causing spectral linewidths of the induced emission to be smaller by several orders of magnitude than those of fluorescence lines emitted by spectral lamps.
4. The possibility of tuning the frequency of a laser line inside a frequency range by several methods, depending on the laser type.
5. The fact that several lasers can generate very short light pulses (down to 10^{-13} sec duration) with high peak powers (up to 10^{13} watts) [16a], which can be used to investigate short term transitions (e. g. lifetime measurements, flash photolysis, etc.).

In view of their importance, these five points will now be discussed in more detail:

1. Table 1 gives wavelengths and output powers for some important laser types operated in a continuous-wave (cw) or pulsed mode. The pulsed lasers normally have much higher peak powers but there are technical or theoretical limitations of the maximum repetition frequency, which means that their time-averaged intensity is often below that of the cw lasers.

For comparison the output power of a high-pressure mercury lamp (Osram HBO 200) also is listed. The reader has to consider, however, that the mercury lamp radiates this power into the unit solid angle (= 60°) distributed over the spectral range from 2000 to 6000 Å, whereas the laser intensity is concentrated at a single wavelength and collimated in a beam with a very small divergence between 10^{-4} and 10^{-7} sterad.

With respect to intensity, most of the laser transitions therefore are superior to conventional lamps, especially for experiments which demand a narrow spectral range or a small solid angle of the incoming light.

Table 1. *Output power of some important laser types*

Wavelength [μ]	Laser medium	Output [watt]	References
Continuous-wave lasers			
337	HCN	$10^{-1}-1$	3, 4)
7–220	H_2O	$10^{-3}-10^{-2}$	5)
10.8	N_2O	$\sim 10^3$	6)
~ 10	CO_2	10^2-10^4	7, 8)
1.06	YAG	10^2-10^3	9)
0.6328	He-Ne	$10^{-3}-10^{-1}$	10)
0.45–0.51	Ar^+	$1-10^2$	11)
0.32 + 0.44	He–Cd	10^{-1}	12)
0.3–300	Gaseous lasers	$10^{-3}-1$	13)
0.5–2	Injection lasers	$10^{-3}-10$	14)*
Pulsed Lasers			
0.69	Ruby	10^5-10^{10}	15)
1.06	Neodymium	10^5-10^{12}	16)
0.4–1	Dye lasers	10^4-10^7	17, 18)
10	CO_2	10^5	19)
	Injection lasers	10^4	20)
0.2–0.6	HBO 200 Mercury lamp High pressure	1.4 watt/Sterad^2	21)

* Meanwhile two important cw-tunable devices have been developed:

a) cw-dye laser (Rhodamin 6 G and Coumarin), 0.4–0.65 μm, $10^{-1}-1$ Watt; 14a)

b) spin-flip laser, 5–100 μm, 1 Watt. 14b)

2. The small divergence of the laser beam, which is limited only by diffraction and by optical inhomogeneities of the laser medium or other optical components in the laser cavity, has several advantages for spectroscopists:

It allows the laser radiation to be focused onto a small area ($\leq 10^{-6}$ cm^2) and the power density to be considerably increased (up to 10^6 watt cm^{-2} with continuous argon-lasers, and more than 10^{14} watt cm^{-2} with pulsed glass lasers) 22). This is, for instance, important for microspectrometric investigations (see Section III.9) and for production of high-temperature plasmas.

The nearly parallel laser beam furthermore allows absorption spectroscopy experiments which realize a long light path at low pressures in the absorption cell without loss in intensity due to beam spread effects; it also eliminates disturbing reflections from cell walls.

In resonance fluorescence, or Raman spectroscopy, the molecules excited by absorption of laser light, because of their short excited lifetimes, reemit the fluorescence or the scattered light essentially along the path of the exciting laser beam. The resulting fluorescence beam can easily be focused onto the entrance slit of a spectrograph, yielding a maximum of collected fluorescence light, which often is essential in these low light level investigations.

For all these experiments the laser may be regarded as a point light source which can be focused by suitable optical components in any desired way.

3. The spectral linewidths of fluorescence lines are determined in most spectral lamps by Doppler effect and pressure broadening and are therefore normally much broader than the natural linewidth, which is approached only by low-pressure hollow cathode lamps 23) operated at liquid helium temperatures.

The wavelength of a laser line, however, is determined by two factors: the fluorescence profile of the corresponding transition in the laser medium and the eigenfrequencies of the laser resonator modes. At normal multimode operation of a laser, where many axial and transverse modes participate in laser oscillation, these eigenfrequencies cover the whole spontaneous line profile nearly uniformly. In these cases the laser linewidth is *not* much smaller than that of the corresponding spontaneous line. In ion lasers for instance, the laser linewidths are especially high because of the high ion temperature in the discharge (up to 5000 °K) 24) and may exceed 5000 Mc/sec (3×10^{10} cycles/sec $\overset{\wedge}{=}$ 1 cm^{-1}) for the Ar^+ line $\lambda = 4880$ Å 25) compared with 1500 Mc/sec for the red Ne laser line at $\lambda = 6328$ Å.

In solid state lasers the fluorescence lines are broadened 26) by statistical Stark fields of the thermal vibrating crystal lattice and furthermore by optical inhomogenities of the crystal. The corresponding laser lines are accordingly, large at multimode operation 27) (5 cm^{-1} for the ruby-laser line $\lambda = 6943$ Å 28) at 300 °K.

In order to realize the extremely small linewidths, attainable because of the temporal coherence of induced emission, care must be taken to ensure that the threshold condition for induced oscillation is fulfilled for only one mode. The transverse modes can be eliminated by an appropriate choice of the cavity dimensions, introducing larger diffraction losses for all but the fundamental (= longitudinal) modes 29). From these a single mode can be selected by reducing the cavity length 30) or by coupling two resonators, as has been done by several authors in different ways 31-34).

The linewidth $\Delta\nu_L$ of such a single mode laser is determined by the bandwidth $\Delta\nu_c$ of the laser cavity (which is inversely proportional to its Q-factor), the laser frequency ν and the output power P at this frequency.

The theoretical lower limit is given by the Townes formula 35):

$$\Delta\nu_L = \frac{2\pi h\, \nu_L \Delta\nu_c^2}{P}$$

which yields for the He-Ne laser ($P = 10^{-2}$ watts, $\Delta\nu_c = 3$ Mc/sec, $\nu_L \approx 5 \times 10^{14}$ sec^{-1}) $\Delta\nu_L = 2 \times 10^{-3}$ sec^{-1}! This means a relative linewidth $\frac{\Delta\nu_L}{\nu_L} = 4 \cdot 10^{-18}$!! Javan *et al.* 36) have proved experimentally that the laser linewidth of a He-Ne laser oscillating at $\lambda = 1.15\,\mu$ is indeed below 1 Hz. They measured the beat frequency and its time variation obtained by mixing two adjacent longitudinal modes. Unfortunately this sensational small linewidth has had no practical importance up to now. The main reason for this is that the laser frequency cannot be stabilized over a sufficiently long period of time and the frequency fluctuations are far larger than the actual linewidth.

With normal efforts for frequency stabilization in the optical frequency region, time-averaged laser linewidths of about 1 Mc/sec have been obtained 37), compared to 1000 Mc/sec in case of spontaneous fluorescence lines.

With special techniques it is possible to stabilize the laser frequency down to some 10^3 sec^{-1} 38, 39), and promising experiments with the infrared line $\lambda = 3.39\mu$ of the He-Ne laser indicate 40) that a stability of 10 cycles/sec or better may be obtained when using the saturated absorption of molecules inside the laser resonator as the stabilizing element (see Section IV.3).

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a) The homogeneous linewidth is that range of wavelengths inside which *each* atom in the considered state can interact with a monochromatic light wave and therefore contribute to its amplification or absorption. All processes faster than the interaction time of the atoms with the light wave contribute to this homogeneous linewidth (e. g. fast collision processes, radiative decay etc). In the case of inhomogeneous line broadening (e. g. doppler broadening) only part of the atoms in the state under investigation have the proper frequency to interact with the monochromatic light field. For more detailed discussion see ref. 42).

The single-mode laser naturally gives less output power than a multimode laser with the same active volume since its induced emission is concentrated into a smaller frequency range. This loss in intensity, however, is much less than one would expect from the ratio of linewidths or from the reduction in oscillating mode number 31, 32, 41). This is due to the fact, that not only atoms with the exact transition frequency can contribute to the induced emission, but also those inside the "homogeneous" linewidth a), which is determined by collision processes in the case of gas lasers 43a) or by crystal line broadening in solid lasers 43b).

A method for obtaining a stabilized and tunable single-mode output from a giant-pulse ruby laser has been reported by Bondarenko *et al.* 43c). The authors injected the light beam from a single-mode ruby laser, operated with frequency stabilization at moderate output power into the high power giant-pulse cavity just at the moment of cavity *Q*-switching. The giant pulse output frequency is then determined by the input trigger frequency and can be tuned with it.

4. The frequency of a single mode laser can be tuned over the line profile of the amplifying medium by changing the length of the resonator. This may be done with piezoelectric crystals 44) on which the cavity mirrors are mounted or with magneto-strictive rods 45).

Another method 34) used a mode selective planeparallel glassplate inside the cavity, which can be tuned to give a continuous frequency shift. The laser intensity depends on the gain at the oscillating frequency and the limits of these methods of frequency tuning are the threshold points on both sides of the gain profile.

A larger frequency shift is possible if the laser is placed in longitudinal or transverse magnetic fields 46, 47) which cause a Zeeman splitting of the upper and lower laser level. With polarizers and quarter wavelength plates one can select the shifted σ_+ or σ_- component 48).

The level splitting and with it the frequency shift of the Zeeman line depends on the Landé g values in both levels. For the Ne line $\lambda = 3.39\ \mu$, for instance, this shift is 1.56 Mc/sec/Gauss 49), for the ruby line $\lambda = 6948$ Å it amounts to 3 Mc/Gauss, and a total shift of 5 cm^{-1} has been obtained at 49 KGauss 50).

In the case of gas lasers the discharge conditions, and therefore also the laser intensity, change with the magnetic field strength, and often the maximum Zeeman frequency shift is not limited by technical considerations (greatest possible magnetic fields) but by the fact that the laser intensity drops to zero 51).

The frequency of solid-laser lines can often be tuned by temperature variation[52a)], as for the ruby line where a shift of 20 cm^{-1} has been obtained[52b)] by varying the temperature between 77 °K and 300 °K. Semiconductor lasers[53)] can be frequency tuned by applying a variable mechanical pressure to the junction in the laser diode[54)].

A much larger tuning range of laser wavelengths is possible in dye lasers[55)] which can be operated in a pulsed and continuous wave mode, with wavelengths covering the visible and near infrared spectral region. By the insertion of wavelength-selecting elements, such as diffraction gratings, prisms or Fabry-Perrot etalons inside the laser cavity, the output wavelengths of different dye lasers can be tuned over a range of several hundred angströms[56)]. With these dispersive elements the laser linewidth decreases from several 100 Å to less than 0.5 Å[57a)]. With a combination of echelette grating and Fabry-Perrot interferometer inside the dye-laser cavity, Bradley *et al.*[57b)] achieved single-mode oscillation with a linewidth of 500 Mc/sec ($\approx$ 0.01 Å). The output power decreased by a factor of four as compared with operation with only a grating, but the linewidth was 50 times smaller[b)]. With this improvement, dye lasers con be used for high resolution spectroscopy (see Section III.5).

The largest continual frequency variation can be obtained with parametric oscillators[58)] which have already been operated in the visible region with appreciable power output when using pulsed lasers as pumping sources[59)]. High power cw lasers, such as argon-ion lasers, can also be used as a pump[60)] to generate continuous parametric oscillation, especially if the frequency-mixing crystal is placed inside the laser cavity. Recently Smith *et al.*[61a)] successfully used a $Ba_2NaNb_5O_{15}$ (banana– crystal) as nonlinear element. They obtained with the frequency-doubled output from a continous YAG-laser (Aluminium-Yttrium-Garnet) lasing at $\lambda = 1.05\ \mu$ as pumping source a parametric output power of 30 m W, at a wavelength continuously tunable between 0.9 μm and 1.2 μm by controlling the temperature of the "banana" crystal.

Amman *et al.*[61b)] even observed output powers as high as 350 mW and 75 % conversion efficiency.

Patel *et al.*[62b)] successfully operated parametric oscillators in the infrared region (2.5 – 25 μm) using the nonlinear characteristics of tellurium and selenium single crystals. This frequency range is important for the molecular spectroscopy of rotational-vibrational

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[b)] In cw-dye lasers, pumped by the focussed beam from an argon laser, linewidths of less than 20 Mc/sec ($\lesssim 10^{-4}$ Å) have been achieved.

transitions, and tunable parametric oscillators promise to replace conventional light sources plus spectrometers.

Growing better crystals [62)] can certainly improve threshold and output power. As soon as the problems of frequency stabilization have been solved satisfactorily [62c)], the perametric oscillator will surpass conventional devices in its intensity and resolving power [62d)].

5. Light pulses with halfwidths of 10^{-8} sec have been generated mainly by Q-switched solid-state lasers [63)] but can be obtained principally with all high-gain laser transitions, as for instance CO_2 lasers [64)], nitrogen lasers [65)] ($\lambda = 3300$ Å), or dye lasers [66, 57b)].

In this Q-switching technique, one of the cavity mirrors is effectively removed during pumping and then suddenly replaced. The build-up time of the giant pulse is determined by the switching speed and the initial gain of the pumped laser.

Through amplification in succeeding amplifier chains of inverted material, the pulse width becomes still smaller [67)] and energy outputs of hundreds of Joules have been reported [67a)].

An electro-optic shutter within the cavity [67b)] in addition to the normal Q-switching produces even shorter light pulses by truncating both edges of the pulse.

With special mode-locking techniques [68)], which have been extensively reviewed by De Maria *et al.* [68a)], it has been possible to obtain high peak-power light pulses (10^6 – 10^{13} Watt) with a halfwidth of several picoseconds. If the spectral width of the laser transition is wide enough, even pulse widths below 10^{-12} secs are possible [68c)]. The shortest light pulse so far reported has a halfwidth of 2.5×10^{-13} sec [70)]. In reference [70a)] the measurement of such short lightpulses is discussed. One method [70b)] uses, for instance, two-photon induced fluorescence: the light pulses pass a fluorescence cell containing a medium which is transparent at the laser wavelength but absorptive at the doubled frequency. The pulse train is reflected back into the cell by a mirror behind it, producing a standing wave pattern. In the region where the incoming and reflected light pulses overlaps, the light intensity is sufficiently high to cause two-photon absorption. The subsequent fluorescence can easily be seen by the naked eye and is a measure of the wave packet dimensions, and with it the pulse duration. Using picosecond laser pulses, Duguay *et al.* [71)] developed a light gate which allows similar short light pulses to be formed with arbitrary light sources.

These techniques are extremely important in investigations of very fast processes and some spectroscopic applications will be discussed in Section III.3, 5 and 6.

III. Spectroscopic Applications of Lasers

The special laser characteristics outlined in the last chapter indeed make the laser a very attractive light source for spectroscopists and many of the applications discussed below were proposed soon after the first successful operation of an optical maser[72-75]. Meanwhile many laboratories are working in this field, and a selection from the numerous spectroscopic experiments will be presented in the following sections.

1. Absorption Spectroscopy

The earliest experiments with lasers in absorption spectroscopy were performed with the high-gain infrared line $\lambda = 3.39\,\mu$ of the He-Ne laser[74], the first gas laser[76]. Several authors[77, 78] discovered that this laser line is absorbed by many hydrocarbon molecules, causing a vibrational-rotational transition in a band which belongs to the excitation of a C-H stretching vibration[79].

Fig. 1 shows the experimental arrangement commonly used for these investigations. The laser may run in multimode or single-mode operation, depending on the required linewidth and the experimental expenditure. A longitudinal magnetic field produces a Zeeman splitting (in the case of Ne, $\lambda = 3.39\,\mu$, up to 0.6 cm^{-1}) of the laser line into two circularly polarized components[c]. A $\lambda/4$ plate with following linear polarizer selects a single (now linearly polarized) component which enters the absorption cell after having passed a beam splitter *ST* and is monitored by a suitable infrared detector

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[c] Because of the different g-values in the upper and lower laser levels, two groups of Zeeman components $\Delta m = \pm 1$ are actually generated, but since this difference is very small ($g_u = 1.333$, $g_e = 1.301$), we may regard each group as one line.

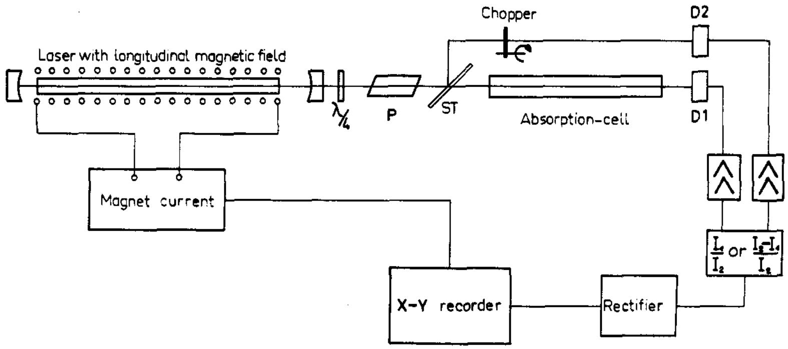

Fig. 1. Experimental arrangement commonly used in absorption spectroscopy with laser lines, tuned by a longitudinal magnetic field

(for instance, a PbS diode). The part of the laser light reflected by the beam splitter ST serves for intensity normalization. Since the laser intensity depends on the magnetic field strength[51], ratio recording of $I/I_0 = e^{-\alpha x}$ or logarithmic amplification of both signals and difference recording of ln I_0 − ln $I = \alpha x$ considerably increases the accuracy[80b],. If the absorption layer is optically thin ($\alpha x \ll 1$), it is, however, easier to measure $\frac{I_0 - I}{I_0} = \alpha x$.

The rotational levels in larger molecules are very close and the laser line therefore can be tuned by this magnetic shift method over several rotation lines of the absorbing gas. Fig. 2 gives an example: the absorption spectrum of C_2H_6 as measured by Gerritsen *et al.*[74]. Here the signal detection was not based on ratio recording so that the dependence of laser intensity on the magnetic field is not eliminated.

While the 3.39 μm He-Ne laser line excites a C-H vibration, the argon laser line λ = 2.7 μm, for instance, causes rotation-vibration transitions associated with O-H vibrations[81].

Several other laser lines have already been used in a similar way[82-90] to measure absorption coefficients and absolute wavelengths of absorption lines, as well as the line profiles and possible fine structures of many polyatomic molecules. By substituting different isotopes, the isotopic shift of absorption lines has been studied[90]. Table 2 shows some of the molecules investigated by the laser line absorption technique, together with the exciting laser wavelengths and some remarks about the kind of measurements performed.

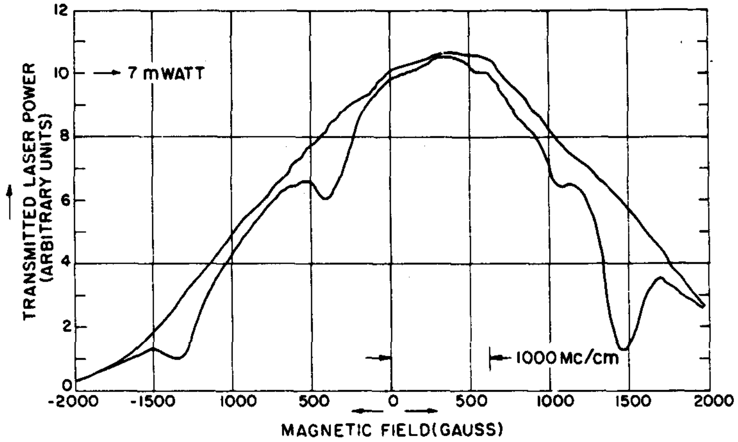

Fig. 2. Absorption spectrum of C_2H_6 obtained with the Zeeman-tuned He-Ne laser line at $\lambda = 3.39\ \mu m$. The dips in the transmission of magnetic field dependent laser intensity are due to different rotational transitions in C_2H_6, their width is determined by doppler broadening. (From: Gerritsen, H.J., ref. 74))

Table 2. *Molecules investigated by laser-absorption technique*

Molecule	Absorbed laser wavelength [μm]	Kind of measurement	References
CH_4	7,70; 7,77	f	80)
CH_4	3,39	f, s, a, l	49, 74, 85, 88)
CCl_4		f	80)
CH_3F	3,39	a, f, l	74)
CH_3Cl	3,39	a, f, l	74)
C_2H_4	7,32; 3,39	a, f	74)
C_2H_6	3,39	a, f	74, 80)
C_3H_8	3,39	a	74, 80)
CO_2	9,4–10,4	f, a, c, l	83, 86, 90)
D_2O	337	a, f, l	98)
HDCO	3,50	f, s, c	84, 85)
H_2CO	3,36; 3,39; 3,50	f, s, c	84, 85)
NH_3	84,1; 171,6	f, s, c	85)
SF_6	9,4–10,4	a, f, l	89, 336)
CD_3CN	337	a, f	87)

a = absolute absorption coefficient
f = frequency of absorption line center
l = line profile
s = Stark splitting
c = calculation of molecular parameters from measurements

The resolution in these measurements is, in the case of singlemode lasers, limited by the doppler width of the absorption lines and reaches 0.001 cm^{-1} [80b, 84] compared to o.o5 cm^{-1} with conventional nearinfrared spectrometers. In Section IV it will be shown that even this limitation may be overcome in favorable cases.

Since the single-mode laser linewidth is small compared to the absorption linewidth, one can probe the absorption profile by tuning the laser line across it, getting more information than by measuring the absorption coefficient averaged over the whole doppler width[86].

The accuracy of wavelength determination depends on the knowledge of the absolute laser wavelength and its specific Zeeman shift $\frac{d\lambda}{dH}$ and on the measurement of the magnetic field strength H. All three parameters can be determined with high precision[82].

It is possible to measure with this method absolute absorption coefficients down to $\alpha \geqq 1 \times 10^{-6}$ cm^{-1} [85].

For the measurement of small absorption coefficients or refractive indices, it is often advantageous to place the probe inside the laser cavity[91]. The sensitivity is then increased by a factor which depends on the quality of the Q factor of the cavity and which can be very large (about 100 or more), since quite small changes in total absorption may cause large changes in laser intensity, especially if the laser is operated close above threshold.

A disadvantage may be the existence of many spontaneous lines from the gas discharge in gas lasers, or the pumped light from the flashlamp in solid state lasers which is superimposed upon the laser light.

To avoid this handicap, Boersch and coworkers[92] used coupled resonators. The first active laser cavitiy generates the radiation whose absorption is to be measured. The probe is placed in a second cavity, which is coupled to the first one and which is undamped by an active medium just below the threshold for self-oscillation. This arrangement enables changes in the refractive index as small as $\Delta n \geqq 10^{-10}$ or absorption coefficients down to $\alpha \approx 10^{-6}$ to be detected.

Instead of tuning the laser line, one can also shift the absorption lines across the laser line by Zeeman or Stark effects. This is especially advantageous in the far-infrared region where the tuning range of laser lines is restricted.

A combination of both methods was realized by Uehara *et al.*[85, 88]. They investigated the Stark spectrum of polyatomic molecules in strong electric fields by probing the different Stark components with the Zeeman-tuned laser line. Since the molecular constants of the vibrational ground state are often known from microwave investigations, the laser-absorption method yields electric dipole moments, polarization and other molecular parameters of the excited state from measurements of the frequency separation and the intensity of the Stark components[92a)]. These excited states are not thermally populated, especially if the exciting line falls in the optical region, and therefore the spectroscopy of these states is not accessible to microwave investigations.

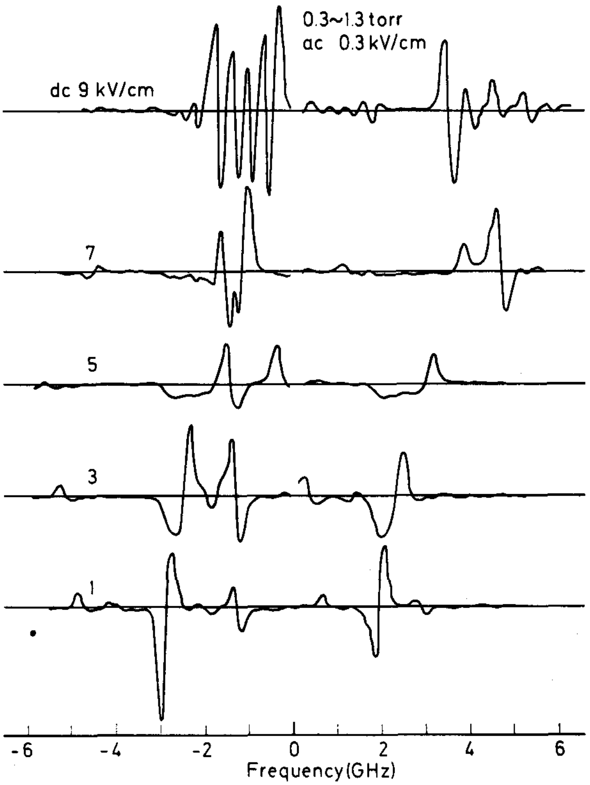

Fig. 3. Stark modulation spectrum of HDCO around 2850.62 cm^{-1}, obtained with a Zeeman-tuned Xe laser line at 3.50 μm. The Stark field is perpendicular to the optical field and increases from the bottom towards the top of the figure resulting in an increasing splitting of the Stark levels; therefore more and more components are separated. (From: Uehara, K.T., Shimizu, T., Shimoda, K., ref. [85)])

By modulating the electric field and using phase-sensitive detection methods, Uehara *et al.*[85] were able to increase the sensitivity considerably and they could even detect Stark splittings of less than the doppler width of the components. Fig. 3 shows the Stark spectrum of HDCO for different electric field strengths. Because of the Stark modulation technique[93], the absorption lines appear differentiated; the zero points represent the center of each line.

Molecular lasers, which can oscillate on many rotational transitions, can be tunded to the different lines[93] by inserting a grating inside the cavity. The CO_2 and N_2O lasers, for instance, have an oscillating line for nearly every wave number of the 9 and 10 μm regions. Therefore vibrational bands of many molecules are entirely covered by these lines[94]. With such a tunable N_2O laser Oppenheim *et al.*[95] studied the absorption of 65 rotational lines in N_2O.

Since the absorption-line profile can be probed by the laser absorption technique, broadening and shifts of these profiles by collision processes can be detected and collision cross-sections may be obtained from the pressure dependence of these line broadenings. The following collision systems have been investigated: CH_4-CH_4[96]; CH_4-noble gases[97]; CH_4-N_2[49]; CH_4-HCl[49]; CO_2-He[83]; HCN-noble gases[98], SF_6-SF_6[97a], Bv_2-Bv_2[97b], Cl_2-Cl_2[97c].

Since the Zeeman tuning of laser lines is limited in the far-infrared spectral range, Duxbury and Burroughs[87] tuned the absorption lines of several gases ($CF_2{=}CH_2$; CD_3CN; C_2H_5CN) over the 337 μm HCN laser line using the pressure shift of the absorption line center and the line broadening. Both parameters could be deduced from the measured change of total absorption with pressure and from comparison with theories of pressure shift and broadening. For increased sensitivity, some of the experiments were performed inside the laser cavity.

Similar investigations of pressure broadening effects in H_2O were accomplished with the HCN laser by Bradley *et al.*[98].

Recent advances in constructing single-mode tunable cw dye lasers with a bandwidth of 20 Mc/sec or less[98a] open the way for high resolution absorption sepectroscopy without the limitations to fixed wavelengths[98b]. One may observe either the total fluorescense intensity, which is proortional to the total absorption, or the decrease of the transmitted laser intensity.

The last method has been pushed to an impressive sensitivity by putting the probe inside the cavity of a cw dye laser oscillating on several modes close above threshold. The sensitivity of such a broad-band dye laser to selective intracavity absorption on a single mode is proportional to the number of oscillating modes due to the coupling between different modes. An increase in absorption sensitivity by a factor of 10^5 as compared to single-pass measurements could be achieved.

This technique bas been demonstrated for the example of molecular iodine absorption, where a layer density of 5 x 10^{-11} g/cm^2 seems to be detectable [98c].

The absorption measurement via observation of the total fluorescence has advantages when the probe cannot be placed inside the laser cavity. It is not necessary to employ any monochromator or spectrograph. The spectral resolution limit, which is set by the finite Doppler width of the absorbing gas and which is already far lower than the resolution of most spectographs, may be drastically reduced by using an atomic or molecular beam perpendicular to the laser beam.

With this technique the Doppler width could be reduced by two orders of magnitude below the natural linewidth, and spectral structures within the Doppler width could be resolved. Examples are the resolution of hyperfine structure components in an I_2-beam using a single-mode argon laser (tunable within a few gigahertz) [98d] or the investigation of the upper state hfs-splitting in the atomic $3P_{1/2}$, $3P_{3/2}$-states of sodium, measured in a well collimated Na beam with a cw dye laser [98e].

With the development of more versatile tunable semiconductor lasers [99a] in the near infrared, high-resolution absorption spectroscopy in this spectral range has been greatly improved. Magnetic field tuned semiconductor lasers [99b] as well as current tunable devices [99c] have been used.

With the recently developed spin-flip laser [99d] a monochromatic and powerful infrared radiation source is available which can be tuned within the 5μm–100μm region.

With a laser linewidth of less than 1KHz spectroscopy has been carried out on water vapor lines around 1885 cm^{-1} ($\sim$ 5,3μm) [99e] with a resolution never obtained before. Application of the spin-flip laser to P- and Q-Branch absorption of NO with 0.08 cm^{-1} resolution has been reported by Wood *et al* [99f].

During recent years lasers have proved their capability for detecting spurious molecular constituents of the atmosphere [100a]. Mainly two methods have been employed: transmission measurements [100b] and laser-induced fluorescence, or Raman spectroscopy [100f]. The first method uses pulsed or cw lasers which can be tuned over a characteristic absorption line of the molecule under investigation [100c]. The change in transmission is detected along a lightpath up to some kilometers.

The second method uses pulsed lasers and the laser-induced fluorescence is detected by telescope. If the telescope and the laser source have a definite base distance, the crossing of laser beam and the acceptance angle of the telescope define the height of the atmospheric layer at which fluorescence is detected. There is also the technique of delayed coincidence, where the time interval between laser pulse and detected fluorescence pulse determines the distance of the observed molecules from the observer (Lidar) 100d) e).

2. Fluorescence Spectroscopy

Many molecules which have absorption bands in the wavelength region of existing laser lines can be excited by absorption of laser photons into single isolated rotational-vibrational levels of the electronic ground state 100-103) (in the case of infrared laser lines) or of an excited electronic state (with visible or ultraviolet lines) 104-113). This has been confirmed experimentally by several authors who investigated mainly diatomic molecules.

Because of the large number of rotational levels in the upper and lower states, the overlap between the exciting laser line and the doppler broadened absorption profile may be nonzero simultaneously for several transitions $(v'', J'') \rightarrow (v', J')$ with different vibrational quantum numbers v and rotational numbers J. This means, in other words, that the energy conservation law allows several upper levels to be populated by absorption of laser photons from different lower levels.

There are, however, certain selection rules for electric dipole transitions which considerably reduce the number of possible transitions. They are extensively discussed and proved in reference 114) and for diatomic molecules consist essentially of the following three rules:

1. The rotational quantum number J for the total angular momentum can only change by $\Delta J = 0$ or ± 1 (conservation of angular momentum for the total system molecule-photon).

2. The probability of a transition $v'' \rightarrow v'$ is determined by the Franck-Condon factor, which is proportional to the squared overlap integral of both vibrational eigenfunctions in the upper and lower state.

3. Transitions are allowed only between states of different symmetry "+" or "–", where the symmetry sign "+" means that the eigenfunction for the rotational level in question remains unchanged when reflected at the origin, and "–" means that it simply changes its sign.

In spite of these selection rules, there normally remain one or several upper levels (v', J') which can be reached by absorption of a laser photon with appropriate energy. By the use of different laser lines, various upper levels can be excited in this way[d].

Because of the high laser intensity, a large population density, comparable to that of the initial ground states, can be obtained in these excited states. With these strongly pumped excited molecules many interesting experiments may be performed, a selection of which will be discussed below.

The excited molecules normally release their energy by spontaneous emission of fluorescence, terminating not only in the initial ground state but on all vibronic levels of lower electronic states to which transitions are allowed. This causes a fluorescence spectrum which consists, for instance, in the case of an excited singlet state in a diatomic molecule, of a progression of either single lines ($\Delta J = 0$ named: Q-lines) or of doublets ($\Delta J = \pm 1$; P- and R-lines)[115].

This spectrum is relatively simple compared to the absorption spectrum of the same molecule and therefore easy to analyze (see Fig. 5). The main advantage is that single lines can be resolved even with medium-resolution instruments and the quantum numbers of the levels involved can often be determined from a preliminary spectrum analysis using a fast monochromator run.

From precise wavelength measurements of the fluorescence spectrum (which may be performed e. g. by interferometric methods[107]), accurate values for the molecular constants can be obtained[106], since the wavelength differences of subsequent lines in the fluorescence progression yield the energy separation of adjacent vibrational and rotational levels as a function of v''. From these spectroscopically deduced molecular constants, the internuclear distance can be calculated[107]. A special computer programm developed by Zare[116] allows the potential curve to be constructed from the measured constants[106, 107], and, if the observed fluorescence progression goes up to high vibrational levels in the electronic ground state, even the dissociation energy can be reliably obtained by extrapolation[111, 109].

Table 3 lists the molecules so far investigated by laserinduced fluorescence.

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[d] If the molecular absorption lines do not overlap within their Doppler width, excitation with single-mode lasers succeeds in populating one single rotational-vibrational level.

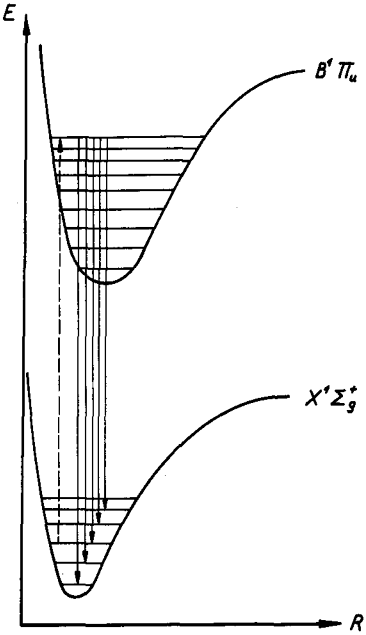

Fig. 4. Excitation of a definite level (v', J') in an upper electronic state of a diatomic molecule by absorption of a laser line, and subsequent fluorescence to different vibrational levels of the electronic ground state (example: Na_2)

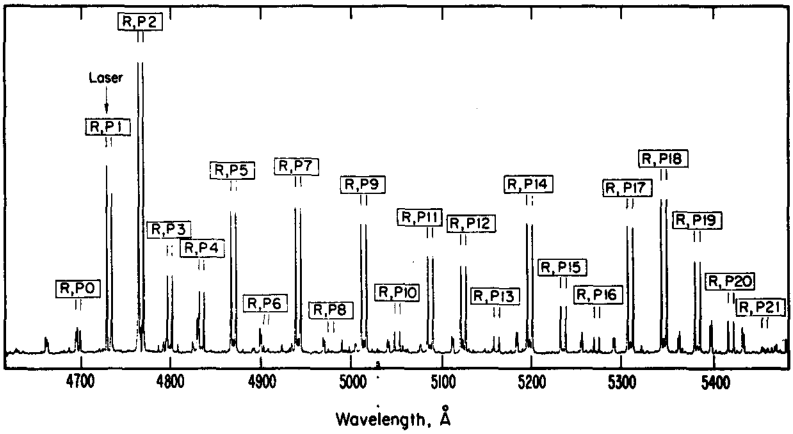

Fig. 5. Fluorescence spectrum of Na_2, from the $B^1\Pi_u$ state ($v' = 10, J' = 39$), excited by the argon laser line $\lambda = 4726$ Å. The fluorescence lines represent transitions with $\Delta J = \pm 1$, terminating at different v'' levels (v'' is labelled at each line) of the electronic ground state. (From ref.[107])

Table 3. *Molecules studied by laser-induced fluorescence technique*

Molecule	Exciting laser line	Kind of measurement	References
a) Electronic excitation (visible laser lines)			
Li_2	Visible argon laser lines	i, w, c	111)
Na_2	” ”	i, w, c, L	107, 122, 128)
K_2	He-Ne laser (0.63 μ)	i, w, c, L	106, 122)
Rb_2	visible argon laser lines	O, L	104, 122)
Cs_2	” ”	O, L	104, 122)
NaLi	” ”		122a)
Cl_2	” ”	i, w	110)
BN_2	” ”	i, w	110)
J_2	He-Ne, arg. + krypton laser lines	o, i, w	105, 110, 108, 109)
CO			110a)
BaO	Visible argon laser lines	i, w, L	112)
CuO	” ”	i, w	113)
NO_2	Argon + krypton laser	i, c	112b)
SO_2			112c)
b) Vibrational excitation (infrared laser lines)			
CO_2	CO_2 laser (10.6 μ)	i, R	150, 150a)
CH_4	He-Ne laser (3.39 μ)	i, L, R	143, 100)
N_2O	N_2O laser (10 μ)	i, R	144, 145)
HCl	HCl laser	i, R	102)

O = Observation of fluorescence
w = wavelength determination
i = identification of absorbing transition with upper and lower state quantum numbers
L = lifetime measurement
c = calculation of molecule parameters from experimental data
R = measurements of collisional relaxation.

The advantages of laser excitation for these fluorescence measurements may be summarized as follows:

1. The high laser intensity enables molecular transitions to be measured even when their Franck-Condon factors are small, so that the fluorescence progression can be followed up to high vibrational levels, thus considerably increasing the accuracy of the molecular constant determination. It furthermore permits fluorescence measurements at low pressures.

2. The obtainable small laser linewidth with tunable wavelength (Section II) improves selection of different molecular transitions and in many cases the selective population of a single excited rotational level can be achieved.

3. The small diameter of the laser beam fixes the local position of excited molecules, and this facilitates many investigations.

3. Measurements of Excited-State Lifetimes

If the intensity of the exciting light is modulated, the fluorescence light also shows a modulation at the same frequency ω, with a smaller degree of modulation and a phase shift $\Delta\varphi$ against the modulation phase of the exciting light [117]. This phase shift is connected with the mean lifetime τ of the excited state (exponential decay anticipated) by $\mathrm{tg}\,\Delta\varphi = \omega \cdot \tau$.

From a measurement of $\Delta\varphi$ therefore, the mean lifetime τ can be obtained with high precision by using the proper modulation frequency [118] With lasers as light sources, the small beam diameter allows Pockel cells [e] with small apertures to be used besides the usual Kerr [120] or supersonic [121] cells as light modulators at high frequencies. These small-aperture Pockel cells have the advantage of operating up to high frequencies with low modulation voltages (~ 100 V at 100 MC/sec compared with 10 kV in Kerr cells) and they transmit over a wide spectral range (2500–12000 Å). When designed as travelling wave modulators, they can be used even up to microwave modulation frequencies [119].

The high intensity of the exciting laser light enables lifetime measurements at molecular pressures of below 10^{-6} torr, which means in many cases that the partial pressure of those molecules in the state (v'', J'') from which absorption of laser light takes place, is about 10^{-9} torr.

With this method lifetimes of excited states in diatomic alkali molecules have been measured [122, 123] by means of the apparatus in Fig. 6.

In measurements at such low pressures the fluorescence intensity is several orders of magnitude smaller than the primary light inevi-

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[e] Pockel cells use the linear electro optic effect in crystals to turn the plane of polarization when an external electric field is applied. A detailed description with references is given in [119].

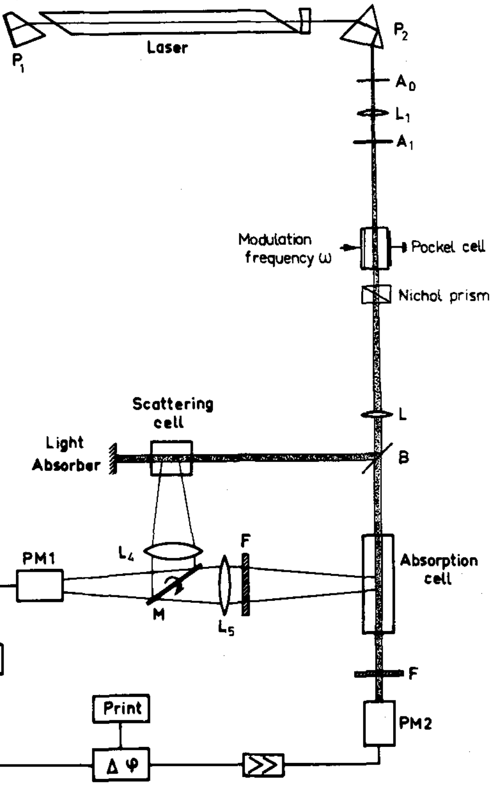

Fig. 6. Experimental arrangement for lifetime measurements by the phase-shift method, using laser excitation. The laser beam is amplitude-modulated by a Pockel cell with analysing Nicol prism and a small part of the beam is reflected by a beam splitter *B* into a water cell, causing Rayleigh scattering. This Rayleigh-scattered light and the fluorescence light from the absorption cell are both focused onto the multiplier cathode *PM1*, where the difference in their modulation phases is detected. (From Baumgartner, G., Demtröder, W., Stock, M., ref. 122)).

tably scattered from the walls of the fluorescence cell. With lasers as exciting light sources, this scattering, which may be a severe handicap, can be reduced because of the excellent beam collimation, especially with the use of Brewster windows which allow the passage of polarized light without reflection.

Another method for lifetime determination uses the level-crossing technique 124), which measures the natural linewidth (and with it the lifetime) from the change of the spatial fluorescence intensity distribution when two levels cross each other (e. g. Zeeman levels of different hyperfine structure states in a magnetic field, or Stark levels in an electric field). The special case of zero field crossing is often called the Hanle effect 125).

This method is equally applicable to atoms 126) and to molecules 127). In molecules the Zeeman splitting depends on the quantum number J' of the total angular momentum and therefore the fluorescence from a single rotational level (v', J') need be observed. Because of this necessarily selective excitation, these molecular level-crossing experiments can be performed much more easily with lasers than with conventional light sources and have been sucessfully performed with Na_2 128) and NaK 129).

Since high rotational levels have a large J, the Landé factor g, which is inversely proportional to $J \cdot (J + 1)$ 130), becomes very small, requiring high magnetic fields to separate the Zeeman levels beyond their natural linewidth. Again the small laser beam diameter helps to perform the experiments inside a small magnet-pole gap, keeping the instrumental expenditure at a modest level.

In a third method for lifetime measurements, the levels to be investigated are excited by a short pulse and subsequently the number of fluorescence quanta is counted as a function of the delay time (e.g. with a multichannel analyzer and a time-to-pulse height converter). The experimental procedure is described by Bennet 131) and has been perfected by several authors using light pulses 132) or electron pulses 133) for excitation.

Compared to the phase-shift method, this technique has the advantage that nonexponential decays can also be investigated.

Because several laser types are able to generate extremely short and powerful light pulses, they are especially useful for this method.

A survey of the application of high-power pulsed lasers to experiments on a nanosecond time scale has been given by Bradley 134). In his article mainly mode-locked tunable dye lasers are discussed. Giant pulse ruby lasers (3 nsec pulse halfwidth) have been successfully used to probe electron densities as a function of time in a rapidly expanding plasma 135). The electron lifetime in the conduction band can be determined with nanosecond semiconductor lasers. By absorption of the laser pulse the electrons in the semiconductor probe are excited into the conduction band, resulting in a definite conductivity. The mean lifetime is obtained by measuring the decrease of conductivity with time 136).

Observations of the decay time of luminescence from activator atoms in crystals excited by laser pulses have enabled lifetimes of different excited states to be determined. Since these lifetimes are often less than 10^{-8} sec, short excitation pulses as provided by lasers are essential.

Haug *et al.* 137) investigated the kinetics of rapid photoprocesses occurring in the time domain between 5 x 10^{-9} to 6 x 10^{-3} sec. The excitation system consisted of a cw argon-ion laserbeam, interupted periodically at frequencies between 4 – 75 Hz. The electro-optic shutter could be switched off within 3 x 10^{-8} sec. The detector system employs a fast photomultiplier and a sampling oscilloscope, the samples being stored digitally in a multichannel analyzer. Careful analysis of the data permits measurement of lifetimes that are much shorter than the switching-off time of the shutter. Because steady-state conditions are established during each cycle and the power density of the laser can be adjusted over the range from 10^{-6} to 10^{4} Watt · cm^{-2}, this system is well suited to an investigation of fast photoprocesses in photosynthetic systems. The authors measured the fluorescence lifetime of rubrene (5,6,11,12-tetraphenylnaphthalene) dissolved in benzene, and obtained $\tau = 16.3 \pm 2.1$ nsecs. Shortening of the lifetime due to the presence of impurities is also discussed.

Applications of the pulse method to measurements of short-lived singlet states in large molecules will be discussed in Section III.5).

Duguay and Hansen 71) measured the relaxation time of the optical Kerr effect 138) in nitrobenzene induced by high power picosecond light pulses from a mode-locked Nd-glass laser. When the light field is switched off, the birefringence induced by the light pulse does not disappear instantaneously but decays in a mean time $\tau = 32 \pm 6$ psecs. From their measurements the authors concluded that this optical Kerr effect is due mainly to the orientation of anisotropically polarized molecules and probably not caused by electron phenomena f).

Another technique for measuring the lifetime of excited activator atoms in solid-state lasers has been published by Gürs 139): If the pulsed laser is operated close above threshold, only a single "spike" (i.e. a short pulse of induced emission) appears, whereas many spikes are emitted when the laser ist running well above threshold. This

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f) Using this "optical Kerr cell" the authors developed a technique to measure the lifetimes of atomic and molecular transitions on a picosecond time scale 138a). See also the reviews by Rentzepis 138b) about "ultrafast processes" and Merkelo 138c).

single spike is emitted exactly at the time when threshold population is reached. Measurements of this time and the shape of the pump light pulse yield the fluorescence lifetime of the upper laser level. Gürs finds $\tau = 3.0$ msecs for the ^2E-state of Cr^{3+} in ruby but only $\tau = 0.127$ msecs for the $^4F_{3/2}$-level of Nd^{3+} in calcium tungstate.

4. Spectroscopic Investigations of Collision Processes

Because of the relatively large population in excited atomic or molecular states attainable through excitation by lasers, even at moderate molecular concentrations, it is possible to study *inelastic* collision processes between *definitely excited* atoms or molecules and arbitrary collision partners by observing pressure-dependent changes in the fluorescence spectrum. In this way fluorescence spectroscopy supplements the investigations of collisions from measurements of line broadening with absorption-spectroscopic techniques, as described in Section III.1. There the line shape is influenced mainly by *elastic* collisions and the upper and lower levels of the absorbing transition are differently affected by the collisional interaction, thus producing a shift and a broadening of the absorption line profile.

With the laser-excited fluorescence technique, collision cross-sections can be obtained either from line-broadening of the fluorescence lines or from measurements of population and deactivation of excited states (by observing the change in fluorescence intensity, which is proportional to the population change in the upper state) or from the appearance of new lines in the spontaneous spectrum. The experimental methods and the kind of inelastic collisions investigated naturally depend on the spectral region. Excitation with infrared laser lines has enabled mainly collision-induced vibrational energy transfer to be studied, and to some extent also rotational relaxation, whereas excitation into an upper electronic state by visible laser lines also allows electronic energy transfer and quenching processes to be observed.

A molecule vibrationally excited by absorption of a laser photon can convert its excitation energy into translational ($V \rightarrow T$ transfer), rotational ($V \rightarrow R$), vibrational ($V \rightarrow V$) or even electronic energy ($V \rightarrow E$) of the collision partners.

These processes have previously been explored mainly in ultrasonic experiments 140) or in shock waves 141). Both methods, however, may thermally populate many levels of the molecules under investigation, and the interpretation of relaxation times in mixtures

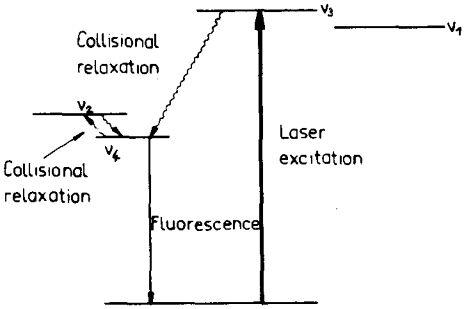

Fig. 7. Vibrational energy level diagram of CH_4 and decay paths after excitation by the He-Ne laser line $\lambda = 3.39\ \mu m$

of molecules with several vibrational degrees of freedom is somewhat ambiguous, since a number of energy transfer processes may be involved. Therefore the excitation of a single level is clearly advantageous.

Yardley and Moore[100)] excited the asymmetric stretching vibration ν_3 of CH_4 (see Fig. 7) with the mechanically chopped output of a He-Ne laser at $\lambda = 3.39 \mu m$. The excited level is rapidly deactivated by collisions with ground state CH_4 molecules, leading to an equilibrium between the ν_3 and ν_4 populations. This can be detected when observing the fluorescence and its modulation phase shift against the exciting light (see Section III.3). Because the ν_3 energy is only slightly larger than twice the ν_4 term energy, on an average 70 collisions are sufficient to generate two excited CH_4 molecules in the ν_4 level from one ν_3 and one ground state molecule. This corresponds to a ν_3 deactivation rate of $\tau_3 \cdot p = (6 \pm 2) \cdot 10^{-9}$ secs · atm, and shows that the collision-terminated lifetime τ_3 at normal pressures is far shorter than the radiative lifetime $\tau_R = 0.037$ sec.

Deactivation of ν_3 and ν_4 in collisions with noble gases is less probable, since here the vibrational energy has to be converted at least partly into translational energy. In CH_4-Ar collisions, for instance, the authors found $\tau_3 p = (68 \pm 20) \cdot 10^{-9}$ secs·atm for the $\nu_3 \rightarrow \nu_4$ transfer but $93 \cdot 10^{-7}$ sec·atm for the ν_4 deactivation.

A detailed description of the laser-excited vibrational fluorescence method and further results on relaxation processes in methane, including $V \rightarrow R$ transfer, have been given in reference[142)]. In this paper, too, a comparison is made between the experimentally obtained $V \rightarrow V$ rates and calculations for the repulsive intermolecular potential responsible for these transitions.

The $V \rightarrow V$ energy transfer from CH_4 (in the ν_4 and ν_2 levels) to O_2 was also investigated by these authors [143] in order to study in more detail the long-known fact that the addition of only 1 % of CH_4 to O_2 can decrease the observed V-T relaxation time of O_2 at 300 °K by more than two orders of magnitude. Again the CH_4 molecule, excited by the 3.39μm laser line, can transfer its vibrational energy to the first vibrational state of O_2 in an CH_4-O_2 mixture. By monitoring the intensity and phase lag of the ν_4 fluorescence at different O_2 mole fractions and at various modulation frequencies, the authors obtained rate constants for $V \rightarrow V$ and $V \rightarrow T$ transfers.

By using a Q-switched N_2O laser [144], the asymmetric stretching vibration of N_2O has been excited and the relaxation rates of N_2O^* have been measured [145] as a function of pressure in mixtures with N_2, H_2, D_2 and noble gases.

The energy transfer from vibrationally excited N_2 onto CO_2 commands special interest, since this is one of the major excitation processes in the CO_2 laser. Witteman [146] found experimentally that additions of He and water to the CO_2-N_2 mixture considerably increase the laser output power. The reason for this is a more efficient deactivation of the lower laser level by these gases. More detailed investigations of these excitation and deactivation processes were necessary in order to gain full understanding of the mechanisms involved. They have been performed by several authors with different methods (see Section V). The laser-excited fluorescence method is especially useful for exploring this field and it has been applied to a study of the $V \rightarrow V$ energy transfer between N_2 and CO_2 [149] and the deactivation of vibrationally excited CO_2 in collisions with noble gases [148] or H_2O and D_2O [149].

Very large rate constants have been found for near resonant energy transfer between infrared active vibrations in CO_2 [150]. Such near-resonant transitions and their dependence on temperature have also been studied for collisions between vibrationally excited CO_2 and other polyatomic molecules as CH_4, C_2H_4, SF_6 *et al.* [103]. The deactivation cross-sections range from 0.28 Å^2 for CH_3F to 4.3 Å^2 for SF_6 at room temperature, and decrease with increasing temperature.

Since the CO_2 laser line corresponds to a transition between two *excited* vibrational levels, only those CO_2 molecules can be excited by absorption of the laser line which are in the (001)-level, populated at 300 °K with about 1 % of the total number of molecules. In spite of this low population density, the laser-excited fluorescence method is easily achieved because of the large exciting laser intensity.

Excitation of CO_2 by a Q-switched CO_2 laser at $\lambda = 10.6\ \mu$ may even lead to a population inversion in the pumped gas, resulting in a new laser transition at 4.3 μ. Hocker *et al.*[150a)] studied vibrational relaxation in CO_2 by this technique.

The effective lifetimes of all these excited states are determined by radiative as well as collisional deactivation, and which contribution is the more significant depends on pressure and transition probability. The simultaneous recording of the absorption and fluorescence spectra yields information about the ratio of radiative to collisioninduced nonradiative decays. This ratio is proportional to the quotient of total fluorescence from the excited level to total absorbed laser light. Such experiments have been started by Ronn[101)].

Pulsed excitation of the $v = 1$ vibrational level in HCl with an HCl laser and subsequent energy transfer from HCl* to CO_2 has been reported by Chen *et al.*[102)]. The energy transfer was so efficient that population inversion in CO_2 was achieved and CO_2 laser emission could be observed. This induced emission could be used as a sensitive tool for the study of time behavior and reaction rates for the activation process[g)].

All the above-mentioned experiments dealt with vibrational excitation of molecules by infrared laser lines. Inelastic collision processes in excited electronic states of molecules can be investigated in a similar way by means of visible or ultraviolet laserlines.

Here collision-induced rotational and vibrational transfer can be studied, as well as electronic energy transfer, total quenching or dissociation from excited states caused by collisions. As an example, the spectroscopic investigation of rotational transfer in excited Na_2 due to collisions with He will be discussed. By absorption of the $\lambda = 4880$ Å line from an argon-ion laser, Na_2 is excited into a rotational level of the $B^1\Pi_\mu$ state ($J' = 43$, $v' = 6$). When 1 torr He is added to the Na-Na_2 mixture (10^{-3} torr Na, 10^{-5} torr Na_2), the excited Na_2 molecule can suffer inelastic collisions with He atoms during its lifetime of 6 nsec; these cause rotational transfer, changing the rotational quantum number by $\pm\,\Delta J$. From these new levels, populated by collisions, the molecule will radiate to the electronic ground state, causing new fluorescence lines which add to the undisturbed fluorescence spectrum. Fig. 8 shows such a collision-indu-

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[g)] For more information about laser spectroscopic investigations of vibrational or rotational energy transfer see ref. [102a–d)].

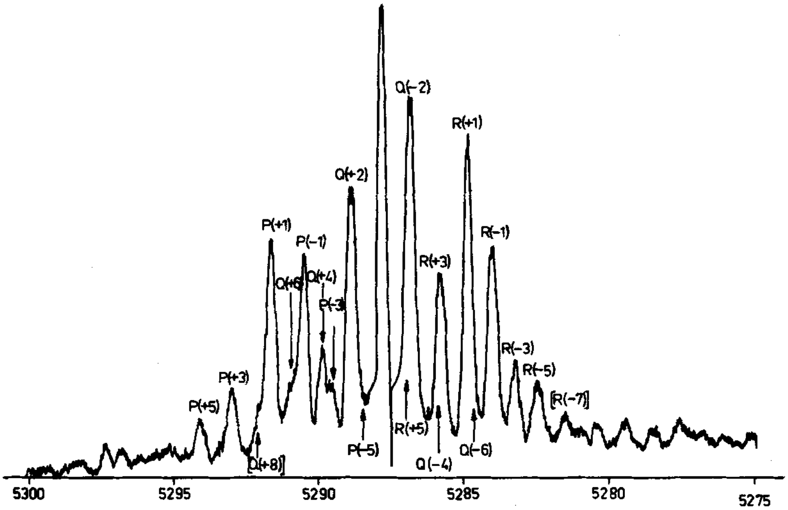

Fig. 8. Collision-induced "satellite spectrum" of Na_2 around $\lambda = 5290$ Å, due to fluorescence originating from rotational levels populated by collision from the $v' = 6, J' = 43$ level in the ${}^1\Pi_u$ state, which was excited by the $\lambda = 4880$ Å argon laser line. (From ref. 151))

ced spectrum around the fluorescence line $\lambda = 5289$ Å $(J' = 43, v' = 6 \to J'' = 43, v'' = 13)$ which was produced by the following processes:

$$\begin{aligned}
Na_2\,({}^1\Sigma_g, J' = 43, v'' = 3) + h\nu_{\text{laser}} &\to Na_2^*\,(B^1\Pi_\mu, J' = 43, v' = 6)\\
Na_2^*\,{}_{J' = 43} + He &\to Na_2^*\,(J' = 43 \pm \Delta J)\\
Na_2^*\,(J' = 43 \pm \Delta J) &\to Na_2 + h\nu_{\text{fluorescence}}
\end{aligned}$$

The Intensity ratio between these "satellite lines" and the main fluorescence line yields the absolute cross sections for the different collision-induced rotational transitions, provided the He pressure and the lifetime of the excited Na_2 state are known. Both parameters have been measured, giving cross sections between $\sigma = 1.5$ Å^2 for $\Delta J = \pm 1$ transitions and $\sigma = 0.3$ Å^2 for $\Delta J = \pm 5$ 151).

Similar measurements for Li_2^* and argon collisions have been performed by Ottinger *et al.* 152) and for vibrational transfer in excited J_2 by Steinfeld *et al.* 153). Exciting different (J', v') levels of the

$A^1 \Sigma$ state of BaO by seven visible Ar^+ laser lines, Sakurai *et al.*[112)] studied rotational and vibrational transitions induced by collisions with He, Ar and N_2. From measurements of the pressure-dependent lifetime ($\tau_{p=0}$ = 12 ± 3 μsec), the authors found for the electronic quenching cross section of the $A^1 \Sigma$ state by He the value $\sigma = 0.25 Å^2$.

In spite of the fact that in alkali vapors, which contain about 1 % diatomic alkali-molecules at a total vapor-pressure of 10^{-3} torr, the atoms cannot absorb laser lines (because there is no proper resonance transition), atomic fluorescence lines have been observed[104)] upon irradiating the vapor cell with laser light. The atomic excited states can be produced either by collision-induced dissociation of excited molecules or by photodissociation from excited molecular states by a second photon. The latter process is not improbable, because of the large light intensities in the exciting laser beam. These questions will hopefully be solved by the investigations currently being performed in our laboratory.

5. Photochemistry and Laser Photolysis

It is mainly three of the qualities discussed in Chapter II which make the laser a powerful tool for studying photochemical reactions: the monochromatic output of frequency controlled lasers, the very short duration of laser pulses, and their high peak power.

The photochemical experiments with lasers performed up to now may therefore be subdivided into three categories according to which one of these laser features was used in the investigation.

In the first group definite states of the molecules to be analyzed are excited by the monochromatic and frequency-tunable laser light, thus inducing selective photochemical reactions.

The second category comprises the flash photolysis experiments using the short high power light pulses from *Q*-switched lasers, furthermore all investigations of time-dependent behavior of excited dye molecules, which play an important role as active material in dye lasers or as saturable absorbers in passive *Q*-switched giant pulse lasers.

In the third category the high intensity of laser pulses is employed to produce multiphoton-induced chemical reactions.

A quite different group of experiments is concerned with the investigation of dye lasers themselves, or of lasers based on the photodissociation of molecules. Studies of the time behavior, concentration, or pressure and temperature dependence of fluorescence and induced emission yield detailed information about radiative and nonradiative decays between initial and final states of the system, about transition probabilities, quenching cross-sections and the mechanism of photodissociation. Examples will be given at the end of this section and in Section V.

a) Selective Photochemistry

One example of selective photochemistry with lasers [154)] is the gasphase photochemical addition of bromine to olefin molecules induced by the monochromatic light near 6940 Å from a pulsed, tunable ruby laser, as studied by Tiffany[154a)].

By tuning the frequency of the laser light through temperature control of the ruby over a range of a few cm^{-1}, various individual absorption lines are covered in the $^3\Pi_{1u} \leftarrow {}^1\Sigma_g^+$ band system of Br_2. The excited vibronic levels are between 500 and 800 cm^{-1} below the dissociation energy. By measuring the dependence of reaction probability on the Br_2 excitation energy controlled by the exciting laser wavelength, Tiffany was able to prove that the addition reaction was not initiated by excited Br_2 molecules but produced by free Br radical chains. By the substitution of different Br_2 isotopes, the following reaction mechanism was elucidated: about 1 % of the excited Br_2 molecules dissociate, the additional energy for dissociation being furnished by collisions with olefin molecules. The excited Br atoms produced by this processes can initiate the addition reaction chain. The remaining 99 % of excited Br_2 molecules relax by collisions to the ground state at a rate somewhat higher than the gas kinetic collision rate.

The experiment also yields deactivation cross-sections in addition to results on the photochemical reaction, and it sets an upper limit for continuous absorption in Br_2 at the ruby laser wavelength.

The same author examined[154b)] the kinetics of gas phase reactions between bromine and unsaturated fluorcarbons.

An interesting application of the selective absorption of laser lines to isotope separation has been demonstrated by several authors [154c), d)]. The essential ingredients for a scheme of isotope separation by lasers are: [154e)]

1. an absorption spectrum with a well-resolved isotope shift;
2. a laser, sufficiently monochromatic and tunable to excite the absorption of one isotope but not the other;

3. a chemical or physical process which acts on excited molecules and separates them from unexcited ones but need not have any inherent isotopic selectivity (e. g. two-step photo dissociation or photo ionization or vibrational photo chemical reactions).

Examples of the use of this technique are the isotopic separation of Br_2 154a), methanol 154f) and formaldehyde 154c).

Another method, based on an old idea about radiation pressure, uses the local separation of different isotopes in atomic or molecular beams. If the laser beam which crosses the molecular beam at right angles is tuned to an absorption line of a defined isotope in a molecular beam containing an isotopic mixture, the recoil from the absorption of the laser photons results in a small additional transverse velocity component. This leads to a beam deflection for the absorbing molecules which enables the desired isotope to be collected in a separate collector 154g).

b) Laser Photolysis

The technique of flash photolysis has been developed by Norrish and Porter 155) and can be described briefly as follows: a short intense light pulse (pump pulse) is focused into the reaction cell where it produces excited molecules or photodissociation fragments which may return into their ground states by fluorescence, nonradiative transitions or collisional relaxation. With the aid of a second, weaker light pulse (analyzing pulse), passing the reaction cell with a controlled time lag as against the pump pulse, the system can be probed at any time by recording the absorption spectrum of this second pulse. For this reason, the absorption pulse should have a broad and uniform spectral intensity distribution in order to obtain simultaneously the whole desired absorption spectrum.

With conventional flashlamps, the pump pulse cannot be made shorter than 10^{-6} secs without suffering a severe loss in intensity. This means that, with a few exceptions 156), only processes lasting longer than 1 μsec have been studied.

Using lasers with pulsewidths between $10^{-4} - 10^{-13}$ sec and huge light intensities enables the class of reactions accessible to flashphotolytic measurements to be substantially enlarged.

The laser has the further advantage of producing monochromatic radiation which excites definite states, whereas flashlamps emit a wavelength continuum which often allows different reactions to occur simultaneously thus complicating the interpretation of results.

Organic dye lasers 57b) are especially useful for nanosecond absorption spectroscopy since their wavelength can be tuned continuously over a range of several hundred angstroms and their output pulses reach several megawatt at pulsewidths down to 10^{-12} sec with mode-locking techniques.

A description of a fast laser photolysis experimental arrangement has been given by Porter and Topp 157) who used a 1.5 Joule, 20nsec ruby giant pulse, frequency doubled in ADP, to measure singlet lifetimes in phenantrene, pyrene and other organic molecules.

Novak and Windsor 158) developed a very elegant and effective method for laser photolysis experiments, using the same laser to produce both pump and analyzing pulses. Their experimental set-up is shown in Fig. 9

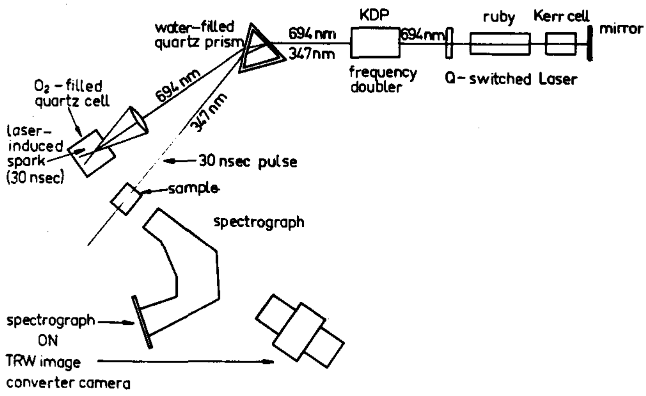

Fig. 9. Experimental arrangement for laser photolysis, using the frequency-doubled output from a giant-pulse ruby laser as pump pulse and the wavelength continuum from a laser-induced high-temperature gas plasma as analysing pulse. (From Novak, J.R., Windsor, M.W., ref. 158))

The output from a ruby giant-pulse laser (2 Joule, 30 nsec halfwidth, $\lambda = 6943$Å) passes a KH_2PO_4 crystal where, due to the nonlinear characteristics of this material, the second harmonic at $\lambda = 3471$ Å is generated with an efficiency of 3 %.The two wavelengths are separated by means of a water filled quartz prism. The ultraviolet light pulse serves as pump pulse.

The nonconverted part of the laser output is focused into a gas-filled cell. A microplasma is produced in the focus (see Section III.9), and this emits a wavelength continuum between 2000–8000 Å having sufficient intensity to be used as lightsource for the analysing pulse. Its pulse duration, as well as the spectral intensity distribution, depends on the gas used in the cell. With 1 atmosphere oxygen, for instance, the pulsewidth is 30 nsec.

One advantage of this method is the automatic synchronization of both pulses to within a few nanoseconds. The second pulse can easily be delayed by changing the length of the light path before generating the microplasma.

When the cell is filled with xenon, the light emission of the plasma lasts for about 10^{-6} sec and the absorption spectrum in the reaction cell can be measured at any time within this microsecond by means of an image converter with high time resolution.

Using this technique, Novak and Windsor were able to measure the absorption spectra of several excited aromatic molecules. The observed transitions started from the first excited singlet state S^* to higher lying states S^{**} 158, 159). The authors could also observe the radiationles singlet-triplet intersystem crossings by measuring the time-dependent decrease of $S^* \rightarrow S^{**}$ absorption and simultaneously the corresponding increase of $T^* \rightarrow T^{**}$ transitions which occur at different wavelength ranges. In benzanthrazene, for instance, the $S^* \rightarrow S^{**}$ absorption band is shifted to the red side of the $T \rightarrow T^*$ band 160, 159).

Similar studies have been performed by Müller and Pflüger 161) on absorption and fluorescence spectra from excited states in cryptocyanin. The authors used a giant pulse ruby laser to produce the pump pulse and a xenon high-pressure lamp for the analyzing pulse. A fast detection system allows time-resolved analysis of the fluorescence and of absorption changes. With this method, not only the singlet lifetimes, but also the extinction coefficients of the higher singlet-transitions $S^* \rightarrow S^{**}$ and the triplet quantum yields can be obtained 161a). The newly observed absorption bands in 1.2-benzanthracene, pyrene and 3-bromopyrene can be assigned by comparison with calculations using the LCAO-MO-SCF method with complete configuration interaction.

Using laser flash photolysis with a frequency-quadrupled neodynium laser, Stevens and al 161b). measured the lifetime of the triplet state of fluoro- and pentafluoro-benzene in the gas phase along with the energy transfer efficiencies to cis-2-butane and oxygen. The triplet transient absorption decay was found to be predominantly first order with a lifetime of 250 μsec and 140 μsec, respectively for fluoro- and pentafluoro-benzene.

Triplet quantum yields for eosin and some other dyes have been determinded by Soep *et al.* [161c)]. The system to be studied is exposed to a dye laser pulse (with tunable wavelength) and the transient absorption changes in the system due to triplet population are recorded with the light from a dc xenon lamp.

The protonation rate constant of the triplet state of thionine has been measured as a function of temperature and hydrogen ion concentration using flash photolysis with a frequency-doubled neodynium laser [161d)].

An interesting method for generation of a broad wavelength continuum with a time duration of some picoseconds has been described by Busch *et al.* [161e)]. By focussing the intense mode locked laser beam from a frequency-doubled neodynium laser into various liquids (H_2O, P_2O, etc.) a light continuum can be generated which spans several thousand wave numbers and yet has a picosecond pulse duration. This enables absorption spectroscopy measurements to be made in the picosecond time scale.

$S^* \rightarrow S^{**}$ absorption and intersystem crossings from the ${}^1B_{3u}$ state of naphthalene in cyclohexane at room temperature were studied by Bonneau *et al.* [162)] using a neodymium laser ($\lambda = 1.0\ \mu$, 50 nsec pulse halfwidths) with two successive frequency doublings down to $\lambda = 2645$ Å.

Since cryptocyanin and other dyes are used as saturable absorbers in *Q*-switched giant-pulse lasers, a thorough understanding of the saturation process is necessary to optimize the selection of a special dye in a concentration which will influence the spectral distribution and the time behavior of the laser giant pulse [163)]. If the relaxation of the excited state to the ground state is fast compared to the laser pulse duration, homogeneous absorption occurs and a broad laser frequency spectrum is produced; if it is short, significant hole-burning takes place and the laser line narrows [164)], sometimes even to a single cavity mode [h)].

A thorough study of the various processes occuring in saturable dyes under the influence of high-intensity light has been performed by Giuliano and Hess [165)], who showed that the optical bleaching processes involves the removal of ground-state molecules to other states having smaller absorption cross-sections at the exciting fre-

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[h)] Measurements of vibrational relaxation of dye molecules have been performed by Ricard [164a] and Riekhoff [164b)].

quency, and that recovery of absorption at this frequency is characterized by a complex relaxation mechanism.

The rate of photobleaching of unisotropic dye molecules in solid polymer matrices has been investigated by Kaminov *et al.*[165a]. The bleaching rate is linearly proportional to the intensiy of the incident radiation from an argon laser, indicating a one-photon process.

The time behaviour of triplet-state absorption of illuminated Rhodamin 6G dye molecules, which plays a fundamental role in dye lasers, has been studied by several authors [165b].

With the picosecond continuum absorption technique Busch *et al.* [161e] measured the picosecond kinetics of a bleachable dye (3,3 – diethyloxodicarbocyanin DODC). They found, that bleaching occurs almost simultaneously across the entire absorption band. There was no evidence that an absorbing species appears during the bleaching process. The recovery time to the original optical density is almost complete 50 p-sec after an initial rapid decay with time constant 10 p-sec.

Huff and DeShazer [166] studied the nonlinear absorption behavior of idanthrone dyes which become opaque at high intensities of incident ruby laser light, in contrast to other dyes (e. g. cryptocyanin) which become more transparent. The experimental data show that not only saturation effects are responsible for this anomalous behavior, but that photochemical processes may be operative, thus forming a highly absorbing state of a new species.

From photolysis of methylene blue by ruby-laser giant pulses, Danzinger *et al.* [167] found that a 0.5 Joule, 30 nsec laser pulse causes almost total conversion of the original molecules into transients, but that the photochemical change is completely reversible. The lifetimes of three transients have been measured as 2, 30 and 140 μsec resp. at a 5.5×10^{-6} M dye solution.

Tanaka *et al.* [168] reported that photoreduction of methylene blue in different solvents is accomplished, not only through the interaction between the lowest triplet state of MB and the reducing agent, but that the excited triplet state also plays an important role owing to the exceedingly high laser intensity.

Because of the low energy of a ruby-laser photon (λ = 6940 Å Λ 1.8 eV), most of the photolysis experiments with ruby laser sources either use frequency doubling or proceed by two-step excitation or two-photon processes.

The nitrogen laser (λ = 3200 Å) [65] supplies a high-power nanosecond ultraviolet light source which allows in many cases direct initiation of photochemical reactions. Sousa [169] excited a 10^{-5}

molar quinine sulfate solution with N_2-laser radiation and measured the average fluorescence decay time, which was $\tau = 18.4$ nsec.

Photodissociation of molecules may also be achieved by depositing energy directly in the vibrational degrees of freedom. With high-power pulsed CO_2 lasers dissociation of molecules which absorb CO_2-laser radiation has been observed to proceed at an initial rate that far exceeds the measured thermal rate 169a). The appearance of luminescence spectra of dissociation products preceding the occurrence of gas breakdown 169b) indicates that a considerable degree of dissociation exists for some time before breakdown.

c) Multiphoton Chemistry

Here we will consider photochemical processes initiated by multiphoton absorption. A theoretical treatment of multiphoton processes was developed as early as 1931 by Goeppert-Mayer 170) but experimental verification was not possible until lasers were available to provide light of the necessary intensity.

Kaiser and Garret 171) first reported two-photon absorptions in CaF_2 crystals activated with E_u^{++}.

The theoretical background of multiphoton spectroscopy and a discussion of experiments published up to November 1966 has been given in a review article by Peticolas 172).

A quantitative determination of two-photon absorption cross-sections from direct measurements of chemical yield was performed by Speiser and Kimel 173) who studied the two-photon-induced photolysis of iodoform with a Q-switched ruby laser.

The reaction followed the scheme:

$$\begin{aligned} CHI_3 + 2\,h\nu_{\text{Laser}} &\rightarrow CHI_2 + I \\ CHI_2 &\rightarrow I + X \\ I + I &\rightarrow I_2 . \end{aligned}$$

The concentration of liberated iodine, as measured by its absorbance at 5000 Å, is proportional to the two-photon absorption probability, since no reactants have absorption bands at the single

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[i] See also the recent review of two-photon spectroscopy by Worlock in: Arrechi, F. T.: Laser handbook, p. 1323 ff. Amsterdam: North Holland Publ. Comp. 1972.

ruby wavelength. Cross-sections for two-photon absorption of CHI_3 in different solvents have been measured and range around $\sigma = 10^{-48}$ cm$^4 \cdot$ sec $\cdot$ photon^{-1} $\cdot$ molecule^{-1}.

Fluorescence in anthracene excited by ruby-laser light has been the subject of many investigations [173a)] since the absorption spectrum had shown that no direct excitation of the singlet state by $\lambda = 6940$ Å light is possible. As the fluorescence intensity is proportional to the square of the laser intensity, Peticolas [174)] assumed two-photon absorptions to be the mechanism exciting the observed fluorescence, whereas other authors [175)] proposed a direct triplet excitation with subsequent collisions between two excited triplet molecules to form one singlet species emitting the blue-green fluorescence. Hall *et al.* [176)] took both mechanisms into account. Jaseja *et al.* [177)] measured quantitatively the fluorescence spectra of anthracene and naphthalene excited by ruby-laser giant pulses and confirmed that two-photon excitation from vibrationally excited levels in the ground electronic state is responsible for the fluorescence.

Rousseau and Leroi [178)] studied the two-photon-induced chemical reaction in AgCl by 30 kW ruby-laser pulses which results in a decomposition of AgCl into collodial silver and chlorine. The resultant blue-green emission was proportional to the square of the laser intensity and the measured quantum yield was 10^{-6}.

Polymerization of styrene and p-isopropylstyrene could be photoinitiated with radiation from the ruby laser in the absence of photosensitizers and oxygen [179)]. Since ordinarily no unsensitized photoinitiation of styrene is detected for wavelengths longer than 4000 Å, the results of this experiments must be due to two-photon processes.

Many other applications of multi-photon absorption spectroscopy have meanwhile been reported in photochemistry [172)] and also in solid state physics, for instance, a new assignment of the band gap in alkali bromides by Froehlich *et al.* [180)]. Some further examples will be discussed in Section III.10).

Sorokin and Lankard [181)] illuminated cesium and rubidium vapors with light pulses from a dye laser pumped by a ruby giant-pulse laser, and obtained two-step excitation of Cs_2 and Rb_2 molecules (which are always present in about 1 % concentration at atomic vapor pressures of $10^{-2} - 1$ torr) [182)]. The upper excited state is a repulsive one and dissociates into one excited atom and one ground-state atom. The resulting population inversion in the $7p$ level of Cs and the $6p$ level of Rb enables laser emission at 3.095 μm in helium-buffered cesium vapor and at 2.254 μm and 2.293 μm in rubidium vapor. Measurements of line shape and frequency shift of the atomic laser transition would yield the velocity distribution of the dissociated atoms, and would therefore give information about the repulsive molecular state and its potential curve [183] from which dissociation starts.

During flash photolysis of either gaseous CF_3I or gaseous CH_3I, Kasper and Pimentel [184] observed laser action at 1.30 μm, due to the $^2P_{1/2} \rightarrow {}^2P_{3/2}$ transition of atomic iodine. The high gain obtained at the laser transition provided the first evidence that CH_3I and CF_3I produce predominantly $^2P_{1/2}$ iodine atoms during flash photolysis. Studies of time behavior and linewidth of laser emission and its dependence on flashlamp intensity and gas pressure provide information about the energy distribution among chemical species produced through rupture of chemical bonds and about possible quenching processes.

These examples should have illustrated the importance of lasers as powerful tools in elucidating many details of photochemical processes which are not accessible with conventional light sources.

6. Raman Spectroscopy

It is certainly no exaggeration to say that the application of lasers in Raman spectroscopy has revolutionized this field, giving new impetus to many investigations and opening up new areas of research. There are several reasons why lasers are in many cases superior to conventional lamps.

1. The high intensity available at many laser wavelengths in the visible and near infrared (see Table 1). The exciting line therefore can be chosen inside a spectral range at the long wavelength side of absorption bands in molecules or crystals. This avoids photochemical effects in the probe and prevents spontaneous emission which would overlap the Raman lines. With red or near-infrared laser lines, Raman spectra have been obtained also from colored substances [185]. The effectiveness of laser excitation is greatly enhanced when the sample is placed inside the laser cavity where the photon flux is $1/\tau$ times larger (τ = transmission of the outcoupling mirror; typical values of τ are 0.01–0.05). This arrangement, however, is restricted to probes with low absorption or scattering losses, since otherwise laser oscillation would be suppressed.

2. The small linewidths of exciting laser lines result in Raman spectra with considerably improved resolution [185a]. Brandmüller *et al.* [186]

demonstrated this when resolving the isotopic structure of the 459 cm^{-1} line of CCl_4 and the structure of the Fermi resonance components of CS_2 at 656 cm^{-1} with a 50 mW He-Ne laser as the exciting source.

3. The small laser beam diameter, its low divergence and the possibility of focusing the beam onto an area of less than 10^{-5} cm^2 allows small samples to be used. Schrader and Meier 187) recorded, for instance, Raman spectra from 5 μl of acetyl-α-oxypropionitrile and from 5 μl CCl_4.

A further advantage is that the illumination geometry is simplified and the scattering angle can be defined more exactly than in conventional, extended arrangements.

4. The controllable polarization of the exciting laser light enables the polarization of Raman lines and their dependence on scattering angle to be studied 188).

5. High-power pulsed lasers offer the possibility of studying nonlinear phenomena such as stimulated Raman scattering, the inverse Raman effect and the hyper-Raman effect. These investigations have contributed much to our knowledge of the solid-state and liquid stucture of matter and its higher order constants.

A comparison between the efficiency of excitation with lasers and mercury lamps has been undertaken by Evans *et al.* 189) and Brandmüller *et al.* 190). Since that time, lasers have improved considerably and a later comparison would be even more in favor of laser applications. Since several commercial laser Raman spectrometers are now available 190a), with He-Ne lasers, Ar^+ or Kr^+-ion lasers and neodymium lasers, most current investigations employ lasers as light sources. j)

We will first discuss spontaneous Raman spectroscopy with lasers (linear Raman effect) and then briefly some investigations of the nonlinear Raman effect.

a) Linear Raman Effect

There are several articles reviewing spontaneous Raman spectroscopy with lasers 191-194) with extensive references to the literature up to 1968. This survey therefore will be restricted to a selection of recent work in this field in order to demonstrate the progress achieved.

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j) See also the review by A Mooradian on Raman Spectroscopy of Solids in: Arrechi, F. P.: Laser handbook, p. 1409 ff. Amsterdam: North Holland Publ. 1972.

In addition to experiments which were possible with conventional lamps but can be much more easily performed with lasers, there are some investigations which have to be done within certain exposure times or signal-to-noise ratios and these have only been possible since lasers have been developed. This group includes the electronic Raman effect 195-197), the observation of Raman scattering in metals 198) where the scattering quasi particles are phonons, Raman studies of vibrational spectra in semiconductor crystals 199), or the resonance Raman effect 200-202).

α) Electronic Raman Effect

Electronic Raman spectroscopy is a relatively new branch of emission spectroscopy and, (except for one early investigation by Rasetti in 1930 on NO 203), was unknown until 1963, when Houghen and Singh reported electronic Raman transitions from a single crystal of $PrCl_2$ 204). With laser excitation, many other electronic Raman effects were found in the laboratory of Koningstein 197). This author showed 196) with $PrCl_3$ as example, that a priori calculations of the intensities for electronic Raman transitions are quite straightforward and not as cumbersome as for the vibrational Raman effect. Therefore experimental results can more easily be compared with theoretical predictions. From the intensities of the Raman lines, for instance, the nonsymmetric polarizibility tensor can be deduced and compared with the calculated values, giving a proof for the electronic eigenfunctions assumed in the theory. Most observed electronic Raman transitions have been of trivalent rare-earth ions 197) in garnet crystals, because these are characterized by relatively narrow electronic levels. The relation between the scattering tensor and the symmetry of the crystal field has been discussed in reference 197a) for the case of electronic Raman transitions of the trivalent europium ion in fields of different symmetries. The cross-sections of the electronic transitions are about 10^{-32} cm^2 compared to 10^{-29} cm^2 for the vibrational Raman line of the benzene molecule with a shift of 992 cm^{-1}. Porto 193) has discussed some applications to solid-state physics of results obtained by measurements of the electronic Raman effect.

A complete study of the electronic states of the f^1 configuration of $CeCl_3$ using the electronic Raman effect has been performed by Kiel *et al.* 205). Two pure antisymmetric transitions were observed which are forbidden by normal symmetric tensor selection rules. In this paper the general features of the electronic Raman effect are discussed, including pseudovector scattering terms and asymmetric scattering intensity. The phonon spectrum of $CeCl_3$ and some anomalies (one of the phonon lines shows a small asymmetry in intensity) are considered.

β) The Resonance Raman Effect

The resonance Raman effect occurs when the exciting line approaches an atomic or molecular resonance transition. The intensity of the Raman lines then starts to rise faster than ν^4 193). Leite *et al.* 195), investigating the resonance behavior of the intensity ratio of one-phonon to two-phonon processes in CdS excited by argon laser lines, were able to prove that near resonance the mechanism responsible for coupling of electro-magnetic radiation to the longitudinal optical phonon in CdS seems to involve the exciton, while all the other excited states in the conduction band play no significant role in Raman scattering efficiency.

When the frequency of a laser falls fully into an absorption band, multiple phonon processes start to appear. Leite *et al.* 206) observed n^{th} order ($n = 1, 2 \dots 9$) Raman scattering in CdS under conditions of resonance between the laser frequency and the band gap or the associated exciton states. The scattered light spectrum shows a mixture of fluorescent emission and Raman scattering. Klein and Porto 207) associated the multiphonon resonance Raman effect with the fluorescent emission spectrum, and suggested a possible theoretical approach to this effect.

Resonance Raman effects in halogen gases have been observed by Holzer *et al.* 207 a). With an appropriate choice of exciting lines from an argon laser either resonance Raman effect or resonance fluorescence could be observed. The difference between the two spectra is discussed. In the case of a strong resonance Raman effect, overtone sequences up to the 14th harmonic could be observed.

Resonance Raman spectra of the halogen methanes have been excited with the ultraviolet nitrogen laser, where the resonance effect was found for the Raman lines of the antisymmetric C-X stretching vibration 207b). With different argon laser lines, RR spectra of the aligned polyvinylene chromopheres in polaroid sheets were detected 207c). The polarization of the scattered light was determined and the corresponding transitions could be assigned. Investigations of RR-spectra of MNO_4 in aqueous solutions and as solids showed high-intensity overtone progressions of the totally symmetric vibration 207d).

γ) *Other Laser-Excited Raman Investigations*

The combination of Raman and phosphorescence spectra studied by Pawlopoulos 208) with phenanzine gives information about a rather strong spin-orbit coupling in this molecule.

Polarized Raman spectra from the alkali fluorides LiF, NaF and CsF habe been observed with argon laser excitations by Evans and Fitchen 209). These spectra are of interest as an extreme test of lattice dynamics theories and polarizability models.

The vibration-rotation gas-phase Raman spectrum of C_3O_2 was obtained for the first time by Smith and Barrett 210) using a 2-watt argon-ion laser. The results of this experiment gave new information about the bonding potential function for the central carbon bonding fundamental.

High-resolution Raman spectroscopy of gases with different He-Ne and Ar^+ laser lines was also performed by Weber *et al.* 211). The authors determined relative scattering cross-sections for the pure rotational Raman spectrum of O_2.

With a He-Ne laser (75 mW) Freeman 212) studied Raman spectra of conformational isomers of isochromans. The spectra were obtained from liquid and solid samples in a 1 mm bore capillary tubing. The presence of a Raman band in the liquid but not in the solid phase of a compund is good evidence that a second conformer is in equilibrium with the conformer present in the solid.

The effect of tetrachlorate ions on water structure has been investigated with laser Raman spectra by Walrafen 213), and Lippincott *et al.* 213a) studied polywater configurations. There are numerous other investigations of laser-excited Raman spectra, the discussion of which would demand a special review article 213b–f).

With single-mode lasers the resolution can be considerably improved since the laser line width is then reduced below $10^{-2}\,\mathrm{cm}^{-1}$. Rotational Raman spectra of gases could be resolved using a multiple-pass Raman cell and a single-mode argon laser 185a). With the development of tunable lasers the possibilities of Raman spectroscopy have been further expanded. As an example we mention the excitation of vibrational levels in homonuclear diatomic molecules through Raman transitions 213g). The molecules were irradiated simultaneously with light from a ruby laser (ω_1) and from a tunable dye laser (ω_2) which was tuned such that $\omega_2 - \omega_1$ equalled a molecular vibrational transition frequency. This permits the excitation of the whole class of vibrational levels connected to a thermally populated level through a Raman active transition and allows the vibrational relaxation ($V \rightarrow T$ transfer) to be studied in gas mixtures.

A recently developed field of research is matrix isolation laser Raman spectroscopy [214a)–d)] which allows the study of vibrational Raman spectra with high resolution. Even small isotopic frequency shifts or the influence of crystal structure on the vibrational frequencies may be determined with high precision. This provides an effective constraint on intermolecular forcefields.

A Raman difference spectroscopic technique has been published by Bodenheimer *et al.* [214e)]. Here the exciting laser beam is split and illuminates two samples simultaneously. By subtracting the signals alternately collected from both samples, unwanted lines can be eliminated.

A very interesting field of research covers the spectroscopy of van der Waals molecules in search of more detailed information about the long range potential and the polarizability. Raman spectra of van der Waals dimers in argon [214f)] have been observed and a vibrational frequency shift for I_2-molecules from 213 cm^{-1} to 197 cm^{-1} has been measured for I_2-Ar-complexes.

b) Nonlinear Raman Effects

With the available high-power lasers the nonlinear response of matter to incident radiation can be studied. We will briefly discuss as examples the stimulated Raman effect, which can be used to investigate induced vibrational and rotational Raman spectra in solids, liquids or gases, and the inverse Raman effect which allows rapid analysis of a total Raman spectrum. A review of the applications of these and other nonlinear effects to Raman spectroscopy has been given by Schrötter [214)].

α) Stimulated Raman Effect

The first observation of the stimulated Raman effect was reported by Woodbury and Ng [215)]. The effect was then thoroughly studied by several authors [216-218)] and its theoretical background developed [219, 220)] (see also the review articles by Zubov *et al.* [221)]). The stimulated Raman effect can be described as a parametric process where the coupling between a light wave at the Stokes frequency ω_s and an optical phonon (vibrational wave) at ω_v is produced by a pump field at $\omega_L = \omega_s + \omega_v$.

The emission at the induced Raman lines has the following characteristics:

1. There exists a definite threshold of excitation.
2. Only those Raman lines which are most intense in the spontaneous spectrum show up in the stimulated spectrum (these are commonly one or two lines).
3. The intensity in the induced Raman lines is comparable to that of the exciting radiation and therefore much higher than in spontaneous lines [222]. Up to 70 % of the laser energy may be converted into the side bands [222a].
4. The lines are highly directional.
5. The linewidth depends on that of the exciting laser line and is often much narrower than the width of spontaneous Raman lines.
6. Through interaction of the Stokes lines with the laser line, stimulated anti-stokes lines can be produced [223].
7. Higher order Stokes or anti-Stokes lines have been observed to occur at exact harmonics of the first vibrational [224] or rotational [225] shifts.

There have been numerous investigations employing these characteristics for Raman spectroscopy, but only a few examples will be given here: the Raman spectrum of $SnCl_4$ has been studied under very high resolution by Rank *et al.* [226].

Using a high-resolution spectrograph and a Fabry-Perrot interferometer, Günther *et al.* [227] resolved a number of equidistant components with a mean separation of 0.04 cm^{-1} in the stimulated Raman spectrum of CS_2, which can be attributed to resonant modes in single medium-scale filaments of self-trapped radiation within the liquid.

Stimulated rotational and vibrational Raman scattering in O_2, CO_2, N_2O and other gases has been observed by Mack *et al.* [228]. The autput of a mode-locked ruby laser [229] producing a train of pulses of 5 psec duration with a maximum peak power of 5 GW was focused into a cell pressurized with the sample gas. Pulse-energy conversion efficiencies into the Raman lines of up to 70 % have been obtained. The induced rotational lines are broadened; this could be due to a strong optical Stark effect [230].

β) Inverse Raman Effect

When a molecular system is irradiated simultaneously by intense monochromatic light at frequency ω_L and by a continuum of higher frequencies, absorption occurs from the continuum at frequencies $\omega_L + \omega_M$, where ω_M is a Raman frequency of the medium.

This phenomenon is known as the inverse Raman effect and was first observed by Stoicheff 231). The inverse Raman spectrum is the analogue of the stimulated Raman emission spectrum and therefore theories of the stimulated Raman effect apply to both emission and absorption. There are, however, significant differences in the corresponding spectra:

The stimulated Raman emission exhibits a threshold and only a few vibrational lines are observed, corresponding to the lines of highest intensity in the normal Raman spectrum. For observation of the inverse Raman spectrum, both the continuum and the monochromatic stimulating radiation are supplied. There is no threshold and therefore the complete Raman active spectrum can be obtained if the continuum light source has a sufficient spectral bandwidth.

There are the further advantages that rotational lines can be studied and that fluorescent substances can be investigated by the inverse Raman effect. Benzene and other molecular liquids have been studied by this method by McQuillan and Stoicheff 232). The required continuum radiation was anti-Stokes emission produced by passing the laser beam in liquid toluene.

Using as the background continuum the short-lived spontaneous fluorescence of rhodamine B or 6 G, McLaren and Stoicheff 233) developed this method further to obtain inverse Raman spectra over the range of frequency shifts 300–3500 cm^{-1} in liquids and solids in a time of 40 nsec! The stimulating monochromatic radiation at 6940 Å is provided by a giant-pulse ruby laser. A small part of the main laser beam is frequency-doubled in a KDP-crystal and serves to excite the rhodamine fluorescence, thus ensuring simultaneous irradiation of the sample by both beams.

7. Light Scattering Observations

In addition to Raman spectroscopy, lasers have very much stimulated investigations of Thomson, Mie, Rayleigh, and Brillouin scattering processes 234 b), where the intensity, angular distribution, polarization and line shape of the scattered light can now be measured with substantially higher precision. The improved experimental technique by giving more reliable results, has also inspired theoreticians to develop models 234) which may enable to interprete and explain the experimental findings.

Before the development of lasers it was not possible, for instance, to study experimentally in any detail the spectral distribution of

Rayleigh scattered light from dense transparent media with nonuniform density. If these nonuniformities are time-independent, there will be no frequency shift of the scattered light. If, however, time-dependent density fluctuations occur, as e. g. in fluids, due to thermal or mechanical processes, the frequency of the scattered light exhibits a spectrum characteristic of this time dependence. The type of information which can be obtained by determining the spectral line profile and frequency shift is described in an article by Mountain 235).

With the availability of lasers, Brillouin scattering can now be used more confidently to study electron-phonon interactions and to probe the energy, damping and relative weight of the various hydrodynamic collective modes in anharmonic insulating crystals.The connection between the intensity and spectral distribution of scattered light and the nuclear displacement-displacement correlation function has been extensively discussed by Griffin 236).

Brillouin scattering of laser light in liquids has been studied by several authors. Shapiro *et al.* 237) measured hypersonic velocities in various liquids and obtained a Brillouin linewidth of 0.011 cm^{-1} in methylene chloride but of less than 0.002 cm^{-1} in benzene, carbon disulfide and chloroform. The broadening of the Brillouin components arises from damping of thermal phonons and is closely connected with the viscosity coefficient of the medium. From the measured linewidths, the lifetimes of the phonons responsible for Brillouin scattering at 89°45′ were calculated to be 4.8×10^{-10} sec for methylene chloride and 7.6×10^{-10} sec for toluene.

Brillouin scattering and its temperature dependence in a liquid crystal was reported by Nordland 238).

The fluctuations in the orientation of anisotropically polarizable molecules in liquids also cause frequency broadening of the scattered light, as investigated for CS_2 in CCl_4 239). CS_2 is a highly polarizable molecule with very different polarizabilities along and perpendicular to the internuclear axis. CCl_4 on the other hand, is a poor scatterer because it is an isotropic molecule. Thus, if CS_2 is mixed with CCl_4, the CS_2 molecules can be studied in a new environment.

For very accurate line profile measurements, a heterodyne technique has been developed 240) which can be briefly explained as follows: the light, scattered into a cone within the angle $\Theta \pm \delta\Theta$ ($\delta\Theta \leq 1°$), is focused onto the cathode of a photomultiplier. The photocurrent is proportional to the square of the incoming light amplitude but cannot follow the rapid light frequency. Any beat frequencies, however, resulting from interference between the different spectral components in the spectral distribution of scattered light will cause fluctuations of the photocurrent inside an easily detectable frequency range. These can be analyzed with commercial spectrum analyzers (which act like tunable electronic frequency filters). A mathematical description of this analysis which uses correlation functions can be found, for instance, in ref. 241).

Application of this technique to measurements of the spectral distribution of light scattered from a pure SF_6 fluid at its critical point was present by Ford and Benedek 240). The scattering is produced by entropy fluctuations which decay very slowly in the critical region. Therefore the spectrum of the scattered light is extremely narrow ($10^1 - 10^4$ cps) and can only be observed by this light beating technique 240a).

This method was also employed by Chu *et al.* 242) who investigated the effects of long range correlation for a critical mixture of polystyrene in cyclohexane at small temperature intervals from the phase seperation temperature.

Rosenberger *et al.* 243) studied with a He-Ne laser changes in intensity and polarization of Rayleigh-scattered light from polymers at a temperature T_g where the plastic displays a phase transition and passes from a glass-like to a rubber-like state. The observed enhanced Rayleigh component and the effects of annealing on the index of refraction are consistent with a model of the plastic which contains a random distribution of strains frozen in during the polymerization process.

Yeh and Keeler 244) extended the method of laser-scattering spectroscopy to probe systems undergoing rapid chemical reactions. They observed the spectral line broadening in light from a single-mode He-Ne laser scattered from multicomponent solutions, as a function of time. The experiment employed a pressure-scanned Fabry-Perrot interferometer and photon counting techniques.

The spectrum of light, scattered from a gas is determined by the motion of the scatterers (Doppler effect) and by collisions and can therefore yield information about collision cross-sections 245). The analytical expressions connecting theory and experimental results are given in ref. 245 a).

The velocity, density and temperature of a streaming gas can be determined by measuring the magnitude, frequency and spectral distribution of Rayleigh-scattered light from two simultaneously pulsed ruby lasers with parallel beams and slightly different frequencies 246).

To prove regular scattering theory 247), the angular distribution of Rayleigh scattering from gases 248) and liquids 249) has been examined and confirmed for different polarizations of the incoming light from cw He-Ne lasers and pulsed ruby lasers.

Concerning transmission of laser light through the atmosphere 250), it is important to know the extent of the influence of turbulence 251) and aerosol attenuation 252). A comparison of measured and predicted aerosol scattering has been given by Setzer 253). His experiment used a He-Ne laser at 6328 Å, the theory being based on Mie's solution for scattering from a single sphere, applied to an aggregate of water droplets.

Air pollutants can be identified by recording the absorption of selected infrared laser lines and their concentration and its local dependence determined. The small beam divergence allows long light paths and therefore high sensitivity 253a).

As in Raman spectroscopy, nonlinear phenomena occur in Rayleigh 254) and Brillouin scattering 220, 255) when high-power lasers act as light sources. The increasing understanding of stimulated scattering processes has opened the way to the determination of material parameters directly from stimulated processes. The experimental investigation of the gain factor in stimulated Brillouin scattering enables, for instance, the spontaneous Brillouin linewidth 256) and phonon lifetimes 257) to be determined.

Stimulated Rayleigh scattering from localised thermal fluctuations in gases 258) and liquids 259) has been reported with measurements of the line shifts, thresholds and critical absorption coefficients.

From nonlinear light scattering in methane, Maker 260) deduced values for the second-order polarizability.

Stimulated effects in nonlinear optics, such as stimulated Brillouin and Raman scattering in liquids and gases and stimulated thermal Rayleigh scattering, have been reviewed by Rank 260a).

8. Plasma Spectroscopy

Lasers have contributed to the understanding of plasma characteristics in a number of different ways.

a) The use of highly sensitive laser interferometer techniques has enabled electron densities and temperatures to be diagnosed 261)–261d) with their variations in time and space, especially in plasmas where other methods (e. g. microwave measurements) could not be employed.

b) Observations of the intensity and spectral distribution of laser light scattered from a plasma, have allowed ion and electron temperatures and density fluctuations to be determined 262).

c) Selective excitation by intense laser light of definite states of atoms seeded in a plasma, and observation of the corresponding fluorescence and its decay can be used to study local values of electron temperature and density in low-temperature plasmas 263a–c).

d) In the focus of powerful laser light pulses, high-temperature microplasmas can be generated in gases 264) or on solid surfaces 265). The investigation of these plasmas gives information about plasma production, heating and expansion. Since highly ionized species are produced, spectroscopic studies of the plasma light yield new data about ionization energy and term values for multiple-charge ions 266).

a) Plasma Diagnosis with the Laser Interferometer

The laser interferometer consists of two coupled resonators, one containing the laser, the other the plasma under investigation (Fig. 10). The laser radiation, reflected back from mirror M_3, which contains phase information about the refractive index of the plasma, interferes with the laser wave in cavity A, resulting in an amplitude modulation of the laser output 267). This modulation can be related to the refractive index and therefore to the plasma frequency and electron density. With a curved rather than a planar mirror M_3, the sensitivity can be increased by utilizing transverse cavity modes 268).

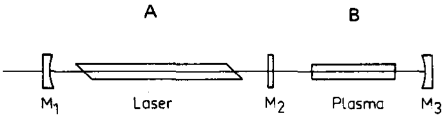

Fig. 10. Laser interferometer for plasma diagnosis

Phase changes as small as $2\pi \times 10^{-3}$ rad have been detected 269) by using a null method where phase drifts of the apparatus are compensated by a calibrated and controllable dielectric in cavity B. The response time of this laser interferometer is less than 5 μsec when operated at 3.39 μm and repetitively pulsed plasmas can therefore be investigated. Gerardo *et al.* 270) even reached a time resolution of about 10^{-8} sec. The time response in their improved interferometer is equal to the time required for the light to make a few passages through cavity *B*.

A new sensitive method which measures the plasma electron density by heterodyning of two frequencies in a ring laser has been proposed by Stefanov 271): In a ring laser 272) two waves travelling in opposite directions are generated. The refractive index of a magnetized plasma is different for the clockwise and counterclockwise running circular polarized waves, resulting in a opposite frequency shift. The beat frequency of both waves therefore is a sensitive detector for the plasma density.

Since the phase shift of light passing through a plasma is proportional to its wavelength, a 337 μm cyanide laser interferometer, described by Kon *et al.* 273), can be 100 times more sensitive than one operated at 3.39 μ.

In partly ionized plasmas, where both the charged and neutral particles are in concentrations large enough to make measurable contributions to the refractive index, single wavelength interferometry cannot separate that part of refractivity resulting from the neutral components.

Because of the relatively large dispersion from the electrons compared with the almost constant refractivity of the neutrals and the negligible contribution of the ions, it is possible, with simultaneous measurements at two different wavelength, to determine independent values of the density of electrons and of the nonelectronic components in the plasma 274). Alcock and Ramsden 275) used the light from a giant-pulse ruby laser and its second harmonic generated in an ADP-crystal (ammonium dihydrogen phosphate) to probe a pulsed plasma and its time-dependent density in a Mach-Zehnder interferometer.

The application of holography to plasma interferometry has several advantages 276): accurate alignment and precision optical elements are not required. A complete three-dimensional record of the interference phenomena is obtained and the technique is well suited to record stationary and transient plasmas. Two-wavelength holographic interferometry of partially ionized plasmas has been performed by Jeffries 277).

b) Scattering of Laser Light from Plasmas

The spectral distribution of light scattered from a plasma depends on its wavelength λ_0, the electron Debye length D_e and the scattering angle θ and can be characterized by a parameter

$$\alpha = \frac{\lambda_0}{4\Pi D_e \sin \cdot \theta/2}$$

For $\alpha \ll 1$ the scattered light spectrum is gaussian with a width determined by the electron temperature, because it is due to the incoherent sum of Thomson scattering from individual, thermally moving electrons. The intensity and spectral linewidth of scattered light therefore yield electron density and temperature.

Such measurements have been performed by Koons and Fiocco [279] in a low-density reflex discharge in helium, using an argon laser at $\lambda = 4880$ Å as light source. The results ($N_e = 4.8 \times 10^{12}$ cm^{-3}, $T_e = 1.3$ eV) are in good agreement with those obtained with a Langmuir probe.

If $\alpha \gg 1$, collective effects play an important role and the light scattering is no longer caused by individual electrons but by electron density fluctuations [280]. In this case the spectrum shows a central line at λ_0 and two narrow lines located symmetrically about λ_0, at a distance governed by the electron plasma frequency. The linewidth is smaller than in the case $\lambda \ll 1$ and is determined rather by the thermal motion of the ions, not that of the electrons. The line shape depends on the ratio of electron to ion temperatures. Therefore, a measurement of the shape and width of this central line allows, under certain assumptions, a direct determination of the ion temperature.

This fact has been used to measure electron and ion temperatures in a theta-pinch plasma [281], and a dense plasma ($n_e = 10^{16}$ cm^{-3}) produced in a carbon arc [282]. Both experiments employed pulsed ruby lasers as light sources.

c) *Selective Excitation*

If an atomic transition is optically pumped by a beam of laser radiation having the appropriate frequency, the population in the upper state can be considerably enhanced along the path of the beam. This causes an intensification of the spontaneous emission from this state, which contains information about the conditions within the pumped region. since the exponential decay time for the intensified emission depends upon both the electron number density and the electron temperature. The latter can be obtained from the intensity ratio of the fluorescence excited from two different lower levels, if local thermal equilibrium is assumed. This method has been discussed and applied to potassium and barium-seeded plasmas by Measures[263], using the fact that the temperature-tuned ruby laser line coincides with transitions between excited states in Ba and K.

The author also studied the possibility of enhancing the electron density and temperature of an alkali-seeded plasma by pumping the resonance lines of the alkali atoms with a suitably tuned laser[283].

A method of evaluating plasma temperature by measuring the transmission of laser radiation that has a resonance with one of the plasma emission lines, has been proposed by Wheeler and Troughton[284]. This technique should be applicable for plasma temperatures between 15 000 – 20 000 °K and for electron densities between $4 \cdot 10^{16}$ and $2 \times 10^{20}\,\mathrm{cm}^{-3}$, and it does not require an exact knowledge of this density. By utilizing the magnetic double refraction (transverse Zeeman effect), the ratio of the magnetic field H in a plasma to the free electron density can be determined by measuring the plasma transmission with respect to the two refracted polarizations of the laser light[285].

d) Laser-Induced Plasmas

Since Meyerand and Haught[286] discovered that focused light from a giant-pulse ruby laser can cause gas breakdown, even in gases which require for ionization more than 12 photons at $\lambda = 6943$ Å, numerous investigations have been performed to study the initial triggering mechanism, the heating processes, and the expansion and decay of these laser-produced plasmas.[286a]

A review of the literature up to 1968 was made by DeMichelis[287]. The phenomena are now essentially understood and may be briefly summarized as follows: by multi-photon absorption[288] some atoms become ionized. The photoelectrons generated can gain sufficient energy from the light field through the process of inverse bremsstrahlung[289] to further excite and ionize atoms and ions. Excited species can be ionized either by multiphoton absorption or by electron impact. The light intensities in the focus of a giant-pulse laser are sufficient to allow these processes to occur in times of less than one nanosecond. Measurements of the far-ultraviolet light emitted from the plasma[290] show that multiply charged ions are present and that plasma temperatures of about $10^4 - 10^6$ °K are reached during the laser pulse[291, 292].

Many of these investigations used a second laser and the methods described above to probe the plasma parameters and their changes on a nanosecond scale[265].

Besides these gas-breakdown phenomena, laser-induced plasmas on solid surfaces have attracted the interest of many physicists, since there may be a chance that nuclear fusion processes will be triggered by laser-produced high-temperature plasmas 293). We will discuss these plasmas and their practical importance for spectroscopy in Section III.9).

9. Chemical Microanalysis and Spectrophotometry

When the light from a pulsed laser is focused onto a solid surface, electrons 292a), ions, and neutral particles are evaporated 293-295) when the laser intensity exceeds a threshold value. Kinetic energy, temperature, degree of ionization and total mass of the expanding vapor cloud depend on incident laser power and pulse duration 296, 297).

These observations have led to various developments:

a) The laser-induced ion emission has been used to construct a pulsed, high-current ion source for mass-spectrometric investigations 293, 298). With this method Megrue was able to analyze the isotopic abundance of the rare gases He^3, He^4, Ne^{20}, Ne^{22} in microvolumes of meteorites 299). The laser-mass spectrometer combination has also been used to study the vapor species emanating from various binary, ternary and quanternary compounds of bismuth, arsenic and antimony with the elements of the VIa group 299a), and it is shown that there is direct correlation in some cases between the vapor composition and the structure of the condensed phase.

b) The fluorescence spectra of excited atoms and ions serve for spectrochemical analysis of the vaporized material. This will be briefly discussed in this section.

c) With the development of extremely powerful light pulses (up to 10^{12} watt), totally ionized plasmas have been induced with temperatures sufficiently high to produce neutrons from irradiated deuterium 300). The investigation of these high-temperature plasmas has attracted increasing interest because of the exciting possibility of triggering controlled nuclear fusion processes 293). A short survey of the literature and measurements on laser induced plasmas from metal surfaces has been published elsewhere 301).

A survey of the applications of lasers in micro- and macro-spectral analysis has been given by Görlich and Moenke-Blankenburg 1b, 302). Their group in Jena has developed the technique of laser microprobing into a reliable and versatile tool for chemical analysis 302a).

The laser microprobe employs a pulsed laser to vaporize minute amounts of the sample. The vapor temperature, however, in the case of low-power lasers is not sufficient to provide adequate excitation for spectrochemical analysis. The sample vapor is therefore further excited as it passes between two auxiliary electrodes above the sample. The optimum excitation conditions have been examined by Quillfeldt 303) using the commercial laser-microspectral analyzer LMA 1 (Carl Zeiss, Jena). Spectrochemical determinations of Fe, Mg, Mn and Ca in garnets with a Jarrell-Ash laser microprobe, using ruby and neodymium lasers 304) have shown that reliable data on the abundance of the different elements can be obtained in a very short time.

The laser microprobe is especially useful for handling toxic or radioactive materials 305) since analysis can be performed with very small samples.

The advantages of this technique are that they are applicable to probes in ultra high vacuum, where any impurities are excluded, and also to samples at atmospheric pressure. The diameter of the evaporated cavity can be varied between 10 μm and 1 mm, and the quantity of the evaporated material may be less than 10^{-6} g. Solids in any desired form, crystalline or powered, are accessible to analysis.

10. Nonlinear Optics and Solid-State Spectroscopy

Besides the spectroscopic investigations of solids by laser-excited spontaneous Raman or Brillouin scattering already discussed in Sections III.6 and 7, much new insight into the optical properties and the structure of solids has been gained by studying nonlinear optical effects. (Surveys and more detailed information about nonlinear optics can be found in refs. 306-308)).

These nonlinear phenomena, long known theoretically 309), but only experimentally realizable with lasers as light sources, are based on the fact that the polarization $\mathfrak{P}$ of a medium, induced by a high-intensity electromagnetic field, is no longer proportional to the electric field vector $\mathfrak{E}$, but contains nonlinear contributions:

$$\mathfrak{P} = \varepsilon_0 \, \chi \cdot \mathfrak{E} + \mathfrak{P}^{NL}$$

By this nonlinear polarization different incident lightwaves, or lightwaves and phonon waves, are coupled together, resulting in the production of sum and difference frequencies and second or third harmonics. (This is to some extent analogous to *rf* frequency mixing in a nonlinear diode).

Taking into account only quadratic terms in $\vec{E}$, the nonlinear part of the polarization can be expressed through the tensor χ_{iJK} of the nonlinear susceptibility:

$$\mathcal{P}_i^{NL} = \sum_{j,K=1}^{3} \chi_{iJK} E_j E_K .$$

One result of studying nonlinear optical phenomena is, for instance, the determination of this susceptibility tensor, which supplies information about the anharmonicity of the potential between atoms in a crystal lattice. A simple electrodynamic model which relates the anharmonic motion of the bond charge to the higher-order nonlinear susceptibilities has been proposed by Levine 310). The application of his theory to calculations of the nonlinearities in α-quarz yields excellent agreement with experimental data.

Calculations which ascribe nonlinear optical polarizabilities in $LiIO_3$ to the individual I-O bonds and relate experimentally measured second harmonic generation coefficients χ_{311} and χ_{313} to theoretical results for the structure of $LiIO_3$, have been performed by Jeggo 311).

By measuring the temperature dependence of second-harmonic generation (SHG) of the neodymium laser wavelength at 1.06 μm in sodium nitride for five different radiation geometries which correspond to the five nonvanishing components of the nonlinear susceptibility tensor, Vogt *et al.* 312) could determine these tensor components and the coherence length $l_c = \frac{\lambda}{4\,(n_2 - n_1)}$ ($n_{1,2}$ are the refractive indices for the fundamental or second harmonic waves respectively) and their temperature dependence. χ^{NL} shows a strong decrease with rising temperature in the ferro-electric phase and in general a sharp drop at the Curie temperature. Domain structures and their influence on SHG are extensively discussed.

Similar measurements on triglycine single crystals with SHG of ruby-laser light have been performed by Svorov and Sonin 313). The nonlinear optical properties of $Ba_2NaNb_5O_{15}$, which is a very efficient material for low-threshold optical mixing and parametric oscillation 314), have been studied in different temperature ranges, where the crystal changes its modification. Between 300 and 560 °C, e. g., it exists in a ferro electric tetragonal phase and is optically uniaxial. Byer *et al.* 315) determined the variation of SHG with temperature in this phase in order to find the optimum range for parametric frequency mixing.

The interest in efficient optical frequency doubling has stimulated a search for new nonlinear materials. Kurtz 316) has reported a systematic approach for finding nonlinear crystalline solids, based on the use of the anharmonic oscillator model in conjunction with Miller's rule to estimate the SHG and electro optic coefficients of a material. This empirical rule states that the ratio of the nonlinear optical susceptibility to the product of the linear susceptibilities is a parameter which is nearly constant for a wide variety of inorganic solids. Using this empirical fact, one can arrive at an expression for the nonlinear coefficients that involves only the linear susceptibilities and known material constants.

Absolute measurements of nonlinear coefficients in GaAs in the millimeter region $10^9 - 10^{12}$ Hz have been determined 317) by mixing adjacent vibrational-rotational lines of a CO_2 laser in a GaAs-filled waveguide which was matched to the difference frequencies. The experiments yielded the astonishing result that the nonlinear coefficient and the dielectric constant show opposite dispersions.

An interesting method of detecting infrared signals with sensitive and fast visible photomultipliers has been demonstrated by Boyd *et al.* 318). The authors used the frequency mixing of infrared signals with visible light (10.6 μ CO_2 laser with 0.6328 μ He-Ne laser) in nonlinear crystals to produce the difference frequency wave (at λ = 0.6729 μ) which can be detected by an S 20 photomultiplier. No additional source of noise due to the mixing process was observed.

The discovery of self-focussing of intense laser beams 318a) and the phenomena of self-induced transparency 318b) have stimulated a whole new class of experimental investigations which give information about the transient interaction between light and matter 318c)

The experiments extend to solids, liquids 318d) and gases 318e).

IV. High-Resolution Spectroscopy Based on Saturation Effects

When a gas is illuminated with laser light, the available laser intensity often is so large that the optical pumping of atoms or molecules into excited states by absorption of laser light may proceed faster than the competing relaxation processes, such as spontaneous emission or collisional relaxations. This means that the initial state, from which the absorption starts, will be depleted, resulting in saturation of the absorbing transition 319). This section discusses the different kinds of saturation phenomena which may occur and which can be used in new methods of high-resolution spectroscopy.

1. Different Kinds of Saturation Effects

Saturation as described above can be observed either when all the molecules in the initial state have the same absorption probability, or when some of the state population is preferentially absorbed, depending on the spatial orientation of the molecules or on their transition frequency, selected from a certain frequency interval. The first case is called homogeneous line saturation, the second is due to inhomogeneous saturation or hole-burning. This different cases will be explained in more detail by discussing some relevant experiments.

a) The first example of the application of saturation effects is an experiment on optical pumping of molecules performed by Drullinger and Zare 320), who used the excitation of Na_2 by absorption of the argon laser line at $\lambda = 4880$ Å. As explained in Section III.2, a definite vibration-rotation level in the excited $B\,^1\Pi_\mu$ state of Na_2 is populated. The excited molecule emits a fluorescence progression as it returns into the electronic ground state. However, not only the initial vibrational level ($v'' = 3$) from which absorption took place is reached by spontaneous emission, but all v'' levels connected by nonvanishing Franck-Condon factors with the excited state (see Figs. 4 and 11.). From these vibrational levels, the $v'' = 3$ level can only be reached by collisional relaxation (since electric dipole transitions between vibrational levels of a homonuclear diatomic molecule are forbidden).

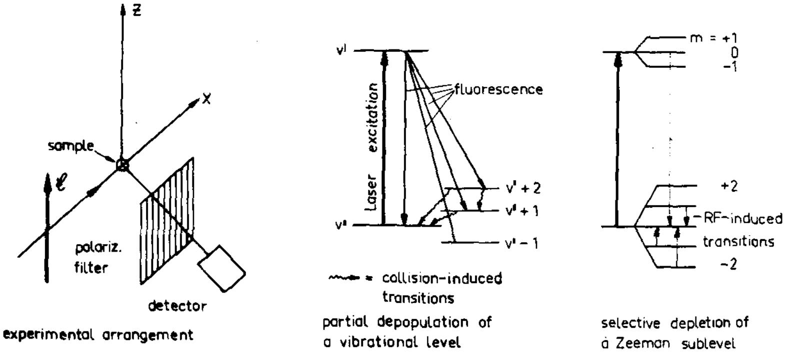

Fig. 11. Optical pumping of molecules and scheme for double resonance experiments on laser-pumped molecules in case of Zeeman splitting of rotational levels of the electronic ground state

If the number of absorbed laser photons per second becomes larger than this relaxation rate, the initial state will be depopulated, thus decreasing the absorption rate, and therefore the fluorescence intensity will rise less than linearly with the laser intensity (Fig. 12).

The absorption probability is proportional to the scalar product $\mu \cdot \mathcal{E} = |\mu| \cdot |\mathcal{E}| \cdot \cos \varphi$, where μ is the transition dipole moment, $\mathcal{E}$ the electric vector of the exciting light wave and φ the angle between $\mathcal{E}$ and μ.

This means that laser photons are preferentially absorbed by molecules with $\mu \, // \mathcal{E}$, which results in a partial polarization of the excited state population and with it the fluorescence.

As soon saturation occurs, those ground-state molecules with $\mu \, // \mathcal{E}$ die out first. This can be detected by observing the corresponding decrease in the fluorescence polarization. Fig. 12 shows the experimental results. This proves that the optical pumping by laser light is even faster than the relaxation rate between molecules of different spatial orientation.

With conventional cw light sources it would not be possible to maintain such a nonthermal population distribution, because the

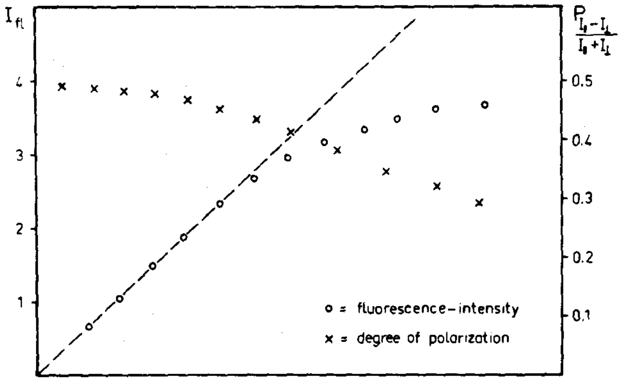

Fig. 12. Optical pumping of molecules: saturation of absorption, resulting in a less than linear increase of fluorescence intensity with exciting laser intensity (left scale) and a decrease of polarization degree (right scale), detected for Na_2 fluorescence excited by the 4880 Å argon laser line. (From Drullinger, R.E., Zare, R.N., ref. [320])

collisional disorientation cross-sections are too large for collision partners with angular momentum. For this reason, nearly all optical pumping experiments have so far been performed on atoms with a spin momentum but with zero angular momentum (spin alignment)[321].

If the molecules are placed in a magnetic field, the different spatial orientations correspond to different Zeeman levels and the selective saturation explained above leads to a nonthermal population of the Zeeman niveaus. By exposing the sample simultaneously to an rf field with the proper frequency, magnetic dipole transitions between the Zeeman levels can occur and the thermal population can be restored. This will again increase the polarization of the fluorescence at most up to its presaturation value. The fluorescence polarization is thus used as detector for the rf transitions.

With this procedure, as with the double-resonance methods in atomic physics, Zeeman and Stark splittings, hyperfine structures and Λ doublings in molecules can be measured with high precision, even if the observed level splittings are far less than the optical doppler width. From the width of the rf resonance and from the time response of the pumped systems, orientation relaxation rates can be evaluated for individual $(v''J'')$ levels. Other possible applications of this promising technique have been outlined by Zare [130]. Experiments to test some of these proposals are currently under investigation and their results will be reported elsewhere.

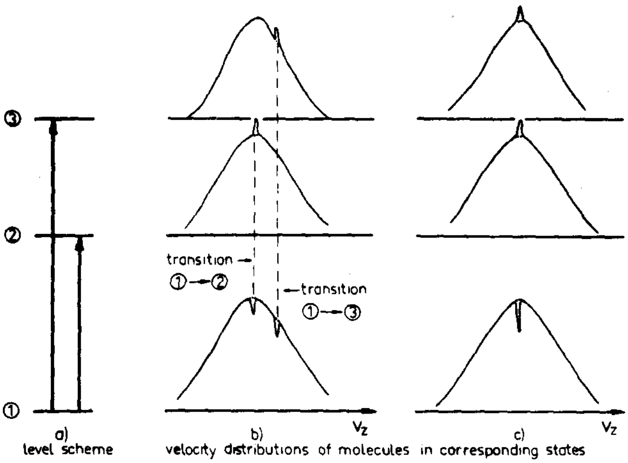

Fig. 13 a-c. "Hole-burning" saturation of two doppler broadened transitions sharing a common lower level

b) Another kind of saturation phenomenon occurs in the case of two doppler-broadened absorbing transitions sharing a common upper or lower level. If one of these transitions is pumped by a monochromatic laser wave propagating in Z direction, the population of both levels is changed selectively because only those molecules with a velocity component $v_z \pm \Delta v_z$ inside the doppler broadened velocity profile have the proper transition wavelength to absorb the monochromatic light (see Fig. 13) [321a)].

In the case of a common upper level the fluorescence from this level due to excitation by the monochromatic wave will reflect this selective population with molecules having only velocity components inside the range $v_z \pm \Delta v_z$. Thus, observing the fluorescence in z direction on any transition from this upper level yields linewidths much smaller than the normal doppler width [322)]. In this way lines which are not resolved in normal fluorescence spectroscopy can be separated even if their frequency difference is much less than their doppler width [323)].

In the case of a common lower level, the second absorption transition would show this narrowing effect when probed with a tunable monochromatic laser line. This example can be realized if atoms or molecules in a magnetic field are pumped by a laser, oscillating simultaneously on two cavity modes [324)]. If the Zeeman splitting of the probe equals the mode spacing of the laser, both transitions are pumped simultaneously and each laser mode selectively "eats away" molecules from the common lower level, which are then not available for the other transition. Thus the absorption profile of one transition is altered by the presence of the other and, as in the fluorescence case, the linewidths of these "resonances", when the Zeeman splitting is tuned over the mode-spacing, are again determined not by doppler-broadening but by the natural or collision-broadened linewidth 325) (see Fig. 13 b u. c).

This method is specially suited for measurements of closely spaced Zeeman or Stark splitting and fine and hyperfine structures, which are separated only within their doppler linewidth 326).

If the absorbing probe is placed inside the laser cavity, this saturation effect causes, through the decreasing absorption losses, a coupling between the two oscillating modes resulting in an intensity change which shows the above-mentioned resonance effect even more markedly when the level spacing of the probe is tuned 327).

Detailed theoretical and experimental investigations 328-330) of such coupling effects show that they are not caused entirely by these "hole-burning" effects, but that double quantum Raman transitions occur and that the interaction between both light fields and the molecule via the common level leads to a dynamic Stark splitting of the probe line 331).

The saturation effects mentioned above can be observed with propagating waves. Another kind of saturation occurs if the probe is placed inside the laser resonator where a standing electromagnetic wave interacts with molecular systems which have inhomogeneously broadened transitions. These saturation phenomena have lead to a new kind of high resolution spectroscopy called Lamb dip spectroscopy after W. Lamb 332) who was the first to give a thoroughly theoretical analysis of the laser, including these saturation effects.

2. Lamb Dip Spectroscopy

Let us consider a laser oscillating at a single frequency (single-mode operation) and gas molecules inside the laser resonator which have absorption transitions at this frequency. Some of the molecules will be pumped by the laser-light into an excited state. If the relaxation processes (spontaneous emission and collisional relaxation) are slower than the excitation rate, the ground state will be partly depleted and the absorption therefore decreases with increasing laser intensity.

The electromagnetic field in the cavity is a standing wave which can be described as a superposition of two travelling waves propagating in opposite directions (± z-axis) (see Fig. 14). The condition that the molecular absorption frequency equals the monchromatic laser frequency is fulfilled for the wave travelling in z direction by molecules with velocity components inside the range $v_{1z} \pm \Delta v_z$, for the wave in -z direction by other molecules with v_z within $v_{2z} \pm \Delta v_z$. This means that generally there are two groups of molecules which can absorb the monochromatic laser light, unless the laser frequency coincides with the center of the doppler-broadened absorption line. In this case only one group with velocity components $v_z = 0 \pm \Delta v_z$ is available for absorption of the laser line. The absorption coefficient therefore has a minimum at the center of the inhomogeneous molecular absorption profile (see Fig. 14 b), and the laser intensity will

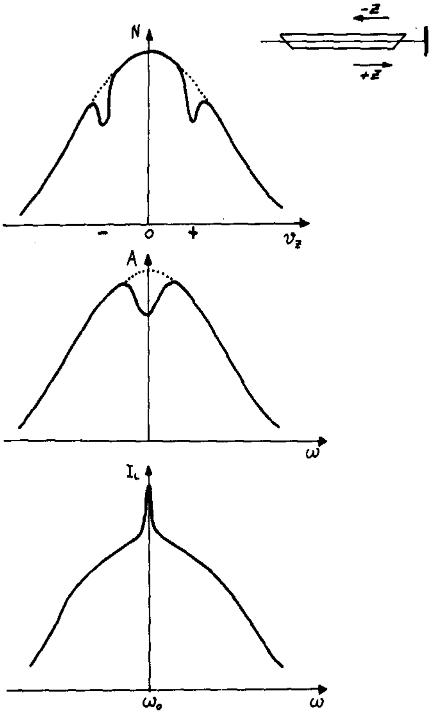

Fig. 14 a-c. "Lamb-dip" saturation of doppler broadened transitions interacting with a standing monochromatic wave inside a laser cavity. a) Lamb dip in the velocity distribution of absorbing ground-state molecules, due to absorption of monochromatic lightwaves travelling in + z and $-z$ directions; b) Absorption coefficient as a function of frequency within the doppler broadened absorbing transition; c) Sharp peak in laser intensity corresponding to the Lamb dip in the absorption profile show a sharp maximum when tuned across the absorption line (Fig. 14 c). If the laser is operated close above threshold this maximum is much more enhanced

This situation corresponds to the well-known saturation effect in the *emission* of most gas laser transitions, where, for the same reason, fewer upper-state molecules can contribute to the gain of the laser transition at the center of the doppler-broadened fluorescence line than nearby. When tuning the laser frequency across the doppler-line profile, the laser intensity therefore shows a dip at the centerfrequency, called the "Bennet hole" or "Lamb dip" after W.R. Bennet Jr.333) who discovered and explained this phenomen, and W.E. Lamb 332) who predicted it in his general theory of a laser.

In both cases (i. e. emission or absorption saturation) the halfwidth of this/Lamb dip is slightly dependent on laser power but mainly determined by the interaction time of the individual molecules with the standing light wave in the cavity. This time may be limited by the finite lifetimes τ_a, τ_b of upper or lower states, by the average time $1/\sigma\bar{v}p$ between two disturbing collisions, or by the transit time τ_t of the gas molecules across the laser beam. This last limitation becomes important at low pressures of the absorbing gas and for transitions between long-lived states (see Section IV.3).

The mathematical expression for the saturable absorption profile of a gaseous probe interacting with a tunable monochromatic standing wave (frequency ω, electric vector $\mathcal{E}$) can be deduced as follows 325):

$$\alpha = \alpha_0 \left[1 - \beta \mathcal{E}^2 \left(1 + \frac{\gamma_{ab}\, \gamma'_{ab}}{(\omega - \omega_0 - \delta)^2 + \gamma_{ab}^2} \right) \right] e^{-[(\omega - \omega_0)\ \Delta\omega_0]^2}$$

This is a Gauss profile with a lorentzian hole, the width of which is determined by the homogeneous linewidth parameters γ_{ab}, γ'_{ab}, with $\gamma_{ab} = \frac{1}{2}(\frac{1}{\tau_a} + \frac{1}{\tau_b} + \frac{1}{\tau_t}) + \sigma\bar{v}p$, depending on the lifetimes τ_a, τ_b of the upper and lower state; the transit time τ_t, and the probability of quenching or phase-interrupting collisions. The center frequency is shifted from ω_0 by an amount δ (which depends on the pressure shift of the absorption profile and on frequency-pulling effects resulting from the coupling between laser frequency and absorption losses) 333a).

The important point is that the Lamb-dip widths for most visible and near infrared transitions at low pressures are several orders of magnitude smaller than the doppler widths and are therefore well suited for high resolution spectroscopy. When probing with a tunable monochromatic laser line the absorption profiles of two closely spaced transitions, their saturation structure may be resolved even when the doppler widths overlap totally.

As a first example for the application of this technique, we mention the investigation of Stark splitting in molecules studied with a CO_2 laser by Brewer *et al.*[334]. The authors shifted the vibration-rotation levels of $N^{14}H_2D$ by an external electric field. With increasing field strength the different Stark components $\Delta M = \pm 1$ of the transition $(v_f'' = 0, 4_{04} \rightarrow v' = 1; 5_{14})$ were tuned across the CO_2 laser line at 944.191 cm^{-1}. This absorption spectrum is shown in Fig. 15a for the absorption of a travelling wave outside the resonator. The absorption lines appear differentiated since the Stark field had been modulated. The linewidth corresponds to the normal doppler width (82 Mc/sec).

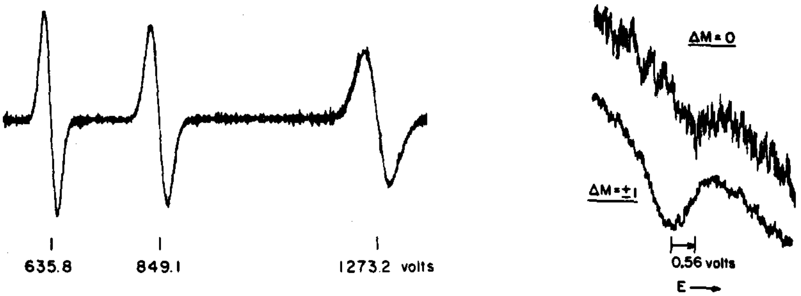

Fig. 15. Lamb dip spectroscopy of $N^{14}H_2D$. Left side: Stark spectrum (with modulated Stark field) for the case of a travelling wave. ($\Delta M = \pm 1$, for deuterium-enriched ammonia, Stark plates 50 cm long at distance of 0.1928 cm). Right side: Stark components $My = \pm 3 \rightarrow \pm 3$ (upper curve) and $My = \pm 3 \rightarrow \pm 4$ (lower curve). (From Brewer, R.G., Kelly, M.J., Javan, A., ref.[334])

When the probe is placed inside the resonator each line exhibits a Lamb dip with a halfwidth of 2.9 Mc/sec, which is mainly limited by inhomogeneities of the electric field (see Fig. 15b).

Comparing two Stark components with a common lower level and slightly different center frequencies ($\Delta\nu = 1.56 \pm 0.05$ Mc/sec), it has been possible to measure the Stark splitting in the excited state and the ratio of the transition probabilities for both transitions. Since the isotopic abundance (and with it the density of $N^{14}H_2D$ molecules) is known, the absolute value of the transition moment can be estimated to $\mu_{12} = 0.33 \pm 0.1$ Debeye.

Line centers of a number of previously unresolved SF_6 transitions in the fundamental ν_3 band have been observed by Rabinowitz *et al.* 335) with this Lamb-dip technique. Measurements of the dip width at small saturation levels yielded a determination of the SF_6-SF_6 cross-sections for phase interrupting collisions.

With a monomode CO_2 laser, delivering a constant power on any rotational line of either the 10.4 μ or the 9.4 μ band, Bordé and Henry 336) studied the shape of Lamb dip profiles in CO_2 which became asymmetric when two rotational lines were allowed to oscillate simultaneously, since the gains are tightly coupled by rotational thermalization.

The hyperfine structure of the R(127) rotational line in the 11-5 band of molecular iodine at $\lambda = 6328$ Å could be resolved 337) by Lamb dip spectroscopy with a halfwidth of 4.5 MHz, and the influence of isotopic substition (I_2^{127} and I_2^{129}) has been studied 338, 338a)k).

These hole-burning effects in intracavity absorbers have attracted increased interest because they are, besides their application to high-resolution spectroscopy, surprisingly useful for extreme frequency stabilization of gas lasers, as will be shown in the next section 339a).

3. Frequency Stabilization by Saturated Absorption

The frequency of a single-mode laser inside the spectral gain profile of its active medium is mainly determined by the eigenfrequency of the active laser cavity mode. Therefore any instability of resonator parameters, such as variation of cavity length, mirror vibrations or thermal drifts of the refractive index will show up as frequency fluctuations and drifts of the laser line.

The idea of stabilizing the laser frequency 37-39) and making it as far as possible independent of cavity parameters, has been realized by many authors in different ways (see for instance the review article by Basov on optical frequency standards 339).

One method which employs the saturable absorption of intracavity gaseous absorbers has turned out to be strikingly successful 333).

As explained in the last section, the absorption profile of a gas interacting with a monochromatic standing wave inside the laser cavity exhibits a sharp minimum at the center of the unsaturated ab-

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k) Meanwhile hfs splittings and quadrupole moments of many atoms and molecules have been measured with lamp-dip spectroscopy, using fixed frequency lasers 338b–c) or tunable dye lasers 338).

sorption line (Lamb dip) due to spectral hole-burning in the velocity distribution of molecules in the lower state. The laser intensity therefore shows a corresponding peak at the same frequency. Its frequency stability is determined by the spectral width of the Lamb dip and by parameters which may affect the energy separations of the upper and lower levels of the absorbing transition (e. g. Stark effects, collisions etc.), but (in first-order approximation) not by cavity parameters.

The idea of using the same medium as absorber and active material has been proposed and realized by several authors [340-343]. Lee and Skolnick [340] used a neon gas discharge at low current and low pressure as saturable absorber inside the cavity of a He-Ne laser oscillating at $\lambda = 6328$ Å. The Lamb-dip halfwidth obtained was 30 Mc/sec compared to 1500 Mc/sec for the doppler line. The disadvantage of this arrangement is that the frequency of the neon transitions depends upon pressure and current [341] in the absorption cell, and this limits the stability and reproducibility of the Lamb dip center frequency.

These frequency-shifting influences are largely excluded in an experiment performed by Barger and Hall [343] who stabilized the $\lambda = 3.39\,\mu$ line of a He-Ne laser by saturable absorption in methane. The $3.39\,\mu$ laser line coincides with a strong absorption line of CH_4, resulting in an excitation of a definite vibronic level. The lifetime of this upper state is very long ($\tau = 37$ msec), corresponding to a natural linewidth of 150 Hz for this transition. Stark and Zeeman shifts are exceedingly small and, because of the spherical symmetry of the methane molecule, collisional frequency shifts are nearly negligible. From preliminary measurements, the authors reported a Lamb dip halfwidth of 150 Kc/sec, which is mainly caused by the transit time of absorbing CH_4 molecules through the laser beam. By cooling the absorption cell and enlarging the beam diameter, this spectral width can be decreased considerably.

The frequency stability obtained up to now is already better than 1×10^{-12} and therefore exceeds the accuracy of the optical wavelength standard (red krypton line) by more than three orders of magnitude [333b, c] [1].

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[1] See also the review by J. L. Hall in: Proceedings of the Third International Conference on Atomic Physics 1972, pp. 615–646. New York: Plenum Press 1973.

4. Investigation of Collision Processes from Line Shape Measurements

Lamb dip spectroscopy provides a very sensitive tool for studying small frequency shifts and broadening of spectral lines which normally would be undetectable because they may be small compared to the doppler width. These investigations yield information about collisions at low pressures, where the effect of far distant collisions is not suppressed by the more effective close collisions. This allows the potential between the collision partners at large intermolecular distances to be examined.

Collision widths considerably smaller than the doppler width have been observed by Szöke and Javan [344] when studying the effects of collisions on the saturation behaviour of the 1.15 μ Ne transition. The measurements showed that, in addition to pressure dependent broadening due to hard collisions, there exists an appreciable broadening due to soft collisions, and that the collisions cause an asymmetry in the average frequency response of individual atoms.

Hall and Barger [343, 40] employed a special "frequency offset locking technique" which allows the stability of an optimized laser to be transferred to another laser, operated under more general conditions. They locked a methane stabilized laser (see Section IV.3), used as the reference frêquency standard, to a second laser without a methane cell, and they could tune the frequency of this second laser against the reference frequency without suffering stability losses. The frequency of a third laser with a methane cell inside its cavity is now locked to that of laser no. 2. When the methane pressure is varied and noble gases added, the Lamb dip profile in laser no. 3 will change and its center frequency will be shifted as against the reference frequency. This can be measured as a function of pressure and for different collision partners with an accuracy of about 100 Hz!

The line broadening for CH_4-CH_4 collisions, for instance, has been measured at (8.1 ± 0.4) KHz/millitorr, whereas the line shift was surprisingly small (75 ± 150 Hz/millitorr).

Toschek and coworkers [345] used a technique called "tuned laser differential spectrometry" which is based on simultaneous interaction of gas atoms with two different laser beams, one of these being a weak "probe" beam the tuning of which scans the saturation on the common level of the two transitions induced by the other beam [346]. The experiment employed the two He-Ne laser lines at $\lambda = 1.15\,\mu$ and $\lambda = 0.6328\,\mu$ which share the common lower $^2P_4$ level.

Atoms that have undergone a transition due to the linearly polarized red laser light field are partially aligned. By varying the mutual polarization direction of "pump beam" and "probe beam", the effect of depolarizing collisions on the saturation profiles could be investigated. An evaluation of the experimental data provides information about the contributions of phase-disturbing and non-phase-disturbing collisions to the line broadening 346a).

A theoretical treatment of the effect of collisions on the spectral characteristics of gas lasers has been given by Rautian 347).

V. Spectroscopy of Laser Media

The last two chapters discussed spectroscopic studies which used coincidences between laser lines and transitions in other atoms or molecules. These investigations have been performed either with lasers as external light sources, or inside the laser cavity. In the latter case coupling phenomena occur between the absorbing species and the laser emission, one example of which is the saturation effect employed in Lamb dip spectroscopy and laser frequency stabilization. This chapter will deal with spectroscopic investigations of the laser medium itself and some perceptions one may obtain from it.

1. Infrared and Submillimeter Wave Spectroscopy [m)]

Soon after the first successful experimental verification of an optical maser 348) the search for possible new laser media began and, especially in the infrared region, numerous stimulated transitions were discovered; many of them had not even been observed previously in spontaneous emission 349).

Because of the essentially higher intensity of most laser lines compared to spontaneous infrared sources, intensity and wavelength measurements could be performed with good signal-to-noise ratio and therefore with higher precision than before, even in spectral ranges where no sensitive detectors are abailable. The small beam diameter, moreover, allows small detector areas to be used, thus restricting the solid angle seen by the detector. This again reduces the background radiation which normally represents the sensitivity-limiting noise in the detection of low-level signals in the medium and far-infrared, and it has the additional advantage for the experimenter that small-aperture (i. e. less expensive) monochromators can be used.

[m)] For more detailed information see the book by G. W. Chantry: Submillimeter spectroscopy. New York: Academic Press, 1971, and the review article by K. J. Button in: Laser Focus 7, 29. August 1971.

Since the doppler width in the far-infrared region is very small but the wavelength relatively large, the laser cavity length L has to be adjusted to $L = m \cdot \frac{\lambda_{max}}{2}$, where λ_{max} is the fluorescence wavelength at the peak of the gain curve. By varying the cavity length continuously, resonances in the laser intensity can be observed every half wavelength. In this way the laser resonator acts as a tunable, long-distance Fabry-Perrot interferometer which allows high-resolution wavelength measurements and which only in some cases needs a low-dispersion preselector to exclude other possible lines.

Many of these infrared laser lines originate from transitions between highly excited states of neutral noble gases, for instance, the neon laser line at $\lambda = 133\ \mu$, which could be assigned to a $10p \rightarrow 9d$-transition [350], or the $4^1P - 4^1D$ He laser line at $\lambda = 216.3\ \mu$[350a]. The precise wavelength determination of these transitions yields excellent experimental proof of approximate calculations for the term energies of highly excited atomic levels, whereas measurements of relative intensities of lines inside the same configuration give information about the relative transition probabilities, which often makes it possible to decide which coupling scheme (e. g. L-S coupling or Racah coupling [351]) is predominant [352].

Most of the infrared laser lines originating from transitions between vibrational-rotational levels in different electronic states of diatomic molecules, e. g. N_2, O_2, H_2, D_2, CO, CN, etc., have been meanwhile correctly indentified [353]. Some lines and term systems have been found [354] which had never been observed before [354a].

It is more difficult to assign lines in laser systems which use polyatomic molecules in pulsed gas discharges [355] since here it is not always easy to decide whether the observed lines belong to transitions of the parent molecule or of dissociation products.

Several investigations concerned with the identification of these lines succeeded, for instance, in the case of H_2O, in elucidating the rotational spectrum in excited vibrational states [356]. Through comparison of wavelengths and intensities of many lines in H_2O^{16}, H_2O^{18} and D_2O^{16} isotopic effects could be studied in these excited vibrational levels [357, 358]. Perturbations of rotational levels by Coriolis resonance which mixes different levels could be cleared up through the assignment and wavelength measurement of some DCN and HCN laser lines [359].

Bridges and Chang [360] obtained very accurate rotational constants of CO_2 from measurements of beat frequencies between CO_2 vibrational-rotational laser lines. They mixed the frequencies from 37 pairs of cw laser lines, each stabilized to line center, in a bulk

Ga-As mixer at room temperature. These beat frequencies, which are in the millimeterwave region of 50–80 GHz, could be measured with an accuracy of better than 1 MHz. The rotational constants deduced for the vibrational levels 00°1, 10°0 and 02°0 are 25 to 200 times more accurate than the previous best results.

2. Excitation Mechanisms and Collision Processes in Gas Discharges

Numerous investigations of the different excitation mechanisms in gas lasers which lead to population inversion and induced oscillation have considerably increased our knowledge about collision processes in gas discharges. There are, for instance, electron-atom collisions, the main excitation process in pure neutral noble gas lasers 361); electron-ion impact, responsible for inversion in ion lasers 362); collisions between excited atoms and ground-state atoms (collisions of the second kind), active in the He-Ne laser 363); vibrational energy transfer in molecular collisions, the main excitation source in CO_2 lasers 364); Penning ionization 365), (where metastable atoms ionize collision partners with ionization potentials lower than the metastable excitation energy); probably one of the pumping processes in He-Cd Lasers 12); rotational energy transfers which thermalize rotational levels in CO_2 lasers 366); and many other collision processes 367). These can be studied when measuring gain, saturation behaviour 368), pressure and discharge current dependence of laser emission and corresponding spontaneous transitions, as will be explained for some examples.

The induced emission on a transition between two levels, *a* and *b*, decrease the population of level *a* by an amount ΔN and increases the number of atoms in level *b* by the same amount ΔN. Periodic interruption of the laser emission (e. g. by a mechanical chopper inside the cavity), enables this change of level population to be detected as a corresponding intensity modulation of spontaneous light originating from levels *a* or *b*. Through observation of fluorescence lines starting from levels adjacent to *a* or *b*, it is possible to study, how the population changes in *a* or *b* affect the population in other levels via collisions or radiative processes (see Fig. 16). By measuring the pressure and current dependence of this modulated fluorescence spectrum, cross-sections for collisional energy transfer between definite excited states can be obtained.

Such measurements have been performed by Parks and Javan 369) for the 2*s* niveaus of neon using the 1.15 μ He-Ne laser line. Besides

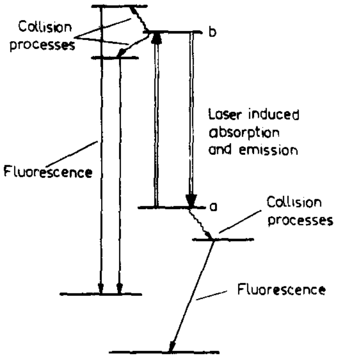

Fig. 16. Spectroscopic investigation of inelastic collisions in a gas discharge: scheme of appropriate levels and corresponding transitions. The level *b* corresponds in case of Ne to the $3s_2$ level (Paschen Notation) which is partly depopulated by the laser transitions at λ = 3.39 μm and λ = 0.6328 μm

collision cross-sections for energy transfer between the different sublevels of the 2*s* group in Ne-Ne collisions, the experiments also yielded the ratio of the spontaneous transition probabilities.

With a similar experimental arrangement, Khaikin[370)] determined cross-sections for electron excitation and atom-atom collisions. Lilly and Holmes[371)] used this method to measure the relative transition probabilities of 12 visible neon lines originating from the 2*s* and 3*s* niveaus and normalized these probabilities by determing the absolute value for one line.

The advantage of this method is that the population change of definite levels is selective and controllable which allows the separate collision processes to be determined in spite of the fact that many other perturbing processes occur simultaneously in the gas discharge.

Detailed information about collision-induced, vibrational, or rotational excitation and deactivation has been collected from much work on molecular lasers, expecially the CO_2 laser[372)]. If the intensity of a laser line is sufficiently high, its gain in an amplifying medium saturates and is then determined by the number of molecules excited per second into the upper laser level and by the depopulation rate of the lower level. Measuring the saturation behaviour under different pressures and discharge currents allows the excitation and deactivating processes to be studied[373, 374)]. Observation of the fluorescence spectra[375)] during laser action gives information about the populations of the different states responsible for energy transfer in lasers with mixed gases.

Karlov *et al.*[376] investigated inversion kinetics in a pulsed CO_2 laser, which was *Q*-switched with a rotating mirror, by shifting the time delay between excitation and *Q*-switch pulses and measuring the laser intensity as a function of delay time and discharge conditions[377]. Similar experiments were performed by Lee *et al.*[378].

The effects of N_2 and He on the rotational relaxation rate in the CO_2 00°1 upper laser level have been measured by Abrams and Cheo[379], who used the output of a *Q*-switched CO_2 laser (1 Kw peak power, 20 nsec) to selectively deplete the population of one rotational level in a flowing CO_2, CO_2 + He and CO_2 + N_2 laser amplifier. The relaxation from neighbouring rotational levels into this depleted state showed up as a recovery of the amplifier gain at the corresponding line which was detected as a function of time with a third cw single-frequency CO_2 laser.

3. Solid-State and Semiconductor Lasers

Most of the solid-state lasers employ as active material crystals or glasses doped with rare-earth or actinide ions, because these ions exhibit a large number of relatively sharp fluorescent lines, covering the whole visible and near-infrared spectrum[2a, b, 380]. The search for new laser materials and investigations of the characteristics of laser emission at different temperatures of the active material and with various pump sources have improved knowledge about the solid state spectra and radiationless transitions in laser media[381].

The spectroscopy of glass lasers[16] has attracted increasing interest because of the large power capability of these devices, which employ activator ions in an *isotropic* host material (in contrast to crystals, the majority of which are nonuniform or birefringent). These glasses can be doped at very high concentrations with excellent uniformity, allowing undisturbed laser beam propagation. Especially important are yttrium - Aluminium - Garnet-crystals, doped with Nd^{3} ± ions. Recently YAG: Nd^{3} laser emission on a cw basis with a linewidth of less than 10^{-9} Å has been claimed to be achieved[382] thus showing that this optical homogenity can also be maintained under continuous pumping conditions. There are not many investigations at the present time on the behavior of ions in glasses, particularly not rare-earth ions. It will therefore be of great interest to study the output characteristics of Nd-glass lasers and their dependence on the host material. By varying the refractive index of the host glass, the laser wavelength can be shifted, and for neodymium the peak of laser emission can be set at any one of a number of wavelength between 1.047 and 1.065 μm 383).

The efficiency of solid-state lasers (that is the ratio of laser output power to pump power) can often be increased by energy transfer from other excited ions with which the crystal was doped additionally 384). In this way energy transfer processes can be studied 385).

Spectroscopic investigations of cross relaxation effects between excited Nd^{3+} ions in glass have been performed by Michon 386) through observation of the time-dependent fluorescence spectrum emitted from a flashlamp-excited neodymium laser under giant pulse conditions. This fluorescence is inhomogeneously broadened (270 Å halfwidth at 300° K) due to a superposition of light from different ions in different environments. The laserline, however, shows a halfwidth of only 20 Å, and the question arises as to whether ions with fluorescence wavelengths outside the laser-emission range may contribute to stimulated emission. Measuring the fluorescence intensity at different wavelengths before and a few nanoseconds after the giant pulse, Michon found that ions within a spectral range of a few hundred angstroms replace the population "eaten away" at the laser frequency in a time of less than 10^{-8} secs, due to cross relaxation.

Similar results were obtained by De Shazer 387), using a different detection technique, where laser oscillations in the sample were forced to develop from the narrow-band radiation, injected from a second small aperture laser into the sample laser cavity. The interionic transfer allowed the feeding of this narrow-band radiation by ions having frequencies outside this interval. The effeciency of energy extraction within the narrow bandwidth and the degree of depolarization of the laser oscillations parametrize the cross relaxation effects.

Since the development of the first gallium arsenide laser 388) the investigation of electroluminescence in semiconductors and the design of optoelectronic devices has made rapid progress. Much of the increased knowledge of luminescence and injection processes acquired during research on diodes for laser developments helped to bring us to the present state of the art. Studies of time behavior of laser output in semiconductor lasers and efforts to increase luminescent efficiency have led to better understanding of radiative recombination and the various competing radiationless processes and their dependence on temperature 389).

Uniaxial stress lowers the threshold current of a Ga-As junction laser and shifts the emission peak to shorter wavelengths 390). This effect can be used to study the influence of crystal asymmetry of the spatial and spectral distributions of emitted photons.

The different pumping methods, such as the commonly used current injection 14), or optical pumping 391), electron beam pumping 392) and avalanche breakdown 393), have been studied in detail (for further refs. see 394) and information has been obtained regarding the excitation probabilities of the different interband transitions. The very short laser pulses (less than 10^{-9} sec) obtained enable rapid processes and their time dependence to be studied.

4. Chemical Lasers

The idea of using the energy released in exothermic chemical reactions for pumping "chemical lasers" and thus producing nonthermal, inverted population in some energy levels of chemical reaction products, has intrigued a number of investigators for several years 396). Such lasers would directly convert chemical energy into electromagnetic radiation and early estimates already show that the conversion efficiency may be higher than in most other laser systems.

The observation of the induced emission, its time behavior and threshold conditions allow to study with new techniques details of chemical reactions which lead to specific states of the molecular or atomic reaction product 397). A quantitative study of such laser systems will also yield information about collisional deactivation rates of the excited states (see also Section III.4).

The first chemical lasers were based on the production of atoms or molecules in excited states by photodissociation of molecules. During flash photolysis of CH_3I and CF_3I Kasper *et al.* 184) observed stimulated emission due to the $^2P_{1/2} \rightarrow {}^2P_{3/2}$ transition of atomic iodine. In a similar way vibrationally excited NO can be formed during flash photolysis of NO Cl 398), resulting in a population inversion between vibrational levels of NO and laser oscillation from 5.95 to 6.30 μm on different vibrational-rotational transitions. These photodissociation lasers do not employ chemical reactions caused by collisions between chemical reactants but rather direct photochemical processes. The first laser based upon excitation by a collision-induced chemical reaction was the HCl laser developed by Kasper and Pimentel 399). It is pumped through the exothermic reaction $H + Cl_2 \rightarrow HCl^* + Cl$, yielding HCl in its vibrational level $v'' = 1$.

A flashlamp is still needed to produce atomic chlorine by photodissociation, which then reacts with H_2 to form atomic hydrogen:

$$Cl_2 + h\nu \rightarrow 2\,Cl$$

$$Cl + H_2 \rightarrow HCl + H$$

The laser emission had a peak power of 10 watts, was centered in a 150 cm^{-1} wide spectral region around 2650 cm^{-1} and could be assigned to various rotational lines of the vibrational transition $v'' = 1 \rightarrow 0$ in HCl. From the gain and intensity ratios of the different laser lines, it was possible to deduce the vibrational and rotational temperatures during the chemical reaction.

Several other chemical lasers with similar excitation schemes soon followed: vibrationally excited CO was formed during flash photolysis of a CS_2-O_2 mixture at 1 torr with 150 torr He buffer gas 400). Investigations of the line spectrum (270 new laser lines have been found 401)), gain and power output of induced emission under various helium pressures and with the addition of CO, established that CO was being selectively excited by different mechanisms into different vibrational levels. The experimental results enabled a few reaction schemes to be selected out of several other possibilities, which could be excluded.

By energy transfer from electronically excited SO_2, the 13th vibrational level of CO can be selectively populated.

(a) $CS_2 + h\nu \rightarrow CS + S$

(b) $S + O_2 \rightarrow SO_2 + 124$ Kcal/mol

(c) $S + O_2 \rightarrow SO + O$

(d) $SO + O \rightarrow SO_2 + 123$ Kcal/mol

$SO_2^* + CO \rightarrow CO^* + SO_2$

During reactions (b) and (d) SO_2 can be formed in the excited $A(^1B_1)$ state, as indicated by a peak at $\lambda = 3640$ Å in the fluorescence spectrum, observed during the reaction 401). Lower vibrational levels ($v'' = 10, 11$) of CO are excited by the reaction

(e) $O + CS_2 \rightarrow CO^* + S_2 + 70$ Kcal/mol whereas still lower levels, for which population inversion could also be obtained, are populated by the following scheme 400):

$$\text{(f)}\quad O + CS_2 \rightarrow COS + S$$

$$COS + O \rightarrow CO^* + SO$$

Lasing from chemically formed CO* in a fast flow has been observed 402) when atomic oxygen (produced in an O_2-He discharge) was mixed with CS_2. Power levels of about 0.1 watt were obtained from an interaction region of 1 cm i. d. x 30 cm long. The maximum of the laser intensity occurs in transitions between $v'' = 10 \rightarrow 9$ of the vibrationally excited CO. This is in good agreement with a mechanism for the chemical reaction producing CO*.

$$\text{(g)}\quad O + CS_2 \rightarrow CS + SO + 32\ \text{Kcal/mol}$$

$$O + CS \rightarrow CO^* + S + 75\ \text{Kcal/mol}$$

Reactions (e) and (g) therefore seem to be responsible for the population of the $v'' = 10$ level of CO.

A detailed experimental and theoretical analysis of pulsed chemical lasers based on the reaction

$$Cl + HBr \rightarrow HCl^* + Br + 15.5\ \text{Kcal/mol}$$

has been given by Airey 403). These lasers are some of the most powerful and efficient pulsed chemical lasers produced to date. Output pulses of 12 Kw/cm^2 with pulse durations between 10–25 μsec have been obtained. Since the ground state of HCl is the lower laser level, the laserpulse is self terminating: the gain for laser oscillation drops to zero as soon as the ground state has been sufficiently populated by stimulated transitions and collisional relaxation.

A chemically pumped CO_2 laser oscillating at 10 μ was reported by Gross 404). In this system vibrationally excited CO_2 molecules are produced by inelastic collisions with vibrationally excited DF which was formed by ultraviolet photolysis of a F_2O-D_2 mixture with a Xe flashlamp, producing free fluorine atoms which could react with D_2

$$F + D_2 \rightarrow DF^* + D.$$

In the absence of CO_2, pulsed laser emission near 4 μ from excited DF* was observed. Similar results have been obtained with F_2O-H_2 mixtures, resulting in laser emission due to vibrationally excited HF* [405].

All chemical laser systems discussed so far were operated in a pulsed mode and they need either flashlamp excitation or a gas discharge to initiate the chemical reaction by producing free radicals. Recently these limitations have been overcome and pure chemical lasers with continuous-wave operation have been developed.

The first investigations about the possibility of obtaining continously vibrational population inversion in reaction products from the reactions

$$H + Cl_2 \rightarrow HCl^* + Cl \quad \text{or}$$

$$H + Br_2 \rightarrow HBr^* + Br$$

have been performed by Polyany and his group [406], who achieved quasi-cw stimulated emission in these systems and measured gains of up to 5 % per meter. Chemical lasers in a quasi-cw operation with higher gain used supersonic mixing of the reactant species $F + HCl \rightarrow HF^* + Cl$ in a shock tunnel [407].

Really continuous laser operation has been achieved by Cool *et al.* [408, 409]. These cw lasers use either different mixtures of CO_2 with DF, HF or HCl, or mixtures of HCl with partly dissociated F_2.

The pumping mechanism for these chemical lasers is near resonant vibrational-rotational energy transfer between excited DF or HCl molecules and ground state CO_2 molecules [n] and a two-step energy transfer in the case of the HF-CO_2 laser [408]. The flow system employed a Pyrex tube with NaCl Brewster windows. In the first experiments [408] a primary flow consisting of helium, mixed with partly dissociated chlorine, fluorine or hydrogen, was introduced into the upstream end of the main flow tube. Initial partial dissociation was achieved with a rf discharge. A secondary flow system, containing CO_2 mixed with one of the molecules Cl_2, HI, DI, F_2, H_2 or D_2, was injected at several points into the primary flow. The excitation of the lasing species followed the reaction:

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[n] Reviews of these chemical transfer lasers have been given by Cool [408a] (cw lasers) and Poehler *et al.* [408b] (pulsed high-pressure lasers).

$$\mathrm{Cl + HI \rightarrow (HCl)^* + I}$$

$$\mathrm{HCl^* + CO_2 \rightarrow HCl + (CO_2)^*}$$

with analogous schemes for the other species, where HI had been formed by H_2 + I → HI + H, and I was dissociated in the radiofrequency discharge.

In later experiments with improved techniques[409)] the initial partial dissociation of F_2, Cl_2 etc. by the *rf* discharge could be replaced by addition of NO to the F_2 flow, thus providing atomic fluorine by the reaction

$$\mathrm{F_2 + NO \rightarrow NOF + F.}$$

This experiment demonstrated the possibility of a purely chemical laser. The new system exhibited large gain and considerable output power. About 500 watts continuous power at 10 μm have been achieved with the DF-CO_2 system and about 1 Watt for the HF-CO_2 laser[409a)].

Spencer *et al.*[410)]obtained 475 watt at 3 μm in a cw HF laser based upton the reaction:

$$\mathrm{H_2 + F \rightarrow (HF)^* + H + 31.7\ Kcal/mol.}$$

The unsaturated gain was 8 %/cm, and 12 % of the chemical energy involved in the above reaction could be converted to laser radiation. The atomic fluorine is produced by thermal dissociation of SF_6 at about 2500 °K.

In high-pressure pulsed CO_2 chemical-transfer lasers, peak output powers of 200 KW with 30 μsec pulse duration have been achieved[408b)].

A very interesting device regarding high output power is the photochemical iodine laser[411)] where excited iodine atoms are formed by photodissociation of CH_3I. Pulses with 5 MW peak power and 5 nsec duration have been produced which could be further amplified in two stages up to 10^9 W. Energies of 1 K Joule seem to be attainable[412)].

The importance of chemical laser studies for basic research aimed at more detailed understanding of chemical reactions results from the possible selective population of definite energy levels of the reacting molecules.

Investigations of vibrational energy transfer and its dependece on temperature, rotational state distribution, energy defect and other parameters, therefore, have been one of the main research subjects[413)–415)].

In some cases the measured *V-V* transfer rates differ from theoretical predictions, which indicates that some improvement is needed in theoretical models. Sophisticated computer analysis has to be employed to transform the experimental data to theoretical parameters 416). The spectroscopic studies of cw and pulsed chemical lasers including the local variation of laser output on different vibration-rotation transitions as a function of distance from the injectory array has been a useful tool, too, for elucidating the different reaction paths and the excited molecular levels involved 417).

Measurements of the relative intensities of different rotational lines in a vibrational transition can give information about the rotational temperature, the efficiency of collision-induced *R-R* transitions and the *J*-dependence of the chemical reaction on angular momentum *J*.

For a more detailed discussion and a comprehensive literature survey of recent research in this field, the reader is referred to a collection of papers from the Third Conference on Chemical and Molecular Lasers which appeared in IEEE J. Quant. Electr. QE9, January 1973, and to a literature review by Arnold and Rojeska 418).

VI. Conclusion

In this reciew the attempt is made to exhibit some of the possibilities of laser applications in modern spectroscopy. The rapid development of new laser types and the improvement of the existing models lend lasers steadily increasing importance as spectroscopic light sources, and it seems that the "laser revolution" is only just beginning. These laser developments lead in different directions:

The efforts to obtain increasing output powers in pulsed and continuous operation, stimulated mainly by military needs but eminently useful for basic spectroscopic research, e. g. in nonlinear optics or in plasma physics, has already resulted in pulsed output powers of 10^{13} watts (neodymium laser) and continuous powers of 30 Kw (CO_2 lasers).

The increased frequency stability of single-mode lasers offers new possibilities in high-resolution spectroscopy, and new techniques for measuring frequencies up to 10^{14} Hz have enabled absolute frequency determinations of infrared laser lines. This opens the way for much more accurate measurements of the speed of light, the basic parameter involved in most spectroscopic quantities.

The development and technical perfection of widely tunable, monochromatic devices, such as dye lasers and optical parametric oscillators, now already at the stage of industrial manufacture, will certainly facilitate and improve many spectroscopic investigations, replacing in some experiments both light source and monochromator.

The reduction of obtainable light-pulse durations down to subpicosecond pulses (halfwidth about 10^{-13} sec) allows fast transient phenomena which were not accessible before to be studied in the interaction of light with matter. One example is the extension of spin echoe-techniques, well known in nuclear-magnetic-resonance spectroscopy, to the photon echoes in the optical region.

A further aspect of laser applications is connected with holography, an important part of modern optics, increasingly used in spectroscopic investigations, too.

The selection of spectroscopic experiments with lasers presented in this review may give an incomplete survey of the state of the art today, but the author would be satisfied if this article conveys to the reader some of the delight he has experienced during his work in this field.

VII. Zusammenfassung

Nach einer kurzen Übersicht im einleitenden Abschnitt über den Aufbau des Artikels und den Zusammenhang der einzelnen Kapitel werden im Abschnitt II die Eigenschaften der Laser behandelt, die für den Spektroskopiker von Bedeutung sind.

Es zeigt sich, daß die meisten *Lasertypen* den konventionellen Lichtquellen überlegen sind hinsichtlich ihrer Ausgangsleistung pro Wellenlängenintervall und Raumwinkeleinheit. Die Vorteile der beim Laser möglichen guten Bündelung der Ausgangsleistung in einen praktisch parallelen Strahl werden für verschiedene spektroskopische Anwendungen diskutiert. Spektrale Linienbreiten, die weit unterhalb der Fluoreszenzbreiten von üblichen Spektrallampen liegen, lassen sich bei Lasern nur unter gewissen Betriebsbedingungen (Oszillation auf nur einer Resonatorfrequenz) realisieren. Mit verschiedenen Methoden können solche fast monochromatischen Linien innerhalb bestimmter Grenzen kontinuierlich in ihrer Wellenlänge verschoben werden, wobei man den größten Abstimmungsbereich mit Farbstoff-Lasern und optischen parametrischen Oszillatoren erreicht. Mit verschiedenen Lasertypen können intensive Lichtpulse mit Pulsdauern bis hinunter zu 10^{-13} sec erzeugt werden, die für die Untersuchung extrem schnell ablaufenden Prozesse von großer Bedeutung sind.

Im dritten Kapitel werden *spektroskopische Untersuchungen* mit Lasern als Lichtquelle beschrieben. Ausführlicher behandelt sind dabei absorptionsspektroskopische Messungen hoher Auflösung, laser-induzierte Fluoreszenz-Spektroskopie und spektroskopische Nachweismethoden für elastische und verschiedene unelastische Stoßprozesse.

Photochemie mit Lasern und neue Wege in der ultraschnellen Flashphotolyse mit Riesenimpulslasern werden diskutiert. Neuere Untersuchungen in linearer und nicht linearer Ramanspektroskopie sind an einigen Beispielen kurz erläutert und die Bedeutung des Lasers für Lichtstreuungs-Messungen (Raman-, Raleigh-, Brillouin- und Thompson-Streuung) wird hervorgehoben.

Zur Diagnostik und zur Erzeugung von *Plasmen* werden Laser in steigendem Maße eingesetzt. Deshalb beschreibt ein Abschnitt interferometrische Methoden zur Messung von Elektronendichten und Temperaturen und Plasma-Untersuchungen aus der Spektralverteilung von gestreutem Laserlicht. Lasererzeugte Plamen werden in der Mikro- und Makro-Spektralphotometrie zur chemischen Analyse kleinster Substanzmengen und für einen schnellen Nachweis der chemischen Zusammensetzung und ihrer lokalen Schwankung innerhalb einer Probe erfolgreich verwendet.

Neue Impulse hat die *Festkörper-Optik* durch die experimentelle Verifizierung optischer Nichtlinearitäten bei der Wechselwirkung intensiver Lichtwellen mit Materie erhalten. Der letzte Abschnitt des 3. Kapitels referiert einige Messungen nichtlinearer Größen, wie der Suszeptibilität, und deren Zusammenhang mit den Bindungskräften im Kristall.

Kapitel IV behandelt einen neuen Zweig der *hochauflösenden Spektroskopie,* der auf Sättigungserscheinungen bei der Wechselwirkung von Licht mit Atomen oder Molekülen beruht. Durch selektive Absorption von monochromatischem Laserlicht wird die thermische Gleichgewichtsverteilung in bestimmten Molekülzuständen gestört. Dies führt zu einer Struktur im inhomogenen Linienprofil des entsprechenden Überganges, deren Linienbreite um Größenordnungen unter den üblichen Absorptionsbreiten (oder Fluoreszenzbreiten in Emission) liegt. Verschiedene Methoden, die diesen Sättigungseffekt ausnutzen, wie optisches Pumpen von Molekülen, Lamb-dip-Spektroskopie und extrem gute Frequenzstabilisierung von Laserübergängen werden diskutiert.

Im letzen Kapitel werden *neue Methoden* der Spektroskopie erläutert, die Untersuchungen am Lasermedium selber betreffen, und die sich die Vorteile der induzierten Emission zunutze machen, um Atom- und Molekül-Linien mit hoher Präzision zu messen, Anregungsmechanismen und Stoßprozesse in Gasentladungen oder Energieaustausch zwischen angeregten Ionen in dotierten Festkörpern zu untersuchen.

Abschließend wird kurz auf die interessante Entwicklung *chemischer Laser* eingegangen, bei denen Bindungsenergie in exothermen chemischen Reaktionen direkt in elektromagnetische Strahlung umgewandelt werden kann. Diese chemischen Laser erlauben neue Nachweismethoden für detaillierte Untersuchungen chemischer Reaktionen, was an einigen Beispielen gezeigt wird.

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