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# Chemical Reviews

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## Lasers and Chemistry

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### Contents

I. Introduction	437
A. Fundamentals of Laser Operation	438
B. Survey of Laser Types	439
C. Properties of Laser Radiation and Nonlinear Effects	441
II. Laser Spectroscopy	442
A. Ultrahigh Resolution Spectroscopy	442
B. Nonlinear Spectroscopy	442
C. Multiphoton Spectroscopy	443
D. Raman Spectroscopy	444
E. Miscellaneous Spectroscopic Applications	445
1. Remote Sensing of Atmospheric Pollutants	445
2. Applications in Analytical Chemistry. Intracavity Studies	446
III. Laser Photophysics	446
A. Fluorescence, Phosphorescence, and Radiationless Transitions	447
B. Excited-State Absorption Spectroscopy. Photoquenching	450
C. Ultrafast Processes	451
IV. Laser Photochemistry	452
A. Flash Photolysis and Transient Photochemistry	452
B. Laser-Induced Chemical Reactions	454
C. Isotope Enrichment	455
D. Nonlinear Photochemistry	461
V. Chemical Control of Laser Action	461
A. Chemical Lasers	461
B. Dye Lasers	463
VI. Appendix. List of Abbreviations	464
VII. References	464

### I. Introduction

Why another review on lasers? In the past few years dozens of reviews have appeared, some of them grouped in book form,<sup>1,2</sup> on specialized applications of lasers in chemistry. Still, we are of the opinion that a survey of the type we are presenting herewith is in order. Briefly, the purpose of this review is threefold:

Firstly, to assist chemists, who plan on utilizing lasers for their research, to orient themselves in the bewildering array of information contained in many hundreds of articles, often written by physicists or engineers for a highly specialized readership.

Secondly, to show to the fast-growing group of chemists who, one way or the other, are "laser consumers", what has been achieved in related chemical disciplines. In this connection, it is gratifying to note the wide-ranging impact chemistry has made on the development of lasers and laser-based techniques.

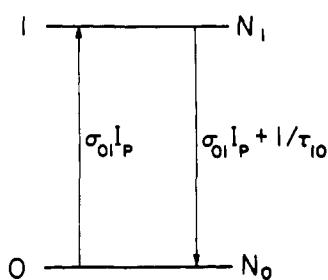
Thirdly, we address ourselves to laser scientists who are not chemists but who, sometimes reluctantly, are led into practicing chemistry, e.g., for chemical lasers, dye lasers, and isotope enrichment. We hope they too will benefit from this exposé, thus furthering the fruitful interdisciplinary effort that has brought the laser field to prominence.

At this point it is, perhaps, appropriate to quote Edward Teller's comment: "Lasers have been discovered by the wrong people, namely, by physicists. The result is that the chemists have not grabbed it to the extent they should. In actual fact, in every laser process, whether it starts with physics or goes through chemistry, much of it will become pure chemistry. The only people who can make real progress are the chemists".<sup>3</sup>

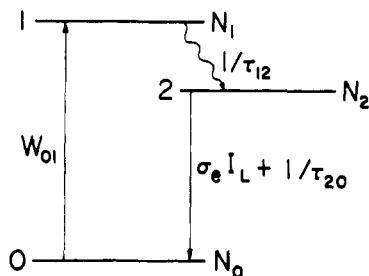
The organization of this review. We discuss in a unified fashion uses of lasers for diverse chemical applications. Along the way we point out some difficulties in interpreting laser-induced phenomena.

The first section treats fundamentals of lasers and summarizes existing laser devices and their properties. It is included here mainly for the sake of completeness and can be skipped by laser practitioners. Sections II, III, and IV demonstrate, respectively, applications of lasers in the areas of spectroscopy, photophysics, and photochemistry. The subject matter reflects to a certain extent the personal interests of the authors. However, we trust that we have presented a balanced view of "Lasers and Chemistry" as it emerges from the current literature (surveyed through 1976). Incidentally, we have been able to mention only a fraction of all the papers on any one subject. An exhaustive list of relevant articles would have numbered many thousands; the complete literature may be gleaned from secondary references cited in the 900-odd references compiled in this review. For convenience, we have organized reported data, as far as possible, in the form of tables which will be of value in their own right.

We have deliberately omitted the following topics as straying beyond the limits set for this review: laser light scattering,<sup>4</sup> photofragment spectroscopy,<sup>5</sup> molecular beam diagnostics,<sup>6</sup> photodetachment,<sup>7</sup> and temperature-jump techniques.<sup>8</sup> Other subjects have been treated rather superficially, partly because of lack of space and partly because reviews and monographs are available. Nonlinear spectroscopy (section II.B), laser Raman



**Figure 1.** Two-level system irradiated by an optical pumping field of intensity  $I_p$ . Shown are rates of absorption  $\sigma_{01}I_p$ , spontaneous emission  $N_1/\tau_{10}$ , and induced emission  $N_1\sigma_{10}I_p$ .



**Figure 2.** Three-level laser medium  $N_i$  is the population density of level  $i$ ,  $\tau_{ij}$  are lifetimes,  $W_{01}$  is the pumping rate,  $\sigma_e$  is the stimulated emission cross section, and  $I_L$  is the laser intensity.

spectroscopy (section II.D), chemical lasers (section V.A), and various energy transfer processes belong to this category.

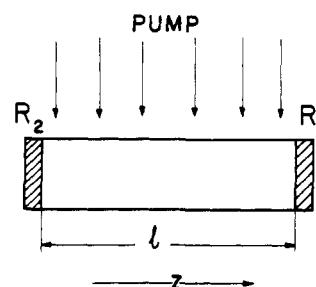
In contrast, we have gone into greater depth regarding the following themes: photophysics (section III), laser-induced chemical reactions (section IV.B), isotope enrichment (section IV.C), and photochemical restrictions imposed on dye laser operation (section V.B). The topics of photoquenching (section III.B) and nonlinear photochemistry (section IV.D) are summarized for the first time.

In the Appendix we have collected the abbreviations used in this review. They are grouped according to category A ("phenomena, devices and techniques") or category B ("materials and compounds"). Finally, we have followed IUPAC recommendations and have used SI units, but occasionally the reader will encounter familiar, though disapproved, units such as the Torr.

## A. Fundamentals of Laser Operation

The purpose of this section is to discuss common features of laser systems. Absorption and emission processes will be discussed, using the consequences of time-dependent perturbation methods,<sup>9-13</sup> in terms of absorption and stimulated emission cross sections and spontaneous emission lifetimes. This enables us to use the formalism of kinetic schemes and rate equations which is familiar to chemists. There are, however, cases where interaction of laser radiation with atoms or molecules cannot be described by this approximation, and more general treatments should be employed.<sup>14</sup>

We start with a discussion of the two-level system depicted in Figure 1. The population density in the ground state is  $N_0$  (particles/cm<sup>3</sup>) and that in the excited state,  $N_1$ . The system is irradiated by a field of intensity  $I_p$  and frequency  $\nu_p = (E_1 - E_0)/h$ , which elevates the species to the upper state. The rate of absorption by species in the ground state is  $\sigma_{01}I_pN_0$ , where  $\sigma_{01}$  denotes the absorption cross section. The rate of emission from the excited state is the sum of a spontaneous emission rate  $N_1/\tau_{10}$ ,  $\tau_{10}$  being the fluorescence lifetime, and of a stimulated emission rate  $N_1\sigma_{10}I_p = N_1\sigma_{01}I_p$ . The population difference  $N_1 - N_0$  is negative except when  $I_p \rightarrow \infty$ , for which  $N_1 \rightarrow N_0$ . Thus in steady-state conditions a radiation field is attenuated after propagating through a two-level medium.



**Figure 3.** Fabry-Perot type laser cavity consisting of two parallel mirrors with reflectivities  $R_1$  and  $R_2$ .

In a laser, a population inversion ( $N_1 > N_0$ ) exists between a pair of levels in a multilevel system, which provides an amplifying medium for an incident resonant radiation field. We first discuss the three-level laser medium shown in Figure 2. Here the total particle density is  $N$ ; a ground-state species is pumped with a rate  $W_{01}$  to the excited level 1 and decays to level 2, usually through a fast radiationless transition at a rate  $N_1/\tau_{12}$ ,  $\tau_{12}$  being the lifetime of state 1. Provided that  $N_2 > N_0$  a radiation field starting from spontaneous emission noise at frequency  $\nu_L = (E_2 - E_0)/h$  can be amplified. If the laser medium is placed inside an optical cavity, oscillations at  $\nu_L$  can be built up in some of the standing waves (modes) that are sustained in the cavity.<sup>9</sup> The rate equations for the population densities corresponding to the three-level kinetic scheme are:

$$dN_0/dt = -W_{01}N_0 + (\sigma_e I_L + 1/\tau_{20})N_2 \quad (1)$$

$$dN_1/dt = W_{01}N_0 - N_1/\tau_{12} \quad (2)$$

$$dN_2/dt = N_1/\tau_{12} - (\sigma_e I_L + 1/\tau_{20})N_2 \quad (3)$$

where  $\sigma_e$  is the stimulated emission cross section at  $\nu_L$  given by

$$\sigma_e = c^2 \phi g(\nu) / 8\pi \nu L^2 \eta^2 \tau_{20} \quad (4)$$

Here  $\phi$  is the quantum yield for fluorescence from level 2 having a fluorescence lifetime  $\tau_{20}$ ,  $g(\nu)$  is the normalized fluorescence lineshape function centered at  $\nu_L$ , and  $\eta$  is the refractive index of the medium.<sup>9</sup> These rate equations are coupled to the rate of change of the laser intensity  $I_L$ , which for a transversely pumped laser system, such as depicted schematically in Figure 3, is<sup>9</sup>

$$dI_L/dt = c[\sigma_e(N_2 - N_0)I_L + N_2/\rho\tau_{20}] / \eta - I_L/t_c \quad (5)$$

where  $t_c$  denotes the photon lifetime in the cavity. For a Fabry-Perot cavity configuration, consisting of two parallel mirrors having reflectivities  $R_1, R_2$ , and separated by a distance  $\ell$ ,  $t_c$  is<sup>9</sup>

$$t_c = 2\eta\ell/c(1 - R_1R_2) \quad (6)$$

The total number of cavity modes  $\rho$  coupled to the fluorescence band and lying within a band width  $\Delta\nu$  is given by

$$\rho = 8\pi^2 \nu_L^2 \Delta\nu V/c^3 \quad (7)$$

$V$  being the volume of the cavity<sup>9</sup> (typically  $\rho \approx 10^{13}$ , but this number can be reduced considerably; cf. section I.C.1).

Different types of three-level lasers can be analyzed by solving the above rate equations under the condition  $N = N_0 + N_1 + N_2$ . The solutions are expressed in terms of the gain coefficient  $G$  defined by Beer's law for amplification (negative absorption),

$$G = (1/I_L) dI_L/dz = (\eta/c I_L) dI_L/dt \quad (8)$$

From the threshold condition,  $G = 0$ , the threshold population ratio  $N_2^{\text{th}}/N$  and the threshold pumping rate  $W_{01}^{\text{th}}$  can be calculated. An analytical solution of the coupled laser rate eq 1, 2, 3, 5, can be obtained only for a steady-state situation. For a laser,

optically pumped with a square-shape pulsed light source of intensity  $I_p$ , such that  $W_{01} = \sigma_{01}I_p$ , the small signal steady-state gain coefficient, for multimode operation near threshold, is given by

$$G = \sigma_e(N_2 - N_0) - \eta/ct_c \\ = N\sigma_e(\tau_{20}\sigma_{01}I_p - 1)/[1 + \sigma_{01}I_p(\tau_{10} + \tau_{21})] - \eta/ct_c \quad (9)$$

where we have used the condition

$$1/\rho\tau_{20} \ll \sigma_e/I_L \ll 1/\tau_{20} \quad (10)$$

Thus we obtain the threshold pump intensity as

$$I_p^{\text{th}} = (1 + a)/\sigma_{01}[a\tau_{20} - (\tau_{21} + \tau_{20})] \quad (11)$$

and the threshold population inversion

$$(N_2 - N_0)^{\text{th}}/N = \eta/Nct_c\sigma_e \equiv 1/a \quad (12)$$

Inspection of eq 11 and 12 shows that optimal results are obtained for laser media for which  $\sigma_{01}$ ,  $\tau_{20}$ , and  $t_c$  are large and  $\tau_{12}$  is small. For typical lasers  $a$  ranges between  $10^2$  and 10.

Analogous kinetic analysis can be performed for a four-level laser such as shown in Figure 4. The results read

$$G = \sigma_e(N_2 - N_3) - 1/t_c \\ = N\sigma_e\sigma_{01}I_p(\tau_{23} - \tau_{30})/[1 + \sigma_{01}I_p(\tau_{21} + \tau_{23} + \tau_{30}) - \eta/ct_c] \quad (13)$$

$$I_p^{\text{th}} = 1/\sigma_{01}[a(\tau_{23} - \tau_{30}) - \tau_{12} + \tau_{23} + \tau_{30}] \quad (14)$$

Invariably, lasing is favorable for a four-level system, compared to a three-level one with similar characteristics, because if the thermal population of the lower laser level  $N_3$  is negligible, it is far easier to achieve population inversion  $N_2 - N_3$  (Figure 4) than  $N_2 - N_0$  (Figure 3).

## B. Survey of Laser Types

To date hundreds of different lasers have been developed, and many have found important applications in chemical research. There are several ways to divide lasers into classes, for example, according to output power, wavelength, or tunability. For the purpose of this review, it is more instructive to divide lasers according to the material properties of the active medium. Each class may contain dozens of lasers having widely different wavelengths and output powers, but all possessing common properties of operation. In this section we shall briefly outline the classes of lasers. For each we mention some of the more prominent members which are available commercially without, however, going into technical details of construction and operation.<sup>15-18</sup> This survey is supplemented in section V, where we discuss some chemical aspects of lasers in more detail.

1. *Solid-state lasers*<sup>16,17</sup> employ ions, doped in a transparent host crystal, as the active medium. Population inversion is attained by optical pumping (see Figure 3), using an intense broad-band flashlamp coupled to the lasing material by an elliptic cylinder-like reflector, inside which the lamp and the laser rod are each positioned along one focal line.<sup>16</sup> The first laser action was discovered in ruby (0.05 wt % Cr<sup>3+</sup> ions in sapphire, crystalline Al<sub>2</sub>O<sub>3</sub>) which constitutes a representative three-level laser (see Figure 2). In spite of the inherent deficiency of operating a three-level laser, which requires that more than 50% of Cr<sup>3+</sup> ions be excited (cf. eq 9-12), the ruby laser is still widely used for chemical applications because of its useful primary wavelength 694.3 nm, or 347.1 nm after frequency doubling (section C), and its high peak power.

The most important four-level solid-state laser (see Figure 4) is based on Nd<sup>3+</sup> ions incorporated as impurities in a variety of host materials such as glass, crystalline CaWO<sub>4</sub>, or YAG (yttrium aluminum garnet, 3Y<sub>2</sub>O<sub>3</sub>:5Al<sub>2</sub>O<sub>3</sub>), each giving rise to somewhat different lasing characteristics. Lasing is obtained at lower ex-

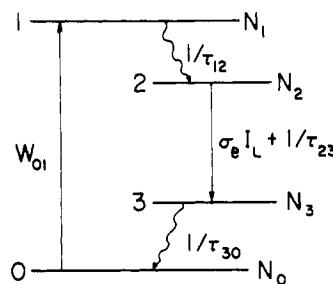


Figure 4. Four-level laser medium. For symbols see Figure 2.

citation thresholds than with ruby (cf. eq 14), and high-repetition pulsed or even quasi-continuous laser output may be achieved with Nd/YAG lasers. Since the primary lasing transition is in the near-infrared region, at 1064 nm, where few compounds possess fundamental absorption bands, this wavelength is often converted for chemical applications, by frequency doubling (to 532 nm), tripling (to 355 nm), or quadrupling (to 266 nm).

2. *Gas lasers*<sup>16,17,19,20</sup> have in common a pumping technique based on the electric discharge present when passing a direct current through a gas or when applying a radio-frequency (rf) electric field to it. Gas lasers are subdivided into atomic lasers, ion lasers, metal vapor lasers, and molecular lasers.

*Atomic lasers* may be exemplified by the He-Ne laser. Some atoms of the gas mixture (1 Torr of He and 0.1 Torr of Ne) are ionized by the discharge, and the free electrons, accelerated by the electric field, excite He to the (un-ionized) metastable levels 2<sup>3</sup>S and 2<sup>1</sup>S. The excited He atoms exchange energy through collisions with ground-state Ne and raise them to the 2S and 3S states, which nearly coincide with the 2<sup>3</sup>S and 2<sup>1</sup>S levels of He. CW laser action is obtained at the Ne transitions 3S → 2p (at 632.8 nm), 2S → 2p (at 1150 nm), or 3S → 3p (at 3390 nm), the particular transition being selected by the choice of coating on the cavity mirrors.

He-Ne lasers, operating at the relatively weak transition of Ne in the red part of the visible spectrum at 632.8 nm, are ubiquitous in chemical laboratories. They provide convenient means for alignment of optical components and instruments. They are also used in scientific and engineering applications such as light scattering,<sup>4</sup> velocimetry, and holography.

For chemical applications, however, *ion lasers* are more effective than the He-Ne laser. In ion lasers transitions occur between highly excited levels of singly ionized atoms; they emit in the blue-green part of the visible spectrum and they can supply high CW power output. Typically, an argon-ion laser delivers about 10 W total power, divided over a small number of spectral lines. With the help of a dispersive prism, output of a few watts may be obtained, at choice, in either of the main lines at 488.0 or at 514.5 nm. Other ion lasers, such as krypton, provide CW laser light in many lines throughout the visible spectral region.

For generating CW ultraviolet laser radiation, one may resort to the helium-cadmium laser with main output at 441.6 and 325.0 nm. Other CW *metal-gas lasers* include helium with Sn, Zn, or Se. Pulsed discharge metal vapor lasers include Cu vapor produced from metal or from copper halides.<sup>21</sup> The most widely applied source for pulsed (~5 ns) radiation in the ultraviolet (at 337.1 nm) is the molecular N<sub>2</sub> gas laser, but some exotic systems pumped by electron beams show promise, notably H<sub>2</sub>, Xe<sub>2</sub>\* excimers, and rare-gas halides (XeF, KrF).<sup>22,23</sup>

*Molecular lasers* are pumped by the same general discharge techniques used for other gas lasers, the only difference being that transitions generally occur between vibrational-rotational levels.<sup>24</sup> The most prominent laser in this class is the carbon dioxide laser. The discharge excites CO<sub>2</sub> molecules to the relatively long-lived [001] vibrational level in the electronic ground state. The integers [n<sub>1</sub>, n<sub>2</sub>, n<sub>3</sub>] denote, respectively, the degree

TABLE I. Some Important Laser Sources<sup>a</sup>

Laser medium	Principal wavelengths <sup>b</sup> (μm)	Predominant mode of operation	Maximum power output (W)	
			Pulsed	CW (multi-mode) or pulsed av
<b>1. Solid-State Lasers</b>				
Ruby	0.694	Pulsed	$10^{10}$	
Nd-glass	1.06	Pulsed	$10^{12}$	
Nd-YAG	1.064	CW	$10^6$	$10^3$
<b>2. Gas Lasers</b>				
He-Ne	0.633	CW		$10^{-2}$
	1.152			$10^{-1}$
	3.391			$10^{-2}$
Ne <sup>+</sup>	0.332	CW		$10^{-1}$
Ar <sup>+</sup>	0.488	CW	$10^2$	10
	0.515			
Kr <sup>+</sup>	0.568	CW		10
	0.647			
Xe <sup>+</sup>	0.526	CW	$10^4$	1
	0.597			
He-Cd	0.325	CW	$10^3$	$10^{-1}$
	0.442			$10^{-1}$
Cu, CuI	0.511	Pulsed	$10^4$	$10^{-1}$
N <sub>2</sub>	0.337	Pulsed	$10^6$	1
H <sub>2</sub>	0.120	Pulsed	$10^4$	
	0.160			$10^5$
Xe <sub>2</sub> *	0.170	Pulsed	$10^6$	
XeF	0.350	Pulsed	$10^9$	
CO <sub>2</sub>	9.6–10.6	Pulsed and CW	$10^{10}$	$10^3$
CO	5.5–5.7	Pulsed	$10^7$	10
H <sub>2</sub> O	7–220	Pulsed	$10^2$	$10^{-1}$
HCN	337	Pulsed	$10^2$	$10^{-1}$
<b>3. Chemical Lasers (see section V.A.2)</b>				
HF	2.8–3.2	Pulsed	$10^8$	$10^3$
HCl	3.6–4.0	Pulsed	$10^3$	
CO	5.0–6.0	Pulsed	$10^4$	
C <sub>3</sub> F <sub>7</sub> I	1.315	Pulsed	$10^{10}$	
<b>4. Semiconductor Lasers</b>				
Ga-As	0.85	Pulsed and CW	$10^2$	$10^{-2}$
In-As-P	2–8			
Pb-Sn-Te	10–35			
<b>5. Dye Lasers</b>				
Coumarins	0.40–0.50	Pulsed and CW	$10^6$	1
Rhodamine-6G	0.56–0.61			

<sup>a</sup> For details on commercial systems see "Laser Focus" Buyers' Guide, 12th ed, January 1977. <sup>b</sup> Complete lists available in "Handbook of Lasers", R. J. Pressley, Ed., CRC Press, Cleveland, Ohio, 1971.

of excitation of the three normal modes of vibration: the symmetric vibrational stretching mode  $\nu_1$ , the bending mode  $\nu_2$ , and the asymmetric stretching mode  $\nu_3$ . Lasing is made more efficient by admixing N<sub>2</sub> and He. A vibrationally excited N<sub>2</sub> molecule (at  $\nu = 2350 \text{ cm}^{-1}$ ) has a long radiative lifetime and, upon collision with a ground-state CO<sub>2</sub> molecule, transfers its energy to the [001] level of CO<sub>2</sub> (at  $\nu_3 = 2349 \text{ cm}^{-1}$ ) with which it is resonant. In this way, population inversion in CO<sub>2</sub> can be established between the level [001] and the level [100] (at  $\nu_1 = 1388 \text{ cm}^{-1}$ ) or the level [020] (at  $2\nu_2, 1285 \text{ cm}^{-1}$ ), thus leading to oscillations in the infrared region around  $961 \text{ cm}^{-1}$  (10.6 μm) or  $1064 \text{ cm}^{-1}$  (9.6 μm), respectively. Collisions with He atoms aid in reverting CO<sub>2</sub> molecules from the lower laser states, [001] or [020], to the ground state [000]. The existence of rotational levels in each vibrational state, together with the standard selection rules for transitions between vibrational sublevels, opens up the possibility of obtaining numerous laser lines. With a diffraction-grating rear-mirror configuration a CO<sub>2</sub> laser can

be tuned discontinuously; that is, it can be made to oscillate at any one of the discrete rotational lines, from P(17) to R(20), which are separated from each other by about  $2 \text{ cm}^{-1}$ . The recent development of high-pressure (~15 atm) CO<sub>2</sub> lasers, in which the individual rotational lines are smeared out by pressure broadening, permits continuous tunability<sup>25</sup> between 930 and  $1100 \text{ cm}^{-1}$ .

The CO<sub>2</sub> laser is the most important molecular laser in use to date. The high CW output power (up to several kW), high intensities (GW/cm<sup>2</sup> in pulses of 100-ns duration), high efficiency (conversion of about 20% of pumping power into radiant power), and the laser wavelengths which fall in a region where many molecules show absorption features, have turned the CO<sub>2</sub> laser into the workhorse of chemists, particularly for the purpose of activating selective reaction pathways (section IV.B).

Vibrotational or pure rotational transitions in other simple molecules such as CO, NO, N<sub>2</sub>O, H<sub>2</sub>O, and HCN, have made available many laser lines in the whole infrared spectral region.<sup>26</sup>

3. *Chemical lasers* differ from other gas lasers in that population inversion is achieved by a chemical reaction, which may be initiated optically, electrically, or thermally. They will be dealt with a more detail in section V.A.

4. *Semiconductor lasers*<sup>27</sup> convert electrical energy directly into coherent radiation. They are different from other lasers in pumping mechanism and operation performance.

Semiconductor lasers are compact ( $\approx 1 \text{ mm}^3$ ), cheap, and highly efficient ( $\approx 30\%$  conversion of electrical energy into optical energy). Some of the major drawbacks, at present, are the need for cooling (often to liquid He temperatures) and the rather low output (typically  $10^{-3} \text{ W}$  in CW operation, or 100-W pulses each of 100-ns duration with kHz repetition rates). Also, they require sophisticated solid-state technology.

The most important application of semiconductor lasers in chemistry is in ultrahigh-resolution spectroscopy (section II.A). The spectral width of a given semiconductor laser is about  $10^6 \text{ Hz}$  ( $\approx 3 \times 10^{-5} \text{ cm}^{-1}$ ) which is two orders of magnitude below the spectral width of the best grating spectrometers.

5. *Liquid lasers* consisting of rare-earth ions in liquid chelates<sup>28</sup> or aprotic solutions<sup>29</sup> have been sparingly used since 1963, the latter mainly as a potential alternative for expensive high-quality Nd-glass rods. However, the discovery in 1966 of the lasing capability of organic dye molecules dissolved in simple solvents such as alcohol or water, and the dramatic development of dye lasers since then, have made the concept of liquid lasers synonymous with dye lasers.<sup>30,31</sup>

Suitable organic dye solutions (section V.B) are pumped with short-duration flashlamps or with other lasers, both of the pulsed type (Q-switched ruby, doubled ruby, doubled Nd, or nitrogen), or of the CW type (tightly focused ion lasers). Lasing action is based on fluorescence in a multilevel scheme consisting of transitions between vibrotational sublevels of two different electronic singlet states.

Coarse tuning of a dye laser in the spectral region between 330 and  $1100 \text{ nm}$  is achieved in practice by employing different dyes, which emit in adjacent parts of the spectrum. The tuning range can be extended into the ultraviolet by frequency doubling and into the infrared by means of parametric devices.<sup>9–13</sup> Equally important is the possibility of continuous fine tuning over the relatively broad fluorescence band ( $\approx 50 \text{ nm}$ ) of a given dye by replacing the rear mirror of the oscillator with a dispersive device such as a rotatable diffraction grating. This will channel the laser radiation, without appreciable loss of total output power, into a narrow ( $\approx 1 \text{ nm}$ ) line. With additional intracavity wavelength-selective elements, such as prisms, etalons, or filters, further narrowing of the spectral line width has been attained,<sup>30</sup> down to  $0.0001 \text{ nm}$ .

Applications of dye lasers are conveyed throughout sections II–IV of this review, while physical-chemical aspects which

control their performance are analyzed in section V.B.

Table I summarizes the characteristics and operating parameters of some of the laser types discussed in this section. The arsenal of commercially available lasers puts at the disposal of the experimenter monochromatic coherent radiation in the wavelength range 250 nm–10 μm, delivered either in CW operation or in pulses of duration ranging from 10<sup>-3</sup> to 10<sup>-12</sup> s and with peak intensities up to 10<sup>14</sup> W/cm<sup>2</sup>.

## C. Properties of Laser Radiation and Nonlinear Effects<sup>9–18</sup>

### 1. Temporal Characteristics of Lasers

Some four-level lasers may be made to emit in the CW mode, e.g., gas lasers, semiconductor lasers, Nd-YAG lasers pumped with continuous lamps, and dye lasers pumped with CW ion lasers.

Most solid-state and dye lasers are operated in pulses. The laser output depends on the temporal characteristics of the input and on the response of the active medium. The properties of the flash lamp and the electric circuitry determine the duration of the pumping pulse which ranges typically from 10<sup>-6</sup> to 10<sup>-3</sup> s. Compared to the ascent of the pumping pulse, laser action starts after a delay necessary to generate population inversion.

Inspection of a "normal-mode" solid-state laser pulse reveals that the output is composed of a random distribution of low-energy submicrosecond pulsations, called spikes, which are due to relaxation oscillations. Spikes start from spontaneous emission noise in regions receiving different amounts of pump energy (because of imperfections in the active medium, uneven thermal expansion or changes of the refractive index); they are terminated by lasing action which depletes the local population inversion.

The erratic output of "normal-mode" operation is undesirable for all applications except those that require thermal irradiation only. Smoothing of the output is achieved by inserting into the cavity a "switch" which suppresses lasing action until a large population inversion has been reached. This technique is called *Q-switching* or *Q-spoiling*, since the resonator quality factor

$$Q = 2\pi\nu_L t_c = 4\pi\eta\ell\nu_L/c(1 - R_1R_2) \quad (15)$$

(cf. eq 6) is deliberately degraded while the population inversion builds up in the laser medium. At the moment of peak inversion the cavity *Q* is abruptly restored and the resonator is allowed to oscillate. This produces a "giant" pulse of about 20 ns duration (for pulse energies of the order of 2 J this corresponds to 10<sup>8</sup> W peak power). In a modified Q-switch technique (pulse transmission mode) the stored energy is dumped out of the cavity during the transit time  $\eta\ell/c \approx 3$  ns.

*Q*-Switching is accomplished by mechanical (rotating mirror),<sup>32</sup> electrooptical<sup>9,10</sup> (Pockels cell) or chemical means.<sup>31</sup> The latter provides the simplest method for *Q*-switching and is named "passive" *Q*-switching. A 1-cm cell containing a bleachable dye solution is placed inside the laser cavity. The dye must be saturable; that is, its opacity decreases with increasing light intensity. In the early stage of pumping the dye solution absorbs the initial low-level spontaneous emission; this extra attenuation reduces the amplification and prevents the buildup of laser oscillations. As a result there is no depletion of the population inversion in the active medium. The absorbed photons decrease the (absorbing) ground-state population of the dye, thus increasing the effective amplification in the cavity by a positive feedback mechanism; at high radiation levels the dye suddenly becomes transparent. The ensuing high *Q* value of the cavity now allows the onset of laser oscillations, and the energy stored in the medium is released in one intense and short burst of oscillations. A main disadvantage of passive *Q*-switching is the jitter ( $\approx 10^{-5}$  s) in the timing of laser emission and consequently the

difficulty of synchronization with other fast events.

*Q*-Switched pulses show temporal structure composed of subnanosecond spikes. Saturable dyes having ultrashort-lived excited states are used for *mode-locking*.<sup>33–35</sup> This can be understood in different ways: in a Fabry-Perot cavity lasing is sustained simultaneously on many longitudinal modes, all with distinct frequency, phase, and amplitude. If the phases of these modes become synchronized or "locked together" they will interfere with one another. The resulting beat effect is observed as periodic intensity pulsations.<sup>36</sup> The laser output will then be in the form of a series, called train, of about 20 regularly spaced ultrashort pulses, separated from one another by the cavity round-trip time  $T = 2\eta\ell/c (\approx 5$  ns). Each pulse is of duration  $T/m$  ( $\approx 5 \times 10^{-12}$  s = 5 ps), where *m* denotes the number of modes locked together.

Conceptually, it is simpler to regard mode-locking as originating in the active medium from emission noise which has the form of a statistically distributed array of spikes.<sup>27</sup> The saturable dye, present in a very thin ( $\approx 1$  mm) cell placed close to one of the cavity mirrors, absorbs weak spikes and preferentially transmits energetic spikes which, momentarily, bleach the dye to transparency. For each spike circulating through the dye-active-medium-system the selection process is repeated and intensified until the resonator contains a single strong spike bounding to and fro between the cavity mirrors. The partially transmitting mirror couples out part of the spike at each reflection and thus produces a train of pulses. The spikes are sharpened up during each round trip since the weaker radiation in the wings of a pulse is more absorbed than that at the pulse center.

It is possible to isolate and switch out electrooptically one individual pulse from the train. The lower limit for the duration  $\tau_p$  of an ultrashort pulse is determined by the inverse spectral band width  $1/\Delta\nu$  of the active medium; this is called a transform-limited pulse; for  $\Delta\nu = 10$  cm<sup>-1</sup> we find  $\tau_p \approx 3$  ps. With pulse-broadening and pulse-compression techniques,<sup>38</sup>  $\tau_p$  may be varied between 10<sup>-10</sup> and 10<sup>-13</sup> s.

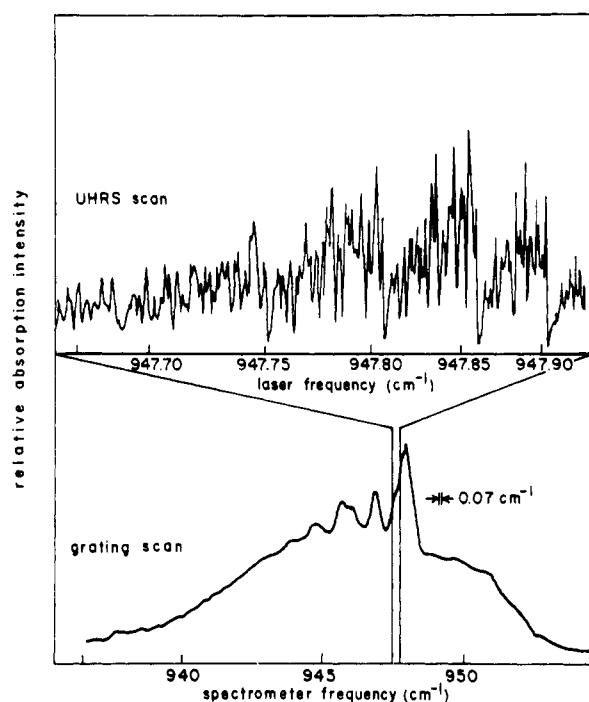
The trade-off in using pulsed laser output is in the rather broad spectral linewidth associated with ultrashort pulses. For some applications *single-mode* operation of lasers is required. This results in extremely narrow linewidths, especially in CW lasers. Transverse or longitudinal laser modes can be selected by inserting, respectively, pin holes and lenses or etalons into the optical cavity.<sup>39–40</sup>

### 2. Coherence

Unlike conventional light sources, lasers are highly coherent,<sup>11–13</sup> and this property is made use of also in chemical applications.

*Time coherence* is related to the monochromatic nature of laser radiation. Classically, it is convenient to consider one spectral line arising from a particular transition at the frequency  $\nu = \Delta E/h$  (s<sup>-1</sup>). Each atom can be thought to emit a Gaussian-shaped wavetrain during the time interval  $\Delta t$  required for the transition to take place. During the lifetime  $\Delta t$  the beam is truly monochromatic, and it is possible to make predictions about the amplitude and phase of the radiation at any point in the wavetrain. The time  $\Delta t$  is called the *coherence time*. Associated with it is the length of the wavetrain, or the *coherence length*  $\Delta L = c\Delta t$ . The link with the spectral properties of the radiation is provided by Fourier analysis, which shows that a wavetrain of single frequency  $\nu$  and of duration  $\Delta t$  is equivalent to a number of infinitely long wavetrains of differing frequencies spread about the central frequency  $\nu$ . A measure for the frequency spread, or the linewidth  $\Delta\nu$ , is given by  $\Delta\nu = 1/\Delta t$ . In terms of the wavelength  $\lambda = c/\nu$  we have

$$\Delta\nu = c\Delta\lambda/\lambda^2 \text{ and } \Delta L = c/\Delta\nu = \lambda^2/\Delta\lambda \quad (16)$$



**Figure 5.** Spectrum of the  $\nu_3$  band of  $\text{SF}_6$ , obtained with a conventional high-resolution spectrometer and with a tunable  $\text{PbSnTe}$  diode laser (after Hinkley<sup>49</sup>).

Space coherence implies that between two chosen points on the wavefront of the radiation there be a constant phase difference that can be maintained over long time intervals. Conventional extended light sources emit random, uncoordinated photons and, typically,  $\Delta L < 10^{-2} \text{ cm}$ . This may be increased to a few centimeters, using a filter–pinhole–lens arrangement, albeit at a large loss of intensity. In contrast, lasers may have a coherence length of several meters. One of the properties resulting from spatial coherence is the fact that laser rays are confined to narrow, low-divergence, directional beams. Simple lenses can focus a beam to a spot, having dimensions of the order of  $\lambda$ . There is a concomitant increase in power density; thus even a low-power He–Ne laser of 1 mW output in a beam of  $0.1 \text{ cm}^2$  cross section, upon focusing to a spot of  $1 \mu\text{m}$  diameter, will yield an intensity of  $\approx 10^4 \text{ W/cm}^2$ . With pulsed  $\text{CO}_2$  lasers it is relatively simple to obtain peak intensities of several terawatts ( $10^{12} \text{ W}$ ) per  $\text{cm}^2$ . Such intensities are being used in molecular photofragmentation studies (see section IV.C).

### 3. Nonlinear Optics in Laser Techniques<sup>9,10</sup>

High-intensity laser radiation propagating within an anisotropic dielectric medium causes optical phenomena which depend in a nonlinear fashion on the electric field strength of the incident wave. The induced electric polarization in the medium corresponds to a forced electric field and its interaction with the incident laser field generates yet another electromagnetic wave. Constructive interference between incident and induced waves in the medium is achieved when all dipole radiators oscillate in phase. This requires conservation of momentum,  $\sum \mathbf{k}_i = 0$ , where  $\mathbf{k}_i = 2\pi\nu_i\eta_i/c$  is the wave vector associated with the field oscillating at  $\nu_i$ . The refractive index  $\eta_i$  depends on the properties of the crystal, its temperature, and its orientation, and also on the properties of the field, its frequency, and its plane of polarization. The phase-match condition may be satisfied for certain uniaxial crystals, such as  $\text{KH}_2\text{PO}_4$  (KDP) or  $\text{NH}_4\text{H}_2\text{PO}_4$  (ADP), possessing large nonlinear coefficients. Crystals are positioned in the beam, usually outside the cavity, and are oriented with the crystal optic axis at the precise phase-match angle with respect to the incident beam.

The most widely used nonlinear optical effect is that of second

harmonic generation (SHG) which creates frequency doubled (FD) radiation. At different phase-match angles efficient frequency tripling (FT) or frequency quadrupling (FQ) may be obtained. Laser systems equipped with an appropriate nonlinear crystal supply coherent radiation at a chosen harmonic frequency; they are widely used in photophysics and photochemistry (see sections III and IV).

Stimulated Raman Scattering (SRS), to be briefly discussed in section II.D, may be employed for (discontinuous) tuning the output of solid-state lasers. Coherent laser-type radiation is created at frequencies shifted from the frequency of the incident source by amounts corresponding to the Raman-active transitions of the irradiated samples. By combining SHG and SRS techniques numerous laser frequencies may be obtained from a single laser source.

## II. Laser Spectroscopy

The unique features of laser sources described in the preceding section make them ideal tools for spectroscopic studies.<sup>2,41–45</sup> The laser has many advantages compared to conventional sources, i.e., enhanced spectral resolution and signal detection (as discussed in this chapter) or improved temporal resolution (section III and section IV.A). Moreover, the laser has created novel types of spectroscopy, such as multiphoton and nonlinear spectroscopy. However, it is important to note that a laser is not just a superior light source; in fact, treating it as such may result in misinterpretation of artifacts, as will be exemplified in this review.

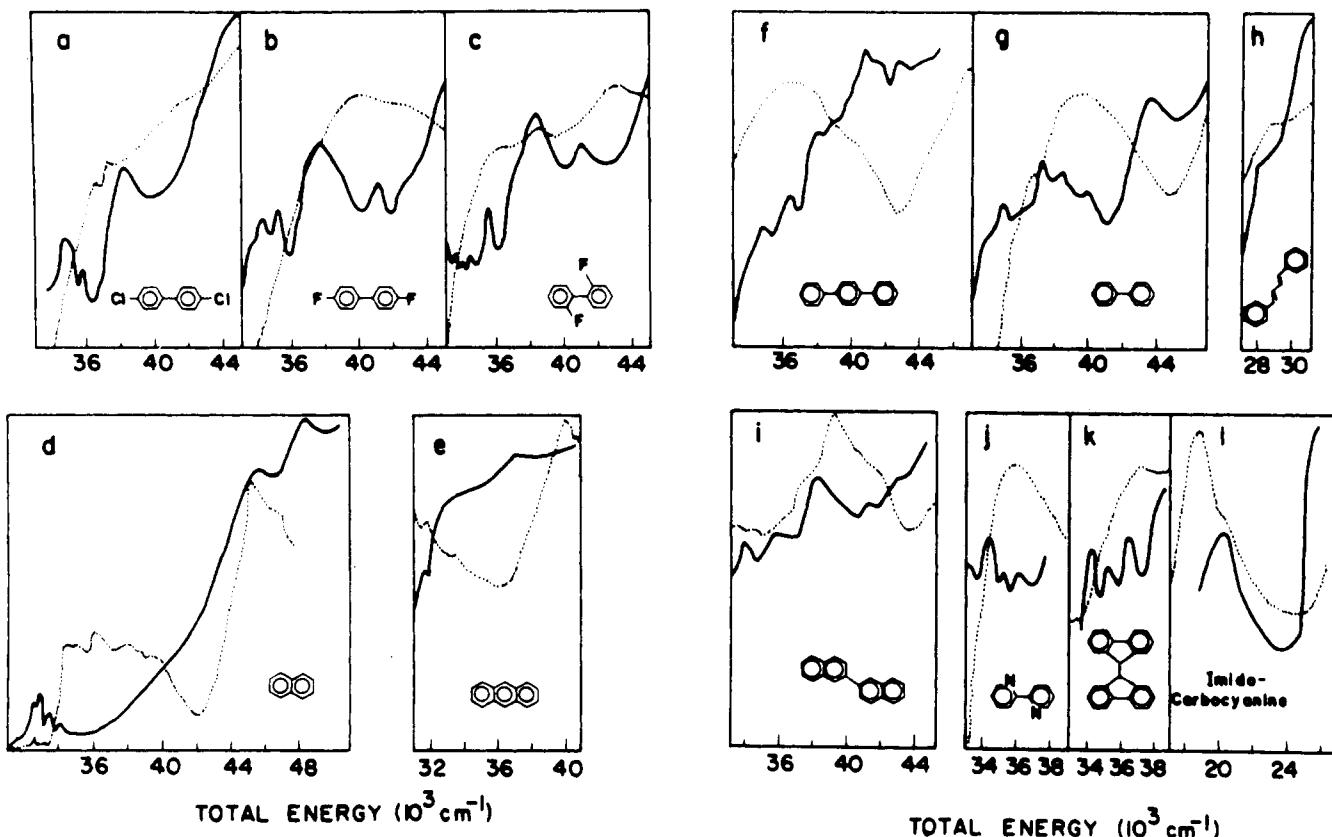
### A. Ultrahigh Resolution Spectroscopy (UHRS)

Narrow linewidth ( $10^{-4} \text{ cm}^{-1}$ ) single-mode gas lasers and tunable narrow band lasers, such as a Hänsch design dye laser<sup>46</sup> or a semiconductor laser,<sup>27</sup> are employed for ultrahigh resolution spectroscopy (UHRS). The most obvious application is in direct absorption spectroscopy which can be performed at much better resolution than that attainable with the best spectrometers. Usually the inhomogeneous Doppler width sets the upper limit of resolution. However, nonlinear techniques may provide resolution within the Doppler width (see section C). Studies of UHRS are indispensable for laser-based isotope enrichment projects (section IV.C). A first effort in this direction was made by Tiffany.<sup>47</sup> With a mode-selected ruby laser, having  $0.04\text{-cm}^{-1}$  line width, he scanned the  ${}^1\Sigma_g^+ \rightarrow {}^3\Pi_{1u}$  band of bromine by thermally tuning the laser output and was able to resolve the spectrum of the two bromine isotopes. Using a single-mode argon-ion laser, Dworetsky and Hozack<sup>48</sup> also resolved spectral lines associated with bromine isotopes.

In Figure 5 we reproduce a spectacular example of UHRS of  $\text{SF}_6$ , obtained with a tunable  $\text{PbSnTe}$  diode laser,<sup>49</sup> showing thousands of resolved absorption features per  $\text{cm}^{-1}$ . For a further discussion the reader is referred to specialized reviews.<sup>42,44,45,50</sup>

### B. Nonlinear Spectroscopy<sup>50–56</sup>

When the monochromaticity of the laser is combined with high intensity, certain nonlinear phenomena can be observed. A rate equation analysis of the type presented in section I.A shows that the conventional Beer's law for absorption does not hold because of saturation. This type of nonlinearity is used in passive Q-switching.<sup>31</sup> If pulses are employed which are short compared to the molecular dephasing time  $T_2$ , coherence phenomena<sup>57–58</sup> such as self-induced transparency (SIT),<sup>59</sup> optical nutation,<sup>60</sup> and photon echoes<sup>61</sup> can be studied. The latter has recently been demonstrated for molecular systems.<sup>62</sup> These phenomena cannot be discussed on a rate equation basis, and a quantum mechanical treatment is required.<sup>14</sup> It is sometimes difficult to determine whether intensity dependence of absorption must be



**Figure 6.** Low-resolution, two-photon absorption spectrum (solid curve) and the corresponding one-photon spectrum (dotted curve) for various centrosymmetric molecules: (a, b, c) ref 90; (d) ref 103; (e) ref 102; (f, g) ref 90; (h) ref 88; (i) ref 89; (j) ref 90; (k) ref 89; (l) ref 95.

attributed to SIT, saturation of absorption, photoquenching,<sup>63</sup> or some other effect. With CW lasers, characterized by narrow linewidths and moderate intensities, novel spectroscopic techniques have been developed;<sup>14,42</sup> among these we mention Lamb-dip spectroscopy, double resonance, and level crossing spectroscopy. The techniques are usually applied to atoms or small molecules and will not be discussed here.

### C. Multiphoton Spectroscopy

Multiphoton spectroscopy deals with the simultaneous absorption of two (or more) photons without the intervention of intermediate stationary energy levels. A quantum mechanical description of two photon absorption (TPA) was first worked out by Göppert-Mayer in 1931, but its potential to chemistry has been realized only with the advent of lasers.<sup>9–13,64,65</sup> The basic theory has been extended to include calculation of TPA cross sections,<sup>66–70</sup> group theoretical analysis of TPA selection rules,<sup>71,72</sup> and polarization effects.<sup>72–74</sup> Experimental results are analyzed through the absorbed laser intensity  $I_{\text{abs}}$  at  $\nu_L$  per unit volume. For one exciting laser source the TPA law<sup>64</sup> reads

$$I_{\text{abs}} = \delta N I_L^2 \ell \quad (17)$$

where  $\delta$  is the TPA cross section ( $\text{cm}^4/\text{s}/\text{photon molecule}$ ) at  $2\nu_L$ ,  $I_L$  the incident laser intensity ( $\text{photons}/\text{cm}^2\text{s}$ ),  $N$  the molecular concentration ( $\text{molecule}/\text{cm}^3$ ), and  $\ell$  the sample cell length. When combining two exciting sources eq 17 has to be modified accordingly.<sup>75</sup> The magnitude of  $\delta$  and its wavelength dependence have been evaluated,<sup>76</sup> but there is still a dispute as to the difference from  $\delta$  calculated for dye molecules on the basis of their one-photon absorption cross section.<sup>76,77</sup> To date, many TPA spectra have been measured, in some cases after having first developed specialized TPA spectrometers.<sup>78–80</sup> The more popular methods are indirect ones in which two-photon fluorescence (TPF)<sup>65,81</sup> or two-photon phosphorescence<sup>82,83</sup> is measured as a function of the excitation wavelength(s). When

using picosecond excitation TPA may be followed by stimulated fluorescence which can also be utilized for the determination of  $\delta$ .<sup>84,85</sup> The use of TPF technique in measuring ps pulse durations is mentioned in section III.C. The TPF technique allows detection of weak TPA transitions but suffers from drawbacks which impede determination of absolute cross sections. For example,  $I_{\text{abs}}$  has to be evaluated from the TPF intensity,  $I_{\text{fl}}$ , through

$$I_{\text{abs}} = \alpha I_{\text{fl}} \quad (18)$$

where  $\alpha$  depends on the fluorescence quantum yield and on the geometry of the experiment.

One of the more important contributions of two-photon spectroscopy (TPS) is in the assignment of electronic transitions. For centrosymmetric molecules, TPS enables one to observe direct  $g \rightarrow g$  transitions which are now allowed in one-photon excitation.<sup>82,87–91</sup> Compounds have been investigated in the crystalline state,<sup>71,86,87,92</sup> in liquid,<sup>73,93</sup> in solution,<sup>81,87–91,94,95</sup> and in the gas phase.<sup>96–100</sup> In Figures 6 and 7 we summarize reported low-resolution TPA spectra and compare them with corresponding one-photon spectra. In most cases, TPA spectra are seen to be different, displaying molecular features which are otherwise difficult to obtain.<sup>65</sup>

Tunable dye laser sources permit moderate<sup>87–92,101–106</sup> and high-resolution<sup>82,97–100,106–111</sup> recording of TPA spectra. In benzene, TPA measurements have been carried out with the purpose of observing the low-lying  ${}^1E_{2g}$  state but, with one possible exception,<sup>112</sup> so far unsuccessfully. Most experiments concentrated on the  ${}^1B_{2u}$  state and revealed features unique to the TPA spectrum<sup>104,108–111</sup> which confirmed theoretical calculations.<sup>68,86,105</sup> For a more complete picture of this subject, the reader is directed to specialized reviews.<sup>64,65,113,114</sup>

The interpretation of TPA phenomena studied either by TPF<sup>65</sup> or by the chemical yield method<sup>94</sup> (section IV.D) or by direct absorption techniques<sup>65,78,79</sup> may be confused by interfering effects. At this point it is, perhaps, appropriate to draw attention

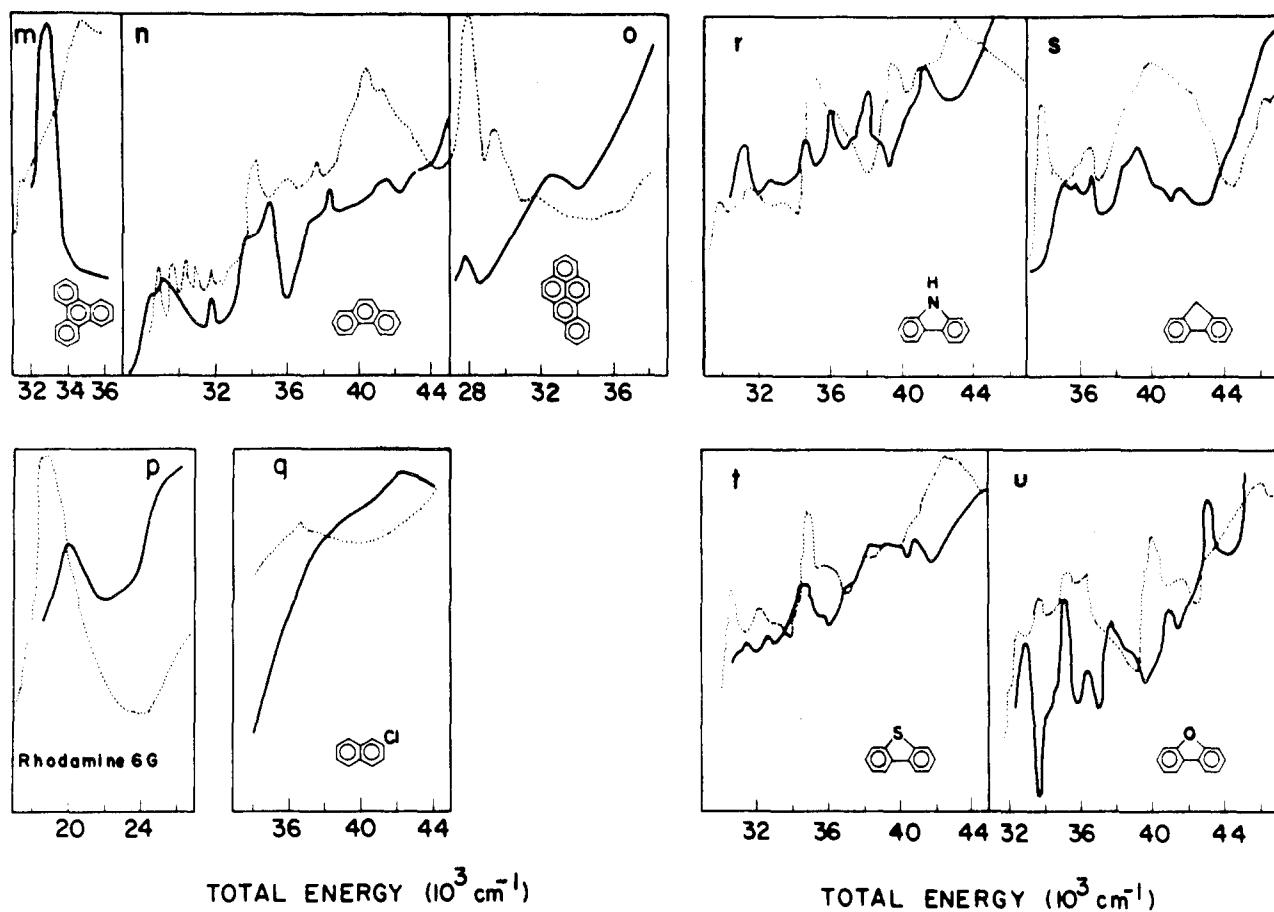


Figure 7. As in Figure 6, for molecules lacking center of symmetry: (m) ref 83; (n) ref 91; (o) ref 81; (p) ref 95; (q) ref 93; (r, s, t, u) ref 91.

to some complications in TPS, which are a direct consequence of the characteristic laser properties. These are different from the difficulties facing traditional spectroscopy when employing intense lasers.<sup>115</sup> TPA is a nonlinear optical process and therefore other nonlinear processes such as photoquenching,<sup>63,116,117</sup> SRS (section D), or self-focusing<sup>94,118,119</sup> should be avoided when performing TPS studies. External focusing influences multiphoton absorption intensities<sup>119–121</sup> and may even mask the correct order of the process (section IV.D). The statistical and coherence properties of the laser light<sup>122–124</sup> and relaxation of the excited state<sup>125,126</sup> may also affect the apparent value of  $\delta$ . Absolute values of  $\delta$  depend foremost on the accurate measurement of the incident laser intensity. It is obvious that fluctuations in the temporal and spatial distribution of the laser beam will have a more pronounced effect in a TPA spectrum than in a one-photon spectrum. The nanosecond envelopes of pulses emitted by Q-switched solid-state lasers,<sup>36,37</sup> or by nitrogen laser pumped dye lasers,<sup>127</sup> contain irregular picosecond spikes of amplified spontaneous noise. Experimental methods<sup>128</sup> and correction factors<sup>129</sup> have been suggested to overcome these intricacies. An attempt to unify experimental approaches, together with a survey of artifacts, has recently been reported.<sup>130</sup> For example, neglect of polarization effects has led to an erroneous assignment for benzene.<sup>98,111</sup>

Using extremely intense and short pulses coherent multiphoton phenomena such as two-photon SIT<sup>131</sup> and coherent TPA<sup>132</sup> have been observed. The transition probabilities for coherent multiphoton absorption processes have been calculated.<sup>133</sup> The situation is complicated further because of possible two-photon saturation effects.<sup>134</sup> The two-photon analog of one-photon saturation spectroscopy<sup>135–137</sup> and Doppler-free TPA permits UHRS of atoms<sup>138–140</sup> and of molecules.<sup>141,142</sup> In conclusion, we note that TPS is a highly important and fast developing field, but securing meaningful results requires recognition of potential sources of error.

#### D. Raman Spectroscopy<sup>143,144</sup>

Raman scattering provides insight into molecular structure and dynamics. It complements information derived from absorption measurements. Vibrational Raman spectroscopy represents an alternative technique for measuring the eigenfrequency  $\nu_M$  of certain symmetrical modes in polyatomic molecules and also of homonuclear diatomics; in addition, it furnishes spectra of compounds in aqueous solutions.

A Raman spectrum displays the intensity of scattered radiation vs. frequency shift from the exciting frequency  $\nu_L$ . A red-shifted (Stokes) frequency  $\nu_S = \nu_L - \nu_M$  or a blue-shifted (anti-Stokes) frequency  $\nu_{AS} = \nu_L + \nu_M$  is associated with, respectively, a net upward or downward transition between two molecular energy levels. Spontaneous Raman emission is due to inelastic scattering of incident photons. It is extremely weak, particularly so for anti-Stokes emission. The much more intense unshifted, or elastic, Rayleigh scattering, at  $\nu_L$ , interferes with measurements of small Raman shifts.

The replacement of mercury lamps as the exciting source by lasers has led to a revival in studies of the Raman effect. At present it has become a routine analytical technique.<sup>143</sup> The narrow line width of gas lasers ( $\approx 0.01 \text{ cm}^{-1}$ ) increases the spectral resolution ( $\approx 0.05 \text{ cm}^{-1}$ ) in Raman spectroscopy. It allows fundamental progress in line-shape studies, and the acquisition of accurate molecular parameters and of reliable scattering cross sections. The perfect polarization of lasers permits measurement of very low depolarization ratios. The intensity and directionality of lasers have resulted in high-quality spectra, obtainable from small samples; however, the efficient collection of isotropically scattered emission remains a problem. These and other aspects of spontaneous Raman scattering with laser excitation are covered in numerous reviews<sup>143–145</sup> and monographs.<sup>146–150</sup>

The use of giant pulse lasers as excitation sources has created

a host of novel effects, e.g., the stimulated Raman, inverse Raman, and hyper-Raman effect. The tunability of laser excitation sources has bred yet additional disciplines, e.g., resonance Raman and coherent anti-Stokes Raman spectroscopy.

*Stimulated* Raman scattering (SRS)<sup>151</sup> originates from spontaneous Raman emission. In a given scattering medium the most intense and spectrally narrow spontaneous Raman Stokes line may become sufficiently intense to build up gain in the direction of the laser propagation. The appearance of a SRS signal is subject to a power threshold. Because the probability for the SRS process is proportional to the product of the radiation densities of both incident and scattered fields, SRS shows exponential growth with pump power, cell length, and sample concentration. It is far less general than spontaneous Raman scattering. For example, in a given compound usually one single transition reaches threshold; moreover, SRS cannot be studied in low-pressure gas samples.

In favorable cases a substantial fraction (up to 30%) of the pump laser power may be converted into SRS signals. This is to be contrasted with typical efficiencies of  $10^{-8}$  normally encountered in the spontaneous Raman effect. The high-intensity SRS Stokes field generated in the medium, in turn, acts as a pump laser at  $\nu_S$  and gives rise to successive SRS Stokes signals,  $\nu_L - 2\nu_M$  and  $\nu_L - 3\nu_M$ . These are, of course, not to be confused with overtone frequencies (no anharmonicity).

In the spontaneous Raman effect anti-Stokes emission is due to thermally populated molecular levels. In contrast, SRS anti-Stokes photons are generated from the interaction between two laser photons and one Stokes photon. This is subject to conservation of energy considerations; thus  $2\nu_L = (\nu_L - \nu_M) + (\nu_L + \nu_M)$  or  $2\nu_L = (\nu_L - 2\nu_M) + (\nu_L + 2\nu_M)$ . Conservation of momentum,  $2\mathbf{k}_L = \mathbf{k}_S + \mathbf{k}_{AS}$ , restricts the anti-Stokes SRS radiation to directions having well-defined conical angles about the laser beam (which precludes observation of anti-Stokes SRS in an intracavity configuration). Here  $k_i$  denotes the wave vector,  $k_i = 2\pi\nu_i\eta_i/c$ , where the refractive index  $\eta_i = \eta(\nu_i)$  depends on  $\nu$ .

Since its chance discovery in 1962, SRS has been intensively investigated and has yielded a wealth of information on electrical and optical properties of molecules. From a practical point of view SRS has found widespread use in chemical tuning of the monochromatic output of solid-state lasers. Some studies of vibrational lifetimes and also of selective laser-induced reactions are based on SRS (see section IV.C).

In order to observe the *inverse* Raman effect,<sup>152,153</sup> a sample is simultaneously irradiated with a giant pulse laser at  $\nu_L$  and continuum radiation, extending on the high-frequency side of  $\nu_L$ . Sharp absorption features within the continuum appear, without threshold, at frequencies  $\nu_L + \nu_M$ . The molecules undergo upward transitions corresponding to Raman-active transitions,  $h\nu_M$ .

In principle, measuring inverse Raman absorption has some advantages compared to spontaneous Raman emission. For one, there is no need for carefully aligned collecting optics, nor for photon-counting detection. More importantly, fluorescing samples are amenable to inverse Raman since measurements are carried out on the high-frequency side of  $\nu_L$ . In practice, however, application of the technique is limited because of technical difficulties in obtaining a sufficiently intense and reproducible radiation continuum that overlaps the giant pulse beam both spatially and temporally. Stimulated anti-Stokes continuum, dye fluorescence, PSFC, and tunable broad-band PLPDL emission have all been employed in inverse Raman investigations.

The *hyper* Raman effect<sup>154,155</sup> is observed when a sample is irradiated with a giant pulse laser, at an intensity just below the threshold level necessary for the production of SRS. The isotropically scattered radiation contains frequencies at  $2\nu_L \pm \nu_M$ . The efficiency of the process is extremely low and the po-

tential advantage of the hyper-Raman effect seems to be mainly in structural determinations. The hyper-Raman selection rules are quite different from the spontaneous Raman ones.<sup>154</sup> For example, all infrared-active transitions are allowed, so are a number of transitions which are inactive in both infrared and Raman spectra.

Resonance Raman spectroscopy is clearly the most rapidly growing branch on the Raman tree, as may be judged from the voluminous reviews by Behringer.<sup>156</sup> Briefly, resonance Raman concerns the very substantial increase in the scattering cross section of certain vibrations when the exciting radiation coincides with some electronic transition of the molecule. In practice, one measures the dependence of the intensity distribution in a Raman spectrum on the exciting frequency. A dye laser is used for the exciting radiation which is tuned through the absorption band(s) of the sample. The resonance Raman effect is intimately related to resonance fluorescence; they can be distinguished by their different spectral and temporal characteristics.<sup>156-159</sup>

The recently developed method of coherent anti-Stokes Raman spectroscopy (CARS)<sup>160,161</sup> promises to become a most valuable analytical tool for detecting low-concentration samples of gases or liquids. CARS exhibits very high Raman efficiency, high spectral resolution, and superb discrimination against fluorescence.

Two sources are employed, usually one fixed frequency laser at  $\nu_1 = \nu_L$ , the other a narrow-band tunable dye laser at  $\nu_2 = \nu_L - \Delta\nu$ . A Raman-active mode  $\nu_M$  is strongly excited at resonance when  $\nu_1 - \nu_2 = \Delta\nu = \nu_M$ , that is,  $\nu_2 = \nu_S$ , the Stokes frequency. The molecular polarizability will then be modulated at  $\nu_1 - \nu_2$ . The scattered wave at  $\nu_1 - \nu_2$  interacts with  $\nu_1$  to generate a wave at

$$\nu_1 + \nu_1 - \nu_2 = 2\nu_L - (\nu_L - \Delta\nu) = \nu_L + \Delta\nu = \nu_{AS}$$

The high-order nonlinear terms in the molecular susceptibility are responsible for the four photon process which involves three incident photons  $\nu_1$ ,  $\nu_1$ ,  $\nu_2$ , and one emitted photon  $\nu_{AS} = 2\nu_1 - \nu_2$ . Therefore, CARS is governed by slightly different selection rules than the spontaneous Raman effect.<sup>160</sup>

The emergent beam is coherent and well collimated which allows simple spatial collection of CARS radiation as opposed to the isotropic scattering encountered in the spontaneous Raman effect. Incidentally, in condensed media the laser beams must, for maximum conversion, be crossed by the phase-matching angle determined by momentum conservation  $2\mathbf{k}_1 - \mathbf{k}_2 = \mathbf{k}_{AS}$ , similar to SRS, since the refractive index  $\eta_i$  is subject to dispersion; in gases all beams are colinear.

## E. Miscellaneous Spectroscopic Applications

### 1. Remote Sensing of Atmospheric Pollutants<sup>162-167</sup>

Remote optical sensing of chemical pollutants such as NO, NO<sub>2</sub>, SO<sub>2</sub>, O<sub>3</sub>, CO, and hydrocarbons in the environmental air is based on passing radiation through the atmospheric section to be investigated and analyzing the transmitted or backscattered radiation. The received optical signal is a function of the transmission, absorption, polarization, and scattering properties of the atmosphere and of the pollutants. Quantitative information can be obtained about specific contaminants and their density and distribution in the atmosphere.

Laser sources for remote sensing have dramatically improved the capability and performance of Light Detection And Ranging (LIDAR) devices,<sup>168</sup> providing means for rapid quantitative analyses of atomic or molecular pollutants with high specificity and sensitivity.

The power and collimation of laser beams enable the detection of atmospheric constituents in well-defined volumes at rather large distances ( $\approx 1000$  m). Also, the short duration of Q-switched pulses permits range discrimination of different air layers by time-gating the returning signal in a radar fashion.

Fixed wavelength as well as tunable lasers are used as LIDAR sources. Some methods are listed as follows:

(a) *Absorption.* Measurements involve direct absorption over a long path through the atmosphere.<sup>168-171</sup> The laser is fine-tuned across a strong absorption line of a given pollutant. It should be noted that retroreflectors or remote detectors are required and also that only the integrated concentration of absorbers over the whole path is measurable without depth resolution. Stratospheric *in situ* measurements have also been performed.<sup>172</sup> Absorption measurements provide the highest overall sensitivity (in the ppb concentration range) of optical monitoring schemes with the least amount of laser power. The sensitivity may be further improved by the derivative technique<sup>173</sup> which involves either frequency modulation of the laser output through the absorption line or amplitude modulation.

(b) *Laser Raman LIDAR.*<sup>174-179</sup> This method requires a fixed-wavelength pulsed laser of high intensity. The emitter and detector are at the same location. The Raman frequencies of a scattering molecule are down converted by the characteristic Stokes shift from the unshifted Mie and Rayleigh components of the backscattered signal. A multicomponent gas mixture is identified unambiguously by polychromatic analysis of the backscattered radiation. A convenient calibration for the absolute concentration of each pollutant (in the ppm range) is provided by ever-present O<sub>2</sub> or N<sub>2</sub> reference Raman lines. They also serve to correct for pulse-to-pulse fluctuations of the pump laser and for ambient atmospheric changes. With a tunable pump laser it may be possible to enhance the scattered signal by the resonance Raman effect. This requires tuning a dye laser to an absorption band of the pollutant.

(c) *Resonance Backscatter and Differential Absorption.* The laser is tuned to a strong transition of a pollutant. Selective excitation will be followed by broad-banded and red-shifted resonance fluorescence which may be detected in the backscattered signal.<sup>180</sup> The differential absorptive method is based on measuring the selective absorption due to atmospheric constituents, of (tunable) radiation "reflected" by natural Mie and Rayleigh scatterers.<sup>181-186</sup>

(d) *Remote Heterodyne Detection.*<sup>187,188</sup> This is a technique for detecting emission at characteristic frequencies from hot effluent sources, such as smokestacks or exhaust plumes of airplanes, without the need to pass radiation through the atmosphere. A semiconductor laser, used as a local oscillator, is frequency tuned through an emission line of the pollutant gas. The amplitude of the beat signal is a measure for the pollutant concentration.

Measurements in the field or in a laboratory-simulated atmosphere have been reported for NO,<sup>172,188</sup> NO<sub>2</sub>,<sup>172,179,180,183,184</sup> SO<sub>2</sub>,<sup>175,179,186,188</sup> O<sub>3</sub>,<sup>172,185,186,188</sup> CO,<sup>168,174,182</sup> and hydrocarbons.<sup>171,174,175,179,186</sup>

## 2. Applications in Analytical Chemistry. Intracavity Studies<sup>189-192</sup>

All optical and spectroscopic methods employed in analytical chemistry have been improved by the introduction of lasers. Tunable lasers operating in the visible<sup>30</sup> and infrared<sup>27</sup> spectral region have revolutionized spectroscopic instrumentation.<sup>42,44,45</sup> For example, the monochromator section in customary absorption spectrophotometers has become redundant. We will briefly discuss applications in analytical chemistry in general and, at this point, we will mention a few salient examples; further references to studies on this topic can be found scattered throughout this review.

The spectral brightness of lasers, i.e., the radiant intensity per unit frequency interval, is many orders of magnitude greater than that of conventional light sources. This is the major reason for enhanced sensitivity. Also, the coherence properties of lasers permit the use of coherent detection techniques, such as het-

erodyning,<sup>187,188</sup> which further increase sensitivity. Moreover, novel techniques have been developed, which include saturation spectroscopy<sup>50,51</sup> and intracavity absorption that are uniquely suited to lasers.

Direct absorption methods in chemical analysis benefit mainly from the high intensity and narrow line width of the laser.<sup>42</sup> For some species detection sensitivities of 1 ppb have been achieved.<sup>189</sup> Some analytical applications have been mentioned, in a different context, in the preceding sections which describe UHRS<sup>44-49</sup> and remote sensing.<sup>168-173,181-186</sup> The high brightness of laser sources has led to the development of saturation spectroscopy,<sup>50,51</sup> which has some proven and many more potential applications for chemical analysis.

The main analytical methods based on light scattering refer to the Raman effect<sup>143-150,152,153,156-161</sup> and to laser excited fluorescence.<sup>52</sup> Special fluorimeters have been developed,<sup>193</sup> and the detection limit has been pushed to below 1 part per trillion<sup>194,195</sup> (which amounts to detecting about 10<sup>4</sup> molecules/cm<sup>3</sup> in a gas sample at 1 Torr pressure or subnanogram detection in solutions). In sections III and IV, we discuss various fluorescence studies, some of which have analytical implications, for example, in the detection of excited or unstable species.

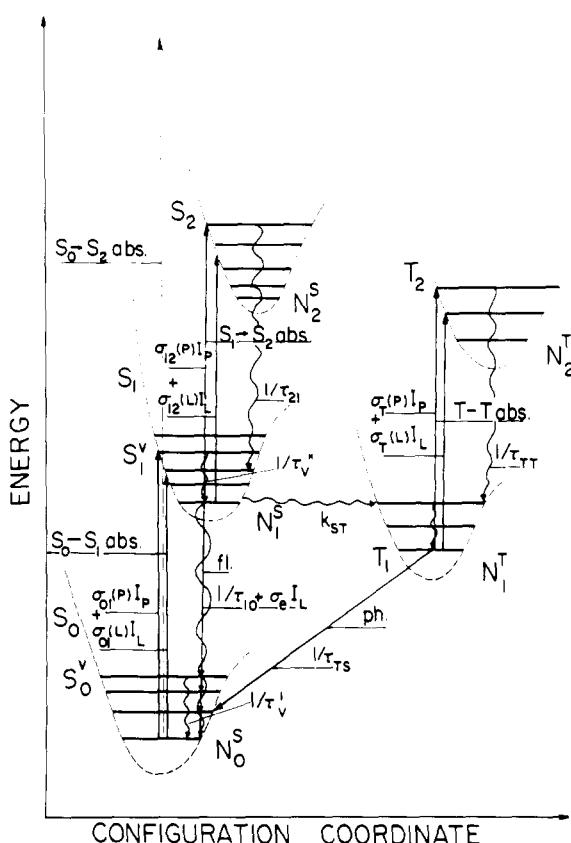
Consider now a cell, containing a compound characterized by narrow absorption features, that is incorporated into the cavity of a broad-band dye laser. At the frequencies where absorption takes place the gain is suppressed and the laser output will be quenched.<sup>196-213</sup> The molecular "amplification" process increases the sensitivity of trace absorptions about 100-fold. Measurements have been reported for Na,<sup>196,203,204,206</sup> Sr,<sup>205</sup> Ba,<sup>203,205</sup> Pr<sup>3+</sup>,<sup>207,208</sup> Eu<sup>3+</sup>,<sup>197,203,208</sup> Ho<sup>3+</sup>,<sup>207</sup> I<sub>2</sub>,<sup>196,198,201,209</sup> NH<sub>2</sub>,<sup>199</sup> HCO,<sup>199</sup> NO<sub>2</sub>,<sup>200,202</sup> anthracene,<sup>79</sup> and stilbene.<sup>79</sup> Theoretical treatments giving a quantitative description of intracavity absorption enhancement have been worked out.<sup>197,201,209,211</sup> The inverse situation of intracavity emission has been used for enhanced flame spectrometry.<sup>212</sup> Quenching of a narrow-band CW dye laser has also been reported.<sup>213</sup>

Finally we mention the use of solid-state and CO<sub>2</sub> lasers in microprobe chemical analysis.<sup>214</sup> The laser beam is focused onto a solid sample, which may be inside an evacuated chamber. The absorbed laser energy vaporizes and excites species from a small area on the sample surface. Conventional spectrographic or mass-spectrometric analysis is then used to determine the concentration of various atomic or molecular fragments in the ejected plume.<sup>214</sup> In this method no demands are made on the monochromaticity or tunability of the laser but rather on the energy/pulse and, of course, on the degree of spatial coherence.

In contrast, laser optoacoustic spectroscopy<sup>215</sup> is based on monochromatic radiation. An infrared laser is tuned to a resonance frequency of the species to be detected in a gaseous mixture, preferably at atmospheric pressure. The energy absorbed by the internal modes of the species is efficiently converted to translational energy (see section IV.B) and results in adiabatic heating of the sample. A modulated or repetitively pulsed laser beam causes periodic expansion of the gas. This is accompanied by pressure waves that can be detected with a pressure transducer or microphone, much in the same way as with a spectrophone apparatus.

## III. Laser Photophysics

Photophysical processes concern the pathways by which an excited species loses its energy, excluding photoionization processes and the formation or destruction of chemical bonds. The photophysical properties of an excited molecule involve all molecular parameters appearing in Figure 8. The kinetic processes shown in Figure 8 apply to solutions or to condensed phases, where radiative processes occur only after complete



**Figure 8.** Diagram of photophysical and kinetic processes occurring in a solution of large organic molecules, typical examples being dye compounds.  $S_i$  and  $T_i$  designate, respectively, singlet and triplet states having populations  $N_i^S$  and  $N_i^T$ . In the singlet manifold the absorption (abs) rates are  $\sigma_{ij}(P)I_P$  and  $\sigma_{ij}(L)I_L$  at the pumping (p) and, if applicable, at the dye laser (L) frequency; in the triplet manifold the absorption rate is designated by  $\sigma_{iT}$ . The lifetime of the vibrational level  $v$  in the ground electronic state is  $\tau_v$ , and  $\tau_{v'}$  in the excited state;  $\tau_{10}$  is the fluorescence (fl) and  $\tau_{TS}$  the phosphorescence (ph) lifetime;  $\tau_{21}$  and  $\tau_{TT}$  denote nonradiative lifetimes and  $k_{ST}$  is the intersystem crossing rate constant.

thermalization within the first excited states  $S_1$  or  $T_1$  has taken place. For isolated molecules, knowledge about the dynamics of single excited vibronic states is also required. Experimentally, photophysics is connected with:

1. UHRS of the molecules, as discussed in the previous section, and if possible, complemented by ultrahigh resolution laser-induced emission spectroscopy.<sup>216-219</sup> This is a prerequisite for any photophysical investigation of isolated molecules.

2. Preparation of a sufficient population of excited molecules in a well-defined vibronic state.

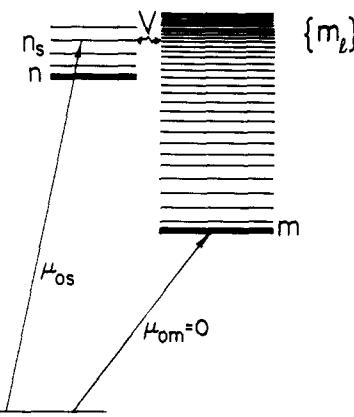
3. Investigation of the temporal evolution of the prepared state which decays via radiative and intramolecular nonradiative channels and/or via intermolecular energy transfer processes. (sections A and C).

4. Absorption spectroscopy of excited molecules (section B).

Although some photophysical studies are still carried out without lasers, the unique properties of the laser enable us to improve techniques so as to experimentally match theoretical advances in this field. Only with lasers can molecules be prepared in well-defined excited states and can lifetimes be measured down to picosecond time scale.

#### A. Fluorescence, Phosphorescence, and Radiationless Transitions

In this section we review the photophysical behavior of molecules. The theoretical treatment of the characteristics of an



**Figure 9.** Diagram showing radiationless transitions from an optically prepared vibronic level  $n_s$  into the manifold  $\{m_e\}$ . The electronic states are designated by 0,  $n$ , and  $m$ ; the transition moments by  $\mu$ ; and the coupling term by the perturbation matrix element  $V$ .

excited molecule provides means for interpretation of experimental data. Extensive reviews of the theory of radiationless transitions and their effects on molecular radiative properties are available.<sup>220-224</sup> We summarize the experimentally relevant predictions of the theory and complement them with illustrative examples.

An isolated molecule is initially prepared in a selected excited state by absorption of a photon. This state depends on the radiation field used and on the interaction time. The preparation stage is important and determines subsequent radiative and nonradiative events.<sup>225</sup> The Hamiltonian of the photoselected molecular system is usually described by the Born-Oppenheimer (B-O) approximation.<sup>221-224,226</sup> For diatomic molecules calculated fluorescence lifetimes,  $\tau_{10}$ , based on the Franck-Condon principle,<sup>226</sup> generally agree with measured quantities.<sup>227-233</sup>

Additional photophysical processes take place when breakdown of the B-O approximation occurs. An initially prepared vibronic state  $n_s$  (see Figure 9) (usually within the first excited singlet state  $S_1$ ) is coupled by a perturbation matrix element  $V$  to the eigenstates  $\{m_e\}$  belonging to a lower electronic state  $m$  ( $S_0$  or  $T_1$ ). The coupling term  $V$  causes nonradiative internal conversion (IC) or intersystem crossing (ISC) processes. States  $\{m_e\}$  do not carry oscillator strength from the ground state ( $\mu_{0m} = 0$ ) and all radiative decay transitions occur from the state  $n_s$ . Depending on the relative values of the molecular parameters, various radiative features can be observed. Experimentally, one measures kinetic parameters and fits them into a kinetic scheme, which can be analyzed in terms of quantum mechanical quantities.<sup>234</sup> We shall discuss the experimental observations as belonging to a statistical, intermediate, or resonance case, a classification suggested by Bixon and Jortner.<sup>235</sup> The resonance limit has been observed only in atoms and will not be reviewed here.

The simplest behavior is exhibited by excited states belonging to the statistical limit characterized by the condition  $\rho V \gg 1$ , where  $\rho$  denotes the density of states. Many large molecules, such as aromatics, are statistical and therefore this limit is also known as the large-molecule limit. Here the nonradiative decay obeys the Fermi "Golden Rule"<sup>226</sup>  $\tau_{nr} = h/2\pi\rho V^2$ , and, in addition, the fluorescence decay is exponential. Nonradiative transitions are intramolecular and irreversible. This is supported by the observation that the fluorescence quantum yield  $\phi$  is smaller than unity and independent of the environment. The criterion for irreversibility is that the maximum experimental time  $\tau_{max}$  available for observing fluorescence from  $n_s$  is larger than the recurrence time  $\tau_R = \hbar\rho$ , that is the time required by a molecule, initially at  $n_s$ , to decay to  $\{m_e\}$  and to return to  $n_s$ .<sup>223,224</sup> Experimentally,  $\tau_R$  depends on the way  $n_s$  was prepared and on the radiation bandwidth. For statistical molecules  $\tau_R \gg \tau_{max}$ ,

TABLE II. Collisionless Fluorescence Lifetimes  $\tau_{10}$  and Collisional Quenching Cross Sections  $\sigma_Q$  for Gaseous Molecular Species Prepared in Single Vibronic States and Studied by Time-Resolved Laser-Induced Fluorescence<sup>a,b</sup>

Species	Vibronic state		$\tau_{10}, \mu\text{s}$	$\sigma_Q$ (at 300 K), $10^{-16} \text{ cm}^2$	Collision partner	Laser system	Ref
	Notation	$v(J)$					
$\text{C}_2^-$	$\text{B}^2\Sigma_u^+$	Various	0.013–0.033		c	$\text{N}_2/\text{dye}$	285
$\text{Li}_2$	$\text{A}^1\Sigma_u^+$		0.018	185–406	Li	$\text{N}_2/\text{dye}$	233b
$\text{Na}_2$	$\text{B}^1\Pi_u$	6, 9, 10, 13, 17	0.0067			$\text{Ar}^+$	233a
	$\text{A}^1\Sigma_u^+$	11, 14, 16	0.1–1			$\text{He}-\text{Ne}$	227
		1–25	0.012			PLPDL	228
$\text{K}_2$	$\text{B}^1\Pi_u$	7	0.012	150 (500 K)	K	$\text{He}-\text{Ne}$	276
		7	0.0096			$\text{Ar}^+$	233a
$\text{Rb}_2$	B		0.017			$\text{Ar}^+$	233a
	C		0.061			$\text{Ar}^+$	
$\text{Cs}_2$			0.012			$\text{Ar}^+$	233a
$\text{Cu}_2$	A,B		0.03, 0.1		Cu	$\text{N}_2/\text{dye}$	302
						$\text{Ar}^+ \text{ CWDL}$	292, 293
$\text{N}_2$	$\text{B}^3\Pi_g$	Various	10	4–7	Ar, $\text{N}_2$	$\text{N}_2$	298
$\text{Cl}_2$	$\text{B}^3\Pi_{ou}^+$		17	8.9		FLPDL	299
${}^{81}\text{Br}_2$	$\text{B}^3\Pi$	1–40	1.2–0.2	176–525	$\text{Br}_2$	$\text{Cl}_2, \text{N}_2$	229b
${}^{79,81}\text{Br}_2$	$\text{B}^3\Pi_{ou}^+$	40 ( $J = 16$ )	3.57	70	${}^{81}\text{Br}_2$	$\text{N}_2/\text{dye}$	277
		45 ( $J = 39$ )	1.57	87	${}^{81}\text{Br}_2$	$\text{Ar}^+$	301
${}^{79,81}\text{Br}_2$		40 ( $J = 19$ )	3.22	80	${}^{81}\text{Br}_2$	Single mode	301
${}^{79,79}\text{Br}_2$		42 ( $J = 32$ )	1.96	84	${}^{81}\text{Br}_2$		301
		46, 47 ( $J = 41$ )	2.70	80	${}^{81}\text{Br}_2$		
$\text{I}^{79}\text{Br}$						CWDL	304
$\text{I}_2$	$\text{BO}_u^+ ({}^3\Pi)$	0–70	1.5–0.7	160–276	$\text{I}_2$	$\text{N}_2/\text{dye}$	279
		9–20	0.33–1.36	62–76	$\text{I}_2$	$\text{N}_2/\text{dye}$	280
$\text{ICl}$	${}^3\Pi$		7.6–10.9	86	ICl	FLPDL	229
	$\text{BO}^+$	1–16	1–3		c	$\text{N}_2/\text{dye}$	281
$\text{BeO}$	$\text{C}^1\Sigma$		0.09			$\text{N}_2/\text{dye}$	289
$\text{BaO}$	$\text{A}^1\Sigma$	0–11	3.57	0.28–2.49	He	$\text{N}_2/\text{dye}$	286
	$\text{A}^1\Sigma$	7, 8	12.5	0.79	He	$\text{Ar}^+$	287
	$\text{A}^1\Pi$	13, 14, 16, 17	8.8–10			$\text{N}_2/\text{dye}$	288
$\text{FeO}$						$\text{Kr}^+$	291
$\text{AlO}$	$\text{B}^2\Sigma^+$	0, 1, 2	0.13			$\text{N}_2/\text{dye}$	290
$\text{LiH}$	$\text{A}^1\Sigma^+$	5 ( $J = 5, 10, 15$ )	0.029–0.033	120–350	Li	$\text{N}_2/\text{dye}$	303
	$\text{A}^1\Sigma^+$	2 ( $J = 3$ )	29.4			$\text{N}_2/\text{dye}$	297
		5 ( $J = 3$ )	30.5				
		7 ( $J = 12$ )	36.9				
$\text{NaH}$	$\text{A}^1\Sigma^+$	8 ( $J = 3$ )	222.7			$\text{N}_2/\text{dye}$	297
$\text{OH}$	$\text{A}^2\Sigma^+$	0	0.79	11.2	$\text{H}_2$	$\text{N}_2/\text{dye}$	231
	$\text{A}^2\Sigma^+$	0	0.82	0.007–5	$\text{H}, \text{H}_2, \text{Ar}$	FLPDL	232
	$\text{A}^2\Sigma^+$	0, 1, 2	0.13–0.74			$\text{N}_2/\text{dye}$	294
	$\text{A}^2\Sigma^+$	0		0.09–25	Various	FD dye	294
	$\text{A}^2\Sigma^+$	0	0.585			$\text{N}_2/\text{dye}$	283
$\text{OD}$	$\text{A}^2\Sigma^+$	0	0.75	10.2	$\text{D}_2$	FD Nd dye	231
	$\text{A}^2\Sigma^+$	0, 1, 2	0.565		c	$\text{N}_2/\text{dye}$	294
	$\text{A}^2\Sigma^+$	0	0.57		c	$\text{N}_2/\text{dye}$	283
$\text{NH}$	$\text{A}^3\Pi$	0, 1, 2	0.165–0.07		c	$\text{N}_2/\text{dye}$	284
$\text{ND}$	$\text{A}^3\Pi$	0, 1, 2	0.170		c	$\text{N}_2/\text{dye}$	284
$\text{CdH}$	$\text{A}^2\Pi$	0, 1	0.07–0.08		$\text{H}_2$	$\text{N}_2/\text{dye}$	300
$\text{CdD}$	$\text{A}^2\Pi$	0, 1	0.07–0.09		$\text{D}_2$	$\text{N}_2/\text{dye}$	300
$\text{CN}$	$\text{B}^2\Sigma^+$	0	0.066	43	$\text{C}_2\text{N}_2$	$\text{N}_2/\text{dye}$	230
$\text{MX}$	Various	Various	0.016–0.051			$\text{N}_2/\text{dye}$	296
M = Ca, Ba, Sr							
X = F, Cl, Br, I							
$\text{NH}_2$	${}^2\text{A}_1$		10–11.9	1.1–11	Various	$\text{N}_2/\text{dye}$	305
$\text{CS}_2$	${}^1\text{A}_2$ or ${}^3\text{A}_2$		2.89	180	$\text{CS}_2$	$\text{N}_2$	307
	${}^3\text{A}_2$						
$\text{NO}_2$	${}^3\text{A}_2$	${}^{10}2^4$	1.20	69	$\text{CS}_2$	$\text{N}_2/\text{dye}$	306
	${}^2\text{B}_{1u}$ , ${}^2\text{B}_{2g}$	Various	70–82			FLPDL	309, 310
	${}^2\text{B}_{1u}$		~1			FLPDL	311
	${}^2\text{B}_{1u}$ , ${}^2\text{B}_{2g}$		45.4–55.5	5.7–10.6	$\text{NO}_2$	FD ruby	312
						FD Nd	
						FLPDL	313
	${}^2\text{B}_{2g}$		30.3, 114			$\text{Ar}^+$	314
	${}^2\text{B}_{1u}$		30			(488 nm) $\text{Ar}^+$ -single mode (514 nm)	
	${}^2\text{B}_{2g}$		100			(514 nm) $\text{Ar}^+$ -single mode (514 nm)	314
	${}^2\text{B}_{1u}$	$K_a = 0$	33	30	$\text{NO}_2$	$\text{N}_2/\text{dye}$	315
	${}^2\text{B}_{1u}$	$K' > 0$	36	10	$\text{NO}_2$	$\text{He}-\text{Cd}$	316

TABLE II. Collisionless Fluorescence Lifetimes  $\tau_{10}$  and Collisional Quenching Cross Sections  $\sigma_0$  for Gaseous Molecular Species Prepared in Single Vibronic States and Studied by Time-Resolved Laser-Induced Fluorescence<sup>a,b</sup>

Species	Vibronic state		$\tau_{10}, \mu\text{s}$	$\sigma_0$ (at 300 K), $10^{-16} \text{ cm}^2$	Collision partner	Laser system	Ref
	Notation	$v (J)$					
SO <sub>2</sub>	<sup>1</sup> B <sub>1</sub>		35.7	250	SO <sub>2</sub>	FQ Nd	312
	<sup>3</sup> B <sub>1</sub>	Thermal	787 <sup>e</sup>	0.12	SO <sub>2</sub>	SRS shifted FD ruby	317
SO <sub>2</sub>	<sup>1</sup> B <sub>1(I)</sub>	Various	80–530	238–412	SO <sub>2</sub>	FD Nd-YAG/dye	318
	<sup>1</sup> B <sub>1(I)</sub>	Various	59	10.1–34.4	SO <sub>2</sub>		
H <sub>2</sub> CO	<sup>1</sup> A <sub>2</sub>	<sup>4</sup> 2 <sup>6</sup> <sup>1</sup>	0.027			N <sub>2</sub>	250
	<sup>1</sup> A <sub>2</sub>		0.020–0.28	39–99	H <sub>2</sub> CO	FD ruby/dye	252
HDCO	<sup>1</sup> A <sub>2</sub>		0.018	310	Air	N <sub>2</sub>	251
	<sup>1</sup> A <sub>2</sub>		0.016	80	Air	N <sub>2</sub>	251
D <sub>2</sub> CO	<sup>1</sup> A <sub>2</sub>		0.08–0.29	18.1–30.3	HDCO	FD ruby/dye	252
Cl <sub>2</sub> CS	<sup>1</sup> A <sub>2</sub>		0.05–4.54	3.7–35.1	D <sub>2</sub> CO	FD ruby/dye	252
CH <sub>3</sub> I		37			Cl <sub>2</sub> CS	FLPDL	331
CrO <sub>2</sub> Cl <sub>2</sub>		0	1.34	250	CrO <sub>2</sub> Cl <sub>2</sub>	FD Nd-YAG/dye	332
trans-Glyoxal	<sup>1</sup> A <sub>u</sub>	0 °	2.1	1.3–17	Various	N <sub>2</sub> /dye	253
	<sup>3</sup> A <sub>u</sub>	Thermal	3300 <sup>e</sup>	0.077–7.2	Various	N <sub>2</sub> /dye	254
cis-Glyoxal	<sup>1</sup> A <sub>u</sub>	Various	0.82–2.41	13	<i>trans</i> -H <sub>2</sub> C <sub>2</sub> O <sub>2</sub>	N <sub>2</sub> /dye	256, 257
	<sup>1</sup> A <sub>u</sub>	Various	(4–11)10 <sup>-3</sup>			N <sub>2</sub> /dye	255
trans-Glyoxal-d <sub>2</sub>	<sup>1</sup> A <sub>1</sub>	0 °	0.96	50	<i>cis</i> -H <sub>2</sub> C <sub>2</sub> O <sub>2</sub>	N <sub>2</sub> /dye	255
	<sup>1</sup> A <sub>u</sub>	0 °	11.4	3.7–35.1	Various	N <sub>2</sub> /dye	253
Propynal	<sup>3</sup> A <sub>u</sub>	Thermal	6.1	0.016	O <sub>2</sub>	N <sub>2</sub> /dye	254
				0.021	<i>trans</i> -D <sub>2</sub> C <sub>2</sub> O <sub>2</sub> ( <sup>1</sup> A <sub>g</sub> )	N <sub>2</sub> /dye	
Methylglyoxal	<sup>1</sup> A <sup>"</sup>	0 °	0.99	7.8–176	Various	N <sub>2</sub> /dye	266
	<sup>3</sup> A <sup>"</sup>	Thermal	383 <sup>e</sup>				
Biacetyl	<sup>1</sup> A <sup>"</sup>	Various	800°				
	<sup>3</sup> A <sup>"</sup>	Various	4, 0.024 <sup>d</sup>	9	Methylglyoxal	FD FLPDL	267
Biacetyl	<sup>1</sup> A <sub>u</sub>	Thermal	0.023	0.012	O <sub>2</sub>	N <sub>2</sub> /dye	261–266
	<sup>1</sup> A <sub>u</sub>		0.005–0.01	0.176			268
Biacetyl	<sup>3</sup> A <sub>u</sub>	Thermal	18, <sup>d</sup> 1850°	1920 <sup>e</sup>	Methylglyoxal	N <sub>2</sub> /dye	269
			0.01–1	(0.18–15)10 <sup>-7</sup>	O <sub>2</sub>	N <sub>2</sub> /dye	269
Methyltriazolinedione	<sup>3</sup> A <sub>u</sub>	Thermal	1510 <sup>e</sup>	<2 × 10 <sup>-6</sup>	Olefins	N <sub>2</sub> /dye	270
	<sup>1</sup> A <sub>u</sub> , <sup>3</sup> A <sub>u</sub>		0.010		Biacetyl	FD ruby	268
Benzoquinone			22 <sup>d</sup>	110	Biacetyl	N <sub>2</sub> /dye	268
	<sup>1</sup> B <sub>1g</sub>		14.7–17.3	47	Various	N <sub>2</sub> /dye	271, 272
Benzoquinone-d <sub>4</sub>	<sup>3</sup> A <sub>u</sub>		27.7	12.6–83 × 10 <sup>-5</sup>	Benzoquinone	FLPDL	275
	<sup>1</sup> B <sub>1g</sub>		10.9–15.1	60	Various	FLPDL	323
s-Tetrazine	<sup>3</sup> A <sub>n</sub>		57		Benzoquinone-d <sub>4</sub>	FLPDL	323
	<sup>1</sup> B <sub>3u</sub>		<0.1			FLPDL	323
Quinoxaline	<sup>3</sup> B <sub>3u</sub>		72 <sup>e</sup>			FLPDL	330
	<sup>1</sup> A <sub>1</sub> , <sup>1</sup> B <sub>2</sub>		1–45	~80	Quinoxaline	FLPDL	330
Diazanaphthalenes	S <sub>1</sub>		1–50			FD FLPDL	329
	S <sub>1</sub>		9.1	30	Benzophenone	FD ruby	321
Benzophenone	T <sub>1</sub>		7200 <sup>e</sup>	0.13	Benzophenone	FD ruby SRS shifted	322
	S <sub>2</sub> ( <sup>1</sup> B <sub>1u</sub> )		0.04			MLFQ Nd	325
Naphthalene	S <sub>2</sub> ( <sup>1</sup> B <sub>1u</sub> )		0.033–0.043			FQ Nd	327
	S <sub>1</sub>	Various	0.16–0.31			FLPDL	328
Pyrene	S <sub>1</sub>		0.4			FQ Nd	324
	S <sub>2</sub>		0.2	13–200	Various	FQ Nd	324
3,4-Benzpyrene	S <sub>2</sub> , S <sub>1</sub>		0.064			MLFQ Nd	325

<sup>a</sup> See Appendix for a list of abbreviations. <sup>b</sup> Based in part on Yardley's review.<sup>306</sup> <sup>c</sup> Matrix isolated molecule. <sup>d</sup> Collisional-induced ISC; observation of fast and slow components of fluorescence decay. <sup>e</sup> Phosphorescence lifetime.

and therefore the process is completely irreversible. In order to follow the time evolution of  $n_s$ , one must use pulses with duration  $\Delta t$  such that  $\Delta t \ll \tau_R$ . For most statistical molecules  $\rho = 10^4 \text{ cm} (= 5 \times 10^{26} \text{ J}^{-1})$  which requires  $\Delta t \ll 50 \text{ ns}$ , a condition easily met by mode-locked lasers. Unfortunately, the photon band width then exceeds the level spacing and  $n_s$  spans a set of many states.

The statistical limit behavior of exponential radiative decay was observed for molecules in condensed media, such as single crystals of s-tetrazines at low temperatures,<sup>236</sup> matrix-isolated Cr(III) complexes,<sup>237,238</sup> rare earth chelates,<sup>239</sup> and solutions.<sup>240–247</sup> A thorough study of the anomalous  $S_2 \rightarrow S_0$  fluo-

rescence of azulene has been performed by Jortner and co-workers.<sup>248</sup> Recently, Zare and co-workers succeeded in demonstrating irreversible nonradiative decay of truly isolated pentacene molecules in a molecular beam experiment.<sup>249</sup>

For the intermediate case, one distinguishes two situations.

a. *Dense intermediate case*, characterized by  $\rho V \approx 1$  and  $\tau_R \approx \tau_{\max}$ . Now we can no longer define average level densities nor average coupling terms; instead we have to consider the specific level distribution. Thus, the measurements will strongly depend on the initially prepared state. We may expect environmental effects which in most cases, however, will not cause

deviations from exponential behavior of radiative decay. Examples are provided by carbonyl compounds such as formaldehyde,<sup>250-252</sup> glyoxal,<sup>253-260</sup> methylglyoxal,<sup>261-265</sup> propenal,<sup>266,267</sup> biacetyl,<sup>268-272</sup> and other systems.<sup>250-252</sup> It was shown that IC and ISC processes are influenced by the addition of quenching agents. From the pressure dependence of  $\tau_{10}$ , which usually follows a Stern-Volmer law, a collisional quenching cross section  $\sigma_Q$  is determined. As expected,  $\sigma_Q$  also depends on the initially prepared vibronic state. The main results for diatomic species,<sup>227-233,276-304</sup> NH<sub>2</sub> radicals,<sup>305</sup> carbonyl compounds,<sup>250-272</sup> and other systems<sup>273-275</sup> are presented in Table II.

b. *Sparse intermediate case*, characterized by  $\rho V > 1$  and  $\tau_{\max} \gg \tau_R$ . Here  $V$  is large for some particular levels, but  $\rho$  is small and the level spacing exceeds the radiation bandwidth. An initially prepared emitting state will evolve in time to other states to which it is strongly coupled, but during the experiment will repeatedly return to the original state. Thus "anomalously long" radiative lifetimes are expected for such molecules,<sup>223,235,306,307</sup> typical examples being CS<sub>2</sub>,<sup>306,308</sup> NO<sub>2</sub>,<sup>309-316</sup> SO<sub>2</sub>,<sup>312,317,318</sup> and NSF.<sup>319</sup> Now the decay is nonexponential and may show oscillatory behavior (quantum beats).<sup>221,320</sup> Lifetimes strongly depend on the particular initial state,  $n_s$ . The quantum yield, which is unity for a completely isolated molecule, decreases at higher pressures where collisional deactivation of  $n_s$  becomes important.<sup>306</sup> This type of "small" molecule behavior also appears in some "large" molecules like benzophenone,<sup>321,322</sup> benzoquinone,<sup>323</sup> pyrene,<sup>324</sup> benzpyrene,<sup>325</sup> naphthalene,<sup>326-328</sup> diazanaphthalenes,<sup>329</sup> s-tetrazine,<sup>326,330</sup> biacetyl,<sup>267-272</sup> thiophosgene,<sup>331</sup> chromyl chloride,<sup>332</sup> and quinoxaline.<sup>273</sup> In biacetyl<sup>271,272</sup> and methylglyoxal,<sup>260-265</sup> reversible intersystem crossing and long-lived collisionally induced phosphorescence have been observed. In addition, the appearance of consecutive fast and slow components<sup>265,271,272</sup> of the fluorescence indicates, as predicted by theory, that in the same molecule features of radiative decay may vary from a completely coherent to an incoherent behavior.<sup>265,272</sup>

We now turn to nonradiative energy-transfer processes. In all gas-phase cases one may observe intermolecular energy transfer of vibrational energy in the ground electronic state to vibrational, rotational, and translational states of collision partners. This subject has been reviewed by many authors<sup>333-335</sup> and will not be discussed here. In condensed phases, in which all molecules behave statistically, intra- and intermolecular electronic transfer processes occur very fast and have to be studied with ps techniques (section C). Still, many energy-transfer studies can be carried out on a nanosecond time scale.<sup>336-345</sup>

## B. Excited-State Absorption Spectroscopy. Photoquenching

In the previous section we were mainly concerned with photophysical decay of an isolated molecule excited to a single vibronic state. Complementary information may be obtained from excited-state absorption, measured by flash spectroscopy methods,<sup>346,347</sup> where a powerful flash source excites the molecules and a synchronized probe source monitors the transient absorption. Absorption measurements of the excited state are less sensitive than studies of emissive properties because of a much lower signal-to-noise ratio. Concentration considerations limit flash spectroscopy experiments to condensed phases, although some laser studies in the gas phase have been reported.<sup>348,349</sup> Prelaser flash experiments were carried out with microsecond time resolution and were therefore limited to studies of triplet states, for which even a CW laser method has been successfully employed.<sup>350</sup> However, the availability of pulsed lasers permits the direct observation of the S<sub>1</sub><sup>v</sup> states (picosecond time scale) or vibrationally relaxed S<sub>1</sub><sup>0</sup> states

(nanosecond time scale).

Following the first laser flash spectroscopy experiment of Weiss and co-workers,<sup>351</sup> most studies use nanosecond pulsed lasers for the excitation stage. These include the Q-switched ruby laser<sup>117,351-354</sup> and its frequency doubled (FD) version,<sup>355-359</sup> the Nd laser operating in its FD,<sup>360-363</sup> tripled (FT),<sup>356,364</sup> or quadrupled (FQ)<sup>360a,365-369</sup> operational mode; and the nitrogen laser<sup>339,360,370-377</sup> and various dye lasers.<sup>347,363,375-377</sup>

Because of the short lifetime of the excited molecule, proper synchronization with the probing light source is crucial. This can be achieved simply by using a CW lamp or a CW laser,<sup>351-354,378</sup> or by an electronically triggered flash lamp (FL).<sup>355,356,359,370-372</sup> Other ingenious methods include laser-induced sparks,<sup>379</sup> laser-induced fluorescence continuum (LIFC),<sup>380,381</sup> dye lasers pumped by the exciting laser,<sup>375,376</sup> or employment of a split-off part of the exciting laser beam,<sup>377,382</sup> all in conjunction with variable optical delays. Extension of these methods to picosecond resolution is described in section C. Geometrical problems of a laser flash spectroscopy set-up have been discussed by Bebelaar<sup>356</sup> and some common difficulties in interpretation by Goldschmidt.<sup>383</sup>

Results for triplet state T<sub>1</sub> and for the singlet state S<sub>1</sub> can be expressed in terms of the absorption cross-sections  $\sigma_T$  and  $\sigma_{12}$ , respectively (see Figure 8). In particular, aromatic molecules (ref 340, 354-359, 369, 380, 384, 392), various charge-transfer (CT) complexes,<sup>372</sup> biological systems,<sup>386,387</sup> and laser dyes (ref 377, 378, 382, 388-391, 393, 405) have been studied.

In Table III we present typical data for  $\sigma_{12}$ , together with experimental details. It is evident from Table III that, particularly for laser dyes,  $\sigma_{12}$  is often so large that the pumping rate  $\sigma_{12}(P)/I_p$  for the transition S<sub>1</sub> → S<sub>2</sub> (see Figure 8) can become comparable to decay processes of S<sub>1</sub><sup>0</sup>. For example, in most dyes  $\sigma_{12}(P) > 10^{-16}$  cm<sup>2</sup>/molecule; therefore, a typical pump intensity  $I_p \approx 10^{26}$  photons/cm<sup>2</sup> sec (corresponding to 100 MW/cm<sup>2</sup> at 350 nm) results in a reabsorption rate  $\sigma_{12}(P)/I_p \approx 10^{10}$  s<sup>-1</sup> which competes with the average fluorescent decay rate<sup>394</sup>  $1/\tau_{10} \approx 10^9$  s<sup>-1</sup>. Since the radiationless decay rate S<sub>2</sub> → S<sub>1</sub> is very fast, molecules subjected to high pump intensities will simply circulate many times between S<sub>1</sub> and S<sub>2</sub> before emitting a fluorescent photon. Consequently, the quantum yield becomes intensity dependent. This photoquenching effect has been observed<sup>126,389,390,393</sup> and has also been interpreted kinetically.<sup>63</sup> The main results of the analysis are the following.

a. The total S<sub>1</sub> → S<sub>0</sub> fluorescence output is intensity dependent. For moderate pump intensities the reciprocal relative quantum yield  $\phi_0/\phi$  follows a Stern-Volmer type law for steady-state photoquenching

$$\phi_0/\phi = 1 + \tau_{10}\sigma_{12}(P)/I_p \quad (19)$$

The importance of eq 19 lies in that one can obtain  $\sigma_{12}(P)$  from a simple photoquenching study without requiring a complete flash spectroscopy set-up.

b. For higher pump intensities the integrated fluorescence signal will reach a maximum at  $I_p$  given by

$$I_p(\text{max}) = [\tau_{21}\tau_{10}\sigma_{01}(P)\sigma_{12}(P)]^{-1/2} \quad (20)$$

This relationship enables us to determine indirectly the otherwise difficult-to-obtain nonradiative lifetime  $\tau_{21}$  of the S<sub>2</sub> → S<sub>1</sub> transition, from measurements of  $I_p(\text{max})$ .

It should be noted that at extremely high pump intensities complications arise caused by bleaching in saturable absorbers, due to resonant stimulated emission<sup>39</sup> or by intense absorption from an S<sub>1</sub><sup>v</sup> state (antibleaching) which both compete with the fast vibrational relaxation; i.e.,  $\sigma_e/I_p \gg 1/\tau_v$ , and  $\sigma_{12}(P)/I_p \gg 1/\tau_v$ . In this case photoquenching, which requires a vibrationally relaxed S<sub>1</sub><sup>0</sup> state, becomes negligible.

Studies of bleaching and antibleaching have been performed

TABLE III. Molecular Cross Section  $\sigma_{12}$ , at the Peak of the  $S_1 \rightarrow S_2$  Absorption Band for Compounds Studied by Laser Flash Spectroscopy<sup>a</sup>

Compound <sup>b</sup>	Laser source	Probing source	Temporal resolution (ns)	$\lambda_{\max}^c$ (nm)	$\sigma_{12}$ ( $10^{-16} \text{ cm}^2$ )	Ref
Naphthalene	FD ruby or FT Nd	FL	3	420	0.016	356
	FD ruby	FL	20	417	0.012	358
Anthracenes	FD ruby	FL	5	420	0.05–0.1	355
Anthracene	$N_2$	Pulsed Xe	10	600	0.04	370
	FD ruby	FL	15	423	1.5	359
	FD ruby	FD ruby	15	At 347.1	1.5	359
1,2 BA	FD ruby	Xe	20	590	0.3	354
	FD ruby	LIFC	10	560	1	380
	FQ Nd	FL	20	485	0.01	358
1,2 BA (vapor)	FD ruby	Arc	10	520	380	
Pyrene	FD ruby	Xe	20	450	0.15	354
Perylene	$N_2$	Pulsed Xe	10	700	0.014	340
Phenanthrene (in PMMA)	FD ruby	LIFC	10	535	0.6	380
Coronene	$N_2$	FL	10	525	0.023	371
	FD ruby	LIFC	10	525	0.023	370
Various aromatics	FD ruby	FL	20	450–700	Rel data only	384
DEA	$N_2$	Pulsed Xe	10	620	$2 \times 10^{-5}$	371
TCNB–aromatics	$N_2$	Pulsed Xe	10	460	0.04	372
CT complex						
PMDA–mesitylene	$N_2$	Pulsed Xe	10	660	$7 \times 10^{-3}$	372
CT complex						
Polymethine dyes	ML ruby	LIFC	$10^{-2}$	800	2–8	405
DCI	Ruby	LIFC	10	550	1.1	390
	Ruby	Ruby	10	At 694.3	7.2	390
HITC	ML ruby	ML ruby	0.3	At 694.3	1.1	382
DTTC	ML ruby	ML ruby	0.3	At 694.3	1.5	382, 388
DTC	ML ruby	ML ruby	0.3	At 694.3	0.7	382
DCI	ML ruby	ML ruby	0.3	At 694.3	1.0	382
R6G	FD Nd	FD Nd	40	At 530	1.2	389
	$N_2$	$N_2$ laser	5	At 337.1	3.7	404
RB	$N_2$	$N_2$ laser	5	At 337.1	3.9	377
Na-fluoresceine	$N_2$	$N_2$ laser	5	At 337.1	3.7	377
DAMC	$N_2$	$N_2$ laser	5	At 337.1	5.5	377
PPO	$N_2$	$N_2$ laser	5	At 337.1	1.5	377
POPOP	$N_2$	$N_2$ laser	5	At 337.1	6.6	377
DiMePOPOP	FD ML	FD ML	0.3	At 347.1	1.8	382
BBO	Ruby	Ruby	0.3	At 347.1	2.1	382
CVP	$N_2$	$Ar^+$ laser	10	At 514.5	3	378

<sup>a</sup> See Appendix for list of abbreviations. <sup>b</sup> All compounds were measured in solution except where indicated otherwise. <sup>c</sup>  $\lambda_{\max}$  denotes the wavelength at maximum absorption unless indicated as "at . . .".

employing laser flash spectroscopy techniques.<sup>400–402</sup> The absorption cross-sections relevant for bleaching have been obtained by kinetic analysis<sup>403</sup> or other methods.<sup>404</sup>

### C. Ultrafast Processes

By the term ultrafast processes we refer to photophysical and photochemical dynamics in the picosecond and subpicosecond time range.<sup>406–408</sup> Observation of these events necessitates the use of mode-locking techniques and ultrafast detection methods as described in section I.C. Although some suitable equipment is available commercially, most experiments call for a sophistication not met by standard available instrumentation. In fact, ultrafast processes have been studied mainly by those few groups that have developed the appropriate equipment and the elegant measuring techniques. Of course, the extremely short pulses and the intrinsic high intensity are likely to amplify artifacts already encountered in nanosecond laser studies, and this may account for discrepancies between results of different laboratories. Absolute values of molecular parameters determined by picosecond methods may well prove to be erroneous.<sup>116,408</sup>

Most primary photophysical and photochemical processes in condensed media occur in the picosecond time range. These include orientational relaxation in liquids,<sup>409–412</sup> dynamical properties of solvated electrons<sup>413–416</sup> and ultrafast energy

transfer<sup>417,418</sup> and decay processes in molecules.<sup>419–423</sup> Many investigations involve dye molecules. For example, the recovery time of the ground state  $S_0$  population determines the mode-locking ability of the dye,<sup>411,424–427</sup> vibrational relaxation of an  $S_1^V$  state determines its Q-switching properties, and the particular values of  $\tau_{10}$ ,  $\tau_{V'}$ ,  $\tau_V$ ,  $k_{ST}$ ,  $\sigma_e$ ,  $\sigma_{12}$ , and  $\sigma_T$  (see Figure 8) control its lasing ability. Most of these parameters have been directly measured using picosecond laser pulses (ref 242, 243, 388, 405, 428–440). The vibrational relaxation in the  $S_0$  state and the vibrational energy transfer have been investigated by monitoring the decay of the anti-Stokes Raman signal of an  $S_0^V$  level populated through an SRS process. The method was initially applied to gases in the nanosecond range<sup>441–447</sup> and was extended to liquids with the aid of picosecond pulses.<sup>449–453</sup>

Generally, ultrafast studies are based on the following techniques: a train of picosecond pulses, or preferably a single picosecond pulse, excites the molecule to some initial state,  $S_1^V$ . The dynamics of this state is then measured by another pulse, called the probe or the interrogation pulse, which is incident on the sample after a variable delay provided by optical means.<sup>406,407</sup> The probing pulse can also be a picosecond continuum (ref 405, 431, 432, 439, 454–465). Ultrafast Kerr shutters and assorted nonlinear optical devices are widely used for synchronization.<sup>412,466</sup> Recently, a novel transient grating method for ultrafast spectroscopy has been reported.<sup>467</sup> The

TABLE IV. Some Photophysical and Photochemical Picosecond Studies of Neat Liquids or Solutions<sup>a</sup>

Species	Process studied or derived parameter	Ref	Species	Process studied or derived parameter	Ref
CS <sub>2</sub> , Kerr liquids	Orientational relaxation in ultrafast light gates	412	Coumarin in CCl <sub>4</sub>	$\tau_v''$ using double pulse excitation	436
CS <sub>2</sub>	Kerr effect, use of self-focusing for time resolved ps spectroscopy	466	Various liquids	Dephasing time and $\tau_v''$ by coherent and incoherent stimulated anti-Stokes Raman scattering	448–451
R6G	Orientational motion in solution	409	CH <sub>3</sub> CCl <sub>3</sub> and CD <sub>3</sub> OD	Rate of intermolecular vibrational energy transfer between proto and deutero modes is $8 \times 10^{10}$ s <sup>-1</sup> .	453
DODCI	Orientational motion in solution	411	Tetracene dianions	ps kinetics studied by double-beam ps spectrometer	423
Electrons in water	Relaxation of the excess electron	413	Anthracene	PSFS using ps continuum; studies in mixed crystals	457, 460
Electrons in ammonia	Relaxation studies	414	ADMA	Solvent induced intermolecular electron transfer by PSFS	458
2Na <sup>+</sup> (tetraphenyl-ethyl-ene) <sup>2-</sup>	Solvent effect on the kinetics of electron photoejection	416	Aromatic ketones	PSFS in solutions	461
Dye molecules	Rise and decay times of S <sub>1</sub> → S <sub>0</sub> fluorescence; quantum efficiency $\phi$ and generation of stimulated emission; S <sub>2</sub> → S <sub>1</sub> IC lifetimes ( $\tau_v'$ = 30 ps for CVP in methanol and 56 ps in ethylene glycol)	394 411 424–429 433–435	1,2-BA s-Tetrazine Transition metal coordination compounds	PSFS study of energy transfer PSFS PSFS	462 463 465
R6G	$\tau_v'' = 8.3$ ps in ethanol	452	DODCI, BDN	PSFS using ps continuum	432
Azulene	$\phi = 10^{-7}$ for S <sub>2</sub> → S <sub>1</sub> fluorescence $\tau_v' = 7.5$ ps in ethanol, rate-determining process in doubt	430	Porphyrrins		
R6G, DPA	Photoquenching of TPF and TPA	116	Polymethyne dyes	$\sigma_{12}$ from PSFS; production of a photoisomer	405
DODCI	Recovery time of S <sub>0</sub> population 10 ps in water. Disagreement with value of 56 ps	411 425, 432 440	DTDC	PSFS	388
CV	IC processes	431	DTTC, DCI	PSFS	439
POPOP	Rate of energy transfer to perylene $5 \times 10^{10}$ s <sup>-1</sup> in vapor phase	438	Kodak, Q-switch dyes	Molecular relaxation studies using crossed beam techniques	428
Benzophenone	$k_{ST} = 6 \times 10^{10}$ s <sup>-1</sup> in ethanol and $3 \times 10^{10}$ s <sup>-1</sup> in benzene; rate of energy transfer to piperylene and naphthalene $\sim 10^{11}$ s <sup>-1</sup>	421, 459	DCI, DDI, DODI, DTDI	Fluorescence and photochemical studies	242, 243
Benzene	Intermolecular collision-induced energy transfer	422	Tetraphenylhydrazine	Dynamics of photodissociation	464
Anthracene-DEA	Excited-state CT interactions and kinetics; critical transfer radius 0.8 nm	417			
I <sub>2</sub> in solution	Collision induced predissociation; dynamics inside (400 ps) and outside (ns range) the solvent cage	418			
D <sub>2</sub> O, H <sub>2</sub> O	Inverse SRS and generation of ps continuum	454, 455			
Alcohols	Time resolved SRS	456			

<sup>a</sup> See Appendix for a list of abbreviations.

techniques and illustrative studies have been reviewed by leading workers in the field.<sup>406–408,468–470</sup> The power of these methods is self-evident and one may expect further rapid development.

In Table IV we summarize dynamical properties of excited species studied by ps techniques, omitting biological systems.<sup>471,472</sup>

#### IV. Laser Photochemistry

In this section we explore the initiation of chemical reactions by laser irradiation. In addition to the use of lasers merely as a light source for conventional photochemistry,<sup>473–476</sup> specific laser-induced effects have been studied. Among these we may include selective photochemical reactions and isotope separation processes, nonlinear photochemistry, and mechanistic kinetic investigations.<sup>477–479</sup>

Many laser-induced chemical reactions were conducted under uncontrolled conditions. In some cases the possibility of breakdown mechanisms due to impurities cannot be ruled out.<sup>480–486</sup> As was shown by Dowley and Peticolas,<sup>487</sup> even small amounts of impurities may affect the product formation

in a high-intensity laser-induced process, causing pyrolysis reactions<sup>488</sup> or initiating other thermal effects,<sup>482,489</sup> some even with incoherent light sources.<sup>490</sup> We shall not discuss these studies any further but shall rather concentrate on quantitative and well-defined laser-induced photochemical processes.

#### A. Flash Photolysis and Transient Photochemistry<sup>346,347</sup>

Whenever an excited molecule does not fluoresce, it loses its excess energy by nonradiative decay routes or by a photochemical transformation. This could be a cis-trans isomerization process,<sup>491</sup> an irreversible photochemical process,<sup>475,476</sup> or a transient photochemical reaction. The short pulse duration obtainable with lasers makes them an ideal tool for investigating transient photochemical events in a standard laser flash set-up, as described in section III.B. All-important information can be obtained on the photochemical behavior of the excited molecule immediately after the excitation process.<sup>492,493</sup> In most cases transient species such as radicals,<sup>117,494–501</sup> excimers,<sup>502,503</sup> exciplexes,<sup>504–511</sup> F centers,<sup>512</sup> solvated electrons,<sup>513–515</sup> singlet oxygen and ozone,<sup>516–521</sup> and biological<sup>387,522–526</sup> or

TABLE V. Representative Studies of Photochemical Processes by Laser Flash Spectroscopy and Related Techniques<sup>a</sup>

Species	Laser source	Probing source	Temporal resolution (ns)	Species detected or process studied	Ref
I <sub>2</sub> (gas phase)	FLPDL	I <sub>2</sub> lamp	10 <sup>3</sup>	I	348
I <sub>2</sub> /water	FD Nd	FL	20	I <sub>2</sub> <sup>-</sup> .	360, 362
I <sub>2</sub> /solvents	FD Nd	FL	20	I-solvent	360, 362
	FT Nd	FL	5	CT complex	364
I <sub>2</sub> + I <sup>-</sup> /t-BuO	FD Nd or FD Nd/dye	Pulsed Xe	20	I <sub>6</sub> <sup>-</sup> .	363
I <sub>2</sub> + I <sup>-</sup> /alcohols	Fd Nd	FL	20	I <sub>4</sub> <sup>-</sup> , I <sub>2</sub> <sup>-</sup> .	361
I <sup>-</sup> /solvents	FQ Nd	FL	20	I + I <sup>-</sup> → I <sub>2</sub> <sup>-</sup>	368
I <sub>3</sub> <sup>-</sup> /water	N <sub>2</sub>	Pulsed Xe	10	I <sub>3</sub> <sup>-</sup> → I <sub>2</sub> <sup>-</sup> + I	558
HgI <sub>2</sub> /water	FQ Nd	FL	20	I <sub>2</sub> <sup>-</sup>	365
CHI <sub>3</sub> /mesitylene	FT Nd	FL	5	I-mesitylene CT complex	364
KI + KBr/water, methanol	FQ Nd	FL	20	I <sub>2</sub> <sup>-</sup> , IBr <sup>-</sup>	530
Br <sub>2</sub> /water	FQ Nd	FL	20	Br-CT complexes	367
Cl <sub>2</sub> /water	FQ Nd	FL	20	Cl-CT complexes	367
Alkali halides (solid state)	Ruby	FL	50	F centers	512
O <sub>2</sub> <sup>1</sup> A <sub>g</sub>	Ruby Nd	Tungsten-I <sub>2</sub> Tungsten lamp	20 20	Energy transfer Various	516-518 516
O <sub>3</sub>	Ruby FLPDL FLPDL	FL O <sub>2</sub> lamp O <sub>2</sub> lamp	20 10 <sup>3</sup> 10 <sup>3</sup>	Various O <sup>3</sup> (P) + O <sub>3</sub> → O <sup>3</sup> (P) + H <sub>2</sub> O →	521 519 520
Hydrocarbons	FD ruby		20	Free electron dynamics	515
VCZ, ECZ	FD ruby	FL	25	Radical ions	499-501
MB/water	Ruby	Tungsten	50	Various	351
	Ruby	Tungsten-I <sub>2</sub>	50	Various	527
MB/p-chlorophenylglycine	Ruby		20	Photoreduction	529
Eosin Y	Ruby	Tungsten-I <sub>2</sub>	50	Various	527
Polymethine dyes/DMSO	ML ruby	LIFC	10 <sup>-2</sup>	Photoisomer	405
Benzene	FQ Nd	Pulsed Xe	20	Excimer	502
Anthracene/THF	N <sub>2</sub>		10	Photocurrent	516
Anthracene/methanol	FD ruby	FL	15	Photoionization	359
Stilbenes	FD ruby	FL	50	Cis-trans Isomerization	528
Methylstyrene	FD ruby	FL	25	Ionic photopolymerization	545
Pyrene	N <sub>2</sub>	FL	10	Radical ion formation, electron transfer to DEA and anthracene	554
	N <sub>2</sub>	FL	10	Photoconductivity	373
Pyrene/micelles	FD ruby	FL	20	Photoionization	514
Pyrene/cyclohexane	N <sub>2</sub>	FL	10	Excimer	503
Mono- and disodium salts of tetracene	Ruby	CW lamp	20	Various	555
Biphenyl radical anion	Ruby	Hg lamp	20	Electron recombination	117
β-Naphthol	N <sub>2</sub>	FL	10	Triplets and solvated electron	513
Aromatics	FQ Nd	FL	20	Triplet state quenching by inorganic ions	369
Diazines, s-triazine	FQ Nd	Xe lamp	20	Radicals	494, 495
Methylated p-benzoquinone	FD ruby	LIFC	10	Deprotonation	492
Benzophenone	FD ruby	FL	20	Hydrogen abstraction, cage effect	532
	FD ruby	FL	25	Triplet quenching by amines	541
Acetophenone/isooctane	FD ruby	Hg lamp	30	Energy transfer	341
Acetophenone/solvents	FQ Nd	FL	20	Ketyl radical photoreduction triplets and photoenolization	531
Carbonyl compounds	FQ Nd	FL	20	Triplet quenching by inorganic ions	369
Indoles	FQ Nd	FL	20	Hydrated electrons	366
Amino acids	FQ Nd	Xe lamp	20	Various	526
Tryptophan/water	FQ Nd	FL	20	Hydrated Electrons	525
Chlorophyll a	FD ruby/dye		20	Photoconductivity	524
PTH/micelles	N <sub>2</sub>	FL	10		544
	FD ruby	FL	25	Photoionization	547
TPMD/isopentane	N <sub>2</sub>		10	Photoconductivity	550
DPPD	FD ruby		25	Photoconductivity	497
TCNB CT complexes	FD ruby	FL	25	Ions	509, 533-540
PMDA CT complexes	FD ruby	FL	25	Ions	509, 533, 539
ADMA	FD ruby	FL	25	CT interactions	458, 544
DMA-pyrene, hydrocarbons	FD ruby	FL	25	Photoconductivity and exciplexes	496, 498
Pyrene-dicyanobenzene	FD ruby	FL	25	Solvated ion-pair	543
TPMD-various molecules	FD ruby or FQ Nd	Pulsed Xe	20	Exciplexes	504
TPMD-naphthalene	N <sub>2</sub>	FL	10	Exciplexes	508
TPMD-biphenyl	N <sub>2</sub>	FL	10	Exciplexes and triplet quenching	508
Pyrene-DEA	N <sub>2</sub>	FL	10	Exciplexes and fluorescence quenching	507
Anthracenes-DEA, TPMD	N <sub>2</sub>	FL	10	Induced ISC with DEA; ion pair formation	506
Aromatics-DEA	N <sub>2</sub>	FL	10	Exciplexes	505

<sup>a</sup> See Appendix for a list of abbreviations.

molecular moieties<sup>351,527-545</sup> can be followed spectroscopically. Transient photoconductivity studies may be used to follow photoionization processes (ref 117, 359, 373, 524, 546-556).

Typical examples of transient photochemistry are summarized in Table V. It can be seen that two types of molecular systems have attracted considerable experimental effort.

a. Iodine atom recombination reactions: here the formation of iodine-solvent CT complex<sup>345,360,362,364</sup> or the formation of iodine radical anions<sup>361,363,368,530,558</sup> is followed. Using picosecond techniques Eisenthal and co-workers could distinguish between recombination inside and outside the solvent cage (Table IV).<sup>418</sup> The appearance of the transient absorption of the iodine-mesitylene CT complex in the laser photolysis of iodoform indicated that the primary photochemical process is the formation of iodine atoms.<sup>364</sup> Similar results were obtained for other halogens and halides.<sup>365,367</sup>

b. Charge-transfer complex formation in the excited state and photoionization processes: this was studied mainly by Ottolenghi and co-workers and by Mataga and co-workers who have also reviewed some of their work on this subject.<sup>559,560</sup>

Often the intensity dependence of transient phenomena is used to deduce the quantum nature of the primary process.<sup>548,550,555</sup> However, inevitable artifacts should then be distinguished from real phenomena.<sup>117</sup>

## B. Laser-Induced Chemical Reactions

The possibility of inducing specific reactions using excitation by lasers is intriguing to chemists. The subject has been reviewed several times in the past few years (ref 333-335, 477, 478, 561-570). We first discuss some general features pertaining to vibrational photochemistry; that is to say, selective (nonthermal) stimulation of elementary chemical reactions in the gas phase through absorption of infrared laser photons by a reactant. The use of visible radiation for activating reactions is covered in section C, under the headings (a) LIR and (b) SPP.

Following absorption of intense (infrared) laser radiation by a low-pressure collisionless sample, the distribution of the molecular population over the energy levels of a preselected vibrational mode becomes non-Boltzmann, and the effective temperature is undefined.<sup>571-573</sup> Monochromatic radiation of frequency  $\nu$  will selectively excite only the particular vibrational normal mode with which it is resonant. Phenomenologically, this may be associated with extension of a localized bond which is now expected to become more reactive.<sup>567,573</sup> This model implies the absence of instantaneous intramolecular randomization processes<sup>249</sup> as can be justified on theoretical grounds<sup>574</sup> and can be supported by experimental evidence discussed in this section. Adding energy in the form of heat leads to equilibrium excitation of all degrees of freedom and usually activates the weakest bond.<sup>575,576</sup> It is worth noting that electronically excited species are not always more reactive than their ground-state counterparts.<sup>577</sup>

For a simplified description<sup>564,578-580</sup> we consider a unimolecular dissociation<sup>581-584</sup> or isomerization reaction<sup>585-588</sup> which obeys the empirical Arrhenius rate equation

$$k_r = A \exp(-E_a/RT) \quad (21)$$

where  $E_a$  denotes the activation energy. Generally,  $E_a = E_a^T$  is measured at thermodynamic equilibrium for the various degrees of freedom, and is dependent on the internal states of the molecule. For small molecules, eq 21 may conceivably serve to describe the dynamics of bimolecular abstraction reactions<sup>575,576,589-593</sup>



involving the dissociation of a specific bond in the reactant BC

and formation of a new bond AB. If the major component of the reaction coordinate is a particular vibrational coordinate of the reactant, a molecule excited in that coordinate to a vibrational level at energy  $Nh\nu$  above the ground state experiences an "effective" barrier  $E_a^L = (E_a^T - Nh\nu)$ , where  $N$  denotes Avogadro's number. Expressed more accurately, the laser does not affect  $E_a$ , but rather channels the energy into the selected reactant mode. Assuming that the preexponential factor  $A$  in eq 21 remains constant, it is then possible to drive a specific reaction at a rate  $k_L$ , enhanced by a factor  $\exp(Nh\nu/RT)$  compared to the thermal reaction rate  $k_T$ . The acceleration may be significant even when  $Nh\nu < E_a$ .<sup>582,583,594-597</sup> For orientation,  $Nh\nu = 12$  kJ/einstein for CO<sub>2</sub> laser radiation,  $RT = 2$  kJ/mol at room temperature, and  $E_a^T \approx 300$  kJ/mol for a typical chemical reaction. Of course, the exact amount of useful radiative energy that must be made available for surmounting the barrier ( $E_a$ ) depends on the shape of the multidimensional potential energy hypersurface for the particular reaction,<sup>598</sup> which also determines the relative utility of vibrational and translational energy.<sup>575,576</sup>

Rapid vibrational to vibrational (V-V) and also slower vibrational to rotational or translational (V-R/T) relaxation processes<sup>385</sup> will drain the initially selective excitation of the reactant. The localized vibrational energy is redistributed over other molecular coordinates and other degrees of freedom, thus contributing to the general heat bath of the medium. Most relaxation processes are collisional in nature<sup>565,599,600</sup> and may be suppressed by working at sufficiently low gas pressures. In this case, however, the efficiency of laser activation is impaired by the rotational "bottleneck" caused by pumping from a single rotational sub-level that contains only a fraction of the total population. This limitation may be serious in molecules for which the rotational line spacing is larger than the power broadening due to the radiation field. It may be overcome by adding an inert diluent gas, such as argon, so as to make the rotational relaxation faster than the laser excitation rate. The optimal pulse duration  $\tau$ , therefore, is  $\tau \gg \tau_{rot}$  to avoid bottlenecking, and  $\tau \ll \tau_{V-T}$  to reduce thermal heating.

Occasionally, intramolecular deactivation channels seem to play a role. For example, the first detailed study<sup>601</sup> of the chemiluminescent reaction of O<sub>3</sub> with NO to form NO<sub>2</sub> indicated that the enhanced reactivity upon vibrational excitation of O<sub>3</sub> with a pulsed CO<sub>2</sub> laser appeared to be delayed. The induction time was attributed to migration of the excitation energy of the stretching mode  $\nu_3 = 1043$  cm<sup>-1</sup> in the O<sub>3</sub> molecule to the bending mode  $\nu_2 = 705$  cm<sup>-1</sup>. The intermediate energy-transfer step presumably caused deviations from an Arrhenius-type first-order reaction augmentation. More recent measurements<sup>602-604</sup> argue in favor of a direct mechanism, so that this example cannot be cited as a measure of the rate of intramolecular transfer of vibrational energy.

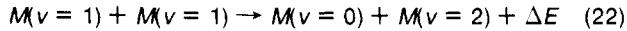
A comprehensive description of laser-driven nonequilibrium reactions involves source parameters such as wavelength, energy, intensity, and irradiation time, and furthermore, system parameters such as sample pressure, ambient temperature, reactive channels, energy distribution over the products, and the rates of reaction and relaxation processes.<sup>582,583,599,605-608</sup> For example, it was shown that for simple abstraction reactions with a given value of  $E_a$  and a comparable value of vibrational excitation of the reactants,  $Nh\nu$  exoergic reactions were barely influenced, while endoergic reactions were speeded up by orders of magnitude.<sup>589-593</sup> In a way, this complements what is said in section V.A regarding chemical lasers; i.e., in some exothermic reactions products are formed in excited vibrational states. Microscopic reversibility<sup>608</sup> then requires that the reverse reactions be speeded up if the reagents are vibrationally excited.

Eventually, (V-R/T) energy dissipation will lead to mere increase of the ambient gas temperature in which  $\Delta T$  may range

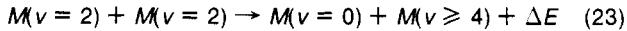
from  $\approx 10$  K when using pulsed CO<sub>2</sub> lasers, to  $\approx 1000$  K for CO<sub>2</sub> CW irradiation.<sup>611</sup> In fact, one of the more difficult experimental and theoretical issues is to distinguish specific-laser from thermal-laser effects.<sup>609-617</sup> This distinction has been ascertained unambiguously only in a few chosen cases, e.g., reactions such as K + HCl or Ba + HF in a crossed-molecular-beam configuration in which all unwanted collisions were eliminated<sup>575,576,618</sup> and conversely, the diametrically opposite case of homogeneous pyrolysis of hydrocarbons where SF<sub>6</sub> or CH<sub>3</sub>F was added to the reactants as a CO<sub>2</sub>-laser-absorbing bath material which acts as a sensitizer.<sup>611-613</sup>

In order for a selective reaction to take place the excited molecules should react before thermalization processes can occur. Generally, this will be true when the energy of the vibrationally excited molecule is comparable to the activation energy. As was noted above, usually  $N\hbar\nu \ll E_a$ ; therefore, absorption of several infrared quanta per molecule would be required for the rate increase to be significant.

Cascade excitation by consecutive absorption cannot be effective: monochromatic radiation in resonance with a particular vibrational-rotational transition  $v = 0, J \rightarrow v = 1, J'$  is, at most, capable of pumping the next few transitions, of the type  $v = 1, J' \rightarrow v = 2, J''$ . Anharmonicity of a molecular oscillator rapidly becomes too large to be compensated by rotational transitions. According to one school of thought (ref 564, 565, 594-597, 619-623), the accumulation of vibrational energy may be brought about by V-V relaxation; this is a faster process than V-R/T relaxation and thus does not cause heating of the sample. At the irradiation densities available with high-flux infrared lasers, the absorbing transition becomes saturated and a large fraction of molecules M will be in the first vibrationally excited state,  $v = 1$ . Upon colliding with one another, redistribution of energy occurs according to

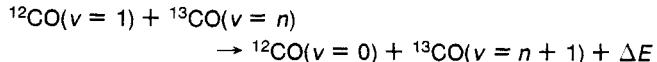


making  $M(v = 0)$  again available for resonant absorption  $v = 0 \rightarrow v = 1$ . Now  $M(v = 1)$  may collide with  $M(v = 2)$ , causing it to reach the state  $v = 3$ . Through further inelastic collisions some molecules rapidly move up the ladder of vibrational energy levels, in steps such as given by eq 22, or in jumps; e.g.,



Unlike radiative transitions which must be in exact resonance (if we neglect power broadening), collisional energy transfer is not sensitive to vibrational anharmonicity. In fact, because of anharmonicity the reactions (eq 22 and 23) are exothermic and the right-hand side products are favored. The (beneficial) excess energy  $\Delta E$  is carried off in the form of translational energy conferred to one or both collision partners. V-V relaxation-induced evolution of the population to high vibrational levels is responsible for the visible fluorescence observed in some gases irradiated with a CW CO<sub>2</sub> laser.<sup>624</sup>

In isotopic mixtures, V-V relaxation pumping may be more pronounced for the heavier species because for them  $\Delta E$  is larger. The mechanism was verified for the reactions of N<sub>2</sub> + O<sub>2</sub> and N<sub>2</sub> + D<sub>2</sub> driven by pulsed discharges<sup>625</sup> and for <sup>12</sup>CO, trapped as impurity in solid argon.<sup>626</sup> Resonant irradiation of the transition  $v = 0 \rightarrow v = 1$  of <sup>12</sup>C<sup>16</sup>O caused luminescence from excited CO (up to  $v = 7 \rightarrow v = 6$ ). The luminescence is predominantly from <sup>13</sup>CO and C<sup>18</sup>O because at the low sample temperatures (10 K) the phonon-assisted excitation transfer of the type



becomes irreversible.<sup>626</sup>

Another approach takes into account the coherent coupling between the radiation field and a molecule undergoing phase-

and energy-changing collisions.<sup>610</sup> Multiphoton absorption, without having to invoke V-V redistribution of the energy, will be treated in subsection C.g describing isotope enrichment through multiphoton decomposition.

Table VI contains a representative collection of selective laser-induced nonthermal reactions.<sup>564-650</sup> Also included are some laser-controlled reactions for which thermal effects have not been unequivocally excluded but which, nevertheless, seem to follow nonthermal pathways. One possible explanation for the fact that different products are obtained is that a laser-heated reacting gas is not in contact with hot cell walls and thus is less prone to surface-catalyzed side reactions.

### C. Isotope Enrichment

Photochemical and photophysical approaches to the separation of isotopes present the more salient challenges of today's laser research in chemistry.<sup>562,651-656</sup> Firstly, because of the intrinsic scientific value, efforts to enrich isotopes have spurred studies of UHRS of atoms<sup>657-661</sup> and molecules<sup>46-49,662-664</sup> and of radiative lifetimes of excited states.<sup>659-661,665</sup> They have promoted the development of tunable lasers. Also, the interaction between radiation and matter has been studied, making use of the degree of isotopic selectivity or isotopic scrambling as a molecular monitoring device. Secondly, there are powerful economic incentives, the major motivation being the enrichment of <sup>235</sup>U for fission fuel in light water nuclear reactors. Projection of the world's nuclear fuel demand for the next 25 years indicate potential net savings of the order of 100 billion dollars when laser-based isotope enrichment technologies can be competitively applied on a large scale.<sup>666</sup> In addition, there is also a promising market for isotopes of lighter elements such as D, <sup>6</sup>Li, <sup>10</sup>B, <sup>13</sup>C, <sup>15</sup>N, <sup>17</sup>O, <sup>18</sup>O, some in connection with energy production (D, Li, B) and others as nonradioactive tracers in analytical, medical, and environmental studies.

Conventional methods for isotope enrichment (with the exception, perhaps, of D/H) are based on inherently inefficient processes involving the minute difference in some property of an isotopically different atom or molecule (isotomer). Each single application of such a process is characterized by a small enrichment factor  $\beta$ . For a mixture of  $N_A$  moles of isotomer A and  $N_B$  moles of (all) the other isotomer (s) B,  $\beta$  is defined as

$$\beta = (N_A/N_B)_{\text{enriched mixture}} / (N_A/N_B)_{\text{natural abundance}} \quad (24)$$

The isotopic ratio  $N_A/N_B$  is related to the mole fraction  $X$  as  $N_A/N_B = X_A/(1 - X_A)$ . In order to achieve even moderate changes in isotopic composition, a series of cascaded enrichment stages is required. This amounts to processing the feed material over and over again, with a concomitant large power consumption.

In contrast, laser-initiated enrichment should, in principle, be highly efficient since the photon energy is supplied exclusively to the isotomer of interest. For an ideal process with quantum efficiency of unity and with total retention of extraction selectivity,  $\beta \rightarrow \infty$ . In that case a single-step photochemical process, say at 400 nm, will yield 1 mol of isotopically pure material per einstein, or per 30 kJ usefully absorbed laser energy. Even for the low overall efficiency ( $\approx 0.1\%$ ) available in existing state-of-the-art dye lasers, this means a total energy consumption of about 100 kWh/mol, which is low compared to that of nonlaser methods. Moreover, unlike a gaseous-diffusion plant, a laser-separation facility has no minimum size constraint and can be operated intermittently.

All laser enrichment strategies have three requirements in common. Firstly, the isotomer must possess absorption features with a well-resolved spectroscopic isotope shift. In the visible or ultraviolet portion of the spectrum of gaseous atoms or molecules, the dense array of electronic transitions displays small isotope shifts (due to different nuclear mass, size, shape, or spin)

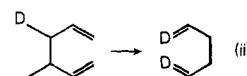
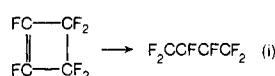
TABLE VI. Selective Chemical Reactions Induced by Laser Excitation

Absorber	Laser	Wavelength and operational mode	Reaction <sup>a</sup>	Reaction features and $k_{\text{rel}}^b$	Ref
H <sub>2</sub> , D <sub>2</sub>	Ruby/SRS shifted	1.1 μm and 0.9 μm 100 mw	H <sub>2</sub> + D <sub>2</sub> → 2HD		446
N <sub>2</sub> F <sub>4</sub>	CO <sub>2</sub>	0.3 J, 0.3 μs 1 J, 1 μs	M → 2NF <sub>2</sub> M + H → M + NO → FNO + NF <sub>3</sub> + F <sub>2</sub> + N <sub>2</sub> M + (CH <sub>3</sub> ) <sub>2</sub> C=CH <sub>2</sub> → CF <sub>4</sub> + HF + N <sub>2</sub> M + N <sub>2</sub> O → NO <sub>2</sub> + NF <sub>3</sub> M + CH <sub>4</sub> → C <sub>2</sub> H <sub>2</sub> + N <sub>2</sub> + H <sub>2</sub> + HF	Explosion Explosion	561 581 567
NH <sub>3</sub>	CO <sub>2</sub>		M → NH <sub>2</sub> + H	Luminescence	642
BCl <sub>3</sub>	CO <sub>2</sub>	CW, 600 W, 30 ms 1.5 J, 200 ns	M + H <sub>2</sub> → Cl <sub>2</sub> + B M + H <sub>2</sub> S → BSCl <sub>2</sub> M + H <sub>2</sub> → BHCl <sub>2</sub> + HCl M + O <sub>2</sub> → BCl + BO	Explosion Luminescence Luminescence	564 631 630 632, 633
B <sub>2</sub> H <sub>6</sub>	CO <sub>2</sub>	CW	M + C <sub>4</sub> H <sub>8</sub> → B <sub>2</sub> H <sub>4</sub> (C <sub>4</sub> H <sub>9</sub> ) <sub>2</sub>	Luminescence	565
	CO <sub>2</sub>	CW, 1.5 W, R (16)	M → B <sub>20</sub> H <sub>16</sub>		628
B(CH <sub>3</sub> ) <sub>3</sub>	CO <sub>2</sub>	CW, 7W, R (12)	M + HBr → B(CH <sub>3</sub> ) <sub>2</sub> Br + CH <sub>4</sub>		629
H <sub>3</sub> BPF <sub>3</sub>	CO <sub>2</sub>	CW, 100 W	2M → B <sub>2</sub> H <sub>6</sub> + 2PF <sub>3</sub>		582
D <sub>3</sub> BPF <sub>3</sub>	CO <sub>2</sub>		2M → B <sub>2</sub> D <sub>6</sub> + 2PF <sub>3</sub>	$E_a^T/E_a^L \approx 8$	583
HF	HF		M(v = 3) + D <sub>2</sub> → HD + DF		641
	HF	0.1 mJ, 0.5 μs	HF(v = 1) + Ba → BaF(v) + H		617
HCl	HCl		M(v = 1) + K → KCl + H	$k_1/k_0 = 100$	575
	HCl		M(v = 1) + O → OH + Cl	$k_1/k_0 = 300$	589, 593
	HCl		M(v = 2) + Br → HBr + Cl	$k_2/k_0 = 10^{11}$	590–592, 606, 607
Br <sub>2</sub>	Ruby	0.5 J, 0.5 ms	M + C <sub>4</sub> F <sub>8</sub> → C <sub>4</sub> F <sub>8</sub> Br <sub>2</sub>	12	47, 631
I <sub>2</sub>	Ar <sup>+</sup>	514.5 nm	<i>o</i> -I <sub>2</sub> → <i>p</i> -I <sub>2</sub>	2	635
		CW, 0.2 W	<i>o</i> -I <sub>2</sub> + 2-hexene → C <sub>6</sub> H <sub>12</sub> I <sub>2</sub>		636, 637
O <sub>3</sub>	CO <sub>2</sub>	200 W/50 Hz	M + NO → NO <sub>2</sub> + O <sub>2</sub> M + O <sub>2</sub> → 2O <sub>2</sub> + O	20	601–604
NO	CO		M + SO → SO <sub>2</sub> + O <sub>2</sub>		580
N <sub>2</sub> O	N <sub>2</sub> O		M + O <sub>3</sub> → NO <sub>2</sub> + O <sub>2</sub>		643
	NO <sub>2</sub> Ar <sup>+</sup> /dye		M + Cu → N <sub>2</sub> + CuO		644
		CW, 5 W	M + CO → NO + CO <sub>2</sub>	1–20	649
CF <sub>2</sub> Cl <sub>2</sub>	CO <sub>2</sub>	CW, 400 W, P(20)	M + C <sub>2</sub> F <sub>4</sub> Cl <sub>2</sub> + Cl <sub>2</sub>		646
		1.5 J, 100 ns	M → CF <sub>3</sub> Cl + C + Cl <sub>2</sub>	100	648
CFCI <sub>3</sub>	CO <sub>2</sub>		M → CCl <sub>4</sub> *	Luminescence	639
CF <sub>3</sub> CL	CO <sub>2</sub>	2 J, 0.2 μs, 0.3 Hz	M → C <sub>2</sub> F <sub>2</sub> Cl <sub>2</sub> + Cl <sub>2</sub> M → C <sub>2</sub> F <sub>6</sub>	2.8% conversion 1.6% per flash	579
CH <sub>3</sub> X (X = F, Cl, Br)		1 J, 200 ns	M + Cl <sub>2</sub> → CH <sub>2</sub> XCl + HCl	MPD	621
CH <sub>3</sub> OH	CO <sub>2</sub>	1.5 J, 100 ns	M → CH* + OH + C <sub>2</sub> *(!)	Luminescence	639
CH <sub>3</sub> CN			M → CN*		639
C <sub>2</sub> H <sub>2</sub>	CO <sub>2</sub>	CW, 300 W, 5 s	M + SF <sub>6</sub> → C	0.3 pyrolysis	612
C <sub>2</sub> H <sub>4</sub>	CO <sub>2</sub>	CW, 660 W, 0.4 s	M → C	$E_a = 192 \text{ kJ/mol}$	615
		CW, 50 W		$k$ (thermal)	616
C <sub>2</sub> H <sub>4</sub>	CO <sub>2</sub>	1.5 J, 100 ns	M → C <sub>2</sub> *	Luminescence	639
			M → C <sub>n</sub>	Polymerization	565
C <sub>2</sub> H <sub>6</sub>	CO <sub>2</sub>	CW, 680 W, 1 s	M + SF <sub>6</sub> → C	Pyrolysis	613, 614
C <sub>2</sub> H <sub>5</sub> Cl	CO <sub>2</sub>	150 W, CW, 972 cm <sup>-1</sup>	M → CH <sub>3</sub> + CH <sub>2</sub> Cl → CH <sub>4</sub>	$k$ (thermal)	617
		200 W, 1 ms, 946 cm <sup>-1</sup>	M → C <sub>2</sub> H <sub>4</sub> + HCl		
C <sub>2</sub> H <sub>2</sub> Cl <sub>2</sub>	CO <sub>2</sub>	100 ns, 60 ns	<i>trans</i> -M → <i>cis</i> -C <sub>2</sub> H <sub>2</sub> Cl <sub>2</sub>	MPD	588
C <sub>2</sub> Cl <sub>4</sub>	CO <sub>2</sub>	6W	M + BCl <sub>3</sub> → C <sub>6</sub> Cl <sub>6</sub>		629
C <sub>2</sub> F <sub>3</sub> Cl			M → C <sub>2</sub> *		638, 639
C <sub>2</sub> F <sub>4</sub> Cl <sub>2</sub>	CO <sub>2</sub>	CW, 4 W	M → C <sub>2</sub> F <sub>4</sub>	$k(921 \text{ cm}^{-1})/k(1052 \text{ cm}^{-1}) = 100$	647
C <sub>4</sub> F <sub>6</sub>	CO <sub>2</sub>	0.4 J, 100 ns	<i>c</i>	90% conversion	587
C <sub>4</sub> H <sub>8</sub>	CO <sub>2</sub>	10 MW, 100 ns	<i>trans</i> -2-butene → <i>cis</i> -2-butene		585
C <sub>4</sub> H <sub>6</sub> O	FLPDLD	10 <sup>-2</sup> W 1 μs, 30 Hz	$\xrightarrow{339 \text{ nm}}$ C <sub>2</sub> H <sub>4</sub> + CH <sub>2</sub> CO <sub>2</sub> , [C <sub>2</sub> ] $\xrightarrow{310 \text{ nm}}$ <i>c</i> -C <sub>3</sub> H <sub>6</sub> + CO, [C <sub>3</sub> ]	[C <sub>3</sub> ]/[C <sub>2</sub> ] = 7.0 [C <sub>3</sub> ]/[C <sub>2</sub> ] = 0.44	645

TABLE VI (Continued)

Absorber	Laser	Wavelength and operational mode	Reaction <sup>a</sup>	Reaction features and $k_{\text{rel}}^b$	Ref
<i>i</i> -C <sub>4</sub> H <sub>9</sub> X (X = Cl, Br, I)		0.3 J, 100 pulses	M → <i>i</i> -C <sub>4</sub> H <sub>8</sub>	MPD	609
C <sub>6</sub> H <sub>12</sub> O <sub>2</sub>	CO <sub>2</sub>	0.3 J, 1 μs, P(20)	M + CH <sub>3</sub> F → 2CH <sub>3</sub> COCH <sub>3</sub>	Luminescence at 410 nm	612
C <sub>6</sub> H <sub>10</sub> D <sub>2</sub>	CO <sub>2</sub>	0.3 MW, 100 ns	<i>e</i>		586
C <sub>6</sub> H <sub>6</sub> D <sub>4</sub>		5000 pulses			
C <sub>6</sub> H <sub>6</sub> D <sub>6</sub>					
C <sub>10</sub> H <sub>16</sub>	CO <sub>2</sub>	CW, 5 W	M → 2C <sub>5</sub> H <sub>8</sub> (isoprene)		584
1-Limonene					
SF <sub>6</sub>	CO <sub>2</sub>	0.8 MW, P(20)	M + HCl	Luminescence	640
UF <sub>6</sub>	CO <sub>2</sub>	CW		100	650

<sup>a</sup> Laser-induced reactions are not presented stoichiometrically; M denotes the laser-excited molecule of column 1, X\* is an electronically excited species. <sup>b</sup>  $k_{\text{rel}}$  denotes the ratio of reaction rates,  $k_L/k_T$ , or, where applicable, [products/reactants]<sub>irrad sample</sub>/[products/reactants]<sub>orig sample</sub>. <sup>c</sup> See reaction i.



<sup>d</sup> c-C<sub>4</sub>H<sub>6</sub>O = cyclobutanone. <sup>e</sup> See reaction ii.

TABLE VII. Isotope Enrichment Experiments: Atomic Beams

Atom	Technique <sup>a</sup>	Laser and mode of operation	Wavelength (nm)	Enrichment factor $\beta$	Ref
<sup>6</sup> Li	TPI	CW Ar <sup>+</sup> /dye	$\lambda_1$ 616.2		703
<sup>40</sup> Ca	TPI	CW Ar <sup>+</sup> , 3 W	$\lambda_2$ 488.8		704
<sup>85</sup> Rb	TPI	Ruby/dye	$\lambda_1$ 794.8		652
		FD ruby	$\lambda_2$ 347.1		699
					700
<sup>138</sup> Ba	RPD	CW Ar <sup>+</sup> /dye	$\lambda_1$ 553.6	2	717
<sup>137</sup> Ba		50 mW/cm <sup>2</sup>	$\lambda_1$ 553.6	13	718
<sup>135</sup> Ba			$\lambda_2$ 582.6		719
<sup>235</sup> U	TPI	N <sub>2</sub> /dye	$\lambda_1$ 426.6	1.5	665
			$\lambda_2$ 360.9		
<sup>235</sup> U	TPI	CW Xe <sup>+</sup> , 70 mW	$\lambda_1$ 378.1	4	670
		CW Kr <sup>+</sup> , 1 W (intracavity 30 W)	$\lambda_2$ 356.4		
			$\lambda_2$ 350.7		

<sup>a</sup> See Appendix for a list of abbreviations.

which range from 1:10<sup>5</sup> to 1:10<sup>8</sup> of the transition energy. In the infrared spectral region the vibrational transitions of molecules are directly related to the reduced mass of constituent atoms, and the relative isotope shift is typically of the order of 1:100 to 1:1000. TPA has been considered for selective excitation of Doppler-broadened transitions.<sup>667</sup> Secondly, the laser must be monochromatic (to the limit of the spectral line width of the absorber) and, preferably, tunable so as to allow selective excitation of the isomer of interest without having to rely on fortuitous coincidences between laser emission lines and isotopic absorption features. Thirdly, there must be an efficient extraction step, which may be magnetic,<sup>668</sup> electrical,<sup>665,668-671</sup> optical,<sup>672,673</sup> thermal,<sup>674</sup> heterogeneous,<sup>675</sup> or chemical (ref 47, 578, 590-592, 606, 607, 676-684), that acts preferentially on the excited species before relaxation, collisional energy transfer, or charge transfer can occur. This turns out to be the more stringent condition for practical implementation of laser enrichment of isotopes. A simple way to preserve selectivity is provided by the method of laser-induced unimolecular photoisomerization, which converts a molecule to a different isomer which can be separated chemically from the unconverted species.<sup>585-588,680</sup>

Several schemes have been explored on a laboratory scale,

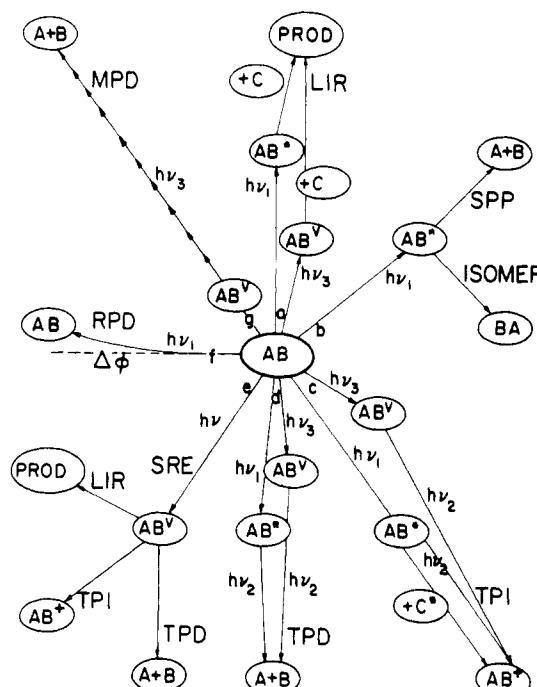


Figure 10. Schematic diagram of laser-based isotope enrichment schemes (a-g) discussed in the text.  $\nu_{1,2}$  designates resonance radiation in the visible or UV spectral region and  $\nu_3$  in the infrared. AB<sup>V</sup>, AB<sup>\*</sup> (or C<sup>\*</sup>), and AB<sup>+</sup> denote, respectively, vibrationally excited, electronically excited, and ionized species. Schemes a, c, and f are also suitable for enrichment of atomic isotopes.

and two are, reportedly, in the pilot plant stage.<sup>665,670</sup> Results published in the unclassified literature up to early 1977 are listed in Tables VII and VIII. The more important methods are reviewed below, where we proceed from single-photon (a, b) via two-photon (c-e) to multiphoton (f, g) processes. They are depicted schematically in Figure 10.

(a) *Laser-Initiated Reactions (LIR)*. This is the oldest spectroscopic procedure for isotope separation. It is based upon the increased reactivity of excited species (section B). This concept has already been applied in the pre-laser era; the best-known example being the production in 1952 of isotopically pure HgO

TABLE VIII. Isotope Enrichment Experiments: Molecules

Absorber	Technique <sup>a</sup>	Laser and mode of operation <sup>b</sup>	Wavelength	Reaction	Enrichment Isotope	Factor $\beta$	Ref
CH <sub>3</sub> OH	LIR	CW HF, 100-W pulsed HF or incoherent source	2.6 $\mu$ m	M + Br <sub>2</sub> → H <sub>2</sub> CO + Br	D	2	681
CD <sub>2</sub> Cl <sub>2</sub>	MPD	1 J, 100 ns, 2 Hz, 3600 pulses	2.6 m 943 cm <sup>-1</sup>	M → HCl + C +	D	1	682
H <sub>2</sub> CO (HDCO, D <sub>2</sub> CO)	SPP	FD ruby	347 nm	M → D <sub>2</sub> + CO	D	6	689
	SPP	FT Nd	353 nm		D	9	694
	SPP	CW He-Cd, 0.5 mW	325 nm	M → HD + CO	D	14	692
H <sub>2</sub> CO	MPD	2 J, 100 ns, 0.5 Hz, 300 pulses	P(20)	M → HD + CO	D	40	638
	SPP	FD ruby/dye doubled	304 nm	M → H <sub>2</sub> + CO	<sup>12</sup> C	80	690
	SPP	FD FLPDL	304 nm				691
BCl <sub>3</sub>	TPD	CW Ne <sup>+</sup> , 20 mW	332.3 nm		<sup>18</sup> O	8	693
	MPD	Pulsed CO <sub>2</sub> Xe-FL	$\lambda_1 = P(20)$ $\lambda_2 \approx 214$ nm	M + O <sub>2</sub> →	<sup>10</sup> B	1.1	709
	MPD	0.1 J, 200 ns 360 000 pulses	P(16) R(30) P(20)	M + H <sub>2</sub> S → B <sub>2</sub> S <sub>3</sub> + HCl M + D <sub>2</sub> S → M + O <sub>2</sub> → BO → B <sub>2</sub> O <sub>3</sub>	<sup>10</sup> B <sup>11</sup> B <sup>10</sup> B	2.2 1.6 8	733 734 725, 632
CF <sub>2</sub> Cl <sub>2</sub> C <sub>2</sub> N <sub>4</sub> H <sub>2</sub> s-Tetrazine	MPD	2 J, 85 ns 1.6 Hz	R(24)	M + HBr → BCl +	<sup>11</sup> B	5	726
	MPD	1.5 J, 200 ns 4000 pulses	P(20)	M + H <sub>2</sub> → BHCl <sub>2</sub> + HCl	<sup>10</sup> B	1.7	732
	SPP	CW Ar <sup>+</sup> /dye (gas)	551.5 nm	M + H <sub>2</sub> →	<sup>13</sup> C <sup>13</sup> C <sup>15</sup> N	1.1 24 6	732 695
N <sub>2</sub>	SPP	N <sub>2</sub> /dye (in matrix at 1.6 K)	653 nm	C <sub>2</sub> N <sub>4</sub> H <sub>2</sub> → N <sub>2</sub> + HCN	<sup>13</sup> C <sup>15</sup> N	10 <sup>4</sup> 10 <sup>4</sup>	696
	SRE-LIR	Ruby	694 nm	N <sub>2</sub> + O <sub>2</sub> → 2NO	<sup>15</sup> N	100	565
		Ruby/SRS Shifted	830 nm				712 713
NH <sub>3</sub>	TPD	CO <sub>2</sub> , 60 mJ, 300 ns	$\lambda_1$ 947.1 cm <sup>-1</sup>	4NH <sub>3</sub> → 2NH <sub>3</sub> + 3H <sub>2</sub> + N <sub>2</sub>	<sup>15</sup> N	4	706 707
		filtered UV spark	$\lambda_2 > 220$ nm				708
O <sub>2</sub> SiF <sub>4</sub>	LIR	ArF	193 nm	O + O <sub>2</sub> → O <sub>3</sub>	A <sup>18</sup> O		678
	MPD	0.8 J, 200 ns 4800 pulses	P(36) 1031.5 cm <sup>-1</sup>	M + H <sub>2</sub> → M + N <sub>2</sub> →	<sup>29</sup> Si <sup>30</sup> Si	1.1	732
SF <sub>6</sub>	MPD	1.5 J, 200 ns 5000 pulses	P(20)	SF <sub>6</sub> + H <sub>2</sub> → SF <sub>5</sub> + HF → SF <sub>4</sub>	<sup>34</sup> S <sup>36</sup> S	33 1200	731
	MPD	2 J, 90 ns 2000 pulses	P(16) P(40)		<sup>34</sup> S <sup>32</sup> S	2800 18	727 726
	MPD	3 J, 90 ns 1000 pulses		SF <sub>6</sub> + H <sub>2</sub> →	<sup>34</sup> S <sup>34</sup> S	47 30	730 729
CCl <sub>4</sub> CF <sub>2</sub> Cl <sub>2</sub> HCl	MPD	17 J, 90 ns	979.7 cm <sup>-1</sup> 971.9 cm <sup>-1</sup>		<sup>13</sup> C <sup>37</sup> Cl	7 1.5	728, 735 732
	TPD	Nd/SRS shifted Xe lamp, FQ Nd	$\lambda_1$ 1180 nm $\lambda_2 > 300$ nm $\lambda_2$ 265 nm	H <sup>35</sup> Cl(v = 3) + NO → NOCl			562, 563
	LIR	Pulsed HCl Pulsed HCl		H <sup>35</sup> Cl(v = 2) + Br → HBr + Cl	<sup>35</sup> Cl	3	590, 592 606
ICl	LIR	CW Ar <sup>+</sup> /dye, 10 mW	605.3 nm	ICl(v = 18) + C <sub>2</sub> H <sub>2</sub> Br <sub>2</sub> intracavity absorption	<sup>37</sup> Cl <sup>37</sup> Cl	1.5 17	683 684
CSCl <sub>2</sub>	LIR	CW Ar <sup>+</sup> FLPDL	465.8 nm 470 nm		<sup>35</sup> Cl <sup>37</sup> Cl	1.2 1.7	578, 676
Br <sub>2</sub>	LIR	Ruby	Temp. tuned	Br <sub>2</sub> + C <sub>4</sub> F <sub>8</sub> → C <sub>4</sub> F <sub>8</sub> Br <sub>2</sub>	<sup>79</sup> Br	1	47
	SPP	FD Nd/YAG	558 nm	M + HI → Br + HI → HBr + I	<sup>81</sup> Br	5	677
CH <sub>3</sub> Br	LIR	CO <sub>2</sub> , CW	R(14)	M + Cl → CH <sub>2</sub> BrCl	<sup>79</sup> Br	1.03	627
I <sub>2</sub>		CW Ar <sup>+</sup>		(intracavity)	<sup>81</sup> Br	1.02	636
OsO <sub>4</sub>	MPD	3 J, 90 ns	R(2) P(2)	M + C <sub>2</sub> H <sub>4</sub> →	<sup>192</sup> Os <sup>187</sup> Os	1.2 1.1	737
	LIR	CO <sub>2</sub> (with UF <sub>6</sub> filter)	P(16)	UF <sub>6</sub> (v <sub>3</sub> + v <sub>4</sub> + v <sub>6</sub> ) + HCl →	<sup>235</sup> U	1.1	663

<sup>a</sup> See Appendix for list of abbreviations. <sup>b</sup> In the MPD technique a pulsed CO<sub>2</sub> laser is used.

by sensitizing a <sup>75</sup>Hg/H<sub>2</sub>O vapor mixture with 253.7-nm resonance radiation from an isotopically pure (or suitably filtered)

Hg lamp.<sup>685</sup> A more recent example is the selective photolysis of <sup>13</sup>CO with 206.2-nm radiation from an iodine lamp.<sup>686</sup> The high

spectral brightness obtainable with lasers has paved the way for novel experiments. For example, irradiation of  $^{79}\text{Br}_2$  vapor with a temperature-tunable ruby laser caused selective electronic excitation (to the  $^3\pi_{1u}$  state) of a specific  $\text{Br}_2$  isomer which was dissociated by subsequent collisions.<sup>47</sup> However, the scavenging reaction of the bromine radicals with olefins turned out to be nonselective, because collisional energy transfer to unexcited  $^{79}\text{Br}_2$  molecules, prior to the addition reaction, caused isotopic scrambling.<sup>47</sup> This is a general drawback of LIR. Isotopic specificity was, however, preserved<sup>677</sup> in the reaction between HI and  $^{81}\text{Br}_2$ , which was excited to the  $^3\pi_0^+$  state by radiation of 558 nm, and produced 85%  $\text{H}^{81}\text{Br}$ .

The first reported isotope enrichment through LIR was that of  $\text{CH}_3\text{OH}$  molecules which absorbed HF laser radiation (at 3644 cm<sup>-1</sup>) and reacted with  $\text{Br}_2$  while admixed  $\text{CD}_3\text{OD}$  molecules appeared to remain inert.<sup>681</sup> Recent quantitative studies were, however, unable to reproduce these rather unusual results.<sup>682</sup> LIR has been successful in enriching Cl isotopes from  $\text{HCl}$ ,<sup>590,592,606</sup>  $\text{ICl}$ ,<sup>683,684</sup> and  $\text{CSCl}_2$ <sup>578,676</sup> (see Table VIII). The efficiency might be improved considerably by direct excitation to the lowest triplet state which reduces isotopic scrambling through resonant transfer.<sup>688</sup> Quite a number of theoretical analyses have been devoted to the LIR method for isotope enrichment.<sup>582,583,594-597</sup>

(b) *Single-Photon Predissociation (SPP)*. In some favorable cases, notably gaseous  $\text{H}_2\text{CO}$ ,<sup>689-693</sup>  $\text{H}_2\text{C}_2\text{O}_2$  (glyoxal),<sup>694</sup>  $\text{Br}_2$ ,<sup>677,678</sup>  $\text{I}_2$ ,<sup>635-637</sup> and gaseous or solid *s*-tetrazine,  $\text{C}_2\text{H}_2\text{N}_4$ ,<sup>695,696</sup> monochromatic ultraviolet or visible radiation will, in one single step, selectively excite a given isomer which will then spontaneously dissociate because the potential energy curve for the bound excited state crosses that of the repulsive dissociating state.<sup>697,698</sup>

(c) *Two-Photon Ionization (TPI)*. A laser is fine-tuned to  $\nu_1$ , corresponding to an absorption peak of the desired isotope (present as a low-density atomic vapor emitted by a long "sheet" vacuum furnace source, coplanar to the laser beam). The laser selectively raises one isotope to an intermediate state while leaving the other isotope(s) unaffected in the ground state. A photon from a second (not necessarily strictly monochromatic) intense source at  $\nu_2$ , such that  $h\nu_2 < E_{\text{ion}} < h(\nu_1 + \nu_2)$ , is subsequently absorbed by the excited isotope to produce a positively charged ion.<sup>652</sup> An electric field removes ions from neutrals in the effusive flow and completes the separation process.

The extremely small absorption cross section ( $\sim 10^{-19}$  cm<sup>2</sup>) associated with the photoionization continuum makes the intensity of the ionizer source at  $\nu_2$  the principal limitation on achieving economical throughput of enrichment. Therefore, it is advantageous to let  $h(\nu_1 + \nu_2)$  terminate on one of the discrete "autoionization" states (characterized by somewhat larger cross sections) which exist above the photoionization threshold,  $E_{\text{ion}}$ .<sup>659,665,699,700</sup> More complex excitation schemes, involving three or four lasers, including a high-power  $\text{CO}_2$  laser to saturate the ionization step, have been proposed to improve overall efficiency.<sup>701</sup> In another modification a catalytic species is added to the isotopic mixture.<sup>702</sup> This species must have a resonance transition at  $h\nu_2$ , which may be transferred to the  $h\nu_1$ -excited isotope by efficient long-range ionizing collisions, albeit at some loss of selectivity. TPI in its various versions (see Table VII) has been applied for the enrichment of  $^{6\text{Li}}$ ,<sup>703</sup>  $^{40}\text{Ca}$ ,<sup>704</sup>  $^{85}\text{Rb}$ ,<sup>652,699,700</sup> and, of course,  $^{235}\text{U}$ .<sup>665,670</sup>

(d) *Two-Photon Dissociation (TPD)*. A molecular isomer is selectively excited with a pulsed laser at  $\nu_1$  (often to a vibrationally excited state but preferably such that  $h\nu_1 \gg kT$  so as to minimize nonselective thermal excitation) and is then brought into the dissociation continuum by means of absorption of pulsed visible or ultraviolet radiation from a laser at  $\nu_2$  or from an incoherent energy source, supplied with a cut-off filter, such that  $h\nu_2 < E_{\text{diss}} < h(\nu_1 + \nu_2)$ , to prevent photolysis of ground-state

molecules.<sup>652,705</sup> The isomer radicals should form stable products or should rapidly react with a premixed scavenger present at sufficient density to prevent back reaction. Representative examples of TPD are provided by  $\text{NH}_3$ ,<sup>706-708</sup>  $\text{HCl}$ ,<sup>562,652</sup> and  $\text{BCl}_3$ .<sup>709</sup> The quantum efficiency and separation factors have been calculated for the case of  $\text{HCl}$ <sup>710</sup> and  $\text{NH}_3$ .<sup>708,711</sup>

(e) *Selective Raman Excitation (SRE)*. The process of (Stokes) stimulated Raman scattering (SRS) is known to generate a substantial molecular population in certain vibrational states (section II.D). Selective Raman excitation (SRE) has been used to enhance, in a controlled way, the reaction rate between  $\text{H}_2$  and  $\text{D}_2$ , to produce  $\text{HD}$ <sup>446,447</sup> or between  $\text{N}_2$  and  $\text{O}_2$ , to produce  $\text{NO}$ .<sup>565,712,713</sup> In the same fashion SRE might be used as a general method in isotope separation processes that require selective vibrational excitation as a primary step, e.g., LIR or TPD. This is particularly important when dealing with nonabsorbing reactants such as homonuclear diatomics.

There are some notable advantages in using SRE, the main ones being its effective tunability and the relinquishment of the requirement for long-term wavelength stability.<sup>714</sup> A host of transitions in the infrared region, where there is a dearth of intense laser sources, may be excited through SRE with a single fixed-wavelength laser operating in the visible spectral region. In addition, there is an inherent selectivity for exciting the major isomer, because of the exponential dependence of the SRS signal on isomer concentration. It might be possible to generate SRS also from a minor isomer by the simple expedient of adding a proper Stokes field, either with a tuned dye laser<sup>443</sup> or with SRS radiation generated in a separate cell which contains that species in pure form.<sup>715,716</sup>

(f) *Radiation Pressure Deflection (RPD)*. This conceptually straightforward photophysical separation technique—to be distinguished from simple photophoresis—was proposed by Ashkin.<sup>672</sup> Saturating radiation from a comparatively low-power CW laser, tuned to the strong resonance line of one isotopic component, is directed perpendicularly onto a collisionless atomic or molecular beam. This setup minimizes Doppler broadening, collision broadening, and power broadening. Each absorbed photon transfers, in the direction of the laser propagation, its linear momentum  $h\nu/c = h/\lambda$  to the absorbing species. Spontaneous emission from the excited state occurs after about  $10^{-8}$  s and scatters the absorbed photons isotropically, whereas the absorption process imparts a resultant net force in the direction of the light. Multiple absorption and emission events during the time of flight of a given species through the region intercepted by the laser are necessary to deflect a neutral isomer out of the beam. This region can be increased by inserting a cylindrical telescope in the optical path. The corresponding decrease in intensity is tolerable down to the saturating intensity for the particular resonance transition. Above this intensity the total momentum transfer rate remains constant anyway. The efficiency of utilization of laser energy is rather low; in fact, almost all the energy of the photons is wasted in the form of randomly scattered radiation.

Spatial extraction of  $^{135}\text{Ba}$ ,  $^{137}\text{Ba}$ , and  $^{138}\text{Ba}$  atoms from a collimated beam of  $^{79}\text{Ba}$  has been demonstrated<sup>717-719</sup> using radiation at  $\lambda = 553.6$  nm corresponding to the resonance transition  $6s^2\ 1\text{S}_0 \rightarrow 6s6p\ 1\text{P}_1$ . An order of magnitude calculation shows that for Ba atoms at 1100 K, moving along a beam with an average velocity  $u_{||} \approx 600$  m/s, the number of absorption/emission cycles required to impart a transverse velocity  $u_{\perp} \approx 1$  m/s, necessary to obtain spatial separation of a beam of 1 mrad divergence, is given by  $138 u_{\perp}/(h/\lambda) \approx 200$  photons per separated Ba atom. This amounts to consumption or more than  $4 \times 10^7$  J/mol separated material (when all other loss mechanisms are neglected) or laser output energy of 10 kWh, implying electrical input energy of over  $10^5$  kWh. More exact calcula-

tions<sup>719,720</sup> show similar values.

Various schemes have been proposed to improve the overall efficiency. These include the use of additional CW laser(s) to depopulate "traps", formed by metastable states at intermediate energies, such as the level 6s5d  $^1D_2$  in Ba, which would otherwise reduce the number of absorption/emission cycles,<sup>718,719</sup> or adding collision partners to the beam.<sup>720</sup> In the method of "fast adiabatic passage" a frequency-swept laser pulse, traveling between mirrors, intersects the atomic beam many times.<sup>721</sup> The incoming pulse causes highly efficient excitation.<sup>722,723</sup> The reflected pulse will cause an excited isomer to revert to the ground state by stimulated emission, thus imparting a unit of recoil momentum. The photon is reemitted along the direction of laser propagation and is reusable in principle.

The RPD technique may, perhaps, become attractive for the separation of optical stereoisomers since circularly polarized laser light will deflect only the component which is chirality-matched with the radiation.

(g) *Multiphoton Dissociation (MPD)*. At this time the most viable enrichment method for molecular isotomers is provided by irradiation of a low-pressure gas sample with a high-intensity pulsed infrared laser, causing collisionless multiphoton dissociation (MPD). The principle of state-selective, chemically irreversible MPD has been applied to a host of reactants and new results are burgeoning at a fast rate, adding to our understanding of this class of fundamental photoprocesses.<sup>724-726</sup>

Typically, a pulsed transversely excited atmospheric pressure (TEA) CO<sub>2</sub> laser (energy 2 J/pulse, pulse duration 100 ns, and pulse repetition rate 1 Hz) is focused into a reaction cell containing an absorbing gas such as SF<sub>6</sub>,<sup>679,724-731</sup> BC<sub>3</sub>,<sup>724-726,732-734</sup> SiF<sub>4</sub>,<sup>732</sup> CCl<sub>4</sub>,<sup>728,735</sup> CF<sub>2</sub>Cl<sub>2</sub>,<sup>732</sup> CD<sub>2</sub>Cl<sub>2</sub>,<sup>736</sup> OsO<sub>4</sub>,<sup>737</sup> or H<sub>2</sub>CO.<sup>738</sup> The laser is tuned close to an absorption line of a particular isomer; the line may be associated with a weak transition or a combination band<sup>735</sup> and the laser may be quite far off resonance.<sup>622,642,738</sup> Irradiation with 500–5000 laser pulses destroys this isomer and progressively leaves the residual gas (sometimes as little as 1% of the initial amount) enriched in the other isomer(s). The enrichment factor  $\beta$  varies exponentially with the number of laser pulses and with the inverse of the initial gas pressure. The total yield also depends on the presence of diluent buffer gases or scavengers, and on numerous laser parameters,<sup>727,729,732,739</sup> leading to the existence of a sharp power threshold for dissociation. The fractional reaction per pulse is determined by eq 26, and this prediction<sup>119</sup> has been confirmed experimentally.<sup>729,739,740</sup> As for temporal laser characteristics, it was claimed that optimal yields are obtained with pulses of about 100 ns duration, while 1 ns pulses<sup>732</sup> (with peak intensities of 10<sup>13</sup> W/cm<sup>2</sup>) or 1  $\mu$ s pulses<sup>733</sup> did not give decomposition. This agrees with the observation that the reaction yield depends on the total energy in the pulse rather than on its peak power. A spectacular enrichment factor of 3000 has been reported<sup>727</sup> for <sup>34</sup>SF<sub>6</sub>, as a result of selective irradiation and photofragmentation of <sup>32</sup>SF<sub>6</sub> using P(16) radiation at 947 cm<sup>-1</sup>. The <sup>34</sup>SF<sub>6</sub> concentration increased from 4.2% in <sup>32</sup>SF<sub>6</sub> to 99% (in the residual gas).

The reasons for isotopic selectivity are only partly understood,<sup>741-751</sup> and considerable experimental effort is now in progress in a number of laboratories<sup>724-726</sup> to elucidate the photolysis mechanism. In early studies it was observed that at irradiation intensities  $I_L$  in excess of 10<sup>8</sup> W/cm<sup>2</sup>, but still below the threshold for optical breakdown ( $I_L \approx 10^{10}$  W/cm<sup>2</sup>), visible luminescence occurred associated with emission lines from electronically excited radicals. For low gas pressures ( $\approx 1$  Torr) luminescence was found to be practically instantaneous (ref 581, 632–634, 638–642, 740). That is, it was discerned after a delay shorter than the mean time between collisions ( $\approx 1$   $\mu$ s). This rules out the V–V exchange mechanism, discussed in section B, as an explanation for bond rupture which requires, typically, over 30 quanta of vibrational energy. The current contention is

that two phases should be distinguished in the MPD mechanism.<sup>632,732,742-744</sup> In the low-energy phase radiative coupling with the anharmonic oscillator causes near-resonance transitions leading to sequential absorption of a few photons by the isolated molecule. A phenomenological model using an ensemble of semiclassical anharmonic oscillators was also proposed to interpret MPD.<sup>745</sup>

The anharmonicity of the vibrational modes may be compensated by rotational transitions or by the anharmonic splitting present in degenerate overtones.<sup>752</sup> Also, power broadening of the absorption lines by the oscillating electric field  $E_L$  of the laser radiation has been invoked<sup>725,732,742</sup> to offset anharmonicity. On the basis of classical arguments<sup>742</sup> the dynamic power broadening (ac Stark effect) may be written as

$$\Delta\nu \approx (\bar{\mu}/hc)E_L \approx (\bar{\mu}/hc)I_L^{1/2}$$

where  $\bar{\mu}$  is the mean value of the transition dipole moment. The laser intensity  $I_L$  necessary to produce a broadening of  $\Delta\nu = 10$  cm<sup>-1</sup> is about 10<sup>9</sup> W/cm<sup>2</sup>. A quantum-mechanical extension for a multilevel system was recently provided by Larsen and Bloembergen<sup>743</sup> and Mukamel and Jortner.<sup>744</sup>

After the molecule has been promoted to the vibrational level  $v = 3$  or 4 at a critical energy of, say, 3000 cm<sup>-1</sup> above the ground state, the second phase of MPD becomes dominant. Now further absorption of the fundamental frequency  $v = 0 \rightarrow v = 1$ , by a coherent single-photon process, coupled with rapid (sub picosecond timescale) intramode energy transfer, can promote molecules to still higher vibrational levels until the dissociation limit is reached. The energy buildup occurs since the density of states, above 3000 cm<sup>-1</sup>, is sufficiently large (particularly in a polyatomic molecule such as SF<sub>6</sub>) to allow the absorber to undergo a fundamental-type transition within the quasi-continuous manifold of all possible states. If the isotope shift is larger than the spectral width  $\Delta\nu$  caused by power broadening, it becomes feasible in the first phase to excite one species in a gaseous mixture of isotomers. Of course, the second phase by itself is not isotopically selective.

The mechanism is corroborated by an elegant experiment performed by Letokhov<sup>748,749</sup> in SF<sub>6</sub> where the isotopic shift is larger than the frequency spread of the P, Q, and R branches. SF<sub>6</sub> first absorbs a low-power (4 MW) CO<sub>2</sub> laser pulse and moves three steps up the photodissociation ladder. The vibrational anharmonicity is compensated by the rotational shift in the absorbing sequence: P-branch ( $v = 0, J \rightarrow v = 1, J - 1$ ), Q-branch ( $v = 1, J - 1 \rightarrow v = 2, J - 1$ ), and R-branch ( $v = 2, J - 1 \rightarrow v = 3, J$ ) transitions. A second CO<sub>2</sub> pulse at 1084.6 cm<sup>-1</sup> is then capable<sup>739</sup> of dissociating SF<sub>6</sub> at a much smaller threshold power (60 MW) than would be required in a single-frequency MPD experiment. Moreover, Letokhov obtained optimal yield<sup>748,749</sup> with the single-frequency laser detuned to 940 cm<sup>-1</sup>, about 10 cm<sup>-1</sup> below the molecular resonance line, in agreement with predictions of Mukamel and Jortner.<sup>744</sup>

It should be noted that one of the advantages of laser isotope separation is lost in MPD when removing the main constituent in the mixture (<sup>11</sup>B, <sup>12</sup>C, <sup>28</sup>Si, <sup>32</sup>S) rather than preferentially enriching the minor isotope. Taking the most favorable cases reported thus far,<sup>727,729</sup> 2  $\times$  10<sup>6</sup> photons were consumed on the average to remove one molecule of <sup>32</sup>SF<sub>6</sub>. Assuming no decomposition of any <sup>34</sup>SF<sub>6</sub> molecules, the quantum efficiency for <sup>34</sup>S enrichment was, at most, 0.042/2  $\times$  10<sup>6</sup>  $\approx 2 \times 10^{-8}$ . In some studies, the more logical route was taken of treating the desired isomer. For example, HD was formed, with an enrichment factor of 40, by selective MPD of natural formaldehyde.<sup>738</sup> Whereas H<sub>2</sub>CO is transparent in the spectral region of the CO<sub>2</sub> laser radiation, HDCO has an absorption line at 951.6 cm<sup>-1</sup> which overlaps to some extent with the main emission line from an untuned CO<sub>2</sub> laser (P (20) at 944 cm<sup>-1</sup>), if power broadening is taken into account. Yet the photon conversion efficiency, deduced from the raw data, is still a meager 7  $\times$  10<sup>-8</sup>.

This will certainly be improved by optimization of the system parameters.

## D. Nonlinear Photochemistry

The term nonlinear photochemistry refers to photochemical reactions induced via simultaneous multiphoton absorption. These processes are related to TPS (section II.C) and to MPD (subsection C.g). Molecules excited to a dissociative state by TPA present an obvious choice for the study of nonlinear photochemistry; such dissociative states appear in TPS as continuous structureless bands.

The first observations of laser-induced two-photon chemical reactions were of a qualitative nature.<sup>753-757</sup> In each case the absorbing molecule was transparent at laser frequency  $\nu_L$  and showed an absorption band at  $2\nu_L$ . The photochemical products of the laser-irradiated molecule were found to be identical with those observed in an one-photon process induced by a light source operating at  $2\nu_L$ . This served as a proof that a two-photon induced photochemical process had indeed taken place, as was demonstrated in the photopolymerization of styrene,<sup>753</sup> and in the hydrogen-chlorine photoreaction.<sup>756</sup>

The first quantitative study of a nonlinear photochemical process was the ruby-laser-induced two-photon-photolysis of iodoform.<sup>94</sup> The process was monitored by measuring the photochemical yield of the liberated iodine as a function of laser intensity. The observed  $I_L^2$  dependence proved the occurrence of a primary photochemical process induced by TPA. The nonlinear photochemical yield  $Y$ , integrated over the whole cell, is given by (cf. eq 17)

$$Y = \gamma \delta N I_L^2 \Delta t \quad (25)$$

where  $\Delta t$  is the duration of the laser pulse, and  $\gamma$  is a factor depending on its temporal and spatial shape<sup>129</sup> ( $\gamma = 0.353$  for a temporally and spatially gaussian profile). Thus using eq 25  $\delta$  can be evaluated from determination of chemical yields. In principle, this procedure is more direct than that based on monitoring the absolute fluorescence yield (cf. eq 18). The main drawback of the photochemical method is that it is not suitable for recording a complete TPA spectrum, for which relative fluorescence measurements are adequate.

Few examples of nonlinear photochemistry have been reported.<sup>758-761</sup> In Table IX we summarize in chronological order the existing data on two-photon photochemical reactions induced by ruby lasers. Not included are nonlinear photoionization and photoconductivity studies,<sup>117,555,762-764</sup> neither is photolysis induced by consecutive absorption of two photons.<sup>391</sup>

The two-photon photolysis study of iodoform has shown<sup>94</sup> that care should be exercised in interpreting nonlinear photochemistry because of the interference of other nonlinear phenomena. In particular, it was found that self-focusing, due to the optical Kerr effect of the solvent,<sup>765</sup> will modify the features of a nonlinear photochemical process. For example, in Kerr solvents such as benzene, it may cause a tenfold increase in  $Y$ . Incidentally, based on this increase, a chemical method for determining the self-focusing parameters of the solvent was established.<sup>94</sup>

A discussion of the effects of external focusing and self-focusing on multiphoton photochemistry has been presented.<sup>119</sup> It was shown quite generally that for any multiphoton process with external focusing of the laser beam and assuming conical geometry, the total yield is no longer given by eq 25 but rather by

$$Y \propto I_L^{3/2} \quad (26)$$

Thus the quantum order of the process cannot be determined in this type of measurement. This prediction has subsequently been confirmed by other calculations.<sup>120,121,766</sup> Experimental support is provided by MPD of SiF<sub>4</sub>,<sup>740</sup> SF<sub>6</sub>,<sup>729,739</sup> and organic

TABLE IX. Chronology of Ruby Laser Induced Two-Photon Photochemical Processes

Molecule	Observed phenomena	$\delta (10^{-50} \text{ cm}^4 \text{ s}/\text{photon molecule})$	Ref
Styrene (liquid)	Polymerization		753
AgCl (solid)	Luminescence and Ag production		754
Phthalocyanine (vapor)	Photolysis		755
H <sub>2</sub> + Cl <sub>2</sub> (gas)	HCl production		756
2-Chloro-3-nitroso-2,3-dimethylbutane (solution)	HNO <sub>2</sub> production		757
Iodoform (solutions)	I <sub>2</sub> production	30	94
Benzene (liquid)	Unidentified products		760
Azoethane (gas)	N <sub>2</sub> production	0.06	758
NO <sub>2</sub> (gas)	O <sub>2</sub> production		771
Potassium ferrioxalate (solution)	Fe <sup>3+</sup> reduction	1.5	759
Nitrobenzene (liquid)	Photolysis	24	761

molecules.<sup>587</sup> It is important to note that the  $I_L^{3/2}$  optical scaling law is valid only for yields integrated over the whole reaction cell and only when the multiphoton transition probability is saturated.<sup>766</sup> The high-order  $I_L^n$  dependence observed in some MPD studies<sup>566,767</sup> must be ascribed to nonintegrated yields, nonfocused geometry, breakdown or, as is the case in atomic multiphoton ionization processes, to unsaturated transition probabilities.<sup>768</sup> Moreover, by using external focusing the threshold for multiphoton induced breakdown and photoionization is usually reached. This may explain the discrepancy between results on the two-photon decomposition of azoethane obtained with<sup>769</sup> and without<sup>758</sup> external focusing. The type and distribution of photolysis products formed in the focused case are similar to those obtained by electrical discharge of azoethane, which suggests that breakdown occurred in the focal region.

Multiphoton processes have been observed in the ruby-laser-induced dissociation of biphenyl<sup>770</sup> NO<sub>2</sub>,<sup>771</sup> the ionization of atoms,<sup>768,772</sup> and molecules,<sup>112,773</sup> and in the whole class of MPD induced by CO<sub>2</sub> laser pulses (section C).

However, many other "nonlinear" photochemical processes were probably initiated via breakdown.<sup>486</sup> These results do not provide molecular cross sections, since the reactions following breakdown mask the quantum order of the primary process. Quantitative information on multiphoton absorption cross sections is limited to those few favorable cases, where no focusing of the laser beam is required to obtain measurable yields.

## V. Chemical Control of Laser Action

### A. Chemical Lasers

#### 1. Principles and Methods

In a chemical laser, elementary chemical reactions lead to an inverted population by selective partitioning of exothermic reaction energy among nonequilibrium vibrationally excited nascent products. The extent to which this occurs is determined by the shape of the potential energy surface along the reaction trajectory.<sup>598,774</sup> Stimulated emission originates from the ensuing spontaneous (infrared) chemiluminescence, which is made to oscillate in an optical cavity. About 10% of the exoergicity is available for lasing.

The spectral and temporal characteristics of the gain provide information about the generation, storage, distribution, and transfer of energy in the primary chemical reactions, and about the radiative and collisional relaxation processes occurring in the medium. Chemical lasers have also been implemented as real-time microprobes for monitoring state specific reaction rate constants outside the resonator (section IV.B), as pumps to

prepare molecules in excited vibrational states, for example, in isotope selective photocatalysis (section IV.C), and in energy transfer studies.

The extensive monograph by Kompa<sup>775</sup> and other reviews<sup>776-780</sup> cover the formative years of the chemical laser field from the discovery<sup>781</sup> of the photodissociation  $\text{CF}_3$  laser by Kasper and Pimentel in 1964 through the spring of 1972. Other surveys deal with the high-power capability of chemical lasers and put more stress on device aspects.<sup>782-784</sup> Chemical lasers are widely used in mechanistics, kinetics, and energy-transfer studies. These particular applications have recently been reviewed in depth by Berry.<sup>785</sup> We confine ourselves here to a brief introduction, aiming not at completeness but rather at an understanding of the principles of chemical lasers and their capabilities in fundamental research in physical chemistry, particularly for systems in thermal disequilibrium.

Laser-producing reactions consume free atoms or radicals, which are generated from suitable precursors either by fast flash photolysis, electrical discharge, or electron-beam injection in a premixed gas, or by thermal dissociation of reactant(s) prior to mixing. "Purely" chemical lasers are self-sustained and derive the excitation energy directly from mixing of stable compounds which act spontaneously without application of auxiliary initiation sources.<sup>786,787</sup> For CW operation rapid and thorough mixing of reagents is essential in order to maintain a vibrationally inverted population of products. Fast pumps or gas dynamic designs are employed in high-power laser configurations.<sup>782-784</sup>

Most chemical lasers operate on vibrational-rotational transitions in diatomic gas molecules,  $vJ \rightarrow v'J'$ , where the prime refers to the lower state, but electronic and rotational transitions may also lead to lasing. Optically allowed transitions are governed by quantum mechanical selection rules. For a rotating vibrator these are, for emission,  $v - v' = +1$  and  $J - J' = -1$  (P-branch) or  $J - J' = +1$  (R-branch). Laser lines are identified as  $P_{v \rightarrow v-1}(J')$  or  $R_{v \rightarrow v-1}(J')$ . The more important chemical laser species are hydrogen halides and CO.

The gain coefficient is proportional to the population inversion between a pair of vibrotational levels,  $\Delta N_{vJ}$ , defined as

$$\Delta N_{vJ} = N_{vJ} - N_{v'J'}g_J/g_{J'}$$

where  $g_J = 2J + 1$  is the statistical weight of sublevel  $J$  in a sample which is assumed to be rotationally thermalized before the onset of lasing (achieved, in practice, through the addition of excess inert gas). Note that this assumption, together with that of long-lived vibrationally excited states (depopulated mainly by radiative transitions), implies different vibrational and rotational temperatures in the sample. Lasing is possible only if  $\Delta N_{vJ} > 0$ . This is more easily achieved for the P-branch, where  $g_J/g_{J'} > 1$ , than for the corresponding R-branch transitions.<sup>775</sup> For some P-lines, gain may be reached even if  $N_v < N_{v-1}$  (partial vibrational inversion). In contrast, lasing at R-lines, Q-lines, or at P-lines with high  $J$  values (achievable, for example, when the molecular rotational constant  $B \ll kT$ ) requires total vibrational population inversion.

Radiative and collisional deexcitation will perturb the initial values of  $\Delta N_{vJ}$  through the combined processes of vibrational cascading and J-switching. Consider, for example, a particular transition  $P_{v \rightarrow v-1}(J')$  which begins to lase when its gain exceeds the cavity loss factors. As a result, the gain of the  $R_{v \rightarrow v-1}(J'-2)$  transition, originating from the same upper level  $vJ$ , is quenched. In fact, R-branch emission is never observed in a free-running chemical laser. Also, depletion of  $N_{vJ}$  facilitates lasing in the adjacent  $v+1 \rightarrow v$  and  $v-1 \rightarrow v-2$  bands and causes dissipation of the nascent population inversion. Thus, as time progresses, the output spectrum of the laser pulse shifts to  $P_{v+1 \rightarrow v}(J'-1)$  and (mostly) to  $P_{v-1 \rightarrow v-2}(J'+1)$ , then, in the course of the thermalization process, to other lines (with lower  $v$  and higher  $J$  values) as the vibrational temperature decreases and the rotational-translational temperature

increases. These qualitative arguments are supported by rate equation treatments and by a thermodynamic analysis, involving entropy changes during the different stages of lasing.<sup>688</sup>

The reaction rates and the radiative and collisional relaxation processes occurring in a chemical laser medium are studied by measuring the spectral composition and relative power of the laser transitions and their pressure, temperature and time dependence, using a combination of the following methods.

(a) Highest-gain method.<sup>789</sup> The first transition to reach threshold in a free-running pulsed chemical laser provides direct evidence about the nascent vibrational population ratio  $N_v/N_{v-1}$ .

(b) Equal-gain temperature method.<sup>790</sup> Here the value of  $N_v/N_{v-1}$  is deduced from the rotational temperature at which two transitions,  $P_{v \rightarrow v-1}(J)$  and  $P_{v \rightarrow v-1}(J+1)$ , have equal gain, i.e.,  $\Delta N_{vJ} = \Delta N_{v,J+1}$ .

(c) Tandem equal-gain method.<sup>791</sup> Two separate tubes containing the same lasing species are placed in one optical resonator. The "driver", which represents a higher gain laser system, forces the "slave" to oscillate on a vibrational band different from its own highest gain transition. The population distribution in the enforced transition is then probed by measuring the temporal evolution of the laser pulse which depends on the gain or loss in the slave section.

(d) Zero-gain temperature method.<sup>792</sup> The temperature in the slave section is varied until transparency is achieved. The slave laser then has zero gain.

A diffraction grating may be incorporated in the configuration of methods b through d. This restricts laser oscillations, at choice, to a particular spectral line or to a pair of adjacent lines.

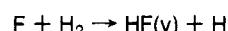
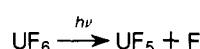
In section 2 we list the more common types of chemical lasers, each illustrated by one example. Complete compilations may be found in the reviews of Kompa<sup>775</sup> and Berry.<sup>785</sup>

## 2. Classification of Chemical Lasers

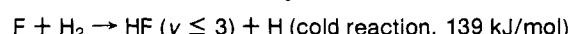
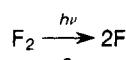
Reactions are actuated by ultraviolet flash photolysis ( $h\nu$ ), electrical discharge (e), electron beams (B), thermal dissociation (heat), or chemical reactions (chem). Radiative decay leads to continuous (CW) or pulsed (p) laser operation. Typical values are presented for pulse duration  $\tau_p$ , powers  $P$ , and energies  $E$ .

### a. Flash-photolysis laser<sup>793</sup>; $p, E = 15 \text{ J}$

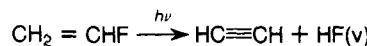
(i) Nonchain reaction;<sup>794</sup>  $\tau_p \approx 5 \mu\text{s}$ , shorter than FL pulse duration



(ii) Chain-branching reaction;<sup>795</sup>  $\tau_p \approx 50 \mu\text{s}$ , longer than FL pulse duration because of reaction chain length which may amount to a few hundred steps.

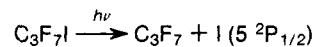


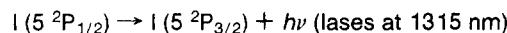
### b. Photoelimination laser;<sup>574,796</sup> $p$



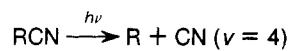
### c. Photodissociation laser;<sup>781,797-799</sup> $p, \tau_p \approx 3 \text{ ns}, E \approx 100 \text{ J}$

Strictly speaking this is not a chemical laser since the decomposition reaction is endothermic and no chemical energy is converted into radiant energy.

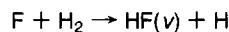
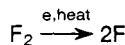




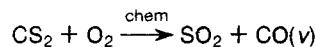
d. Predissociation laser<sup>800</sup>



e. Flow chemical laser;<sup>786,801</sup> CW,  $P \approx 5 \text{ kW}$  for supersonic transverse flow and for 10 Torr operating pressure.

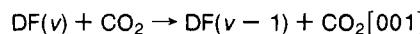
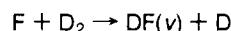
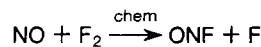


f. Free-burning flame laser;<sup>802</sup> CW,  $P \approx 25 \text{ W}$ , pressure about 10 Torr

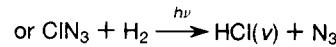
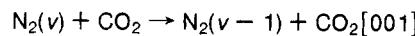
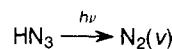


g. Energy transfer laser;<sup>786,787,803,804</sup> CW,  $P \approx 15 \text{ kW}$ , operating pressure 60 Torr

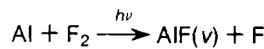
In this purely chemical laser, energy stored in the vibrational manifold of DF(v) is transferred to the long-lived upper laser level [001] of CO<sub>2</sub>. In this way deleterious vibrational redistribution between hydrogen halides is minimized.



h. Thermal-explosion laser;<sup>805</sup>  $p, \tau_p \approx 10 \mu\text{s}$



i. Exploding-wire laser;<sup>806</sup>  $p$



## B. Dye Lasers<sup>30</sup>

Organic dye lasers have become the most widespread source for coherent, tunable, and monochromatic light (section I.B). General reviews of this expanding field are available,<sup>30,31,807-810</sup> as are partial bibliography lists<sup>811,812</sup> to which we refer for details regarding design or operational techniques. In this section we shall review the chemical approach to dye lasers. Our goal here is not to add yet another survey of dye lasers, but to analyze the properties of the lasing medium.

Dye lasers can be investigated using kinetic techniques, but a complete analysis is beyond the scope of this review. We will present the case of a dye amplifier operating near threshold under steady-state conditions.<sup>813</sup> Most of the conclusions of this simple model are applicable to real-life dye lasers for which more general treatments are available.<sup>808,814-817</sup> Using the kinetic scheme presented in Figure 8, we can, to a first approximation, discuss laser dyes as a four level system. Molecules are pumped at a rate of  $\sigma_{01}(\text{P})/I_p$  to some vibronic level S<sub>1</sub><sup>v</sup> (or S<sub>n</sub><sup>v</sup>), from which they subsequently relax nonradiatively to S<sub>1</sub><sup>0</sup> at a rate  $1/\tau_v$ . Laser action is initiated by the spontaneous fluorescence noise, characterized by a fluorescence lifetime  $\tau_{10}$ , a line shape,  $g(v)$ , and a quantum yield  $\phi$ . Together they determine the stimulated emission cross-section  $\sigma_e$  (see eq 4). The fluorescence transitions take place between the S<sub>1</sub><sup>0</sup> and the S<sub>0</sub><sup>v</sup> states, which ultimately return nonradiatively to S<sub>0</sub><sup>0</sup> at a rate  $1/\tau_v$ . The spontaneous noise is amplified through stimulated

emission at a rate  $\sigma_e I_L$ , thus leading to laser action in the dye medium. Using typical data for the molecular parameters of laser dyes in condensed media (section III.B and Table III), we are justified in assuming that  $\sigma_{10}(\text{P})/I_p \ll 1/\tau_v$ . From eq 13 an expression for the gain G of a dye laser amplifier may be obtained

$$G = \tau_{10}\sigma_e\sigma_{01}(\text{P})/I_p N / [1 + \tau_{10}\sigma_{01}(\text{P})/I_p] \quad (27)$$

which would imply that no threshold power exists. This indicates that the four-level model is rather naive. In fact, a dye laser consists of a multilevel molecular medium, and generally the complete singlet and triplet manifolds have to be taken into account.

We divide dye laser systems into three categories according to the pumping technique employed: (a) CW dye lasers (CWDL) pumped by Ar<sup>+</sup> or Kr<sup>+</sup> lasers; (b) flash lamp pumped dye lasers (FLPDL); (c) pulsed laser pumped dye laser (PLPDL) systems. Here pumping is provided by a FD ruby or Nd laser, or a nitrogen laser.

In CWDL and FLPDL the pumping duration,  $\tau_p$ , is long compared to the reciprocal ISC rate constant  $1/k_{ST}$ . For this reason, triplet state formation limits the laser performance. The steady-state analysis of a CWDL or FLPDL amplifier yields the following expressions for the gain and for the threshold pump intensity  $I_p^{\text{th}}$ .

$$G = \xi N [\sigma_e - \sigma_{12}(\text{L}) - \tau_{TS}\sigma_T(\text{L})k_{ST} - \sigma_{01}(\text{L})(1 + \tau_{10}k_{ST})/\tau_{10}\sigma_{01}(\text{P})/I_p] \quad (28)$$

and

$$I_p^{\text{th}} = \sigma_{01}(\text{L})(k_{ST}\tau_{10} + 1)/\tau_{10}\sigma_{01}(\text{P})[\sigma_e - \sigma_{12}(\text{L}) - \sigma_T(\text{L})k_{ST}\tau_{TS}] \quad (29)$$

with

$$\xi = \tau_{10}\sigma_{01}(\text{P})/I_p / \{ \tau_{10}[\sigma_{01}(\text{P})/I_p + k_{ST}] + 1 + k_{ST}\tau_{10}\tau_{TS}\sigma_{01}(\text{P})/I_p [1 + \tau_{TS}\sigma_T(\text{P})/I_p] \} \quad (30)$$

where all the molecular parameters are defined in Figure 8.

Lasing is most easily achieved in PLPDL systems. Here  $\tau_p \ll 1/k_{ST}$  so that triplet-state formation can be neglected. However, now we must take into account photoquenching due to absorption of the pump radiation by molecules in S<sub>1</sub><sup>0</sup>, at a rate  $\sigma_{12}(\text{P})/I_p$ . The results for G and  $I_p^{\text{th}}$  in a PLPDL small-signal amplifier are

$$G = \zeta N [\sigma_e - \sigma_{12}(\text{L}) - \sigma_{01}(\text{L})/\tau_{10}\sigma_{01}(\text{P})/I_p] \quad (31)$$

and

$$I_p^{\text{th}} = \sigma_{01}(\text{L})/\tau_{10}\sigma_{01}(\text{P})[\sigma_e - \sigma_{12}(\text{L})] \quad (32)$$

where

$$\zeta = \tau_{10}\sigma_{01}(\text{P})/I_p / [1 + \tau_{10}\sigma_{01}(\text{P})/I_p + \tau_{10}\tau_{21}\sigma_{01}(\text{P})\sigma_{12}(\text{P})/I_p^2] \quad (33)$$

Inspection of eq 29 and 32 shows that the necessary molecular operation criterion for any dye laser is that  $\sigma_e > \sigma_{12}(\text{L})$ . The cross-section  $\sigma_{01}(\text{L})$  influences the value of  $I_p^{\text{th}}$  and also the high-frequency tuning limit of the dye. Equation 28 shows that for FLPDL and CWDL G decreases in systems having increasing  $k_{ST}$ ,  $\sigma_T(\text{P})$ ,  $\sigma_T(\text{L})$ , or  $\tau_{TS}$ ; thus even when  $\sigma_e > \sigma_{12}(\text{L})$  the triplet parameters may determine the operational conditions. While  $k_{ST}$ ,  $\sigma_T(\text{P})$ , and  $\sigma_T(\text{L})$  are only slightly affected by external perturbations, the value of  $\tau_{TS}$  can be manipulated by adding triplet quenchers such as oxygen<sup>808,818,819</sup> or cyclooctatetraene.<sup>820</sup> In PLPDL systems, photoquenching sets an optimum for the efficiency of the dye laser, since there exists a maximum gain, given by eq 20.<sup>813,814</sup> This was confirmed by efficiency measurements<sup>820</sup> and through the intensity dependence of the gain as measured by Shah and Leheny.<sup>378,822</sup> In addition, indirect observations of photoquenching effects on PLPDL performance

have been reported.<sup>813,814,823-825</sup> Molecular reorientation,<sup>826,827</sup> bleaching,<sup>828</sup> and photodegradation of dyes<sup>829-832</sup> are also relevant to PLPDL. Bleaching, which is utilized in passive Q-switching, will quench dye laser action completely since at these pump powers  $\sigma_{01}(P)/I_p \gg 1/\tau_v$ . Thus no laser action is possible; i.e., complete vibrational relaxation of the  $S_1$  state is needed prior to laser action.

We may conclude that for all dye lasers the relative values of the molecular parameters determine their performance.<sup>833,834</sup> These parameters are a function of the chemical structure of the dye molecule. Efforts in dye synthesis to improve the lasing characteristics are important and may prove fruitful in reducing some of the molecular loss mechanisms discussed above. Enhanced photochemical stability of dye molecules is also significant in practical systems.<sup>835,836</sup> Another approach to overcome losses is to modify the lasing state. For example, protonation by acidifying the medium<sup>809</sup> or formation of exciplexes,<sup>837-839</sup> as in coumarin systems, have been effective in extending the lasing range. However, it is not clear whether this should be attributed to reduced photoquenching, which normally is sizable in these systems due to the large value  $\sigma_{12}(P)$ .<sup>377</sup> Similar effects on the lasing state can be achieved by utilizing energy transfer between a donor-pumped molecule and an acceptor-lasing dye.<sup>344,345</sup> Energy transfer dye lasers (ETDL) have been used to extend the range of PLPDL systems to the infrared spectral region.<sup>840-842</sup> As was shown in a recent analysis of ETDL, the threshold power is lowered and sometimes photoquenching can be minimized.<sup>843</sup>

As in other studies of laser photophysics, dye laser investigations provide a wealth of information concerning molecular parameters and molecular dynamics. The novel technique of gain spectroscopy can be employed to yield better insight into molecular properties<sup>844,845</sup> responsible for optimum dye laser operation. The diverse uses of dye lasers by chemists are demonstrated throughout this review. In addition there is a strong and continuing effort to explore new aspects of dye lasers, and to improve the performance of dyes through a better understanding of their photophysical and photochemical properties.<sup>846</sup> A combined effort by physical and organic chemists to "engineer" laser dyes<sup>833,835</sup> for a given application may prove mutually rewarding.

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## VI. Appendix. List of Abbreviations

### A. Phenomena, Devices and Techniques

CARS	Coherent anti-Stokes Raman scattering
CT	Charge transfer
CW	Continuous wave
CWDL	Continuous wave dye laser
ETDL	Energy transfer dye laser
FD	Frequency doubled
FL	Flash lamp
FLPDL	Flash lamp pumped dye laser
FQ	Frequency quadrupled
FT	Frequency tripled
IC	Internal conversion
ISC	Intersystem crossing
LIDAR	Light detection and ranging
LIFC	Laser induced fluorescence continuum
LIR	Laser-induced reaction
ML	Mode locked
MPD	Multiphoton decomposition
PLPDL	Pulsed laser pumped dye laser
PSFC	Picosecond fluorescence continuum
PSFS	Picosecond flash spectroscopy

RF	Radiofrequency
RPD	Radiation pressure deflection
SHG	Second harmonic generation
SIT	Self-induced transparency
SPP	Single photon predissociation
SRE	Stimulated Raman excitation
SRS	Stimulated Raman scattering
TEA	Transversely excited atmospheric pressure
TPA	Two-photon absorption
TPD	Two-photon dissociation
TPF	Two-photon fluorescence
TPI	Two-photon ionization
TPS	Two-photon spectroscopy
UHRS	Ultrahigh resolution spectroscopy

## B. Materials and Compounds

ADMA	<i>p</i> -(9'-Anthryl)- <i>N,N</i> -dimethylaniline
BA	Benzanthracene
BBO	2,5-Bis(4-phenyl)oxazole
BDN	Bis(4-dimethylaminodithiobenzil)nickel(II)
CV	Cresyl violet
CVP	CV perchlorate
DAMC	7-Diethylamino-4-methylcoumarin
DCI	Cryptocyanine (1,1'-diethyl-4,4'-carbocyanine iodide)
DDI	1,1'-Diethyl-2,2'-dicarbocyanine iodide
DEA	<i>N,N</i> -Diethylaniline
DiMe-	1,4-Bis[2-(4-methyl-5-phenyloxazolyl)]benzene
· POPOP	
DMA	<i>N,N</i> -Dimethylaniline
DMSO	Dimethyl sulfoxide
DODCI	3,3'-Diethyloxadicarbocyanine iodide (DODI)
DPA	Diphenylanthracene
DPPD	<i>N,N</i> -Diphenyl- <i>p</i> -phenylenediamine
DTC	1,1'-Diethyl-2,2'-tricarbocyanine iodide
DTDC	3-Ethyl-2-[5-(3-ethyl-2-benzothiazolinylidene-1,3-pentadienyl]benzothiazolium iodide
DTDI	3,3'-Diethylthiadadicarbocyanine iodide
DTTC	3,3'-Diethylthiatricarbocyanine iodide
DPPD	<i>N,N</i> -Diphenyl- <i>p</i> -phenylenediamine
ECZ	<i>N</i> -Ethylcarbazole
HITC	1,3,3,1',3',3'-Hexamethyl-2,2'-indotricarbocyanine iodide
MB	Methylene blue
PMDA	Pyromellitic dianhydride
PMMA	Poly(methyl methacrylate)
POPOP	[2,2'- <i>p</i> -Phenylenebis(5-phenyloxazole)]
PPO	Phenylbiphenylyloxadiazole
PTH	Phenothiazine
RB	Rhodamine B
R6G	Rhodamine 6G
TCNB	1,2,4,5-Tetracyanobenzene
THF	Tetrahydrofuran
TPMD	<i>N,N,N',N'</i> -Tetramethyl- <i>p</i> -phenylenediamine
VCZ	<i>N</i> -Vinylcarbazole

## VII. References

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