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Lasers and Chemistry

SOL KIMEL* and SHAMMAI SPEISER

Department of Chemistry, Technion—Israel Institute of Technology, Haifa, Israel

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Contents

I. Introduction

Why another review on lasers? In the past few years dozens of reviews have appeared, some of them grouped in book form,[1,2] 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".[3]

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,[4] photofragment spectroscopy,[5] molecular beam diagnostics,[6] photodetachment,[7] and temperature-jump techniques.[8] 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

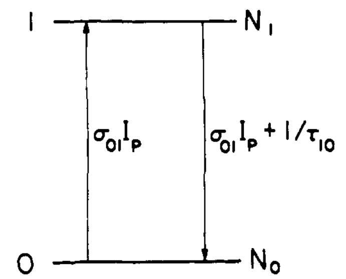


Figure 1. Two-level system irradiated by an optical pumping field of. intensity I_p. Shown are rates of absorption $\sigma_{01}I_p$, spontaneous emission τ_{10}^{-1}, and induced emission $\sigma_{10}I_p$.

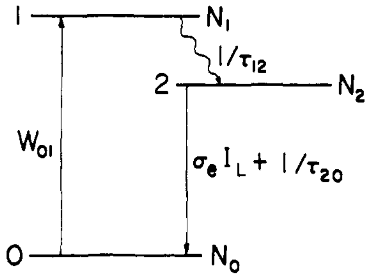


Figure 2. Three-level laser medium N_i is the population density of level i, τ_{ij} are lifetimes, W_{01} is the pumping rate, σ_e is the stimulated emission cross section, and I_L is the laser intensity.

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,[9-13] 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.[14]

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^3) 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 σ_{01} denotes the absorption cross section. The rate of emission from the excited state is the sum of a spontaneous emission rate N_1/τ_{10}, τ_{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.

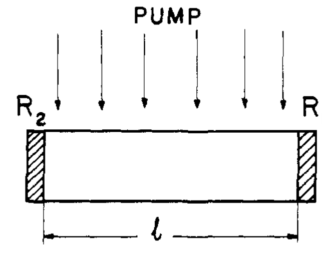


Figure 3. Fabry-Perot type laser cavity consisting of two parallel mirrors with reflectivities R_1 and R_2.

In a laser, a population inversion ($N_1 > N_0$) exists btween 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/τ_{12}, τ_{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 ν_L can be built up in some of the standing waves (modes) that are sustained in the cavity.[9] The rate equations for the population densities corresponding to the three-level kinetic scheme are:

$$dN_0/dt = -W_{01}N_0 + (\sigma_eI_L + 1/\tau_{20})N_2 \tag{1}$$

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

$$dN_2/dt = N_1/\tau_{12} - (\sigma_eI_L + 1/\tau_{20})N_2 \tag{3}$$

where σ_e is the stimulated emission cross section at ν_L given by

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

Here ϕ is the quantum yield for fluorescence from level 2 having a fluorescence lifetime τ_{20}, $g(\nu)$ is the normalized fluorescence lineshape function centered at ν_L, and η is the refractive index of the medium.[9] 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[9]

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

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 ℓ, t_c is[9]

$$t_c = 2\eta\ell/c(1 - R_1R_2) \tag{6}$$

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

$$\rho = 8\pi^2\nu_L^2\Delta\nu V/c^3 \tag{7}$$

V being the volume of the cavity[9] (typically $\rho \simeq 10^{13}$, 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),

$$G = (1/I_L)\,dI_L/dz = (\eta/cI_L)\,dI_L/dt \tag{8}$$

From the threshold condition, $G = 0$, the threshold population ratio N_2^{th}/N and the threshold pumping rate W_{01}^{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

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

where we have used the condition

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

Thus we obtain the threshold pump intensity as

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

and the threshold population inversion

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

Inspection of eq 11 and 12 shows that optimal results are obtained for laser media for which σ_{01}, τ_{20}, and t_c are large and τ_{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

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

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

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.[15-18] This survey is supplemented in section V, where we discuss some chemical aspects of lasers in more detail.

1. *Solid-state lasers*[16,17] 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.[16] The first laser action was discovered in ruby (0.05 wt % Cr^{3+} ions in sapphire, crystalline Al_2O_3) 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^{3+} 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^{3+} ions incorporated as impurities in a variety of host materials such as glass, crystalline $CaWO_4$, or YAG (yttrium aluminum garnet, $3Y_2O_3{:}5Al_2O_3$), each giving rise to somewhat different lasing characteristics. Lasing is obtained at lower excitation 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).

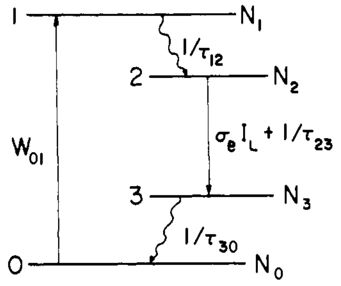


Figure 4. Four-level laser medium. For symbols see Figure 2.

2. *Gas lasers*[16,17,19,20] 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 2^3S and 2^1S. 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 2^3S and 2^1S 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,[4] 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.[21] The most widely applied source for pulsed (~5 ns) radiation in the ultraviolet (at 337.1 nm) is the molecular N_2 gas laser, but some exotic systems pumped by electron beams show promise, notably H_2, Xe_2^* excimers, and rare-gas halides (XeF, KrF).[22,23]

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.[24] The most prominent laser in this class is the carbon dioxide laser. The discharge excites CO_2 molecules to the relatively long-lived [001] vibrational level in the electronic ground state. The integers $[n_1, n_2, n_3]$ denote, respectively, the degree

TABLE I. Some Important Laser Sources[a]

Laser medium	Principal wavelengths[b] (μm)	Predominant mode of operation	Maximum power output (W)	
			Pulsed	CW (multimode) or pulsed av
	1. Solid-State Lasers			
Ruby	0.694	Pulsed	10^{10}	
Nd-glass	1.06	Pulsed	10^{12}	
Nd-YAG	1.064	CW	10^6	10^3
	2. Gas Lasers			
He-Ne	0.633	CW		10^{-2}
	1.152			10^{-1}
	3.391			10^{-2}
Ne^+	0.332	CW		10^{-1}
Ar^+	0.488	CW	10^2	10
	0.515			
Kr^+	0.568	CW		10
	0.647			
Xe^+	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_2	0.337	Pulsed	10^6	1
H_2	0.120	Pulsed	10^4	
	0.160		10^5	
Xe_2^*	0.170	Pulsed	10^8	
XeF	0.350	Pulsed	10^9	
CO_2	9.6-10.6	Pulsed and CW	10^{10}	10^3
CO	5.5-5.7	Pulsed	10^7	10
H_2O	7-220	Pulsed	10^2	10^{-1}
HCN	337	Pulsed	10^2	10^{-1}
	3. Chemical Lasers (see section V.A.2)			
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_3F_7I	1.315	Pulsed	10^{10}	
	4. Semiconductor Lasers			
Ga-As	0.85	Pulsed and CW	10^2	10^{-2}
In-As-P	2-8			
Pb-Sn-Te	10-35			
	5. Dye Lasers			
Coumarins	0.40-0.50	Pulsed and CW	10^6	1
Rhodamine-6G	0.56-0.61			

[a] For details on commercial systems see "Laser Focus" Buyers' Guide, 12th ed, January 1977. [b] 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 ν_1, the bending mode ν_2, and the asymmetric stretching mode ν_3. Lasing is made more efficient by admixing N_2 and He. A vibrationally excited N_2 molecule (at $\nu = 2350$ cm^{-1}) has a long radiative lifetime and, upon collison with a ground-state CO_2 molecule, transfers its energy to the [001] level of CO_2 (at $\nu_3 = 2349$ cm^{-1}) with which it is resonant. In this way, population inversion in CO_2 can be established between the level [001] and the level [100] (at $\nu_1 = 1388$ cm^{-1}) or the level [020] (at $2\nu_2$, 1285 cm^{-1}), thus leading to oscillations in the infrared region around 961 cm^{-1} (10.6 μm) or 1064 cm^{-1} (9.6 μm), respectively. Collisions with He atoms aid in reverting CO_2 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 vibrotational sublevels, opens up the possibility of obtaining numerous laser lines. With a diffraction-grating rear-mirror configuration a CO_2 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 cm^{-1}. The recent development of high-pressure (~15 atm) CO_2 lasers, in which the individual rotational lines are smeared out by pressure broadening, permits continuous tunability[25] between 930 and 1100 cm^{-1}.

The CO_2 laser is the most important molecular laser in use to date. The high CW output power (up to several kW), high intensities (GW/cm^2 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_2 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_2O, H_2O, and HCN, have made available many laser lines in the whole infrared spectral region.[26]

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*[27] convert electrical energy directly into coherent radiation. They are different from other lasers in pumping mechanism and operation performance.

Semiconductor lasers are compact (≃1 mm^3), cheap, and highly efficient (≃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} 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 Hz (≃3×10^{-5} 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[28] or aprotic solutions[29] 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.[30,31]

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 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.[9-13] Equally important is the possibility of continuous fine tuning over the relatively broad fluorescence band (≃50 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 (≃1 nm) line. With additional intracavity wavelength-selective elements, such as prisms, etalons, or filters, further narrowing of the spectral line width has been attained,[30] down to 0.0001 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^{-3} to 10^{-12} s and with peak intensities up to 10^{14} W/cm^2.

C. Properties of Laser Radiation and Nonlinear Effects[9–18]

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^{-6} to 10^{-3} 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

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

(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 10^8 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 $\eta\ell/c \simeq 3$ ns.

Q-Switching is accomplished by mechanical (rotating mirror),[32] electrooptical[9,10] (Pockels cell) or chemical means.[31] 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 ($\simeq 10^{-5}$ 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.*[33–35] 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.[36] 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 $T = 2\eta\ell/c$ ($\simeq 5$ ns). Each pulse is of duration T/m ($\simeq 5 \times 10^{-12}$ 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.[27] The saturable dye, present in a very thin ($\simeq 1$ 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 τ_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^{-1} we find $\tau_p \simeq 3$ ps. With pulse-broadening and pulse-compression techniques,[38] τ_p may be varied between 10^{-10} and 10^{-13} 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.[39–40]

2. Coherence

Unlike conventional light sources, lasers are highly coherent,[11–13] 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^{-1}). Each atom can be thought to emit a Gaussian-shaped wavetrain during the time interval Δt required for the transition to take place. During the lifetime Δt 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 Δt 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 ν and of duration Δt is equivalent to a number of infinitely long wavetrains of differing frequencies spread about the central frequency ν. 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

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

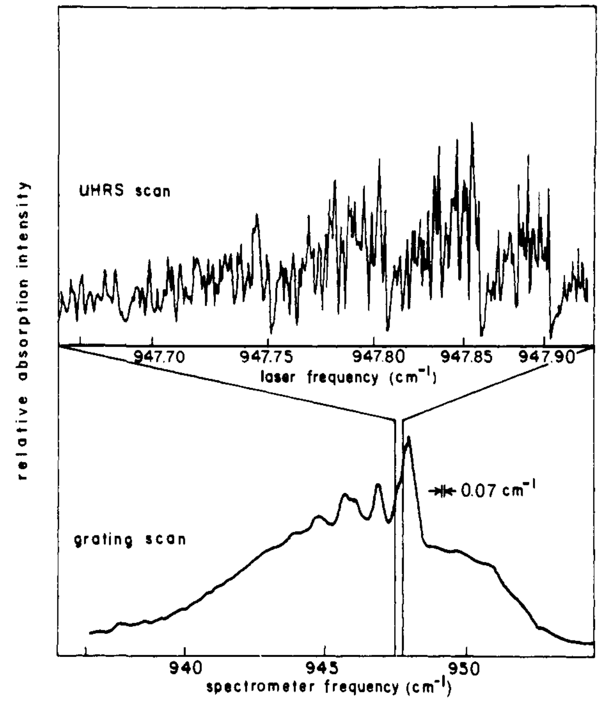


Figure 5. Spectrum of the ν_3 band of SF_6, obtained with a conventional high-resolution spectrometer and with a tunable PbSnTe diode laser (after Hinkley[49]).

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, $\Delta L < 10^{-2}$ 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 λ. 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 cm^2 cross section, upon focusing to a spot of 1 μm diameter, will yield an intensity of $\simeq 10^4$ W/cm^2. With pulsed CO_2 lasers it is relatively simple to obtain peak intensities of several terawatts (10^{12} W) per cm^2. Such intensities are being used in molecular photofragmentation studies (see section IV.C).

3. *Nonlinear Optics in Laser Techniques*[9,10]

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, $\Sigma \mathbf{k}_i = 0$, where $k_i = 2\pi\nu_i\eta_i/c$ is the wave vector associated with the field oscillating at ν_i. The refractive index η_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 KH_2PO_4 (KDP) or $NH_4H_2PO_4$ (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.[2,41–45] 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} cm^{-1}) single-mode gas lasers and tunable narrow band lasers, such as a Hänsch design dye laser[46] or a semiconductor laser,[27] 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.[47] With a mode-selected ruby laser, having 0.04-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[48] also resolved spectral lines associated with bromine isotopes.

In Figure 5 we reproduce a spectacular example of UHRS of SF_6, obtained with a tunable PbSnTe diode laser,[49] showing thousands of resolved absorption features per cm^{-1}. For a further discussion the reader is referred to specialized reviews.[42,44,45,50]

B. Nonlinear Spectroscopy[50–56]

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.[31] If pulses are employed which are short compared to the molecular dephasing time T_2, coherence phenomena[57–58] such as self-induced transparency (SIT),[59] optical nutation,[60] and photon echoes[61] can be studied. The latter has recently been demonstrated for molecular systems.[62] These phenomena cannot be discussed on a rate equation basis, and a quantum mechanical treatment is required.[14] It is sometimes difficult to determine whether intensity dependence of absorption must be

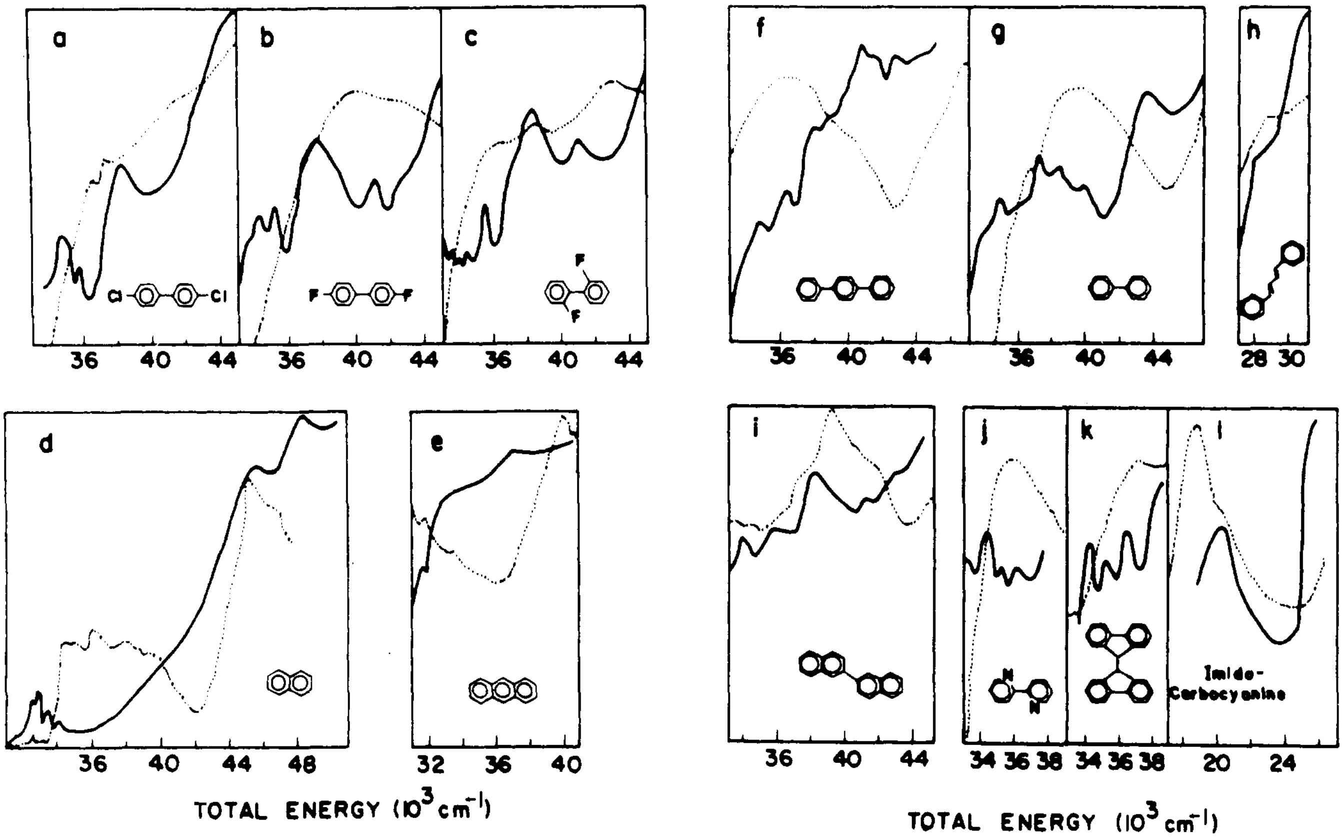


Figure 6. Low-resolution, two-photon absorption spectrum (solid curve) and the corresponding one-photon spectrum (dotted curve) for various centrosymmetric molecules: (a, b, c) ref 90; (d) ref 103; (e) ref 102; (f, g) ref 90; (h) ref 88; (i) ref 89; (j) ref 90; (k) ref 89; (l) ref 95.

attributed to SIT, saturation of absorption, photoquenching,[63] or some other effect. With CW lasers, characterized by narrow linewidths and moderate intensities, novel spectroscopic techniques have been developed;[14,42] 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.[9-13,64,65] The basic theory has been extended to include calculation of TPA cross sections,[66-70] group theoretical analysis of TPA selection rules,[71,72] and polarization effects.[72-74] Experimental results are analyzed through the absorbed laser intensity I_{abs} at ν_{L} per unit volume. For one exciting laser source the TPA law[64] reads

$$I_{\mathrm{abs}} = \delta N I_{\mathrm{L}}^2 \ell \qquad (17)$$

where δ is the TPA cross section (cm^4 s/photon molecule) at $2\nu_{\mathrm{L}}$, I_{L} the incident laser intensity (photons/cm^2 s), N the molecular concentration (molecule/cm^3), and ℓ the sample cell length. When combining two exciting sources eq 17 has to be modified accordingly.[75] The magnitude of δ and its wavelength dependence have been evaluated,[76] but there is still a dispute as to the difference from δ calculated for dye molecules on the basis of their one-photon absorption cross section.[76,77] To date, many TPA spectra have been measured, in some cases after having first developed specialized TPA spectrometers.[78-80] The more popular methods are indirect ones in which two-photon fluorescence (TPF)[65,81] or two-photon phosphorescence[82,83] 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 δ.[84,85] 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_{abs} has to be evaluated from the TPF intensity, I_{fl}, through

$$I_{\mathrm{abs}} = \alpha I_{\mathrm{fl}} \qquad (18)$$

where α 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 → g transitions which are now allowed in one-photon excitation.[82,87-91] Compounds have been investigated in the crystalline state,[71,86,87,92] in liquid,[73,93] in solution,[81,87-91,94,95] and in the gas phase.[96-100] 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.[65]

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

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

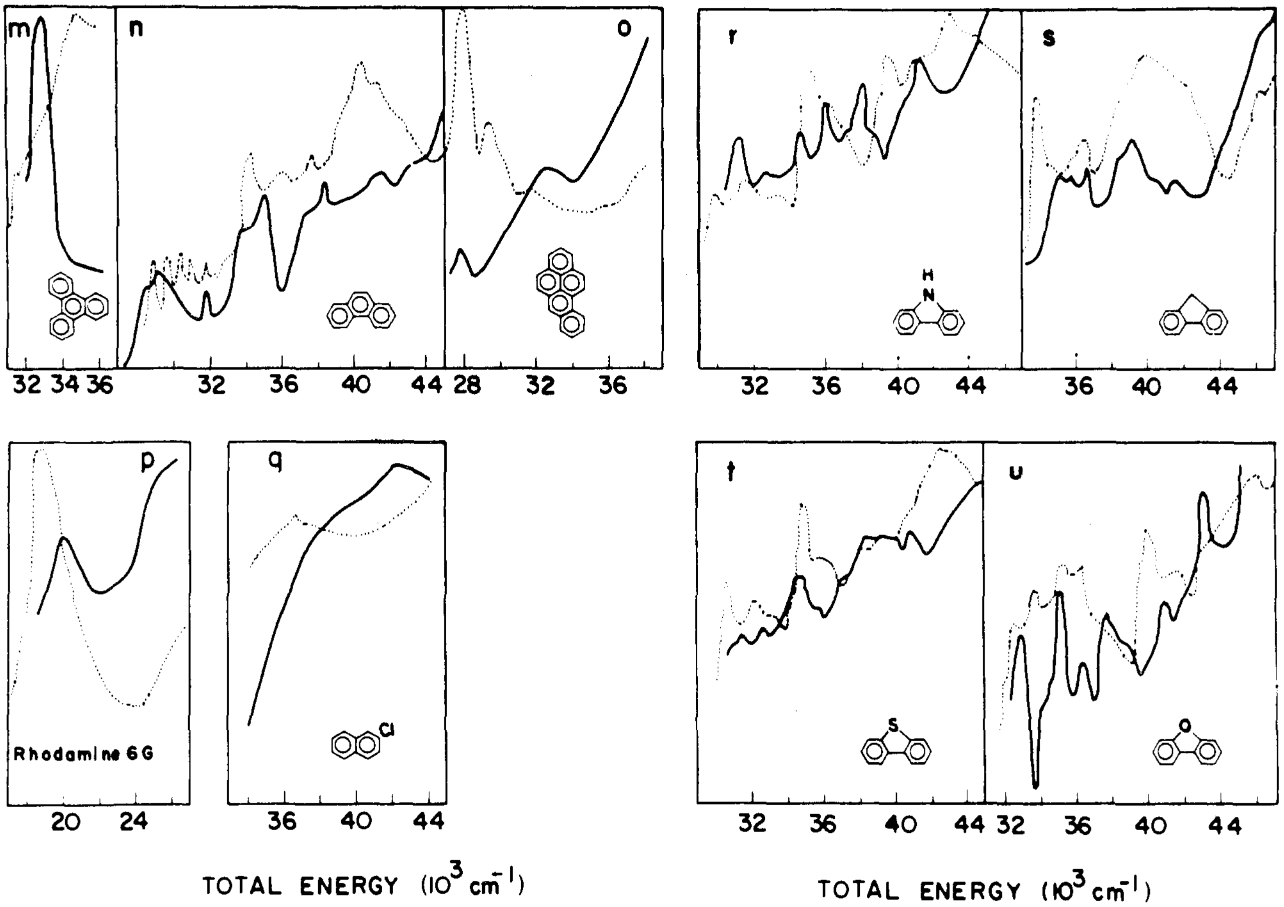


Figure 7. As in Figure 6, for molecules lacking center of symmetry: (m) ref 83; (n) ref 91; (o) ref 81; (p) ref 95; (q) ref 93; (r, s, t, u) ref 91.

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.[115] TPA is a nonlinear optical process and therefore other nonlinear processes such as photoquenching,[63,116,117] SRS (section D), or self-focusing[94,118,119] should be avoided when performing TPS studies. External focusing influences multiphoton absorption intensities[119-121] and may even mask the correct order of the process (section IV.D). The statistical and coherence properties of the laser light[122-124] and relaxation of the excited state[125,126] may also affect the apparent value of δ. Absolute values of δ 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,[36,37] or by nitrogen laser pumped dye lasers,[127] contain irregular picosecond spikes of amplified spontaneous noise. Experimental methods[128] and correction factors[129] have been suggested to overcome these intricacies. An attempt to unify experimental approaches, together with a survey of artifacts, has recently been reported.[130] For example, neglect of polarization effects has led to an erroneous assignment for benzene.[98,111]

Using extremely intense and short pulses coherent multiphoton phenomena such as two-photon SIT[131] and coherent TPA[132] have been observed. The transition probabilities for coherent multiphoton absorption processes have been calculated.[133] The situation is complicated further because of possible two-photon saturation effects.[134] The two-photon analog of one-photon saturation spectroscopy[135-137] and Doppler-free TPA permits UHRS of atoms[138-140] and of molecules.[141,142] 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[143,144]

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 ν_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 ν_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 ν_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.[143] The narrow line width of gas lasers ($\simeq$0.01 cm^{-1}) increases the spectral resolution ($\simeq$0.05 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[143-145] and monographs.[146-150]

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)[151] 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 ν_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 ν.

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,[152,153] a sample is simultaneously irradiated with a giant pulse laser at ν_L and continuum radiation, extending on the high-frequency side of ν_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 ν_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[154,155] 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 potential 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.[154] 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.[156] 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.[156-159]

The recently developed method of *coherent anti-Stokes* Raman spectroscopy (CARS)[160,161] 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 ν_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 ν_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 ν_1, ν_1, ν_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.[160]

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 η_i is subject to dispersion; in gases all beams are colinear.

E. Miscellaneous Spectroscopic Applications

1. *Remote Sensing of Atmospheric Pollutants*[162-167]

Remote optical sensing of chemical pollutants such as NO, NO_2, SO_2, O_3, 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,[166] 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 (≃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.[168–171] 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.[172] 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[173] which involves either frequency modulation of the laser output through the absorption line or amplitude modulation.

(b) *Laser Raman LIDAR.*[174–179] 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_2 or N_2 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.[180] 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.[181–186]

(d) *Remote Heterodyne Detection.*[187,188] 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,[172,188] NO_2,[172,179,180,183,184] SO_2,[175,179,186,188] O_3,[172,185,186,188] CO,[168,174,182] and hydrocarbons.[171,174,175,179,186]

2. Applications in Analytical Chemistry. Intracavity Studies[189–192]

All optical and spectroscopic methods employed in analytical chemistry have been improved by the introduction of lasers. Tunable lasers operating in the visible[30] and infrared[27] spectral region have revolutionized spectroscopic instrumentation.[42,44,45] 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 heterodyning,[187,188] which further increase sensitivity. Moreover, novel techniques have been developed, which include saturation spectroscopy[50,51] 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.[42] For some species detection sensitivities of 1 ppb have been achieved.[189] Some analytical applications have been mentioned, in a different context, in the preceding sections which describe UHRS[44–49] and remote sensing.[168–173,181–186] The high brightness of laser sources has led to the development of saturation spectroscopy,[50,51] 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[143–150,152,153,156–161] and to laser excited fluorescence.[52] Special fluorimeters have been developed,[193] and the detection limit has been pushed to below 1 part per trillion[194,195] (which amounts to detecting about 10^4 molecules/cm^3 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.[196–213] The molecular "amplification" process increases the sensitivity of trace absorptions about 100-fold. Measurements have been reported for Na,[196,203,204,206] Sr,[205] Ba,[203,205] Pr^{3+},[207,208] Eu^{3+},[197,203,208] Ho^{3+},[207] I_2,[196,198,201,209] NH_2,[199] HCO,[199] NO_2,[200,202] anthracene,[79] and stilbene.[79] Theoretical treatments giving a quantitative description of intracavity absorption enhancement have been worked out.[197,201,209,211] The inverse situation of intracavity emission has been used for enhanced flame spectrometry.[212] Quenching of a narrow-band CW dye laser has also been reported.[213]

Finally we mention the use of solid-state and CO_2 lasers in microprobe chemical analysis.[214] 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.[214] 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[215] 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

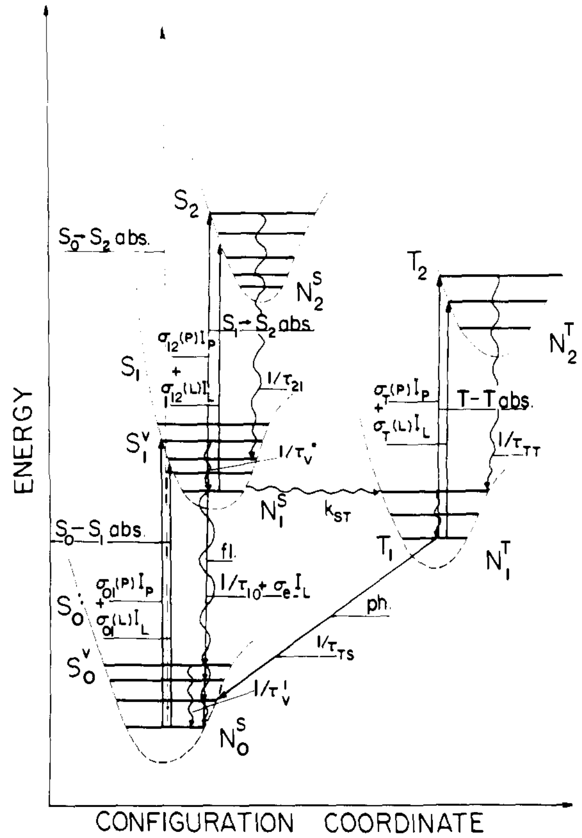


Figure 8. Diagram of photophysical and kinetic processes occurring in a solution of large organic molecules, typical examples being dye compounds. S_i and T_i designate, respectively, singlet and triplet states having populations N_i^S and N_i^T. In the singlet manifold the absorption (abs) rates are $\sigma_{ij}(p)I_p$ 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 $\sigma_T I$. The lifetime of the vibrational level v in the ground electronic state is $\tau_{v'}$, and $\tau_{v'}$ in the excited state; τ_{10} is the fluorescence (fl) and τ_{TS} the phosphorescence (ph) lifetime; τ_{21} and τ_{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.[216-219] 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 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.[220-224] We summarize the experimentally relevant predictions of the theory and complement them with illustrative examples.

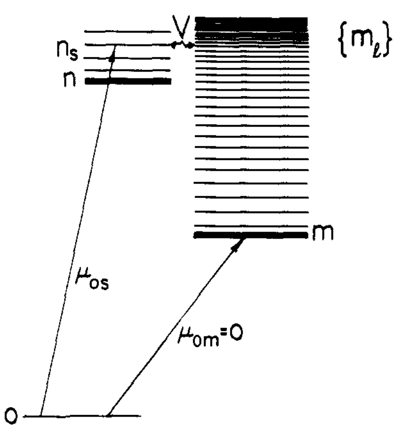


Figure 9. Diagram showing radiationless transitions from an optically prepared vibronic level n_s into the manifold $\{m_\ell\}$. The electronic states are designated by 0, n, and m; the transition moments by μ; and the coupling term by the perturbation matrix element V.

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.[225] The Hamiltonian of the photoselected molecular system is usually described by the Born–Oppenheimer (B–O) approximation.[221-224,226] For diatomic molecules calculated fluorescence lifetimes, τ_{10}, based on the Franck–Condon principle,[226] generally agree with measured quantities.[227-233]

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 $\{m_\ell\}$ 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 $\{m_\ell\}$ 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.[234] We shall discuss the experimental observations as belonging to a statistical, intermediate, or resonance case, a classification suggested by Bixon and Jortner.[235] 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 ρ 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"[226] $\tau_{nr} = \hbar/2\pi\rho V^2$, 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 ϕ is smaller than unity and independent of the environment. The criterion for irreversibility is that the maximum experimental time τ_{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 $\{m_\ell\}$ and to return to n_s.[223,224] Experimentally, τ_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 τ_{10} and Collisional Quenching Cross Sections σ_Q for Gaseous Molecular Species Prepared in Single Vibronic States and Studied by Time-Resolved Laser-Induced Fluorescence[a,b]

Species	Vibronic state		τ_{10}, μs	σ_Q (at 300 K), 10^{-16} cm^2	Collision partner	Laser system	Ref
	Notation	v (J)					
C_2^-	$B^2\Sigma_u^+$	Various	0.013-0.033		*c*	N_2/dye	285
Li_2	$A^1\Sigma_u^+$		0.018	185-406	Li	N_2/dye	233*b*
Na_2	$B^1\Pi_u$	6, 9, 10, 13, 17	0.0067			Ar^+	233*a*
	$A^1\Sigma_u^+$	11, 14, 16	0.1-1			He-Ne	227
		1-25	0.012			PLPDL	228
K_2	$B^1\Pi_u$	7	0.012	150 (500 K)	K	He-Ne	276
		7	0.0096			Ar^+	233*a*
Rb_2	B		0.017			Ar^+	233*a*
	C		0.061			Ar^+	
Cs_2			0.012			Ar^+	233*a*
Cu_2	A,B		0.03, 0.1		Cu	N_2/dye	302
						Ar^+ CWDL	292, 293
N_2	$B^3\Pi_g$	Various	10	4-7	Ar, N_2	N_2	298
						FLPDL	299
Cl_2	$B^3\Pi_{ou}^+$		17	8.9		Cl_2, N_2	229b
$^nBr_2$	$B^3\Pi$	1-40	1.2-0.2	176-525	Br_2	N_2/dye	277
$^{81,81}Br_2$	$B^3\Pi_{ou}^+$	40 (J = 16)	3.57	70	$^nBr_2$		301
						Ar^+	
		45 (J = 39)	1.57	87	$^nBr_2$		
						Single	
$^{79,81}Br_2$		40 (J = 19)	3.22	80	$^nBr_2$		
						mode	301
$^{79,79}Br_2$		42 (J = 32)	1.96	84	$^nBr_2$		301
		46, 47 (J = 41)	2.70	80	$^nBr_2$		
$I^{79}Br$						CWDL	304
I_2	BO_u^+ ($^3\Pi$)	0-70	1.5-0.7	160-276	I_2	N_2/dye	279
		9-20	0.33-1.36	62-76	I_2	N_2/dye	280
ICl	$^3\Pi$		7.6-10.9	86	ICl	FLPDL	229
	BO^+	1-16	1-3		*c*	N_2/dye	281
BeO	$C^1\Sigma$		0.09			N_2/dye	289
BaO	$A^1\Sigma$	0-11	3.57	0.28-2.49	He	N_2/dye	286
	$A^1\Sigma$	7, 8	12.5	0.79	He	Ar^+	287
	$A^1\Pi$	13, 14, 16, 17	8.8-10			N_2/dye	288
FeO						Kr^+	291
AlO	$B^2\Sigma^+$	0, 1, 2	0.13			N_2/dye	290
LiH	$A^1\Sigma^+$	5 (J = 5, 10, 15)	0.029-0.033	120-350	Li	N_2/dye	303
	$A^1\Sigma^+$	2 (J = 3)	29.4			N_2/dye	297
		5 (J = 3)	30.5				
		7 (J = 12)	36.9				
NaH	$A^1\Sigma^+$	8 (J = 3)	222.7			N_2/dye	297
OH	$A^2\Sigma^+$	0	0.79	11.2	H_2	N_2/dye	231
	$A^2\Sigma^+$	0	0.82	0.007-5	H, H_2, Ar	FLPDL	232
	$A^2\Sigma^+$	0, 1, 2	0.13-0.74			N_2/dye	294
	$A^2\Sigma^+$	0		0.09-25	Various	FD dye	294
	$A^2\Sigma^+$	0	0.585			N_2/dye	283
OD	$A^2\Sigma^+$	0	0.75	10.2	D_2	FD Nd dye	231
	$A^2\Sigma^+$	0, 1, 2	0.565		*c*	N_2/dye	294
	$A^2\Sigma^+$	0	0.57		*c*	N_2/dye	283
NH	$A^3\Pi$	0, 1, 2	0.165-0.07		*c*	N_2/dye	284
ND	$A^3\Pi$	0, 1, 2	0.170		*c*	N_2/dye	284
CdH	$A^2\Pi$	0, 1	0.07-0.08		H_2	N_2/dye	300
CdD	$A^2\Pi$	0, 1	0.07-0.09		D_2	N_2/dye	300
CN	$B^2\Sigma^+$	0	0.066	43	C_2N_2	N_2/dye	230
MX	Various	Various	0.016-0.051			N_2/dye	296
M = Ca, Ba, Sr							
X = F, Cl, Br, I							
NH_2	$^2A_1$		10-11.9	1.1-11	Various	N_2/dye	305
CS_2	$^1A_2$ or		2.89	180	CS_2	N_2	307
	$^3A_2$						
	$^3A_2$	1^02^4	1.20	69	CS_2	N_2/dye	306
NO_2	$^2B_1$, $^2B_2$	Various	70-82			FLPDL	309, 310
	$^2B_1$		~1			FLPDL	311
	$^2B_1$, $^2B_2$		45.4-55.5	5.7-10.6	NO_2	FD ruby	312
						FD Nd	
	$^2B_2$		30.3, 114			FLPDL	313
	$^2B_1$		30			Ar^+	314
						(488 nm)	
	$^2B_2$		100			Ar^+-single mode	314
						(514 nm)	
	$^2B_1$	$K_a = 0$	33	30	NO_2	N_2/dye	315
	$^2B_1$	$K' > 0$	36	10	NO_2	He-Cd	316

TABLE II. Collisionless Fluorescence Lifetimes τ_{10} and Collisional Quenching Cross Sections σ_Q for Gaseous Molecular Species Prepared in Single Vibronic States and Studied by Time-Resolved Laser-Induced Fluorescence[a,b]

Species	Vibronic state		τ_{10}, μs	σ_Q (at 300 K), 10^{-18} cm^2	Collision partner	Laser system	Ref
	Notation	*v* (*J*)					
SO_2	$^1B_1$		35.7	250	SO_2	FQ Nd	312
	$^3B_1$	Thermal	787[e]	0.12	SO_2	SRS shifted FD ruby	317
SO_2	$^1B_1$(I)	Various	80–530	238–412	SO_2	FD Nd–YAG/dye	318
	$^1B_1$(I)	Various	59	10.1–34.4	SO_2		
H_2CO	$^1A_2$	4^26^1	0.027			N_2	250
	$^1A_2$		0.020–0.28	39–99	H_2CO	FD ruby/dye	252
	$^1A_2$		0.018	310	Air	N_2	251
HDCO	$^1A_2$		0.016	80	Air	N_2	251
	$^1A_2$		0.08–0.29	18.1–30.3	HDCO	FD ruby/dye	252
D_2CO	$^1A_2$		0.05–4.54	3.7–35.1	D_2CO	FD ruby/dye	252
Cl_2CS	$^1A_2$		0.03–0.05	82–214	Cl_2CS	FLPDL	331
CH_3I		37			*c*	N_2/dye	282
CrO_2Cl_2		0	1.34	250	CrO_2Cl_2	FD Nd–YAG/dye	332
trans-Glyoxal	^1A_u	0 °	2.1	1.3–17	Various	N_2/dye	253
	^3A_u	Thermal	3300[e]	0.077–7.2	Various	N_2/dye	254
	^1A_u	Various	0.82–2.41	13	*trans*-$H_2C_2O_2$	N_2/dye	256, 257
	^1A_u	Various	$(4–11)10^{-3}$			N_2/dye	255
cis-Glyoxal	$^1A_1$	0 °	0.96	50	*cis*-$H_2C_2O_2$	N_2/dye	255
trans-Glyoxal-d_2	^1A_u	0 °	11.4	3.7–35.1	Various	N_2/dye	253
	^3A_u	Thermal	6.1	0.016	O_2	N_2/dye	254
				0.021	*trans*-$D_2C_2O_2$ (^1A_g)	N_2/dye	
Propynal	$^1A''$	0 °	0.99	7.8–176	Various	N_2/dye	266
	$^3A''$	Thermal	383[e]				
			800[e]		*c*	FDFLPDL	267
Methylglyoxal	$^1A''$	Various	4, 0.024[d]	9 <0.08	Methylglyoxal, Ar	N_2/dye	261–266
	$^3A''$	Various	1920[e]	0.012	Methylglyoxal	N_2/dye	
Biacetyl	^1A_u	Thermal	0.023	0.176	O_2	FD ruby	268
	^1A_u		0.005–0.01			N_2/dye	269
	^3A_u	Thermal	18,[d] 1850[e]			N_2/dye	269
			0.01–1	$(0.18–15)10^{-7}$	Olefins	N_2/dye	270
				$<2 \times 10^{-8}$	Biacetyl		
	^3A_u	Thermal	1510[e]			FD ruby	268
	^1A_u, ^3A_u		0.010			N_2/dye	268
			22[d]	110	Biacetyl	N_2/dye	271, 272
Methyltriazolinedione	$^1AA'(^1B_1)$		0.059–0.12	1–12	Various	N_2/dye	275
Benzoquinone	$^1B_{1g}$		14.7–17.3	47	Benzoquinone	FLPDL	323
	^3A_u		27.7	$12.6–83 \times 10^{-5}$	Various	FLPDL	323
Benzoquinone-d_4	$^1B_{1g}$		10.9–15.1	60	Benzoquinone-d_4	FLPDL	323
	^3A_n		57			FLPDL	323
s-Tetrazine	$^1B_{3u}$		<0.1			FLPDL	330
	$^3B_{3u}$		72[e]			FLPDL	330
Quinoxaline	$^1A_1$, $^1B_2$		1–45	~80	Quinoxaline	FLPDL	273
Diazanaphthalenes	S_1		1–50			FD FLPDL	329
Benzophenone	S_1		9.1	30	Benzophenone	FD ruby	321
	T_1		7200[e]	0.13	Benzophenone	FD ruby SRS shifted	322
Naphthalene	$S_2(^1B_{1u})$		0.04			MLFQ Nd	325
	$S_2(^1B_{1u})$		0.033–0.043			FQ Nd	327
	S_1	Various	0.16–0.31			FLPDL	328
Pyrene	S_1		0.4			FQ Nd	324
	S_2		0.2	13–200	Various	FQ Nd	324
3,4-Benzpyrene	S_2, S_1		0.064			MLFQ Nd	325

[a] See Appendix for a list of abbreviations. [b] Based in part on Yardley's review.[306] [c] Matrix isolated molecule. [d] Collisional-induced ISC; observation of fast and slow components of fluorescence decay. [e] 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 Δt such that $\Delta t \ll \tau_R$. For most statistical molecules $\rho = 10^4$ cm ($=5 \times 10^{26}$ J^{-1}) which requires $\Delta t \ll 50$ 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,[236] matrix-isolated Cr(III) complexes,[237,238] rare earth chelates,[239] and solutions.[240-247] A thorough study of the anomalous $S_2 \rightarrow S_0$ fluorescence of azulene has been performed by Jortner and coworkers.[248] Recently, Zare and co-workers succeeded in demonstrating irreversible nonradiative decay of truly isolated pentacene molecules in a molecular beam experiment.[249]

For the intermediate case, one distinguishes two situations.

a. *Dense intermediate case*, characterized by $\rho V \simeq 1$ and $\tau_R \simeq \tau_{max}$. 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,[250-252] glyoxal,[253-260] methylglyoxal,[261-265] propynal,[266,267] biacetyl,[268-272] and other systems.[250-252] It was shown that IC and ISC processes are influenced by the addition of quenching agents. From the pressure dependence of τ_{10}, which usually follows a Stern–Volmer law, a collisional quenching cross section σ_Q is determined. As expected, σ_Q also depends on the initially prepared vibronic state. The main results for diatomic species,[227-233,276-304] NH_2 radicals,[305] carbonyl compounds,[250-272] and other systems[273-275] 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 ρ 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,[223,235,306,307] typical examples being CS_2,[306,308] NO_2,[309-316] SO_2,[312,317,318] and NSF.[319] Now the decay is nonexponential and may show oscillatory behavior (quantum beats).[221,320] 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.[306] This type of "small" molecule behavior also appears in some "large" molecules like benzophenone,[321,322] benzoquinone,[323] pyrene,[324] benzpyrene,[325] naphthalene,[326-328] diazanaphthalenes,[329] *s*-tetrazine,[326,330] biacetyl,[267-272] thiophosgene,[331] chromyl chloride,[332] and quinoxaline.[273] In biacetyl[271,272] and methylglyoxal,[260-265] reversible intersystem crossing and long-lived collisionally induced phosphorescence have been observed. In addition, the appearance of consecutive fast and slow components[265,271,272] 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.[265,272]

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[333-335] 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.[336-345]

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,[346,347] 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.[348,349] 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.[350] However, the availability of pulsed lasers permits the direct observation of the $S_1{}^v$ states (picosecond time scale) or vibrationally relaxed $S_1{}^0$ states (nanosecond time scale).

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

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,[351-354,378] or by an electronically triggered flash lamp (FL).[355,356,359,370-372] Other ingenious methods include laser-induced sparks,[379] laser-induced fluorescence continuum (LIFC),[380,381] dye lasers pumped by the exciting laser,[375,376] or employment of a split-off part of the exciting laser beam,[377,382] 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[356] and some common difficulties in interpretation by Goldschmidt.[383]

Results for triplet state T_1 and for the singlet state S_1 can be expressed in terms of the absorption cross-sections σ_T and σ_{12}, respectively (see Figure 8). In particular, aromatic molecules (ref 340, 354–359, 369, 380, 384, 392), various charge-transfer (CT) complexes,[372] biological systems,[386,387] and laser dyes (ref 377, 378, 382, 388–391, 393, 405) have been studied.

In Table III we present typical data for σ_{12}, together with experimental details. It is evident from Table III that, particularly for laser dyes, σ_{12} is often so large that the pumping rate $\sigma_{12}(P)I_p$ for the transition $S_1 \rightarrow S_2$ (see Figure 8) can become comparable to decay processes of $S_1{}^0$. For example, in most dyes $\sigma_{12}(P) > 10^{-16}$ cm^2/molecule; therefore, a typical pump intensity $I_p \simeq 10^{26}$ photons/cm^2 sec (corresponding to 100 MW/cm^2 at 350 nm) results in a reabsorption rate $\sigma_{12}(P)I_p \simeq 10^{10}$ s^{-1} which competes with the average fluorescent decay rate[394] $1/\tau_{10} \simeq 10^9$ s^{-1}. Since the radiationless decay rate $S_2 \rightarrow S_1$ is very fast, molecules subjected to high pump intensities will simply circulate many times between S_1 and S_2 before emitting a fluorescent photon. Consequently, the quantum yield becomes intensity dependent. This photoquenching effect has been observed[126,389,390,393] and has also been interpreted kinetically.[63] The main results of the analysis are the following.

a. The total $S_1 \rightarrow S_0$ fluorescence output is intensity dependent. For moderate pump intensities the reciprocal relative quantum yield ϕ_0/ϕ follows a Stern–Volmer type law for steady-state photoquenching

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

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

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

This relationship enables us to determine indirectly the otherwise difficult-to-obtain nonradiative lifetime τ_{21} of the $S_2 \rightarrow S_1$ transition, from measurements of I_p(max).

It should be noted that at extremely high pump intensities complications arise caused by bleaching in saturable absorbers, due to resonant stimulated emission[39] or by intense absorption from an $S_1{}^v$ 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 $S_1{}^0$ state, becomes negligible.

Studies of bleaching and antibleaching have been performed

TABLE III. Molecular Cross Section σ_{12}, at the Peak of the $S_1 \rightarrow S_2$ Absorption Band for Compounds Studied by Laser Flash Spectroscopy[a]

Compound[b]	Laser source	Probing source	Temporal resolution (ns)	λ_{max}[c] (nm)	σ_{12} (10^{-16} 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	2×10^{-5}	371
TCNB-aromatics CT complex	N_2	Pulsed Xe	10	460	0.04	372
PMDA-mesitylene CT complex	N_2	Pulsed Xe	10	660	7×10^{-3}	372
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

[a] See Appendix for list of abbreviations. [b] All compounds were measured in solution except where indicated otherwise. [c] λ_{max} denotes the wavelength at maximum absorption unless indicated as "at . . .".

employing laser flash spectroscopy techniques.[400-402] The absorption cross-sections relevant for bleaching have been obtained by kinetic analysis[403] or other methods.[404]

C. Ultrafast Processes

By the term ultrafast processes we refer to photophysical and photochemical dynamics in the picosecond and subpicosecond time range.[406-408] 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.[116,408]

Most primary photophysical and photochemical processes in condensed media occur in the picosecond time range. These include orientational relaxation in liquids,[409-412] dynamical properties of solvated electrons[413-416] and ultrafast energy transfer[417,418] and decay processes in molecules.[419-423] 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,[411,424-427] vibrational relaxation of an $S_1{}^v$ state determines its Q-switching properties, and the particular values of τ_{10}, $\tau_{v''}$, $\tau_{v'}$, k_{ST}, σ_e, σ_{12}, and σ_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[441-447] and was extended to liquids with the aid of picosecond pulses.[449-453]

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.[406,407] 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.[412,466] Recently, a novel transient grating method for ultrafast spectroscopy has been reported.[467] The

TABLE IV. Some Photophysical and Photochemical Picosecond Studies of Neat Liquids or Solutions[a]

Species	Process studied or derived parameter	Ref
CS_2, Kerr liquids	Orientational relaxation in ultrafast light gates	412
CS_2	Kerr effect, use of self-focusing for time resolved ps spectroscopy	466
R6G	Orientational motion in solution	409
DODCI	Orientational motion in solution	411
Electrons in water	Relaxation of the excess electron	413
Electrons in ammonia	Relaxation studies	414
$2Na^+$ (tetraphenylethylene)$^{2-}$	Solvent effect on the kinetics of electron photoejection	416
Dye molecules	Rise and decay times of $S_1 \rightarrow S_0$ fluorescence; quantum efficiency ϕ and generation of stimulated emission; $S_2 \rightarrow S_1$ IC lifetimes ($\tau_v{}' = 30$ ps for CVP in methanol and 56 ps in ethylene glycol)	394 411 424–429 433–435
R6G	$\tau_v{}'' = 8.3$ ps in ethanol	452
Azulene	$\phi = 10^{-7}$ for $S_2 \rightarrow S_1$ fluorescence $\tau_{v'} = 7.5$ ps in ethanol, rate-determining process in doubt	430
R6G, DPA	Photoquenching of TPF and TPA	116
DODCI	Recovery time of S_0 population 10 ps in water. Disagreement with value of 56 ps	411 425, 432 440
CV	IC processes	431
POPOP	Rate of energy transfer to perylene 5×10^{10} s^{-1} in vapor phase	438
Benzophenone	$k_{ST} = 6 \times 10^{10}$ s^{-1} in ethanol and 3×10^{10} s^{-1} in benzene; rate of energy transfer to piperylene and naphthalene $\sim 10^{11}$ s^{-1}	421, 459
Benzene	Intermolecular collision-induced energy transfer	422
Anthracene–DEA	Excited-state CT interactions and kinetics; critical transfer radius 0.8 nm	417
I_2 in solution	Collision induced predissociation; dynamics inside (400 ps) and outside (ns range) the solvent cage	418
D_2O, H_2O	Inverse SRS and generation of ps continuum	454, 455
Alcohols	Time resolved SRS	456
Coumarin in CCl_4	$\tau_{v''}$ using double pulse excitation	436
Various liquids	Dephasing time and $\tau_{v''}$ by coherent and incoherent stimulated anti-Stokes Raman scattering	448–451
CH_3CCl_3 and CD_3OD	Rate of intermolecular vibrational energy transfer between proto and deutero modes is 8×10^{10} s^{-1}.	453
Tetracene dianions	ps kinetics studied by double-beam ps spectrometer	423
Anthracene	PSFS using ps continuum; studies in mixed crystals	457, 460
ADMA	Solvent induced intermolecular electron transfer by PSFS	458
Aromatic ketones	PSFS in solutions	461
1,2-BA	PSFS study of energy transfer	462
s-Tetrazine	PSFS	463
Transition metal coordination compounds	PSFS	465
DODCI, BDN Porphyrins	PSFS using ps continuum	432
Polymethyne dyes	σ_{12} from PSFS; production of a photoisomer	405
DTDC	PSFS	388
DTTC, DCI	PSFS	439
Kodak, Q-switch dyes	Molecular relaxation studies using crossed beam techniques	428
DCI, DDI, DODI, DTDI	Fluorescence and photochemical studies	242, 243
Tetraphenylhydrazine	Dynamics of photodissociation	464

[a] See Appendix for a list of abbreviations.

techniques and illustrative studies have been reviewed by leading workers in the field.[406–408,468–470] 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.[471,472]

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,[473–476] 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.[477–479]

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.[480–486] As was shown by Dowley and Peticolas,[487] even small amounts of impurities may affect the product formation in a high-intensity laser-induced process, causing pyrolysis reactions[488] or initiating other thermal effects,[482,489] some even with incoherent light sources.[490] 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[346,347]

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,[491] an irreversible photochemical process,[475,476] 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.[492,493] In most cases transient species such as radicals,[117,494–501] excimers,[502,503] exciplexes,[504–511] F centers,[512] solvated electrons,[513–515] singlet oxygen and ozone,[516–521] and biological[387,522–526] or

TABLE V. Representative Studies of Photochemical Processes by Laser Flash Spectroscopy and Related Techniques[a]

Species	Laser source	Probing source	Temporal resolution (ns)	Species detected or process studied	Ref
I_2 (gas phase)	FLPDL	I_2 lamp	10^3	I	348
I_2/water	FD Nd	FL	20	$I_2^-\cdot$	360, 362
I_2/solvents	FD Nd	FL	20	I–solvent	360, 362
	FT Nd	FL	5	CT complex	364
$I_2 + I^-$/*t*-BuO	FD Nd or FD Nd/dye	Pulsed Xe	20	$I_6^-\cdot$	363
$I_2 + I^-$/alcohols	Fd Nd	FL	20	$I_4^-\cdot$, $I_2^-\cdot$	361
I^-/solvents	FQ Nd	FL	20	$I + I^- \rightarrow I_2^-$	368
I_3^-/water	N_2	Pulsed Xe	10	$I_3^- \rightarrow I_2^- + I$	558
HgI_2/water	FQ Nd	FL	20	I_2^-	365
CHI_3/mesitylene	FT Nd	FL	5	I–mesitylene CT complex	364
KI + KBr/water, methanol	FQ Nd	FL	20	I_2^-, IBr^-	530
Br_2/water	FQ Nd	FL	20	Br–CT complexes	367
Cl_2/water	FQ Nd	FL	20	Cl–CT complexes	367
Alkali halides (solid state)	Ruby	FL	50	F centers	512
$O_2\ {}^1\Delta_g$	Ruby	Tungsten–I_2	20	Energy transfer	516–518
	Nd	Tungsten lamp	20	Various	516
	Ruby	FL	20	Various	521
O_3	FLPDL	O_2 lamp	10^3	$O^3(P) + O_3 \rightarrow$	519
	FLPDL	O_2 lamp	10^3	$O^3(P) + H_2O \rightarrow$	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_2	50	Various	527
MB/*p*-chlorophenylglycine	Ruby		20	Photoreduction	529
Eosin Y	Ruby	Tungsten–I_2	50	Various	527
Polymethine dyes/DMSO	ML ruby	LIFC	10^{-2}	Photoisomer	405
Benzene	FQ Nd	Pulsed Xe	20	Excimer	502
Anthracene/THF	N_2		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_2	FL	10	Radical ion formation, electron transfer to DEA and anthracene	554
	N_2	FL	10	Photoconductivity	373
Pyrene/micelles	FD ruby	FL	20	Photoionization	514
Pyrene/cyclohexane	N_2	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_2	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_2	FL	10		544
	FD ruby	FL	25	Photoionization	547
TPMD/isopentane	N_2		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_2	FL	10	Exciplexes	508
TPMD–biphenyl	N_2	FL	10	Exciplexes and triplet quenching	508
Pyrene–DEA	N_2	FL	10	Exciplexes and fluorescence quenching	507
Anthracenes–DEA, TPMD	N_2	FL	10	Induced ISC with DEA; ion pair formation	506
Aromatics–DEA	N_2	FL	10	Exciplexes	505

[a] See Appendix for a list of abbreviations.

molecular moieties[351,527–545] 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[345,360,362,364] or the formation of iodine radical anions[361,363,368,530,558] is followed. Using picosecond techniques Eisenthal and co-workers could distinguish between recombination inside and outside the solvent cage (Table IV).[418] 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.[364] Similar results were obtained for other halogens and halides.[365,367]

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.[559,560]

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

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.[571–573] Monochromatic radiation of frequency ν 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.[567,573] This model implies the absence of instantaneous intramolecular randomization processes[249] as can be justified on theoretical grounds[574] 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.[575,576] It is worth noting that electronically excited species are not always more reactive than their ground-state counterparts.[577]

For a simplified description[564,578–580] we consider a unimolecular dissociation[581–584] or isomerization reaction[585–588] which obeys the empirical Arrhenius rate equation

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

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[575,576,589–593]

$$A + BC \rightarrow AB + C$$

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 $h\nu$ 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 $Nh\nu < E_a$.[582,583,594–597] For orientation, $Nh\nu = 12$ kJ/einstein for CO_2 laser radiation, $RT = 2$kJ/mol at room temperature, and $E_a^T \simeq 300$ 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,[598] which also determines the relative utility of vibrational and translational energy.[575,576]

Rapid vibrational to vibrational (V–V) and also slower vibrational to rotational or translational (V–R/T) relaxation processes[385] 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[565,599,600] 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 τ, therefore, is $\tau \gg \tau_{rot}$ to avoid bottlenecking, and $\tau \ll \tau_{V\text{-}T}$ to reduce thermal heating.

Occasionally, intramolecular deactivation channels seem to play a role. For example, the first detailed study[601] of the chemiluminescent reaction of O_3 with NO to form NO_2 indicated that the enhanced reactivity upon vibrational excitation of O_3 with a pulsed CO_2 laser appeared to be delayed. The induction time was attributed to migration of the excitation energy of the stretching mode $\nu_3 = 1043$ cm^{-1} in the O_3 molecule to the bending mode $\nu_2 = 705$ cm^{-1}. The intermediate energy-transfer step presumably caused deviations from an Arrhenius-type first-order reaction augmentation. More recent measurements[602–604] 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.[582,583,599,605–608] 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, $vNh\nu$ exoergic reactions were barely influenced, while endoergic reactions were speeded up by orders of magnitude.[589–593] 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[608] 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 ΔT may range from ≃10 K when using pulsed CO_2 lasers, to ≃1000 K for CO_2 CW irradiation.[611] In fact, one of the more difficult experimental and theoretical issues is to distinguish specific-laser from thermal-laser effects.[609–617] 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[575,576,618] and conversely, the diametrically opposite case of homogeneous pyrolysis of hydrocarbons where SF_6 or CH_3F was added to the reactants as a CO_2-laser-absorbing bath material which acts as a sensitizer.[611–613]

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 $Nh\nu \ll E_a$; 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

$$M(v = 1) + M(v = 1) \rightarrow M(v = 0) + M(v = 2) + \Delta E \quad (22)$$

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 vibrationl energy levels, in steps such as given by eq 22, or in jumps; e.g.,

$$M(v = 2) + M(v = 2) \rightarrow M(v = 0) + M(v \geqslant 4) + \Delta E \quad (23)$$

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 ΔE 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_2 laser.[624]

In isotopic mixtures, V–V relaxation pumping may be more pronounced for the heavier species because for them ΔE is larger. The mechanism was verified for the reactions of $N_2 + O_2$ and $N_2 + D_2$ driven by pulsed discharges[625] and for ${}^nCO$, trapped as impurity in solid argon.[626] Resonant irradiation of the transition $v = 0 \rightarrow v = 1$ of ${}^{12}C^{16}O$ caused luminescence from excited CO (up to $v = 7 \rightarrow v = 6$). The luminescence is predominantly from ${}^{13}CO$ and $C^{18}O$ because at the low sample temperatures (10 K) the phonon-assisted excitation transfer of the type

$$\begin{aligned} &{}^{12}CO(v = 1) + {}^{13}CO(v = n) \\ &\qquad \rightarrow {}^{12}CO(v = 0) + {}^{13}CO(v = n + 1) + \Delta E \end{aligned}$$

becomes irreversible.[626]

Another approach takes into account the coherent coupling between the radiation field and a molecule undergoing phase- and energy-changing collisions.[610] 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.[564–650] 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.[562,651–656] Firstly, because of the intrinsic scientific value, efforts to enrich isotopes have spurred studies of UHRS of atoms[657–661] and molecules[46–49,662–664] and of radiative lifetimes of excited states.[659–661,665] 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 ${}^{235}U$ 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.[666] In addition, there is also a promising market for isotopes of lighter elements such as D, ${}^6Li$, ${}^{10}B$, ${}^{13}C$, ${}^{15}N$, ${}^{17}O$, ${}^{18}O$, 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 β. For a mixture of N_A moles of isotomer A and N_B moles of (all) the other isotomer (s) B, β 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 (≃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)

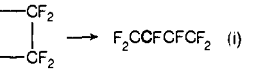
TABLE VI. Selective Chemical Reactions Induced by Laser Excitation

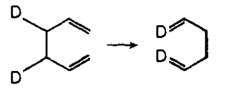
Absorber	Laser	Wavelength and operational mode	Reaction[a]	Reaction features and k_{rel}[b]	Ref
H_2,D_2	Ruby/SRS shifted	1.1 μm and 0.9 μm 100 mw	$H_2 + D_2 \rightarrow 2HD$		446
N_2F_4	CO_2	0.3 J, 0.3 μs	$M \rightarrow 2NF_2$	Explosion	561
			$M + H \rightarrow$		581
			$M + NO \rightarrow FNO + NF_3 + F_2 + N_2$		
		1 J, 1 μs	$M + (CH_3)_2C{=}CH_2 \rightarrow CF_4 + HF + N_2$	Explosion	567
			$M + N_2O \rightarrow NO_2 + NF_3$		
			$M + CH_4 \rightarrow C_2H_2 + N_2 + H_2 + HF$		
NH_3	CO_2		$M \rightarrow NH_2 + H$	Luminescence	642
BCl_3	CO_2	CW, 600 W, 30 ms	$M + H_2 \rightarrow Cl_2 + B$	Explosion	564
			$M + H_2S \rightarrow BSCl_2$	Luminescence	631
		1.5 J, 200 ns	$M + H_2 \rightarrow BHCl_2 + HCl$		630
			$M + O_2 \rightarrow BCl + BO$	Luminescence	632, 633
B_2H_6	CO_2	CW	$M + C_4H_8 \rightarrow B_2H_4(C_4H_9)_2$		565
	CO_2	CW, 1.5 W, R (16)	$M \rightarrow B_{20}H_{16}$	Luminescence	628
$B(CH_3)_3$	CO_2	CW, 7W, R(12)	$M + HBr \rightarrow B(CH_3)_2Br + CH_4$		629
H_3BPF_3	CO_2	CW, 100 W	$2M \rightarrow B_2H_6 + 2PF_3$		582
D_3BPF_3	CO_2		$2M \rightarrow B_2D_6 + 2PF_3$	$E_a^T/E_a^L \simeq 8$	583
HF	HF		$M(\nu = 3) + D_2 \rightarrow HD + DF$		641
	HF	0.1 mJ, 0.5 μs	$HF\ (\nu = 1) + Ba \rightarrow BaF(\nu) + H$		617
HCl	HCl		$M(\nu = 1) + K \rightarrow KCl + H$	$k_1/k_0 = 100$	575
	HCl		$M(\nu = 1) + O \rightarrow OH + Cl$	$k_1/k_0 = 300$	589, 593
	HCl		$M(\nu = 2) + Br \rightarrow HBr + Cl$	$k_2/k_0 = 10^{11}$	590–592, 606, 607
Br_2	Ruby	0.5 J, 0.5 ms	$M + C_4F_8 \rightarrow C_4F_8Br_2$	12	47, 631
I_2	Ar^+	514.5 nm	$o\text{-}I_2 \rightarrow p\text{-}I_2$	2	635
		CW, 0.2 W	$o\text{-}I_2$ + 2-hexene $\rightarrow C_6H_{12}I_2$		636, 637
O_3	CO_2	200 W/50 Hz	$M + NO \rightarrow NO_2 + O_2$	20	601–604
			$M + O_2 \rightarrow 2O_2 + O$		
			$M + SO \rightarrow SO_2 + O_2$	2	580
NO	CO		$M + O_3 \rightarrow NO_2 + O_2$		643
N_2O	N_2O		$M + Cu \rightarrow N_2 + CuO$		644
	NO_2Ar^+/dye		$M + CO \rightarrow NO + CO_2$	1–20	649
		CW, 5 W	$M + C_2F_4Cl_2 + Cl_2$		646
CF_2Cl_2	CO_2	CW, 400 W, P(20)	$M \rightarrow CF_3Cl + C + Cl_2$	100	648
		1.5 J, 100 ns	$M \rightarrow CCl^*$	Luminescence	639
$CFCl_3$			$M \rightarrow C_2F_2Cl_2 + Cl_2$		
CF_3CL	CO_2	2 J, 0.2 μs, 0.3 Hz	$M \rightarrow C_2F_6$	2.8% conversion 1.6% per flash	579
CH_3X (X = F, Cl, Br)		1 J, 200 ns	$M + Cl_2 \rightarrow CH_2XCl + HCl$	MPD	621
CH_3OH	CO_2	1.5 J, 100 ns	$M \rightarrow CH^* + OH + C_2^*(!)$	Luminescence	639
CH_3CN			$M \rightarrow CN^*$		639
C_2H_2	CO_2	CW, 300 W, 5 s	$M + SF_6 \rightarrow C$	0.3 pyrolysis	612
C_2H_4	CO_2	CW, 660 W, 0.4 s	$M \rightarrow C$	E_a = 192 kJ/mol	615
		CW, 50 W		k (thermal)	616
C_2H_4	CO_2	1.5 J, 100 ns	$M \rightarrow C_2^*$	Luminescence	639
			$M \rightarrow C_n$	Polymerization	565
C_2H_6	CO_2	CW, 680 W, 1 s	$M + SF_6 \rightarrow C$	Pyrolysis	613, 614
C_2H_5Cl	CO_2	150 W, CW, 972 cm^{-1}	$M \rightarrow CH_3 + CH_2Cl \rightarrow CH_4$	k(thermal)	617
		200 W, 1 ms, 946 cm^{-1}	$M \rightarrow C_2H_4 + HCl$		
$C_2H_2Cl_2$	CO_2	100 ns, 60 ns	*trans*-M $\rightarrow$ *cis*-$C_2H_2Cl_2$	MPD	588
C_2Cl_4	CO_2	6W	$M + BCl_3 \rightarrow C_6Cl_6$		629
C_2F_3Cl			$M \rightarrow C_2^*$		638, 639
$C_2F_4Cl_2$	CO_2	CW, 4 W	$M \rightarrow C_2F_4$	$k(921\ cm^{-1})/k(1052\ cm^{-1}) = 100$	647
C_4F_6	CO_2	0.4 J, 100 ns	[c]	90% conversion	587
C_4H_8	CO_2	10 MW, 100 ns	*trans*-2-butene → cis-2-butene		585
C_4H_6O	FLPDLFD	10^{-2} W	c-C_4H_6O[d] $\xrightarrow{339\ nm} C_2H_4 + CH_2CO$, $[C_2]$	$[C_3]/[C_2] = 7.0$	645
		1 μs, 30 Hz	c-C_4H_6O[d] $\xrightarrow{310\ nm}$ c-$C_3H_6 + CO$, $[C_3]$	$[C_3]/[C_2] = 0.44$	

TABLE VI (Continued)

Absorber	Laser	Wavelength and operational mode	Reaction[a]	Reaction features and k_{rel}[b]	Ref
i-C_4H_9X (X = Cl, Br, I)		0.3 J, 100 pulses	$M \rightarrow i$-C_4H_8	MPD	609
$C_6H_{12}O_2$	CO_2	0.3 J, 1 μs, P(20)	$M + CH_3F \rightarrow 2CH_3COCH_3$	Luminescence at 410 nm	612
$C_6H_{10}D_2$ $C_6H_8D_4$ $C_6H_6D_6$	CO_2	0.3 MW, 100 ns 5000 pulses	e		586
$C_{10}H_{16}$ 1-Limonene	CO_2	CW, 5 W	$M \rightarrow 2C_5H_8$ (isoprene)		584
SF_6	CO_2	0.8 MW, P(20)		Luminescence	640
UF_6	CO_2	CW	$M + HCl$	100	650

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





[d] c-C_4H_6O = cyclobutanone. [e] See reaction ii.

TABLE VII. Isotope Enrichment Experiments: Atomic Beams

Atom	Technique[a]	Laser and mode of operation	Wavelength (nm)	Enrichment factor β	Ref
^{6}Li	TPI				703
^{40}Ca	TPI	CW Ar^+/dye CW Ar^+, 3 W	λ_1 616.2 λ_2 488.8		704
^{85}Rb	TPI	Ruby/dye FD ruby	λ_1 794.8 λ_2 347.1		652 699 700
^{138}Ba	RPD	CW Ar^+/dye	λ 553.6	2	717
^{137}Ba		50 mW/cm^2	λ_1 553.6	13	718
^{135}Ba			λ_2 582.6		719
^{235}U	TPI	N_2/dye	λ_1 426.6 λ_2 360.9	1.5	665
^{235}U	TPI	CW Xe^+, 70 mW CW Kr^+, 1 W (intracavity 30 W)	λ_1 378.1 λ_2 356.4 λ_2 350.7	4	670

[a] See Appendix for a list of abbreviations.

which range from 1:10^5 to 1:10^8 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.[667] 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 isotomer 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,[668] electrical,[665,668-671] optical,[672,673] thermal,[674] heterogeneous,[675] 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.[585-588,680]

Several schemes have been explored on a laboratory scale, and two are, reportedly, in the pilot plant stage.[665,670] 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.

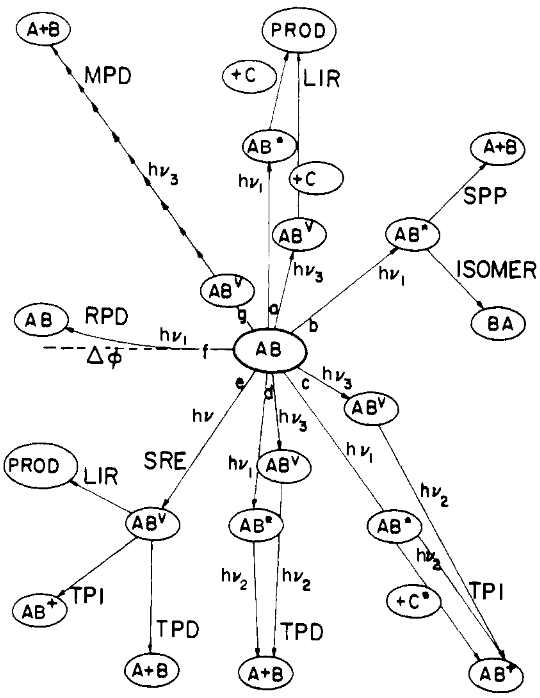


Figure 10. Schematic diagram of laser-based isotope enrichment schemes (a–g) discussed in the text. $\nu_{1,2}$ designates resonance radiation in the visible or UV spectral region and ν_3 in the infrared. AB^v, AB* (or C*), and AB$^+$ denote, respectively, vibrationally excited, electronically excited, and ionized species. Schemes a, c, and f are also suitable for enrichment of atomic isotopes.

(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[a]	Laser and mode of operation[b]	Wavelength	Reaction	Enrichment Isotope	Enrichment Factor β	Ref
CH_3OH	LIR	CW HF, 100-W	2.6 μm	$M + Br_2 \rightarrow H_2CO + Br$	D	2	681
		pulsed HF or incoherent source	2.6 m		D	1	682
CD_2Cl_2	MPD	1 J, 100 ns, 2 Hz, 3600 pulses	943 cm^{-1}	$M \rightarrow HCl + C +$	D	1.2	736
H_2CO (HDCO, D_2CO)	SPP	FD ruby	347 nm	$M \rightarrow D_2 + CO$	D	6	689
	SPP	FT Nd	353 nm		D	9	694
	SPP	CW He-Cd, 0.5 mW	325 nm	$M \rightarrow HD + CO$	D	14	692
	MPD	2 J, 100 ns, 0.5 Hz, 300 pulses	P(20)	$M \rightarrow HD + CO$	D	40	638
H_2CO	SPP	FD ruby/dye doubled	304 nm	$M \rightarrow H_2 + CO$	^{12}C	80	690
	SPP	FD FLPDL	304 nm				691
	SPP	CW Ne^+, 20 mW	332.3 nm		^{18}O	8	693
BCl_3	TPD	Pulsed CO_2	$\lambda_1 = P(20)$	$M + O_2 \rightarrow$	^{10}B	1.1	709
		Xe-FL	$\lambda_2 \simeq 214$ nm				
	MPD	0.1 J, 200 ns	P(16)	$M + H_2S \rightarrow B_2S_3 + HCl$	^{10}B	2.2	733
		360 000 pulses	R(30)	$M + D_2S \rightarrow$	^{11}B	1.6	734
			P(20)	$M + O_2 \rightarrow BO \rightarrow B_2O_3$	^{10}B	8	725, 632
	MPD	2 J, 85 ns	R(24)		^{11}B	5	726
		1.6 Hz		$M + HBr \rightarrow BCl +$	^{10}B	20	726
	MPD	1.5 J, 200 ns	P(20)	$M + H_2 \rightarrow BHCl_2 + HCl$	^{10}B	1.7	732
		4000 pulses					724
CF_2Cl_2	MPD			$M + H_2 \rightarrow$	^{13}C	1.1	732
$C_2N_4H_2$	SPP	CW Ar^+/dye	551.5 nm		^{13}C	24	695
s-Tetrazine	(gas)	10 mW			^{15}N	6	
				$C_2N_4H_2 \rightarrow N_2 + HCN$			
	SPP	N_2/dye	653 nm		^{13}C	10^4	696
	(in matrix at 1.6 K)				^{15}N	10^4	
N_2	SRE-	Ruby	694 nm	$N_2 + O_2 \rightarrow 2NO$	^{15}N	100	565
	LIR	Ruby/SRS Shifted	830 nm				712
							713
NH_3	TPD	CO_2, 60 mJ,	λ_1 947.1	$4NH_3 \rightarrow 2NH_3 + 3H_2 + N_2$	^{15}N	4	706
		300 ns	cm^{-1}				707
		filtered UV spark	$\lambda_2 > 220$ nm				708
O_2	LIR	ArF	193 nm	$O + O_2 \rightarrow O_3$	$A^{18}O$		678
SiF_4	MPD	0.8 J, 200 ns	P(36)	$M + H_2 \rightarrow$	^{29}Si	1.1	732
		4800 pulses	1031.5 cm^{-1}	$M + N_2 \rightarrow$	^{30}Si		
SF_6	MPD	1.5 J, 200 ns	P(20)	$SF_6 + H_2 \rightarrow SF_5 + HF \rightarrow SF_4$	^{34}S	33	731
		5000 pulses			^{36}S	1200	
	MPD	2 J, 90 ns	P(16)		^{34}S	2800	727
		2000 pulses	P(40)		^{32}S	18	726
	MPD	3 J, 90 ns		$SF_6 + H_2 \rightarrow$	^{34}S	47	730
		1000 pulses			^{34}S	30	729
CCl_4	MPD	17 J, 90 ns	979.7 cm^{-1}		^{13}C	7	728, 735
CF_2Cl_2			971.9 cm^{-1}		^{37}Cl	1.5	732
HCl	TPD	Nd/SRS shifted	λ_1 1180 nm	$H^{35}Cl(v = 3) + NO \rightarrow NOCl$			562, 563
		Xe lamp,	$\lambda_2 > 300$ nm				
		FQ Nd	λ_2 265 nm				
	LIR	Pulsed HCl		$H^{35}Cl(v = 2) + Br \rightarrow HBr + Cl$	^{35}Cl	3	590, 592
		Pulsed HCl					606
ICl	LIR	CW Ar^+/dye, 10 mW	605.3 nm	$ICl(v = 18) + C_2H_2Br_2$	^{37}Cl	1.5	683
				intracavity absorption	^{37}Cl	17	684
$CSCl_2$	LIR	CW Ar^+	465.8 nm		^{35}Cl	1.2	578, 676
		FLPDL	470 nm		^{37}Cl	1.7	
Br_2	LIR	Ruby	Temp. tuned	$Br_2 + C_4F_8 \rightarrow C_4F_8Br_2$	^{79}Br	1	47
Br_2	SPP	FD Nd/YAG	558 nm	$M + HI \rightarrow Br + HI \rightarrow HBr + I$	^{81}Br	5	677
CH_3Br	LIR	CO_2, CW	R(14)	$M + Cl \rightarrow CH_2BrCl$	^{79}Br	1.03	627
			P(10)	(intracavity)	^{81}Br	1.02	
I_2		CW Ar^+					636
OsO_4	MPD	3 J, 90 ns	R(2)	$M + C_2H_4 \rightarrow$	^{192}Os	1.2	737
			P(2)		^{187}Os	1.1	
UF_6	LIR	CO_2 (with UF_6 filter)	P(16)	$UF_6(\nu_3 + \nu_4 + \nu_6) + HCl \rightarrow$	^{235}U	1.1	663

[a] See Appendix for list of abbreviations. [b] In the MPD technique a pulsed CO_2 laser is used.

by sensitizing a $^nHg/H_2O$ vapor mixture with 253.7-nm resonance radiation from an isotopically pure (or suitably filtered) Hg lamp.[685] A more recent example is the selective photolysis of ^nCO with 206.2-nm radiation from an iodine lamp.[686] The high spectral brightness obtainable with lasers has paved the way for novel experiments. For example, irradiation of $^{n}Br_2$ vapor with a temperature-tunable ruby laser caused selective electronic excitation (to the $^3\pi_{1u}$ state) of a specific Br_2 isotomer which was dissociated by subsequent collisions.[47] However, the scavenging reaction of the bromine radicals with olefins turned out to be nonselective, because collisional energy transfer to unexcited $^{n}Br_2$ molecules, prior to the addition reaction, caused isotopic scrambling.[47] This is a general drawback of LIR. Isotopic specificity was, however, preserved[677] in the reaction between HI and $^{81}Br_2$, which was excited to the $^3\pi_{0}{}^{+}{}_{u}$ state by radiation of 558 nm, and produced 85% $H^{81}Br$.

The first reported isotope enrichment through LIR was that of CH_3OH molecules which absorbed HF laser radiation (at 3644 cm^{-1}) and reacted with Br_2 while admixed CD_3OD molecules appeared to remain inert.[681] Recent quantitative studies were, however, unable to reproduce these rather unusual results.[682] LIR has been successful in enriching Cl isotopes from HCl,[590,592,606] ICl,[683,684] and $CSCl_2$[578,676] (see Table VIII). The efficiency might be improved considerably by direct excitation to the lowest triplet state which reduces isotopic scrambling through resonant transfer.[688] Quite a number of theoretical analyses have been devoted to the LIR method for isotope enrichment.[582,583,594–597]

(b) *Single-Photon Predissociation* (*SPP*). In some favorable cases, notably gaseous H_2CO,[689–693] $H_2C_2O_2$ (glyoxal),[694] Br_2,[677,678] I_2,[635–637] and gaseous or solid *s*-tetrazine, $C_2H_2N_4$,[695,696] monochromatic ultraviolet or visible radiation will, in one single step, selectively excite a given isotomer which will then spontaneously dissociate because the potential energy curve for the bound excited state crosses that of the repulsive dissociating state.[697,698]

(c) *Two-Photon Ionization* (*TPI*). A laser is fine-tuned to ν_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 ν_2, such that $h\nu_2 < E_{ion} < h(\nu_1 + \nu_2)$, is subsequently absorbed by the excited isotope to produce a positively charged ion.[652] 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^2) associated with the photoionization continuum makes the intensity of the ionizer source at ν_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_{ion}.[659,665,699,700] More complex excitation schemes, involving three or four lasers, including a high-power CO_2 laser to saturate the ionization step, have been proposed to improve overall efficiency.[701] In another modification a catalytic species is added to the isotopic mixture.[702] 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}Li,[703] ^{40}Ca,[704] ^{85}Rb,[652,699,700] and, of course, ^{235}U.[665,670]

(d) *Two-Photon Dissociation* (*TPD*). A molecular isotomer is selectively excited with a pulsed laser at ν_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 ν_2 or from an incoherent energy source, supplied with a cut-off filter, such that $h\nu_2 < E_{diss} < h(\nu_1 + \nu_2)$, to prevent photolysis of ground-state molecules.[652,705] The isotomer 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 NH_3,[706–708] HCl,[562,652] and BCl_3.[709] The quantum efficiency and separation factors have been calculated for the case of HCl[710] and NH_3.[708,711]

(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 H_2 and D_2, to produce HD[446,447] or between N_2 and O_2, to produce NO.[565,712,713] 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.[714] 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 isotomer, because of the exponential dependence of the SRS signal on isotomer concentration. It might be possible to generate SRS also from a minor isotomer by the simple expedient of adding a proper Stokes field, either with a tuned dye laser[443] or with SRS radiation generated in a separate cell which contains that species in pure form.[715,716]

(f) *Radiation Pressure Deflection* (*RPD*). This conceptually straightforward photophysical separation technique—to be distinguished from simple photophoresis—was proposed by Ashkin.[672] 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 isotomer 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}Ba, ^{137}Ba, and ^{138}Ba atoms from a collimated beam of ^{n}Ba has been demonstrated[717–719] using radiation at $\lambda = 553.6$ nm corresponding to the resonance transition $6s^2\ {}^1S_0 \rightarrow 6s6p\ {}^1P_1$. An order of magnitude calculation shows that for Ba atoms at 1100 K, moving along a beam with an average velocity $u_\parallel \simeq 600$ m/s, the number of absorption/emission cycles required to impart a transverse velocity $u_\perp \simeq 1$ m/s, necessary to obtain spatial separation of a beam of 1 mrad divergence, is given by $138\ u_\perp/(h/\lambda) \simeq 200$ photons per separated Ba atom. This amounts to consumption or more than 4×10^7 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 calculations[719,720] 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,[718,719] or adding collision partners to the beam.[720] In the method of "fast adiabatic passage" a frequency-swept laser pulse, traveling between mirrors, intersects the atomic beam many times.[721] The incoming pulse causes highly efficient excitation.[722,723] The reflected pulse will cause an excited isotomer 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 collisonless 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.[724-726]

Typically, a pulsed transversely excited atmospheric pressure (TEA) CO_2 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_6,[679,724-731] BCl_3,[724-726,732-734] SiF_4,[732] CCl_4,[728,735] CF_2Cl_2,[732] CD_2Cl_2,[736] OsO_4,[737] or H_2CO.[738] The laser is tuned close to an absorption line of a particular isotomer; the line may be associated with a weak transition or a combination band[735] and the laser may be quite far off resonance.[622,642,738] Irradiation with 500–5000 laser pulses destroys this isotomer and progressively leaves the residual gas (sometimes as little as 1% of the initial amount) enriched in the other isotomer(s). The enrichment factor β 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,[727,729,732,739] leading to the existence of a sharp power threshold for dissociation. The fractional reaction per pulse is determined by eq 26, and this prediction[119] has been confirmed experimentally.[729,739,740] As for temporal laser characteristics, it was claimed that optimal yields are obtained with pulses of about 100 ns duration, while 1 ns pulses[732] (with peak intensities of 10^{13} W/cm^2) or 1 μs pulses[733] 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[727] for $^{34}SF_6$, as a result of selective irradiation and photofragmentation of $^{32}SF_6$ using P(16) radiation at 947 cm^{-1}. The $^{34}SF_6$ concentration increased from 4.2% in $^nSF_6$ to 99% (in the residual gas).

The reasons for isotopic selectivity are only partly understood,[741-751] and considerable experimental effort is now in progress in a number of laboratories[724-726] to elucidate the photolysis mechanism. In early studies it was observed that at irradiation intensities I_L in excess of 10^8 W/cm^2, but still below the threshold for optical breakdown ($I_L \simeq 10^{10}$ W/cm^2), *visible* luminescence occurred associated with emission lines from electronically excited radicals. For low gas pressures ($\simeq$1 Torr) luminescence was found to be practically instantaneous (ref 581, 632–634, 638–642, 740). That is, it was discerned after a delay shorter than the mean time between collisions ($\simeq$1 μs). 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.[632,732,742-744] 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.[745]

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

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

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^{-1} is about 10^9 W/cm^2. A quantum-mechanical extension for a multilevel system was recently provided by Larsen and Bloembergen[743] and Mukamel and Jortner.[744]

After the molecule has been promoted to the vibrational level $v = 3$ or 4 at a critical energy of, say, 3000 cm^{-1} 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^{-1}, is sufficiently large (particularly in a polyatomic molecule such as SF_6) 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[748,749] in SF_6 where the isotopic shift is larger than the frequency spread of the P, Q, and R branches. SF_6 first absorbs a low-power (4 MW) CO_2 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_2 pulse at 1084.6 cm^{-1} is then capable[739] of dissociating SF_6 at a much smaller threshold power (60 MW) than would be required in a single-frequency MPD experiment. Moreover, Letokhov obtained optimal yield[748,749] with the single-frequency laser detuned to 940 cm^{-1}, about 10 cm^{-1} below the molecular resonance line, in agreement with predictions of Mukamel and Jortner.[744]

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 (^{11}B, ^{12}C, ^{28}Si, ^{32}S) rather than preferentially enriching the minor isotope. Taking the most favorable cases reported thus far,[727,729] 2×10^6 photons were consumed on the average to remove one molecule of $^{32}SF_6$. Assuming no decomposition of any $^{34}SF_6$ molecules, the quantum efficiency for ^{34}S enrichment was, at most, $0.042/2 \times 10^6 \simeq 2 \times 10^{-8}$. In some studies, the more logical route was taken of treating the desired isotomer. For example, HD was formed, with an enrichment factor of 40, by selective MPD of natural formaldehyde.[738] Whereas H_2CO is transparent in the spectral region of the CO_2 laser radiation, HDCO has an absorption line at 951.6 cm^{-1} which overlaps to some extent with the main emission line from an untuned CO_2 laser (P (20) at 944 cm^{-1}), if power broadening is taken into account. Yet the photon conversion efficiency, deduced from the raw data, is still a meager 7×10^{-8}.

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.[753-757] In each case the absorbing molecule was transparent at laser frequency ν_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,[753] and in the hydrogen-chlorine photoreaction.[756]

The first quantitative study of a nonlinear photochemical process was the ruby-laser-induced two-photon-photolysis of iodoform.[94] 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)

$$Y = \gamma \delta N I_L^2 \Delta t \tag{25}$$

where Δt is the duration of the laser pulse, and γ is a factor depending on its temporal and spatial shape[129] ($\gamma = 0.353$ for a temporarily and spatially gaussian profile). Thus using eq 25 δ 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.[758-761] 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,[117,555,762-764] neither is photolysis induced by consecutive absorption of two photons.[391]

The two-photon photolysis study of iodoform has shown[94] 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,[765] 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.[94]

A discussion of the effects of external focusing and self-focusing on multiphoton photochemistry has been presented.[119] 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

$$Y \propto I_L^{3/2} \tag{26}$$

Thus the quantum order of the process cannot be determined in this type of measurement. This prediction has subsequently been confirmed by other calculations.[120,121,766] Experimental support is provided by MPD of SiF_4,[740] SF_6,[729,739] and organic molecules.[587] 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.[766] The high-order I_L^n dependence observed in some MPD studies[566,767] must be ascribed to nonintegrated yields, nonfocused geometry, breakdown or, as is the case in atomic multiphoton ionization processes, to unsaturated transition probabilities.[768] 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[769] and without[758] 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.

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

Molecule	Observed phenomena	δ (10^{-50} cm^4 s/photon molecule)	Ref
Styrene (liquid)	Polymerization		753
AgCl (solid)	Luminescence and Ag production		754
Phthalocyanine (vapor)	Photolysis		755
$H_2 + Cl_2$ (gas)	HCl production		756
2-*Chloro*-3-*nitroso*-2,3-dimethylbutane (solution)	HNO_2 production		757
Iodoform (solutions)	I_2 production	30	94
Benzene (liquid)	Unidentified products		760
Azoethane (gas)	N_2 production	0.06	758
NO_2 (gas)	O_2 production		771
Potassium ferrioxalate (solution)	Fe^{3+} reduction	1.5	759
Nitrobenzene (liquid)	Photolysis	24	761

Multiphoton processes have been observed in the ruby-laser-induced dissociation of biphenyl,[770] NO_2,[771] the ionization of atoms,[768,772] and molecules,[112,773] and in the whole class of MPD induced by CO_2 laser pulses (section C).

However, many other "nonlinear" photochemical processes were probably initiated via breakdown.[486] 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.[598,774] 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[775] and other reviews[776-780] cover the formative years of the chemical laser field from the discovery[781] of the photodissociation CF_3I 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.[782-784] Chemical lasers are widely used in mechanistics, kinetics, and energy-transfer studies. These particular applications have recently been reviewed in depth by Berry.[785] 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.[786,787] 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.[782-784]

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, ΔN_{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.[775] 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 ΔN_{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.[688]

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.[789] 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.[790] 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.[791] 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.[792] 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[775] and Berry.[785]

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 τ_p, powers P, and energies E.

a. Plash-photolysis laser[793]; p, $E = 15$ J

(i) Nonchain reaction,[794] $\tau_p \simeq 5\ \mu s$, shorter than FL pulse duration

$$UF_6 \xrightarrow{h\nu} UF_5 + F$$

$$F + H_2 \rightarrow HF(v) + H$$

(ii) Chain-branching reaction;[795] $\tau_p \simeq 50\ \mu s$, longer than FL pulse duration because of reaction chain length which may amount to a few hundred steps.

$$F_2 \xrightarrow[e]{h\nu} 2F$$

$$F + H_2 \rightarrow HF\ (v \leq 3) + H \text{ (cold reaction, 139 kJ/mol)}$$

$$H + F_2 \rightarrow HF\ (v \leq 10) + F \text{ (hot reaction, 420 kJ/mol)}$$

b. Photoelimination laser;[574,796] p

$$CH_2 = CHF \xrightarrow{h\nu} HC{\equiv}CH + HF(v)$$

c. Photodissociation laser;[781,797-799] p, $\tau_p \simeq 3$ ns, $E \simeq 100$ J

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

$$C_3F_7I \xrightarrow{h\nu} C_3F_7 + I\ (5\ ^2P_{1/2})$$

$$\mathrm{I}\,(5\ {}^2\mathrm{P}_{1/2}) \rightarrow \mathrm{I}\,(5\ {}^2\mathrm{P}_{3/2}) + h\nu \text{ (lases at 1315 nm)}$$

d. Predissociation laser[800]

$$\mathrm{RCN} \xrightarrow{h\nu} \mathrm{R} + \mathrm{CN}\,(v = 4)$$

e. Flow chemical laser;[786,801] CW, $P \simeq 5$ kW for supersonic transverse flow and for 10 Torr operating pressure.

$$\mathrm{F}_2 \xrightarrow{\text{e,heat}} 2\mathrm{F}$$

$$\mathrm{F} + \mathrm{H}_2 \rightarrow \mathrm{HF}(v) + \mathrm{H}$$

f. Free-burning flame laser;[802] CW, $P \simeq 25$ W, pressure about 10 Torr

$$\mathrm{CS}_2 + \mathrm{O}_2 \xrightarrow{\text{chem}} \mathrm{SO}_2 + \mathrm{CO}(v)$$

g. Energy transfer laser;[786,787,803,804] CW, $P \simeq 15$ 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_2. In this way deleterious vibrational redistribution between hydrogen halides is minimized.

$$\mathrm{NO} + \mathrm{F}_2 \xrightarrow{\text{chem}} \mathrm{ONF} + \mathrm{F}$$

$$\mathrm{F} + \mathrm{D}_2 \rightarrow \mathrm{DF}(v) + \mathrm{D}$$

$$\mathrm{DF}(v) + \mathrm{CO}_2 \rightarrow \mathrm{DF}(v-1) + \mathrm{CO}_2[001]$$

h. Thermal-explosion laser;[805] p, $\tau_\mathrm{p} \simeq 10\ \mu$s

$$\mathrm{HN}_3 \xrightarrow{h\nu} \mathrm{N}_2(v)$$

$$\mathrm{N}_2(v) + \mathrm{CO}_2 \rightarrow \mathrm{N}_2(v-1) + \mathrm{CO}_2[001]$$

$$\text{or } \mathrm{ClN}_3 + \mathrm{H}_2 \xrightarrow{h\nu} \mathrm{HCl}(v) + \mathrm{N}_3$$

i. Exploding-wire laser;[806] p

$$\mathrm{Al} + \mathrm{F}_2 \xrightarrow{h\nu} \mathrm{AlF}(v) + \mathrm{F}$$

B. Dye Lasers[30]

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,[30,31,807-810] as are partial bibliography lists[811,812] 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.[813] Most of the conclusions of this simple model are applicable to real-life dye lasers for which more general treatments are available.[808,814-817] 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 $\sigma_{01}(\mathrm{P})I_\mathrm{p}$ to some vibronic level $\mathrm{S}_1{}^\mathrm{v}$ (or $\mathrm{S}_n{}^\mathrm{v}$), from which they subsequently relax nonradiatively to $\mathrm{S}_1{}^0$ at a rate $1/\tau_{\mathrm{v}''}$. Laser action is initiated by the spontaneous fluorescence noise, characterized by a fluorescence lifetime τ_{10}, a line shape, $g(\nu)$, and a quantum yield ϕ. Together they determine the stimulated emission cross-section σ_e (see eq 4). The fluorescence transitions take place between the $\mathrm{S}_1{}^0$ and the $\mathrm{S}_0{}^\mathrm{v}$ states, which ultimately return nonradiatively to $\mathrm{S}_0{}^0$ at a rate $1/\tau_{\mathrm{v}'}$. The spontaneous noise is amplified through stimulated emission at a rate $\sigma_\mathrm{e}I_\mathrm{L}$, 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 $\sigma_{10}(\mathrm{P})I_\mathrm{p} \ll 1/\tau_{\mathrm{v}'}$. From eq 13 an expression for the gain G of a dye laser amplifier may be obtained

$$G = \tau_{10}\sigma_\mathrm{e}\sigma_{01}(\mathrm{P})I_\mathrm{p}N/[1 + \tau_{10}\sigma_{01}(\mathrm{P})I_\mathrm{p}] \qquad (27)$$

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^+ or Kr^+ 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, τ_p, is long compared to the reciprocal ISC rate constant $1/k_\mathrm{ST}$. 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 $I_\mathrm{p}{}^\mathrm{th}$.

$$G = \xi N[\sigma_\mathrm{e} - \sigma_{12}(\mathrm{L}) - \tau_\mathrm{TS}\sigma_\mathrm{T}(\mathrm{L})k_\mathrm{ST} - \sigma_{01}(\mathrm{L})(1 + \tau_{10}k_\mathrm{ST})/\tau_{10}\sigma_{01}(\mathrm{P})I_\mathrm{p}] \qquad (28)$$

and

$$I_\mathrm{p}{}^\mathrm{th} = \sigma_{01}(\mathrm{L})(k_\mathrm{ST}\tau_{10} + 1)/\tau_{10}\sigma_{01}(\mathrm{P})[\sigma_\mathrm{e} - \sigma_{12}(\mathrm{L}) - \sigma_\mathrm{T}(\mathrm{L})k_\mathrm{ST}\tau_\mathrm{TS}] \qquad (29)$$

with

$$\xi = \tau_{10}\sigma_{01}(\mathrm{P})I_\mathrm{p}/\{\tau_{10}[\sigma_{01}(\mathrm{P})I_\mathrm{p} + k_\mathrm{ST}] + 1 + k_\mathrm{ST}\tau_{10}\tau_\mathrm{TS}\sigma_{01}(\mathrm{P})I_\mathrm{p}[1 + \tau_\mathrm{TS}\sigma_\mathrm{T}(\mathrm{P})I_\mathrm{p}]\} \qquad (30)$$

where all the molecular parameters are defined in Figure 8.

Lasing is most easily achieved in PLPDL systems. Here $\tau_\mathrm{p} \ll 1/k_\mathrm{ST}$ 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 $\mathrm{S}_1{}^0$, at a rate $\sigma_{12}(\mathrm{P})I_\mathrm{p}$. The results for G and $I_\mathrm{p}{}^\mathrm{th}$ in a PLPDL small-signal amplifier are

$$G = \zeta N[\sigma_\mathrm{e} - \sigma_{12}(\mathrm{L}) - \sigma_{01}(\mathrm{L})/\tau_{10}\sigma_{01}(\mathrm{P})I_\mathrm{p}] \qquad (31)$$

and

$$I_\mathrm{p}{}^\mathrm{th} = \sigma_{01}(\mathrm{L})/\tau_{10}\sigma_{01}(\mathrm{P})[\sigma_\mathrm{e} - \sigma_{12}(\mathrm{L})] \qquad (32)$$

where

$$\zeta = \tau_{10}\sigma_{01}(\mathrm{P})I_\mathrm{p}/[1 + \tau_{10}\sigma_{01}(\mathrm{P})I_\mathrm{p} + \tau_{10}\tau_{21}\sigma_{01}(\mathrm{P})\sigma_{12}(\mathrm{P})I_\mathrm{p}{}^2] \qquad (33)$$

Inspection of eq 29 and 32 shows that the necessary molecular operation criterion for *any* dye laser is that $\sigma_\mathrm{e} > \sigma_{12}(\mathrm{L})$. The cross-section $\sigma_{01}(\mathrm{L})$ influences the value of $I_\mathrm{p}{}^\mathrm{th}$ 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, $\sigma_\mathrm{T}(\mathrm{P})$, $\sigma_\mathrm{T}(\mathrm{L})$, or τ_TS; thus even when $\sigma_\mathrm{e} > \sigma_{12}(\mathrm{L})$ the triplet parameters may determine the operational conditions. While k_ST, $\sigma_\mathrm{T}(\mathrm{P})$, and $\sigma_\mathrm{T}(\mathrm{L})$ are only slightly affected by external perturbations, the value of τ_TS can be manipulated by adding triplet quenchers such as oxygen[808,818,819] or cyclooctatetraene.[820] In PLPDL systems, photoquenching sets an optimum for the efficiency of the dye laser, since there exists a maximum gain, given by eq 20.[813,814] This was confirmed by efficiency measurements[820] and through the intensity dependence of the gain as measured by Shah and Leheny.[378,822] In addition, indirect observations of photoquenching effects on PLPDL performance have been reported.[813,814,823-825] Molecular reorientation,[826,827] bleaching,[828] and photodegradation of dyes[829-832] 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.[833,834] 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.[835,836] Another approach to overcome losses is to modify the lasing state. For example, protonation by acidifying the medium[809] or formation of exciplexes,[837-839] 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 $\sigma_{12}(P)$.[377] Similar effects on the lasing state can be achieved by utilizing energy transfer between a donor-pumped molecule and an acceptor-lasing dye.[344,345] Energy transfer dye lasers (ETDL) have been used to extend the range of PLPDL systems to the infrared spectral region.[840-842] As was shown in a recent analysis of ETDL, the threshold power is lowered and sometimes photoquenching can be minimized.[843]

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[844,845] 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.[846] A combined effort by physical and organic chemists to "engineer" laser dyes[833,835] 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	*p*-(9′-Anthryl)-*N*,*N*-dimethylaniline
BA	Benzanthracene
BBO	2,5-Bis(4-phenylyl)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	*N*,*N*-Diethylaniline
DiMe-POPOP	1,4-Bis[2-(4-methyl-5-phenyloxazolyl)]benzene
DMA	*N*,*N*-Dimethylaniline
DMSO	Dimethyl sulfoxide
DODCI	3,3′-Diethyloxadicarbocyanine iodide (DODI)
DPA	Diphenylanthracene
DPPD	*N*,*N*-Diphenyl-*p*-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′-Diethylthiadicarbocyanine iodide
DTTC	3,3′-Diethylthiatricarbocyanine iodide
DPPD	*N*,*N*-Diphenyl-*p*-phenylenediamine
ECZ	*N*-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′-*p*-Phenylenebis(5-phenyloxazole)]
PPO	Phenylbiphenylyloxadiazole
PTH	Phenothiazine
RB	Rhodamine B
R6G	Rhodamine 6G
TCNB	1,2,4,5-Tetracyanobenzene
THF	Tetrahydrofuran
TPMD	*N*,*N*,*N*′,*N*′-Tetramethyl-*p*-phenylenediamine
VCZ	*N*-Vinylcarbazole

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