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Chemical Effects of Laser Radiation

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This review deals with the chemical effects observed under the influence of laser light. The operating principle of the laser, the main types of laser, and the properties of laser radiation are briefly described. The application of laser techniques to the production and investigation of short-lived excited states is discussed. One-photon and multi-photon processes induced by laser radiation are considered. Several examples of the specificity of the reactions initiated by laser light are given. 140 references.

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I. INTRODUCTION

In the hands of scientists and engineers, lasers have proved an important new tool to study interactions with matter. The physical principles of laser action were formulated as a result of the fundamental researches on quantum electronics carried out in the USSR (by Basov and Prokhorov's team) and in the USA (by Townes and Schawlow's team). In 1958 Schawlow and Townes[1] drew attention to the possibility of producing an optical quantum generator (laser) based on stimulated (or induced) radiation processes†. The first solid-state laser, using ruby, was constructed by Maiman[2] in 1960, and one year later Javan, Bennett, and Herriott assembled the first gas (helium–neon) laser[3]. At about this time, suggestions that laser light could be used to study chemical processes began to appear in the literature[4,5]. The most attractive properties of laser light for this purpose are its high intensity and monochromaticity, and also its accurate collimation, which enables the laser energy to be transmitted over long distances or concentrated into small, isolated regions of matter. The radiation of many lasers lies in the i.r. region of the spectrum, i.e. in a region where absorption is accompanied by the excitation of intramolecular vibrations. The availability of high-intensity, monochromatic light sources for this spectral region gave a new impetus to infrared photochemistry, i.e. to the excitation of specific molecular vibrations, and to the selective initiation and control of chemical reactions.

Many papers (both theoretical and experimental) have been written in recent years on the effect of laser radiation on matter and on the chemical reactions induced by laser light. Some overall trends are becoming apparent, and we can attempt to generalise some of the published results.

II. PROPERTIES OF LASER LIGHT. VARIOUS TYPES OF LASER

Lasers are devices for the generation or amplification of light by stimulated emission. Consider a vessel exposed to a flux of incident light. The atoms and molecules in the vessel will absorb light and undergo transitions. The transition from an excited level to the ground level can occur either spontaneously or by induced (stimulated) processes (see Fig. 1). The number of absorbtions and of induced emissions per unit time in unit volume is given by

$$\Delta N_{ik} = B_{ik}u_\nu N_i \quad (1)$$

$$\Delta N_{ki} = B_{ki}u_\nu N_k \quad (2)$$

where, as shown by Einstein in 1917,

$$B_{ik} = B_{ki} \quad (3)$$

(u_ν is the photon flux; N_i and N_k are the numbers of atoms in the i-th and the k-th level per unit volume; B_{ik} and B_{ki} are the Einstein coefficients).

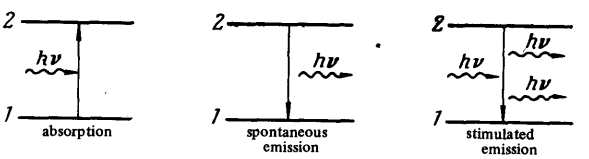


Figure 1. Model of absorption, spontaneous emission, and stimulated emission processes: *1*) ground level, *2*) excited level.

The fall in intensity of the light beam per unit volume along the direction of the incident beam is given by the formula

$$-\Delta U = B_{ik}N_i u_\nu \Delta E - B_{ki}N_k u_\nu \Delta E \quad (4)$$

where $\Delta E = h\nu = E_k - E_i$ (E_k and E_i are the energies of the k-th and the i-th level; ν is the frequency corresponding to the transition).

Using Eqn. (3),

$$-\Delta U = u_\nu B_{ik}N_i \Delta E\left(1 - \frac{N_k}{N_i}\right) \quad (5)$$

Under conditions of thermodynamic equilibrium

$$\frac{N_k}{N_i} = e^{-\frac{\Delta E}{kT}} \quad (6)$$

† This principle for the amplification of light had been suggested earlier (in 1940) by V.A. Fabrikant.

and, since $\Delta E > 0$, the exponential factor in the expression

$$-\Delta U = u_\nu B_{ik} N_i \Delta E \left(1 - e^{-\frac{\Delta E}{kT}}\right) \quad (7)$$

is always less than unity and therefore the stream of radiation must lose energy at any finite temperature (in the limit of $T \to \infty$, $\Delta U \to 0$). The condition for light amplification (or "negative absorption") is

$$\frac{N_k}{N_i} > 1 \quad (8)$$

This condition can be satisfied only by non-equilibrium processes. A population of energy levels corresponding to the inequality (8) is termed a population inversion. The more substantial the population inversion, the greater is the amplification of the light beam. Let us consider the ways in which population inversion can be induced. Assume that the atomic or molecular system can exist in three energy levels *0*, *1*, and *2* (see Fig. 2). Population inversion arises when the probability of a $1 \to 0$ transition is less than the probability of a $2 \to 1$ transition under conditions such that the rate of the $2 \to 0$ transition is sufficiently low.

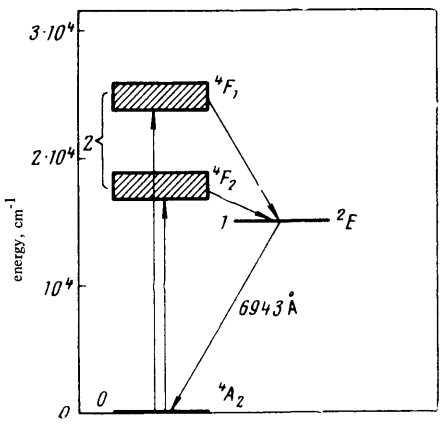


Figure 2. Energy levels of ruby ($Cr^{3+} \cdot Al_2O_3$).

Lasers consist of an active medium (i.e. the substance whose optical transitions are used to generate light), a pump (to excite the system), and suitable resonators (mirrors) to cause excitation of specific vibrations in the active medium. The active medium can be solid, gaseous, or liquid. Pumping, i.e. the production of a population inversion, is achieved in a variety of ways, depending on the type of laser: solid-state lasers are pumped optically, semiconductor lasers by electrical impulses, and gas lasers are usually pumped by electrical discharges. The resonator usually consists of a system of two plane-parallel mirrors.

Fig. 2 represents the system of energy levels for the ruby laser. Irradiation of the ruby crystal from a xenon flash tube causes inversion of the population of the ^2E level. The radiation density u_ν increases as a result of multiple reflections from the silvered end-faces of the crystal, and stimulated emission appears. The intensity of emission increases very rapidly until level *1* becomes depleted. The duration of the light pulse ("spike") is 10^{-6} s, and the total duration of the stream of separate spikes is of the order of 10^{-3} s. This operating regime for a pulsed laser is termed free generation.

Lasers can also be operated in a different regime: the so-called modulated Q-factor or giant pulse regime, or in English terminology the Q-switched regime[6]. By inserting a shutter between the crystal and one of the mirrors, the photon flux in the active medium of the laser is decreased, thus decreasing the number of stimulated transitions per unit time and hence enhancing the population inversion. A very powerful light pulse is obtained when the optical shutter is momentarily opened. Although the total energy of the giant pulse is about an order of magnitude lower than that obtained in the free generation regime, the length of the pulse can be as small as 10^{-8} s, and therefore power levels of hundreds of megawatts can be obtained. The optical shutter usually consists of a solution of a dye, which is decolorised by a very intense light beam (see Section III).

Even shorter (10^{-11}–10^{-12} s) and more powerful pulses have been generated as a result of recent advances in the Q-switching method. Picosecond pulses of laser light have been produced by the mode-locking method. The radiation from a solid-state laser consists of many modes or frequencies of vibration, close to the fundamental frequency. Some dyestuffs behave as amplitude modulators when irradiated: they amplify the frequencies of highest amplitude and they attenuate all the other frequencies. As a result, the many frequencies generated by the laser become phase-locked, and a series of narrow pulses (of length inversely proportional to the width of the corresponding frequency component) is produced[7,8] as a result of constructive and destructive interference.

The main types of laser are listed in Table 1 together with some properties of their radiation. The light emitted by lasers has some unique properties, not found in ordinary light sources (coherence, high monochromaticity, intensity, etc.). Not all of these are equally important from the point of view of initiating chemical reactions: the most valuable property of laser light in this respect is the intensity of the radiant energy available over a narrow range of frequencies. As Table 1 shows, the generated band-width in any laser is much narrower than the absorption band of the molecules. It is also possible to increase the density of laser radiation by focussing the beam. A monochromatic, low-divergence laser beam can be focussed into a spot 10^{-6}–10^{-4} cm^2 in area. Because of the coherence of laser radiation, interference can take place in the focal region: the amplitude of the radiation field will vanish, or increase by a factor of two, between points half a wavelength apart. Since many of the effects of laser radiation are non-linear, i.e. they vary as the square (or some higher power) of the intensity of radiation, interference can be expected to enhance some of the high-intensity effects of laser radiation. Such giant intensities of radiation are accompanied by substantial values of the electric and magnetic vector of the light wave. Thus, an electric field strength of 10^6 V cm^{-1} is set up when a pulse from a 1 MW ruby laser is focussed into a spot 0.2 mm in diameter. This level of field strength is comparable with the electric fields present within molecules. It follows that the electric field associated with the light waves can induce strong perturbations, leading to polarisation (and, in the limit, ionisation or dissociation) of the molecules.

When laser radiation is used to initiate chemical reactions, it would be desirable to have a smooth control over the wave length of the light (to suit the particular system)

Table 1. Main types of laser.

Active medium	Operating regime	Pump	Wave length	Monochromaticity, Δλ	Duration of emission, s	Power	Light flux[a] photons/cm^2 s	Comments	Ref.
Doped crystals and glasses									
Ruby (Cr^{3+}/Al_2O_3)	pulse[b]	optical	6943 Å	<1 Å	10^{-3}	1—100 kW	$3\cdot10^{21}$—$3\cdot10^{23}$	efficiency <1%	9
	Q-switch[c]			0.08—0.5 Å	10^{-8}	10—100 MW	$3\cdot10^{26}$—$3\cdot10^{29}$		
Nd^{3+}/glass	pulse		1.06 μm	100 Å	10^{-3}	1—100 kW	$5\cdot10^{21}$—$5\cdot10^{23}$		
	Q-switch			20—100 Å	10^{-8}	10—100 MW	$5\cdot10^{28}$—$5\cdot10^{29}$		
Semiconductor lasers									
GaAs	pulse	current pulses	9020 Å	5—10 Å	10^{-6}—10^{-7}	1—60 W at 10^4—10^5 pulses s^{-1}	$4\cdot10^{18}$—$3\cdot10^{20}$	at 300° K	10
	pulse		8430 Å	5—10 Å				at 77° K	
Gas lasers									
He-Ne	continuous[d]	discharge	6328 Å	10^{-4} Å or less	—	1—100 MW	$3\cdot10^{15}$—$3\cdot10^{17}$		11
			1.15 μm						
CO_2	continuous[d]	discharge or optical	10.6 μm	0.01 Å	—	50 W—8 kW	$2\cdot10^{21}$—$4\cdot10^{23}$	50-80 W per metre of discharge tube	12
N_2	*Q*-switch	discharge	3371 Å	0.01 Å	10^{-8}	50 kW	$8\cdot10^{22}$		13
He—Cd	continuous	discharge	3250 Å	—	—	5—50 MW	$8\cdot10^{15}$—$8\cdot10^{16}$		14
			4416 Å					efficiency	15
Dye lasers	*Q*-switch	single laser pulse or optical	4000—12000 Å	0.6—300 Å	10^{-8}	1—10 MW	$2\cdot10^{27}$—$6\cdot10^{28}$	from 0.001% to 90%	16

[a] Flux calculated for an unfocussed beam of 1 cm^2 diameter.
[b] Pulsed, free generation regime.
[c] Pulsed, *Q*-switched regime.
[d] Continuous regime.

while retaining its high power and monochromaticity. Laser emission consists of discrete lines, usually in the i.r. region of the spectrum or close to the red end of the visible region. However, radiation in the u.v. region or close to the u.v. limit of the visible region would be much more appropriate in chemical applications (photon energy 4—7 eV). Only two gas lasers emit in this region of the spectrum: the N_2 pulsed laser[13], which has a relatively low power, and the recently discovered helium—cadmium laser, which can be operated in the continuous wave regime[14]. Laser radiation in the u.v. region can be obtained also by frequency doubling, which involves transmitting strong laser pulses through certain crystals (KH_2PO_4, $NH_4H_2PO_4$). In this way we can obtain light with λ = 3471 Å (by doubling the frequency of the ruby laser) or λ = 2650 Å (by twice doubling the frequency of the Nd^{3+} laser). Thus, by using the harmonics of laser light, we can increase the number of available discrete wave length and produce powers of the order of 0.1 MW in the short-wave region. Lasers based on organic dyes[15,16] offer an even better choice of wave lengths in the region of interest. The emission from these lasers can be controlled over fairly wide wavelength limits (several hundreds of Ångstroms). Dye lasers were discovered quite recently (in 1967), but the number of dyes in which laser action has been observed already exceeds the number of active media used in all other types of laser. In principle, the number of dyes capable of laser action is almost infinite, and it should be possible to synthesise dyes having the required properties (frequency, amplification coefficient) and to use a special laser for each of a large number of narrow frequency ranges. Thus, with the help of lasers based on solutions of organic dyes we expect to progress from a discrete and limited choice of frequencies (obtained from solid-state lasers) to a practically free choice of frequencies in the visible and near infrared regions of the spectrum. Generation from a 4-methylumbelliferone laser beginning at 3850 Å, i.e. in the u.v. region, has recently been reported[17].

III. MECHANISM OF THE EFFECT OF LASER RADIATION

1. Effects Associated with Electronic Excitation

a. One-photon effects

Direct excitation to the triplet state. When a substance having a singlet ground state is irradiated with light of relatively low frequency, direct excitation of triplet levels is not observed, because the extinction coefficients of light with a frequency corresponding to these transitions are 10^5—10^6 times smaller than the extinction coefficients for allowed transitions. Although the lowest triplet level of most molecules is located between the ground and the first excited singlet level (Fig. 3), the electronic spectra of molecules show their first absorption at frequencies corresponding to the $S_1 \leftarrow S_0$ transition. With ordinary photochemical excitation by light of low intensity, triplet states can arise only by $T_0 \leftarrow S_1$ transitions from excited singlet states (Fig. 3).

However, direct population of triplet levels can be induced by using laser light. In spite of the low probability of $T_0 \leftarrow S_0$ transitions, sufficiently intense radiation can make these transitions observable. Direct triplet excitation has been observed in a number of aromatic hydrocarbons and dyes with low-lying excited states[18-21] (see also a discussion[22] of the criteria for the direct formation of triplet states). The most convenient material for a study of this effect is anthracene, because the frequency of the transition to the triplet state in this material (14 750 cm^{-1}) is close to the frequency of radiation from the ruby laser (14 400 cm^{-1}). Phosphorescence has been observed in anthracene irradiated with light from a ruby laser[23] operated in the *Q*-switched mode. Since the quantum energy of the ruby laser is lower (by 350 cm^{-1}) than the excitation energy of anthracene, direct absorption can occur with a small activation energy, which may even

exceed 350 cm^{-1}, if a vibrationally excited triplet of anthracene is formed during absorption.

In molecular oxygen the ground level is triplet. However, transitions to the singlet, vibrationally excited $O_2(^1\Delta_g + v)$ level can be induced [24] by Nd^{3+} laser light

$$O_2(^3\Sigma_g^-) \rightarrow O_2(^1\Delta_{g+v})$$

and in this way the reactions of singlet oxygen can be initiated.

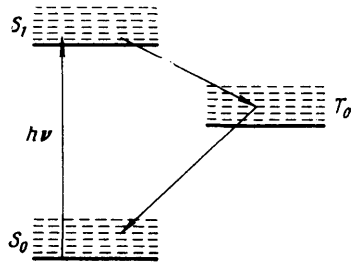


Figure 3. Energy levels of an organic molecule (the broken lines denote vibrational sublevels).

The one-photon mechanism of transition to a triplet state acting as an intermediate in a chemical reaction has been convincingly demonstrated [25] in one system only: the gas-phase photochemical bromination of perfluoro-olefins, initiated by light from a ruby laser. (The rate of the dark reaction is very low for these compounds.) During normal photobromination with light of wavelength below 6800 Å the Br_2 molecule dissociates into atoms and the reaction proceeds by a radical-chain mechanism. The energy of a light quantum corresponding to $\lambda = 6940$ Å is not sufficient for direct photodissociation of Br_2, but this quantum can excite a transition from the ground to the lowest excited state ($^3\Pi_{1u} \leftarrow {}^1\Sigma_{g^+}$). The vibrational energy of this state of the Br_2 molecule can be altered also by varying the radiation frequency [26] within several cm^{-1}. In this way, the addition to a double bond of bromine molecules in the triplet state and in exactly known vibrational states has been investigated. It has been shown that the reaction rate is very sensitive to the wavelength (within the absorption band) and is directly proportional to the intensity of the incident light at constant wavelength. Thus, the reaction is not caused by direct dissociation of the Br_2 molecules, corresponding to the appearance of a continuum in the spectrum. At the same time, participation of atomic bromine is suggested by the inhibiting effect of traces of NO. Mass spectrometric analysis of the products obtained in bromination experiments with labelled $^{79}Br-{}^{79}Br$ and $^{81}Br-{}^{81}Br$ molecules confirmed the absence of isotopic enrichment of the reaction products, which would be expected if the addition of Br_2 occurred by a molecular mechanism. The primary photobromination product, $Br_2(^3\Pi_{1u})$, has a closely spaced set of vibrational levels, the difference in energy between successive levels being less than kT at room temperature. Hence, the probability of vibrational energy transfer is high. Since the dissociation energy of this state of the Br_2 molecule is only 6 kcal $mole^{-1}$, the $Br_2(^3\Pi_{1u})$ molecule can acquire, by collision, the vibrational energy necessary for dissociation into Br atoms, which then enter into the chain reaction leading to the brominated product. The contribution to the reaction from the molecular mechanism is negligibly small.

Excitation into singlet states. The main feature of the excitation of singlet levels by giant laser pulses is the fact that the pulses are very intense and of short duration (shorter than, or comparable with, the mean life time of the singlet excited states). Because of the high intensity, excited levels can be highly populated. As a result, the spectral properties of the material are changed, and observation of the absorption spectra of excited singlets becomes possible. The short duration of the laser pulse enables us to monitor processes occurring in nanoseconds [27], and even picoseconds, provided that the reaction is accompanied by fast emission [28]. The frequencies of transitions into excited singlet states of organic molecules lie in the u.v. region. Since lasers which emit at these frequencies are not powerful enough, one-photon excitation to singlet states is usually carried out by utilising the higher harmonics of the light from very powerful pulsed lasers. Excited singlets, and their reactions, have been investigated by an extension of Norrish and Porter's [29] flash photolysis and spectroscopy method. An intense flash of light creates macroscopic concentrations of the primary photochemical dissociation product in the irradiated material: free atoms, radicals, or molecules in excited states. The excited system can be investigated either spectroscopically or kinetically. In the former case a second (test) pulse of light is transmitted through the system after a predetermined interval, and the absorption spectrum of the short-lived products is recorded. In the kinetic method, light of wavelength corresponding to the absorption maximum of the short-lived product is continuously passed through the cell, and changes in transmission are monitored for a predetermined period following excitation. The classical flash photolysis method uses pulses of 10^{-6} s duration, obtained from a discharge tube, which limits the application of the method to processes with rates $<10^6$ s^{-1}. Processes 100–1000 times faster can be studied by using laser-pulse excitation. The apparatus used by Porter and Topp [30,31] to record the absorption spectra of the excited singlets of aromatic compounds is shown in Fig. 4. The spectra were measured a known time after excitation by a giant pulse of the first harmonic of a ruby laser (3470Å). Part of the light, selected by a beam splitter, was focussed on a cell containing the solution of the experimental compound. The other part of the beam passed through the splitter, was reflected by a mirror back to the splitter, and to a cell containing the scintillator intended to generate a continuum in the spectral region of interest. The test pulse passed through the cell into the spectrograph, where the spectrum of the singlet excited states produced by the laser pulse was recorded. The time delay is determined by the distance between the beam splitter and the mirror: for example, a distance of ~3.5 m will produce a delay of 25 ns. For kinetic measurements, the test source of light can be a flash from a discharge tube of duration (several milliseconds) large compared to that of the excitation pulse from the laser. In practice, it is possible to use a small part of the light output of the lamp used for optically pumping the laser. It is important that the intensity of this light source remains practically constant during the measurement.

Novak and Windsor [32] used a slightly different method to generate their test pulse. They used a prism to isolate the beam of primary laser radiation, which is usually lost when a crystal of KH_2PO_4 is used for frequency doubling, and focussed it on to a cell containing an inert gas. The luminescence produced by the dielectric breakdown of this gas, having a continuous spectrum, could be used as the test pulse. Time resolution was obtained by directing the test radiation to a fast-response photocathode after it had passed through the cell. Obviously, the time delay can be controlled, as in the previous apparatus [31], by varying the distance between the prism and the inert gas cell with the help of a mirror. Lastly, by using a monochromator, the absorption spectra of excited singlets can be investigated from the time-resolved absorbance curves for several different wavelengths. This method has been used by a number of workers [33-38].

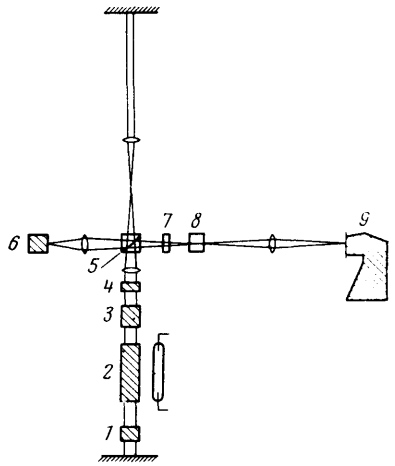


Figure 4. Apparatus for spectral measurements on short-lived products in the nanosecond region: *1*) Q-switch; *2*) ruby laser; *3*) $NH_4H_2PO_4$ crystal; *4*) filter; *5*) beam splitter; *6*) source of test pulses; *7*) attenuator; *8*) cell containing experimental compound; *9*) spectrograph.

Using this method, Porter and Topp [31] obtained the $S_X \leftarrow S_1$ absorption spectra for many aromatic hydrocarbons, and they were able to measure the mean life time of the first excited singlet. The latter quantity can also be measured independently from the rate of decay of fluorescence: in most cases the results obtained by the two methods were practically identical. The interpretation of singlet–singlet absorption spectra is complicated by the accumulation of the T_0 triplet in solution as the excited S_1 singlet disappears, so that the observed spectrum is not a simple one. With some hydrocarbons (pyrene, coronene) the apparent lifetime of the excited singlet is found to be much greater than the duration of the laser pulse, and therefore the spectra observed at very short delay times are characteristic of the excited singlet only. The isolation of the $S_X \leftarrow S_1$ absorption spectrum from the $T_X \leftarrow T_0$ background, which increases with time, is further complicated [33,34] by the great similarity between these spectra. This similarity has been reported for many hydrocarbons: naphthalene and benzanthracene [33,34], anthracene [36], biphenyl [39], pyrene, and coronene [31], and therefore it must be a general phenomenon, as theoretically predicted [40]. However, absorption from S_1 and T_0 levels has different polarisations [36,41]. The absorption spectra of excited singlets have been observed also for halogenated hydrocarbons [35,42].

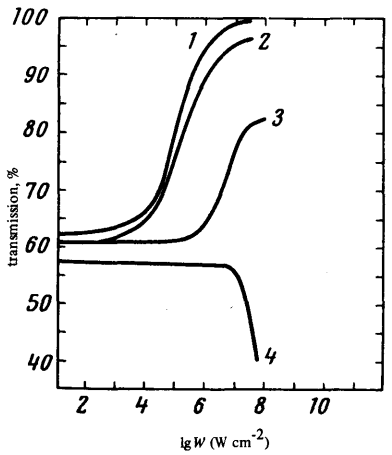


Figure 5. Transmission of dye solutions against intensity of laser radiation [30]: *1*) phthalocyanine in chloronaphthalene solution; *2*) vanadyl phthalocyanine in toluene; *3*) cryptocyanine in isopropanol; *4*) Sudan Black in acetic acid.

With dyes, whose electronic absorption spectra lie in the visible region, one-photon excitation of singlet levels can be induced by the radiation of the ruby laser. These processes are involved in the bleaching of the dyes used as passive optical shutters in Q-switching. Under the influence of a high-intensity beam the population of ground state dye molecules decreases, and as a result deviations from Beer's law are observed and the transmittance of the solution increases with light intensity. This behaviour is shown by solutions of phthalocyanine and cryptocyanine (see Fig. 5). At least two different mechanisms for this process can be suggested. According to the first [43,44], the dye acts as a two-level system, and the transition saturates when the populations of the ground and the excited state are equalised and the rates of absorption and stimulated emission are also equalised. However, it has been shown [45] that for most dyes at experimentally accessible photon fluxes the rate of stimulated radiative transitions from an excited level is smaller than the rate of intersystem crossing, as a result of which the triplet levels become populated. Thus, the dye should be treated as a multilevel system. The condition necessary for bleaching is that the cross-section for absorption of light of the laser generation frequency by molecules raised to the excited level should be less than the absorption cross-section for the ground state. In the opposite case—as with the dye Sudan Black, see Fig. 5—an increase in absorbance is observed. However, these phenomena can be explained only by assuming multi-photon excitation.

b. Multi-photon processes

Many of the effects of laser radiation are produced by multi-photon processes. Such processes are important in two respects. When laser radiation gives rise to excitation, ionisation, or chemical reaction, the process usually involves the absorption of more than one quantum, since the quantum energy of currently available lasers is several times smaller than bond dissociation energies, electronic excitation energies, or ionisation potentials. The rate of a multi-photon process is proportional to I^n, where $n > 1$. Hence, the larger n, the faster does the relative importance of multi-photon processes increase with intensity of illumination. Cross-sections for n-photon absorption are listed in Table 2: it can be seen that even at a flux of 10^{30} photons cm^{-2} s^{-1} the probability of two-photon excitation is less than the probability of one-photon excitation. However, the role of multi-photon processes may be enhanced by the non-linear self-focussing effect [47].

Table 2. Cross-sections for n-photon absorption.

n	Cross-section
1	10^{-17}–10^{-18} cm^2 $molecule^{-1}$
2	10^{-48}–10^{-54} cm^4 s $photon^{-1}$ $molecule^{-1}$
3	10^{-75}–10^{-85} cm^6 s^2 $photon^{-2}$ $molecule^{-1}$
4	10^{-115} cm^8 s^3 $photon^{-3}$ $molecule^{-1}$

Multi-photon (in particular, two-photon) processes were first observed in classical photochemistry, i.e. at relatively low light intensities [48]. In this case multi-photon processes can be favoured by producing high concentrations of metastable triplet states: the necessary increase in the life time of the triplet states is achieved by freezing the irradiated compound in a solid matrix. Two-photon excitation includes intersystem crossing and triplet–triplet absorption. Several reactions of the excited T_1 triplet have been observed: solvent interactions, decomposition, and photoionisation. The rate of a two-photon process is $r \propto I^2$, or more precisely $r \propto I_{\nu_1} I_{\nu_2}$. It is an interesting peculiarity of two-photon photochemical reactions that they require simultaneous irradiation with light of frequencies ν_1 and ν_2. The quantum yields of multi-photon processes are small: for two-photon processes, they are of the order of 10^{-2} for light intensities of 10^{14}–10^{17} photons cm^{-2} s^{-1}. However, at higher light intensities their yield (and therefore also the relative importance of multi-photon processes in competition with one-photon processes) is expected to increase. By using pulsed incoherent light sources, or better still lasers, multi-photon processes can be induced without special precautions to ensure long life times of the metastable states. In this case densely populated triplet levels are obtained not by lowering the probability of transitions from the triplet level, but by a high rate of generation of triplets under the influence of intense light. We shall now examine in detail some multi-photon processes induced by laser radiation.

Multi-photon excitation. Multi-photon (mostly, two-photon) excitation of aromatic molecules by a giant laser pulse has been observed by many workers [23,49–52]. In most cases, the excitation was detected by fluorescence or absorption, which depend (for two-photon processes) on the square of the intensity of the exciting light. A fluorescence yield proportional to the square of the intensity of a ruby laser has been reported [53] for benzoquinone, naphthaquinone, anthraquinone, N-ethylacridone, and many other aromatic molecules. All these molecules do not absorb (by the normal one-photon mechanism) light of wavelength 6490 Å, but they can be excited by u.v. light of wavelength close to one-half that of the radiation from the ruby laser. If a two-photon transition takes place, the experimental compound contains excitation levels of energy double that of the quantum. Hence, we may think of two-photon and multi-photon spectroscopy as a method of determining electronic excitation levels [54]. Resonance conditions are fairly easy to satisfy, because the electronic absorption bands of organic molecules usually contain vibrational fine structure and therefore are relatively broad. Hence, two-photon transitions will give rise to a vibrationally excited singlet state, as for example in the excitation of anthracene by light from a ruby laser [23]. An important feature of two-photon transitions is the fact that they obey quantum-mechanical selection rules different from those of ordinary one-photon transitions. Transitions involving a change in the parity of the initial and the final states are allowed in the one-photon excitation of molecules with a centre of symmetry, whereas in two-photon excitation transitions without parity changes are allowed [55,56]. Thus, states which are not accessible to ordinary optical excitation can be excited by using two-photon transitions. These transitions have been observed, for example, in coronene, 1,2-benzanthracene, and other aromatic hydrocarbons [32].

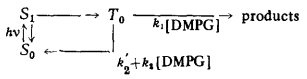
Since two-photon transitions have been observed with ordinary incoherent light sources as well as with lasers, the role of the coherence and monochromaticity of laser light has been questioned. Weiss and coworkers [57] compared the two-photon excitation cross-sections of naphthalene and anthracene with a laser and a xenon flash tube respectively. They found very similar values. A theoretical analysis [58] also led to the conclusion that the effect of coherence is negligible.

The degree of polarisation of the exciting light may have a stronger influence on the cross-section for two-photon absorption [59]. It has been shown [60] that the transition probabilities in anthracene and in 9,10-dichloroanthracene are several times greater in linearly polarised than in circularly polarised exciting light. The vibrational sub-level of the final excited state also depends on the polarisation of the light.

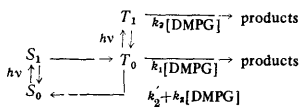
Multi-photon ionisation. Multi-photon ionisation in gases under the influence of laser radiation has been studied in detail [60–63]. Much less is known about multi-photon ionisation (photoconductivity) in the liquid phase. It has been shown [64] that light pulses from a nitrogen laser can generate photoconductivity, by a two-step mechanism, in solutions of N,N,N',N'-tetramethyl-p-phenylenediamine in non-polar solvents. The intermediate products may consist of triplet and singlet excited states, and possibly also charge-transfer complexes (CTC). Another paper [65] deals with the role of the solvent in the photoionisation of the same compound. The reaction $Fe^{2+} \rightarrow Fe^{3+}$ also appears to involve a metastable intermediate produced by a two-photon mechanism [66].

Chemical reactions induced by multi-photon excitation. The excitation which precedes

two-photon chemical reactions can occur either with formation of metastable (triplet) states or by the simultaneous absorption of two photons. It is suggested[56] that the latter process includes the formation of an intermediate virtual state. The mechanism of two-photon chemical reactions of the first type is similar to that of ordinary two-photon photochemical processes[48]. The photolysis of Methylene Blue by giant pulses from a ruby laser, studied by Tanaka and coworkers[67], is a good example of reactions of this type. The photo-reduction of Methylene Blue by ordinary light involves interaction between the reducing agent and the lowest triplet state of the dye. α-Dimethylphenylglycine (DMPG) was the reducing agent used. At low intensities of laser radiation the reaction follows the scheme



where the ratio $\frac{k_1 + k_2}{k_2'}$ is identical to the values found in ordinary photolysis. However, an increase in light intensity is accompanied by an apparent increase in the value of k_1. This increase was ascribed to the onset of triplet–triplet absorption in Methylene Blue, producing an excited triplet which takes part in the reaction and increases the rate of photo-reduction:

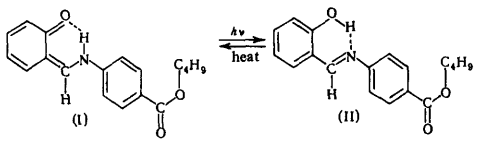


The above scheme is identical to two-photon excitation in ordinary photolysis‡. In the present case two-photon excitation arises because of the high rate of population of S_1 under conditions leading to sufficiently fast $T_0 \leftarrow S_1$ intersystem crossing, and also because the levels T_0–T_1 and S_0–S_1 are equidistant. The fact that in laser photolysis the metastable level can be excited only by a photon of energy equal to that used to excite the ground level limits the number of systems capable of undergoing chemical change under the influence of laser radiation. In this sense, the initiation of two-photon processes with two ordinary light sources of different wavelengths is a more flexible procedure. In principle, chemical reactions can be induced by using two laser lines of different wavelength (for example, with a gas laser, which radiates at different frequencies), or with a laser synchronised to a flash tube[70]. However, no system has yet been investigated by these methods.

Very high populations of triplet levels have been observed in studies of the *cis–trans*-isomerisation of substituted indigo dyes initiated by laser light[71]. A sharp decrease in transmission occurs at a radiation intensity of 10^{26} photons cm^{-2} s^{-1}: it is ascribed to the high population of a level with a higher absorption at 6940 Å than the ground level. The authors estimate that 62% of the molecules of *N,N*-dimethylindigo pass into the triplet state, whereas only 6% are present in the form of excited singlets.

‡ It should be noted that the mechanism of excitation of Methylene Blue by giant pulses from a ruby laser is much more complicated. In aqueous solutions, the dye exists in a partly associated form, as dimers[68]. Laser radiation gives rise[69] to a triplet of the monomer and a triplet of the dimer, which forms an additional excited state (probably a charge-transfer complex).

Prokhorov and coworkers[53] studied a number of multiphoton chemical reactions induced by laser radiation. Some azomethine dyes can undergo tunnelling hydrogen transfer under the influence of u.v. light:



accompanied by a change in the electronic configuration of the molecule and detected by a shift in the maximum of the fluorescence band. Fluorescence characteristic of compound (II) was observed by irradiating (I) with light from a ruby laser operated in the *Q*-switched mode. Since $I_{\text{fluor.}} \sim I^2_{\text{exc.}}$, the hydrogen transfer process must involve two-photon excitation. Free radicals produced by giant pulses from a ruby laser in triphenylmethane, α-nitronaphthalene, and other aromatic compounds frozen at 77°K have been detected by ESR. The triphenylmethyl radical $(C_6H_5)_3C^{\cdot}$, formed when $(C_6H_5)_3CH$ is irradiated with ordinary light with a quantum energy of 5.5 eV, was detected during irradiation of $(C_6H_5)_3CH$ with ruby laser light. It is evident that a three-photon mechanism must be involved, since $I_{\text{fluor.}} \sim I^3_{\text{exc.}}$, and the energy of three quanta of ruby radiation is close to 5.5 eV.

Porter and Steinfeld[72] studied the photolysis of phthalocyanine vapour at 420–430°C, a temperature at which the compound is stable. A pulse from a ruby laser with an energy of 40 J (equivalent to a power of 50 kW) did not cause decomposition, whereas a giant pulse of energy ~2 J but corresponding to a power of 100 MW produced decomposition of approximately 50% of the material in the path of the beam. The steep variation of reaction yield with intensity is evidence for a multi-photon mechanism. A reaction product with an absorption maximum in the u.v. region, characteristic of indole derivatives, was observed. The existence of a metastable or resonance level, excited by laser light, seemed probable in all the reactions considered.

Two-photon reactions have been observed also in systems where the electronic excitation of the reactants involved the simultaneous absorption of two quanta. Porter[73] exploited the two-photon initiation of the hydrogen–chlorine reaction in a lecture demonstration. When a mixture of $Cl_2 + H_2$ was illuminated with light from a ruby laser in the free generation regime (30 J) no reaction was observed, since both hydrogen and chlorine are transparent to red light, but an explosive reaction was induced by introducing a solution of cryptocyanine dye in the laser cell (even though the energy of the laser pulse had been decreased by a factor of 10). The explosion was initiated by the two-photon dissociation of chlorine, since the energy of two quanta of ruby laser light (3.57 eV) falls within the range of electronic absorption of chlorine (3.0–5.2 eV). The reaction $Cl_2 + CH_4$ involves a similar mechanism[74]. All possible chloro-substituted methanes are found among the reaction products, which points to a radical mechanism. Rousseau and coworkers[75] observed two-photon excitation and decomposition of AgCl under the influence of ruby laser light. AgCl is transparent to light of λ = 693 nm, but it absorbs at 347 nm. The reaction produces colloidal silver, identified by its absorption spectrum; it is accompanied by luminescence ($\tau = 10^{-4}$ s), with $I_{\text{lum.}} \sim I^2_{\text{exc.}}$ Light from a He–Ne laser (633 nm) of much lower intensity produced no reaction at the same (fully absorbed) energy.

2. Effects Associated With Vibrational Excitation

Lasers are powerful sources of radiation in the near and medium i.r. region. The absorption of radiation of frequency 10^2-10^4 cm^{-1} produces vibrational excitation in molecules. If the irradiated material is a sufficiently strong absorber at the frequency generated by the laser, it will display high, non-equilibrium occupancies of its vibrational levels. Deactivation of these excited states can occur either radiatively (by i.r. fluorescence), or by a non-radiative mechanism involving various relaxation processes. As long as the radiated power of the laser is not too high, very high vibrational temperatures can be reached without raising the translational temperature, i.e. without heating the material. With the most powerful lasers, infrared heating of the material can occur. The difference between this process and normal heating is that the whole of the absorbed energy is transferred to vibrations in the first instance, before being redistributed among other degrees of freedom. Ultimately, excitation of all the vibrational, rotational, and translational degrees of freedom can be expected, with the possibility of decomposition of the molecule. If the system can equilibrate between all degrees of freedom before decomposition sets in, the laser-induced reaction will not differ in any way from normal thermal decomposition at moderately high temperatures. However, if the chemical reaction begins before all the relaxation processes have gone to completion it may exhibit entirely different kinetic parameters (rate constants, activation energies). This is particularly true when absorption of a quantum raises the molecule to an excited vibrational level close to the dissociation threshold, and there is a finite probability of further thermal activation leading to dissociation (see, for example, Ref. 25). An alternative path to non-equilibrium chemical reactions involves multi-photon vibrational excitation. Examples of both types of process are discussed below.

Vibrational excitation by laser radiation. Measurement of the time dependence of the i.r. fluorescence from molecules which have been excited by laser radiation is a powerful new method of studying energy transfer processes in gases. Upwards of 20 compounds have been examined by this method, including methane, ethane, ethylene, and CO_2. The main results are discussed in recent reviews [76,77]. Recent developments in laser technology, by making available picosecond pulses, have enabled intramolecular vibrational relaxation to be studied [78] in complex molecules over times of the order of 7.5×10^{-12} s, i.e. over a few tens of vibrations.

Decomposition under the influence of laser radiation. As we have already pointed out, vibrational excitation can lead to decomposition of the irradiated compound at sufficiently high radiated powers. This type of decomposition has been observed by irradiating various hydrocarbons with light from a CO_2 laser [79,80]. Further work [81] showed that the decomposition of ethylene, propene, allene, and divinyl becomes appreciable only at pressures above a definite threshold. Thus, the decomposition of ethylene begins at pressures above 120 mmHg, and at pressures above 220 mmHg it is accompanied by strong self-heating, formation of carbon and resins, and visible luminescence. This steep pressure dependence arises from the pressure-induced broadening of the absorption bands. The greater the broadening, the more fully is the laser radiation absorbed by the compound. The distribution of reaction products is almost the same as in the thermal reactions of the hydrocarbons.

Decomposition of CO_2 is responsible for the relatively low power available from the sealed gas laser (in which circulation of the gas mixture is not provided) [82,83]. It has been shown [82] that the extent of conversion of CO_2 is large because the equilibrium $CO_2 \rightleftharpoons CO + \frac{1}{2}O_2$ in the system is displaced towards the right by adsorption or chemical reaction of the products (O_2 or O) with the electrodes or the walls of the discharge tube.

Multi-photon vibrational excitation and dissociation. With powerful modern lasers,

$$(2-3)\hbar\omega \approx D \text{ and } \omega \approx 10\omega_e$$

where $\hbar\omega$ is the quantum energy, and D and ω_e are "typical" values of the dissociation energy and natural vibration frequency of a chemical bond. It follows that direct photodissociation (without a predissociation step) can occur by a multi-photon mechanism with resonance transitions through several vibrational levels. The theory of "oscillating" molecular vibrations and photodissociation in a powerful field of laser radiation has been discussed by Askar'yan [84,85] and by Bunkin and coworkers [86].

There are two possible regimes of vibrational excitation and dissociation of molecules under the influence of laser light. The first occurs when the force acting on a molecule in an intense light field is linearly related to the field and has a frequency equal to that of the light field. This state of affairs is usually found with polar molecules. The molecules are set oscillating in the field when their mean dipole moment interacts with the electric component of the radiation field. The probability of two- and three-photon purely vibrational transitions (i.e. not involving a change in the electronic state) has been evaluated [86] for diatomic molecules in the anharmonic oscillator approximation. Molecular vibrations can interact with the field only as a result of their anharmonicity, which ensures that transitions with $|\Delta n| > 1$ are allowed. The probability of the process depends essentially on whether the discrete vibrational spectrum includes resonant transitions defined by the condition

$$(\omega - \omega_{n,0})^2 \ll \left(\frac{\mu\varepsilon}{\hbar}\right)^2$$

where $\omega_{n,0} = \frac{1}{\hbar}(E_n - E_0)$; ϵ is the electric field strength of the electromagnetic wave; μ is the dipole moment. It is evident from this formula that the resonance conditions is most easily satisfied by highly polar molecules in a field of high intensity. With a field of 3×10^7 V cm^{-1}, resonant transitions are more probable than non-resonant transition by a factor of 10^3. The difference is even greater at higher fields. Three-photon transitions without resonance are improbable at 10^7 V cm^{-1}, but at $\epsilon = 3 \times 10^8$ V cm^{-1} their probability is quite large.

The second excitation regime describes the situation when the force for excitation has a frequency different from that of the light wave. A force of this type may arise from atom polarisability, i.e. from the excitation of homopolar as well as heteropolar molecules. This force is proportional to the square of the field, and therefore it can only give rise to new spectral absorption lines in very strong light fields [84,85].

Evidence of initiation of a chemical reaction by the above mechanism is given in two papers only. Eisenthal and coworkers [87] studied the effect of ruby laser pulses (0.1–5 MW cm^{-2}) on biphenyl. The power density of

these pulses corresponded to a peak field strength of $10^{-4}-10^{5}$ V cm^{-1}. The observed fast luminescence spectrum was different from the fluorescence and the phosphorescence spectrum of the compound, and its intensity was proportional to the cube of the light intensity. Hence it was concluded that three-photon vibrational excitation and dissociation into two phenyl radicals can take place in laser light. The luminescence is produced by dissociation products with an excess of energy of ~30 kcal mole^{-1}. A similar mechanism is probably involved also in the photodissociation of dibenzofuran, dibenzthiophen, and also dibenzyl, for which a two-photon mechanism has been proposed.

Prokhorov and coworkers[53] observed the decomposition of α-nitronaphthalene irradiated with light from a dysprosium laser ($h\nu$ = 0.5 eV). This reaction probably involves stepwise excitation to vibrational sublevels of the electronic ground state, followed by dissociation of the bond (~1.1 eV bond strength).

IV. HIGH-TEMPERATURE REACTIONS

When solids are irradiated with laser pulses, instantaneous heating and evaporation occur, accompanied by plasma formation at the highest powers. Hence, lasers have been used for the mass-spectrometric[88] and emission-spectrometric[89] analysis of solids, and also in pyrolytic gas chromatography[90].

Hydrocarbons have been synthesised[74] from carbon (heated by a giant laser pulse) and hydrogen: the products included acetylene (90%), methane, ethylene, allene, methylacetylene, and diacetylene. Subsequent work[91,92] showed that the formation of acetylene (which can be observed also with normal laser pulses) is the result of interaction between C_2 and hydrogen or hydrocarbons in the gas phase. Some other reactions can also be ascribed to the diatomic C_2 radical[93]. Laser heating of silicon and germanium in a hydrogen atmosphere, and of carbon in an atmosphere of chlorine, has yielded SiH_4, GeH_4, and CCl_4 respectively[74]. A method for producing diamond from graphite in a laser beam has been patented[94].

The gas phase formed when solids are impulsively heated with laser radiation often differs in composition from the vapour evolved on slow heating. This type of phenomenon has been observed[95] with the oxides, sulphides, selenides, and tellurides of arsenic, antimony, and bismuth. The gas phase obtained by laser vaporisation is characterised by particles of the type Bi_3X: a probable explanation is that critical conditions are approached in the region subjected to instantaneous heating.

As already pointed out, dielectric breakdown can occur in transparent liquids and gases exposed to strong optical fields. Multi-photon processes play an important role in dielectric breakdown[60]. However, once a plasma has been formed, the medium becomes opaque to the laser radiation, and thereafter it can be heated to very high temperatures by the laser beam. Breakdown can initiate the fixation of atmospheric nitrogen[74] and the formation of acetylene from methane[96], but attempts to prepare ammonia by this method from a stoichiometric mixture of nitrogen and hydrogen have been unsuccessful[74]. Breakdown due to pulses from a ruby laser was shown[97] to produce C_2, C, C^+, C^{2+}, Cl, and O^+ in organic vapours (CCl_4, $CHCl_3$, CH_3COCH_3, CH_3OH, and n-C_6H_{14}). The vibrational state of C_2 was different in CCl_4 and $CHCl_3$ vapours. Chloroform and carbon tetrachloride gave C_2Cl_4, C_2Cl_6, C_6Cl_6, and octachloronaphthalene. Methanol gave only high-molecular products.

V. CHEMICAL EFFECTS OF LASER LIGHT IN VARIOUS SYSTEMS

We have considered the various types of excitation produced by laser radiation, and the corresponding mechanisms by which chemical reactions can be induced by laser light. Often the mechanism of a particular reaction is not known, and in some cases the observed changes can be ascribed to more than one factor. Systems of this type are best described without attempting to associate them with any particular mechanism.

1. Decomposition of Organic Compounds

Wiley and Weeravagu[98] studied the chemical effects of focussed light from a ruby laser operated in the free generation regime (pulse energy 3.5 J) on various solid or frozen aromatic compounds. According to the distribution of reaction products, all the compounds examined can be classified into three types (see Table 3). The first is characterised by the formation of acetylene in much larger amounts than methane. Compounds of the second group give comparable yields of methane and acetylene.

Table 3. Decomposition products of organic compounds[98].

Compound	Products, vol.%				
	CH_4	C_2H_2	C_2H_4	C_2H_6	$C_3H_6+C_4H_8$
Biphenyl	7	84	6	Tr*	3
Naphthalene	4	87	4	Tr	5
Anthracene	4	85	3	Tr	8
Phenanthrene	2	91	1	Tr	6
Benzoic acid	3	85	1	Tr	11
Benzil	15	65	19	1	—
Anthraquinone	3	86	2	Tr	9
Methyl Yellow	28	57	8	7	Tr
Toluene	38	51	10	1	—
p-Xylene	42	48	9	1	—
Mesitylene	46	40	13	1	—
Methylene Blue	44	43	8	3	2
Benzene	56	16	21	1.5	—
N,N-Dimethylaniline	77	2	12	5	—
N,N-Diethylaniline	51	9	26	7	—

*Traces.

Lastly, irradiation of some compounds (benzene, *N,N*-dimethylalanine, and *N,N*-diethylalanine) yields much larger amounts of methane than of acetylene. In addition to CH_4 and C_2H_2, appreciable amounts of ethylene, vinylacetylene, and diacetylene are produced in many cases.

The unexpected distribution of reaction products, summarised in Table 3, allows us to exclude a purely thermal decomposition mechanism at the focus of the laser beam. On the other hand, the high yields of methane from compounds such as benzene and benzil, which do not contain methyl or methylene groups, and also the CH_4/C_2H_2 ratios for pairs of compounds such as benzene–biphenyl and benzene–benzoic acid, make it very difficult to interpret the results. As Table 3 shows, chemically and structurally very different compounds fall in the same group.

The authors suggest that the reactions of hot atoms or radicals (CH, CH_2 or CH_3) formed "under specific focussing conditions of the laser beam" may be responsible for the formation of large amounts of methane and acetylene. Although reactions of atomic carbon sometimes give the same products[99] as the decomposition of aromatic compounds under the influence of laser light, the formation of particles like C or CH requires such large energy expenditure as to be inadmissible, except by a multi-photon mechanism, whose probability is low, however, at the relatively low intensities of a laser beam in the free generation regime. Whereas the above results suggest some measure of specificity in the effect of ruby laser light on solid aromatic compounds—in particular on frozen benzene—other results by Bragin and coworkers[100,101] show that laser radiation can initiate non-specific pyrolysis reactions in liquid benzene (and other aromatic compounds), with hydrogen and carbon as the only products. Liquid benzene was irradiated with unmodulated pulses of laser radiation, of energy in the range 1–8 J (i.e. of the same order of magnitude as the luminous fluxes used by Wiley and Weeravagu[98]). The wavelength of the laser light did not appear to play any part, but a sharp energy threshold of the laser pulses was identified below which no decomposition occurred. Above the energy threshold the formation of solid reaction products was accompanied by generation of shock waves. The threshold energy depended on whether a finely divided suspension was present in the liquid benzene, but not on its chemical nature. These observations, together with the anomalously high quantum yield (0.33), forced the authors to the conclusion[101] that the reaction is initiated by the temperature rise of the microscopic solid particles always present in a liquid, and proceeds by a chain mechanism. However, this mechanism fails to explain why the reaction follows an entirely different course in solid benzene irradiated with laser light, with a specific rather than thermal mechanism (as shown by the nature of the products). On the other hand, if laser radiation can initiate the pyrolysis of benzene, it is not clear why acetylene was not detected among the products although it is the commonest product of high-temperature decompositions of hydrocarbons. Studies of the laser photolysis of benzene[38,102] (λ = 3471 and 2645 Å) have revealed an intermediate with an absorption maximum close to 5000 Å and a life time of 2×10^{-8} s. This absorption was originally ascribed to the $^1E_{1u} \leftarrow {}^1B_{2u}$ singlet–singlet transition, but a more careful comparison with pulse radiolysis data[103] led to the conclusion that the particle responsible for this absorption is an excimer of benzene, formed by a two-photon mechanism. The excimer is formed from highly excited states of benzene with an energy of ~7 eV. At the same time, stable products are formed, and they accumulate in solution after prolonged irradiation (trienes, and fulvene derivatives). It is probable that laser radiation causes opening of the aromatic ring, which may explain the formation of CH_4 in Wiley's experiments[98]. The benzene biradical may be an intermediate in this reaction[103].

The data reviewed by Wolfgang[99], and also some recent experimental results[104,105] on the effect of laser radiation on a number of gaseous unsaturated hydrocarbons, suggest that hydrogen transfer reactions may be involved. We have detected[104] ethylene and ethane in acetylene irradiated with light from a Nd^{3+} laser (10^{-3} s, 1–10 J). As Table 4 shows, C_2 hydrocarbons are predominant among the products of this reaction.

We were unable to detect any higher hydrocarbons, in particular benzene—a familiar product of the photolysis of acetylene. Significant amounts of hydrogen, carbon black, and pyrolytic carbon were also absent. It is evident, from the composition of the products, that the radiation from a neodymium laser has a specific effect on acetylene, quite unrelated either to pyrolysis or to ordinary photolysis. The vibrational spectrum of acetylene includes a strong $3\nu_3$ overtone whose frequency (9640 cm^{-1}) is close to that of neodymium laser light (9400 cm^{-1}).[106] If this fortuitous agreement between the frequency of the laser radiation and the natural vibration frequency of the irradiated compound is responsible for the chemical reaction, we may expect both the absorption and the reaction to disappear if an isotopic frequency shift is introduced by replacing C_2H_2 by C_2D_2. However, we find that C_2D_2 also undergoes chemical reaction when irradiated with neodymium laser light, but in this case the product consists mainly of ethane. Irradiation of an equimolar mixture of C_2H_2 and C_2D_2 leads to isotope exchange with formation of C_2HD. The products obtained by irradiating ethylene with neodymium laser light included methane, acetylene, and divinyl in the ratio 3 : 1 : 1. The high relative yield of methane is remarkable, since neither pyrolysis nor ordinary photolysis of ethylene gives significant amounts of methane. Wiley and Reich[105] also obtained unexpectedly high yields of methane in their work on the irradiation of acetylene with light from a ruby laser in the free generation regime (Table 5).

Table 4. Products obtained from acetylene by the action of radiation from a neodymium laser in the free generation regime[104].

Starting material	Gaseous products, vol.%				
	ethane	ethylene	divinyl	vinylacetylene	diacetylene
C_2H_2	—	71.7	0.5	13.7	13.2
C_2D_2	71	2.0	5.5	21.3	—

Table 5. Products obtained from gaseous hydrocarbons by the action of radiation from a ruby laser in the free generation regime[105].

Hydrocarbon	Products				
	CH_4	C_2H_2	C_2H_4	C_2H_6	Higher
Cyclopropane	26.5	none	11.5	62	none
Ethylene	4.3	none	—	95.7	none
Acetylene	59.3	none	40.7	—	none
Ethane	32.1	—	not measured	67.9	none
Butane	25.4	1.2	26.9	43.4	3.6*

*Propene.

The material balance of these reactions suggests that in some cases (C_2H_4) large amounts of hydrogen must have been formed, in others (C_3H_6, C_2H_2) carbon must have been formed, or polymers with a low hydrogen content.

2. Polymerisation

Pulses of laser light can initiate polymerisation reactions. In the earliest experiments[107] polymerisation was

obtained in the presence of a dye sensitiser. When acrylamide was irradiated with argon laser light (4880 Å) in the presence of a sensitiser (4,5-dibromofluorescein + N,N,N',N'-tetramethylethylenediamine) the polymerisation yield was 10^3 per absorbed photon[108]. The polymerisation of vinyl acetate, initiated by giant laser pulses (λ = 3472 Å) in the presence of 2-azo-bis-isobutyronitrile, is described in the Patent literature[109]. Polymerisation without sensitisers was first reported by Pao and Rentzepis[110], who irradiated styrene frozen at 77°K with light from a ruby laser (0.3 MW). A two-photon mechanism was suggested. The yield of polymer was 0.01% per pulse. The i.r. spectrum of the polymer was indistinguishable from that of polystyrene, and its molecular weight was 3.6×10^6. Because styrene does not absorb strongly at 3470 Å, it can only be polymerised in a rigid matrix (not in the liquid phase). Other monomers which are better absorbers at this frequency (e.g. p-isopropylstyrene) were successfully polymerised at room temperature. Polymerisation of the chloro-derivatives of styrene was easier still.

The possibility of polymerising styrene with giant ruby laser pulses was later confirmed by Apletalin and coworkers[111]. However, these workers described the process not in terms of two-photon excitation of the lower electronic levels, but in terms of multi-photon dissociation (probably by Bunkin's mechanism[86]) and ionisation, giving rise to a breakdown phenomenon accompanied by visible luminescence with a continuous spectrum.

3. Disintegration and Degradation of High-molecular Compounds

In opaque polymers, the energy of laser pulses is absorbed in a very small volume, and therefore the material is locally heated to very high temperatures (see Section IV). The mechanical degradation processes observed when powerful laser pulses are focussed within transparent polymers are very much harder to interpret[60]. Mechanical disintegration is evidently associated with chemical degradation of the polymer, which may result in the appearance of paramagnetic centres in the polymer[112]. These changes are sometimes preceded by phase transformations (melting and recrystallisation of some of the structural elements of the polymer)[113]. A study[114] of the decomposition of poly(methyl methacrylate), PMMA, under the influence of ruby and neodymium laser pulses has shown that gases are formed by a two-photon or a three-photon process, depending on the photon energy. The composition of the gaseous decomposition products of PMMA included CO, CO_2, and CH_4, whereas normal thermal degradation of PMMA yields only the monomer (at low temperatures) or a complex mixture of secondary reaction products—mainly acetylene and ethylene—at higher temperatures[115]. Hence, we can dismiss the purely thermal mechanism of degradation of transparent polymers exposed to laser radiation.

Many investigations[116-120] have been devoted to the action of laser radiation on opaque polymers (phenolic resins, elastomers) and on coal. The gaseous degradation products were found to consist predominantly of acetylene and hydrogen. The composition of the reaction products was quite different from the composition of the products of low-temperature (500–900°) degradation of these materials, and also from the composition of the products obtained by the action of a xenon flash tube[119]. A study of the laser degradation of coal in a time-of-flight mass spectrometer has shown that the primary products are H atoms and methyl radicals. The strongest peak in the mass spectrum was due to acetylene[121].

(Added in proof)

Several relevant papers have appeared since this review was submitted for publication. The most interesting results relate to the possibility of selectively initiating chemical reactions by monochromatic laser light, using resonant excitation of selected intramolecular vibrations. It has been shown[122] that the dissociation of BCl_3 under the influence of CO_2 laser light occurs by a cascade mechanism (i.e. by an n-photon mechanism with $n \gg 1$), and high vibrationally excited states, close to the dissociation threshold, have been observed spectroscopically. Mixtures of BCl_3 and H_2 react explosively when irradiated. The initiation of chemical reactions by excitation of molecular vibrations has been demonstrated in a number of other systems[124-126], including N_2F_4 in mixtures with N_2, H_2, and CH_4, and also CH_3OH mixed with CD_3OD. This work has shown that in many cases the anharmonicity of vibrations is not an insuperable obstacle to selective bond breaking. Two-stage excitation is proposed[127] for systems in which the vibrational–translational relaxation processes can compete with resonant excitation processes at levels not high enough to reach the dissociation threshold. Using this method, the photodissociation of HCl and the photoionisation of rubidium vapour have been demonstrated[128].

Barashev and Tal'roze[129] have developed a criterion for distinguishing photochemical from purely thermal effects of laser radiation on matter. A group of papers[130-132] deals with a theoretical analysis of the initiation of chemical reactions by laser light. Several reviews of the properties and applications of various types of laser have appeared: dye lasers[133], lasers based on compounds of the rare-earth elements[134], and pulsed gas lasers[135]. Further work on the laser photolysis of benzene has been reported[136]. Lastly, the laser photolysis of acetophenone[137], thiocyclobutanes and thiocyclopentanes[138], the two-photon gas-phase decomposition of azoethane[139], and the photoionisation of water[140] have been described.

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