Lasers

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The advent of the laser light source has given rise to a minor revolution in the study of various optical phenomena and has allowed many experiments to be performed which would not otherwise have been possible. A brief inspection of the scientific literature should serve to convince the reader that there have been appreciably more papers published on lasers than there are words in this article, so that a comprehensive review of the subject would hardly be possible. However, since this article is concerned primarily with experiments which relate directly to chemistry, comparatively few of these papers are of immediate interest. The term LASER is an abbreviation for Light Amplification by Stimulated Emission of Radiation, light in this context frequently being taken to include sources from the ultraviolet to the far infrared, that is all but microwave devices.

The characteristics of lasers that distinguish them from other radiation sources are the extreme directionality, the very high output powers available, the polarisation, line width and the coherence, both longitudinal and lateral, of the output. Since the construction of the first laser, the pulsed ruby laser, by Maiman *et al.*[1] in 1960, so many laser transitions have been discovered that it would clearly not be possible to give more than a brief résumé of developments in this field in an article of this nature: to date several thousand laser transitions have been discovered and the development of the subject is, as yet, in its infancy. Although these lasers have been developed in such a wide variety of conditions, particularly with regard to the excitation methods involved, certain principles are fundamental to the laser process and to appreciate fully the value of these light sources it is essential to have some understanding of the basic theory involved.

1 Spontaneous and Stimulated Emission of Radiation

We consider an atomic (or molecular) system having energy states ϵ_i, ϵ_j, ϵ_k, . . . (for simplicity we assume each of these states to be singly degenerate), the number of atoms in each state at any time being N_i, N_j, N_k, . . . Under conditions of thermal equilibrium the number of atoms in any state i is proportional to the Boltzmann factor, $\exp(-\epsilon_i/\boldsymbol{k}T)$. For a system containing a total of N atoms, the fraction in any state is given by

$$\frac{N_i}{N} = \frac{\exp(-\epsilon_i/\boldsymbol{k}T)}{\Sigma_i \exp(-\epsilon_i/\boldsymbol{k}T)} \tag{1}$$

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[1] T. H. Maiman, R. H. Hoskins, I. J. D'Haenens, C. K. Asawa, and V. Evtuhov, *Phys. Rev.*, 1961, **123**, 1145 and 1151.

For any atomic system in thermal equilibrium this fraction is sensibly independent of time since changes occurring among these states are such as to maintain the distribution given by equation (1). Further, if we neglect considerations of degeneracy, there will always be fewer atoms in a higher energy state than in one of lower energy.

Considering the radiative transitions which may occur between two energy states i and j, with $\epsilon_i > \epsilon_j$, we have to take account of three processes, the frequency of these transitions being related to the energies of the states involved by the Bohr frequency condition

$$\epsilon_i - \epsilon_j = h\nu_{ij} \tag{2}$$

If we imagine the atomic system immersed in a radiation field of energy density $\rho(\nu_{ij})$ at the incident frequency ν_{ij}, then atoms originally in the state j (Figure 1) may be induced to absorb a quantum of radiation of this frequency and transfer to the excited state i. The fraction of the atoms originally in state j excited in this way is proportional to the intensity of radiation at that frequency and hence the number of transitions occurring in unit time is

$$B_{ij}\, N_j\, \rho(\nu_{ij}) \tag{3}$$

where B_{ij} is the Einstein transition probability of (induced) absorption. (The convention used here is that the first subscript refers to the final level, the second to the level from which the transition originates.)

Of those atoms originally present in excited state i, decay to the lower state j with emission of radiation quanta of frequency ν_{ij} may occur by two processes termed spontaneous and stimulated emission. One of these is analogous to the absorption process in that the rate at which the quanta are emitted is proportional to the number of atoms in the state i and to the intensity of radiation at the frequency ν_{ij}. This process is termed stimulated emission and the number of transitions occurring in unit time is given by

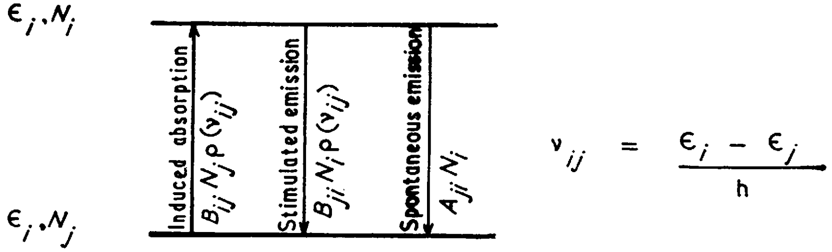

Figure 1 *The three types of process giving rise to radiative transitions between levels* i *and* j

$$B_{ji}\, N_i\, \rho(\nu_{ij}) \tag{4}$$

B_{ji} is the Einstein transition probability of stimulated emission. In addition, decay to the state j with emission of radiation quanta of frequency ν_{ij} can occur by a process which does not depend on the presence of radiation of frequency ν_{ij}. This process, termed spontaneous emission, depends only on the number of atoms in state *i* and occurs at a rate given by

$$A_{ji} N_i , \tag{5}$$

A_{ji} being the Einstein transition probability of spontaneous emission.

In any real system many levels other than those considered have to be taken into account. However, for a system in thermal equilibrium with the radiation field, the number of atoms arriving on a particular level must equal the number leaving that level. Since the numbers of atoms in states *i* and *j* are constant, the number of atoms leaving level *i* *via* the transition $j \leftarrow i$ must be equal to the number arriving at *i* *via* the transition $i \leftarrow j$. That is, we have the relation

$$A_{ji} N_i + B_{ji} N_i \rho(\nu_{ij}) = B_{ij} N_j \rho(\nu_{ij}) \tag{6}$$

From the Boltzmann expression

$$N_j = N_i \exp (h\nu_{ij}/kT) . \tag{7}$$

Thus from (6) and (7),

$$\rho(\nu_{ij}) = A_{ji} / [B_{ij} \exp (h\nu_{ij} / kT) - B_{ji}] \tag{8}$$

Since the system is in thermal equilibrium with the radiation field for all ν_{ij}, equation (8) must be identical with the expression for the Planck radiation law which, expressed in terms of the energy density of the radiation, is

$$\rho(\nu_{ij}) = \frac{8\pi h\nu^3}{c^3} . \frac{1}{[\exp (h\nu / kT) - 1]} \tag{9}$$

so that for singly degenerate levels

$$\left.\begin{aligned} B_{ij} &= B_{ji} , \text{ and} \\ \frac{A_{ji}}{B_{ji}} &= \frac{8\pi h \, \nu^3{}_{ij}}{c^3} \end{aligned}\right\} \tag{10}$$

It is the existence of the stimulated emission process which is of relevance to the operation of a laser, since the presence of radiation at a particular frequency can induce suitably excited atoms to radiate at that particular frequency. Under suitable conditions the original radiation can be amplified to many times its original value and give rise to an extremely intense beam of radiation, the laser radiation.

For a consideration of the practicalities of an operating laser it is necessary to consider in a little more detail the implications of equations (9) and (10). An atom excited to the state *i* can revert to the state *j* and radiate its energy at a frequency ν_{ij} by either the spontaneous or stimulated emission processes. The relative rates of these two processes are given by

$$\frac{A_{ji}}{B_{ji} \rho(\nu_{ij})} = [\exp (h\nu_{ij} / kT) - 1] \tag{11}$$

The rates of decay of i atoms by these two processes are equal when $\exp(h\nu_{ij} / kT) = 2$, so that for an atomic system at a temperature of 1000°K, the frequency ν_{ij} is found to be *ca.* $1{\cdot}44 \times 10^{13}$ sec.$^{-1}$, or a wavelength of approximately 21 μm. For a system emitting in the visible region of the electromagnetic spectrum at a wavelength of 5000 Å, the proportion of spontaneous to stimulated emissions is $10^{12{\cdot}5}$. It is apparent that for a system in thermal equilibrium with its surroundings the rate of removal of the excited state atoms by stimulated emission can compete with the spontaneous emission only for long wavelength radiation. For the ammonia maser, which operates between certain of the inversion-doublet components of the ground vibrational state, the emitted wavelength is *ca.* 1·25 cm. For a suitably large radiation density at these long wavelengths the proportion of spontaneous to stimulated emissions is negligible. It is possible to separate physically molecules in the excited states of the inversion-doublet components[2] and since, once separated, these molecules remain in the excited state, they can be induced to emit maser radiation *via* the stimulated emission process.

For systems excited to very high energy states, such as can give rise to transitions in the visible or near-infrared regions, most of the excited states are removed *via* spontaneous emission and, consequently, for a source in thermal equilibrium the stimulated emission process is generally of little consequence. In addition, even if high intensity radiation of the appropriate frequency ν_{ij} were introduced into the system, since $B_{ij} = B_{ji}$ and $N_j > N_i$ for a system in thermal equilibrium, equations (3) and (4) indicate that the radiation has a greater probability of being absorbed rather than giving rise to an amplification of the original beam. Thus, most of the radiation of frequency ν_{ij} would be emitted by the spontaneous emission process indicated in equation (5). It is thus apparent that in order for appreciable amplification of the original beam to occur it is necessary that there be a substantially greater number of atoms in the upper state i than in the lower state j. This phenomenon is termed inversion of population and its explanation in terms of the Boltzmann expression implies the existence of a negative temperature. This concept of a negative temperature, however, is extremely misleading since it implies the acceptance of a system in thermal equilibrium whereas under the conditions for which population inversion is obtained this is not the case.

Given that it is possible to establish an appreciable population inversion between two levels which can combine with emission of radiation, one of the conditions necessary for laser action is established. One of the other necessary conditions is that this population inversion be established in an environment which allows of an appreciable amplification of a primary wave. Such an amplification can be achieved by enclosing the active medium between a pair of parallel, highly reflecting, mirror surfaces. This optical cavity is, in effect, a normal parallel-plate Fabry-Perot interferometer, the separation of the plates being necessarily very much longer than the wavelength of the laser radiation. Since lasers are, in effect, light oscillators rather than light amplifiers, the primary

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[2] J. P. Gordon, H. J. Zeiger, and C. H. Townes, *Phys. Rev.*, 1954, **95**, 282.

wave arises as a result of a spontaneously emitted photon of the appropriate frequency propagated along the axis of the Fabry-Perot interferometer. Amplification of this wave can occur as it passes through the active medium and, if this amplification is sufficient to overcome the losses inherent in any optical cavity, this radiation will continue to grow in intensity by reflection at the end plates and subsequent passage through the active medium. In reality a standing wave pattern is maintained between the end mirrors and since, for such a standing wave to be maintained in an optical cavity, certain resonance conditions have to be accurately satisfied, the laser beam is very highly directional and extremely well collimated—a beam divergence of a fraction of a mrad. being quite commonplace. A 2 mm. diameter laser beam having a divergence of 1 mrad. would project a spot only 1 m. in diameter at a distance of 1 km. from the source. In addition, since the amplification occurs as a result of the stimulated emission process, the emitted photon must be in phase with the exciting radiation. For a plane wave set up in a cavity of this nature the phase of the radiation at any instant across a plane perpendicular to the direction of propagation of the beam is the same: that is, the plane wave produced by the laser beam is spatially coherent. With a rather different cavity configuration, perhaps employing spherical in place of plane mirrors, the radiation is also coherent but the surface of constant phase will not necessarily be a plane. This coherence property of the laser is not met with in conventional sources since these emit radiation by the spontaneous emission process in which the atoms emit independently of one another and hence the phase of this radiation fluctuates randomly. This coherence property of the laser is readily observed in the wide range of interference phenomena, such as the Young's slit experiment, which can be performed readily using these sources.

Having considered briefly some of the factors which are of relevance to the laser process it is now necessary to consider a little more fully some of the finer details involved in such processes.

A. The Three-level Laser.—Perhaps the simplest theoretical picture in which it is possible to discuss the conditions necessary for laser action is for the three-level laser. A relevant energy level scheme is shown in Figure 2.

In this system it is assumed that laser action occurs between states i and j and, for simplicity, we assume that level i is populated through absorption of radiation from the ground state k. After the steady-state condition has been reached the populations of states i, j, and k, are respectively N_i, N_j, and N_k. We assume further that only radiative transitions of the sort indicated in Figure 2 need be considered. Under steady-state conditions, and neglecting stimulated emission from state j as compared with the spontaneous emission from this state and the population N_i with respect to N_k, we have

$$0 = \frac{\mathrm{d}N_i}{\mathrm{d}t} = B_{ik}N_k\,\rho(\nu_{ik}) - A_{ki}N_i - A_{ji}N_i - B_{ji}N_i\,\rho(\nu_{ij}) \qquad (12)$$

$$0 = \frac{\mathrm{d}N_j}{\mathrm{d}t} = A_{ji}N_i + B_{ji}N_i\,\rho(\nu_{ij}) - A_{kj}N_j \qquad (13)$$

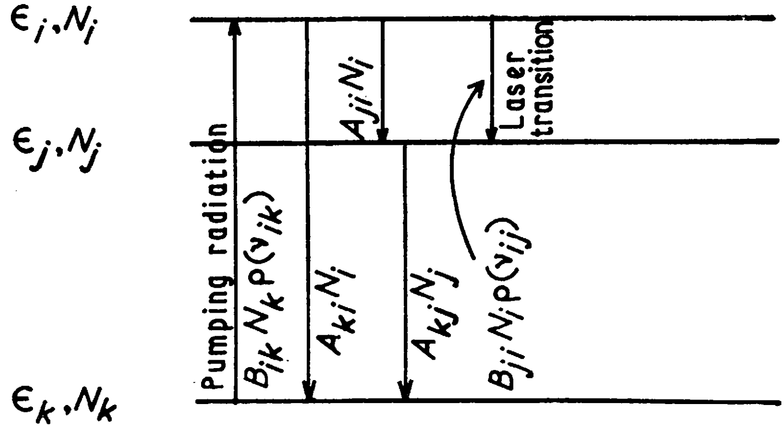

Figure 2 *The energy level diagram for a typical three-level laser system*

$$0 = \frac{dN_k}{dt} = A_{ki}N_i + A_{kj}N_j - B_{ik}N_k\,\rho(\nu_{ik}) \tag{14}$$

If, for the present, we neglect the stimulated emission process from state i and consider depletion of this state to occur purely by spontaneous emission, equations (12), (13), and (14) may be solved to yield for the ratios of the steady-state populations,

$$\frac{N_i}{N_k} = \frac{B_{ik}\,\rho(\nu_{ik})}{A_{ki} + A_{ji}} \tag{15}$$

$$\text{and } \frac{N_i}{N_j} = \frac{A_{kj}}{A_{ji}}\,. \tag{16}$$

In order that there shall be an excess of population in state i over state j, the levels involved in the laser transition, it is essential that the transition probability for spontaneous emission A_{kj} be greater than A_{ji}. In the event that the transition probability A_{kj} is sufficiently high there will be a population inversion between states i and j and, in principle, laser action will be possible at the frequency ν_{ij}. However, in order that oscillation shall build up to a substantial extent it is necessary that there be a large excess in population for state i over state j. Then, providing that $N_i \ll N_k$, the ratio of this excess population compared with those atoms remaining in state k is given by,

$$\frac{N_i - N_j}{N_k} = \frac{B_{ik}\,\rho(\nu_{ik})}{(A_{ki} + A_{ji})}\left[1 - \frac{A_{ji}}{A_{kj}}\right] \tag{17}$$

For this fraction to be high it is essential that A_{kj} be larger than A_{ji}, and that A_{ki} should be small relative to A_{ji}. However, since B_{ik} and A_{ki} are interrelated by equation (10), a low value of A_{ki}, and hence of B_{ik}, means that in order to produce an appreciable inversion of population between states i and j intense pumping radiation of frequency ν_{ik} is necessary. If sufficiently intense pumping of this kind is supplied so that lasing action in a suitable cavity can occur, then depletion of the level i by the stimulated emission to state j becomes appreciable and the simple treatment given above is no longer adequate. Under these conditions the true relative populations of states i, j, and k must be obtained by solutions of equations (12), (13), and (14), an analysis which, for a very similar three-level system and in a far more sophisticated fashion than suggested here, has been carried out by Bloembergen[3] and Maiman.[1]

Since, in principle, transition probabilities can be calculated from first principles by quantum mechanical methods from the eigenfunctions of the atomic states involved in the transition, it should be possible to calculate the pumping power necessary to achieve a certain population inversion among suitable states. In practice, however, such an approach is not possible since the computation is generally too involved and the simplicity of the system assumed here is not maintained in practice.

B. Other Energy Level Schemes.—In principle, the two-level system (Figure 3a) is appreciably simpler than the three-level system described above. However, the lower level in such a system is invariably the ground state of the energy level scheme; to produce the requisite population inversion in such a system over half of the atoms have to be excited into the upper state. This is an extremely difficult task since methods of pumping the atoms into the upper state are invariably efficient at depleting this state and no purely two-level lasers have as yet, been constructed. A disadvantage of the three-level system as described above arises from the fact that, for an efficient laser, as we shall see later, it is essential that the line width of the laser, and hence the widths of the energy levels involved, be extremely small. Consequently, it is not possible to achieve appreciable population of the upper level by optical pumping methods. This disadvantage is overcome in the three- and four-level systems indicated in Figures 3b and 3c.

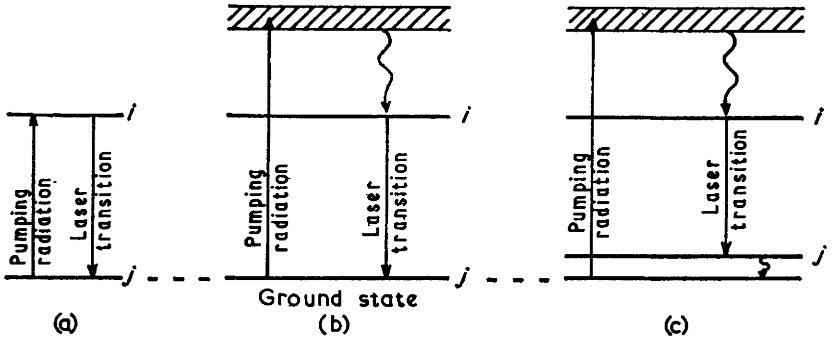

Figure 3 *Some typical energy level schemes for two-, three-, and four-level lasers. The laser transition occurs between levels* i *and* j

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[3] N. Bloembergen, *Phys. Rev.*, 1956, **104**, 324.

In Figures 3b and 3c broad-band pumping radiation matched, in so far as possible, to the broad absorption band of the sample serves to populate the metastable state i very efficiently. In the system of Figure 3b more than half the atoms have again to be raised into the state i, although this is an achievable condition if state i is a metastable state and the pumping radiation is sufficiently intense: this disadvantage is not met with in the system of Figure 3c since under conditions of thermal equilibrium the fraction of atoms in state j, given by the Boltzmann factor, is extremely small. For this system, however, it is necessary that the lifetime of the state j be appreciably less than that of state i. Systems b and c relate to the situation in the ruby and doped-glass lasers respectively, ruby being one of the few lasers which operates on a purely three-level laser system. These three- and four-level systems are of relevance also to many of the gas lasers, although in these cases the method of excitation is rarely by means of optical pumping but invariably by means of electron-impact methods which occur in d.c. and r.f. excited discharges in the gases.

C. Laser Action.—Prior to laser oscillation the atoms are excited by various means, such as optical pumping or electrical discharges in low-pressure gases, to the upper level involved in the laser transition. If the pumping power is sufficiently intense to overcome the losses due to spontaneous emission and various non-radiative processes then an inversion of population may be established between the two laser levels. If the system is contained in an optical cavity which allows of amplification of a primary wave, then laser oscillation will occur when the amplification of this wave during a single pass through the cavity is sufficient to overcome the losses due to imperfections in the optical components used in the cavity. From equation (12) it may be seen that for a particular population in level i, the rate of decay from this state increases with increasing radiation density $\rho(\nu_{ij})$, so that increasing the rate at which i atoms are supplied over and above that required for lasing action goes primarily to increasing the output power of the laser. The spontaneous radiation remains approximately constant and, with increasing pumping power, removal of atoms from the excited state i occurs primarily through the stimulated emission process.

The intensity of illumination (that is, the radiation density multiplied by the wave velocity) in an amplifying medium propagating with a gain coefficient g is attenuated by the factor exp (gx), if x is the length of the amplifying medium, *i.e.*

$$I = I_0 \exp(gx) \qquad (18)$$

The gain coefficient relates to the amplification which occurs at a specific frequency. The laser levels i and j, of course, are not infinitely narrow and the radiation emitted spontaneously for a transition between levels i and j has a finite spectral width, albeit very small. The width of the emission line from a gas at low temperature is due primarily to Doppler-broadening and the line contour may be expressed in terms of the gain by the relation

$$g = g_0 \exp[-K(\nu - \nu_0)^2] \qquad (19)$$

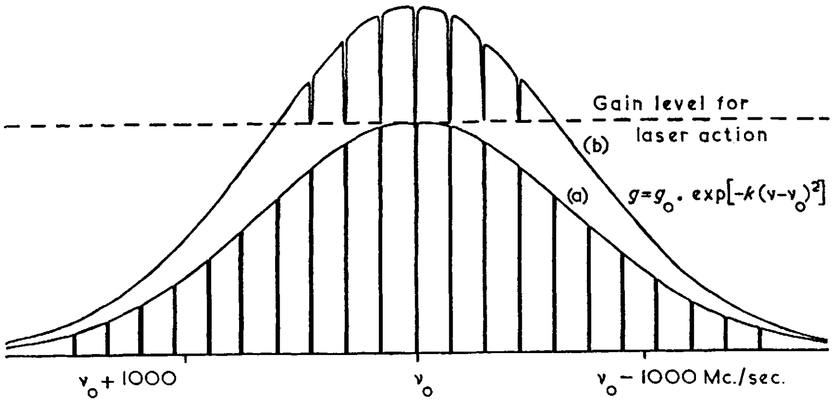

Figure 4 *Spontaneous emission line profile at threshold* (a) *and the positions of the various cavity resonances (solid lines). It is assumed in this diagram that one of the resonances of this axial mode lies at the peak of the spontaneous emission line, consecutive resonance positions being displaced from this one by* 150 Mc./sec. *The width of the spontaneous emission line is* 1600 Mc./sec. *In* (b) *the gain is increased considerably above laser threshold, the gain at positions corresponding to the various cavity resonances being reduced due to the stimulated emission process*

The shape of such an emission line is shown in Figure 4, the area under this spectral curve, of course, being the total radiation emitted in the transition from state i to state j. Then, since $\int_0^\infty g\,\mathrm{d}\nu = g_0\sqrt{\frac{\pi}{K}}$, and $\Delta\nu$, the line width at half-peak height is given by $\Delta\nu = 2\sqrt{\frac{\ln.2}{K}}$, we have that

$$\int_0^\infty g\,\mathrm{d}\nu = g_0 \cdot \tfrac{1}{2}\sqrt{\frac{\pi}{\ln.2}} \cdot \Delta\nu \qquad (20)$$

A very similar expression to this may be derived for other applicable line shapes and, in general, will differ from equation (20) by only a small constant. It can be readily shown* that

$$\int_0^\infty g\,\mathrm{d}\nu = \frac{\lambda_0^2}{8\pi} \cdot A_{ji}(N_i - N_j), \qquad (21)$$

and replacing the transition probability A_{ji} by the radiative lifetime τ ($A_{ji} = 1/\tau$), we have that

$$\int_0^\infty g\,\mathrm{d}\nu = \frac{\lambda_0^2}{8\pi} \cdot \left(\frac{N_i - N_j}{\tau}\right). \qquad (22)$$

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* See, C. C. Eaglesfield, 'Laser Light', Macmillan, London, 1967.

Then from equations (20) and (22),

$$g_0 = \frac{2\sqrt{\ln . 2}}{\sqrt{\pi}} \cdot \frac{\lambda_0^2}{8\pi} \cdot \left(\frac{N_i - N_j}{\tau \ \Delta\nu}\right) \tag{23}$$

$\Delta\nu$ being the width of the spectral line and λ_0 the wavelength at its centre. The importance of the line width, $\Delta\nu$, in lasing action is apparent from equation (23), since the population inversion required increases as the Doppler-width of the spontaneous emission increases.

If there are more atoms in the lower level of the laser transition, $(N_i - N_j)$ is negative and the primary wave will be absorbed in the medium. If, on the other hand, an inversion of population has been achieved, $(N_i - N_j)$ is positive and amplification can occur. All radiation losses in the system can be approximated by assuming that the optical cavity as a whole has a reflectance R, the fraction of the radiation lost by reflections at interfaces, transmission through the mirrors, absorption by windows, *etc.*, is then $(1 - R)$. For oscillation to occur the gain through amplification must exceed the losses, so that

$$\left.\begin{aligned} I/I_0 &\geqslant 1/R\,,\ \text{or} \\ R\exp(gx) &\geqslant 1 \end{aligned}\right\} \tag{24}$$

If the radiative lifetime, τ, of the transition is known as well as the spectral band width, $\Delta\nu$, it is possible to estimate the number of excited-state atoms which must be supplied in unit time to maintain oscillation, *i.e.* $\frac{N_i - N_j}{\tau}$. The minimum pumping power is then given by

$$P_{\text{min.}} = \left(\frac{N_i - N_j}{\tau}\right) . \, h\nu \tag{25}$$

Thus it is possible from these parameters to calculate the minimum pumping power necessary to produce laser action. However, it should be stressed that this is only a very approximate calculation since the methods of excitation do not specifically pump one particular level and many levels other than the ones considered here have to be taken into account. Further, radiative and non-radiative processes between these states tend to destroy the simple picture developed above. In addition, of course, for those lasers such as the ruby or doped-glass lasers which employ optical pumping methods, the geometry of the pumping system is of critical importance. Consequently, the estimate of the minimum pumping power necessary is very approximate and is usually very much less than that which is required for lasing action.

D. The Optical Cavity.—In order to obtain appreciable laser output the nature of the optical cavity which has to be employed is of critical importance. Generally the system employed consists of a normal Fabry-Perot interferometer with the amplifying medium contained between the plates. The system is different from the Fabry-Perot interferometer used for high-resolution spectroscopy, however, in that the plates are of small diameter and very widely spaced, typically 1 in.

diameter mirrors at a separation of roughly 1 m. Further, the design of the amplifying medium, the ruby rod perhaps or the discharge tube for a gas laser, restricts the aperture of the system so that only waves propagating along or close to the axis of the laser will have enough gain to lase.

In a parallel-plate Fabry-Perot laser cavity the steady oscillation built up between the mirrors can be compounded from two plane parallel waves propagating in opposite directions along the axis of the cavity: that is, a standing wave pattern is set up between the walls of the cavity, the condition for this being that there be an integral number of half-waves between the two mirrors. In the optical region the dimensions of the resonator are many orders of magnitude greater than the wavelengths of the radiation emitted but, nevertheless, for very high-order modes near the axis of the cavity one or more modes of oscillation at very specific frequencies are favoured.

The Fabry-Perot interferometer as normally used for high-resolution spectroscopy is, in reality, an optical filter which transmits radiation in directions such that a wave of a particular frequency passing through the filter directly is reinforced by another of the same phase which has been reflected twice through the cavity, and so on. This reinforcement of transmitted and reflected waves is obtained providing the condition

$$n\lambda/2 = D\,, \tag{26}$$

is satisfied for waves propagating along the axis of the cavity, or

$$n\lambda/2 = D\cos\theta \tag{27}$$

for waves inclined to this axis at an angle θ. These criteria must also be satisfied for the standing wave pattern set up inside the laser cavity so that the cavity acts as a resonator whose Q (Quality factor) is low for all except a few modes satisfying equation (27). A particular value of the wavelength can be satisfied for many values of n and θ, waves reflected back and forth in the cavity at a value of θ small, but different from zero, moving sideways across the cavity until they strike the walls of the tube. For these low-order modes also then appreciable amplification may occur since the Q of these modes may also remain high. Laser action may thus occur on modes which are inclined at a small angle to the axis of the tube, although as the angle θ increases the optical losses for a particular mode configuration tend to increase rapidly so that only small values of θ are generally observed. By suitable choice of the length of the cavity and by keeping the diameter of the amplifying medium down to a minimum, the losses in the transverse modes can be increased sufficiently so that laser action on the axial mode only is observed. For this longitudinal mode propagating along the axis of the cavity, $\theta = 0$, and the resonance condition is given by

$$n\,\lambda/2 = D$$

For this axial mode there are a number of values of n which satisfy the resonance condition, each different value of n implying a slightly different wavelength for the resonance. For a typical gas laser, for example the helium–neon laser at

6328·2 Å, with a distance between the mirrors of exactly 1 m., the mode number nearest this wavelength is obtained from equation (26) and is found to be 3,160,456. Because n is such a large number the frequency separation between adjacent modes differing in n value by unit is extremely small, being given by

$$\nu_{n+1} - \nu_n = c/2D, \text{ since } \nu = c/\lambda$$

For the typical cavity considered this axial mode separation is 150 Mc./sec. The natural line width is many times greater than this, typically 1600 Mc./sec. for the transition considered above, so that there will be many resonance frequencies within this line width (Figure 4). On increasing the pumping power to a laser which has a geometry such that axial modes only are allowed, the first resonance frequency to oscillate is the one nearest to the peak of the spontaneous emission line. If the laser power is increased considerably above this oscillation threshold several of these frequency modes are simultaneously excited. It is apparent then that for true single-mode operation the output power for this single mode is of necessity very low, typically *ca.* 100 μw in the visible region. While the oscillation line width of such a single-mode laser is incredibly low, values of $\Delta\nu/\nu$ as low as 10^{-13}—10^{-14} having been measured, the long-term frequency stability is not so pronounced, being limited by the nature of the discharge and thermal and mechanical variations of the interferometer spacing. The overall performance in regard to the line width, frequency stability, and output power, however, is many orders of magnitude greater than has been achieved with conventional sources.

For a less restrictive cavity there may be, in addition, a number of angular modes corresponding to different values of θ, and for a fixed value of θ a number of resonances corresponding to different values of n. In a multimode laser then there will be very many resonances within the profile of the spontaneous emission line and many of these will have enough gain to lase. Consequently, within the spectral profile of the laser beam there may be considerable sub-structure corresponding to the individual modes, the spectral width of any one mode being very much less than that of the overall laser contour.

Mode structure of this sort is observed in most gas lasers, although it is generally absent in solid-state lasers due to inhomogeneities in the laser medium.

E. The Ruby Laser.—Since the ruby laser was the first to operate successfully,[1] it is of considerable interest, particularly since the extremely high output powers which can be achieved with this laser have given rise to such a range of exciting new effects. Ruby consists of a crystal of aluminium oxide in which a small proportion, typically 0·05%, of the aluminium ions has been replaced by chromium (Cr^{3+}) ions. It is the spectroscopic behaviour of these chromium ions which is responsible for the red colour of ruby. The relevant energy level scheme is shown in Figure 5. Excitation of the ruby to the upper level involved in the laser transition occurs *via* the $^4F_1$ and $^4F_2$ levels. These levels are populated by absorption of radiation in the violet and green regions of the spectrum respectively and, since the absorption bands are intense and extremely broad, they

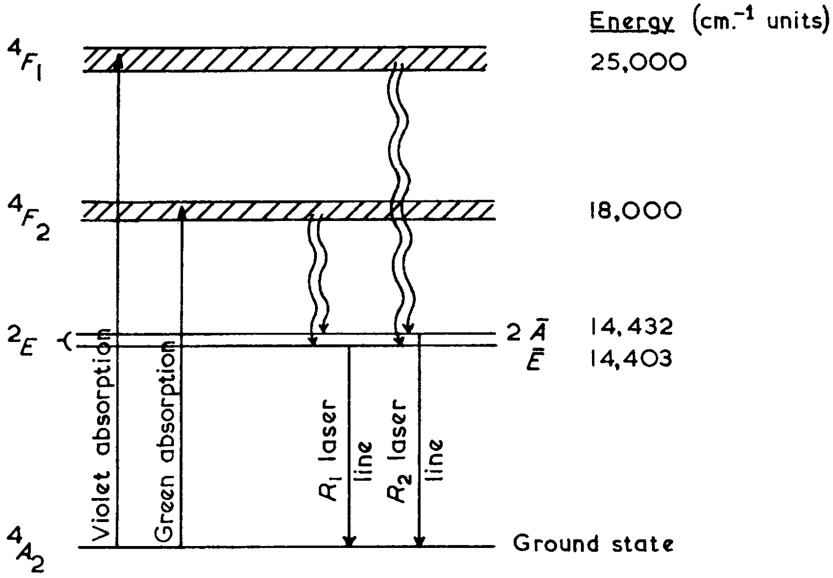

Figure 5 *Energy level diagram and transitions for the ruby* (0·05% Cr^{3+}) *laser*

can absorb large amounts of the optical pumping radiation. Consequently, large numbers of chromium ions can be excited *via* these states into the metastable ^2E state of ruby, from where they return to the ground state with emission of the characteristic fluorescence of ruby. When the exciting radiation becomes sufficiently intense this ^2E level, being metastable, may contain more chromium ions than exist in the ground state. Under these conditions radiation near 6943 Å, corresponding to the energy difference between the ^2E and $^4A_2$ ground state, instead of being absorbed by the crystal, may be amplified. This amplification is reflected in the decreased spectral width of the fluorescence radiation near 6943 Å with increasing pumping power to the $^4F_1$ and $^4F_2$ levels.

In the crystal the ^2E state is split into two levels, $2\bar{A}$ and $\bar{E}$, separated by 29 cm^{-1}. The normal ruby laser radiation occurs from the lower of these, $\bar{E}$, to the ground state: this transition, occurring at 6943 Å at room temperature is called the R_1 transition of ruby. Laser action on the R_2 transition, from the $2\bar{A}$ level to the ground state, may also be observed, although to achieve this it is necessary to introduce loss at the R_1 transition (usually by using reflectors which selectively reflect R_2 radiation), since the latter transition has a much lower threshold for laser action and tends to dominate the emission. The actual wavelength of the R_1 laser line is temperature-dependent, occurring at 6943·25 Å at 20° and varying by 0·065 Å per degree centigrade over the range -20—$+80°$.

In order to obtain sufficiently intense pumping for laser action the simplest method is to utilise extremely intense flash lamps, usually xenon-filled, with pulse durations of *ca.* 1 msec. in an arrangement such as that shown in Figure 6. By discharging a large number of condensers through the lamps they dissipate

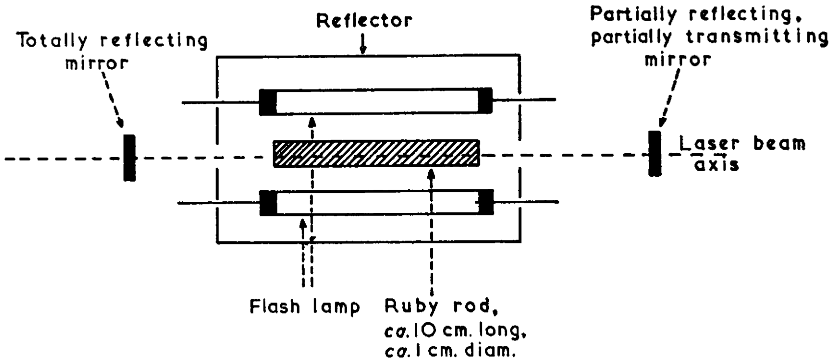

Figure 6 *Schematic diagram of the ruby laser*

several thousand joules in this time but since the output of the laser is generally less than 1 joule it is apparent that the overall efficiency of the system is very low. To increase the efficiency of the excitation system the flash lamps are surrounded by elaborate reflectors to reduce the amount of pumping radiation required for laser action. When the mirrors are accurately aligned with the axis of the ruby rod, laser action is usually observed as an intense burst of red radiation from the partially transmitting mirror, the pulse having a duration of *ca.* 0·5 msec. and commencing shortly after the start of the excitation flash.

For an output energy of *ca.* 1 joule from a laser pulse of duration *ca.* 1 msec. the output power is approximately 1 kw. When the output of such a laser is examined as a function of time it is found that within the temporal width of the pulse there is a large number of very sharp pulses, each of duration less than 10^{-6} sec. This suggests that the power in each of these individual pulses would be very much greater than suggested above. By a technique called 'Q-switching' most of the laser radiation can be produced in a pulse of duration *ca.* 10^{-8} sec.; 1 joule of energy in this short time is equivalent to a power of *ca.* 10^8w. This 'Q-switching' technique is most easily achieved by rotating the totally reflecting mirror about an axis at high speed. Then for all positions of this mirror but that at which it is aligned with the axis of the ruby rod, the Q of the cavity is very low. By synchronising the rotation of the mirror with the time at which the lamps are discharged it is possible to pump a large number of ions into the excited state before the mirror is in the cavity configuration in which laser action can occur. Power outputs in excess of 10^9 w have already been achieved and such 'giant-pulse' lasers are currently in use for applications similar to those described in later sections of this article.

F. Other Laser Systems.—Quite naturally it would not be possible in this article to consider in detail either the theory or practice or the operation of the many individual lasers which have been constructed to date. For those interested in obtaining further details on some of the more common lasers in use today, the spectral characteristics, operating conditions, and appropriate references to their theory and construction, are given in the Table.

Table *Some details regarding the more common lasers*

Laser	*Medium*	*Cavity configuration*	*Wavelength* μm.	*Output power*	*Refs.*
c.w. He–Ne	Gas, Ne:He = 1:5 (Total pressure = 0·6 torr.) D.C. or R.F. excitation	*ca.* 2-m. gas discharge tube, *ca.* 7 mm. diam. Brewster end windows. Dielectric coated mirrors	0·63282	*ca.* 100 mw	*a*
			1·152	*ca.* 100 mw	
			3·3913	*ca.* 20 mw	
c.w. argon–ion	Pure argon gas at total pressure 0·5 torr. D.C. or R.F. excitation	*ca.* 80 cm. gas discharge tube, *ca.* 2 mm. diam. Brewster end windows. Dielectric coated mirrors	0·45793	*ca.* 40 mw	*b*
			0·47649	*ca.* 100 mw	
			0·48799	*ca.* 500 mw	
			0·49651	*ca.* 100 mw	
			0·51453	*ca.* 500 mw	
c.w. carbon dioxide	Gas CO_2:N_2:He 1:1:8 (Total pressure *ca.* 10 torr.) D.C. or R.F. excitation	*ca.* 2 m. gas discharge tube, *ca.* 30 mm. diam. Gold-coated mirrors, output hole coupled	Many lines of the 001–020 and 001–100 transitions near 10 μm.	*ca.* 50 w total	*a* and *c*
Ruby	(Solid state) Al_2O_3+0·05% Cr^{3+}. Excitation by intense flash lamp pulse	Ruby rod, *ca.* 10 cm. × 1 cm., dielectric coated mirrors, *ca.* 30 cm. cavity	0·6943, but depends on operating temp.	*ca.* 10^3 w conventional, pulse duration *ca.* 1 msec.	*d*, *e*, and
				ca. 10^7 w Giant pulse, duration *ca* 10^{-8} sec.	*d*, *e*, and *f*

[a] W. R. Bennett, *Appl. Optics*, Suppl. 2, 1965.
[b] R. A. Paananen, 'Spectrum', I.E.E.E., June, 1966, p. 88.
[c] S. Koozekanani, J. McCoys, D. Rensch, *Amer. J. Phys.*, 1966, **34**, 989; T. J. Bridges and C. K. N. Patel, *Appl. Phys. Letters*, 1965, **7**, 244.
[d] C. C. Eaglesfield, 'Laser Light', Macmillan, London, 1967.
[e] T. P. Melia, 'An Introduction to Masers and Lasers', Chapman and Hall, London, 1967.
[f] O. S. Heavens, 'Optical Masers', Methuen, London, 1965.

2 Applications of Lasers in Chemistry

Before discussing some of the applications of lasers in chemistry it is worth reviewing briefly some of the characteristics of laser sources. Probably the most significant of these characteristics is the extremely high output power available in what is, frequently, a very narrow spectral line. Further, because of the very well collimated nature of the beam, this high output power may be used very efficiently as compared with a conventional light source and it may be made remarkably free of extraneous radiation. In addition, of course, the very long coherence length and the extremely well-defined state of polarisation of the beam for certain lasers are of immense value in certain specialised applications. Other sources possess certain of the properties of laser resonators but none have their unique characteristics allied to the extremely high output powers available.

Lasers can be built for use from the ultraviolet region near 3000 Å to the far-infrared, and since they can operate continuously, or in a variety of pulsed fashions, it is clear that here we have a family of devices with an incredibly wide field of application.

As befits a device which received its major impetus from an understanding of the nature of light emitting processes, the major application of the laser has been in spectroscopy, and it is this particular application which will concern us initially.

One of the first applications of one of the earliest lasers was that of Porto and Wood:[4] they obtained the Raman spectra of liquid carbon tetrachloride and benzene with 50 pulses from a ruby laser, each pulse being of *ca.* 1 msec. duration and containing *ca.* 1 joule of energy at 6943 Å. The total exposure time was thus only about 50 msec., an extraordinarily short time for the observation of Raman spectra. However, due to heating effects which occur in the ruby during each pulse, the laser was fired at a rate of only three per minute, so that the practical exposure time was not 1/20 sec. but about 20 min. With a continuously operating ruby laser with an output power of only 1 w a similar exposure could have been achieved in about 1 min. This example immediately illustrates the fact that in certain experiments it is necessary to supply a suitably large number of laser photons in the minimum overall time; for such studies low-power, continuously operating, lasers are often the most efficient, conventional Raman spectroscopy and fluorescence studies falling within this category. In certain other cases, however, the extremely high powers available with pulsed lasers give rise to extremely interesting non-linear phenomena such as the stimulated Raman effect and various two-photon absorption processes.

A. Conventional Spectroscopy with Lasers.—(i) *Raman spectroscopy.* The study of Raman spectroscopy is ideally suited to take full advantage of the unique characteristics of lasers. Almost invariably continuously operating lasers have been employed, the most widely used being the 6328 Å radiation from a helium–neon laser with an output power in the region of 100 mw. This laser compares very well with conventional mercury arcs as a Raman source,[5] and since it operates well into the red region of the spectrum it is of considerable value for obtaining spectra from highly coloured and photosensitive liquids or solids.[6] Because of the well collimated nature of the beam it is possible nowadays to obtain spectra from samples $<\mu$l.[7] so that the technique compares very favourably with infrared spectroscopy in absolute sensitivity. In addition, it has become possible, for the first time, to obtain very accurate measures of the

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[4] S. P. S. Porto and D. L. Wood, *J. Opt. Soc. Amer.*, 1962, **52,** 251.

[5] D. Cossart, G. Taieb, C. Troyanowsky, R. Cagnard, and J.-L. Otto, *Compt. rend.*, 1965, **260B,** 1127; M. V. Evans, T. M. Hard, and W. F. Murphy, *J. Opt. Soc. Amer.*, 1966, **56,** 1638; R. C. Hawes, K. P. George, D. C. Nielson, and R. Beckwith, *Analyt. Chem.*, 1966, **38,** 1842.

[6] P. J. Hendra, *Spectrochim. Acta*, 1967, **23,** 1275; G. C. Hayward and P. J. Hendra, *Spectrochim. Acta*, 1967, **23,** 2309; D. V. Luce, C. Clément, and R. Lafont, *Compt. rend.*, 1967, **264B,** 1822.

[7] G. F. Bailey, S. Kint, and J. R. Scherer, *Analyt. Chem.*, 1967, **39,** 1040.

depolarisation ratios for both Rayleigh and Raman scattering of liquids and gases.[8]

The helium–neon laser has been incorporated as a source into many commercially available Raman spectrometers and has proved to be so successful that it is unlikely to be displaced for the study of routine spectra for some considerable time. In addition it has even been found to be of value in the excitation of pure-rotational Raman spectra of gases,[9] and because of the extremely narrow width of the spectral line, it could prove of immense value for the study of such spectra under extremely high resolution.[10] For the study of weakly scattering materials, however, particularly for gas samples, this laser is being replaced in many research laboratories by the ion-lasers: the argon-ion laser has been particularly popular and with an output power of up to 1 w in several lines in the blue-green region of the spectrum, those at 4880 Å and 5145 Å being the most intense, this laser is ideal for the study of gas-phase Raman spectra. This laser, since it operates at a considerably shorter wavelength than the helium–neon laser, has the advantage that the Raman scattering, governed by the ν^4 law, is appreciably more intense and detectors operating in the blue-green region of the spectrum are appreciably more sensitive than those operating in the red. By using such sources it has been possible to obtain photographically and photoelectrically[11] pure-rotation and vibration–rotation spectra from many gas samples, spectra which could only be obtained with appreciable difficulty with conventional sources.

A natural extension of the applicability of lasers in Raman spectroscopy is in the study of the spectra of solids, particularly single-crystal spectra, where the state of polarisation of the beam and its directionality are so well defined that it is ideal for determining the molecular geometry and the various lattice modes of the crystal. Loudon[12] and Porto[13] have provided excellent accounts of the background theory associated with such spectra and the following references to the study of the first- and second-order Raman spectra of crystals provide an indication of the interest in this field: GaP,[14] CaWO,[15] $LiNbO_3$,[16] $CaWO_4$, $SrWO_4$, $CaMoO_4$, and $SrMoO_4$,[17] $SrTiO_3$,[18] $BaTiO_3$,[19] $KTaO_3$,[20] europium

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[8] N. J. Bridge and A. D. Buckingham, *J. Chem. Phys.*, 1964, **40**, 2733; R. C. C. Leite, R. S. Moore, and S. P. S. Porto, *J. Chem. Phys.*, 1964, **40**, 3741; S. P. S. Porto, *J. Opt. Soc. Amer.*, 1966, **56**, 1585; J. R. Lalanne and P. Bothorel, *J. Chim. phys.*, 1966, **63**, 1538; J. R. Lalanne and P. Bothorel, *Compt. rend.*, 1966, **263B**, 693; W. F. Murphy, M. V. Evans, and P. Bender, *J. Chem. Phys.*, 1967, **47**, 1836.

[9] A. Weber and S. P. S. Porto, *J. Opt. Soc. Amer.*, 1965, **55**, 1033.

[10] E. J. Allin, A. D. May, B. P. Stoicheff, J. C., Stryland, and H. L. Welsh, *Appl. Optics*, 1967, **6**, 1597.

[11] A. Weber, S. P. S. Porto, L. E. Cheesman, and J. J. Barrett, *J. Opt. Soc. Amer.*, 1967, **57**, 19; J. J. Barrett and N. I. Adams, *J. Opt. Soc. Amer.*, 1968, **58**, 311.

[12] R. Loudon, *Adv. Phys.*, 1964, **13**, 423; R. Loudon, *Proc. Roy. Soc.*, 1963, *A*, **275**, 218.

[13] S. P. S. Porto, 'The Spex Speaker', Spex Industries Inc., 1968, Metuchen, N. Jersey, U.S.A.

[14] M. V. Hobden and J. P. Russell, *Phys. Letters*, 1964, **13**, 39.

[15] J. P. Russell and R. Loudon, *Proc. Phys. Soc.*, 1965, **85**, 1029.

[16] R. F. Schaufele and M. J. Weber, *Phys. Rev.*, 1966, **152**, 705.

[17] S. P S. Porto and J. F. Scott, *Phys. Rev.*, 1967, **157**, 716.

[18] R. F. Schaufele and M. J. Weber, *J. Chem. Phys.*, 1967, **46**, 2859.

[19] A. Pinczuk, W. Taylor, E. Burstein, and I. Lefkowitz, *Solid State Comm.*, 1967, **5**, 429.

[20] W. G. Nielsen, *J. Chem. Phys.*, 1967, **47**, 1413.

yttrium gallium garnet (electronic Raman spectrum).[21]

(ii) *Brillouin spectra.* Because of the extreme narrowness of the 6328 Å spectral line of the helium–neon laser this source has been used for very high resolution studies of Brillouin scattering in liquids. Brillouin spectra are produced as a result of thermally excited sound waves present in the scattering medium. Periodic changes of refractive index produced by such waves may scatter incoming photons at a displaced frequency giving rise to the Brillouin scattering. In this scattering both energy and momentum must be conserved and the frequency separation of the Brillouin components to high and low frequencies of the central (Rayleigh) line are given by

$$\Delta\nu = 2Vn/c \;.\; \nu_0 \;.\; \sin\phi/2$$

V being the velocity of the acoustical wave of frequency $\Delta\nu$ in the medium, n the index of refraction at the frequency ν_0, c the velocity of light, and ϕ the scattering angle. The separations of the Brillouin components from the Rayleigh are typically 0·2 cm.^{-1} for 90° scattering so that for observation of the triplet structure of the scattered radiation extremely high resolution is necessary. This resolution is usually achieved by means of high-dispersion spectrographs or Fabry-Perot interferometers, the spectra being observed either photographically or photoelectrically by pressure-scanning the interferometer. With the very high resolution available extremely accurate values for these hypersonic velocities have been obtained in both liquid, solid, and high-pressure gas samples.[22] These determinations on the whole agreed very well with the known ultrasonic velocities in these media. Cummins and Gammon[23] in a detailed study of the effect were able to obtain good agreement between the measured values for the ratios of the intensities of Brillouin to Rayleigh scattering and their modification of the Landau–Placzek theory of light scattering in liquids. Significant broadening of the Brillouin as compared with the Rayleigh components for acetic and formic acids was observed by Chiao and Stoicheff.[22] From this they were able to obtain the decay time of the sound wave in the medium ($\tau = 2{\cdot}2 \times 10^{-10}$ sec. for acetic acid) and they suggest the relevance of the technique for the study of relaxation processes and very fast chemical reactions as an extension of the existing techniques at ultrasonic frequencies. In addition, Rank, Hollinger, and Eastman[24] were able to show that in most cases the Brillouin components were strongly polarised and were able to infer the presence of a certain ordering in some liquids on the basis of the temperature dependence of the depolarisation ratio of the Rayleigh component.

(iii) *Tuned laser spectroscopy.* In a rather novel application of lasers in high-

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[21] J. A. Koningstein, *J. Opt. Soc. Amer.*, 1966, **56**, 1405.

[22] R. Y. Chiao and B. P. Stoicheff, *J. Opt. Soc. Amer.*, 1964, **54**, 1286; G. B. Benedeck, J. B. Lastovka, K. Fritsch, and T. Greytak, *J. Opt. Soc. Amer.*, 1964 **54**, 1284; J. Stone, *J. Opt. Soc. Amer.*, 1966, **56**, 1136; G. R. Hanes, R. Turner, and J. E. Piercy, *J. Acoust. Soc. Amer.*, 1965, **38**, 1057; E. G. Rawson, E. H. Hara, A. D. May, and H. L. Welsh, *J. Opt. Soc. Amer.*, 1966, **56**, 1403.

[23] H. Z. Cummins and R. W. Gammon, *J. Chem. Phys.*, 1965, **44**, 2785.

[24] D. H. Rank, A. Hollinger, and D. P. Eastman, *J. Opt. Soc. Amer.*, 1966, **56**, 1057.

resolution infrared spectroscopy, and one indicative of the sort of experiment which will become possible in a much refined form in the future, Gerritsen and Heller[25] carried out a study of the widths of methane absorption lines in the vicinity of 2947·9 cm.$^{-1}$. They used a helium–neon laser operating on the 3·39 μm infrared transition and by the application of an axial magnetic field they were able to vary the operating frequency of this laser over a range of +0·11 cm.$^{-1}$ from the unperturbed frequency of 2947·903 cm.$^{-1}$. By comparing the intensity of radiation transmitted through a sample cell, with and without methane present, they were able to observe certain absorption lines of the methane sample. Since the resolution of the instrument was 0·003 cm.$^{-1}$ they were able to observe the broadening effect of inert gases at a total pressure of only 40 mm. Hg and hence to obtain collision diameters for these systems more accurately than had been previously possible. The experiment was limited in scope of course by the small frequency range covered, but the authors suggest that by the use of pressure-scanned injection lasers[26] this range could be increased substantially.

The rather specific absorption of 3·39 μm. helium–neon laser radiation by methane has been used to estimate the amount of methane present in the atmosphere[27] and to improve the output of a 6328 Å helium–neon laser by removal of the competing laser process at 3·39 μm.

The technique of tuned laser spectroscopy has been applied to the study of spectra of other molecules in this region[28] and has been extended by the use of a helium–xenon laser operating at 3·507 μm[29] and has even allowed the observation of the Stark effect of certain vibration–rotation lines of the formaldehyde molecule.[30]

(iv) *Relaxation studies in gaseous systems.* As an extension of the studies on the absorption of the 3·39 μm. helium–neon laser radiation, Yardley and Moore[31] observed vibrational fluorescence from the triply degenerate deformation vibration ν_4 of methane populated *via* absorption of the laser into the triply degenerate ν_3 vibrational state. By a careful consideration of the phase of the scattered radiation they were able to determine vibrational relaxation times for deactivation of the ν_4 mode and for the transfer of energy from ν_3 to ν_4 and the number of CH_4–CH_4 collisions necessary for the latter process.

The very high output power of a carbon dioxide laser was recently employed by Ronn[32] to study the infrared fluorescence of ethylene. In this study the emitted radiation was resolved with an infrared spectrometer and since the vibrational relaxation was relatively slow (*ca.* 0·1—10 msec.) the fluorescence spectrum was found to be very similar to the absorption spectrum due to very rapid rotational

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[25] H. J. Gerritsen and M. E. Heller, *Applied Optics*, Suppl, No. 2, 1965, 73.

[26] J. M. Besson, *J. Phys.*, Colloque C2, Suppl., 3-4, 1967, **28**, 247; J. M. Besson, J. F. Butler, A. R. Calawa, W. Paul, and R. H. Rediker, *Appl. Phys. Letters*, 1965, **7**, 206

[27] T. S. Chu and D. C. Hogg, *Bell System Tech. J.*, 1966, **45**, 301.

[28] H. J. Gerritsen, *Phys. Quant. Elect.*, 1965, 581; H. Brunet, *J. Quantum Elect.*, 1966, **2**, 382.

[29] K. Sakurai, K. Shimoda, and M. Takami, *J. Phys. Soc. Japan*, 1966, **21**, 1838 and 1842; K. Sakurai and K. Shimoda, *Japan J. Appl. Phys.*, 1966, **5**, 938.

[30] K. Sakurai, K. Uehara, M. Takami, and K. Shimoda, *J. Phys. Soc. Japan*, 1967, **23**, 103.

[31] J. T. Yardley and C. B. Moore, *J. Chem. Phys.*, 1966, **45**, 1066.

[32] A. M. Ronn, *J. Chem. Phys.*, 1968, **48**, 511.

relaxation in the excited state. Ezekiel and Weiss[33] were able to study the resonance fluorescence of a molecular beam of iodine excited by 5145 Å radiation from an argon-ion laser. They were able to measure the oscillator strength for the transition as well as the lifetime in the excited state (3 μsec.) at a pressure of I_2 in the beam chamber of less than 3×10^{-7} mm. Hg.

With a view to obtaining a more detailed understanding of the operation of the carbon dioxide laser, there has been extensive study of the lifetimes and collision half-widths in the CO_2–N_2 molecular system,[34] this laser also having been employed for an infrared-microwave double-resonance experiment[35] on methyl bromide.

No discussion of the relevance of lasers in relaxation studies would be complete without a reference to their application in shock-wave studies of vibrational relaxation. Kiefer and Lutz[36] have described a quantitative Schlieren method for a shock-tube study of the vibrational relaxation in D_2–Ar mixtures with a He–Ne 6328 Å laser. Because the beam was narrow and well collimated they were able to obtain substantially increased sensitivity and accuracy as compared with the techniques previously employed. The work has been extended to the study of hydrogen[37] and oxygen[38] and the technique is undoubtedly of some value in shock-tube studies.

B. Non-linear phenomena.—Because of the very great power of giant pulse lasers, extremely high electric-field strengths, typically 10^6—10^8 v/cm., can be achieved at the focus of a converging lens. With such high field strengths a whole range of new effects has been observed. One of the earliest of these effects to be observed was the generation of an optical harmonic of the ruby laser radiation at one half of its wavelength (3471·5 Å).[39] Nowadays, second-harmonic conversion efficiencies of more than 20% can be achieved using giant-pulse lasers so that it is possible to obtain roughly 1 Mw of radiation at, say, 3471·5 Å from a giant pulse ruby laser. Melia and Heavens (see footnotes *e* and *f* to the Table) provide concise accounts of the mechanism of harmonic generation, and while this phenomenon is perhaps of less interest to the chemist than some of the others in this section, it is a very worthwhile method of extending the range of giant pulse lasers and promises to be of particular value in the field of reaction kinetics.

The stimulated Raman effect. Perhaps the most interesting of these non-linear phenomena is the generation of coherent Raman radiation *via* the stimulated Raman effect. This effect was observed initially by Woodbury and Ng[40] when they used liquid nitrobenzene in a Kerr cell arrangement inside the cavity for Q-switching a ruby laser. They observed, in addition to the intense line at

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[33] S. Ezekiel and R. Weiss, *Phys. Rev. Letters*, 1968, **20**, 91.

[34] C. Rossetti and P. Barchewitz, *Compt. rend.*, 1966, **262B**, 1199 and 1684; P. K. Cheo, *J. Appl. Phys.*, 1967, **38**, 3563.

[35] A. M. Ronn and D. R. Lide, *J. Chem. Phys.*, 1967, **47**, 3669.

[36] J. H. Kiefer and R. W. Lutz, *J. Chem. Phys.*, 1966, **44**, 658.

[37] J. H. Kiefer and R. W. Lutz, *J. Chem. Phys.*, 1966, **44**, 668.

[38] R. W. Lutz and J. H. Kiefer, *Phys. Fluids*, 1966, **9**, 1638.

[39] P. A. Franken, A. E. Hill, C. W. Peters, and G. Weinreich, *Phys. Rev. Letters*, 1961, **7**, 118.

[40] E. J. Woodbury and W. K. Ng, *Proc. Inst. Radio. Eng.*, 1962, **50**, 2367.

6943 Å, an additional line at 7670 Å with an intensity which was a substantial fraction of that of the laser. The separation of this line from the laser line coincided with one of the vibrational frequencies of the nitrobenzene molecule at 1344 cm.$^{-1}$. Eckardt *et al.*[41] studied the effect in rather more detail and with a greater variety of liquids and found a definite threshold both with regard to the pumping intensity and length of liquid column required. In addition, substantial narrowing of the spectral line was observed with increased pumping power and the degree of beam collimation appeared to be the same as that of the laser, all features characteristic of the production of laser action at the Raman-shifted line wavelength. In addition, very intense lines were observed at *exactly* twice and three times the frequency shift, although in these experiments no anti-Stokes components were observed. In subsequent experiments on solids, liquids, and gases[42] it was found that the effect could be produced outside the laser cavity by placing the Raman cell at the focus of a converging lens. In these cases many Stokes-shifted components were observed as well as a number of anti-Stokes components, the latter exhibiting a pronounced angular dependence.[43] The effect has been studied in some considerable detail both in liquids and high pressure gases[44] and considerable interest has been aroused in the theory of this remarkable process.[45] Since only the strongest, narrowest, Raman lines are observed in this effect, it is of little value for the study of conventional Raman spectra but it has stimulated considerable discussion of the nature of the scattering process and has increased the number of possible laser transitions by many thousand.

Following on this work on stimulated Raman scattering, Chiao, Townes, and Stoicheff[46] were able to observe stimulated Brillouin scattering in quartz and sapphire, an observation which was soon followed by others on various solids and liquids[47] and on aspects of the theory of this effect.[48] This process is analogous to the Raman laser action but with the molecular vibration replaced by an acoustic wave of frequency *ca.* 3×10^{10} sec.$^{-1}$, the acoustic and scattered light waves being emitted in very specific directions. Chiao *et al.* suggest that stimul-

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[41] G. Eckardt, R. W. Hellwarth, F. J. McClung, S. E. Schwarz, D. Weiner, and E. J. Woodbury, *Phys. Rev. Letters*, 1962, **9**, 455.

[42] See for example, R. W. Minck, R. W. Terhune, and W. G. Rado, *Appl. Phys. Letters*, 1963, **3**, 181; B. P. Stoicheff, *Phys. Letters*, 1963, **7**, 186; J. J. Barrett and M. C. Tobin, *J. Opt. Soc. Amer.*, 1966, **56**, 129; S. Yoshikawa, Y. Matsumura, and H. Inaba, *Appl. Phys. Letters*, 1966, **8**, 27.

[43] R. Chiao and B. P. Stoicheff, *Phys. Rev. Letters*, 1964, **12**, 290; E. Garmire, *Phys. Quantum Elect.*, 1965, 167.

[44] R. V. Wick, T. A. Wiggins, and D. H. Rank, *Appl. Optics*, 1966, **5**, 473; P. Lallemand, P. Simova, and G. Bret, *Phys. Rev. Letters*, 1966, **17**, 1239; F. M. Johnson, J. A. Duardo, and G. L. Clark, *Appl. Phys. Letters*, 1967, **10**, 157; J. A. Duardo, L. J. Nugent, and F. M. Johnson, *J. Chem. Phys.*, 1967, **46**, 3585.

[45] R. W. Terhune, *Solid State Design*, 1963, **4**, 38; E. Garmire, F. Pandarese, and C. H. Townes, *Phys. Rev. Letters*, 1963, **11**, 160; R. W. Hellwarth, *Phys. Rev.*, 1963, **130**, 1850; Y. R. Shen and N. Bloembergen, *Phys. Rev.*, 1965, **137**, 1787.

[46] R. Y. Chiao, C. H. Townes, and B. P. Stoicheff, *Phys. Rev. Letters*, 1964, **12**, 592.

[47] E. Garmire and C. H. Townes, *Appl. Phys. Letters*, 1964, **5**, 84; R. G. Brewer, *Phys. Rev.*, 1965, **140**, 800; A. S. Pine, *Phys. Rev.*, 1966, **149**, 113.

[48] See for example, J. Walder and C. L. Tang, *Phys. Rev.*, 1967, **155**, 318.

ated Brillouin scattering affords a method of generating intense hypersonic waves of power *ca.* 1 kw at frequencies as high as 60,000 Mc/sec.

Among the interesting new phenomena observed with these pulsed lasers was the inverse Raman effect.[49] In their study of this effect Jones and Stoicheff irradiated the scattering medium simultaneously with intense ruby laser radiation of frequency ν_0 and with an intense continuum in the region of certain of the anti-Stokes lines of the molecules under study. Under this excitation the molecules are stimulated to emit radiation at ν_0 and, at the same time, to absorb radiation at $\nu_0 + \nu_{\text{vib}}$ or $\nu_0 - \nu_{\text{vib}}$ from the continuum, the net effect being to change their energy states by $+h\nu_{\text{vib}}$ or $-h\nu_{\text{vib}}$ respectively, ν_{vib} being one of the vibrational frequencies of the molecule. The transitions representing this stimulated emission process are shown in Figure 7b, along with the resulting

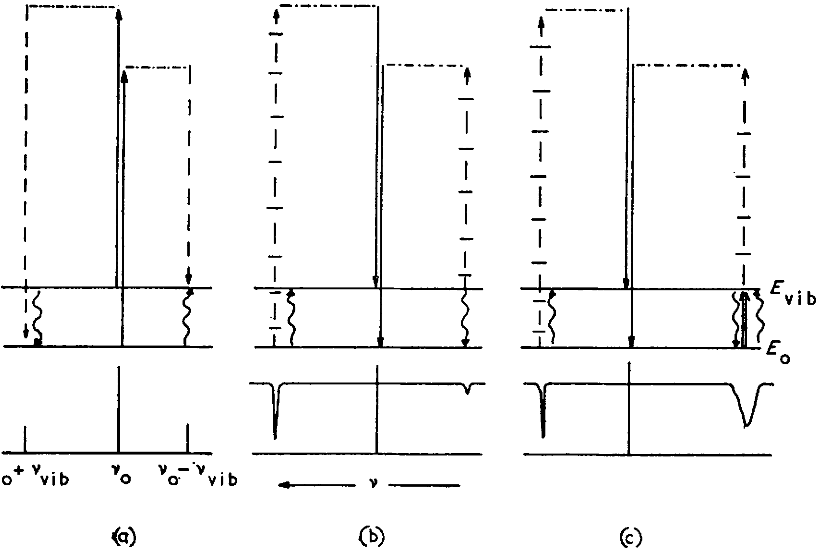

Figure 7 *Diagrammatic representation of molecular transitions leading to stimulated Raman scattering* (a), *inverse Raman absorption* (b), *and stimulated inverse Raman absorption* (c). 6943 Å *radiation* ——→ ; *stimulated Raman radiation* – – – → ; *background continuum radiation* - | - | - | → ; *phonon wave excitation* → ; *change produced in vibrational state* ⌒→ .

absorption spectrum. Conveniently, background radiation spanning the frequency $\nu_0 + \nu_{\text{vib}}$ could be generated readily using certain of the anti-Stokes lines produced by the stimulated Raman effect from the same or a different liquid. The absorptions did not exhibit a threshold nor was any appreciable line narrowing observed, the widths of the lines being comparable to those observed in conventional Raman spectroscopy. The inverse Raman spectrum is the analogue of the stimulated Raman emission spectrum and one would expect to find similar characteristics in the two spectra. However, since stimulated Raman

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[49] W. J. Jones and B. P. Stoicheff, *Phys. Rev. Letters*, 1964, **13**, 657.

emission is usually excited with light of one frequency it exhibits a threshold so that, in general, only one or two vibrational lines are observed corresponding to the lines of highest intensity per bandwidth in the normal Raman spectrum. In the inverse Raman spectrum, however, both the continuum and the stimulating radiation have already been supplied so that there is no threshold and the complete Raman-active spectrum should be observable. This is of some importance in the development of Raman spectroscopy since, with the development of a suitably broad band continuum synchronised with the laser pulse, it should be possible to investigate the inverse Raman spectra of solids, liquids, and perhaps gases, in times of the order of 10^{-8} sec. Dumartin and his co-workers[50] confirmed these findings and extended the results by generating a very much broader continuum which extended on both the Stokes and anti-Stokes side of the laser by focusing the laser beam into cells of compressed krypton gas. They observed not only the conventional inverse Raman absorption on the anti-Stokes side but also what they call the inverse stimulated Raman absorption on the Stokes side. They observed absorption from the Stokes continuum at the frequency $\nu_0 - \nu_{\text{vib}}$ (Figure 7c), the absorption having a breadth which was very much greater than that of the anti-Stokes absorption and, unlike the anti-Stokes absorption, the Stokes absorption was observed to exhibit a definite threshold. In accounting for this phenomenon Dumartin and his co-workers[51] assume that generated in the liquid there will be a wave of optical phonons, as well as a wave of Stokes photons, with a definite threshold for their generation. They claim that these optical phonons are responsible for the population inversion of the vibrational level necessary to produce a strong Stokes absorption. Interaction of these vibrationally excited molecules with the Stokes continuum and subsequent stimulated emission at frequency ν_0 leads to the observation of strong absorption at a frequency $\nu_0 - \nu_{\text{vib}}$. The appreciable width of the absorption is thought to be a consequence of the large spectral width of the band of optical phonons because of the short lifetime of these phonons due to their strong absorption in the medium.

3 Multiple-photon Absorption Processes

A. Fluorescence Studies.—The possible application of intense laser beams for observing two-photon absorption processes was first considered by Kleinman[52] and observed in $CaF_2:Eu^{2+}$ by Kaiser and Garrett.[53] The latter authors observed intense blue fluorescence around 4250 Å on illuminating a calcium fluoride crystal doped with 0·1% Eu^{2+} ions with the 6943 Å radiation from a ruby laser. They found that the intensity of the blue fluorescence was proportional to the square of the incident laser intensity, as expected for a two-photon process, and were able to determine the efficiency of this process. The versatility of the technique for fluorescence studies was illustrated by Abella[54] who was able to study

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[50] S. Dumartin, B. Oksengorn, and B. Vodar, *Compt. rend.*, 1965, **261**, *B*, 3767.
[51] S. Dumartin, B. Oksengorn, and B. Vodar, *Compt. rend.*, 1965, **261**, *B*, 4031.
[52] D. A. Kleinman, *Phys. Rev.*, 1962, **125**, 87.
[53] W. Kaiser and C. G. B. Garrett, *Phys. Rev. Letters*, 1961, **7**, 229.
[54] I. D. Abella, *Phys. Rev. Letters*, 1962, **9**, 453.

the fluorescence of caesium vapour excited by two-photon absorption of the 6943 Å ruby laser radiation. For a double photon transition to occur, the energy of the excited level must be twice that of a single incident photon, and the initial and final states must be of the same parity. For two electric-dipole transitions these conditions were satisfied for the change $9^2D_{3/2} \longleftarrow 6^2S_{1/2}$, having $\Delta l = 2$, $\Delta J = 1$, the absorption being detected by observing the fluorescent decay $6^2P_{3/2} \longleftarrow 9^2D_{3/2}$ at 5847 Å. The Doppler width for the two-photon transition was 0·04 cm.$^{-1}$ so that the necessity for obtaining a coincidence between this sharp resonance and the laser frequency imposed stringent experimental requirements on thermal tuning of the laser.

Since this early work many authors have studied fluorescence from inorganic[55] and organic[56] crystals and anthracene in particular has been very intensively studied[57] using these sources. Singh[58] observed a three-photon absorption in naphthalene, Regensburger and Pannizza[59] a two-photon absorption spectrum of a single crystal of CdS, one of the photons being provided by the Nd–glass laser the other through absorption from a xenon continuum synchronised with the laser, and more recently Wang and Chang[60] were able to report on the observation of coherent fluorescence from a zinc sulphide crystal excited by two-photon absorption of radiation from a giant pulse ruby laser.

B. Interactions of Lasers with Solid Surfaces.—By letting an intense laser beam strike a solid surface many extremely interesting effects have been observed. Such effects have included the emission of multiply charged ions,[61] removal of surface adsorbed species,[62] electron thermionic, photoelectric and *X*-ray emission,[63] as well as the observation of photoconductivity in certain crystals.[64] In analytical chemistry the vapourisation of metal surfaces and the production of charged ions has proved to be of some considerable value[65] since the samples can be studied under high vacuum conditions and the technique is extremely sensitive for the study of adsorbed gases and localised impurities. In addition

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[55] S. Singh and B. P. Stoicheff, 'Proceedings of the Symposium on Optical Masers', Polytechnic. Institute of Brooklyn, 1963, p. 385.

[56] W. L. Peticolas, J. P. Goldsborough, and K. E. Rieckhoff. *Phys. Rev. Letters*, 1963, **10,** 43; M. W. Dowley, K. B. Eisenthahl, and W. L. Peticolas, *J. Chem. Phys.*, 1967, **47,** 1609.

[57] See for example, S. Singh, W. J. Jones, W. Siebrand, B. P. Stoicheff, and W. G. Schneider, *J. Chem. Phys.*, 1965, **42,** 330; M. Ianuzzi and E. Polacco, *Phys. Rev.*, 1965, **138A,** 806; D. Fröhlich and H. Mahr, *Phys. Rev. Letters*, 1966, **16,** 895; D. F. Williams and W. G. Schneider, *J. Chem. Phys.*, 1966, **45,** 4756.

[58] S. Singh and L. T. Bradley, *Phys. Rev. Letters*, 1964, **12,** 612.

[59] P. J. Regensburger and E. Panizza, *Phys. Rev. Letters*, 1967, **18,** 113.

[60] S. Wang and C. C. Chang, *Appl. Phys. Letters*, 1968, **12,** 193.

[61] S. Namba, P. H. Kim, and A. Mitsuyama, *J. Appl. Phys.*, 1966, **37,** 3330; B. C. Fawcett and N. J. Peacock, *Proc. Phys. Soc.*, 1967, **91,** 973.

[62] J. F. Ready, E. Bernal, and L. P. Levine, *Proc. Nat. Elect. Conf.*, 1966, **22,** 993.

[63] F. Giori, L. A. Mackenzie, and E. J. McKinney, *Appl. Phys. Letters*, 1963, **3,** 25; H. Sonnenberg, H. Heffner, and W. Spicer, *Appl. Phys. Letters*, 1965, **5,** 95; M. C. Teich, J. M. Schroeer, and G. J. Wolga, *Phys. Rev. Letters*, 1964, **13,** 611; C. M. Verber and A. H. Adelman, *J. Appl. Phys.*, 1965, **36,** 1522; W. L. Knecht, *I.E.E.E., J. Quantum Elect.*, 1966, **2,** 103.

[64] K. Hasegawa and W. G. Schneider, *J. Chem. Phys.*, 1963, **39,** 1346; K. Maeda, *Appl. Phys. Letters*, 1966, **9,** 92.

[65] J. Debras-Guedon and N. Liodec, *Compt. rend.*, 1963, **257B,** 3336; E. F. Runge, F. R. Bryan, and R. W. Minck, *Canad. Spectroscopy*, 1964, **9,** 80; W. D. Hagenah, *Z. Angew. Math. Phys.*, 1965, **16,** 130.

the technique can be employed for generating and studying flames,[66] Jeunhomme and Schwenker[67] employing it to determine the oscillator strength of the C_2 (Swan) system of bands near 4000 Å.

There have been many other applications of these remarkable light sources in subjects bordering on chemistry, for example in the generation of plasmas[68] and for electron density and temperature determinations in these media.[69] One of the most remarkable effects generated by the giant pulse lasers is the observation of an intense flash of light accompanied by an audible 'snap' when the beam is brought to a focus, with a short focal length lens, in a gas. This breakdown is due to multiple ionisation of the atoms (or molecules) of the gas due to the very high field strengths prevailing at the focus.[70]

C. Applications of Lasers in Reaction Kinetic.—The scope for the application of these devices in the field of reaction kinetics is potentially enormous although as yet comparatively little work has been done. Thus, production of molecules in selectivity excited electronic states by absorption of laser radiation, or the production of ions and radicals by intense pulses of u.v. laser radiation, could initiate certain reactions or radically alter the course of others. Such changes in the course and rates of chemical reactions could also be effected by selectively populating certain vibrational states, for example by absorbing radiation from the extremely intense carbon dioxide laser at 10·6 μm. Tiffany *et al.*[71] used a pulsed ruby laser in selective photocatalysis of certain bromine reactions, while Epstein and Sun[72] carried out a preliminary study of some chemical reactions induced in gases by the same source. These results, naturally, are of a preliminary nature but suggest the scope for the technique in this field of study.

Besides these applications in chemistry the laser has also been of immense value in many other fields of study, interferometry, holography, instrumentation, communications, medicine, astronomy and micro-machining, being but a few. In addition, of course, one should not forget the benefits to chemistry arising from research into laser materials and the intensive study of fluorescent lifetimes, collision cross sections, spectral line widths, and methods of production of excited-state species in the many types of laser which have been constructed to date. Some years ago it might have been true to say that the laser was a perfect answer in search of a problem, the same statement could hardly be made today.

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[66] B. P. Stoicheff, in Proceedings of the Xth Colloquium Spectroscopicum Internationale; ed. E. R. Lippincott and M. Margoshes, Spartan Books, Washington, D.C., 1963, J. E. Mentall and R. W. Nicholls, *J. Chem. Phys.*, 1967, **46**, 2881; A. G. Sharkey, J. L. Shultz, and R. A. Friedel, *Adv. Chem.*, 1966, Ser. No. 55, p. 643.

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[68] E. Archbold and T. P. Hughes, *Nature*, 1964, **204**, 670; M. M. Litvak and D. F. Edwards, *I.E.E.E., J. Quantum Elect.*, 1966, **2**, 486.

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[70] R. G. Tomlinson, *Phys. Rev. Letters*, 1965, **14**, 489; M. Young, M. Hercher, and C-Y. Wu, *J. Appl. Phys.*, 1966, **37**, 4938; M. Berry, *Compt. rend.*, 1966, **262**, *B*, 1395.

[71] W. B. Tiffany, H. W. Moos, and A. L. Schawlow, *Science*, 1967, **157**, 40.

[72] L. M. Epstein and K. H. Sun, *Nature*, 1966, **211**, 1173.