

# LASERS AND LASER SPECTROSCOPY

## 2.1 General discussion of lasers

### 2.1.1 General features and properties

The word 'laser' is an acronym derived from 'light amplification by the stimulated emission of radiation'. If the light concerned is in the *microwave* region then the alternative acronym 'maser' is often used. Although the first such device to be constructed was the ammonia maser in 1954 it is the lasers made subsequently which operate in the infrared, visible or ultraviolet regions of the spectrum which have made a greater impact.

In Section 2.2 we saw that emission of radiation by an excited atom or molecule  $M^*$  may be by a spontaneous (Equation 2.4) or by an induced, or stimulated, process

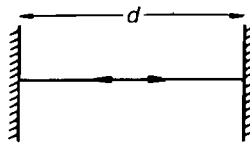


as in Equation (2.5).

Laser radiation is emitted entirely by the process of stimulated emission, unlike the more conventional sources of radiation discussed in Chapter 3, which emit through a spontaneous process.

For induced emission from the upper energy level  $n$  of the two-level system in Figure 2.2(a) to dominate absorption (Equation 2.3) there must be a population inversion between the two levels, that is  $N_n > N_m$  where  $N_i$  refers to the population of state  $i$ . To disturb the normal Boltzmann population distribution (Equation 2.11), in which  $N_n < N_m$ , requires an input of energy. The process by which such a population inversion is brought about is known as pumping. A system, which may be gaseous, solid or liquid and in which a population inversion has been created is referred to as an active medium. According to Equation (9.1) the active medium is capable of acting as an amplifier of radiation falling on it. The equation shows that, for every photon entering the active medium, two photons are emitted from it.

To make an oscillator from an amplifier requires, in the language of electronics, positive feedback. In lasers this is provided by the active medium being between two mirrors, both of them highly reflecting but one rather less so in order to allow some of the stimulated radiation to leak out and form the laser beam. The region bounded by the mirrors is called the laser cavity. Various mirror systems are used but that shown in Figure 9.1, consisting of



**Figure 9.1** Laser cavity with two plane mirrors

two plane mirrors a distance  $d$  apart, is one of the simplest. The mirror separation must be an integral number of half-wavelengths,  $n\lambda/2$ , apart, necessitating extremely accurate alignment. The resonant frequency  $\nu$  of the cavity is then given by

$$\nu = \frac{nc}{2d}$$

### Worked example 9.1

*Question.* A laser cavity is 10.339 96 cm long and is operating at a wavelength of 533.647 8 nm. How many half-wavelengths are there along the length of the cavity? By how much would the length have to be changed to increase this number by one? What consequences does this result have for the tuning of such a cavity? How long does it take for the radiation to complete one round-trip of the cavity (to four significant figures)?

*Answer.* Since wavelength  $\lambda$  and frequency  $\nu$  are related by

$$c = \nu\lambda$$

Equation (9.2) gives

$$\begin{aligned} \therefore \lambda &= \frac{c}{\nu} = \frac{2d}{n} \\ \therefore n &= \frac{2d}{\lambda} = \frac{2 \times 10.339\,96 \times 10^7 \text{ nm}}{533.647\,8 \text{ nm}} \\ &= 3.875\,200 \times 10^5 \end{aligned}$$

Increasing  $n$  by one gives

$$\begin{aligned} n &= 3.875\,210 \times 10^5 \\ \therefore d &= \frac{n\lambda}{2} = \frac{3.875\,210 \times 10^5 \times 533.647\,8 \times 10^{-7} \text{ cm}}{2} \\ &= 10.339\,99 \text{ cm} \end{aligned}$$

Therefore the  
tune the cavity  
one of the m  
One round-

The reflect  
and low diele  
specific laser v  
highly reflect  
to emerge as t

Photons of  
Those that sm  
flux to reach a  
active median  
Laser radia

1. *Directional*  
parallel, w  
mirrors D

2. *Monochrom*  
a gaseous  
range of t  
the laser  
wavelength

3. *Brightness*  
unit solid  
reason fo  
0.5 mW l

4. *Coherence*  
electrom  
general  
coherenc  
Coherenc  
as in me

Therefore the cavity has been increased in length by  $0.000\ 03\ \text{cm} = 0.3\ \mu\text{m}$ . This means that to tune the cavity to a half wavelength of the radiation requires an extremely accurate movement of one of the mirrors forming the cavity.

One round-trip of the cavity covers a distance of  $20.680\ \text{cm}$

$$\begin{aligned}\therefore \text{time taken} &= \frac{20.680\ \text{cm}}{2.997\ 9 \times 10^{10}\ \text{cm s}^{-1}} \\ &= 6.898 \times 10^{-10}\ \text{s}\end{aligned}$$

The reflecting surfaces of the mirrors are specially coated, with alternate layers of high and low dielectric materials such as  $\text{TiO}_2$  and  $\text{SiO}$ , to give almost total reflection at the specific laser wavelength. The usual aluminium, silver or gold coatings are not sufficiently highly reflecting. One of the mirrors is coated so as to allow 1 to 10 per cent of the radiation to emerge as the laser beam.

Photons of energy  $hc\bar{\nu}$  are generated initially in the cavity through spontaneous emission. Those that strike the cavity mirrors at  $90^\circ$  are retained within the cavity causing the photon flux to reach a level which is sufficiently high to cause stimulated emission to occur, and the active medium is said to lase.

Laser radiation has four very remarkable properties:

1. *Directionality.* The laser beam emerging from the output mirror of the cavity is highly parallel, which is a consequence of the strict requirements for the alignment of the cavity mirrors. Divergence of the beam is typically a few milliradians.
2. *Monochromaticity.* If the energy levels  $n$  and  $m$  in Figure 2.2(a) are sharp, as they are in a gaseous active medium, the Planck relation of Equation (2.2) limits the wavelength range of the radiation. However, whatever the nature of the active medium, the fact that the laser cavity is resonant only for the frequencies given by Equation (9.2) limits the wavelength range.
3. *Brightness.* This is defined as the power emitted per unit area of the output mirror per unit solid angle and is extremely high compared with that of a conventional source. The reason for this is that, although the power may be only modest, as in, for example, a  $0.5\ \text{mW}$  helium-neon gas laser, the solid angle over which it is distributed is very small.
4. *Coherence.* Conventional sources of radiation are incoherent, which means that the electromagnetic waves associated with any two photons of the same wavelength are, in general, out of phase. The coherence of laser radiation is both temporal and spatial, the coherence lasting for a relatively long time and extending over a relatively large distance. Coherence of laser radiation is responsible for its use as a source of intense local heating, as in metal cutting and welding, and for holography.

9.1.2 Methods of obtaining population inversion

Equation (9.1) may give the impression that in the stimulated emission process we are getting something for nothing—putting in one quantum of energy and getting out two. The process does involve an amplification of the radiation (hence the ‘light amplification’ which appears in the acronym) but energy has to be put into the system to excite  $M$  to  $M^*$  so there is no energy gain. Not only is there no energy gain but the efficiency of the overall process is very low. For example, a nitrogen gas laser has an efficiency of less than 0.1 per cent and a semiconductor (diode) laser, one of the best in this respect, has an efficiency of about 30 per cent.

Before we look at the various methods of pumping we shall consider the types of energy level scheme encountered in lasing materials.

So far we have thought of the stimulated emission occurring in a lasing material as being in a simple two-level system like that shown in Figure 9.2(a). In fact, a laser operating through such a two-level system is very unusual – the excimer laser discussed in Section 9.2.8 is such an example. The reason for this is that, under equilibrium conditions, level 2 will have a much lower population than will level 1 (see Equation 2.11). If level 2 is a high-lying vibrational, or an electronic, energy level the population will be negligibly small. Pumping with energy  $E_2 - E_1$  results, initially, in net absorption, which continues until the populations are equal, a condition known as saturation and encountered in Section 2.3.4.2. At this point further pumping results in absorption and induced emission occurring at the same rate so that population inversion cannot normally be achieved.

Commonly, a three-level or four-level system, illustrated in Figures 9.2(b) and 9.2(c), is necessary for population inversion to be obtained between two of the levels.

In the three-level system of Figure 9.2(b) population inversion between levels 2 and 1 is achieved by pumping the 3–1 transition. The 3–2 process must be efficient and fast in order to build up the population of level 2 while that of level 1 is depleted. Lasing occurs in the 2–1 transition.

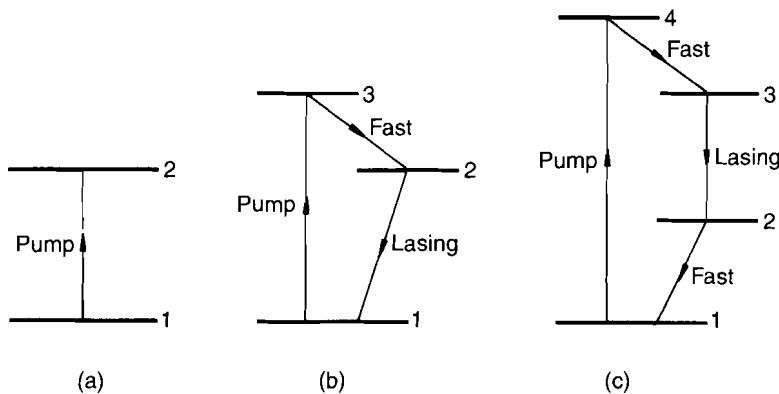


Figure 9.2 (a) Two-level (b) three-level and (c) four-level lasing systems

The four-level population inversion efficiency is that population of level

In more complex all involved in fast systems.

Population inversion laser systems the continuously. For source which del continuous wave

Methods of pu be pulsed or CW

Optical pump source and is as obtained over a photolysis. desc that of the pump continuously as

Electrical pu electrical discharge cell or by a high collisions betw translational en

In some gas where  $N$  serv energy to  $M$  b

Ideally,  $N^*$  is  $M^*$  which is

9.1.3 Laser ca

The cavity radiation Th has modes c axial (or l propagator

The tran magnetic

The four-level system in Figure 9.2(c) is even more efficient in the creation of a population inversion, in this case between levels 3 and 2. The reason for the greater efficiency is that, not only is level 3 populated through the fast 4-3 process, but the population of level 2 is rapidly depleted by the fast 2-1 process.

In more complex systems there may be more levels between 4 and 3 and between 2 and 1, all involved in fast processes to lower levels, but they are still referred to as four-level systems.

Population inversion is difficult not only to achieve but also to maintain. Indeed, for many laser systems there is no method of pumping which will maintain a population inversion continuously. For such systems inversion can be brought about only by means of a pumping source which delivers short, high-energy pulses. The result is a pulsed laser as opposed to a continuous wave, or CW, laser which operates continuously.

Methods of pumping, irrespective of the type of level system and of whether lasing is to be pulsed or CW, fall into two general categories—optical and electrical pumping.

Optical pumping involves the transfer of energy to the system from a high-intensity light source and is used particularly for solid and liquid lasers. A very high photon flux can be obtained over a short period of time from inert gas flashlamps of the type used in flash photolysis, described in Section 3.5.4. The result is a pulsed laser, the repetition rate being that of the pumping source. CW optical pumping may be achieved in some lasers by a continuously acting tungsten-iodine, krypton, or high-pressure mercury arc lamp.

Electrical pumping is used for gas and semiconductor lasers. In a gas laser this involves an electrical discharge in the gas which may be induced by microwave radiation outside the gas cell or by a high voltage across electrodes inside the cell. The pumping is achieved through collisions between the gaseous atoms or molecules and electrons produced with high translational energy in the discharge.

In some gas lasers it is preferable to use a mixture of the lasing gas M and a second gas N, where N serves only to be excited to  $N^*$  by collisions with electrons and to transfer this energy to M by further collisions:

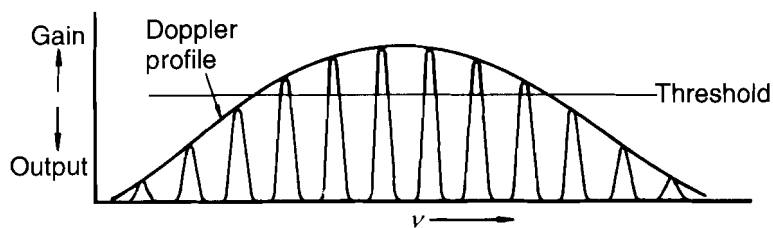


Ideally,  $N^*$  is a long-lived, metastable state with an energy similar to that of the level of  $M^*$  which is being pumped.

### 9.1.3 Laser cavity modes

The cavity of a laser may resonate in various ways during the process of generation of radiation. The cavity, which we can regard as a rectangular box with a square cross-section, has modes of oscillation, referred to as cavity modes, which are of two types, transverse and axial (or longitudinal). These are, respectively, normal to and along the direction of propagation of the laser radiation.

The transverse modes are labelled  $TEM_{m\ell}$ , where TEM stands for transverse electric and magnetic (field);  $m$  and  $\ell$  are integers that refer to the number of vertical and horizontal



**Figure 9.3** Doppler limited laser line with twelve axial modes within the line width

nodal planes of the oscillation, respectively. Usually it is preferable to use only the TEM<sub>00</sub> mode, which produces a laser beam with a gaussian intensity distribution (see Figure 2.5) normal to the direction of propagation.

The variety of possible axial modes is generally of greater consequence. The various frequencies possible are given by Equation (9.2) so that the separation  $\Delta\nu$  of the axial modes is given by

$$\Delta\nu = \frac{c}{2d} \quad (9.4)$$

For a cavity length of, for example, 50 cm the axial mode separation is 300 MHz ( $0.01 \text{ cm}^{-1}$ ).

In practice the laser can operate only when  $n$ , in Equation (9.2), takes values such that the corresponding resonant frequency  $\nu$  lies within the line width of the transition between the two energy levels involved. If the active medium is a gas this line width may be the Doppler line width (see Section 2.3.2). Figure 9.3 shows a case where there are twelve axial modes within the Doppler profile. The number of modes in the actual laser beam depends on how much radiation is allowed to leak out of the cavity. In the example in Figure 9.3 the output level has been adjusted so that the so-called threshold condition allows six axial modes in the beam. The gain, or the degree of amplification, achieved in the laser is a measure of the intensity.

It is clear from Figure 9.3 that the laser line width for a single axial mode is much less than the Doppler line width. Normally a laser will operate in multimode fashion but for many purposes, for example in high-resolution spectroscopy using a laser source, it is desirable that the laser be made to operate in a single mode. One possible way of achieving this is clear from Equation (9.4). By making the cavity length  $d$  sufficiently short that only one axial mode lies within the Doppler profile, single-mode operation results. This method is applicable mostly to infrared lasers where the Doppler line width, of the order of 100 MHz, is relatively small. Whatever method is used for single-mode operation there is a considerable loss of laser power compared with multimode operation.

### 9.1.4 Q-switching

The quality factor  $Q$  of a laser cavity is defined as

$$Q = \frac{\nu}{\Delta\nu} \quad (9.5)$$

where  $\Delta\nu$  is the line width defined in Equation (9.4). Single-mode operation results in a laser line width related to the energy

Q-switching is achieved in a laser by preventing the laser from operating continuously. This is done by preventing the laser action building up. The laser is allowed to increase in intensity. Since the pulse width

a much shorter pulse. Various methods are used to achieve this. One simple in principle is to use a Pockels cell.

A Pockels cell (a crystal that changes its refracting index when an electric field is applied) passes through the laser beam. The laser beam is pure crystalline potassium dihydrogen phosphate ( $\text{KD}_2\text{PO}_4$ ,  $\text{KD}$ ).

Figure 9.4 shows a laser cavity in which the laser beam is plane polarized. The cavity is plane polarized. The laser beam is circularly polarized. The laser beam is of circular polarization. The laser beam is plane-polarized. The laser beam is polarized. It is from the output of the laser. The length of the laser

Fig

where  $\Delta\nu$  is the laser line width.  $Q$  can be regarded as the 'resolving power' of the cavity, as defined in Equation (3.3) for the dispersing element of a spectrometer. Single-mode operation results in a smaller  $\Delta\nu$  and, therefore, a higher  $Q$  than multimode operation.  $Q$  is related to the energy  $E_c$  stored in the cavity and the energy  $E_l$  allowed to leak out in time  $t$  by

$$Q = \frac{2\pi\nu E_c t}{E_l} \quad (9.6)$$

$Q$ -switching is an operation whereby the  $Q$  of a laser cavity is reduced for a short period of time by preventing the radiation from being reflected backwards and forwards between the cavity mirrors. During this time the population of the upper of the two levels involved in laser action builds up to a much higher value than it would be if  $Q$  remained high. Then  $Q$  is allowed to increase rapidly and the cycle is repeated, resulting in very short laser pulses. Since the pulse duration  $\Delta t$  is related to the pulse power  $P_p$  and energy  $E_p$  by

$$P_p = \frac{E_p}{\Delta t} \quad (9.7)$$

a much shorter pulse leads to a large increase in power. The resulting pulse is referred to as a giant pulse. Various methods of  $Q$ -switching are used. A rotating mirror in the laser cavity is simple in principle but a Pockels cell is used more often.

A Pockels cell is made from an electro-optic material which becomes birefringent (doubly refracting) when a voltage is applied across it. The result is that, if plane polarized radiation passes through the material, it emerges, in general, elliptically polarized. Such materials are pure crystalline ammonium dihydrogen phosphate  $[(\text{NH}_4)\text{H}_2\text{PO}_4]$ , abbreviated to ADP, potassium dihydrogen phosphate ( $\text{KH}_2\text{PO}_4$ , KDP), and potassium dideuterium phosphate ( $\text{KD}_2\text{PO}_4$ , KD\*P). All may be used in a laser operating in the visible region.

Figure 9.4 shows how a Pockels cell may be used in a laser cavity. The radiation in the cavity is plane-polarized by the polarizer P and passes to the Pockels cell, where it becomes circularly polarized when the voltage is applied. On reflection at the mirror  $M_1$  the direction of circular polarization is reversed. On passing through the Pockels cell a second time it is plane-polarized but at  $90^\circ$  to the original plane and, therefore, is not transmitted by the polarizer. It is only when the voltage is switched off that a  $Q$ -switched giant pulse emerges from the output mirror  $M_2$ . The timing of the voltage switching determines the power and length of the output pulses.

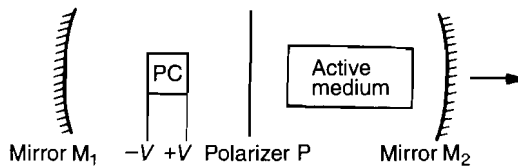


Figure 9.4 Use of Pockels cell (PC) in a laser cavity to produce  $Q$ -switching

9.1.5 Mode locking

Although *Q*-switching produces shortened pulses, typically 10–200 ns long, if we require pulses in the picosecond ( $10^{-12}$  s) or femtosecond ( $10^{-15}$  s) range the technique of mode locking may be used. This technique is applicable only to multimode operation of a laser and involves exciting many axial cavity modes but with the correct amplitude and phase relationship. The amplitudes and phases of the various modes are normally quite random.

Each axial mode has its own characteristic pattern of nodal planes and the frequency separation  $\Delta\nu$  between modes is given by Equation (9.4). If the radiation in the cavity can be modulated at a frequency of  $c/2d$  then the modes of the cavity are locked both in amplitude and phase since  $t_r$ , the time for the radiation to make one round-trip of the cavity (a distance  $2d$ ), is given by

$$t_r = \frac{2d}{c} \tag{9.8}$$

The result is that, for the case of a cavity operated with, say, seven modes, the output is like that in Figure 9.5 when the cavity is mode locked. Only the modes which have a node at one end of the cavity are output from the laser and all others are suppressed.

The width  $\Delta t$  of the pulse at half-height is given by

$$\Delta t = \frac{2\pi}{(2N + 1)\Delta\nu} \tag{9.9}$$

where  $(2N + 1)$  is the number of axial modes excited and  $\Delta\nu$  is their frequency separation.

One method of mode locking a visible laser is by placing an acoustic modulator in the cavity and driving it at a frequency of  $c/2d$ .

An important consequence of shortening a laser pulse is that the line width is increased as a result of the uncertainty principle as stated in Equation (1.16). When the width of the pulse is very small there is difficulty in measuring the energy precisely because of the rather small number of wavelengths in the pulse. For example, for a pulse width of 40 ps there is a frequency spread of the laser, given approximately by  $(2\pi\Delta t)^{-1}$ , of about 4.0 GHz ( $0.13 \text{ cm}^{-1}$ ).

Pulse lengths of  $< 100$  fs (1 femtosecond =  $10^{-15}$  s) have been achieved by mode locking.

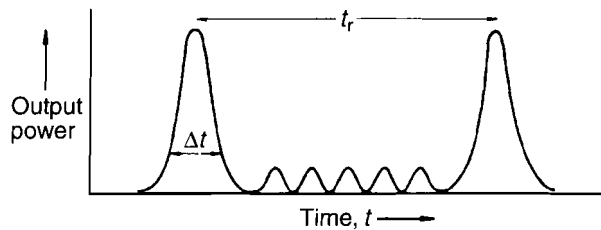


Figure 9.5 Suppression of five out of seven axial cavity modes by mode locking

9.1.6 Harmonic

In the context of electric field  $E$  by

In fact, this eq. in  $E$

where  $\beta$  is effects due to because they the very important. The magn

where  $A$  is

the radiat twice the t called frequ Equation

Worked

Question frequency genera

Answer when

### 9.1.6 Harmonic generation

In the context of discussion of the Raman effect, Equation (5.43) relates the oscillating electric field  $E$  of the incident radiation, the induced electric dipole  $\mu$  and the polarizability  $\alpha$  by

$$\mu = \alpha E \quad (9.10)$$

In fact, this equation is only approximate and  $\mu$  should really be expressed as a power series in  $E$

$$\begin{aligned} \mu &= \mu^{(1)} + \mu^{(2)} + \mu^{(3)} + \dots \\ &= \alpha E + \frac{1}{2}\beta E \cdot E + \frac{1}{6}\gamma E \cdot E \cdot E + \dots \end{aligned} \quad (9.11)$$

where  $\beta$  is known as the hyperpolarizability and  $\gamma$  the second hyperpolarizability. Any effects due to the second (or higher) terms in the series are referred to as non-linear effects because they arise from terms which are non-linear in  $E$ . These effects are usually small but at the very high power, and therefore  $E$ , characteristic of laser radiation causes them to be important.

The magnitude of the oscillating electric field is given by

$$E = A \sin 2\pi \nu t \quad (9.12)$$

where  $A$  is the amplitude and  $\nu$  the frequency. Since

$$E^2 = A^2 (\sin 2\pi \nu t)^2 = \frac{1}{2} A^2 (1 - \cos 4\pi \nu t) \quad (9.13)$$

the radiation scattered by the sample contains, due to the  $\mu^{(2)}$  term, some radiation with *twice* the frequency (or *half* the wavelength) of the incident radiation. The phenomenon is called frequency doubling or second harmonic generation. In general, higher-order terms in Equation (9.11) can result in third, fourth, etc., harmonic generation.

#### Worked example 9.2

*Question.* Show that the third term in Equation (9.11) results in the generation of radiation of frequency  $3\nu$  when radiation of frequency  $\nu$  is incident on a crystal capable of third harmonic generation.

*Answer.* The third term in equation (9.11) involves the cube of the oscillating electric field which (cf. Equation 9.13) is given by

$$E^3 = A^3 (\sin 2\pi \nu t)^3$$

But, in general,  $\sin^3 \theta = \frac{3}{4} \sin \theta - \frac{1}{4} \sin 3\theta$

$$\therefore E^3 = A^3 \left( \frac{3}{4} \sin 2\pi\nu t - \frac{1}{4} \sin 2\pi 3\nu t \right)$$

Because the second term in the brackets contains  $3\nu$  in the sine function, radiation at a frequency which is three times that of the incident radiation is generated. This is referred to as third harmonic generation. The first term in brackets indicates that some radiation of unchanged frequency also results.

There are several pure crystalline materials which may be used for frequency doubling. Examples are ADP, KDP and KD\*P, mentioned in Section 9.1.4, potassium pentaborate ( $\text{KB}_5\text{O}_8$ , KPB),  $\beta$ -barium borate ( $\text{BaB}_2\text{O}_4$ , BBO) and lithium niobate ( $\text{Li}_3\text{NbO}_4$ ). Each material being suitable for incident radiation of only a limited wavelength range in the visible region. The importance of these materials is that a laser operating in the visible region, of which there are a relatively large number, can be made to operate in the near-ultraviolet, where there are relatively few.

The efficiency of frequency doubling is quite low, often only a few per cent, but it may be as high as 20 to 30 per cent.

## 9.2 Examples of lasers

### 9.2.1 The ruby and alexandrite lasers

After the ammonia maser, operating in the microwave region and constructed by Townes *et al.* in 1954, the next major step forward was the ruby laser, operating in the red region of the spectrum and demonstrated in 1960 by Maiman. This is a solid state laser employing a ruby crystal consisting of aluminium oxide,  $\text{Al}_2\text{O}_3$ , containing 0.5 per cent by weight of  $\text{Cr}_2\text{O}_3$ , giving it a pale pink colour.

The lasing constituent is the  $\text{Cr}^{3+}$  ion which is in such low concentration that it can be regarded as a free ion. The ground configuration of  $\text{Cr}^{3+}$  (see Table 7.1) is  $KL3s^23p^63d^3$ , which gives rise to eight terms (see Table 7.2) of which  $^4F$  is, according to Hund's rules (see Section 7.1.2.3b), the lowest lying (ground) term. Of the others  $^2G$  is the lowest excited term. Each  $\text{Cr}^{3+}$  ion is in a crystal field (see Section 7.3.1.4a) of approximately octahedral symmetry. In the octahedral point group  $O_h$ , the  $^4F$  ground term gives  $^4A_2$ ,  $^4T_1$  and  $^4T_2$  states, and the  $^2G$  excited term gives  $^2A_1$ ,  $^2E$ ,  $^2T_1$  and  $^2T_2$  states. Of these,  $^4A_2$  is the ground state and  $^4T_1$ ,  $^4T_2$ ,  $^2E$  and  $^2T_2$  are relatively low-lying excited states: all are shown in Figure 9.6(a).

The  $^4T_1$  and  $^4T_2$  states are broadened as a result of slight variations in the crystal field. The  $^2T_2$  and  $^2E$  states are sharper but the  $^2E$  state is split into two components,  $29\text{ cm}^{-1}$  apart, because of the slight distortion of the octahedral field. Population inversion and

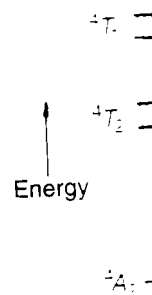


Figure 9.6.

consequent laser pumping into the  $^4T_2$  state. The ruby laser uses the  $^4T_2$  and  $^4T_1$  states of the  $\text{Cr}^{3+}$  ion. The flashlamp of the ruby laser is the ruby crystal itself, which is a mirror material 2 cm in diameter.

The transition from  $^4T_2$  to  $^4A_2$  is respectively, but

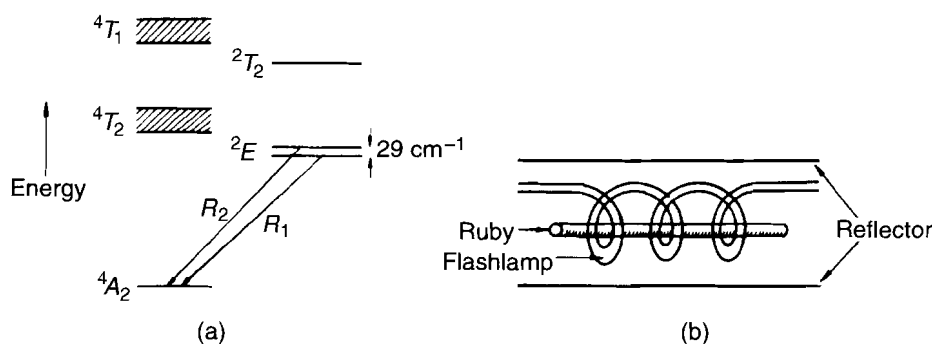
The laser noise of a large amount

The efficiency

Alexandrite laser is chrysoberyl ( $\text{Al}_2\text{O}_3$ ) in positions which are  $^4A_2$  ground state of the crystal

Lasing occurs in ruby (see Figure 9.6) of much greater. Because both alexandrite and ruby are both the electric dipole wide wave-length advantage over

A further advantage is a four-level laser with zero-point level and zero-point level



**Figure 9.6** (a) Low-lying energy levels of Cr<sup>3+</sup> in ruby. (b) Design for a ruby laser

consequent laser action occurs between the  $^2E$  and  $^4A_2$  states. This is achieved by optical pumping into the  $^4T_2$  or  $^4T_1$  states with 510–600 nm or 360–450 nm radiation, respectively. The ruby laser is seen to be a three-level laser, illustrated in Figure 9.2(b). The broadness of the  $^4T_2$  and  $^4T_1$  states contributes to the efficiency of pumping, which is achieved with a flashlamp of the type described in Section 3.5.4. This may be in the form of a helix around the ruby crystal as shown in Figure 9.6(b), the whole being contained in a reflector. The mirror material is deposited directly on to the ends of the crystal, which may be as large as 2 cm in diameter and 20 cm in length.

The transitions labelled  $R_1$  and  $R_2$  in Figure 9.6(a) are at 694.3 nm and 693.4 nm, respectively, but laser action involves principally  $R_1$ .

The laser normally operates in the pulsed mode because of the necessity of the dissipation of a large amount of heat between pulses.

The efficiency of a ruby laser is less than 0.1 per cent, typically low for a three-level laser.

Alexandrite, like ruby, contains Cr<sup>3+</sup> ions but they are substituted in the lattice of chrysoberyl, BeAl<sub>2</sub>O<sub>4</sub>. The chromium ions occupy two symmetrically non-equivalent positions which would otherwise be occupied by aluminium ions. In this environment the  $^4A_2$  ground state of Cr<sup>3+</sup> is broadened, compared with that in ruby, by coupling to vibrations of the crystal lattice.

Lasing occurs at 680.4 nm in alexandrite, the transition involved being analogous to  $R_1$  in ruby (see Figure 9.6a) and not involving any vibrational excitation in the  $^4A_2$  state. However, of much greater importance in alexandrite is laser action between the  $^4T_2$  and  $^4A_2$  states. Because both the  $^4T_2$  state and the  $^4A_2$  state are broadened by vibrational coupling the alexandrite laser is sometimes referred to as a vibronic laser. As a result of this broadening of both the electronic states involved in the  $^4T_2$ – $^4A_2$  transition the laser can be tuned over a wide wavelength range: 720–800 nm. This tunability gives the alexandrite laser a great advantage over the ruby laser, which is limited to just two wavelengths.

A further advantage is the higher efficiency of the alexandrite laser because of its being a four-level laser. In the illustration in Figure 9.2(c), level 4 is a vibronic level and level 3 the zero-point level of the  $^4T_2$  state. Level 2 is a vibronic level of the  $^4A_2$  state and level 1 the zero-point level. Because of the excited nature of level 2 it is almost depopulated at room

temperature so that a population inversion between levels 3 and 2 is relatively easy to achieve. In fact, level 2 is a continuous band of vibronic levels covering a wide energy range resulting in the wide wavelength range over which the laser is tunable.

Pumping is with a flashlamp, as in the case of the ruby laser, and a pulse energy of order 1 J may be achieved. Frequency doubling (second harmonic generation) can provide tunable radiation in the 360–400 nm region.

### 9.2.2 The titanium–sapphire laser

Despite the fact that the first laser to be produced (the ruby laser, Section 9.2.1) has the remarkable property of having all its power concentrated into one or two wavelengths, a property possessed by most lasers, it was soon realized that the inability to change these wavelengths appreciably, that is to tune the laser, is a serious drawback which limits the range of possible applications.

Historically, the first type of laser to be tunable over an appreciable wavelength range was the dye laser, to be described in Section 9.2.10. The alexandrite laser (Section 9.2.1), a tunable solid state laser, was first demonstrated in 1978 and then, in 1982, the titanium–sapphire laser. This is also a solid state laser but tunable over a larger wavelength range, 670–1100 nm, than the alexandrite laser, which has a range of 720–800 nm.

The lasing medium in the titanium–sapphire laser is crystalline sapphire ( $\text{Al}_2\text{O}_3$ ) with about 0.1 per cent by weight of  $\text{Ti}_2\text{O}_3$ . The titanium is present as  $\text{Ti}^{3+}$  and it is between energy levels of this ion that lasing occurs.

The ground configuration of  $\text{Ti}^{3+}$  (see Table 7.1) is  $KL3s^23p^63d^1$ . The crystal field experienced by the ion splits the  $3d$  orbital into a triply degenerate lower-energy  $t_2$  orbital and a doubly degenerate higher-energy  $e$  orbital (see Figure 7.38). If the electron is in the lower orbital a  ${}^2T_2$  ground state results and, if it is in the upper orbital, a  ${}^2E$  excited state results. These states are about  $19\,000\text{ cm}^{-1}$  apart but each is split into further components and is also coupled to the vibrations of the crystal lattice. In a similar way to that in alexandrite (Section 9.2.1) population inversion can be created between these two sets of levels resulting in a four-level vibronic laser with a tunable range of 670–1100 nm.

A further advantage, compared with the alexandrite laser, apart from a wider tuning range, is that it can operate in the CW as well as in the pulsed mode. In the CW mode the  $\text{Ti}^{3+}$ –sapphire laser may be pumped by a CW argon ion laser (see Section 9.2.6) and is capable of producing an output power of 5 W. In the pulsed mode pumping is usually achieved by a pulsed  $\text{Nd}^{3+}$ :YAG laser (see Section 9.2.3) and a pulse energy of 100 mJ may be achieved.

In 1991 a remarkable discovery was made, accidentally, with a  $\text{Ti}^{3+}$ –sapphire laser pumped with an  $\text{Ar}^+$  laser. Whereas we would expect this to result in CW laser action, when a sharp jolt was given to the table supporting the laser, mode locking (Section 9.1.5) occurred. This is known as self-locking of modes, and we shall not discuss further the reasons for this and how it can be controlled. One very important property of the resulting pulses is that they are very short. Pulse widths of a few tens of femtoseconds can be produced routinely and with high pulse-to-pulse stability. Further modification to the laser can

produce pulses  
widths of less than

### 9.2.3 The neodymium laser

Laser action can be achieved in various matrices, including yttrium aluminium garnet.

The neodymium ion has a ground state consisting of the terms arising from  $S = \frac{3}{2}$ , giving a multiplet structure as shown in Figure 9.7(a). Also shown is the laser action transition.

Laser action is not the ground state, consequently the ground state is not the ground state.

In free  $\text{Nd}^{3+}$  the ground state is  ${}^4F_{3/2}$  and  $\Delta J = 1$ . In  $\text{Nd}^{3+}$  in a crystal field the ground state is split into several levels, as shown in Figure 9.7(b).

Figure 9.7

produce pulses as short as 8 fs. Commercially, such lasers are available producing pulse widths of less than 100 fs at a repetition rate of 80 MHz with a peak power of 1 W.

### 9.2.3 The neodymium-YAG laser

Laser action can be induced in  $\text{Nd}^{3+}$  ions embedded in a suitable solid matrix. Several matrices, including some special glasses, are suitable but one of the most frequently used is yttrium aluminium garnet ( $\text{Y}_3\text{Al}_5\text{O}_{12}$ ), which is referred to as YAG.

The neodymium atom has the ground configuration  $\dots 4d^{10}4f^45s^25p^66s^2$  and a  $^5I_4$  ground state (see Table 7.1). The ground configuration of  $\text{Nd}^{3+}$  is  $\dots 4d^{10}4f^35s^25p^6$  and, of the terms arising from it,  $^4I$  and  $^4F$  are important in the laser. For the  $^4I$  term  $L = 6$  and  $S = \frac{3}{2}$ , giving  $J = \frac{15}{2}, \frac{13}{2}, \frac{11}{2}, \frac{9}{2}$  in the Russell-Saunders approximation (see Section 7.1.2.3). The multiplet is normal, that is, the lowest value of  $J$  has the lowest energy, as in Figure 9.7(a). Also shown in Figure 9.7 is the normal multiplet arising from the  $^4F$  term.

Laser action involves mainly the  $^4F_{3/2} - ^4I_{11/2}$  transition at about  $1.06 \mu\text{m}$ . Since  $^4I_{11/2}$  is not the ground state, the laser operates on a four-level system (see Figure 9.2c) and consequently is much more efficient than the ruby laser.

In free  $\text{Nd}^{3+}$  the  $^4F_{3/2} - ^4I_{11/2}$  transition is doubly forbidden, violating the  $\Delta L = 0, \pm 1$  and  $\Delta J = 0, \pm 1$  selection rules (see Section 7.1.6). In the YAG crystal the  $^4I_{11/2}$  state of  $\text{Nd}^{3+}$  is split by crystal field interactions into six and the  $^4F_{3/2}$  state into two components, as shown in Figure 9.7(b). There are eight transitions, grouped around  $1.06 \mu\text{m}$ , between the

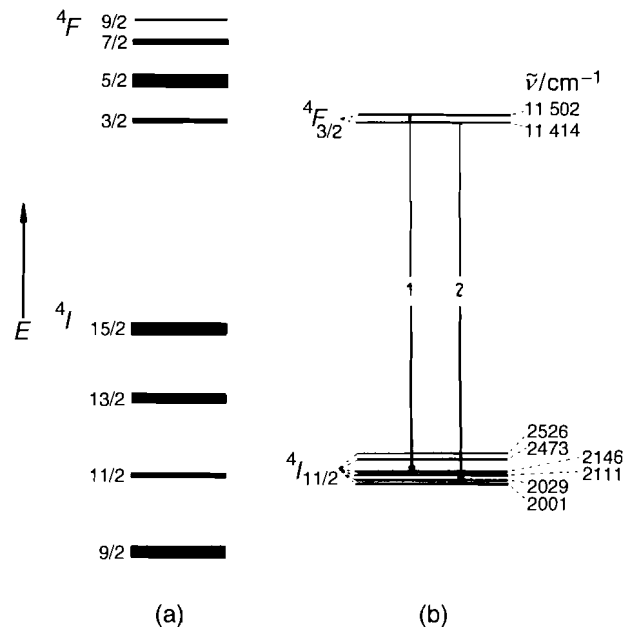


Figure 9.7 Energy levels in (a) free  $\text{Nd}^{3+}$  and (b)  $\text{Nd}^{3+}$  split by crystal field interactions

components but only the two marked in the figure are important. At room temperature transition 1 at  $1.0648 \mu\text{m}$  is dominant but at  $77 \text{ K}$  transition 2 at  $1.0612 \mu\text{m}$  is dominant.

A krypton arc lamp may be used for CW pumping or a flashlamp for much higher power pulsed operation.

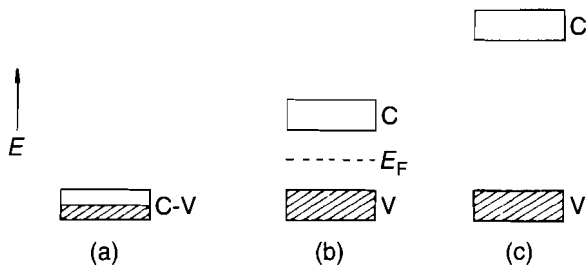
The  $\text{Nd}^{3+}$ :YAG rod is a few centimetres long and contains 0.5 to 2.0 per cent by weight of  $\text{Nd}^{3+}$ . In pulsed operation the peak power of each pulse is sufficiently high for generation of second, third or fourth harmonics at  $533 \text{ nm}$ ,  $355 \text{ nm}$  and  $266 \text{ nm}$ , respectively, using suitable crystals.

### 9.2.4 The diode or semiconductor laser

A diode, or semiconductor, laser operates in the near-infrared and into the visible region of the spectrum. Like the ruby and  $\text{Nd}^{3+}$ :YAG lasers it is a solid state laser but the mechanism involved is quite different.

Figure 9.8(a) shows how the conduction band<sup>1</sup> C and the empty valence band V are not separated in a conductor whereas Figure 9.8(c) shows that they are well separated in an insulator. The situation in a semiconductor, shown in Figure 9.8(b), is that the band gap between the conduction and valence bands, is sufficiently small that promotion of electrons into the conduction band is possible by heating the material. For a semiconductor the Fermi energy  $E_F$ , such that at  $T=0 \text{ K}$  all levels with  $E < E_F$  are filled, lies between the bands as shown.

Semiconductors may also be made from a material which is normally an insulator by introducing an impurity, a process known as doping. Figure 9.9 shows two ways in which an impurity may promote semiconducting properties. In Figure 9.9(a) the dopant has one more valence electron per atom than the host and contributes a band of filled impurity levels I close to the conduction band of the host. This characterizes an n-type semiconductor. An example is silicon ( $KL3s^23p^2$ ) doped with phosphorus ( $KL3s^23p^3$ ), which reduces the band gap to about  $0.05 \text{ eV}$ . Since  $kT$  at room temperature is about  $0.025 \text{ eV}$ , the phosphorus



**Figure 9.8** Conduction band, C, and valence band, V, in (a) a conductor, (b) a semiconductor and (c) an insulator

<sup>1</sup> Bands in the solid state can be regarded as grossly delocalized orbitals extending throughout the sample.

**Figure 9.9** Impurity band and  $V$  the valence band

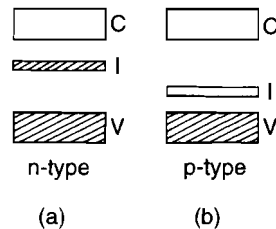
converts silicon to a semiconductor.

Alternatively, an impurity contributes an impurity band (KL3s<sup>2</sup>3p<sup>3</sup>) in the valence band.

A semiconductor can be an n-type or a p-type. A semiconductor with an n-type impurity is called a semiconductor with n-type conduction and is shown in Figure 9.9.

If a voltage is applied across the n and p regions, current flows in the opposite direction to the Fermi energy. This is an example of the Seebeck effect, as seen in Section 9.1.

**Figure 9.9** Impurity band and voltage across



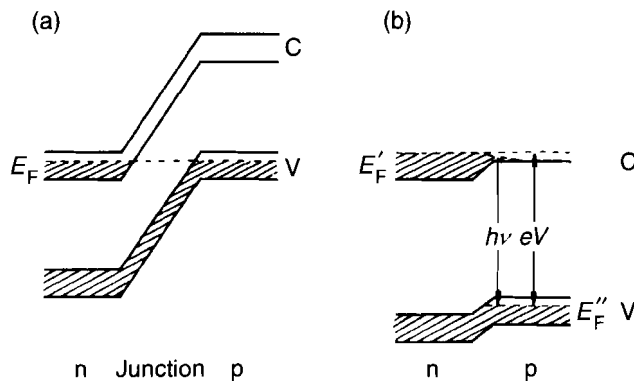
**Figure 9.9** Impurity levels I in (a) an n-type and (b) a p-type semiconductor; C is the conduction band and V the valence band

converts silicon from a high-temperature semiconductor into a room-temperature semiconductor.

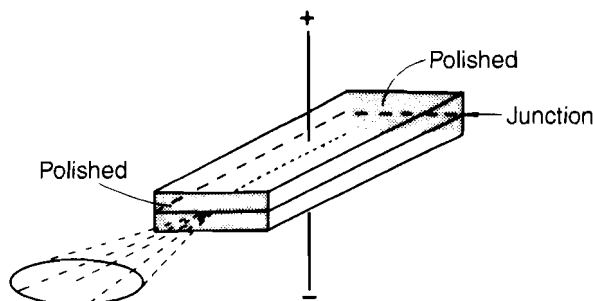
Alternatively, as in Figure 9.9(b), a dopant with one valence electron fewer than the host contributes an impurity band I which is empty but more accessible to electrons from the valence band. An example of such a p-type semiconductor is silicon doped with aluminium ( $KL3s^23p^1$ ) in which the band gap is about 0.08 eV.

A semiconductor laser takes advantage of the properties of a junction between a p-type and an n-type semiconductor made from the same host material. Such an n-p combination is called a semiconductor diode. Doping concentrations are quite high and, as a result, the conduction and valence band energies of the host are shifted in the two semiconductors, as shown in Figure 9.10(a). Bands are filled up to the Fermi level with energy  $E_F$ .

If a voltage is applied to the junction with the negative and positive terminals attached to the n and p regions, respectively, electrons flow from the n to the p region, and positive holes in the opposite direction. The levels are also displaced, as shown in Figure 9.10(b), and the Fermi energies  $E'_F(n)$  and  $E''_F(p)$  are now unequal, resulting in a population inversion in the region of the junction and leading to laser action. The semiconductor laser is, unusually, an example of a two-level system, but the population inversion is not obtained by pumping: we saw in Section 9.1.2 that this could not be done.



**Figure 9.10** (a) The Fermi level  $E_F$  in the region of a p-n junction. (b) The result of applying a voltage across the junction; C is the conduction band and V the valence band



**Figure 9.11** A semiconductor, or diode, laser

A typical semiconductor laser, shown in Figure 9.11, is small, only a few millimetres long and with an effective thickness of about  $2\ \mu\text{m}$ .

A variety of materials are used depending on the region in which the laser is required to operate. For example, a range of lead alloy semiconductors such as  $\text{Pb}_{1-x}\text{Sn}_x\text{Se}$  and  $\text{PbS}_{1-x}\text{Se}_x$  covers the range  $2.8\text{--}30\ \mu\text{m}$ . Semiconductor lasers can be tuned but the tuning range of a particular laser is small so that a whole series of them is necessary to cover an appreciable wavelength range. Gross tuning of the wavelength is achieved by surrounding the laser with a refrigeration unit to control and vary the temperature.

The two ends of the laser diode in Figure 9.11 are polished to increase internal reflection. As a consequence of the cavity geometry the laser beam is, unlike that of most lasers, highly divergent.

Semiconductor lasers are some of the most efficient of all lasers, with an efficiency of about 30 per cent.

### 9.2.5 The helium–neon laser

The helium–neon laser is a CW gas laser which is simple and reliable to operate and, if the laser is of relatively low power, quite inexpensive.

Laser action takes place between excited levels of the neon atoms, in a four-level scheme, the helium atoms serving only to mop up energy from the pump source and transfer it to neon atoms on collision. The energy level scheme is shown in Figure 9.12.

Pumping is electrical, a discharge being created in a helium–neon gas mixture by applying either a high voltage through internal electrodes or by applying microwave radiation externally. Helium atoms are excited, on collision with electrons present in the discharge, to various excited states. Of these the  $2^3S_1$  and  $2^1S_0$  states are metastable, and therefore long-lived, because transitions to the  $1^1S_0$  ground state are forbidden (see Section 7.1.5).

The ground configuration of Ne is  $1s^22s^22p^6$ , giving a  $1^1S_0$  state. The excited configurations give rise to states to which the Russell–Saunders approximation does not apply. Nevertheless, any  $\dots 2p^5ns^1$  or  $\dots 2p^5np^1$  configuration, with  $n > 2$ , gives rise to four or ten states, respectively, as would be the case in the Russell–Saunders approximation (see

**Figure 9.12**  
of states and...

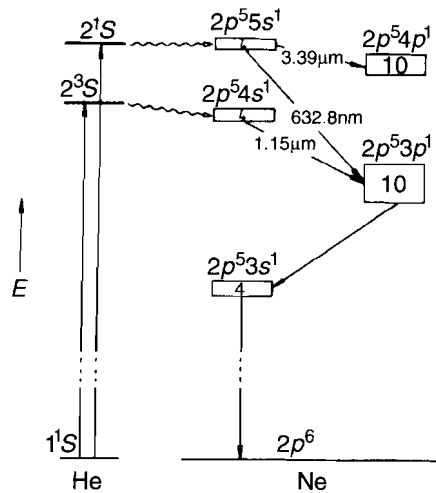
Section 7.1.2  
the approxi...

The states  
energy as the  
population of  
of Ne lie ju  
 $\dots 2p^5ns^1$  st  
 $\dots 2p^5np^1$  st  
inversion bet

The first l  
infrared clos  
being at 1.3  
red region. t

Infrared l  
not particu  
they deple  
The 3.39  $\mu$   
specifically  
to deflect th

Decay fro  
are relativel  
of the ...  
trapping. th  
632.8 nm t



**Figure 9.12** Energy levels of the He and Ne atoms relevant to the helium–neon laser. The number of states arising from each Ne configuration is given in a ‘box’

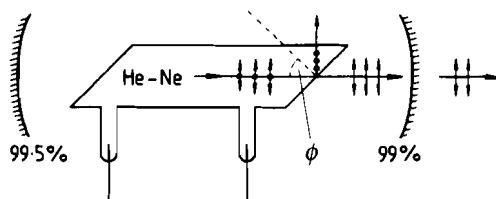
Section 7.1.2.3) and as is indicated in boxes in Figure 9.12. We shall not be concerned with the approximation which is appropriate for describing these states.

The states arising from the  $\dots 2p^5 5s^1$  configuration of Ne have very nearly the same energy as that of the  $2^1S_0$  state of He so that collisional energy transfer results in efficient population of these Ne states. Similarly, the states arising from the  $\dots 2p^5 4s^1$  configuration of Ne lie just below the  $2^3S_1$  state of He and are also populated by collisions. All the  $\dots 2p^5 ns^1$  states have lifetimes of the order of 100 ns compared with 10 ns for the  $\dots 2p^5 np^1$  states. These conditions are ideal for four-level lasing in Ne with population inversion between the  $\dots 2p^5 ns^1$  and  $\dots 2p^5 np^1$  states.

The first laser lines to be discovered in the He–Ne system were a group of five in the infrared close to 1.15  $\mu\text{m}$  and involving  $\dots 2p^5 4s^1 - \dots 2p^5 3p^1$  transitions, the strongest being at 1.1523  $\mu\text{m}$ . Similarly, the  $\dots 2p^5 5s^1 - \dots 2p^5 3p^1$  transitions give laser lines in the red region, the one at 632.8 nm being the strongest.

Infrared laser lines involving  $\dots 2p^5 5s^1 - \dots 2p^5 4p^1$  transitions in the 3.39  $\mu\text{m}$  region are not particularly useful. However, they do cause some problems in a 632.8 nm laser because they deplete the populations of the  $\dots 2p^5 5s^1$  states and decrease the 632.8 nm intensity. The 3.39  $\mu\text{m}$  transitions are suppressed by using multilayer cavity mirrors designed specifically for the 632.8 nm wavelength or by placing a prism in the cavity orientated so as to deflect the infrared radiation out of the cavity.

Decay from the  $\dots 2p^5 3p^1$  states to the  $\dots 2p^5 3s^1$  states is rapid but the  $\dots 2p^5 3s^1$  states are relatively long-lived. Their populations tend to build up and this increases the probability of the  $\dots 2p^5 3p^1 \rightarrow \dots 2p^5 3s^1$  radiation being reabsorbed, a process known as radiation trapping, thereby increasing the  $\dots 2p^5 3p^1$  population and decreasing the laser efficiency at 632.8 nm (and 1.15  $\mu\text{m}$ ). Depopulation of the  $\dots 2p^5 3s^1$  states occurs on collision with the



**Figure 9.13** A helium–neon laser

walls of the discharge tube. For this reason narrow tubes, only a few millimetres in diameter, are used.

Figure 9.13 illustrates the construction of a helium–neon laser. In this example the discharge in the gas mixture (typically ten parts of He to one of Ne at a total pressure of about 1 Torr) is excited by internal electrodes. On the ends of the discharge tube are Brewster angle windows to prevent excessive light loss from multiple transmissions. If a window is at  $90^\circ$  to the optic axis of the laser a certain percentage is lost every time the radiation passes through. However, if the window is oriented at Brewster's angle  $\phi$ , as shown, some is lost by reflection on the first transmission but no more is lost on subsequent transmissions. As the figure also shows, for unpolarized radiation incident from inside the cavity, the transmitted and reflected radiation are plane polarized, the planes being at  $90^\circ$  to each other. The laser beam is, therefore, plane polarized.

One of the mirrors forming the laser cavity is as close to 100% reflecting as possible (99.5%); the other is coated to allow 1% of the radiation to emerge as the laser beam.

Brewster's angle is given by

$$\tan \phi = n \quad (9.14)$$

where  $n$  is the refractive index of the window material. Since  $n$  varies with wavelength, so does  $\phi$  but, for glass in the visible region,  $\phi \simeq 57^\circ$  and varies little with wavelength.

### 9.2.6 The argon ion and krypton ion lasers

Laser action occurs in the noble gas ions  $\text{Ne}^+$ ,  $\text{Ar}^+$ ,  $\text{Kr}^+$  and  $\text{Xe}^+$  but that in  $\text{Ar}^+$  and  $\text{Kr}^+$  produces the most useful lasers.

These ion lasers are very inefficient, partly because energy is required first to ionize the atom and then to produce the population inversion. This inefficiency leads to a serious problem of heat dissipation, which is partly solved by using a plasma tube, in which a low-voltage high-current discharge is created in the Ar or Kr gas, made from beryllium oxide,  $\text{BeO}$ , which is an efficient heat conductor. Water cooling of the tube is also necessary.

Most  $\text{Ar}^+$  and  $\text{Kr}^+$  lasers are CW. A gas pressure of about 0.5 Torr is used in a plasma tube of 2–3 mm bore. Powers of up to 40 W distributed among various laser wavelengths can be obtained.

The spectroscopic lasers because lasers were first

The ground orbital into excited states arise from promotion of one of the  $3p$

The  $\text{Ar}^+$  laser being at 488.0 nm 800 nm region contains a wide range of wavelengths

### 9.2.7 The nitrogen laser

The molecular configuration rise to the singlet and particular to equilibrium

In a high two electrodes because it whereas the near u

<sup>2</sup> The rest of the usual

The spectroscopy of ion lasers is generally less well understood than that of neutral atom lasers because of the lack of detailed knowledge of ion energy-level schemes. Indeed, ion lasers were first produced accidentally and attempts to assign the transitions came later.

The ground configuration of  $\text{Ar}^+$  is  $KL3s^23p^5$ , giving an inverted  $^2P_{3/2}, ^2P_{1/2}$  multiplet. The excited states involved in laser action involve promotion of an electron from the  $3p$  orbital into excited  $4s, 5s, 4p, 5p, 3d, 4d, \dots$  orbitals. Similarly, excited states of  $\text{Kr}^+$  involved arise from promotion of an electron from the  $4p$  orbital. In  $\text{Ar}^+$  the  $KL3s^23p^4$  configuration gives rise to  $^1S, ^3P, ^1D$  terms (see Section 7.1.2.3). Most laser transitions involve the core in one of the  $^3P$  states and the promoted electron in the  $4p$  orbital.

The  $\text{Ar}^+$  laser produces about ten lines in the 454 nm to 529 nm region, the most intense being at 488.0 nm and 514.5 nm. The  $\text{Kr}^+$  laser produces about nine lines in the 476 nm to 800 nm region, with the 647.1 nm line being the most intense. Quite commonly, a laser contains a mixture of argon and krypton gases and is capable of producing a fairly wide range of wavelengths.

### 9.2.7 The nitrogen ( $\text{N}_2$ ) laser

The molecular orbital configuration of  $\text{N}_2$  has been described in Section 7.2.1.1. The ground configuration of Equation (7.57) can be abbreviated to  $\dots(\sigma_u^*2s)^2(\pi_u2p)^4(\sigma_g2p)^2$  and gives rise to the  $X^1\Sigma_g^+$  ground state. When an electron is promoted to a higher-energy orbital, singlet and triplet states result. We shall be concerned here with only the triplet states and, in particular, the  $A^3\Sigma_u^+, B^3\Pi_g$  and  $C^3\Pi_u$  states.<sup>2</sup> The orbital configurations and values of  $r_e$ , the equilibrium internuclear distance, for these states are given in Table 9.1.

In a high-voltage discharge through nitrogen gas there is a deep pink glow due mainly to two electronic band systems in emission. The  $B-A$  system, or so-called first positive system because it was thought initially to be due to  $\text{N}_2^+$ , stretches from the red to the green region whereas the  $C-B$  system, or so-called second positive system, stretches from the blue into the near ultraviolet.

**Table 9.1** Molecular orbital (MO) configurations and equilibrium bond lengths  $r_e$  of  $\text{N}_2$

State	MO configuration	$r_e/\text{\AA}$
$X^1\Sigma_g^+$	$\dots(\sigma_u^*2s)^2(\pi_u2p)^4(\sigma_g2p)^2$	1.0977
$A^3\Sigma_u^+$	$\dots(\sigma_u^*2s)^2(\pi_u2p)^3(\sigma_g2p)^2(\pi_g^*2p)^1$	1.2866
$B^3\Pi_g$	$\dots(\sigma_u^*2s)^2(\pi_u2p)^4(\sigma_g2p)^1(\pi_g^*2p)^1$	1.2126
$C^3\Pi_u$	$\dots(\sigma_u^*2s)^1(\pi_u2p)^4(\sigma_g2p)^2(\pi_g^*2p)^1$	1.1487

<sup>2</sup> The reader is reminded that the labels  $A, B, C$  rather than  $a, b, c$  for triplet states of  $\text{N}_2$  do not follow the usual convention.

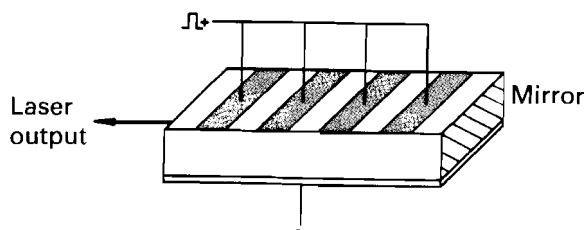


Figure 9.14 Nitrogen laser cavity

Laser action has been obtained in a few transitions in both these systems but the  $C-B$  laser action has proved to be more important because it resulted in the first ultraviolet laser. It is only this system that we shall consider here.

The values of the equilibrium internuclear distance  $r_e$  for the various states, listed in Table 9.1, indicate that the minimum of the potential for the  $C$  state lies almost vertically above that of the  $X$  state, as in Figure 7.20(b), whereas those of states  $B$  and  $A$  are shifted to high  $r$ . The result is that the electron-molecule collisional cross-section for the transition from  $v'' = 0$  in the  $X$  state to  $v' = 0$  in the  $C$  state is greater than that for analogous transitions in the  $A-X$  and  $B-X$  systems. A population inversion is created between the  $v = 0$  level of the  $C$  state and the  $v = 0$  level of the  $B$  state. Lasing has been observed in the 0-0 transition, as well as in the 0-1 transition, of the  $C-B$  system. However, the laser action is self-terminating because the lifetime of the lower state  $B$  (10  $\mu$ s) is longer than that of the upper state  $C$  (40 ns). This does not render laser action impossible but necessitates pulsing of the input energy with a pulse length shorter than the lifetime of the  $C$  state.

A design for a nitrogen laser is shown in Figure 9.14. A pulsed high voltage of about 20 kV, triggered by a spark gap or a thyratron, is applied transversely across the cavity. A single mirror is used to double the output. Laser pulses of about 10 ns length are typical. Peak power can be as much as 1 MW. The maximum repetition rate is about 100 Hz with longitudinally flowing gas. Much higher repetition rates are possible for transverse flow.

The operating wavelength of a nitrogen laser is 337 nm for the 0-0 transition of the  $C-B$  system.

### 9.2.8 The excimer and exciplex lasers

An excimer is a dimer which is stable only in an excited electronic state but dissociates readily in the ground state. Examples of these are the noble gas dimers such as  $\text{He}_2$ , discussed in Section 7.2.5.6. This molecule has a repulsive  $X^1\Sigma_g^+$  ground state but a bound  $A^1\Sigma_u^+$  excited state, as illustrated in Figure 7.24(a).

Such a situation suggests the possibility of creating a population inversion and laser action between two such states, since any molecules in the repulsive ground state have an extremely short lifetime, typically a few picoseconds. A laser operating by this mechanism is a

two-level laser state molecule of two atoms, of fairly high, a

An  $\text{Xe}_2$  e importance a and bound e consisting, n electronic st between an excimer lase

Excimer l and  $\text{XeI}$  as t

The meth electrical di such an exc

In an exc pumped aro

The exam (308 nm) a

Because th bound, ther

In the case supports a t

The excu power of up

Figure 9. bound exc

two-level laser but population of the upper state is not, of course, caused by pumping ground state molecules. Molecules in the upper state are created in a discharge by collisions between two atoms, one or both of which may be in an excited state. The efficiency of such lasers is fairly high, about 20 per cent.

An  $\text{Xe}_2$  excimer laser has been made to operate in this way, but of much greater importance are the noble gas halide lasers. These halides also have repulsive ground states and bound excited states: they are examples of exciplexes. An exciplex is a complex consisting, in a diatomic molecule, of two *different* atoms, which is stable in an excited electronic state but dissociates readily in the ground state. In spite of this clear distinction between an excimer and an exciplex it is now common for all such lasers to be called excimer lasers.

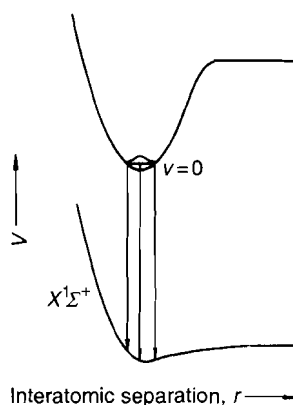
Excimer lasers employing NeF, ArF, KrF, XeF, ArCl, KrCl, XeCl, ArBr, KrBr, XeBr, KrI, and XeI as the active medium have been made.

The method of excitation was, in the early days, by an electron beam but now a transverse electrical discharge, like that for the nitrogen laser shown in Figure 9.14, is used. Indeed such an excimer laser can be converted to a nitrogen laser by changing the gas.

In an excimer laser the mixture of inert gas, halogen gas, and helium, used as a buffer, is pumped around a closed system consisting of a reservoir and the cavity.

The examples of ArF (193 nm), KrF (248 nm), XeF (351 nm), KrCl (222 nm), XeCl (308 nm) and XeBr (282 nm) indicate the range of wavelengths from excimer lasers. Because the ground states of these molecules are not totally repulsive but very weakly bound, there is a very shallow minimum in the potential curve, as illustrated in Figure 9.15. In the case of XeF the potential energy minimum is relatively deep, about  $1150 \text{ cm}^{-1}$ , and supports a few vibrational levels. As a result the laser may be tuned over several transitions.

The excimer laser radiation is pulsed with a typical maximum rate of about 200 Hz. Peak power of up to 5 MW is high compared with that of a nitrogen laser.



**Figure 9.15** Potential energy ( $V$ ) curves for a very weakly bound ground state and a strongly bound excited state of a noble gas halide

### 9.2.9 The carbon dioxide laser

The CO<sub>2</sub> laser is a near-infrared gas laser capable of very high power and with an efficiency of about 20 per cent. CO<sub>2</sub> has three normal modes of vibration:  $\nu_1$ , the symmetric stretch,  $\nu_2$ , the bending vibration, and  $\nu_3$ , the antisymmetric stretch, with symmetry species  $\sigma_g^+$ ,  $\pi_u$ , and  $\sigma_u^+$ , and fundamental vibration wavenumbers of 1354, 673, and 2396 cm<sup>-1</sup>, respectively. Figure 9.16 shows some of the vibrational levels, the numbering of which is explained in footnote 4 of Chapter 4 (page 93), which are involved in the laser action. This occurs principally in the  $3_0^1 2_2^0$  transition, at about 10.6  $\mu\text{m}$ , but may also be induced in the  $3_0^1 1_1$  transition, at about 9.6  $\mu\text{m}$ .

Population of the  $3^1$  level is partly by electron-molecule collisions and partly by energy transfer from nitrogen molecules in the  $v = 1$  level, this being metastable due to the fact that the transition to  $v = 0$  is forbidden (see Section 6.1.1). Energy transfer from nitrogen is particularly efficient because the  $v = 1$  level is only 18 cm<sup>-1</sup> below the  $3^1$  level of CO<sub>2</sub> (Figure 9.16). Because of near-degeneracies of higher vibrational levels of nitrogen and the  $\nu_3$  stack of CO<sub>2</sub>, transfer to levels such as  $3^2, 3^3, \dots$  also occurs. Transitions down the  $\nu_3$  stack are fast until the  $3^1$  level is reached.

Decay of the  $1^1$  and  $2^2$  lower levels<sup>3</sup> of the laser transitions are rapid down to the  $2^1$  level; this is depopulated mostly by collisions with helium atoms in the CO<sub>2</sub>:N<sub>2</sub>:He gas mixture which is used.

Lifetimes of upper and lower states are governed by collisions and that of the upper is always longer than that of the lower in the gas mixtures used.

The energy input into a CO<sub>2</sub> laser is in the form of an electrical discharge through the mixture of gases. The cavity may be sealed, in which case a little water vapour must be added in order to convert back to CO<sub>2</sub> any CO which is formed. More commonly, longitudinal or, preferably, transverse gas flow through the cavity is used. The CO<sub>2</sub> laser can operate in a CW or pulsed mode, with power up to 1 kW possible in the CW mode.

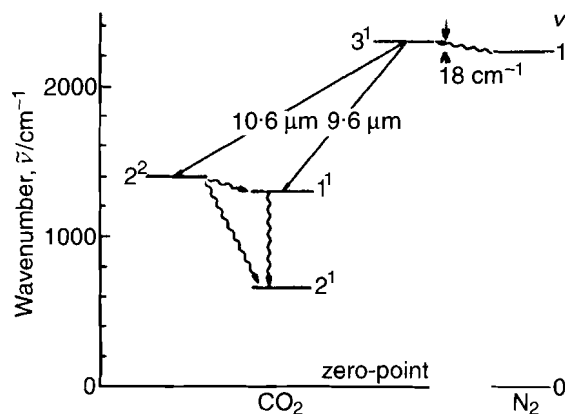


Figure 9.16 Vibrational levels of N<sub>2</sub> and CO<sub>2</sub> relevant to the CO<sub>2</sub> laser

<sup>3</sup> The assignments of these levels was reversed in 1965. The new assignments are used here.

Each of the  
for linear mo  
and R branch  
Figure 6.25

Unless the  
the highest  
highest popu  
temperatures  
of rotational

The cavity  
one of the m

### 9.2.10 The dye laser

Laser action  
This led to  
range. Dye

One char  
electronic st  
of a dye is  
Equation 2  
Equation 7

Figure 9.  
the typical

Figure  
(5 × 10<sup>7</sup>  
and that  
Chapter 4  
Dekker.

Each of the lasing vibrational transitions has associated rotational fine structure, discussed for linear molecules in Section 6.2.4.1. The  $3_0^1 1_0^+$  transition is  $\Sigma_u^+ - \Sigma_g^+$  with associated  $P$  and  $R$  branches, for which  $\Delta J = -1$  and  $+1$ , respectively, similar to the  $3_0^1$  band of HCN in Figure 6.25. The  $3_0^1 2_0^+$  band is, again,  $\Sigma_u^+ - \Sigma_g^+$  with a  $P$  and  $R$  branch.

Unless the cavity is tuned to a particular wavelength the vibration-rotation transition with the highest gain is the  $P$ -branch transition involving the rotational level which has the highest population in the  $3^1$  state. This is  $P(22)$ , with  $J'' = 22$  and  $J' = 21$ , at normal laser temperatures. The reason why this  $P$ -branch line is so dominant is that thermal redistribution of rotational level populations is faster than the population depletion due to emission.

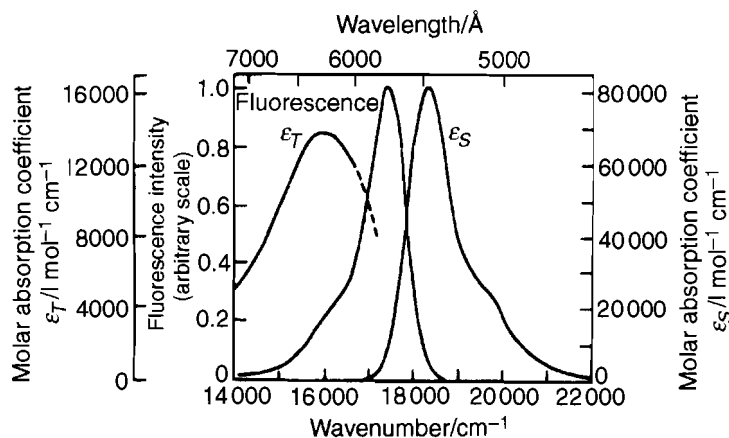
The cavity may be tuned to a particular transition by a prism or, preferably, by replacing one of the mirrors (not the output mirror) at one end of the cavity by a diffraction grating.

### 9.2.10 The dye laser

Laser action in some dye solutions was first discovered by Lankard and Sorokin in 1966. This led to the first laser which was continuously tunable over an appreciable wavelength range. Dye lasers are also unusual in that the active medium is a liquid.

One characteristic property of dyes is their colour due to absorption from the ground electronic state  $S_0$  to the first excited singlet state  $S_1$  lying in the visible region. Also typical of a dye is a high absorbing power characterized by a value of the oscillator strength  $f$  (see Equation 2.18) close to 1, and also a value of the fluorescence quantum yield  $\Phi_F$  (see Equation 7.135) close to 1.

Figure 9.17 illustrates these features in the case of the dye rhodamine B. The maximum of the typically broad  $S_1 - S_0$  absorption occurs at about 548 nm with a very high value of



**Figure 9.17** Absorption and fluorescence spectra of rhodamine B in methanol ( $5 \times 10^{-5}$  mol l $^{-1}$ ). The curve marked  $\epsilon_T$  is for the  $T_2 - T_1$  absorption (process 8 in Figure 9.18) and that marked  $\epsilon_S$  for process 1. (Reproduced, with permission, from Dienes, A. and Shank, C. V., Chapter 4 in *Creation and Detection of the Excited State* (Ed. W. R. Ware), Vol. 2, p. 154, Marcel Dekker, New York, 1972)

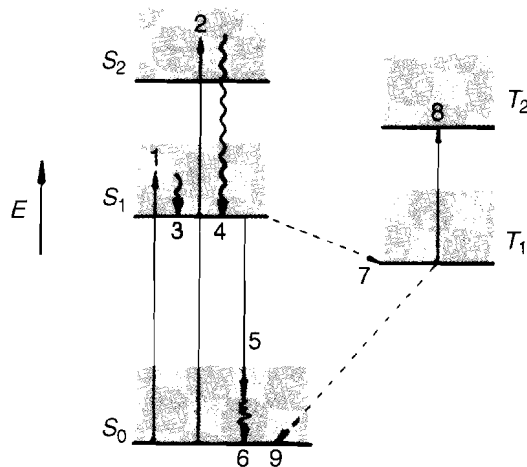
$80\,000\text{ l mol}^{-1}\text{ cm}^{-1}$  for  $\epsilon_{\text{max}}$ , the maximum value of the molar absorption coefficient (Equation 2.16). The fluorescence curve shows, as usual, an approximate mirror image relationship to the absorption curve. It has the additional property, important for all laser dyes, that the fluorescence and absorption maxima do not coincide: if they did, a large proportion of the fluorescence would be reabsorbed.

Figure 9.18 shows a typical energy level diagram of a dye molecule including the lowest electronic states  $S_0$ ,  $S_1$  and  $S_2$  in the singlet manifold and  $T_1$  and  $T_2$  in the triplet manifold. Associated with each of these states are vibrational and rotational sub-levels broadened to such an extent in the liquid that they form a continuum. As a result the absorption spectrum, such as that in Figure 9.17, is typical of a liquid phase spectrum showing almost no structure within the band system.

Depending on the method of pumping, the population of  $S_1$  may be achieved by  $S_1 - S_0$  or  $S_2 - S_0$  absorption processes, labelled 1 and 2 in Figure 9.18, or both. Following either process collisional relaxation to the lower vibrational levels of  $S_1$  is rapid by process 3 or 4 for example the vibrational-rotational relaxation of process 3 takes of the order of  $10\text{ ps}$ . Following relaxation the distribution among the levels of  $S_1$  is that corresponding to thermal equilibrium, that is, there is a Boltzmann population (Equation 2.11).

The state  $S_1$  may decay by radiative (r) or non-radiative (nr) processes, labelled 5 and 7, respectively, in Figure 9.18. Process 5 is the fluorescence, which forms the laser radiation and the figure shows it terminating in a vibrationally excited level of  $S_0$ . The fact that it does so is vital to the dye being usable as an active medium and is a consequence of the Franck-Condon principle (see Section 7.2.5.3).

The shape of the broad absorption curve in Figure 9.17 is typical of that of any dye suitable for a laser. It shows an absorption maximum to low wavelength of the  $0_0^0$  band position, which is close to the absorption-fluorescence crossing point. The shape of the absorption curve results from a change of shape of the molecule, from  $S_0$  to  $S_1$ , in the



**Figure 9.18** Energy level scheme for a dye molecule showing nine processes important in laser action

direction of  
absorption is  
level of  $S_1$   
fluorescence  
whereas the  
following pro  
 $S_1$  and vibrat  
levels are of

The popul  
molecule fro  
non-radiativ  
discussed in  
9.18, which  
order of  $10^9$

Since  $\tau$  is  $10^{-8}$

The lifeti  
9.18, is sp  
amount of d  
result is th  
many dye m  
9.18, overl  
decreasing  
process is  $10^{-10}$

In order  
rate low er  
sufficiently  
overlap wi

There ar  
which, tog  
930 nm m  
mol l<sup>-1</sup> to

Taking  
provide t  
intensity  
dye laser

A puls  
the dye is  
and with  
low - up

direction of one or more normal coordinates, so that the most probable transition in absorption is to a vibrationally excited level of  $S_1$ . Similarly, in emission from the zero-point level of  $S_1$ , the most probable transition is to a vibrationally excited level of  $S_0$ . The fluorescence lifetime  $\tau_r$  for spontaneous emission from  $S_1$  is typically of the order of 1 ns whereas the relaxation process 6, like process 3, takes only about 10 ps. The result is that, following processes 1 and 3, there is a population inversion between the zero-point level of  $S_1$  and vibrationally excited levels of  $S_0$  to which emission may occur, provided that these levels are of sufficiently high energy to have negligible thermal population.

The population of  $S_1$  may also be reduced by absorption of the fluorescence taking the molecule from  $S_1$  into  $S_2$ , if the wavelengths of the two processes correspond, as well as by non-radiative transitions to either  $S_0$  (internal conversion) or  $T_1$  (intersystem crossing), as discussed in Section 7.3.6. In dye molecules it is the  $S_1 - T_1$  process, labelled 7 in Figure 9.18, which is the most important. This is a spin-forbidden process with a lifetime  $\tau_{nr}$  of the order of 100 ns. The lifetime  $\tau$  of the state  $S_1$  is related to  $\tau_{nr}$  and the radiative lifetime  $\tau_r$  by

$$\frac{1}{\tau} = \frac{1}{\tau_r} + \frac{1}{\tau_{nr}} \quad (9.15)$$

Since  $\tau_r$  is of the order of 1 ns, fluorescence is the dominant decay process for  $S_1$ .

The lifetime  $\tau_T$  of the state  $T_1$  is long because the  $T_1 - S_0$  transition, process 9 in Figure 9.18, is spin-forbidden. Depending on the molecule and on the conditions, particularly the amount of dissolved oxygen, it may be anywhere in the range 100 ns to 1 ms. If  $\tau_T > \tau_{nr}$  the result is that the concentration of molecules in  $T_1$  can build up to a high level. It happens in many dye molecules that the intense, spin-allowed,  $T_2 - T_1$  absorption, process 8 in Figure 9.18, overlaps with, and therefore can be excited by, the  $S_1 - S_0$  emission, thereby decreasing the efficiency of the laser considerably. Figure 9.17 shows how important this process is in rhodamine B.

In order to prevent this occurring a pulsed method of pumping is used with a repetition rate low enough to allow time for  $T_1 - S_0$  relaxation. For CW operation either  $\tau_T$  must be sufficiently short or another dye has to be used for which  $T_2 - T_1$  absorption does not overlap with the fluorescence.

There are many dyes available, each of which can be used over a 20–30 nm range and which, together, cover a wavelength range from about 365 nm in the ultraviolet to about 930 nm in the near-infrared. Dye concentrations are low, typically in the range  $10^{-2}$  mol  $l^{-1}$  to  $10^{-4}$  mol  $l^{-1}$ .

Taking into account the possibility of frequency doubling (Section 9.1.6) dye lasers can provide tunable radiation throughout the range 220–930 nm but with varying levels of intensity and degrees of difficulty. The tunability and the extensive wavelength range make dye lasers probably the most generally useful of all visible or ultraviolet lasers.

A pulsed dye laser may be pumped with a flashlamp surrounding the cell through which the dye is flowing. With this method of excitation pulses from the dye laser about 1  $\mu$ s long and with an energy of the order of 100 mJ can be obtained. Repetition rates are typically low – up to about 30 Hz.

More commonly a pulsed dye laser is pumped with a nitrogen, excimer, or  $\text{Nd}^{3+}$ :YAG laser. Both the nitrogen laser, operating at 337 nm, and a xenon fluoride excimer laser operating at 351 nm, excite the dye initially into a singlet excited state higher in energy than  $S_1$ . The  $\text{Nd}^{3+}$ :YAG laser is either frequency doubled to operate at 532 nm or frequency tripled to operate at 355 nm depending on the dye that is being pumped. However, because of the low efficiency of frequency tripling, it is more usual to mix the frequency-doubled dye radiation, of wavelength  $\lambda_D$ , with the  $\text{Nd}^{3+}$ :YAG laser fundamental, of wavelength  $\lambda_F$  (1.0648  $\mu\text{m}$ ), in a non-linear crystal such as KDP (Section 9.1.6) to give a wavelength  $\lambda$  where

$$\frac{1}{\lambda} = \frac{1}{\lambda_D} + \frac{1}{\lambda_F} \quad (9.15a)$$

Pulse rates of about 50 Hz are typical.

CW dye lasers are usually pumped with an argon ion laser, up to about 1 W of continuous dye laser power being produced, compared with about 1 MW peak power which may be produced in a pulsed dye laser.

In both CW and pulsed lasers the dye solution must be kept moving to prevent overheating and decomposition. In a pulsed laser the dye is continuously flowed through the containing cell. Alternatively, magnetic stirring may be adequate for low repetition rates and relatively low power. In a CW laser the dye solution is usually in the form of a jet flowing rapidly across the laser cavity.

### 9.2.11 Laser materials in general

In choosing the examples of lasers discussed in Sections 9.2.1 to 9.2.10 many have been left out. These include the CO,  $\text{H}_2\text{O}$ , HCN, colour centre, and chemical lasers, all operating in the infrared region, and the green copper vapour laser. The examples that we have looked at in some detail serve to show how disparate and arbitrary the materials seem to be. For example, the fact that Ne atoms lase in a helium-neon laser does not mean that Ar, Kr and Xe will lase also – they do not. Nor is it the case that because  $\text{CO}_2$  lases, the chemically similar  $\text{CS}_2$  will lase also.

The potential for laser activity is not anything we can demand of any atom or molecule. We should regard it as accidental that among the extremely complex sets of energy levels associated with a few atoms or molecules there happens to be one (or more) pairs between which it is possible to produce a population inversion and thereby create a laser.

## 9.3 Uses of lasers in spectroscopy

From 1960 onwards, the increasing availability of intense, monochromatic laser sources provided a tremendous impetus to a wide range of spectroscopic investigations. The most immediately obvious application of early, essentially non-tunable, lasers was to all types of Raman spectroscopy in the gas, liquid or solid phase. The experimental techniques,

employing laser  
spectra which  
the pure rota  
rotation Raman  
obtained with

Laser radi  
from, for exa  
As a result, v

In addition  
of Raman e  
effects which  
the oscillati  
non-linear l

For bran  
appear to b  
particularly  
devised for  
the transi  
achieved b  
spectrosc  
resonance

A usefu  
laser, is co  
are appre

In regio  
obtain an  
oscillator  
Absorbar  
technique  
electroni  
secondar  
occurred  
followin  
resulting  
closely

It ma  
sources  
wide va  
possibi

### 9.3.1 Hy

We ha  
falling