Tunable Lasers

By J. K. Burdett and M. Poliakoff
DEPARTMENT OF INORGANIC CHEMISTRY, THE UNIVERSITY,
NEWCASTLE-UPON-TYNE NE1 7RU

1 Introduction

Since the review by Jones[1] in 1969 there has been considerable progress in laser technology, and in particular in the field of tunable lasers. Until recently tunable laser radiation could only be obtained by changing the temperature, pressure, or magnetic field of some existing fixed-frequency laser. In every case, the tuning range was very limited. For example, the output wavelength of a ruby laser changes by $\sim 0.6\ cm^{-1}\ K^{-1}$ at room temperature, and in the Zeeman tuned gas laser (ZTG) the atomic energy levels of, *e.g.*, Ne (in an He–Ne laser) may be slightly shifted by applying an axial magnetic field. In this review we describe truly tunable lasers with much larger tuning ranges. We shall concentrate on the four main types available at the moment and will outline the physical principles of their operation, which are somewhat different from those of non-tunable lasers, familiar to most chemists. We shall describe typical tuning ranges, linewidths, and powers. Already several commercial tunable lasers are available covering parts of the ultraviolet, visible, and infrared regions. In such a brief review we can only mention a few of the potential chemical applications of these devices. We refer readers who wish to read more comprehensive accounts of tunable laser operation and applications to several reviews[2–7] which contain more extensive bibliographies.

2 Dye Lasers

Dye lasers[4] produce tunable radiation in the visible and near-i.r. regions. They exploit the very intense absorption and fluorescence of organic dyes, such as Rhodamine 6G, in solution. Figure 1 shows schematically the lowest electronic levels of such a dye. Absorption of light promotes an electron from the ground state S_0 to a vibrationally excited level b of the first excited state S_1. There is rapid radiationless decay from b into the lowest vibrational level B, of S_1, and a

[1] W. J. Jones, *Quart. Rev.*, 1969, **23**, 73.
[2] C. K. N. Patel in 'Coherence and Quantum Optics', ed. L. Mandel and E. Wolf, Plenum Press, 1973.
[3] E. D. Hinkley, K. W. Nill, and F. A. Blum in 'Laser Spectroscopy of Atoms and Molecules', ed. H. Walther, Springer-Verlag, Heidelberg, to be published 1974.
[4] B. B. Snaveley, *Proc. IEEE*, 1969, **57**, 1374; 'Topics in Applied Physics', Vol. I, 'Dye Lasers', ed. F. P. Schäffer, Springer-Verlag, New York, 1973.
[5] S. E. Harris, *Proc. IEEE*, 1969, **57**, 2096.
[6] Proceedings of the Conference on Laser Spectroscopy, Vail, Colorado, 1973, ed. R. G. Brewer and A. Mooradian, Plenum Press, 1974.
[7] W. Demtröder, *Phys. Reports*, 1973, **7C**, 225.

population inversion is produced between this state and the vibrationally excited states, *a*, of S_0, since the relaxation $a \rightarrow A$ is very fast. Thus laser action can occur on the transition $B \rightarrow a$. Since the system involves four sorts of levels, ground and excited states of both S_1 and S_0, it is possible to maintain a continuous population inversion and the laser can operate in both *continuous wave* (CW) and *pulsed* modes. The state S_1 can also cross into the lowest triplet state, T_1. The transition $T_1 \rightarrow S_0$ is spin-forbidden and, upon irradiation, molecules can be 'trapped' in the relatively long-lived T_1 state, preventing CW operation unless a triplet quencher, such as O_2, is added to the solution.[4]

Experimentally the dye laser consists of a short-path-length cell, containing the dye solution, placed between two mirrors which constitute the *resonant cavity*. The dye is 'optically pumped' using either a flash lamp or a fixed-frequency laser (*e.g.* N_2 or Ar ion). The dye is usually made to flow rapidly through the cell to prevent excessive heating. (Under the high illumination required for CW operation even quartz windows have been known to 'burn'). The *spontaneous linewidth* of such a simple laser is relatively broad, 3—4 nm, but the linewidth can be drastically reduced by placing a *Fabry–Pérot etalon* inside the laser cavity. An etalon consists of a narrow air gap between two parallel transparent plates. Interference effects only allow light of a particular wavelength (dictated by the length of the air gap) to pass through the etalon undeviated. Laser action can occur only at this wavelength where the optical gain is maintained. Thus, the etalon acts not merely as a filter but concentrates all the latent laser power into a narrow bandwidth. Limited tuning can be achieved by rotation of the etalon relative to the axis of the laser cavity (*i.e.* by changing the effective length of the air gap).

The dye laser is tunable because the vibrationally excited states of S_0 (Figure 1)

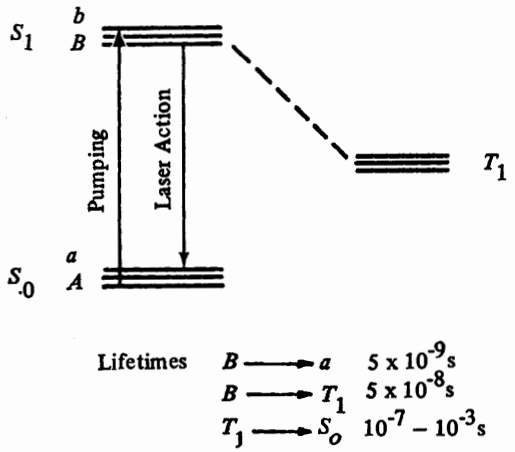

Figure 1 *Schematic energy levels of an organic dye, showing transitions involved in laser action*

are broadened by interaction with the solvent so that they virtually form a continuum and the transition from B to a large part of this continuum can be amplified. The *laser threshold* (the population of the excited state required for laser action) is a function of wavelength, dye concentration, and mirror reflectance, and, for a particular laser, light will be emitted at the wavelength corresponding to the minimum threshold. Tuning involves changing either the dye concentration or the mirror reflectance. In practice, the latter is preferred. High wavelength dependence of reflectivity is obtained by replacing one of the cavity mirrors by a diffraction grating or mirror–prism combination, and the laser output is then tuned by rotating the grating or prism. The laser is, however, not continuously tunable. The output wavelength, λ, is related to the *optical length*, L, of the laser cavity (physical length × refractive index) by the *Fabry-Pérot relationship*,

$$m\lambda = 2L$$

and, since only integral values of m are allowed, *mode-hopping* from one value of m to the next will be observed. Continuous tuning can only be obtained if the cavity length is also changed during tuning. This is achieved experimentally by using a piezoelectric mirror mount which can be moved through small distances by applying a voltage across it.

The tuning range of a particular dye is 60—70 nm although the range can be extended by suitable solvent changes. Most dyes fluoresce at wavelengths longer than 500 nm but, by incorporating a frequency-doubling crystal (see below) into the laser cavity, near-u.v. light can also be generated. Thus a typical commercial pulsed system can be tuned over discrete ranges in the region 265—800 nm, and tuning ranges are constantly being extended as new dyes are discovered. Pulsed powers are high, typically as much as 25 MW. Laser-pumped dye lasers tend to have a higher peak power but lower overall pulse energies than flash-lamp-pumped systems. CW powers are usually in the range 10 mW—1 W.

The linewidth of the laser output is essentially limited by mechanical vibration of the optical components and turbulence in the dye cell. Mechanical vibration is, in practice, the principal cause of frequency instability in most tunable lasers. There are CW dye lasers in regular use[4] with linewidths of 1 MHz* using invar stabilization and vibration-free mountings. Pulsed lasers have somewhat larger linewidths, ~10 MHz. It must be remembered, however, that linewidth and pulse length are related by the Heisenberg Uncertainty Principle. Thus a picosecond pulse (10^{-12} s), which can be produced by a laser operating under *mode-locked* conditions, is limited to a linewidth of ~5 cm^{-1}. If such a pulse is made more nearly monochromatic using an etalon it will simultaneously be stretched in time.

3 Non-linear Devices

These devices[3,5] are based on the interaction of high-intensity laser beams with

* 1 cm^{-1} = 30 GHz; 1 GHz = 3 × 10^{-2} cm^{-1}; 1 MHz = 3 × 10^{-5} cm^{-1}; 1 kHz = 3 × 10^{-8} cm^{-1}; 1 MHz, equivalent to a wavelength change of 10^{-6} nm at 600 nm.

non-linear materials. For such materials it is convenient to relate the dipole moment P, induced by the electric field E, and the susceptibility tensor χ, by the expression

$$P = \chi E = (\chi_0 + \beta E)\, E \ .$$

In low fields P is linearly dependent on E, whereas in high fields, such as exist in laser beams, the total susceptibility becomes field-dependent and the second term oscillates with the frequency of the laser input.

This expression for the susceptibility is reminiscent of the Raman polarizability tensor,[8] one component of which oscillates with a vibrational frequency of the molecule, giving scattered photons of frequency $\nu_{\text{input}} \pm \nu_{\text{vibration}}$. Thus, using a derivation, mathematically almost identical to the classical derivation of the Raman effect, it can be shown that two input laser photons of frequency ν_1 and ν_2 will give rise to $\nu_3 = \nu_1 + \nu_2$ (the two photon mixer, TPM) and $\nu_3 = \nu_1 - \nu_2$ (difference frequency generator, DFG). The well known effect of frequency doubling is a special case of TPM, with $\nu_1 = \nu_2$.

A more rigorous mathematical treatment shows that it is possible to have a process whereby a single input photon produces two photons of different frequency, $\nu_1 = \nu_2 + \nu_3$ (by conservation of energy). This is the exact opposite of the TPM process.

For a multi-photon process momentum as well as energy must be conserved. If $\boldsymbol{k}$ ($\boldsymbol{k} = 2\pi \boldsymbol{r}/\lambda$, where $\boldsymbol{r}$ is a unit vector in the direction of propagation) is the wavevector of a photon, momentum conservation implies

$$\sum_{\text{input}} \boldsymbol{k} = \sum_{\text{output}} \boldsymbol{k}$$

Momentum is normally conserved by the propagation of input and output beams in different directions. However, in an efficient non-linear device it is vital that the input and output beams should be parallel. How this is achieved is best understood by considering the frequency doubler, which, for example, converts red light into blue using a crystal of KDP (KH_2PO_4).[9] Momentum conservation dictates that $k_{\text{blue}} = 2k_{\text{red}}$ and, since wavelength and frequency are related by the speed of light and the refractive index, n, of the material, n_{blue} must equal n_{red}. In an isotropic substance this condition cannot be fulfilled because of the dispersion of the material. In a birefringent (optically anisotropic) material, light is propagated as two rays, ordinary and extraordinary, which have different refractive indices, n_{ord} and n_{ext}, and which give rise to double refraction. n_{ext} varies with the orientation of the crystal whereas n_{ord} does not. In KDP, since the birefringence ($n_{\text{ord,blue}} - n_{\text{ext,blue}}$) is greater than the dispersion ($n_{\text{ord,blue}} - n_{\text{ord,red}}$), it is possible to orient the crystal so that $n_{\text{ord,red}} = n_{\text{ext,blue}}$. Figure 2 shows how rotation of the optic axis of the KDP

[8] D. A. Long, *Chem. in Britain*, 1971, **7**, 108.
[9] P. D. Maker, R. W. Terhune, M. Nisenoff, and C. M. Savage, *Phys. Rev. Letters*, 1962, **8**, 21.

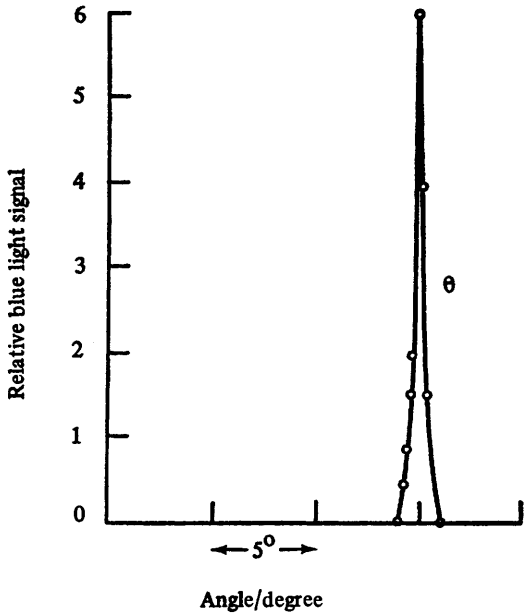

Figure 2 *Blue light intensity as a function of crystal orientation (angle between optic axis and red laser beam) for a KDP frequency doubler*
(Adapted by permission from *Phys. Rev. Letters*, 1962, **8**, 21)

crystal relative to the red laser beam affects the intensity of the blue light emitted parallel to the red. The intensity rises dramatically at the angle where the two refractive indices are equal. This process is called *phase matching*.

TPM devices, adding together photons of different frequency, have been produced. For example, millimetre wavelength microwave radiation and the output of a CW CO_2 laser have been successfully mixed in a GaAs-loaded waveguide.[10] The laser is tuned by changing the microwave frequency; obviously the tuning range is rather small, but eventually it should be possible to cover the entire range of the CO_2 laser. The power is low (~ 1 μW) and the linewidth quite narrow (~ 10 MHz). The advantage of this device is that the frequency of the output is very accurately known. With the majority of other tunable lasers precise frequency measurement presents a serious problem.

The DFG subtracts the photons of two pump-laser beams. Tuning, in this case, is achieved by tuning one of the pump lasers, while the other remains at a fixed frequency, and rotating the crystal to preserve the phase-matching condition. Radiation above 5 μm has been generated using a dye laser and fixed-frequency

[10] V. J. Corcoran, R. E. Cupp, J. J. Gallagher, and W. T. Smith, *Appl. Phys. Letters*, 1970, **16**, 316.

visible laser (Ar ion or ruby). Powers have been low, 0.5 μW, with a linewidth of 50 MHz (1.6×10^{-4} cm^{-1}) CW and 1 W (linewidth 10 cm^{-1}) pulsed. The DFG is experimentally complicated since several components have to be tuned simultaneously. A $LiNbO_3$ optical parametric oscillator (1.5—1.7 μm) (see below) and a Nd YAG laser (1.32 μm) have been successfully used with a $AgGaSe_2$ crystal to produce *continuously* tunable radiation from 7 to 12 μm (1400—850 cm^{-1}) with a lidewidth of 2 cm^{-1}.[11] Spectra taken with this device are similar to those of a medium-resolution conventional i.r. spectrometer.

The best developed tunable non-linear device is the *optical parametric oscillator*, OPO, in which two i.r. photons are generated from a single input photon of visible or near-i.r. radiation. The non-linear crystal is situated in a resonant cavity which amplifies the signal at either one or both of these new frequencies. The two arrangements are known as *singly* or *doubly resonant oscillators* (SRO and DRO) respectively. The SRO is normally used as the DRO suffers from substantial mode-hopping instability ($\sim$20 cm^{-1}), so called *clustering*. The frequencies of these two beams, conventionally called *signal* (higher frequency) and *idler* (lower frequency), are dictated by phase-matching requirements in the crystal. Thus the OPO is tuned by altering the phase-matching conditions, by either rotating, heating, or compressing the crystal hydrostatically to change its refractive index. The tuning range is limited by (*a*) the crystal 'running out' of birefringence, (*b*) thermal decomposition, and (*c*) absorption of light by the crystal (*e.g.* $LiIO_3$ absorbs below 1750 cm^{-1}). Figure 3 shows typical tuning characteristics of a commercially available $LiNbO_3$ OPO with temperature tuning and a Nd YAG pump laser.

Etalons are required to reduce the relatively broad bandwidth of the OPO output (*cf.* dye laser). Linewidths better than 0.001 cm^{-1} (30 MHz) have been achieved at wavelengths shorter than 4 μm (2500 cm^{-1}), with relatively low CW power (μW or mW). Piezoelectric mirror mounts (*q.v.*) are required to prevent mode-hopping during tuning. Pulsed lasers have higher powers, *e.g.* $LiIO_3$, which attains 10 kW from a 100 kW pump pulse. Tunable radiation has been generated in the entire region 1—20 μm, but OPO's operating below 5 μm are still under development.

4 The Spin-flip Raman Laser (SFRL)

This laser[2,3] operates *via* stimulated Raman scattering[8] from the electronic energy levels of the conduction band of an n-type semiconductor. It has already produced tunable radiation in the i.r. around 5—6 μm, 1950—1830 cm^{-1} pulsed, 1950—1600 cm^{-1} CW, and 10 μm, 995—890 cm^{-1} pulsed. True laser action occurs if the gain associated with the stimulated Raman process is large enough to overcome losses in the Raman scattering medium (due to absorption, reflection, *etc.*). In general, the output frequency of such a laser is given by the usual Raman scattering energy conservation relationship,

[11] R. L. Byer, M. M. Choy, R. L. Herbst, D. S. Chemla, and R. S. Feigelson, *Appl. Phys. Letters*, 1974, **24**, 65.

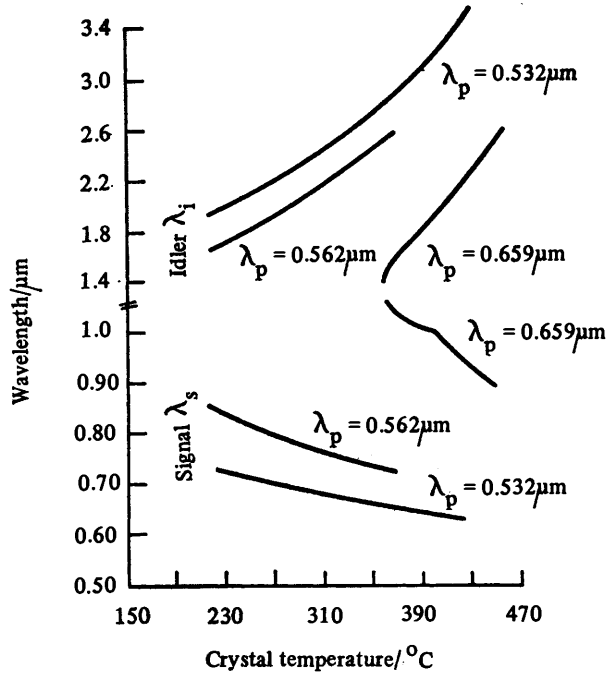

Figure 3 *Tuning curves of a commercially available parametric oscillator (Chromatix Model* 1020) *using a* $LiNbO_3$ *crystal pumped with different lines from a frequency-doubled* Nd *YAG laser* (0.532, 0.562, and 0.659 μm)

$$h\nu_{\text{output}} = h\nu_{\text{input}} \pm mh\nu_{\text{ex}} \quad (m = 1, 2, 3 \ldots)$$

where ν_{ex} is the frequency of the excitation involved in the scattering mechanism (for $\nu_{\text{output}} < \nu_{\text{input}}$ Stokes radiation is produced, for $\nu_{\text{output}} > \nu_{\text{input}}$ anti-Stokes). Chemists will be most familiar with the situation where ν_{ex} is a molecular vibration frequency, but Raman scattering can also occur from the mobile electrons in n-type semiconductors. Stimulated 'spin-flip' Raman scattering from these electrons in InSb (probably the best understood of all semi-conductors) has been extensively developed[12] since 1970. A simplified explanation of the process is as follows. In a magnetic flux density B, the conduction band of a semi-conductor is split into several well-defined states (*Landau levels*) with energies

$$E = (n + \tfrac{1}{2})\, h\nu_{\text{c}}$$

ν_{c} is the cyclotron frequency and n is an integral quantum number (0, 1, 2 . . .)

[12] C. K. N. Patel and E. D. Shaw, *Phys. Rev. Letters*, 1970, **24**, 451; R. L. Allwood, S. D. Devine, R. O. Mellish, S. D. Smith, and R. A. Wood, *J. Phys.* (*C*), 1970, **3**, L186.

(see Figure 4). Each Landau level is further split by electron spin into two levels ('spin-up' and 'spin-down') separated by $g\mu_B B$ where g is the *g-factor* associated with the conduction band electrons and μ_B is the Bohr magneton. The spin-flip

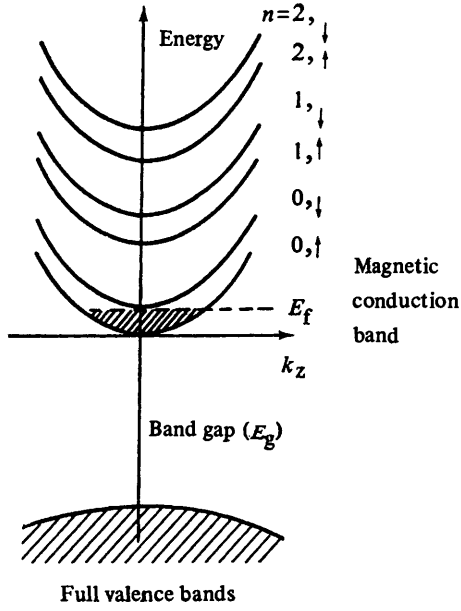

Figure 4 *The structure of the conduction band of an n-type semiconductor in a magnetic field, illustrating the splitting of the Landau levels (designated by integral values n) into spin-up and spin-down levels. E_F is the Fermi level*

transition occurs *via* net promotion of an electron from the 'spin-up' level of $n = 0$ to the 'spin-down' level of $n = 0$. For InSb, g is large and negative, -45 (*cf.* the free electron value of $+2$). The Raman laser output frequency is therefore given by

$$\nu_{\text{output}} = \nu_{\text{input}} \pm m|g\mu_B B| \quad (m = 1, 2, 3 \ldots .)$$

and may be tuned by varying the applied magnetic field, with a tuning rate for InSb, since g is so large, of ~ 20 cm^{-1} T^{-1}.

The stimulated Raman effect has two features of great importance to laser physics. Firstly, there is a considerably higher ratio of Raman scattered intensity to pump (exciting) radiation than in the spontaneous (or normal) Raman effect, there being up to 50% conversion[8] of the incident pump radiation into Stokes Raman radiation, compared with 10^{-4}% in the normal effect. Secondly, the process results in a sizeable narrowing of the Raman scattered linewidth

over that associated with the spontaneous Raman effect. For CW operation the theoretical limit of the stimulated Raman scattered linewidth is as low as 1 Hz (3×10^{-11} cm^{-1}) for an output power of 1 W.

Experimentally, a rectangular single crystal of n-type InSb is located in a powerful magnetic field and is cooled to cryogenic temperatures by contact with liquid helium. Two opposite faces of the crystal are highly polished, optically flat, and almost parallel, to form the ends of the resonant cavity where the stimulated process occurs. The pump laser beam enters the crystal through one of these faces and the stimulated Raman radiation and the unconverted pump radiation emerge from the crystal through the opposite face. The tunable radiation has well-defined polarization and may be separated from the pump radiation by the use of filters or a monochromator. (This also serves to separate the double Stokes, Stokes, and anti-Stokes radiation which are produced simultaneously.)

All existing spin-flip lasers use InSb crystals. This means that any pump radiation must be lower than the InSb band gap, ~ 1900 cm^{-1},* to avoid direct absorption by the crystal. However, if the pump frequency is close to the band gap then resonant enhancement of the stimulated Raman process occurs and the conversion efficiency from pump to Raman-scattered radiation is improved enormously. This effect, equivalent to the familiar resonance Raman effect, is a vital factor in the operation of the SFRL in both the pulsed and CW modes.

The pulsed SFRL is normally pumped with a pulsed or Q-switched CO_2 laser. This produces a series of lines in the region of 10.6 μm (943 cm^{-1}), any of which can be frequency-doubled (*q.v.*) using a tellurium crystal to give radiation at 5.3 μm (1887 cm^{-1}) close to the band gap of InSb. Peak SFRL output powers of 1 kW (Stokes) and 100 W (double Stokes and anti-Stokes) at frequencies of *ca.* 5.3 μm have been obtained for pump powers of ~ 1 MW. The pulse length of the SFRL output is of course related to the pulse length of the pump laser. Although the linewidth is limited by the uncertainty principle (*via* nanosecond 'spikes' in the input pulse) to 100 MHz (0.003 cm^{-1}) the narrowest tunable linewidth so far observed is ~ 0.02 cm^{-1} (700 MHz). If the undoubled CO_2 10.6 μm radiation is used as a pump, tunable radiation is produced in this region of the spectrum with similar power to that in the 5 μm region but with slightly greater linewidths.

A superconducting magnet is preferred since very high magnetic fields can be obtained. Varying the field from 0 to 10 T gives a total theoretical tuning range with a combination of anti-Stokes and double Stokes radiation of ~ 480 cm^{-1} for a given pump frequency. In practice the range is less than this owing to absorption of the Raman radiation across the band gap and by losses, induced by the magnetic field, which prevent the stimulated process occurring. A typical tuning curve is shown in Figure 5.

* The exact position of the band gap is dependent on temperature, the applied magnetic field and carrier concentration of the semiconductor.

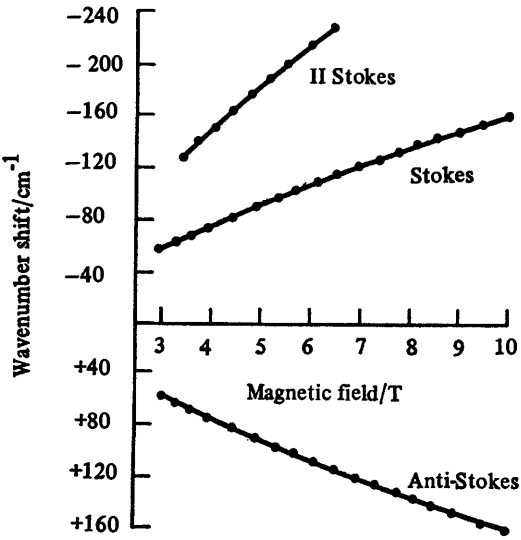

Figure 5 *Typical tuning curve of a pulsed spin-flip laser. Note that the slope of the double-Stokes curve is approximately twice that of the Stokes*

Since the SFRL has a finite magnetic threshold, there is an inaccessible region close to the pump frequency. This threshold decreases with decreasing carrier concentration and can be as low as ~0.05 T. The frequency gaps can be covered by using adjacent lines of the pump laser. There is also a power threshold for SFRL operation. This presents no problem in pulsed operation, where the input powers are ~1 MW.

Using InSb, CW operation is only possible in the 5.3 μm region, where stimulated Raman scattering is very efficient, since the threshold at 10.6 μm is so high that CW heating effects would be enormous. Normally a CW CO gas laser is used for pumping and SFRL output powers of 100 mW—1 W have been achieved. Since the CO laser has a large number of different lines, the SFRL can be tuned by using either a single CO line and a superconducting magnet or a whole series of CO lines and less powerful conventional magnets. An ingenious arrangement allows use of a permanent magnet.[13] The longer-wavelength limit (~6.2 μm) is imposed by decreasing pump laser powers and increasing power thresholds for CW operation.

The theoretical linewidth of this system is 1 Hz for an output power of 1 W and using the heterodyne technique a linewidth as small as 1 kHz (3×10^{-8} cm^{-1}) has been experimentally observed.[2] The usable linewidth is ~ 1—10 MHz (*i.e.* about 10^{-4} cm^{-1}) but this may be reduced to *ca.* 30 kHz (~10^{-6} cm^{-1}) by using

13 S. R. J. Brueck, and A. Mooradian, *IEEE J. Quantum Electron.*, 1973, **QE9**, 1157.

a second CO laser for heterodyne stabilization.[14] The discrepancy between the observed linewidth and the theoretical minimum is due to pump-laser instability and mechanical vibration.

5 Semiconductor Diode Lasers (SDL)

By pumping the band gap of a semiconductor, electrons are promoted to the conduction band leaving a hole in the valence band. Stimulated emission of radiation of frequency $\nu = h^{-1}E_g$ may be produced by recombination of these electron–hole pairs. Population inversion can be achieved by optical pumping (at a frequency where the radiation is absorbed), by electron beam excitation, or by electron injection at a p–n junction. Tunable lasers using electron injection have been the most extensively developed and are called *diode lasers*.[3,6] Figure 6

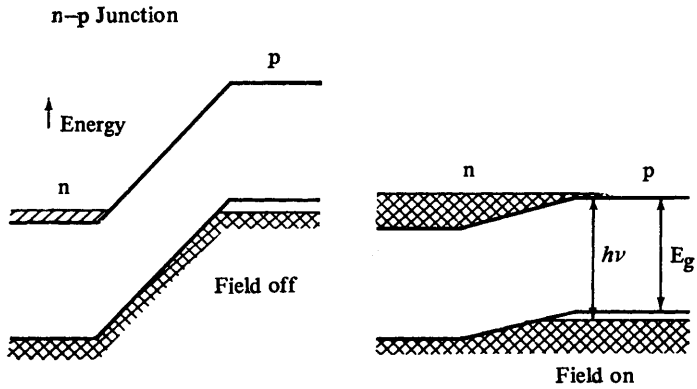

Figure 6 *Schematic illustration of the method of producing a population inversion at the p–n junction of a semiconductor diode by applying an electric field (applied voltage across the junction)*

shows, schematically, the relative energies of the conduction and valence bands of the p and n sides of a p–n junction. When a voltage is applied across this junction, a population inversion now exists on the p side. Stimulated emission occurs simply by the 'flow' of electrons from the conduction band of the n side into the conduction band of the p side and across the band gap E_g. Semiconductor materials where the band gap is in the i.r. region include such binary compounds as InAs, InSb, GaSb, PbS, and the ternary systems $Pb_{1-x}Sn_xTe$ and $Pb_{1-x}Sn_xSe$. In the visible and near-i.r. region, other materials such as $GaAs_{1x}-P_x$ can be used.

The diodes are made by cleaving single crystals of the semiconductor material such that each contains a p–n junction. A typical size of such a diode is 0.1 × 0.04 × 0.02 cm. Low-resistance contacts are cold-welded to the p and n sides

[14] S. R. J. Brueck, *Bull. Amer. Phys. Soc.*, 1973, **18**, 400; S. R. J. Brueck and A. Mooradian, *IEEE J. Quantum Electron.*, in the press.

of the junction and the diode is attached to the cold finger of a Dewar. At present liquid helium is used as the refrigerant for CW operation although pulsed operation of the laser is possible at 77 K. (CW operation is also possible at 10 K using a closed-cycle cooler.) A steady d.c. current is applied across the junction for CW operation or a current pulse of short duration sent through the crystal for pulsed operation.[3]

The nominal i.r. emission frequency is set by the energy of the band gap and may be 'tailored' by altering the chemical composition of the semiconductor. Thus for $Pb_{1-x}Sn_xTe$, emission can occur anywhere between 6.5 and 32 μm (1690—312 cm^{-1}) and crystal-growing techniques are such that a laser can be produced to emit a particular frequency with an error of less than 5 cm^{-1} by correct choice of x. Once a diode laser has been fabricated, further adjustment of its energy gap is possible by changing the applied hydrostatic pressure, temperature, or magnetic field. PbSe diode lasers, for example, can be pressure-tuned from 8 to 22 μm (1250—450 cm^{-1}). The limit is set by the fact that the pressurizing helium gas solidifies[15] at 14 kbar at 77 K.

The bandwidth associated with the spontaneous *recombination radiation* across the band gap may be of the order of 5—50 cm^{-1}. However, the frequency of the stimulated (laser) radiation occurring within this bandwidth will be dictated by the optical length of the laser cavity (*via* the Fabry-Pérot condition), formed by the cleaved ends of the semiconductor crystal. The p–n junction layer runs perpendicular to these faces and the stimulated recombination occurs in this junction zone. Laser action can then only occur at wavelengths which are allowed cavity modes. Fine tuning of the laser frequency is achieved either by applying pressure to alter the physical length of the cavity or by changing the temperature or magnetic field to alter the refractive index and hence optical length of the cavity. The most frequently used method of tuning is variation of the diode current. Changes in the current alter the temperature and hence the refractive index of the diode. Because of the small thermal mass of the laser this heating is very rapid and the laser output may readily be modulated at frequencies[3] as high as 10 kHz. A typical current tuning range for one of these crystals is *ca.* 40 cm^{-1}, although only about half of this range is accessible in practice because of mode-hopping (*q.v.*) (Figure 7). The diode laser is a multimode device in that laser action can occur on several cavity modes simultaneously, although one is usually predominant in power. For a normal-size diode crystal cavity modes are separated by *ca.* 2 cm^{-1}, and a simple monochromator is sufficient to separate a single frequency from the output. Gaps in the tuning range can be filled in by applying an external magnetic field or by selecting a different mode with the monochromator.

The maximum power output for a diode laser to date[3] has been $\sim$1 mW in a single mode for CW operation, although typical powers are lower, $\sim$10 μW. A peak power of 10 W has been achieved using a pulsed diode at 77 K. Higher output powers should be possible with optical pumping of the band gap, where

[15] J. M. Besson, W. Paul, and A. R. Calawa, *Phys. Rev.*, 1968, **173**, 699.

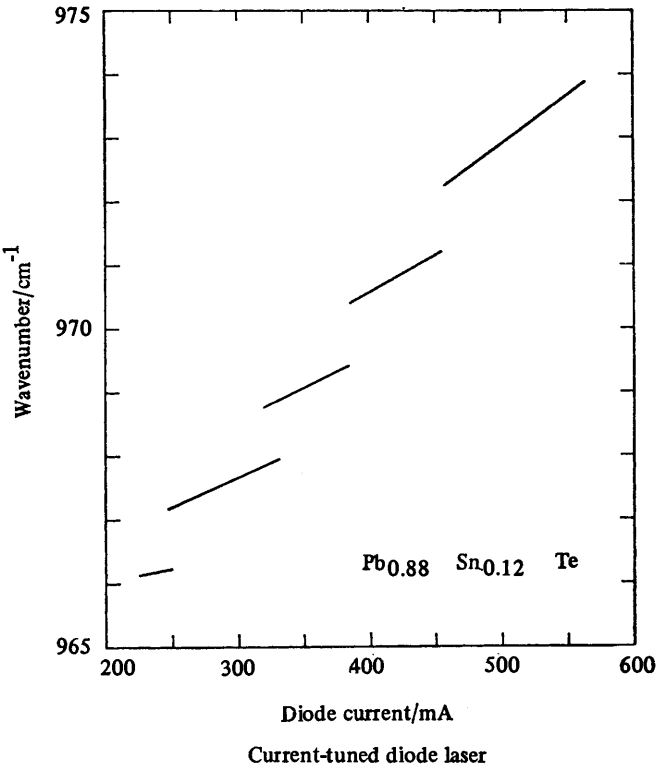

Figure 7 *Typical current-tuning curve for a diode laser indicating mode-hopping* (Adapted by permission from E. D. Hinkley and A. R. Calawa, ACS Meeting Dallas, Texas, April, 1973)

the output radiation is tuned by altering an applied magnetic field.[16] The linewidth of the CW SDL is very narrow; 54 kHz (2×10^{-6} cm^{-1}) has been obtained[17] as a usable bandwidth for a 0.24 mW $Pb_{0.88}Sn_{0.12}$ diode laser operating at 10.6 μm. The linewidth of the pulsed version is considerably larger, since heating of the crystal changes the temperature and the refractive index (and hence the emission wavelength) during the lifetime of the pulse. This process is called *chirping* and is typically 20 MHz ns^{-1}.

6 Spectroscopy using Tunable Lasers

Tunable lasers are likely to revolutionize high-resolution spectroscopy, especially in the i.r. The resolution of a conventional i.r. spectrometer is usually limited

[16] R. Grisar, C. Irslinger, H. Wachering, and H. O. Hafele. *Optics Comm.*, 1971, **3**, 415.
[17] E. D. Hinkley and C. Freed, *Phys. Rev. Letters*, 1969, **23**, 277.

by the decreasing amounts of energy reaching the detector as the slit width is reduced. The minimum practicable power at most detectors is $\sim 10^{-9}$ W, and a typical black-body source at 2000 K produces a usable power of 10^{-7} W cm at 10 μm (1000 cm^{-1}), limiting the resolution to ~ 0.01 cm^{-1}. On the other hand a CW diode laser can easily achieve 100 μW in a bandwidth of 200 kHz (10^{-5} cm^{-1}). Furthermore the output beam of the laser is directional and collimated, which means that its *spectral brightness* (W cm^{-1} sr^{-1}) is *ca.* 10^{14} times as high as that of the black body. An i.r. spectrometer inevitably has a resolution which is much worse than the Doppler-limited width (~ 100 MHz, or 0.003 cm^{-1}) of typical gas-phase absorptions. Figure 8 gives a comparison of linewidths of the different types of tunable laser and shows that all have 'resolution' better than the best

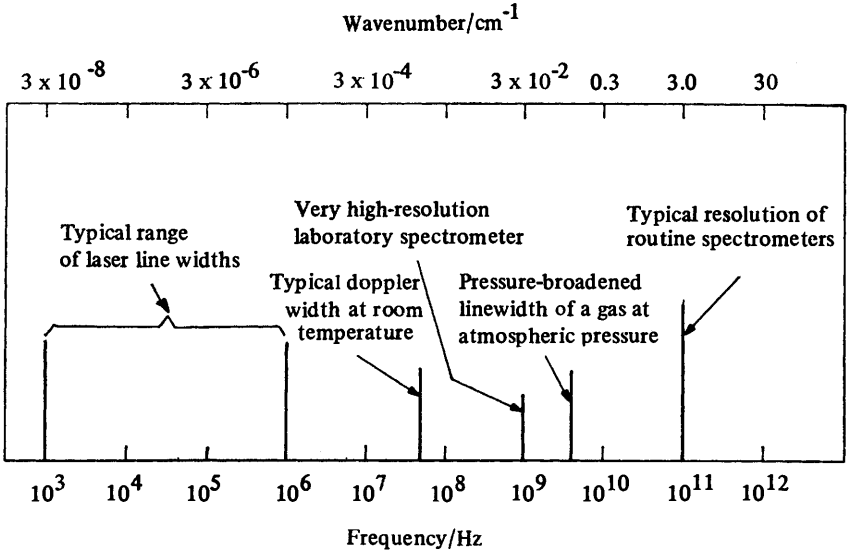

Figure 8 *Resolution requirements for spectroscopy compared with conventional and tunable laser linewidths*
(Courtesy E. D. Hinkley)

i.r. spectrometers; most are better than the Doppler limit. This increase in resolution is amply demonstrated by Figure 9. The lower half shows the best available grating spectrum of the ν_3 rotation–vibration band of gas-phase SF_6, while the other half shows the fine structure observed in just a small part of the spectrum using a diode laser.[3,18] (The fine structure has been partially attributed to second-order Coriolis effects.) Other impressive spectra include resolution of

[18] E. D. Hinkley, *Appl. Phys. Letters*, 1970, **16**, 351.

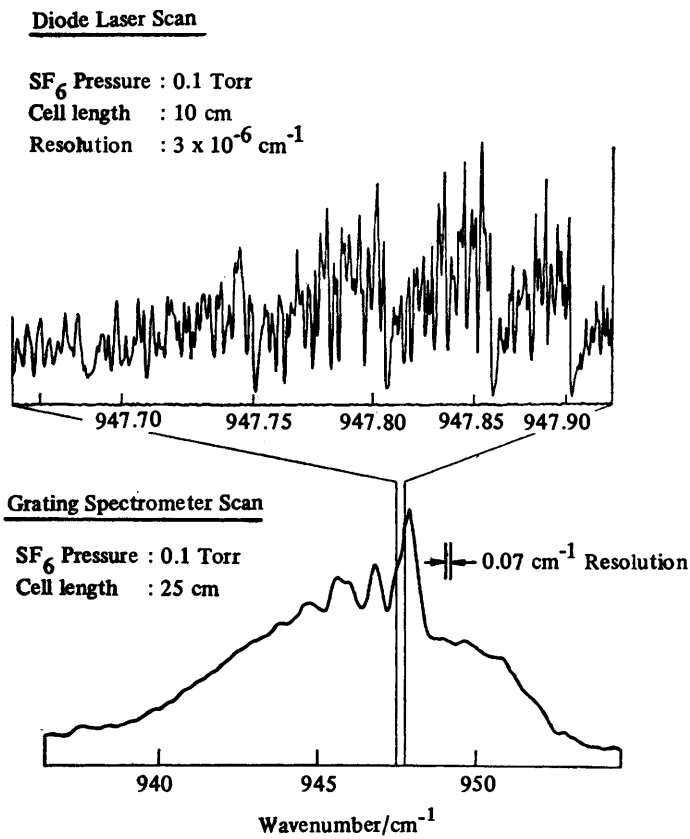

Figure 9 *A section of the i.r. vibrational spectrum of* ν_3 *of* SF_6 *using a diode laser (above) compared with the best available spectrum (below), obtained using a very high-resolution conventional spectrometer*
(Adapted by permission from *Appl. Phys. Letters*, 1970, **16**, 351)

nuclear hyperfine splittings[19] in NO and the self-broadening[20] of the vibration–rotation bands of H_2O. Dye lasers have already enabled saturation techniques (Lamb-dip *etc.*) to be used to observe fine structure normally obscured by Doppler broadening in atomic spectra.[21] Tunable i.r. lasers should allow these techniques to be applied to i.r., rotation–vibration spectra.[22]

[19] F. A. Blum, K. W. Nill, A. R. Calawa, and T. C. Harman, *Chem. Phys. Letters*, 1972, **15**, 144.
[20] R. S. Eng, A. R. Calawa, T. C. Harman, P. L. Kelley, and A. Javan, *Appl. Phys. Letters*, 1972, **21**, 303.
[21] T. W. Hansch, I. S. Shahin, and A. L. Schawlow, *Phys. Rev. Letters*, 1971, **27**, 707; M. S. Feld and V. S. Letokhov, *Sci. Amer.*, 1973, **229**, No. 6, p. 69.
[22] A. C. Luntz and R. G. Brewer, *J. Chem. Phys.*, 1971, **54**, 3641; R. G. Brewer, *Science*, 1972, **178**, 247.

The high powers and signal to noise ratios of tunable lasers greatly simplify the recording of spectra under adverse conditions where very weak signals are obtained. These include long path lengths (> 1 km), highly absorbing solvents, very low-concentration gas mixtures (*e.g.* NO in city air, using the highly sensitive opto-acoustic cell[23]) spectra of high-temperature species (in presence of strong emission from a furnace *etc.*), and short-lived moelcules[2] (*e.g.* from flash photolysis where the sampling time is very short, ~ 1 μs). The high power levels of these lasers also make possible two-step photodissociation processes,[24] which may become increasingly important in the field of isotope separation.[25]

7 Future Developments and Conclusions

It is obviously impossible to make accurate forecasts of future developments. Nevertheless it is likely that the existing tunable lasers will be further refined with increases in tuning range and power and reductions in linewidth. New dyes and non-linear materials will be exploited, and new types of tunable laser will be developed. One of the more promising of these is the *high-pressure gas* laser (HPG). Present-day, low-pressure gas lasers produce a series of narrow bandwidth lines corresponding to the rotational levels of the gas. If the pressure of the gas were to be substantially increased these rotational lines would be broadened into a quasi-continuum and continuous i.r. tuning analogous to that of the dye laser would be possible. Initial experiments have been promising[26] but much development is still needed.

Nevertheless, it must be admitted that tunable lasers have already been developed to a stage where they are potentially useful to the chemist. It is to be expected that over the next few years tunable lasers will be extensively applied to chemistry.

[23] W. R. Harshburger and M. B. Robin, *Accounts Chem. Res.*, 1973, **6**, 329; L. B. Kreuzer, *J. Appl. Phys.*, 1971, **42**, 2934.
[24] R. V. Ambartzumian and V. S. Letokhov, *Appl. Optics*, 1972, **11**, 354.
[25] C. B. Moore, *Accounts Chem. Res.*, 1973, **6**, 323.
[26] N. G. Basov, V. A. Danilychev, O. M. Kerimov, and A. S. Podsosannyi, *Zhur. exp. i teor. Fiz. Pis'ma Redakts*, 1973, **17**, 147.