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#### *General references and further reading*

- A non-mathematical account of laser saturation spectroscopy is given in the article by  
 Feld, M. and Letokhov, V.S. (1973). *Sci.Amer.* 229, No.6, p.69.  
 A comprehensive review of mode selection techniques in lasers is given by  
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## Tunable dye lasers and atomic spectroscopy

### 14.1. Introduction

In the previous three chapters we have discussed the properties of gas lasers and have shown how they can be designed for single frequency oscillation, and also how the output frequency may be tuned continuously over the bandwidth of the Doppler-broadened gain curve. Unfortunately this tuning range is relatively narrow and the application of these gas lasers to atomic and molecular spectroscopy is restricted to studies of the laser transitions themselves, or to accidental coincidences with molecular absorption lines. It would therefore seem that the new and powerful technique of saturated absorption spectroscopy was also of relatively limited applicability.

Fortunately, in the past decade, several different types of narrow-bandwidth widely tunable lasers have been developed and of these the organic dye laser has played the most prominent role in atomic and molecular spectroscopy. These dye lasers provide tunable coherent radiation throughout the wavelength range from the near ultraviolet to the near infrared, and moreover, by optical harmonic and laser difference frequency generation, the accessible spectral region can be extended into the vacuum ultraviolet and the far infrared.

This new device has led to a rapid growth in the nonlinear spectroscopy of atoms and molecules. In addition the narrow spectral bandwidth and great intensity per unit spectral range of these dye lasers have made it possible to extend the range of classic spectroscopic techniques such as absorption and fluorescence spectroscopy. Even the more precise spectroscopic methods such as the Hanle effect, the optical double resonance, and the optical pumping techniques have all benefitted from the increasing availability of tunable dye lasers. Selective step-wise excitation using dye

lasers now enables atomic energy levels to be studied which have the same parity as the ground state and which consequently cannot be efficiently excited by conventional lamps.

Thus dye lasers have led to an enormous increase in activity in many areas of atomic physics. In the sections which follow we will briefly discuss the principles of dye laser operation and the construction of some typical laser systems. We will then consider a few of the recent applications of these devices to atomic spectroscopy. Further information on dye lasers and their spectroscopic applications is contained in the excellent collections of review articles edited by Schäfer (1973), Walther (1976) and Shimoda (1976).

#### 14.2. Tunable organic dye lasers

14.2.1. Principles of dye laser operation. Many organic compounds that absorb strongly in certain regions of the visible spectrum also fluoresce very efficiently, emitting radiation which covers a large wavelength range. The first descriptions of stimulated emission from these fluorescent organic dyes in liquid solution were reported almost simultaneously by Sorokin and Lankard (1966) and Schäfer *et al.* (1966). It was not long before Soffer and McFarland (1967) had demonstrated that the stimulated emission was also tunable and the rapid development of tunable dye lasers had commenced.

The energy-level scheme of a typical organic dye molecule in dilute solution is shown schematically in Fig. 14.1. It consists of a ground state  $S_0$  and a series of excited singlet levels  $S_1, S_2, \dots$  together with another series of triplet levels  $T_1, T_2, \dots$  in which the lowest level lies about  $15\,000\text{ cm}^{-1}$  above the ground state  $S_0$ . The energy level separation  $S_0-S_1$  is typically about  $20\,000\text{ cm}^{-1}$ . In the singlet states the spin of the active electron and that of the remainder of the molecule are antiparallel, while in the triplet states the spins are parallel. Transitions between states of the same multiplicity give rise to the in-

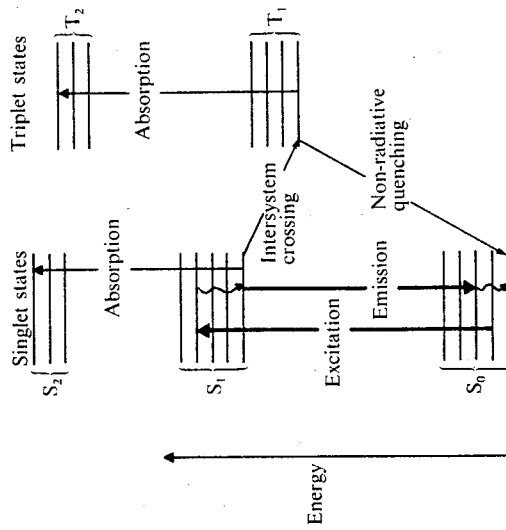


Fig.14.1. Schematic energy level diagram of typical dye molecule. (After Hänsch (1973).)

tense absorption and fluorescence spectra of the dye while singlet  $\leftrightarrow$  triplet radiative transitions involve a spin flip and are therefore far less probable. Each electronic level is also associated with an array of vibrational and rotational levels. The vibrational levels are spaced by intervals of  $1400-1700\text{ cm}^{-1}$  while the spacing of the rotational levels is smaller by a factor of approximately 100 and consequently is too small to be shown in Fig.14.1. Due to rapid relaxation processes the rotational and vibrational levels are smeared out to form broad continuous energy bands. These account for the continuous absorption and emission spectra, examples of which are shown in Fig.14.2 for the case of the well-known laser dye rhodamine 6G in ethyl alcohol solution. The colour of the dye is determined by the broad absorption band  $S_0 \rightarrow S_1$  which results from the excitation of an electron in a  $\pi$ -orbital.

When the dye solution is illuminated by light whose wavelength falls in the absorption band, molecules are op-

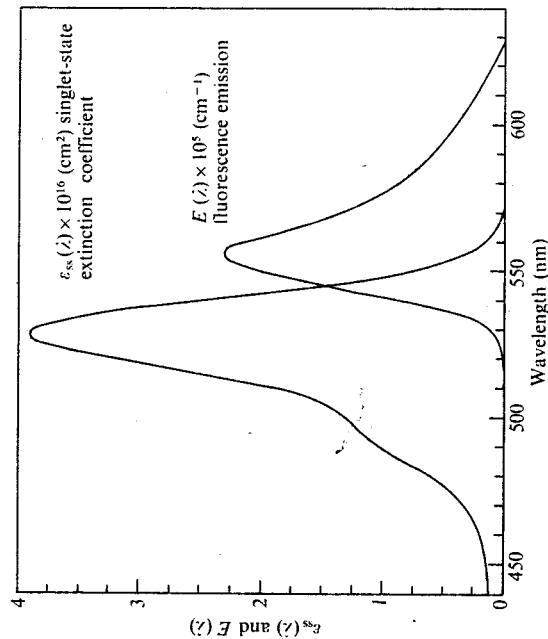


Fig.14.2. Absorption and fluorescence spectra of the laser dye rhodamine 6G in ethanol solution. (After Hänsch (1973).)

tically excited from the level  $S_0$  into some rotational-vibrational level  $b$  belonging to the excited singlet state,  $S_1$ . Following the excitation, rapid collisions with other molecules dissipate the excess vibrational-rotational energy and the molecule relaxes to the lowest vibrational level of the  $S_1$  state in a time of the order of  $10^{-11}$ - $10^{-12}$  s. From here the molecule can decay by spontaneous emission, with a radiative lifetime  $\tau_s \approx 10^{-9}$  s, to any of the rotational-vibrational levels of the ground state. Consequently the emitted light is of longer wavelength than the pumping radiation. Finally non-radiative relaxation processes return the molecule to the  $v=0$  level of the electronic ground state,  $S_0$ .

If the intensity of the pumping radiation is very high, exceeding about  $100 \text{ kW cm}^{-2}$ , a population inversion between  $S_1$  and  $S_0$  may be attained. Light amplification by the stimu-

lated emission of radiation is then possible over almost the entire fluorescence band with the exception of that part which is effectively overlapped by the absorption band of the molecule. In the absence of frequency-selective feedback, the dye laser will oscillate on a band approximately 10-50 Å wide close to the peak of the fluorescence curve. However, due to the rapid thermalization of the vibrational and rotational levels, the spectral profile of the gain curve is essentially homogeneously broadened and it is possible to channel almost the entire available energy into a narrow spectral range by using a laser cavity with wavelength-selective feedback. Thus continuously tunable dye laser oscillation may be obtained.

Unfortunately there are several processes which compete with the fluorescent decay mode of the molecule and therefore reduce the efficiency of the laser. The most important of these are non-radiative relaxation to the ground state  $S_1 \rightarrow S_0$ , and non-radiative intersystem crossing  $S_1 \rightarrow T_1$ . This latter process is particularly undesirable since a large population of molecules may build up in the triplet level owing to the relatively long lifetime,  $\tau_T = 10^{-3}$ - $10^{-7}$  s, of this metastable state. Absorption on the allowed transition such as  $T_1 \rightarrow T_2$  can then cause considerable cavity losses if these absorption bands overlap the  $S_1 \rightarrow S_0$  fluorescence band, and laser oscillation may be quenched or prevented completely. This triplet loss may be reduced by adding small quantities of chemicals such as cyclooctatetrene to the dye solution, for these favour the non-radiative transitions  $T_1 \rightarrow S_0$  and thus shorten the effective lifetime of the  $T_1$  level.

To date laser action has been achieved on several hundred organic dyes, many of which are listed in the survey by Warden and Gough (1971). Examples of some of the most useful dyes together with their respective tuning ranges are shown in Fig.14.3. The tuning range of certain dyes can be extended by adjusting the pH value of the solvent. Thus Shank *et al.* (1970) have been able to cover the entire

14.2.2. Flashlamp - pumped dye lasers. Many laser dyes with emission bands ranging from the near ultraviolet to the infrared have been successfully pumped using flashlamps. These lamps consist of quartz tubes filled with xenon or some other gas at a relatively high pressure and they are excited by a pulsed high-current discharge from a storage capacitor. Flashlamps with short risetimes, of the order of 100 ns or less, are the most suitable for use with dye lasers. The flashlamp and dye cell may be coaxial or alternately the lamp and cell may be held at the foci of an elliptical cylindrical reflector as indicated schematically in Fig.14.4. Difficulties are encountered in these lasers

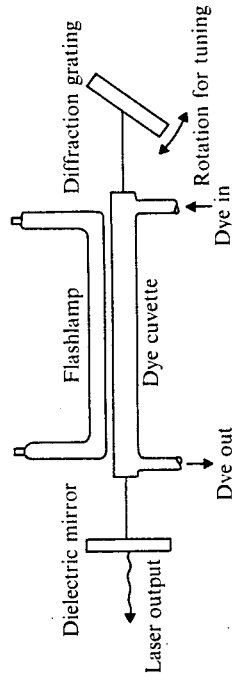


Fig.14.4. Schematic diagram of flashlamp-pumped dye laser. (After Hänsch (1973).)

because of the large amount of thermal energy transferred to the dye solution. This causes refractive index variations throughout the dye cell and leads to very large diffraction losses in the optical cavity. In order to overcome these thermal schlieren effects, the solution is usually circulated rapidly through the dye cuvette by means of a small pump.

In order to achieve a narrow bandwidth tunable output one mirror of the normal laser cavity is usually replaced by a diffraction grating as shown in Fig.14.4. The grating normal makes an angle  $\theta$  with the axis of the cavity and in this Littrow arrangement the condition

$$2 d \sin\theta = m\lambda \quad m = 1, 2, \dots \quad (14.1)$$

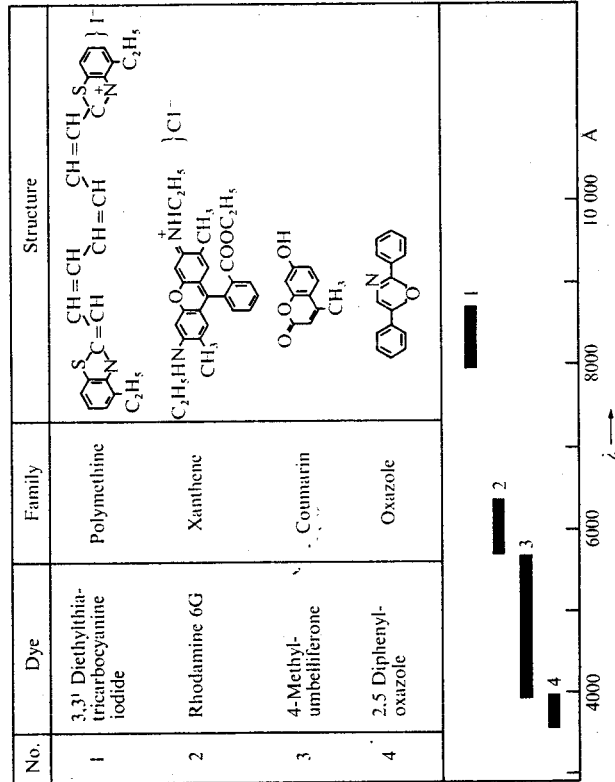


Fig.14.3. Examples of laser dyes, their structure and respective tuning ranges. (After Hänsch (1973).)

range of the spectrum from the near ultraviolet to the yellow, 390-544 nm, using 4-methyl-umbelliferone and its excited acidic complex. Mixtures of different dyes in the same solution have also been used to extend the tuning range or to transfer energy to a dye whose absorption bands did not match the emission of the pump source. However, for use in high-resolution spectroscopy wide tuning range in a single dye is of less importance than high fluorescence efficiency. Happily new dyes which have been especially synthesized for high efficiency over particular spectral regions are becoming increasingly available. The fluorescence efficiency, the triplet losses, and the absorption spectrum of the dye all impose stringent requirements on the properties of the dye laser pump source and we now turn to a consideration of the main types of sources used at present.

must be satisfied for radiation to be reflected back along the cavity axis. In this equation  $\lambda$  is the oscillating wavelength of the laser and  $d$  is the grating spacing. Light of other wavelengths is not reflected back along the cavity axis and consequently this radiation sees a very lossy resonator and oscillation is prevented. Thus narrow bandwidth laser output is obtained and wavelength tuning may be accomplished simply by rotating the grating. Prisms, Fabry-Perot étalons, and combinations of these elements with diffraction gratings have all been used as tuning elements in flashlamp-pumped dye lasers and the bandwidths obtained range typically from 0.3-3.0 Å. Flashlamp-pumped dye lasers can be very cheap and simple to make and output energies of up to several Joules per pulse have been obtained. Generally, however, the pulse repetition rate is too low and the output spectral bandwidth is too large to permit their use in high-resolution atomic spectroscopy.

#### 14.2.3. Laser-pumped dye lasers - pulsed systems.

(a) Solid state laser-pumped dye lasers. The first reported dye lasers were pumped by giant pulse (Q-switched) solid state lasers such as the ruby laser at 694.3 nm and the frequency-doubled neodymium laser at 530.0 nm. These pump sources continue to play an important part in applications requiring very high peak powers. The inherently short pulse length of the Q-switched solid state lasers, 5-100 ns, effectively eliminates the problems of triplet state absorption and dye laser efficiencies of up to 50 per cent have been reported in certain cases.

These laser-pumped dyes exhibit very large gain coefficients,  $\approx 10^3 \text{ mm}^{-1}$ , and low-Q optical cavities containing several rather lossy tuning elements may be used. Thus by combining a Littrow mounted échelle grating and one or more Fabry-Perot étalons, single mode operation with bandwidths of less than 0.01 Å can be achieved. Ruby laser pumping is essential for most of the infrared dye lasers since the absorption bands of these molecules lie towards the red end

of the spectrum and moreover these dyes are easily destroyed by photodissociation when sources of shorter wavelength are used. However, solid state laser-pumped dyes are not restricted to the long wavelength end of the spectrum, for efficient second and fourth harmonic generation makes the ruby (347.2 nm) and neodymium (265.0 nm) lasers very effective pump sources for dye lasers in the near ultraviolet.

Laser pumping certainly provides the easiest route to tunable dye laser radiation once the pump laser exists. Unfortunately the very low repetition rate of many of the Q-switched solid state lasers is a great disadvantage in experiments in atomic and molecular spectroscopy.

(b) Molecular nitrogen laser-pumped dye lasers. A particularly reliable and convenient pump source is the pulsed nitrogen laser operating at 337.1 nm. The short wavelength of this laser radiation excites many dyes to high-lying singlet levels, but in all cases the molecules relax very quickly to the bottom edge of the lowest excited singlet level, dissipating the excess energy in the solvent, and dye laser oscillation occurs on the  $S_1 \rightarrow S_0$  transition. Since most dyes have a strong absorption band in the ultraviolet region the nitrogen laser provides an almost universal pump source. The short pulse length and high repetition frequency of this laser provide a convenience similar to that of C.W. operation and it is one of the most widely used systems in atomic spectroscopy.

A schematic diagram of the nitrogen laser-pumped dye laser system developed by Hänsch (1972) is shown in Fig. 14.5. The nitrogen laser consists of a rectangular channel  $\approx 1 \text{ m}$  long through which a rapid discharge is passed from a triggered high-voltage capacitor system. Nitrogen molecules are excited to the  $C^3\Pi_u$  state by collisions with fast electrons and a transient inversion is created on the  $B^3\Pi_g \leftarrow C^3\Pi_u$  ultraviolet emission band. The radiation emitted by the laser is self-terminating because the lower level has a longer lifetime than that of the upper level and in most of these devices the output consists of a pulse of amplified spontaneous emission

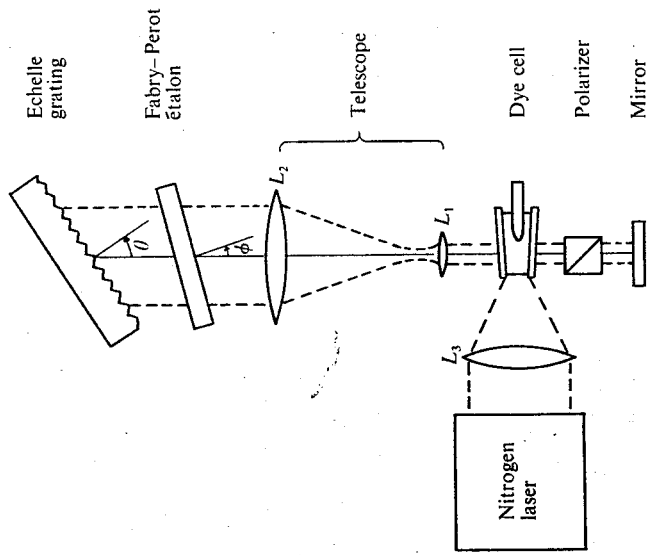


Fig.14.5. Dye laser with narrow bandwidth output pumped by pulsed nitrogen laser. (After Hänsch (1973).)

at 337.1 nm lasting 7-10 ns and having a peak power of  $\approx 300$  kW.

The radiation from the nitrogen laser emerges in the form of a beam of rectangular cross-section, approximately 5 mm  $\times$  40 mm, which is focussed by a spherical quartz lens into a line near the inner wall of the dye cell. The active volume of the dye forms a cylindrical filament about 0.2 mm diameter and 10 mm long having a single pass gain which approaches  $10^3 \text{ mm}^{-1}$  under these conditions. The optical cavity of the dye laser is about 40 cm long and consists of a plane dielectrically-coated mirror at one end and a Littrow-mounted diffraction grating at the other. Owing to diffraction, the rather small active cross-section in the dye results in a substantial angular spread of the emerging radiation and this

would normally limit the bandwidth obtainable with angle-dependent wavelength selectors such as gratings and étalons. However, this problem may be overcome by using a telescope as a beam expander within the cavity so illuminating the whole aperture of the grating. In this system a bandwidth of 0.03-0.05 Å can be obtained using the grating and telescope alone and the output bandwidth can be reduced by a further factor of ten by inserting a tilted Fabry-Perot étalon into the cavity. As explained in section 13.7.4 this acts simply as a narrow bandpass filter with the transmission maxima determined by the condition

$$2 \mu t \cos \phi = n \lambda \quad (14.2)$$

where  $\phi$  is the tilt angle, and  $\mu$  and  $t$  are the refractive index and thickness of the étalon respectively. The laser wavelength can be tuned continuously over a range of several Ångstroms by altering the tilt angles of the étalon and grating simultaneously. The wavelength stability is limited by temperature changes in the étalon, but can be as good as 0.01 Å over several hours.

In dye lasers of this type the efficiency can be as high as 20 per cent. At low repetition rates thermal schlieren effects are absent because the pulse length is so short, 5-10 ns, and the output beam is nearly diffraction limited. However, for repetition rates above 10 Hz it is necessary to circulate the dye transversely through the cell. Peak optical output powers of several kW can then be generated at repetition rates approaching 100 Hz.

14.2.4. Argon laser-pumped dye lasers - C.W. systems. The very high intensity required to pump dye lasers on a C.W. basis can so far be obtained only by using the tightly focussed beam of an argon or krypton ion laser, as shown in Fig.14.6. In this particular design, developed by Kogelnik *et al.* (1972), the argon laser beam enters the dye laser cavity through a Brewster angle prism and is focussed to a spot of approximately 10  $\mu\text{m}$  diameter in the tilted dye cell

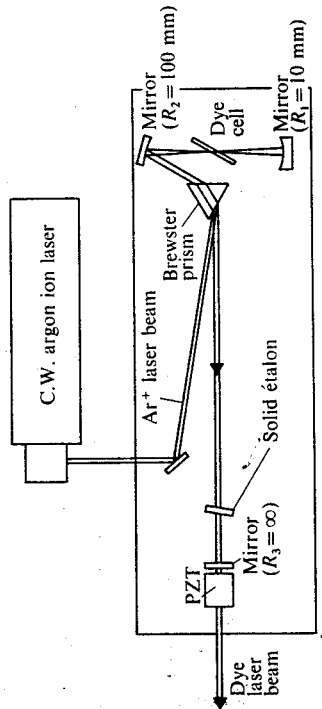


Fig. 14.6. Argon ion laser-pumped C.W. dye laser using three mirror cavity. (After Walther (1974).)

by an off-axis, short radius of curvature mirror. The folded arrangement of three mirrors and the Brewster angle prism then form the dye laser cavity and astigmatism is compensated by careful choice of the radii of curvature of the mirrors. Unlike the pumping schemes discussed previously, the single pass gain in C.W. systems seldom exceeds a few per cent and a low-loss optical cavity is necessary for successful dye laser oscillation. This means that diffraction gratings cannot be used as tuning elements; however, even the low dispersion provided by a single prism is sufficient to reduce the output bandwidth to  $\approx 0.25 \text{ \AA}$ , for the amplified radiation now makes a much larger number of transits before leaving the cavity.

In order to reduce the bandwidth still further it is first essential to provide high thermal and mechanical stability, for instance by mounting all the optical components on a massive invar base. Oscillation on a single cavity mode can then be achieved by employing a tilted intracavity étalon and bandwidths as low as 1.5-5.0 MHz have been attained. With this étalon fixed, the dye laser output can be tuned over the free spectral range,  $c/2L \approx 500 \text{ MHz}$ , of the main cavity by mounting one of the mirrors on a piezo-

electric drive and thus varying the length of the cavity. Continuous tuning over the bandwidth determined by the prism is considerably more difficult and requires synchronous tuning of the lengths of both the cavity and the mode-selecting étalon.

For many experiments in atomic and molecular spectroscopy C.W. dye lasers would seem to be the natural choice were it not for the fact that, of all the systems we have discussed, they are the most difficult to operate successfully. Moreover their output is often limited to the 5400-6500  $\text{Å}$  region by the fact that only a few dyes such as rhodamine 6G, rhodamine B and coumarin 6 can be made to oscillate on a C.W. basis when the strong blue-green argon lines at 4880  $\text{Å}$  and 5145  $\text{Å}$  are used as the pump. It is possible to extend the operating range to 4000-7000  $\text{Å}$  by pumping with the ultraviolet lines of the krypton or argon ion lasers, but here pump powers of 10-15 W or more are usually necessary.

14.2.5. Comparison of different dye lasers. Representative values of the output power, pulse duration, and tuning range of dye lasers pumped by the four schemes we have just considered are given in Table 14.1. The table also includes values of the minimum output bandwidth but these should be treated with some caution since results in individual cases are very largely determined by the alignment and stability of the dye laser cavity. Moreover this figure may be increased by several orders of magnitude should the number of frequency selective elements in the cavity be reduced.

The range of tunable dye laser radiation may be extended down to 230 nm by frequency doubling or optical sum-frequency generation using non-linear optical materials. Similarly coherent infrared radiation can be generated using difference frequency mixing in non-linear crystals or by stimulated Raman scattering in alkali metal vapours, as indicated in Table 14.2. However, the efficiency of these conversion processes is often rather low, especially in the infrared region, and experiments outside the normal

Operating parameters of dye lasers

Pump source	Output power (peak value)	Pulse duration (ns)	Repetition rate (Hz)	Approximate bandwidth (MHz)	Wavelength range (nm)
Flashlamp	20 - 50 kW	300 - 500	10 - 100	4	350 - 850
Ruby or neodymium laser	0.5 - 5.0 MW	5 - 20	≈ 1	50	350 - 1200
Molecular nitrogen laser	2.0 - 200 kW	2 - 8	30 - 500	500	350 - 1200
Argon ion laser	50 - 500 mW	—	C.W.	0.5	400 - 700

TABLE 14.1.

TABLE 14.2

Wavelength range of ultraviolet and infrared radiation generated by dye laser sum and difference frequency mixing in non-linear media

Non-linear optical material	Wavelength range	Input power (peak)	Conversion efficiency (per cent)
Ammonium dihydrogen phosphate (ADP)	280 - 290 nm	20 MW	10
Cooled ADP	250 - 325 nm	60 kW	10
Lithium formate monohydrate	230 - 300 nm	50 kW	2
Proustite (Ag <sub>3</sub> AsS <sub>3</sub> )	3.2 - 5.6 μm	900 kW	2
Lithium iodate	4.1 - 5.2 μm	4 MW	10 <sup>-2</sup>
Proustite	10.1 - 12.7 μm	290 kW	10 <sup>-6</sup>
Sodium/potassium vapour	2.21 - 23.4 μm	20 kW	10 <sup>-5</sup>

tuning range of dye lasers are still rather difficult.

When shorter pulse lengths are necessary these can be generated by mode locking a dye laser as discussed in section 13.6. The very wide gain bandwidth of dye lasers should theoretically permit the generation of sub-picosecond pulses, but dispersion in the cavity optics and other problems have so far imposed a lower limit of about 1.5 ps on the attain-