

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-

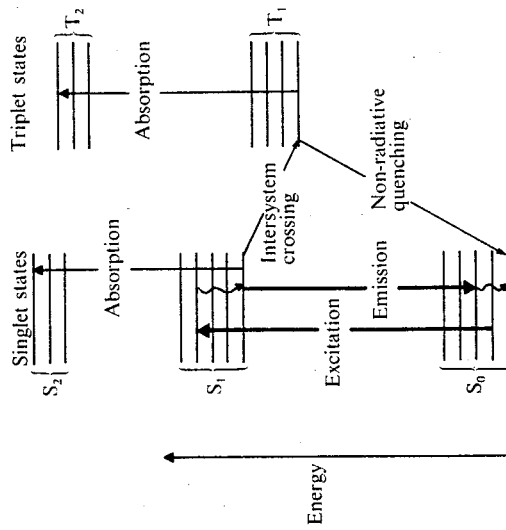


Fig.14.1. Schematic energy level diagram of typical dye molecule. (After Hänsch (1973).)

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 $1400\text{--}1700\text{ cm}^{-1}$ 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 π -orbital.

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