



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 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