# CHAPTER TWO

## FUNDAMENTAL BASIS OF DYE LASERS

### 2.1 BASIC PRINCIPLES OF DYE LASERS

Organic dyes are characterized by a strong absorption band in the visible region of the electromagnetic spectrum. Such a property is found largely in organic compounds that contain an extended system of conjugated bonds, with alternating single and double bonds. The long-wavelength absorption band of dyes is attributed to the transition from the electronic ground state $S_0$ to the first excited singlet state $S_1$. The reverse process $S_1 \rightarrow S_0$ is responsible for the spontaneous emission known as fluorescence and for the stimulated emission in dye lasers.

When the dye laser is pumped with an intense light source, the dye molecules are excited typically to some higher level in the singlet state, from which they then relax to the lowest vibronic level of $S_1$. The molecules remain in this level until they are called on for stimulated emission.

Direct relaxation to ground state $S_0$ or internal conversion and intersystem crossing to the triplet manifold are the non-radiative process that compete with the light emission and thus reduce the laser efficiency. The considerable triplet-triplet absorption resulting from the relative long lifetime of the triplet-state molecules is known to inhibit lasing action.

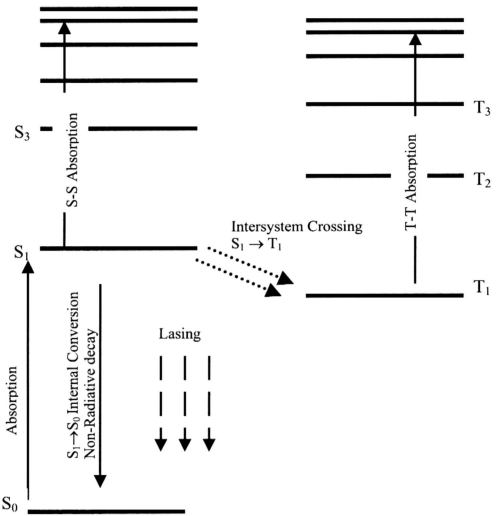


Figure 2.1. Energy level diagram of an organic dye molecule (taken from reference [2])

## 2.2 PHYSICAL PROPERTIES OF EFFICIENT DYE LASERS

The molecular structure and the lasing properties of organic dyes have a strong relationship to each other, and this must be considered in the design of the new laser dyes. A rigid planar molecular structure favors high laser efficiency as such as architecture inhibits structural mobility and increases conjugation, as may be illustrated by the dye 6-cyanobenzquinuclidine [28]. Structural mobility increases the rate of non-radiative internal conversion $S_1 \rightarrow S_0$ that is illustrated by the dyes Rhodamine 6G, Rhodamine B, Coumarin 30 and Coumarin 2 [41]. However, other factors can affect the overall laser performance such as dye concentration, thickness of the active region, photophysical limits of the samples and excitation parameters/geometry.

On the other hand, hydrogen atoms attached directly to the chromophore group of the dye will influence the non-radiative process $S_1 \rightarrow S_0$. This mechanism becomes increasingly effective with the decreasing energy difference between $S_1$ and $S_0$. The replacement of hydrogen by deuterium should reduce the rate of non-radiative decay.

If a part of the dye molecule is strongly electron-donating or withdrawing, a reversible charge transfer may occur between this portion and the excited chromophore, which will result in the loss of electronic excitation. Thus, when a nitro group is introduced into the carboxyphenyl substituent of a rhodamine dye, a non-fluorescent derivative is obtained.

Circulating electrons create an orbital magnetic moment that couples with the spin of the electron. This increased spin-orbit coupling then enhances the rate of the intersystem crossing, another non-radiative decay process. In a dye where the $\pi$-electrons of the chromophore can make a loop when oscillating between the end groups, the triplet yield will be higher than a related compound whose loop is blocked. Oxazine dyes and their compounds that contain tetrahedral carbon atom in place of oxygen

lingkages do not allow any π-electron to pass over the bridge and thus provide low triplet yields.

The intersystem-crossing rate can be greatly enhanced if the dye is substituted with heavier elements, which increases spin-orbit coupling. The triplet yield of eosin, in which hydrogen is replaced by bromine of fluorescein, in alkaline solution was found to be 76%, compared with that for fluorescein itself. The effect is also noticeable if an organic dye is merely dissolved in a solvent that contains heavy-atom substituents, e.g., iodomethane and iodobenzene.