

a torsional motion of the quinolyl group and the phenyl group respectively. All previous picosecond studies on these compounds have been made at a single excitation wavelength. In this work the excitation wavelength was varied between 555 and 633 nm. As a result of this study we found a large change in the lifetime τ of ground state recovery. For instance, in the cyanine dye DQOCI in butanol τ is 35 ps at 633 nm and 55 ps at 585 nm and in the triphenylmethane dye ethyl violet in hexanol τ is 12 ps at 630 nm and 37 ps at 580 nm. The most outstanding feature of this wavelength dependence in DQOCI and ethyl violet is a fast rise in the lifetimes as the 0-0 transition is passed from the low energy side. As an explanation for this strong τ versus λ dependence we propose a model where S_1 is close to another singlet state S_2 . The crossing between the potential surfaces of S_1 and S_2 occurs close to the zeroth vibrational state in S_1 and there is no potential barrier for the crossing to occur. Excitation to a higher vibrational state of S_1 leads to a slower rate of internal conversion.

Quenching of triplet states of dyes by inorganic ions in aqueous solutions

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The quenching of triplet states of organic dyes (fluorescein, eosin and acridine orange) by transition metal ions (d and f elements) was studied in aqueous solutions by flash photolysis. The values of the quenching rate constants for the triplet states were determined. It was shown that the efficiency of quenching depends on the position of the triplet level of the dye and the redox properties of the dyes and metal ions. The general pattern of the triplet state quenching was considered, involving energy transfer, electron transfer and the external heavy atom effect. A method of distinguishing between the three major quenching mechanisms is proposed. The relationship between the quenching rate constants and the free-energy change of the electron transfer and energy transfer steps is discussed. The formation of solvated radical ions was established for some dye-metal ion couples. The efficiency of the formation of radical ions was found to be due to the competition of dissociation and recombination processes occurring in ion pairs. The values of dissociation and recombination rate constants were determined.