

# Charge transfer symmetry breaking in excited quadrupolar molecules in protic solvents

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A threshold-type dependence of the fluorescence quenching of a centro-symmetric acridine-dione in mixtures of protic (methanol) and aprotic (DMF) solvents is analyzed theoretically. The following assumptions are made: 1) fluorescence quenching occurs due to the formation of an H-bond between the fluorophore and the protic solvent and 2) only sufficiently long clusters of methanol molecules can form strong complexes with the fluorophore and cause an excited state charge transfer symmetry breaking and a strong fluorescence quenching. The assumptions allow explaining the observed absence of quenching at methanol concentrations below 9 M. The developed theory provides both quantitative description for the concentration dependence of the fluorescence yield and non-exponential fluorescence decay kinetics measured experimentally [1]. Since charge transfer dissymmetry degree is sensitive to the interaction energy between the fluorophore and the clusters this opens up new possibilities for studying the details of H-bond clustering in protic solvents.

A model of H-bond effect on charge transfer symmetry breaking in excited quadrupolar fluorophores is proposed. Such a fluorophore has two symmetrically arranged H-bond acceptors. The effect of H-bonding is described in terms of two quantities: 1) the free energy of H-bond formation by an excited symmetric fluorophore with a protic solvent, and 2) a parameter determining the susceptibility of the H-bond strength to the charge of the H-bond acceptor. The model bases on the fact that an increase in fluorophore dissymmetry makes one acceptor more negative and the other less negative. This results in strengthening of the H-bond on one branch and weakening on the other. An analytical solution of the mathematical model is obtained. Regardless of the strength of the H-bond, the effect of the H-bonding on the symmetry breaking degree is shown to be small, as long as the free energy of formation of the weaker H-bond is negative. A strong effect is expected only if this free energy becomes positive, that is, when the H-bond is formed on only one arm. An unexpected result of weakening of the dissymmetry degree caused by the strengthening of the H-bond is predicted and discussed. An approach for quantitative determination of the susceptibility of the H-bond strength to the charge of the H-bond acceptor is proposed.

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[1] S.L. Bondarev, T.F. Raichenok, S.A. Tikhomirov, N.G. Kozlov, T.V.

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