

Selective Energy Flow in Solution through Anisotropic Inter-molecular Interaction.

Haruo Inoue

Department of Applied Chemistry, Graduate Course of Engineering, Tokyo Metropolitan University,

1-1 Minami-ohsawa, Hachiohji, Tokyo 192-0397 Tokyo JAPAN

e-mail: inoue-haruo@c.metro-u.ac.jp

A radiationless deactivation from an electronic excited state produces a highly vibrationally excited molecule. Unstable intermediates on a reaction pathway are sometimes highly vibrationally excited. Generally the excess energies of the highly vibrationally excited molecules in a condensed phase have been accepted to dissipate very rapidly into thermal energy of low temperature. The dissipation is known to be a random process. It is most interesting, if the excess energy of the highly vibrationally excited molecule (Hot molecule) could be transferred selectively to another molecule. This process may be called a "Selective energy flow."

As a model reaction of the selective vibrational energy flow in fluid system from a "Hot molecule" to another molecule through a specific interaction such as hydrogen bonding, vibrationally sensitized decomposition of peroxide coupled with a radiationless deactivation of an excited organic molecules was attempted. The lowest excited singlet states (intramolecular CT) of aminoanthraquinones and aminofluorenones are known to suffer a substantial deactivation in ethanol due to an intermolecular hydrogen bond between the carbonyls of quinones and the hydroxyl group of alcohol. Fluorescences of aminoanthraquinones and aminofluorenones in benzene upon selective excitation of the aromatic carbonyls were also quenched by cumylhydroperoxide (CHP) through intermolecular hydrogen bonding interaction to result in an effective sensitized decomposition of the peroxide, while benzoyl peroxide (BPO) which can not form hydrogen bonds with the carbonyls of quinones did not suffer any sensitized decomposition even on prolonged irradiation. Molecular mechanism of the energy dissipation through the quenching by alcohol molecules was intensively studied. Detailed time resolved fluorescence emission and transient absorption studies revealed that dual modes of anisotropic hydrogen bonding interactions of 1) in-plane mode and 2) out-of-plane one with the hydroxyl group of alcohol are involved in the relaxation processes of the excited aromatic carbonyls. The in-plane mode interaction leads to form a weakly emissive species, while the out-of-plane one results in an efficient radiationless deactivation.

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