1-4-2. Hydrogen Bonding Interactions in the Excited States

Overview

One of the important primary processes in the excited state of a molecule is the formation of intramolecular or intermolecular hydrogen bonds. Photoexcitation of a molecule significantly changes the electron density distribution from the ground state, and when the electron density of a specific atom in the molecule increases, intermolecular hydrogen bonds are often enhanced compared to the ground state, resulting in an important non-radiative deactivation process. Recently, anisotropic interactions at the molecular level have been revealed, such as the existence of two types of interactions: in-plane and out-of-plane, when the negative charge is concentrated on the carbonyl oxygen atom in the intramolecular charge transfer state.

Current Status and Frontiers

One of the important primary processes in the excited state of a molecule is the formation of intramolecular or intermolecular hydrogen bonds. In a pioneering report, Mataga et al. discovered that the fluorescence of the aromatic alcohol β-naphthol changes significantly in various solvents, and discussed the hydrogen bonding in the excited state.[1] Aromatic molecules that absorb visible or ultraviolet light often exhibit a significant change in electron density distribution in their excited states compared to their ground states. In particular, when the intramolecular charge transfer state (ICT) is the lowest excited state, the electron density of specific atoms within the molecule changes significantly in the excited state, enhancing intermolecular hydrogen bonding to result in a nonradiative deactivation process as an important primary process. Typical examples are summarized in Table 1. When an aromatic molecule in the excited state exhibits hydrogen bond donating properties against another aromatic molecular as hydrogen bond acceptor, the hydrogen bonding interaction can be expressed in conjunction with charge transfer interaction (Fig. 1).[2–4] Details of hydrogen bond dynamics have been revealed using femto-picosecond spectroscopy.[3,4]

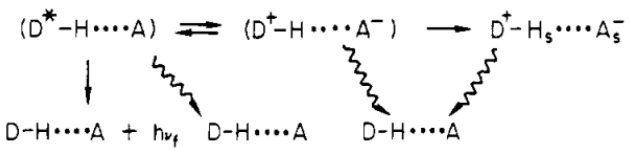


Figure 1. Hydrogen bonding interaction among two aromatic molecules (D: PyOH, AP, A: Py in Table 1).

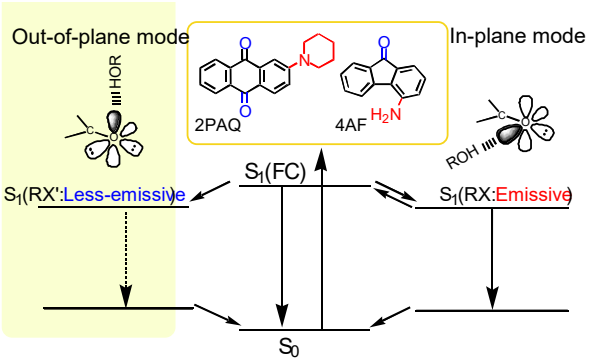
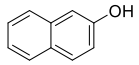
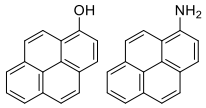
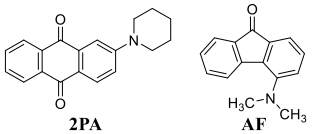


Figure 2. Anisotropic hydrogen bonding in the excited state.

On the other hand, aminoanthraquinones (2PA) and aminofluorenones, which are typical molecules whose lowest excited states are ICT, serves as hydrogen-bonding acceptor in their lowest excited state. In

ICT, charge transfer occurs primarily from the amino nitrogen to the intramolecular carbonyl oxygen atom. Then, aliphatic alcohol, such as ethanol, strongly interacts with the carbonyl oxygen of the ICT excited state of 2PA, essentially jumping on it, and induces highly efficient non-radiative deactivation through enhanced intermolecular hydrogen bonding.[5–7] The fluorescence of 2PA is quenched by ethanol with a deuterium isotope effect, whereby the fluorescence quenching effect is reduced when the alcohol hydroxyl group is changed from -OH to -OD. Detailed dynamic observations and analysis using a femtosecond laser pulse have revealed anisotropic interactions at the molecular level, including the existence of two types of interactions: in-plane and out-of-plane (Fig. 2).[8] Furthermore, in the case of the hydroperoxide ROOH, which has an alcohol-type hydroxyl group, the non-radiative deactivation of PA via intermolecular hydrogen bonding induces an efficient decomposition of the hydroperoxide. This is expected to be developed as an energy coupling model of chemical reaction in which non-radiative deactivation through high vibrational energy transfer within a supramolecular system induces an actual chemical reaction.

Table 1. Hydrogen bonding interactions in the excited states.

Donor	Acceptor	Interactions	Reference
 β-naphthol	Dioxane, alkyl acetate, triethylamine, etc.	Hydrogen bonding through enhanced acidity in the excited state	1, 2
 **PyOH** **AP**	 **Py**	Hydrogen bonding coupled with charge transfer	3, 4
ROH	 **2PA** **AF**	Hydrogen bonding	5–8

References

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Future Perspectives and Directions

Issues that need to be resolved and realized within the next 10 years: Realizing the construction of an energy coupling among chemical reactions through hydrogen bonding interactions as a “chemical soliton” model in supramolecular systems, etc.

(Author: Haruo Inoue)