1-4-1. Photoinduced Electron Transfer Processes

Overview

Photoinduced electron transfer processes have been long studied extensively in the field of photochemistry from various viewpoints. These include experimental research exploring the verification of the theoretical study of electron transfer reactions, fundamental processes in light energy conversion such as natural/artificial photosynthesis, developments in photofunctional molecules, utilization as photo-reducing or oxidizing agents for subsequent chemical reactions, and so forth. In these years, electron transfer reactions using multiple photon processes have been reported, such as consecutive photoinduced electron transfer where radical anions generated by one-photon reaction are further excited to enhance their reducing ability to other molecules, and selective electron transfer from highly excited states generated via multiple photon excitation leading to the formation of charge separated state which cannot be produced from the lowest excited state. These reactions can open new fields in photoinduced electron processes.

Current Status and Frontiers

Electron transfer reactions were considered as one of the mechanisms of fluorescence quenching, and various studies have been long conducted in the field of photochemistry such as exciplex and excited state CT complexes. Because the photoinduced electron transfer starts with the time origin of photoexcitation, reaction rates can be determined in detail using time-resolved measurements. Therefore, experimental studies on the determination of photoinduced electron transfer rates were conducted for various systems to explore correspondence with theories on the electron transfer reactions on the relation between the rate and the energy gap of the reaction. Furthermore, concerning fundamental processes in the electron transfer reactions, experimental and theoretical studies on the dynamic responses of solvents have also been extensively reported. Solvent fluctuations play a crucial role in electron transfer reactions, in particular, in polar solvents and stabilization by the solvation of the excited molecules are one of the important factors for Stokes shifts in absorption and fluorescence as shown in the Mataga-Lippert equation.

On the fundamental process in light energy conversion, various intramolecular donor-acceptor molecular systems have been synthesized and studied to systematically unveil the relation between the electron transfer rate and the energy gap of the reaction. Focus of these studies progressed from simple donor-acceptor systems to multi-chromophore complex systems. Alongside deepening understanding of electron transfer reaction mechanisms, research evolved toward artificial photosynthesis involving charge shifts within molecules, applying the principles of electron transfer reactions. Particularly in Japan, a large number of researchers have led this field by using organic and inorganic molecular systems. In porphyrin-fullerene conjugated systems, charge separation living in orders of seconds has been achieved.

Research has expanded beyond organic/inorganic molecules to include systems utilizing semiconductors and metal dots as electron donors or acceptors. Additionally, electron transfer reactions in biomolecules, complex systems with very strong interactions between electron donors and acceptors, and electron occurring at interfaces are widely studied.

Recently, a new type of electron transfer reactions has been developed by using multiphoton absorption processes (Fig. 1). In consecutive photoinduced electron transfer, a radical anion generated by a single-photon electron transfer reaction is further excited to enhance its reducing power to other molecules. For the production of a charge-separated state with an energy level higher than the lowest excited state, selective electron transfer proceeding from a high-energy excited state generated by multiple excitations has been reported. These multiphoton electron transfers can be applied in a new stage of the photoinduced electron transfer.

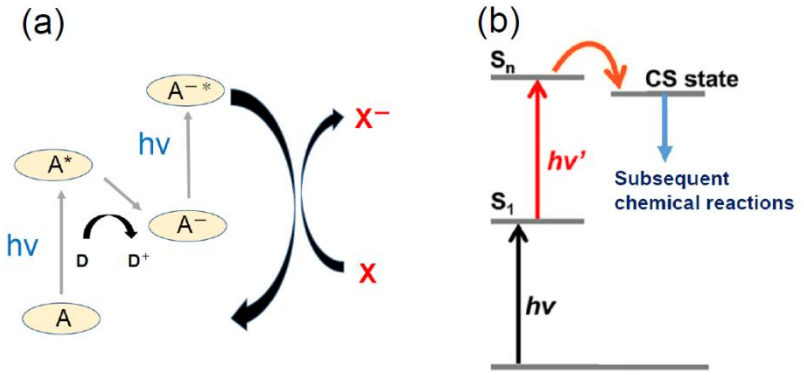

Figure 1. Examples of electron transfer reactions using two-photon absorption. (a) Consecutive electron transfer, and (b) Generation of a high-energy charge-separated (CS) state by multiple excitation, leading to subsequent chemical reaction.

References

1. N. Mataga, H. Miyasaka, *Adv. Chem. Phys.*, **107**, 431–496 (1999).
2. N. Mataga, et al., *J. Photochem. Photobiol. C*, **6**, 37–59 (2005).
3. H. Imahori, et al., *J. Am. Chem. Soc.,* **123**, 6617–6628 (2001).
4. N. Mataga, et al., *Bul. Chem. Soc. Jpn.*, **28**, 690–691 (1955).
5. Y. Kobayashi, et al., *J. Am. Chem. Soc.,* **138**, 5930–5938 (2016).
6. T. Uno, et al., *J. Phys. Chem. Lett.*, **8**, 7098–7105 (2018).
7. D. Yoshioka, et al., *Nanoscale*, **13**, 1823–1831 (2020).

Future Perspectives and Directions

Challenges to be resolved or realized within the next 10 years: Establishment of a theoretical framework enabling the understanding of various electron transfer reactions. Development into socially implementable devices such as efficient solar cells, photocatalysts, and artificial photosynthesis systems.

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