STM investigation of energy conversion and transfer at a single molecule

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Excitation of molecules by light irradiation triggers various important energy conversion processes, such as luminescence, photochemical reactions, and photovoltaics. Detailed understanding of the molecular excited states is crucial to improve and develop organic energy conversion devices based on opto-electronic/opto-chemical processes.

In this talk, I will discuss two issues focusing on the interaction between a single molecule and localized surface plasmon to describe fundamental aspects of energetics on the solid surfaces.

Absorption spectroscopy is a powerful tool to describe the molecular excitations and the combination with emission (luminescence) spectroscopy which deals with deexcitation processes is effective to investigate the excited states. Single-molecule luminescence detection has progressed rapidly and become indispensable in quantum physics, physical chemistry, and biophysics. However, despite considerable effort and progress, absorption spectroscopy is far behind; number of molecules are still necessary to obtain an absorption spectrum. A difficulty lies in the difference between the diffraction limit of excitation light and absorption cross section of a single molecule. Here I introduce our recent progress in measurement of the single molecule luminescence and absorption spectra of a single molecule using a scanning tunneling microscope (STM) equipped with optical detection facilities, which is applied to the real-space investigation of energy transfer between two molecules.

Localized surface plasmon (LSP) induced chemical reactions of molecules adsorbed on metal nanostructures are attracting increased attention as novel photocatalytic reactions. Most of previous papers explained that the reactions occur through the indirect hot-electron transfer mechanism. However, the proposed indirect mechanism has been discussed on the basis of ensemble observations of the local reactions and is, therefore, still controversial. Here, I propose a novel reaction mechanism on the basis of real-time and real-space observation of single-molecule chemical reaction induced by a LSP. This is achieved by optically exciting the LSP in the gap between a plasmonic Ag tip of an STM and a metal substrate. The LSP-induced reaction will be explained in detail by comparing with visible-light-induced photoreaction of the molecule.

References

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