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分子内水素移動反応の制御と直接観察

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Control and Visualization of Intramolecular H-atom Transfer Reaction

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Molecular processes and functions are fundamental in nature and play a key role for molecular devices in nanotechnology. The atomic-scale environment of individual molecules is known to have significant impact on the potential energy landscape of chemical processes and thus the reaction rates [1]. However, such influences are extremely difficult to examine at the level of individual molecules and the effect from single atoms on chemical reactions has never been studied so far. On the other hand, H-atom transfer reaction is one of the most common and important processes in chemistry [2]. Especially, the transfer in a two-state system, i.e., intramolecular H-atom transfer (tautomerization), includes key problems, which is related with elementary processes in photochromism and enzymatic reactions. Although tautomerization has been investigated by conventional spectroscopic method, few studies reported in heterogeneous systems, i.e., on surfaces. Recent STM studies demonstrated to engineer and directly observe H-atom(bond) dynamics at the single-molecule level on a metal surface [3], which paves a novel way to explore the fundamental processes.

In the presentation, we show the precise control of tautomerization within a single molecule using STM under ultra-high vacuum conditions. The molecule is deposited onto a clean metal surface and investigated at 5 K. The tautomerization is controlled by an electron injection of STM into a molecule, where the yield shows clear position-dependence of the injection with sub-molecular scale, and using a deuterium-substituted molecule it is revealed that the tautomerization is induced by vibrational excitation. We find that the tautomerization rates can be tuned up and down in a controlled fashion by placing a single adatom with atomic precision nearby a molecule, which shows the high sensitivity of the process not only to the presence but also to the exact position of individual atoms with respect to the molecule, surprisingly also at rather large distances, i.e. more than van der Waals radius. Furthermore, we extended our experiment to molecular assemblies where even the H-atom arrangement in neighbour molecules influences the reaction rate, resulting in positive and negative cooperativity effects. Our results highlight the importance of controlling the environment of molecules with atomic precision and demonstrate the potential to regulate a single-molecule function.

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- [2] J.T. Hynes, J.P. Klinman, H.-H. Limbach, R.L. Schowen, *Hydrogen-Transfer Reactions*, WILEY, 2007.
- [3] T. Kumagai, *Visualization of Hydrogen-Bond Dynamics – Water-Based Model Systems on a Cu(110) surface*, Springer 2012.