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Visualization of Hydrogen-Bond Dynamics

Water-Based Model Systems
on a Cu(110) Surface

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Takashi Kumagai

Visualization of Hydrogen-Bond Dynamics

Water-Based Model Systems
on a Cu(110) Surface

Doctoral Thesis accepted by
Kyoto University, Japan

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Supervisor's Foreword

The water molecule, H_2O , is one of the most familiar molecules around us. Its unique ability to develop an H-bond network plays a central role in so many areas of chemistry and biology, yet it remains poorly understood at the microscopic level. Furthermore, H-bond dynamics, such as bond rearrangements and proton transfer, are difficult to probe and researchers have invariably relied on spectroscopic probes to infer H motions. In his Ph.D. work, Takashi Kumagai achieved a direct probe of the H-bond dynamics on a metal surface using a scanning tunneling microscope (STM). By combining its manipulation capabilities with single-molecule imaging, he was able to construct a variety of H-bond structures on the surface. Properties and dynamics of individual H-bonds in water clusters, hydroxyl clusters, and water-hydroxyl complexes were studied in conjunction with density functional theory. Most notably, concerted proton relay reactions, which are frequently invoked across many fields of chemistry, were visualized and controlled by tunneling electrons. One of the key aspects that distinguishes this work from others is the rational choice of a Cu(110) surface as the substrate. Because water molecules interact weakly with copper surfaces, it was not feasible to controllably manipulate a water molecule with the STM on low-index surfaces, such as Cu(111) and (100). The relatively “open” structure of the (110) plane makes the outermost Cu atoms electron-deficient, which causes water molecules to be moderately bound on the surface. Furthermore, the 2-fold symmetry of the substrate makes the dynamics of water and its derivatives anisotropic, which allows us to investigate them in a straightforward way. Takashi Kumagai's great efforts and patience that always must accompany STM experiments were certainly essential. This thesis paves the way for studying H-bond dynamics in real space, providing an important contribution to fields beyond surface chemistry.

Hiroshi Okuyama

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Chapter 1

Introduction

Abstract The main topic of this thesis is visualization of H-bond dynamics within water-based model systems assembled on a metal surface. Scanning tunneling microscope (STM) is employed to image and engineer such model systems at the single molecule level. H-bond dynamics of water molecules, i.e., the bond exchange, H-atom transfer reactions, are a pretty simple and important process in chemistry and biology, which also deeply relates to fundamentals of life activities. It is usually very difficult to investigate H-bond dynamics in chemical and biological systems at the single molecule level because complicated environmental effects cannot be eliminated in conventional spectroscopies in which the signal stems from the ensemble of the system. In this thesis I show the characterization of H-bonding nature and dynamics within water-based model systems at the spatial limit. Experiments under ultra-high vacuum and low temperature conditions eliminate the environmental effects and thermal fluctuations. General discussions and previous studies of H-bond dynamics of water are described in [Sect. 1.1](#). Previous studies of water on metal surfaces are summarized in [Sect. 1.2](#). The evolution of single atom/molecule science using STM is described in [Sect. 1.3](#). Finally, I mention the motivation and scope in [Sect. 1.4](#).

Keywords Hydrogen-bond dynamics • Water molecules on metal surfaces • Single atom/molecule science • Scanning tunneling microscope

1.1 Dynamics of Hydrogen Bond in Water

H bond is a moderate interaction between molecules. The strength of H bond is larger than that of van-der-Waals interaction while it cannot be comparable to that of covalent or ionic bonds. This intermediate strength is responsible for a wide variety of importance in chemistry and biology. For instance, H bond is commonly

used in protein folding and the structures of DNA. H bond is also the path of H-atom transfer that is one of the most elementary and significant reactions in synthetic, environmental and biological processes. For instance, H-atom transfer is essential in biological catalysis because the transportation of H atom into the correct site and timing can enhance the process in enzyme reactions.

H bond in water is a quite ubiquitous question in nature. The H bond is formed between an H atom and an electronegative O atom, which provides unique properties of water [1], e.g., the relatively high boiling point, the lower density in solid than that in liquid, and the tendency to form dome-like droplets on solid surfaces. A water molecule can form four H bonds, thus two donating and two accepting H atoms. Although water molecules build three-dimensional networks in the liquid, continuous annihilation/re-creation of H bond and changes of molecular orientations/distances takes place with the time scale from femtosecond to picosecond. This flexibility of H bond gives rise to an abundant phase behavior in the pressure–temperature diagram. The dynamical fluctuation of H bond is also associated with various chemical and physical processes, e.g., solvation, acid–base reactions in solution, and freezing processes. For this reason, it has been a long-standing challenge to elucidate the net structure and dynamics of H bond in liquid water and numerous experimental [2–21] and theoretical [22–34] efforts have been devoted in the past. Infrared absorption, Raman scattering, depolarized light scattering, inelastic neutron scattering, and x-ray absorption spectroscopy have been employed to probe H-bond dynamics indirectly. The vibrational spectroscopies have been proven to be a powerful tool observing H-bonding nature and dynamics of water. A water molecule has three fundamental vibrations, i.e., the symmetric and asymmetric stretching modes at 3657 and 3756 cm^{-1} , respectively and the bending mode at 1595 cm^{-1} [34]. Especially, it is beneficial to detect the O–H stretching mode of water molecules because its frequency is quite sensitive to the H-bonding nature, like the number and relative strengths of H bond. Specifically, the frequency shows redshift as a water molecule forms H bond due to a weakening of the covalent OH bond. This weakening results from the substantial charge transfer from covalent O–H bond to the vicinity of H bond. In addition to the redshift, a spectral broadening can also arise from several reasons; anharmonic coupling to low-frequency modes, Fermi resonances with overtone and inhomogeneous broadening due to different H-bonding geometries [35–38]. Although linear vibrational spectroscopy provides a direct evidence of H-bonding interaction of steady states, it is quite difficult to gain insights of its dynamics because such spectroscopy gives only time-averaged signals. Ultrafast time-resolved vibrational spectroscopy is a powerful tool to investigate the dynamics of liquid water, which enables us to probe H-bond dynamics in real-time. Infrared pump-probe spectroscopy has often used to observe the ultrafast dynamics of the H-bond network of water [39–46]. However, the experimental data have often interpreted in only qualitative way. The difficulty to reproduce H-bonding dynamics mainly results from the complex potential energy landscape as well as a large number of possible network configurations. Moreover, quantum effects, i.e., tunneling, zero-point energy, become pronounced due to its small mass of H-atom, making it further