

## Chapter 11

# Conclusions

I described the real space observation of H-bond dynamics within water-based model systems assembled on a metal surface. Low-temperature scanning tunneling microscope was employed to image, assemble and characterize such systems at the single molecule level. The combination of manipulation and controlled dissociation of individual water molecules made it possible to construct a variety of H-bonded systems. In addition to the assembly of desirable model systems, the time-resolved measurement of STM was proven to be useful to unveil the process of H-bond dynamics at the single molecule level. The voltage and current dependence of a motion or a reaction provided the key to elucidate the elementary processes. Especially, the voltage dependence is directly associated with vibrational excitations of molecule and quite useful for chemical identifications of adsorbates as well as for determining dynamical properties.

This research shed a new light on understanding of H-bond dynamics at a heterogeneous system in terms of the single molecule limit. In particular, visualization of quantum dynamics, such as H-bond interchange tunneling in a water dimer, single-proton flip motion in hydroxyl group and a symmetric H-bond in a water-hydroxyl complex, is highlighted. Furthermore, H-atom relay reactions, like the Grotthuss mechanism, were directly observed in one-dimensional H-bonded complexes for the first time. However, the time-resolution of STM was still limited to capture the transition state of the reaction process. To improve the time-resolved imaging would pave a novel way to elucidate detailed processes of H-bond dynamics. Additionally, the investigation of the temperature dependence of those processes gives abundant information of potential landscape determining the dynamical properties. Water and hydroxyl spontaneously form a wide variety of ordered structures on material surfaces. The combination of this self-assembling nature with STM manipulation gives a way to realize much more sophisticated and complex systems to examine H(-bond) dynamics.