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Review

Direct observation and control of hydrogen-bond dynamics using low-temperature scanning tunneling microscopy



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ABSTRACT

Hydrogen(H)-bond dynamics are involved in many elementary processes in chemistry and biology. Because of its fundamental importance, a variety of experimental and theoretical approaches have been employed to study the dynamics in gas, liquid, solid phases, and their interfaces. This review describes the recent progress of direct observation and control of H-bond dynamics in several model systems on a metal surface by using low-temperature scanning tunneling microscopy (STM). General aspects of H-bond dynamics and the experimental methods are briefly described in chapter 1 and 2. In the subsequent four chapters, I present direct observation of an H-bond exchange reaction within a single water dimer (chapter 3), a symmetric H bond (chapter 4) and H-atom relay reactions (chapter 5) within water-hydroxyl complexes, and an intramolecular H-atom transfer reaction (tautomerization) within a single porphycene molecule (chapter 6). These results provide novel microscopic insights into H-bond dynamics *at the single-molecule level*, and highlight significant impact on the process from quantum effects, namely tunneling and zero-point vibration, resulting from the small mass of H atom. Additionally, local environmental effect on H-bond dynamics is also examined by using atom/molecule manipulation with the STM.

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Contents

1.	Introduction	240
1.1.	Brief remarks on the H bond	240
1.2.	Tunneling dynamics of the H bond in a double-well potential	241
1.3.	The role of zero-point energy in H-bond dynamics	242
1.4.	H-atom (proton) transfer reactions	244
1.5.	Intramolecular H-atom transfer reactions	245
2.	Methods	246
2.1.	Direct observation and control of molecular processes using scanning tunneling microscopy	246
2.2.	Experimental details	248
2.3.	DFT calculations	248
3.	Tunneling dynamics of the H-bond exchange reaction; water dimers on Cu(110)	249
3.1.	Background	249
3.2.	Direct observation of a water dimer	250
3.3.	Rate of the H-bond exchange reaction	251
3.4.	Mechanism of the H-bond exchange reaction	252
3.5.	Vibrationally assisted tunneling of the H-bond exchange reaction	253
3.6.	Impact of local environments on the H-bond exchange reaction	254
4.	Symmetric H bond; water–hydroxyl complex on Cu(110)	255
4.1.	Background	255
4.2.	Formation of water–hydroxyl complexes	255
4.3.	Structure of water–hydroxyl complexes	257
4.4.	Symmetric H bond within a water–hydroxyl complex	259
5.	H-atom relay reactions; water–hydroxyl chain complexes on Cu(110)	261
5.1.	Background	261
5.2.	Assembly of H ₂ O–(OH) ₂ chain complex	261
5.3.	Structure of H ₂ O–(OH) ₂ chain complex	262
5.4.	H-atom relay reactions induced by STM	263
5.5.	Theoretical analysis of vibrationally-induced H-atom relay reaction	266
5.6.	Reaction pathway of the H-atom relay reaction within H ₂ O–(OH) ₂	269
6.	Intramolecular H-atom transfer reaction; porphycene molecule on Cu(110)	270
6.1.	Background	270
6.2.	Structure of a single porphycene molecule	271
6.3.	Thermally induced <i>cis</i> – <i>cis</i> tautomerization	272
6.4.	STM-induced <i>cis</i> – <i>cis</i> tautomerization	273
6.5.	Mechanism of STM-induced tautomerization	277
6.6.	Control of tautomerization within a single porphycene molecule using single Cu atoms	280
6.7.	Tautomerization of individual porphycene molecules in molecular assemblies	284
7.	Outlook	286
	Acknowledgements	286
	References	287

1. Introduction

1.1. Brief remarks on the H bond

The hydrogen bond (H bond) is a non-covalent bond (electrostatic attractive interaction) [1] that occurs between polar molecules in which an H atom is bound to an electronegative atom such as fluorine (F), oxygen (O), or nitrogen (N). The minimum structural motif consists of an H bond donor X, an acceptor Y, and an H atom, and is represented as X–H···Y where X–H and H···Y stand for a covalent- and H bond, respectively. The strength of the H bond is typically in the range of 1–7 kcal/mol, which is considerably weaker than covalent or ionic bonds, but about 10 times larger than the van der Waals interaction. This intermediate strength makes it possible to create and break H bonds in a reversible fashion. In this context, the H bond can be viewed as “flexible”, and its dynamics are

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