



Review article

Atomic-scale investigation of nuclear quantum effects of surface water: Experiments and theory

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ABSTRACT

Quantum behaviors of protons in terms of tunneling and zero-point motion have significant effects on the macroscopic properties, structure, and dynamics of water even at room temperature or higher. In spite of tremendous theoretical and experimental efforts, accurate and quantitative description of the nuclear quantum effects (NQE) is still challenging. The main difficulty lies in that the NQEs are extremely susceptible to the structural inhomogeneity and local environments, especially when interfacial systems are concerned. In this review article, we will highlight the recent advances of scanning tunneling microscopy and spectroscopy (STM/S), which allows the access to the quantum degree of freedom of protons both in real and energy space. In addition, we will also introduce recent development of *ab initio* path-integral molecular dynamics (PIMD) simulations at surfaces/interfaces, in which both the electrons and nuclei are treated as quantum particles in contrast to traditional *ab initio* molecular dynamics (MD). Then we will discuss how the combination of STM/S and PIMD are used to directly visualize the concerted quantum tunneling of protons within the water clusters and quantify the impact of zero-point motion on the strength of a single hydrogen bond (H bond) at a water/solid interface. Those results may open up the new possibility of exploring the exotic quantum states of light nuclei at surfaces, as well as the quantum coupling between the electrons and nuclei.

1. Introduction

1.1. Nuclear quantum effects (NQEs)

Water is vital to human's daily life and has been extensively investigated throughout the history of science. However, the molecular-level understanding of the structure and many unusual properties of water still remains a great challenge in spite of the persistent development of new scientific instruments and theoretical methods. The mystery of water mainly arises from the

Abbreviations: STM, Scanning tunneling microscopy; STS, Scanning tunneling spectroscopy; IETS, Inelastic electron tunneling spectroscopy; EELS, Electron energy loss spectroscopy; SFG, Sum-frequency generation spectroscopy; NMR, Nuclear magnetic resonance; XRD, X-ray diffraction; IR spectroscopy, Infrared spectroscopy; nc-AFM, Noncontact atomic force microscopy; NV center, Nitrogen-vacancy center; PIMD, Path-integral molecular dynamics; MD, Molecular dynamics; MC simulations, Monte-Carlo simulations; DFT, Density functional theory; VASP, Vienna *ab initio* simulation package code; PES, Potential energy surface; TI, Thermodynamic integration; cNEB, Climbing image nudged elastic band; NQEs, Nuclear quantum effects; H bond, Hydrogen bond; DOS, Density of states; HOMO, Highest occupied molecular orbital; LUMO, Lowest unoccupied molecular orbital; PDOS, Projected density of states; E_F , Fermi level; vdW, Van der Waals; ZPM, Zero-point motion; ZPE, Zero-point energy; D, Deuterium; H₂S, Hydrogen sulfide; HF, Hydrogen fluoride; C₆H₁₂, Cyclohexane; AS, Anticlockwise state; CS, Clockwise state

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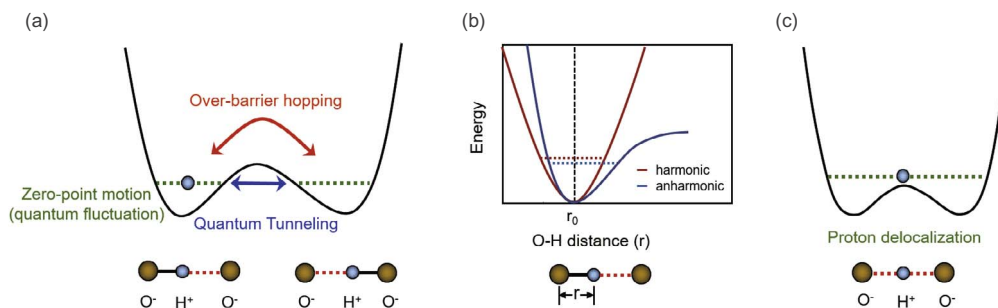


Fig. 1. Nuclear quantum effects of H bond. (a) Symmetric double-well potential of interconversion between covalent bond and H bond via proton transfer. Red and blue double-ended arrows denote over-barrier hopping and quantum tunneling of proton, respectively. The zero-point motion (quantum fluctuation) of protons is depicted by dotted green lines. (b) Schematic of the harmonic (red) and anharmonic (blue) zero-point motion of the proton. r_0 denotes the equilibrium O–H distance under the harmonic potential. (c) Reduction of the reaction barrier leading to the proton delocalization and, consequently, symmetric H bond.

intermolecular hydrogen-bonding (H-bonding) interaction. It is well known that H bonds have a strong classic component coming from electrostatics. However, its quantum component can be exceptionally prominent due to the quantum motion of light H nuclei (proton), which play important roles in the structure, dynamics, and macroscopic properties of H-bonded materials [1–10]. Therefore, the accurate assessment of NQEs has been a key issue for the understanding of many extraordinary physical and chemical properties of water.

The NQEs of water mainly arise from quantum tunneling and zero-point motion (ZPM) of protons. In water, the H atom links two oxygen atoms via a covalent bond on one side and a H bond at the other side. Classically, the covalent bond and H bond could be switched through over-barrier proton hopping, as shown in Fig. 1a. Nevertheless, such a switching can be also realized by proton tunneling (Fig. 1a) when the height and width of the potential barrier is sufficiently small, which has been observed in many H-bonded systems [1,11–17]. Another quantum nature of proton is ZPM or quantum fluctuation. Unlike classical particles, which are localized in the local minimum of potential well, protons constantly fluctuate at zero-point energy (ZPE) state due to the Heisenberg uncertainty principle. In a harmonic potential well, the ZPM is symmetric, making the averaged position of the proton coincides with the local minimum of potential well (Fig. 1b). However, the real potential profile of O–H...O has an anharmonic character. The anharmonic ZPM of H nuclei causes the O–H covalent bond to expand with respect to the case under harmonic potential, thus the H-bonding strength is enhanced (Fig. 1b). Once the reaction barrier of the proton transfer is significantly reduced, the ZPE plays a decisive role. In this situation, the proton will be totally delocalized and equally shared by the oxygen atoms, leading to a symmetric H bond (Fig. 1c).

1.2. The impact of NQEs on the structure and properties of water and ice

The NQEs usually show up in isotopic substitution experiments. When replacing hydrogen (H) atoms with heavier deuterium (D) atoms, macroscopic properties of water exhibit significant isotope effects, which have been explicitly summarized in a recent review [7]. For example, the melting temperature is increased by 3.82 K upon substituting D with H [18,19] and the temperature of the maximum density is 7.21 K higher in D_2O compared with H_2O [20,21]. Upon deuteration, the viscosity increases 23% accompanied by a 23% decrease in water diffusion [19,20,22,23]. Spectroscopic studies of liquid water at ambient temperature provide evidence that D_2O is more structured than H_2O [2,24–27]. These observations suggest that the H-bonding strength is enhanced when exchanging H with D, namely, the NQEs incline to weaken the H-bonding strength in liquid water at room temperature. However, the opposite trend appears at higher temperature [18,28] and conflicting theoretical simulations also exist [29]. So far, a consensus is not reached and it remains an open question how large the quantum component of H bond is.

The NQEs in water/ice become more prominent at low temperature or when the O–O distance of water molecules is small [1,30,31], for example, under high pressure, confined in the nano-cavity or at interfaces. The proton dynamics in ice I_h (hexagonal ice) and ice I_c (cubic ice) does not freeze out even down to 5 K, suggesting the existence of the concerted proton tunneling [17]. However, the direct evidence of the concerted proton tunneling is still lacking and under debate [11,17,32–34]. In particular, high-pressure ice has received considerable attention since the intermolecular distance can be continuously tuned by applying high pressure. As the pressure is increased, the ice undergoes phase transition from ice VIII to ice VII, which is believed to be driven by proton tunneling [1]. Symmetric ice X appears at even higher pressure as a result of zero-point fluctuations, in which the proton sits exactly halfway between the two oxygen atoms [1,35–37].

The adsorption of water on various solid surfaces gained extensive attention as well, as it is ubiquitous in nature and plays a crucial role in a great many environmental, biophysical, catalysis and even technological processes [3,38–44]. The distance between adjacent water molecules is subjected to the atomic arrangement of the surfaces because of the water-substrate interaction. Li et al. reported the substrate dependent NQEs of the H bond by quantum calculations, where the magnitude of proton delocalization between two oxygen atoms was determined by the substrate lattice constant, resulting in partially (on Pt(111) and Ru(0001)) or totally (on Ni(111)) symmetric H bonds [45]. Meanwhile, Kumagai et al. discovered the symmetric H bond in a water-hydroxyl complex on Cu(110) from real-space experiments [46]. In addition, the high diffusion rate of water dimers on Pd(111) at low

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