



Research paper

Resolving H(Cl, Br, I) capabilities of transforming solution hydrogen-bond and surface-stress

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ABSTRACT

A combination of differential phonon spectrometrics (DPS) and DFT calculations verified the essentiality of $H^+ \leftrightarrow H^+$ point fragilization and X^- polarization dictating the surface stress of HX (X = Cl, Br, I) solutions. $H^+ \leftrightarrow H^+$ repulsion breaks the network regularly; X^- polarization shortens and stiffens the H–O bonds but lengthens and softens the O:H nonbonds in its hydration shell. The X^- capability of hydrogen bond and surface stress transformation follows the order of $I > Br > Cl$. Observations provide fresh insight into the acid solvation network dynamics. DPS resolves solute capabilities of transforming the bonds and surface stress.

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1. Introduction

Although the HX (X = Cl, Br, I) protonated aqueous solutions are ubiquitously important to fields varying from agriculture, biochemistry, corrosion and protection, to medical and pharmaceutical sciences, it remains yet unclear how the H^+ proton and the X^- anions interact with the solvent H_2O molecules despite intensive investigations made since 1900s when Svante Arrhenius [1] won the 1903 Nobel prize for his definition acid-base solvation, and subsequently, Brønsted–Lowry, [2] and Lewis [3] defined the acid compounds in terms of H^+ or electron pair donation.

Typically, the acid solution is corrosive, dilutive, and surface stress (or surface tension) destructive [4–8]. Understanding the solute–solvent interaction in the acid solutions implicates to some kinds of drugs whose molecules are sided with excessive H–O dangling bonds [9,10] that functionalize cells through solution–protein interactions [11,12]. Unfortunately, such knowledge was hindered by the lacking knowledge of water structure and response of the hydrogen bond (O:H–O or HB) to the ionic perturbation in the hydration networks. Perception of the amorphous hydrogen bonding network of liquid water prevents researchers from thinking about this matter in an ordered manner.

The investigation of the hydrogen bonding network is a long-standing issue involving spectroscopies of Raman scattering, sum frequency generation (SFG), time-dependent infrared (t-IR) absorption, neutron scattering, terahertz and many other experimental methods. The SFG probes the sublayer-resolved dipole orientation or surface dielectrics, at the air–solution interface [13,14]. The t-IR resolves the solute or water molecular diffusive motion dynamics in terms of phonon lifetime and the viscosity of the solutions [15,16] in terms of ‘structural diffusion’ or ‘solute delocalization’. Neutron scattering probes the density of states of phonons in the substance of interest. Generally, one decomposes the high-frequency Raman spectroscopic data of water around 3200 cm^{-1} into various number (from 2 to 5) of components in terms of sub-layer contributions.

Tremendous work has been done in past two centuries on the ‘proton transport dynamics’ that has formed a subject of fierce debating [17–20]. It was assumed that the mobility of protons in liquid water is considerably high compared with H_2O molecules. The explanations for the proton mobility began with Grotthuss [21] in terms of ‘structural diffusion’ nearly two centuries ago. Subsequent explanations have refined this concept by invoking thermal hopping [22], proton tunneling or solvation fluctuating [23]. In 1960s, Eigen [24] proposed the formation of an $H_9O_4^+$ complex in which an H_3O^+ core is strongly hydrogen-bonded to three H_2O molecules and leave the lone pair of the H_3O^+ free. Zundel [25] supported the notion of an $H_5O_2^+$ complex in which the proton

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is shared by two H₂O molecules. Using the *ab initio* path integral simulations, Marx et al. [26] noted that the hydrated proton forms a fluxional defect in the hydrogen-bonded network, with both H₉O₄⁺ and H₅O₂⁺ occurring only in the sense of 'limiting' or 'ideal' structures. The defect can become delocalized over several hydrogen bonds owing to quantum fluctuations. The thermally induced hydrogen-bond breaking in the second solvation shell determines the rate of proton diffusion.

An ultrafast 2DIR spectroscopy investigation by Thämer and co-workers [17] suggested that the proton prefers the manner of Zundel structure accommodated by two H₂O at a time, [H(H₂O)₂]⁺, rather than the Eigen structure in which the protons piggyback on individual molecules. Similarly, Wolke et al. [27] studied deuterated prototypical Eigen clusters, [D(D₂O)₄]⁺, bound to an increasingly basic series of hydrogen bond acceptors. By tracking the frequency of every O-D stretch vibration in the complex as the transferring hydrogen is incrementally pulled from the central hydronium to a neighboring water molecule.

Moreover, *ab initio* molecular dynamics (AIMD) [28,29] suggest that 'bond switch' occurs in the first H₃O⁺ hydration shell. The key for these explanations is the H⁺ that hopping from one H₂O molecule to another by switching the H₂O ↔ H₃O⁺ on and off randomly due to thermal and quantum fluctuation [26]. Nevertheless, the 'proton transfer' seems to be a topic of continuing debating.

However, little attention has been paid to the full scan of the Raman spectra and the correlation between the frequency shifts of different components. It has been poorly known how the H⁺ functionalizes the solvent H₂O molecules and how the H⁺ determines the functionality of the hydration network of the acid solutions [30–32]. One needs to find the link between the solute dynamics to the solvent network relaxation and performance upon acid solvation.

We show in this communication that the understanding of the hydrogen bond (HB or O:H—O with ':' being the electron lone pair) cooperativity in water ice [33,34] has enabled us to resolve this solute capability of bond and surface stress transformation using Raman phonon spectrometrics (DPS) and density functional theory (DFT) calculations. Observations verified that the H⁺ ↔ H⁺ fragilization and X⁻ polarization dictate the performance of acid solutions.

2. Principles

2.1. HB cooperative relaxation and H ↔ H fragilization

Due to its intrinsic 2sp orbital hybridization [35], one oxygen atom is always associated with two H—O polar covalent bonds and two nonbonding lone pairs of electrons ':'. If a specimen contains *N* oxygen atoms, the specimen will have 2*N* pairs of ':' and 2*N* H—O bonds, conserving in the temperature range of 5 K and above. The O:H—O bond is the unique form of interaction between neighboring oxygen ions, which remains even in the ionic phase under 2000 K temperature and 2 TPa pressure [36] and in the phase of equal O:H and H—O lengths (at 60 GPa over all temperatures) [34], or in aqueous solutions [37,38].

Fig. 1a inset shows the (H₂O)₂ unit cell [33,34] with central replacement of an H₃O⁺. Hydration of an HX acid molecule creates an X⁻ anion and an H⁺ proton. The H⁺ proton bonds to one of its four neighbors by replacing a ':' and then turns this H₂O molecule into the H₃O⁺ hydronium. The H₃O⁺ remains the tetrahedron configuration having three H—O bonds and one lone pair which is equivalent to form the H_{2n+1}O_{2n}⁺ clusters with *n* = 2 (the present unit cell) and 4 (extended to a cubic unit cell of 8 molecules [34]) in the solution [26]. This process breaks the 2*N* conservation with an additional pair of H⁺ protons. The H⁺ ↔ H⁺, called anti-HB, is the only way of interaction between the H₃O⁺ and the H₂O.

Freely drift motion or translational tunneling of the H⁺ between two H₂O molecular for 2H₂O ↔ H₃O⁺: HO⁻ occurs at extreme conditions (2000 K and 2 TPa pressure) [36] is very unlikely because the H—O bond is 4.0 eV and over [34], requiring at least 121.6 nm laser to dissociate the H—O bond [39].

Fig. 1b inset shows that the radial electric field of an X⁻ cation that aligns, clusters and stretches the O:H—O bond in its hydration shell through polarization. The O:H—O bond contains the weaker O:H intermolecular nonbond (denoted as L, ~0.1 eV under the ambient conditions) and the stronger H—O intramolecular covalent bond (denoted as H, ~4.0 eV). The HB is characterized by the short-range repulsive force between electron pairs on the adjacent oxygen anions [34]. The long-range and nuclear quantum entanglement interactions can be averaged as the common background. The combination of an external excitation and the repulsion between the adjacent oxygen anions relaxes the H—O and the O:H cooperatively. Both O ions dislocate along the HB in the same direction but by different amounts. The O:H always relaxes more than the H—O does, as shown in the inset.

As an external excitation, the H⁺ ↔ H⁺ repulsion will compress the O:H nonbond that lies along the force direction slightly and elongates the H—O bond besides the local network termination. This network termination destructs the acid solution surface stress. The depolarization (decrease of dipole moment) of neighboring O:H—O bond and the weakening of neighboring H—O covalent bond by anti-HB makes the acid solution corrosive, dilutive, and destructs the solution surface stress. The H ↔ H terminates locally the HB network as the H⁺ ion does regularly in metals as hydrogen embrittlement [40].

As it does in the salt solutions [41,42], the X⁻ (X = Cl, Br, I) stretches and polarizes water molecules to form the hydration shells [43]. The X⁻ polarization lengthens and softens the O:H nonbond but shortens and stiffens the H—O bonds in the meshes. The competition of the H⁺ ↔ H⁺ repulsion and X⁻ hydration polarization governs the performance of the acid hydration networks. However, the H—O hardly relaxes in computations using the rigid and non-polarizable scheme.

2.2. Phonon spectrometrics

Raman shift Δω_x (x = H or L) probes the HB stiffness cooperative shift that depends functionally on the segmental length *d*_x and energy *E*_x, irrespective of the source nature of stimulation [34],

$$\Delta\omega_x \propto \sqrt{E_x/\mu_x}/d_x \propto \sqrt{(k_x + k_c)/\mu_x} \quad (1)$$

The O:H nonbond is characterized by the stretching vibration frequency at ~200 cm⁻¹ and the H—O bond by the frequency of ~3200 cm⁻¹ in the bulk water. The *k*_x and *k*_c are the force constants or the second differentials of the intra/inter molecular interaction and the O—O repulsion. The Δω_x also varies with the reduced mass μ_x of the specific *x* oscillator. Thus, Raman spectroscopy resolves unambiguously the effect of the X⁻ ions and the H ↔ H anti-HB on the solution network relaxation and the solution structural transition [44].

Raman measurements of 150 μL deionised water and aqueous solutions injected into a silica stage were conducted using the confocal micro Raman spectrometer (Renishaw inVia) with a 532-nm He-Ne laser as the light source [41,45]. We examined the details of phonon relaxation with focused on the difference between the spectra measured from solutions and from the deionized water upon all ω_x spectra. Before the operation, we corrected the spectral background and normalized the spectral peak. This differential phonon spectrometrics (DPS) purifies the phonon abundance transition and removes the commonly shared spectral features [33].

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