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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.

Keywords: Acid solution; surface stress; phonon spectrometrics; anti-hydrogen-bond; fragilization

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Content entry

Highlight

- H_3O^+ formation with $\text{H}^+ \leftrightarrow \text{H}^+$ point fragilization destructs the surface stress
- The X^- elongates and polarizes the $\text{O}:\text{H}-\text{O}$ bonds in its hydration shell
- DPS resolves solute capability of $\text{O}:\text{H}-\text{O}$ bond and surface stress transformation
- Nonlinear coefficient features X^--X^- correlation weakening the ionic field.

1 Introduction

Although the HX ($X = \text{Cl}, \text{Br}, \text{I}$) 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, 3] and Lewis [4] 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.[5-9] 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 [10, 11] that functionalize cells through solution-protein interactions.[12, 13] Unfortunately, such knowledge was hindered by the lacking knowledge of water structure and response of the hydrogen bond ($\text{O}:\text{H}-\text{O}$ 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 [14, 15]. The t-IR resolves the solute or water molecular diffusive motion dynamics in terms of phonon lifetime and the viscosity of the solutions [16, 17] 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 sublayer contributions.

Tremendous work has been done in past two centuries on the “proton transport dynamics” that has formed a subject of fierce debating [18-25]. It was assumed that the mobility of protons in liquid water

is considerably high compared with H₂O molecules. The explanations for the proton mobility began with Grotthuss [26] in terms of “structural diffusion” nearly two centuries ago. Subsequent explanations have refined this concept by invoking thermal hopping [27], proton tunneling [28] or solvation fluctuating [29]. In 1960s, Eigen [30] proposed the formation of an H₉O₄⁺ complex in which an H₃O⁺ core is strongly hydrogen-bonded to three H₂O molecules and leave the lone pair of the H₃O⁺ free. Zundel [31] supported the notion of an H₅O₂⁺ complex in which the proton is shared by two H₂O molecules. Using the *ab initio* path integral simulations, Marx et al [32] 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 [18] 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.* [33] 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)[34-37] 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 [32]. 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 [38-40]. 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 [41, 42] 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 $H^+ \leftrightarrow H^+$ fragilization and X^- polarization dictate the performance of acid solutions.

2 Principles

2.1 *HB cooperative relaxation and $H \leftrightarrow H$ fragilization*

Due to its intrinsic $2sp$ orbital hybridization [43], 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 $2N$ pairs of “:” and $2N$ 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 [44] and in the phase of equal O:H and H-O lengths (at 60 GPa over all temperatures) [42], or in aqueous solutions [45, 46].

Figure 1a inset shows the $(H_2O)_2$ unit cell [41, 42] with central replacement of an H_3O^+ . 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 H_2O molecule into the H_3O^+ hydronium. The H_3O^+ 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 [42]) in the solution [32]. This process breaks the $2N$ conservation with an additional pair of H^+ protons. The $H^+ \leftrightarrow H^+$, called anti-HB, is the only way of interaction between the H_3O^+ and the H_2O . Freely drift motion or translational tunneling of the H^+ between two H_2O molecular for $2H_2O \leftrightarrow H_3O^+ : HO^-$ occurs at extreme conditions (2000K and 2TPa pressure) [44] is very unlikely because the H-O bond is 4.0 eV and over [42], requiring at least 121.6 nm laser to dissociate the H-O bond [47].

Figure 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 [42]. 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 $H^+ \leftrightarrow H^+$ 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 $H \leftrightarrow H$ terminates locally the HB network as the H^+ ion does regularly in metals as hydrogen embrittlement [48].

As it does in the salt solutions [49, 50], the X^- ($X = \text{Cl}, \text{Br}, \text{I}$) stretches and polarizes water molecules to form the hydration shells [51]. 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 $H^+ \leftrightarrow H^+$ 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 $\Delta\omega_x$ ($x = \text{H}$ 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 [42] ,

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

The O:H nonbond is characterized by the stretching vibration frequency at $\sim 200 \text{ cm}^{-1}$ and the H-O bond by the frequency of $\sim 3200 \text{ cm}^{-1}$ 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 $\Delta\omega_x$ 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 $H\leftrightarrow H$ anti-HB on the solution network relaxation and the solution structural transition [52].

Raman measurements of 150 μ L 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.[49, 53] 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.[41]

3 Results and discussion

3.1 *Phonon cooperative relaxation dynamics*

Firstly, as compared in **Error! Reference source not found.**, we collected the full-frequency range Raman spectra for HX solutions at 0.1 molar concentration and HI of different concentrations with respect to the spectrum of deionized water under the same ambient conditions. Evolution of the characteristic peaks for the O:H and the H-O stretching vibration cantered at $< 200\text{ cm}^{-1}$ and at $3200\text{--}3700\text{ cm}^{-1}$, respectively, would suffice to make conclusion, so we omitted the rest vibration modes due to bond bending for simplicity. The inset in **Error! Reference source not found.**a illustrates the formation of $H\leftrightarrow H$ anti-HB breaker between the H_3O^+ and a H_2O and inset b the polarization effect by anion on the O:H-O bond relaxation. This superposition of the pont breaker and the point fragilization is critical to the properties of acid solutions.

A spectral peak represents the Fourier transformation of all vibrating bonds in the same frequency from the real space, irrespective of the location or orientation of the bonds or the liquid, solid, or vapor phase of the substance. One can only probe the statistic mean of the vibrations and its fluctuation. The spectral peak frequencies correspond to the respective bond stiffness [41]. As the frequency is sensitive to the

bond length and energy, a spectroscopy probes intrinsically the change of the bonding identities without being able to discriminate the sources of stimuli. Dominating the spectral peaks shift, the O:H-O bond segmental length and energy vary in the same H-O elongation manner of with mechanical compression and base solvation [54], and H-O contraction of liquid heating and molecular undercoordination . From the full-frequency Raman spectra, one could hardly be able to gain quantitative information on the transformation of the stiffness, fraction, and fluctuation of bonds being functionalized by solvation.

The full-range Raman spectra show consistently that in the HX solution, the ω_H (H-O) is indeed stiffened because the X^- polarizes and shortens the H-O bond and lengthens the O:H nonbond. Meanwhile, H-bond network termination by H^+ induces the fragilization and depolarization of neighboring O:H-O bond.

Figure 1 Full-frequency Raman Spectroscopy for (a) the type at 0.1 molar concentration and (b) HI concentration dependence for HX proton acid solutions. Insets show the structures for (a) $H \leftrightarrow H$ creation that does not polarize neighboring O:H-O bond but supplies repulsion and for (b) X^- ionic point polarization. Inset a illustrates the $H \leftrightarrow H$ anti-HB formation and b the X^- polarization that shortens the H-O but lengthens the O:H in its hydration shell.

To examine the details of O:H-O bond relaxation and the surface stress, we measured the contact angle between the solution droplet and glass substrates. A differential phonon spectrometry (DPS) was also conducted to calibrate the solute capability for bond transformation. We subtract the specific H-O and O:H segmental spectral peaks of the solutions by the respective peaks of deionized water as references upon both sets of spectral areas being normalized. The normalization excludes the artifacts of

measurements and to ensure that the phonon abundance remain constant – the abundance loss equals to its gain upon hydration [41]. The integral of the normalized peak represents the number of detected bonds being taken as unity. This process not only distills the fraction (< 1 unity) of phonons or bonds being transformed upon solvation but also removes the commonly shared spectral areas that is of no direct meaningful.

The Raman modes and their cross-section for the O:H-O bond due the compressed matrix and polarized hydration shell with different relaxation may be different, which is beyond the resolution of currently available means. Calibration shows that the relative change of the cross-section is 10^{-3} order for NaCl solutions at 0-300° C temperature difference, which is too tiny to be within the resolution of most available means [55]. However, the spectral peak normalization does minimize the effect of cross-section difference. Furthermore, the cross-section difference does not affect the nature or concentration trends of the fraction coefficients that feature the capability of solutes transforming the bonds but only affects the prefactors of the formulations, as demonstrated shortly.

Figure 2 Concentration dependence of the ω_H DPS for (a) HCl/H₂O, (b) HBr/H₂O, (c) HI/H₂O and (d) the fraction of O:H-O bond being polarized by X⁻ anions in the HX solutions. The tiny valley at 3620 cm⁻¹ and small feature at $\omega_H < 3100$ cm⁻¹ results from H $\leftrightarrow$ H repulsion. The nonlinear numerical fitting to the fraction coefficient indicates that X⁻X⁻ interaction weakens the local electric field of the X⁻ hydration shells. The H⁺ proton does not contribute to the polarization because of H₃O⁺ formation.

Figure 3 Concentration dependence of the ω_L DPS for (a) HCl, (b) HBr, (c) HI, and (d) the contact angle between solution and glass substrate for HX solutions. Transformation of ω_L results from X⁻ polarization and H $\leftrightarrow$ H repulsion.

Figure 2 and Figure 3 show segmental ω_x DPS and the fraction coefficient that is the abundance of the excessively peak representing the fraction of bonds being polarized by X⁻ anions. The ω_x relaxes indeed cooperatively for all solutions. As the concentration increases from 0.02 to 0.1, the X⁻ electrification

shifts the ω_H from 3200 to $\sim 3500 \text{ cm}^{-1}$ associated with ω_L red shifting from 180 to 110 cm^{-1} as the joint effect of X^- polarization and $H \leftrightarrow H$ repulsion. For salt without $H \leftrightarrow H$ repulsion the shift is to 80 cm^{-1} [53]. The $H \leftrightarrow H$ repulsion shifts the ω_L from 80 to 110 cm^{-1} . The ω_H valley at 3620 cm^{-1} suggests the H-H repulsivity in the skin region, which stiffens the characteristic phonon of the dangling H-O bond and screens its signals during detection.

The slight hump at $< 3100 \text{ cm}^{-1}$ features the effect of $H \leftrightarrow H$ repulsion that lengthens its neighboring H-O bond, as being the case of mechanical compression [50] and $O \leftrightarrow O$ point compression in base solution [54]. However, this feature attenuates and disappears when the X turns from Li to K (see Figure 2d) as the stronger polarizability of K annihilates the effect of $H \leftrightarrow H$ repulsion.

The phonon abundance transition represents the number of the bonds contributing to the fragmented hydration. The phonon spectrometrics could hardly resolve the effect of X^- polarization. With the established database, $(d_H, E_H, \omega_H) = (0.10 \text{ nm}, 4.0 \text{ eV}, 3200 \text{ cm}^{-1})_{\text{Bulk}}$, one may evaluate the hydrated HB energy $(0.095 \text{ nm}, 4.5 \text{ eV}, 3450 \text{ cm}^{-1})_{\text{acid}}$ using eq (1).

Figure 2d shows the concentration (mole fraction) dependence of the polarizability (f_{HX}) of proton acid HX solutions. The f_{HX} corresponds to the number fraction of bonds being polarized by X^- . Since the stiffer H-O bond allows H^+ only form a H_3O^+ firmly, the polarization due to H^+ is absent, $f_H^+ = 0$. Therefore, the $f_{HX} = f_X$ that follows the relation $f_{HX} = f_X = A[1 - \exp(-x/B)]$, where A and B are fitting constants and c is the mole fraction. The polarizability approaches to saturation because of the $X^- - X^-$ correlation that weakens the ionic electronic field in the hydration shell at lower concentrations.

3.2 Surface stress destruction

The contact angles were estimated with a drop shape analysis system (Krüss GmbH, Germany). Figure 3d shows the contact angles between HX solution droplets and a glass support with reference of water at $\angle 48^\circ$. Increasing the acid concentration destructs the solution skin stress, leading to the decrease of the contact angle. The $H \leftrightarrow H$ fragilization depolarizes the HBs and destructs the skin stress of the acid solution. The X^- anion polarizes and stretches the H_2O molecules to form a hydration shell like in salt solution, but takes less effect on acid solution than H^+ dose. The $H^+ \leftrightarrow H^+$ anti-hydrogen bond between

the H_3O^+ and H_2O breaks the hydration network and extends the neighboring H-O bonds, leading to the radical states and depolarization states, destructing the solution skin stress. Quantum fragilization and depolarization resolve the corrosive, dilutive, and skin-stress destructive nature of the solution.

3.3 *DFT calculations*

Structural optimizations of pure water, water containing H^+ , water containing X^- anions were performed by Dmol³ code. Perdew and Wang's (PW91)[56] functional was chosen to describe the exchange-correlation energy. We chose two schemes without the dispersion-correction (PW91) and with the dispersion-correction by OBS-PW [57]. All-electron calculation was performed based on double numeric and polarization basis sets. The self-consistency threshold of total energy was set at 10^{-6} Hartree. In the structural optimization, the tolerance limits for the energy, force and displacement were set at 10^{-5} Hartree, 0.002 Hartree/Å and 0.005 Å, respectively. Harmonic vibrational frequencies were computed by diagonalizing the mass-weighted Hessian matrix.

3.3.1 *O:H-O bond cooperative relaxation*

Two schemes (PW91 and OBS-PW) derived O:H and H-O bond length relaxation in water, $\text{H}_2\text{O}-\text{H}^+$, $\text{H}_2\text{O}-\text{X}^-$ are shown in Table 1. The relative change $\Delta\epsilon$ is calculated by the average of specific bond lengths in ion systems divided by the average value in pure water. There are two inequivalent bonds in the pure water unit cell. For $\text{H}_2\text{O}-\text{H}^+$, the two H-O bond lengths and the two weak O:H interaction distances in the anti-HB are considered. Besides, the neighboring O:H-O bonds around the proton were also considered as labeled in Figure 4b. For $\text{H}_2\text{O}-\text{X}^-$, three covalent bonds and X:H nonbonds in X:H-O interaction are considered. Besides, the O:H-O bond relaxation of second-neighboring under-coordinated O atoms, as labeled in Figure 4c, are also considered in the X^- hydration shell.

Results in Table 1 shows that two schemes of DFT calculation give the same trend of O:H-O relaxation of ions. H^+ makes the H-O like free radical, H-O bond is shortened by 3.08%, and the O:H distance is extended by 63.4%. However, the neighboring O:H-O bonds are shortened by the termination of H-bond network, leading to a weaker and longer H-O bond in the acid solution and the depolarization of the O:H-O bond (the reducing of the dipole moment due to the contraction of the O:H-O bond). The average extension except the anti-H-bond of the acid structure is up to 4.38%.

Results in Table 1 also indicate that X^- attracts the neighboring protons and forms three $X:H-O$ bonds. Since the $X:H$ interaction is weaker than the $O:H$. As the nuclei of X increases, the $X:H$ interaction continue to drop weak, and thus the $H-O$ bond becomes shorter and stronger. In H_2O-I^- , $H-O$ bond is shortened by 1.09%. The second-neighboring under-coordinated O atoms of the X^- hydration shell indicates that the $O:H-O$ bond is elongated due to under-coordination. In the I^- hydration shell, second-neighboring under-coordinated $O-H$ is shortened by 0.91%.

Table 1 DFT derived bond relaxation in pure water, H^+ - and X^- contained water (unit in %)

		OBS-PW		PW91	
		$\Delta\epsilon_{H-O}$	$\Delta\epsilon_{O:H}$	$\Delta\epsilon_{H-O}$	$\Delta\epsilon_{O:H}$
H_2O		0	0	0	0
$H_2O - H^+$	Anti-HB	-3.08	63.4	-2.99	59.2
	Neighbor	4.38	-12.5	3.48	-10.3
$H_2O - Cl^-$	$Cl:H-O^*$	-0.91	24.1	-0.98	28.1
	Neighbor [#]	-0.80	20.5	-0.65	19.2
$H_2O - Br^-$	$Br:H-O^*$	-1.05	31.6	-1.08	30.1
	Neighbor [#]	-0.83	22.8	-0.73	22.9
$H_2O - I^-$	$I:H-O^*$	-1.09	40.5	-1.11	42.7
	Neighbor [#]	-0.91	27.5	-0.76	29.8

*Values in the line are taken from $X:H-O$ bonds.

#Values in the line are taken from the second-neighboring under-coordinated O atoms as labeled in Figure 4c.

Figure 4 shows the optimized structures of pure water, water containing H^+ , water containing X^- ($X = Cl, Br, I$). Proton (H^+) forms anti-HB with a neighboring water molecule, generating two $O-H$ radical and terminating the continuous H -bond network. The DFT calculation considers the structure under the temperature of 0K. Since this work examined the effect of ions on the relaxation of the $O:H-O$ bond, thermal fluctuation may expand the peak width but not determine the relaxation direction. Due to the termination, the neighboring $O-H$ bond was extended (as labeled by numbers in Figure 4b) and weakened. X^- attracts three proton and forming three $X:H-O$ bonds, forming the hydration shell. The

formation of X:H-O bonds makes three second-neighboring O atoms not fully coordinated, as numbered in Figure 4c.

Figure 4. DFT optimized structures of (a) pure water in cubic structure, (b) H⁺-contained (yellow) water with anti-HB (black arrow) formation. (c) X⁻ - contained water with hydration. Number 1-3 denotes the undercoordinated O²⁻ anions due to the X⁻ hydration shell formation.

3.3.2 Vibrational spectra

Figure 5. (a) DFT-derived vibration spectra of $\text{H}_2\text{O}-\text{H}^+$ and pure water. (b) The difference of vibration spectra between $\text{H}_2\text{O}-\text{H}^+$ and pure water. Red shifts of the anti-HB O:H stretching and bending modes and blue shift of neighboring O:H modes are observed. (c) The $\text{H}_2\text{O}-\text{H}^+$ radical mode at 49 cm^{-1} : the anti-HB stretching mode; (d) the neighboring O:H depolarization mode at 412 cm^{-1} : O:H stretching mode with molecule translation movement; (e) The radical mode at 406 cm^{-1} : anti-HB bending mode; (f) the neighboring O:H depolarization mode at 895 cm^{-1} : O:H bending mode with molecule rotation movement.

Figure 5 shows the OBS-PW-derived vibration spectra of $\text{H}_2\text{O}-\text{H}^+$ and pure water. The difference of vibration spectra between $\text{H}_2\text{O}-\text{H}^+$ and pure water indicates the red shift of O:H stretching and bending mode blue shift of neighboring O:H modes. The spectra include two parts - O:H stretching modes with molecular translation movement and bending modes with molecular rotation movement. Results indicate that $\text{H}^+ \leftrightarrow \text{H}^+$ anti-HB induces a radical state with lower frequency and a depolarization state with higher frequency for both parts. For stretching part, the pure water modes around $200\sim 300\text{cm}^{-1}$ shift below 100cm^{-1} , which are the anti-HB radical modes, and above 400cm^{-1} , which are neighboring O:H depolarization modes. For bending part, the pure water modes around $700\sim 800\text{cm}^{-1}$ shift below 600cm^{-1} , which are the anti-HB radical bending modes, and above 800cm^{-1} , which are neighboring O:H depolarization bending modes.

Figure 6. (a) DFT-derived vibration spectra of $\text{H}_2\text{O}-\text{X}^-$ and pure water. (b) The difference of vibration spectra between $\text{H}_2\text{O}-\text{X}^-$ and pure water. Blue shifts of H-O symmetric and asymmetric stretching modes are observed. (c) The $\text{H}_2\text{O}-\text{X}^-$ characteristic mode around 3200 cm^{-1} : the X^- hydration shell induced

neighboring H-O symmetric stretching mode. (d) The $\text{H}_2\text{O-X}^-$ characteristic mode around 3400 cm^{-1} : the H-O asymmetric stretching mode in X:H-O .

Figure 6 shows the DFT-derived vibration spectra of $\text{H}_2\text{O-X}^-$ and pure water. The difference of vibration spectra between $\text{H}_2\text{O-X}^-$ and pure water indicates blue shifts of H-O symmetric and asymmetric stretching modes. The $\text{H}_2\text{O-X}^-$ characteristic mode around 3200 cm^{-1} is the X^- terminated H-O symmetric stretching mode. The $\text{H}_2\text{O-X}^-$ characteristic mode around 3400 cm^{-1} is the H-O asymmetric stretching mode in X:H-O . As the nuclei increases from Cl to I, the attractive force of X:H decreases, leading to the more significant hardening of H-O phonon. Thus, the characteristic mode increases from Cl^- to Br^- to I^- .

4 Conclusion

Without any assumption or approximation, an incorporation of the classical acid theory to the known water structure and HB relaxation dynamics has enabled the specification of acid solution. The discovery of the intrinsic $\text{H}^+ \leftrightarrow \text{H}^+$ quantum fragilization and X^- polarization and its effect on the nature of the solute-solvent-functionality chain of the acid solutions may lead to complementary definition of acids on their abilities of generating the excessive H^+ or the $\text{H}^+ \leftrightarrow \text{H}^+$ anti-HB point breakers when hydrated. These quantum fragilization and polarization shall be the keys to the respective hydration-networks.

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