

Hydrogen-bond transition from the vibration mode of ordinary water to the (H, Na)I hydration states: Molecular interactions and solution viscosity



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ABSTRACT

With the aid of differential phonon spectrometrics (DPS) and surface stress detection, we show that HI and NaI solvation transforms different fractions of the H—O stretching phonons from the mode of ordinary water centred at ~ 3200 to the mode of hydration shell at ~ 3500 cm^{-1} . Observations suggest that an addition of the H \leftrightarrow H anti-hydrogen-bond to the Zundel notion, $[\text{H}(\text{H}_2\text{O})_2]^+$, would be necessary as the H—O bond due H_3O^+ has a 4.0 eV energy, and the H \leftrightarrow H fragilization disrupts the solution network and the surface stress. The I^- and Na^+ ions form each a charge centre that aligns, stretches, and polarize the O:H—O bond, resulting in shortening the H—O bond and its phonon blue shift in the hydration shell or at the solute-solvent interface. The solute capabilities of bond-number-fraction transition follow: $f_{\text{H}}=0$, $f_{\text{Na}} \propto C$, and $f_{\text{I}} \propto 1 - \exp(-C/C_0)$ toward saturation, with C being the solute molar concentration and C_0 the decay constant. The $f_{\text{H}}=0$ evidences the non-polarizability of the H^+ because of the H \leftrightarrow H formation. The linear $f_{\text{Na}}(C)$ suggests the invariance of the Na^+ hydration shell size because of the fully-screened cationic potential by the H_2O dipoles in the hydration shell but the nonlinear $f_{\text{I}}(C)$ fingerprints the $\text{I}^- \leftrightarrow \text{I}^-$ interactions at higher concentrations. Concentration trend consistency between Jones–Dole's viscosity and the $f_{\text{NaI}}(C)$ coefficient may evidence the same polarization origin of the solution viscosity and surface stress.

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1. Introduction

Solvation of acid and salt, taking HI and NaI as representatives, is of ubiquitously important to fields such as biochemistry, organic chemistry, food and medicine, health care and life quality of human beings [1–3]. However, it remains yet uncertain how the H^+ , Na^+ and I^- solvation transform their respective hydrogen-bond network, or the solute-solvent interface bonding dynamics,

despite intensive investigations made since centuries long ago [4] with focus mainly on the solute diffusive motion dynamics [5], hydration-shell thickness [6,7], characteristic phonon life time [8–11], and interface dipole orientation [12,13].

The proton mobility in acid solutions was explained firstly by Grotthuss [4] two-century ago in terms of 'structural diffusion' that was subsequently refined by invoking mechanisms of thermal hopping [14], proton tunnelling [15], and fluctuating [16]. In 1960s, Eigen [17] proposed an H_9O_4^+ complex in which a H_3O^+ core is strongly hydrogen-bonded to three H_2O molecules and leaves its lone pair free. Zundel [18] proposed a $[\text{H}(\text{H}_2\text{O})_2]^+$ in which the proton is shuttling alternatively between two H_2O molecules. From the *ab initio* path integral simulations, Marx et al. [19] noted that the hydrated proton forms a fluxional defect in the hydrogen-bonded network, with both $[\text{H}(\text{H}_2\text{O})_2]^+$ and $[\text{H}(\text{H}_2\text{O})_4]^+$ occurring only in the sense of 'limiting' or 'ideal' structures. The defect can

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become delocalized over several hydrogen bonds owing to quantum fluctuations.

An ultrafast 2DIR spectroscopy investigation [10,20] suggested that the proton prefers the manner of Zundel structure accommodated by two H₂O at a time, rather than the Eigen structure in which the protons piggyback on individual molecules. In contrast, another work [11] favours deuterated prototypical Eigen clusters, [H(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 neighbouring water molecule. Clearly, debate on proton performance continues. However, we should focus not only on the proton performance but also its capabilities of transforming the solution matrix bonds and electrons and the solute-solvent interface bonding dynamics and the solution-surface performance.

Salt solvation not only changes the surface stress of the solution but also varies the solution ability of dissolving proteins, which has been explained from perspectives of interaction length scales [21], ionic specificity [22,23], ion-skin induction [24], quantum dispersion [25], structural order and disorder making [21,26–29], etc. Based on measurements of 1 M potassium halide solutions with 14 mol % HOD in D₂O, Smith et al. [30] contended that the Raman ω_H blue shift for the salt solutions from that of the deionized water arises primarily from the electric fields rather than from rearrangement of the hydrogen bonds beyond the first hydration shell or from structure breaking [31].

Recent MD computations [32] suggested that an external fields in the 10⁹ V/m order can slow down water molecules and even crystallize the system. The fields generated by the Na⁺ ions act rather locally but can reorient the hydrated neighbouring water molecules. MD computations [33] also suggested that HCl hydration make water clusters into smaller ones by fragmentation.

Recent progress [34–37] demonstrated that serving as charge centres, the (Li, Na, K, Rb, Cs)⁺ cations and the (Cl, Br, I)[−] anions in alkali halide solutions form each a polarization centre that aligns and clusters water molecules, and stretches the neighbouring hydrogen bonds. The only difference between the cations and anions upon solvation is that the cation hydration shell is smaller than those of the anions and the opposite directions of the electric fields. Ionic polarization shortens and stiffens the H–O bonds and meanwhile lengthens and softens the O:H nonbonds in the hydration shells, resulting in the respective H–O phonon frequency blue shift and O:H phonon frequency redshift [34,36]. However, little is known yet on the ionic and protonic effect on transforming the solution matrix

hydrogen bond upon acid and salt solvation though the solute behaviour has been well understood [3,10,11,19].

With the aid of the Raman differential phonon spectrometrics (DPS) and the contact angle measurements, we show herewith comparatively how the H⁺, Na⁺ and I[−] react with the solution hydrogen bonds and how the DPS can resolve solute capabilities of transforming the solution bonds from the mode of ordinary water to the hydration shells and how the transformed bond relaxes.

2. Principles and processes

2.1. Phonon frequency and spectroscopy

A phonon spectral peak features the Fourier transformation of all bonds vibrating in the same frequency irrespective of their locations or orientations in the solid, liquid, or vapour phase of a substance. One can only probe the statistic mean of the vibrations and its fluctuation. The phonon frequency features the respective bond stiffness, $\omega_x^2 \propto E_x/d_x^2$, (bond stiffness is the product of its elasticity Y and length d , $Yd = Ed/d^3$, energy density times bond length) [38]. The ω_x , E_x and d_x are the phonon wavenumber shift, O:H–O segmental energy and length, respectively. The subscript $x = L$ and H denotes the respective O:H and the H–O segment. The 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 and base solvation [39], and the other way around under liquid heating [40], compressing [41], salting [42], and molecular undercoordination, [38] as well.

As compared in Fig. 1, we collected the full-frequency Raman spectra for NaI/H₂O and HI/H₂O solutions at different molar concentrations (or molecular number ratios that could be more convenient than using mole per litre water) with respect to the spectrum of deionized water probed under the same conditions. Evolution of the characteristic peaks for the O:H and the H–O stretching vibration centered at <200 cm^{−1} and at >3000 cm^{−1}, respectively, would suffice to examine the O:H–O segmental cooperativity, so one can omit the rest modes due to bond bending and torsional motion for simplicity. The bending and torsional vibrations are featured in the 300–1600 cm^{−1}, which contributes insignificantly to the O:H–O cooperative stretching vibrations that follow the $\omega_x^2 \propto E_x/d_x^2$ relation. From the full-frequency Raman spectra, one could hardly be able to gain quantitative information on the solvation transformed stiffness, fraction, and

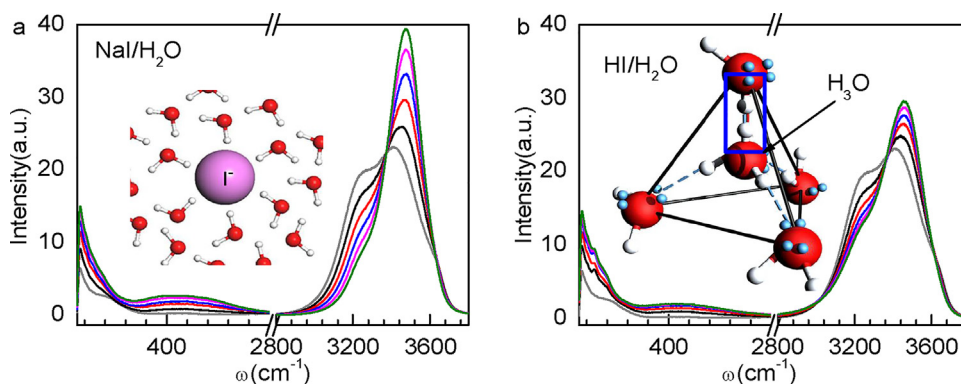


Fig. 1. Concentration dependence of the full-frequency Raman spectroscopy for (a) NaI and (b) HI solutions with concentration varying from 0.02 to 0.10 molar fraction (number ratio will be more convenient than using the unit of M/L). Inset **a** illustrates the process of ionic polarization that stiffens the H–O phonon and softens the O:H phonons because of the O:H–O bond cooperativity. Inset **b** shows the structure unit cell of water with a H₃O⁺ replacement for the central H₂O upon HI solvation. The framed H → H anti-hydrogen-bond prevents H⁺ from being able to polarize its neighbours or from translational tunnelling between water molecules, but serves as a point breaker disrupting the hydrogen network and the surface tension of the acidic solutions.

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