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Mediating relaxation and polarization of hydrogen-bond in water by NaCl salting and heating

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Abstract

Infrared spectroscopy and contact-angle measurements revealed that NaCl salting effects identically to heating on O:H phonon softening and H-O phonon stiffening but the opposite on skin polarization of liquid water. The mechanics of thermal modulation of O-O Coulomb repulsion [Sun, et al., *J. Phys. Chem. Lett.*, 2013, 4: 3238] may suggest a possible mechanism for this NaCl involved Hofmeister effect, aqueous solution can modulate surface tension and its ability of protein dissolution, from the perspective of Coulomb meditation of interaction within the O:H-O bond.

Key words: Water, hydrogen bond, Hofmeister series, Coulomb interaction

The behavior of aqueous ions has profound impact on biological molecules such as proteins and DNA, and thus, implications for health care and disease curing. Ions added in the form of salts, acids, sugar, or buffer agents to protein solution are crucial to maintaining protein stability. Different ions are better or worse at preventing aggregation and self-association of DNA in activating or deactivating ion channeling [1-3].

Smith et al [4] compared the H-O stretching Raman phonon (ω_H) spectra of HOD/D₂O with and without presence of 1 M KX (X = F⁻, Cl⁻, Br⁻, and I⁻), see appendix and found that larger ions with lower electronegativity stiffen the ω_H more than the otherwise. Using ultrafast 2-dimensional infrared (2DIR) spectroscopy and molecular dynamics (MD) simulations, Park and coworkers [5] found that 5% NaBr addition to HOD in H₂O shifts the O-D stretching frequency from 2509 to 2539 cm⁻¹ and the extent of shift varies with the relative number (8, 16, 32) of H₂O molecules attached to a Br⁻ ion. Adding varied concentration of NaBr to its aqueous solutions can disrupt the O:H-O bond network. HOD molecules are H-bonded to ions as HOD-Br⁻, DOH-Br⁻, and HDO-Na⁺ in the hydration shells around the ions. Salt ions such as NaCl [6], NaBr [5], LiCl [7], NaClO₄ and Mg(ClO₄)₂ [8-10] also shift positively the ω_H of the hydroxyl group (-OH or -OD). Aqueous LiCl performs the same to adding H₂O/LiCl ratio from 100 to 6.7 in dropping the supercooling temperature from 248 K to 190 K [7]. The vibration frequency also changes with the pH value of aqueous solution containing organic compound such as NH₄H₂PO₄ [11].

Likewise, salt anions also affect the phase transition temperature characterized by enthalpies and the specific heat under constant pressure (C_p) of the methylcellulose aqueous solutions. Xu et al [12, 13] found in their differential scanning calorimetric measurement that NaCl exhibits the salt-out and NaI salt-in effect. Increasing NaCl concentration lowers the C_p peak temperature but raises the peak intensity but NaI does oppositely on the peak temperature.

The effect of adding salts into solutions of nonelectrolytes is very complicated, due to different types of intermolecular interactions that involve ions, solvents, and the solute molecules [1, 14]. There are several possible mechanisms explaining this Hofmeister effect [15] from the perspective of interaction length scales [16]. One is that ions produce long-range effects on the structure of water, leading to changes in water's ability of letting proteins fall out of, or stay dissolved in, a solution. The currently popular view is that Hofmeister effect stems largely from the varying abilities of different salt ions to replace water at the nonpolar molecular or macroscopic surfaces. The surface potential difference and surface tension at an air-salt solution interface could explain how ions affect protein stability and solubility through indirect interactions at the protein-solution interface [17]. Models based solely on electrostatics cannot explain ion specific properties of electrolyte solutions without considering dispersion interactions of ions with other ions and with water molecules [18].

Calculations based on Colin's rule establish dispersion interactions to ionic interactions, which explained several puzzling properties of electrolyte solutions: the variation in solvation energy among ions of the same size, the small repulsion of iodide from the air-water interface, and the affinity of large ions for each other in water embodied in Collins's rules. Conversely, Liu et al [19] observed strong Hofmeister effect in $\text{Ca}^{2+}/\text{Na}^+$ exchange on a permanently charged surface over a wide range of ionic strengths and argued that this observation could not be attributed to dispersion forces, classical induction forces, ionic size, or hydration effects other than a new force active in the ion-surface interactions. The strength of this force was up to 104 times that of the classical induction force, and could be comparable to the Coulomb force. Coulomb, dispersion and hydration effects appeared to be intertwined to affect the force. The presence of the observed strong non-classical induction force implied that energies of non-valence electrons of ions/atoms at the interface might be underestimated, and possibly just those underestimated energies of non-valence electrons determined Hofmeister effects. However, theoretical framework can hardly predict or explain this phenomenon from the perspective of ion replacement induced O:H-O relaxation due to short-range interactions [1-3].

Recent progress [20, 21] suggests that hydrogen bond (O:H-O) cooperative relaxation and its associated charge entrapment and polarization determine the anomalous behavior of water ice under various stimuli. All anomalies of water ice are correlated. In this communication, we extend our understanding to the NaCl salting effect on the phonon and surface contact angle relaxation, in comparison to the heating effect whose mechanism has been established [22, 23].

An extension of the Ice rule [24] has resulted in a tetrahedron that contains two water molecules and four identical O:H-O bonds. This extended tetrahedron has unified the length scale, geometric configuration, and the mass density of molecular packing tetrahedrally in water ice [25]. This extension has also turned out, as shown in Figure 1a, the O:H-O bond with asymmetric, short-range O:H, H-O and O---O interactions [26]. The O:H-O performs as a pair of asymmetric oscillator coupled by Coulomb repulsion between electron pairs on oxygen atoms (red sphere with pairing dot as the electron pairs). Under the Coulomb coupling, external excitation such as cooling [22], compressing [27], and clustering [28] always relaxes the O:H and the H-O cooperatively in the same direction by different amounts.

Segmentation of the O:H-O bond is necessary into a shorter and stiffer H-O covalent bond with a stronger exchange interaction and a longer and softer O:H nonbond with a weaker nonbond (vdW-like) interaction [27, 28]. The vdW-like interaction contains electrostatic interaction between the lone-pair and the H^+ proton, so the nonbond interaction is slightly stronger than the ideal vdW bond that denotes purely dipole-dipole interaction. The H^+ proton always remains closer to the O (right-hand side of Figure 1a) without any frustration and keeps away from the other O atom because of the much stronger H-O exchange interaction than the weaker O:H nonbond. The O:H-O bond links the O-O in both the solid and liquid H_2O phase, regardless of phase

structures [25]. The inset shows the charge localization that forms the foundation introducing the inter-oxygen repulsion [20].

Figure 1b shows the forces acting on oxygen and the associated O:H-O bond relaxation subjected to salting and heating. Averaging the background long-range interactions due to other H₂O molecules or protons [29] and omitting the nucleus quantum effect on fluctuations [30], the forces acting on the electron pairs of oxygen include:

- 1) Coulomb repulsion between electron pairs on adjacent O²⁻ ions is the first-order differentiation of the Coulomb potential, $f_q = -\partial V_c(r)/\partial r$, out of equilibrium. Replacing one O²⁻ ion with an ion of acid, salt, sugar, protein, or a biomolecule or a cell, mediates the Coulomb repulsion f_q by varying the ionic size and charge quantity. This replacement may mediate the O:H dissociation energy and the functionalities of the O:H-O bond and the solubility of water solution [31].
- 2) Pointing either towards or away from the coordinate origin, the force dislocates oxygen atoms f_{dx} ($x = L$ for the O:H and $x = H$ for the H-O bond). An applied stimulus (e.g. mechanical compression, molecular undercoordination, thermal excitation, chemical reaction, etc.) provides this driving force.
- 3) The force of deformation recovery, $f_{rx} = -\partial V_x(r)/\partial r$, approximates to the first-order differentiation of the respective $V_x(r)$ at equilibrium. The f_{rx} always points opposite to the direction of deformation.

During liquid heating, the O:H nonbond follows the regular rule of thermal expansion but the resultant of the Coulomb repulsion and H-O exchange interaction shortens the H-O bond, stiffens its ω_H phonons, and simultaneously softens ω_L phonons, as confirmed in [6, 22, 32]. The O:H elongates more than the H-O contracts when heating lowers the mass density of liquid. This O:H-O bond has an memory to emit heat at a rate depending on the its initial storage, which resolved the Mpemba effect – hot water freezes faster [23].

It is expected that salting effects the same to heating on modulating the Coulomb interaction $V_c(r_O)$ and the associated phonon frequency shift $\Delta\omega_x$ that is correlated to the segmental stiffness in terms of length d_x and energy E_x by [26, 33]:

$$\begin{cases} \Delta\omega_x = (2\pi c)^{-1} \sqrt{\frac{k_x + k_c}{m_x}} \propto \sqrt{E_x} / d_x & \text{(Phonon frequency)} \\ V_c(r_O) = \frac{q_O^2}{4\pi\epsilon_i\epsilon_0 r_O} & \text{(O---O potential)} \end{cases} \quad (1)$$

where c is the velocity of light travelling *in vacuo*. The force constants k_x and k_c correspond to the second differentials of the respective potentials. The m_x is the reduced mass of the H₂O:H₂O oscillator. The r_O is O-O

distance. The ϵ_r and ϵ_0 are the relative and the vacuum dielectric constant. One can adjust the Coulomb potential by adjusting the charge quantity q_0 , dielectric constant ϵ_r , and r_0 .

There are three factors in the $V_c(r_0)$ potential. One can modulate it by changing the ϵ_r , r_0 , or q_0 . Heating lengthens the r_0 and possibly ϵ_r ; ion replacement modulates the $V_c(r_0)$ or adding a potential by changing the charge quantity, ion size, and the ϵ_r . The replacement of O^{2-} ions with salt ions should effect similar to heating on modulating the Coulomb interaction and polarization. Figure in Appendix shows that the F^- , Cl^- , Br^- , and I^- ions and results in [5-10] do follow this expectation. One can identify the dominating factor of the Hofmeister effect by monitoring the phonon frequency and contact angle relaxation conveniently.

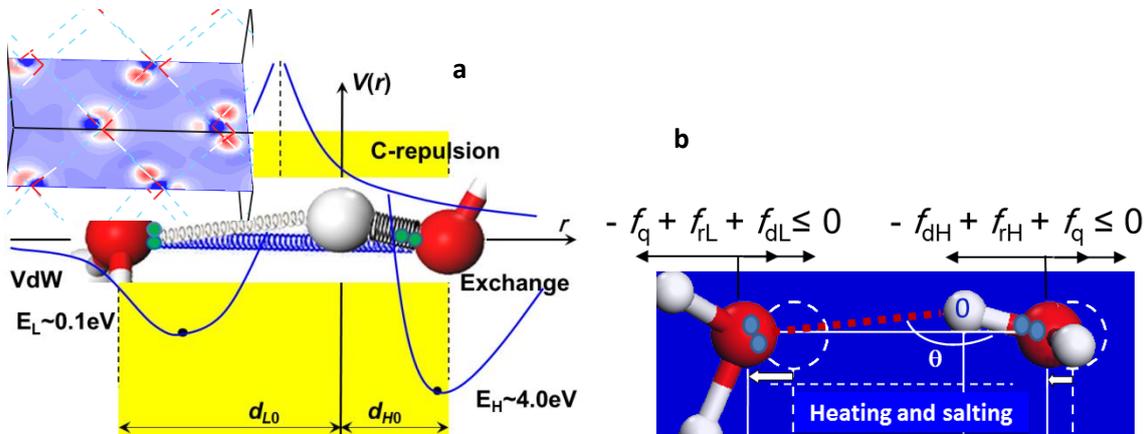
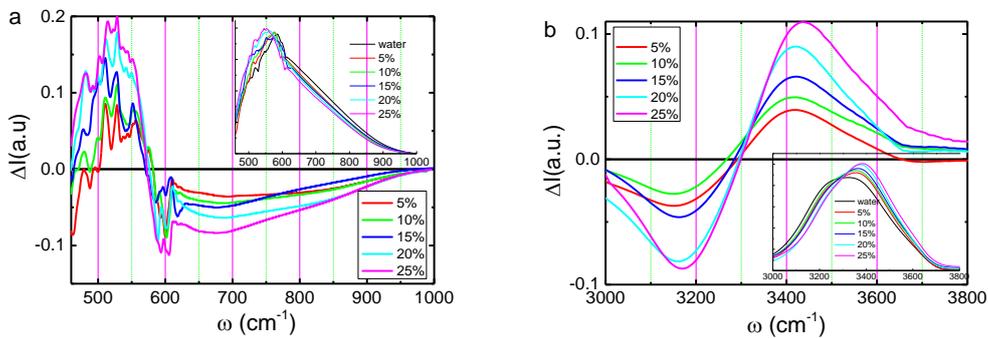


Figure 1 (a) Asymmetrical, short-range potentials for the segmented O:H-O bond include the O:H van der Waals (vdW)-like nonbond interaction (left-hand side), the H-O bond exchange (right-hand side) interaction, and the Coulomb repulsion between electron pairs on adjacent O^{2-} ions. One switches off a particular potential and the other on at the boundary, or at the atomic site, when it moves across the boundary [25]. The inset shows the localization of the residual charge density of an ice-VIII unit cell. The residual charge density is the difference between the charge of an H_2O molecule and that of an isolated O atom. The positive regions (red) correspond to the gain of electrons. The negative regions (blue) correspond to the charge loss. (b) Forces and relaxation dynamics of the segmented O:H-O bond with H^+ as the coordinate origin. Forces include the Coulomb repulsion f_q , deformation recovery f_{rx} , and the external force driving relaxation f_{dx} ($x = L$ for the O:H and $x = H$ for the H-O bond). Coulomb repulsion and external stimulus dislocate O atoms in the same direction but by different amounts. The O:H always relaxes more than H-O. Weakening of the inter-oxygen (paring dots denote electron pair on oxygen that is in red) Coulomb repulsion by O---O thermal expansion or by charge reduction during ion replacement lengthens-and-softens the O:H and shortens-and-stiffens the H-O segment. Arrows indicate the amount and direction of displacement with respect to H^+ as the coordination origin.

In order to verify our expectations, we firstly measured the relaxation of the O:H bending and H-O stretching phonons in the frequency range of 400 – 4000 cm^{-1} using Fourier transformation infrared (FTIR) absorption spectroscopy from deionized water at 278 K. This spectrum serves as a reference. We then probed the FTIR spectra of water at heating from 278 to 328 K with 10 K step by program controlling and of water by adding NaCl up to 25 mass% in a 5% step. In order to test the salting and heating effect on polarization that determines the surface energy [33], we also measured the contact angle of water on glass in the same heating and salting conditioning procedures. It would be necessary to focus on the Hofmeister effect of one kind ion and then the others systematically.

Figure 2 shows the raw (insets) and the residual phonon spectra (RPS) of the conditioned water. One can obtain the RPS by subtracting the reference spectrum for pure water from those being conditioned upon background correction and peak area normalization. The RPS distills conditioning as new peaks and the reference background as a valley. Results show that the ω_{BI} ($\sim 600 \text{ cm}^{-1}$ corresponding to the $\angle\text{O:H-O}$ bending mode) undergoes redshift and the ω_{H} ($3150 \sim 3450 \text{ cm}^{-1}$) blueshift upon being heated or NaCl salted, which confirmed our expectations. The ω_{H} shifts from 3170 gradually to the skin value of 3450 cm^{-1} [33, 34] at 25% salting, which are the same to that reported in [6, 35] for salting. Meanwhile, salting shifts the ω_{BI} from 600 to 520 cm^{-1} . In comparison, heating stiffens the ω_{H} from gradually 3170 to the same value of 3450 with presence of a shoulder at 3650 cm^{-1} that corresponds to the H-O dangling bond. However, heating softens the ω_{BI} from 600 to 470 cm^{-1} , which is softer than that derived by slating.

According to eq (1), phonon softening/stiffening indicates bond stiffness loss/gain. Excitingly, NaCl salting and heating effect the same on the ω_x relaxation despite the $50 \text{ cm}^{-1} \Delta\omega_{\text{BI}}$ difference. This trend agreement indicates that salting indeed modulates the Coulomb repulsion between ions in a common mechanism to liquid heating with minus extent difference [22].



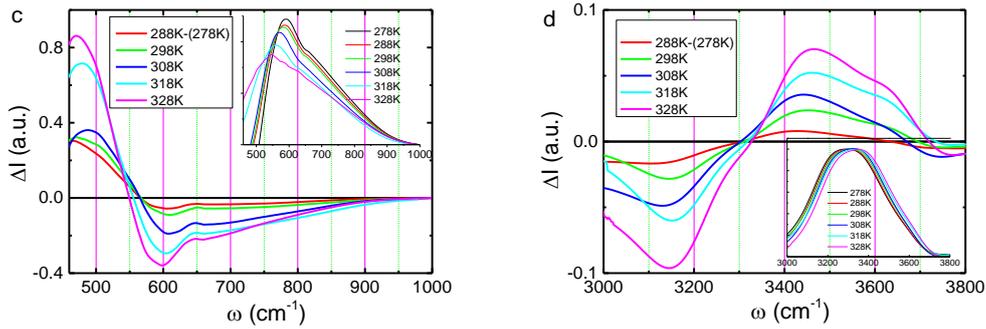


Figure 2 FTIR (a, c) ω_{B1} and (b, d) ω_H residual spectra of water as a function of (a, b) salinity (mass% NaCl) and (c, d) heating temperature with respect to the referential spectrum collected from unsalted water at 278 K. Insets show the raw spectra. Heating shifts the ω_{B1} from 600 to 470 cm^{-1} while salting shifts the ω_{B1} to 520 cm^{-1} . Heating and salting shifts the ω_H from 3150 to 3450 cm^{-1} but heating creates a shoulder at 3650 cm^{-1} .

Figure 3 shows the experimental set up and the temperature and NaCl concentration dependence of the contact angle of water on glass substrate. Surprisingly, Heating and NaCl salting show trends opposite to that of phonon relaxation. Heating lowers but salting raises, the contact-angle (an indication of surface tension or polarization) though both relax the ω_x phonon in the same manner. The slight $\Delta\omega_{B1}$ difference may elaborate this paradox. Heating softens the O:H nonbond through depolarization, which shifts the $\Delta\omega_{B1}$ to 470 cm^{-1} but salting does oppositely shifting the $\Delta\omega_{B1}$ to 520 cm^{-1} . The polarization further stiffens but depolarization softens the O:H phonon. Therefore, the RPS is very powerful in identifying the effect of polarization and depolarization due to chemical, Coordinational, and thermal effect on the phonons and the macroscopic properties of liquid water [33].

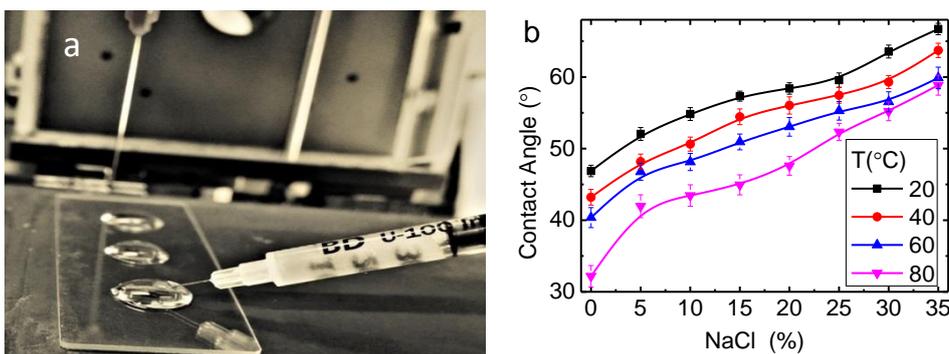


Figure 3 (a) The set up for contact-angle measurements of water on glass as a function of (b) NaCl concentration and heating temperature. Results revealed that heating weakens while salting enhances the polarization that modulates the skin tension.

These observations thus verified our expectations from the perspectives of O:H-O bond cooperative relaxation and potential modulation. The known mechanism ω_x thermal relaxation for liquid water [22, 23] explains the salting effect. The same trend of phonon relaxation induced by salting and heating indicates that they share the same mechanism of Coulomb modulation of O---O interaction by varying ion size, ion charge, and O---O distance. Heating mediates the interaction by O---O elongation but salting by varying ion size and charge quantity. Thus, larger ions with lower ionicity would weaken the Coulomb repulsion and stiffens the ω_H more than the otherwise, which is exactly the situation reported by Smith et al [4] who found that the amount of the $\Delta\omega_H$ is in the order of $F^- < Cl^- < Br^- < I^-$, see Figure 4.

In summary, NaCl salting effects identically to heating on the O:H-O bond stiffness relaxation. Both heating and salting share the common mechanism of O:H-O bond Coulomb modulation. However, heating and salting effects oppositely on surface tension because of their functionality of O:H-O polarization. Findings and understanding may suggest a possible mechanism for the effect of salts, acids, and sugar on the performance of water.

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Appendix: Hofmeister series

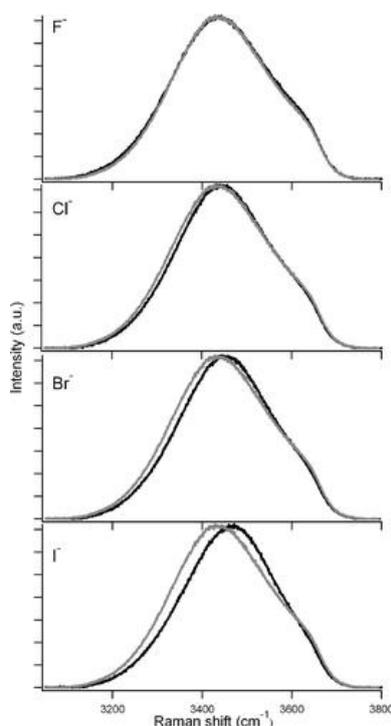


Figure 4. Comparison of the normalized ω_H for 1 M KX (X = F⁻, Cl⁻, Br⁻, and I⁻) in HOD/D₂O (black lines) with that of pure HOD/D₂O (grey lines). The alkali halides in liquid water change the H-O vibrational frequency instead of the actions of ions' electric fields on adjacent water molecules. The order of the frequency shift follows the F⁻ < Cl⁻ < Br⁻ < I⁻ order of ion size and ionicity. (Reprinted with permission from [4].)

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