Unprecedented $O:\rightleftharpoons:O$ compression and $H\leftrightarrow H$ fragilization in Lewis solutions

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Perspective

H $\leftrightarrow$ H fragilization and O: $\rightleftharpoons$:O compression in Lewis solutions

Chang Q Sun^{1,2}

Abstract

Charge injection in terms of ions, lone pairs ‘:’, and protons, upon acid and base solvation mediates the hydrogen bonding network and properties of Lewis solutions, which is ubiquitously important to many subject areas of Chemical Physics and has been attracting increasing attention. This work features the recent progress and future trends in this aspect with focus on the solute-solvent interactions and hydrogen bonds (O:H–O or HB) transition from the vibration mode of ordinary water to the hydrating states. A combination of the O:H–O bond cooperativity notion, differential phonon spectrometrics, calorimetric and surface stress detection, and quantum computations clarified the solute capabilities of O:H–O bond transition in YOH and HX (Y = Li, Na, K; X = Cl, Br, I) solutions. The H⁺ and the lone pair do not stay alone to move or shuttle freely between adjacent H₂O molecules but they are attached to a H₂O to form the (H₃O⁺, OH[−])-4H₂O motifs, which transits an O:H–O bond into the H $\leftrightarrow$ H anti-HB point breaker in the acidic solutions and into the O: $\rightleftharpoons$:O super-HB compressor and polarizer in the basic solutions, respectively. The H $\leftrightarrow$ H disrupts the solvent network and surface stress, having the same effect of liquid heating or thermal fluctuation. The O: $\rightleftharpoons$:O compression lengthens and weakens the solute H–O bond, which heats up the solution at solvation. The H–O bonds due H₃O⁺ contracts by 3% and due OH[−] shrinks by 10%. The Y⁺ and X[−] perform the same as they do in salt solutions to form hydration shells through electrostatically screened polarization. Focusing more on the O:H–O bond transition would be much more promising and revealing than on the manner and mobility of lone pair or proton transportation.

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Graphic abstract

Charge injection in terms of protons, lone pairs, cations and anions by acid and base solvation mediate the HB network and properties of the Lewis solutions through $H \leftrightarrow H$ fragilization, $O \leftrightarrow O$ compression and polarization, ionic polarization and hydrating H_2O dipolar screen shielding, anion-anion repulsion, compressed solvent $H-O$ bond elongation and undercoordinated solute $H-O$ bond contraction.

Content entry

Contents

Perspective	1
H$\leftrightarrow$H fragilization and O:$\rightleftharpoons$:O compression in Lewis solutions.....	1
1. Wonders of Lewis solutions	4
1.1. Charge and Molecular Motion Dynamics.....	4
1.2. Raman Spectroscopy of Lewis Solutions	9
2. Conservation Rules and O:H–O Bond Cooperativity	10
3. DPS characterization.....	13
3.1. Lewis Solutions: Conservation Rules Broken	13
3.2. Acidic Solvation: H $\leftrightarrow$ H Fragilization and X ⁻ Polarization	14
3.3. Incapability of Proton Polarization.....	16
3.4. Basic Solvation: O: $\rightleftharpoons$:O Compression and Solute H–O Contraction	17
3.5. Hydrogen Bonds and Surface Stress Transition	20
4. DFT: X ⁻ and H ₃ O ⁺ Hydration Shells	23
5. Calorimetric Detection: Basic Exothermic Solvation Energetics	26
6. Concluding Remarks.....	29
Acknowledgement	32
References	33

Authors Biography

Chang Q Sun, FRSC, FInstP, received his PhD in Physics at Murdoch University in 1996 and then joined Nanyang Technological University. He has been working on the theme of *Extraordinary Coordination Bonding and Nonbonding Electronics* and pioneered theories of Bond Relaxation and Hydrogen Bond (O:H–O) Oscillator Pair Cooperativity and holds multiple patents on the Electron and Phonon Spectrometrics. His contribution has been documented in *Solvation Dynamics: A Notion of Charge Injection*, Springer-Nature, 2019; *The Attribute of Water: Single Notion, Multiple Myths*, Springer 2016; *Relaxation of the Chemical Bond*, Springer 2014 and their Chinese versions, as well as over 20 treatises published in *Chemical Reviews*, *Progress in Materials Science*, etc. He was bestowed with the first rank of the Khwarizmi International Award in 2012 and the Inaugural Nanyang Award 2005.

1. Wonders of Lewis solutions

1.1. Charge and Molecular Motion Dynamics

Solvation of YOH bases and HX acids mediates the hydrogen bonding network and properties of the Lewis solutions, which is ubiquitously important to health care and daily life (1-4) ($Y = \text{Li, Na, K}$; $X = \text{F, Cl, Br, I}$). Overwhelming contributions with focus mainly on the proton and lone pair motion dynamics have been made since 1900's when Arrhenius (5), Brønsted–Lowry (6, 7), and Lewis (8) defined the acid and base dissolution based upon the ways of electron pairs sharing. A Lewis acid is a substance that accepts a pair of electrons from another atom and a Lewis base donates a pair of electrons to another to form a new bond.

Regarding the motion dynamics of protons and lone pairs, Grotthuss (9, 10) firstly proposed in 1903 a mechanism of “proton structural diffusion” or “concerted random hopping” from one H_2O motif to another without restriction. The proton mobility was assumed higher than that of a H_2O molecule. The century-old notion regarded an OH^- hydroxide as a H_2O molecule missed an H^+ proton. Such a “proton hole” in basic solutions follows the same H_3O^+ motion dynamics in acidic solutions. One often simply alters the excessive proton with the electron lone pair or simply reverse the H_3O^+ polarity to the OH^- with an alteration number of the lone pairs from one to two. Subsequent development refined “concerted random hopping” notion by invoking proton thermal hopping (11), structural fluctuating (12), and quantum tunneling (13). Although this widely-accepted scheme captures the concept of long-range charge translocation, numerous basic questions still remain regarding the rapidly evolving structure of an aqueous proton (14).

In 1964, Eigen (15) proposed an H_9O_4^+ ($\text{H}_3\text{O}^+ \cdot 3\text{H}_2\text{O}$) complex and suggested that an H_3O^+ core is strongly O:H nonbonded to three H_2O molecules and leave the lone pair of the tetrahedrally-structured H_3O^+ free, as Figure 1a illustrates. The lone pairs of the neighboring three H_2O molecules oriented simultaneously in such a way that they are facing to the H^+ of the H_3O^+ to form the O:H–O bonds. In contrast, as illustrated in Figure 1b, Zundel (16) favors in 1976 a $[\text{H}_5\text{O}_2]^+$ complex in which the proton shuttles randomly or frustrates between two positions off midway of two O^{2-} anions, nonbonded ($\text{H}^+ \cdot 2\text{H}_2\text{O}$) (16) or covalently bonded ($\text{H}^+ \cdot 2\text{H}_2\text{O}$) (17) to the adjacent H_2O neighbors. This scenario is the same to the transitional quantum tunneling of Bernal–Fowler proposed in 1932 (18) and the ice rule of frustration proposed by Pauling in 1935 (19).

Figure 1. Models for (a, b) proton and lone-pair motion and (c, d) O:H–O bond transition in Lewis solutions. (a) The $[\text{H}_9\text{O}_4]^+$ (or $\text{H}_3\text{O}^+ \cdot 3\text{H}_2\text{O}$) complex of Eigen (15) and (b) the $[\text{H}_5\text{O}_2]^+$ (nonbonded $\text{H}^+ \cdot 2\text{H}_2\text{O}$ (16) or covalently bonded $\text{H}^+ - 2\text{H}_2\text{O}$ (17) to the H_2O molecules) configuration of Zundel. A central replacement of the $2\text{H}_2\text{O}$ unit cell (22) forms (c) the $(\text{H}_3\text{O}^+, \text{OH}^-) \cdot 4\text{H}_2\text{O}$ motifs for Lewis solutions, which transits an O:H–O bond into the $\text{H} \leftrightarrow \text{H}$ anti-HB and an $\text{O} \rightleftharpoons \text{O}$ super-HB, respectively, (Reproduced from refs (20, 21) with permission from Elsevier, copyright [2017])

Tremendous theoretical efforts have been made in past century focusing on the “charge motion dynamics” (23–32). Density functional theory (DFT) calculations suggest that the OH^- hydration shell contains the $\text{OH}^- \cdot 3\text{H}_2\text{O}$ Eigen complex (33) and the hydrating molecular structure undergoes evolution by reorientation at heating (34). DFT calculations and phonon spectroscopic studies (35) suggested that water molecules act either as single donor or acceptor, a double-proton-donor, or a double-donor-single-acceptor in both the first and the second hydration shell of the OH^- . Interconversion among the isomers appears to be rapid as manifested in the observed spectra dominated by the broad and congested absorptions. The strong nonlinear coupling between intra- and inter-molecular vibrations and the non-adiabatic vibrational relaxation was suggested to take the responsibility for the rapid dynamics of phonon relaxation. The phonon frequency blueshift is associated with a longer phonon lifetime, or slower molecular dynamics, and a higher viscosity of the solution due to stronger polarization (35).

The OH^- was ever suggested highly active in solutions compared to the Y^+ and X^- ions that serve each as a point charge center of screened polarization (36–38). The performance of the basic solution is in

so far best explained in terms of “structural diffusion” or “solute delocalization” (39-41) - hydration complexes interconversion driven by the ionic solvation shell fluctuations. First-principles calculations

Using the *ab initio* path integral approximations, Tuckerman et al (42) suggested that an interplay between the hydration complexes and nuclear quantum effects determines the OH⁻ transport dynamics in basic solution. For acid, Marx et al (43, 44) suggest that the hydrated proton forms a fluxional defect in the hydration network, with a mixture of both the [H₉O₄]⁺ and the [H₅O₂]⁺ complexes occurring only in the sense of ‘limiting’ or ‘ideal’ structures. The defect is delocalized over several hydrogen bonds owing to quantum fluctuations and the protons transfer collectively in ice. The manner of H⁺ motion varies with temperature because of the involvement of thermal fluctuations and quantum effect. Moreover, AIMD calculations suggest that “bond switch” occur in the first H₃O⁺ hydration shell (45-47) and that HCl hydration makes water clusters into smaller ones by fragmentation (48). Recent quantum computations (49) suggest that the extra proton weakens the O–H bond due the H₃O⁺ ion since the lower bond order of the O–H bond in a H₃O⁺ ion compared with H₂O molecules, which softens the O–H stretching vibration mode due H₃O⁺.

Numerous dynamic and static electron/photon/phonon/neutron spectroscopies have been employed to investigate Lewis solutions. The sum frequency generation (SFG) spectroscopy probes the sublayer-resolved water dipolar orientation or the surface dielectrics, at the air-solution interface (39, 40); time-resolved two-dimensional infrared (2DIR) spectroscopy resolves the solute or water molecular diffusive motion dynamics in terms of phonon lifetime (23, 42, 50) that is related to the “structural diffusion”, “solute delocalization”, “molecular residing time” in the hydration shells. Neutron scattering probes the phonon density of states for the interested solutions (51, 52).

An ultrafast 2DIR spectroscopy investigation (23) suggests that the proton prefers Zundel motion manner accommodated by two H₂O at a time, [H₅O₂]⁺, rather than the Eigen structure, H₉O₄⁺. However, Wolke et al.(53) studied deuterated prototypical Eigen clusters, [D₉O₄]⁺, bound to an increasingly basic series of hydrogen bond acceptors. By tracking the frequency of every H–O stretching vibration in the complex as the transferring hydrogen is incrementally pulled from the central H₃O⁺ to one of its neighboring water molecules.

The pump-probe phonon spectroscopy investigation (54) of OH⁻ vibration energy relaxation suggests that excitation for the OH⁻ solvation decays in 200 fs and this process is followed by a thermalization

that becomes slower with the increase of solute concentration. The thermalization is suggested to proceed by water molecular rotation, reorientation, and diffusion (55). Dynamic studies of YOH hydration in bulk water (23) and in water molecular clusters (56) revealed two processes of vibration phonon relaxations. One is the rapid processes on 200 ± 50 fs time scales and the other slower dynamics on 1–2 ps scales (41, 57). The vibrational energy exchange between the bulk-like water and the hydrated water (or transition from the mode of ordinary water to the solvated state) takes place in ~ 200 fs.

An addition of 7M-NaOH solute could fold the phonon lifetime and increase four-fold the viscosity of the solution from that of pure water (23). On the other hand, NaOH hydration broadens the IR spectra between 800 and 3500 cm^{-1} with an association of redshift transiting the phonon abundance from above 3000 cm^{-1} to its below, refer to Figure 2b of similar observations. This transition was attributed to the strong interactions between the OH^- ion and its hydrating water molecules in an unclear manner. In conjunction with harmonic vibrational analysis of an $\text{OH}^-(\text{H}_2\text{O})_{17}$ cluster, it was suggested that the H–O stretching vibrations of aqueous hydroxides arise from coupling of multiple water molecules that dissolve the ions (56). Likewise, the free and hydrogen-bonded OH^- stretches the $\text{OH}^-(\text{H}_2\text{O})_{4,5}$ clusters phonon band substantially in the frequency range $2650\text{--}3850\text{ cm}^{-1}$ under the estimated 170 K temperature (58).

FTIR spectroscopy of 1% HOD in varying concentrations of NaOD/D₂O with the D₂O background subtracted revealed that as the NaOD concentration increases. A new feature appeared at 3600 cm^{-1} was attributed to the OH^- stretching, and a strong broadening appeared at low frequency was ascribed as the HOD molecules bonded to the DO^- ions (59), which is similar to the spectra in Figure 2b. The broadening of the IR spectra was explained in terms of Zundel model as proton shuttling motions between two oxygen atoms driven by the strong, rapidly fluctuating electrical fields of the surrounding polar solvent molecules (23, 50, 53).

Excises insofar are focused on the motion manner and dynamics of the excessive hydrated charge (proton and line-pair) and molecules with debating mechanisms proposed by Grotthuss, Eigen, and Zundel with little attention to the O:H–O bond relaxation and transition by solvation. The charge either hops freely from one H₂O molecule to another by switching the $\text{H}_2\text{O} \leftrightarrow \text{H}_3\text{O}^+$ on and off due to thermal and quantum fluctuation (43, 60) or firmly forms a H₃O⁺ hydronium without restriction to its O:H–O bond orientations in the ordered water molecules. One often considers the solute motion dynamics in

terms of phonon or molecular lifetime in the hydrating states, drift motion diffusivity, by taking the H₂O motif as the basic structural unit. Unfortunately, progress in understanding the solute capabilities of mediating the solution HB network and properties is slower than it supposed to be because there is a knowledge gap of the solvent O:H–O bond attributes. Little attention has been paid to the full-frequency scan of the Raman spectra or the correlation between the frequency shifts of the H–O and the O:H characteristic peaks – O:H–O bond segmental phonon cooperativity. It is unclear how the H⁺, OH[–], Y⁺, and X[–] ions functionalize collaboratively the hydration network and properties of the Lewis solutions. It is essential to correlate the manner and mobility of solute or molecular motion to the O:H–O bonding network deformation that determines the performance of a solution.

One amazing issue associated with YOH base solvation is the energy exchange in terms of exothermic and endothermic reaction, which is of great importance to both the basic and engineering sciences (33, 61, 62), as well as the efficiency of drug functioning (63). How the OH[–] hydration releases energy to heat up its solution is unclear. Rosenholm (64) and Ratkova and co-workers (65) comprehensively reviewed the thermodynamic chemistry occurred in liquids, solids, and semiconductor materials and suggested that the concurrent understandings are mainly within the framework of classical thermodynamics in terms of enthalpy (65, 66) and Gibbs free energy (67). The heat generation at reaction is attributed to the solute-solvent electron transportation (64, 68), solute-solvent correlation (69), water molecular interactions (70) and molecular motion (71). The inter- and intra-molecular cooperative interactions govern the path, ultimate outcome, and efficiency of aqueous thermic solvation (72) though formation and quantification of the energy exchange is still open for clarification.

In place of the solute motion dynamics, this practitioner and collaborators considers the capabilities of the excessive H⁺ that is attached to a H₂O to form a H₃O⁺ and one additional pair of lone pairs on a OH[–] tetrahedral motif (20, 73). The H⁺ or the ‘:’ neither stands alone nor moves freely between adjacent O^{2–}. As shown in Figure 1c and d, the central H₂O replacement of the 2H₂O unit cell with an H₃O⁺ turns one O:H–O bond into the H⁺↔H⁺ anti-HB point breaker for acidic solution. The OH[–] substitution for the central H₂O transits the O:H–O bond into the O:↔:O super-HB point compressor and polarizer in the basic solution. One must note that the orientations of the neighboring four molecules remain unchanged because of the structure geometry and intermolecular interactions (74).

The aim of this presentation is to show that focusing on the solute capabilities of transiting the HB from the mode of ordinary water to hydrating using the differential phonon spectrometrics (DPS), calorimetric detection, and DFT calculations is promising. Observations verified the expectations of $H\leftrightarrow H$ formation and the acidic solution network and the surface stress disruption and the $O:\leftrightarrow:O$ super-HB formation and its ability of compression and polarization. The screened X^- and Y^+ in Lewis solutions serve as point polarizers associated with each a supersolid hydration shell (75). The combination of the ionic polarization and the $H\leftrightarrow H$ fragilization or the $O:\leftrightarrow:O$ compression, and the undercoordinated solute H–O bond contraction mediate the HB network and the performance of Lewis solutions. As it is seen, this premise is much more profoundly revealing than focusing on the solute motion dynamics to the understanding of acid and basic solvation dynamics, solute-solvent interactions and solute extraordinary capabilities on HB transition.

1.2. Raman Spectroscopy of Lewis Solutions

Figure 2 compares the full-frequency Raman spectra for the 0.1 molar-ratio concentrated YOH/H_2O and HX/H_2O solutions against the spectrum of deionized water collected under the same ambient conditions. Focusing on the evolution of the characteristic peaks for the O:H stretching vibrations centered at $< 200\text{ cm}^{-1}$ and the H–O at $> 3000\text{ cm}^{-1}$ would suffice. Insets recap the reaction at solvation:

The X^- and Y^+ ions align, polarize and stretch the H_2O molecules in the hydration shells, and in turn, the ordered hydrating H_2O dipoles screen the ions, as they do in salt solutions (76). The superposition of the ionic point polarization and the $H\leftrightarrow H$ point fragilization or the $O:\leftrightarrow:O$ point compression and polarization dictate the properties of Lewis solutions.

However, the full-frequency Raman spectra could hardly resolve their differences unless the new peak at 3610 cm^{-1} and the broadening of the 3200 cm^{-1} to the lower frequencies for the basic solutions. No features of solute-solvent bonding could be resolved from the phonon spectroscopy except for the relaxation of the H–O bond centered at 3200 cm^{-1} and the O:H at 200 cm^{-1} . In acid solutions, only the X^- polarization shifts the O:H–O phonons into the hydrating states while the $H\leftrightarrow H$ does not polarize

the network of the HX solutions (20). It is unlikely to attribute the asymmetrical peak shape to the nonlinear contribution or artifacts but arises from the intrinsic bond vibrational identities.

Figure 2 Full-frequency Raman spectroscopy for the 0.1 molar concentrated (a) HX/H₂O and (b) YOH/H₂O solutions. Insets illustrate the framed H $\leftrightarrow$ H and O: $\leftrightarrow$:O formation and the ionic hydration shell formation through polarization and the hydrating H₂O dipole screen shielding (Reproduced from refs (20, 21) with permission from Elsevier, copyright [2017]).

The vibration mode features the Fourier transformation of bonding vibrating in the similar frequencies regardless of their orientations and locations in real space. The peak shape is the population function and the peak maximum the highest popularity, the peak central ω_x represent the stiffness of the vibrating bonds as a function of bond length d_x and bond energy E_x , $(\omega_x)^2 \propto E_x/d_x^2$. The peak integral is proportional to the number of bonds contributing to the phonon abundance of the specific mode x . Thus, one can distill the fraction-stiffness transition of the O:H–O phonons by differentiating the spectrum for the deionized water as a reference from those collected from solutions or water under perturbation such as heating and compressing upon all the spectral peak area being normalized (76). This differential phonon spectrometrics (DPS) strategy (77, 78) gives direct information on the O:H–O bonds transition from its vibration mode of ordinary water to the hydrating in terms of the number fraction (phonon abundance), stiffness (frequency shift), and fluctuation (line width) with much more ease and quantitative information than using the conventional spectral peak Gaussian-type decomposition.

2. Conservation Rules and O:H–O Bond Cooperativity

Figure 1c illustrates the 2H₂O unit cell having four oriented O:H–O bonds bridging oxygen anions if the central H₂O is recovered from the present H₃O⁺. Transiting from the V-shaped H₂O motif of C_{2v}

symmetry to the 2H₂O unit cell of C_{3v} symmetry aims to resolving the O:H–O cooperativity. As the basic structure and energy storage unit, the O:H–O bond integrates the intermolecular weaker O:H nonbond (or called van der Waals bond with ~0.1 eV energy) and the intramolecular stronger H–O polar-covalent bond (~4.0 eV) (76). The asymmetrical and short-range interactions of the segmented O:H–O bond are coupled with the ever-overlooked Coulomb repulsion between electron pairs on adjacent oxygen ions.

Figure 3. O:H–O bond relaxation in the segmental (a) length $d_x(P)$ and (b) the $\omega_x(P)$ for 80 K ice (79). (c) The $d_x(T)$ was derived from the measured density $\rho(T)$ profile (80) and (d) the measured $\omega_x(T)$ (81). The d_x is derived from ρ using eq (1). with EXP—MD denoting the MD matching to the measured $\rho(P)$ profile (82, 83). The MD derived the same trend of the measured $\omega_x(T)$ despite the accuracy due to the artifacts of calculation program. The offset is made to match to low-temperature experimental $\omega_x(T)$. (Reproduced from refs (81, 83) with permission from ACS and RSC, copyright [2012,2013])

Liquid water performs like a crystallite with well-defined lattice geometry, strong correlation, and high fluctuation. For a specimen having N number of oxygen atoms, there will be $2N$ numbers of

protons H^+ and lone pairs ‘:’ to form the O:H–O bonds uniquely, except for the dangling H–O radicals and the dangling lone pairs at the network terminals. The 2N numbers and the O:H–O bond configuration conserve regardless of structural phase (84) unless an excessive number of H^+ or ‘:’ is introduced.

The motion of a H_2O molecule or the proton H^+ in pure water is subject to strict restriction. If the central molecule rotating above 60° around the C_{3v} symmetrical axis of the $2H_2O$ unit cell, the $H \leftrightarrow H$ and $O \leftrightarrow O$ repulsion will come into play, which is energetically forbidden. Because of the H–O bond energy of ~ 4.0 eV, the H^+ translational tunneling or shuttling between adjacent H_2O molecules is also forbidden. In fact, only can 121.6 nm wavelength laser radiation breaks the H–O bond in the vapor phase (85).

With the known H–O and O:H segmental length relaxation derived from $\rho(P)$ ($1/V(P)$) profile measured from compressed ice (79, 83) and the framework of tetrahedral-coordination for a water molecule (86), one can correlate the size d_H , separation d_{OO} , bond geometry, and mass density ρ of molecules packed in water and ice in the following manner (87),

$$\begin{cases} d_{oo} = 2.6950\rho^{-1/3} & (\text{Molecular separation}) \\ \frac{d_L}{d_{L0}} = \frac{2}{1 + \exp[(d_H - d_{H0})/0.2428]}; & (d_{H0} = 1.0004 \text{ and } d_{L0} = 1.6946 \text{ at } 4^\circ\text{C}) \end{cases} \quad (1)$$

As illustrated in Figure 3, an external stimulus dislocates the O^{2-} along the segmented O:H–O bond in the same direction but by different amounts because of the O:H nonbond and the H–O bond segmental disparity and the O–O coupling (73, 81, 83, 88). The softer O:H nonbond always relaxes more than the stiffer H–O bond with respect to the H^+ as the coordination origin. For instance, a compression shortens and stiffens the O:H but the H–O responds to compression contrastingly (83). Molecular undercoordination and electric polarization have an opposite effect of compression (89).

The $\angle O:H-O$ angle θ relaxation contributes to the geometry and mass density. The H–O relaxation absorbs or emits energy and the O:H relaxation dissipates energy capped at 0.1 eV. The O:H–O bond segmental energy and specific heat disparity dictate the extraordinary adaptivity, cooperativity recoverability, sensitivity, properties of water and ice under external stimulus such as mechanical compression and thermal excitation.

Heating from 273 to 377 K lengthens the O:H nonbond from 1.695 to 1.750 Å, but the H–O bond responds to heating contrastingly from 1.000 to 0.985 Å. The segmental disparity defines the manner of O:H–O thermal relaxation. The O:H having a lower specific heat follows the regular thermal expansion, which shortens the H–O bond by the O–O coupling (81). Compression always shortens the O:H and lengthens the H–O regardless of the phase structures. The O:H nonbond contracts from 1.78 to 1.10 Å under compression up to 60 GPa when transits from the VII/VIII phase into phase X of identical O:H and H–O lengths. The segmental energy E_x varies with a certain power of its inverse length d_x . The phonon spectroscopy probes the length and energy as the phonon frequency shift, or segmental stiffness, in the form of $(\Delta\omega_x)^2 \propto (E/d^2)_x$, as demonstrated in Figure 2 b and d.

3. DPS Characteristics and Solution Performance

3.1. Lewis Solutions: Conservation Rules Broken

Upon solvation, an HX acid molecule dissolves into an H^+ proton and an X^- anion. The H^+ does not stay freely but bonds firmly to a H_2O molecule to form a tetrahedral H_3O^+ hydronium with one lone pair and three H^+ . The H_3O^+ replaces a H_2O in the center of the $2H_2O$ unit cell while its four neighbors remain their orientations because of the O:H–O regulation of interactions with their rest neighbors (35, 74), as illustrated in Figure 1c. The alteration of the ‘:’ with a H^+ at the $H_2O \rightarrow H_3O^+$ transition breaks the $2N$ conservation with derivative of $2N+1$ number of protons and $2N-1$ lone pairs in the solution. The excessive $2N+1 - (2N-1) = 2$ protons drive the $H_3O^+ \cdot 4H_2O$ motif uniquely and turns one O:H–O bond into the $H^+ \leftrightarrow H^+$ anti-HB without any other choice.

Likewise, the YOH base is dissolved into a Y^+ cation and a hydroxide (HO^- is HF-like tetrahedron with three lone pairs and one H^+ , which forms the $OH^- \cdot 4H_2O$ motif), see Figure 1d. The OH^- addition transits the $2N$ conservation into $2N+3$ number of lone pairs ‘:’ and $2N+1$ number of protons. The excessively unbalanced $2N+3 - (2N+1) = 2$ lone pairs can only form the $O:\leftrightarrow:O$ point compressor between the central OH^- and one of its H_2O neighbors that reserve their molecular orientations. This $O:\leftrightarrow:O$ compressor pertaining to each hydroxide has the same effect of but stronger mechanical compression on the network HB relaxation (73) because of the clustering of the two pairs of lone pairs and their weak binding energy to O^{2-} . The clustering of four electrons and weak bonding to O^{2-} specify the point polarizer instead of a point breaker.

3.2. Acidic Solvation: $H \leftrightarrow H$ Fragilization and X^- Polarization

Figure 4 and Figure 5 show the segmental ω_x DPS for the concentrated HX/H_2O solutions (20) compared with that for the heated water (38). The ω_L and the ω_H relax indeed cooperatively for all acidic solutions and the heated water. As the concentration increases from 0 to 0.1, X^- polarization transits the ω_L from 180 to 75 cm^{-1} and the ω_H from 3200 to 3480 cm^{-1} (36). $H \leftrightarrow H$ repulsion reverts the ω_L from 75 cm^{-1} to 110 cm^{-1} . The DPS also resolves the effect of the $H \leftrightarrow H$ repulsion on the H–O bond elongation featured as small humps below 3050 cm^{-1} . The $H \leftrightarrow H$ repulsion lengthens its neighboring H–O bonds, as being the case of mechanical compression and $O:\rightleftharpoons O$ point compression in basic solutions (73). The fraction of H–O bonds elongation by $H \leftrightarrow H$ repulsion decreases when the X^- turns from Cl^- to Br^- and I^- as the stronger polarizability of I^- annihilates the effect of $H \leftrightarrow H$ repulsion. The small spectral valley at 3650 cm^{-1} results from the preferential skin occupation of X^- that strengthens the local electric field. The stronger electric field stiffens the dangling H–O bond but the X^- screening weakens the signal of detection.

Acid solvation shares the same effect of segmental length and phonon stiffness relaxation and surface stress depression albeit different origins. X^- polarization and H–O thermal contraction stiffen the ω_H , X^- polarization and O:H thermal expansion softens the ω_H . $H \leftrightarrow H$ fragilization and thermal fluctuation lowers the surface stress.

With the established database, $(d_H, E_H, \omega_H) = (0.10 \text{ nm}, 4.0 \text{ eV}, 3200 \text{ cm}^{-1})_{\text{water}}$, one may evaluate the hydrated HB identities as $(0.095 \text{ nm}, 4.5 \text{ eV}, 3500 \text{ cm}^{-1})_{\text{solution}}$, which indicates the H–O bonds in the X^- supersolid hydration shell of the acidic solutions are indeed shorter and stiffer than those in the deionized water. For those featured at 3050 cm^{-1} and below, the H–O bond is longer and softer, being the same to the effect of mechanical compression and base solvation (57).

Figure 4. Comparison of the ω_H DPS for the concentrated (a) HCl/H₂O, (b) HBr/H₂O, and (c) HI/H₂O solutions and (d) the heated water. The X⁻ polarization transits the ω_H from 3200 to 3480 cm⁻¹. H $\leftrightarrow$ H repulsion softens a fraction H–O bond to $\omega_H < 3050$ cm⁻¹. The <3050 cm⁻¹ feature attenuates when the X turns from Cl to I because of the stronger I⁻ polarization, which overtones the effect of H $\leftrightarrow$ H repulsion. The skin X⁻ stronger polarization and its preferential occupancy results in the tiny valley at 3650 cm⁻¹ (reprinted with copyright permission from (20, 38) with permission from Elsevier and RSC, copyright [2007,2014]).

Figure 5. Comparison of the ω_L DPS for the concentrated (a) HCl/H₂O, (b) HBr/H₂O, and (c) HI/H₂O solutions and (d) the heated water. The X⁻ polarization transits the ω_L from 180 to 75 cm⁻¹ but the H $\leftrightarrow$ H repulsion reverts the ω_L partly to 120 cm⁻¹ and > 250 cm⁻¹. Heating softens the ω_L to 80 cm⁻¹ (reprinted with copyright permission from (20, 38) with permission from RSC and Elsevier, copyright [2017, 2014]).

3.3. Incapability of Proton Polarization

Integration of the DPS ω_H peaks gives rise to the phonon abundance transition from the ordinary water to the hydrating, or the number fractions of the transited H–O bonds (89). The following shows the incapability of proton polarization, $f_H(C) \equiv 0$, $f_{HI}(C) \equiv f_i(C)$, and $f_{Na}(C) = f_{NaI}(C) - f_{HI}(C)$, by employing the ω_H DPS for NaI and HI solutions (20, 22). One can assume that the I⁻ in the NaI and the HI solutions has the same concentration dependence of capability of hydration and Na⁺ and H⁺ are different. The ω_H DPS integrals for NaI Figure 6a and HI in Figure 4 c give rise to the fraction coefficients $f_{NaI}(C) = 0.4441 \times (1 - \exp(-C/0.1013))$ and $f_{HI}(C) = 0.1652 \times (1 - \exp(-C/0.0529))$ and Figure 6b (diamond) shows the difference $f_{Na}(C) \equiv f_{NaI}(C) - f_{HI}(C)$.

Letting $f_{NaI} = f_{Na} + f_i$ and $f_{HI} = f_H + f_i$, the f_{NaI}/f_{HI} ratio

$$f_{NaI}/f_{HI} = (f_{Na} + f_i)/(f_H + f_i) = 1 + (f_{Na} - f_H)/(f_H + f_i)$$

reorganizing,

$$f_{Na} - f_H = (f_H + f_i)(f_{NaI}/f_{HI} - 1) = f_{NaI} - f_{HI} = f_{Na},$$

thus,

$$f_{\text{Na}} - f_{\text{H}} \equiv f_{\text{Na}} \text{ and } f_{\text{H}} \equiv 0.$$

The $f_{\text{Na}}(C)$ line in Figure 6b (stars) increases linearly with the solute concentration, which is identical to the assumed $f_{\text{NaI}} - f_{\text{HI}}$ (diamond shape). It is thus proven that $f_{\text{H}}(C) \equiv 0$. The H^+ does not polarize water molecules but bonds to a H_2O molecule to form the H_3O^+ hydronium or the $\text{H}_3\text{O}^+ \cdot 4\text{H}_2\text{O}$ motif.

Figure 6. The ω_{H} DPS for (a) the NaI/H₂O and HI/H₂O solutions (Figure 4 c) measured at 298 K (20, 22) and (b) their integrals $f_{\text{NaI}}(C)$ and $f_{\text{HI}}(C)$ and the assumed (diamond) and proven $f_{\text{Na}}(C) \equiv 0.15C$. The $f_{\text{H}}(C) \equiv 0$ and $f_{\text{Na}}(C) - f_{\text{H}}(C) \equiv f_{\text{Na}}(C)$. (reprinted with copyright permission from (20, 22) with permission from RSC and Taylor & Francis, copyright [2017, 2018]).

3.4. Basic Solvation: $\text{O} \rightleftharpoons \text{O}$ Compression and Solute H–O Contraction

The solute type and concentration resolved DPS shown in Figure 7 and Figure 8 confirmed that YOH solvation indeed softens the ω_{H} phonon – $\text{O} \rightleftharpoons \text{O}$ compression lengthens the neighboring H–O bond and softens its phonon to 3100 cm⁻¹ and below (56, 59, 90). Besides, a sharp peak appears at 3610 cm⁻¹ that is identical to the dangling H–O bond at water surface. The sharp peaks feature the H–O bond due to the less ordered OH⁻ solute. The ω_{x} is less sensitive to the type of the alkali cations of the same concentration. These observations confirm that the $\text{O} \rightleftharpoons \text{O}$ super-HB has the same but stronger effect of mechanical compression (91) and that the bond order-length-strength (BOLS) correlation (92) applies to aqueous solutions - bonds between undercoordinated atoms become shorter and stronger.

Figure 7. DPS ω_H for the concentrated (a) LiOH/H₂O, (b) NaOH/H₂O, and (c) KOH/H₂O solutions and the (d) compressed water. All solutions share the same compression effect of O: $\rightleftharpoons$:O and mechanical pressure on the distant solvent H–O bond elongation ($< 3100 \text{ cm}^{-1}$), and the bond-order-deficiency induced solute H–O bond contraction (3610 cm^{-1} , being identical to the dangling H–O of 10% shorter than it is in bulk water). The O: $\rightleftharpoons$:O compression is much stronger than 1.33 GPa for the room-temperature ice formation (d) (reprinted with copyright permission from ref (57) with permission from Elsevier, copyright [2016]).

Observations justify that the O: $\rightleftharpoons$:O super–HB point compression ($< 3100 \text{ cm}^{-1}$; $> 220 \text{ cm}^{-1}$) has the same but much stronger effect of mechanically bulk compression ($< 3300 \text{ cm}^{-1}$; $> 200 \text{ cm}^{-1}$) at the critical pressure 1.33 GPa for the room-temperature water-ice transition (73), compared to the compression effect on water and ice shown in Figure 7d and Figure 8d. The $\Delta\omega_L$ for the YOH solutions at lower concentrations duplicates the $\Delta\omega_L$ feature of the mechanically compressed water, because of the compression and polarization (83). Compression lengthens the solvent H–O bond and softens its phonon but relaxes the O:H nonbond contrastingly. The strong effect of compression overtones the

effect of Y^+ polarization. The excessive peak at 3610 cm^{-1} features the bond-order-deficiency induced H–O contraction of the due OH^- solute, which is identical to the surface H–O dangling bond of 10% shorter, shorter and stiffer than the skin H–O bond featured at 3450 cm^{-1} for ice and water, and bulk water at 3200 cm^{-1} (93).

The broad hump at $\omega_H < 3100\text{ cm}^{-1}$ shows the distant dispersion of the $\text{O}:\rightleftharpoons:\text{O}$ compression forces acting on its subsequent H_2O neighbors. The sharp feature at 3610 cm^{-1} for the YOH indicates the strong localized nature of the solute H–O bond contraction. These DPS H–O vibration peaks clarify the origin for the two ultrafast processes in terms of phonon lifetime (23, 56). The longer $200 \pm 50\text{ fs}$ lifetime features the slower energy dissipation of higher-frequency solute H–O bond vibrating at 3610 cm^{-1} and the other shorter time on 1–2 ps characterizes the elongated solvent H–O bond at lower-frequency of vibration $<3100\text{ cm}^{-1}$ upon OH^- solvation (57). In the pump-probe ultrafast IR spectroscopy, the phonon population decay, or vibration energy dissipation, rate is proportional to the phonon frequency – the dynamics of higher frequency phonon is associated with a slower process.

Figure 8. DPS ω_L for the concentrated (a) LiOH/H₂O, (b) NaOH/H₂O, and (b) KOH/H₂O solutions and the (d) compressed water. All solutions share the same compression and polarization effect of O: $\leftrightarrow$:O and mechanical pressure on the O:H phonons ($\sim 120\text{ cm}^{-1}$, $>250\text{ cm}^{-1}$), (reprinted with copyright permission from ref (57) with permission from Elsevier, copyright [2016]).

3.5. Solution Performance

Figure 9a and b show the linear form $f(C) \propto C$ for the OH⁻ transiting the ordinary H–O bond to the elongated solvent H–O bonds ($< 3100\text{ cm}^{-1}$) and the solute H–O phonons (3610 cm^{-1}) in YOH solutions. The fractions of solvent H–O bonds and the solute H–O are proportional to the solute concentration. The effect of Y⁺ ionic polarization was annihilated by the O: $\leftrightarrow$:O compression and the undercoordinated solute H–O contraction.

Figure 9c shows the solute capabilities of HB transition and surface stress disruption of HX/H₂O solutions. Since the stronger H–O bond ($\sim 4.0\text{ eV}$) only allows H⁺ to form a H₃O⁺ firmly, the polarization due to H⁺ is absent, $f_H(C) = 0$. Therefore, $f_{HX}(C) \cong f_X(C)$. The nonlinear concentration trends $f_X(C) \propto 1 - \exp(-C/C_0)$ corresponds to the number fraction of bonds being polarized by X⁻ in its closest hydration shells. The slope of the $f_X(C)$ is proportional to the number of bonds within the X⁻ hydration shell. The pronounced X⁻ $\leftrightarrow$ X⁻ repulsion at higher concentrations, or smaller solute separations, weakens the ionic electronic field in the hydration shells, which indicates that the number inadequacy of the highly ordered H₂O dipoles in the crystal-like semi-rigid hydration shells could not fully screen the X⁻ solute (76). The H $\leftrightarrow$ H fragilization disrupts the solvent network and the surface stress. Therefore, H $\leftrightarrow$ H fragilization resolves the corrosive, dilutive, and skin-stress destructive nature of the acidic solutions. Results are consistent with MD calculations on the hydration shell molecular dynamics and the H⁺ induced network fragmentation (48).

The electrical conductivity of the concentrated HCl/H₂O, LiOH/H₂O, and /H₂O solutions, shown in Figure 9d follows the trend the $f(C)$ for YX solutions, or the Jones-Dale notion for viscosity (22), indicating a common yet unclear mechanism of charge transportation.

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Figure 9. Fraction of O:H–O bonds transition due to (a) the $\text{O} \leftrightarrow \text{O}^+ \text{O}^-$ compression and (b) the undercoordinated H–O contraction in YOH solutions and (a) X^- polarization in acid solutions. Electrical conductivity of HCl/H₂O and LiOH/H₂O compared with that of the LiCl/H₂O solutions. Insets a shows the corresponding solvent ($< 3100 \text{ cm}^{-1}$) and b the solute (3610 cm^{-1}) phonon peaks (reprinted with copyright permission from ref (20, 21) with permission from Elsevier, copyright [2017, 2018]).

Figure 10 a and b compare the surface stress of the concentrated HY and YOH solutions. Acid solvation shares some of the heating effect on the O:H–O phonon relaxation, shown in Figure 4. X^- polarization stiffens the ω_{H} and softens the ω_{H} because of the electric field but heating did the same by specific heat disparity. Furthermore, both acid solvation and heating depress the surface stress because of the thermal fluctuation (38) and $\text{H} \leftrightarrow \text{H}^+$ disruption (20). The YOH solutions have the similar polarization effect on the surface stress. YOH solvation constructs the surface stress through polarization by both cation and $\text{O} \leftrightarrow \text{O}^+ \text{O}^-$ polarization. Compared with the $\text{H} \leftrightarrow \text{H}^+$ in acidic solutions, the $\text{O} \leftrightarrow \text{O}^+ \text{O}^-$ repulsivity

is much greater as the two pairs of lone pairs packed closely. Figure 10 c and d show the viscosity of the HCl and LiOH solutions.

Comparison of the $f(C)$ functions, the electric conductivity (Figure 9), surface stress, and the relative viscosity for the concentrated HCl and LiOH solutions (Figure 10) revealed the following:

- 1) The conductivity follows the respective $f(C)$ trends except for the LiOH solution whose $f(C)$ depends linearly on the concentration but the $\sigma(C)$ follows the Jones-Dale expression for the viscosity. The viscosity of (H, Li)Cl solutions is proportional to the respective $f(C)$. The $H \leftrightarrow H$ and $O \leftrightarrow O$ fragmented hydration volumes shall ease charge transportation, which leads to the $\sigma_{HCl} > \sigma_{LiOH} > \sigma_{LiCl}$ order at higher concentrations. Ions and their hydration volume may serve as carriers for the current flow that is subject to scattering as an added mechanism of transporting. Further investigation under variation of the measuring electric field would derive the carrier mobility in solutions.
- 2) However, the η_{HCl} increases with solute concentration in contrasting to the surface stress. The $H \leftrightarrow H$ fragilization disrupt the surface stress and the $H \leftrightarrow H$ and the $X^- \leftrightarrow X^-$ repulsions governs the viscosity of acid solutions. The η_{HCl} increases slightly slower than the η_{LiCl} because of the $H \leftrightarrow H$ fragmentation.
- 3) The $O \leftrightarrow O$ strong repulsion derives the much greater viscosity with $d^2\eta/dC^2 > 0$ for LiOH solutions. This unexpected concentration trend of viscosity elevation is consistent to those of the divalent (Ma, Ca, Cs)(Cl, Br)₂ solutions (94, 95) and the NaClO₄ and LiClO₄ (96) solutions. The strong $O \leftrightarrow O$ and multiple solutes repulsion should be responsible for the viscosity of the basic, divalent and complex salt solutions.

Figure 10. Surface stress of the concentrated (a) HX and (b) YOH solutions and the relative viscosity for the concentrated (c) HCl and (d) LiOH solutions. $H \leftrightarrow H$ fragilization depresses the surface stress and X^- polarization and $O \rightleftharpoons O$ compression raises the viscosity in different manners (reprinted with copyright permission from ref (20, 21) with permission from Elsevier, copyright [2017, 2018]).

4. DFT: X^- and H_3O^+ Hydration Shells

Structural optimization derived the segmental bond lengths and vibration frequencies of the pure, H^+ -contained, and X^- -contained water using both the (PW91) (97) and the dispersion-corrected OBS-PW (98) calculation methods. The OBS-PW method invokes the hydrogen bond weak interactions. All-electron calculations were performed based on the double numeric and polarization basis sets. The self-consistency threshold of total energy was set at 10^{-6} Hartree. The energy tolerance limit, 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 (99). The DFT calculation considers the structure under the temperature of 0 K.

Figure 11a-c compares the optimized H^+ and X^- solution structures with ordinary water. The H^+ forms an anti-HB with a neighboring water molecule, as the arrow denoted in Figure 11b, which results in two H–O radicals ending the continuous solvent network. The $H \leftrightarrow H$ repulsion elongates and softens its neighboring H–O bonds. The X^- attracts three protons to form three $X \cdot H-O$ bonds in its closest hydration shells (Figure 11c).

Figure 11. DFT optimized cubic structure of (a) pure water, (b) H⁺-contained (yellow) water with anti-HB (black arrow) and (c) X⁻-contained water with hydrating neighbors. Number 1-3 denote the undercoordinated O²⁻ anions in the X⁻ hydration shell. (reprinted with copyright permission from ref (20) with permission from Elsevier, copyright [2017]).

Table 1 features the calculated O:H and H–O segmental lengths associated with the H₃O⁺ and the X⁻ solutes. The ϵ_x is the solvation-induced strain at different locations. For the H₃O⁺ induced bond relaxation, one must consider the H–O bonds due H₃O⁺ solute and its second nearest neighbors, as labeled in Figure 11b. For the X⁻ hydration shell, three X·H–O bonds form the closest hydration shells with “·” representing for the Coulomb interaction between the X⁻ and the H⁺, which is weaker than the regular O:H nonbond. The X⁻ hydration shell extends to the second O:H–O bond length with inclusion of the under-coordinated O atoms, because of the X·H termination, as labeled in Figure 11c.

Results in Table 1 show that both DFT schemes give the same trend of intrinsic O:H–O relaxation upon acid solvation. The H–O bonds due H₃O⁺ are 3% shorter and its O:H counterpart is 60% longer than they are in pure water, which means that the H₃O⁺ volume is smaller than a H₂O but a larger separation between its neighboring water molecules. However, the network disruption by H $\leftrightarrow$ H repulsion shortens the next neighboring O:H–O bonds, which lengthens the H–O bond by 4% and shortens the O:H by about 11%, according to the calculations (20). The O:H–O bond contraction reduces its dipole moment and depolarizes the local network. The 4% elongation corresponds to the H–O vibration feature at <3100 cm⁻¹ and the 11% contraction for the O:H transition of its vibration frequency from 75 to 110 cm⁻¹.

Results in Table 1 and Figure 11c also indicate that the X⁻ anion attracts its three neighboring protons to form the X·H–O bonds in the closest hydration shells. The hydration shell extends to the subsequent

O:H–O bonds oriented slightly towards the X^- charge center. Since the $X^- \cdot H^+$ interaction is weaker than the $O^{2-} : H^+$ nonbond and the number increase of the X^- with concentration also weakens the electric field in the hydration shell because of the $X^- \leftrightarrow X^-$ repulsion (76). Calculations confirm that the X^- polarization does shorten the H–O bond and lengthens the O:H and the X·H nonbond compared with the respective segment in pure water (20). The X^- capability of relaxing the nearest X·H–O and the subsequent O:H–O follows the Hofmeister series order: $I > Br > Cl$. The H–O bond in the first I^- hydration shell is 1.1% shorter and the I·H is 41% longer than they are in the bulk water. The O:H–O bond in the second hydration shell of the X^- anion becomes longer. The H–O bond contracts by 0.8% and the O:H expands by 28% in the second shell, for instance.

The calculated DPS between H_3O^+ -solvated and pure H_2O showed the splitting of the stretching and bending modes into two components. The red shift is attributed to the nearest neighboring elongated O:H nonbonds of the H_3O^+ and the blue shift to the next nearest neighboring O:H elongation. For the stretching part, the pure water modes around $200\sim300\text{ cm}^{-1}$ shift to 110 cm^{-1} and below, resulting from the first nearest neighboring O:H nonbond elongation. The mode above 400 cm^{-1} corresponds to the neighboring O:H depolarization and $H \leftrightarrow H$ repulsion, which is consistent with the O:H length relaxation as shown in Table 1 and spectral profiles in Figure 4. The O:H–O bond cooperative relaxation also holds for the X^- hydration shells.

Table 1. DFT derived bond strain ε (%) surround H^+ and X^- solutes (reprinted with copyright permission from (20))

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

* Neighbor – the O:H–O bonds in the second-nearest hydration shells as labeled in Figure 11c.

5. Calorimetric Detection: Basic Exothermic Solvation Energetics

From the perspective of O:H–O cooperativity (35) and the solute-solvent O:⇌:O super-HB compression induced solvent H–O bond elongation and the solute undercoordinated H–O bond contraction (57), one can correlate the solution temperature T(C) to the fraction f(C) of bonds transition at base solvation. According to Pauling (100), chemical bonds are the ingredient of energy storage. Energy emission or absorption proceeds by bond relaxation – the equilibrium atomic distance and binding energy change under non-conservative perturbation (92) such as aqueous solvation or mechanical compression. Table 2 summarizes the thermodynamic processes involved in the YOH solvation (21).

Energy absorption, emission and dissipation are involved in solvation. Bond dissociation and elongation emit energy, but bond formation and bond contraction absorb energy, leading to the respective exothermic and endothermic reaction. Molecular motion and structure fluctuation dissipate energy within the range of O:H cohesive energy at 0.1 eV, which contribute little to the change of solution temperature. Table 3 suggests the possible thermodynamics involved in the YOH solvation under the non-adiabatic calorimetric detection and their significance of energy change. H₂O₂ solvation is not subject to YOH molecular dissolution but only H–O relaxation and molecular motion and structure fluctuation.

Table 2. Thermodynamics of base solvation (reprinted with permission from (21))

YOH + H ₂ O → Y ⁺ + OH [−] + H ₂ O + (heat ↑)	Three pairs of lone pairs ‘:’ attached to the tetrahedrally coordinated OH [−] hydroxide, forming an O:⇌:O compressor.
O:⇌:O repulsion shortens the O:H and lengths the solvent H–O that emits energy to heat up the solutions	

Table 3. Thermodynamics of YOH solvation (reprinted with permission from (21)).

Heat absorption	solvent H–O bond thermal contraction (81)	significant
Q _a	Undercoordinated solute H–O bond contraction (74)	significant

	hydrating H–O bond contraction by Y^+ polarization (37)	Negligible because YX solvation and polarization change little the solution temperatures
Heat emission Q_e	YOH dissolution into Y^+ and OH^- (57)	
	O: $\rightleftharpoons$:O compressed solvent H–O bond elongation (57)	
	Y^+ polarization elongated O:H nonbond (37)	Negligible O:H energy dissipation
Heat dissipation Q_{dis}	molecular motion and structure fluctuation	With little contribution to energy absorption or emission
	heat loss due to the non-isothermal calorimetric detection	Cause error of tolerance

According to the proposed thermal dynamics framework in Table 3, one may estimate the energy exchange during base solvation. The total energy should conserve if counts the three significant processes of emission, absorption and dissipation:

$$\sum_3 Q_{e,i}(C) - \sum_3 Q_{a,j}(C) - \sum_2 Q_{dis,l}(C) = 0$$

The energy Q_0 heating up one mole mass solution from the initial T_i to final T_f by increasing the solute concentration up to its maximal C_M equals ($h_0 = 4.18 \text{ J}(\text{g}\cdot\text{K})^{-1} = 0.00039 \text{ eV}(\text{bond}\cdot\text{K})^{-1}$ is the specific heat for liquid water):

$$\int_0^{Q_0} dq = h_0 \int_0^1 dm \int_0^{C_M} \frac{dT(C)}{dC} dC = h_0 T(C_M) \quad (2)$$

The $T(C_M)$ is the highest solution temperature measured at the maximal concentration C_M , show in Figure 12. The energy difference between exothermic solvent H–O elongation Q_e by O: $\rightleftharpoons$:O compression and the endothermic solute H–O contraction Q_a by bond-order-deficiency heats up the solution (h_e and h_a are the energy emission and absorption per bond),

$$\int_0^{Q_e} dq_e - \int_0^{Q_a} dq_a = \left[h_e \int_0^{f_e} dm_e - h_a \int_0^{f_a} dm_a \right] \int_{T_i}^{T_f} dt = [h_e f_e - h_a f_a] T(C_M) \quad (3)$$

Where f_e and f_a are the fraction coefficients for H–O elongation ($< 3100 \text{ cm}^{-1}$) and contraction (3610 cm^{-1}). One can obtain the heat emission from the H–O bond elongation,

$$Q_e = h_e T(C_M) = \frac{h_0 T(C_M)}{f_e - f_a} \frac{h_a}{h_e} \approx \frac{h_0 T(C_M)}{f_e - f_a}, (\text{with } h_e \approx h_a) \quad (4)$$

One may approximate that the h_a is compatible to the h_e for estimation. Table 4 tabulates the outcome showing that the H–O elongation by $\text{O}:\rightleftharpoons:\text{O}$ compression emits at least 150% the O:H cohesive energy of 0.1 eV at room temperature (74). It is thus verified that the energy remnant of the solvent H–O exothermic elongation and the solute H–O endothermic contraction heats up the solution, which has little to do with energy dissipation of molecular motion or structure fluctuation.

One can also estimate the energy emission from H–O bond elongation with the documented values of $(d_H, E_H, \omega_H) = (1.0 \text{ \AA}, 4.0 \text{ eV}, 3200 \text{ cm}^{-1})$ for the mode of bulk water (87), and for basic hydration $(1.10\sim 1.05 \text{ \AA}, E_2, 2500\sim 3000 \text{ cm}^{-1})$ using the $\omega^2 \propto E/d^2$ relation:

$$\Delta E = 2E \left(\frac{\Delta d}{d} + \frac{\Delta \omega}{\omega} \right) = 2 \times 4 \left(\frac{0.10 \sim 0.05}{1} + \frac{(2500 \sim 3000) - 3200}{3200} \right) = \begin{cases} -0.95 & (2500 \text{ cm}^{-1}) \\ -0.1 & (3000 \text{ cm}^{-1}) \end{cases} \quad (5)$$

Table 4. Derivative of energy emission from the H–O bond elongation by $\text{O}:\rightleftharpoons:\text{O}$ compression. C is the molar concentration (reprinted with permission from (21)).

YOH	C_M	f_e/C	f_a/C	T_M/C	h_e/h_0	Q_e (eV/bond)	Q_e/E_L
LiOH	0.08	0.981	0.321	253.8	1.515	0.150	1.58
NaOH	0.1	1.773	0.970	296.1	1.245	0.144	1.52
KOH	0.1	0.875	0.371	285.4	1.984	0.221	2.33

The H–O bond elongation losses its cohesive energy from 4.0 by 0.1~1.0 eV depending on the frequency shift. Although the 0.15 eV energy emission may be underestimated, the exothermic H–O bond elongation by $\text{O}:\rightleftharpoons:\text{O}$ compression is certainly the intrinsic and primary source for heating up the YOH solution. The elongated H–O bond emits $>150\%$ the O:H cohesive energy at 0.095 eV that caps the energy dissipation by molecular motion and thermal fluctuation. Therefore, the

intramolecular H–O bond relaxation driven by the bond-order-deficiency and intermolecular $O:\rightleftharpoons:O$ repulsion governs the hydration bonding thermodynamics and the performance of the solutions.

A calorimetric detection has confirmed the correlation between the $T(C)$ and the $f(C)$ for the solvent H–O elongation and the undercoordinated H–O bond contraction. The calorimetric detection was conducted using a regular thermometer to record the solution temperature in a glass beaker under the ambient temperature. The solution was stirred using a magnetic bar rotating in the beaker in 5 Hz frequency. For concept proofing, it is reasonable to omit the energy loss due to non-adiabatic detection and the stirring friction, as these artefacts only influence the accuracy of detection but not the nature and trend of observations.

Figure 12 shows the solution temperature $T(C) \propto C$ and the time taken to reach the highest temperature as a function of the base concentration. LiOH is more easily dissolved than the rest two. This thermal relaxation time in second or minute scale is completely different from that used in the time-resolved infrared spectroscopy for spectral signal decay at the fs ~ ps level with involvement of the water molecular and solute drift motion (101). Furthermore, the less capability of the H_2O_2 than YOH of raising the $T(C)$, the solution surface stress and the $f(C)$ of H–O bonds transiting from water to the solvated states further confirms the effect of bond-order-deficiency.

Figure 12. Solution self-heating upon YOH solvation. (a) solution $T(C)$ and the (b) solvation time to the highest temperature at fixed value of concentration (reprinted with copyright permission from ref (21) with permission from Elsevier, copyright [2018]).

6. Concluding Remarks

A combination of the O:H–O bond cooperativity notion, DPS detection, contact angle measurements, calorimetric detection has enabled the described progress. The following clarifies the solvation dynamics, molecular interactions, and solute capabilities on the O:H–O bond relaxation:

- 1) Charge injection in forms of H^+ , lone pairs, Y^+ and X^- by acid and base solvation mediate the HB network and properties of the Lewis solutions through $H \leftrightarrow H$ point fragilization, $O:\leftrightarrow:O$ compression and polarization, X^- and Y^+ polarization and hydrating H_2O dipolar screen shielding, $X^- \leftrightarrow X^-$ repulsion, and solvent H–O bond elongation and solute H–O bond contraction.
- 2) Acid solvation shares the same effect of liquid water heating that stiffens the ω_H and softens the ω_L associated with surface stress depression governed by different mechanisms. X^- polarization in acid solution and the O:H–O segmental specific heat disparity of liquid water dictate the same trend of O:H and H–O phonon frequency shift. The $H \leftrightarrow H$ fragilization in acid solution and liquid water thermal fluctuation depress the surface stress.
- 3) In acid solution, the H–O bond due H_3O^+ contracts by 3% and the O:H distance expands by 60%. The next neighboring H–O lengthens by 4% and its O:H counterpart shortens by 11%. The X^- forms the $X-H-O$ and the next O:H–O hydration shells. The H–O bond in the first hydration shell contracts by 1.1% and contracts by 0.8% and the O:H expands by 28% in the second hydration shell, The I-H distance is 41% longer than the O:H in the bulk water. According DFT calculations.
- 4) Base solvation shares partly the effect of mechanical compression on softening solvent ω_H from above 3100 cm^{-1} to below and recovering ω_L from the polarized 75 to 100 cm^{-1} . The $O:\leftrightarrow:O$ compression is much stronger than the 1.35 GPa for room-temperature water icing. The undercoordinated solute H–O bond contracts by 10% of it is in the bulk, which also the length of the dangling H–O radicals featured at 3610 cm^{-1} .
- 5) Energy emission by the solvent H–O bond elongation and energy absorption by the solute H–O bond contraction, heats up the base solutions. The solution temperature increases linearly with the number fraction of the ordinary O:H–O bonds transiting into their hydration states. The elongated H–O bond emits >150% the O:H cohesive energy of 0.1 eV that caps the energy dissipating by molecular motion, thermal fluctuation, diffusion, and even evaporation.

- 6) The X^- and Y^+ ions performed the same as they do in salt solutions but the effect of Y^+ is annihilated by the effect of $O:\leftrightarrow O$ compression and solute $H-O$ contraction. $X^-\leftrightarrow X^-$ repulsion comes into play at higher solute concentration, which weakens the X^- electric field and the hydration shell size.

One may be recommended the essentiality of the following in consideration:

- 1) Water and solvent matrix form the highly ordered, strongly correlated, and fluctuating crystals packed with tetrahedrally-coordinated water molecules, which follow the conservation rules of the number of protons and lone pairs and the $O:H-O$ configuration and the restriction to molecular motion and proton tunneling transition. $O:H-O$ bond cooperative relaxation and its transition upon solvation from the mode of ordinary water to the hydrating would be critical to the understanding of solvation.
- 2) One can consider the solvation as a process of charge injection with multiple interactions. Protons and lone pairs cannot stay alone or move freely but they are attached to H_2O molecule to form the H_3O^+ or OH^- tetrahedron, respectively. The H_3O^+ or the OH^- may undergo Brownian motion under fluctuation or drift diffusion under a graded electric or thermal field. The $H\leftrightarrow H$ anti-HB fragilization, $O:\leftrightarrow O$ super-HB compression and polarization, the screened ionic polarization, and the undercoordinated solute $H-O$ bond contraction dictate the solvation dynamics, molecular interaction, and the HB network and property mediation.
- 3) Focus on the $O:H-O$ bond energetic/spatial/temporal transition would be more revealing than on the solute spatial/temporal transportation. Molecular motion dissipates energy capped at the scale of $O:H$ binding energy that is only about 3% of the $H-O$ energy. The $H-O$ absorbs or emits energy through relaxation. Any detectable quantities are functional dependence on the bond length and energy.
- 4) The DPS is proven a powerful tool probing quantitative information on the fraction-stiffness transition of the $O:H-O$ bonds from the mode of ordinary water to hydrating. The combination of the DPS and the time-resolved electron/phonon spectroscopy and interdisciplinary investigation would be more fruitful.

Understanding may extend to water-protein interaction, biochemistry, environmental and pharmaceutical industries. It would be very promising for one to keep arm and mind open towards developing experimental strategies and innovating theories to unveil the solvation bonding dynamics.

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