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2018

Sun, C. Q. (2018). Supersolidity of undercoordinated and hydrating water. *Physical Chemistry Chemical Physics*, 20(48), 30104-30119. doi:10.1039/c8cp06115g

<https://hdl.handle.net/10356/144930>

<https://doi.org/10.1039/c8cp06115g>

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Perspective

Supersolidity of undercoordinated and hydrating water

Chang Q Sun^{1*}

Abstract

Supersolidity of water ice, proposed in 2013 and intensively verified since then [*J Phys Chem Letter* 4: 2565; *ibid* 4: 3238], refers to those water molecules being polarized by molecular undercoordination pertained to the skin of bulk water ice, nanobubbles, and nanodroplets (often called confinement) or by electrostatic fields of ions in salt solutions [*PCCP* 16: 22995 (2014); *J Phys Chem B* 122: 1228 (2018)]. From the perspective of hydrogen bond (O:H–O or HB with “:” being the lone pairs on O²⁻) cooperative relaxation and polarization, this work features the recent progress and recommends future trends in understanding the bond-electron-phonon correlation in the supersolid phase. The supersolidity is characterized by the shorter and stiffer H–O bond and the longer and softer O:H nonbond, deeper O1s energy band, and longer photoelectron and phonon lifetime. The supersolid phase is less dense, viscoelastic, mechanically and thermally more stable. The O:H–O bond cooperative relaxation offsets boundaries of structural phases and raises the melting point and meanwhile lower the freezing temperature of water ice – known as supercooling and superheating.

Keywords: hydration; undercoordination; electron spectroscopy; phonon spectroscopy; hydrogen bond; ice friction; ice floating; phase transition

Highlight

- *Molecular undercoordination and ionic hydration effect the same on O:H–O relaxation*
- *XPS O 1s and K-edge absorption energy shifts in proportional to the H–O bond energy*
- *Electron hydration probes the site- and size-resolved bounding energy and the electron lifetime*
- *DPS, SFG, and calculations confirm the site-resolved H–O contraction and thermal stability*

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Electrostatic polarization or molecular undercoordination endows the supersolidity by shortening and stiffening the H–O bond and lengthening and softening the O:H nonbond, deepening the O1s energy level, and prolonging the photoelectron and phonon lifetime. The supersolid phase is less dense, viscoelastic, mechanically and thermally more stable, which offsets boundaries of structural phases and critical temperatures for phase transition of the coordination-resolved core-shell structured water ice such as the ‘no man’s land’ supercooling and superheating.

Contents

1.	Wonders of H ₂ O Molecular Undercoordination and Salt Hydration.....	3
2.	O:H–O Bond Oscillator Pair	6
2.1.	Basic Rules for Water.....	6
2.2.	O:H–O Bond Potentials and Cooperativity	7
2.3.	Specific Heat and Phase Transition	9
3.	Supersolidity and Quasisolidity.....	10
3.1.	Significance of Supersolidity and Quasisolidity.....	10
3.2.	Supercooling of Supersolid Phase	13
4.	Electron and Phonon Spectrometrics.....	13
4.1.	STM and STS: Strong Polarization	13
4.2.	SGF: Site Resolved H–O Bond Length and Stiffness	15
4.3.	DPS: Fraction of O:H-O Bond Transition.....	17
4.4.	Ultrafast IR: Phonon Energy Dissipation	17
4.5.	Ultrafast PES: Nonbonding Electron Polarization	19
4.6.	XPS, XAS, and DPS: Supersolid Thermal Stability.....	21
5.	Perspectives	26

1. Wonders of H₂O Molecular Undercoordination and Salt Hydration

As independent degrees of freedom, water molecular undercoordination and electrostatic polarization by ions in salt solutions make the mysterious water ice even more fascinating (1). Undercoordinated water molecules are referred to those with fewer than four nearest neighbors ($CN < 4$) as they occur in the bulk interior of water and ice. Molecular undercoordination takes place in the terminated hydrogen bonded network, in the skin of a large or small volume of water and ice, molecular clusters, ultrathin films, snowflakes, clouds, fogs, nanodroplets, nanobubbles, and in the vapor phase.

Such a kind of water molecules shows the extraordinary features of hydrophobic, less dense, elastoviscous, melting point (T_m) elevation, freezing temperature (T_N) depression, superfluidity in microchannels (2-6). A few molecular-layer of ice can form at the room temperature on SiO₂ substrate (7). Nanobubbles are long lived, mechanically stronger and thermally more stable. The T_N drops from 258 K to even 150 K when the droplet size is reduced – called supercooling or “no man’s land” (4, 8). Likewise, nuclear magnetic resonance and differential scanning calorimetry measurements revealed that the melting of ice in porous glass having different pores sizes proceeds inhomogeneously. There exists a 0.5 nm thick interface liquid layer between the pores surface and the ice crystal (9). The superfluidity occurs at most six-layer molecular thickness sandwiched between two graphene sheets (10).

Excessive properties also include the longer O–O distance, stiffer H–O phonons and softer O:H phonon, deeper O 1s core level, and longer photoelectron and H–O phonon lifetimes (11-16). The dynamics of water molecules in the confined geometries and near different types of surfaces are substantially slower than in the bulk (about one order of magnitude) (8, 17). These features become more pronounced as the molecular coordination number decreases.

Salt solvation differs the local physical–chemical properties of solutions in the hydration shells from those of the ordinary bulk water. Intensive pump–probe spectroscopic investigations have been conducted to pursue the mechanism behind molecular performance in the spatial and temporal domains. For instance,

the sum frequency generation (SFG) spectroscopy resolves information on the molecular dipole orientation or the skin dielectrics, at the air–solution interface (18), while the ultrafast two–dimensional infrared absorption (2DIR) probes the solute or water molecular diffusion dynamics in terms of phonon lifetime and the viscosity of the solutions (19).

Salt solutions demonstrate the Hofmeister effect (20) on regulating the solution surface stress and the solubility of proteins with debating mechanisms of structural maker and breaker (21), ionic specification (22), quantum dispersion (23), skin induction (24), quantum fluctuation (25), and solute–solvent interactions (26). Increasing the chloride, bromide and iodide solute concentration stiffens the H–O stretching vibration mode to higher frequencies. The H–O phonon blueshifts are usually referred to that the Cl^- , Br^- , and I^- ions weaken their surrounding O:H nonbond, known as water structure breaking (27, 28).

An external electric field in the 10^9 V/m order slows down water molecular motion and even crystallizes the solution matrix. The field generated by a Na^+ ion acts rather locally to reorient and even hydrolyze its neighboring water molecules according to molecular dynamics (MD) computations (29). A cation can form a stiffer cylindrical volume between the cation and the graphite-oxide (negatively charged) defects of the adjacent layers in a “(-) ~ (+) ~ (-)” fashion perpendicular to the graphene sheets. This stiffer hydration volume expands the graphene-oxide interlayer spacing up to 1.5 nm and the modulated layer separation varies with the type of cations (30, 31). Strikingly, charge injection in terms of ions separation by salt solvation shares the same effect of molecular undercoordination on the hydrogen bond (O:H–O or HB) segmental length and stiffness and the H-O phonon lifetime (32-34).

Salt hydration and water molecular undercoordination have been intensively investigated using the following multiscale approaches:

- 1) Classical continuum thermodynamics (35-37) embraced the dielectrics, diffusivity, surface stress, viscosity, latent heat, entropy, nucleation, and liquid/vapor phase transition in terms of free energy, though this approach has faced difficulties in dealing with solvation dynamics and the properties of water and ice.

- 2) MD computations and the ultrafast phonon spectroscopies (38-40) are focused on the spatial and temporal performance of water and solute molecules as well as the proton and lone pair transportation behavior. Information includes the phonon relaxation or the molecular residing time at sites surrounding the solute or under different coordination conditions or perturbations.
- 3) Nuclear quantum interactions (41, 42) simulation has enabled visualize the concerted quantum tunneling of protons within the water clusters and quantify the impact of zero-point motion on the strength of a single hydrogen bond at a water/solid interface. An interlay of STM/S and the *ab initio* path-integral molecular dynamics (PIMD) verify unambiguously that the sp^3 -orbital hybridization takes place at 5 K temperature. The proton quantum interaction elongates the longer part and shortens the shorter part of the O:H-O bond.
- 4) O:H-O bond cooperativity (1, 43-45) enables resolution to multiple mysteries of water and ice. A combination of the Lagrangian mechanics, MD and density functional theory (DFT) computations with the static phonon spectrometrics has enabled quantification of O:H-O transition from the mode of ordinary water to the conditioned states. Obtained information includes the fraction, stiffness, and fluctuation order transition upon perturbation and their consequence on the solution viscosity, surface stress, phase boundary dispersity, and the critical pressure and temperature for phase transition.

However, knowledge insufficiency about the O:H-O bond cooperativity and polarizability (46) has hindered largely the progress in understanding the effect of molecular undercoordination and salt solvation in terms of bonding dynamics, solute capabilities, and inter- and intramolecular interactions. It has been hardly possible to resolve the network O:H-O bond segmental cooperative relaxation induced by salt solvation and molecular undercoordination. It is yet to be known how the cation and anion mediate the O:H-O network and properties of salt solutions such as the surface stress, solution viscosity, solution temperature, and critical pressures and temperatures for phase transition (27, 47). It is also unclear how the undercoordinated water molecules define the supercooling and superheating processes and the unusual performance of nanodroplets, nanobubbles, and the skins of water ice. Fine-resolution detection and consistently deep insight into the intra- and intermolecular interactions and their consequence on the solution and undercoordination derived properties of water have been an area of increasingly active study.

According to Pauling (48), the nature of the chemical bond bridges the structure and property of a crystal and molecule. Therefore, bond formation and relaxation and the associated energetics, localization, entrapment, and polarization of electrons mediate the macroscopic performance of substance accordingly (32). O:H–O bond segmental disparity and O–O repulsivity form the soul dictating the extraordinary adaptivity, cooperativity, recoverability, and sensitivity of water and ice (43). One must focus on the chemical bond relaxation (48) and the valence electron polarization (32, 43) in the skin region or in the hydration volume with the afore-mentioned multiscale approaches for improved knowledge .

This perspective shows the electronic and phononic spectrometric evidence for the bond–electron–phonon correlation of the undercoordinated and the hydrated O:H–O bond network and the supersolid state. Ions in salt solutions form each a center of electric field that clusters, stretches and polarizes its neighboring H₂O molecules that in turn screen the electric field of the ions to form the hydration shell of limited sizes (33). Molecular undercoordination shortens the H–O bond spontaneously and lengthens the O:H nonbond associated with the polarization (33). Molecular undercoordination and salt solvation share the same effect of O:H–O relaxation and polarization on the bonding network and properties such as the prolonged H–O phonon lifetime and the mediated critical conditions of phase transition.

2. O:H–O Bond Oscillator Pair

2.1. Basic Rules for Water

Water prefers the statistic mean of the tetrahedrally-coordinated, two-phase structure in a core-shell fashion of the same geometry but different O:H–O bond lengths (1, 43). Figure 1a illustrates the 2H₂O unit cell having four oriented O:H–O bonds bridging oxygen anions. 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).

The asymmetrical and short-range interactions of the segmented O:H–O are coupled with the ever-overlooked Coulomb repulsion between electron pairs on adjacent oxygen ions, which dictates the extraordinary adaptivity, cooperativity, recoverability sensitivity of water ice when subjecting to

perturbation (1). O:H–O bond angle and length determines the crystal geometry and mass density of water ice. The segmental stretching vibration frequencies ω_x determine the respective Debye temperatures Θ_{Dx} of their specific heats through the Einstein relation, $\Theta_{Dx} \propto \omega_x$, (subscript X = L and H denotes, respectively, the O:H and the H-O interactions). The segmental binding energy E_x correlated to the thermal integration of the specific heat $\eta_x(T/\Theta_{Dx})$ in Debye approximation. O:H–O bond length and its containing angle relaxation changes the system energy, but fluctuation contributes little to the system energy on average.

It is essential to treat water as a crystalline-like structure with well-defined lattice geometry, strong correlation, and high fluctuation. For a specimen containing N 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 (49) unless excessive H^+ or “:” is introduced. The H^+ or the “:” cannot stay alone of moving freely but attach to a H_2O .

Excessive H^+ injection by acid solvation will bond to a H_2O to form the H_3O^+ hydronium and the $H \leftrightarrow H$ anti-HB (50). Base or H_2O_2 solvation introduces excessive number of “:” in the form of HO^- hydroxide that form the $O:\leftrightarrow O$ super-HB with one of its neighboring H_2O (51). The H_3O^+ or the HO^- replaces the central H_2O in Figure 1a but the neighboring H_2O remain their orientations because of the lattice geometry and interactions with other neighboring H_2O molecules. The H_3O^+ or the HO^- may undergoes Brownian motion or drift diffusion under a graded electric or thermal field.

The motion of a H_2O molecule or the proton H^+ transportation is subject to restriction. If the central molecule rotating above 60° around the C_{3v} symmetrical axis of the $2H_2O$ unit cell, $H \leftrightarrow H$ and $O:\leftrightarrow O$ repulsion will come into play, which is energetically forbidden. Because of the H–O bond energy of ~ 4.0 eV, translational tunneling of the H^+ between adjacent H_2O molecules is also forbidden. In fact, only can 121.6 nm wavelength laser radiation breaks the H–O or the D–O bond in the vapor phase (52, 53). The 121.6 nm wavelength corresponds to 5.1 eV energy that is greater than the 4.0 eV estimated by resolving the T_C - P profiles of ice Regelation (54, 55). The least molecular coordination number of the gaseous monomer shortens and stiffens the H–O bond most.

2.2. O:H–O Bond Potentials and Cooperativity

Figure 1b illustrates the asymmetrical, short-range, coupled three-body potentials for the segmented O:H-O bond (44, 45). The proton serves as the coordination origin. The left-hand side is the O:H van der Waals (vdW) interaction and the right-hand side is the H-O polar-covalent bond. The Coulomb repulsion between electron pairs on neighboring O^{2-} couple the O:H-O bond to be an oscillator pair.

Figure 1. (a) The $2H_2O$ primary unit cell containing four oriented O:H-O bonds defines liquid water as a crystal with molecular and proton motion restrictions. (b) The asymmetrical, short-range, coupled three-body potentials for the segmented O:H-O bond. (c) Cooperative relaxation of the segmental O:H-O bond proceeded by elongating one part and contracting the other with respect to the H^+ coordination origin. (d) Superposition of the segmental specific heats η_x defines the phases from high temperature downward of

the Vapor ($\eta_L = 0$, not shown), Liquid and Ice I_{h+c} ($\eta_L/\eta_H < 1$), Quasisolid (QS) ($\eta_L/\eta_H > 1$), XI ($\eta_L \cong \eta_H \cong 0$), and the QS boundaries ($\eta_L/\eta_H = 1$) closing to T_m and T_N , respectively (2). Electrification (ionic polarization)(33) or molecular undercoordination (34) disperses the QS boundaries outwardly (reprinted with permission from (2, 34, 56)).

The O:H nonbond and the H–O bond segmental disparity and the O–O coupling dislocate the O^{2-} of the segmented O:H–O bond in the same direction but by different amounts under an external stimulus, see Figure 1c. The softer O:H nonbond always relaxes more than the stiffer H–O bond with respect to the H^+ as the coordination origin. The $\angle O:H-O$ angle θ relaxation contributes mainly to the geometry and mass density. The O:H–O bond bending has its specific vibration mode that does not interfere with the H–O and the O:H stretching vibrations (1). The O:H–O bond cooperativity determines the properties of water and ice under external stimulus such as molecular undercoordination (5, 6, 57-59), mechanical compression (27, 47, 54, 60), thermal excitation (2, 61), solvation (62) and determines the molecular behavior such as solute and water molecular thermal fluctuation, solute drift motion dynamics, or phonon relaxation.

2.3. Specific Heat and Phase Transition

Figure 1d shows the superposition of the specific heat $\eta_x(T/\Theta_{Dx})$ of Debye approximation for the O:H and the H–O segments (2). The segmental specific heat meets two conditions. One is the Einstein relation, $\Theta_{Dx} \propto \omega_x$, which directly correlates the shape of the specific heat curve to the measured phonon frequency ω_x . The specific heat curves vary with external perturbation through the Einstein relation. The other is the thermal integration that is proportional to the bond energy E_x . The (ω_x, E_x) are $(200 \text{ cm}^{-1}, \sim 0.1 \text{ eV})$ for the O:H nonbond and they are $(3200 \text{ cm}^{-1}, \sim 4.0 \text{ eV})$ for the H–O bond. The superposition of the segmental specific heats η_x defines the phases from high temperature downward of Vapor (not shown), Liquid, Quasisolid (QS), I_{h+c} ice, XI, and the QS boundaries of extreme densities that are closing to the T_m and the T_N (2, 4).

The thermodynamics of water ice is subject to its segmental specific heat difference in terms of the η_L/η_H ratio. The segment having a lower specific heat follows the regular rule of thermal expansion, but the other

segment responds to thermal excitation contrastingly. The thermodynamics and density oscillation of the bulk water ice under the ambient pressure proceed in the following phases (2, 4):

- 1) In the Vapor phase (≥ 373 K), $\eta_L \cong 0$, the O:H interaction is negligibly weak though the H₂O motifs still hold.
- 2) In the Liquid phase (277, 373K), $\eta_L/\eta_H < 1$, O:H cooling contraction and H–O elongation take place, but the O:H contracts more than H–O contracts, cooling contraction of water take place, reaching to the value of $d_{OO} = d_H + d_L = 1.0004 + 2.6946$ Å.
- 3) In the QS phase (258, 277 K), $\eta_L/\eta_H > 1$, H–O cooling contracts less that the O:H expands; O:H–O expands, which triggers ice floating.
- 4) At the QS boundaries (258, 277 K), $\eta_L/\eta_H = 1$, the density drops from its maximum 1.0 to its minimum of 0.92 gcm^{-3} . No apparent singularity presents to the specific heat or to the density profile, so the 277 K is recommended be the temperature for phase transition from Liquid to the QS phase. The 258 K corresponds to the T_N for the homogeneous ice nucleation.
- 5) The I_{c+h} ice (258, 100 K), $\eta_L/\eta_H < 1$, repeats the thermodynamics of the Liquid phase at a lower transition rate, transiting the density from 0.92 to 0.94 gcm^{-3} .
- 6) In the XI phase, $\eta_L \cong \eta_H \cong 0$, neither O:H nor H–O responds sensitively to thermal excitation, so the density remains almost constant except for the slight $\angle\text{O:H–O}$ angle expansion at cooling.

One should note that any relaxation of the O:H–O bond length and energy under perturbation will offset the phase boundaries through the Einstein relation: $\Theta_{DX} \propto \omega_X$; and therefore, the O:H–O bond oscillation and relaxation dictate the thermodynamics of water ice and aqueous solutions.

3. Supersolidity and Quasisolidity

3.1. Significance of Supersolidity and Quasisolidity

The concept of supersolidity was initially extended from the ⁴He fragment at mK temperatures, demonstrating elastic, repulsive and frictionless between the contact motion of ⁴He segments (63) because of the atomic undercoordination induced local densification of charge and energy and the associated electron polarization at the fragment surfaces (64). The supersolidity features the behavior of water and ice under polarization by coordination number reduction or under electrostatic fields. When the molecular

CN is less than four the H–O bond contracts spontaneously associated with O:H elongation and strong polarization. At the surface, the H–O bond contracts from 1.00 to 0.95 Å and the O:H expands from 1.70 to 1.95 Å associated with the O:H vibration frequency transiting from 200 to 75 cm⁻¹ and the H–O from 3200 to 3450 cm⁻¹ (65). The shortened H–O bond raises its vibration frequency to a higher value that increases again with further reduction of the molecular CN.

The quasisolidity describes phase transition from Liquid density maximum of 1.0 gcm⁻³ at 4 °C to Solid density minimum of 0.92 gcm⁻³ at -15 °C. The unusual property of the QS phase is its $\eta_L/\eta_H < 1$ defined cooling expansion and the QS boundaries tunability. Cooling the QS phase shortens the H–O bond and lengthens the O:H and enlarges the $\angle\text{O:H-O}$ angle from 160 to 165° for bulks specimen (2).

The O:H–O bond relaxation under perturbation shifts its segmental phonon in opposite directions, which offsets the phase boundaries accordingly, including the T_C for the I_c –XI transition dropping from 100 K to 60 K with the droplet size (66, 67). The outward dispersion of the QS phase boundaries by molecular undercoordination or electrostatic polarization depresses the T_N for homogenous ice nucleation and raises the T_m for melting, which accounts for the room-temperature thin ice formation (7) and mechanical and thermal stability of nanobubbles (68). The supercooling of water nanodroplets to the “no man’s land” could arise from the QS boundary dispersion due to the high fraction of undercoordinated molecules (1). However, compression has contrasting effect on the QS boundary dispersion, raising the T_N and lowering the T_m , resulting in the ice Regelation – compression depresses the T_m that reverse when and the pressure is relieved (55).

Because of the strong polarization and O:H–O relaxation, the skin of water and ice is offered with a supersolid skin that is elastoviscous, less dense (0.75 unit), and mechanically and thermally more stable. The high elasticity of the softer O:H phonons, $\Delta\omega_L < 0$, ensures the high adaptivity and the densely-packed surface dipoles secures the contacting interface repulsivity, resulting in the slipperiness of ice (69), nanobubble endurability (68), and the toughest water skin (70). It is the supersolid skin lower density that raise the skin thermal diffusivity for the heat transport in the Mpemba effect (71).

Salt solvation derives cations and anions dispersed in the solution (33). Each of the ions serves as a source center of electric field that aligns, clusters, stretches and polarizes the neighboring O:H–O bonds, resulting

the same supersolidity within the hydration shell whose size is subject to the screening of the hydrating H₂O dipoles and the ionic charge quantity and volume size.

3.2. Supersolidity of the “pathological Polywater”

Polywater is a hypothesized polymerized form of water that was firstly noted by two Soviet physicists, which had aroused interest of the western world in 1960s' and sparked fears of a "polywater gap" in the US in 1969. The Pentagon put bankrolling efforts to push the polywater technology ahead (72). It was thought as the cause for increasing resistance on trans-Atlantic phone cables, while others predicted that if polywater were to contact ordinary water, it would convert that water into polywater, causing a disaster or a war. By the 1970s, polywater was well known in the general population.

However, some experimentalists were able to reproduce the matter, while others failed. Several theories were advanced to explain the phenomenon. Several people questioned the authenticity of the polywater. The main concern was contamination of the water. Denis Rousseau and Sergio Porto of Bell Labs (73) carried out infrared spectrum analysis which showed polywater was made mostly of chlorine and sodium, which has also the identical phonon spectroscopic feature of sweat. Rousseau (74) then suggested that polywater was nothing more than water with small amounts of biological impurities. Examination of polywater via electron microscopy showed that it also contained small particles of various solids from silica to phospholipids, explaining its greater viscosity. When the experiments that had produced polywater were repeated with thoroughly cleaned glassware, the anomalous properties of the resulting water vanished, and even the scientists who had originally advanced the case for polywater agreed that it did not exist. In August, 1973, the Soviet physicists who initiated Polywater published a letter in *Nature* in which they wrote (75), "*these anomalous properties should be attributed to impurities rather than to the existence of polymeric water molecules.*"

Nevertheless, the story is over but the mechanism for the ionic effect remains open for discussion. The unanswered question remains why do organic and inorganic impurities even the sweat make the solution - polywater denser, more viscous, and thermally more stable than regular water? The phenomenon is within the description of the present notion of supersolidity. The molecular undercoordination between the hydrophobic impurities and liquid water interface and the ionic polarization of the solute impurities enhance each other on H-O bond contraction and O:H nonbond elongation. Polarization of the molecular

undercoordination and charged impurities disperses outwardly the QS phase – higher T_m and lower T_N associated with high viscosity. The higher density arises from the masses of impurities.

3.3. Supercooling of Supersolid Phase

Figure 2 shows the T_N depression by droplet size reduction and by salt solvation. As illustrated in Figure 1d, the QS boundaries offset outwardly by the phonon frequency shift $\Delta\omega_H > 0$ and $\Delta\omega_L < 0$ that disperses the Debye temperatures Θ_{Dx} , resulting in the supercooling at freezing and superheating at melting, as one observes as the “no man’s land”. XRD, Raman, and MD observations show that 1.2 nm sized droplet freezes at 173 K (5), and the $(H_2O)_{3-18}$ clusters do not form ice even at 120 K (6).

Figure 2. Ice nucleation temperature T_N depression (a) by H_2O droplet size-reduction from 258 K for the bulk to 200 K for 1.4 nm droplet (2-6) and (b) by concentrated NaCl and $CaCl_2$ solvation (76) with inset showing the salt anti-icing. (Reprinted with permission from (2, 76, 77)).

4. Electron and Phonon Spectrometrics

4.1. STM and STS: Strong Polarization

Figure 3 shows the orbital images and the dI/dV spectra of a H_2O monomer and a $(H_2O)_4$ tetramer deposited on a NaCl(001) surface probed using scanning tunneling microscopy/spectroscopy (STM/S) at 5 K temperature (78). The highest occupied molecular orbital (HOMO) below the E_F of the monomer appears as a double-lobe structure with a nodal plane in between, while the lowest unoccupied molecular

orbital (LUMO) above E_F appears as an ovate lobe developing between two HOMO lobes. STS spectra at different depths discriminate the tetramer from the monomer in the density of states (DOS) crossing E_F .

Figure 3. STM images of (a) a H_2O monomer and (b) a $(\text{H}_2\text{O})_4$ tetramer, and (c, d) the respective dI/dV spectra obtained under conditions of $V = 100$ mV, $I = 100$ pA, and dI/dV collected at 50 pA of different heights at 5 K temperature. Grid in images denotes the Cl^- lattice of the $\text{NaCl}(001)$ substrate. The LUMO ($> E_F$) and HOMO ($< E_F$) indicated in (c) denote the orbital energy states (Reprinted with permission from (78).)

These STM/S observations (78) confirmed the occurrence of sp^3 -orbit hybridization of oxygen in H_2O monomer occurs at 5 K or lower and the intermolecular interaction involved in $(\text{H}_2\text{O})_4$. Therefore, the 2N number conservation of protons and “:” holds regardless of temperature. Even at extreme conditions of 2000 K temperature and 2 TPa pressure, when the $2\text{H}_2\text{O}$ transits into $\text{H}_3\text{O}^+:\text{HO}^-$ the superionic state (79), the 2N number conservation of protons and lone pairs remains. According to the bond–band–barrier correlation (32, 80), the HOMO located below E_F corresponds to the energy states occupied by electron

lone pairs of oxygen, and the LUMO to states yet to be occupied by electrons of antibonding dipoles. The image of the monomer showing the directional lone pairs that point into the open end of the surface. As the H^+ protons share its unpaired electron with oxygen, the Cl^- ion in the NaCl substrate interacts with the H^+ only electrostatically.

4.2. SGF: Site Resolved H–O Bond Length and Stiffness

The SFG probes the molecular orientation and dielectrics at the interface as a function of vibration frequency (18). SFG measurements, shown in Figure 4a (81), confirmed that in the outermost subsurface, the first (B1) and the second (B2) bilayer, the O:H nonbond of the $O_{B1}-H:O_{B2}$ is weaker than that of the $O_{B1}:H-O_{B2}$. The subsurface O–O distance is laterally altered, depending on the direction of H–O bond along the surface normal: H–up or H–down, which is in contrast with bulk O:H nonbonds. This discovery is consistent with the DFT derivatives (82) and the present O:H–O bond cooperativity notion expectation (44, 45). The least coordinated $H-O_{B1}$ in the first sublayer is shorter and stiffer than the second sublayered $H-O_{B2}$ and hence the $O_{B2}:H$ is longer and softer than the $O_{B1}:H$.

Figure 4. SFG spectrum for the H–O oscillators lined along the c -axis of ice $I_h(0001)$. Insets illustrate the $O_{B1}:H-O_{B2}$ and the $O_{B1}-H:O_{B2}$ segmental bond lengths, orientations, and the H–O stretching vibration frequencies. The positive peak ($< 3270 \text{ cm}^{-1}$) corresponds to the $H-O_{B2}$ (shaded in green) and the valley ($> 3270 \text{ cm}^{-1}$) to the $O_{B1}-H$ (shaded in blue). The less coordinated $O_{B1}-H$ is shorter and stiffer and its $H:O_{B2}$ is longer and softer than the inverse (reprinted with permission from (81)). (b) the DPS of water and ice collected at 87 and 0° polar angles (inset b) (83) decomposed the ω_H into the bulk (3200 cm^{-1}) and

skin (3450 cm^{-1}) components (inset a) with an additional feature for the H–O free radical at 3600 cm^{-1} (reprinted with permission from (65)).

The differential phonon spectrometrics (DPS) is the difference between the characteristic D–O or H–O spectrum of bulk water from those of the nanodroplets and salt solution upon all the spectral peak area being normalized. These DPS peaks show the transition of the D–O bond from the mode of ordinary water as valleys to the droplets and the hydrated modes as peaks, in terms of phonon abundance (peak area), stiffness ($\Delta\omega_D$), and fluctuation order (line width). The phonon peak frequency follows the $\omega^2 \propto E(\mu d^2)^{-1}$ relation with μ being reduced mass and E_H the binding energy and d the length of the H–O or D–O vibrating dimer. The DPS profiles in Figure 4b were obtained by subtracting the spectra collect at angle closing to the surface normal from the ones collected in gracing angles and all of them being spectra area normalized (83). The DPS shows that the $-(15-20)\text{ }^\circ\text{C}$ ice and the $25\text{ }^\circ\text{C}$ water share the same skin supersolidity – characterized by the identically shortened and stiffened H–O bond (65).

DFT calculations by Wang and collaborators (37, 84) examined the site–resolved electronic binding energy and H–O stretching vibration frequency for medium sized $(\text{H}_2\text{O})_n$ clusters ($n = 17-25$). They classify the H–O bonds into five groups: the dangling H–O bonds, the H–O bonds associated with the dangling H_2O molecules, those with undercoordinated H_2O molecules without dangling H–O bonds, those forming the tetrahedral–coordination of the central H_2O and the others in its neighbor four molecules. The neighboring four molecules and the outer undercoordinated molecules form cages covering the central H_2O . Computations resolved that these two regions interact competitively, showing complementary interaction energy with the change of cluster size. Calculated phonon spectra in Figure 5 reveal the site–resolved vibration frequencies. The dangling bond frequency features keep constant while others vary with cluster size. Observations confirm the effect of coordination environments on the H–O bond contraction, H–O bond energy gain, and its vibration frequency blue shift (1).

Figure 5. Computational H–O stretching vibration modes in the $(\text{H}_2\text{O})_n$ clusters. The black dashed lines convolute the H–O vibration modes of the entire clusters. The sharp feature D corresponds to the H–O dangling bonds, C to the H–O bonds associated to the undercoordinated molecules. Features A and B to the H–O bonds inside the clusters. Reprinted with copyright permission from (84).

4.3. Ultrafast IR: Phonon Energy Dissipation

The pump–probe time–dependent IR spectroscopy probes the decay time of a known intramolecular (H–O or D–O) vibrational phonon lifetime τ . The lifetime features the rate of population decay or vibration energy dissipation depending on the solution viscosity and Stokes–Einstein molecular drift diffusivity $D(\eta, R, T)$ (35) and the solute concentration C resolved Jones–Dole viscosity $\eta(C)$ (87),

$$\begin{cases} \frac{D(\eta, R, T)}{D_0} = \frac{k_B T}{6\pi\eta R} & (\text{Drift}) \\ \frac{\Delta\eta(C)}{\eta(0)} = A\sqrt{C} + BC & (\text{Viscosity}) \end{cases}.$$

Where D_0 , R , T are the diffusivity at $\eta(0)$, drifting particle size, and temperature, respectively.

The ultrafast phonon photoelectron spectroscopies is very much the same in principle to optical fluorescent (88, 89). The signal lifetime is proportional in a way to the density and distribution of the defects and impurities. The impurity or defect states prevent the thermalization of the

electron/phonon/photon transiting from the excited states to the ground for exciton (or electron–hole pair) recombination. One switches off/on the pump/probe simultaneously and monitors the population decay that features the rate of vibration energy dissipation during the wave propagation in the solution.

Using the ultrafast IR spectroscopy, Park and co-workers (85) confirmed that confinement by an interface to form a nanoscopic water pool is a primary factor governing the dynamics of nanoscopic water rather than the presence of charged groups at the interface. The H–O phonon lifetime increases from 2.6 to 3.9 and 6.7 ps as the water transits into NaBr solution with concentration increasing from 32 to 8 H₂O per NaBr and increases from 18 to 50 ps when the water droplet size is reduced from 4.0 to 1.7 nm (85).

4.4. DPS: Fraction of O:H-O Bond Transition

The phonon abundance transition from the valley to the peak in both cases show that the D–O bond turns to be shorter and stiffer in the hydration shell and in the droplet skin. From the $f(1/D)$ in Figure 6d and the fact of the droplet sized resolved T_N , one can infer that a droplet holds the two phase structure in terms of coordination–resolved core–shell configuration rather than the domain resolved high/low density random patches. Figure 6a and b show the infrared spectra of water nanodroplets and NaBr solvation in a 5%D₂O + 95%H₂O solvent (85). Replacing some H with D is for better resolution in detection.

An integration of the DPS peak gives rise to the fraction of bonds transiting from the mode of water to the ionic hydration and in the skin of the droplets, as shown in Figure 6c and d. The solute concentration C and the droplet size D resolved fraction coefficients and their slopes follow the relations:

$$f_{\text{NaBr}}(C) \propto 0.196 \times [1 - \exp(-C/0.117)]; \quad df_{\text{NaBr}}(C)/dC = 1.675 \times \exp(-C/0.117)$$

$$f_{\text{droplet}}(D) = 0.54D^{-1}; \quad df_{\text{droplet}}(D)/d(1/D) = 0.54 \text{ nm}$$

The exponential drop of the slope $df_{\text{NaBr}}(C)/dC$ towards saturation indicates the hydration shell volume or the solute electric field decreases with solute concentration, due to anion–anion repulsion (33). The small cations have been fully-screened by the hydrating H₂O dipoles and thus cations do not interact with any other solutes. The $df_{\text{droplet}}(D)/dD$ clarifies the presence of the supersolid covering sheet of a constant thickness ΔR . One can estimate the shell thickness ΔR of a spherical droplet of $V \propto R^3$: $f(R) \propto \Delta V/V =$

$\Delta N/N = 3\Delta R/R$, and the skin thickness $\Delta R_{\text{skin}} = f(R)R/3 = 0.90 \text{ \AA}$ is exactly the dangling H–O bond length (1) featured at 3610 cm^{-1} wavenumber of vibration (34). The dangling H–O bond is 10% shorter than it is in the bulk. The next shortest H–O bond in the skin is about $0.95 \text{ \AA}$ featured at 3550 cm^{-1} (84). The DPS distills only the first hydration shell and the outermost layer of a surface (86) without discriminating the intermediate region between the bulk and the outermost layer.

Figure 6. (a, b) D–O phonon DPS and (c, d) the fraction coefficient for (a, c) the concentrated NaBr solutions and (b, d) the sized water droplets. Insets a and b show the peak-area normalized D–O peaks sourced from (85). Inset a illustrates the O:H–O elongation by polarization due to salt solvation and molecular undercoordination (33, 34). Inset c illustrates the hydration volume and d water droplet of D across.

4.5. Ultrafast PES: Nonbonding Electron Polarization

Molecular undercoordination induced skin polarization have been detected using an ultrafast pump–probe liquid–jet ultra-violet photoelectron spectroscopy (UPS) (89). A free electron injected into water (90) will be trapped by locally oriented solvent molecules and transiently confined within a roughly spherical cavity defined by H–O bonds oriented toward the hydrated electron (91). The hydrated electron serves as a probe to the local environment without changing the solvent geometry. Using the ultrafast pump–probe photoelectron spectroscopy, Verlet et al (13) discovered that an excess electron can bound to the surface of a water cluster and to the ambient water/air interface. The internally solvated electron bound energy for $(D_2O)_{50}^-$ is centered at -1.75 eV and surface localized states are centered at -0.90 eV. These two states vary with the cluster size and from $(D_2O)_{50}^-$ to $(H_2O)_{50}^-$ slightly. The vertical bound energies (being equivalent to work function) of the hydrated electrons is 1.6 eV in the skin and 3.2 eV in the bulk interior of pure water. The bound energy decreases with the number n of the $(H_2O)_n$ clusters toward zero (92, 93).

The hydrated electrons live longer than 100 ps near the surface compared with those solvated inside the bulk interior. The unexpectedly long lifetime of solvated electrons bound at the water surface is attributed to a free-energy barrier that separates surface and interior states (89). Observations evidence that molecular undercoordination substantially enhances nonbonding electron polarization (34), which increases the viscoelasticity and hence lowers the skin molecular mobility. The anchored skin dipoles allow nanodroplet interacting with other substance through electrostatic, van der Waals, and hydrophobic interactions without exchanging electrons or bond formation, named non-additivity (94).

The nonbonding electrons are subject to dual polarization when the molecular CN is reduced (1). Firstly, H–O bond contraction deepens the H–O potential well and entraps and densifies electrons in the H–O bond and those in the core orbitals of oxygen. This locally and densely entrapped electrons polarize the lone pair of oxygen from the net charge of -0.616 e to -0.652 eV according to DFT calculations for ice skin (65). The increased charge of O^{2-} further enhances the O–O repulsion as the second round of polarization. This dual polarization raises the valence band energy up.

Further reduction of cluster size, or the molecular CN, enhances this dual polarization, resulting observations in Figure 7a – cluster trend of the solvate electron polarization. Therefore, electronic dipoles formed on the flat and the curved skins enhances the polarization, which creates the repulsive force, making liquid water hydrophobic and ice slippery. Nonbonding electron polarization notion indicates that

molecular undercoordination polarizes nonbonding electrons in two rounds by the densely entrapped H–O bonding electrons and by the repulsion between electron pairs on adjacent oxygen anions (1).

Figure 7. (a) $(\text{H}_2\text{O})_n^-$ ($n = 2-11$) cluster size and molecular site resolved bound energy of hydrated electron (92, 93) with inset showing the size-resolved H–O phonon frequency (95, 96); (b) The lifetime of hydrated electrons (13)). The relaxation time scales are given after electronic excitation of the surface isomers at 0.75 eV (open symbols) and internal isomers at 1.0 eV (solid symbols) of $(\text{H}_2\text{O})_n^-$ (circles) and $(\text{D}_2\text{O})_n^-$ (squares) (Reprinted with permission from (89).)

The hydrated electron can reside at the water/air interface, but remain below the dividing surface, within the first nanometer, shown in Figure 7a (93, 97). Comparatively, the neutral $(\text{H}_2\text{O})_N$ size-resolved H–O vibration frequency (inset a (19)) and photoelectron lifetime (Figure 7b) shifts linearly with the inverse of cluster size (95, 96, 98). The longer lifetime of the surface phonons and electrons than the internal states indicates the slower electron/phonon energy dissipation in the supersolidity phase. These cluster size and molecular site resolved electron bound energy, phonon stiffness, and electron phonon lifetimes confirm consistently the molecular undercoordination induced supersolidity.

4.6. XPS, XAS, and DPS: Supersolid Thermal Stability

Molecular undercoordination imparts to H–O bond contraction and the local charge densification, binding energy entrapment, and nonbonding electron polarization (89). X-ray photoelectron spectroscopy (XPS) shown in Figure 8a confirmed that the O1s level shifts more deeply from 536.6 eV to 538.1 eV and to

539.7 eV when one moves from the bulk interior to its skin and then to a monomer in gaseous phase (99-101). The O1s binding energy shift is a direct measure of the H–O bond energy E_H , $\Delta E_{1s} \propto E_H$, and the contribution from the O:H nonbond energy of ~ 0.1 eV is negligibly small, according to the tight-binding approximation (86).

Figure 8 b and c compares the near-edge X-ray fine structure adsorption spectroscopy (NEXFAS) profiles of nanobubbles (102), vapor, liquid skin, and bulk water (103). The spectra show three majors at 535.0 to 536.8 and 540.9 eV corresponding, respectively, to the molecular coordination resolved bulk interior, skin, and H–O dangling bond radicals.

Figure 8. (a) XPS O1s spectra of water containing emissions from the liquid skin at 538.1 eV and from the gaseous phase at 539.9 eV (reprinted with permission from (101)). (Reprinted with permission from (104).) NEXFAS spectra of (b) nanobubbles (102) and (c) vapor, liquid skin, and bulk liquid (103). The spectra resolve discrete peaks that correspond to the bulk, skin, and H–O dangling bond radicals.

The NEXFAS energy conservation mechanism is different from that of the XPS (86). The NEXFAS involves the shift of both the valence band and the O1s core band but the XPS involves the O 1s band only. The NEXFAS pre-edge shift is the relative shift of the O1s core level ΔE_{1s} and its valence band shift ΔE_{vb} (occupied $4a_1$ orbital) from their energy levels of the isolated O atom: $\Delta E_{edge} = \Delta E_{vb} - \Delta E_{1s} \propto \Delta E_H > 0$ (H–O bond energy) (34). The ΔE_{vb} is always greater than the ΔE_{1s} because of the shielding of electron in the outer electronic orbitals (86).

Strikingly, the NEXFAS measurements (105) revealed that Li^+ , Na^+ , and K^+ cations shift the pre-edge component peak energy more than the Cl^- , Br^- , and I^- anions and the pre-edge component associated with the first hydration shell of Li^+ ion is thermally more stable than those beyond, see Figure 9. At 25 °C, the

cation effect on the pre-edge shift from the value of 534.67 eV in alkali chlorides is remarkable: Li^+ (0.27 eV), Na^+ (0.09 eV), and K^+ (0.00 eV). The energy shift of Li^+ ion in 5 M LiCl solution (0.30 eV) is close to that in 3 M. On the other hand, in sodium halides, the anion effect is small: Cl^- (0.09 eV), Br^- (0.04 eV), and I^- (0.02 eV). The energy trend of the pre-edge shifts is the same as the DPS $\Delta\omega_{\text{H}}$ of the solutions and the skin of water (106).

Contributions from the Li:O polarization or the O:H binding energy change are negligibly small. At polarization, the H–O bond becomes shorter and stiffer; the stiffer H–O bond is thermally more stable than those in the bulk of ordinary water, as it does in the skin of deionized water (106). The identical $\text{O}_{\text{fw}} - \text{O}_{\text{bw}}$ and $\text{O}_{\text{bw}} - \text{O}_{\text{bw}}$ thermal expansion in both the pure water and in the 5M LiCl solution indicates the invariance of the Li^+ hydration shell size, which does not interfere the O–O thermal behavior between the hydrated and non-hydrated oxygen anions.

Figure 10 shows the full-frequency Raman spectra of the deionized water heated from 5 to 95 °C revealed that heating shifts the ω_{H} upwardly and the ω_{L} downwardly because heating stiffens the H–O bond and softens the O:H nonbond due to the O:H–O cooperativity (106). Inset a shows the ω_{H} decomposition into the bulk (3200 cm^{-1}), skin (3450 cm^{-1}) and the H–O free radical (3600 cm^{-1}) components. Panel b shows that the H–O bond in the bulk and in the skin undergoes thermal contraction and phonon stiffening, but the dangling H–O bond is subject to thermal expansion and softening because the dangling H–O bond lacks the O–O coupling at the open end of water surface. However, the skin $\omega_{\text{H}}(\text{T})$ component is thermally more stable than the bulk component (106).

Figure 9. Site and temperature resolved (a) NEXFAS pre-edge component energy shift for LiCl solution. (b) The E_{edge} for the first hydration shell (O_{fw}) shifts more than those beyond (O_{bw}) yet the O_{fw} energy is thermally more stable. The energy shifts still undergo thermal entrapment but the hydration E_{edge} shifts slower than that of pure bulk water (Reprinted with permission from (105)).

Figure 10. (a) Full-frequency Raman spectra of the deionized water heated from 5 to 95 °C denoted with the ω_{H} (H–O stretching vibration) and the ω_{L} (O:H vibration) phonon frequencies in opposite detraction. The ω_{H} is decomposed into the bulk (3200 cm^{-1}) and skin (3450 cm^{-1}) components with an additional feature for the H–O free radical at 3600 cm^{-1} (inset a). (b) Both the skin $\omega_{\text{H}}(T)$ and the bulk $\omega_{\text{H}}(T)$ components undergo thermal stiffening and the dangling H–O is subject to thermal softening. (Reprinted with permission from (106)).

Table 1 lists the MD estimation and neutron diffraction resolved the first $O^{2-}:Y^+$ and $O^{2-}\leftrightarrow X^-$ hydration shell sizes of the solutes (105), which agree with the DFT derived segmental strains of the O:H–O bonds surrounding X^- solutes (50). The consistency between the DPS of the skin and the confined deionized water and the NEXFAS for salt solution and computations evidences for the thermal stability of the supersolid states of the Y^+ hydration shell and the skin of pure water (107):

- 1) The H–O bond energy undergoes thermal gain but for regular substance the bond energy is subject to thermal loss (108). The H–O energy gain results from the O:H–O cooperativity when the O:H is elongated by ionic polarization, liquid heating (28), skin molecular undercoordination (34). These

observations showed that the O:H–O bond in the supersolid phase follows the regular thermodynamics outside the QS phase temperatures: $dd_L/dT > 0$, $dd_H/dT < 0$.

- 2) The shortened H–O bonds are thermally and mechanically more stable because the stiffened bonds are less sensitive to perturbation. The shorter H–O bond is harder to be further shortened by heating or to be lengthened by compression because of the O:H–O cooperativity nature (27, 47): $(d|E_H|/dT)_{\text{super}}/(d|E_H|/dT)_{\text{regular}} < 1$ and $(d\omega_H/dT)_{\text{super}}/(d\omega_H/dT)_{\text{regular}} < 1$.
- 3) The QS upper boundary is at 4 °C for regular water and it seems at 25 °C for the supersolid states according to the curve slopes in Figure 9b.
- 4) The local electric field of small cations is stronger than that of a larger anions because of the $X^- \leftrightarrow X^-$ repulsion due to the high-order molecular structure of the supersolid hydration shells with insufficient number of dipoles screening the electric field (33).

Table 1. The O:Y⁺ and O²⁻↔X⁻ distances (Å) in the YX solutions (105, 109, 110)

	Li ⁺ :O ²⁻ (5M LiCl)	Na ⁺ :O ²⁻ (Å)	K ⁺ :O ²⁻ (Å)
Y ⁺ :O ²⁻ distance	2.00 (5°C)	—	—
MD (105)	1.99 (25°C)	2.37	2.69
	1.98 (80 °C)	—	—
Neutron diffraction (105, 109, 110)	1.90	2.34	2.65
MD (105)	Cl ⁻ ·H ⁺ –O ²⁻	Br ⁻ ·H ⁺ –O ²⁻	I ⁻ ·H ⁺ –O ²⁻
X ⁻ ↔O ²⁻ distance	3.26	3.30	3.58
DFT(acid) (50)*	Cl ⁻ ·(H–O:H)	Br ⁻ ·(H–O:H)	I ⁻ ·(H–O:H)
1 st (ε _H ; ε _L)%	–0.96; +26.1	–1.06; +30.8	–1.10; + 41.6
2 nd (ε _H ; ε _L)%	–0.73; +19.8	–0.78; +22.8	–0.83; +28.6
XAS (5 M LiCl) (105)	Li ⁺ :(first O:H–O)	Li ⁺ :(next O:H–O)	O:H–O (H ₂ O)
5°C	d _{O–O} = 2.71 (at 4 °C, d _{O–O} = d _H + d _L = 1.0004 + 1.6946 = 2.695 (56))		
80 °C	2.76 (Δd _L > –Δd _H (<0))		

$*(\epsilon_H; \epsilon_L)\%$ is the DFT derived segmental strain for the first and the second O:H–O bonds radially surrounding X^- anions in acid solutions. The strain is referred to the standard values of $d_H = 1.0004$ and $d_L = 1.6946$ Å for 4 °C water (56). $X^- \cdot H$ represents the anions and H^+ Coulomb interaction.

5. Perspectives

A combination of the STM/S, XPS, XAS, SFG, DPS, and ultrafast UPS and FTIR observations and quantum calculations reveals consistently the bond–electron–phonon correlation of the supersolidity of the confined and the hydrating water. Molecular undercoordination and charge dispersion by salt solvation share the same effect on the O:H–O bond relaxation and nonbonding electron polarization, which modulate the local hydrogen bonding network and the water properties through H–O bond contraction and O:H nonbond elongation. The O 1s energy shifts deeper, electronic vertical bound energy decreases but the electron and phonon lifetimes become longer. The supersolid phase is less dense, elastoviscous, mechanically and thermally more stable with the hydrophobic and frictionless surface. The O:H–O bond cooperative relaxation disperses outwardly the quasisolid phase boundary to raise the melting point and meanwhile lower the freezing point of water ice.

From what we have learnt in the described exercises, one can be recommended the following ways of thinking and approaching to complement the available premises:

- 1) The nonbonding electron lone pairs pertained to N, O, F and their neighboring elements in the Periodic Table form the primary element being key to our life, which should receive deserved attention. The lone pair is related to DNA folding and unfolding, regulating, and messaging. NO medication and CF_4 anticoagulation in synthetic blood are realized through lone pairs interaction with living cells. The lone pair forms the O:H and the $O:\rightleftharpoons:O$ interactions together with the $H\leftrightarrow H$ determines the molecular interactions. However, the presence and functionality of the localized and weak lone pairs interactions have long been overlooked. Without lone pairs, neither O:H–O bond nor oxidation could be possible; molecular interaction equilibrium could not be realized. Extending the knowledge about lone pairs and their functionality of polarization to catalysis, solution-protein, drug-cell, liquid-solid, colloid-matrix, interactions and even energetic explosives and other molecular crystals would be even more fascinating.

- 2) The key to the O:H–O bond is the O–O coupling. Without such a coupling none of the cooperative relaxation or the mysterious of water ice and aqueous solutions such as ice floating, ice slipperiness, regelation, supercooling/heating or the negative thermal expansion, warm water cooling faster. Unfortunately, the O–O coupling has been long overlooked in practice. It is necessary to think about water and solvent matrix as the highly ordered, strongly correlated, and fluctuating crystals, particularly, the supersolid phase caused by salt solvation and molecular undercoordination rather than the amorphous or multiphase structures. Water holds the two-phase structure in the core-shell configuration, rather than the randomly domain-resolved mixture of density patches. Liquid water and the matrix of aqueous solutions must follow the conservation rules for the $2N$ number of protons and lone pairs and for the O:H–O configuration despite its segmental length and energy relaxation unless excessive H^+ or lone pairs are introduced.
- 3) As a degree of freedom, atomic and molecular undercoordination forms the foundation of and reconciles the defect and surface science, nanoscience and engineering. The undercoordination derived bond contraction and the associated electron and energy entrapment and local polarization govern the performance of the undercoordinated systems. One can consider the solvation as a process of charge injection with multiple interactions. Charge injection in terms of hydrated electrons, protons, lone pairs, cations, anions, and even molecular dipoles mediate the HB network and properties of a solution. Salt solvation and molecular undercoordination share the same effect of polarization on the viscosity, surface stress, phonon stiffness and lifetime transition. The quasisolid (quasiliquid) of negative thermal extensivity due to O:H–O bond segmental specific disparity, the supersolidity due to molecular undercoordination and electric polarization are both important to water, ice and aqueous solutions. The quasisolid phase boundary dispersion by perturbation determines the solution O:H–O bond network and thermodynamic behavior such critical pressures and temperatures for phase transition.
- 4) Focusing on the bond-electron-phonon-property correlation and interlaying the spatially- and temporarily-resolved electron/phonon/photon spectrometrics would substantiate the advancement of related studies. Combining the spatially resolved electron/phonon DPS and the temporarily resolved ultrafast pump-probe spectroscopies not only distill the phonon abundance-stiffness-

lifetime-fluctuation due to liquid conditioning but also fingerprint the electron/phonon energy dissipation and the ways of interactions. Molecular residing time or drift motion under a certain coordination environment fingerprints the way of energy dissipation but these processes could hardly give direct information of energy exchange under perturbation. Polarization, entrapment, and absorption determine the energy dissipation. Embracing the emerged O:H–O bond segmental disparity and cooperativity and the specific heat difference would be even more revealing.

Understanding may extend to water-protein interaction, biochemistry, environmental and pharmaceutical industries. Hydrophobic interface is the same to free surface. Charge injection by salt and other solute solvation provides the local electric fields. As the important degrees of freedom, molecular undercoordination and electric polarization are ubiquitous to our daily life and living conditions. It would be very promising for one to keep mind open and be on the way to developing experimental strategies and innovating theories toward resolution to the wonderful world.

Acknowledgement

Financial support from the National Natural Science Foundation (Nos. 21875024; 11872052) and National Science Challenge Project (No. TZ2016001) of China are all gratefully acknowledged.

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