

A common supersolid skin covering both water and ice

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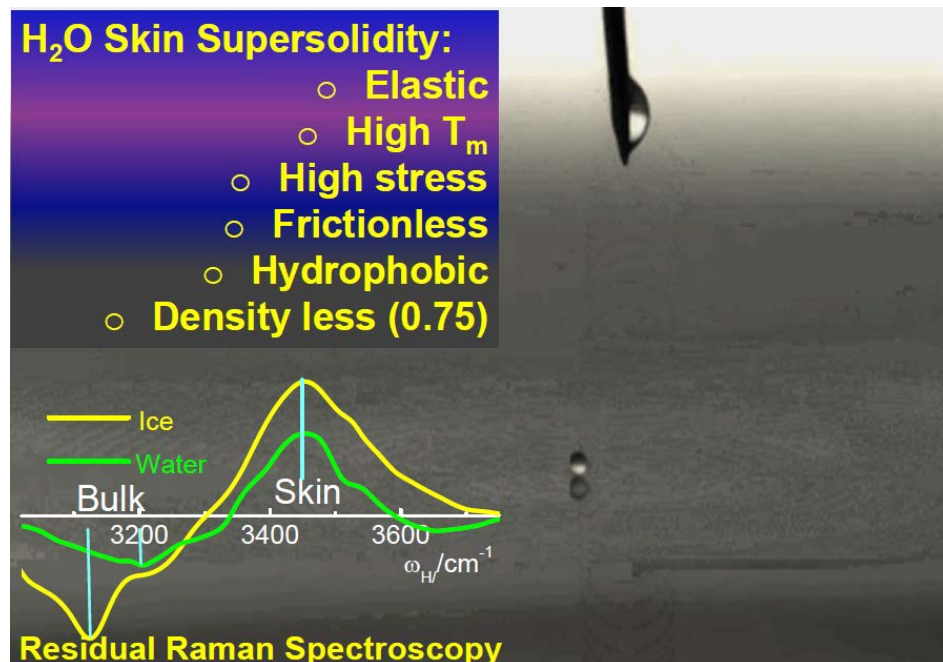
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Abstract

Ice is most slippery and the skin of liquid water is toughest of ever known. However, mechanisms behind these anomalies and their correlation remain challenging since 1859 when Faraday firstly proposed that a quasi-liquid skin presents lubricating ice. Here we show that consistency between theoretical calculations and experimental observations confirmed our predictions of water ice skin supersolidity – elastic, hydrophobic, frictionless, thermally stable, and density less. Firstly, hydrogen bond (O:H-O) forms a pair of asymmetric and H-bridged oscillators coupled by Coulomb repulsion between electrons on adjacent oxygen ions. Secondly, molecular undercoordination shortens the H-O bond (molecular size) spontaneously by ~5% and lengthens the O:H nonbond (molecular separation) by ~25% through Coulomb repulsion, which lowers the mass density of ice/water from the known bulk values of 0.92/1.0 to 0.75 g·cm⁻³. H-O bond contraction stiffens the high-frequency phonon from 3150~3200 cm⁻¹ to the same value of 3450 cm⁻¹ for both skins, raises the melting temperature from 273 to ~300 K, and entraps the O 1s binding energy from the bulk value of 536.6 eV to 538.1 eV. Two processes of nonbonding electron polarization by the densely entrapped bonding electrons due to H-O contraction and O---O repulsion enhance the elasticity, viscosity, and dipole moment of the skins, which is responsible for the high tension of water skin and the slippery of ice.

Keywords: Ice; water; slippery; surface tension; hydrogen bond; Coulomb repulsion

1. Introduction

Ice remains slippery while one is standing still on it without involvement of pressure melting or friction heating [1-3], whose lubrication enabled moving heavy stones from far distance away to the Forbidden City in ancient China [4]. The high surface tension, 72 dynes/cm at 25 °C [5], toughens water skin with fascinations [6]. For instance, small insects such as a strider can walk and glide freely on water because: (i) it weighs insufficiently to penetrate the skin and (ii) the interface between its paddle and the skin of water is hydrophobic. If carefully placed on the surface, a small needle floats on the water even though its density is times higher than that of water. If the surface is agitated to break up the tension, then the needle will sink quickly. A high-speed video clip [7] revealed that a water droplet dances repeatedly and continuously on water surface, which evidences the elasticity and hydrophobicity of the skin.

The extraordinary hydrophobicity and toughness of water skin are commonly attributed to the presence of a layer of molecules in solid state [8, 9] while the slippery of ice is perceived as the presence of a liquid or a quasi-liquid skin even at temperature below freezing [10, 11] to serves as the lubricant [12]. Additional mechanisms such as pressure-promoted melting [13] and friction-induced heating [14] have also been proposed to explain the slippery of ice.

However, pressure melting only happens to temperature at -22 °C and above while slippery remains at even lower temperatures. Furthermore, the phase diagram of ice below -22 °C shows that pressure induces only solid-solid transition rather than solid-liquid [13, 15]. On the other hand, if a liquid skin lubricant exists on ice, the vibration amplitudes of the skin molecules should be folds greater than that in the bulk but interfacial force microscopy measurements excluded this possibility [1]. The skin layer is, however, rather viscoelastic in the -10 to -30 °C range, evidencing the absence of the liquid layer at such low temperatures. Sum frequency generation spectroscopy (SFGS) measurements and molecular dynamics (MD) calculations suggested that the outermost two layers of water molecules are ordered “ice like” at room temperature [16]. The surface pre-melting is in conflicting with the ice-like nature of ultrathin films of water at the ambient [9, 17].

Does a liquid skin form on ice or a solid skin on water? Solutions to these questions are yet to be certain. In this communication, we show that molecular undercoordination and inter-oxygen repulsion shortens the H-O bond and lengthens the O:H nonbond [18] with strong polarization. The cooperative relaxation of the hydrogen bond (O:H-O) and the associated quantum entrapment and polarization result in the common supersolid phase that is responsible for the anomalies of skins for both water and ice.

2 Principle and predictions

2.1 Principle: O:H-O bond cooperative relaxation

Figure 1 illustrates the O:H-O bond and the short-range potentials [18]. The O:H-O bond is composed of the weaker-and-longer O:H nonbond (left-hand side) and the shorter-and-stronger O-H polar-covalent bond (right-hand side) coupled with the Coulomb repulsion between electron pairs (green pairing dots) on adjacent O atoms. The O:H-O bond performs like a pair of asymmetric, coupled, H-bridged oscillators with ultra-short interactions [19, 20]. The motion dynamics of this pair of coupled oscillators can be resolved using Lagrangian-Laplace transformation. With the measured segmental lengths and vibration frequencies (d_x , ω_x , $x = H$ and L represent for the H-O bond and the O:H nonbond, respectively) one is able to obtain the respective force constants and binding energies (k_x , E_x)[20].

According to the BOLS (bond order-length-strength) and NEO (nonbonding electron polarization) notations [21], the intramolecular H-O bond undergoes spontaneous contraction as the molecular coordination number (CN) is reduced. The Coulomb coupling and the external excitation (compression, thermal excitation, and molecular undercoordination, etc.) drive the segmented O:H-O bond relaxes cooperatively. O atoms always move in the same direction but by different amounts along the O:H-O bond [22]. For O:H-O bond in the undercoordinated skin region, the softer O:H (d_L in length) bond elongates more than the stiffer H-O (d_H) contracts: $|\Delta d_L| > |\Delta d_H|$, resulting in mass density reduction. The spontaneous H-O contraction will deepen the H-O potential accordingly [21].

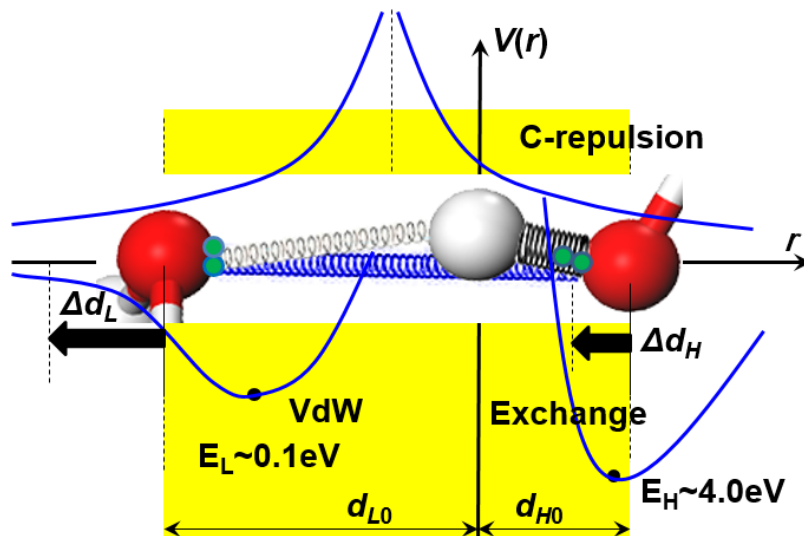


Figure 1 Asymmetric, local, short-range potentials for the segmented O:H-O bond. Interactions include the

short-range van der Waals (vdW left hand side), the exchange (right hand side) interactions, and the Coulomb (C-repulsion) repulsion between electron pairs on adjacent oxygen atoms [19]. The C-repulsion and molecular undercoordination ($CN < 4$) drive the O:H-O bond to relax cooperatively. As the molecular CN reduces, the d_L expands more than the d_H shortens, reducing the mass density. The shortened d_L stiffens the H-O phonon ω_H ($\sim 3000 \text{ cm}^{-1}$), deepens the O_{1s} binding energy, and raises the critical temperature of phase transition. The repulsion lengthens the d_L and polarizes the nonbonding electrons with enhancement of elasticity.

2.2 Predictions and evidence: Skin supersolidity

Undercoordination and inter-oxygen repulsion relax the O:H-O bond cooperatively and anomalously, which is ubiquitously important to skins, defects, hydration shells, and ultrathin films of H_2O . The bond-energy-electron relaxation determines the macroscopic performance of the skin of water and ice, which follows the relationships [21]:

$$\left. \begin{matrix} T_C \\ \Delta E_{1s} \\ \Delta \omega_x \end{matrix} \right\} \propto \left\{ \begin{matrix} E_H \\ E_H \\ \sqrt{E_x} / d_x = \sqrt{Y_x d_x} = \sqrt{(k_x + k_c) / \mu_x} \end{matrix} \right. \quad (1)$$

E_x is the cohesive energy of the respective bond ($x = L$ and H represent for the O:H and the H-O segment respectively). Theoretical reproduction of the critical temperature (T_C) for ice VII-VIII phase transition under compression confirmed that the H-O bond energy determines the T_C [22] with an estimation of $E_H = 3.97 \text{ eV}$ for ice. The shift of the O_{1s} binding energy (ΔE_{1s}) from that of an isolated oxygen atom is proportional to the E_H . The phonon frequency shift is proportional to the square root of the respective bond stiffness, which is the product of the Young's modulus ($Y_x \propto E_x d_x^{-3}$) and the bond length [22, 23]. The force constants of k_x and k_c correspond to the second derivatives of the interatomic and inter-electron-pair coupling potentials, respectively [20]. There are two processes of polarization [18]. One is the polarization of the nonbonding electron by the densely entrapped bonding electron due to H-O contraction and the other is the O---O repulsion. The polarization stiffens the O:H-O bond networks with enhanced viscosity and elasticity.

Recent DFT calculations [18] (Fig S1) estimated that as the number N of $(H_2O)_N$ cluster is reduced from 6 to 2, the d_H shortens from 0.99 to 0.97 Å and the d_L elongates from 1.65 to 1.92 Å. The H-O stretching phonon ω_H stiffens from 3100 to 3600 cm^{-1} , agreeing with measurements [24, 25]; the O:H phonon softens from 250 to 180 cm^{-1} . The calculated d_x values may vary subjecting to algorithms but the size trends retain during cluster size reduction. Undercoordination lengthens the O—O distance, resulting in volume expansion [26-29], as reported in [19, 28] the skin d_{OO} expands by 5.9 ~ 10.0 % at the ambient. Likewise, the 4.0% and 7.5%

volume expansion of water molecules confined, respectively, in the 5.1 and 2.8 nm sized hydrophobic TiO_2 pores [30] provide further evidence for the predicted low mass density at the hydrophobic water skin. The H-O bond contraction not only raises the density of binding energy and bonding electrons [31-34] but also deepens the interatomic potentials, which entraps binding energy [31, 35-37]. The H-O bond stiffening also raises the critical temperature for phase transition.

3. Experimental and numerical verification

3.1 Methods

In order to verify our predictions, we analyzed the Raman data collected by Donaldson and co-workers [2] and conducted quantum calculations using the DFT-MD and the dispersion-corrected DFT packages. Calculations were focused on resolving the O:H-O cooperative relaxation in length and stiffness in the skin and the skin charge accumulation. MD calculations were performed using the Forcite code with COMPASS force field [38]. Ice interface is relaxed in NPT ensemble at 180 K for 100 ps to obtain equilibrium. The time step is 0.5 fs. Nose-hoover thermostat with Q ratio of 0.01 is adopted to control the temperature. Dispersion-corrected DFT structural optimizations of ice surface were performed using Dmol³ code based on the PBE functional[39] in the general gradient approximation and the dispersion-corrected Tkatchenko-Scheffler scheme [40] with the inclusion of hydrogen bonding and vdW interactions. The all-electron method was used to describe the wave functions with a double numeric and polarization basis sets. The self-consistency threshold of total energy was set at 10^{-6} Hartree. In the structural optimization, the tolerance limits for the energy, force and displacement were set at 10^{-5} Hartree, 0.002 Hartree/Å and 0.005 Å, respectively.

Calculations also extend to examine the charge densification, viscosity, and surface tension at the skin region of 200 K ice. The conventionally used super-cell [41] as shown in Figure 2 was used in calculations. A vacuum slab is inserted into the super-cell to approximate the liquid-vapor interface or the skin that contains free H-O radicals.

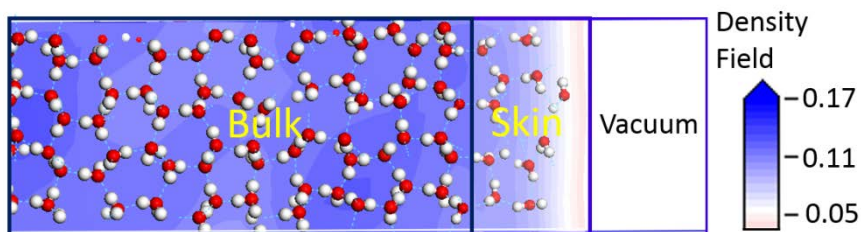


Figure 2 H_2O super-cell with a vacuum slab represents the supersolid skin of ice (200 K) with even undercoordinated H-O radicals. Color indicates the MD-derived mass density field. The current work turns out the skin reduces the H_2O molecular volume but inflates molecular distance and thus lower the mass

density at surface skin.

4. Results and discussion

4.1 O:H-O bond cooperative relaxation under various conditions

Figure 3 shows O:H-O cooperative relaxation under various stimuli. Results confirm consistently that in a certain panel, if one segment contracts the other lengthens; the two curves in one panel change in a way either ‘face to face’ or ‘back to back’ when the segments are relaxed. Results indicate the following: (a) compression shortens the O:H and lengthens the H-O towards O:H and H-O length symmetrization [42]; (b) cooling below T_m , the H-O shortens less than the O:H lengthens, resulting in volume expansion; (c) cooling at temperature above T_m the O:H and the H-O relax opposing to that at $T < T_m$, resulting in densification [43]; (d) Molecular undercoordination effects oppositely to compression [18]. In the liquid and the solid phase, the O:H follows the rule of thermal expansion but the H-O oppositely, resulting in the mass density and phonon stiffness oscillation in the full temperature range of water and ice [43]. These derivatives evidence the essentiality of the inter-oxygen repulsion dominating the unusual behavior of the hydrogen bond under excitation.

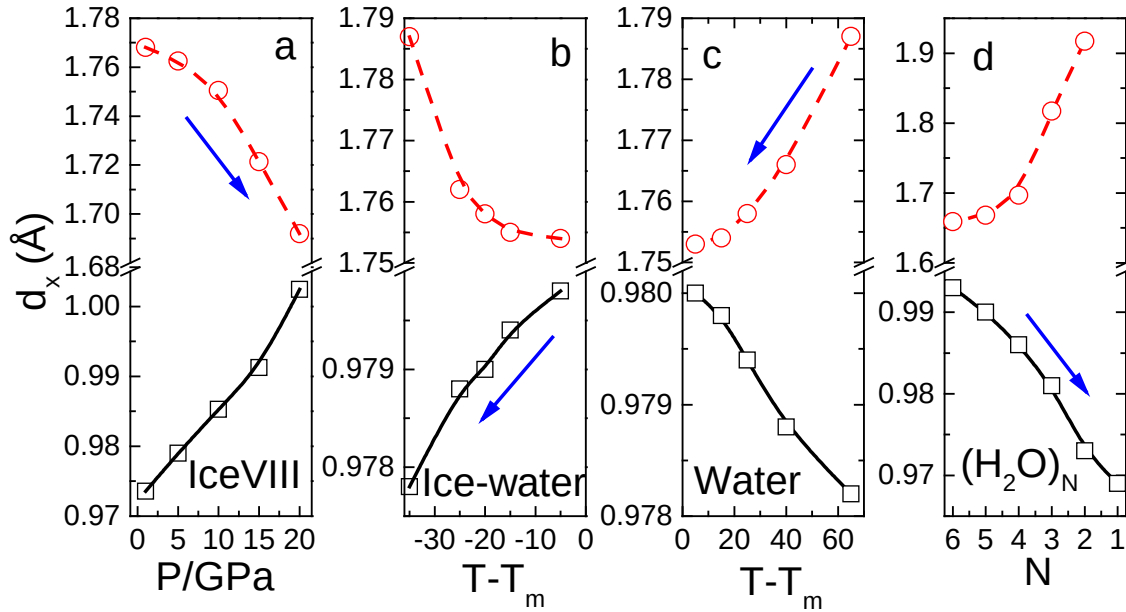


Figure 3 MD-derived cooperative O:H and H-O relaxation of the segmented O:H-O bond (a) under compression; cooling (b) below and (c) above the melting point (T_m), and (d) cluster size reduction. Arrows indicate the driving segments and their relaxation directions. Either the O:H or the H-O shrinks the other one expands, disregarding the stimuli applied or the structural phases because of the inter-oxygen repulsion.

4.2 Skin-resolved O:H-O bond relaxation

Figure 4 features the residual length spectra (RLS) for the MD-derived O-H and O:H bond of ice. The RLS is obtained by subtracting the spectrum of a fully-filled unit cell from that containing the vacuum slab, see Figure 2. The RLS turns out that the O-H bond contracts from ~ 1.00 in the body to ~ 0.95 at the skin. The O:H elongates from ~ 1.68 in the body to ~ 1.90 Å (average) at the skin, resulting in a 6.8% d_{OO} elongation or a 20% volume expansion. The $d_H = 0.93$ Å peak and the wide d_L peak correspond to the even undercoordinated H-O radicals that are associated 3650 cm^{-1} vibration frequency [18]. This result agrees with the trend that the H-O bond contracts from 0.9732 Å at the center to 0.9659 Å at the skin of a water droplet containing 1000 molecules in previous MD calculations [44].

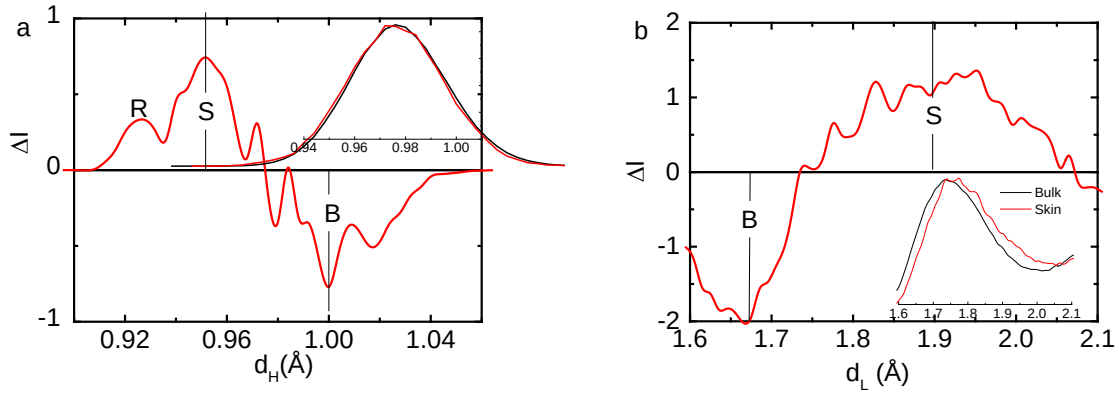


Figure 4 MD-derived RLS of (a) d_H contraction from ~ 1.00 to ~ 0.95 Å for skin (S) and 0.93 Å for radicals (R) and (b) d_L elongation from ~ 1.68 to ~ 1.90 Å (high fluctuation). Insets show the raw data of calculations with and without the skin vacuum slab. B represents the H-O in the bulk.

Furthermore, the measured d_{OO} ($= 2.965$ Å) [28] in the water skin turns out, using eq (1), $d_H = 0.8406$ Å and $d_L = 2.1126$ Å, corresponding to the $0.75\text{ g}\cdot\text{cm}^{-3}$ density that is much lower than the bulk ice of $0.92\text{ g}\cdot\text{cm}^{-3}$. Therefore, the numerical RLS and the experimental derivatives verified the expectation of the ultra-low density of the skins of both water and ice, resulting from d_H contraction and d_L elongation. Table 1 lists the experimentally-derived bond length (d_{OO} , d_x) and density (ρ) (eq 1), vibration frequency (ω_x), and bond energy (E_x) that was transformed from Lagrangian solution to the O:H-O oscillators with the measured d_{OO} and ω_x as input [20]. Clearly, skins of water and ice share the same identity of density, bond length, bond strength, vibration frequency, etc., at temperatures of 25 and -20 °C.

Table 1 Skin supersolidity (ω_x , d_x , E_x , ρ) of water and ice converted from eq (1) and Lagrangian solution with the known data (indicated with refs) as input [19, 20].

	Water (298 K)		Ice ($\rho_{\min}$)	Ice	Vapor
	bulk	skin	bulk	80 K	dimer
$\omega_H(\text{cm}^{-1})$	3200[2]	3450[2]	3125[2]	3090[43]	3650[45]
$\omega_L(\text{cm}^{-1})$ [43]	220	~ 180 [18]	210	235	0
$d_{\text{OO}}(\text{\AA})$ [19]	2.700[46]	2.965[28]	2.771	2.751	2.980[28]
$d_H(\text{\AA})$ [19]	0.9981	0.8406	0.9676	0.9771	0.8030
$d_L(\text{\AA})$ [19]	1.6969	2.1126	1.8034	1.7739	≥ 2.177
$\rho(\text{g}\cdot\text{cm}^{-3})$ [19]	0.9945	0.7509	0.92[47]	0.94[47]	≤ 0.7396

4.3 Phonon frequency and thermal stability

The supersolid skin of water and ice share the common $\omega_H = 3450 \text{ cm}^{-1}$ associated with T_m elevation, eq(2). As demonstrated in [18], the temperature of melting is proportional to the H-O bond energy. Therefore, the supersolid skin of water performs like ice at room temperature. This derivative also applies to water droplets encapsulated in hydrophobic nanopores [29,66,67] and defects elevated local T_m [48, 49]. According to the E_H derived in Table 1, the skin T_m is twice that of the bulk, but the T_m is subject to the temperature of evaporation T_{evap} that requires energy breaking the H:O bond (0.925 eV[21]). Therefore, the monolayer water melts at temperature about 315 K [50].

Figure 5(a, b) features the calculated residual phonon spectra (RPS) of ω_L and ω_H of ice in comparison to (c) the ω_H measurements from water and ice with insets showing the original raw spectra [2]. The RPS were obtained by subtracting the spectrum collected at smaller angles (between the surface normal and the reflection beam) from the one collected at larger angles upon the spectral area being normalized. The valleys of the RPS represent the bulk feature while the peaks the skin attributes. Proper offset of the calculated RPS is necessary as the calculation code overestimates the inter- and inter-molecular interactions [43].

As expected, the ω_L undergoes a redshift while the ω_H splits into three peaks. Two ω_H frequencies arise from the undercoordination induced contraction of the bonded (T) and the free H-O radicals (R). The ω_L redshift arises from O-O repulsion and polarization. The polarization in turn screens and splits the interatomic potential, resulting in another ω_H peak (P) below the bulk valley. The R peak corresponds to the even lower-coordinated H-O radicals.

Most strikingly, the measured RPS shows that skins of water and ice share the common ω_H value at 3450 cm^{-1} , which indicates that both skins are identical in nature. This finding agrees with the DFT-MD derivative that the H-O vibration frequency shifts from $\sim 3250 \text{ cm}^{-1}$ at a 7 $\text{\AA}$ depth to $\sim 3500 \text{ cm}^{-1}$ at the 2 $\text{\AA}$ skin of water

liquid [41]. Therefore, neither ice skin forms on water nor does the otherwise. One can refer such abnormal skins to the supersolid state. The concept of supersolidity is adopted from the superfluidity of solid ^4He at mK temperatures. The skins of ^4He fragments are highly elastic and frictionless with repulsive force between them at motion[51].

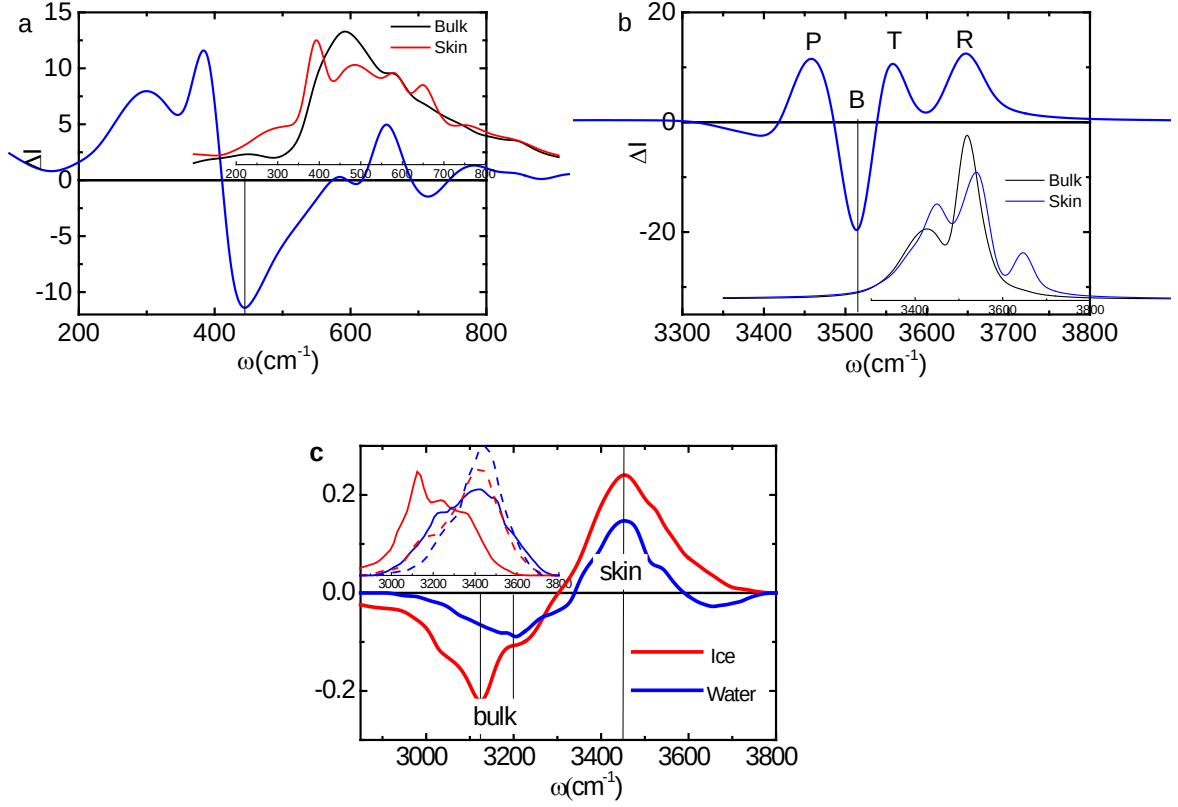


Figure 5 RPS of the MD-derived (a) ω_L and (b) ω_H of ice and (c) the measured ω_H of water (at room-temperature) and ice (at -20 and -15 °C) [2]. The ω_L undergoes redshift while the ω_H splits into three. Features T and R correspond to the H-O skin bond and the free H-O radicals and P to the screen and splitting effects on the crystal potentials by the undercoordinated O:H in numerical derivatives. Water and ice skins share the identical ω_H of 3450 cm $^{-1}$, which clarifies that neither liquid skin forms on ice nor solid skin on water, but the common supersolid skin.

The supersolid skin is thermally stable, whose melting point is proportional to the E_H . Water freezing starts preferentially at sites of molecules with full-coordination neighbors of four. According to MD calculations [48], freezing starts firstly in the subsurface of water instead of the top layer that remains disordered during freezing. The bulk melting is mediated by topological defects that preserve the coordination environment of the tetrahedral-coordinated network. Such defects form a region with a longer lifetime than the ideal bulk [49]. Water droplet on roughened Ag surface (with nanocolumnar structures) having a greater contact angle melts

62 sec later than the latter at -4°C compared with the droplet with smaller contact angle on a smooth Ag surface[52]. The critical temperature for transiting the contact the initial contact angle of a droplet to zero is proportional to the its initial value (curvature)[53]. Transition happens at 185, 234, and 271°C for water droplets on quartz, sapphire, and graphite with initial contact angles of 27.9, 64.2, and 84.7° , respectively (Fig S4). Likewise, water droplets encapsulated in hydrophobic nanopores[54] and ultrathin water films on graphite, and silica behave like ice at room temperature, i.e. they melt at a temperature higher than the melting point of water in bulk (monolayer ice melts at 325K)[50]. The monolayer film of water is hydrophobic [17, 55]. These findings indicate that water molecules at highly curved skin are thermally even more stable.

4.4 Skin charge entrapment and polarization-repulsive forces

The skins do entrap bonding and core electrons, which polarizes nonbonding charge, raises the thermal stability, and creates electronic repulsive force. Table 2 features the DFT derived charge polarization at the skin of water. The net charge of a water molecule increases from 0.022 in the body to -0.024 at the skin. SFG measurements confirmed that two adjacent water molecular layers are highly ordered at the hydrophobic contacts than those at the water-air interface [56]. As expected, bonding electron gain does happen at the skin. The charge gain and the nonbonding electron polarization provide the sources for the Coulomb repulsive force that reduces the friction at the interface between ice and other materials.

Table 2 DFT-derived charge polarization at the skin of ice. Negative sign represents net electron gain.

	Skin	Bulk
q_{O}	-0.652	-0.616
q_{H}	0.314	0.319
Net	-0.024	0.022

Undercoordination induced charge entrapment and polarization have been confirmed experimentally. For instance, the O1s level energy is 536.6 eV in the bulk of water [57], 538.1 eV in the surface of water, and 539.8 eV in gaseous molecules [58] (Fig S2). The densification and entrapment of bonding electrons polarize the nonbonding electrons. As it has been discovered using an ultra-fast liquid jet vacuum ultra-violet photoelectron spectroscopy [32], the dissociation energy for an nonbonding electron in solution changes from

a bulk value of 3.3 eV to 1.6 eV at the water skin. The dissociation energy, as a proxy of work function and surface polarization, decreases further with molecule cluster size (Fig S3).

Measurements have revealed the presence of the repulsive forces between a hydrated mica-tungsten contacting pair at 24 °C [59]. Such repulsive interactions appear at above 20% relative humidity (RH) and are fully developed in the range of 38-45% RH. The repulsion corresponds to an elastic modulus of 6.7 GPa. Monolayer ice also forms on graphite surface at 25% RH and room temperature [60]. These experimental and numerical findings evidence the presence of the supersolidity with repulsive forces as a result of surface polarization and bonding charge accumulation and the elevated melting point resulting due to H-O strength gain.

4.5 Stress, viscosity, and elasticity

Water and ice skins share high tension and viscosity. The surface tension γ is defined as the difference between the stress components in the direction parallel and perpendicular to the interface [61, 62],

$$\gamma = \frac{1}{2} \left(\frac{\sigma_{xx} + \sigma_{yy}}{2} - \sigma_{zz} \right) \cdot L_z \quad (2)$$

where σ_{xx} , σ_{yy} , and σ_{zz} are the stress tensor element and L_z is the length of the super-cell in the z direction.

Green [63] and Kubo [64] correlated the surface shear viscosity η_s to the bulk stress σ in the way:

$$\eta_s = \frac{V}{kT} \int_0^\infty \langle \sigma_{\alpha\beta}(0) \sigma_{\alpha\beta}(t) \rangle dt \quad (3)$$

where the $\sigma_{\alpha\beta}$ denote the three equivalent off-diagonal elements of the stress tensors. The bulk viscosity η_v is related to the decay of fluctuations in the diagonal elements of the stress tensor as follows:

$$\begin{aligned} \eta_v &= \frac{V}{kT} \int_0^\infty \langle \delta\sigma(0) \delta\sigma(t) \rangle dt \\ \delta\sigma &= \sigma - \langle \sigma \rangle \end{aligned} \quad (4)$$

Based on these notations, we calculated the γ using the MD-derived stress tensors. The auto-correlation functions of stress tensors can also be calculated and hence η_s and η_v are obtained according to eq (4) and (5). Table 3 features the MD-derived thickness-dependent γ , η_s , and η_v of ice skin. Reduction of the number of

water molecule layers increases the values of γ , η_s , and η_v , which agrees with our expectations. The O:H-O cooperative relaxation and the associated entrapment and polarization enhance the stress tensors to reach the values of 73.6 for 5 layers, approaching the measured 72 dyn/cm at 25 °C.

Table 3 Thickness-dependent surface tension and viscosity of ice skin.

Number-of-layer	15	8	5
γ dyn/cm	31.5	55.2	73.6
η_s	0.0007	0.0012	0.0019
η_v	0.0027	0.0029	0.0032

Skin supersolidity slipperizes ice. The H-O contraction, core electron entrapment and nonbonding electron polarization yield the high-elasticity, self-lubrication, and low-friction of ice and the hydrophobicity of water surface as well. The mechanism of frictionless and self-lubricate of ice [3] is the same to that of metal nitride surfaces [21]. The friction coefficient of ice and some nitrides are in the same order of 0.1 or below. The elastic recovery coefficient of TiCrN and GaAlN surfaces reaches 100% under a critical indentation load of friction (< 1.0 mN) at which the lone pair breaks. The involvement of lone pairs makes the ice and the nitride skins more elastic and slippery at loads under the critical values.

5 Summary

Experimental and numerical results evidence consistently our prediction of the common supersolid skin covering both water and ice. Molecular undercoordination and inter electron-pair repulsion drive O:H-O bond cooperative relaxation in length and energy and the associated charge entrapment and polarization. Molecular undercoordination shortens and stiffens the H-O bond and meanwhile lengthens and polarizes the O:H bond thorough inter-oxygen repulsion. In the skin region, molecular becomes smaller but the molecular separation becomes longer and hence the density of the skin drops substantially ($0.75 \text{ g}\cdot\text{cm}^{-3}$). The shortening of the H-O bond raises the density of the core and the bond electrons, which in turn polarize the lone pairs, resulting in the high elasticity and the high density of dipoles. The supersolid skin slipperizes ice and enhances the surface tension of liquid. Neither liquid skin forms on ice nor ice skin forms on water.

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Supporting Information on experimental observations of (i) elastic and hydrophobic water skin, (ii) length and vibration frequency cooperative relaxation of hydrogen bond between water molecules with fewer than four neighbors, (iii) O 1s bonding electron entrapment and nonbonding electron polarization, and (iv) curvature dependence of the thermal stability of water droplet skin is available free of charge via the Internet at <http://pubs.acs.org>.

FOOT NOTES

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