

Review of: "Asymmetric response of interfacial water to applied electric fields"

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VSFG investigation [1] revealed the asymmetrical response of the surface heavy water (D₂O) dipoles to the charge polarity of the graphene electrode, evidencing the nonlinearity of the surface water dielectrics. A peak of non-hydrogen-bonded OD groups at a frequency of 2,700 cm⁻¹ is presented. The OD points away of water surface at a 5×10¹² electrons/cm² negative electrode charge density. However, at neutral or positive electrode potentials, this 'free-OD' peak disappears abruptly, and the spectra display broad peaks of hydrogen-bonded OD species (2,300–2,650 cm⁻¹). This observation demonstrates the nonlinear dielectric response of the surface water to electric fields of about ±3×10⁸ V/m. Furthermore, the G-mode frequency of the graphene electrode undergoes a blueshift by some 10 cm⁻¹ under electrification. The findings contributed to knowledge of the interfacial water dielectrics at the atomic scale and discovered the graphene G-mode response to electrification.

This reader would like to share his experience, as supplementary information, in exploring the effect of atomic undercoordination and directional electrostatic polarization on the phononic performance of the skin water [2-4] and graphene [5]:

1. The phonon frequency shift that is proportional to $(E/d^2)^{1/2}$ reflects the perturbation to the oscillator energy E and length d . The blue shift indicates the stiffening of the the electrode C—C bond and stiffness distribution of the D—O bonds in different coordination environment.
2. Molecular undercoordination shortens and stiffens the intramolecular H(D)—O bond, and meanwhile, lengthens and softens the O:H(D) nonbond associated with strong polarization of the lone pair electrons (<https://www.qeios.com/read/FO6KAP>). Being gel-like, viscoelastic, less dense, hydrophobic, frictionless (for ice), mechanically and thermally stable, the supersolid skins of water and ice share the identical H—O bond of 3450 cm⁻¹ vibration frequency. Thus, vibration frequency of the free H(D)—O radical is higher than that of water skin and even higher than it is in the bulk.
3. Directional field electrification enhances the effect of molecular under-coordination on the skin supersolidity. DFT calculations [6] confirmed that H₂O molecules of the (H₂O)₆₋₂₀ clusters remain their tetrahedral structures with titled orientation under polarization. The electrification stretches the O:H from 1.86 till break at 1.91 Å, for instance. The breaking limit varies with cluster size. If the field

intensity is sufficiently strong, molecular dipoles will reorient oppositely along the field direction; at the critical intensity, the O:H(D) will break, easing evaporation but hindering H(D)—O dissociation, as electrification shortens and stiffens the H—O [4].

- Water electrification exhibits many anomalies such as Armstrong's water floating bridge [7], Dufour's electrofreezing [8], and Asakawa's electro-evaporation [9].
- How the electrification stiffens the C—C bond of the electrode remains an open question. That electrification shortens the intramolecular C—C bond is very challenging, which appears to happen to the strongly coupled systems – the nonbonding pair-electron may play a certain yet unclear role.

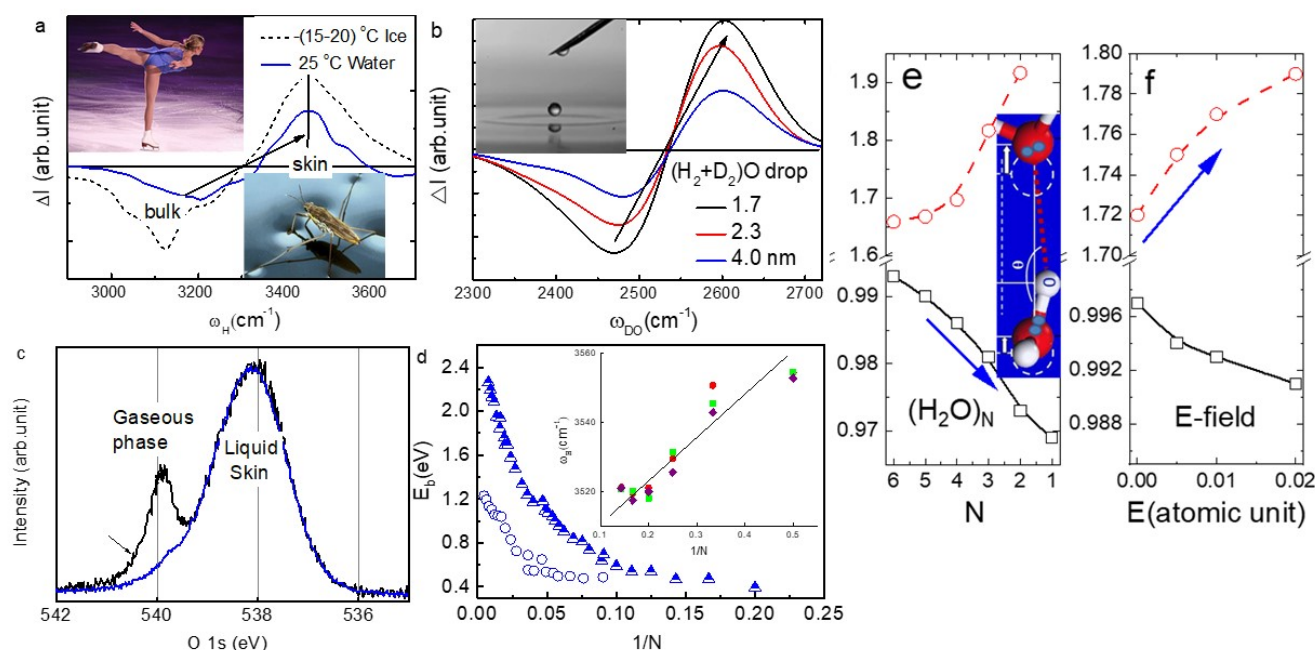


Fig.1 H—O bond stiffness transition from the bulk reference to the supersolid skins of (a) 298 K water, 258 K ice [10], and (b) $(0.05\text{D}+0.95\text{H})_2\text{O}$ nanodroplets [11]. The H—O contraction entraps (c) O1s electrons from the bulk (536 eV) to the skin (538) and the gaseous water (530 eV) [12]. The densely entrapped core electrons polarize in turn (d) the nonbonding electrons from the bulk core (3.2 eV) to the interior (2.4 eV) and the skin (1.2 eV) for the sized droplets (N). Droplet size reduction enhances the polarization till 0.4 eV for $N = 5$ [13]. Inset d shows the cluster size reduction induced H—O frequency blueshift. (e) Cluster $(\text{H}_2\text{O})_N$ size reduction and (f) electrostatic polarization do shorten the H—O bond and lengthens the O:H, according to the Force-field calculations [14].

I hope this supplementary could help in understanding the performance of the interfacial water under electrification from the perspective of hydrogen bonding cooperativity (Fig 1 inset e). Critiques and comments are welcome and appreciated.

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