Abstract

We present recent progress in understanding the anomalous behavior of water ice under mechanical compression, thermal excitation, and molecular undercoordination (with fewer than four neighbors in the bulk) from the perspective of hydrogen (O:H-O) bond cooperative relaxation. Extending the Ice Rule suggests a tetrahedral block that contains two H2O molecules and four O:H-O bonds. This block unifies the length scale, geometric configuration, and mass density of molecular packing in water ice. This extension also clarifies the flexible and polarizable O:H-O bond that performs like a pair of asymmetric, coupled, H-bridged oscillators with short-range interactions and memory. Coulomb repulsion between electron pairs on adjacent oxygen atoms and the disparity between the O:H and the H-O segmental interactions relax the O:H-O bond length and energy cooperatively under stimulation. A Lagrangian solution has enabled mapping of the potential paths for the O:H-O bond at relaxation. The H-O bond relaxation shifts the melting point, O 1s binding energy, and high-frequency phonon whereas the O:H relaxation dominates polarization, viscoelasticity, and the O:H dissociation energy. The developed strategies have enable clarification of origins...
of the following observations: (i) pressure-induced proton centralization and phase transition–temperature depression; (ii) thermally-induced four-region oscillation of the mass density and the phonon frequency over the full temperature range; and (iii) molecular-undercoordination-induced supersolidity that is elastic, hydrophobic, thermally stable, with ultra-low density. The supersolid skin is responsible for the slipperiness of ice, the hydrophobicity and toughness of water skin, and the bi-phase structure of nanodroplets and nanobubbles. Molecular undercoordination mediates the O:H and H-O bond Debye temperatures and disperses the liquid-solid transition phase boundary, resulting in freezing point depression and melting point elevation. O:H-O bond memory and water-skin supersolidity ensures a solution to the Mpemba paradox – hot water freezes faster than its cold. These understandings will pave the way towards unveiling anomalous behavior of H2O interacting with other species such as salts, acids and proteins, and excitation of H2O by other stimuli such as electrical and magnetic fields.

**Keywords**: Water structure; ice rule; H-bond potentials; phonon relaxation; pressure; temperature; molecular cluster; Raman; FTIR; XPS; phase transition; viscoelasticity; polarization; specific heat; slipperiness of ice; water surface tension; Coulomb coupling; multiple fields; correlation and fluctuation; Fourier fluid thermodynamics; water-protein interaction; hydrophobicity; polarization; negative thermal expansion; electro- and magneto-freezing; supersolidity; superheating and supercooling; Mpemba paradox; Hofmeister series; Leidenfrost effect.

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Hydrogen-bond relaxation dynamics: Resolving mysteries of water ice (42 k words), Coord Chem Rev, in press

A: In this article, authors discuss broad research area on water based on the intermolecular interactions between two water molecules. The article is quite long and its coverage is broad. It was also conducive for me to read such a massive review article, while I found some unconvincing descriptions.

B: This manuscript is a review of the latest works related with the atomic structures of ice, water and chemical-physical properties related including the explanation of some anomalies of water-ice behaviour. It is an exhaustive review with almost 400 references with interesting results and concepts, like the water-skin, Mpemba Paradox and thermodynamics explanations. However, it looks like that has been written too fast, even after the revision, because this manuscript is a revision version, and some improvements should be applied. I think that this manuscript could be published only after a carefully major revision addressing the following comments.

C: I would agree that there is scope for such a review, and the outline appears reasonably comprehensive. Other recent reviews may have some relevance but appear to have a different emphasis. E.g. George Malenkov 2009 "Liquid water and ices: understanding the structure and physical properties" J. Phys.: Condens. Matter 21 283101 doi:10.1088/0953-8984/21/28/283101

Prof Sun’s forays into water ice studies are relatively recent but he has transferred expertise and tools from materials science to make a significant contribution already, developing models that are consistent with much experimental data.

Other comments:

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