

Aqueous surface and interface: Hydrogen-bond transition dynamics

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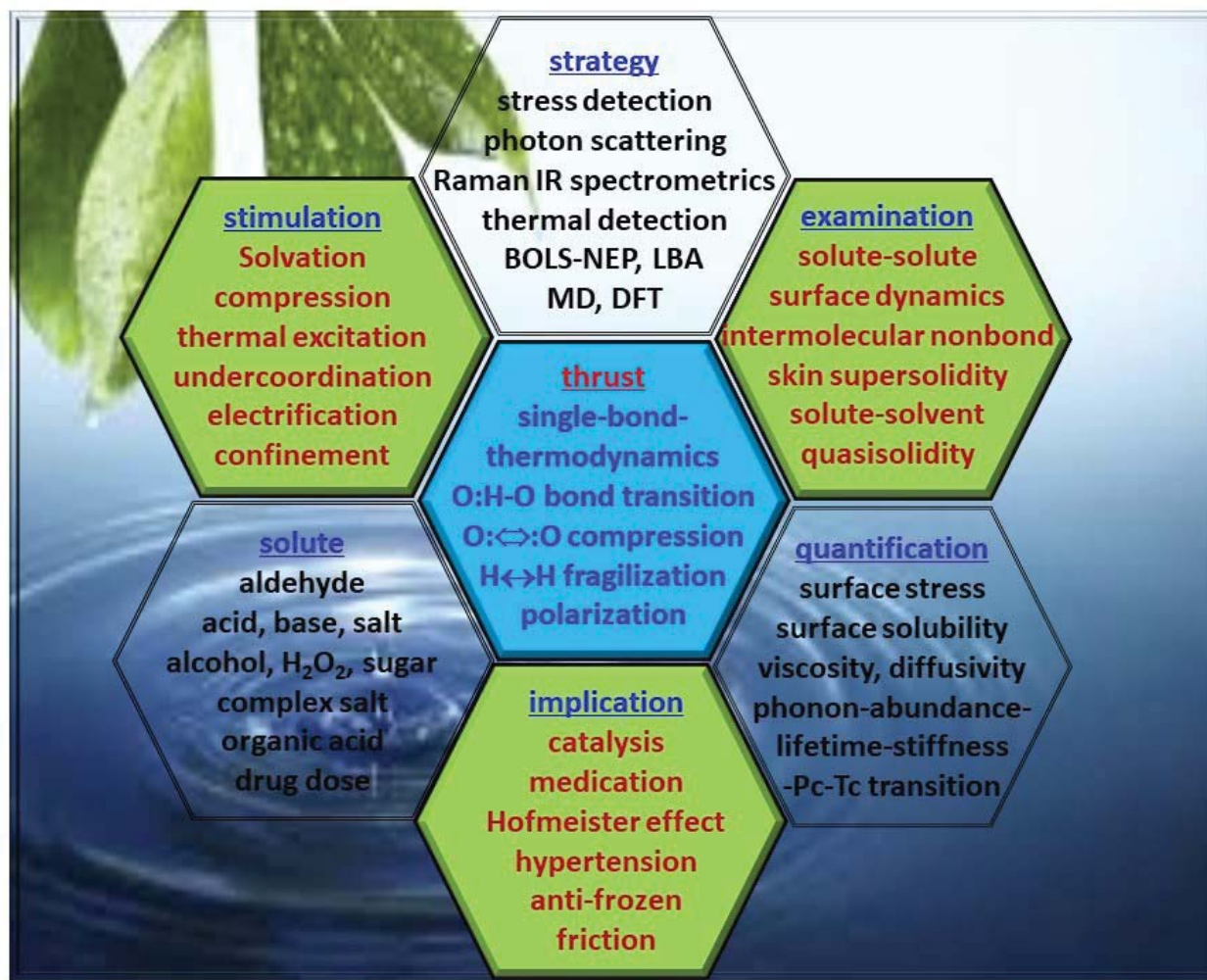
Synopsis

A combination of the hydrogen bond (O:H—O) cooperativity notion and the differential phonon spectrometrics (DPS) strategy has resolved transition of O:H—O bonds from the mode of ordinary water to their hydration in terms of their number fraction and stiffness upon solvation and confinement, which reconciles the molecular interactions, bonding thermodynamics, and solute capabilities of mediating molecular diffusivity, critical pressures and temperatures for phase transition, phase boundary dispersion, phonon lifetime, solute-solute interactions, surface stress, solution viscosity, etc.

Understanding may extend the surface and interface to the atomic scale of solvation and nanoconfinement for deeper and consistent insight into the bonding dynamics with novel yet straightforward means of direct detection.

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Keywords- content entry



Highlight

- O:H, H $\leftrightarrow$ H, O: $\leftrightarrow$:O or ionic or dipolar polarization govern aqueous molecular intercalations
- Bond-nonbond cooperative relaxation and transition dictates the performance of a solution
- DPS resolves O:H—O bond transition from the mode of ordinary water to hydration shells.
- Amplifying surface and interface to atomic scale solvation and confinement is fascinating.

Abstract

Compatible to surface chemisorption, aqueous solvation is ubiquitously important to our daily life and living conditions. Pursuing fine-resolution detection and consistently-deep insight into the solvation interface bonding dynamics has becoming a subject area of increasingly active. Extending the hydrogen bond (O:H–O or HB with “:” being the electron lone pairs of oxygen) cooperativity theory and the differential phonon-electron spectrometrics (DPS) strategy has amplified here the solvation study from the perspectives of continuum thermodynamics and molecular dynamics to the solvation hydrogen bonding dynamics and single-bond thermodynamics. This amplification has enabled resolution of the following issues:

- 1) the number fraction and phonon stiffness of HBs transiting from the mode of ordinary water to hydration shells;
- 2) cooperative relaxation of the intermolecular nonbonds (electrostatic polarization, O:H attraction, $H \leftrightarrow H$ and $O \leftrightarrow O$ repulsion without charge sharing or orbital overlap) and the intramolecular H–O covalent bonds;
- 3) the local electric field, the O:H–O segmental phonon frequency shift, and the hydration shell size; and,
- 4) the interdependence of skin stress, solution viscosity, molecular diffusivity, solvation thermodynamics, phase boundary dispersion, and critical pressures and temperatures for phase transitions.

Solvation examination revealed the following:

- 1) the excessive protons in the H(Cl, Br, I) solutions create the $H \leftrightarrow H$, called anti-HB point breaker, that has the same effect of heating on disrupting its solution network and surface stress;
- 2) the excessive lone pairs in the H_2O_2 and in the (Li, Na, K)OH solutions generate the $O \leftrightarrow O$, named super-HB point compressor, that has the same effect of pressure on shortening and stiffening the O:H nonbond and relaxing the intramolecular H–O bond contrastingly; the bond-order-deficiency shortens and stiffens the solute H–O bond due H_2O_2 and OH^- ;
- 3) ions in the Na(Cl, Br, I), (Na, K, Rb, Cs)I and Na(HSO_4 , NO_3 , ClO_4 , SCN) solutions serve each as a charge center that aligns, clusters, stretches and polarizes their neighboring HBs to form hydration shells; and,
- 4) solvation of alcohols, aldehydes, complex salts, organic and formic acids, and sugars demonstrate the dipolar solute - solvent interface structural distortion with introduction of the anti-HB or the super-HB to functionalize the solutions.

The $f_H(C) = 0$, $f_{OH}(C) \propto f_{cation}(C) \propto C$, and $f_X(C) \propto 1 - \exp(-C/C_0)$ feature the solute capabilities of transiting the fraction number of HBs in the concentrated solutions (C). The invariant $df(C)/dC$ for the alkali, OH^+ , and organic solutes, suggests the constant hydration shell size that is insensitive to interference by other solutes because the hydration H_2O dipoles fully-screen the solute electric field. The number inadequacy of the H_2O dipoles in the highly-ordered hydration shells could, however, not fully-screen the anion's electric field and thus anion-anion repulsion persists in the relevant solutions. Besides, $f_{droplet}(D) \propto D^{-1}$ clarifies the core-shell configuration of water droplet of D size. For salt solutions the phonon relaxation time $\tau_{solution}(C) \propto f(C)$ but for nanodroplet $\tau_{droplet}(D)$ results from skin supersolidity and geometric confinement inhibiting vibration energy dissipation. Evidencing the essentiality of intermolecular nonbond and intramolecular bond cooperativity, exercises not only lead to consistent insight into the hydration interface bonding thermodynamics but also exemplify the efficient yet straightforward DPS towards solvation phonon spectrometrics. Understanding may amplify the surface and interface to the

atomic scale of solvation and nanoconfinement for deeper and consistent insight into the bonding dynamics with efficient means of direct detection. Extending the developed knowledge and strategies to catalysis, solution-protein, drug-cell, and other molecular interactions towards discoveries in molecular crystals and liquids would be even more challenging, fascinating, and rewarding.

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