# Springer Series in Chemical Physics

Volume 121

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Chang Q Sun

# Solvation Dynamics

## A Notion of Charge Injection

Springer

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ISSN 0172-6218
Springer Series in Chemical Physics
ISBN 978-981-13-8440-0 ISBN 978-981-13-8441-7 (eBook)
https://doi.org/10.1007/978-981-13-8441-7



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The registered company address is: 152 Beach Road, #21-01/04 Gateway East, Singapore 189721, Singapore

*Hydration of anions, cations, electrons, lone pairs, protons, and dipoles mediates the O:H–O bonding network and properties of a solution through O:H formation, H↔H fragilization, O:⇔:O compression, screened polarization, solute-solute interaction, and intra-solute bond contraction.*

—Chang Q Sun

*Solvation Dynamics—A Notion of Charge Injection*

Springer Series of Chem Phys 121, 2019

*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.*

—Chang Q Sun and Yi Sun
*The Attribute of Water—Single Notion, Multiple Myths*
Springer Series of Chem Phys 113, 2016

*Bond and nonbond relaxation and the associated energetics, localization, entrapment, and polarization of electrons mediate the performance of substance accordingly.*

—Chang Q Sun
*Relaxation of the Chemical Bond*
Springer Series of Chem Phys 108, 2014

*Spectrometrics of electron emission and diffraction, liquid and solid multifield phonon relaxation refines quantitative, ever-unexpected information of the bonding, nonbonding, electronic and lattice dynamics pertaining to chemisorption, solvation, irregular atomic-coordination, mechanical and thermal excitation.*

—Chang Q Sun
*Electron and Phonon Spectrometrics*
Springer, 2019

*In memory of and dedicated to my parents*

# Preface

The high molecular polarity endows water as an excellent solvent capable of impinging into and then dissolving a soluble crystal into charge carriers to disperse in the aqueous solvent matrix. Charge injection in forms of electrons, electron lone pairs, ions, protons, and molecular dipoles by solvation mediates the hydration network and properties of a solution, which is ubiquitously important to our health and life. Pursuing means of fine-resolution detection and consistent insight into solvation dynamics, molecular interactions, and solute functionalities on the hydrogen bonding network and solution properties has become an increasingly active subject area. Numerous issues are to be ascertained, despite intensive investigations since the 1880s, when Franz Hofmeister discovered the effect known as the Hofmeister series order and Svante Arrhenius defined the acid, base, and their combination of adduct.

Interactions between solute charge carriers and water molecules have profound impacts on many chemical, biological, and environmental topics such as DNA engineering, cell culturing, finding cures for diseases and healthcare. The solvation of salts changes the solutions' viscoelasticity, thermal stability, critical temperatures and pressures for solution phase transition, and even lowers the frictional coefficient, when salt solutions are used as wet lubricants. Ionic hydration forms a stiffer volume, which expands the graphene-oxide interlayer spacing from 0.34 up to 1.5 nm and the modulated layer separation varies with the type of cations.

Salt solutions demonstrate the Hofmeister effect on regulating the solution surface stress and its solubility of DNA and proteins. The ability of anions to precipitate certain proteins not only follows the Hofmeister series order, but the extent of solvation modulation also varies with solute concentration. Debating mechanisms for salt solvation include water structure maker and breaker, ionic specification, quantum dispersion, skin induction, and interaction length scale of hydration.

From the perspective of proton and lone pair acceptance and donation, Svante Arrhenius (1884), Brønsted–Lowry (1923) and Gilbert Lewis (1923) defined the acid, base, and adduct. Regarding the transport manner and mobility of protons and lone airs in Lewis solutions, Theodor Grotthuss proposed in 1903 the "structural diffusion" or the "concerted random hopping" from one $H_2O$ motif to another. The proton mobility was thought high compared to the mobility of the $H_2O$ molecules. Later development refined this concept by invoking proton thermal hopping, structural fluctuating, and quantum tunneling.

In 1964, Eigen proposed an $H_9O_4^+$ ($H_3O^+$:3$H_2O$) complex, in which an $H_3O^+$ core is strongly bounded to three $H_2O$ molecules and leaves the lone pair of the tetrahedrally-structured $H_3O^+$ hydronium free. The lone pairs of the neighboring three $H_2O$ molecules were orientated simultaneously toward the $H^+$ protons, forming the hydrogen bonds (O:H–O or HB with ":" as the electron lone pairs of oxygen). Zundel favors in 1967, however, a $[H_5O_2]^+$ ($H^+$:2$H_2O$ nonbonded or $H^+$–2$H_2O$ covalently bonded) complex in which the proton shuttles randomly between two $H_2O$ molecules. Protons frustrate in two positions off midway between adjacent two oxygen anions, which is the same as the transitional quantum tunneling of Bernal–Fowler–Pauling proposed in the 1930s. Protons and lone pairs were thought to follow the same motion dynamics albeit their polarity inversion.

The known mechanisms for proton and lone pair transportation are in contradiction to the fact that an H–O bond possesses ~4.0 eV energy, which requires at least 121.6 nm wavelength laser irradiation for the H–O bond to dissociate in the gaseous phase. On the other hand, the conservation of the 2N number of protons and lone pairs and the O:H–O configuration and orientation endow liquid water as a highly ordered fluctuating crystal. One has to constrain the motion of $H_2O$ molecules and protons in water solvent.

Organic molecular solvation makes the situation even more complicated. For instance, carboxylic acids (such as alcohols) modify the HBs of vodka and whiskey and because these distilled spirits to taste differently one from another; aldehydes and carboxylic acids could damage DNA, causing cancer; glycine and its N-methylated derivatives denature proteins; salt (NaCl) and sodium glutamate ($NaC_5H_8NO_4$) could cause hypertension, but ascorbic acids (vitamin C) can lower blood pressure. The addition of sugar could lower the freezing temperature, which enables low-temperature storage of bio-species without crystallization. The understanding of organic molecular solvation is still in its infancy.

From the perspectives of molecular spatial and temporal performance, proton transportation, nuclear quantum interaction, and O:H–O bond and electronic cooperativity, the following multiscale approaches have made important contributions to understanding water and solutions:

1. Classical continuum thermodynamics scheme takes water ice as a collection of neutral particles and correlates its properties directly to the applied stimulus with focus on the Gibbs free energy. This approach embraces the dielectrics, diffusivity, surface stress, viscosity, latent heat, entropy, liquid/vapor phase transition, though this scheme has faced difficulties in dealing with solvation dynamics and the anomalous properties of water and ice.

2. Molecular dynamics (MD) premises treat water ice as a collection of flexible or rigid, polarizable or non-polarizable molecular dipoles. The combination of MD computations and the ultrafast phonon spectroscopies explores the spatial and temporal performance of water and solute molecules as well as the proton and lone pair motion and transportation behavior. Information includes the phonon relaxation or the molecular residing time at sites nearby the solute or under different coordination conditions or under perturbations.
3. Nuclear quantum interactions approach is focused on visualizing the concerted quantum tunneling of the light 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 the scanning tunneling microscopy/ spectroscopy (STM/S) has verified the $sp^3$-orbital hybridization at 5 K and the magic number of $Na{\cdot}3H_2O$ for interface fast transport. The proton quantum interaction elongates the longer part and shortens the shorter part of the O:H–O bond, being the result of electrostatic polarization.
4. O:H–O bond cooperativity and electron polarization notion is focused on the cooperativity of the intra- and intermolecular interactions and nonbonding electron polarization under perturbation. The cooperativity of the segmented O:H–O bond and its segmental specific heat disparity dictate the phase structures and thermodynamics of water and ice. A combination of the Lagrangian oscillation mechanics, MD and DFT computations with the static phonon spectrometrics seeking for the O:H–O bond cooperativity and its transition from the mode of ordinary water to the conditioned states and the associated electron polarization. Obtained information includes the fraction, stiffness, and fluctuation order transition upon perturbation and their consequences on the solution viscosity, surface stress, phase boundary dispersivity, and the critical pressure and temperature for phase transition.

In fact, solvation is a process of aqueous charge injection. Charged species react in their respective ways but cooperatively with the solvent molecules, which mediates the hydrogen bonding network and properties of the solutions. The key challenge is to gain consistent insight into the discriminative roles of various solutes interacting with solvent and other solutes and to develop efficient means for fine detection.

This book is focused on the solvation dynamics, molecular nonbond interactions, and the extraordinary functionalities of various solutes on the solution bond network and properties from the perspectives of ionic and dipolar electrostatic polarization, O:H nonbond attraction, H↔H anti-HB and O:⇔:O super-HB repulsion. A combination of the O:H–O bond cooperativity notion and the differential phonon spectrometrics (DPS) has enabled quantitative information on the following issues: (i) the number fraction and phonon stiffness of HBs transiting from the mode of ordinary water to hydration; (ii) solute–solvent and solute–solute molecular nonbond interactions; (iii) discriminative functionalities of individual solutes; and, (iv) interdependence of skin stress, solution viscosity, molecular diffusivity, solvation thermodynamics, and critical pressures and temperatures for phase transitions.

Systematic examination of solvation dynamics has clarified the following:

(1) Charge dispersive injection by solvation mediates the hydrogen bond network and properties of a solution through electrostatic polarization, $H_2O$ dipolar shielding, O:H van der Waals bond formation, H↔H and O:⇔:O repulsion, solute–solute interactions, as well as undercoordinated intra-solute bond contraction.

(2) Lone pair or proton injection breaks the 2N number conservation to form the stereo ($H_3O^+$, $HO^-$)·$4H_2O$ motifs, turning one O:H–O bond into the H↔H anti-HB point breaker, and the O:⇔:O super-HB point compressor and polarizer, in Lewis solutions.

(3) The H↔H fragilization disrupts the acidic solution network and surface stress; the O:⇔:O compression shortens the O:H nonbond but lengthens the H–O bond in basic and $H_2O_2$ solutions; yet, bond-order-deficiency shortens and stiffens the solute H–O bond due $H_2O_2$ and $OH^-$ solutes.

(4) Exothermal solvation of base and $H_2O_2$ arises from energy emission of solvente H–O bond expansion by O:⇔:O compression and energy absorption from the solute H–O bond contraction in solvation. The energy gain heats up the respective solution at solvation. Molecular motion and evaporation dissipate energy capped by the O:H bounding of 0.1–0.2 eV being less than 5% of the H–O bond energy. The H↔H repulsion governs the exothermal solvation of alcohols.

(5) As an inverse of a monovalent cation, the hydrated electron is entrapped by $H_2O$ dipoles, which serves as a probe to the molecular-site and cluster-size resolved HB polarization and the lifetime of photoelectron energy dissipation.

(6) Ions each serve as a charge center that aligns, clusters, stretches, and polarizes their neighboring HBs to form supersolid hydration volumes. Ions prefer eccntrically the hollow sites of the cubic unit cell containing four $2H_2O$ motifs. The small cation retains its hydration volume because the hydrating $H_2O$ molecules fully screen its electric field; however, the number insufficiency of the ordered hydrating $H_2O$ molecules only partly screen the local electric field of anions and anion-anion repulsion reduces the hydration volume at higher solute concentrations.

(7) Solvation of alcohols, aldehydes, complex salts, carboxylic and formic acids, glycine and sugars distort the solute–solvent interface structures with involvement of the anti-HB or the super-HB.

(8) Pressure, temperature, charge injection, and molecular undercoordination act jointly on the critical pressures and temperature for the phase transition and quasisolid phase boundary dispersion of a solution.

(9) Oxidation-solvation-hydration of alkali metals (Y) and the molten alkali halides (YX) fosters their aquatic unconstrained explosion that can be formulated by [$Y^+$↔$Y^+$ + 2($H_2O$:⇔:$OH^-$) + heat] + ($H_2$ or HX)↑. The $Y^+$↔$Y^+$ Coulomb fission initiates and the O:⇔:O super-HB fosters the explosion.

(10) The combination of the X:H–Y tension and X:⇔:Y or H↔H repulsion dictates the sensitivity, energy density, and detonation velocity of energetic substance. The X:H–Y tension determines the sensitivity of the constrained explosion.

As key elements to solvation, O:H–O bond polarization and segmental cooperativity, O:H–O segmental specific heats derived five phases over the full temperature range, and the charge injection derived nonbond interactions and the perturbation dispersed phase boundaries, as well as the bond order deficiency resolved intra-solute bond contraction continue to challenge the limitations of available theories and computational methods. A combination of the spatially-resolved phonon spectrometrics for the phonon abundance-stiffness-fluctuation transition with the X-ray absorption, sum frequency generation, and temporally-resolved pump-probe phonon and photoelectron spectroscopies would be even more revealing for solvation bonding energetic-spatial-temporal evolution dynamics.

It is my great pleasure and obligation to share these personal learnings from the perspective of aqueous charge injection and hydrogen bond transition. Further refinement and improvement are welcome, and critiques from readers are much appreciated.

I hope that this volume, underscoring the essentiality of quasisolidity, supersolidity, anti-HB, super-HB, and O:H–O bond cooperativity to solvation could inspire ways of thinking about and dealing with solvation dynamics, which also stimulate more interest and activities toward correlating the bond-electron-phonon cooperativity to the performance of aqueous and living substances. Directing effort to the areas of extraordinary coordination bond engineering, nonbonding electrons, molecular crystals, and life science could be even more challenging, fascinating, promising, and rewarding.

I would like to express my sincere thanks to colleagues, friends, and peers for their encouragement, invaluable input, and support, to my students and collaborators for their contributions, and to my family, my wife Meng Chen and daughter Yi, for their assistance, patience, support, and understanding throughout this fascinating and fruitful journey.

Singapore
March 2019

Chang Q Sun

# Contents

# About the Author

**Chang Q Sun** received his BSc in 1982 from Wuhan University of Science and Technology and an MSc in 1987 from Tianjin University and served on its faculty until 1992. He earned his PhD in Physics at Murdoch University in 1997 and then joined Nanyang Technological University.

Dr. Sun has been working on the theme of *Extraordinary Coordination Bonding and Nonbonding Electronics.* He has pioneered theories of Bond Relaxation and Hydrogen Bond (O:H–O) Oscillator Pair Cooperativity and holds multiple patents on the Coordination-Resolved Electron and Multifield Phonon Spectrometrics. His contribution has been documented in *Electron and Phonon Spectrometrics, Springer 2019; Solvation Dynamics: A Notion of Charge Injection, Springer 2019; The Attribute of Water: Single Notion, Multiple Myths, Springer 2016; Relaxation of the Chemical Bond*, *Springer 2014* and their Chinese versions. He has published over 20 treatises in *Chemical Reviews*, *Progress in Materials Science*, etc. He was bestowed with the inaugural Nanyang Award in 2005 and the first rank of the 25$^{th}$ Khwarizmi International Award in 2012.

# Nomenclature

| | |
|---|---|
| $\theta$ | Contact angle between the solution droplet and a certain substrate features the solution surface stress |
| $\eta(C)$ | Solute concentration C resolved solution viscosity |
| $\Theta_{DX}(\omega_X)$ | Debye temperature (characteristic phonon frequency) of the x segment of the O:H–O bond |
| $\omega_x$ | O:H–O bond x-segment vibration frequency |
| $\eta_x(T)$ | Segmental specific heat featured by the $\Theta_{DX}$ and its integral that is proportional to the bond energy $E_x$ |
| AFM | Atomic force microscopy |
| BOLS | Bond-order-length-strength correlation for undercoordinated atoms and molecules |
| CN | Coordination number |
| DFT | Density functional theory |
| DPS | Differential phonon spectrometrics |
| $d_x/E_x$ | O:H–O bond x segmental length and bond energy (x = L for the O:H and H for the H–O bond) |
| f(C) | Solute concentration C resolved volume or number fraction of the hydrogen bonds transiting from the vibration mode of ordinary water to hydration states |
| FTIR | Fourier transformation infrared absorption |
| FWHM | Full width at half maximum, $\Gamma$ |
| H↔H | Anti-HB due to excessive $H^+$ injection serves as a point beaker fragilizing the HB network |
| LBA | Local bond average approach features the Fourier transformation |
| MD | Molecular dynamics |
| NEXAFS | Near edge X-ray absorption fine structure spectroscopy, XAS |
| $n_H(C)$ | Number of the first vicinal hydrating $H_2O$ dipoles |
| O:⇔:O | Super-HB due to excessive lone pair injection serves as a point compressor and polarizer |
| O:H–O | Hydrogen bond (HB) coupling inter- and intramolecular interactions |

| | |
|---|---|
| $P_C/T_C$ | Critical pressure/temperature for phase transition |
| PIMD | Path-integral molecular dynamics |
| QS | Quasisolid phase bounded at (−15, 4) °C due to O:H–O segmental specific heat superposition, which disperses under external perturbation |
| S/CIP | Separated/contacted ion pair |
| SFG | Sum frequency generation spectroscopy |
| STM/S | Scanning tunneling microscopy/spectroscopy |
| t-2DIR | Time-resolved two-dimensional infrared absorption |
| $T_m/T_N$ | Melting/freezing temperature closing to the intersections of segmental specific-heat curves and dominated by the $E_H$ /$E_L$ |
| VLEED | Very-low energy electron diffraction |