

第 6 回極限物質科学研究会
The 6th Workshop for Extreme Materials Science
“Water and Ice”

Date: 13:30-17:00 Jan. 18th (Fri), 2019.

2019年1月18日(金) 13:30-17:10

Place: Small Meeting Room 1(west), Welfare and Conference Bldg. (C61), Riken, Wako.

理研和光 統合支援施設小会議室1(西)建物番号C61

http://www.riken.jp/en/access/wako-map/#campus_map

Organizers: Tsutomu Kawatsu (tsutomu.kawatsu@riken.jp), Toshiaki Iitaka (tiitaka@riken.jp)

Participation: Free

Sponsor: **Post-K Computer Challenging Problems, “Challenge of Basic Science”**,

Subproject C “Structure and Properties of Materials in deep Earth and Planets”

ポスト「京」萌芽的課題「基礎科学の挑戦」

サブ課題C「地球惑星深部物質の構造と物性」

<http://www.iitaka.org/~xmat/en/>

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Scope

Water is one of the most important components to discuss the evaluation of the Earth and planetary systems. The water can be gas (vapor), liquid, and solid (ice) on the ground surface of current Earth, and the eighteen ice phases are reported under various pressure-temperatures. In this meeting four distinguished researchers will talk about their recent experimental and theoretical study on water and ice.

Program

13:30-13:40 Toshiaki IITAKA: Opening

13:40-14:40 Chang Qing SUN (孙长庆) (Nanyang Tech.) 【INVITED】

O:H–O bond transition by aqueous charge injection

http://research.ntu.edu.sg/expertise/academicprofile/Pages/StaffProfile.aspx?ST_EMAILID=ECQSUN

<https://scholar.google.com/hk/citations?user=M6d5ZQsAAAAJ&hl=en>

(Break 10 min)

14:50-15:30 Ryo YAMANE (山根峻) (Univ. of Tokyo) 【INVITED】

High-pressure dielectric measurements of ice VII using a newly developed high-pressure cell

<http://www.eqchem.s.u-tokyo.ac.jp/laboratories/kagi/Homepage/member.html>

<https://aip.scitation.org/doi/10.1063/1.4980154>

(Break 20 min)

15:50-16:30 Hiroshi FUKUI (福井宏之) (Univ. of Hyogo) 【INVITED】

X-ray Induced molecular dissociation of H₂O in dense ice

https://www.researchgate.net/profile/Hiroshi_Fukui2

<https://www.nature.com/articles/srep26641>

16:30-17:10 Tsutomu KAWATSU (河津励) (RIKEN) 【INVITED】

A computational study of the protonic quantum fluctuations on the high-pressured hydrogen bond of the ice and hydrous alumina

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https://www.researchgate.net/scientific-contributions/2082167612_Tsutomu_Kawatsu

Closing

O:H–O bond transition by aqueous charge injection

Chang Q Sun¹

This presentation shows that charge injection in forms of electrons, protons, lone pairs, ions, and molecular dipoles by solvation mediates the O:H–O (or HB) bonding network and properties of a solution through O:H formation, H \leftrightarrow H fragilization, O: \leftrightarrow :O compression, electrostatic polarization, H₂O dipolar shielding, solute-solute interaction, and undercoordinated solute H–O bond contraction [1-3]. A combination of the O:H–O bond cooperativity notion [4] and the differential phonon spectrometrics (DPS)[5] has enabled quantitative information on the following: (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; and, (iii) interdependence of skin stress, solution viscosity, molecular diffusivity, solvation thermodynamics, and critical pressures and temperatures for phase transitions. A systematic examination of solvation dynamics has clarified the following: (i) The excessive protons create the H \leftrightarrow H (H₃O⁺·4H₂O), or anti-HB point breaker, to disrupt the acidic solution network and surface stress. (ii) The excessive lone pairs generate the O: \leftrightarrow :O (HO⁻·4H₂O), or super-HB point compressor, to shorten the O:H nonbond but lengthen the H–O bond in basic solutions; yet, bond-order-deficiency shortens and stiffens the H–O bond due OH⁻ solutes. (iii) Ions serve each as a charge center that aligns, clusters, stretches and polarizes their neighboring HBs to form hydration shells screened by the hydrating H₂O molecules. Anion-anion repulsion comes into play reducing the hydration volume with solute concentration, yet cations retain their hydration volumes because of the fully-screened electric fields by the ordered solvent crystals.



CQ Sun received his PhD in Physics at Murdoch University in 1996 and then joined NTU where he works presently. He has been working on the theme of *Extraordinary Coordination Bonding and Nonbonding Electronics* and 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 *The Attribute of Water: Single Notion, Multiple Myths*, Springer 2016; *Relaxation of the Chemical Bond*, Springer 2014 and their Chinese versions, as well as 20 treatises published in *Chem Rev*, *Prog Mater Sci*, etc. He was bestowed with the Khwarizmi International Award in 2012.

1. Sun, C.Q., *Aqueous charge injection: solvation bonding dynamics, molecular nonbond interactions, and extraordinary solute capabilities*. International Reviews in Physical Chemistry, 2018(DOI: 10.1080/0144235X.2018.1544446).
2. Sun, C.Q., *Perspective: supersolidity of the undercoordinated and the hydrating water*. Physical Chemistry Chemical Physics, 2018(10.1039/C8CP06115G).
3. Sun, C.Q., *Perspective: O:H-O bond transition onto the O:=:O and H-H by lone pair and proton injection*. Physical Chemistry Chemical Physics, 2018. **revised**.
4. Huang, Y.L., et al., *Hydrogen-bond relaxation dynamics: Resolving mysteries of water ice*. Coordination Chemistry Reviews, 2015. **285**: p. 109-165.
5. Liu, X.J., et al., *Coordination-resolved electron spectrometrics*. Chemical Reviews, 2015. **115**(14): p. 6746-6810.

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Title: High-pressure dielectric measurements of ice VII using a newly developed high-pressure cell

Ryo YAMANE (Univ. Tokyo)

Abstract:

Ice has 18 polymorphs. They are classified into two groups, disordered and ordered ice, by site occupancies of their hydrogen atoms and these occupancies take 50 and 100% in disordered and ordered ice, respectively. The disordered and ordered states make a variety of ice polymorphs, and so that these states are notable structural and physical properties of ice.

Ice VII is a high-pressure disordered phase in a wide pressure region, from 2 GPa to 60 GPa, at room temperature. Pressure dependence of the disordered state of ice VII has long been studied, and it is known from dielectric measurements that the disordered state is dominated by orientation (or rotation) of H₂O in lower pressure region (below 5 GPa) [1]. In much higher pressure region (above 40 GPa), proton translation mainly induced by a quantum effect on O-H...O bond dominates the disordered state of ice VII [2].

Hernandez & Caracas recently reported from their DFT simulation that the rotational disordered state changes into the translational disordered state at around 15 GPa [3], where a number of measurements anomalies were reported, such as Raman scattering, X-ray diffraction, and electrical conductivity measurements [4,5,6]. Pruzan et al., who first reported the anomaly in [4], also suggested a scenario of the transition of ice VII disordered state from their Raman scattering anomaly in [1]; FWHM of symmetry stretching mode of H₂O had a minimum at around 11 GPa.

In order to confirm the disordered state transition, dielectric measurement would be an effective experimental method because the H₂O rotation and H translation, which is mainly induced by classical hopping at around the anomalous pressure region, occur in time scale of 10⁻⁶ – 10³ s [7] and the time scale is appropriate for dielectric measurements without considering difficulties of dielectric measurements under high pressure.

In the presentation, I will show results of high-pressure dielectric measurements of ice VII up to 12 GPa with technical developments of newly developed high pressure cell.

[1] P. Pruzan et al., *Journal of Chemical Physics*, **99**, 12 (1993)

[2] E. Sugimura et al., *Physical Review B*, **77**, 214103 (2008)

[3] J. Hernandez and R. Caracas, *Journal of Chemical Physics*, **148**, (2018)

[4] P. Pruzan et al., *Europhysics Letters*, **13**, 81 (1990)

[5] M. Somayazulu et al., *Journal of Chemical Physics*, **128**, 064510 (2008)

[6] T. Okada et al., *Scientific Reports*, **4**, 5778 (2014)

[7] E. Pettinelli et al., *Reviews of Geophysics*, **53**, 593 (2015)

X-ray Induced molecular dissociation of H₂O in dense ice

Hiroshi Fukui

Graduate School of Material Science, University of Hyogo, Japan

Water ice exhibits various thermodynamically stable and metastable phases at temperatures up to 2000 K and pressures up to 100 GPa [1]. At high pressures above 2 GPa, ice has high-density packing structures consisting of interpenetrating diamond-like sublattices, in which each oxygen atom is surrounded by eight nearest neighbors but is connected to only tetrahedrally coordinated four neighbors with hydrogen bonds. Ices with a body-centered sublattice of oxygen atoms are called dense ices; they are ice VII, ice VIII, and ice X.

Ice VII undergoes photochemical reaction or dissociation of H₂O molecules by irradiation of intense 10-keV X-ray [2]. The dissociation yield was found to have a maximum at 14 GPa [3]. Some anomalies were reported to occur at around this pressure. One of them is the maximum of electric conductivity [4]. From the similar pressure dependence of the electric conductivity to the dissociation yield, it is expected that the mobility of hydrogen (or proton) in the oxygen sublattice of dense ice is strongly related to the x-ray induced molecular dissociation. A recent progress to measure temperature dependence of the dissociation will be presented in the workshop.

[1] Chaplin, M. Water phase diagram, In *Water Structure and Science* (2000).

http://www1.lsbu.ac.uk/water/water_phase_diagram.html (Accessed on 4th of January 2019).

[2] Mao, W. L. *et al.*, *Science* **314**, 636 (2006).

<https://doi.org/10.1126/science.1132884>

[3] Fukui, H. *et al.*, *Sci. Rep.* **6**, 26641 (2016).

<https://doi.org/10.1038/srep26641>

[4] Okada, T. *et al.*, *Sci. Rep.* **4**, 5778 (2014).

<https://doi.org/10.1038/srep05778>

A computational study of the protonic quantum fluctuations on the high-pressured hydrogen bond of the ice and hydrous alumina

Tsutomu Kawatsu

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The ice is characterized by the hydrogen bond and its networks. Each water molecule typically has four hydrogen bonds; two hydrogen donors and two acceptors in ice. The ice has various phases depending on the pressure and temperature and these are numbered using Roman numerals in the order reported. The Ice VII and X, which are high-pressure phases of the ice, have similar structure of the oxygen atom order, however, different for the position of the hydrogen and the symmetry of the hydrogen bond. Under the lower pressure condition, Ice VII appears and has an asymmetric hydrogen-bond structure, and Ice X at extreme higher pressure has a symmetric hydrogen bond [1].

Hydrous alumina, δ -AlOOH is a phase of minerals known as diaspore and böehmite [2] at high temperature and high pressure. The material was catalyzed in laboratory and suggested to be produced on subducting slab in the Earth's interior [3]. It has similar hydrogen-bond structure to Ice VII and Ice X and similar phase transition in lower pressure region [2,3] and can be a model system of the Ice VII-X.

The path integral molecular dynamics (PIMD) method [5] includes the effect of quantum fluctuations of atomic coordinates, and the first principle PIMD method can treat the hydrogen-bond recombination. We used Shiga's "PIMD" program [6] for PIMD method with Quantum Espresso 6.0 package [7], on-the-fly, for the density functional calculations with PAW potential for rectangular cells including two water molecules for ice and two pairs of AlOOH for δ -AlOOH, respectively. In present study, we calculated the structure of ice VII-X and δ -AlOOH models in various pressures. We focused on the hydrogen-bond structure and the protonic quantum fluctuation on the hydrogen bond: The region where the proton is confined are determined by the symmetric-asymmetric transition of the hydrogen-bond structure in pressures, and the region determines the zero-point vibrational energy of the proton.

[1] E. Sugimura et al., Phys. Rev. B, **77**, 214103 (2008).

<https://doi.org/10.1103/PhysRevB.77.214103>

[2] T. Kuribayashi, et al., Phys. Chem. Minerals., 41, (2014), 303.

<http://dx.doi.org/10.1007/s00269-013-0649-6>

[3] A. Sano, et al., Geophys. Res. Letts., 35, (2008), L03303.

<http://dx.doi.org/10.1029/2007GL031718>

[5] M. E. Tuckerman, et al., J. Chem. Phys., **99**, 2796 (1993)

<https://doi.org/10.1063/1.465188>

[6] <http://ccse.jaea.go.jp/ja/download/pimd/index.en.html>.

[7] <http://www.quantum-espresso.org>