H₂O Under Pressure

Russell J. Hemley

Geophysical Laboratory
Carnegie Institution of Washington
Washington, DC

Workshop on Fundamental Challenges in our Understanding of the Physics and Chemistry of Water, January 16-17, 2015
High-pressure behavior of water continues to present new questions and surprises

- Origin of stability?
  - ~20 stable and metastable phases

- Novel transitions?
  - non-molecular
  - amorphization
  - superionic
  - liquid/liquid trans

- High P-T fluid?

- Electronic prop.?

- New chemistry?

- Breakdown of H₂O?

- Supporting life at extreme P-T?
Mission: To accelerate the discovery and synthesis of new energy materials using extreme conditions

Carnegie:
- Director: R. J. Hemley
- Assoc. Director: T. S. Strobel
- Admin. S. Gramsch, M. Phillips

University Partners:
- Penn State: J. Badding, N. Alem, Crespi
- Cornell: R. Hoffmann, N. Ashcroft
- Colorado School Mines: C. Taylor
- Caltech: B. Fultz
- Lehigh: K. Landskron

DOE Facilities
- APS, ANL (X-ray)
- SNS, ORNL (Neutron)
- NSLS II, BNL (IR)
Continuing puzzles in ice VII

- O atoms lie on bcc lattice
- Two interpenetrating ice Ic lattices
- Retains tetrahedral motif seen in lower pressure ice phases
- Predicted H-bond symmetrization

[Kamb & Davis, PNAS (1964)]
Continuing puzzles in ice VII

- **Nature of the proton ordering**

- **Structural transitions observed in ice VII**

- **Is there a ferroelectric form?**
- **Higher P-T behavior?**

Ice VII proton disordered

Ice VIII anti-ferroelectric

Hypothetical polar ice VIII (ferroelectric)
Ferroelectricity in dense H$_2$O

- AFE-FE nearly degenerate
- Fit to x-ray data
- Mixed domains of FE and AFE
- Stabilized by pressure and epitaxial growth?

[Caracas & Hemley, to be published]
Water splitting in dense ice

THEORY: ‘When is H$_2$O not water?’


• Molecular alloy of H$_2$-O$_2$
• Metastable energetic material
• Similar results found for NH$_3$
  [Lazor *et al.*, to be published]
• Mechanism not understood

X-ray-induced reaction

Hard (>7 keV) x-ray photons
Improved measurement of high $P$-$T$ melting

[Ahart et al., *High Pressure Res.* (2014)]

- Clear melting signature
- $v_s$ (eos) for high $P$-$T$ liquid
- High P-T relations, structures, dynamics?
Neutron scattering at extreme $P-T$ conditions

- Underutilized (compare x-ray)
- Low-Z cross sections (e.g., D)
- Extensively used at low $P-T$
- Previous limit 27 GPa
  - [Guthrie, Ph.D. thesis (2002)]
- Transitions at higher pressure

SNAP: Spallation Neutrons at Pressure

C. A. Tulk
A. M. dos Santos
J. Moliason

SNAP’s dedicated high pressure diffractometer, came online 2006

Highly versatile: can study single crystals, powders, liquids
New cell designs of high-pressure neutron scattering

Enhancing sample volume

[Boehler et al., High Pressure Res. (2013)]
Neutron diffraction of ice VII (300 K)

- Excellent S/N to 50 GPa
- Shifts in positions and intensities

D$_2$O ice VII

0.05 mm$^3$

(6 hour datasets)

~50 ug sample!

5.3 GPa

43 GPa

[Guthrie et al., PNAS (2013)]
Failure of the conventional model for ‘proton centering’

- Rietveld refinement
- Low pressure data agree well with previous work
- Abrupt reduction in quality of fit above 25 GPa

Observed intensities consistent with scattering density in the octahedral voids of O lattice

[Guthrie et al., PNAS (2013)]
Interstitial protons in ice VII above 30 GPa (300 K)

- Not reproduced by DFT calculations (classical nuclei)
- Quantum diffusion? (path integrals?)
- Improved theory or other models?

[Guthrie et al. PNAS (2013)]
Partial dissociation to form additional defects

*MD DFT-GGA (50 GPa, 300 K)*

- Partial breakdown of $\text{H}_2\text{O}$
- $\text{H}_3\text{O}...\text{OH}$ defects
- H-H-O-H molecules

[Caracas et al. *in preparation*]
Interstitial protons and superionicity

(Meta)stability of interstitial H defects at high temperatures

300 K: Interstitial H defect?

1000 K: Melt/ Superionic?

Need confirmation by neutron scattering

MD DFT-GGA (50 GPa, 300 K)

[Caracas et al. in preparation]
Ultrahigh-pressure phases of $\text{H}_2\text{O}$: theoretical predictions

[Militzer et al. Phys. Rev. Lett. (2010); see also Caracas, ibid. (2008); Hermann et al., PNAS (2012)]
Neutron diffraction at megabar pressures

Increase sample volume by x100 at 100 GPa
(10^{-4} \text{ mm}^3 \text{ to } \sim 2 \times 10^{-2} \text{ mm}^3)

[Boehler et al., High Pressure Res. (2013)]
Oxygen under pressure

ε-oxygen: \((O_2)_4\) clusters (>8 GPa)

Neutron scattering shows magnetic collapse

Hydrogen under pressure

‘Graphenic’ hydrogen at 230 GPa (phase IV)

Neutron diffraction of $D_2$ to 30 GPa (phase I)

[Glazkov et al., JETP Lett. (1988)]

Rotational disordered hcp
Novel Dense Molecular Compounds

**CH$_4$(H$_2$)$_4$**
33.4 wt% H$_2$


**(H$_2$O)$_2$H$_2$**
α-quartz-type

[Strobel et al., J. Phys. Chem. (2011)]

**(H$_2$S)$_2$H$_2$**
Al$_2$Cu type


**H$_2$O-H$_2$**
11.3 wt% H$_2$


**Xe(H$_2$)$_7$**
Insulating to >255 GPa

[Somayazulu et al., Nature Chem. (2009)]

Higher pressure: Superconductor: $T_c = 190$ K (!)

[Eremets et al., to be published]
A bright future for studies of the behavior of water under extreme conditions
## ACKNOWLEDGEMENTS

### Collaborators

**CARNEGIE INSTITUTION**
- Reini Boehler
- Ivan Naumov
- Guoyin Shen
- Viktor Struzhkin
- Timothy Strobel
- Zhenxian Liu
- Yingwei Fei
- Zhenxian Liu
- S. Michida
- M. Somayazulu
- Ronald E. Cohen
- Ho-kwang Mao
- Muhetaer Aihaiti
- Stephen Gramsch
- Changsheng Zha
- Kuo Li
- S. Sinogeikin

**OTHER INSTITUTIONS**
- Chris Tulk (ORNL)
- Jamie Molaison (ORNL)
- A.M. dos Santos (ORNL)
- N. Pradhan (ORNL)
- Razvan Caracas (Lyon)
- Neil Ashcroft (Cornell)
- Roald Hoffman (Cornell)
- A. Hermann (Cornell)

### Financial Support

- DDOE/SC/BES, DOE/NNSA, A. P. Sloan Foundation, N.S.F., Carnegie Institution