First Principles Studies of Aqueous Solutions at Ambient and Extreme Conditions

Viktor Rozsa

CELEBRATING SSGF 15 YEARS

THE UNIVERSITY OF CHICAGO

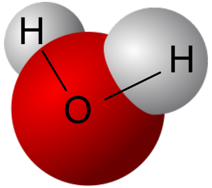
PRITZKER SCHOOL OF MOLECULAR ENGINEERING
THE UNIVERSITY OF CHICAGO

Outline

- **Motivation**
- **Strategies for Computational Modeling of Water**
- **4 Vignettes about water**
  - Statistically robust studies on monovalent ions in bulk water
  - Pure water and solvated ions confined in carbon nanotubes
  - First principles spectroscopy and conductivity of water under high pressure/temperature
  - Characteristics of ion solvation under high pressure/temperature
- **Conclusions**

Motivation: Why water?

- **Importance of water:**
  - Most abundant substance on Earth, necessary ingredient to all life, key to industrial processes, geophysical systems. Deep cultural and geopolitical significance



- **Uniqueness of water:**
  - Universal solvent, increased density upon melting, high viscosity, high surface tension, density maximum
- **How do perturbations affect its properties?**
  - Solvation of ions
  - Physical confinement
  - High pressure and temperature

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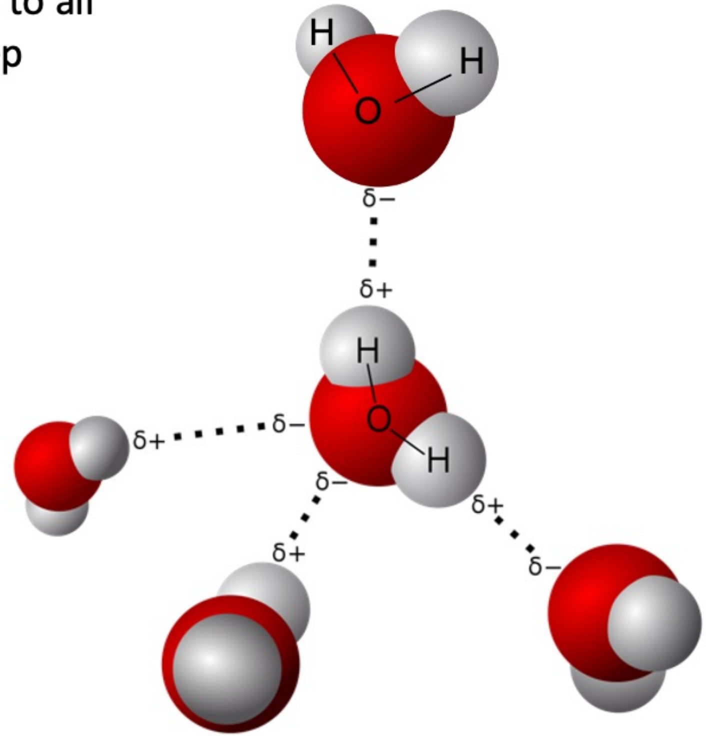
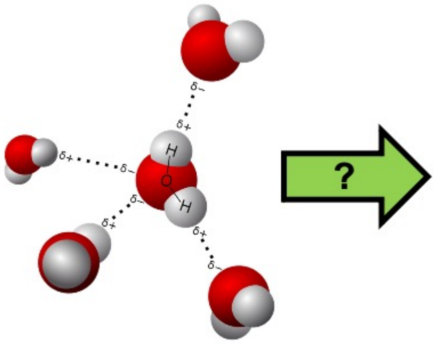


Computational Modeling of Water

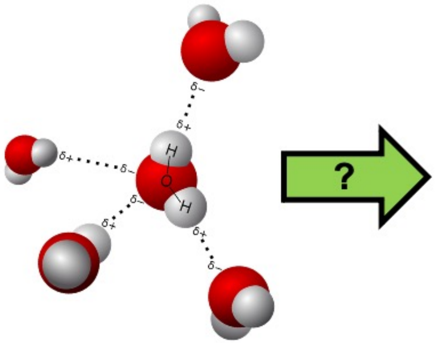


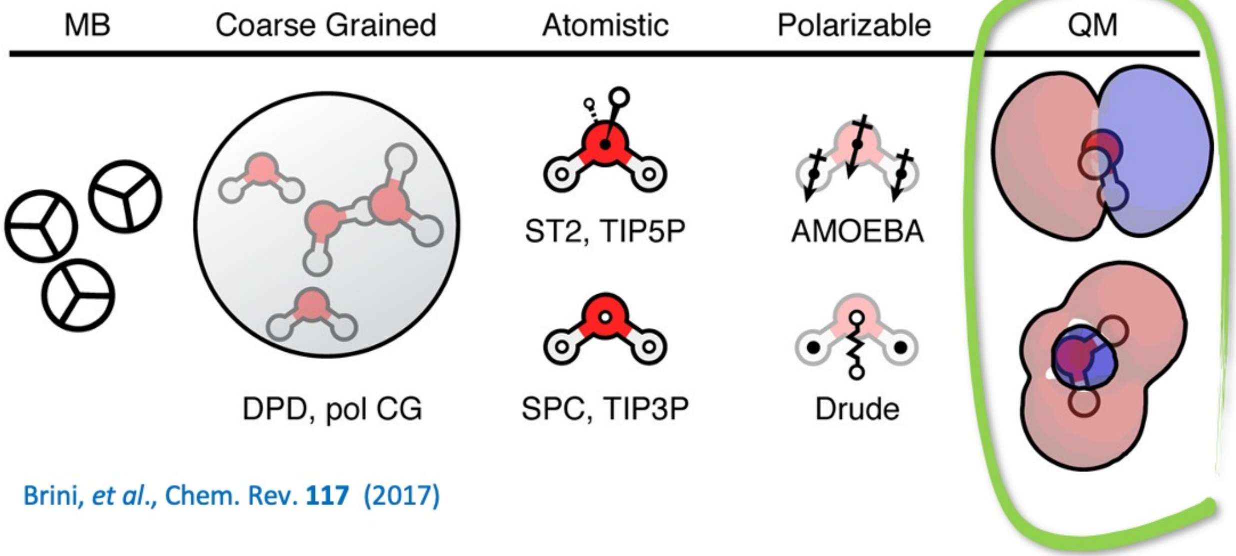
AVIDAC, 1953

El Capitan, 2023

- **Enduring challenge**: sufficiently capturing properties of water at feasible computational cost.
- **Early models:** Stillinger, Rahman (1971): tetrahedral charges on Lennard Jones sites
- **State of the art:** Quantum mechanical – properties of water are used as benchmark of new computational theories

Computational Modeling of Water





Brini, *et al.*, Chem. Rev. **117** (2017)

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Our Strategy: First Principles MD

- Need a method that captures subtle time-dependent information in water

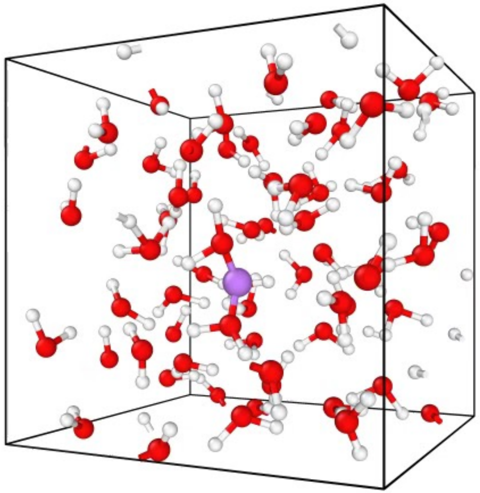
Molecular dynamics (MD):

$$-\frac{\partial E(\{\mathbf{R}_j\})}{\partial \mathbf{R}_i} = m_i \ddot{\mathbf{R}}_i$$

- Need theory that can account for polarizable environments, allows for bond breaking

Density Functional Theory:

$$H_{KS}\psi_i(\mathbf{r}) = \varepsilon_i \psi_i(\mathbf{r})$$



63 H2O w/ Li⁺ at 11 GPa, 1000 K

- Our strategy is the combination: **First Principles Molecular Dynamics**, as implemented in the Qbox code →

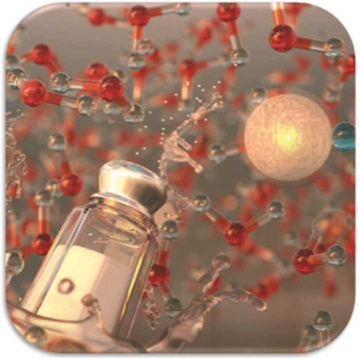
R. Car and M. Parrinello, Phys. Rev. Lett., **55**, (1985)

Qbox

http://qboxcode.org/

F. Gygi IBM J. Res. Dev. , **52**, (2008)

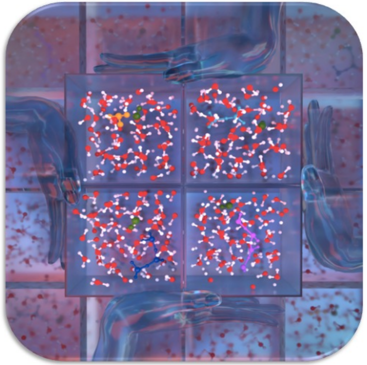
4 Vignettes about Water



Statistically robust studies on monovalent ions in bulk water

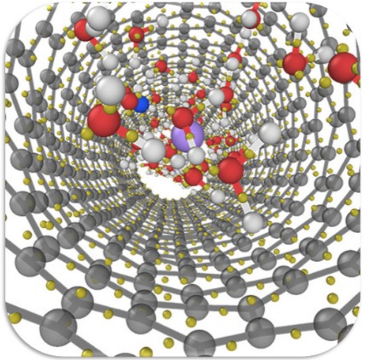
Rozsa *et al.*, J. Chem. Phys, **152** (2020)

Zeng, Rozsa, *et al.*, ACS Earth Space Chem., **3**, (2019)



Ab initio spectroscopy and ionic conductivity in water at high pressure and temperature

Rozsa *et al.*, PNAS, **115**, (2018)



Pure water and ion solutions under confinement in carbon nanotubes

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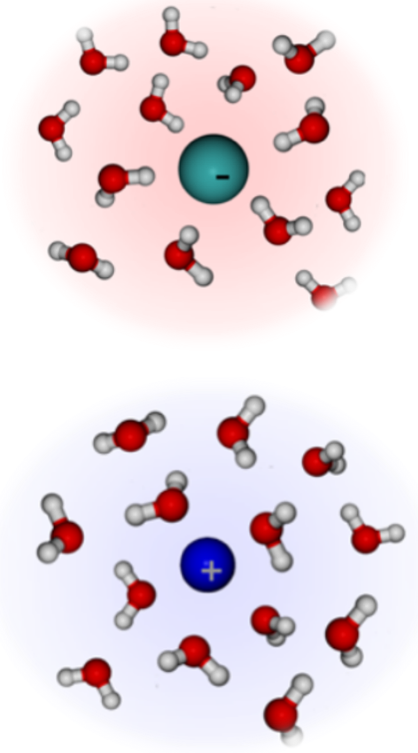
Ions in bulk Water: Motivation



- **Fundamental chemistry:** How does water's hydrogen bond network respond to perturbation due to ion solvation?
- **Extensive application**: biochemical processes, molecular engineering of energy materials

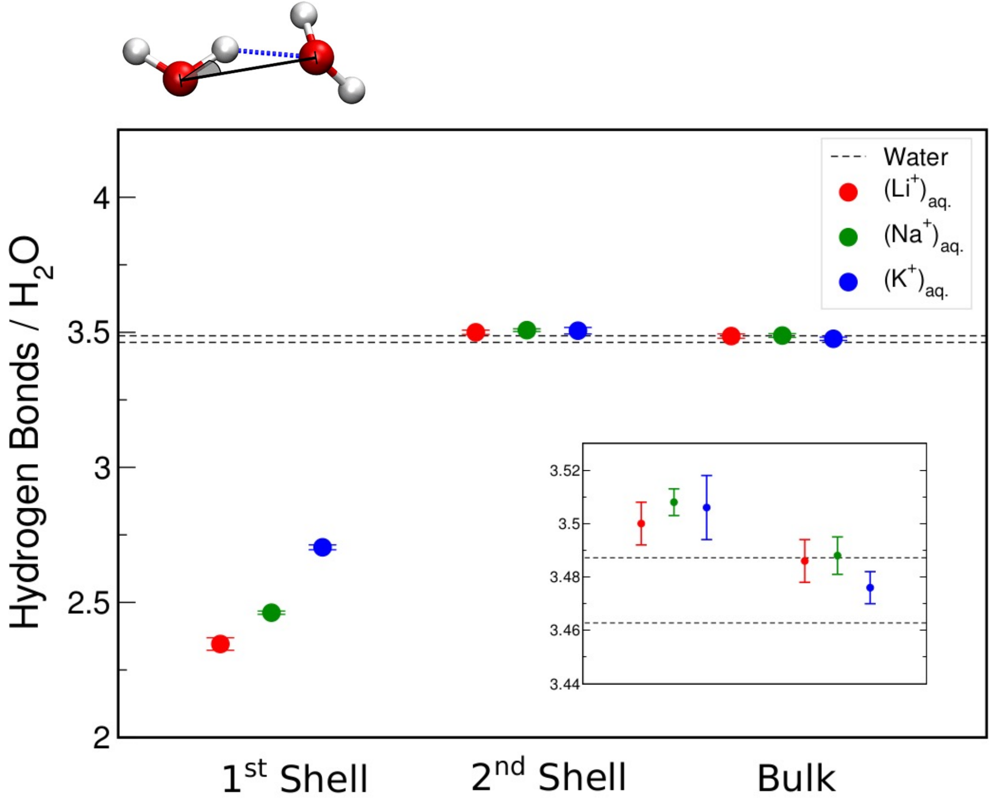
- **Long history in both experimental and computational literature:**
  - Relative consensus on local solvation properties
  - Controversies on long-range properties:

    \- Global effects: THz dielectric relaxation, neutron diffraction

    \- Local effects: fs-IR, X-ray absorption spectroscopy, Raman scattering

Gaiduk *et al.*, J. Phys. Chem. Lett. **8**, (2017)

Bulk Ions: Hydrogen Bonding

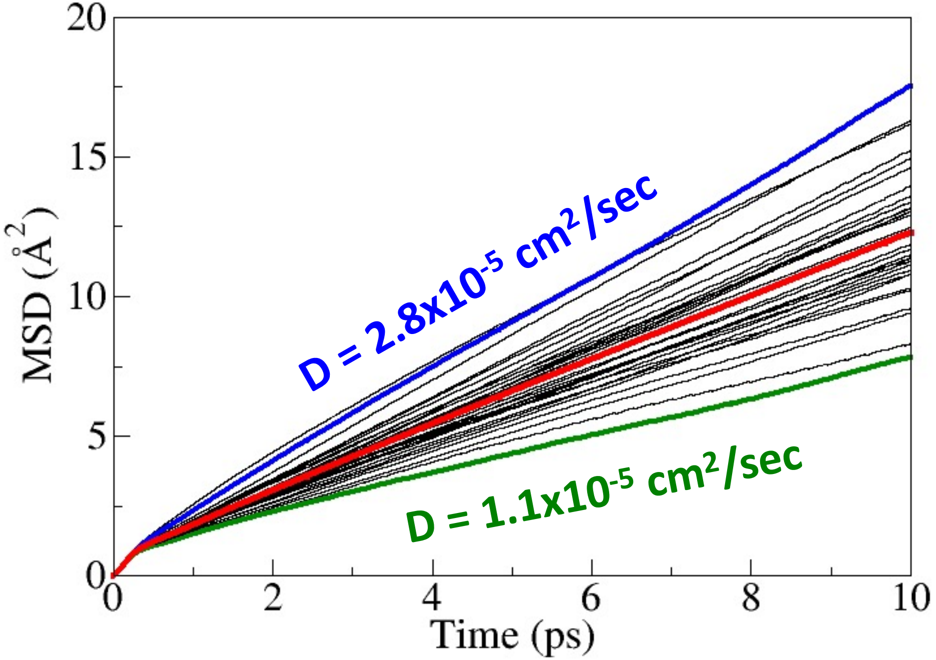


- Statistically robust (10 independent samples ~60 ps each) simulations of Li+, Na+, and K+ in PBE water
- Statistically significant H-bond density increase in 1st shell: **Li+** < **Na+** < **K+**
- No statistically significant H-bond differences in 2nd shell, or bulk
- None of Li+, K+, or Na+ are "structure maker/breaker" in bulk water (PBE model)

Rozsa *et al.*, J. Chem. Phys, **152** (2020)
Dawson *et al.*, J. Chem. Phys. **148**, (2018)

Bulk Ions: Diffusion

$$\mathrm{MSD} \equiv \langle (x - x_0)^2 \rangle = \frac{1}{T} \sum_{t=1}^{T} (x(t) - x_0)^2$$



Dawson *et al.*, J. Chem. Phys. **148**, (2018)

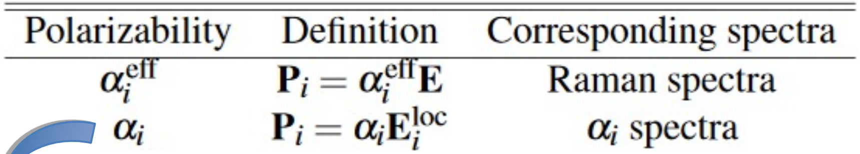
- 32 independent water trajectories @ PBE level, 400 K, ~60 ps each: **1.86 ns.** Average **D: 1.95(27) x10^{-5} cm^2/s**: (Error from "Students' T-test" w/ 95% confidence). Importance of **many independent runs** for sampling

- **Li+: D[O] = 1.90 (30)**
- **Na+: D[O] = 2.1 (34)**
- **K+: D[O] = 2.43 (39)**

- Cannot statistically conclude Li+, K+, or Na+ are "structure maker/breaker" from diffusion analysis in PBE water (contrary to previous reports)

Molecular Polarizability, α_i

- α_i is a measure of how sensitive molecular charge density is to applied electric fields



Polarizability	Definition	Corresponding spectra
α_i^{eff}	$\mathbf{P}_i = \alpha_i^{\mathrm{eff}}\mathbf{E}$	Raman spectra
α_i	$\mathbf{P}_i = \alpha_i\mathbf{E}_i^{\mathrm{loc}}$	α_i spectra

Earlier methods:

$$\boldsymbol{\alpha_i = \alpha_i^{eff} - \alpha_i^{DID}}$$

$$\mathbf{E}_i^{\mathrm{loc}} = \mathbf{E} + \sum_{i\neq j}\mathbf{T}_{ij}\mathbf{P}_j,$$

$$T_{ij}^{\mu\nu} = \frac{r_{ij}^2\delta_{\mu\nu} - 3r_{ij}^{\mu}r_{ij}^{\nu}}{r_{ij}^5},$$

DID interaction tensor computed using **ewald** technique

Wan et al, JCTC, (2014)

Method used here:

$$\boldsymbol{\alpha_i = \alpha_i^{eff} - \alpha_i^{Multipole}}$$

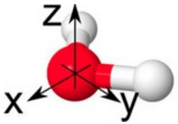
$$\vec{E}_{env} = \frac{1}{N_{orb}}\sum_{i}^{N_{orb}}\int \vec{e}'(\vec{r})|w_i(\vec{r})|^2 d\vec{r}\,,$$

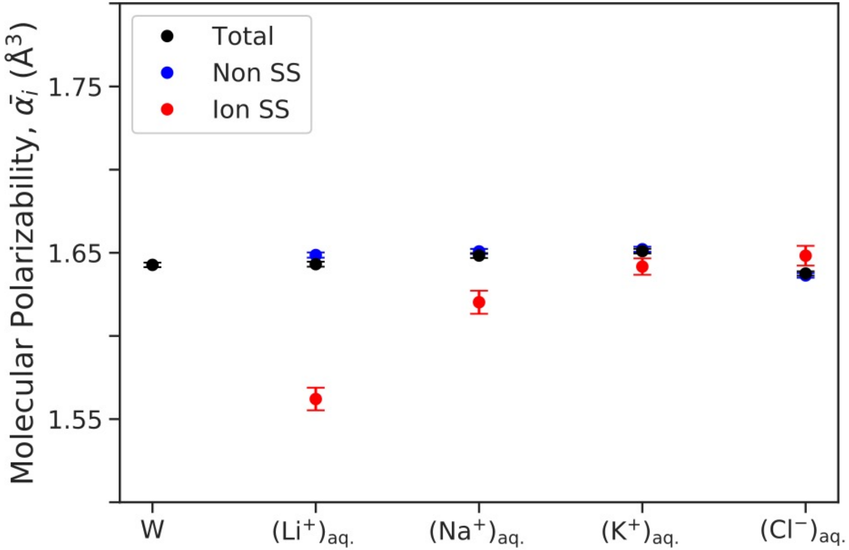
Computed using inverse dielectric matrix

Pan et al, J Chem Phys, (2018)

- Uses all multipoles in α_i , not just DID interaction
- No ewald summation, single SCF calculation

Molecular Polarizability, α_i





Rozsa *et al.*, J. Chem. Phys, **152** (2020)

- Molecular Polarizability, α_i computed as in Pan et al., J. Chem. Phys **152**, (2018)

- **Large sensitivity to local solvation shells:**
  - Cation solvation shells reduced: Li+ ~6%, Na+ ~2% and K+ ~1%

- Out of plane molecular polarizability, α_i^{POP} is most sensitive to H-bonding: largest changes

- **Verification and generalization** of conclusions of Gaiduk et al., J. Phys. Chem. Lett **15**, (2015)

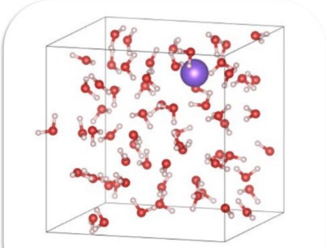
- Molecular polarizabilities are fingerprints of longer-range effect

Aqueous bulk ions: Conclusions

- Long timescale (1.5 ns total) AIMD simulations (@PBE) of H_2O+ monovalent cation solutions show that **while ions affect 1st solvation shell H-bonding, there is no bulk effect**
- None of Li+, Na+, or K+ affect solvated water's global diffusion in a statistically significant (95%) manner. **Diffusion is not a sensitive probe** of **global effects** of solvated monovalent cations at PBE level of theory.
- **Molecular polarizability is a sensitive probe** of ion effects in water, able to detect changes beyond the second solvation shell

- Aqueous K+ simulations also applied to isotopic fractionation study including K and Rb-rich minerals

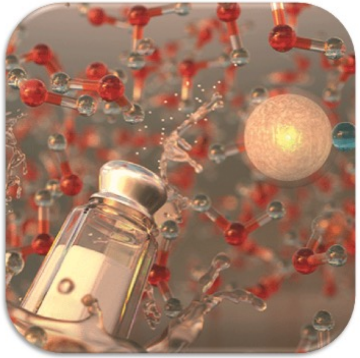
Lawrence Livermore National Laboratory



$[K(H_2O)_{63}]^+$

H. Zeng, V. Rozsa, et al., ACS Earth Space Chem. **3**, (2019)

4 Vignettes about Water



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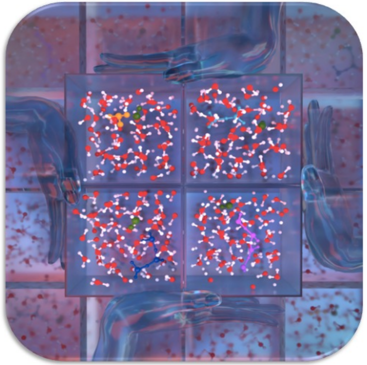

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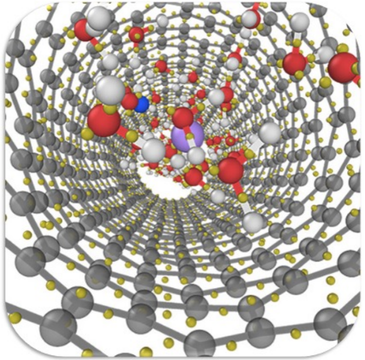

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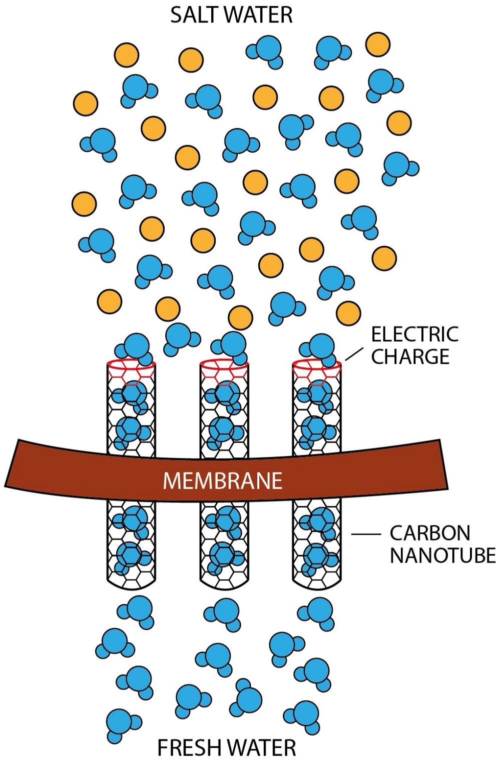
Confined Solutions: Motivation

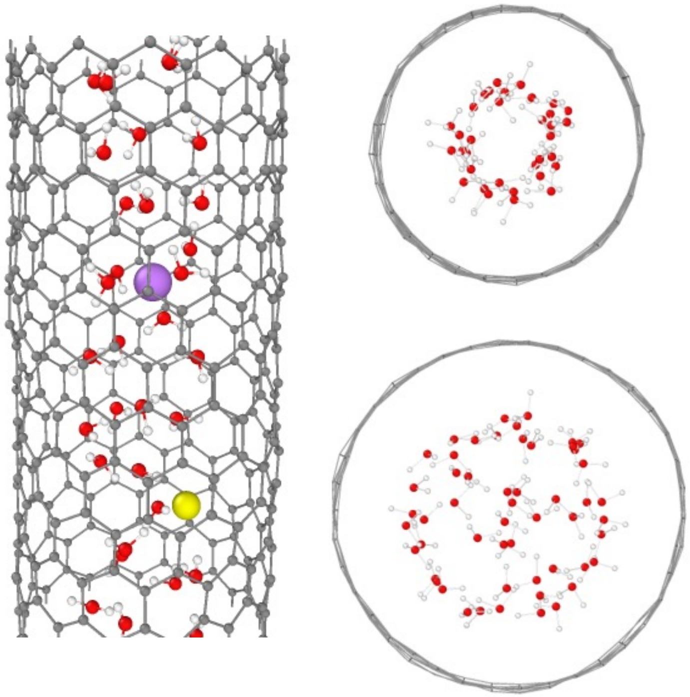


https://helix.northwestern.edu/article/freshwater-scarcity-and-future-filtration

- **Fundamental chemistry:** How does water's hydrogen bond network respond to perturbation due to confinement?
- **Extensive application**: bio capillaries, molecular engineering of desalination technology, molecular sensors, nanofluidics

- **Water's anomalies under confinement:**
  - Diameter-dependent phase transitions, including novel phases
  - Enhancements of water diffusion
  - Anisotropic dielectric properties
  - Effect of ions particularly unknown

Confined Solutions: Structure



1.1 nm
diameter CNT:
Pure, LiCl, KCl

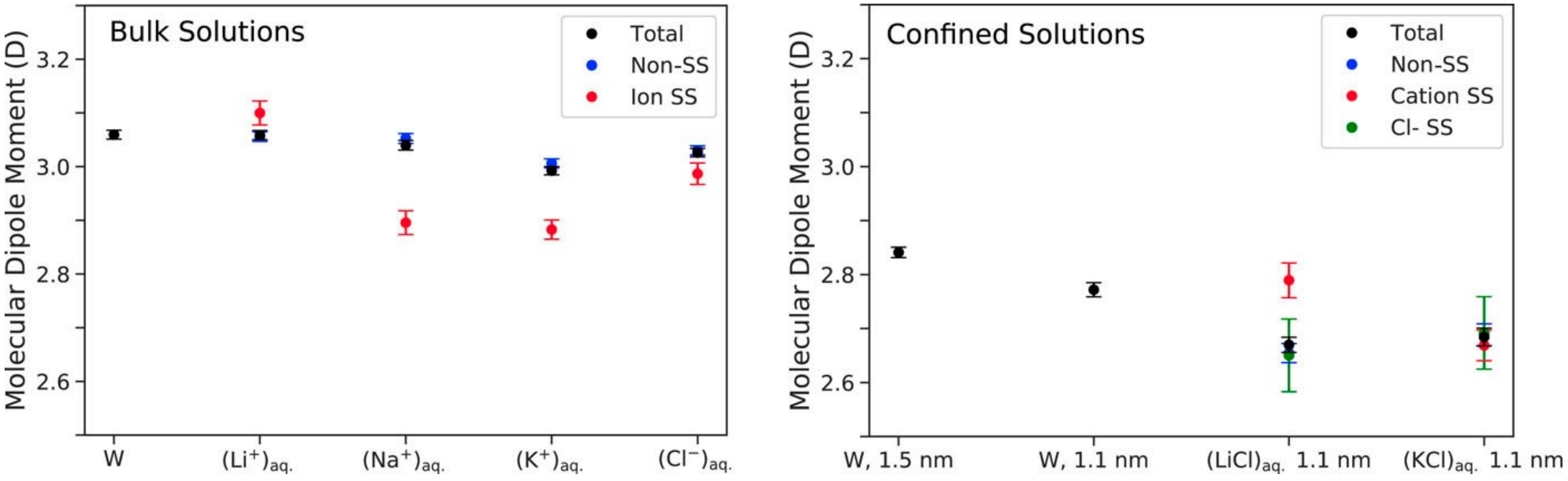
1.5 nm
diameter CNT:
Pure

- 1.1 nm confinement: cylindrical arrangement, with **void in center**
- 1.5 nm confinement: **occupied inner region**
- Ion residence in 1.1 nm solutions: All Li+, K+, and Cl- occupy space towards center of tube, with K+ being most interior
- Coordination shell changes:
  - Li+ SS maintains 4 coordination
  - Desolvation of K+, Cl- ions: decrease by ~1-2.

Rozsa *et al.*, J. Chem. Phys, **152** (2020)

Confined Dielectric Properties

Dipole Moment, μ_i



- **Dipole moments:** Reduced relative to bulk (9% and 7% for 1.1, 1.5 nm CNTs)
- **Molecular polarizabilities:** 3% enhanced relative to bulk for 1.1 nm, 1.5 nm unchanged. Degree of enhancement in ion solutions is greater
- **Radial dependence** of both effects… interfacial origin?

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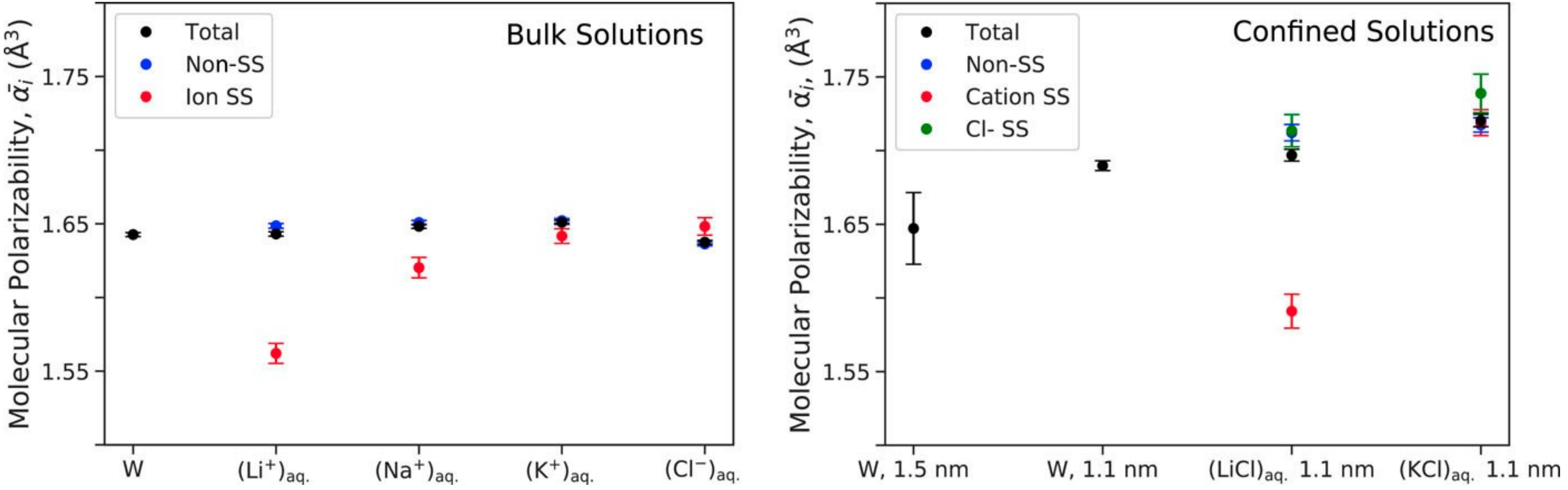

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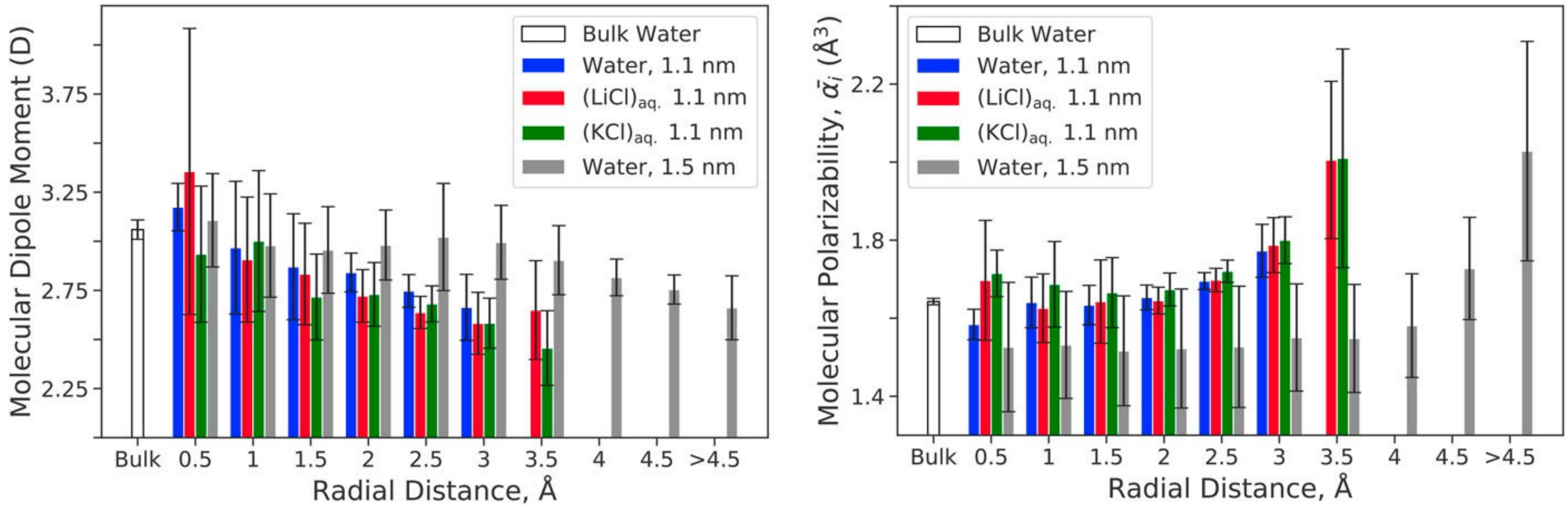
Confined Dielectric Properties

Radial dependence μ_i and α_i



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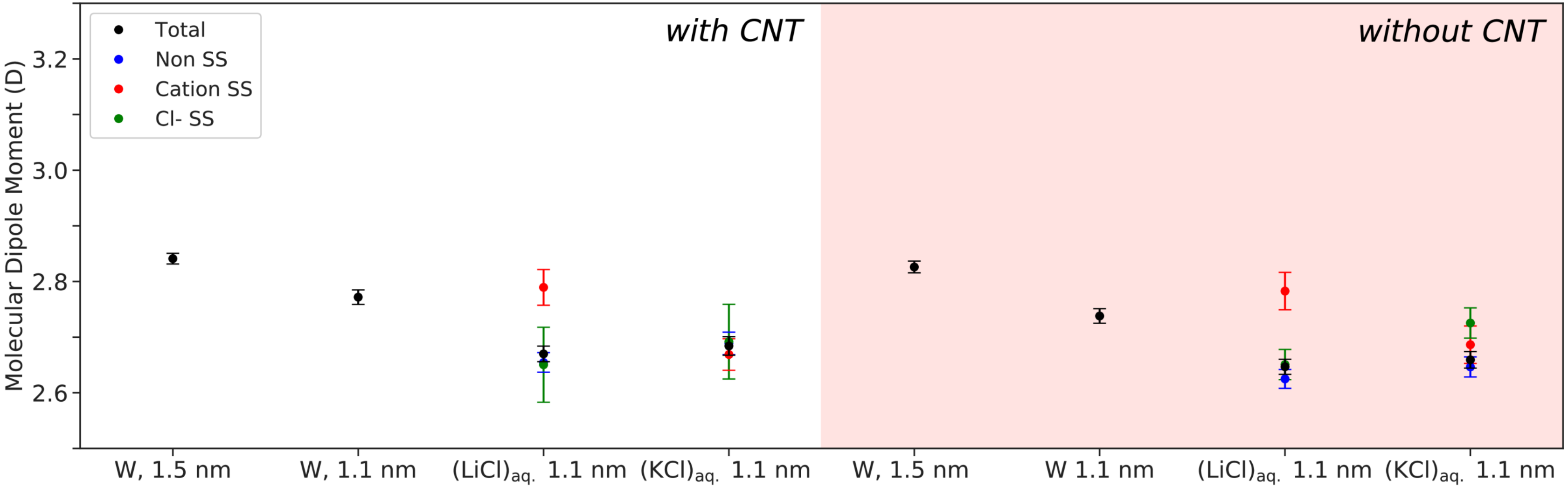

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- **Molecular polarizabilities:** effect of CNT is considerable. w/ CNT: enhancements to α in all solutions relative to bulk. w/out CNT: no enhancements in α_i , and even reductions relative to bulk
- **α_i :** competing effect of broken H-bonds (reduces α_i) and CNT interface (enhances α_i)

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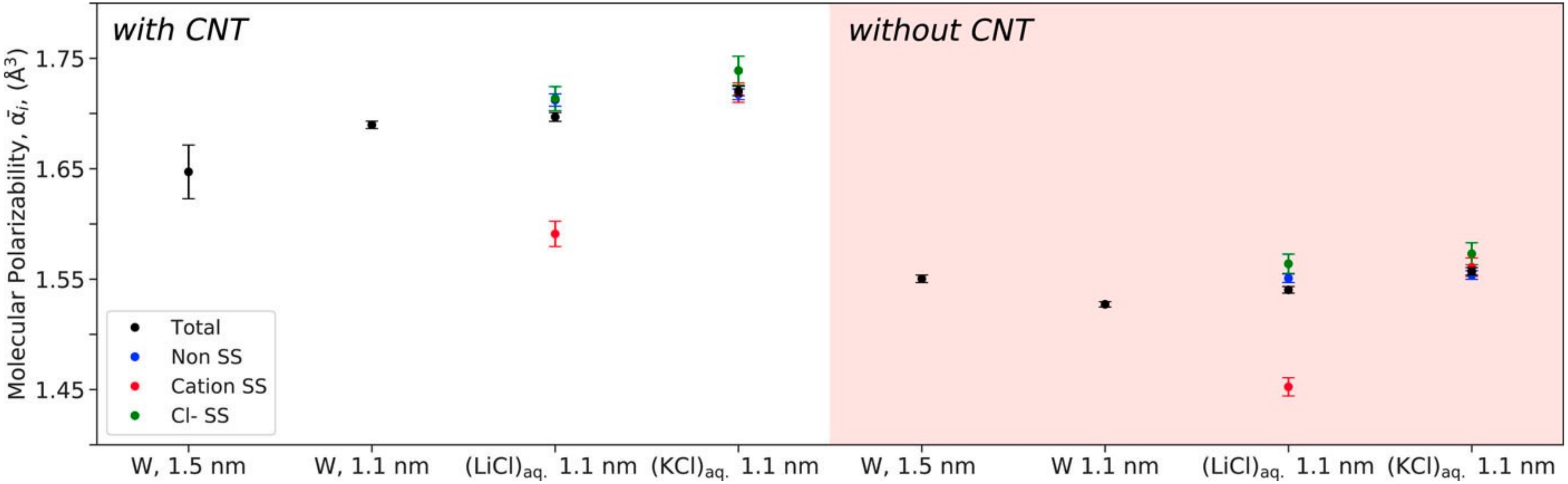

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Confined solutions: Conclusions

- Performed first principles simulations of pure water confined in CNT at 1.1 and 1.5 nm diameter. LiCl and KCl in water at 1.1 nm diameter, **verified structural behavior**
- Confinement has a **reducing effect on dipole moment**, and an **enhancement effect molecular polarizability,** which is radially dependent. Ions may amplify these effects confinement.
- Two **competing effects on molecular polarizability** under confinement: reduction due to broken hydrogen bonds and enhancement from the interaction of water with CNT interface.
- Demonstrate the usefulness of **molecular polarizability as a fingerprint to perturbations** due to confinement

Lawrence Livermore National Laboratory

Confined solutions: Conclusions

ions … CNT at 1.1

in w

AIP Scilight

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Nanoconfinement of salty water results in complex effects

Savannah Mandel

Quantum mechanical simulations reveal the effects of ions and nanoconfinement on the structural and electronic properties of water.

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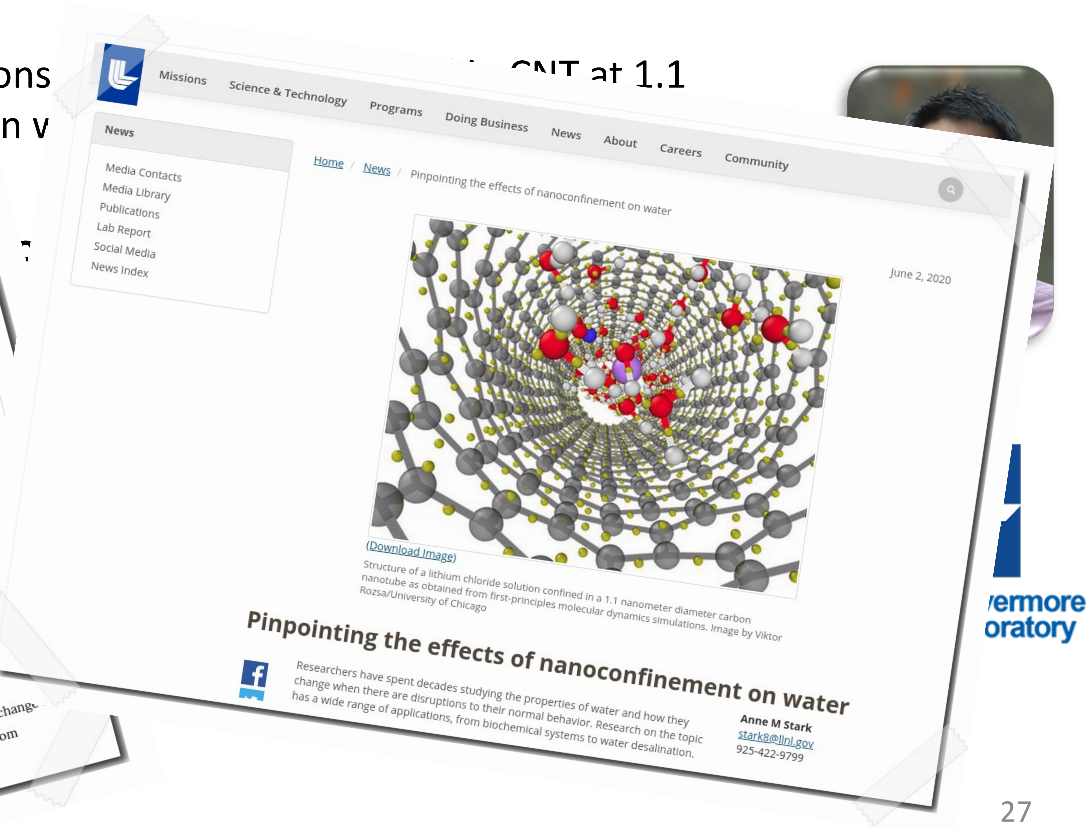
PPT | High-resolution

Researchers have spent decades studying the properties of water and how they change various perturbations. Research on the topic has a wide range of applications from … systems to water desalination.



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June 2, 2020

(Download Image)

Structure of a lithium chloride solution confined in a 1.1 nanometer diameter carbon nanotube as obtained from first-principles molecular dynamics simulations. Image by Viktor Rozsa/University of Chicago

Pinpointing the effects of nanoconfinement on water

Researchers have spent decades studying the properties of water and how they change when there are disruptions to their normal behavior. Research on the topic has a wide range of applications, from biochemical systems to water desalination.

Anne M Stark
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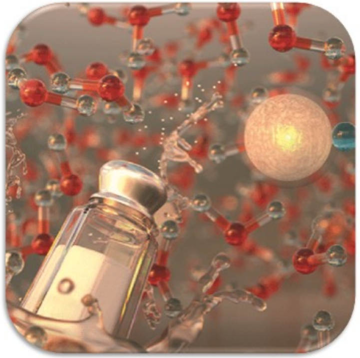
4 Vignettes about Water



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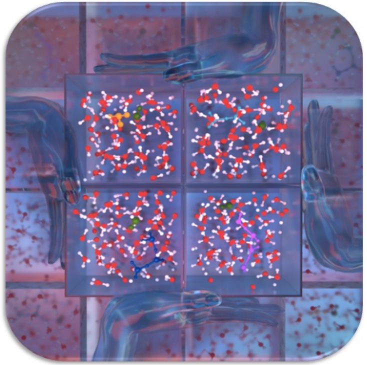

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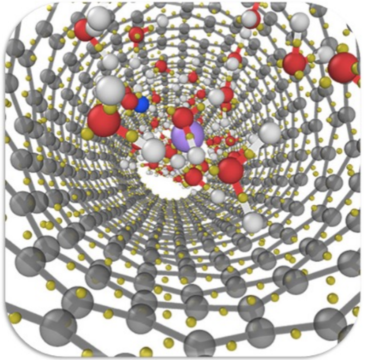

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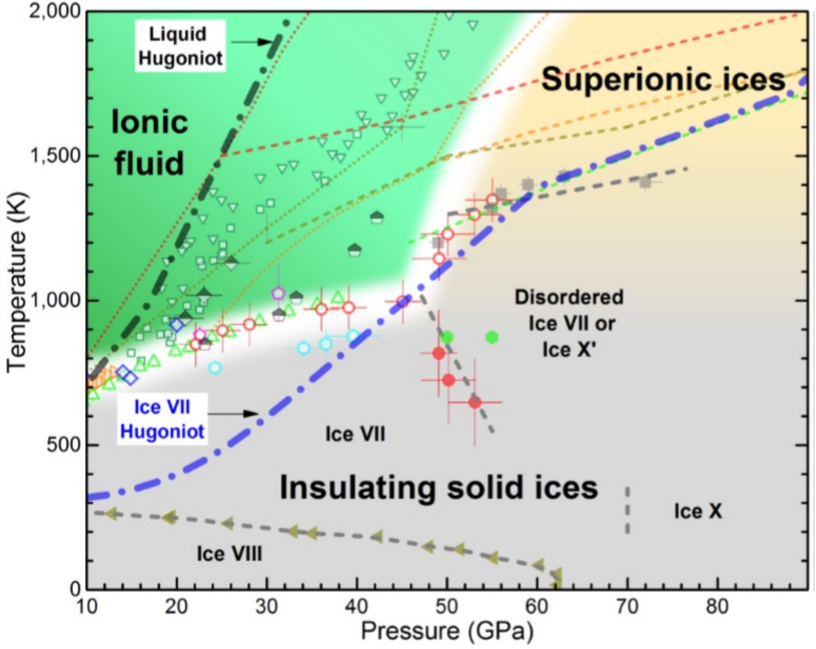
HPHT Water: Motivation



Millot *et al.*, Nat. Phys., **14** (2018)

- **Planetary science**: deep water, global carbon cycle, magnetic fields
- **Fundamental physics** of hydrogen-bonded systems at extreme conditions
- 18 known crystalline phases of ice
- **High-pressure, high-temperature region:**
  - Mixed, contradictory experimental results
  - Experimental tools: Raman, IR, Brillouin spectroscopy, Conductivity, Neutron scattering

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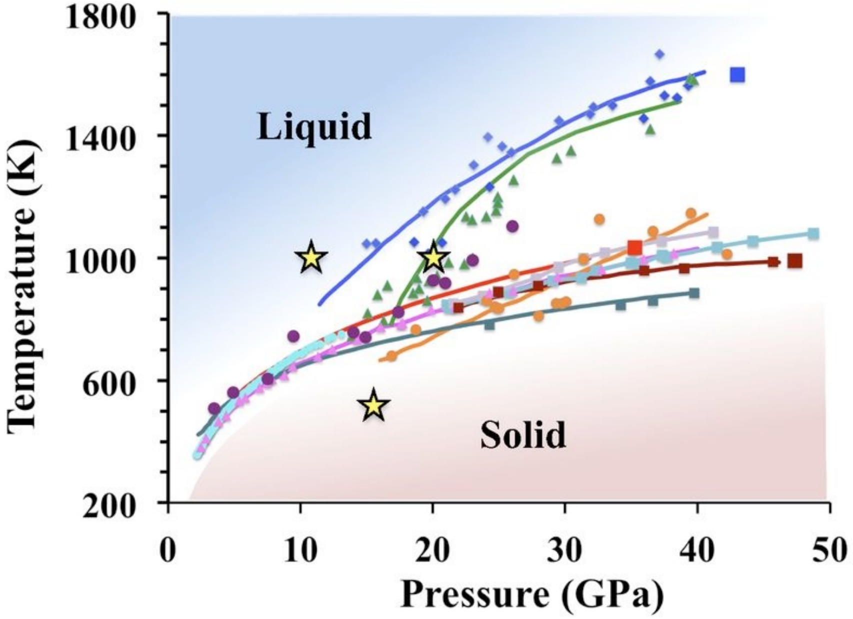

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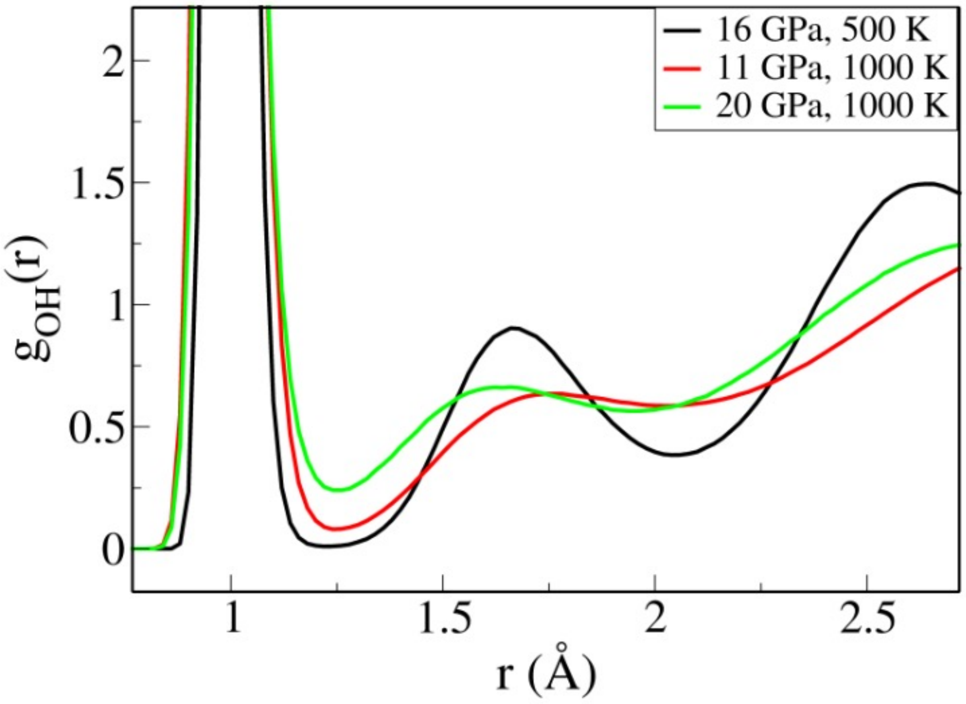
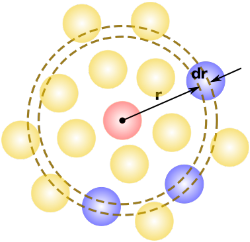
Effect of High P/T on structure



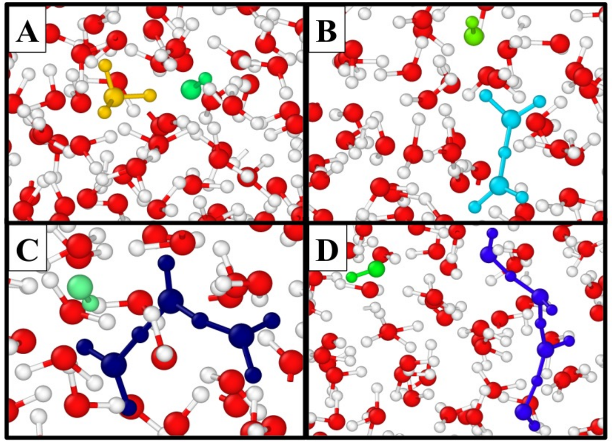
- O-H structure:
  - No large differences in covalent peak maximum
  - First peak minimum is signature of proton dissociation

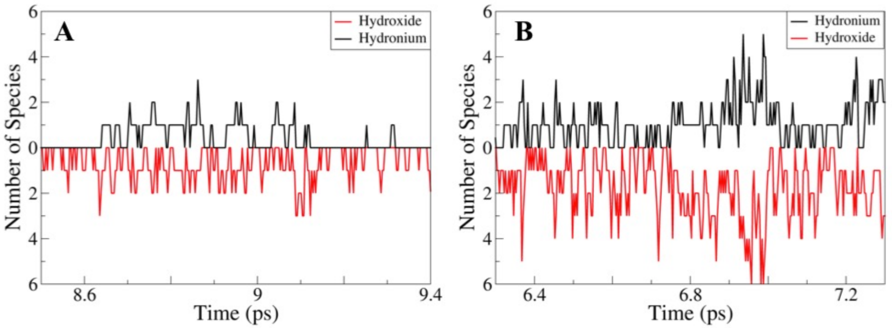


- O-MLWF indicates significant dissociation
- **Structural observations indicate molecular dissociation in both fluids,** with more occurring in 20 GPa than 11 GPa

Rozsa *et al.*, PNAS, **115** (2018)

Dissociative Species in High P/T Water





Rozsa *et al.*, PNAS, **115** (2018)

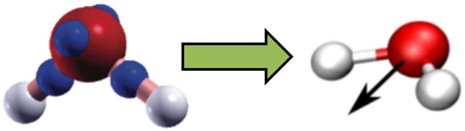
- Dissociation events lead to **exotic short-lived ionic species** (fs lifetimes) including hydronium/hydroxide, Zundel-like $H_5O_2^+$ species (cyan) with a nearby hydroxide. $H_7O_3^+$ species $H_7O_4^-$
- Dissociation is **never unimolecular**. Hydroxide/hydronium formations are highly correlated. We find **no free protons** in the fluid

First Principles Ionic Conductivity, σ

- Experimental measurements show large increases in conductivity, but first principles simulation has not fully explained the phenomena

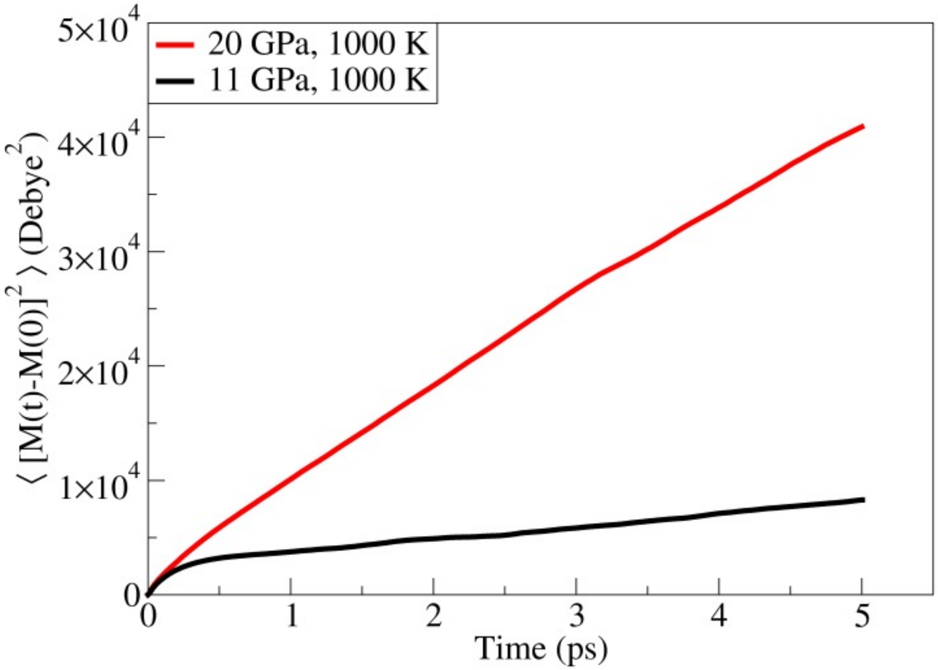
- We use here a **Green Kubo relation**, which is a general result describing the collective dissipative response of any system to a fluctuation. The sample dipole moment is computed with the aid of maximally localized Wannier centers (MLWFs)

$$\mathbf{M}(t) = e \cdot \sum_{i=1}^{N_H} \vec{R}_i^H(t) + 6e \cdot \sum_{i=1}^{N_O} \vec{R}_i^O(t) - 2e \cdot \sum_{i=1}^{N_{MLWF}} \vec{R}_i^{MLWF}(t)$$



$$\sigma = \frac{1}{3k_bTV}\int_0^\infty \langle \dot{\mathbf{M}}(0)\dot{\mathbf{M}}(t)\rangle dt \quad \Longleftrightarrow \quad \boxed{\sigma = \lim_{t\to\infty}\frac{1}{6tk_bTV}\langle[\mathbf{M}(t) - \mathbf{M}(0)]^2\rangle}$$

First Principles Ionic Conductivity, σ



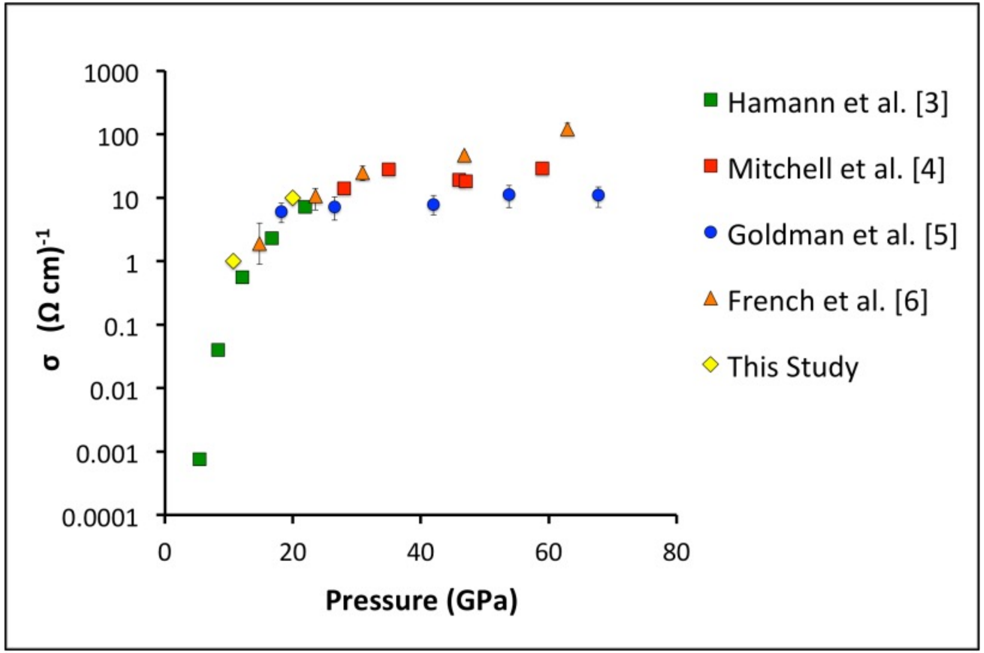
- We find large enhancements of ionic conductivity relative to ambient conditions:

  11 GPa, 1000 K: σ = ~1 $(\Omega\text{cm})^{-1}$
  20 GPa, 1000 K: σ = ~10 $(\Omega\text{cm})^{-1}$

- σ results are 6 and 7 orders of magnitude greater than to ambient water

- Computed σ values are consistent with experimental measurements of massive increase in conductivity

First Principles Ionic Conductivity, σ



[3] Hamann *et al.*, Trans. Farad. Soc., **62** (1966)
[4] Mitchell *et al.*, J. Chem. Phys*,* **76** (1982)
[5] Goldman *et al.*, J. Chem. Phys., **130** (2009)
[6] French *et al.*, Phys. Rev. B., **82** (2010)

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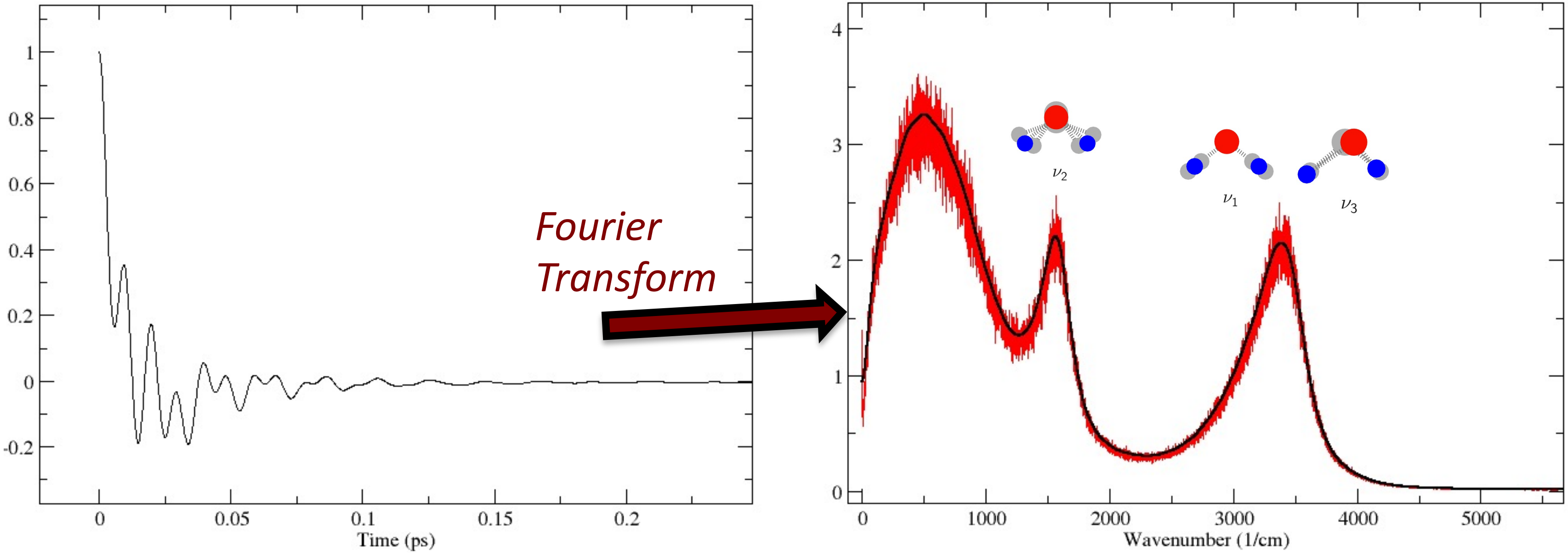
From Autocorrelation to Spectrum

$$\langle \dot{\boldsymbol{r}}(\tau)\dot{\boldsymbol{r}}(t+\tau)\rangle_\tau$$

$$\int \langle \dot{\boldsymbol{r}}(\tau)\dot{\boldsymbol{r}}(t+\tau)\rangle_\tau \mathrm{e}^{-i\omega t}\mathrm{d}t$$



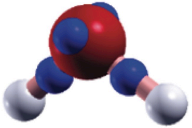
Fourier Transform

All vibrational spectra are Fourier transforms of autocorrelation functions

Raman and IR Spectra: Theory

Fourier transform of dipole moment time correlation function is proportional to IR spectrum:

$$A(\omega) \propto \frac{2\pi\omega^2\beta}{3cV}\int dt e^{-i\omega t}\langle \mathbf{M}(0)\mathbf{M}(t)\rangle$$



Where M(t) are calculated from maximally localized Wannier functions

Fourier transform of polarizability time correlation function is proportional to Raman spectrum:

$$R_{iso}(\omega) \propto \frac{\hbar\omega}{kT}\int dt e^{-i\omega t}\left\langle \overline{\alpha}(0)\overline{\alpha}(t)\right\rangle$$

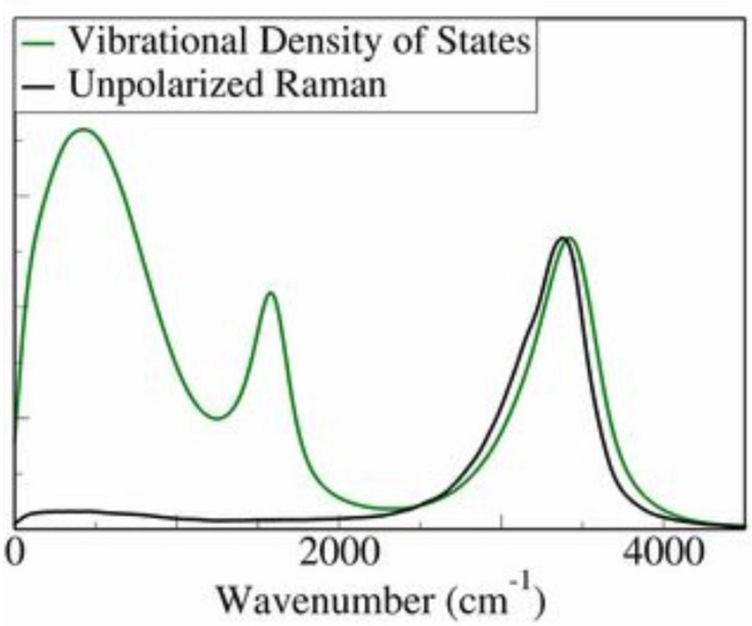
$$R_{aniso}(\omega) \propto \frac{\hbar\omega}{kT}\int dt e^{-i\omega t}\left\langle \frac{2}{15}\mathrm{Tr}\beta(0)\beta(\mathrm{t})\right\rangle$$

$$\bar{\alpha} = \frac{1}{3}\mathrm{Tr}\alpha$$

$$\beta = \alpha - \bar{\alpha}\mathbf{I}$$

Where in our case α(t) are calculated by finite field methods or density functional perturbation theory

Raman and IR Spectra: Signatures?



- VDOS is **not a valid substitute** for Raman spectra: difference in O-H stretch frequency and incorrect in lower modes.
- First principles prediction of Raman spectra – **excellent agreement** with experiment. Also inter/intra breakdown of OH shoulder
- Quenched phase: **liquid-like** Raman spectra from quenched phase
- No new signatures from Raman, but **continuum signature** in IR

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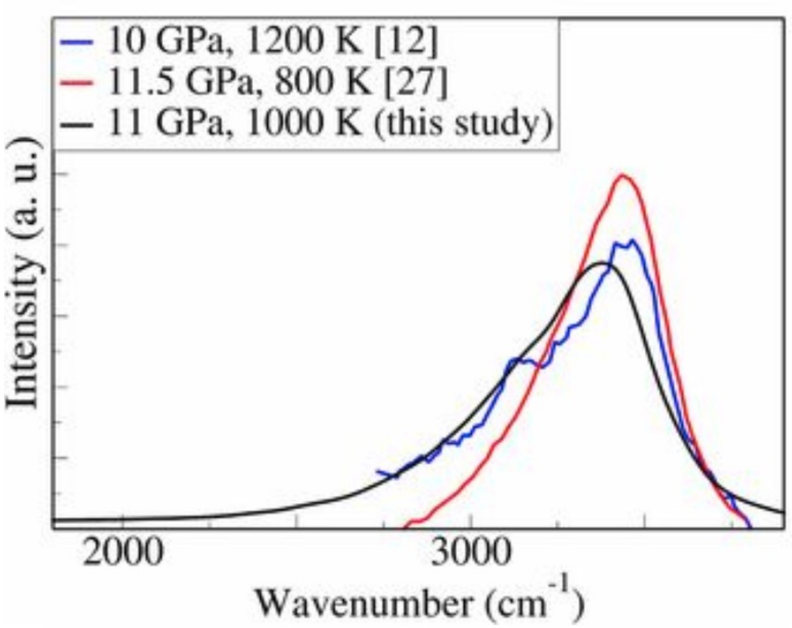

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[41] Lin *et al.*, Geophys. Res. Let., **32** (2005)

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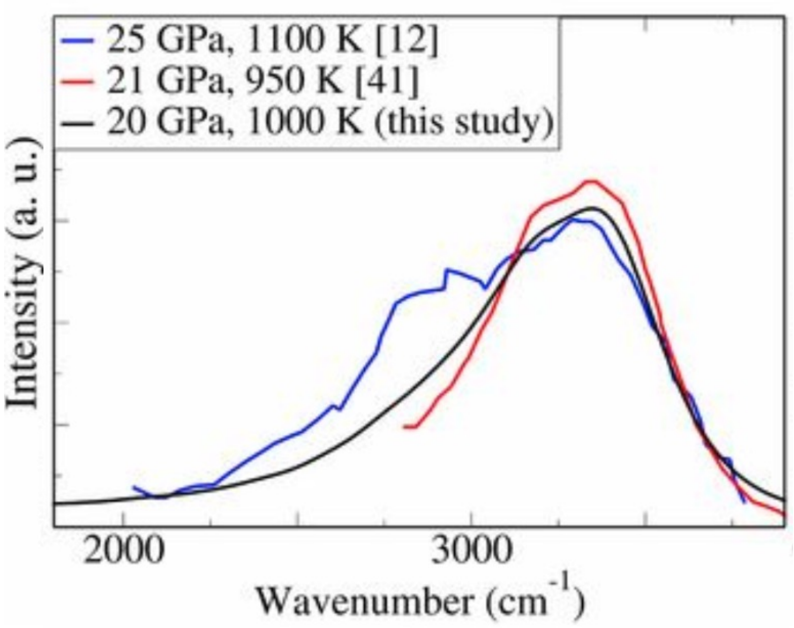

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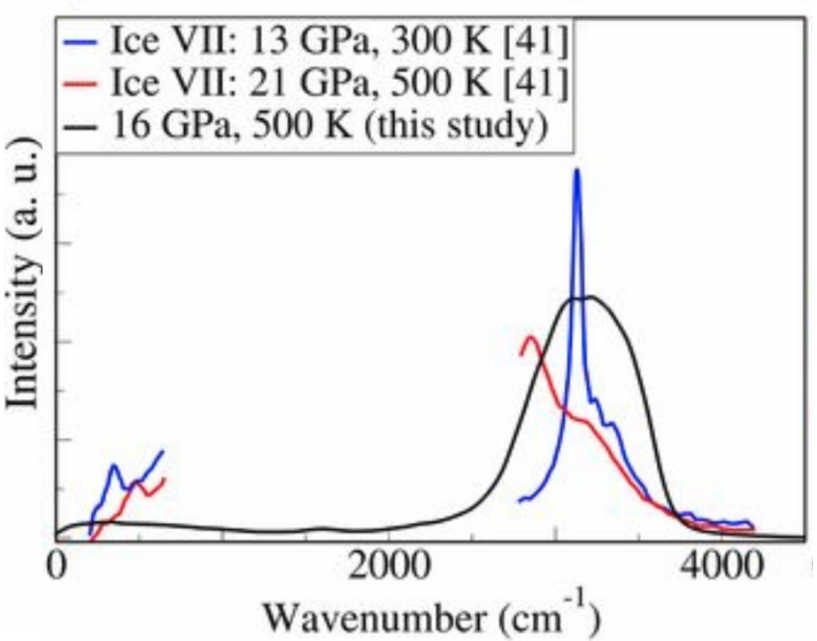

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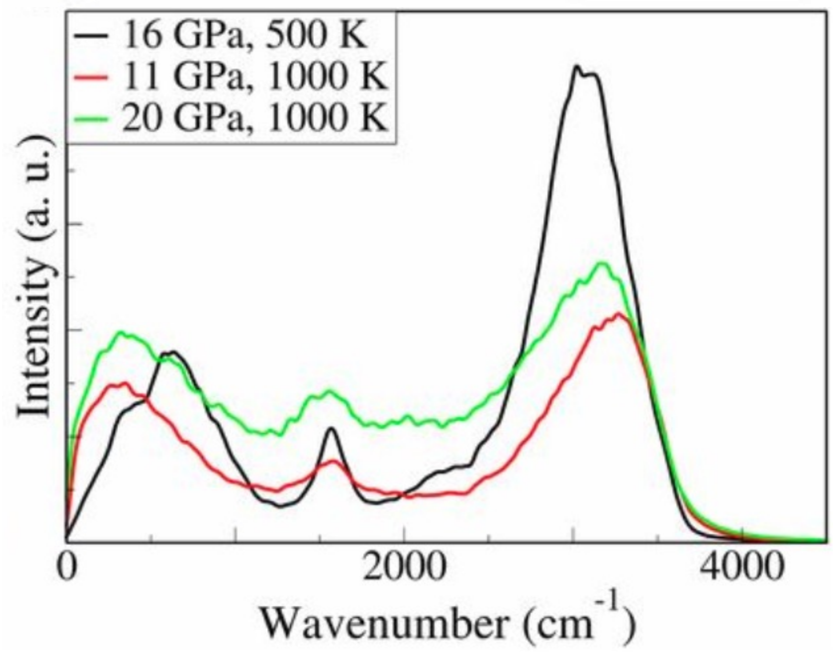

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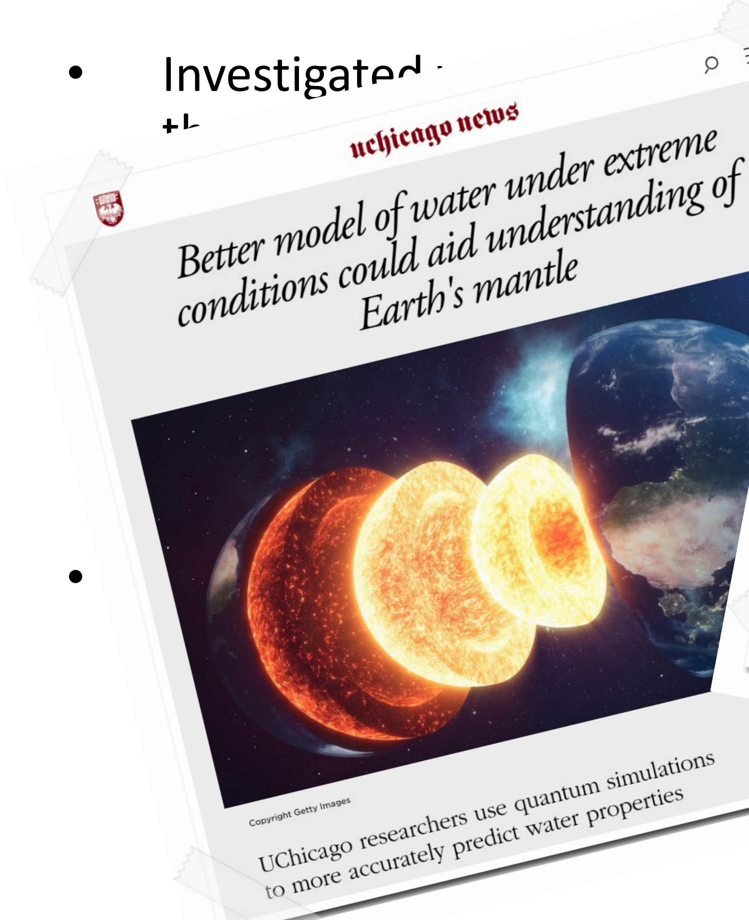
High P/T: Conclusions

- Investigated water under pressure at 11 GPa and 20 GPa, along the 1,000-K isotherm, using ab initio MD. Results consistent with a **lower melting line of Ice VII**
- Along the 1,000-K isotherm, liquid water exhibits rapid molecular dissociation events occurring via a bimolecular mechanism, which support an **enhancement of ionic conductivity on the order of 6 and 7 orders of magnitude** greater than ambient for 11, 20 GPa
- First **ab initio calculations of Raman spectra** at these conditions. No vibrational signatures of hydroxide and hydronium ions in Raman spectra, but signature in **continuum increase of IR spectra**

High P/T: Conclusions

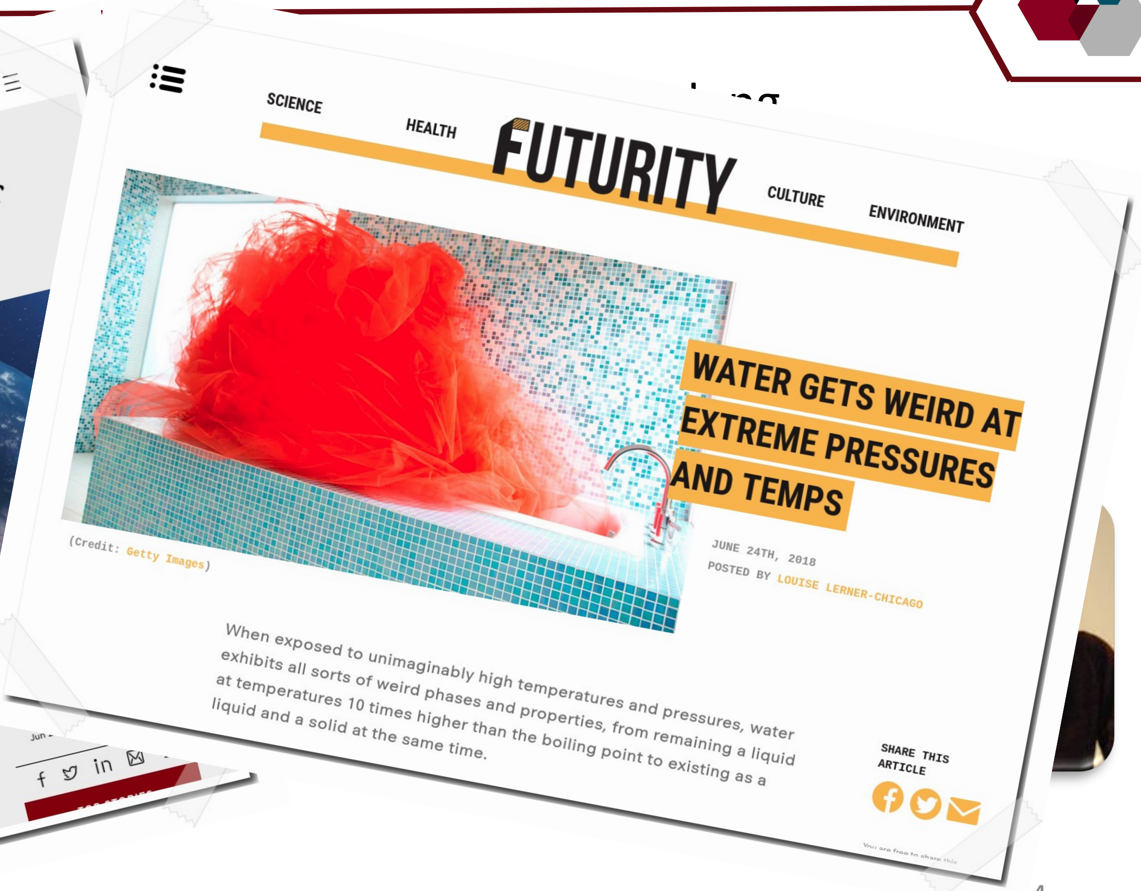
- Investigated



Better model of water under extreme conditions could aid understanding of Earth's mantle

Copyright Getty Images

UChicago researchers use quantum simulations to more accurately predict water properties



WATER GETS WEIRD AT EXTREME PRESSURES AND TEMPS

(Credit: Getty Images)

JUNE 24TH, 2018

POSTED BY LOUISE LERNER-CHICAGO

When exposed to unimaginably high temperatures and pressures, water exhibits all sorts of weird phases and properties, from remaining a liquid at temperatures 10 times higher than the boiling point to existing as a liquid and a solid at the same time.

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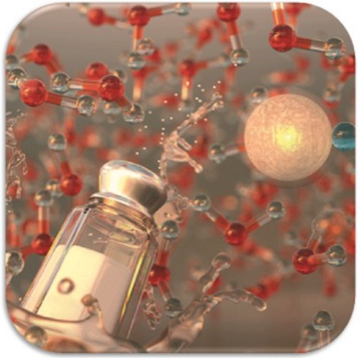
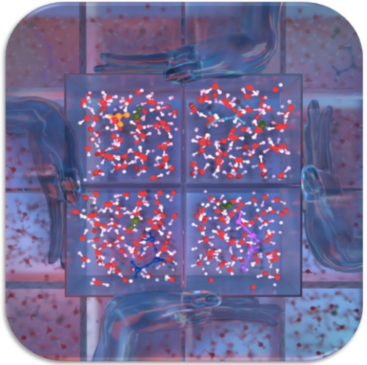
4 Vignettes about Water



Statistically robust studies on monovalent ions in bulk water

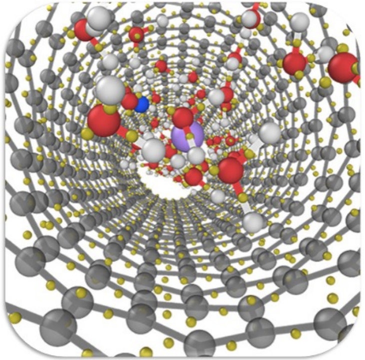
Rozsa *et al.*, J. Chem. Phys, **152** (2020)

Zeng, Rozsa, *et al.*, ACS Earth Space Chem., **3**, (2019)



Ab initio spectroscopy and ionic conductivity in water at high pressure and temperature

Rozsa *et al.*, PNAS, **115**, (2018)



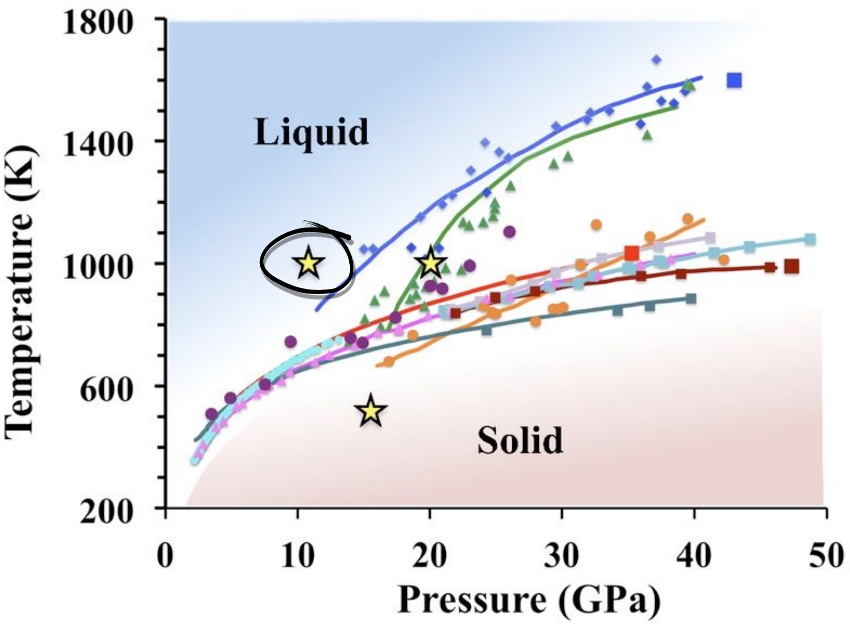
Pure water and ion solutions under confinement in carbon nanotubes

Rozsa *et al.*, J. Chem. Phys, **152**, 6952 (2020)

The effect of monovalent ion solvation on water at high pressure and temperature

Rozsa *et al.*, J. Chem. Phys, **154** (2021)

HPHT Ions: Motivation



Rozsa *et al.*, PNAS, **115**, 6952 (2018)

- **Planetary science**: deep water, deep carbon, mineral solubility/transport
- **Fundamental physics** of hydrogen-bonded systems at extreme conditions
- Solvation properties of **ions** in *highly dissociative* water are **virtually unexplored**

LiF to 6 GPa, 1000 K:

Jahn *et al.*, Geochim. Cosmochim. Acta, **73**, (2009)

NaOH to 0.85 GPa, 700 K:

Stefanski *et al.*, Phys. Chem. Chem. Phys, **33**, (2018)

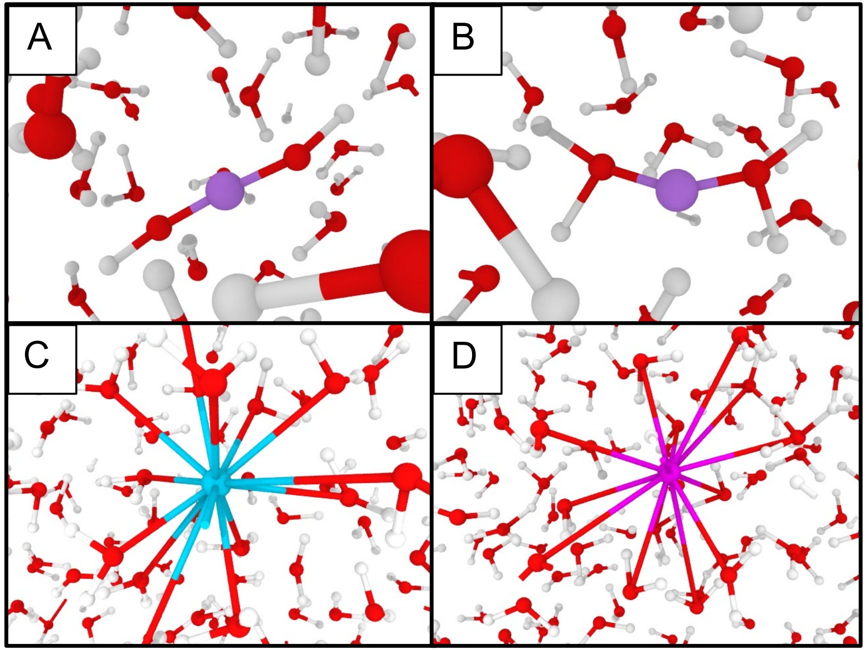
$MgSO_4$ to 1.4 GPa, 700 K:

Jahn *et al.*, J. Phys. Chem. B, **33**, (2010)

Structural Motifs in High P/T Water + Ions

- **Li+ Solution:** Formation of long-lived (~10s ps) H_xLiO_2 (x=2:4) complex

- **K+, Cl- Solutions:** Large ion solvation shells, no long-lived molecular species

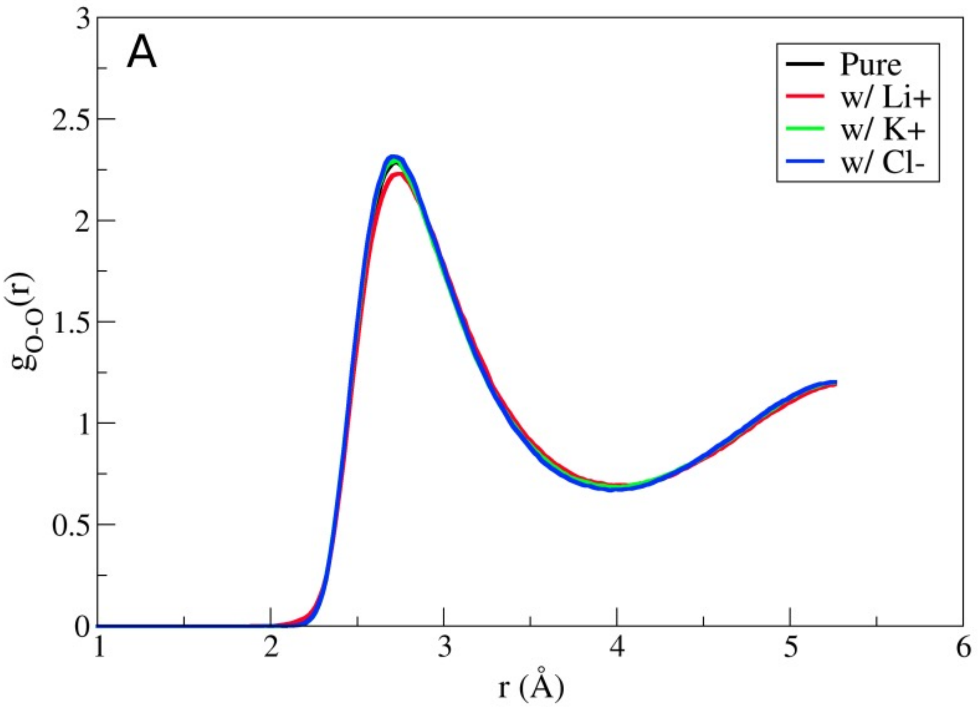


All structural motifs verified with the ***O-O**, **O-H**, **H-Ion**, **O-Ion*** *radial distribution functions AND larger simulation cell sizes*

✓

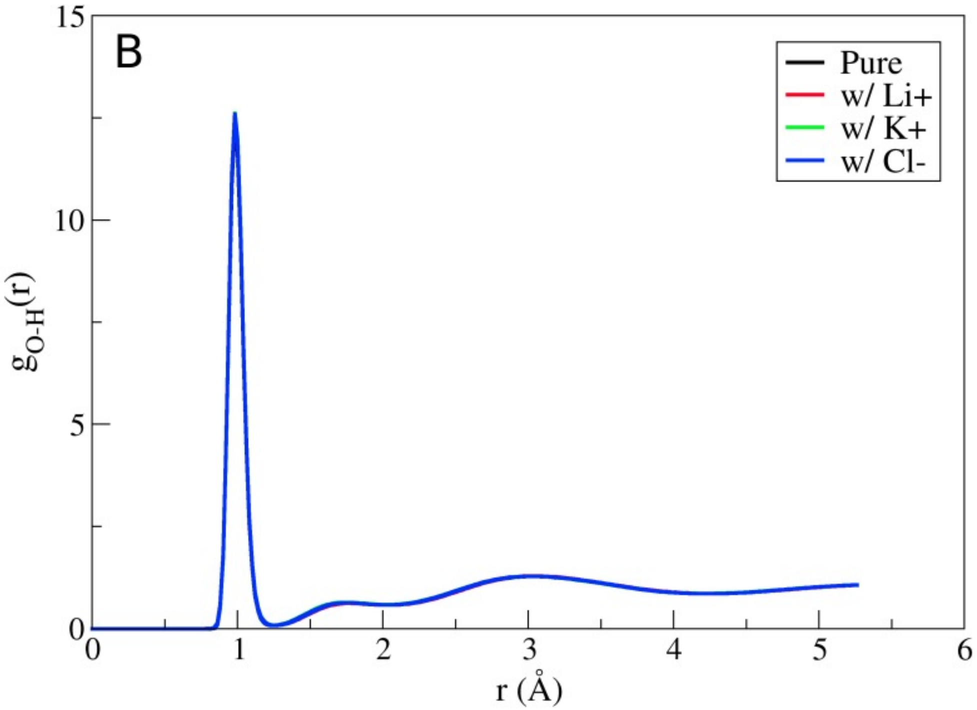
Rozsa *et al.*, J. Chem. Phys, **154** (2021)

Effect of ions on structure



- O-O structure is unaffected by ion solvation
- O-H structure, is unaffected by ion solvation
- O-MLWF structure is unaffected by ion solvation
- **The effect of ions on structural properties of water, including dissociation, is minimal.**

Effect of ions on structure



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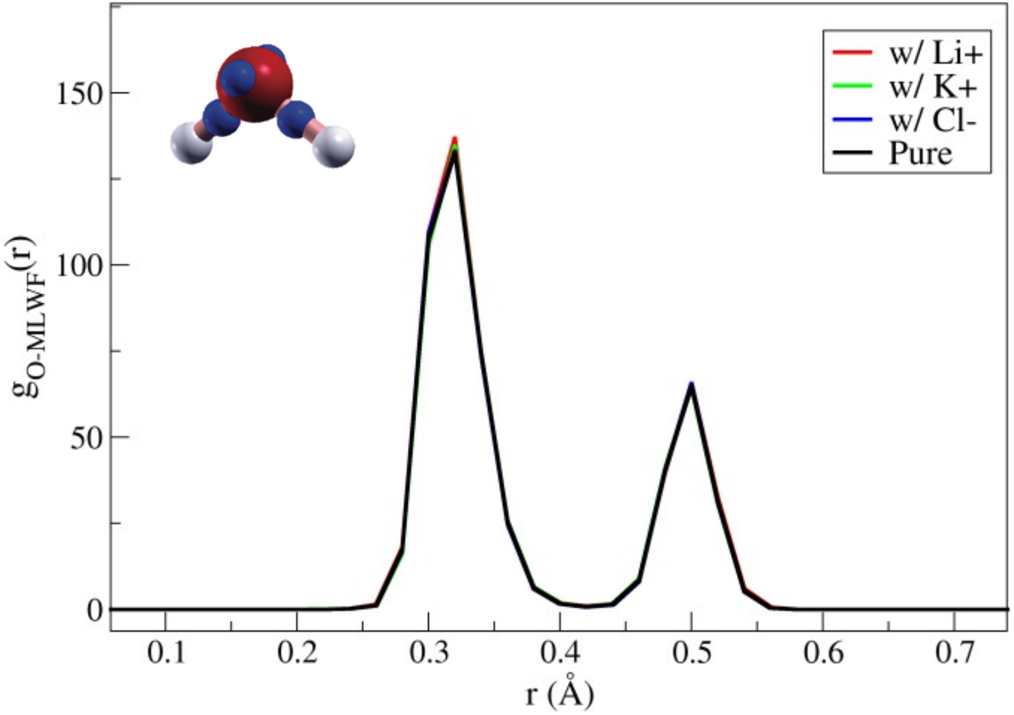

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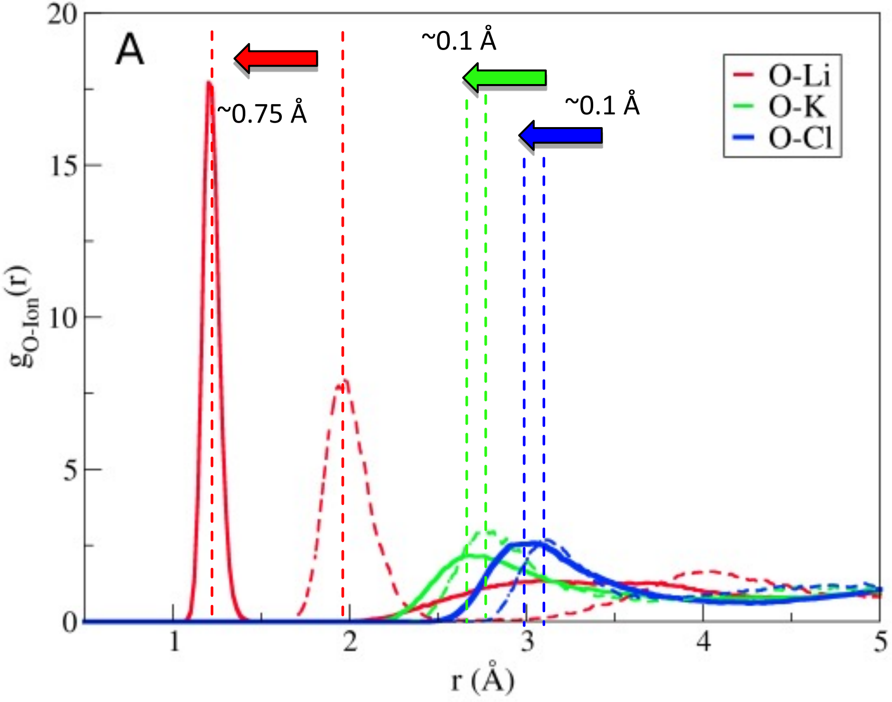
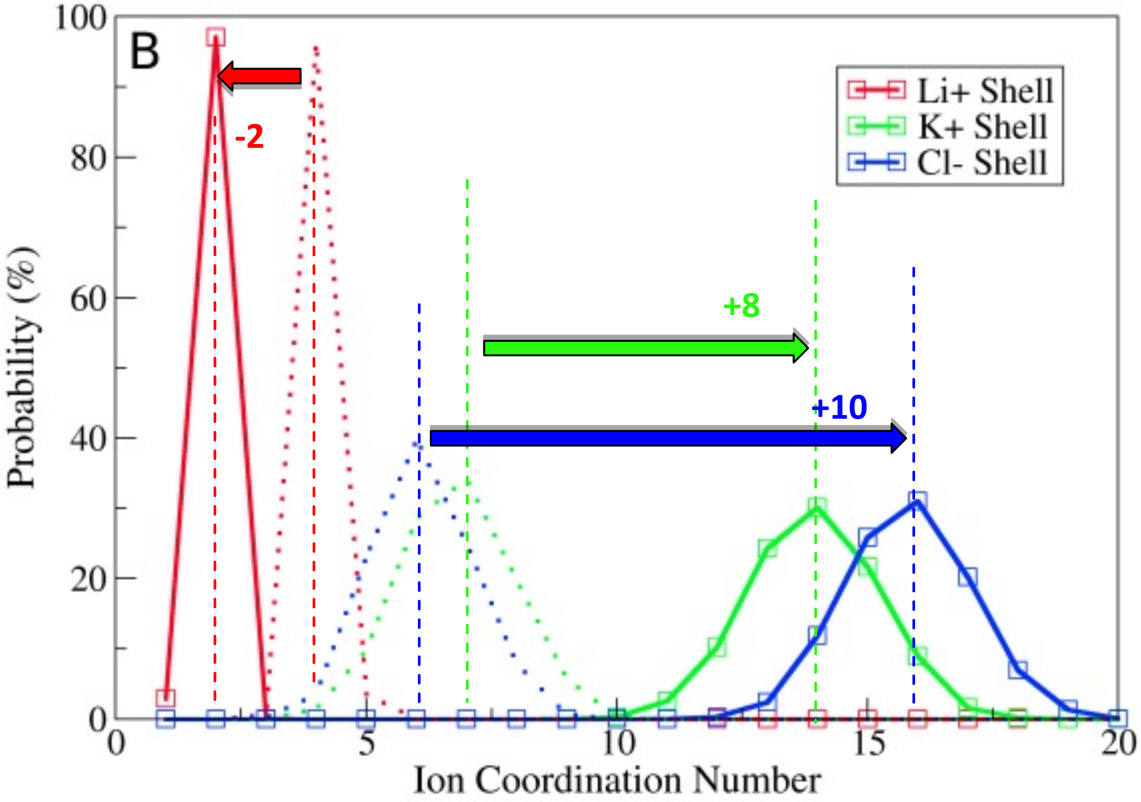
Changes to Ion Solvation Shells: Structure



- **Li+ shifts to much smaller first shell – corresponds to flanking oxygens of** H_xLiO_2 (x=2:4)

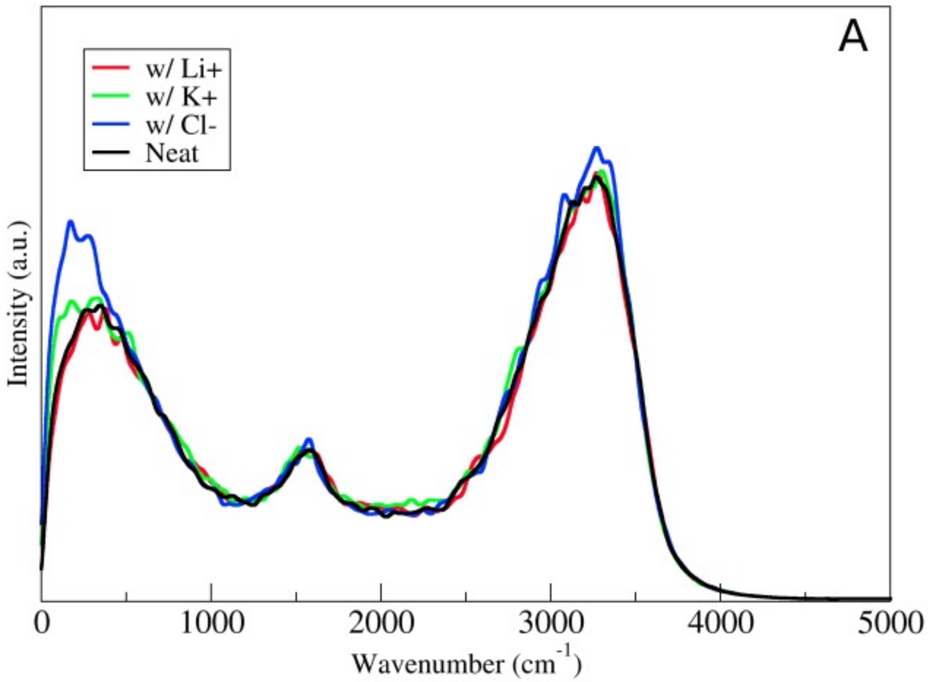
- **K+ and Cl- both have slightly smaller first shells, and behave very similar to each other** with respect to the effect of high P/T

Changes to Ion Solvation Shells: Coordination



- **Li+ decreases** from almost perfectly tetrahedral at ambient conditions **to 2-coordinated (H_xLiO_2 (x=2:4))**
- **K+, Cl- greatly increase in coordination**
  - **N_{Cl-} +10, N_{K+} +8**
  - Distributions have same shape (characteristic of shell “floppiness”)

Unchanged Raman and IR



- **Infrared:**
  - Same **signatures of dissociation** (mid-frequency continuum)
  - **No differences among ions** – dipole moment distributions not sensitive probe
- **Raman:**
  - No differences in OH stretching modes among ions

  - **Overall no new spectroscopic signatures of new species, even the H_xLiO_2**

Rozsa *et al.*, J. Chem. Phys, **154** (2021)

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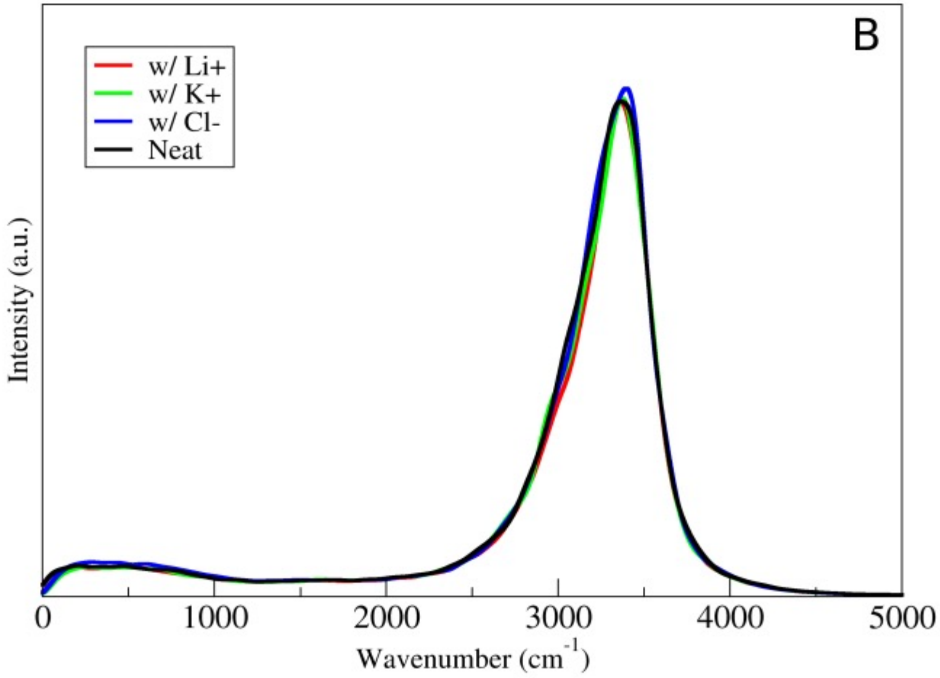

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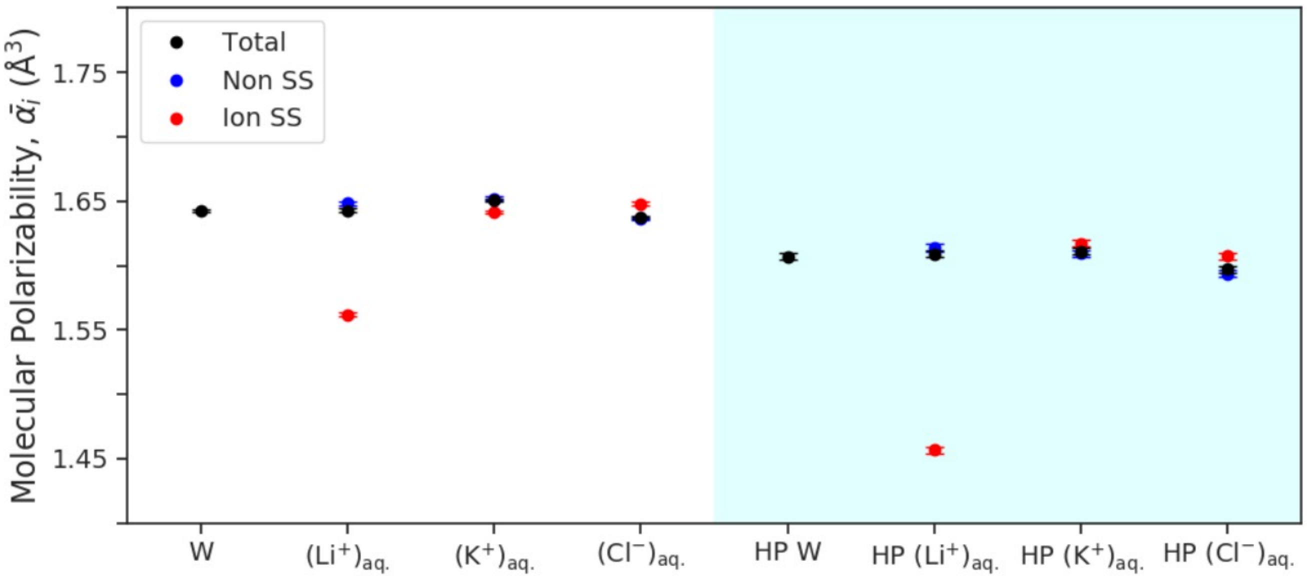
Rozsa *et al.*, J. Chem. Phys, **154** (2021)

Molecular Polarizability



- Reduction in all molecular polarizabilities (~4%)
- Within a given ion solution, qualitative behavior of SS vs non-SS is similar to bulk
- Among ions, effect non-SS is same as bulk
- Molecular Polarizability continues to be a **sensitive probe of perturbations, though changes are small**

Rozsa *et al.*, J. Chem. Phys, **154** (2021)

Dielectric Constant: Crucial to Geochem. Models

$$\varepsilon_0 = 1 + \frac{4\pi}{3k_B TV}\left(\langle \mathbf{M}^2 \rangle - \langle \mathbf{M} \rangle^2\right)$$

The Helgeson-Kirkham-Flowers model for aqueous species requires **Gibbs free energy of formation of an aqueous species**, based on the Born function for the average Gibbs energy of solvation,

$$\Delta\overline{G}_{s,j} = \omega_j \left(\frac{1}{\varepsilon_0} - 1\right)$$

Where ω_j is the electrostatic Born parameter for ion *j.* ε_0 is the **static dielectric constant of the solvating water**

Helgeson *et al.*, Am. J. Sci, **274**, 1089 (1974)

Recent AIMD calculations of **pure water ε_0** have allowed for a reparameterization of deep earth water models

Pan *et al.*, PNAS, **110**, 6646 (2013)
Sverjensky *et al.*, Geoche et Cosm. Act., **129** (2014)

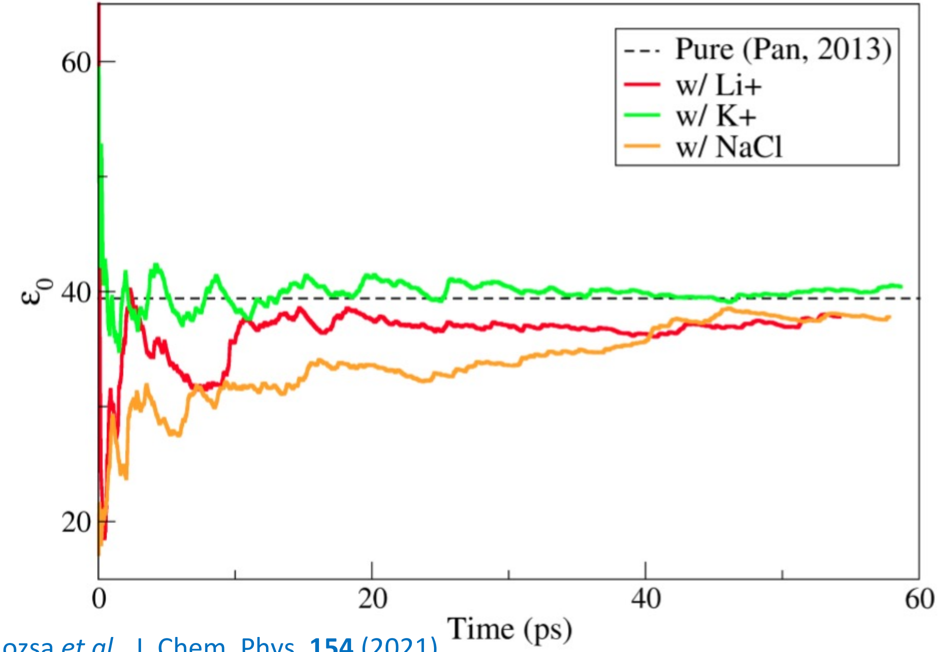
*"In real fluids containing mixed solvents, a **contribution from the dielectric constant of the mixed solvent** should be used in the non-standard state, extended-term contributions to the aqueous activity coefficient, e.g. an additional term …"*

Sverjensky., J. Geol. Soc. (2019)

Dielectric Constant: ε_0

$$\varepsilon_0 = 1 + \frac{4\pi}{3k_BTV}\left(\langle \mathbf{M}^2\rangle - \langle \mathbf{M}\rangle^2\right)$$

128 H_2O



Rozsa *et al.*, J. Chem. Phys, **154** (2021)

Consistent w/ AIMD:
Pan *et al.*, PNAS, **110**, 6646(2013)

Pure: ~39

K+: ~39 > **Li+: ~37** > **Cl-: ~35**

No Change **~5% decrease** **~10% decrease**

Ab initio prediction that pure water is an **upper limit on ε_0** relative to solvated ions.

Consistent with empirical predictions from:

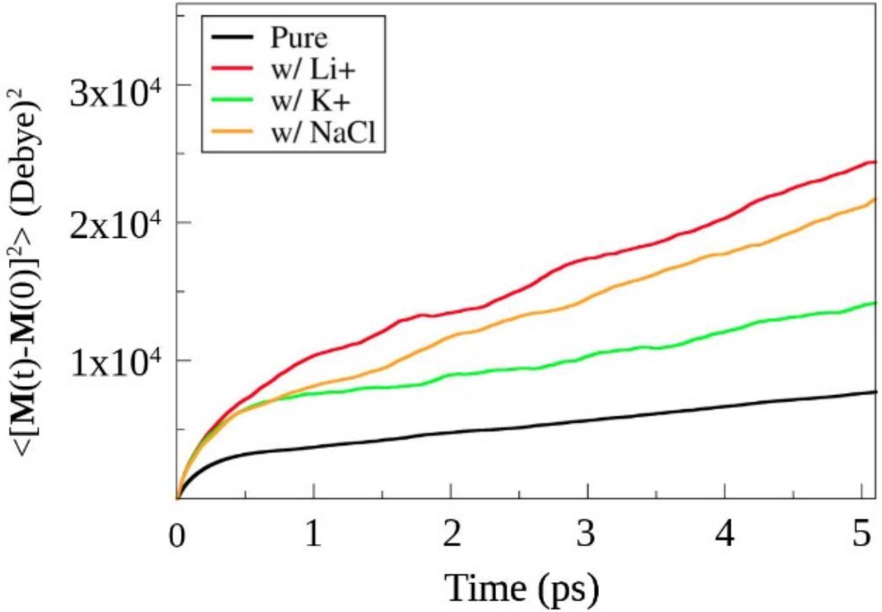
- NaCl: 6-12 GPa, 800-1100 K (Foustoukos, Chem. Geol. 447 (2016)
- C-O-H: 3 GPa, 1200 K (Galvez et al., Earth Planet. Sci. Lett 430 (2015)

Larger cells: **consistent pattern in dielectric constants** (K+ > Li+ > NaCl), though larger change for Li+ (~10% decrease)

Ionic Conductivity

$$\mathbf{M}(t) = e \cdot \sum_{i=1}^{N_H} \vec{R}_i^H(t) + 6e \cdot \sum_{i=1}^{N_O} \vec{R}_i^O(t) - 2e \cdot \sum_{i=1}^{N_{MLWF}} \vec{R}_i^{MLWF}(t)$$

$$\sigma = \lim_{t \to \infty} \frac{1}{6tk_bTV} \langle [\mathbf{M}(t) - \mathbf{M}(0)]^2 \rangle$$



Rozsa *et al.*, J. Chem. Phys, **154** (2021)

Li+ σ = 3.8 (0.5) S/cm
K+ σ = 4.2 (0.5) S/cm
NaCl σ = 4.0 (0.6) S/cm

Overall**, all ions exhibit enhancement of σ**

Enhancements are factor of 3 or 4 at most, and distinguishability between ions is difficult to establish

High P/T ions: Conclusions

- We have detailed analysis of how structures of how **solvation shells are altered** differently by high P/T. Global water structure RDFs are **unaffected by ions**
- Vibrational spectra (Raman/IR) show **no new modes as signatures of ions or high P/T ionic species.** However, **VDOS shows signature spectra** of suppressed vibrational spectrum of Li+ solvation shell, and K+/Cl- show qualitative similarities in their coupling to vibrational modes.
- Molecular polarizabilities are **reduced across the board**, though qualitative behavior of solvation shell waters is very similar to ambient conditions. Polarizability continues to be sensitive to perturbations.
- Dielectric constants of **pure HPHT water is an upper limit** for solvated ion solutions
- Conductivity is **enhanced in high P/T solutions by no more than a factor of ~4.**

Summary and General Conclusions

- To understand water at extreme conditions, **need first principles theory**
- **Molecular polarizability is a consistently effective fingerprint** of perturbations to water
- Demonstrated **viability of computing ionic conductivity** in liquids from first principles
- **IR, not Raman spectroscopy** detects changes changes due to water dissociation at high P/T
- **Resilience of water** to perturbations extreme conditions:
  - Ions at ambient have little global effect, and differences among ions are similar to bulk
  - At high P/T, no new vibrational modes despite big changes, ion solvation similarities to bulk properties

Acknowledgments

Ding Pan, Anh Pham, Federico Giberti, Alex Gaiduk, Francois Gygi, Arin Greenwood, and many more

Giulia Galli

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RESEARCH COMPUTING CENTER