Role of Polarizability in the Structure and Dynamics of liquid water

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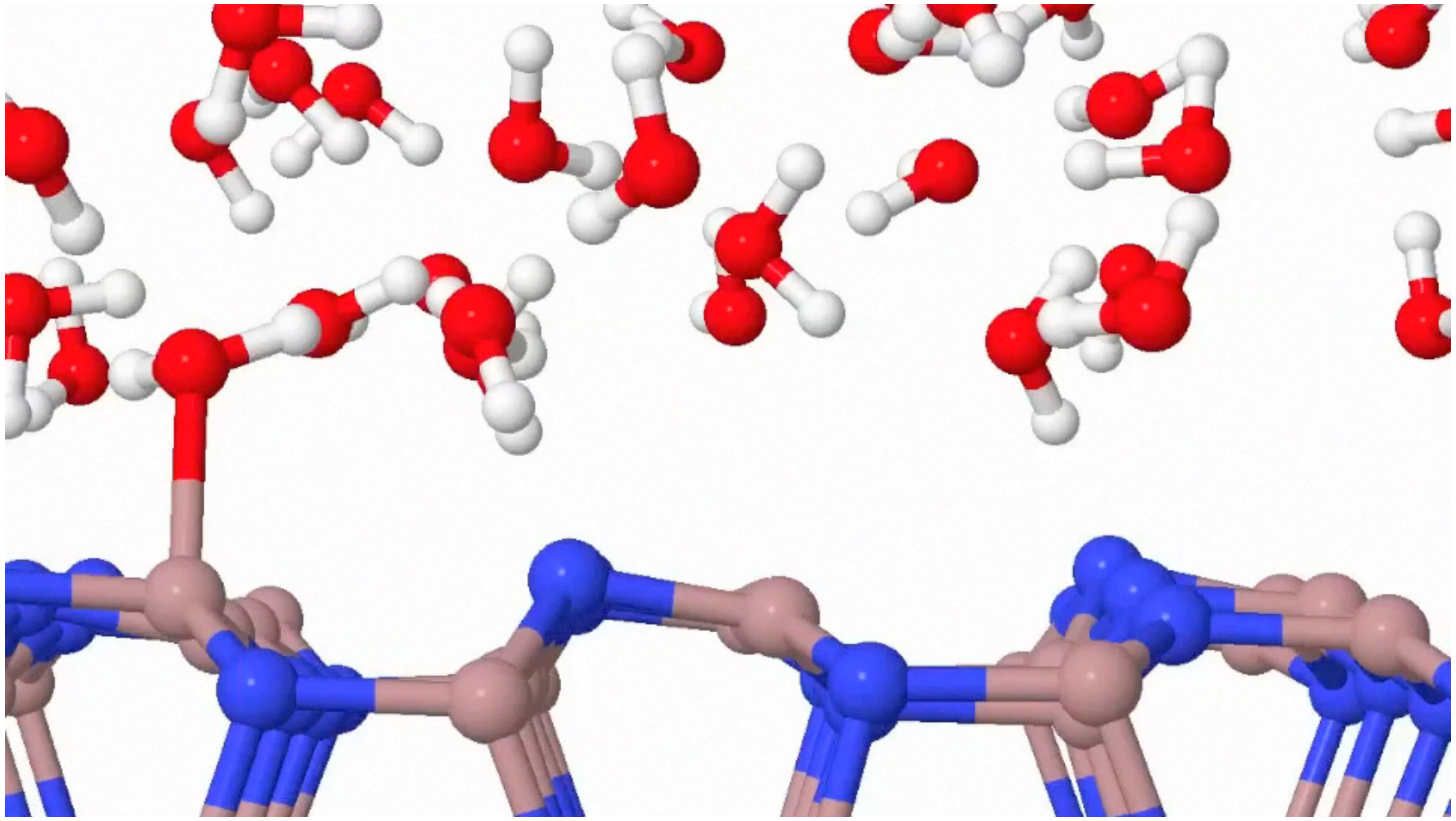

ANOMALIES IN WATER

Superco

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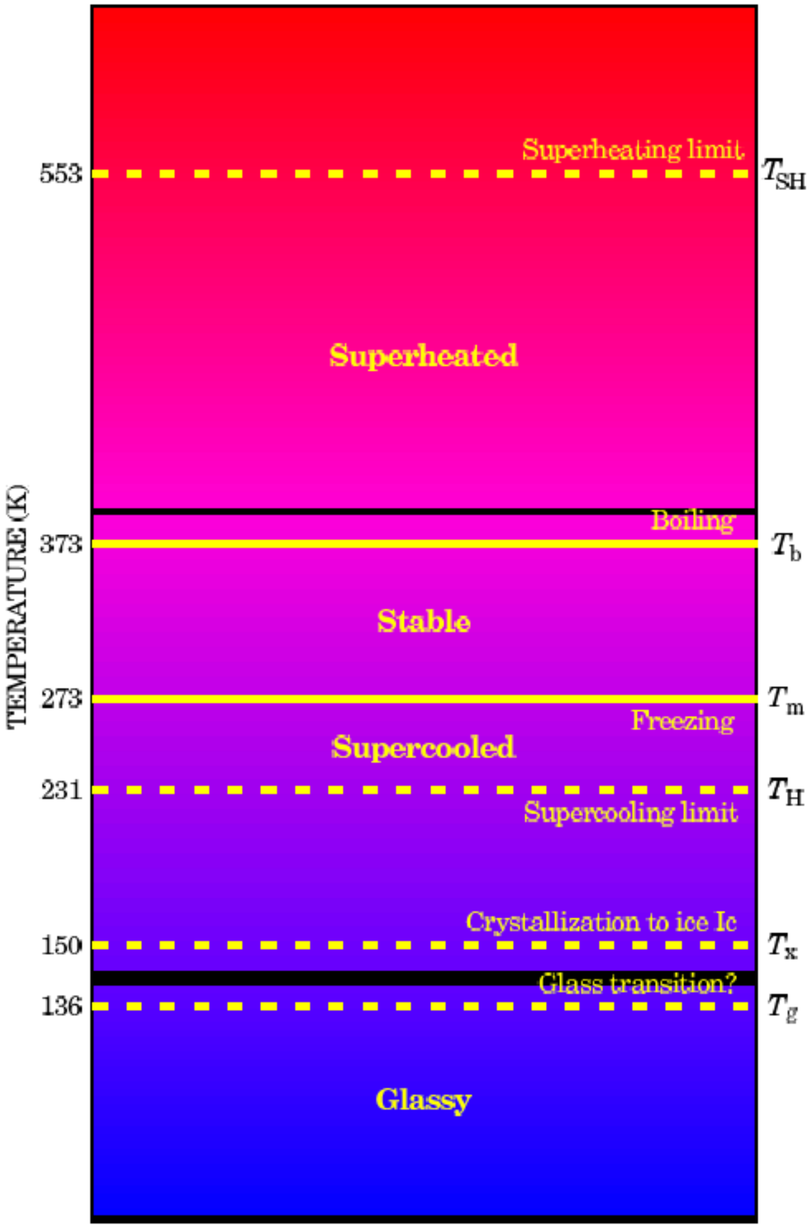
locat

Poole,

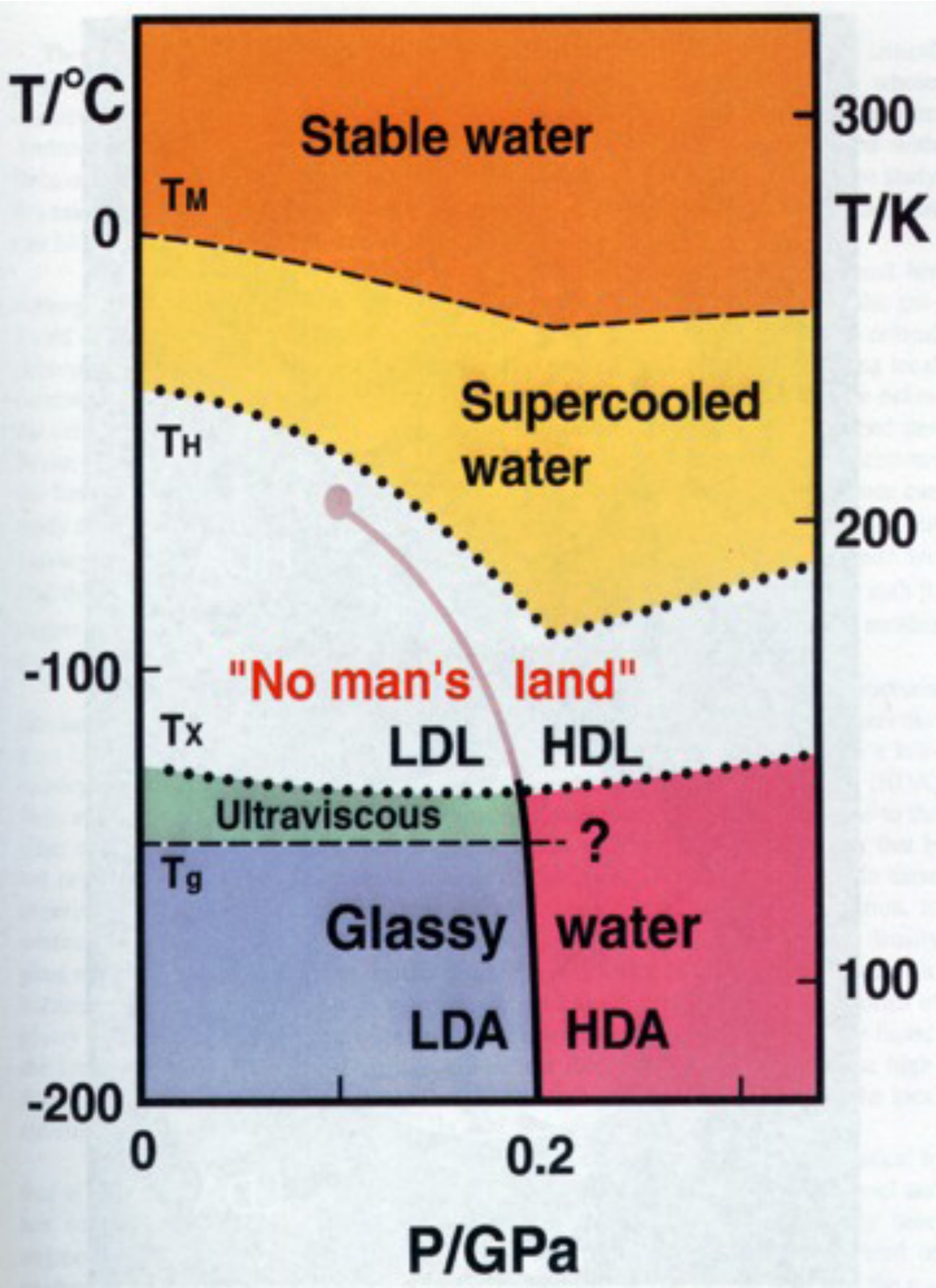
OVERSIMPLIFIED PHASE DIAGRAM

"hypothesized phase diagram"



Poole, P. H., Sciortino, F., Essmann, U., Stanley, H. E. (1992) *Nature* 360:324–328

. G. Debenedetti and **H. E. Stanley**, "Supercooled and Glassy Water," Physics Today **56 [issue 6]**, 40-46 (2003)



Homogeneous nucleation temperature T_M=231 K: T cannot be supercooled below this.

T_{glass}=130 K: LDA melts into a highly viscous liquid.

Tx=150 K, a highly viscous liquid crystalizes into cubic ice Ic

150 K < No man's Land < Tm (231 K)

TWO FLUCTUATING LIQUIDS

REVIEW

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OPEN

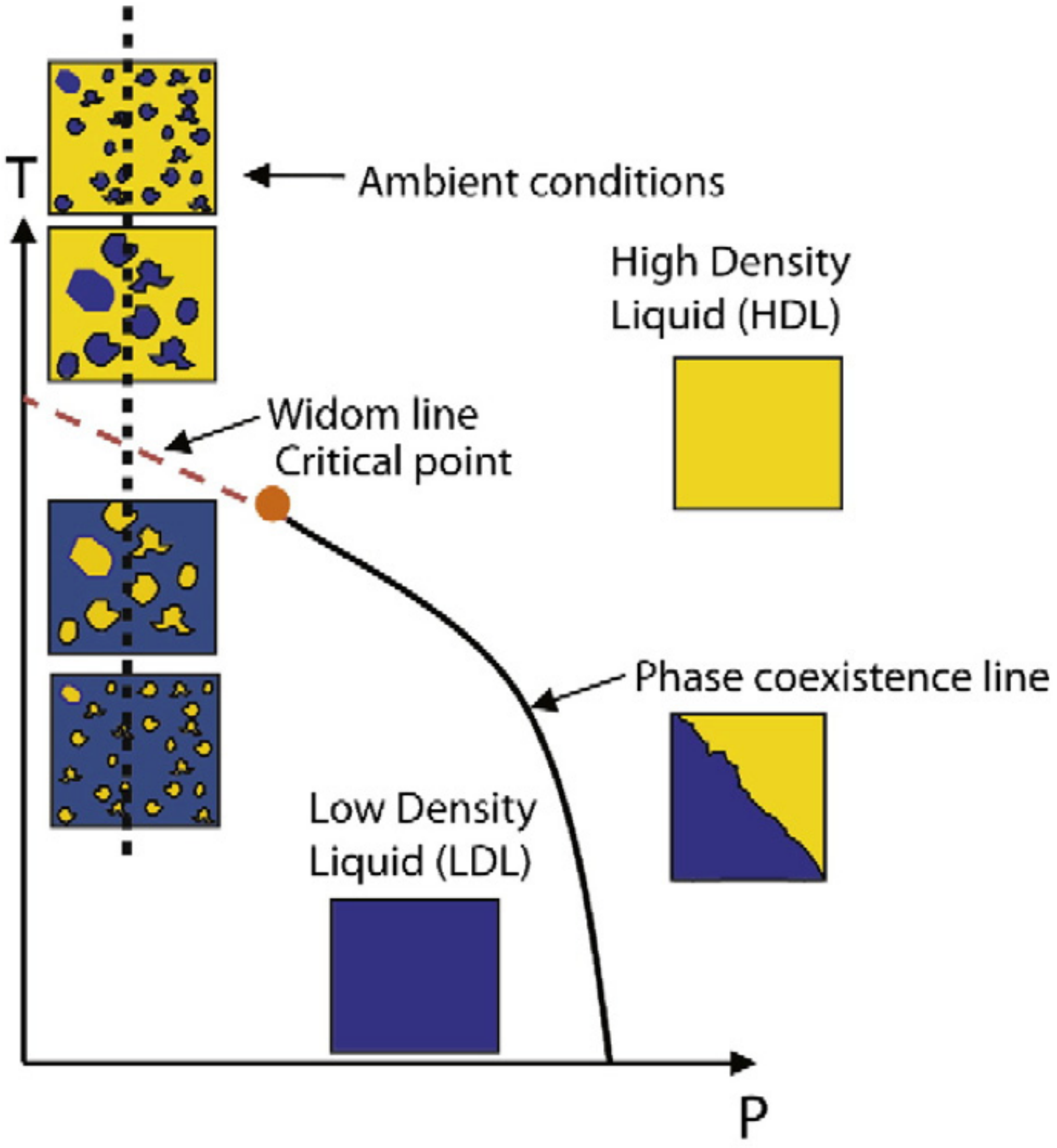
The structural origin of anomalous properties of liquid water

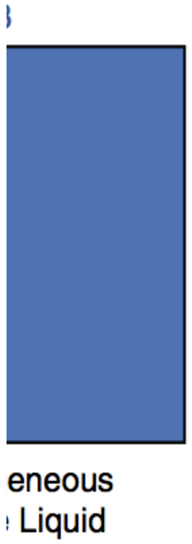
Anders Nilsson[1] & Lars G.M. Pettersson[1]

How can the hypothesis be tested?

- Experiments: No access to no ma interpretation, confined water.
- Models: 2-scale models, designed LLCP
- Simulations: Based on fitted mode reproduce the full phase diagram

If experiments are not conclusive, only well converged ab initio simulations can give an unbiased answer



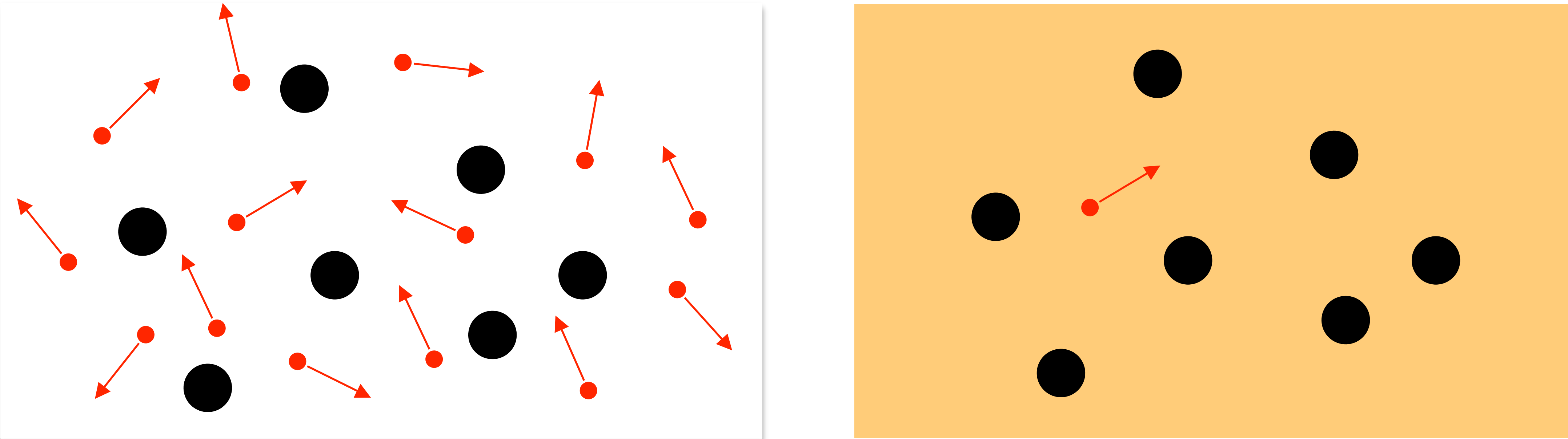


DENSITY FUNCTIONAL THEORY

$$H = \sum_{i=1}^{n_e}\left[-\frac{\hbar}{2m_e}\nabla_i^2 + V_N(\mathbf{r}_i)\right] + \frac{1}{2}\sum_{\substack{i,j=1\\ i\neq j}}^{n_e}\frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|}$$

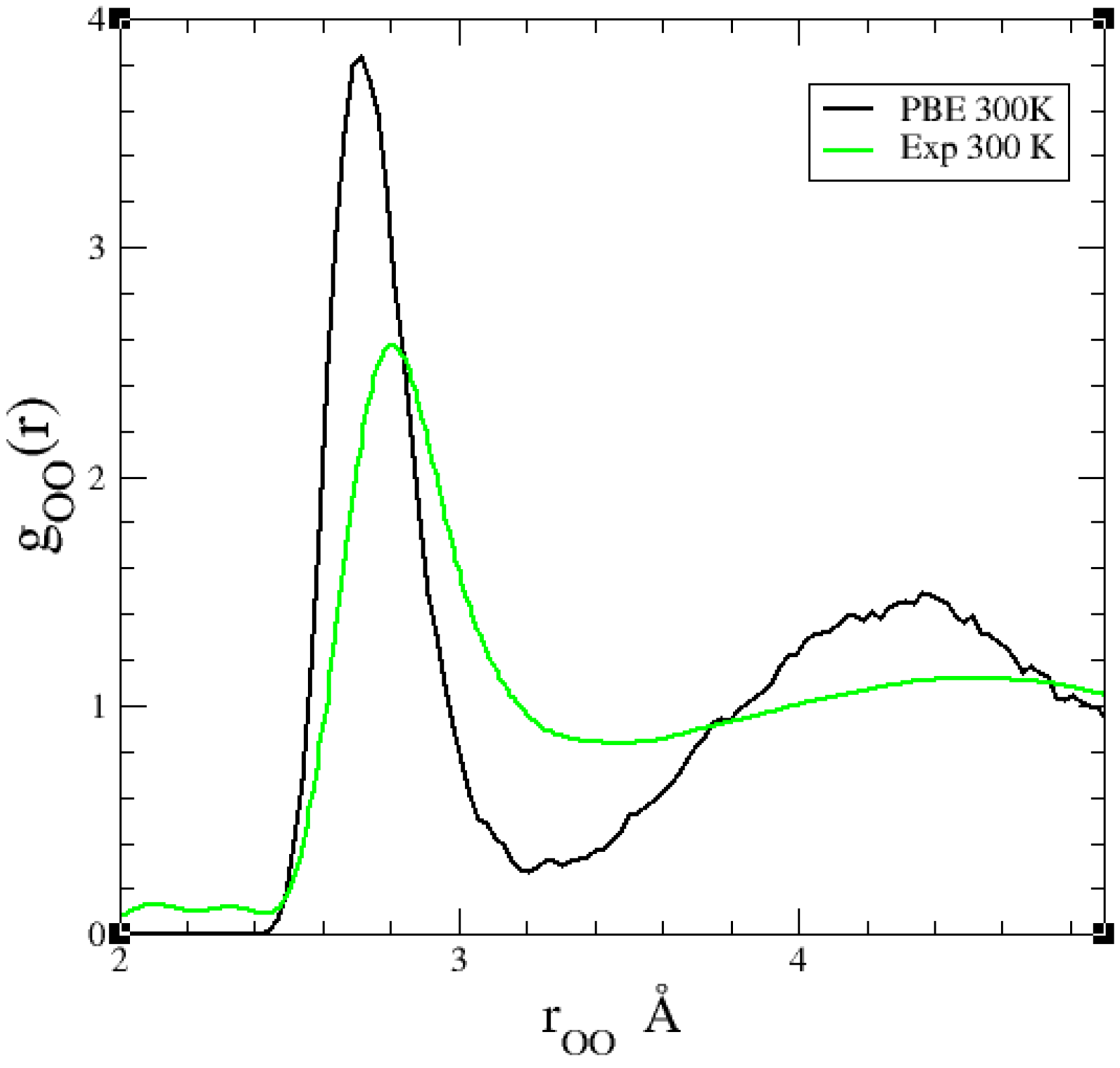
$$H_{DFT} = \sum_{i=1}^{n_e}\left[-\frac{\hbar}{2m_e}\nabla_i^2 + V_N(\mathbf{r}_i) + V_H(\mathbf{r}_i) + V_{XC}(\mathbf{r}_i)\right]$$

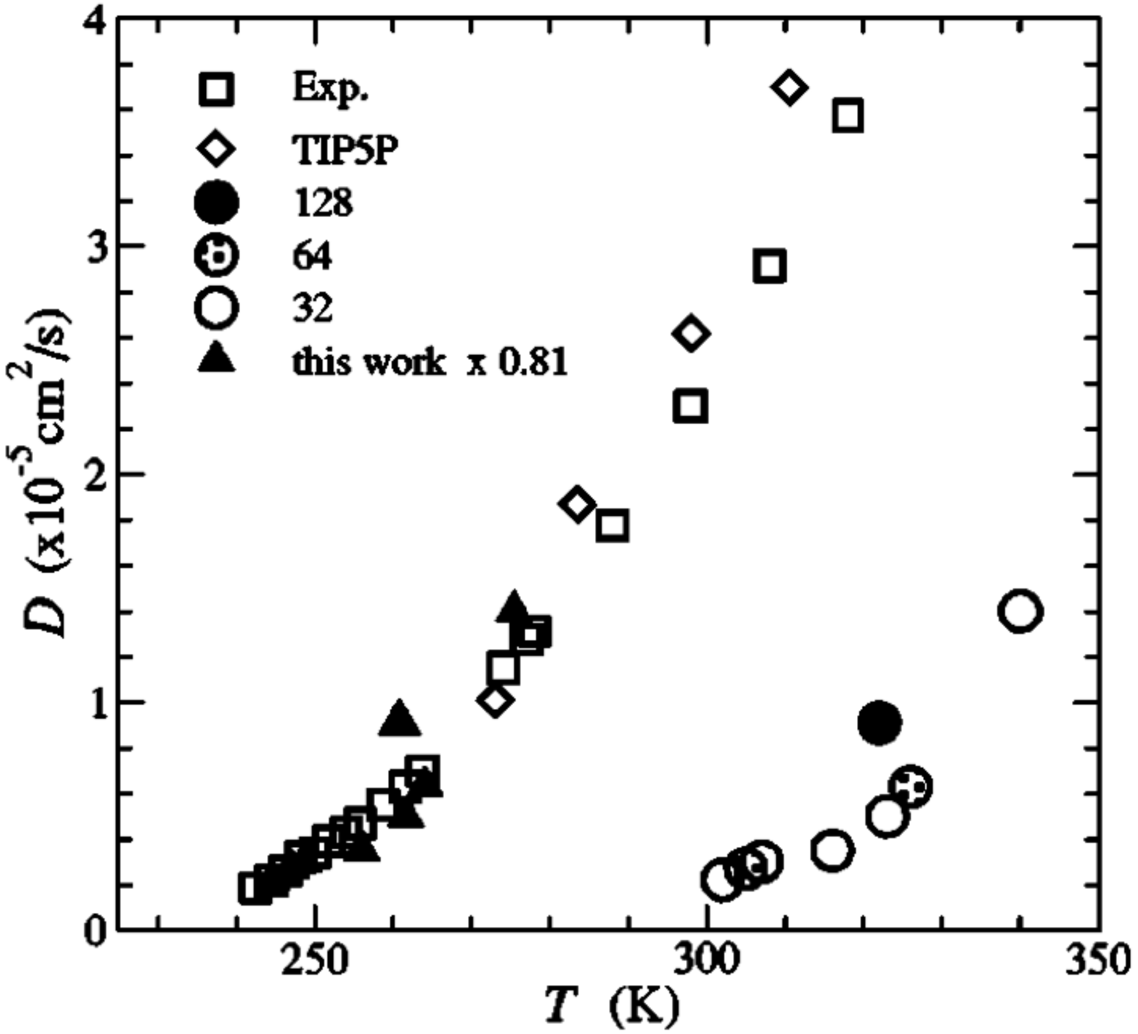
$$V_H(\mathbf{r}) = \int d^3\mathbf{r}'\,\frac{\rho_e(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}$$



$$\Psi(r_1,\ldots,r_N) \rightarrow \psi_1(r_1)\,\psi_2(r_2)\,\ldots\,\psi_N(r_N)$$

NON VDW DENSITY FUNCTIONALS





Exp: L. B. Skinner, C. Huang, D. Schlesinger, L. G. M. Pettersson,
A. Nilsson, and C. J. Benmore, J. Chem. Phys. 138, 074506 (2013).

M.V Fernandez-Serra and E. Artacho. J. Chem. Phys.121, 11136-11144 (2004).

VDW XC DENSITY FUNCTIONAL

Dion, Rydberg, Schröder, Langreth, and Lundqvist (DRSLL) PRL 92, 246401 (2004)

$$E_{xc} = E_x^{\text{GGA-revPBE}} + E_c^{\text{LDA}} + E_c^{nl}$$

$$E_c^{nl} = \frac{1}{2}\iint d\mathbf{r}_1\, d\mathbf{r}_2\, n(\mathbf{r}_1)\, n(\mathbf{r}_2)\, \Phi(q_1, q_2, r_{12})$$

$$q(n, \nabla n) = \left[1 + \frac{\varepsilon_c^{LDA}(n)}{\varepsilon_x^{LDA}(n)} - \frac{Z_{ab}}{9}\left(\frac{k_G}{2k_F}\right)^2\right] k_F$$

$$Z_{ab} = -0.8491 \qquad k_F = \left(3\pi^2 n\right)^{1/3} \qquad k_G = \frac{\nabla n}{n}$$

Other proposals:

O.A.Vydrov and T.Van Voorhis, PRL 103, 063004 (2009)

J.Klimes, D.R.Bowler, and A.Michaelides, JPCM 22, 22201 (2010)

J.Wellendorff et al, Topics Catal. 53, 378 (2010)

K. Berland and Per Hyldgaard, PRB 89, 035412 (2014)

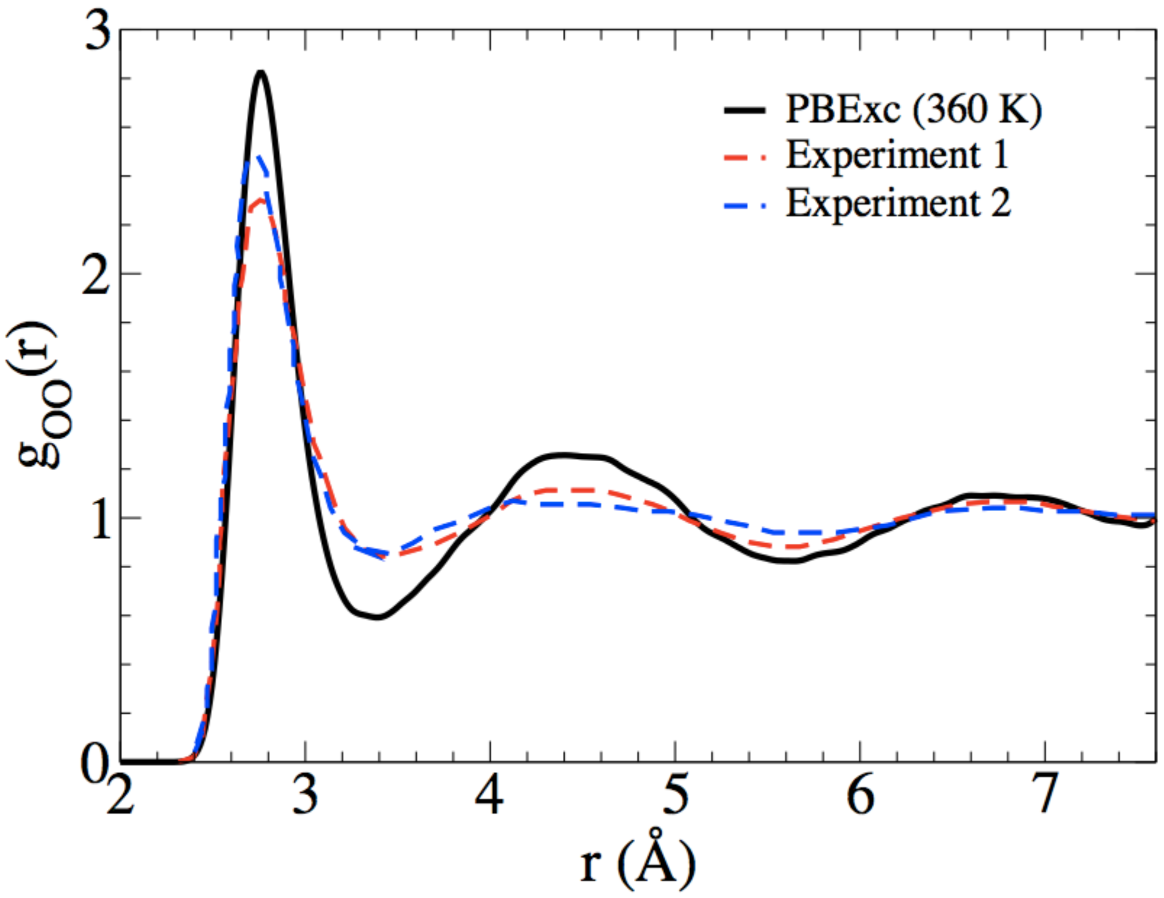
Non local kernel factorization:
Roman-Perez & Soler, PRL 2009

O(N log(N)) cost

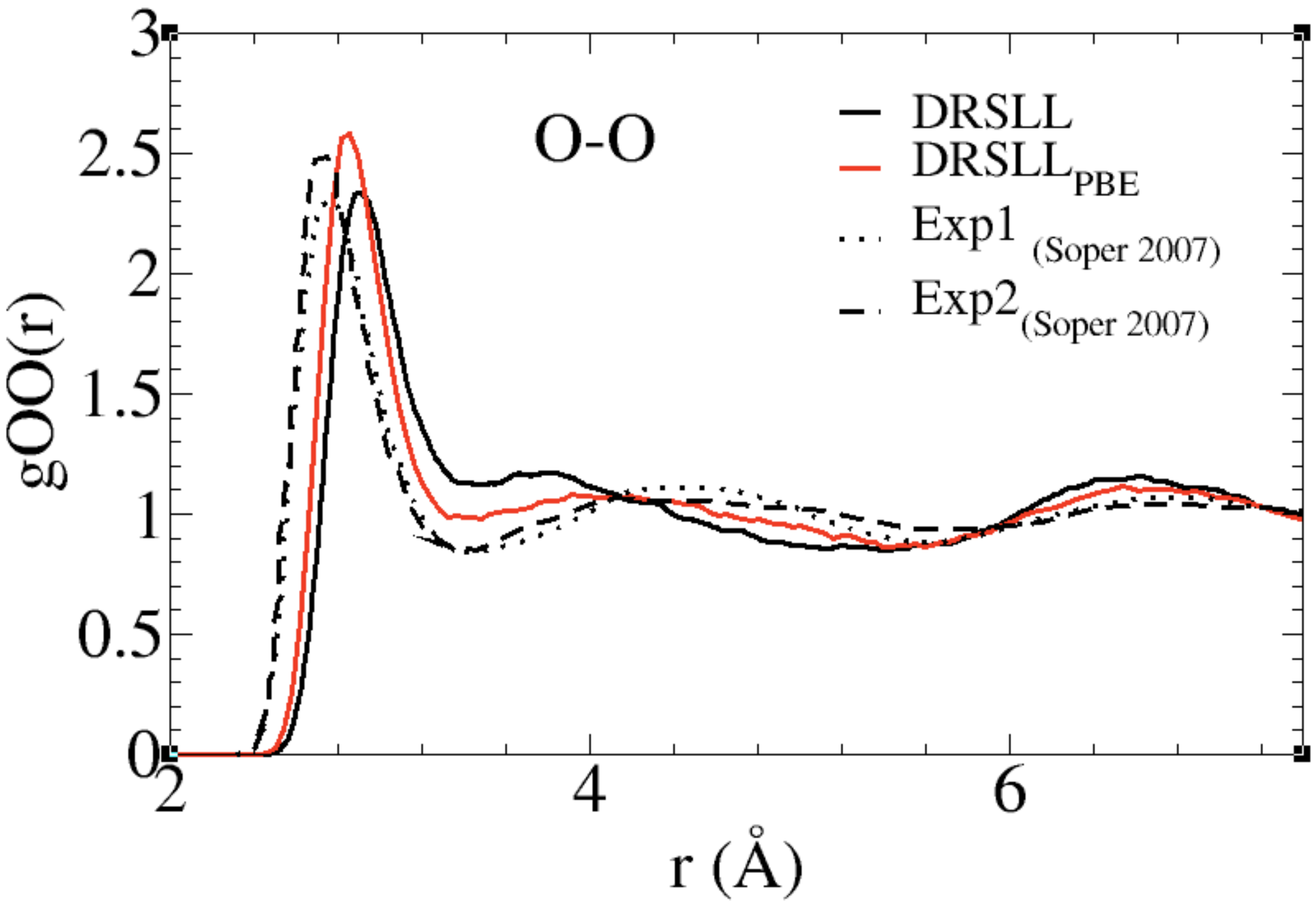
1.- DFT Liquid Water
vdW effects in Density
vdW effects in Structure

Pair distribution functions

semi-local XC



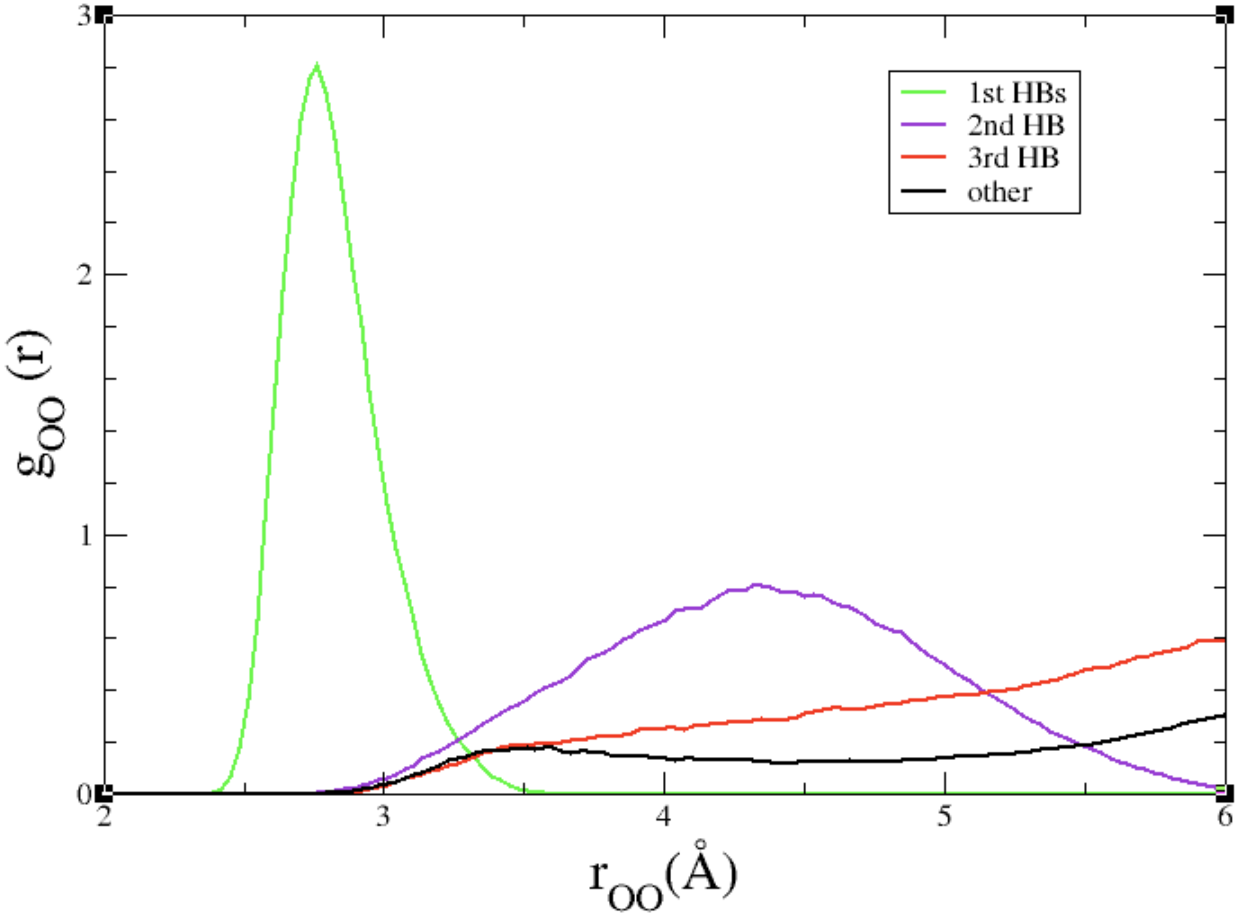
semi-local XC + non local C



$\rho=1 g/cm^3$

H–bond network

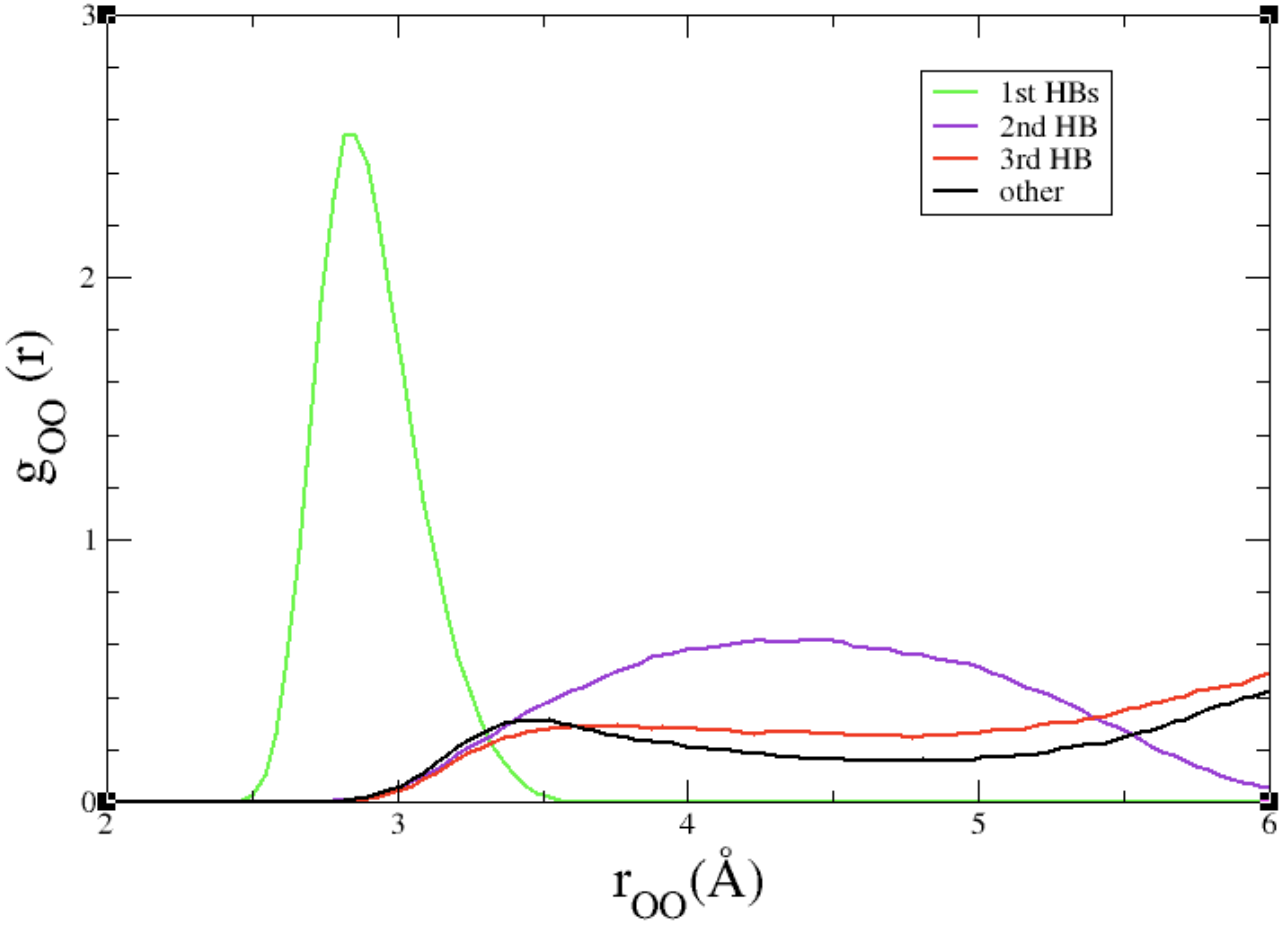
PBE (ρ=1g/cm^3, 64 mol) PBE-VdW-DF, (ρ=1g/cm^3,64 mol)



3.81 H–bonds/molecule

$<r_{HB}>=2.85$

1.26 vdW bonds/molecule



3.76 H–bonds/molecule

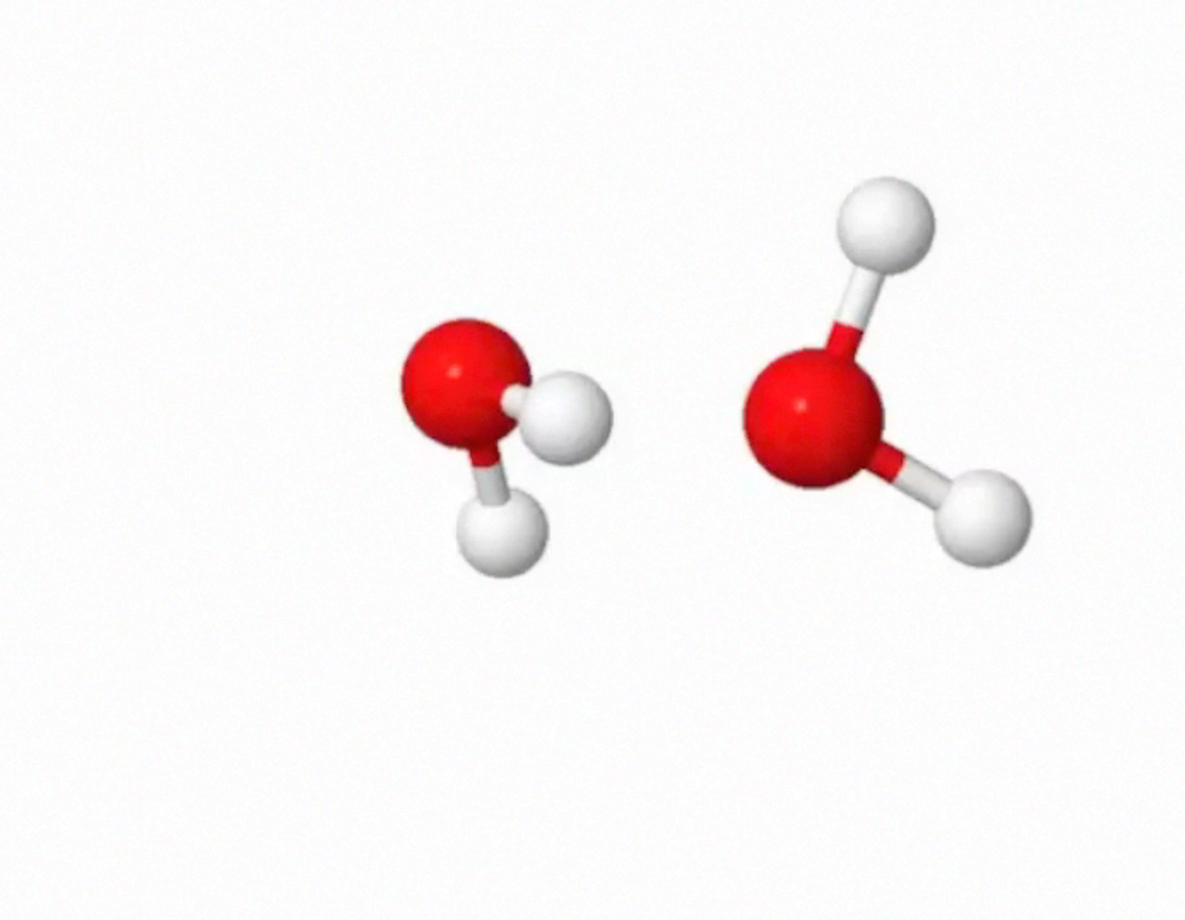
$<r_{HB}>=2.93$

1.99 vdW–bonds/molecule

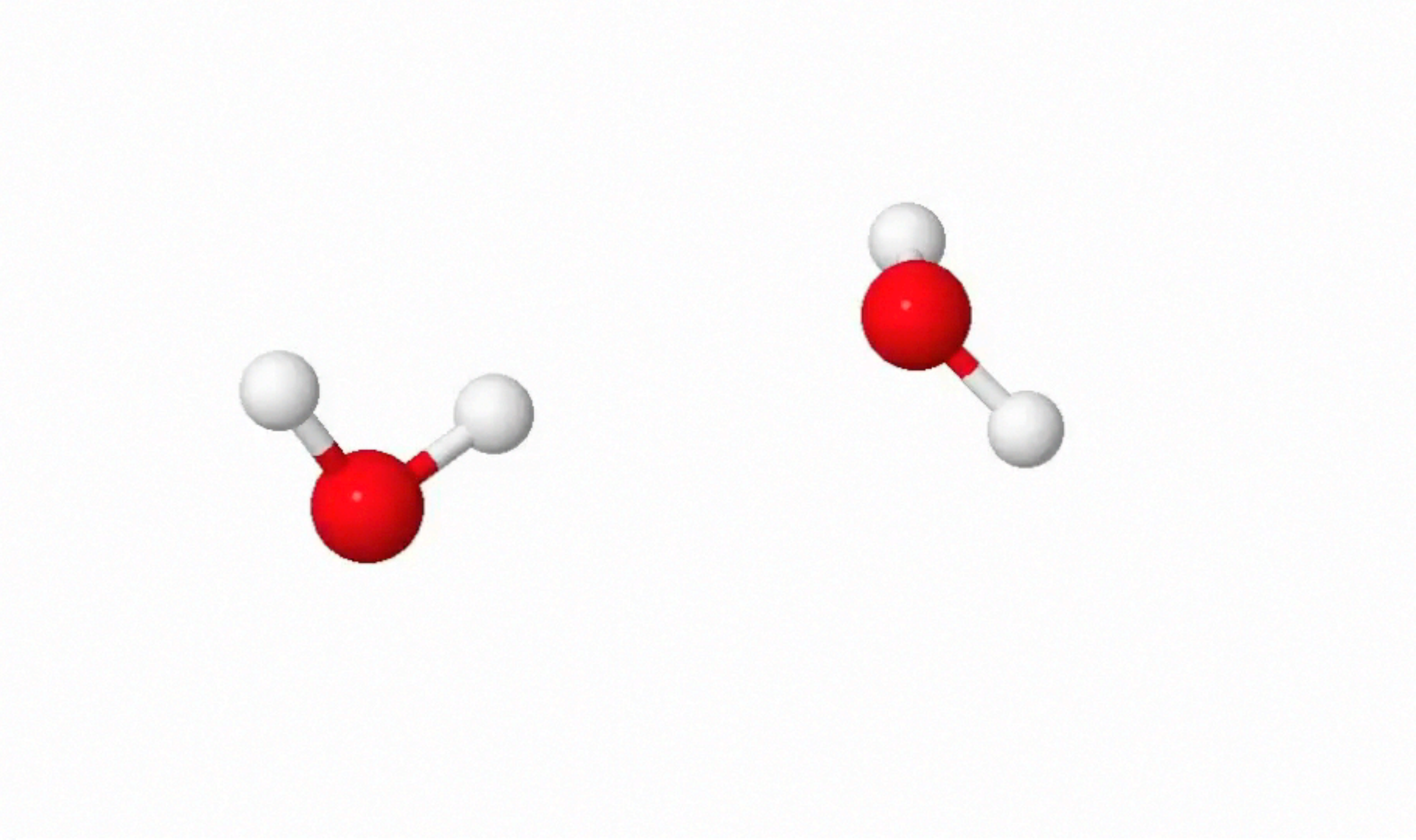
Density, structure and dynamics of water: the effect of Van der Waals interactions Jue Wang, G. Roman-Perez, Jose M. Soler, Emilio Artacho, and M.-V.Fernandez-Serra, J. Chem. Phys. 134, 024516 (2011).

HBONDS AND VDW BONDS

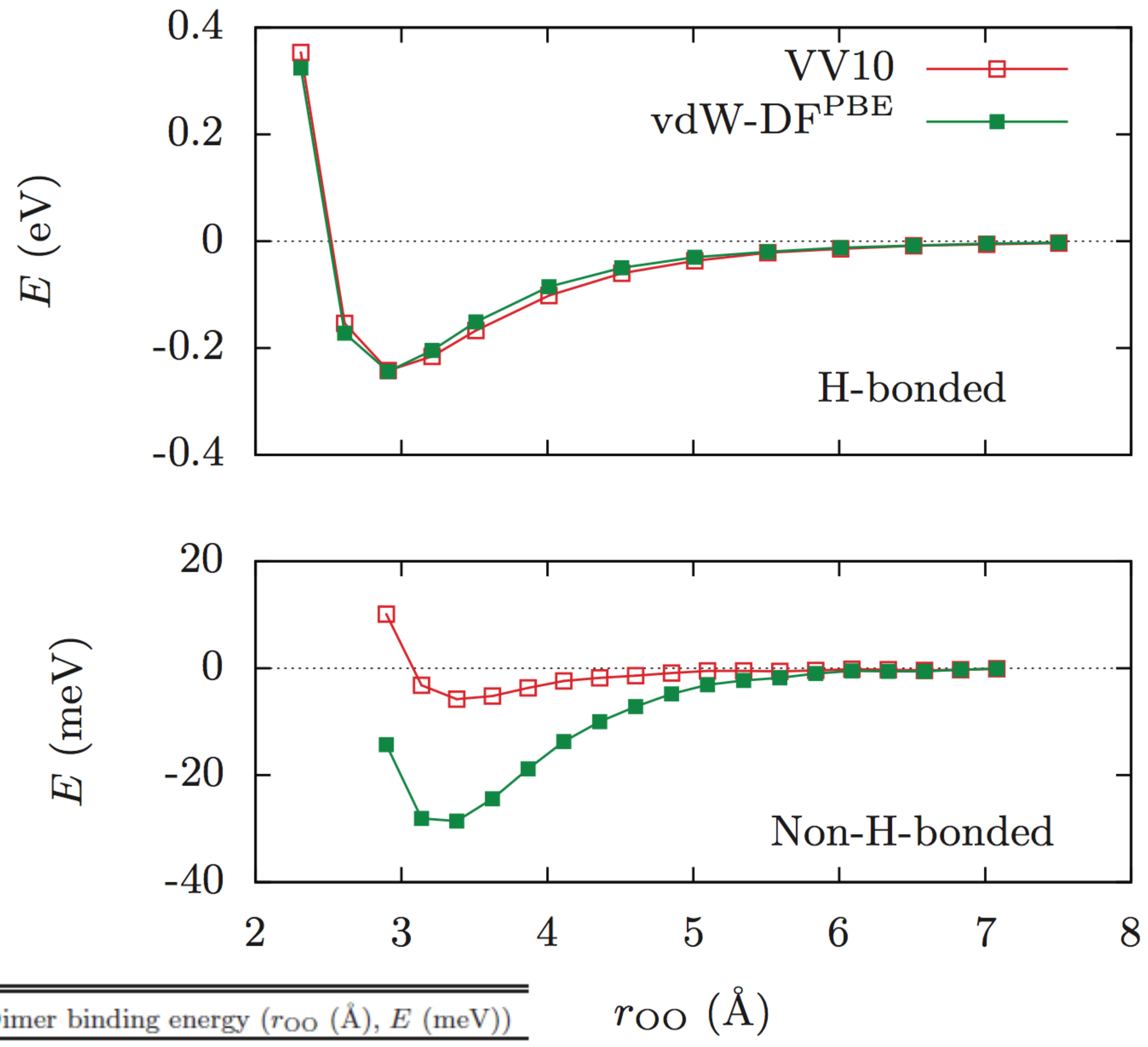
No vdW



with vdW



Dimer interaction energies



xc	Dimer binding energy (r_{OO} (Å), E (meV))	
	H-bonded	Non-H-bonded
VV10	(2.87, 247)	(3.39, 6)
vdW-DF$^{\mathrm{PBE}}$	(2.92, 245)	(3.27, 29)

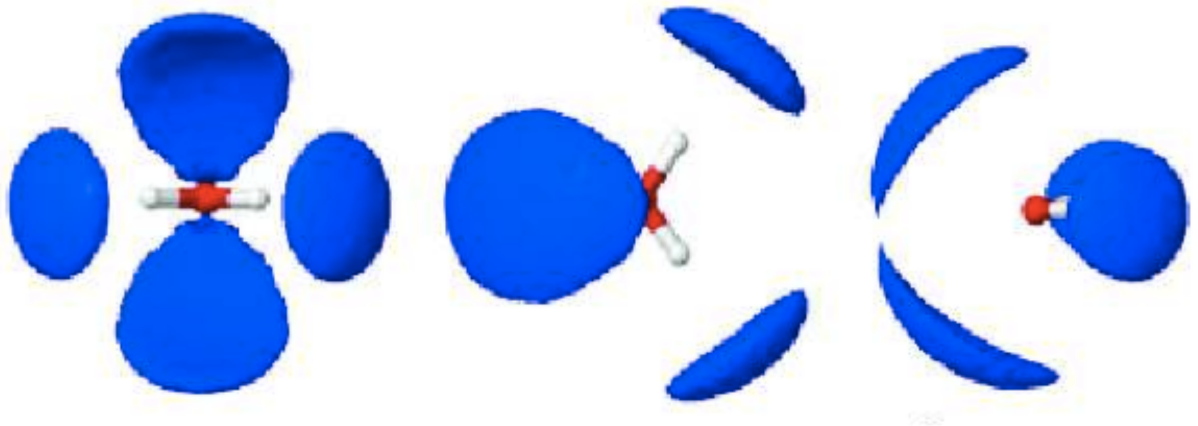
Fabiano Corsetti, Emilio Artacho, José M. Soler, S. S. Alexandre, M.-V. Fernández-Serra, J. Chem. Phys. 139, 194502 (2013).

‘Interstitial shell’

Spatial Distribution function

First shell

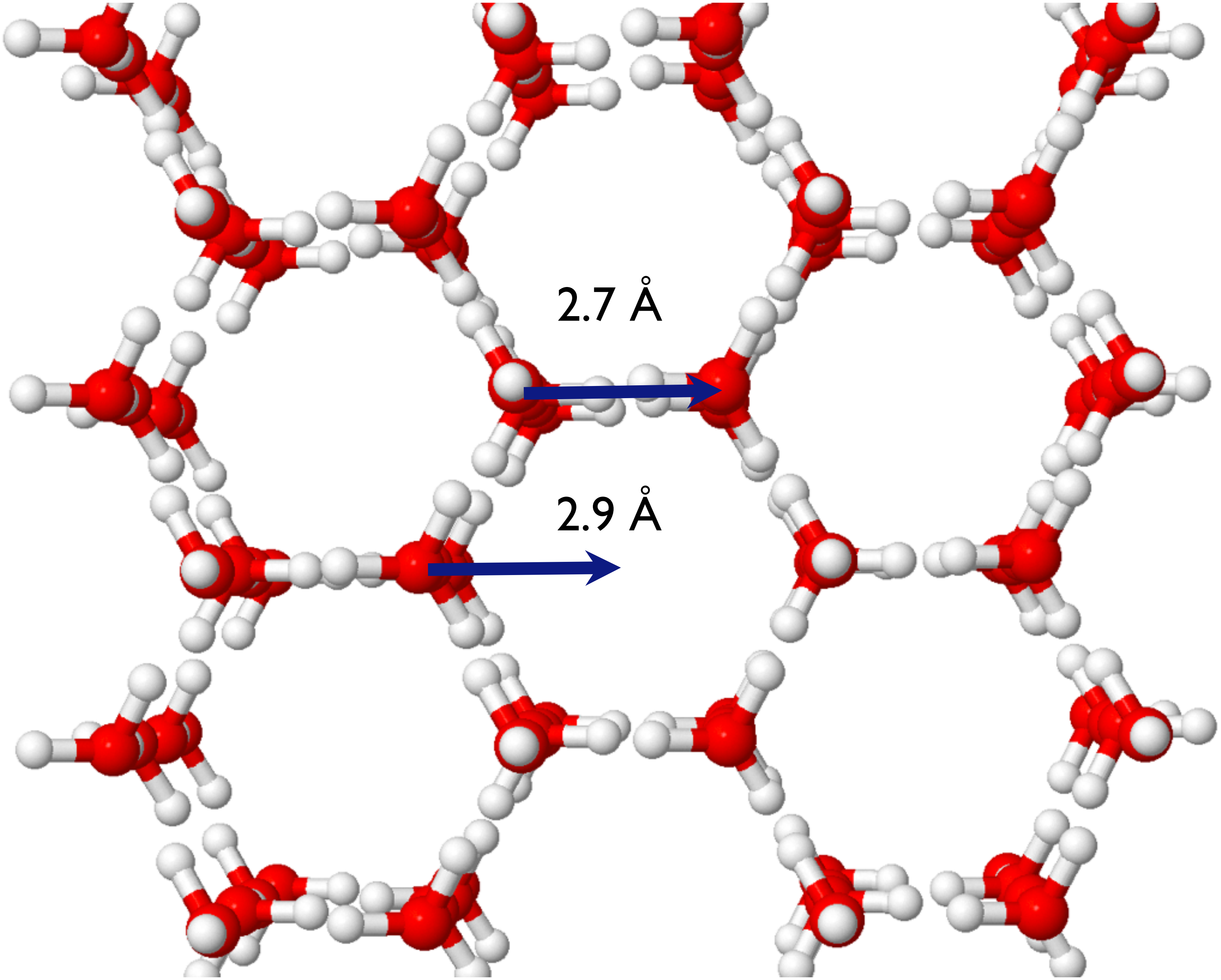
r = 2.8 Ang



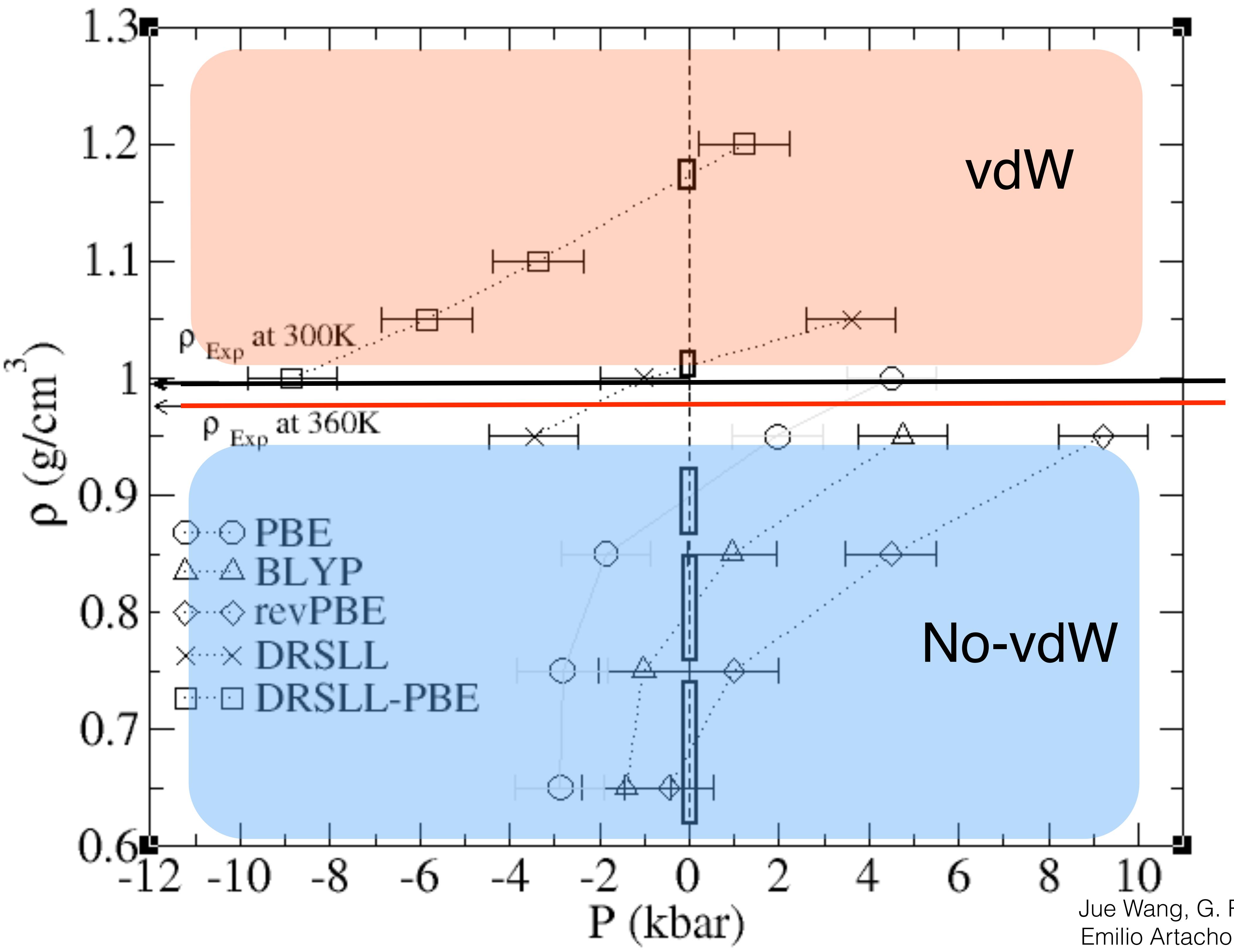
r = 3.5 Ang

Density, structure and dynamics of water: the effect of Van der Waals interactions Jue Wang, G. Roman-Perez, Jose M. Soler, Emilio Artacho, and M.-V.Fernandez-Serra, J. Chem. Phys. 134, 024516 (2011).

Interstitial sites: Ice–IH



Pressure–density curves



64 H2O
T=300 K vdW-DF
T=340 K GGA
only

Jue Wang, G. Roman-Perez, Jose M. Soler,
Emilio Artacho, and M.-V.Fernandez-Serra,
J. Chem. Phys. 134, 024516 (2011).

PHYSICS, PHYSICS, PHYSICS EVERYWHERE…

- Anomalous isotope effects in water and ice
  - Anomalous Nuclear Quantum Effects in Ice, B. Pamuk, J. M. Soler, R. Ramirez, C. P. Herrero, P.W. Stephens, P. B. Allen, and M.-V. Fernandez-Serra. Phys. Rev. Lett. 108, 193003 (2012).
  - Quasi-harmonic approximation of thermodynamic properties of ice Ih,II, and III, R. Ramirez, N. Neuerburg, M.V. Fernández-Serra, and C. Herrero. J. Chem. Phys. 137, 044502 (2012)

- Zero point effects and the phase diagram of Ice
  - Electronic and nuclear quantum effects on the ice XI/ice Ih phase transition. Pamuk, Philip B. Allen, and M.-V. Fernández-Serra Phys. Rev. B 92, 134105, 2015

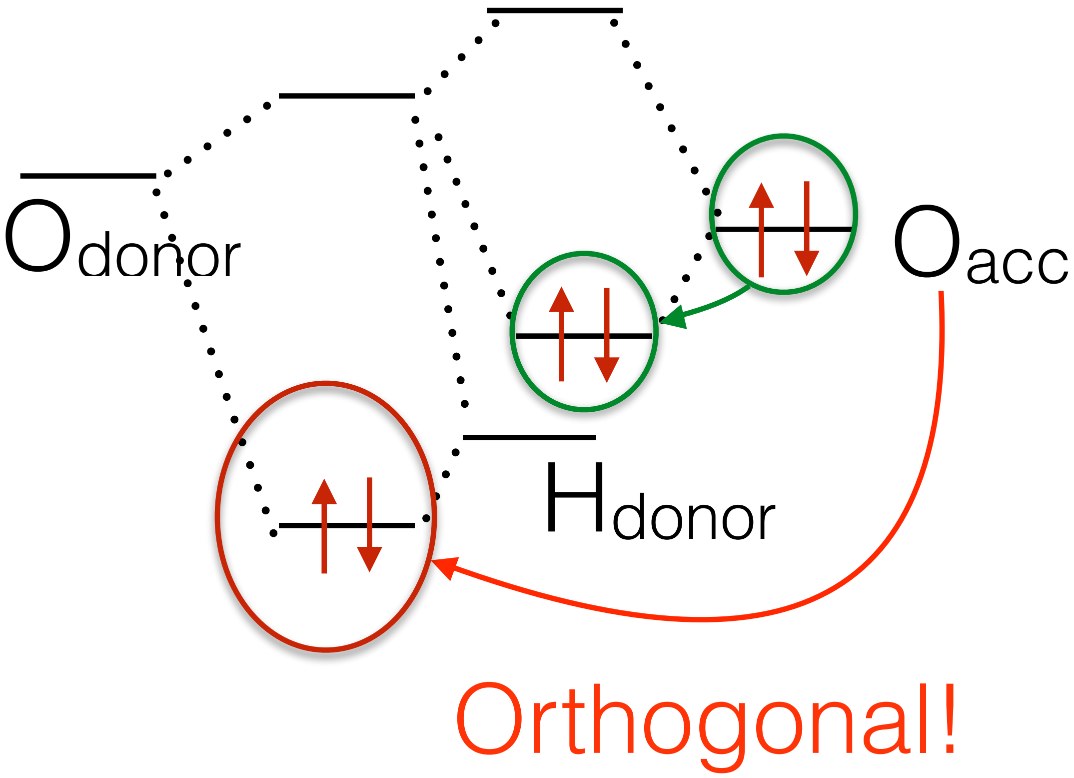
- Thermal conductivity of Ice: what can we learn about proton order?
  - Proton order and thermal conductivity of ice, J. T. Siebert, K. Chen, P. B. Allen and M.V Fernandez-Serra (in prep.)

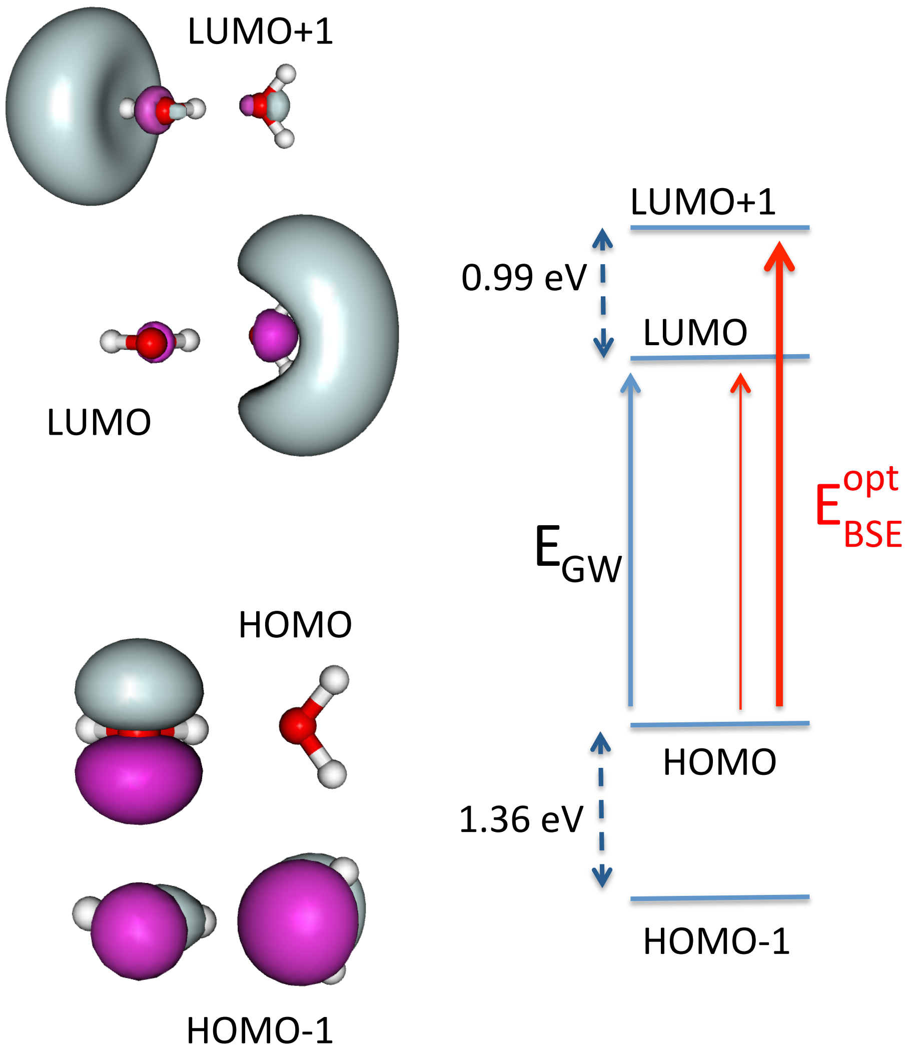
- Polar order in liquid water
  - Polar nanoregions in water - a study of the dielectric properties of TIP4P/2005, TIP4P2005f and TTM3F, Daniel C. Elton, M.V. Fernández-Serra, J. Chem. Phys, 140 , 124504 (2014).

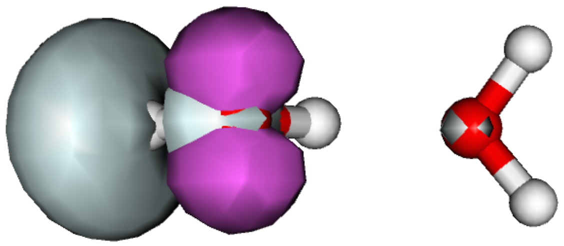
- Phonons in liquid water: Is water closer to a polar solid o to a polar liquid?
  - The hydrogen bond network of water supports propagating optical phonon-like modes" arxiv.org/abs/1507.06363 Nature Communications 2016

H-BOND INTERACTION

Quantum-mechanical (electronic) component of the H-bond: intermolecular polarization, with mixing. Acceptor molecule's HOMO partially fills the LUMO of the donor molecule. This is the anti bonding of the covalent OHd bond, therefore weakening this covalent bond






Exciton S1

M.V Fernandez-Serra and E. Artacho. Phys. Rev. Lett, 96, 016404 (2006).

X. Blase, P. Boulanger, F. Bruneval, M. Fernandez-Serra, and I. Duchemin, JCP (2016)

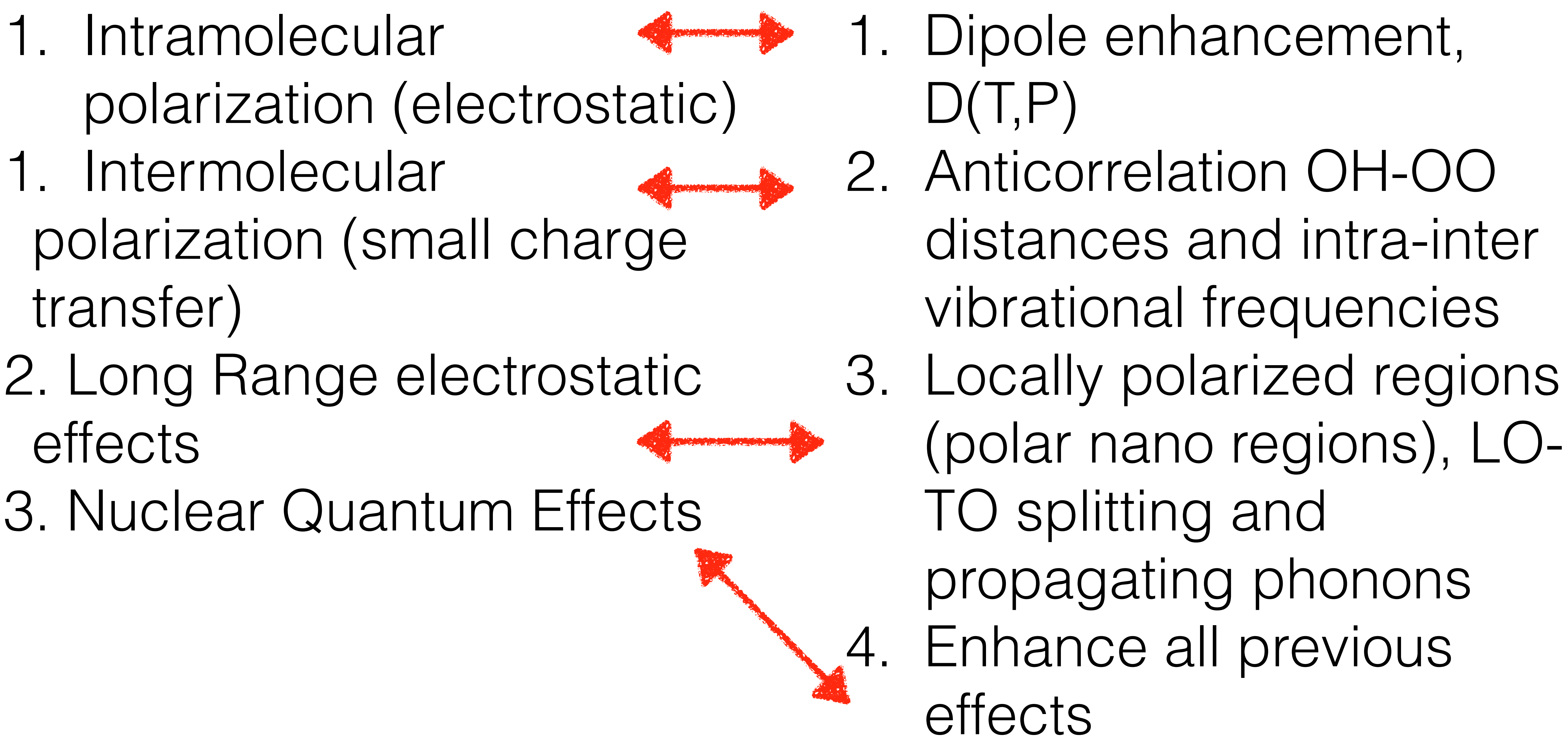
COOPERATIVITY (MANY BODY EFFECTS)

- Many body effects have been shown to be critical to observe the existence of a LLPT in Giancarlo Franzese's many-body coarse grained model.
- The model reproduces most of the thermodynamical anomalies of water and presents a liquid-liquid phase transition ending in a critical point in the universality class of the two-dimensional (2D) Ising model.
- In the model these "quantum many body effects" are linked to the cooperative nature of the H-bond interaction.

Franzese, G., Marques, M. I. & Stanley, H. E. Intramolecular coupling as a mechanism for a liquid-liquid phase transition. Phys. Rev. E 67, 011103 (2003).

Franzese, G., Malescio, G., Skibinsky, A., Buldyrev, S. V. & Stanley, H. E. Generic mechanism for generating a liquid-liquid phase transition. Nature 409, 692 (2001).

COOPERATIVITY (MANY BODY EFFECTS)



Different Physical Sources

1\. Intramolecular polarization (electrostatic)

1\. Intermolecular polarization (small charge transfer)

2\. Long Range electrostatic effects

3\. Nuclear Quantum Effects

Manifestation

1\. Dipole enhancement, D(T,P)

2\. Anticorrelation OH-OO distances and intra-inter vibrational frequencies

3\. Locally polarized regions (polar nano regions), LO-TO splitting and propagating phonons

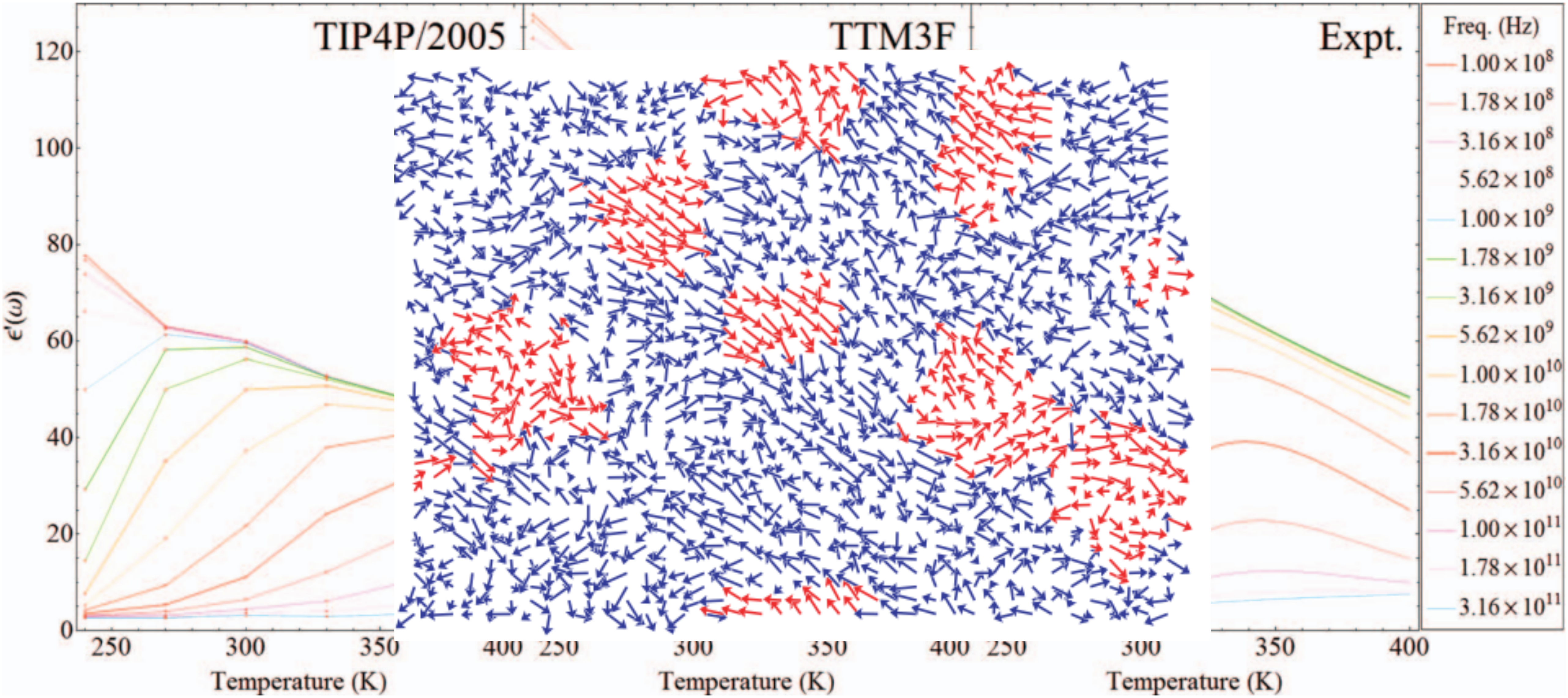
4\. Enhance all previous effects

Intramolecular Polarization

Both and electronic and ionic contribution
Present in all flexible and polarizable force fields

Temperature dependence of the dipole moment

Density dependence of the dipole moment



- TTM3F better reproduces Δε(0) / ΔT and Δε(0) / ΔV
- Change in entropy in E field is proportional to Δε(0) / ΔT[1]

öhlich, *Theory of Dielectrics (Oxford Uni. Press*,1949).

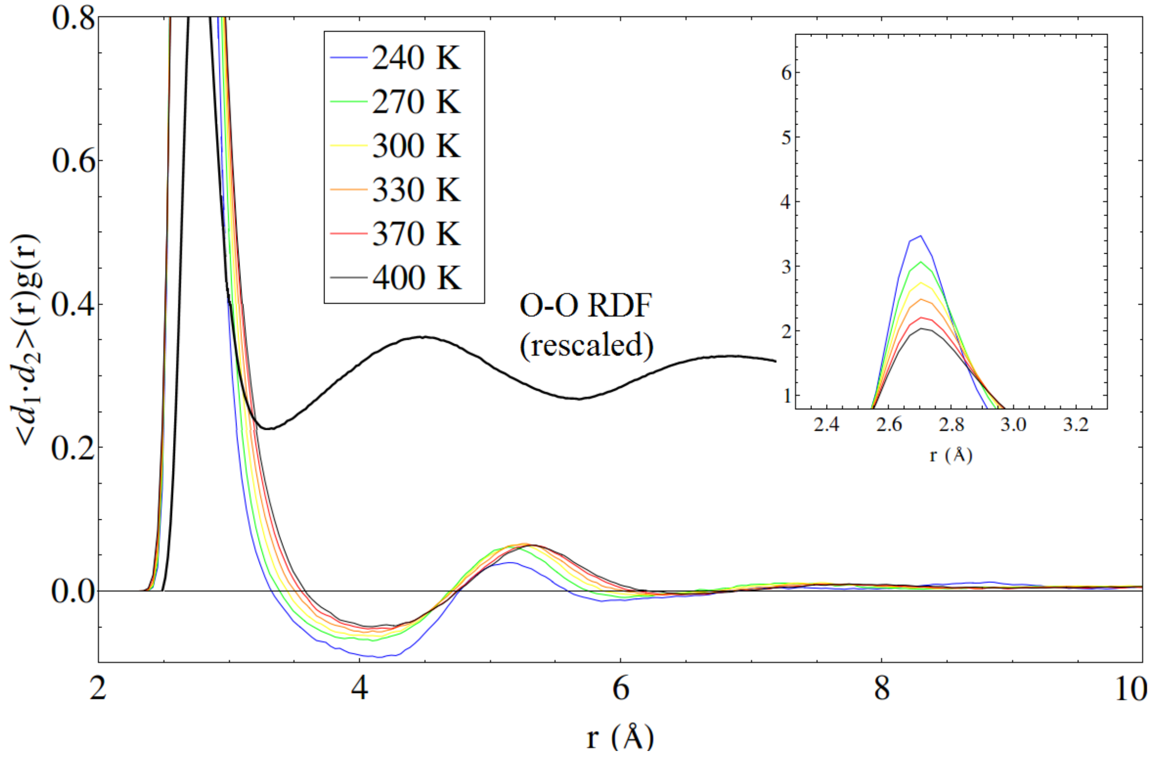
Daniel C. Elton, M. V. Fernández-Serra, J. Chem. Phys, 140 , 124504 (2014).

DIPOLE LONG RANGE ORIENTATIONAL ORDER

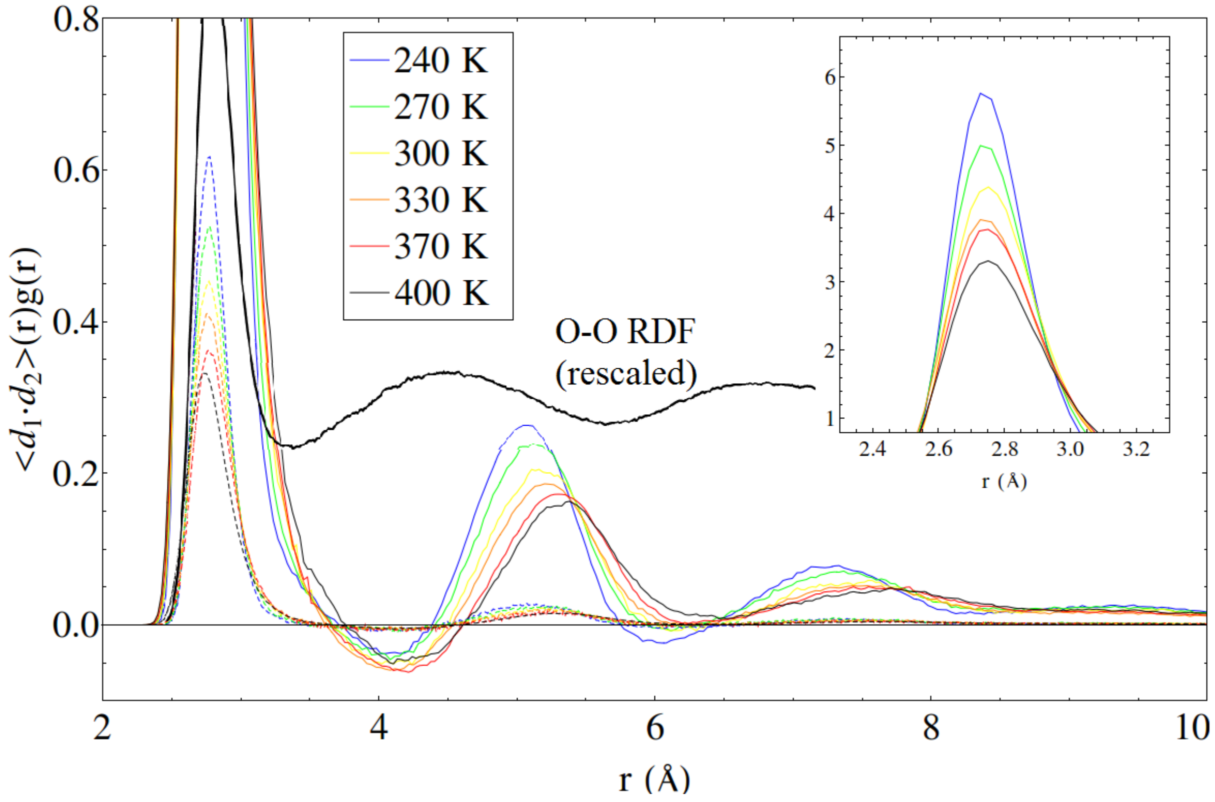
“dip-dip correlation function” – gives average angle, weighted by density of molecules (O-O RDF)

$$\phi(r) = \frac{1}{N_{\mathrm{gas}}(r)} {\sum_{i,j}}' \boldsymbol{\mu}_i \cdot \boldsymbol{\mu}_j \qquad r < r_{ij} < r + \delta r$$
$$= \langle \boldsymbol{\mu}_1 \cdot \boldsymbol{\mu}_2 \rangle (r) g_{OO}(r)$$

TIP4P/2005f dip-dip correlation function



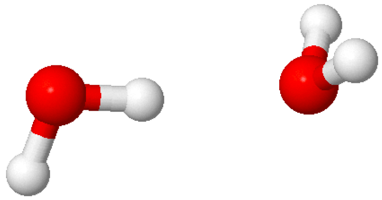
TTM3F dip-dip correlation function



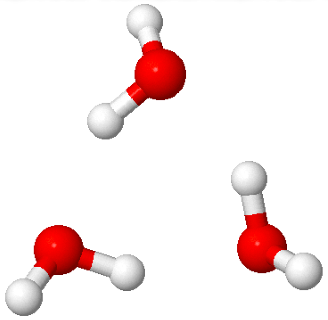
Polar Nanoregions (PNRs): Cooperative rearranging regions
Same behavior as Relaxor Ferroelectric materials

Daniel C. Elton, M. V. Fernández-Serra, J. Chem. Phys, 140 , 124504 (2014).

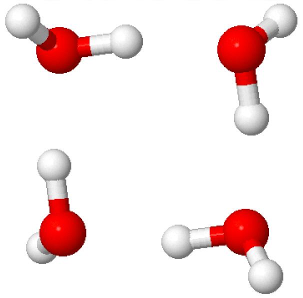
COOPERATIVITY IN HBOND CHAINS



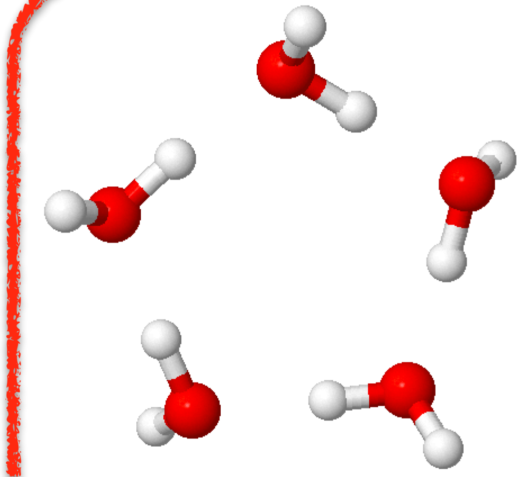
$r_{OO}=2.91$ Å
$r_{OH}=0.98$ Å
$E_b=0.227$



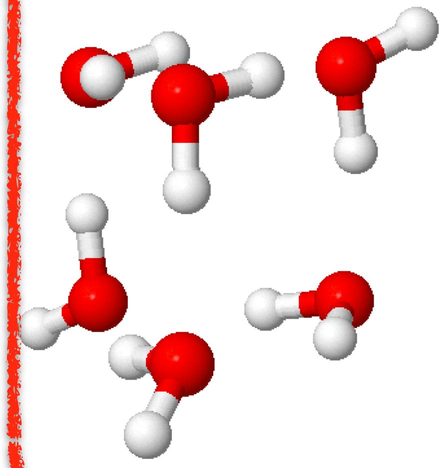
$r_{OO}=2.80$ Å
$r_{OH}=0.99$ Å
$E_b=0.245$



$r_{OO}=2.69$ Å
$r_{OH}=1.0$ Å
$E_b=0.35$



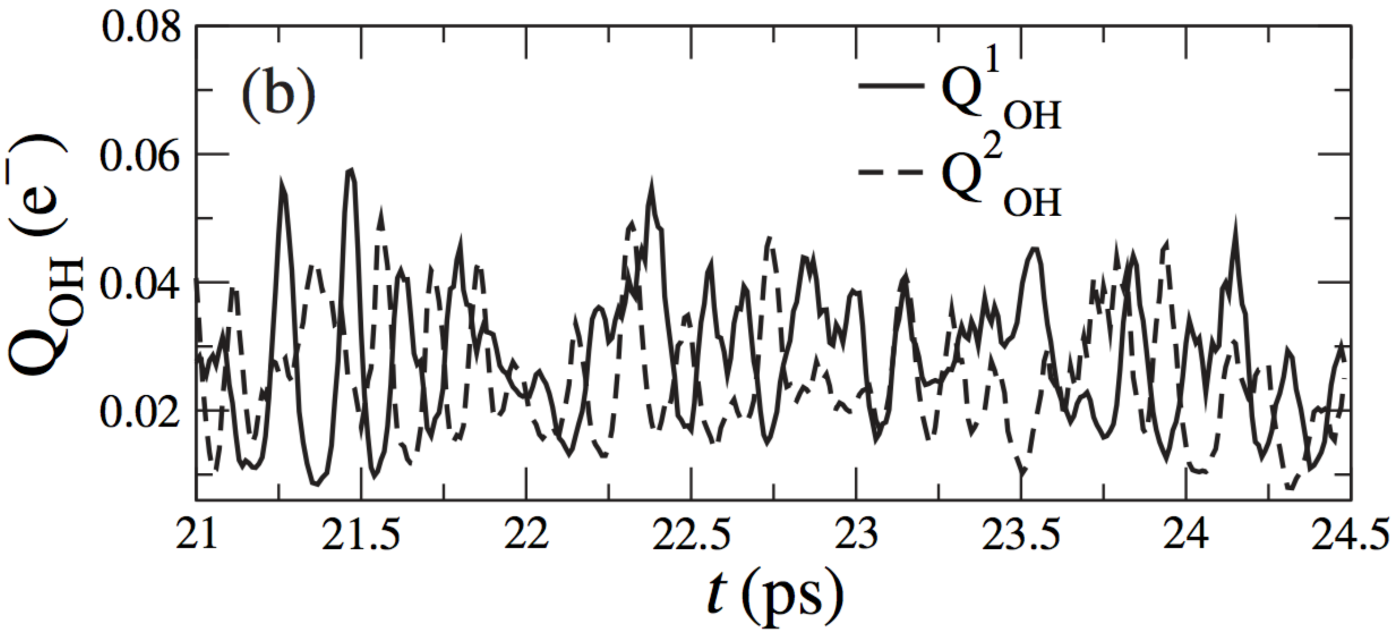
$r_{OO}=2.69$ Å
$r_{OH}=1.0$ Å
$E_b=0.37$



$r_{OO}=2.81$ Å
$r_{OH}=0.99$ Å
$E_b=0.27$

ELECTRONIC COOPERATIVITY IN LIQUID WATER

The main source of enhanced Hbond interaction is liquid water are the intra- and inter-molecular polarization effects. In addition, there is an observed electronic beat which alternates between strong and weak Hbonds, that can be delocalized along a chain of several Hbonded molecules.



M.V Fernandez-Serra and E. Artacho.
Phys. Rev. Lett, 96, 016404 (2006).

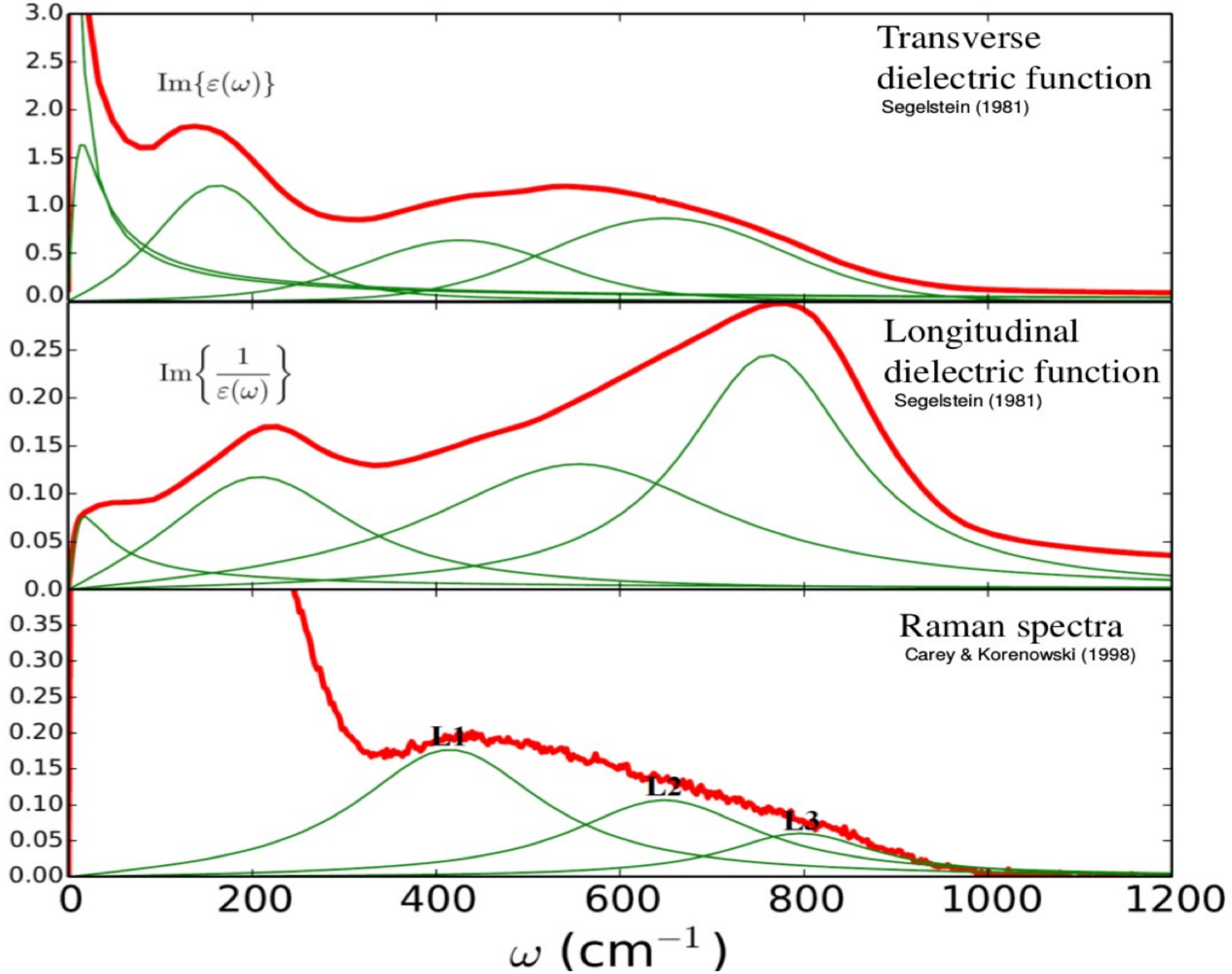
T. D. Kuhne, R. Z. Khaliullin.

“Electronic signature of the instantaneous asymmetry in the first coordination shell of liquid water.”

Nature Communications, 4, 1450 (2013)

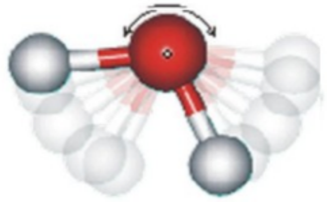
VIBRATIONAL PROPERTIES OF WATER

Problematic peak assignments

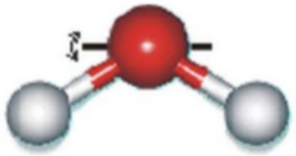


Librational motions of a single water molecule

L1 = "twisting"



L2 = "rocking"
IR active

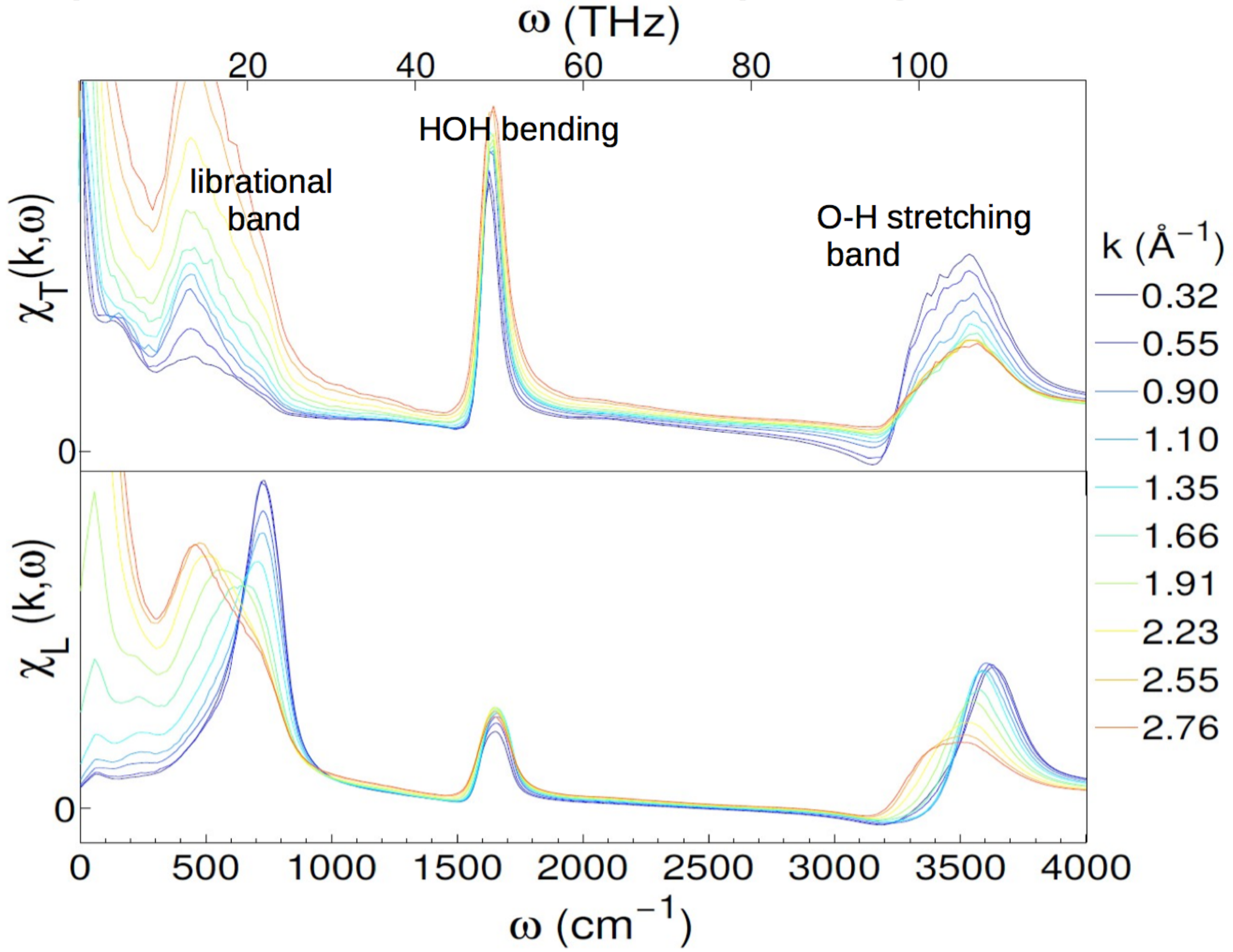


L3 = "wagging"
IR active

"The hydrogen bond network of water supports propagating optical phonon-like modes",

D. Elton and M. V. Fernández-Serra, Nature Communications 7, Article number: 10193, (2016)

VIBRATIONAL PROPERTIES OF WATER



k-dependent dielectric susceptibility of TTM3F

$$\phi(k,t) = \left\langle \sum_i \mathbf{p}_i(k,0) \cdot \sum_j \mathbf{p}_j(k,t) \right\rangle$$

$$\chi_{\mathrm{L/T}}(k,\omega) = \chi_{\mathrm{L/T}}(k,0) \int_0^\infty \dot{\Phi}_{\mathrm{L/T}}(k,t) e^{i\omega t} \mathrm{d}$$

$$\chi_L(k \to 0, \omega) = 1 - \frac{1}{\varepsilon(\omega)}$$

$$\chi_T(k \to 0, \omega) = \varepsilon(\omega) - 1$$

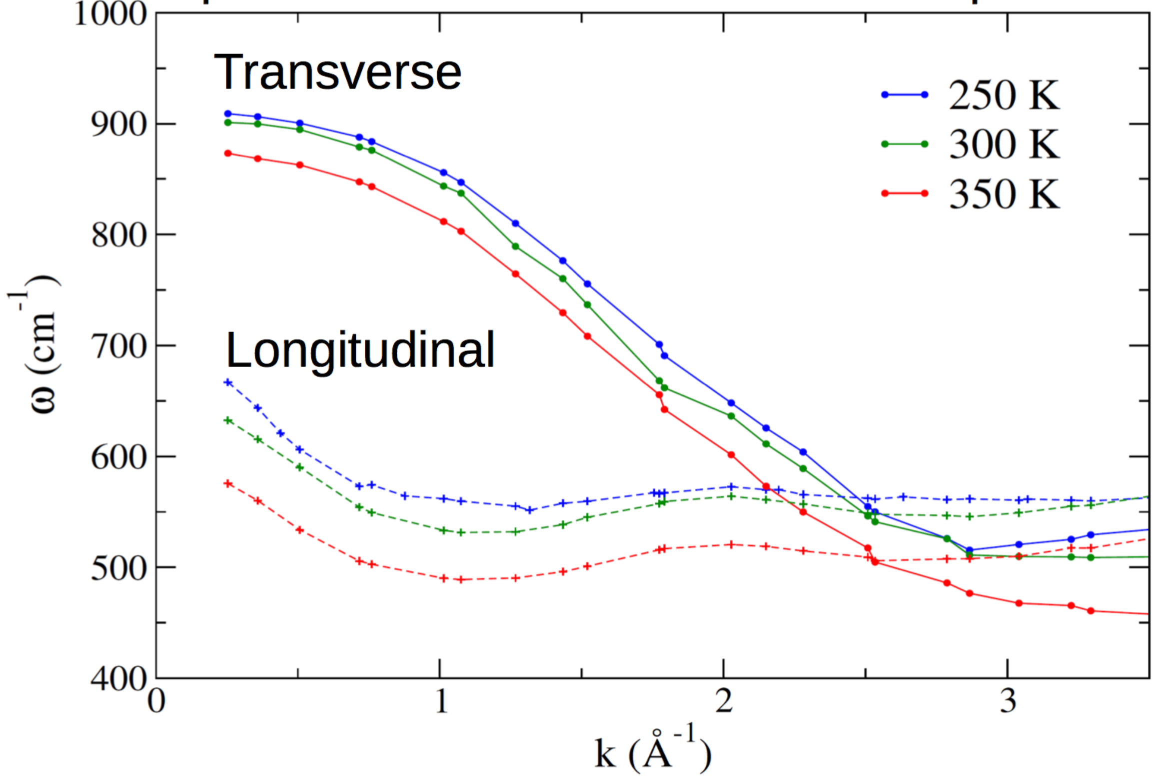
$$\begin{aligned} \varepsilon'(\omega) &= n^2(\omega) - k^2(\omega) \\ \varepsilon''(\omega) &= 2n(\omega)k(\omega) \end{aligned}$$

“The hydrogen bond network of water supports propagating optical phonon-like modes”,

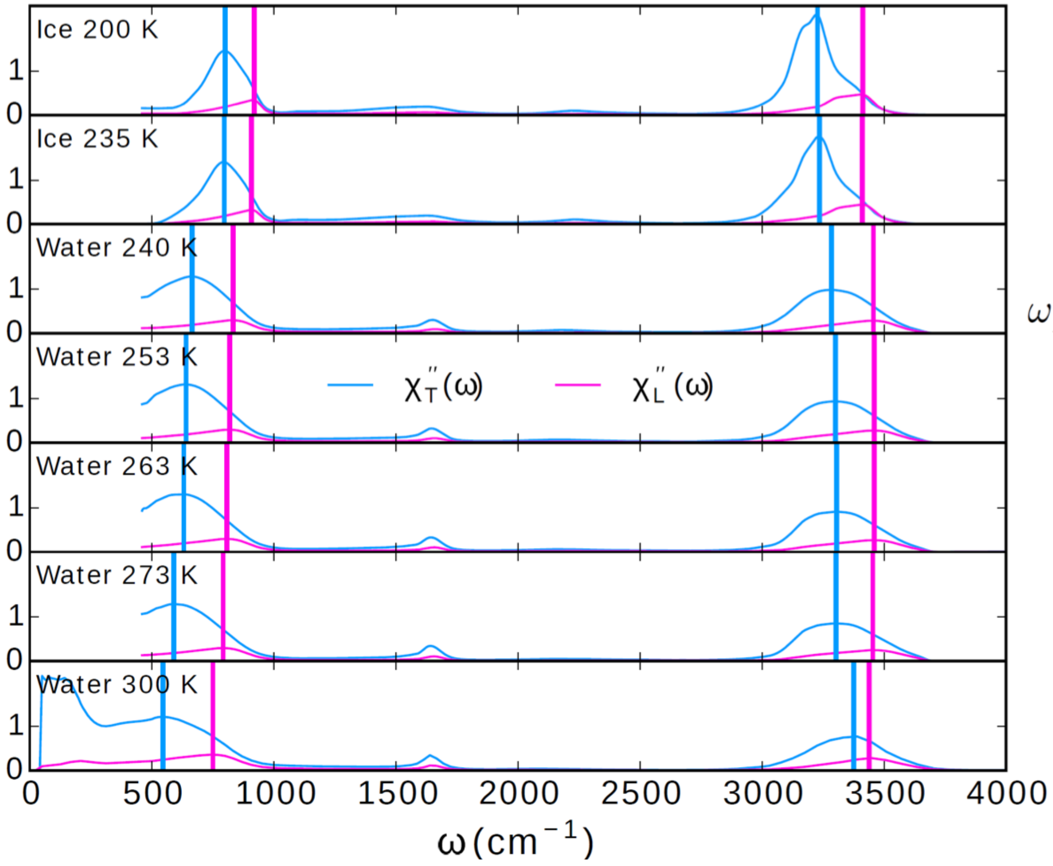
D. Elton and M. V. Fernández-Serra, Nature Communications 7, Article number: 10193, (2016)

VIBRATIONAL PROPERTIES OF WATER

Dispersion relations for the librational peak



LO-TO splitting



Relation to crystal structure:

$$\omega_{Lk}^2 - \omega_{Tk}^2 = \frac{4\pi C}{3v}\left(\frac{\partial \boldsymbol{\mu}}{\partial Q_k}\right)^2$$

v = volume per unit cell

C = depends on crystal structure

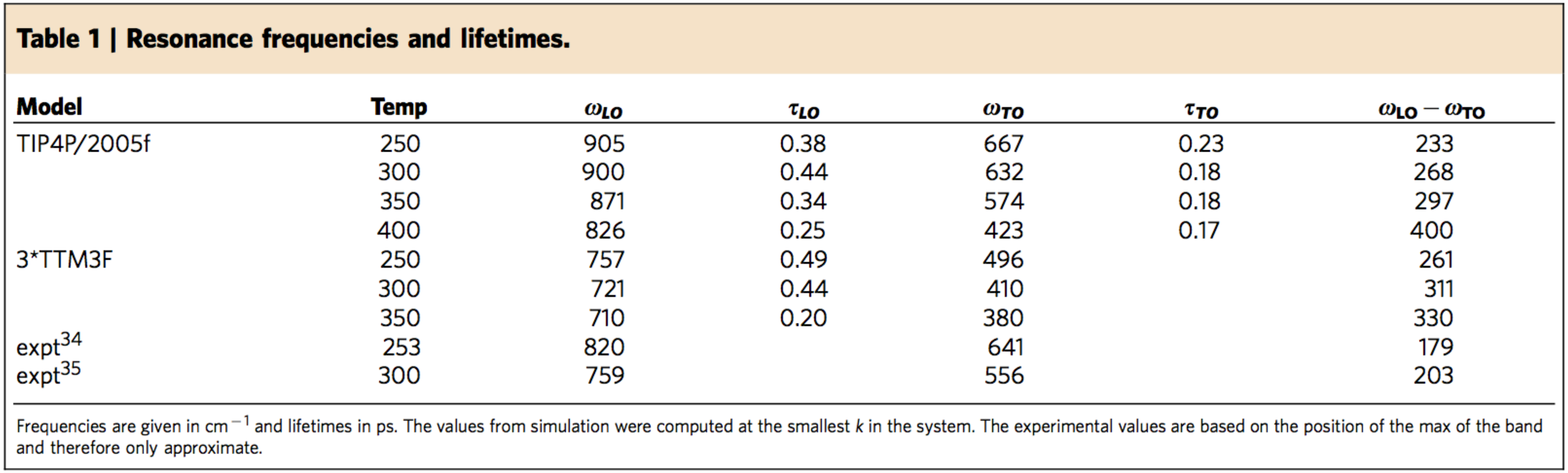


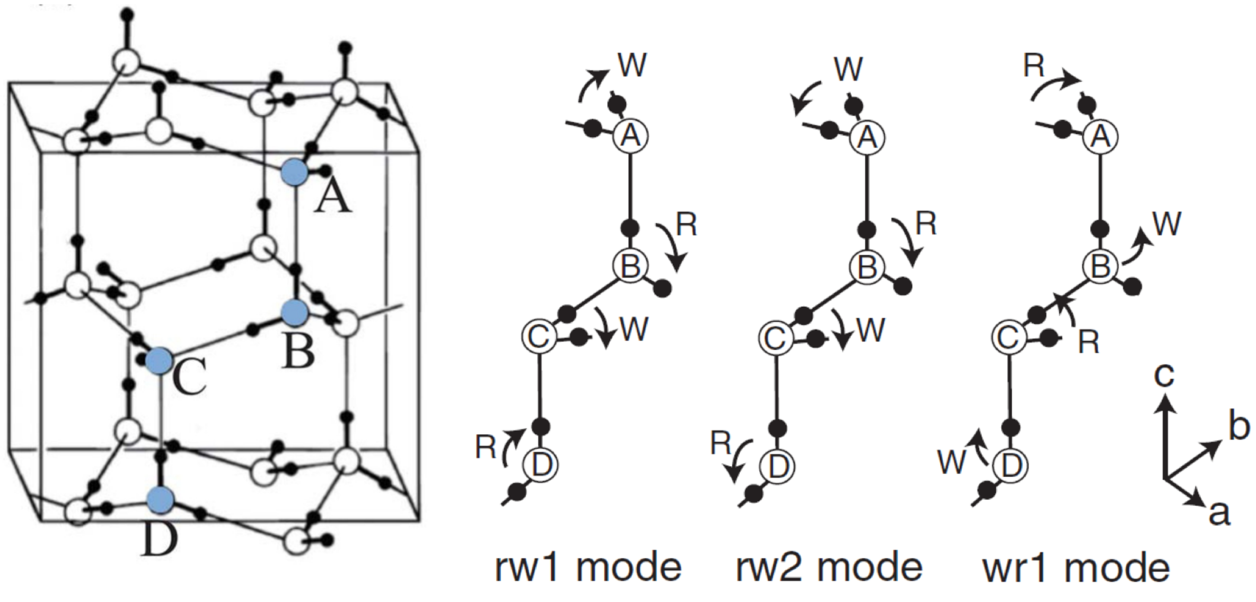
Table 1 | Resonance frequencies and lifetimes.

Model	**Temp**	ω_{LO}	τ_{LO}	ω_{TO}	τ_{TO}	$\omega_{LO} - \omega_{TO}$
TIP4P/2005f	250	905	0.38	667	0.23	233
	300	900	0.44	632	0.18	268
	350	871	0.34	574	0.18	297
	400	826	0.25	423	0.17	400
3*TTM3F	250	757	0.49	496		261
	300	721	0.44	410		311
	350	710	0.20	380		330
expt[34]	253	820		641		179
expt[35]	300	759		556		203

Frequencies are given in cm^{-1} and lifetimes in ps. The values from simulation were computed at the smallest *k* in the system. The experimental values are based on the position of the max of the band and therefore only approximate.

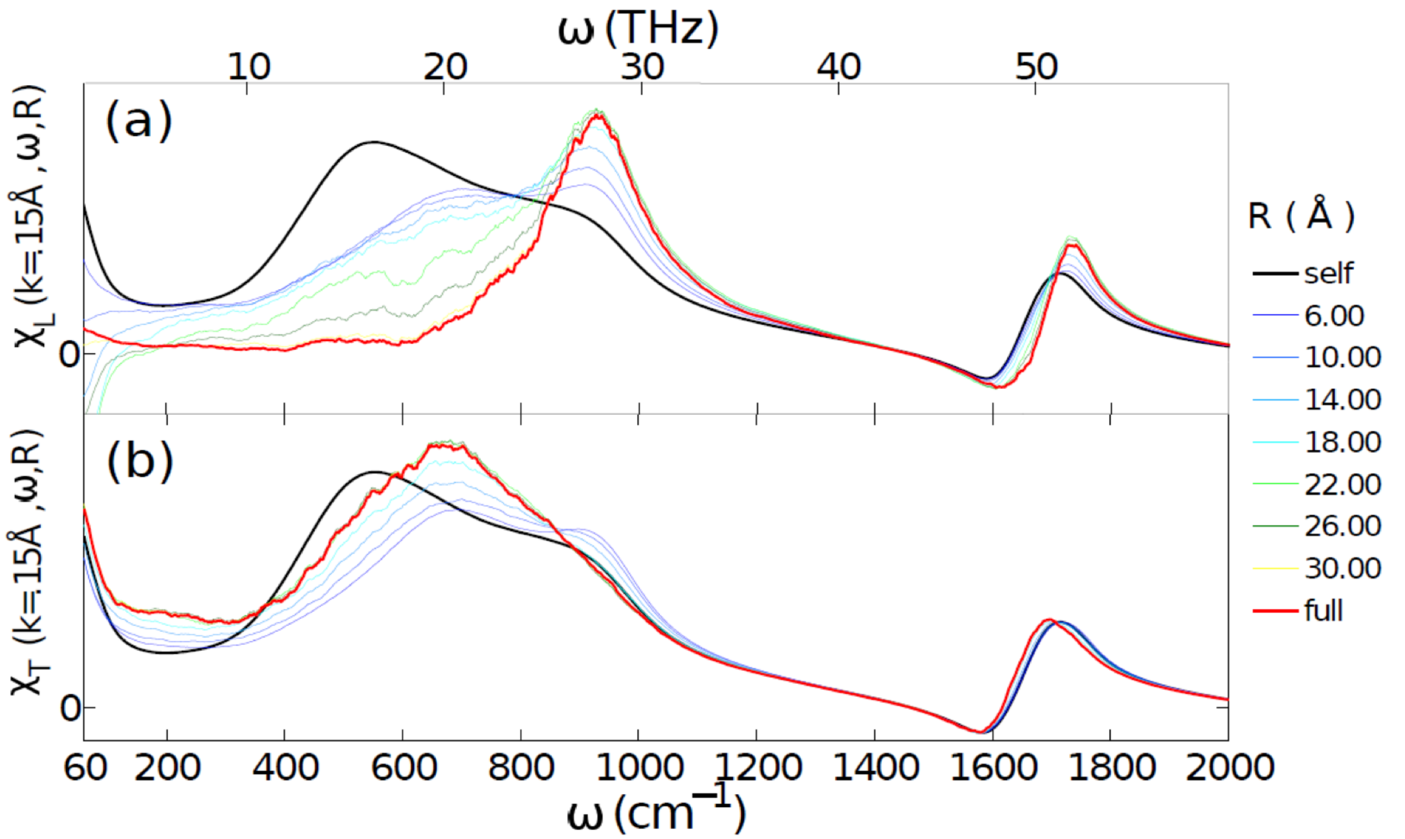
PHONONS IN ICE AND RANGE OF PROPAGATION

Corresponding librational modes in ice XI



Ref: Iwano et al. *J. Phys. Soc. Jap.* **79**, 063601 (2010).

Distance decomposition of the spectra

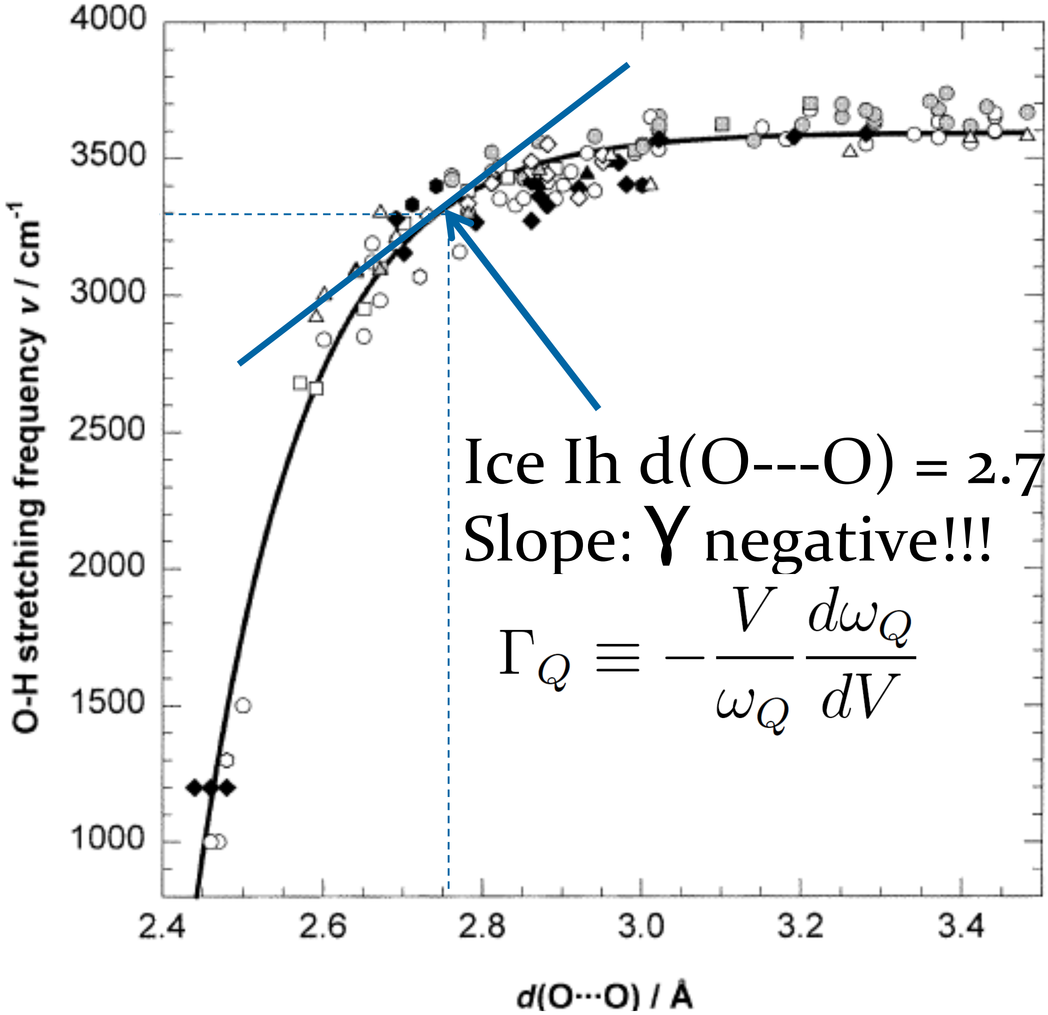


- The dynamics of water are closer to that of ice than previously thought.
- We reassign librational & stretching spectral peaks to phonon-like modes.
- The librational modes correspond to coupled rocking and waging motions
- lifetimes of ~.1 – .5 ps
- propagation distances of up to 2 nm
- modes exhibits LO-TO splitting
- LO-TO splitting is a novel probe of local structure

Example of DFT success: Anomalous Isotope effects in ice and water

OH--O ANTI-CORRELATION EFFECT

- Well know effect in water and ice
- Common in Hbonded systems.



Ice Ih d(O---O) = 2.75 Å

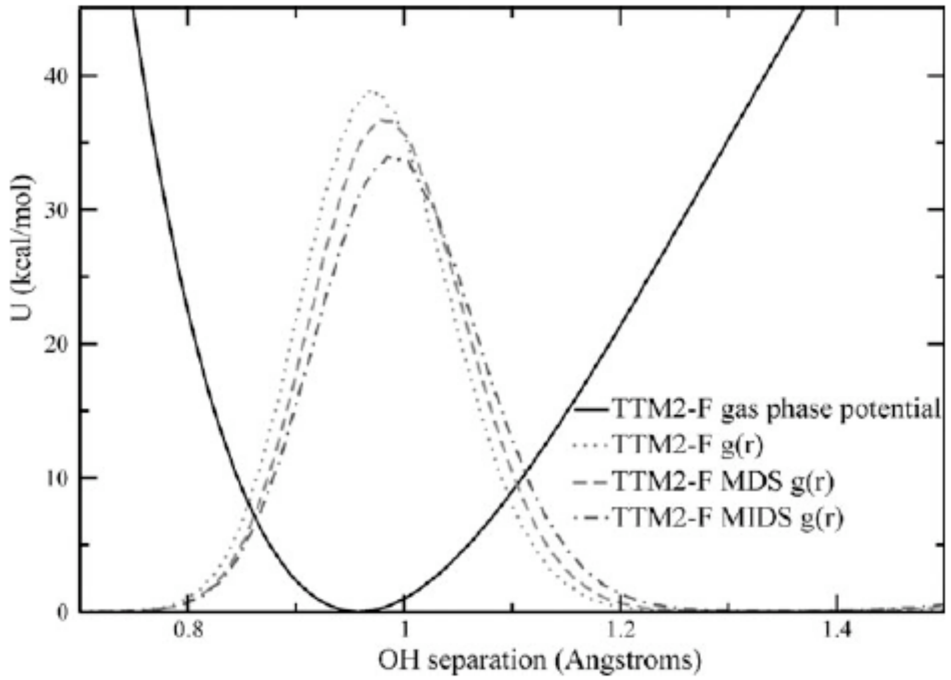
Slope: γ negative!!!

$$\Gamma_Q \equiv -\frac{V}{\omega_Q}\frac{d\omega_Q}{dV}$$

E. Libowitzky, 1999

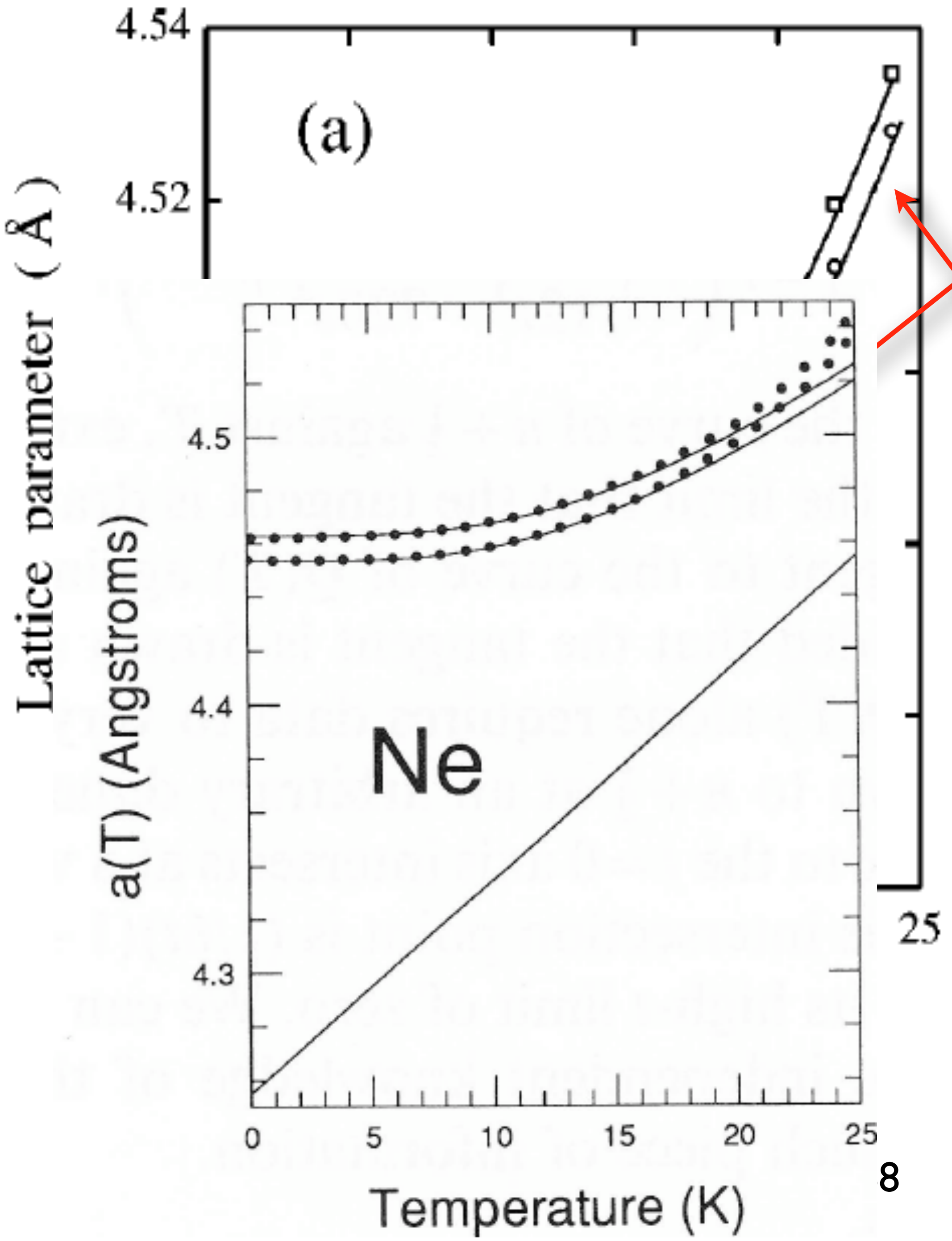
Fig. 1. Plot of the $d(\mathrm{O}\cdots\mathrm{O})$ – frequency correlation; open symbols represent straight H bonds, shaded symbols mark bent H bonds, and filled ones denote copper compounds; circles – silicates, squares - (oxy)hydroxides, hexagons – carbonates, diamonds – sulfates, triangles – phosphates and arsenates; the regression curve was calculated for distances < 3.5 Å ($n = 124$) in the form $\nu = 3592 - 304 \cdot 10^9 \cdot \exp(-d/0.1321)$, $R^2 = 0.96$

C. J. Burnham, G. F. Reiter, J. Mayers, T. Abdul-Redah, H. Reichert and H. Dosch, **On the origin of the redshift of the OH stretch in Ice Ih: evidence from the momentum distribution of the protons and the infrared spectral density**, Phys. Chem. Chem. Phys., 2006, 8, 3966

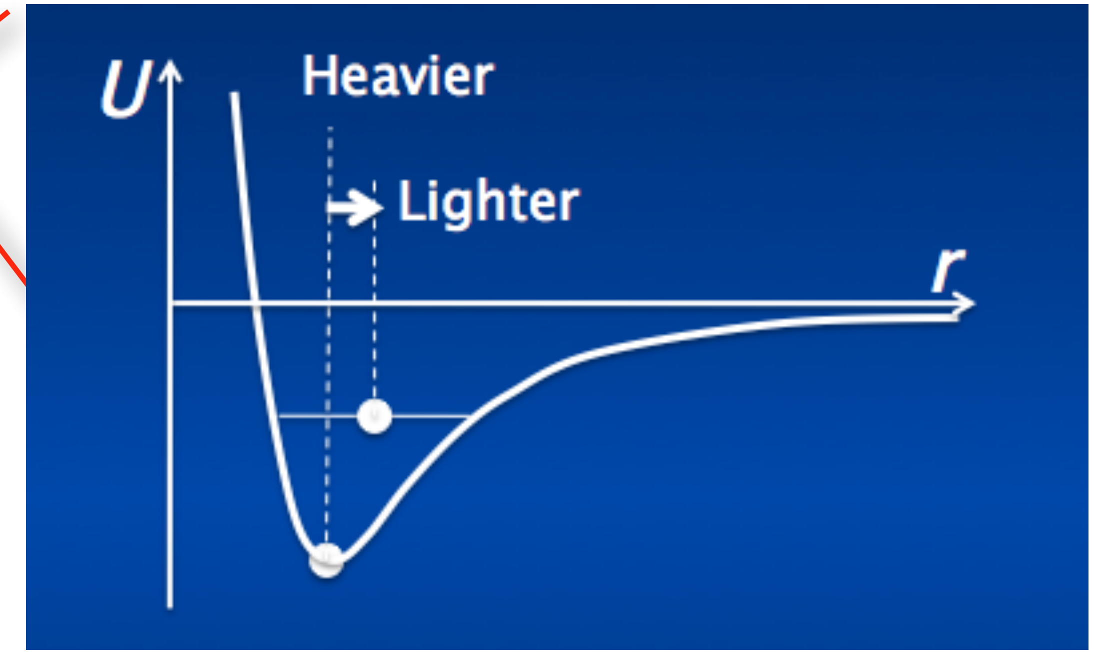


Isotope shift of lattice constant

Bolz and Mauer, 1962
Batchelder, Losee, and Simmons, 1968
Phil Allen, 1994, Herrero 96



Heavy neon (^{22}Ne) occupies 0.19% less space than light neon (^{20}Ne) at T=0.



T.

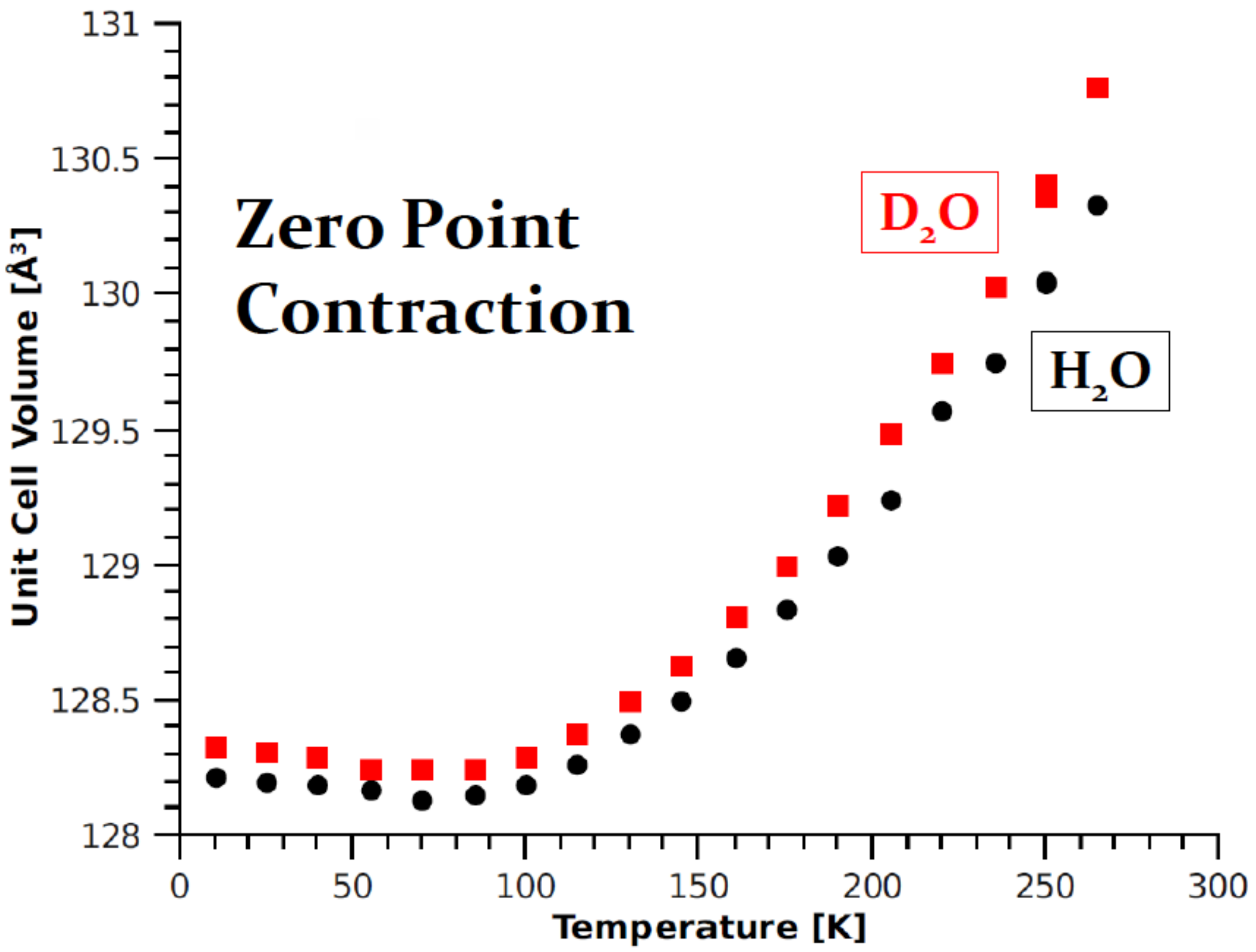
Extrapolated bare lattice constant a=4.255A

~12% zero point volume expansion

Isotope effects in ice: experiments

K. Röttger, A. Endriss, J. Ihringer, S. Doyle and W. F. Kuhs

Lattice constants and thermal expansion of H_2O and D_2O ice Ih between 10 and 265K
Acta Cryst. (1994). B50, 644-648
Acta Cryst (2012)



- Inverse isotope effect!
- $V(H_2O) < V(D_2O)$ by 0.09%
- Deviation is increasing rather than decreasing as T increases

Should V_0 be
> exps. or < exps?

Theory of zero point and thermal lattice expansion (I)

- To find V at T=0, we minimize:

$$E_{gs} = E_{el,0} + \sum_q \frac{\hbar\omega_q}{2} \longleftarrow \mathrm{E}_{\mathrm{zp}}$$

- At T>0 the equilibrium V minimizes the Helmholtz free energy:

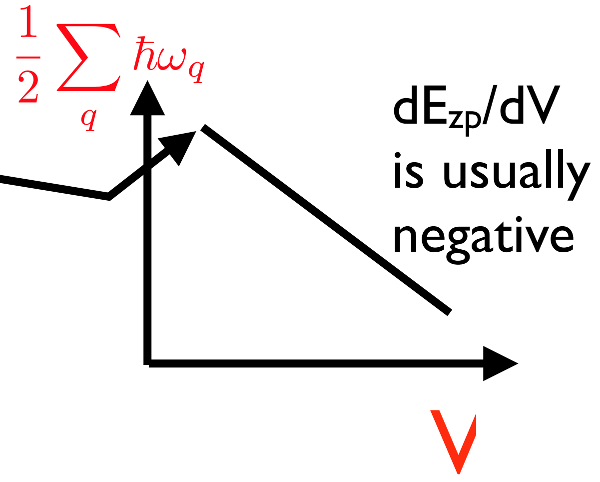
$$F(V,T) = E_0(V) + \sum_q \left[\frac{\hbar\omega_q}{2} + k_B T \ln\left(1 - e^{\frac{-\hbar\omega_q}{k_B T}}\right)\right]$$

- Volume dependent Quasiharmonic approximation: Frequencies depend only on V(T).

$$\omega_q(V) = \omega_q(V_0)\left[1 - \frac{(V - V_0)}{V_0}\gamma_q\right]$$

- Grüneisen parameter

$$\gamma_q \equiv -\left(\frac{V_0}{\omega_q}\right)\left(\frac{\partial\omega_q}{\partial V}\right)_{V_0}$$



dE$_{zp}$/dV is usually negative

ICE STRUCTURES

Different Ice Structures

ice Ih (BF structure, proton ordered)

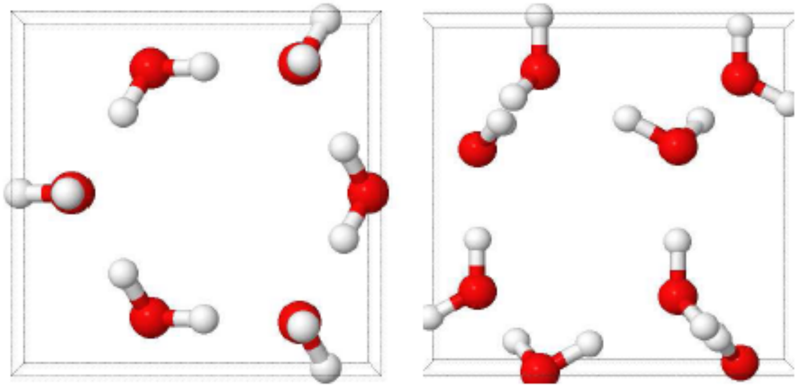


FIG. 2. Bernal-Fowler ice Ih structure. The image on the right is the top view of the x-y plane; the image on the left is the side view of the x-z plane.

ice XI

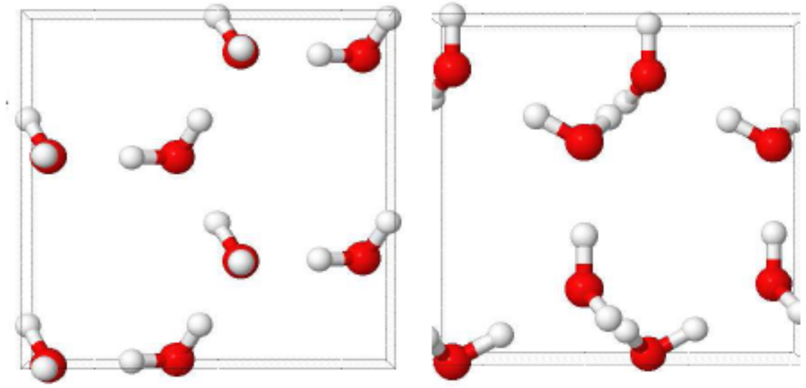


FIG. 1. Unit cell of the H-ordered ice XI structure. The image on the right is the top view of the x-y plane; the image on the left is the side view of the x-z plane.

ice Ih, 96 H2O, proton disordered

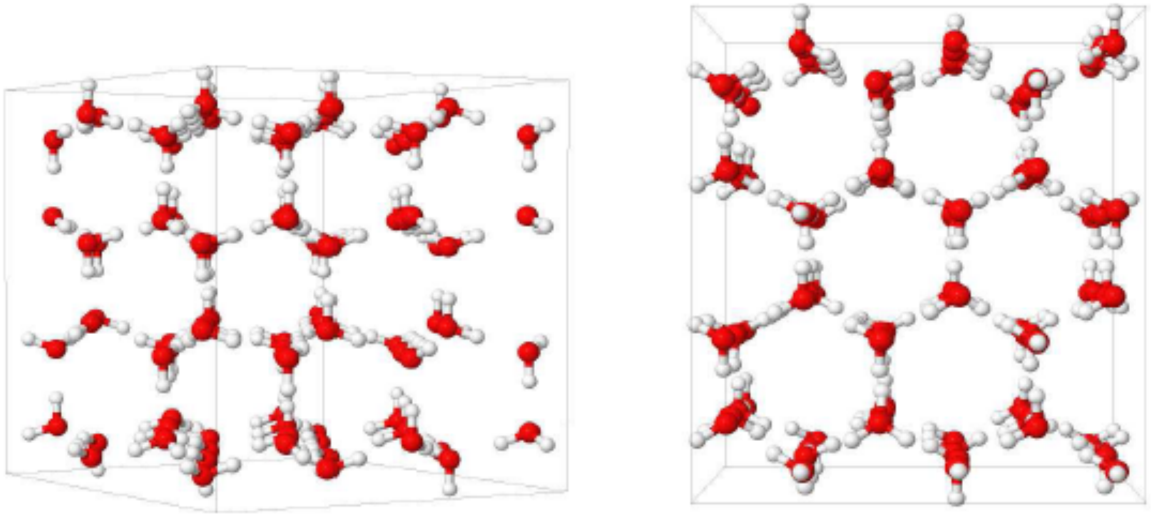
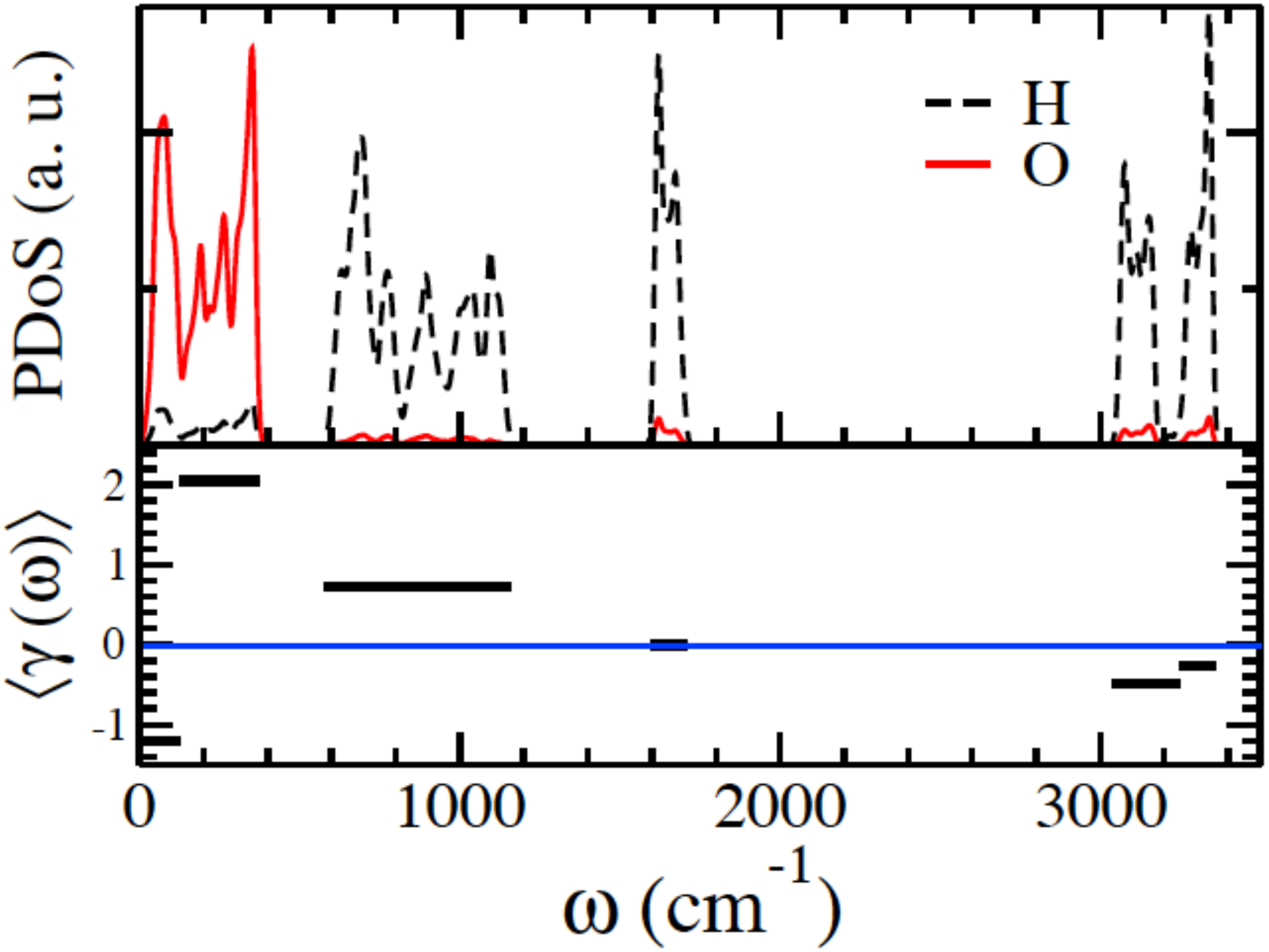


FIG. 3. H-disordered ice Ih structure. The image on the right is the top view of the x-y plane; the image on the left is the side view of the x-z plane.

Phonon Density of States

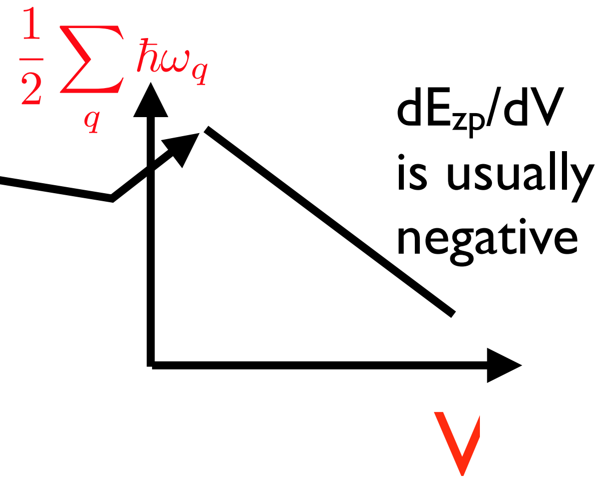


OH--O anti-correlation:

Stronger H-bond⇒

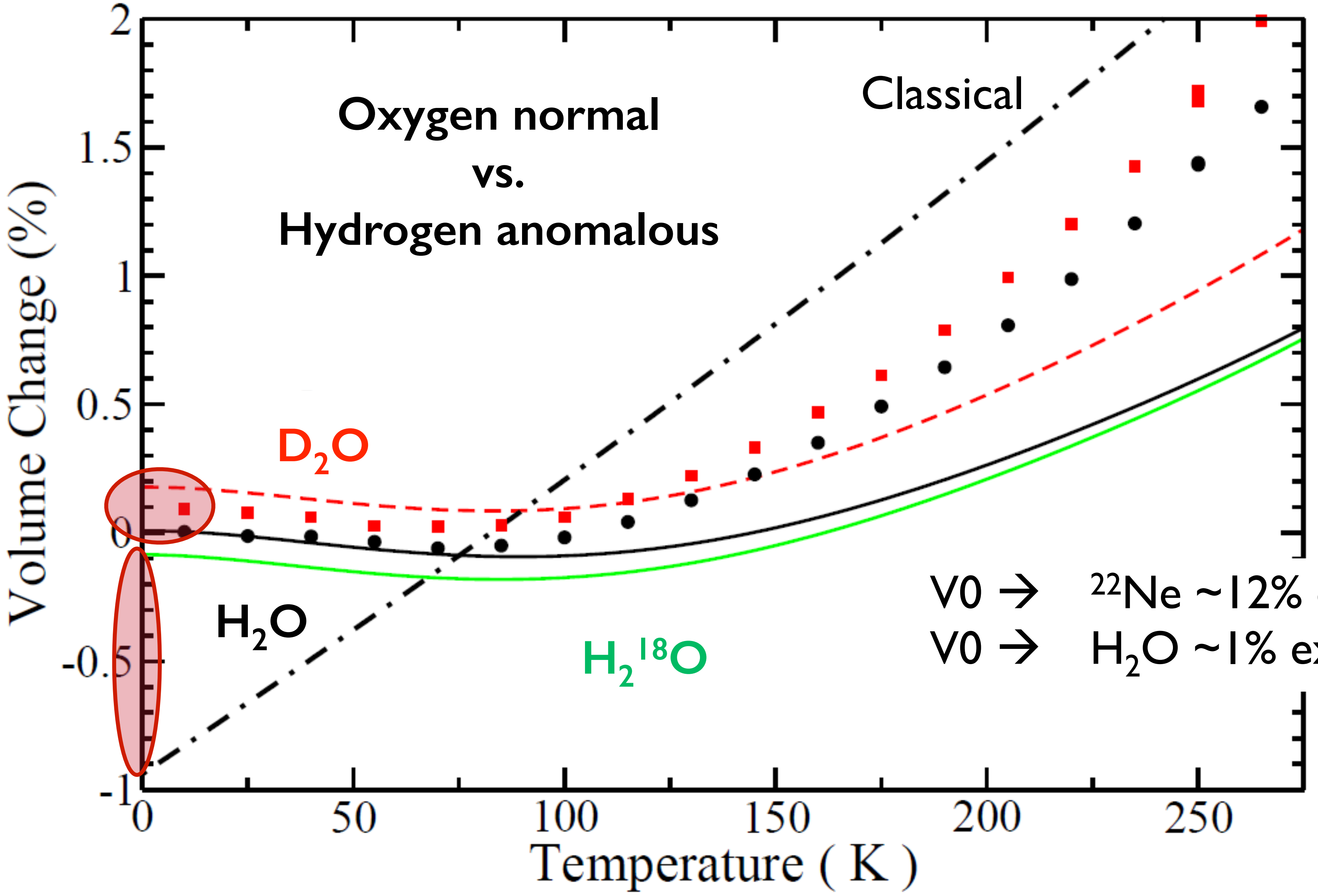
Weaker OH covalent bond

- Grüneisen parameter $$\gamma_q \equiv -\left(\frac{V_0}{\omega_q}\right)\left(\frac{\partial \omega_q}{\partial V}\right)_{V_0}$$



dE_{zp}/dV is usually negative

Temperature dependence: vdW-DF-PBE

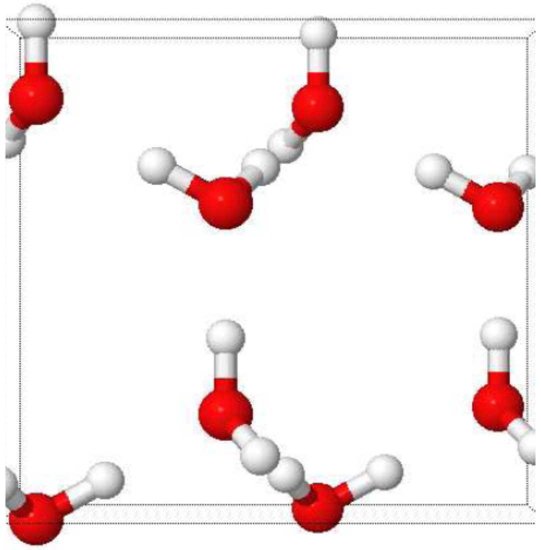


B. Pamuk et al, PRL 108, 193003 (2012)

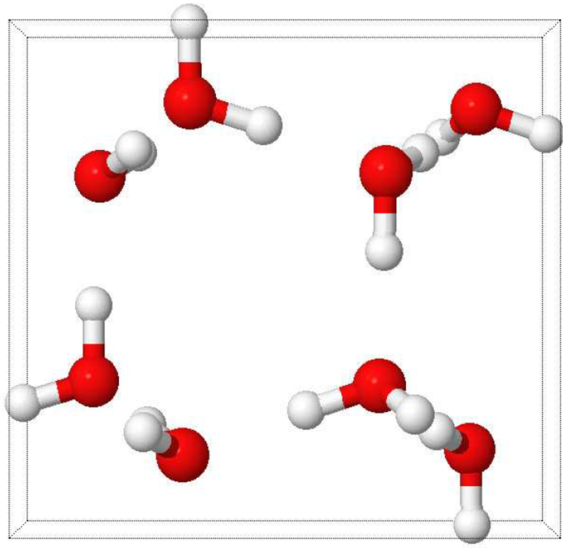
V0 → ^{22}Ne ~12% expansion
V0 → H_2O ~1% expansion

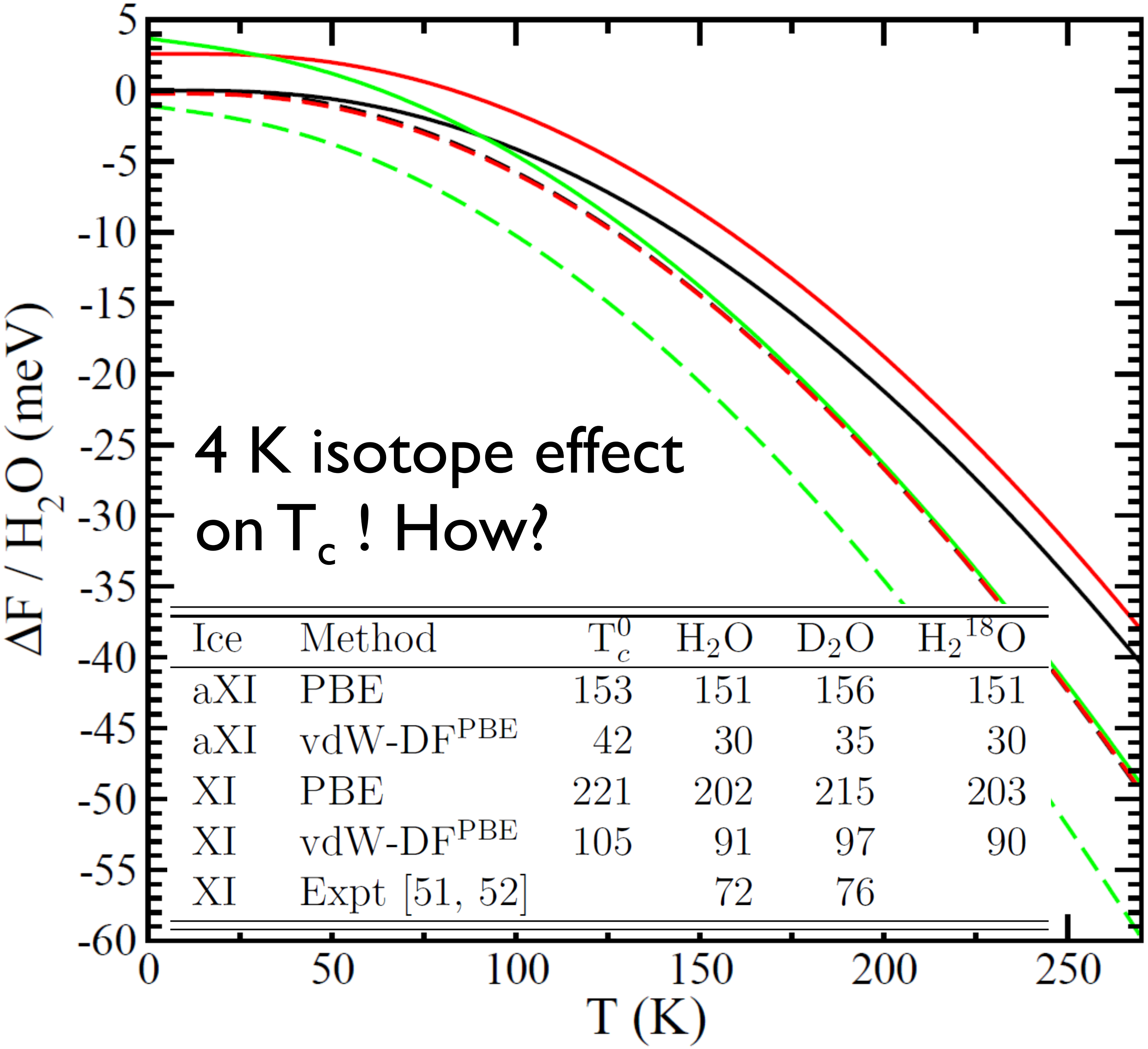
ICE I-XI ORDER DISORDER PHASE TRANSITION

Ferroelectric
ordered ice XI



Antiferroelectric
ordered ice XI

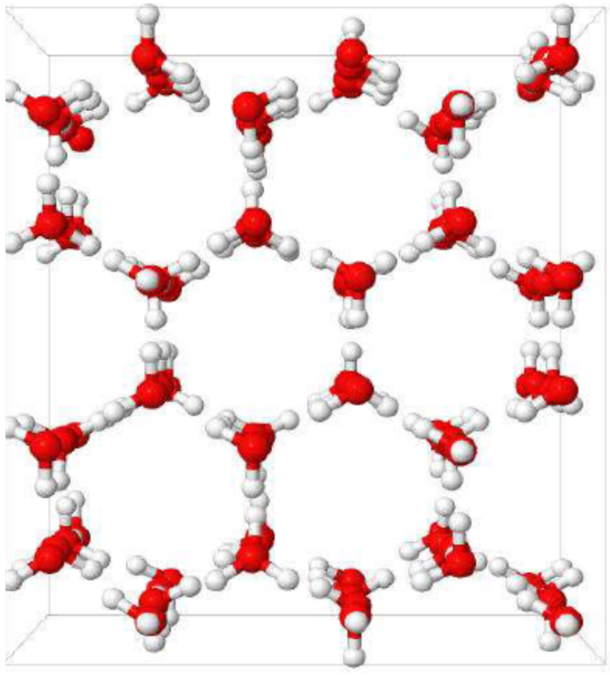




4 K isotope effect on T_c ! How?

Ice	Method	T_c^0	H_2O	D_2O	$H_2{}^{18}O$
aXI	PBE	153	151	156	151
aXI	vdW-DF^{PBE}	42	30	35	30
XI	PBE	221	202	215	203
XI	vdW-DF^{PBE}	105	91	97	90
XI	Expt [51, 52]		72	76	

Disordered
Ice Ih



ICE I-XI ORDER DISORDER PHASE TRANSITION

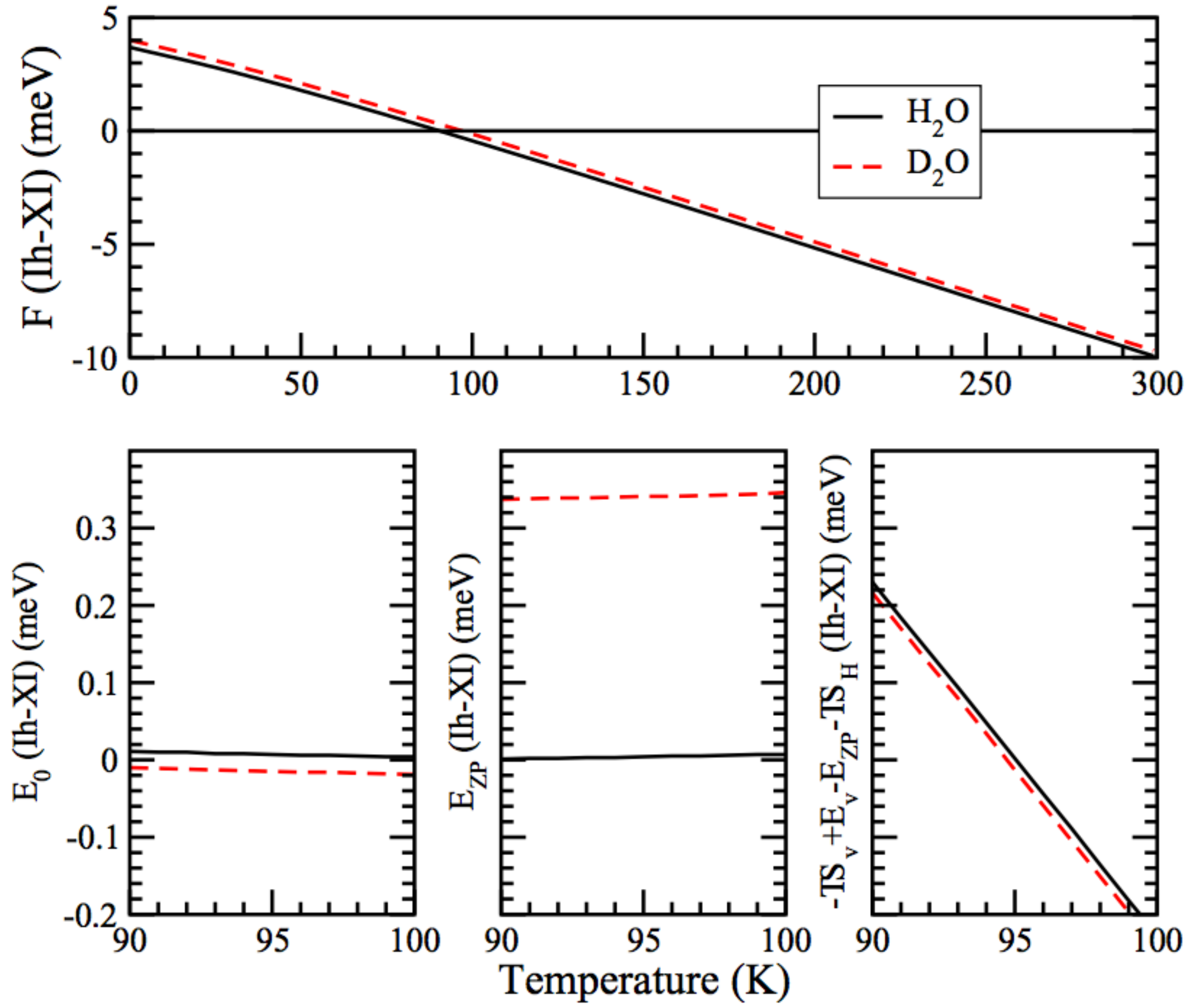


FIG. 5. (Color online) (Top) Free energy difference per molecule between ice Ih and ice XI calculated with vdW-DF^{PBE} functional in the region of the phase transition. (Bottom) Contributions to this free energy difference by each term in Eq. (4). (Left) Frozen lattice electronic term. (Middle) Zero-point vibrational energy. (Right) Remaining terms. All the energies on the bottom plots have been shifted to allow them to be compared in the same energy scale.

$$F(V,T) = E_0(V) + \sum_k \left[\frac{\hbar\omega_k(V)}{2} + k_B T \ln\left(1 - e^{-\hbar\omega_k(V)/k_B T}\right)\right] - T S_H. \tag{4}$$

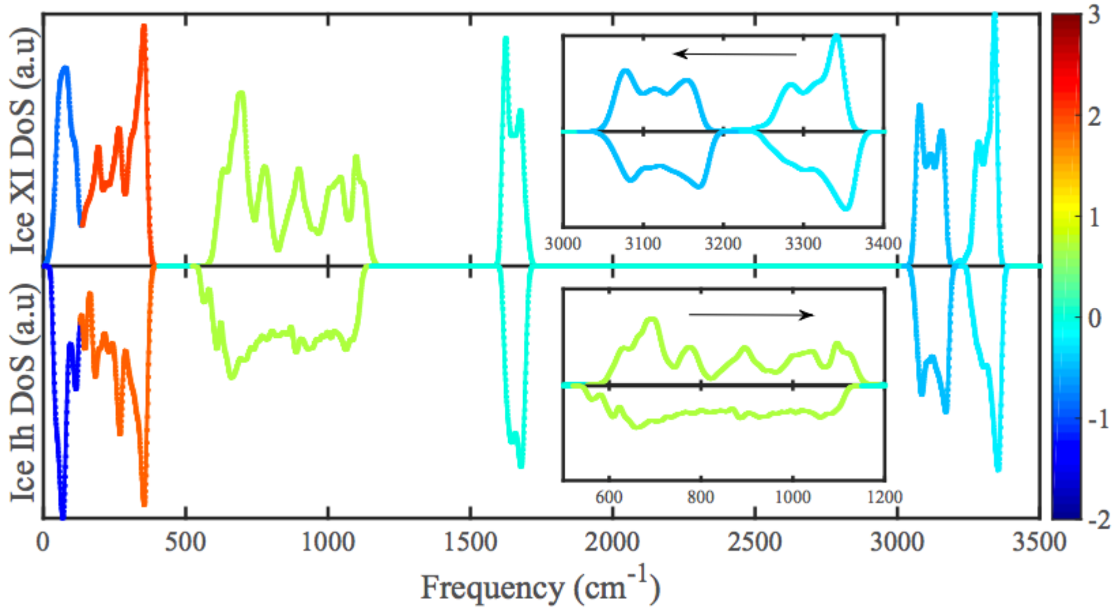


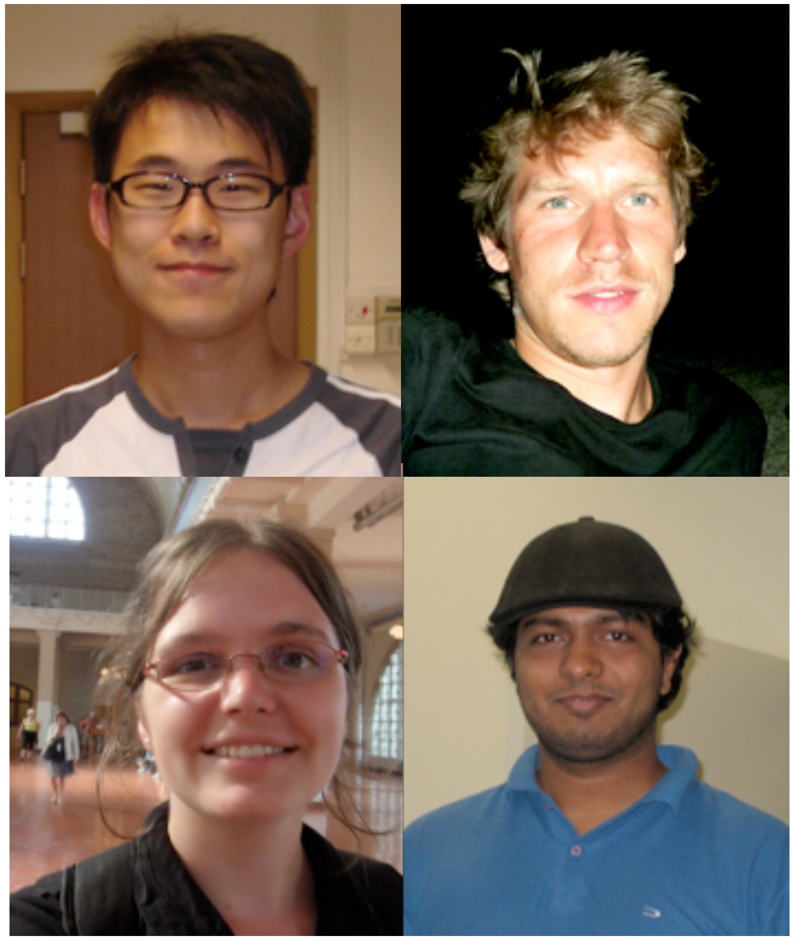
FIG. 6. (Color online) Vibrational density of states for H_2O for proton-ordered ice XI and disordered Ih structures, as obtained with vdW-DF^{PBE} functional. Average Grüneisen constants of the different modes are given in color code. The inset above zooms into the stretching modes and shows the redshift, while the inset below zooms into the librational modes and shows the blueshift in ice XI with respect to ice Ih.

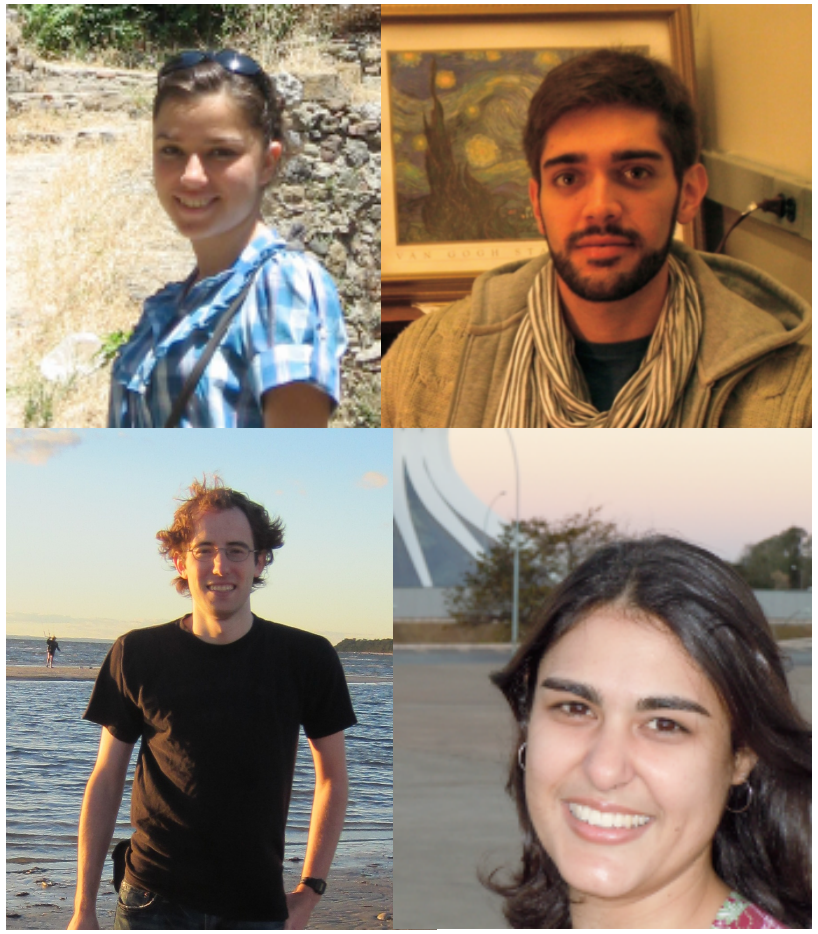
- Pamuk, Philip B. Allen, and M.-V. Fernández-Serra. Phys. Rev. B 92, 134105, 2015

Conclusions

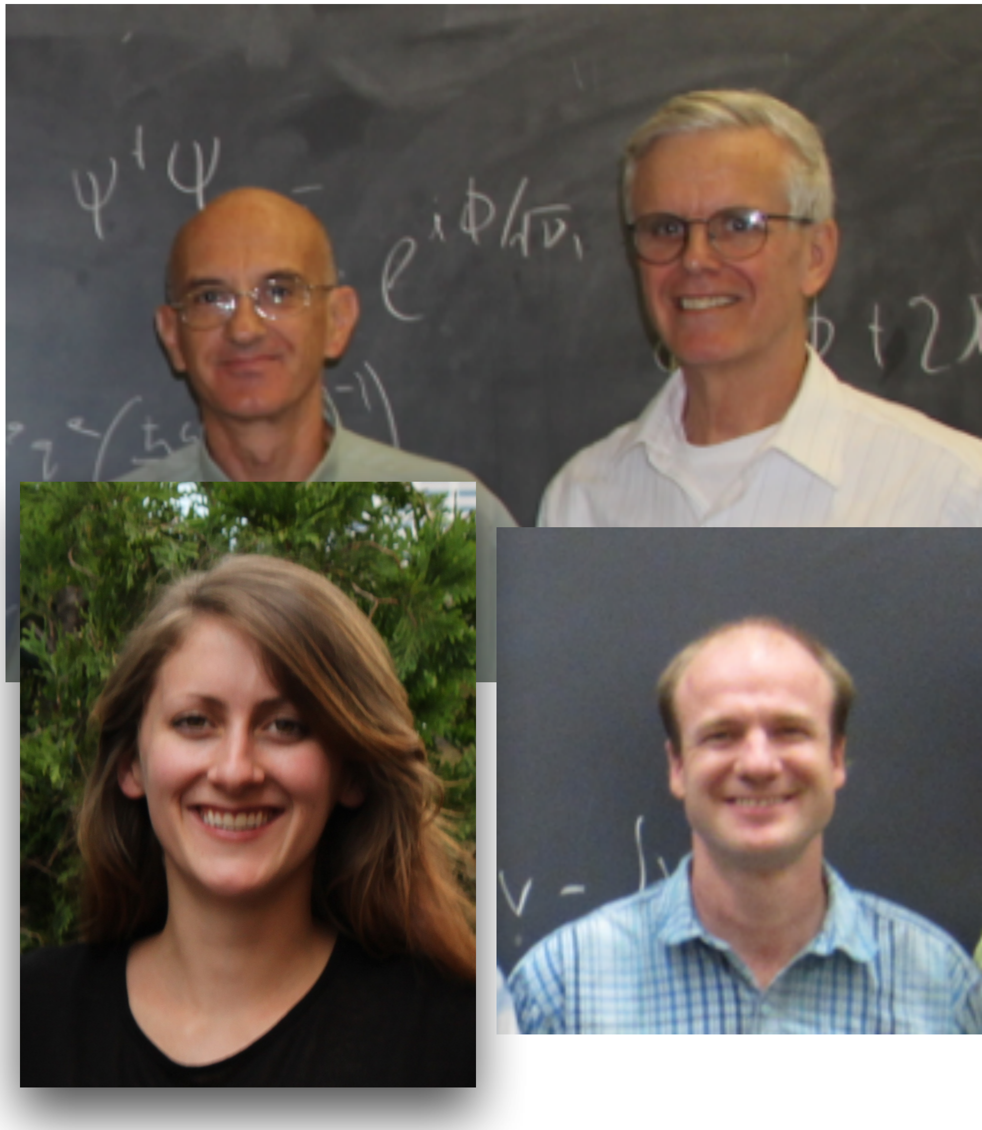
- The physics of water is rich. A book on condensed matter physics could be written using mostly water examples
    - phonons, thermal conductivity, dielectric properties, thermal expansion, phase transitions, ferroelectricity…
- In computational condensed matter physics water challenges us to develop new simulation methods and testing current methods
    - New density functionals, new molecular dynamics algorithms, simulation of nuclear quantum effects, efficient and accurate sampling.
- Lots of progress achieved in the last 10 years, and much more to come!

ACKNOWLEDGMENTS





Closer Collaborators



DOE Early Career DE-SC0003871
DOE: DE-FG02-09ER16052

DIPOLE LONG RANGE ORIENTATIONAL ORDER

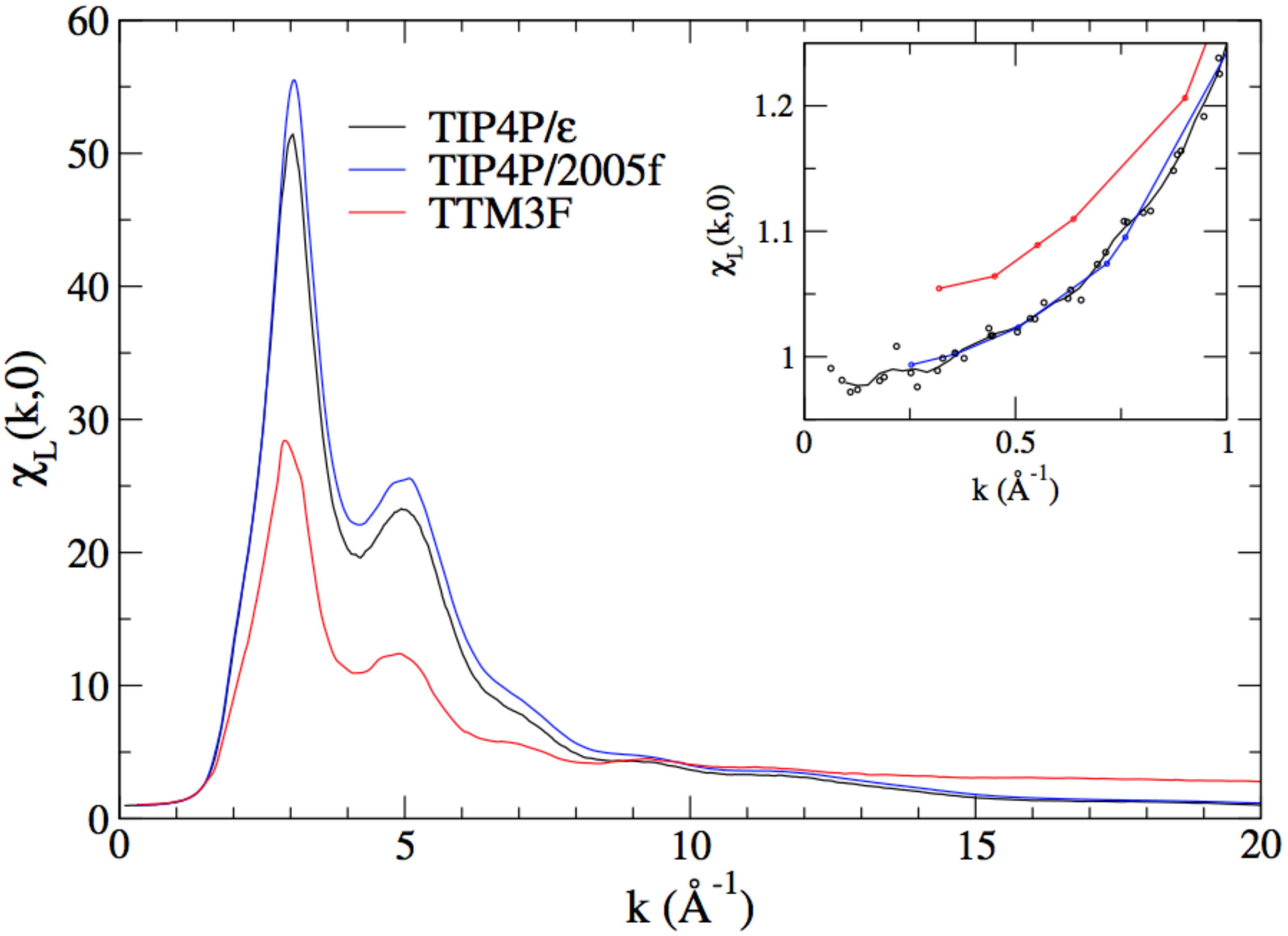
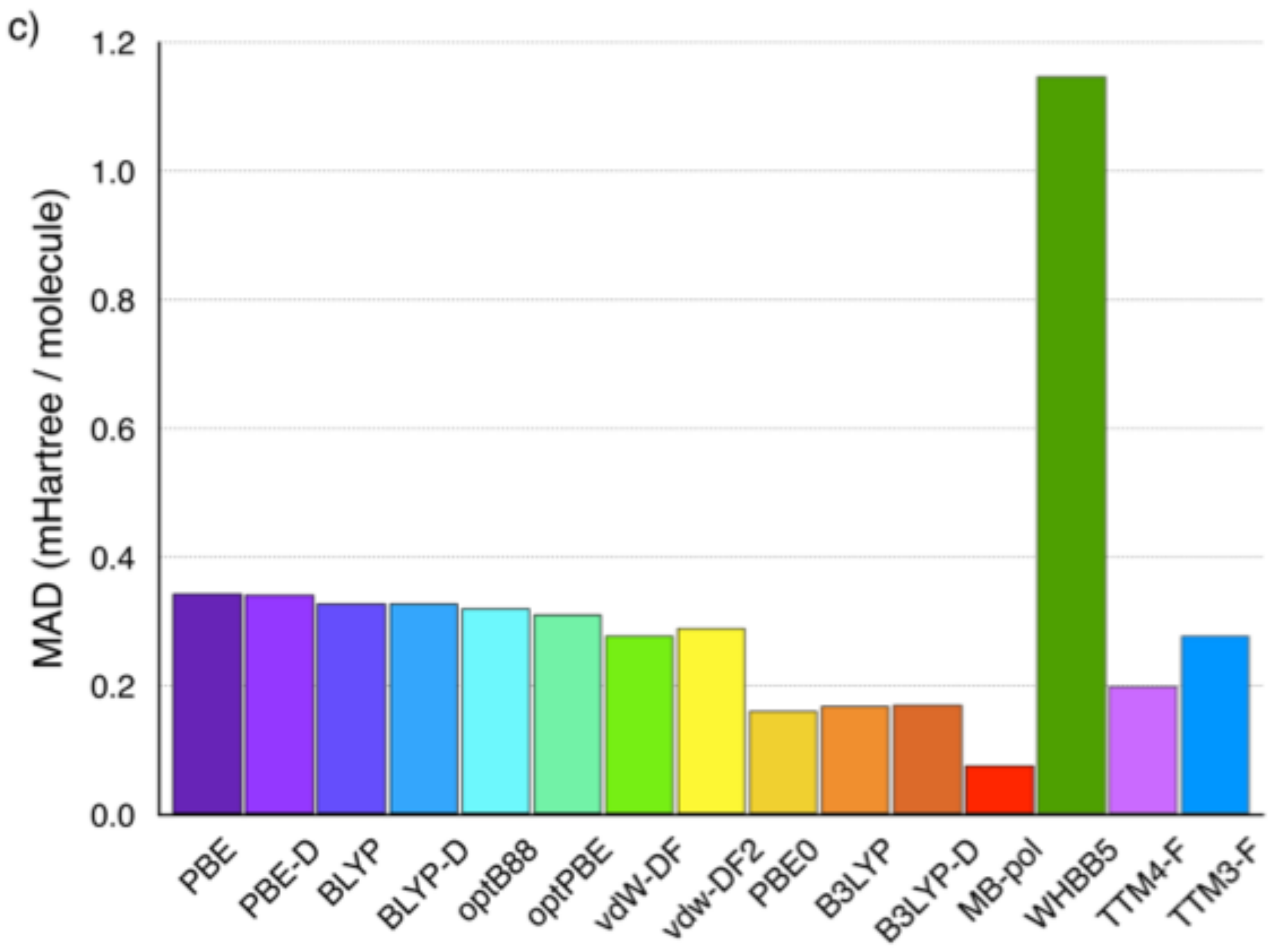


Figure 9.4: Static longitudinal susceptibility for three different models.

STATE OF THE ART IN THE WATER SIMULATION COMMUNITY: MB-POL

MB-POL: 2 and 3 body interactions at CCSD(T) level.

- V. Babin, C. Leforestier, and F. Paesani, J. Chem. Theory Comput., 9, 5395 (2013).
- V. Babin, G. R. Medders, and F. Paesani, J. Chem. Theory Comput., 10, 1599 (2014).



Medders et al. 2015

- Derived from fits to CCSD(T) energies calculated for both water dimers and trimers in the complete basis set (CBS) limit.
- Many-body effects: polarization model employed by the TTM4-F potential.
- To date MB-pol is the only many-body potential that accurately predicted the properties of water from the gas to the condensed phase.
- 47 times more expensive than TIP4P

MOTIVATION TO OPTIMIZE A DFT

- **Can we optimize a density functional for water using the information produced to fit the MB-POL potential?**

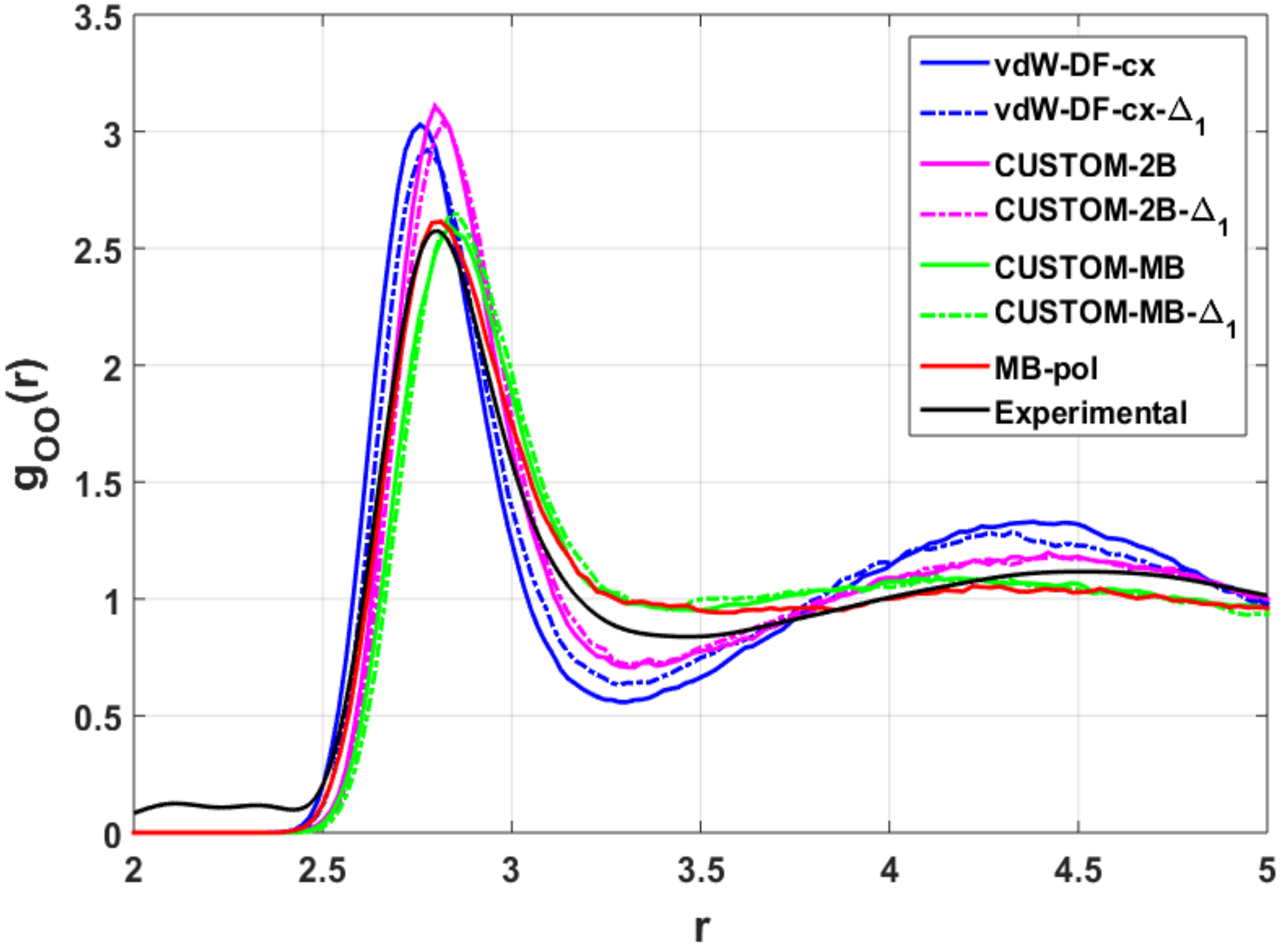
- In practice, there is not one ab initio DFT, but many.
- Trial and error: does a functional fit the data?
- While hybrid functionals might work better, they are not yet as accurate as MB-pol and their computational cost is still too large.

We choose to take the MB-pol approach, and fit a GGA +vdW-Df functional. The method is called Data Projection on The parameter Subspace, DPPS.

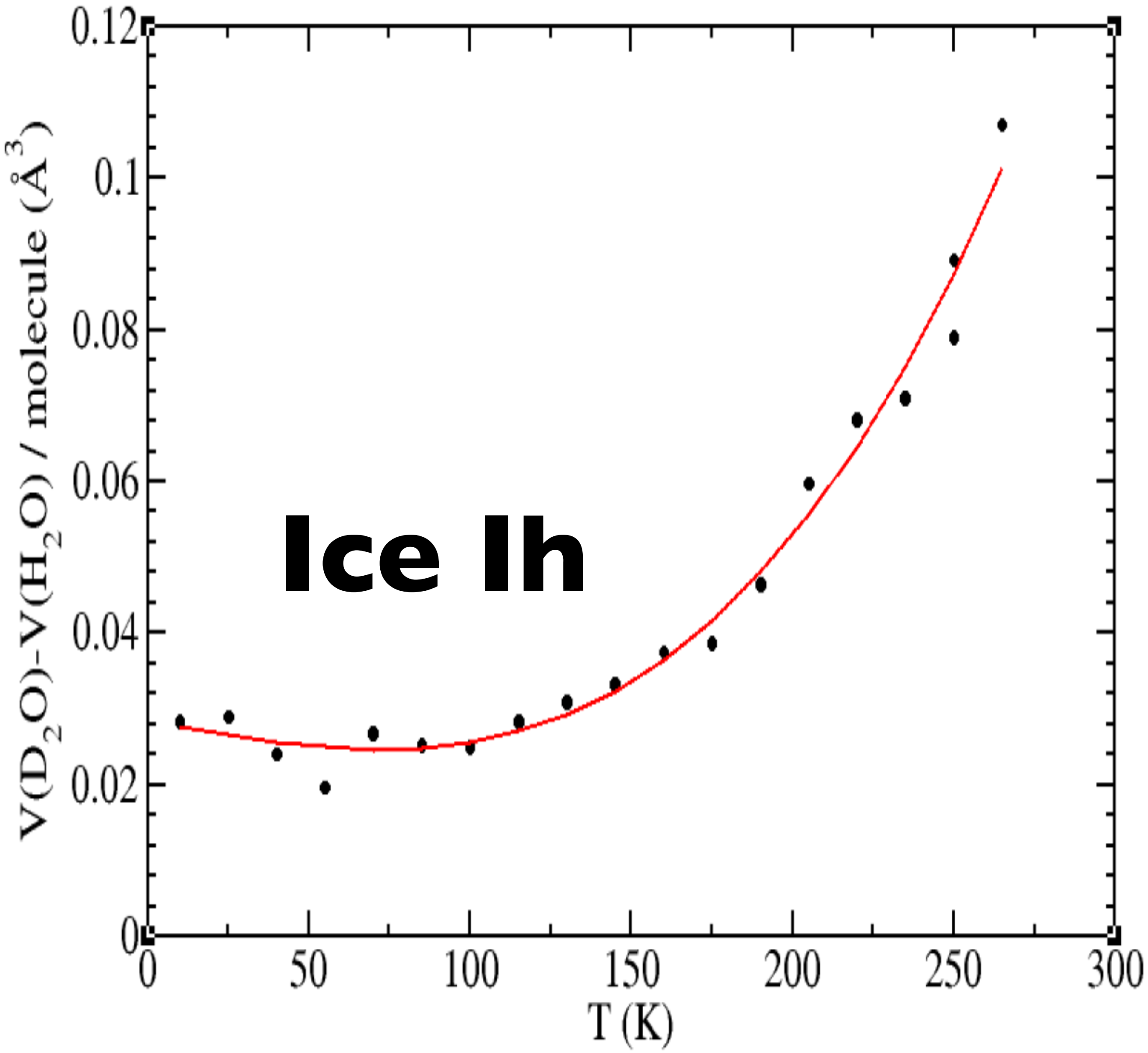
DPPS: what functional fits best the data?

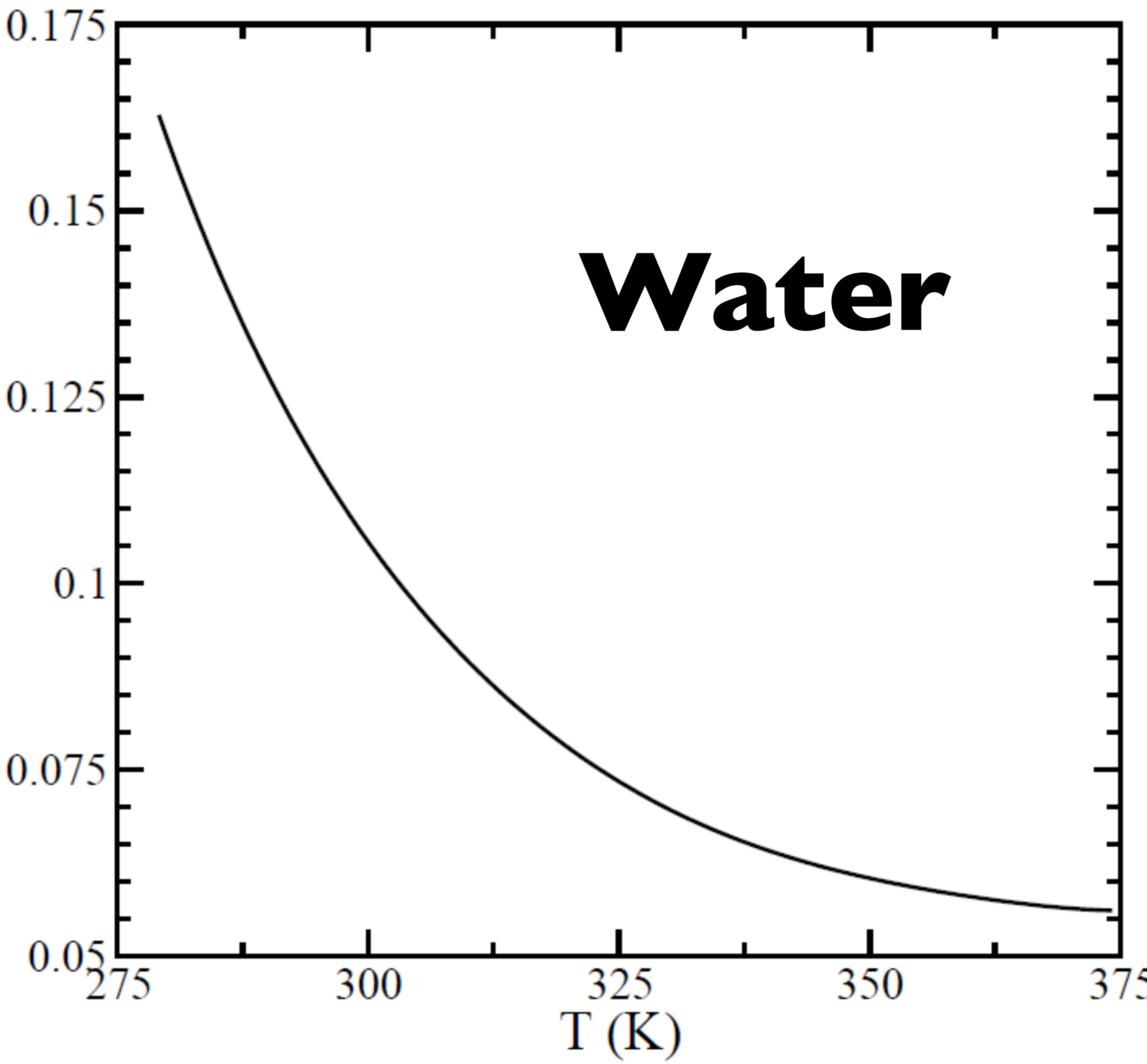
Optimization of an exchange-correlation density functional for water, Michelle Fritz, Marivi Fernandez-Serra and Jose M. Soler, JCP (2016), submitted

CUSTOM FUNCTIONAL: STRUCTURE



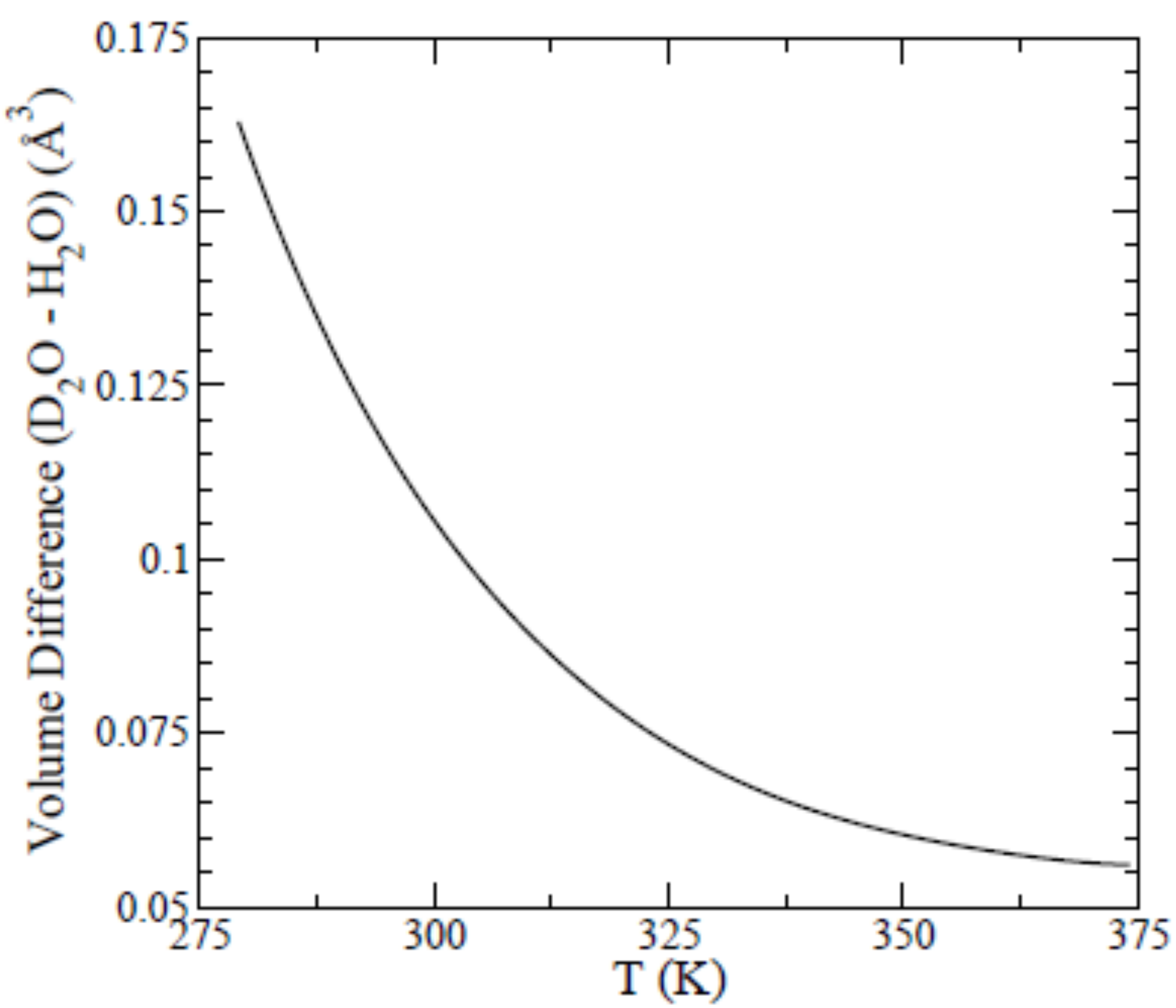
Anomalous Isotope Effect



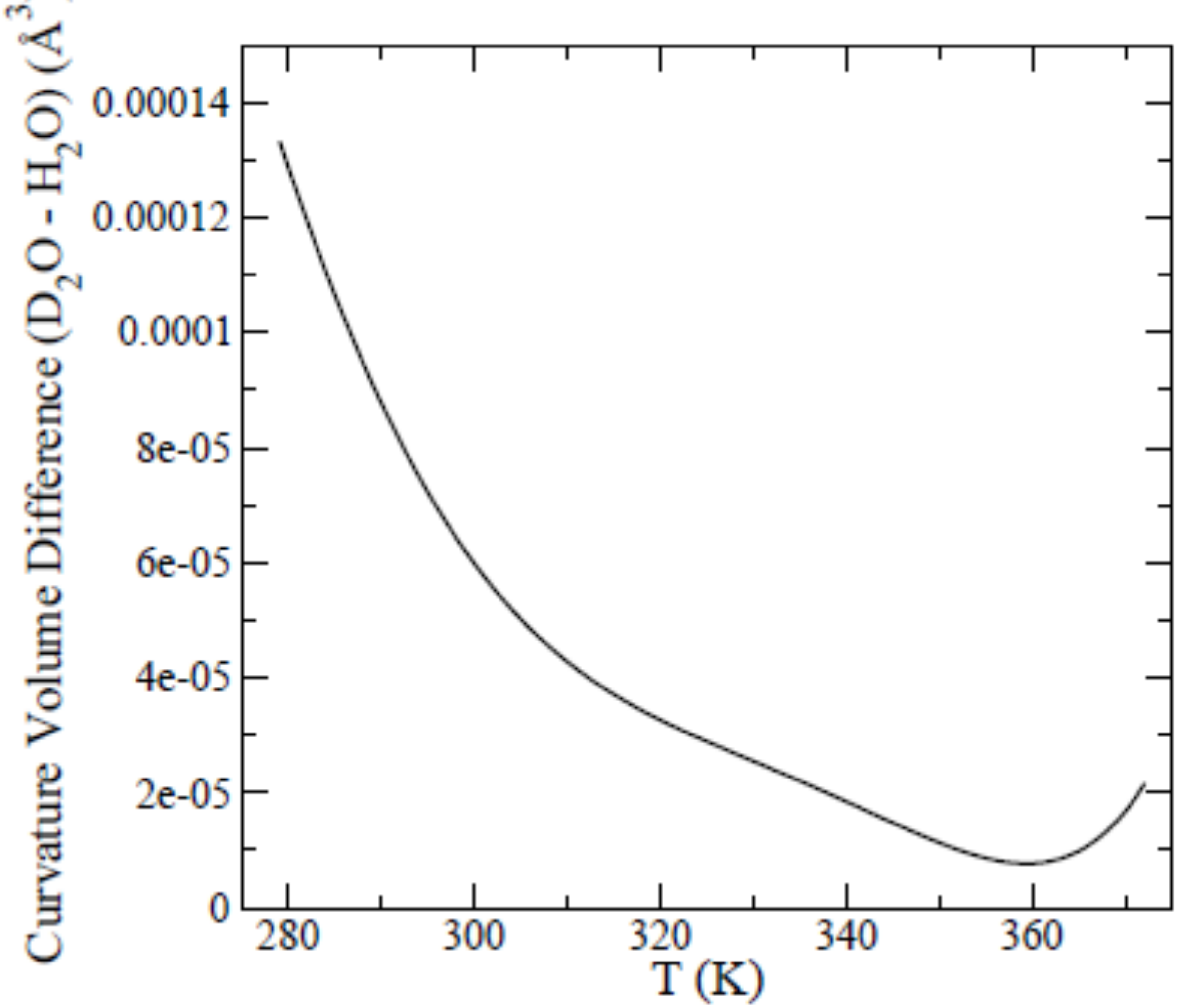


K. Röttger *et. al.*, Acta Cryst. **B50,** 644 (1994).
G. S. Kell, J. Phys. Chem. Ref. Data **6,** 1109 (1977).

From Ices to Liquid Water

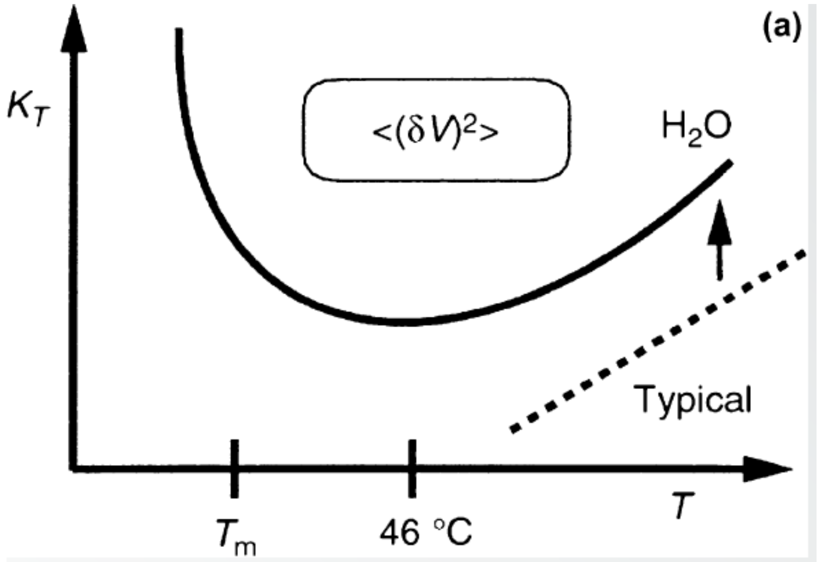


(a) Isotope effect in water.

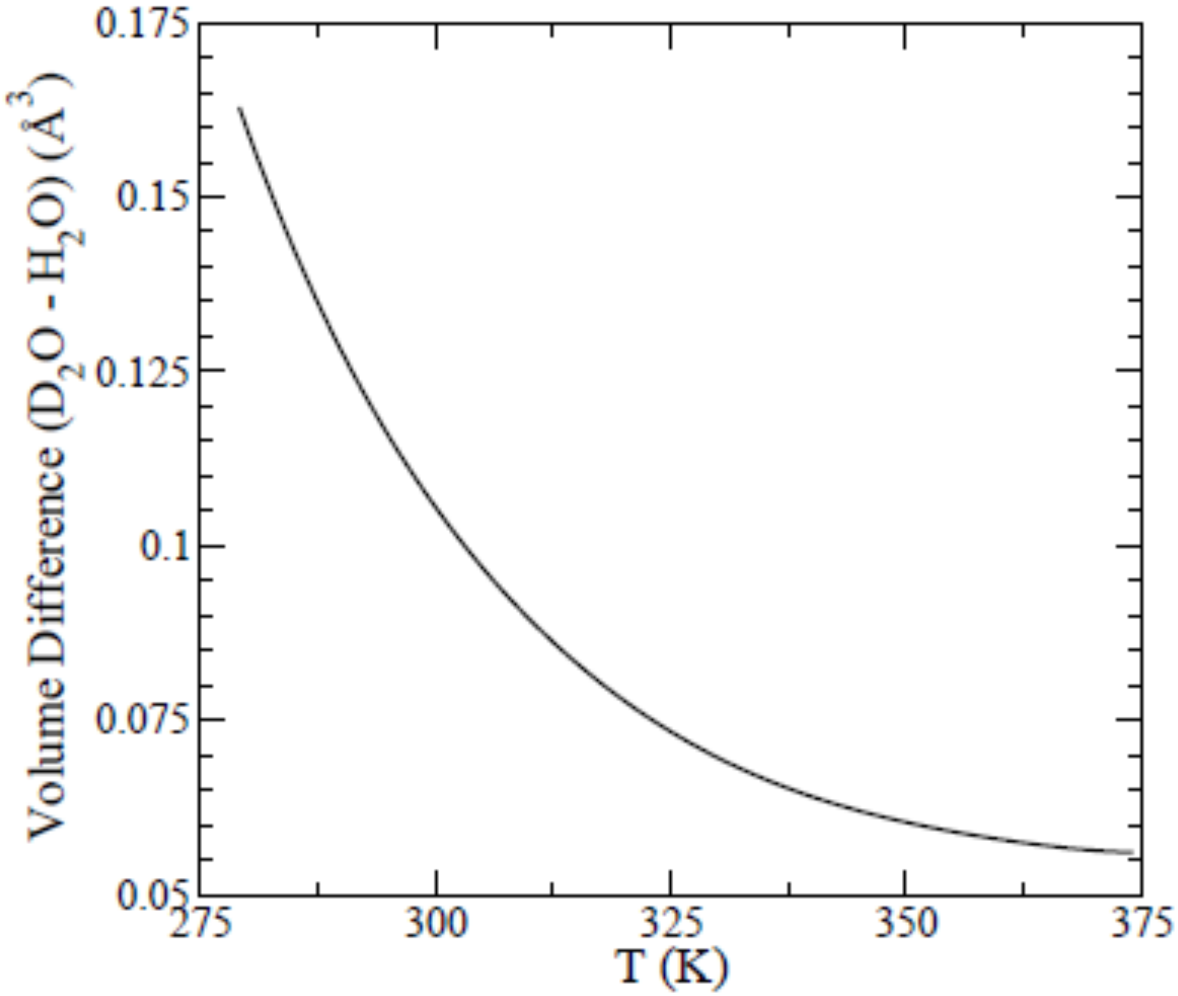


(b) Curvature of isotope effect in water.

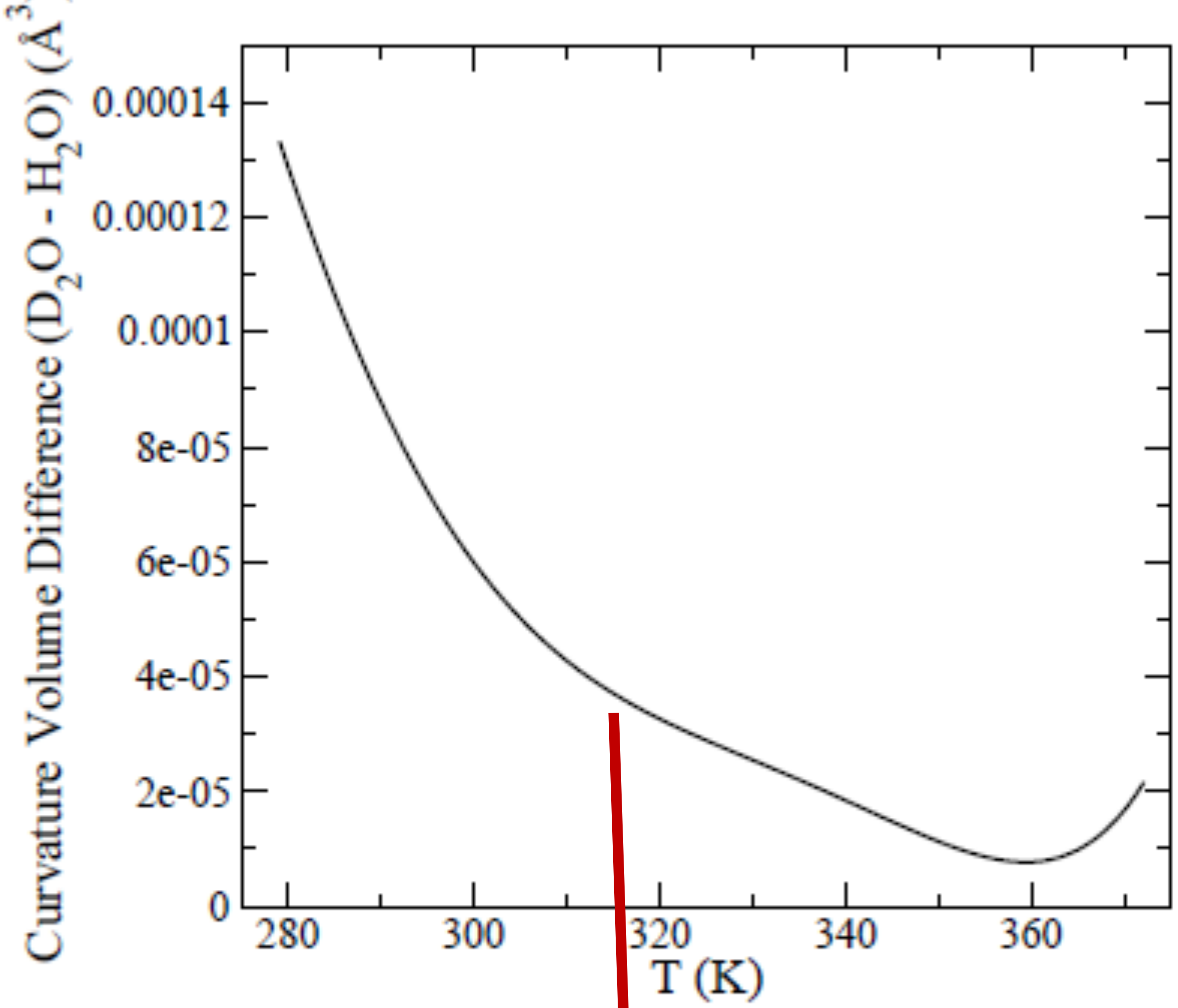
Isothermal compressibility



From Ices to Liquid Water



(a) Isotope effect in water.



(b) Curvature of isotope effect in water.

Isothermal compressibility