The anomalous electron-proton ground state of nano- confined water, with some remarks on coherent delocalization of protons in water at interfaces

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Outline of Talk

Deep Inelastic Neutron Scattering-Neutron Compton Scattering: Momentum distributions as a probe of quantum effects

Variation of proton momentum distributions for water at Interfaces-kinetic binding energies

Nano-confined water-a distinct quantum ground state

Properties of Nano-confined water-work by others

Kinematical space for VESUVIO - e.VERDI

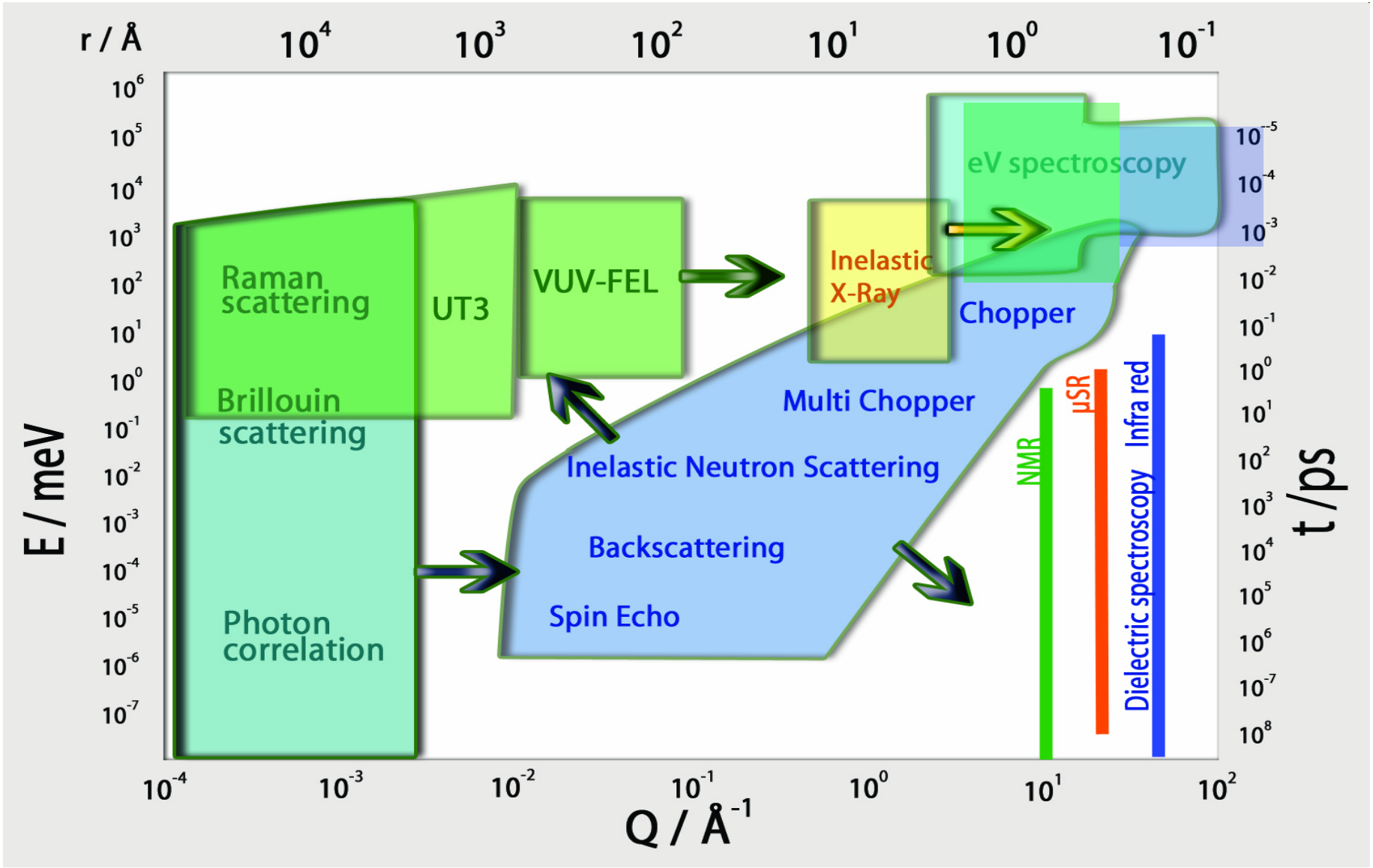
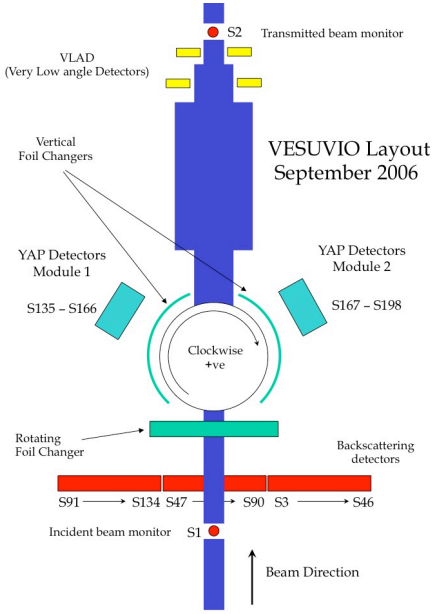
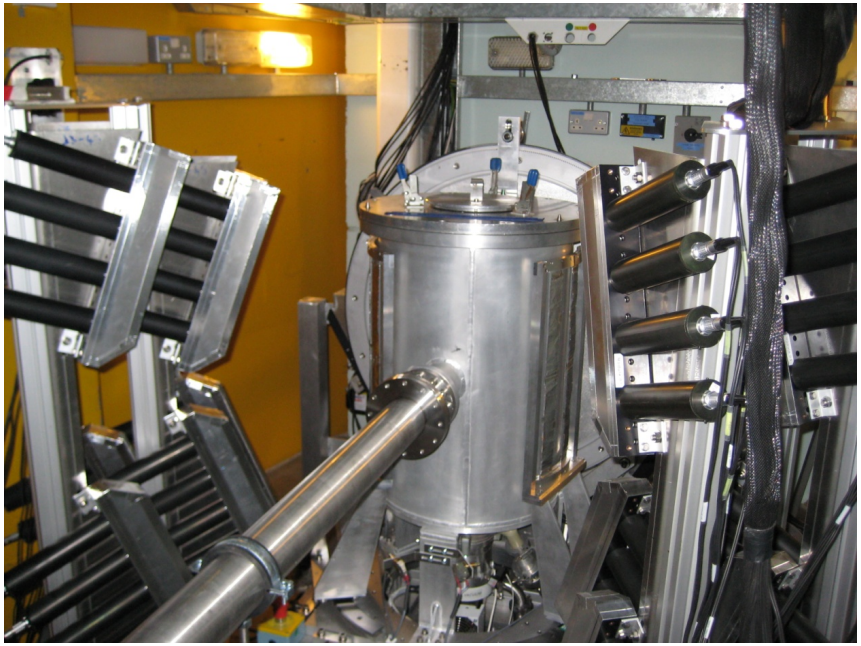


Figure from Carla Andreani

VESUVIO instrument at ISIS only existing instrument. ELVIS proposed at SNS would have 60-100 times the count rate





Detectors set final state energy to ~5eV

Principle of Measurement

At high enough transferred wavevector q, the "Impulse Approximation" is valid. The scattering function decays so rapidly(10^{-16}-10^{-17}s) that the struck particles trajectory is a straight line during this period, and the scattering is as though the particle were free of external forces.

Initial Kinetic Energy

$$\kappa_i = p^2 / 2M$$

Final Kinetic Energy

$$\kappa_f = (\vec{p} + \vec{q})^2 / 2M$$

Momentum transfer

Energy transfer

$$\omega = \frac{(\vec{p} + \vec{q})^2}{2M} - \frac{p^2}{2M}$$

Momentum along $\hat{q}$

$$y = \vec{p}.\hat{\vec{q}} = \frac{M}{q}\left(\omega - \frac{q^2}{2M}\right)$$

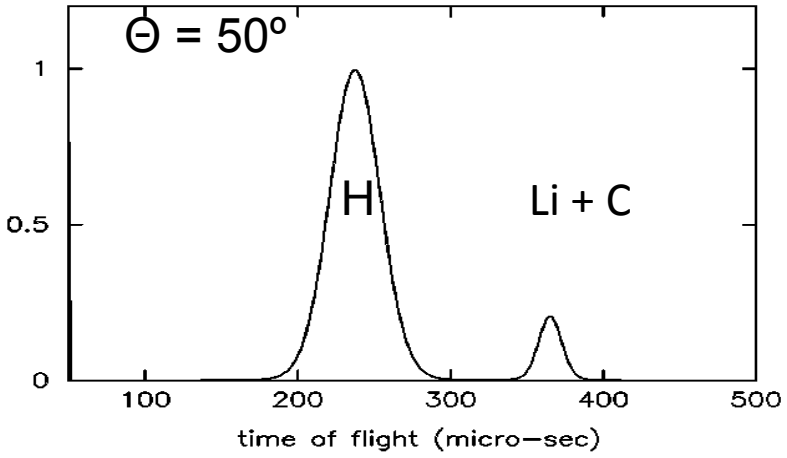
DINS is inelastic neutron scattering in the limit of large momentum transfer, q (~30-100 Å^{-1}). $S(\mathrm{q},\omega)$ in this limit takes the form:

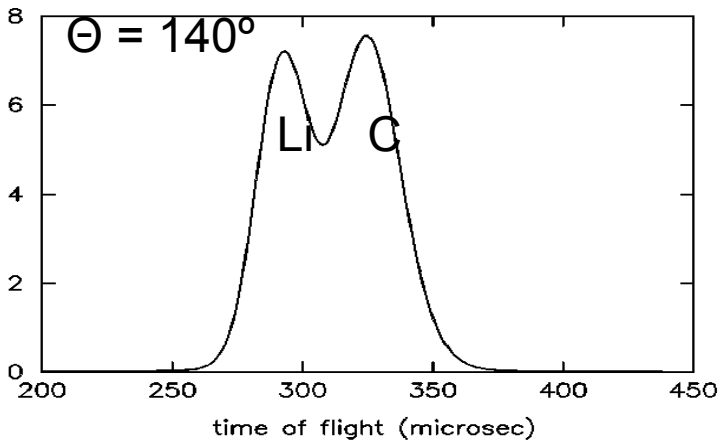
$$S(\boldsymbol{q},\omega) = \int n(\boldsymbol{p})\delta(\omega - \frac{\hbar q^2}{2M} - \boldsymbol{p}\cdot\boldsymbol{q})\boldsymbol{dp}$$

$$= \frac{M}{q}\int n(\boldsymbol{p})\delta(y - \boldsymbol{p}\cdot\hat{\boldsymbol{q}})d\boldsymbol{p} = \frac{M}{q}J(y,\hat{\boldsymbol{q}})$$

Momentum distribution

Compton profile





One Particle in an Effective Potential Approximation

Particle at center of inversion

$$\Phi(\mathbf{p}) = \pm\sqrt{n(\mathbf{p})}$$

$$\Psi(\mathbf{x}) = \int \Phi(\mathbf{p}) e^{i\mathbf{p}\circ\mathbf{x}} d\mathbf{x}$$

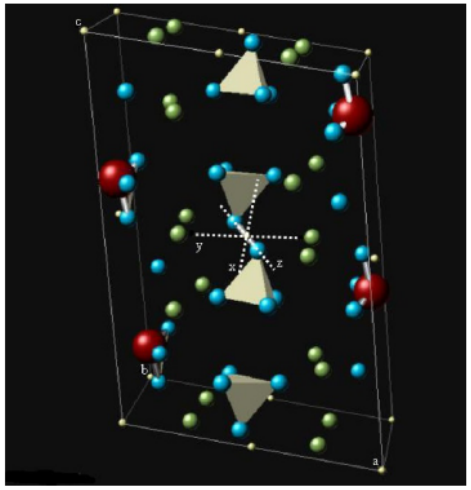
$$E - V(\mathbf{x}) = \frac{\int \frac{p^2}{2M} \Phi(\mathbf{p}) e^{i\mathbf{p}\circ\mathbf{x}} d\mathbf{p}}{\int \Phi(\mathbf{p}) e^{i\mathbf{p}\circ\mathbf{x}} d\mathbf{x}}$$

D. Homouz et al, Phys.Rev. Letts. . **98**, 15502 (2007)

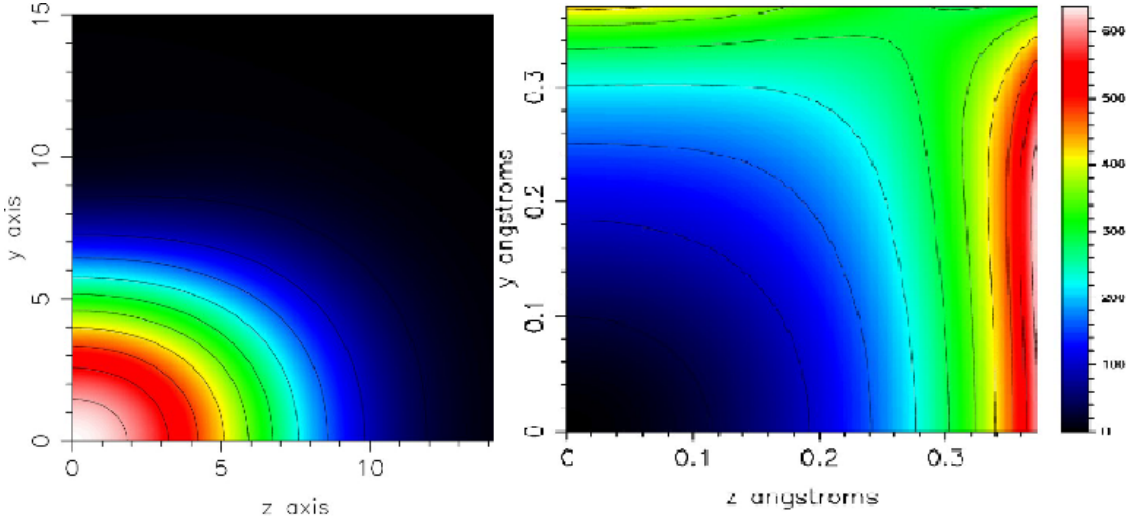
DINS can be used to measure Born-Oppenheimer potentials

$$n(\vec{p}) = \frac{1}{(2\pi\hbar)^3}\left|\int \psi(\vec{r})\exp(i\vec{p}.\vec{r})dr\right|^2 \qquad \tilde{\psi}(\mathbf{p}) = \int \psi(\mathbf{r})e^{i\mathbf{p}.\mathbf{r}}d\mathbf{r}$$

$$E - V(\mathbf{r}) = \frac{\int e^{i\mathbf{p}.\mathbf{r}}\dfrac{p^2}{2M}\tilde{\psi}(\mathbf{p})d\mathbf{p}}{\int e^{i\mathbf{p}.\mathbf{r}}\tilde{\psi}(\mathbf{p})d\mathbf{p}}$$



$Rb_3H(SO_4)_2$

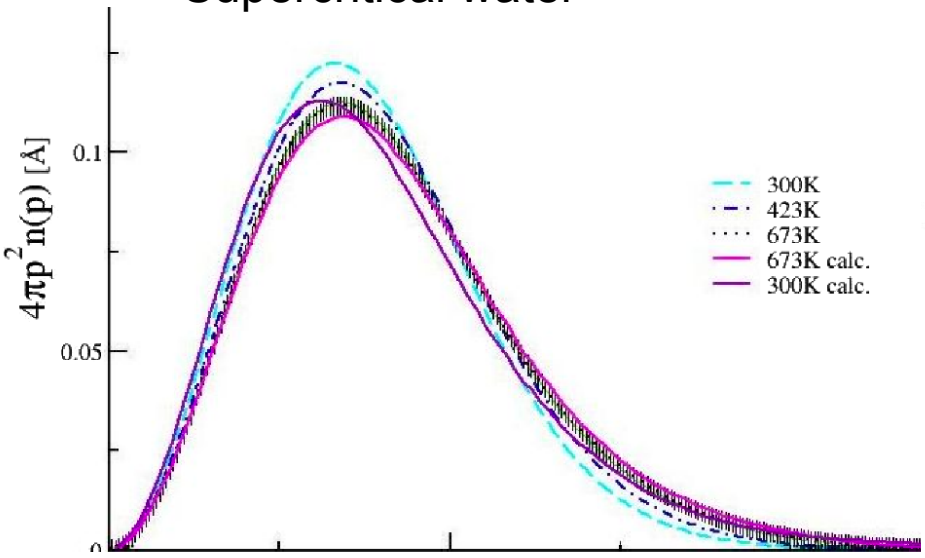


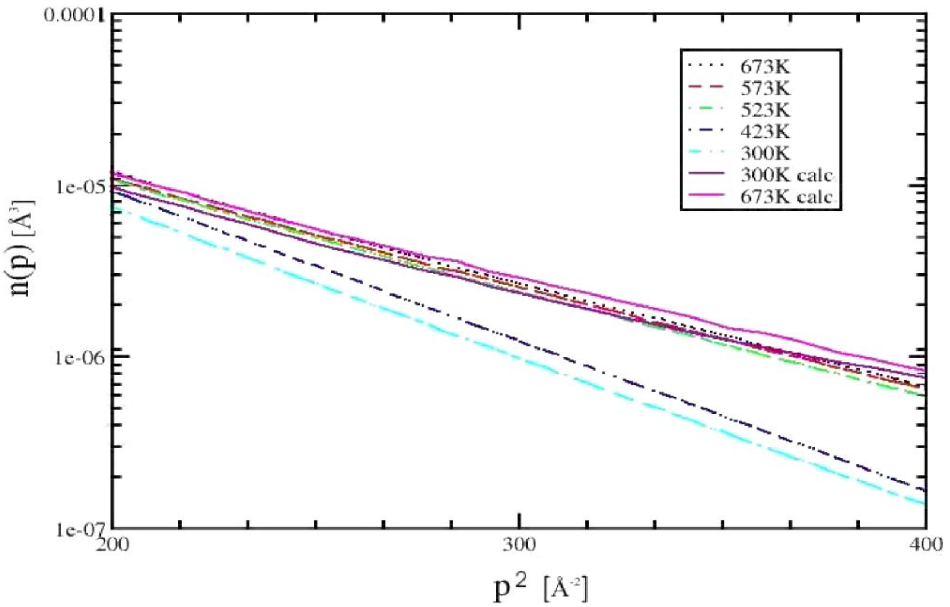
D. Homouz, G. Reiter, J. Eckert and R. BlincPhys. Rev. Letts. 98, 15502 (2007

DINS a precise local probe of environment of the protons.

Weakly interacting molecule (TTM4F)model unable to account for the softening of the proton potential in dense phases of water

Supercritical water

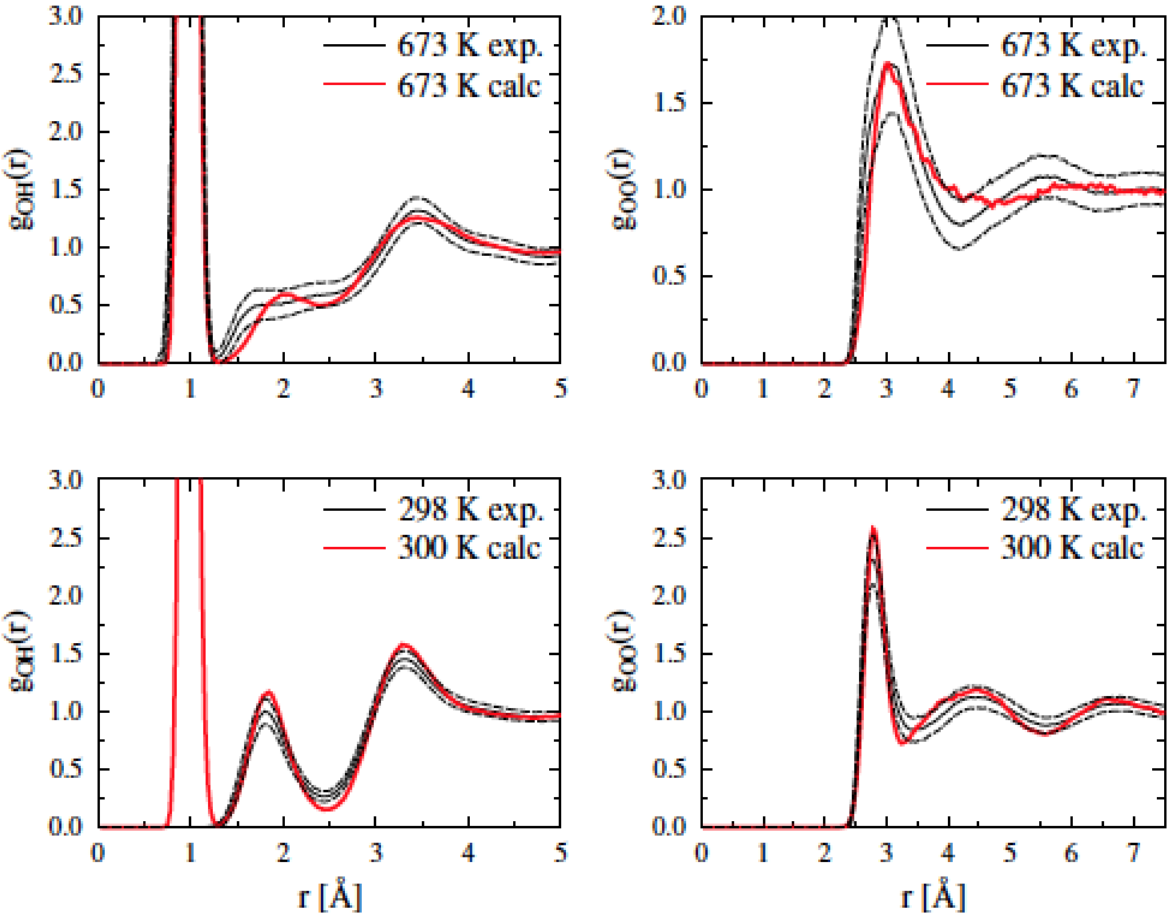




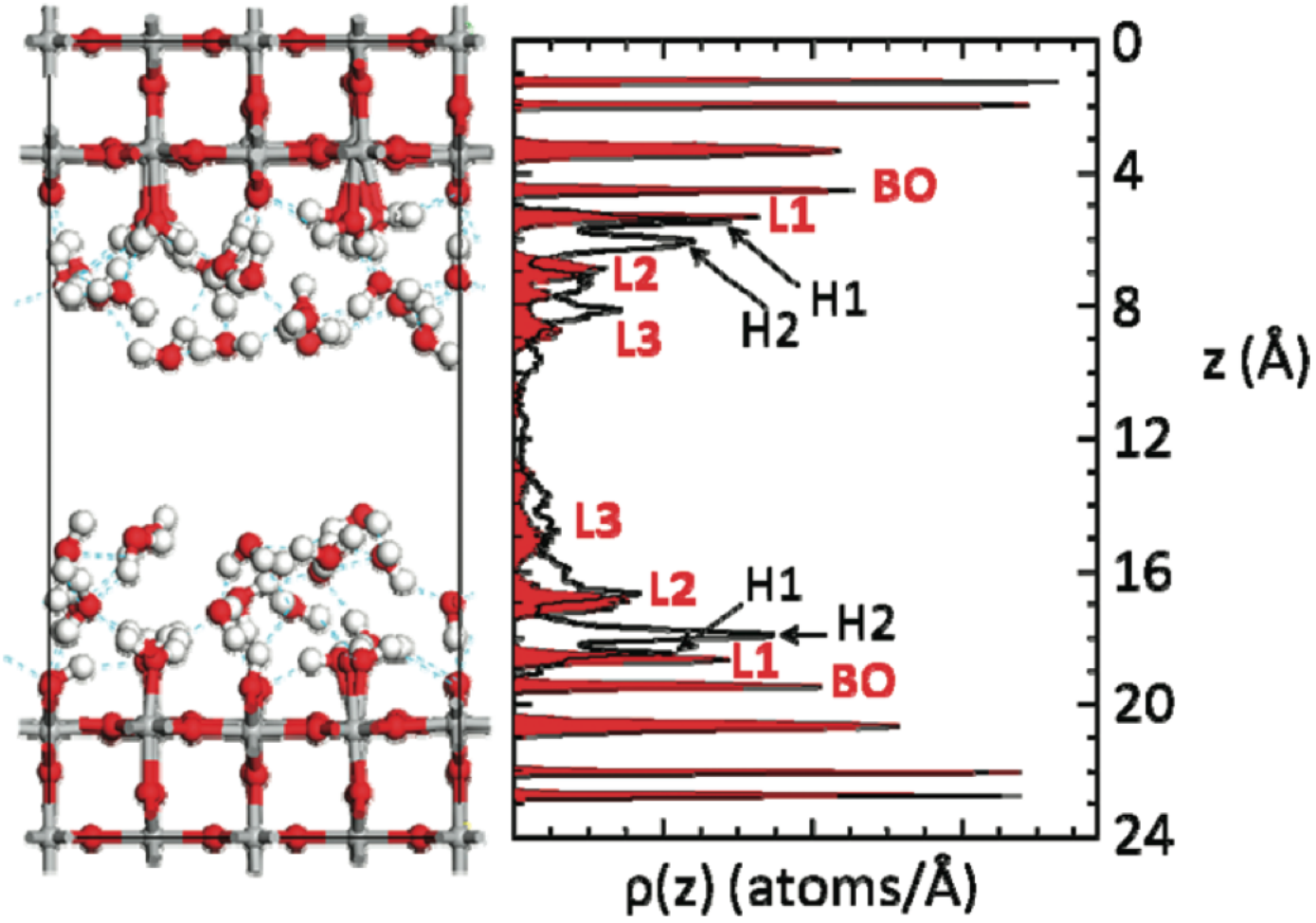
High momentum tail

C. Pantalei A. Pietropaolo, R. Senesi, S. Imberti, C. Andreani, J. Mayers, C. Burnham, and G. Reiter, Phys. Rev. Letts. 100, 177801(2008)

Fit to water g(r) with empirical potential(TTM4-F) based on weakly interacting molecule model

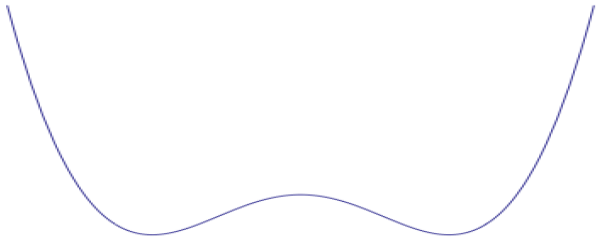


. C. Pantalei A. Pietropaolo, R. Senesi, S. Imberti, C. Andreani, J. Mayers, C. Burnham, and G. Reiter, in Phys. Rev. Letts. 100, 177801(2008)

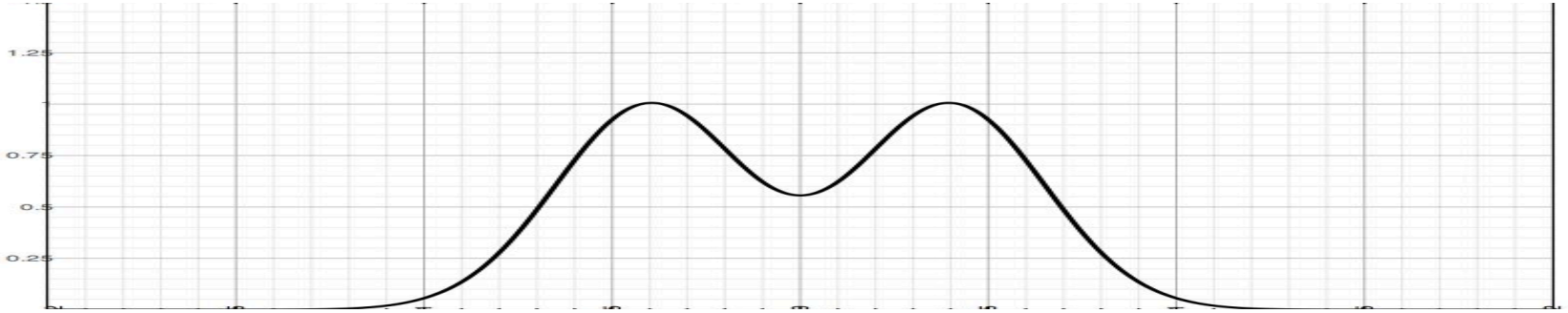


N. Kumar et al, J. Phys. Chem. C, 113, 13732 (2009)

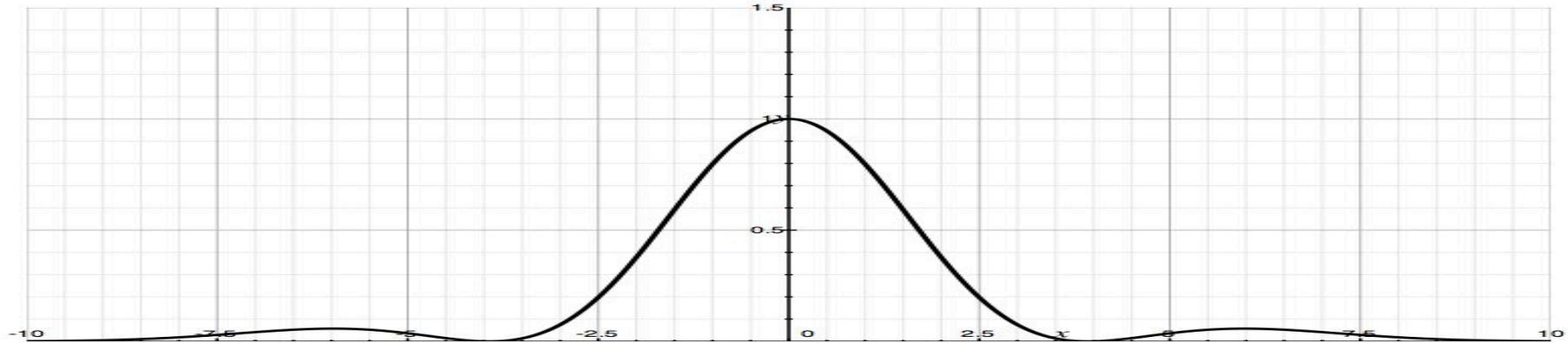
If the potential is a double well

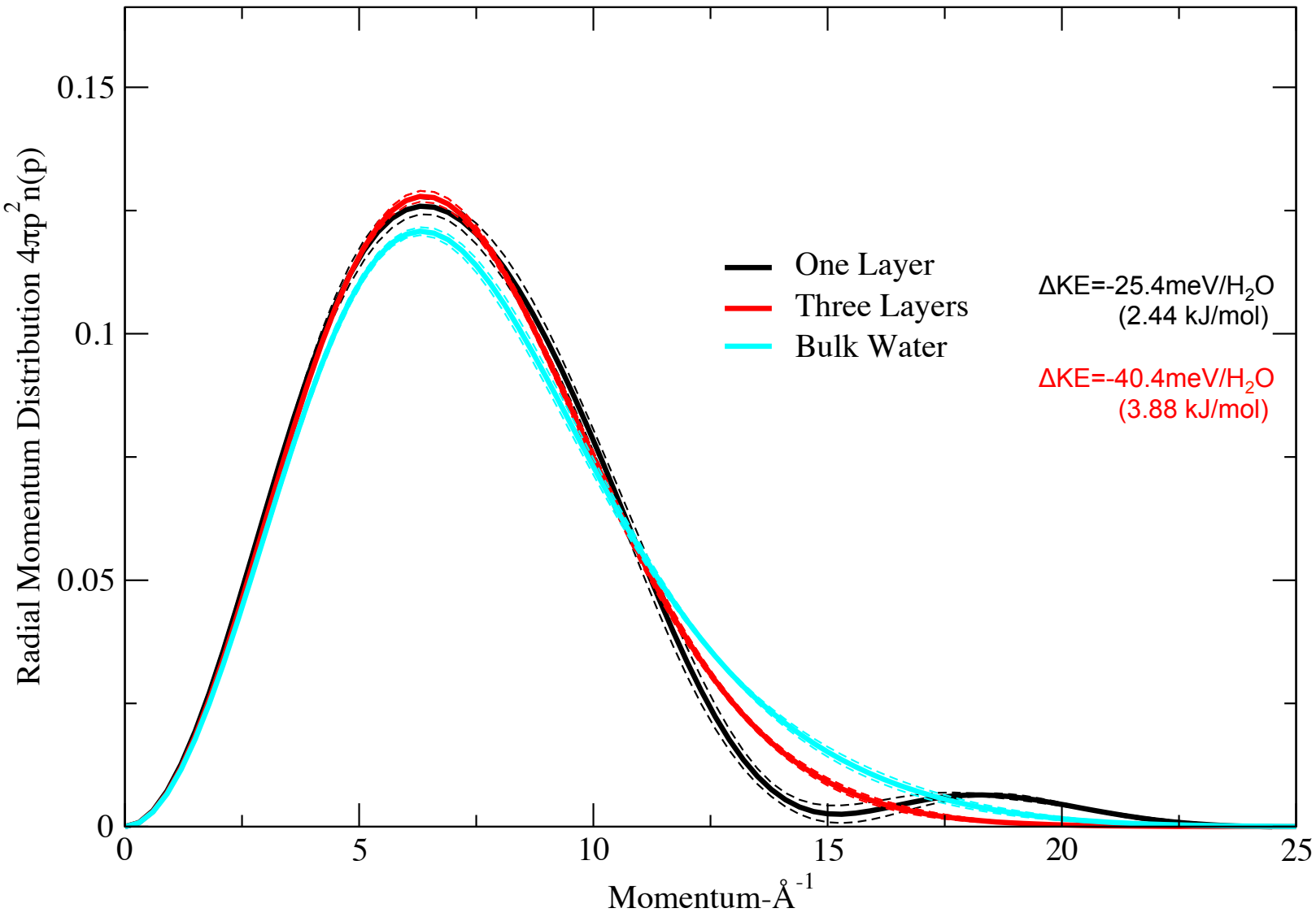


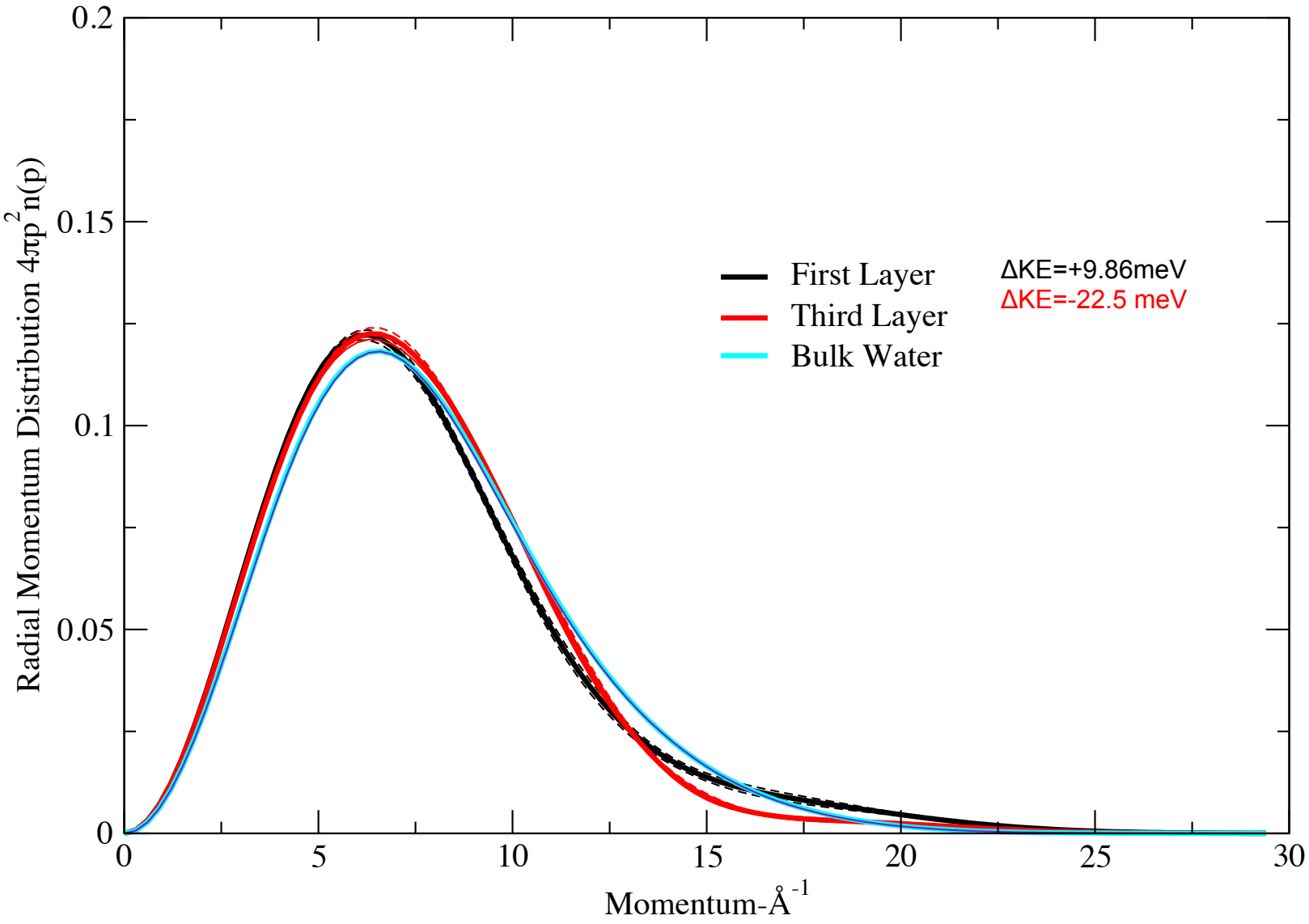
The ground state wavefunction will look like



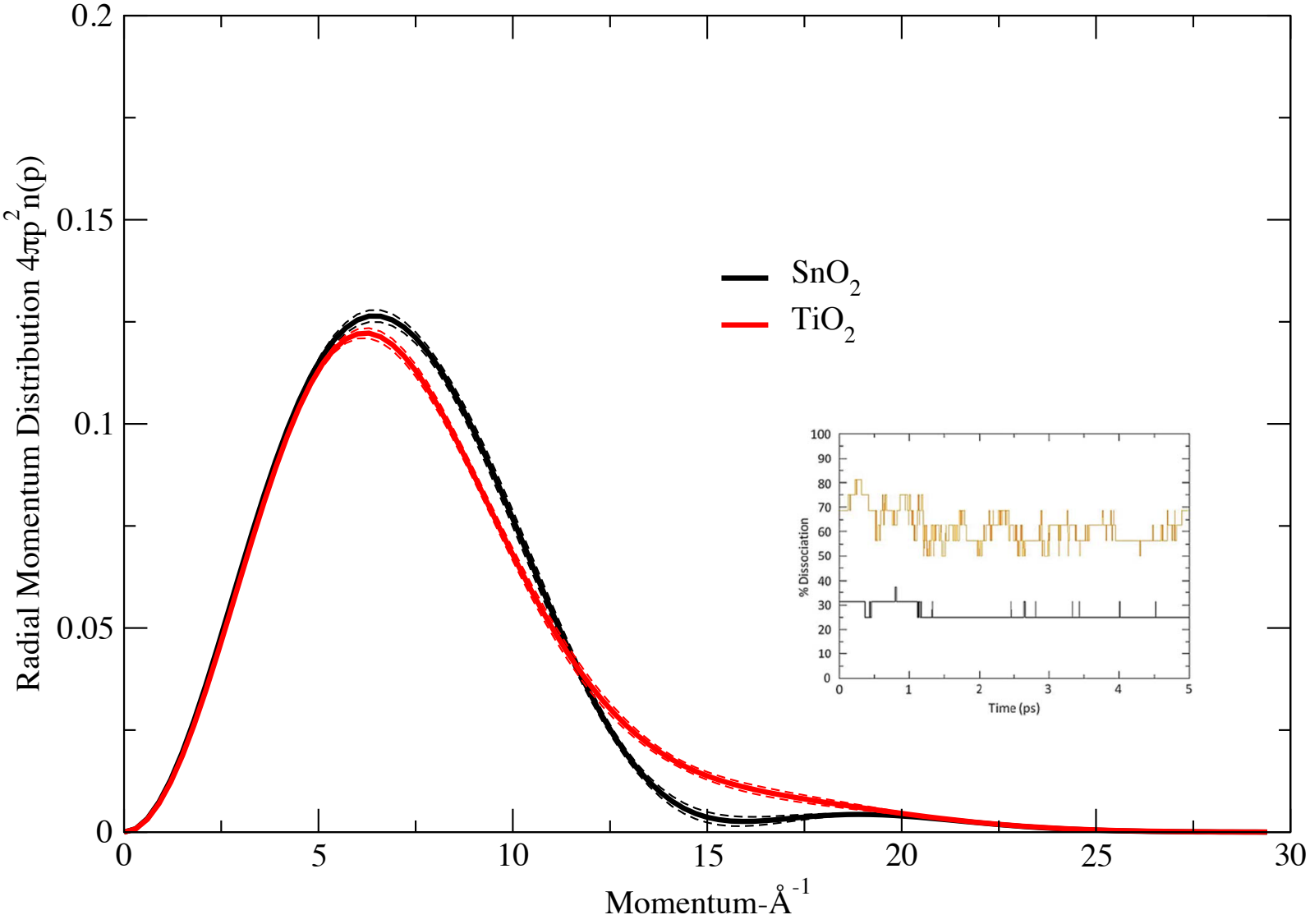
And the momentum distribution will look like



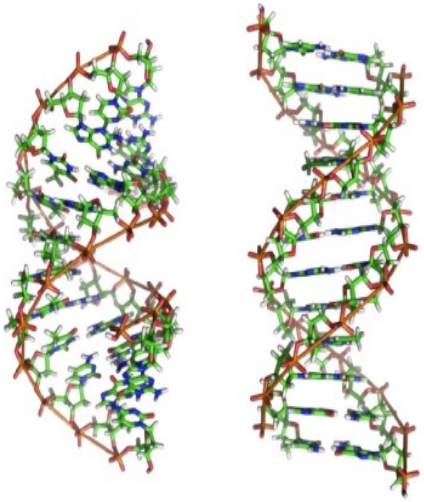

Water on SnO2
Radial Momentum Distribution 4πp2 n(p)
0.15
0.1
0.05
0
0
5
10
15
20
25
Momentum-Å-1
One Layer
Three Layers
Bulk Water
ΔKE=-25.4meV/H2O
(2.44 kJ/mol)
ΔKE=-40.4meV/H2O
(3.88 kJ/mol)


Water on TiO2
Radial Momentum Distribution 4πp2n(p)
Momentum-Å-1
First Layer
Third Layer
Bulk Water
ΔKE=+9.86meV
ΔKE=-22.5 meV
0
0.05
0.1
0.15
0.2
0
5
10
15
20
25
30

First Water Layers on TiO_2 and SnO_2

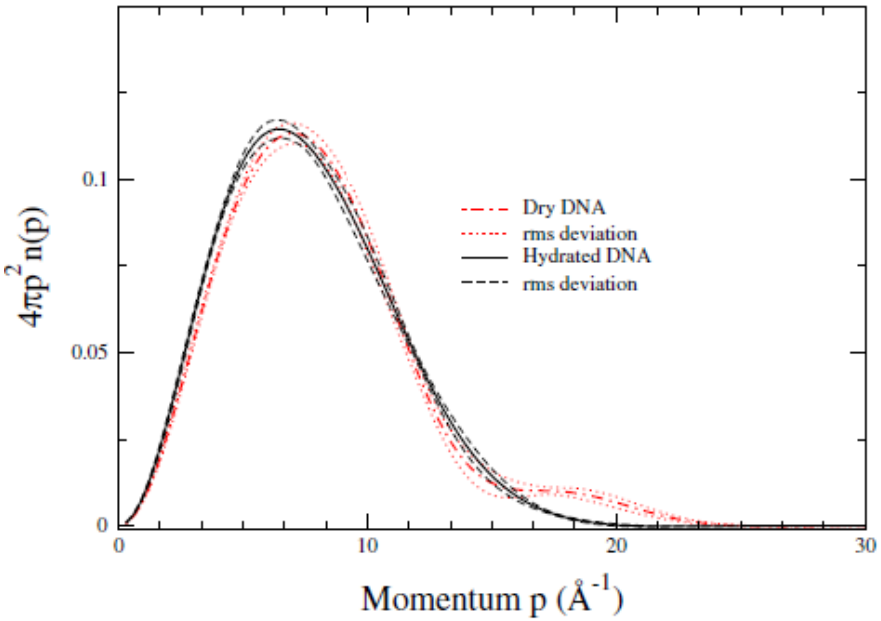


Changes in the kinetic energy(zero point motion) are biologically significant



Dry A phase
Biologically
Inactive

Hydrated B phase
Biologically active

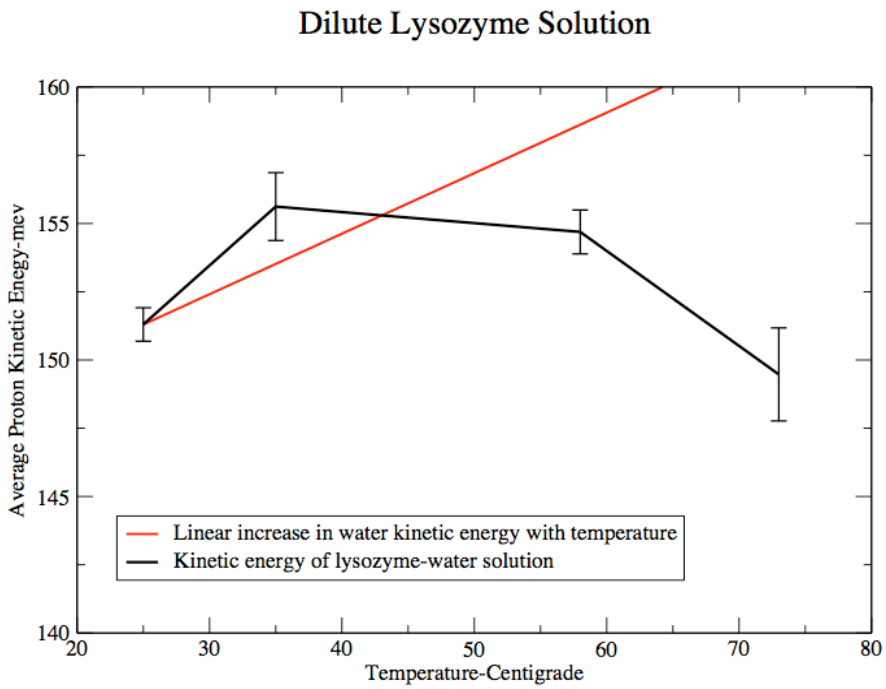


Changes in the zero point energy of protons completely
accounts for enthalpy change in A to B phase for 6 mol/bp of water, 3.02±.5 kJ/mol

PHYSICS WORLD.COM Feb 4 2011
http://physicsworld.com/cws/article/news/45037

G. F. Reiter, R. Senesi and J. Mayers, Phys. Rev.Letts. 105, 148101 (2010)

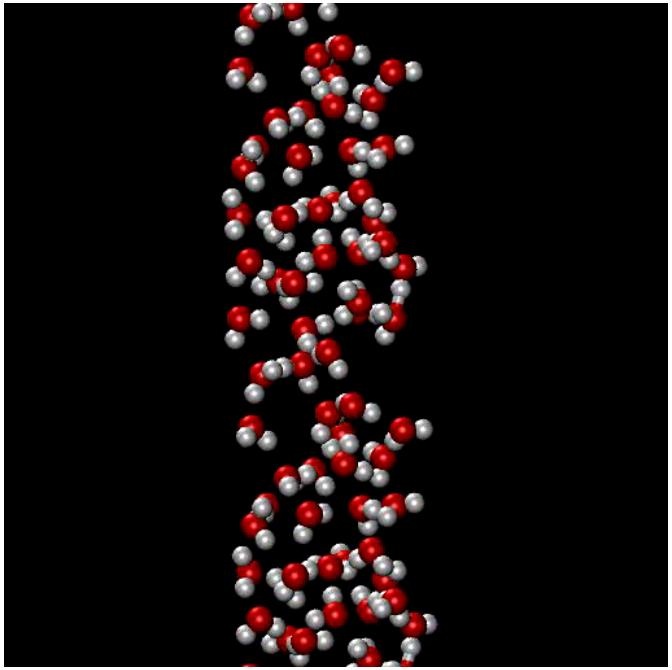
The making and breaking of hydrogen bonds as a protein unfolds with temperature

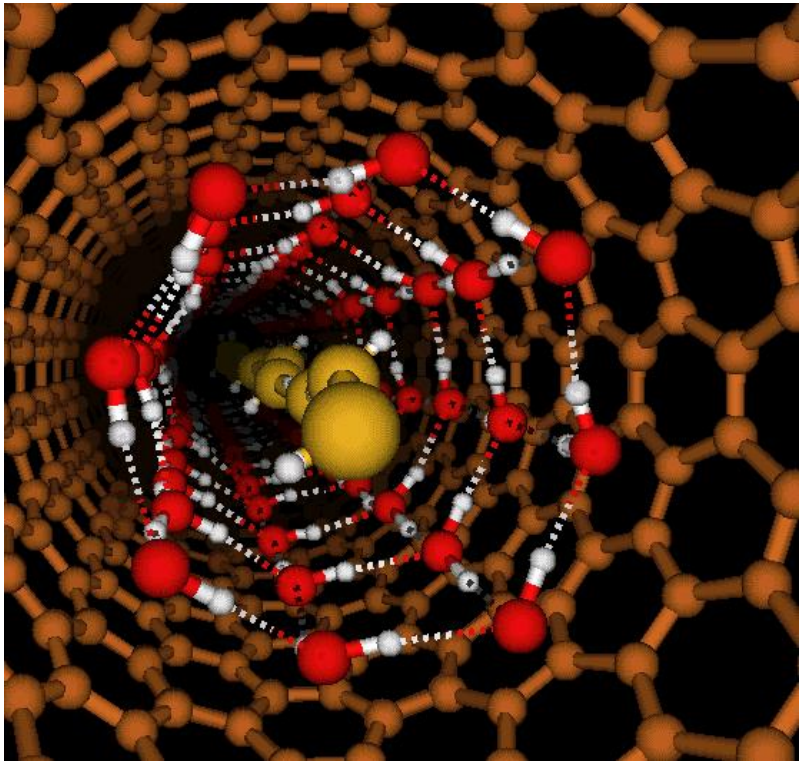


Variation of kinetic energy of the protons in a dilute lysozyme solution as the protein unfolds with temperature. Red line is what is to be expected if there are no changes in the proton quantum state

Reiter. Senesi, Mayers unpublished

MD simulations and proposed nanotube-water structure



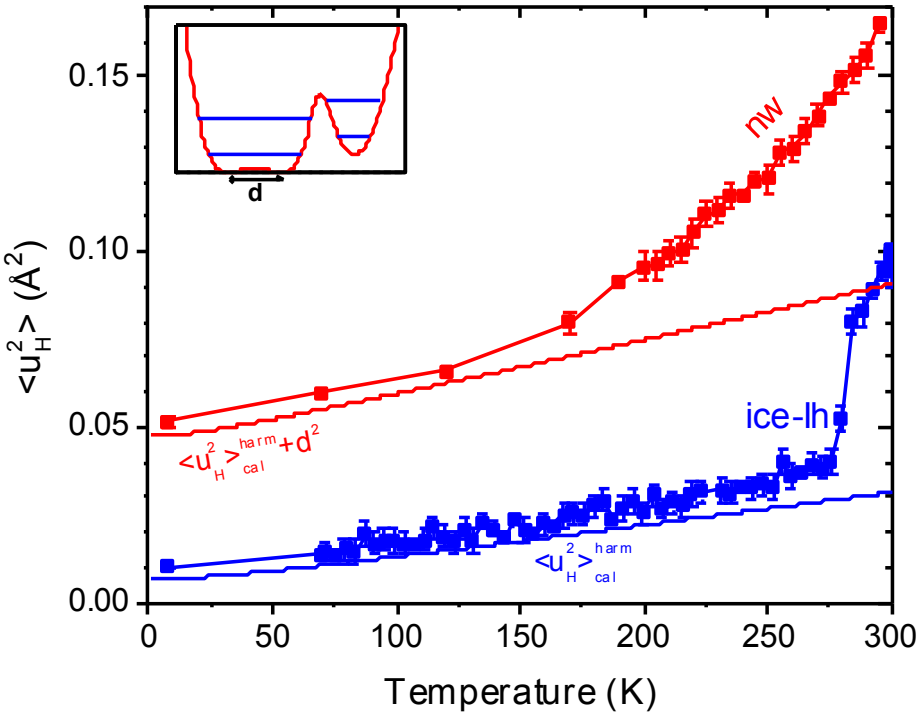


Proposed structure of nanotube-water. The interior "chain" water molecules have been colored yellow to distinguish them from the exterior "wall" water molecules (colored red).

MD calculations have been performed using the **TTM2-F** polarizable flexible water model (uses smeared charges and dipoles to model short range electrostatics) [1]. Our MD simulations consist of a rigid carbon nanotube of length 40 Å in periodic boundary conditions that interacts with water through the Lennard-Jones potential [2].

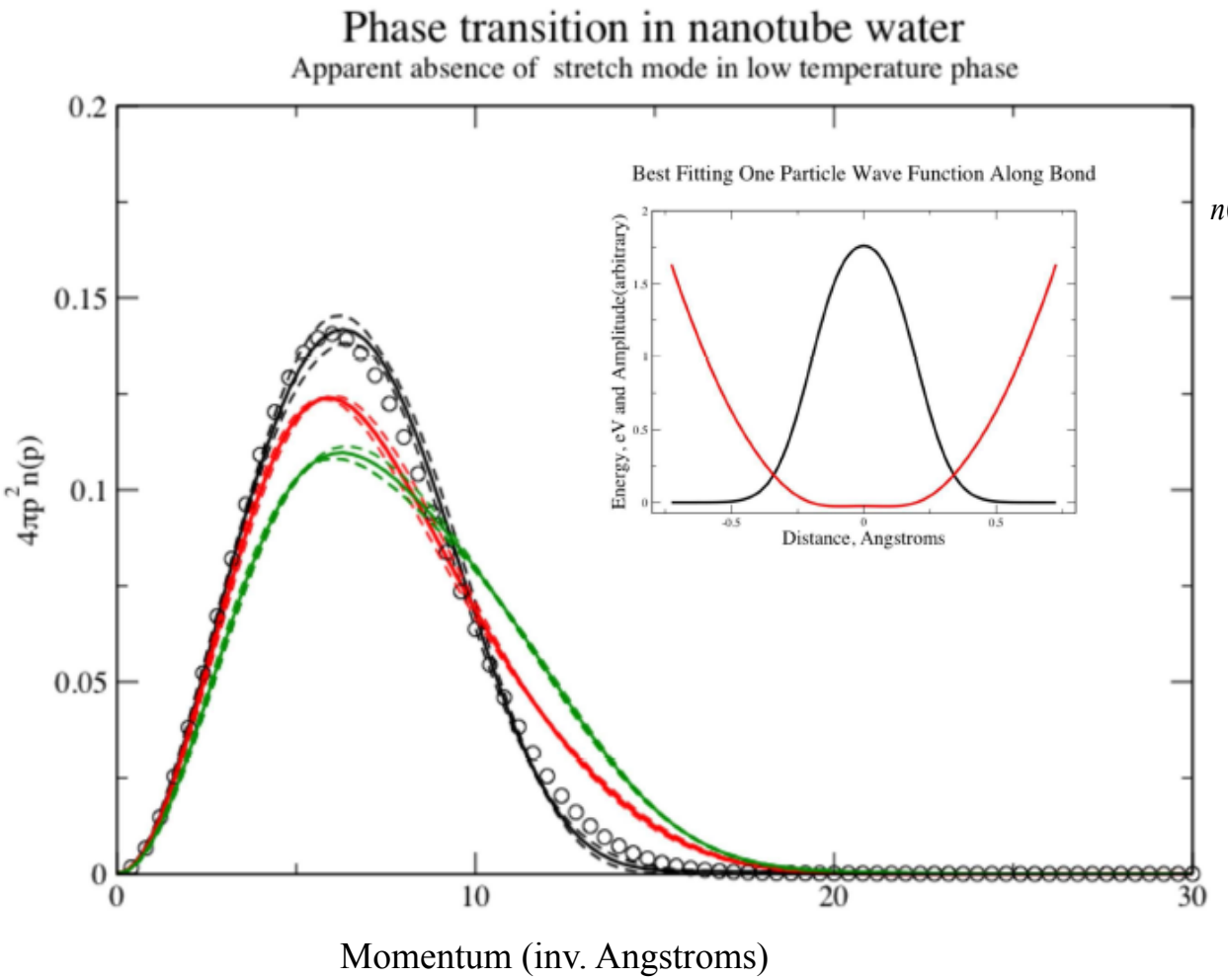
[1] Burnham & Xantheas, J. Chem. Phys. (2002); [2] Walther et al., J. Phys. Chem. (2001)

First evidence of something new happening in confined water



To describe $\langle u_H^2 \rangle$ for nanotube-water the calculated curve was vertically shifted by supposed delocalization, d~0.2 Å, of the hydrogen atoms due to the flat bottom of its potential (insert).

A. I. Kolesnikov, J.-M. Zanotti, C.-K. Loong, P. Thiyagarajan, A. P. Moravsky, R. O. Loutfy, and C. J. Burnham, Phys. Rev. Lett. **93,** 035503 (2004).



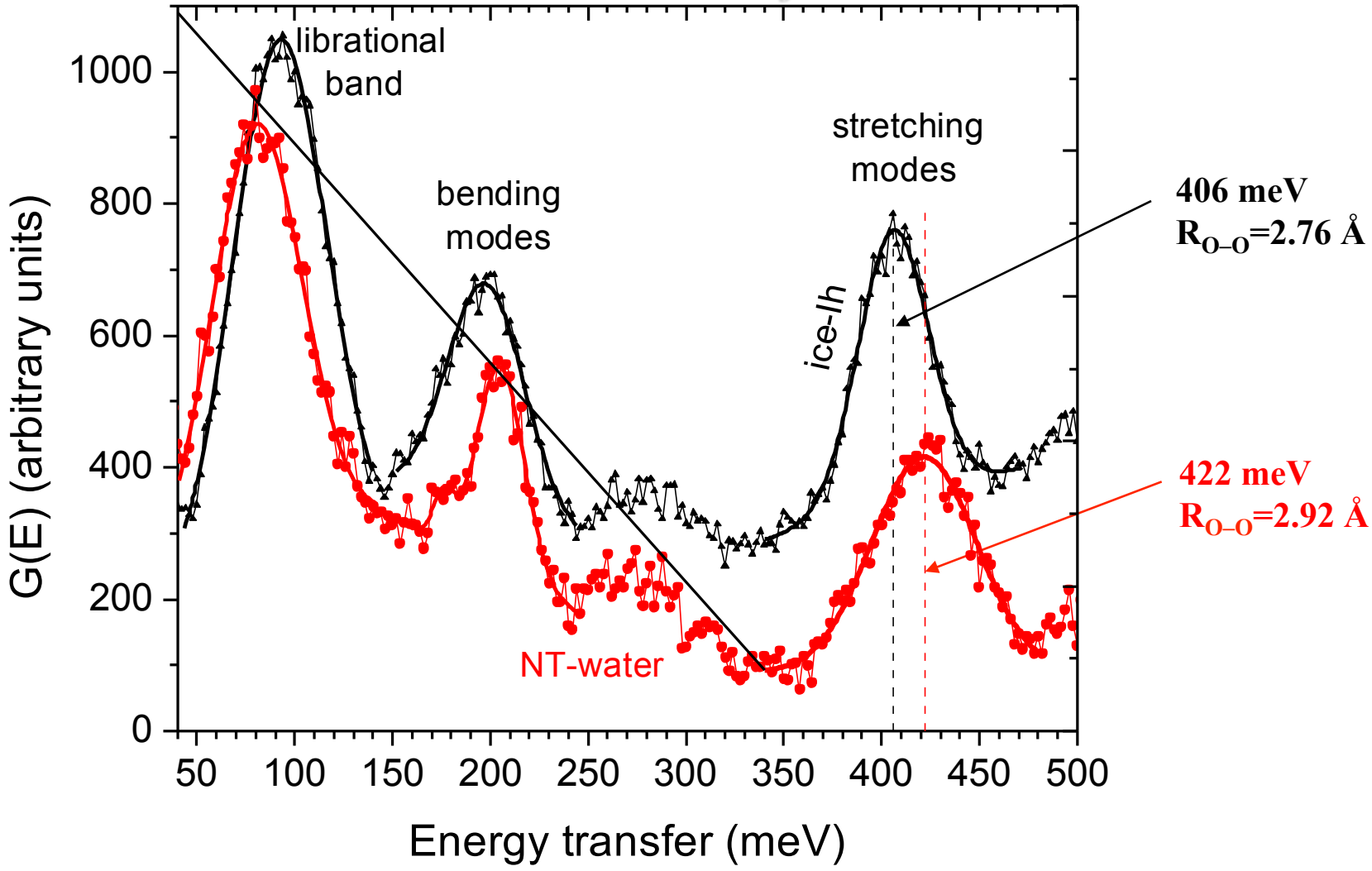
$$n(p_x, p_y, p_z) = \frac{2\cos^2(\frac{p_z d}{2\hbar})}{1+\exp(-\frac{d^2\sigma_z^2}{2\hbar^2})} \prod_i \frac{\exp(-\frac{p_i^2}{2\sigma_i^2})}{\sqrt{2\pi\sigma_i}}$$

K.E of N.T water=106 meV

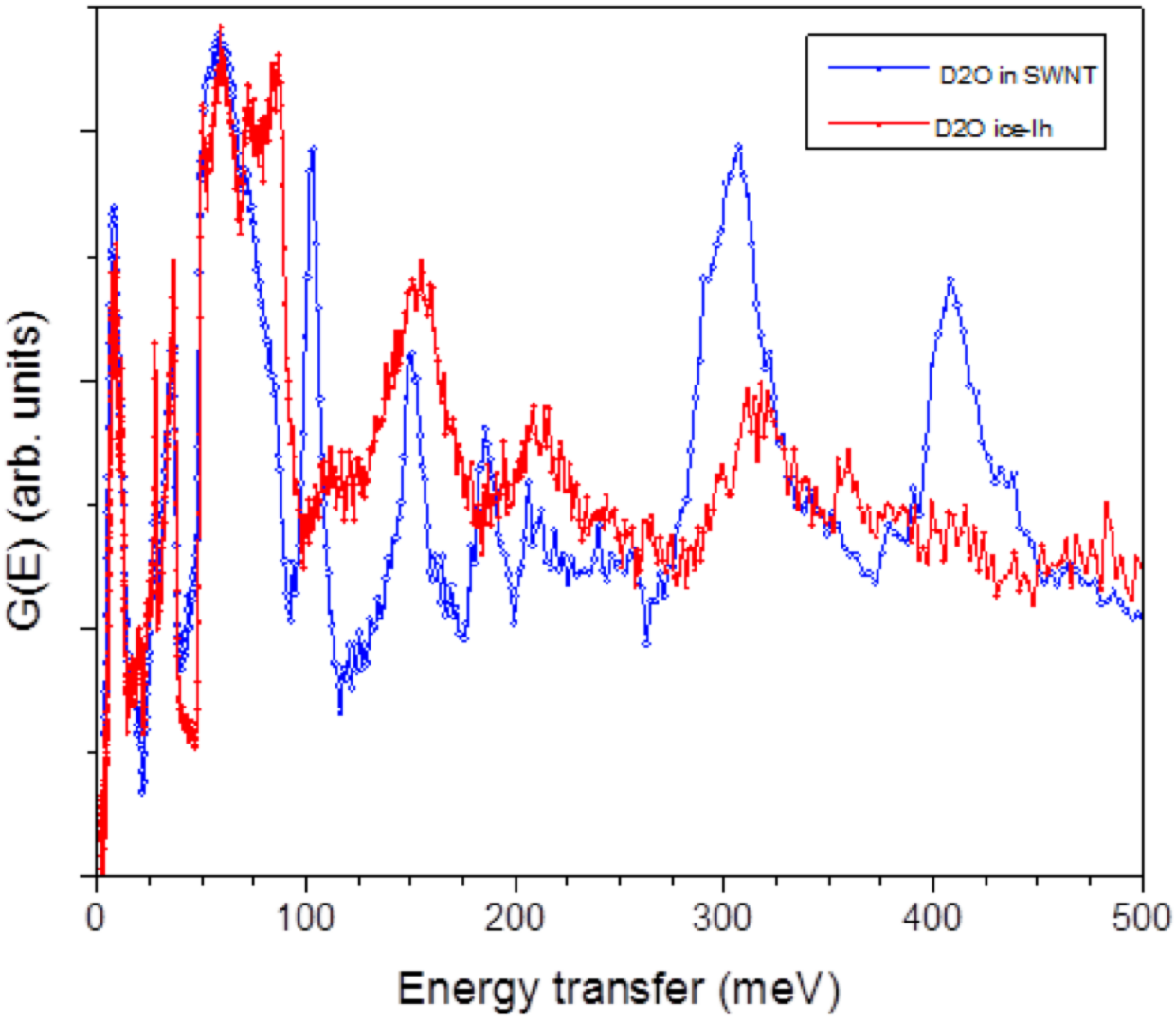
K.E. of bulk water=148 meV

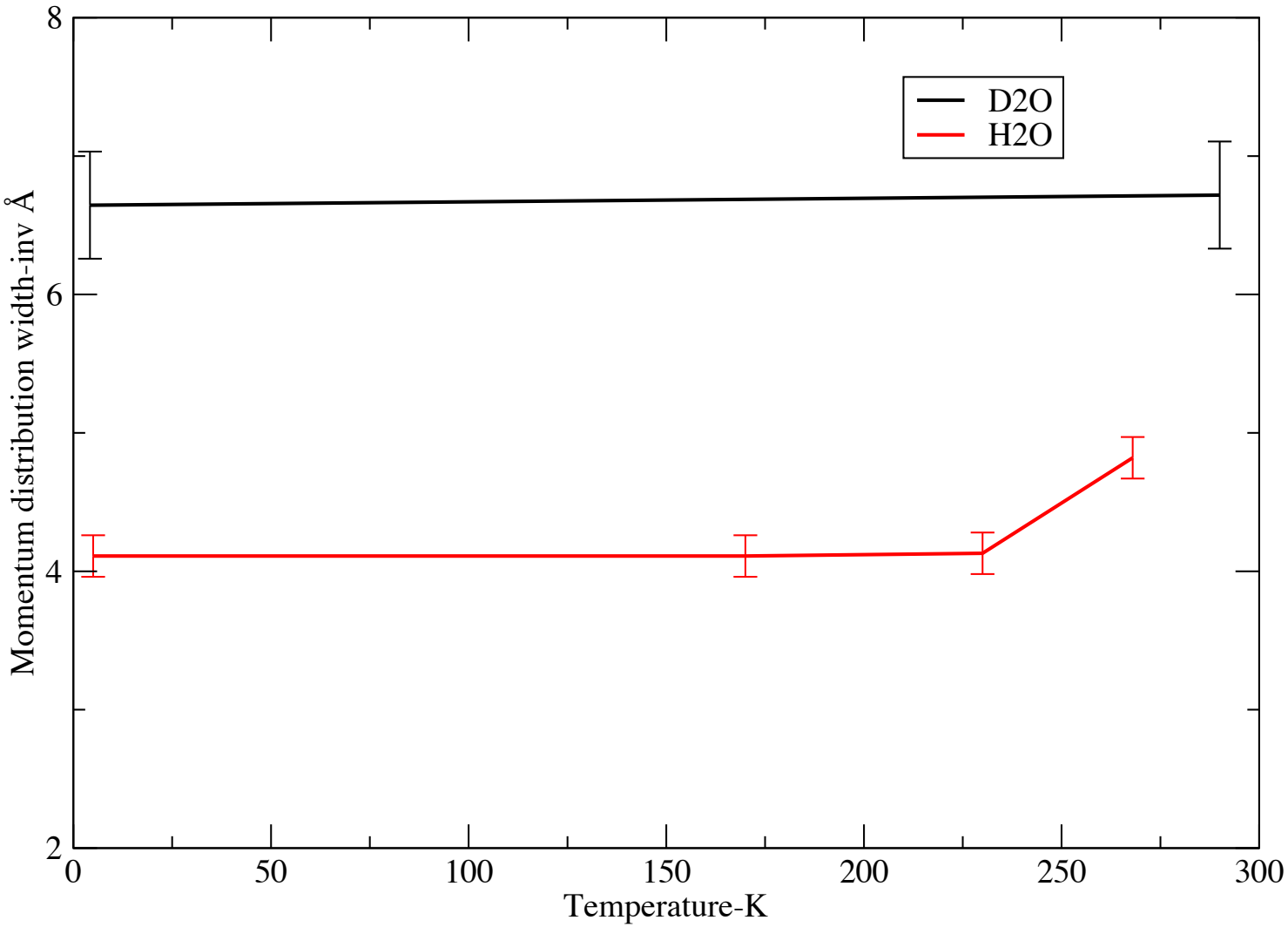
Momentum distributions for NT-water at 268 K (green) and 5 K (black), and ice-Ih at 269 K (red). The circles are a fit to a model in which the water proton is delocalized in a double well potential. The potential (red) and wave-function (black) are shown in the inset.

A Significantly Weaker Hydrogen-Bond Network in Nanotube-Water- Stretch mode blue shifted

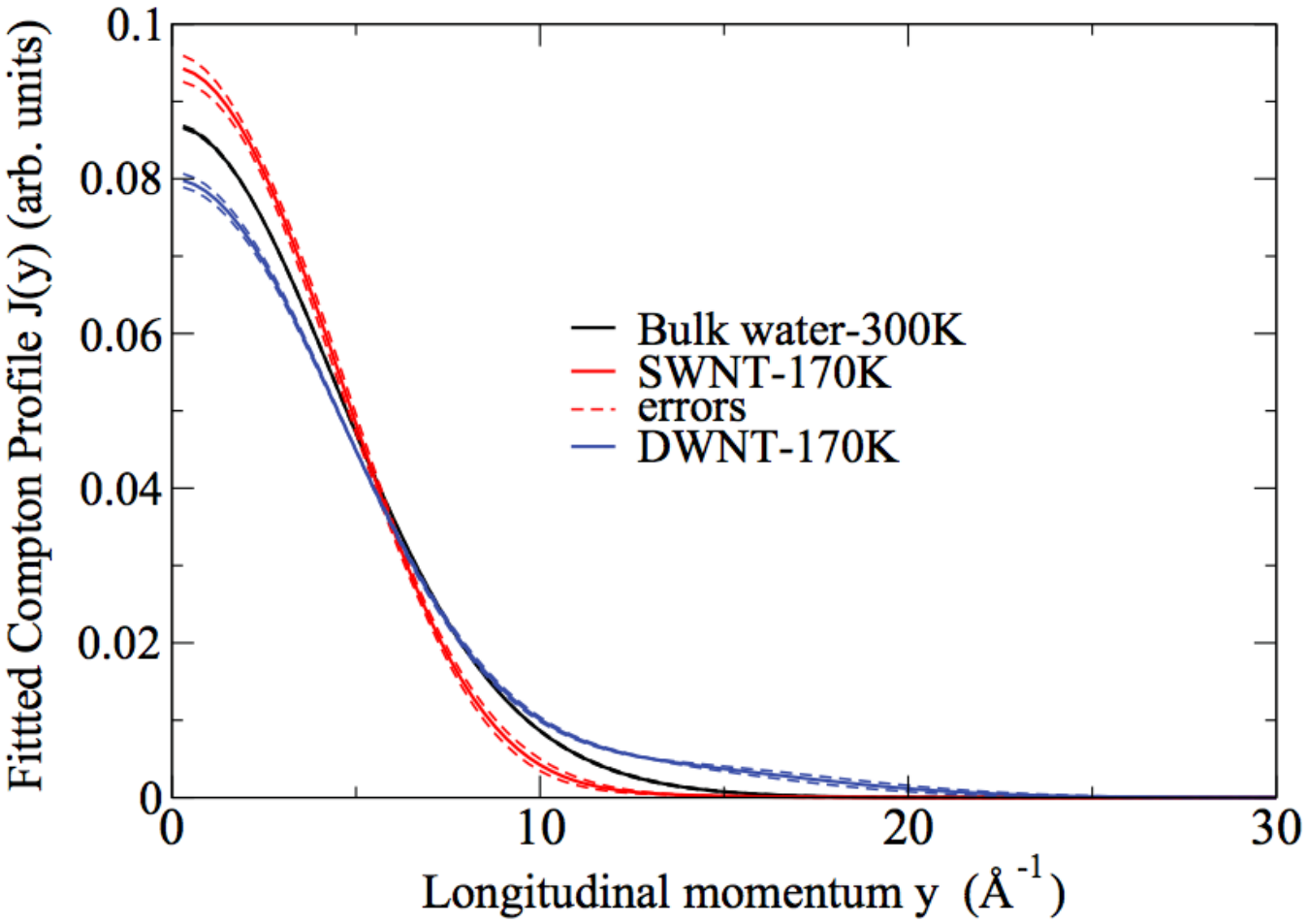


But red shifted in D2O!

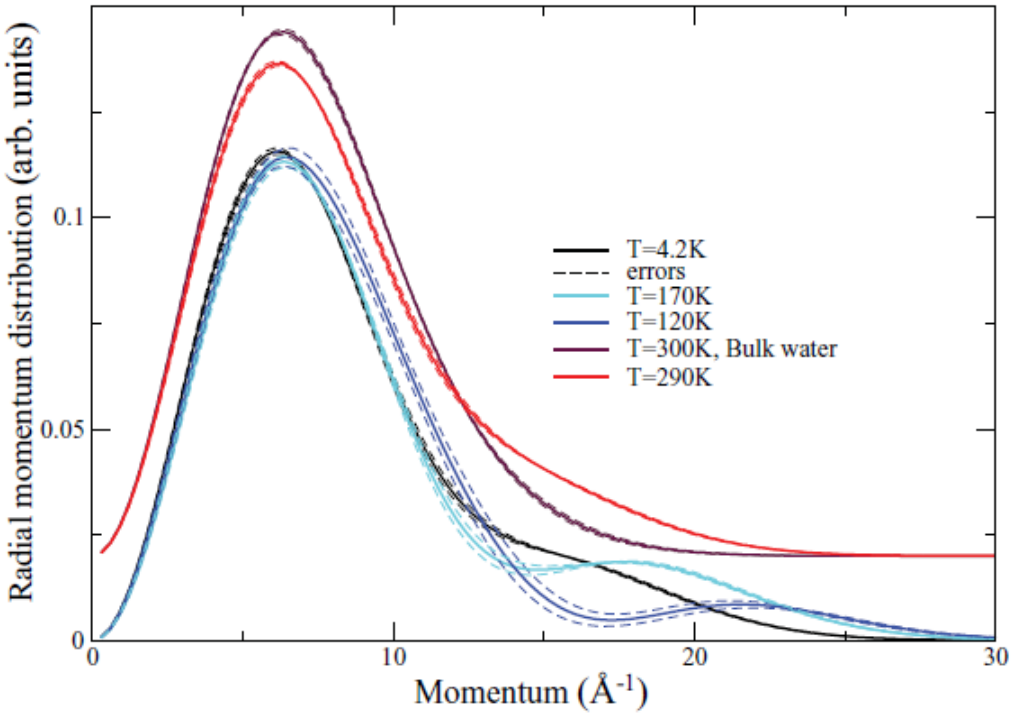



Momentum width, D2O, H2O
D2O
H2O
Momentum distribution width-inv Å
Temperature-K
8
6
4
2
0
50
100
150
200
250
300

SWNT(dia. 14Å) compared with DWNT(dia. 16Å)

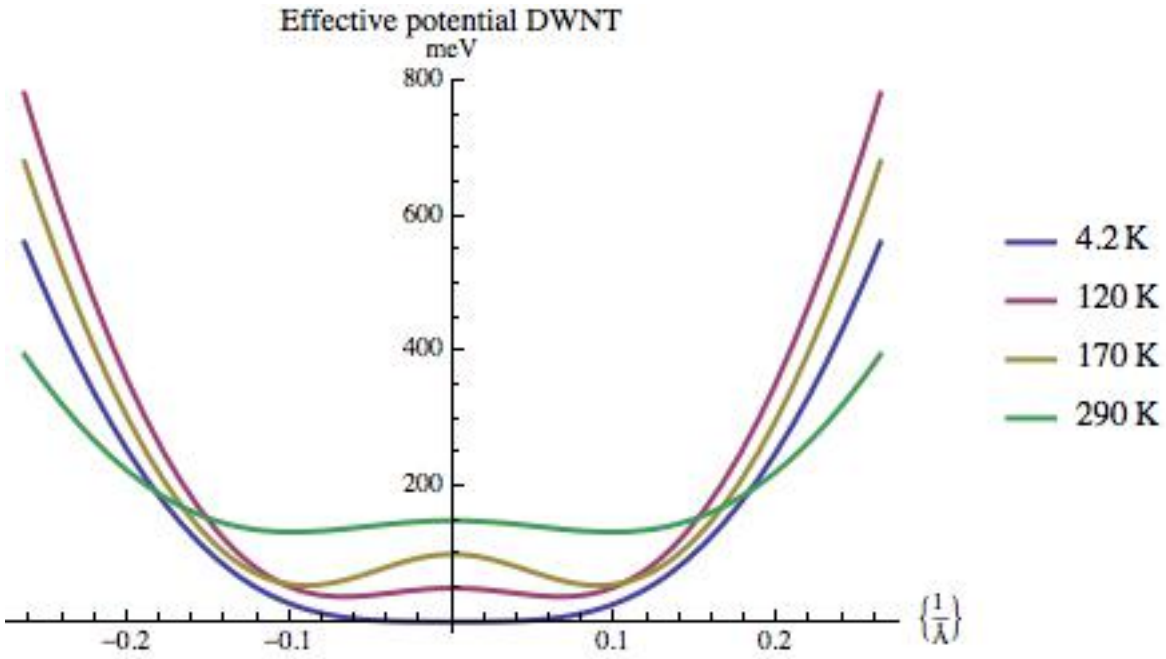


Double wall nanotubes-16Å diameter



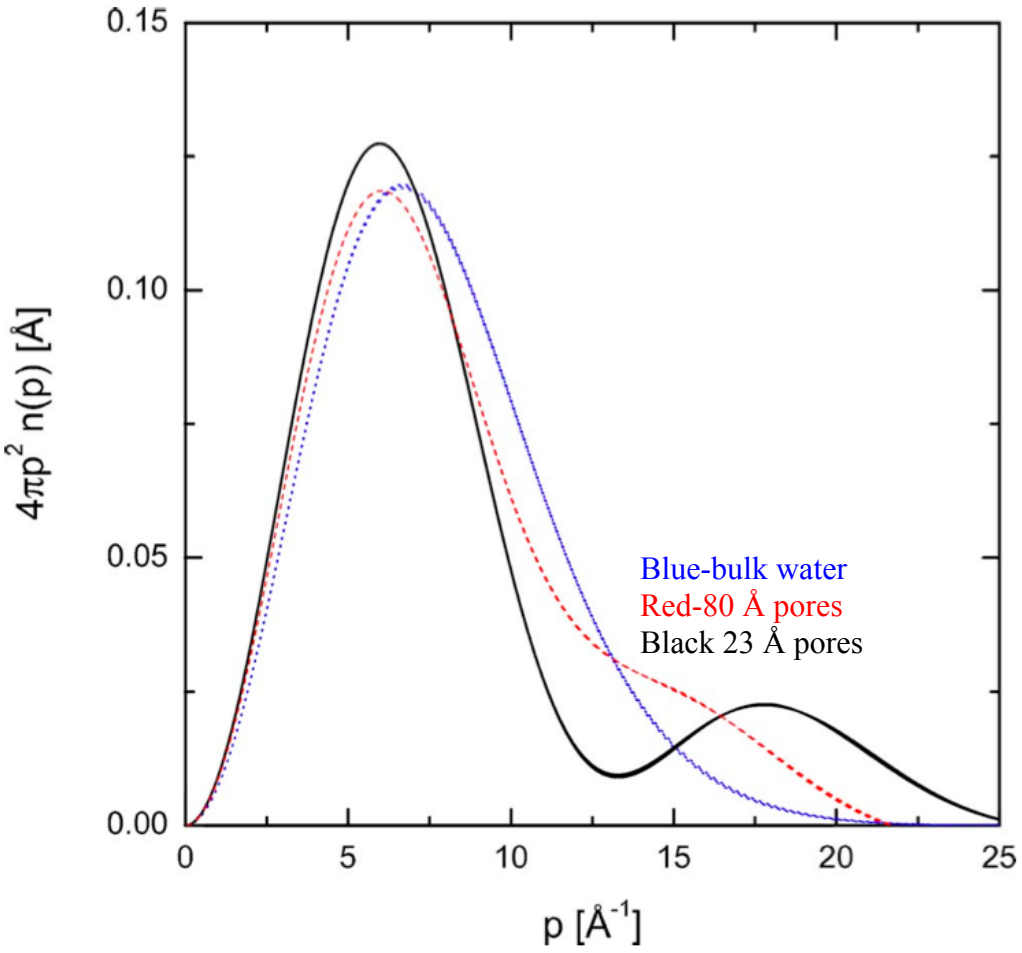
The radial momentum distribution, $4\pi p^2 n(p)$, of the water protons in 16 Å DWNT at different temperatures, compared with that of bulk water at room temperatures. The 290 K signal and the bulk water signal have been displaced upward by 0.02 units for clarity.

G. F. Reiter, R. Senesi and J. Mayers, Phys. Rev. B 105, 148101 (2010)

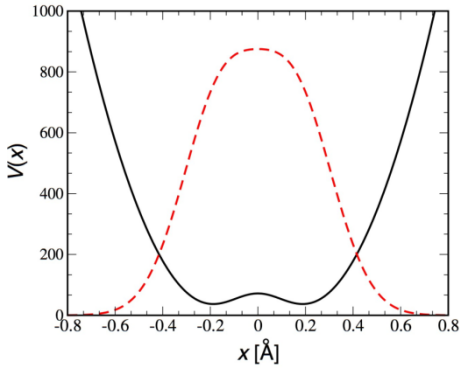


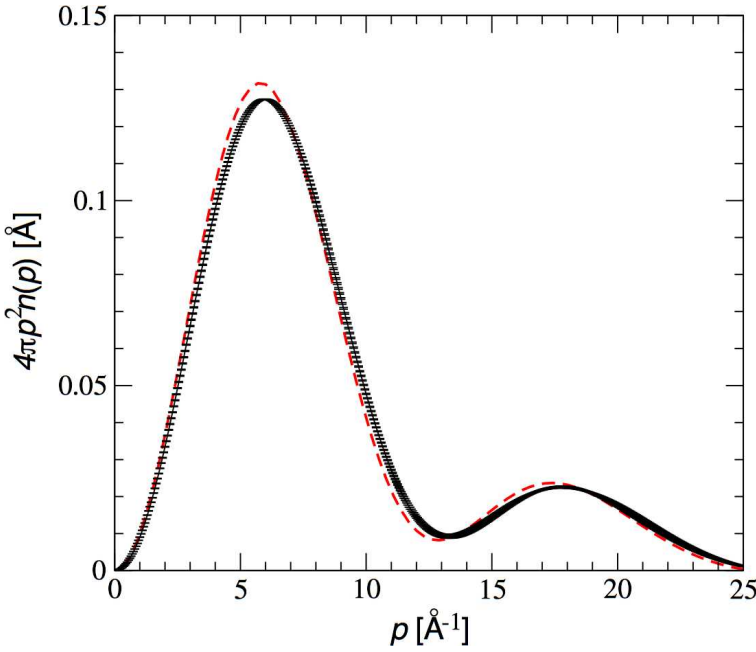
Temperature dependence of the effective potential for the protons in DWNT. The 120K, 170K, and 290K curves have been shifted up by 50, 100 and 150 meV respectively from the 4.2K curve.

Water in xerogel-room temperature



V. Garbuio, C. Andreani, S. Imberti, A. Pietropaolo, G. F. Reiter, R. Senesi, and M. A. Ricci, J. Chem. Phys. **127,** 154501 (2007).

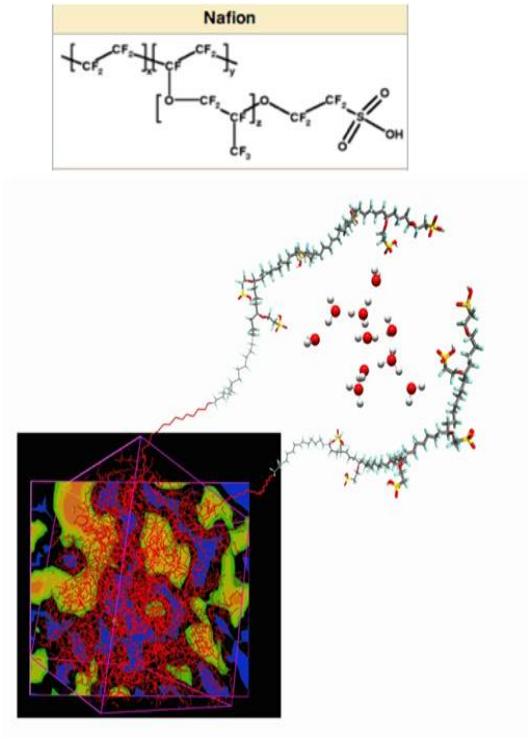


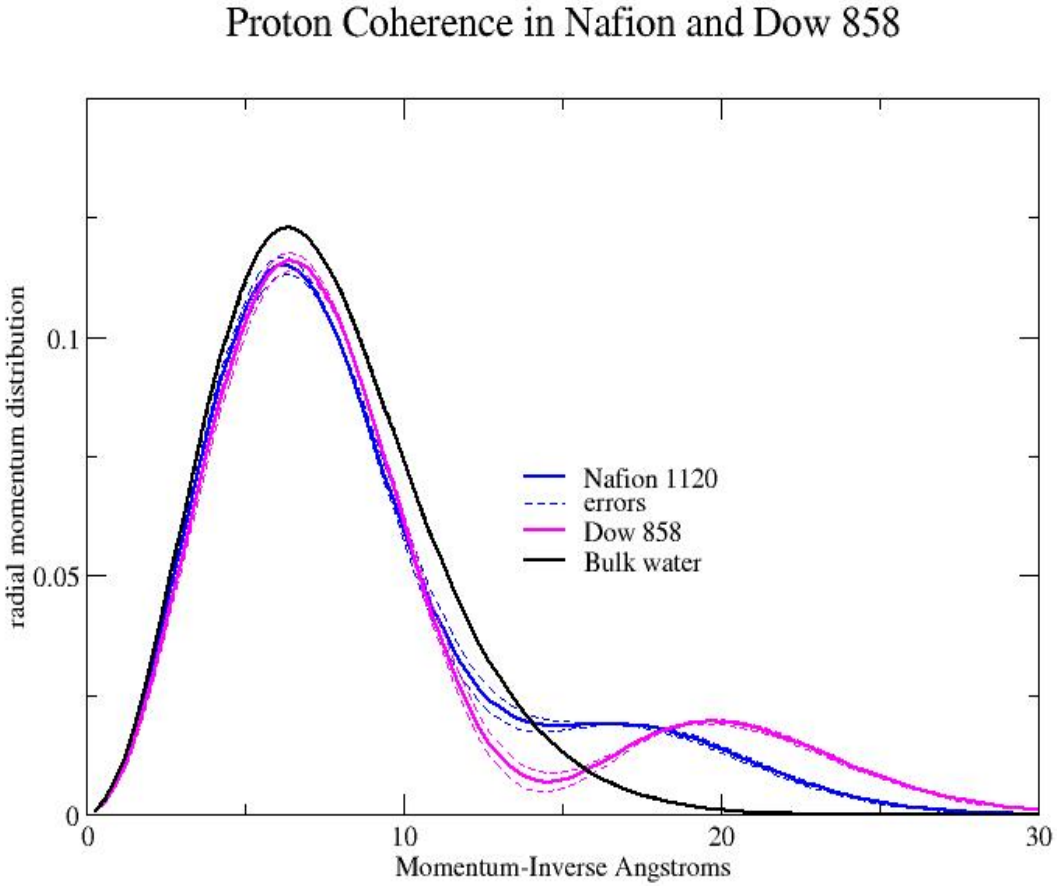


Water in xerogel 23 Å pores (T=300 K). The dashed red line is a fit to the data with a single particle in a double-well model (top figure) [1].

[1] V. Garbuio *et al., J. Chem. Phys.* **127** (2007) 154501.

Water in Nafion, Dow 858- Room temperature



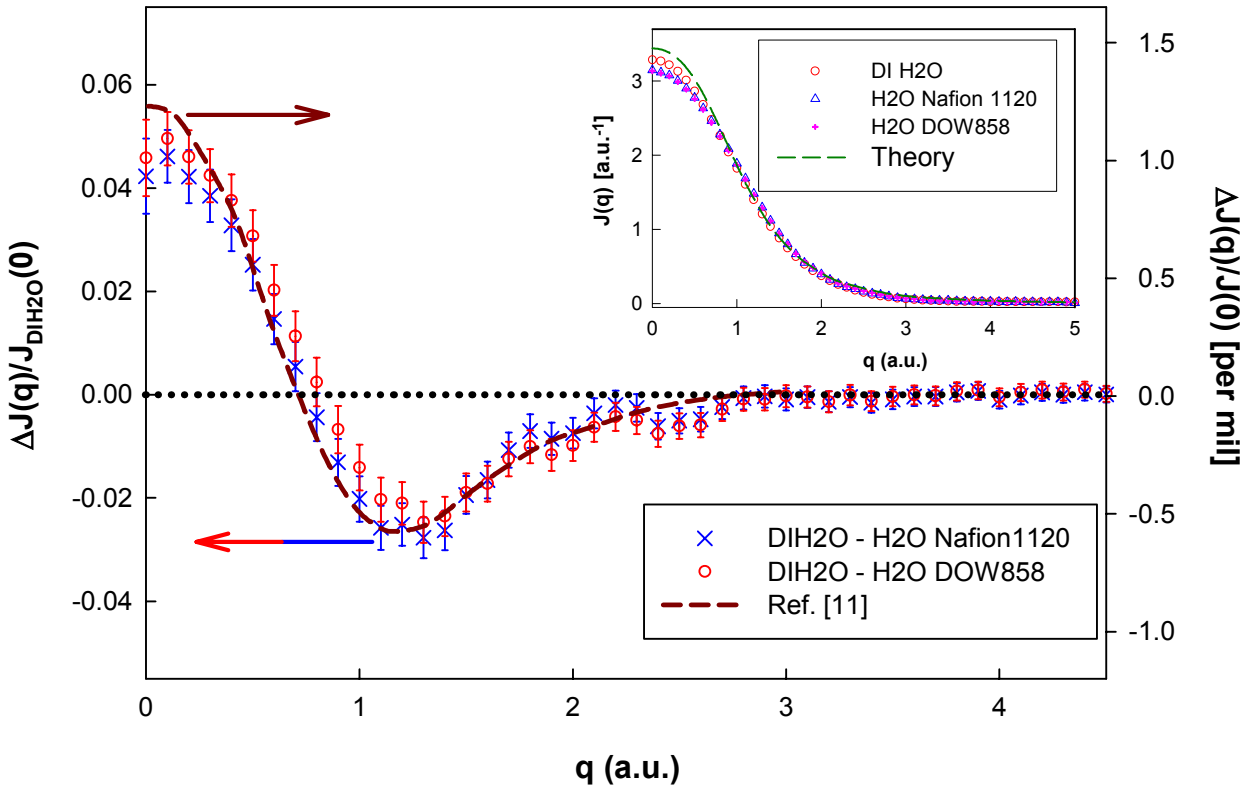


The radial momentum distribution, $4\pi p^2 n(p)$, of the protons in Nafion1120 (blue) and Dow 858 (magenta) compared with that of bulk water (black), all at room temperature.

G. F. Reiter, R. Senesi and J. Mayers, Phys. Rev. 105, 148101 (2010)

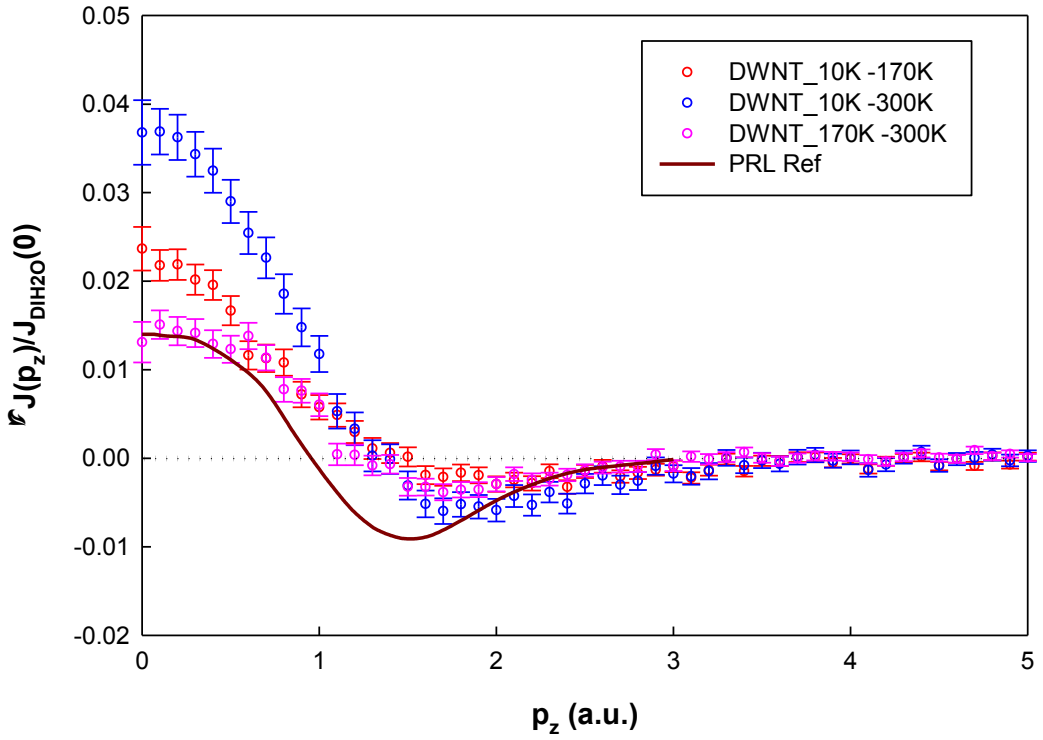
Water Sample	$\sigma(\mathring{A}^{-1})$	K.E.-meV
Bulk-300K	$4.72 \pm .03$	138
DWNT-4,2K	$5.40 \pm .36$	181
DWNT-120K	$5.65 \pm .06$	198
DWNT-170K	$5.97 \pm .15$	221
DWNT-290K	$5.26 \pm .08$	172
SWNT-170K	$4.09 \pm .07$	104
Nafion1120-300K	$6.28 \pm .40$	245
Dow858-300K	$6.50 \pm .27$	262

Difference profiles: Bulk water-water in Nafion, Dow 858

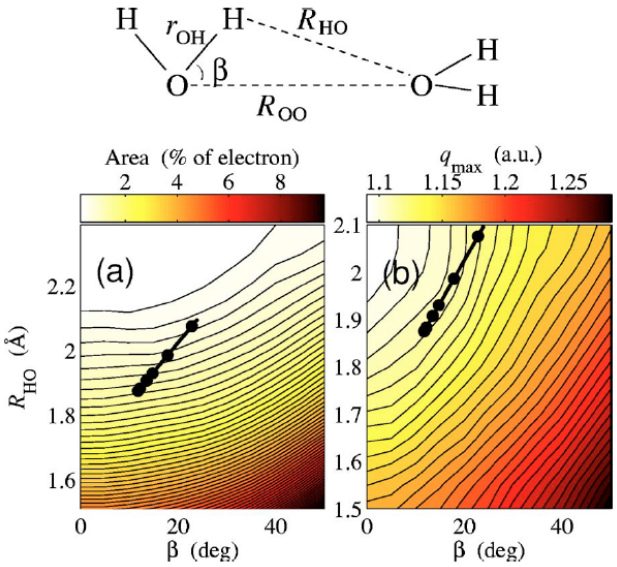


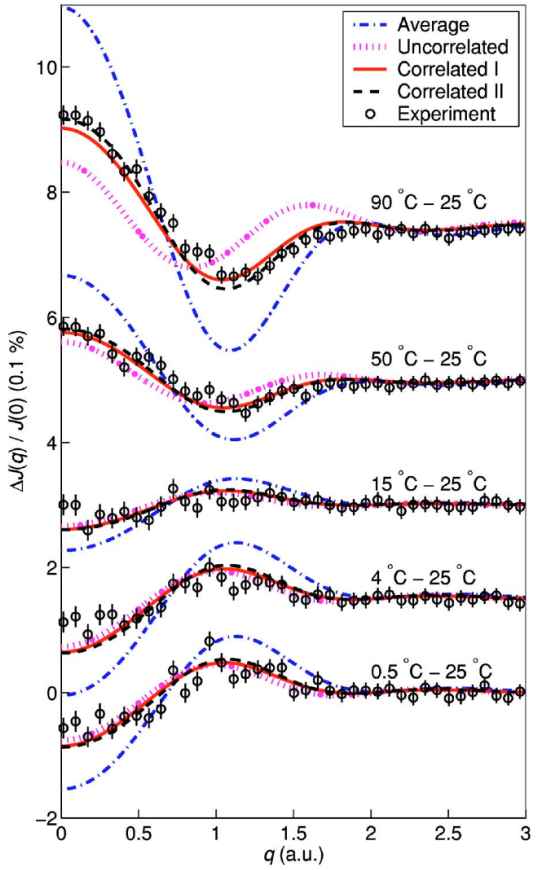
G. F. Reiter, A. Deb, Y. Sakurai, M. Itou, V. G. Krishnan and S. J. Paddison, PRL 111, 036803 (2013)

Electron Compton profile-DWNT Differencewith Bulk



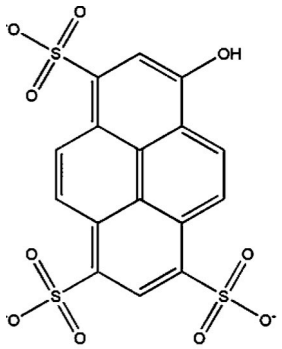
X-Ray Compton scattering from bulk water, using molecular model for interpretation. Note scale of variation of Compton profile with temperature.



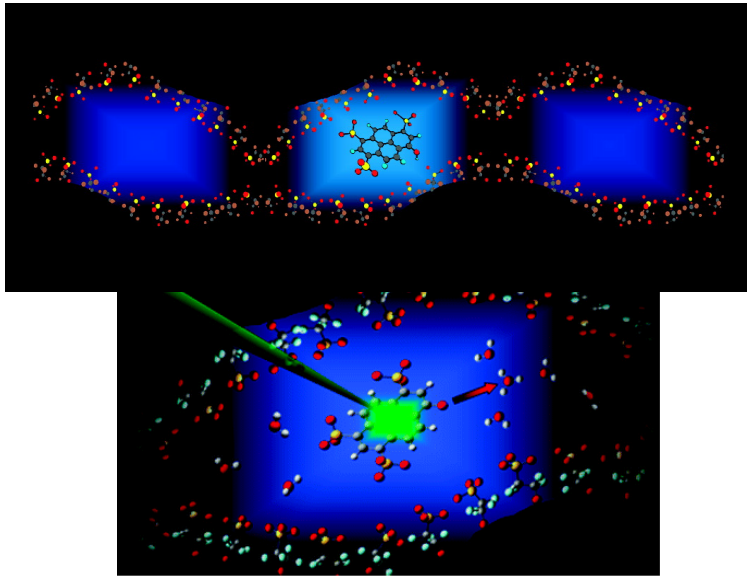


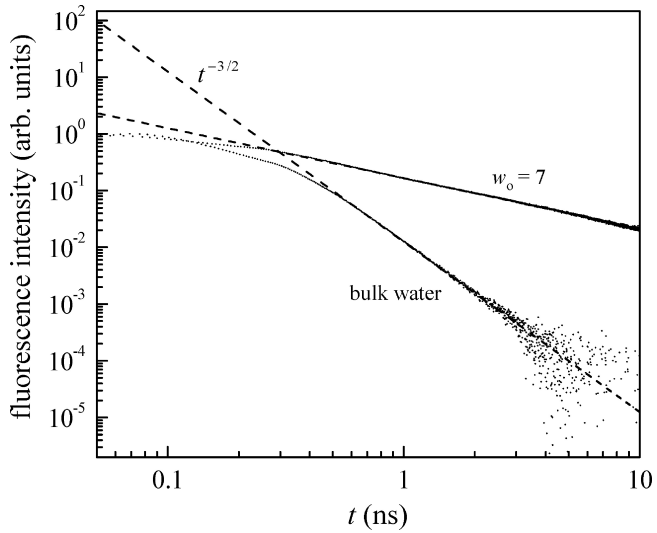
M. Hakala et al, J. Chem. Phys. 125, 084504 (2006)

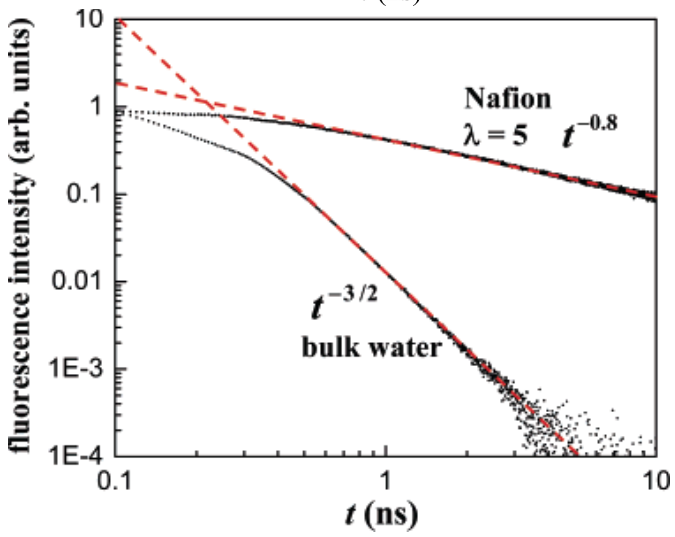
AOT



HPTS







D. E. Moilanen, D. B. Spry and M. D. Fayer, Langmuir 24 (8), 3690-3698 (2008)

Direct electronic de-excitation of excited state possible in nano-confined water

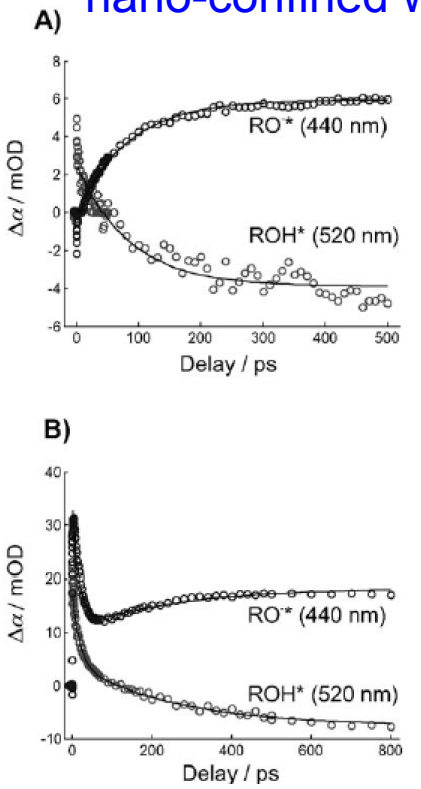


Figure 3. A) The signal as a function of pump-probe delay time at a wavelength of 440 and 520 nm for large reverse micelles ($w = 15$). The lines are obtained by fitting the data to Equation (1). B) The signal as a function of pump-probe delay time at a wavelength of 440 and 520 nm for medium size reverse micelles ($w = 8$). The lines are obtained by fitting the data to Equation (2).

Klaas Jan Tielrooij, M Jocelyn Cox, and Huib J Bakker, ChemPhysChem 10, 245 (2009)

Summary

- The momentum distribution of water confined to distances of the order of 20 Å is unlike that of bulk water and sensitive to the global nature of the confinement.

- Changes in proton kinetic energy of water on surfaces is thermodynamically significant.

- The quantum ground state of the electrons and protons in nano-confined water is qualitatively different from that of bulk water. The usual model of molecules interacting weakly electrostatically does not apply.

- The changes in zero point energy of the protons is observable in the transformations in shape of biological molecules, and hence, most biological processes

- 20Å is the characteristic distance between the elements of biological cells. It is unlikely that evolution has not made use of the properties of this state. We should understand its properties if we want to understand the role quantum mechanics has played in the origin of life.