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MEETINGS & EVENTS

ACS SPRING 2021

MACROMOLECULAR CHEMISTRY: THE SECOND CENTURY

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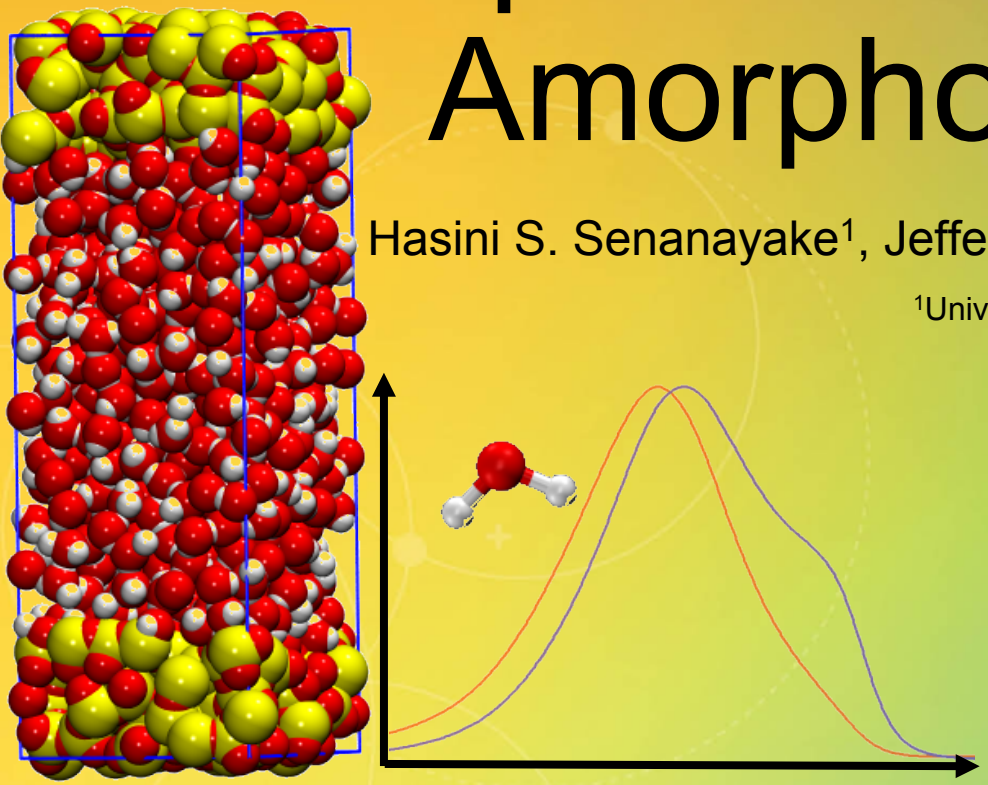
ACS SPRING 2021

MACROMOLECULAR CHEMISTRY: THE SECOND CENTURY

Simulations of the IR and Raman Spectra of Water Confined in Amorphous Silica Slit Pores



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Paper ID:3554066

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MEETINGS & EVENTS

Water confined in mesoporous silica

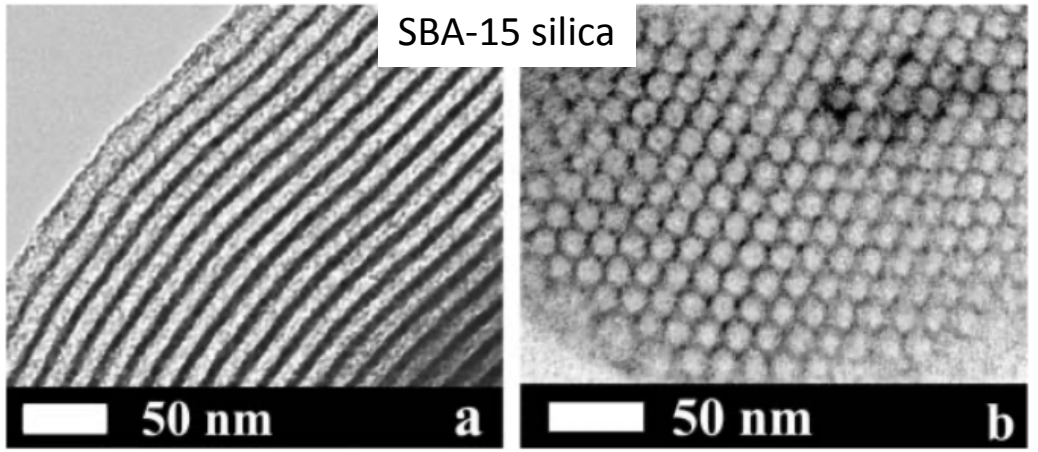
Confined water - soil and sedimentary rocks

Difficult to prepare nano pores from real rocks/minerals

Mesoporous silica - synthetic analogs to look at mineral-fluid interactions

To predict or control how water and aqueous species move

- contaminant transport
- remove or store material (CO_2,nuclear waste)



Chen *et al.*,*Chem. Commun.*, **42**, 5343-5345 (2005)

Theoretical spectra for confined water

How does the pore width affect the dynamics of the confined liquid?

How do the spectroscopic properties relate to the molecular details?

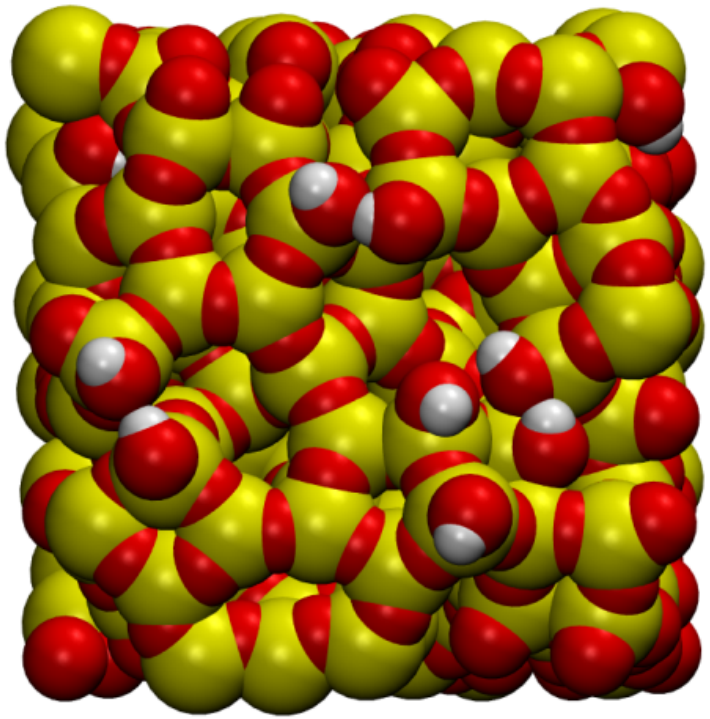
We will be looking at :

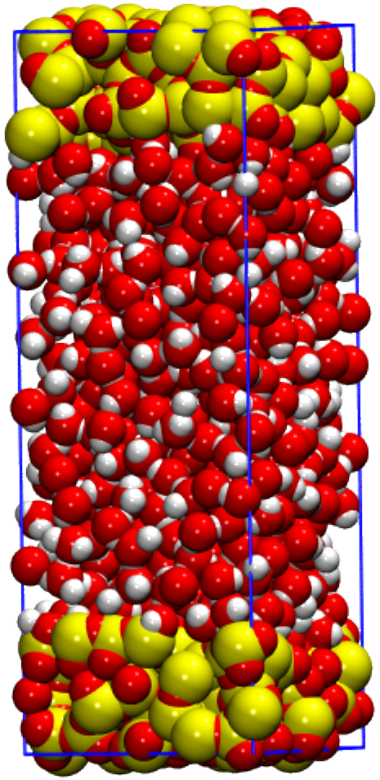
Effect of pore width on confinement

H-bonding between water molecules and pore surface atoms

Effect of surface hydroxyl density on confinement

Amorphous silica slit pore generation





Dr. Pubudu Wimalasiri

MD simulations - LAMMPS
Rectangular periodic box with x and y = 21.055 Å
Gulmen-Thompson force field – Silanol and Geminal interactions
SPC/E model - water interactions

Calculation of vibrational frequencies

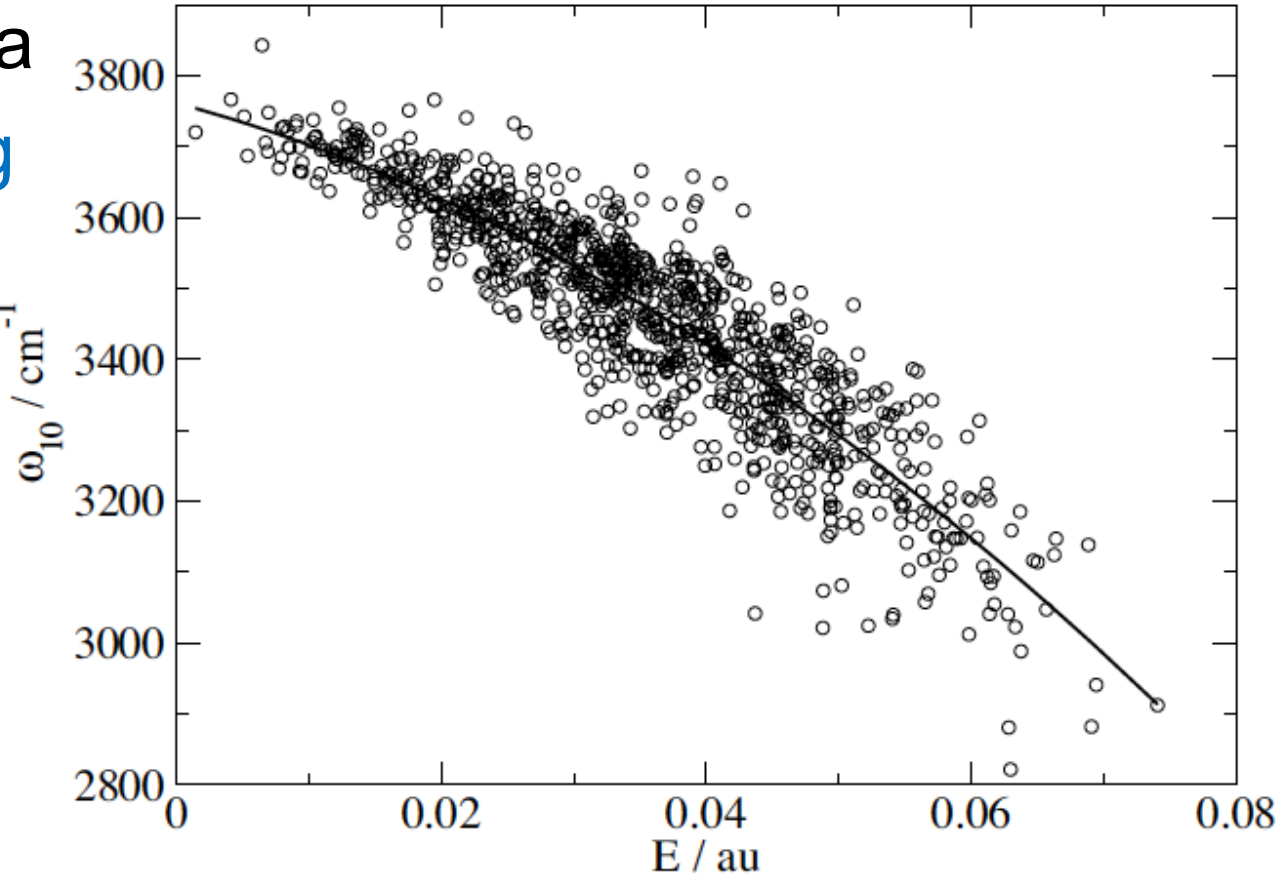
HOD in D_2O – For simplified spectra

Empirical (or Electrostatic) mapping

$$\omega_{01}^{i}(t) = c_0 + c_1 E_i(t) + c_2 E_i(t)^2$$

Fundamental vibrational frequency for stretching evaluated for the i^{th} OH at time t

Total electric field evaluated for the i^{th} OH at time t

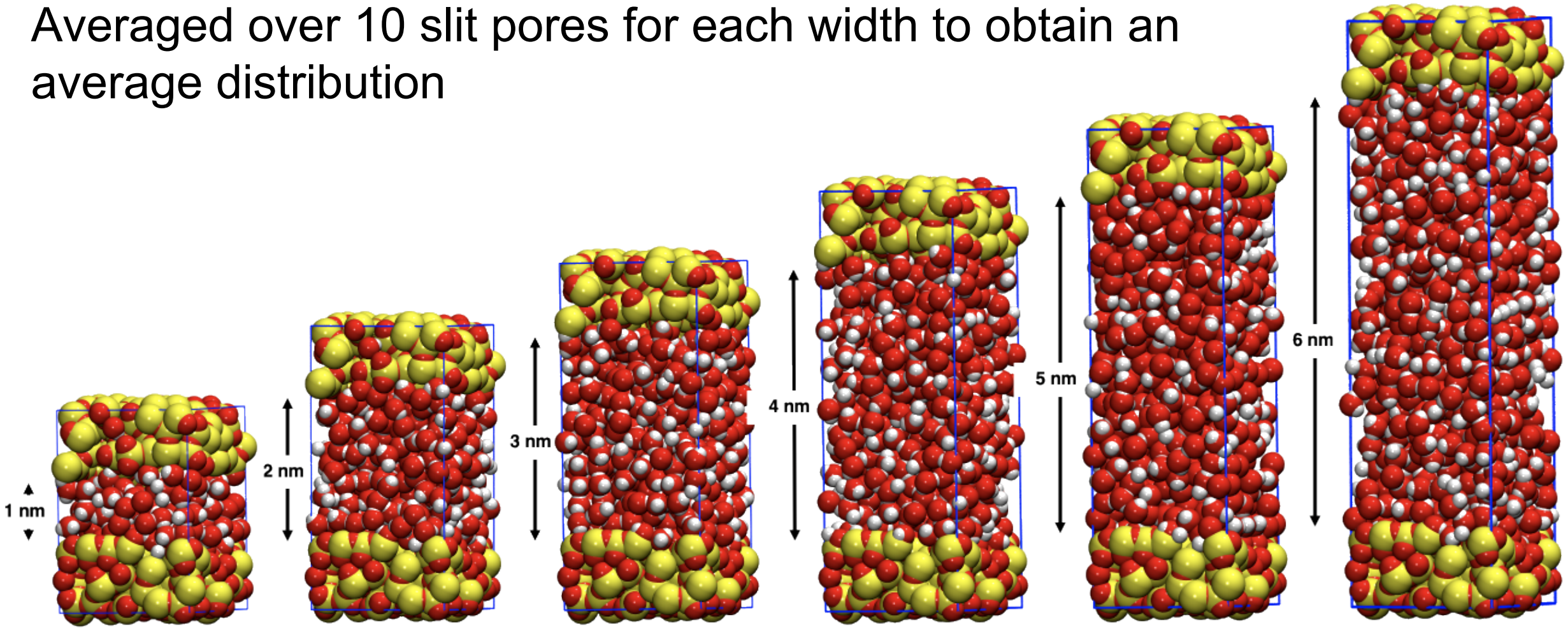


Calculated OH stretch frequencies versus electric field E. Solid line is the best quadratic fit

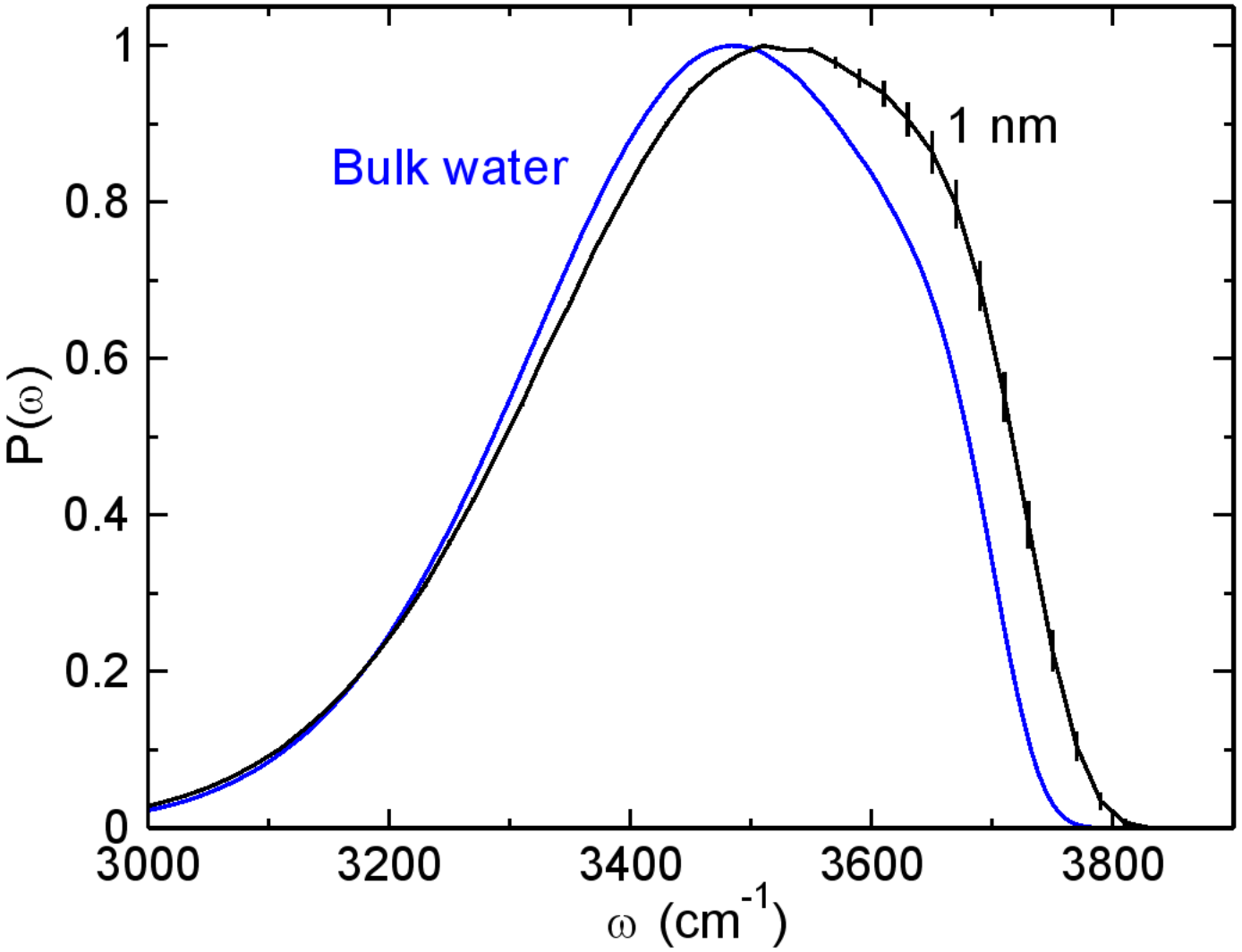
Auer *et al.*,*Proc. Natl. Acad. Sci* **104**, 14215 (2007)

Effect of pore width

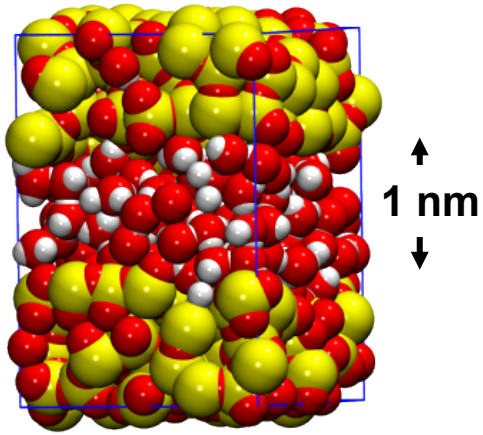
Averaged over 10 slit pores for each width to obtain an average distribution



Effect of pore width on frequency distribution



The frequency distributions for confined water is prominently blue shifted



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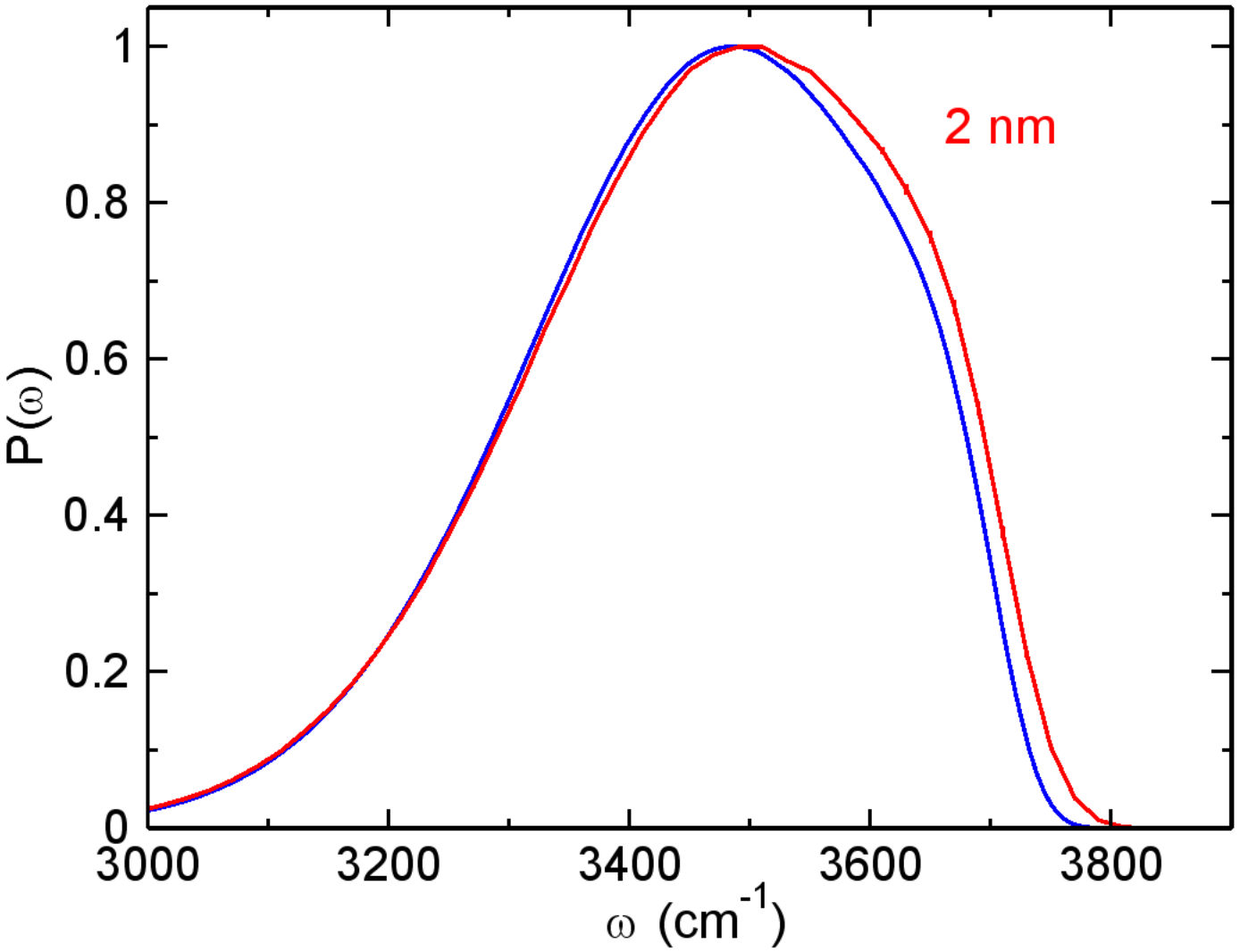
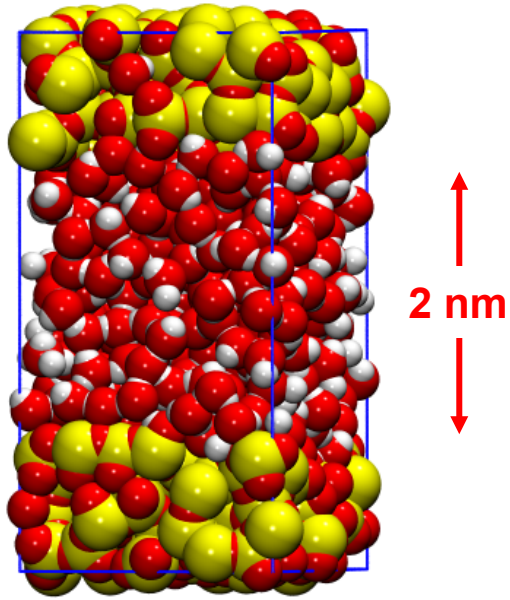
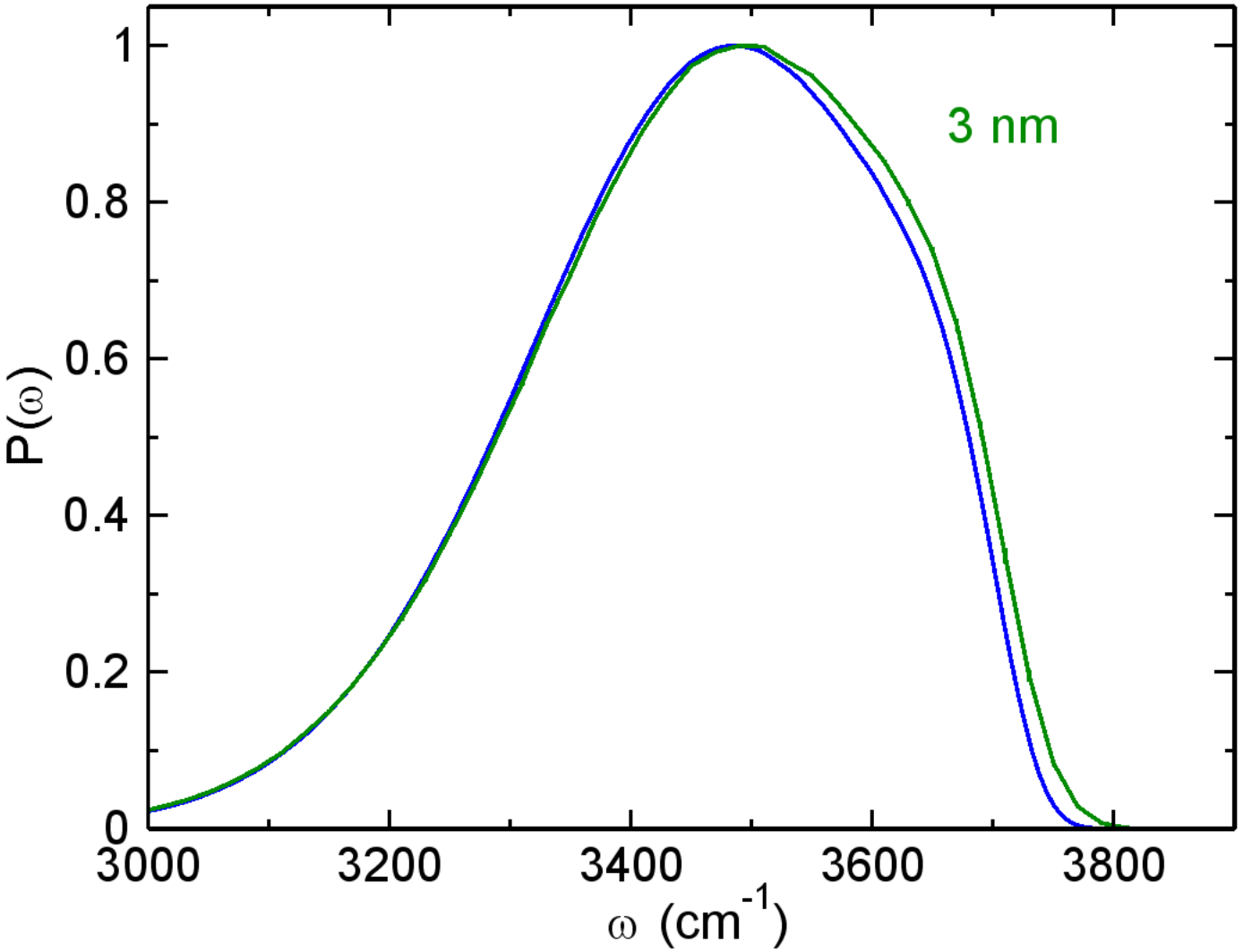


The distribution shifts towards bulk water when increasing the pore width



Effect of pore width on frequency distribution



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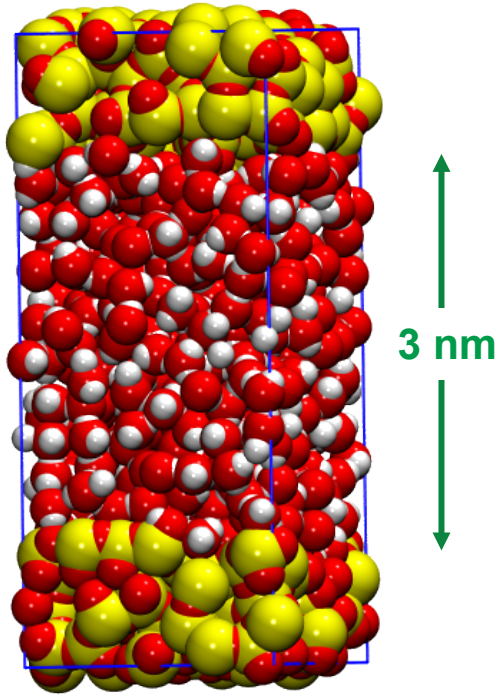
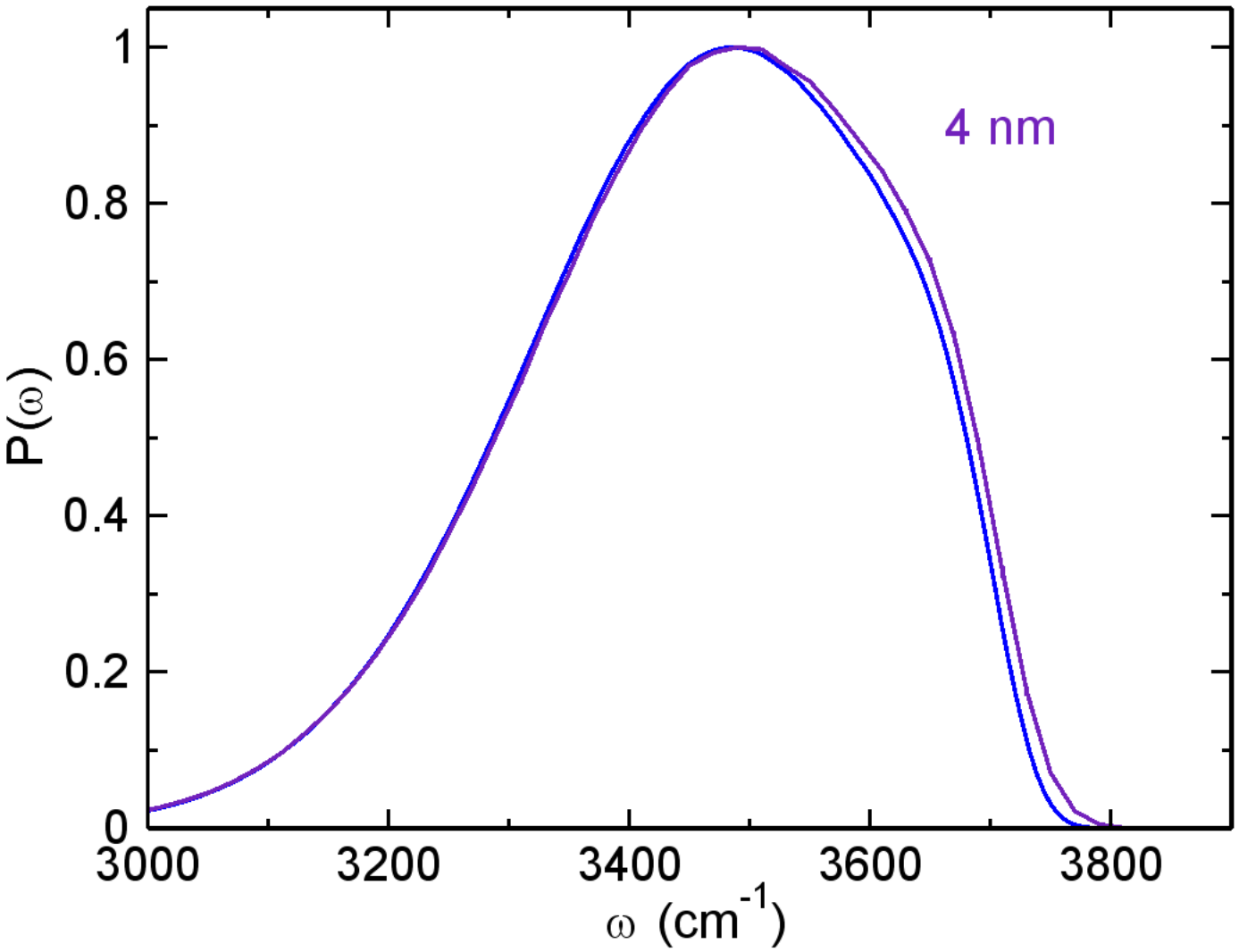
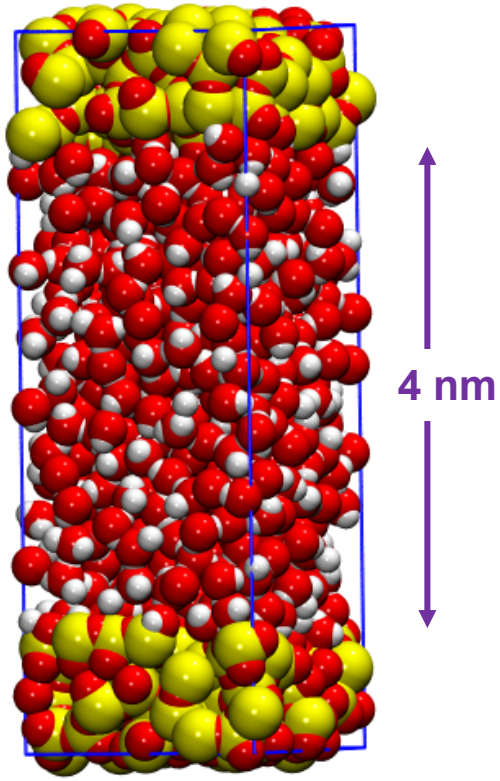
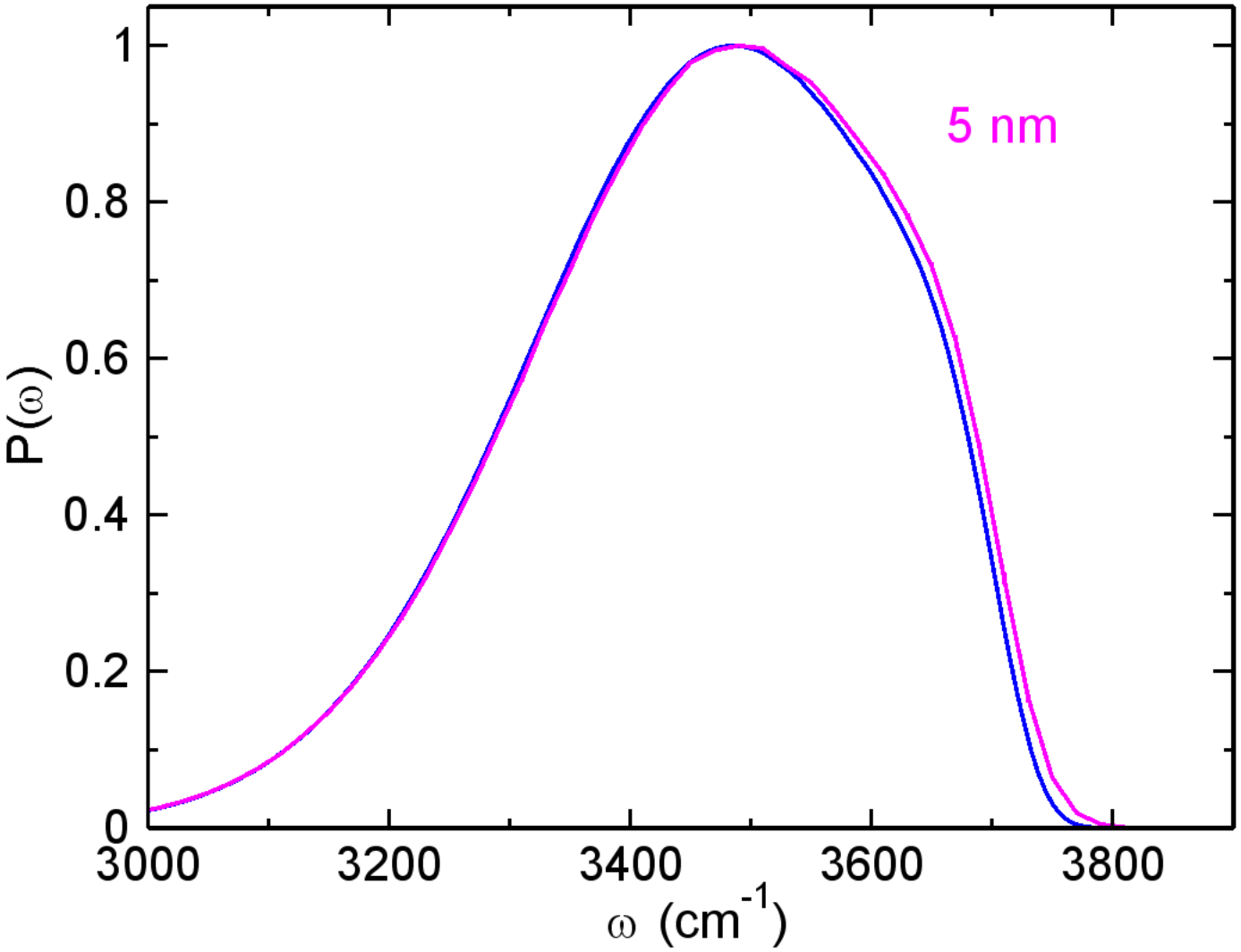


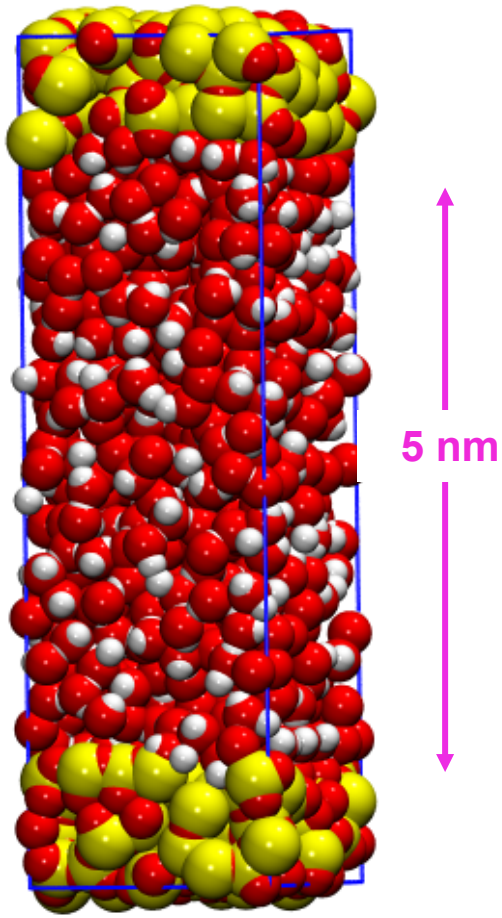
Effect of pore width on frequency distribution



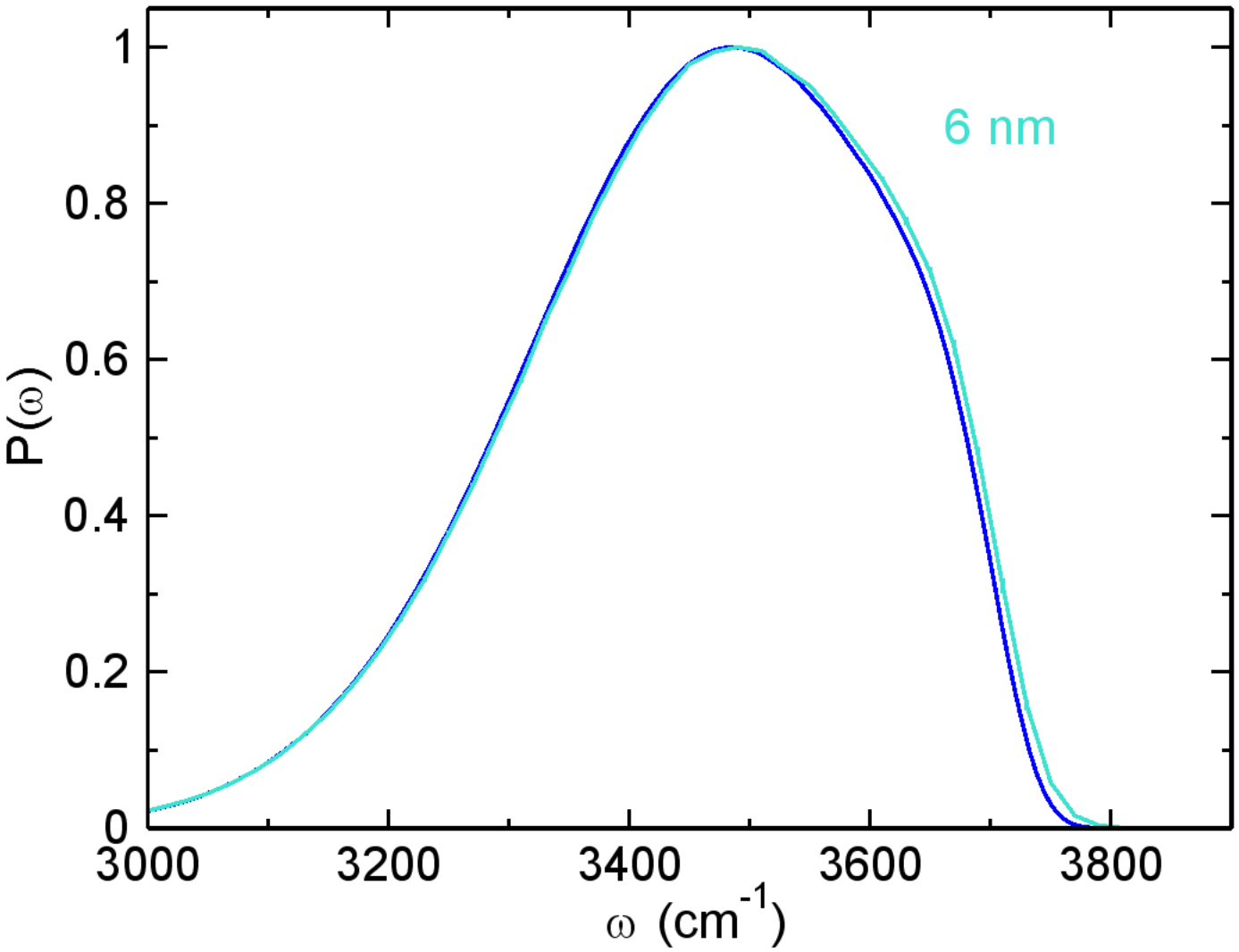


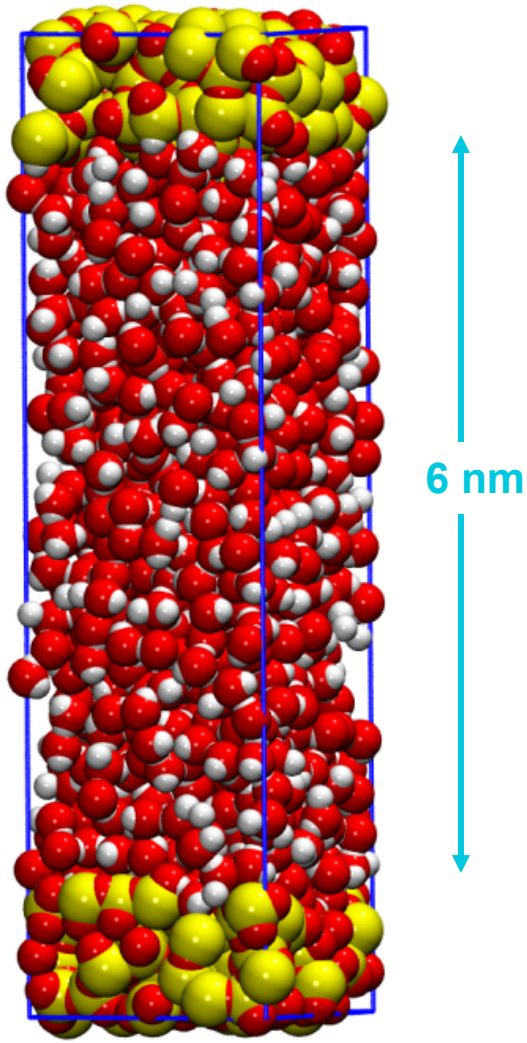
Effect of pore width on frequency distribution



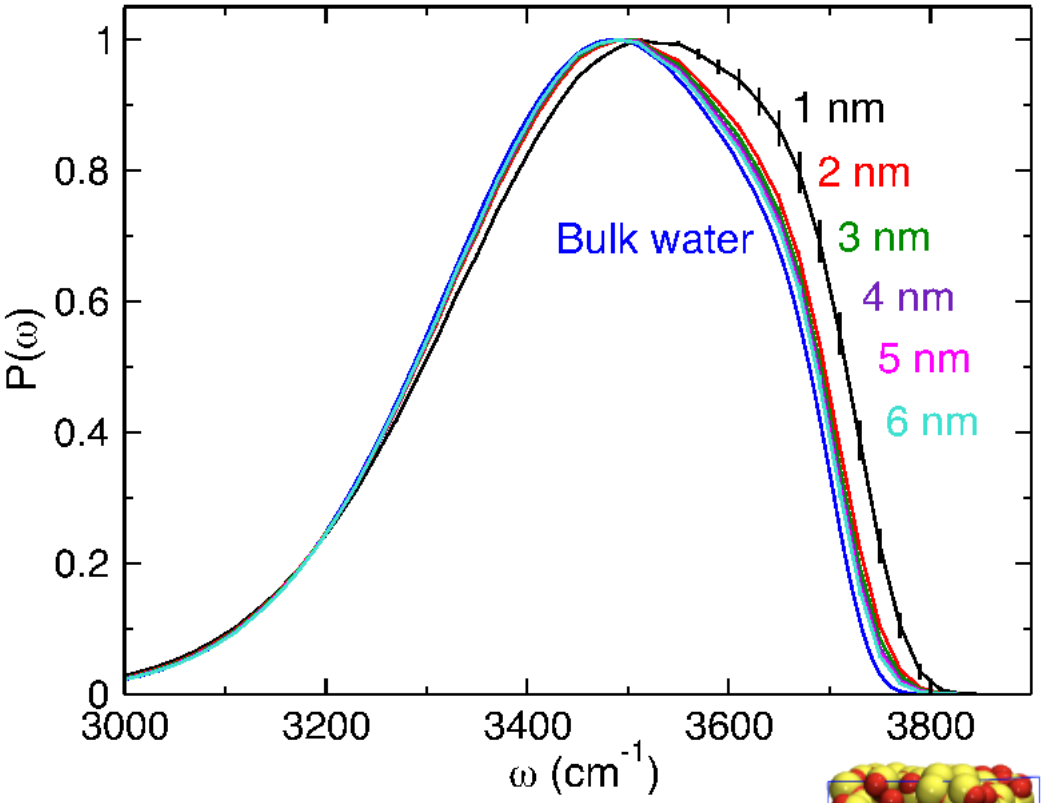


Effect of pore width on frequency distribution





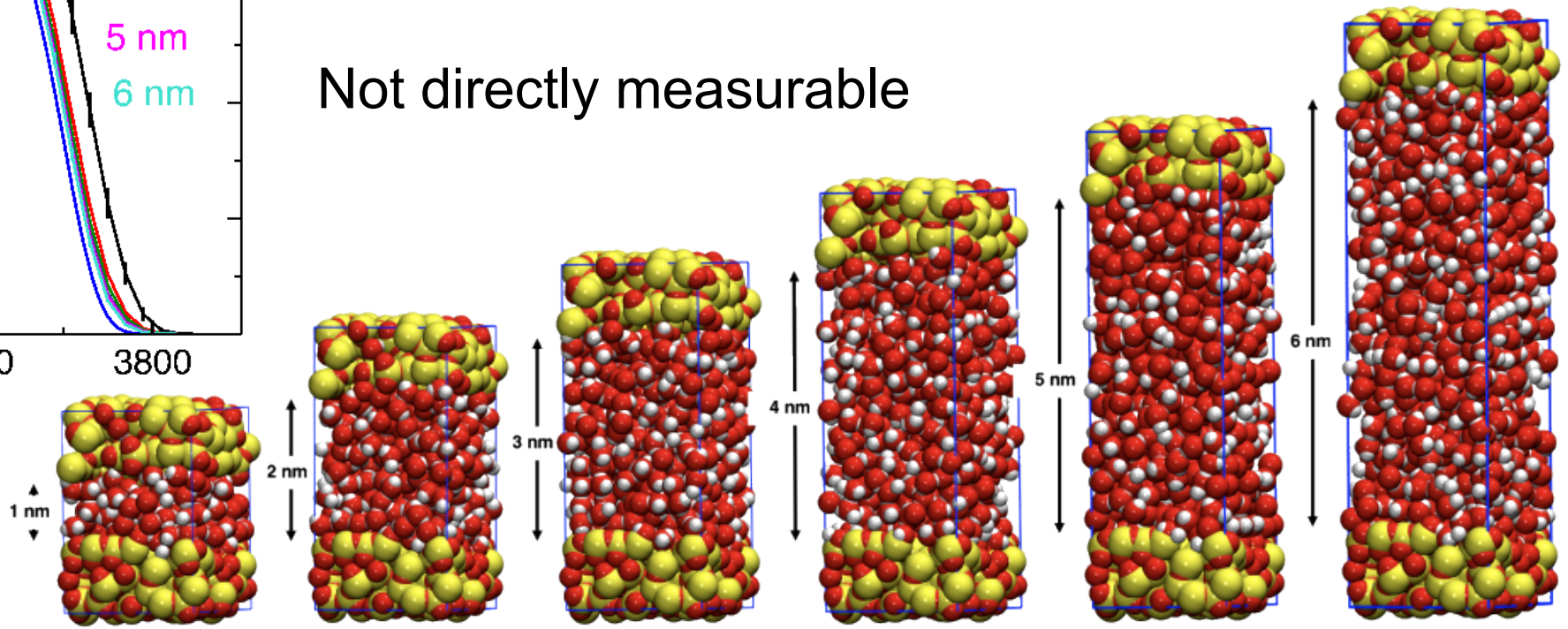
Effect of pore width on frequency distribution



The distribution shift towards bulk water when increasing the pore width.

The effects are small except for the 1 nm pore.

Not directly measurable



Senanayake *et al., J. Chem. Phys.* **154**, 104503 (2021)

Calculation of IR lineshapes

$$I(\omega) = \frac{1}{2\pi}\int_{-\infty}^{\infty} e^{-i\omega t}\phi(t)dt$$

$$I_{IR}(\omega) \longrightarrow \phi_{\mu}(t)$$

Dipole-dipole response function

$$\phi_{\mu}(t) = e^{-|t|/2T1}\left\langle \vec{\mu}_{01}(0).\vec{\mu}_{01}(t)e^{i\int_0^t \omega(\tau)d\tau}\right\rangle$$

Vibrational lifetime (700 fs)

Transition dipole vector

Transition frequency

Skinner *et al.*, *J. Chem. Phys.* **120**, 8107 (2004)

Calculation of Raman lineshapes

$$I(\omega) = \frac{1}{2\pi}\int_{-\infty}^{\infty} e^{-i\omega t}\phi(t)dt$$

$$I_{Raman}(\omega) \longrightarrow \phi_\alpha(t)$$

Polarizability response function

$$\phi_\alpha(t) = e^{-|t|/2T1}\left\langle \vec{\alpha}_{01}(0).\vec{\alpha}_{01}(t)e^{i\int_0^t \omega(\tau)d\tau}\right\rangle$$

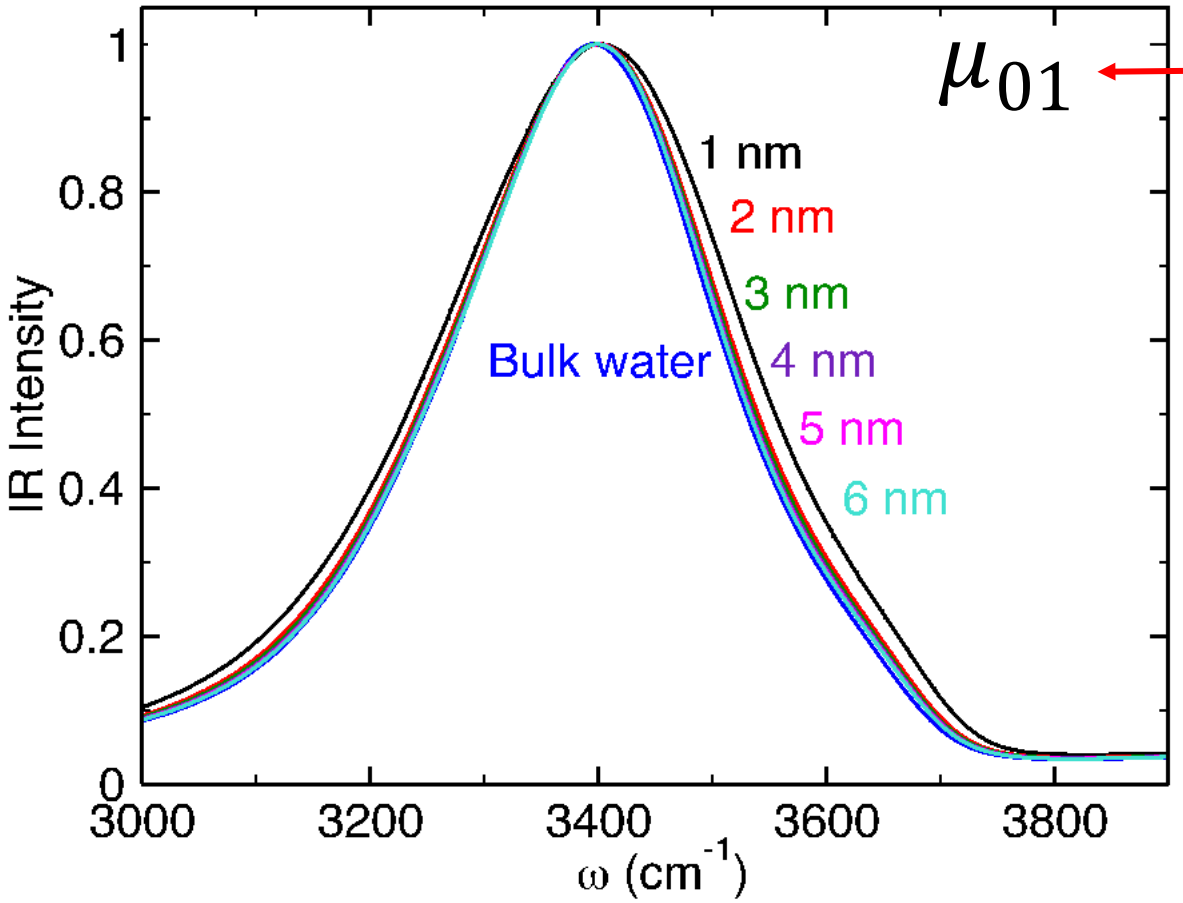
Vibrational lifetime (700 fs)

Transition polarizability

Transition frequency

Skinner et al.,*J. Chem. Phys*. **120**, 8107 (2004)

Effect of pore width on IR spectra



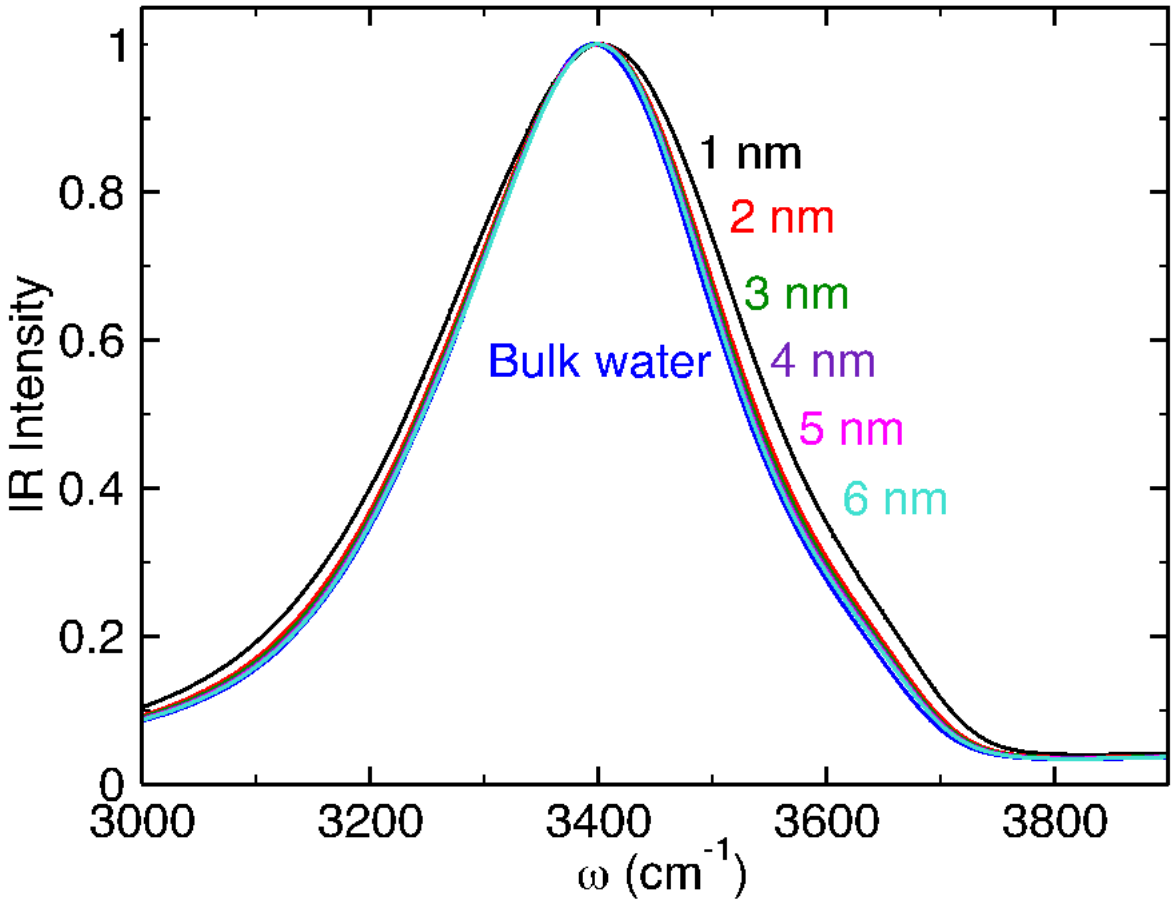
non-Condon effect

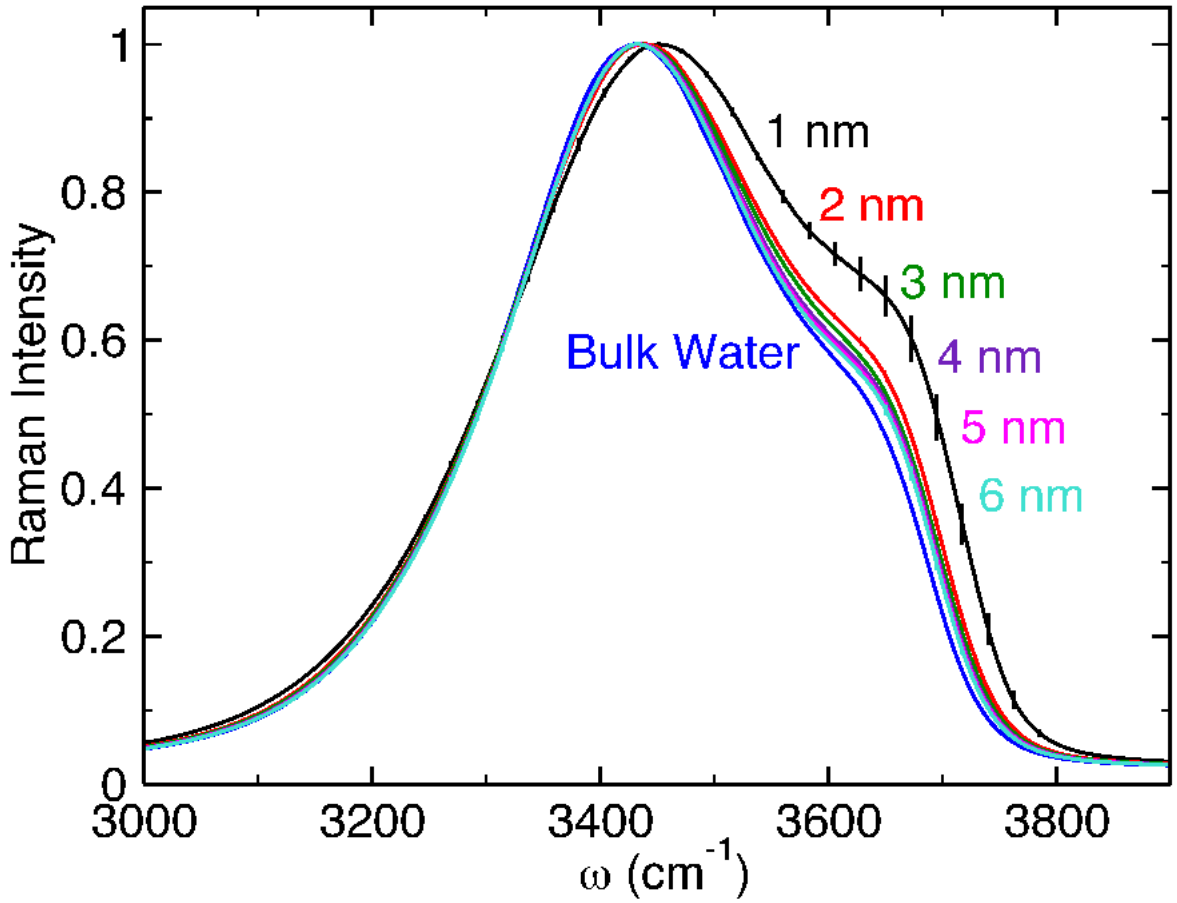
Sensitive to different environments of the OH bond

Makes the transition dipole moment smaller for weaker H-bonded OH groups

Senanayake *et al., J. Chem. Phys.* **154**, 104503 (2021)

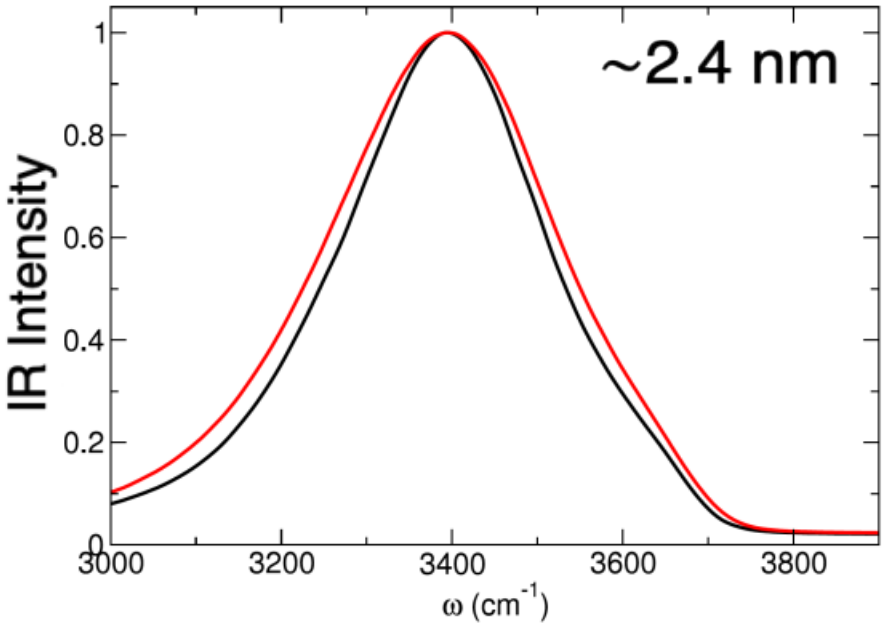
Effect of pore width on IR and Raman spectra

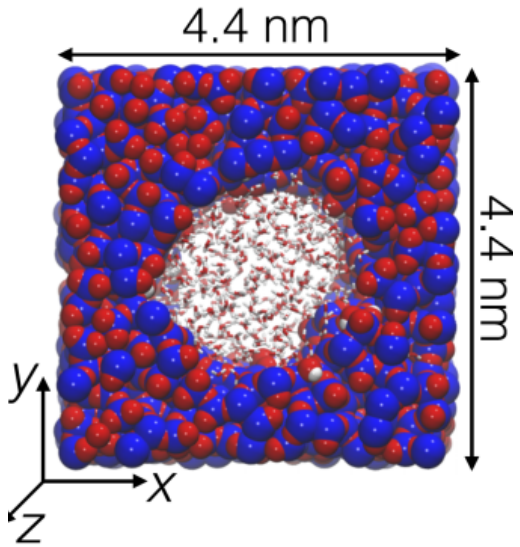


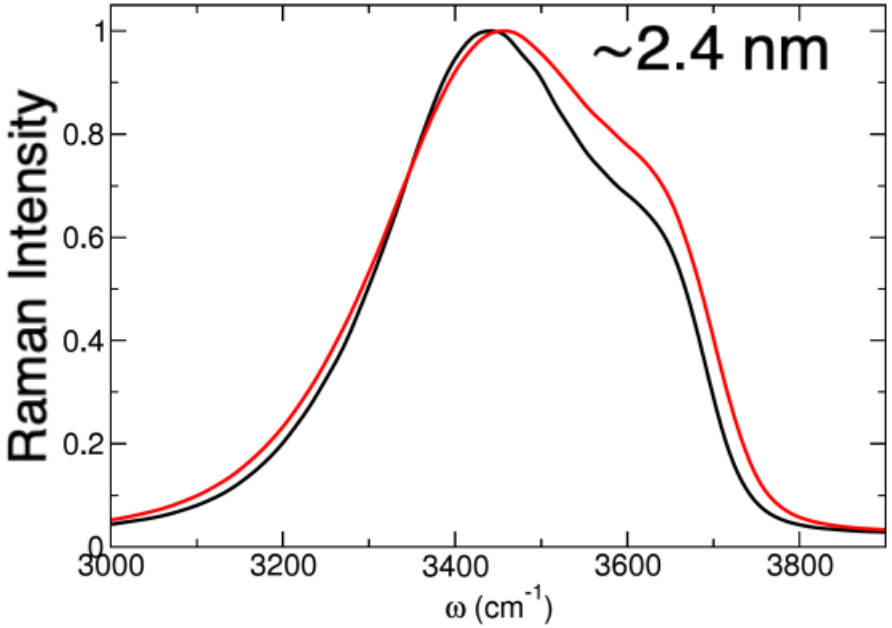


Senanayake *et al., J. Chem. Phys.* **154**, 104503 (2021)

Comparison with cylindrical pores





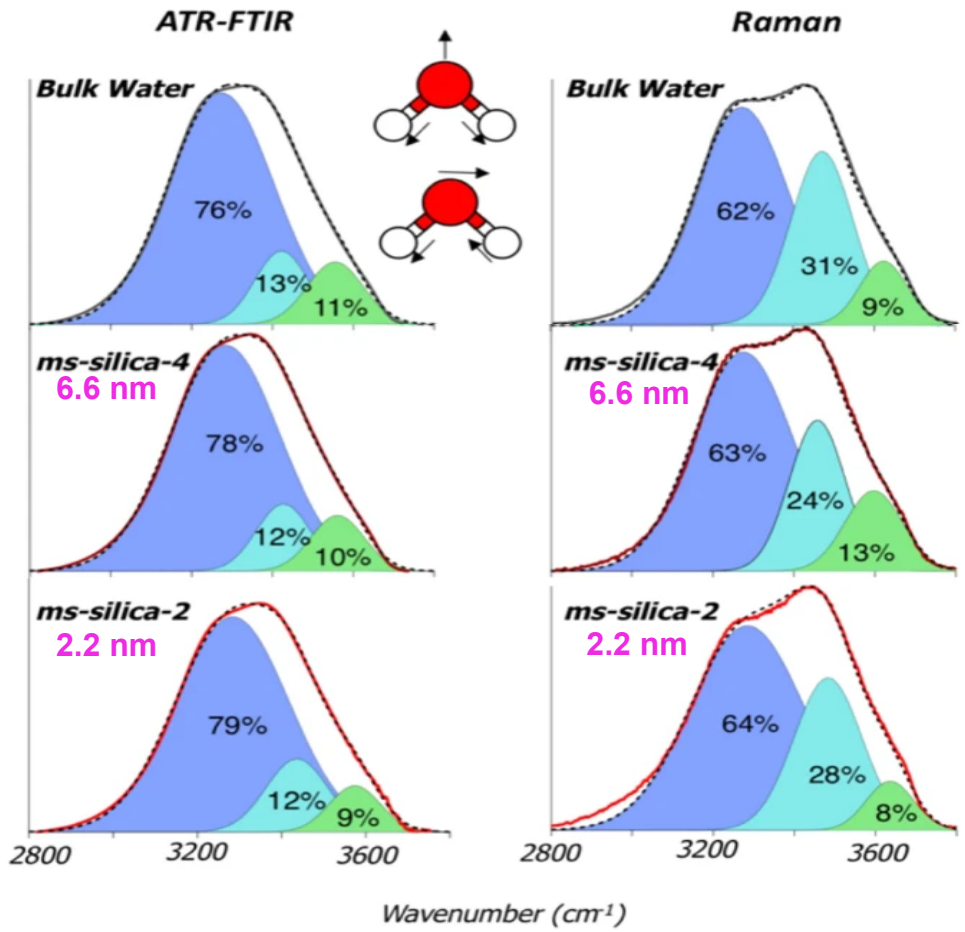


Simulated linear IR spectrum of the OH fundamental for bulk water (black) and water confined in a ~2.4 nm hydrophilic silica pore (red)

Simulated Raman spectrum of the OH fundamental for bulk water (black) and water confined in a ~2.4 nm hydrophilic silica pore (red)

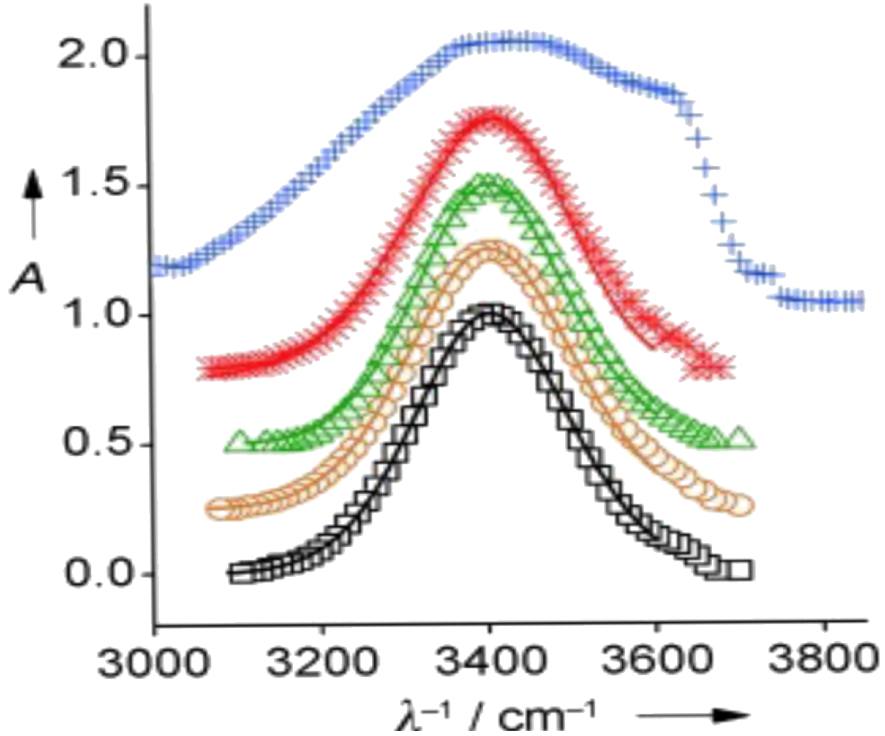
Burris *et al., J. Chem. Phys.* **144,** 194709 (2016)

Comparison with experimental spectra



ATR-FTIR and Raman spectra showing the O-H stretching band of free bulk water, *ms*-silica-4, and *ms*-silica-2

Knight *et al., Sci Rep* **9,** 8246 (2019)

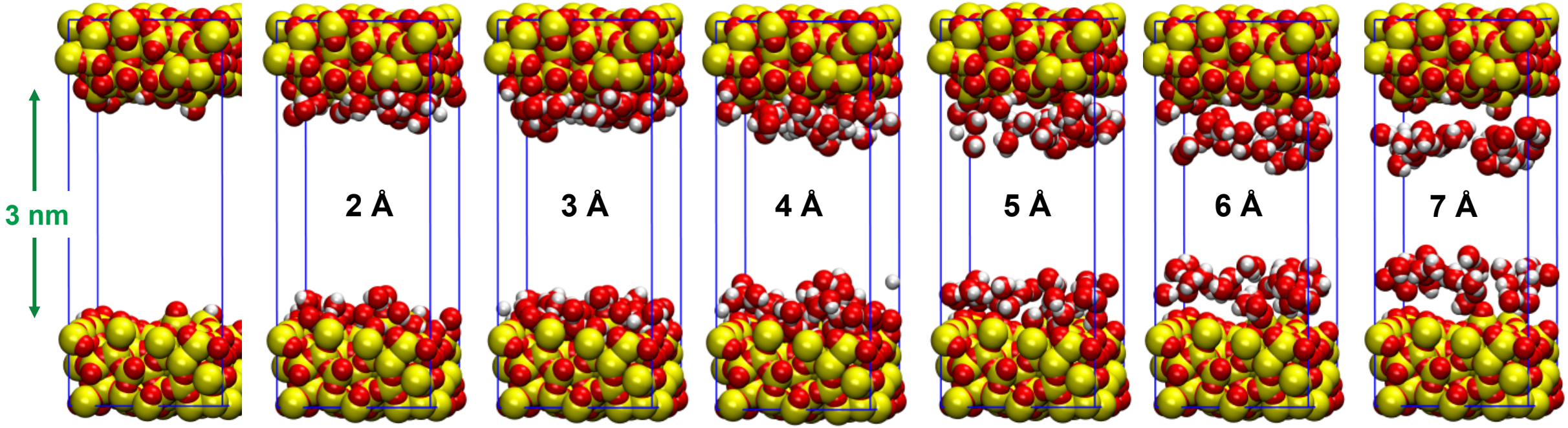


IR spectra of H2O in bulk water (red), partially hydrated 1 nm diameter (blue) and fully hydrated hydrophilic 50 nm (green), 13 nm (brown), and 1 nm (black) diameter silica pores.

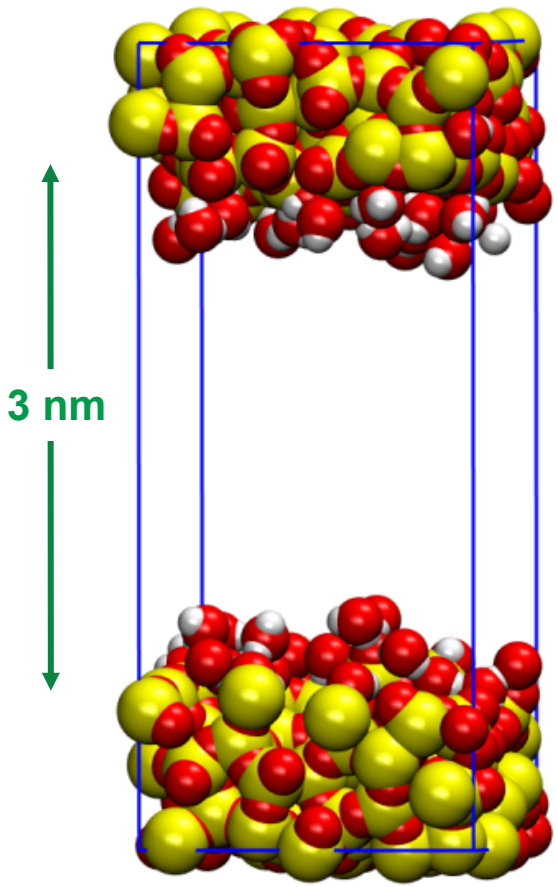
Musat *et al.*, *Angew. Chem., Int. Ed.* **47**, 8033–8035 (2008)

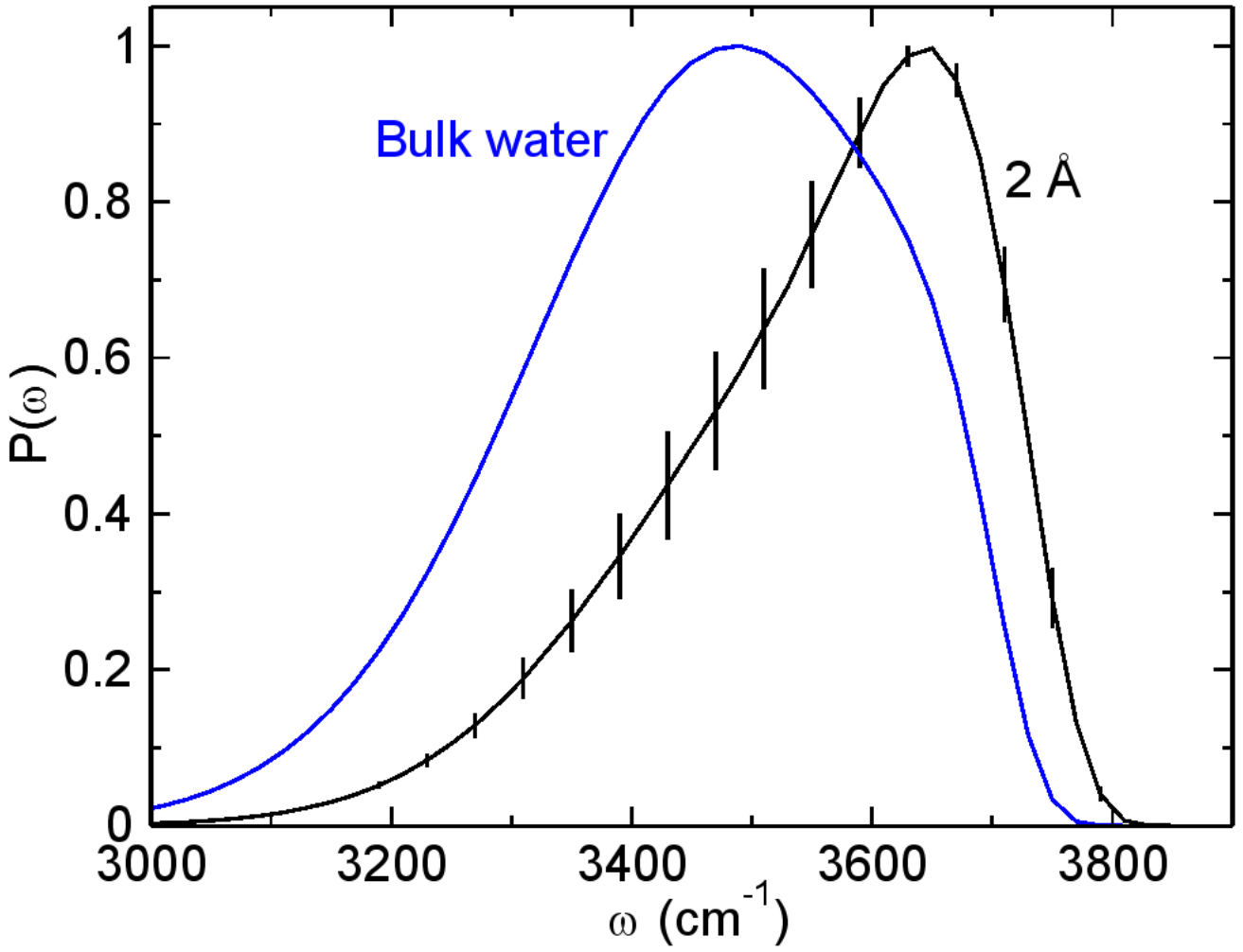
Effect of distance from the silica surface

The distributions can be decomposed depending on the distance from the OH to the nearest pore oxygen atom



Distance dependent frequency distribution

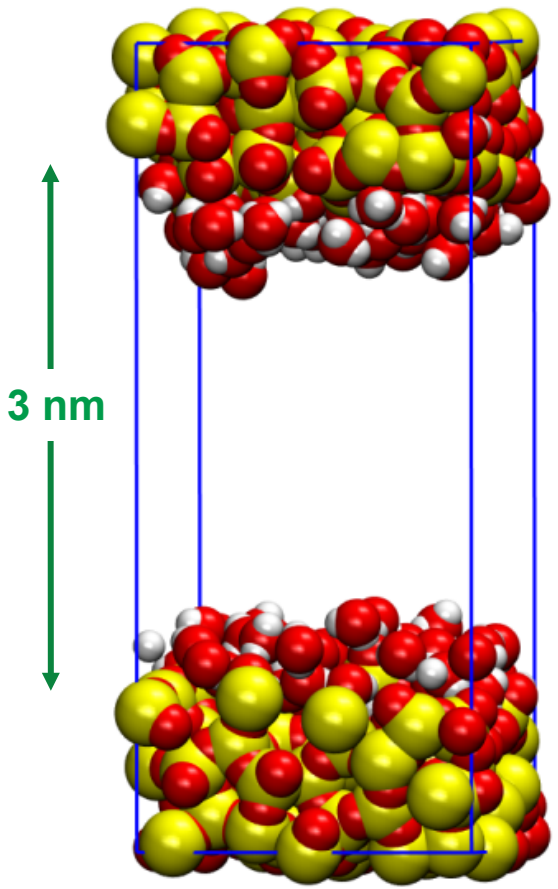


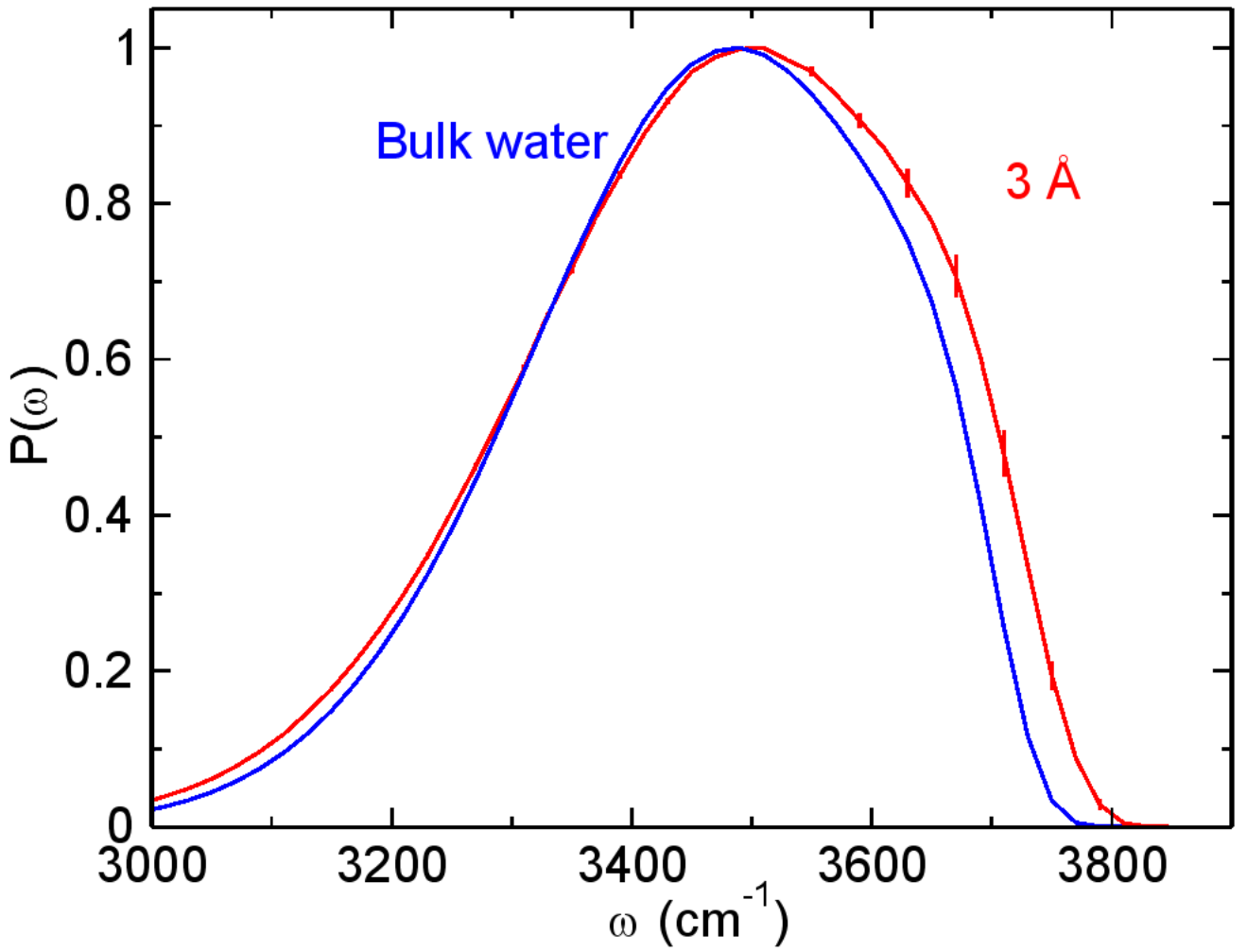


A prominent blue shift relative to bulk water.

weaker H-bonds formed with the surface oxygen atoms

Distance dependent frequency distribution

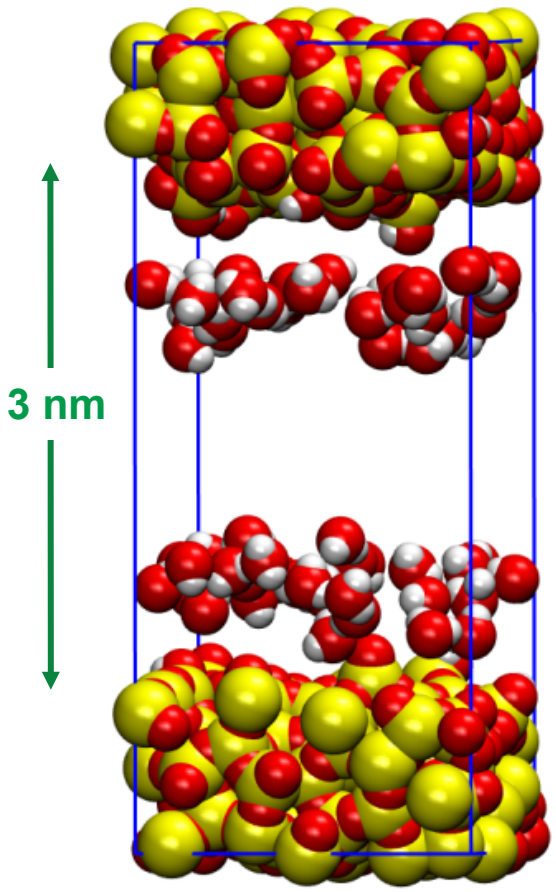


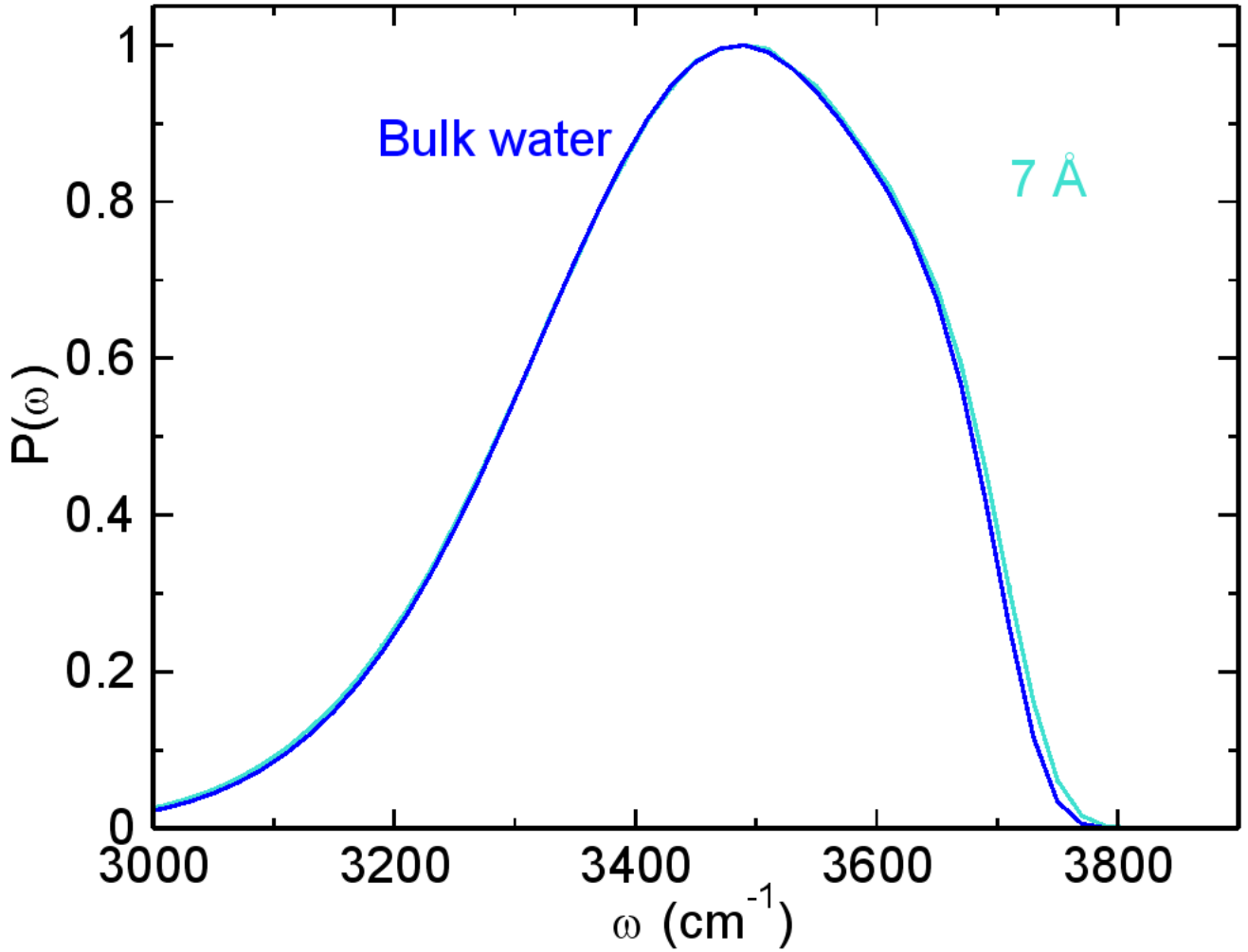


A slight blue shift relative to bulk water.

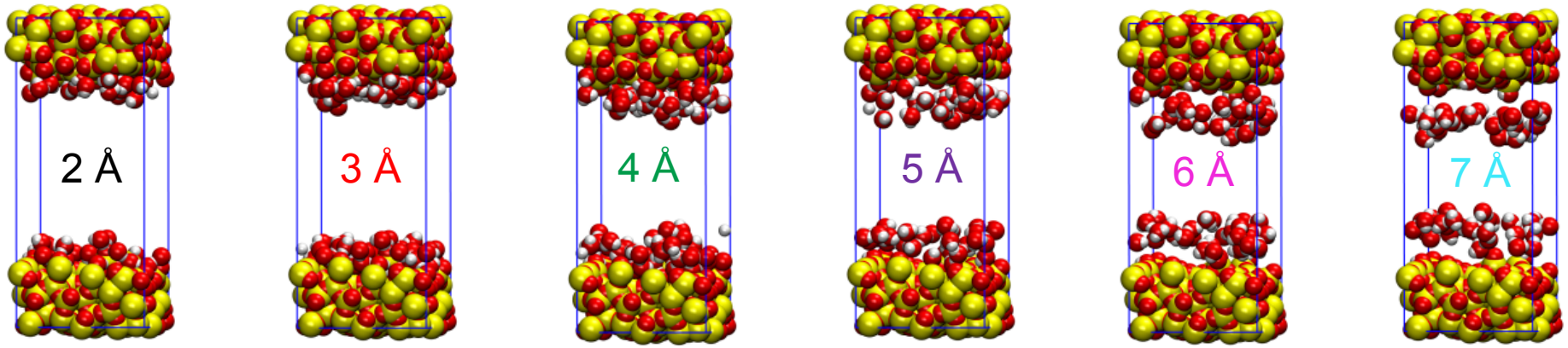
This is due to weaker H-bonds formed with the surface oxygen atoms

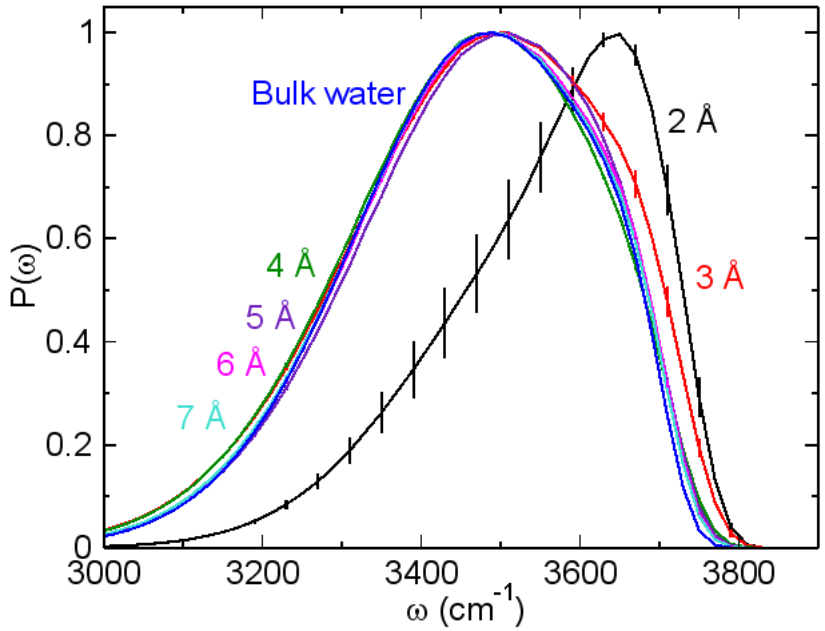
Distance dependent frequency distribution





Distance dependent frequency distribution

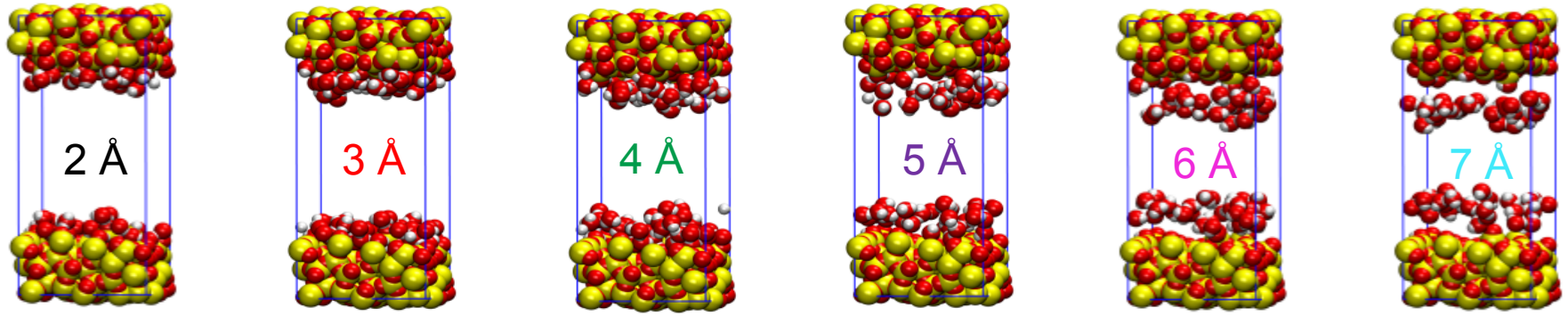


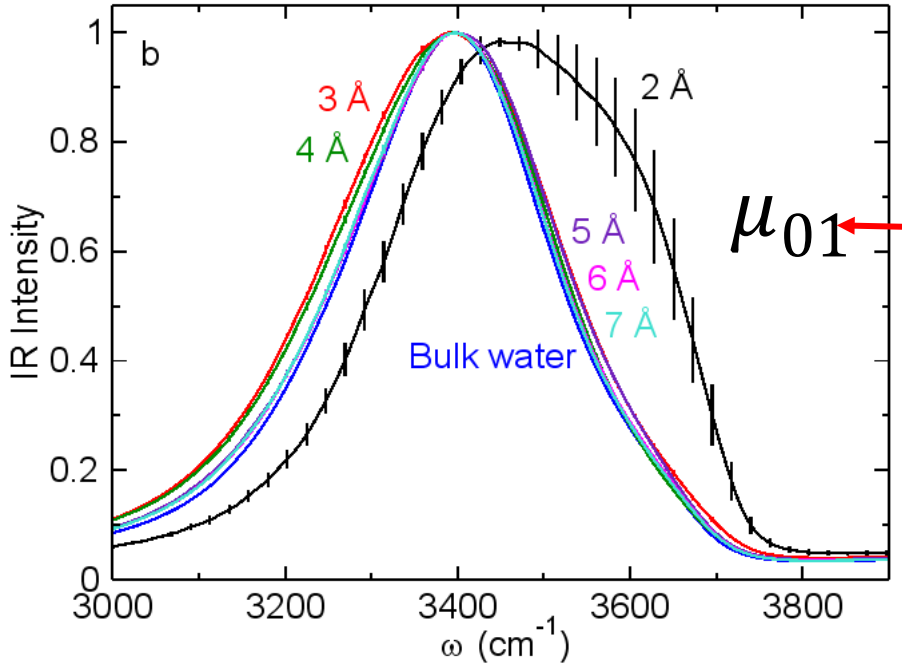


Blue-shifted relative to bulk water due to surface effects

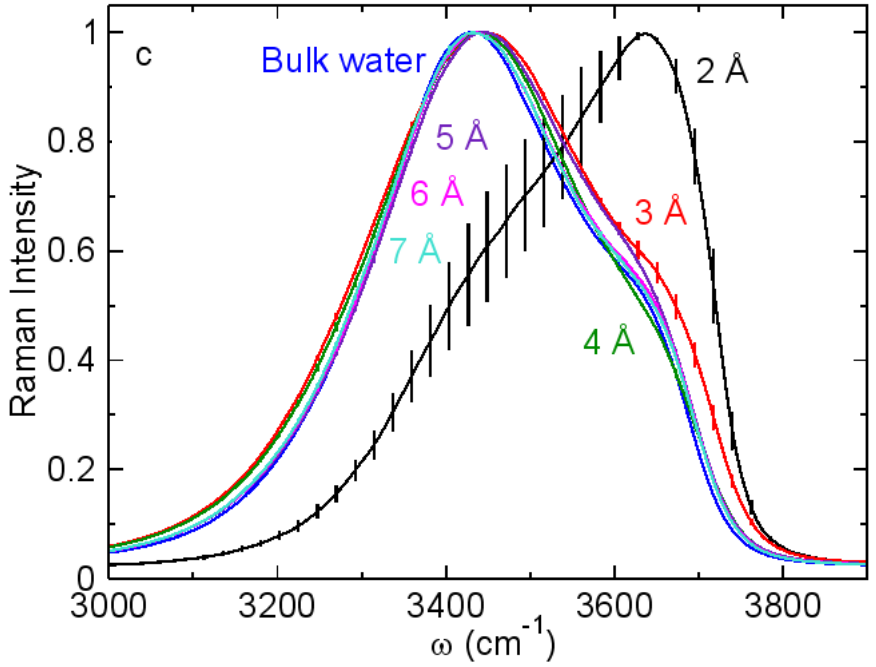
Senanayake *et al., J. Chem. Phys.* **154**, 104503 (2021)

Distance dependent IR and Raman spectra





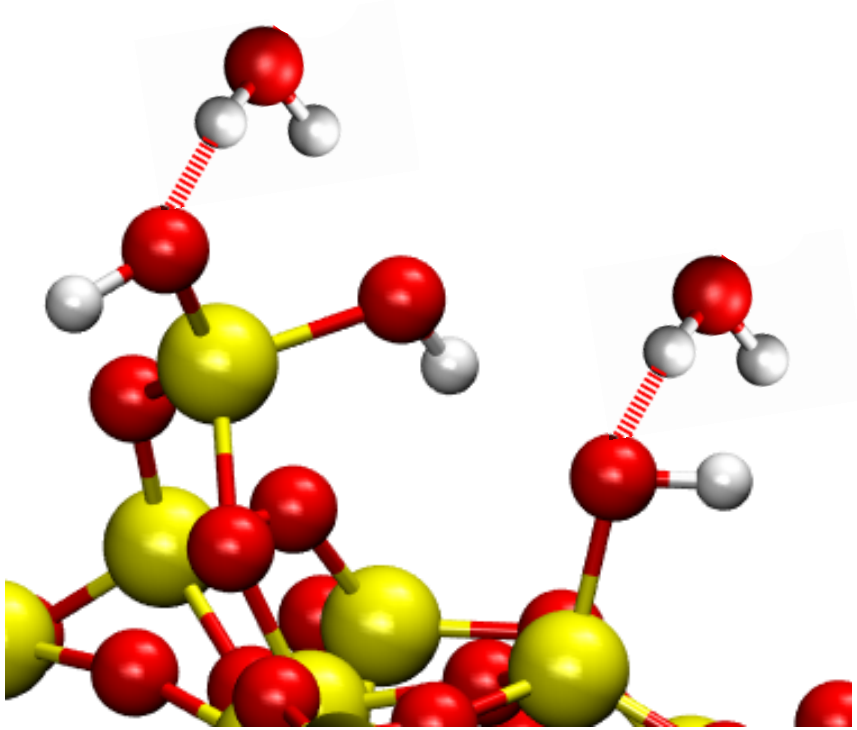
μ_{01} ← **non-Condon effect**



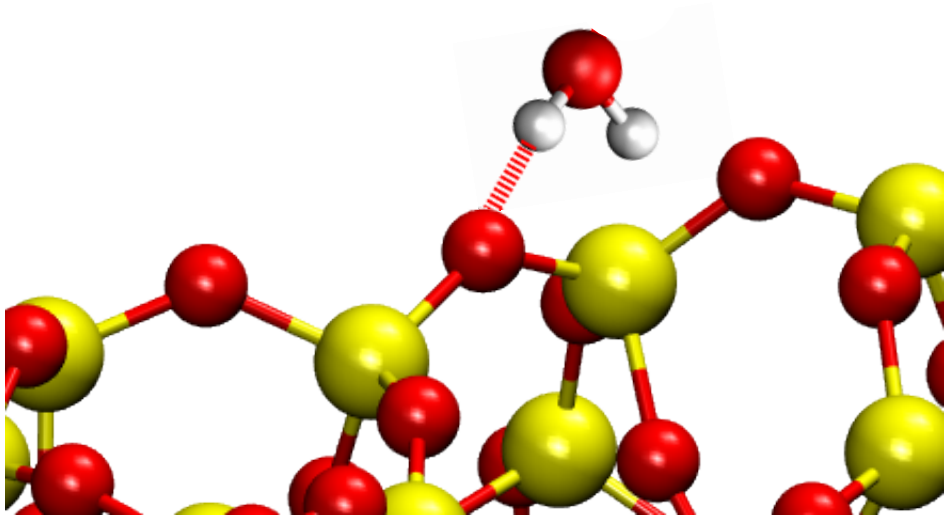
Senanayake *et al., J. Chem. Phys.* **154**, 104503 (2021)

H-bond acceptor based lineshapes

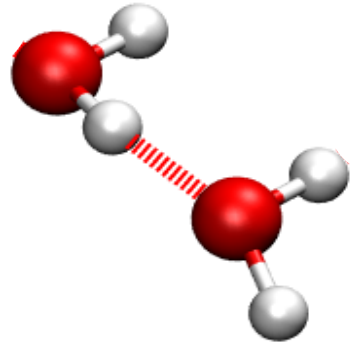
Silanol Oxygen



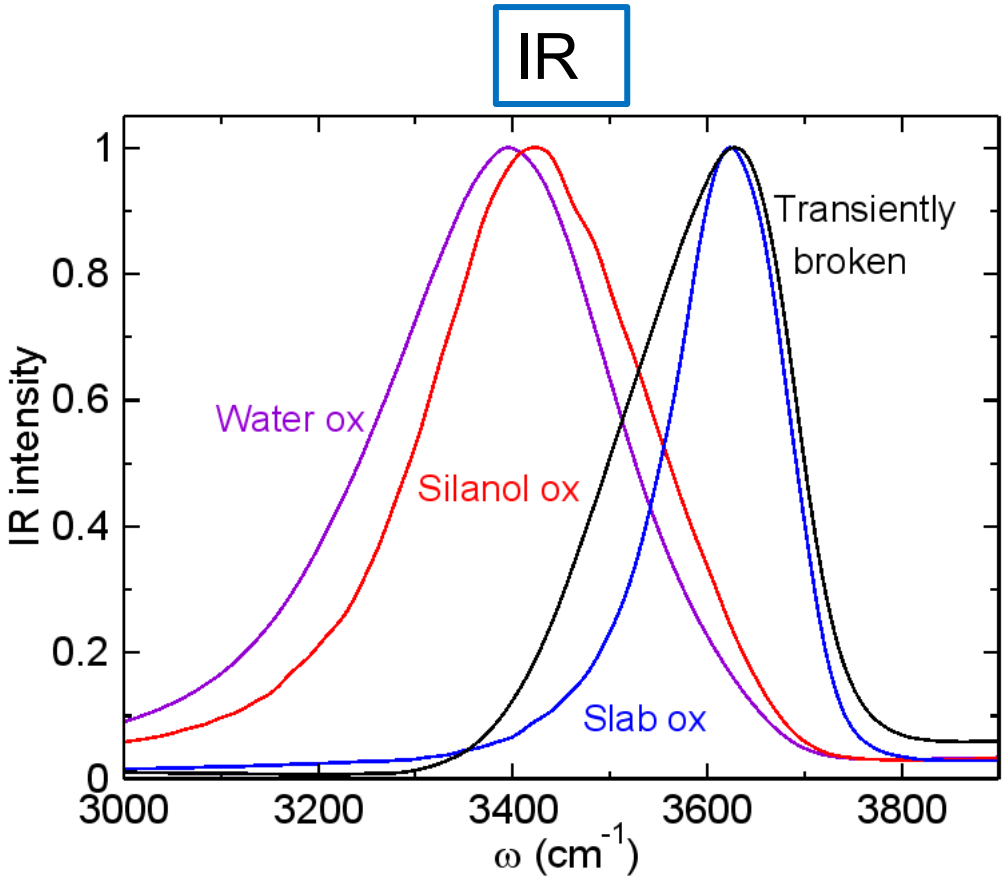
Slab Oxygen

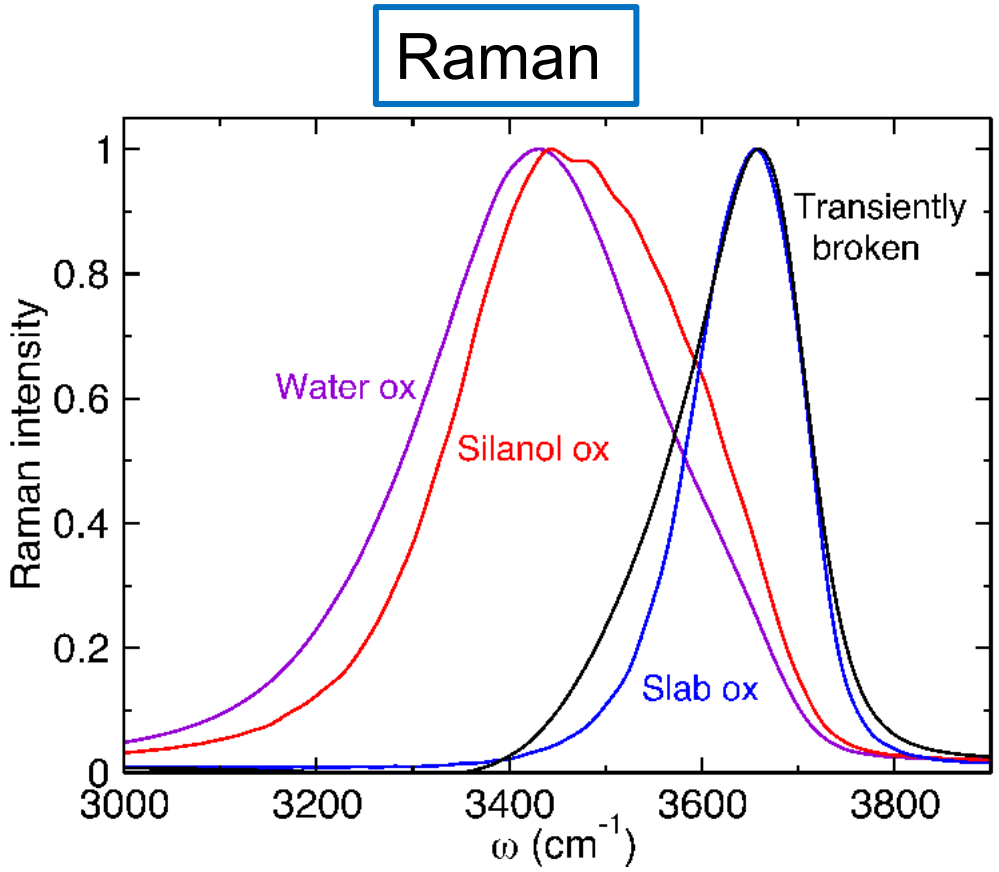


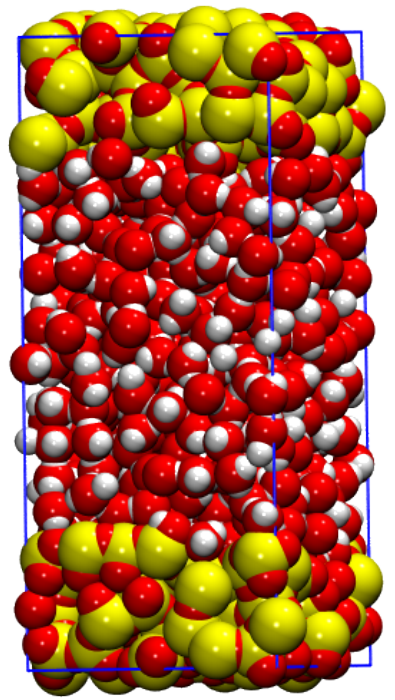
Water Oxygen



H-bond acceptor based lineshapes



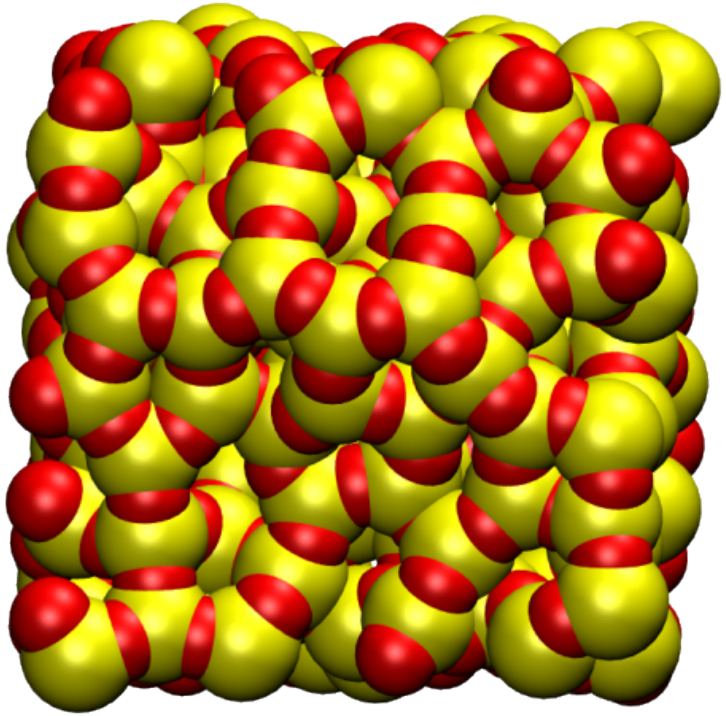




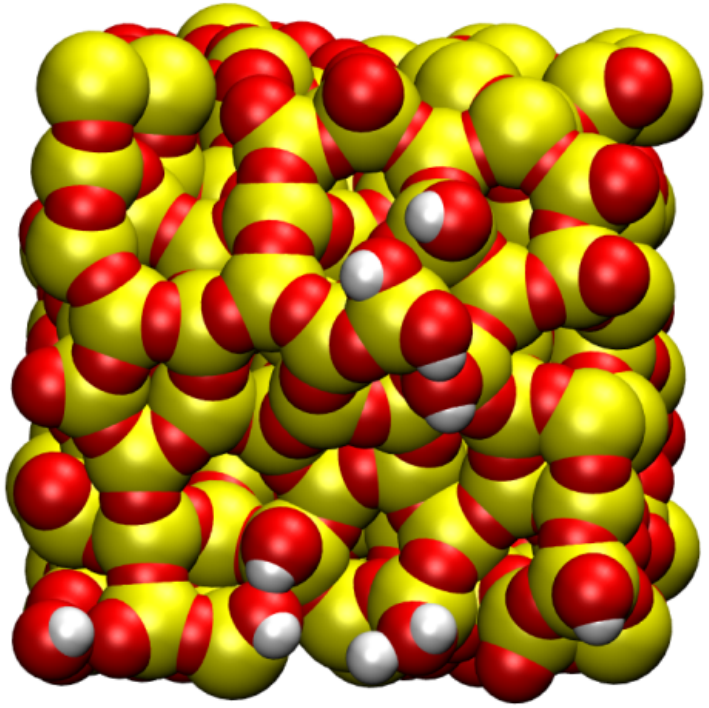
Senanayake *et al., J. Chem. Phys.* **154**, 104503 (2021)

Effect of hydroxyl density

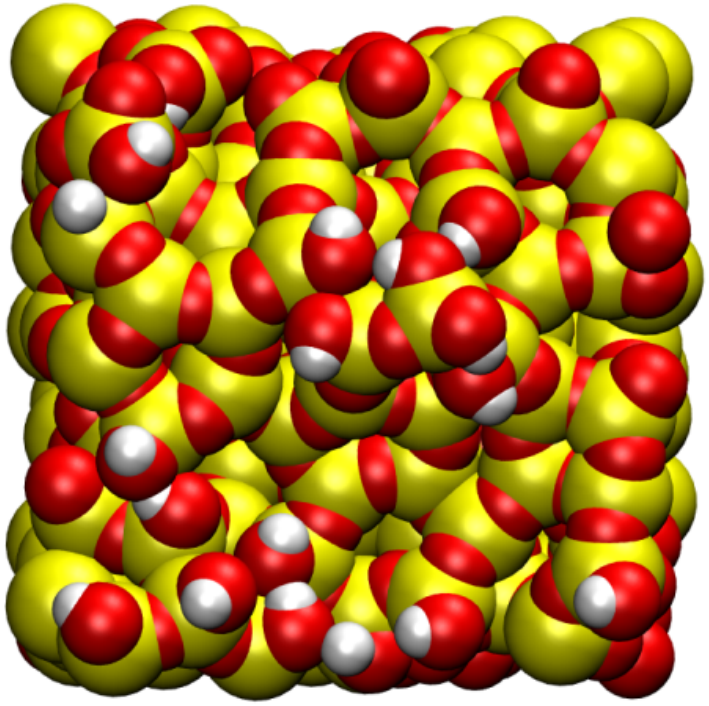
Slabs were generated by functionalizing the most strained Si-O bonds on the surface.



No hydroxyls

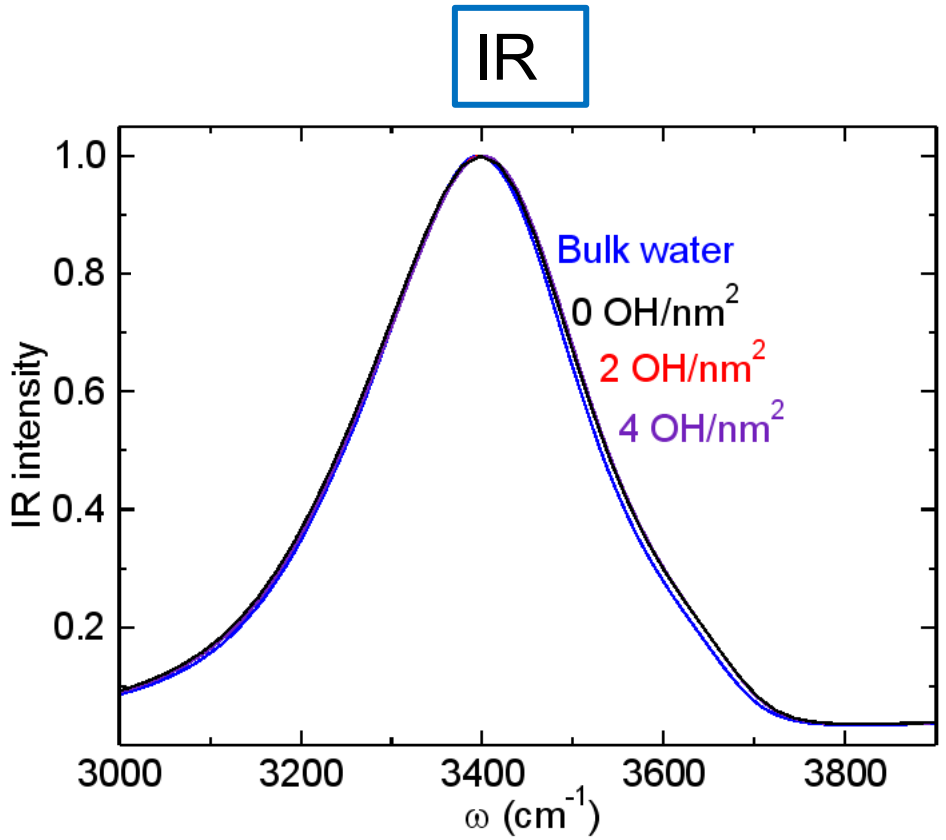


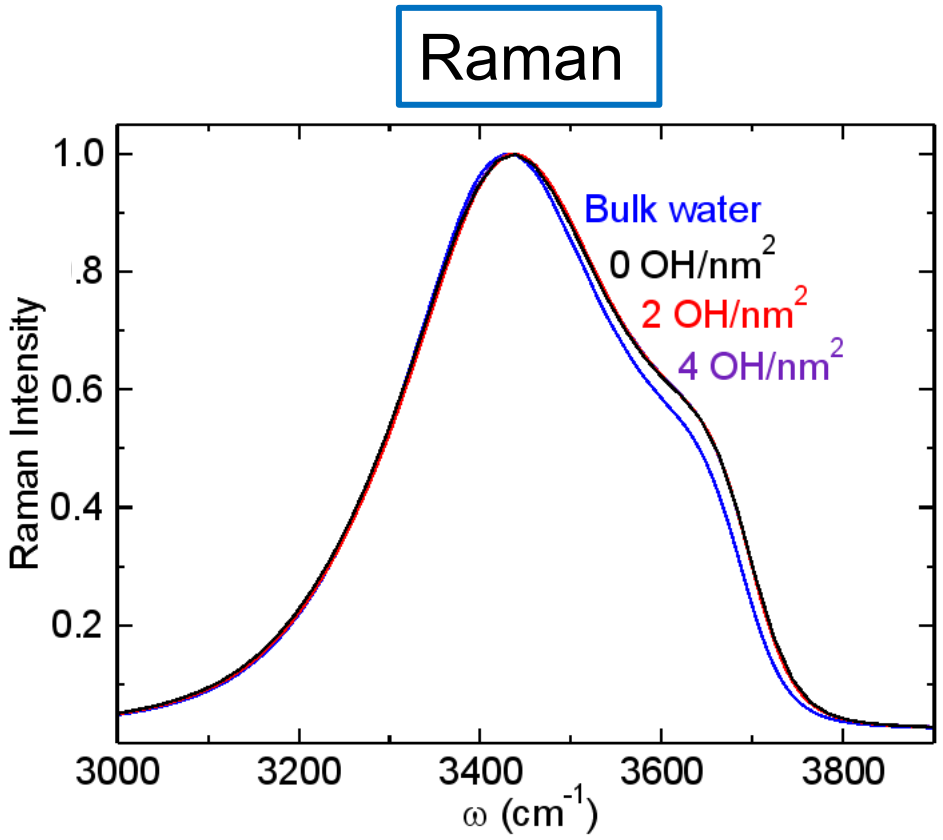
2 hydroxyls /nm^2

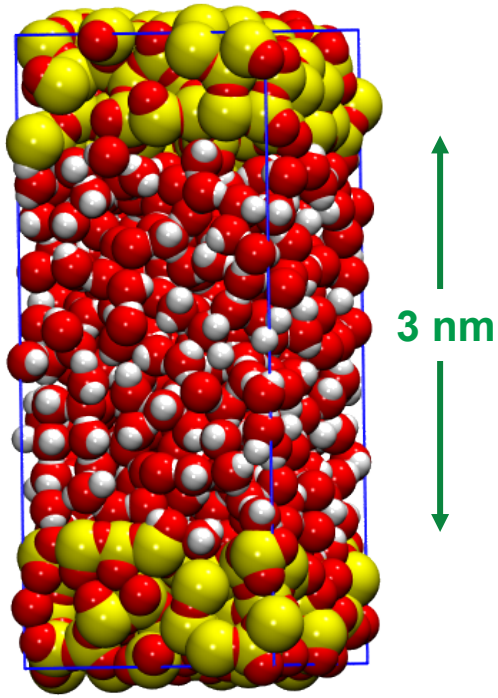


4 hydroxyls /nm^2

Effect of hydroxyl density







No visible effect of hydroxyl density. Because majority is bulk water

Senanayake *et al., J. Chem. Phys.* **154**, 104503 (2021)

Conclusions

The primary effect of confinement - blueshift in the frequency due to weak H-bonding with the silica surface

Raman spectroscopy is more sensitive to the confinement effects compared to IR

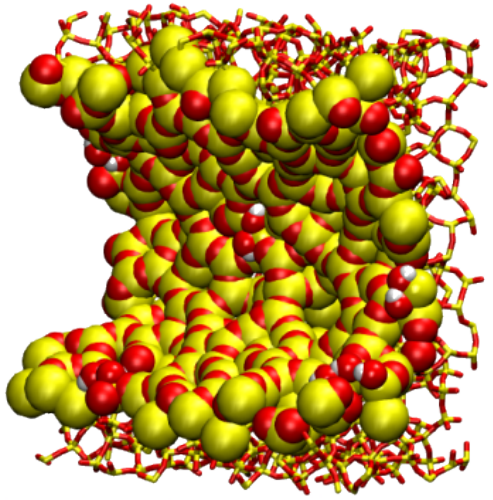
No visible effect of OH density in IR or Raman spectra

Future work

Explore the effects of :

- Salt solutions
- Charged surfaces
- Temperature
- Curvature of the pore

on the IR and Raman spectra



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Acknowledgments

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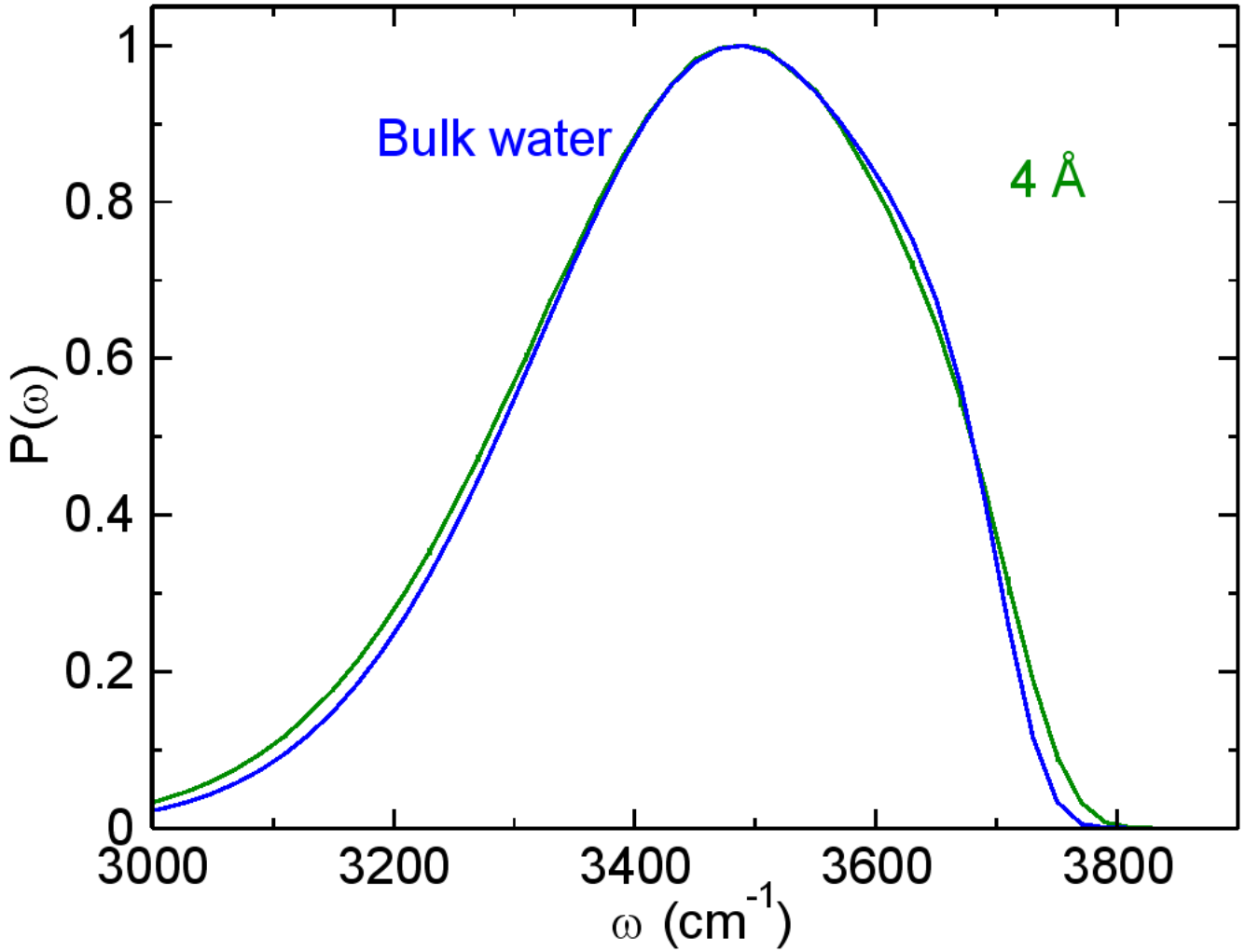
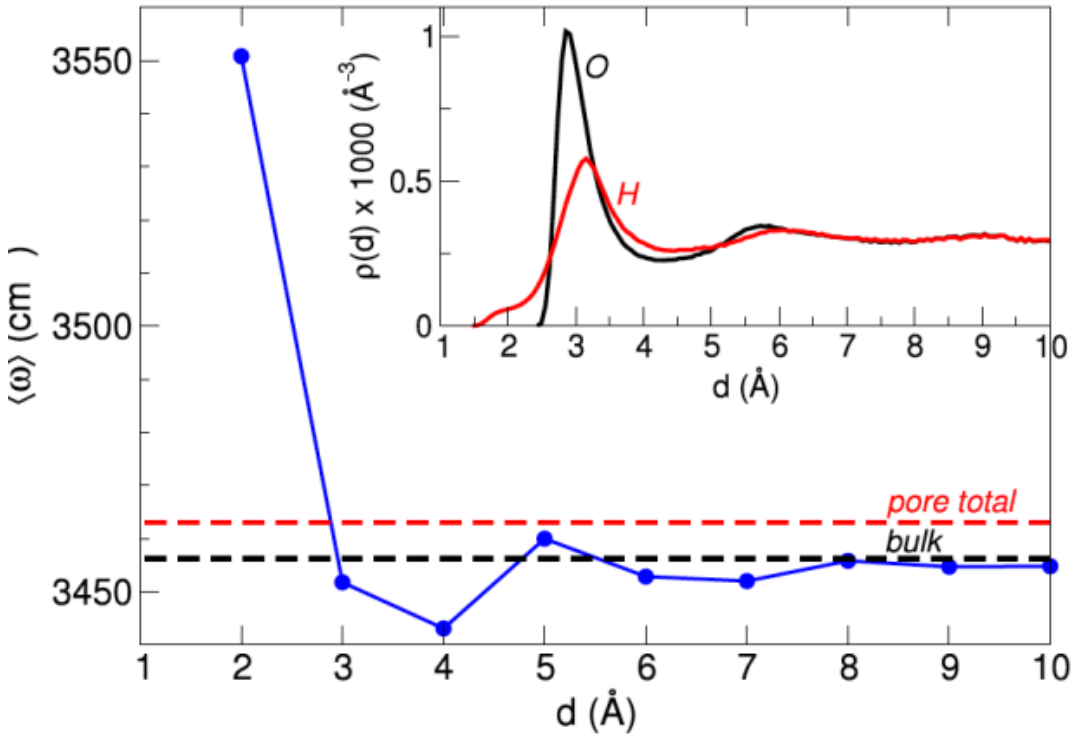


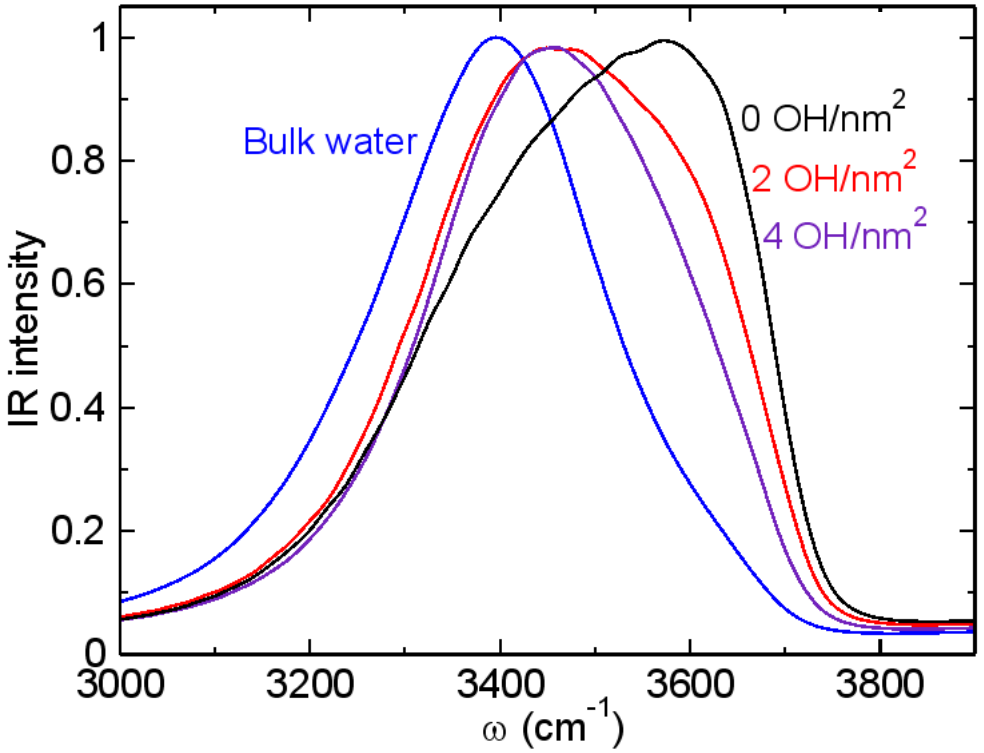


Atomic densities as a function of d for water oxygen (O) and hydrogen (H) atoms

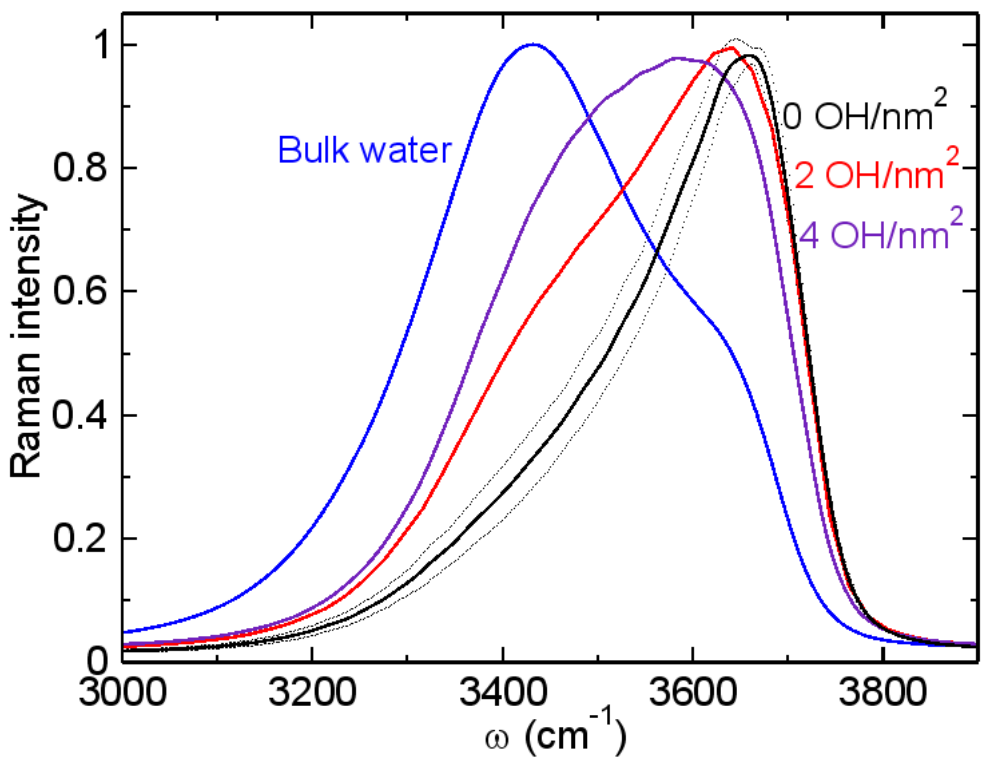
P. C. Burris, D. Laage, W. H. Thompson, J. Chem. Phys. 144, 194709 (2016)

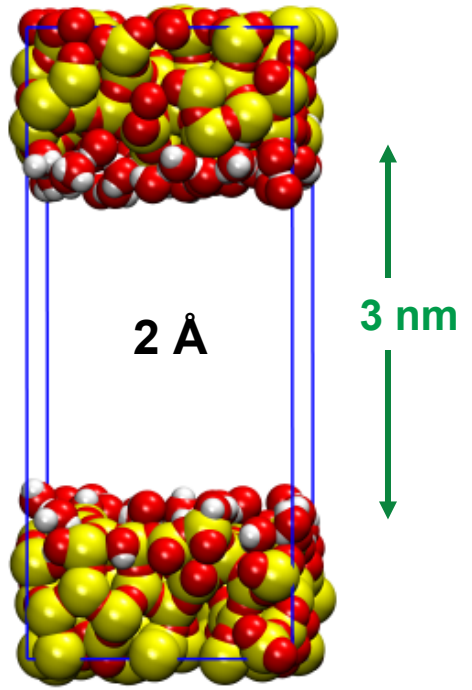
Effect of hydroxyl density on surface water

IR



Raman

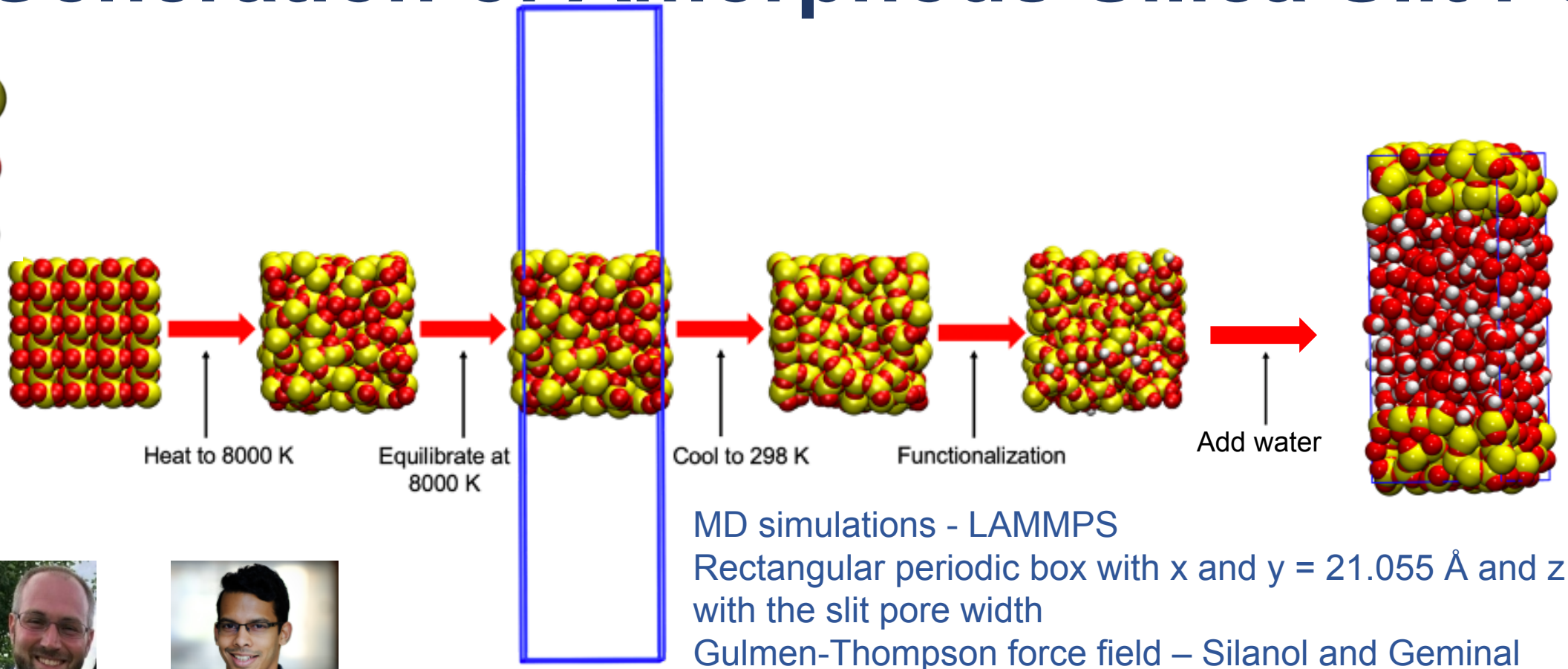




Effect of hydroxyl density on the 2 Å lineshape is investigated.

With the increase in hydroxyl density the lineshape shifts towards bulk water

Generation of Amorphous Silica Slit Pores



MD simulations - LAMMPS
Rectangular periodic box with x and y = 21.055 Å and z varying with the slit pore width
Gulmen-Thompson force field – Silanol and Geminal interactions


Dr. Jacob Harvey

Dr. Pubudu Wimalasiri

Calculation of vibrational frequencies

HOD in D_2O – For simplified spectra

Empirical (or Electrostatic) mapping

B. Auer, R. Kumar, J. R. Schmidt, and J. L. Skinner, *Proc. Natl. Acad. Sci* **104**, 14215 (2007).

$$\omega_{01}^{(i)}(t) = 3761.6 - 5060.4\epsilon_i(t) - 86225\epsilon_i^2(t)$$

$\epsilon_i(t)$ is given by ;

$$\epsilon_i(t) = \vec{e}_{OH,i}(t).\vec{\epsilon}_{tot}(r_{H,i}, t)$$

$\vec{\epsilon}_{tot}(r_{H,i}, t)$ - total electric field

$\vec{e}_{OH,i}(t)$ - unit vector pointing towards H