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Probing electrolyte–silica interactions through simulations of the infrared spectroscopy of nanoscale pores

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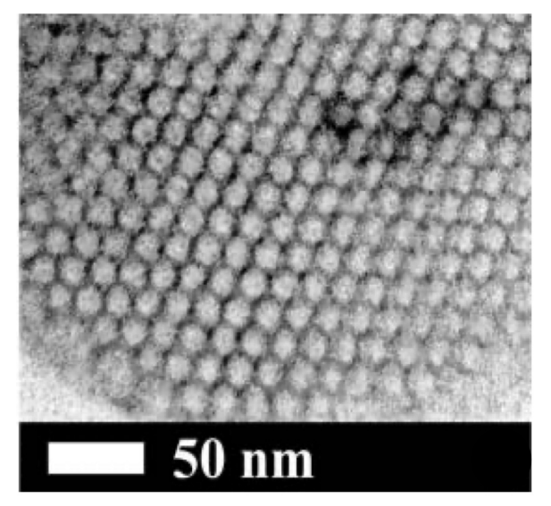
Why study electrolytes in mesoporous silica?

Mesoporous silica - synthetic analogs to look at confinement effects in real rocks and minerals.

Electrolyte is confined on nano-scale, strongly modifies the structural and dynamical properties. Our understanding of these confinement effects is significantly incomplete.



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

Advantage of using vibrational spectroscopy

An excellent probe of the local structure and dynamics.

We use classical MD to simulate the spectra.

Why simulations of spectra?

Challenging to interpret spectra

Experimental spectra can not do a site-by site interpretation.

Surface-sensitive spectroscopies can not be applied to porous materials.

Calculating spectra

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

IR lineshape

$$\phi_{IR}(t) = e^{-|t|/2T_1}\left\langle \vec{\mu}_{01}(0)\cdot\vec{\mu}_{01}(t)e^{i}\int_0^t \omega_{01}(\tau)d\tau\right\rangle$$

Dipole-dipole response function

Transition dipole vector

Transition frequency

Depolarized Raman lineshape

$$\phi_{depol}(t) = e^{-|t|/2T_1}\left\langle \vec{\alpha}_{01}(0)\cdot\vec{\alpha}_{01}(t)e^{i}\int_0^t \omega_{01}(\tau)d\tau\right\rangle$$

Polarizability response function

Vibrational lifetime (Expt. 700 fs)

Transition polarizability

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

Temperature derivative

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

$$\boxed{\frac{\partial}{\partial\beta}\phi(t) = -\delta H\phi(t)}$$

$$\beta = \frac{1}{k_BT}$$

$$H(0) - \langle H\rangle = \delta H \leftarrow$$

Fluctuation in the total energy

Predicting the spectrum at different temperatures

$$I_{pred}(\omega;T_b) = \frac{I(\omega;T_a)e^{-(\beta_b-\beta_a)\Delta U(\omega)}}{\int_0^\infty P(\omega;T_a)e^{-(\beta_b-\beta_a)\Delta U(\omega)}d\omega}$$

Vibrational frequency distribution

Effective internal energy

Piskulich *et al.*, *J. Phys. Chem. A* **123** (33), 7185-7194 (2019)

Reorientation dynamics

Can be directly measured using time-resolved pump–probe IR anisotropy

$$C_2(t) = \langle P_2[\vec{e}_{OH}(0)\cdot\vec{e}_{OH}(t)]\rangle$$

Reorientational time correlation function

Second Legendre polynomial

Unit vector along the OH

Laage et al., *J. Phys. Chem. B* **112**, 14230–14242 (2008).

Spectral diffusion

Can be measured from two-dimensional IR (2D-IR) photon echo measurements

$$C_\omega(t) = \frac{\langle\delta\omega_{01}(0)\delta\omega_{01}(t)\rangle}{\langle\delta\omega_{01}^2\rangle}$$

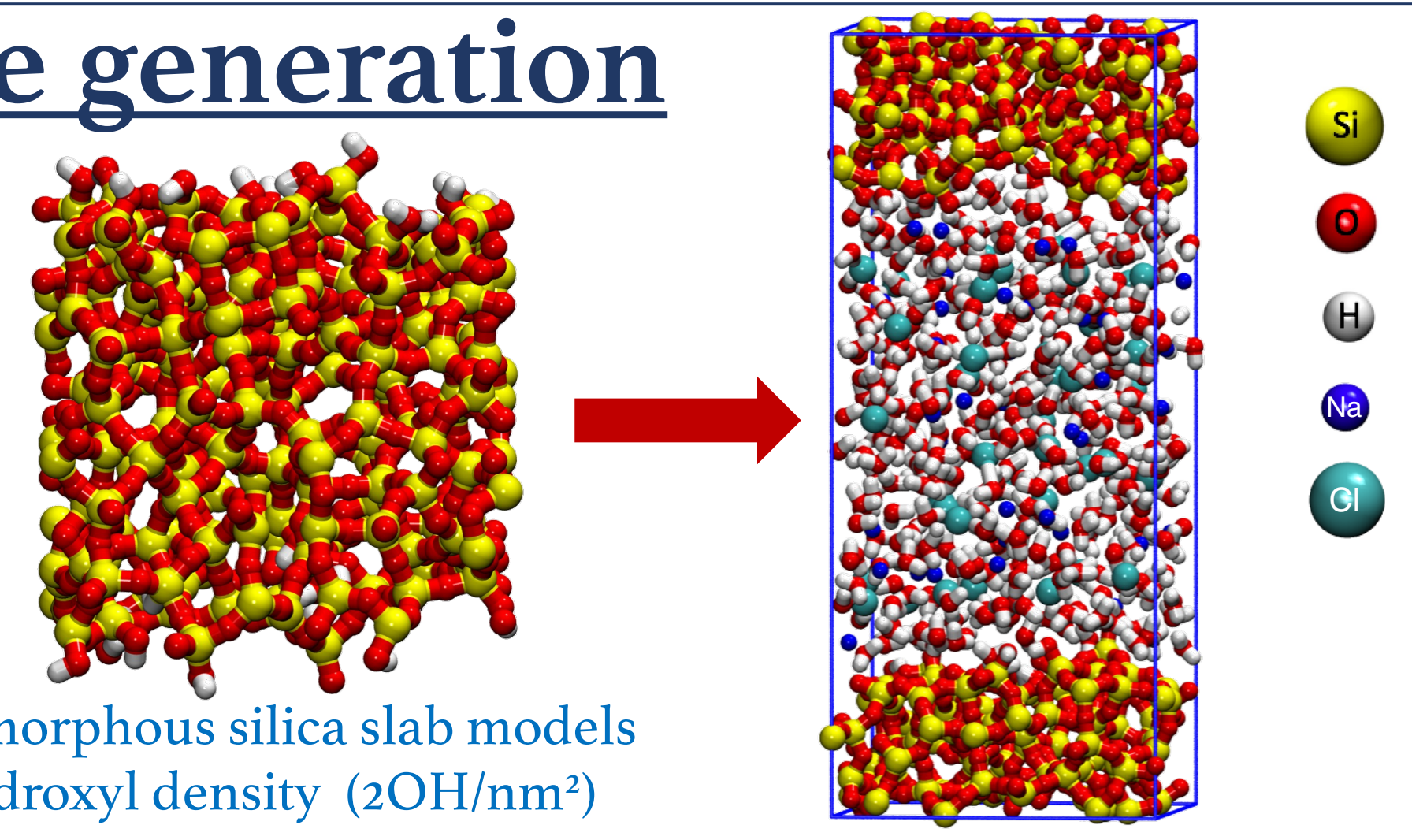
Normalized frequency–frequency time correlation function (FFCF)

$$\delta\omega_{01}(t) = \omega_{01}(t) - \langle\omega_{01}\rangle$$

Piskulich *et al.*, *J. Chem. Phys.* **154**, 064501 (2021)

Slit pore generation

Dr. Pubudu Wimalasiri

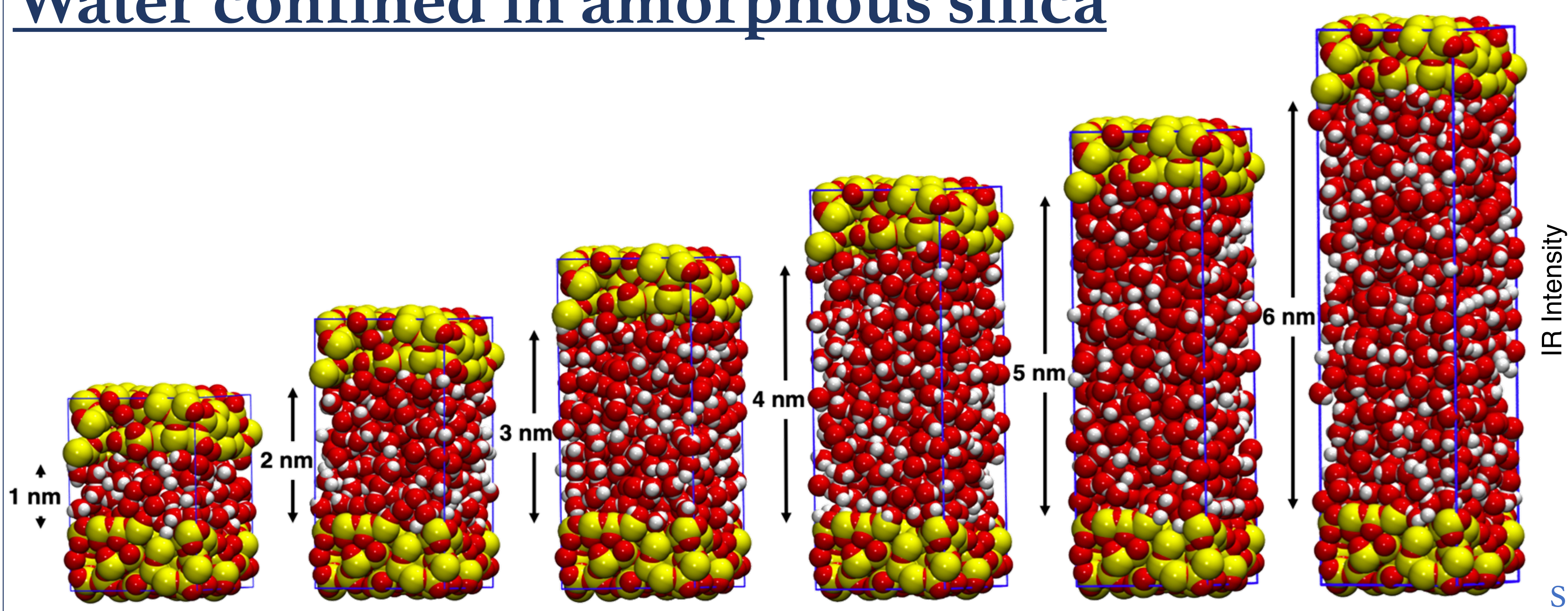


Amorphous silica slab models hydroxyl density (2OH/nm²)

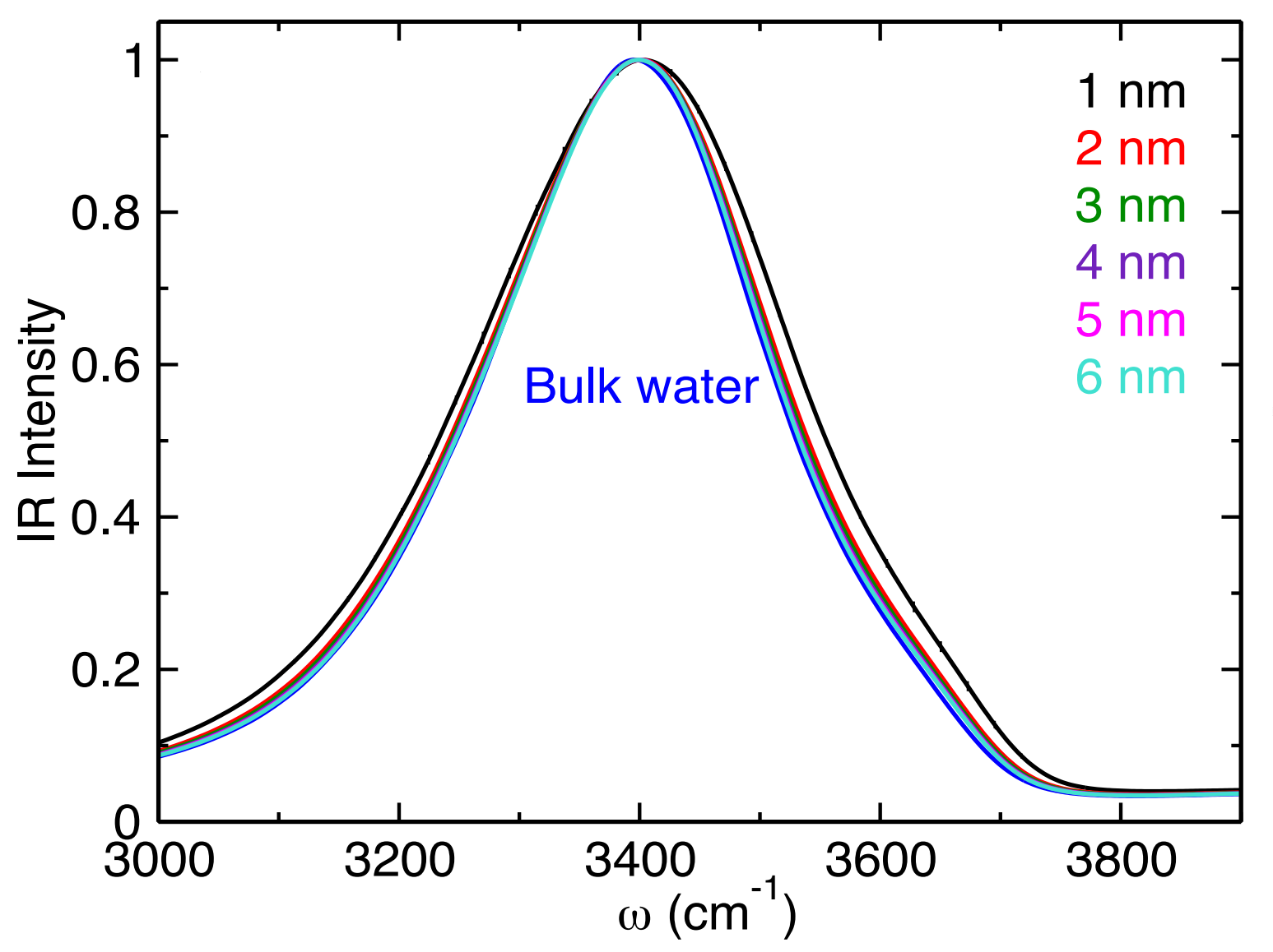
Gulmen-Thompson force field – Silanol and Geminal interactions
SPC/E model - water interactions
Jung-Cheatham model – ion interactions

P. N. Wimalasiri, N. P. Nguyen, H. S. Senanayake, B. B. Laird, and W. H. Thompson *J. Phys Chem C* **125** (**42**), 23418-23434(2021)

Water confined in amorphous silica

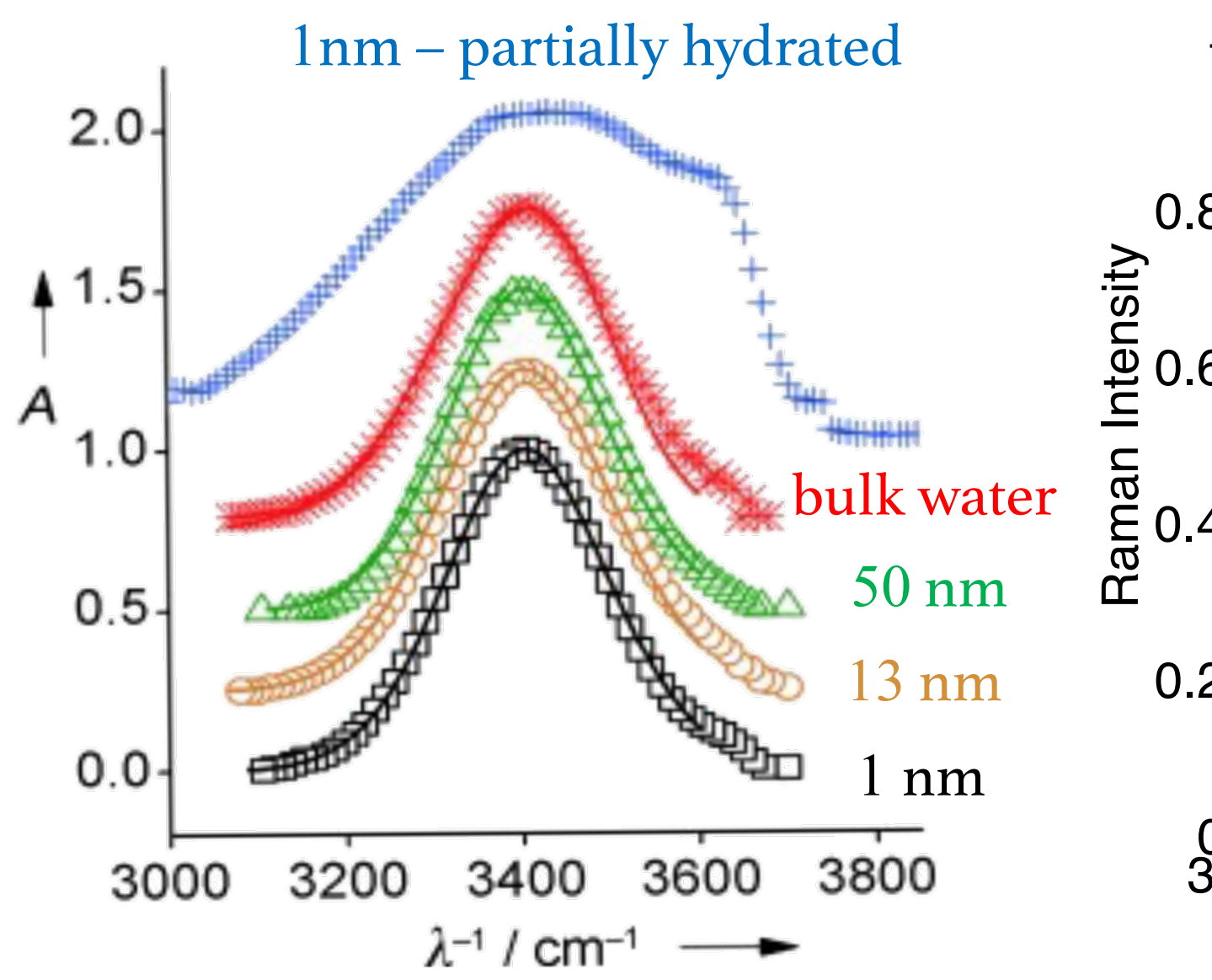


Simulated IR spectrum



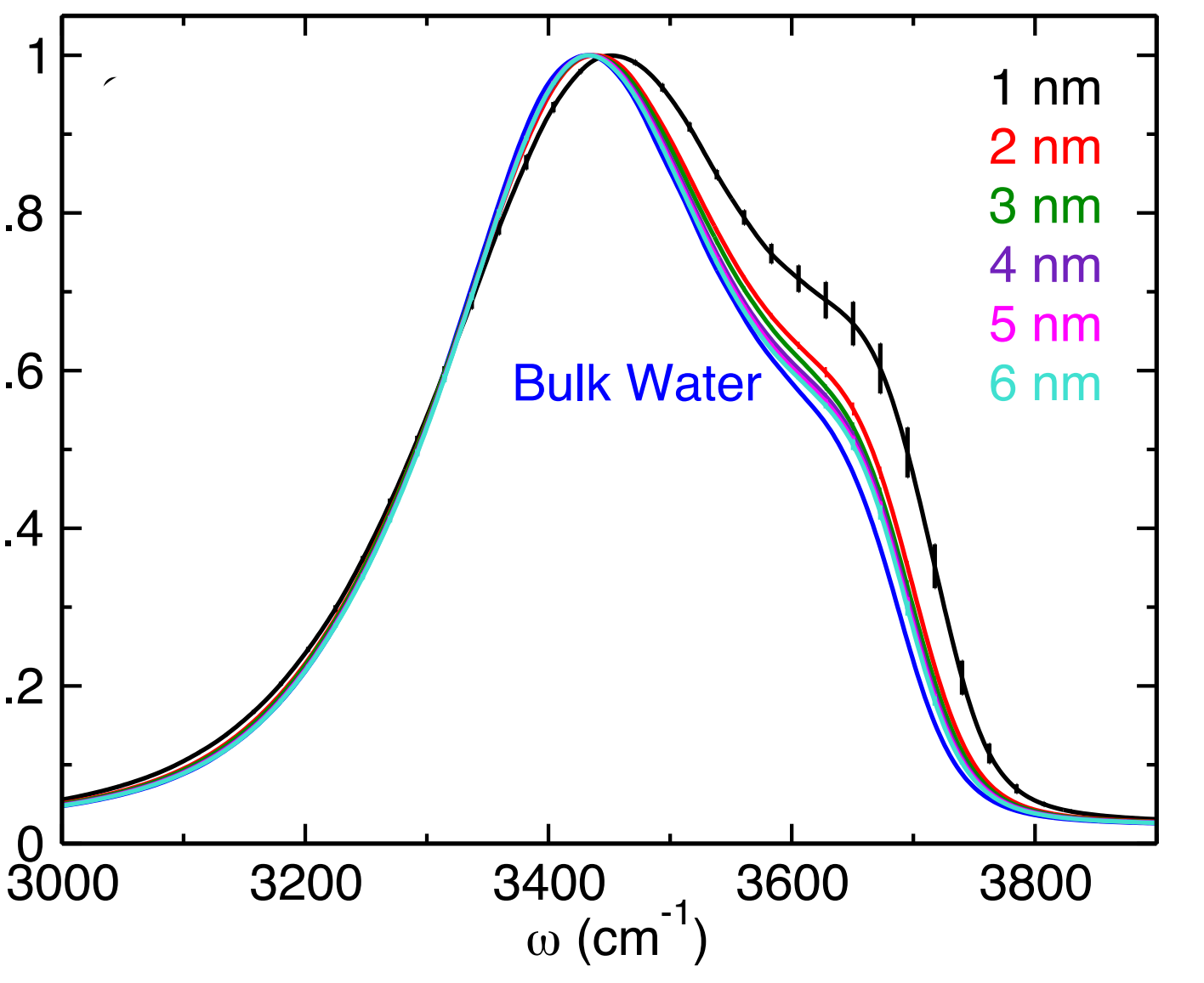
Senanayake *et al.*, J. Chem. Phys. 154, 104503 (2021)

Experimental IR spectrum



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

Simulated Raman spectrum

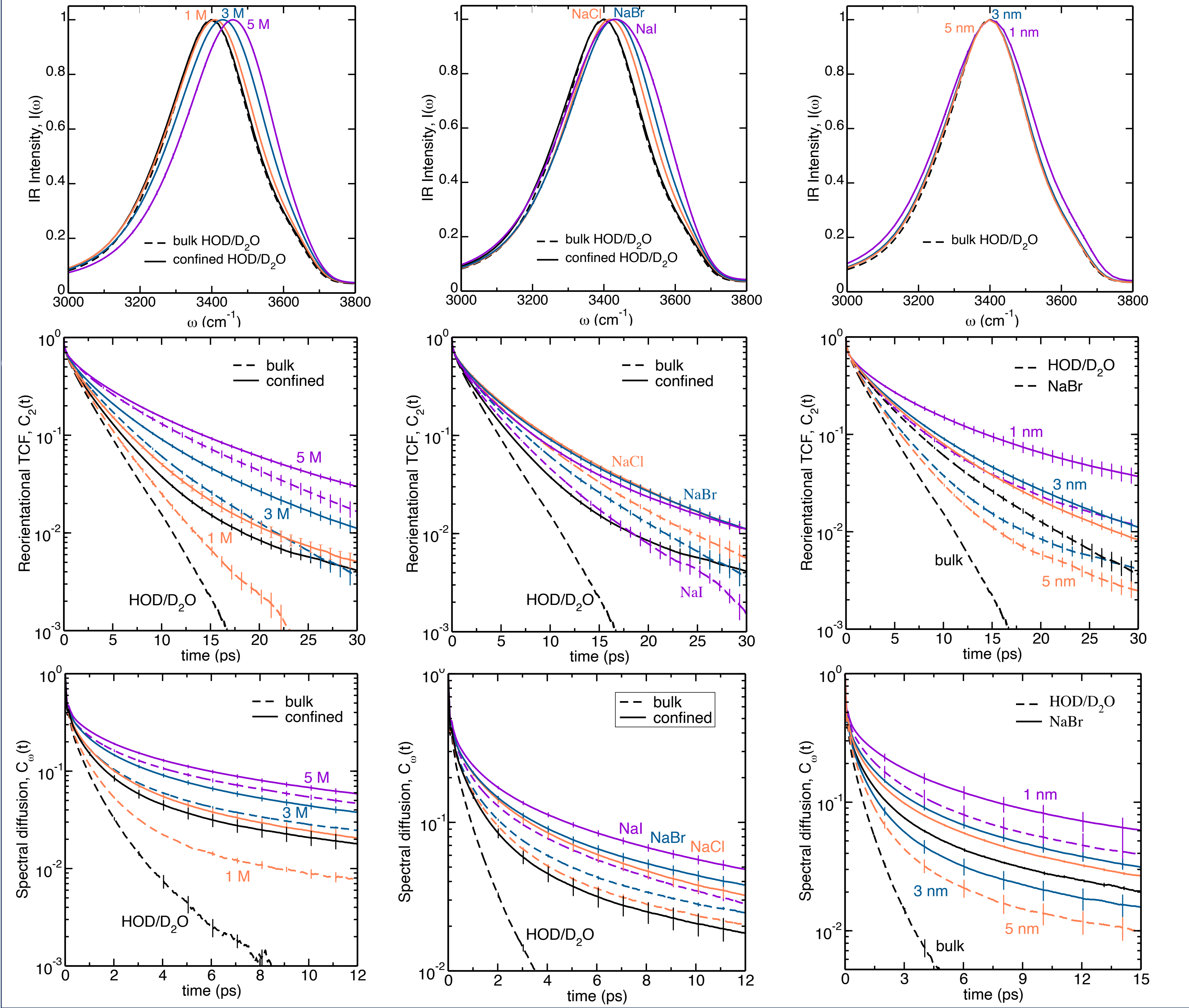


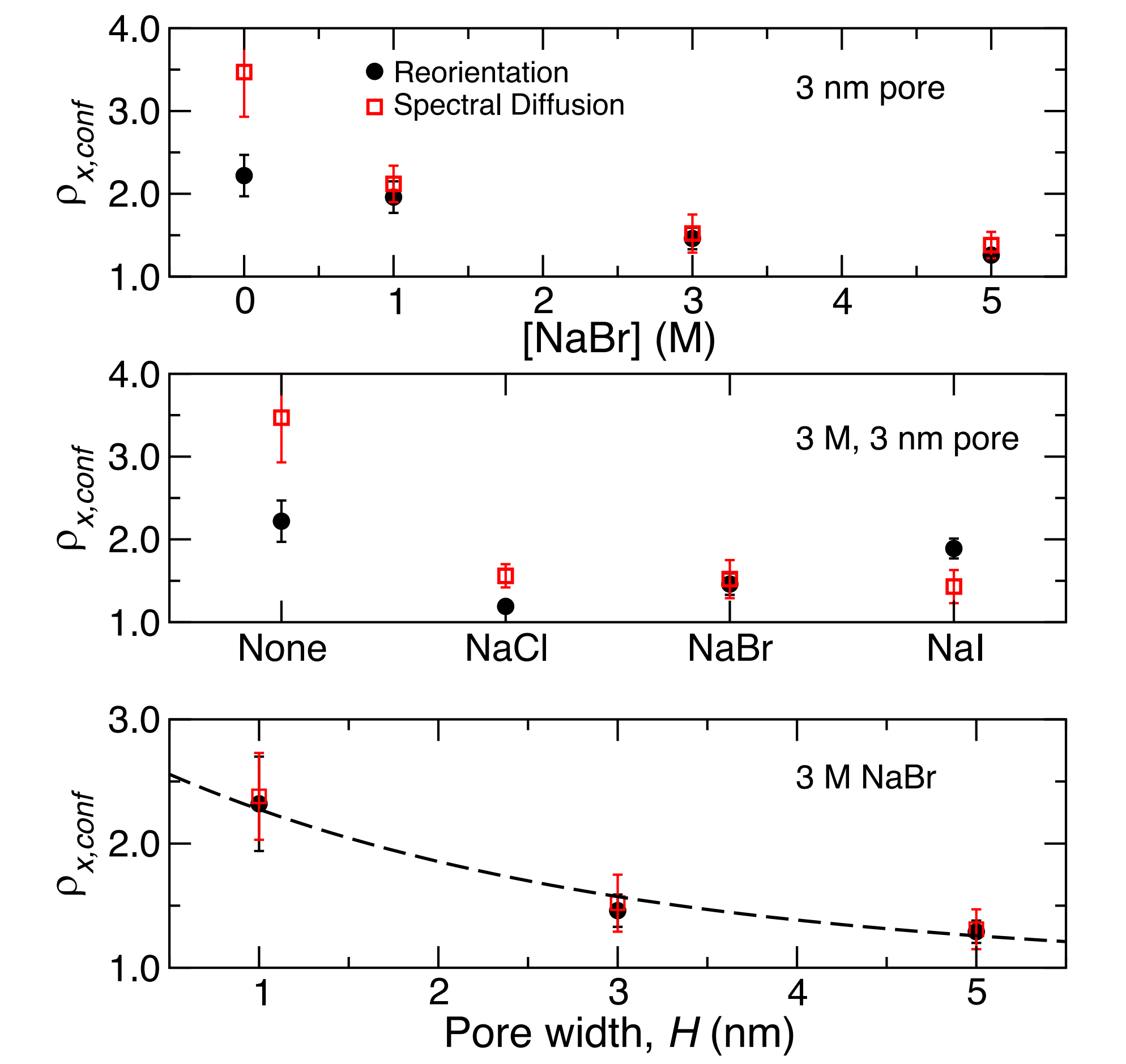
Electrolytes confined in amorphous silica

Effect of concentration

Effect of halide

Effect of pore width





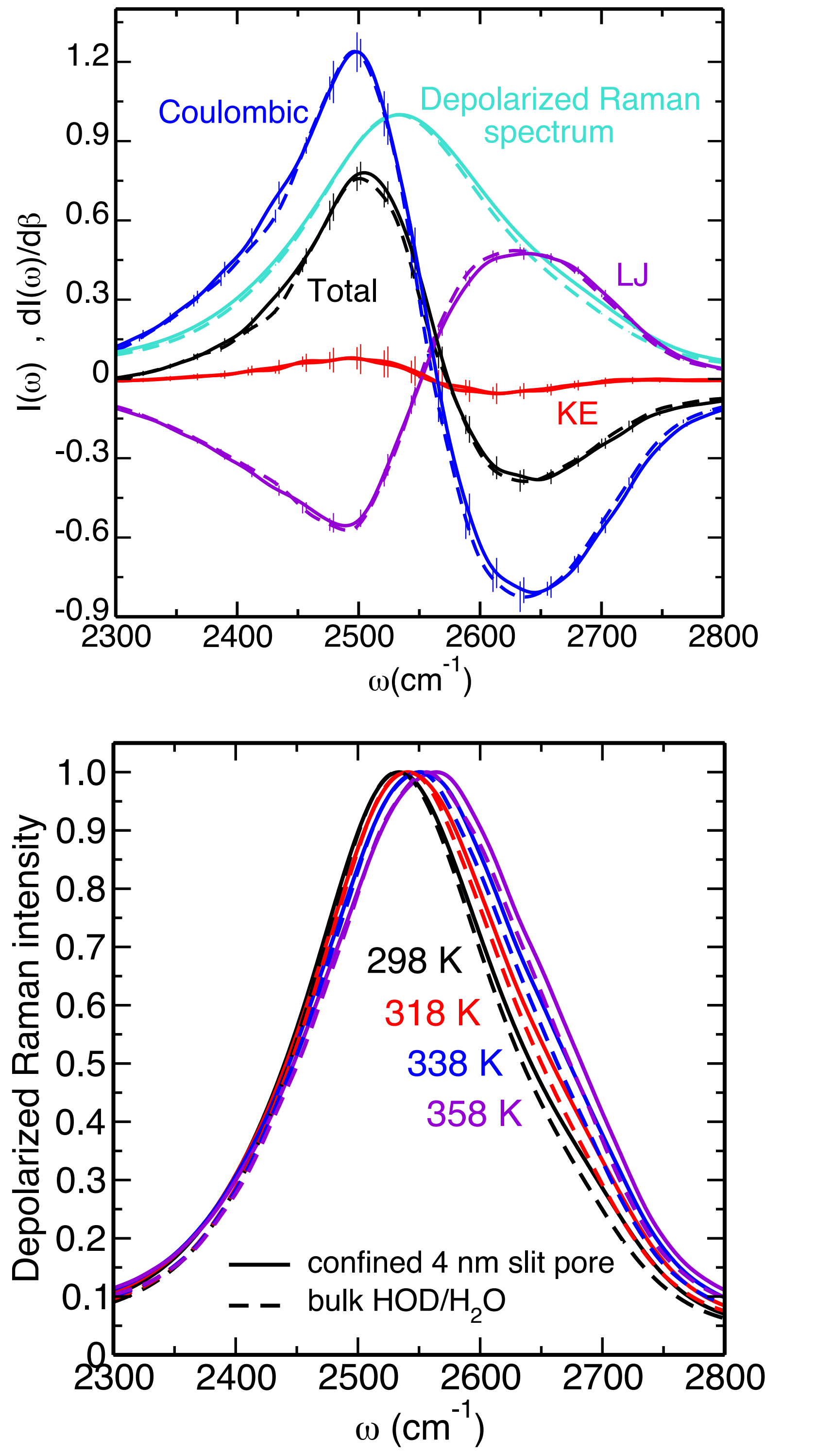
$\rho_{x,conf}$ - The ratio of the confined to bulk timescales

The weaker H-bonding of water molecules with the silica surface leads to smaller transition dipole moments hence the interfacial OH groups are suppressed in the IR spectrum.

Slowdown factors are most prominent in neat water and decrease with salt concentration and pore width.

Senanayake *et al.*, *J. Chem. Phys.* 157, 034702 (2022);

Temperature dependence



Conclusion

Trends in frequency shifts are in good agreement with experimental spectra for water confined in silica nanopores.

IR spectra show only modest differences between confined and bulk electrolyte solutions in amorphous silica slit pores.

Confinement effects are suppressed as the concentration increases.

The larger the halide, the more blue-shifted the IR spectrum.

OH reorientational dynamics are significantly slowed by confinement even at the lowest concentrations.

Acknowledgments

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