SAND2022-3181C

Simulations of vibrational and solvation properties of nano-confined electrolyte solutions

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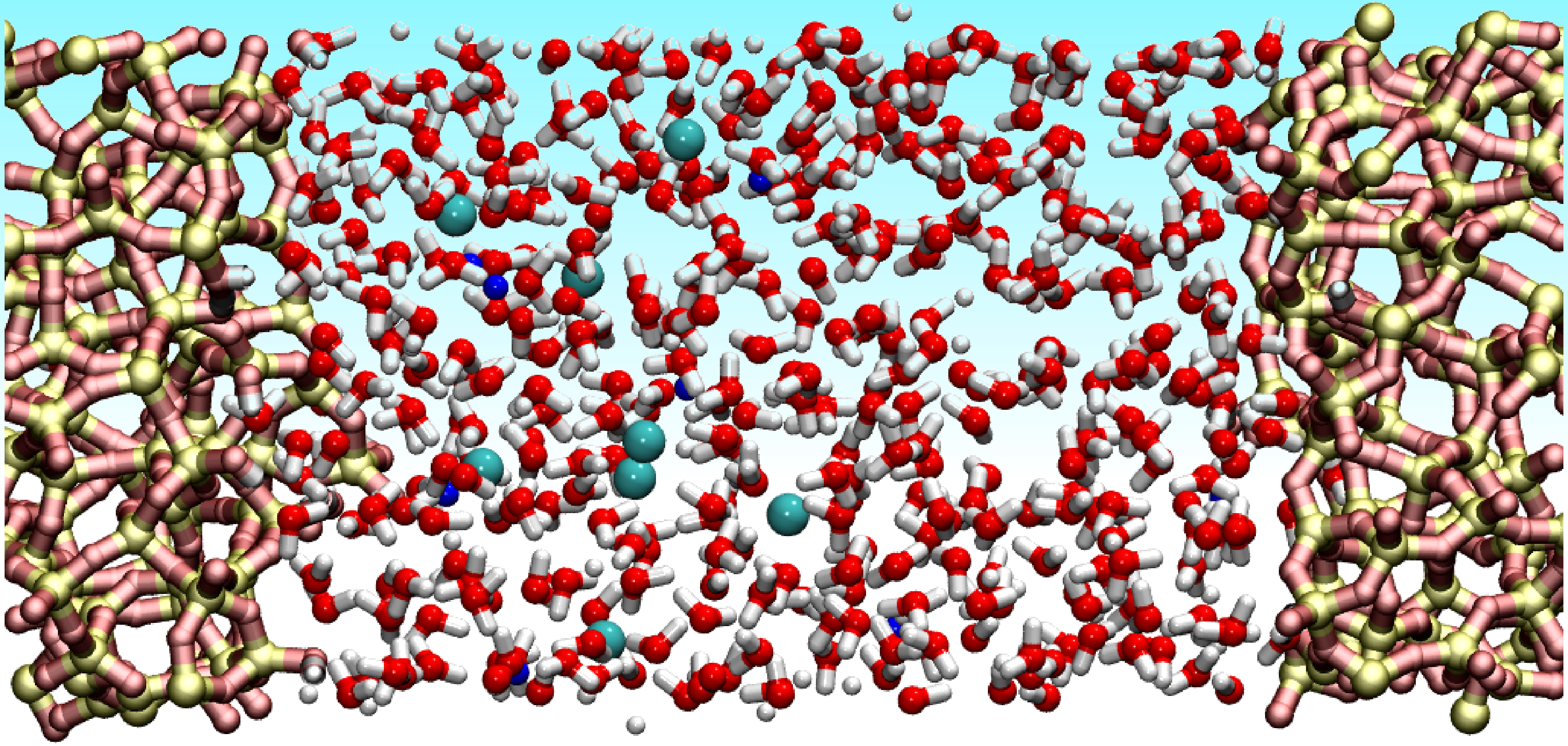

This work was supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, Chemical Sciences, Geosciences, and Biosciences Division. Sandia National Laboratories is a multi-mission laboratory managed and operated by National Technology and Engineering Solutions of Sandia LLC, a wholly owned subsidiary of Honeywell International Inc. for the U.S. ... 003525

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Electrolytes confined in mesoporous silica

In collaboration with Geochemistry Department of Sandia National Laboratories, NM

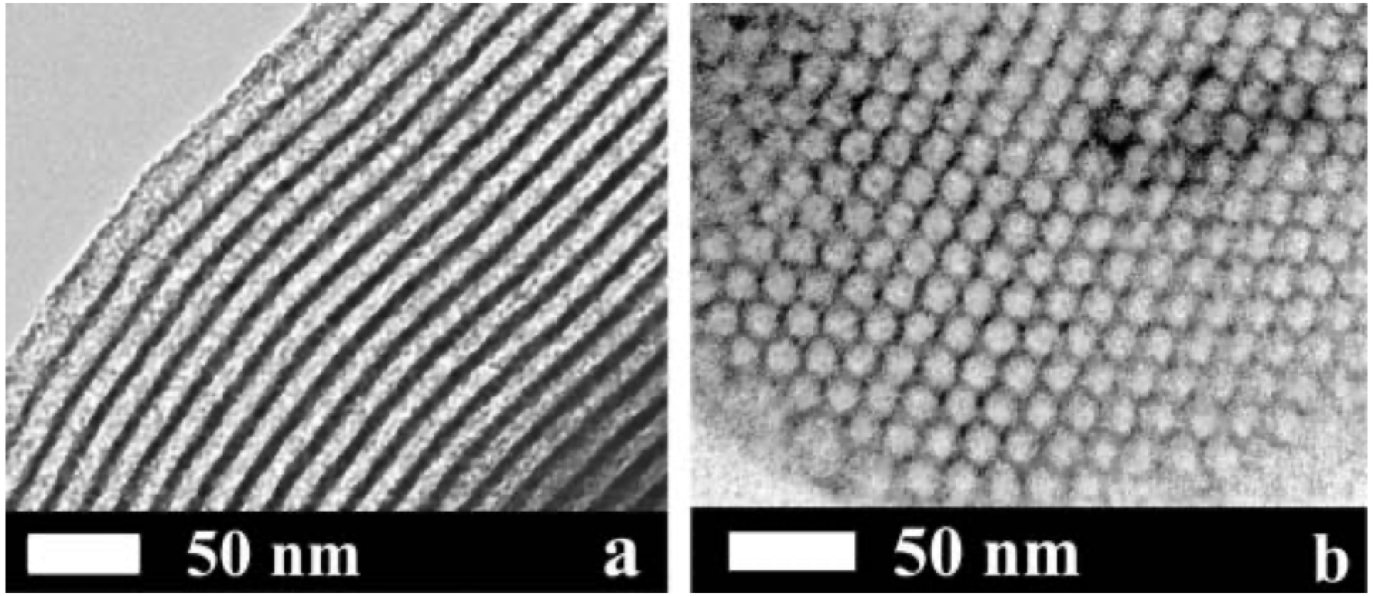
Confined water and electrolytes - soil and sedimentary rocks

Difficult to prepare nanopores from real rocks/minerals

Mesoporous silica - synthetic analogs to look at confinement effects

To predict or control

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



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

Vibrational spectroscopy

An excellent probe of the local structure and dynamics

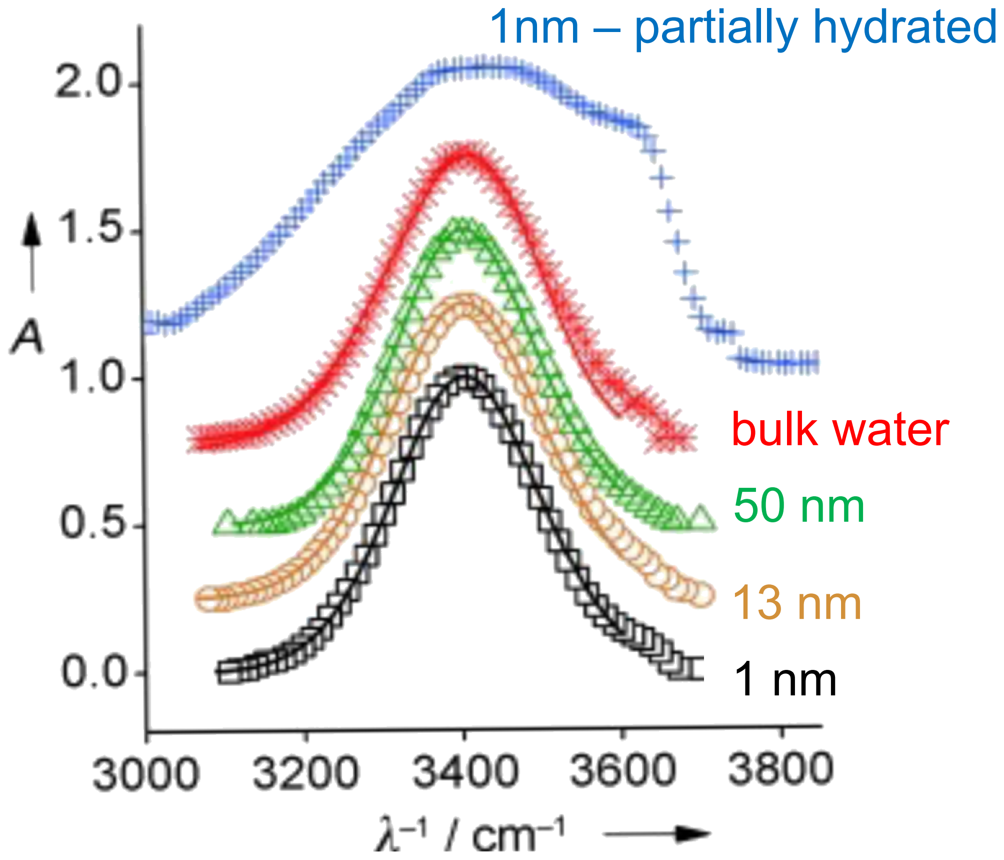
We use classical MD to simulate the spectra

Why simulations of spectra?

Challenging to interpret spectra

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

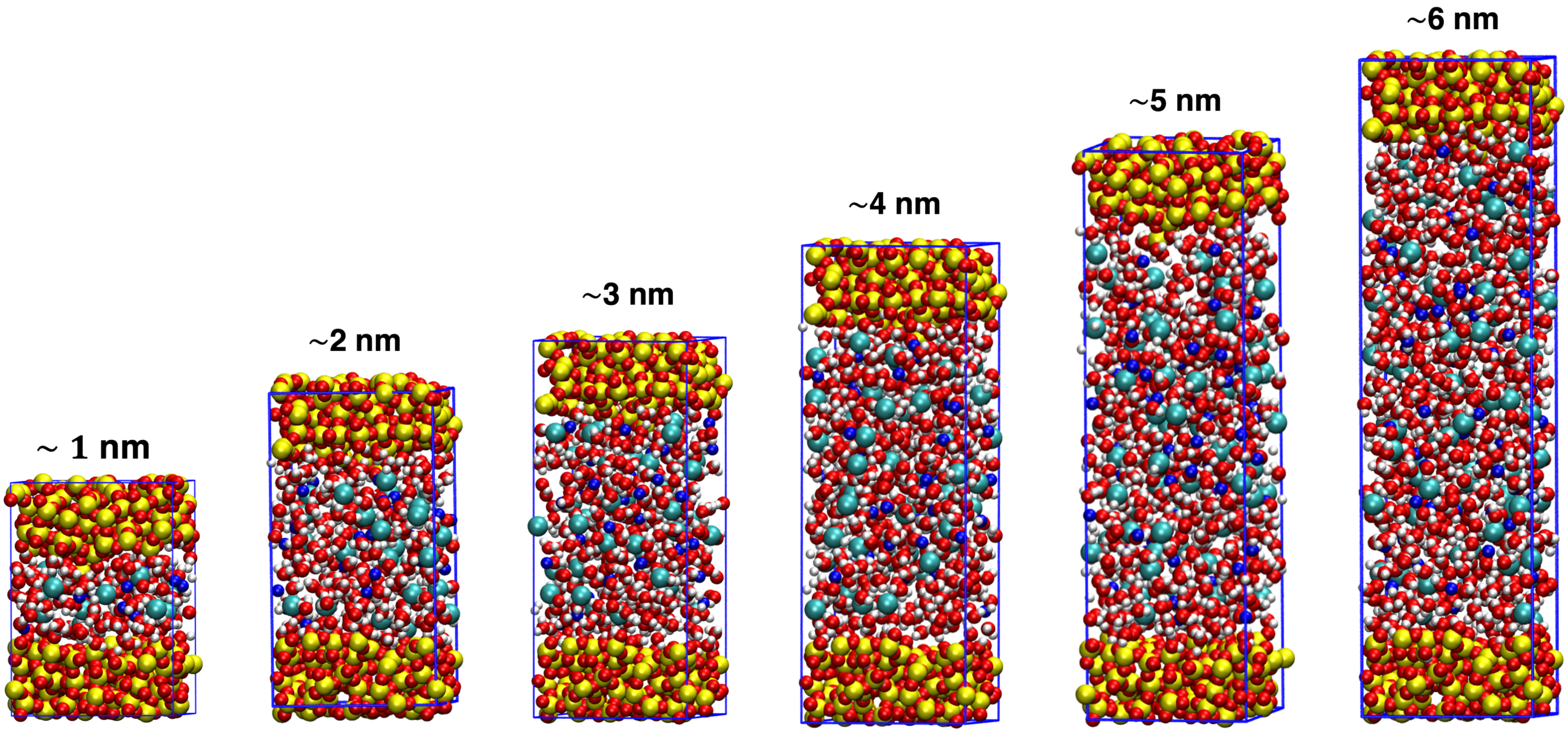
Surface-sensitive spectroscopies can not be applied to porous materials



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

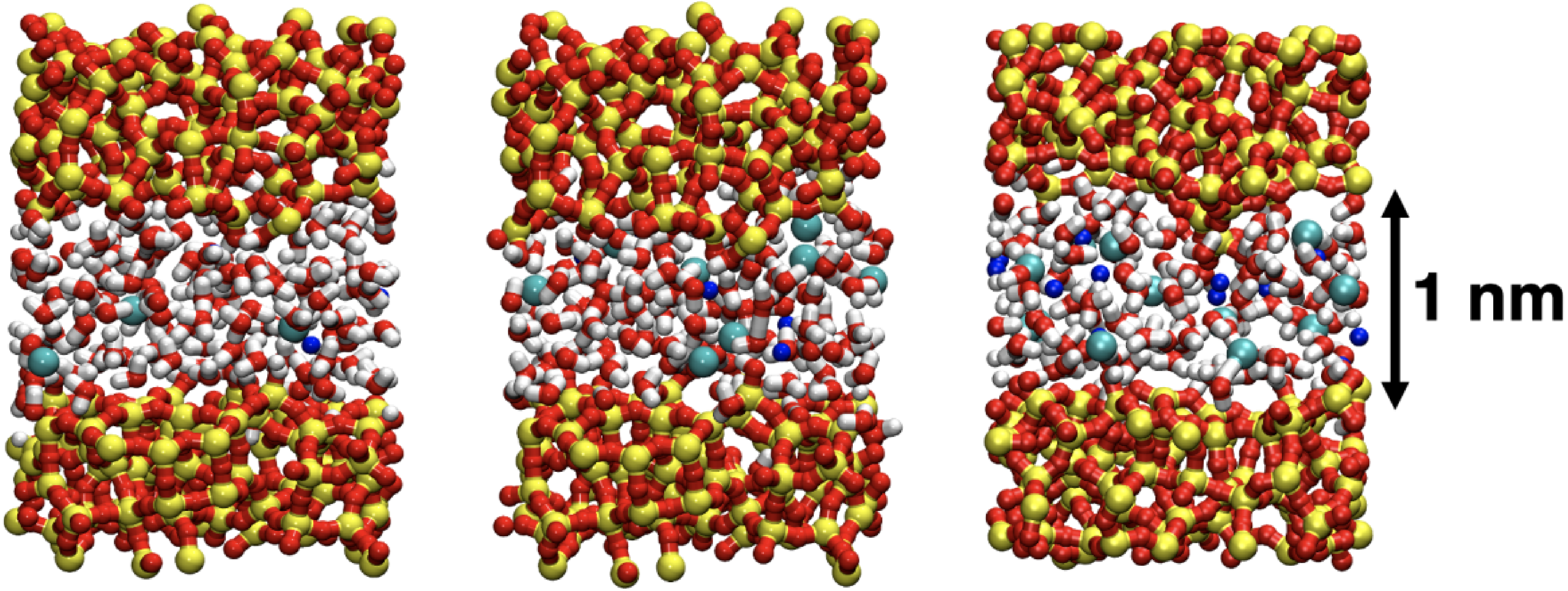
Outline

How water vibrational properties are affected by the slit pore width



Outline

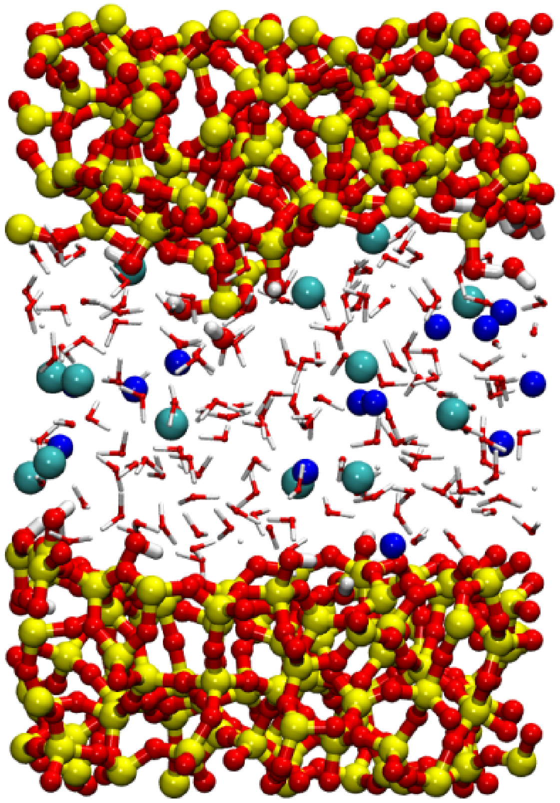
How water vibrational properties are affected by NaCl concentration



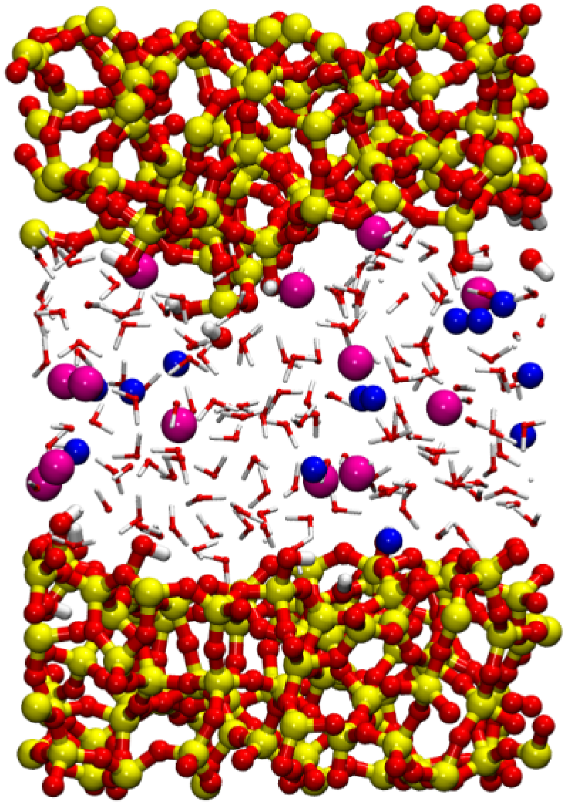
NaCl 1 M NaCl 3 M NaCl 5 M

Outline

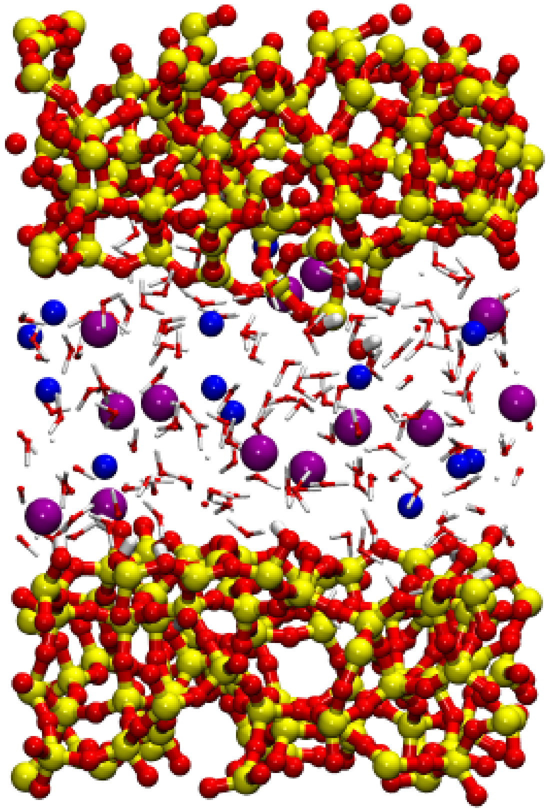
How water vibrational properties are affected by the type of halide



NaCl



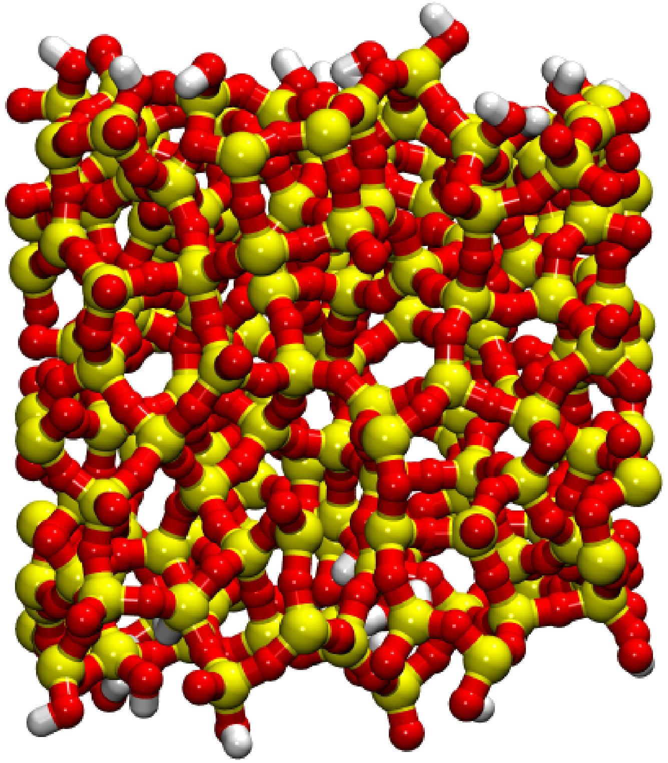
NaBr



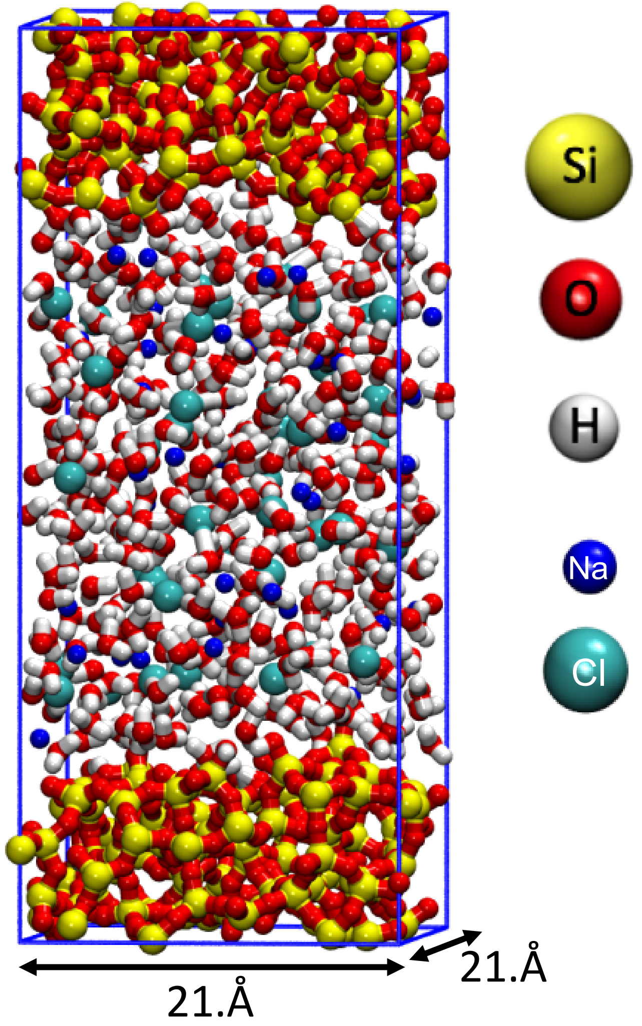
NaI

Generation of amorphous silica slit pore models

Dr. Pubudu Wimalasiri



Amorphous silica slab models
hydroxyl density (2OH/nm^2)



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

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

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)

How to calculate IR intensity

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

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

Dipole-dipole response function

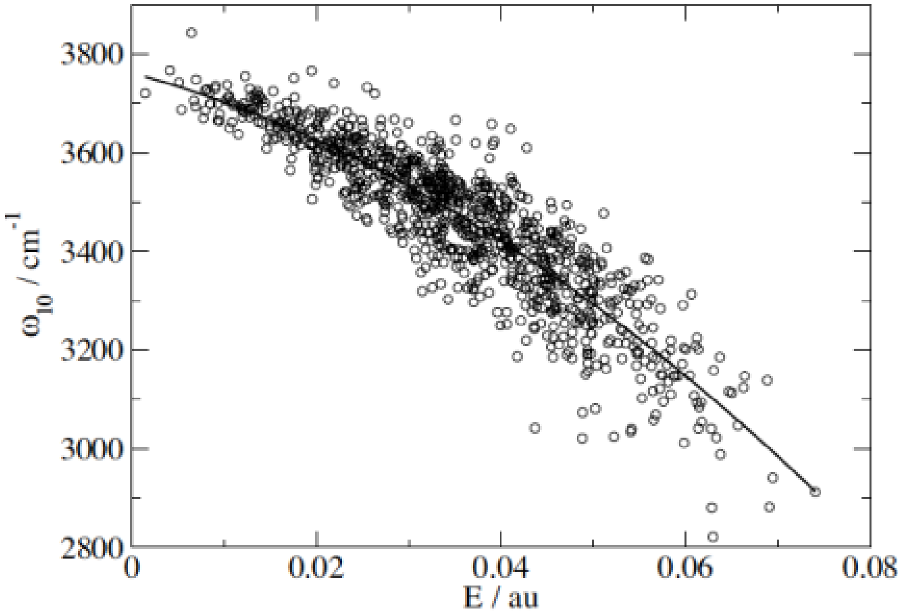
Vibrational lifetime (Expt. 700 fs)

Transition dipole vector

Transition frequency

Empirical (or Electrostatic) mapping

HOD in D_2O – To avoid resonance vibrational coupling



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)

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

Vibrational spectra of confined water

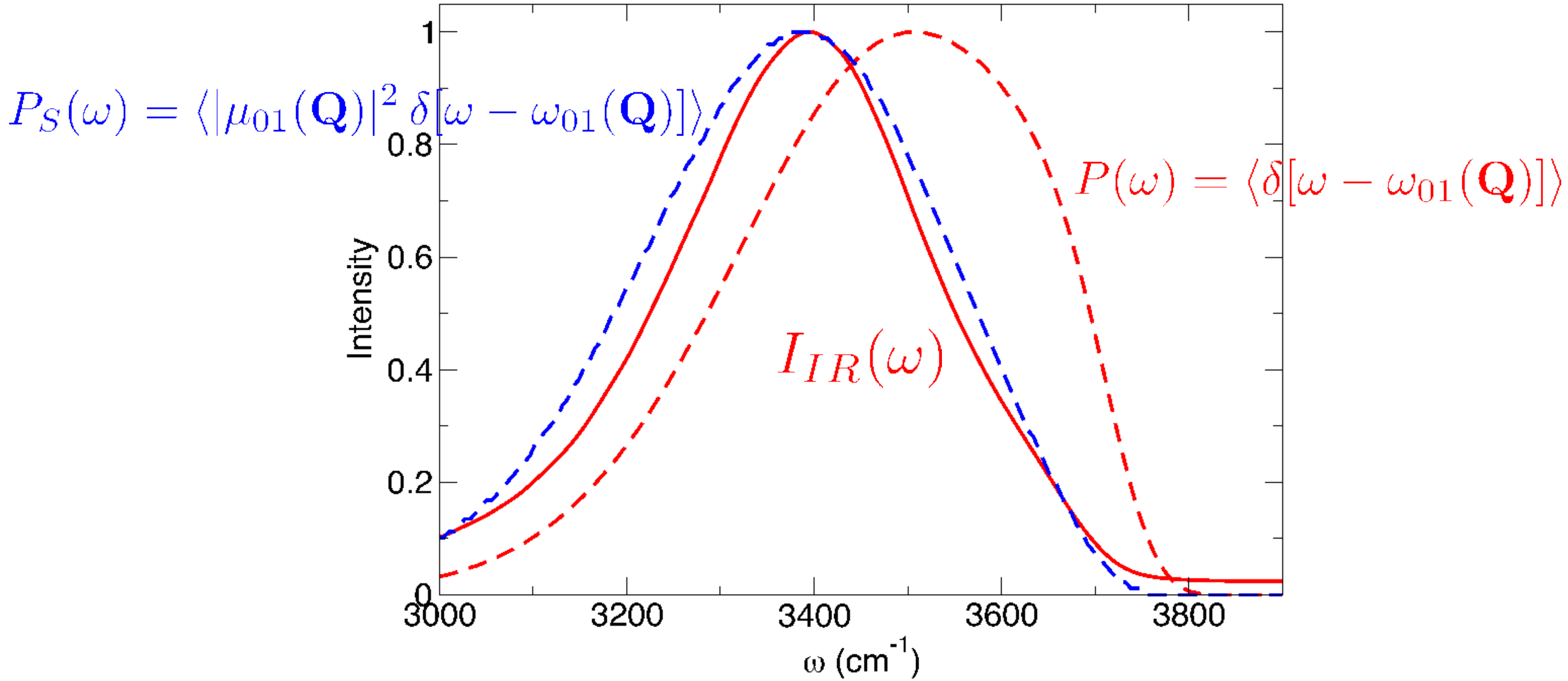
$$I(\omega) = \frac{1}{2\pi}\int_{-\infty}^{\infty} e^{-i\omega t}\phi(t)dt$$

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

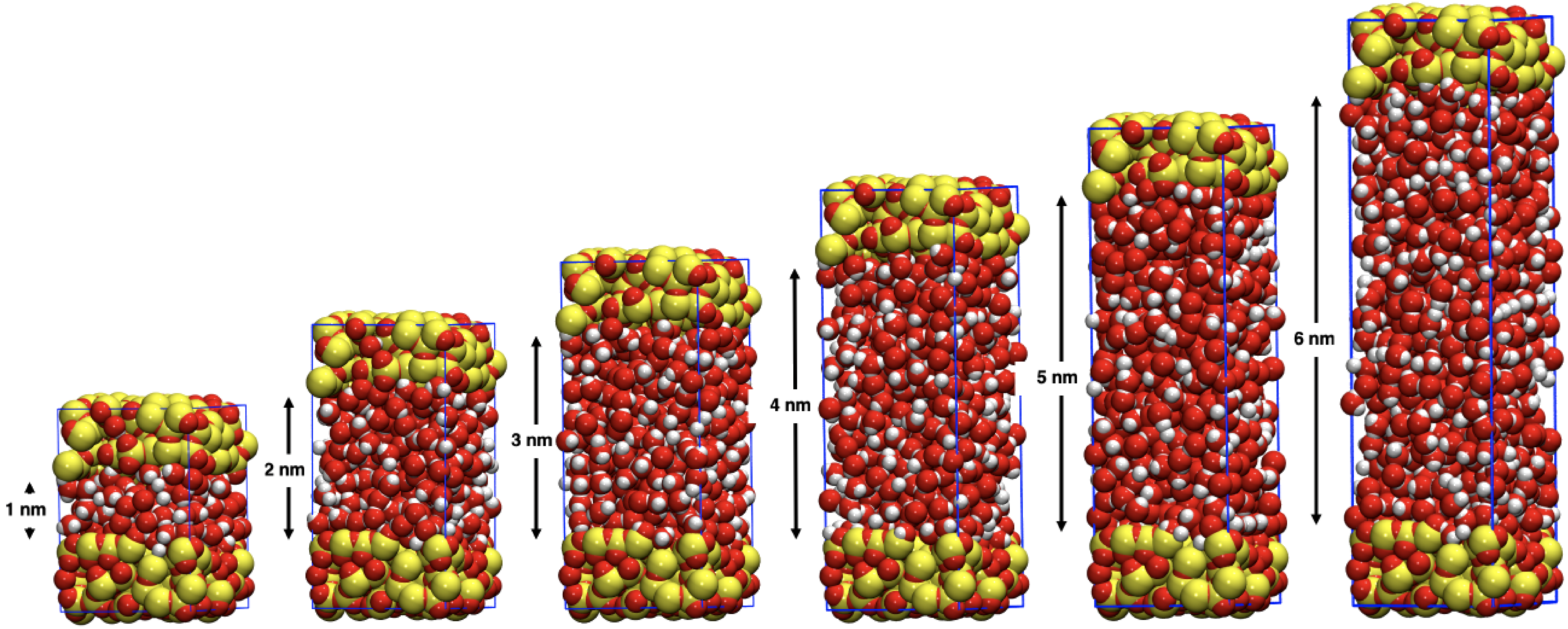
Vibrational lifetime (Expt. 700 fs)

Transition dipole vector

Transition frequency

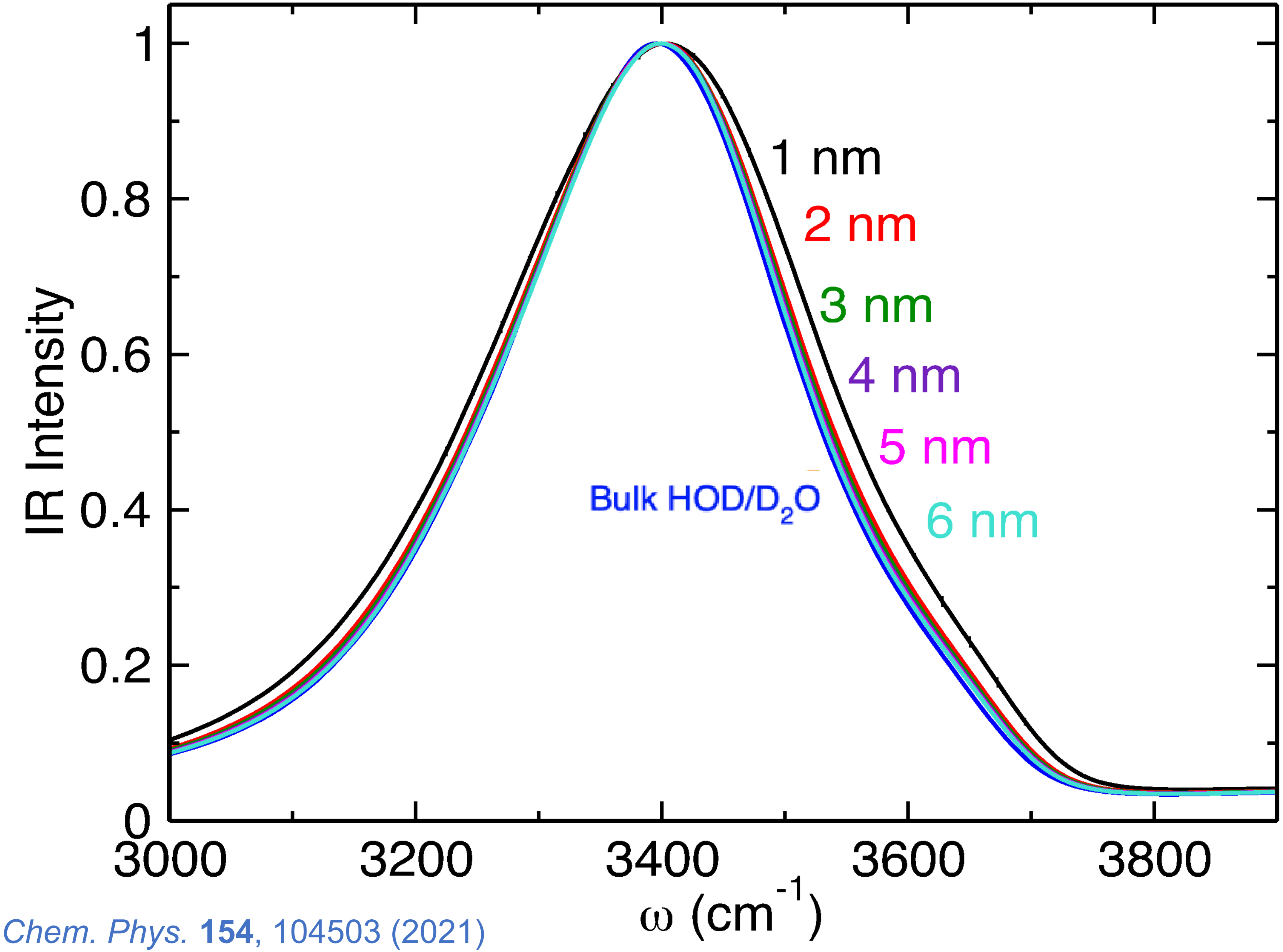


Effect of pore width on confined water vibrational properties



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

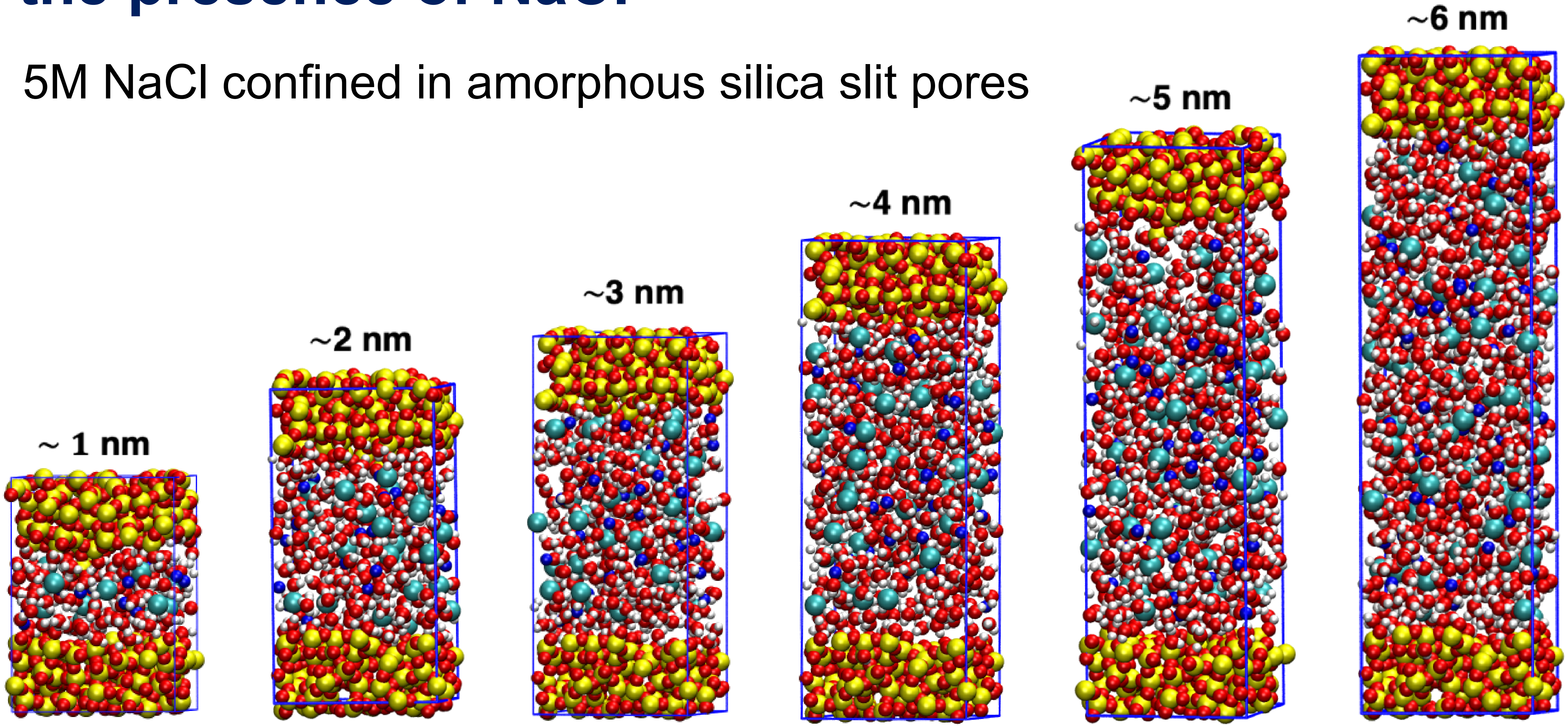
Effect of pore width on confined water IR spectrum



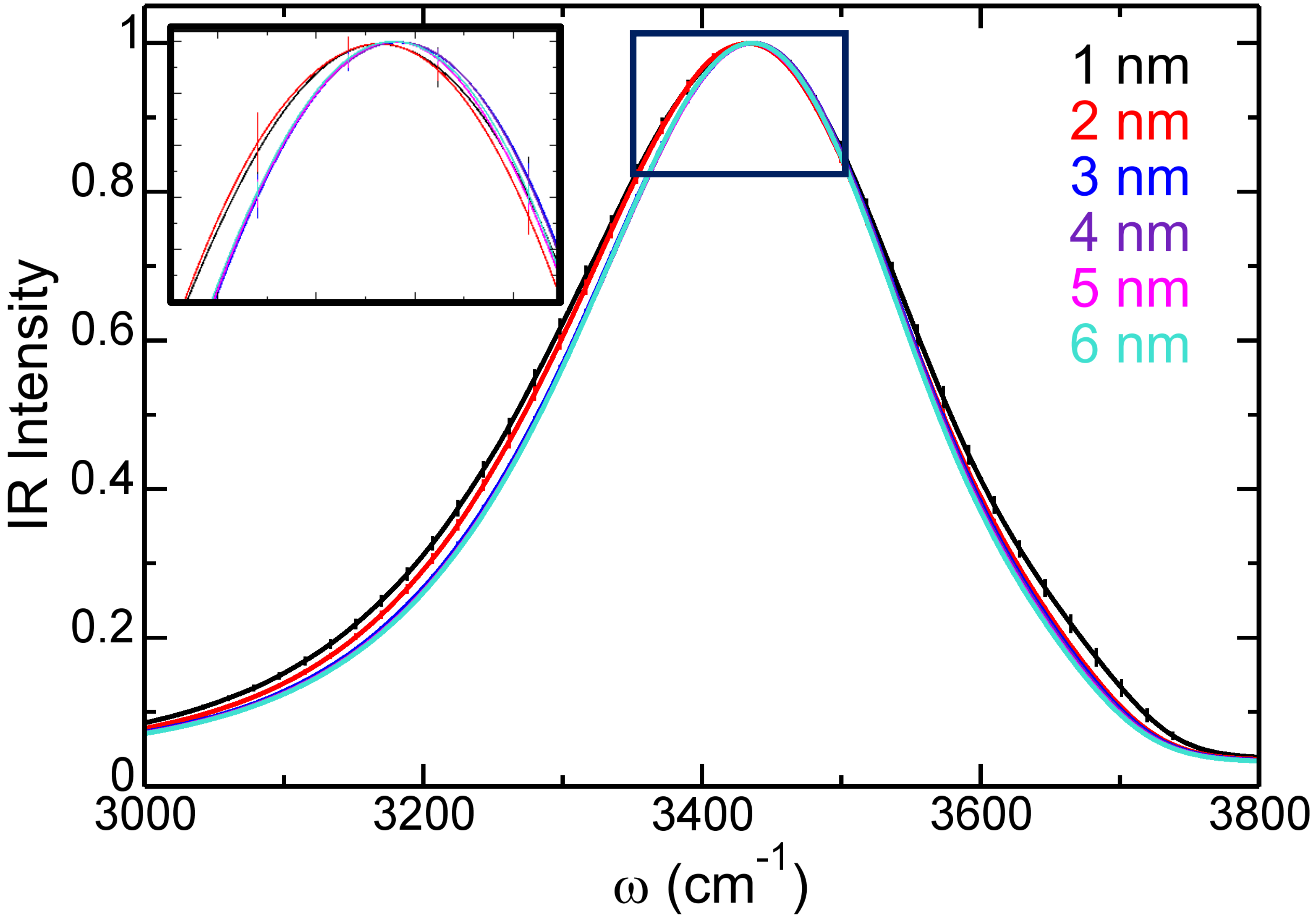
Senanayake *et al.*, *J. Chem. Phys.* **154**, 104503 (2021)

Effect of pore width on confined water IR spectrum in the presence of NaCl

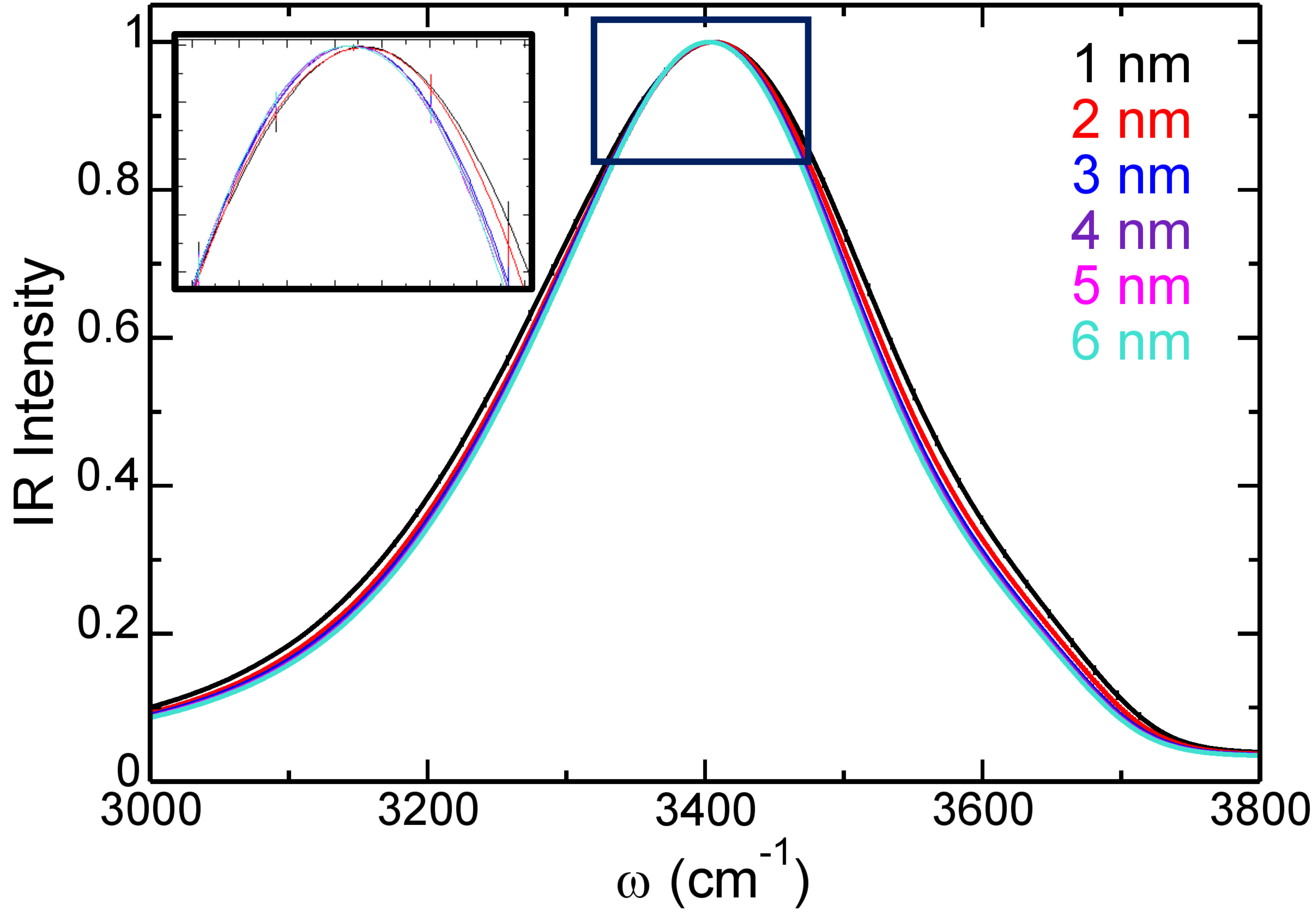
5M NaCl confined in amorphous silica slit pores



Effect of pore width on confined aqueous NaCl (~5M) IR spectrum

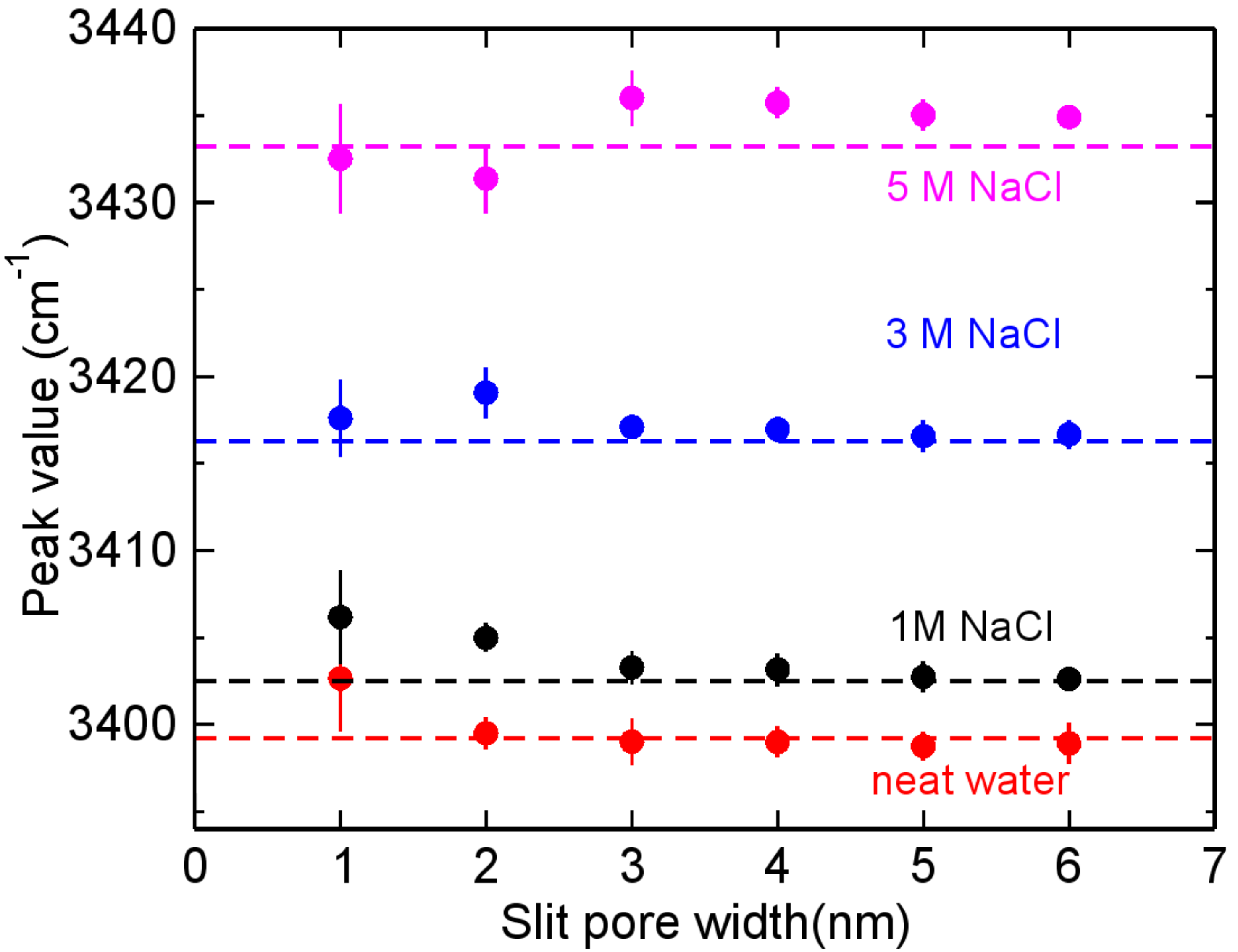


Effect of pore width on confined aqueous NaCl (~1M) IR spectrum



Effect of pore width on confined aqueous NaCl IR spectra

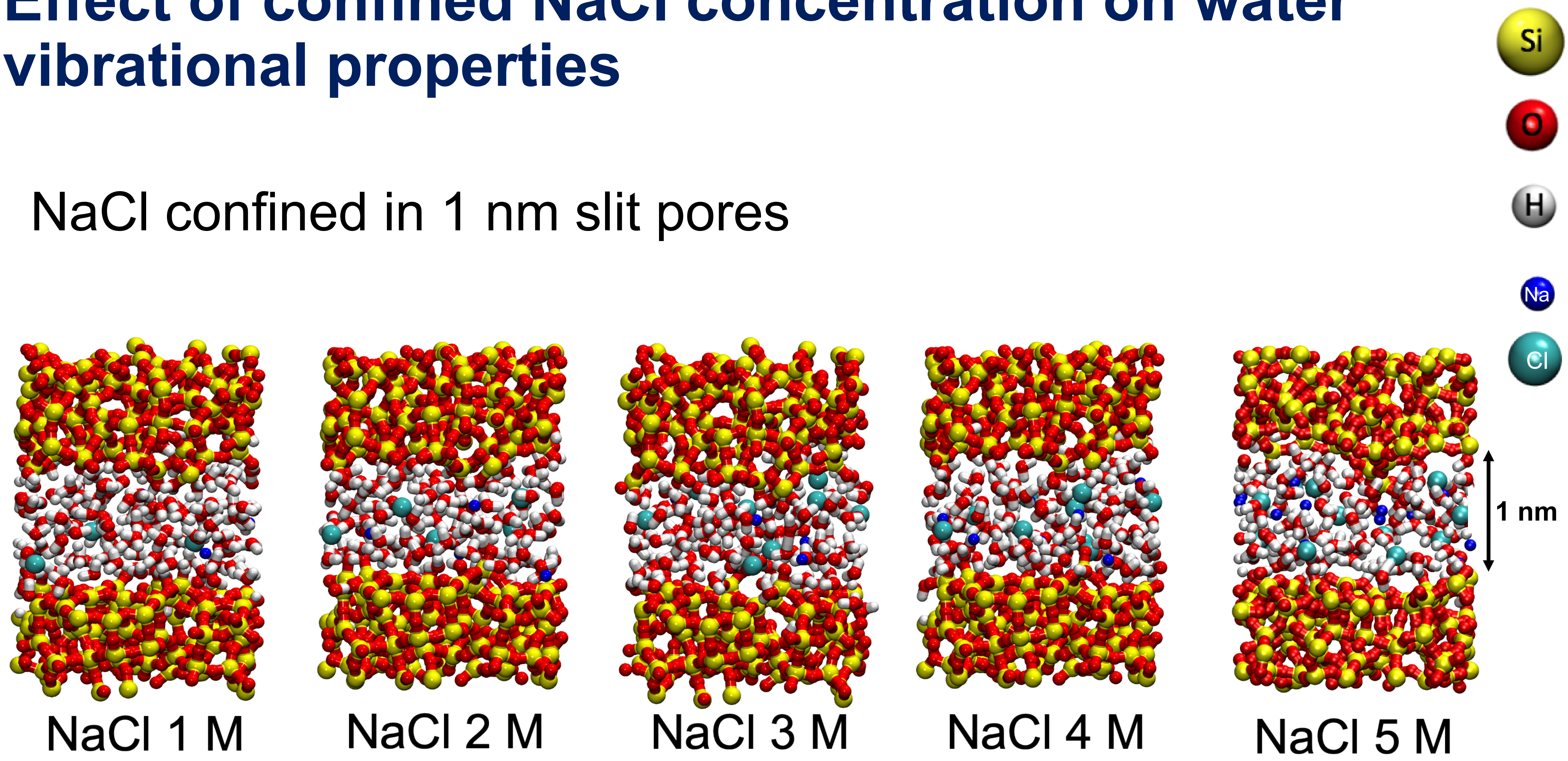
Comparison of peak frequency at different concentrations



dashed line – bulk NaCl
circles – confined NaCl

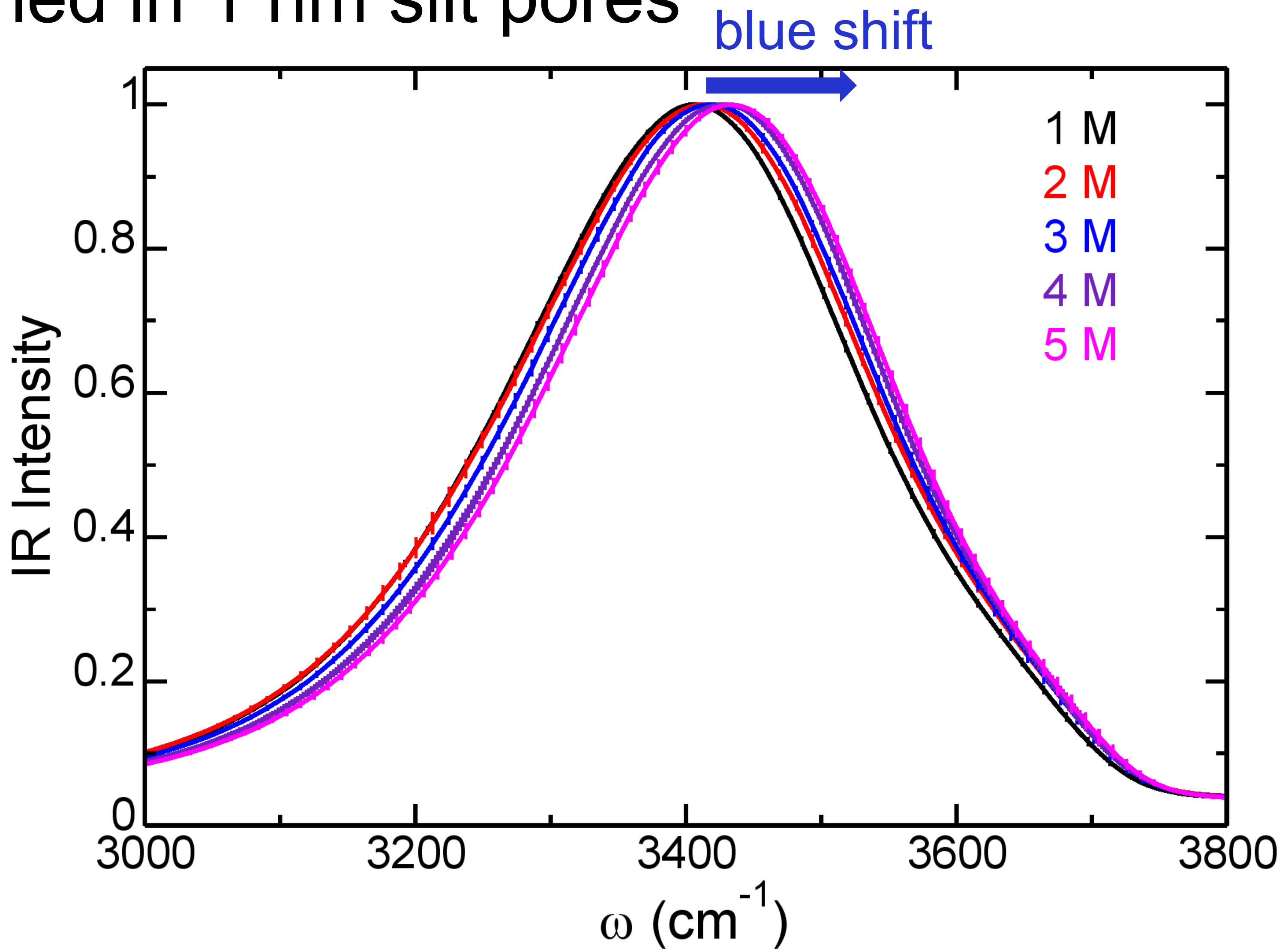
Effect of confined NaCl concentration on water vibrational properties

NaCl confined in 1 nm slit pores



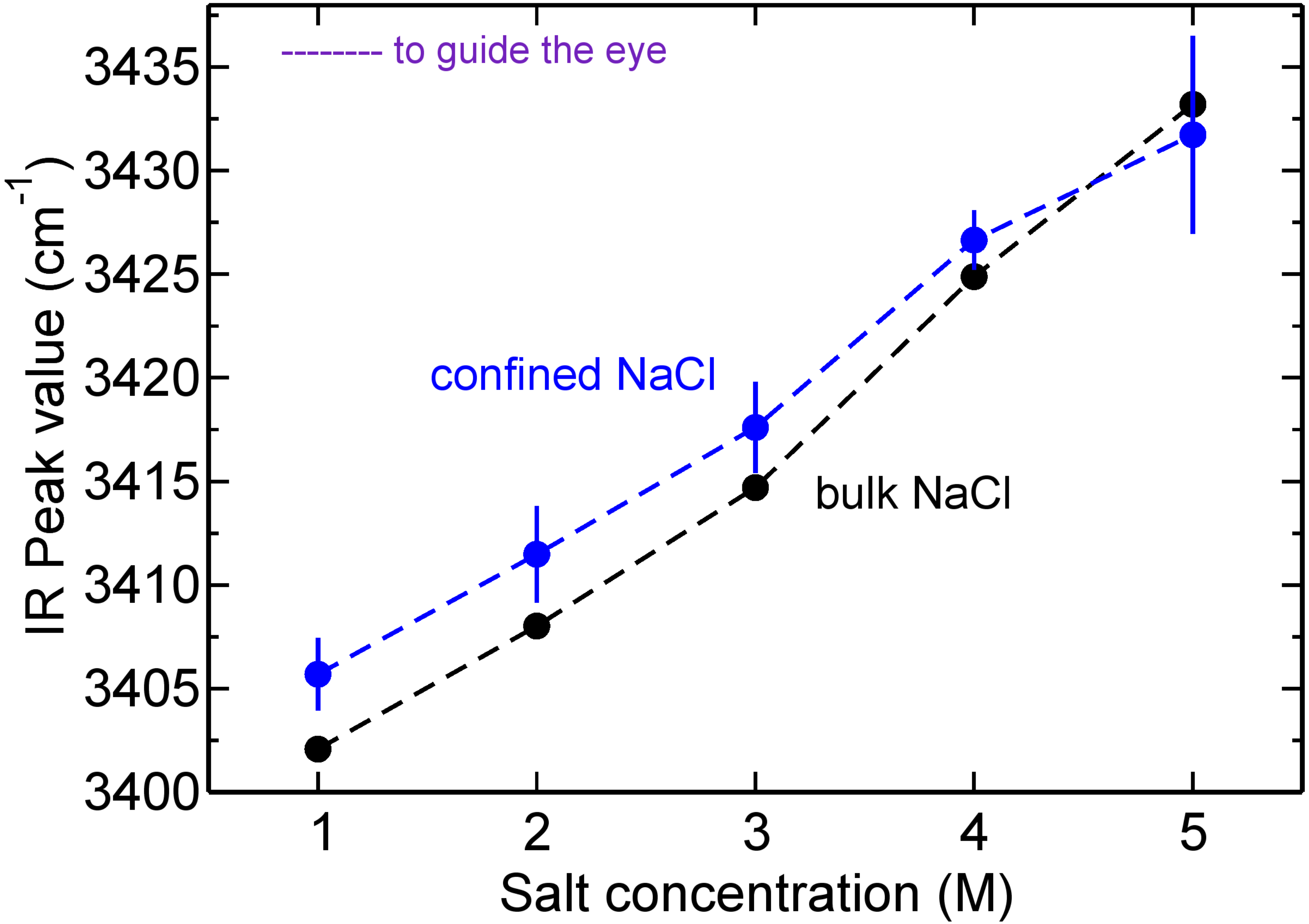
Effect of NaCl concentration on confined water IR spectrum

NaCl confined in 1 nm slit pores



Effect of NaCl concentration on IR spectra

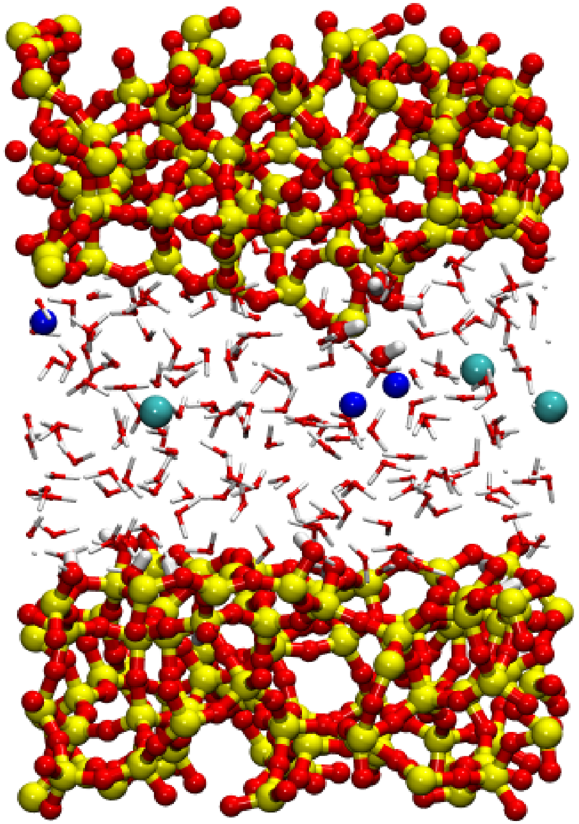
Comparison of peak frequency : NaCl confined in 1 nm slit pore



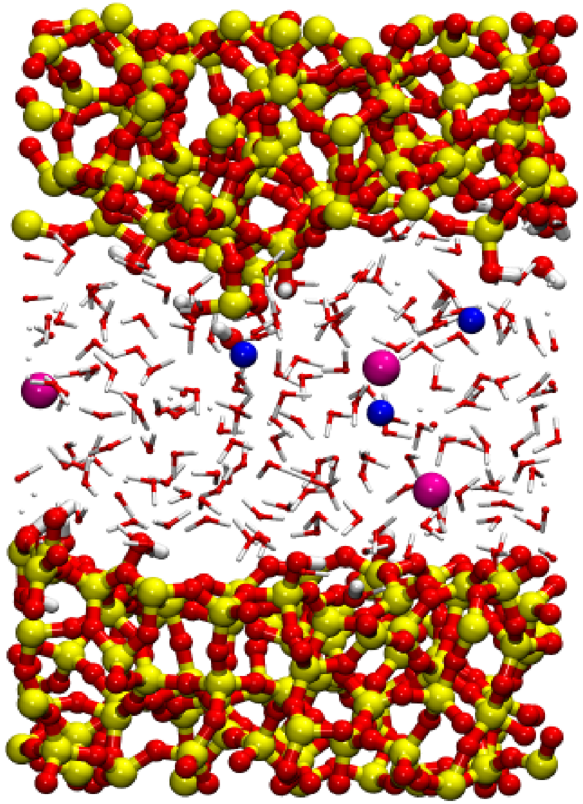
Effect of the type of halide on water vibrational properties

1M solutions confined in 1nm slit pores

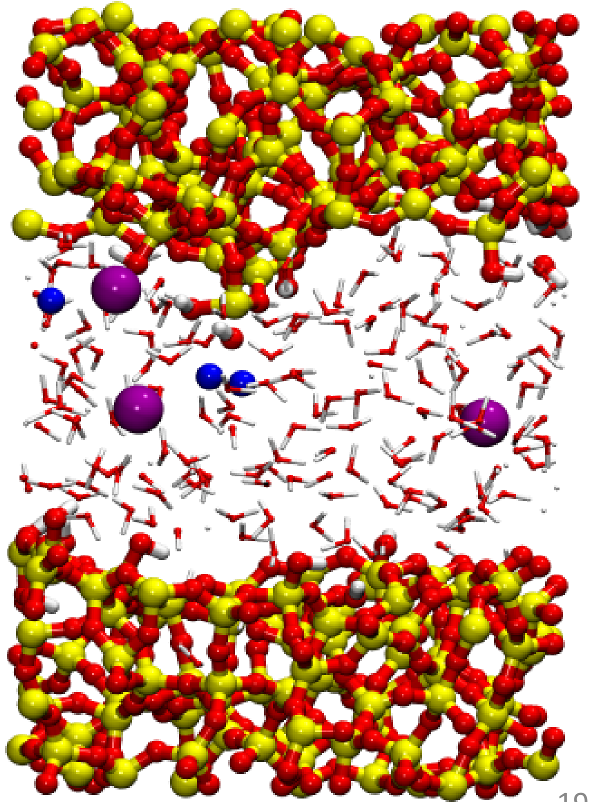
NaCl



NaBr

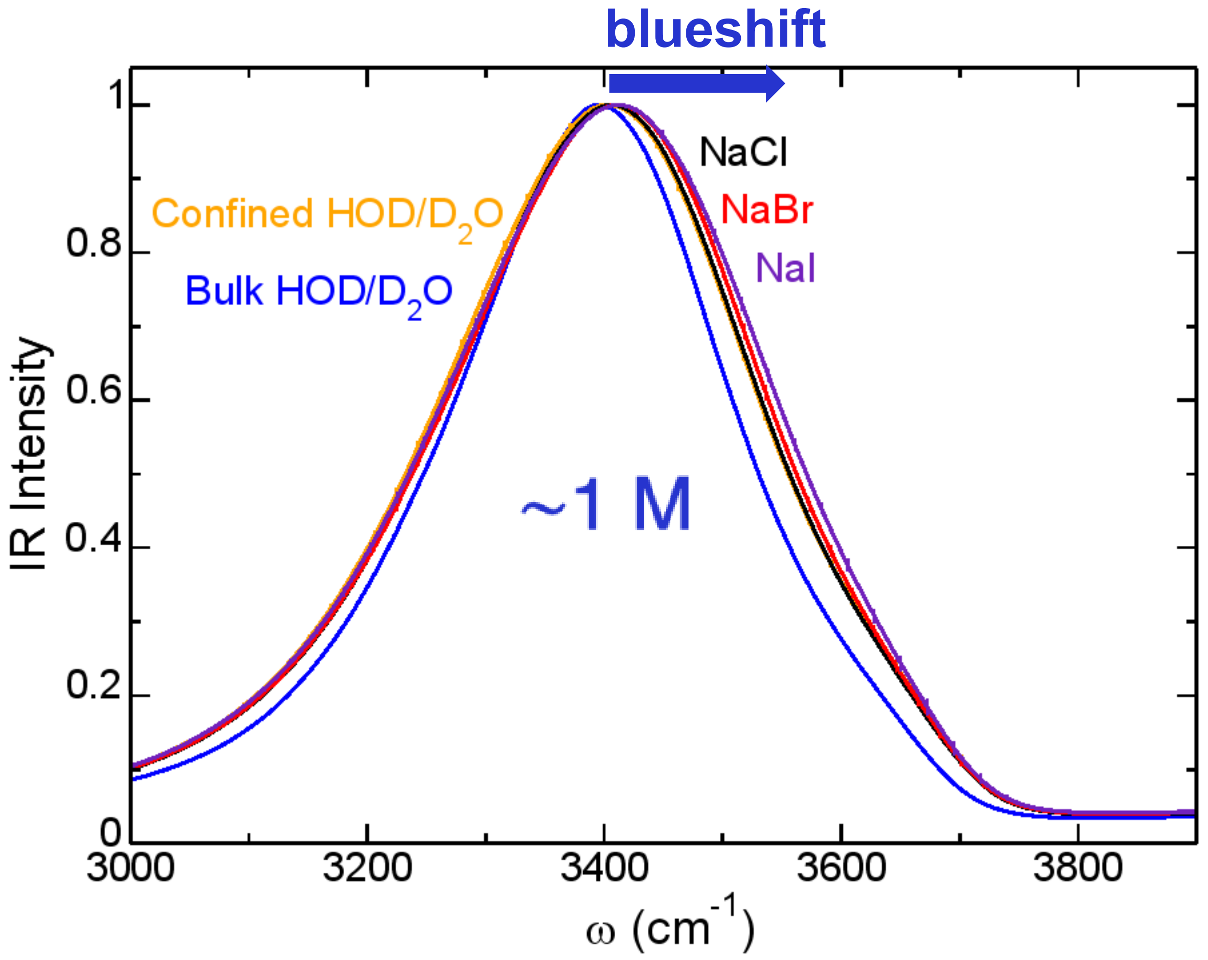


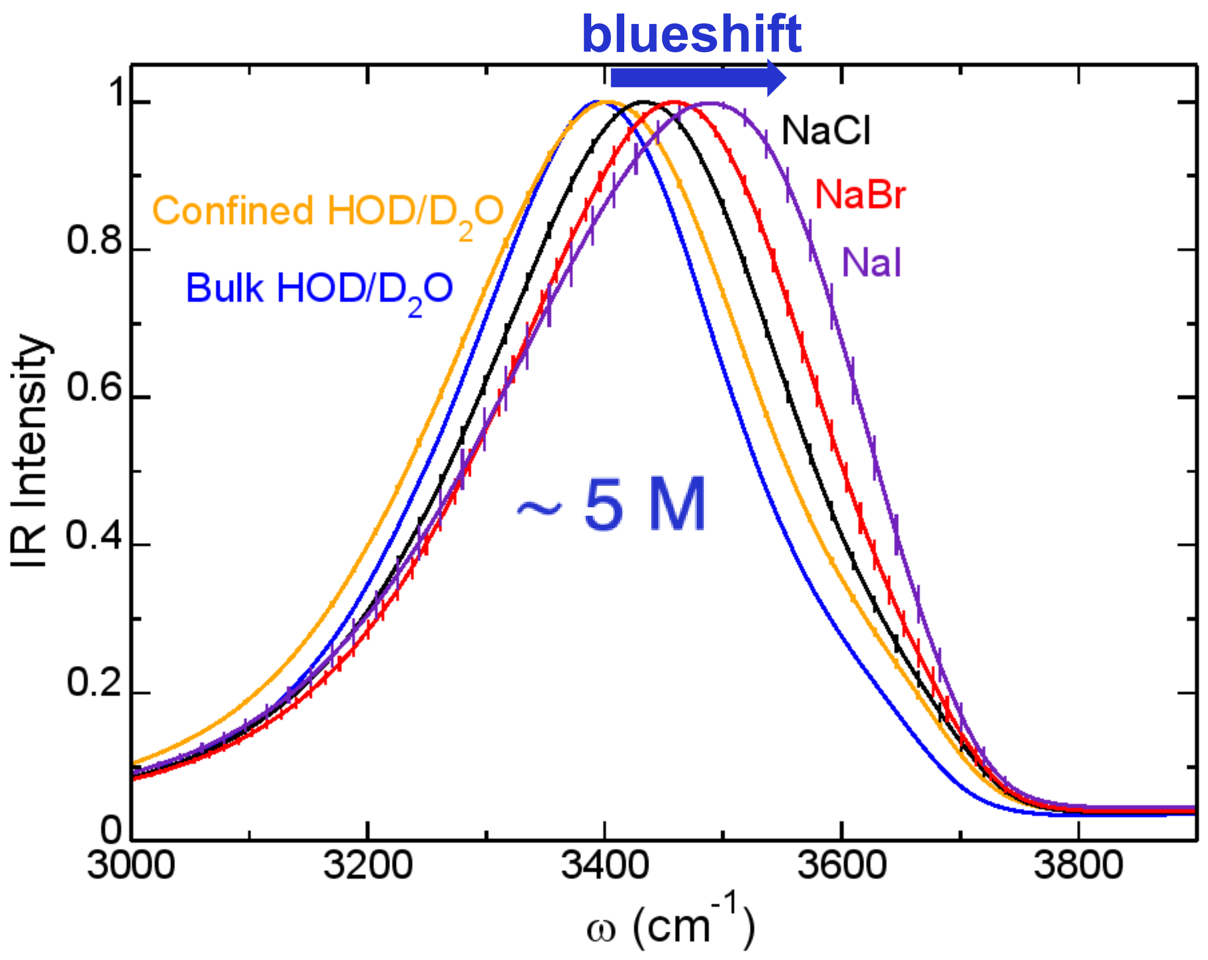
NaI



Effect of halide on confined water IR spectrum

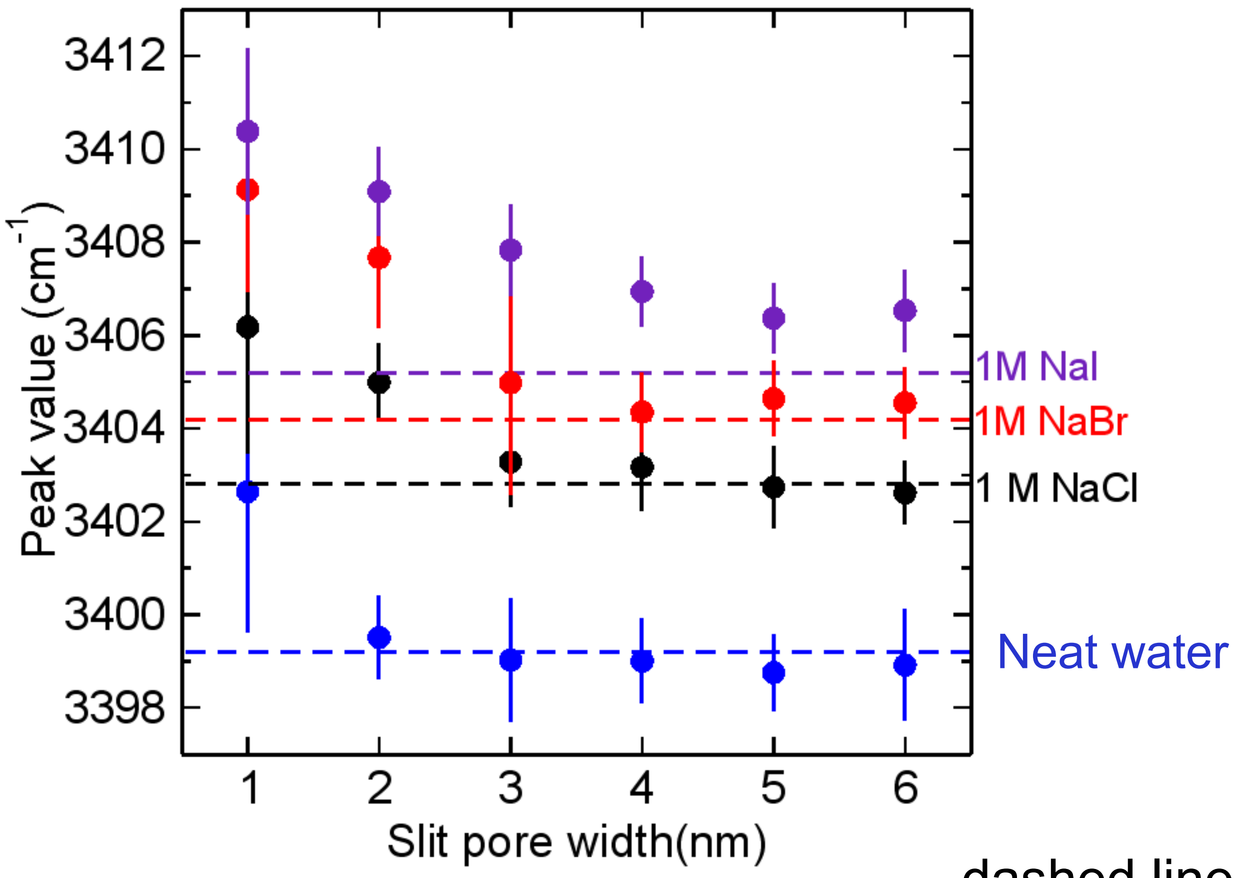
NaX confined in 1 nm slit pores

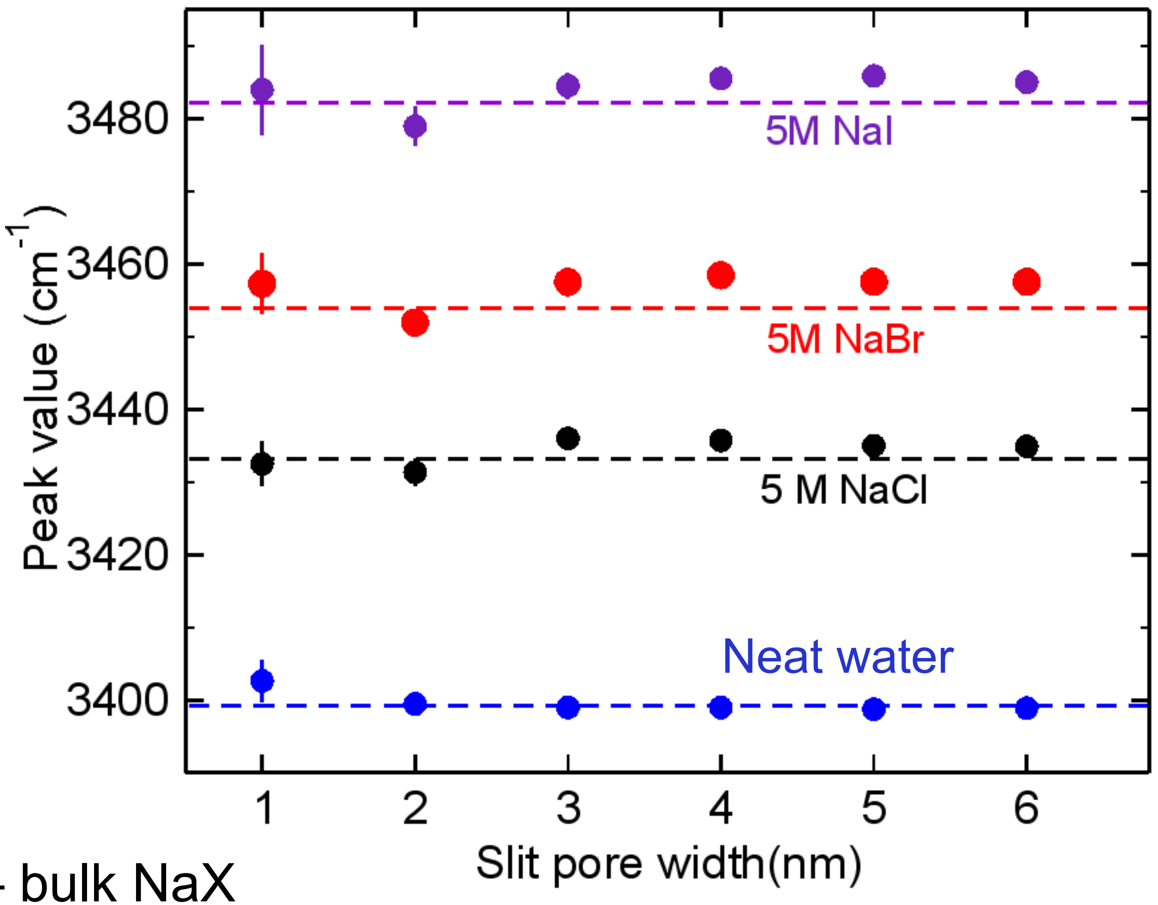




Effect of the type of halide on confined water IR spectra

Comparison of peak frequency



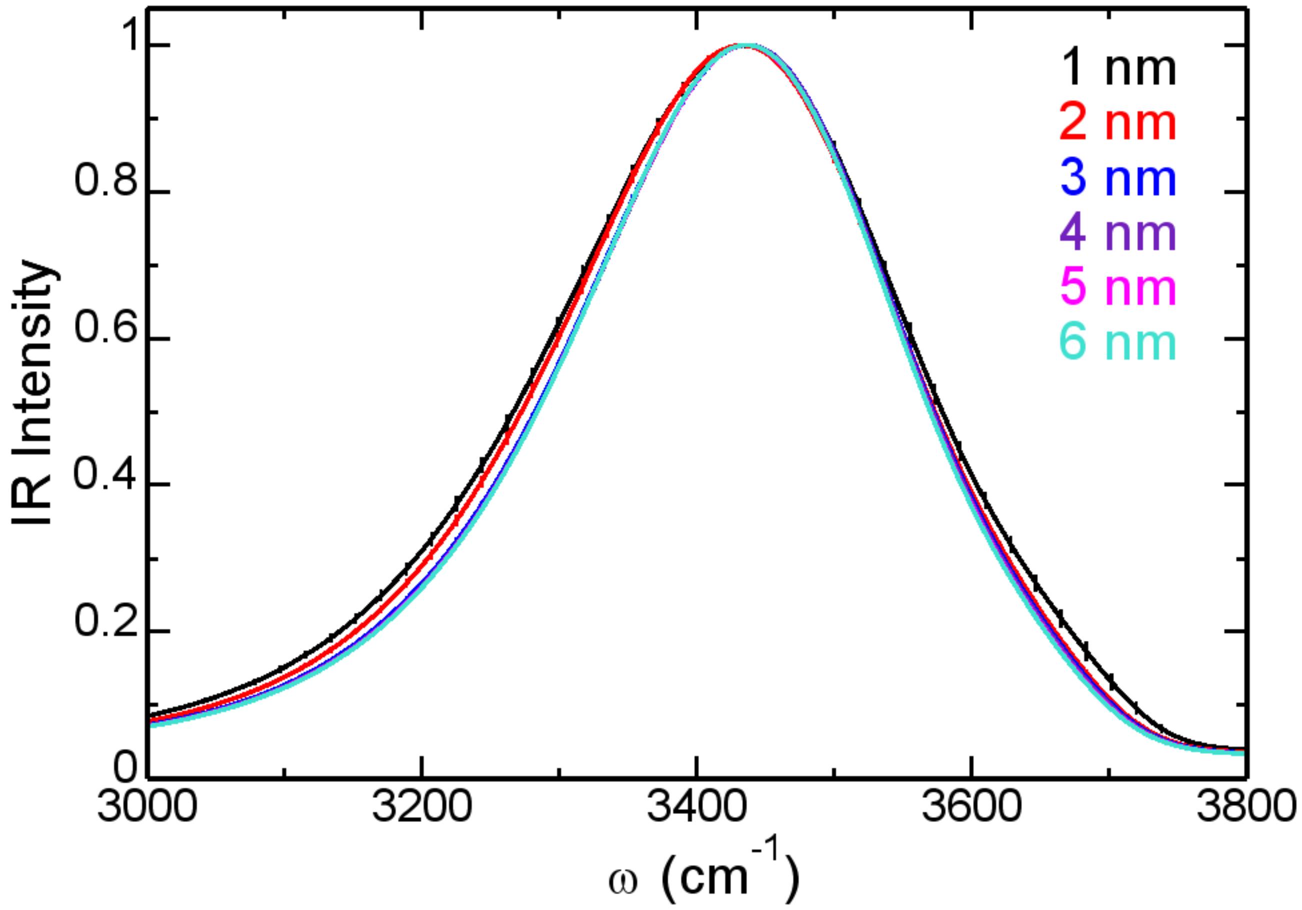


dashed line – bulk NaX
circles – confined NaX

Conclusion

Confined water IR spectra are

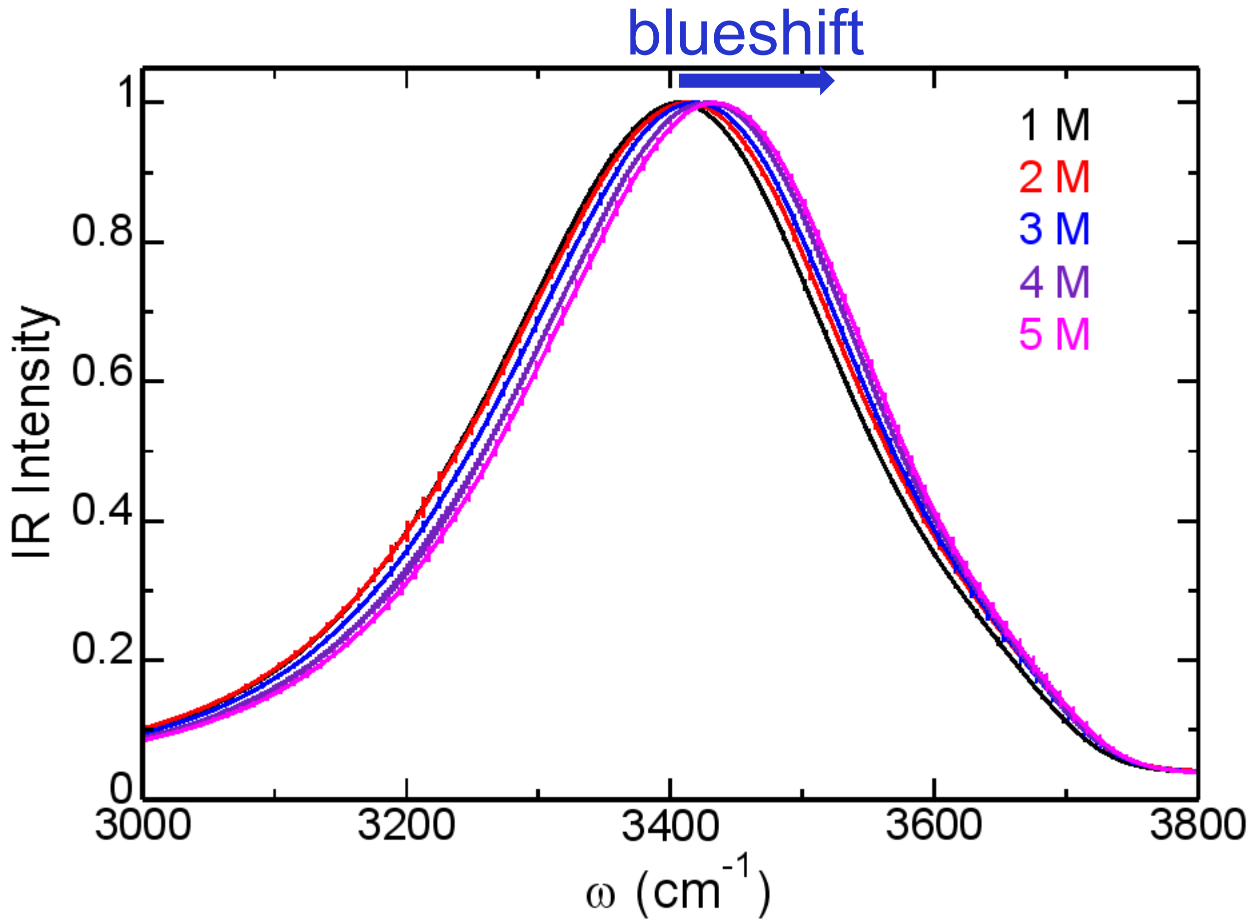
- less sensitive to the pore width



Conclusion

Confined water IR spectra are:

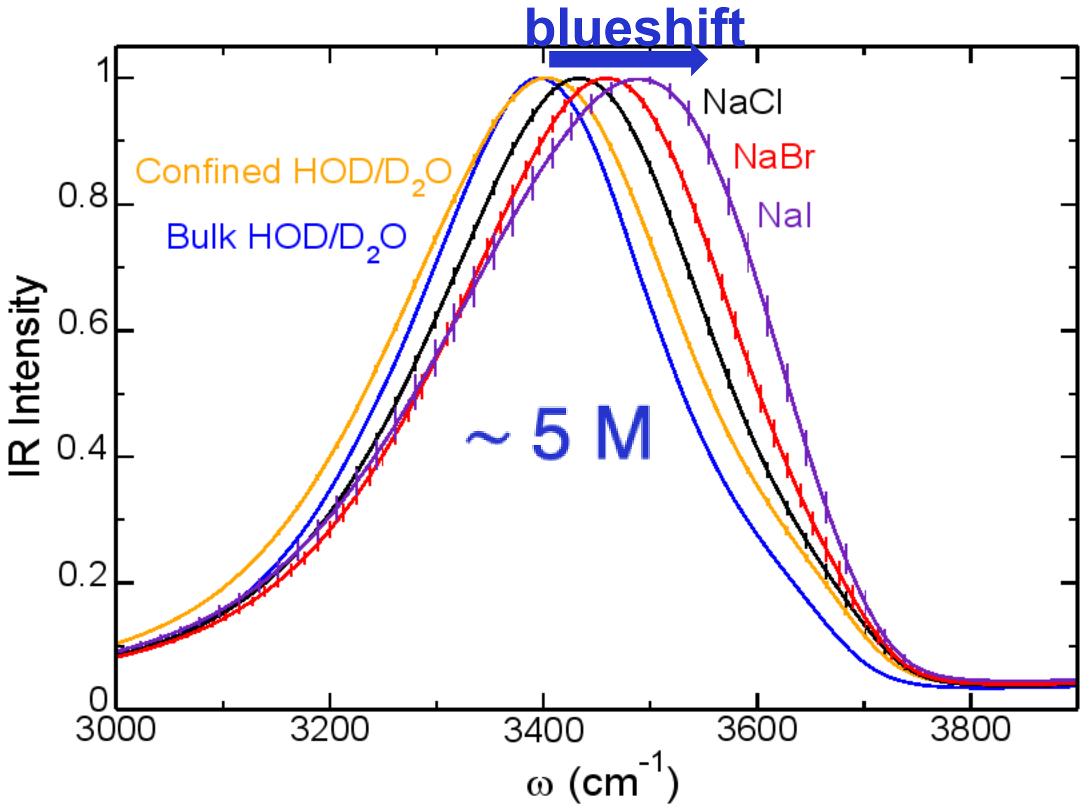
- ➢less sensitive to the pore width
- ➢less sensitive to the halide concentration



Conclusion

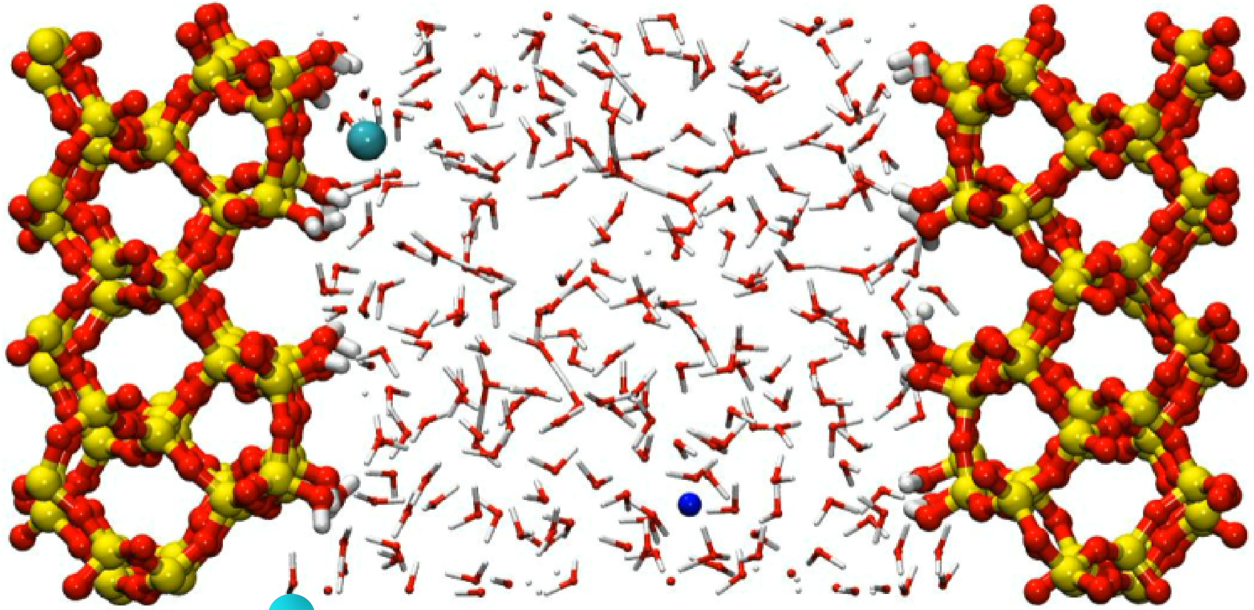
Confined water IR spectra are:

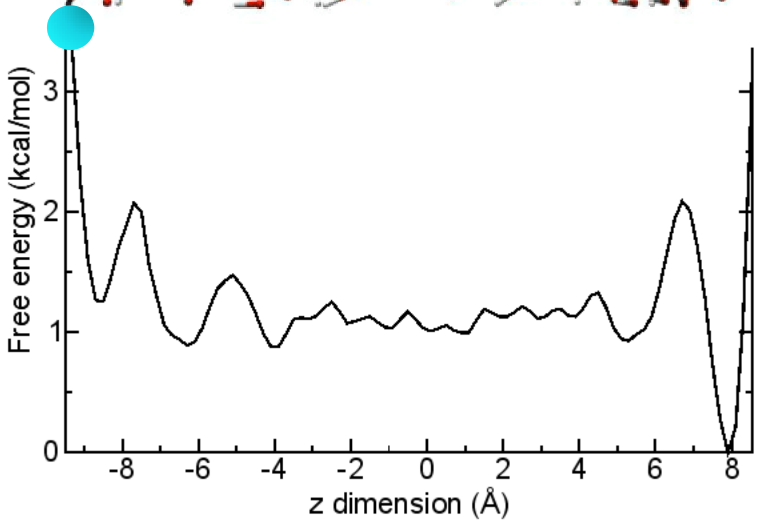
- ➢less sensitive to the pore width
- ➢less sensitive to the halide concentration
- ➢More sensitive to the halide type



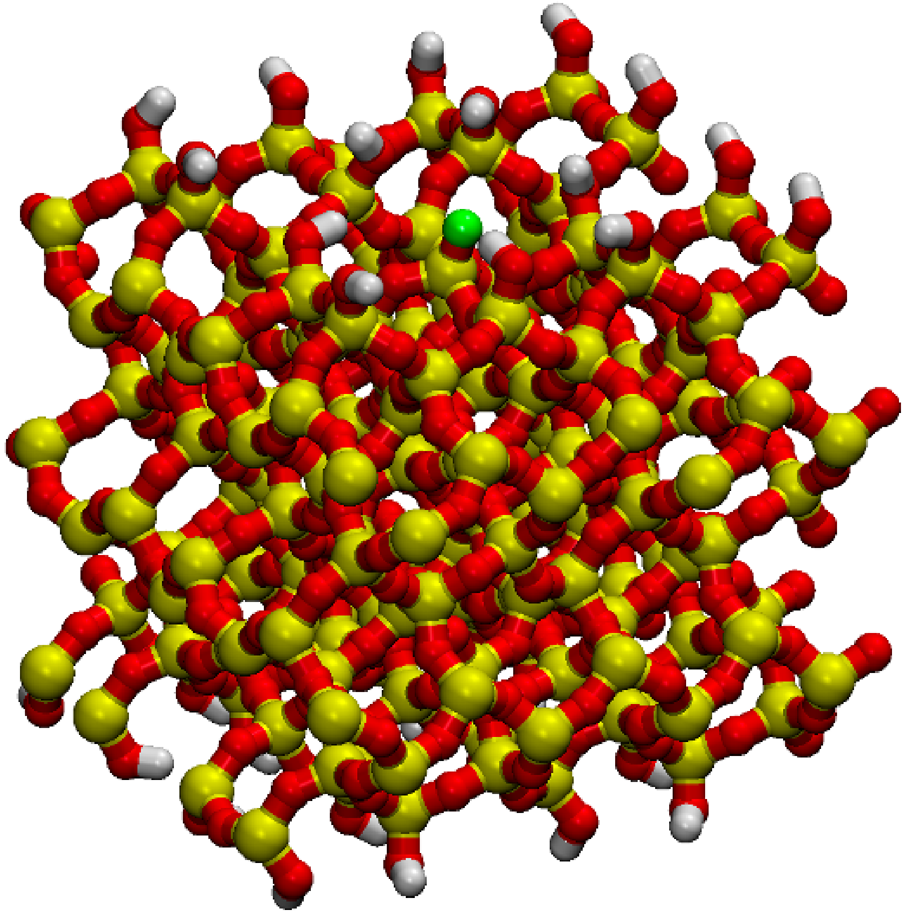
Future work

- Understanding the interactions of halides with the surface through solvation free energies





- Effect of pH on water vibrational properties : Charged silica surfaces



Acknowledgments

Collaborators

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Grant: DE-NA0003525