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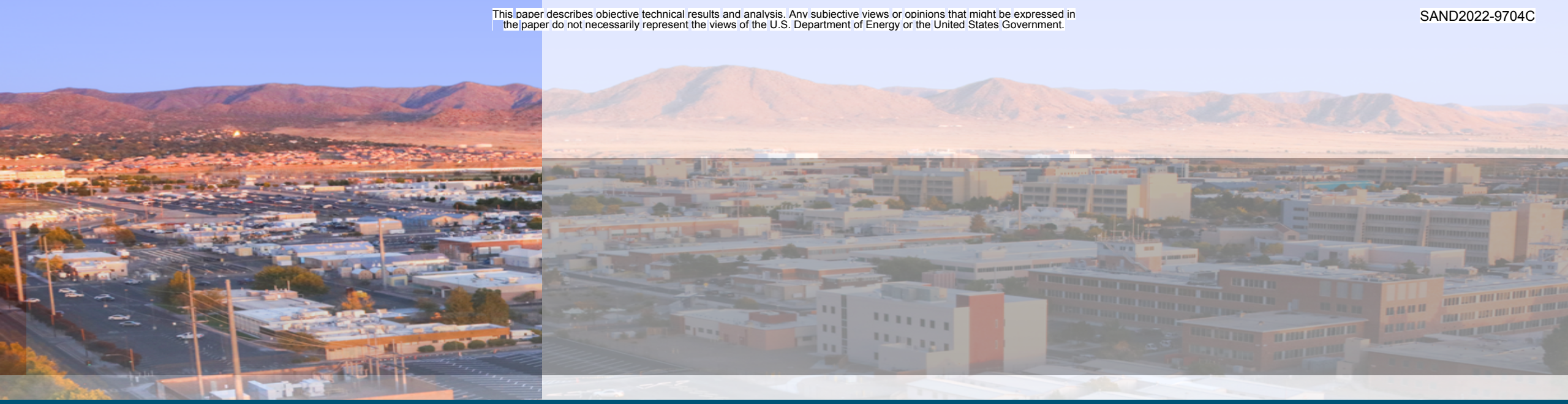

Sandia National Laboratories

Hydrogen-bonding networks in nanoconfined water

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U.S. DEPARTMENT OF ENERGY | Office of Science

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Acknowledgements

Funding: Basic Energy Sciences, DOE

User Facilities: APS, Argonne National Lab

Collaborators: Andrew Knight, Sandia National Labs
Kevin Leung, Sandia National Labs
Louise Criscenti, Sandia National Labs
Eric Coker, Sandia National Labs
Nikolai Kalugin, NM Tech University
Nadine Kabengi, Georgia State University

This material is based upon work supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences.

This research used resources of the Advanced Photon Source, a U.S. Department of Energy (DOE) Office of Science User Facility operated for the DOE Office of Science by Argonne National Laboratory under Contract No. DE-AC02-06CH11357.

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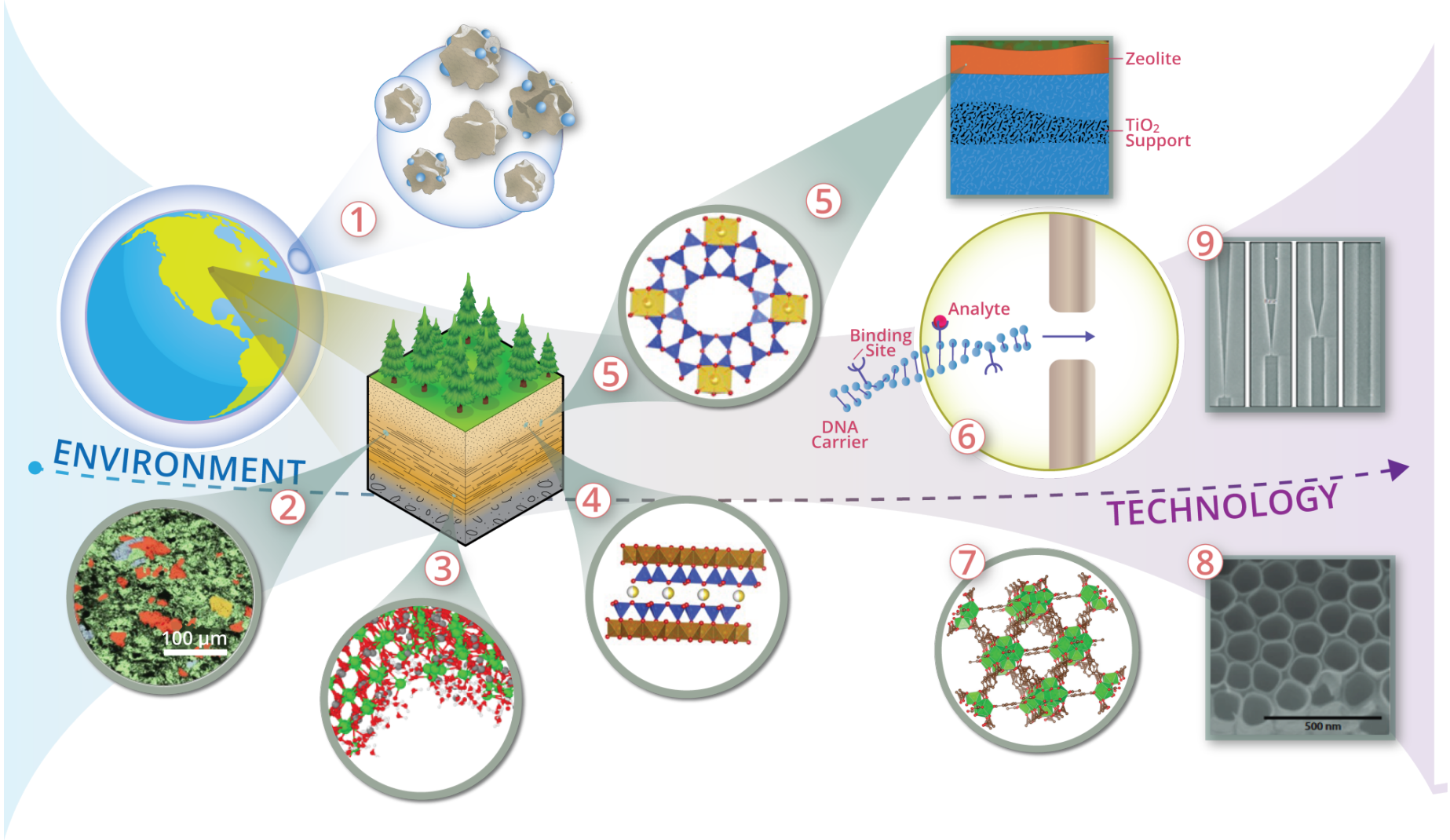
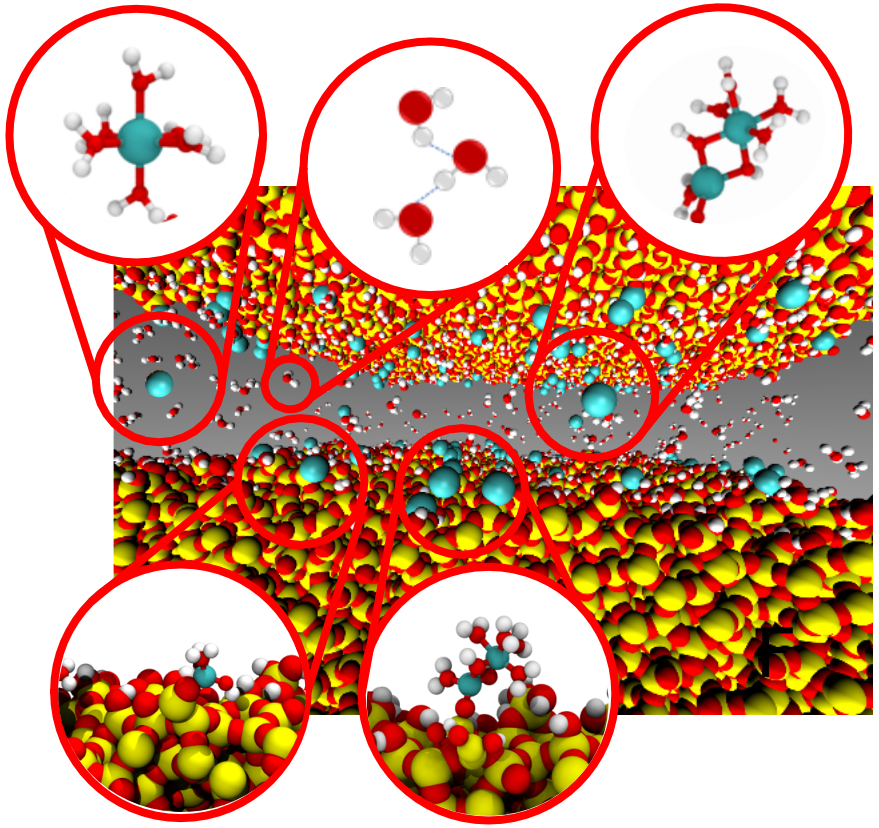
Nanoconfined chemical environments are important in the fate and transport of elements and in technological applications.



(1) atmospheric dust with nanopores and nm-scale thin water films; (2) nanopores in soil particles and sedimentary rocks; (3) nano-scale cracks in rocks; (4) nanochannels in clay minerals; (5) nanocages in natural zeolites, which are also used in industrial applications of catalysis, ion exchange, and in hierarchical membranes with nanoporous active layers (from Caro Chem. Soc. Rev., 2016. 45: 3468); (6) nanopore sensing and chemical analysis (adapted from Albrecht Annu. Rev. Anal. Chem. 2019. 12:371–87); (7) Synthetic metal organic frameworks UiO-66; (8) nanoporous TiO2 electrode in water splitting applications (from Baxter et al., Annu. Rev. Phys. Chem. 2014. 65:423–47); (9) nanofluidic «lab-on-a-chip» (from Zhou et al., Annu. Rev. Anal. Chem. 2011. 4:321–41). *Mineral structures were from American Mineralogist Crystal structure database and visualized with the Vesta 3.3.9 program.

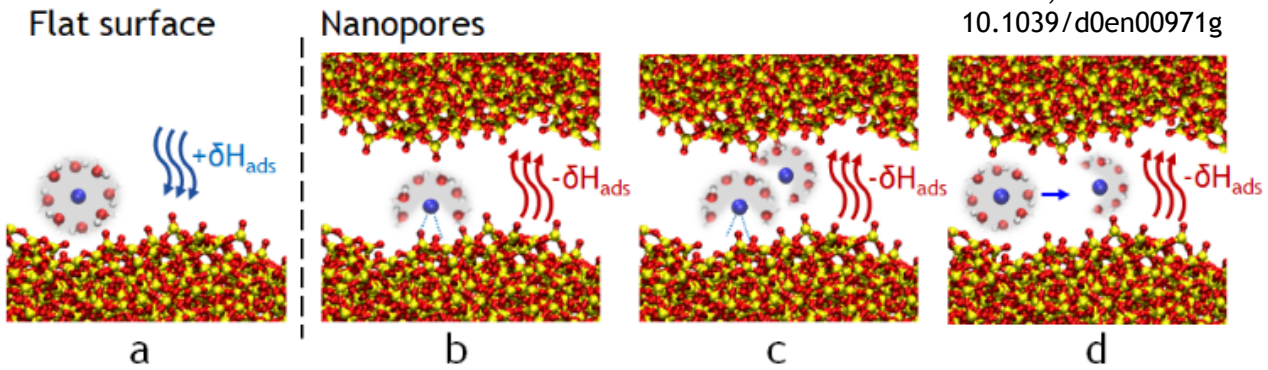


Emergent chemical behaviors in nanopores:

- Decreased dielectric constant[1-2], surface tension[3], and density of water.[3]
- Decreased solvation energies of metal cations.[4]
- Increased inner-sphere coordination of metal cations.[4]
- Enhanced metal adsorption[5-6], modified diffusion properties.[7,8]

Adsorption in SiO_2 nanopores:

Ilgen et al. Environ. Sci. Nano 8, 2021 DOI: 10.1039/d0en00971g



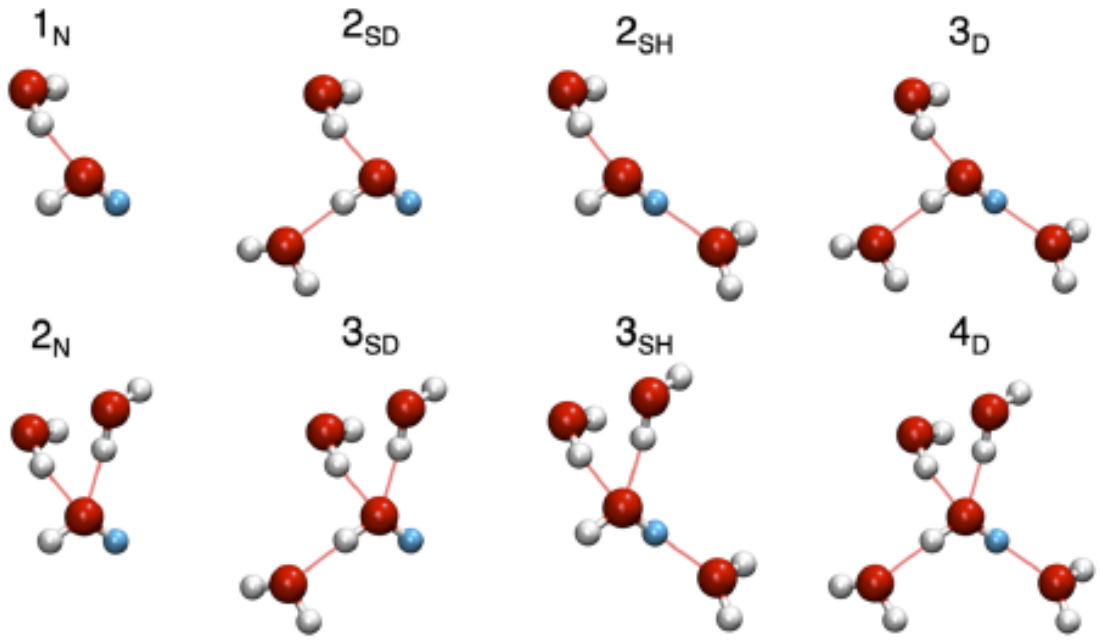
Proposed Ln^{3+} adsorption mechanisms which can result in an *endothermic* (+δH) or an *exothermic* (-δH) signal. (a) Ln^{3+} adsorption as an outer-sphere complex on unconfined SiO_2 surface; (b) Ln^{3+} adsorption as an inner-sphere complex on confined SiO_2 surface; (c) Ln^{3+} adsorption as an inner-sphere dimer complex on confined SiO_2 surface; (d) Decrease in ΔG_{hydr} under nanoconfinement.

Ion solvation thermodynamics and structures are dictated by thermodynamics and structure of H_2O in nanopores

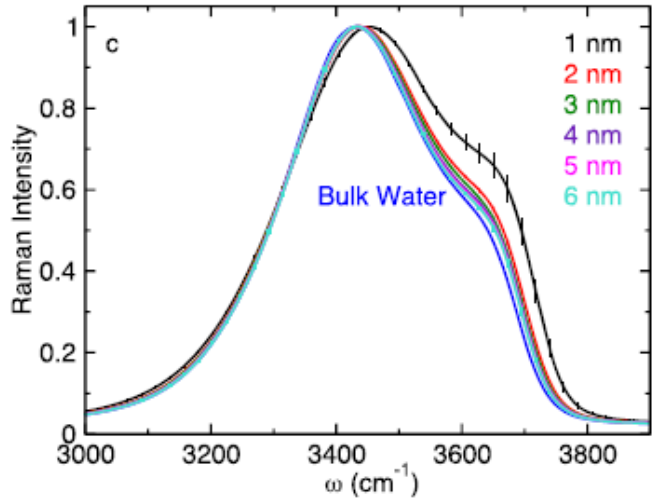
[1]Marti et al., *J. Phys. Chem. B* (2006)
[2]Senapati et al., *J. Phys. Chem. B* (2001)
[3]Takei et al., *Colliod Polym. Sci.* (2000)
[4]Kalluri et al., *J. Phys. Chem. C* (2011)
[5]Wang et al., *Geology* (2003)
[6]Zimmerman et al., *Environ. Sci. Techol.* (2004)
[7]Samsom and Biggin, *Nature* (2001)
[8]Ma et al., *JACS* (2019)

H_2O structures in nanopores: hydrogen bonding

Possible HB structures in dilute D_2O in H_2O



- Slower H_2O re-orientation dynamics;
- HB networks in H_2O confined within SiO_2 nanopores: near surface-H_2Os characterized by HB with Si-OH and Si-O-Si sites[1,2];
- H_2O populations are distinguishable in experimental Raman spectra: HB and not-HB components;

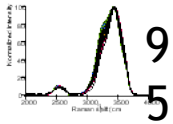


Senanayake et al. J. Chem. Phys. 154, 2021 DOI: 10.1063/5.0040739

[1]Harting et al., (2000)
[2]Senanayake et al. J. Chem. Phys. 154, (2021)

Methods

Raman spectroscopy measurements



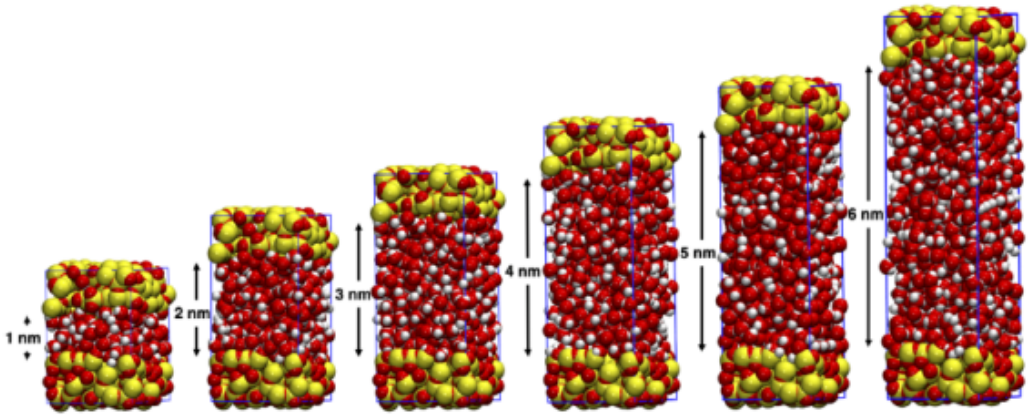
95 vol% H_2O /
5 vol.% D_2O

v_1, v_3 OH

v_1, v_3 OD

- XploRA Plus Raman microscope (HORIBA Scientific);
- Cooled CCD detector (Jobin Yvon's Synapse camera);
- Unpolarized 532 nm laser, ~100 mW power at 10-25% power;
- 10x magnification, NA 0.25; laser spot diameter 2.6 microns;
- 20 sec exposure, 30 scans average, range 2000 to 4000 cm^{-1}.
- Spectrometer calibration every 24 hours on Si(0) wafer;
- Dilute D_2O in H_2O to exclude resonant vibrational coupling ~3200 cm^{-1}.

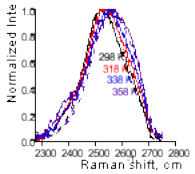
Molecular Dynamics simulations



- Classical MD simulations – LAMMPS software;
- The SPC/E model - to describe the water interactions;
- The silica slab (Si & O) - kept frozen throughout the simulation silanol and geminal interactions - Gulmen–Thompson force field;
- Intermolecular interactions evaluated with a cutoff of 10.5 Å;
- Long-range electrostatic interactions - three-dimensional periodic boundary conditions and the particle–particle particle mesh (PPPM) solver with a tolerance of 10−4;
- Each slit-pore trajectory was run for 1 ns with a 1 fs time step;
- Data collected every 2 fs.

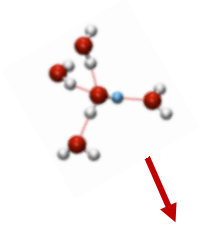
Results: OD stretching in H_2O / D_2O with increasing temperature

Raman spectroscopy measurement

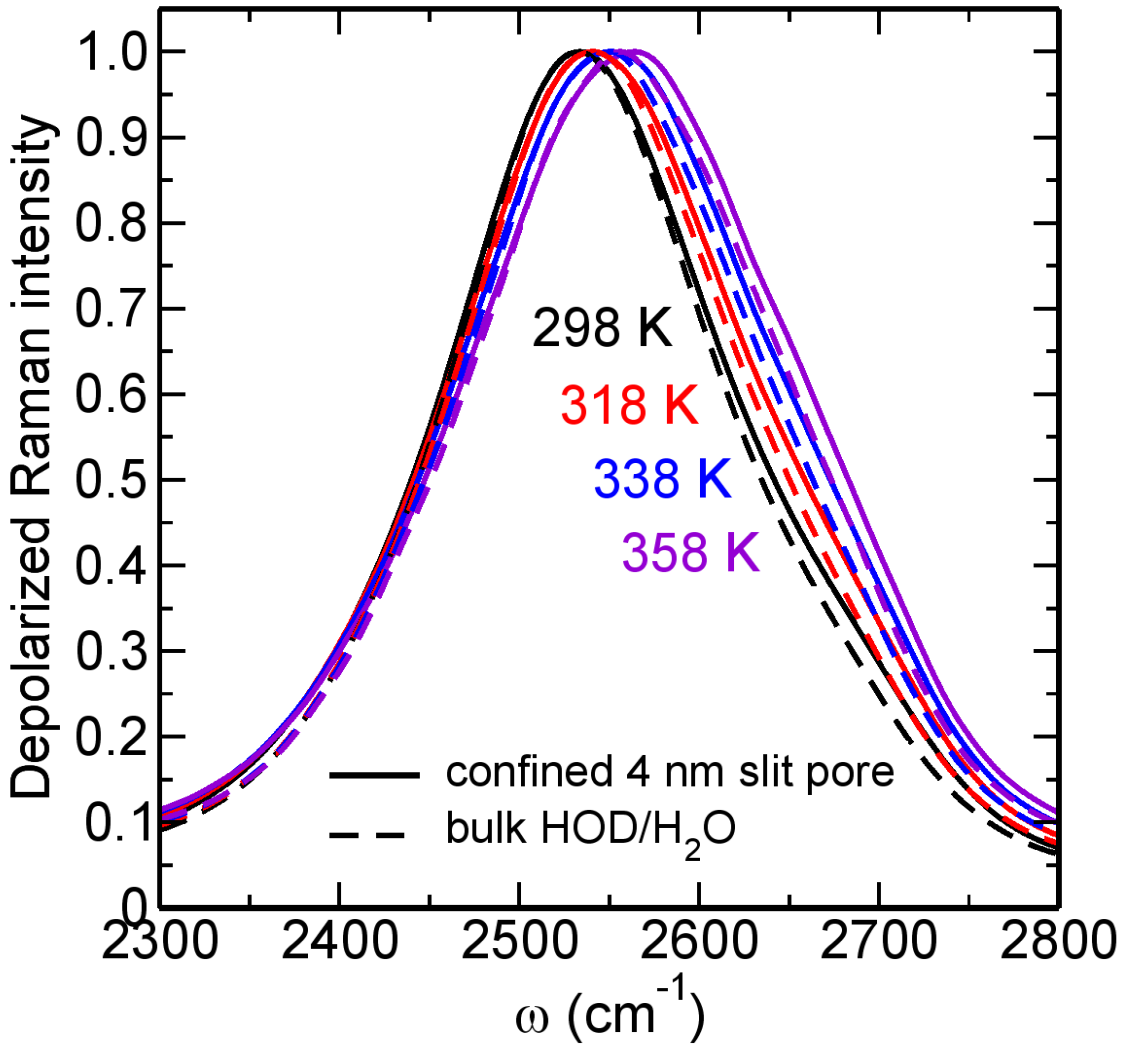


4 nm cylindrical pore

bulk H_2O/D_2O



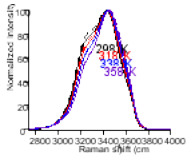
2440

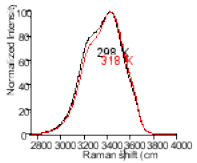


- 2440 cm^{-1}: 4-coordinated, ice-like scatterers, higher contribution in 4 nm pores compared to bulk. Blue shift: HBs get weaker with increasing T, non-HB contribution increases with T; HBs are weaker in SiO_2 pores due to nanoconfinement and HBs with SiO_2 surfaces.

Results: OH stretching in H_2O / D_2O with increasing temperature

Raman spectroscopy measurements





4 nm pore
bulk H_2O/D_2O

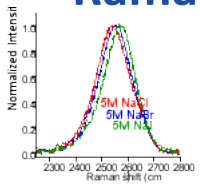
7 nm pore
bulk H_2O/D_2O

- 3200 cm^{-1} intensity: interoscillator coupling,[1] the intensity is lower in 4 nm pores, may indicate distorted directional character of HB interactions (in-phase vibrational coupling); this effect is not seen in 7 nm pores;
- Blue shift: HBs are weaker with increasing T.

[1]Hare and Sorenson, J/ Chem P*hys. (1991)*

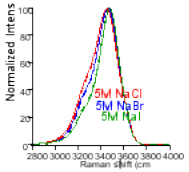
Results: H_2O / D_2O + salt solutions at RT

Raman spectroscopy measurements



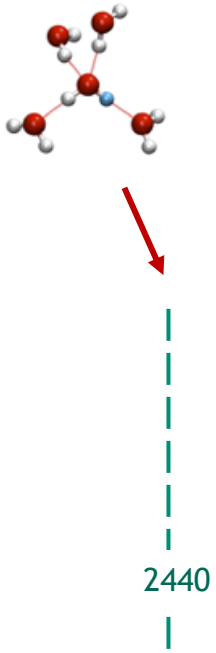
OD stretching

ΔG_{solv} (Cl^-) =-340 kJ/mol
ΔG_{solv} (Br^-) =-315 kJ/mol
ΔG_{solv} (I^-) =-275 kJ/mol



OH stretching

4 nm cylindrical pore
bulk solution



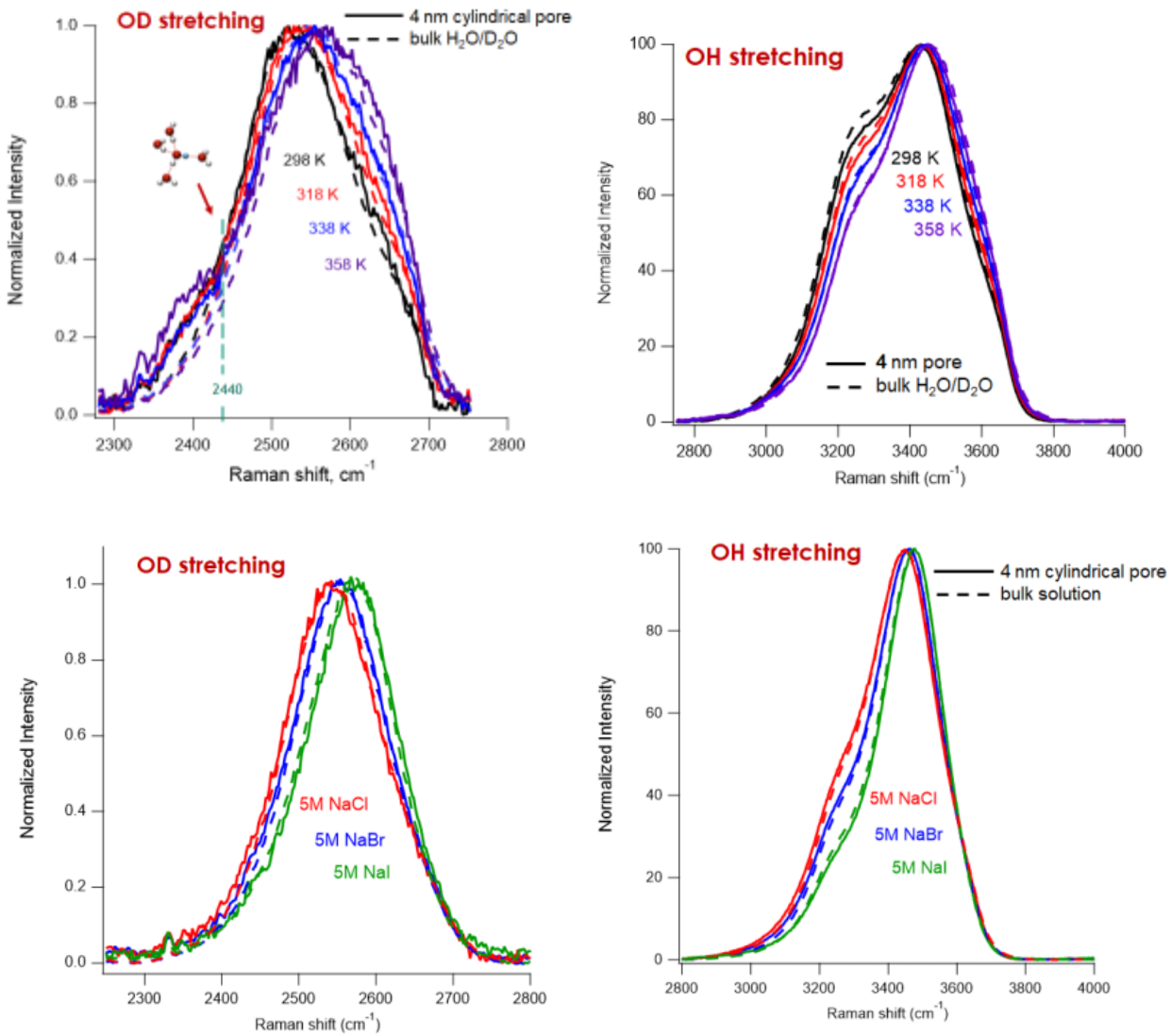
- 2440 cm^{-1}: 4-coordinated, ice-like scatterers, slightly higher contribution in 4 nm pores.
- 3200 cm^{-1} intensity: interoscillator coupling,[1] the intensity is slightly lower in 4 nm pores for Cl^-, Br^-, but not I^-
- Blue shift: with decrease in anion's solvation energy.

Summary

- Nanoconfinement effects on HB structures are more pronounced for pure D_2O/H_2O compared to 5M salt solutions because the electrical double layer estimated as Debye length is vastly different:
  - ~1000 nm in water, and
  - <0.01 nm in 5M NaX solutions

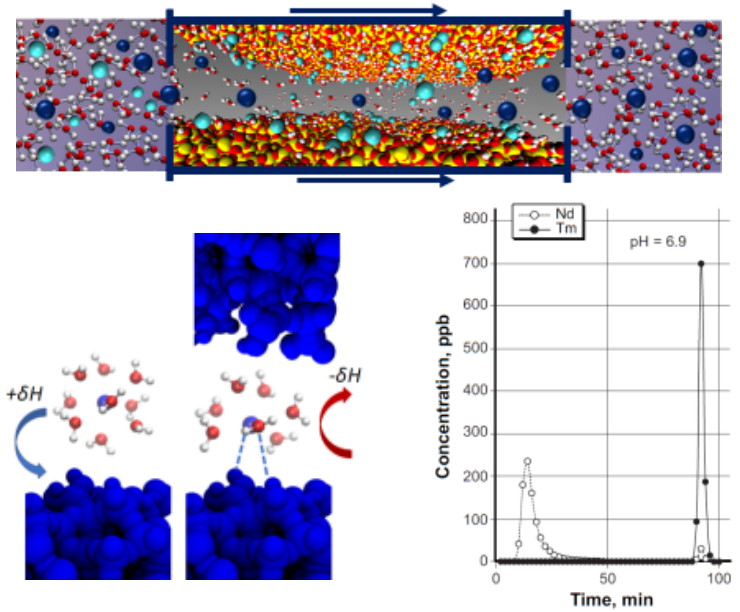
- Nanoconfinement and SiO_2-H_2O interactions may produce two populations of H_2O in nanopores (2440 cm^{-1} contribution in 4 nm pores indicate 4-coordinated, ice-like scatterers, and the increased intensity in ~ 2650 cm^{-1} region indicative of H_2O population with broken or weak HBs)

Raman spectroscopy measurements



Broader impacts

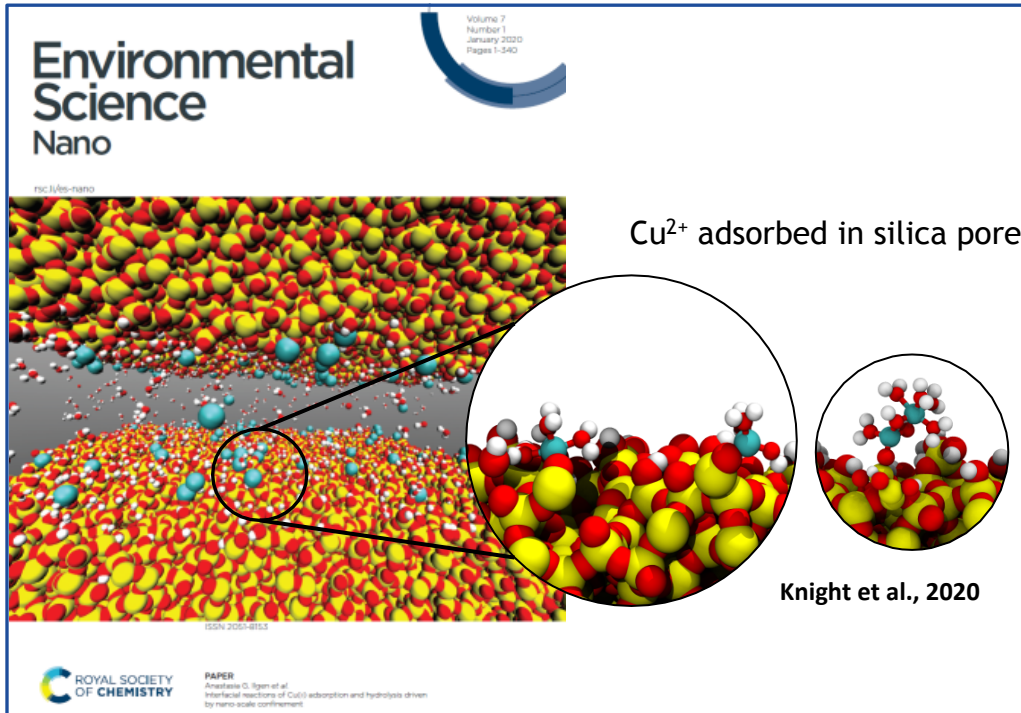
Separation Science



Understanding how Ln^{3+} adsorption structure and energetics change under confinement, enables improved separation strategies for critical rare earth elements.

Patent:
Ilgen, Non-provisional patent application "Systems and Methods for Separating Rare Earth Elements Using Mesoporous Materials". Filed on 3/11/2020.

Environmental Fate and Transport



Understanding how ion adsorption structure and energetics change under confinement, enables improved fate and transport models for contaminants.

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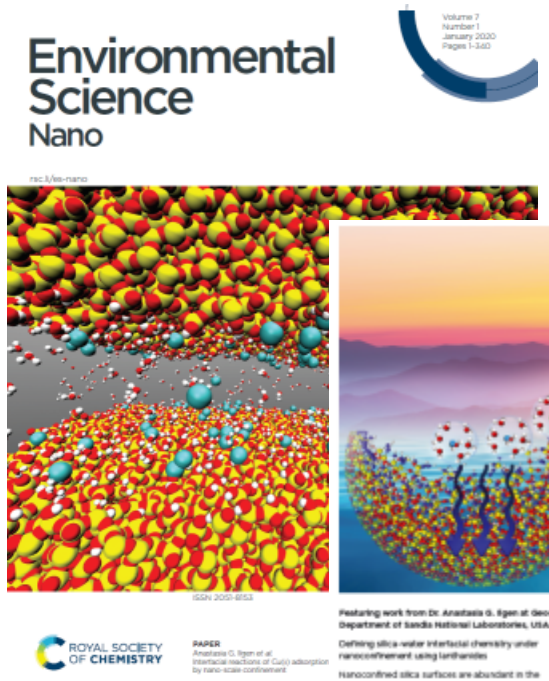
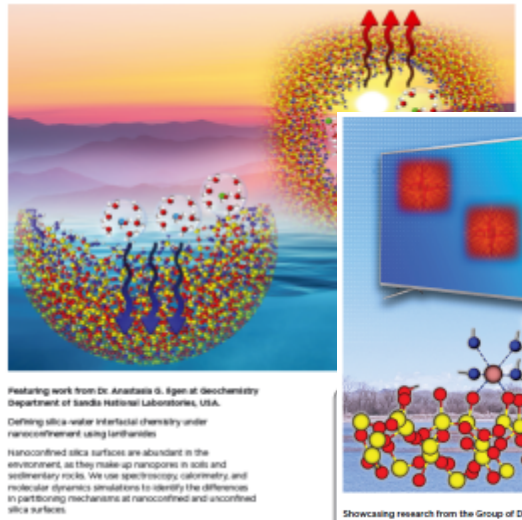
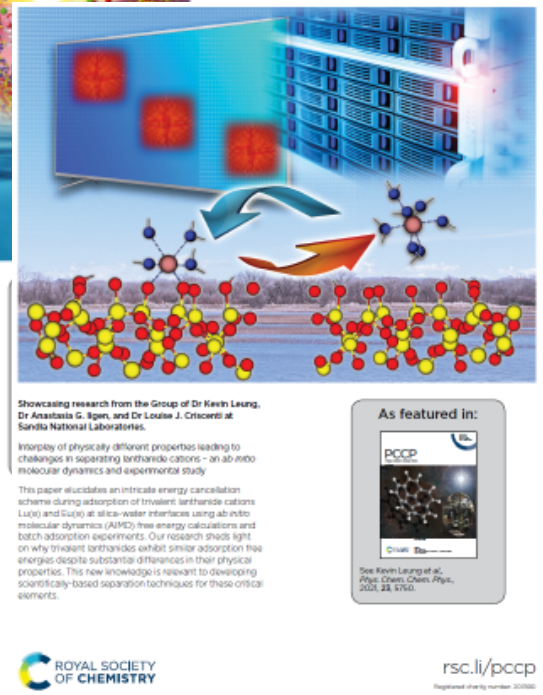
Thank you.



Knight et al.,
Environmental
Science Nano, 2020



Ilgen et al.,
Environmental
Science Nano, 2021



Leung et al.,
Environmental
Science Nano, 2021

Simulations of the IR and Raman spectra of water confined in amorphous silica slit pores

Cite as: J. Chem. Phys. 154, 104503 (2021); doi: 10.1063/5.0040739
Submitted: 15 December 2020 • Accepted: 16 February 2021 •
Published Online: 8 March 2021

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Senanayake et al., Journal of
Chemical Physics, 2021

Greathouse et al.,
Environmental
Science Nano, 2021