

Sandia National Laboratories

Geochemistry in Nanopores

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Nanoscale Confinement: Similar to temperature effects, the physical and chemical properties of water when confined in porous materials, diverge from the bulk as evidenced by a measurable decrease in the dielectric constant¹⁻², surface tension³, and density of water³. Solvation energies of metal cation decrease with pore size leading to a greater tendency to form inner sphere coordination⁴⁻⁶.

Physical Measurements: Physical measurements, including thermal gravimetric analysis and differential scanning calorimetry along with water and N₂ adsorption measurements, were made to assess H-bonding interactions and deviations in water properties upon confinement relative to the bulk.

Research Goals and Hypothesis : The *goal* of this project is to understand how nano-scale confinement affects the energetics and kinetics of geochemical reactions. To achieve this goal, we focused on the properties of water in confinement using synthetic, mesoporous material as the implications resulting from deviations in water chemistry affect cation adsorption chemistry. *We hypothesize that these nano-scale confinement effects can be linked to deviations in water properties, and that these water properties are a result of changes to the H-bonding network.*

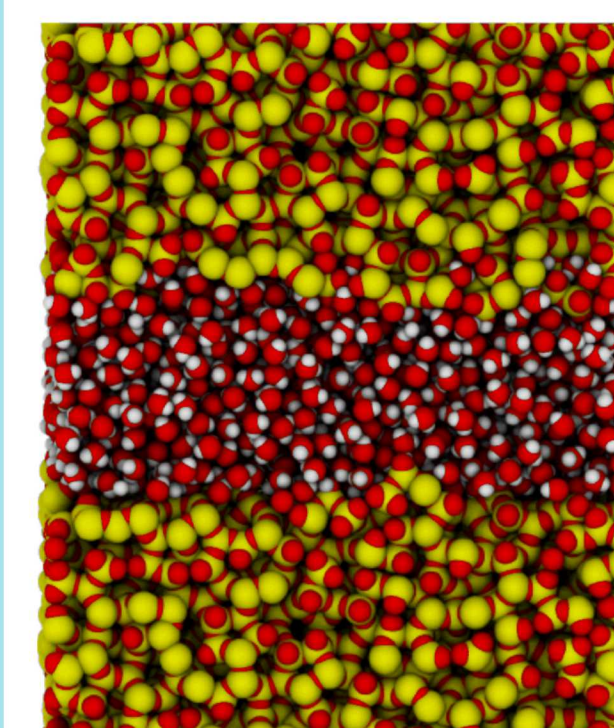


Figure 1. Model of a silica water pore

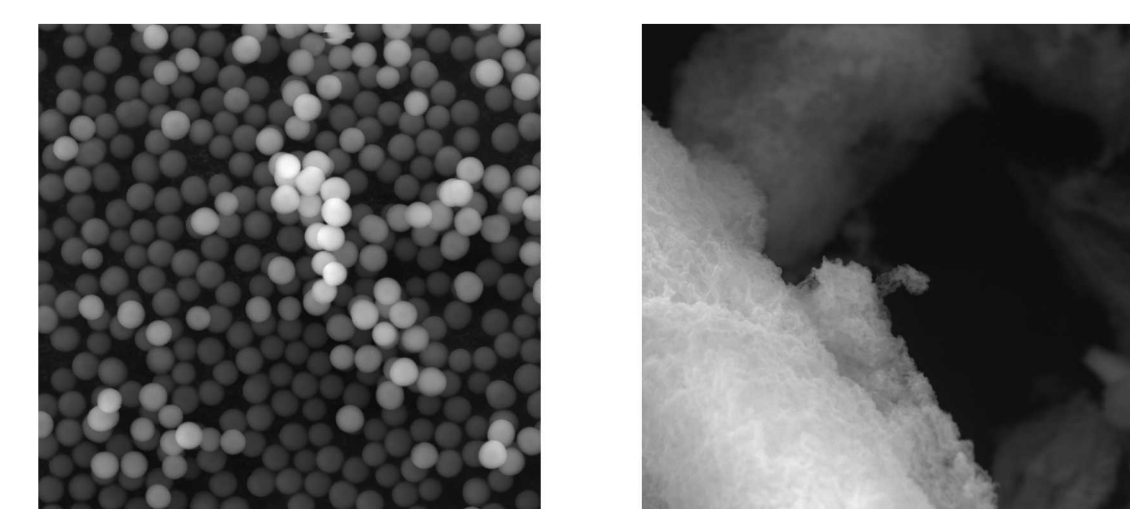


Figure 2. SEM images of ms-silica and SBA-15 silica materials

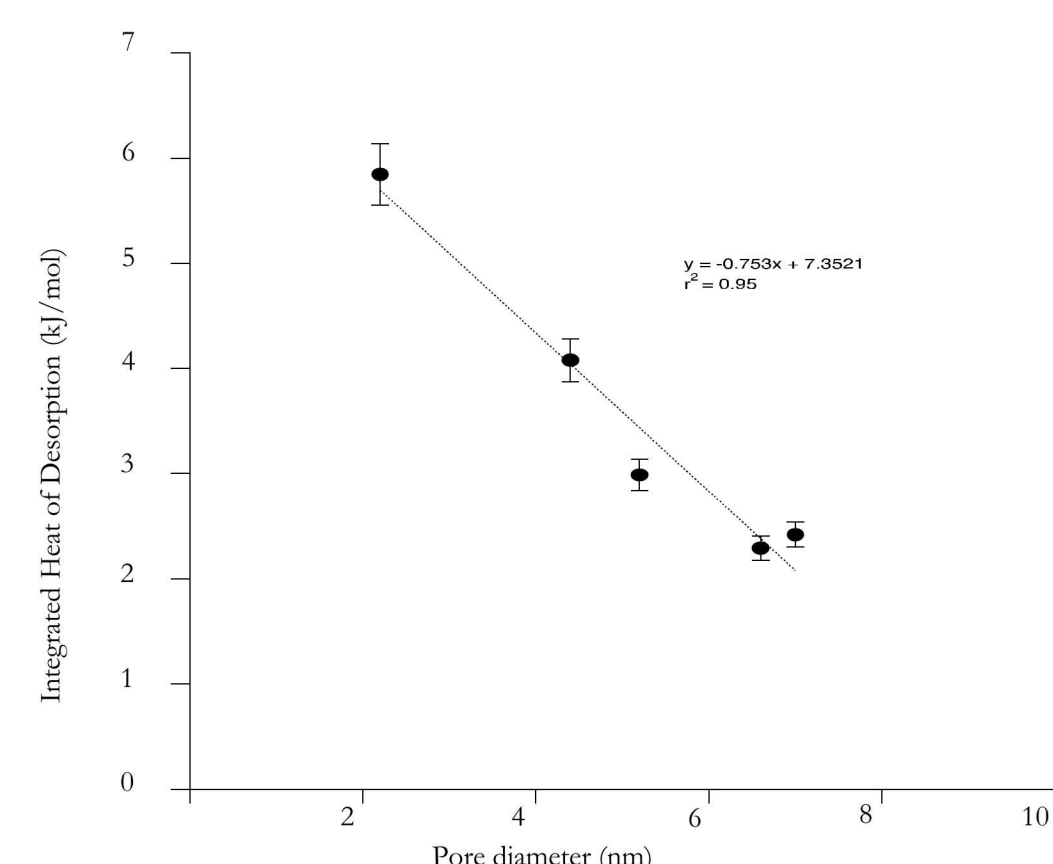


Figure 3. Integrated heats of desorption versus pore diameter

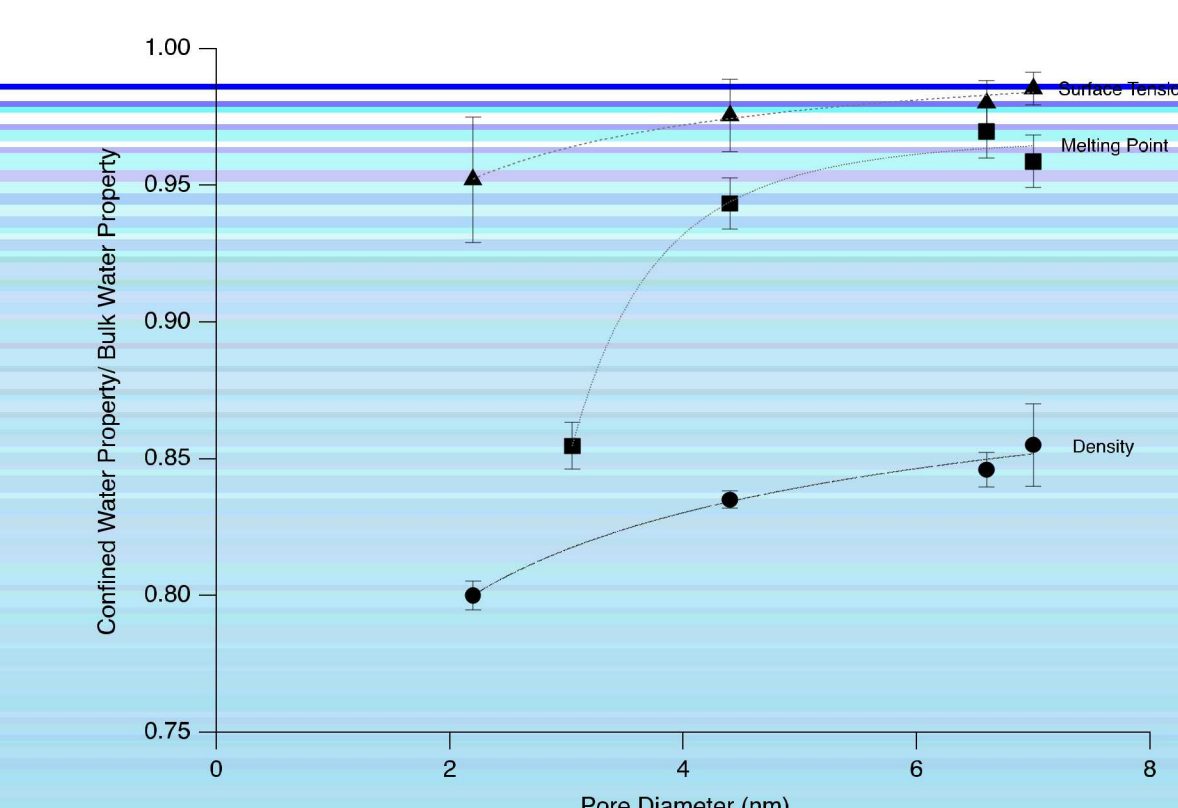


Figure 5. Confined water properties relative to bulk water, including surface tension, density, and melting point temperature versus pore diameter

References: ¹Marti et al., *J. Phys. Chem. B* (2006), ²Senapati et al., *J. Phys. Chem. B* (2001), ³Takei et al., *Colloid Polym. Sci.* (2000), ⁴Kalluri et al., *J. Phys. Chem. C* (2011), ⁵Wang et al., *Geology* (2003), ⁶Zimmerman et al., *Environ. Sci. Technol.* (2004), ⁷Malash et al., *Chem. Eng. J.* (2010), ⁸Knight et al. (2018) *Geochemical Transactions*

Table 1. Table of physical properties of the silica materials used in this study

Material	Pore size (nm)	BET Surface Area (m ² /g)	Pore Volume (cm ³ /g)	-OH-density (-OH/nm ²)	Reference
SBA-15-8	7.0 ± 0.3	661 ± 5	1.21 ± 0.03	1.8 ± 0.2	Knight et. al. (2018)
SBA-15-6	5.2 ± 0.2	603 ± 16	0.87 ± 0.03	1.9 ± 0.2	Knight et. al. (2018)
SBA-15-4	4.4 ± 0.1	580 ± 13	0.67 ± 0.04	2.3 ± 0.2	Knight et. al. (2018)
ms-silica-4	6.6 ± 0.1	253 ± 3	0.45 ± 0.03	2.6 ± 0.3	This study
ms-silica-2	2.2 ± 0.2	1090 ± 19	0.50 ± 0.02	1.1 ± 0.2	This study
MCM-41	1.55 ^a	861 ^a	0.865 ^a	0.59 ± 0.3 ^b	^a Takei et al. (2000), ^b This study

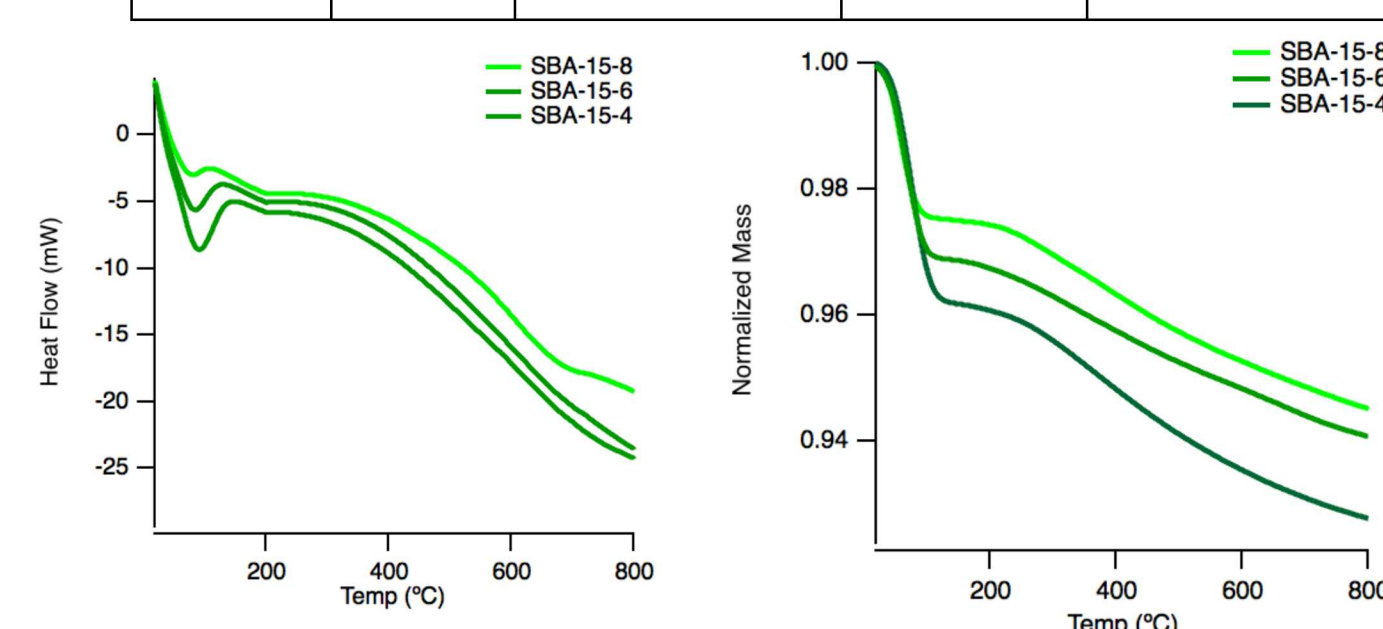


Figure 4. DSC and TGA analyses of SBA-15-8, SBA-15-6, and SBA-15-4

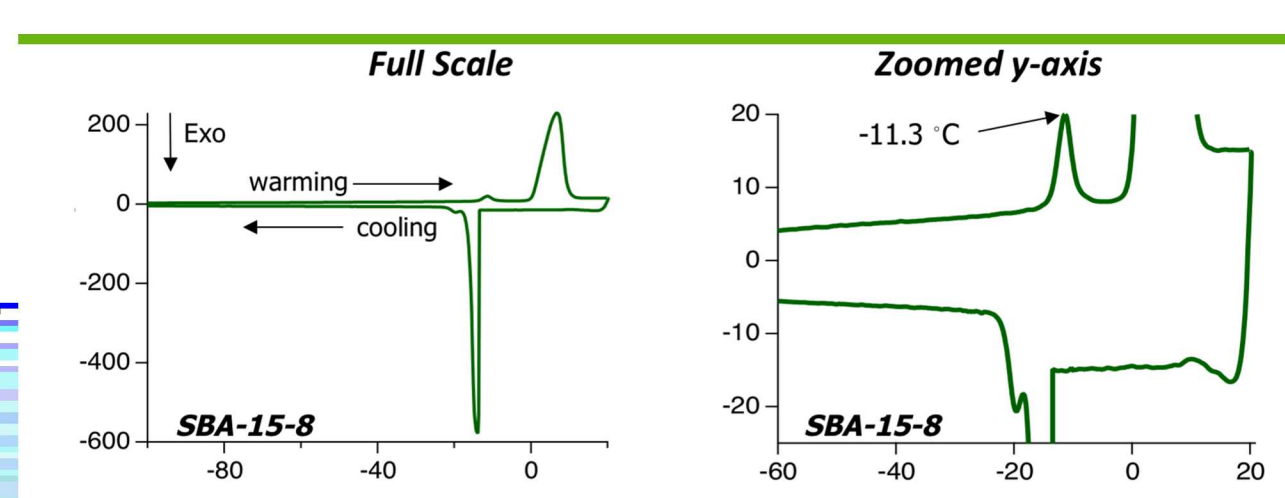


Figure 6. Melting point temperature determination of SBA-15-8

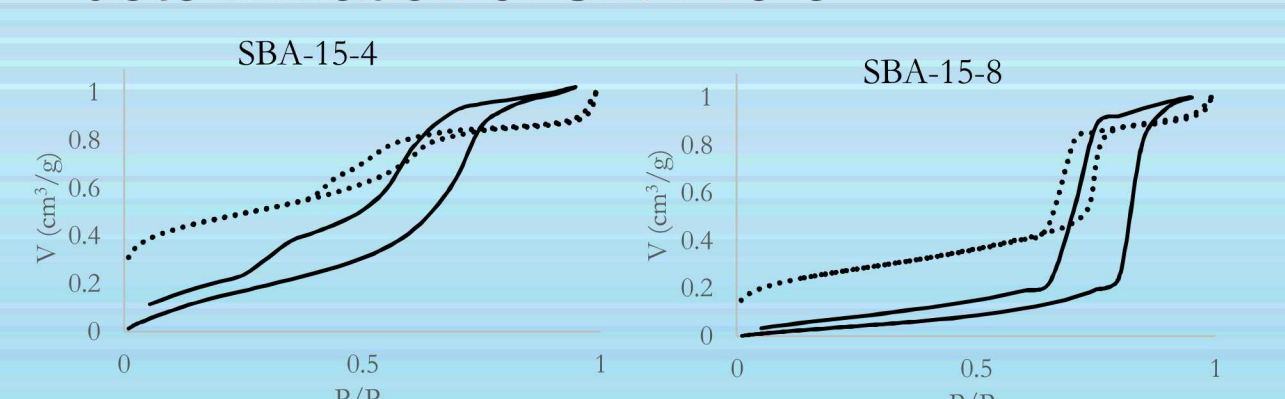
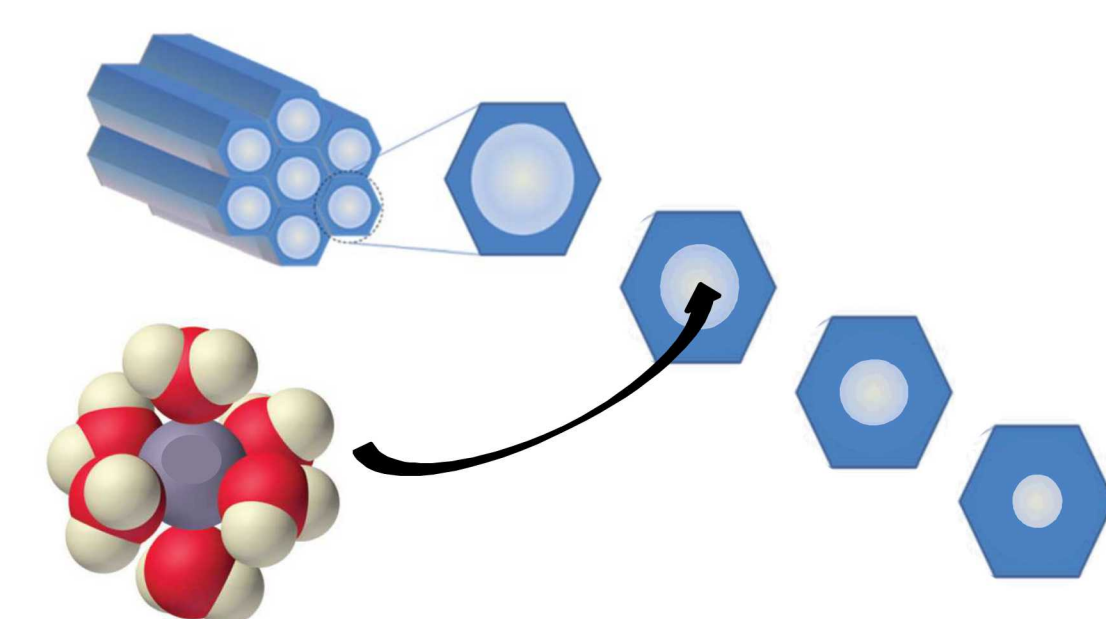


Figure 7. Water and Nitrogen adsorption isotherms for SBA-15-4 and SBA-15-8 used to determine the density and surface tension of water in the pores.



Vibrational Spectroscopy: Vibrational measurements, including Raman scattering and ATR-FTIR, were used to probe changes in the H-bonding network resulting from confinement. This was done by evaluating the connectivity band, libration band, bending band, and O-H stretch band of water.

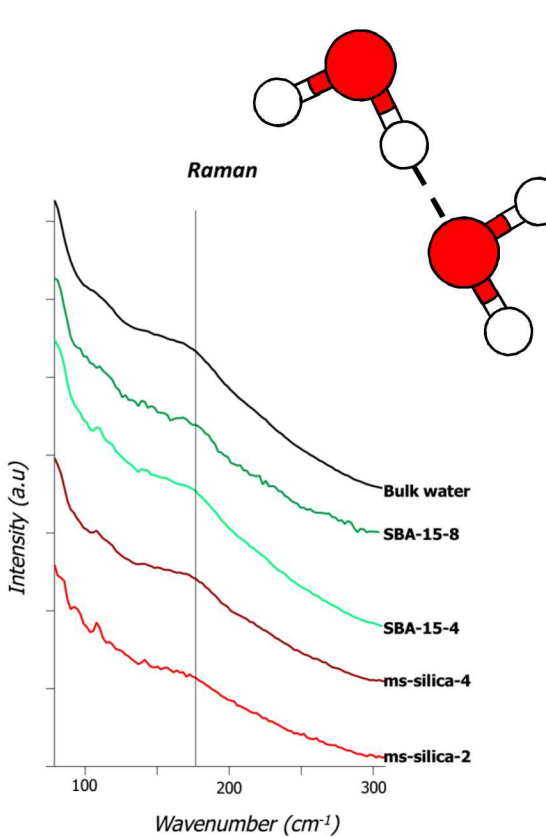


Figure 8. Raman spectra showing the connectivity band of free bulk water, SBA-15-8, SBA-15-4, ms-silica-4, and ms-silica-2.

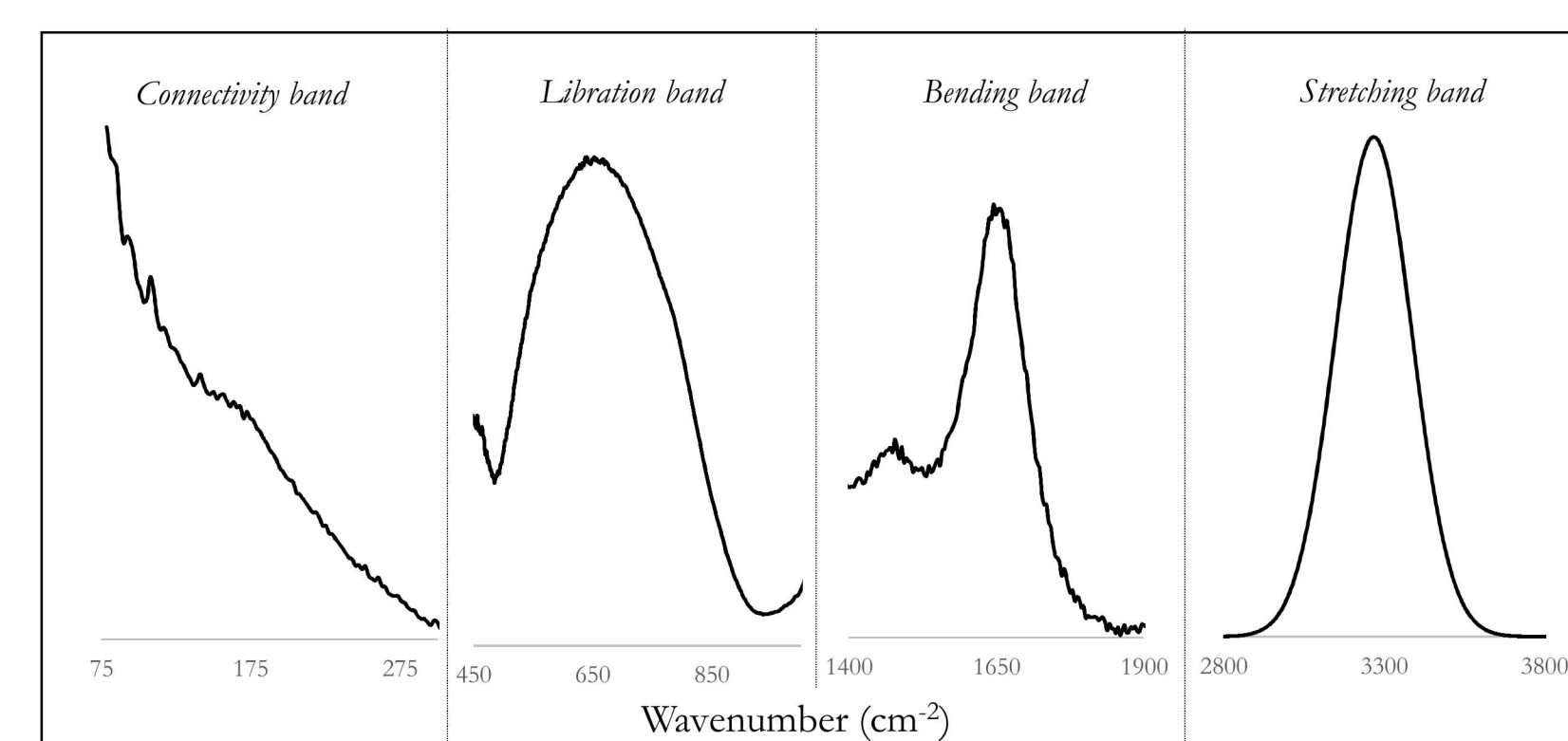


Figure 9. Spectroscopic summary of the vibrational bands evaluated to understand the changes to H-bonding as a function of pore diameter. While the connectivity and O-H stretch regions showed changes, the Libration and bending bands did not deviate much between nano-confined water and bulk.

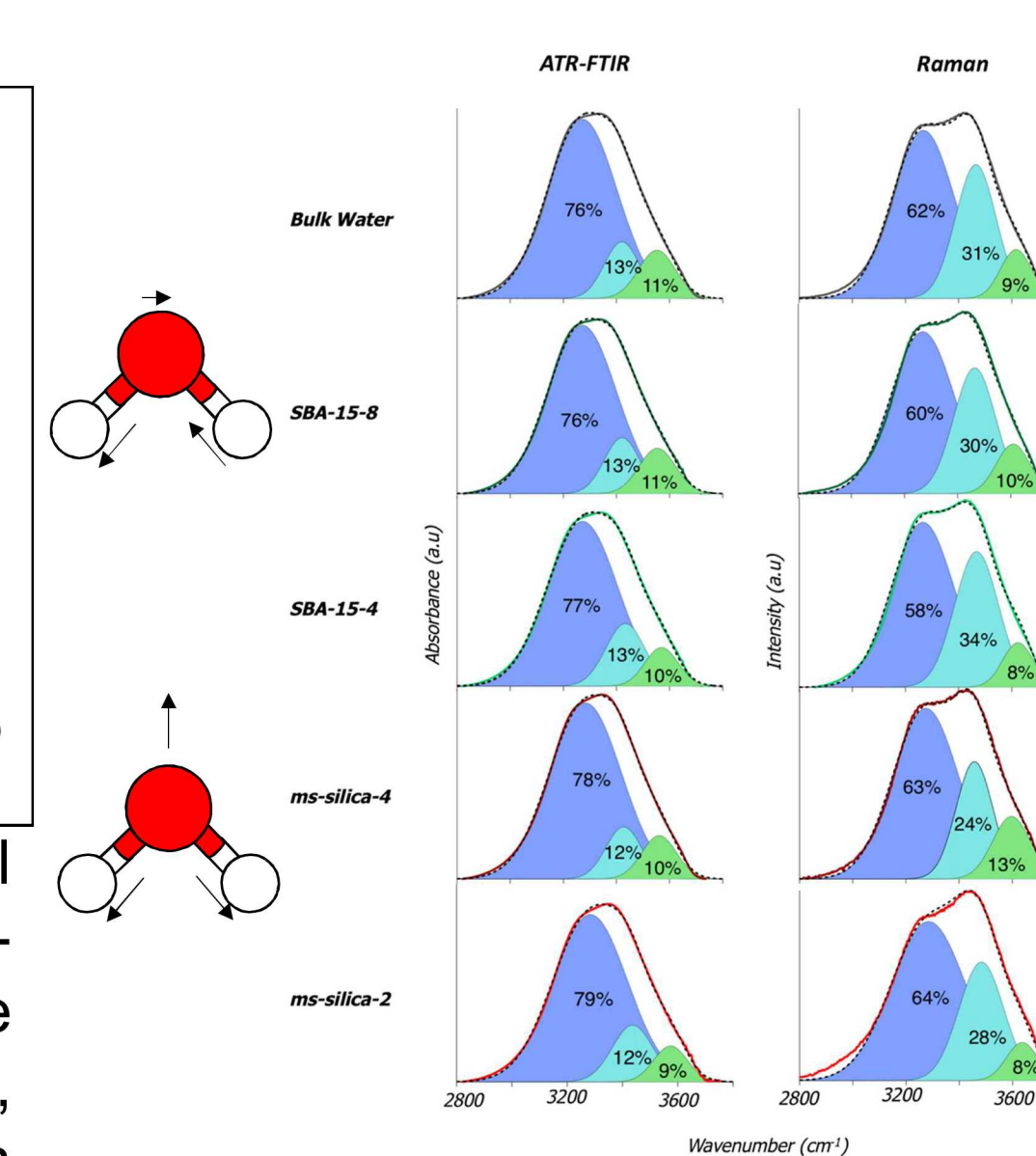


Figure 10. ATR-FTIR and Raman spectra showing the O-H stretching band of free bulk water, SBA-15-8, SBA-15-4, ms-silica-4, and ms-silica-2. The adsorption was fit with three features describing different H-bonding environments, specifically network water (NW), intermediate water (IW), and multimer water (MW). The dotted line in the ATR-FTIR data represents the global peak fit.

Conclusions: From TGA/DSC measurements, we observed an increased water desorption energy as pore diameter, likewise; a decrease in the density, surface tension, and melting point temperature of confined water. Vibrational results of the connectivity band show a blue shift and decrease in full width half maximum as pore diameter decreases, suggesting stronger H-bonding interactions. The O-H stretch region shows increased population of network water and decreased population of multimeric water along with a red shift in the peak positions. In sum these results indicate that H-bonding interactions are increased for water in confinement. Future work will incorporate deuterium to provide further vibrational spectroscopic understanding.

Implications: Changes to water properties in confinement leads to additional deviations in cation adsorption behavior and has demonstrated changes in both the adsorption chemistry and coordination chemistry of copper (Cu) on mesoporous silica.⁸ Nano-scale confinement enhanced both the adsorption maximum values as well as the reaction rate constant. Additionally, there is likely an increased tendency to form inner sphere complexes in confinement.

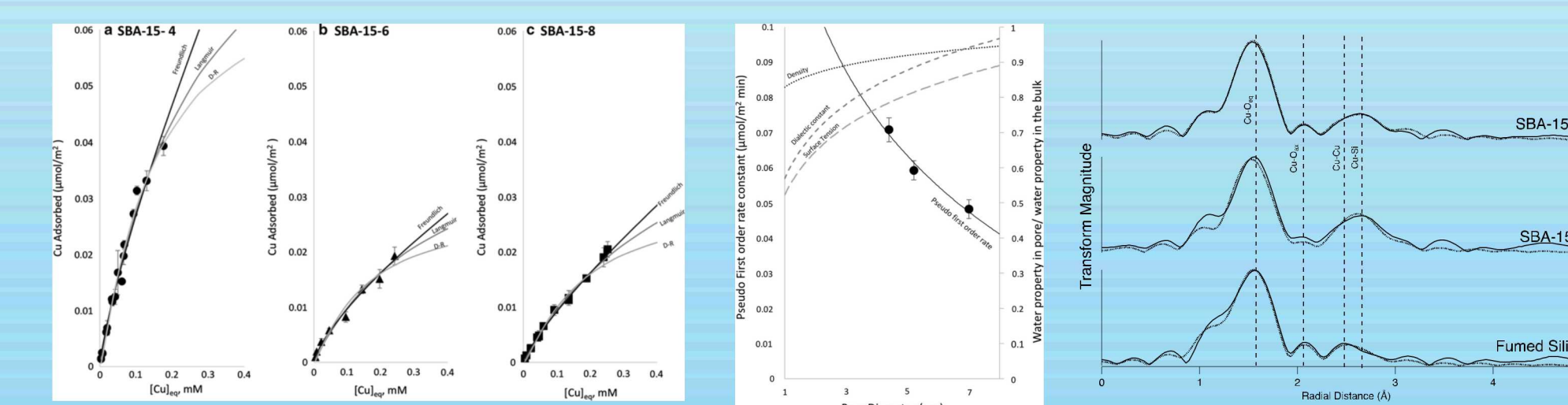


Figure 11. Figures showing the impact of nano-scale confinement on the adsorption and coordination chemistry of copper on mesoporous silica. An enhanced adsorption maximum, increased pseudo first order rate were observed with adsorption studies, along with increased propensity to form inner sphere complexes and dimers observed by XAFS.