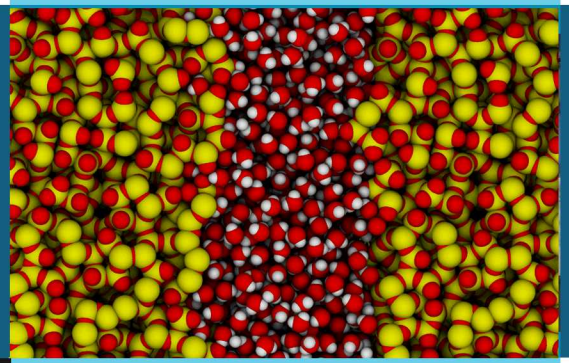
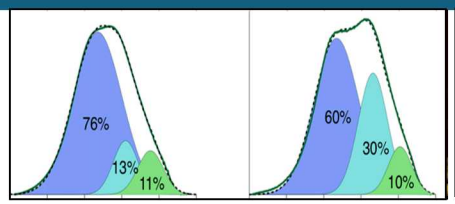
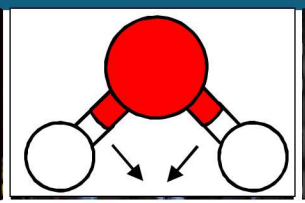
SAND2018-8274C

Properties of Nano-scale Confined Water







PRESENTED BY

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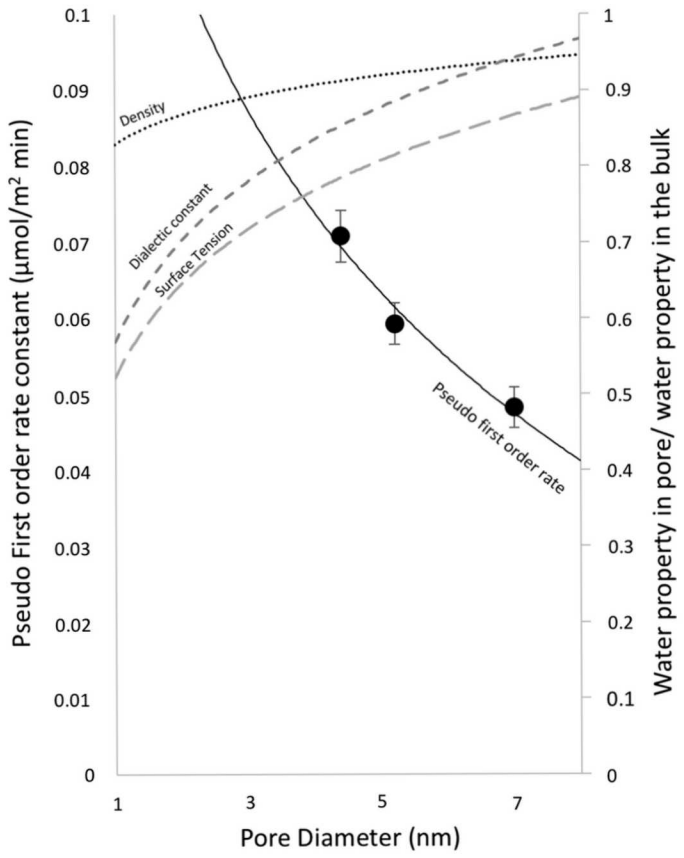
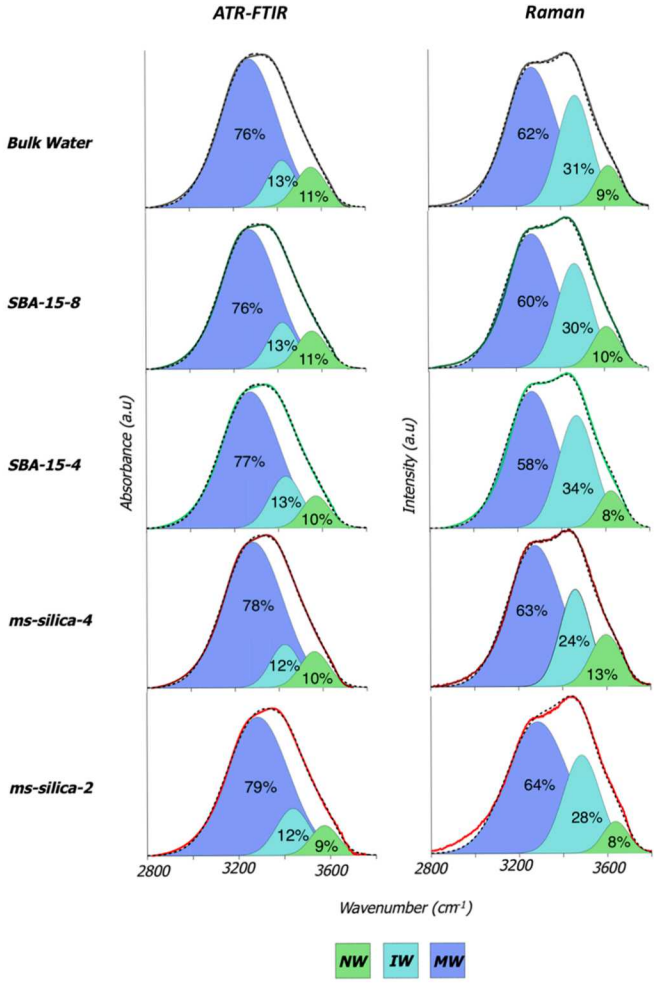
Chemistry in Nano-pores

1. Pore Size Effects on Trace Metal Adsorption

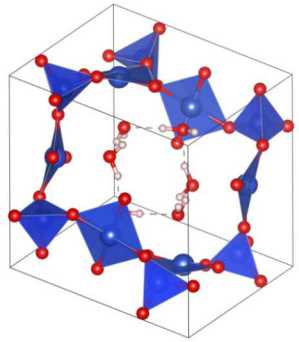


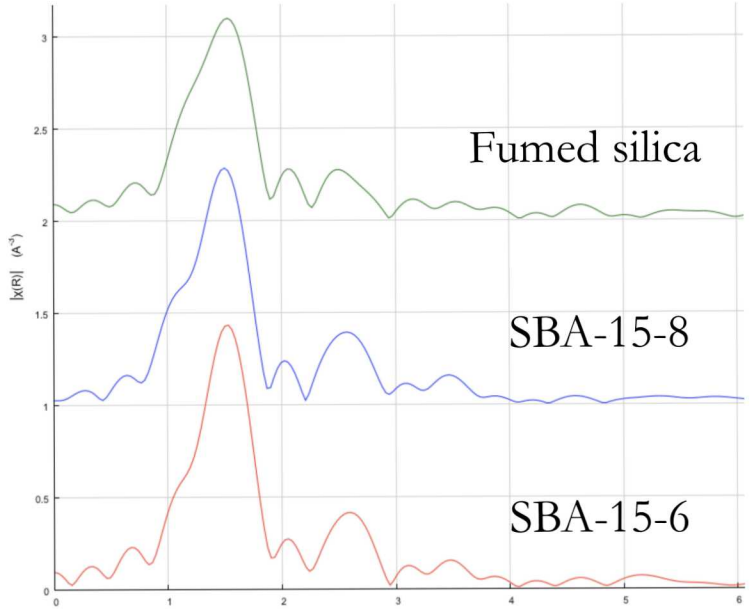
Knight, A.W., Tigges, A.B., A. G. Ilgen (2018) *Geochem. Trans.* 19(13)

2. Emergent Properties of Confined Water



3. Coordination Chemistry in Confinement



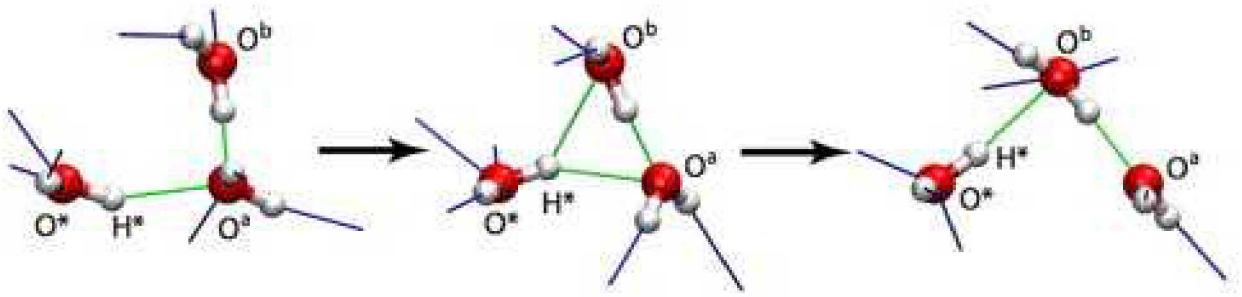


Temperature-Dependent Properties of Water at the Molecular Scale

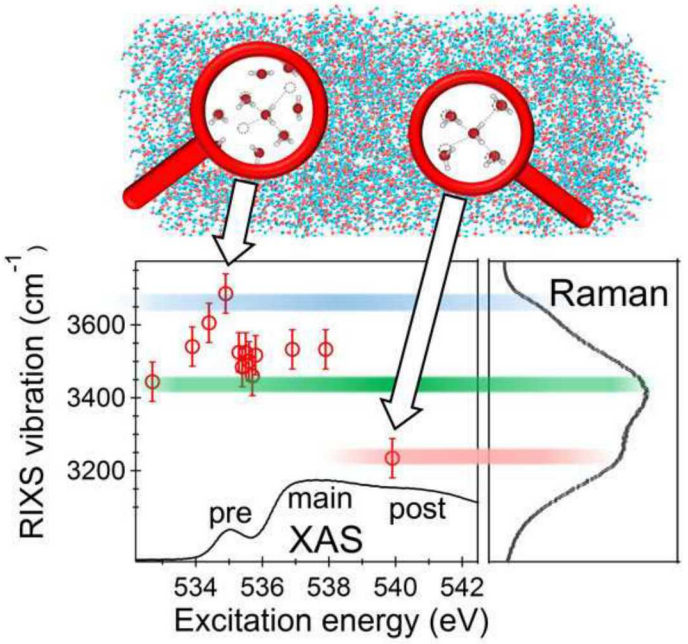
Molecular shape and dipole dictate physical properties of water

- Anomalous liquid behavior
  - High melting and freezing points, heat capacity, surface tension, and viscosity
- Divergent trends near/below the freezing point
  - Density, isothermal compressibility, and heat capacity differ from typical liquid behavior

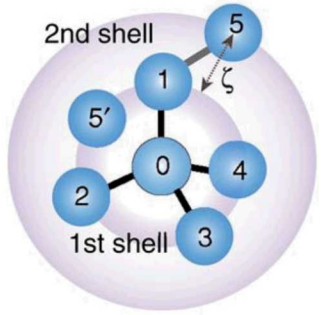
Hydrogen bonding network



Russo, J. and Tanaka, H. (2014). *Nature Comm.* 5.



Harada, et. al. (2017). J. Phys. Chem. Let. 8(22).

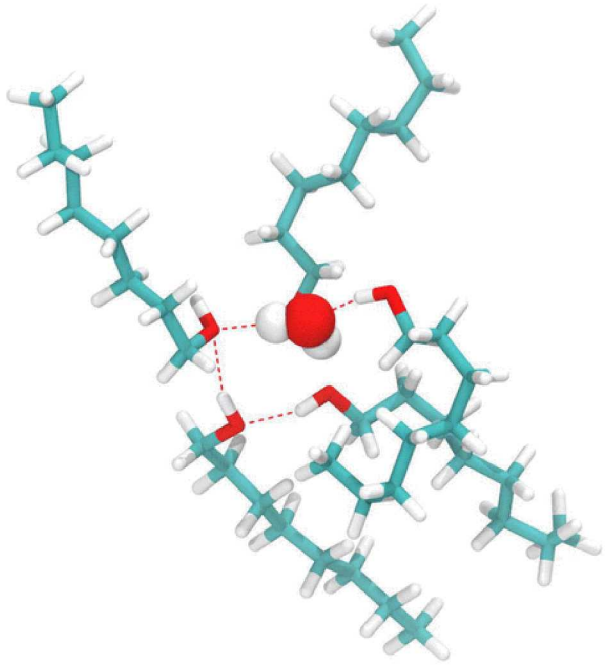


Laage, D.; Hynes, J. T. (2006). Chem. Phys. Lett. 43(80).

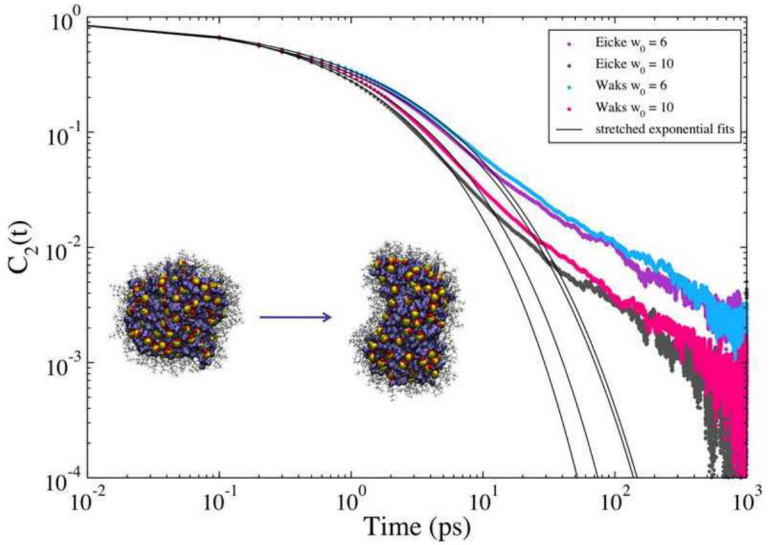
Water in Confinement

Relevant to applications in :

- Geosciences
- Biological Sciences
- Condensed matter (micro-emulsion and reverse micelles)
- Catalysis
- Membrane



Knight, A. W, et al (2017) *Langmuir*, 33 (15)



Martinez, V. A. et al (2013) *J. Phys. Chem. B.*, 117 (24)

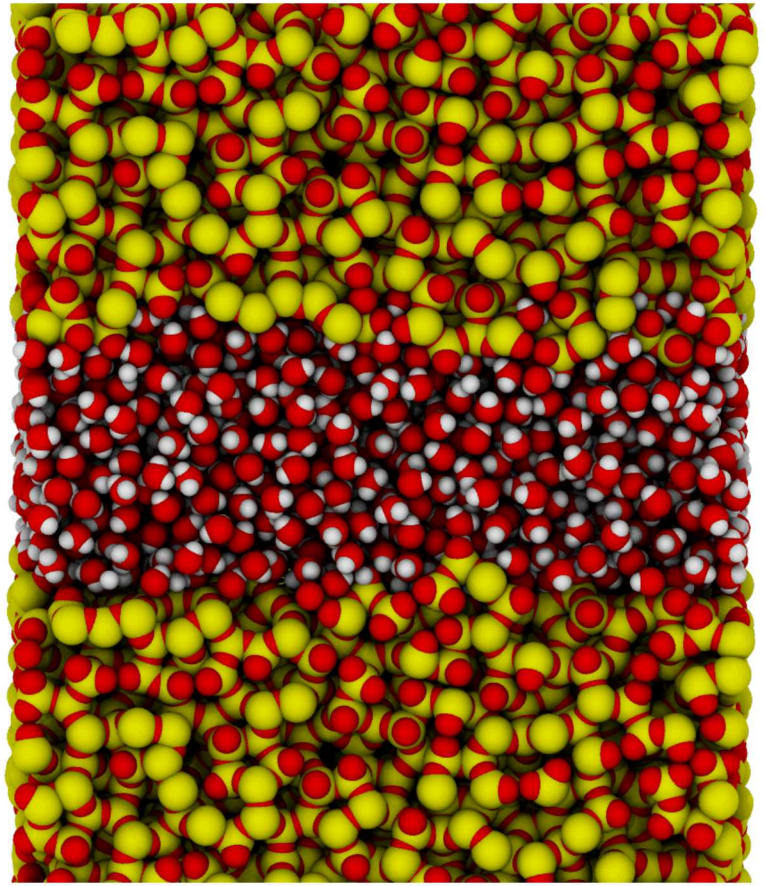


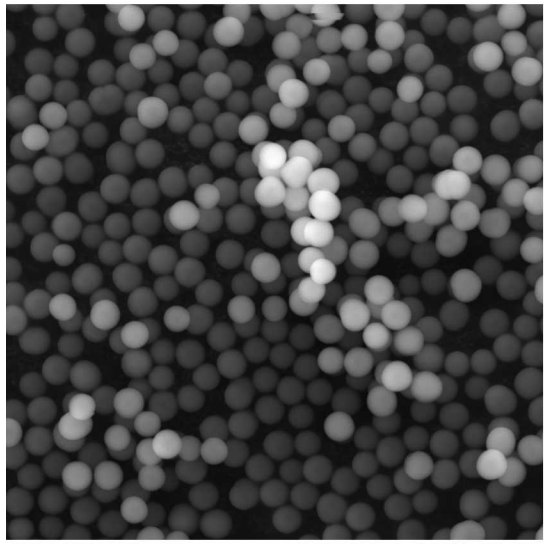
Image from simulation by Jacob Harvey

How are physical and chemical properties of water affected by confinement in incrementally smaller pores

Hypothesis: The dependence of nano-scale confinement and pore size can be quantified by physical and vibrational methods by probing changes in the H-bonding network

Surface Properties of Silica Materials

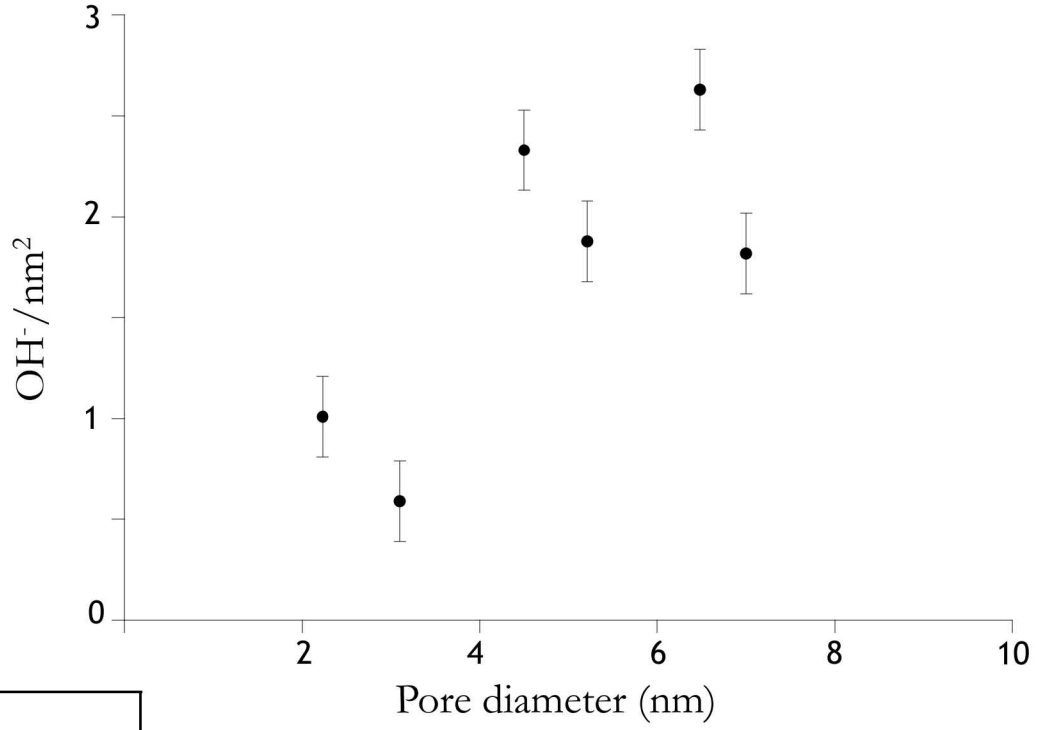
Pore diameter and OH^- density are not independent



ms-silica, 3 um particle, 5 kx mag

SBA-15, <150 um particle, 5 kx mag

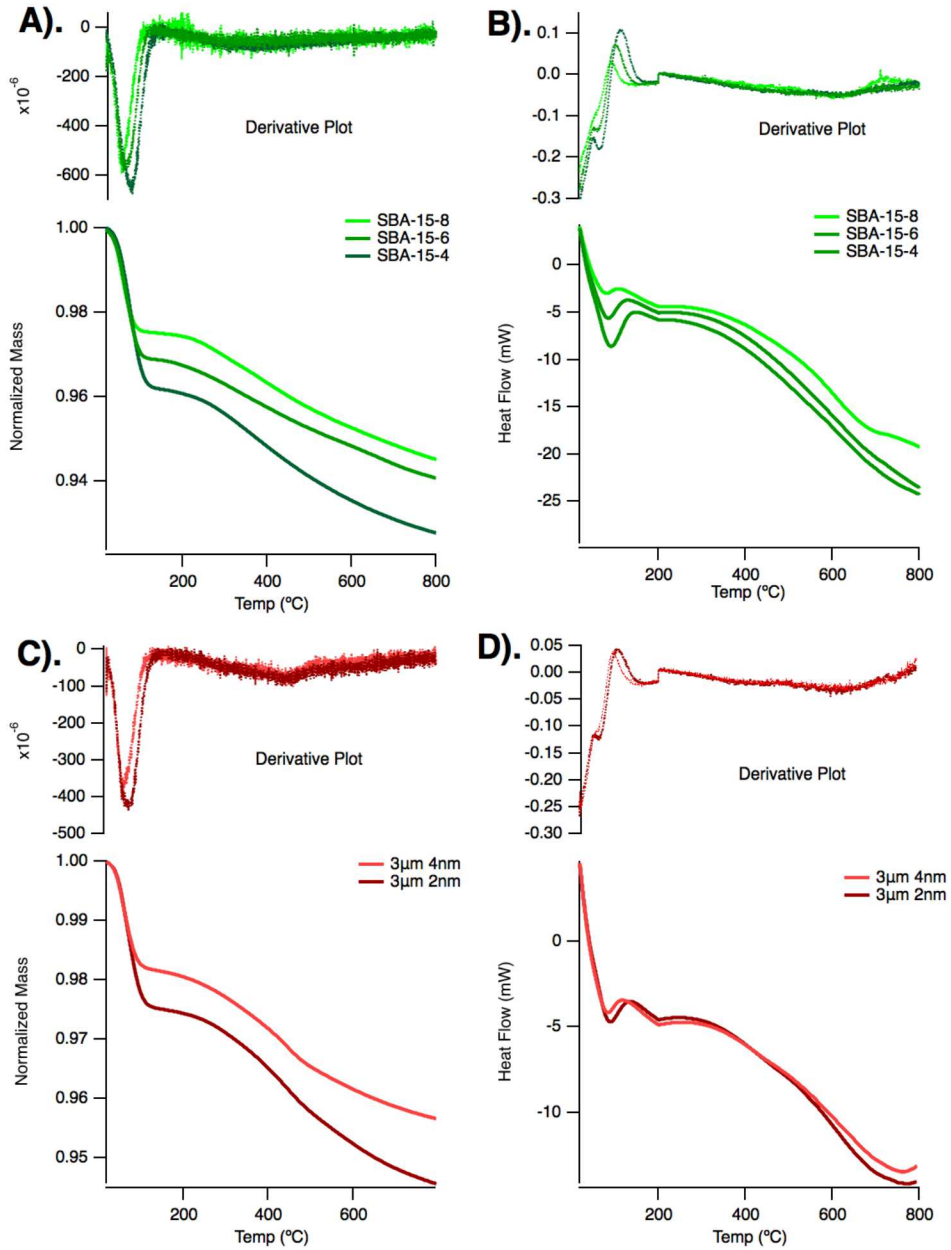
Material	Pore size (nm)	BET Surface Area (m^2/g)	Pore Volume (cm^3/g)	−OH-density ($-OH/nm^2$)	Reference
SBA-15-8	7.0 ± 0.3	661 ± 5	1.21 ± 0.03	1.8 ± 0.2	Knight et. al. (2018)
SBA-15-6	5.2 ± 0.2	603 ± 16	0.87± 0.03	1.9 ± 0.2	Knight et. al. (2018)
SBA-15-4	4.4 ± 0.1	580 ± 13	0.67 ± 0.04	2.3 ± 0.2	Knight 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[1]	861[1]	0.865[1]	0.59 ± 0.3[2]	[1]Takei et. al. (2000), [2]This study

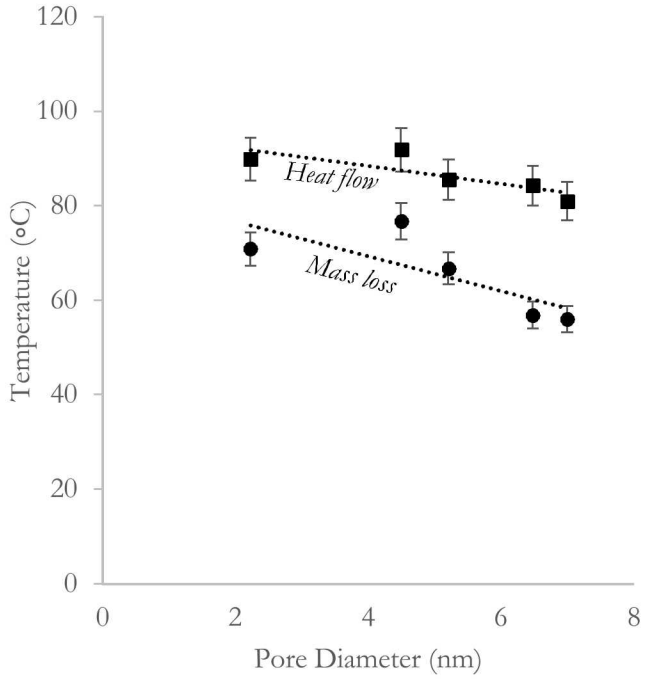


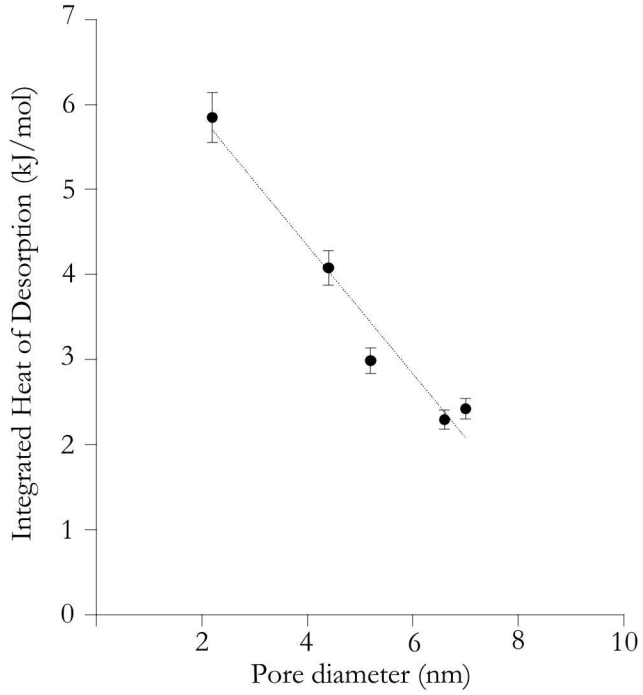
Low OH^- is a result of synthesis

- Annealed at 600-800 ∘C

Thermal Gravimetric and Calorimetry Analyses





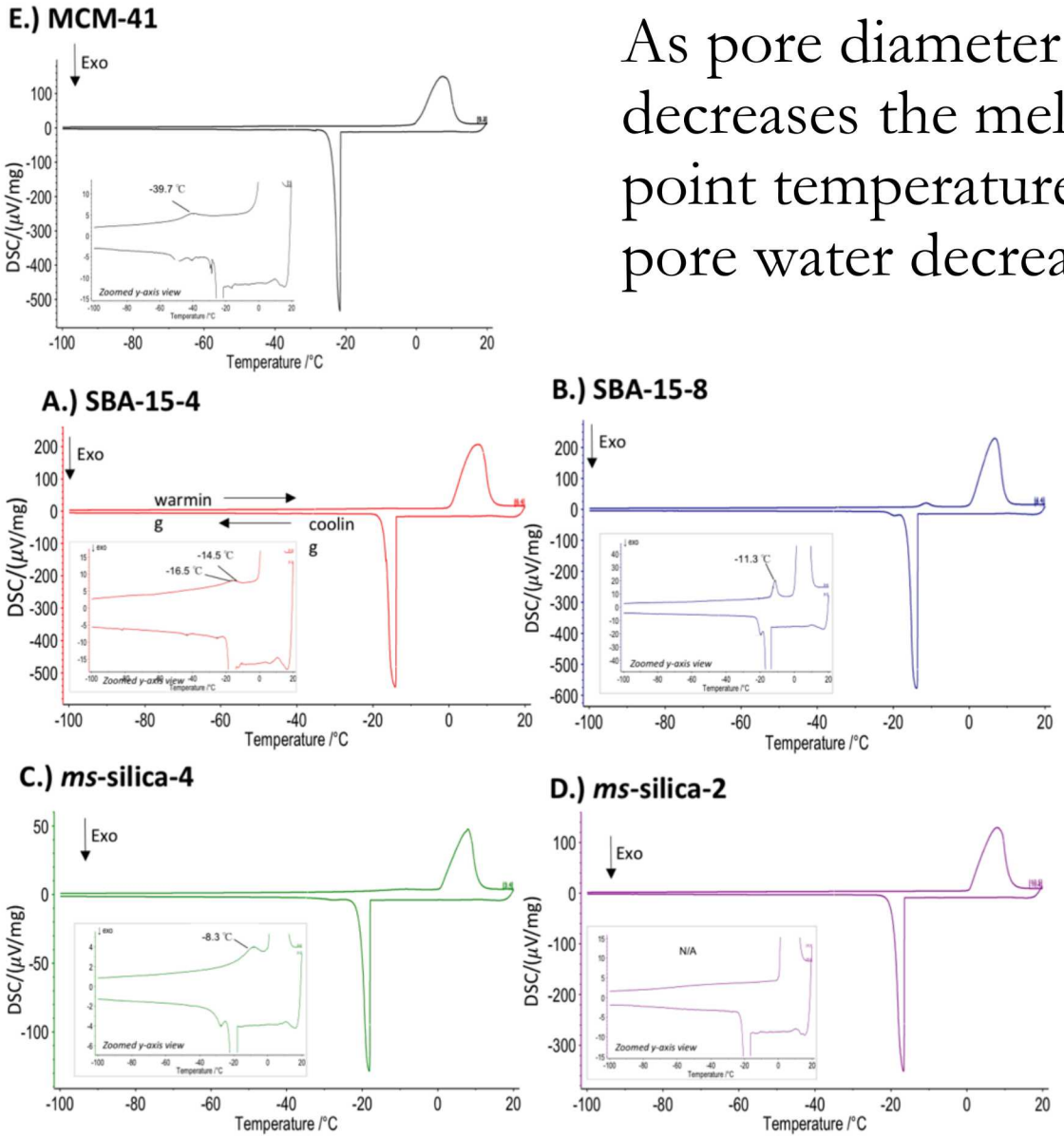


As pore diameter decreases:

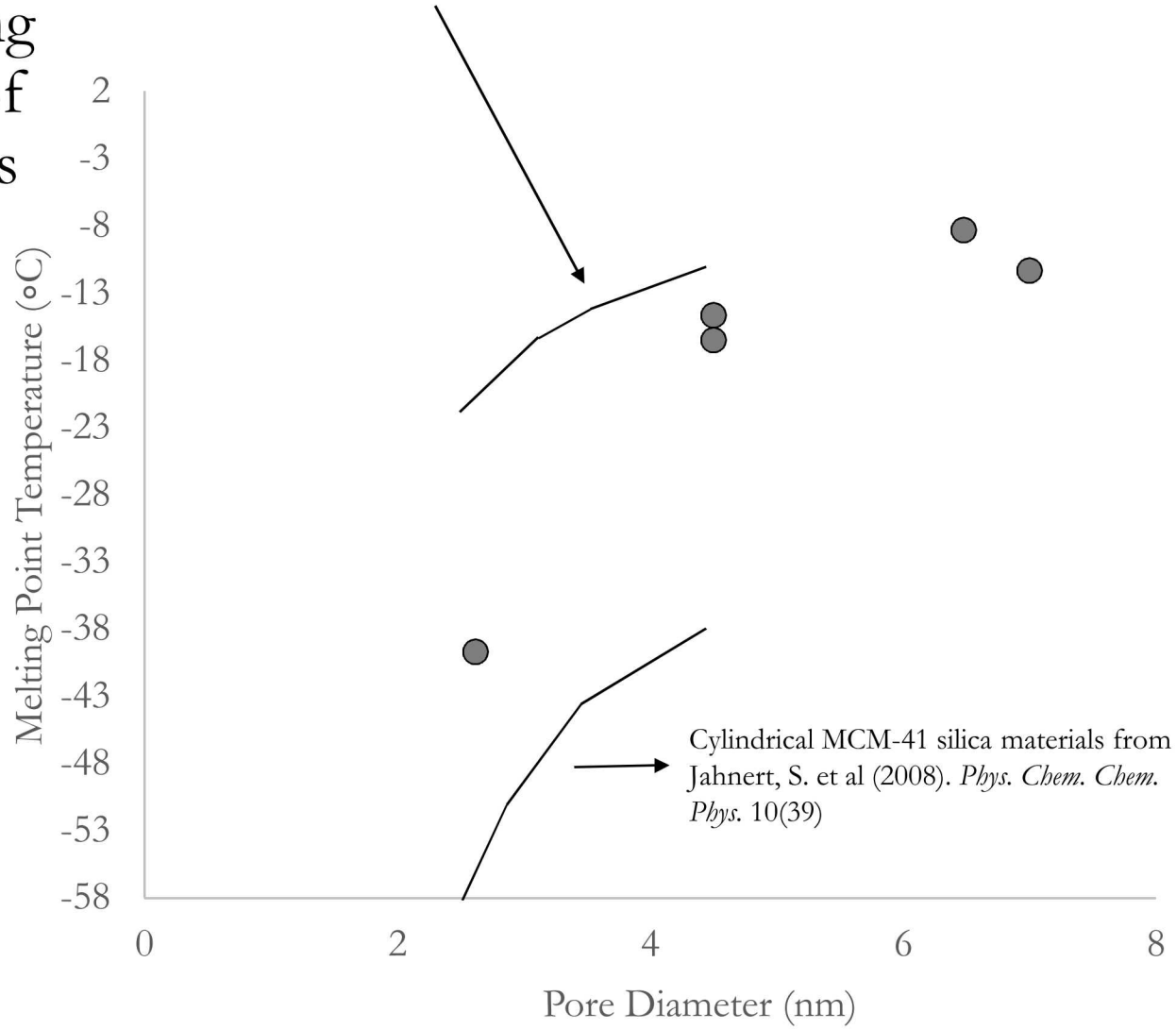
- The temperature and magnitude of maximum mass rate loss increases
- The temperature and magnitude of maximum heat flow increases
- The energy required to desorb water increases

Melting Point Temperature

As pore diameter decreases the melting point temperature of pore water decreases



Silica gels from Webber, B. and Dore, J. (2004). *J. Condens. Matter. 16.*

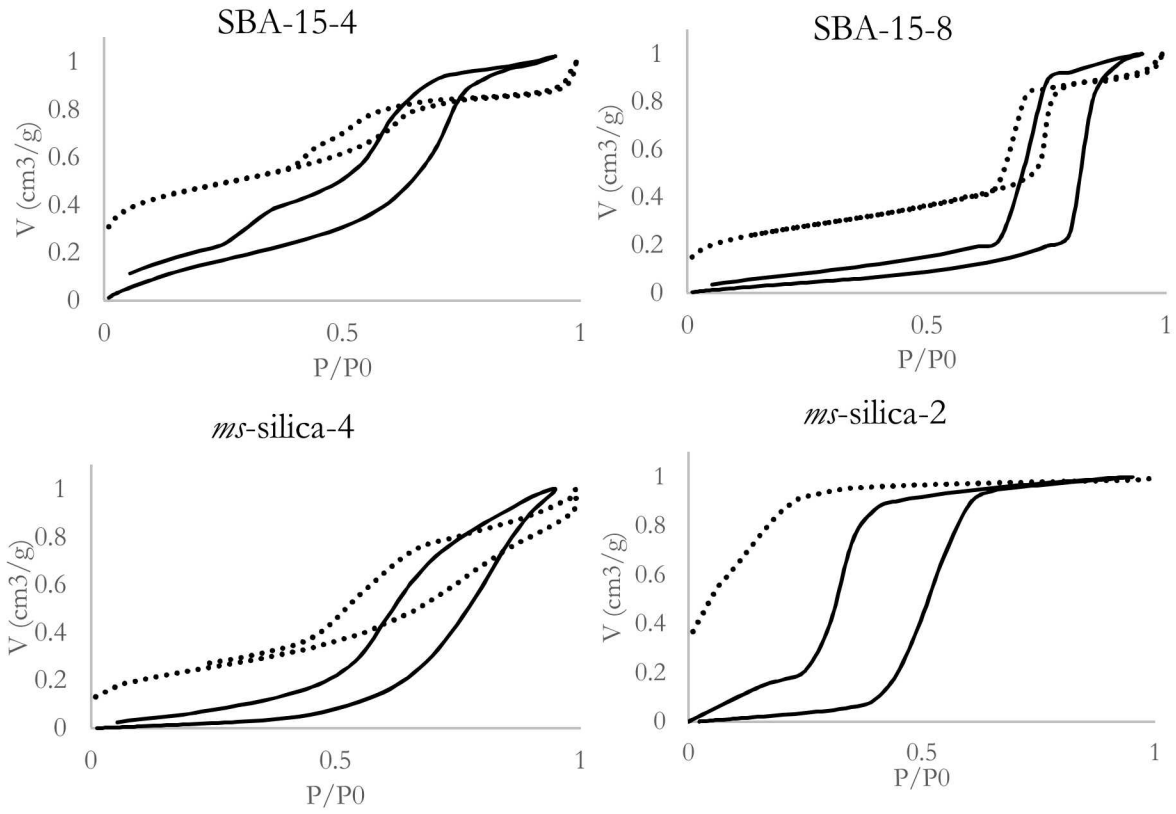


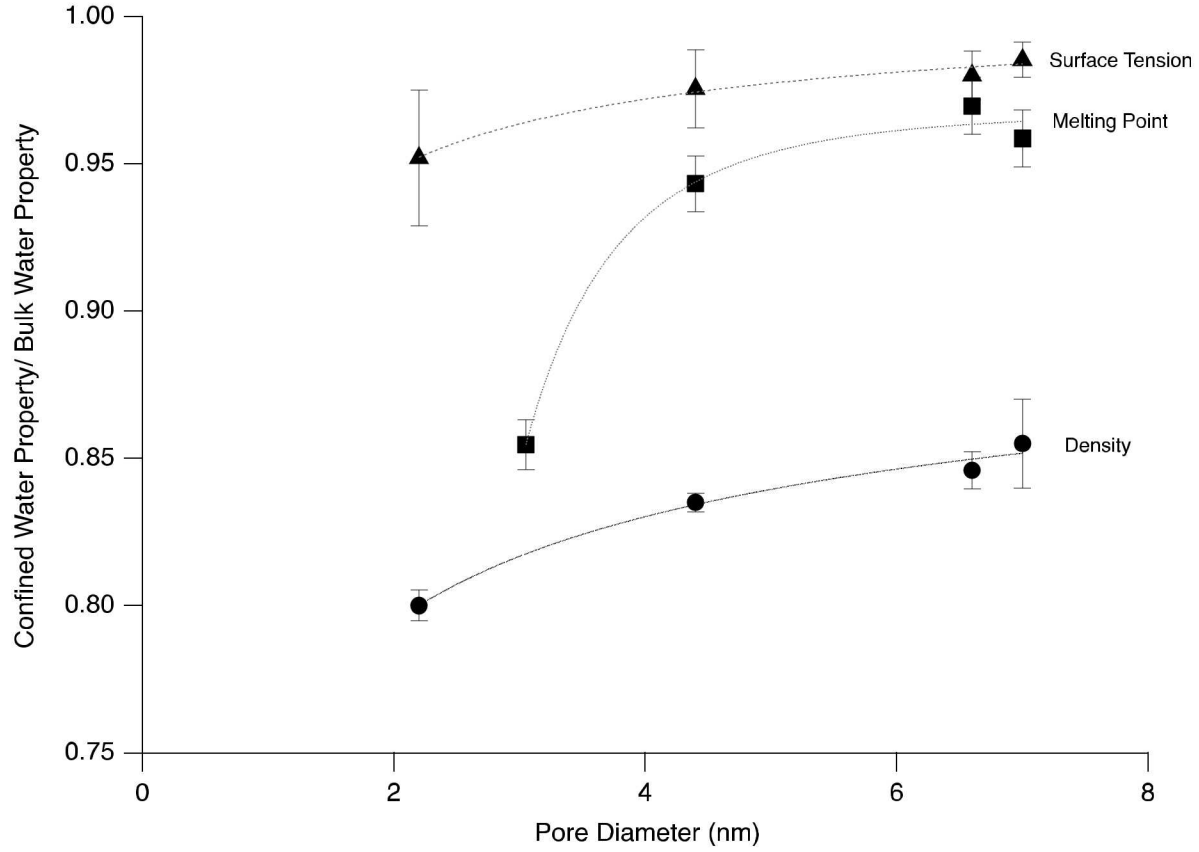
Cylindrical MCM-41 silica materials from Jahnert, S. et al (2008). *Phys. Chem. Chem. Phys.* 10(39)

Density and Surface Tension of Water

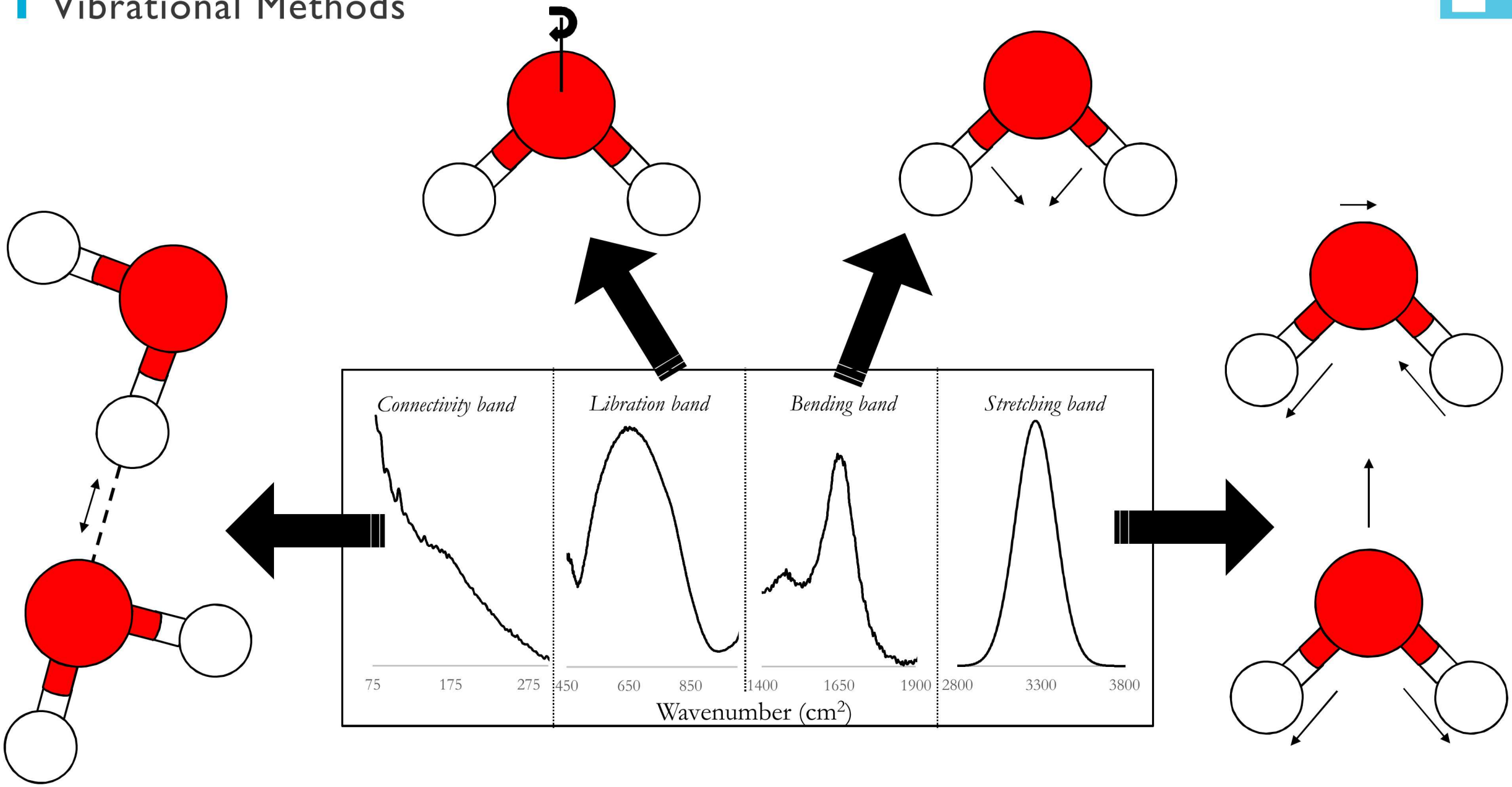
Surface tension and density of water decrease with decreasing pore diameter

- Decrease in water coordination number -- Takei et. al (2000). *Colloid Polym. Sci.* 278.
- Increase in nearest neighbor distance -- Takei et. al (2000). *Colloid Polym. Sci.* 278.
- Change in the OH – H angles -- Takei et. al (2000). *Colloid Polym. Sci.* 278.
- Mean radius of curvature of the meniscus -- Melrose J. C. (1966). *AIChE Journal.* 12(5).





Vibrational Methods



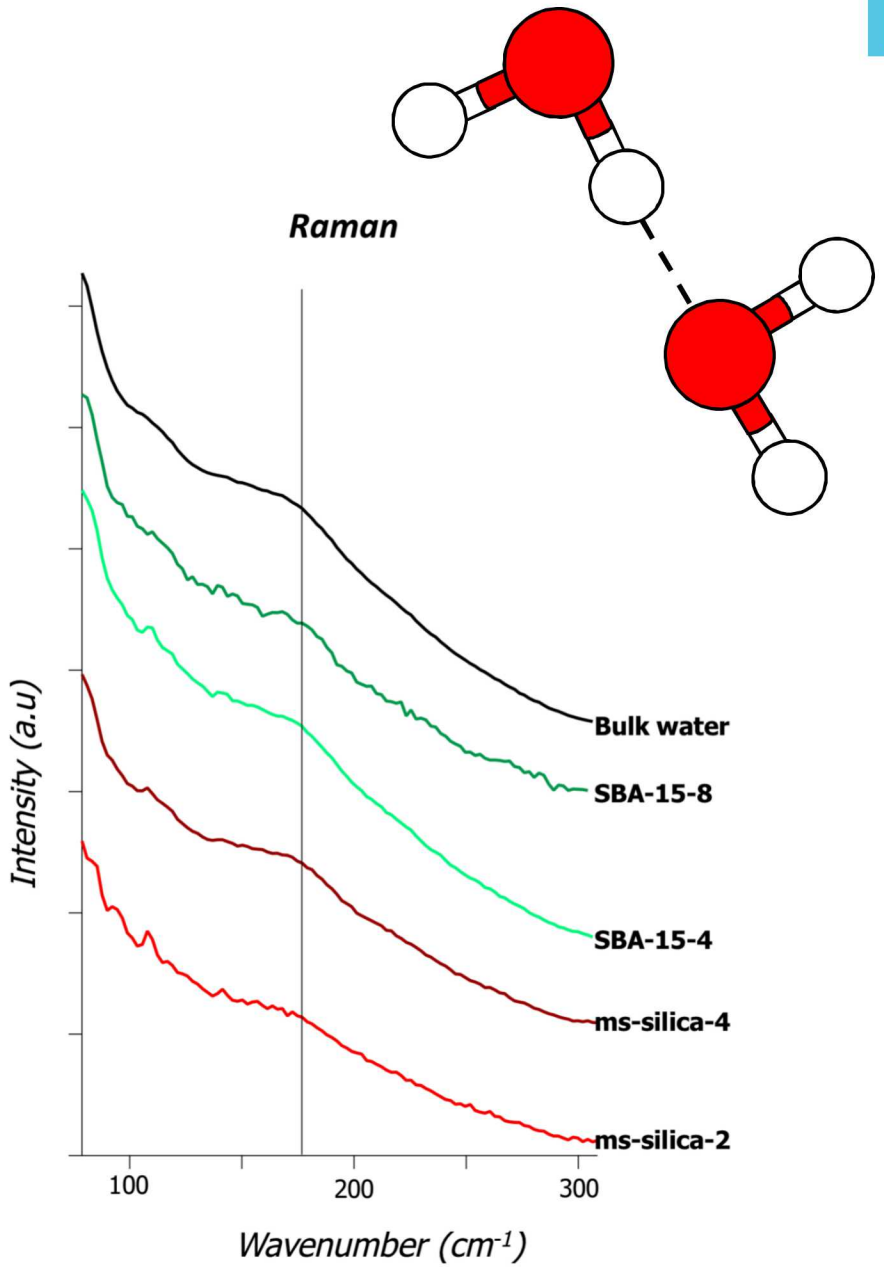
Connectivity Vibrational Mode

As pore diameter decreases:

- Blue shift in peak positions occurred, suggesting stronger H-bonding network
- FWHM decreased, suggesting a narrower distribution of H-bonding energies

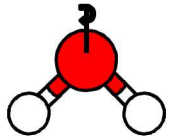
Confinement results in more ordered water

Raman		
Material	**Position (cm^{-1})**	**FWHM (cm^{-1})**
Bulk water	173	35
SBA-15-8	172	24
SBA-15-4	177	24
***ms*-Silica-4**	174	25
***ms*-Silica -2**	176	26

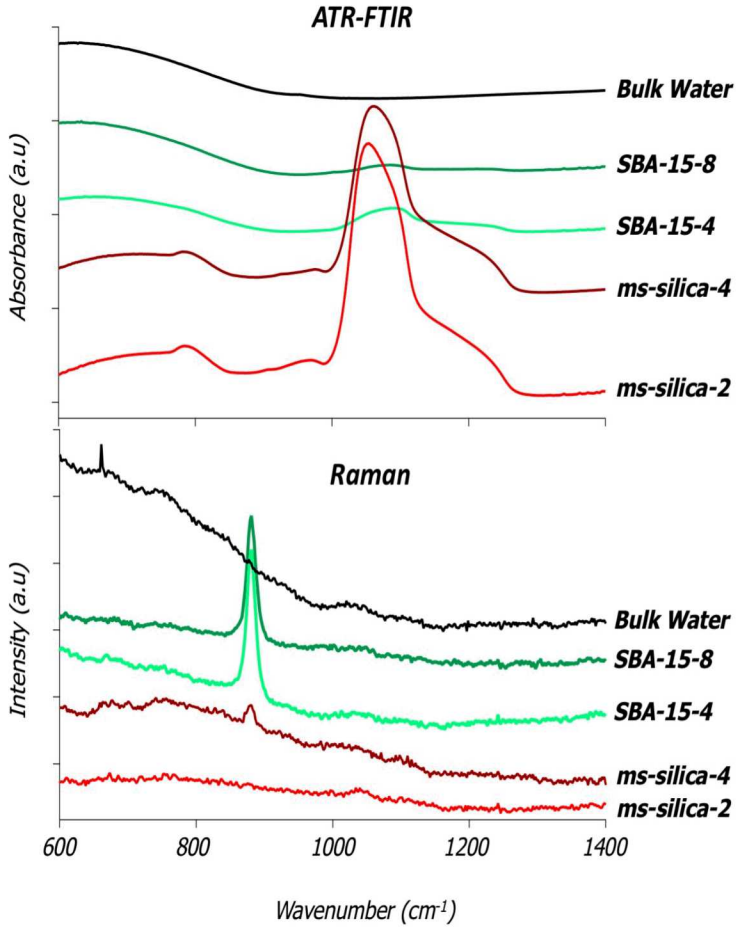


Water Bending and Libration Bands

Libration band

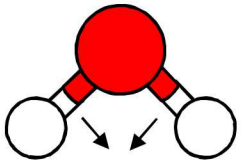


- Dominated by silica vibrations
- No nano-scale confinement observations

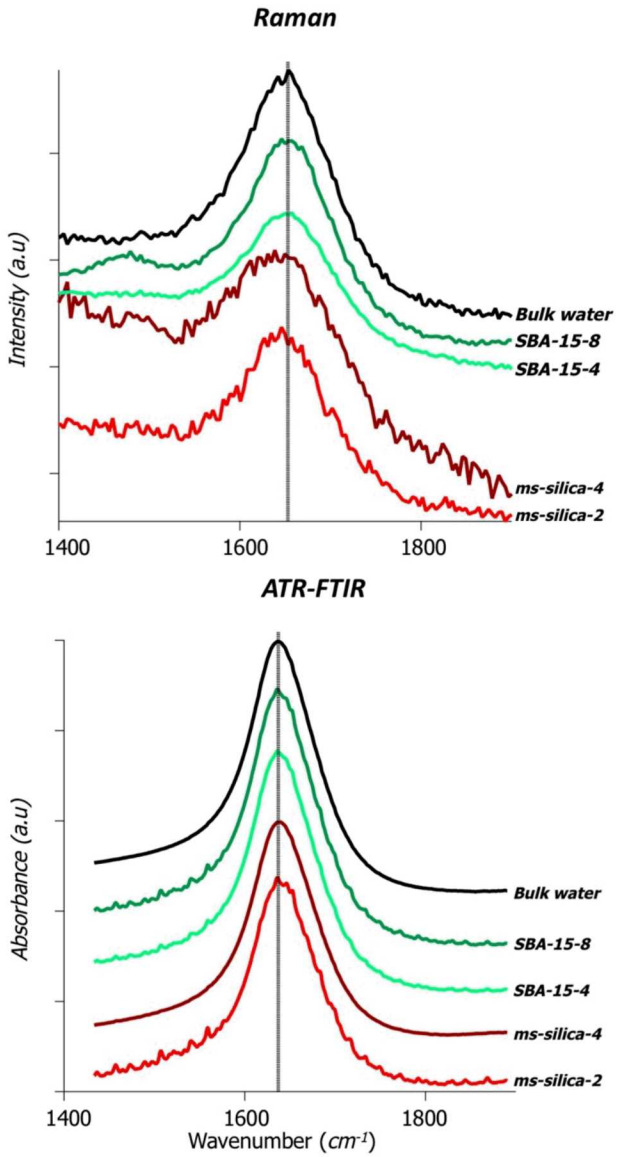


Water bending band

- No major changes resulting upon confinement
- Slight changes were observed for *ms*-silica-2



Material	*ATR-FTIR*		*Raman*	
	Position (cm^{-1})	FWHM (cm^{-1})	Position (cm^{-1})	FWHM (cm^{-1})
Bulk water	1640	91	1652	54
SBA-15-8	1640	91	1653	48
SBA-15-4	1640	92	1653	56
ms-Silica-4	1641	90	1652	49
ms-Silica -2	1642	91	1646	50

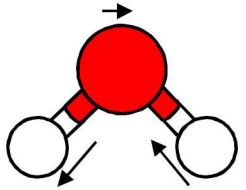


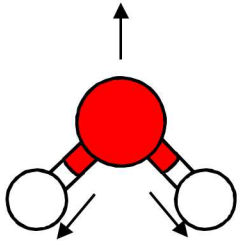
O-H Stretch Region

As pore diameter decreases:

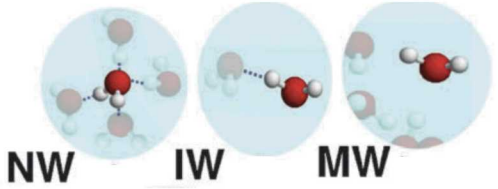
- NW population grows and MW population declines
  - Suggest more ordering occurs
- Red peak shift occurs
  - Weaker O-H stretch, in response to stronger intermolecular interactions

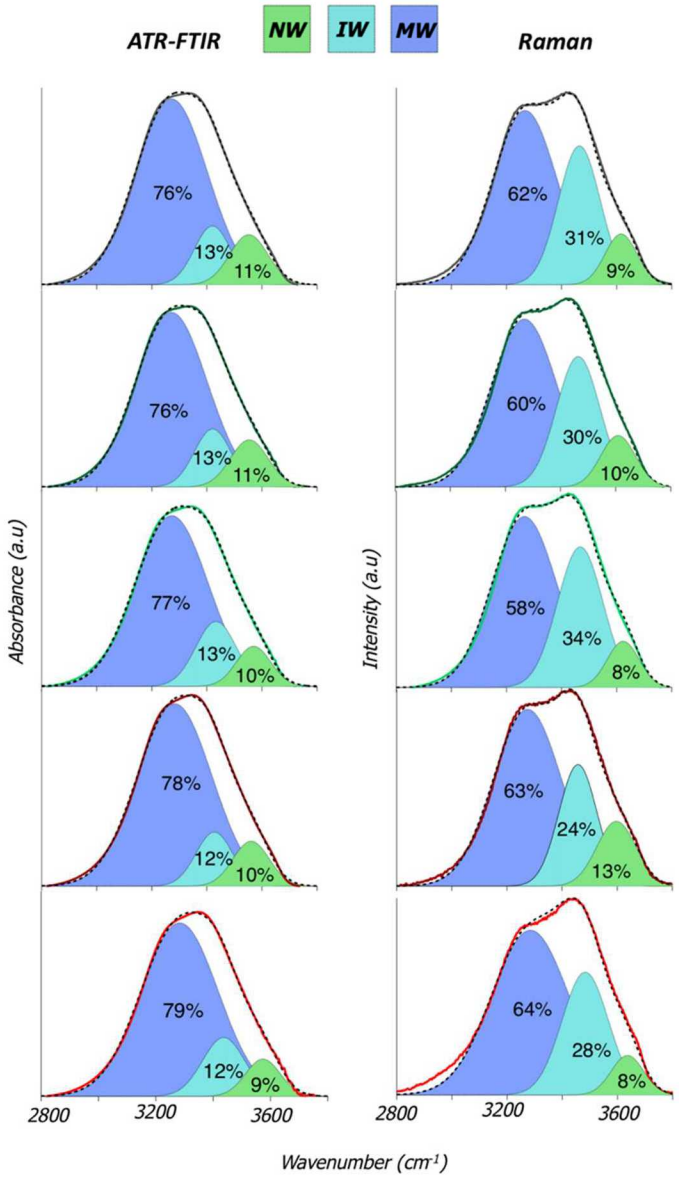
ATR-FTIR										
Material	NW (Network Water)			IW (Intermediate Water)			MW (Multimer Water)			
	Position (cm^{-1})	FWHM (cm^{-1})	Percent (%)	Position (cm^{-1})	FWHM (cm^{-1})	Percent (%)	Position (cm^{-1})	FWHM (cm^{-1})	Percent (%)	r^2 of fit
Bulk water	3272	308	76	3421	156	13	3554	163	11	0.997
SBA-15-8	3271	306	76	3420	156	13	3553	164	11	0.996
SBA-15-4	3474	315	77	3426	161	13	3560	158	10	0.997
***ms*-Silica-4**	3279	315	78	3425	156	12	3558	159	10	0.992
***ms*-Silica -2**	3285	320	79	3429	160	12	3564	153	9	0.994
Raman										
Material	NW (Network Water)			IW (Intermediate Water)			MW (Multimer Water)			
	Position (cm^{-1})	FWHM (cm^{-1})	Percent (%)	Position (cm^{-1})	FWHM (cm^{-1})	Percent (%)	Position (cm^{-1})	FWHM (cm^{-1})	Percent (%)	r^2 of fit
Bulk water	3267	137	60	3465	90	31	3616	69	9	0.998
SBA-15-8	3268	140	60	3464	93	30	3608	74	10	0.998
SBA-15-4	3265	139	58	3468	98	34	3624	68	8	0.997
***ms*-Silica-4**	3277	146	63	3458	82	24	3597	84	13	0.996
***ms*-Silica -2**	3283	165	64	3483	99	28	3636	69	8	0.993





Le Caer, S., et al., (2011). *Phys. Chem. Chem. Phys.* 13(39)

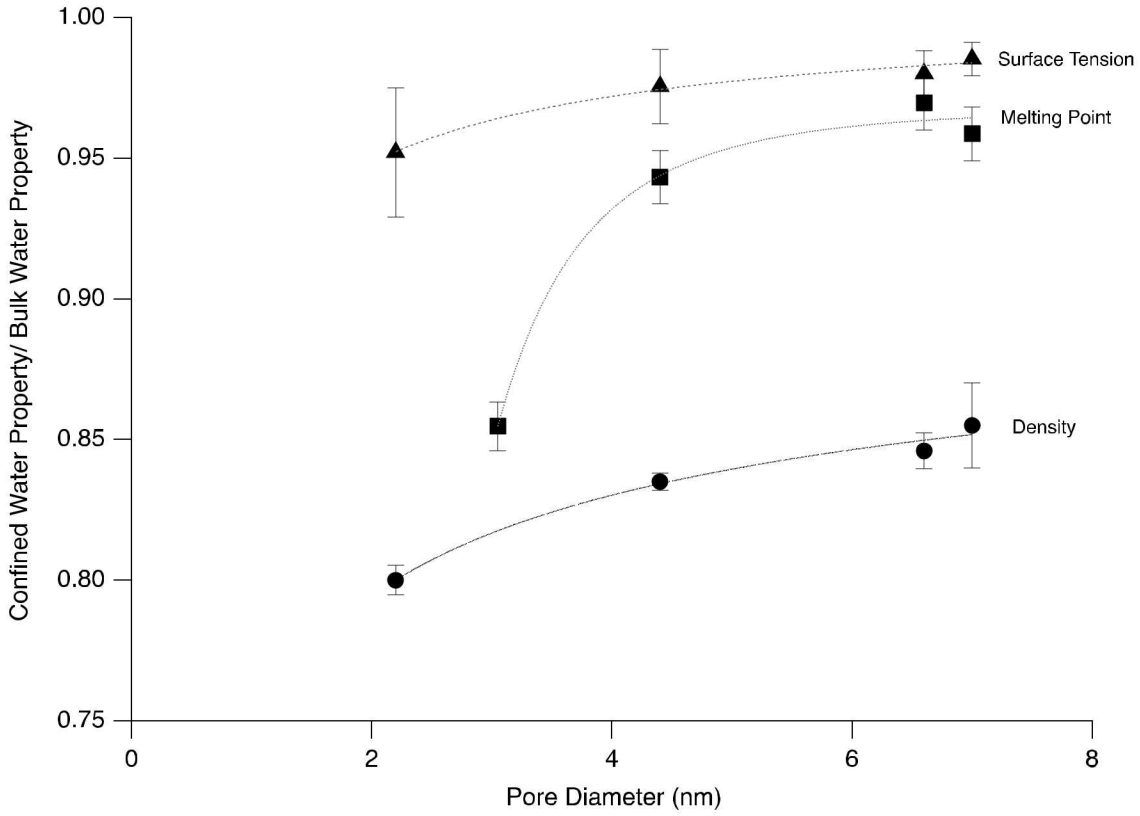


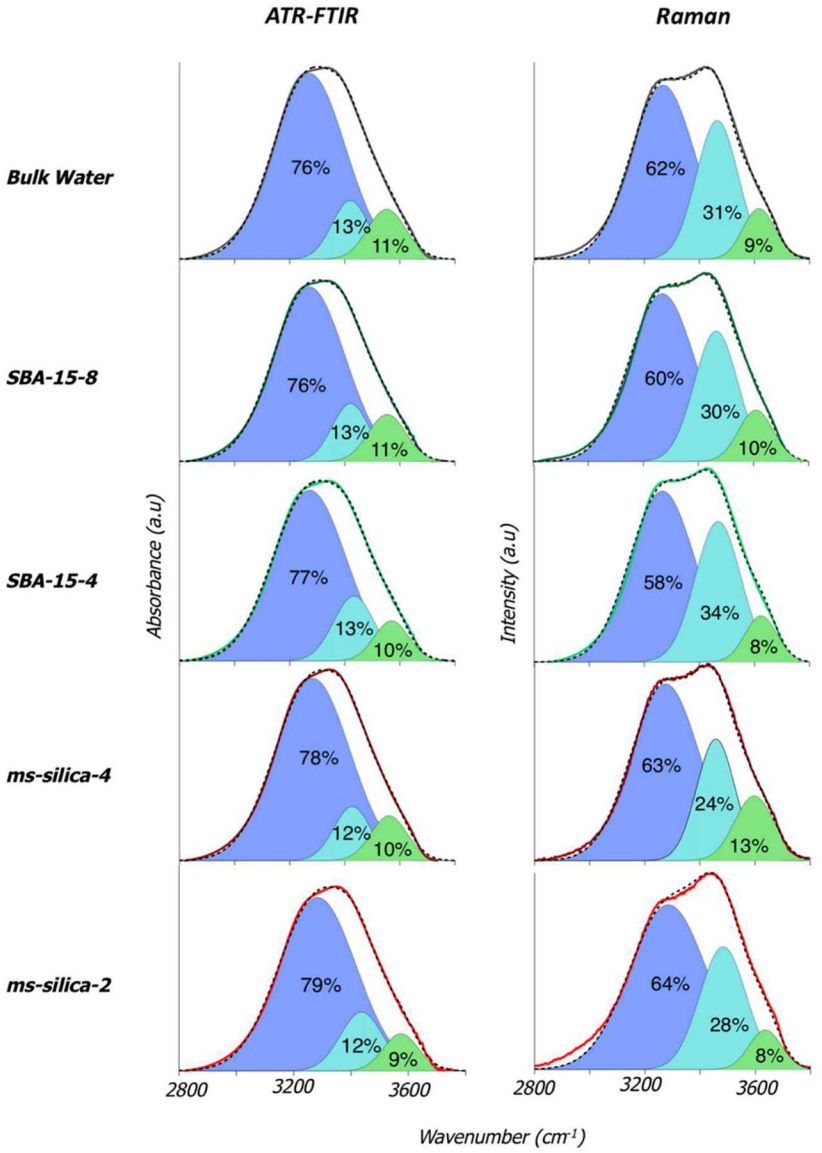


Conclusions

The changes in both physical properties of water and vibrational spectra highlight nano-scale confinement effects

- Lower density, surface tension, and melting point
- Larger heat of desorption and populations of networked water
- Increased strength of H-bonding interactions and structure.





Thank you and Acknowledgments

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