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Nanoconfined Water in Clinoptilolite and Heulandite Microporous Zeolites

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Objective

Correlation of experimental and large-scale MD data surrounding the behavior of nanconfined water within ordered zeolitic materials.

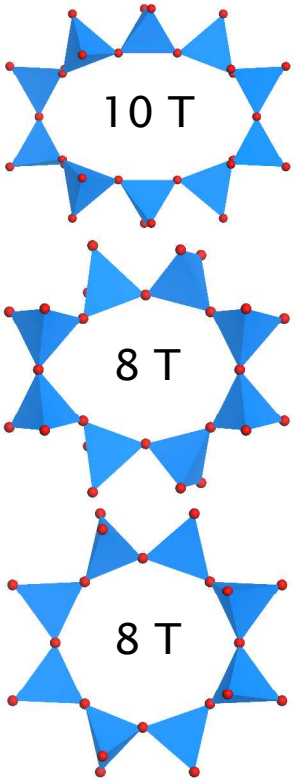
Clinoptilolite / Heulandite

$$[X]_{4\text{-}6}[Al_6(Al,Si)_4Si_{26}O_{72}] \cdot x\ H_2O$$

- Most commonly occurring natural zeolite
- Abundant supply for many industrial applications
- Variable Si/Al ratio, water and ion content
- Relatively high ion exchange capacities

Structure of Clinoptilolite and Heulandite

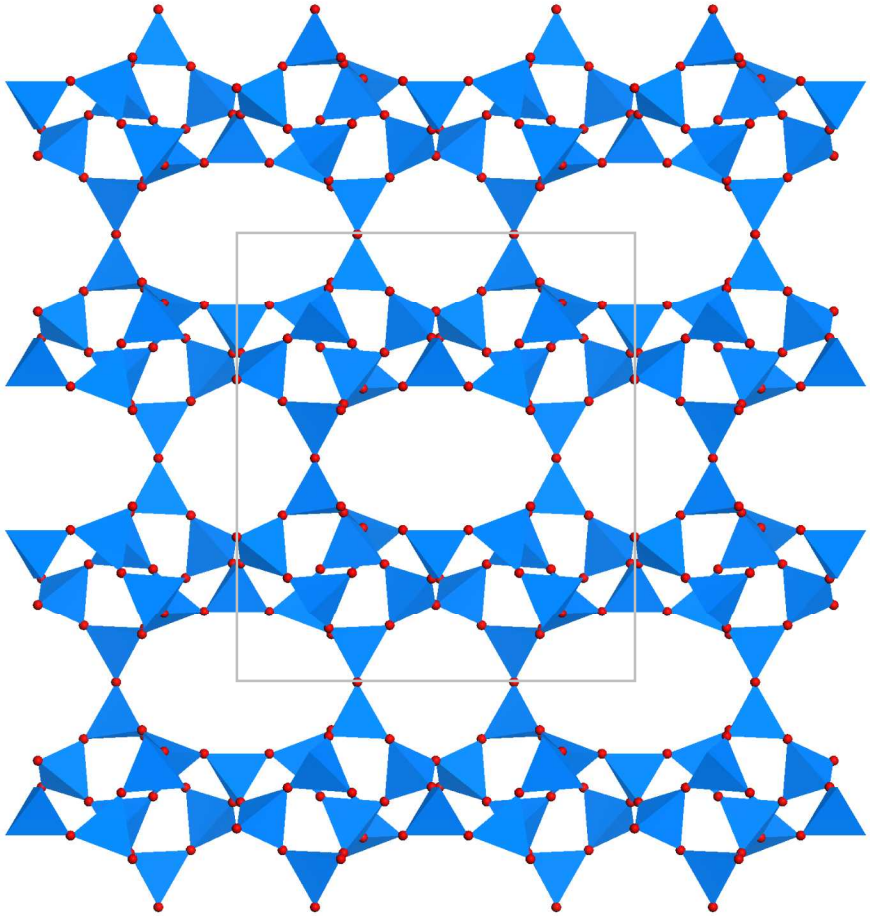
$[Ca,Na,K,Li]_{4-6}[Al_6(Al,Si)_4Si_{26}O_{72}] \bullet 24H_2O$



7.2 x 4.4 Å
orthonormal to *z*-axis

5.5 x 4.0 Å
orthonormal to *x*-axis

4.7 x 4.1 Å
diagonal to 10 T channels



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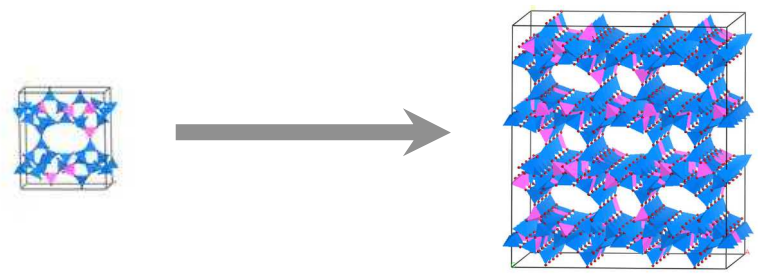
Large-scale Molecular Dynamics

LAMMPS (ZEOFF & SPC water)	Clinoptilolite (Si/Al = 5.0)	Heulandite (Si/Al = 3.5)
Alkali	Li^{+}, Na^{+}, K^{+}, Rb^{+}, Cs^{+}	Li^{+}, Na^{+}, K^{+}, Rb^{+}, Cs^{+}
Alkaline Earth	Mg^{+2}, Ca^{+2}, Sr^{+2}, Ba^{+2}	Mg^{+2}, Ca^{+2}, Sr^{+2}, Ba^{+2}
Water Content	0→32/u.c.	0→32/u.c.
1 u.c. 114-210 atoms	Supercell (2x2x5 u.c.) 2300-4200 atoms	500 ps Equilibrations 250 ps Productions Energetic Structural Spectroscopic
		

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Framework-Water-Ion Behavior

$Cs^{+} < Rb^{+} < Ba^{+2} < K^{+} < Sr^{+2} < Na^{+} < Ca^{+2} < Li^{+} < Mg^{+2}$

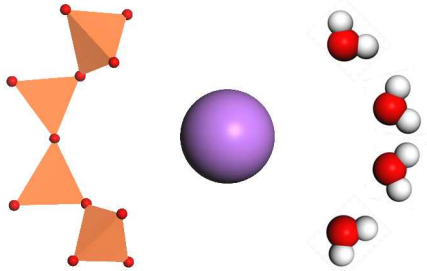
Lowest Hydration Energy

Highest Hydration Energy

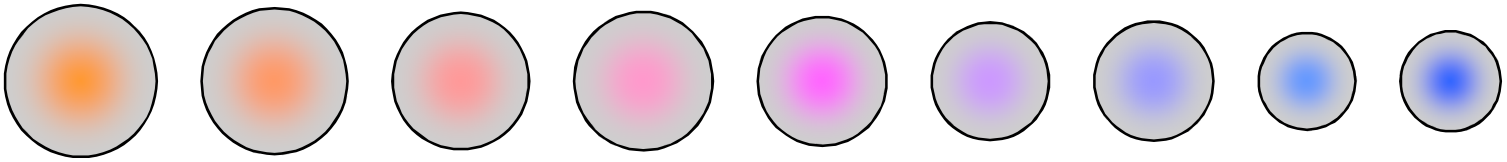
Weakly Hydrated

Strongly Hydrated

Framework-Ion Interactions Dominate



Water-Ion Interactions Dominate



Largest Ionic Radius

Smallest ionic Radius

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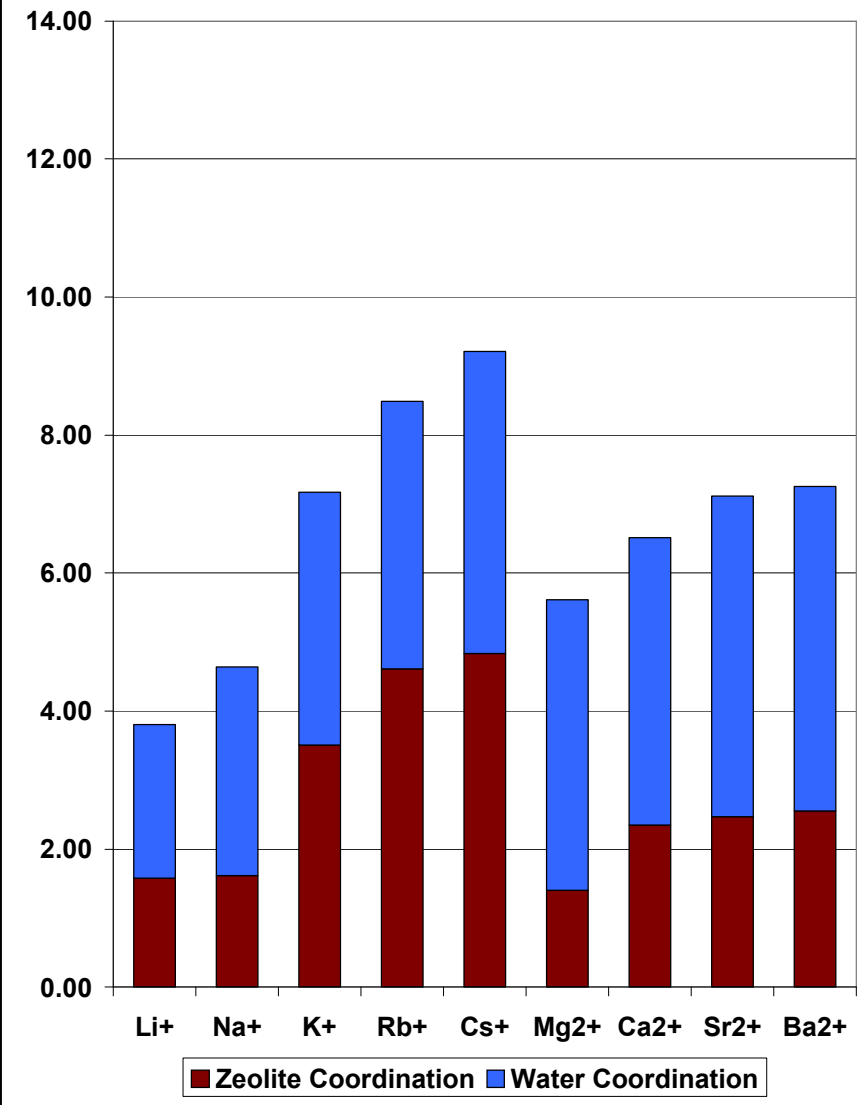
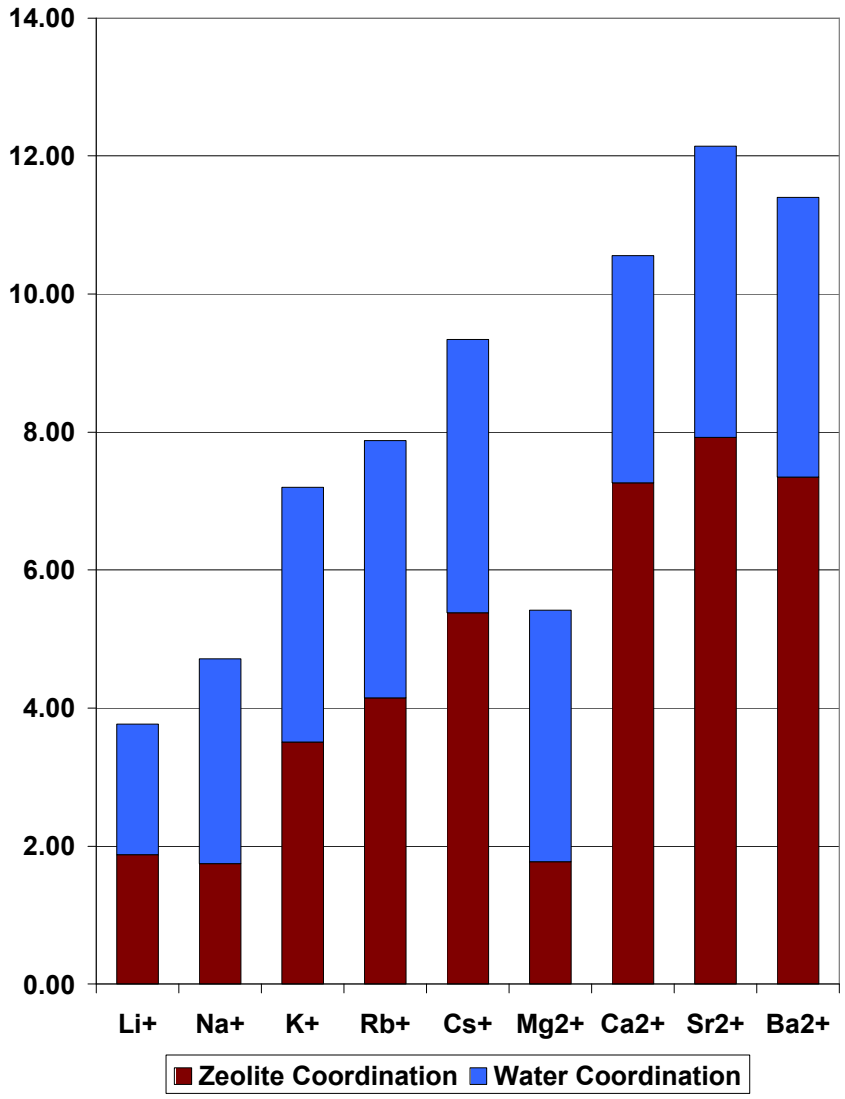
Ion Coordination in Clinoptilolite



Less Negatively Charged Framework

Ion Coordination in Heulandite



More Negatively Charged Framework

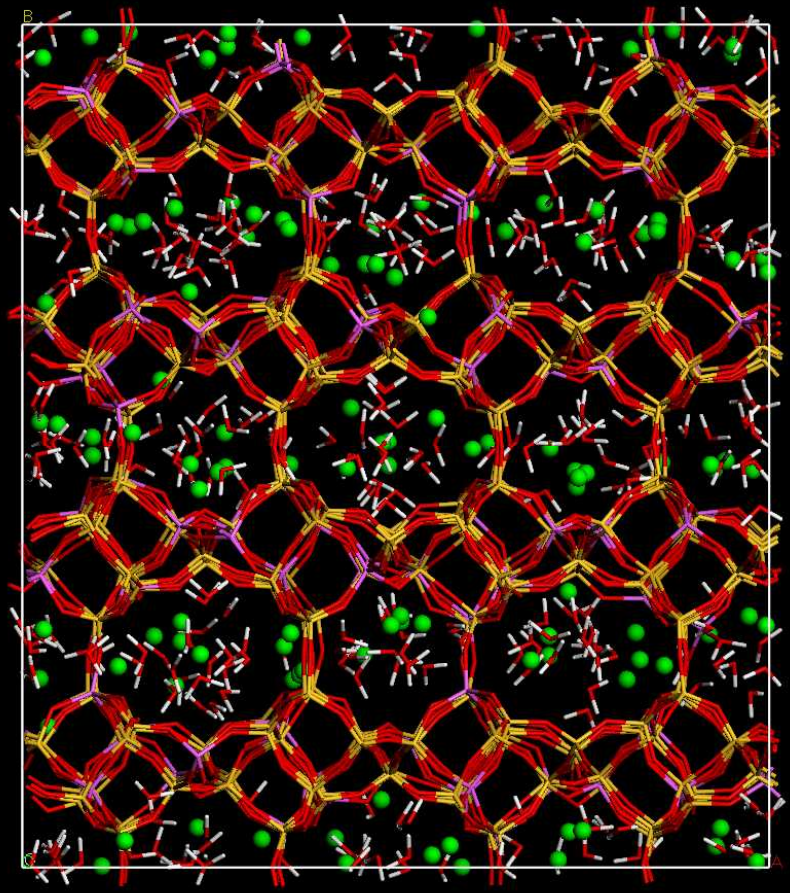
Ion-O_w Distances (Å)

	Li^+	Na^+	K^+	Rb^+	Cs^+	Mg^{+2}	Ca^{+2}	Sr^{+2}	Ba^{+2}
Pure H_2O (*exp*)	2.10	2.41	2.80	2.92	3.14	2.07	2.33	2.60	2.90
Pure H_2O (*calc*)	1.88	2.33	2.83	2.98	3.18	2.23	2.60	2.98	2.93
CLI-H_2O (*calc*)	1.88	2.29	2.82	2.94	3.06	1.99	2.43	2.68	2.75
HEU-H_2O (*calc*)	1.89	2.28	2.81	2.92	3.02	1.98	2.91	3.15	3.19

Ion Hydration Enthalpies (kcal/mol)

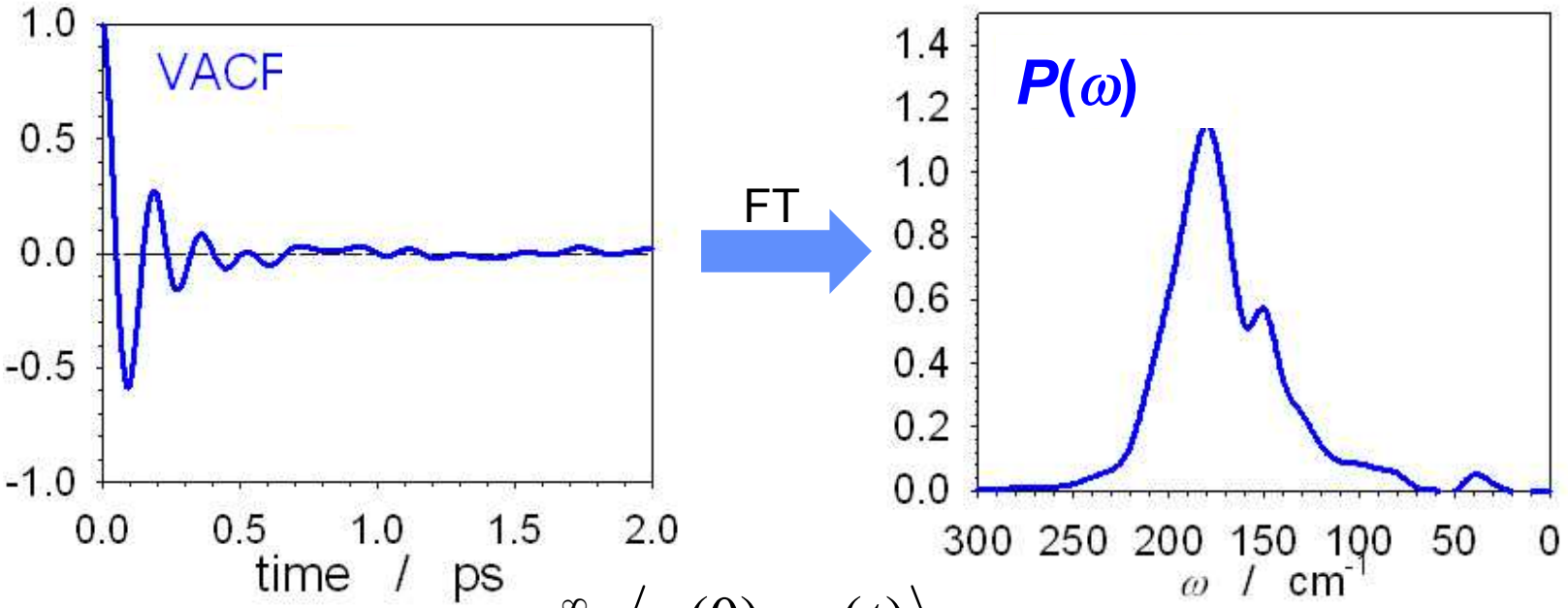
	Li^+	Na^+	K^+	Rb^+	Cs^+	Mg^{+2}	Ca^{+2}	Sr^{+2}	Ba^{+2}
Ion (*exp*)	-124	-97	-77	-71	-66	-459	-377	-345	-312
Ion (*calc*)	-127	-101	-69	-66	-62	-433	-358	-311	-314
CLI (*calc*)	-16.0	-14.2	-12.8	-12.4	-12.2	-98.8	-18.4	-17.6	-16.8
HEU (*calc*)	-18.1	-15.2	-13.0	-12.6	-11.9	-95.0	-15.5	-15.3	-15.1

CLI & HEU calculated on a per H_2O Basis


B
C
A

Dynamics of Individual Atoms
VACFs and Power Spectra

$$\mathrm{VACF} \equiv C_{vv}(t) = \frac{\langle \mathbf{v}(0)\cdot\mathbf{v}(t)\rangle}{\langle \mathbf{v}(0)^2\rangle} = \frac{1}{\langle \mathbf{v}(0)^2\rangle}\int \mathbf{v}(0)\cdot\mathbf{v}(\mathrm{t})\, d\Gamma$$



$$P(\omega) = \int_0^\infty \frac{\langle \mathbf{v}(0)\cdot\mathbf{v}(t)\rangle}{\langle \mathbf{v}(0)^2\rangle}\cos(\omega\, t)\, dt$$

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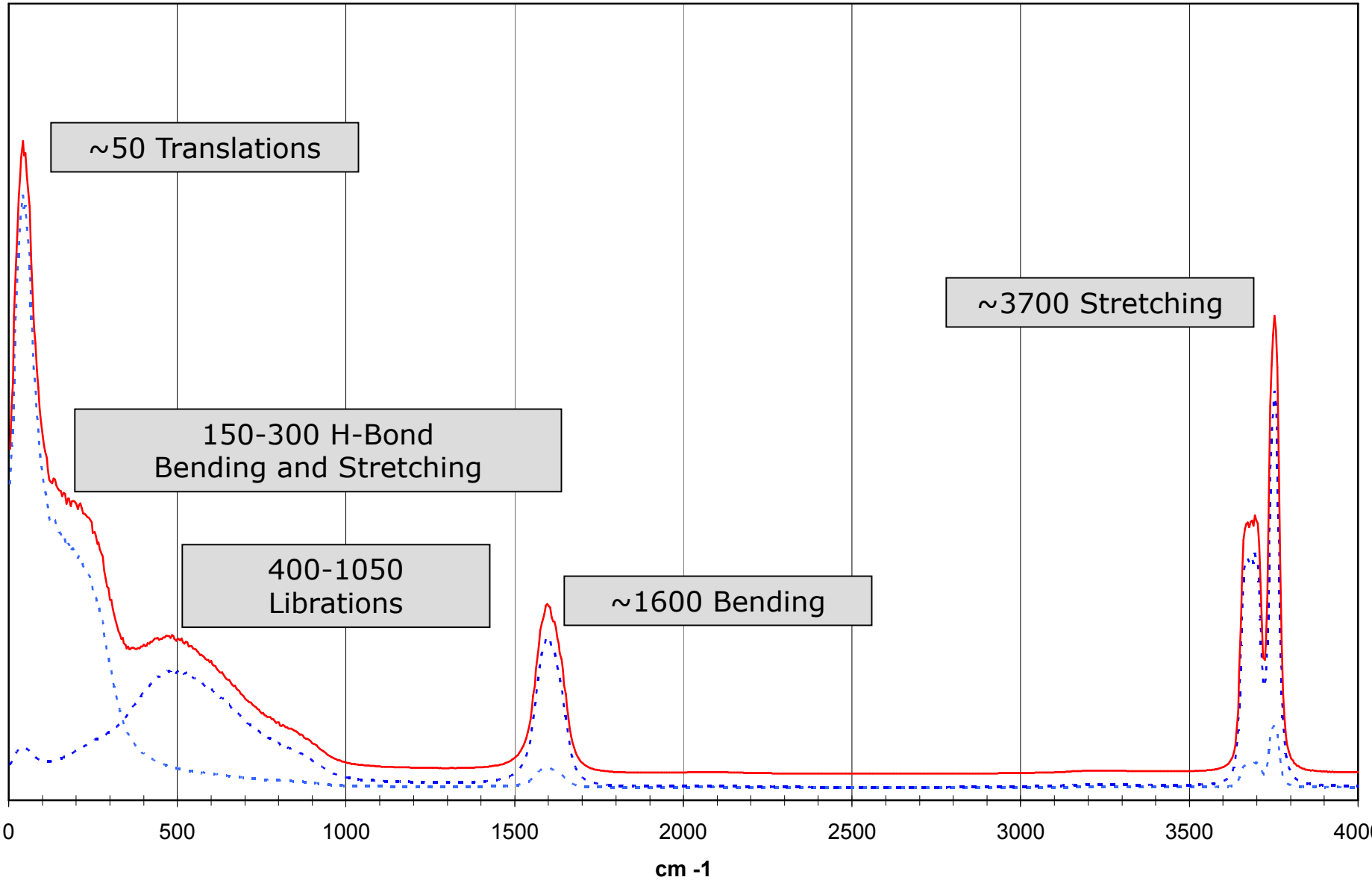
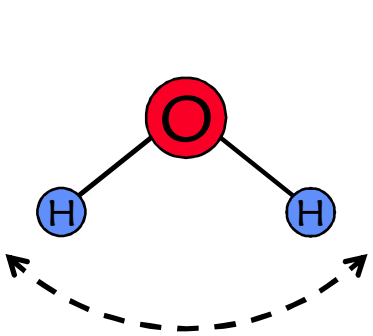
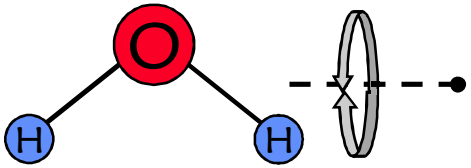
Power Spectra of Water



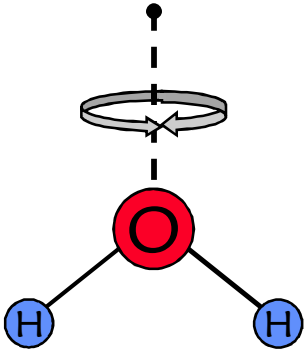
H_2O Molecular Libration Modes



"rocking" (R)



"wagging" (W)



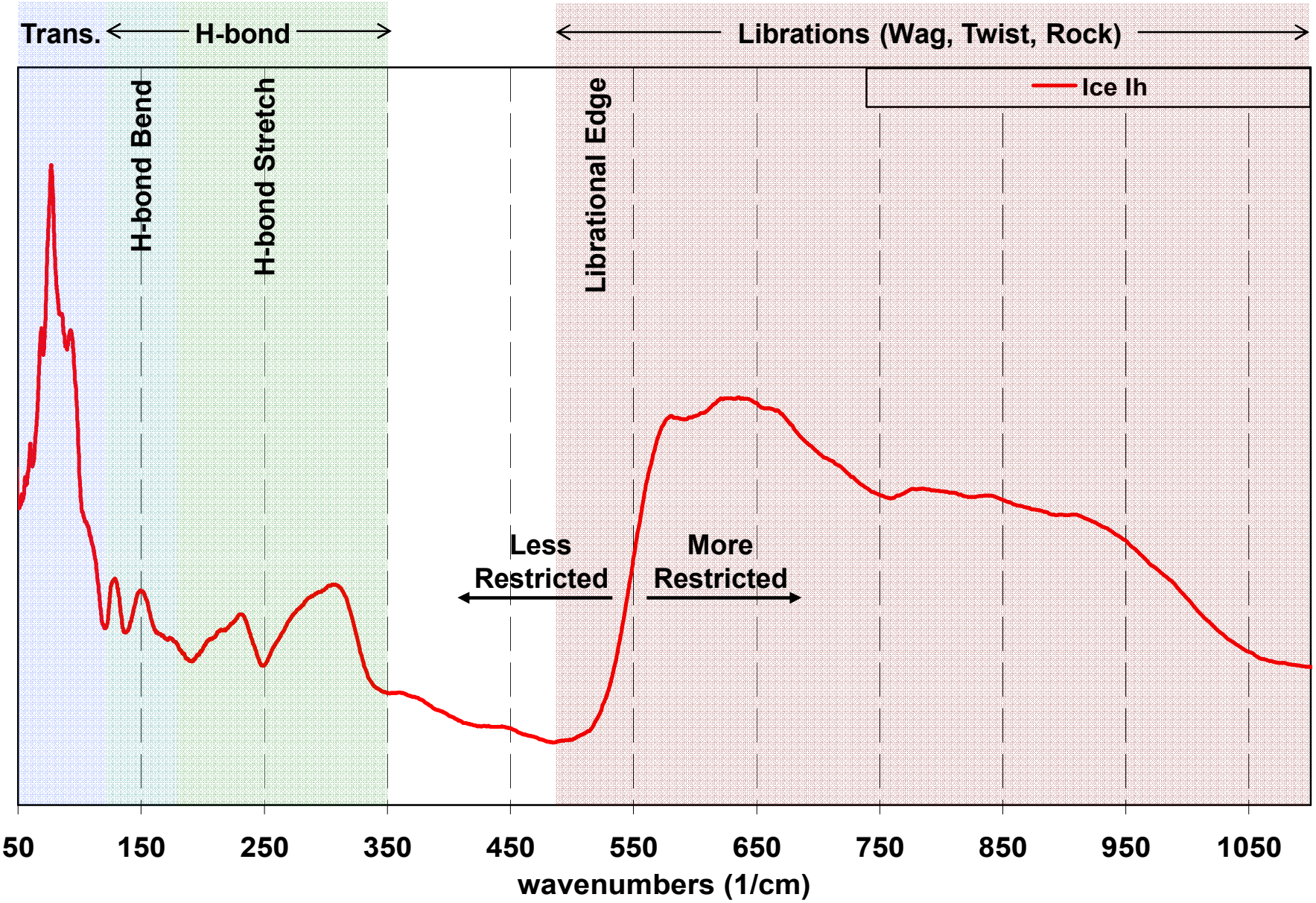
"twisting" (T)

Typically centered around ~500 cm^{-1}.

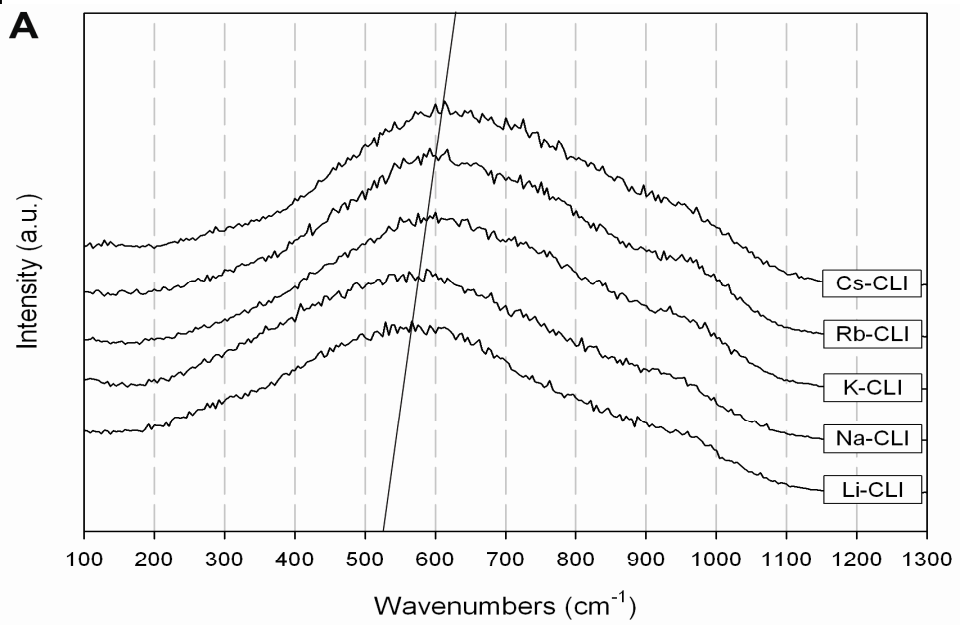
Extremely sensitive to environment. (H-bonding, Ion Coordination, Sterics)

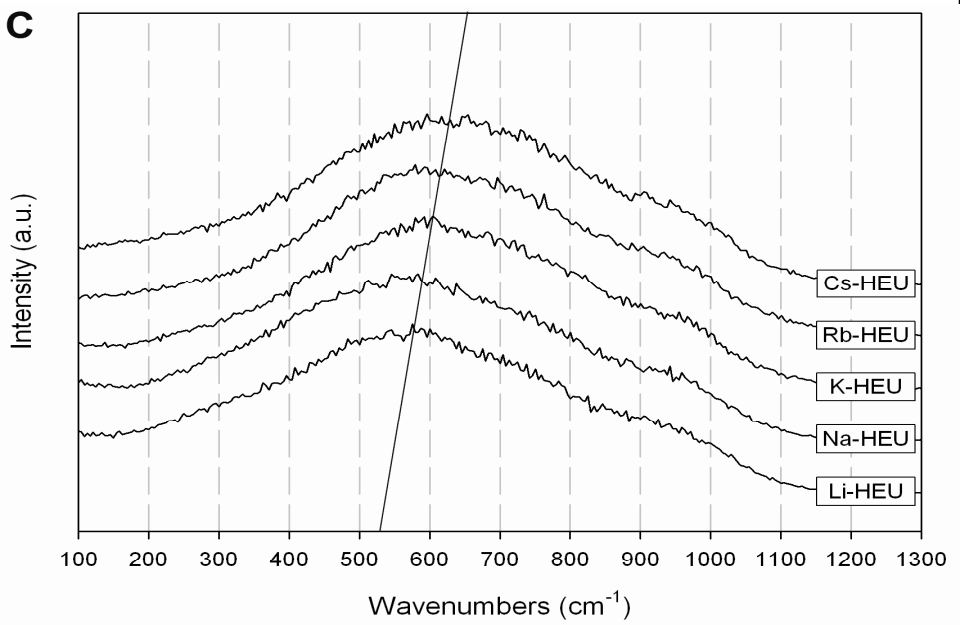
Intensity decreases and strong broadening with H_2O disorder (multiple configurations) and gives rise to Librational Edge.

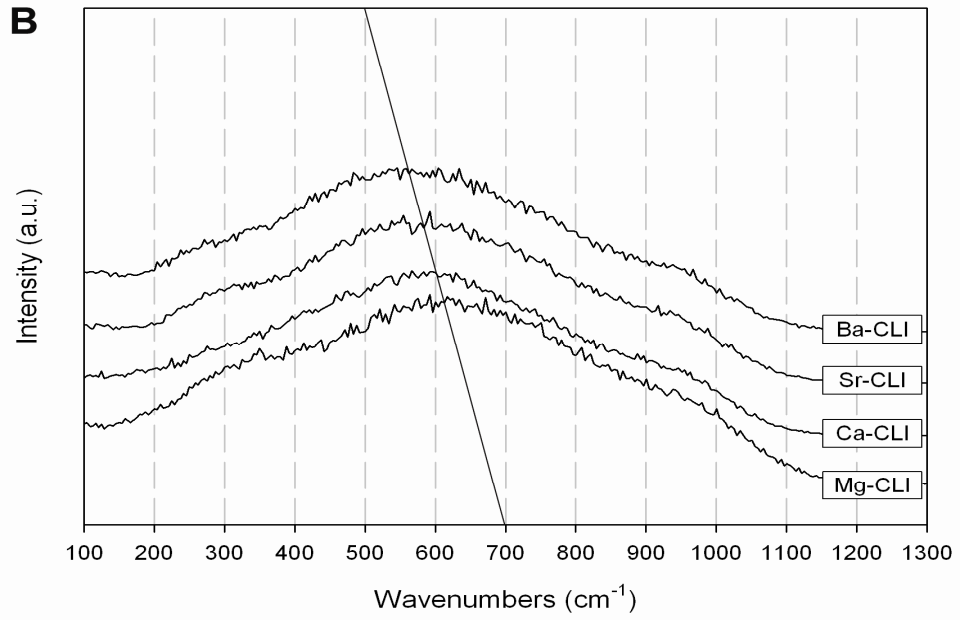
Inelastic neutron Scattering (INS) of Water

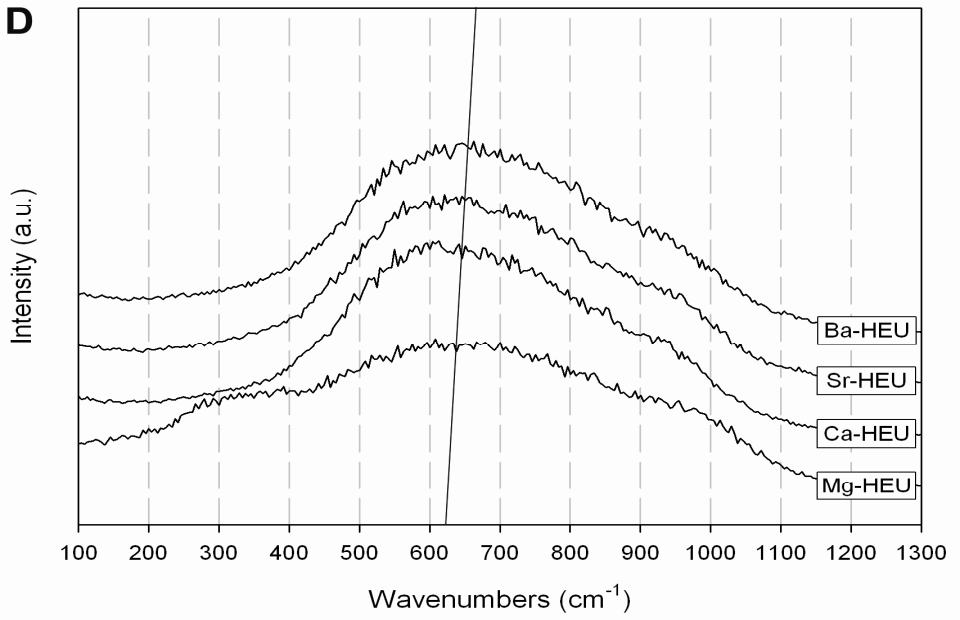


Librational features of H_2O in X-CLI and X-HEU @ 300K

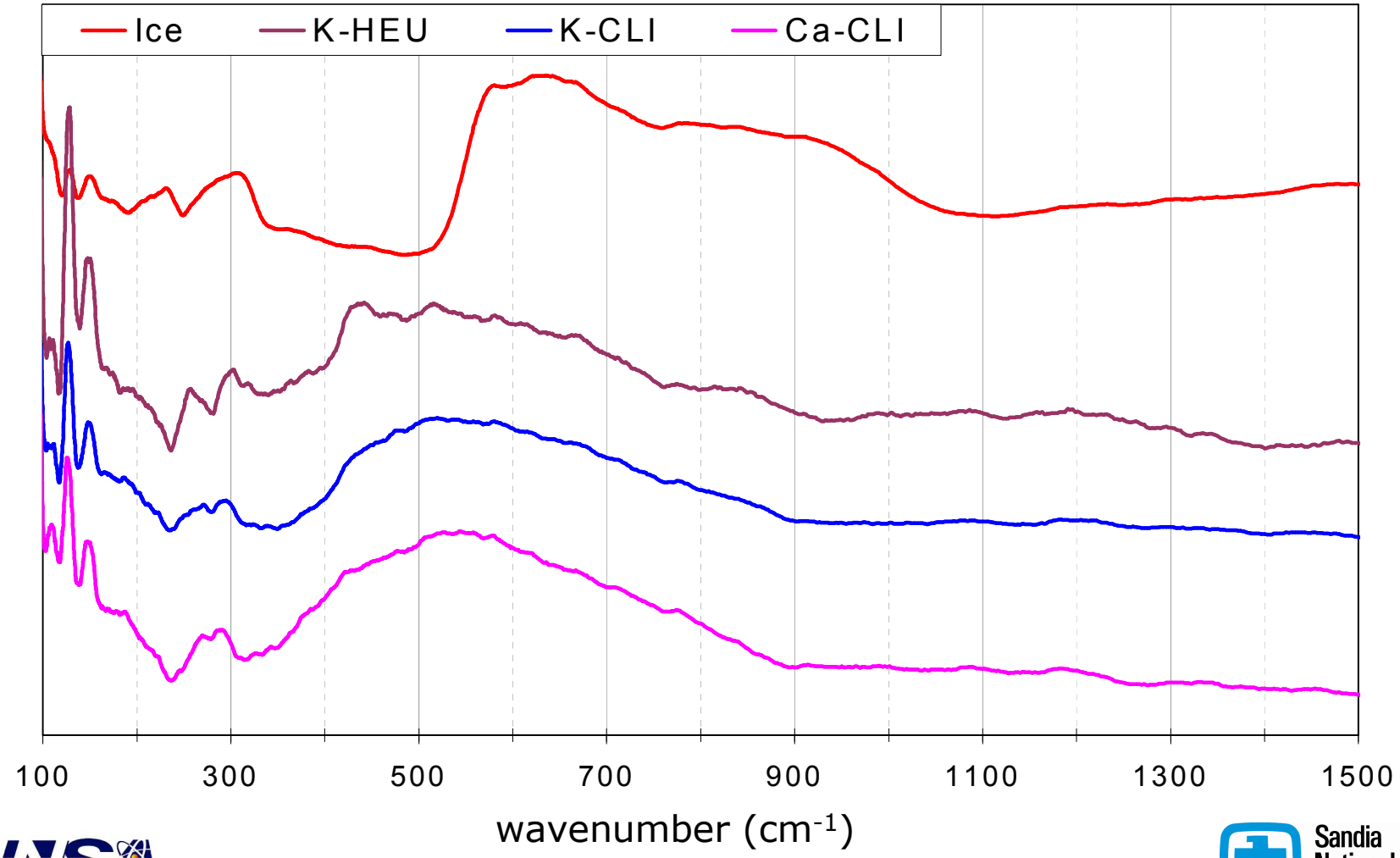








LANSCE-Inelastic Neutron Scattering (INS) Data



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Conclusions

Large-scale MD simulations are an effective method for determination and analysis of the dynamic behavior of water, ions, and framework

Ion and zeolite charge densities have finite impacts on the rotational (libration) motions of confined H_2O.

The balance between these two electrostatic fields governs dynamic behavior.

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