Low-energy XAFS at high temperatures and pressures: Ca^{2+} *and* Cl^- *K*-edge spectra of supercritical aqueous solution

PNC-XOR Sector 20

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Ion Solvation and Chemistry in High-Temperature Water

At high temperatures, the cations and anions of salts dissolved in water begin to strongly associate to form contact-ion pairs. In ongoing studies at the PNC-CAT (Advanced Photon Source) we are using x-ray absorption fine structure (XAFS) to elucidate, for the first time, the exact structures of these ion-water and ion-ion species under high-temperature conditions. The improvement in our understanding of these structures will have an impact on all systems that contain water (biochemistry, chemistry, geochemistry, waste destruction, corrosion, ion separations).

The high-brilliance, PNC–CAT beam enables studies of solutions through the small diamond-windows of the high-pressure cells (to 1 kbar). Many different ion-water systems have been studied with XAFS starting with an early landmark investigation of Sr^{2+} in supercritical water. All ionic species undergo dramatic structural transitions leading to the formation of contact ion pairs.

Importance:

- There is a need to develop a universal understanding of ion pairing covering the liquid, supercritical and gas states.
- Need to obtain the first experimental results to test simulation and statistical mechanical models of ions in hydrothermal *and* liquid water.
- Determine the strength of cation/anion "bonds" for ion-pair species
- Improve ion-water and ion-ion intermolecular potential models
- Coordination structure and redox chemistry
- Relevant to organometallic chemistry.
- Organic synthesis and oxidation reactions under hydrothermal conditions
- Salt separation and solubility
- Geochemistry

Applications:

- Environmental remediation
- Thermochemical water splitting
- Atmospheric chemistry
- Corrosion and fouling in the power generation industry.
- Hanford tank waste processing
- All processes involving ions in solution

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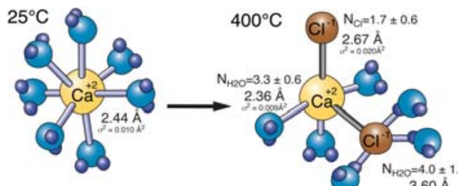
Conclusions:

- XAFS is a powerful tool to characterize structure and chemistry in high-temperature water.
- The structure of the Ca^{2+}/Cl^- ion pairs have been precisely determined using XAFS, XANES and the pre-edge region. (number, position, disorder)
- XAFS can be used to refine water-ion potentials.
  - ✓Existing intermolecular potentials don't completely capture the ion-water structure.
- These results are of fundamental importance to all aqueous systems that operate under ambient, hydrothermal or supercritical conditions.

High-Temperature Structures from Ca *and* Cl XAFS

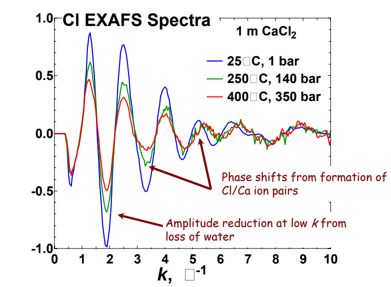


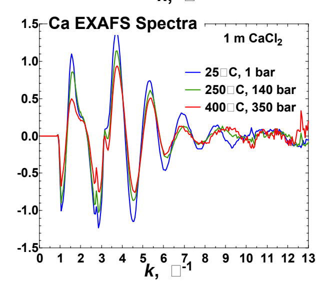
Structures derived from EXAFS fits to FEFF8 standards and from XANES and Pre-Edge features

Summary of Approach/Results

- *First* XAFS spectra of Cl^- (*K*-edge at 2822 eV) under high pressure (350 bar).
- Precise measure of the contact ion pair structure obtained including: ion-ion distances, coordination numbers, symmetry and positional disorder.
- Important for understanding geochemical and biochemical processes.
- Test case for ion pair simulations via MD.

The XAFS spectra….





Conclusion for Ca^{2+}/Cl^- Ion Pairs

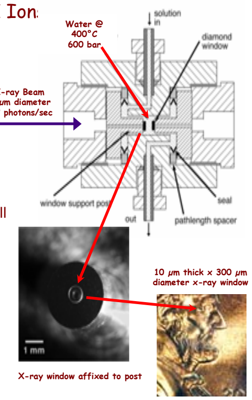
- Dramatic changes in the first shell structure
  - ✓Loss of over half the waters of hydration
  - ✓Contact ion pairing with approximately 2 chloride counter ions.
  - ✓Direct measure of the Ca-Cl interaction with bond distances and disorder.
- First successful study of a low-Z atom. (Cl *K*-edge at 2822 eV)
- Structural results are important for understanding various geochemical and biochemical systems.
- Good test case for contact ion pair simulations

Diamond-Window XAFS Cell for Low-Z Ions Cl^-, K^+, Ca^{2+}

Microbeam XAFS at APS

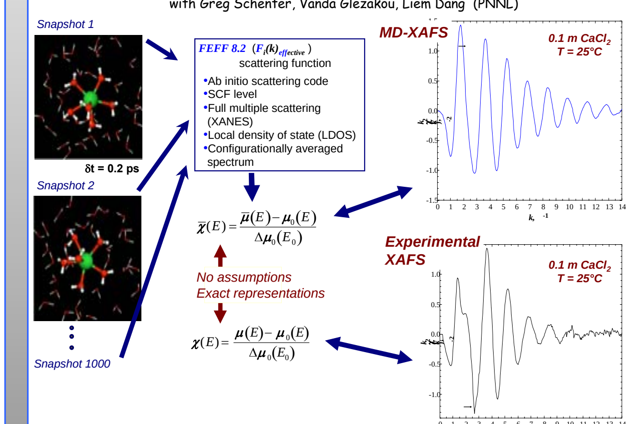
- Almost no structural studies of lighter elements under high temperature by any technique.
- Low-Z, low energy XAFS.
- Precise pressure and temperature control
- Rapid sample changes

Design Parameter	Liquid cell	Supercritical cell
Temperature	25°C	Up to 500°C
Pressure	1 bar	0.6 kbar
Beamsize	1 x 4 mm	150 x 150 µm
Incident Photon Flux	6 x 10^8	6 x 10^8
Window thickness	4 µm	10 µm
Window material	Polypropylene	[110] diamond
Pathlength	50-250 µm	50-250 µm
Concentrations	0.2 to 5 molal	0.2 to 5 molal
Transmission	20%	10%
Harmonic rejection	$>10^6$	$>10^6$
Lowest energy	2750 eV	2750 eV

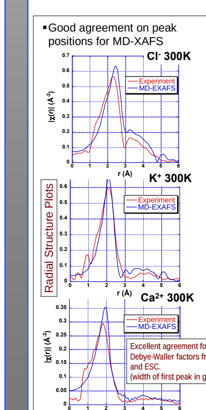


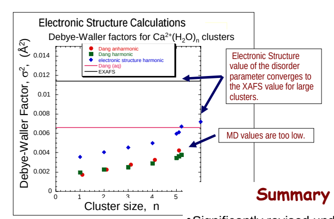
Molecular Dynamics Generation of XAFS Spectra (MD-XAFS)

with Greg Schenter, Vanda Glezakou, Liem Dang (PNNL)



Electronic Structure Calculations (ESC) vs. MD and experiment





Ion	Method	*R*, Å Ion-water distance	σ^2, Å^2 Ion-water disorder
Cl^-	XAFS	3.11	***0.029***
	ESC		***0.027***
	MD	3.22	0.033
K^+	XAFS	2.73	***0.029***
	ESC		***0.028***
	MD	2.77	0.022
Ca^{2+}	XAFS	2.43	***0.011***
	ESC		***0.011***
	MD	2.45	0.007

Summary

- Significantly revised understanding of Cl^-, K^+ and Ca^{2+} hydration. Water is more ordered than previously believed from *all other* experimental measurements.
- Good agreement for ion-water distances with MD.
- Electronic structure calculations of the ion-water peak width agree with XAFS results but not MD or neutron diffraction (NDIS) suggesting the higher accuracy of XAFS