



Details of Ion Hydration and Ion-Pair Structure from X-ray Absorption Spectroscopy and Molecular Dynamics Simulations

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Ion Hydration and Ion-Pairing in Ambient and High-Temperature Water

In ongoing studies at the third-generation synchrotron (APS) at Argonne National Lab we are using x-ray absorption fine structure (XAFS) to determine the molecular-level structure of ion hydration and ion-ion interactions in water and to improve models of these systems. By conducting these experiments over a wide range of temperatures (up to 500°C), it is possible to modulate the amount of cation-to-anion coordination without changing the chemical composition of the systems. Under ambient conditions, most cations and anions are fully dissociated. However, at high temperatures the contact-ion pairs form. The results have yielded important new information about the transitions in the coordination structure about ions in water.

Another important outcome of the research is that we have found an effective way to test and develop intermolecular potentials that are used in simulations. These ion-water and ion-ion intermolecular potentials are used both for high-temperature and ambient water studies. The existing ion-water models do not accurately predict structure in high-temperature water. From the XAFS experimental results we have implemented improvements to these models that have significantly boosted their performance.

Many different ion-water systems have been studied with XAFS starting with an early landmark investigation of Sr^{2+} in supercritical water. We have found significant dehydration occurring under supercritical water conditions for mono- and di-valent cations (Sr^{2+} and Rb^+) and for a monovalent anion (Br^-). More recently we have explored the fascinating changes in the coordination structure that occur for ion-pair species of the transition metal, Ni^{2+} and Cu^+ . In the most recent studies, we have produced a definitive study of Ca^{2+} and Sr^{2+} hydration under ambient conditions.

Importance:

- Fundamental properties of ion hydration in water (ambient and high-T)
- Simulation and statistical mechanical models of ions.
- Improving ion-water and ion-ion intermolecular potentials
- Coordination structure and redox chemistry
- Relevant to organometallic chemistry. Simple coordination chemistry
- Organic synthesis and oxidation reactions under hydrothermal conditions
- Salt separation and solubility
- Geochemistry

Applications:

- Environmental remediation
- Waste destruction in SCW oxidation.
- Metal ion separations
- Corrosion and fouling in the power generation industry.
- Hanford tank waste processing
- All processes involving ions in solution

References

- "An XAFS Study of Strontium Ions and Krypton in Supercritical Water." D. M. Pfund, J. G. Darab, and J. L. Fulton, *J. Phys. Chem.*, **98**, 13102-13107, (1994).
- "Direct Modeling of XAFS Spectra from Molecular Dynamics Simulations", B. J. Palmer, D. M. Pfund, J. L. Fulton, *J. Phys. Chem.*, **100**, 13393-13398, (1996).
- "The Ion Pairing and Hydration of Ni^{2+} in Supercritical Water at 425°C and 680 bar determined by X-ray Absorption Fine Structure and Molecular Dynamics Studies", S. L. Wallen, B. J. Palmer, J. L. Fulton, *J. Chem. Phys.*, **108**, 4039-4046, (1998).
- "A Transition in the Ni²⁺ Complex Structure from Six- to Four-Coordinate upon Formation of Ion Pair Species in Supercritical Water: An XAFS, NMR and MD Study" M. M. Hoffmann, J. G. Darab, B. J. Palmer, and J. L. Fulton, *J. Phys. Chem. A*, **103**, 8471-8482, (1999)
- "Copper(I) and Copper(II) Coordination Structure under Hydrothermal Condition at 325°C: An XAFS, and MD Study", Fulton, Hoffmann, M. M., Darab, J. G., Palmer, B. J., Stern, E. A., *J. Phys. Chem. A*, **105**, 11651-11653, (2000).
- "An X-ray Absorption Fine Structure Study of Copper(II) Chloride Coordination Structure in Water up to 325°C", J. L. Fulton, M. M. Hoffmann, and J. G. Darab, *Chemical Physics Letters*, **330**, 300-308, (2000)
- "An Infrared and X-ray Absorption Study of the Structure and Equilibria in Chromate, Bichromate, and Dichromate Aqueous Solutions to High Temperature", *J. Phys. Chem. A*, **105**, 6876-6885, (2001).
- "Understanding the Effects of Concentration on the Solvation Structure of Ca^{2+} in Aqueous Solution: The Perspective on Local Structure from XAFS and XANES", J. L. Fulton, S. M. Heald, Y. S. Badyal, J. M. Samson, *J. Phys. Chem. A*, **107**, 4686-4696 (2003)

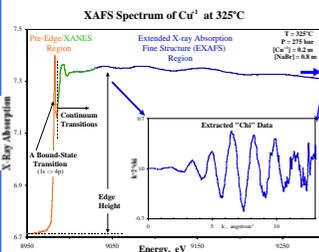
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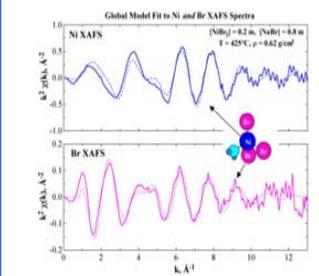
Conclusions:

- XAFS is a powerful tool to characterize ion hydration structure.
- The structure of the Ni/Br , Cu/Br , Cu/Cl , Ca/Cl ion pairs have been precisely determined (number, position, disorder)
- XAFS can be used to refine water-ion and ion-ion potentials.
- Existing intermolecular potentials don't completely capture the ion-water structure. Many serious deficiencies in anion-cation potential models.
- These results are of fundamental importance to all aqueous systems that operate under ambient, hydrothermal and supercritical conditions

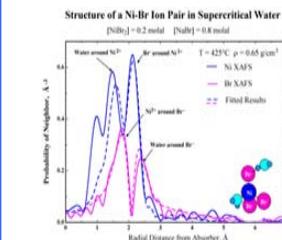
The XAFS spectrum....



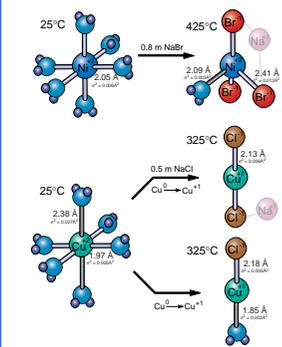
The fitted data....



The transformed spectra....

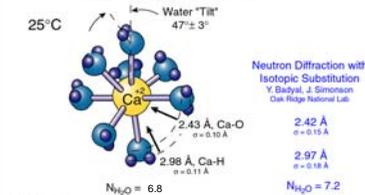


Contact Ion Pairs: High-Temperature Structures from Ni/Cu and Br XAFS

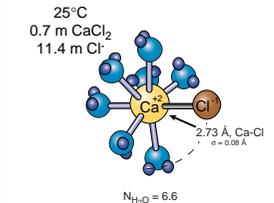


XAFS Structures....

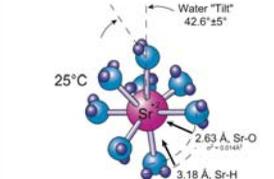
Calcium Hydration: XAFS vs Neutron Scattering



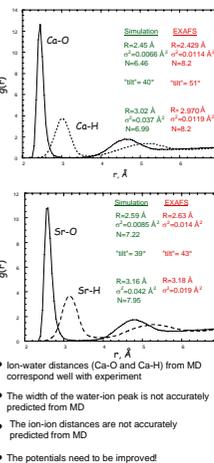
Calcium Chloride Contact Ion Pair



Strontium Hydration Structure

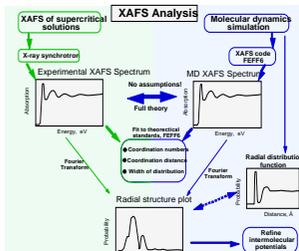


MD-XAFS Comparison to Experiment

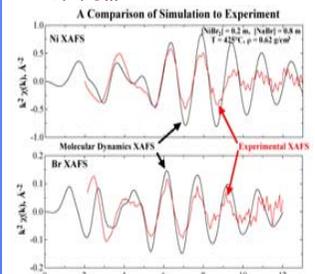


- Ion-water distances (Ca-O and Ca-H) from MD correspond well with experiment
- The width of the water-ion peak is not accurately predicted from MD
- The ion-ion distances are not accurately predicted from MD
- The potentials need to be improved

Molecular Dynamics Generation of XAFS Spectra



MD vs. experimental XAFS...

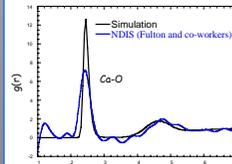


MD results...

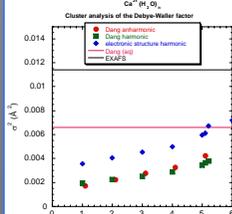
Qualitative agreement between XAFS data and MD simulation for ions in a hydrothermal environment, but significant errors in distances and binding energy. XAFS can be used to refine the water-ion intermolecular potential models that are currently only parameterized at standard temperature and pressure.

The Water-Ion Distance Disorder

Simulated peak width is too narrow compared to neutron scattering results.



XAFS peak width appears to agree with electronic structure calculations but not with the MD simulated peak width.



XAFS vs. MDXAFS vs. Neutron Diffraction: Results of comparative studies

- Good agreement for ion-water distances by all three techniques including ion-oxygen and ion-hydrogen distances
- From MD studies, we have shown that the water "tilt" is due to thermal "wagging" of the water molecular on the water surface.
- Ion-water distance disorder from simulation is much smaller than from either XAFS or neutron diffraction. Need improved potential models.
- Electronic structure calculations of the ion-water peak width agree with XAFS results but not MD or neutron diffraction
- Contact ion pair distances are 0.1-0.2 angstroms shorter than predicted from MD simulations. Need improved potential models.