X−ray absorption spectroscopy investigations of aqueous solutions at high pressure

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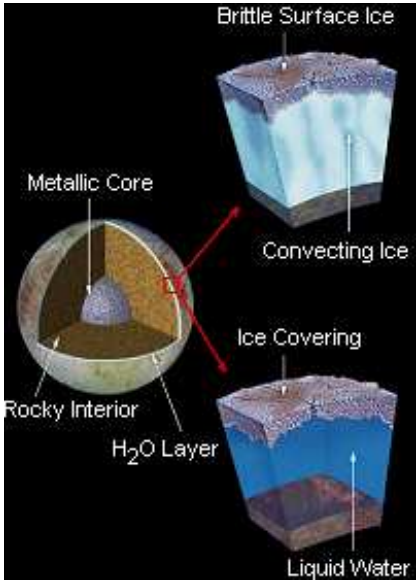
Talk Outline − main issues

- 1. Scientific motivations
- 2. Why X−ray absorption spectroscopy is useful
- 3. Experimental techniques for High Pressure and Temperature
- 4. Examples of investigations of aqueous solutions
- 5. Nature and importance of the achievable information

Roma, 101° Congresso Nazionale SIF, 21−25 Settembre 2015

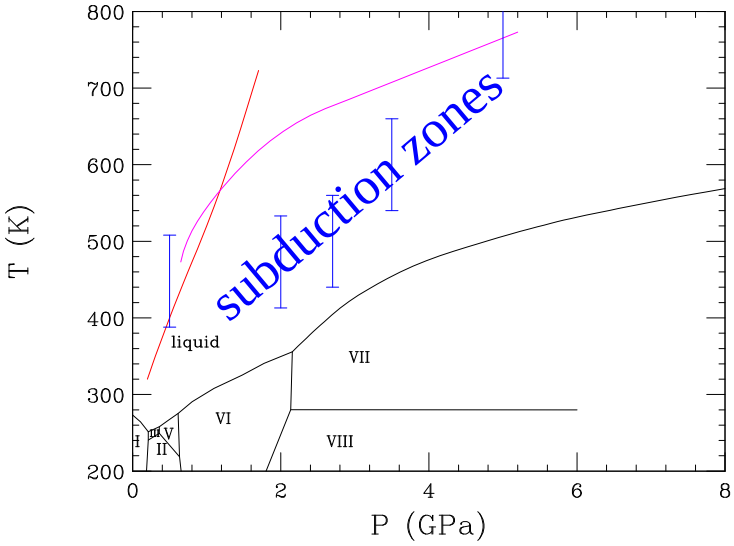
X−ray absorption spectroscopy studies of aqueous solutions at High−Pressure

Scientific motivation:
Understanding the behaviour of water as a solvent at high−pressure



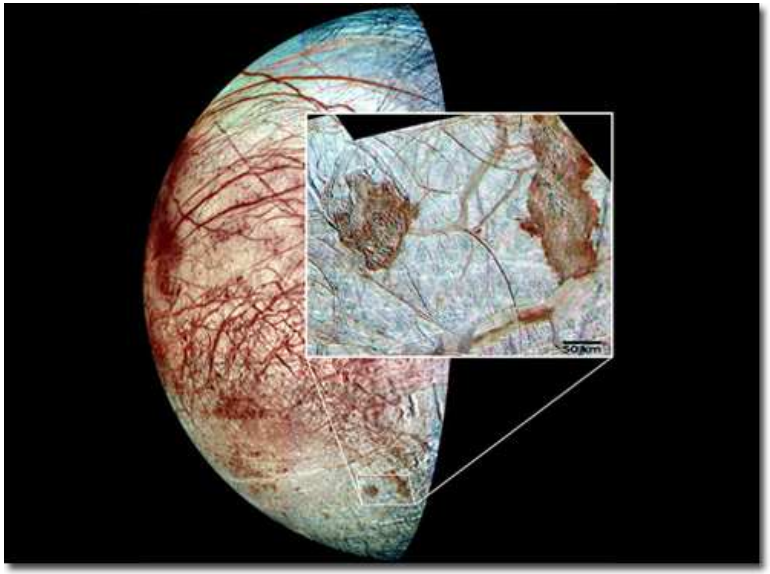
Relevant to:
- Basic chemical physics science
- Earth and Planetary science

Earth crust/upper mantle



H_2O phase diagram

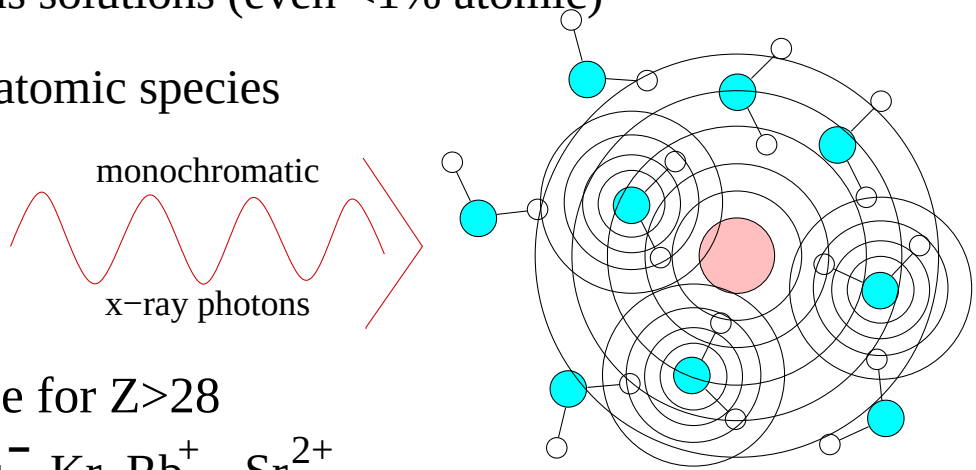
Europa buried ocean



Fields where X−ray Absorption Spectroscopy is unique

- Crystalline structures: diffraction techniques tell almost everything, however XAFS can play a role when correlated local units exist.
- Liquid or amorphous bulk structures: XAFS provides important complementary information on the short−range features of the partial radial distribution functions.
- Sensitivity to triplet correlations through MS (still partly unexploited)
- Electronic properties can be probed in many ways, but XAFS probes them simultaneously with the structure. Can be exploited in the case of I<−>M transitions or to probe the integrity of molecular strucutres.
- Diluted species (in low−Z environment) in disordered matter: impurities, diluted alloys, aqueous solutions (even <1% atomic)

  XAS at the edge of the minority atomic species



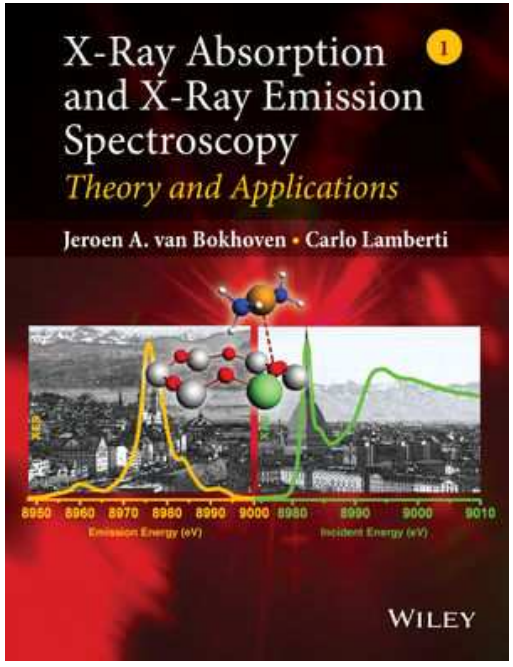
→ HP experiments are possible for Z>28

Cu^{2+}, Zn^{2+}, Ga, Ge, As^{3+}, Br^{-}, Kr, Rb^{+} , Sr^{2+}, ...

The learn more about XAS $\rightarrow$ the new Book

X-Ray Absorption and X-Ray Emission Spectroscopy: Theory and Applications

Editors:
Jeroen van Bokhoven, Carlo Lamberti
ISBN: 978-1-118-84423-6
Wiley (2015)



Chapter 25: "XAS in Liquid Systems"
by Adriano Filipponi and Paola D'Angelo

25.5.3 Transition metal aqua ions

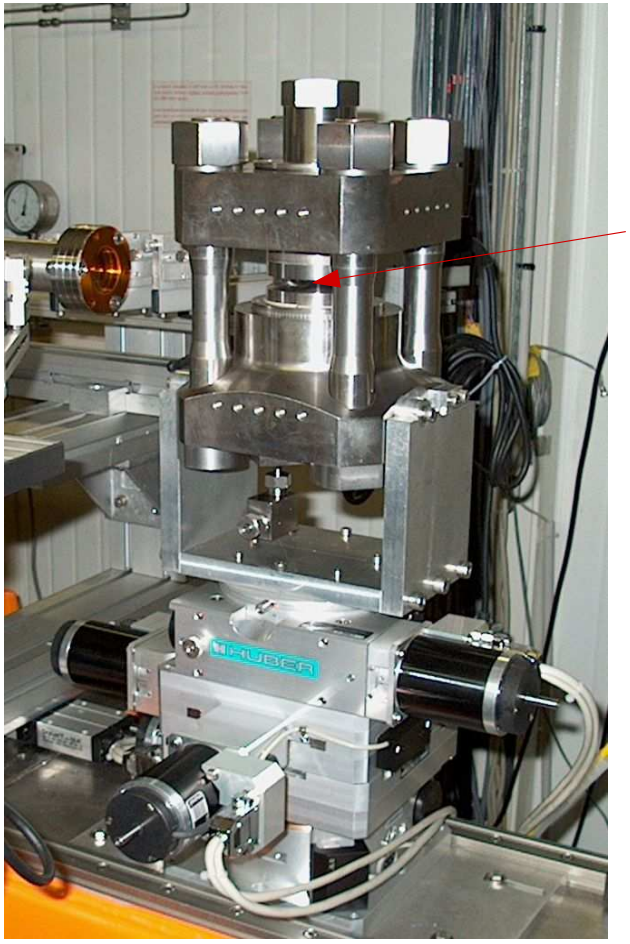
25.5.4 Lanthanide aqua ions

25.5.5 Halide aqua ions: the bromide case

Paris−Edinburgh press and sample confinement

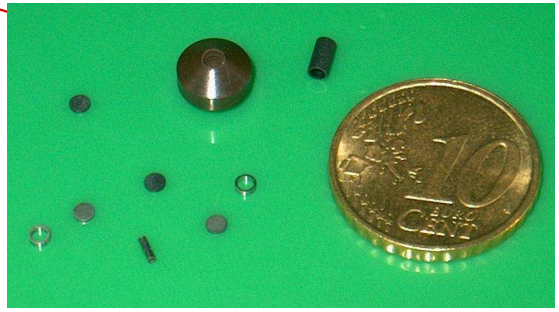
In collaboration with Jean Paul Itié (Paris)

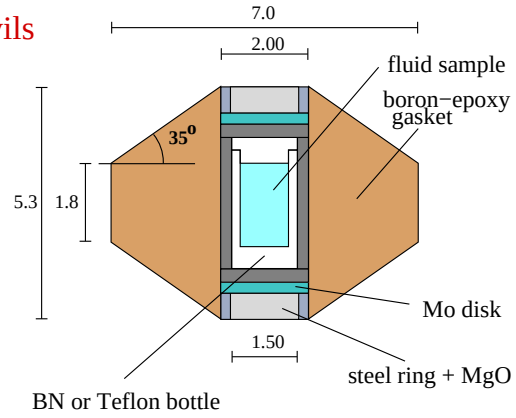
high−pressure large−volume technique
P: 0.2−8 GPa, T: 300−1000 K



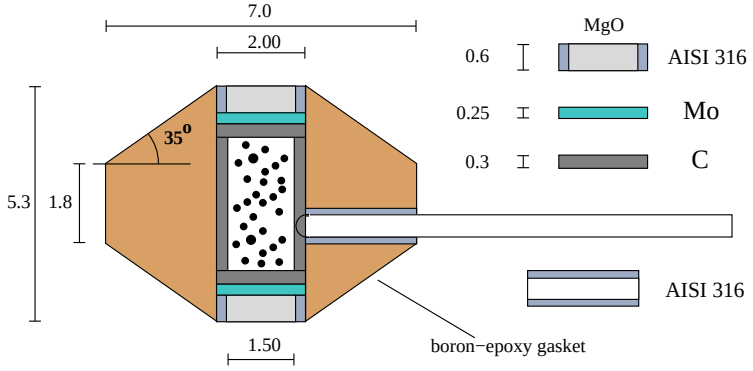
7mm gasket

Sample mounting components

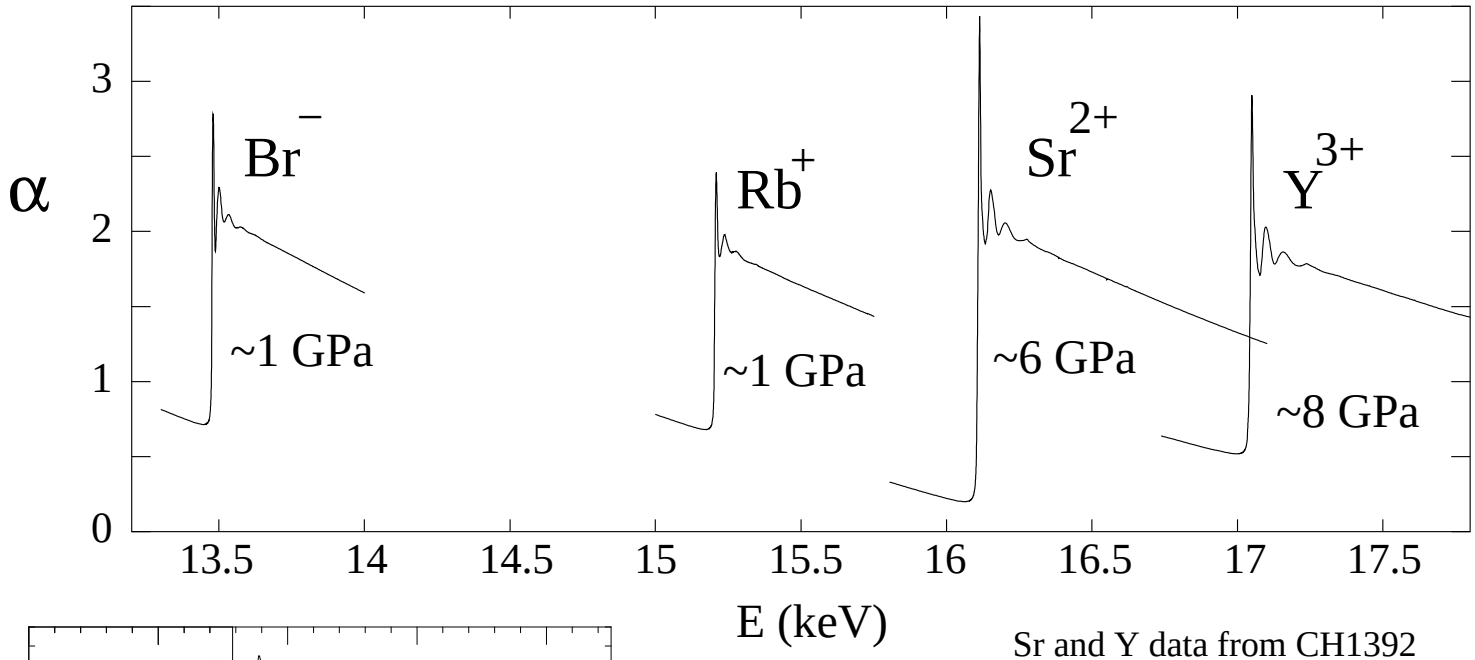




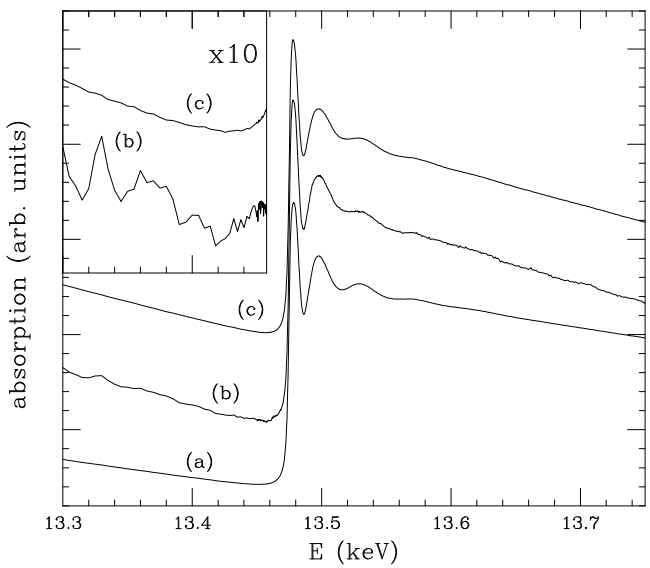
an aqueous solution sample



X−ray absorption spectra of aqueous solutions at HP



Sr and Y data from CH1392
(with S. Ramos and A. Barnes)

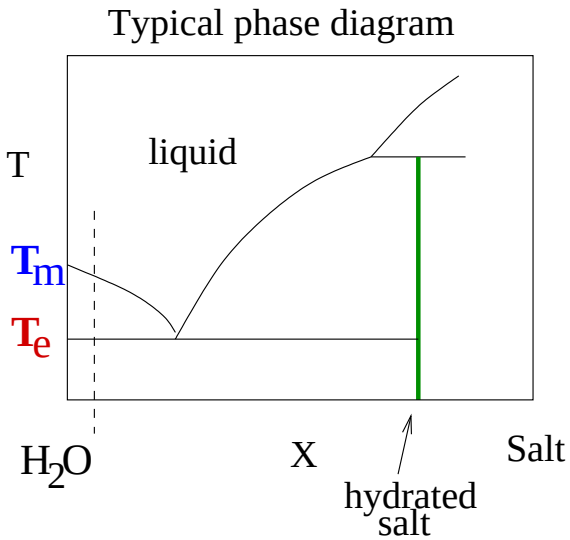


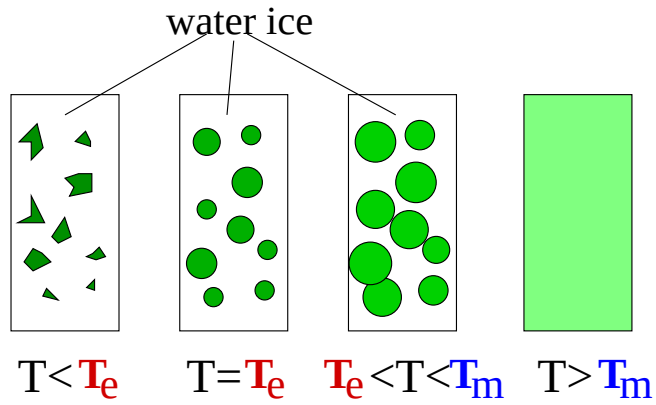
High quality x−ray absorption spectra can be collected also under extreme conditions of high pressure and temperature $\Delta\alpha / \alpha \sim 10^{-4}$

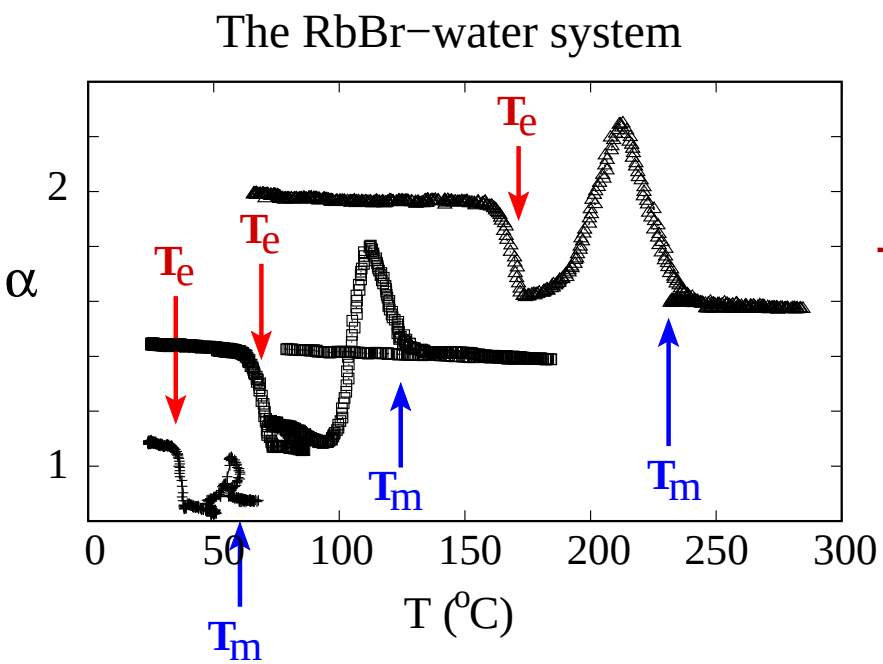
Aqueous solutions XAFS investigations at room and HP (●)

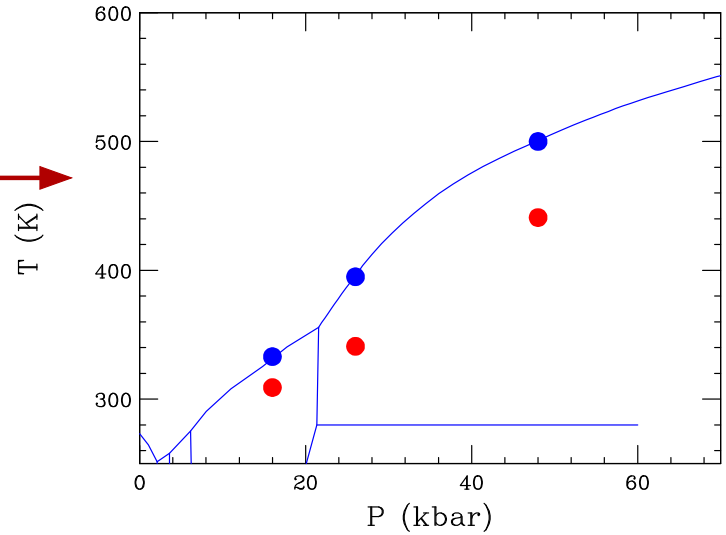
- A. Filipponi, S. De Panfilis, C. Oliva, M. A. Ricci, P. D'Angelo, and D. T. Bowron, *"Ion hydration under pressure."*, Phys. Rev. Lett. **91**, 165505 (2003).
- P. D'Angelo, S. De Panfilis, A. Filipponi, and I. Persson, *"High-Energy X-ray Absorption Spectroscopy: A New Tool for Structural Investigations of Lanthanoids and Third-Row Transition Elements."*, Chemistry - A European Journal **14**, 3045-3055 (2008).
- V. Migliorati, G. Mancini, G. Chillemi, A. Zitolo, and P. D'Angelo, *"Effect of the Zn(2+) and Hg(2+) Ions on the Structure of Liquid Water."*, J. Phys. Chem. A **115**, 4798-4803 (2011).
- P. D'Angelo, A. Zitolo, V. Migliorati, G. Chillemi, M. Duvail, P. Vitorge, S. Abadie, and R. Spezia, *"Revised Ionic Radii of Lanthanoid(III) Ions in Aqueous Solution."*, Inorganic Chemistry **50**, 4572-4579 (2011).
- V. Migliorati, G. Mancini, S. Tatoli, A. Zitolo, A. Filipponi, S. De Panfilis, A. Di Cicco, and P. D'Angelo, *"Hydration Properties of the Zn^{2+} Ion in Water at High Pressure."*, Inorganic Chemistry **52**, 1141-1150 (2013).
- P. D'Angelo, F. Martelli, R. Spezia, A. Filipponi, and M. A. Denecke, *"Hydration Properties and Ionic Radii of Actinide(III) Ions in Aqueous Solution."*, Inorganic Chemistry **52**, 10318-10324 (2013).
- P. D'Angelo and V. Migliorati, *"Solvation Structure of Zn^{2+} and Cu^{2+} Ions in Acetonitrile: A Combined EXAFS and XANES Study."*, J. Phys. Chem. B **119**, 4061-4067 (2015).

X−ray absorption temperature scans to investigate water−salt phase diagrams



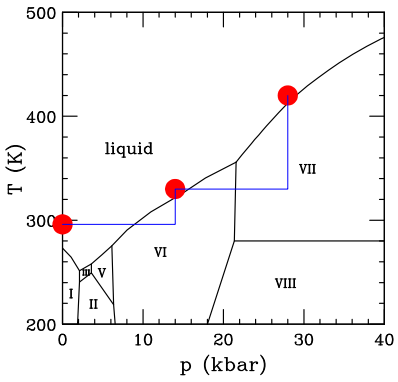




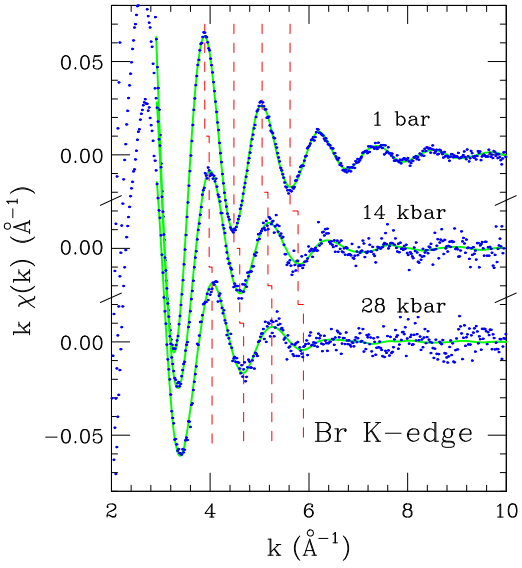


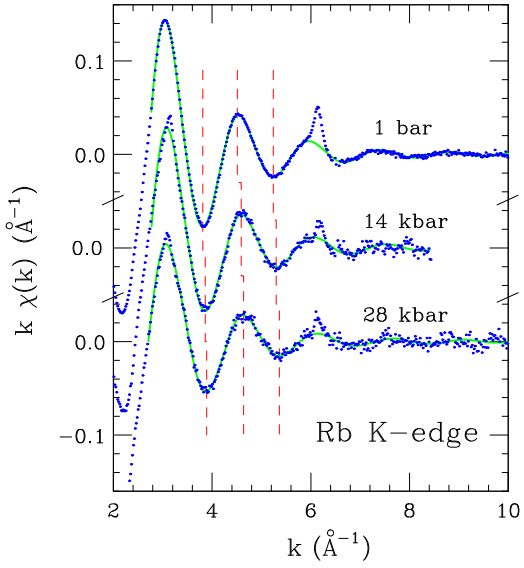
The hydration structure around Rb^+ and Br^- up to 2.8 GPa

P−T sample history

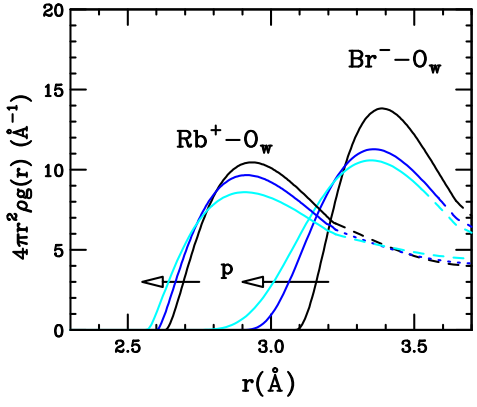


EXAFS of a RbBr aqueous solution





Pressure effect on the Ion−O distribution

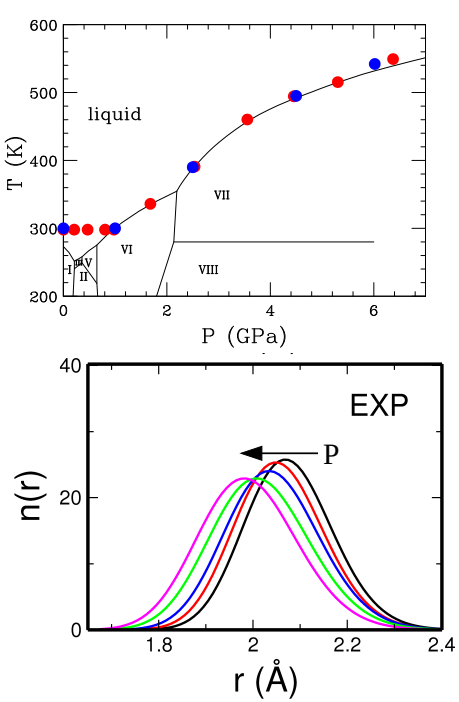


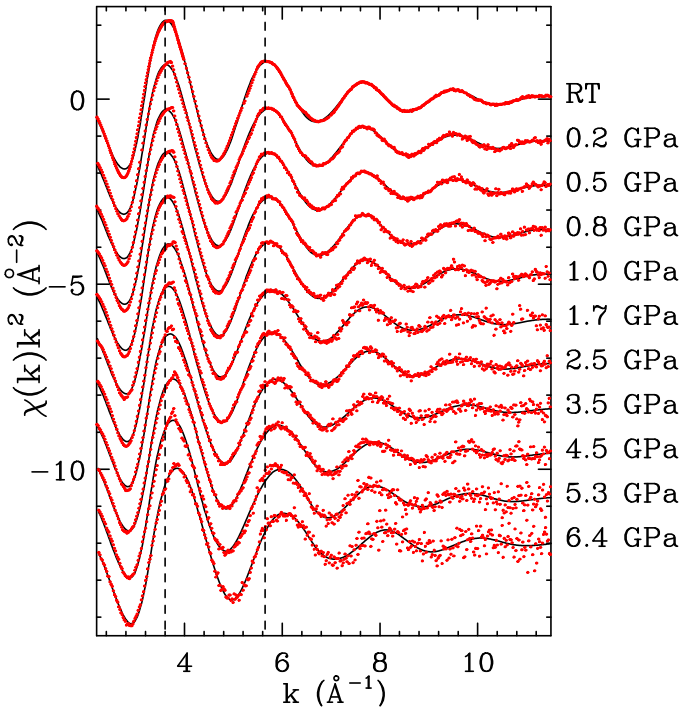
- A. Filipponi, S. De Panfilis, C. Oliva, M. A. Ricci, P. D'Angelo, and D. T. Bowron, "Ion hydration under Pressure", Phys. Rev. Lett. 91, 165505 (2003).

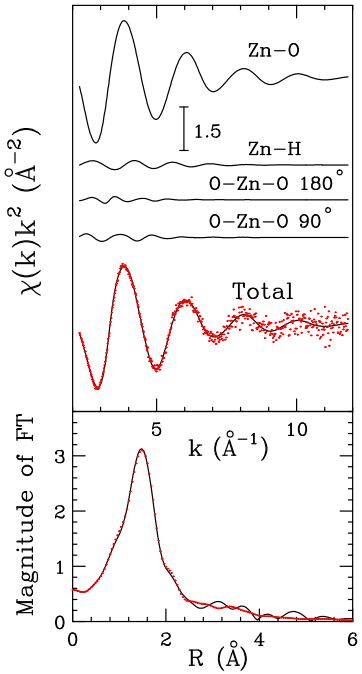
The hydration shell of Zn^{2+} as a function of pressure

V. Migliorati, G. Mancini, S. Tatoli, A. Zitolo, A. Filipponi, S. De Panfilis, A. Di Cicco, and P. D'Angelo, *"Hydration Properties of the Zn^{2+} Ion in Water at High Pressure."*, Inorganic Chemistry **52**, 1141-1150 (2013).

The octahedral coordination of the Zn^{2+} ion is well assessed, but ...







an evident compression of the Ion-Oxygen distance distribution occurs with increasing P at RT and then following the water melting line up to $\simeq 6$ GPa.

Conclusions

X-ray absorption spectroscopy investigations of aqueous solutions at ambient and high pressure can provide important information on the water salt systems, in particular:

- High-Pressure experiments up to 6-8 GPa in the molten water range are possible using the large-volume Paris-Edinburgh press technique. Ions from Cu^{2+} ($Z \geq 29$) can be investigated.
- Temperature scans provide evidence for the major temperature markers (T_e and T_m) in the water-salt phase diagrams at various pressures.
- Signal from the Ion-Oxygen distance distribution can be clearly detected providing information on the evolution (compression) and integrity of the hydration shell.
- XAS data provide severe constraints to interaction potential models used in computer simulations.

Thank you for your attention!