![ESRF logo] **ESRF**	**Experiment title:** Hydratation study of GaBr$_3$ aqueous solution in supercritical conditions by X-ray Absorption Spectroscopy	**Experiment number**: 30.02.747
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Compared to water at ambient conditions, supercritical water (SCW) is unique in that it exhibits both gas-like and liquid-like. A decrease of the dielectric constant of SCW leads to a lowering of the solubility of inorganic salts. By characterizing the ion-water (hydration), ion-ion (ion pairing) and water-water (hydrogen bonding) interactions, the unique properties of such a system can be inspected. One of the most appropriate technique for the structural study of the local order around the ions in solution is the X-ray Absorption Spectroscopy (XAS). A High Temperature and High Pressure (HP/HT) cell dedicated to fluorescence XAS measurements, among other techniques, was developed and is now used routinely.[1]

The behaviour with P and T of the bromide anion bonded to monovalent[2] or divalent cations such as Zn[3], Mn[4], Ni[5] in aqueous solutions is now well understood. In this study we focus on a trivalent cation, Ga(III). The main aim of this experiment was to determine the structure of the ionic hydration and/or pairing at various P and T in aqueous GaBr$_3$ solutions. Previous results from XAS, X-ray Diffraction and Raman experiments on the GaBr$_3$ system showed the ion pairing effect occurred at ambient conditions in concentrated aqueous solutions[6] and is not observed for concentrations lower than 1 mol/l.[7]

The isobaric experiments have been performed with the HP/HT cell at 30 MPa from ambient temperature to 400°C for two GaBr$_3$ concentrations (0.017 and 0.17 mol/l). XAS measurements have been made, both at the Ga and Br K-edges on these aqueous GaBr$_3$ solutions. Analysis has been carefully performed on the different part of the signal: height of the edge measured in the transmission mode (concentration of the dissolved probed element), EXAFS and XANES spectra.

EXAFS spectra obtained for the concentrated solutions are shown on figure 1. At room temperature, Ga and Br atoms are fully solvated, surrounded by O atoms at 1.97Å (Ga-O) and 3.37Å (Br-O). When the temperature increases, Ga atoms precipitate as GaO(OH) in the [100 - 330°C] range while Br atoms remain completely solvated. For higher temperature, Ga atoms are remarkably re-dissolved (25% and 50% for 0.017 and 0.17 mol/l respectively), ion pairing occurs and tetrahedral GaBr$_4$ complexes are formed (R$_{Ga-Br}$=R$_{Br-Ga}$=~2.31Å). This determination is done from:

- EXAFS calculation at the Ga K-edge (N$_{Ga-Br}$=3.3±0.2, N$_{Ga-O}$=0.6±0.2 at 333°C and 0.17mol/l)
- EXAFS calculation at the Br K-edge (N$_{Br-Ga}$=0.9±0.2, N$_{Ga-O}$=2.0±0.2 in the same conditions)
- XANES calculations at the Ga K-edge (figure 2)

This structure is in good agreement with what was obtained at ambient conditions in concentrated solutions[6] but also with the analogous system InCl$_3$ in supercritical conditions where InCl$_4$ clusters are formed.[8] The main differences with the divalent systems are the dissolution of Ga from solid GaO(OH) close to the

supercritical region and the formation of $GaBr_4$ molecule in comparison with MBr_nO_{4-n} molecules (M= Zn^3, Mn^4, Ni^5, n=$2^{3,4}$ or 1^5).
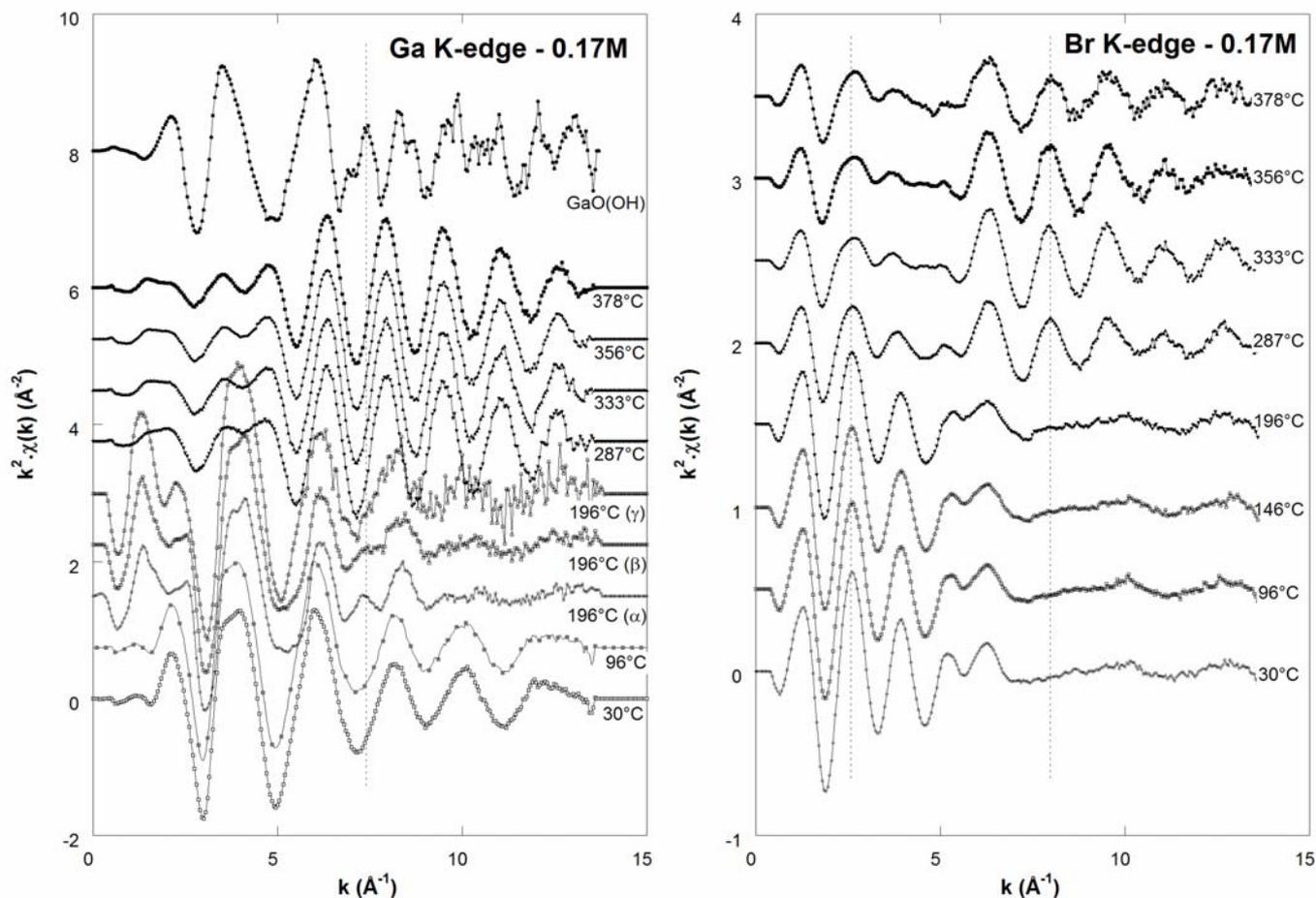

Figure 1: $k^2.\chi(k)$ EXAFS spectra obtained for the $GaBr_3$ aqueous solutions ([$GaBr_3$]=0.017M) at the Ga (left) and Br (right) K-edges.
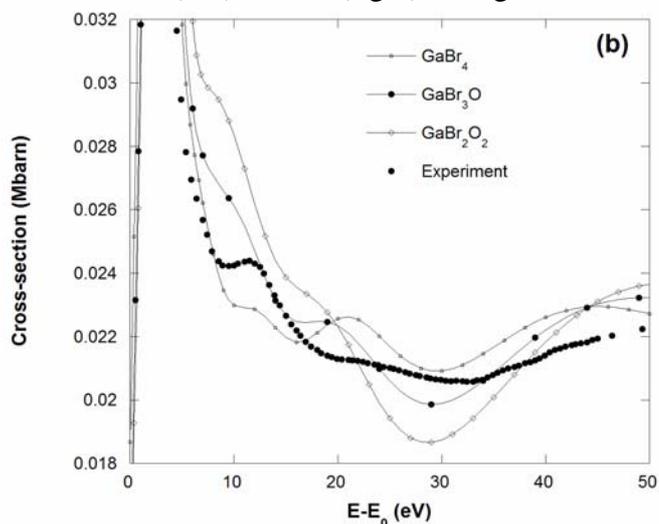

Figure 2: Experimental and convoluted calculated spectrum for $GaBr_{4-n}O_n$. Caluclations performed using the Finite Difference Method (FDM) where the electronic potential is calculated by the direct resolution of the Schrödinger equation on the node points of a three-dimensional grid.[9] The various resonance peaks experimentaly obtained (at ~11 and ~21eV) are consistent with the pure $GaBr_4$ tetrahedral structure

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