



<b>Experiment title:</b> The solvation of cations around the metal-nonmetal transition in metal-ammonia solutions.	<b>Experiment number:</b> CH540	
<b>Beamline:</b> BM29	<b>Date of experiment:</b> from: 13 <sup>th</sup> Dec 1998 to: 17 <sup>th</sup> Dec 1998	<b>Date of report:</b> 20 <sup>th</sup> Feb. 1999
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**Report:**

The aim of this experiment was to obtain information on the coordination environment of Rb in the Rb-NH<sub>3</sub> solutions. BM29 was used with the Si[311] monochromator crystals configuration and data about the Rb K-absorption edge at  $\approx 15.20\text{keV}$  was obtained. A typical experimental scan covered a range of X-ray energies from to 14.9 to 15.8keV. Furthermore, EXAFS data of a concentrated RbBr-NH<sub>3</sub> solution were collected, the structural information from which will provide an insight into how the short range order of Rb is affected by the presence of Br in the ammonia solutions, and act as a benchmark in which we know the Rb valence. Moreover, in studying RbBr both the Rb and Br edges (the latter at  $\approx 13.46\text{keV}$ ) were accessible using BM29 allowing for the solvation of the Br<sup>-</sup> ion in the ammonia solution to be studied. Crystalline RbBr was chosen as the reference compound for the ammonia solution data. The EXAFS data are the subject of on-going data analysis, although preliminary results are given in this report.

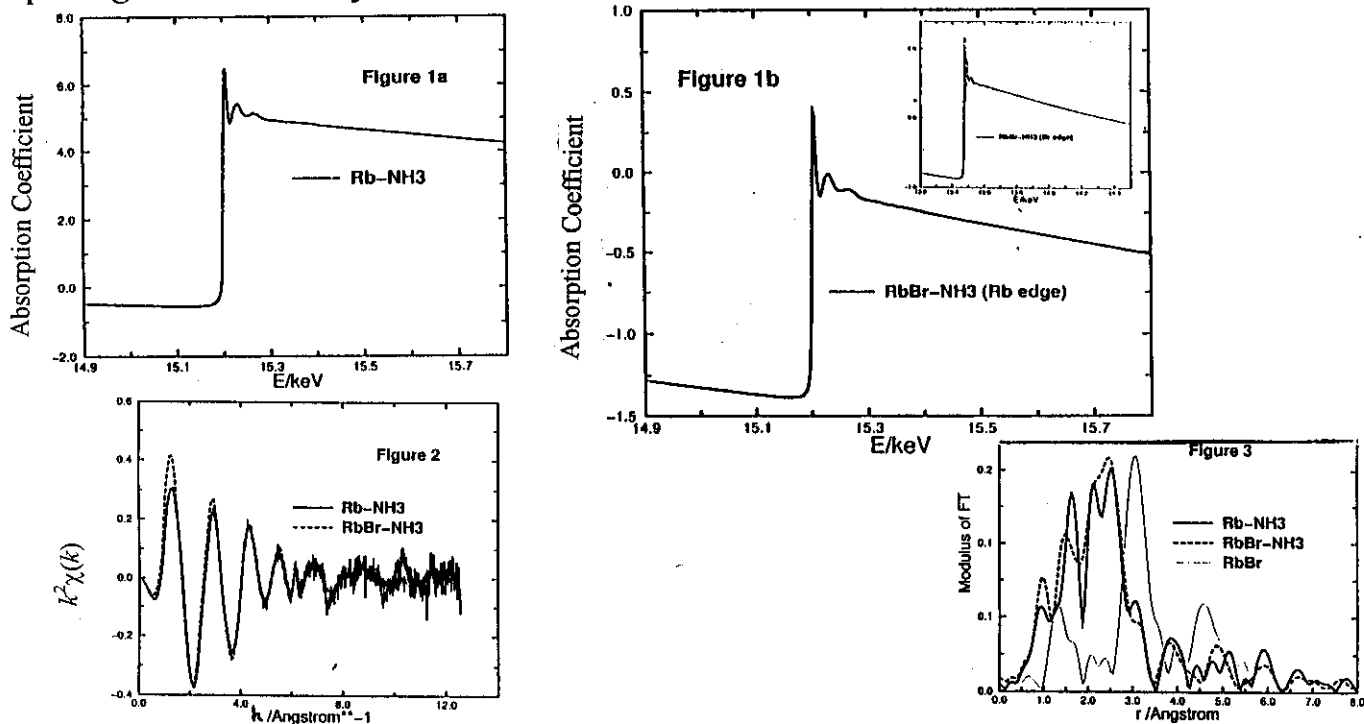
The solutions were made *in-situ* at the beamline by condensing ammonia onto the metal or salt at the sample position and excellent EXAFS data were obtained above the K-absorption edge of Rb for both Rb-NH<sub>3</sub> (3MPM- Mole Percent Metal) and concentrated RbBr-NH<sub>3</sub> solutions at 210K. Unfortunately, it was not possible to investigate fully the solvation of the Rb<sup>+</sup> ion in ammonia solutions by varying the ammonia concentration or the solution temperature. This was as a result of the teething problems encountered while trying to obtain a leak-tight sample environment in which to prepare high quality solutions. However, such a

working environment was successfully achieved by using a stainless steel gas-rig assembly connected to the cryostick of BM29, despite the time consuming problems posed in obtaining a seal at the sample cell (using a 2-piece polyethylene sample cell). Such hindrances were further compounded by the slow rate of condensation of the ammonia onto the Rb metal and loss of beam for approximately 1/2 a day.

During the sample changes of the Rb metal solutions, involving the neutralisation of the residual Rb mirror, EXAFS data for the RbBr-NH<sub>3</sub> solutions were collected. As a result the coordination environment of both solvated ions could be studied. The preliminary results for a concentrated RbBr-NH<sub>3</sub> solution are presented, together with the data for a 3MPM Rb-NH<sub>3</sub> solution in the figures below.

In figures 1a and 1b the Rb *K*-absorption edge is shown for the Rb-NH<sub>3</sub> and RbBr-NH<sub>3</sub> solutions at 210K. Preliminary analysis shows this absorption edge to occur at 15,199eV in both solutions, yet the visible contrast in size of the absorption edge jump for the data set may be attributed to a large amount of Rb-NH<sub>3</sub> solution being exposed to the X-ray beam. The inset shows the Br *K*-absorption edge for the RbBr-NH<sub>3</sub> solution at 210K.

In figures 2 and 3 the  $k^2\chi(k)$  functions and the corresponding real space Fourier transforms for the Rb<sup>+</sup> ion obtained using the "jesf" program at BM29 are given. These data sets are uncorrected for the phase shift of the backscattering atoms. Similarities between the Rb<sup>+</sup> environment in both the metal and metal salt ammonia solutions are apparent in these raw data sets, and from a comparison with the real space data set for the RbBr standard, Rb<sup>+</sup>-Br<sup>-</sup> pairings are tentatively identified in the RbBr-NH<sub>3</sub> solution.



In carrying out this experiment on BM29, our ability to use a gas-rig assembly to dispense and condense ammonia onto a rubidium metal surface has been highlighted. Furthermore, without the use of the high quality argon glove box of the Chemistry Laboratory the safe handling of the rubidium metal would not have been made possible. However, the suitability of polyethylene cells to hold the rubidium plus minor changes in their design need to be investigated further for future experiments. A pyramid shaped sample cell will aid in optimizing the absorption edge jump.