ESRF	**Experiment title:** Atomic x-ray absorption in Ba and Sr	**Experiment number**: HD-370
Beamline: BM-29	**Date of experiment**: from: 24/06/2009 to: 30/06/2009	**Date of report**: 05/03/2010
Shifts: 18	**Local contact(s)**: Dr Matthew RUFFONI	*Received at ESRF:*

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Report:

In molecular or solid-state aggregates the x-ray photoabsorption cross section of an atom is modified by a structural signal, a result of the interference of the photoelectron wavefunction with wavelets scattered from the neighbor atoms. A measurement of the absorption on a sample of free atoms yields the pure atomic cross section, comprising smooth shell or subshell contributions, upon which small sharp spectral features of collective excitations of the atomic system are superposed. The experimental data provide useful information for advanced atomic models, particularly on the effects of electron corelation. Atomic absorption of an element is also useful as the atomic absorption background (AAB) for EXAFS analysis of strongly disordered samples with a weak structural signal.

Apart from the monatomic noble gases, a state of free atoms is difficult to prepare and maintain in stability for a spectroscopy measurement. In most experiments, inherently monatomic metal vapors have been used. The experimentally most accessible K edge energy region has been extensively studied. The experiments in the L edge region, more difficult for the lower penetration power of soft x-rays, are currently under way [1].

In a planned experiment on Ba, a new high-temperature absorption cell with Be windows in a helium atmosphere has been devised, to be used in the high-temperature oven of BM29 and with its advanced alignment tools. The conflicting data on Ba vapor pressure in the literature suggested that in a cell with maximum practical length (30 cm) a sufficient attenuation μd ~0.3 for a successful experiment might be reached. Absorption scans of several Ba cells in the L edge region were measured during the warming up and at the maximum temperature, using the Si 111 monochromator with the resolution of ~0.7 eV, and ionization detectors filled with 240 mbar, 1500 mbar, and 2000 mbar of N_2, respectively, and topped up with He to 2000 mbar. However, consistently negative results led to the conclusion that the more conservative estimates of vapor pressure were right and that the atomic absorption of Ba was inaccessible with the current experimental technique with a temperature limit of 950 ^{0}C.

A less ambitious goal of Ba atomic absorption background could still be achieved by a different approach. In absorption spectra of samples with a weak and simple EXAFS, the structural signal can be removed by modelling of the atomic neighborhood, preferably in an crosswise iteration of two independent samples. A sequence of AAB in a contiguous series of elements from Ga to Rb has been determined in this way [2].

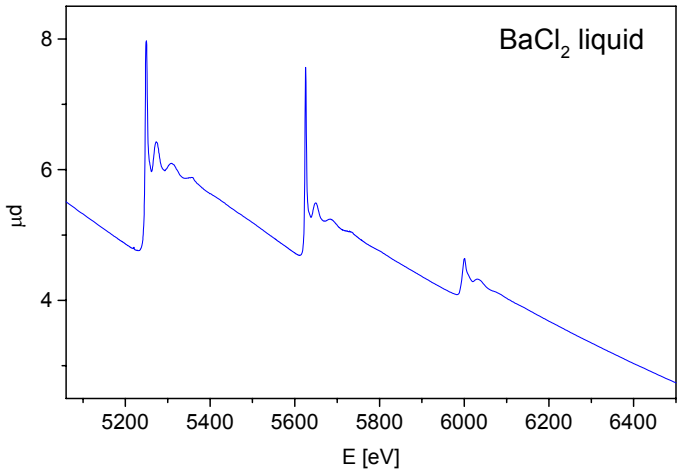

Figure 1.

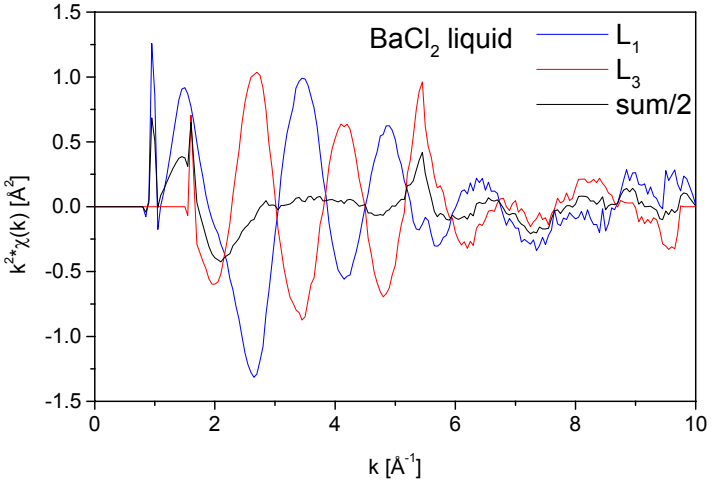

Figure 2.

Aqueous solution of $BaCl_2$, providing a sample of quasi-free Ba^{2+} ions – ions with a strongly disordered neighborhood – was prepared. The absorption spectrum of ~0.25 mm thick layer of the solution in a liquid-absorption cell was repeatedly measured in the experimental setup described above. Fig. 1 shows the spectrum over the three L edges, with a short-range EXAFS signal above each edge, providing at least two independent combinations of the structural signal and AAB. An approximate AAB can be obtained simply by the cancellation of the structural signal above L_3 and L_1 edges (Fig. 2). It shows a strong peak due to a resonant transition to a double core vacancy state [2(p,s)4d] at ~ 5.5 Å^{-1}, conspicuous already in each edge segment itself.

A better approximation of AAB is obtained by modelling the simple structural signal of the ion with a single neighbor shell of oxygen atoms. A simultaneous modelling of the signal at the three edges is used to improve the accuracy of the result. The best-fit model of the L_3 structural signal in the k-range 2.8 – 9.5 $Å^{-1}$, with the standard quality-of-the-fit measure r-factor of 2.9 %, is shown in R-space (Fig 3a). After its removal from the measured absorption signal in E-space, the residual is AAB (Fig 3b).

The application of the absorption background is demonstrated in a practical EXAFS analysis of $BaFe_{12}O_{19}$ nanoparticles with an extremely weak structural signal (Fig. 4).

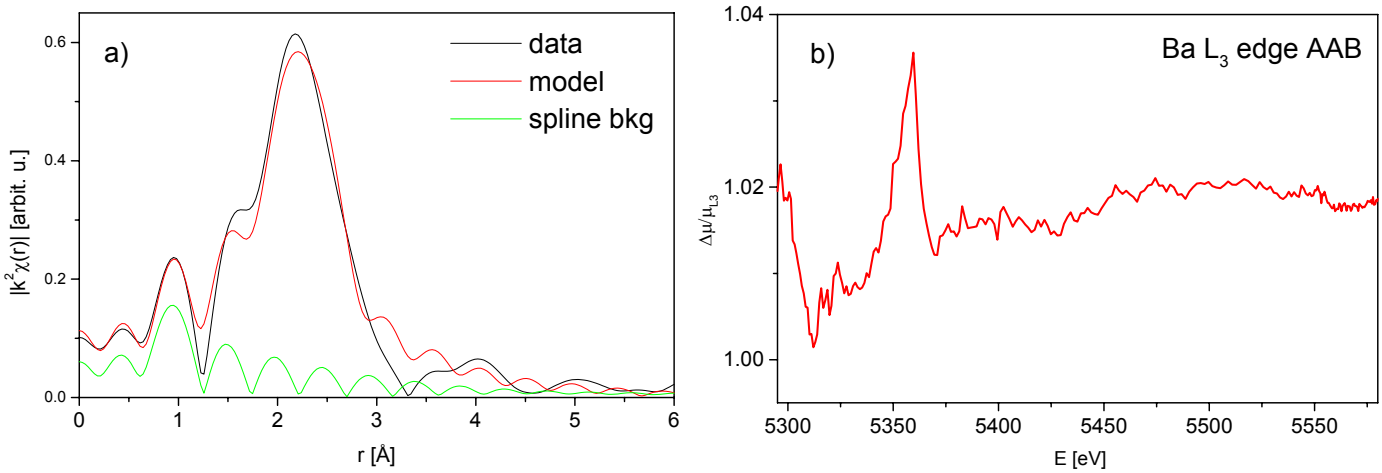

Figure 3.

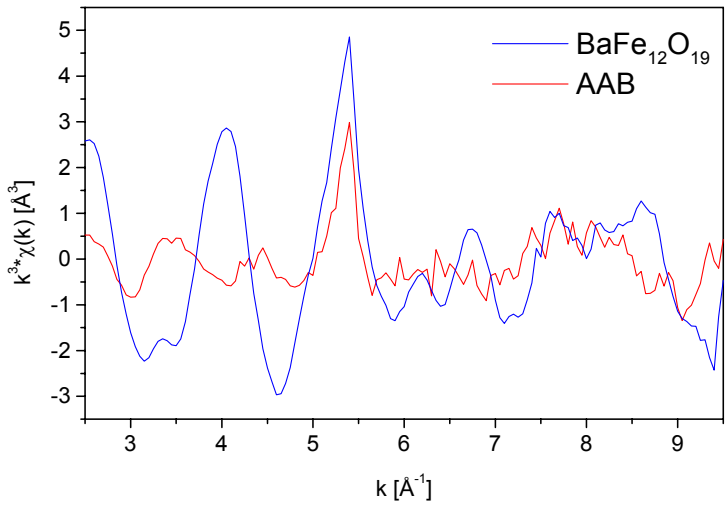

Figure 4.

References:

[1] A. Kodre, I. Arčon, J. Padežnik Gomilšek, 14th International conference on X-ray absorption fine structure, Camerino, Italy, 26-31 July 2009: program and abstracts, (2009) 110.

[2] J. Padežnik Gomilšek, A. Kodre, I. Arčon, A. M. Loireau-Lozac'h, S. Benazeth, Phys. Rev. A 59 (1999) 3078-3081.