Separation of weak EXAFS signal from atomic background in Br and Rb samples

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In EXAFS analysis of Rb-doped silicate glasses and of cetyl-trimethylammonium bromide (CTAB) adsorbed on carbon black, the spline approximation of the atomic background is inadequate. Instead, a residuum obtained from absorption spectra of Rb and Br ions in aqueous solution after removal of the structural signal is used. Another iteration cycle whereby the residuum from one sample in the atom-ion pair is used in analysis of the other one, gives satisfactory convergence. In this way, definite FEFF models of Rb glass and CTAB are constructed, and a better approximation for atomic absorption obtained as residual.

Keywords: atomic absorption background, Rb ion EXAFS, Br ion EXAFS, disordered materials

As a prerequisite for the standard EXAFS analysis in the FEFF code (Stern *et al.*, 1995, Rehr *et al.*, 1992), the atomic absorption background (AB) is eliminated from the EXAFS signal in the form of a spline constructed from the non-structural long-wavelength components. The procedure is unfeasible for strongly disordered samples with very weak EXAFS signal. There, some a priori knowledge of AB is required. Useful information is provided in a short review of AB measurements (Filipponi, 1995) and in examples of construction of AB from atomic data (Di Cicco *et al.*, 1996) and of iterative refinement (Li *et al.*, 1992; Bridges *et al.*, 1995),

In Fig. 1 the EXAFS spectra of Br in CTAB on carbon black and Rb in silicate glass are shown together with K edge absorption spectrum of the neighbor element Kr. Evidently, a considerable part of the Br and Rb signal must be due to AB contribution consisting of multielectron excitations to [1s3d].. and [1s3p].. states, identified in Kr spectrum (Schaphorst *et al.*, 1993). Hence, the standard procedure of a spline approximation to AB, as implemented in the UWXAFS code, cannot be expected to produce satisfactory results. The spline of the Kr spectrum, constructed by the same procedure, follows general trend satisfactorily, but misses the sharp spectral features. From these, spurious structural components will most likely be generated in subsequent EXAFS analysis of the Br and Rb spectra. Thus, it is more important in analysis of weak EXAFS signals to eliminate the sharp features of the AB than the long-period components: these can be recognized as non-structural by their position in the FT spectrum anyway.

An initial approximation of the AB can be obtained from another sample of the element with sufficiently simple EXAFS, in the present case from aqueous solutions of KBr and RbCl: the strong EXAFS signal is mostly due to the first-neighbor solvation shell. Although the parameters of the shell are not known a priori,

they can be determined with sufficient precision from the UWXAFS procedure with the standard "autobk" routine and best fit of the single-shell FEFF model. Fig. 2 shows the resulting decomposition of the KBr solution spectrum into the model EXAFS signal and the residuum AB[1]. The latter comprises the AB proper and some contribution of the structural components not included in the model, and the experimental noise.

This residuum is used instead of the spline AB in the analysis of the CTAB EXAFS. It removes satisfactorily the sharp edges from the spectrum and gives a recognizably simple harmonic EXAFS signal which is well described by a FEFF model of a single oxygen atom neighbor. Now, the model is removed from the original CTAB spectrum to yield the next approximation AB[2] of the Br atomic background. Because of the low amplitude of the CTAB EXAFS signal even a moderate accuracy of the FEFF model provides an essential improvement over the earlier AB approximation.
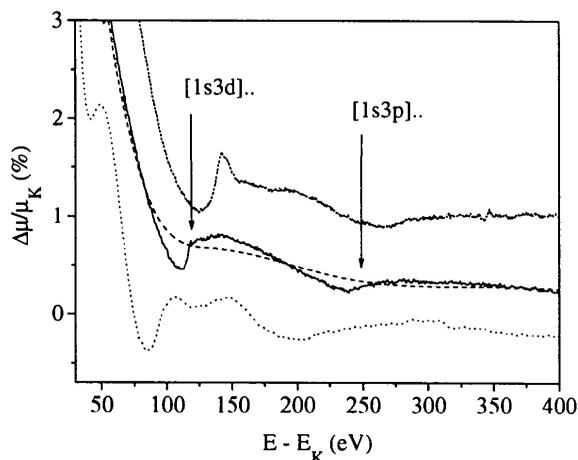
Figure 1.

K edge absorption spectra of Br in CTAB adsorbed on carbon black (dotted line), Kr (solid line) and Rb dopant in silicate glass (short dashed line) after removal of the general Victoreen trend. Spline approximation to AB (dashed line) is superposed onto the Kr spectrum. The energies of multielectron excitations in Kr are indicated by arrows.
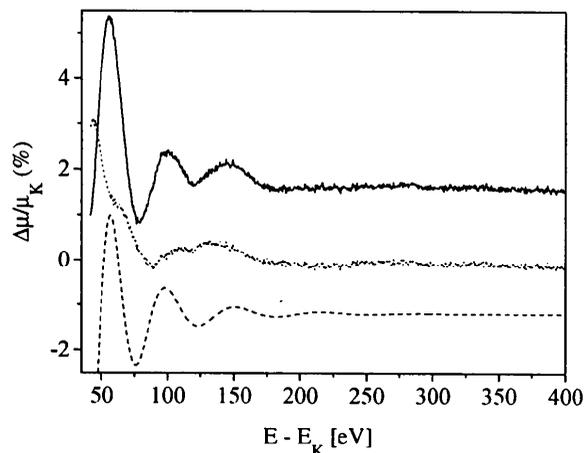
Figure 2.

The initial decomposition of Br absorption spectrum in KBr solution (solid line) into the model EXAFS (dashed line) and AB[1] (dotted line).

The entire procedure is lead through another iteration step, using AB^2 on KBr spectrum and refining the solvation-shell FEFF model to produce AB^3. With the latter, the CTAB structure can be reliably refined with another neighbor shell consisting of three carbon atoms, supposedly derived from the carbon-black surface, to which the Br atom is adsorbed via an -O- link (Bele et al., 1998). The residual AB^4 of the CTAB spectrum can be adopted as the generally applicable atomic background of Br (Fig. 3).

The analogous procedure involving the Rb-doped glass and RbCl solution EXAFS spectra (Fig. 4) yields a model of the glass structure around the Rb ion with two oxygen shells with 1 atom at
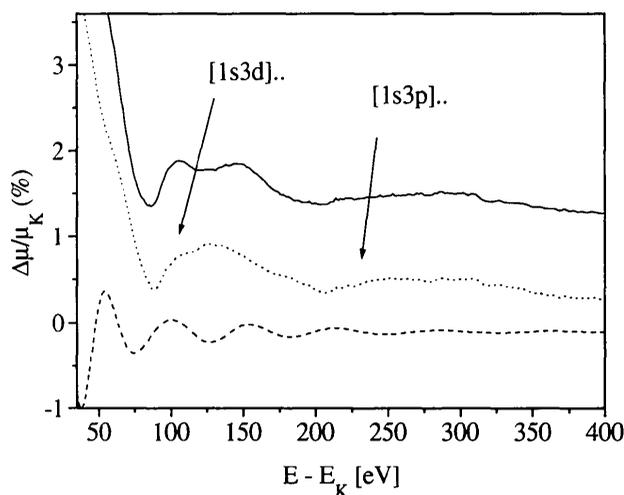
Figure 3.
The final decomposition of the Br absorption spectrum in CTAB on carbon black (solid line) into the structural signal (dashed line) and the atomic background AB^4 (dotted line).
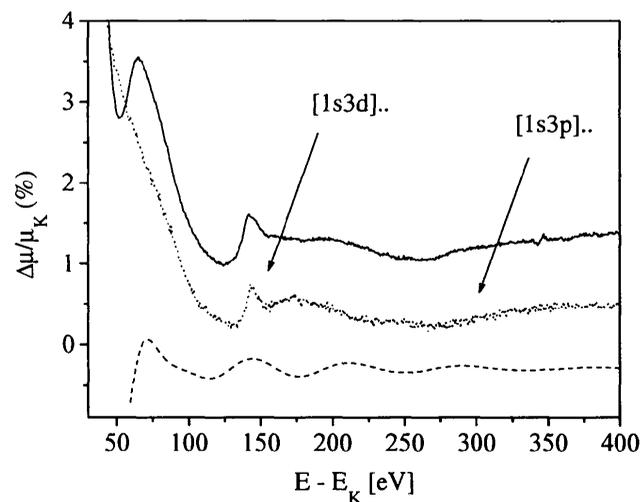
Figure 4.
The analysis of the Rb absorption spectrum in Rb-doped silicate glass (solid line): the structural signal (dashed line) obtained with the help of the RbCl atomic absorption residuum (AB^3 - dotted line).

2.79 A and 5.3 at 3.08 A. The resulting AB can be compared to the Rb vapor absorption (Kodre et al., 1995): the AB spectra are practically identical within the noise level. The only major difference is the strong peak at the [1s3d] edge, attributed to the shake-up of the white line, which shows prominently at the Rb-ion K edge and is barely visible in Rb vapor absorption. Thus, all features of the AB can be explained as a result of atomic collective excitations, without resorting to specific intra-atomic XAFS effects (AXAFS) (Rehr et al., 1994).

In comparison with approximate AB extracted for Rb and Br in a similar procedure from single strong EXAFS spectra (Li et al., 1992, D'Angelo et al., 1993), the present analysis improves on the sharpness of detail by starting from weak EXAFS spectra in which the AB signal is the dominant component. With the use of the auxiliary sample, the noise and unresolved XAFS components are averaged out to some extent. The transferability of AB, implied in the procedure, is enhanced by the similar local environment of oxygen atoms attached to the monovalent Br or Rb ion. For the application of the extracted AB for samples of the investigated elements in general, however, further transferability tests are required. The comparison of the Rb-ion and Rb vapor AB, and the results on Ge from a related contribution at this conference (Padežnik Gomilšek et al., 1998) indicate that the problem may not be severe. In the EXAFS region of interest, the multielectron excitations comprising the AB involve mostly the electrons from subvalence states which are less susceptible to the chemical environment.The transferability is thus mainly achieved by adjusting for strong resonant multielectron excitations (as in Rb) and for the chemical shift induced by the specific environment and oxidation state.

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