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K edge absorption spectra of elements from Ge to Br in gaseous hydrides were measured at the BM 29 station of ESRF with noise level as low as 2×10⁻⁵, so far achievable only on noble gases. The dominant feature of the spectra is the atomic background similar to that of Kr and comparable to it in the quality of detail. Onto the background, a smooth weak EXAFS signal due to the hydrogen neighbors is superposed. For the very simple molecules such as these, its contribution can be calculated ab initio, with exact treatment of the effect of molecular vibrations, so that no best-fit adjustment to the experimental data is necessary. In comparison to the main constituent of the atomic background, i.e. the shake-up absorption edges, the EXAFS signal is of minor importance in HBr with a single H neighbor, but of the same order of magnitude in GeH₄.

Keywords: Atomic absorption background, Ge, As, Se, Br hydride EXAFS

1. Introduction

Detailed analysis of absorption spectra reveals fingerprints of collective excitations of the atom, mostly as tiny resonances and jumps above K and L absorption edges. Although most of the experimental evidence has been accumulated from experiments on noble gases (Schaphorst et al., 1993), the results are relevant also for the EXAFS analysis. The collective excitations occupy the same spectral region as the EXAFS signal and thus comprise its non-structural part, the atomic absorption background (AAB). In routine EXAFS work, the background is conveniently separated from the structural signal in the transform space: it is reconstructed by a spline from the low wavenumber components. However, the sharp features of the collective excitations occupy a broad wavenumber interval, so that some leakage into the structural signal is inevitable (Frahm et al., 1984; Kochur et al., 1986; Kodre et al., 1994; Chaboy et al., 1994; Kodre et al., 1995; Filipponi & Di Cicco, 1995; D’Angelo et al., 1996; Kodre et al., 1997; Kodre et al., 1999; Paděžnik Gomilšek et al., 1999). For precision EXAFS analysis, an independently determined AAB is thus required. The basic assumption, however, is that of transferability: the atomic background depends mainly on intra-atomic dynamics and not on the environment of the atom (Kodre et al., 2000).

The scarce data on the independent AAB have been collected in several ways. A direct measurement is only possible on monatomic gases. Beside noble gases, hardly interesting for EXAFS, some metal vapors have been studied (Filipponi et al., 1993; Prešeren et al., 1996; Kodre et al., 1997; Arčon et al., 1997; Prešeren et al., 1999; Prešeren & Kodre, 1999-a). By a reverse analysis, AAB can be obtained as a remainder of an EXAFS signal after the structural signal of sample with a well-known (or a very simple) structure has been removed. This technique has been exploited in AXAFS (atomic EXAFS) investigations (Holland et al., 1978; Rehr et al., 1994). By combining two or more samples, the need for a well-known structure is dispensed - in this way, AAB of the series of 4p elements have been determined (Paděžnik Gomilšek et al., 1999-a). In some cases, an iterative procedure on a single sample succeeded without additional information (Li et al., 1992; D’Angelo et al., 1993; D’Angelo et al., 1995; Bridges et al., 1995; D’Angelo et al., 1996). There is also a semiempirical approach, where AAB is constructed from atomic binding energies and cross sections (Di Cicco, 1995; Di Cicco et al., 1996; Arčon et al., 1997). It is simplified by the fact that only multielectron excitations of core + first subvalence electrons contribute to the EXAFS AAB. The excitations involving valence electrons are limited to within 30 eV of the edge in the XANES region, while those involving deeper shells appear more than 1000 eV above the edge.

In the present study, we demonstrate that gaseous hydrides of 4p elements Ge, As, Se, Br can be used in determining the AAB with the same precision as that of elemental monatomic samples, exploiting the low-noise gas absorption spectroscopy and the fact that the small structural signal of scattering on hydrogen can be determined ab initio. Bromine hydride has been studied in this way before (D’Angelo et al., 1993). The non-negligible scattering...
The decomposition of the hydride absorption spectra of Fig. 1 into the ab initio calculated EXAFS signal (dashed line) and AAB (solid line). Average linear trend is subtracted from the AAB spectra for better comparison with the EXAFS spectra. A relative energy scale with origin at the K edge is used. The spectra are displaced vertically for clarity.

3. Results and discussion

The above-edge region of the absorption spectra is shown in Fig. 1. Notably, there is hardly any recognizable structural signal, the spectra are all similar to the absorption spectrum of Kr, added below for comparison. They reveal two distinct absorption edges which can, in analogy with Kr, be attributed to multielectron excitations involving 3d and 3p electrons. Another edge, involving 3s excitation, can be discerned at higher energies. The identification of the edges is confirmed by Dirac-Fock estimates of the excitation energies.

The structural signal of the hydrides can be constructed from known scattering amplitudes and phases (Rehr et al., 1992; Stern et al., 1995). The width of the hydrogen neighbor shell can be calculated from the spectrum of molecular vibrations, which, due to the simple geometry of the molecules, allows exact treatment (Cyvin, 1968; Greenwood & Earnshaw, 1984). In this way, the structural signal is constructed entirely ab initio: the best-fit determination of the EXAFS parameters which would be unreliable in view of the prevalence of the AAB in the experimental spectrum, is completely avoided. We can see (Fig. 2) that the structural signal is not really negligible: in a curious coincidence, however, the waves of the EXAFS signal follow the rise of the two absorption edges of the AAB so that the oscillatory component of the spectrum remains inconspicuous.

The comparison of the AAB in Fig. 2 with the earlier data from solid samples of the same set of elements (Padežnik Gomilšek et al., 1999-a) shows more than a tenfold improvement in accuracy. In the earlier set, the noise of the results comprises mostly the unresolved high-wavenumber structural components while in the present case we believe the noise at the level of $2 \times 10^{-5}$ in As and Se data is negligible: in a curious coincidence, however, the waves of the EXAFS signal follow the rise of the two absorption edges of the AAB so that the oscillatory component of the spectrum remains negligible in As and Se data is limited to the detector statistics. The high quality of the experimental data shows, for the first time, fine structure of the AAB features (Fig. 3). In a detailed analysis, the features are completely resolved into contributions of atomic double excitation resonant, shake-up and shake-off channels (Prešeren, 2000), with an essential modification due to the molecular coupling of final states. The important point, however, is that the AAB can be described by the dynamics of the atom, and that apart from details of multiplet structure which show fingerprints of the molecule, a transferable AAB is defined with sufficient precision even for most sensitive EXAFS analysis (see also Kodre et al., 2000).

The fine structure of the AAB features can also be used to estimate the contribution of AXAFS, a long-wave interference pattern arising from the scattering at the atom boundary (Rehr et al., 1994). It has been proposed as an alternative, or at least complementary, interpretation of AAB. Since sharp features and multiplet structures by which the major part of the extracted AAB signal is explained,
are not predicted in AXAFS, its contribution in the AAB spectra of the investigated hydrides seems to be of minor importance.

![Graph](image)

**Figure 3**
Multiplot structure of 1s3d and 1s3p MPE features in SeH2. AAB. Dots – experiment; contributions of atomic double excitation channels: resonances - (dashed line), shake-up (dash-dot line) and shake-off (dotted line) channels. Sum of individual MPE channels – (solid line).

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**References**


