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Atomic background and EXAFS of gaseous hydrides of Ge, As, Se and Br

Rok Prešeren,^a Alojz Kodre,^{ab*} Iztok Arčon^{cb} and Michael Borowski^d

^aFaculty of Mathematics and Physics, University of Ljubljana, Jadranska 19, 1000 Ljubljana, Slovenia, ^bInstitute Jozef Stefan, Jamova 39, 1000 Ljubljana, Slovenia, ^cNova Gorica Polytechnic, POB 301, Vipavska 13, 5001 Nova Gorica, Slovenia, ^dEuropean Synchrotron Radiation Facility (ESRF), BP 220, 38043 Grenoble Cedex, France.
Email:alozj.f.kodre@ijs.si

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, 1995; Filipponi & Di Cicco, 1995; D'Angelo *et al.*, 1996; Kodre *et al.*, 1997; Kodre *et al.*, 1999; Padežnik 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 (Padežnik 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.

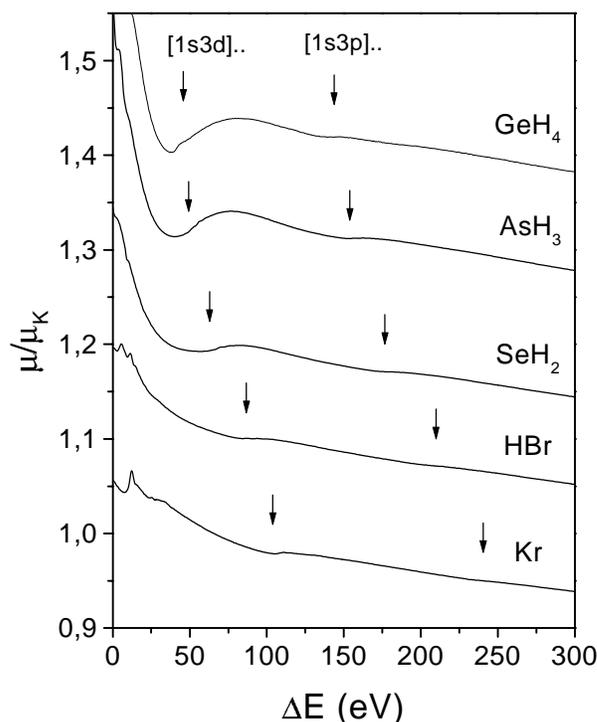


Figure 1

Normalised K edge absorption spectra of GeH₄, AsH₃, SeH₂, and HBr. The spectrum of Kr is added for comparison. A relative energy scale with origin at the K edge is used. Thresholds for [1s3d] and [1s3p] multielectron excitations are indicated by arrows. The spectra are displaced vertically for clarity.

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

contribution of hydrogen neighbors has already been demonstrated in an experiment on germane (Bouldin *et al.*, 1981).

2. Experiment

Germane (GeH_4), arsine (AsH_3), hydrogen selenide (SeH_2), and hydrogen bromide (HBr) have been synthesised for the purpose and sealed in 12 cm long glass cells with kapton windows. For the aggressive HBr, a cell with thin (0.3 mm) glass windows had to be used, with subsequent tenfold increase in the noise level. The gas pressure in the cells was chosen to ensure absorption length $\mu \sim 2$ at the K edge.

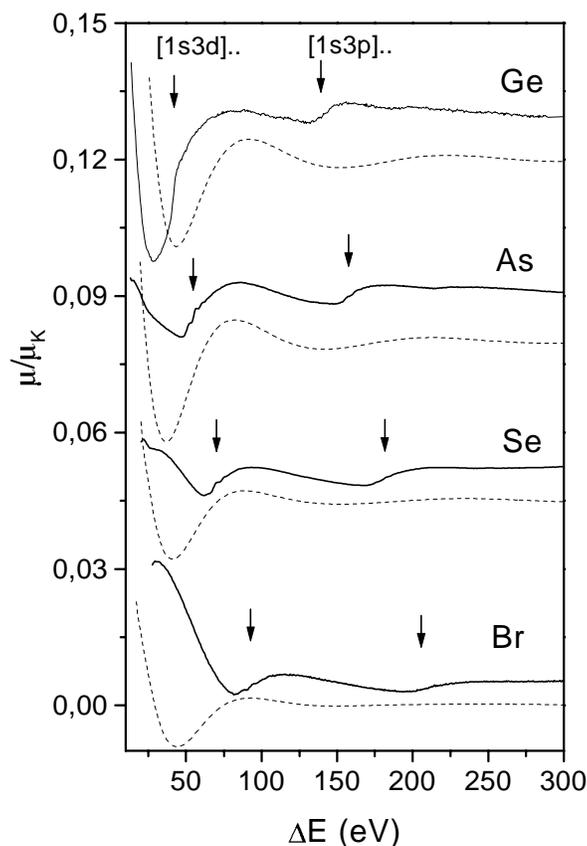


Figure 2

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. Multielectron excitation [1s3d] and [1s3p] shake-up edges in the AAB spectra are indicated by arrows. The spectra are displaced vertically for clarity.

The experiments were performed at the beamline BM 29 of the European Synchrotron Radiation Facility ESRF in Grenoble, France and at the beamline ROEMO2 (X1.1) in Hamburger Synchrotronstrahlungslabor HASYLAB at Deutschen Elektronen - Synchrotron DESY (Hamburg, Germany). At both beamlines a Si(311) fixed-exit double-crystal monochromator was used with 0.8 eV and 1.5 eV resolution at 12 keV, respectively. Harmonics were effectively eliminated by detuning the monochromator crystal using

a stabilization feedback control. Ionization cells filled with argon were used to detect incident and transmitted flux of the monochromatic X-ray beam through the sample.

The absorption spectra were recorded in 0.5 eV energy steps with an integration time of 2 s/step. Ten experimental runs were superimposed to improve the signal-to-noise ratio. Exact energy calibration was established with the simultaneous absorption measurements on the Pt metal foil and from a measurement on Kr with a well defined K edge.

The absorption cells were equipped with a side chamber into which the gas could be frozen *in situ* and thus removed from the beam, to obtain a precision reference measurement of the window transmission and energy dependence of detector efficiency.

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 2×10^{-5} 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.

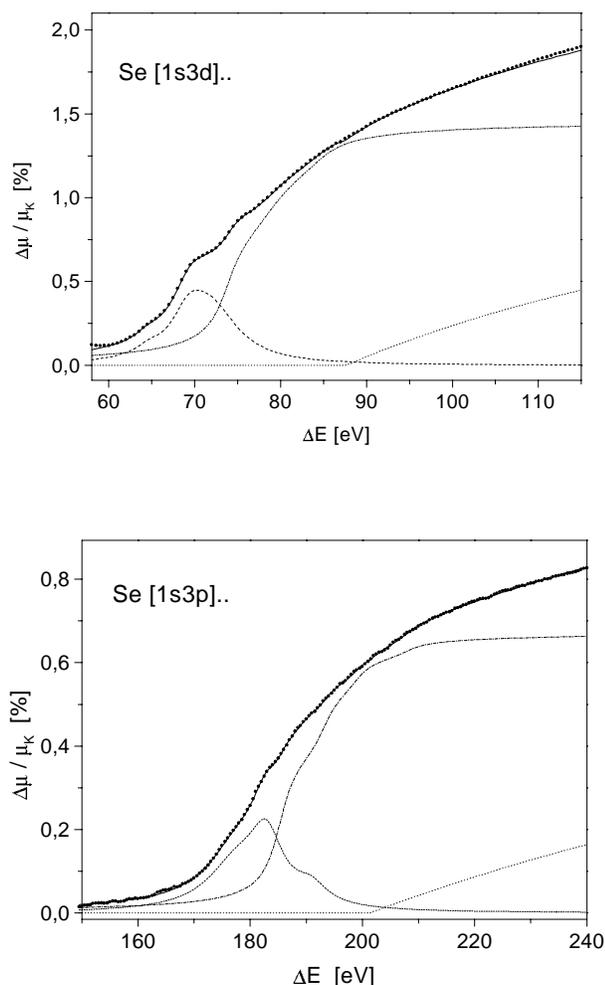


Figure 3

Multiplet structure of 1s3d and 1s3p MPE features in SeH_2 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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