A study of transferability of atomic background on EXAFS spectra of simple gaseous compounds of As

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From EXAFS spectra of As and As_2O_3 vapors and arsine gas AsH_3 the *ab initio* calculated structural signal is removed. The remainders comprise small absorption edges due to shake-up channels involving electrons from 3d or 3p subshell. With enhanced resolution, the edges reveal a fine splitting and a varying contribution of resonance channels, due to individual molecular energy-level structure of the samples. On the resolution level appropriate for routine EXAFS analysis the remainders coincide, representing a unique and transferable atomic absorption background for the range of As valence states spanned by the samples.

Keywords: Atomic background transferability, **As K-edge EXAFS, As, As_2O_3 and AsH_3 gases**

1. Introduction

In precision EXAFS structure determination, the conventional spline reconstruction of low-wavenumber components cannot satisfactorily describe non-structural, intra-atomic effects. In particular, sharp features such as small resonances and absorption edges, introduced into absorption spectra by multielectron excitations, contribute non-negligible high-wavenumber components which can interfere with the structural signal (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; Kodre *et al*., 1997; Arčon *et al*., 1997; Padežnik Gomilšek *et al.*, 1999). Thus, a true atomic absorption background (AAB) from an independent measurement or calculation is required. Some of the scarce available data on AAB is constructed from semi-empirical models (Di Cicco, 1995; Di Cicco *et al.*, 1996; Arčon *et al*., 1997), some is recovered from standard EXAFS samples (Li *et al*., 1992; D'Angelo *et al.*, 1993; Bridges *at al*., 1995; D'Angelo *et al.*, 1995; D'Angelo *et al.*, 1996; Padežnik Gomilšek *et al.*, 1999-a). A similar approach has been exploited in AXAFS (atomic EXAFS) investigations (Holland *et al.*, 1978; Rehr *et al*., 1994). For a very small number of elements AAB can be measured directly and with high accuracy on monatomic gaseous samples (Schaphorst *et al*,. 1993; Filipponi *et al.*, 1993, Kodre *et al*., 1997, Prešeren *et al.*, 1996; Prešeren *et al.* 1999; Prešeren & Kodre, 1999-a). It has been shown that simple molecular gases can also be used for the purpose (D'Angelo *et al.*, 1993; Prešeren *et al.*, 2000). Exploiting this approach we have devised a direct test of the transferability of AAB of an element. The concept of transferability is generally assumed, in view of the intra-atomic origin of the AAB, but it has hardly been supported by convincing experimental evidence. (However, in the AXAFS interpretation, the transferability is limited to similar environments of the atom.) In this study, we compare AAB extracted from three gaseous compounds of arsenic.

2. Experiment

Arsine, AsH_3, is a stable gas at room temperature. A 60 mm long glass absorption cell with kapton windows was filled with 40 kPa of arsine, yielding absorption $\mu d \sim 1.7$ at the As K edge. Arsenic trioxide, As_2O_3, sublimates at temperatures above 300°C. As its vapor reacts slowly with most of conventional cell and window materials, a sample of 12 mg of As_2O_3 was sealed in a 200 mm long absorption cell of Duran glass with 0.3 mm thick windows of the same material. The absorption in the windows contributed $\mu d \sim 2$, and the absorption in the sample, when completely vaporized at 320°C, $\mu d \sim 1.7$. At this temperature, it took ~1 hour before the oxide reacted with glass appreciably.

Elemental arsenic is also known to sublimate above 500°C. At this temperature, it reacts vigorously with standard high-temperature cell and window materials, stainless steel, quartz, and glass. In the latter, however, the reaction is relatively slow, so that a single spectrum of 20 min duration could be recorded. A 300 mm long Duran cell with 0.3 mm thick Duran windows was used, operated at 490°C, yielding $\mu d \sim 0.3$ at the As K edge.

The As K edge absorption spectra of As_2O_3 vapor and AsH_3, were measured at BM 29 of the European Synchrotron Radiation Facility (ESRF) in Grenoble, France. The absorption spectrum of As vapor was measured at the X1 station of the Doris ring in Hamburger Synchrotronstrahlungslabor HASYLAB at Deutschen Elektronen-Synchrotron DESY (Hamburg, Germany). At both beamlines a Si(311) fixed-exit double-crystal monochromator was used. The resolution at 12 keV was 0.8 eV at BM29 and 1.5 eV at X1. Harmonics were effectively eliminated by detuning the monochromator crystal using a stabilization feedback control. Ionization cells filled with argon were used to detect the incident flux of the monochromatic x-ray beam and the flux transmitted through the sample.

The absorption cell of arsine was equipped with a side chamber into which the gas could be frozen in situ to obtain a precision reference measurement of the window transmission and energy dependence of detector efficiency. Reference spectra for arsenic trioxide and elemental arsenic were taken on the cells at room temperature before heating.

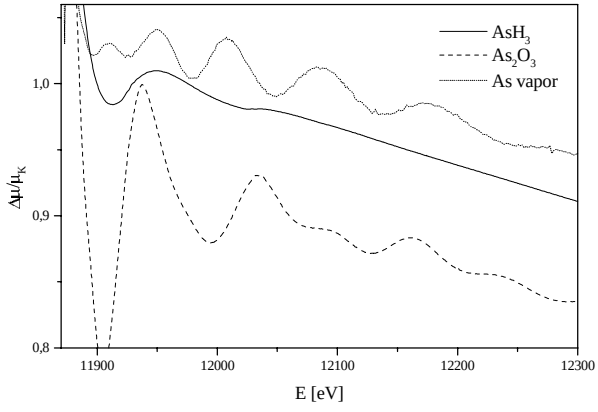

Figure 1
The normalized As K edge absorption spectra of gaseous AsH_3 (solid line), As_2O_3 vapor (dashed line) and As vapor (dotted line). The spectra are slightly displaced along vertical axis for clarity.

3. Experimental results

The quality of the spectra (Fig. 1) differs considerably between the three compounds, as a consequence of different experimental conditions. The stable gas arsine, in a cell with kapton windows, gives a spectrum comparable to the state-of-the-art noble-gas spectra. With superposition of 10 independent scans, the signal-to-noise ratio of 4×10^4 is achieved. The resolvable level of detail is very high as shown in the derivative spectra in the insets of Fig. 2. The structural signal, resulting from the photoelectron scattering on the H neighbors is smooth and relatively weak so that the sharp features of the As AAB are plainly visible.

The quality of the spectrum of arsenic oxide is appreciably diminished by the strong absorption in the windows. The structural signal of O and As neighbors is prevailing, so that the features of the AAB cannot be readily observed. The noise level is larger than in arsine by an order of magnitude.

The noise level in the spectrum of arsenic vapor is larger still, of the order of 10^{-3}, mainly due to the lower density and the absorption in glass windows. The spectrum exhibits a strong structural signal of As neighbors since the vapor contains As_4 molecules.

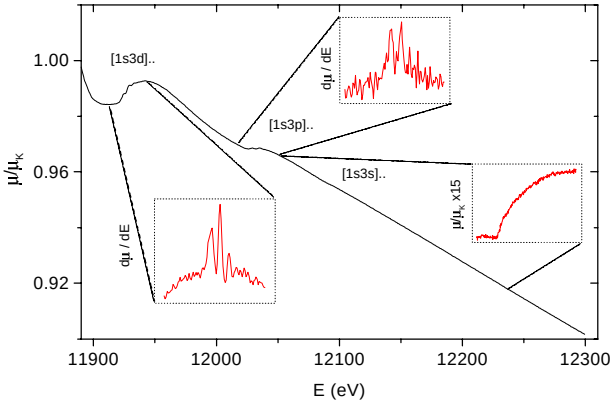

Figure 2
The normalized As K edge absorption spectrum of AsH_3 gas. The insets show derivatives of the spectrum in the region of 1s3d and 1s3p multielectron photoexcitation and a magnified region of the 1s3s excitation.

4. Analysis

In order to extract AABs, the structural signal for all three molecules was modeled in FEFF 6 code (Rehr *et al.*, 1992; Stern *et al.*, 1995) and removed from the spectra. For AsH_3, it is possible to construct the EXAFS signal *ab initio* from known interatomic distances and angles (Greenwood & Earnshaw, 1984), scattering factors, and vibrational modes of the molecule (Cyvin, 1968). The *ab-initio* construction is imperative since there is little possibility of adjusting the FEFF model parameters by a best-fit procedure to the indinstinct structural signal in the measured spectrum.

For As_2O_3 vapor, the conventional semiempirical FEFF model is employed: the geometry of the molecule, a tetrahedron of As atoms with O atom links along edges, actually corresponds to the dimer As_4O_6. Positions of the atoms and the scattering data are introduced ab initio. The Debye-Waller factors, however, are determined by best-fit to the well-resolved structural signal. The model contribution of the first (O) and the second (As) neighbors, together with some weak higher order-scattering, explains the two major peaks in the FT spectrum remarkably well. However, after removal of the model signal, the remaining atomic background still shows a small contribution of short-wave components that cannot be accounted for by the scattering paths within the molecule. They are mostly explained as an absorption signal from a very small quantity of crystalline As_2O_3, adsorbed on the cell windows. Indeed, with addition of scattering paths in solid As_2O_3 to the model, the quality-of-fit-measure in the FEFFIT procedure, the r-factor of 0.001 is obtained.

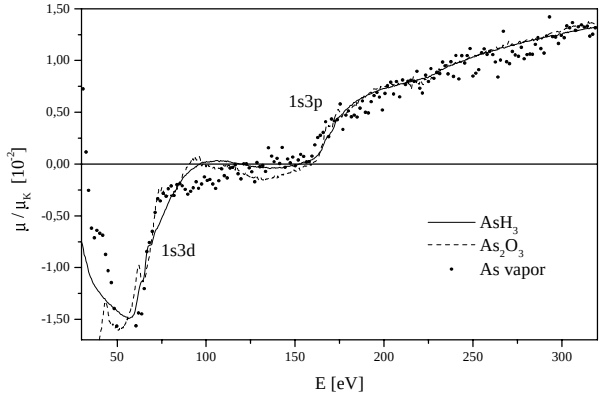

Figure 3
The comparison of AAB extracted from absorption spectra of three As molecules. The common energy scale is defined relative to the respective energies of the As K-edge.

For As vapor, the same semiempirical approach is employed, with an additional modification. According to chemical data (Cyvin, 1968; Greenwood & Earnshaw, 1984), the As molecule in the vapor is tetraatomic in the range of temperatures in the experiment. The FEFFIT procedure, however, gives an essential improvement in the fit at the non-integer number of neighbors N = 3.8, indicating a mixture of tetraatomic molecules and larger aggregates.

5. Conclusions

The AABs of the three As molecules are shown in Fig. 3. Although they differ appreciably in quality, the As_2O_3 background ridden by residual shortwave components and the As background by the large noise, the three spectra are clearly identical with relative deviations below 3×10^{-3} and on the level of resolution of routine EXAFS analysis, so that a unique As atomic background can be defined for most practical purposes. The non-transferable part of AAB, due to alternative mechanisms such as AXAFS, is thus limited to a smooth contribution with amplitude of deviations mentioned above.

The sharp features of the background have been identified as fingerprints of two-electron excitations (Prešeren, 2000-a): indeed, they can be decomposed into contributions of resonant and shake channels for the two major excitation groups, 1s3d and 1s3p (Fig. 4). The energies of the channels lie within a few eV of energies calculated by a Dirac-Fock relativistic self-consistent model of the As atom. For an atomic calculation, the mismatch is relatively large. It is caused by the fact that the excited states are molecular in character: the hybridization of electronic orbitals in a molecule introduces a shift of a few eV from the corresponding atomic energy levels which are modelled in the self-consistent calculation.

The complete decomposition of the sharp AAB features of AsH_3 and As_2O_3 shown in Fig. 4 testifies that they arise entirely from the internal atomic dynamics, namely, the collective response to the photoexcitation. There is another remarkable fact in support of the finding: the parameters by which the components are described - energies, amplitudes and linewidths - are identical within experimental error for both molecules, with exception of the width

parameter. The smaller effective width of resonances in the oxide spectrum accounts for their relative prominence. Thus, the transition probabilities which define the shape of the jumps in AAB are essentially the same for both molecules. The observed small differences between the two sharp AAB features can be attributed merely to different widths of the lowermost unoccupied molecular levels.

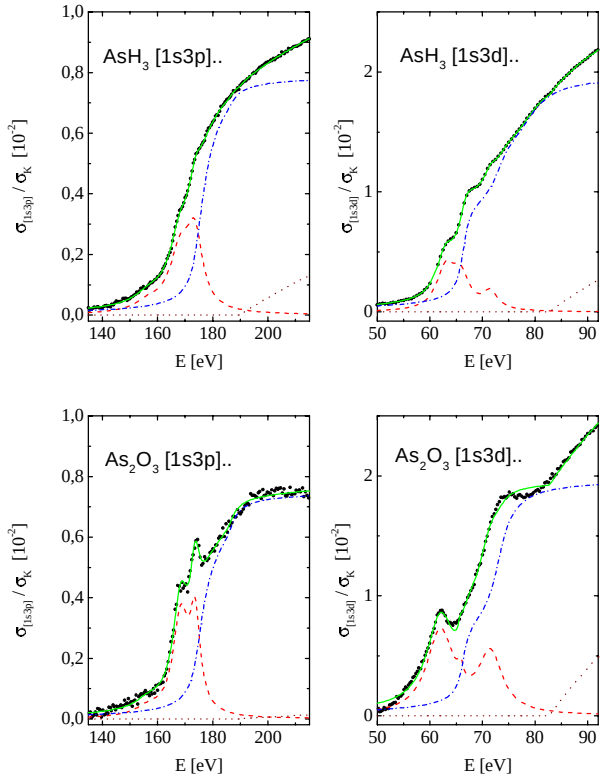

Figure 4
The [1s3p] and [1s3d] multielectron photoexcitation features in AsH_3 and As_2O_3 absorption spectra decomposed into contributions of resonant (dashed line), shake-up (dot-dashed line) and shake-off channels (dotted line). Sum (solid line) and experiment (bullets).

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