Direct experimental determination of atom–molecule–solid binding energy shifts for Sb and Bi

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Abstract. Binding energy shifts Bi–Bi2–Bi (solid) and Sb–Sb2–Sb4–Sb (solid) have been measured for the first time directly for Bi4f and Sb4d core levels by applying synchrotron radiation excited photoelectron spectroscopy. Atomic, molecular and solid state spectra are obtained by varying the temperature of evaporated metal vapours by means of a special multichamber oven and letting the vapour condensate on a cool solid tip. Vapour and solid state spectra are created simultaneously in similar experimental conditions, making direct and accurate shift determinations possible. The effects of the multiplet fine structure of the open shell atoms are pointed out.

Binding energy (BE) shifts of atomic core levels between free atoms, molecules and their solid samples are very fundamental data for different branches of electron spectroscopy and the theory of the electronic structures of molecules, clusters and solids. The early triumph of electron spectroscopy was mainly based on the precise determination of the BE shifts of the same element in different chemical compounds, and finding the ‘fingerprints’, the chemical shifts of each element in various chemical surroundings, a method called electron spectroscopy for chemical analysis (ESCA) [1]. A large number of papers have been published on this subject. A much less studied field is the BE shifts on going from free atoms to elemental solid or molecules [2–4]. Besides their basic theoretical importance, the accurate atom–solid binding energies and their shifts are also very useful reference values in the experimental studies of clusters [4, 5], as the cluster size determinations by means of photoelectron spectroscopy strongly rely on these asymptotic values. The atom–solid BE shifts are, however, not very

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accurately known experimentally. The main reason is that for free atoms and molecules these values are measured using gaseous calibration lines and vacuum level as the reference energy level, whereas the solid state values are measured with respect to the Fermi level. In order to bring the values to the common energy scale, solid state values should be corrected by the appropriate work function of the sample. The values of the work function are rather difficult to measure accurately and they depend e.g. on the crystal structures and the surface conditions. Therefore the previously reported values vary significantly. If the vapour–solid BE shifts are obtained combining the results from three different measurements (BE for vapour and solid, and the determination of the work function), they also involve the inaccuracies of these three different measurements. Therefore it is very desirable to obtain shift values directly from one single experiment. Only a few attempts [6, 7] have been made in order to achieve an absolute reference level for solid samples without a common success. Furthermore, the photoelectron spectra (PESs) of free atoms may display very different features due to the open shell multiplet structure of atomic PES than the spectra of closed shell molecular and solid species.

The present high-intensity synchrotron radiation sources provide completely new possibilities for free atom–molecule–solid shift studies with superior resolution and count rates. In the course of our metal vapour studies, we have developed a simple method in order to simultaneously observe both vapour and solid state spectra in identical experimental conditions. The idea is to locate a cool needle-like surface into the vapour beam and to simultaneously observe the spectra both from the vapour around the tip and from the condensed solid layer. The surface of the solid sample is covered by the negative work function potential and the vapour atoms are in this potential in the vicinity of the surface. Therefore the spectra have the same reference energy level and no work function correction is needed.

In this study, we will report results obtained using this method for the 4f photolines of Bi and the 4d photolines of Sb. These samples are especially interesting because they are known to evaporate as molecular species [8] that can be fragmented further pyrolytically with a special multichambered oven system, shown schematically in figure 1. This provides a very interesting possibility to experimentally determine the consecutive atom–molecule–solid shifts. New accurate atomic BE values for Bi and Sb and their atomic fine structure will be reported elsewhere [9, 10] and, in this paper, we will concentrate on the atom–molecule and molecule–solid state shifts.

Synchrotron radiation from undulator beamline I411 [11] at the MAXII storage ring in MAX-laboratory Lund, Sweden, was used to ionize the vapour phase samples. An effusive vapour beam from the inductively heated oven (figure 1) and the synchrotron radiation light crossed at right angles and electrons were detected at the ‘magic’ 54.7° angle with respect to the polarization vector of the horizontally polarized synchrotron radiation. A modified Scienta SES-100 electron energy analyzer [12] was used to record the emitted electrons. The electron spectrometer is equipped with a resistive anode position sensitive detection system, making possible the gating of the detection of electrons during short inductive heating intervals. The energy of the ionizing radiation was 90 and 220 eV in the measurements of Sb and Bi, respectively.

Bismuth evaporates almost equally as atomic Bi and diatomic Bi$_2$ molecules and antimony dominantly as Sb$_4$ molecules. The atom/molecule ratio of the vapour cannot be manipulated solely by increasing the evaporation temperature [8]. In order to vary the atom–molecule ratio in the vapour, a special multichambered oven (figure 1) with a molybdenum crucible consisting of two or three parts in different temperatures was used. The evaporated molecular species can...
be further fragmented to atomic Bi or to Sb$_3$, Sb$_2$ and Sb by concentrating a heating field on the uppermost part of the oven system via strongly increasing the temperature of it, which induces a lot of collisions of the molecules, but keeping the vapour flow from the reservoir part in control by its cooler temperature.

For the measurement of the solid state spectra, a copper wire with a sharpened tip has been used. The wire was attached to the water cooling coils of the oven system and bent over the oven so that the sharpened tip of the wire was about 1.5 cm above the hole of the crucible. The temperature of the tip is not known, because there was not a thermometer attached to it, but it can be said that the temperature of the tip is much cooler than the temperature of the oven.

The following procedure was used for data handling in Bi measurements. First, the vapour spectra were calibrated by introducing Kr gas into the interaction region and recording the well-known Kr 3d PES. By doing so, we were able to calibrate both the energies and the linewidths. The values of 93.788 and 95.038 eV used for the binding energies of the Kr 3d$_{3/2}$ and 3d$_{5/2}$ lines, respectively, were from King et al [13]. The experimental broadening, caused by our experimental setup, of the measured lines was determined by fitting a Voigt function to the Kr 3d lines and subtracting the known lifetime broadening of the Kr 3d lines (88 meV from [14]) from the fitted function. The measured vapour spectra were fitted, keeping the experimental broadening constant. In the case of antimony, a similar data handling procedure was used, and in the BE calibration, recently reported values for Sb$_4$ 4d photolines [15] based also on Kr reference lines were used.

The experimental spectra from the solid–vapour BE shift measurements were then fitted, keeping the parameters for the vapour photolines constant (the parameters were taken from the previously fitted spectrum, where only the vapour photolines were measured). The instrumental broadening was also kept constant to the solid photolines, but extra broadening compared to the vapour photolines was allowed to be included in the solid peaks. A Doniach–Sunjic-type lineshape was assumed for the solid photolines, keeping the asymmetry parameter as a free parameter. A free fit to the linewidths of the vapour peaks was also performed to make sure...
that the introduction of the needle into the interaction region did not affect the widths of the vapour photolines, and no such effect was observed. In the case of the vapour sample, a linear background was subtracted from the experimental spectra. In the simultaneous measurements of the vapour and solid samples, linear and Shirley-type backgrounds were subtracted from the spectra to eliminate the background caused by scattered electrons from the solid sample.

Figure 2 shows the 4f spectrum taken at 220 eV photons simultaneously from vapour and solid Bi samples. Three doublets of spin–orbit split 4f_{7/2} and 4f_{5/2} components from Bi, Bi_2 and solid Bi are well resolved. Binding energies decrease when going from the atom to the molecule and further to the solid, as expected. The solid state peaks were fitted with surface and bulk components with the energy difference of 0.22 eV, the bulk component having larger BE [17]. The surface and bulk components of the solid 4f photolines were approximated to have a Doniach–Sunjic profile with equal linewidths, and the line shape analysis gave inherent width of 330 meV for these lines compared with the 230–280 meV width of the atomic and molecular lines [9]. In vapour phase Bi, it was observed in [9] that the molecular Bi lines are about 50 meV narrower than the atomic lines. It was concluded that the multiplet splitting in the atomic lines is a larger factor when determining the linewidth than the vibrational broadening in the diatomic Bi molecule. In this study, it was found that the solid peaks are about 100 meV wider than the molecular lines. It seems that in solid Bi the phonon broadening as well as the final state vibrational broadening (see e.g. [18] and references therein) may cause an extra broadening of the linewidths, despite the observation that in the Bi_2 molecule the lifetime broadening seems to dominate over the vibrational broadening. The BE values for the line components are given in table 1.

As was pointed out in [9], the 4f photolines of atomic Bi contain multiplet splitting because of the 6p^3 open shell structure. Nevertheless, this splitting is so small that it cannot be distinguished from the experimental spectrum. Therefore the obtained BE values for the atomic 4f_{5/2} (4f_{7/2}) photoline represent a sort of average BE of the states having configuration...
Table 1. 4f binding energies (in eV) of solid Bi, Bi$_2$ and solid Bi with respect to vacuum level. The BE shift is given with respect to atomic Bi BE.

| Sample        | $E_b$ (4f$_{7/2}$) | $E_b$ (4f$_{5/2}$) | BE shift |
|---------------|--------------------|--------------------|----------|
| Bi$^a$        | 164.76 ± 0.03      | 170.09 ± 0.03      | –        |
| Bi$^b$        | 163.80 ± 0.03      | 169.13 ± 0.03      | 0.96     |
| Solid Bi$_{surface}$ | 160.91 ± 0.05      | 166.21 ± 0.05      | 3.87     |
| Solid Bi$_{bulk}$   | 161.13 ± 0.05      | 166.43 ± 0.05      | 3.65     |

$^a$ Patanen et al [9].

Figure 3. Antimony 4d spectra taken at increasing temperatures and different vapour compositions with 90 eV photons. (a) Simultaneously measured vapour and solid spectra. The vapour consists mainly of Sb$_4$ and a minor fraction of Sb$_2$. (b) A vapour spectrum consisting mainly of Sb$_4$ and Sb$_2$ components; the fraction of Sb$_4$ is about twice the fraction of Sb$_2$. (c) An almost pure Sb$_2$ vapour spectrum. (d) The vapour consists mainly of Sb and Sb$_2$ components; the fraction of Sb$_2$ is slightly larger than the fraction of Sb. (e) An almost pure atomic Sb spectrum. Dashed lines connect the positions of the main peaks.

with a 4f$_{5/2}$ (4f$_{7/2}$) core hole. For the atom–diatom shift we obtain a value of 0.96 eV, and for atom–solid (bulk) shift 3.65 eV.

Figure 3 shows how the BE of the 4d$^{-1}$ states evolves when going from the solid to the atomic Sb. The 4d PES of antimony vapour taken at increasing temperatures of the upper part of the oven in figures 3(b)–(e) emphasizes how the composition of the vapour can be varied smoothly. At the lowest temperatures the spectrum consists purely of Sb$_4$, but increasing the temperature enhances the pyrolytic fragmentation, increasing signal from Sb$_2$, and finally an almost pure atomic spectrum is observed. In the spectrum of figure 3(a), there might also be a small Sb$_3$ contribution (<10%), which has been reported in previous studies [19, 20]. One may notice a dramatic change in the fine structure of the atomic spectrum compared with the
Figure 4. Antimony 4d spectrum taken simultaneously from Sb$_4$ (red line), Sb$_3$ (violet line), Sb$_2$ (green line) and solid (blue line) samples with 90 eV photons. The red circles are measured data points, the solid black line represents the total fitted spectrum and the dashed black line is the Shirley background. The dotted black curve is the difference between the measured data points and the fit.

Table 2. 4d binding energies (in eV) of solid Sb, Sb$_4$, Sb$_2$ and Sb atoms with respect to vacuum level and the 4d BE shifts (eV) determined by the energy difference of the average center-of-gravity BE of the 4d$^{-1}$ configurations. See the text for details.

| Sample       | $E_b$ (4d$_{5/2}$) | $E_b$ (4d$_{3/2}$) | $E_{av}$ | BE shift |
|--------------|--------------------|--------------------|----------|----------|
| Sb           | 40.19 ± 0.03 ($^3D_3$) | 41.45 ± 0.03 ($^1D_3$) | 40.88    | –        |
| Sb$_2$       | 39.08 ± 0.03       | 40.32 ± 0.03       | 39.50    | 1.38     |
| Sb$_3$       | 38.77 ± 0.1        | 40.03 ± 0.1        | 39.28    | 1.60     |
| Sb$_4$       | 38.51 ± 0.03       | 39.77 ± 0.03       | 39.01    | 1.87     |
| Solid Sb$_{surface}$ | 36.55 ± 0.03   | 37.80 ± 0.03       | 37.07    | 3.81     |
| Solid Sb$_{bulk}$ | 36.30 ± 0.03  | 37.55 ± 0.03       | 36.82    | 4.06     |

molecular spectra. The atomic open shell structure is clearly observable, splitting the 4d lines into their fine structure components. This makes the determination of the atom-to-molecule shifts complicated. The atomic 4d$^{-1}$ PES will be reported in detail elsewhere [1]. From the energies of the multiplets, we obtained the average energy of the 4d$^{-1}$ configuration ($E_{av}$) of atomic Sb to be 40.88 eV by weighting all the binding energies of the multiplets with their fitted intensity. This value corresponds to the combined binding energies of all the 4d$_{5/2}$ and 4d$_{3/2}$ multiplets, and allows us to determine the BE shifts more accurately if a corresponding average energy is also used for the spin–orbit split components of the molecular/solid state spectra.

The 4d PES taken simultaneously from the vapour and solid phase Sb is shown in more detail in figure 4. Again the surface and bulk components were both fitted with the Doniach–Sunjic lineshape to the spectrum with the reported energy difference of 0.25 eV [21], but in contrast to Bi, the surface component has larger BE. Table 2 presents the 4d$_{3/2}$ and 4d$_{5/2}$ binding energies as well as the average energy of the configuration for atomic, dimer, trimer, tetramer and solid antimony. In table 2, we also give the energies of the two intense
photoelectron lines of the atomic 4d\(^{-1}\) PES having 4d\(_{3/2}\)\(^{-1}\) and 4d\(_{5/2}\)\(^{-1}\) configurations, but these energies do not correspond to the energies of the 4d\(_{3/2}\) and 4d\(_{5/2}\) hole states solely, because, owing to the multiplet splitting, the 4d\(^{-1}\) states have been scattered to the energy range of 4 eV, creating several lines to the spectrum [10]. The values for the trimer have larger uncertainty in the energies, because no clear peak but a shoulder aside the tetramer peak was associated with the Sb\(_3\) 4d\(^{-1}\) PES.

In this paper, we have demonstrated a method of measuring simultaneously vapour and solid spectra and reported new BE shift values for Bi–Bi–Bi (solid) and Sb–Sb–Sb–Sb (solid). Accurate values for shifts are needed e.g. in cluster studies, where the size determination of the clusters is strongly affected by the reference BE values of the atomic and solid samples. It is worth pointing out that also the new solid state BE values obtained here are measured with respect to vacuum level and no determination of the work function of the solid sample is needed. The obtained binding energies for solid Bi, 161.13 ± 0.05 eV and 166.43 ± 0.05 eV (bulk) for 4f\(_{7/2}\) and 4f\(_{5/2}\) levels, respectively, and 160.91 ± 0.05 eV and 166.22 ± 0.05 eV (surface), are in satisfactory agreement with the previously reported values 161.0 ± 0.1 eV and 166.3 ± 0.1 eV obtained by McGilp et al [22] by a completely independent method.

In addition, the multiplet splitting of an open shell atom is converted to an average energy of the hole configuration, and so too is the BE of the spin–orbit split components seen in molecular/solid state spectra. Both facts, the inaccurate values of work functions and the confusion due to the multiplet splitting of an open shell atom, may have created great uncertainties in the determination of atom–solid shifts published previously. Based on the same footing, the values reported here are believed to serve as a calibration for clusters studies and as test values for the development of the theoretical calculation methods.

The method used in this work has also been used to determine the BE shifts of materials that are insulators in solid state. The photoelectron spectroscopy of insulators is usually difficult due to the charging effects, but using this direct measurement method, charging effects can be sidestepped. In a forthcoming article, this subject will be discussed in more detail and the results for the BE shifts for molecular LiCl and solid LiCl will be presented.

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