Free atom 4f photoelectron spectra of Au, Pb, and Bi

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ABSTRACT

High resolution 4f photoelectron spectra have been measured from Au, Pb, and Bi vapors using synchrotron radiation. New accurate binding energy values are found to deviate more than 0.3 eV for Au from the previous results demonstrating the need for new precise values, e.g. for chemical shift and cluster studies. For Bi both atomic and diatomic lines have been observed simultaneously, molecular lines at 0.96 eV lower binding energies. Fine structure splitting created by the coupling of the 4f core hole to the open 6p shell has been found to manifest itself in this high resolution experiment as slightly different line widths for 4f spin components. The fine structure has been investigated also theoretically by calculating the 4f photoionization energies, intensities, and lifetimes using the multiconfigurational Dirac–Fock approach.

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1. Introduction

High resolution electron spectroscopy pioneered by professor Kai Siegbahn and his group in Uppsala about 40 years ago caused a real revolution in the determination accuracy of electron binding energies in atoms and molecules. This made possible the great success of ESCA (electron spectroscopy for chemical analysis) based on the directly observed shifts of core binding energies of the studied element in its different chemical states. The observed chemical shifts were found to be up to several eV's, whereas these shifts in X-ray spectra as the differences of two energy levels were roughly one order of magnitude smaller. The first pioneering studies were presented in the well known two "ESCA–bibles" [1] of electron spectroscopy. Enormous amount of studies of chemical shifts have been published since then and the theory of chemical shifts has developed to its present high quality state. Most studies were performed using Al Kα soft X-rays as exciting radiation, either directly from the X-ray tubes or monochromatized by crystal monochromators. The success of ESCA was based mainly on the high accuracy electron spectrometers. Limiting factors were broadness and weakness of the used X-ray lines. The line widths (≈ 1.0 eV for Al Kα) set the minimum for observed width of the photoelectron lines and also for the peak position determination.

Development of synchrotron radiation sources during the last 20 years with very large range tunable photon energies and enormous intensities has meant a second revolution in the history of electron spectroscopy. Due to the very high inherent photon flux from synchrotron radiation sources, very narrow photon energy bands can be selected by high resolution monochromators to ionize atoms in the source point. The usable photon bandwidths in the gas phase measurements can be typically some tens of meV in soft X-ray region and even in μ eV range for UV radiation. Photon energies can easily be selected for optimal ionization or resonant excitations making possible a completely new field of electron spectroscopy, resonant Auger spectroscopy.

Accurate core level binding energies for free atoms are very important because they are the natural references for the corresponding values and ESCA shifts from different chemical compounds. In addition presently very active cluster studies need reliable free atom reference values for binding energy shifts. Most of the elements are solids in their natural form but evaporate usually as free atoms or small molecules. Only rare gases appear as free atoms in their natural form. Therefore vapor phase studies are very important source of experimental free atom values. The basic difficulty in vapor studies is the low target density in the vapor beams corresponding typically to partial pressure of 10^{-6}–10^{-5} mbar in the source point. Vapor beams are advantageous in order to avoid harmful contamination of nearby surfaces, e.g. electron lens elements, by the condensing vapor.

In this special issue of ELSPEC in memory of professor Kai Siegbahn we present new high accuracy 4f binding energy values for Au, Pb, and Bi atoms measured in the Swedish national synchrotron radiation laboratory Max-lab in the frame of the long Finnish–Swedish collaboration. Pb and Bi are of special interest in this connection, because they were studied in the very pioneering vapor phase work by Siegbahn and co-workers [2].

2. Experiments

Measurements were carried out using synchrotron radiation from undulator beamline I411 (Swedish–Finnish beamline) [3] at MAXII storage ring in MAX-laboratory Lund, Sweden. The beamline

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is equipped with high resolution plane grating monochromator SX-700 [4]. An inductively heated oven was used to evaporate the solid samples. The heating method was successfully introduced in electron spectroscopy by prof. Jonathan's group in Southampton [5]. It was used also by our group in 1980s for electron beam excited Auger electron studies of atomic Au [6], Pd [7], Fe, Co, and Ni [8]. This heating method has turned out to be very convenient in generating high temperatures for low volatile samples. It is much faster than resistive heating in reaching the operating temperatures, but due to the generated magnetic fields the heating needs usually to be pulsed: when the heating is applied the electron signal from detector is rejected. This causes some unavoidable decrease in data collection efficiency, typically 10–30%. Our present setups have been described in some more detail in Refs. [9–11].

Bi is known to evaporate in almost one to one ratio as atomic Bi and diatomic Bi_2 molecules. Therefore in Bi measurements a special molybdenum crucible consisting of two parts with different temperatures was used to effectively control the ratio between Bi and Bi_2. A modified Scienta SES-100 electron energy analyzer [10] was used to record the emitted electrons at the "magic" 54.7° angle with respect to the polarization vector of the horizontally polarized synchrotron radiation, corresponding to the angle-independent measurements. The electron spectrometer is equipped with resistive anode positive sensitive detection system making possible gating of the detection of electrons during short inductive heating intervals in order to avoid disturbances of the high frequency induction field. The energy of the ionizing radiation was 170 eV, 200 eV, and 220 eV in the measurements of Au, Pb, and Bi, respectively. The vapor spectra were calibrated by introducing Kr gas to the interaction region and recording very well known Kr 3d photoelectron spectrum simultaneously with the vapor lines. The estimated oven temperatures were 1420 °C, 720 °C, and 675° C for Au, Pb, and Bi, respectively.

2.1. Data handling

The following procedure was used in data handling in all measurements. First, both the energies and line widths of the vapor spectra were calibrated with respect to Kr 3d lines. The values 93.788 eV and 95.038 eV were used for binding energies of Kr $3d_{5/2}$ and $3d_{3/2}$ lines, respectively, from King et al. [12]. A Voigt profile was fitted to the lines, and as the lifetime broadening of the Kr 3d lines is known (88 meV from [13]), we obtained the total Voigt-type experimental broadening caused by our experimental setup to the measured lines. The measured vapor spectra were fitted keeping the experimental broadening constant. Fitted experimental values for binding energies are presented in Table 1.
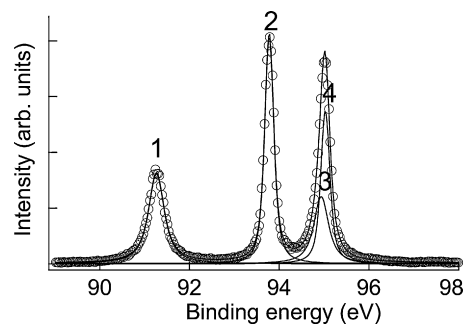

Fig. 1. Au $4f_{7/2}$ (1) and $4f_{5/2}$ (3) and Kr $3d_{5/2}$ (2) and $3d_{3/2}$ (4) lines measured with 170 eV photons. Circles refer to measured datapoints and solid curve to fitted Voigt functions.
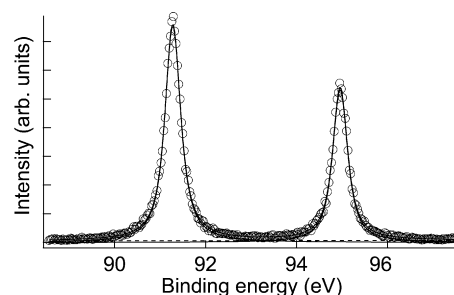

Fig. 2. Au 4f lines measured with 170 eV photons. Circles refer to measured datapoints and solid curve to fitted Voigt functions. Dashed line represents the subtracted background.

2.2. Au 4f binding energies

Accurate 4f binding energy values of free gold atoms are of special interest, for example, because 4f lines from solid gold are important and commonly used reference energies in solid state studies. As far as we know atomic 4f photoelectron spectra have not been measured earlier. Until now values obtained by Aksela et al. [6] from experimental atomic 4f Auger energies and optical double hole final state energies, 91.60 ± 0.20 eV and 95.25 ± 0.20 eV for the $4f_{7/2}$ and $4f_{5/2}$, respectively, have been used. The main source of inaccuracy in these values is the inaccurate value of second ionization potential of Au in optical data [14]. In this study we have measured the 4f photoelectron spectrum from atomic Au vapor with high accuracy using well known 3d photolines from Kr for the energy calibration. It turned out that Au $4f_{7/2}$ and Kr $3d_{3/2}$ photolines overlap almost completely as shown in Fig. 1 where Au 4f and Kr 3d photolines are shown to form three peaks. The Au 4f photolines (circles) are shown in Fig. 2 with the Voigt func-

Table 1
Experimental and theoretical 4f binding energies (eV) and inherent linewidths (meV) (consisting of lifetime broadening and multiplet splitting of the states) of Au, Pb, and Bi.

Atom	Experiment		Theoretical		Experiment		Theoretical	
	$E_b(4f_{5/2})$	$E_b(4f_{7/2})$	$E_b(4f_{5/2})$	$E_b(4f_{7/2})$	$\Gamma(4f_{5/2})$	$\Gamma(4f_{7/2})$	$\Gamma(4f_{5/2})$	$\Gamma(4f_{7/2})$
Au	94.95 ± 0.03 [a] 95.25 ± 0.20 [b]	91.28 ± 0.03 [a] 91.60 ± 0.20 [b]	95.58	91.80	280 ± 10 [a]	300 ± 10 [a]	350	320
Pb	149.17 ± 0.03 [a]	144.30 ± 0.03 [a] ≈ 144 [c]	148.74	143.92	290 ± 10 [a]	280 ± 10 [a]	230	220
Bi	170.09 ± 0.03 [a]	164.76 ± 0.03 [a] 164.9 [c]	169.40	164.15	280 ± 10 [a]	260 ± 10 [a]	240	250
Bi_2	169.13 ± 0.03 [a]	163.80 ± 0.03 [a]			240 ± 10 [a]	230 ± 10 [a]		

[a] This work.
[b] Ref. [6].
[c] Ref. [2].