



Atom–solid binding energy shifts for K 2p and Rb 3d sublevels

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ABSTRACT

Binding energy shifts between free and solid state atoms for K 2p and Rb 3d photolines have been determined by measuring the vapor and solid state spectra simultaneously in similar experimental conditions applying synchrotron radiation excited photoelectron spectroscopy. This method has the important benefit that the work function is not needed to correct for different reference energy levels, therefore much more accurate values for binding energy shifts are obtained.

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1. Introduction

Binding energy shifts between free atoms and atoms in solid state are an interesting topic in electron spectroscopy as they link atoms and solids to each other. Experimental binding energy shift values between atomic vapor and solid are not accurate if the vapor values are calibrated with respect to vacuum and solid state values with respect to Fermi level, due to inaccuracies in the determination of work function of solid samples and cumulative inaccuracies of two separate measurements. The determination of work function can be avoided if the vapor and solid state measurements are done simultaneously with respect to a common reference level observing the electrons from vapor atoms very close to tip surface in the surface potential. Accurate values for binding energies and shifts are very important, e.g. in cluster studies, as the commonly used cluster size determination model is strongly dependent on these values. Tchapyguine et al. [1] studied core-level binding energy shifts between free atom and large clusters for several elements. They used large clusters instead of infinite solids in their experiments, which may result in a significant difference in shift values if compared to real atom–solid binding energy shifts.

Johansson and Mårtenson [2] calculated core-level binding energy shifts for various elements including K and Rb using the semiempirical thermochemical model. They calculated outer shell binding energies using the assumption of a fully screened final state in the metallic case and the $(Z + 1)$ approximation. The calculations were done with the help of the Born–Haber cycle which connects the initial state with the final state of the core-ionization process.

Alkali metals are widely studied as atoms, recently Jänkälä et al. reported the 2p photoelectron spectrum (PES) of K [3] and 3d PES of Rb [4]. Size, charge and plasmons of free alkali metals clusters have been studied recently [1,5–10]. 3p photolines of solid K and 4p photolines of solid Rb were recorded, e.g. by Wertheim et al. [11–13] and 3d PES of solid Rb, e.g. by Leiro and Minni [14].

In this paper K 2p and Rb 3d PES are recorded simultaneously from free atoms and solid sample and accurate binding energy shifts between them are determined in the same way as in [15]. No simultaneous measurements of K 2p and Rb 3d photolines from vapor and solid phase have been reported previously. Our results provide also new references for cluster studies of K and Rb.

2. Experiment and results

The measurements were carried out at the I411 beamline of the MAX II [16] synchrotron radiation storage ring. A resistively heated oven was used to evaporate the solid samples. Spectra were recorded at the magic angle of 54.7° with respect to the polarization direction of the synchrotron radiation beam. The emitted electrons were recorded with a modified Scienta SES-200 electron analyzer [16]. The 2p PES of K (in Fig. 1) were measured with the photon energy of 365 eV and the 3d PES of Rb (in Fig. 2) with the photon energy of 200 eV. Corresponding kinetic energies of the electrons emitted from the solids were 66–69 eV and 85–87 eV for K and Rb, respectively. Referring to the escape depths of the electrons from solids [17] the photon energies used lead to surface sensitive measurements. In these measurements a needle like surface was located into the vapor beam and the spectra from the vapor around the tip and from the condensed solid layer were simultaneously observed. Condensed solid layer was presumably polycrystalline but we were not able to study the layer in more detail. The vapor atoms in the vicinity of the solid tip are very accurately in

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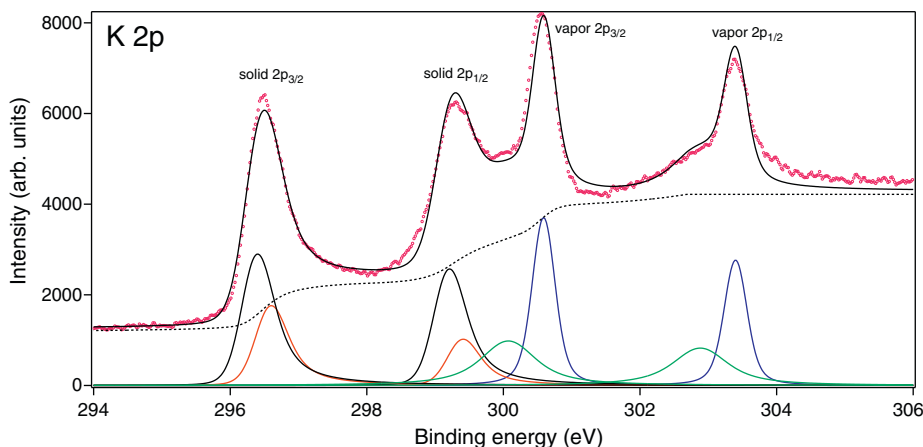


Fig. 1. K 2p PES taken simultaneously from vapor and solid sample. Blue lines corresponds to $2p_{1/2}$ and $2p_{3/2}$ vapor lines. Red line for solid is the surface and black line the bulk peak. Green lines correspond the bulk plasmons. Red circles are measured data points, solid black line is the total fitted spectrum and dashed black line is the Shirley background. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

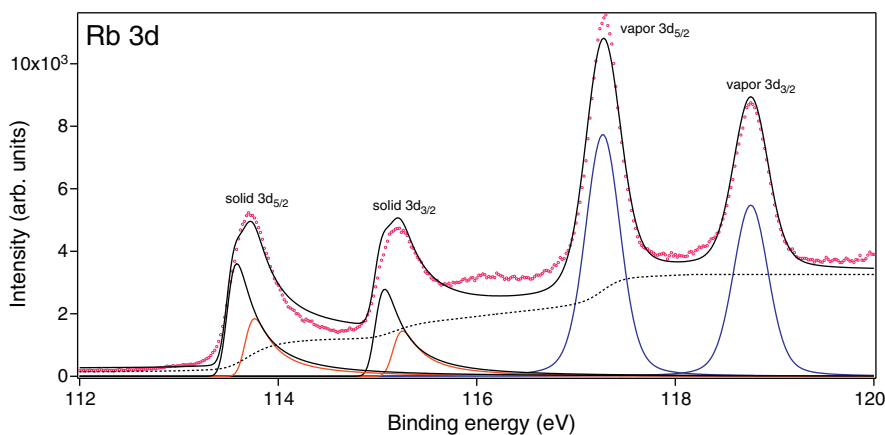


Fig. 2. Rb 3d PE taken simultaneously from vapor and solid sample. Blue lines corresponds to $3d_{3/2}$ and $3d_{5/2}$ vapor lines. Red line for solid is the surface and black line the bulk peak. Red circles are measured data points, solid black line is the total fitted spectrum and dashed black line is the Shirley background. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

the potential of the solid surface which form the joint reference potential.

When electrons from solid atoms enter to the source volume of emitting vapor atoms they have lost kinetic energy by the amount of work function relative to Fermi level and shift is automatically observed. In the simultaneous measurements the vapor atoms are ionized at distance less than the diameter of the exciting beam from the solid surface. At distance zero, potential is certainly the negative work function potential. At some distance d within the beam diameter the potential may change very slightly because the potential at that point is affected also by the surface potentials of surrounding metal surfaces. It can be estimated that maximal change is roughly of the order of 10 meV.

Alkali metals are very reactive due to one valence electron reacting strongly with oxygen (see, e.g. [18–20] and references therein). This tends to broaden the observed photolines of alkali metals [20]. By preheating the copper needle and applying continuous evaporation and condensation during the measurements this was tried to be minimized. K 2p and Rb 3d PES from simultaneous measurements are shown in Figs. 1 and 2, respectively.

The binding energies of the atomic K 2p and Rb 3d photolines (K $2p_{1/2}$ 303.39 eV, $2p_{3/2}$ 300.58 eV and Rb $3d_{3/2}$ 118.76 eV, $3d_{5/2}$ 117.27 eV) were obtained from Jänkälä et al. [3,4] for energy calibration. Spectra were fitted using the Voigt profile for vapor photolines and the Doniach–Sunjic type lineshape [21] for solid photolines. At first a Shirley-type background [22] was subtracted from solid state

part of the spectra to eliminate the background caused by scattered electrons in solid sample. Linear background was subtracted under the vapor peaks. The data was fitted keeping the linewidths of atomic photolines (Lorentzian linewidths: 150 meV for K [3] and 100 meV for Rb [4]) as well as the spin-orbit splitting of the atomic and solid photolines fixed (2.81 eV [3] for K and 1.49 eV [4] for Rb) whereas Gaussian linewidths which represent the spectrometer broadening were linked to one peak. For the solid photolines Lorentzian linewidths and asymmetry parameter as well as Gaussian linewidths were linked to one peak.

The photolines from solids are known to show usually two components corresponding atoms on the surface and in the bulk. In alkali metals the core electrons are more bounded at the surface than in the bulk, i.e. the bulk component has a smaller binding energy if compared to surface component [10–13]. In the case of K solid lines the separation of the surface and bulk lines has been reported to be 0.2 eV [10] and for Rb 0.18 eV [9]. Binding energies for K $2p_{1/2}$ and $2p_{3/2}$ and Rb $3d_{3/2}$ and $3d_{5/2}$ vapor, surface and bulk peaks, the intensity weighted average energy of these peaks as well as the binding energy shifts are shown in Tables 1 and 2.

3. Discussion

Photolines in solid K and Rb spectra are several eV's at lower binding energies relative to photolines in vapor. This is mainly due the extra atomic relaxation (screening) [23–25] of the ionized final

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