

# **HIGH RESOLUTION SPECTROSCOPY**



# HIGH-RESOLUTION X-RAY PHOTOELECTRON SPECTROSCOPY STUDIES OF THIOL-DERIVED SELF-ASSEMBLED MONOLAYERS

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We have firstly applied the synchrotron-based high resolution XPS to study thiol-derived self-assembled monolayers (SAMs) with an emphasis on the SAM/metal interface. The measurements were performed at the synchrotron storage ring MAX II at MAX-Lab in Lund, Sweden. The variable photon energy of the synchrotron light and a high energy resolution of the spectrometer (better than 0.1 eV) enabled us to resolve the bulk and surface components of the substrate emission peaks (Au4f/Ag3d) and monitor the evolution of these components upon the formation of SAMs from both thioaliphatic [C12: CH<sub>3</sub>(CH<sub>2</sub>)<sub>11</sub>SH] and thioaromatic [BPT: CH<sub>3</sub>(C<sub>6</sub>H<sub>4</sub>)<sub>2</sub>SH] molecules (Fig. 1). Simultaneously, the interaction of the thiol-derived molecules with the substrate was followed by monitoring the S 2p doublet attributed to the sulfur head group of these molecules (Fig. 2). Only one sulfur species was found in the densely packed SAMs, which implies an equivalent bonding geometry for all adsorbed molecules. In SAMs comprising of specially designed, mixed aliphatic-aromatic molecules a periodical, "odd-even" shift of the S 2p binding energy with the varying length of the aliphatic part was observed. This shift was attributed to the distortion of the substrate-S-C bonding angle resulting from either the favorable or unfavorable package conditions occurring at the varying length of the aliphatic part. This work has been supported by the German Bundesministerium für Bildung und Forschung through grant No. 05 SL8VHA 2 and by DAAD (313/S-PPP-pz).

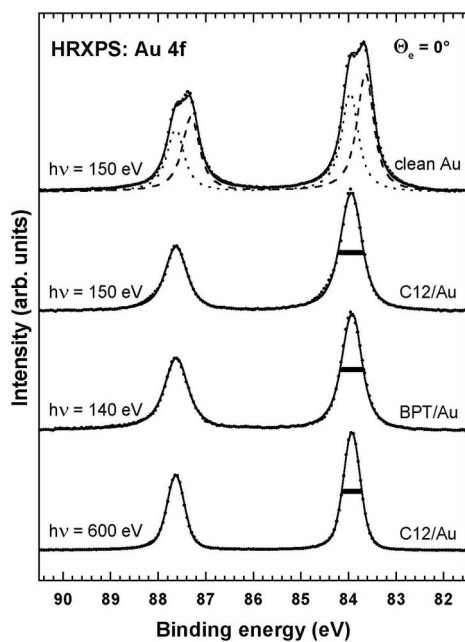


Figure 1: Au 4f HRXPS spectra of clean and C12/BPT covered gold substrate.

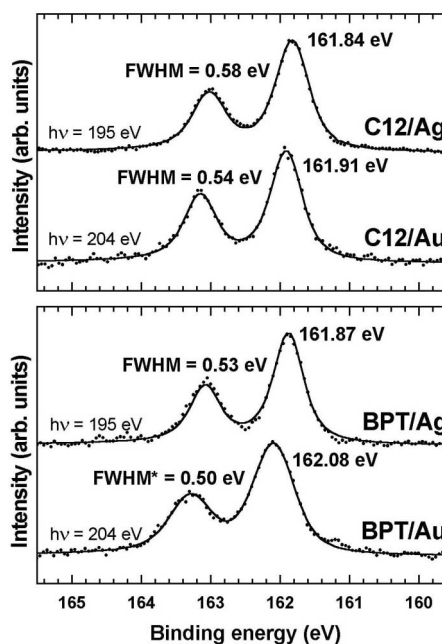


Figure 2: S 2p HRXPS spectra of AT and BPT SAMs on Au and Ag. The BEs and FWHMs of the S 2p<sub>3/2,1/2</sub> peaks are indicated.

## High Resolution Si 2p Photoelectron Spectroscopy For Molecular Adsorption on Si(100)c(4x2)

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In recent years, there has been a great interest in molecule-silicon systems, concerning the application to molecular scale devices [1,2]. For the systems, the interface bonding between molecule and Si substrate is very important. High resolution Si 2p spectroscopy provides crucial information about the interface bonding and the charge transfer between molecule and Si. In the present study, we have investigated several molecule-silicon systems by means of high resolution Si 2p photoelectron spectroscopy.

The experiments were performed using a BL-16B with an undulator radiation source of Photon Factory at High Energy Accelerator Research Organization in Tsukuba, Japan. In the experiments, the total energy resolution was estimated to be below 80 meV at the photon energy of 130 eV. Photoelectron spectra were measured at ~100 K for clean Si(100)c(4x2) surface and chemisorption layer on Si(100)c(4x2).

For the clean Si(100)c(4x2) surface, we could resolve five components in the Si 2p spectra by carefully analyzing the spectra recorded at several photon energies and emission angles. They are attributed to the bulk, up dimer atom, down dimer atom, subsurface, and unidentified species [3]. After adsorption of unsaturated hydrocarbon molecules (ethylene, cyclopentene, and 1,4-cyclohexadiene), the peaks corresponding to the up and down atoms of the asymmetric dimers almost vanish, while new peaks are observed between 215 and 398 meV relative to the bulk Si peak. These new peaks are assigned to the Si-C bonds, considering that the C atom is more electronegative than the Si atom and the area intensity of the Si-C peak is almost the same as the sum of consumed intensities of both up and down dimer atom peaks. Furthermore, we have estimated the charge transfers between the adsorbed molecules and the Si surface, where they depend on the molecules.

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# HIGH-RESOLUTION ANGLE-RESOLVED ION-YIELD SPECTRA OF NO<sub>2</sub> IN THE N AND O K-EDGE REGIONS

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The photochemistry of nitrogen dioxide (NO<sub>2</sub>) molecule is practically of interest from the environmental viewpoint, playing a critical role in the stratospheric NO<sub>x</sub> cycle and also in the atmospheric photochemical smog cycle [1]. The NO<sub>2</sub> molecule presents some similarities to the CO<sub>2</sub> molecule from the physicochemical point of view, because it is an oxide where the central atom is replaced by the nitrogen. It is a bent triatomic molecule with terminal oxygen atoms, similar to O<sub>3</sub> in this sense. Despite these fundamental interests and practical needs for photochemical information for NO<sub>2</sub>, spectroscopic studies are still rare, especially in the soft X-ray region. Thus, in the present study we have measured the high-resolution angle-resolved ion-yield spectra of NO<sub>2</sub> in the N and O *K*-edge regions. It is well known that the inner-shell angle-resolved ion-yield spectroscopy is a powerful probe of symmetries of the excited states as well as the geometric structures [2].

The experiments were performed on the soft X-ray photochemistry beamline BL27SU at SPring-8. A pair of energetic-ion detectors of retarding-potential type is mounted horizontally and vertically in the main chamber. Angle-resolved energetic-ion yield curves of the NO<sub>2</sub> were measured with the applied retarding voltage of 6.4 V. The sample gas was introduced coaxially with the photon beam from a gas nozzle positioned downstream. We also measured the total ion-yield (TIY) curve simultaneously with the energetic-ion yield curves.

The N *1s* and O *1s* spectra of NO<sub>2</sub> obtained in the present study are similar to those reported by Zhang et al. [3], but are resolved much better especially for the Rydberg transitions. For example, peaks with the principal quantum numbers of up to 6, at least, are discernable in the present N *1s* TIY spectrum. Under the axial-recoil approximation and utilizing the simple vector algebra, the symmetries of the inner-shell excited states can be deduced from angular distribution of the fragment ions. A shoulder at 409.97 eV in the TIY spectrum, for example, is assigned as the transition to *3pb*<sub>1</sub>, because this peak is observed only in the spectrum recorded in the direction perpendicular to the polarization vector. In this way, we could establish the assignments unambiguously of the N *1s* and O *1s* inner-shell spectra of NO<sub>2</sub> based on the angular distribution data for the energetic ions.

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# PHOTOELECTRON SPECTROMETRY OF ATOMIC Fe IN THE REGION OF THE $3p \rightarrow 3d$ GIANT RESONANCE

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To date, wide ranging and systematic studies of open-shell atoms are still largely lacking [1], particularly when compared to the enormous amount of work that has been carried out on closed-shell atoms, chiefly the rare gases. Due to the non-isotropic charge distribution in the ground state of most open-shell atoms, interesting effects in the photoionization process can arise which will not occur in a closed-shell atom.

Atomic Fe,  $[Ar]3d^64s^2(^5D_4)$ , is an intriguing candidate for study because of its partially filled  $d$  subshell. In this poster we will present a systematic and comprehensive study of the partial cross sections of the  $3d$  and  $4s$  mainlines and associated satellites in the region of the  $3p \rightarrow 3d$  giant resonance. One characteristic of open-shell atoms is the multiplet structure of the residual photoion. Following the removal of a  $3d$  electron in atomic Fe, five  $3d$  photopeaks are produced: the  $3d^{-1}(^6S)$ ,  $3d^{-1}(^4G)$ ,  $3d^{-1}(^4P)$ ,  $3d^{-1}(^4D)$ , and  $3d^{-1}(^4F)$ . The relative partial cross sections of each of these lines is shown in figure 1. All spectra have been normalized with respect to each other so that a direct comparison of their relative intensity can be made. As can be seen from the data, all lines except the  $3d^{-1}(^6S)$  clearly show the presence of two broad asymmetric resonances. Our results are in accord with earlier measurements at lower resolution with poorer statistics [2]. In contrast to those measurements, however, we were able to completely separate the  $3d(^4G)$  and  $3d(^4P)$  peaks.

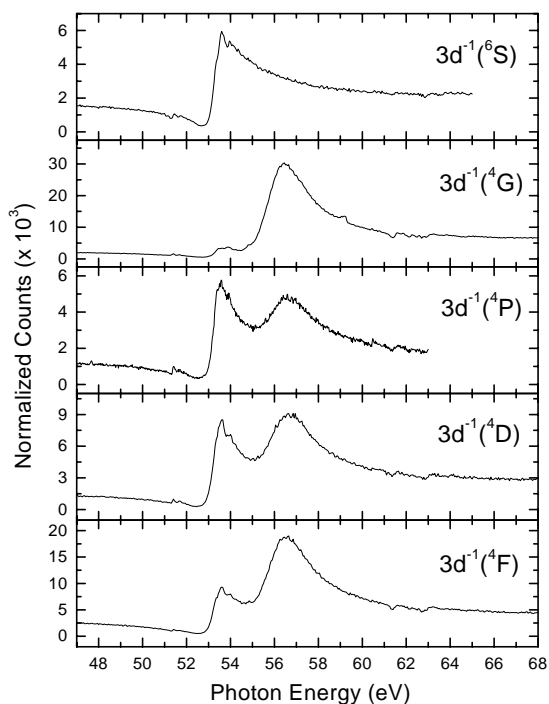


Figure 1: Atomic Fe  $3d$ -mainlines in the region of the  $3p \rightarrow 3d$  giant resonance.

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## **Disorder broadening of core level lineshapes in alloys: Surface contributions.**

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The electrostatic energy of arrays of charges has attracted attention since the work of Madelung and the concepts of electronegativity and ionicity are important in chemistry. However “charge transfer” is not a quantum mechanical observable and the lack of an agreed definition has limited the usefulness of the concept. This is a particular difficulty in the study of metal alloys where the effects of charge transfer between alloy constituents play an important role in order-disorder transitions.

Recently a new method of defining and measuring charge transfer based on high resolution measurements of core level photoelectron lines has been developed [1,2]. In the analysis of such data it is important to allow for the effects of surface core level shifts. In this work the influence of surface core level shifts on the analysis of the disorder broadening of core level lineshapes in CuPd alloys is considered.

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# HIGH-RESOLUTION SURFACE CORE-LEVELS OF GaAs(001) SURFACES

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GaAs(001) surface is the most widely used surface for high-speed and opto-electronic devices. This surface has been extensively investigated in the last two decades with its various surface reconstructions. However, only few photoemission studies have been done because of the difficulty in the combination of synchrotron radiation photoemission system with MBE.

In this contribution, we have installed an MBE system to the photoemission endstation at BL-1C of the Photon Factory [1], and measured a high-resolution core-levels for GaAs(001) – c(4x4), (2x4), (4x2) and (4x6) surfaces. An n+-GaAs(001) epitaxially substrate was used. After removing surface oxides, a 3000Å GaAs buffer layer was grown under optimized conditions. The surface structures were monitored by RHEED during the growth. The photoemission measurements were carried out with the photon energy of 100 eV. Figure 1 shows the photoemission spectra of As 3d and Ga 3d core-levels with 0° and 60° emission angles. The surface structures were checked by LEED before and after each measurement. We have determined the surface core-level shift (SCLS) from chemically inequivalent surface sites and compared with the previously proposed surface structure models. We have successfully determined the surface structures and chemical bondings for the reconstructed surfaces.

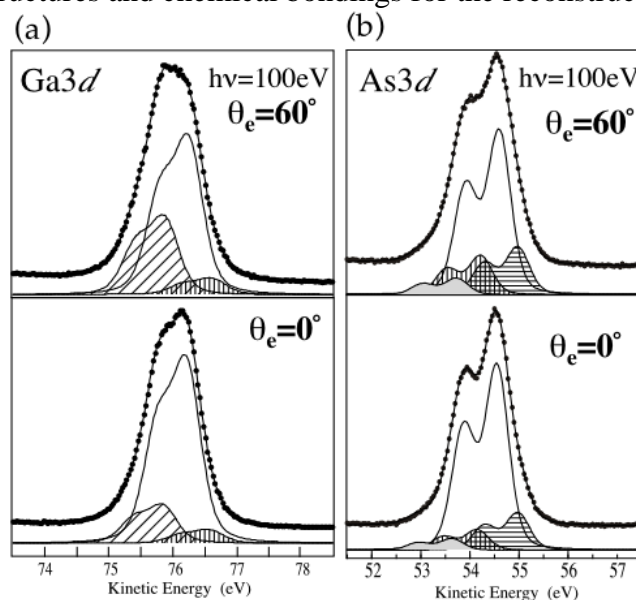


Figure 1: (a) Ga 3d, and (b) As 3d photoemission spectra for the c(4x4)-GaAs(001) surface with 0° and 60K emission angles.

## References

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# INTERFERENCE EFFECTS IN AUTOIONIZATION SPECTRA OBSERVED AT La 3d EXCITATIONS IN LaF<sub>3</sub> AND LaCl<sub>3</sub>

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Resonant photoemission by using tuneable radiation with high monochromaticity has been an important tool in the study of interference phenomena in the region of autoionization resonances. A resonant enhancement of the electron emission from core levels is caused by an indirect process associated with the Auger decay of the intermediate state reached by the photoexcitation, which has the same initial and final states as a direct photoemission process. Adding the amplitudes of both paths give rise to interferences that produce the characteristic Fano type profile, for example, in the constant initial state spectra.

The resonant photoemission spectra from lanthanum 4d, 5p and 5s core levels in LaF<sub>3</sub> and LaCl<sub>3</sub> have been measured in the vicinity of the M<sub>45</sub> absorption edges of La. It is shown that the spectra excited at 3d<sup>10</sup> → 3d<sup>9</sup>4f autoionization resonances exhibit a very strong interference effects. The anomalous behaviour of the intensity ratio of 4d<sub>3/2</sub> and 4d<sub>5/2</sub> as well as 5p<sub>1/2</sub> and 5p<sub>3/2</sub> photolines of La at the resonance excitation energies is found and attributed to the strong term-dependence of the autoionization process. For instance, in Fig. 1 we have demonstrated how the destructive interference for larger photon energies yields to the complete cancellation of La 5s photoline. The experiments have been performed at beamline D1011 at MAX-II and at beamline 22 of MAX-I storage ring in MAX-lab (Lund, Sweden).

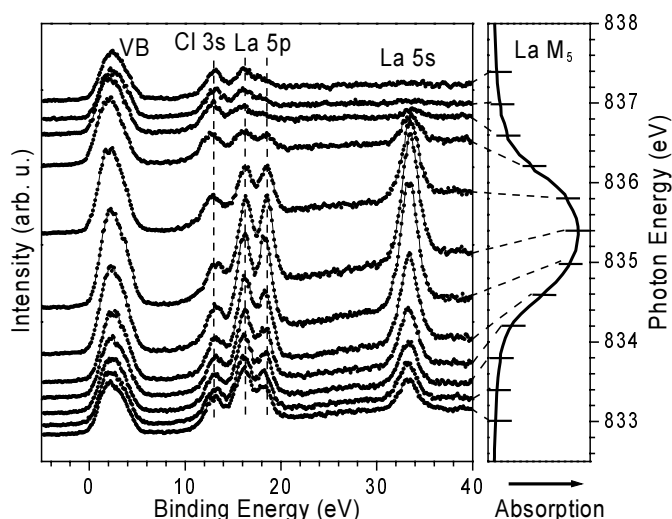


Figure 1: Resonant photoemission spectra for LaCl<sub>3</sub> in the region of La 5p and 5s photolines (left panel) excited around the lanthanum M<sub>5</sub> absorption maximum (right panel).

# HIGH-RESOLUTION SURFACE CORE-LEVELS OF GaAs(111)B SURFACES

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GaAs is the most widely used compound semiconductor for high-speed and opto-electronic devices. GaAs(111)B surface is used as a substrate for InGaAs quantum wells which exhibit a large piezoelectric effect in opto-electronic devices. Although GaAs(001) surface has been extensively investigated in the last two decades, GaAs(111)B surface is very poorly understood.

We have installed an MBE system to the photoemission endstation at BL-1C of the Photon Factory [1], and measured high-resolution core-levels for GaAs(111)B – (2x2) and ( $\sqrt{19} \times \sqrt{19}$ ) surfaces. An n+-GaAs(111)B epitaxial substrate was used. After removing surface oxides, a 1000Å GaAs buffer layer was grown under optimized conditions. The surface structures were monitored by RHEED during the growth. The photoemission measurements were carried out with the photon energy of 100 eV. The photoemission spectra of As 3d (results in (2x2) surface is shown in Fig. 1) and Ga 3d core-levels with 0° and 60° emission angles were measured. The surface structures were checked by LEED before and after each measurement. We have determined the surface core-level shift (SCLS) from chemically inequivalent surface sites and compared with the proposed surface structure models. We have successfully determined the surface structures and chemical bondings for the reconstructed surfaces of GaAs(111)B.

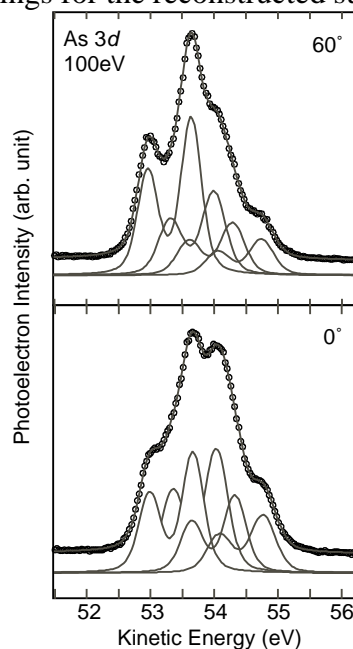


Figure 1: As 3d photoemission spectra for the (2x2)-GaAs(111)B surface with 0° and 60° emission angles.

## References

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# HIGH-RESOLUTION Si 2P CORE-LEVEL STUDY OF THE K/Si(111)-(3x1) SURFACE

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Semiconductor surfaces modified by adsorption of metal atoms have been a topic of experimental investigation for the creation of nanoscale quantum structures with high perfection. Among the great number of metal induced surface reconstructions, the alkali metal (AM) adsorbed Si(111)-(3x1) surface is one of the most well known. Several structural models have been proposed until now for the atomic geometry of this surface. Among them, the honeycomb-chain-channel (HCC) model [1] is the energetically most stable one. However, though the presence of at least three Si 2*p* surface components is suggested for the HCC model theoretically [1], only two components are observed experimentally [2] up to now. Since the Si 2*p* core-level reflects well the underlying surface geometry and the bonding configuration of the adsorbates, it is important to measure the Si 2*p* core-level with high-resolution to obtain a proper understanding on the structure of the AM/Si(111)-(3x1) surface.

In this study, we have measured the Si 2*p* core-level of the K/Si(111)-(3x1) surface by photoelectron spectroscopy. The high-resolution core-level PES studies were performed at beamline 33 at the MAX-I synchrotron radiation facility in Lund, Sweden. For the most surface sensitive measurement, we have used a photon energy of 130 eV and an emission angle of 60° from the surface normal direction, and for the most bulk sensitive measurement, a photon energy of 108 eV and an emission angle of 0° were used. Analyzing the spectra by a least-squares-fitting method using spin-orbit split Voigt functions, we recognize the presence of five Si 2*p* surface components. Among these five components, the energy shifts of three of them agree well with the previous theoretical calculation [1]. The good agreement of these three components shows the appropriateness of the HCC model. Moreover, the agreement in energy shifts suggests their origins to be the first layer Si atoms. We will also discuss the origin of the two other components in relation to the HCC model.

## References

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# Determination of the Scandium 2p ionization thresholds using high resolution electron spectroscopy

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Up to now only values for the Scandium 3p ionization thresholds have been measured [1]. As an outcome of photoionization studies in the region of 2p excitation carried out at the BESSY II synchrotron radiation facility, data for the atomic 2p ionization thresholds can now be presented (Figure 1). The data were acquired at the U49/1-SGM beamline using a high resolution hemispherical electron analyzer (Scienta SES 200).

The experimental results show a very good agreement with numerically calculated data. The calculations were carried out using the relativistic Hartree-Fock algorithm (Cowan code). Line assignments were done based on the numerical data.

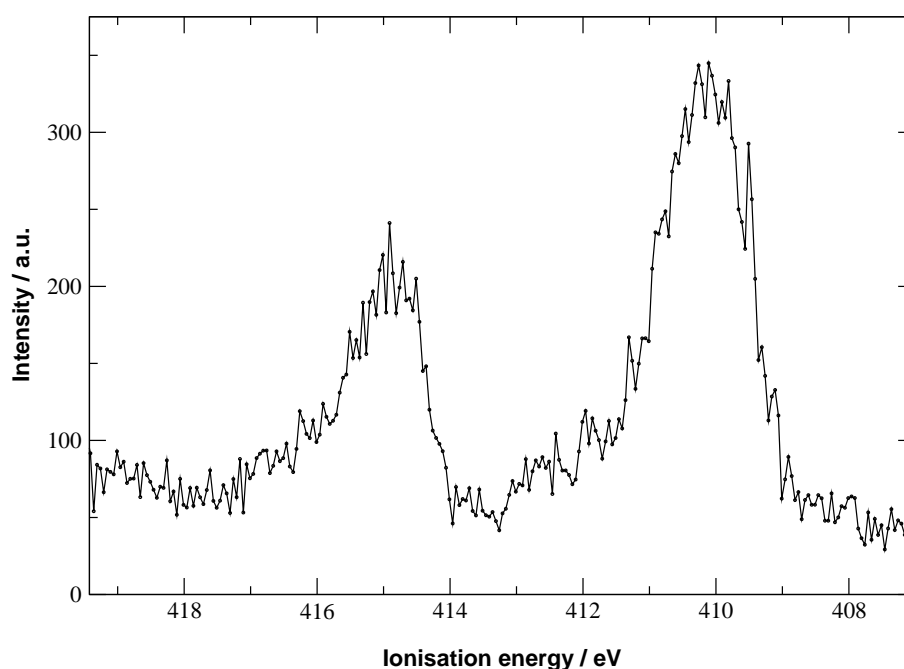


Figure 1: Energy resolved photoelectron spectrum of directly ionized 2p Scandium electrons. The structure is dominated by the fine structure splitting of the 2p core hole.

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