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Increased photoelectron transmission in High-pressure photoelectron spectrometers using “swift acceleration”



Mårten O.M. Edwards^a, Patrik G. Karlsson^a, Susanna K. Eriksson^b, Maria Hahlin^c, Hans Siegbahn^c, Håkan Rensmo^c, Juhan M. Kakk^d, Ignacio J. Villar-Garcia^d, David J. Payne^d, John Åhlund^{a,*}

^a VG Scienta AB, Box 15120, 750 15 Uppsala, Sweden

^b Department of Chemistry-Ångström, Uppsala University, Box 523, 751 20 Uppsala, Sweden

^c Department of Physics and Astronomy, Uppsala University, Box 516, 751 20 Uppsala, Sweden

^d Department of Materials, Imperial College London, Exhibition Road, London SW7 2AZ, UK

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ABSTRACT

A new operation mode of a HPXPS (high-pressure X-ray photoelectron spectroscopy) analyzer is evaluated on a HPXPS system fitted with an Al K α X-ray source. A variety of metal foil samples (gold, silver and copper) were measured in different sample gas environments (N₂ and H₂O), and a front aperture diameter of 0.8 mm. The new design concept is based upon “swiftly” accelerating the photoelectrons to kinetic energies of several keV after they pass the analyzer front aperture. Compared to the standard mode, in which the front section between the two first apertures is field-free, this gives a wider angular collection and a lower tendency for electron losses in collisions with gas molecules within the analyzer. With the swift-acceleration mode we attain, depending on the experimental conditions, up to about 3 times higher peak intensities in vacuum and about 10 to 20 times higher peak intensities in the 6–9 mbar regime, depending on kinetic energy. These experimental findings agree well with simulated transmission functions for the analyzer. The new mode of operation enables faster data acquisition than the standard mode of operation, particularly valuable in a home laboratory environment. Further demonstrations of performance are highlighted by measurements of the valence band structure in dye-sensitized solar cell photoelectrodes under a 2 mbar H₂O atmosphere, a molecularly modified surface of interest in photoelectrochemical devices.

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1. Introduction

High pressure X-ray photoelectron spectroscopy (HPXPS) has in recent years become a powerful and increasingly popular method for studying chemical species at solid and liquid surfaces at pressures closer to ambient conditions. This has created an opportunity to study a wide range of materials and phenomena, related to surface gas and liquid interactions, that previously have not been possible to study with conventional ultra high vacuum (UHV) photoelectron spectroscopy [1].

Photoelectrons with kinetic energies up to a few keV are more strongly scattered by gas molecules due to higher electron scattering cross-sections at these energies. This result in photoelectron signal intensities, many orders of magnitude lower than in standard XPS measurements. This is a reason why most HPXPS experiments are performed at synchrotron facilities with high

photon fluxes by teams specializing in large-scale UHV instrumentation [1–6]. To become a widespread laboratory-based method, available to the wider scientific and industrial communities, it is crucial that high-pressure spectra can be recorded on a reasonable timescale [2,7,8]. In this work we present an analyzer high-voltage operation mode “swift acceleration” that widens the angular collection and drastically reduces the internal electron collision losses found in lab-based HPXPS analyzers, and consequently greatly reduces the data acquisition times. The swift acceleration mode differs from the standard mode of operation in that it has a high voltage potential close to the first aperture of the instrument. This allows for faster acceleration of the electrons in this mode and hence a higher transmission is realized. In this work we compare the new swift acceleration lens table with the standard transmission mode lens table, used in Ref. [6], with regard to the analyzer transmission and spectral quality for a wide range of analyzer slit-widths, pass energies, and sample pressures. The swift mode of operation was evaluated using gold, silver and copper samples under various nitrogen and water pressures and the swift acceleration mode performance was further validated

* Corresponding author.

E-mail address: john.ahlund@vgsienta.com (J. Åhlund).

using a photoelectrochemically active interface consisting of a mesoscopic TiO₂ photoelectrode sensitized with a Ru-based dye molecule under a water vapor pressure of 2 mbar. Such electrochemical systems are interesting for energy applications such as molecular solar cells and are also closely related to many systems used for photocatalysis.

We find that with the swift-acceleration mode we attain, depending on the experimental conditions, up to about 3 times higher peak intensities in vacuum and in the range of 10 to almost 20 times higher peak intensities in the 6–9 mbar regime. No Corona/dielectric breakdown was observed during any of the experiments, due to the high potential in the front of the instrument. This enables stable operation with higher transmission using the swift acceleration mode. A consequence of the extended pressure regime is that larger front cone apertures can be used in HPXPS, giving improved electron collection and facilitating the use of large X-ray sample spots.

2. Experimental

The experiments were performed at the HPXPS system at VG Scienta AB in Uppsala, Sweden, whose main components are a Scienta MX 650 HP X-ray source, a Scienta R4000 HiPP-2 electron analyzer, an analysis chamber with a manipulator-controlled sample holder array, and a preparation chamber for sample loading. For a detailed description and schematic views of the set-up, see Ref. [6]. The peak energy and width of the Bragg reflected Al K α radiation from the X-ray monochromator is 1486.7 eV and \sim 200 meV, respectively, and the incidence angle on the sample is 62.5° for central X-rays. The X-ray source settings (200 W power, 12.0 kV electron acceleration voltage) and the alignment of the whole source and the monochromator crystals were kept constant throughout the experimental series.

The electron analyzer consists of (i) a straight energy-retarding and differentially pumped section and (ii) an energy-analyzing 180° hemisphere with a mean radius of 200 mm, nine interchangeable slits, and a 2D MCP/CCD type detector. Emitted photoelectrons from the sample enter the differential pumping stage lens through a small aperture in the conical front. For operation in different sample pressure regimes several exchangeable analyzer front cones with different aperture diameters are available [6]. The analyzer slit width can be varied from 200 μ m to 4 mm. For these experiments a set of curved slits (0.1 mm, 0.2 mm, 0.3 mm, 0.4 mm and 0.8 mm) and a set of straight slits (1.5 mm, 2.5 mm and 4 mm) were used. The analyzer can be operated using pass energies from 50 to 500 eV [6]. The so-called lens table describes the optimum high-voltage configuration of the analyzer lens elements, and its dependence on kinetic energy and pass energy. The lens table is a unique property for a specific analyzer type which is derived through electron-optics simulations of element voltages for a limited number of kinetic energies and interpolation between the simulated points [9,10]. Of particular interest in this work are the geometry and the voltage configuration of the elements at the front of the analyzer. Another conical element, with a several mm wide central circular opening, is situated 10 mm downstream from the front cone, and on further downstream there is also a mesh lens element, electrically connected to the second cone. The front cone is permanently grounded, and in previous work [6] the second cone and the mesh element were also grounded to keep the zone from the sample to the mesh field-free. This keeps aberrations at a minimum and is, in particular, advantageous for angular measurements. Associated with this field-free front operation are standard-operation lens tables, e.g. transmission mode and angular mode lens tables. To attain higher analyzer transmission we have developed a swift-acceleration operation mode, wherein the electrons are accelerated from ground to around 4.5 keV, about three times higher than the Al K α X-ray

excitation energy, along a 10 mm path between the front (first) and second cone. The lens table associated with this mode of operation is tailored for Al K α X-ray excitation sources to further streamline the use of home laboratory and soft X-ray HPXPS systems.

The modes of operation were evaluated using silver, gold, and copper foil samples (99.95% from A. Rasmussen a.s.; 99.99% from KarAna AB; and 99.99% from Goodfellow Ltd., respectively). Nitrogen (99.999% Alphagaz 1™ from Air Liquide AB) was used as the sample gas in the analysis chamber unless explicitly stated otherwise. Complementary tests are performed with water vapor as the sample gas. Water vapor from heated water in a test tube is introduced in the analysis chamber through a leak valve. Prior to the measurements dissolved gases in the test tube water are eliminated by repeated freeze-pump-thaw cycles. To keep sample contamination at a minimum the metal sample surfaces are mechanically etched prior to insertion into vacuum. In the experiments the sample surface is always oriented normal to the axis of the straight retarding analyzer section. The dye-sensitized solar cell sample consisting of a mesoscopic TiO₂ photoelectrode sensitized with a Ru-based dye molecule was prepared in a similar way as described in [11,12]. The sample was measured in vacuum and in a 2 mbar H₂O atmosphere.

A 0.8 mm diameter front cone is used throughout the measurement series and, if not explicitly stated otherwise, the sample surface is located at a distance of one front cone diameter from the front cone (i.e. 0.8 mm). At this distance the sample surface is in the entrance focal point of the analyzer, and furthermore the true pressure at the sample surface is approximately equal (less than 10% difference) to the measured pressure in the rest of the analysis chamber [13]. For all metal samples, spectra were acquired with an energy step size of 0.05 eV (0.54 eV for pass energy 300 eV) and a dwell time of 1 s. The Ag, Au, and Cu regions were recorded with windows of 13 eV, 10 eV, and 13 eV, respectively. The full width half maximum (FWHM) and the peak intensities, expressed as the area under the peak, are evaluated by fitting the spectral line with a Voigt function using a Shirley background.

At no time during the experiments, discharges or arcing was observed despite the fact that these types of problems are quite common in the field of HPXPS. Discharges are more likely to occur in HPXPS than XPS due to the higher pressures in the former, and the risk is especially high in the Corona discharge region. Discharges will show up as spikes in the recorded data and they might cause malfunction or even destruction of the equipment since induced currents stress the high voltage electronics of the analyzer. In the present system, red LED's on the high voltage cards is able to indicate discharges or other instabilities, but no such conditions have been observed.

3. Results and discussion

3.1. Effects on line shape for the different lens modes

Fig. 1 displays a set of normalized Ag 3d spectra for the standard mode of operation and the swift acceleration mode for a set of different slits using a pass energy of 200 eV. For small slit sizes, e.g. 0.3 mm (Fig. 1a) to fairly large slit sizes of i.e. 1.5 mm (Fig. 1b) the swift acceleration mode and standard mode peak line profiles are almost identical. For larger slits the peak profiles shows an asymmetry, with a tail on the low-kinetic-energy side (high binding energy side), as seen in Fig. 1c where the largest slit (4.0 mm) of the analyzer is used. It is also worth noting that the spectral line shape and position of the asymmetric Ag 3d_{5/2} peak (recorded using the 4.0 mm slit) does not change with sample distance. That is, up to slit widths of 1.5 mm (the smallest straight slit) the swift-acceleration lens table can be used without precautions regarding the asymmetry, which is further supported by measurements using pass

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