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## Auger Photoelectron Coincidence Spectroscopy of Molecules Adsorbed on a Gold Wire Surface.

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**Abstract :** In this paper, we present the results on Auger/Photoelectron Coincidence Spectroscopy (APECS) of molecules - propanethiol and Bovine Serum Albumin (BSA)- deposited on a gold wire surface, using a magnetic bottle electron time-of-flight spectrometer. Although this study is preliminary and conducted under low vacuum ( $\sim 10^{-7}$  mbar) conditions in comparison to surface science standards, it demonstrates the APECS method's high efficiency in probing complex molecules. We also establish its versatility and potential for easy extension to other various systems.

### **Introduction:**

Auger electron spectroscopy (AES) and X-ray photoelectron spectroscopy (XPS) are widely employed for material characterization due to the specific inner-shell ionization energies of different chemical elements within a given environment. The significance of this technique was recognized with the Nobel Prize in 1981, awarded to Kai Siegbahn for his work on ESCA (Electron Spectroscopy for Chemical Analysis) [1]. Moreover, it has been long acknowledged [2, 3] that detecting Auger electrons in coincidence with associated photoelectrons - known as Auger Photoelectron Coincidence Spectroscopy (APECS) - can significantly enhance the interpretation of Auger spectra, which may otherwise be complex or/and congested. Although initial APECS results were obtained in the late 1970s [4], the experiments utilized two separate electron analyzers with limited solid angle detection ( $\sim 1\%$ ) and resulted in low coincidence rates with a limited energy resolution. In our present experiment, we have used a magnetic bottle electron spectrometer (MB-TOF) with an acceptance angle close to  $4\pi$  for all electron energies (up to 200 eV) simultaneously. This setup allowed us to investigate molecules deposited on gold wire surfaces. A prior study, using a similar MB-TOF spectrometer, was published by Hikosaka *et al.* [5], where they examined the inner-shell photoionization of condensed water (ice) on a copper wire. In the present study, we explored more complex molecules: propanethiol and Bovine Serum Albumin (BSA), which can be easily deposited on gold wires. Although we did not meet ultra-high vacuum conditions, auspicious results have been obtained.

### **Experimental set-up:**

The experimental setup has been previously described in detail [6, 7]. It relies on a 2 m long horizontal magnetic bottle electron spectrometer. A cylindro-conical ( $\theta = 80^\circ$ ) shaped permanent magnet (SmCo, diameter: 24mm, length: 40 mm) produces a strong magnetic field ( $B \sim 0.8$  T at the contact and  $B \sim 0.4$  T at 2 mm in the interaction region) that decreases rapidly ( $\partial B/\partial z \sim 0.1$  T/mm where  $z$  is the distance from the tip of the magnet along the axis of the flight tube). This configuration creates a magnetic mirror, reflecting all the outgoing electrons produced in the interaction region toward a time-of-flight tube. The electron trajectories are parallelized over a short distance ( $\sim$ cm) by the B-field gradient [8], and

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subsequently guided by the homogeneous field ( $\sim 1$  mT) of a solenoid wound around the TOF tube towards a microchannel plate (MCP) detector. The electron time-of-flight  $t$  is measured relative to the ionizing photon pulse using a time-to-digital converter (TDC) with a resolution of 275 ps, and is then converted to velocity and kinetic energy:  $E_k = 1/2m_e(L/t)^2$  where  $L$  is the length of the flight tube. The typical energy resolution is  $\Delta E/E = 2\%$  and the absolute energy resolution can be improved by slowing down the electrons with a negative potential on the flight tube. We have been utilizing this setup for many years to study multiple ionization of atoms and molecules in the gas phase, the collection efficiency is close to the full  $4\pi$  solid angle and the MCP detection efficiency using funnelled MCP is more than 70%. For outgoing electrons from a surface, as it is the case for a gold wire, a maximum  $2\pi$  solid angle can be expected.

The photons are provided by the PLEIADES beamline at the SOLEIL French synchrotron. To measure the electron time-of-flight with the magnetic bottle spectrometer, it is mandatory to use the single bunch filling mode of the synchrotron with a period of  $T = 1.18 \mu\text{s}$ . Additionally, an asynchronous mechanical chopper [9] is used, which is based on a modified turbomolecular pump rotating at 48000 r.p.m. and equipped with 100 equidistant slits (160  $\mu\text{m}$  wide) in a 90 mm diameter cylinder. This chopper selects one bunch out of every ten at a frequency of 80 kHz. The photon pulse that passes through the chopper is detected downstream by a channeltron and is utilized to gate the ring-clock signal. This ring-clock signal serves as the time reference for the electrons and is sent to one STOP channel of the TDC (referred to as CH1). The START signal for the TDC is provided by the arrival of the first electron. The same electron signal is sent to another (multi-)STOP channel (referred to as CH2), and the time-of-flight for all the electrons is obtained by calculating the difference between the time in CH1 and CH2, with a time shift determined after time-to-energy calibration using known electron energies (see Methods section below). The time window is opened for 12  $\mu\text{s}$  before another START signal can trigger a new process. To minimize the occurrence of random coincidences, it is essential to keep the electron count rate well below the photon repetition rate of 80 kHz. In gas phase studies, the target density can be lowered (as long as it doesn't reach the base vacuum), and the slits of the monochromator can be closed to reduce the photon flux. However, when using a solid target, the only feasible method to reduce the photon flux is by closing the slits and by detuning the undulator. Hence, an electron count rate of 2 kHz was chosen to effectively limit random coincidences in this experiment.

The target is a 250  $\mu\text{m}$  diameter gold wire mounted on a connector (Fig.1) that is plugged on a holder consisting in two 6 mm diameter copper tubes mounted on an electrical CF40 feedthrough. This allows to polarize the target and may also allow for outgassing of the wire through resistive heating.

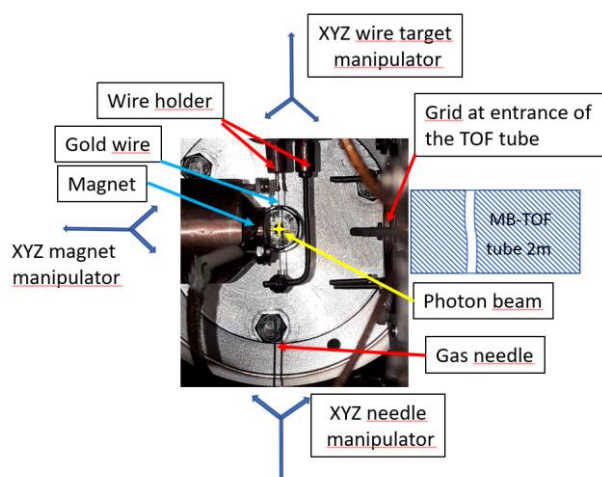


Fig 1: View of the wire inserted in the chamber close to the permanent magnet and aligned with the photon beam. Three XYZ manipulators allow to align the magnet, the wire and the gas needle with respect to the photon beam and the MB-TOF tube axis.

A 25 cm Z translation enables us to insert the wire inside the chamber. It can be extracted and isolated from the main chamber by a CF100 valve, allowing an easy exchange of the wire holder. The Z translation system is positioned on top of the chamber and is accompanied by an XY 25 mm translation, which enables us to position precisely the wire within the photon beam and along the axis of the MB-TOF spectrometer. This arrangement ensures accurate alignment for optimal experimental conditions. Below the chamber, we have retained the system for gas injection through a needle. This system allows for the introduction of gases into the experimental setup, for calibration purpose.

The size of the photon beam at the focal point is approximately (H x V): 250  $\mu\text{m}$  X 150  $\mu\text{m}$ , matching the diameter of the wire. Aligning the wire within the photon beam is a straightforward task and can be monitored using a YAG fluorescent screen or a photodiode that can be inserted behind the interaction region at the end of the chamber. However, the alignment of the wire with the axis of the magnetic bottle and with the magnet requires more care. The position of the magnet can also be adjusted using an XYZ manipulator, and its precise positioning is crucial. When using a gaseous target, we often noticed oscillations in the transmission depending on electron velocity, corresponding to the cyclotron frequency in the solenoid. To minimize the amplitude of these oscillations, it was necessary to adjust the position of the magnet. In this configuration, the interaction volume occurs at the intersection between the photon beam and the effusive gas target, with the needle placed  $\sim 2$  mm away from the photon beam to avoid any electron from the needle. The interaction region forms approximately a 2 mm long cylinder along the photon beam, visible on the phosphor screen that collects the electron signal from the MCPs. The typical magnification of the source volume onto the MCP detector is  $\sim 20$  and corresponds to the square root of the ratio between  $B_i$  and  $B_f$  (where  $B_i$  is 0.4 T at the source point and  $B_f$  is 1 mT in the solenoid).

When using the wire target, the alignment of the wire and the magnet with respect to the axis of the TOF tube became more critical. After optimizing the position of both the wire and the magnet to smooth the oscillations in transmission, we found the magnet to be off-center by a few mm with respect to the TOF axis. Several hypotheses could explain this fact. Ideally, the system should possess cylindrical symmetry around the TOF axis and be perfectly centred. However, the presence of a transverse B-field can break this symmetry. This transverse B-field may result from a parasitic external field or from a tilt of the permanent magnet (or inhomogeneous magnetization). Due to the parallelization of trajectories occurring over a short distance and the rapid decrease of the B-field from the permanent magnet, a tilt of the magnet might inject the electrons into the solenoid at an angle, leading to an off-axis cyclotron motion within the solenoid and causing these oscillations. By adjusting the magnet and target positions, we can re-align the tilted trajectories onto the TOF axis, and this alignment is especially critical for the wire target, requiring a precision of about 50  $\mu\text{m}$ . In contrast, with the gas target, some averaging in the target volume reduces the impact of this effect, making the alignment easier.

## **II. Methods**

After unsuccessful attempts with acetonitrile (injected through the gas needle in the chamber) on platinum wires, we decided to switch to gold wires and 1-propanethiol ( $\text{CH}_3\text{CH}_2\text{CH}_2\text{SH}$ ). The target was prepared in our laboratory by immersing the gold wire on its holder in liquid 1-propanethiol 99% (CAS Number: 107-03-9 from Sigma-Aldrich), overnight. It is well-known that thiol molecules readily adsorb on gold surfaces as monolayers [10, 11].

As our primary objective was to demonstrate the feasibility of APECS on complex molecules on surfaces, we have conducted the experiments on low vacuum conditions with respect to ultrahigh vacuum required for surface science experiments. The quality of the vacuum was ensured by Viton gaskets and the ultimate vacuum was  $\sim 1 \times 10^{-7}$  hPa.

To convert time to energy, we measured Ar (2p) photoelectrons time-of-flight at different known photon energies. We introduced the Argon into the chamber through the needle opposite the wire holder. The

needle, like the gold wire, was grounded. However, it's important to consider that contact potentials and work function due to different metals can modify the electron kinetic energy. If an insulating layer is created on the surface, ionization by the synchrotron light can also induce a positive potential on the wire. Consequently, the absolute electron energy for electrons from the surface can be shifted with respect to the calibration performed with Argon gas. A strong signal due to low energy electrons [0- 20 eV] is observed that results from secondary electron processes. To suppress this signal, a 30 V retardation potential has been applied on the TOF tube between two parallel high transparency (90%) grids at 0 V and -30V at the tube entrance (see Fig. 1).

We have studied the photoionisation of 1-propanethiol  $\sim 50$  eV above the S (2p) ionisation threshold ( $h\nu=222$  eV) and  $\sim 50$  eV above the C (1s) threshold ( $h\nu=340$  eV) with 30 V retardation on the TOF tube. In Fig. 2 the S (2p) photoelectrons are clearly identified and appear in coincidence with electrons from 0 to 120 eV in kinetic energy. A random coincidence 2D map has been generated by multiplying the electron spectrum by itself and normalizing this product in a region where no coincidences are expected since electrons are due to valence single ionization. The electrons detected in coincidence with S 2p photoelectrons near 110-120 eV correspond to unscattered Auger electrons. We also detect electrons of lower energy, down to 0 eV, in coincidence with S 2p photoelectrons: they correspond to inelastically scattered Auger electrons.

The Au  $4f_{5/2,7/2}$  photoelectron lines are visible in the photoelectron spectrum, however they give only random coincidences and thus it was not possible to observe the corresponding Auger electrons [12] around 70-75 eV in coincidence with the photoelectron lines. Unfortunately, the electron signal had also a rebound at 50 ns that generates false coincidences (also visible in Fig.3 in ref [5]) that could mask the possible coincidence signal from the gold wire. In addition, we observe an additional photoelectron peak at 83 eV that, surprisingly, increased regularly in time with respect to S and Au photoelectron peaks and indicates the deposit of a chemical element on the wire. The photoelectron energy gives an ionization threshold around  $\sim 100$  eV and true coincidence with Auger electrons up to 80 eV. One possibility is that Rb atoms that were previously studied in this chamber desorb from the chamber to stick on the gold wire. Since the experiments were carried out with vacuum level in the  $10^{-7}$  hPa range the deposition of the residual gas on the wires is inevitable. Even in ultrahigh vacuum condition of the synchrotron beamlines the carbon pollution of the optics is a serious problem and may result in a severe flux drop around the C 1s edge [13]. Nevertheless, in these conditions it is clearly evidenced that it is possible to observe APECS for propanethiol above the S 2p edge in a reasonable time (1h with electron count rates of 2 kHz). It would certainly be possible to accept higher electron count rates up to 20 kHz as far as subtraction of random coincidences remains possible.

The coincident S 2p Auger spectrum is obtained by projection of a 5 eV wide energy band around the S2p photoelectron peak and by subtracting the same signal from an adjacent band with no photoelectron peak. In these conditions the false signal due to the crossing with the Rb vertical band disappears. We plot the Auger spectrum on the same figure with the kinetic energy corrected for the 30V deceleration.

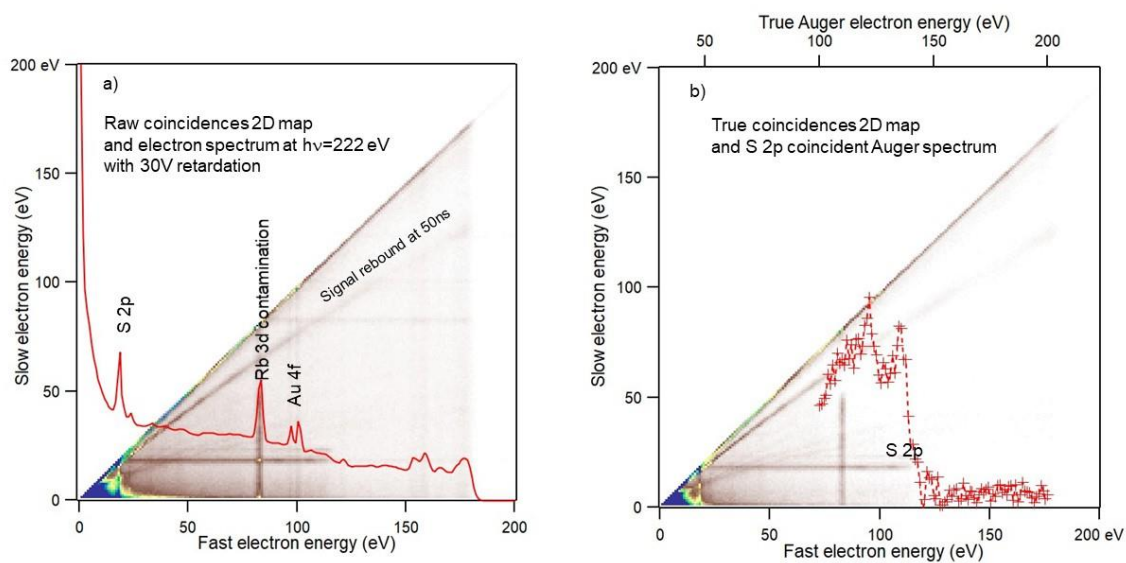


Fig. 2: Coincident electron spectrum at  $h\nu = 222$  eV about 50 eV above the S(2p) ionisation thresholds with 30 V retardation. a) raw coincidence 2D map and electron spectrum. b) true coincidence 2D map after subtraction of random coincidences deduced from the electron spectrum. The S2p coincident Auger spectra is shown with the good energy scale.

For a photon energy ( $h\nu = 340$  eV),  $\sim 50$  eV above the C 1s threshold the obtained spectra is shown in Fig. 3. We identify the C 1s photoelectron but the strongest signal is due to carbon contamination of the surface. However, a smaller peak at lower kinetic energy is certainly due to one of the C atoms of the 1-propanethiol molecule but it cannot be excluded that other peaks are masked by the prominent C 1s contamination peak.

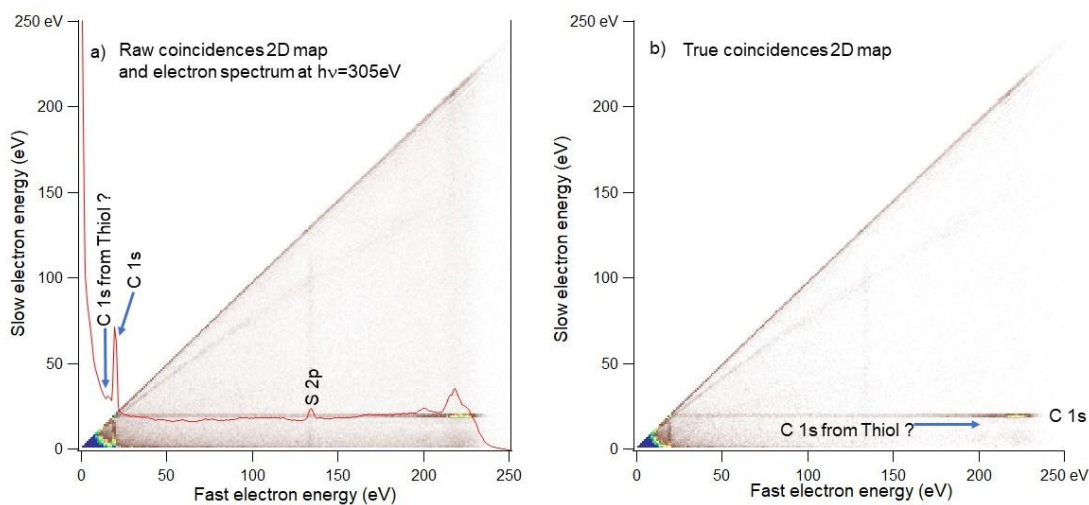


Fig. 3: Coincident electron spectrum at  $h\nu=340$  eV about 50 eV above the C(1s) ionisation thresholds with 30V retardation. a) raw coincidence 2D map and electron spectrum. b) true coincidence 2D map after subtraction of random coincidences deduced from the electron spectrum.

To confirm the possibility to measure APECS with C 1s photoelectrons we have performed another experiment on a macromolecule: BSA (Bovine Serum Albumin) protein. This protein was already studied by X-ray electron spectroscopy, by a some of the co-authors, either solvated, in an under vacuum liquid microjet, or in its solid state deposited on a copper substrate [14]. BSA was extensively studied by XPS, deposited on various kinds of substrates (see table S2 in appendix of Ref 14), and in liquid droplet by near ambient electron spectrometry technique [15]. By soaking a gold wire in a BSA solution (Lyophilized Bovine Serum Albumin from Sigma-aldrich, A0281, dissolved at 36 g/L and dialyzed in pure water, see materials and methods section of reference 14 for more details), it is possible to attach the protein on the surface. While in a liquid jet there are no problem with carbon contamination, it becomes a problem with a surface when the vacuum is not good enough. In a recent experiment using a magnetic bottle dedicated to liquid jet studies it was possible to study sodium benzoate solutions [16]. However, we had not the possibility to study BSA in a liquid jet with the MB-TOF to perform APECS. Our goal was here to see if it was possible to obtain complementary information from BSA deposited on gold wires.

A partial view of the coincidence 2D map is shown in Fig. 4 a) with the C1s photoelectron spectrum. In Fig.4 b), we compare the C1s photoelectron spectra for 1-propanethiol and BSA. The dominant C1s peak due to carbon contamination of the surface is very similar in both cases. At lower kinetic energy the spectra are clearly different: a difference attributed to C1s ionization of the molecules on the surface.

For BSA the energy spacing of 1.25 eV between the two peaks corresponds well with the previous electron spectroscopic studies. The overall shape of the C1s XPS spectrum of BSA is recognizable, with a higher intensity peak that regroups the contributions of carbon linked only to carbon and hydrogen and of carbon singly bounded to nitrogen or oxygen. At lower kinetic energy, a smaller intensity peak produced by carbonyl and/or amide carbon and carboxyl carbon is visible. The intensity ratio between the peak is impacted by the background tail of low energy electrons. Although the statistics is poor it

should be possible to extract the specific Auger decay for the two different peaks in BSA as it was performed for sodium benzoate in liquid jet [15].

With these two examples, we have proved that APECS can be performed for complex molecules deposited on wires (most probably as monolayers) as it was also the case for H<sub>2</sub>O ice by Hikosaka *et al.* [5].

Recently, APECS was also performed on Ag MNN Auger lines and for molecular O<sub>2</sub> adsorbed on Ag(111) using two ArTOF (Angle-resolved Time-Of-Flight) spectrometers at BESSY synchrotron [17]. The two analyzers accept electrons on  $\pm 14^\circ$  and  $\pm 24^\circ$  that is 1.5% and 4% of the full solid angle and the expected coincidence efficiency of  $6 \times 10^{-4}$  is much lower than what can be achieved with a MB-TOF. The very high collection efficiency of the MB-TOF allows high coincidence count rates even if the electrons emitted from the surface are only in a  $2\pi$  solid angle. Indeed, for a cylindrical wire target (as for a liquid microjet) only one side of the target is exposed to the photon beam and the electrons are reflected by the magnetic mirror towards the TOF tube. They have to travel far enough compared to the size of the wire to be able to turn around it. To improve the resolution and to keep good conditions for coincidence measurements it is possible to decelerate the electron before they enter in the flight tube. This has a first advantage of improving the resolution for fast electrons and also to remove the slow electrons (specially below 10 eV that are due to collisions on the surface) from the spectra. It's enough to select the photon energy in the good energy range to have the photoelectron faster or slower than the Auger ones. This was done by us on C<sub>6</sub>H<sub>6</sub> in ref [18] and could also be performed for molecules on surfaces.

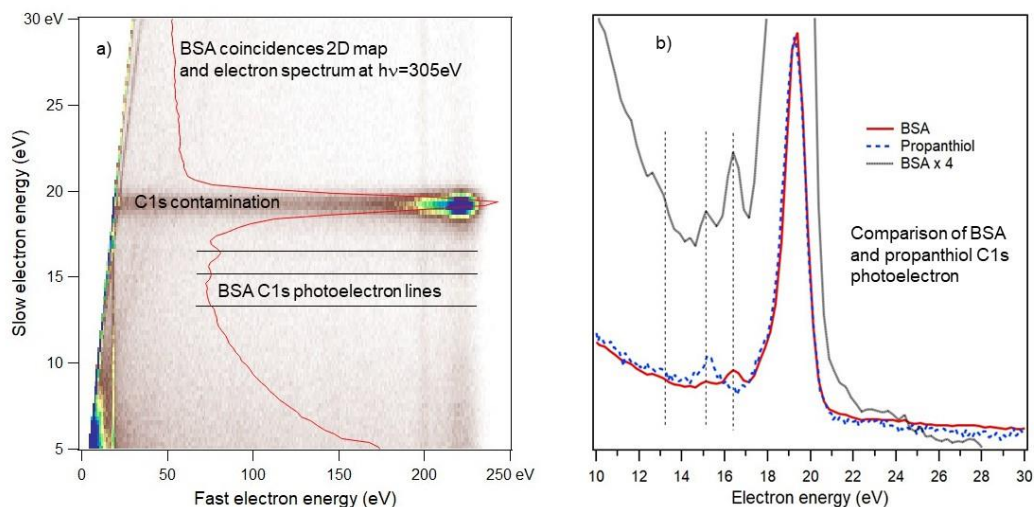


Fig. 4: a) Coincident electron spectrum at  $h\nu=340$  eV about 50 eV above the C(1s) ionisation thresholds with 30 V retardation for BSA (Bovine Serum Albumin). b) comparison of the C1s photoelectron spectra for BSA and 1-propanethiol .

### **Conclusions and perspectives:**



We have made a proof of principle of APECS with a MBTOF spectrometer for molecules deposited on gold surfaces. Only one previous study with a similar set-up was published earlier [5] and, here, we have shown that it will be possible to perform APECS with high efficiency on complex molecular systems. The actual limitations come from carbon contamination of the surfaces due to limited vacuum conditions in our experiment. This limitation can be easily resolved by working in ultra-high vacuum conditions and in a suitable sample environment (sample preparation and cleaning conditions). The energy resolution ( $\Delta E/E=2\%$ ) of the MB-TOF could be improved by decelerating the electrons [17] to obtain filtered Auger spectra with a resolution comparable to commonly used  $180^\circ$  hemispherical deflection analyzers (HDA  $180^\circ$ ). Another possible development could be to exploit the loss angle of the magnetic bottle that corresponds to electrons going towards the magnet that is about  $\pm 10^\circ$  and corresponds to  $\sim 1\%$  of  $4\pi$  solid angle while 99% of the electrons are reflected toward the magnetic bottle. Using a hollow magnet as in [19] it should be possible to analyse the electron going through the hole with a high-resolution analyser. The coincidence efficiency should be close to 1% because the second electron is always detected in the MB-TOF (with the only limit of MCP detection efficiency). In a very preliminary experiment, it has been possible to detect electrons going through the magnet hole with the ion TOF spectrometer [19] by changing the MCP polarities to detect electrons rather than ions. However, no true coincidences could be observed because the regions seen by the two spectrometers were probably different if the magnet was tilted. Although technical developments will be necessary to make such experiment more straightforward, the MB-TOF guarantees a very high detection efficiency for all energies simultaneously and remains the best option for high coincidence count rate. It is also the only system that allows the detection of more than 2 electrons in coincidence (that remains possible with two analyzers [17]). When three or more electrons are detected in coincidence, the complete story of the ionization and decay processes becomes available which provides unprecedented results for surface studies as it was possible for isolated species.

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