High resolution photoelectron spectroscopy of solids

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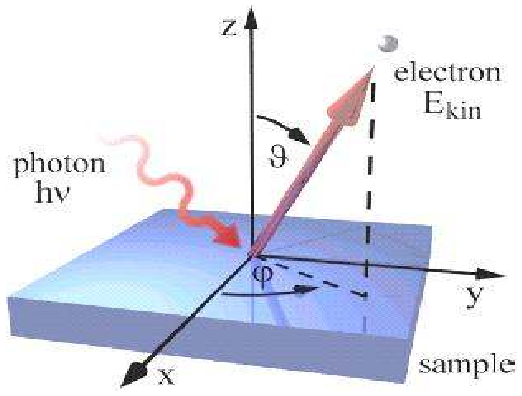
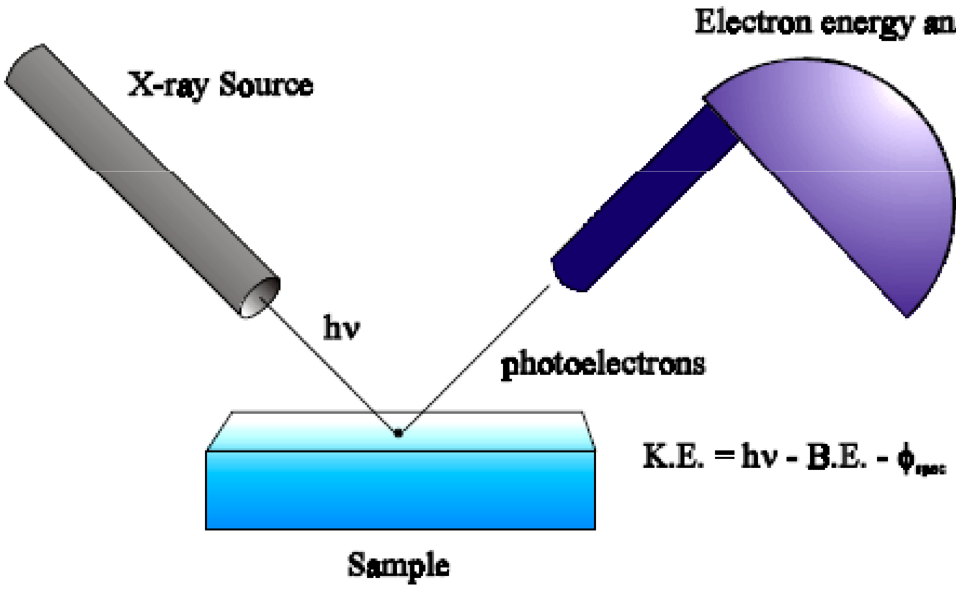
Photoelectron spectroscopy



- based on ‘photoelectric effect’
  - first observed by Heinrich Hertz (1887)
  - theoretical explanation by Albert Einstein (1905)



Photoemission intensity depends on

- photon energy
- energy of the emitted electrons
- direction of electron emission
- temperature
- area (for inhomogeneous samples)

Photoelectrons are analyzed based on

- Kinetic energy
- Direction of emission
- Orientation of spin

Energy resolution in PES

- **Low energy resolution - provides qualitative and quantitative information of elements present**
- **High energy resolution - information on the chemical state and bonding of those elements**

Overall energy, $\Delta E = (\Delta E_x^2 + \Delta E_A^2 + \Delta E_2^2)^{1/2}$

ΔE_x is the FWHM of the X-ray line,
ΔE_A is the width of the energy analyser window (adjusted)
ΔE_2 is the natural line width of the orbital of the atom (fixed)

Resolution is obtained by measuring the width of a narrow core line or the width of the Fermi edge of a noble metal at low temperatures. Generally the 4f line of metallic Au or the valence p level in a rare gas is measured.

Need for High resolution PES of solids:

- ❖ The electronic structures of the bulk of a solid can be different from those in the surface region, due to surface reconstruction or relaxation.

- ❖ Band structure measurements or Fermi surface maps of solids require an energy resolution of about 50 meV.

- ❖ To study the many-body effects in photoemission spectra

- ❖ A quantitative study of fine spectral features of solids near fermi level is directly related to low energy excitations in the material, this requires very high resolution measurements

- ❖ Investigations on some physical properties of solids, such as superconductivity and magnetism require high absolute energy resolution

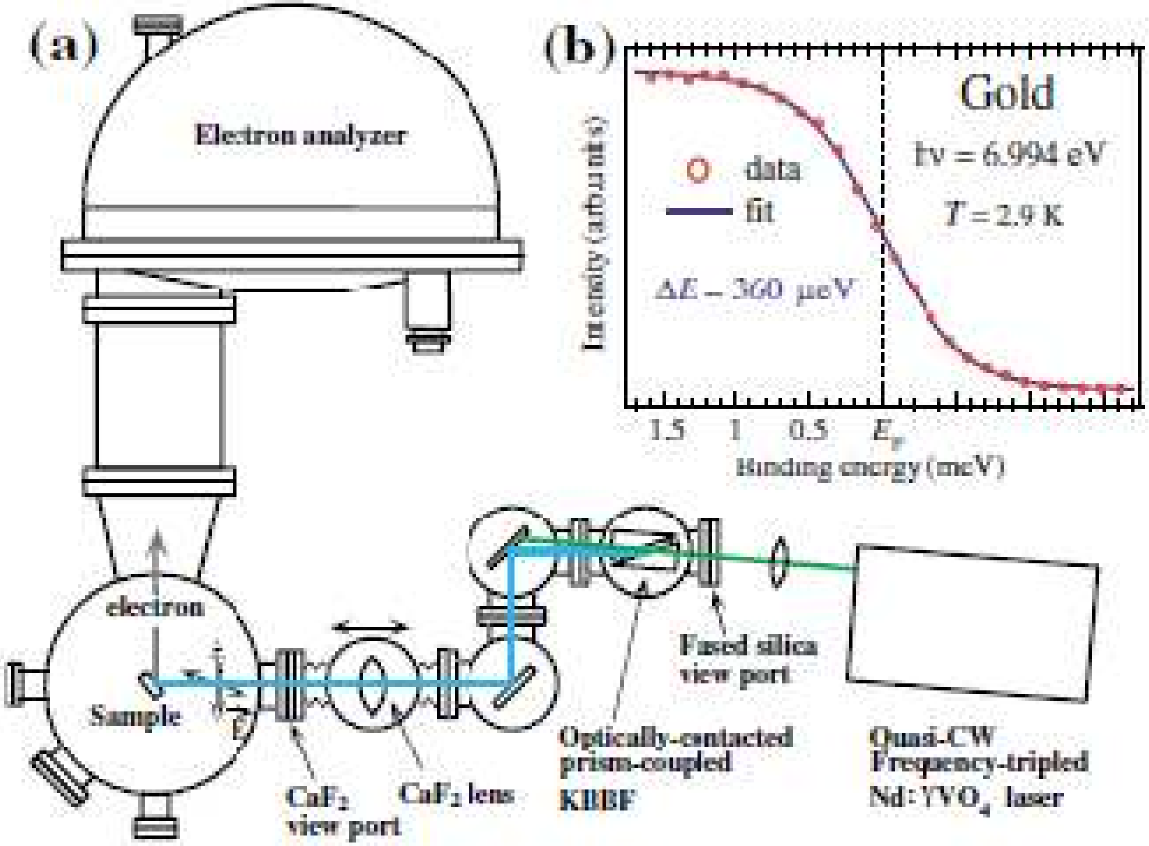
- ❖ To resolve the closely lying vibrational energy states.

Applications of High resolution PES of solids

Evidence for gap anisotropy in an f-electron superconductor ($CeRu_2$)

- Due to the extremely small energy scales of the superconducting gaps of f- electron superconductors, very high resolution photoelectron spectroscopy is needed.

- Laser PES with a resolution of 1 meV is used.



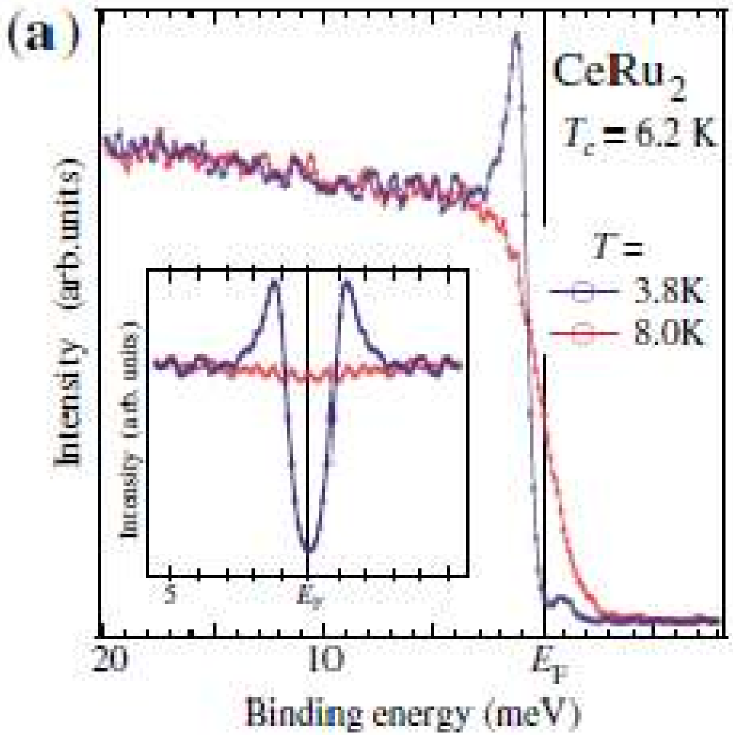
Ultra high resolution measurement of gold Fermi edge spectrum at 2.9 K

- Here, vacuum UV laser ($NdYVO_3$, 6.994 eV) with sub-meV resolution is used for measuring the bulk superconducting gap of $CeRu_2$.

- A high precision hemispherical analyzer (GAMMADATA SCIENTA R-4000) is combined with a quasi-continuous laser system for achieving high resolution.

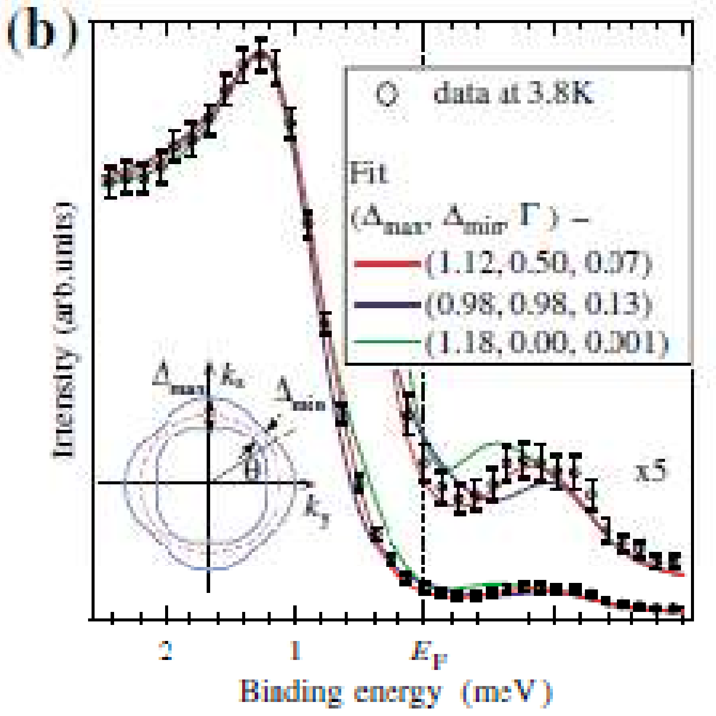
Phys. Rev. Lett. 2005, *94*, 057001

Temperature dependent spectra near E_f. Inset shows the symmetrised spectra.



The spectrum at 8 K has a Fermi edge while, that at 3.8 K shows a sharp peak at 1.35 meV with a leading-edge shift to higher biding energy, which indicates the opening of the SC gap. The small peak above Ef of the SC spectrum corresponds to thermally excited electrons across the gap. The formation of the gap across Tc is more clearly seen in the inset

Normalized SC DOS at 3.8 K.



Normalized SC spectrum, compared with three calculated spectra with (Δmax, Δmin, Γ) = (0.98, 0.98, 0.13, isotropic case), (1.12, 0.50, 0.90, anisotropic case), and (1.18, 0.00, 0.001, maximum anisotropy) in units of meV

Phys. Rev. Lett. **2005**, *94*, 057001

- Success in probing the bulk superconducting electronic states of $CeRu_2$ opens up important opportunities in solid state physics.

- This technique can be applied to any other material having differing surface and bulk electronic states.

- In conclusion, ultra high resolution PES using a laser as a photon source has been proven to be useful for the measurement of bulk SC gap of an f-electron superconductor.

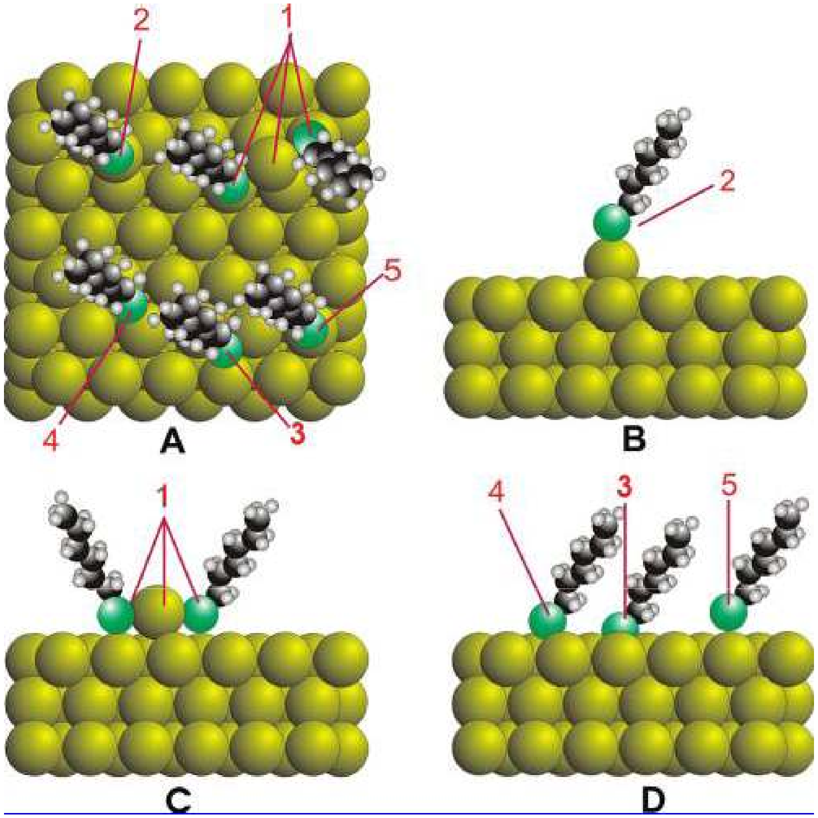
Phys. Rev. Lett. 2005, *94*, 057001

Analysis of the structure of interface in long chain alkanethiol SAMs

- The structure of the interface between a self-assembled monolayer (SAM) of alkanethiolates (AT) and the underlying Au(111) substrate was probed.

- SAMs of hexanethiolate and dodecanethiolate on Au(111) was studied using synchrotron-based high resolution X-ray photoelectron spectroscopy (HRXPS)

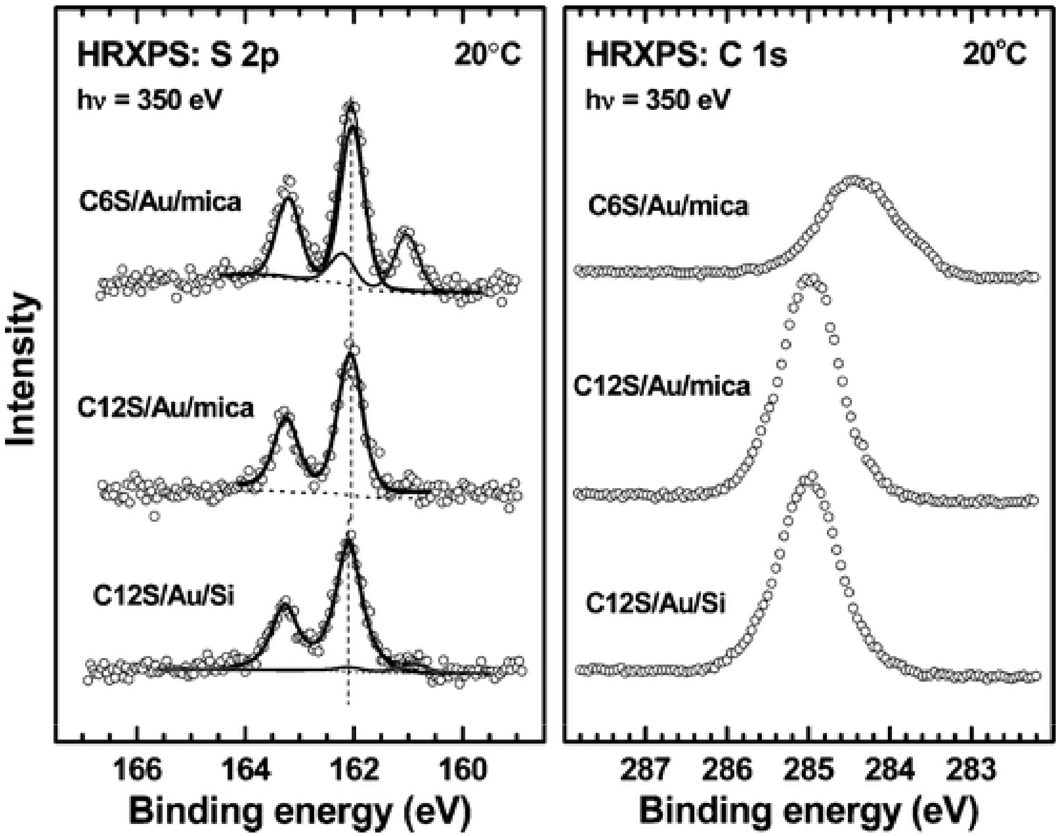
- The emphasis of the HRXPS characterization was put on the Au 4f emission of the substrate, which could be decomposed into the components related to the bulk and surface. The behavior of the surface component upon formation of hexanethiolate and dodecanethiolate SAMs was monitored in detail.



Schematic view of the proposed local binding geometries for the bonding of ATs to Au(111) substrate; A, top view; B-D, side views. (1) Au-adatom-dithiolate bonding configuration; (2) Au-adatom monothiolate bonding configuration; (3-5) adsorption into hollow, bridge, and atop site on the unreconstructed (111) surface, respectively.

J. Phys. Chem. C, Vol. 114, No. 15, 2010

HRXPS spectra of S 2p (left panel) and C 1s (right panel) for C6S/Au/mica, C12S/Au/mica and C12S/Au/ Si acquired at a photon energy of 350 eV. SAMs were prepared at room temperature.

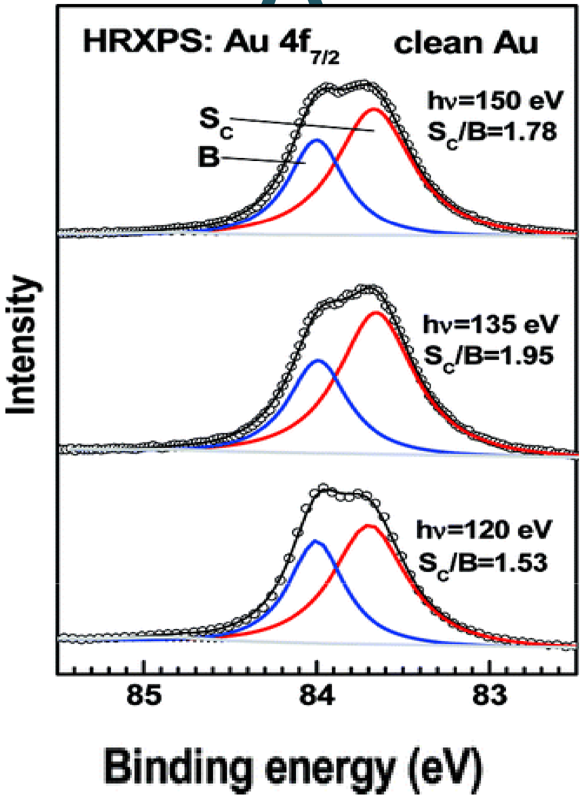


- For C12S the doublet is the only feature suggesting that all the thiolates are attached to the substrate in the same manner.
- For C6S there are actually two doublets. This possibly originates from another type of thiolate sulphur with different binding chemistry.
- Another feature in this spectra is smaller fwhm for films Au/mica (0.50 eV) than on Au/Si (0.58) and this is the manifestation of highly homogeneous AT film formation on Au/mica.

- For C1S spectra, both binding energy and fwhm for C12S and C6S are distinctly different.
- Two different BE (284.95 and 284.4 eV) for two different AT SAMs is due to screening of photoemission hole by the conduction electrons of substrate, this effect decreases with distance between the excitation site and the substrate.

Au 4f emission of the substrate upon formation of hexanethiolate and dodecanethiolate SAMs was monitored

A



B

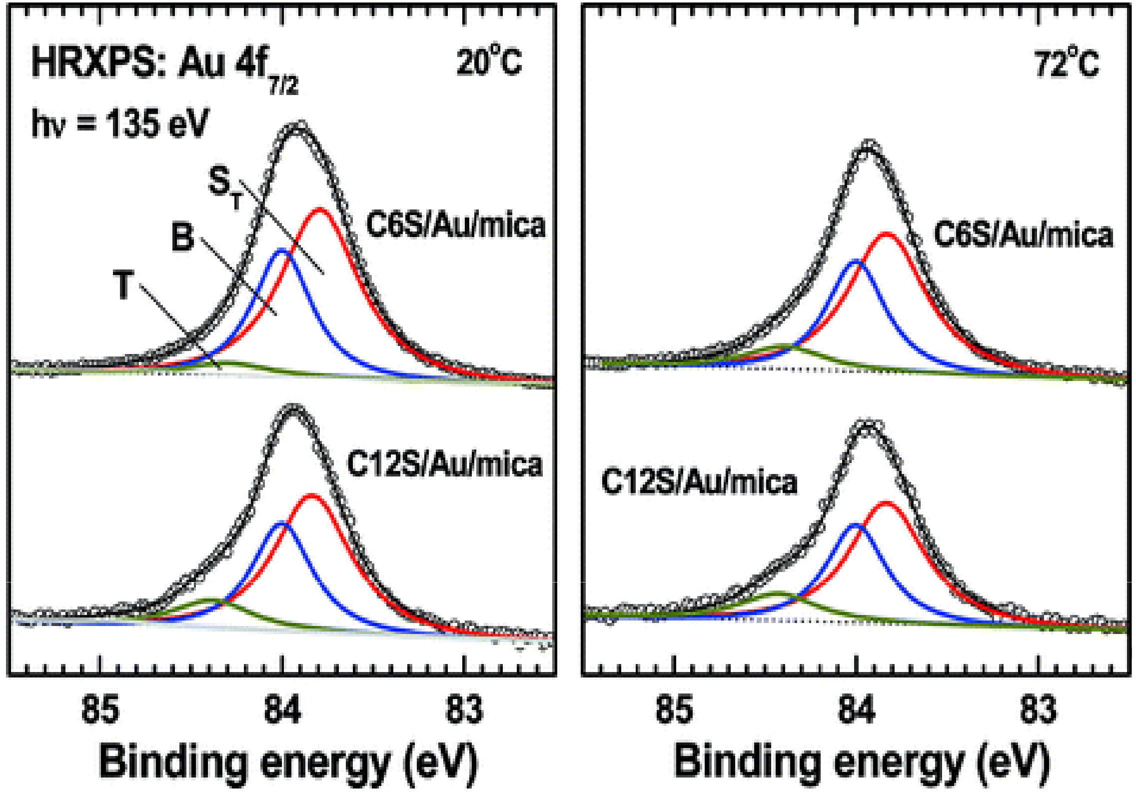


Fig. A Au $4f_{7/2}$ HRXPS spectra of clean Au surface acquired at photon energies 120, 135 and 150 eV. In each cases the spectra are decomposed into the bulk (B; blue trace) and surface (S_c; red trace).

Fig. B Au $4f_{7/2}$ HRXPS spectra of C6S/Au/mica and C12S/Au/mica prepared at 20^0C (left panel) and at 72^0C(right panel). The spectra are decomposed into the bulk (B; blue line), and two surface (S_T and T; red and green trace respectively)components.

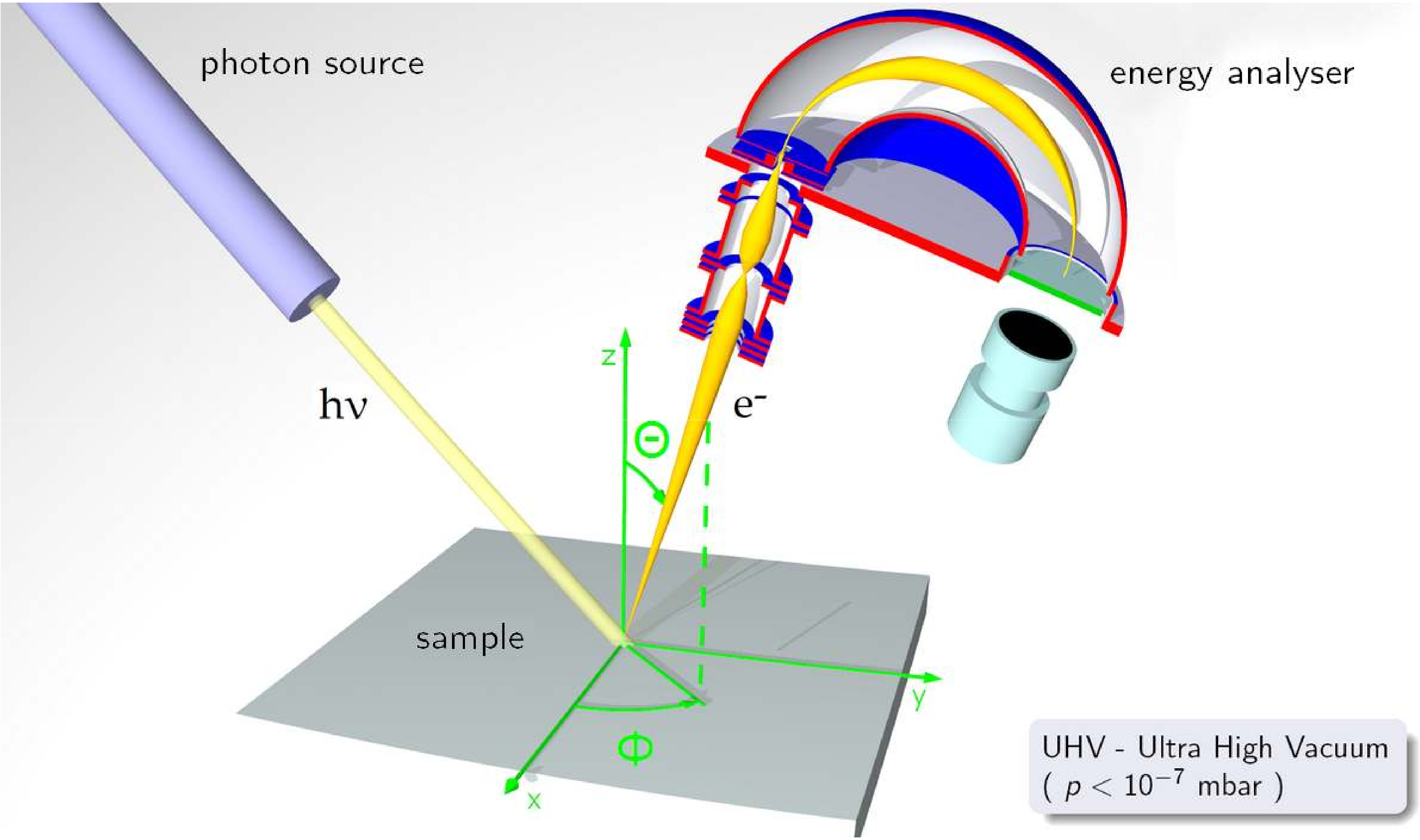
The most important difference is the difference in intensity between shifted surface component and the shoulder (S_T/T). This was found to be around 3 for C4S and C1S previously, but for C12S it has been found to be around 5 and for C6S a value of 15 has been obtained.

❖ The exact structure of the interface seems to be different for the short chain and long chain AT SAMs.

❖The S_T/T ratio which is considered to be the fingerprint for different adsorption models has been found to be quite different for the long chain thiols than the values reported for the short chain counterparts.

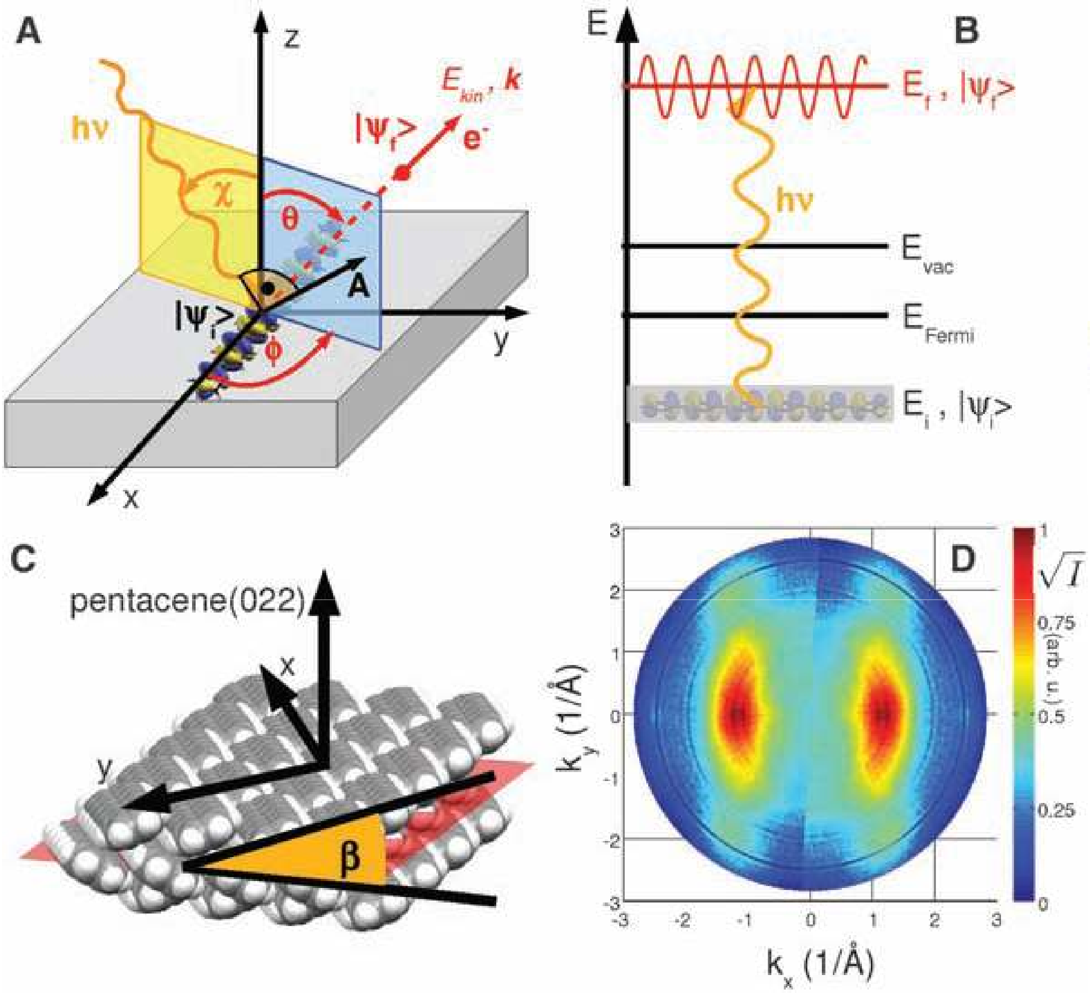
❖At this moment this is not very clear though whether this difference is significant and new model is required or not but the data provides strong evidence about the presence of adatoms at the interface between AT headgroups and Au(111) substrate.

An Experimental Setup of Angle-Resolved Photoemission Spectroscopy:



http://en.wikipedia.org/wiki/Angle_Resolved_Photoemission_Spectroscopy

Reconstruction of molecular orbital densities from photoemission data

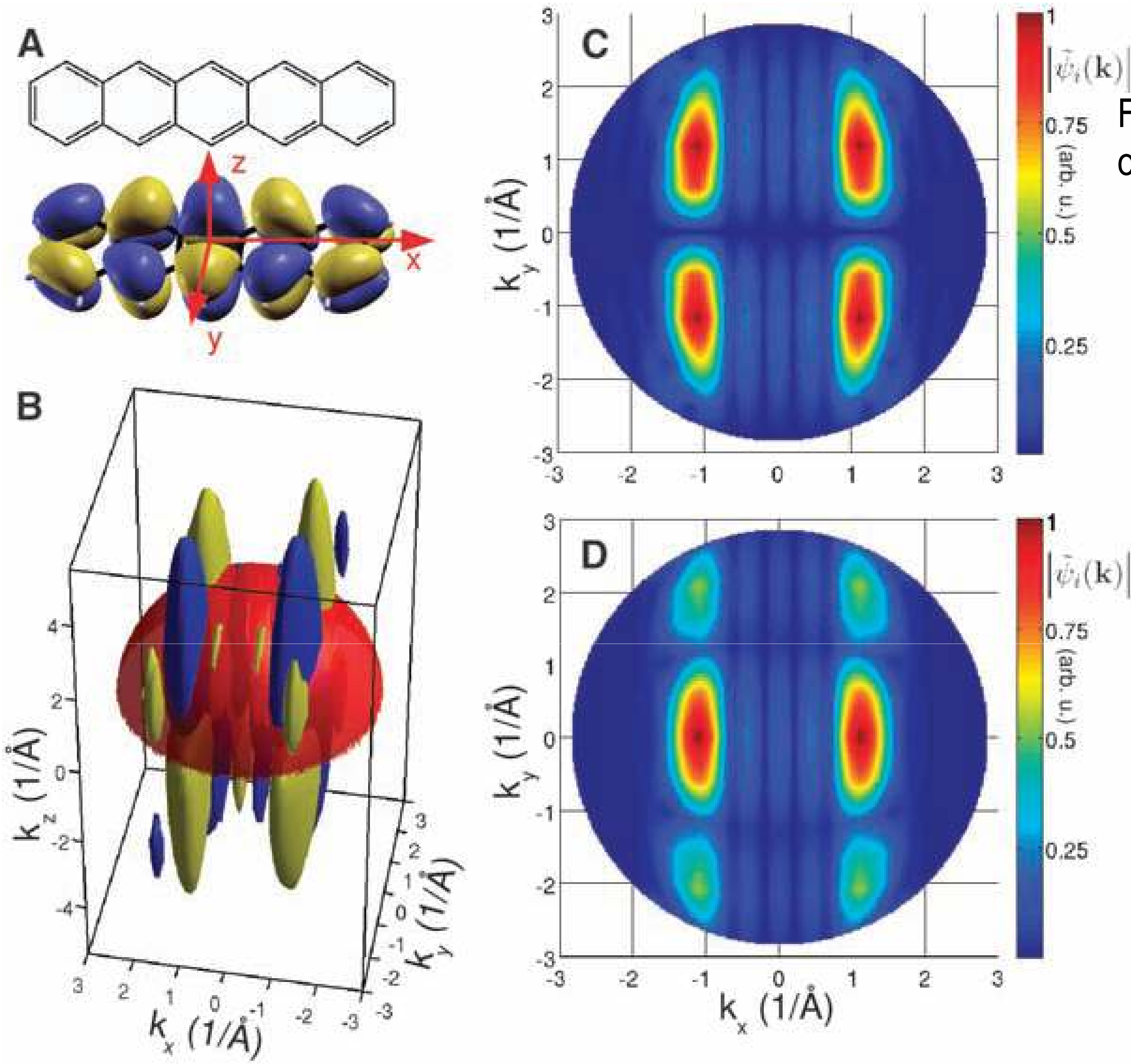


$$I(\theta,\phi;E_{\mathrm{kin}}) \propto \sum_i \left|\langle \psi_f(\theta,\phi;E_{\mathrm{kin}})|\mathbf{A}\cdot\mathbf{p}|\psi_i\rangle\right|^2 \times \delta(E_i+\Phi+E_{\mathrm{kin}}-\hbar\omega) \qquad (1)$$

$$|\tilde{\psi}_i(\mathbf{k})| \propto \frac{\sqrt{I_i(\theta,\phi)}}{|\mathbf{A}\cdot\mathbf{k}|} \qquad (2)$$

Momentum maps in angle-resolved PE experiments. (A) The incident photon with energy hn and vector potential A excites an electron from the initial state yi to the final state yf characterized by the kinetic energy Ekin and the momentum vector k. The polar and azimuthal angles q and f, respectively(B) Schematic energy-level diagram (C) Model of the pentacene multilayer arrangement on a Cu(110)-(2 × 1)O Surface (D) Square root of the PE intensity as a function of azimuthal and polar angle after conversion to momentum (azimuthal scan) at a constant binding energy of 1.3 eV (hv = 35 eV) corresponding to the pentacene HOMO.

***SCIENCE*, 2009, *326*, 702**



FT is calculated at constant binding energy on a hemisphere of radius

$$k = \sqrt{(2m/\hbar^2)E_{\text{kin}}}$$

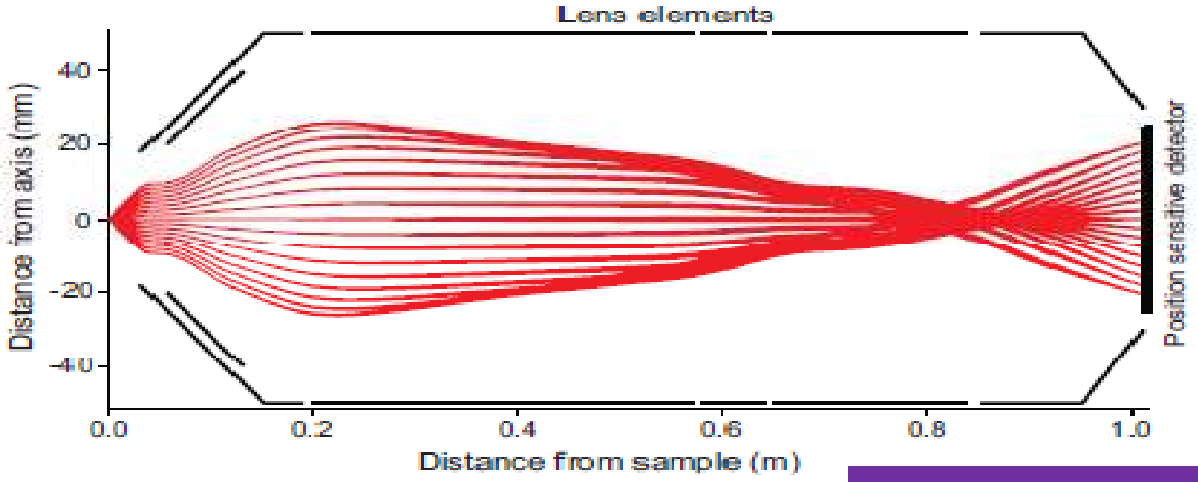
The value of the FT on that hemisphere for a kinetic energy of 29.8 eV .

Fig. 2. Calculation of the PE intensity from the FT of the molecular orbital. (A) Line drawing and HOMO of pentacene as obtained from a DFT calculation for an isolated molecule. (B) Three-dimensional FT of the HOMO as an isosurface plot; blue indicates negative and yellow, positive values, together with a hemisphere of radius $k = \sqrt{(2m/\hbar^2)E_{\text{kin}}}$ with a kinetic energy Ekin = 29.8 eV. (C) Absolute value of the HOMO FT on the hemisphere shown in (B). (D) Simulation of PE intensity of the pentacene multilayer film, taking into account molecules with tilt angles of β = +26° and β = −26° out of the xy plane

***SCIENCE*, 2009, *326*, 702**

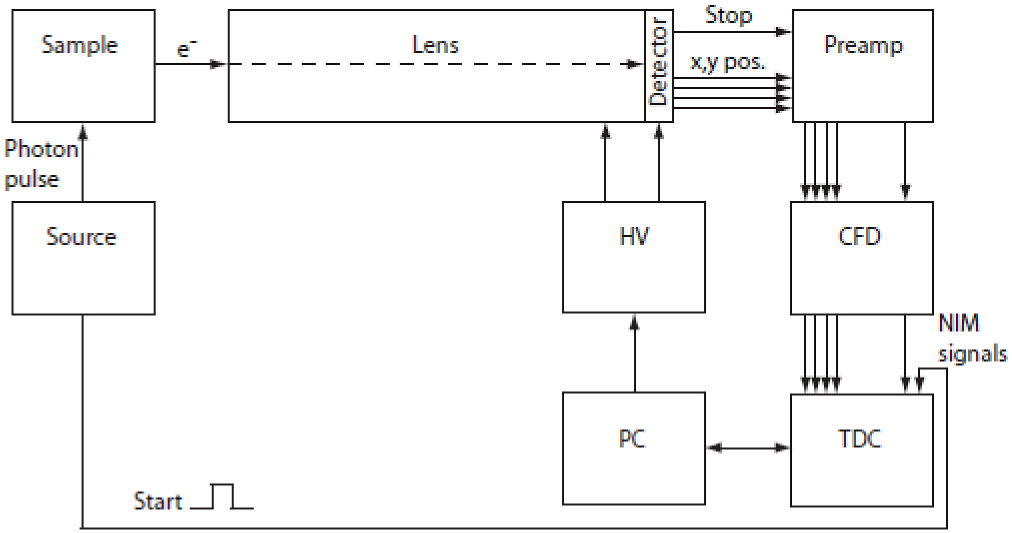
Latest instrumentation

Simulated trajectories through the ARTOF flight tube



Simulated trajectories through the ARTOF flight tube for 10 eV electrons and an angular magnification allowing polar angles approximately within the range ± 15° to reach the detector. The source diameter is 0.2 mm.

Signal-flow in the ARTOF 10k. HV indicates the high voltage supplies, PC is the computer, TDC is the Time to Digital Converter, and CFD is the Constant Fraction Discriminator.



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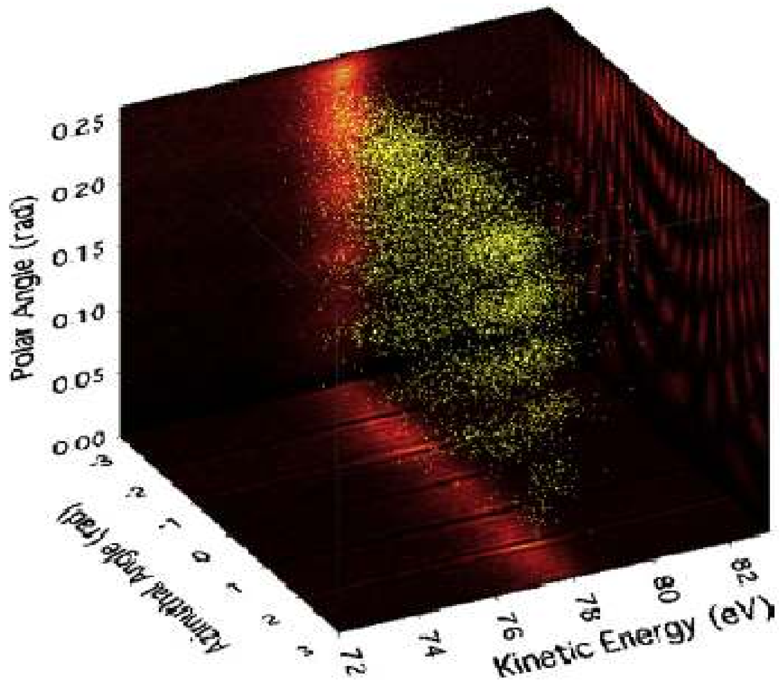
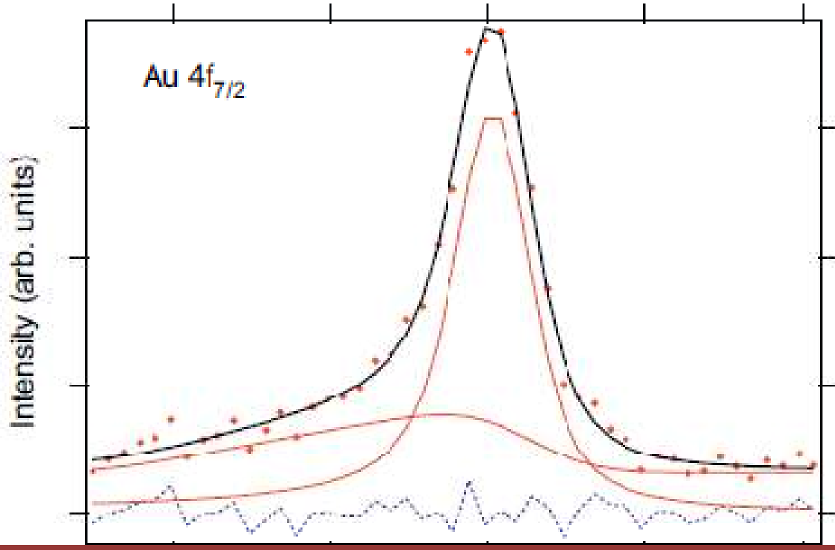


3D representation of the C1s peak after transformation to the (θ, φ, E_k) space

Synchrotron radiation 363 eV

Angle integrated spectrum of Au 4f $_{7/2}$ line

Synchrotron radiation 318eV



Angle integrated electron spectrum showing the Au $4f_{7/2}$ photoelectron line, recorded using the photon energy of 318 eV. The dots represent data points; the thick solid line is a fit of the data; the thin solid lines are the Doniach-Sunjic and Shirley profiles used in the fit, and the dashed line is the residue. A linear background has been subtracted.

THANK YOU