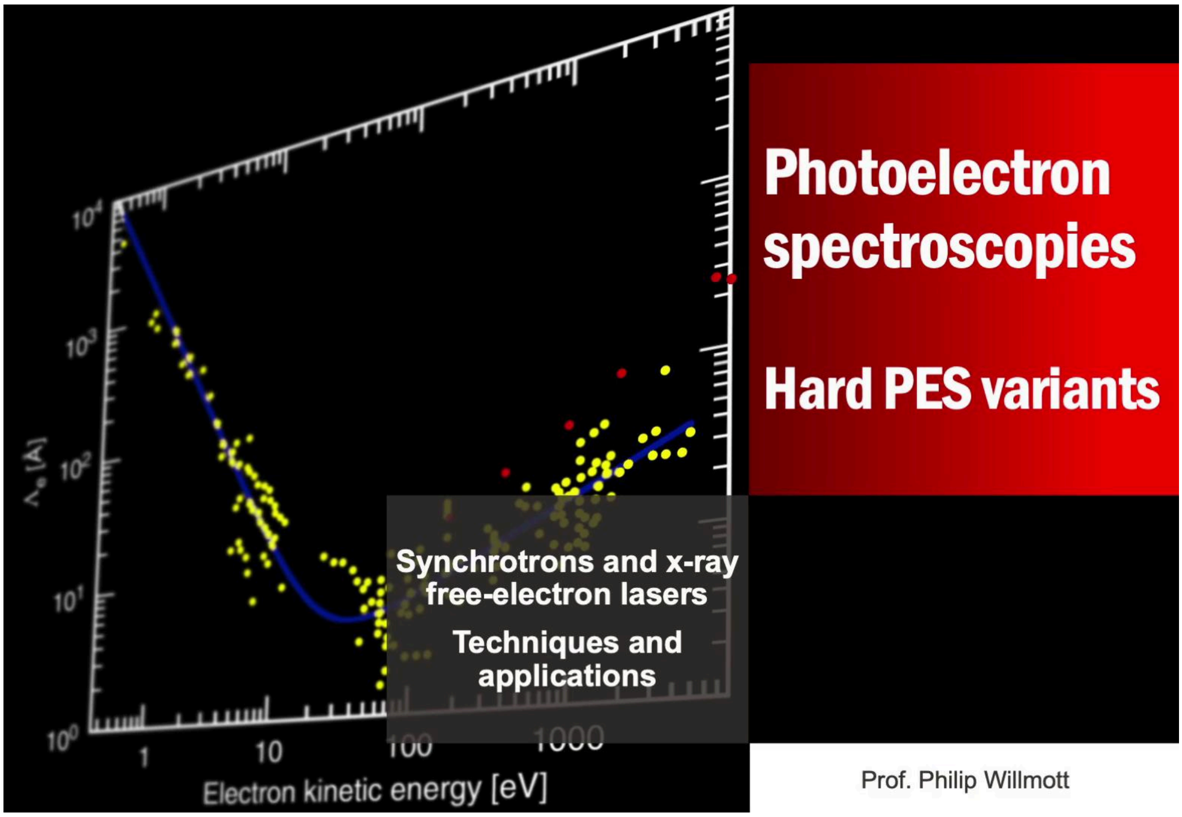
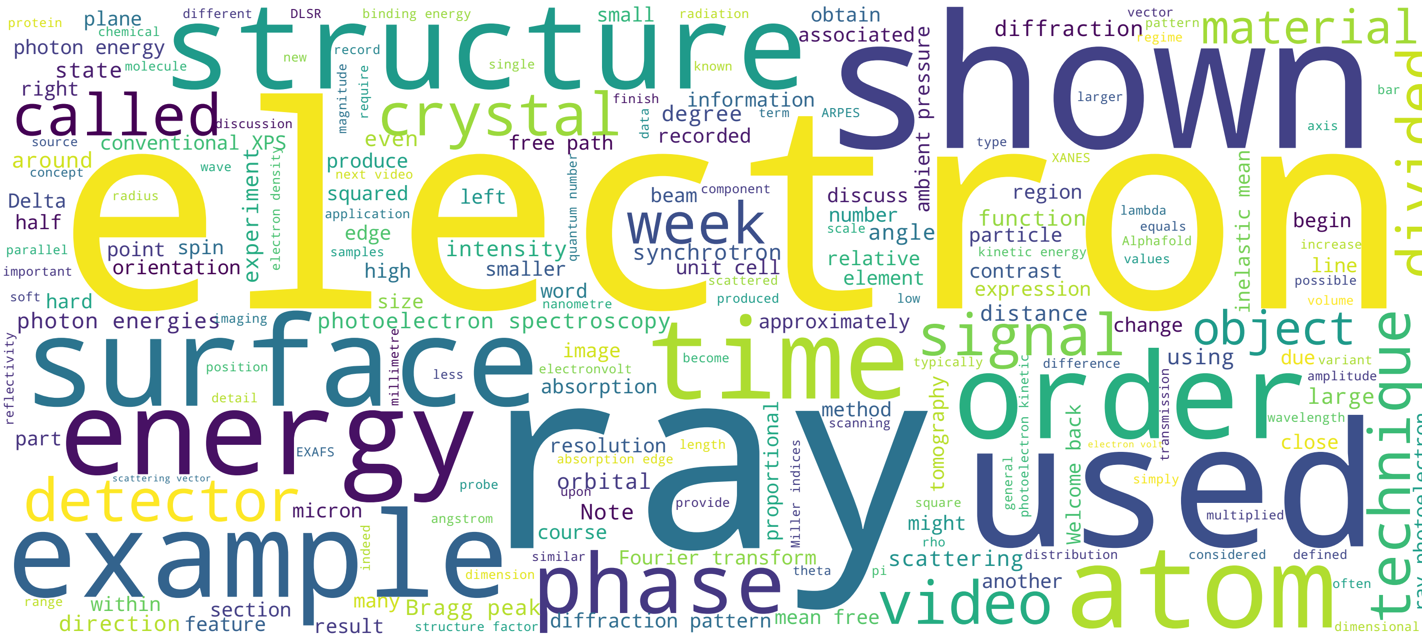
EPFL



École polytechnique fédérale de Lausanne

Prof. Philip Willmott



Search MOOC

Video

EPFL

Contents and objectives of this video

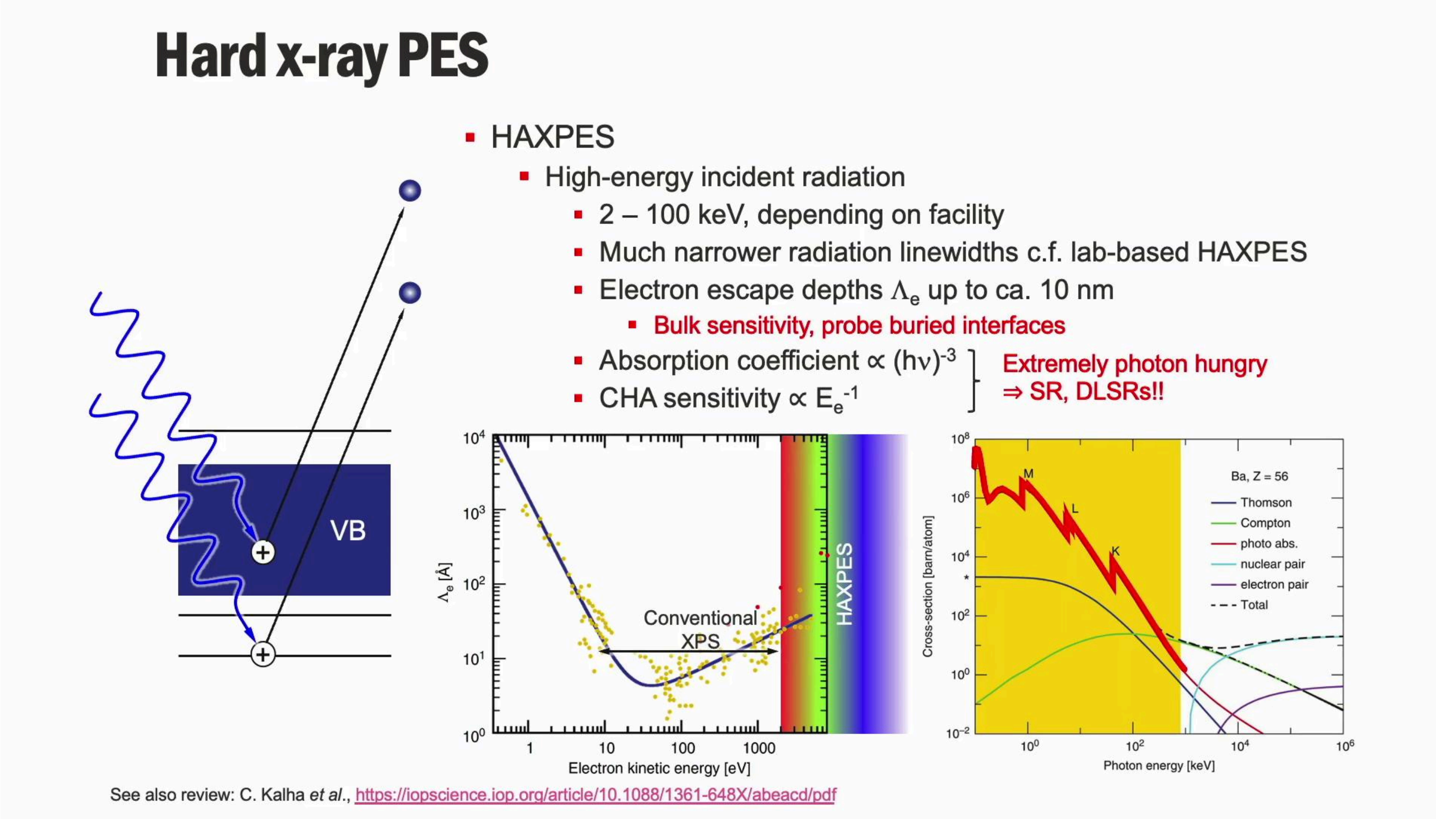
- HAXPES
- HARPES
- AP-HAXPES

Welcome back to the last video of week four of this course on synchrotron and XFEL radiation techniques and applications. In this video, we briefly cover variants of photoelectron spectroscopy in which higher incident photon energies are employed, which lead to higher photoelectron kinetic energies and an associated higher inelastic mean-free path. The three variants discussed here, HAXPES, HARPES, and ambient pressure HAXPES, if not exhaustive, give a taste of how photoelectron spectroscopy is moving increasingly towards the investigation of realistic systems found in operando devices such as battery cells or in electronic device structures, for example.

Notes

Summary

0m 05s



Hard X-ray photoelectron spectroscopy or HAXPES, is simply conventional XPS using high photon energies. For a given binding energy, the photoelectron produced by absorption of a photon with X eV higher energy will therefore have a correspondingly higher kinetic energy. So in contrast to conventional XPS, which extends up to about two kiloelectronvolts, HAXPES begins at this energy and can extend as high as 100 kiloelectronvolts, depending on the facility. The advantage of synchrotron-based HAXPES is that because the escape depths are up to an order of magnitude larger than in conventional XPS, it has bulk sensitivity, meaning that all momentum quantum numbers; kx, ky and kz are good, and that buried interfaces can be probed. The technical obstacles to HAXPES include a much-reduced photoabsorption coefficient, which drops off with the inverse third power of the incident photon energy and a reduced analyzer sensitivity, which is proportional to the inverse photoelectron kinetic energy. This makes all hard X-ray photoelectron spectroscopies extremely photon-hungry, necessitating the use of synchrotrons, and in particular, DLSRs. The number of HAXPES facilities is burgeoning since the advent of DLSRs with MAX IV in 2016.

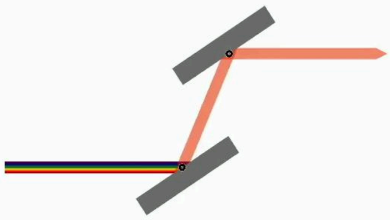
Notes

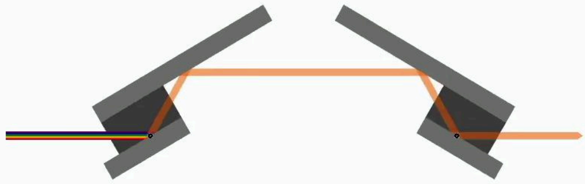
Summary

0m 51s

Hard x-ray PES

- $\Delta E/E \sim 1/10000$ or better
  - DCM/CCM/4BM combination Si and/or Ge
  - High Miller indices e.g., (333), (400), (444)
    - Access high photon energies at reasonable Bragg angles (i.e., $\lambda = 2d_{hkl} \sin \theta \Rightarrow$ small d_{hkl})





Because the absolute bandwidth Δv of the binding energy should remain similar to that produced in conventional XPS at lower photon energies, the relative bandwidth Δv upon v must be much smaller, setting stringent specifications on the monochromator design. This is typically achieved by combining conventional DCM monochromators, which have a nondispersive geometry regarding the Bragg angle of the second crystal with a four-bounce mono or double-crystal cut mono, typically using different Miller indices or indeed different crystal types. The Miller indices also tend to be higher due to their smaller interplanar separations, allowing one to more easily access higher photon energies at non-glancing Bragg angles.

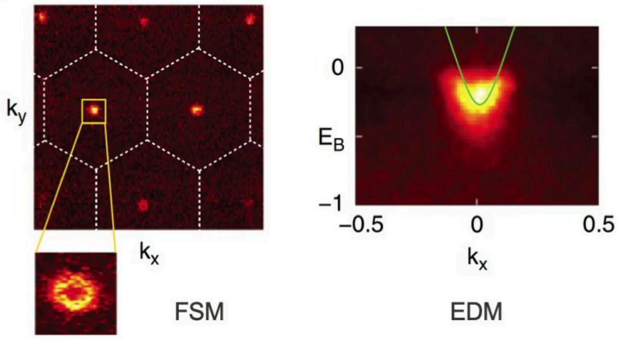
Notes

Summary

2m 28s

Hard x-ray angle-resolved PES

- HARPES – hard x-ray ARPES (see Video w4s2v4)
  - Up to 2 keV, "SX-ARPES"
  - ≡ angle-resolved HAXPES
  - Extremely low PE-excitation cross-sections
    - ⇒ SR, DLSR, XFEL
  - Bulk excitation
    - All momentum quantum numbers are good, including k_z
    - Less sensitive to surface contaminations ⇒ partially relaxed vacuum conditions
    - Hugely expanded range of easily prepared sample materials
  - In-situ/operando experiments



ARPES features of $Al_xGa_{1-x}N$ buried quantum well structure
See: L.L. Lev *et al.*, Nature Comms.

When HAXPES is combined with angle-resolved signal, one obtains HARPES, the hard X-ray variant of ARPES. This is often referred to rather confusingly to the uninitiated as soft X-ray ARPES, but this is for photon energies below around two kiloelectronvolts, but still significantly higher than those energies which are normally employed in conventional ARPES. These rarely extend past 250 or maybe 500 electronvolts. As we've already intimated, the photoabsorption cross-sections are extremely small at these higher energies, requiring very high, brilliant beamlines. The bulk excitations induced in HARPES means not only that momentum quantum numbers are preserved in all directions, but also that experimental results are less sensitive to surface contaminations, thus relaxing sample preparation procedures, the vacuum conditions, and also hugely expanding the range of materials that lend themselves to such experiments. Soft X-ray ARPES and HARPES are already producing exciting results in the fields of in-situ and operando systems, such as shown here for the electronic structure of aluminium gallium nitride buried quantum-well structures.

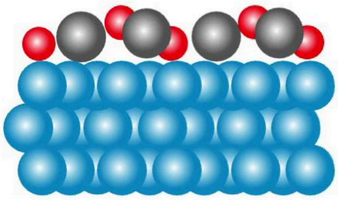
Notes

Summary

3m 18s

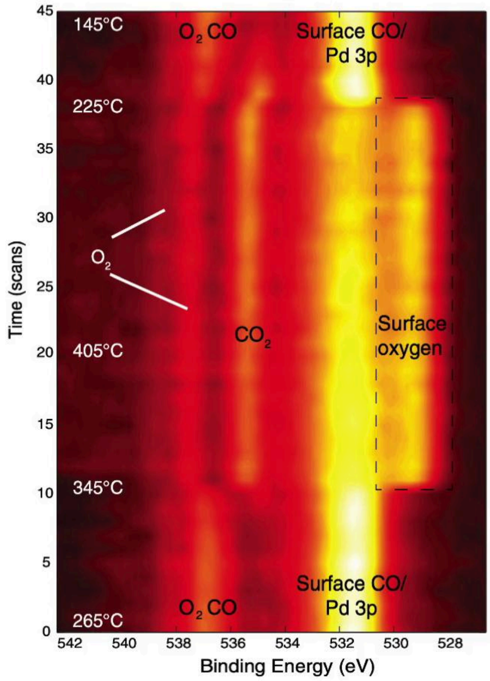
Ambient-pressure hard x-ray PES

- AP-HAXPES
  - Extended inelastic mean-free path
  - ⇒ Higher ambient pressures
  - ⇒ Thicker liquid layers
  - Interfaces under realistic chemical conditions



Example: Change in spectra around the O 1s region during temperature ramp in CO oxidation on Pd(100) @ 0.2 mbar O_2/CO
hν = 650 eV

S. Blomberg *et al.*, http://dx.doi.org/10.1103/PhysRevLett.110.117601

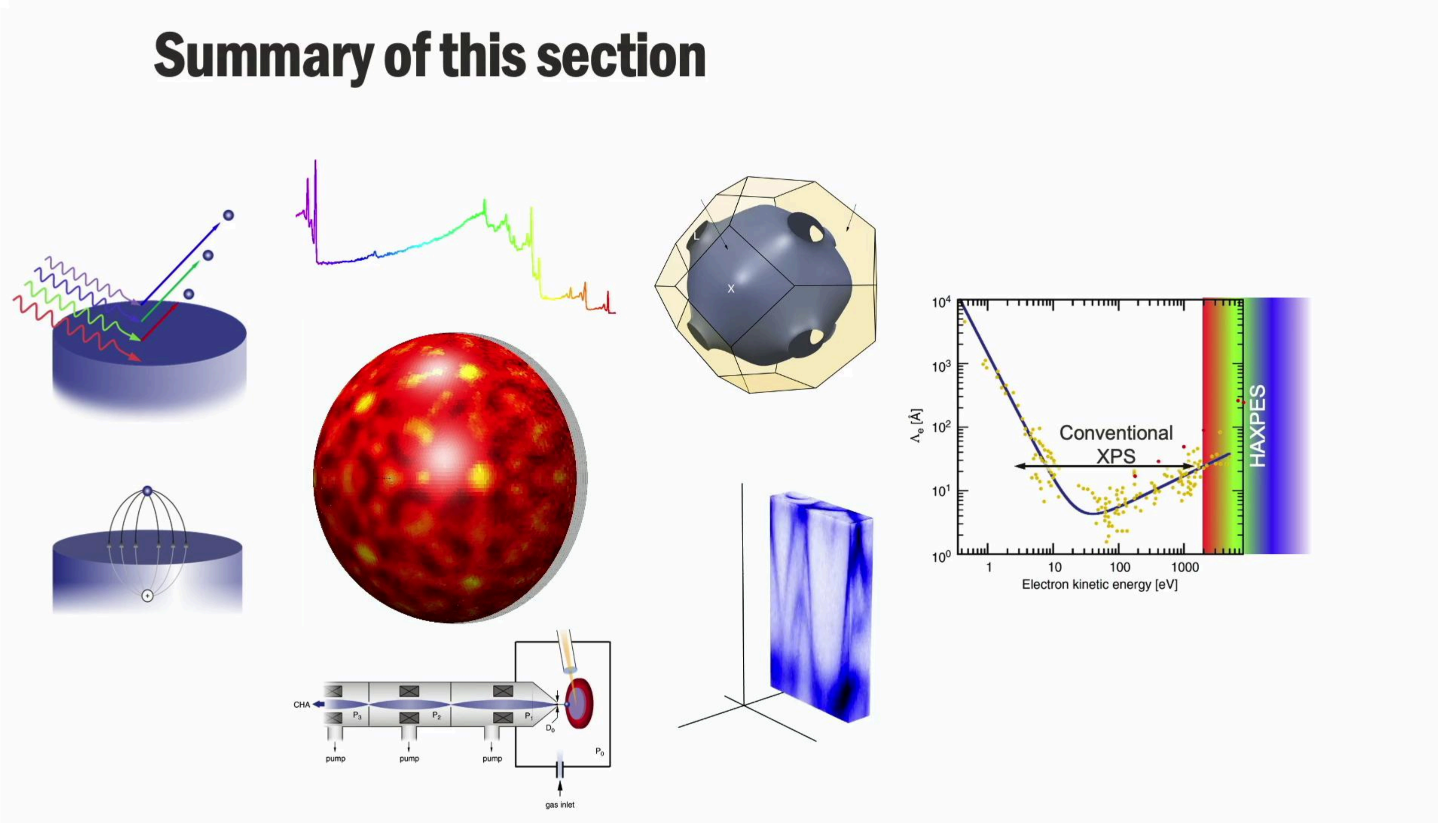


Finally, ambient pressure hard X-ray photoelectron spectroscopy exploits the larger inelastic mean-free path of the photoelectron, not while it is emerging from dense matter, but during its journey from the surface or interface to the differentially pumped electron analyzer. This means either that thicker liquid layers can be used in solid-liquid interface experiments or higher gas pressures in solid-gas or liquid-gas setups. Thus, ever more realistic physicochemical conditions can be achieved in ambient pressure HAXPES, such as shown here in an early example of the technique used in the study of carbon monoxide oxidation on the surface of the palladium.

Notes

Summary

4m 44s



To summarise this second week devoted to synchrotron-based spectroscopies, we first recapped the photoelectric effect explained by Einstein in 1905, and the work function. We then proceeded to explain conventional XPS or ESCA and the interesting phenomenon of pronounced forward scattering exploited in X-ray photoelectron diffraction to investigate the structural features of crystalline surfaces. One of the drawbacks of XPS is the relative ease with which photoelectrons can be scattered and lost by background gas interactions. We introduced the technical innovation of near-sample photoelectron extraction and differential pumping in near-ambient pressure photoelectron spectroscopy developed to study systems that are close to those used in real systems, such as catalytic reactors, batteries or heterogeneous surface chemistry. We then considered both the theoretical background, including bandstructure and the Fermi surface, and the very powerful technique itself of angle-resolved photoelectron spectroscopy, or ARPES. We finished this week with a brief overview of variants of photoelectron spectroscopies in which higher photon energies are used and correspondingly, higher photoelectron kinetic energies are produced with their associated larger inelastic mean-free paths.

Notes

Summary

5m 31s

Next week...

Next week will be the first of two concentrating on imaging techniques, in which we discuss X-ray computed tomography and Zernike and dark field microscopies. I look forward to seeing you then.

Notes

Summary

7m 01s