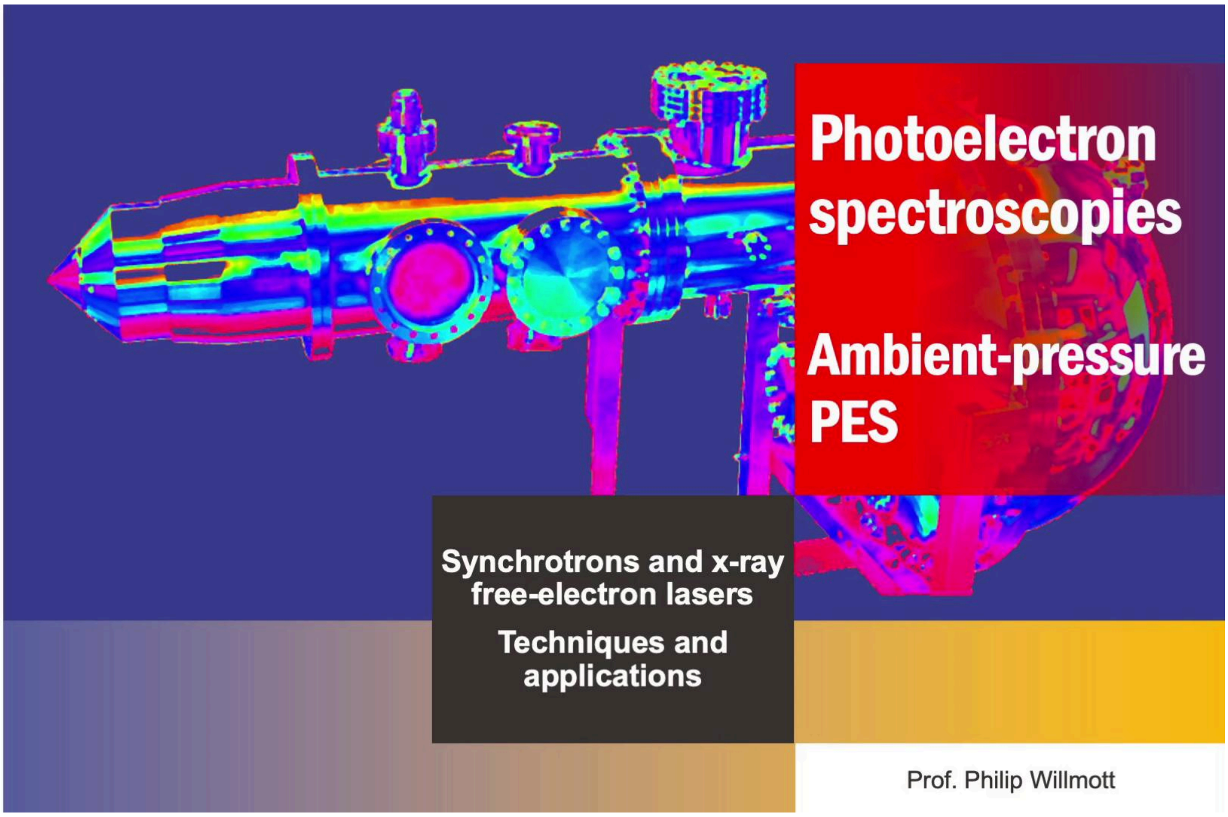
EPFL



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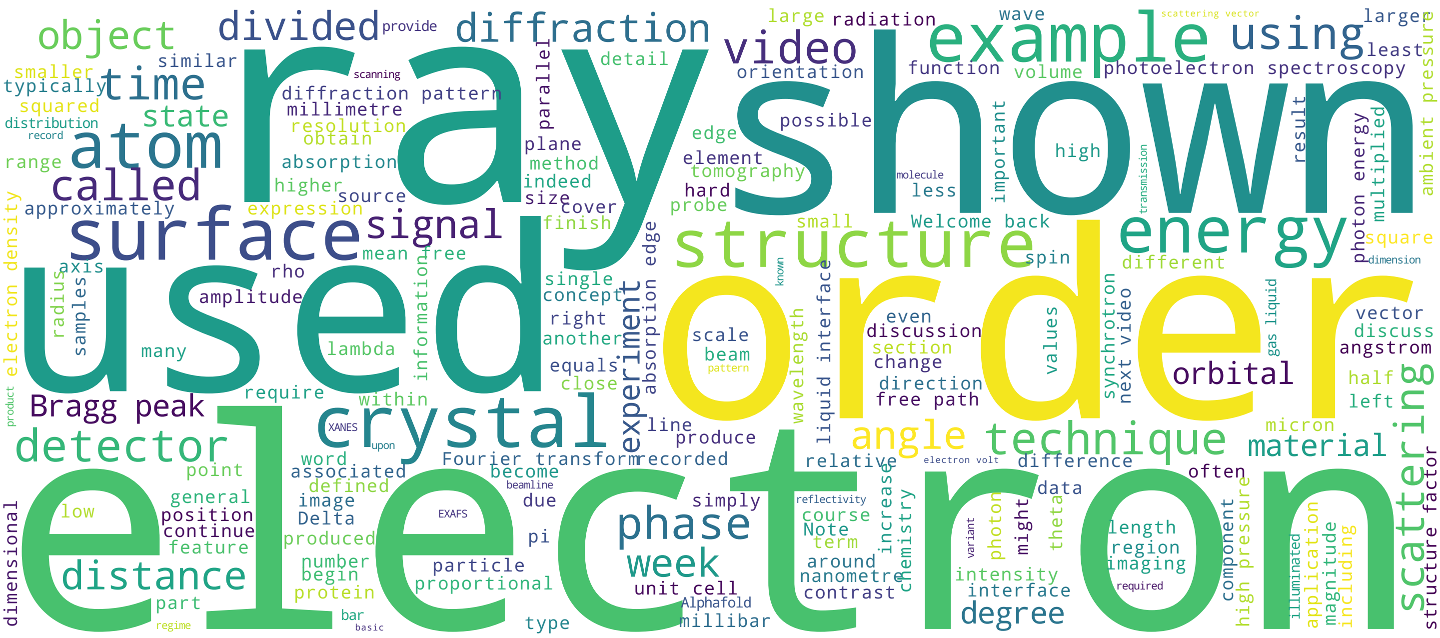


Search MOOC

Video

EPFL

Contents and objectives of this video

- APPES overview
- Handling high pressure environments
  - IMFP in gases and liquids
  - Differential pumping
- Solid-liquid interfaces

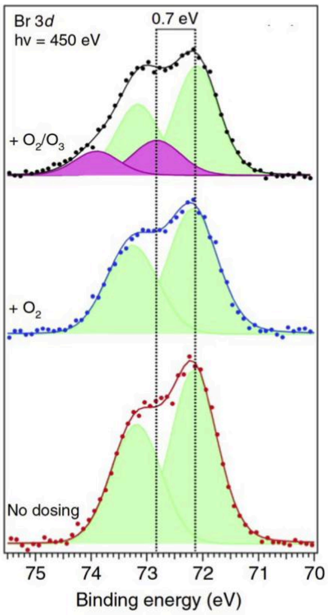
Welcome back to week 4 of this course on synchrotron and XFEL radiation techniques and applications. We continue our discussions of photoelectron spectroscopies in this video by considering ambient pressure photoelectron spectroscopy or APPES. This variation of photoelectron spectroscopy is extremely important in heterogeneous chemistry, not least in catalysis. It's similar to X-ray photoelectron spectroscopy, the main new ingredient being that the sample is in a high-pressure environment. Here the term high pressure means significantly higher than that normally used in XPS and typically ranges from a fraction of a millibar to many millibars. This increase in ambient pressure comes with technical issues regarding extraction of the photoelectron signal which we will discuss next. In addition to gas-solid and gas-liquid interfaces, it's also possible to investigate solid-liquid interfaces which we'll also discuss at the end of this video.

Notes

Summary

0m 05s

Ambient-pressure PES



- XPS in realistic reaction conditions
- Chemical information
  - Shifts in binding energy
  - Relative intensities
- Angular distribution of photoelectrons
- Dependence on polarization vector relative to interface
- Effect of external parameters
  - Temperature
  - pH
  - Gas type
  - Pressure
  - Applied voltage
  - …

From L. Artiglia *et al.*, Nature Communications

Traditionally, XPS has required the highest vacuum conditions for two main reasons. Uncontrolled physi- and chemisorption of gaseous species generally has an impact on the physical, chemical, and electronic properties of materials in the near surface region. In conventional XPS, this is of course to be avoided as one is investigating pure and unsullied materials. Moreover, the photoelectrons have a certain cross-section with residual gas particles and thus a too high pressure reduces the distance they can travel before they are inelastically scattered and can't be measured. Nonetheless, there is much interest in studying gas-solid and gas-liquid interfaces as most interesting and commercially relevant chemical reactions occur at interfaces and use pressures far in excess of those of traditional XPS. APPES was developed to fulfil that need and study the effect of external physicochemical parameters. In order to overcome the problem of scattering of the photoelectrons, the entrance to a differentially pumped extraction and measurement system is placed extremely close to the region of interest that is being illuminated by the X-rays. This is described quantitatively in just a moment.

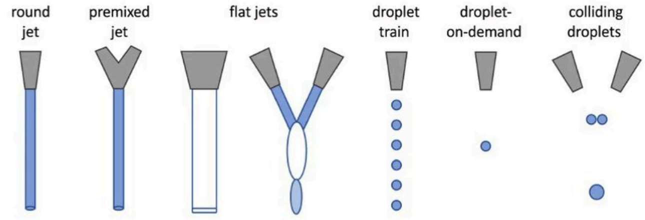
Notes

Summary

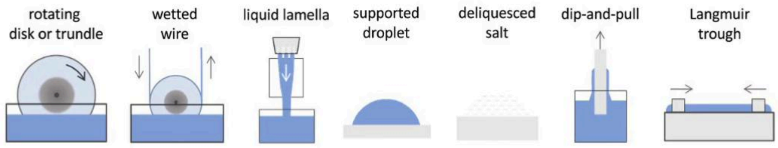
1m 15s

Ambient-pressure PES

Sample delivery, ~ ms-dynamics



Sample delivery, ~ s-dynamics



Images and see also: R. Dupuy *et al.*, doi: 10.1063/5.0036178

- Synonyms
  - Ambient-pressure PES (APPES)
  - Near-ambient-pressure PES (NAPP)
  - Ambient-pressure XPS (APXPS)
  - High-pressure XPS (HPXPS)
  - …
- Large pressure range ~ mbar – bar
- Gas-liquid, gas-solid, solid-liquid interfaces
  - Kinetics
  - Dynamics
  - “Realistic” chemical conditions
- Typical research fields
  - Environmental sciences/atmospheric chemistry
  - Battery research
  - Photochemistry
  - Chemistry of ice
  - Corrosion

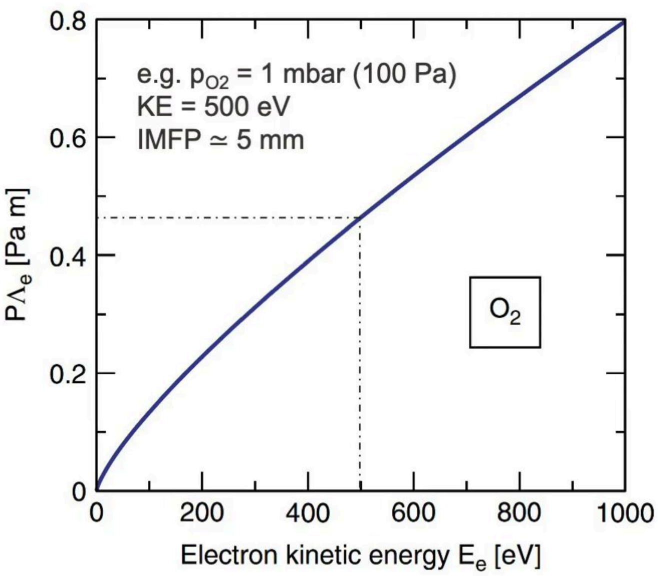
Before we continue, it should be mentioned that there isn't as yet a universal consensus as to how to name or abbreviate this relatively novel technique of ambient pressure photoelectron spectroscopy, varying according to the type of experiment one is attempting. The pressure range can be very different from below the millibar range to the order of one atmosphere. All combinations of gas, liquid, solid interfaces can be investigated for research, typically in the broad field of chemistry and in particular related to energy, catalysis, and the environment. How the interfaces are produced are also very varied, depending a lot on the timescale of any dynamical processes that might be involved.

Notes

Summary

2m 46s

Handling high pressures



- Short inelastic mean-free path of photoelectrons in ambient gas
- Reduction of ambient pressure P_0 to UHV pressure regime < 10^{-9} mbar
  - Multiple differential pumping stages
    - Up to reduction by factor 10^{10}
    - Each stage $p_{n+1}/p_n \sim 10^{-2} - 10^{-4}$
    - Separated by small holes
    - Electron-focusing optics
- Opening to first differentially pumped stage = $D_0 \sim 100 - 500\ \mu m$
  - Sample-opening distance ~ few x D_0
    - Too small? Interacts with process
    - Too large? Too small solid angle
  - Maximum allowed pressure $\propto 1/D_0$
  - Photoemission signal $\propto D_0^2$

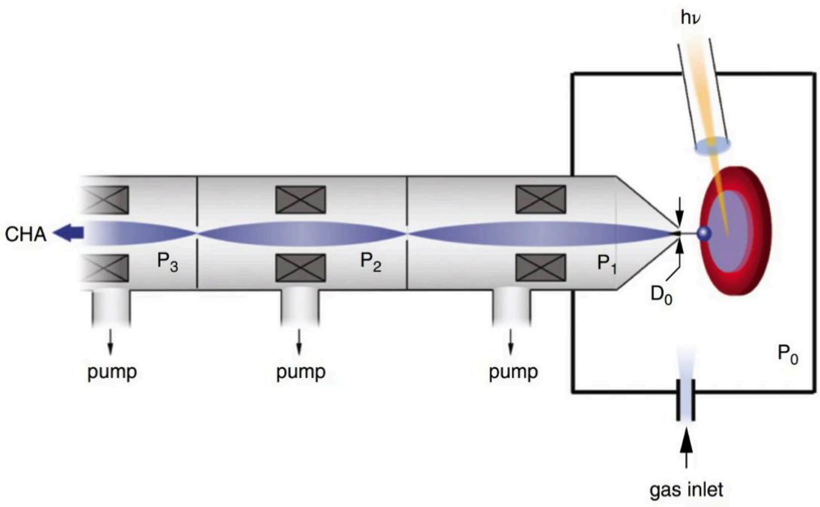
In order to handle high ambient pressures, one has to consider the photoelectron's energy and its corresponding mean-free path for the pressure being used. For example, 500 electronvolt electrons travelling through 1 millibar of oxygen have a product of pressure times mean-free path of approximately 0.46 pascal metres. One millibar is equal to 100 pascals, hence the mean-free path is 4.6 millimetres.

Notes

Summary

3m 35s

Handling high pressures



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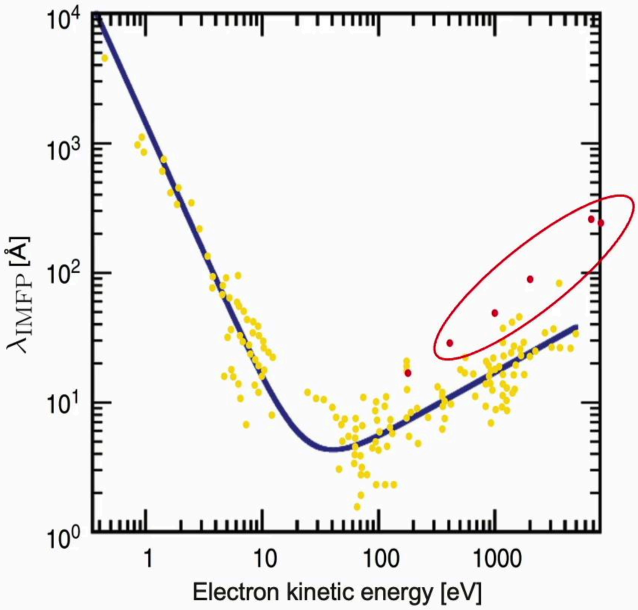
The extraction nozzle of the electron energy analyser must therefore be approximately this distance or smaller from the point of X-ray irradiation. The electron enters a first stage of differential pumping which will reduce the pressure by a factor of around 100-10,000, and thus increasing the mean-free path correspondingly. Typically, there are three or four such differentially pumped stages until the pressure drops to the order of 10 to the minus 9 millibars or less. Each stage contains electron focusing optics in order to collect as much photoelectron signal as possible. The initial opening has a diameter D0, which is typically between 0.1 and 0.5 millimetres. As a rule of thumb, the irradiation point to extraction opening distance is a few times this opening diameter. The maximum allowed pressure is inversely proportional to D0, while the photoemission signal intensity is proportional to the square of D0.

Notes

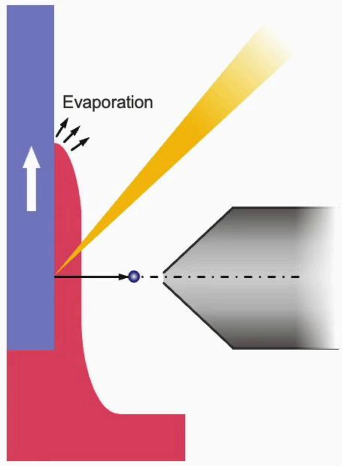
Summary

4m 10s

Solid-liquid interfaces



- Water IMFP @ HXR energies ~ 20 – 30 nm
- Thin layers < 25 nm required
  - "Dip and pull" meniscus layer



Solid-liquid interfaces are particularly interesting in the case of water and high photoelectron energies, as the mean-free path is unusually high, of the order of 20-30 nanometres, as highlighted here, allowing for a thin film of water to be used in a dip and pull process, as shown schematically here on the right.

Notes

Summary

5m 22s

In the next video...

In the next video, we tackle the basics of the theoretical background to angle-resolved photoelectron spectroscopy or ARPES.

Notes

Summary

5m 48s