X-ray photoemission - XPS principles and applications.

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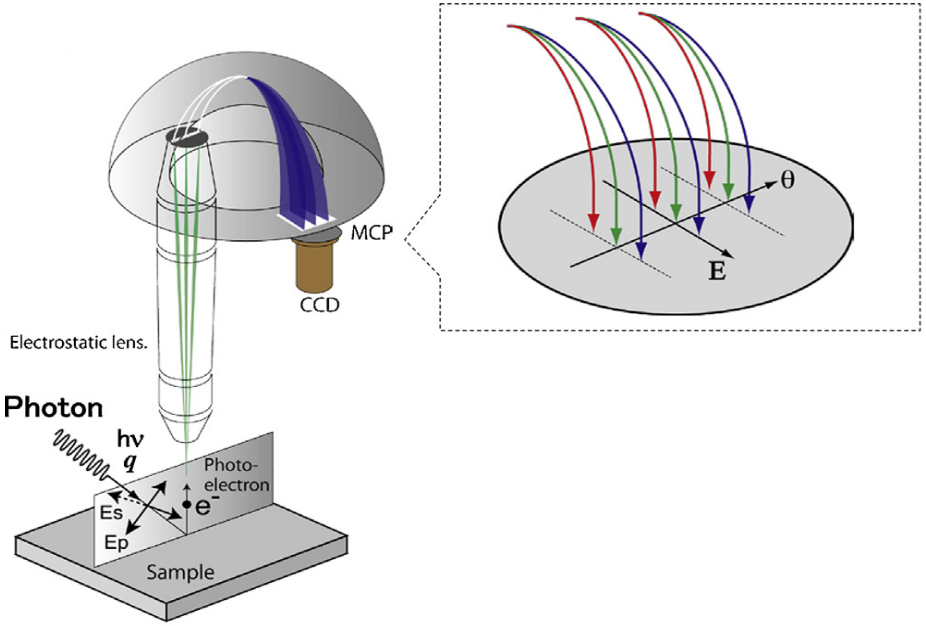
Hemispherical electron analyzer

Spectrometers widely used at all synchrotron radiation facilities



→ Angle Resolved PhotoElectron Spectroscopy (ARPES)

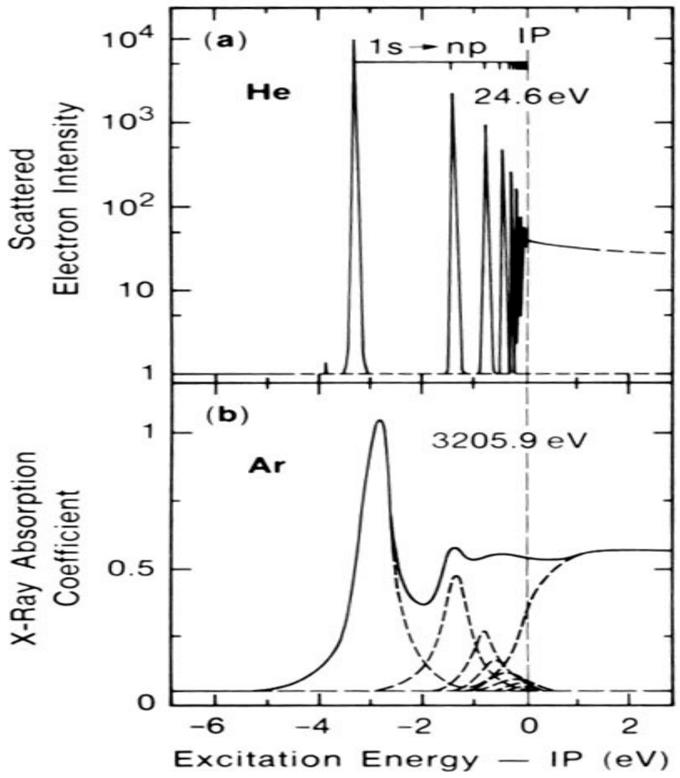
Hemispherical analysers allow to measure simultaneously kinetic energies and angle of emission thanks to a 2D detector

Excellent compromise between resolution and transmission thanks to modern electrostatic lens.

Absorption spectrum below the ionization threshold

Below the ionization threshold, electronic transitions corresponding to the promotion of an electron from an inner shell electron toward an unoccupied orbital are occuring.

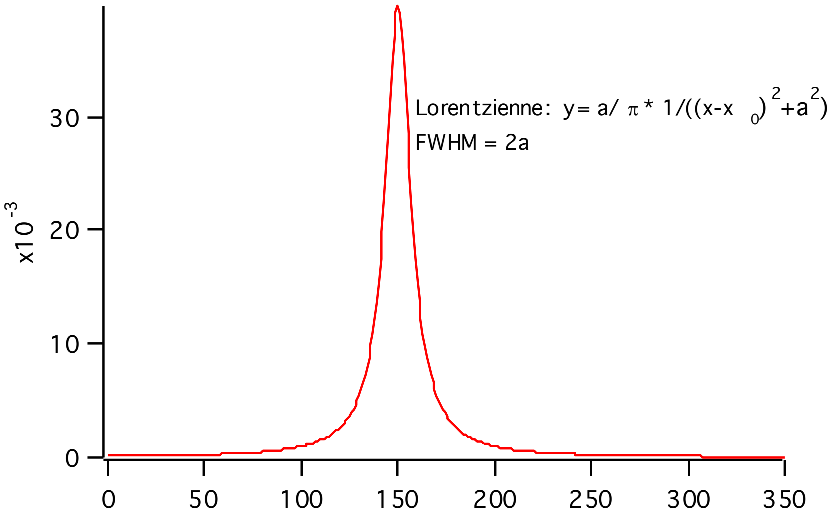
Lifetime of the core-hole: 1 femtosecond



Comparison of 1s→ np Rydberg series for helium and argon converging to the ionization threshold as a fun ction of term values (excitation energy – IP (eV)). Dash lines for argon indicate the Lorentzian lifetime broadening.

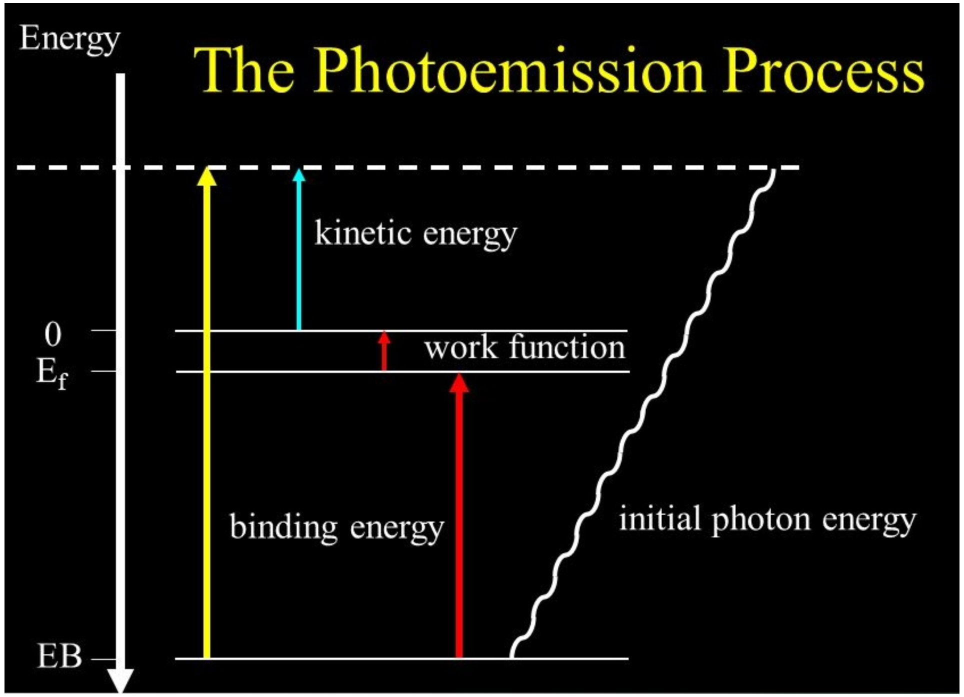
Inner shell excitation produces an unstable intermediate state. At infinite resolution, the FWHM Γ is due to the lifetime (τ) broadening of the intermediate state following the Heisenberg uncertainty principle $\Gamma.\tau = h/2\pi$.

$$h/2\pi = 6.6 \,.\, 10^{-16}\ \text{eV.s}$$



Absorption spectra are systematically broadened by the bandwidth of the monochromator (Gaussian) and by the lifetime broadening.

XPS X-ray Photoelectron Spectroscopy, also called ESCA Electron Spectroscopy for Chemical Analysis



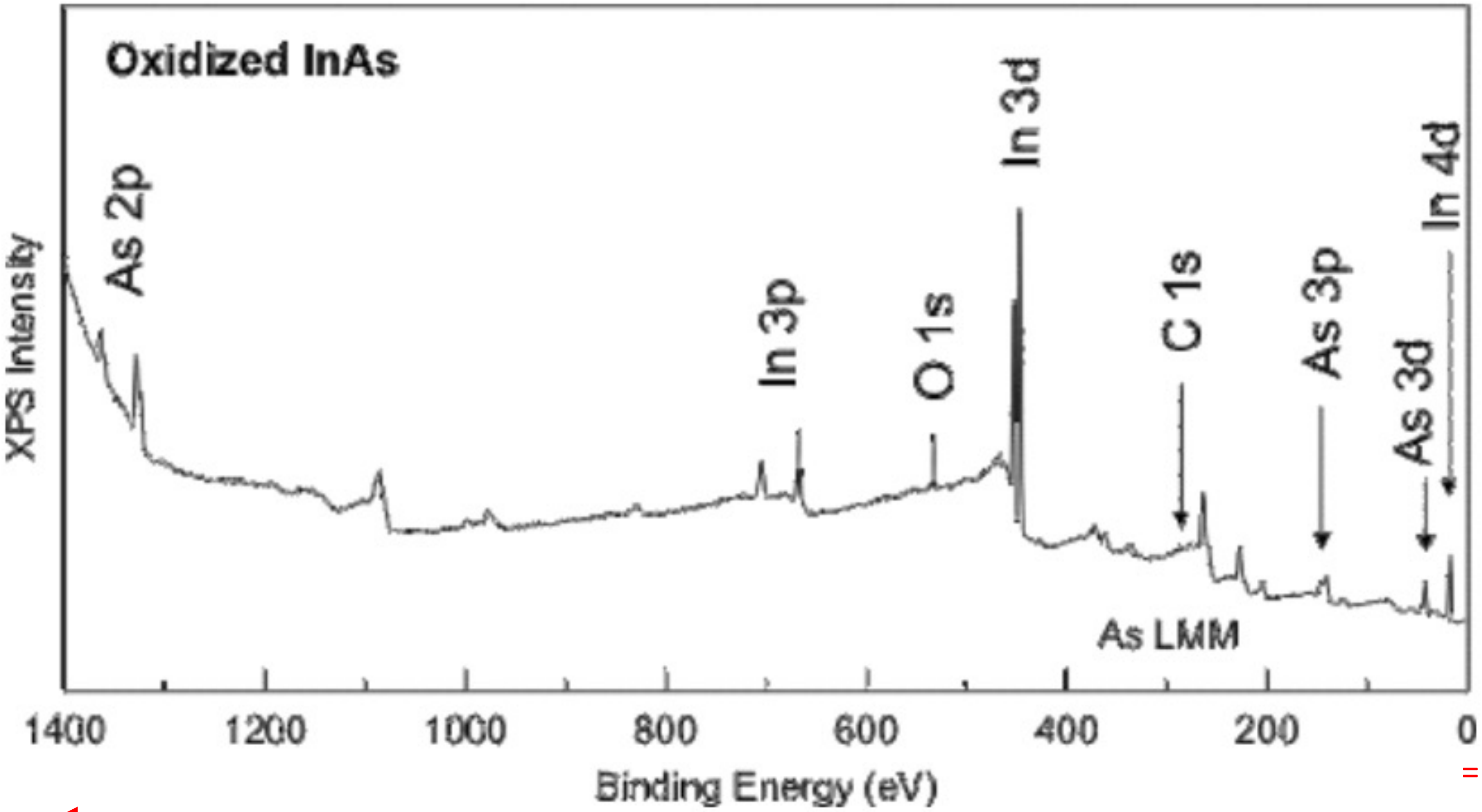
Energy Conservation

$h\nu = KE + BE + \Phi_A$

$h\nu$: photon energy
KE: Kinetic Energy
BE: Binding Energy
Φ_A: Work Function

No work function in gas phase !

$$h\nu = KE + BE + \Phi_A$$



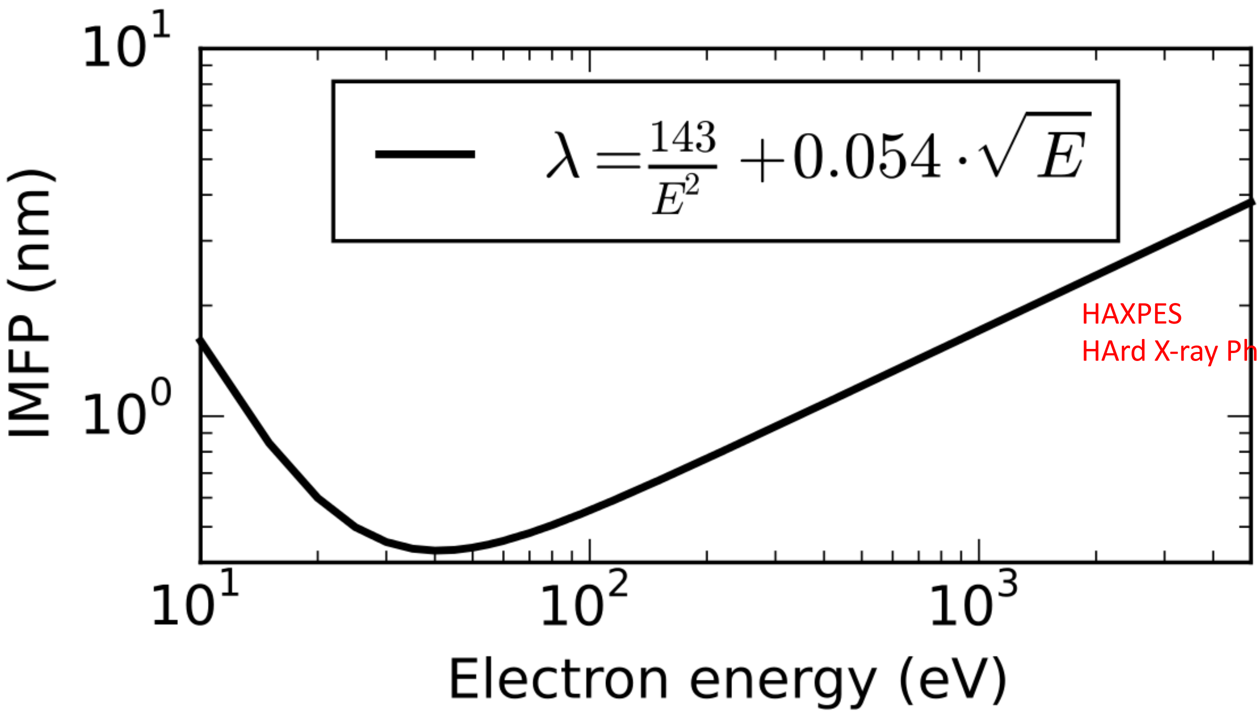
$= E_{Fermi}$

Deeper Core Level

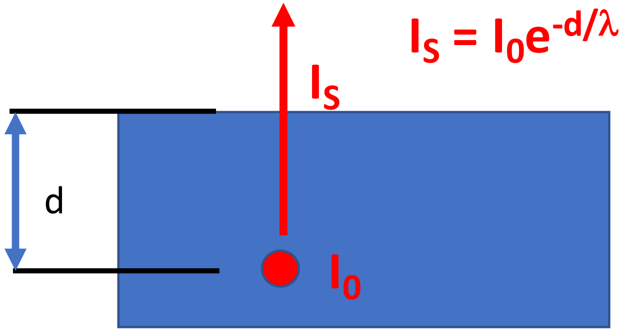
X-ray Photoelectron Spectroscopy: Sampling Depth

Ionization of an Atom in a solid

Inelastic Mean Free Path: IMFP (universal curve)



HAXPES
HArd X-ray PhotoElectron Spectroscopy



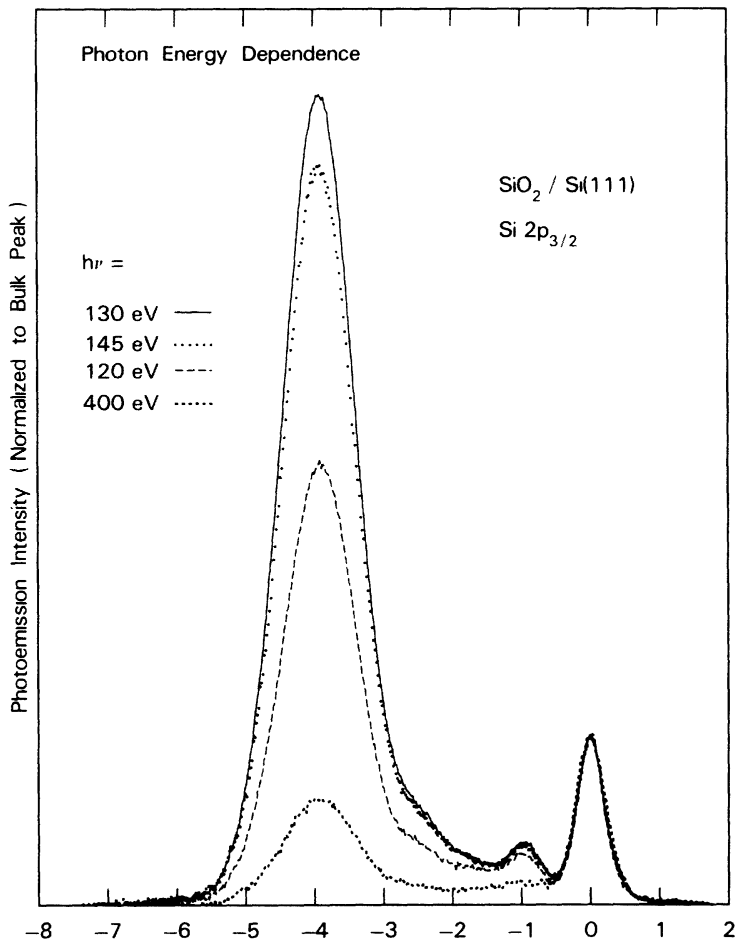
$$I_S = I_0 e^{-d/\lambda}$$

At 50 eV of kinetic energy, XPS only sensitive to the surface (few nm)

At high kinetic energies (HAXPES), bulk sensitivity.

Core level X-ray Photoelectron Spectroscopy, Depth profiling

By varying the photon energy and thus photoelectron kinetic energies



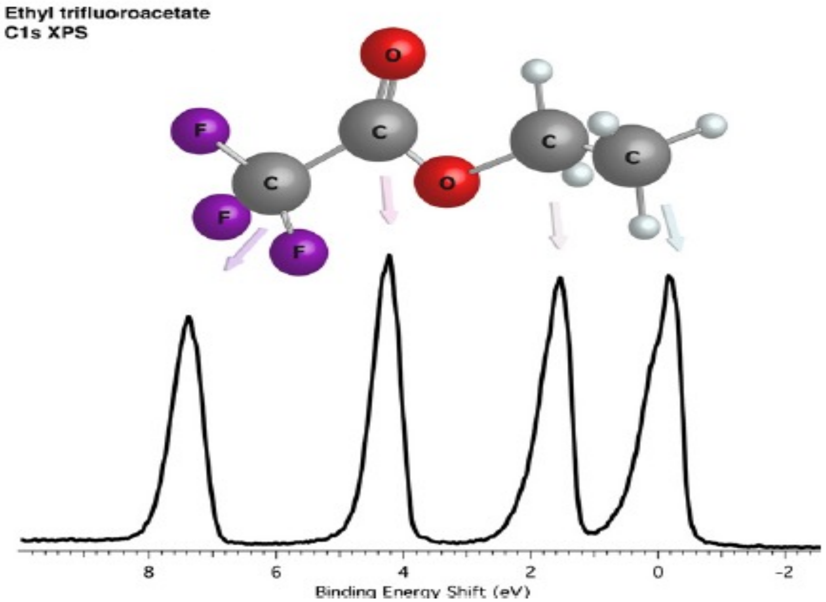
Study of the microscopic structure of SiO_2/Si interface (14 Å of oxide on Si(111)).

Himpsel, Phys. Rev. B 38 6084 (1988)

→ HArd X-ray PhotoElectron Spectroscopy (HAXPES) to probe the bulk or buried interfaces overall few tens of nm is becoming a routine technic.

Core level X-ray Photoelectron Spectroscopy, Chemical Aspects

ESCA Electron Spectroscopy for Chemical Analysis
Physics Nobel Prize 1981 : Kai SIEGBAHN



Chemical shift: change in binding energy between 2 chemical forms of the same atomic species

→ Applications: Provides informations on chemical environment, functional groups, oxydation states, distinguish isolated Atoms and in clusters, between bulk and surface Atoms…

X-ray Photoelectron Spectroscopy: from UHV to NAP (Near Ambient Pressure)

XPS is usually performed in Ultra High Vacuum (10^{-9} mbar) in order to:

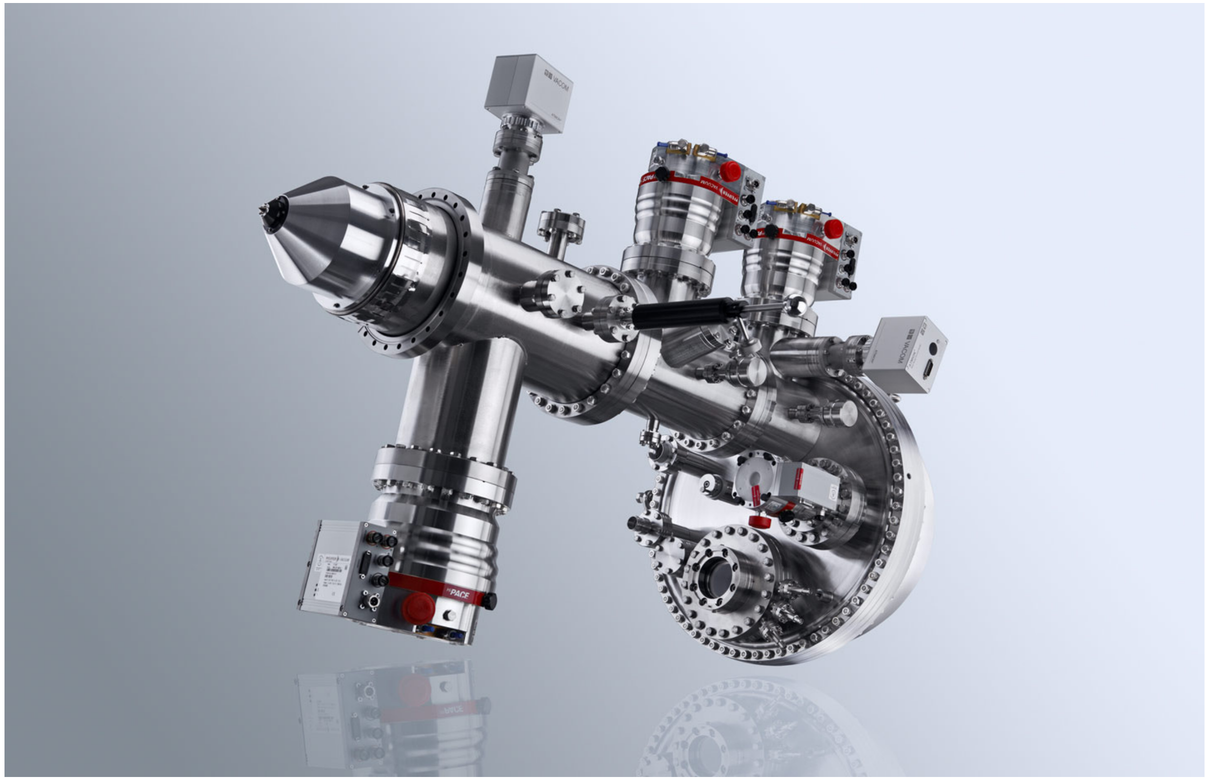
- minimize photoelectron attenuation in their way up to the detector
- minimize sample contamination
- preserve electron detector
- increase photon mean free path

But it can be interesting to measure surfaces in realistic conditions:

- study of gas-solid interfaces: heterogenous catalysis, corrosion, oxidation
- study of gas-liquids interfaces: surfaces wetting, electrochemistry, hydrated molecules, liquids in equilibrium with their vapor pressure

→ Near Ambient Pressure (NAP) Photoemission

X-ray Photoelectron Spectroscopy: from UHV to NAP (Near Ambient Pressure)

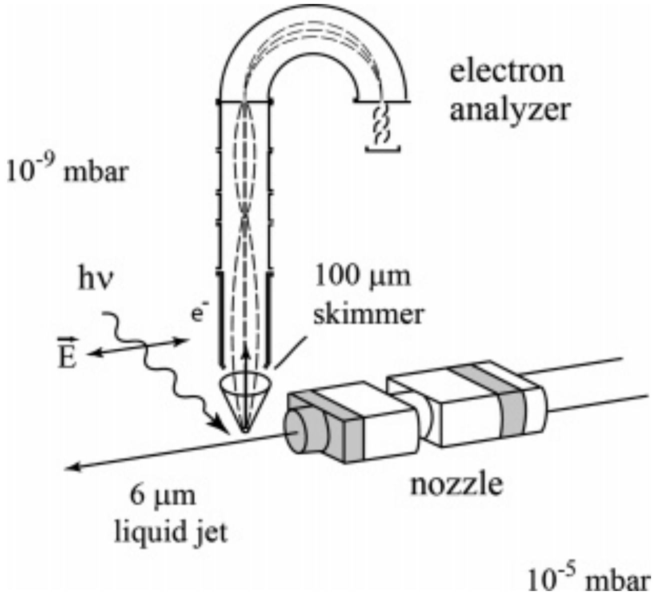


Successive differential pumping stages combined with electromagnetic lens system

H. Bluhm, Journal of Electron Spectroscopy and related Phenomena 177 71 (2010)

Technic available in most of the Synchrotron Radiation facilities

Liquid jet photoemission



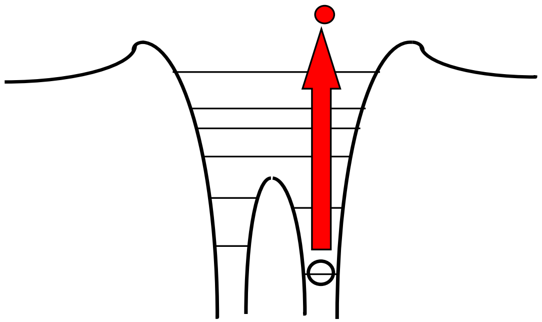
The pressure in the interaction chamber is ~10^{-5} mbar, and the jet velocity is 120 ms^{-1}

Photoemission from liquid aqueous solutions

Dissolved salts, molecules, influence of PH…

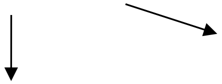
B. Winter and M. Faubel, Chemical Reviews 106 1176 (2006)

Photoionisation



Inner shell photoionization

If the photon energy is high enough, an inner shell electron is ejected into the continuum leaving a singly charged ion highly excited.

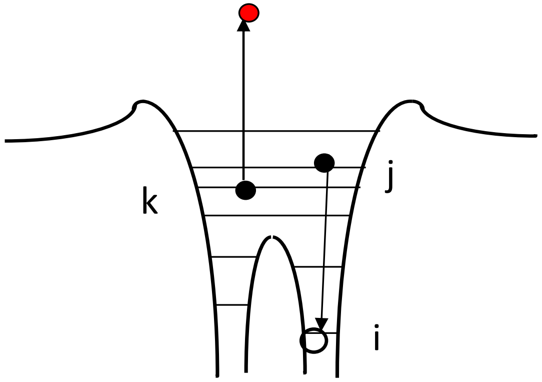


$$\mathbf{Ec = h\nu - Eb - \Phi a}$$

Work function

Binding Energy

Innershell relaxation: the Auger effect



Auger effect

Due to the Coulomb interaction between the inner shell and outer shell electron: the core hole is filled and an outer shell electron (Auger electron) is ejected into the continuum leaving a doubly charged ion.

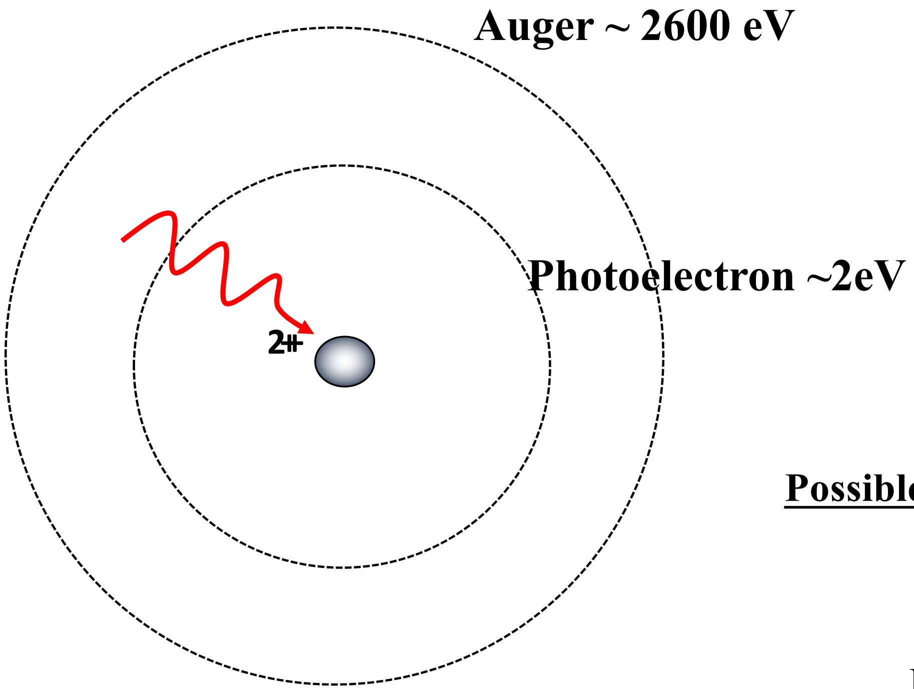
Matric element:

$$\underbrace{< \varphi_i \chi}_{\text{final}} \left| \frac{1}{r_{12}} \right| \underbrace{\varphi_j \varphi_k >}_{\text{initial}}$$

Photoionisation and Auger effect are sequential processes

POSTCOLLISION INTERACTION MECHANISM

Argon 1s photoionization: $\hbar\omega = IP + 2$ eV



Auger ~ 2600 eV

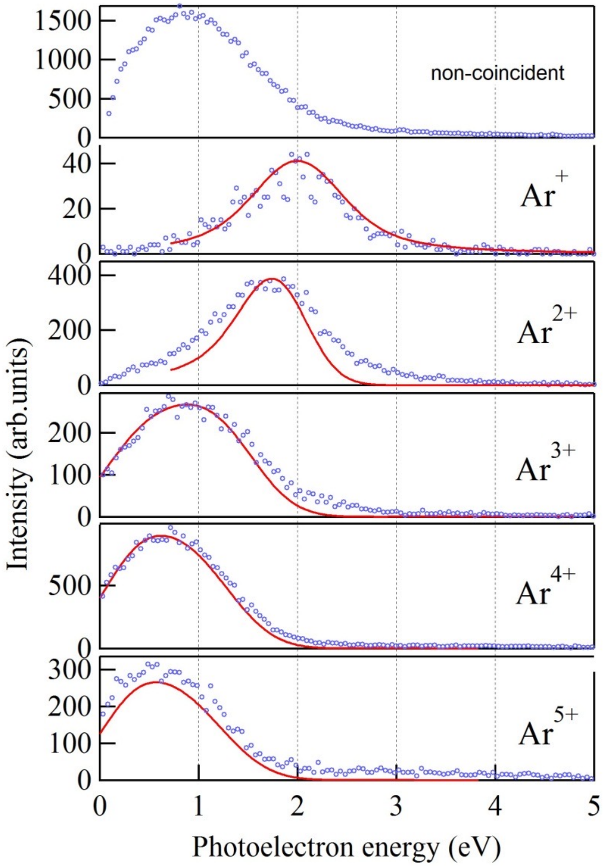
Photoelectron ~2eV

<u>Possible post-collision interactions:</u>

Ion/photoelectron
Ion/Auger
Photoelectron/Auger

Post Collision Interaction → Dynamics of the intermediate states

Ultrafast dynamics in postcollision interaction after multiple Auger decays in Argon 1*s* photoionization



Semi-classical calculations by Sergei Sheinerman:

- Negligible interaction between Auger and photoelectron
- Coulomb interaction between ion and photoelectron
- Photoelectron has no effect on the ion decay
- Sudden Auger emission and change of ionic charge
- Classical, linear electron trajectories

The PCI shift $\Delta E = \xi \Gamma / 2$

$\xi = \Delta Z / V_{ph}$

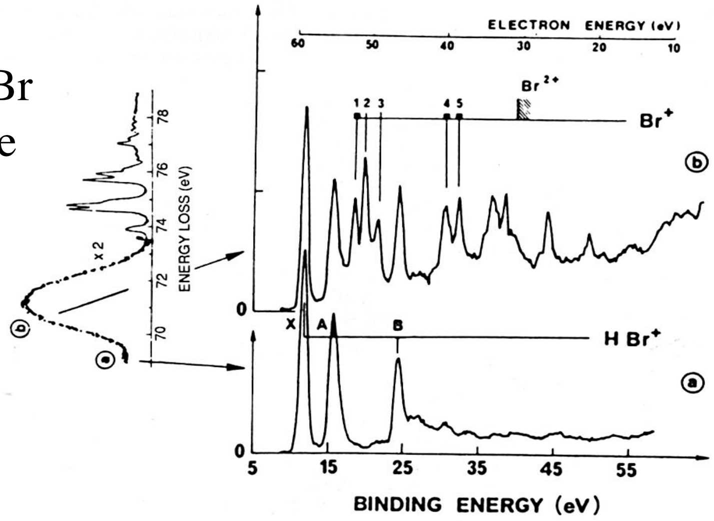
$\Gamma = \tau^{-1}$

Lifetime!

R. Guillemin et al., Phys. Rev. Lett. 109, 013001 (2012)

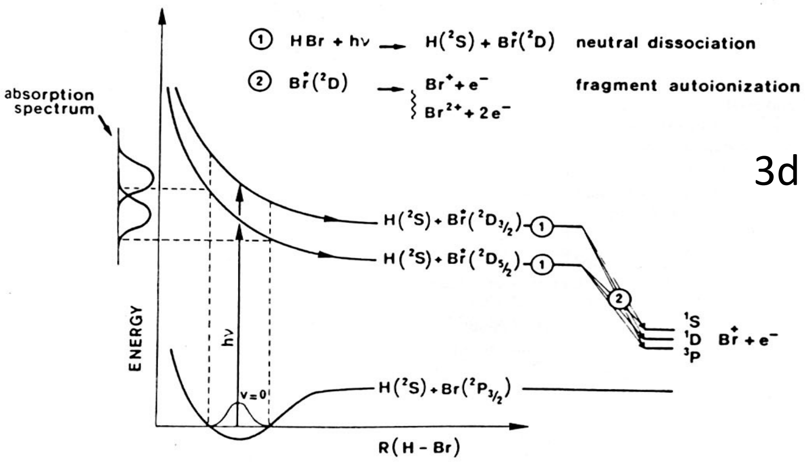
Ultrafast fragmentation: Fragmentation faster than the core-hole lifetime

HBr Molecule HBr excited around the Br 3d level



Electron spectrum measured on top of the resonance

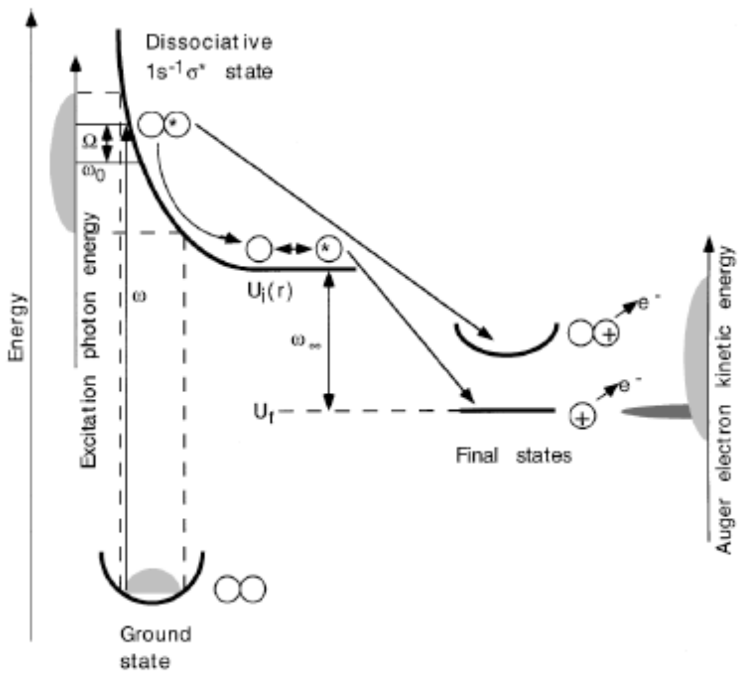
Off resonance photoelectron spectrum



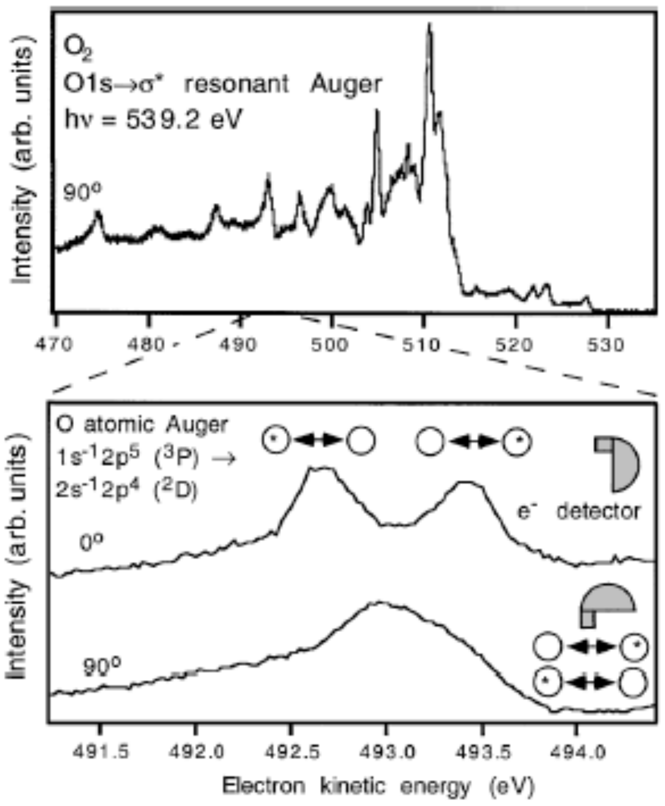
3d core-hole lifetime: 7 femtoseconds

P. Morin et I. Nenner, Phys. Rev. Lett. 56, (1986) 1913

Doppler broadening observed on 01s core excited O_2 molecule



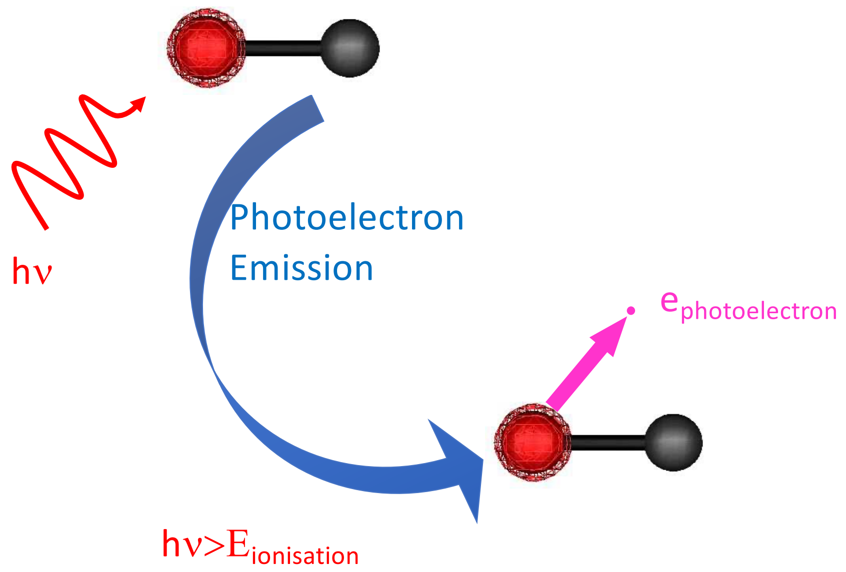
Schematic representation of ultrafast fragmentation of core excited O_2 molecule



Spectre Auger résonant mesuré sur la résonance O1s-->σ* pour deux orientations de l'analyseur d'électron par rapport au vecteur polarisation

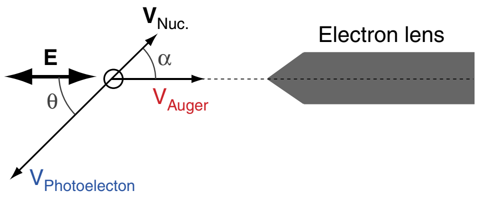
Björneholm et al., Phys. Rev. Lett. 84, (2000) 2826

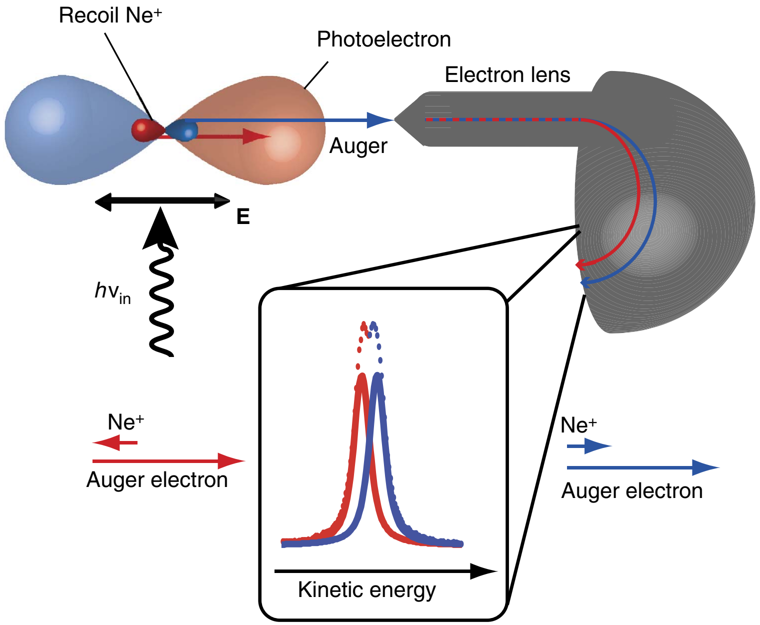
Recoil effects
High KE photoelectron (HAXPES)

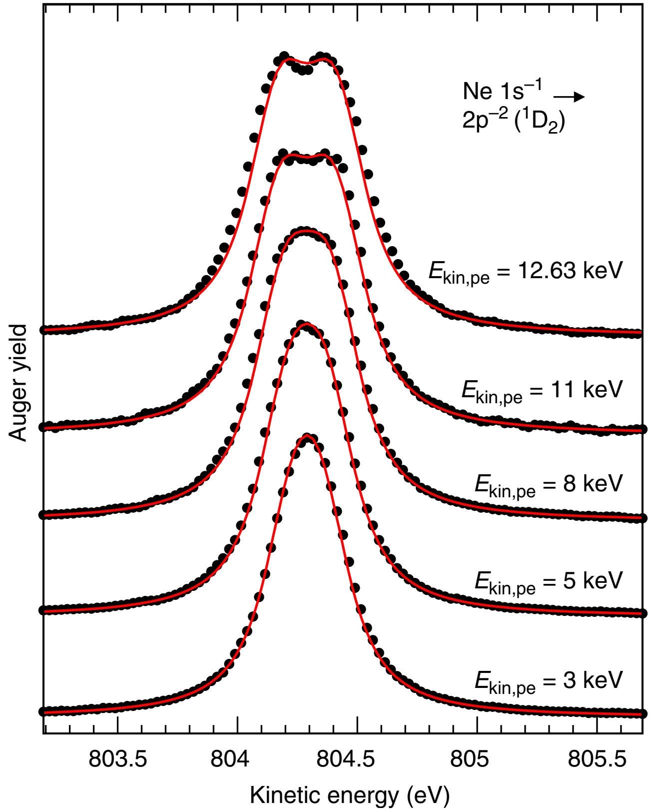


High kinetic energy of the photoelectron → translational recoil
Photoelectron emitted along the molecular axis → vibrational recoil
Photoelectron emitted perpendicular to the molecular axis → rotational recoil

Atomic Auger Doppler effects on emission of fast photoelectrons: Ne as showcase

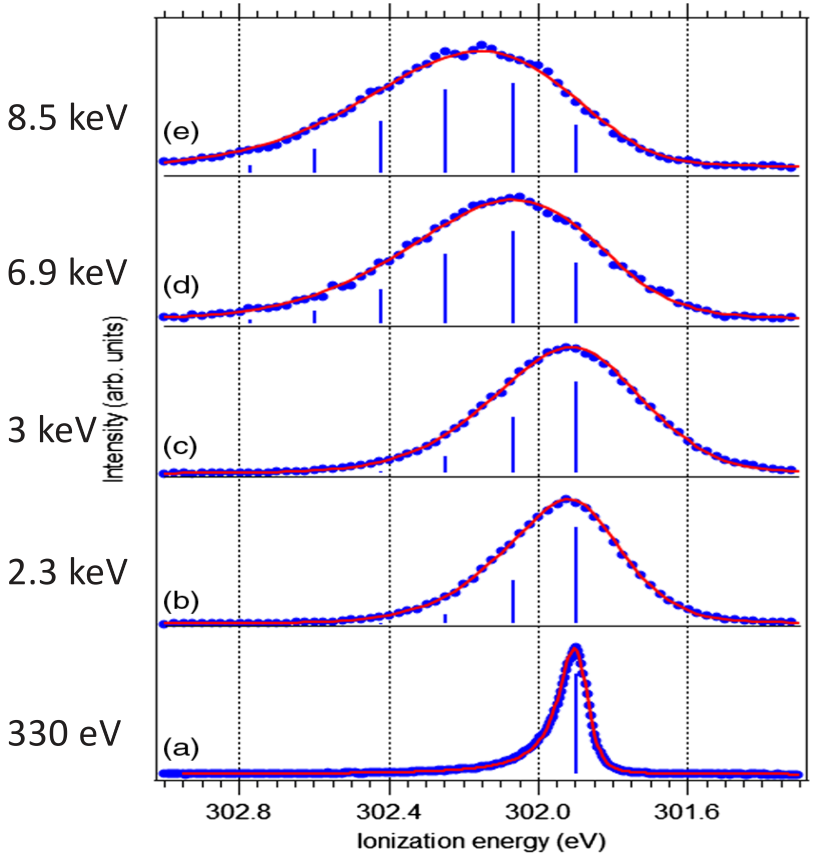






M. Simon et al., Nature Communications 5 4069 (2014)

Vibrational recoil of the CF_4 molecule



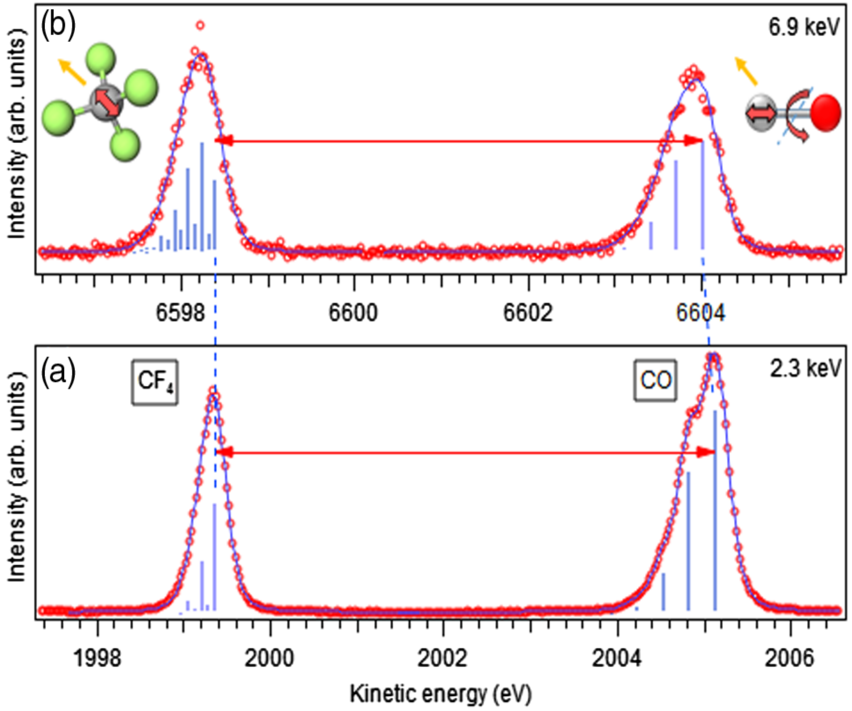
Carbon 1s photoelectron spectrum of the CF_4 molecule

No Franck-Condon excitation at 330 eV, PCI tail toward lower kinetic energy

Mainly asymmetric stretching mode

E. Kukk et al., Phys. Rev. Lett. 121 073002 (2018)

Vibrational and rotational recoil of the CO molecule



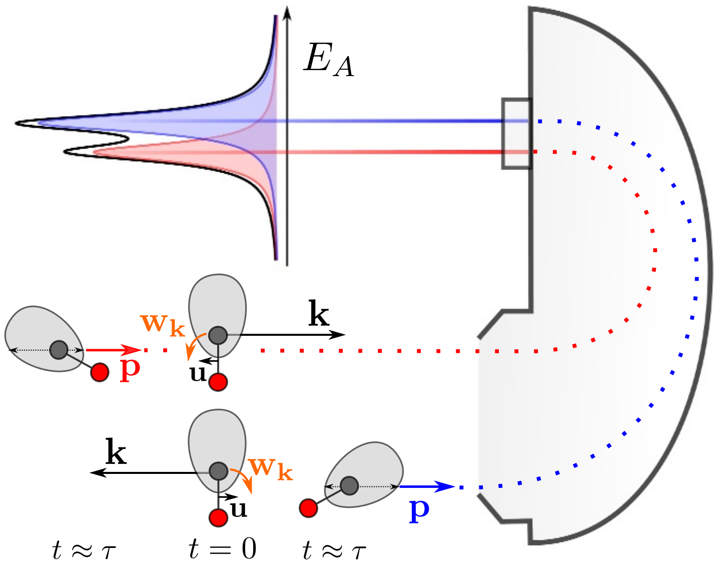
Mixture of CO and CF_4 molecules

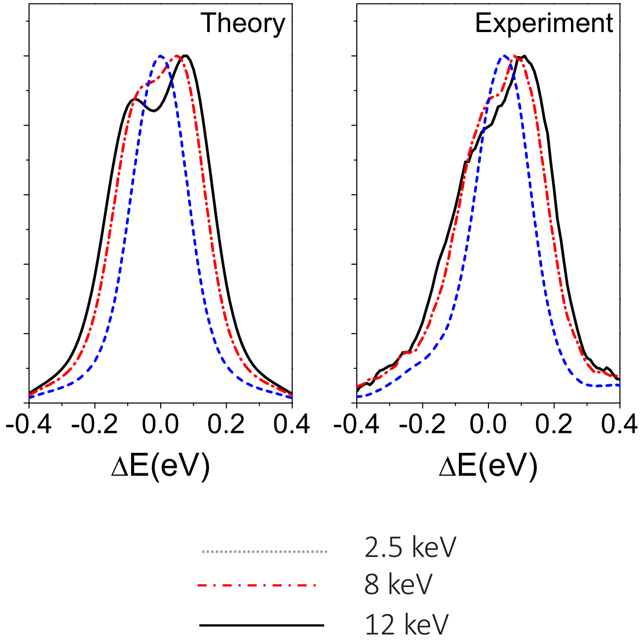
90 meV of rotational recoil

Carbon 1s photoelectron spectrum of CF_4 and CO molecules

E. Kukk et al., Phys. Rev. Lett. 121 073002 (2018)

Recoil induced ultrafast molecular rotation of the CO molecule probed by dynamical rotational Doppler effect



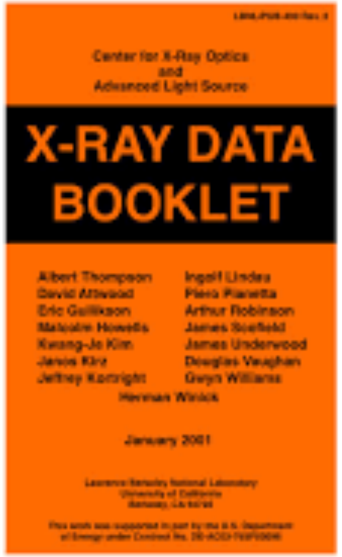


→ Rotational period shorter than the C1s core-hole lifetime (5 fs)

D. Céolin et al.; Proceedings of the National Academy of Sciences 116 4877 (2019)

X-ray spectroscopy

- **Element-specific**
- **Shell-specific**



Center for X-Ray Optics
and
Advanced Light Source

X-RAY DATA
BOOKLET

Albert Thompson
David Attwood
Eric Gullikson
Malcolm Howells
Kwang-Je Kim
Janos Kirz
Jeffrey Kortright
Ingolf Lindau
Piero Pianetta
Arthur Robinson
James Scofield
James Underwood
Douglas Vaughan
Gwyn Williams
Herman Winick

January 2001

https://xdb.lbl.gov

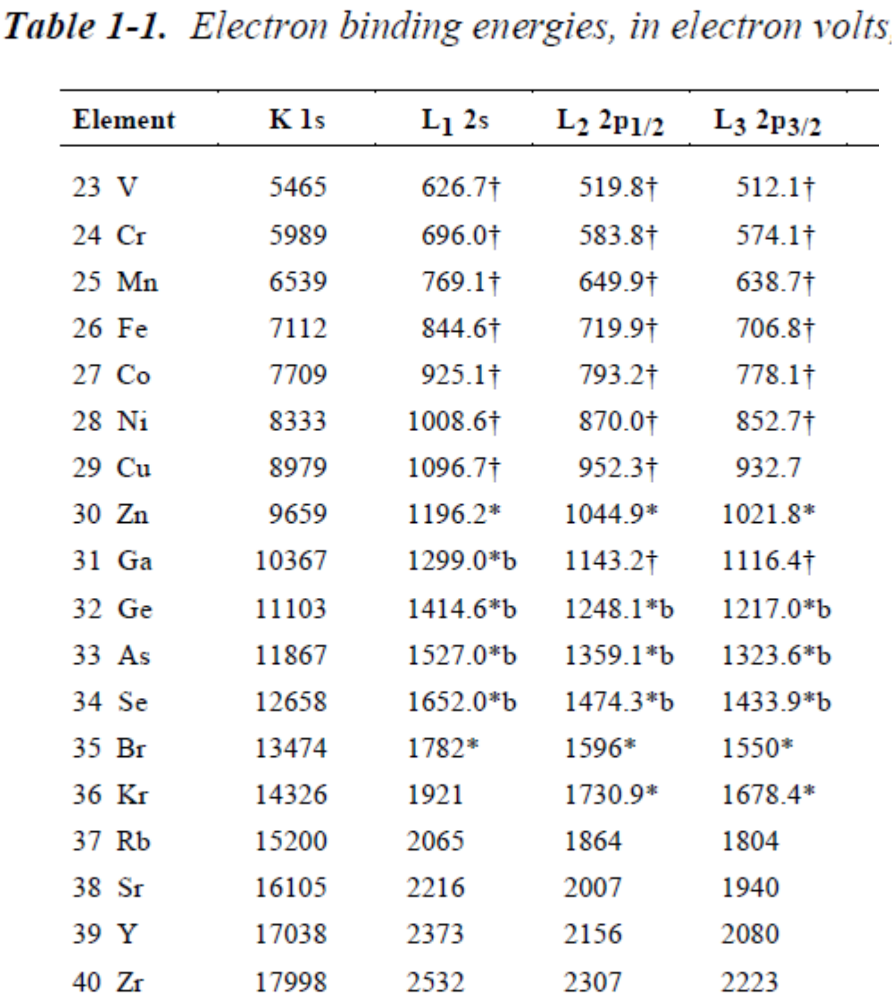


Table 1-1. *Electron binding energies, in electron volts*

Element	K 1s	L_1 2s	L_2 $2p_{1/2}$	L_3 $2p_{3/2}$
23 V	5465	626.7†	519.8†	512.1†
24 Cr	5989	696.0†	583.8†	574.1†
25 Mn	6539	769.1†	649.9†	638.7†
26 Fe	7112	844.6†	719.9†	706.8†
27 Co	7709	925.1†	793.2†	778.1†
28 Ni	8333	1008.6†	870.0†	852.7†
29 Cu	8979	1096.7†	952.3†	932.7
30 Zn	9659	1196.2*	1044.9*	1021.8*
31 Ga	10367	1299.0*b	1143.2†	1116.4†
32 Ge	11103	1414.6*b	1248.1*b	1217.0*b
33 As	11867	1527.0*b	1359.1*b	1323.6*b
34 Se	12658	1652.0*b	1474.3*b	1433.9*b
35 Br	13474	1782*	1596*	1550*
36 Kr	14326	1921	1730.9*	1678.4*
37 Rb	15200	2065	1864	1804
38 Sr	16105	2216	2007	1940
39 Y	17038	2373	2156	2080
40 Zr	17998	2532	2307	2223

A. C. Thompson et al., X-ray data booklet, Lawrence Berkeley National Laboratory, University of California (2009)