Spectroscopy from experimentalist's viewpoint II

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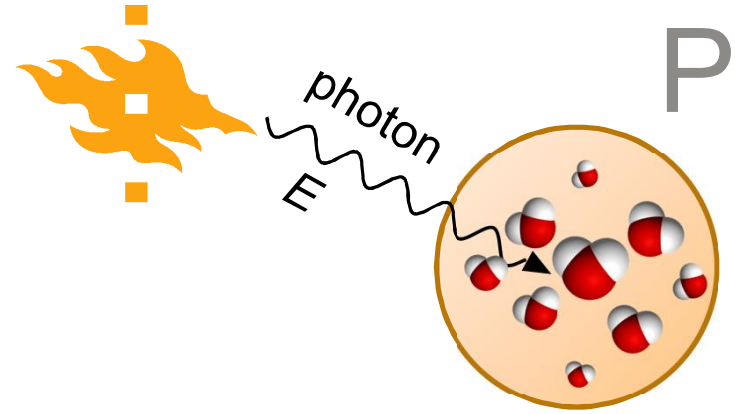
TDDFT school, Benasque, Spain, January 2014

UNIVERSITY OF HELSINKI

Photon absorption

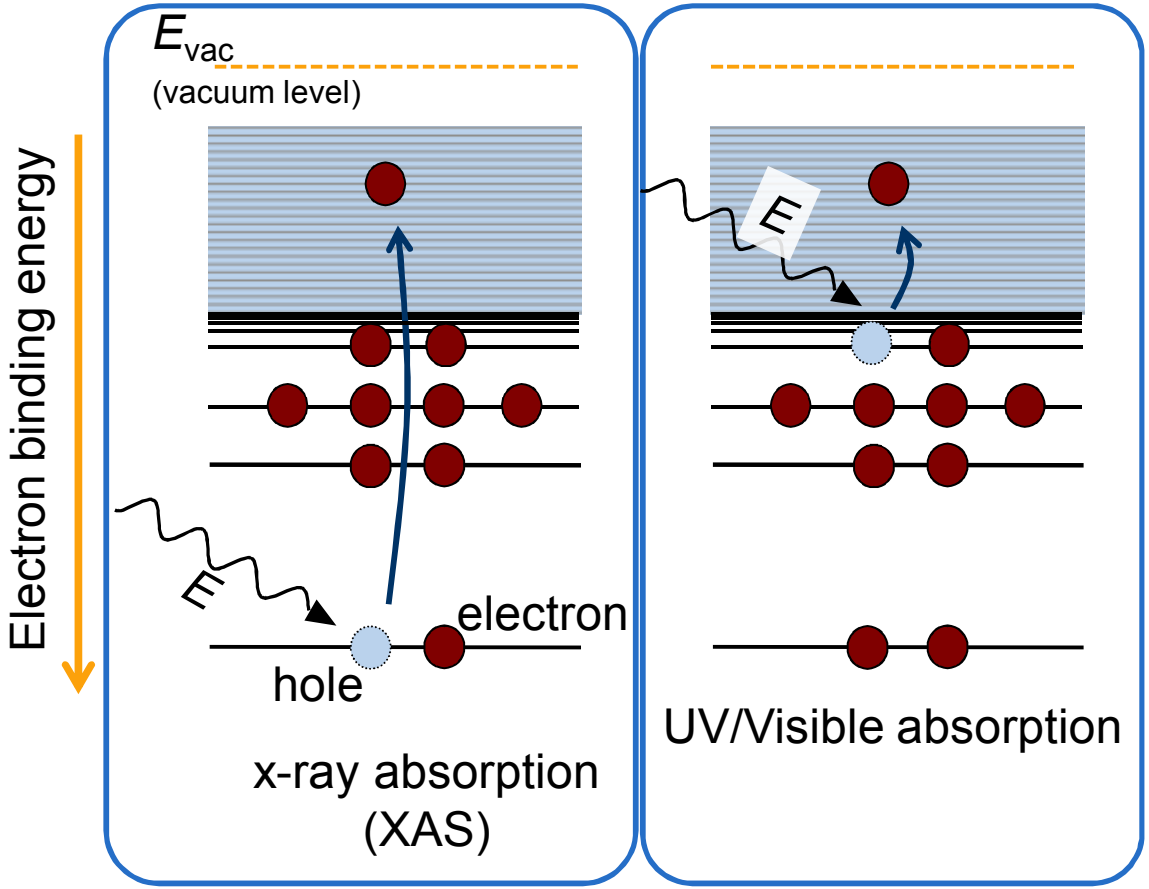


What is used:

Photon energy *E*, polarisation

Interaction term:

$\mathbf{p} \cdot \mathbf{A}$ term in first order



Quantity:

Optical terminology

α [1/cm] = attenuation coefficient

X-ray terminology

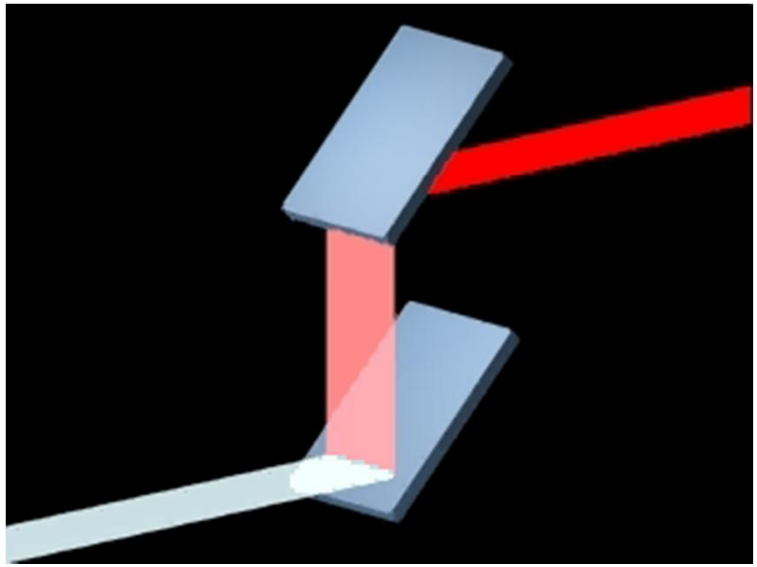
μ [1/cm] = absorption coefficient

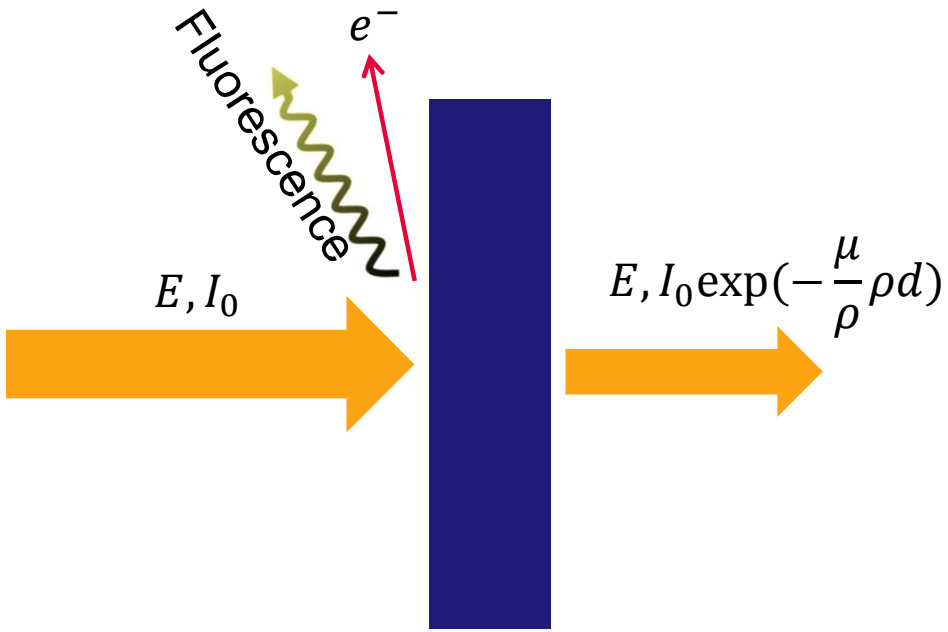
α/ρ or μ/ρ [cm²/g]
= mass attenuation coefficient

Beer-Lambert law: $I = I_0 e^{-\alpha x}$

Absorption spectroscopy

Need monochromatic radiation!
A double-crystal x-ray monochromator:
perfect Si crystals
Optical grating for UV/Vis

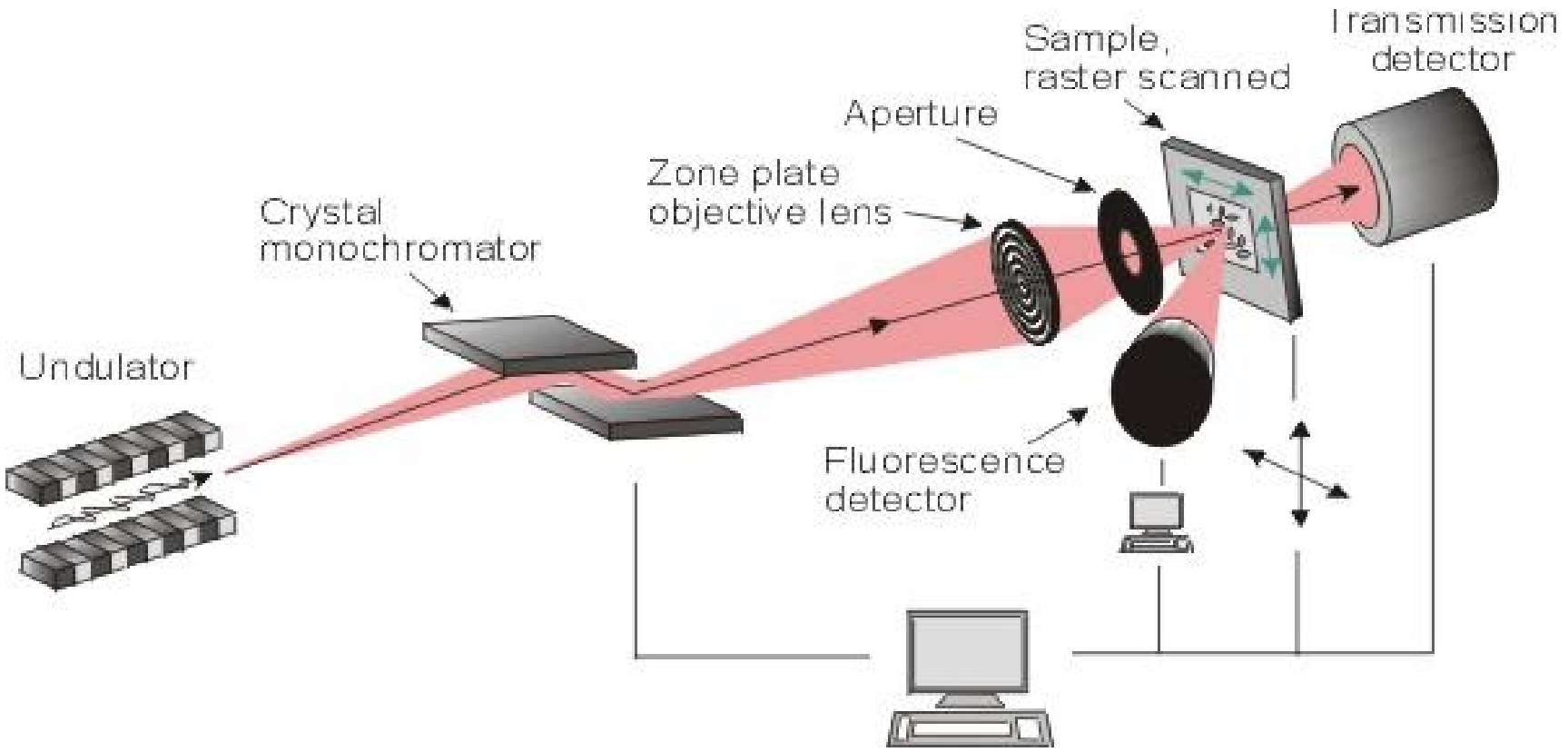




Measure at least one of:
- transmission
- fluorescence yield
- electron yield

Bragg's law: $\lambda = 2d \sin\theta$

Vacuum ultraviolet + x-ray absorption



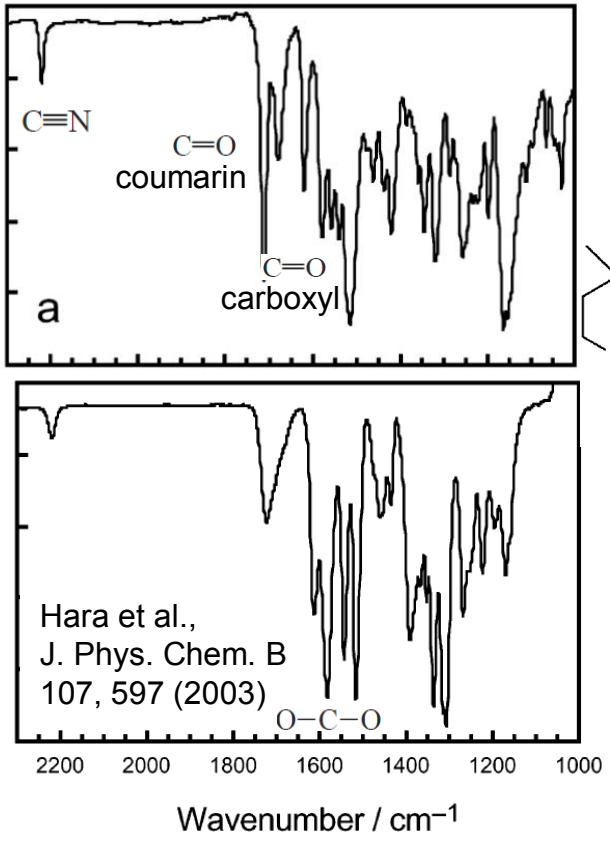
Scanning x-ray microscope, ESRF ID21

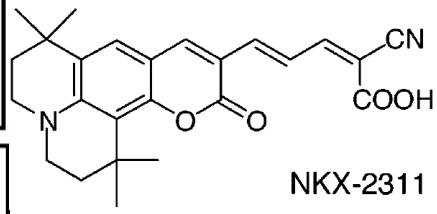
http://www.esrf.eu/UsersAndScience/Experiments/Imaging/ID21/Sxm/Sxm

Fourier transform IR

Fourier transform of signal as a function of wave path length difference

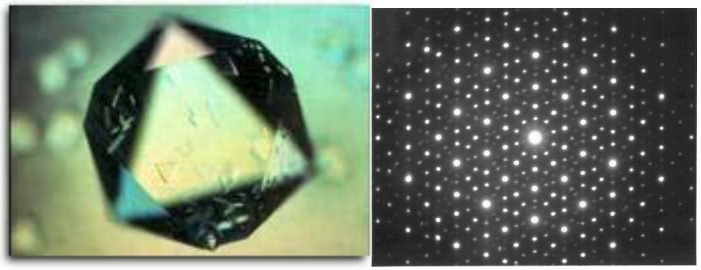
$$T(\omega) = \int_0^\infty I(x)\cos(\alpha\omega x)\,dx$$



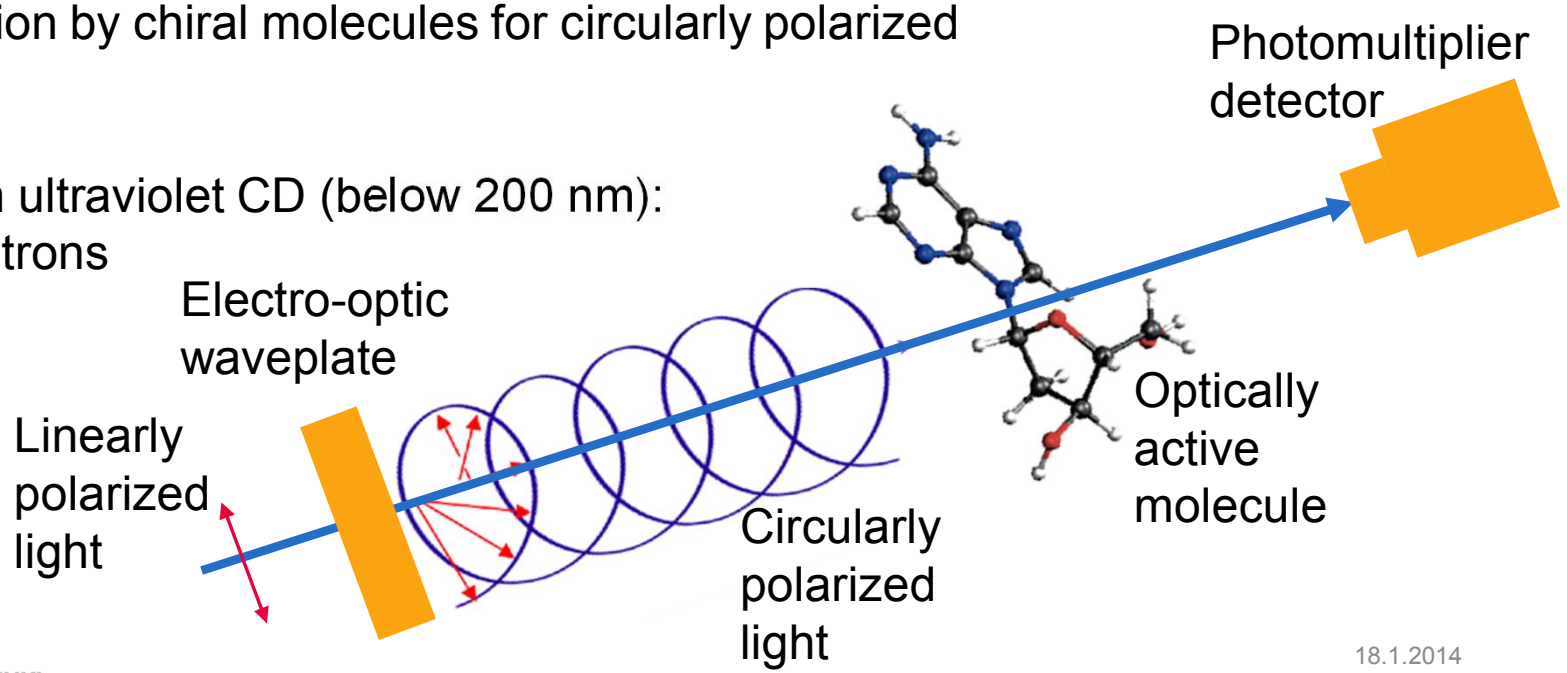


NKX-2311

Circular Dichroism

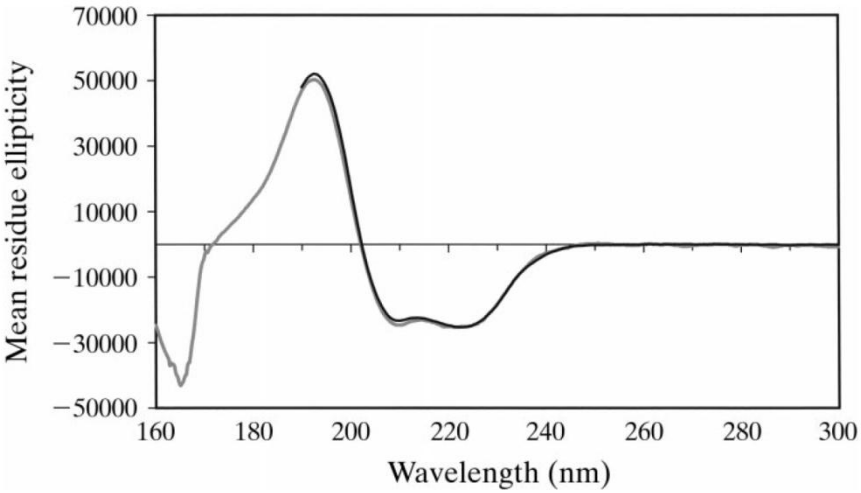


- Crystallography is an excellent tool for structure solving but needs crystals.
- Absorption spectroscopy is a good tool for studies of proteins in solution or molecules in gas phase
- Circular dichroism (CD) is the difference of light absorption by chiral molecules for circularly polarized light
- Vacuum ultraviolet CD (below 200 nm): synchrotrons

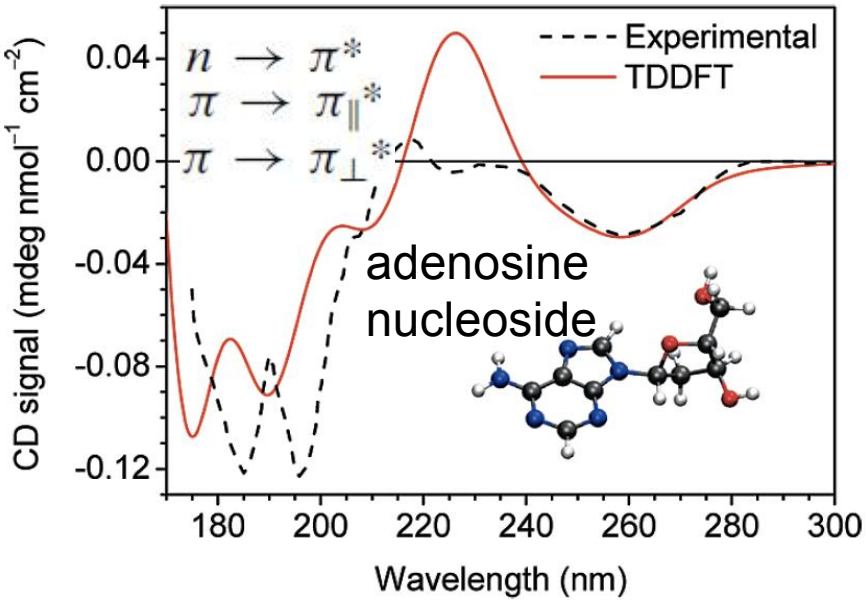


Circular Dichroism

- Each secondary structure of an optically active molecule has a unique fingerprint in the spectrum
- Time resolved studies, formation and change of structures in real conditions
- Traditional UV lamps in laboratory equipment
- Synchrotron radiation sources powerful sources of vacuum UV (<200 nm)



Wallace, J. Synchrotron Radiat. 7, 289 (2000)

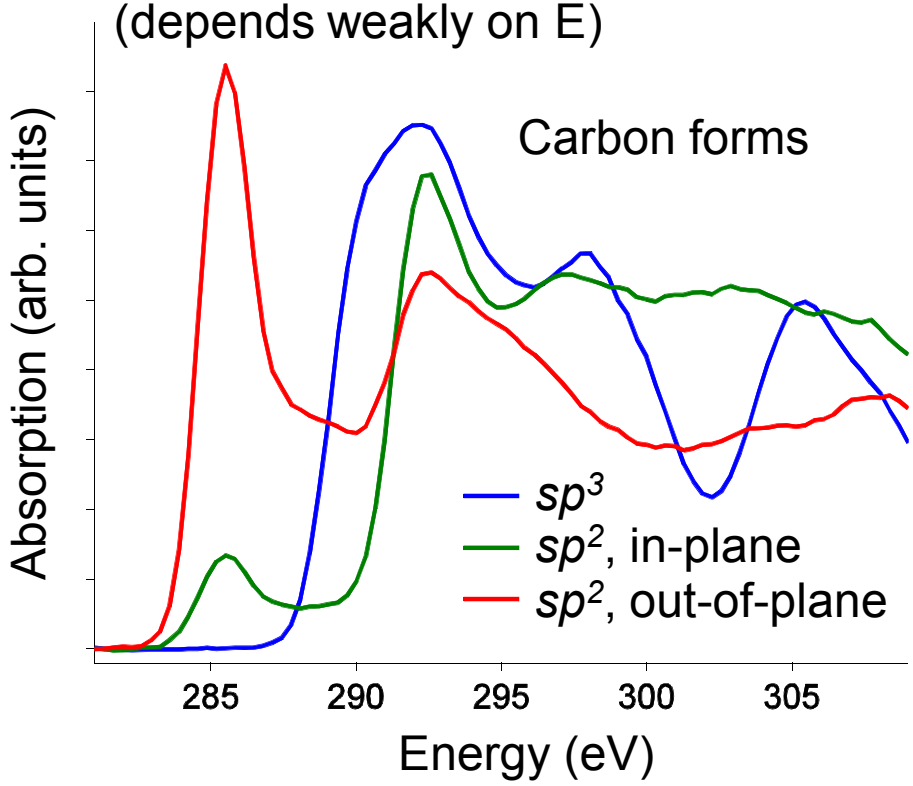


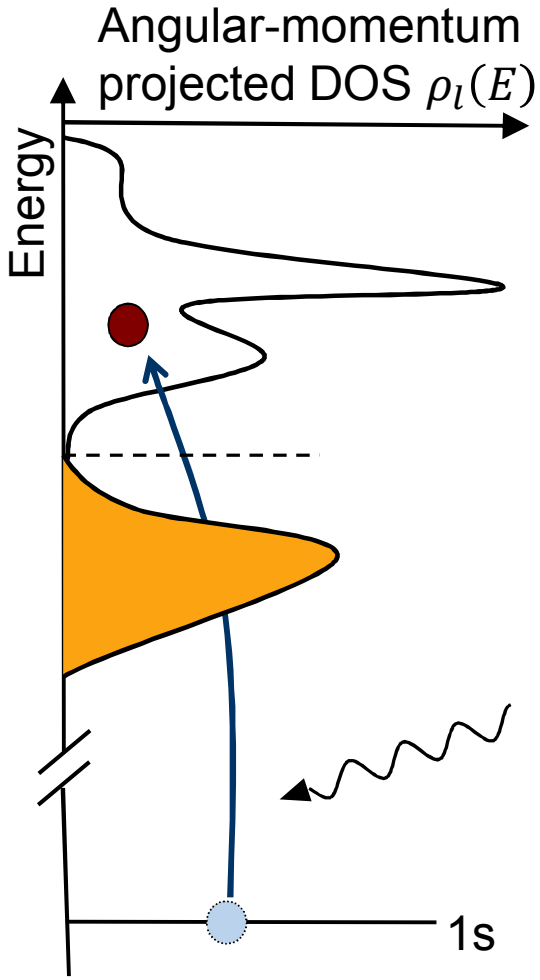
Nielsen *et al.*, J. Phys. Chem. B 113, 9614 (2009)

X-ray absorption

$\mathbf{p} \cdot \mathbf{A}$ term in first order

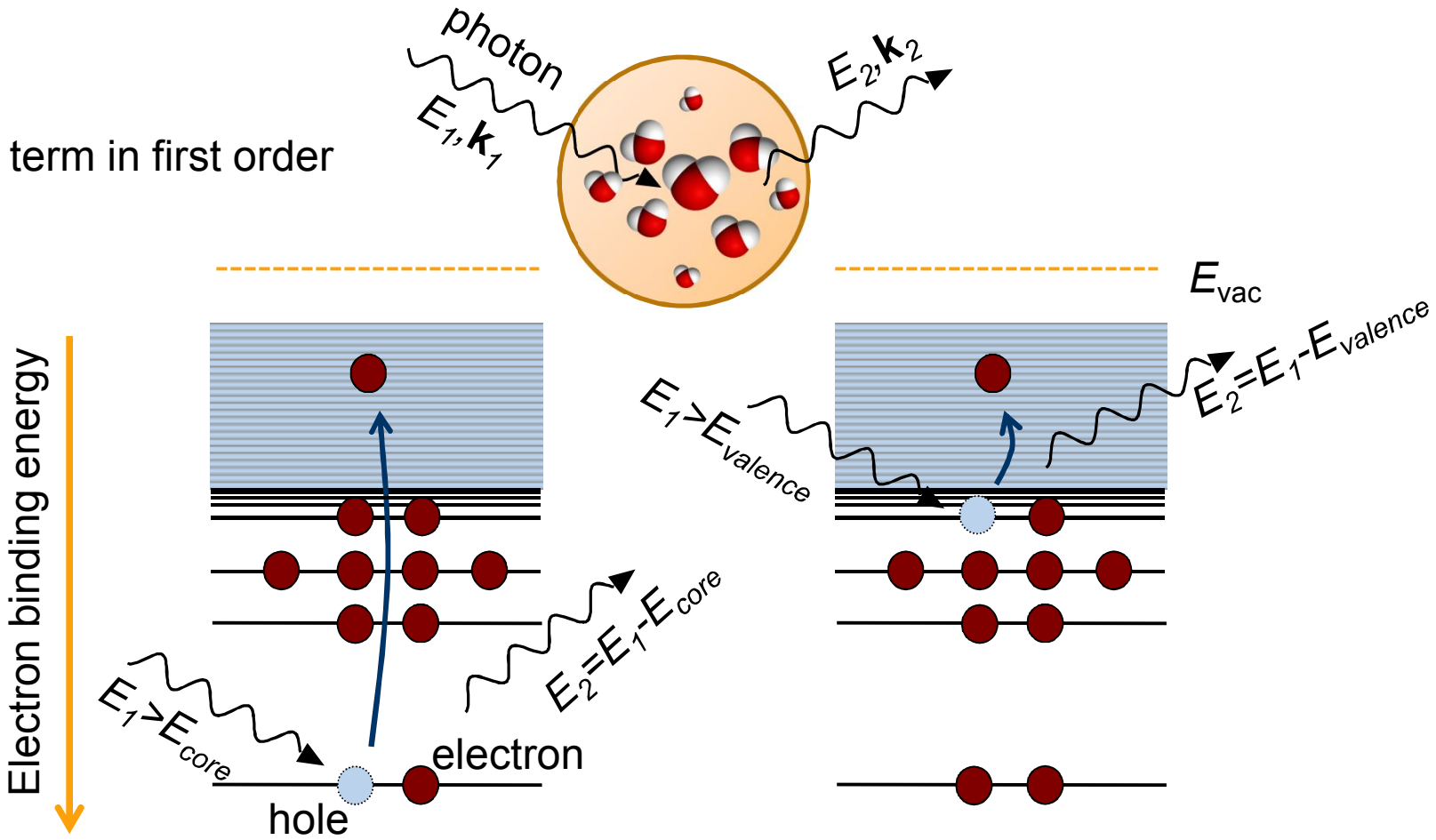
$\mu(E) = M(E)\rho_l(E)$
$M(E)$ is the matrix element
(depends weakly on E)





Inelastic scattering

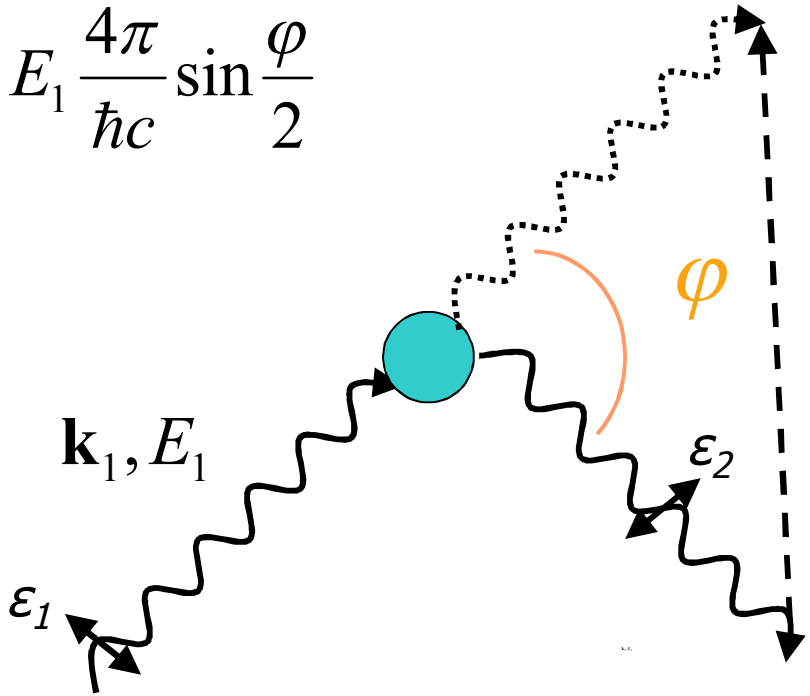
$\mathbf{A} \cdot \mathbf{A}$ term in first order



Energy transfer $E=E_1-E_2$
Momentum transfer $q=k_1-k_2$

Non-resonant x-ray scattering

$$Q \approx E_1 \frac{4\pi}{\hbar c} \sin\frac{\varphi}{2}$$



$$\mathbf{Q} = \mathbf{k}_1 - \mathbf{k}_2$$

$$\frac{d^2\sigma}{dE\, d\Omega} = r_e^2 (\boldsymbol{\epsilon}_1 \cdot \boldsymbol{\epsilon}_2)^2 \, S(\mathbf{Q}, E)$$

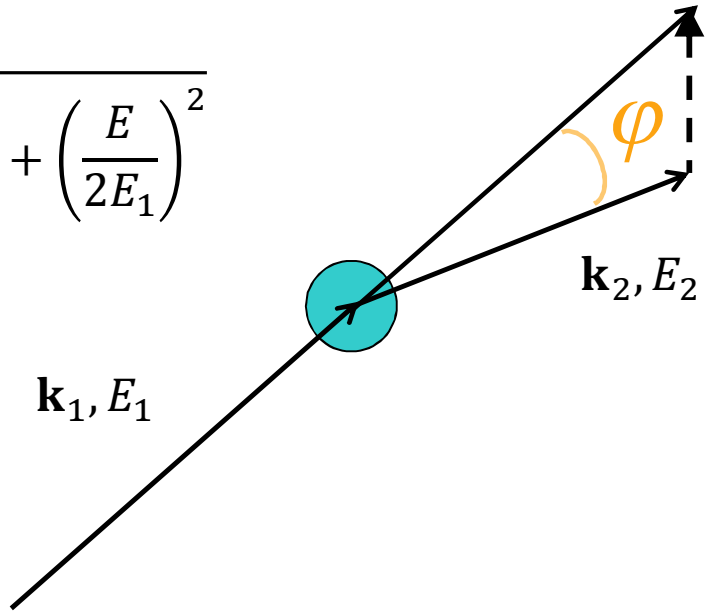
Momentum transfer	$\mathbf{Q} = \mathbf{k}_1 - \mathbf{k}_2$
Energy transfer	$E = E_1 - E_2$

*Dynamic structure factor S(**Q**,E)*

$$S(\mathbf{Q}, E) = \frac{Q^2}{4\pi^2 n} \mathrm{Im}\left[\frac{-1}{\varepsilon(\mathbf{Q}, E)}\right]$$

Electron scattering

$$Q = k_1 \sqrt{\varphi^2 + \left(\frac{E}{2E_1}\right)^2}$$



$$\mathbf{Q} = \mathbf{k}_1 - \mathbf{k}_2$$

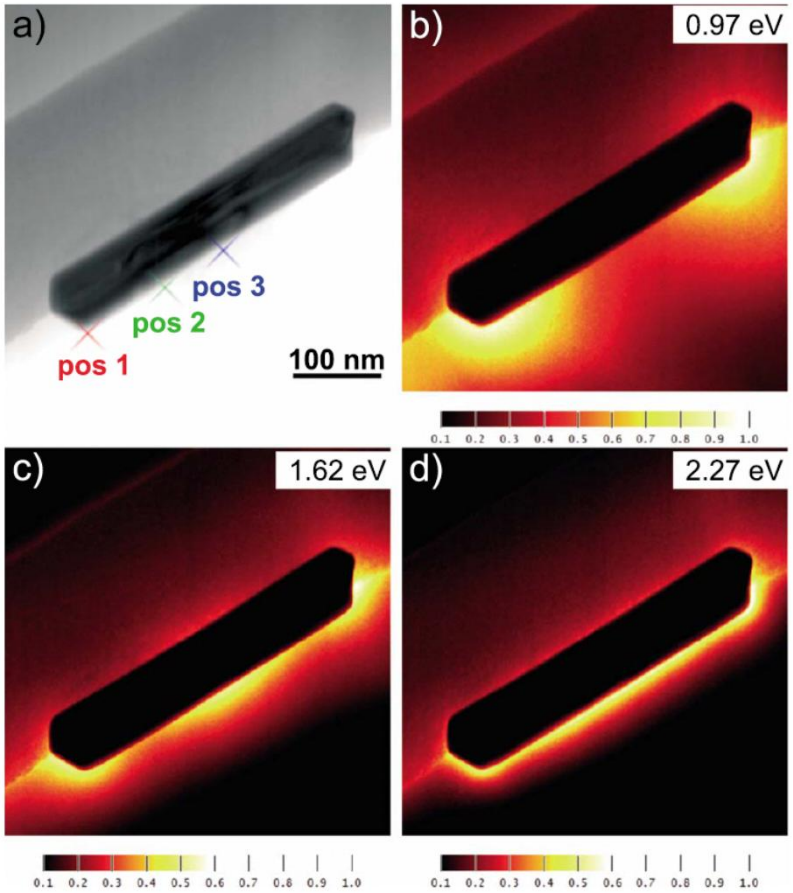
$$\frac{d^2\sigma}{dE\ d\Omega} = \frac{4\hbar\gamma^2}{a_0^2 Q^4} S(\mathbf{Q}, E)$$

*Dynamic structure factor S(**Q**,E)*

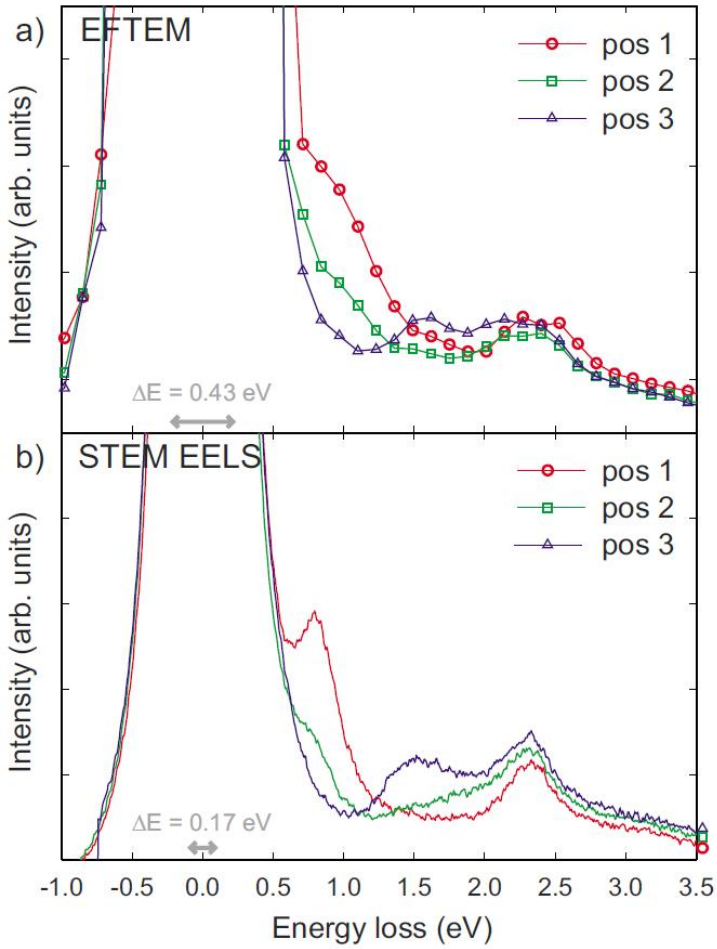
Momentum transfer	$\mathbf{Q} = \mathbf{k}_1 - \mathbf{k}_2$
Energy transfer	$E = (\hbar^2/2m)(k_1 - k_2)$

$$S(\mathbf{Q}, E) = \frac{Q^2}{4\pi^2 n} \mathrm{Im}\left[\frac{-1}{\varepsilon(\mathbf{Q}, E)}\right]$$

Electron microscopy



Plasmon eigenmodes of a gold nanoparticle



B. Schaffer et al. PRB 79, 041401(R) (2009)

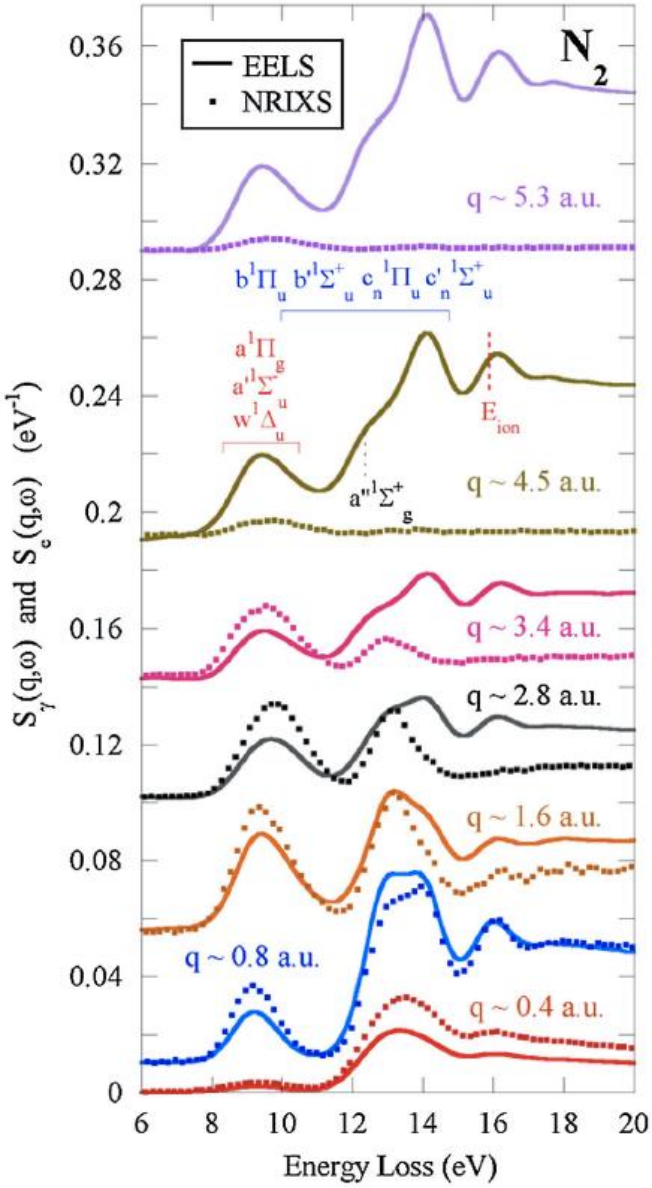
First Born approximation

Comparative study of EELS and IXS valence excitations from nitrogen molecule

J. A. Bradley et al.,
PRL 105, 053202 (2010)

$$\left(\frac{d^2\sigma}{d\Omega d\omega}\right)_{\gamma,e} = \left(\frac{d\sigma}{d\omega}\right)_{\mathrm{Th,Ru}} S(\mathbf{q},\omega)$$

In principle..
But true for all dynamic range?

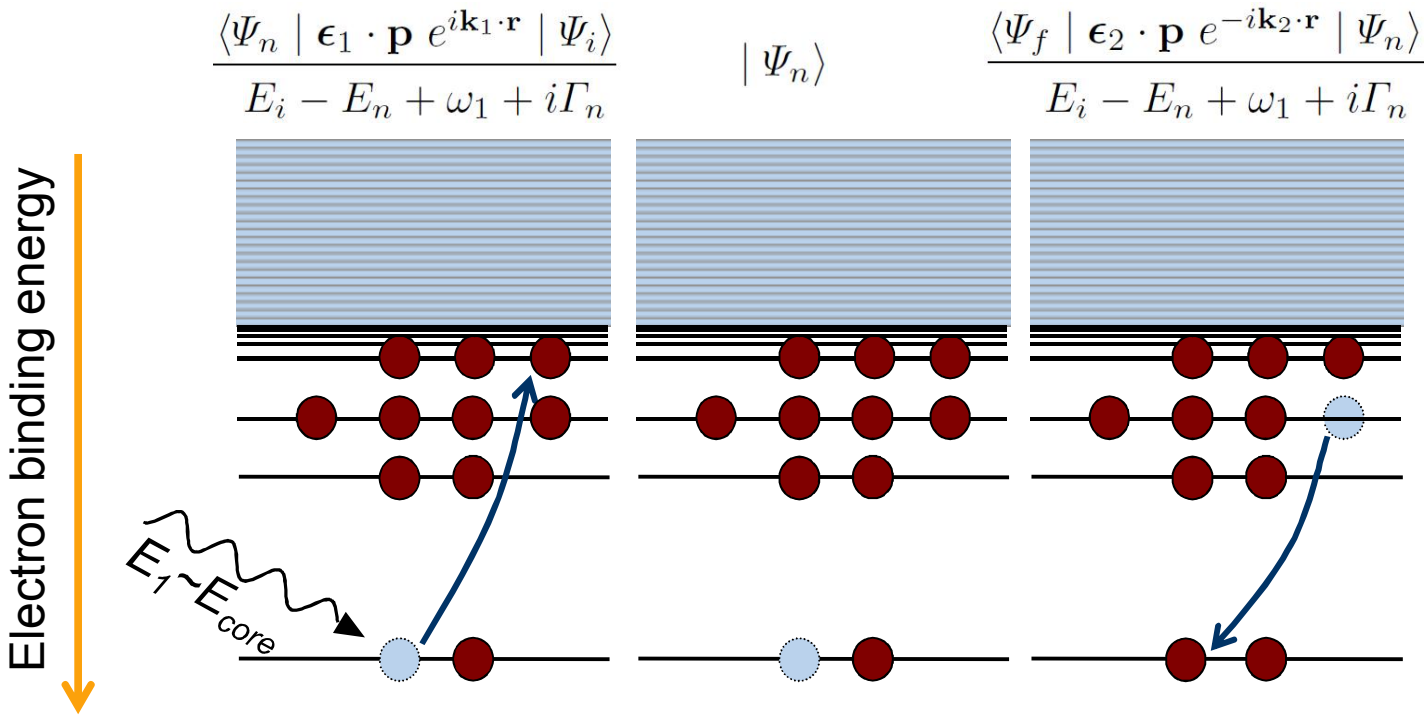


Lyman-Birge-Hopfield (LBH) band

Resonant inelastic scattering

$\mathbf{p} \cdot \mathbf{A}$ term in second order

Ground state ⟶ Intermediate state ⟶ Final state



Photon energies E_1, E_2, polarisation, momentum

ID20 @ ESRF: Resonant IXS

ESRF

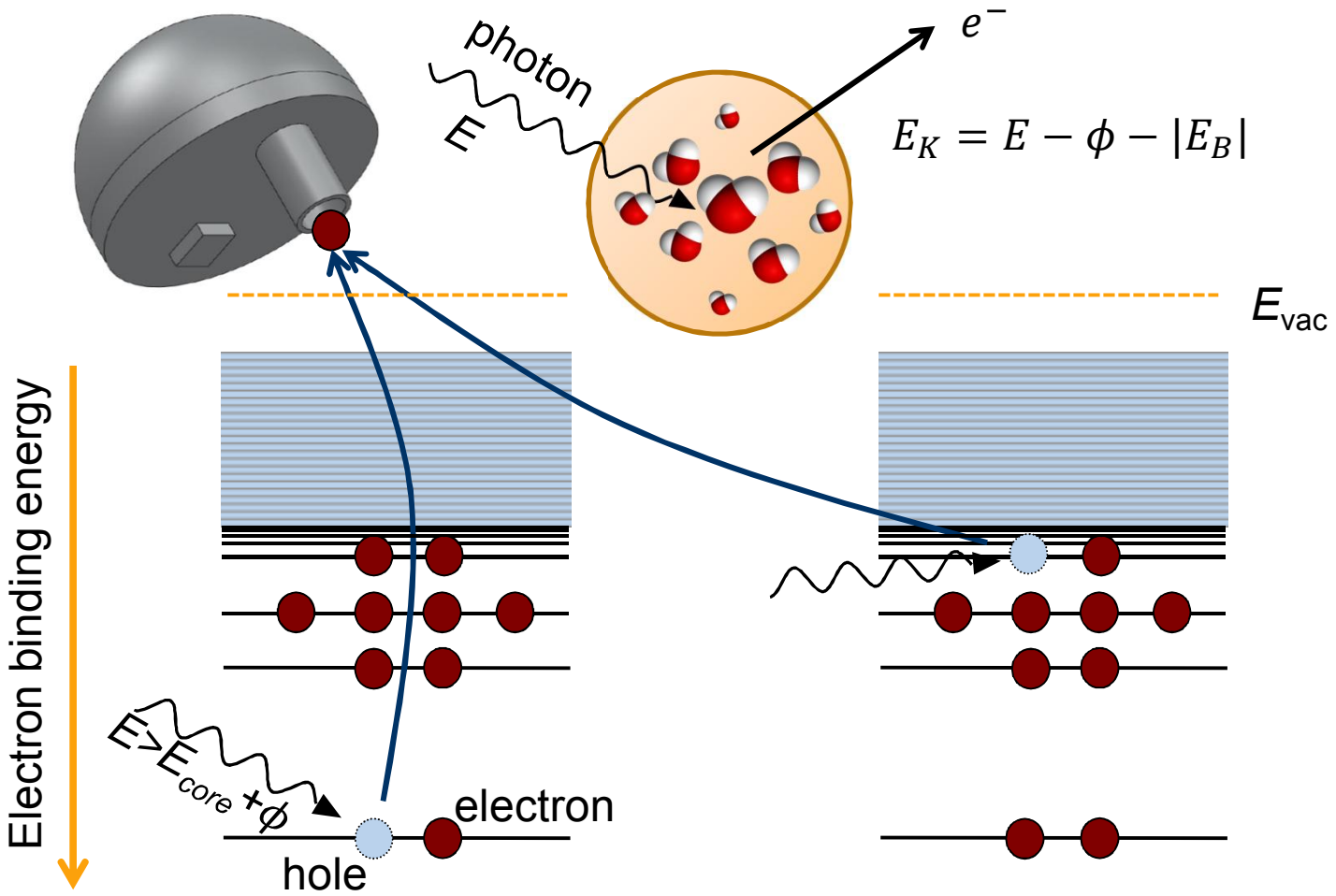
5 individual scattered photon detectors

$\Delta E \sim 25$ meV @ 10 keV

High flux and/or several **q**'s

Credit: ID20 team (Laura Simonelli, M. Moretti Sala, Ali Al-Zein, R. Verbeni, M. Krisch, G. Monaco, et al.)

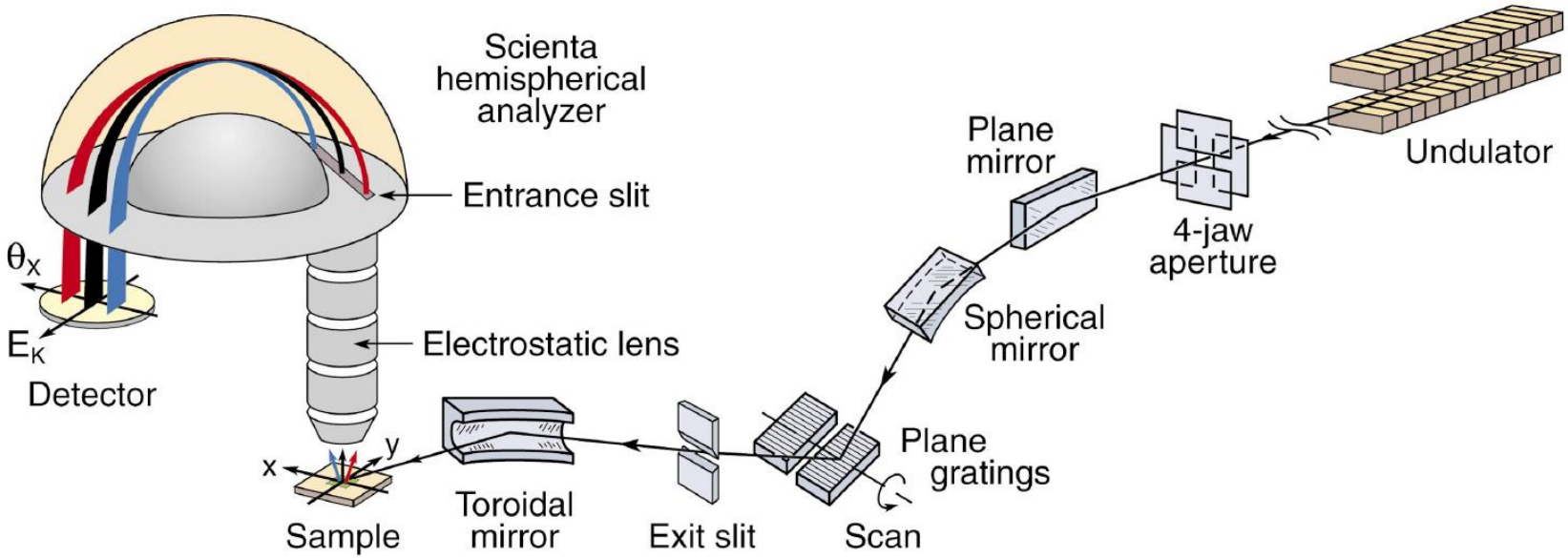
Photoemission



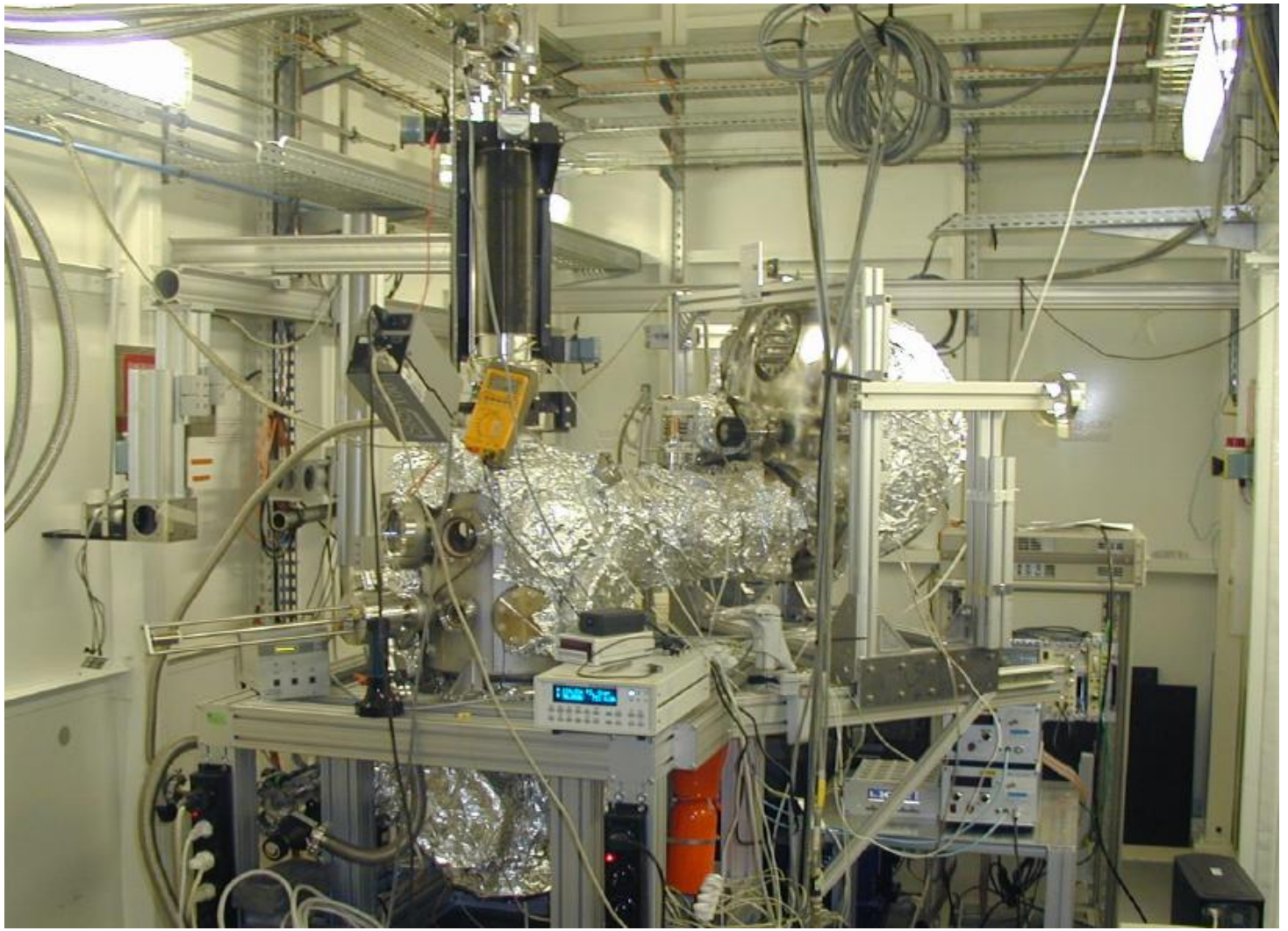
Photon energy *E*, polarisation, momentum...

Photoemission

A. Damascelli et al., Rev. Mod. Phys 75, 473 (2003)



Powerful tool for
- ESCA (electron spectroscopy for chemical analysis): identification of core levels, shifts, shape
- Valence PES for band mapping (ARPES)
- Circular dichroism

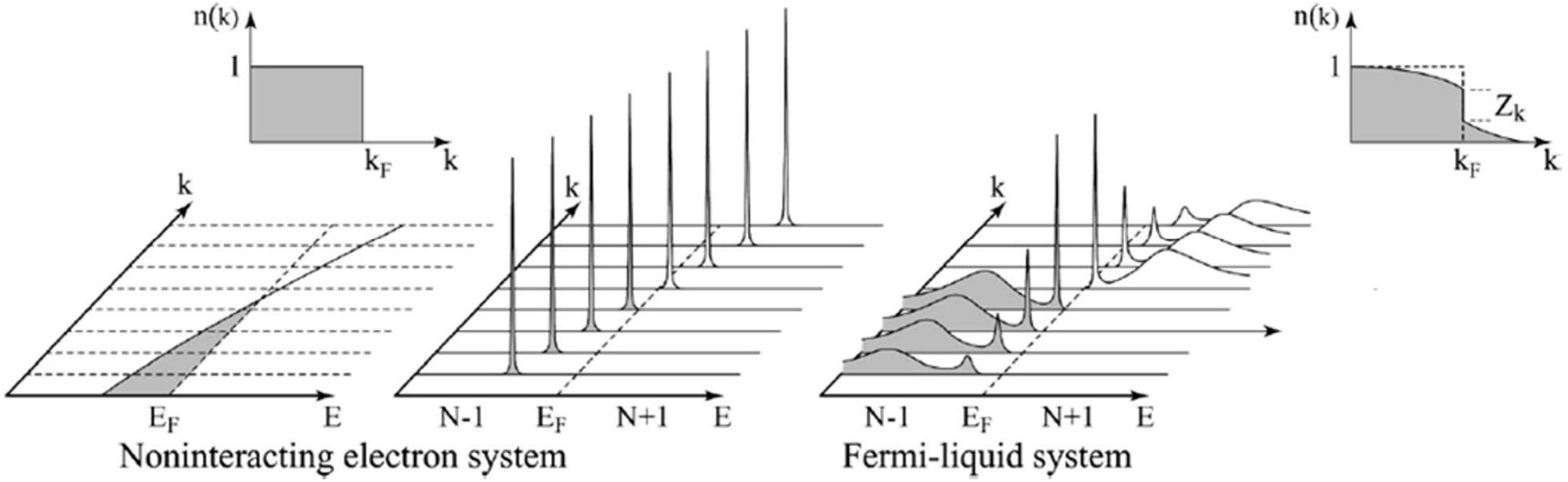


The Volume Photoemission (VOLPE) spectrometer at ESRF
(G. Panaccione, M. Sacchi, et al.)

Photoemission

A. Damascelli et al., Rev. Mod. Phys 75, 473 (2003)

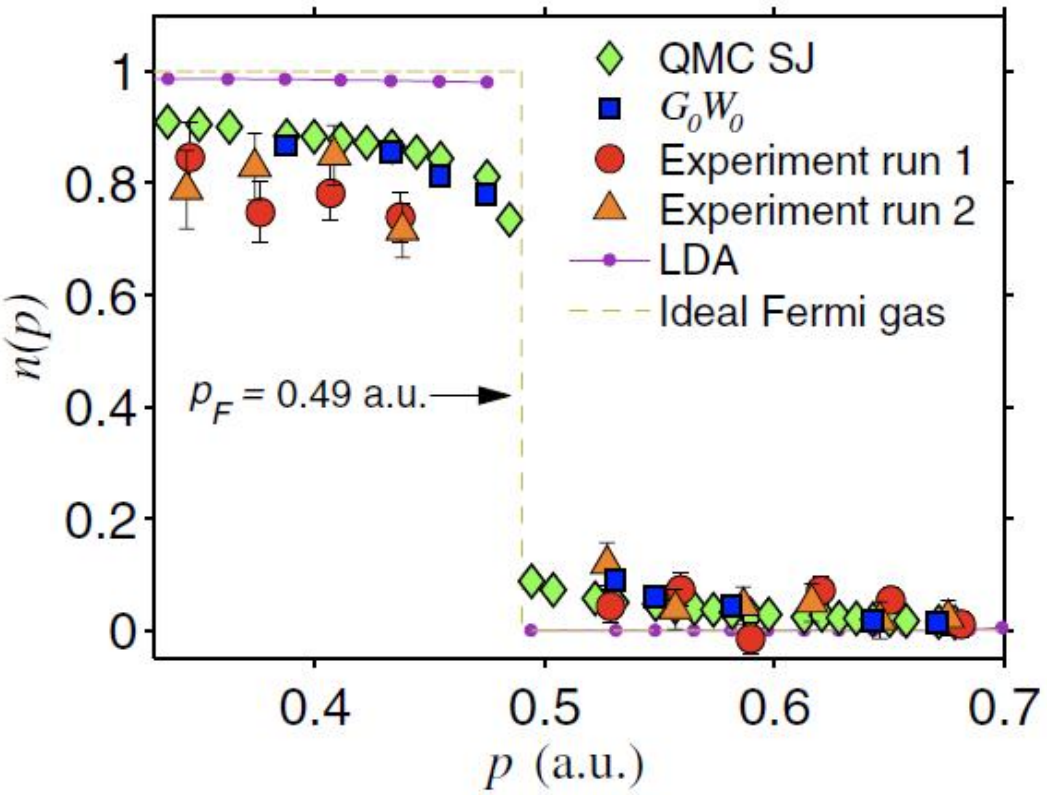
One-electron removel and addition spectra in a crystal



$$\mathrm{PES} \propto \sum_{f,i} \left| M_{f,i}^{\mathbf{p}} \right|^2 A(\mathbf{p}, E) \delta \left(E_K + E_m^{N-1} - E_i^N - \omega_1 \right)$$

Spectral function

Quasiparticle renormalisation factor



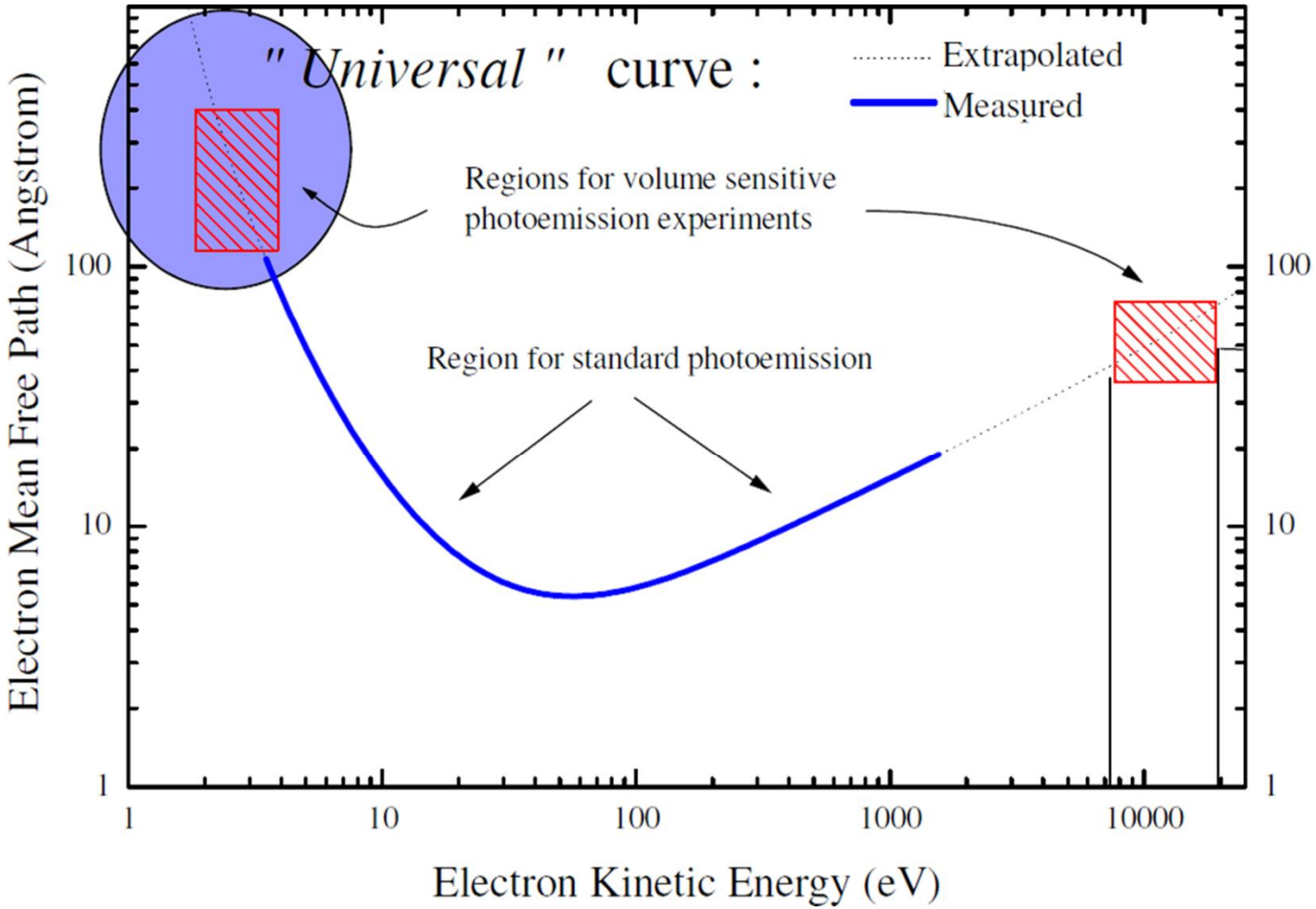
For Na ($r_s = 3.99$), experimental

$$Z_{k_F} = 0.58 \pm 0.07$$

Method: Compton spectroscopy

S. Huotari, J. A. Soininen, T. Pylkkänen, K. Hämäläinen, A. Issolah, A. Titov, J. McMinis, J. Kim, K. Esler, D. M. Ceperley, M. Holzmann, V. Olevano, Phys. Rev. Lett. 105, 086403 (2010)

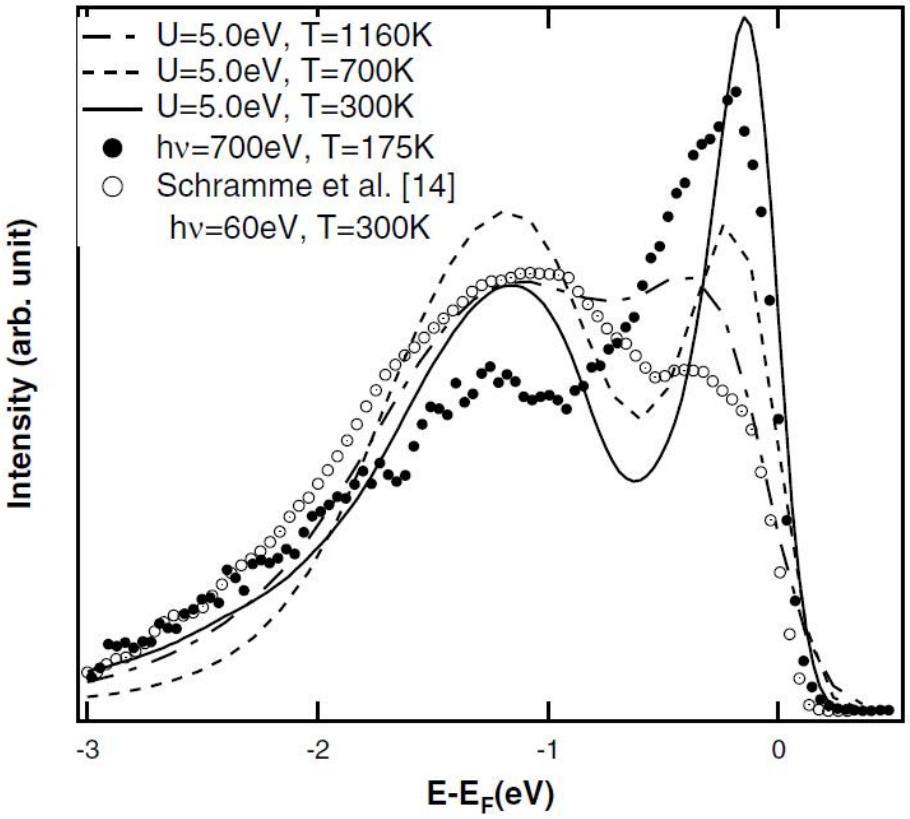
Bulk-sensitive photoemission

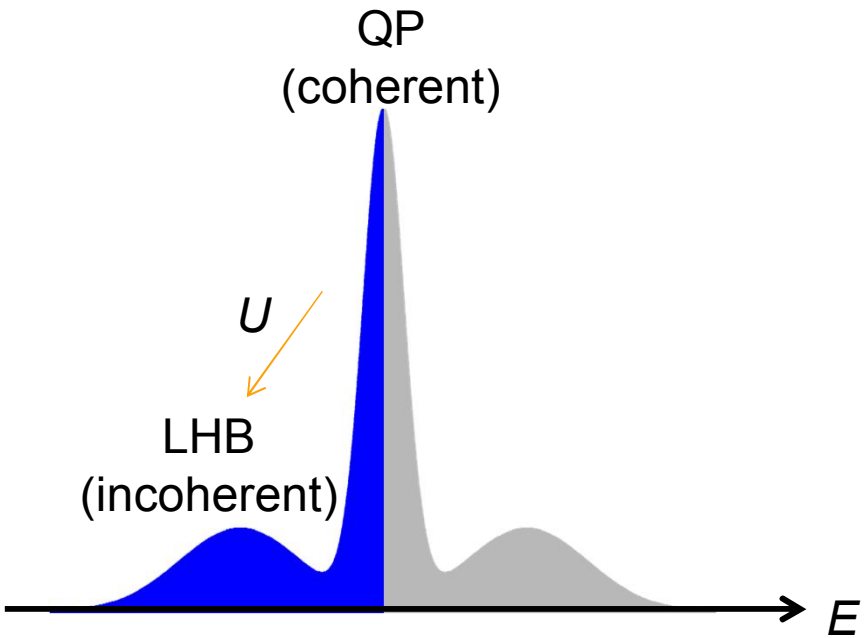


Bulk-sensitive photoemission

The Mott-Hubbard insulator V_2O_3

S.K. Mo et al., PRL 90, 186403 (2003)

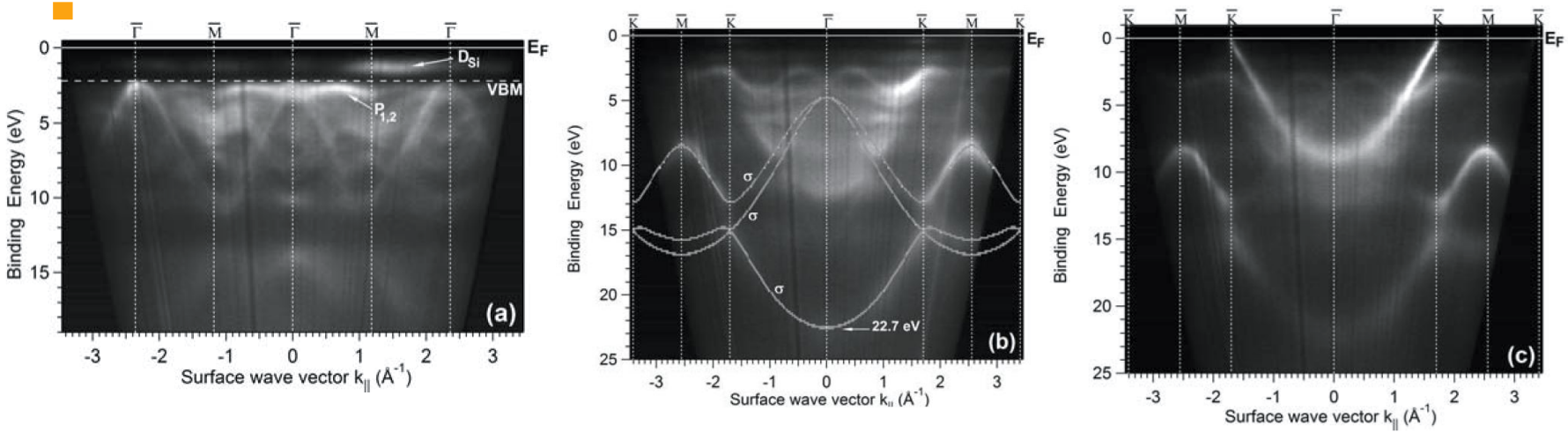


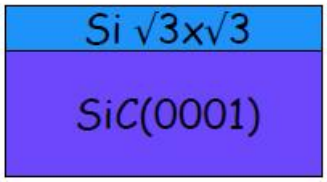


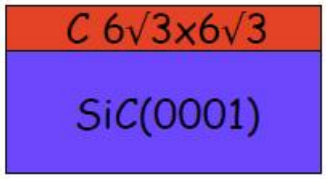
Half-filled one-band Hubbard model

U = on-site Coulomb repulsion

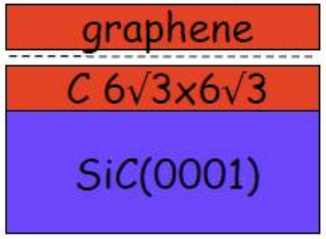
Band mapping by ARPES







sp^2-bonded p_z hybridized with SiC; π band not developed

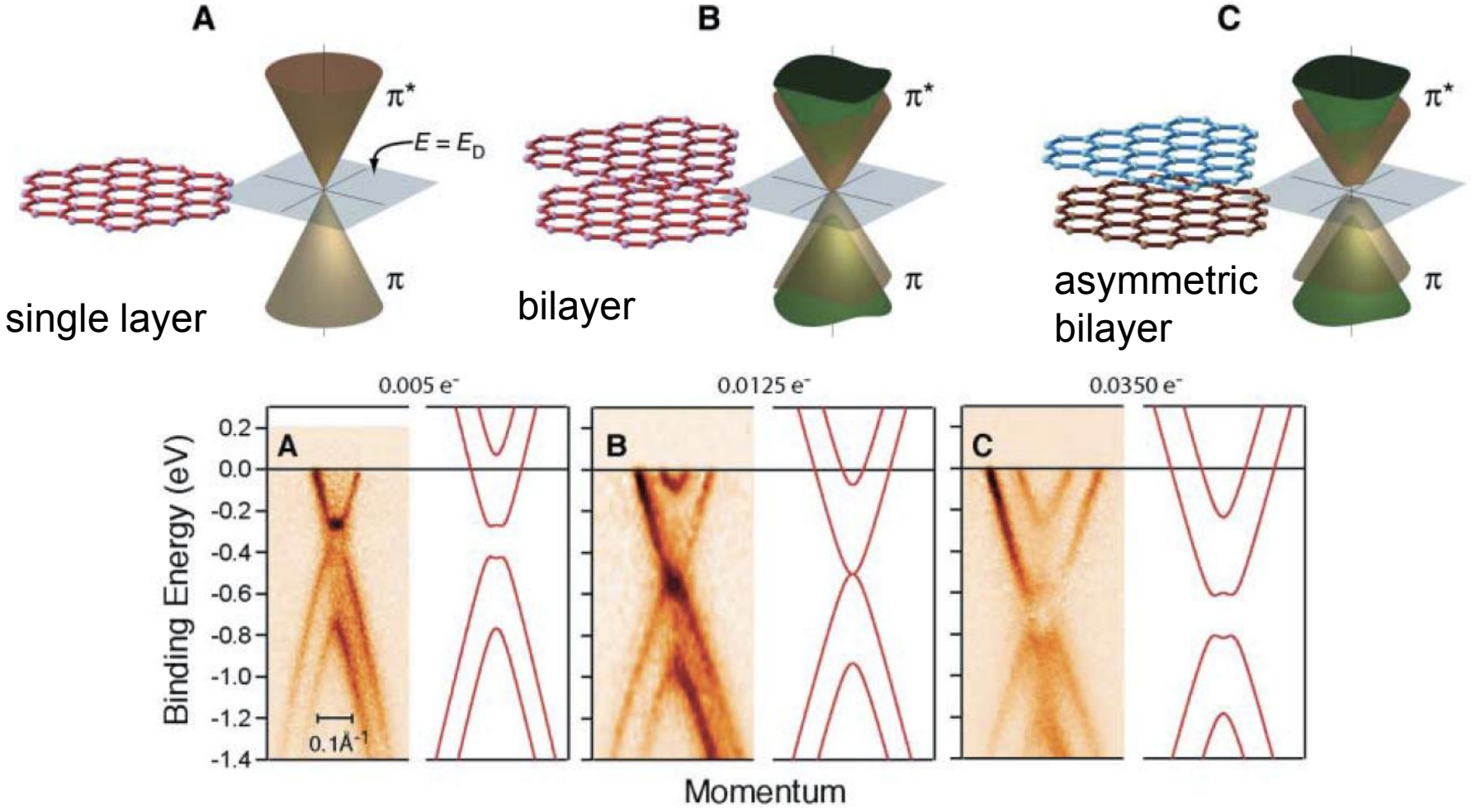


sp^2-bonded p_z derived band, van der Waals-bonded to 6√3 layer

K. V. Emtsev et al., http://arxiv.org/abs/cond-mat/0609383

Credits: from a talk by K.Horn et al.
www.uv.es/wsetld/archivos/Tuesday/WS10-Horn.pdf

Controlling the Electronic Structure of Bilayer Graphene



T. Ohta et al., Science 313, 951 (2006)

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