Resonant inelastic x-ray scattering (RIXS) - an element specific tool to map electronic structure and elementary excitations

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Center for Free-Electron Laser Science

Outline

- Basic considerations

- Instrumental aspects
  - soft x-rays
  - hard x-rays („real photons“)

- RIXS as element and site specific electronic structure tool
  - molecular orbitals
  - band mapping
  - interference effects

- RIXS and elementary excitations
  - Molecular vibrations
  - Phonons
  - Magnons, Orbitons,….

- RIXS – dynamical aspects
  - intermediate state wave packet dynamics
  - electron-phonon coupling

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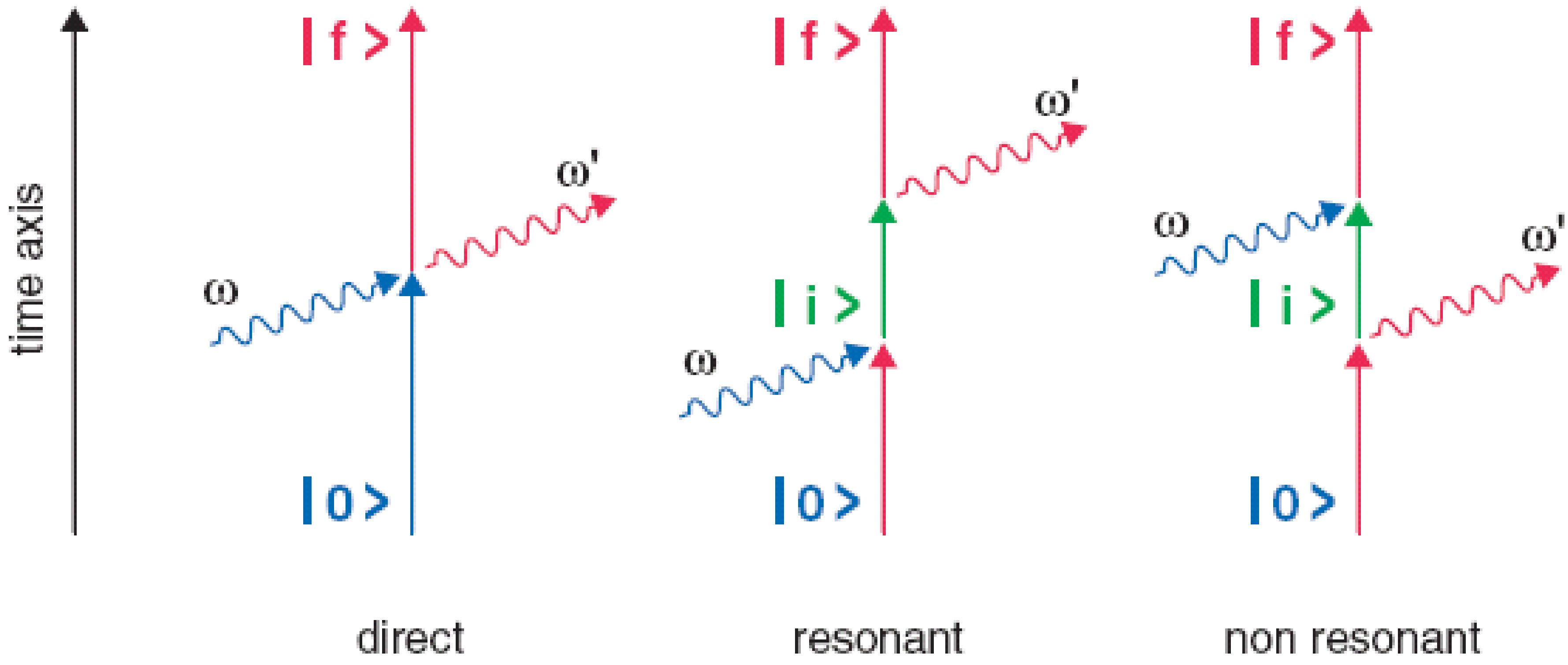
Schematics

Energy transfer $\Delta E = E_f - E_g = \hbar\omega - \hbar\omega'$

Momentum transfer/ħ $\vec{q} = \vec{k}_f - \vec{k}_i$

„Photon in – photon out" spectroscopy

Relevant diagrams

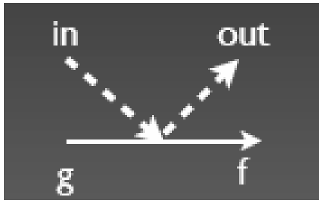


Second order perturbation theory yields Kramers-Heisenberg formula

in

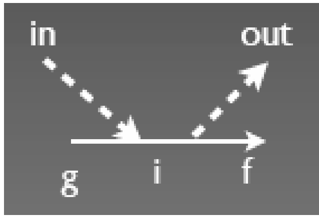
„direct" term

$$\sigma^{scatt} \propto \sum_f \left| (\vec{\epsilon}_{-\vec{k},\omega_{out}} \cdot \vec{\epsilon}_{\vec{k},\omega_{in}}) \langle f | \sum_Z e^{\imath(\vec{k}_{out}-\vec{k}_{in})\vec{r}} | g \rangle \right.$$



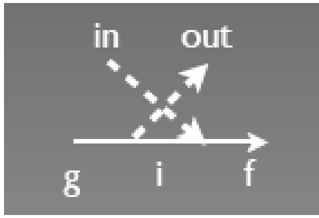
„resonant" term

$$+ \sum_i const \cdot \left[\frac{\langle f | \vec{\epsilon}_{-\vec{k},\omega_{out}} \cdot \vec{d}_{-\vec{k},\omega_{out}} | i \rangle \langle i | \vec{\epsilon}_{\vec{k},\omega_{in}} \cdot \vec{d}_{\vec{k},\omega_{in}} | g \rangle}{\hbar\omega_{in} - E_i + E_g + \imath\Gamma_i/2} \right.$$



„non-resonant" term

$$\left. - \frac{\langle f | \vec{\epsilon}_{-\vec{k},\omega_{in}} \cdot \vec{d}_{-\vec{k},\omega_{in}} | i \rangle \langle i | \vec{\epsilon}_{\vec{k},\omega_{out}} \cdot \vec{d}_{\vec{k},\omega_{out}} | g \rangle}{\hbar\omega_{out} + E_i - E_g} \right] \Bigg|^2$$



energy conservation

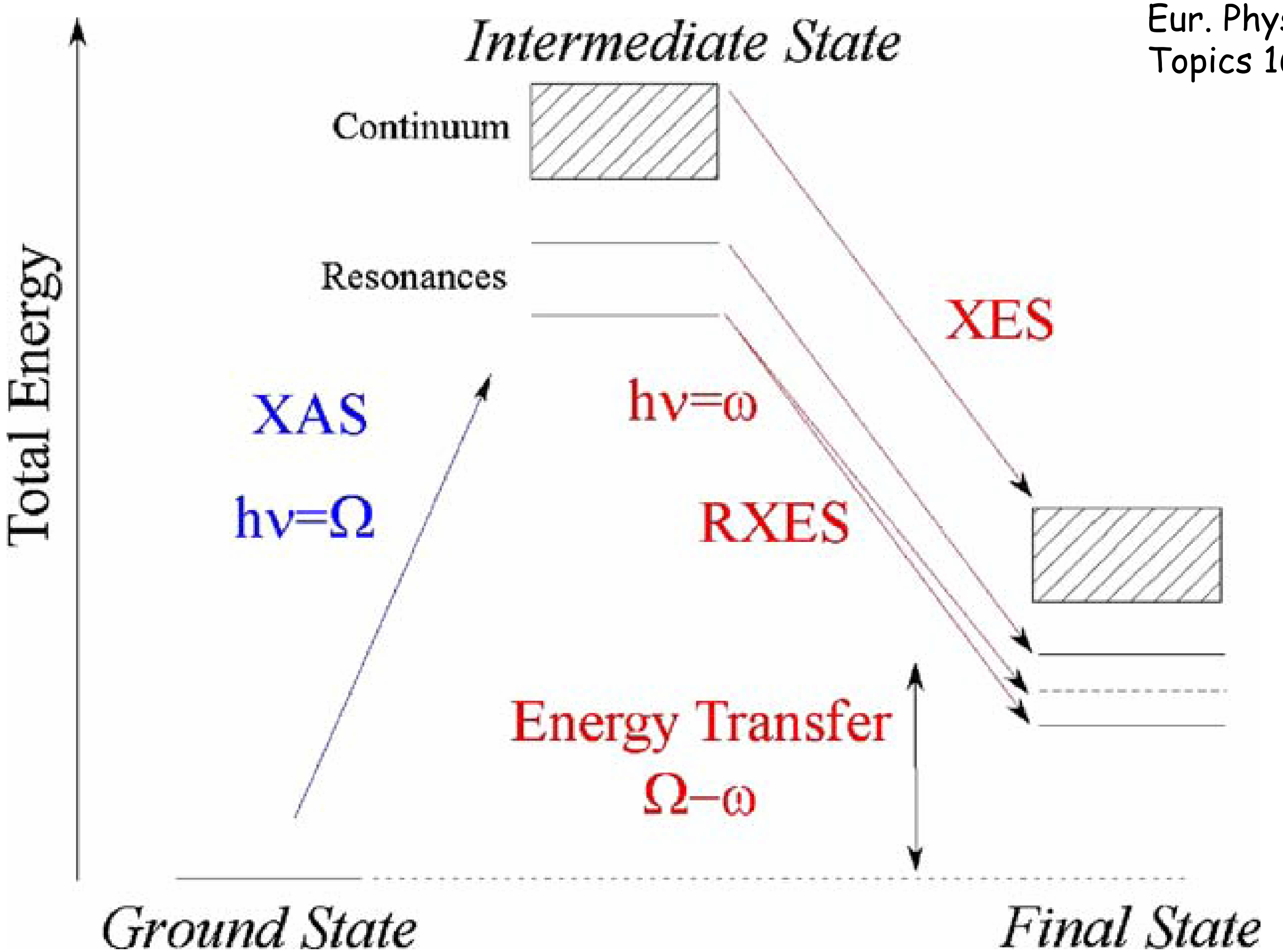
$$\cdot \frac{\Gamma_f}{2\pi \left[(\hbar\omega_{out} + E_f - E_g - \hbar\omega_{in})^2 + \left(\frac{\Gamma_f}{2}\right)^2 \right]}$$

„Lorentzian" line width only determined by final state lifetime

after M. Beye Ph.D thesis

Resonant inelastic scattering

After P. Glatzel et al., Eur. Phys. J. Special Topics 169, 207 2009)



Sometimes also termed resonant x-ray emission, resonant fluorescence and resonant x-ray Raman

Resonant inelastic scattering

Including interference effects (sum over intermediate states)

$$F(\Omega,\omega) = \sum_f \left| \sum_n \frac{\langle f|T_2|n\rangle\langle n|T_1|g\rangle}{E_g - E_n + \Omega - i\frac{\Gamma_n}{2}} \right|^2 \times \frac{\frac{\Gamma_f}{2\pi}}{(E_g - E_f + \Omega - \omega)^2 + \frac{\Gamma_f^2}{4}}\,.$$

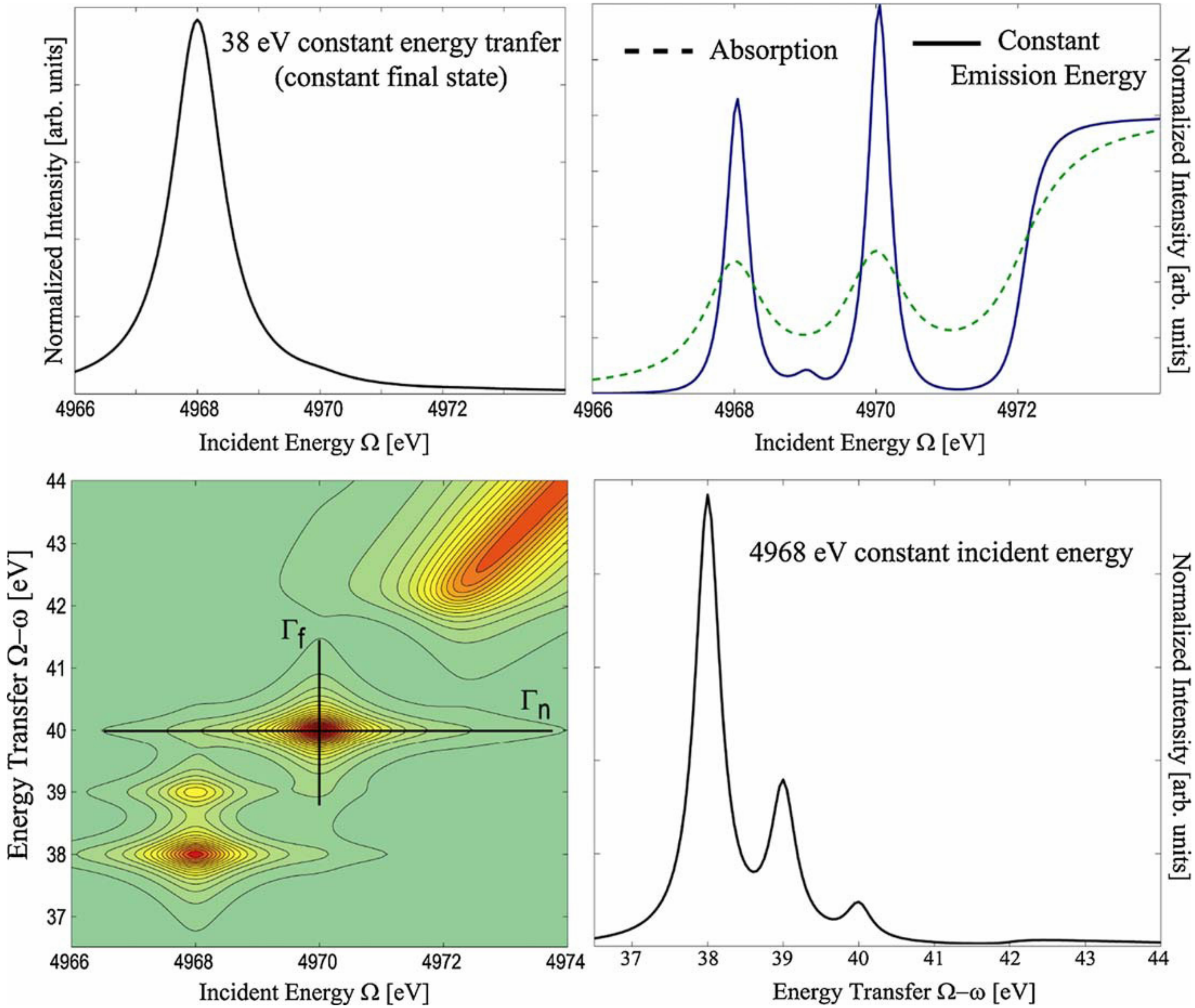
neglecting interference effects (sum outside brackets)

$$F(\Omega,\omega) = \sum_f \sum_n \frac{\langle f|T_2|n\rangle^2\langle n|T_1|g\rangle^2}{(E_g - E_n + \Omega)^2 + \frac{\Gamma_n^2}{4}} \times \frac{\frac{\Gamma_f}{2\pi}}{(E_g - E_f + \Omega - \omega)^2 + \frac{\Gamma_f^2}{4}}\,.$$

width ~Γ_n width ~Γ_f

After P. Glatzel et al., Eur. Phys. J. Special Topics 169, 207–214 (2009)

Lifetime broadening effects – model system

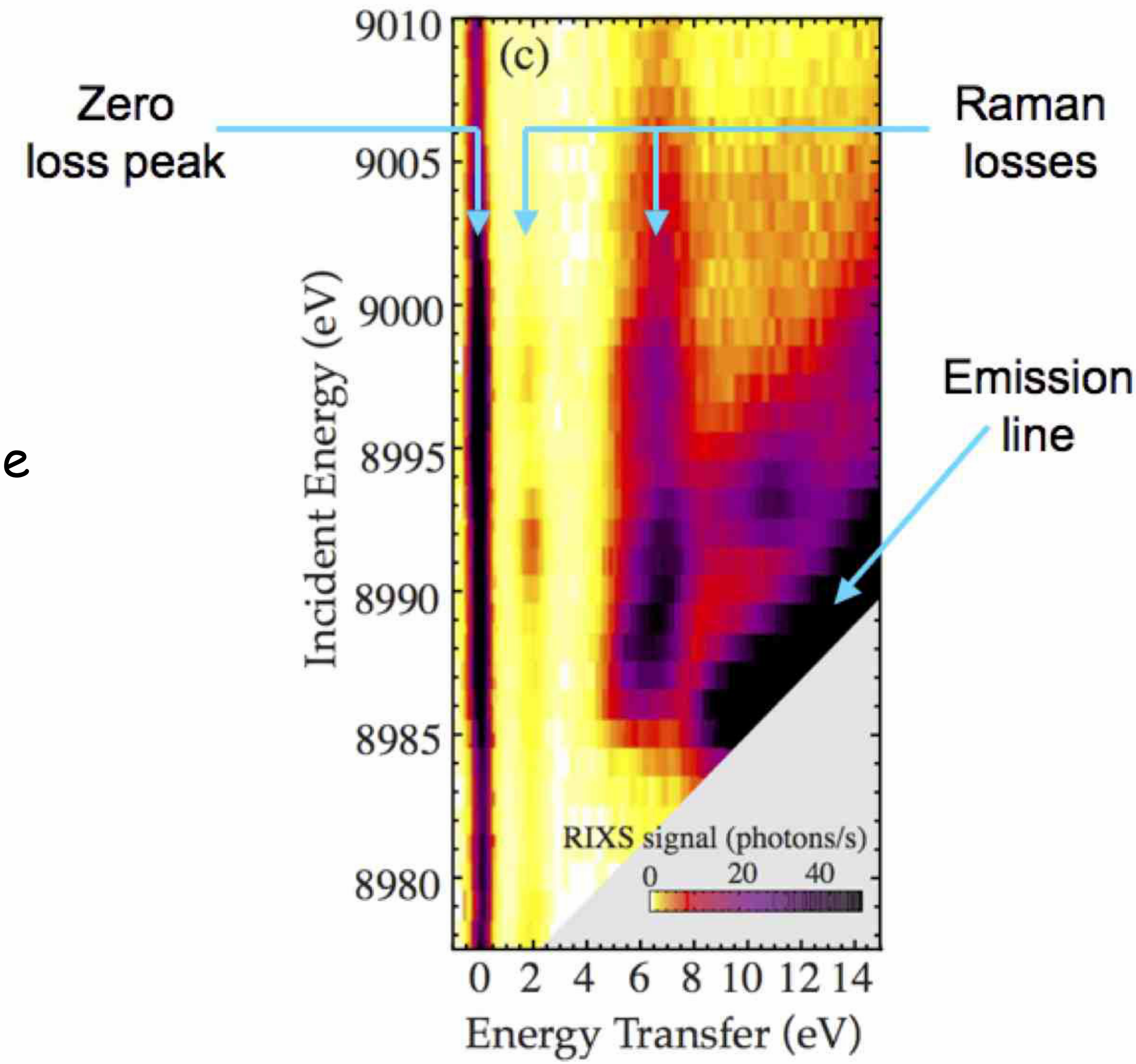


After P. Glatzel et al., Eur. Phys. J. Special Topics 169, 207-214 (2009)

Raman features vs. emission lines

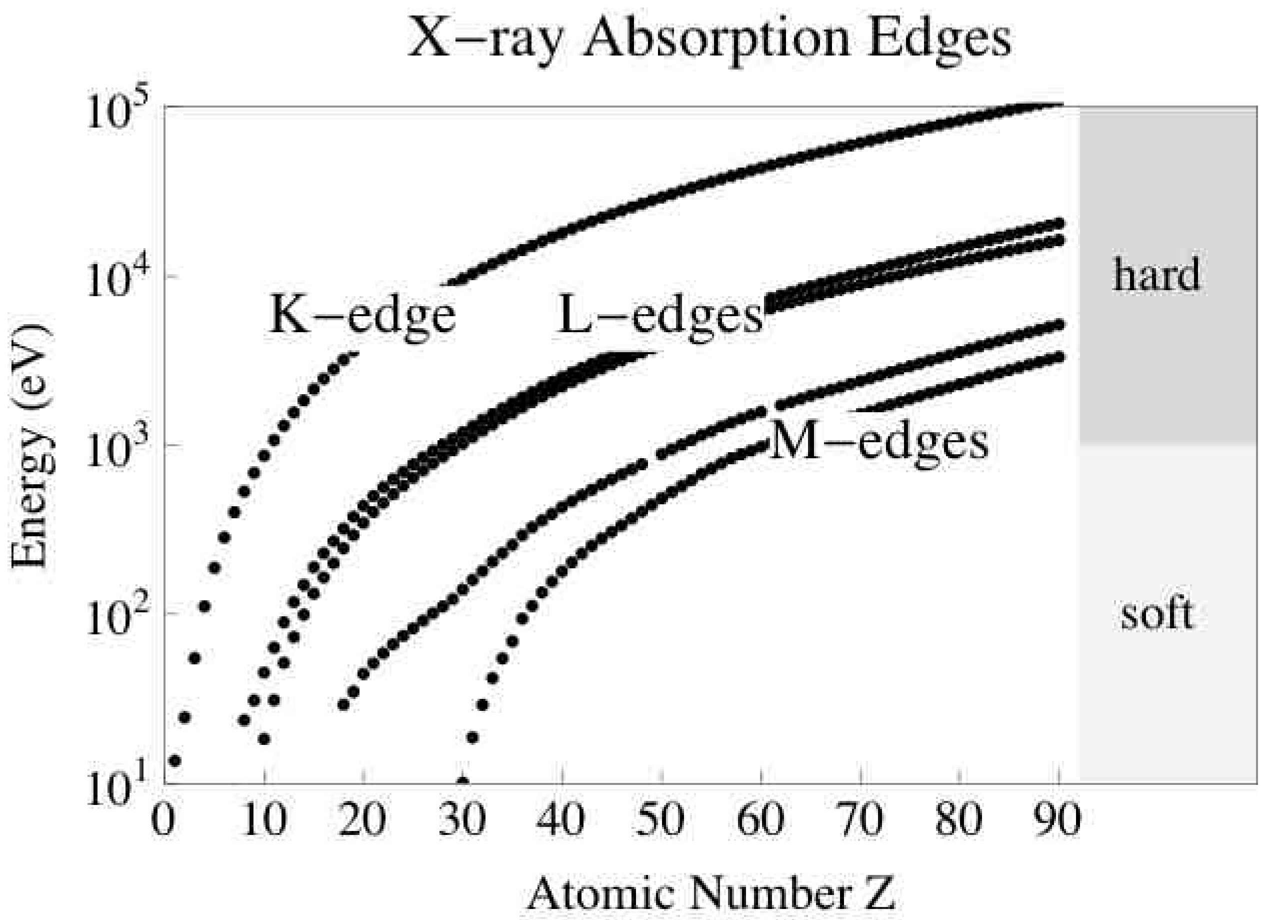
CuB_2O_4

Cu K-edge



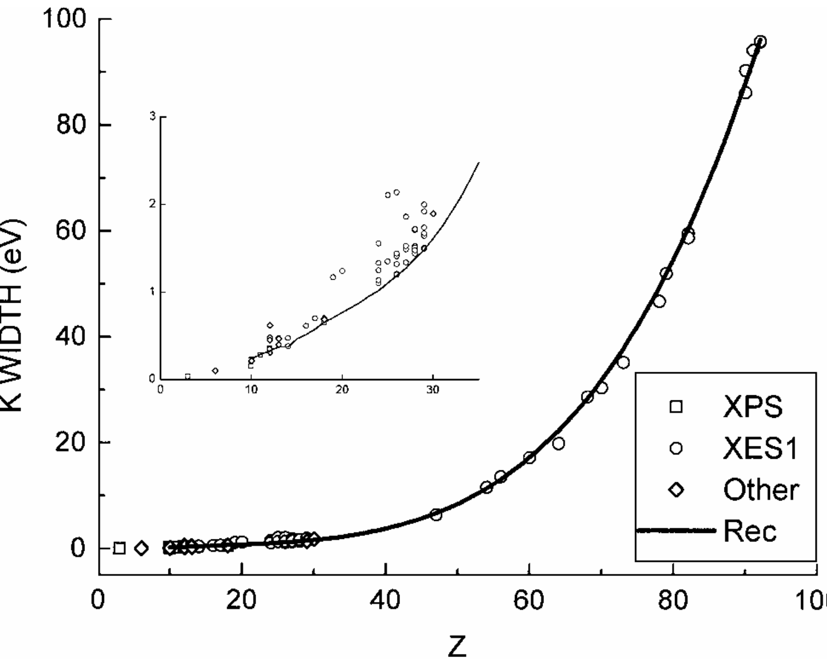
J.N. Hancock et al., Phys. Rev. B 80, (2009) 092509

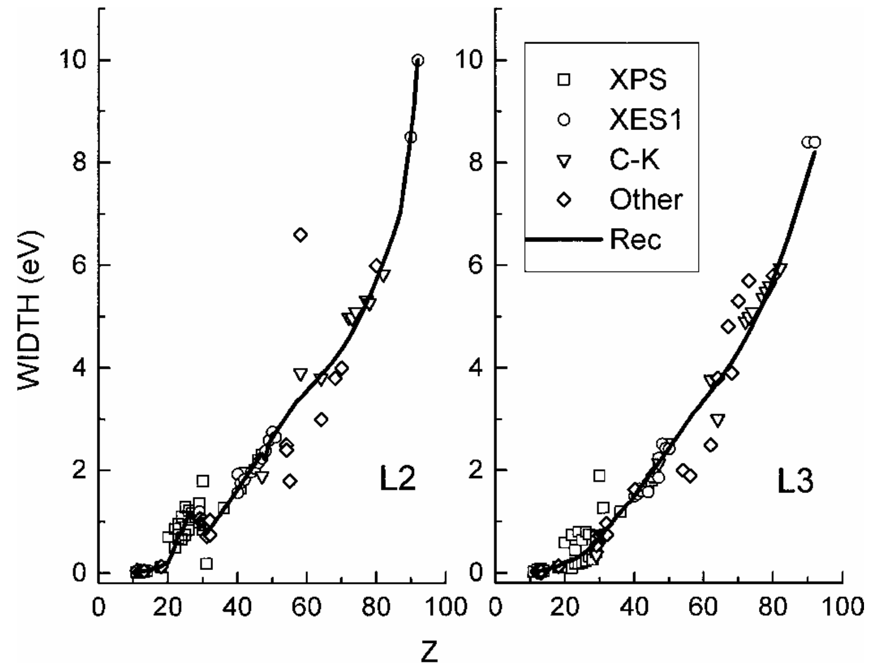
Core level energies

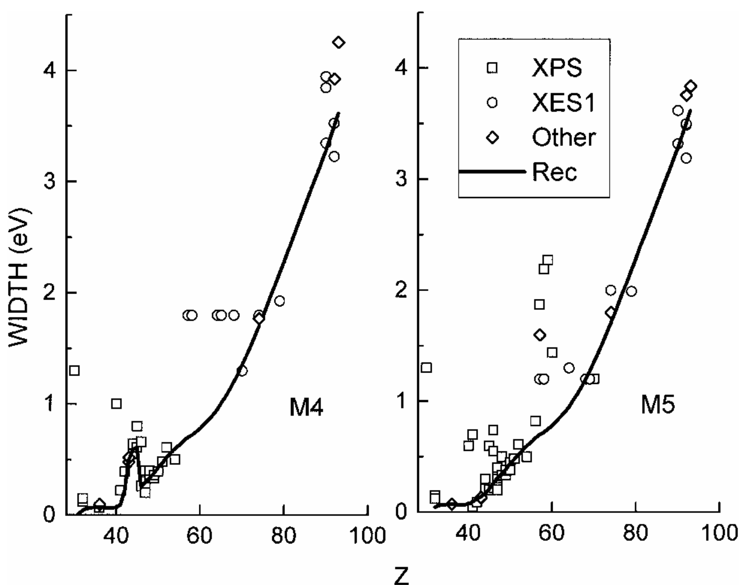


From L. J.P. Ament et al. to appear in Rev. Mod. Phys.

Natural linewidth

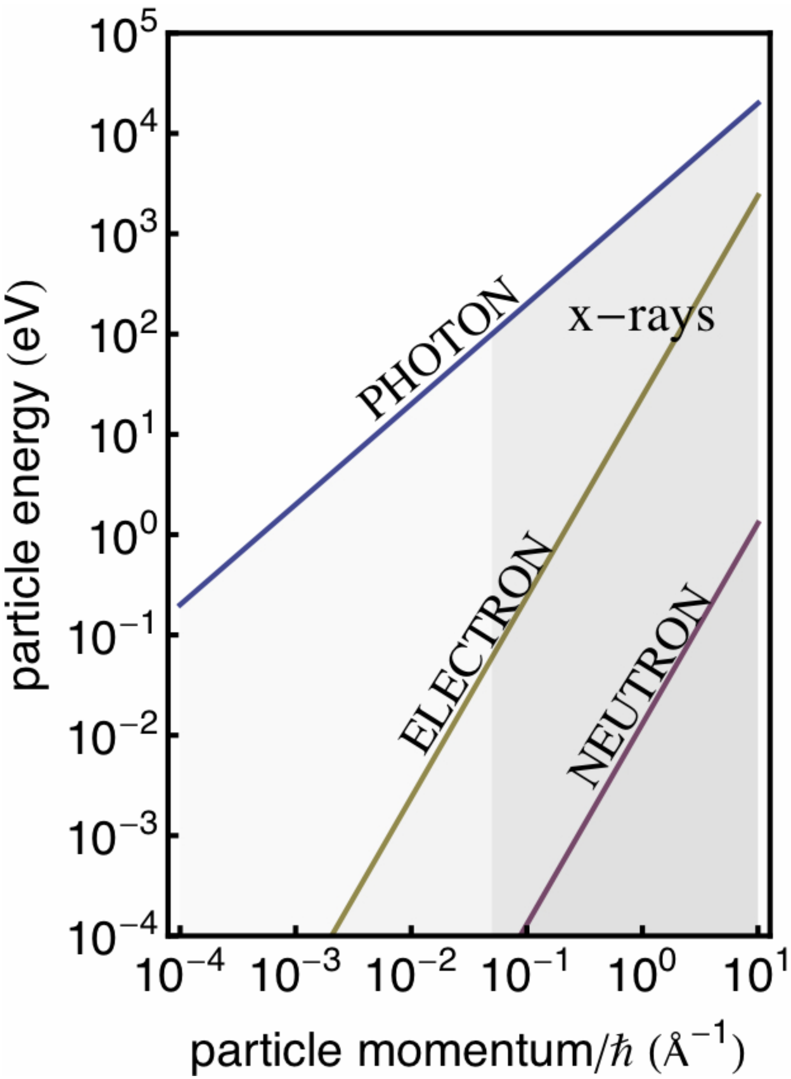






J. L. Campbell and T. Papp,
Atomic Data and Nuclear Data Tables
77, 1–56 (2001)

Momentum transfer



Inelastic x-ray scattering

Electron energy loss spectroscopy

Inelastic neutron scattering

From L. J.P. Ament et al. to appear in Rev. Mod. Phys.

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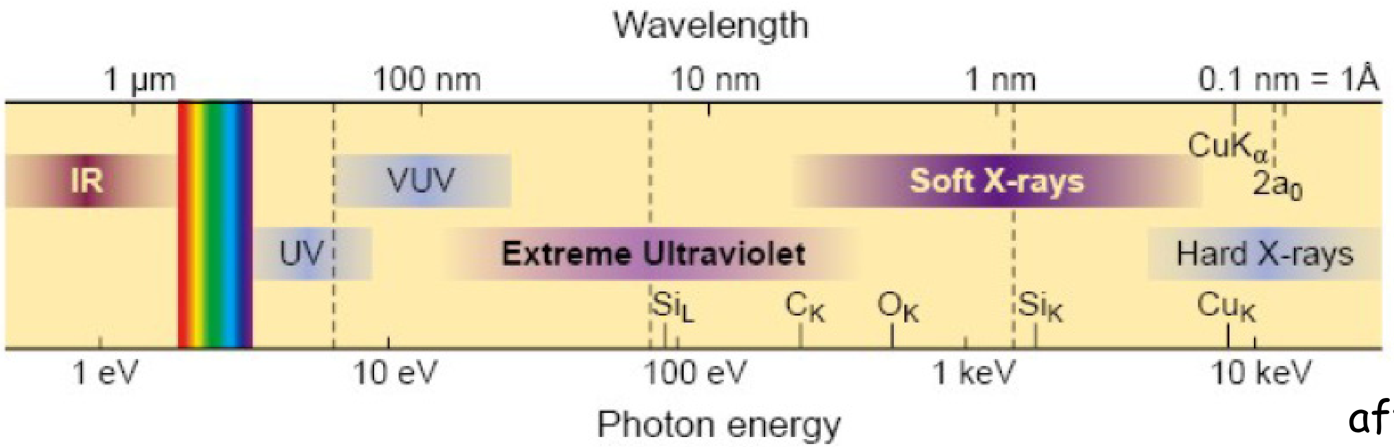
Tunable source

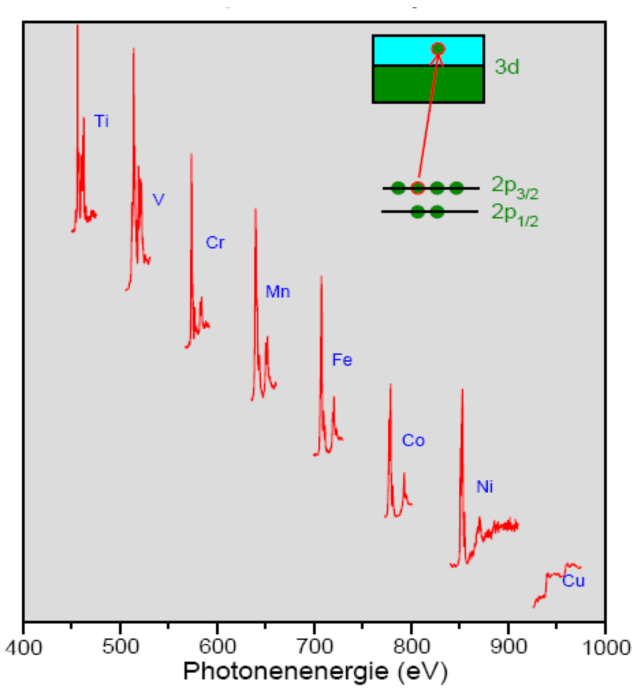
Synchrotron radiation from a storage ring or a free-electron laser

X-rays and their properties



after D. Attwood

element-specific
chemical state selective

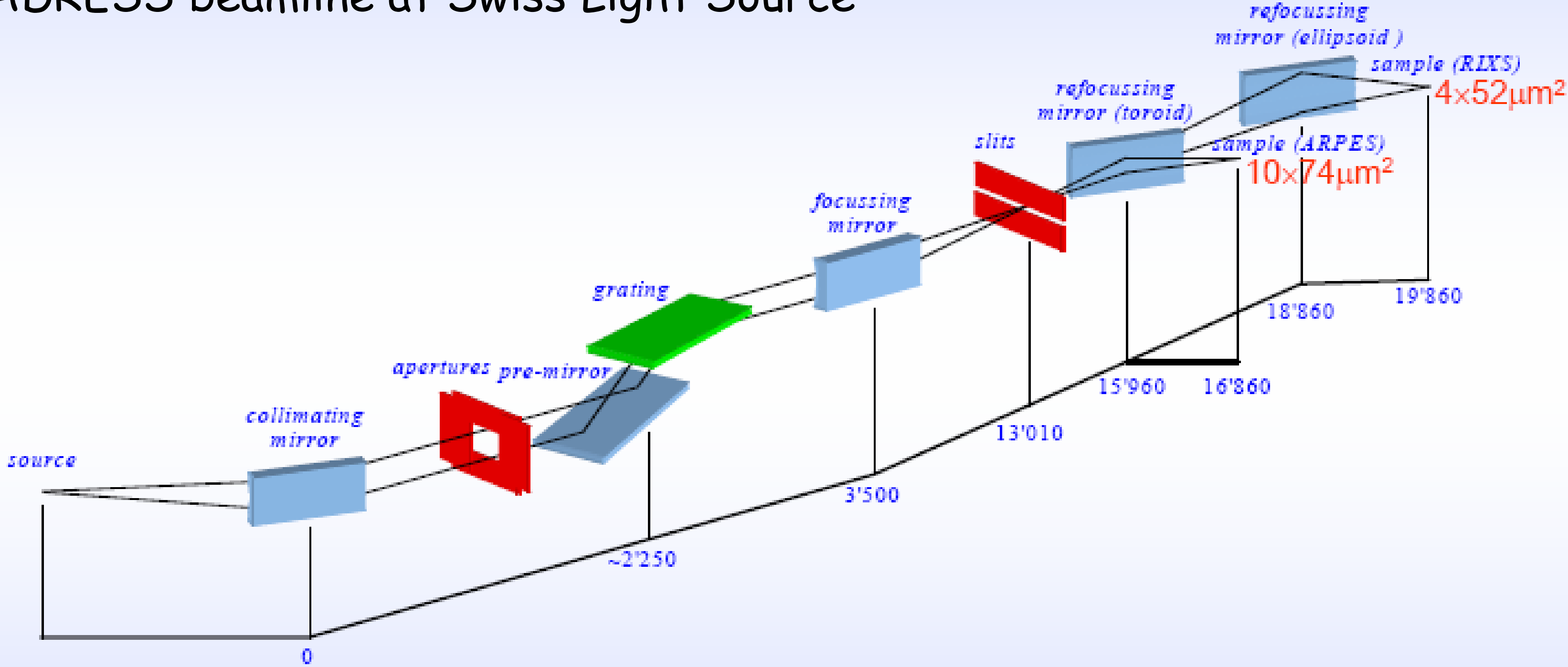


	Hard	**Soft**
Penetration depth	mm-m	nm-µm
Wavelength	1Å-0.1Å	~ 10-1 nm
Photon momentum	$\sim Å^{-1}$	$\sim 10^{-2} Å^{-1}$
optics	Crystals, lenses, waveguides	Mirrors and gratings with grazing incidence
Detectors	CCD	MCP+Phosphor+ CCD

Soft x-ray beamline

Optical scheme : Collimated-light PGM

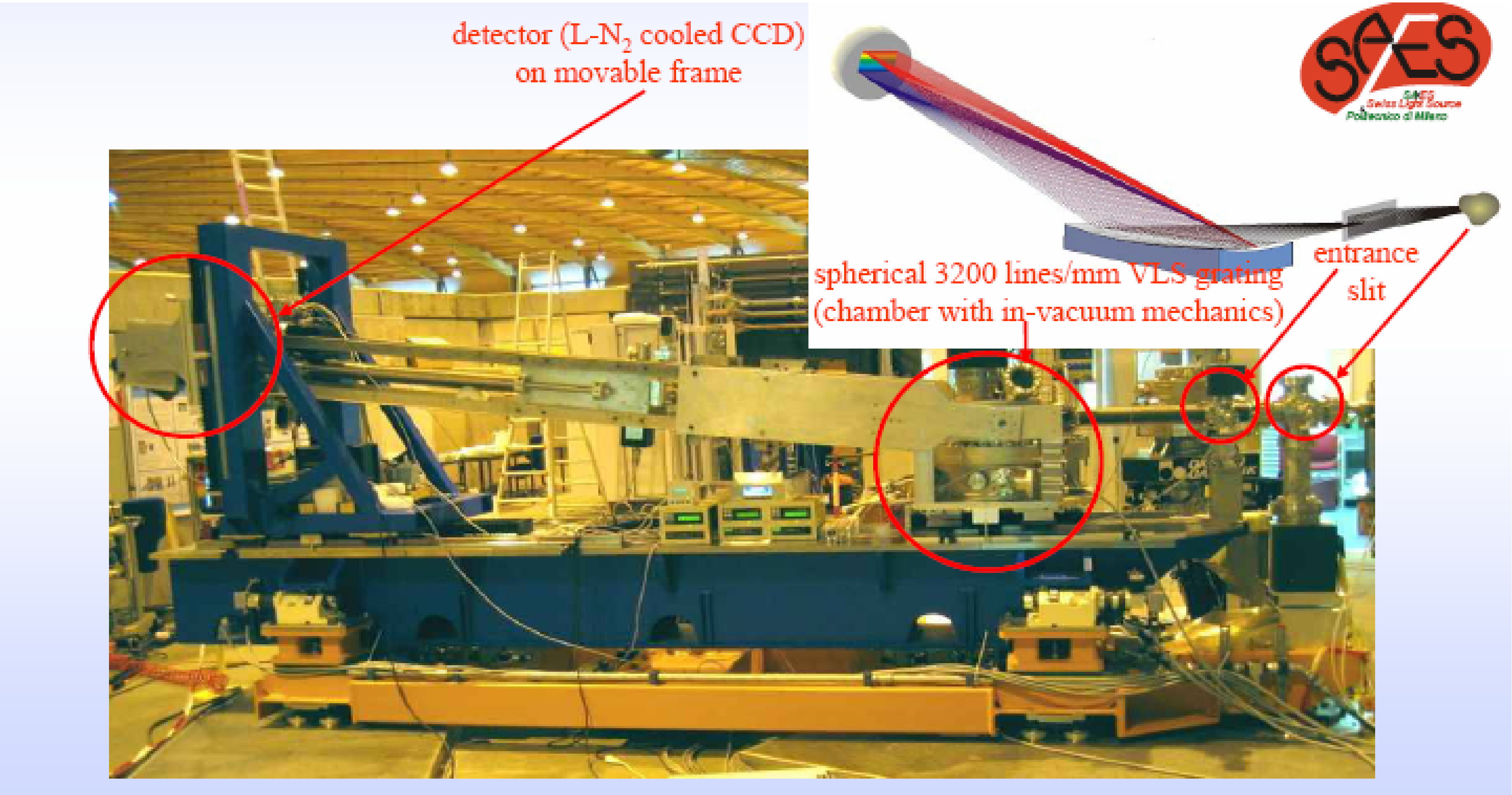
ADRESS beamline at Swiss Light Source



- high resolution
- no entrance slit: high flux
- wide energy range
- resolution, flux and HIOS optimization by C_{ff}
- proven design and flawless operation @ SLS

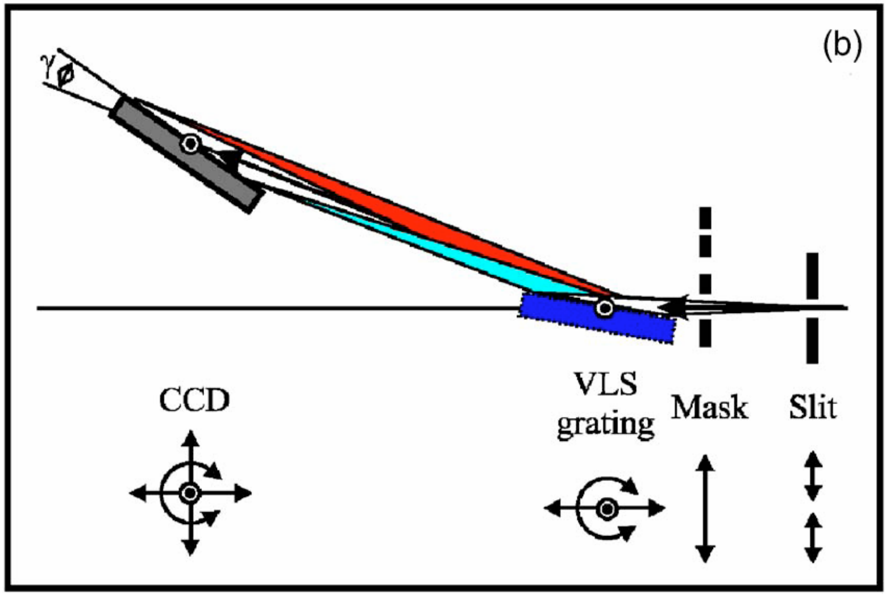
After V. Stroscov and T. Schmitt

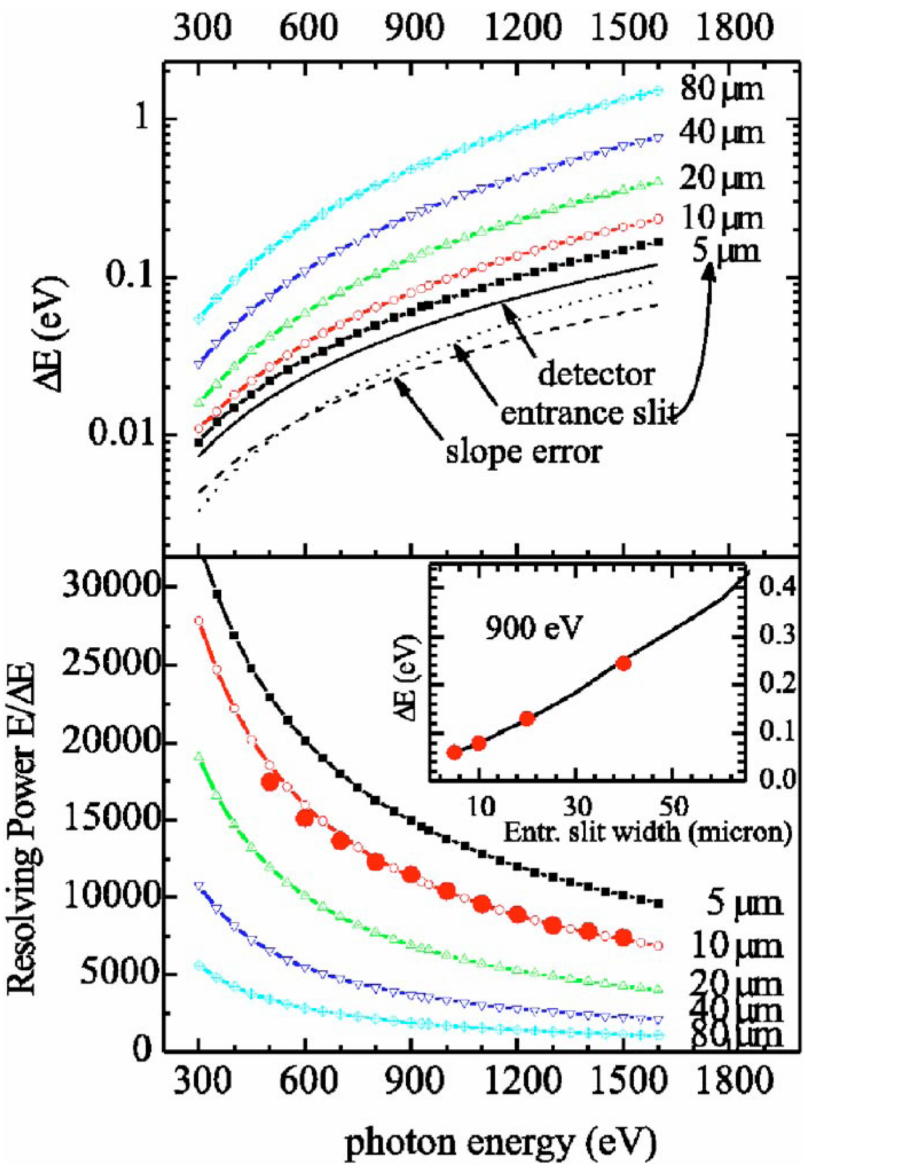
Grating spectrometer – 400-1600 eV



G. Ghiringhelli et al, Rev. Sci. Instrum. 77, 113108 (2006)

State of the art performance

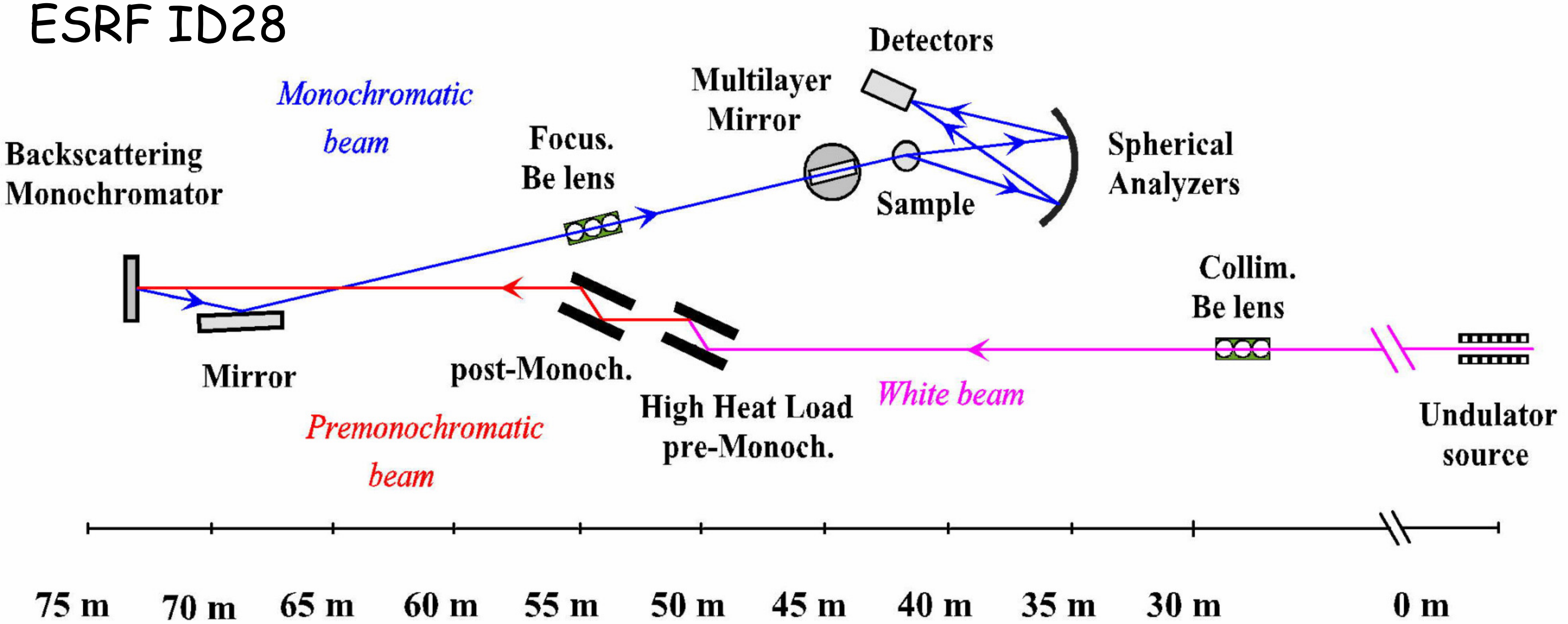




G. Ghiringhelli et al, Rev. Sci. Instrum. 77, 113108 (2006)

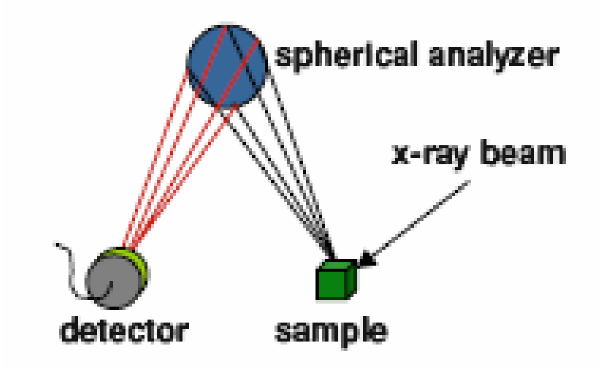
Hard x-ray beamline

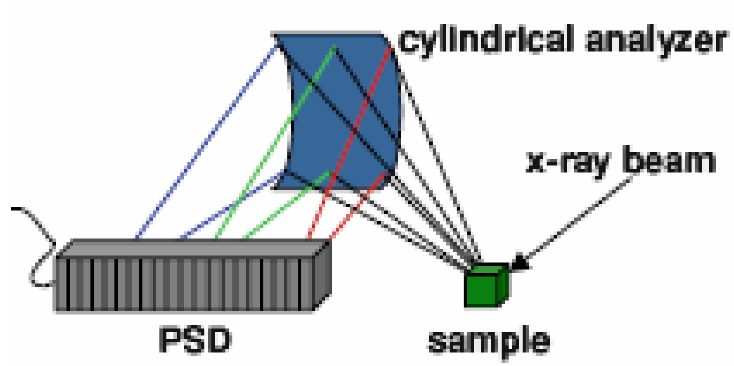
ESRF ID28

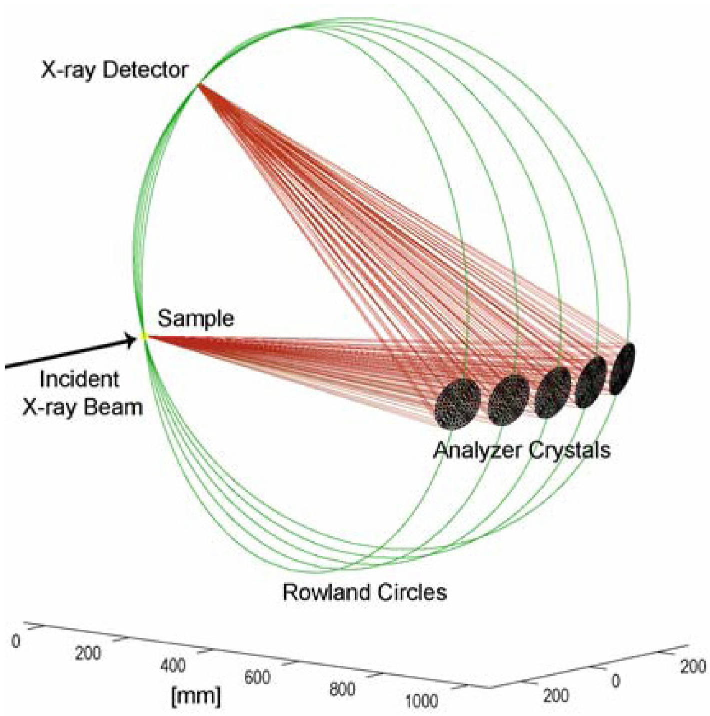


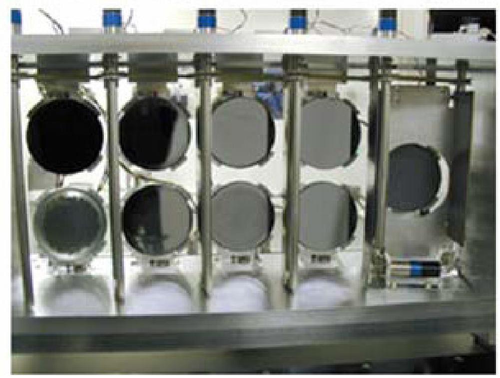
- Incident photon energy: 13840, 15817, 17794 and 21747 eV
- Energy resolution of 7.0, 5.5, 3.0 and 1.5 meV.
- Energy transfer: 0-200 meV
- Momentum resolution: typically 0.03 nm^{-1} (can be further improved by slits).
- Momentum transfers from 1-100 nm^{-1}

Crystal spectrometers









U. Bergmann, P. Glatzel, Photosynth Res (2009) 102:255

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History: x-ray emission spectroscopy

M. Siegbahn
Nobel prize
1924

O´Bryan and Skinner, Phys. Rev. 45, 370 (1934)

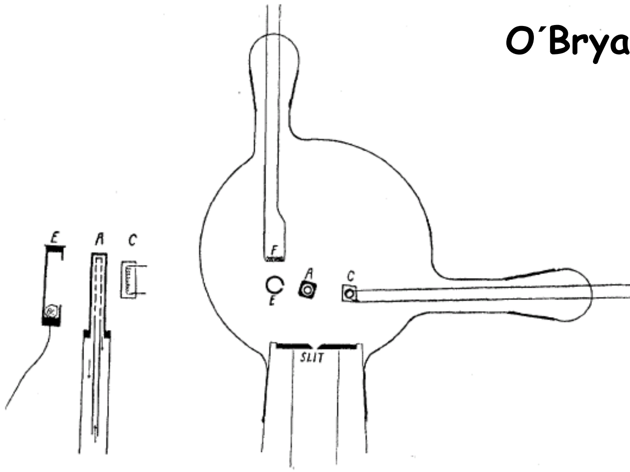
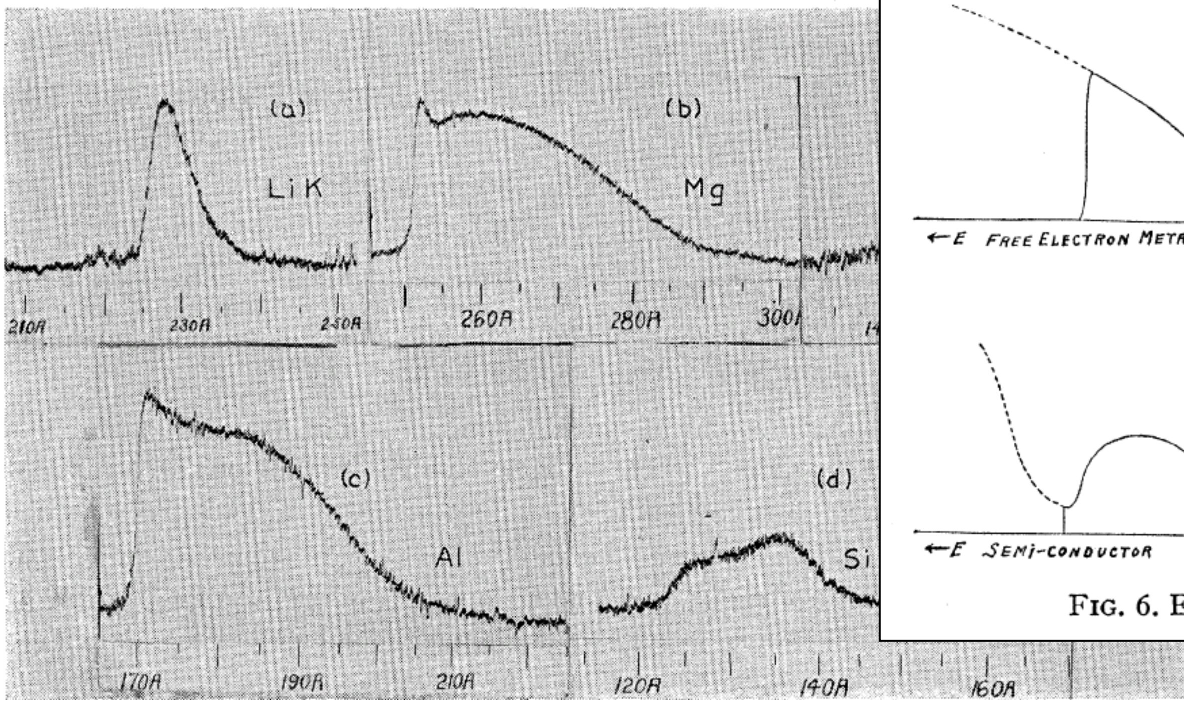


Fig. 1. X-ray tube and evaporating oven.

2m grating spectrometer
30000 lines/inch
Detector: photographic plates



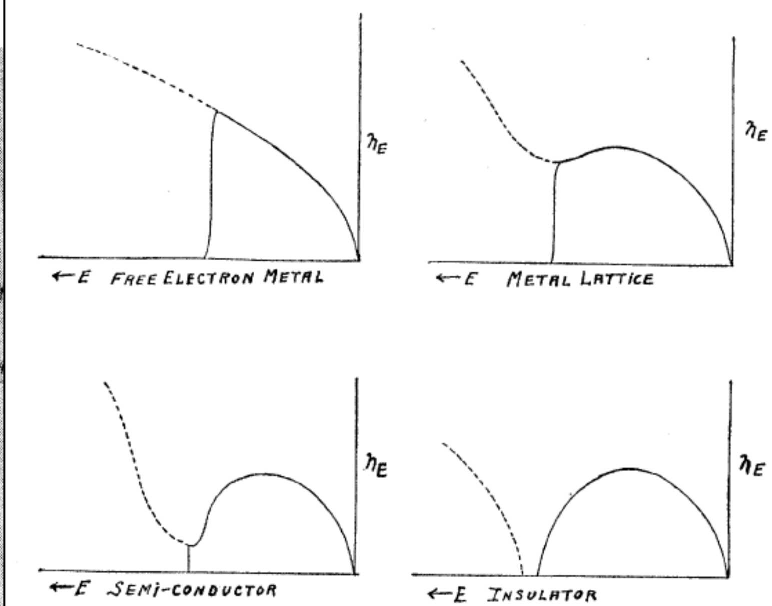
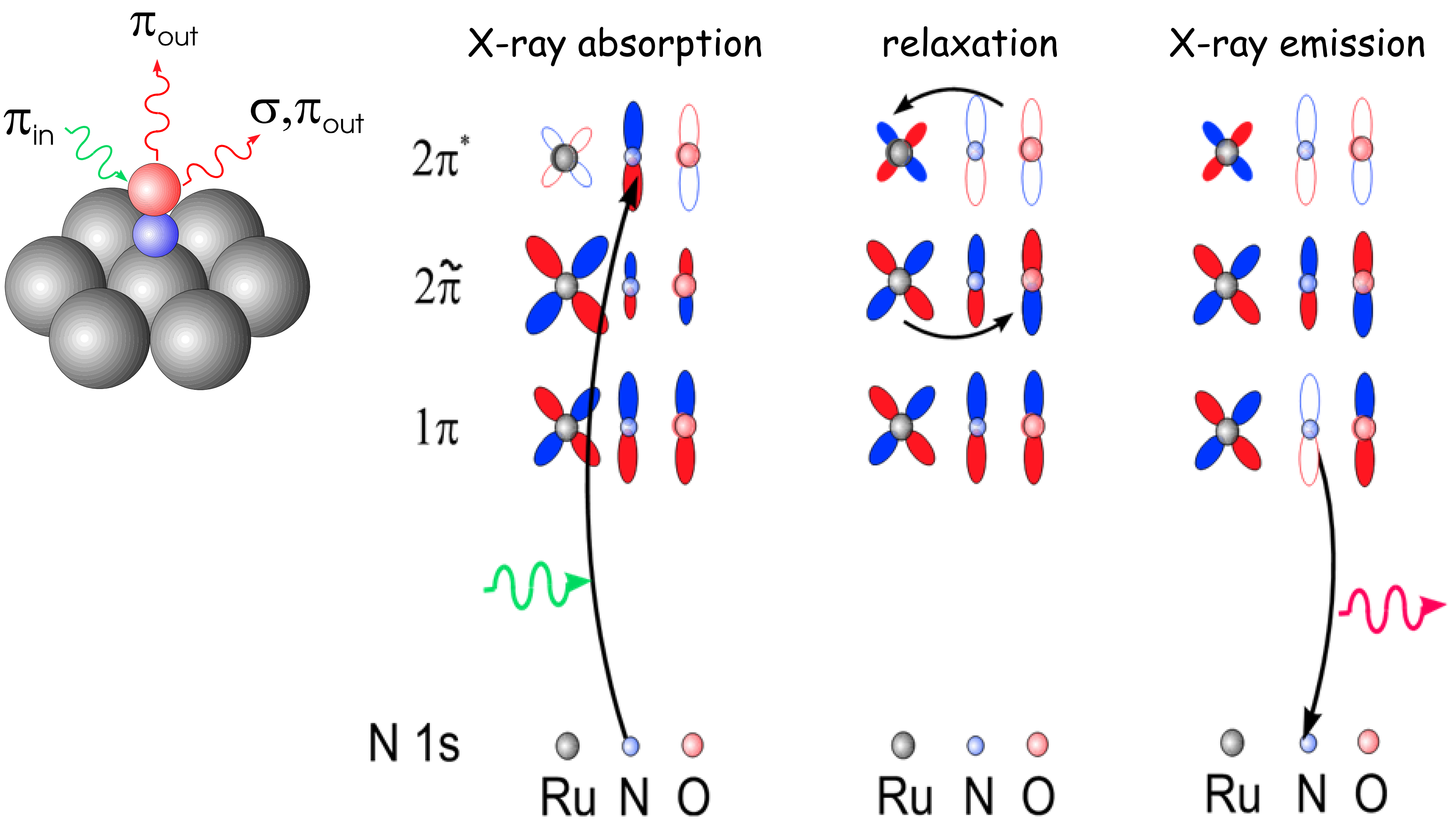
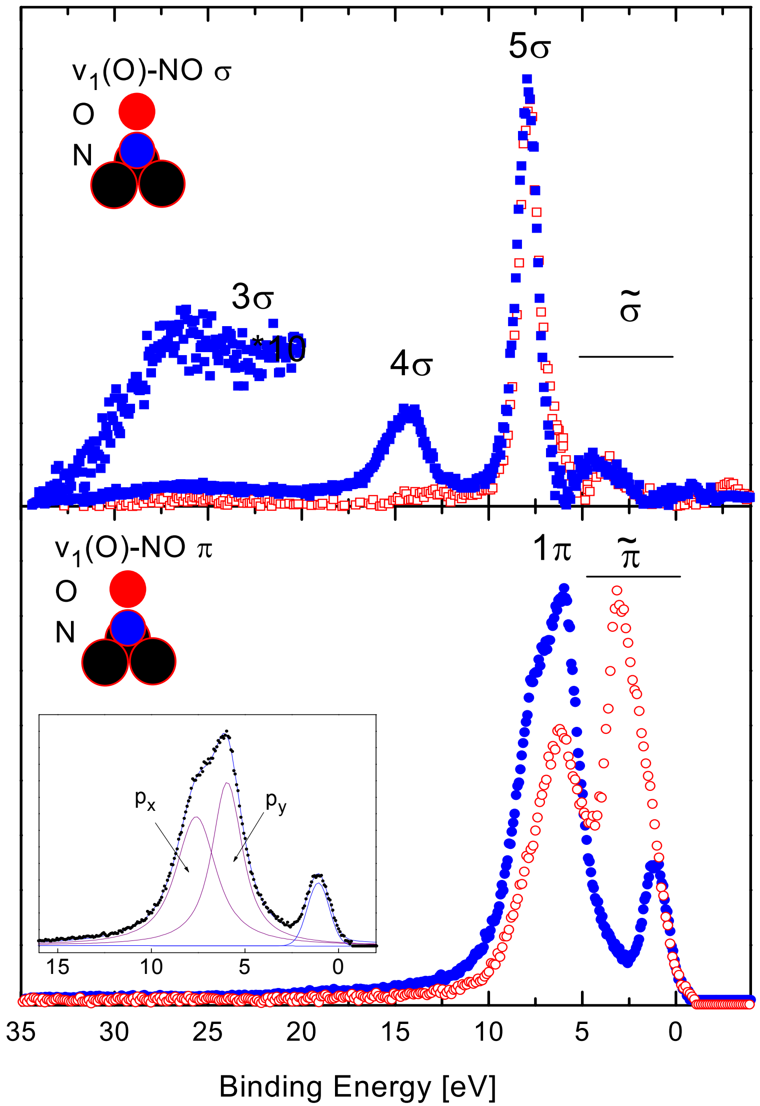


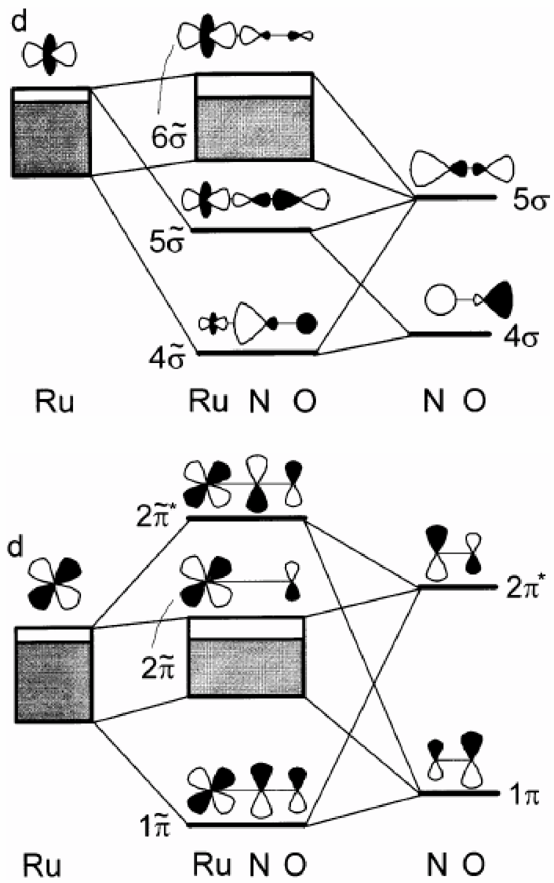
Fig. 6. Energy states in solids.

Resonant x-ray emission



Mapping of molecular orbitals



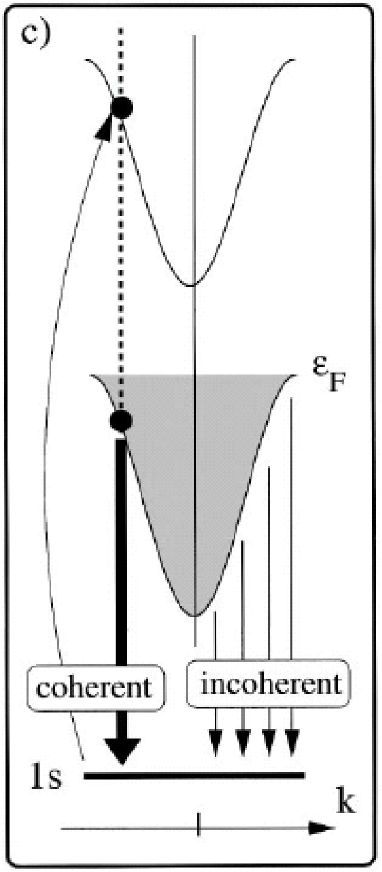


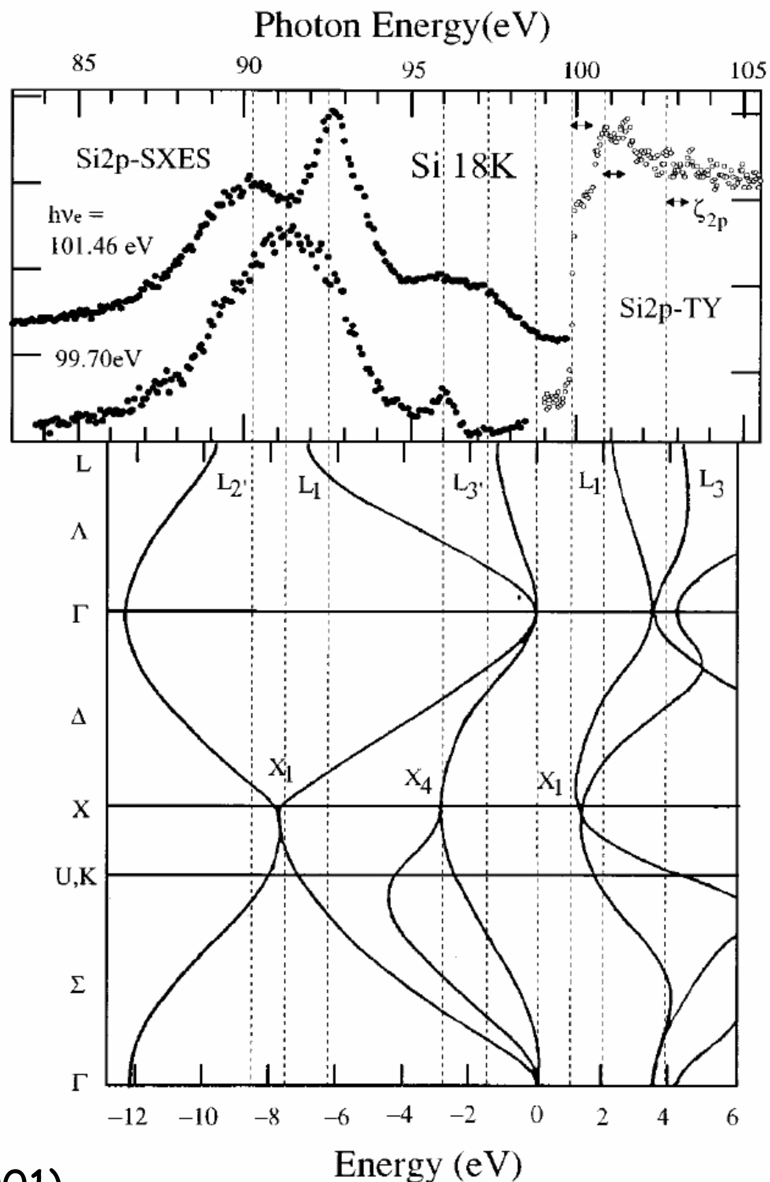
M. Stichler et al., Surf. Sci. 448 (2000) 164

Band mapping

Si(100)

Momentum conservation

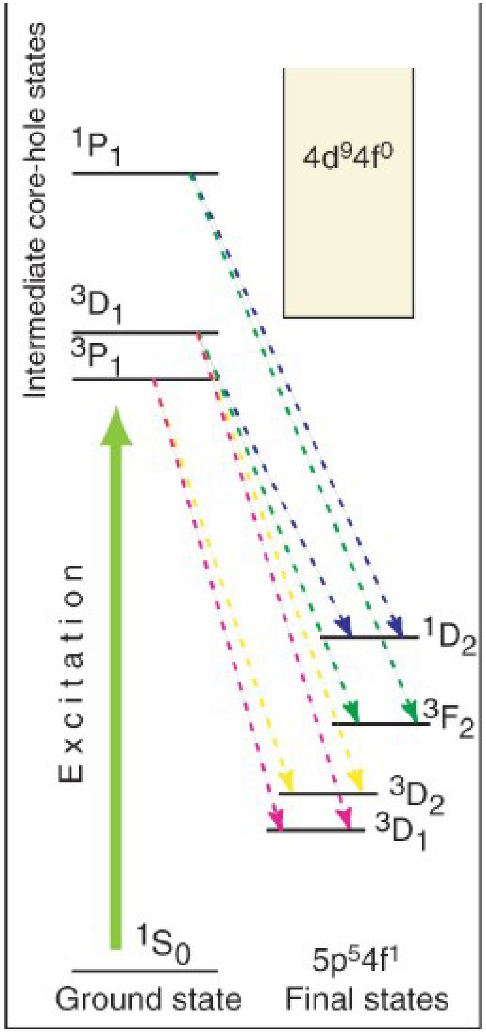




A. Kotani, S. Shin, Rev, Mod. Phys. 73, 203 (2001)

Interference effects

$$F(\Omega,\omega)=\sum_f\left|\sum_n\frac{\langle f|T_2|n\rangle\langle n|T_1|g\rangle}{E_g-E_n+\Omega-i\frac{\Gamma_n}{2}}\right|^2\times\frac{\frac{\Gamma_f}{2\pi}}{(E_g-E_f+\Omega-\omega)^2+\frac{\Gamma_f^2}{4}}.$$

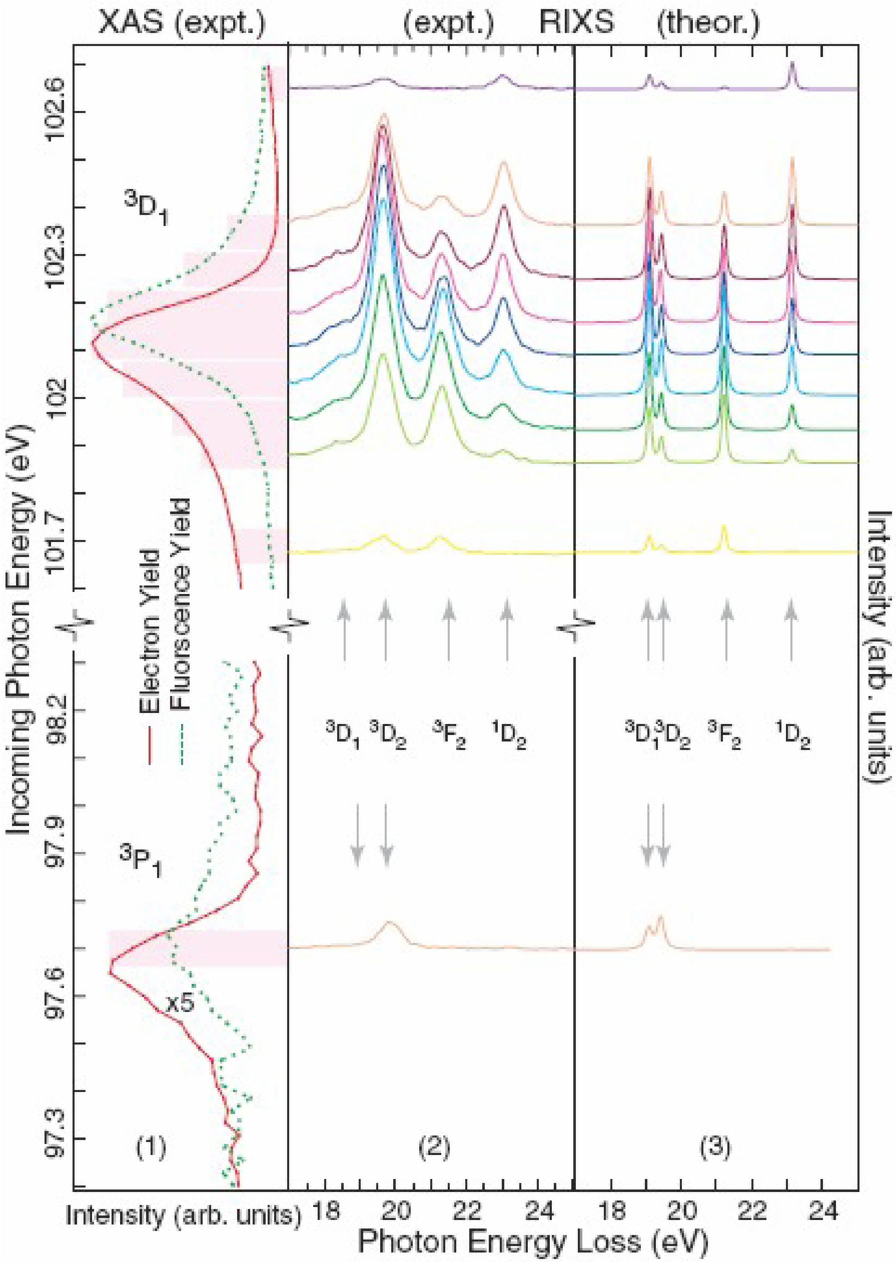


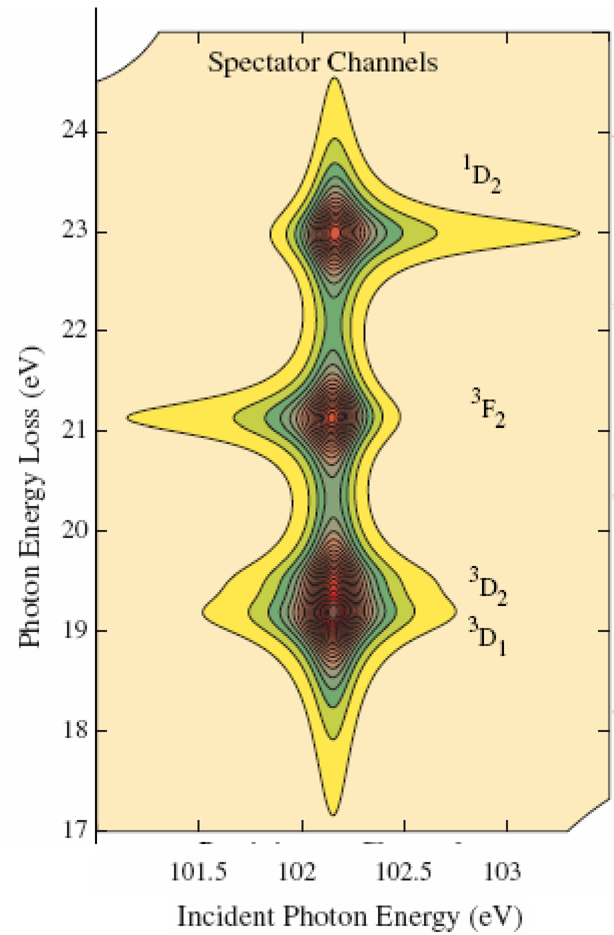
La^{3+} in $LaPO_4$ nano crystals

Electronic excitations 5p→4f

E. Suljoti et al, PRL 103, 137401 (2009)

Interference effects





E. Suljoti et al, PRL 103, 137401 (2009)

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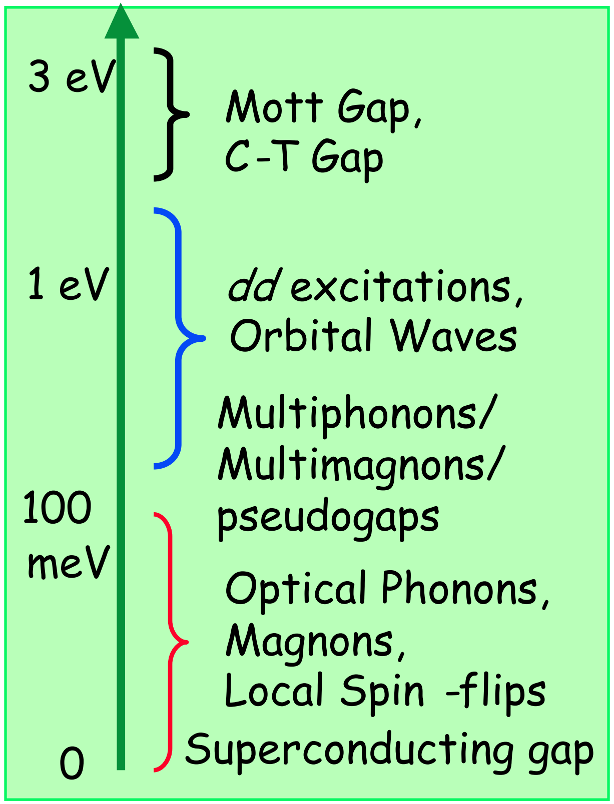
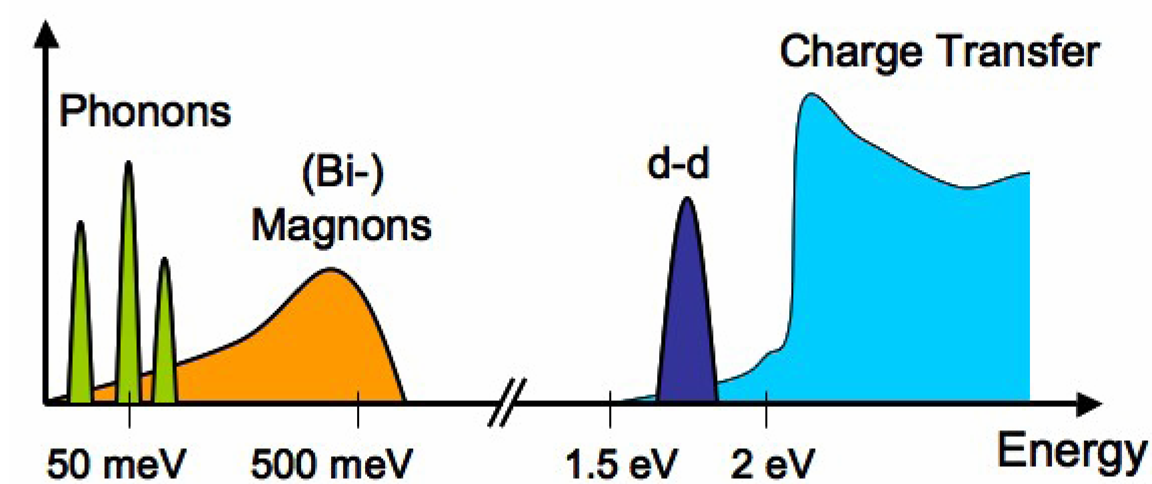
Advantages of X-ray Raman ?

Measure $S(q,\omega)$ (finite q)

- Element specific
- Bulk sensitive
- Spectroscopy of dipole forbidden transitions (e.g. d-d, f-f)
- Direct coupling to charge
- Spectroscopy in the presence of
  - Electric fields
  - Magnetic fields
  - High pressure
  - High temperature
  - .....
- High energy resolution
  (given by monochromator, analyzer and final state widths)

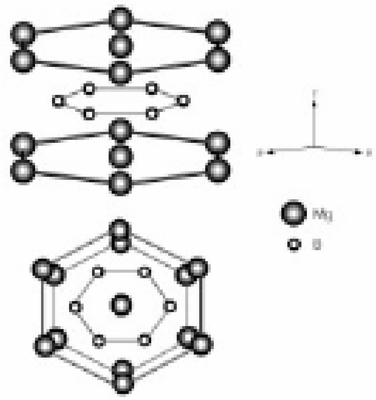
Elementary excitations- strongly correlated materials



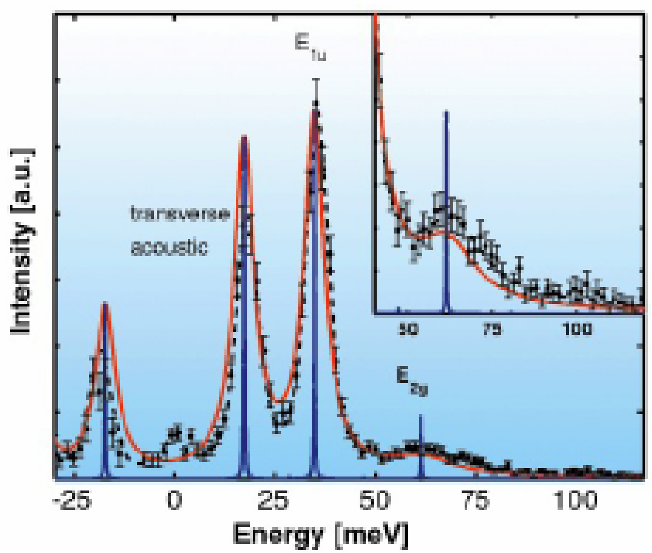


L. J.P. Ament et al. to appear in Rev. Mod. Phys.

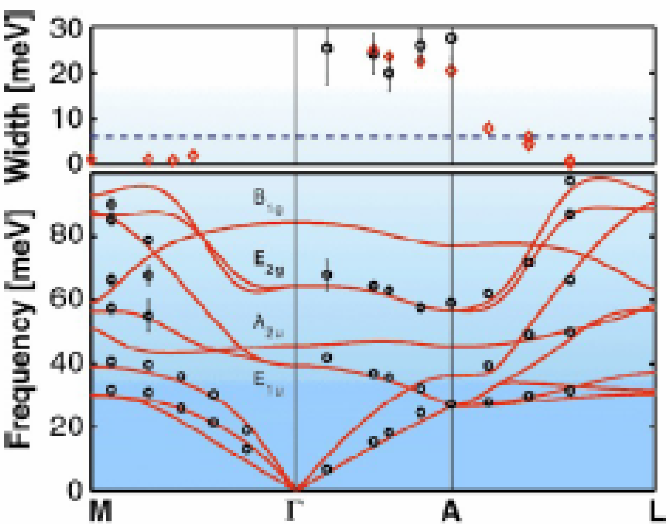
Phonon dispersion



Magnesiumdiborid super conductor $T_c = 39K$



measured at ESRF beamline ID 28, E=15,816keV

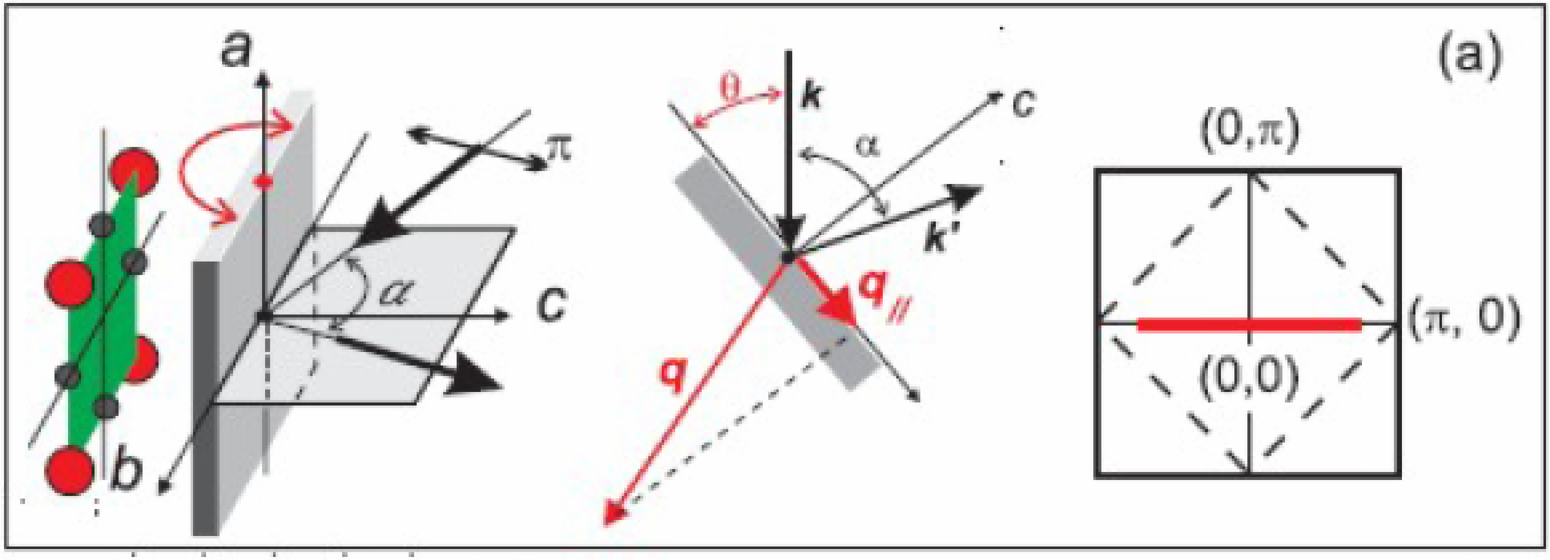


A. Shukla et al. Physical Review Letters 90, 095506,2003

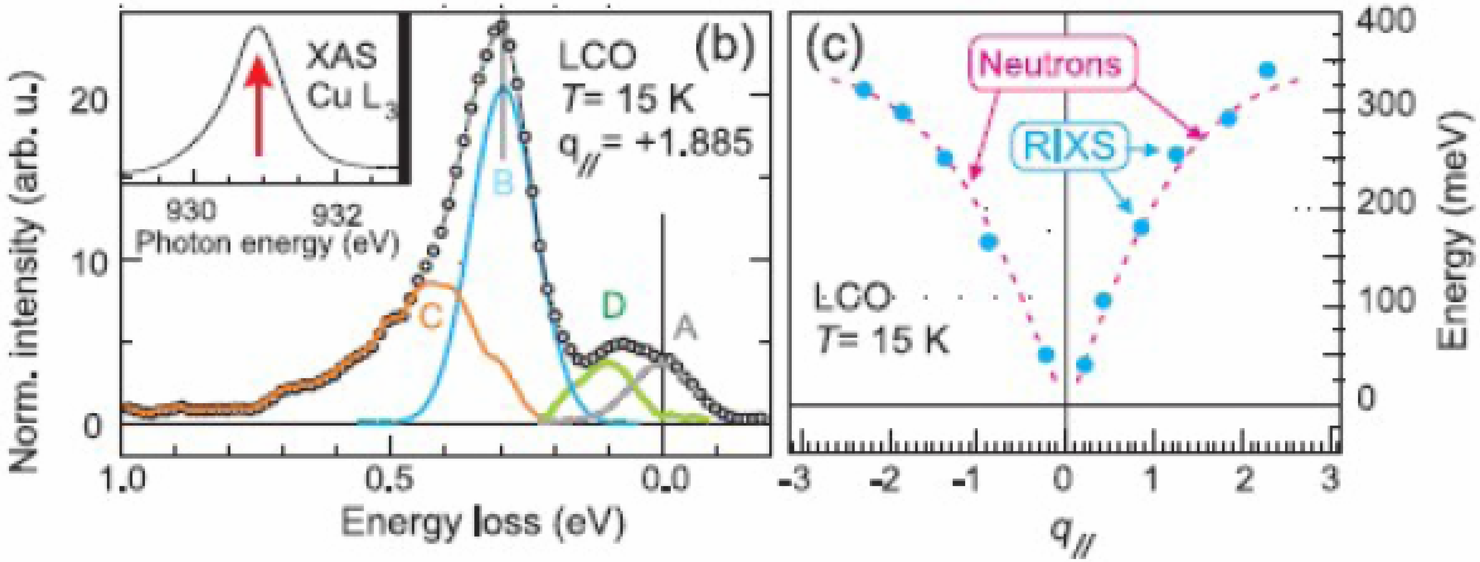
Spin-flip excitations - magnons

- resonant inelastic x-ray scattering from La_2CuO_4:
  $|0\rangle 2p^6 3d^9 \rightarrow |i\rangle 2p^5 3d^{10} \rightarrow |f\rangle 2p^6 3d^{9*}$
- $3d^{9*}$ dd-excitation or spin-flip
- spin-flip allowed for certain geometries (symmetries) through spin-orbit coupling

scattering geometry



from L. Braicovich et al., PRL 104, 077002 (2010) magnon dispersion

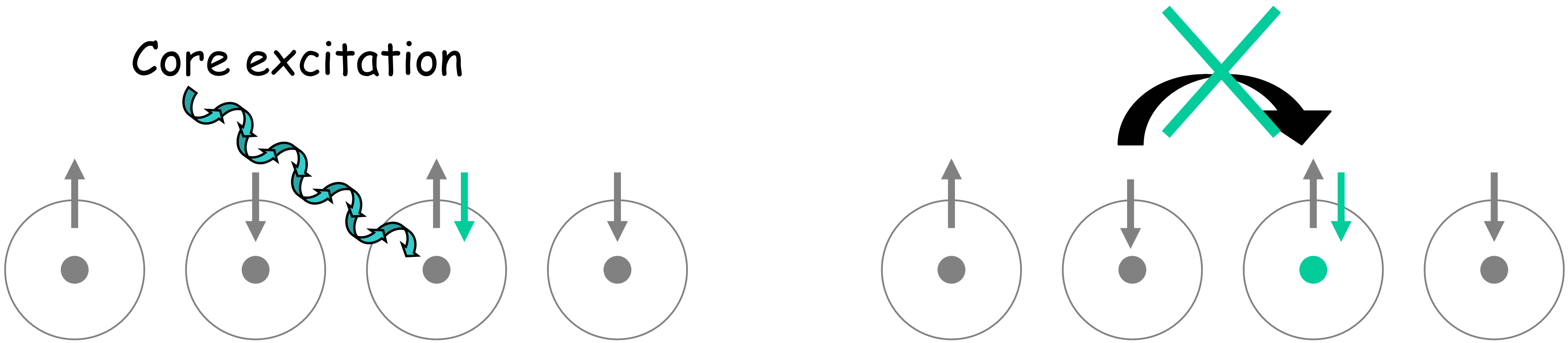


- peak A: elastic peak
- peak B: single magnon
- peak C: multiple magnon
- peak D: optical phonon

from L. Braicovich et al., PRL 104, 077002 (2010)

Direct coupling to magnons

Hubbard-model with antiferromagnetic order



Superexchange (Cu-O-Cu) changed by 2p→3d transition

After L. J. P. Ament

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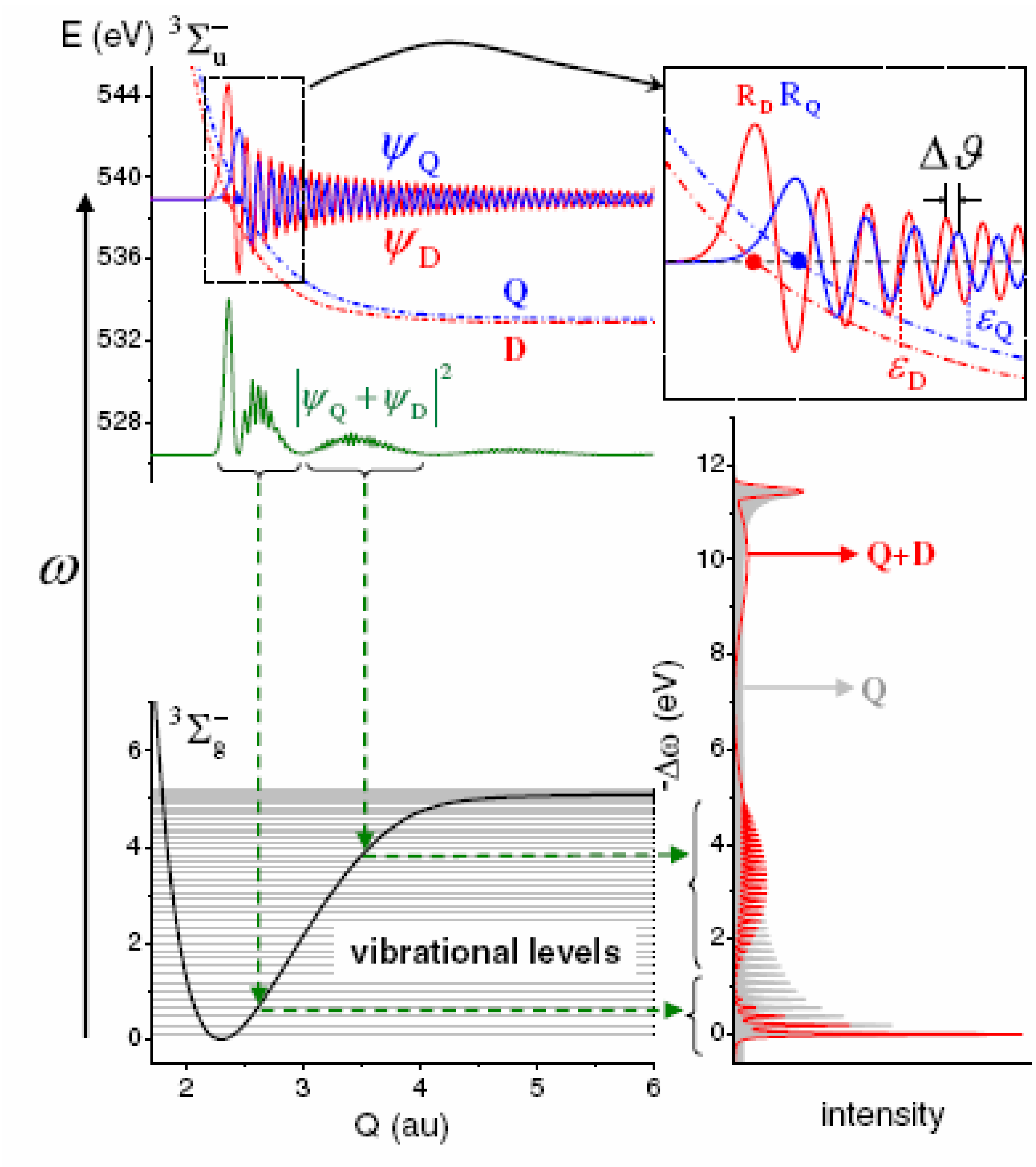
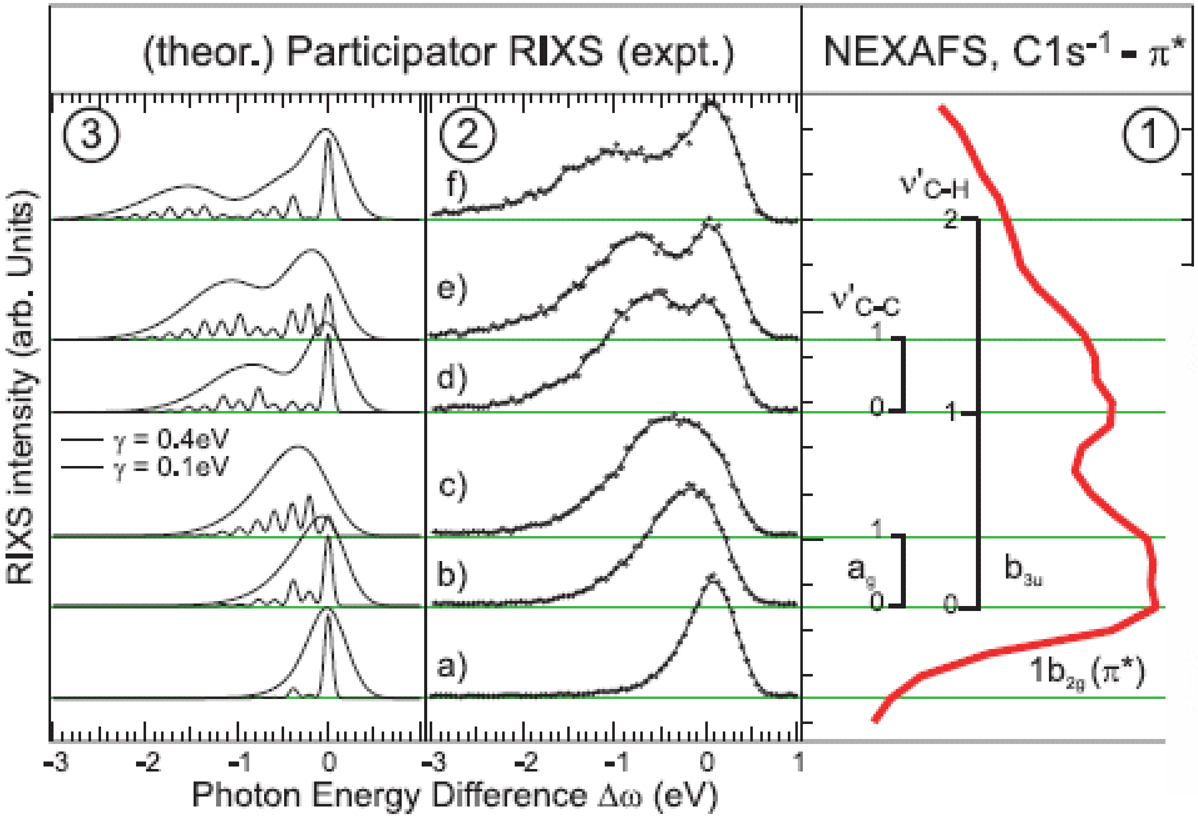
Quantum Beats in Vibrational Resonant Inelastic Soft X-Ray Scattering at Dissociating States in Molecular Oxygen

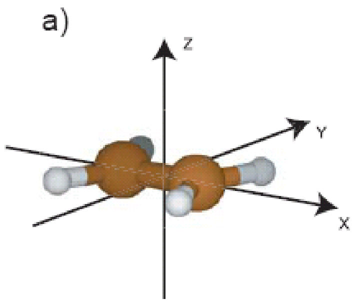


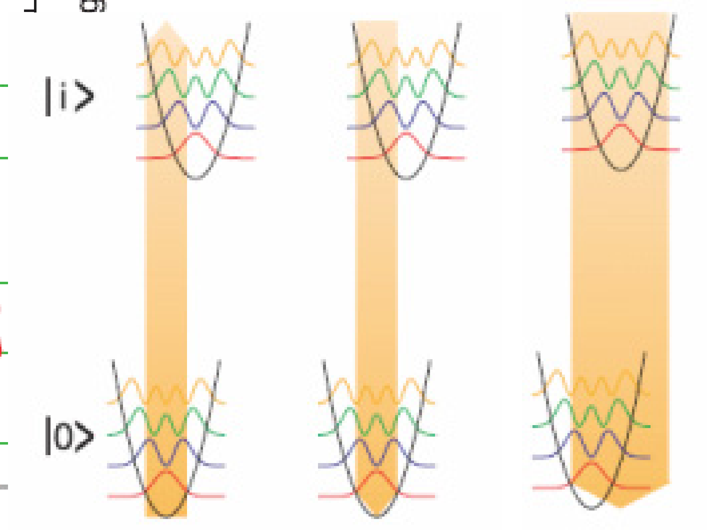
A.Pietzsch et al.,
PRL 106, 153004 (2011)

Nuclear dynamics in the intermediate state

Condensed ethylene







Electronic final state = ground state

$$\tau = 1/\sqrt{\Omega^2 + (\Gamma/2)^2}$$

F. Hennies et al PRL 95, 163002 (2005).

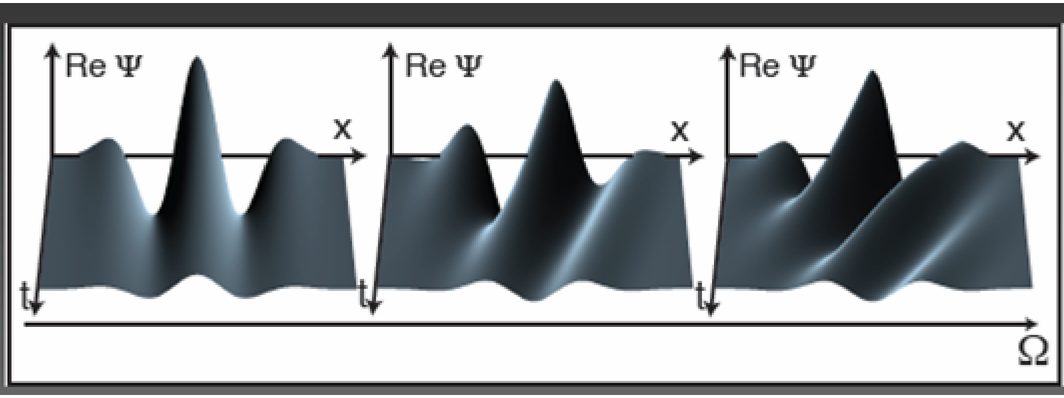
Concept of scattering duration

Scattering duration time

Consider time-evolution of intermediate state wave packets

1eV ~ 0.6 fs

$$
\begin{aligned}
\Psi\left(\vec{r},t\right) &= \psi\left(\vec{r}\right)\cdot e^{\imath\mathcal{H}t} \\
\mathcal{H} &= \left(\Omega+\imath\Gamma_i/2\right)/\hbar \\
\Omega &:= \hbar\omega_{in}-E_i+E_g \\
\Psi\left(\vec{r},t\right) &= \psi\left(\vec{r}\right)\cdot e^{\frac{\Gamma_i}{2\hbar}t}\cdot e^{\imath\frac{\Omega}{\hbar}t}
\end{aligned}
$$

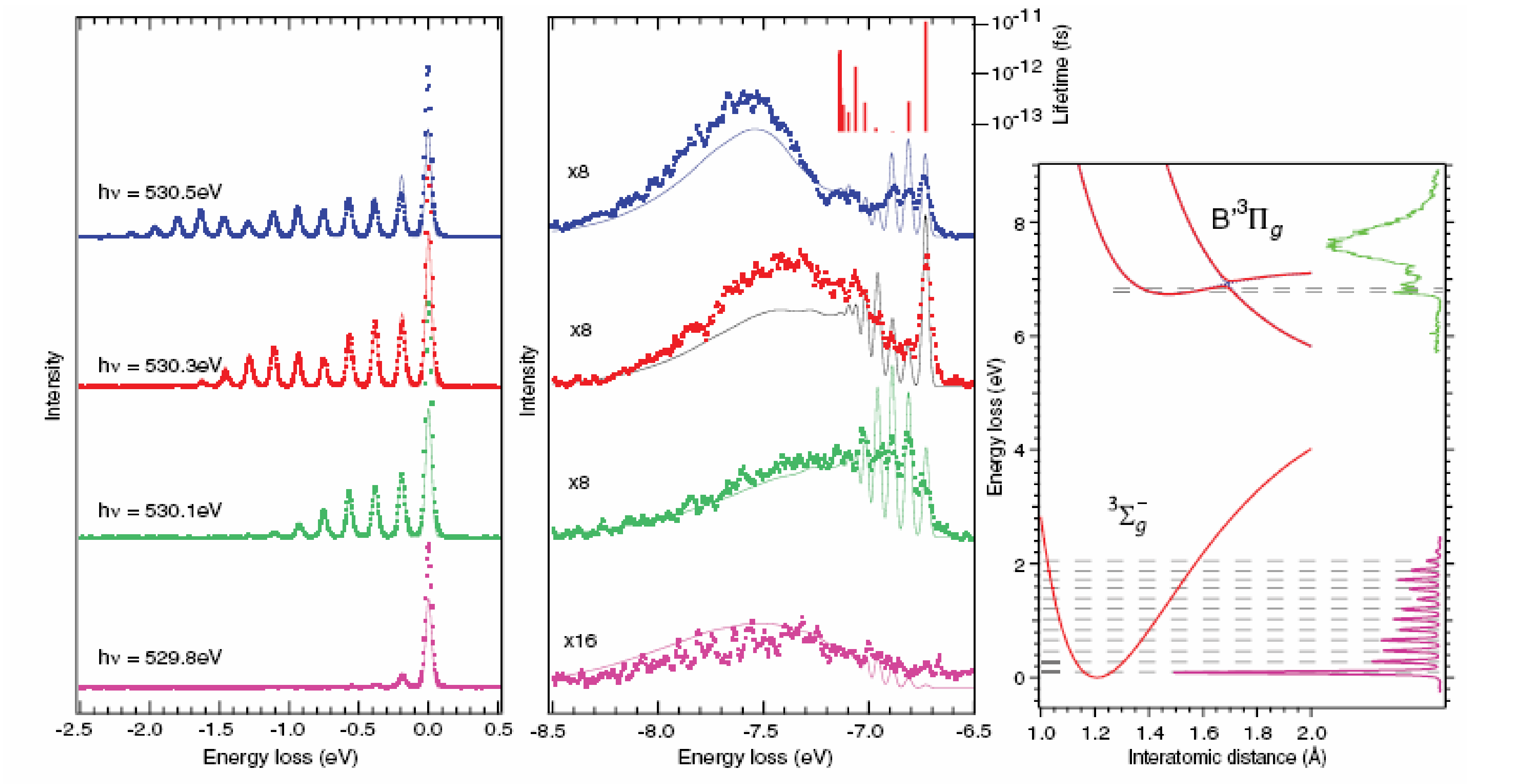


$$
t_{RIXS}=\frac{1}{\sqrt{\Omega^2+\left(\frac{\Gamma_i}{2}\right)^2}}
$$

After M. Beye

F. Gelmukhanov et al., Duration of x-ray Raman scattering, PRA 59, 380 (1999)

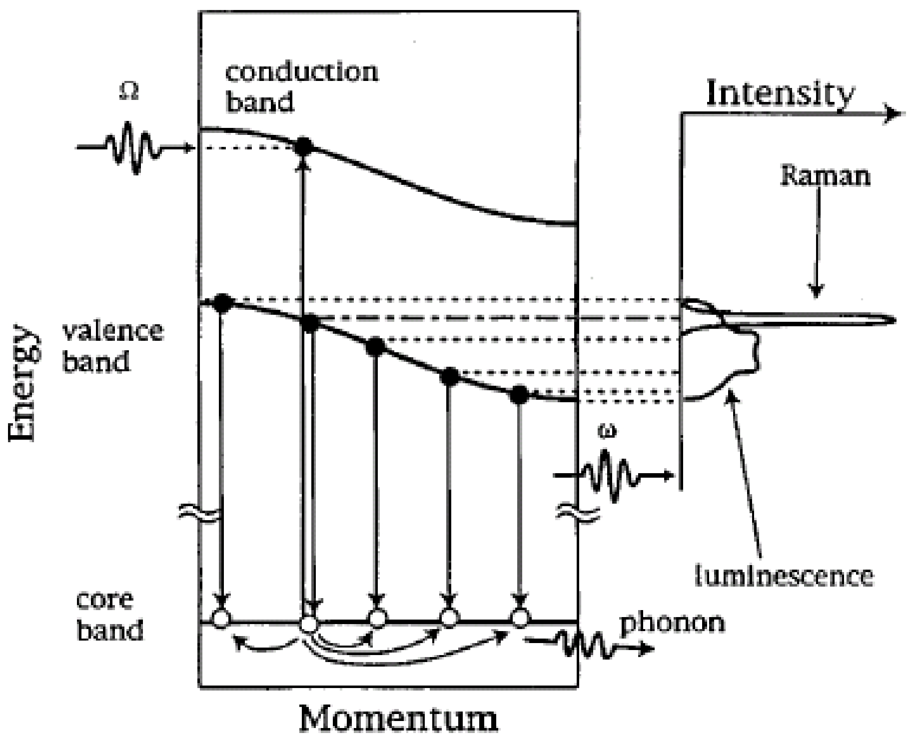
Wave packet evolution for molecular oxygen

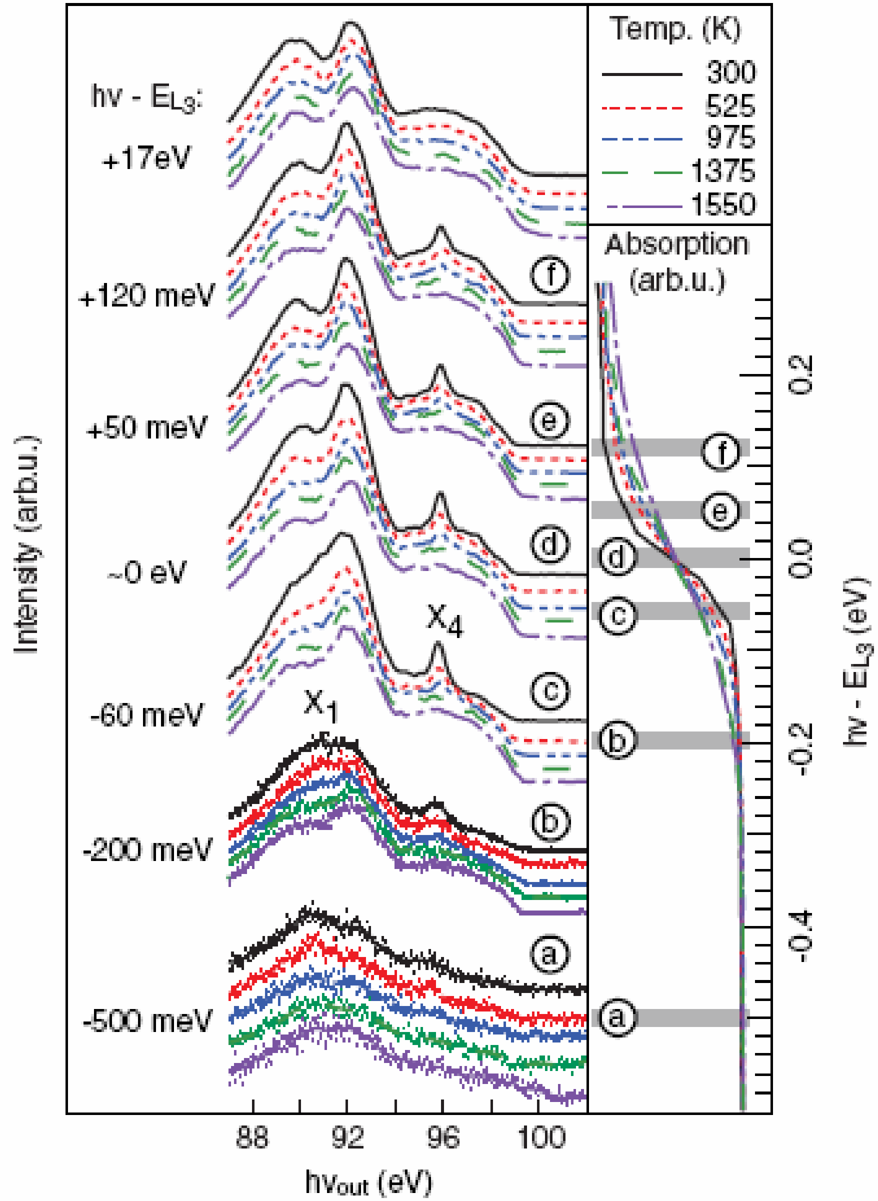


F. Hennies et al., PRL 104, 193002 (2010)

„RIXS intermediate state dynamics –electron-phonon coupling"

„Dephasing"





M. Beye et al., PRL 103, 237401 (2009)