Resonant Inelastic Soft X-ray Scattering
Photons in and Photons out

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5th School on X-Ray Spectroscopy Methods, Campinas 23/8 2016

Outline

- *General Introduction*
  - *Local Partial Density of State*
  - *Site Selectivity*
  - *Typical attenuation length: 1000Å*
- *Instrumentation*
  - *Soft X-ray spectroscopy*
  - *High Brilliance Synchrotron Radiation*
- *RIXS; Resonant Inelastic Soft X-ray Scattering*
  - *Always a one-step process*
  - *Energy conservation*
  - *Momentum conservation*
  - *Symmetry selectivity*
  - *Dynamics*
- *Applications*
  - *Molecular Materials*
  - *Materials with electron correlation and spin-orbit coupling*
- *Stimulated RIXS?*

X-ray emission: Characteristic radiation?

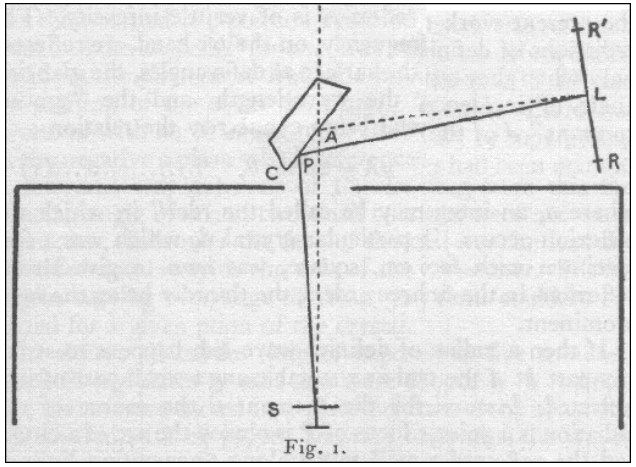


Fig. 1.

H. G. J. Moseley, M. A.
Phil. Mag. (1913), p. 1024

$$Z \propto \sqrt{h\nu}$$

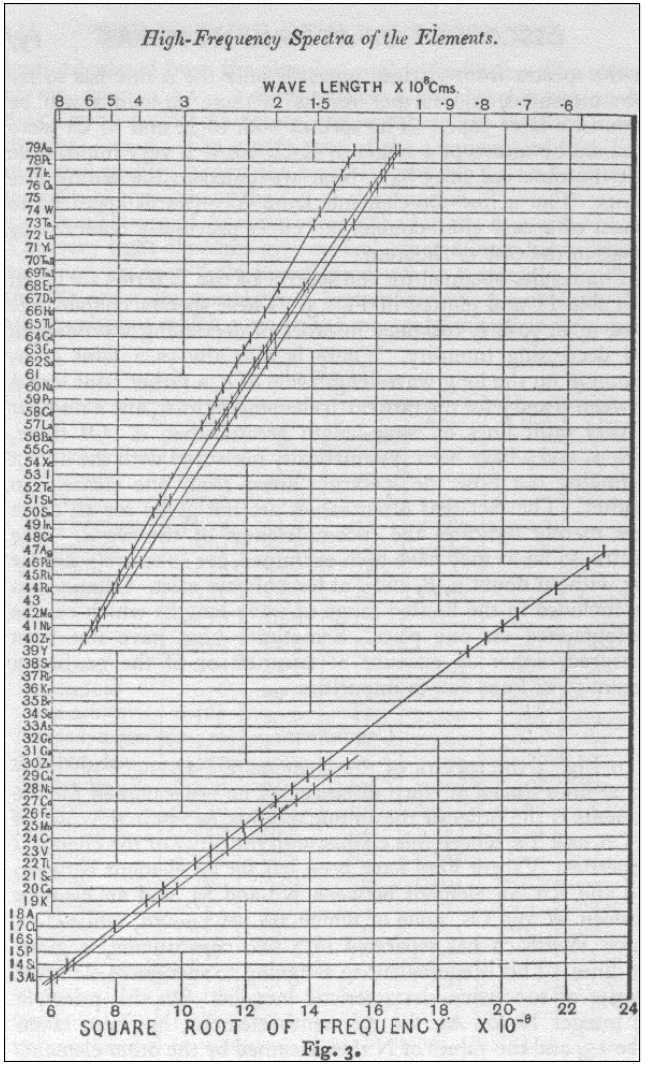


Fig. 3.

Yes, but also uncharacteristic

Valence electronic struture

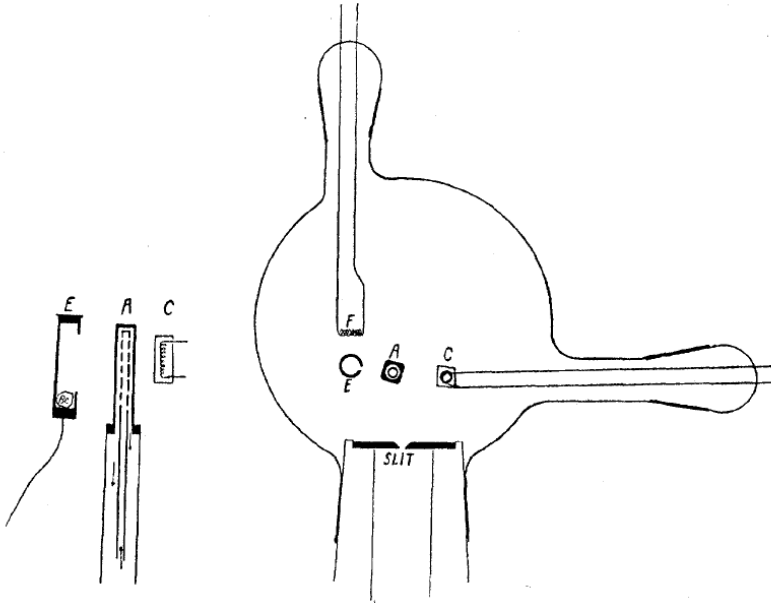


FIG. 1. X-ray tube and evaporating oven.

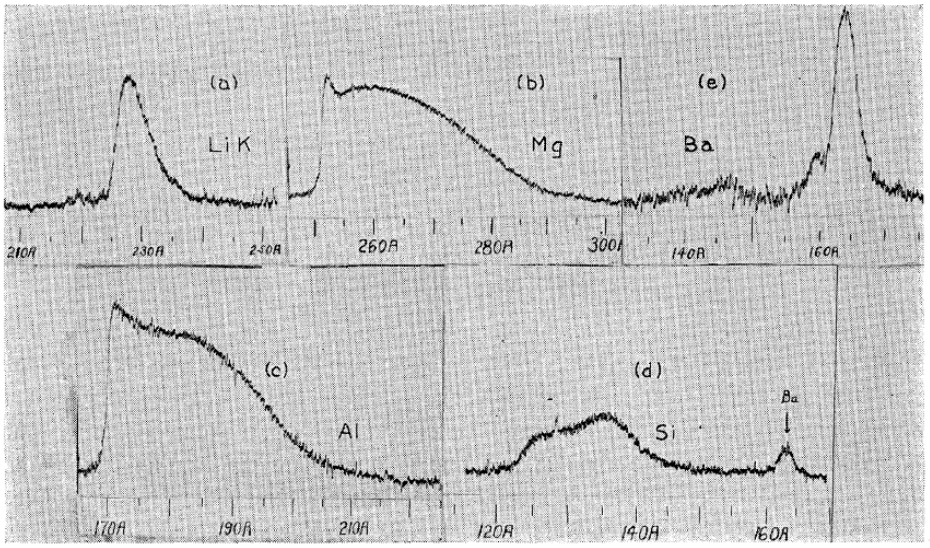
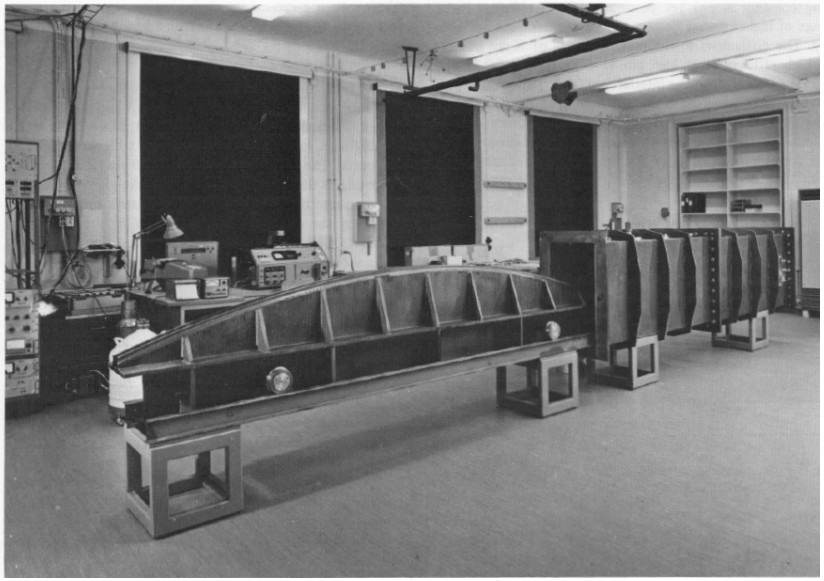
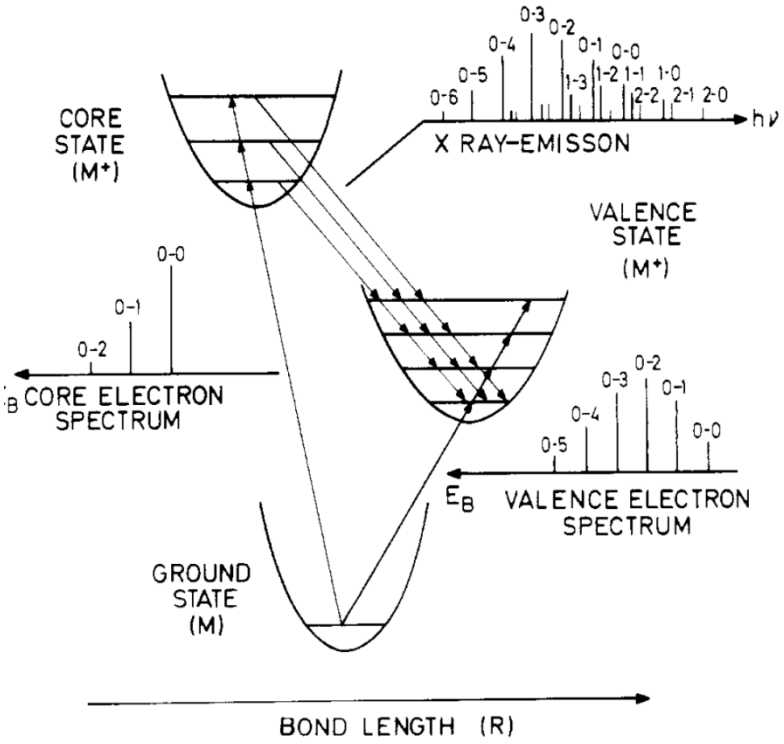


FIG. 4. Photometer curves of x-ray lines.

Phys. Rev. 45, 370 (1935)


SWEDEN
Norwegian Sea
Abisko National Park
Sarek National Park
Sjt Kebnekaise (2111m)
Muddus National Park
Arctic Circle
Jokkmokk (Dálvadis)
Vindeltjällens Nature Reserve
Pieljekaise National Park
Luleå
Storuman
0 300 km
0 150 miles
Umeå
Trondheim
Östersund
FINLAND
ATLANTIC OCEAN
Sundsvall
Sälen
Gulf of Bothnia
Fulufjället
NORWAY
Helsinki
Borlänge
Uppsala
Oslo
Drammen
Örebro
Stockholm
Tallinn
RUSSIA
ESTONIA
Lake Vänern
Vadstena
Gotland
Gothenburg
Visby
Lake Vättern
Riga
LATVIA
Växjö
DENMARK
Helsingborg
Öland
Baltic Sea
LITHUANIA
Copenhagen
Trelleborg
Vilnius

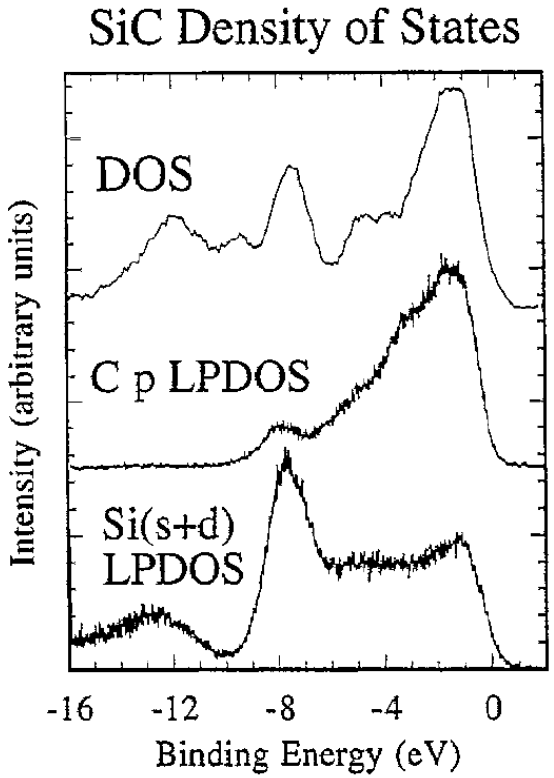


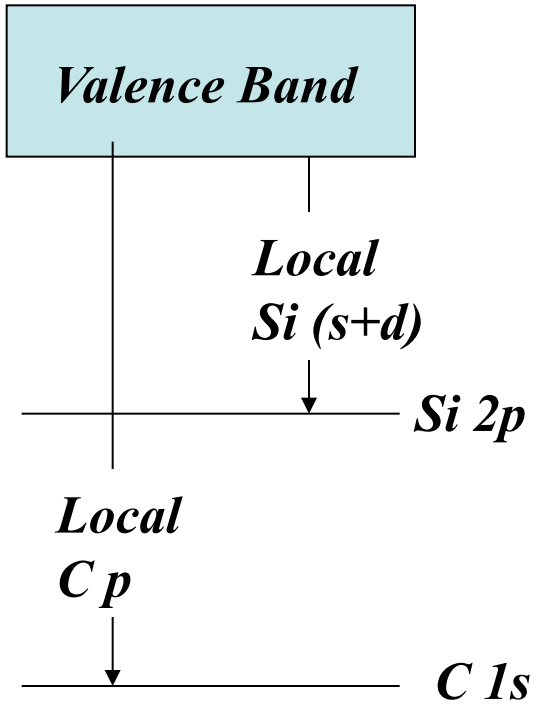

CORE STATE (M+)
X RAY-EMISSON
hν
VALENCE STATE (M+)
0-0
0-1
0-2
E_B CORE ELECTRON SPECTRUM
0-3
0-2
0-4
0-1
0-0
0-5
E_B VALENCE ELECTRON SPECTRUM
GROUND STATE (M)
BOND LENGTH (R)

Core levels are atomic-like:
Local Properties

Dipole Selection rules are valid:
Symmetry Selectivity

$$\Delta l = \pm 1$$



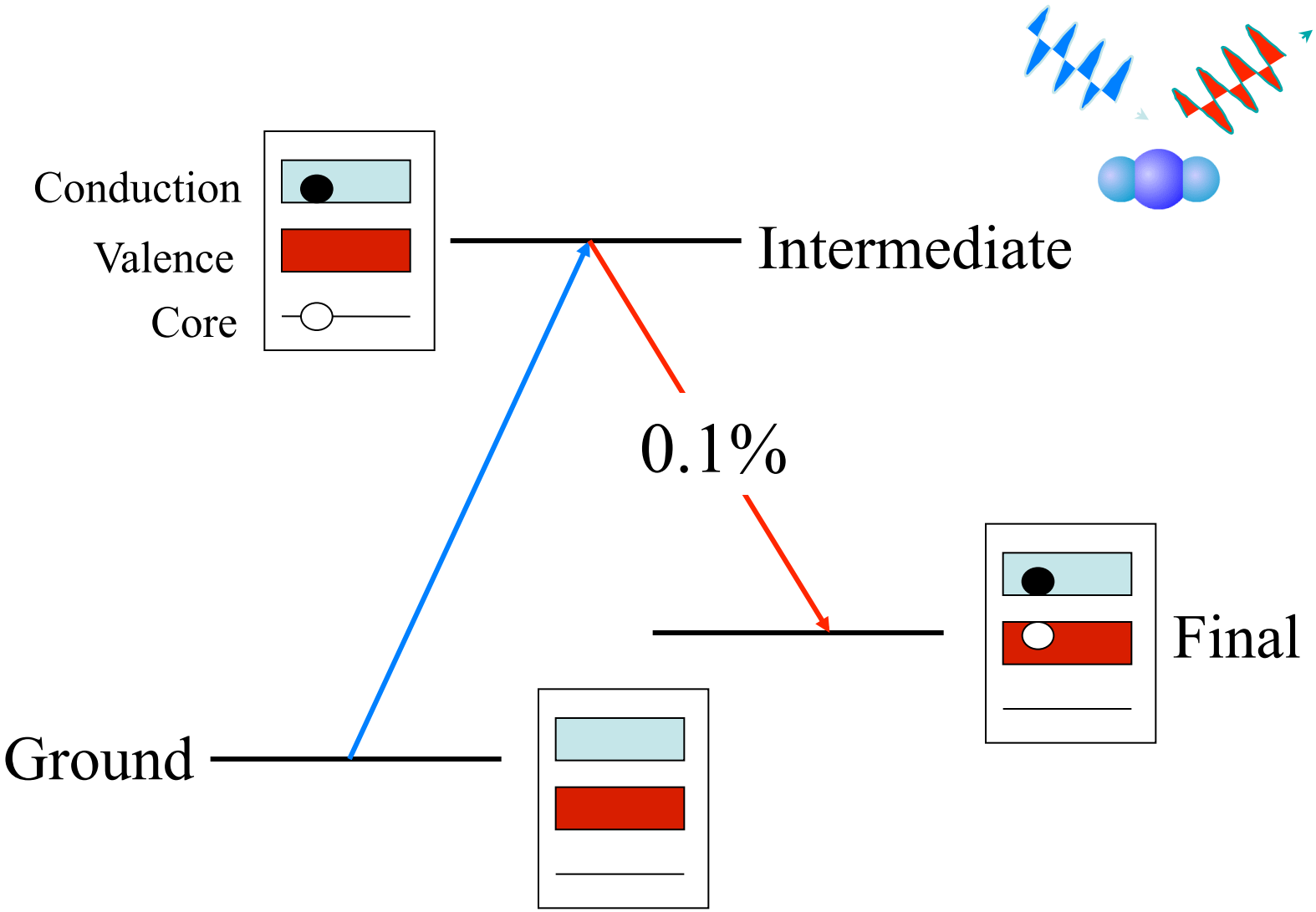


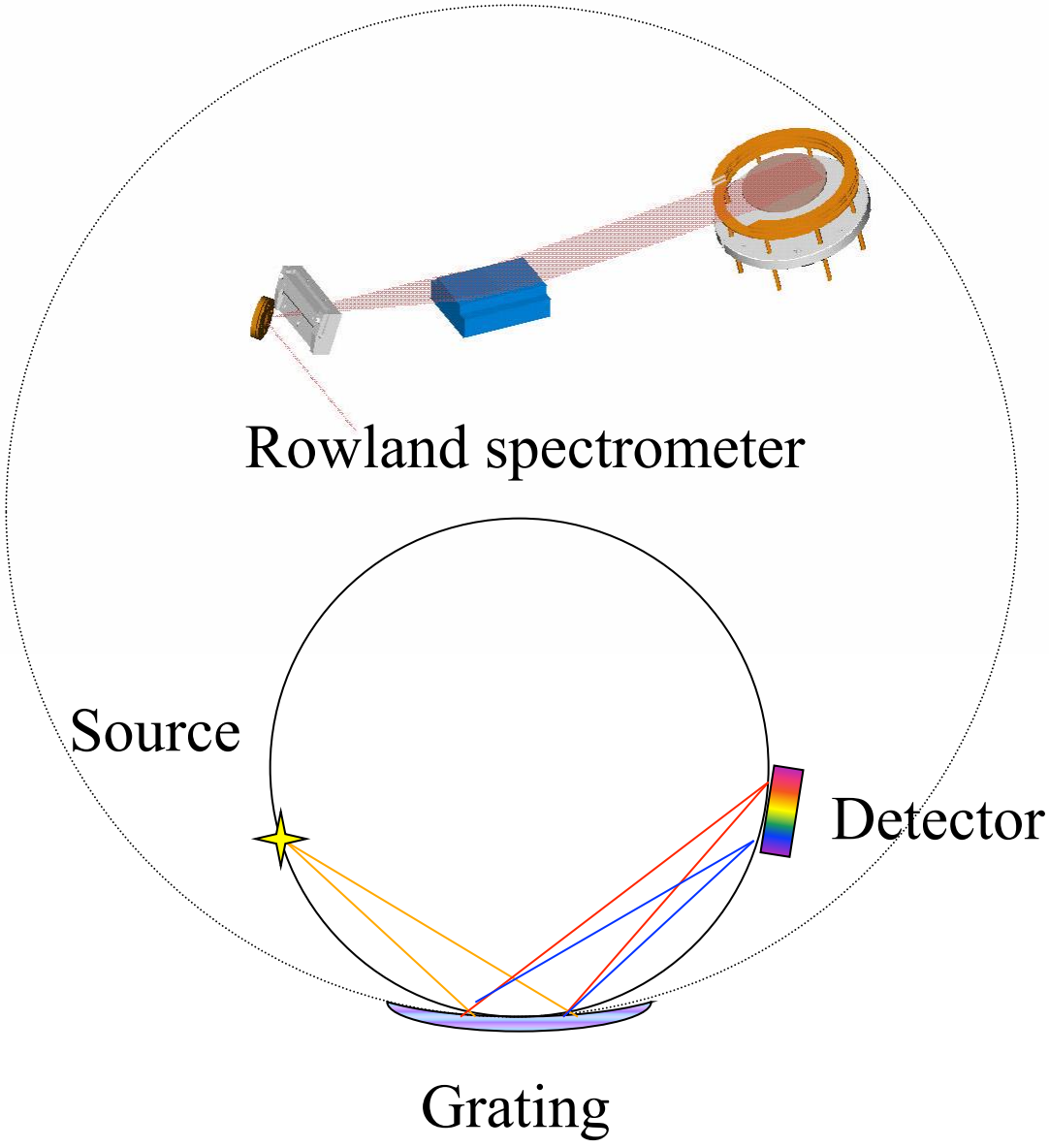
Local Partial Density of States

Almost the same information as electrons, but: photon-in-photon-out

- Deep probing (>1000Å)
- True bulk properties
- Buried structures
- Ambient Conditions
- Liquids and Gases
- Independence of external fields and charging.

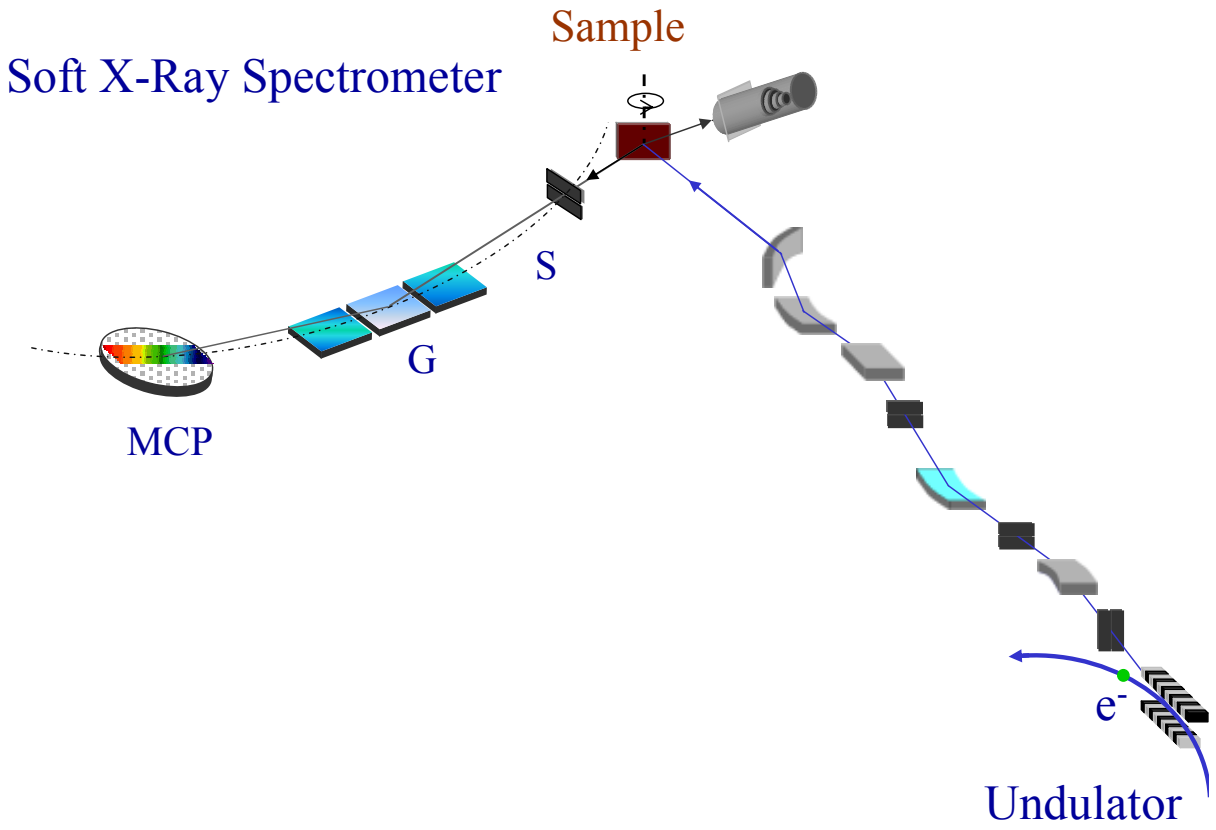
Notoriously low count rates



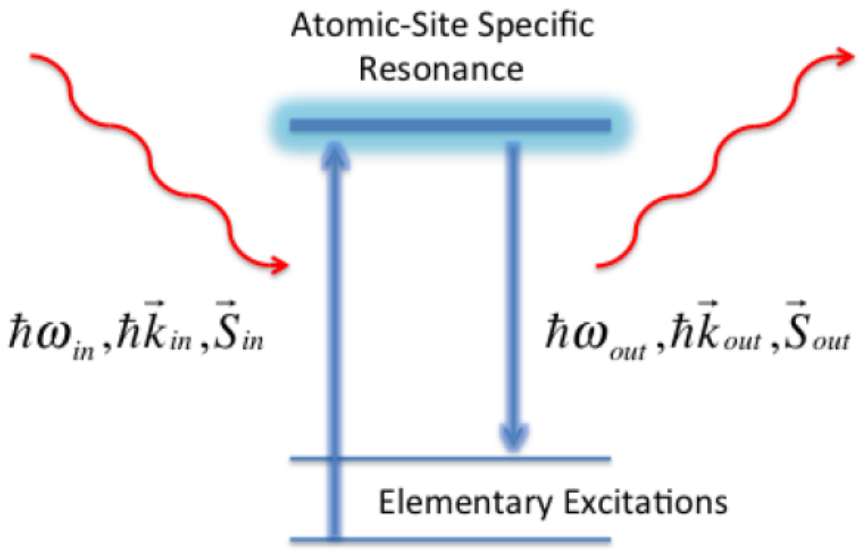


Combining the focussing properties of a sphere with the dispersive properties of a grating

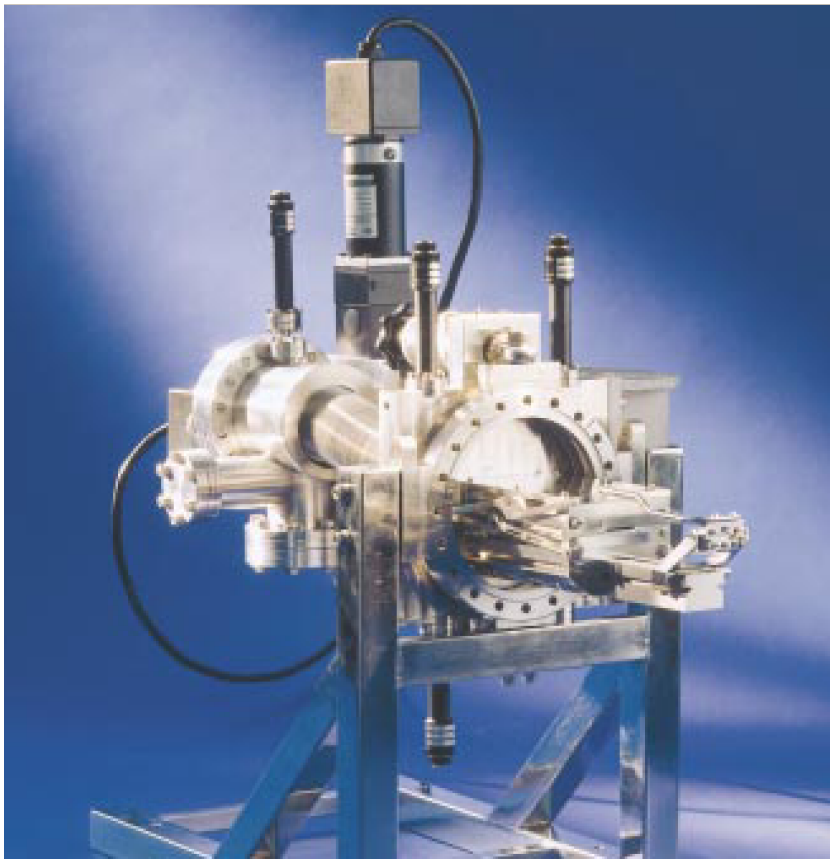
Experiment



Resonant Inelastic X-ray Scattering

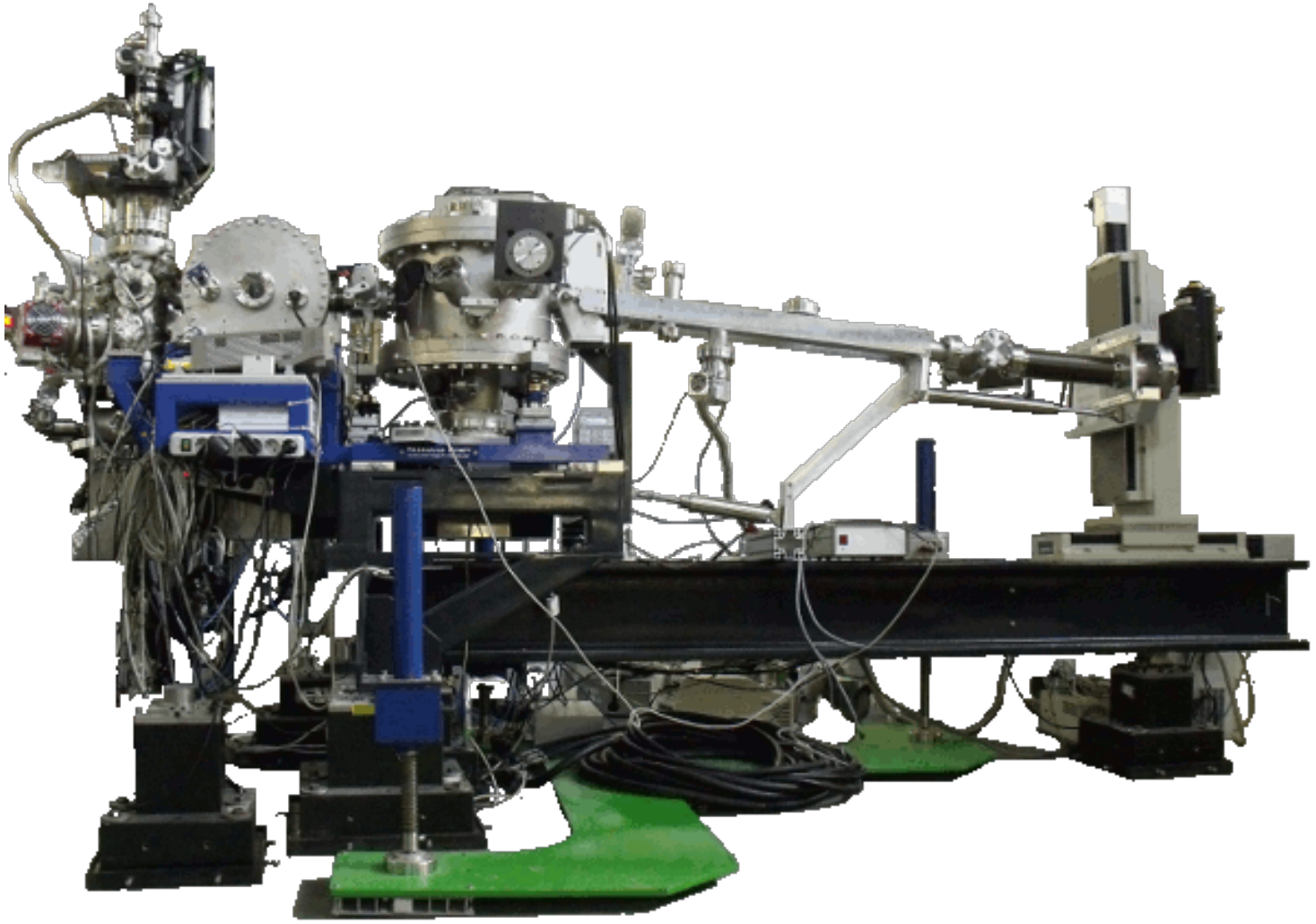


Joseph Nordgren design from mid-80:s

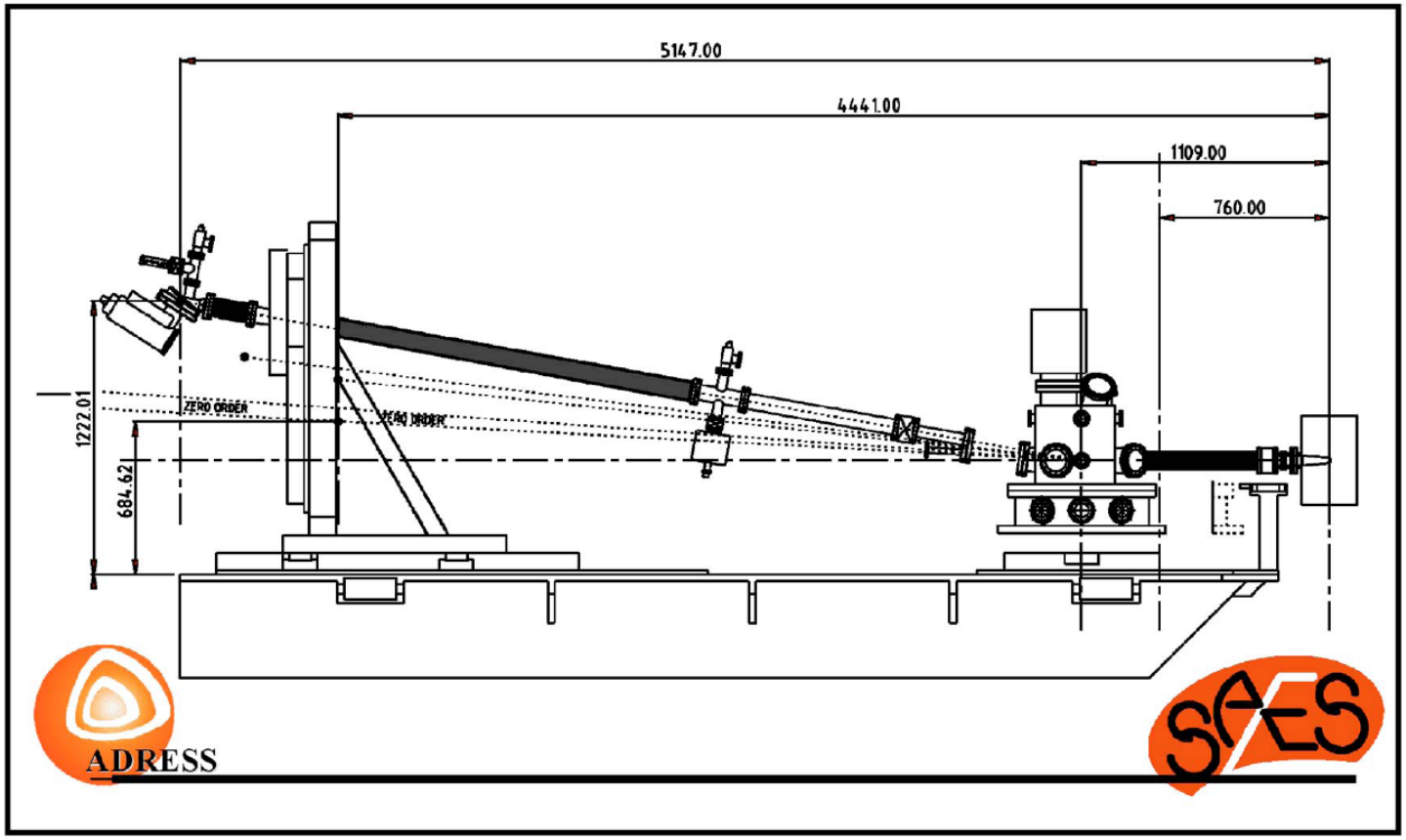


still going strong…

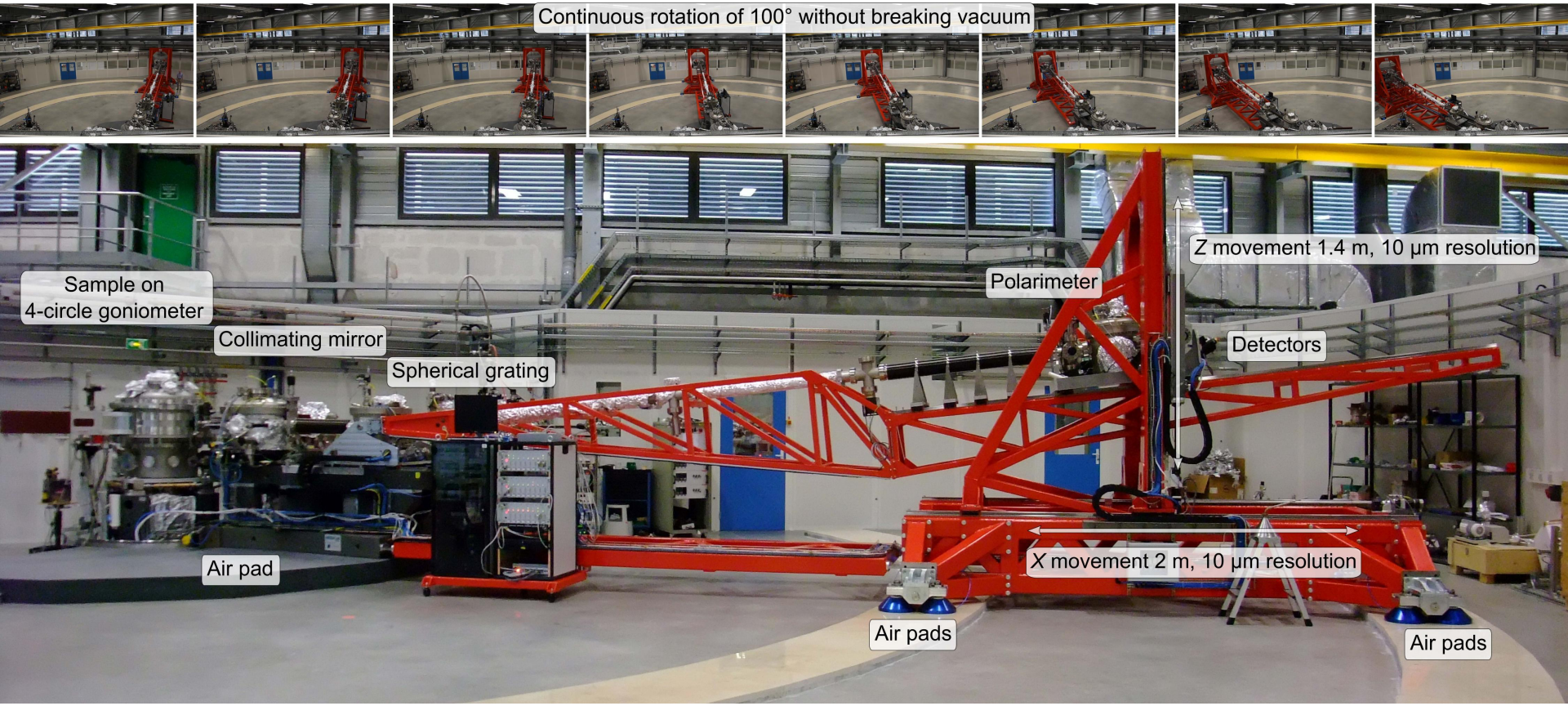
AERHA@SEXTANTS@SOLEIL



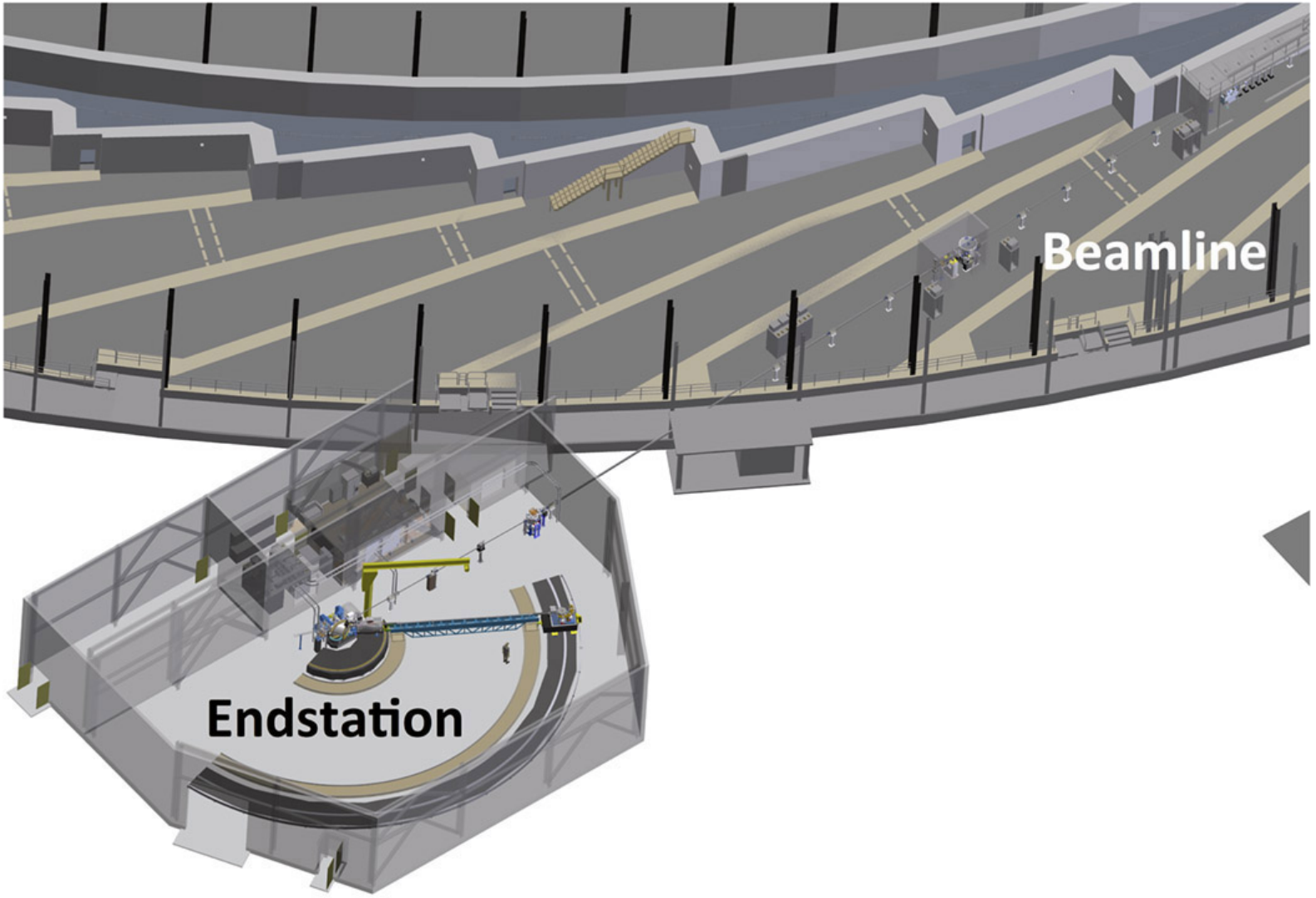
SAXES@ADRESS@SLS



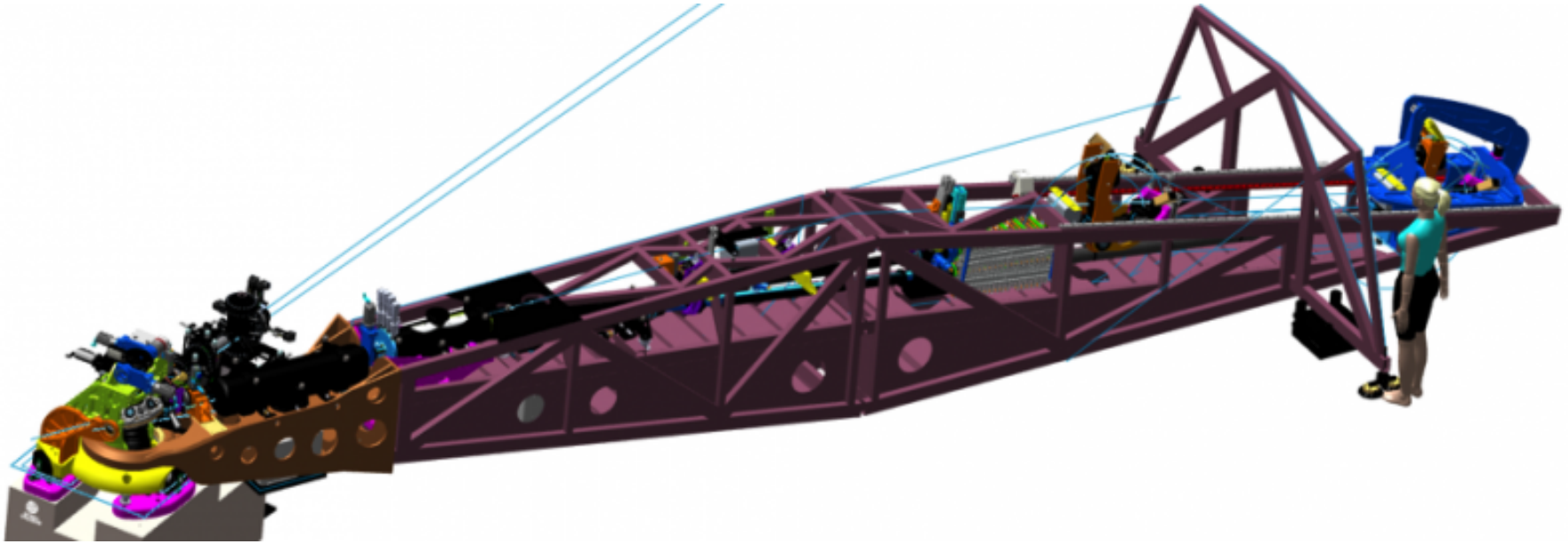
ERIXS@ESRF


Continuous rotation of 100° without breaking vacuum
Sample on
4-circle goniometer
Collimating mirror
Spherical grating
Air pad
Polarimeter
Z movement 1.4 m, 10 µm resolution
Detectors
X movement 2 m, 10 µm resolution
Air pads
Air pads

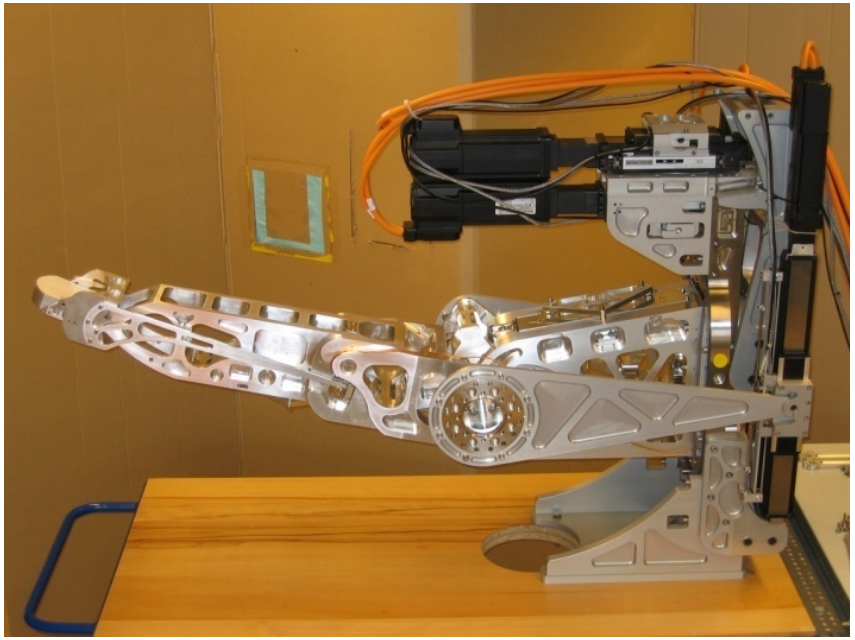
SIX@NSLS-II



VERITAS@MAX IV

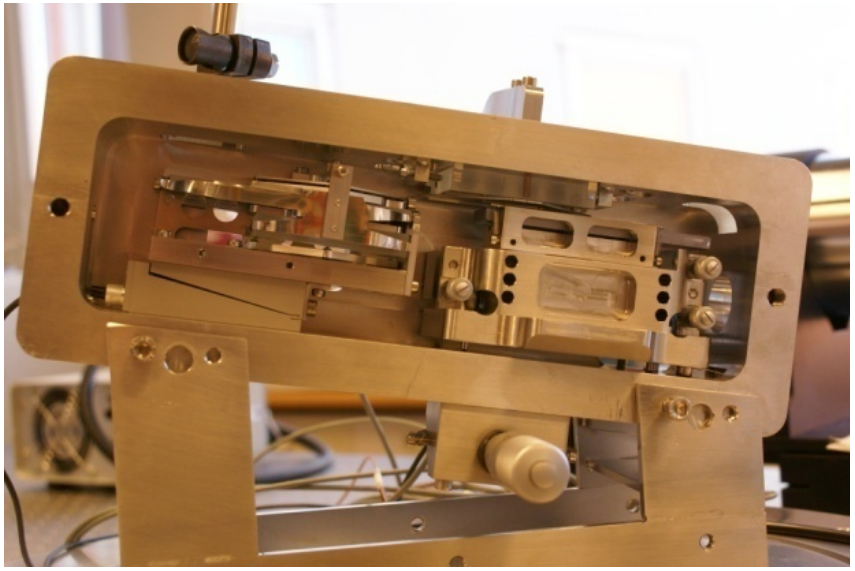


New Concepts for efficiency and resolution



PGS:
Plane grating spectrometer

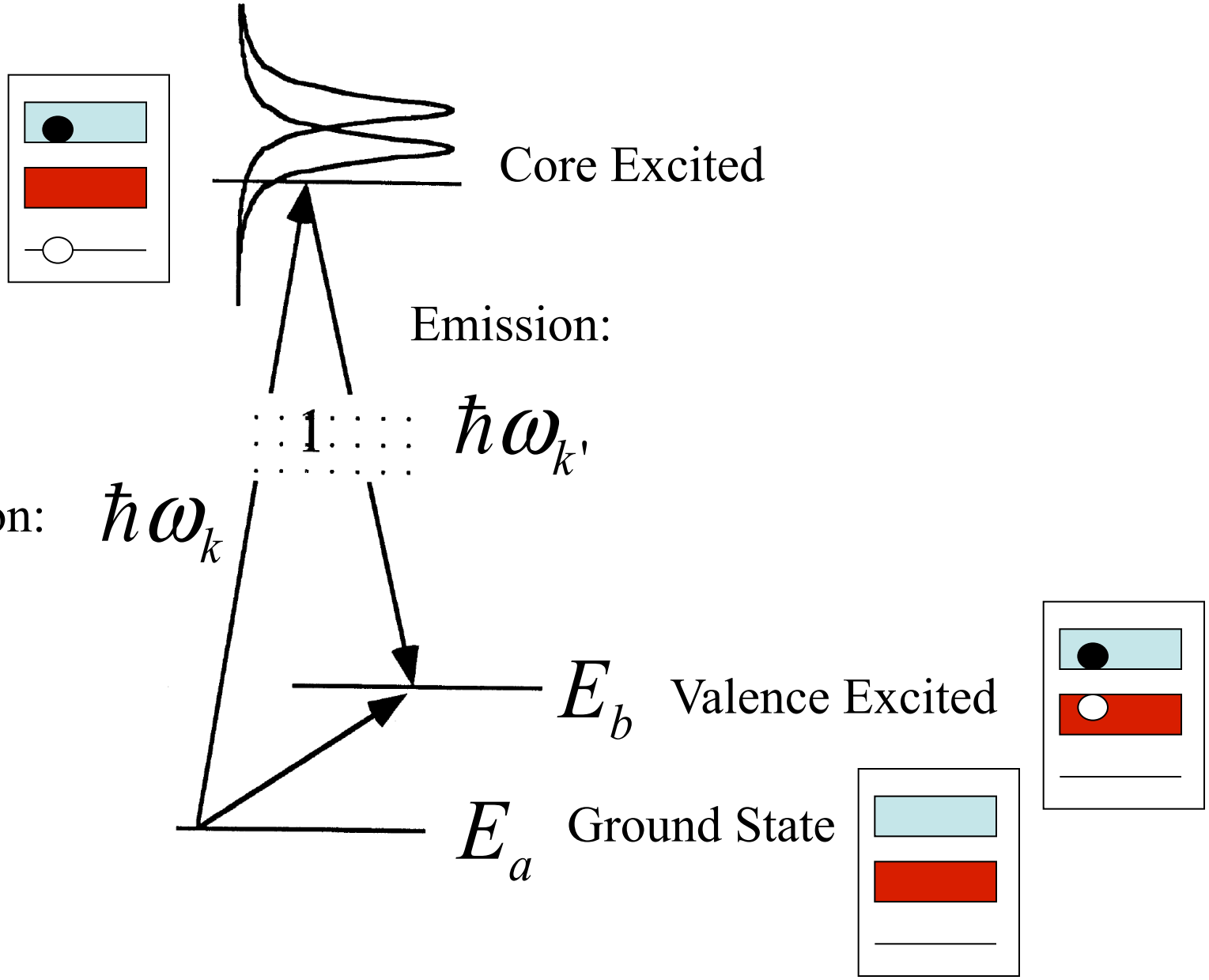
Two parabolic mirrors and
a plane grating



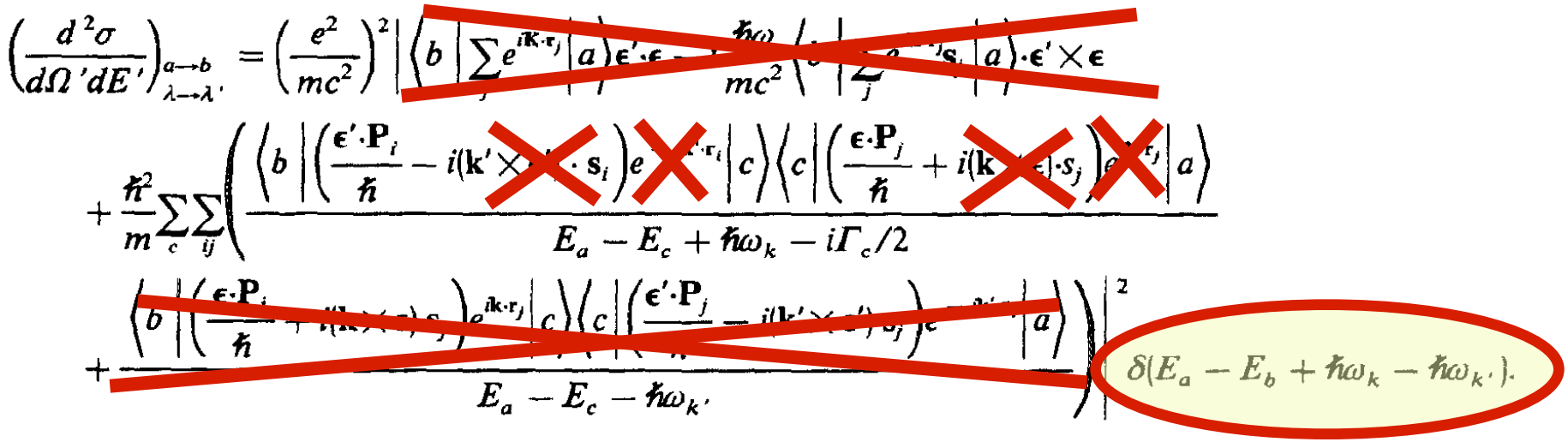
FTS:
Fourier Transform Spectrometer

Wavefront Beamsplitters and
mirrors in grazing incidence

X-ray scattering; always a one-step process

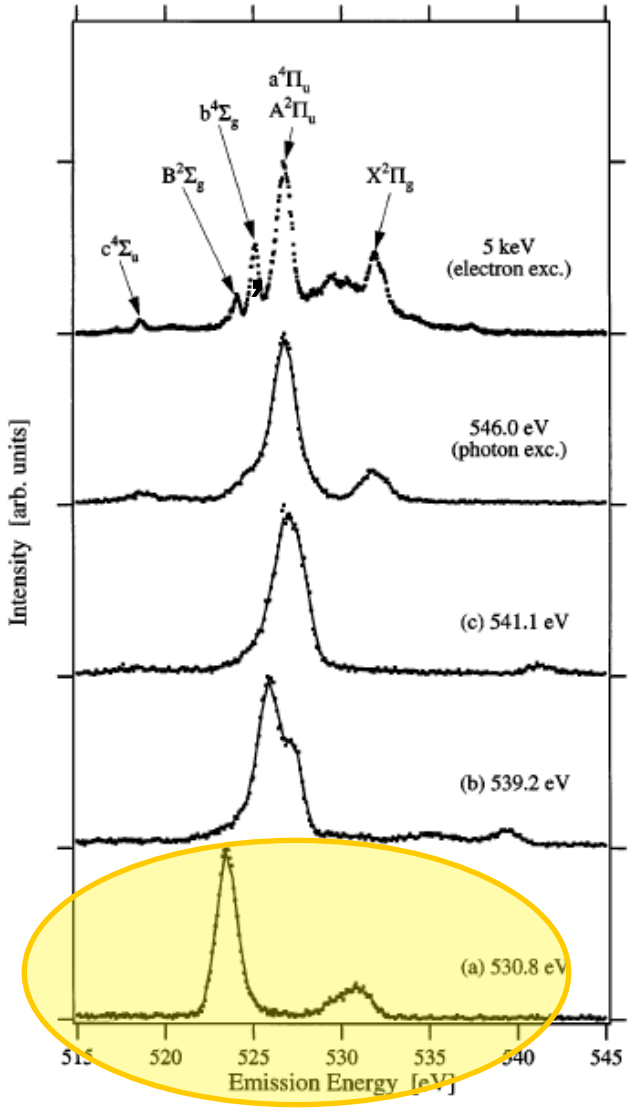


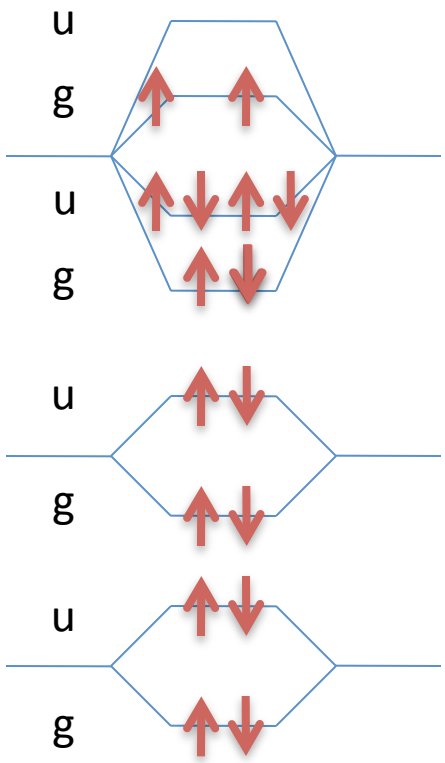
Linear approximation



M. Blume, J. Appl. Phys. 57, 3615 (-85): This equation ' accounts for most scattering phenomena to the order of $\left(\frac{\hbar\omega}{mc^2}\right)^2$,

The oxygen molecule: inversion symmetry





Where is the core hole?

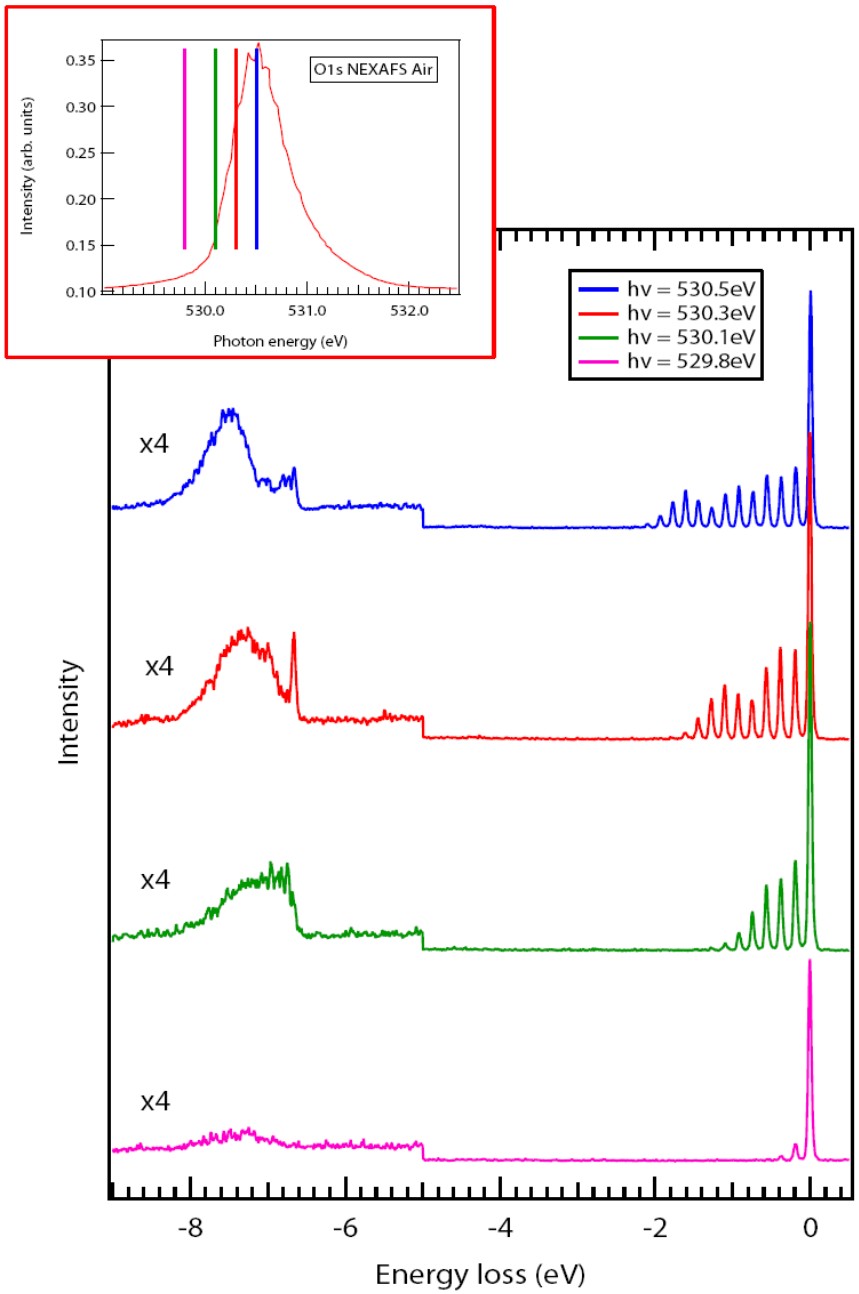
Right? O O

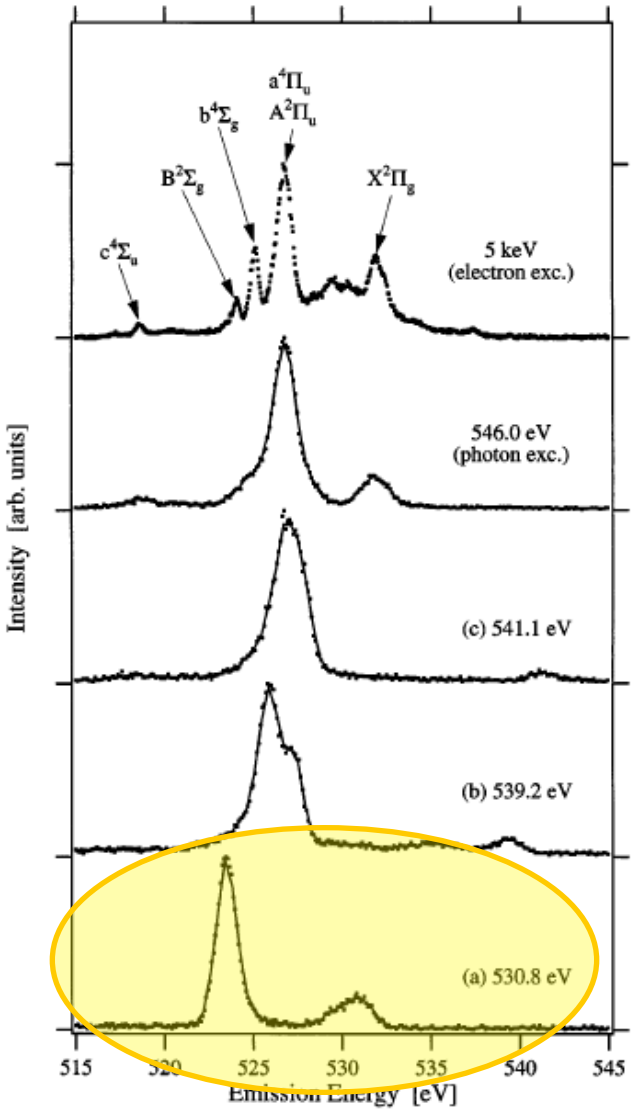
Left? O O

Both?

Strict dipole selection rules apply:
Gerade→Ungerade→Gerade
Inversion symmetry is not broken

P. Glans, et al. PRL 76, 2488 (-96)

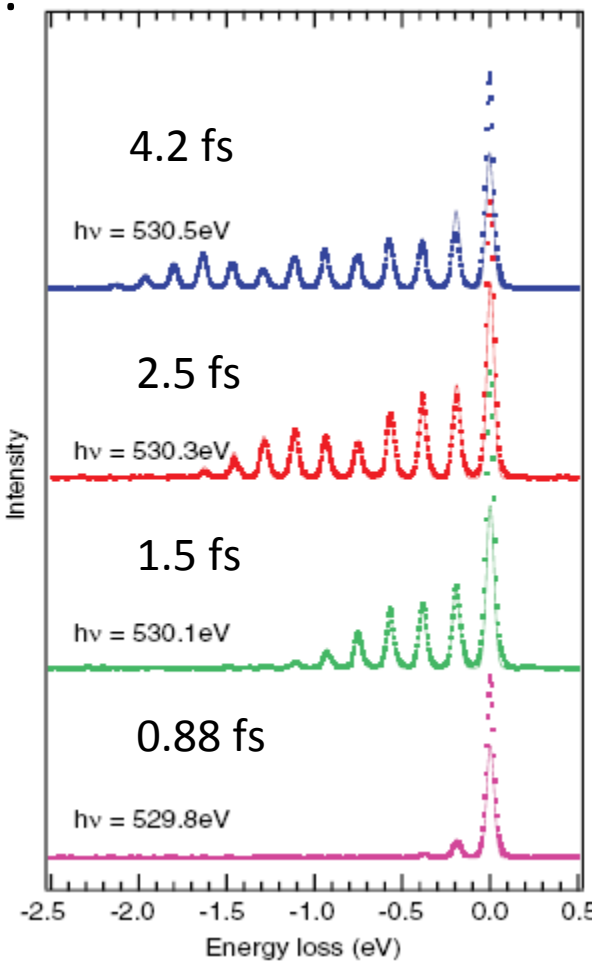




Hennies, et al. PRL. 104, 193002 (2010)

Controlling the nuclear motion

Potential surface and lifetime of the core excited state.



$$\Gamma = 150 \pm 1 \quad \text{meV}$$

$$r_0 = 1.35 \pm 0.01 \quad \text{Å}$$

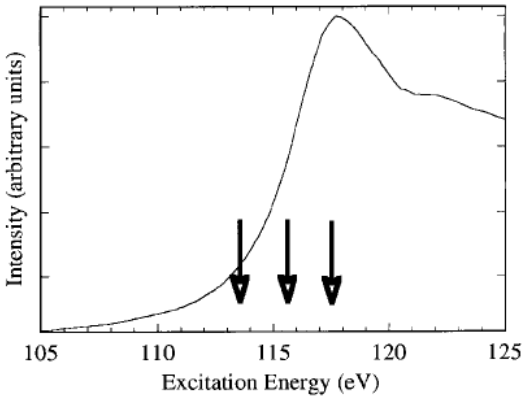
Scattering Duration Time

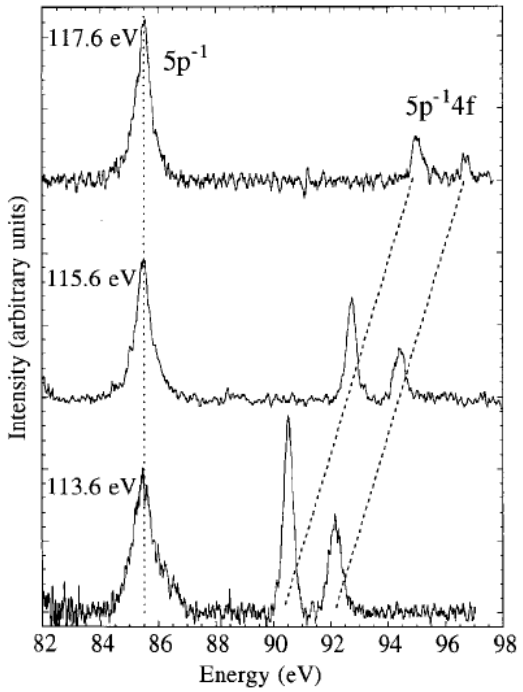
$$\tau = \frac{\hbar}{\sqrt{\Gamma^2 + \Omega^2}}$$

Constant-Γ approximation ”valid”
Constant-fluorescence-yield approximation

Concept developed by Faris Gel’mukhanov and Hans Ågren

The Ultrafast Core-hole Clock





4d→4f resonance in LaF_3

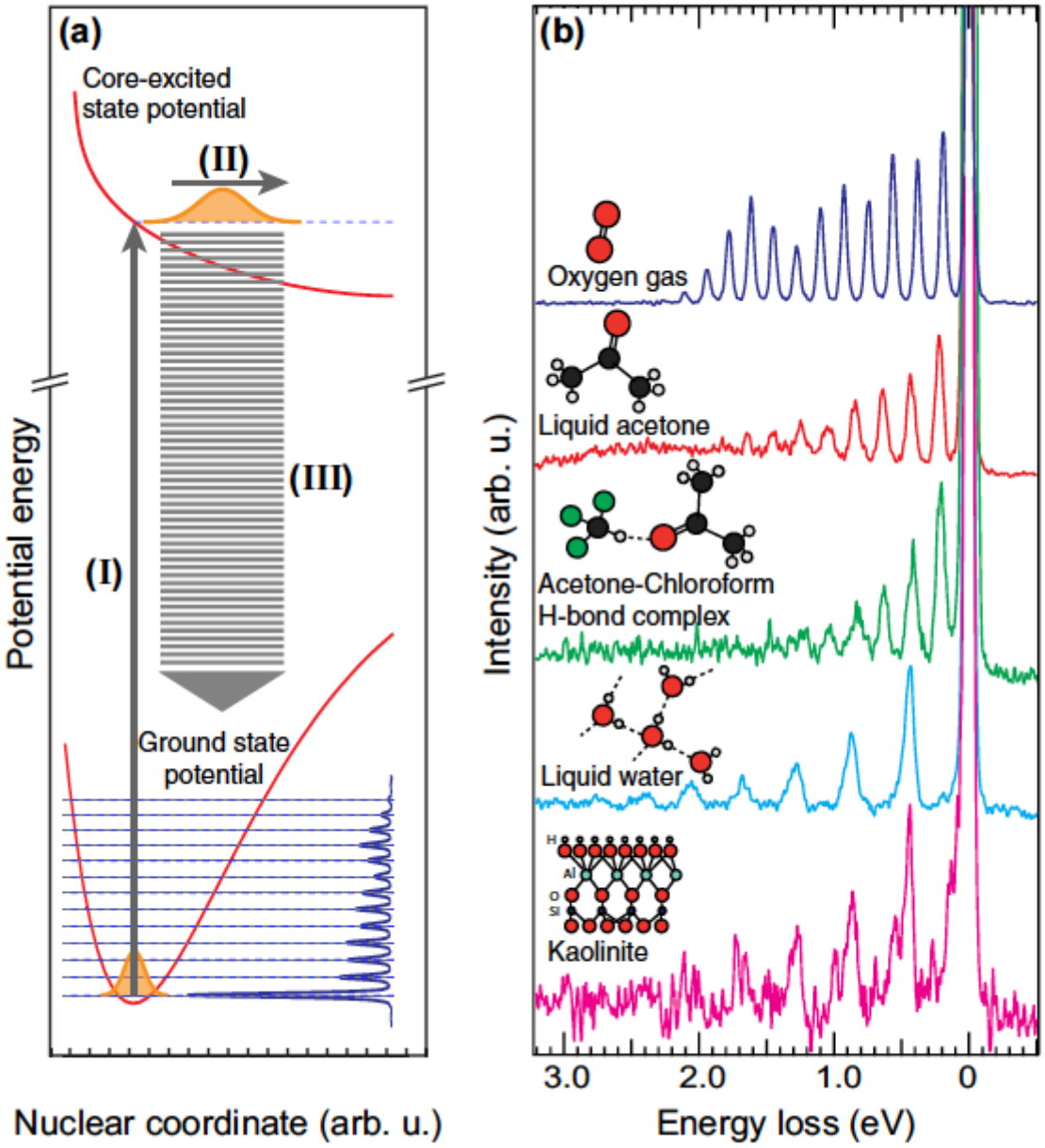
Scattering:

$$GS \rightarrow 4d^{-1}4f \rightarrow 5p^{-1}4f$$

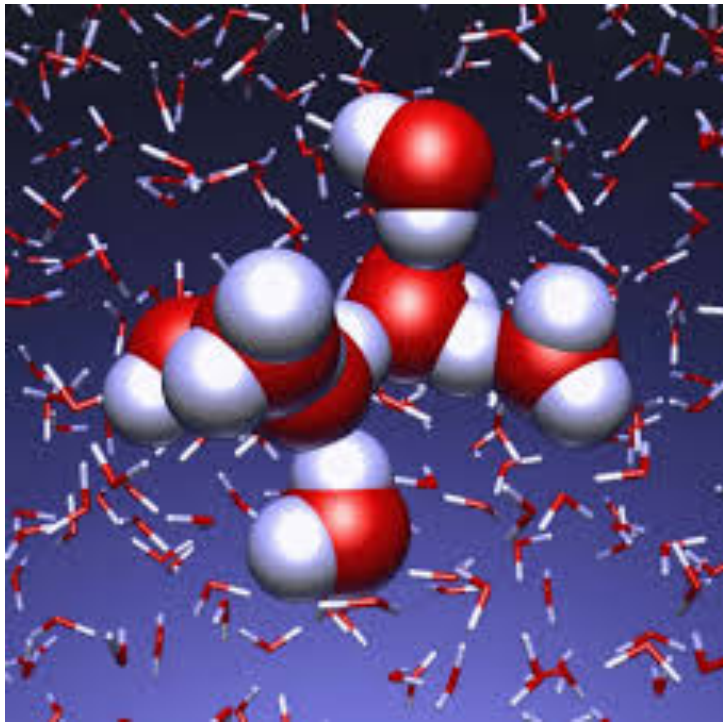
Gives narrow peaks.

$GS \rightarrow 5p^{-1}\varepsilon$ intensity indicates that the *4f* electron escapes during the process:

Molecular Materials and Processes



S. Schreck et al., Sci Rep. 6, 20054 (2016)

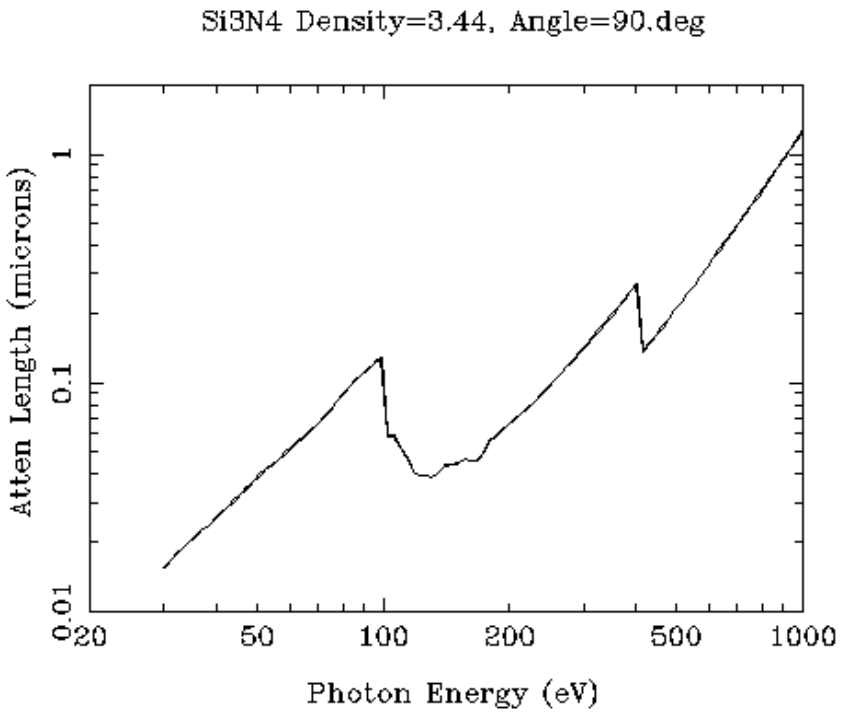


High-Resolution RIXS gives access to

- **local potential surfaces** of the electronic ground state of complex molecular systems
- coupling of local vibrational **combination** modes

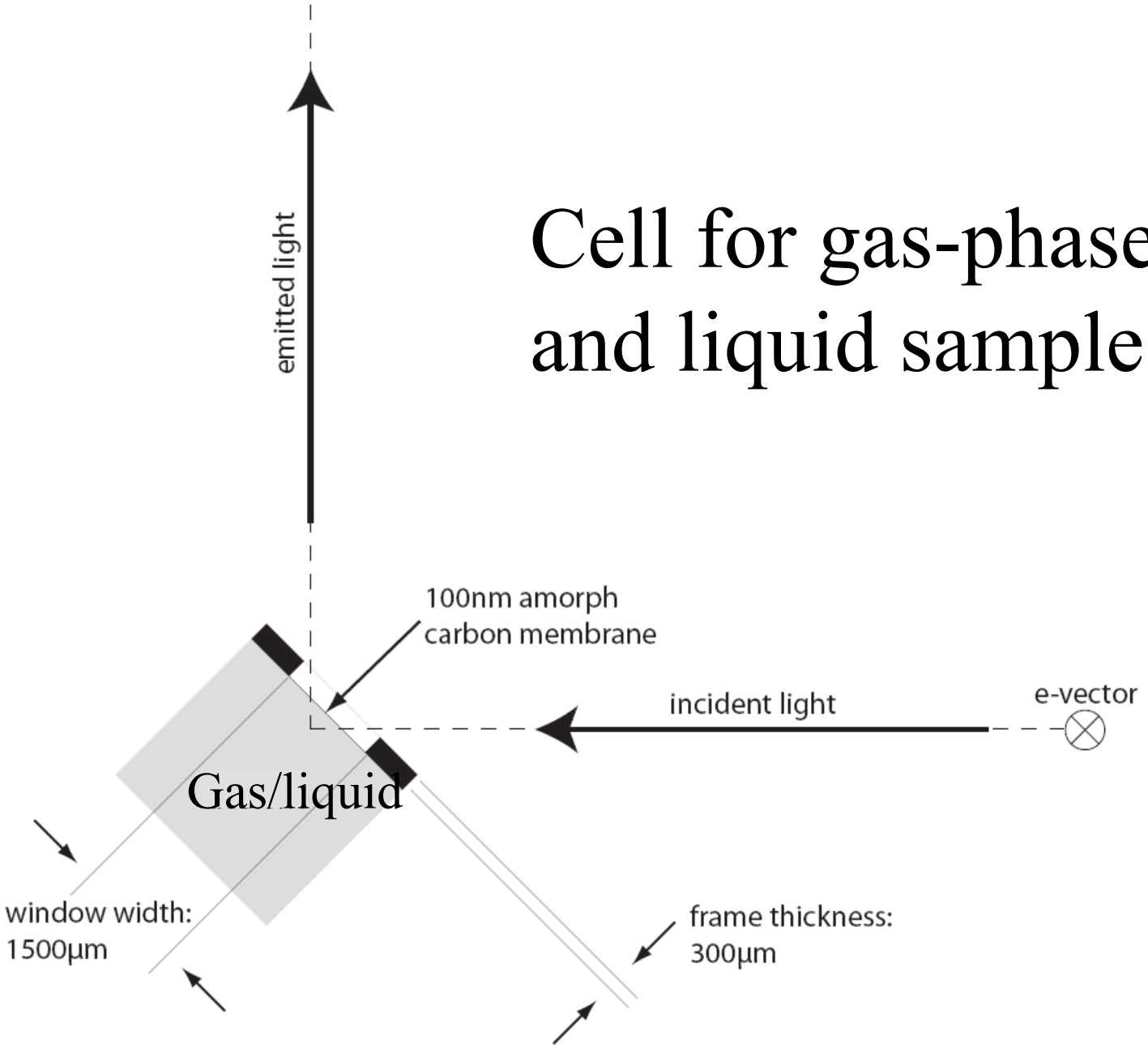
Looking Through Windows

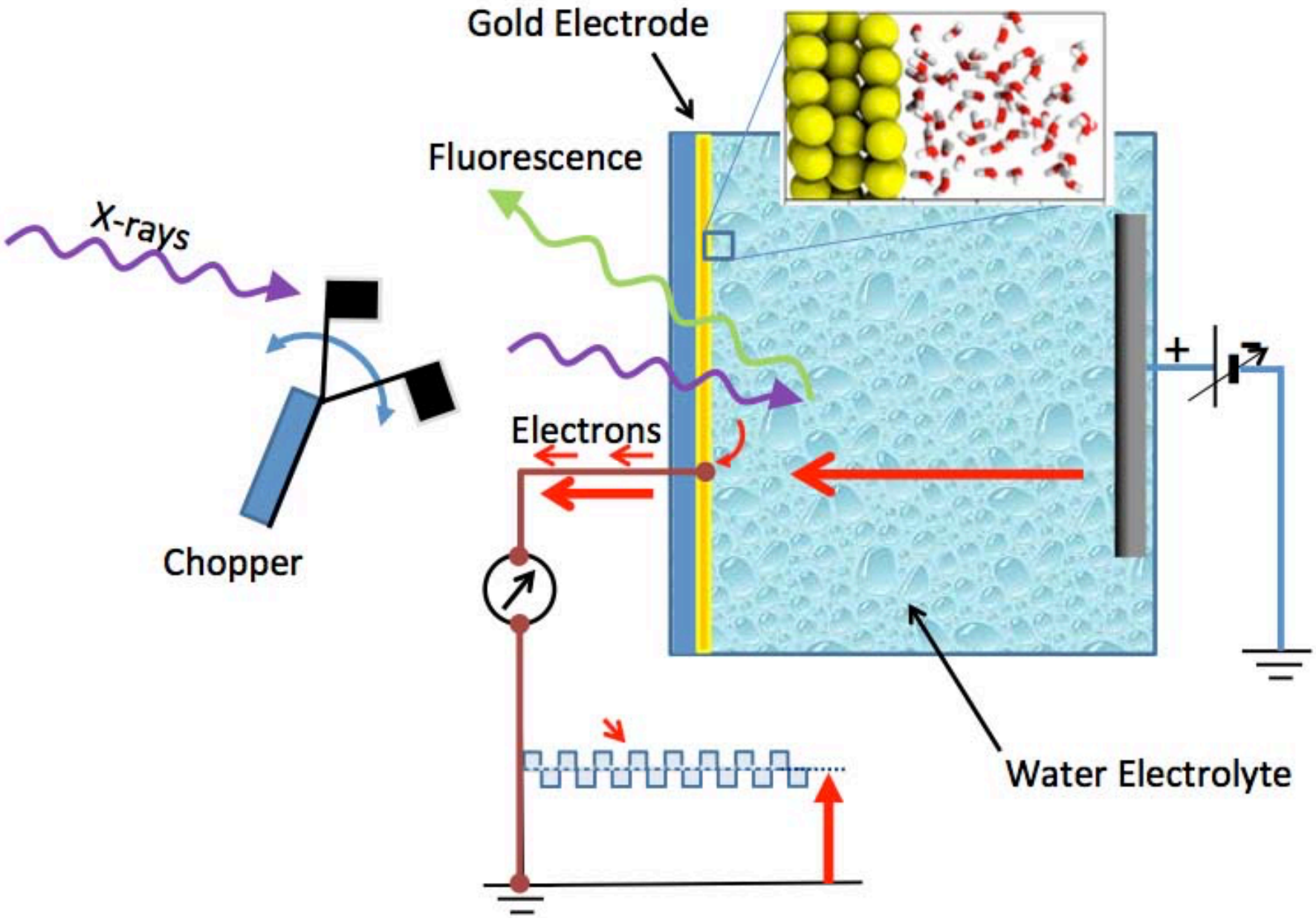
Several 1000 Ångström



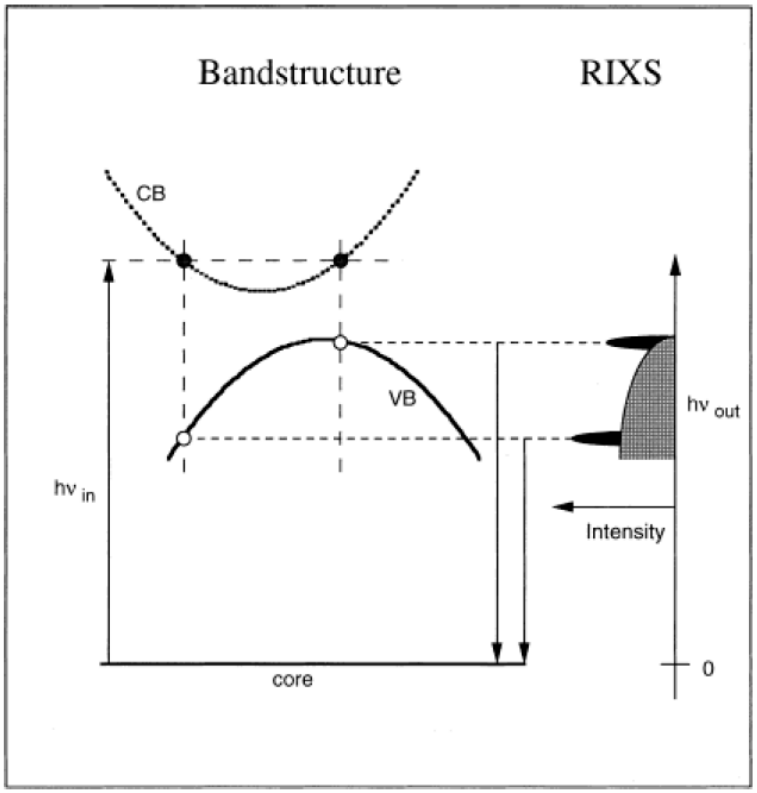
-true bulk properies
-gases
-liquids
-gas/liquid/solid interfaces

Cell for gas-phase and liquid samples



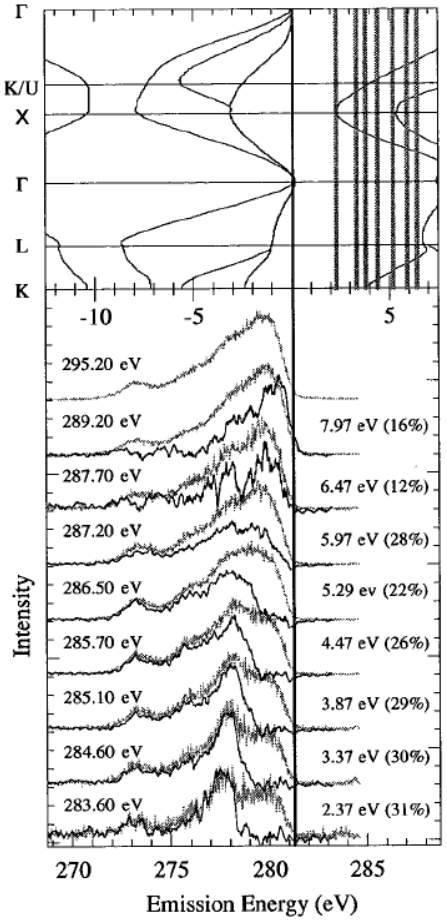

Gold Electrode
Fluorescence
X-rays
Electrons
Chopper
+
Water Electrolyte
Pulsed current from molecular layer

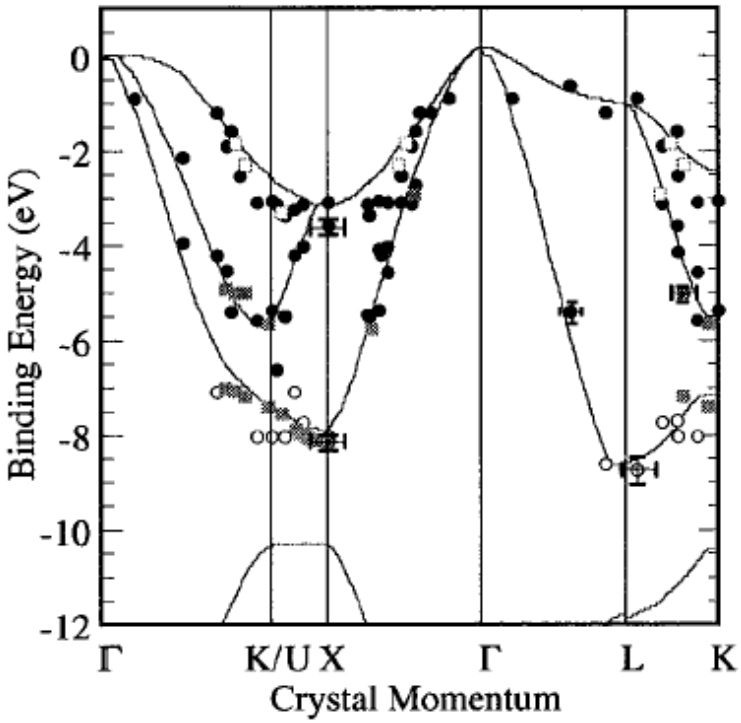
Momentum Conservation



And band mapping

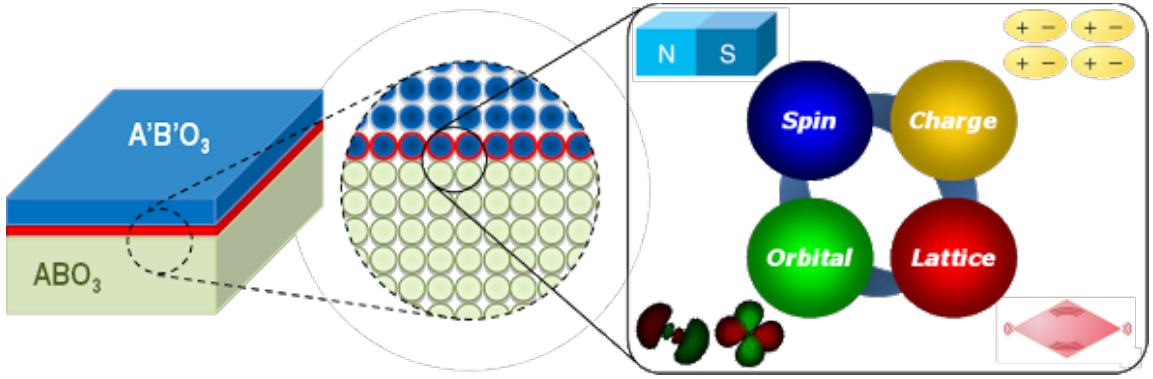
Silicon Carbide again

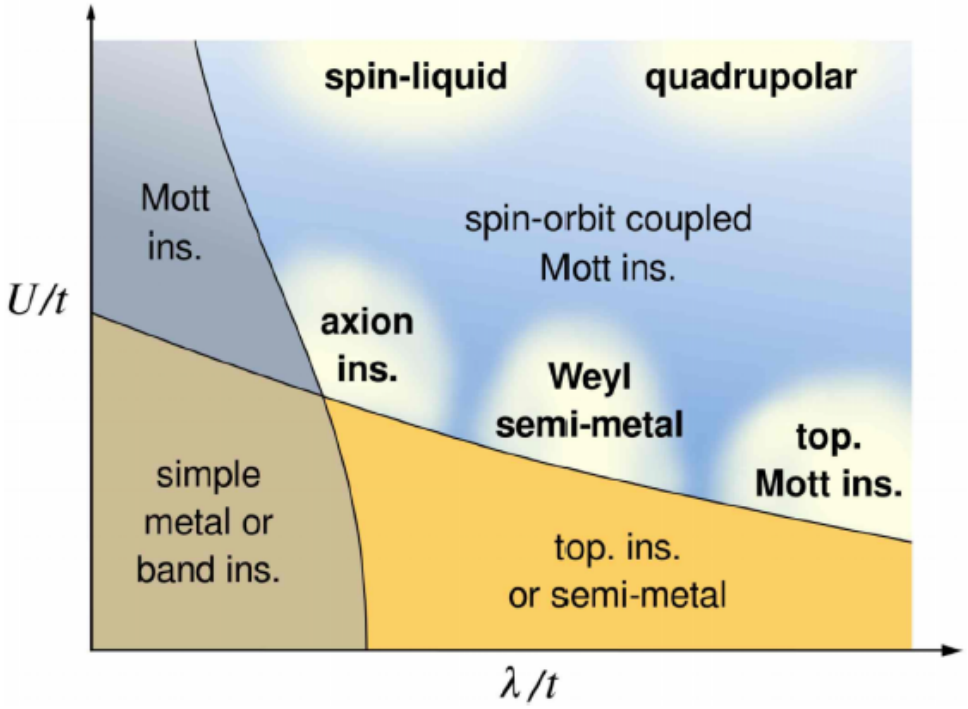


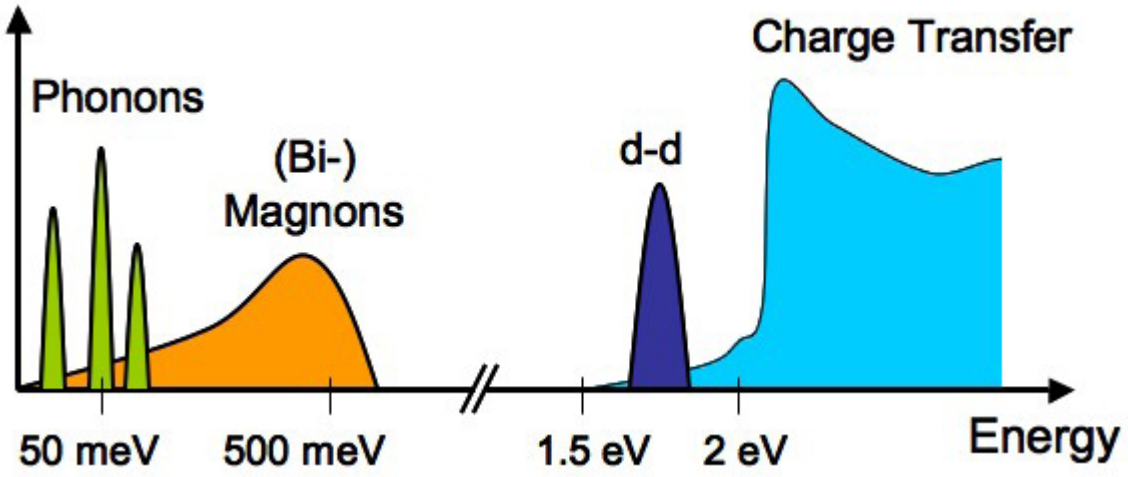


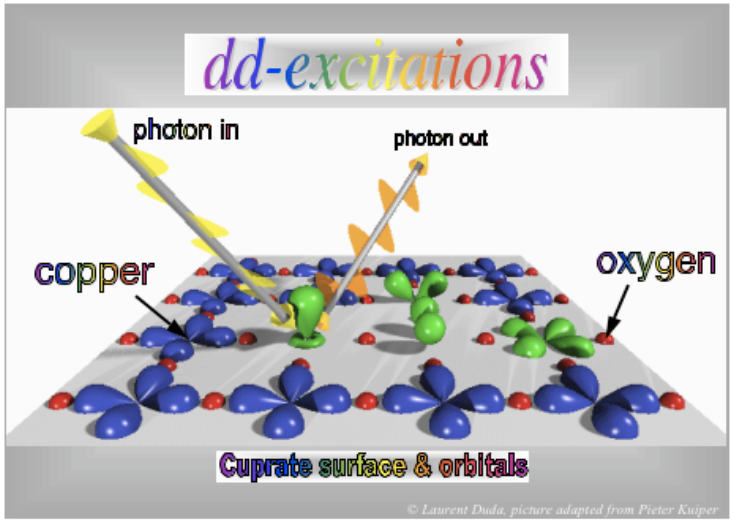
J. Lüning et al., PRB56 -97

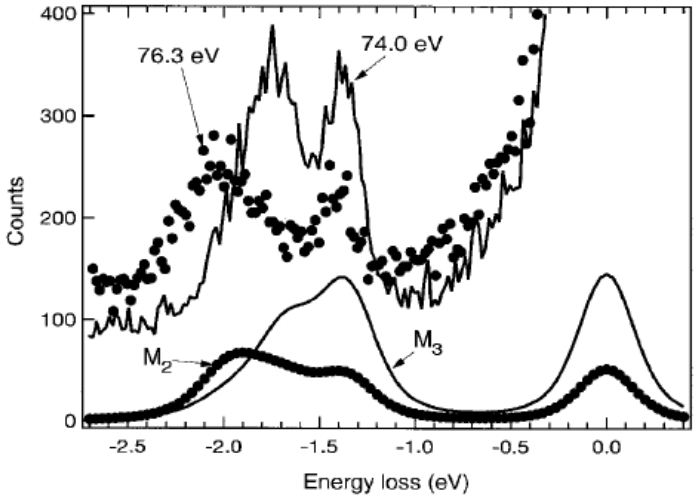
Correlated Electron Materials



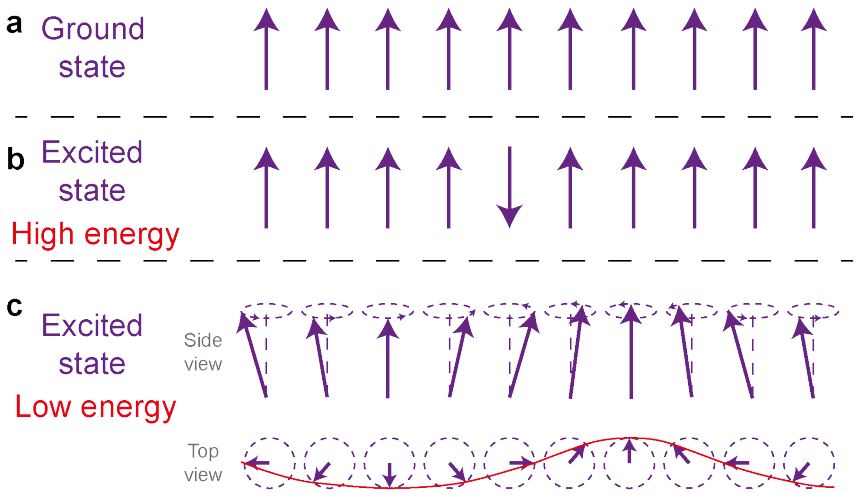


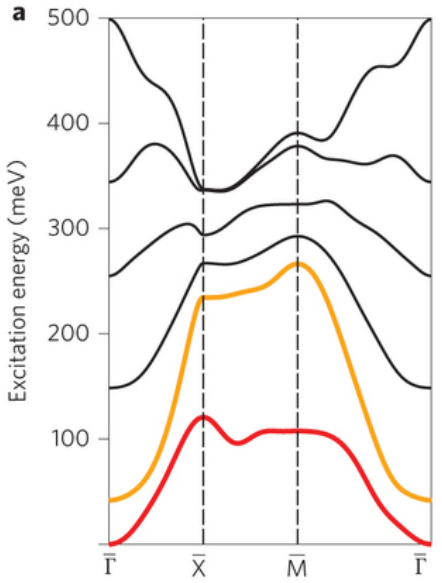

Charge Transfer
Phonons
(Bi-)
Magnons
d-d
50 meV
500 meV
1.5 eV
2 eV
Energy


dd-excitations
photon in
photon out
copper
oxygen
Cuprate surface & orbitals
© Laurent Duda, picture adapted from Pieter Kuiper


76.3 eV
74.0 eV
M2
M3
Counts
Energy loss (eV)
400
300
200
100
0
-2.5
-2.0
-1.5
-1.0
-0.5
0.0

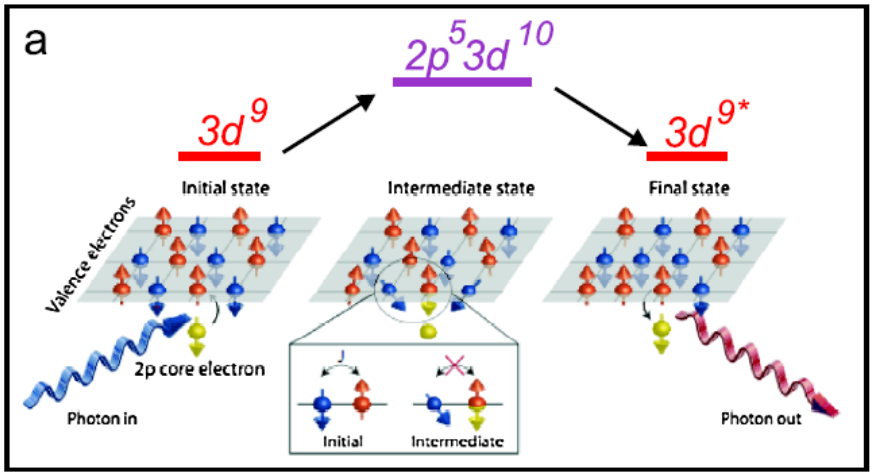
Magnon energy depends on momentum

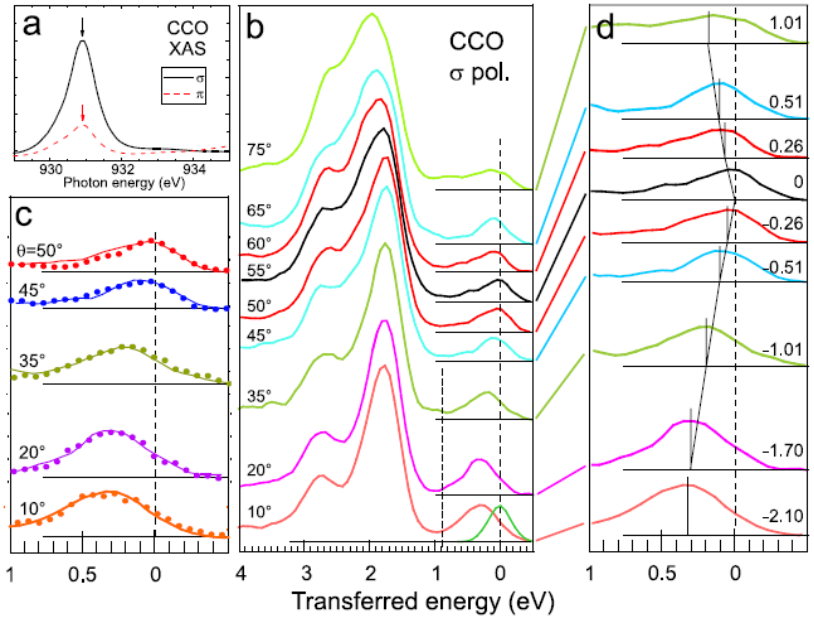




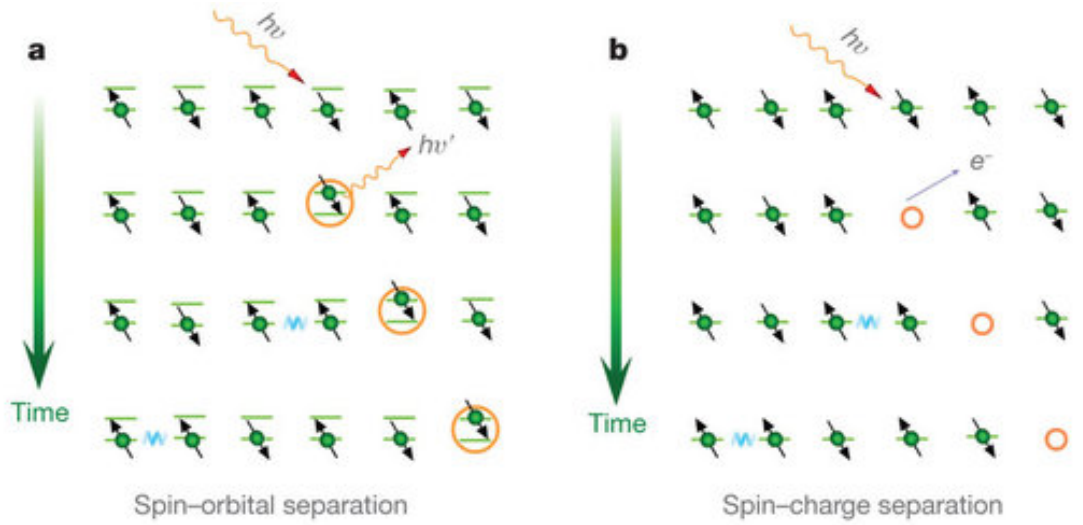
Dispersion of Magnetic Excitations in the Cuprate La_2CuO_4 and $CaCuO_2$ Compounds Measured Using Resonant X-Ray Scattering

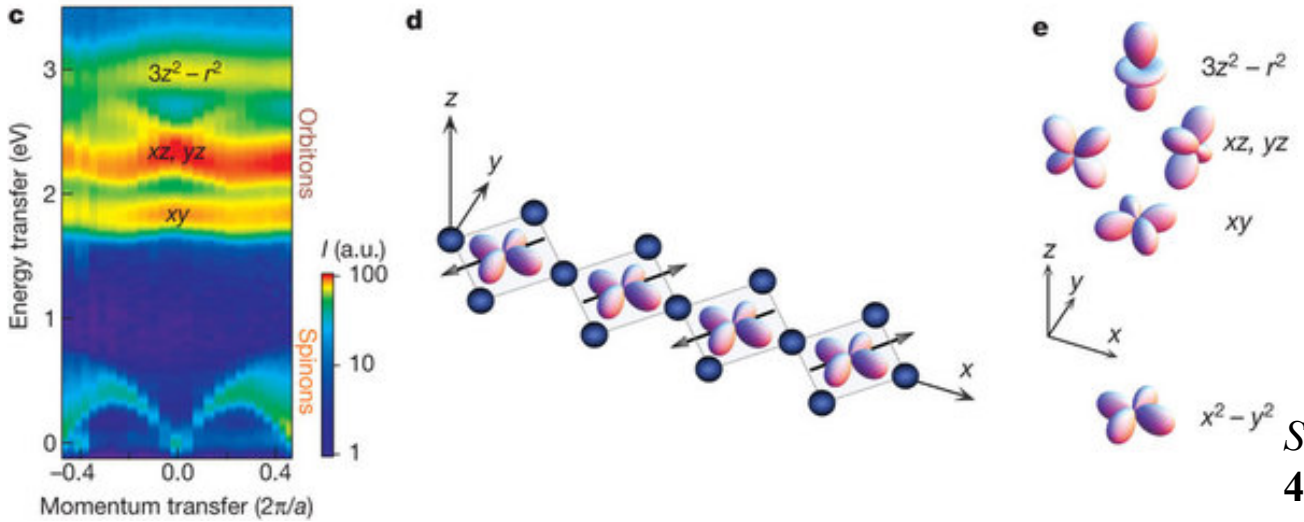
L. Braicovich,[1] L. J. P. Ament,[2] V. Bisogni,[3] F. Forte,[2,4] C. Aruta,[5] G. Balestrino,[6] N. B. Brookes,[3] G. M. De Luca,[5] P. G. Medaglia,[6] F. Miletto Granozio,[5] M. Radovic,[5] M. Salluzzo,[5] J. van den Brink,[2,7] and G. Ghiringhelli[1]





Orbiton-Spinon Separation

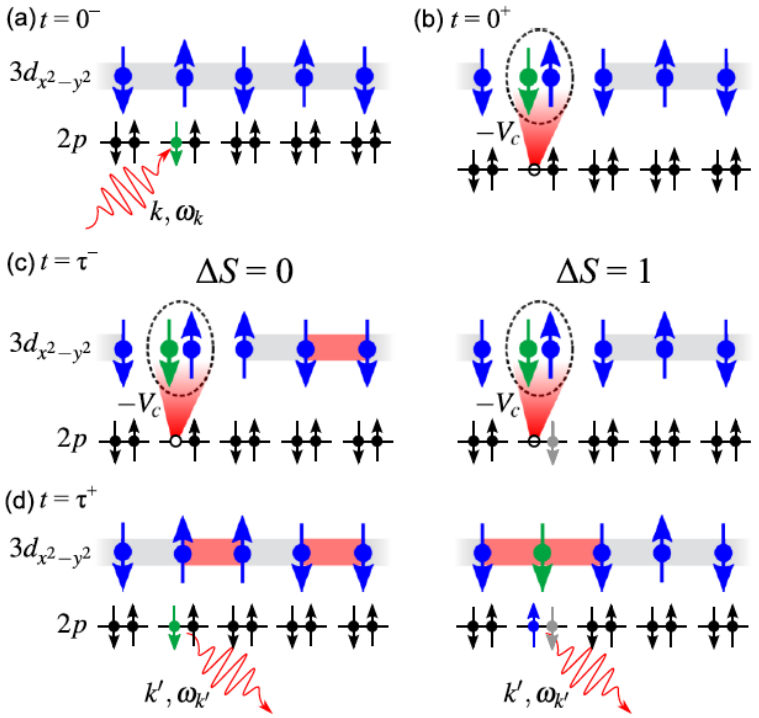


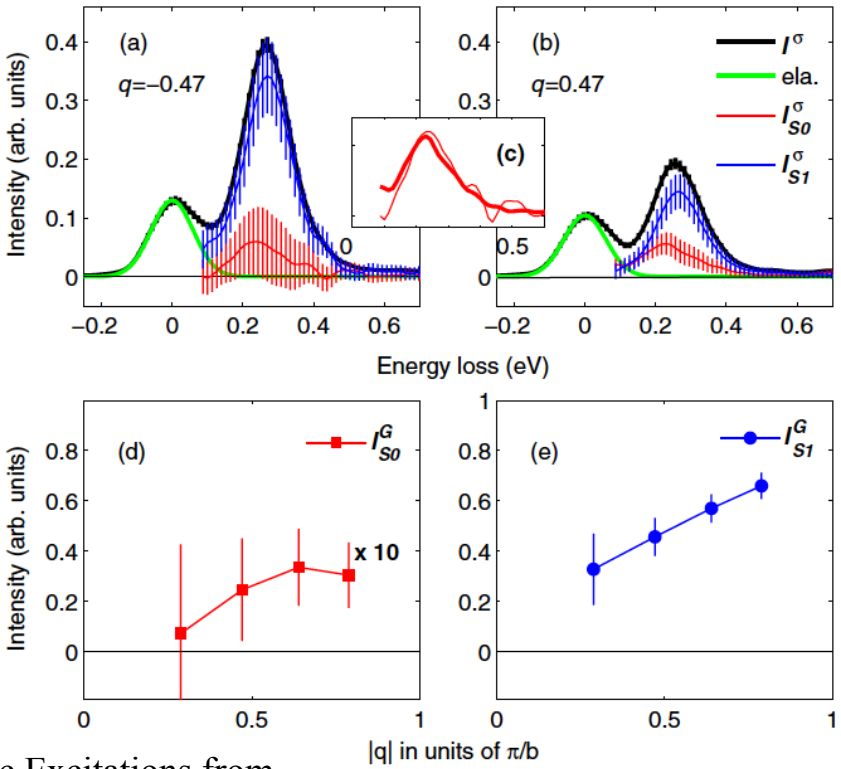


Schlappa et al., Nature **485**, 82–85 (2012)

Magnetism and Magnetization Dynamics

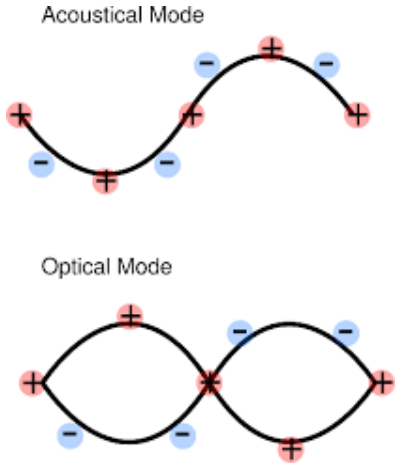
Double spin-flips depend on the spin-spin interaction strength, whereas the spin-orbit coupling is faster

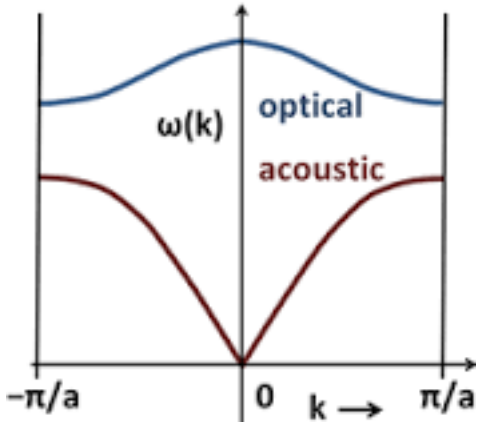




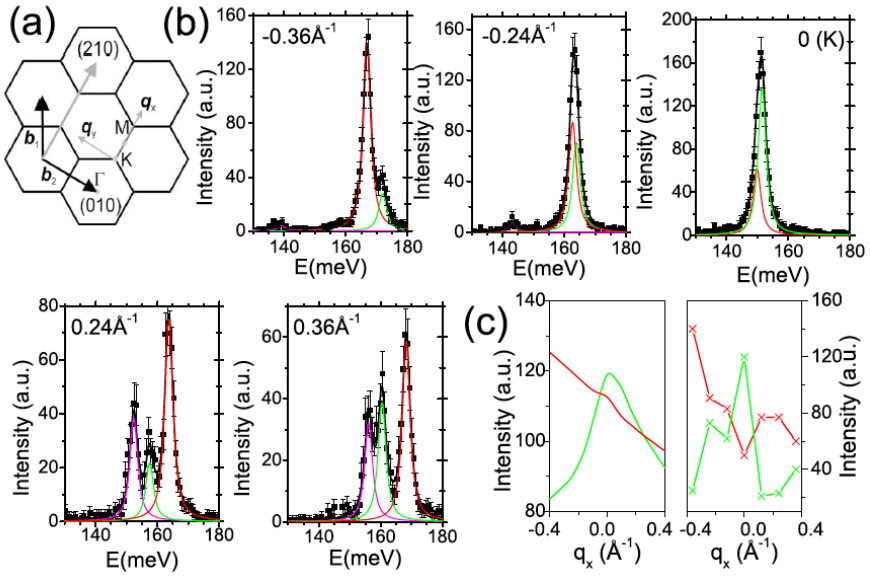
Femtosecond Dynamics of Momentum-Dependent Magnetic Excitations from Resonant Inelastic X-Ray Scattering in $CaCu_2O_3$.
V. Bisogni et al. PRL. 112, 147401 (2014)

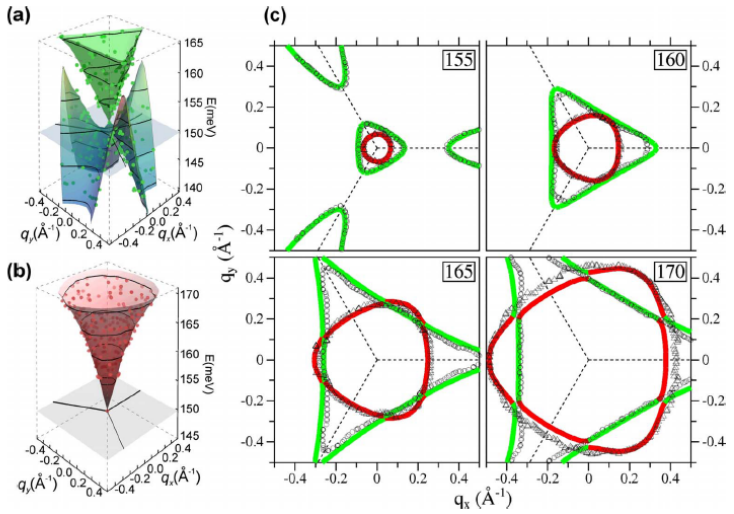
Phonon energy depends on momentum





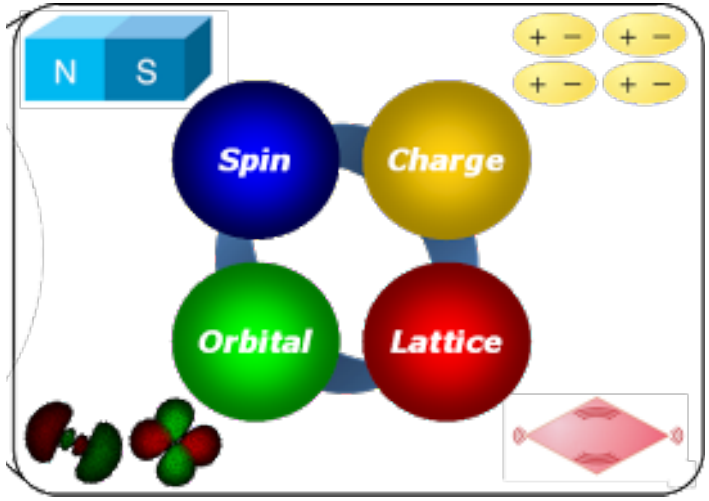
Phonon-electron-magnon-orbiton coupling





Phonon surface mapping of graphite, Grüneis et al., PRB 80, 085423 (2009)

Property-determining interactions



accessible in high-resolution RIXS

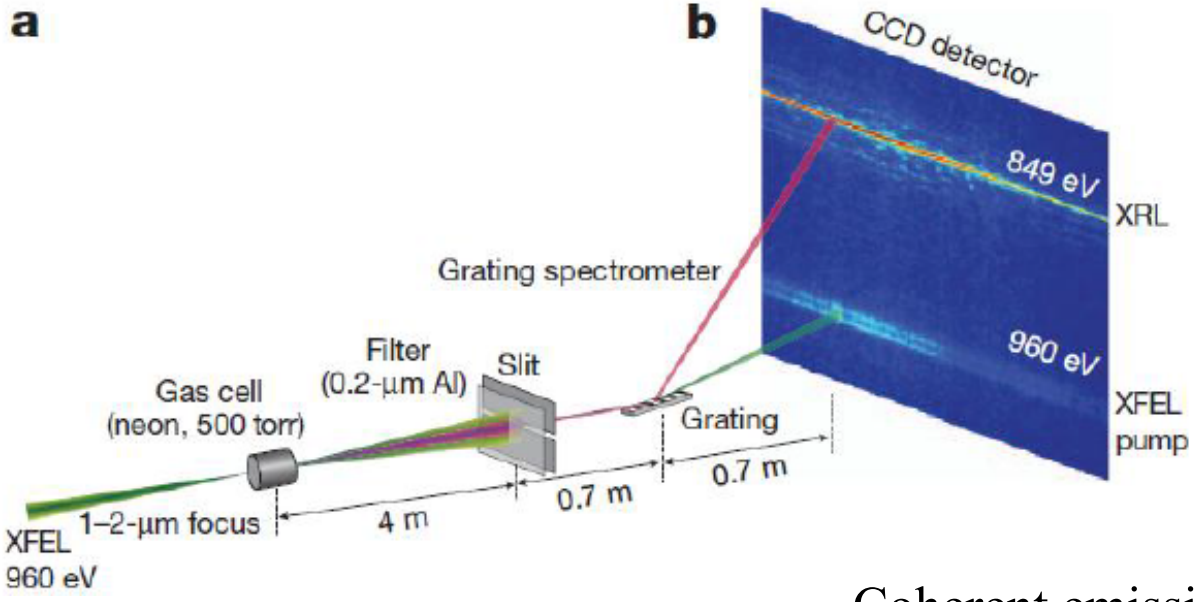
Main messages

- High resolution RIXS requires high brilliance, and large instruments
- Local potential surfaces in molecular materials can be determined
- Interaction between spin, charge, orbital and lattice in correlated electron systems can be determined

At free-electron lasers

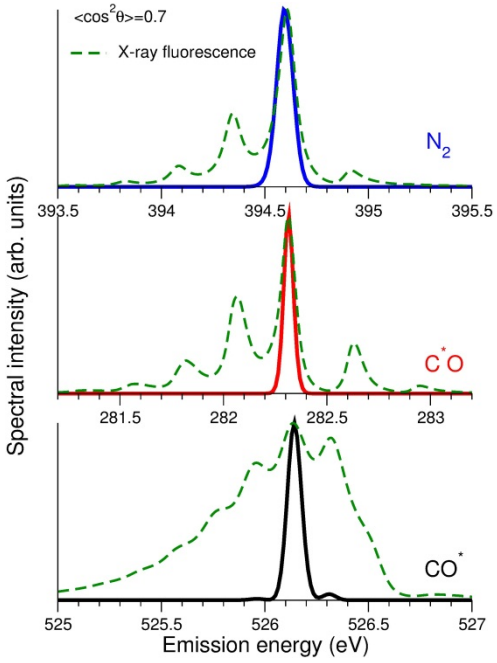
Stimulated X-ray Emission and Stimulated Resonant Inelastic Scattering

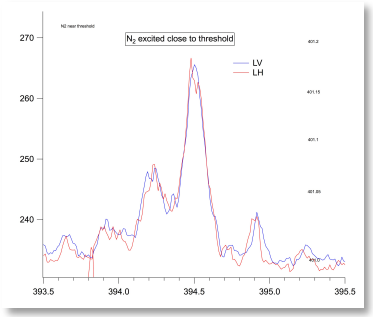
Collimated scattered light opens up new experimental opportunities

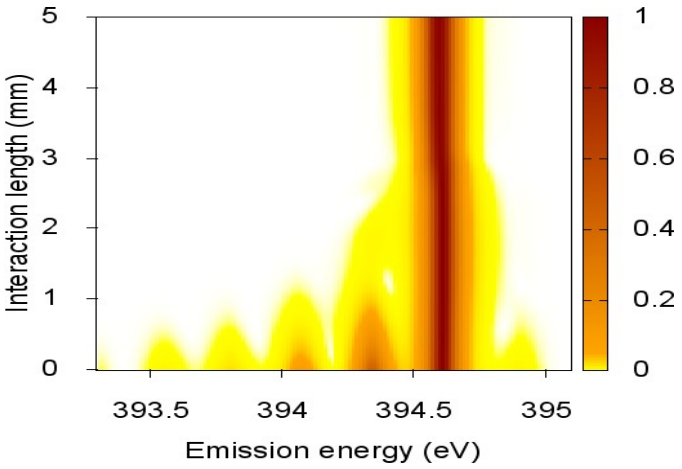


Coherent emission, Rohringer et al., Nature 481, 488 (2012))

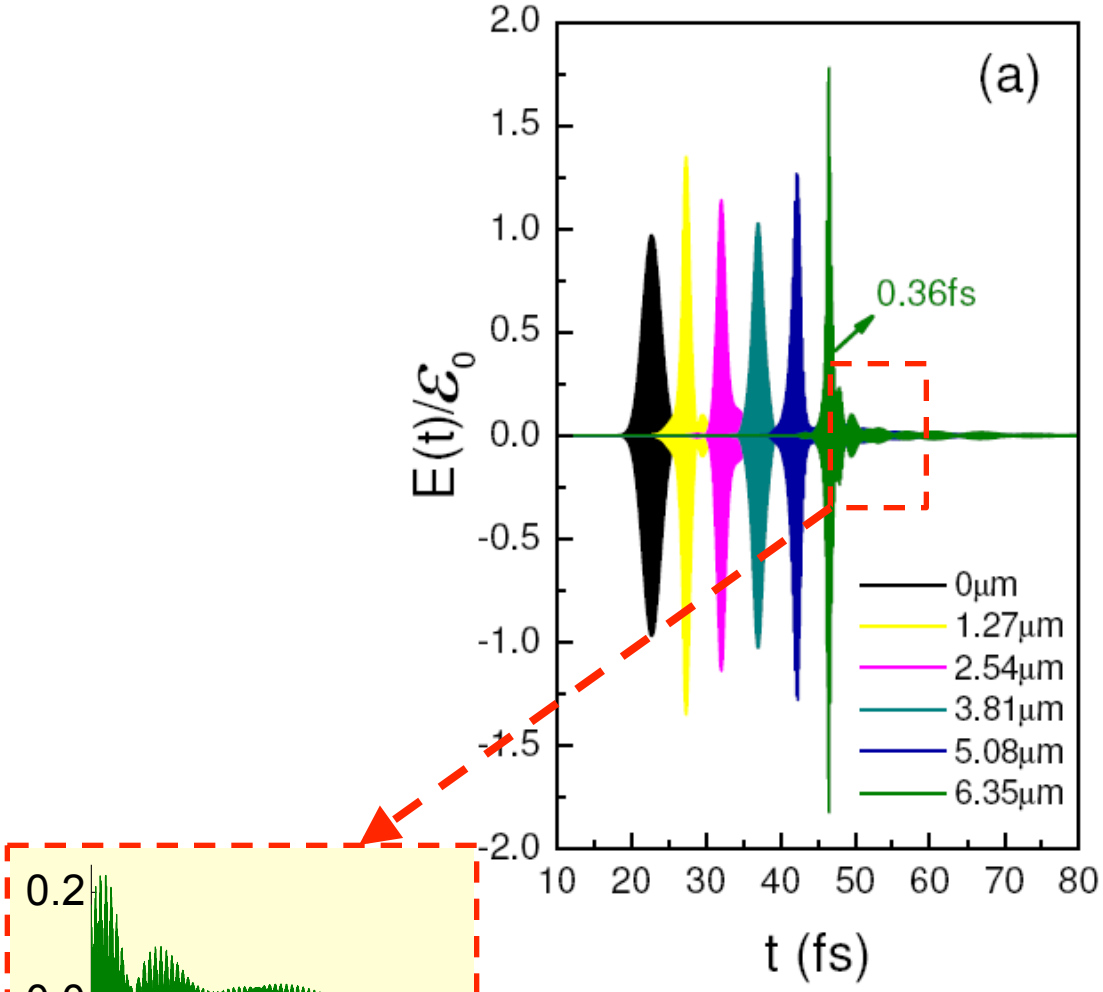
Control of the nuclear dynamics

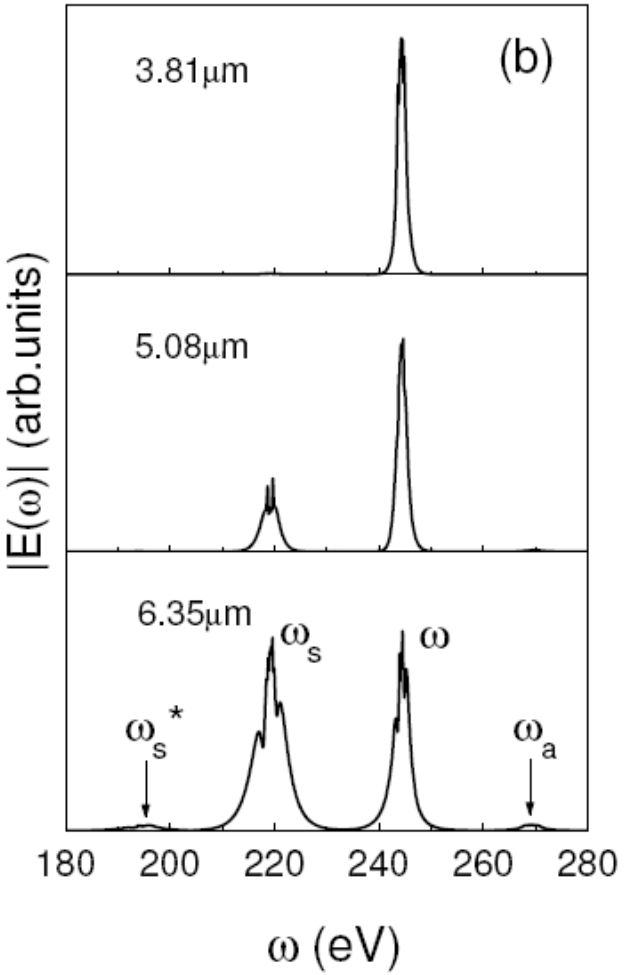






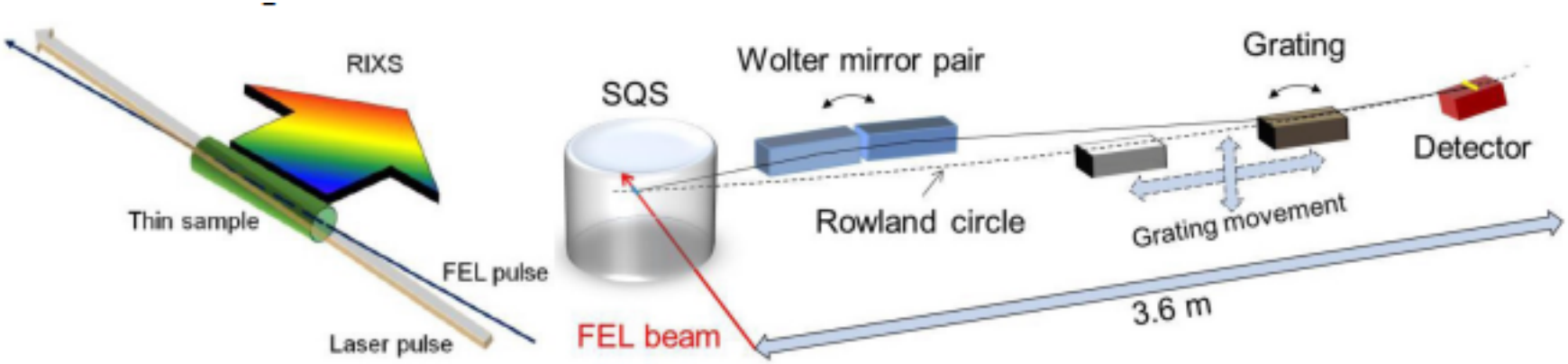
Pulse compression, Burnham-Chiao modulation and four wave mixing





Phys Rev A 81 (2010) 013812
Phys Rev A 81 (2010) 043412
EuroPhys.Lett. 87(2009)64002
J. Phys.B:At.Mol.Opt.Phys. 42(2009)201001
Ph D Thesis of Y.-P. Sun 2011

1-D imaging spectrometer as an in-kind contribution the European XFEL



Thank you

Summary

- *General Introduction*
  - *Local Partial Density of State*
  - *Site Selectivity*
  - *Typical attenuation length: 1000Å*
- *Instrumentation*
  - *Soft X-ray spectrometers: Resolution, resolution, resolution and the new PGS*
  - *Synchrotron radiation: Brilliance, brilliance, brilliance and MAX-IV*
- *RIXS; Resonant Inelastic Soft X-ray Scattering*
  - *Always a one-step process*
  - *Energy conservation*
  - *Momentum conservation*
  - *Symmetry selectivity*
  - *Dynamics*
    - *Interference and vibronic coupling*
    - *Core-hole clock*
- *Applications*
  - *Complex Systems*
- *Stimulated RIXS?*