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

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Uppsala University

Photon Matter Interaction, NORDITA, 04.10.16

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*
- *The non-linear…*

X-ray emission: Characteristic radiation?

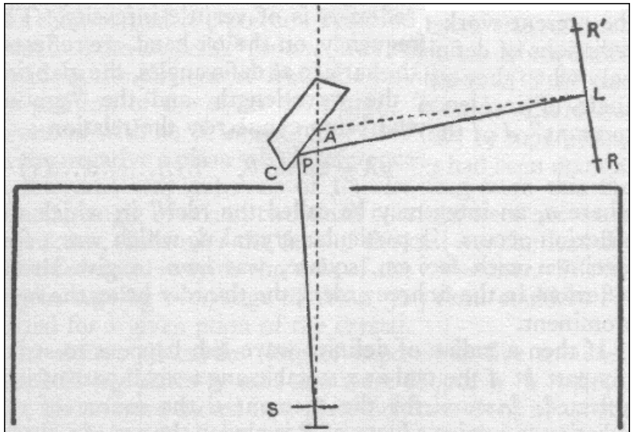


Fig. 1.

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

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

High-Frequency Spectra of the Elements.

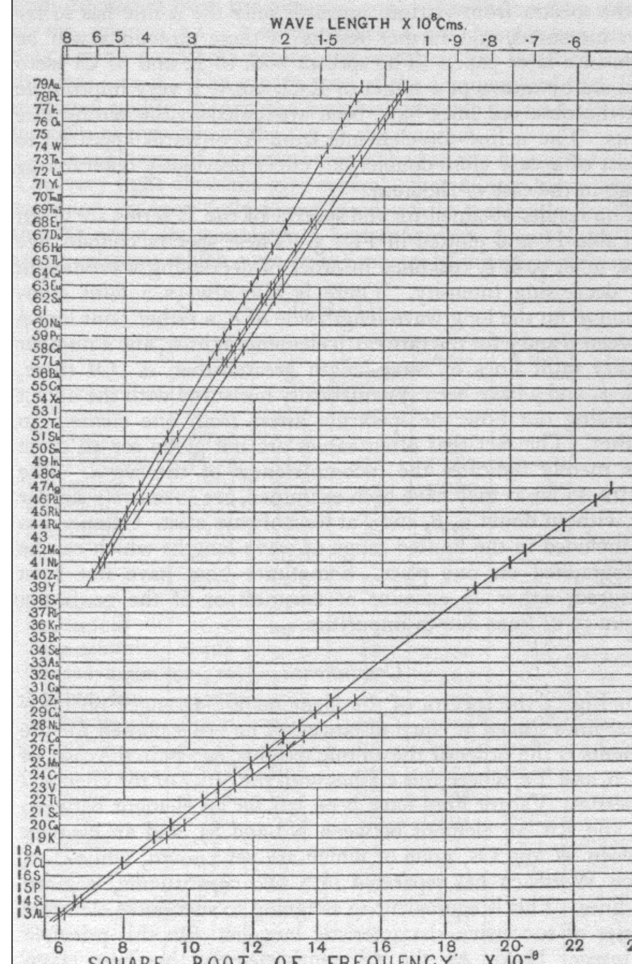


Fig. 3.

Yes, but also uncharacteristic
Valence electronic struture

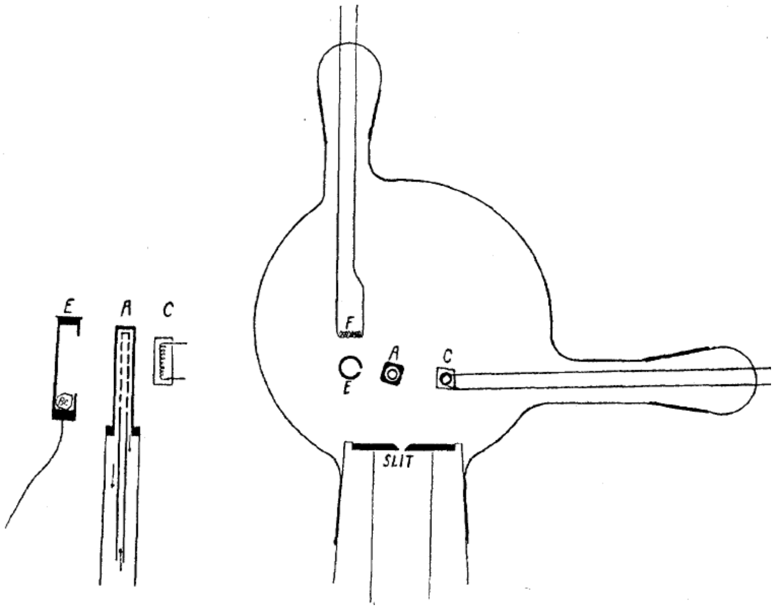


FIG. 1. X-ray tube and evaporating oven.

H. M. O'BRYAN AND H. W. B. SKINNER

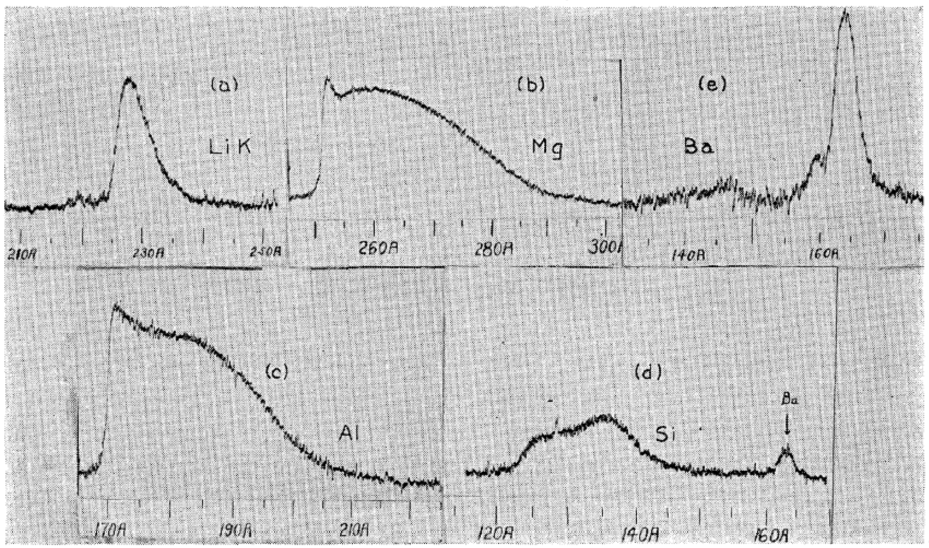
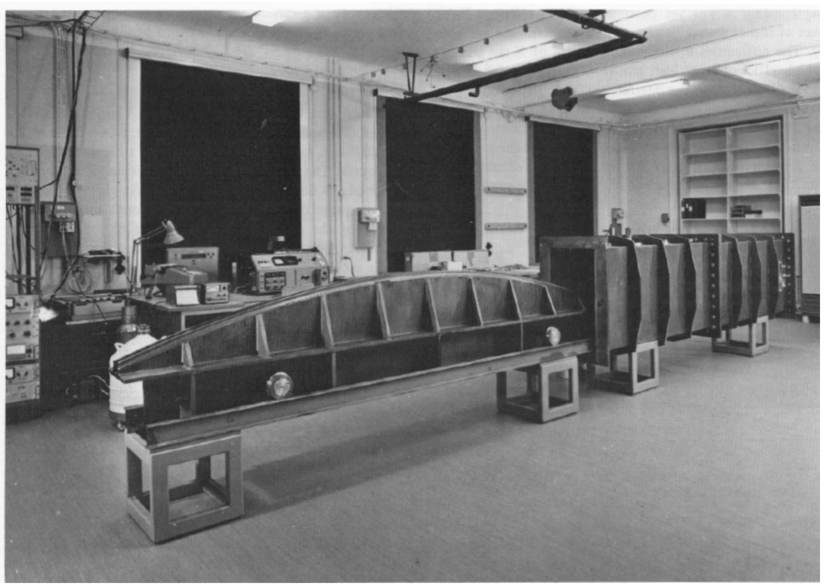
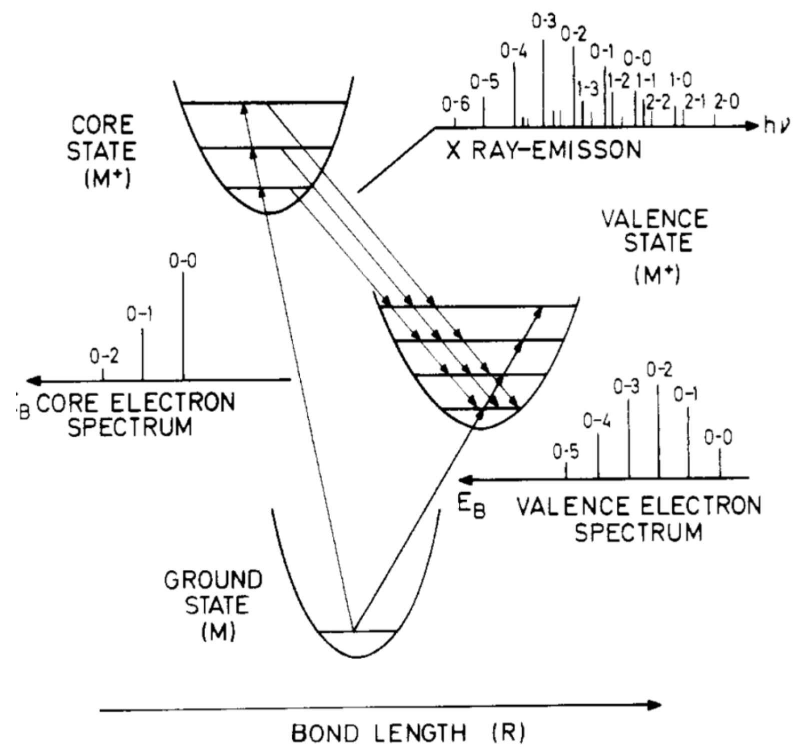


FIG. 4. Photometer curves of x-ray lines.

Phys. Rev. 45, 370 (1935)


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

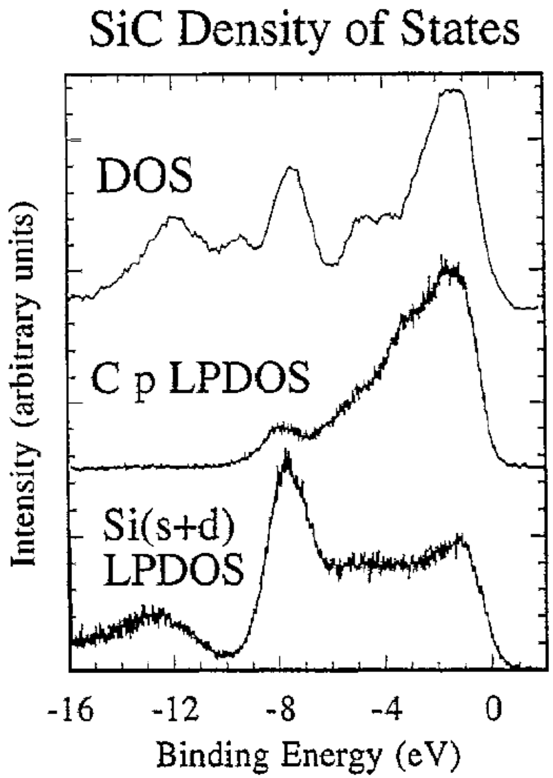


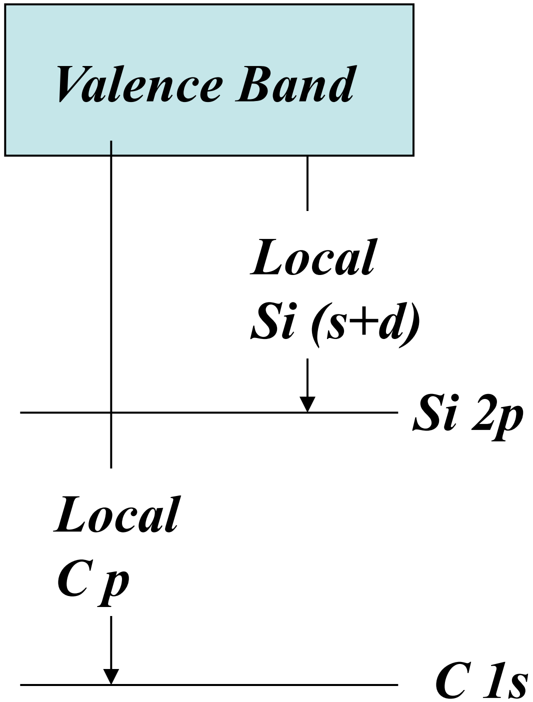

CORE STATE (M+)
X RAY-EMISSON
hν
0-6
0-5
0-4
0-3
0-2
0-1
0-0
1-3
1-2
1-1
1-0
2-2
2-1
2-0
VALENCE STATE (M+)
0-0
0-1
0-2
CORE ELECTRON SPECTRUM
E_B
0-5
0-4
0-3
0-2
0-1
0-0
E_B
VALENCE ELECTRON SPECTRUM
GROUND STATE (M)
BOND LENGTH (R)

Core levels are atomic-like:
Local Properties

Dipole Selection rules are valid:
Symmetry Selectivity

$$\Delta l = \pm 1$$



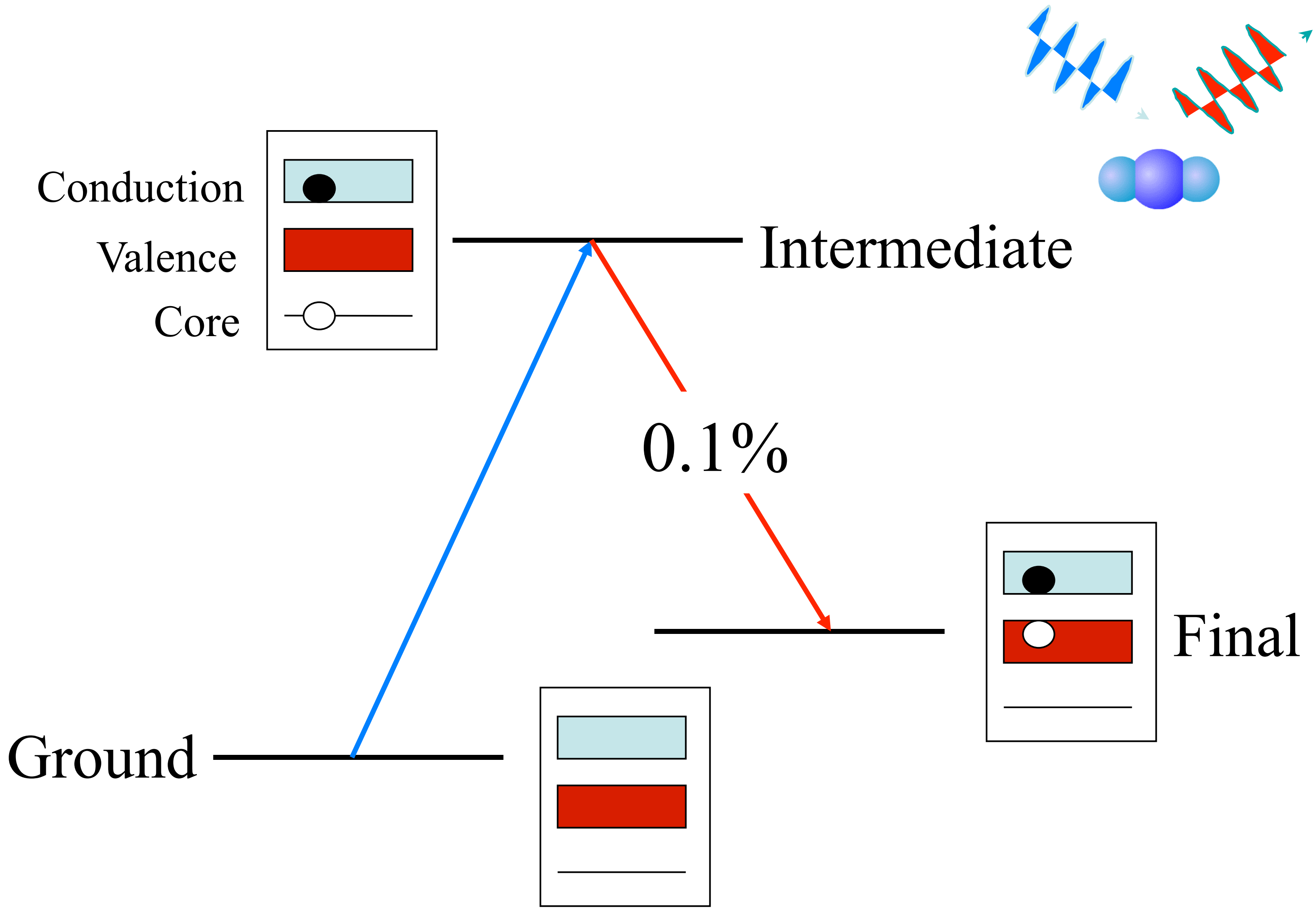


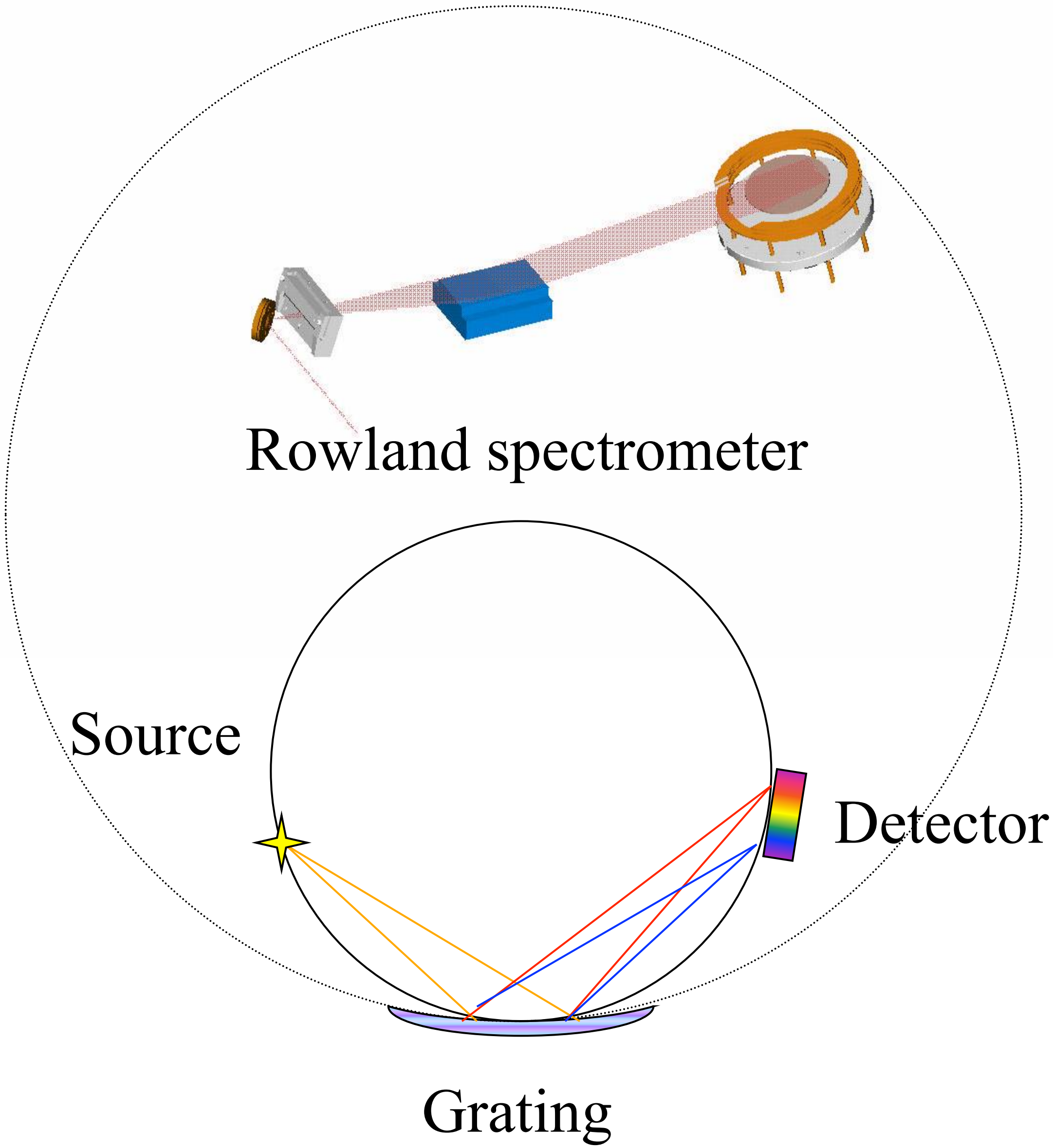
Local Partial Density of States

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.

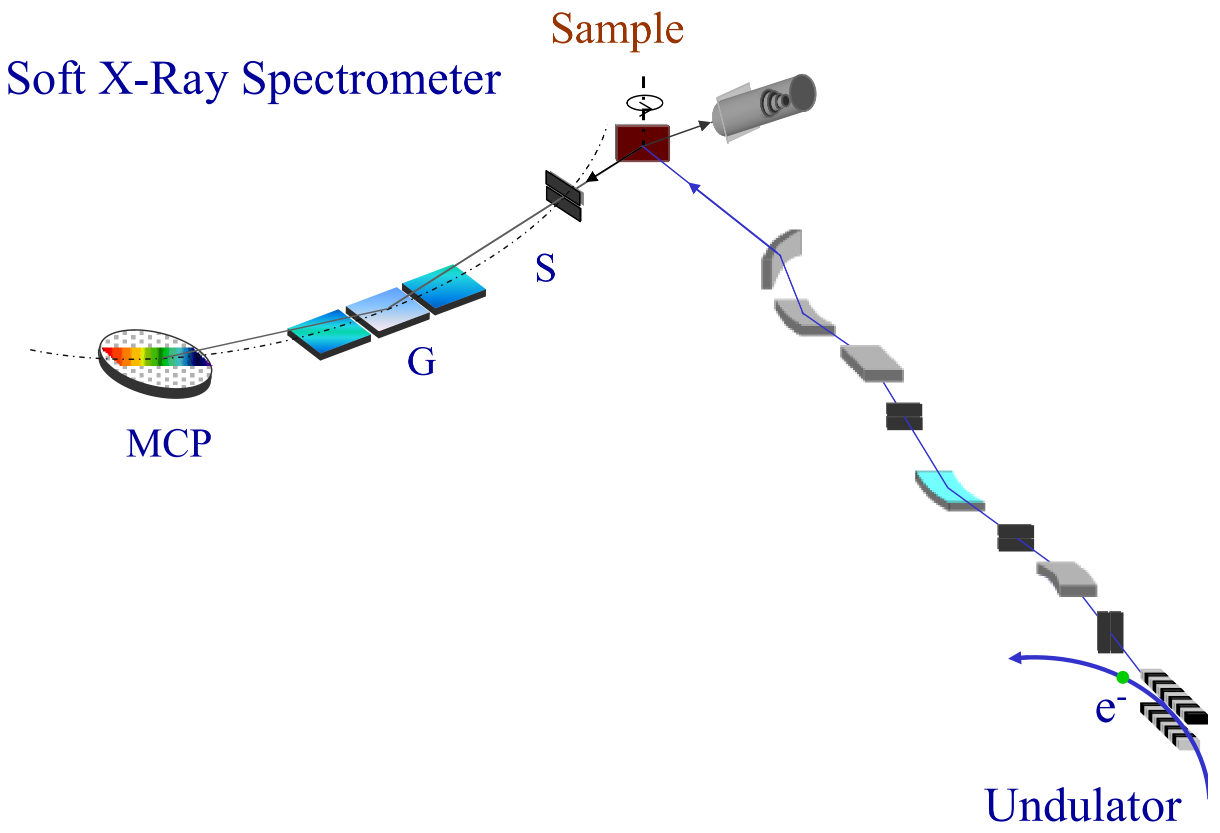
Notoriously low count rates



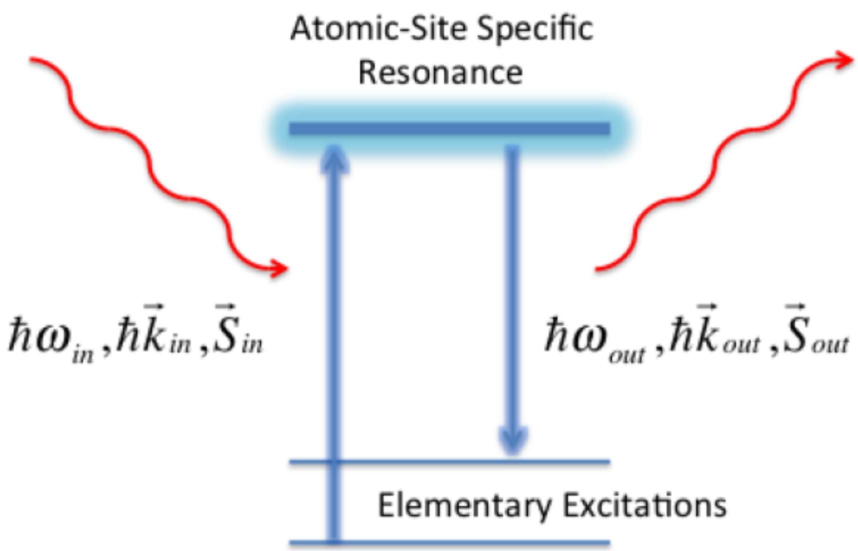


Combining the focussing properties of a sphere with the dispersive properties of a grating

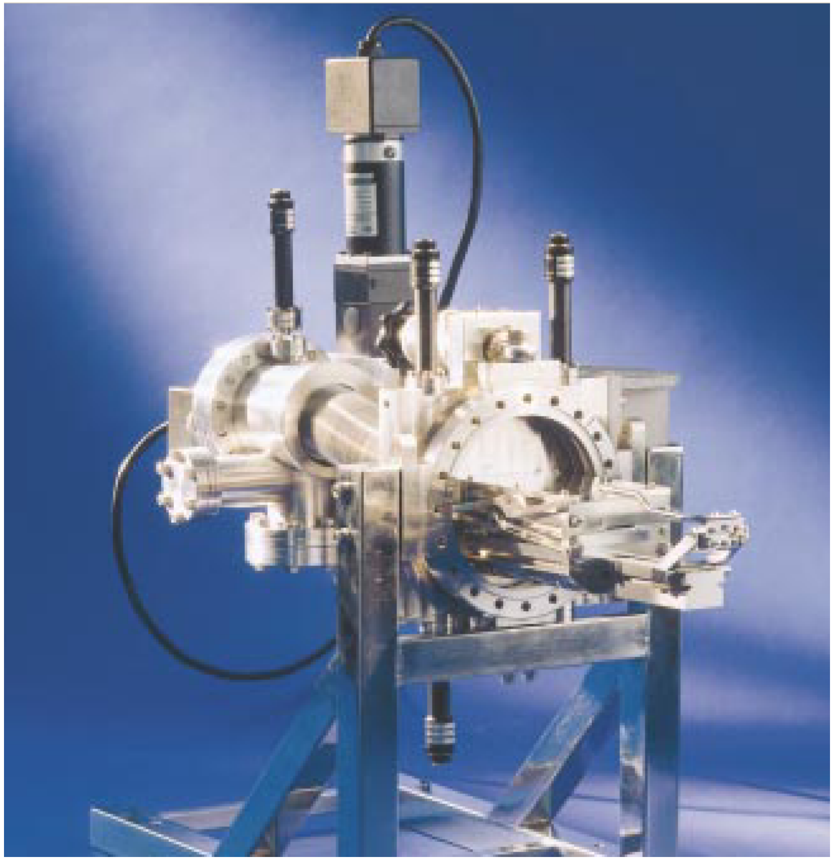
Experiment



Resonant Inelastic X-ray Scattering

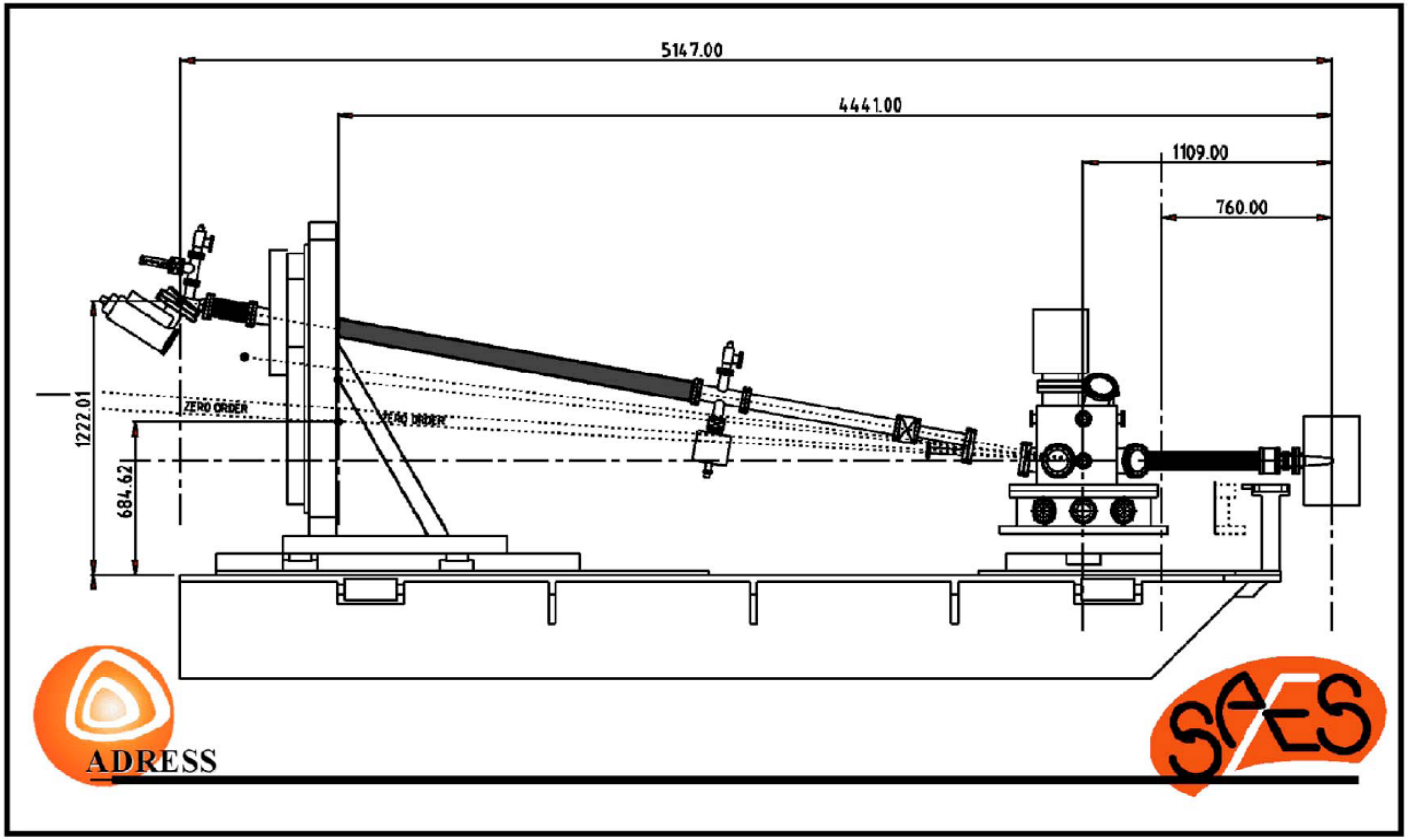


Joseph Nordgren design from mid-80:s

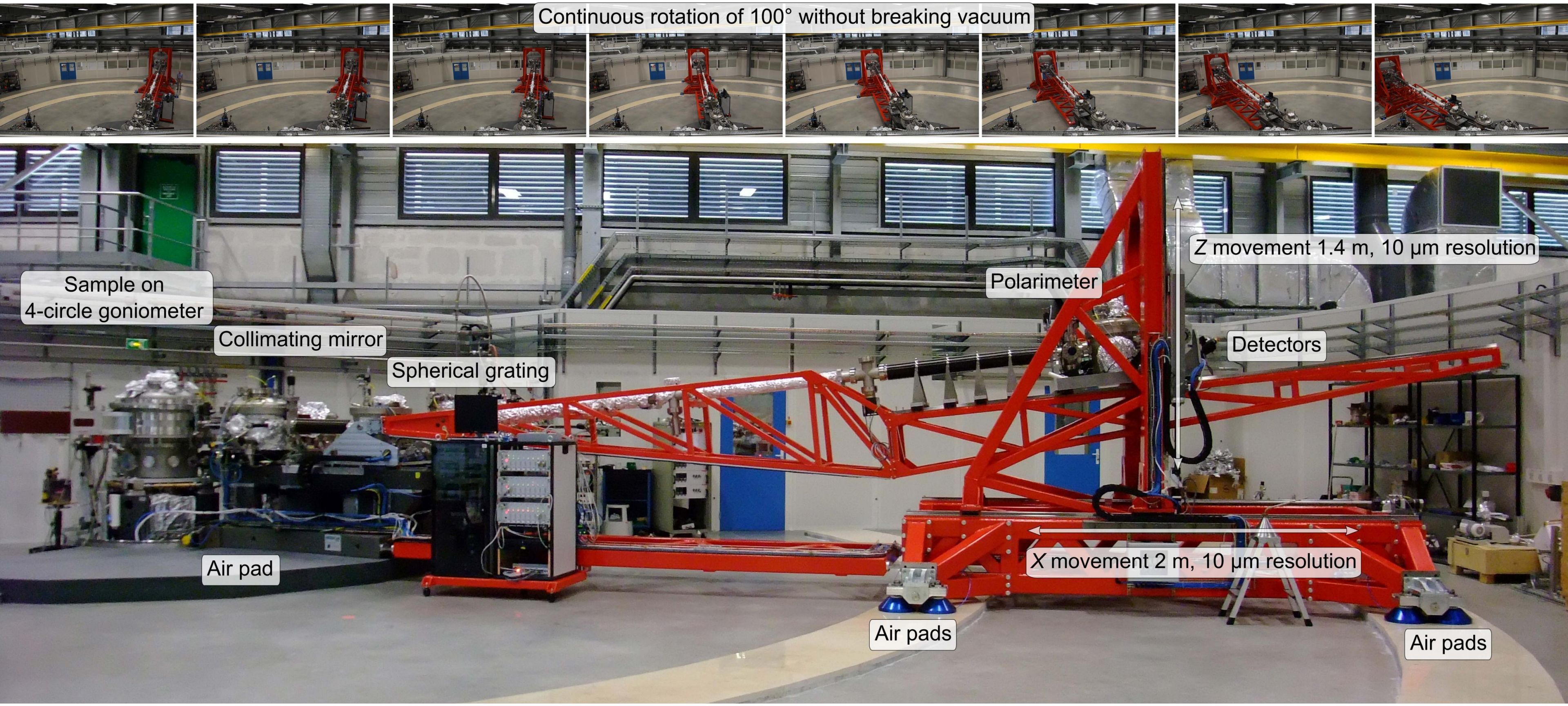


still going strong…

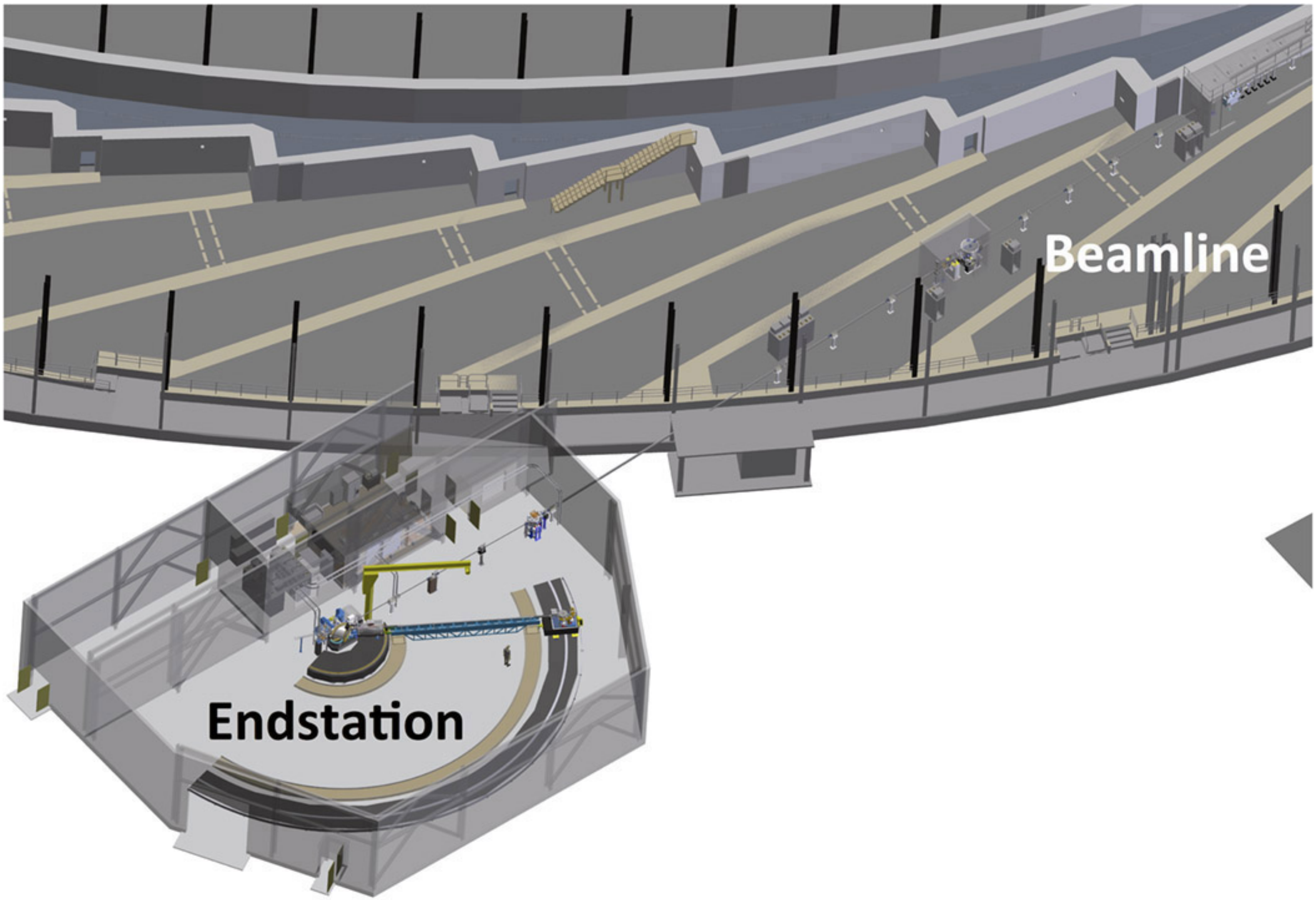
SAXES@ADRESS@SLS



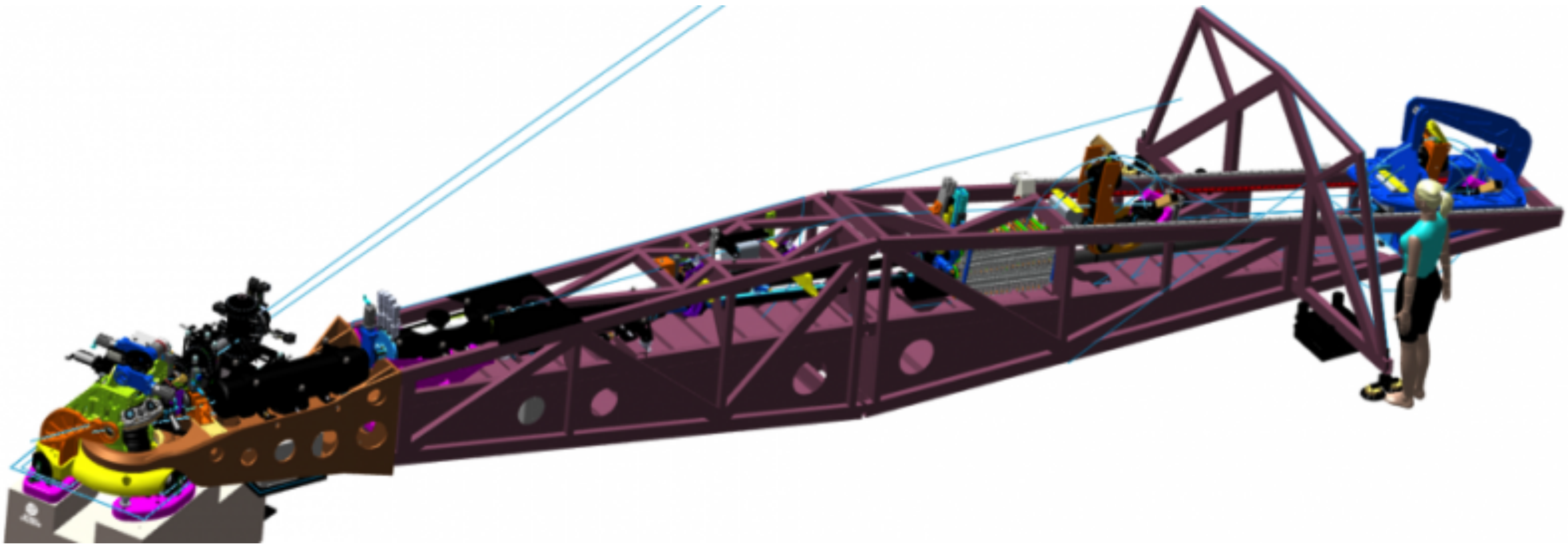
ERIXS@ESRF


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

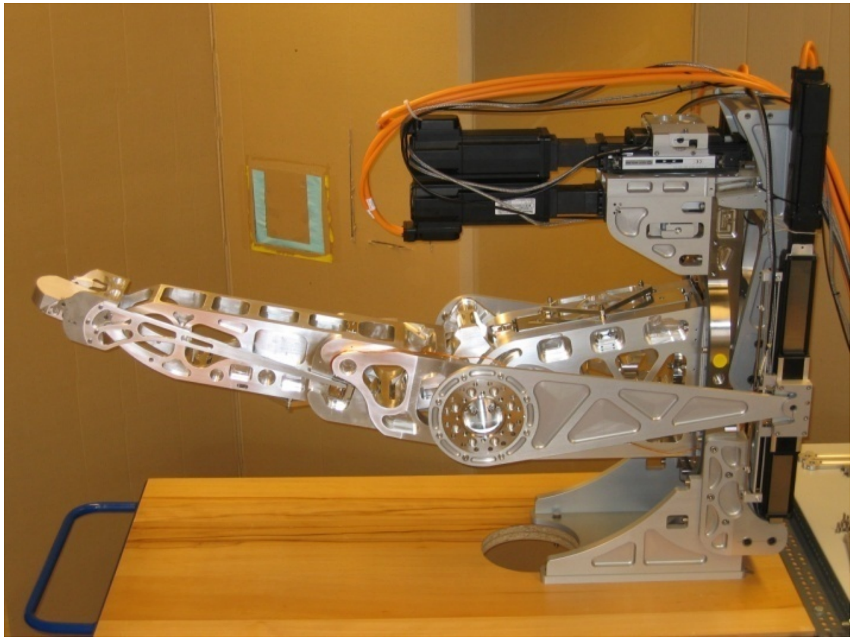
SIX@NSLS-II



VERITAS@MAX IV

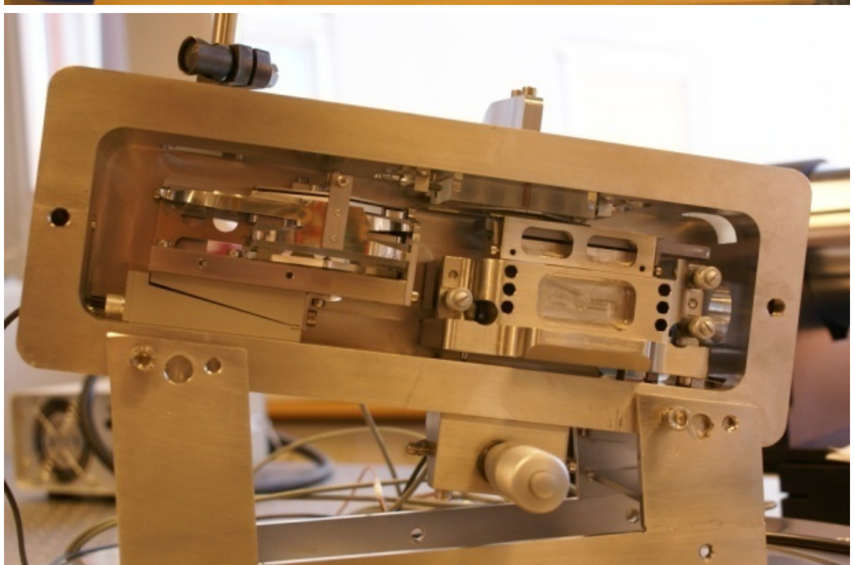


New Concepts for efficiency and resolution



PGS:
Plane grating spectrometer

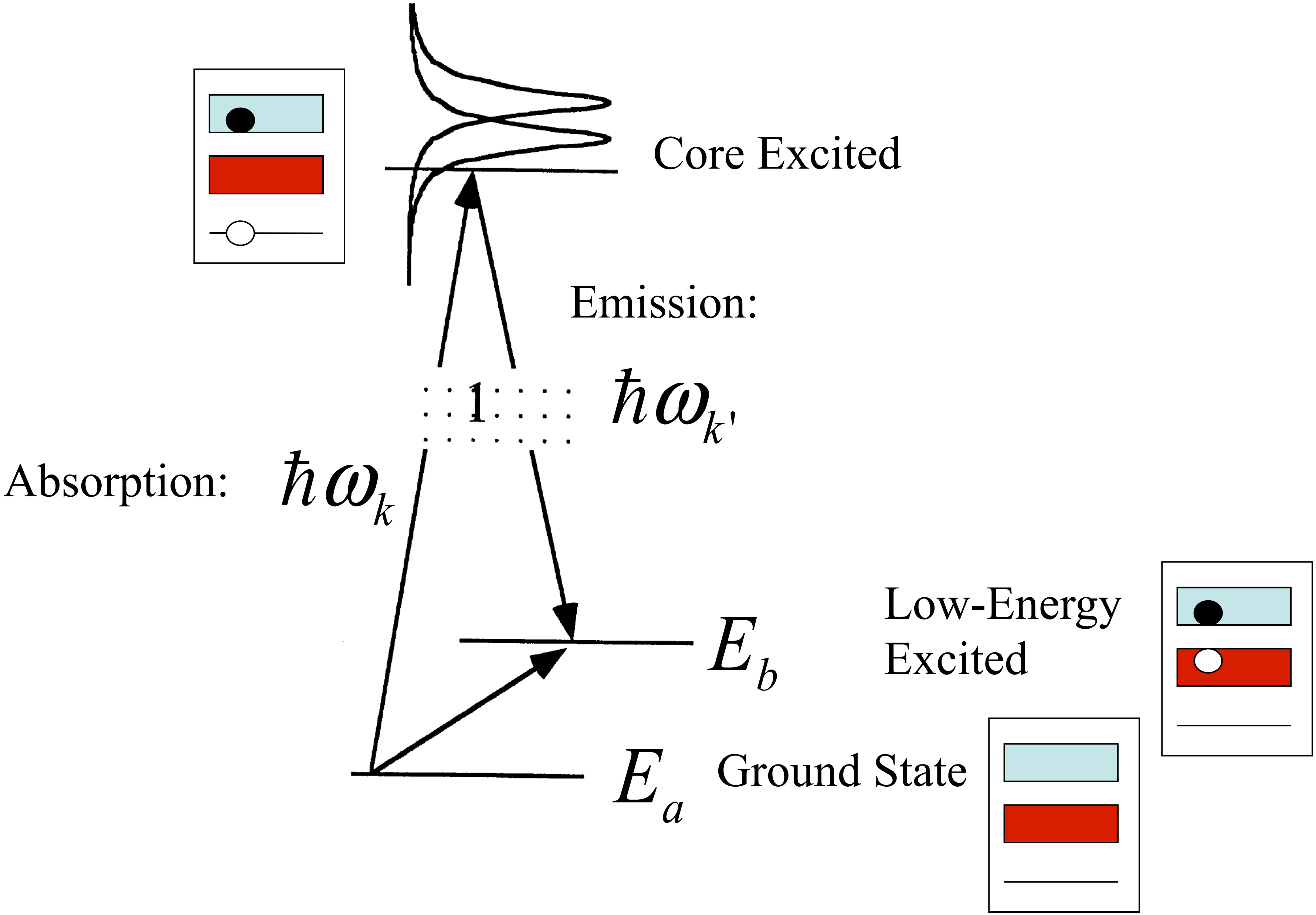
Two parabolic mirrors and
a plane grating



FTS:
Fourier Transform Spectrometer

Wavefront Beamsplitters and
mirrors in grazing incidence

X-ray scattering; always a one-step process



Linear approximation

$$\left(\frac{d^2\sigma}{d\Omega' dE'}\right)_{\substack{a\to b\\ \lambda\to\lambda'}} = \left(\frac{e^2}{mc^2}\right)^2 \Bigg| \left\langle b \left| \sum_j e^{i\mathbf{K}\cdot\mathbf{r}_j} \right| a \right\rangle \boldsymbol{\epsilon}'\cdot\boldsymbol{\epsilon} - i\frac{\hbar\omega}{mc^2}\left\langle b \left| \sum_j e^{i\mathbf{K}\cdot\mathbf{r}_j}\mathbf{s}_j \right| a \right\rangle \cdot \boldsymbol{\epsilon}'\times\boldsymbol{\epsilon}$$

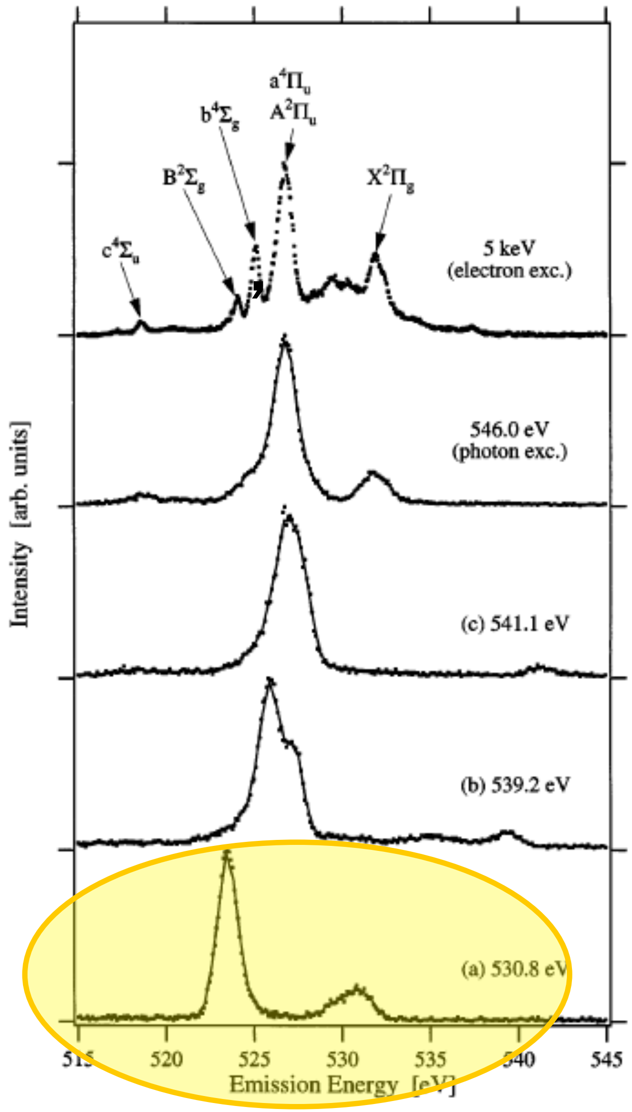
$$+ \frac{\hbar^2}{m}\sum_c\sum_{ij}\Bigg(\frac{\left\langle b \left| \left(\frac{\boldsymbol{\epsilon}'\cdot\mathbf{P}_i}{\hbar} - i(\mathbf{k}'\times\boldsymbol{\epsilon}')\cdot\mathbf{s}_i\right) e^{-i\mathbf{k}'\cdot\mathbf{r}_i} \right| c \right\rangle \left\langle c \left| \left(\frac{\boldsymbol{\epsilon}\cdot\mathbf{P}_j}{\hbar} + i(\mathbf{k}\times\boldsymbol{\epsilon})\cdot\mathbf{s}_j\right) e^{i\mathbf{k}\cdot\mathbf{r}_j} \right| a \right\rangle}{E_a - E_c + \hbar\omega_k - i\Gamma_c/2}$$

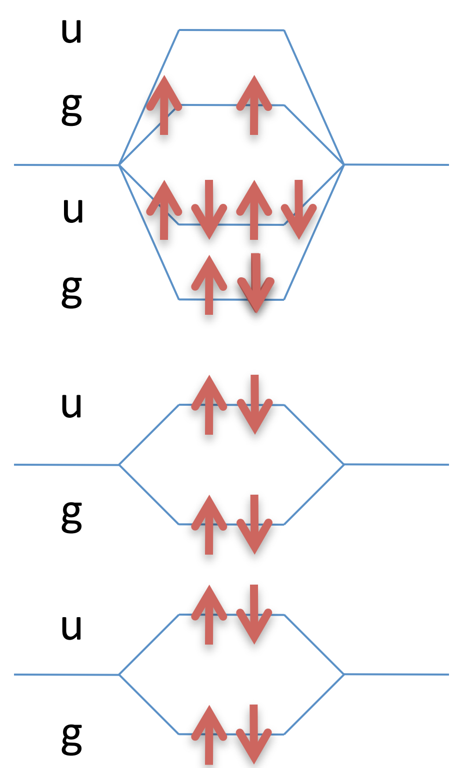
$$+ \frac{\left\langle b \left| \left(\frac{\boldsymbol{\epsilon}\cdot\mathbf{P}_i}{\hbar} + i(\mathbf{k}\times\boldsymbol{\epsilon})\cdot\mathbf{s}_i\right) e^{i\mathbf{k}\cdot\mathbf{r}_i} \right| c \right\rangle \left\langle c \left| \left(\frac{\boldsymbol{\epsilon}'\cdot\mathbf{P}_j}{\hbar} - i(\mathbf{k}'\times\boldsymbol{\epsilon}')\cdot\mathbf{s}_j\right) e^{-i\mathbf{k}'\cdot\mathbf{r}_j} \right| a \right\rangle}{E_a - E_c - \hbar\omega_{k'}} \Bigg)\Bigg|^2 \delta(E_a - E_b + \hbar\omega_k - \hbar\omega_{k'}).$$

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

$$I = (a+b)^2 = a^2 + b^2 + 2ab$$

The oxygen molecule: inversion symmetry

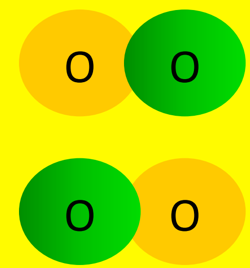




Where is the core hole?

Right?

Left?



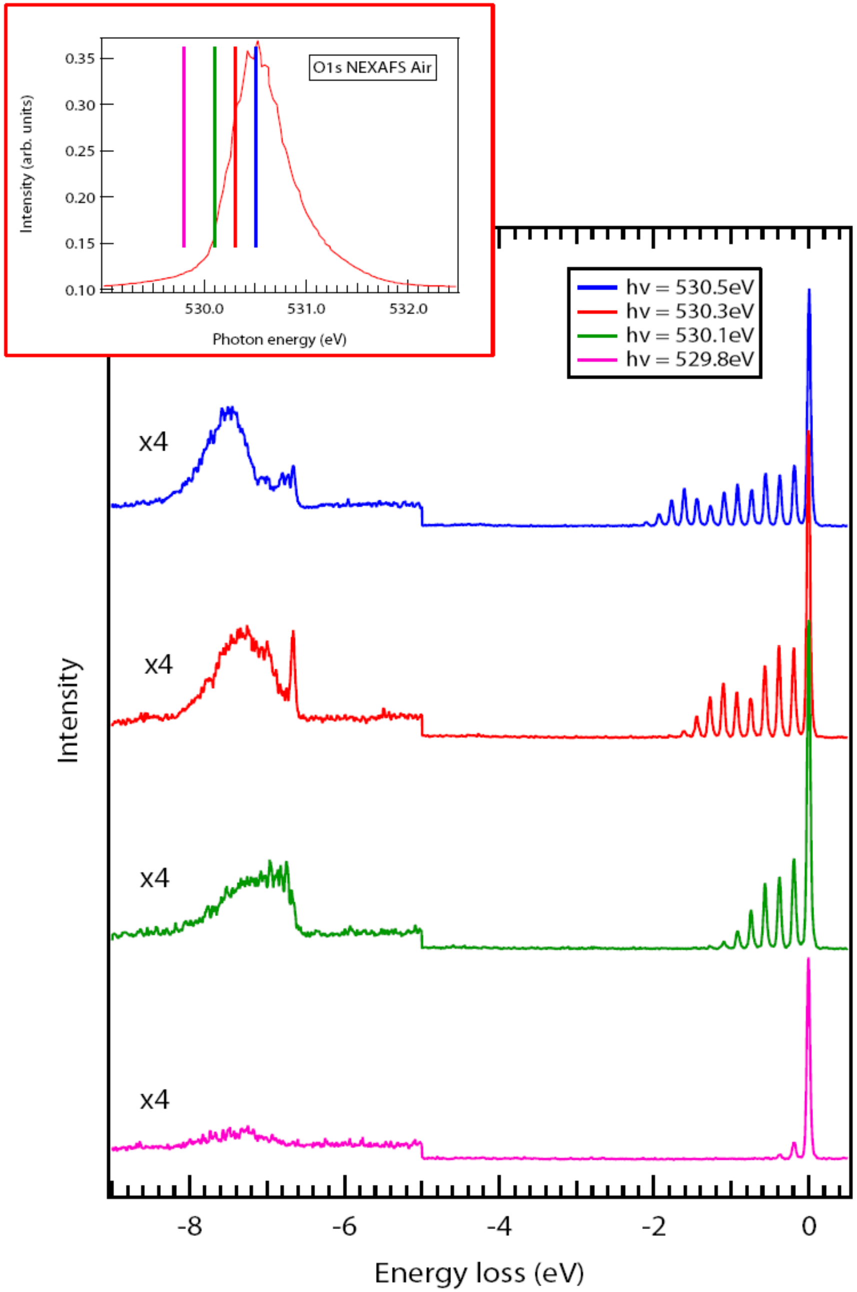
Both?

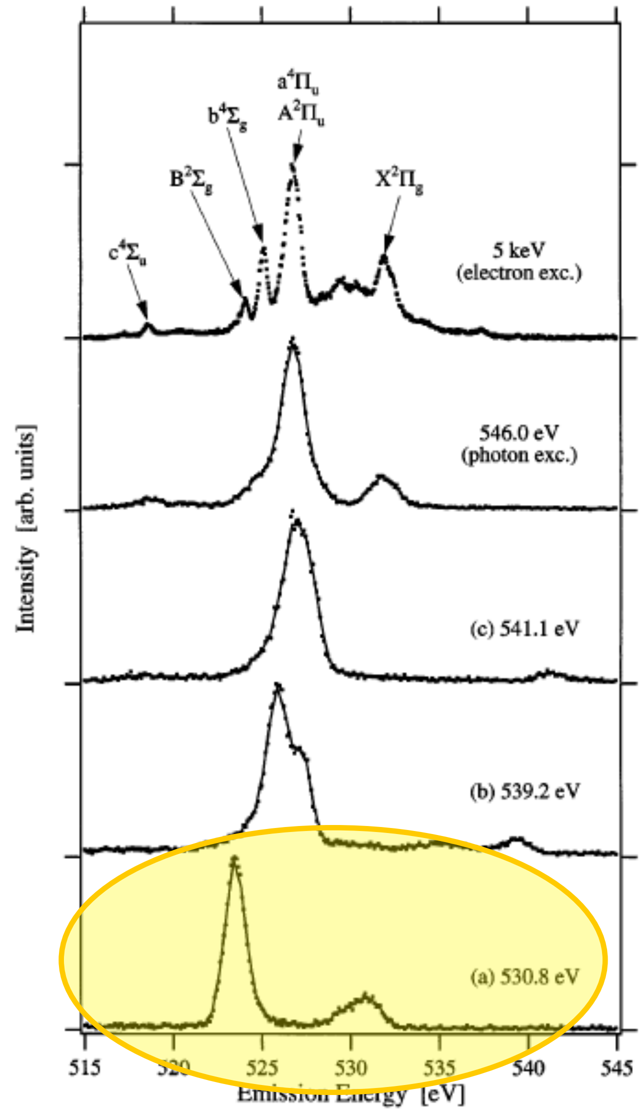
Strict dipole selection rules apply:

Gerade→Ungerade→Gerade

Inversion symmetry is not broken

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

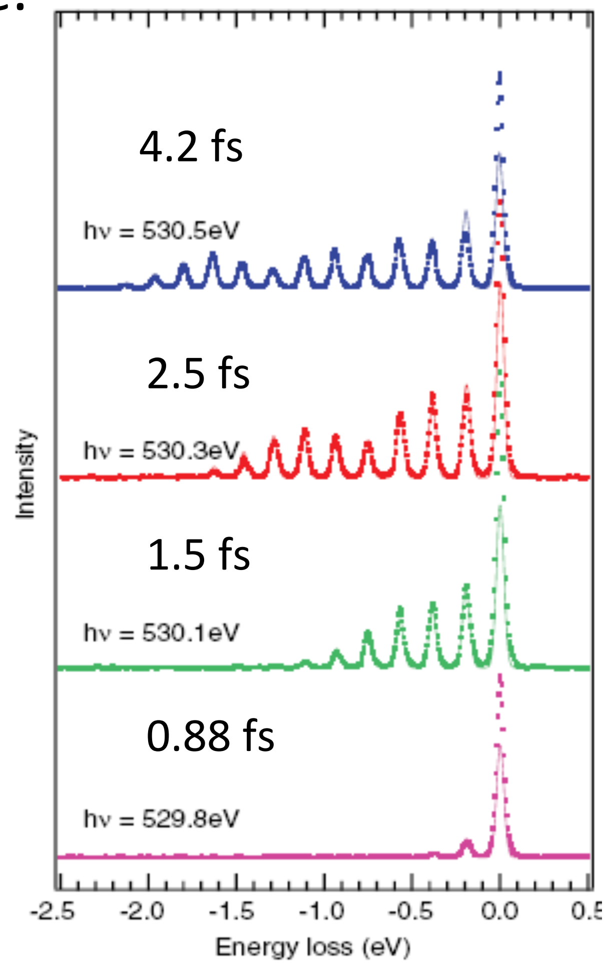




Hennies, et al. PRL. 104, 193002 (2010)

Controlling the nuclear motion

Potential surface and lifetime of the core excited state.



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

$$r_0 = 1.35 \pm 0.01 \ \text{Å}$$

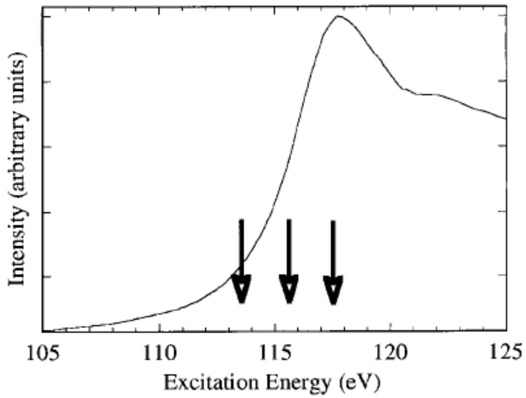
Scattering Duration Time

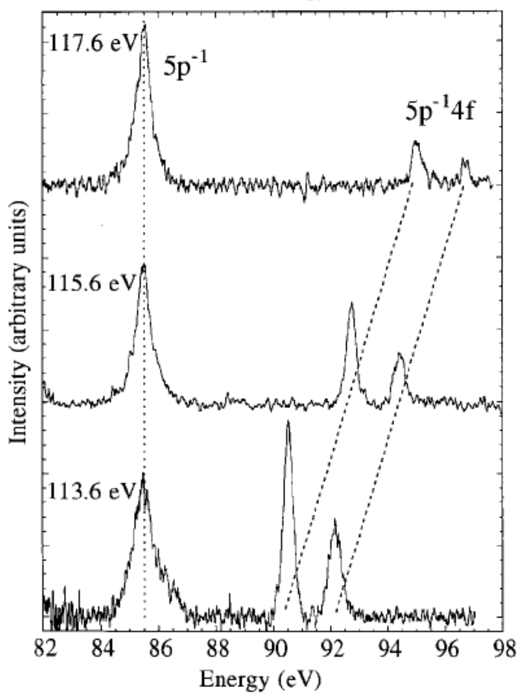
$$\tau = \frac{\hbar}{\sqrt{\Gamma^2 + \Omega^2}}$$

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

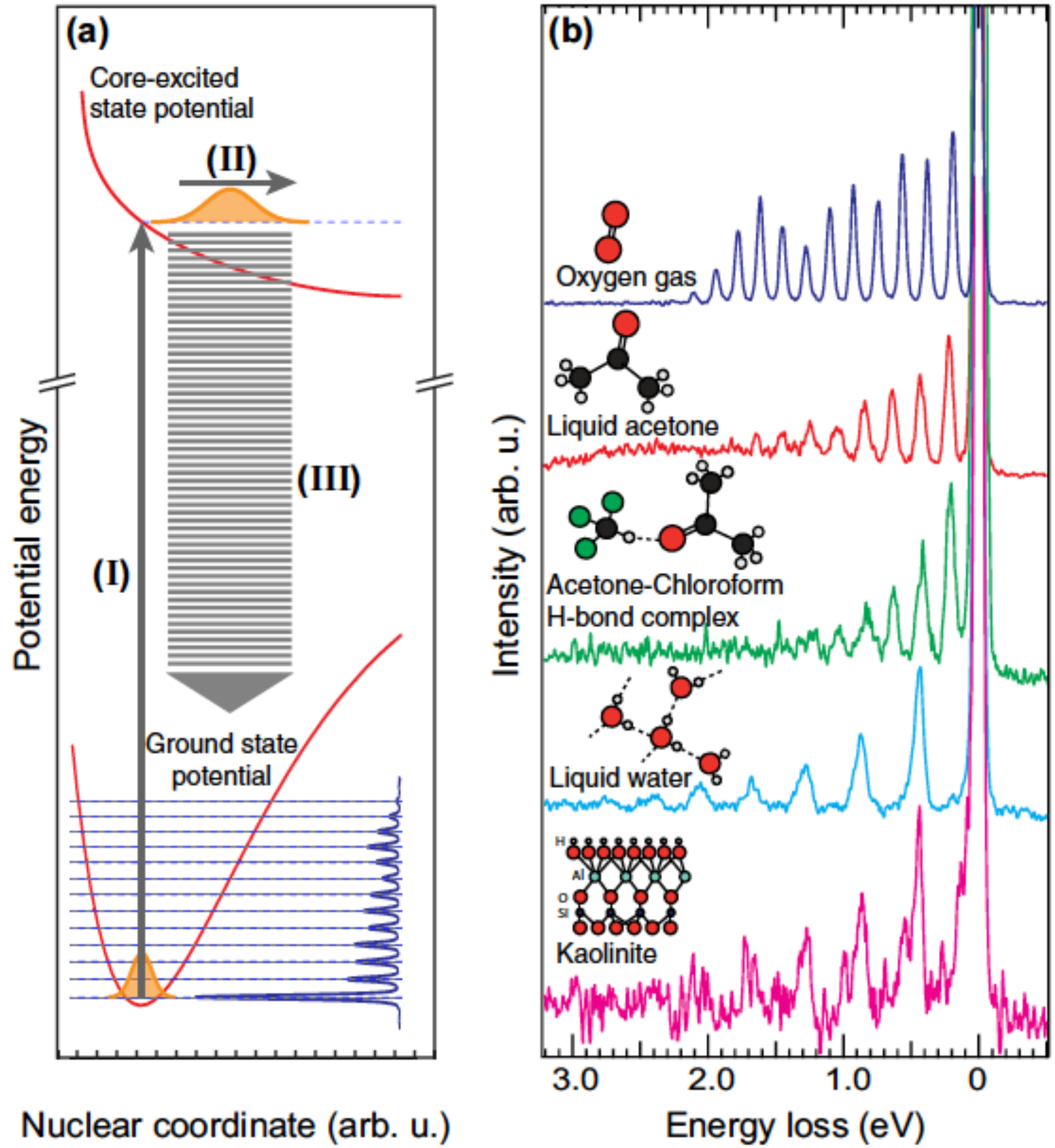
Scattering:

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

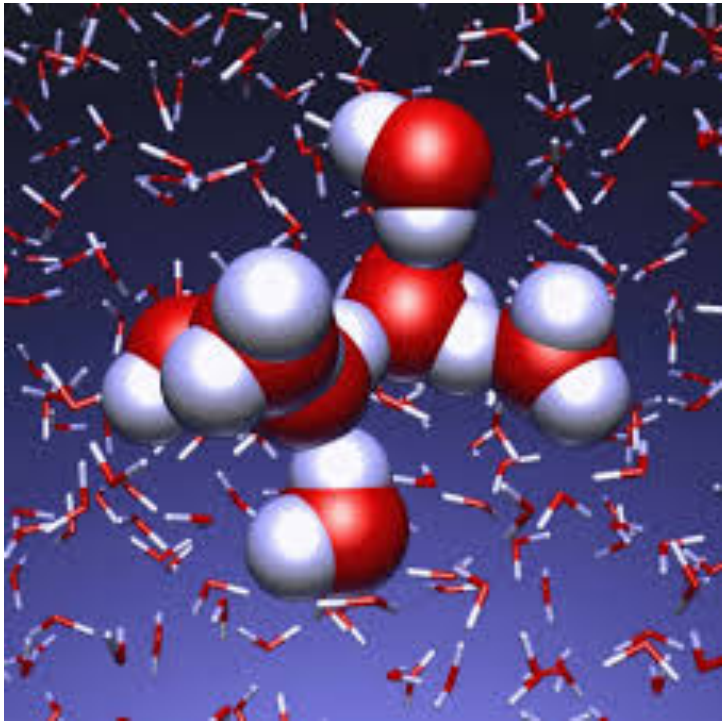
Gives narrow peaks.

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

Molecular Materials and Processes



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



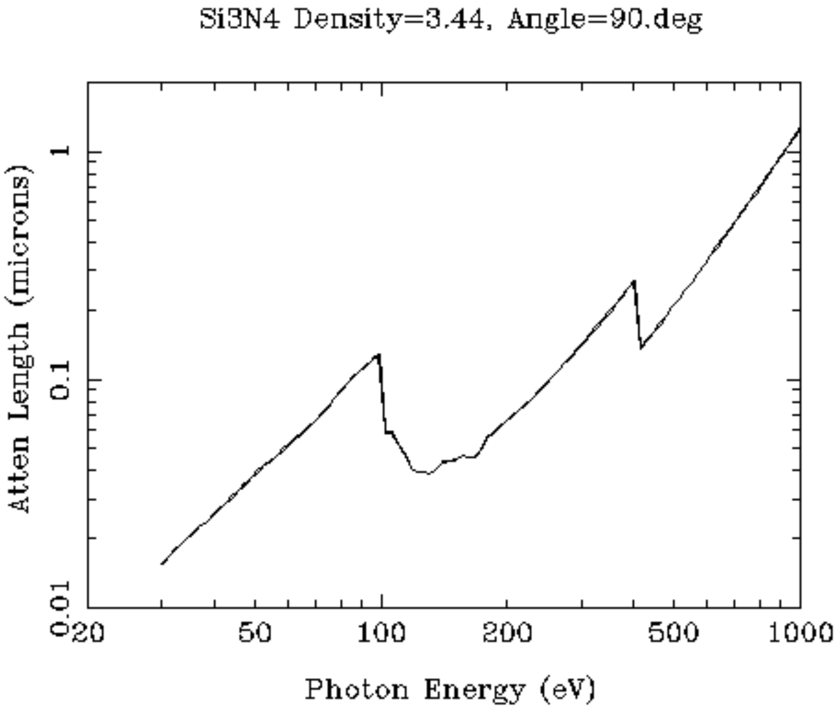
High-Resolution RIXS gives access to

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

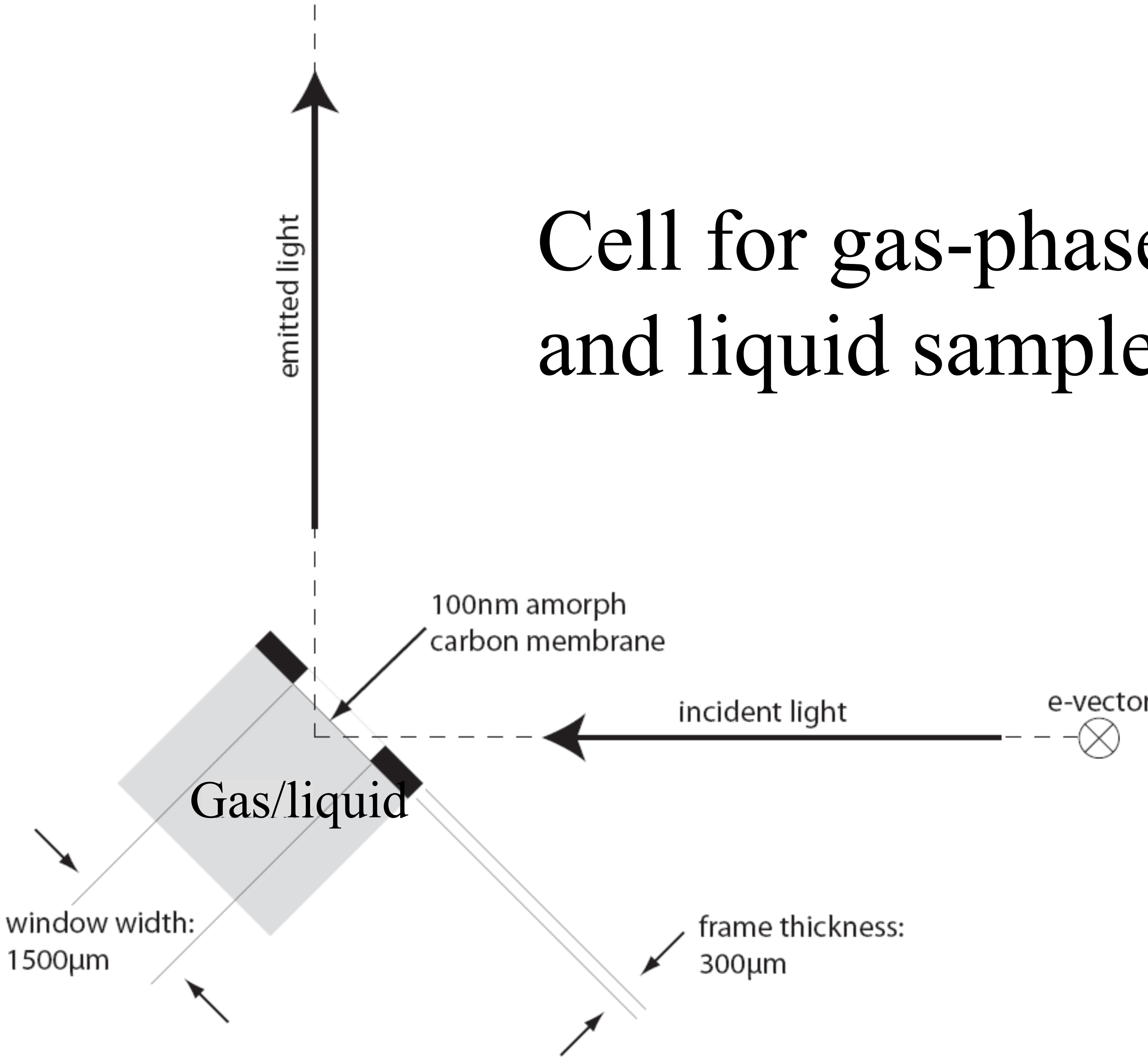
Looking Through Windows

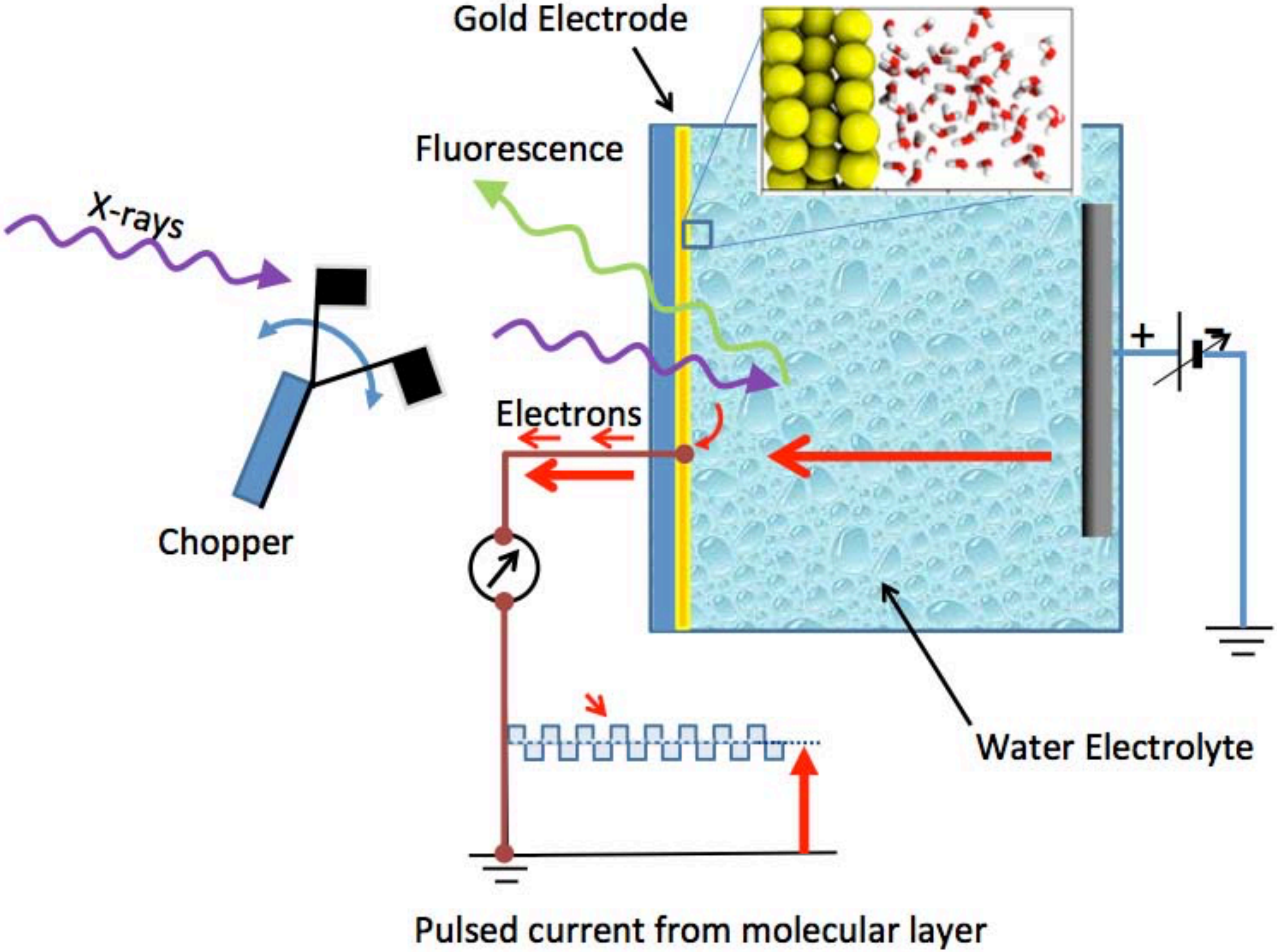
Several 1000 Ångström

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

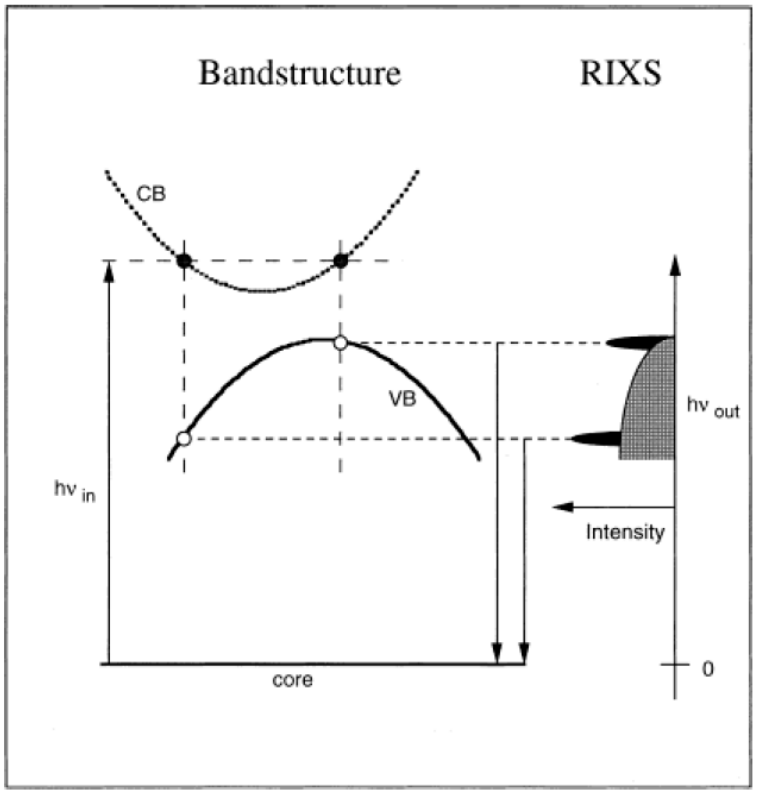


Cell for gas-phase and liquid samples



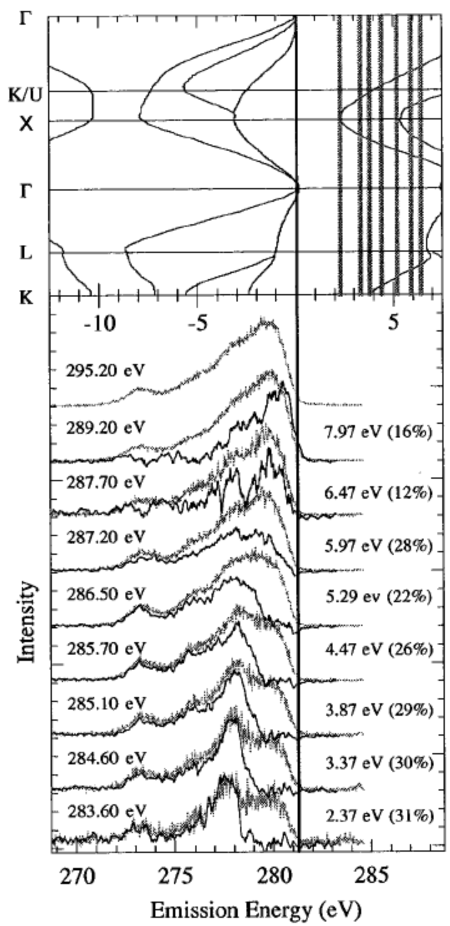

Gold Electrode
Fluorescence
X-rays
Chopper
Electrons
+
Water Electrolyte
Pulsed current from molecular layer

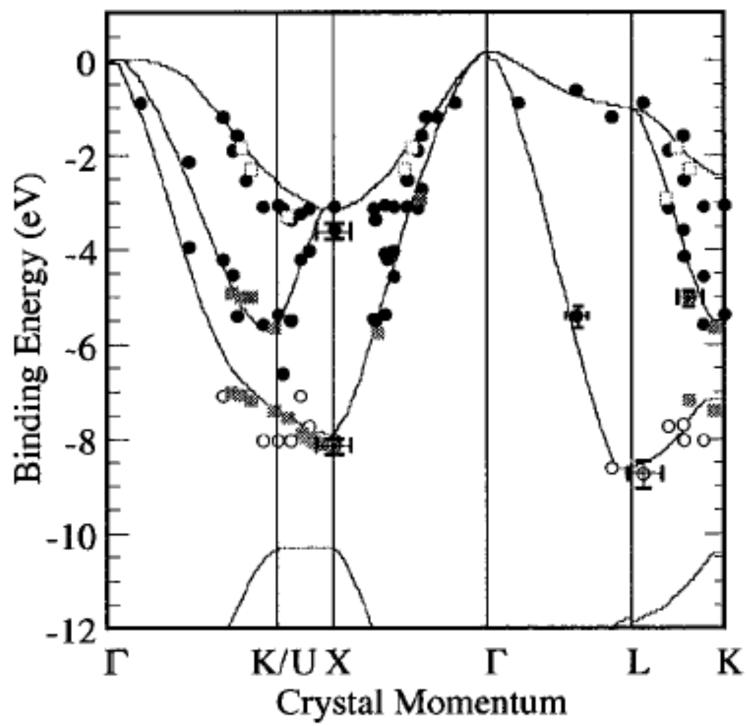
Momentum Conservation



And band mapping

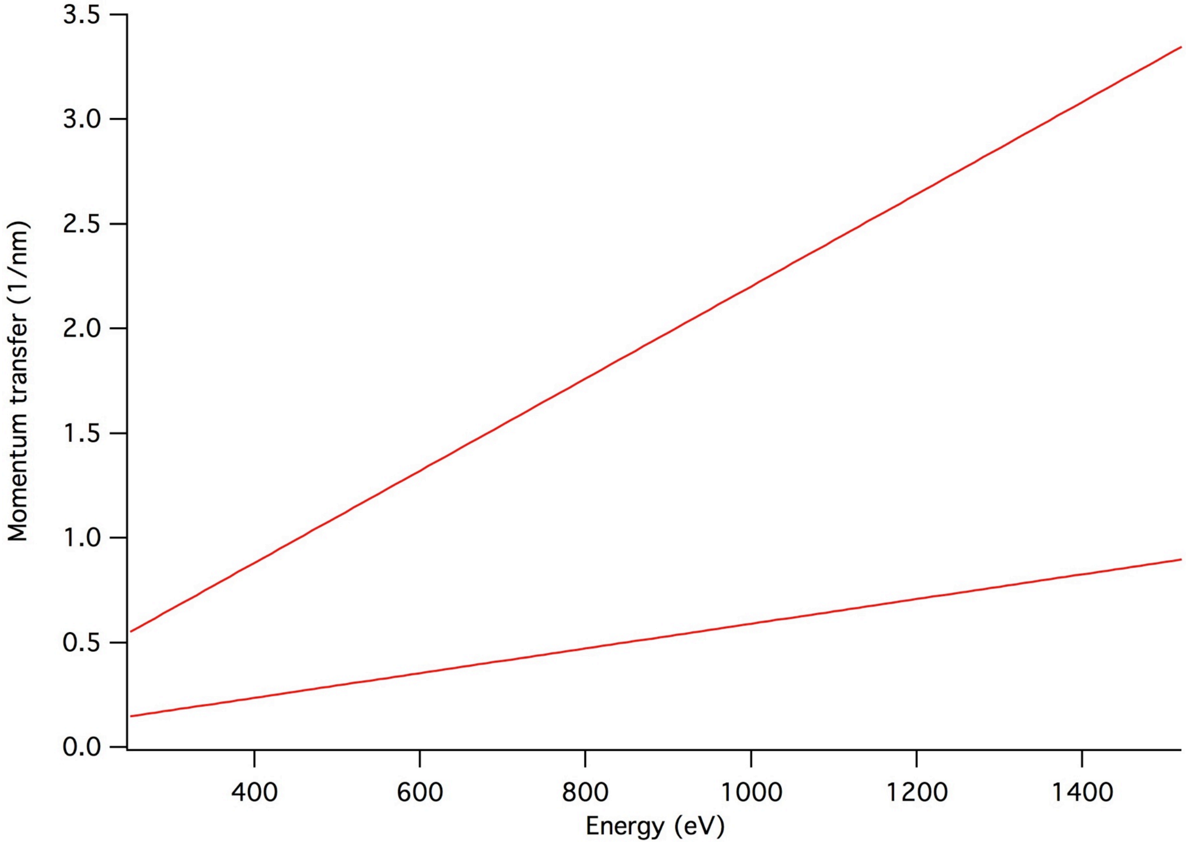
Silicon Carbide again



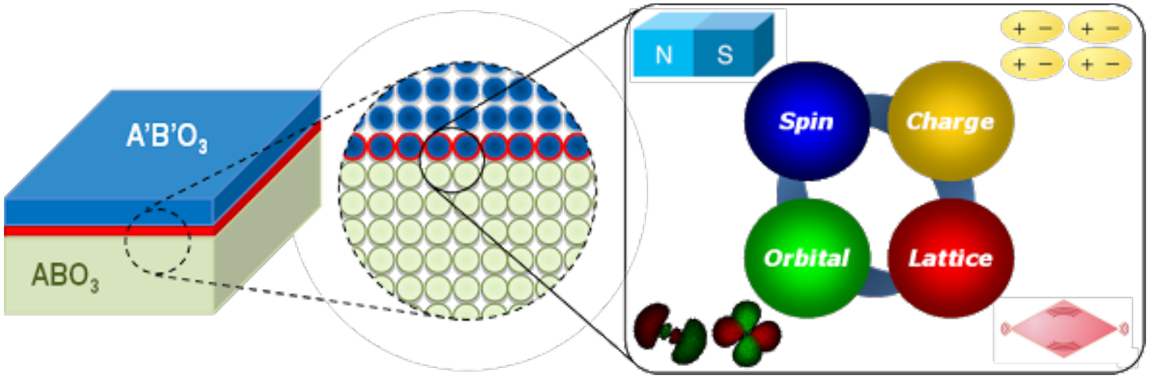


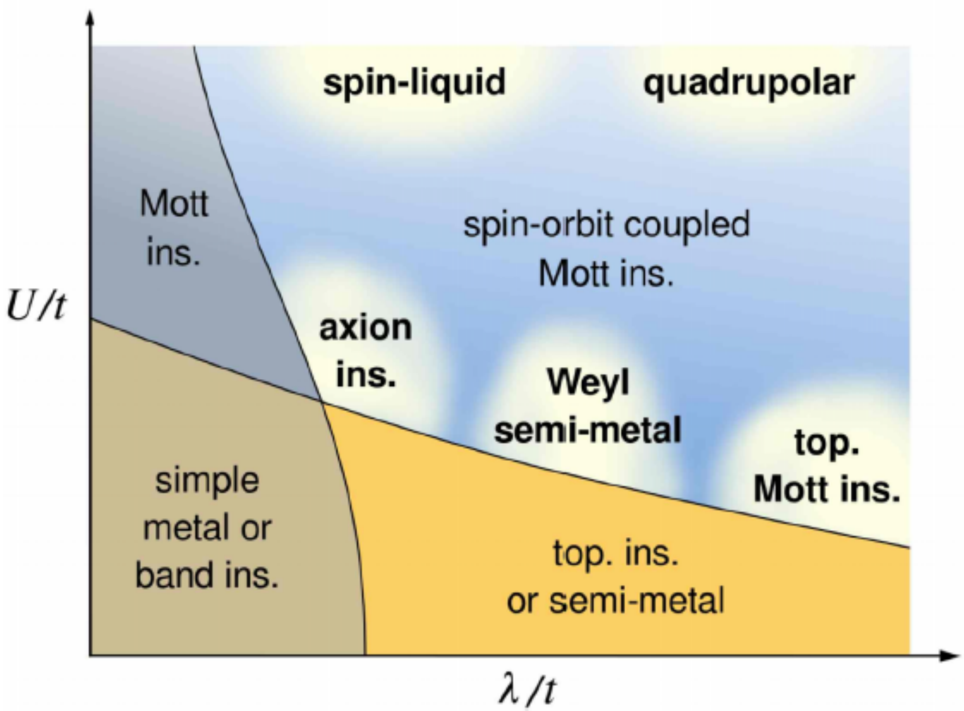
J. Lüning et al., PRB56 -97

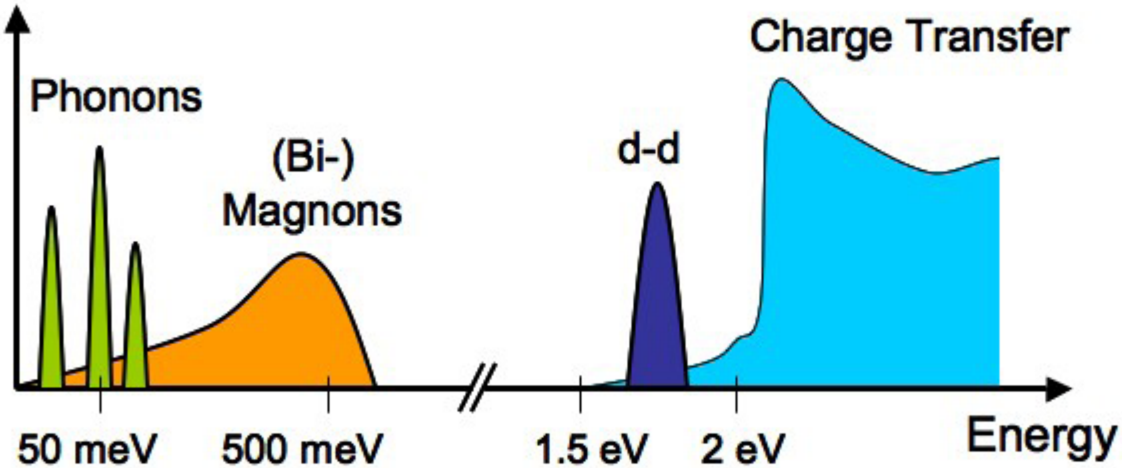
Momentum Transfer at VERITAS

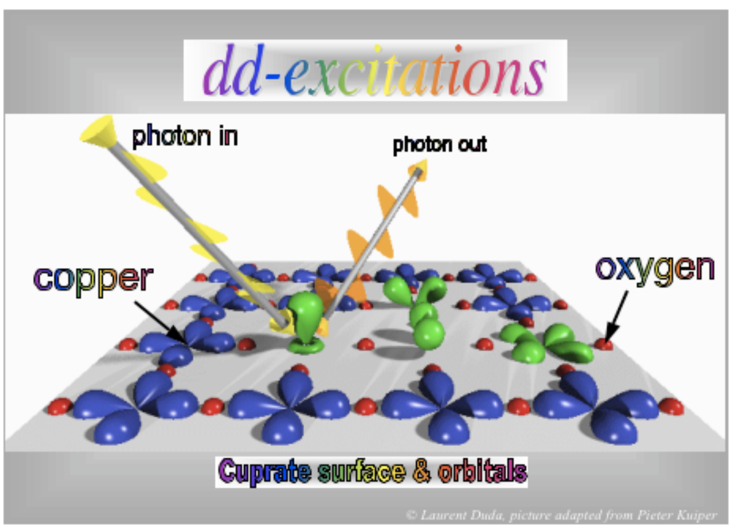


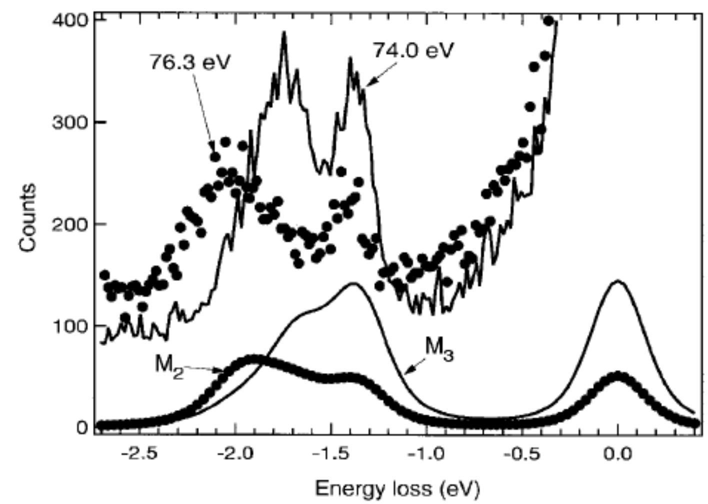
Correlated Electron Materials



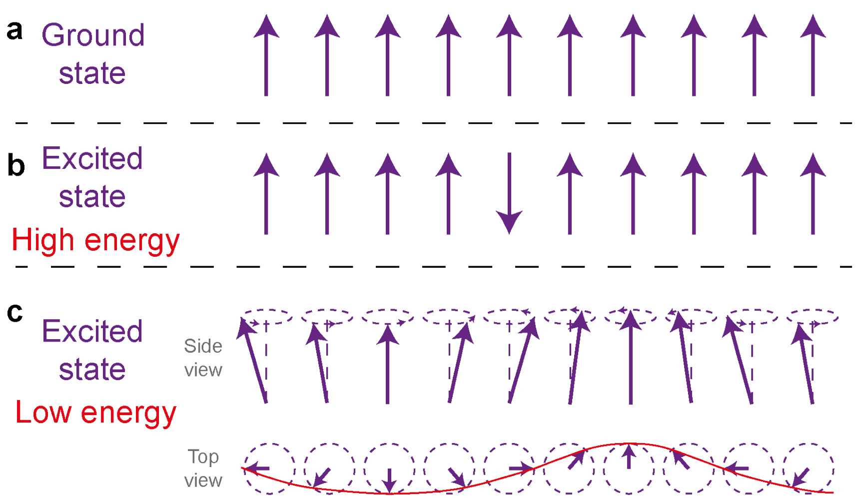


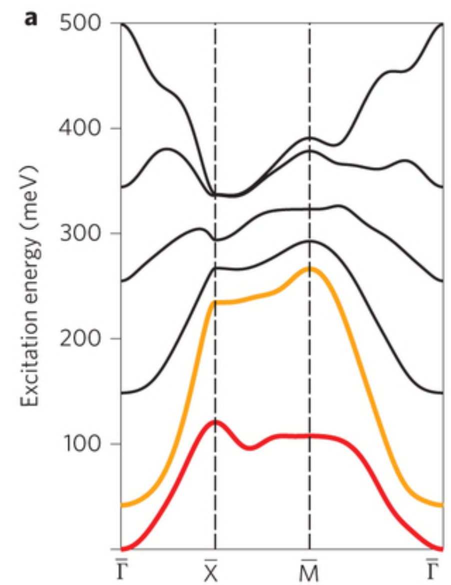

Phonons
(Bi-)
Magnons
d-d
Charge Transfer
50 meV
500 meV
1.5 eV
2 eV
Energy


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


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

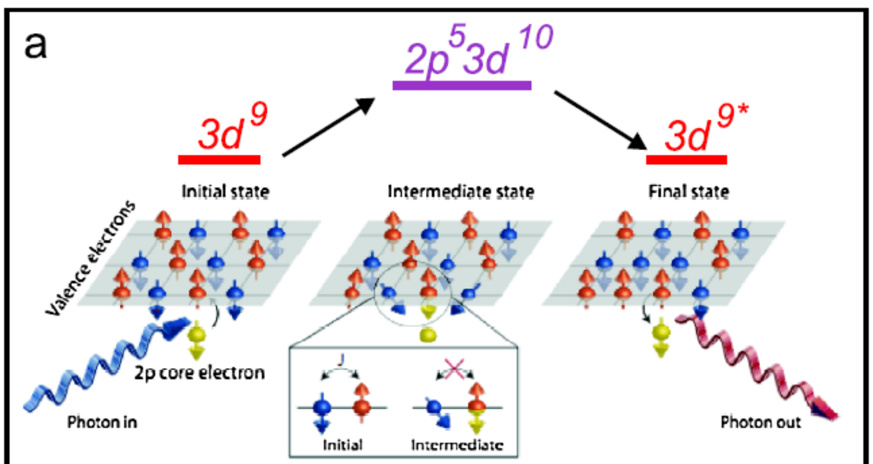
Magnon energy depends on momentum

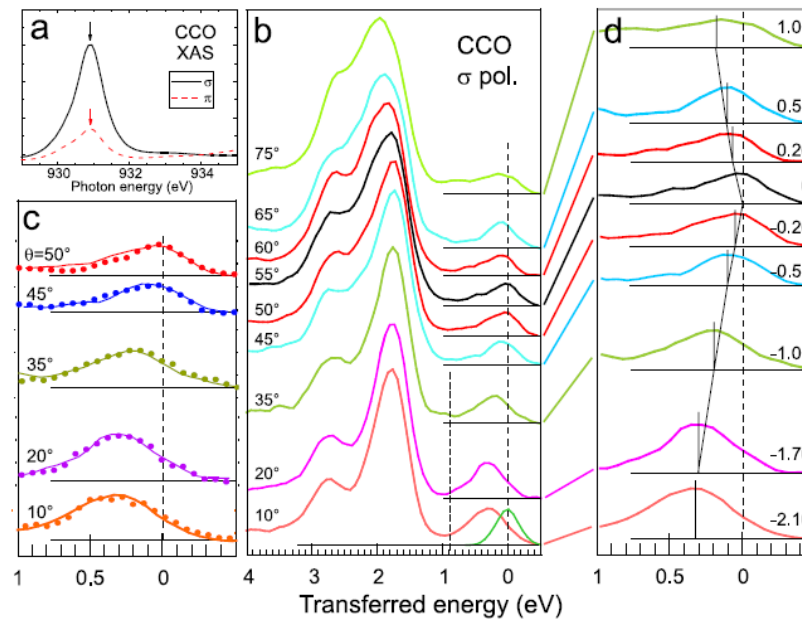




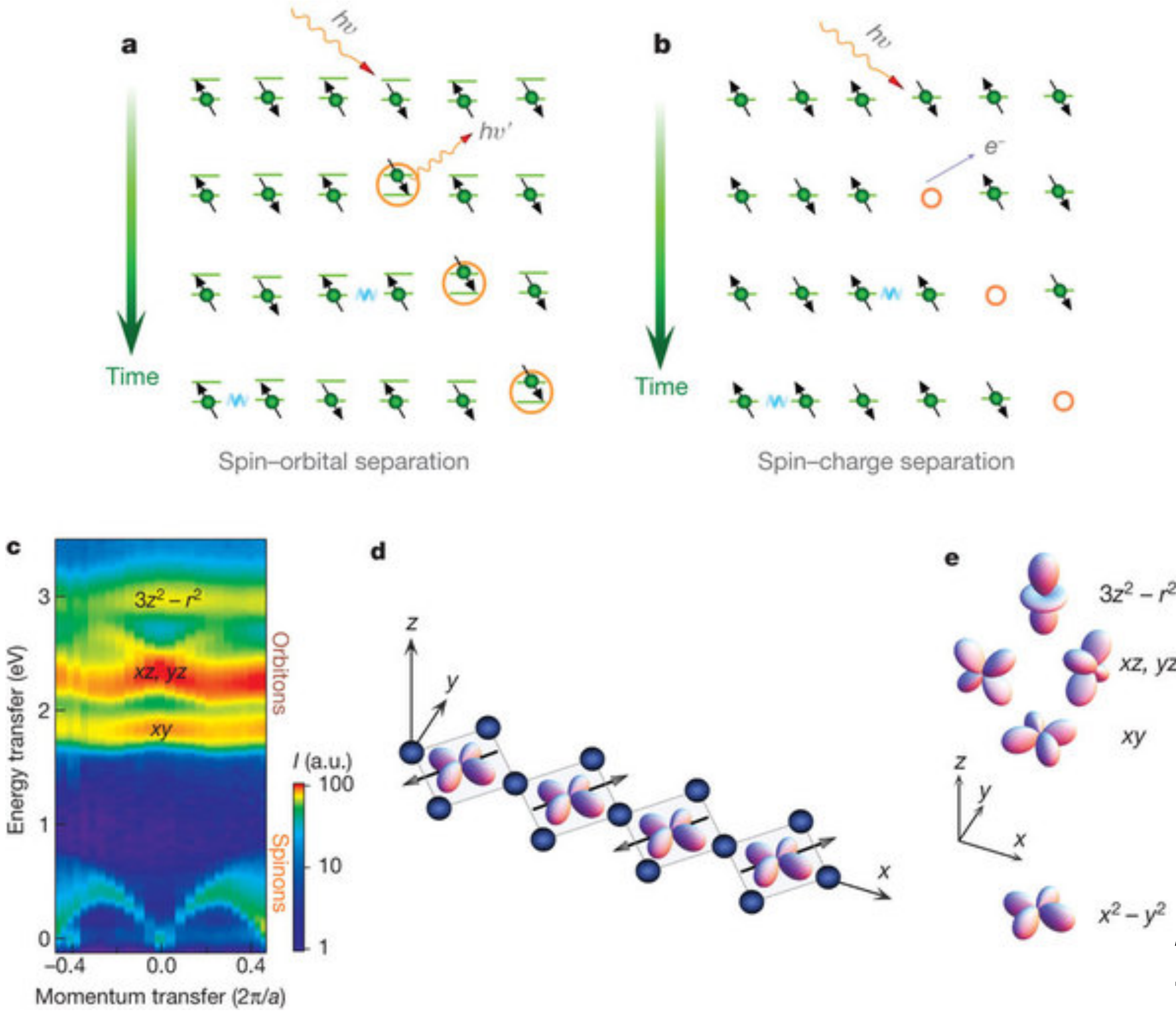
Dispersion of Magnetic Excitations in the Cuprate La_2CuO_4 and $CaCuO_2$ Compounds Measured Using Resonant X-Ray Scattering

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]





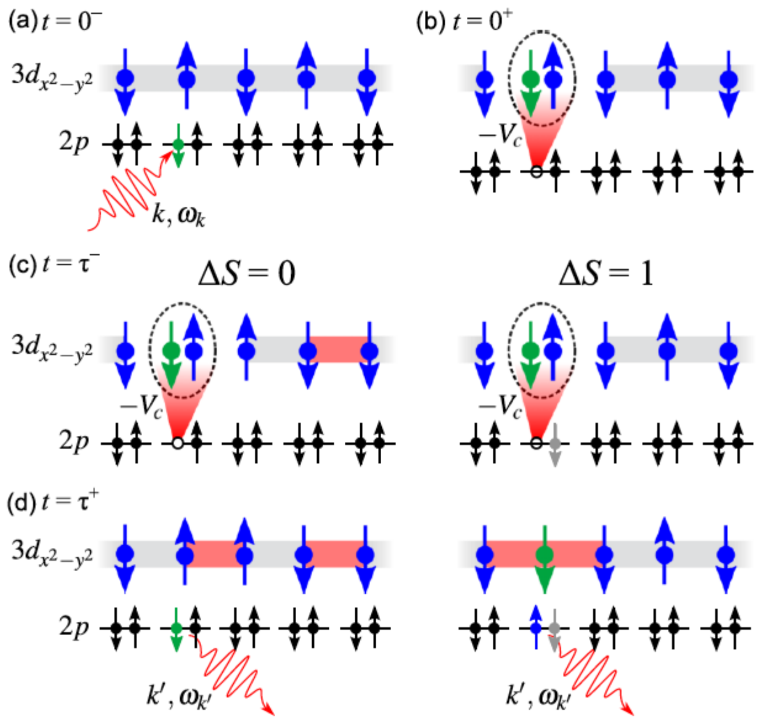
Orbiton-Spinon Separation

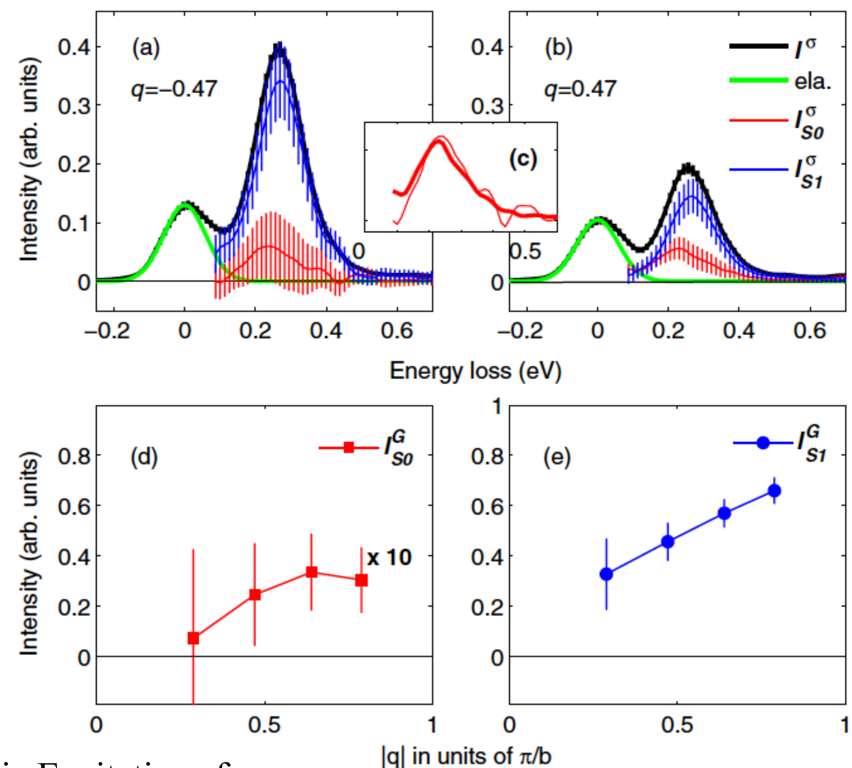


Schlappa et al., Nature **485**, 82–85 (2012)

Magnetism and Magnetization Dynamics

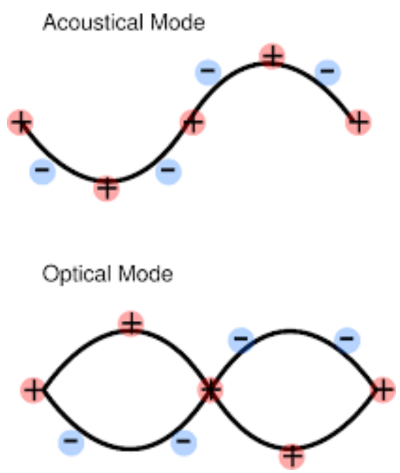
Double spin-flips depend on the spin-spin interaction strength, whereas the spin-orbit coupling is faster

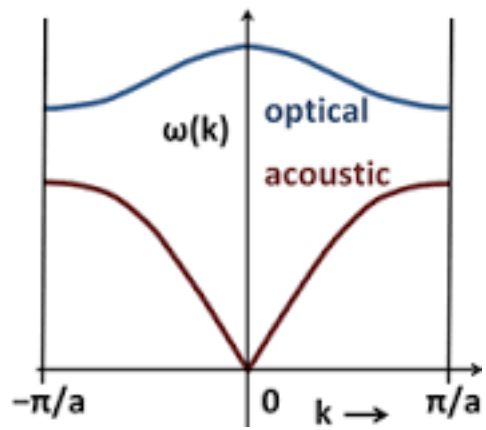




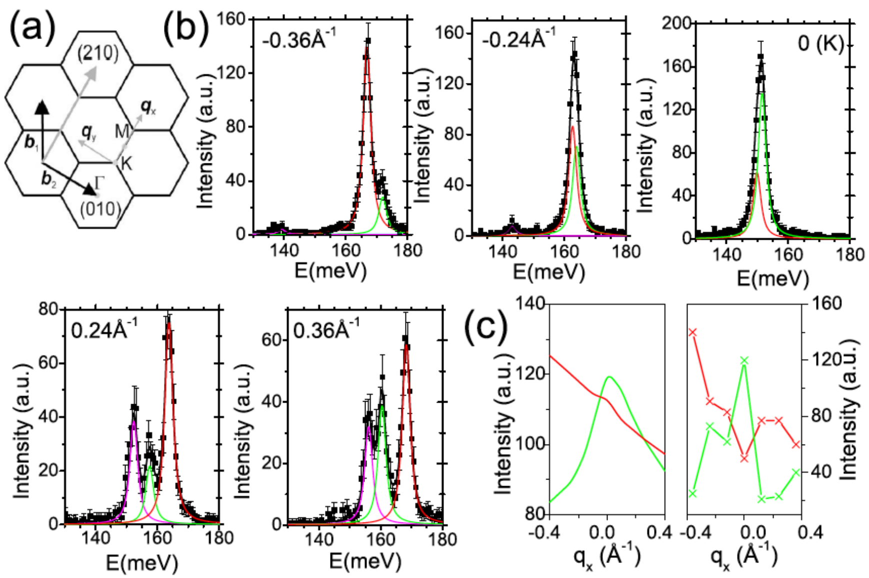
Femtosecond Dynamics of Momentum-Dependent Magnetic Excitations from Resonant Inelastic X-Ray Scattering in $CaCu_2O_3$.
V. Bisogni et al. PRL. 112, 147401 (2014)

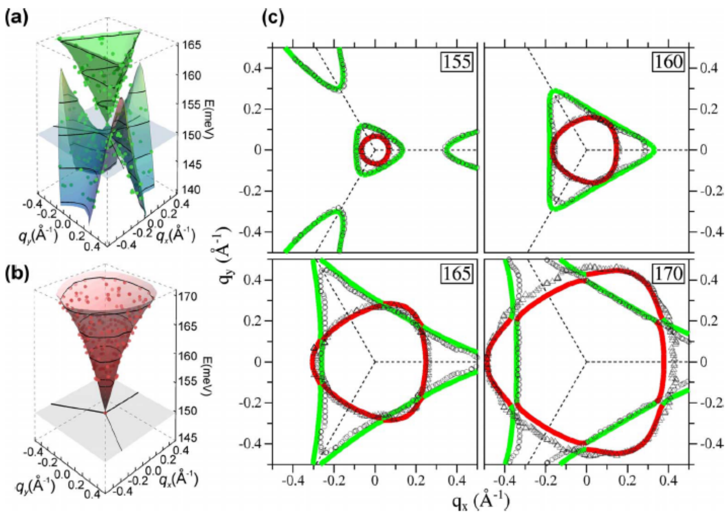
Phonon energy depends on momentum





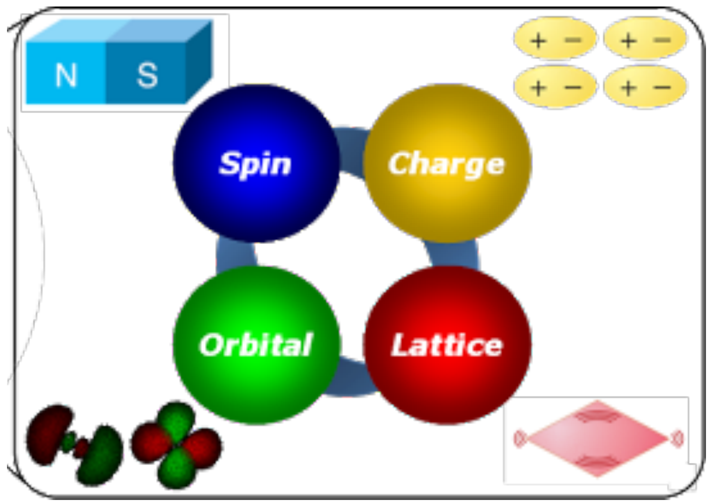
Phonon-electron-magnon-orbiton coupling





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

Property-determining interactions



accessible in high-resolution RIXS

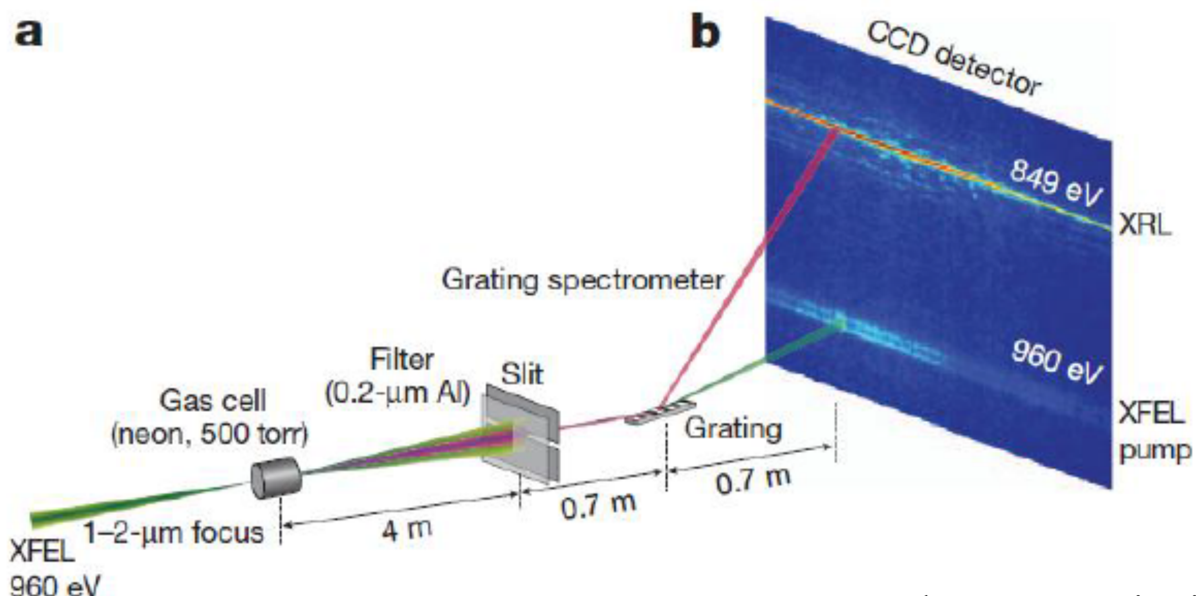
Main messages

- 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

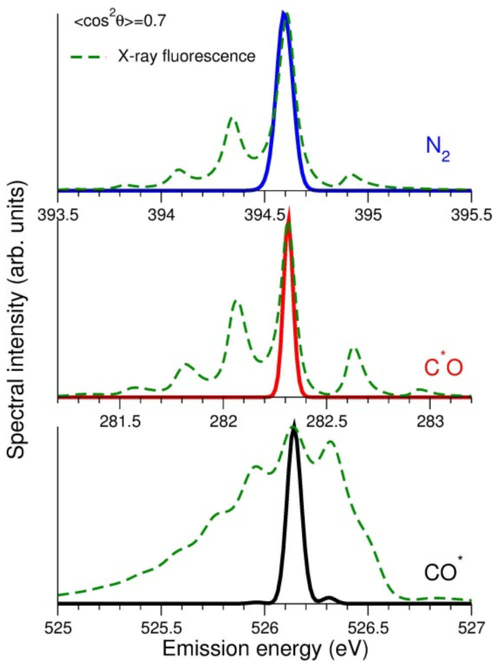
Stimulated X-ray Emission and Stimulated Resonant Inelastic Scattering

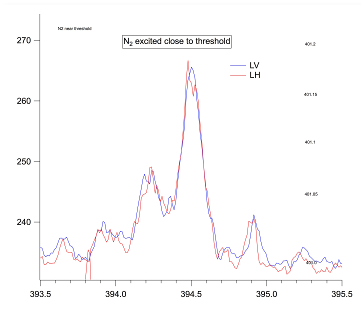
Collimated scattered light opens up new experimental opportunities

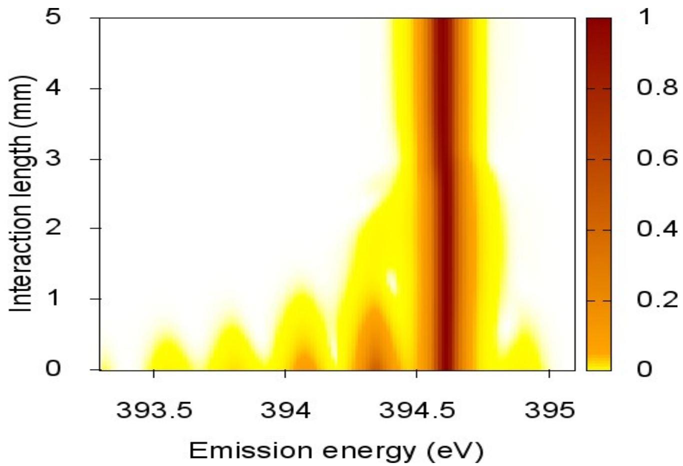


Coherent emission, Rohringer et al., Nature 481, 488 (2012))

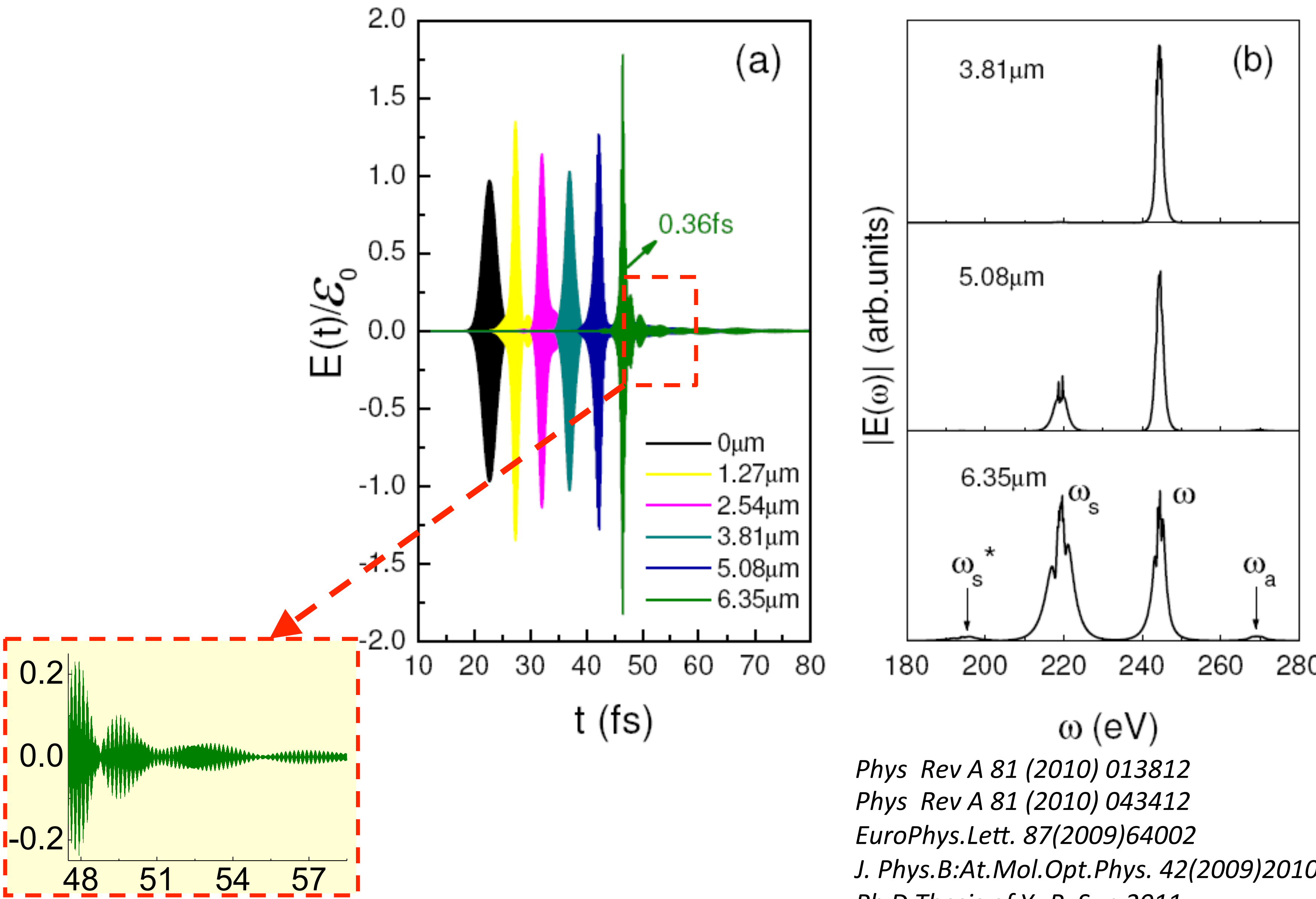
Control of the nuclear dynamics







Pulse compression, Burnham-Chiao modulation and four wave mixing



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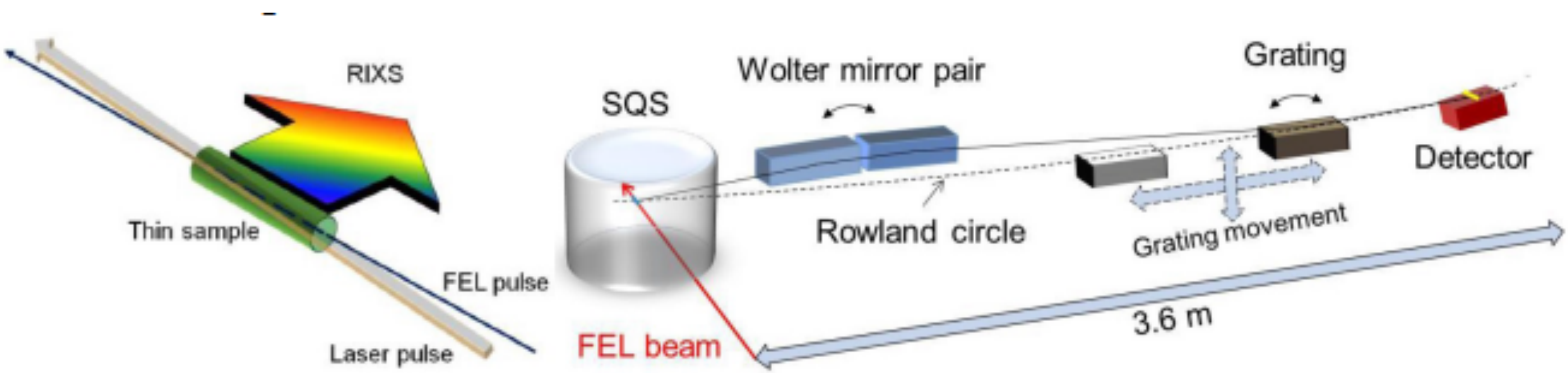
Ph D Thesis of Y.-P. Sun 2011

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



Thank you