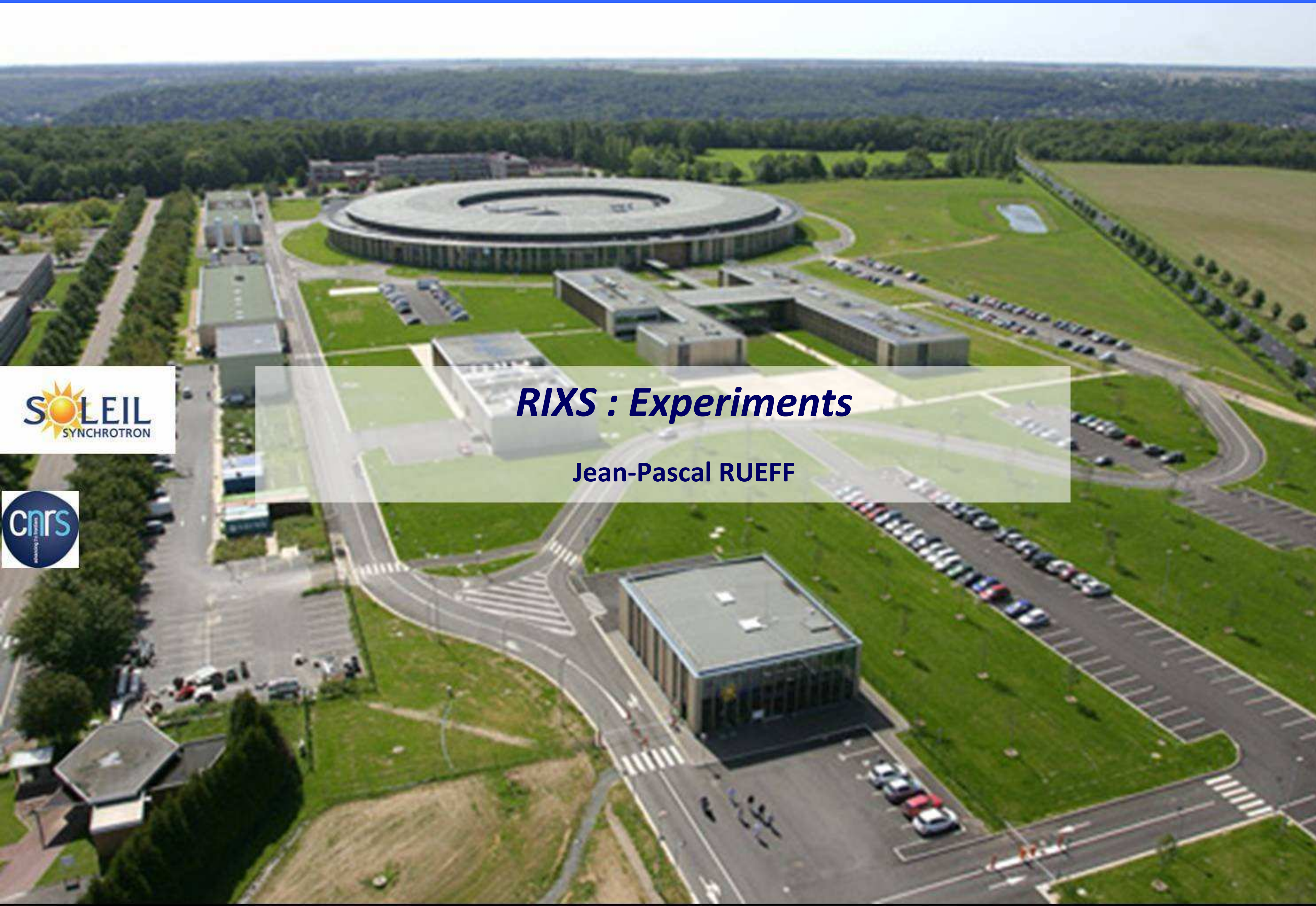
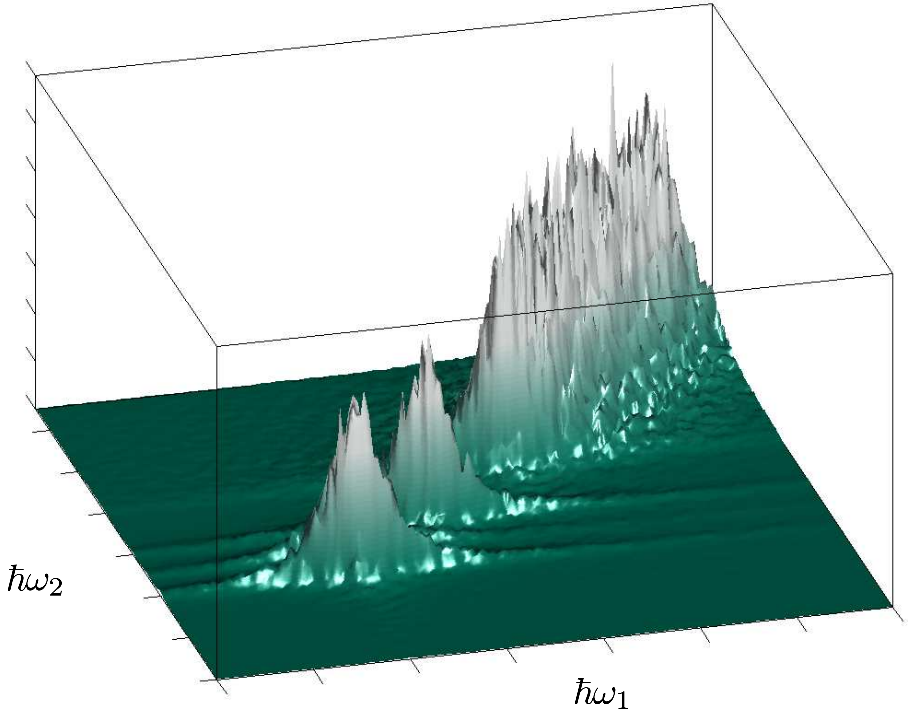


RIXS : Experiments

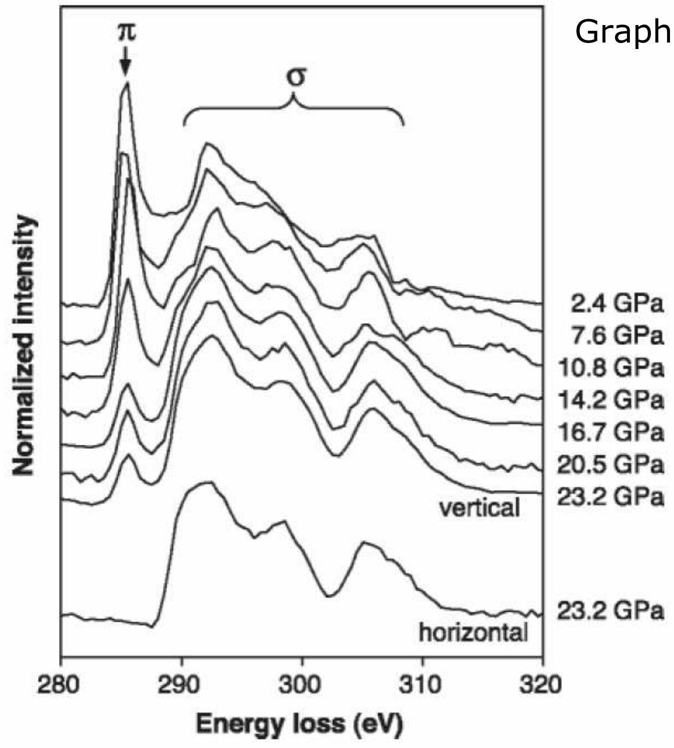
Jean-Pascal RUEFF


$\hbar\omega_2$
$\hbar\omega_1$

Is it possible to…

- Acquire soft x-ray spectra with a hard x-ray probe ?
- See under the white line ?
- "Image" the chemical environment ?
- Probe forbidden transition, … and their dispersion ?
- Do spectroscopy in constraint sample environments ?
- Measure phonons with x-rays ?

☑ Acquire soft x-ray spectra with a hard x-ray probe ?



Graphite – C K edge

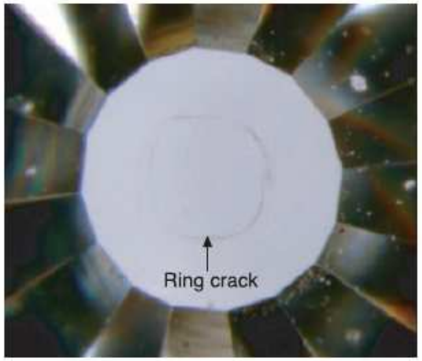
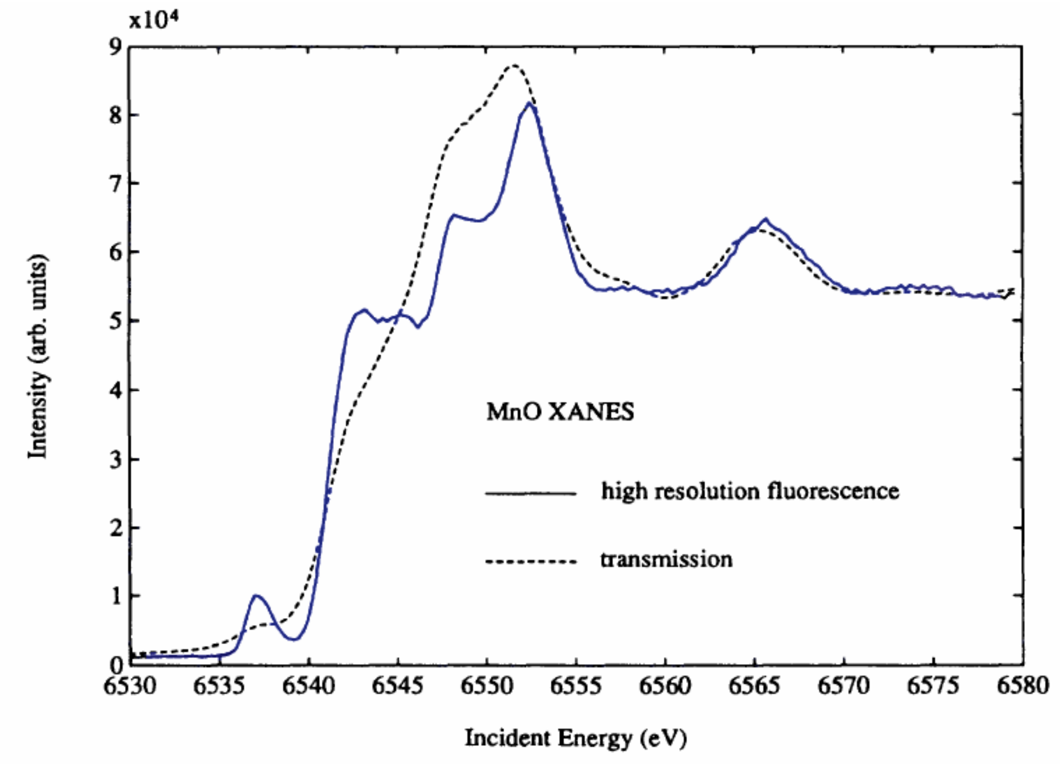


Fig. 3. Photomicrograph showing indention (ring crack) of diamond anvil by the high-pressure form of cold-compressed graphite.

W. Mao, Science (2003)

☑ See under the white line ?

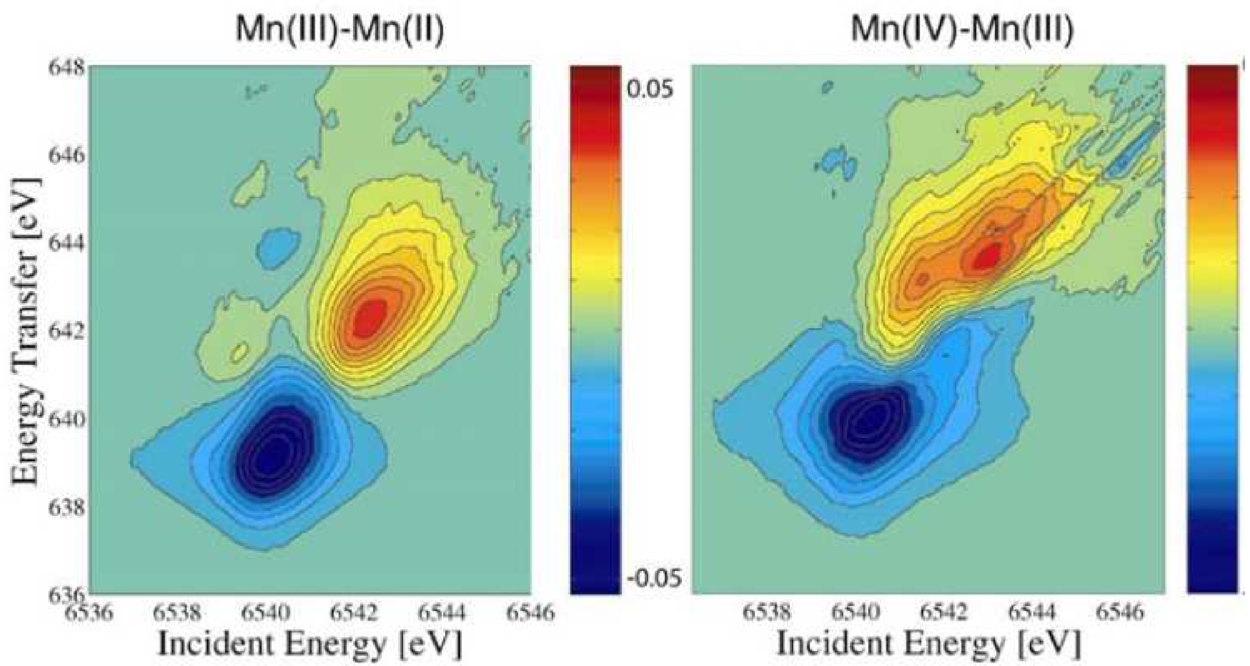


MnO - Mn K edge

K. Hämäläinen et al., Phys. Rev. B (1992)

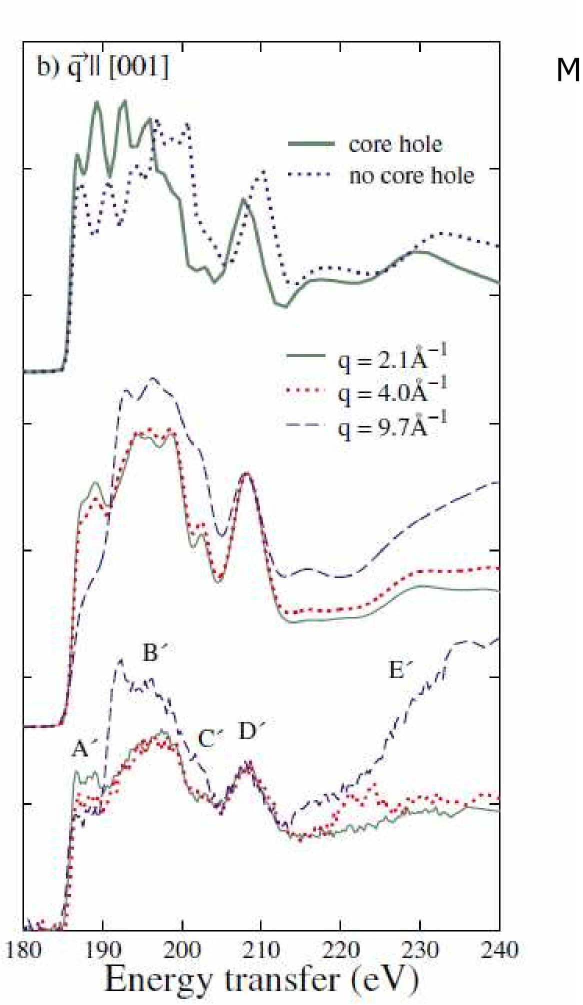
☑ "Image" the chemical environment ?

Mn complexes- Mn K edge / Kα emission

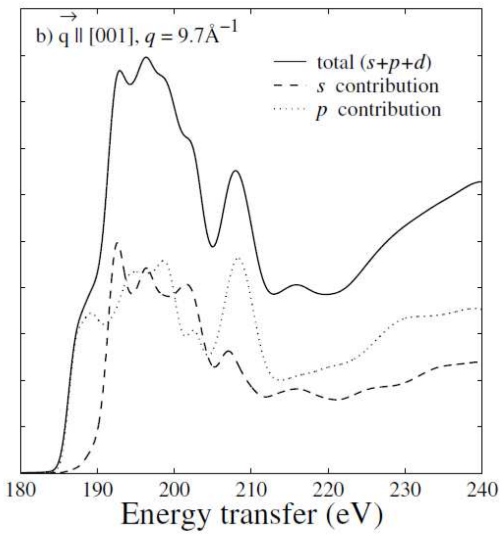


P. Glatzel, J. Am. Chem. Soc. (2004)

☑ Probe forbidden transition ?



MgB_2 – B K edge

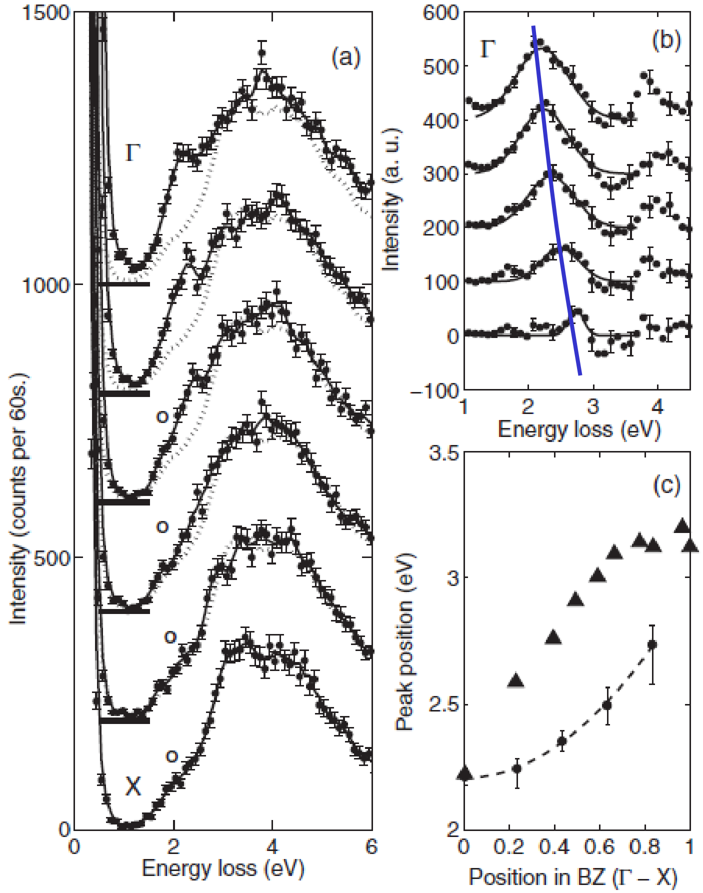


$1s \rightarrow p$

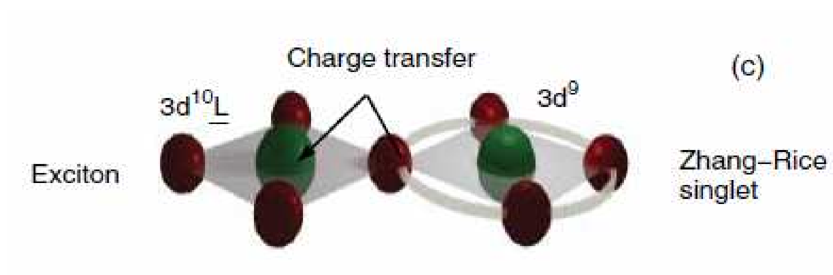
$1s \rightarrow s$

A. Mattila, Phys. Rev. Lett., (2005)

☑ … and their dispersion ?



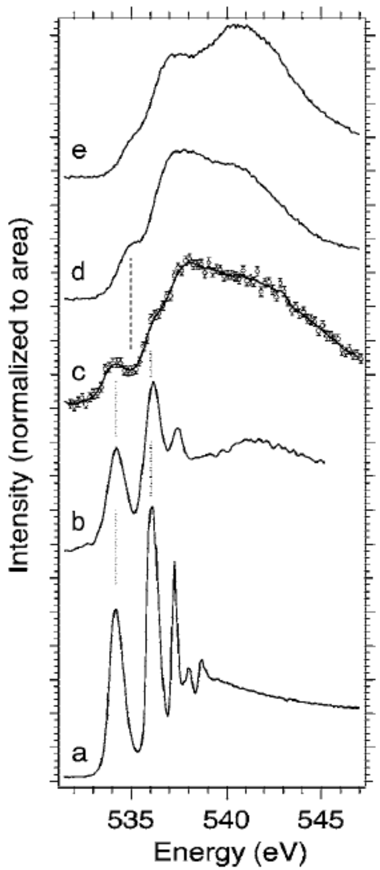
La_2CuO_4, energy loss

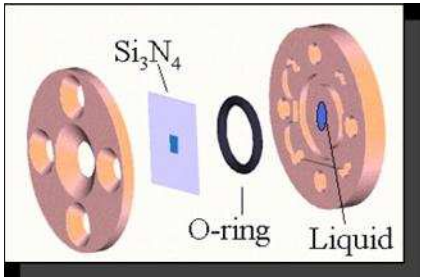


E. Collart, Phys. Rev. Lett. (2006)

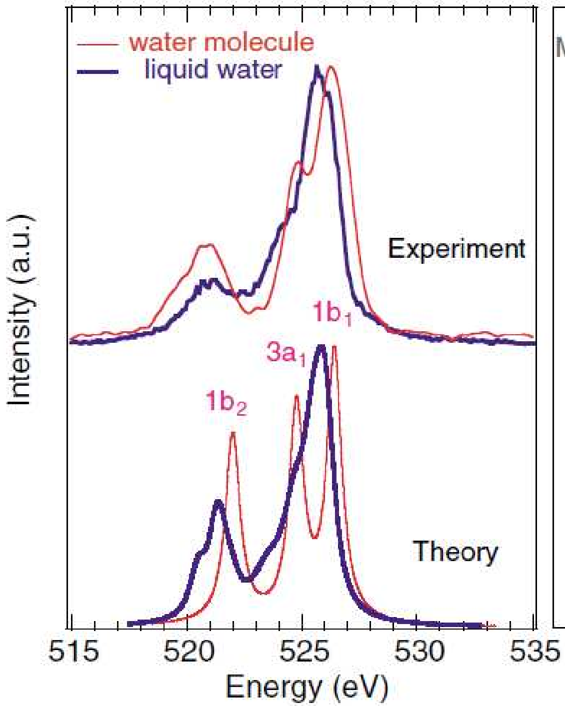
☑ Do spectroscopy in constraint sample environments ?

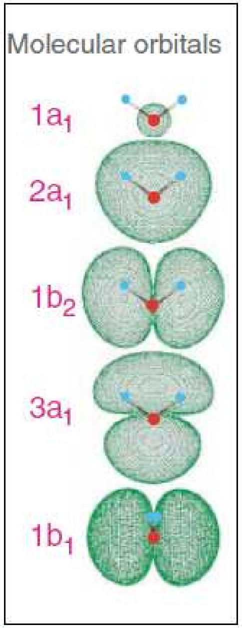
H_2O – O K edge





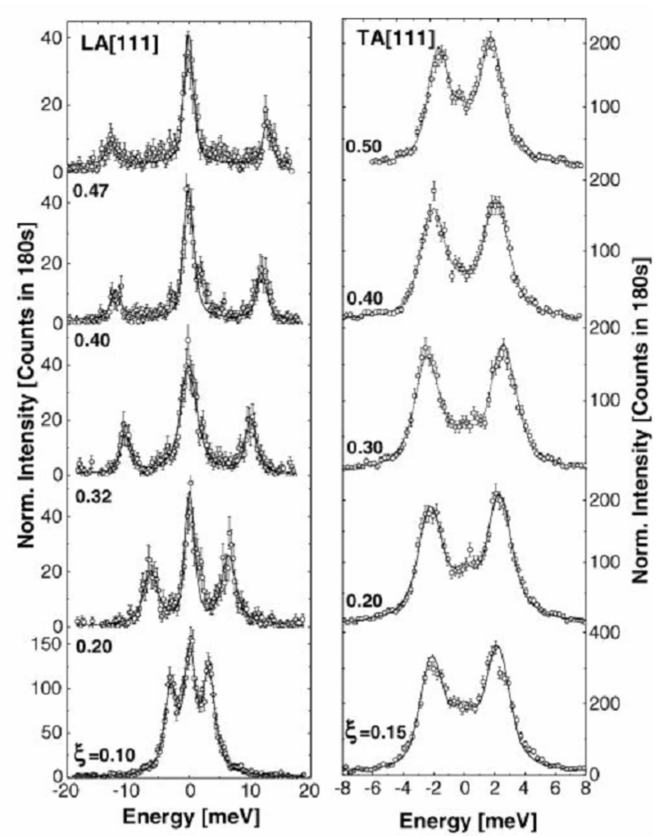
H_2O – O Kα emission



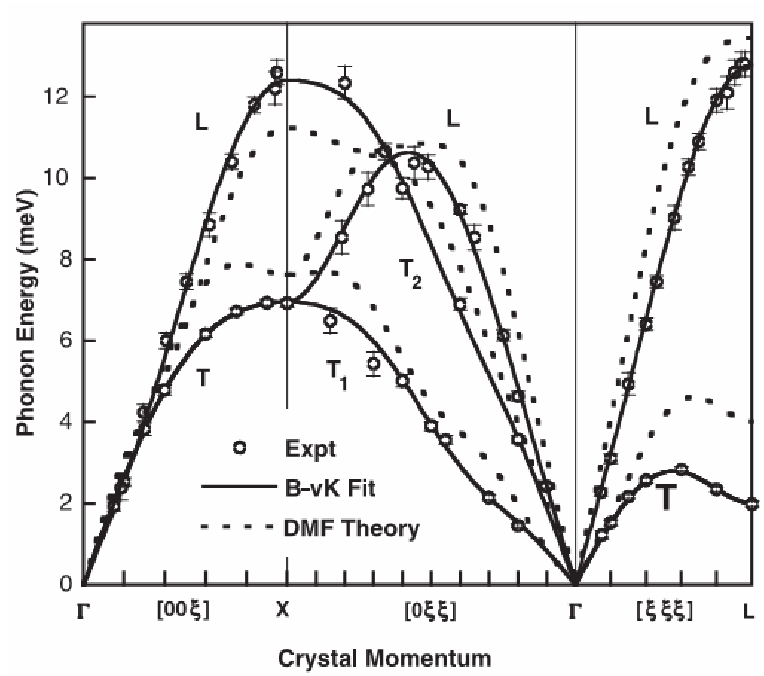


P. Wernet, J. Chem. Phys. (2005) ; J. Guo, Phys. Rev. Lett. (2002)

☑ Measure phonons with x-rays ?



δ-Pu – phonons



J. Wong et al., Science (2003)

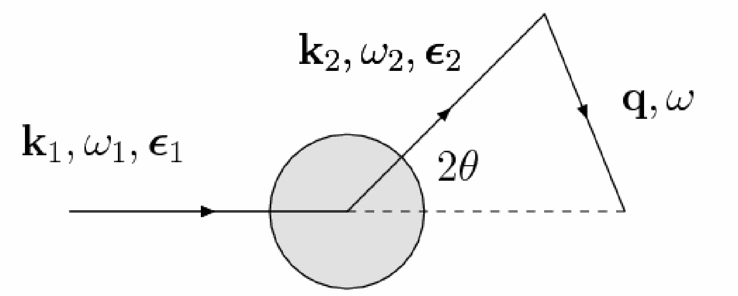
Outline

- Motivations
- Introduction: a Reminder
  - Non-resonant IXS
  - RIXS
- Applications
  - High pressure
  - Coordination Chemistry
  - Strongly correlated materials
- Perspectives
  - New experiments

INTRODUCTION

General principle

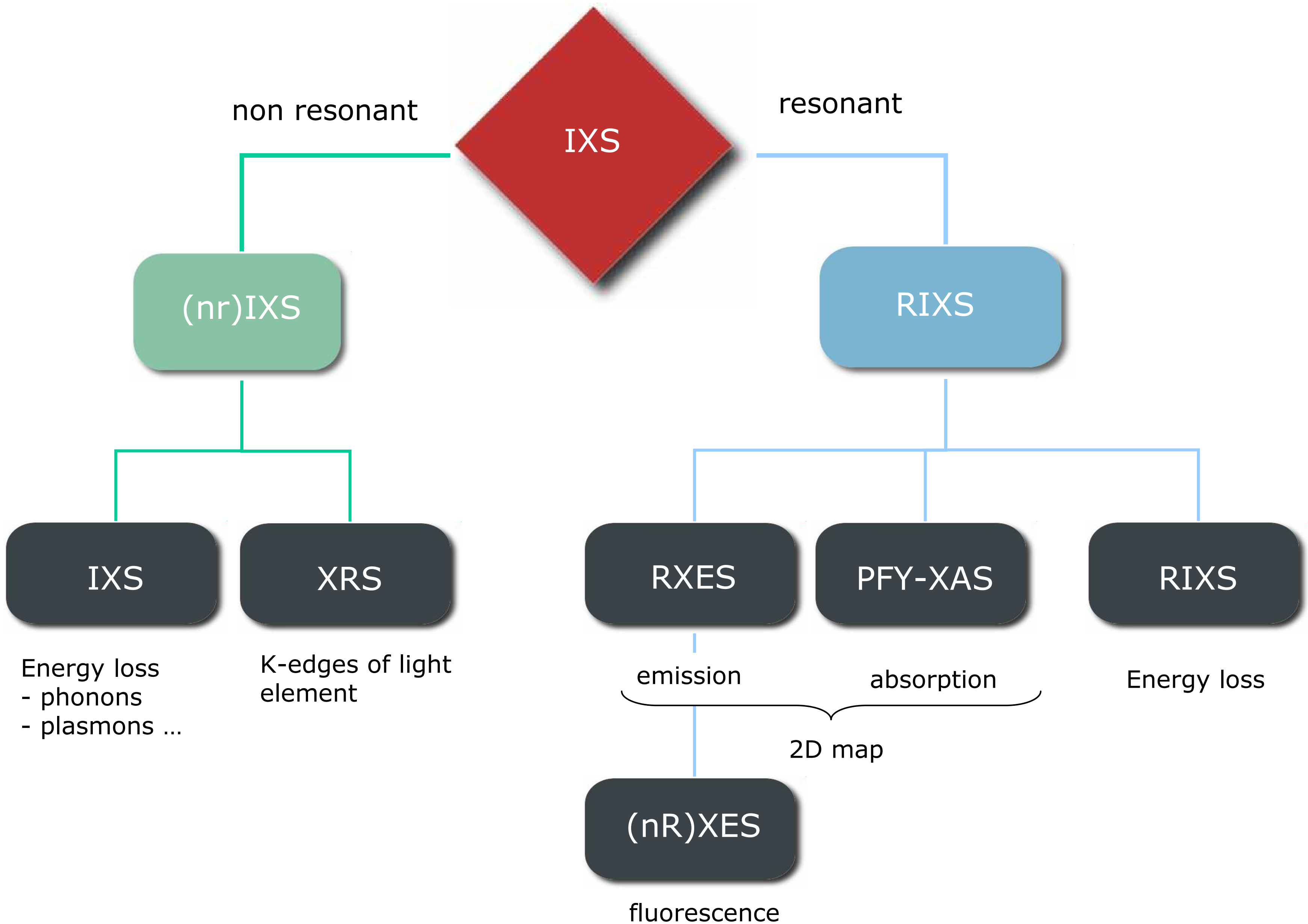
There are only three basic actions to produce all the phenomena associated with light and electrons: A photon goes from place to place, an electron goes from place to place, an electron emits or absorbs a photon, QED, Richard Feyman



$\hbar\omega = \hbar\omega_1 - \hbar\omega_2$ Transfer energy

$q \approx 2k_1 \sin(\theta)$ Transfer momentum

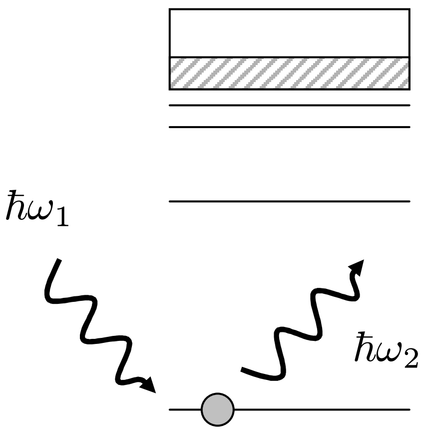
Overview


IXS
non resonant
resonant
(nr)IXS
RIXS
IXS
XRS
RXES
PFY-XAS
RIXS
Energy loss
- phonons
- plasmons …
K-edges of light element
emission
absorption
Energy loss
2D map
(nR)XES
fluorescence

Resonant vs. Non resonant

Non resonant IXS

2 photons

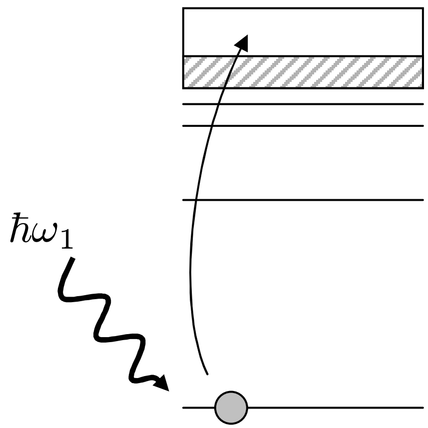


$$\frac{e^2}{2m}\mathbf{A}^2$$

1st order

absorption

1 photon + 1 electron

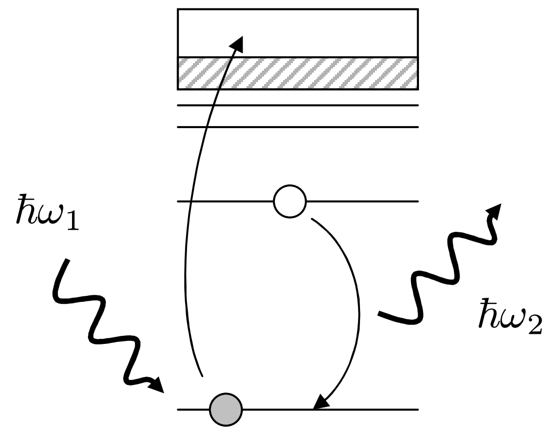


$$\frac{e}{m}\mathbf{p}\cdot\mathbf{A}$$

1st order

RIXS

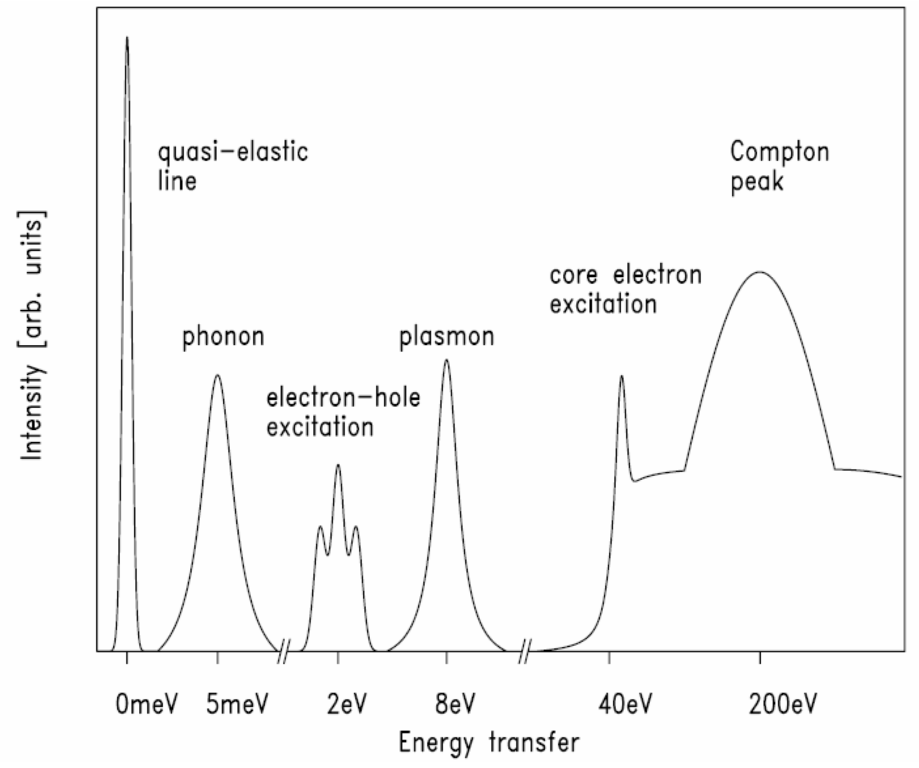
2 photons + 2 electrons

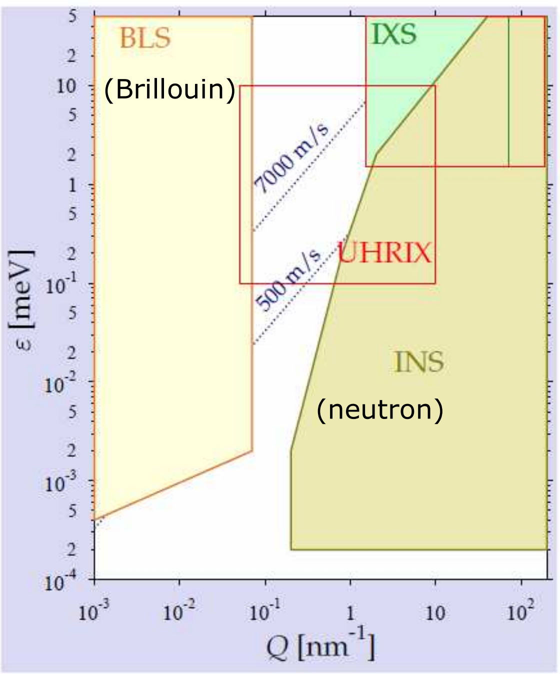


$$\left(\frac{e}{m}\mathbf{p}\cdot\mathbf{A}\right)^2$$

2nd order

• **Dynamical structure factor** $S(\mathbf{q}, \omega)$





(source ESRF)

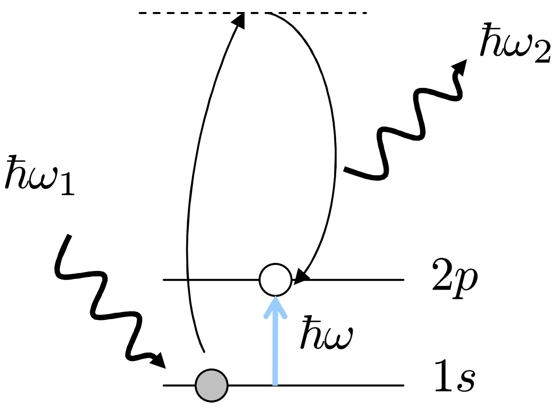
(nr)IXS

Equivalence with x-ray absorption

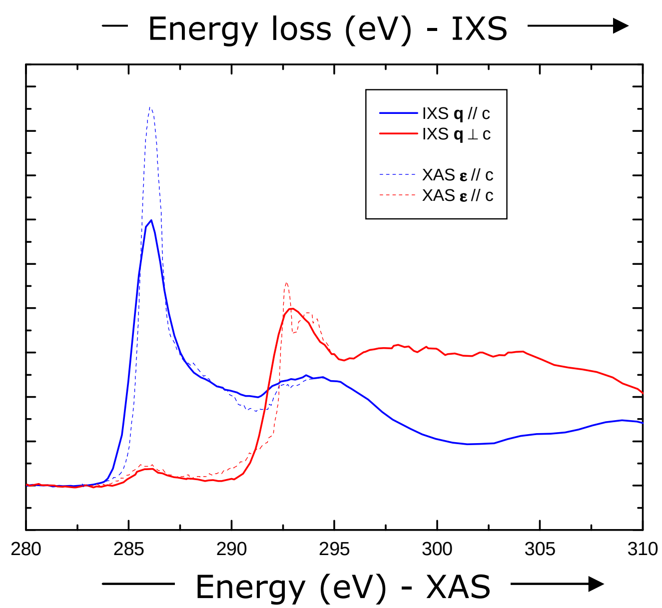
$$S(\mathbf{q},\omega) = \sum_{i,f} \left| \langle f | \sum_j \exp(i\mathbf{q}\cdot\mathbf{r}) | i \rangle \right|^2 \times \delta\left(E_f - E_i - \hbar\omega\right)$$

$$\exp(i\mathbf{q}\cdot\mathbf{r}) = 1 + i\mathbf{q}\cdot\mathbf{r} + (i\mathbf{q}\cdot\mathbf{r})^2/2 + \dots$$

$\mathbf{q}$ plays the role of $\boldsymbol{\epsilon}$



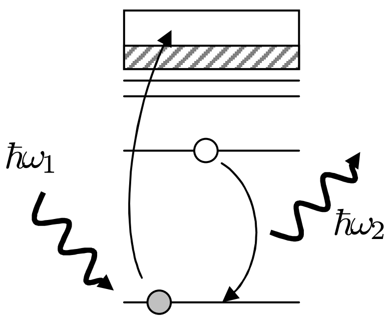
C - K edge



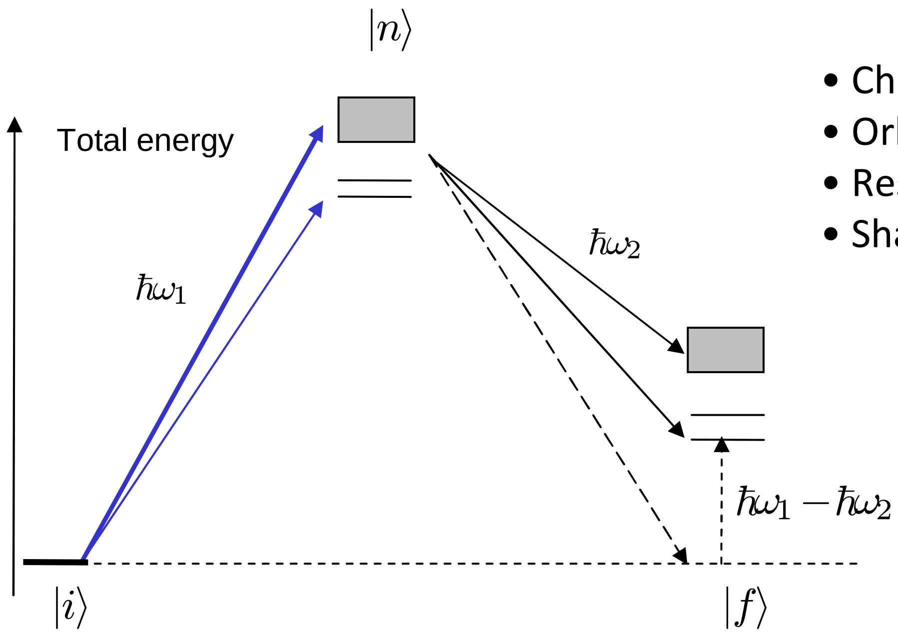
(nr)IXS

Y. Mizuno and Y. Ohmura, J. Phys. Soc. Japan (1967)

- **Kramers-Heisenberg equation**



XAS ⊗ XES



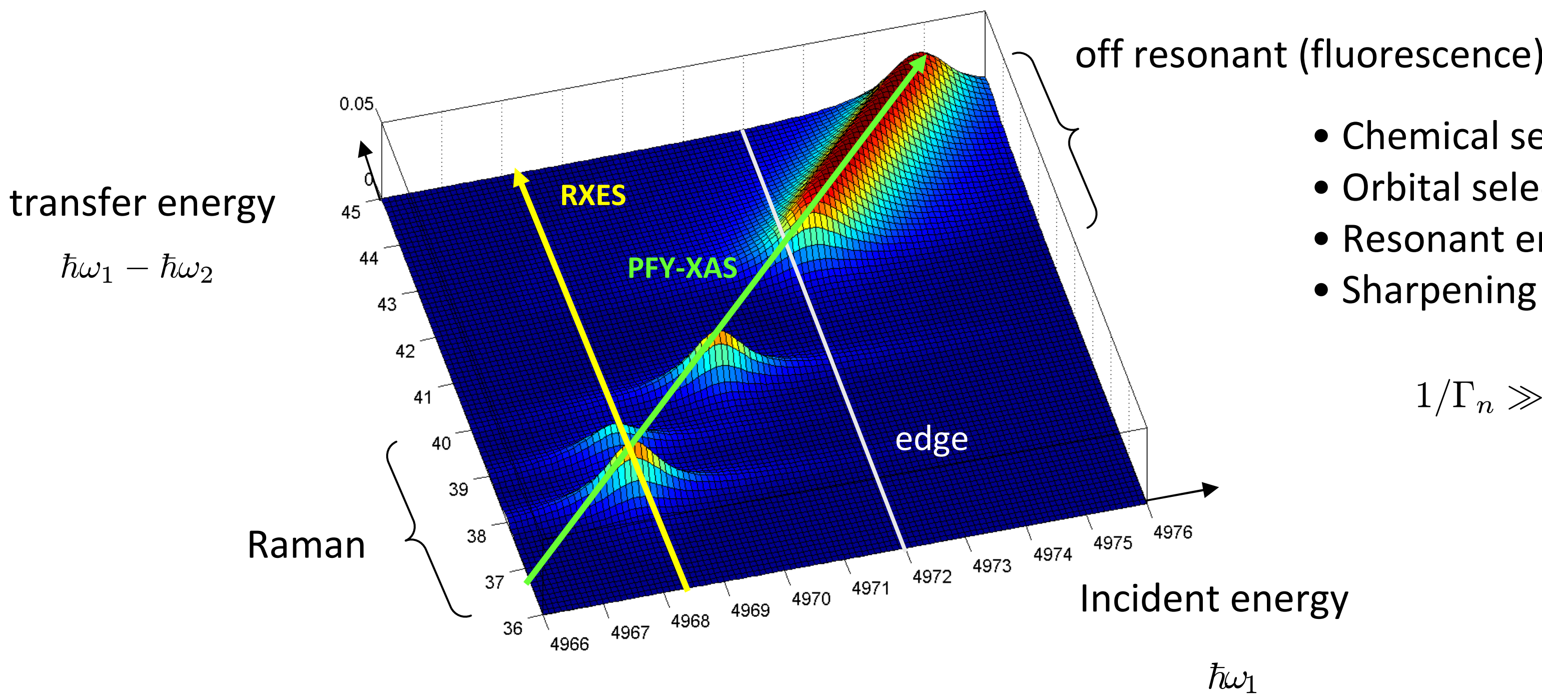
- Chemical selective
- Orbital selective
- Resonant enhancement
- Sharpening effect

$$1/\Gamma_n \gg 1/\Gamma_f$$

RIXS

Spectral sharpening effect

- **Kramers-Heisenberg equation**

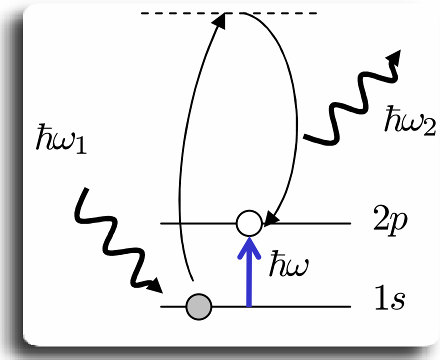


- Chemical selective
- Orbital selective
- Resonant enhancement
- Sharpening effect

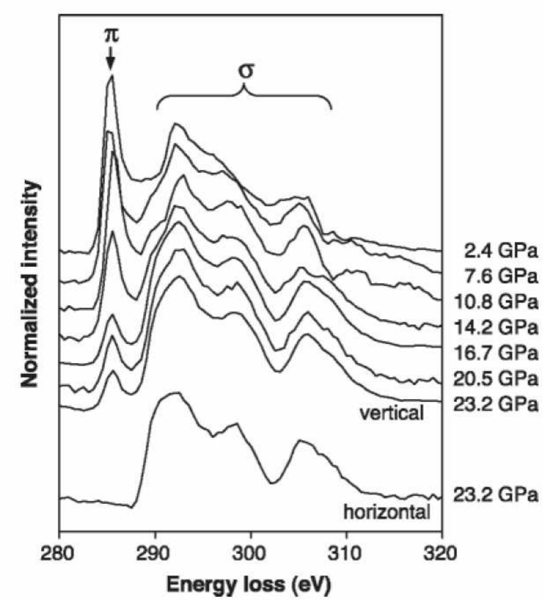
$$1/\Gamma_n \gg 1/\Gamma_f$$

APPLICATIONS

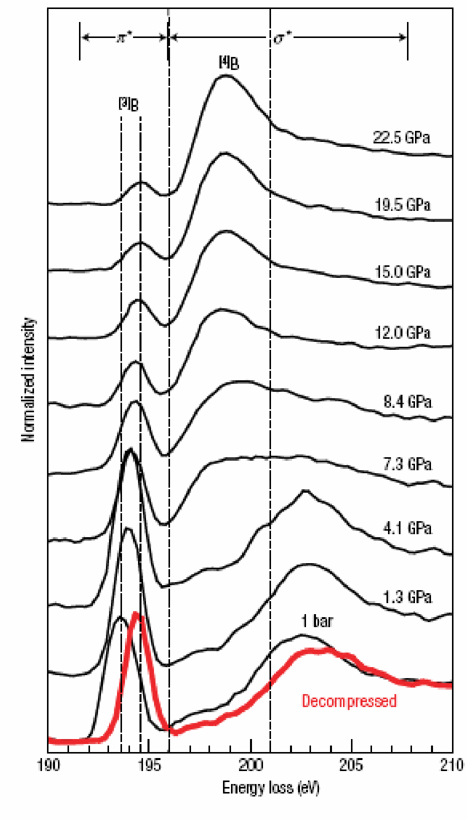
Bonding changes under pressure

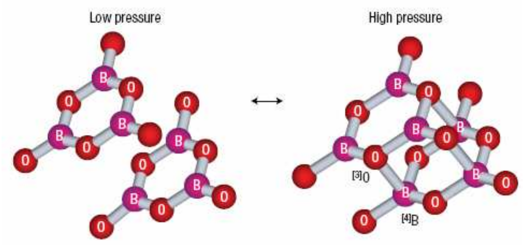


graphite



B_2O_3



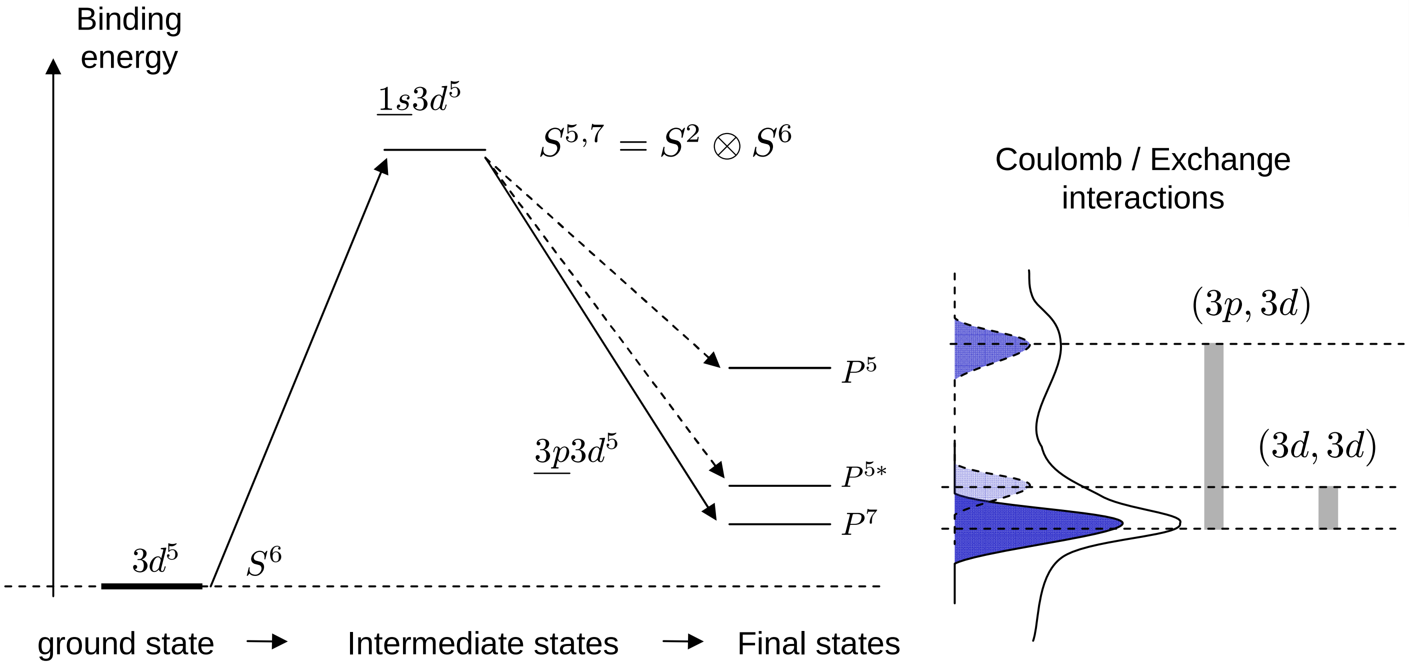


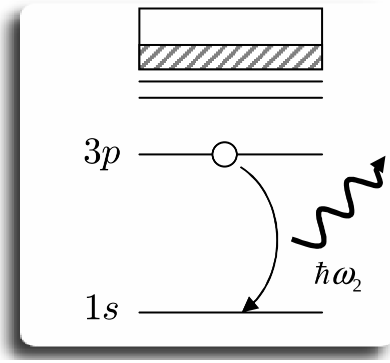
(nr)IXS

W. Mao, Science (2003); Lee et al. Nature Materials (2005)

Spin state transition in transition metal

Kβ - XES





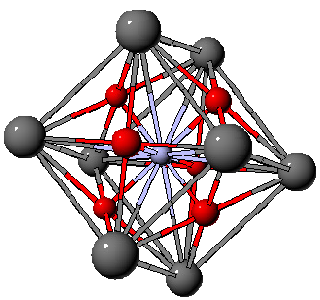
> local probe of the 3d magnetism in transition metal
> No applied magnetic field
> Compatible with high pressure

> $L\gamma_1$ emission in rare-earth for 4f magnetism

RIXS

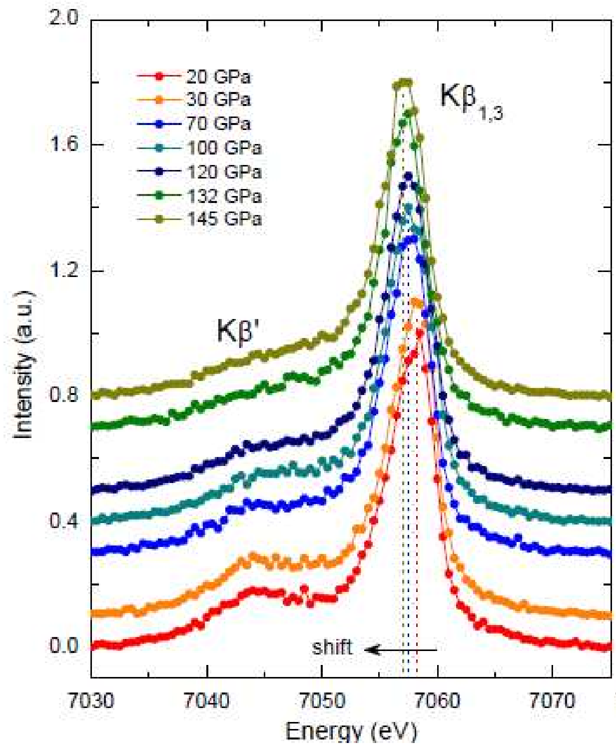
G. Peng, J. Am. Chem. Soc. (1994)

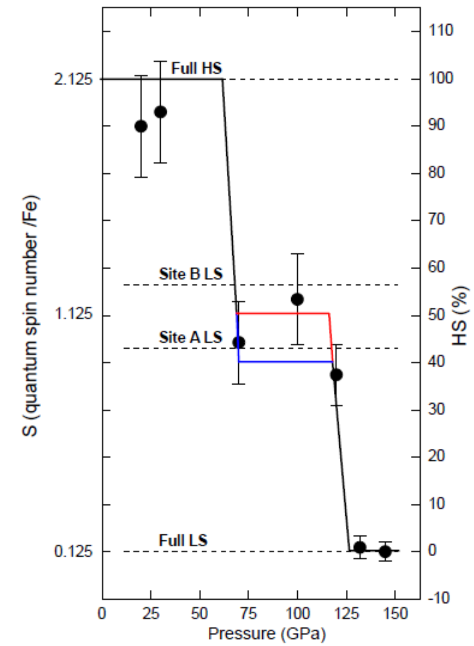
Magnetic collapse in (Mg,Fe)SiO2



$75\%\ Fe^{2+}$, $25\%\ Fe^{3+}$

- A (Ih) site :
  - 75% of Fe^{2+}
- B (Oh) site :
  - 25% of Fe^{2+}
  - 100% of Fe^{3+}

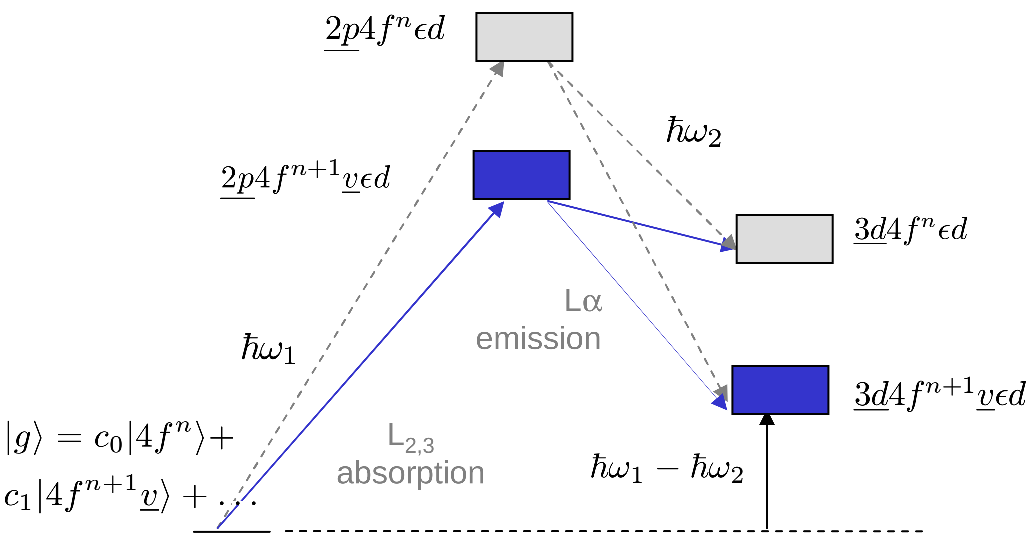




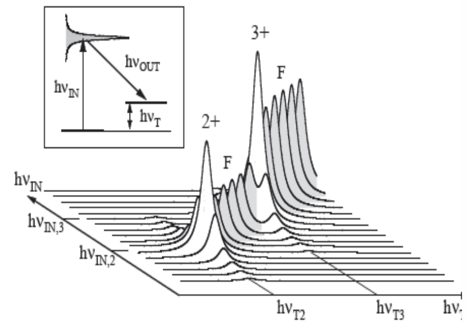
RIXS

J. Badro et al., Science (2004)

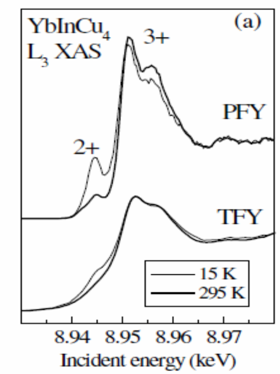
2p3d - RXES



ground state → Intermediate states → Final states



RXES



PFY

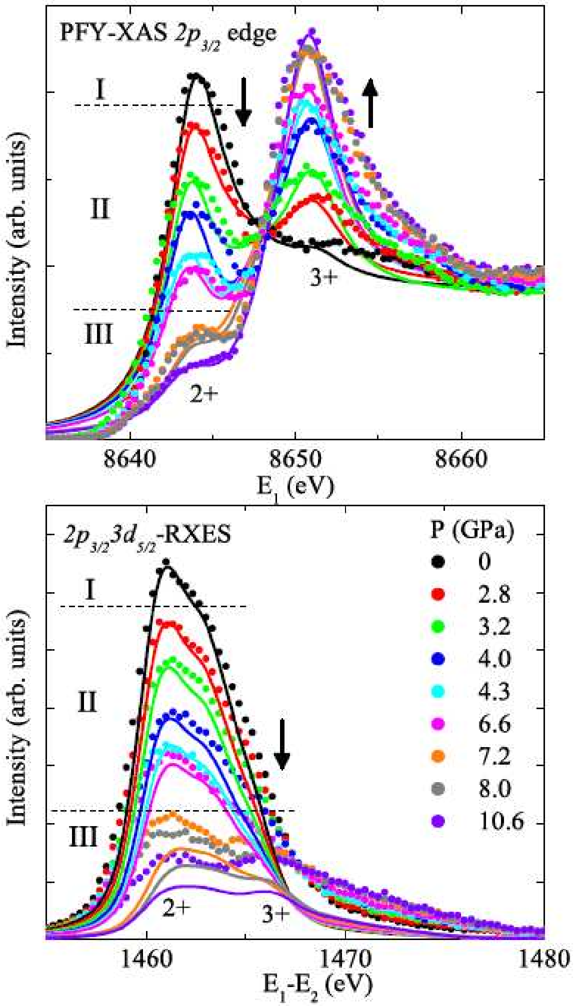
$$v = 2 + \frac{I_{\mathrm{RIXS}}(3+) + I_{\mathrm{RIXS}}(2+)}{I_{\mathrm{RIXS}}(2+)}$$

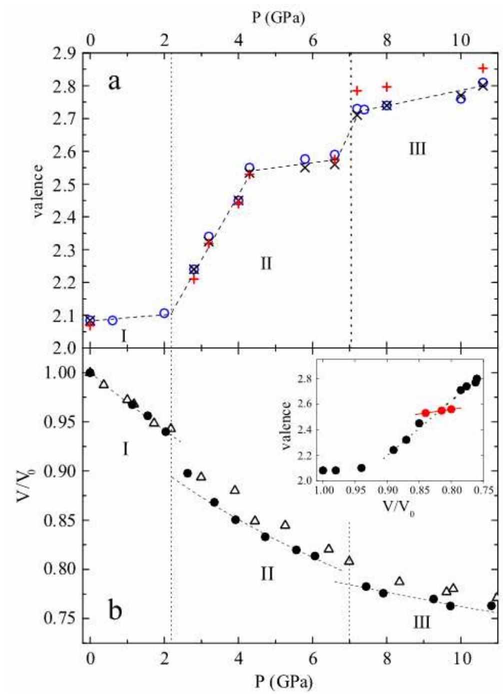
> Core hole potential separates the different mixed states
> Sharpening effect due to resonant effects
> Great accuracy in the determination of the valent state
> 4f,5f systems

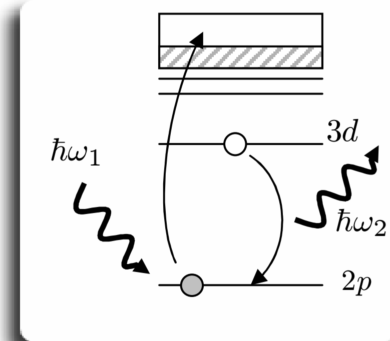
RIXS

Dallera et al., Phys. Rev. Lett. (2002)

Mixed valent state: TmTe under pressure



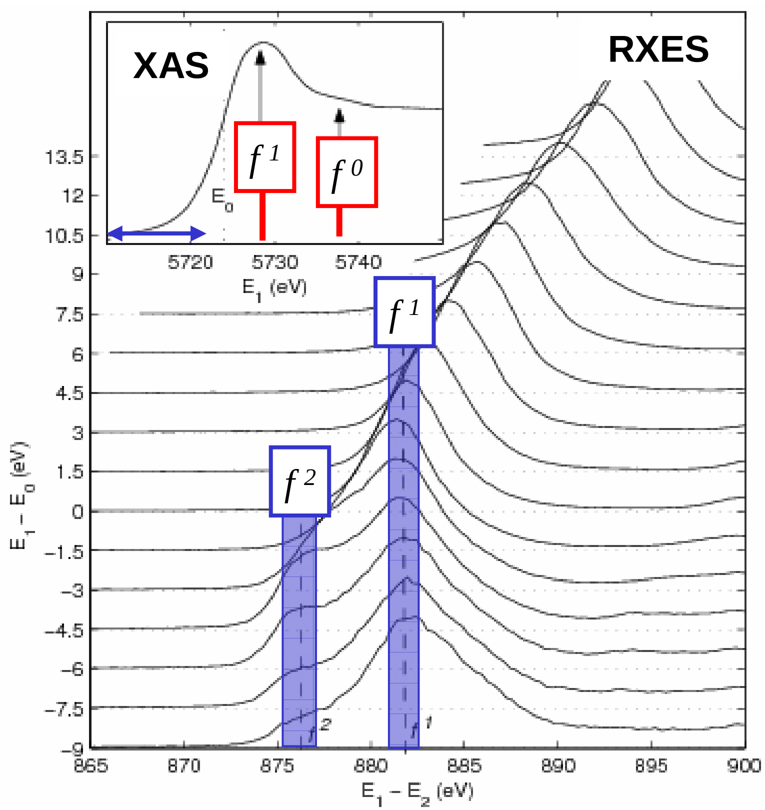


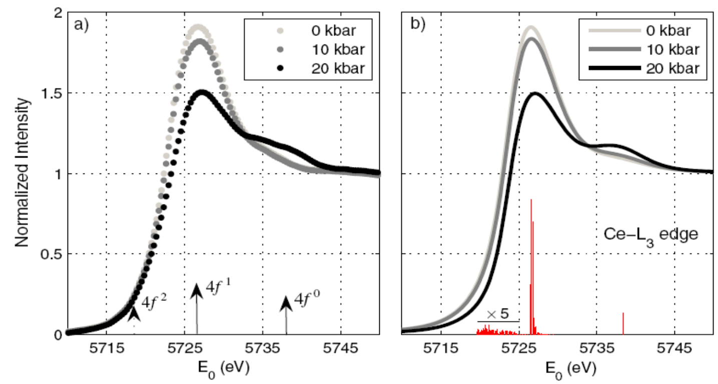


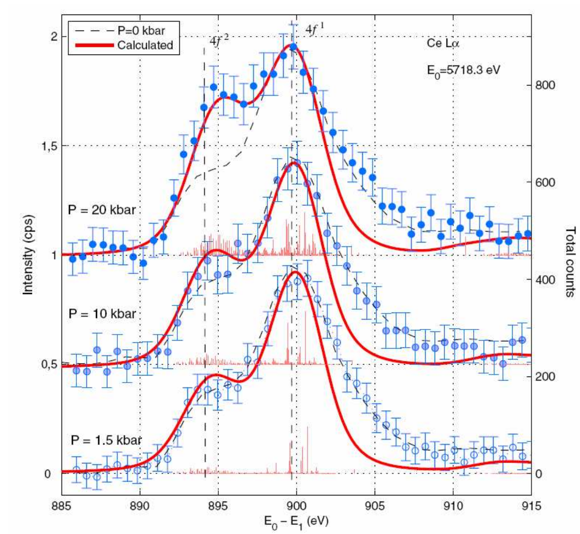
RIXS

I. Jarrige et al., Phys. Rev. Lett. ***101****, 127401 (2008)*

α-γ transition in Ce



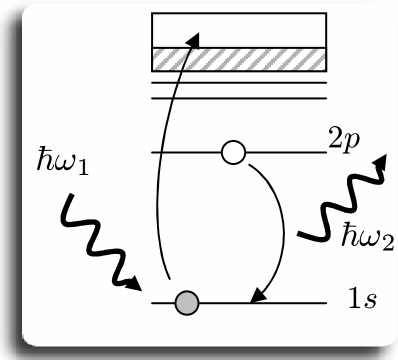




RIXS

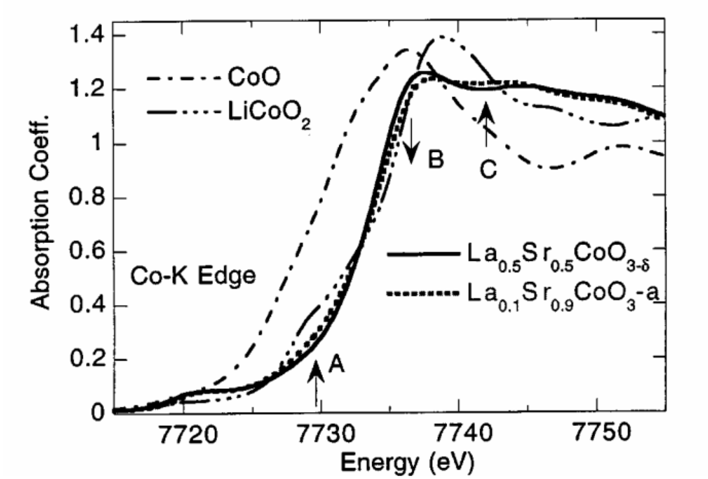
JPR, Phys. Rev. Lett. (2006)

Nature of the Pre K-edge in TM oxides

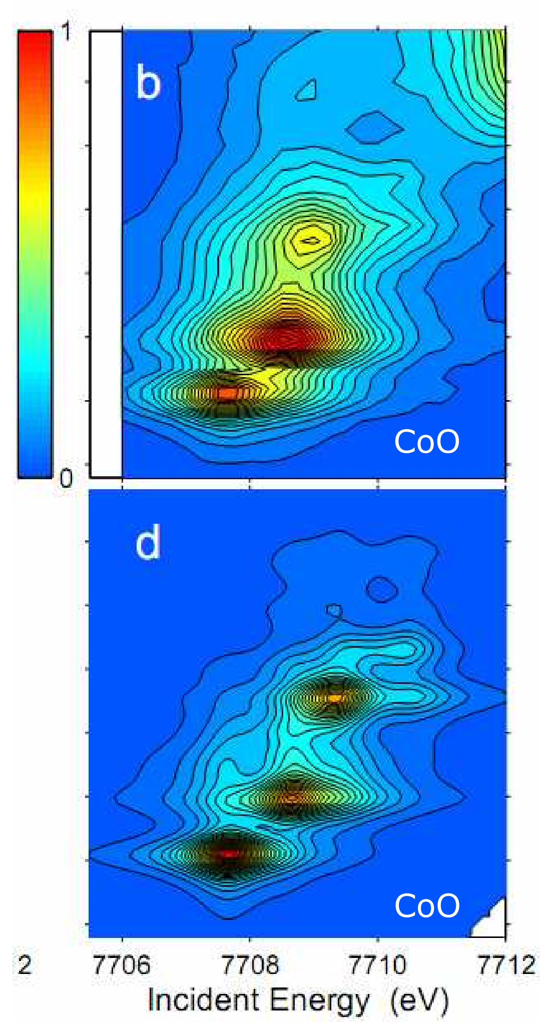


RXES

XAS – Co K-edge



E$_2$: $1s \rightarrow 3d$ E$_1$: $1s \rightarrow 4p$



(experiment)

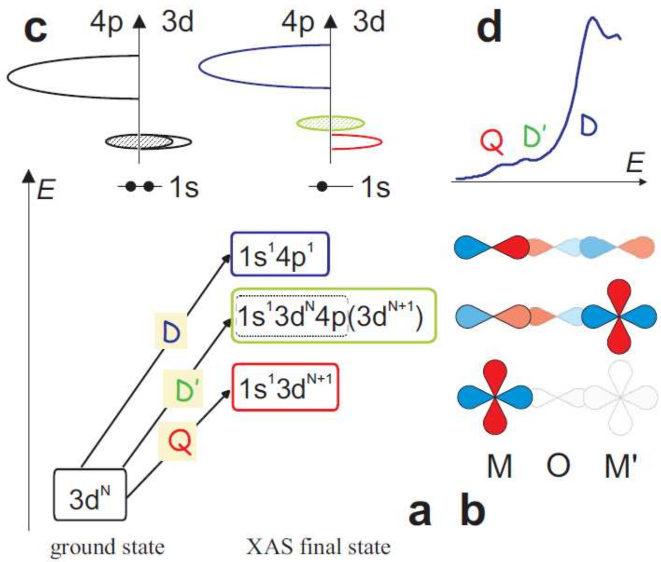
(multiplet calculations)

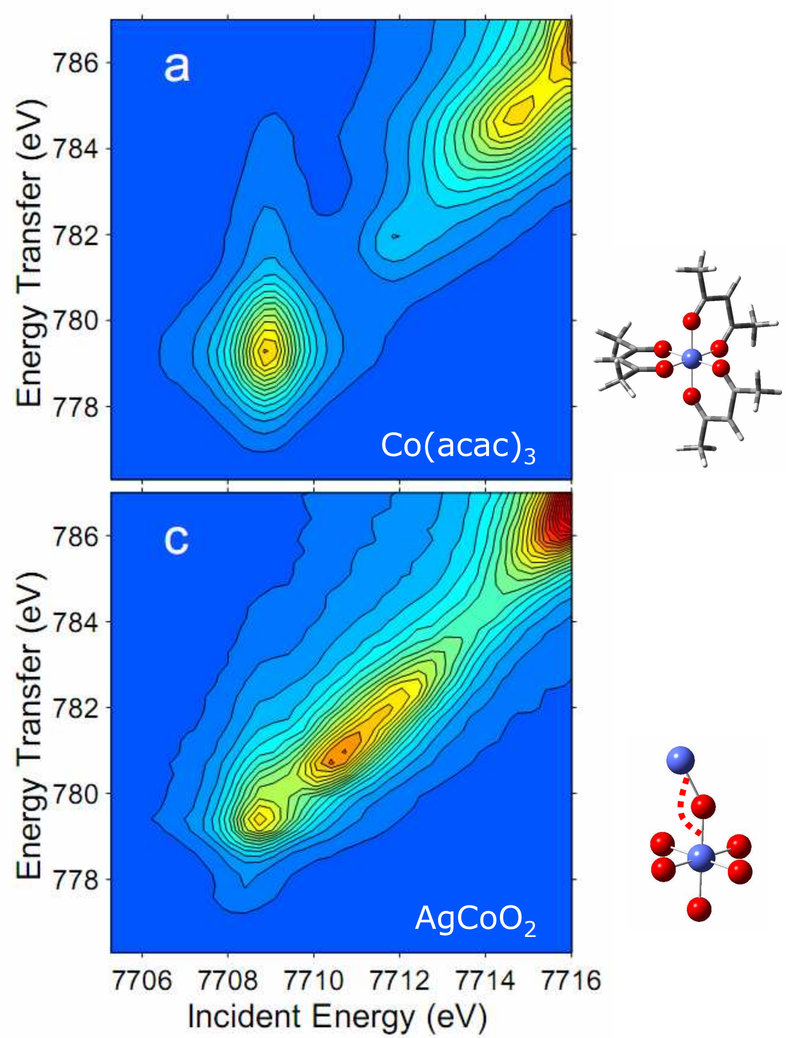
RIXS

G. Vanko et al., cond-mat (2008)

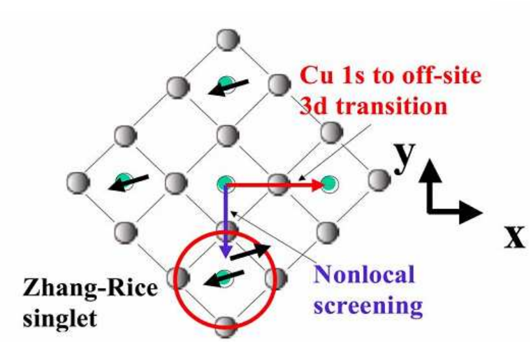
On site vs. off site screening processes

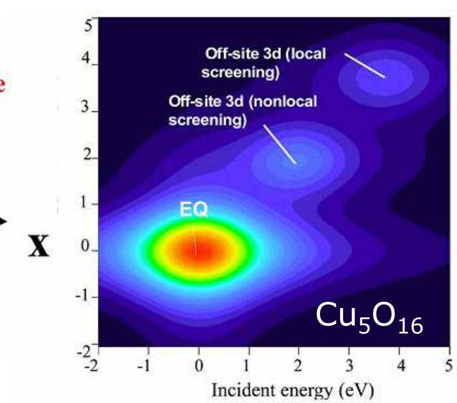
1s2p - RXES





Other screening process





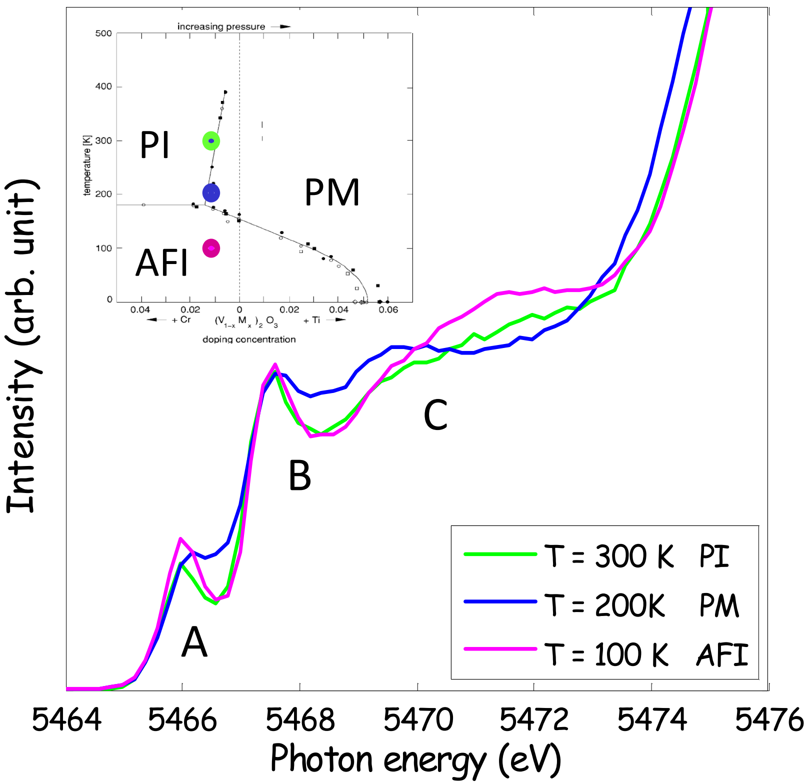
RIXS

G. Vanko et al., cond-mat (2008); A. Kotani, Phys. Rev. B (2008)

Mott transition in V_2O_3

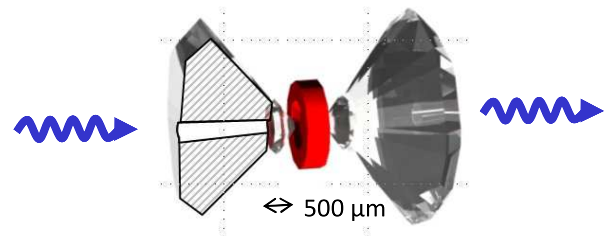
PFY-XAS

temperature

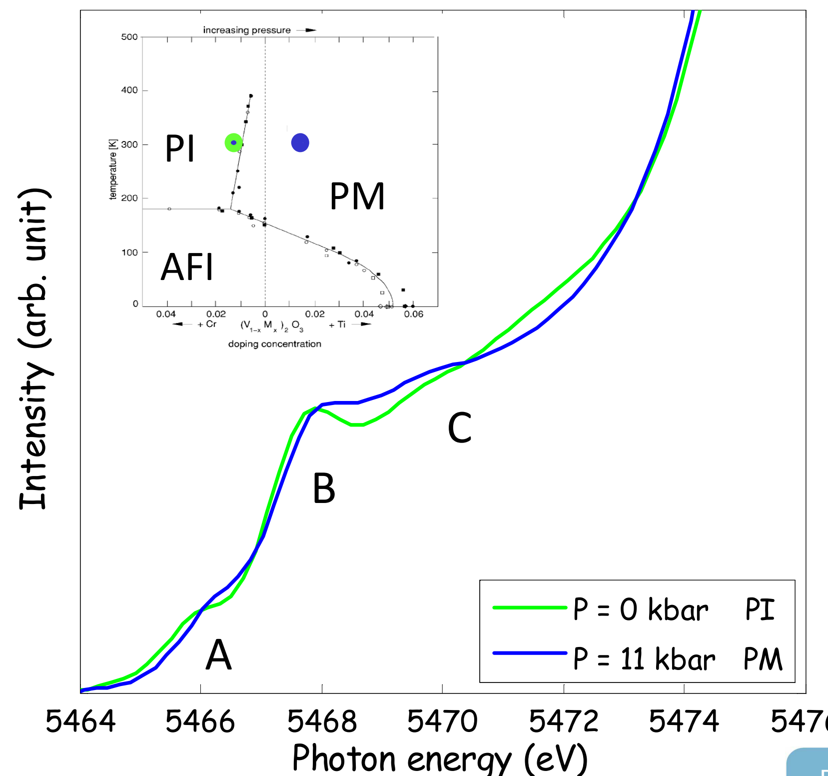


Perforated diamonds

pressure

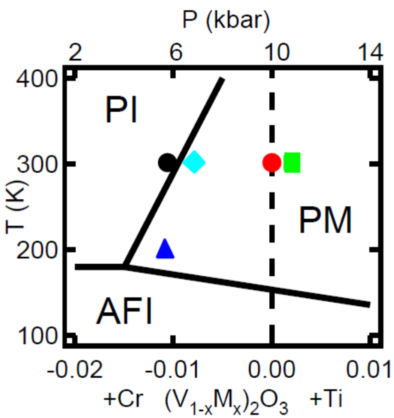


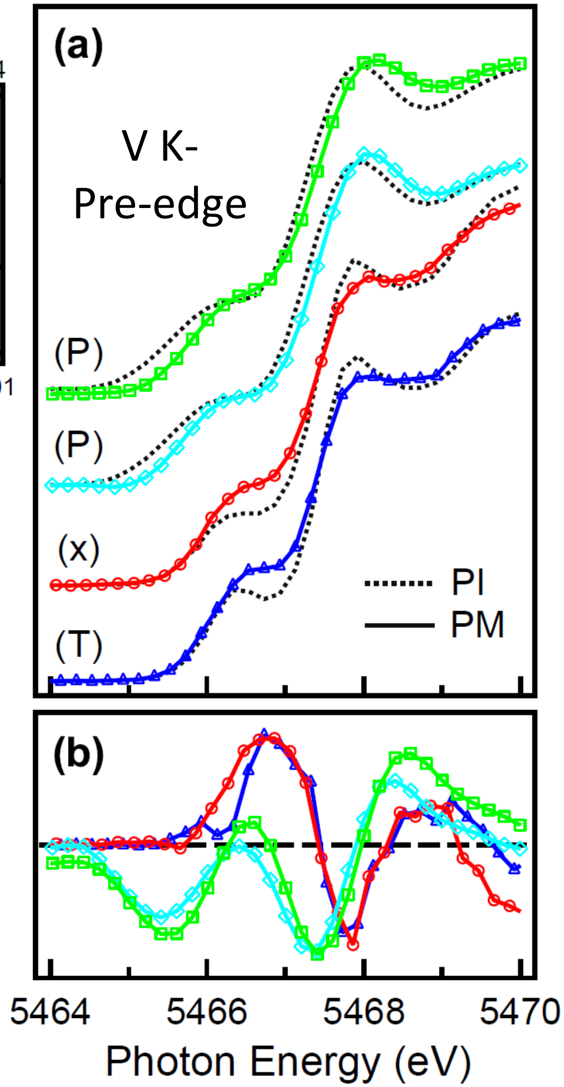
XAS - transmission



RIXS

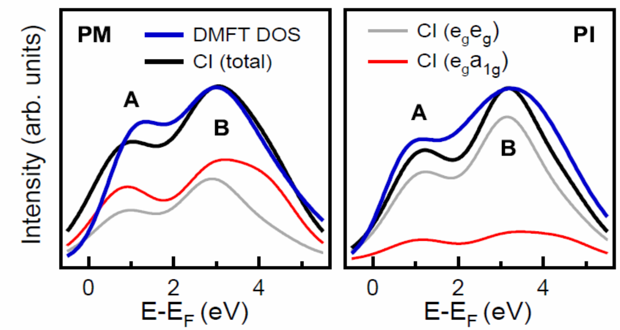
Mott transition in V_2O_3

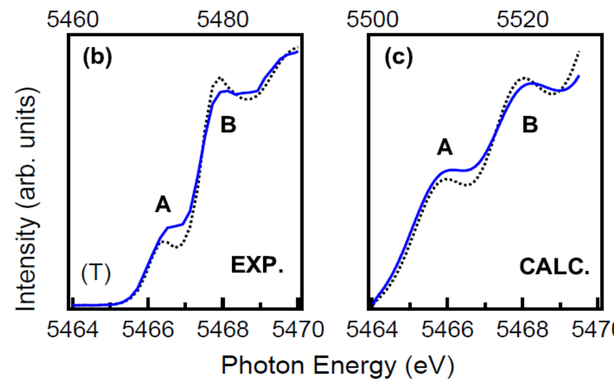




differences

DMFT Incoherent part



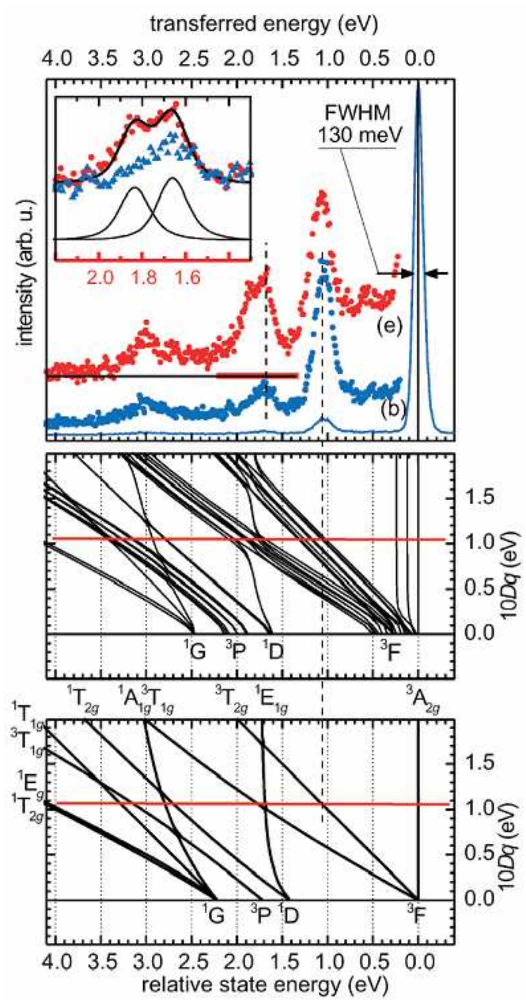


Two metallic phases : P different from T

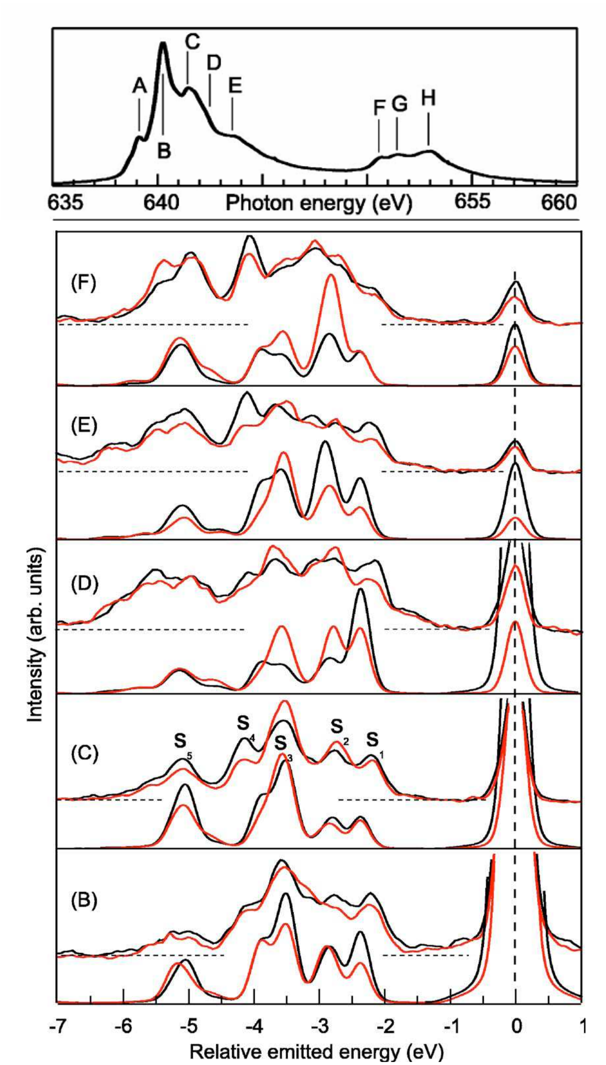
F. Rodolakis et al., submitted

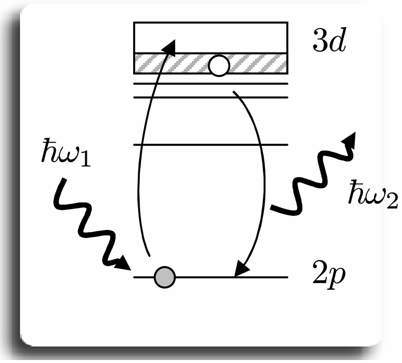
dd excitations in transition metals

NiO



MnO

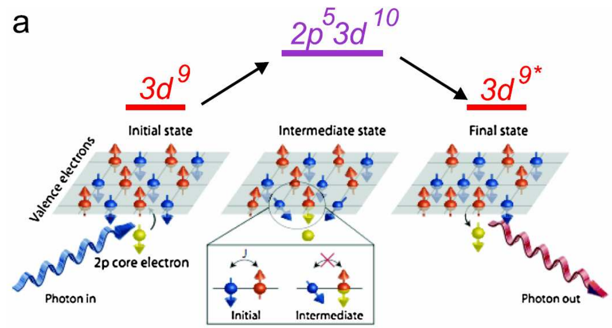


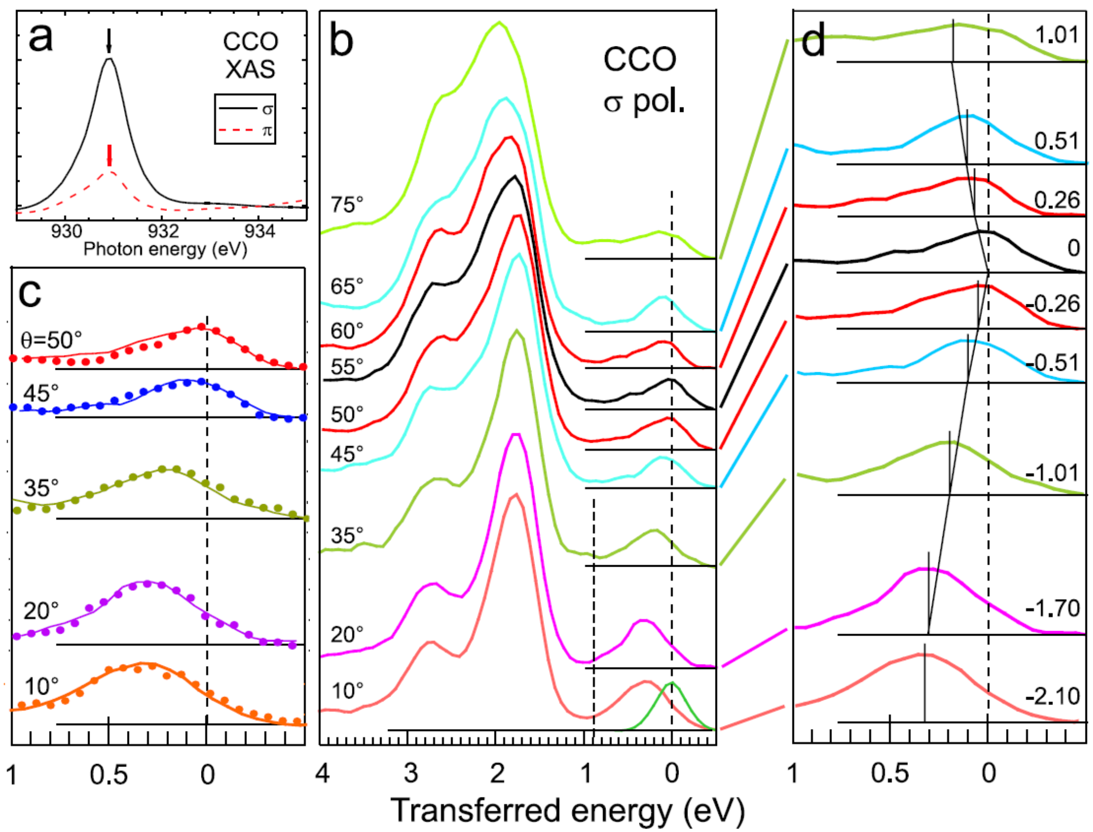


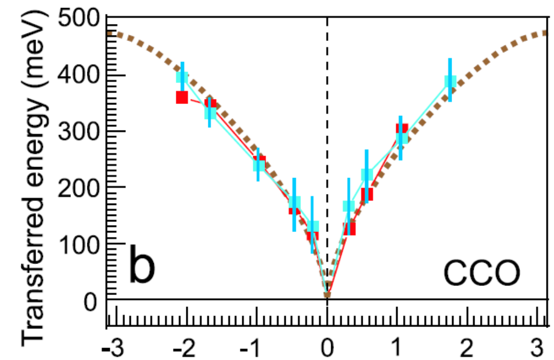
RIXS

S. Chiuzbaian et al., PRL (2005); Ghiringhelli et al., PRB (2006)

Magnetic excitations viewed by x-rays



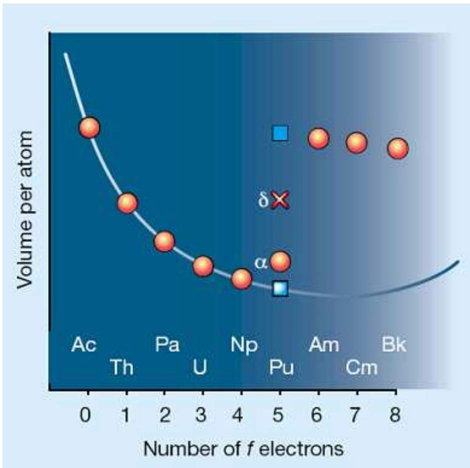


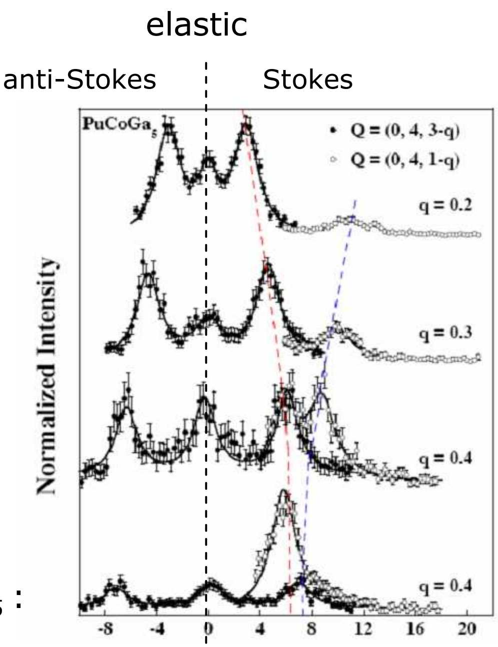


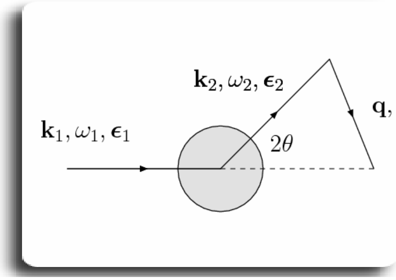
RIXS

*L. Braicovich, Phys. Rev. Lett. **102**, 167401 (2009)*

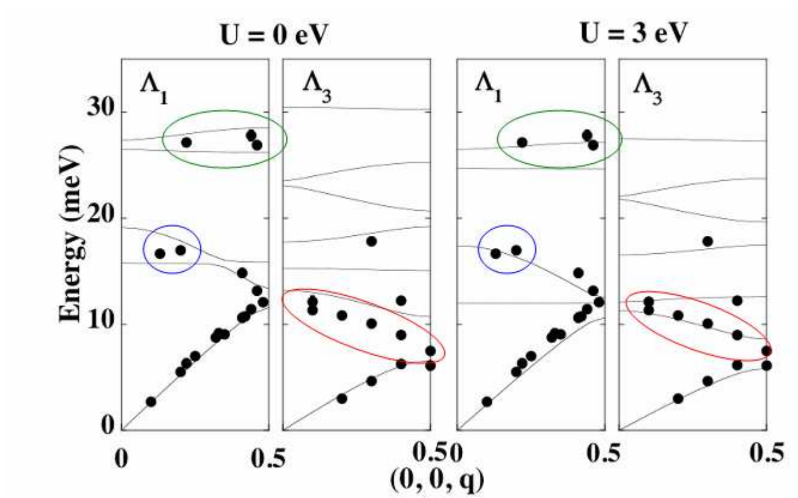
phonons in actinides







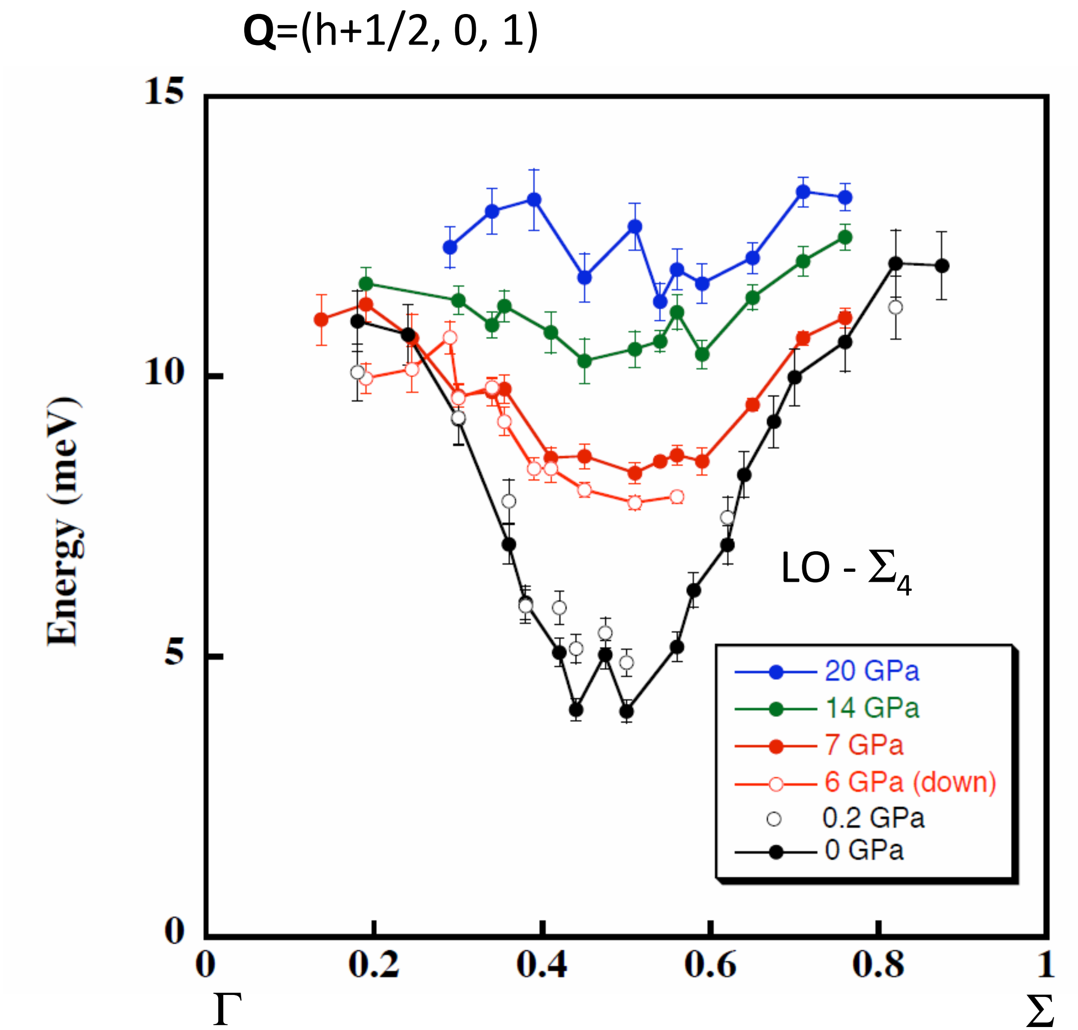
> encapsulated single crystals : $^{242}PuCoGa_5$:



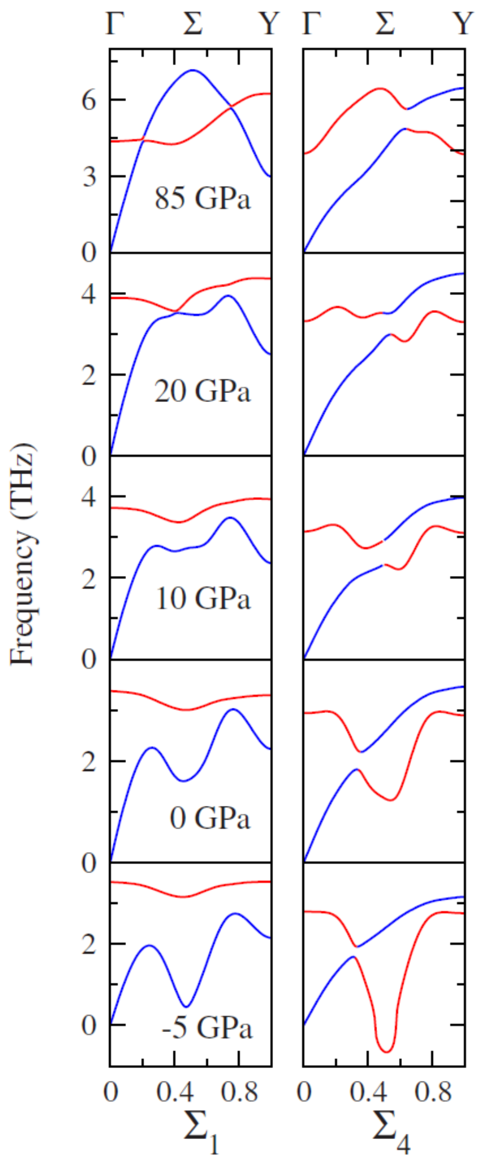
(nr)IXS

S. Raymond, Phys. Rev. Lett. (2006)

CDW in α-U under pressure



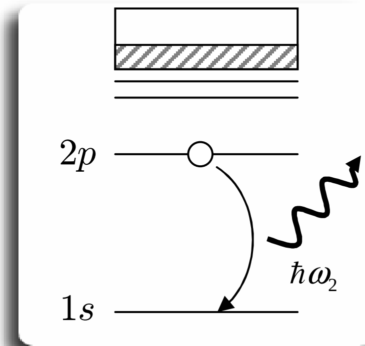
S. Raymond et al. (2009)



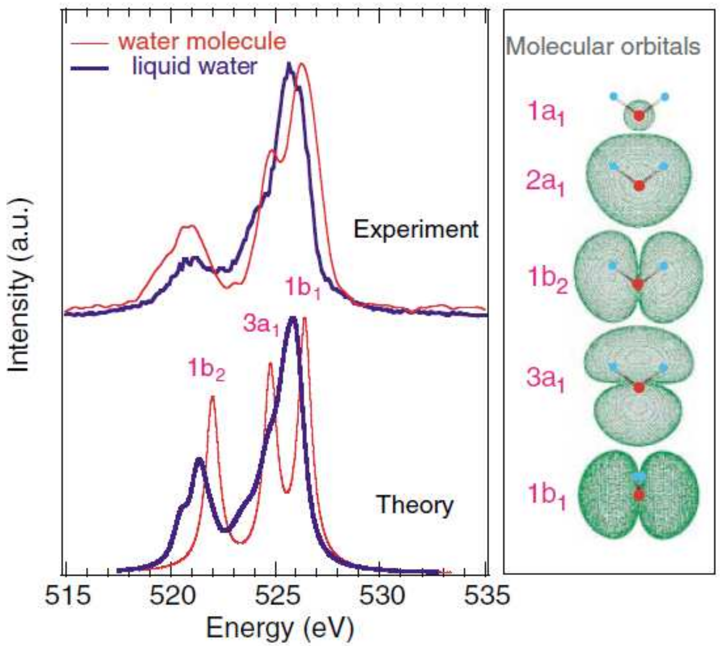
*J. Bouchet, Phys. Rev. B, **77**, 024113 (2008)*

O-binding and molecular conformation

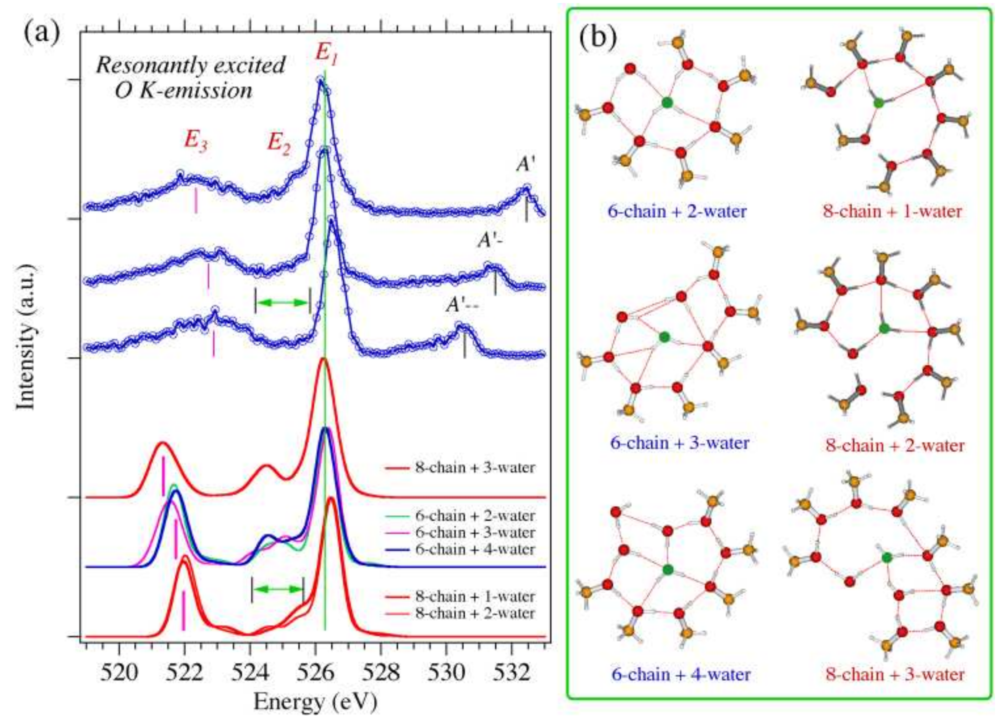
Kα XES



water



water + alcohol

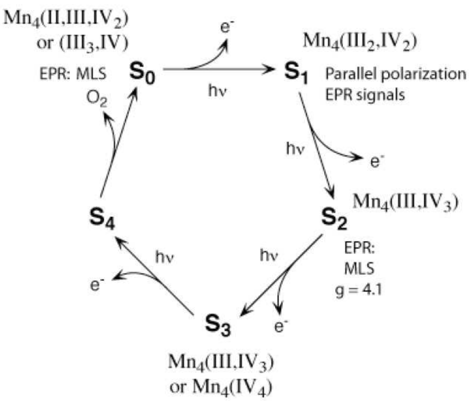


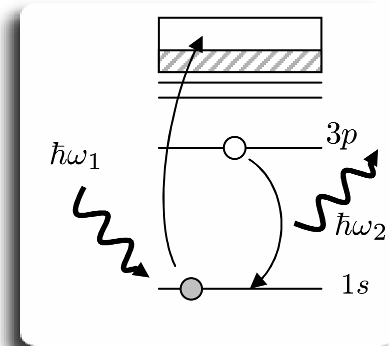
RIXS

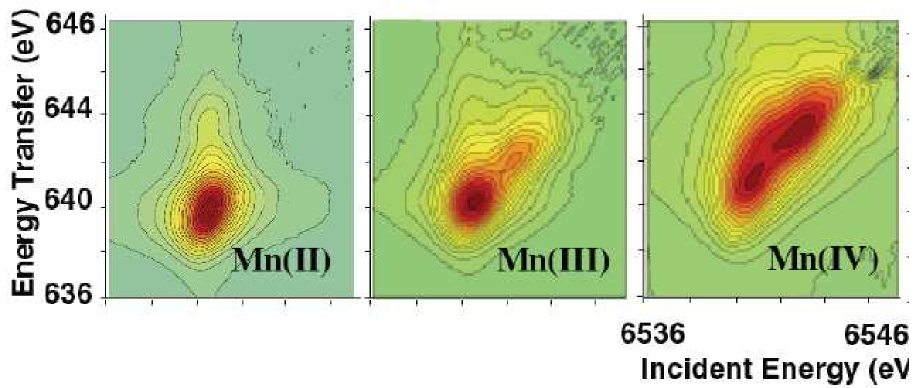
J. H. Guo et al. Phys. Rev. Lett. (2002)

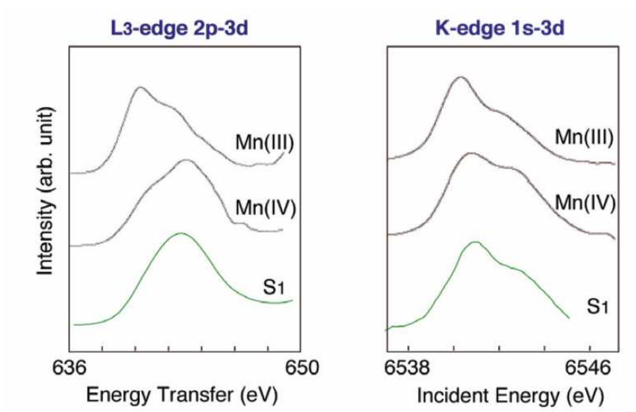
nature of photosystem II complexes

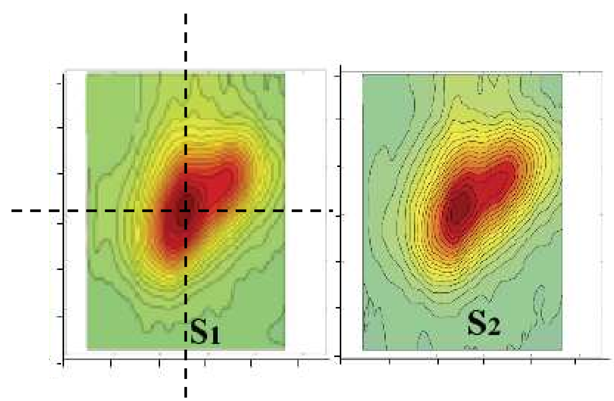
1s3p - RXES









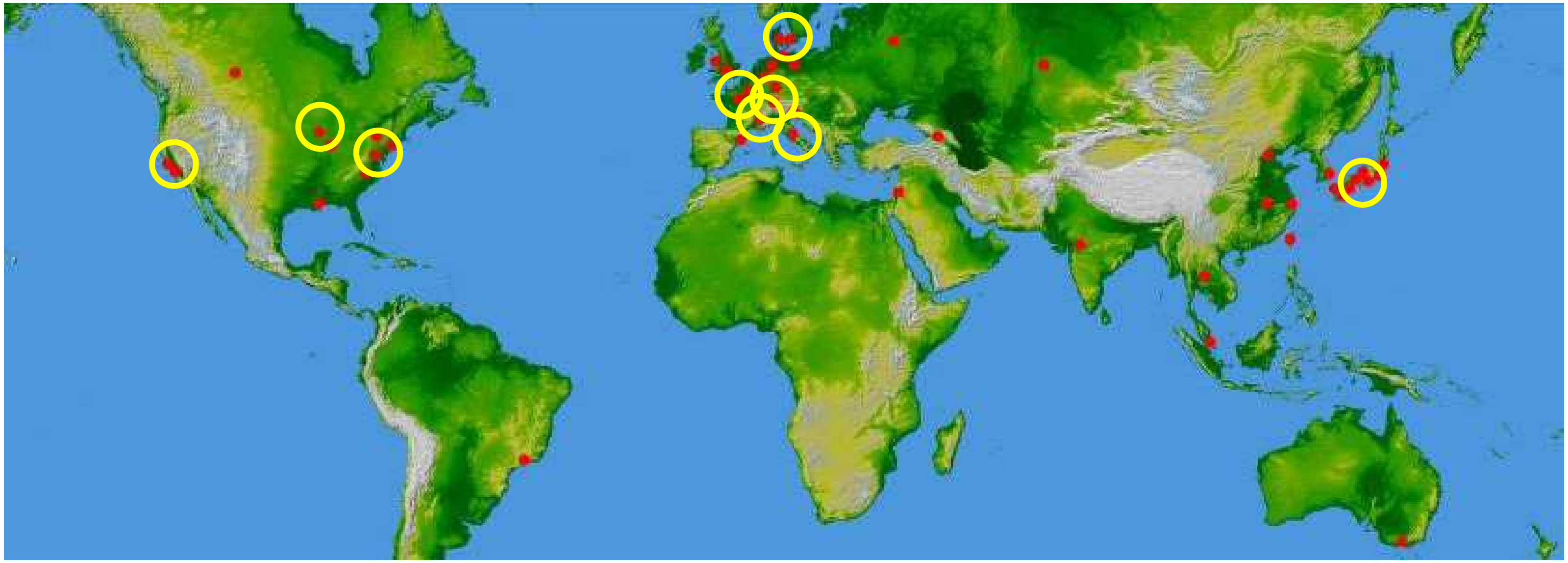


RIXS

J. Yano, Proceedings XAFS13 (2007); P. Glatzel et al., JACS (2004)

PERSPECTIVES

IXS stations world wide



(soft x-ray / hard x-ray)

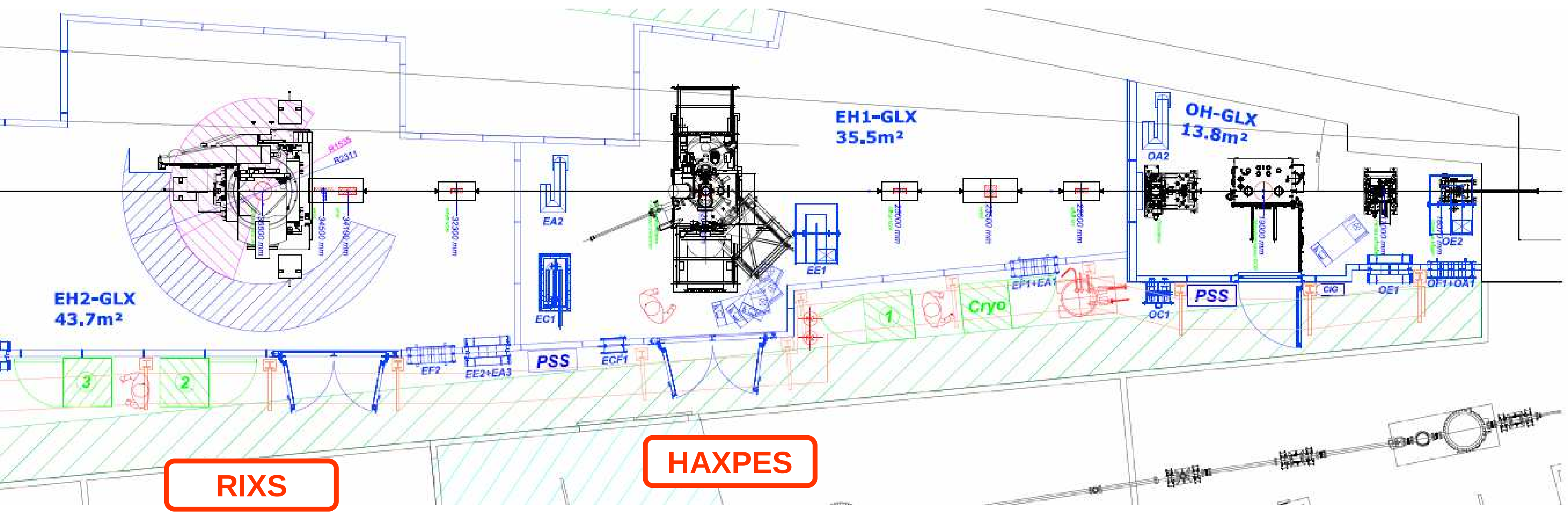
Ring	Nbr	Beamline	Energy range	Country
ESRF	4	ID8 / ID-16, 26, 28	0.4-1.6 keV / 5-23 keV	France
Spring-8	1	BL12XU	5-30 keV	Japan
APS, SSRL, ALS	4	IXS-CAT, BL 6.2; BL 7.0	5-25 keV / 0.06-1.2 keV	USA
NSLS-2		IXS beamline*	> 5 keV	
MAX II	1	I5-11	0.05-1.5 keV	Sweden
Elettra	1	IUVS	5 - 11 eV	Italy
SLS	1	ADDRESS	0.4-1.8 keV	Swiss
SOLEIL	**2**	**MicroFocus* / GALAXIES***	**0.05-1.5 keV / 2-12 keV**	**France**

(*) not yet operational 2010 / 2011

Inelastic x-ray scattering and Electron spectroscopy

- U20 undulator, energy Range : 2.2-12 keV
- Two experimental stations
    - RIXS
    - HAXPES

- High resolution ΔE = 100 meV – 1 eV
- Micro Focalization:
    - > High-Flux: 80×35 µm²
    - > Micro-Focus: 5×5 µm²



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