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Advanced School on Synchrotron and Free Electron Laser Sources and their Multidisciplinary Applications

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Resonant Inelastic X-ray Scattering

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Italy

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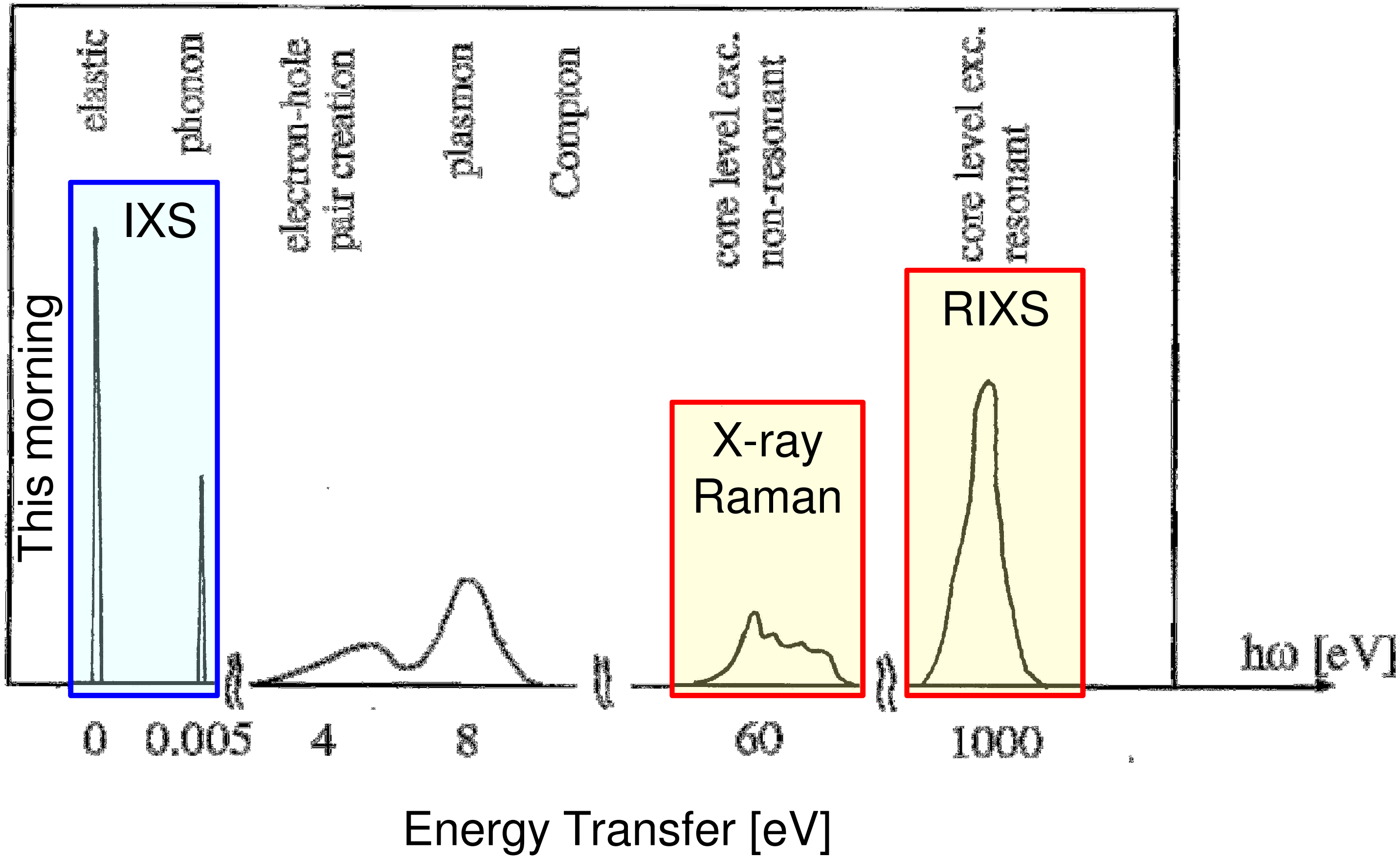
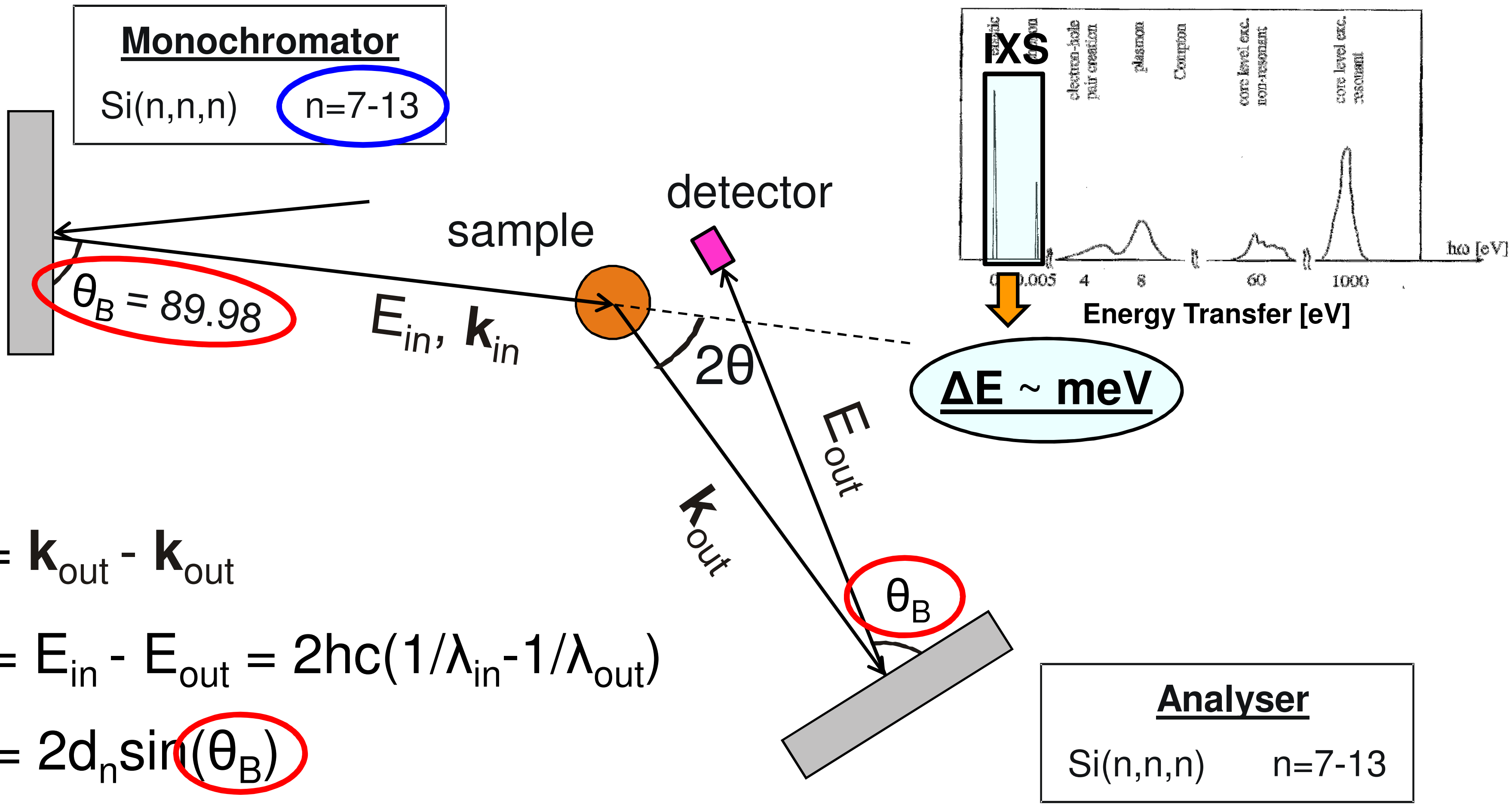
OUTLINE

Introduction: inelastic X-ray spectrum



Basic IXS instrumentation

IXS (this morning)



$\mathbf{k} = \mathbf{k}_{out} - \mathbf{k}_{out}$

$E = E_{in} - E_{out} = 2hc(1/\lambda_{in} - 1/\lambda_{out})$

$\lambda = 2d_n \sin(\theta_B)$

backscattering + **high order reflections** = **ΔE ~ meV**

Basic IXS instrumentation

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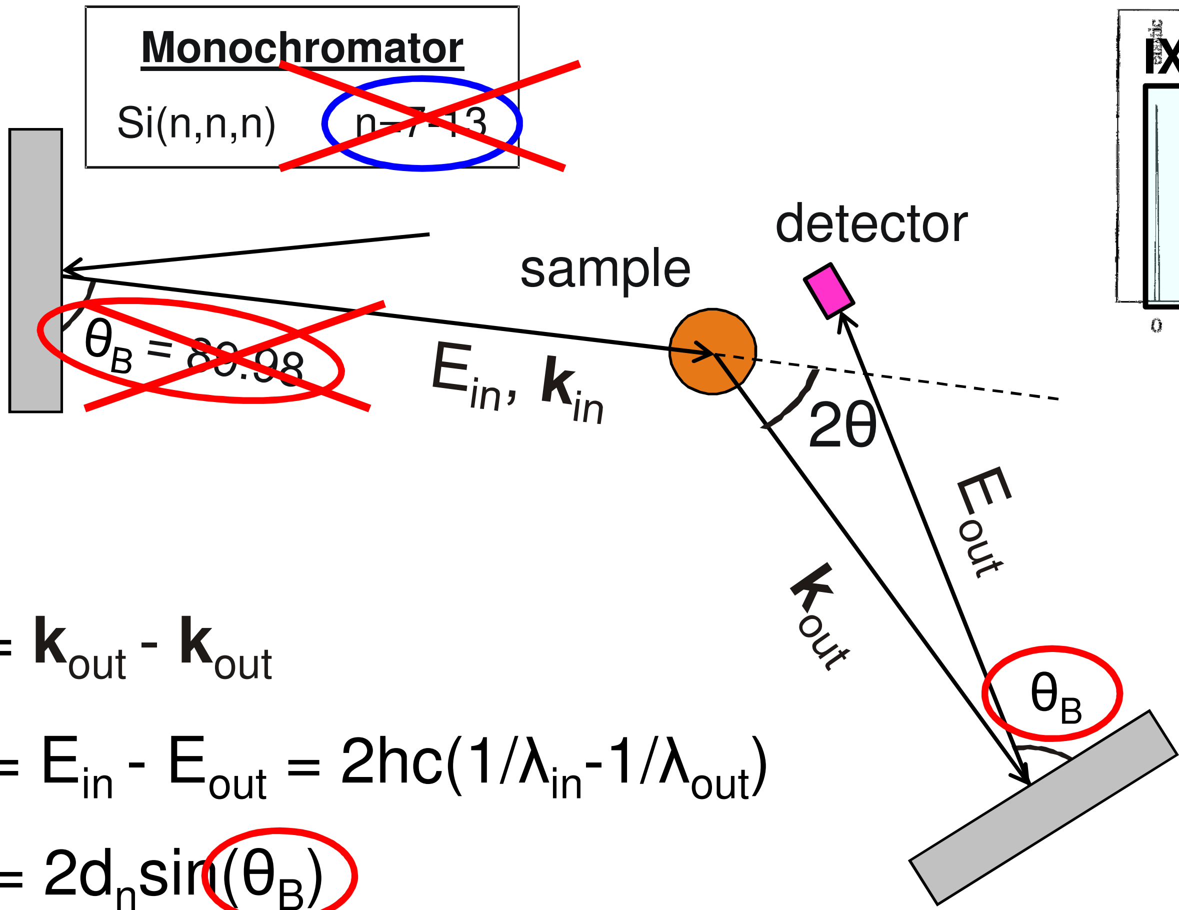

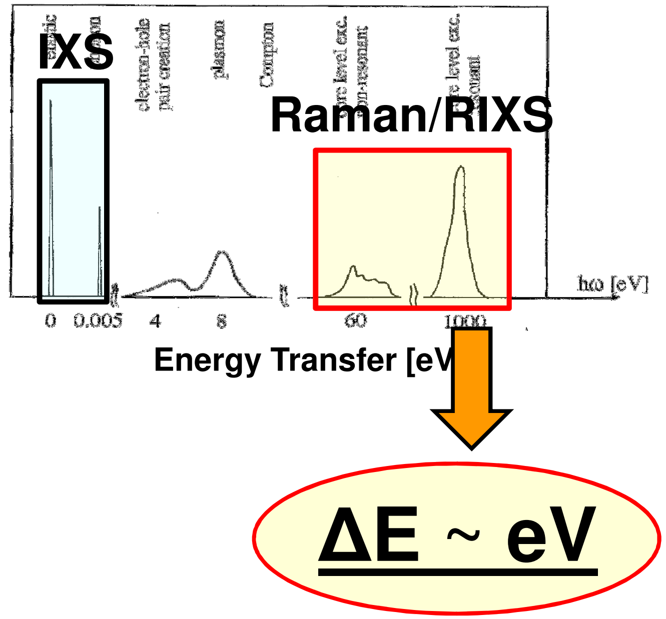

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~~backscattering~~ + ~~high order reflections~~ = ~~ΔE ~ meV~~

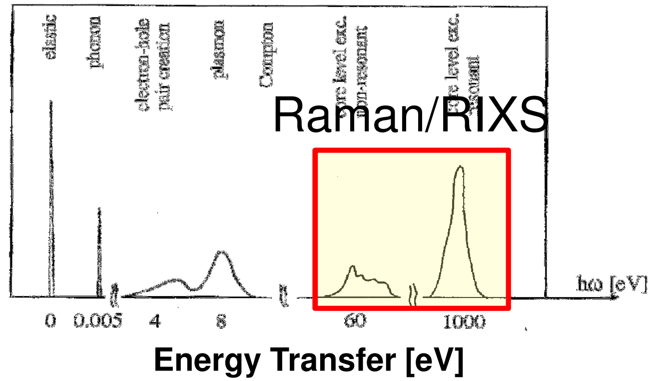
Basic IXS instrumentation

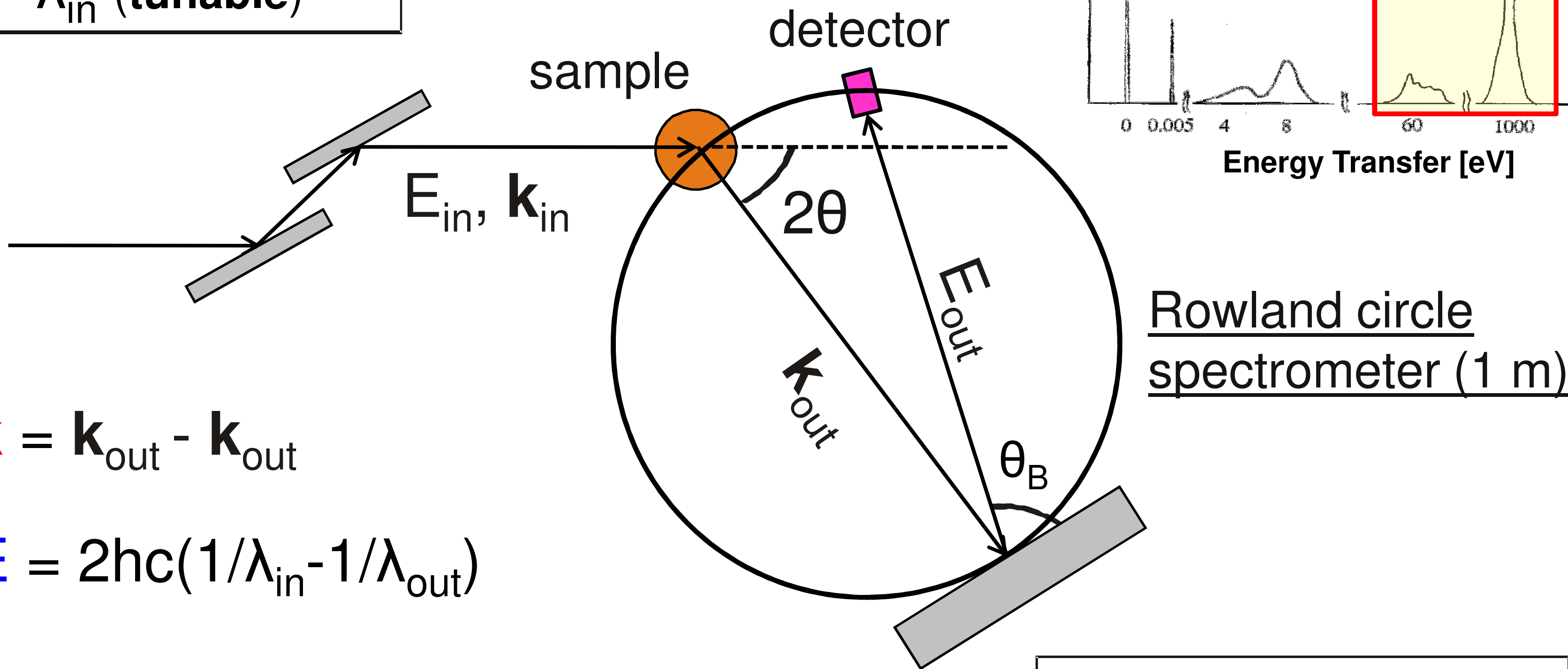
Raman / RIXS

Monochromator

Si(1,1,1); (2,2,0); …

λ_{in} (**tunable**)





$\mathbf{k} = \mathbf{k}_{out} - \mathbf{k}_{out}$

$E = 2hc(1/\lambda_{in} - 1/\lambda_{out})$

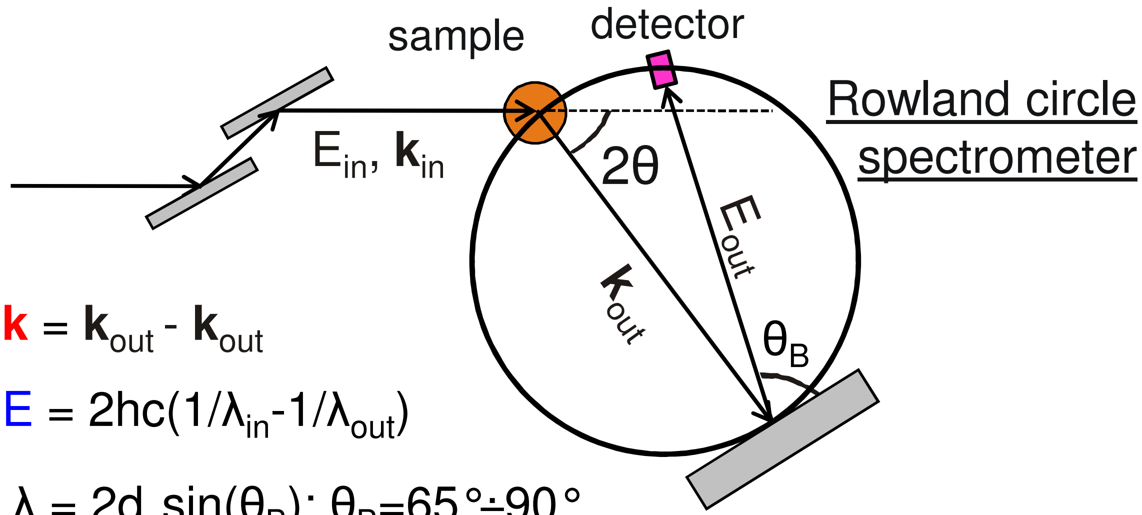
$\lambda = 2d_n \sin(\theta_B)$; $\theta_B = 65° \div 90°$

Analyser

Si(h,k,l) λ_{out} (**tunable**)

Basic IXS instrumentation

Raman / RIXS



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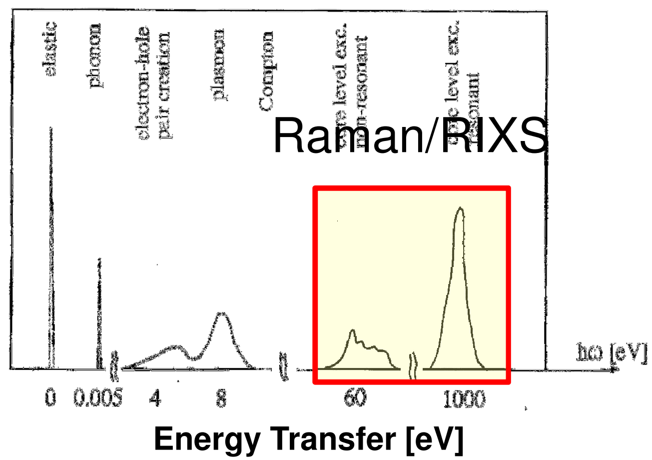


Scanning strategy

1. E_{out} fixed, scanning E_{in} — non-resonant IXS, RIXS
2. E_{in} fixed, scanning E_{out} (rotating crystal and follow with the detector) — RIXS
3. Scanning E_{in} and E_{out} keeping E constant — RIXS

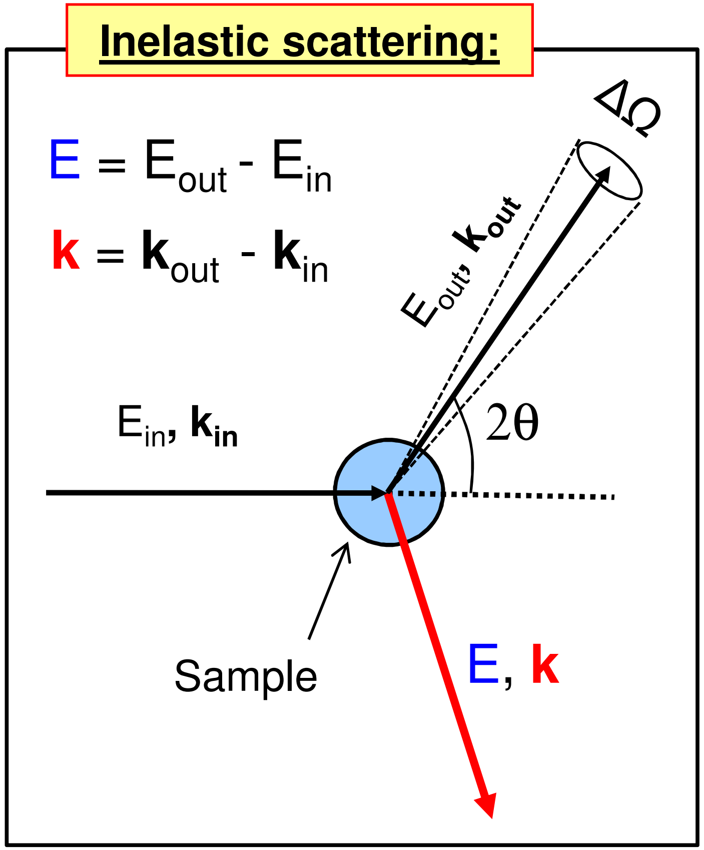
Basic theoretical aspects

$$H_{int}=(e/m_e c)\sum_j[(e/2c)\mathbf{A}_j\cdot\mathbf{A}_j+\mathbf{A}_j\cdot\mathbf{p}_j]$$

A: vector potential of electromagnetic field

P: momentum operator of the electrons

j: summation over all electrons of the system



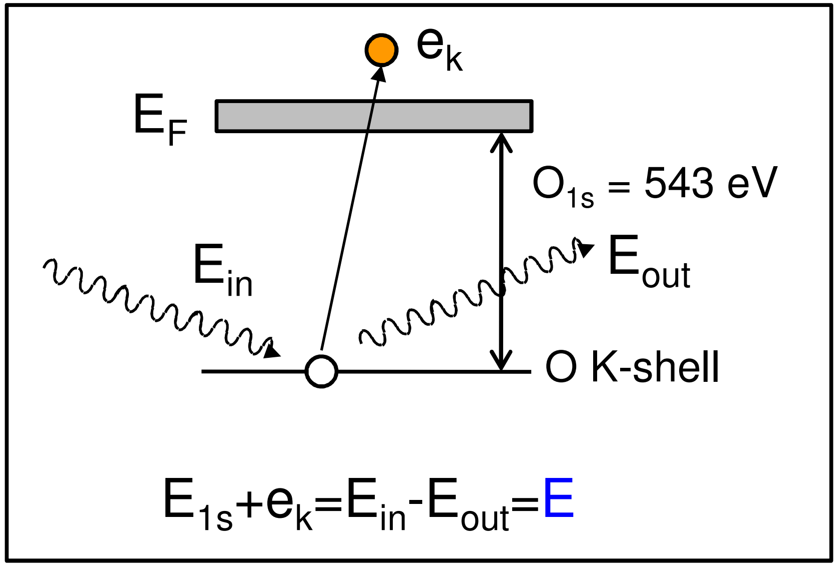
A·A → non-resonant scattering (example this morning: IXS)

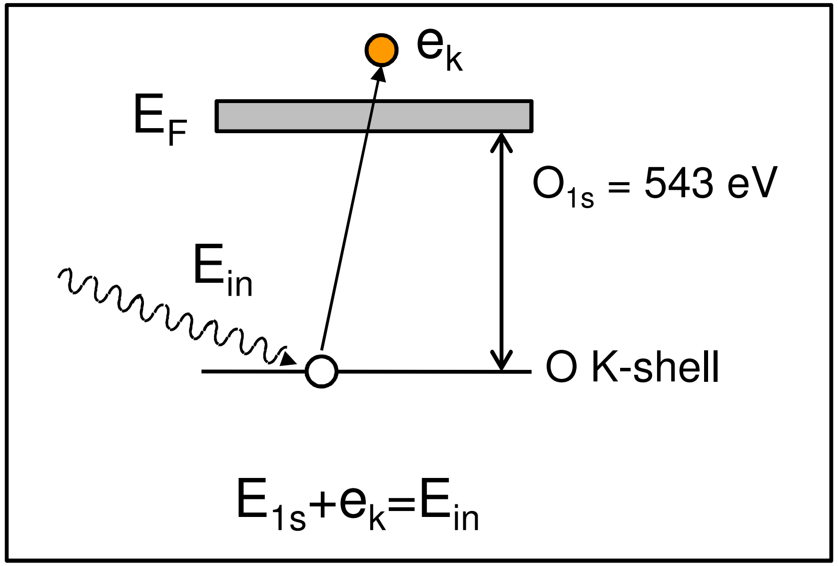
A·p → resonant scattering, absorption followed by emission

Basic theoretical aspects

Non resonant IXS cross section:

$$\frac{\partial^2\sigma}{\partial\Omega\partial E} = r_0^2(\boldsymbol{\varepsilon}_{in}\cdot\boldsymbol{\varepsilon}_{out})^2(k_{in}/k_{out})\sum_I P_I|\langle I|\exp\{i\mathbf{k}\cdot\mathbf{r}_j\}|F\rangle|^2\delta(E-E_F+E_I)$$





X-ray absorption cross section (dipolar approximation):

$$\frac{\partial\sigma}{\partial E_{in}} = 4\pi^2\alpha E_{in}\sum_I P_I|\langle I|\boldsymbol{\varepsilon}_{in}\cdot\mathbf{r}_j|F\rangle|^2\delta(E_{in}-E_F+E_I)$$

Basic theoretical aspects

Non resonant IXS cross section:

$$\frac{\partial^2\sigma}{\partial\Omega\partial E} = r_0^2(\boldsymbol{\varepsilon}_{in}\cdot\boldsymbol{\varepsilon}_{out})^2(k_{in}/k_{out})\sum_I P_I|\langle I|\exp\{i\mathbf{k}\cdot\mathbf{r}_j\}|F\rangle|^2\delta(E-E_F+E_I)$$

$$\mathbf{k}\cdot\mathbf{r}_j \ll 1 \rightarrow e^{i\mathbf{k}\cdot\mathbf{r}} \sim 1 + i\mathbf{k}\cdot\mathbf{r}_j$$

$\mathbf{k}\cdot\mathbf{r}_j \ll 1$ → Dipolar regime: identical to photon absorption, where:

i) The momentum transfer ($\mathbf{k}$) plays the role of the photon polarization vector ($\boldsymbol{\varepsilon}_{in}$)

ii) The energy transfer (E) plays the role of the incident energy (E_{in})

X-ray absorption cross section (dipolar approximation):

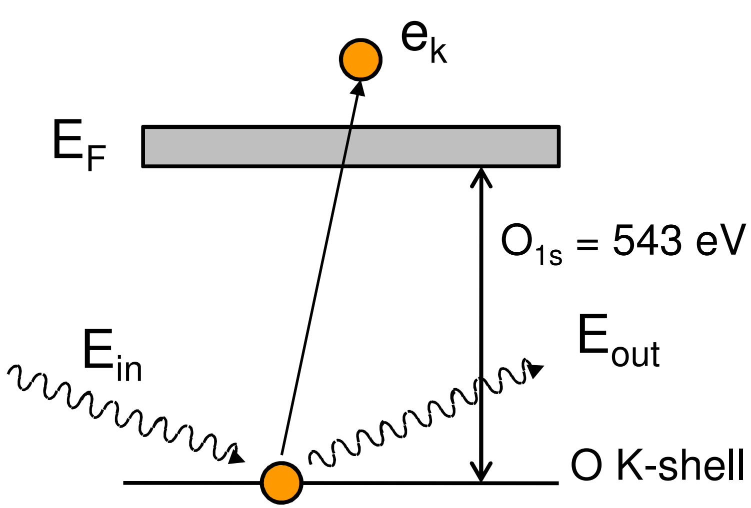
$$\frac{\partial\sigma}{\partial E_{in}} = 4\pi^2\alpha E_{in}\sum_I P_I|\langle I|\boldsymbol{\varepsilon}_{in}\cdot\mathbf{r}_j|F\rangle|^2\delta(E_{in}-E_F+E_I)$$

Basic theoretical aspects

Non resonant IXS cross section:

$$\frac{\partial^2\sigma}{\partial\Omega\partial E} = r_0^2(\boldsymbol{\varepsilon}_{in}\cdot\boldsymbol{\varepsilon}_{out})^2(k_{in}/k_{out})\sum_F P_F|\langle I|\exp\{i\mathbf{k}\cdot\mathbf{r}_j\}|F\rangle|^2\delta(E-E_F+E_I)$$

X-ray Raman Scattering (XRS)



$E_{1s}+e_k=E_{in}-E_{out}=E$

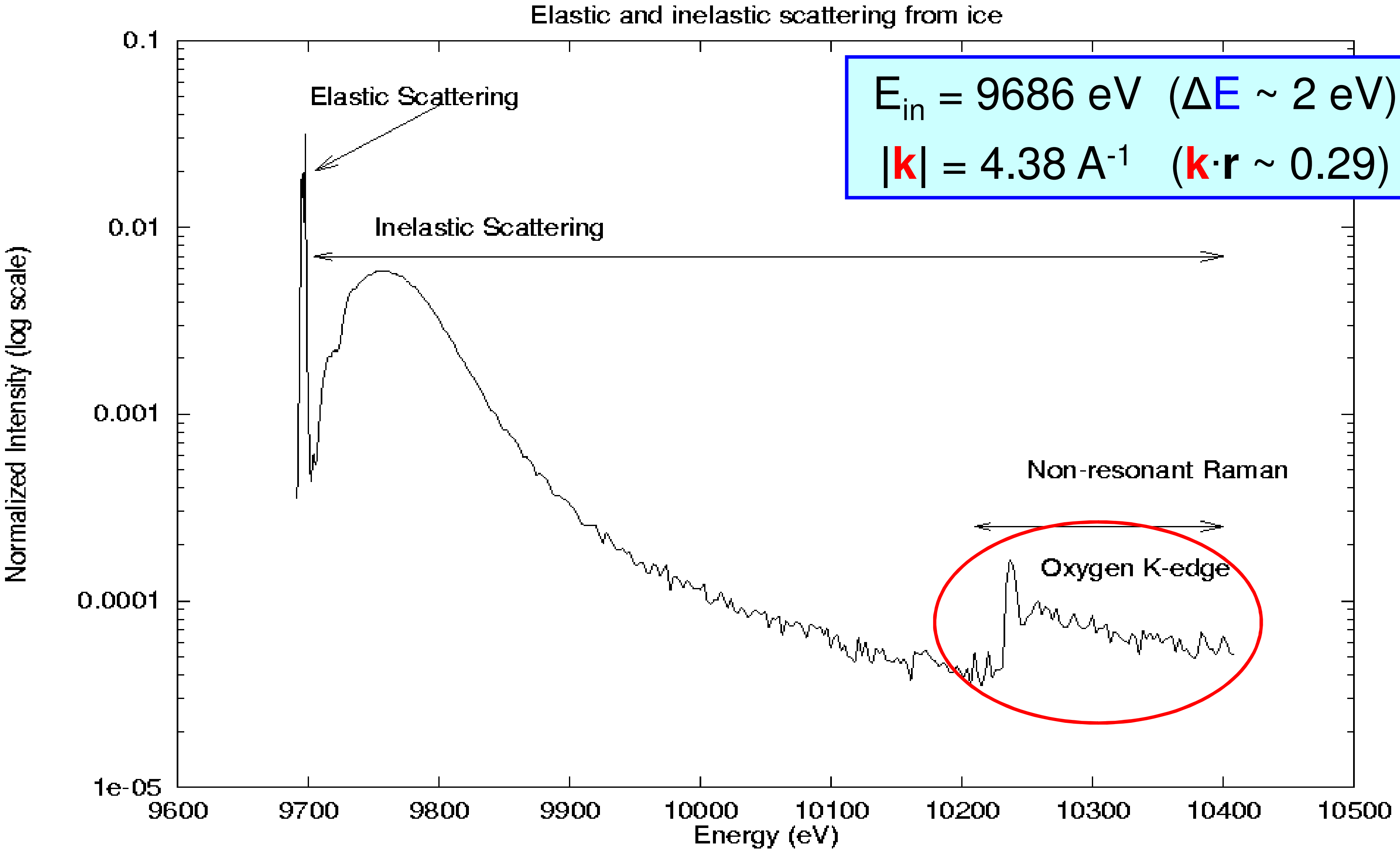
Motivation: element-selective probe for local atomic structure

XRS is alternative to:

- Neutron scattering (with isotopic substitution)
- X-ray (anomalous) scattering
- XANES and EXAFS

Experimental highlights (XRS)

XRS from O K-edge in water and ice



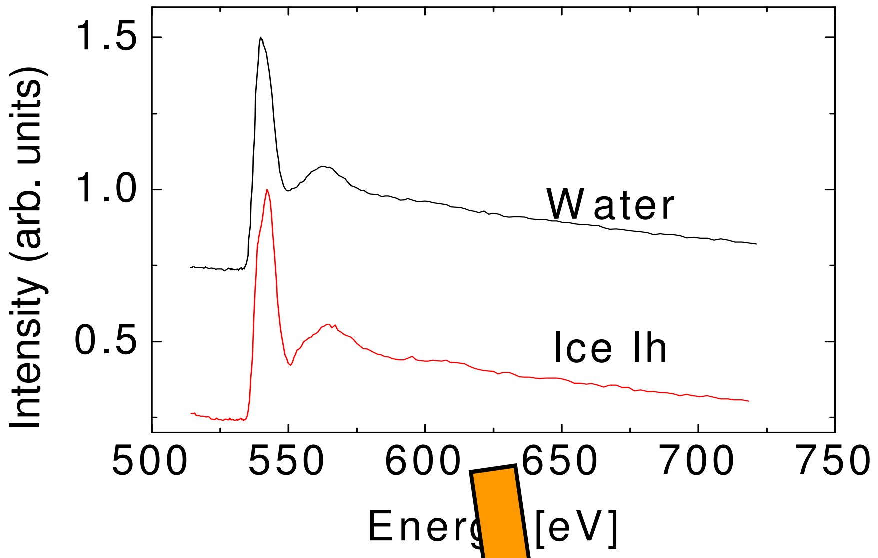
E_{in} = 9686 eV (ΔE ~ 2 eV)

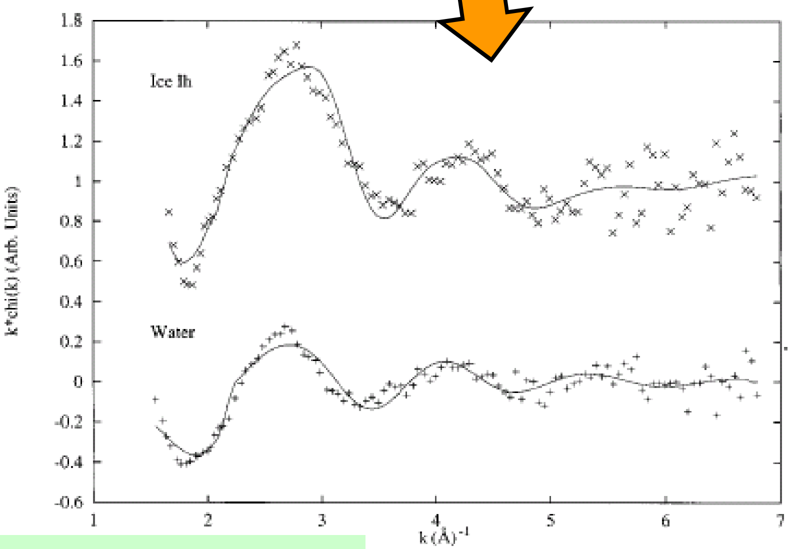
|**k**| = 4.38 A^{-1} (**k**·**r** ~ 0.29)

PRB 62, R9223 (2000)

Experimental highlights (XRS)

XRS from O K-edge in water and ice (EXAFS)

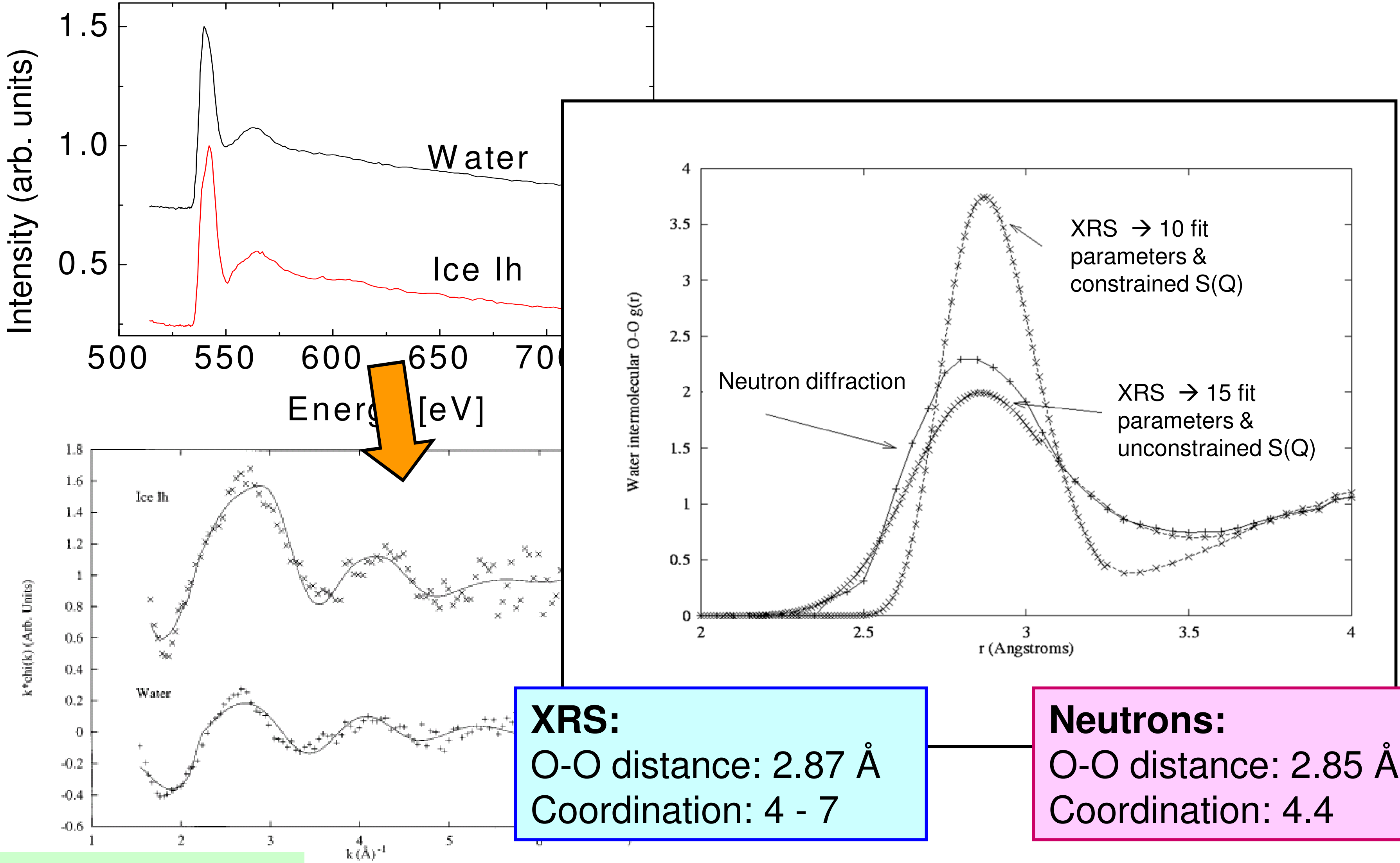




PRB 62, R9223 (2000)

Experimental highlights (XRS)

XRS from O K-edge in water and ice (EXAFS)



XRS:
O-O distance: 2.87 Å
Coordination: 4 - 7

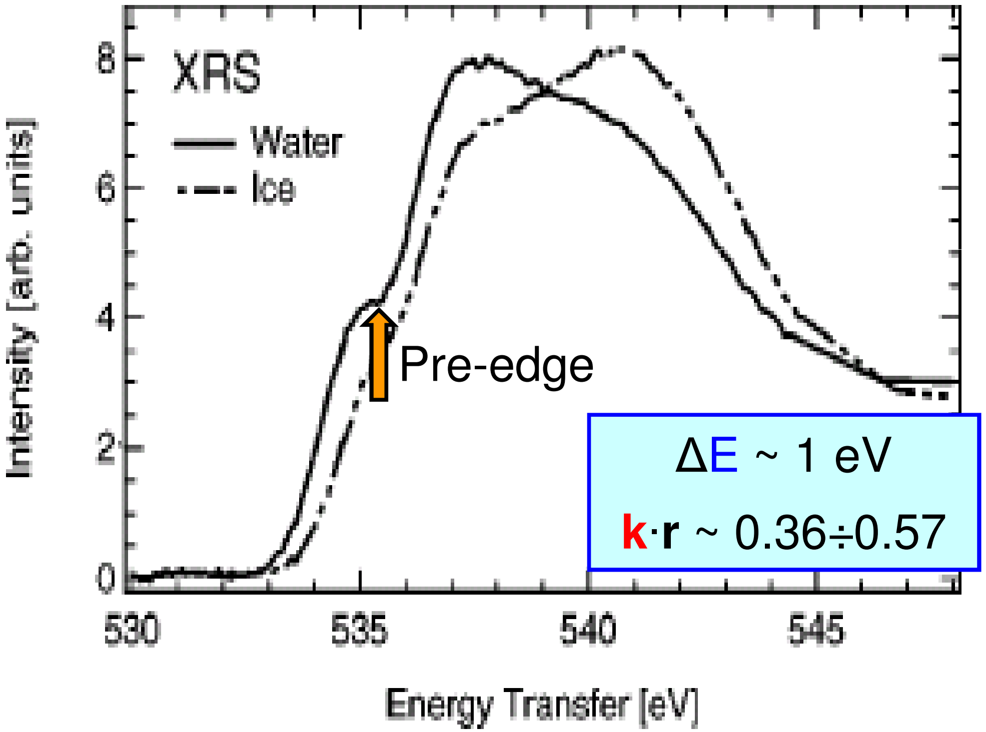
Neutrons:
O-O distance: 2.85 Å
Coordination: 4.4

PRB 62, R9223 (2000)

Experimental highlights (XRS)

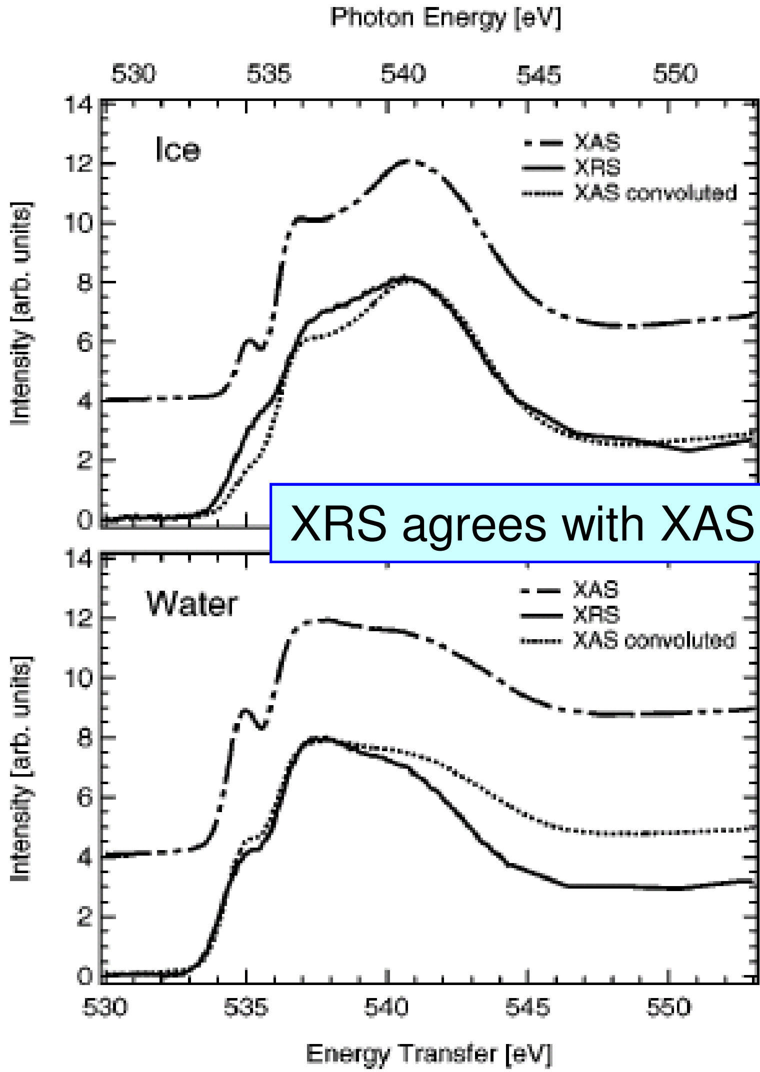
XRS from O K-edge in water and ice (XANES)

XANES sensitive to the number and “type” of hydrogen bonds (HB)



$\Delta E \sim 1$ eV

$\mathbf{k}\cdot\mathbf{r} \sim 0.36 \div 0.57$



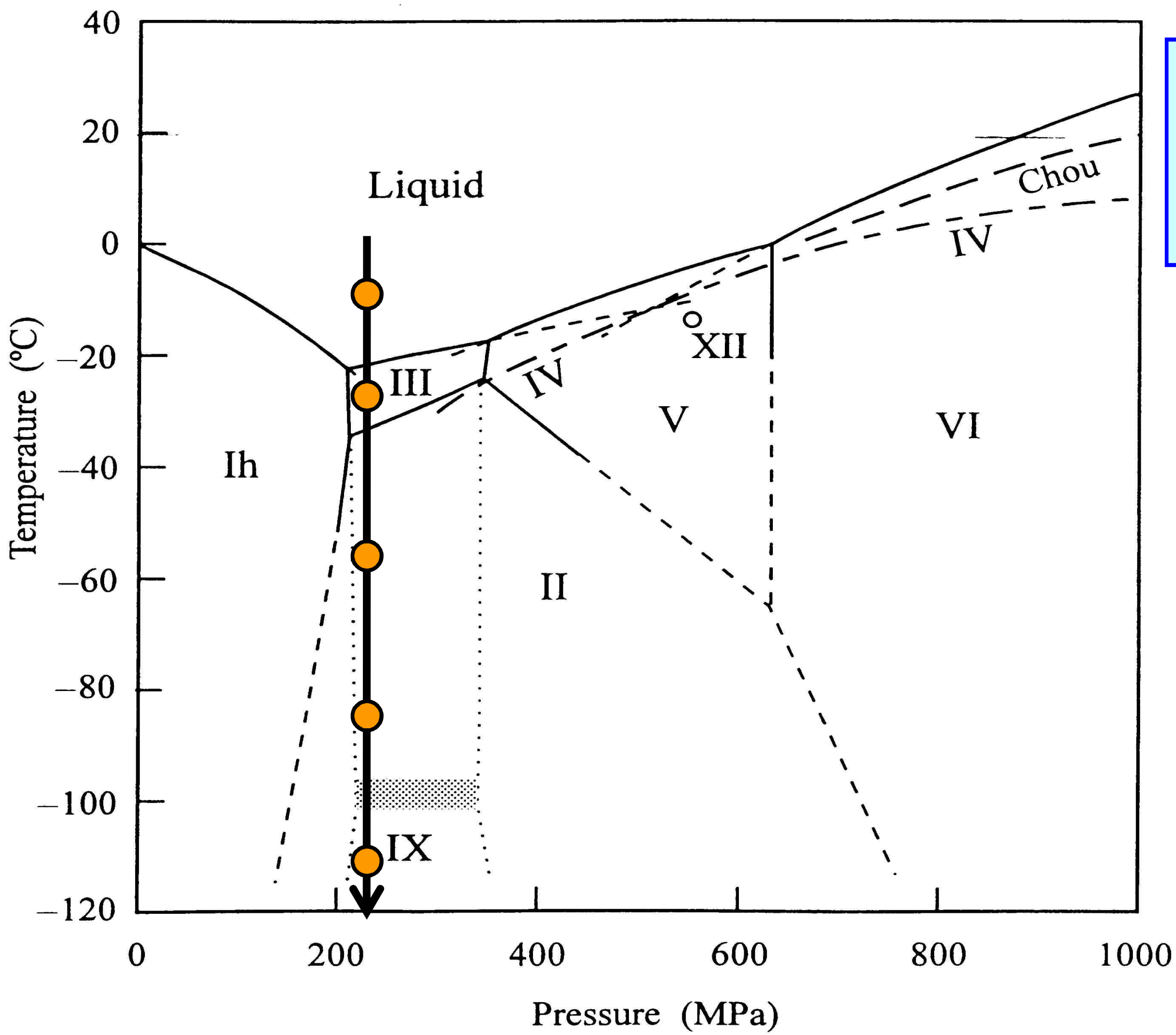
XRS agrees with XAS

- Pre-edge indicates a large number (~ 70%) of distorted or broken HB (supported by calculation)

PRB 66, 092107 (2002)

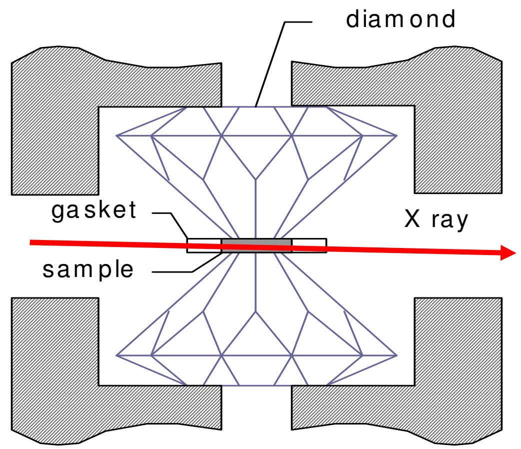
Experimental highlights (XRS)

XRS from O K-edge in ice under high pressure



E_{out} = 9885 eV
(ΔE ~ 0.2÷0.3 eV)
|**k**| ~ 3 A^{-1} (**k**·**r** ~ 0.2)

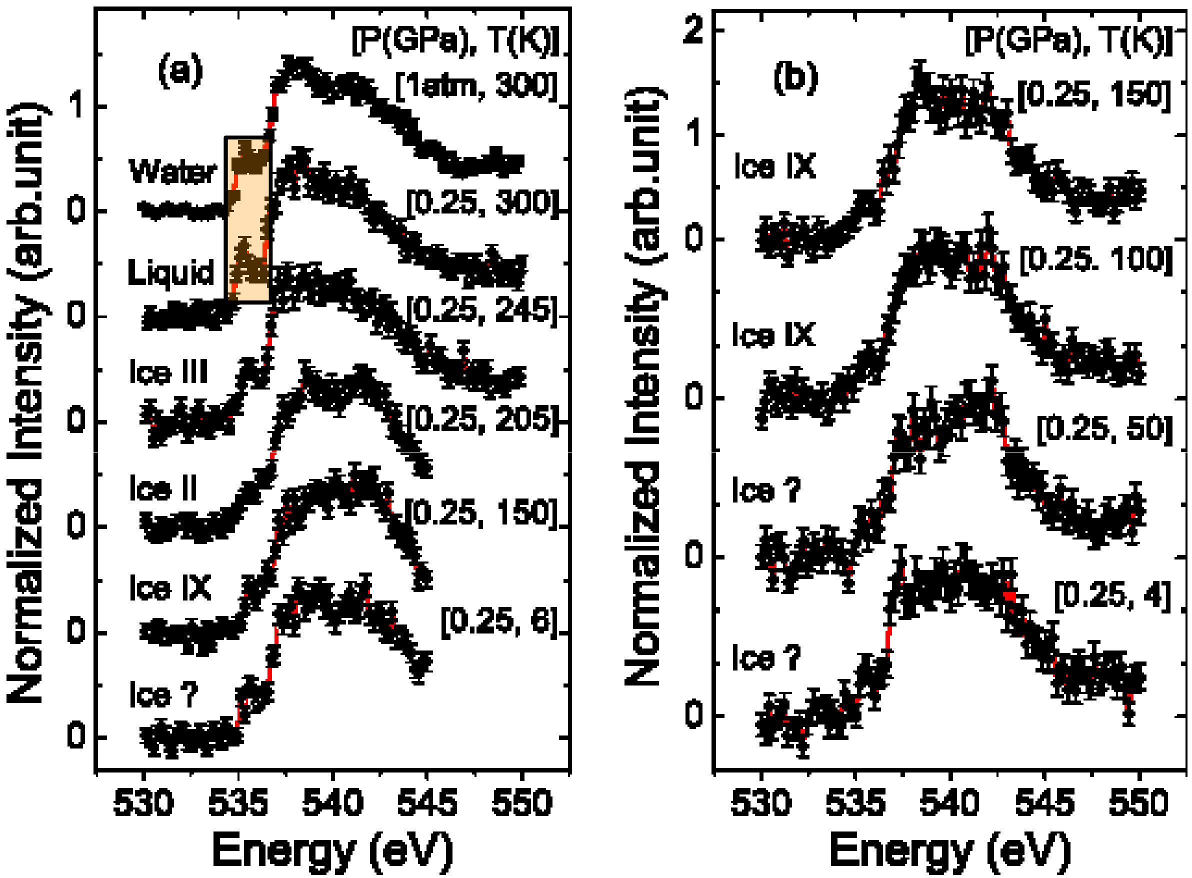
DAC sample environment: hard x-ray needed



PRL 94, 025502 (2005)

Experimental highlights (XRS)

XRS from O K-edge in ice under high pressure



- Slight increase of pre-edge with P (<u>larger HB distortion</u>)
- Increasing order of HB from liquid → Ice III (tetrahedral) → Ice II / IX
- New pre-edge increase @ low-T: new Ice phase?

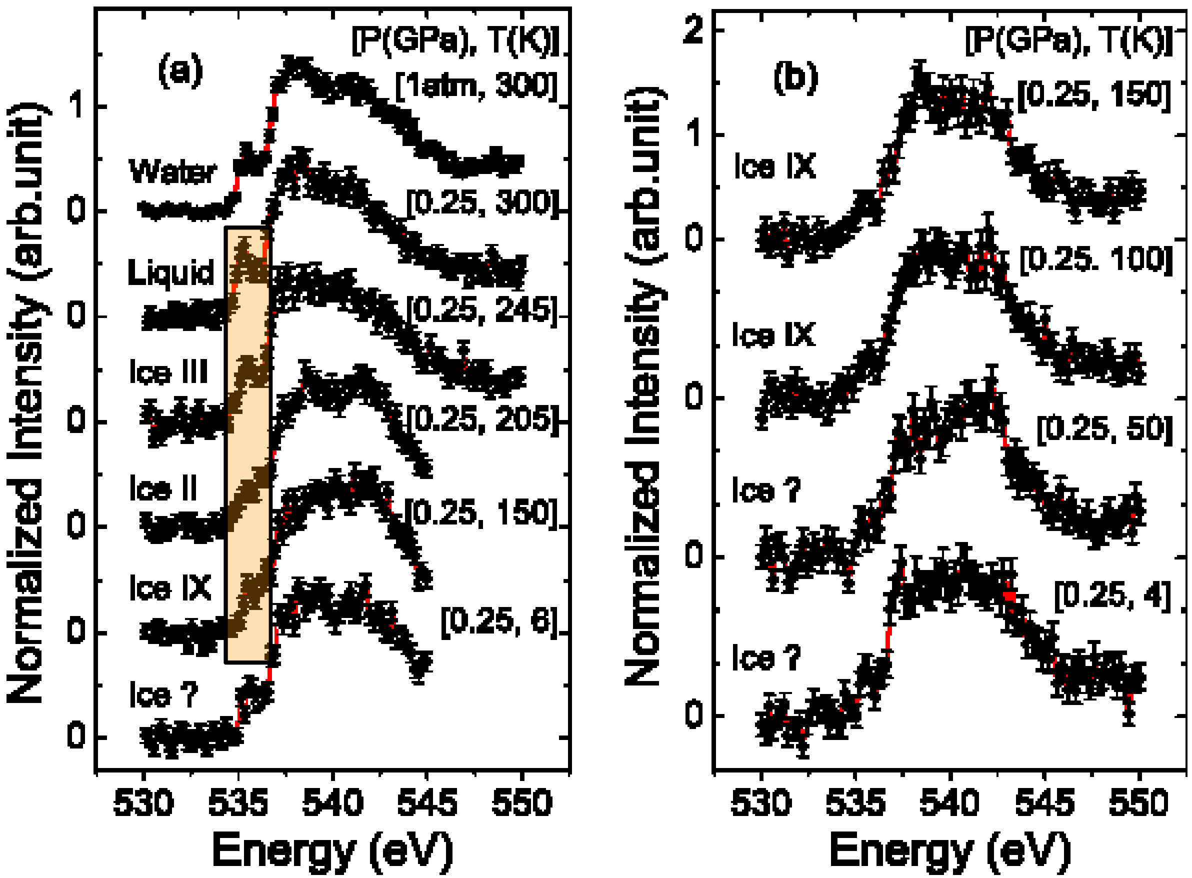
<u>Observation of spectral changes:</u>

<u>Need of much better statistics and theory to extract quantitative information</u>

PRL 94, 025502 (2005)

Experimental highlights (XRS)

XRS from O K-edge in ice under high pressure



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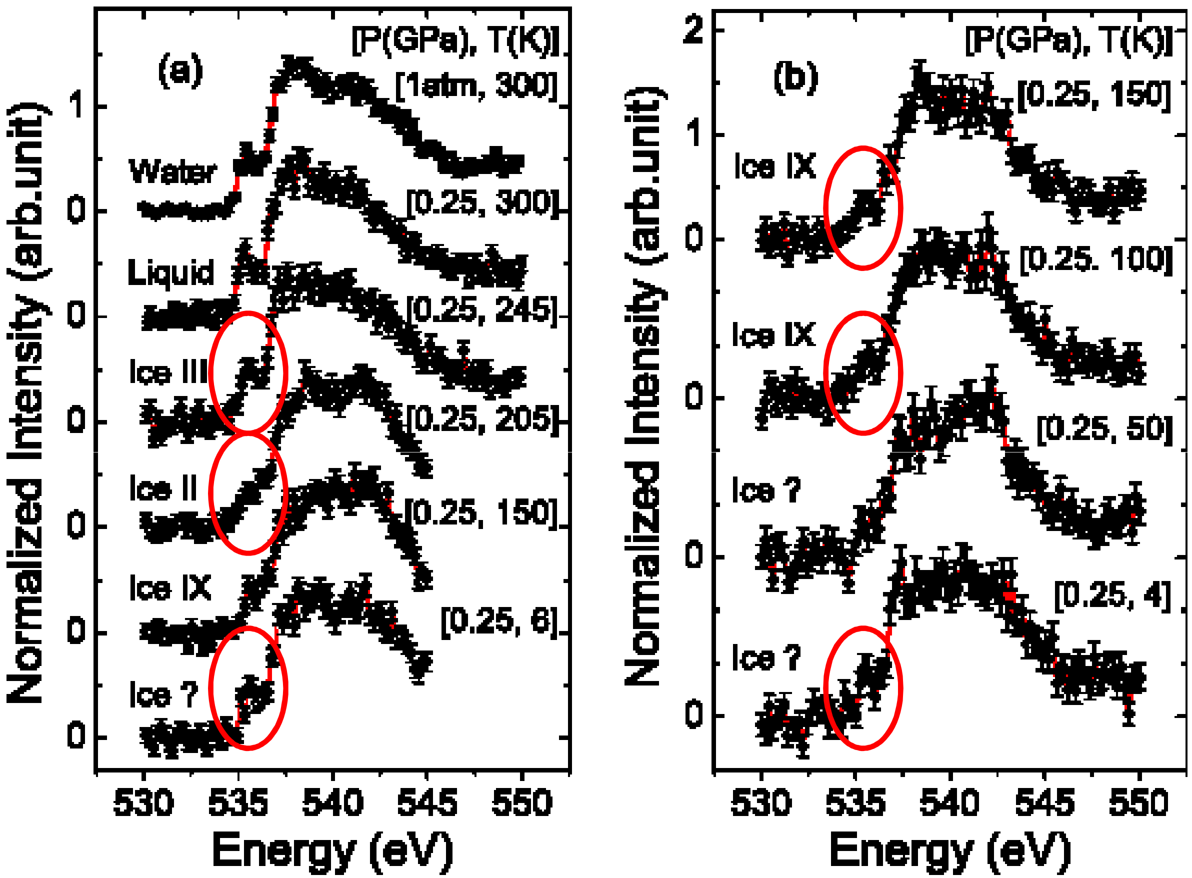

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PRL 94, 025502 (2005)

Experimental highlights (XRS)

XRS in summary:

Soft x-ray spectroscopy in the hard x-ray regime

Advantages

- "simple" sample environment (high pressure/temperature, etc…)
- bulk sensitive
- access "exotic" final states
- indicated for studying (bulk) Oxygen and Carbon

Drawbacks

- "weak probe" (practically limited to $Z < 14$)
- limited quality for structural analysis (EXAFS)
- reasonable quality in the XANES region

Exploit information in the near-edge region

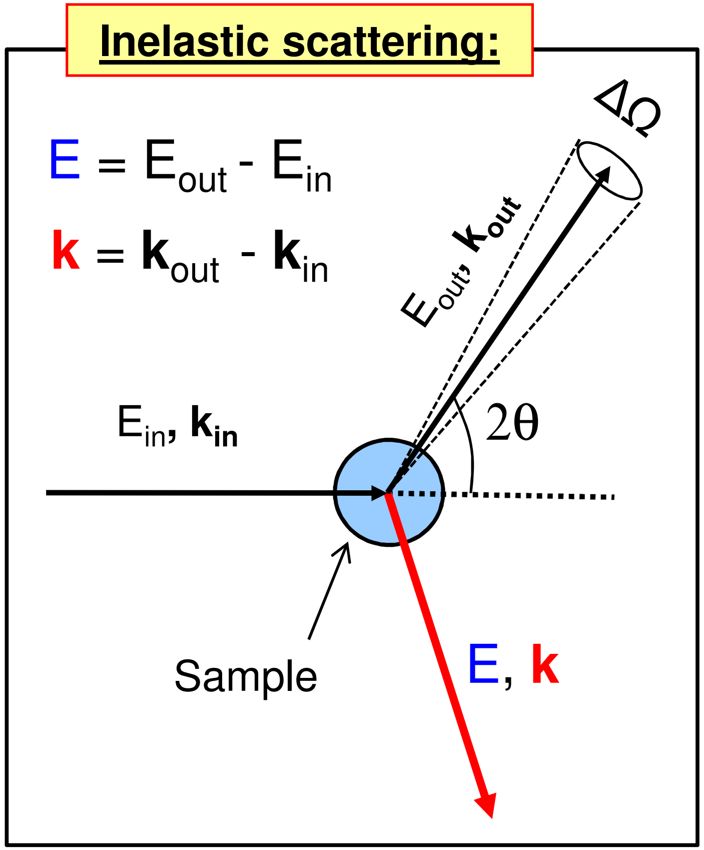
Basic theoretical aspects

$$H_{int}=(e/m_e c)\sum_j[(e/2c)\mathbf{A}_j\cdot\mathbf{A}_j+\mathbf{A}_j\cdot\mathbf{p}_j]$$

A: vector potential of electromagnetic field

P: momentum operator of the electrons

j: summation over all electrons of the system



A·A → non-resonant scattering (IXS - XRS)

A·p → resonant scattering, absorption followed by emission

Basic theoretical aspects

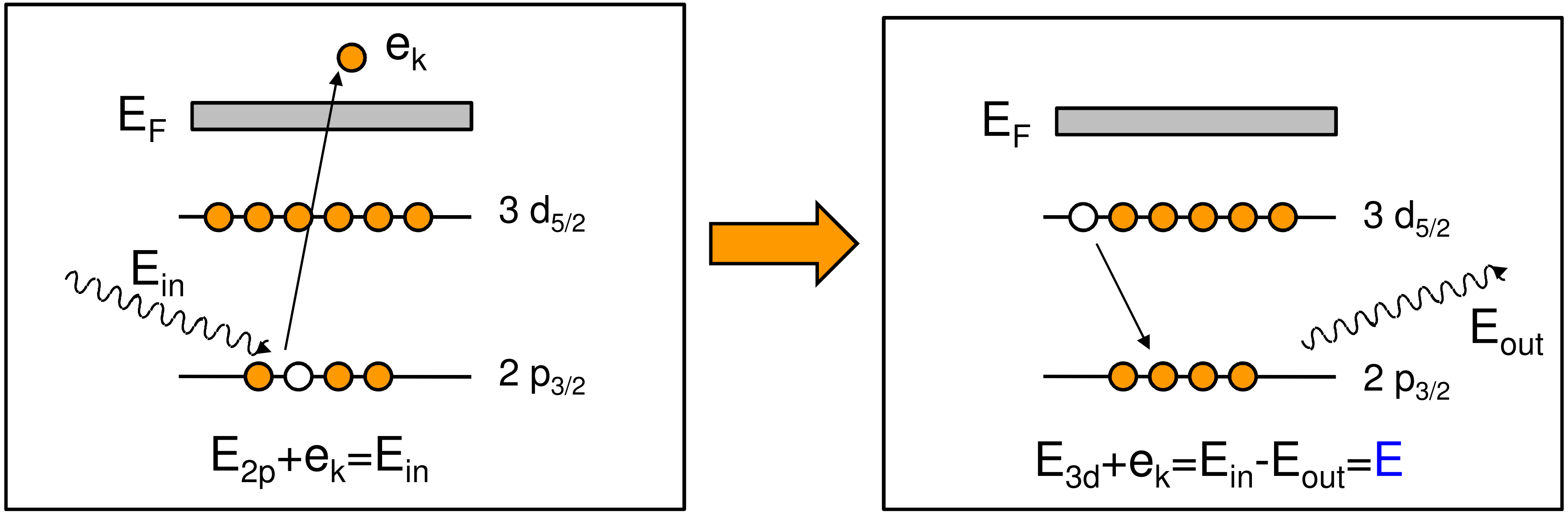
Resonant IXS cross section:

Absorption: $\langle I|C_k|N\rangle$ **Emission**: $\langle N|C_k^{+}|F\rangle$

$$\frac{\partial^2\sigma}{\partial\Omega\partial E} \sim \sum_F \left| \sum_n \frac{\langle I|C_k|N\rangle \langle N|C_k^{+}|F\rangle}{E_N - E_I - E_{in} - i\Gamma_N} \right|^2 \delta(E - E_F + E_I)$$

Resonant denominator: $E_N - E_I - E_{in} - i\Gamma_N$

$$C_k = \sum_j (\boldsymbol{\varepsilon}\cdot\mathbf{p}_j)\exp\{i\mathbf{k}\cdot\mathbf{r}_j\}$$



Basic theoretical aspects

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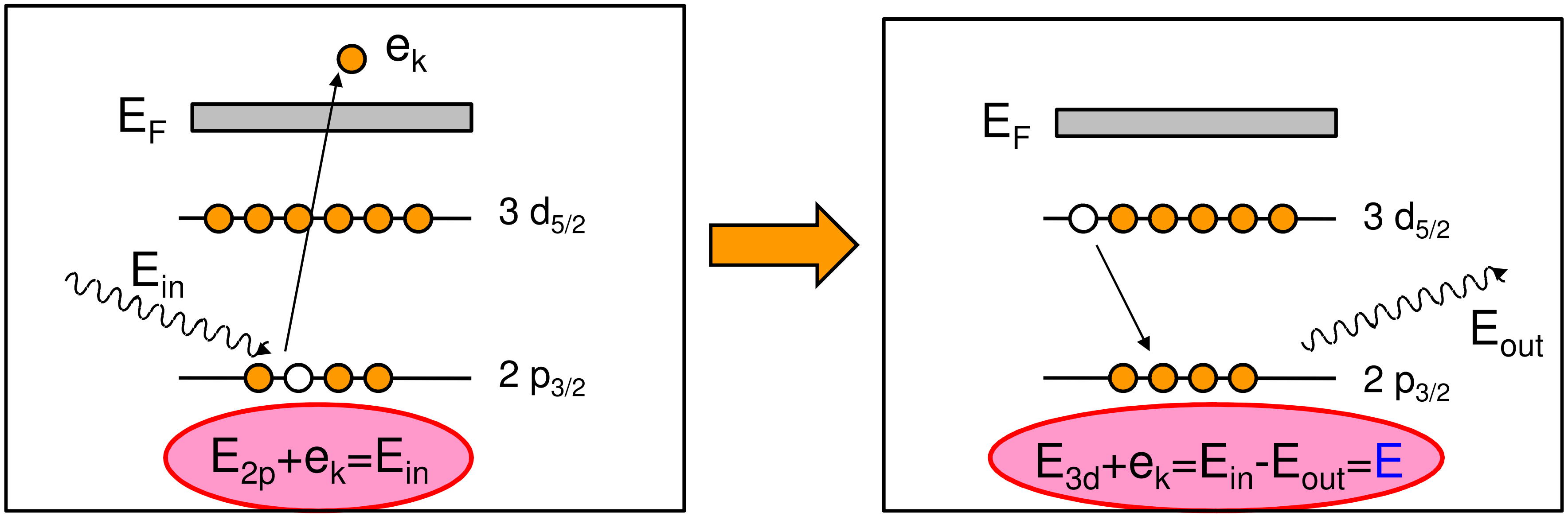
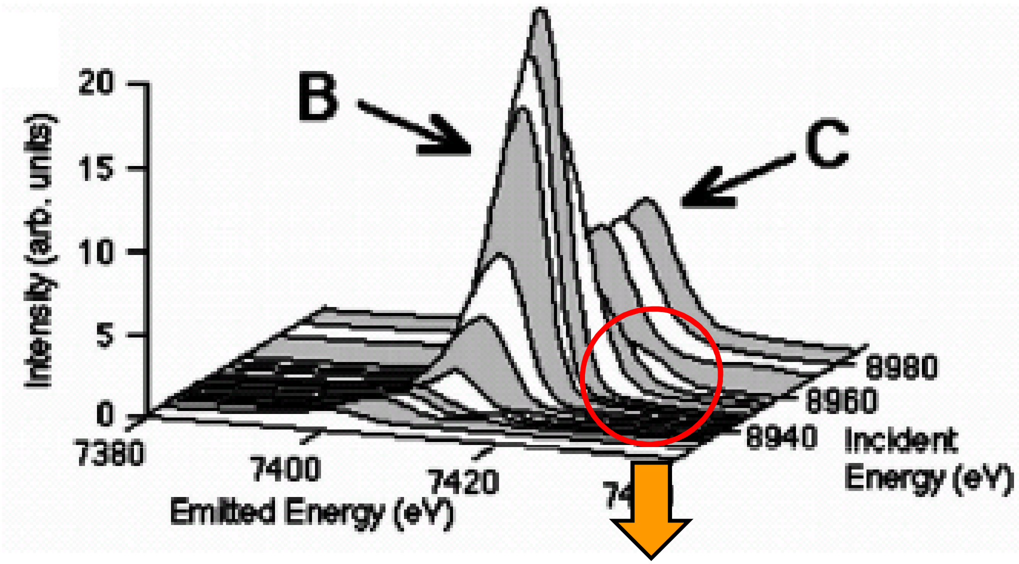
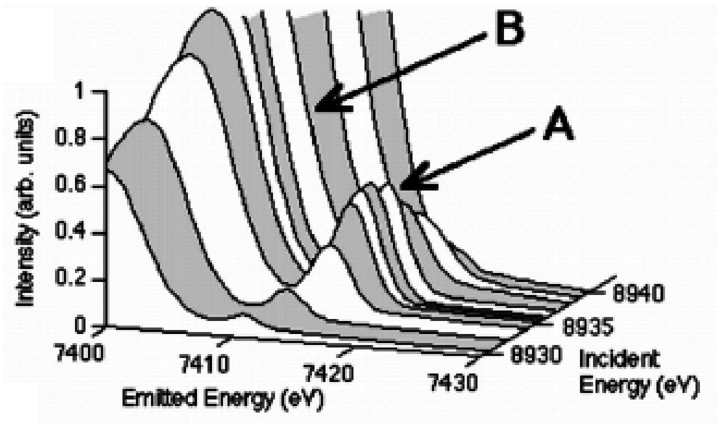
Final states for XAS are intermediate for RIXS (resolution ~ Γ_N)

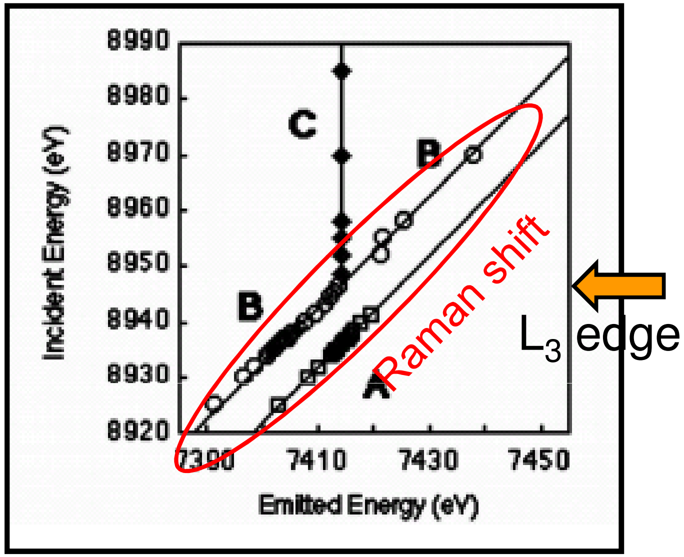


Experimental highlights (RIXS)

RIXS in Rare-Earths ($Yb_2Fe_{14}B$)







A: very weak, visible in the pre-edge region, observed at constant energy transfer (E=E_{out}-E_{in})
B: strong, observed at constant E
C: cannot be separated below edge, above is observed at increasing E

Energy resolution ~ 3-7 eV for Rare-Earths ($\Gamma_{3d} << \Gamma_{3d}$)

PRB 60, 13497 (1999)

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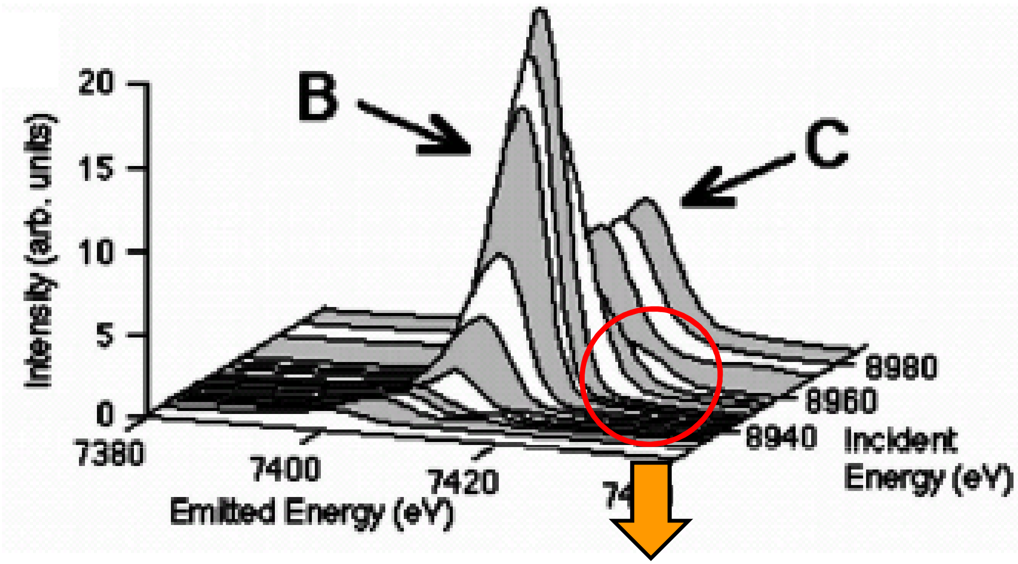
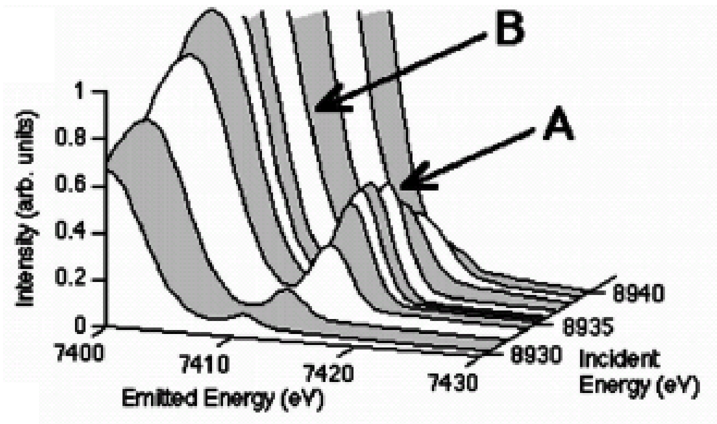
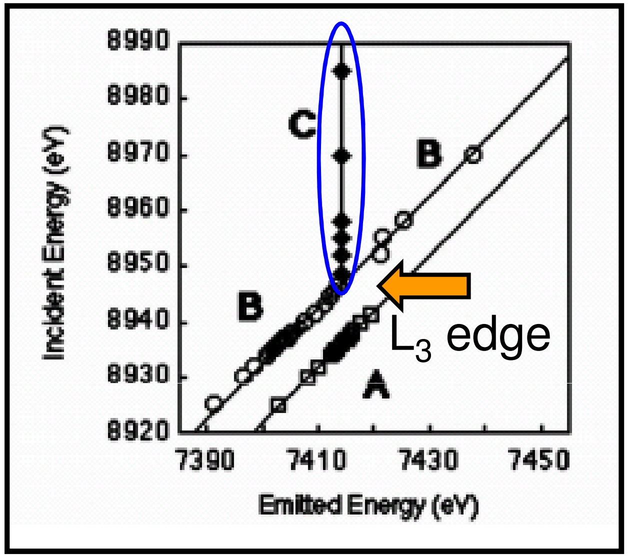




Fluorescence



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B: strong, observed at <u>constant E</u>
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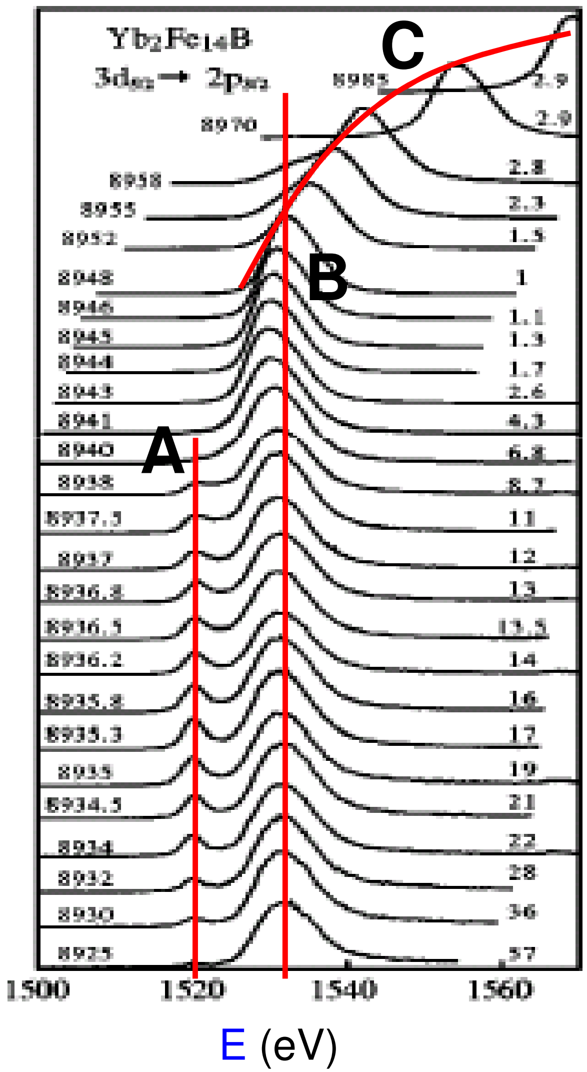


L_3 edge

Ground: $|4f^{13}d^{n*}>$

A: **Quadrupolar: 2p → 4f channel**

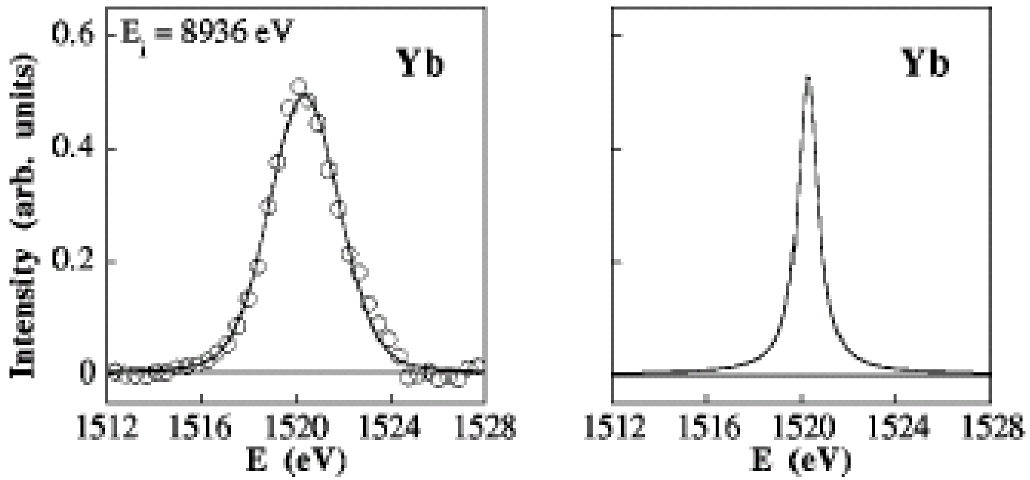
$|N> = |2p^5 4f^{14} 5d^{n*}> \rightarrow |F> = |3d^9 4f^{14} 5d^{n*}>$

B: **Dipolar: 2p → 5d channel**

$|N> = |2p^5 4f^{13} 5d^{n*+1}> \rightarrow |F> = |3d^9 4f^{13} 5d^{n*+1}>$

C: **$L_{\alpha 1}$ fluorescence: 2p→continuum**

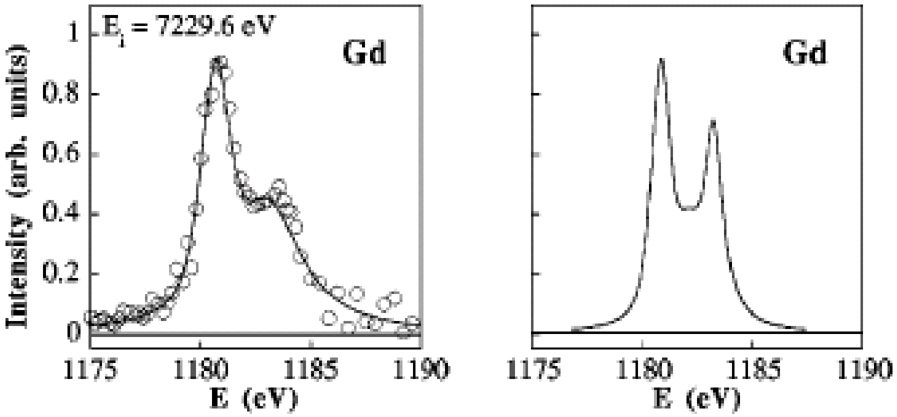
Quadrupolar excitation (A): agreement calculations



PRB 60, 13497 (1999)

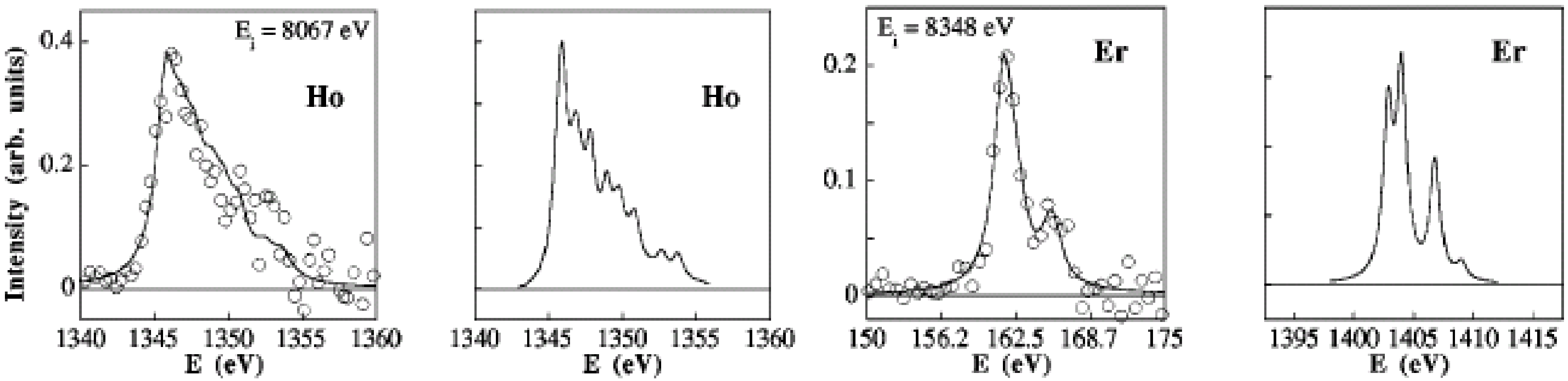
Experimental highlights (RIXS)

RIXS in Rare-Earths (quadropolar 2p→4f)



RIXS data vs. Theory:

The shape of quadrupolar 2p → 4f transition agrees with calculations



PRB 60, 13497 (1999)

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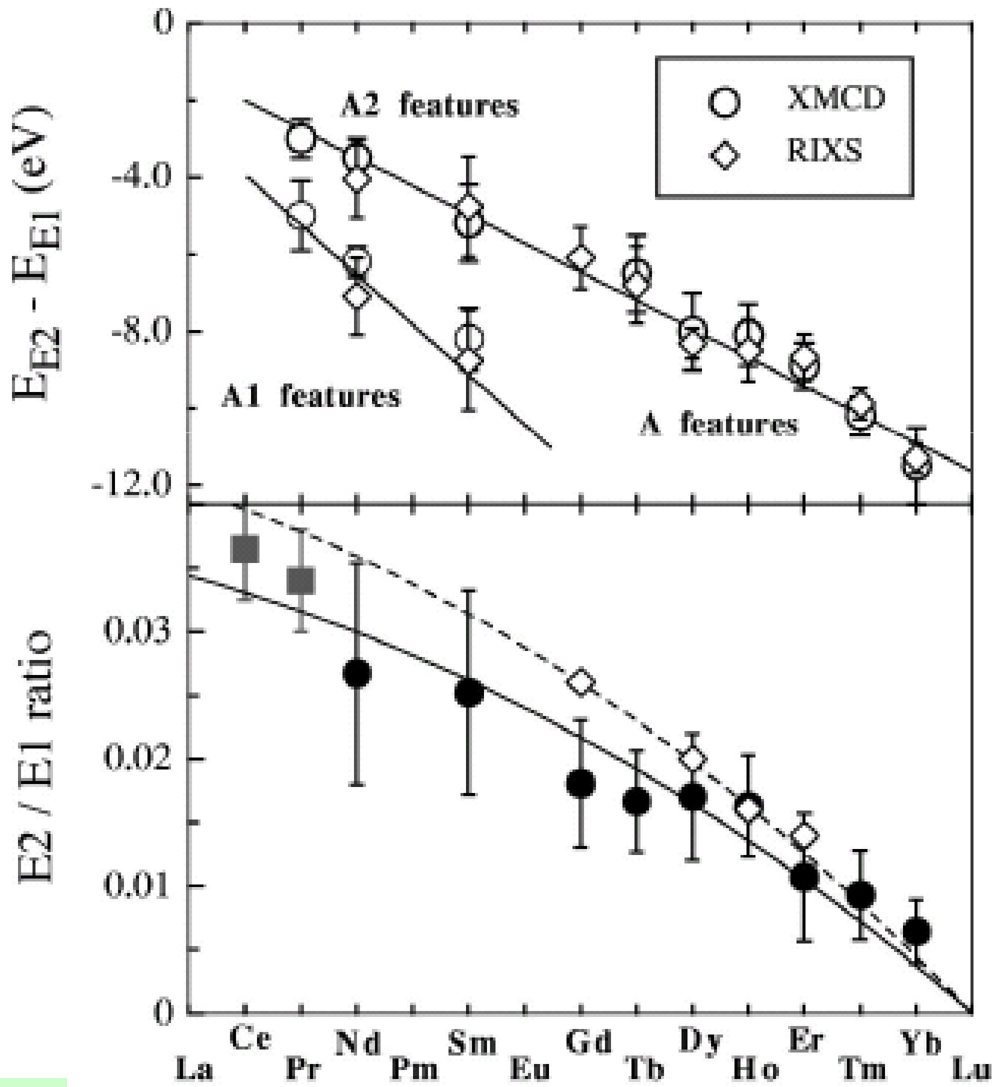
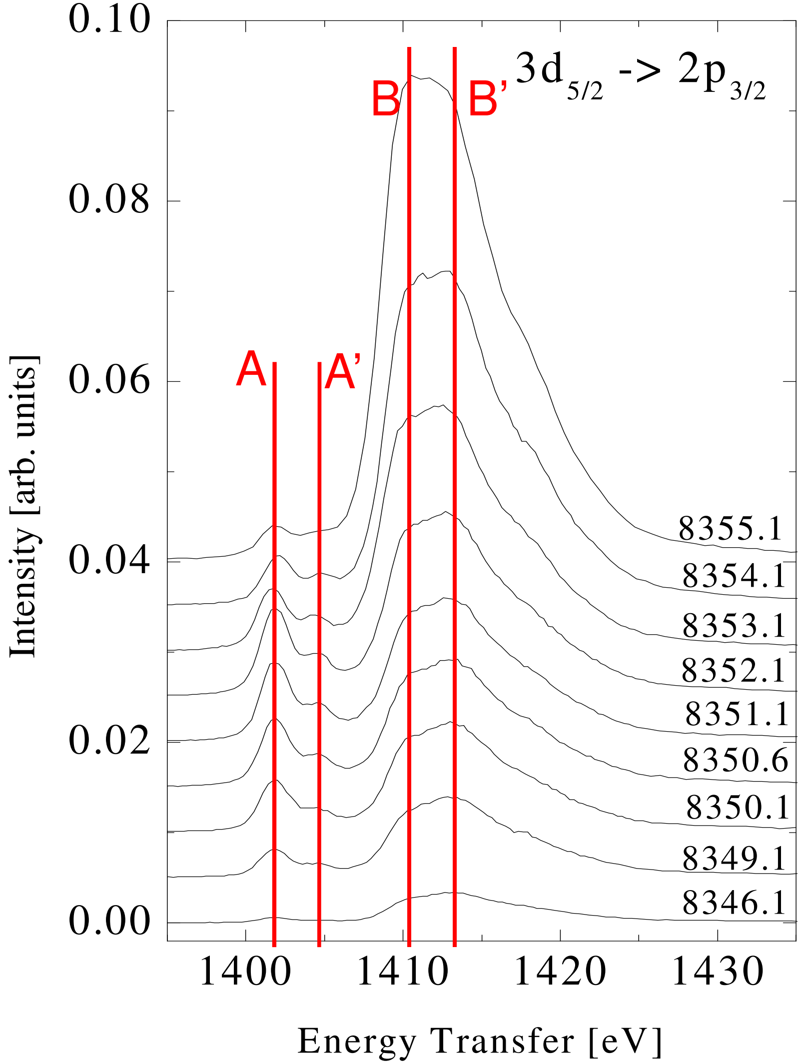
RIXS in Rare-Earths (quadropolar 2p→4f)

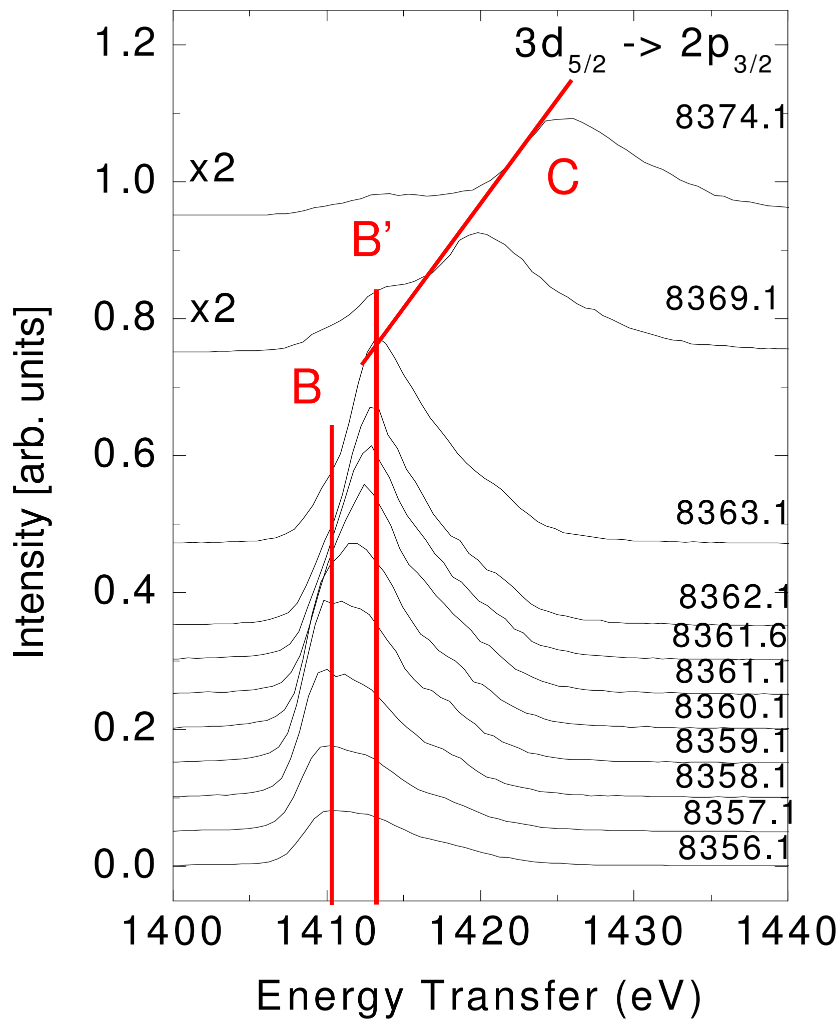


PRB 60, 13497 (1999)

Experimental highlights (RIXS)

RIXS in Rare-Earths (Er_2O_3)

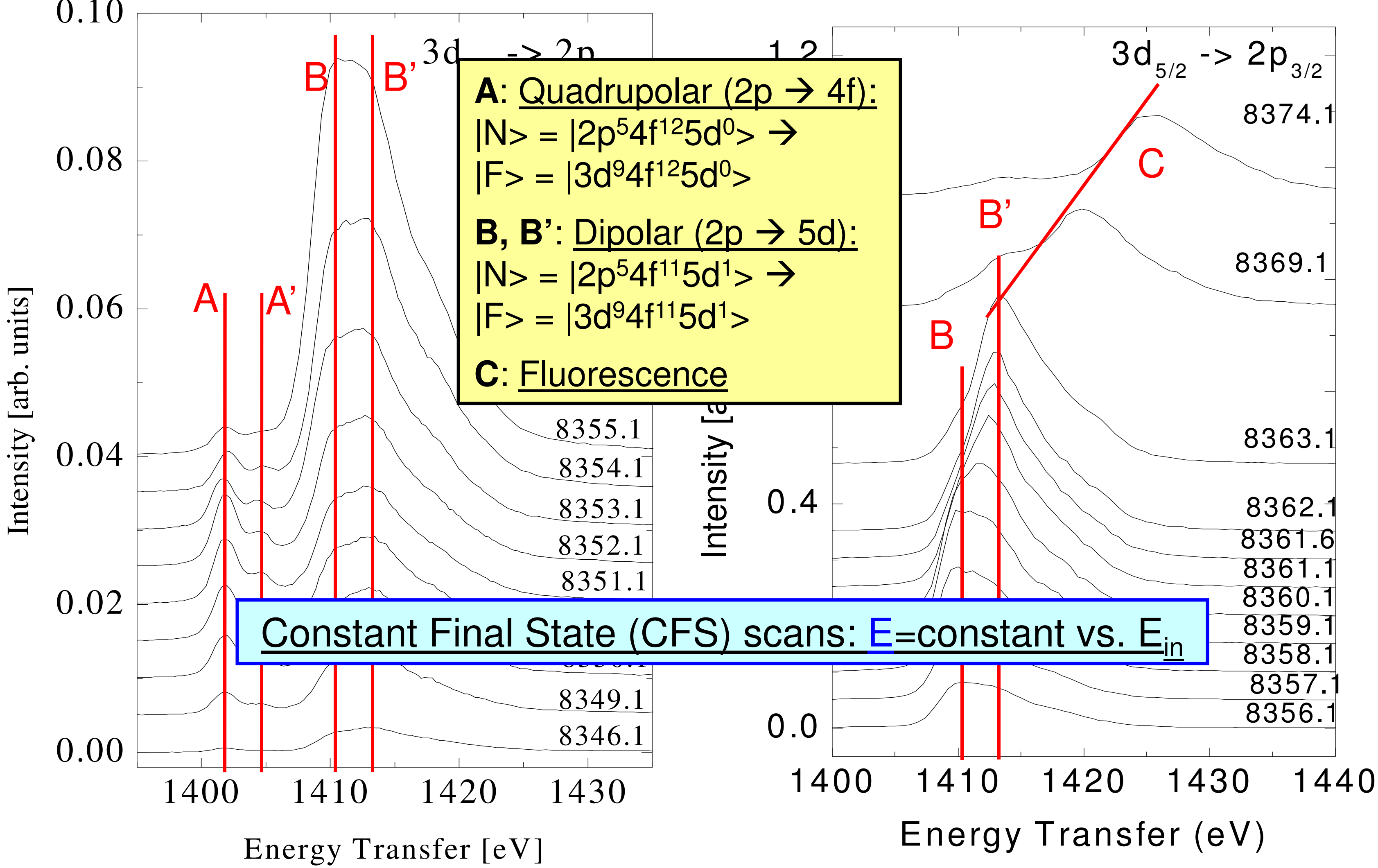




Experimental highlights (RIXS)

RIXS in Rare-Earths (Er_2O_3)

Ground: |4f¹¹d⁰>



A: Quadrupolar (2p → 4f):
|N> = |2p⁵4f¹²5d⁰> →
|F> = |3d⁹4f¹²5d⁰>

B, B': Dipolar (2p → 5d):
|N> = |2p⁵4f¹¹5d¹> →
|F> = |3d⁹4f¹¹5d¹>

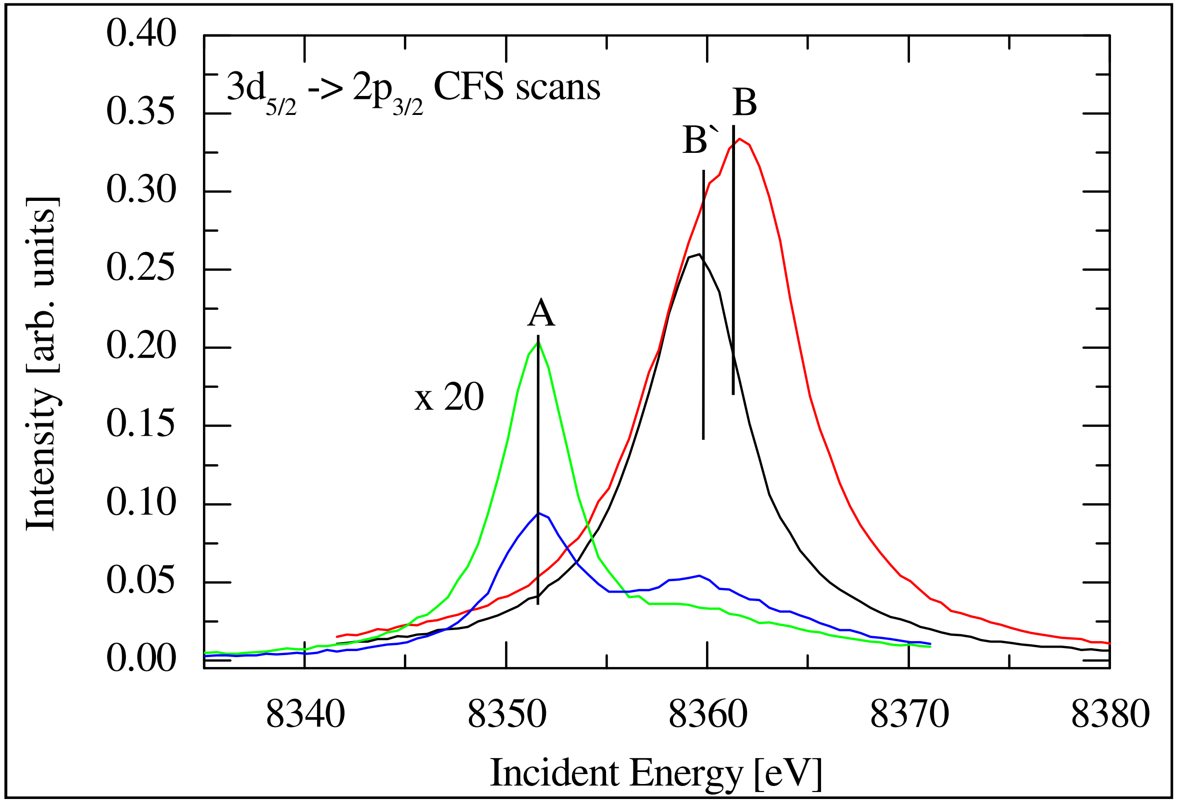
C: Fluorescence

Constant Final State (CFS) scans: E=constant vs. E_{in}

Experimental highlights (RIXS)

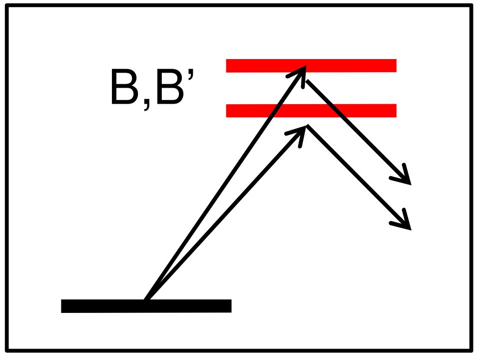
RIXS in Rare-Earths (Er_2O_3)

Constant final state scans: E = constant & E_{in} through the absorption edge



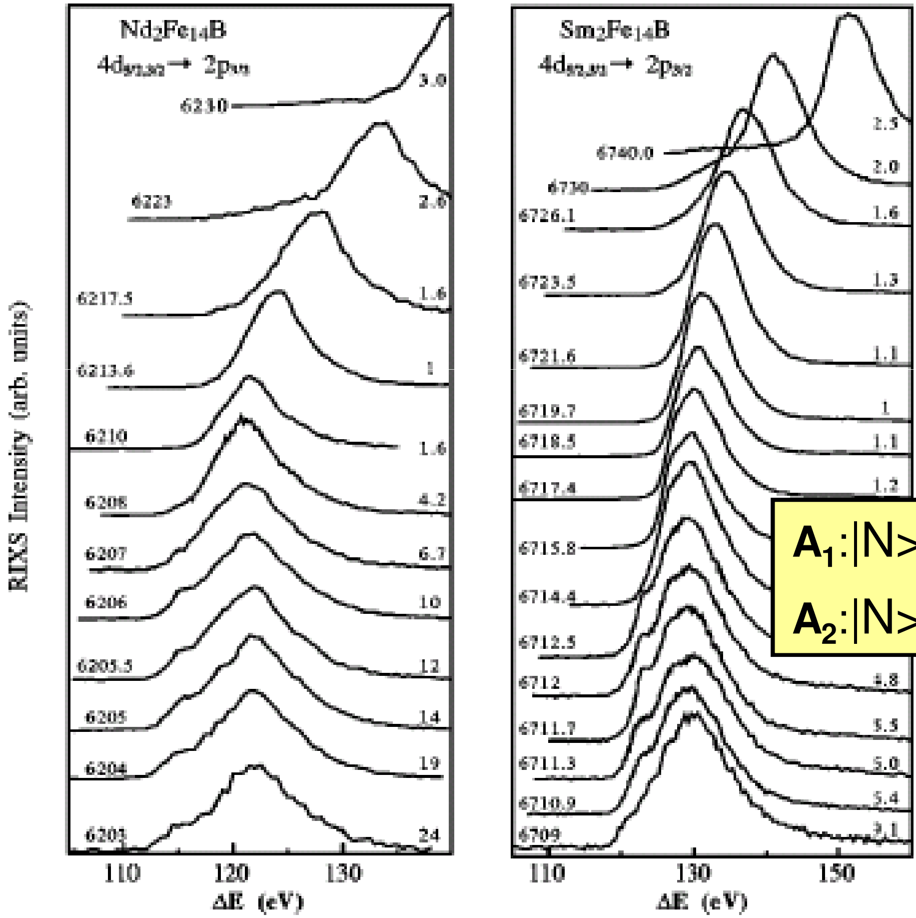
B and B*: 2p → 5d dipolar transitions. Different intermediate states, cubic field splitting of the 5d states: ΔE = 2.3 eV

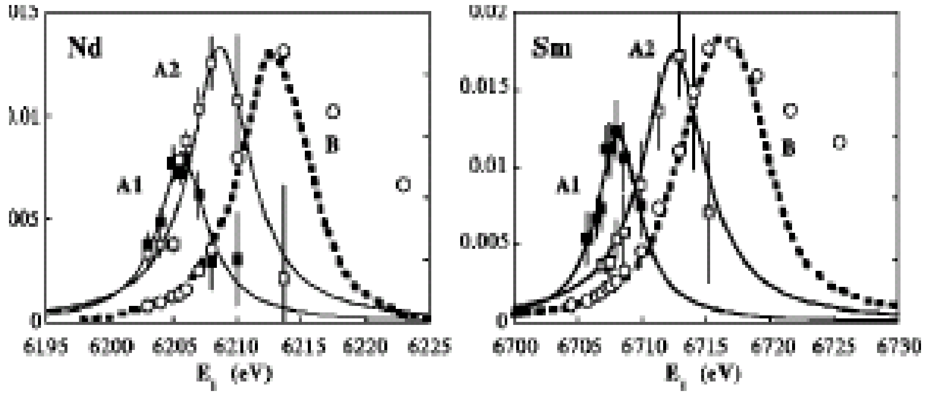
A and A*: 2p → 4f. Same intermediate state



Experimental highlights (RIXS)

RIXS in Rare-Earths (Nd & Sm)





A_1:$|N\rangle = |2p^5 4f^{(n-1)\uparrow} 5d^{n^*}\rangle \rightarrow |F\rangle = |2d^9 4f^{14} 5d^{n^*}\rangle$

A_2:$|N\rangle = |2p^5 4f^{n\uparrow+1\downarrow} 5d^{n^*}\rangle \rightarrow |F\rangle = |2d^9 4f^{14} 5d^{n^*}\rangle$

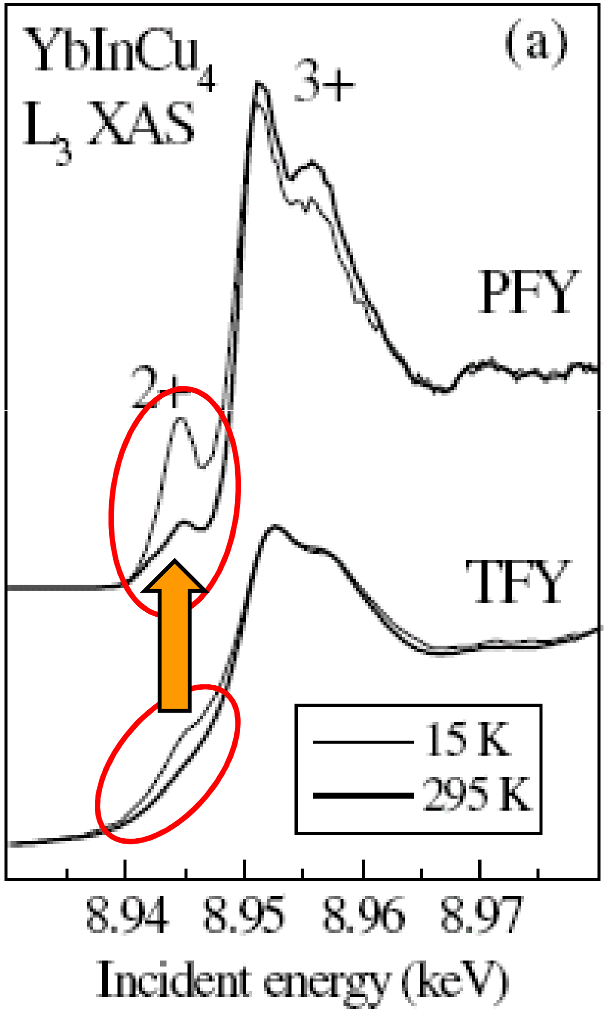
A2 and A2: 2p → 4f transitions

Different intermediate states due to partially filled f sub-shells. Compatible with calculations and with XMCD results

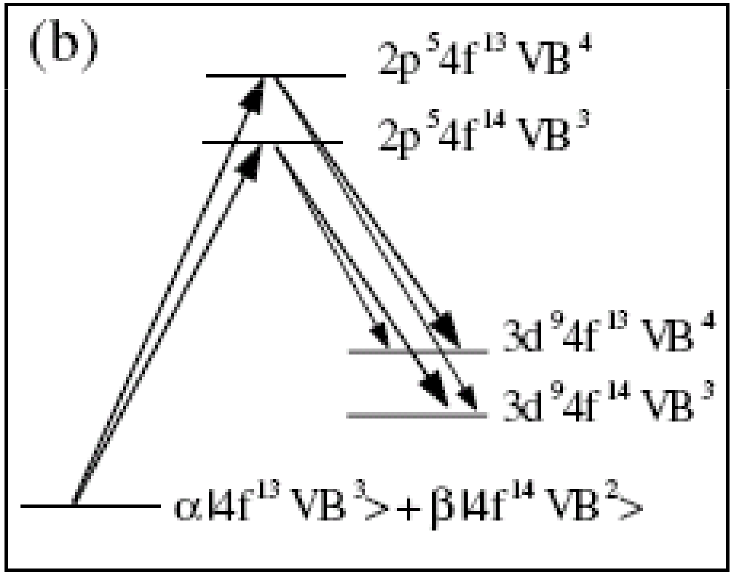
PRE 60, 13497 (1999)

Experimental highlights (RIXS)

RIXS in Rare-Earths (valence transition)



- Mixed ground state (Yb^{2+}; Yb^{3+})
- Pre-edge → larger Yb^{2+} at low-T
- XAS final = RIXS intermediate

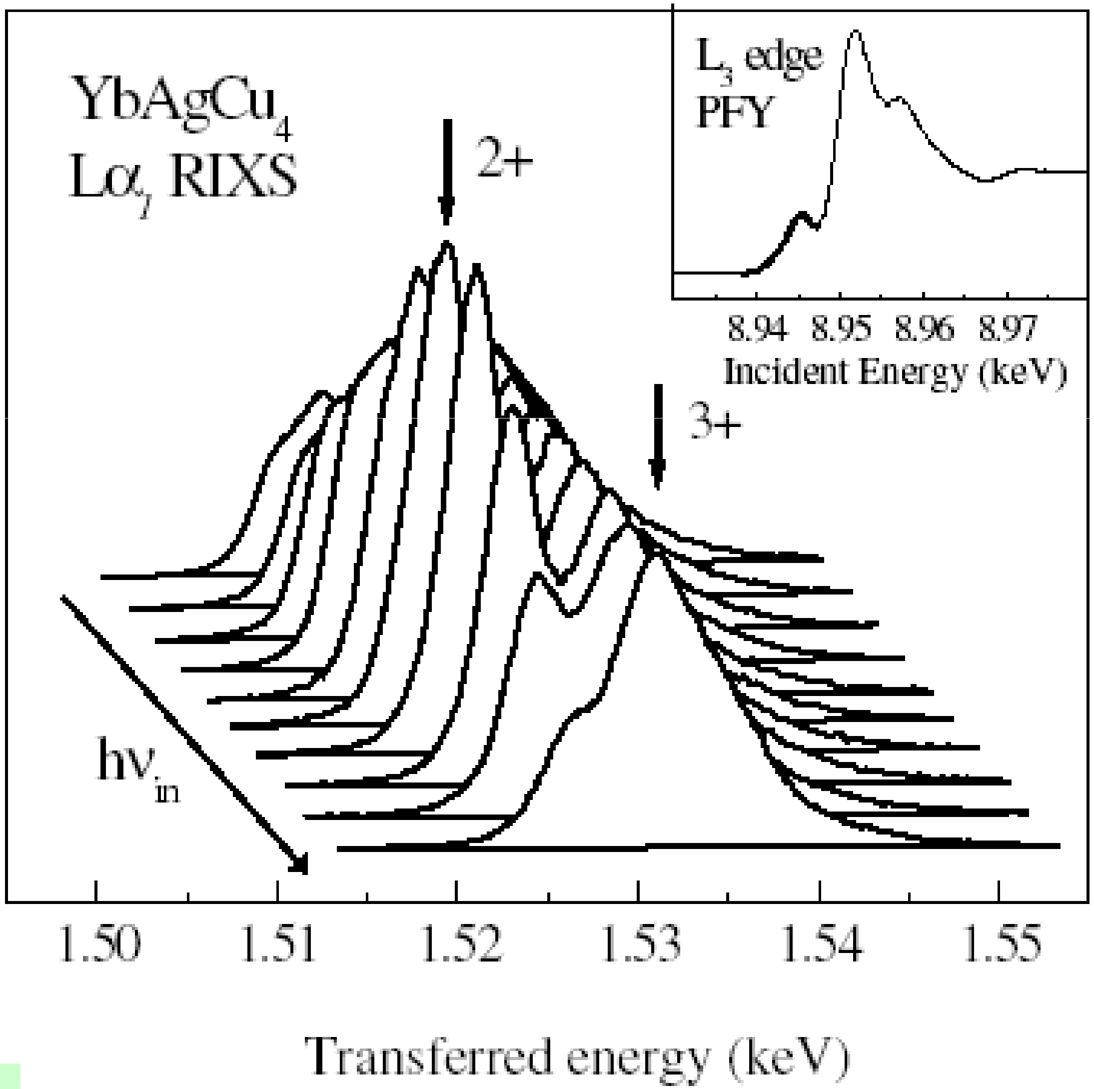


PRL 88, 196403 (2002)

Weak Yb^{2+} feature can be resonantly enhanced: possible to study T-dependence

Experimental highlights (RIXS)

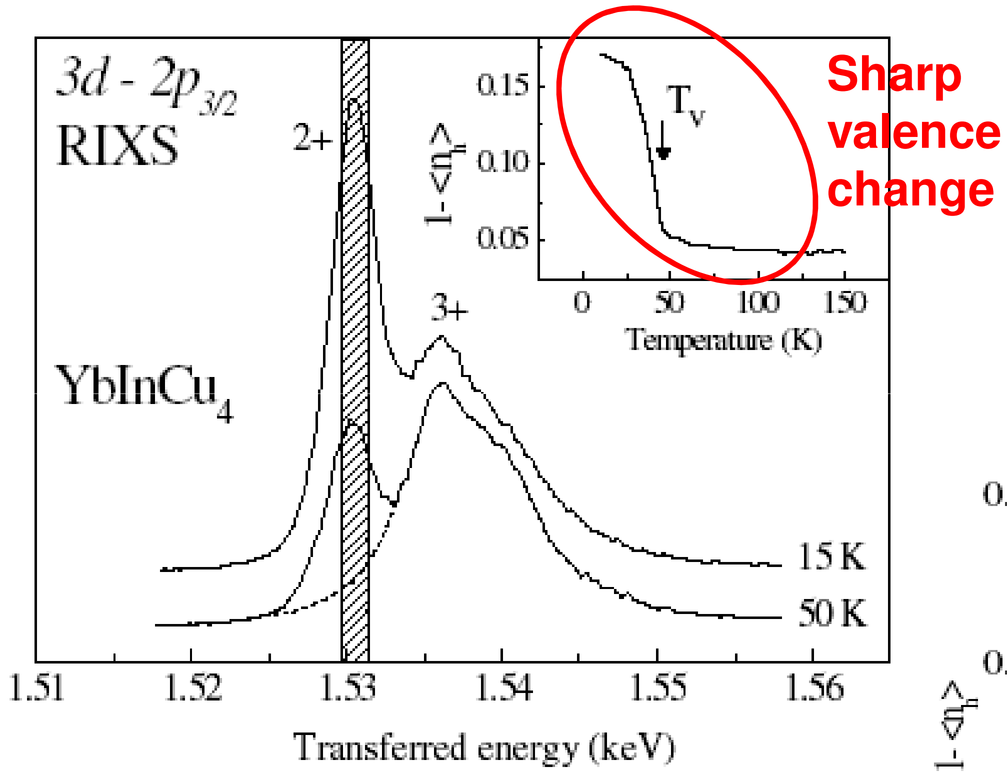
RIXS in Rare-Earths (valence transition)



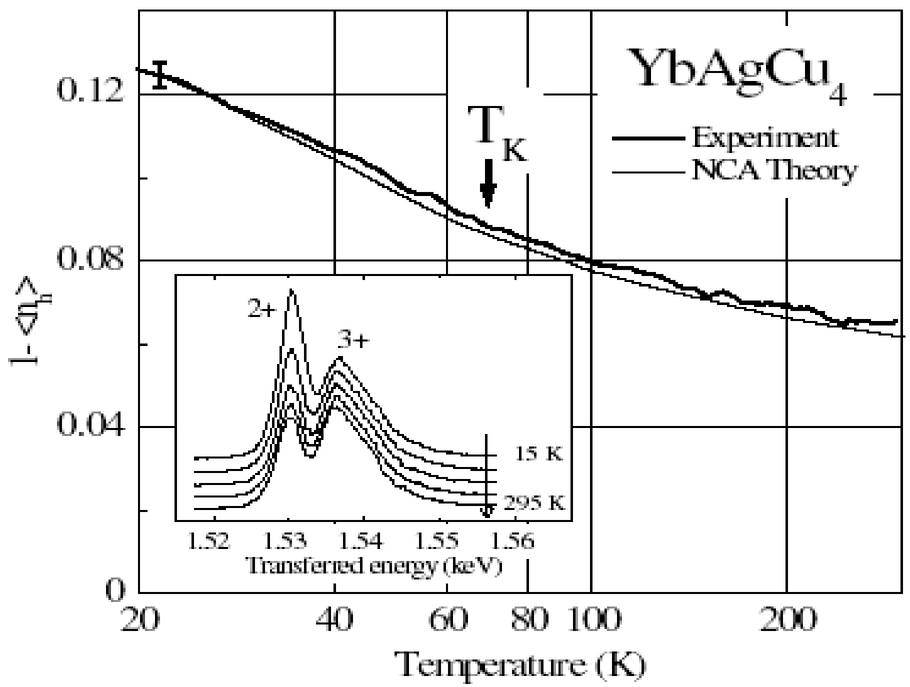
PRL 88, 196403 (2002)

Experimental highlights (RIXS)

RIXS in Rare-Earths (valence transition)



Smooth valence change



PRL 88, 196403 (2002)

Experimental highlights (RIXS)

RiXS in summary:

Final state core-hole lifetime < energy separation of the multiplet families

↓

RIXS allows the separation of different excitation channels which are obscured in a standard absorption measurement

Keeping E fixed and tuning E_{in} through edge (CFS scan)

↓

Resonant enhancement of "subdle" intermediate states