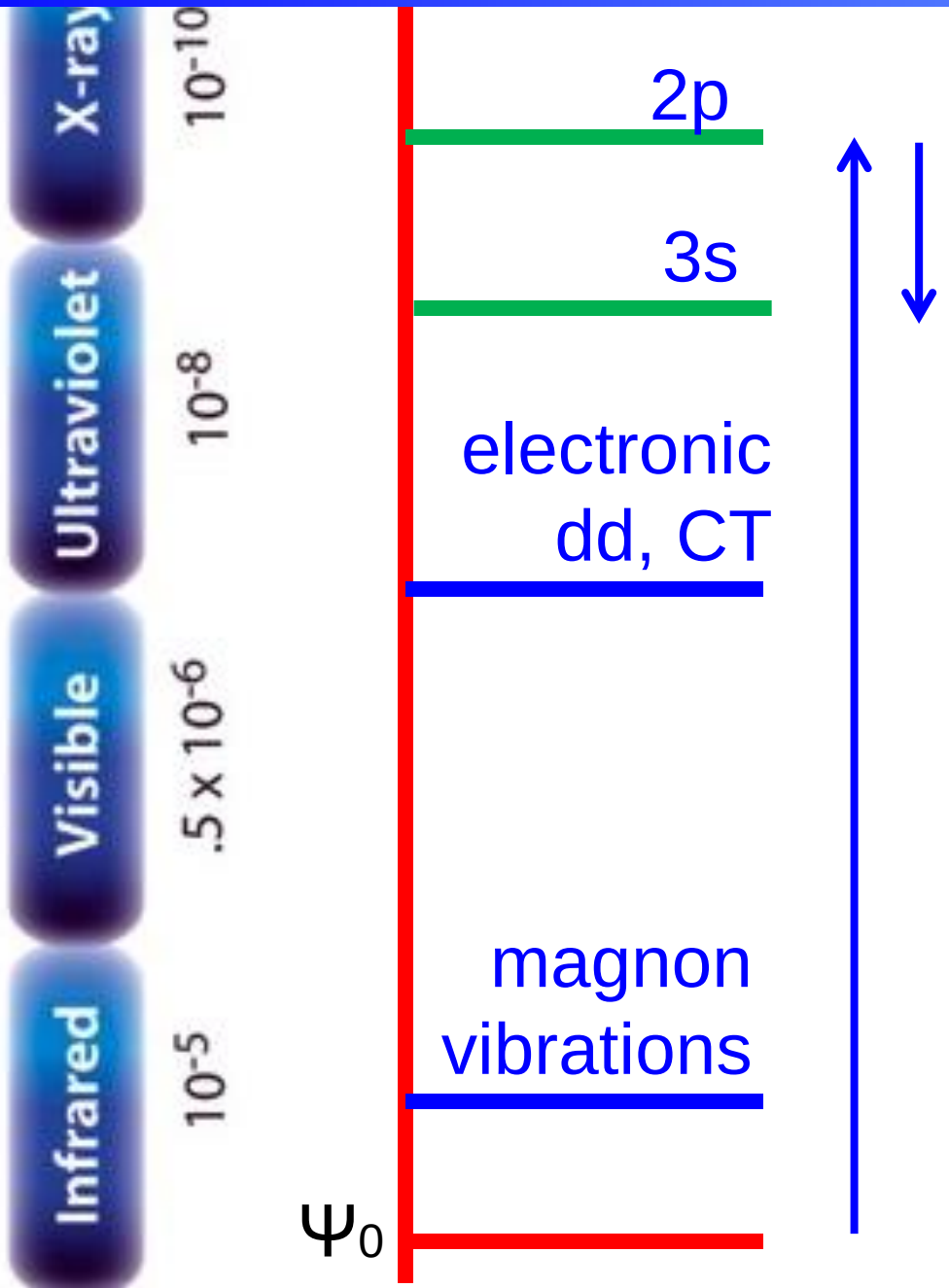
Resonant Inelastic X-ray Scattering

core-core RIXS

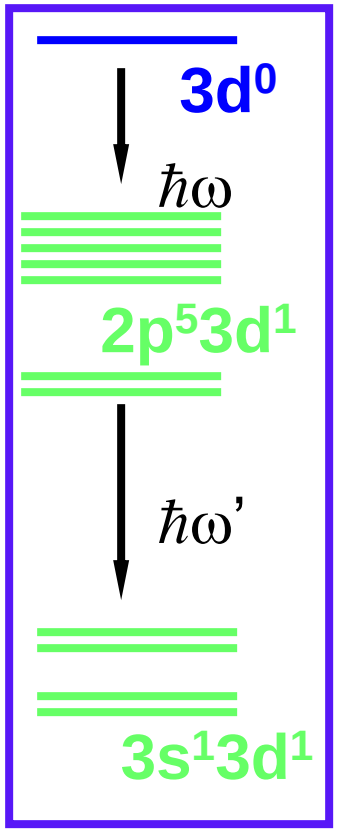
core-valence RIXS

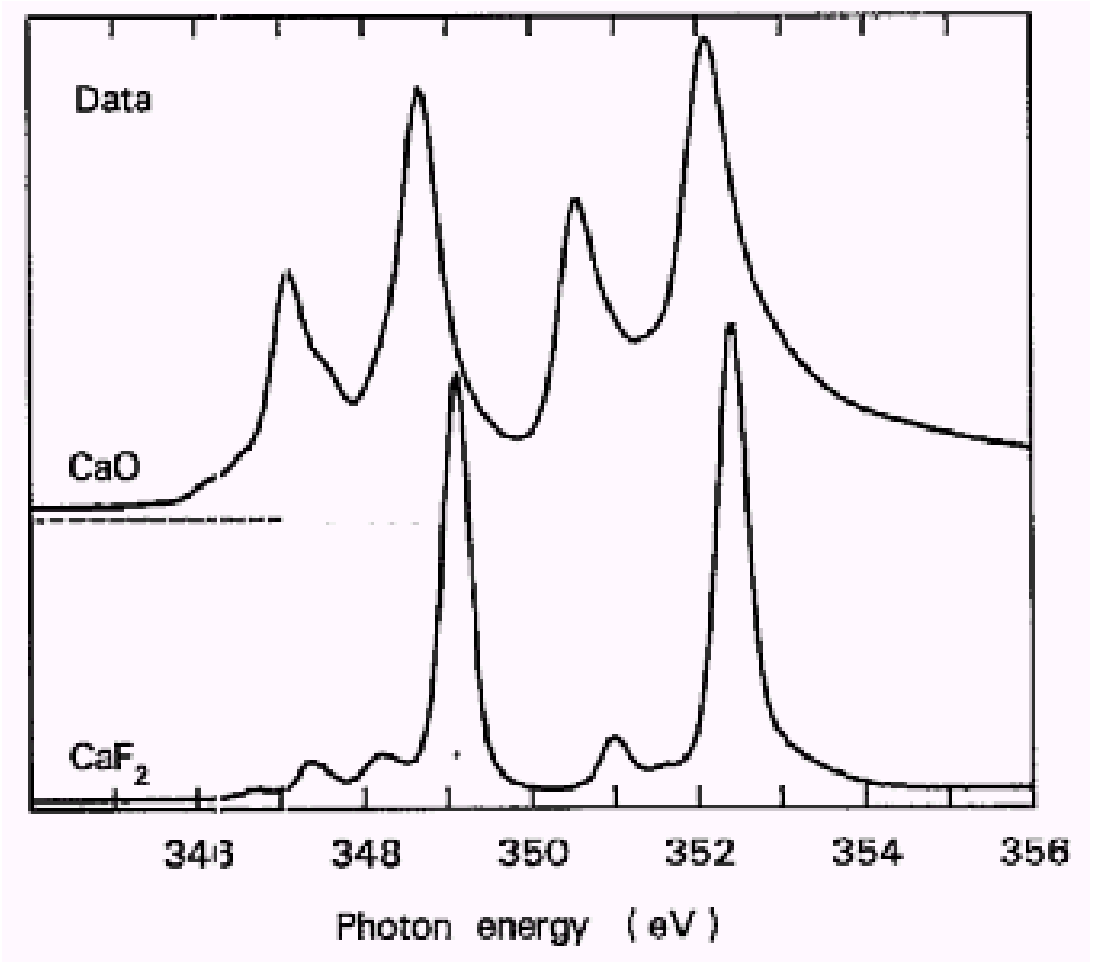
Core-core RIXS



2p3s RIXS of CaF_2

2p XAS of CaF_2



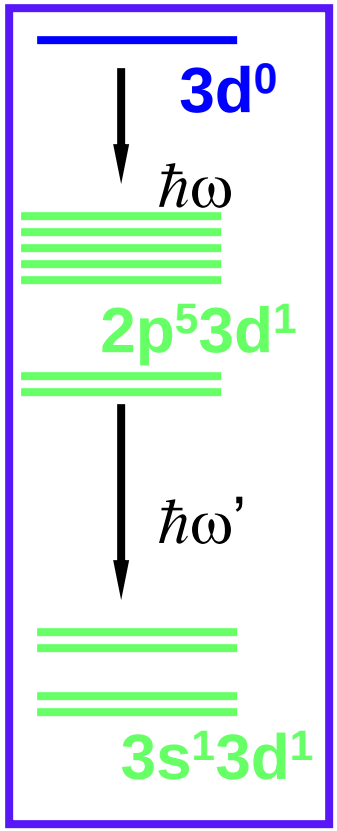


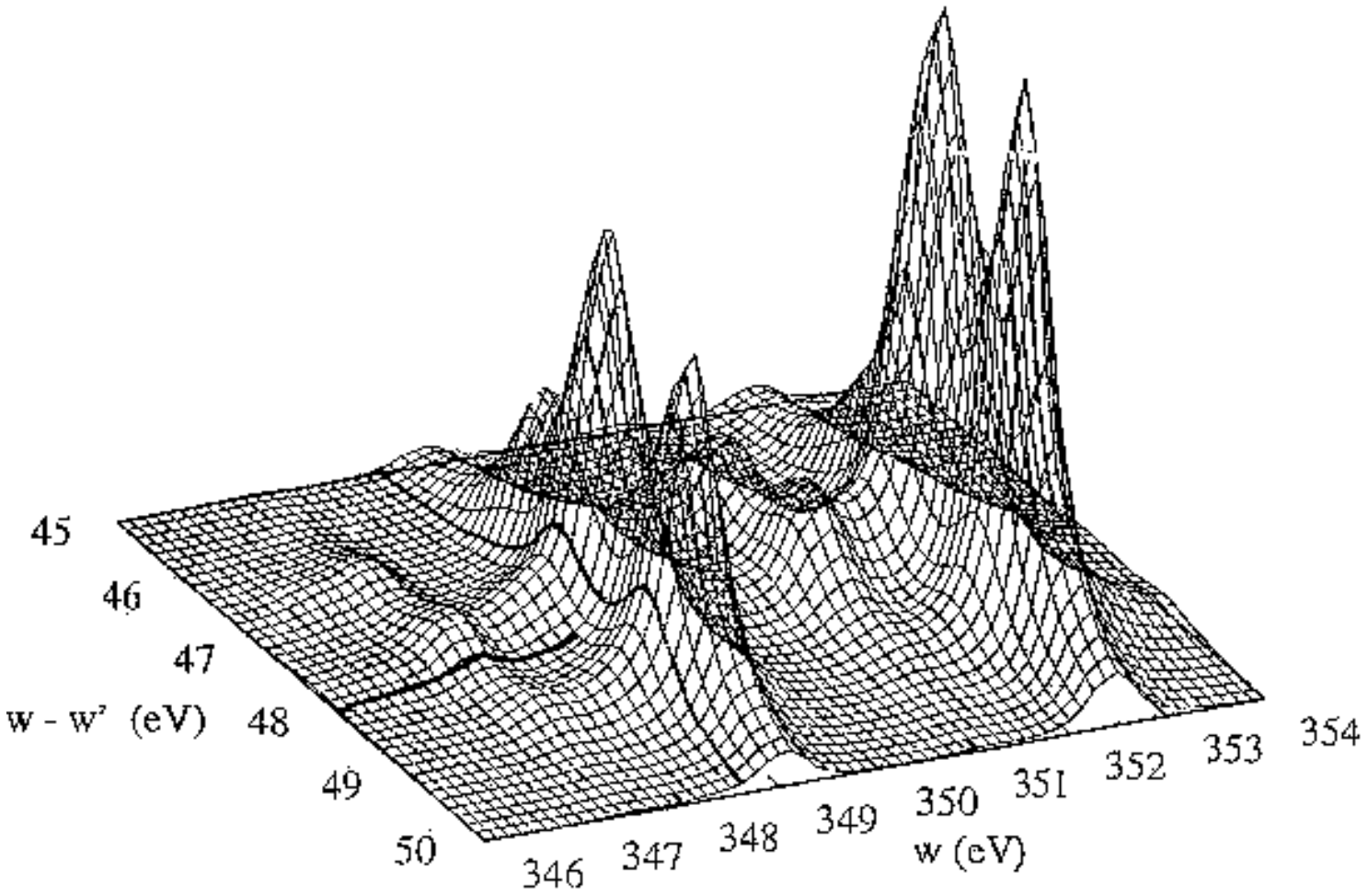
2p3s RIXS of CaF_2

- Ground state is $3d^0$
- Excitation (i_0) $3d^0 \rightarrow$ (x) $2p^5 3d^1$
- Decay (x) $2p^5 3d^1 \rightarrow$ (f) $3s^1 3d^1$

$$I(\omega,\omega') = \sum_f \left| \sum_x \frac{\langle f|r_q|x\rangle\langle x|r_q|i_0\rangle}{E_{i_0}+\omega-E_x-i\Gamma_x} \right|^2 L_f(\omega-\omega')G_E,$$

2p3s RIXS of CaF_2





Phys. Rev. B. 53, 7099 (1996)

1s2p RIXS of transition metal ions

10^{-10}

10^{-8}

$.5 \times 10^{-6}$

10^{-5}

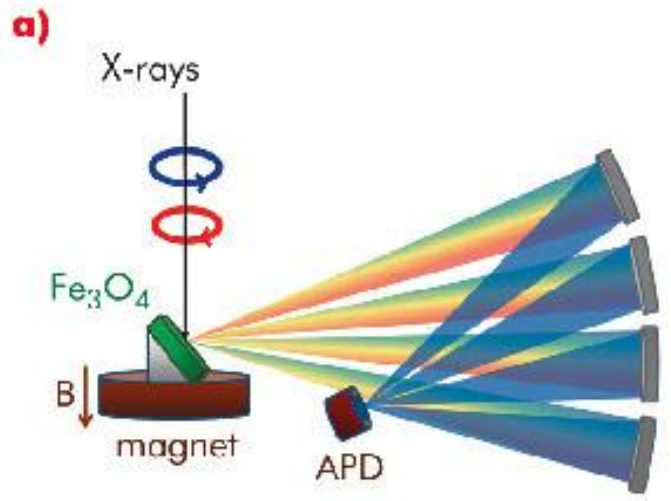
1s

2p

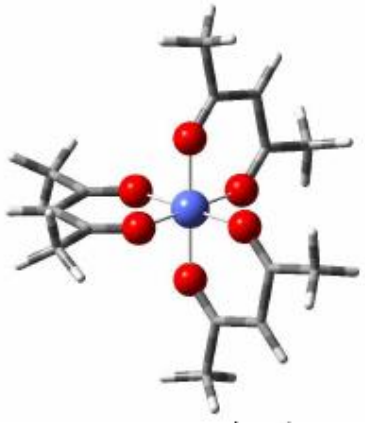
electronic
dd, CT

magnon
vibrations

Ψ_0

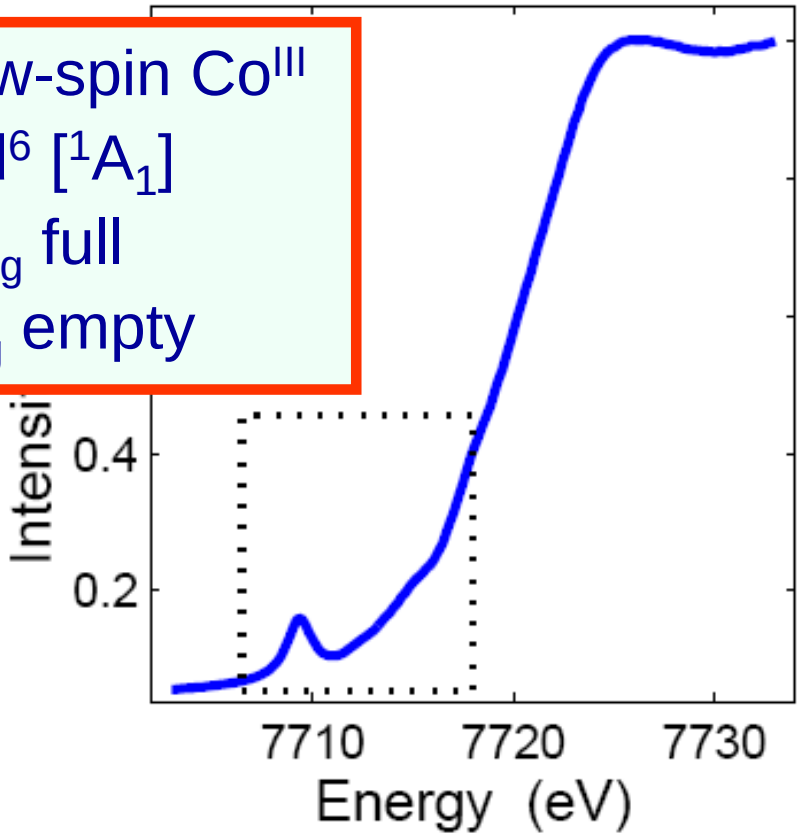


1s2p RIXS of transition metal ions



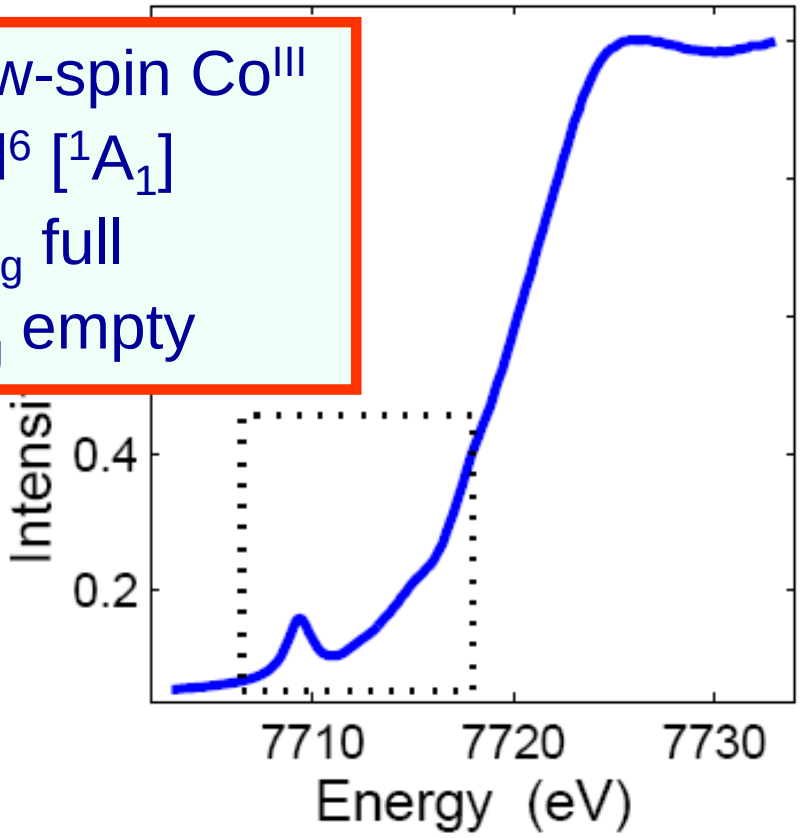
$Co(acac)_3$

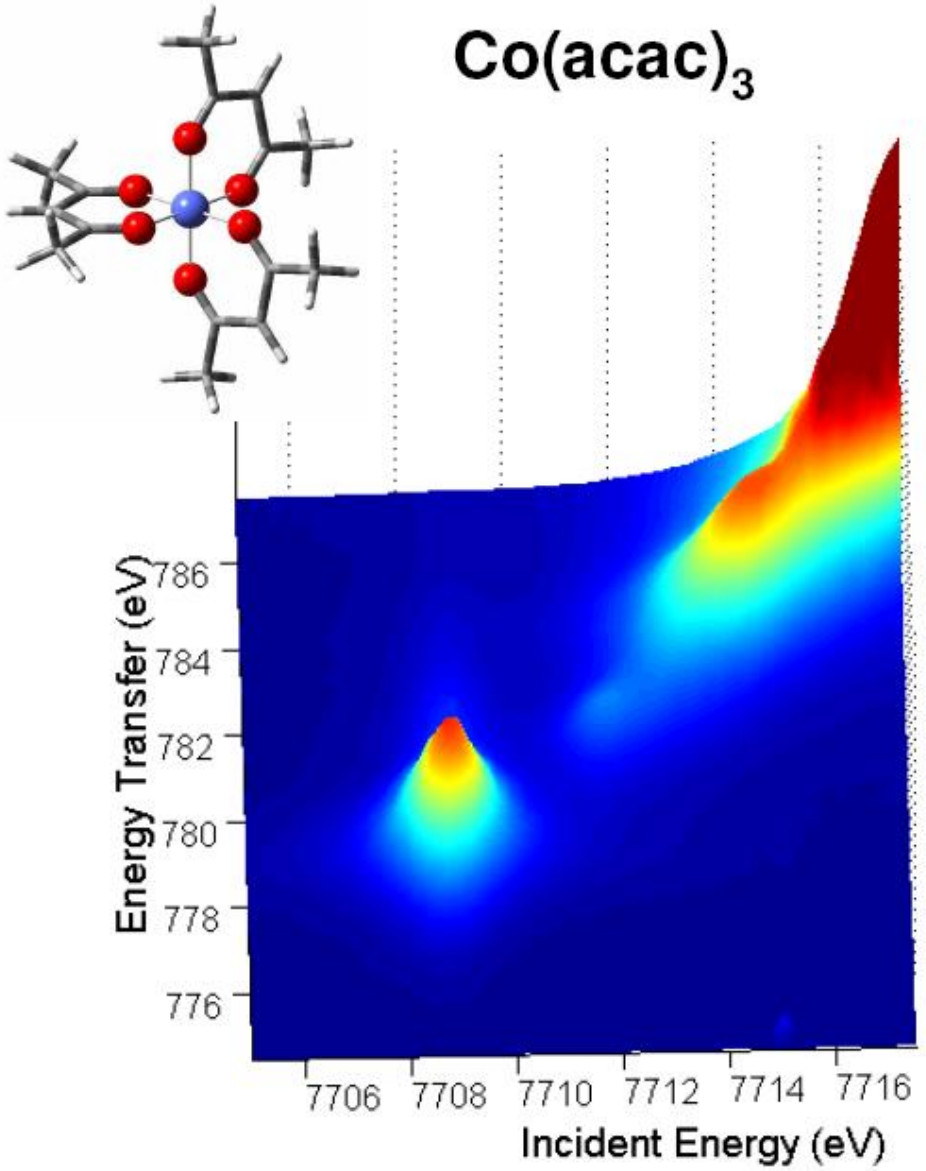
low-spin Co^{III}
$3d^6$ $[^1A_1]$
T_{2g} full
E_g empty



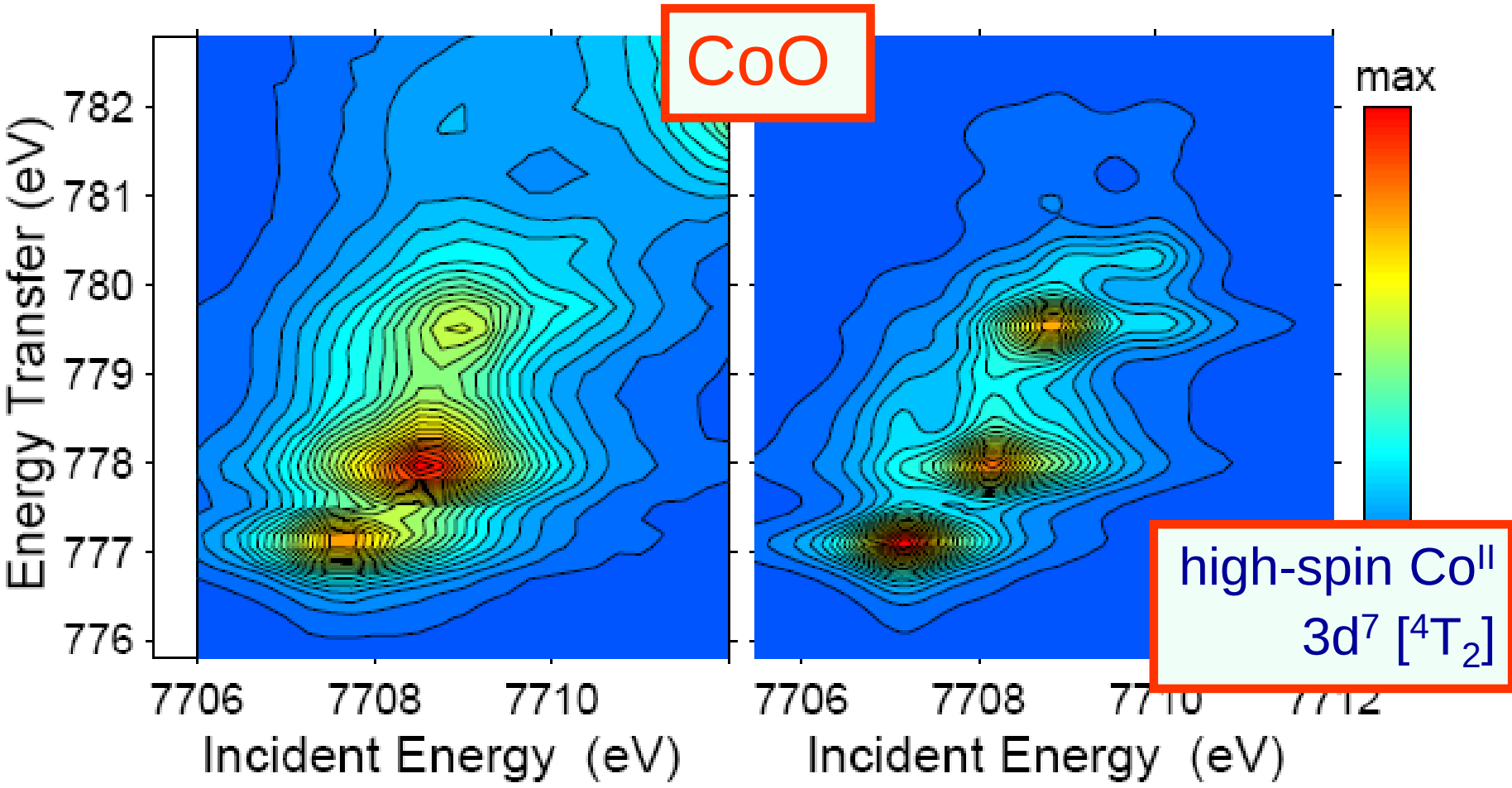
1s2p RIXS of transition metal ions

low-spin Co^{III}
$3d^6$ [$^1A_1$]
T_{2g} full
E_g empty





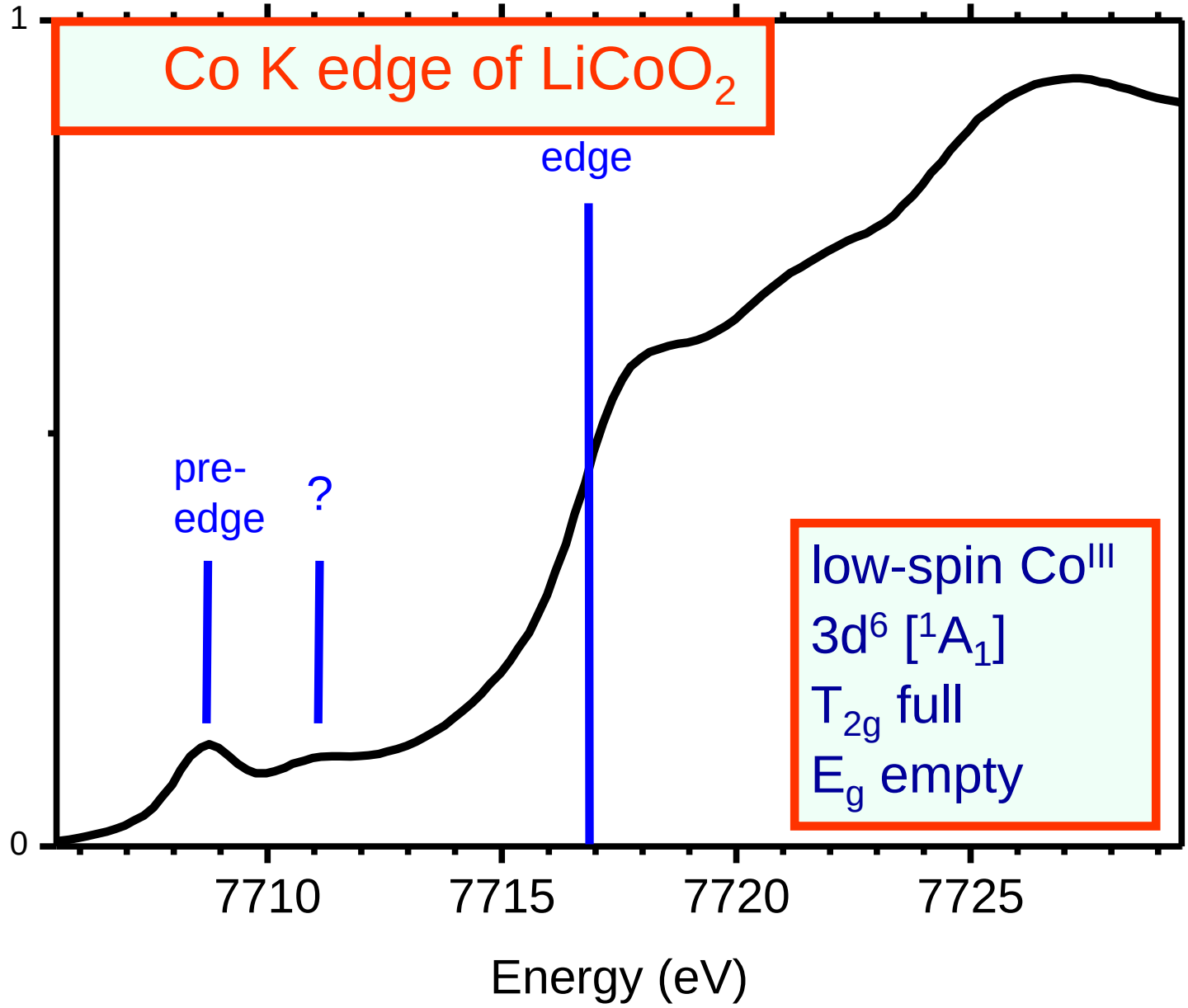
Sharper pre-edge structures in 1s XAS



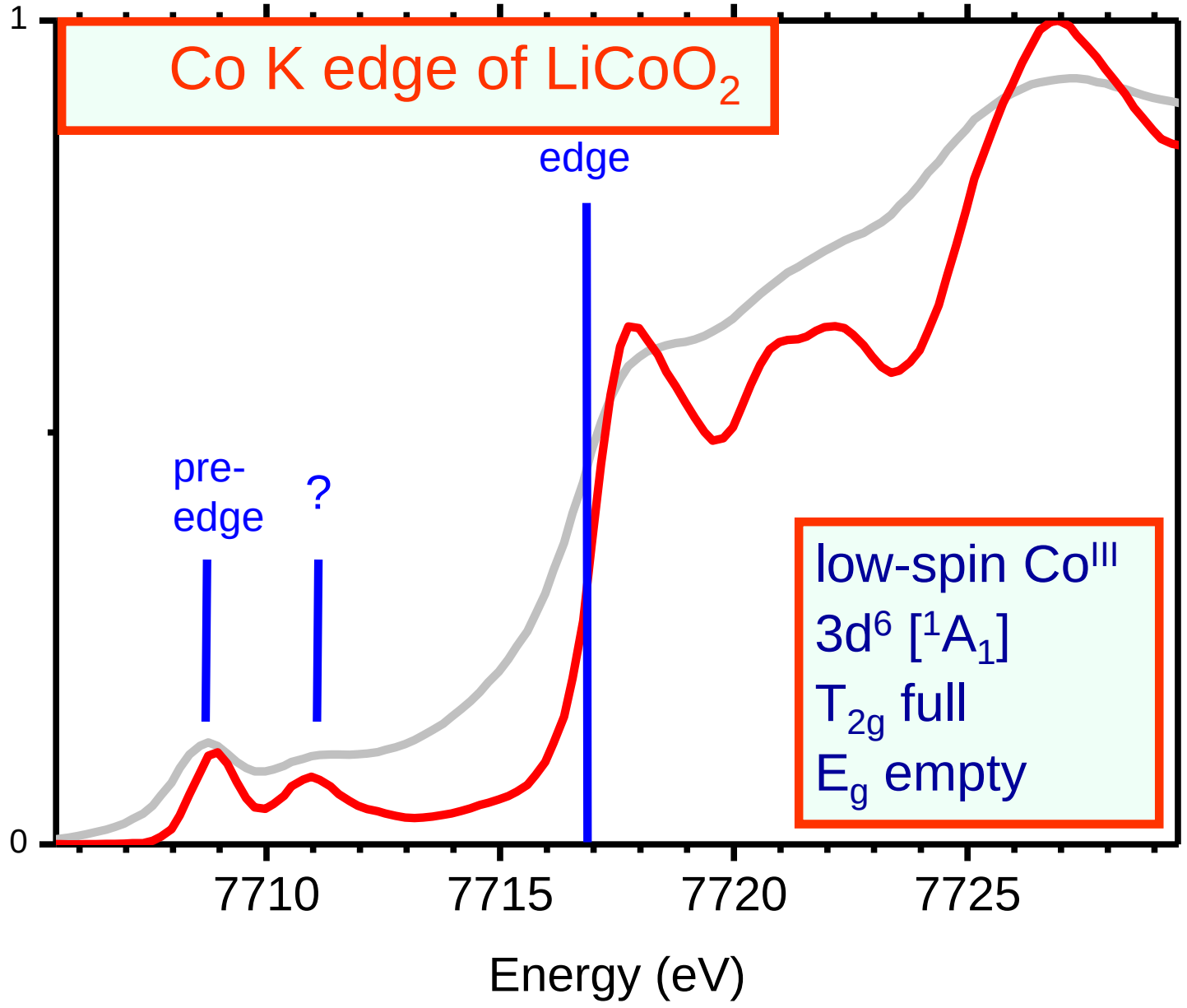
Only quadrupole peaks visible

$3d^7 \rightarrow 1s^1 3d^8 \rightarrow 2p^5 3d^8$

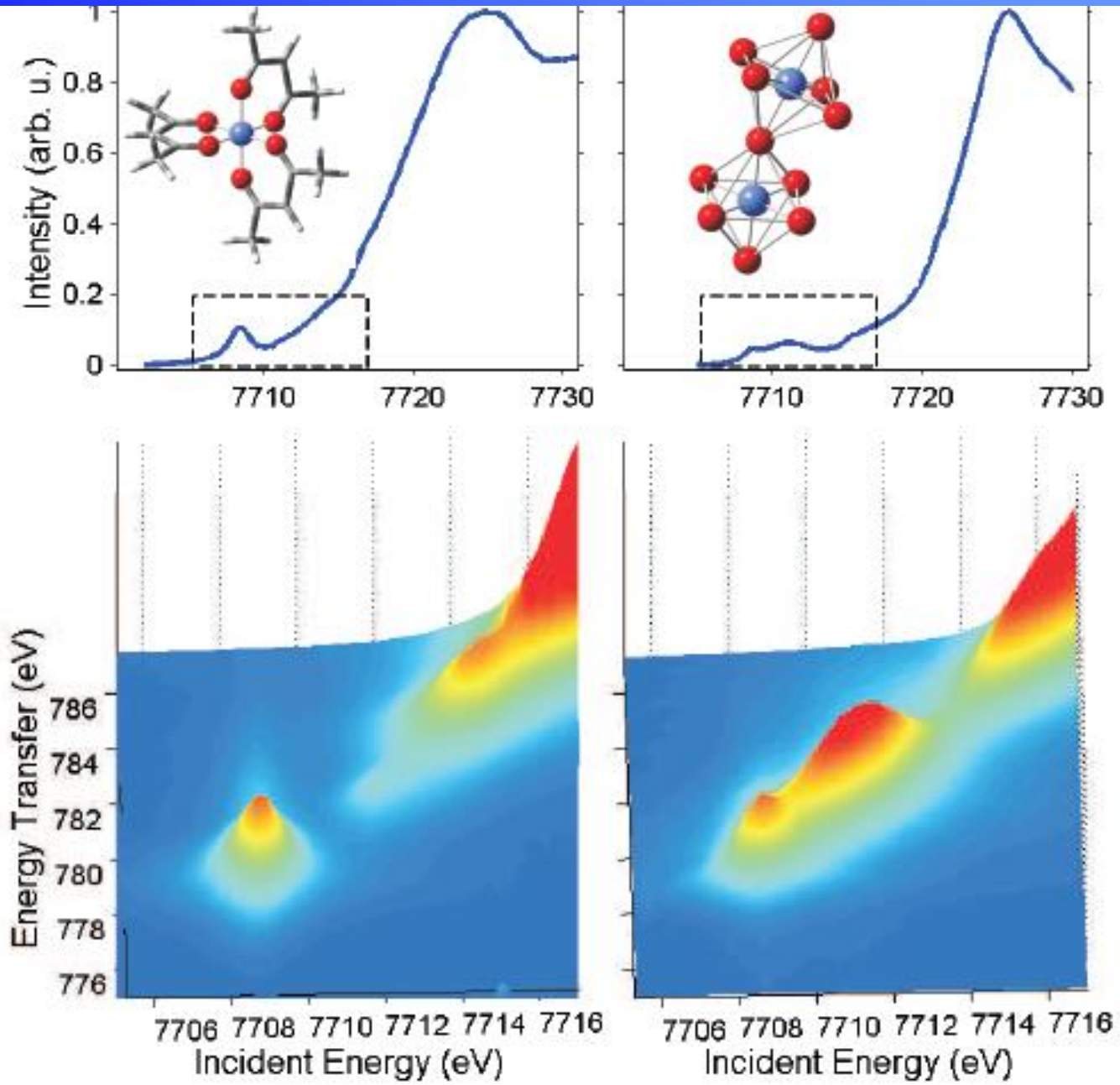
Pre-edges structures in 1s XAS



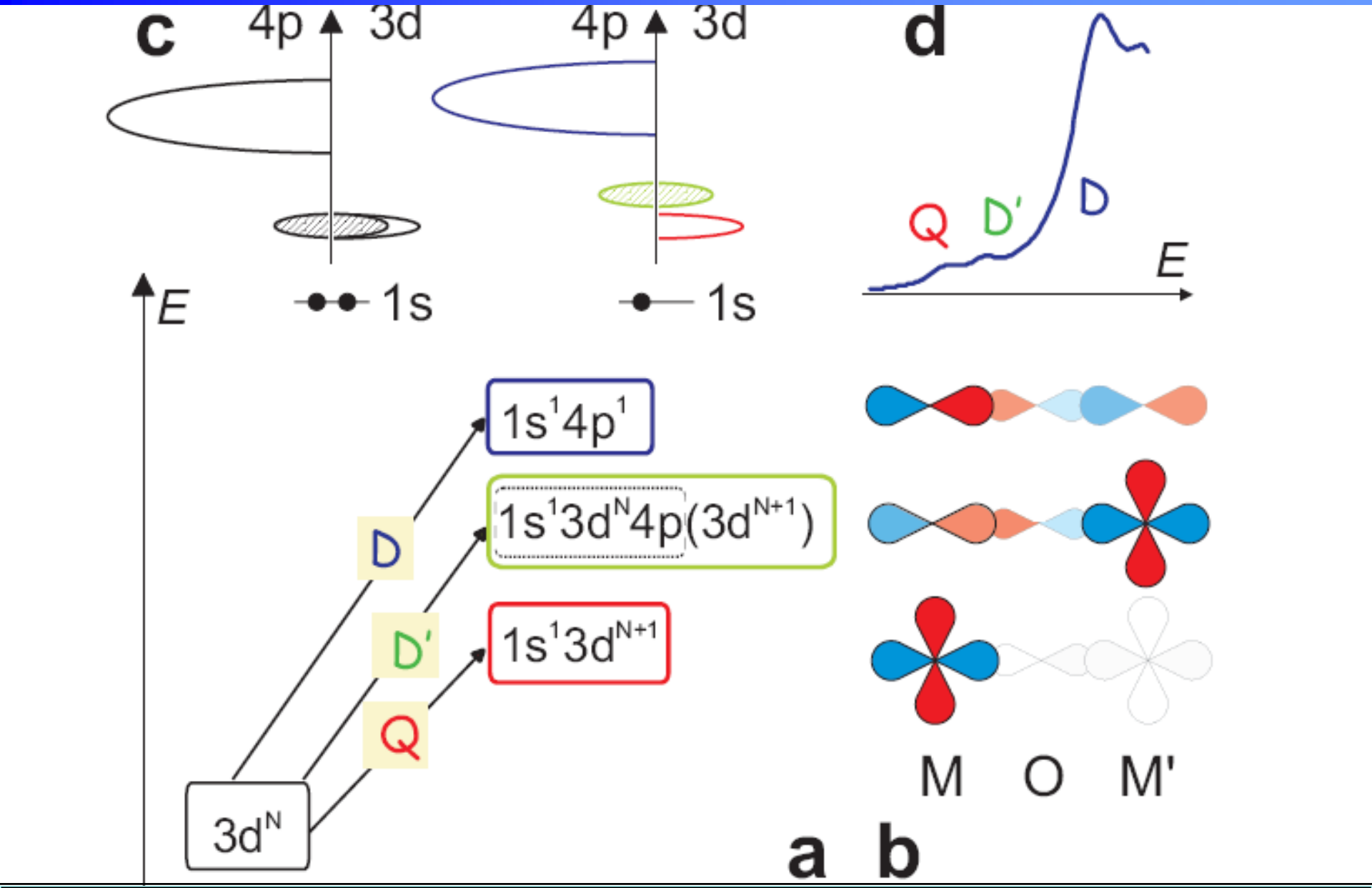
Pre-edges structures in 1s XAS



Pre-edges structures in 1s XAS

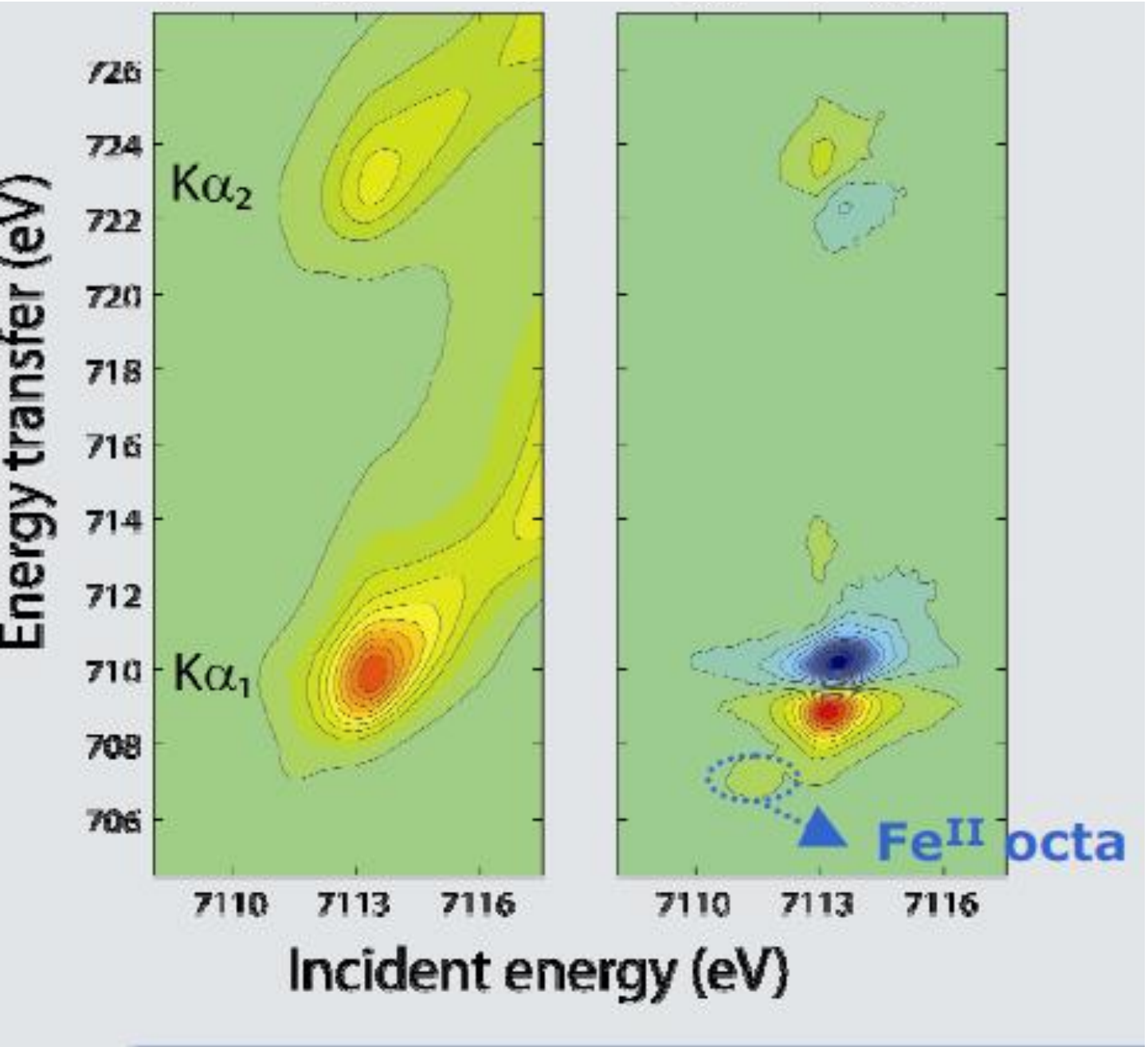


Pre-edges structures in 1s XAS

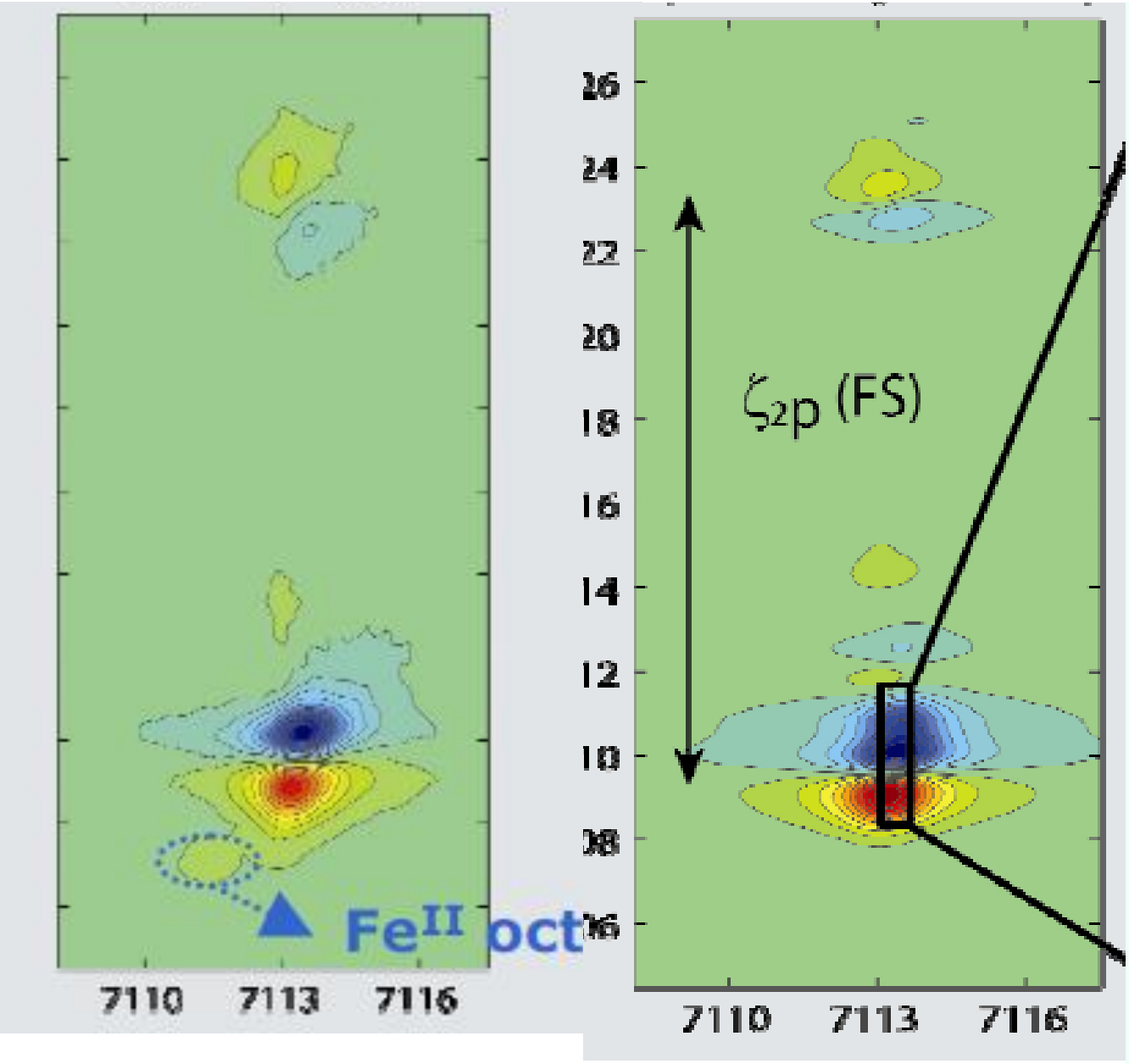


J. Phys. Cond. Matt. 21, 104207 (2009); Phys. Rev. B. 81, 115115 (2010)

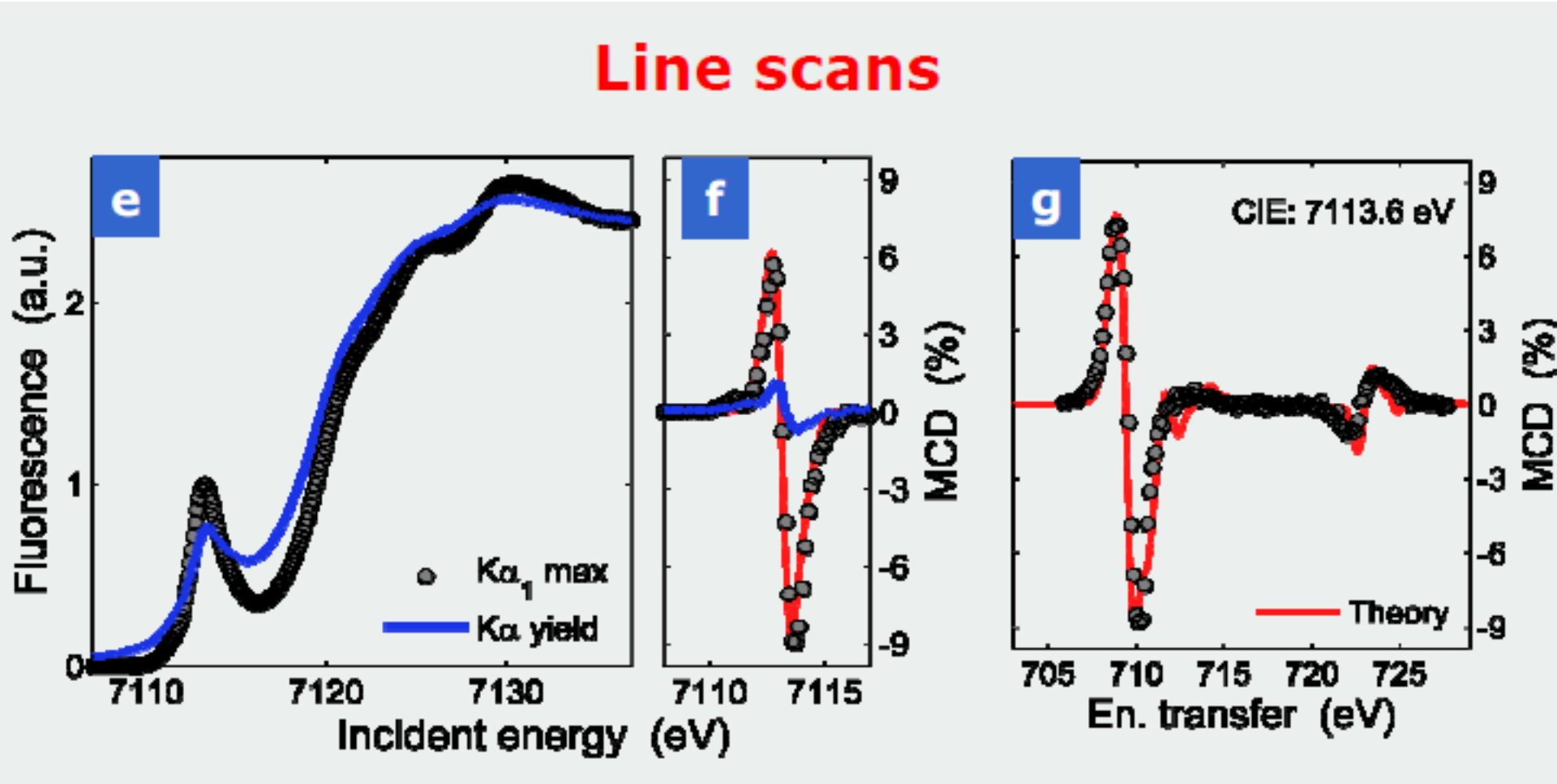
RIXS-MCD at the K pre-edge of Fe_3O_4



RIXS-MCD at the K pre-edge

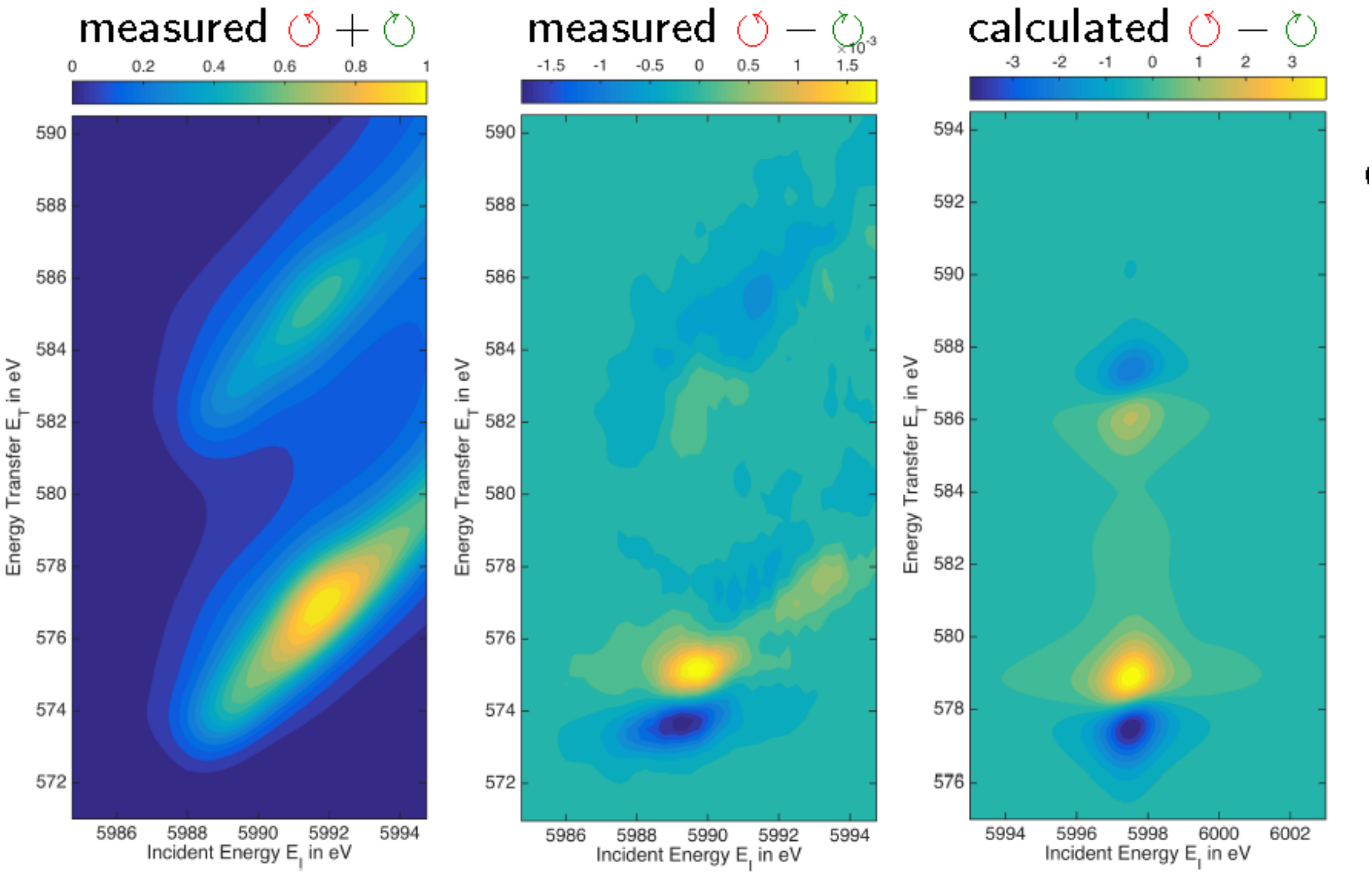


RIXS-MCD at the K pre-edge



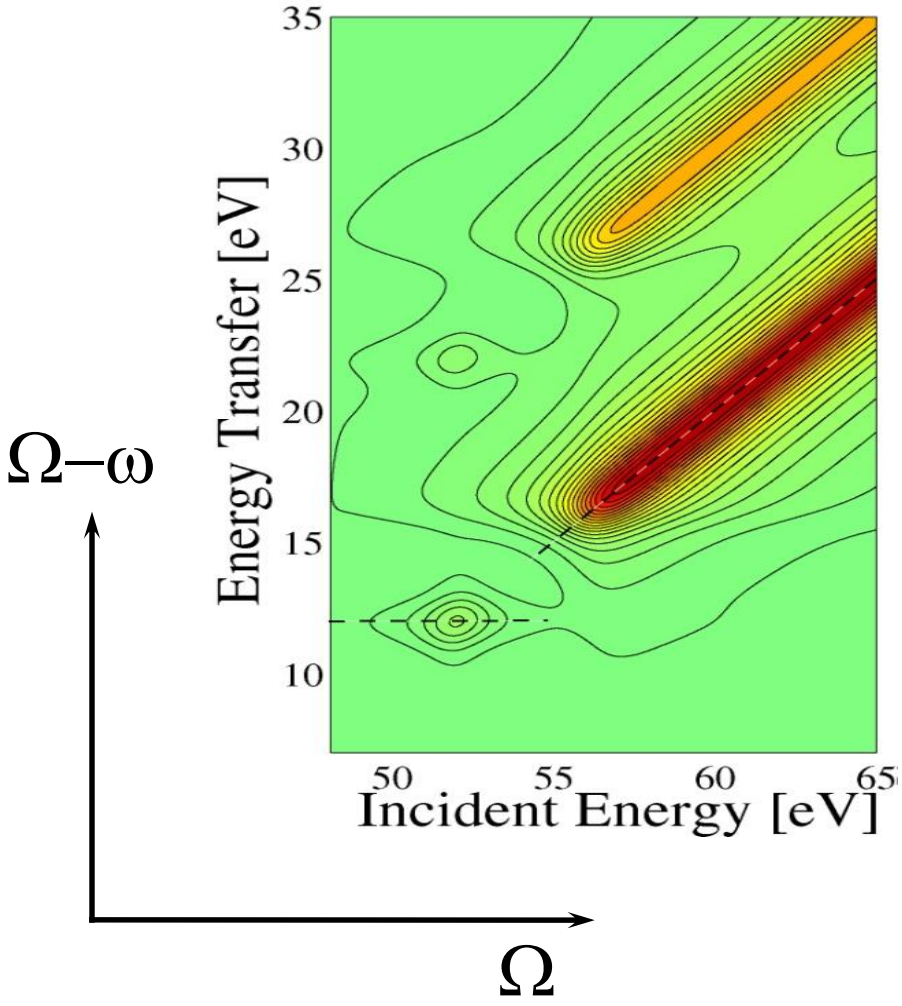
XMCD at high-pressure

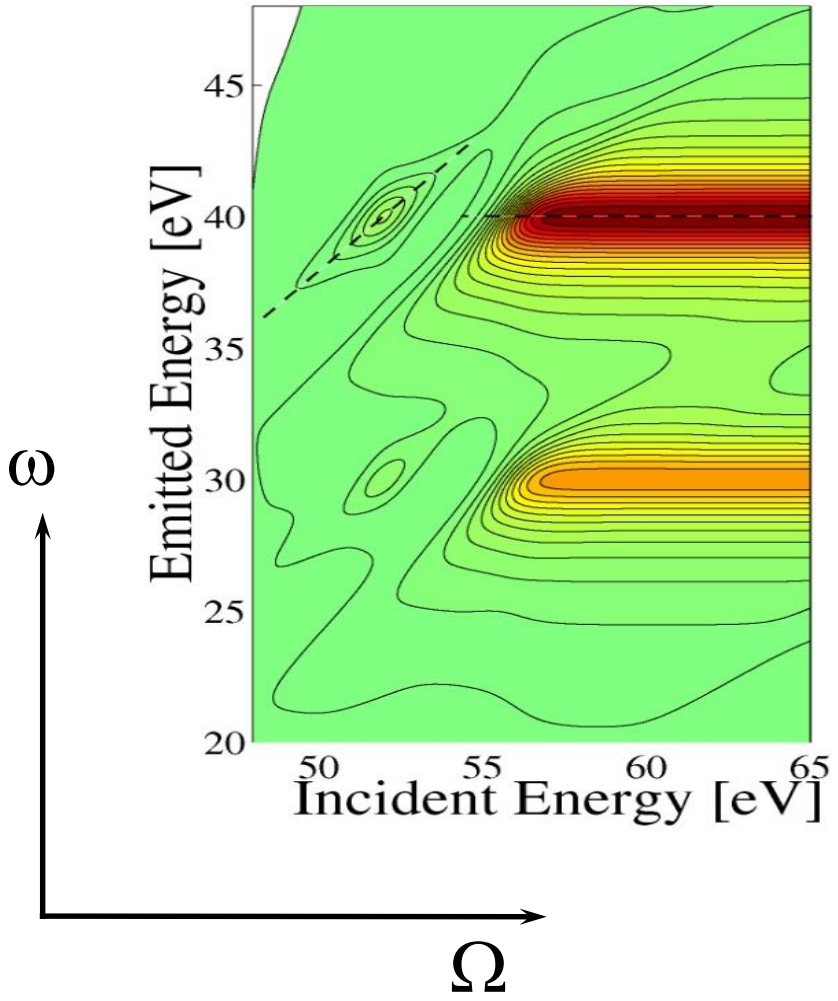
RIXS-MCD of CrO_2



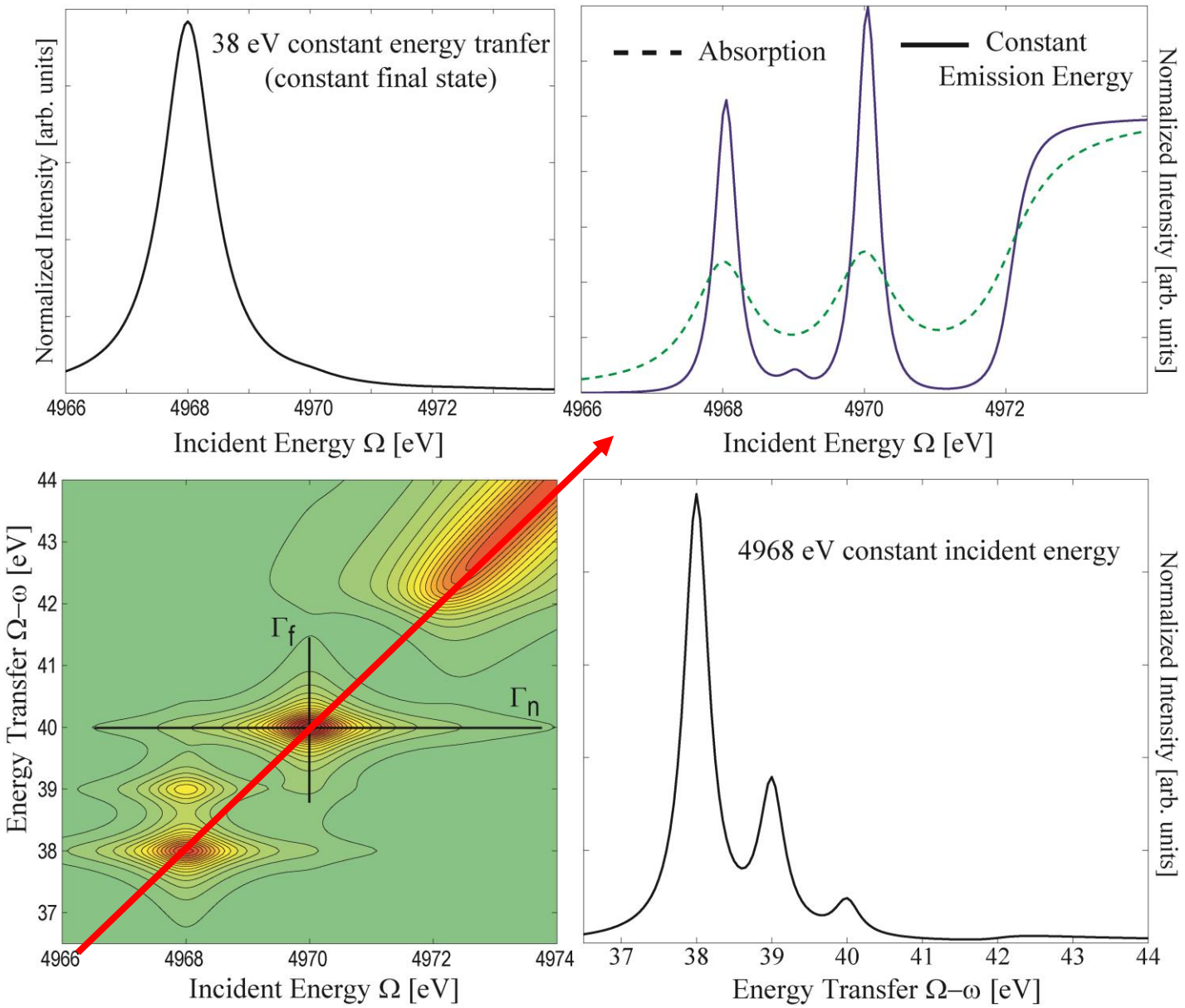
[Zimmermann et al. J. Elec. Spec (2017)]

1s2p RIXS: the RIXS plane





1s2p RIXS: the RIXS plane



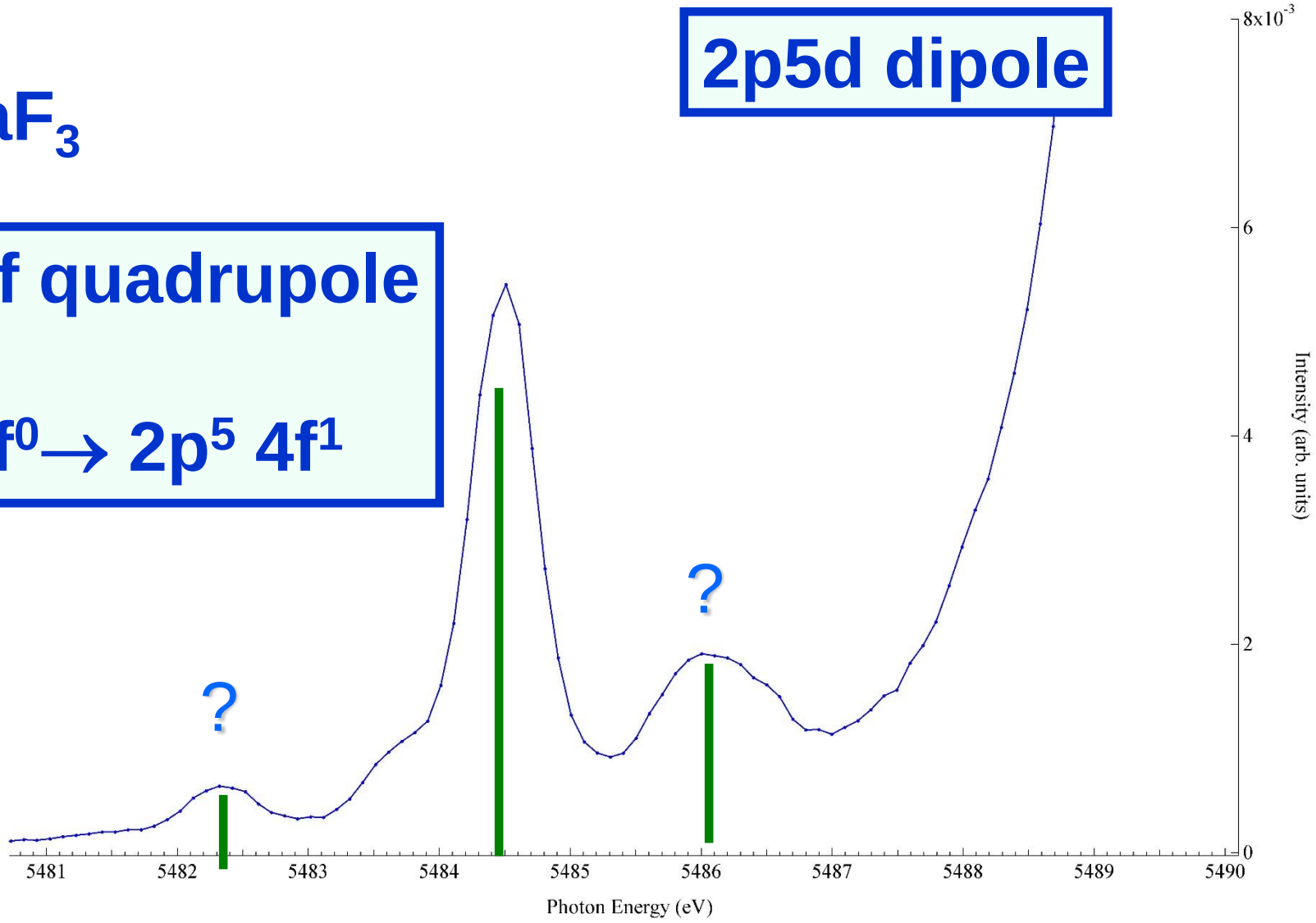
Does HERFD measure X-ray Absorption?

LaF_3

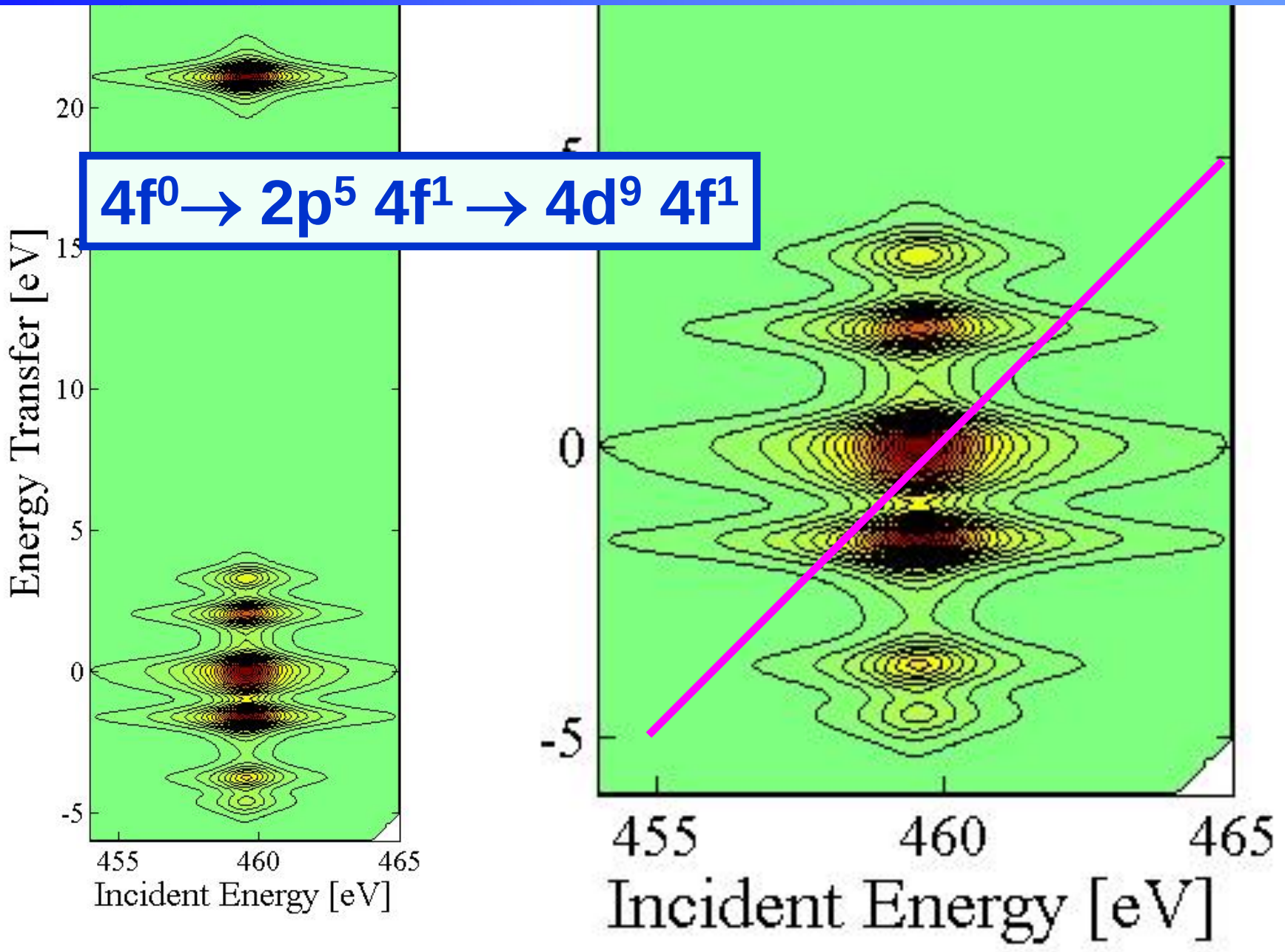
2p4f quadrupole

$4f^0 \rightarrow 2p^5\ 4f^1$

2p5d dipole



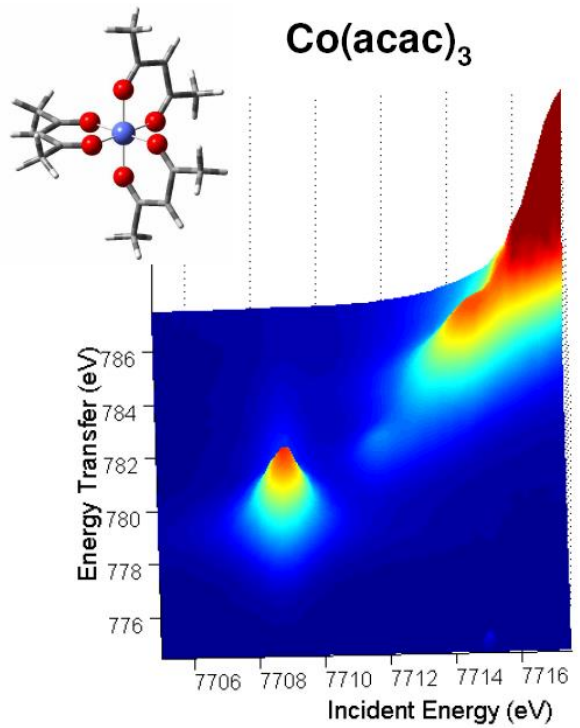
2p4d RIXS of LaF_3



RIXS of transition metal systems

- Reduce lifetime from 1.5 to 0.2 eV
- Reveal new features at pre-edge

- Valence specific EXAFS
  [Inorg. Chem. 41, 3121 (2002)]
- Spin-polarized XAS
- Range extended EXAFS
- Background free FY for low conc.
- RIXS-MCD



Core-valence RIXS

RIXS

Resonant Inelastic X-ray Scattering

or

Resonant X-ray Raman Scattering (RXRS)

Resonant X-ray Emission Spectroscopy (RXES)

or

Resonant X-ray Energy Loss Spectroscopy (R-XELS)

2p3d RIXS of transition metal ions

10^{-10}

10^{-8}

$.5 \times 10^{-6}$

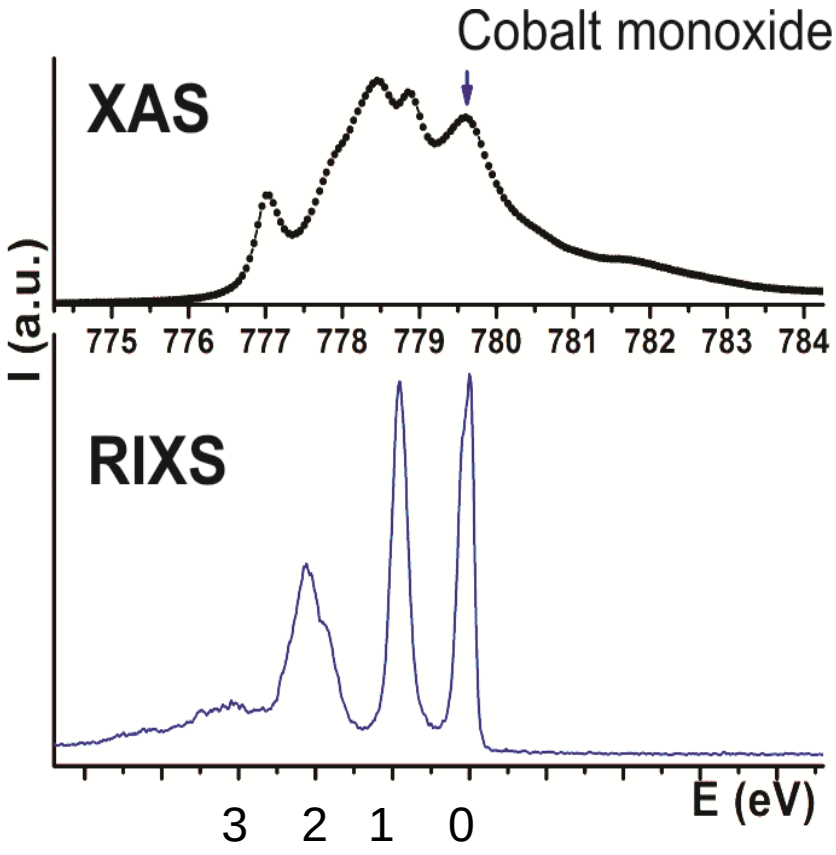
10^{-5}

core

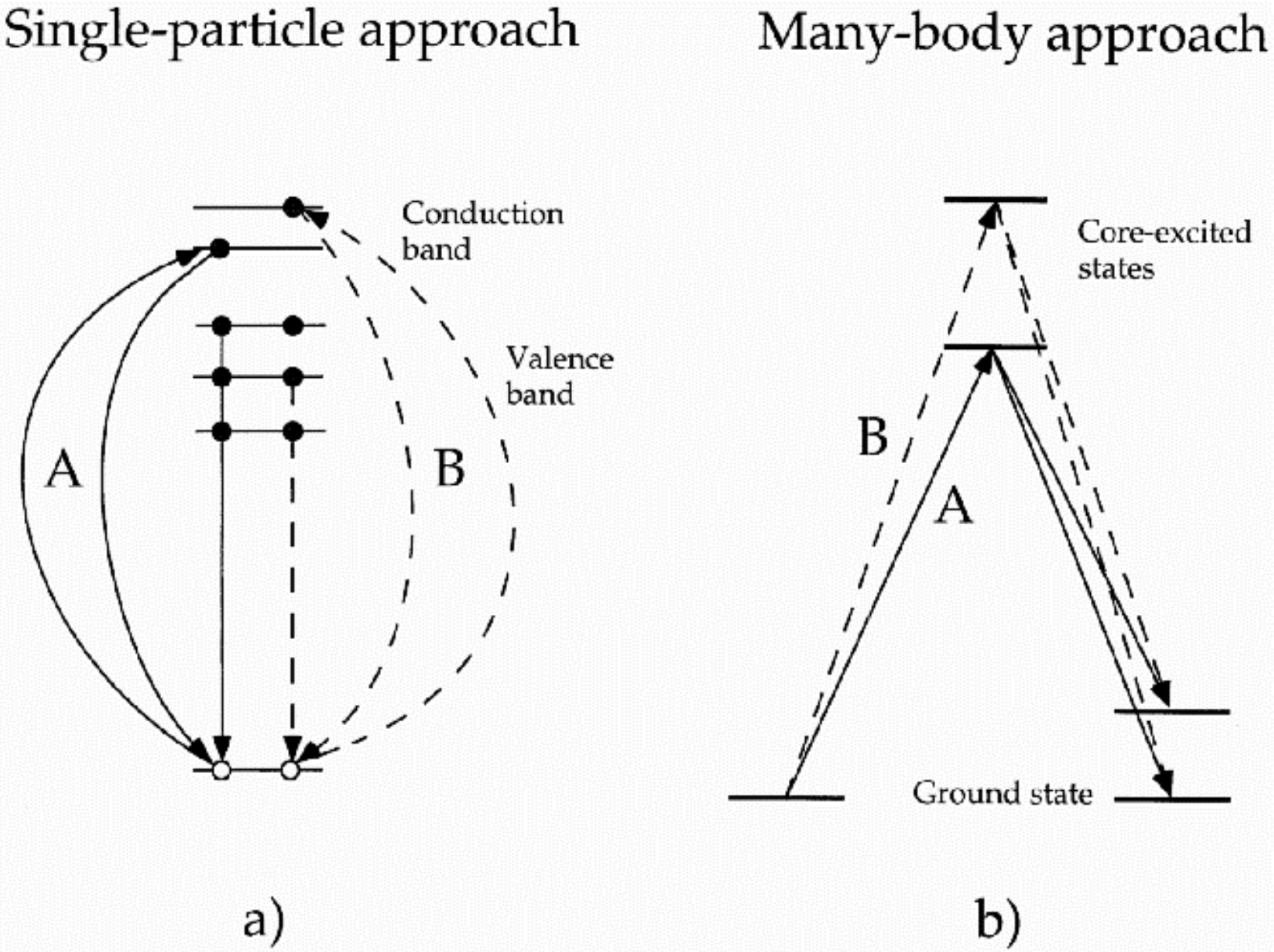
electronic
dd, CT

magnon
vibrations

Ψ_0

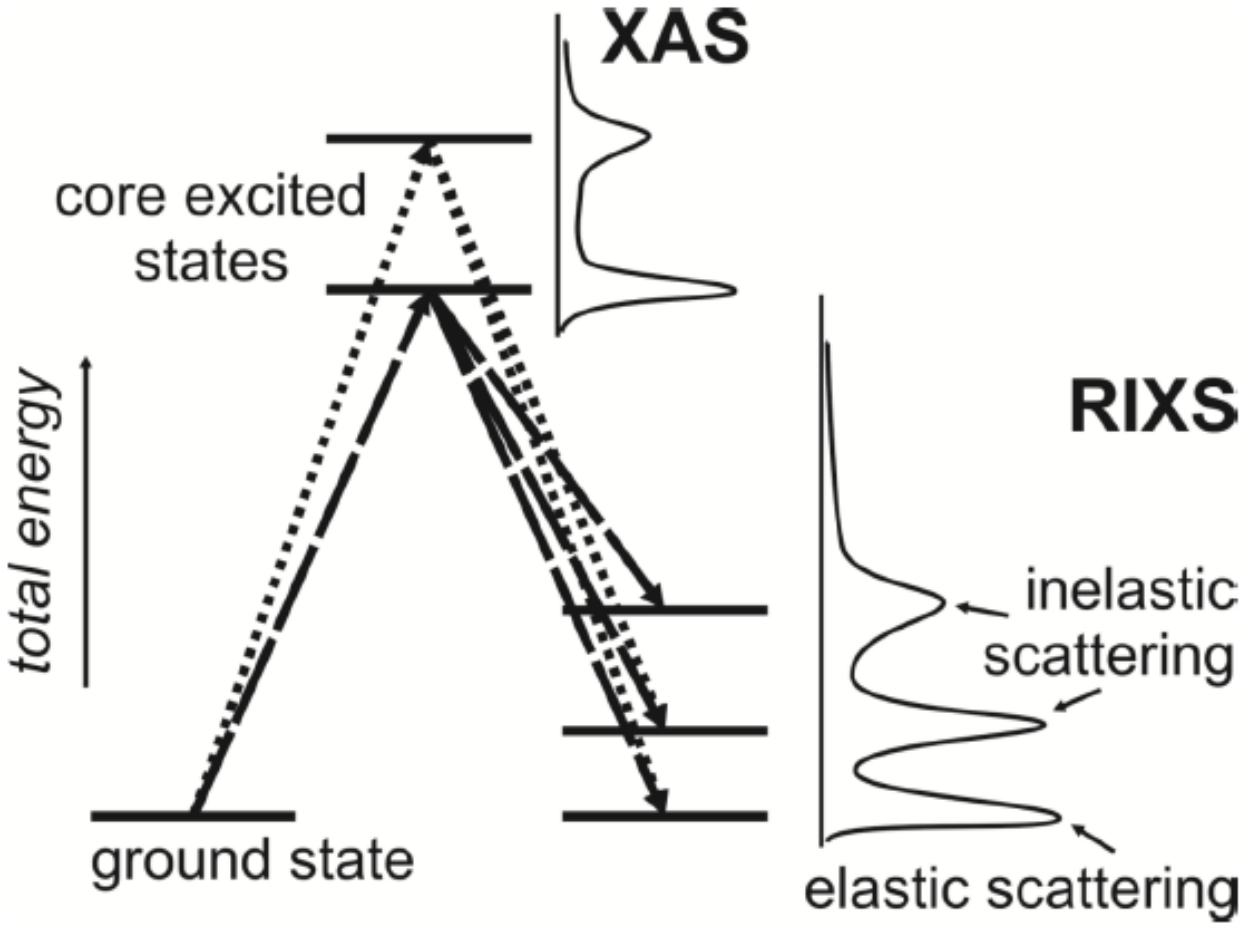


Resonant Inelastic X-ray Scattering



Butorin J. Elec. Spec 110, 213 (2000)

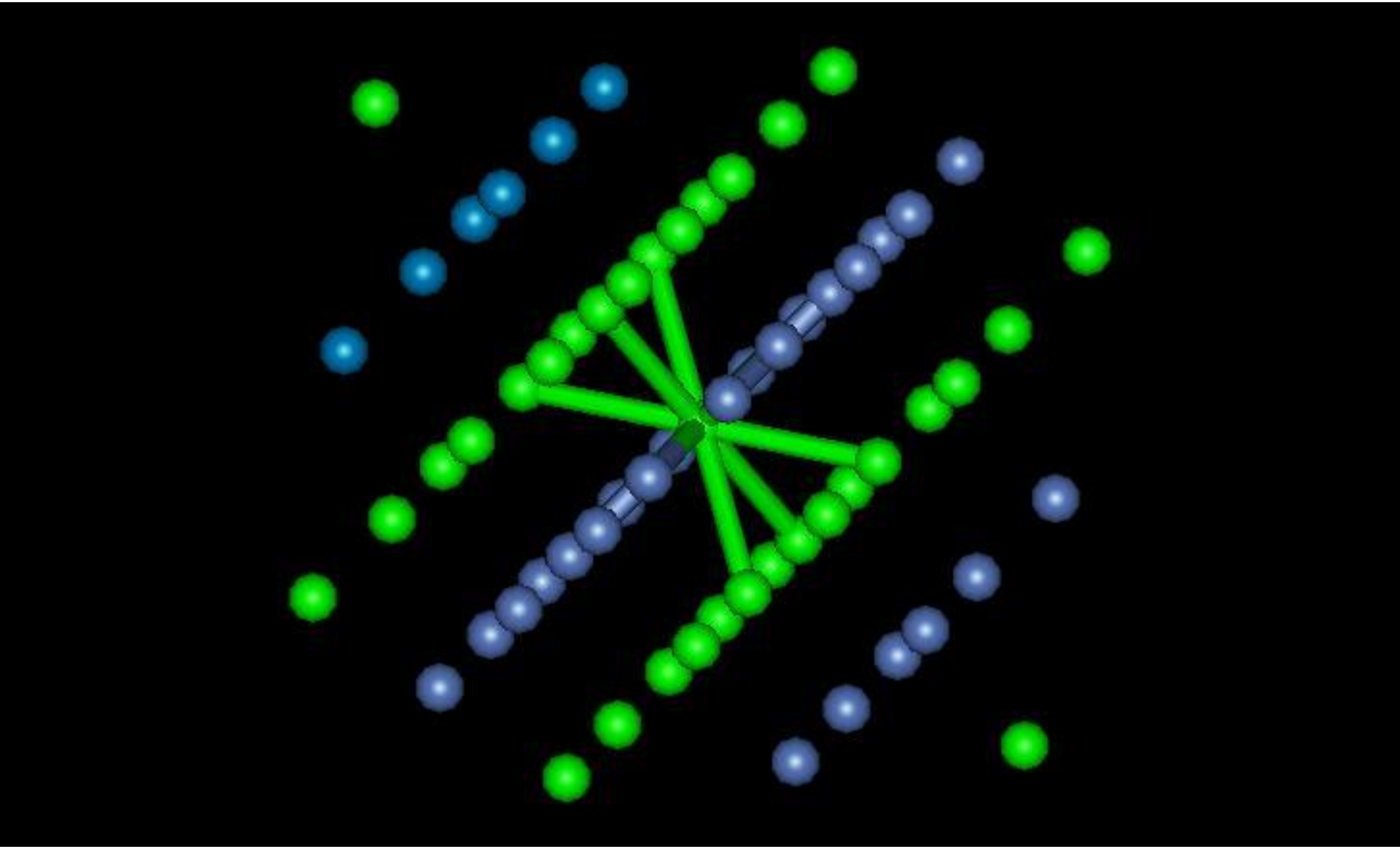
resonant inelastic x-ray *spectroscopy*



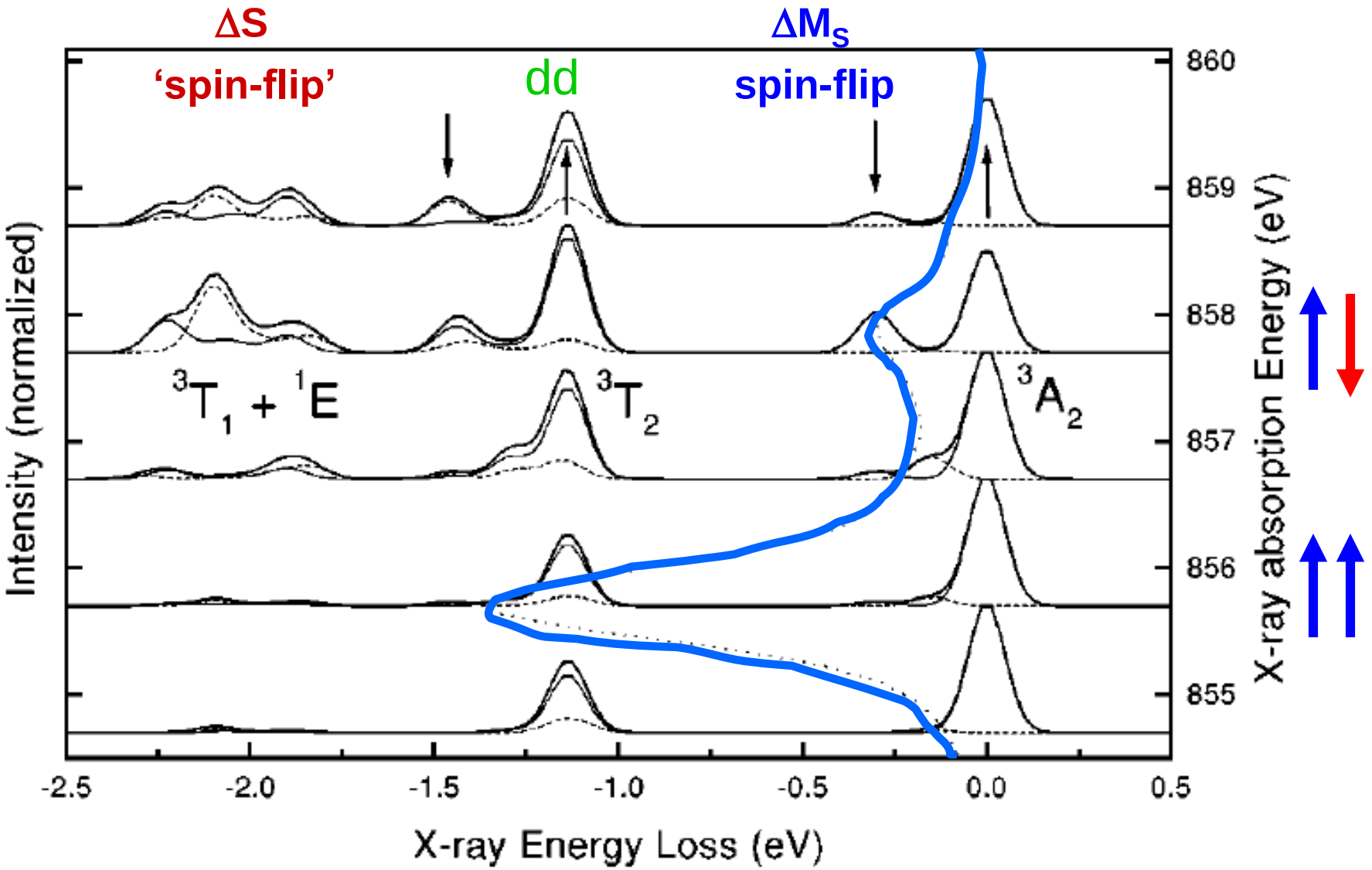
$$F(\Omega,\omega)=\sum_j\left|\sum_i\frac{<f|T_2|i><i|T_1|g>}{E_g+\hbar\Omega-E_i+\mathrm{i}\Gamma_i}\right|^2\times\frac{\Gamma_f/2\pi}{(E_g+\hbar\Omega-E_f-\hbar\omega)^2+\Gamma_f{}^2/4}$$

2p3d RIXS of NiO

Ni^{II} $3d^8$ [↑↑] → $2p^5 3d^9$[jj] → $3d^8$[↓↓]

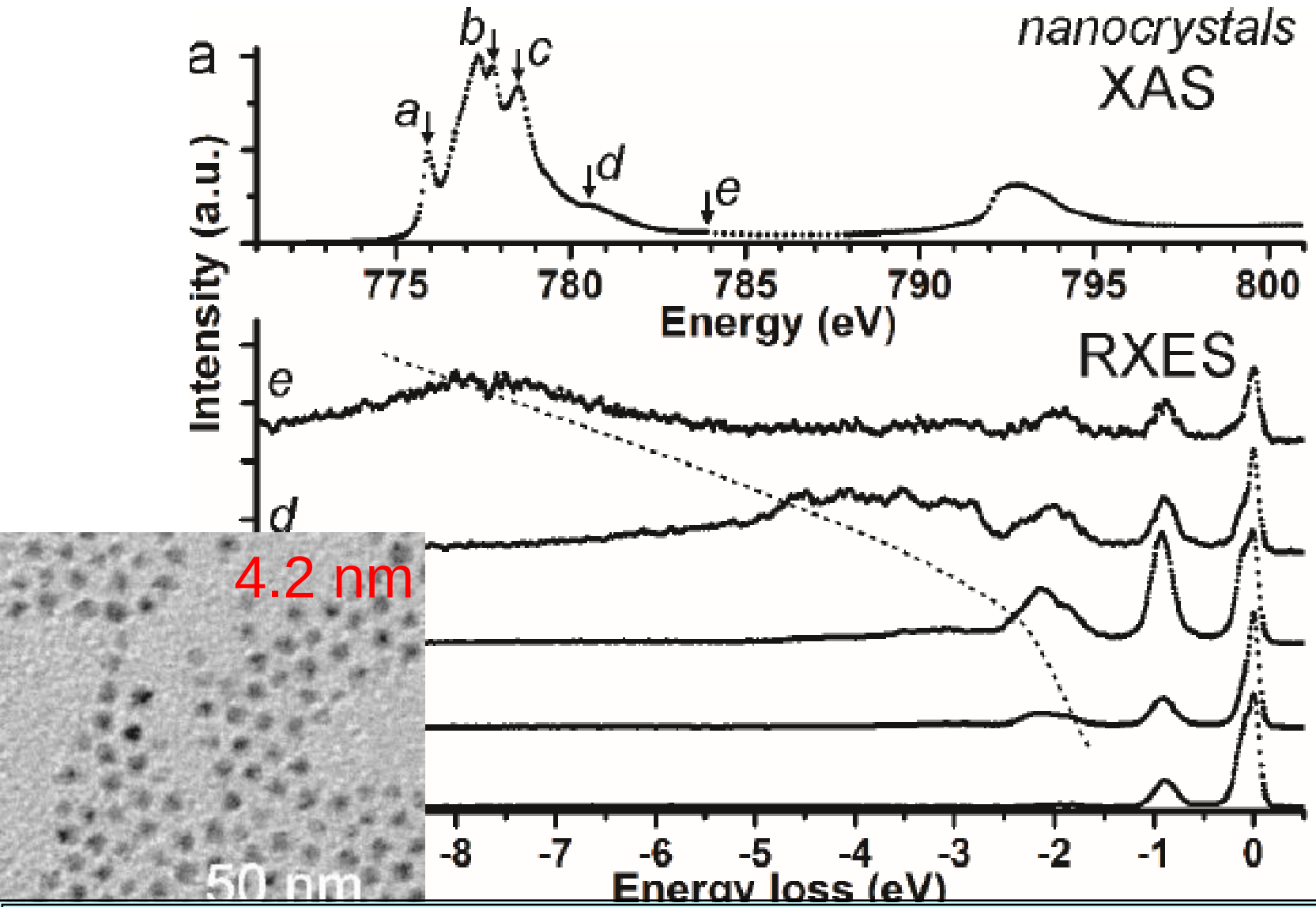


2p3d RIXS of NiO



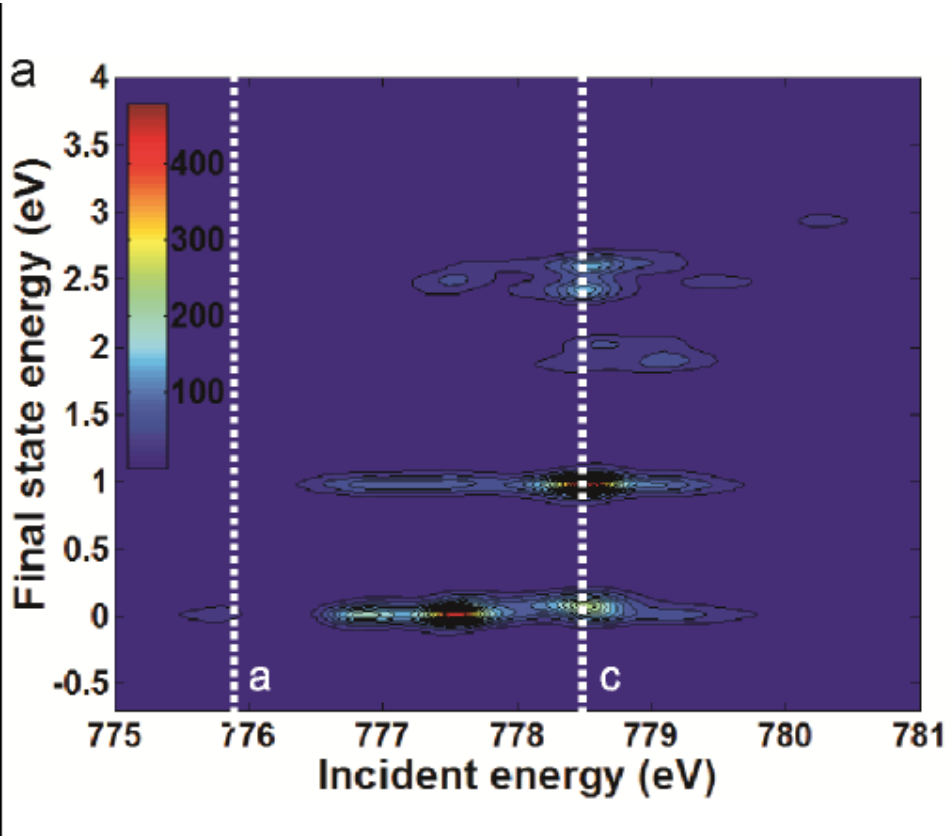
Phys. Rev. B. 57, 14584 (1998)

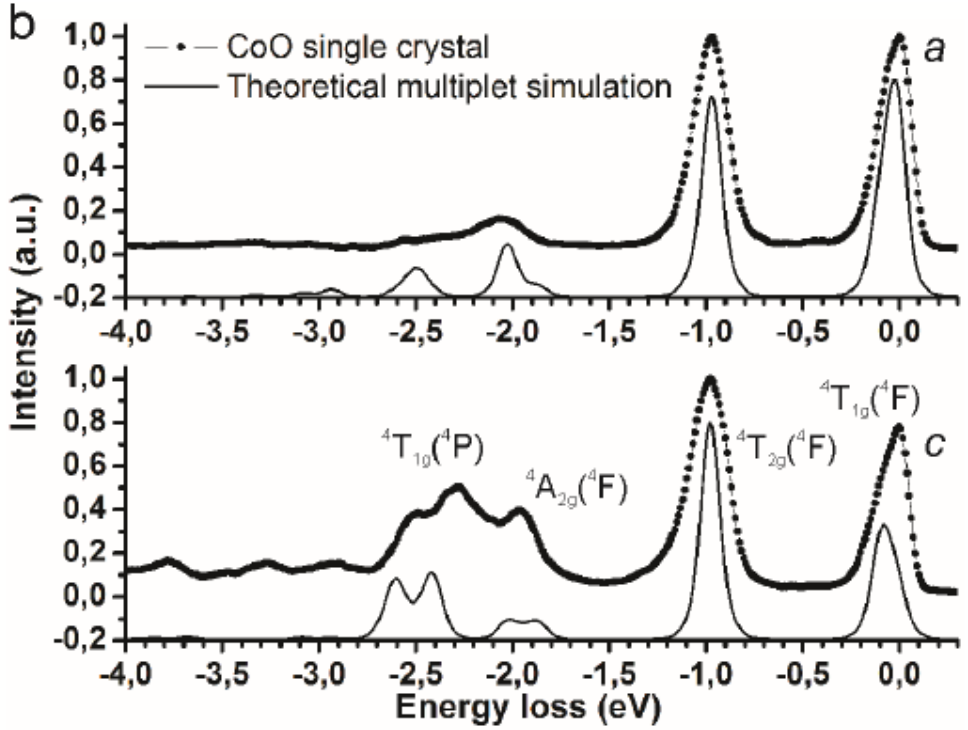
2p3d RIXS of CoO



van Schooneveld et al., J. Phys. Chem. C 116, 15218 (2012)

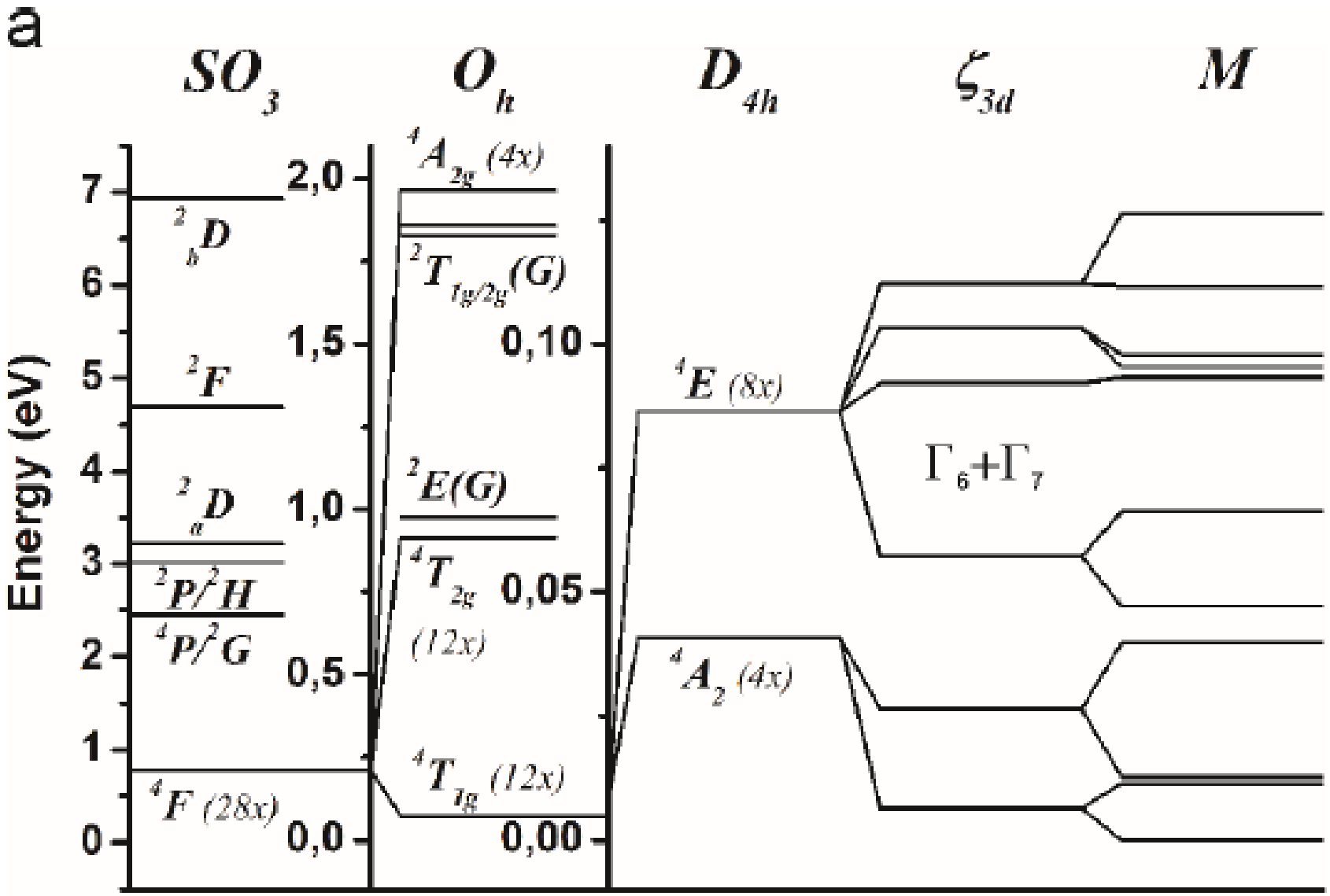
2p3d RIXS of CoO





van Schooneveld et al., J. Phys. Chem. C 116, 15218 (2012)

2p3d RIXS of CoO



van Schooneveld et al., J. Phys. Chem. C 116, 15218 (2012)

2p3d RIXS

polarization, angles
(in, sample, out)

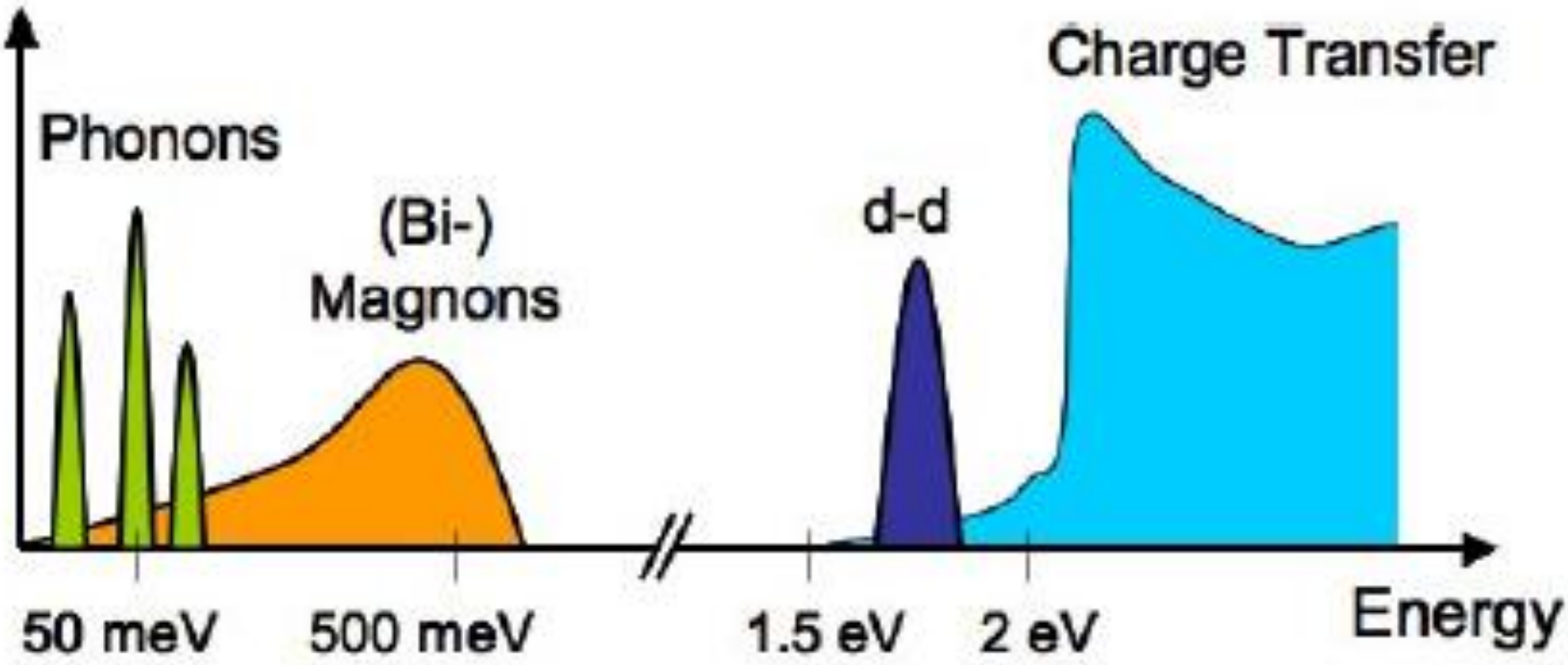
eV
electron-electron
crystal field
charge transfer

meV
spin-orbit, magnetic
distortions
vibrations

RIXS1998:
500 meV

RIXS 2018:
30 meV

Energy dependence in 2p3d RIXS



In 2p3d RIXS the intensity of charge transfer is smaller than dd-excitations

[Ament et al., Rev. Mod. Phys. 83, 705 (2011)]

Energy dependence in 2p3d RIXS

2 eV – 10 eV
- charge transfer

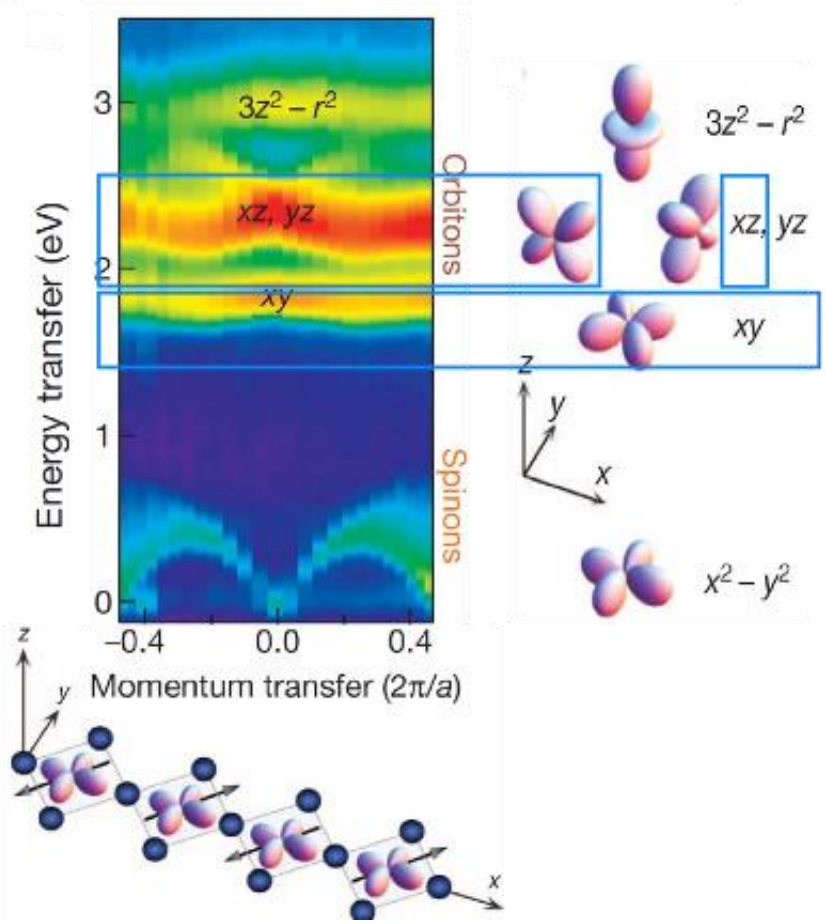
0.5 eV – 6 eV
- dd excitations (atomic + crystal field)

0.0 – 0.5 eV
- spin-flip (magnon)
- symmetry distortions
- HS-LS transition point
- spin-orbit coupling

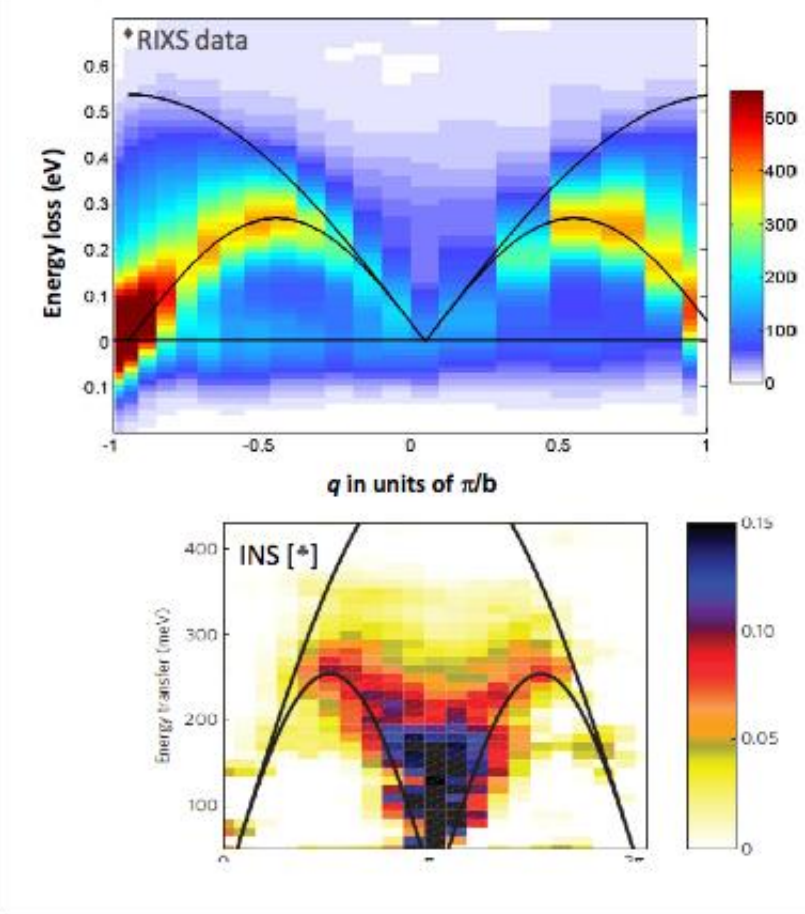
0.0 – 0.2 eV
- vibrations (phonon)

2p3d RIXS in cuprates

Sr_2CuO_3



$CaCu_2O_3$

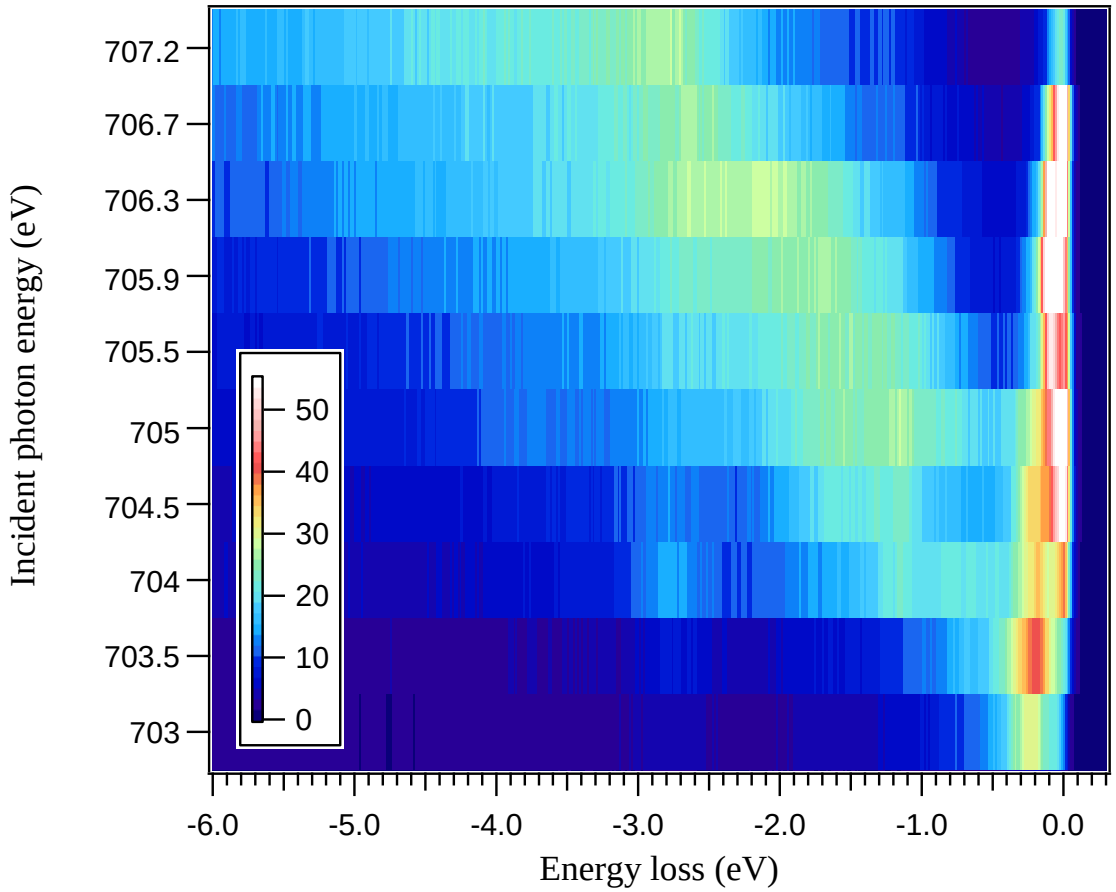


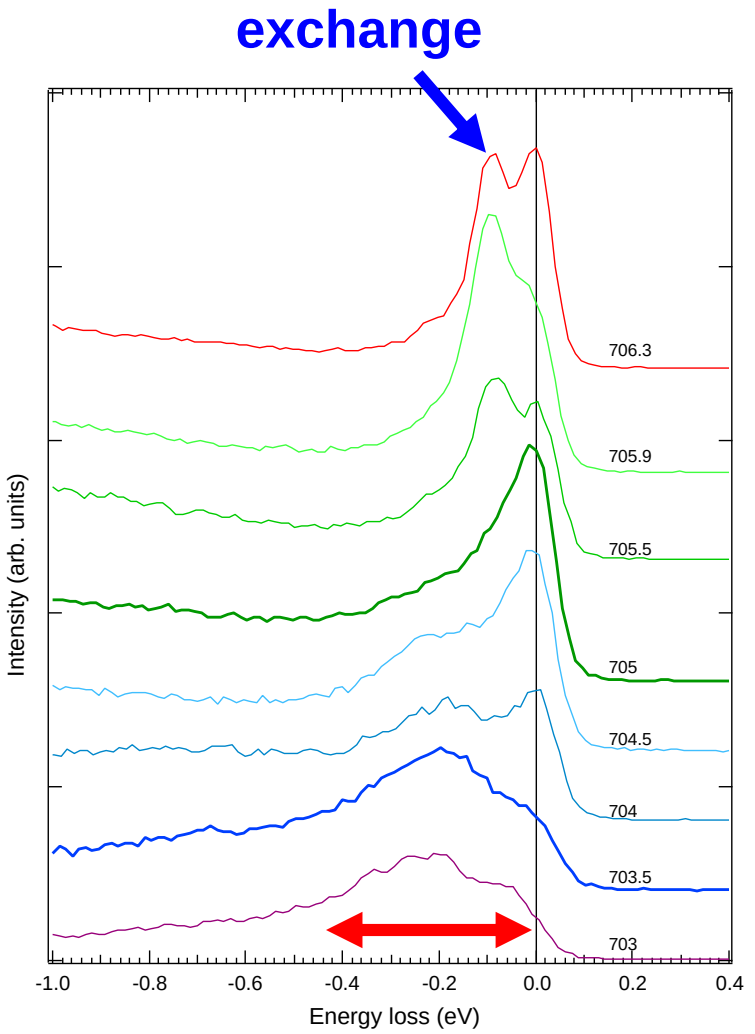
2p3d RIXS

Schlappa et al., Nature (2012)

Bisogni et al., arXiv:1310.8346

Select specific states in 2p3d RIXS (Fe_3O_4)

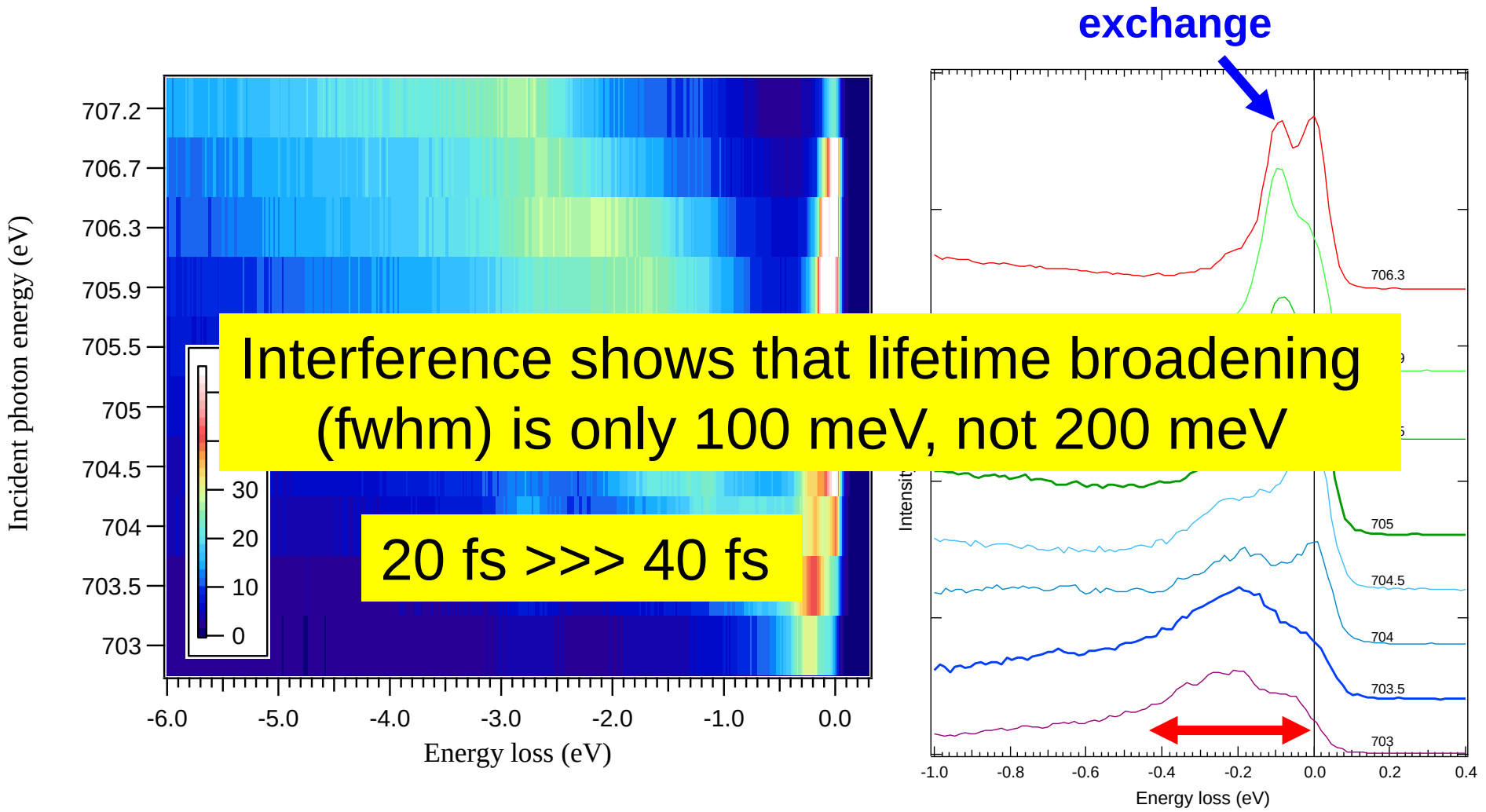




spin-orbit + exchange

[Huang et al. Nature Comm. 8, 15929 (2017)]

Select specific states in 2p3d RIXS (Fe_3O_4)

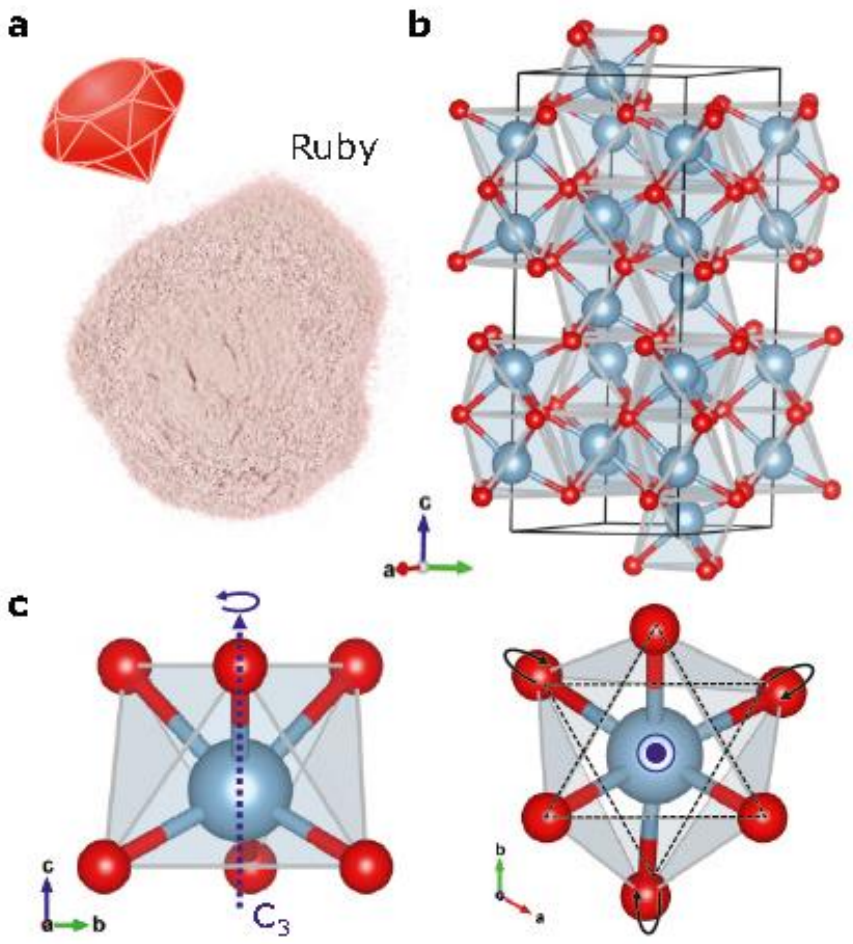


Interference shows that lifetime broadening (fwhm) is only 100 meV, not 200 meV

20 fs >>> 40 fs

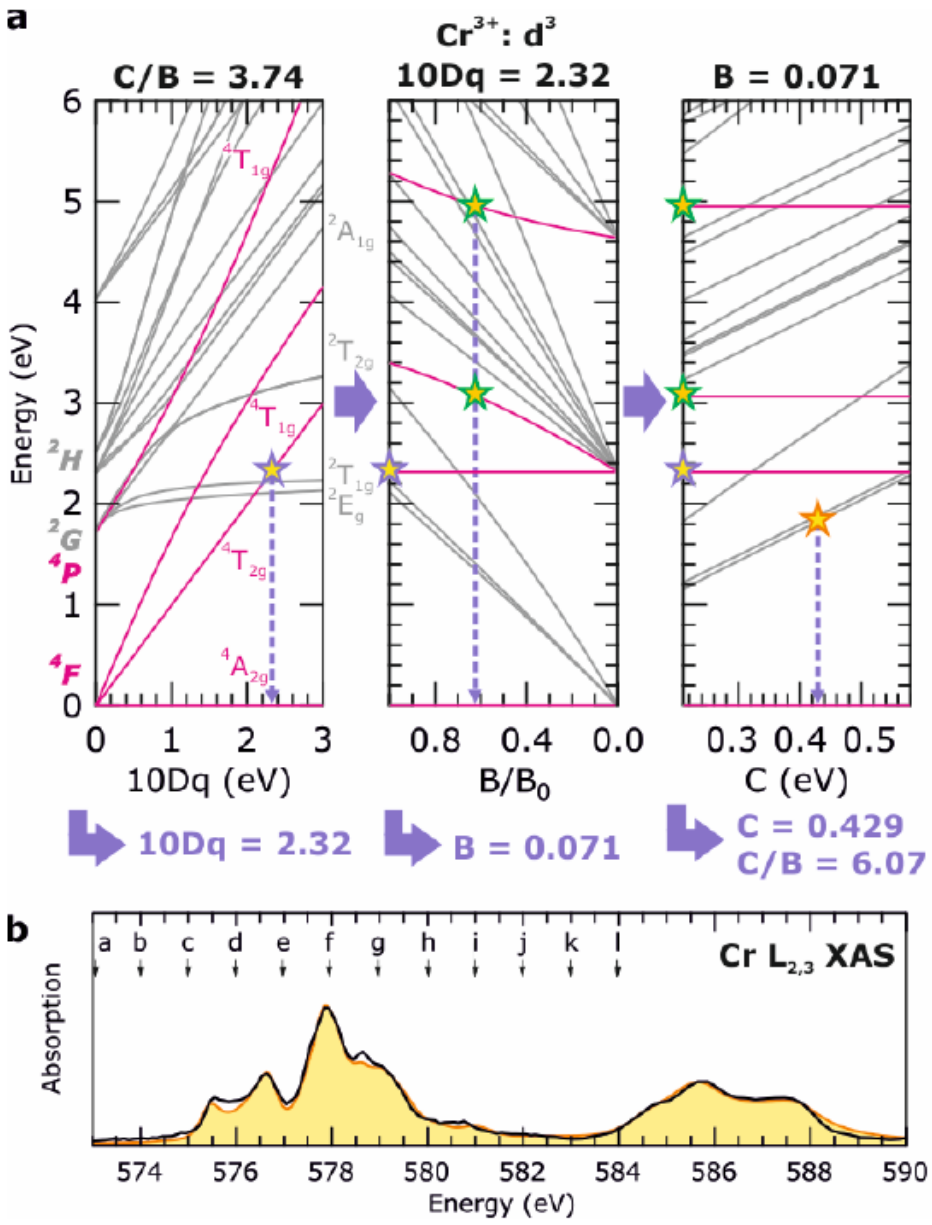
[Huang et al. Nature Comm. 8, 15929 (2017)]

2p3d RIXS of isolated chromium ions (ruby)

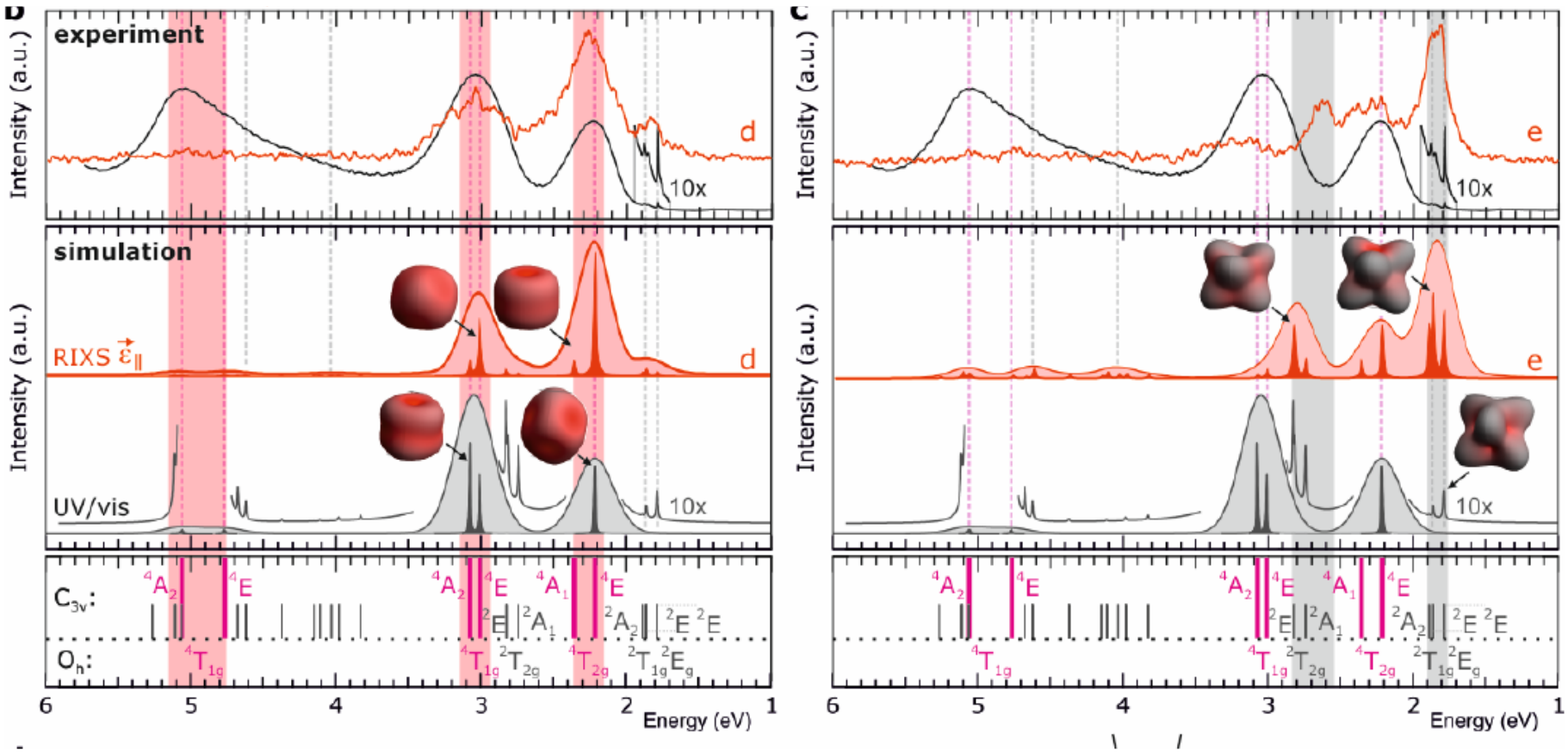


[Van Schooneveld, Hunault et al., unpublished]

Multiplet challenge: 2p3d RIXS on Cr^{3+}



Multiplet challenge: 2p3d RIXS on Cr^{3+}



- Optical resolution can be 0.01 meV

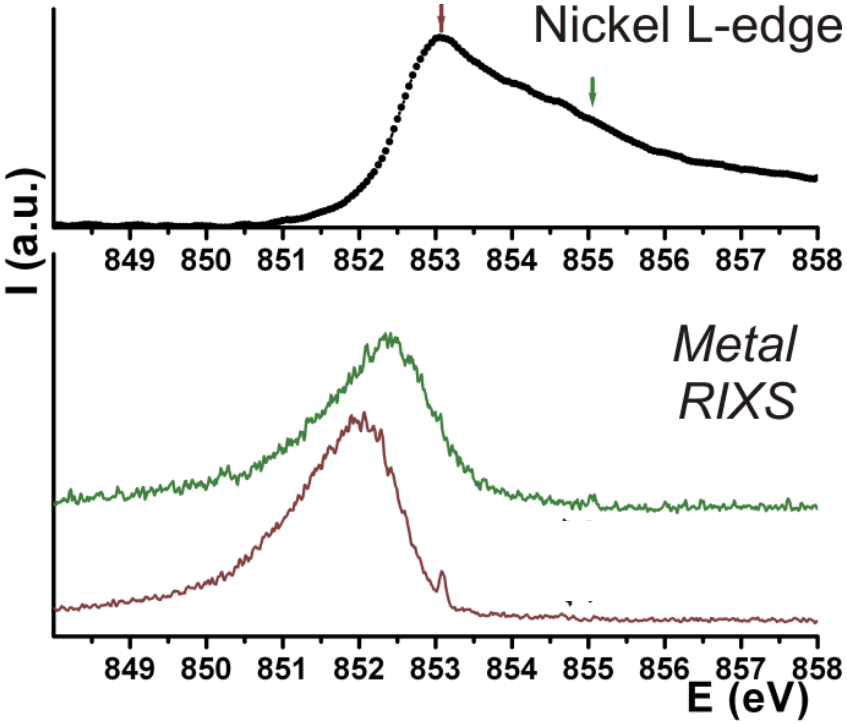
Spin-forbidden dd-excitations limited by experimental resolution

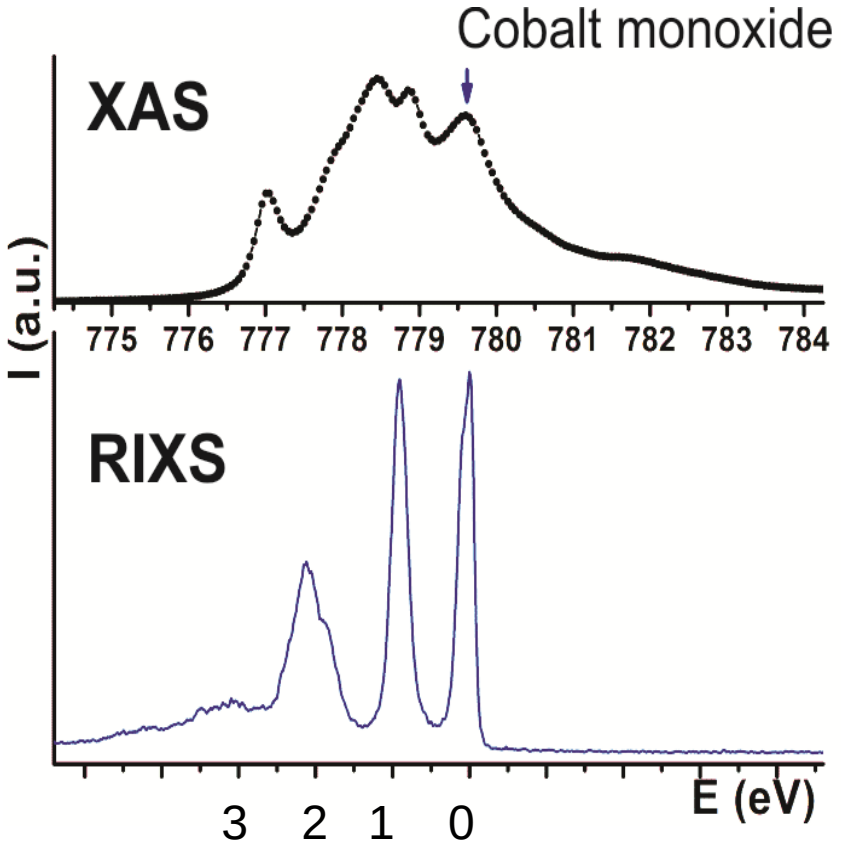
[Hunault, van Schooneveld, submitted]

RIXS and fluorescence

CoO: excitons → RIXS

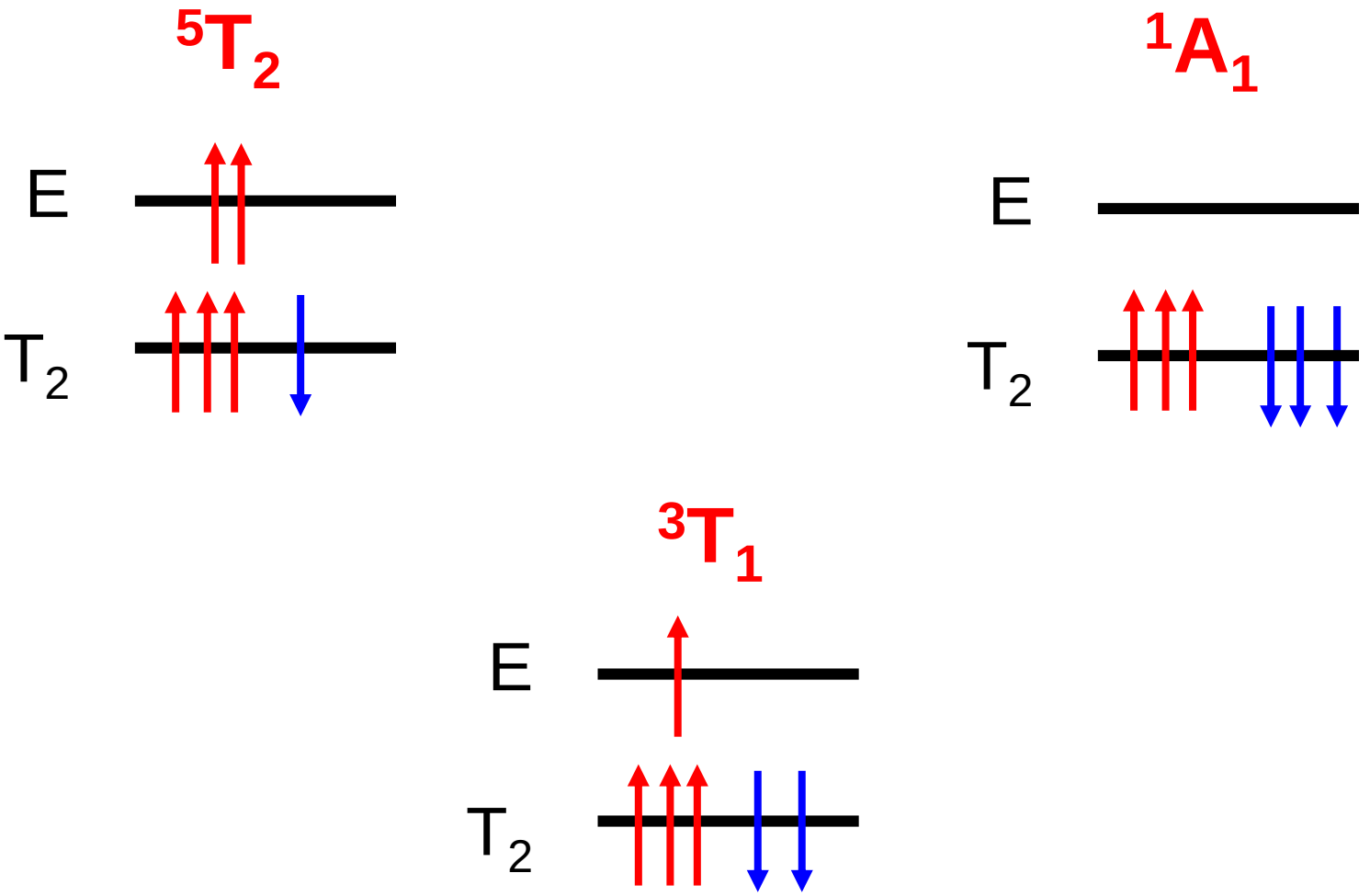
Ni metal: band excitations → fluorescence





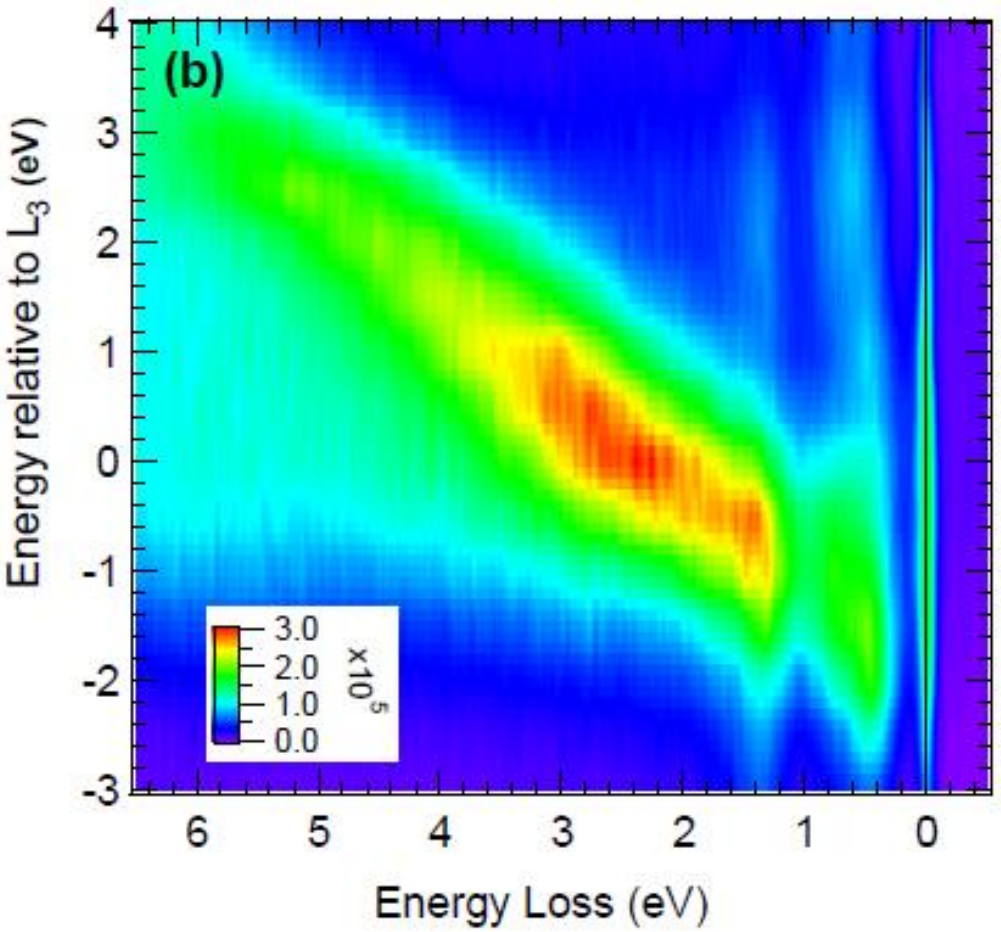
Spin-state in $LaCoO_3$ (single crystal)

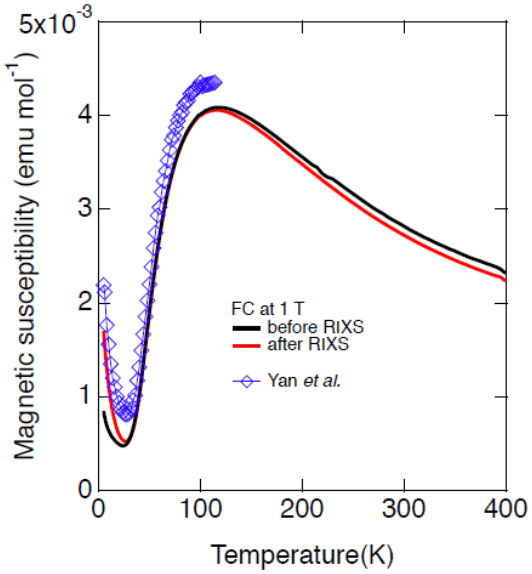
Spin state of $LaCoO_3$

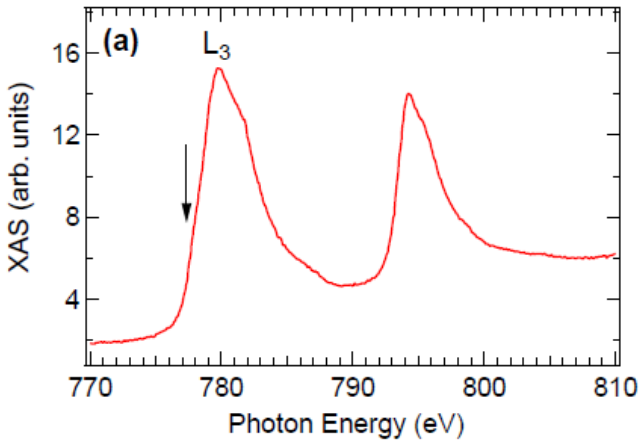


NOTE: Term symbols and orbital occupations are only indications: they are mixed by electron-electron, spin-orbit, etc.

Spin state of $LaCoO_3$



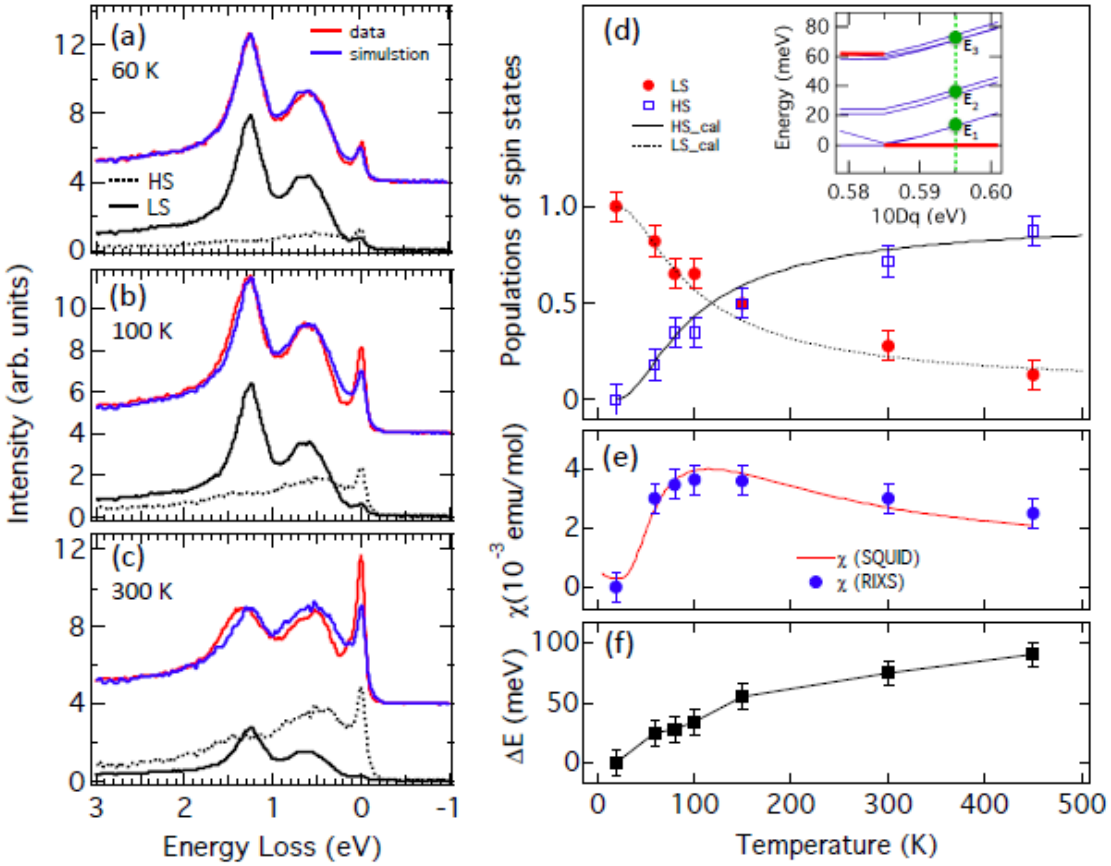




dd-excitations + fluorescence

[Tomiyasu et al. PRL 8, 119, 196402 (2017)]

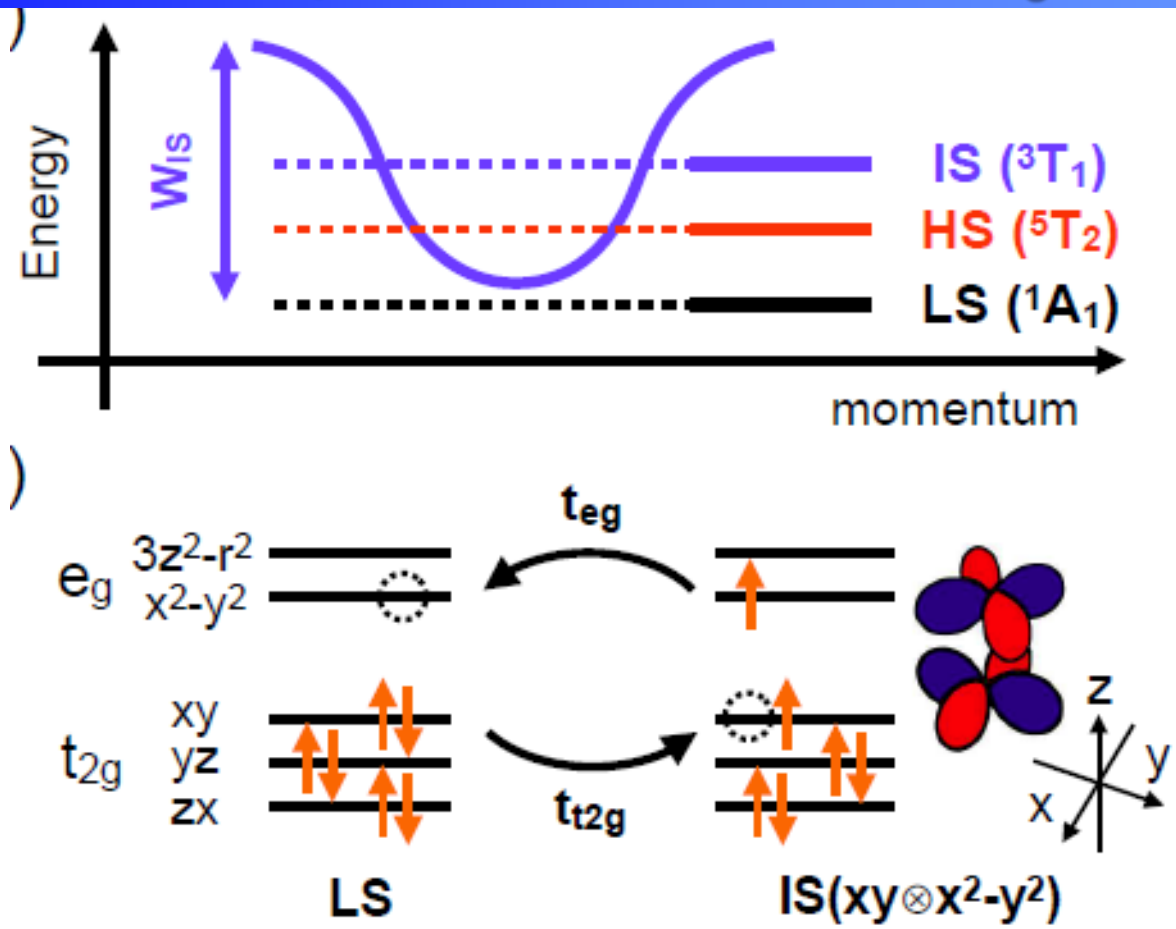
Spin state of $LaCoO_3$



Spin transition is from low-spin to high-spin,
. . . . but is it really high-spin?

[Tomiyasu et al. PRL 8, 119, 196402 (2017)]

Spin state of $LaCoO_3$



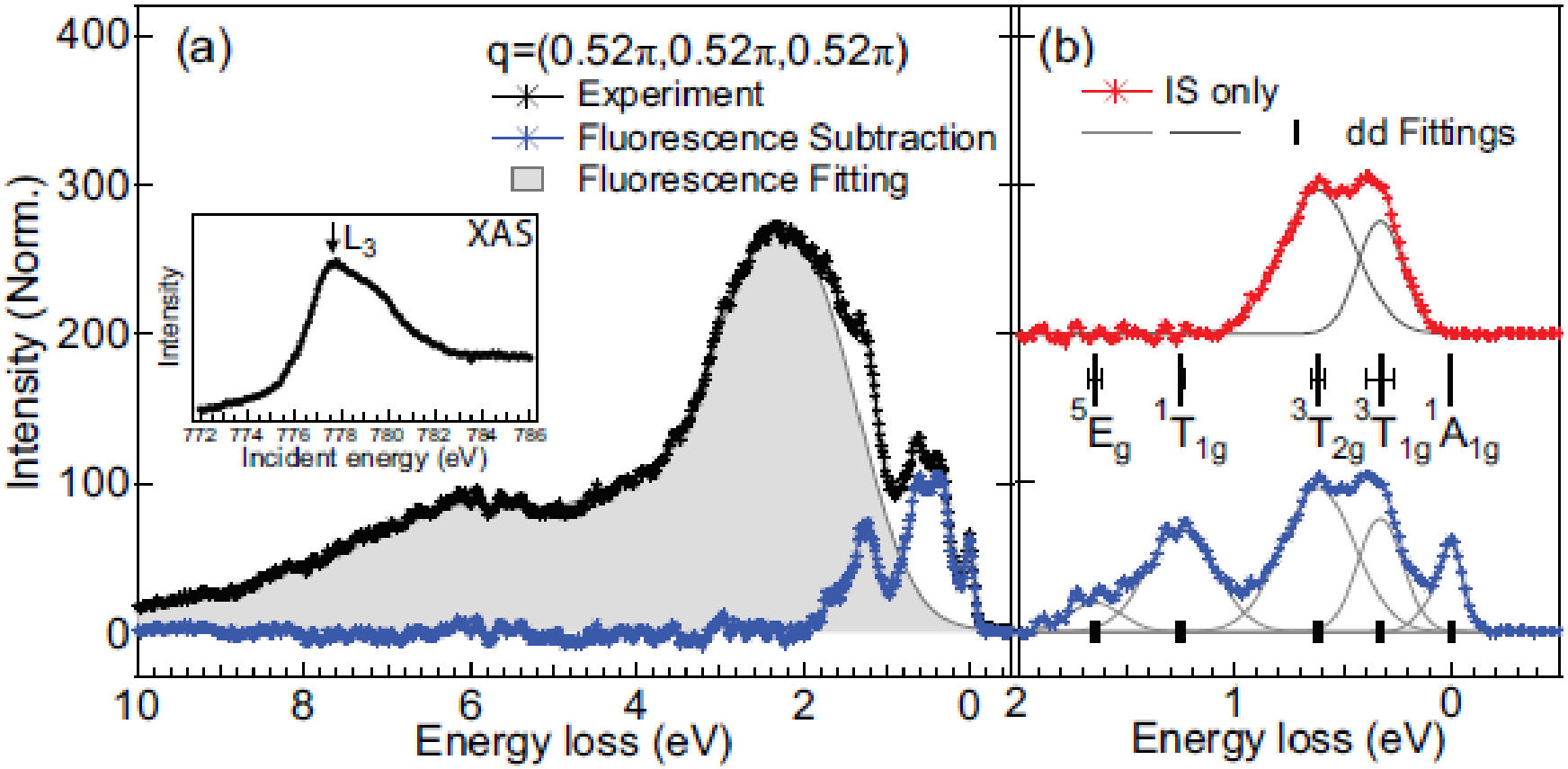
Order of states at zero Kelvin: LS < HS < IS

Strong coupling between LS and IS (not with HS)

Large dispersion of IS: **Excitonic Insulator**

[Sotnikov & KUnes, Sci. Rep 6, 30510 (2016); Wang et al. submitted]

Spin state of $LaCoO_3$

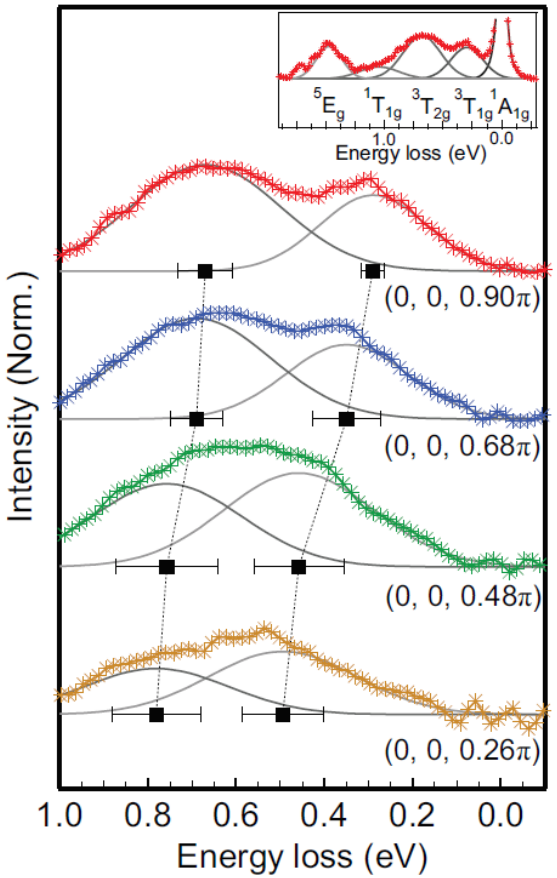


q-dependent RIXS with 90 meV resolution at 20 K

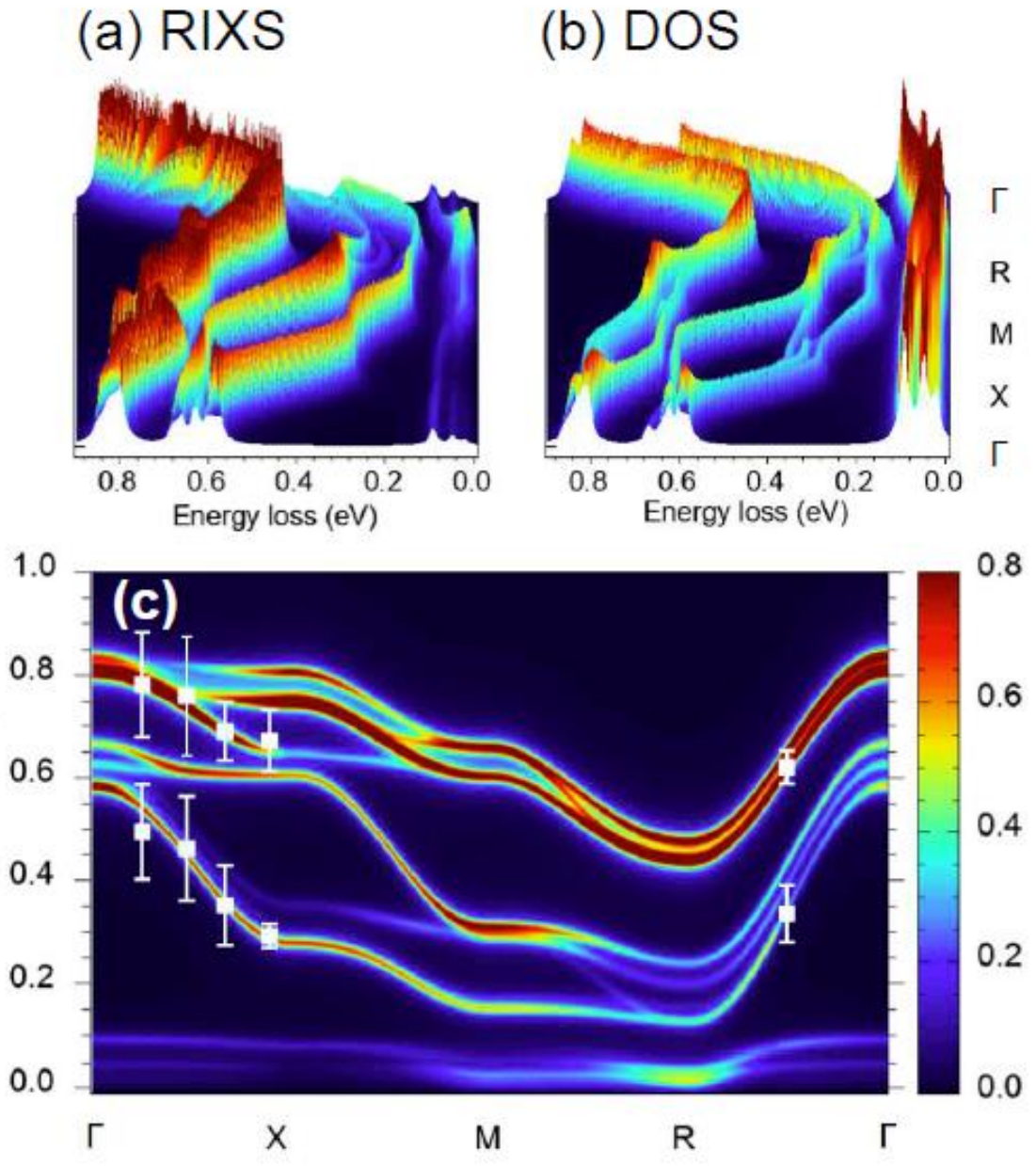
[data treatment: remove fluorescence and isolate states related to the triplet states (IS)]

[Wang et al. submitted]

Spin state of $LaCoO_3$



q-dep. RIXS



[Wang et al. submitted]