The future of XAS

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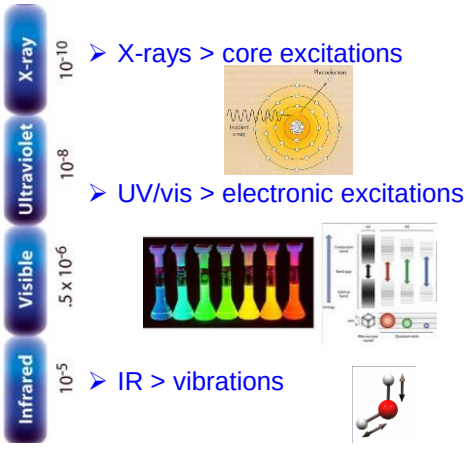
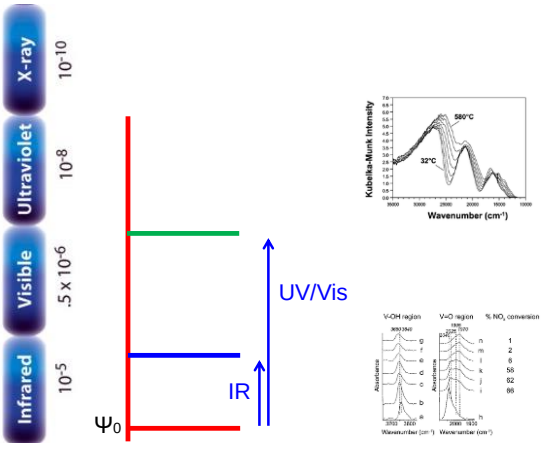
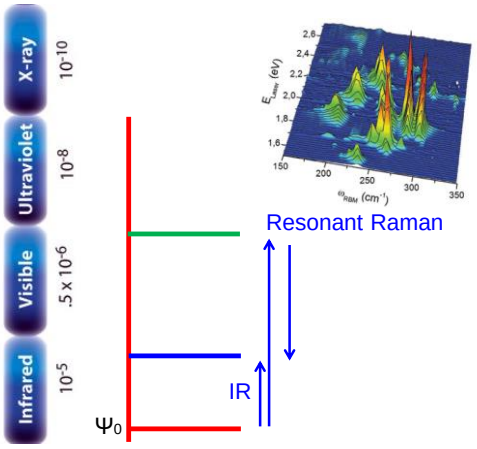
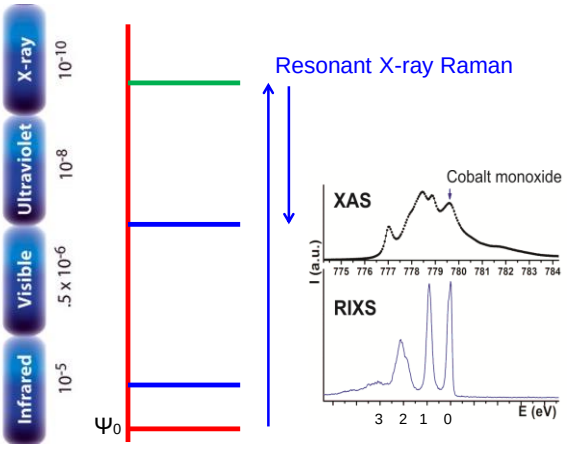
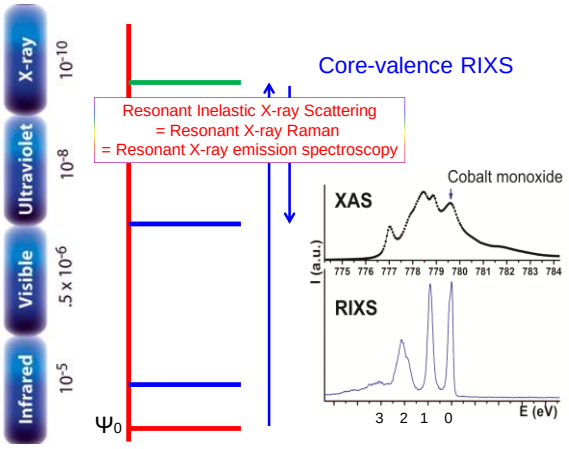
- ENERGY: resonant experiments
- TIME: time-resolved XAS
- SPACE: x-ray spectromicroscopy







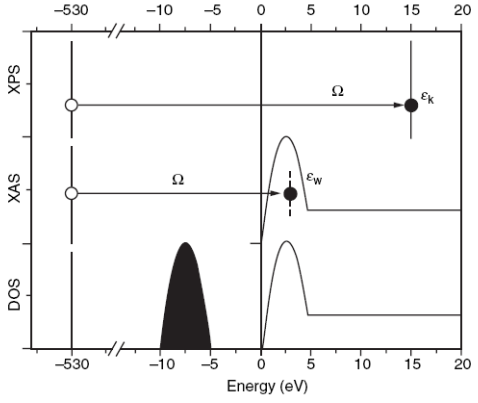




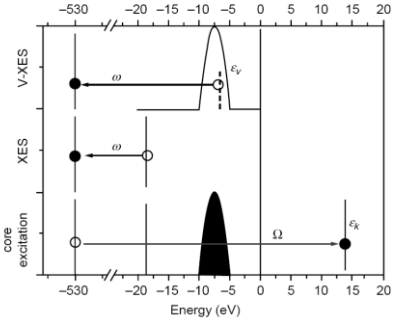
Why core-valence RIXS?

- Measure optical spectra with x-rays
  >> in-situ, element specific
- dd-transitions > electronic structure
- Magnetic excitations
- Reveal ~1% active sites

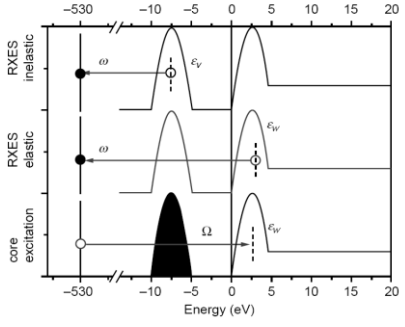
X-ray absorption and X-ray photoemission



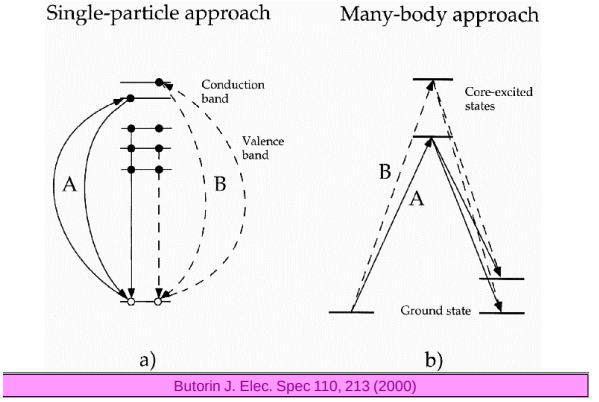
X-ray emission



Resonant X-ray emission spectroscopy

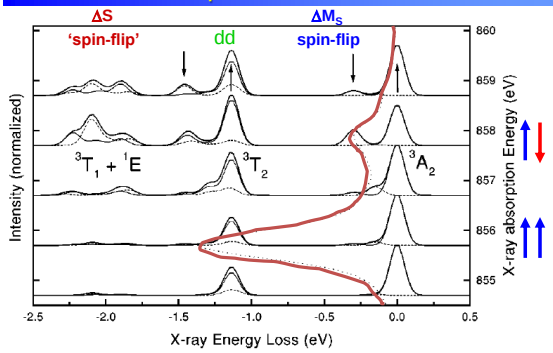


Resonant Inelastic X-ray Scattering



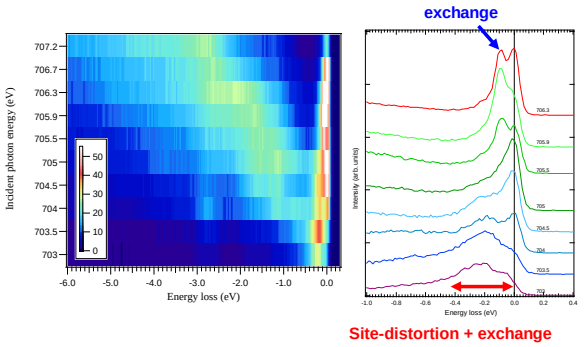
Butorin J. Elec. Spec 110, 213 (2000)

2p3d RIXS of NiO



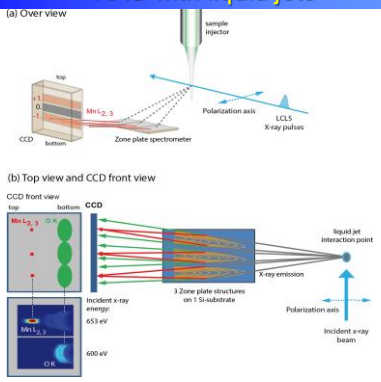
Phys. Rev. B. 57, 14584 (1998)

2p3d RIXS of Fe_3O_4



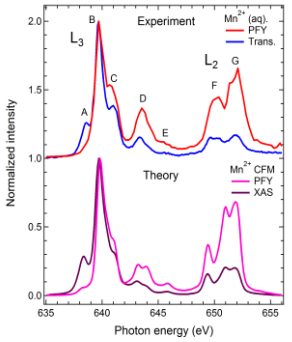
Huang, Wang, et al. (unpublished)

XAS with liquid jets



Mitzner et al, J. Phys. Chem. Lett. 4, 3641 (2013)

XAS: transmission & FY

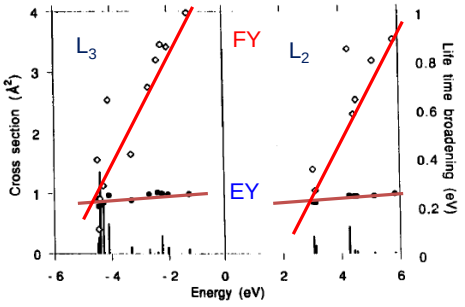


Fluorescence does not measure XAS spectrum

- Saturation
- State-dependent decay

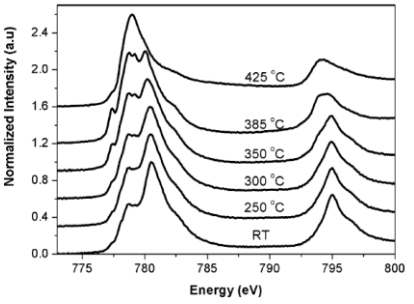
Mitzner et al, J. Phys. Chem. Lett. 4, 3641 (2013)

FY detection: State dependent decay



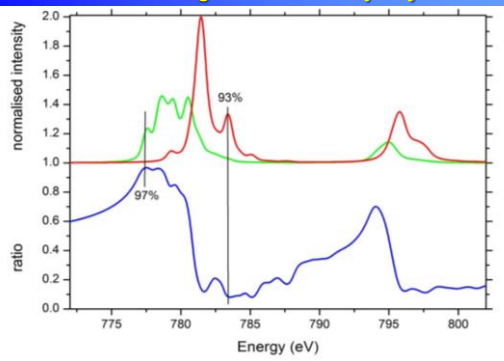
Solid State Comm. 92, 991 (1994)

Removing the silent majority

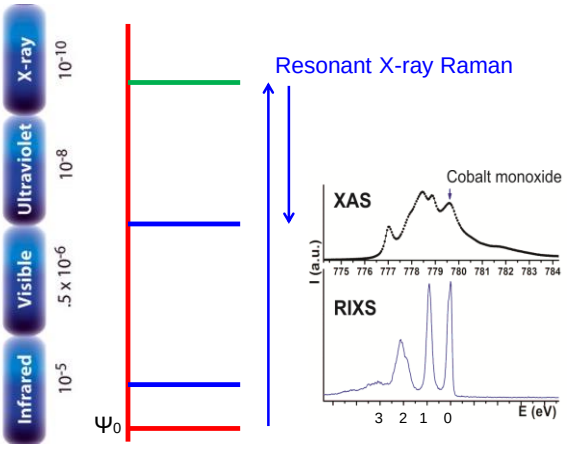


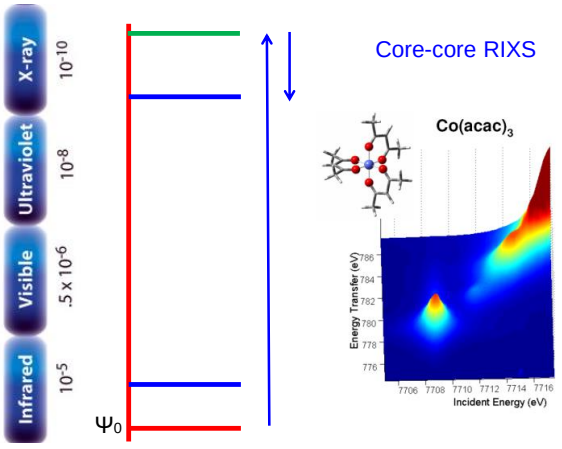
XAS is linear in number of atoms

Removing the silent majority



RIXS can enhance a specific state by 97%





Why core-core RIXS?

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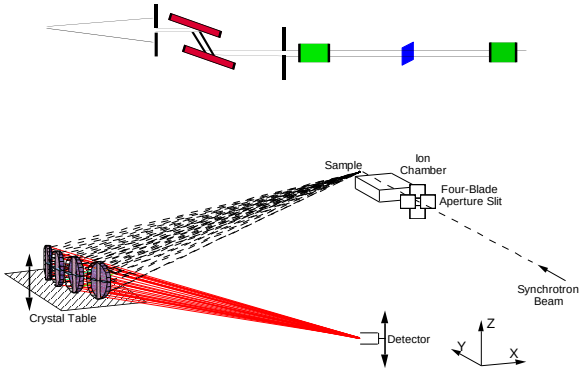
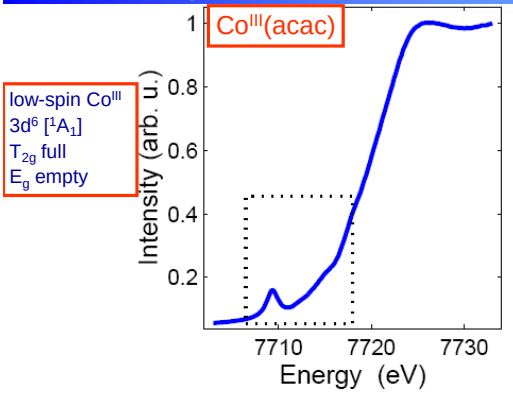
- Remove lifetime broadening
- Reveal new features in pre-edges
- Selective XAS (valence sel. EXAFS)
- Range extended EXAFS

Resonant Inelastic X-ray Scattering



Pre-edges structures in 1s XAS



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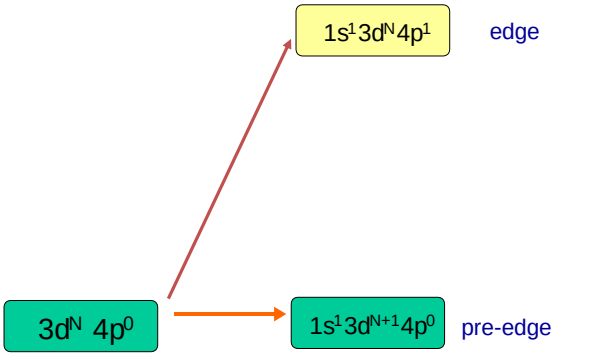

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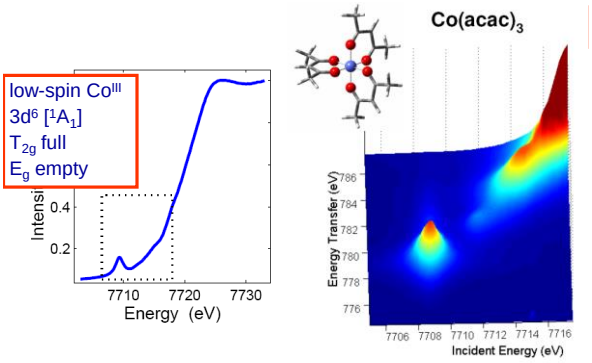
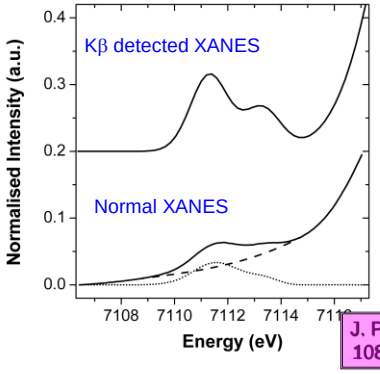


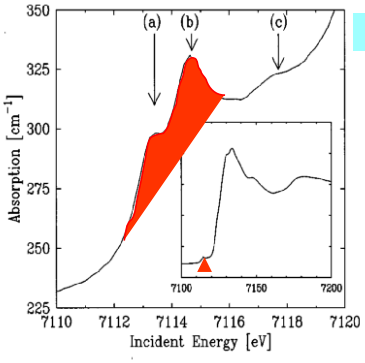
Vanko et al. (submitted)

Spectral Sharpening



J. Phys. Chem. B. 108, 10002 (2004)

Resonant Inelastic X-ray Scattering



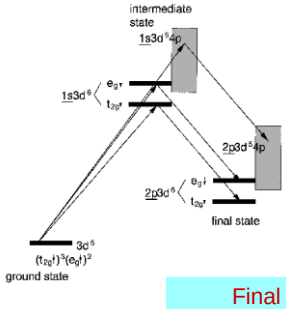
1s XAS of Fe_2O_3

K edge:
1s to 4p

Pre-edge:
1s to 3d

Phys. Rev. B. 58, 13452 (1998)

Resonant Inelastic X-ray Scattering



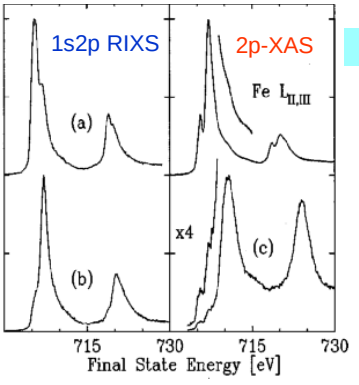
1s2p RIXS of Fe_2O_3

Quadrupole to 3d-states
Dipole to 4p-states

Decay of 2p-electron into 1s-hole

Final state identical to 2p XAS

Resonant Inelastic X-ray Scattering

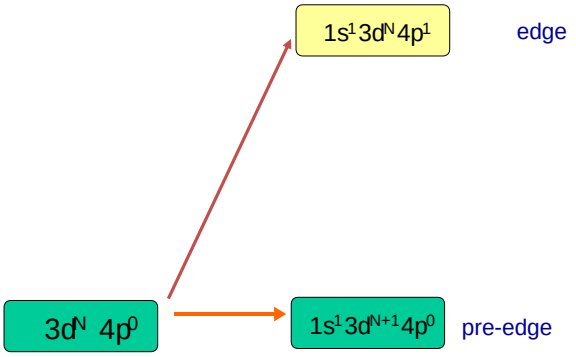


1s2p RIXS of Fe_2O_3

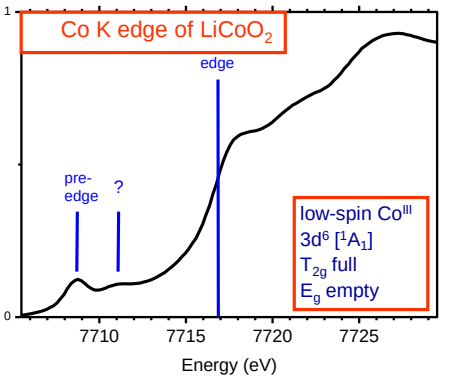
'soft x-ray spectra with hard x-rays'

Phys. Rev. B. 58, 13452 (1998)

Pre-edge and edge



K edge X-ray Absorption Spectroscopy



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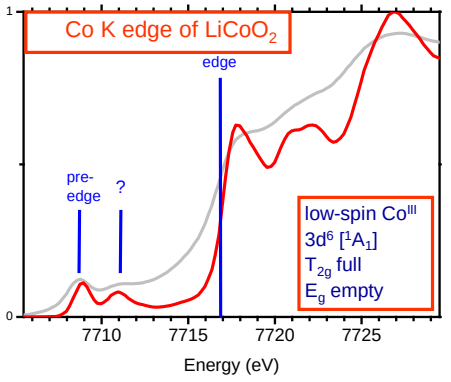

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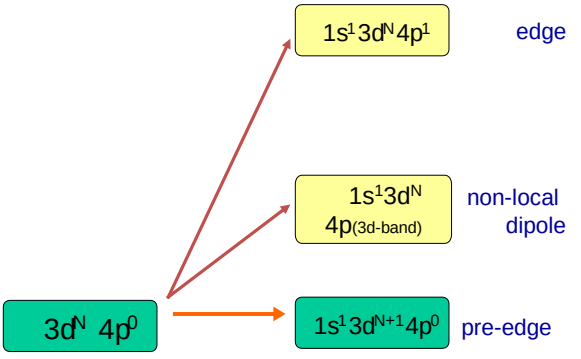

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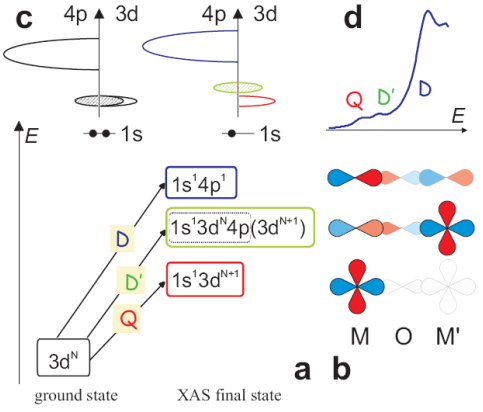
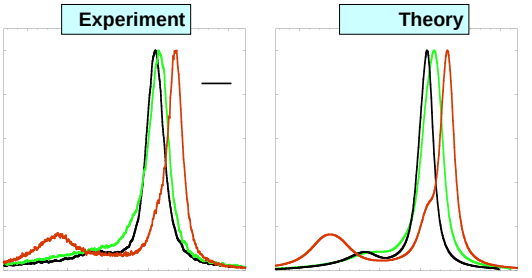


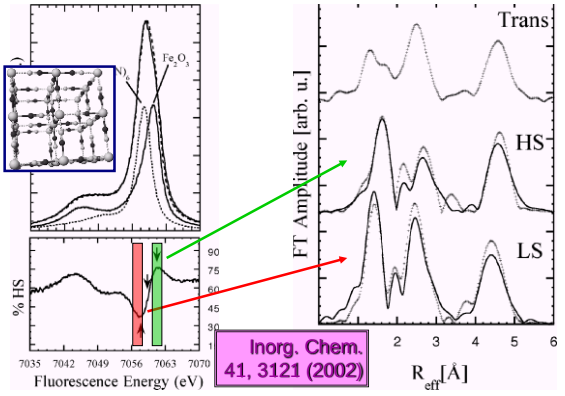
Valence shifts in RIXS

Chemical Dependence of Kβ Emission

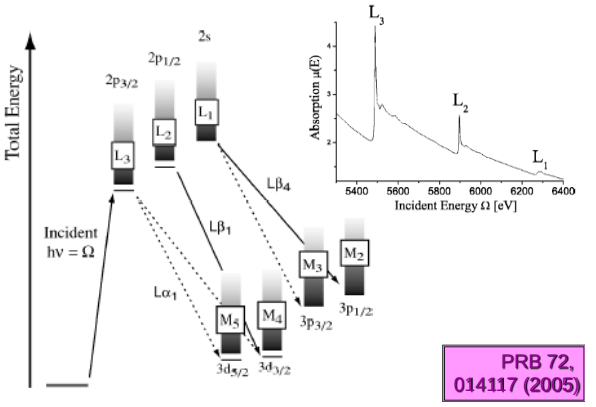


Equal center-of-gravity energies used in calculations!

Valence selective XAS



Range extended EXAFS



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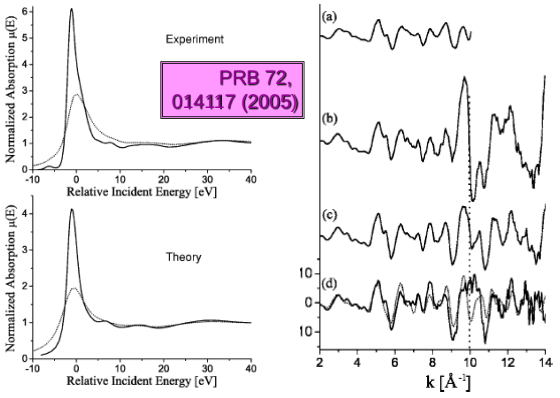

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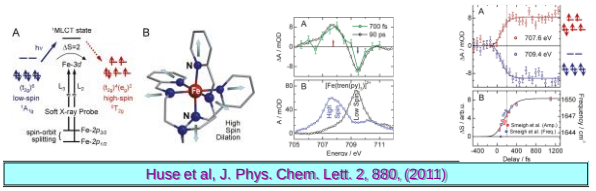
Time-resolved XAS

- measure XAS of ground state
- transient spectrum of laser excited state at certain delay time
- fit ground state and excited state
- determine time-evolution

Time-resolved XAS @ synchrotron

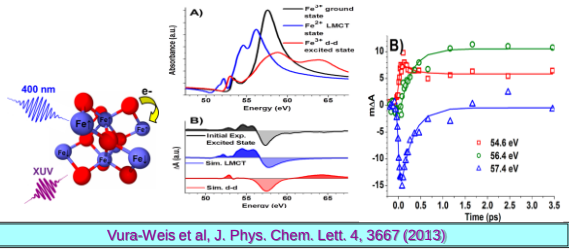
- measure iron 2p XAS of ground state
- transient spectrum of laser excited state at certain delay time
- fit ground state and excited state
- determine time-evolution



Huse et al, J. Phys. Chem. Lett. 2, 880, (2011)

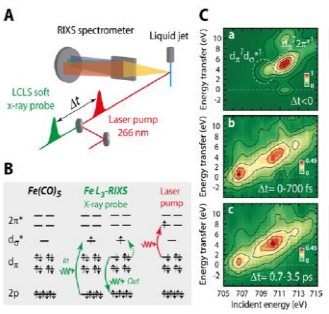
Time-resolved XAS @ laboratory

- measure iron 2p XAS of ground state
- transient spectrum of laser excited state at certain delay time
- fit ground state and excited state
- determine time-evolution



Vura-Weis et al, J. Phys. Chem. Lett. 4, 3667 (2013)

Time resolved RIXS with liquid jets



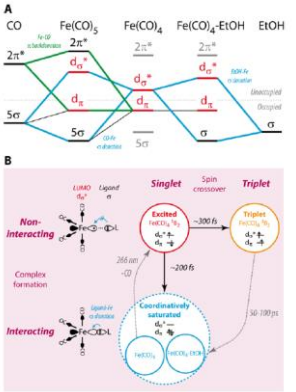
RIXS of ground state

After 700 fs: Peak at 707 eV due to hole in d_π

→ Track time-evolution of the electronic states.

[with Wernet et al., Nature 520, 78 (2015)]

Time resolved RIXS with liquid jets



Model of time-dependent electronic structure changes on femtosecond timescale.

→ Track time-evolution of a chemical reaction.

[with Wernet et al., Nature 520, 78 (2015)]