



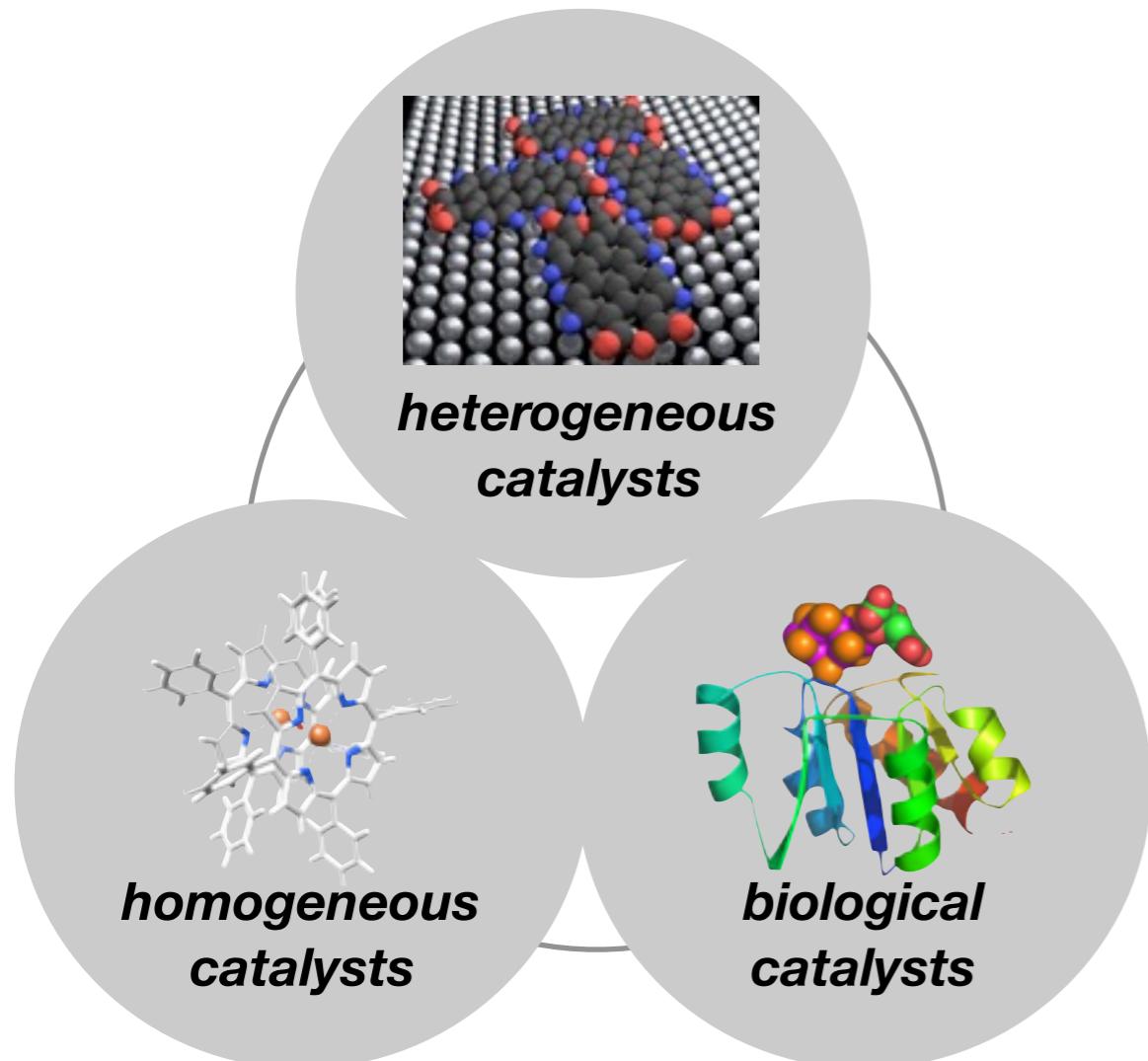
Advanced X-ray Spectroscopy

Serena DeBeer
Max-Planck-Institut für Chemische Energiekonversion

Penn State Bioinorganic Workshop
June 2016



Understanding Catalytic Connections...



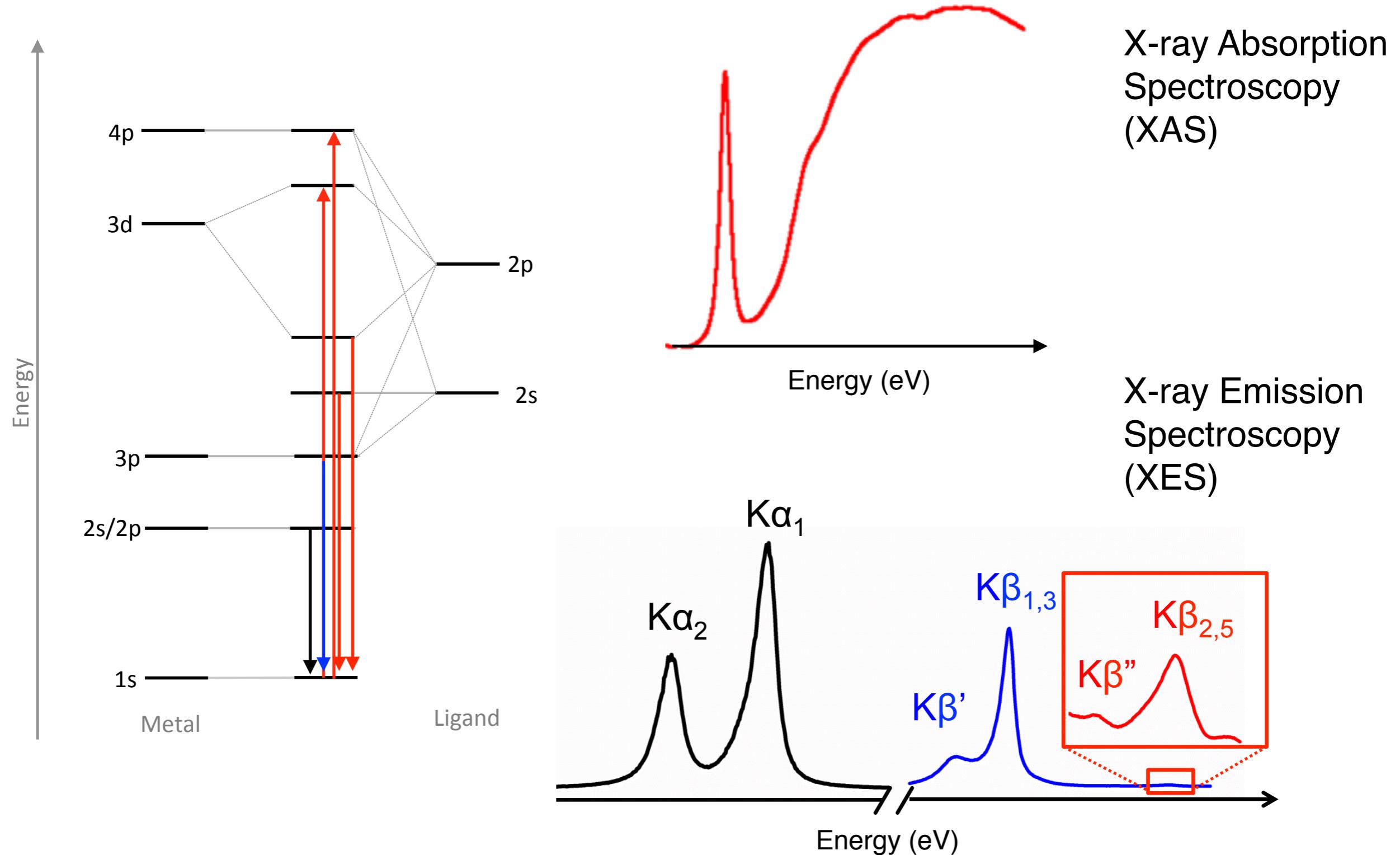
Key Reactions in Energy Research



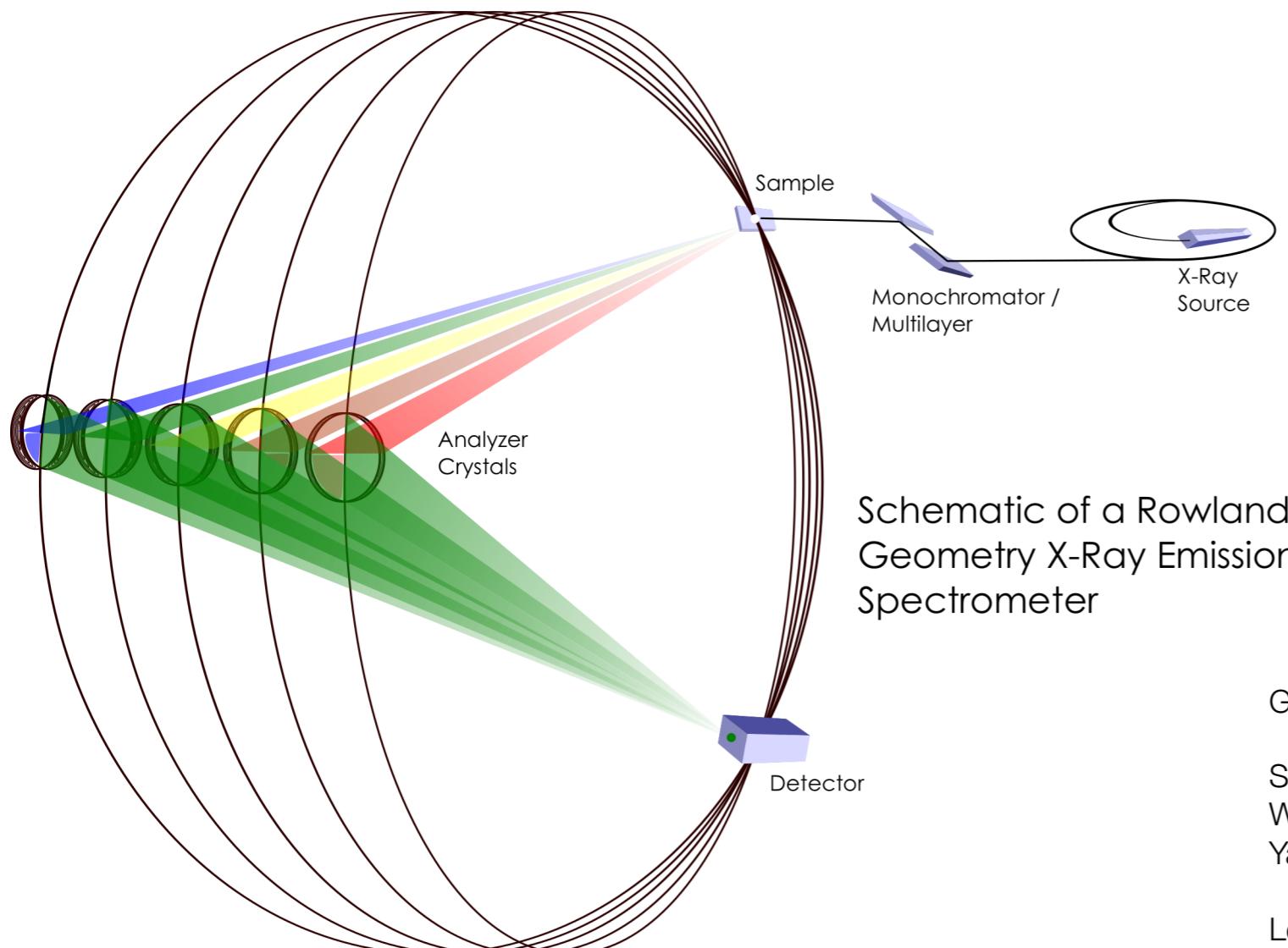
How can sustainable, earth-abundant base metals enable the activation of strong chemical bonds?

Requires an atomic level understanding of the geometric and electronic structure changes which occur over the course of catalysis.

X-ray Spectroscopy



A High-Energy Resolution XES Setup



The increased resolution of modern setups, increased sensitivity and developments in theory have opened up all new chemical applications...

Glatzel, P.; Bergmann, U. *Coord. Chem. Rev.* **2005**, 249, 65.

Smolentsev, G.; Soldatov, A. V.; Messinger, J.; Merz, K.; Weyhermueller, T.; Bergmann, U.; Pushkar, Y.; Yano, J.; Yachandra, V. K.; Glatzel, P., *JACS*, **2009**, 131, 13161.

Lee, N.; Petrenko, T.; Bergmann, U.; Neese, F.; DeBeer, S., *JACS*, **2010**, 132, 9715.

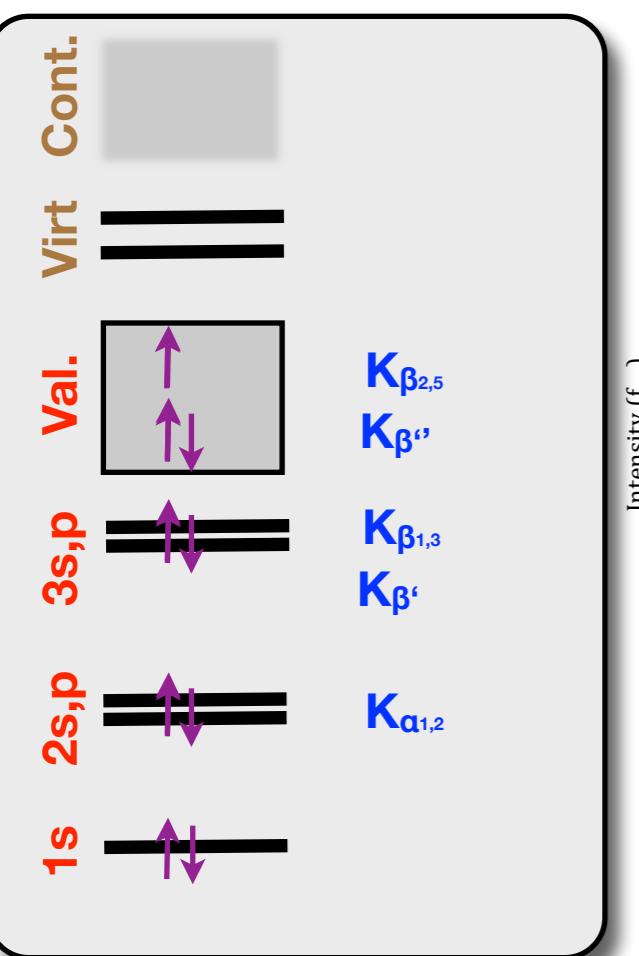
Pushkar, Y.; Long, X.; Glatzel, P.; Brudvig, G. W.; Dismukes, G. C.; Collins, T. J.; Yachandra, V. K.; Yano, J.; Bergmann, U. *ACIES*, **2010**, 49, 800.

Lancaster, K. M.; Roemelt, M.; Ettenhuber, P.; Hu, Y.; Ribbe, M. W.; Neese, F.; Bergmann, U.; DeBeer, S. *Science* **2011**, 334, 974.

Figure J. A. Rees

X-Ray Emission Spectra

N. Lee, T. Petrenko, U. Bergmann, F. Neese, S. DeBeer, J. Am. Chem. Soc., 2010, 132, 9715-9727.



Outline

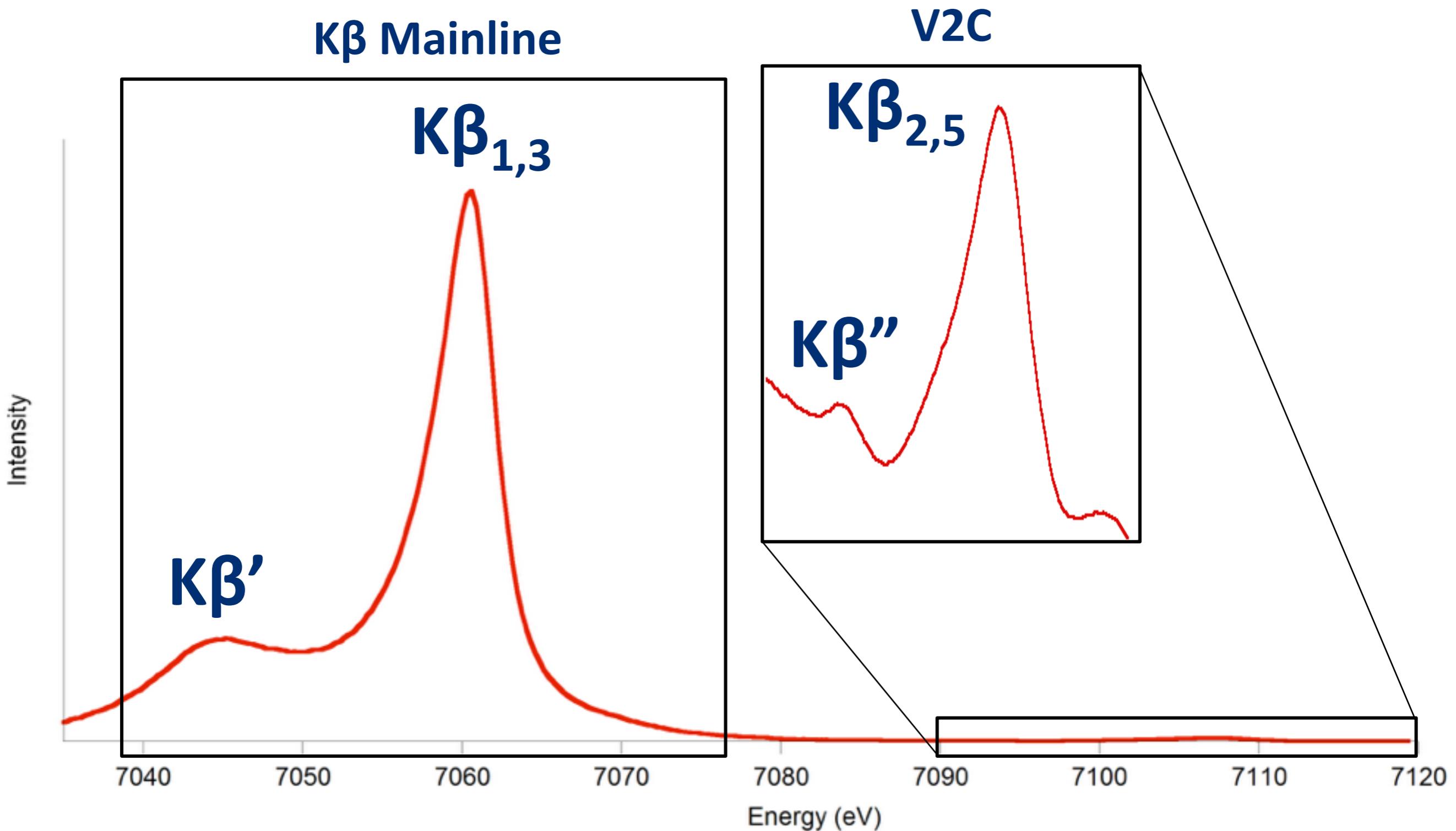
- **Non-resonant X-ray Emission Spectroscopy (XES)**

- **K-Beta XES**
- **Valence to Core XES**
- (K-alpha XES)

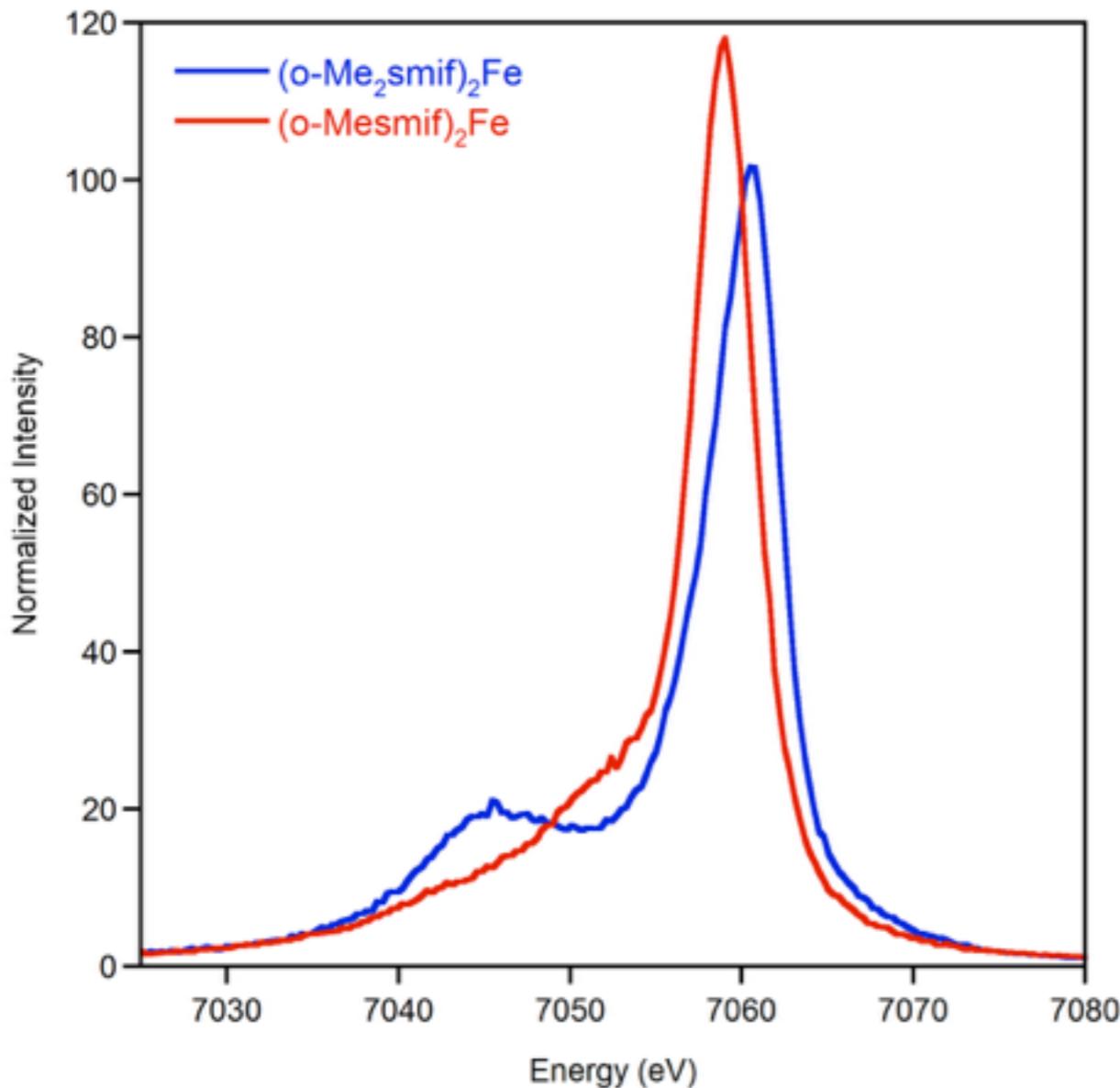
- Resonant X-ray Emission Spectroscopy (RXES or RIXS)

- XAS + XES 2D measurement
- Higher resolution XAS
- Oxidation State and Spin State Selective XAS
- Ligand Selective XAS?
- Combine Mb-XES instrument
- 2p3d RIXS

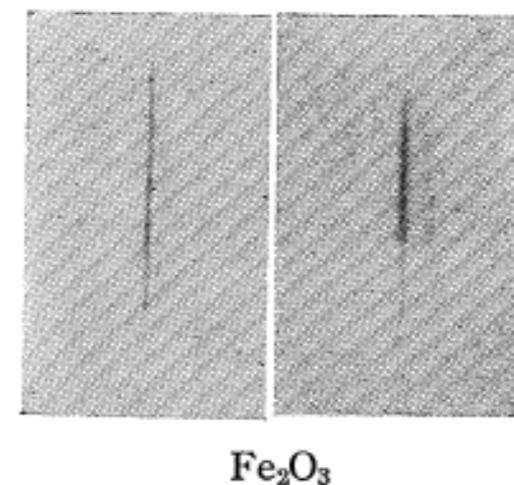
K-Beta Main Line and Valence to Core Regions



K-Beta Main Lines: A fingerprint for Spin State?

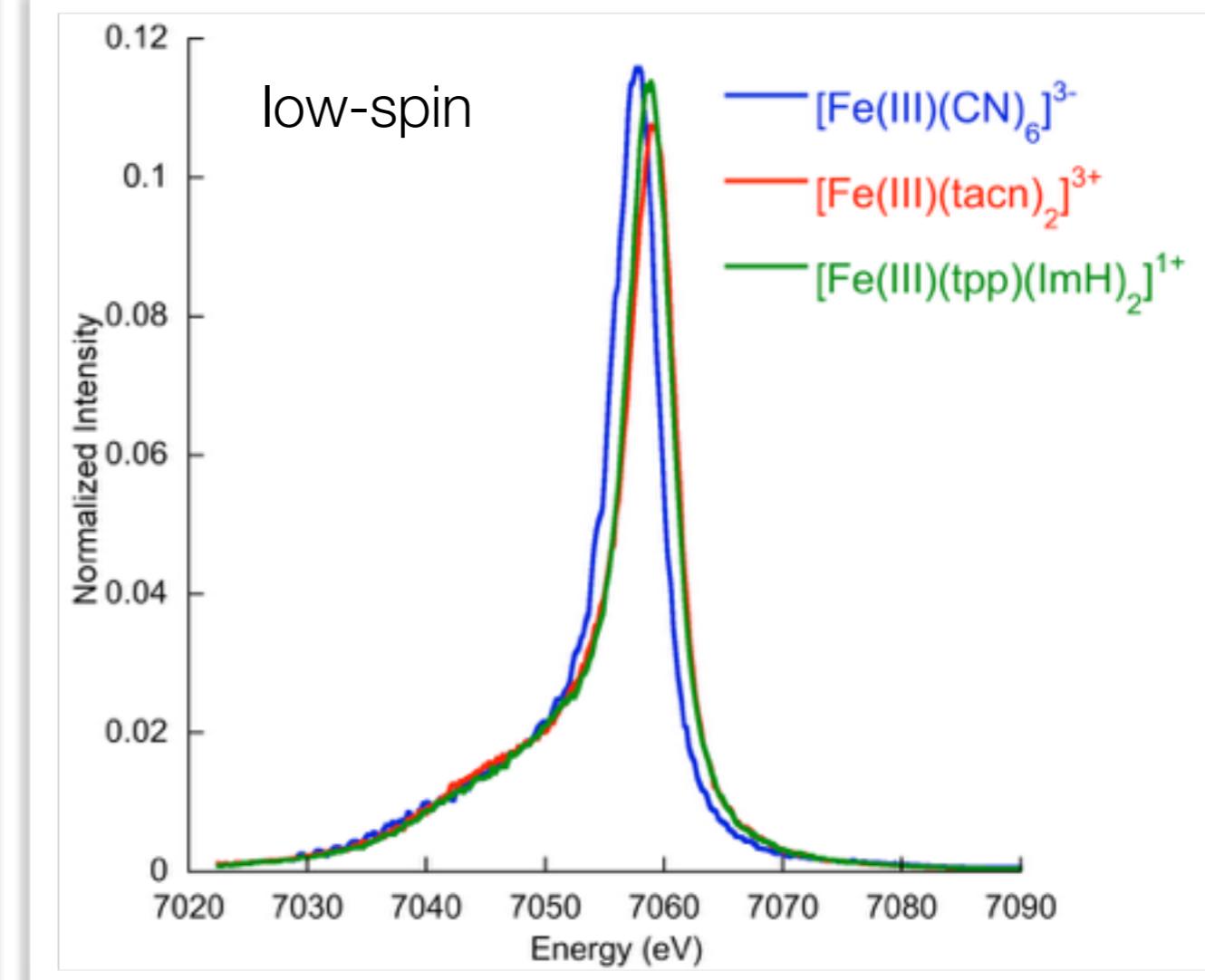
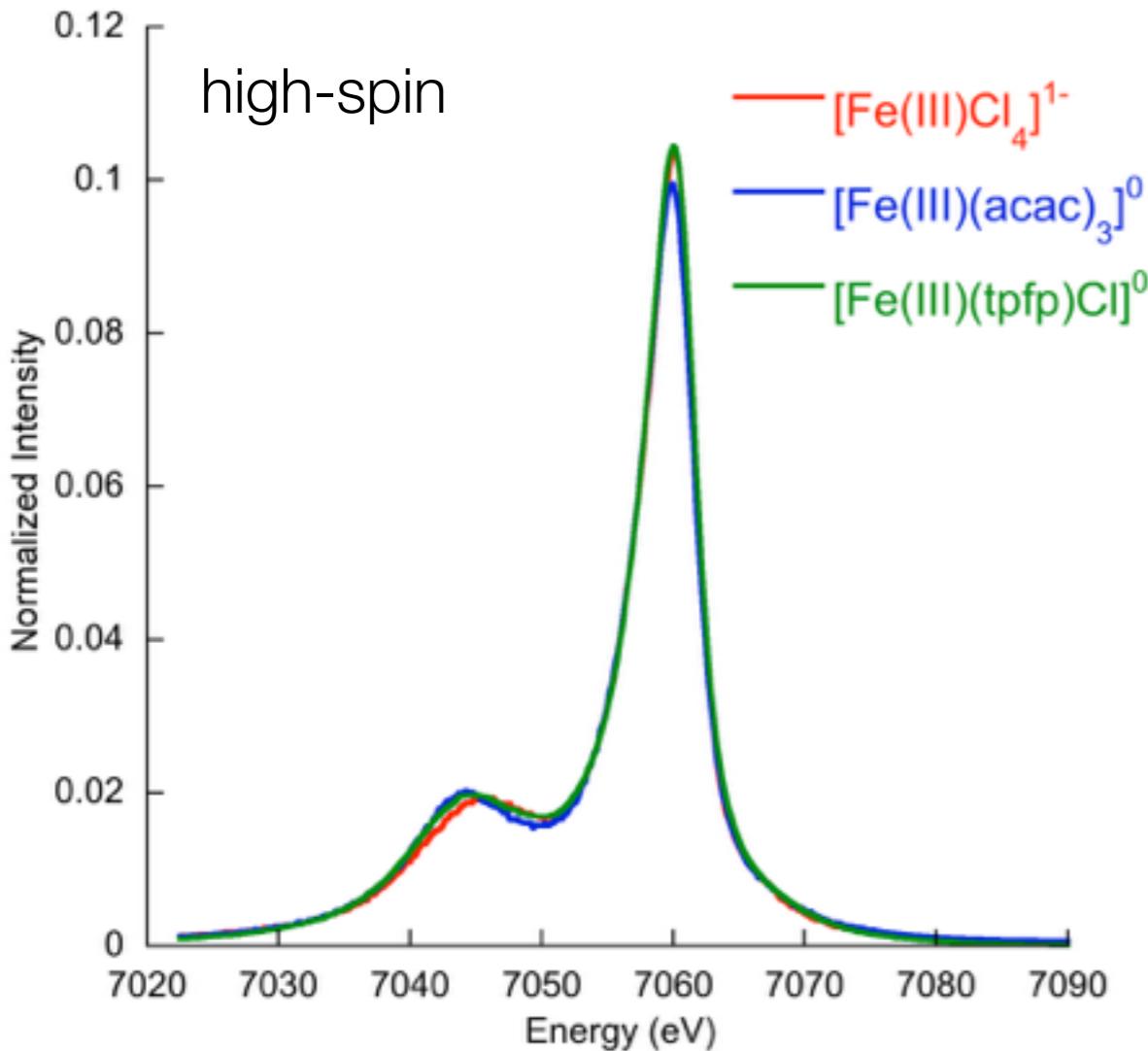


- High-spin Fe complexes exhibit a shoulder which is (essentially) absent in low spin analogues
- Similar observations can be made for other metals....
- Correlation first made in 1959
Tsutsumi et al., J. Phy. Soc. Jap.
Vol. 14, 12

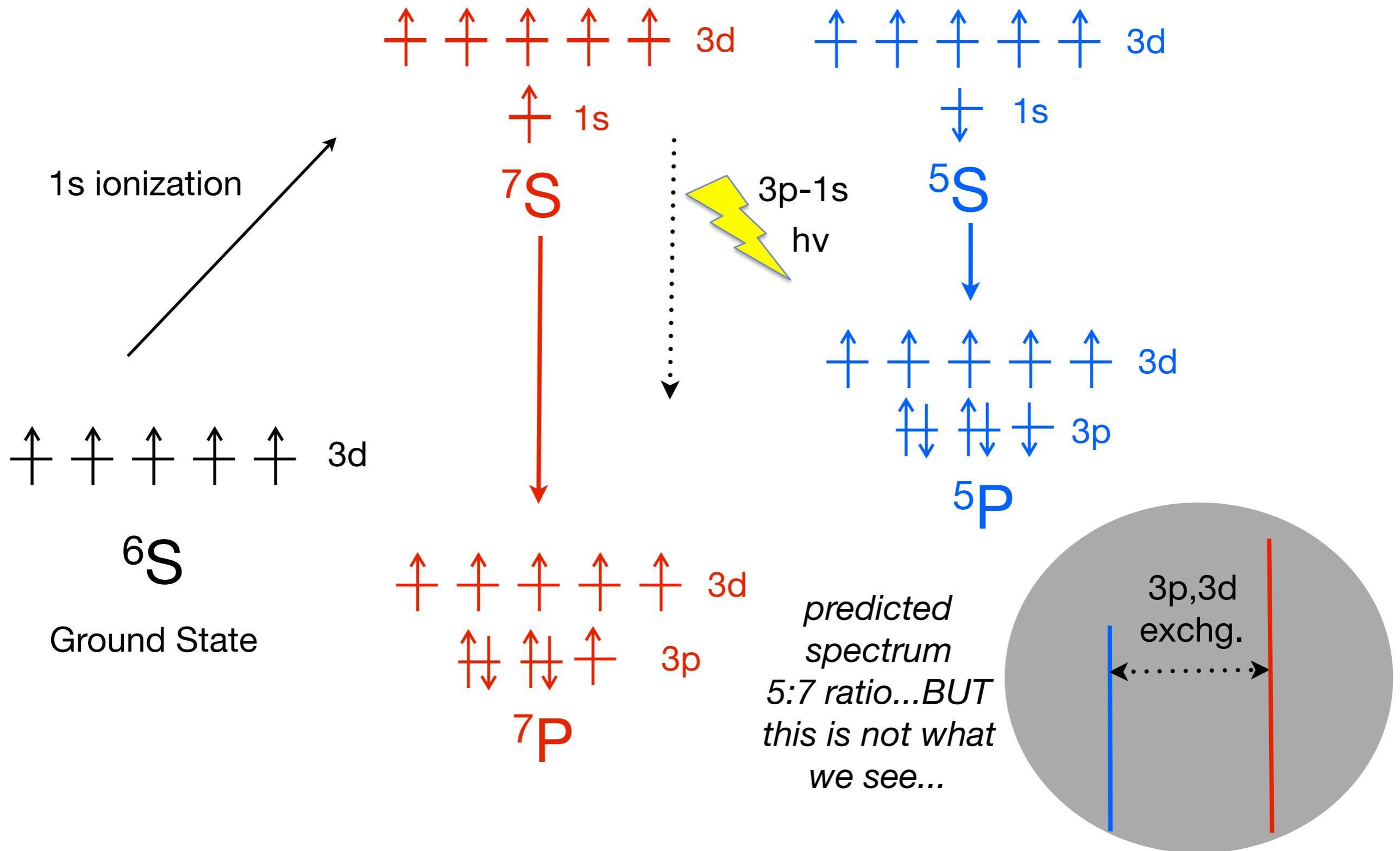


C.J. Pollock, P.T. Wolczanski, S. DeBeer, unpublished results.

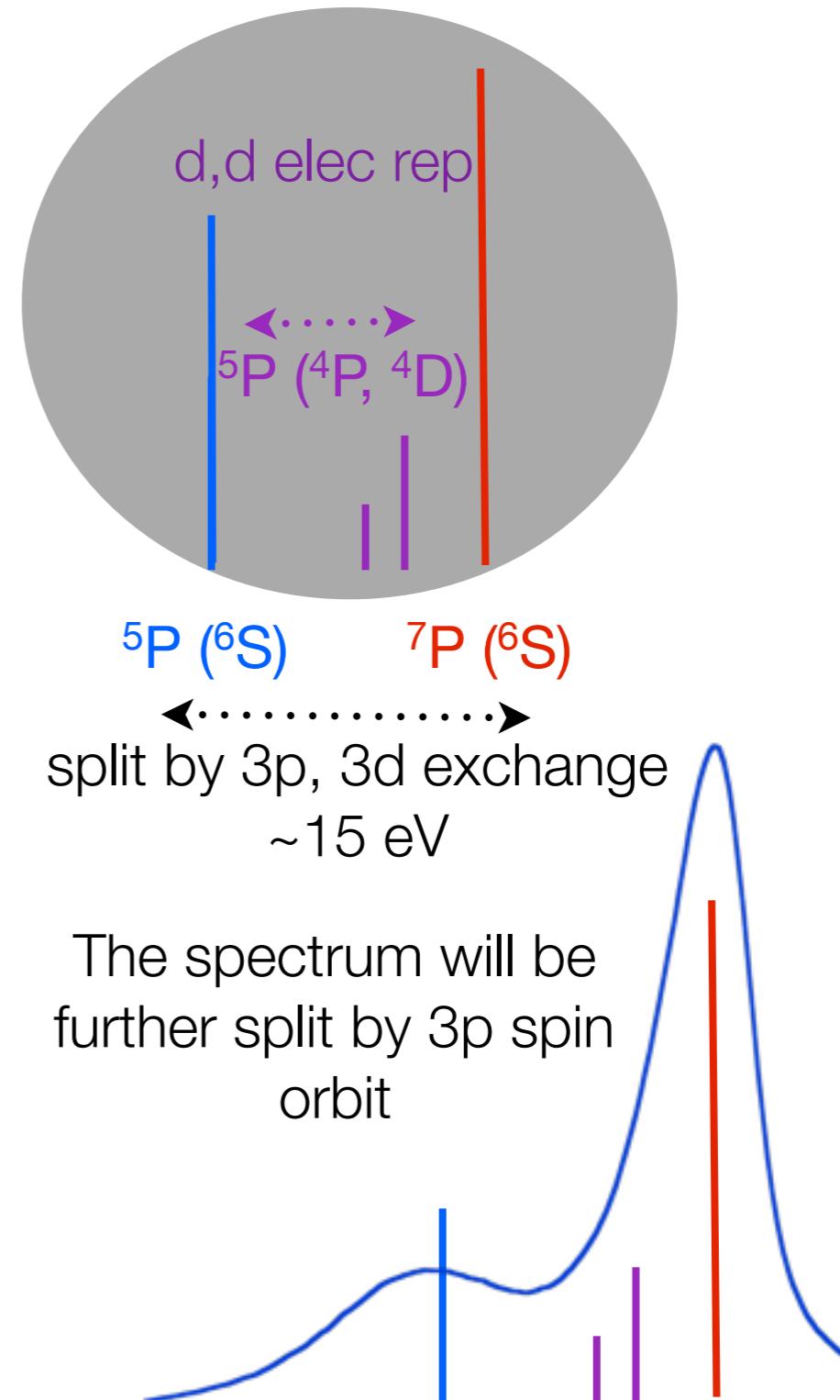
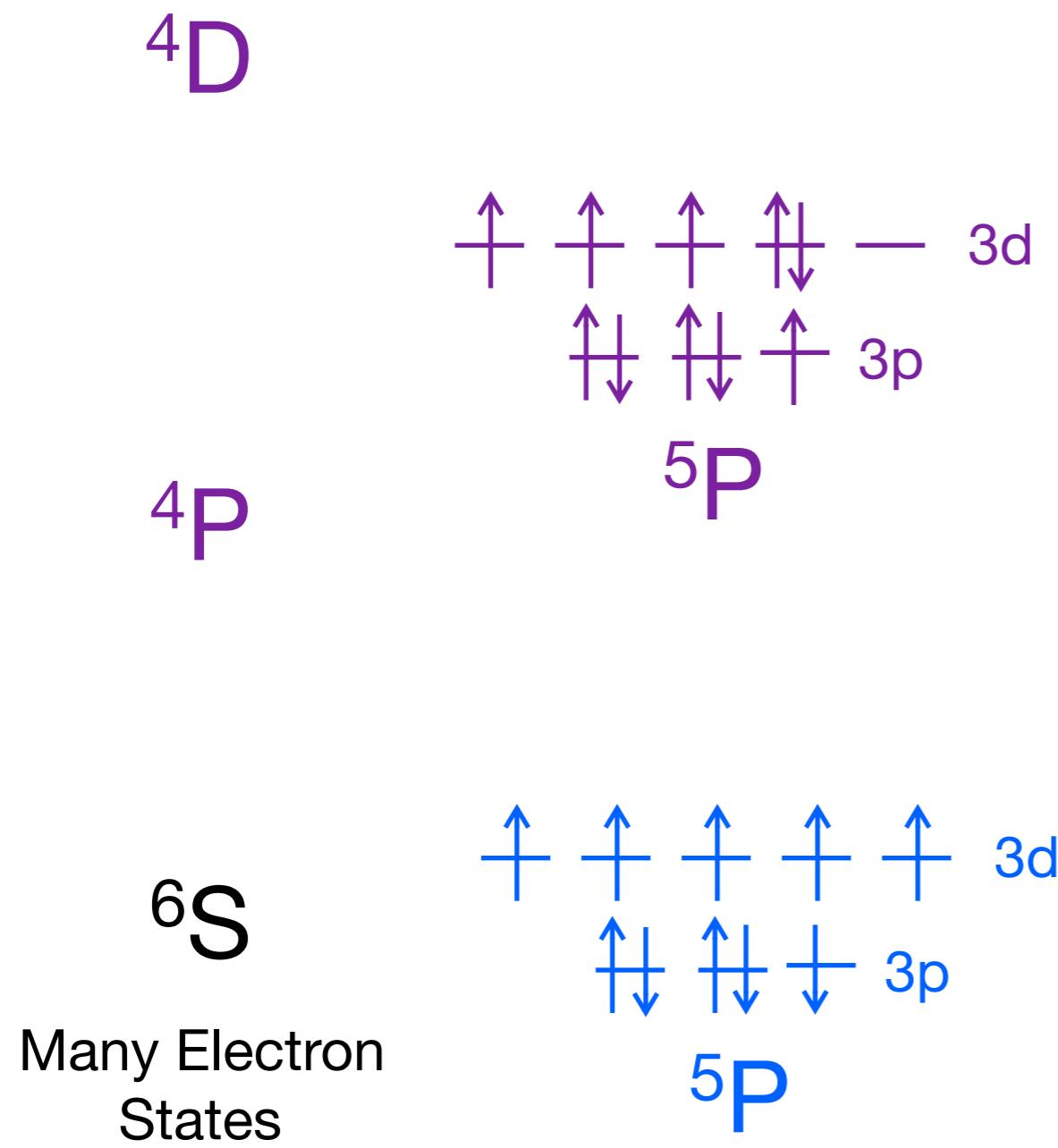
HS vs LS generalization for K-Beta Mainlines



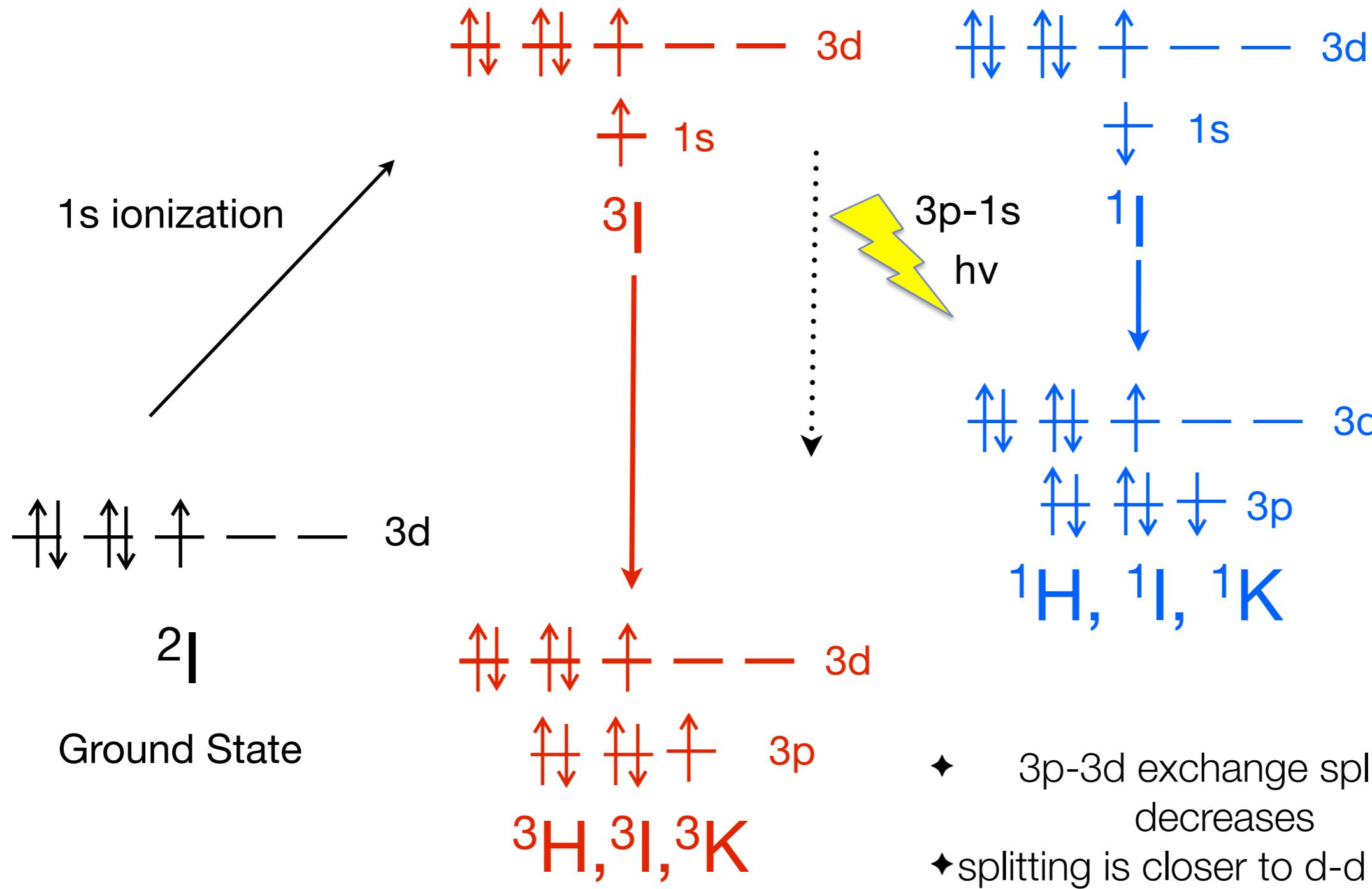
Origins of K-Beta Main Line Splitting: HS Fe(III)



Origins of K-Beta Main Line Splitting: HS Fe(III)



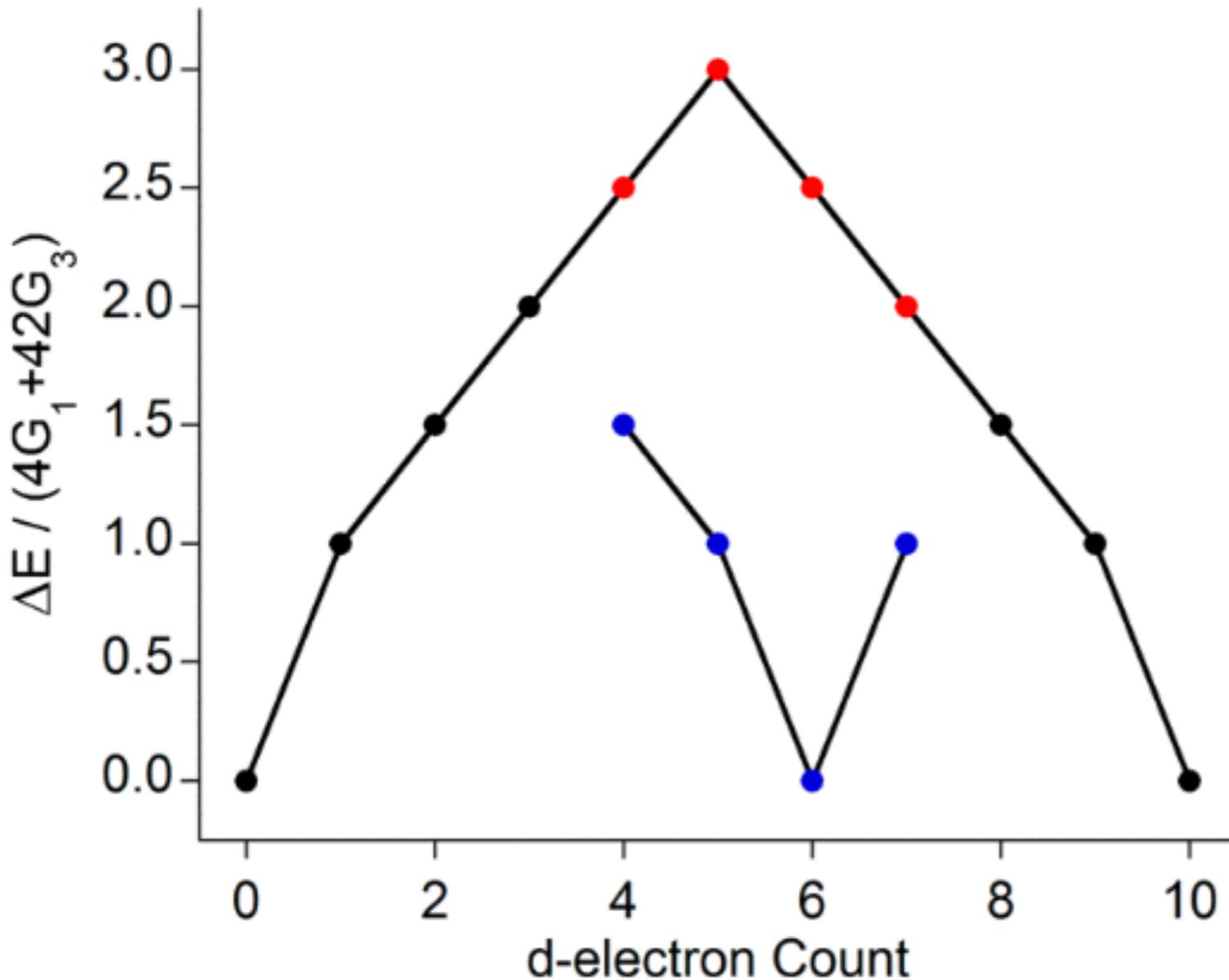
Origins of K-Beta Main Line Splitting: LS Fe(III)



- ◆ 3p-3d exchange splitting decreases
- ◆ splitting is closer to d-d electron repulsion

Analytical Expressions for the K β Mainline Splittings

Energy Splitting of the Mainline: Free Ion Case

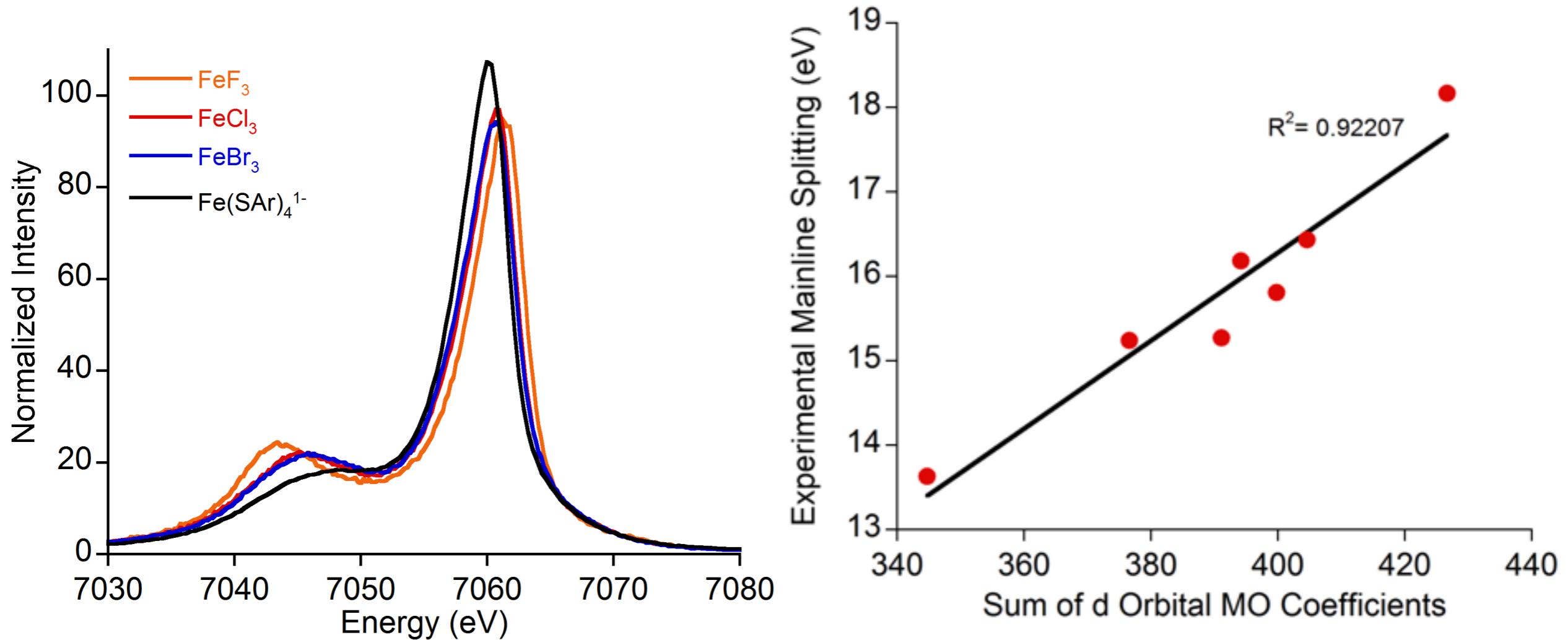


The mainline splitting can be expressed in terms of the p-d exchange ($4G_1 + 42G_3$) for every d-count



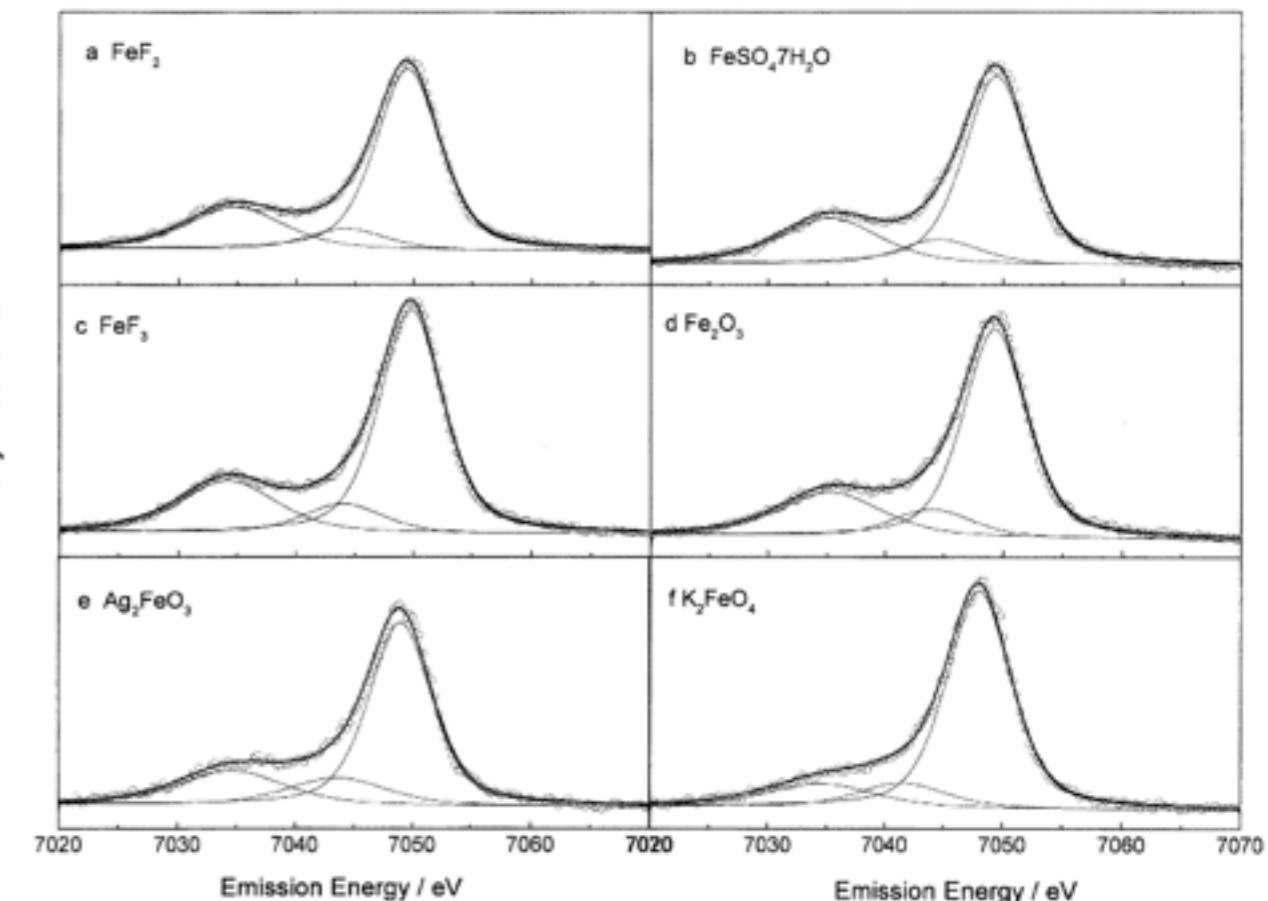
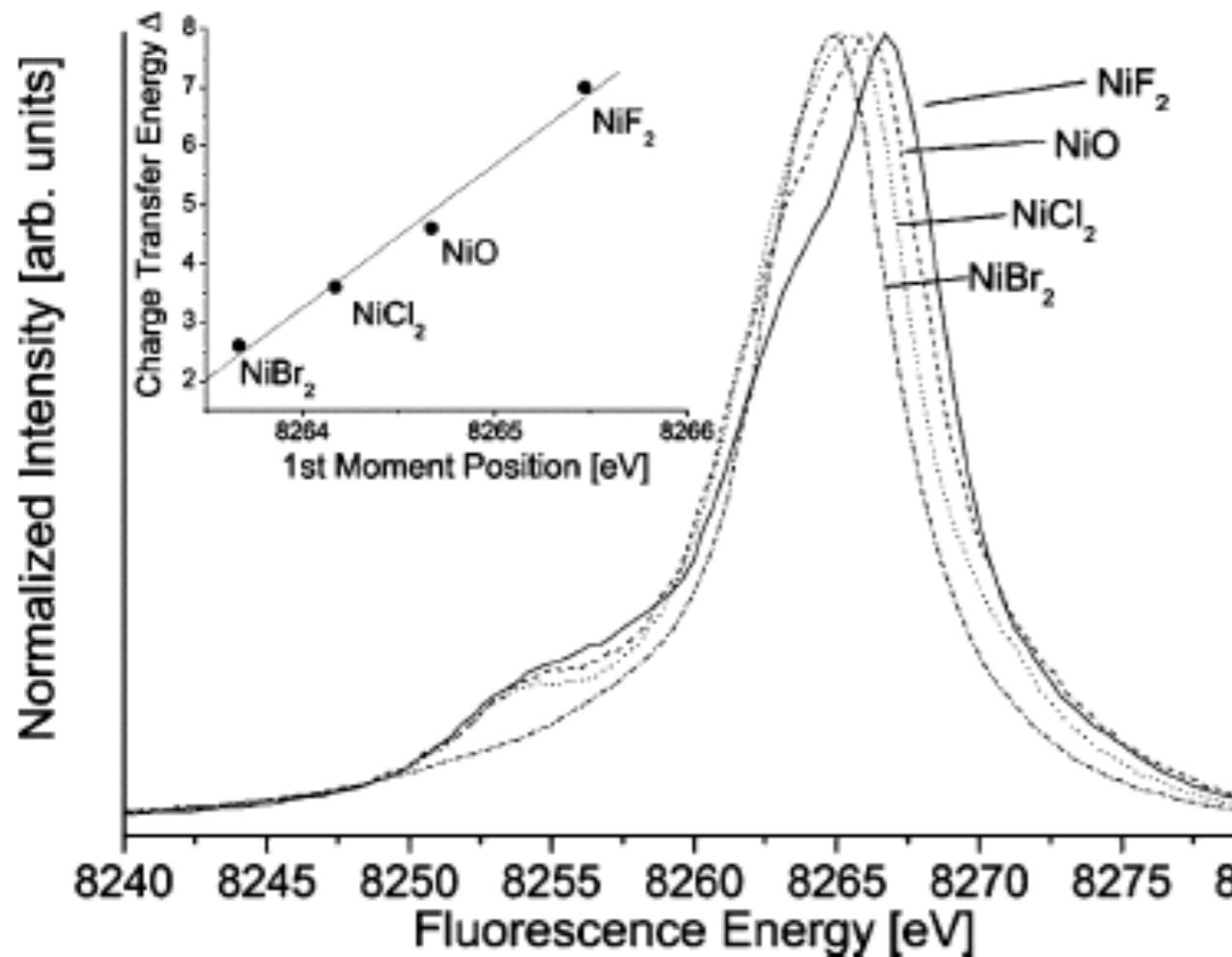
Simple take home message
- The more unpaired electrons the bigger the splitting?

K-Beta Mainline and Covalency



Exchange interaction scales with covalency of the 3d manifold, so ΔE dependent on 3d orbital composition

Previous Observations



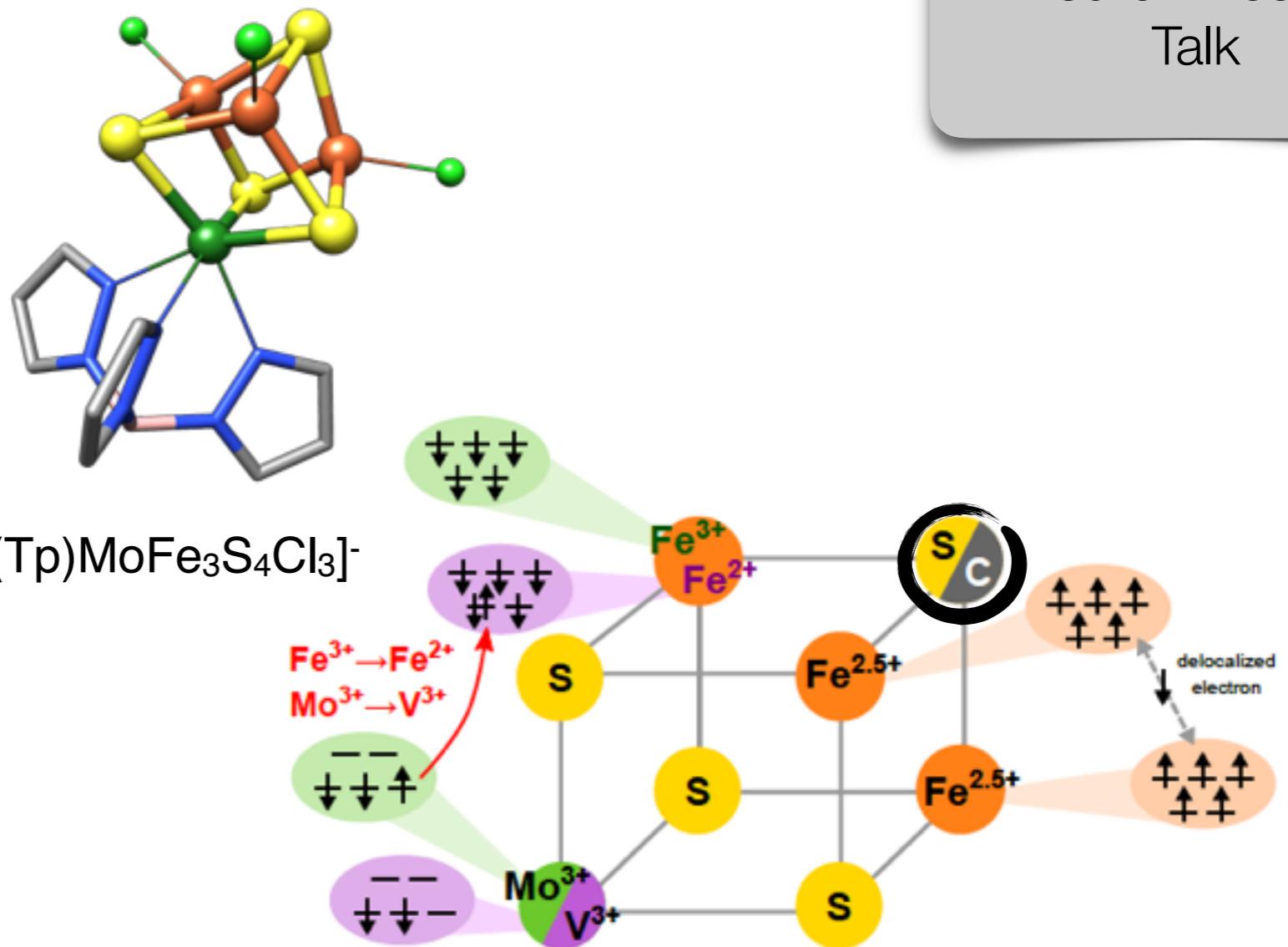
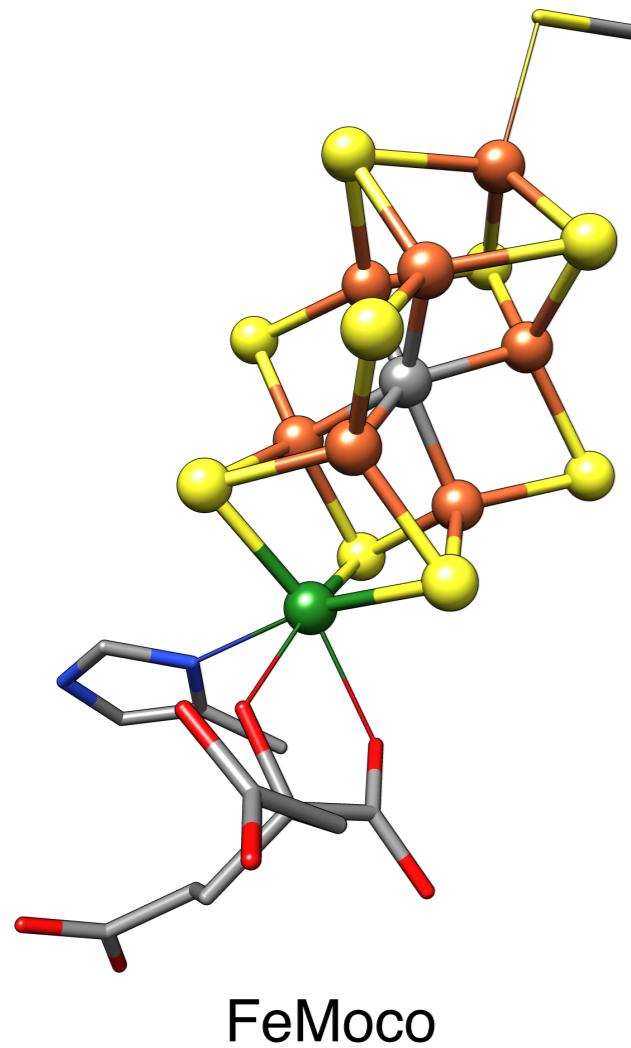
Bergmann, et al, Coord. Chem. Rev., 2005, 249, 65.

Cramer, et al, J. Synchrotron Rad., 1997, 4, 236.

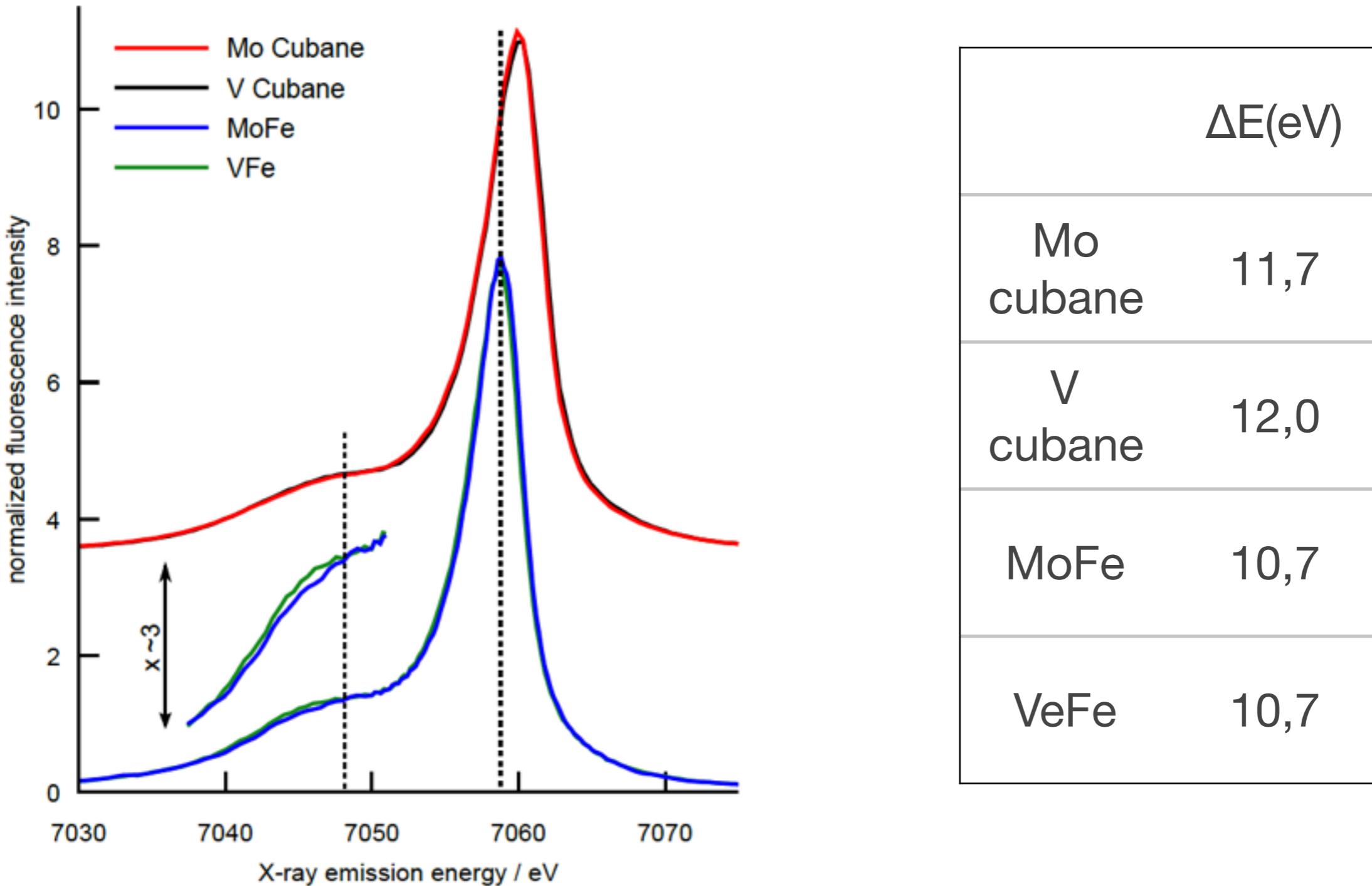
Urch, et al, J. Electron Spectrosc. Relat. Phenom., 2001, 113, 179.

K-Beta XES to Understand the Role of the Carbon?

Julian Rees'
Talk

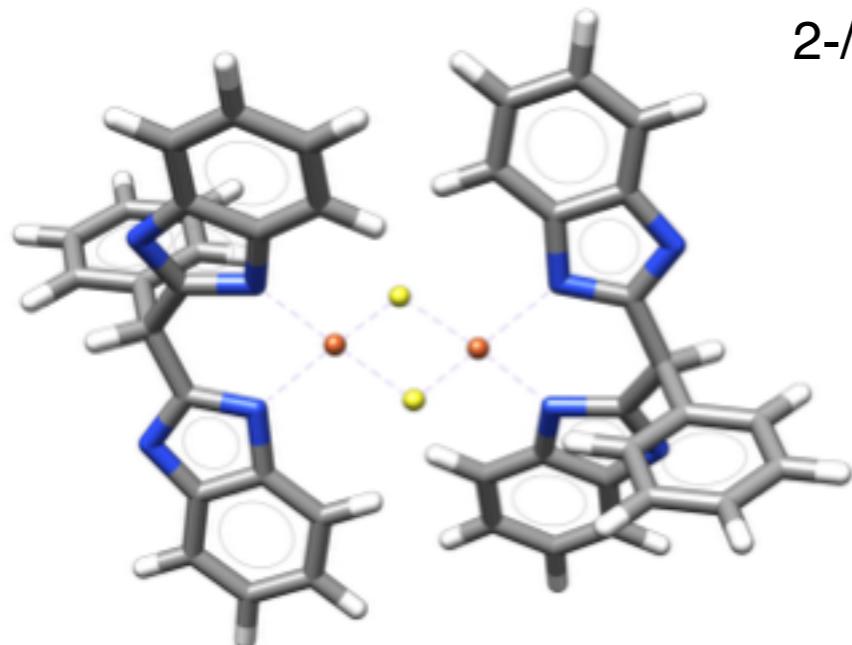


K-Beta Mainline of Cubanates vs. N₂ases



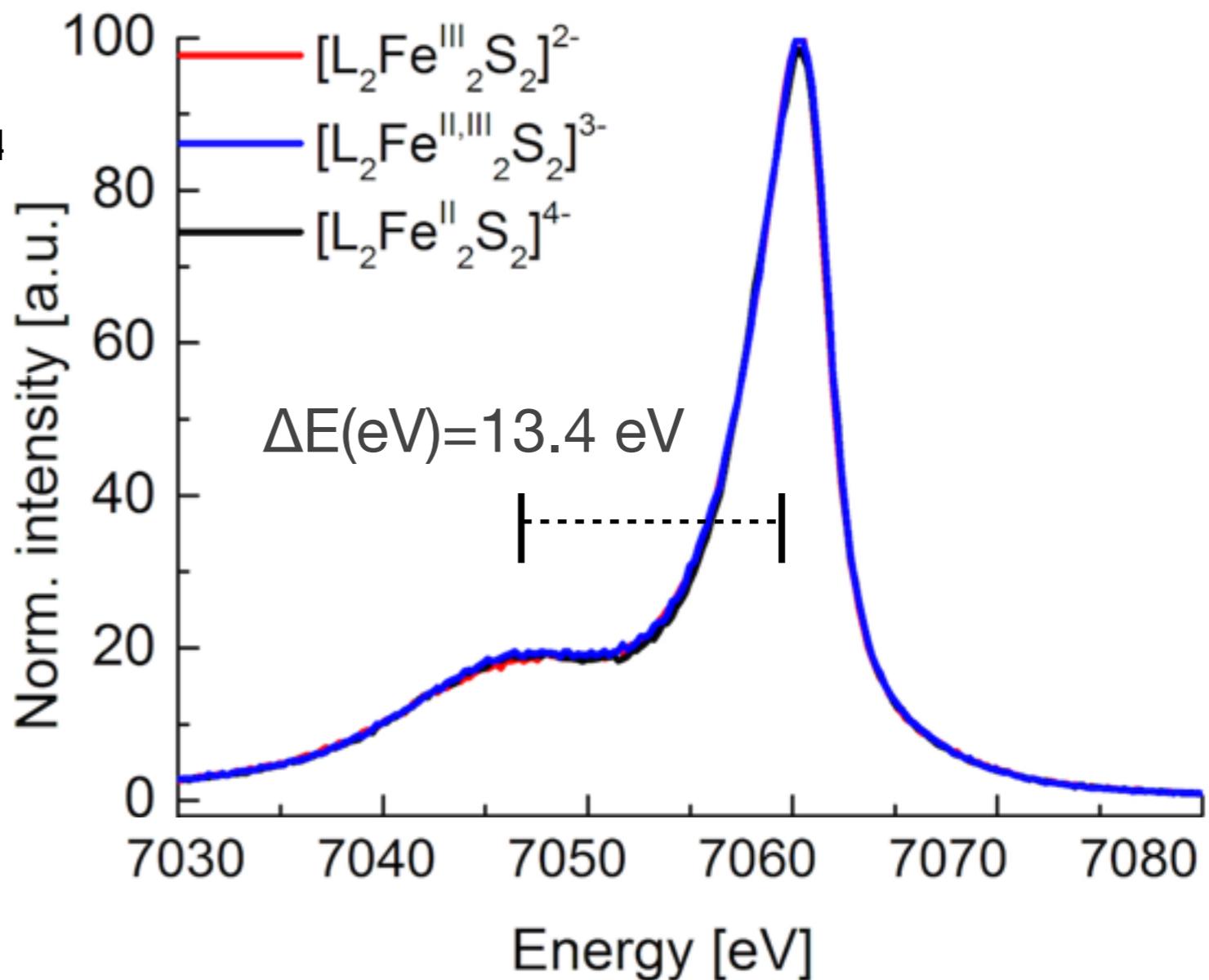
Lessons from Model Studies

In Collaboration with
F. Meyer (Göttingen)



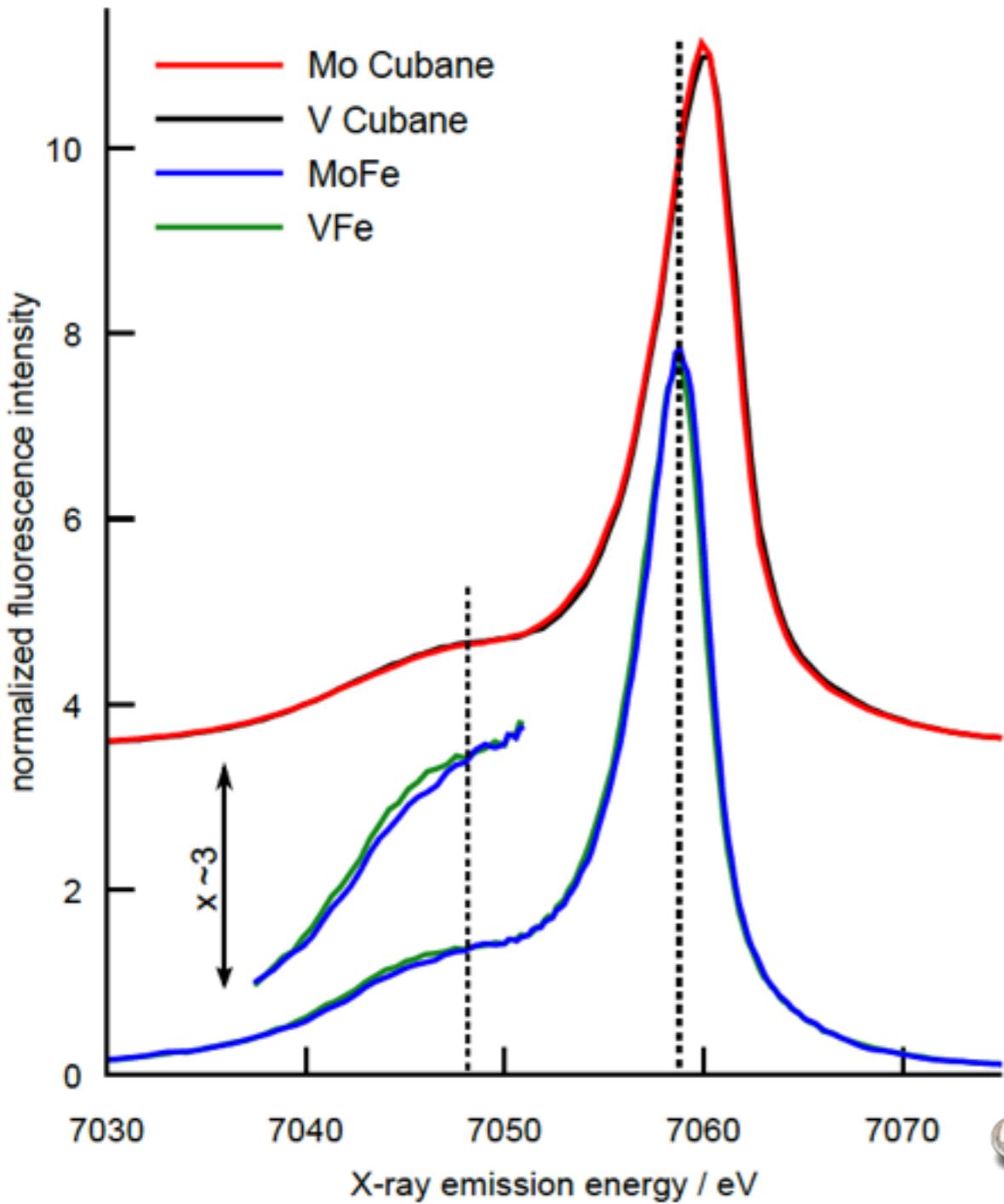
2-3/4

- A. Albers *et al.*, *Angew. Chem. Int. Edit.*, **2011**, *9191* (39)
A. Albers *et al.*, *J. Am. Chem. Soc.*, **135**, *2013*, *1704*.
J. Kowalska *et al.*, *Inorg. Chem.*, **2016**, *in press*.



Contributions due to change in oxidation state
and covalency completely cancel!

K-Beta Mainline of Cubanes vs. N2ases



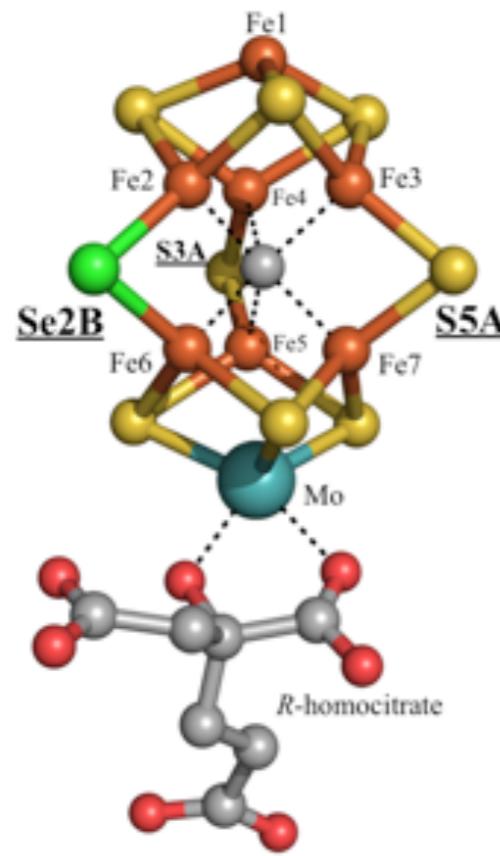
$\Delta E(\text{eV})$	
Mo cubane	11,7
V cubane	12,0
MoFe	10,7
VFe	10,7
$[\text{L}_2\text{Fe(III)}_2\text{S}_2]^{2-}$	13,4
$[\text{L}_2\text{Fe(II,III)}_2\text{S}_2]^{3-}$	13,4
$[\text{L}_2\text{Fe(II)}_2\text{S}_2]^{4-}$	13,4
P-cluster	13,1



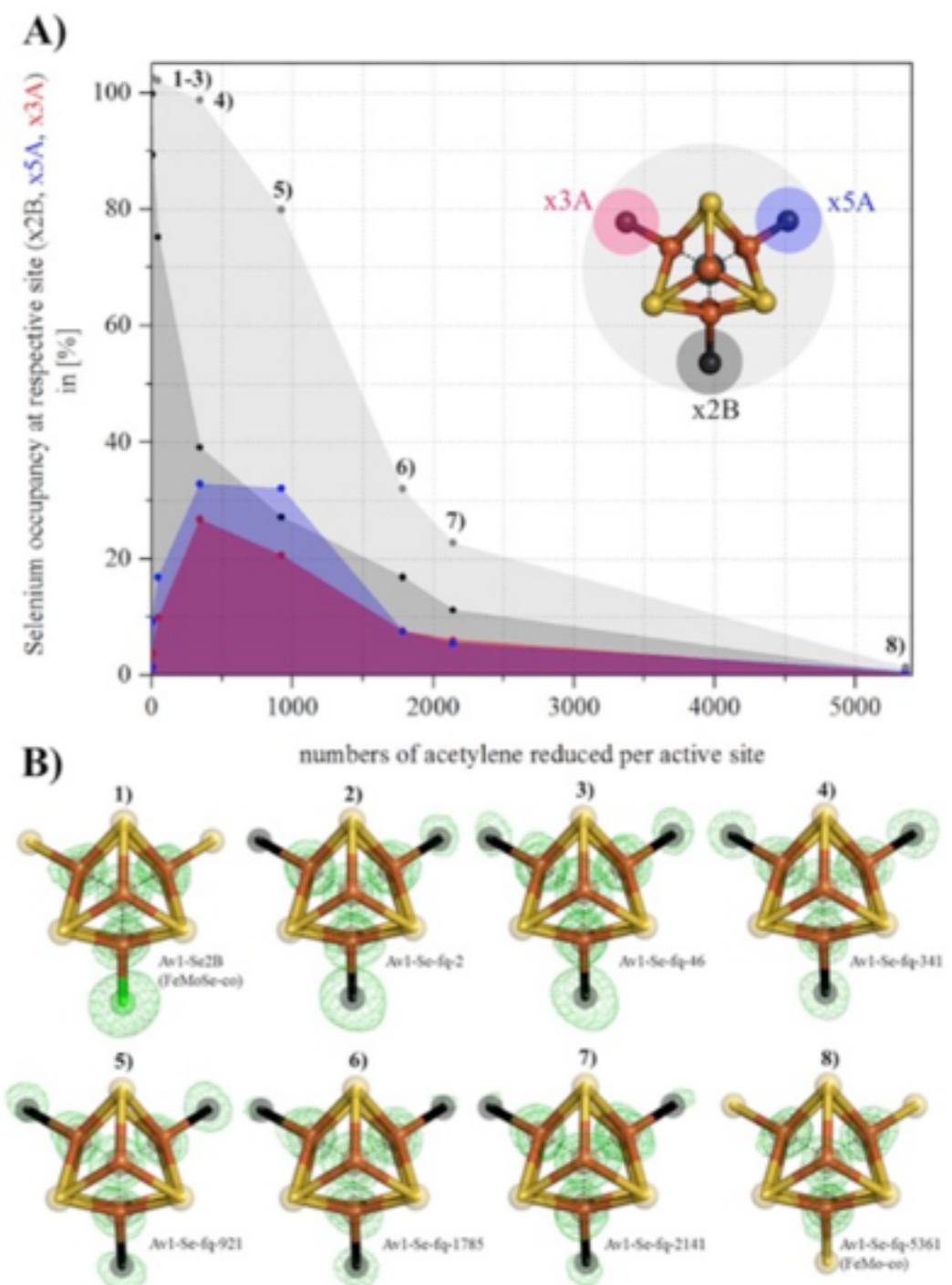
MoFe/VFe smallest ΔE of any FeS cluster. Likely attributed to covalency of carbon.

Se HERFD to Interrogate Intermediates

T. Spatzal *et al.*, *ELife*, 2015, 4:e11620

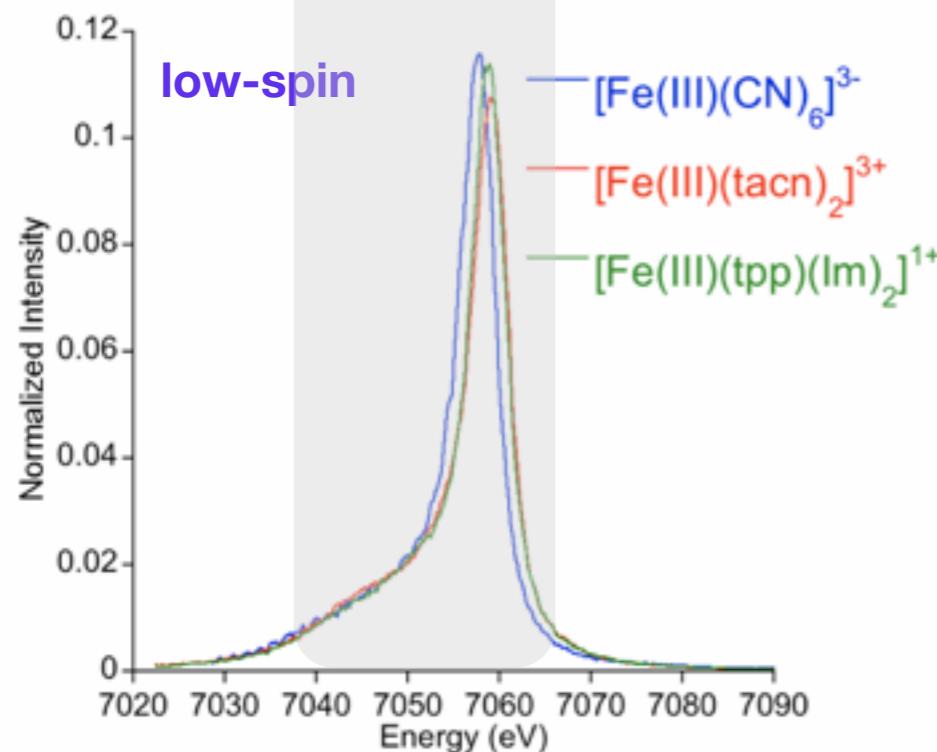
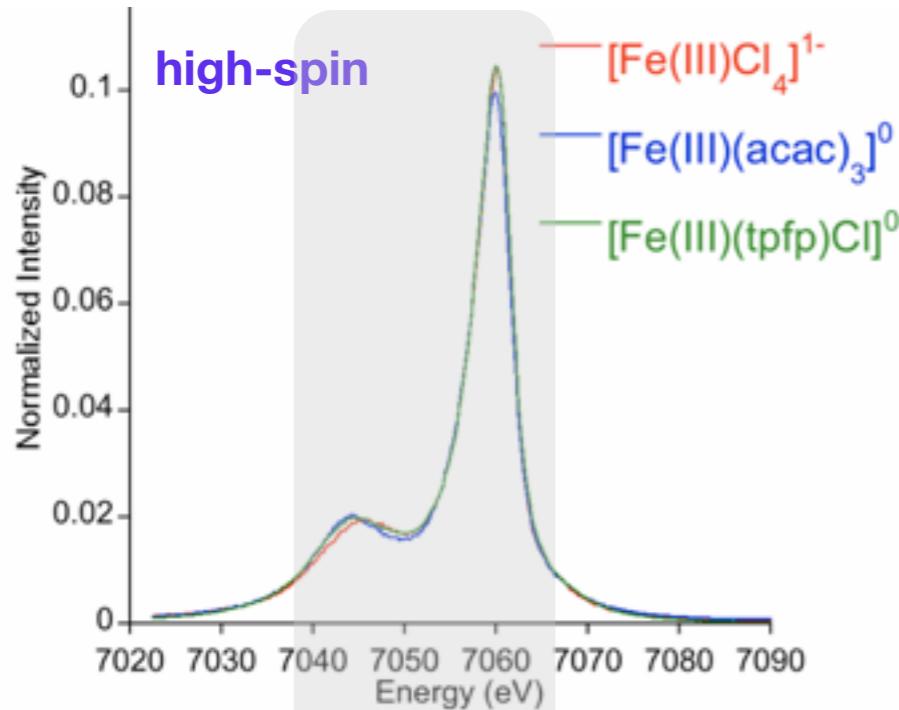


- Se can place the S2B belt sulfur
- Se migrates to S3A and S5A at later stages of catalysis
- FeMoco may be more dynamic than previously thought
- The central carbon, may provide structural stability

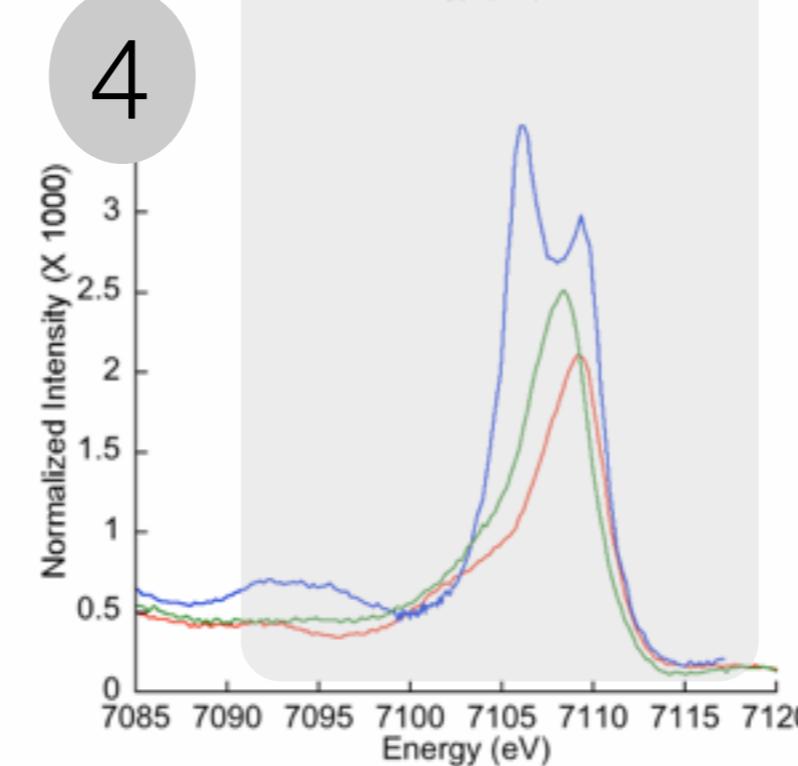
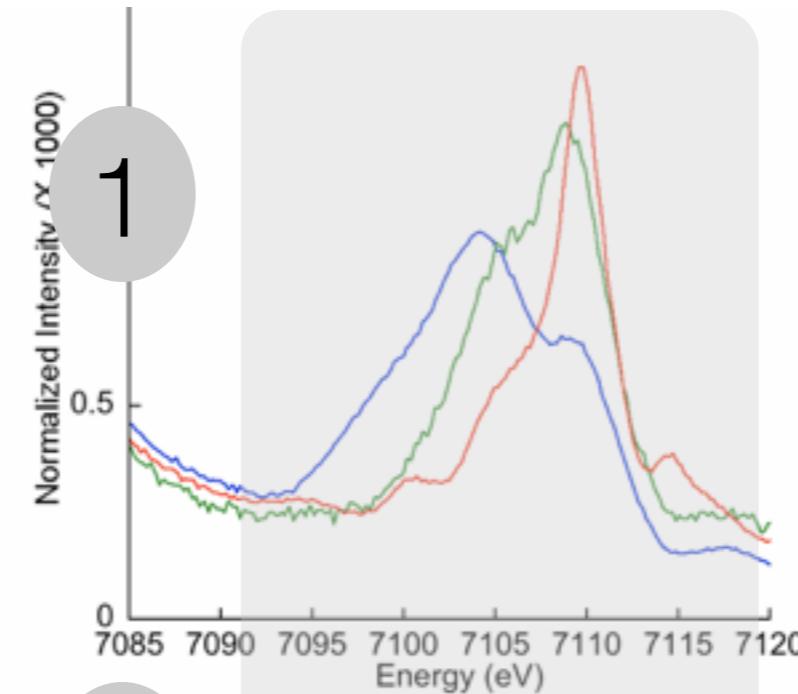


K β and Valence to Core XES of Ferric complexes

K β Main Line



K β Valence to Core



► K-Beta main line shows a strong dependence on spin state (both energy and shape of spectra)

► Valence to core region show greater sensitivity to the chemical environment

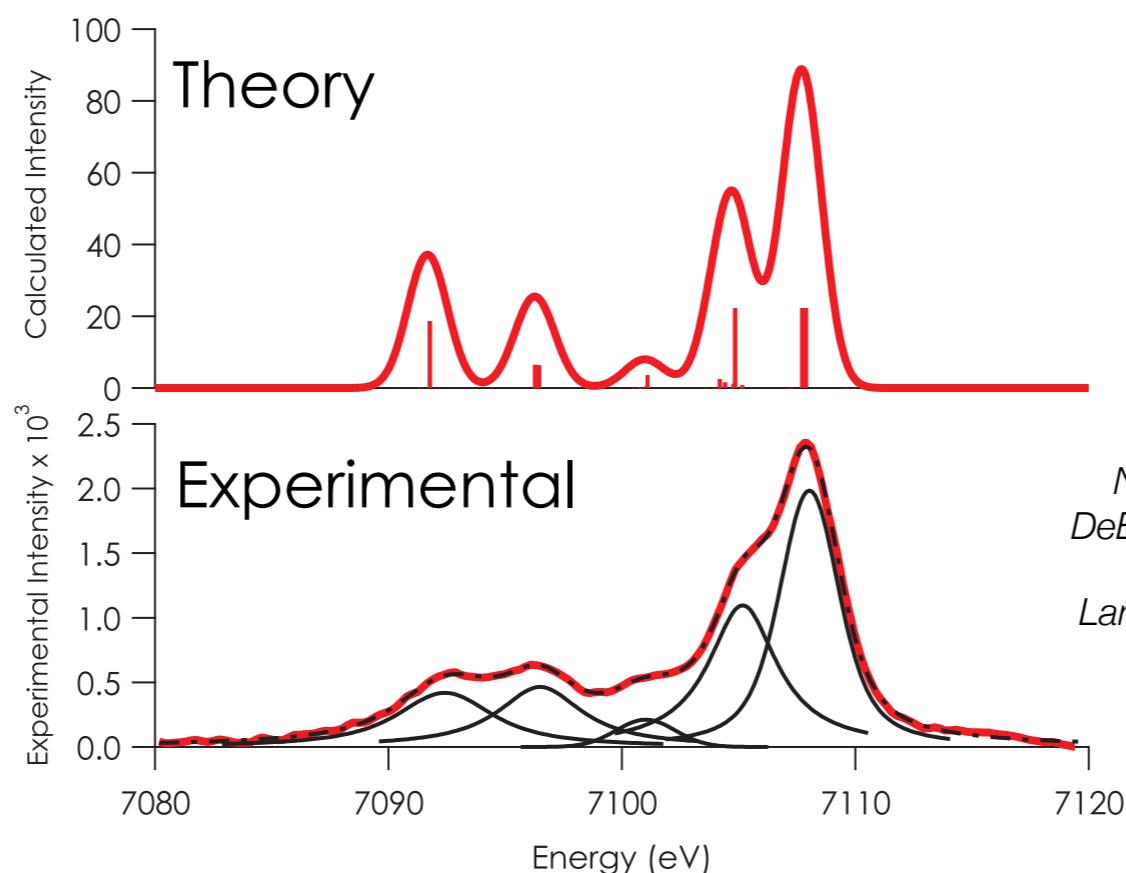
► High-spin complexes show broader features and lower intensities in valence to core region

N. Lee, T. Petrenko, U. Bergmann,
F. Neese, S. DeBeer,
J. Am. Chem. Soc., **2010**, 132,
9715-9727.

Predicting V2C XES with DFT Calculations

$$\sigma(\omega_{em}) = \frac{4\pi}{3} \omega_{em} \sum_{i_\sigma j_\sigma} \sum_{\alpha=x,y,z} \frac{\left| \langle i_\sigma | m_\alpha | j_\sigma \rangle \right|^2 \Gamma}{(\omega_{FI} - \omega_{em})^2 + \frac{1}{4} \Gamma^2} = \frac{4\pi}{3} \omega_{em} \sum_{i_\sigma j_\sigma} \sum_{\alpha=x,y,z} \left| \langle i_\sigma | m_\alpha | j_\sigma \rangle \right|^2 f(\omega_{em}, \omega_{ij}, \Gamma)$$

- Emission energies calculated as **ΔE between one-electron Kohn-Sham orbitals**
- Transitions require **metal character** in molecular orbitals involved in the emission process
- Intensity is governed by the **electric dipole moment operator** (m_α)

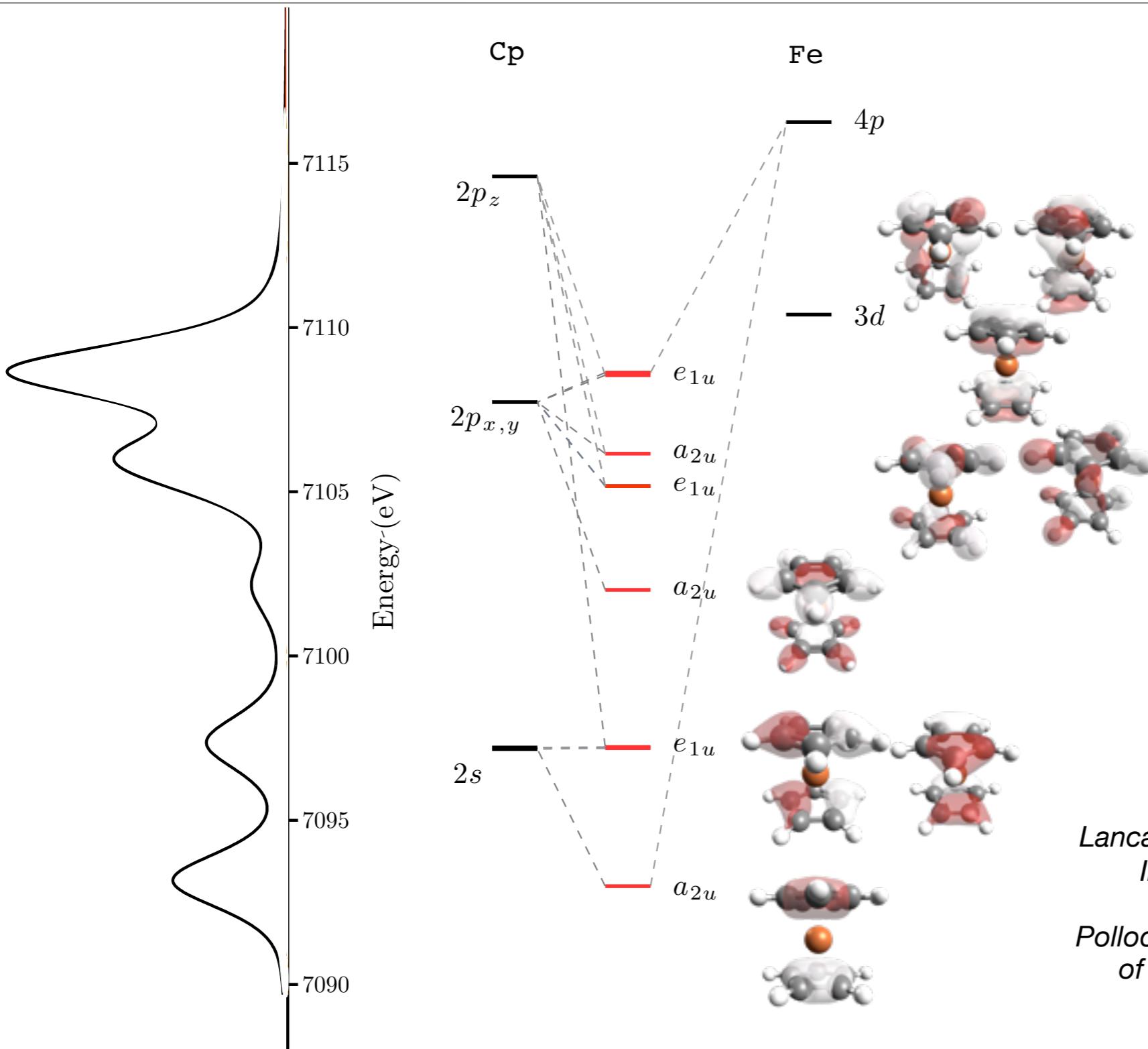


ORCA
F. Neese

N. Lee, T. Petrenko, U. Bergmann, F. Neese, S. DeBeer, J. Am. Chem. Soc., **2010**, 132, 9715-9727.

Lancaster, K.M.; Finkelstein, K.D.; DeBeer, S. Inorg. Chem. **2011**, 50, 6767-6774.

Electronic Structural Insights from VtC XES...



✓ All contributions result from metal np mixing into filled Fc MOs

✓ Maps out filled ligand MOs from perspective of a given metal

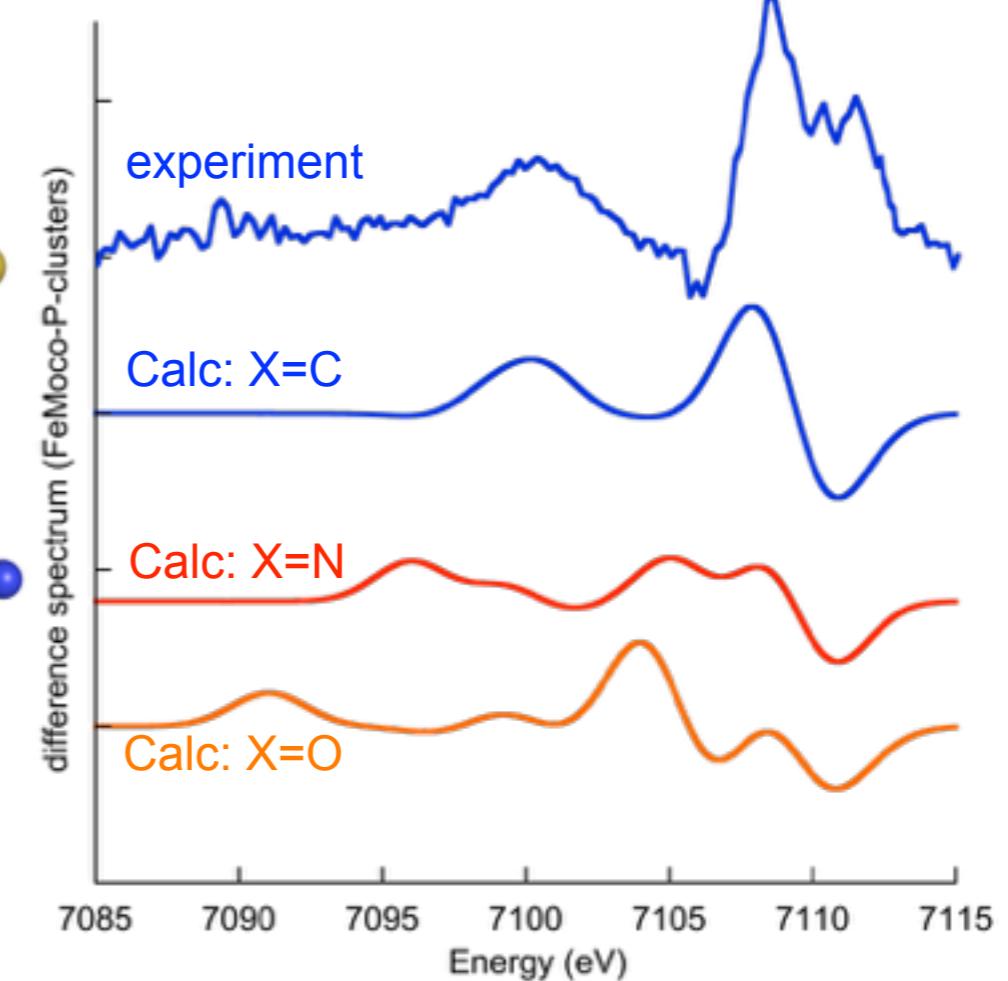
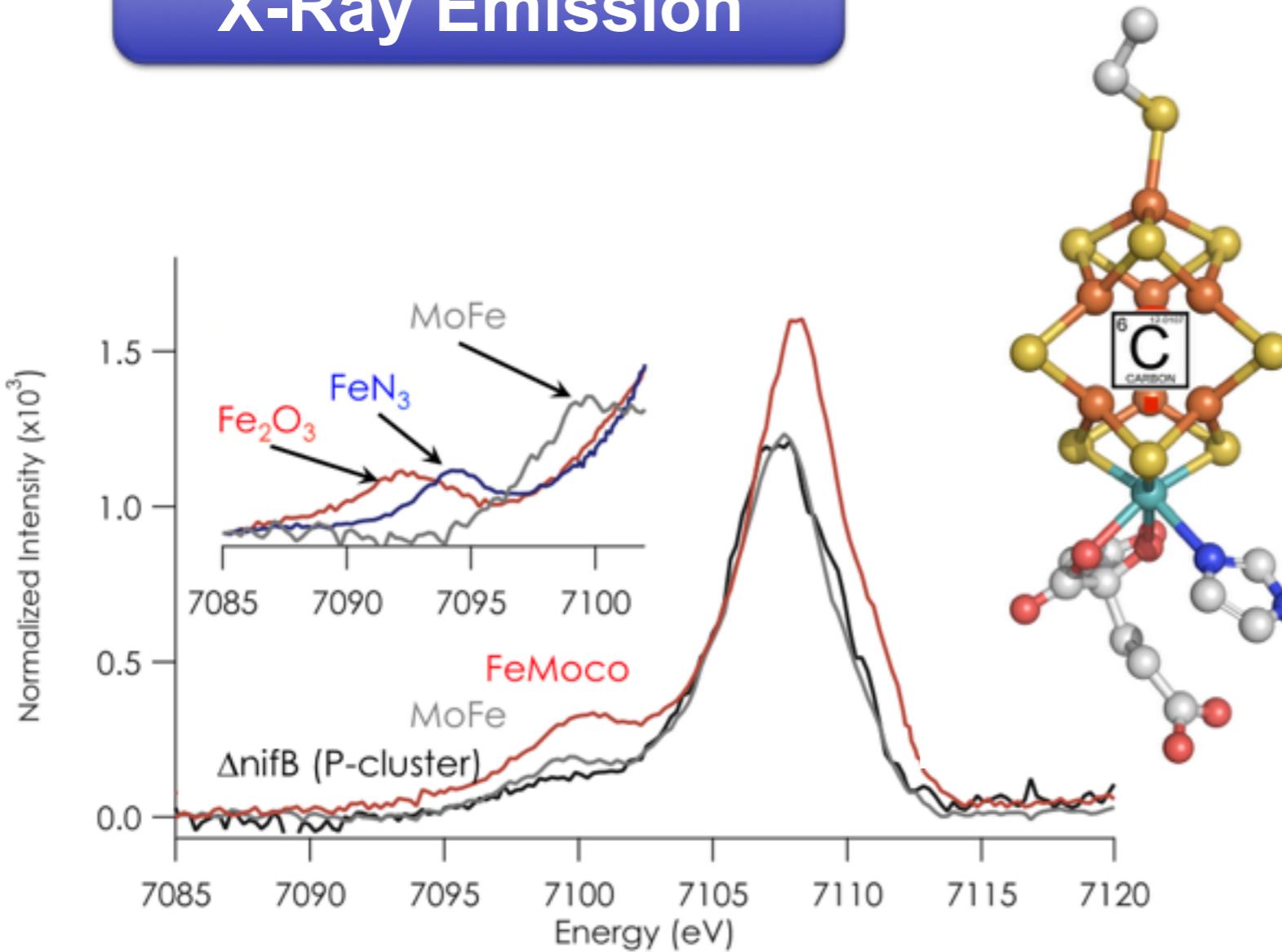
Lancaster, K.M.; Finkelstein, K.D.; DeBeer, S. Inorg. Chem. **2011**, 50, 6767-6774.

Pollock, C. J. and DeBeer, S. **2015**, Accounts of Chemical Research, 48, 2967-2975.

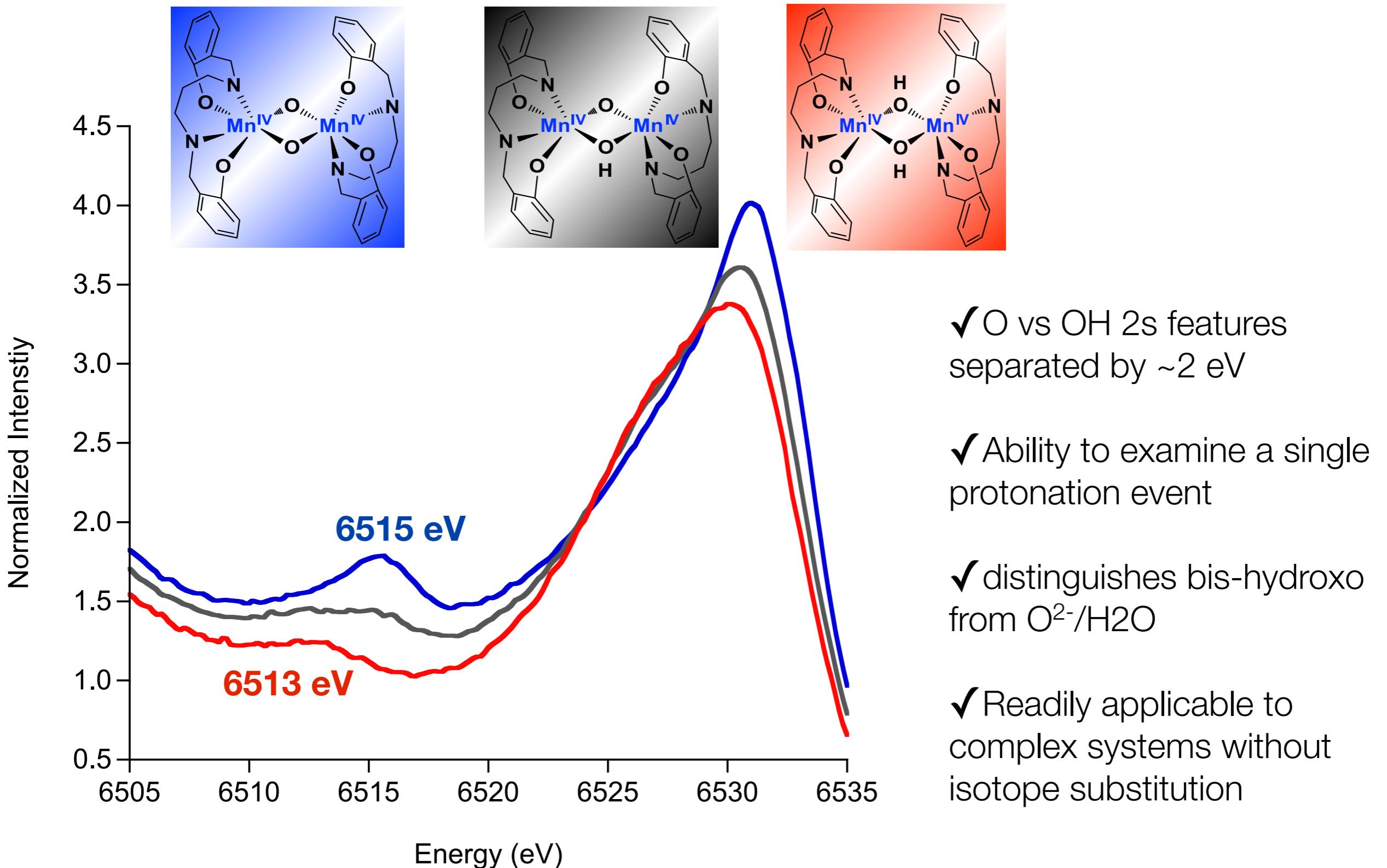
Identifying the Central Atom in FeMoco

Novel Spectroscopy:
X-Ray Emission

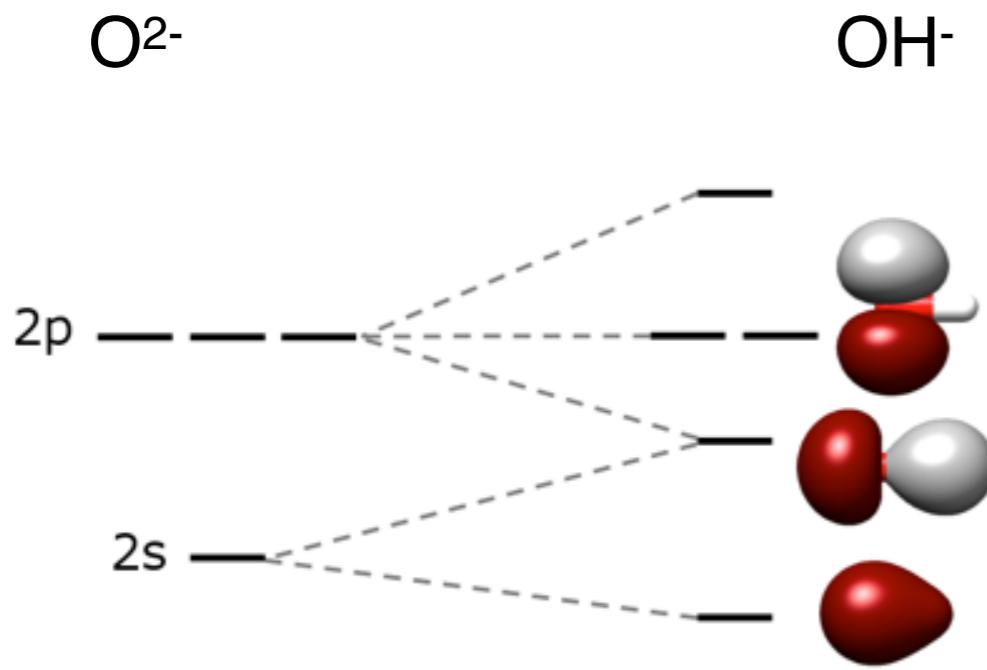
Quantum Chemistry



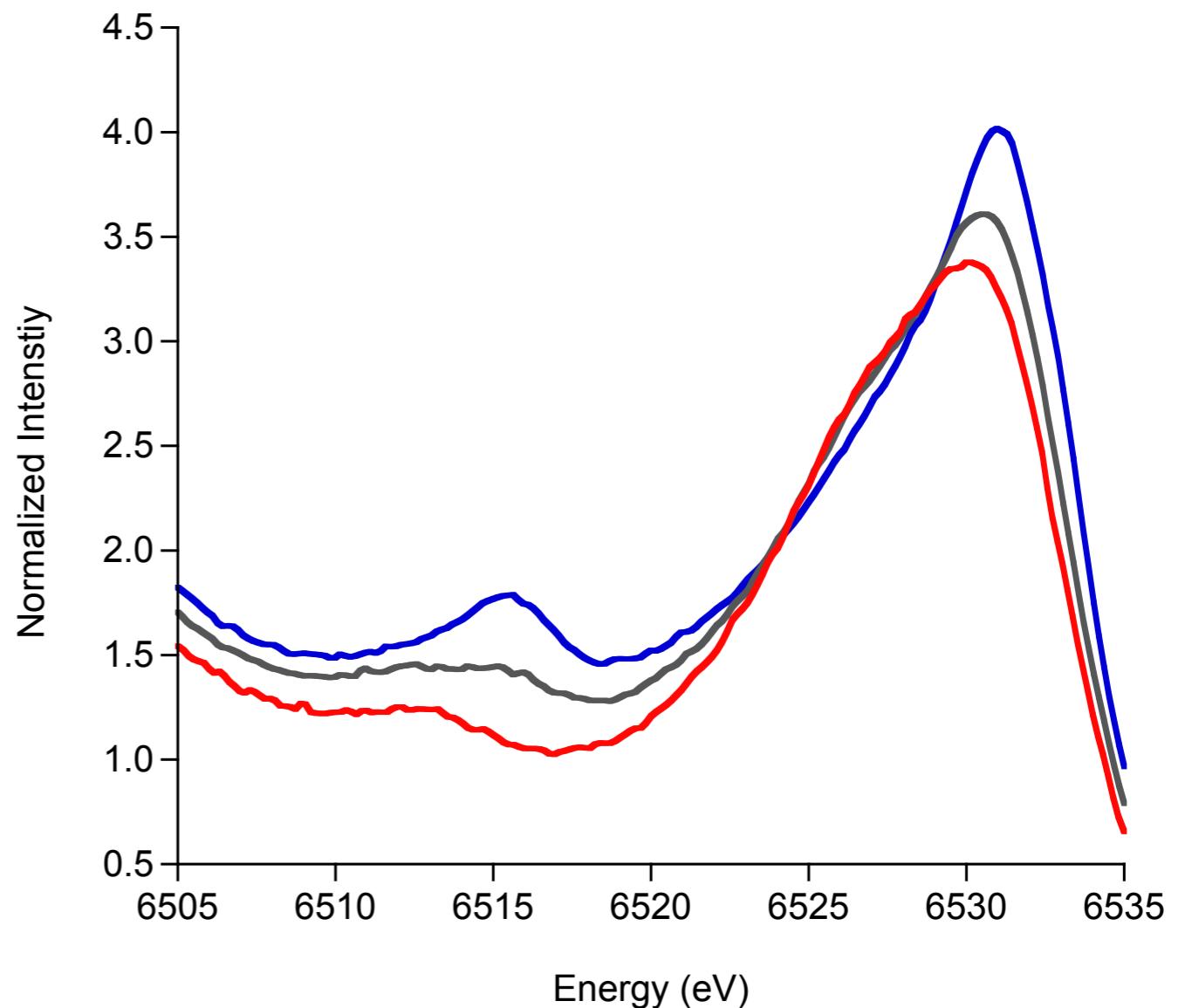
XES is directly sensitive to protonation



Effect of protonation on the MOs....



- ✓ Protonation lowers the 2s energy
- ✓ Delocalizes electrons into the O-H bond, thus lowering intensity
- ✓ Similarly a lower energy shoulder appears in the KB2,5



Outline

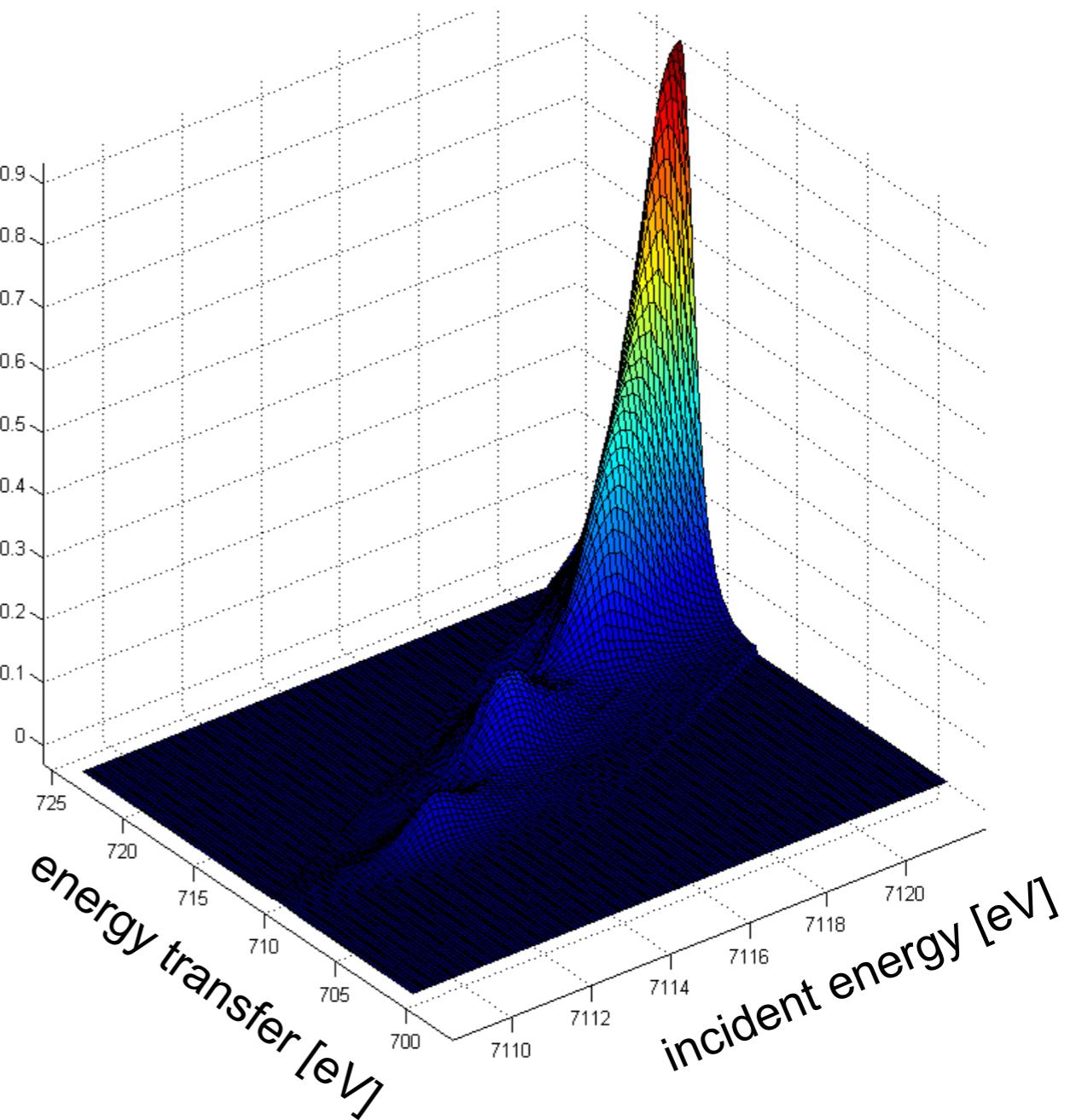
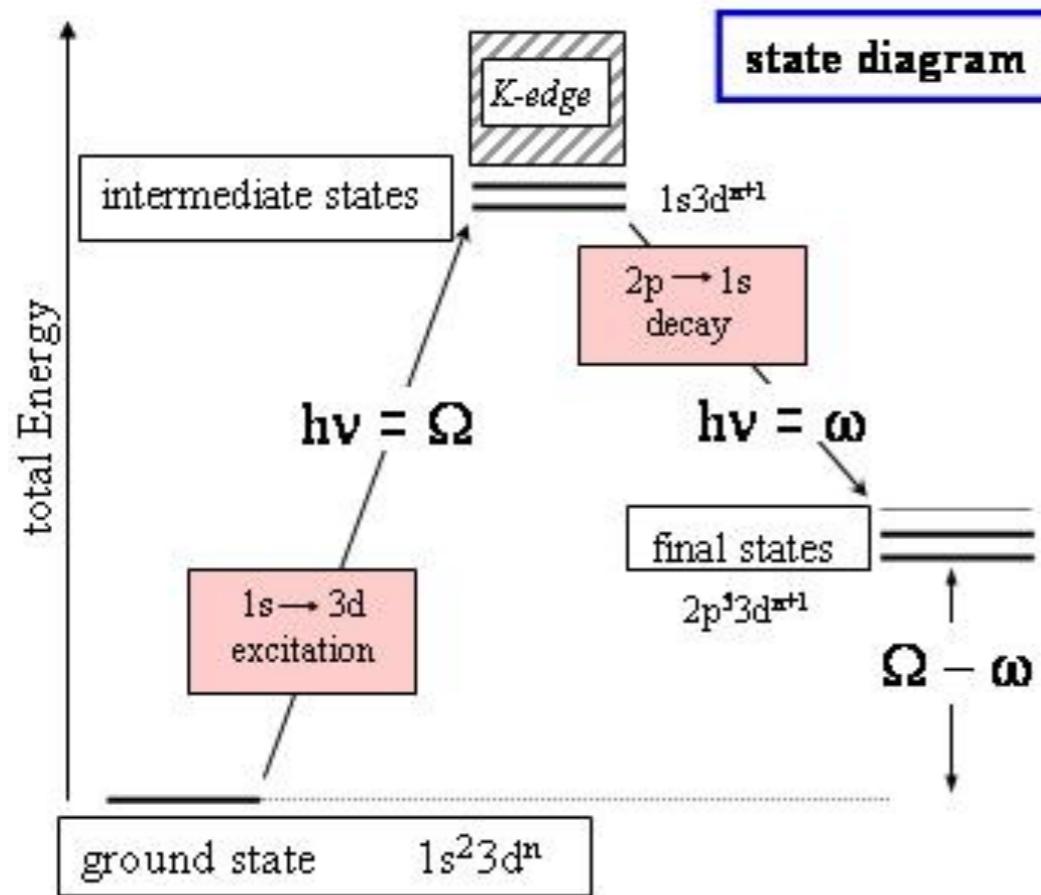
- Non-resonant X-ray Emission Spectroscopy (XES)

- K-Beta XES
- Valence to Core XES
- (K-alpha XES)

- **Resonant X-ray Emission Spectroscopy (RXES or RIXS)**

- XAS + XES 2D measurement
- Higher resolution XAS
- Oxidation State and Spin State Selective XAS
- Ligand Selective XAS?
- Combine Mb-XES instrument
- 2p3d RIXS

RIXS: Adding Another Dimension...



- * L-edge like probe with hard X-rays!
- * Expands in situ possibilities (high pressure, solutions, etc)
- * Reduced damage

1s2p RIXS: Applications to the OEC

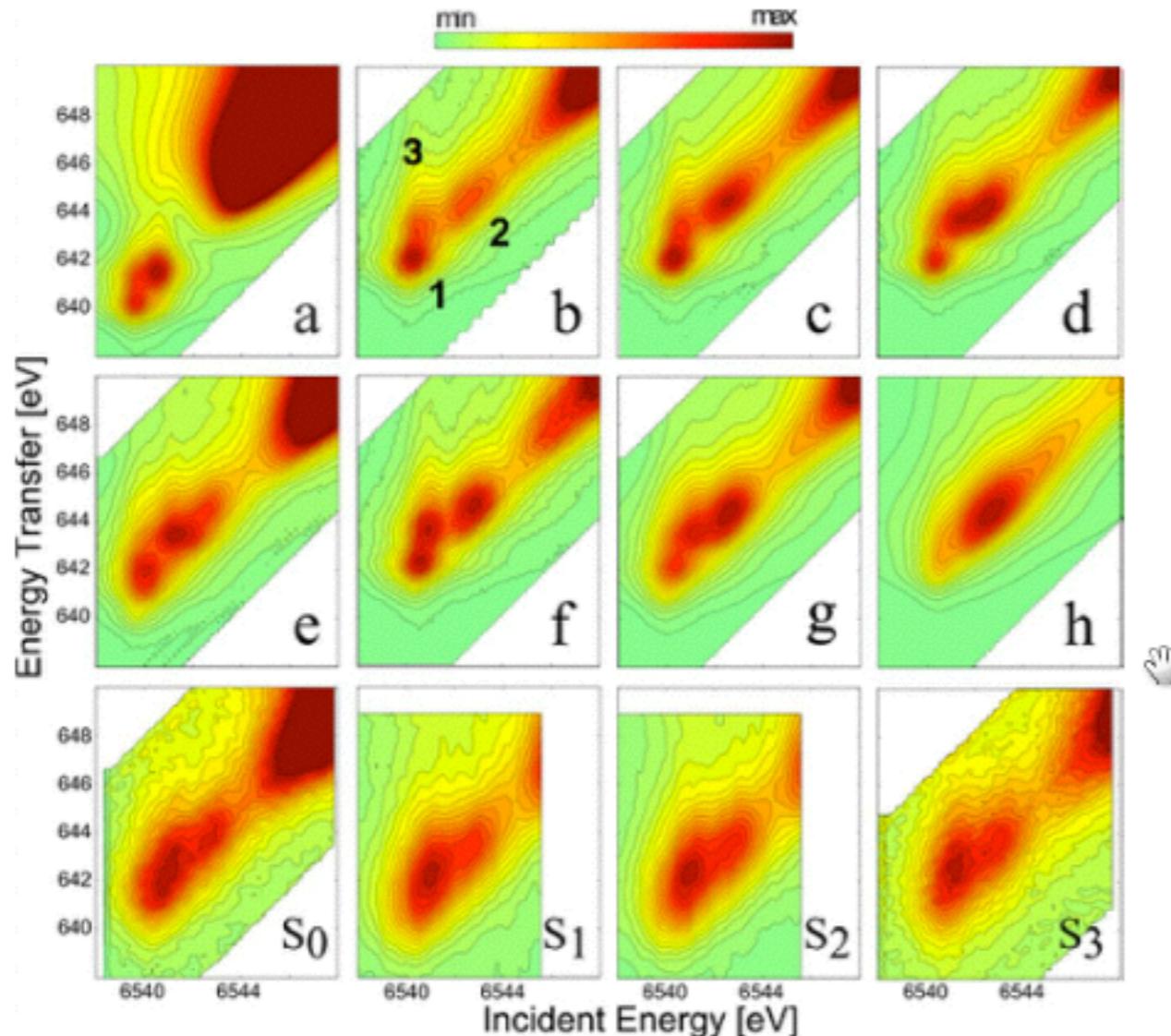


Figure 1. Contour plots of Mn 1s2p RIXS planes of model compounds and the OEC in PS II in the S_0 to S_3 states: (a) Mn^{II}O; (b) salpn₂Mn^{IV}₂(OH)₂; (c) salpn₂Mn^{IV}₂(O)(OH); (d) salpn₂Mn^{IV}₂(O)₂; (e) phen₄Mn^{IV}₂(O)₂; (f) Mn^{IV}₃Ca₂; (g) Mn^{IV}₃(O)₄Acbpy; (h) Mn^{IV}(O)₂. The energy axes are identical for all spectra. The intensity is normalized to the maximum in the preedge region for all spectra.

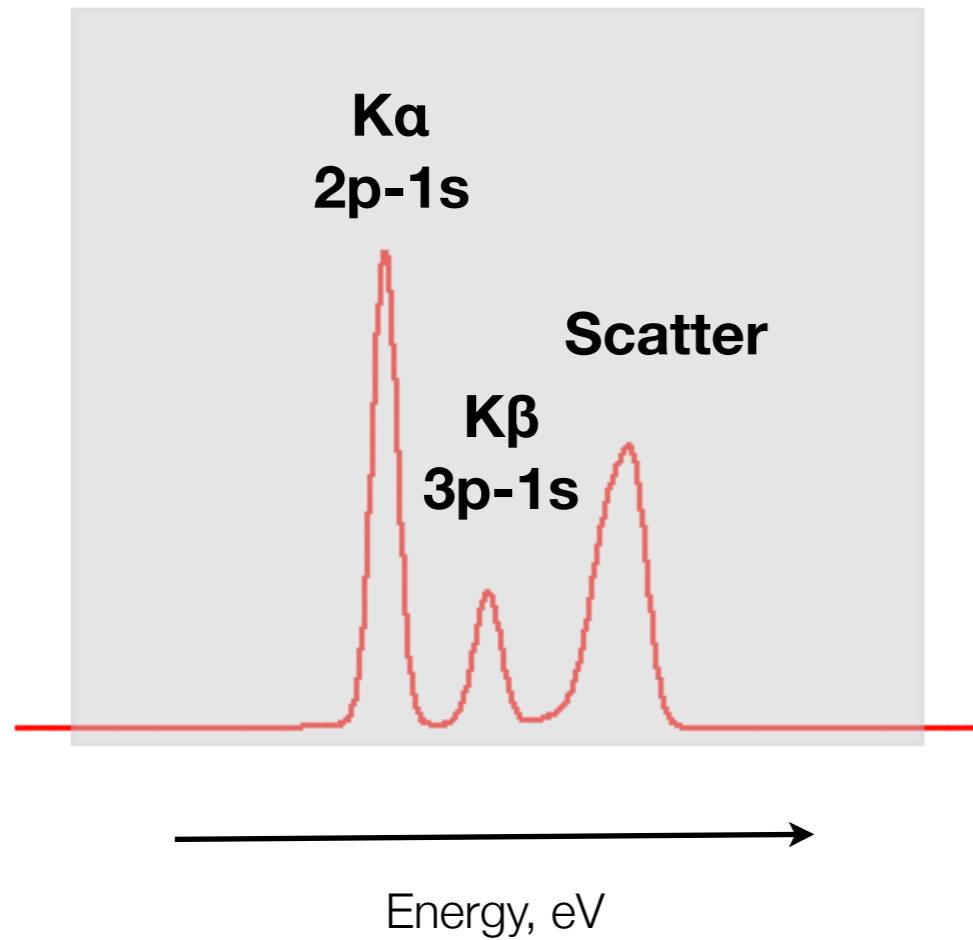
- * Readily applied to complex systems *in situ*
 - * Able to obtain data on dilute metalloprotein
 - * provides a much more detailed “fingerprint” for the assignment of oxidation states within complex systems.
- 
- * BUT, more theory development is needed for proper treatment (ROCIS in progress)
 - * Cuts through RIXS plane can provide higher resolution XANES...

Glatzel et al., Inorg. Chem, 2013, 52, 5642.

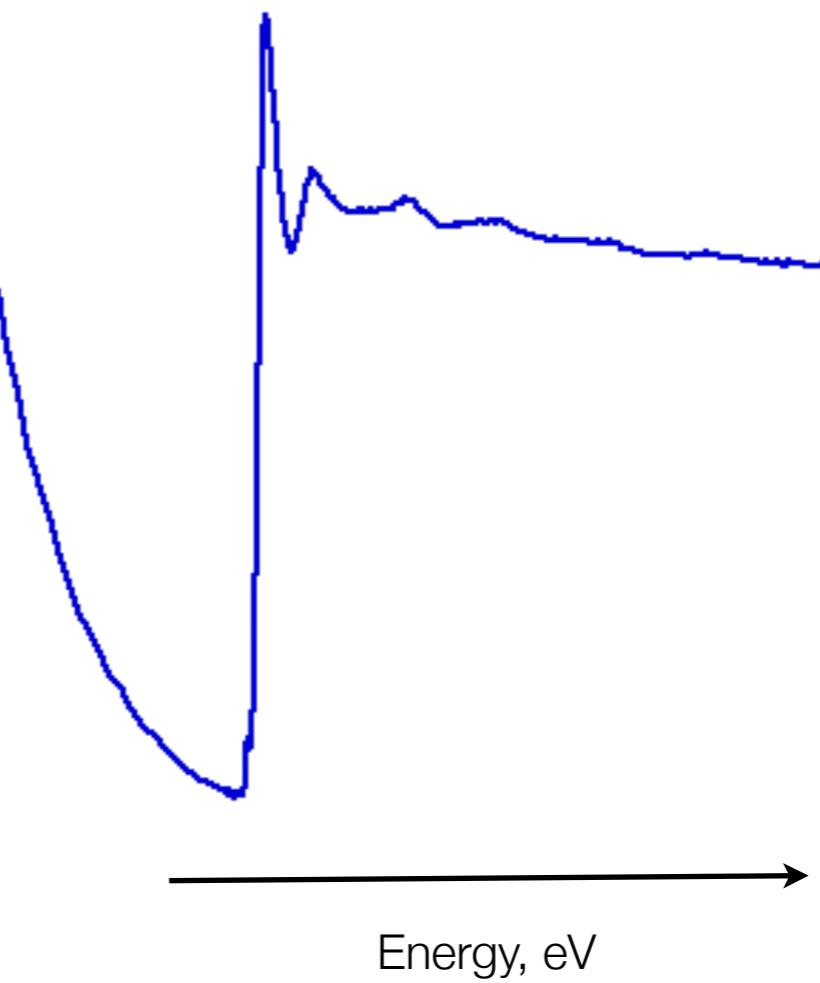
Standard vs High-Resolution XAS Detection

In the dilute limit XAS is measured as proportional to fluorescence

Total fluorescence detection:



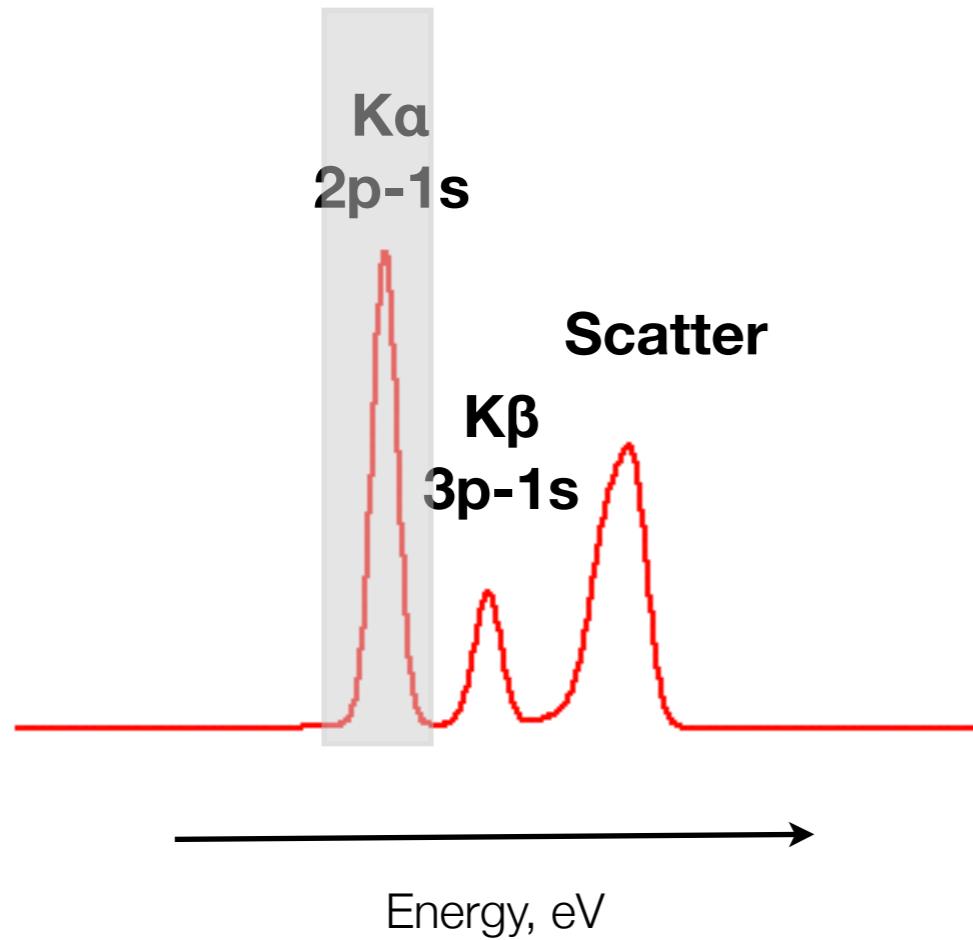
Resultant XAS Spectrum:



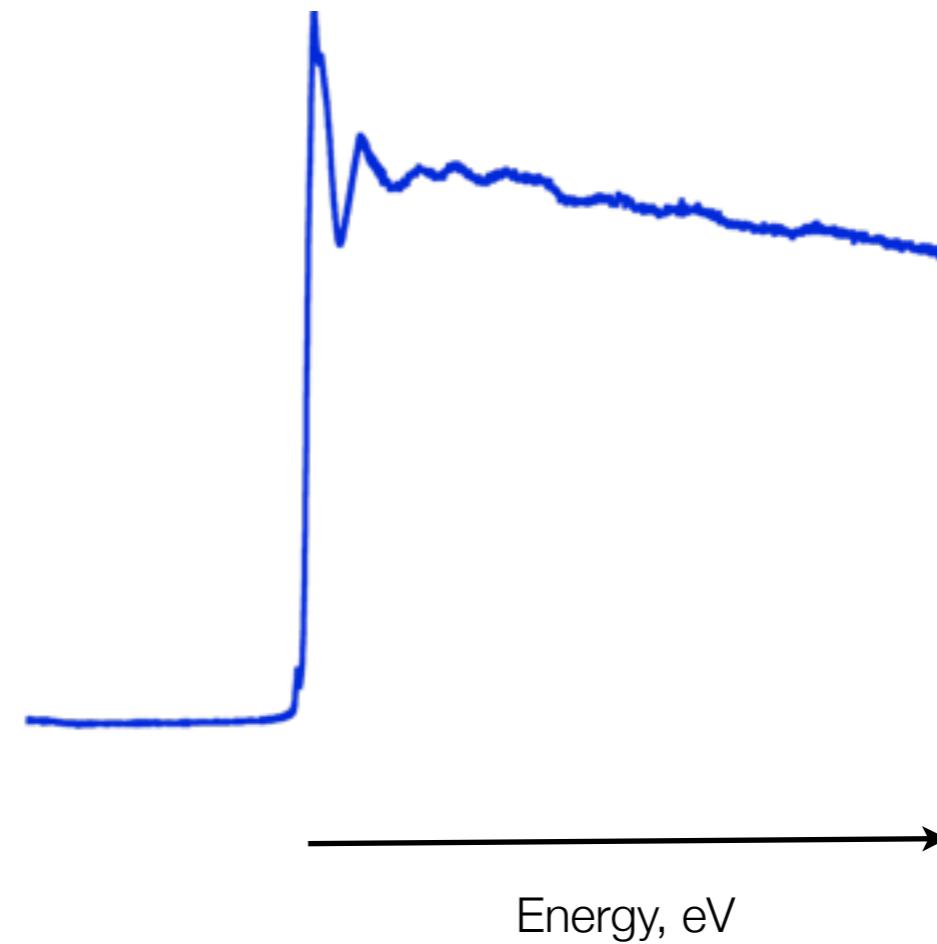
Standard vs High-Resolution XAS Detection

Solid State Detectors can repress the “scatter” background

Partial fluorescence detection:



Resultant XAS Spectrum:

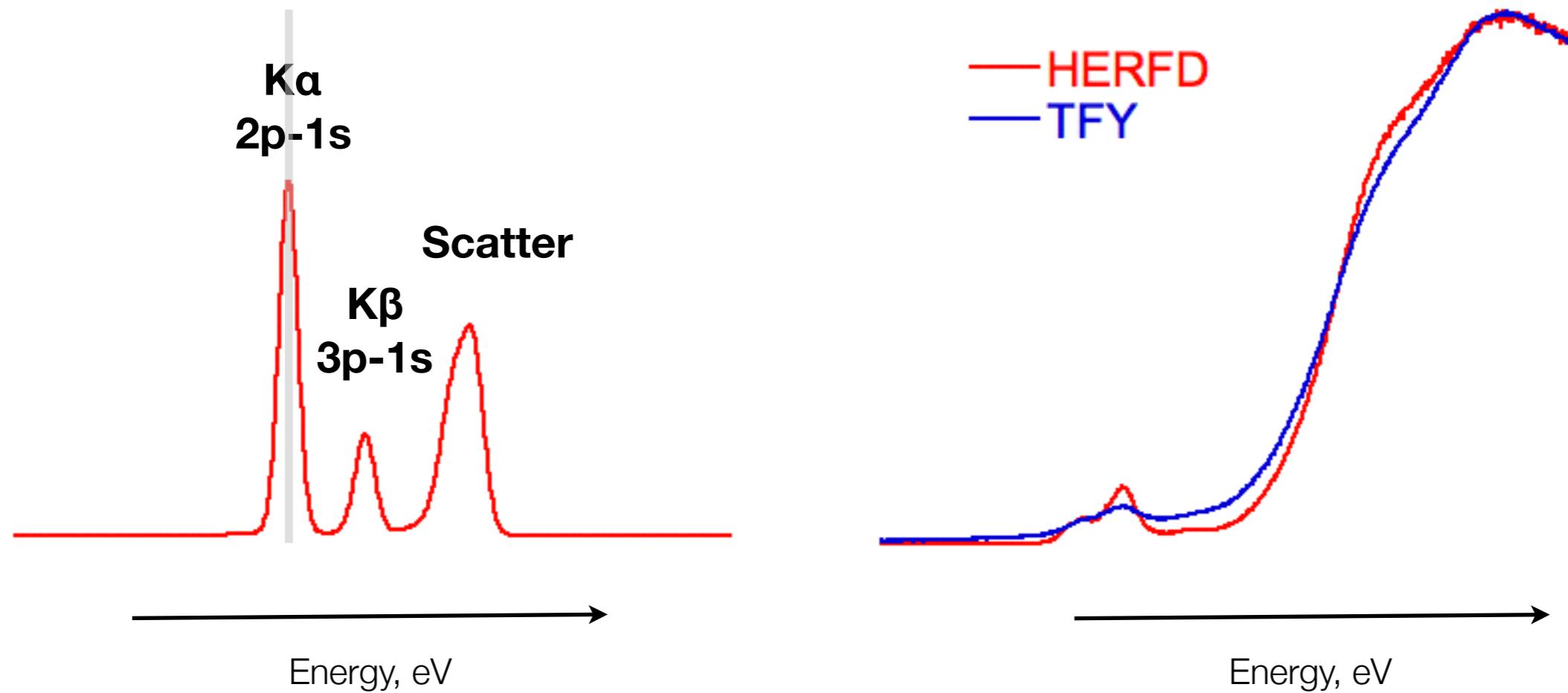


Standard vs “HERFD” XAS Detection

High-energy resolution fluorescence detection XAS uses a ~2 eV slice through the K-alpha line.

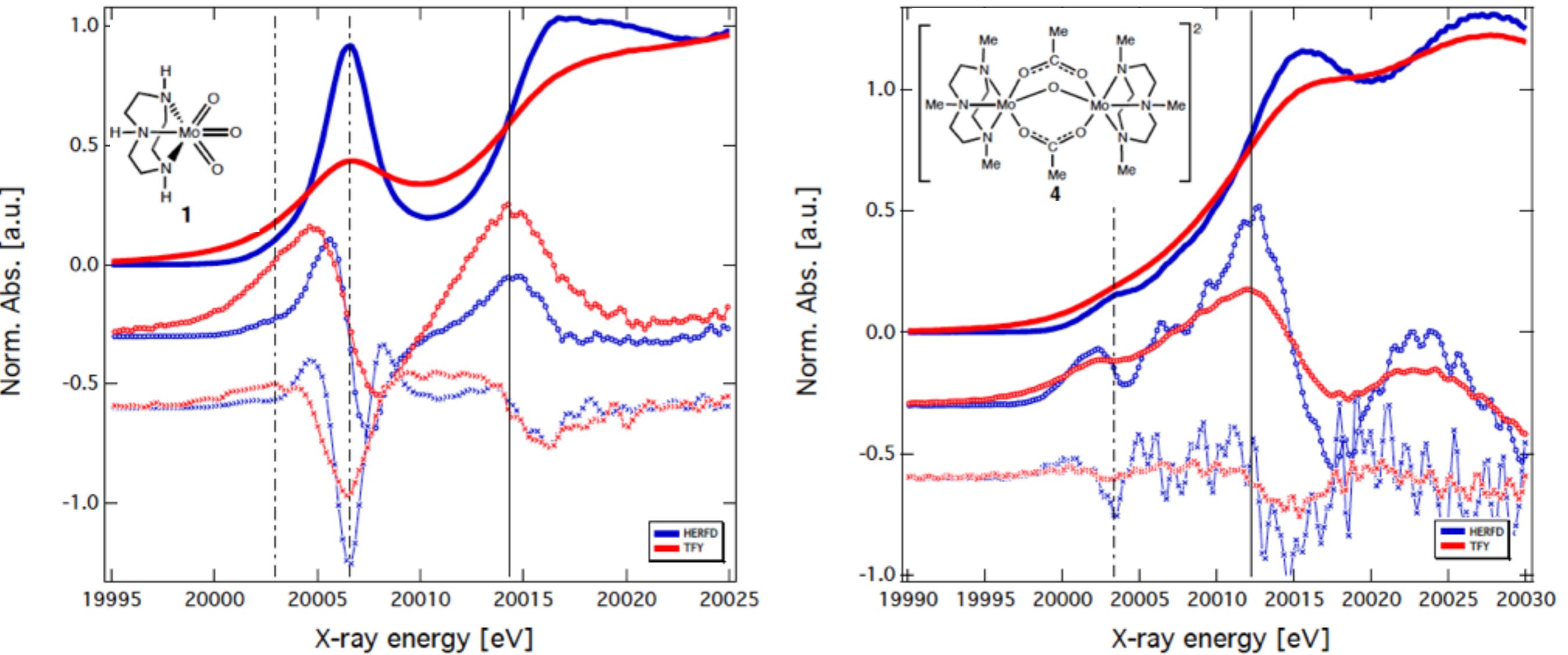
Resolution dominated by 2p rather than 1s core hole.

HERFD detection:



K. Hämäläinen, D. P. Siddons, J.B. Hastings, L. Berman, Phys. Rev. Lett., 1991, 67,20.

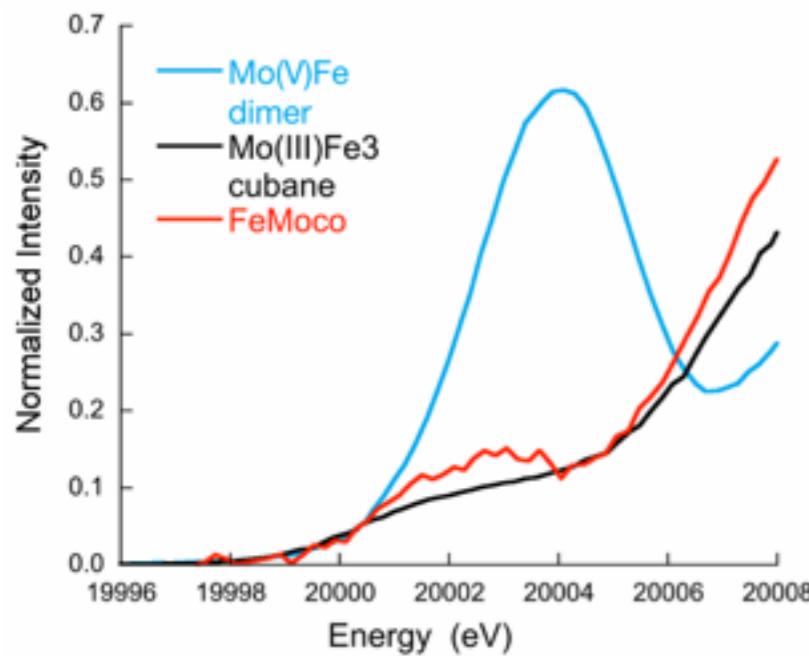
Improved resolution in Mo HERFD XAS



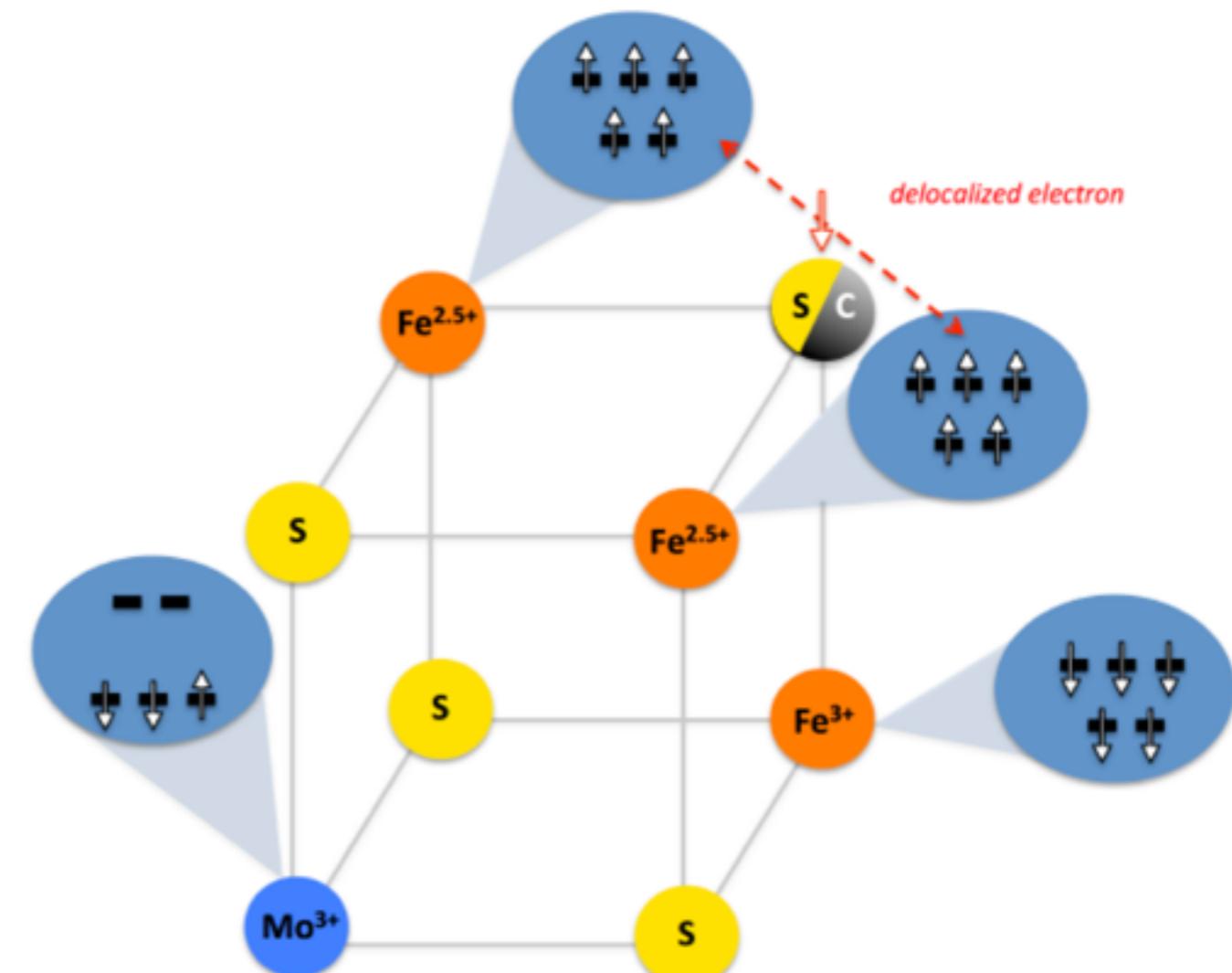
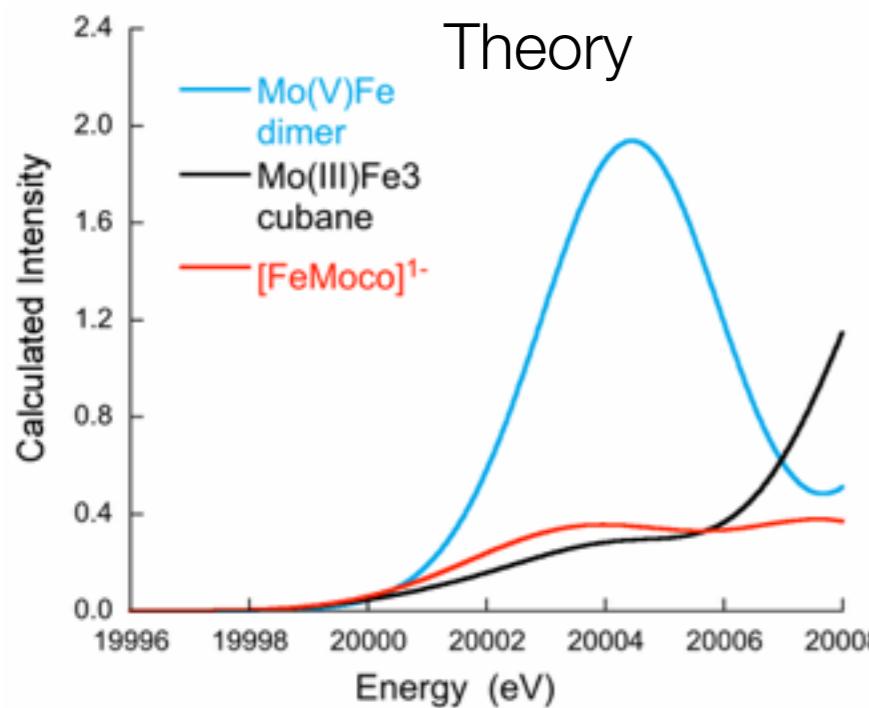
A Spin-coupled Mo(III) in FeMoco

Mo HERFD XAS

Experiment



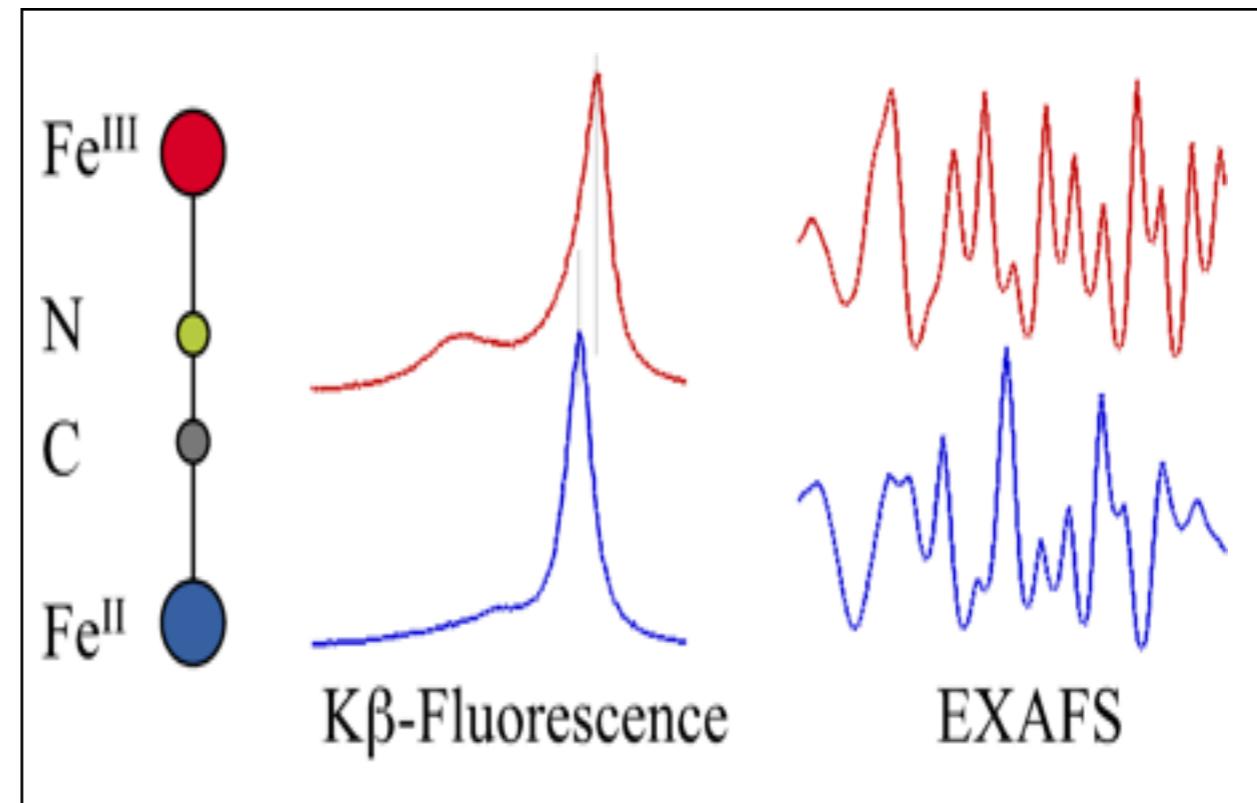
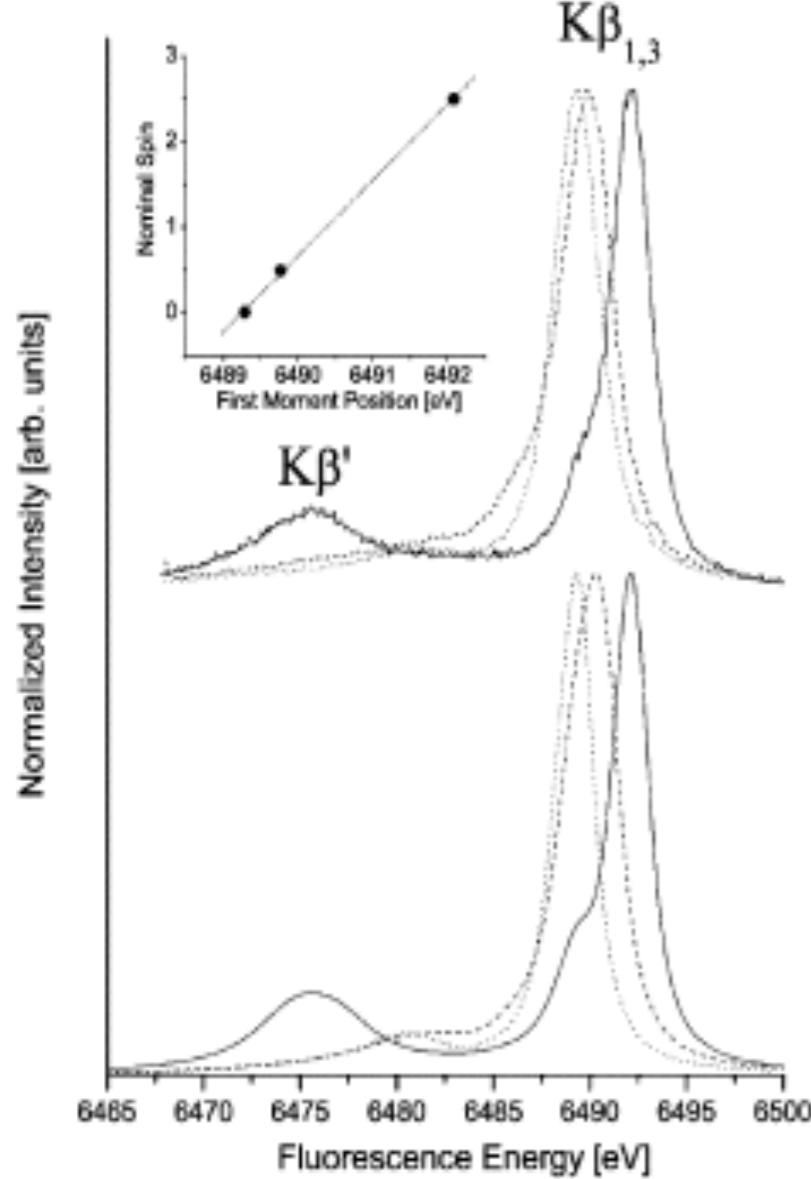
Theory



Total charge on FeMoco, however, still an open question.
We need to know the iron oxidation state distribution....

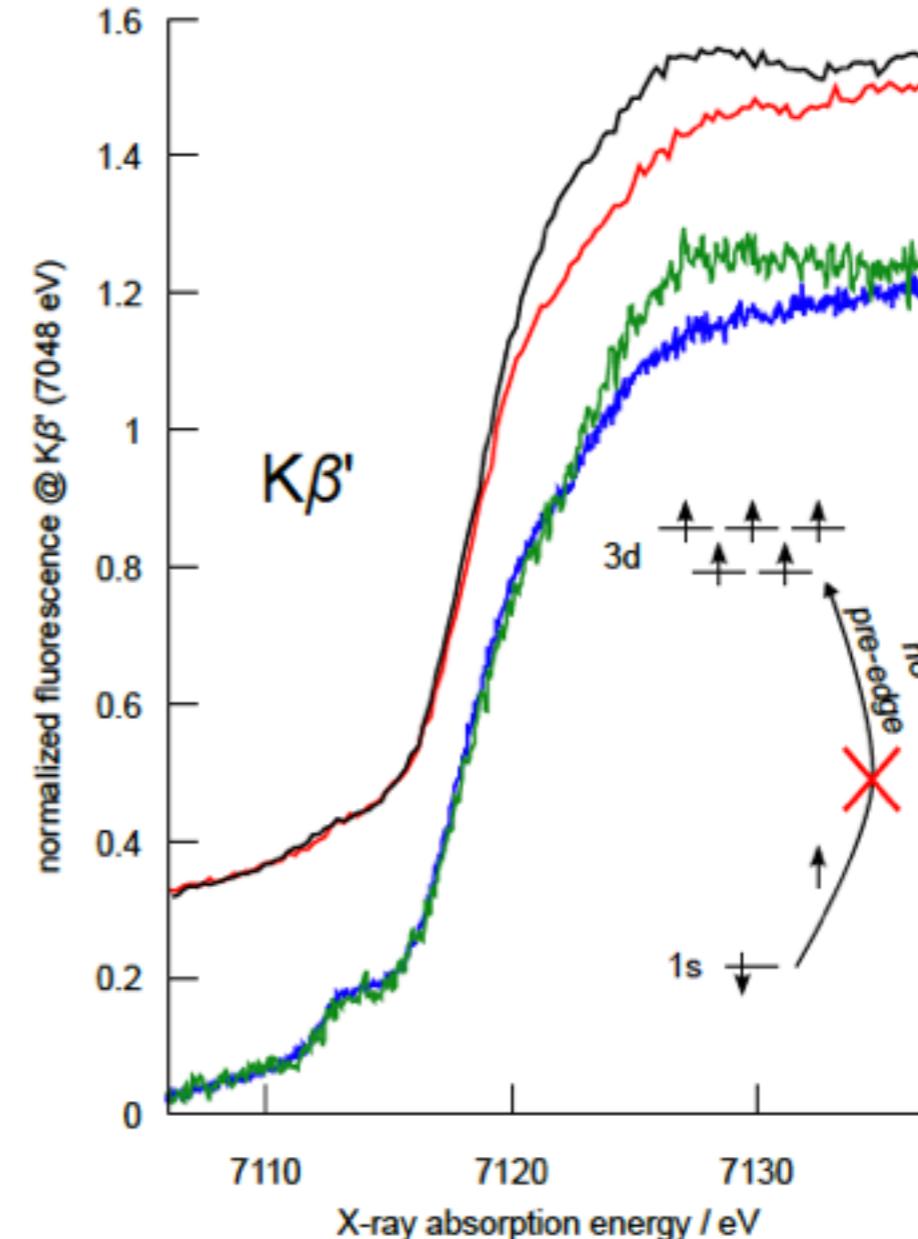
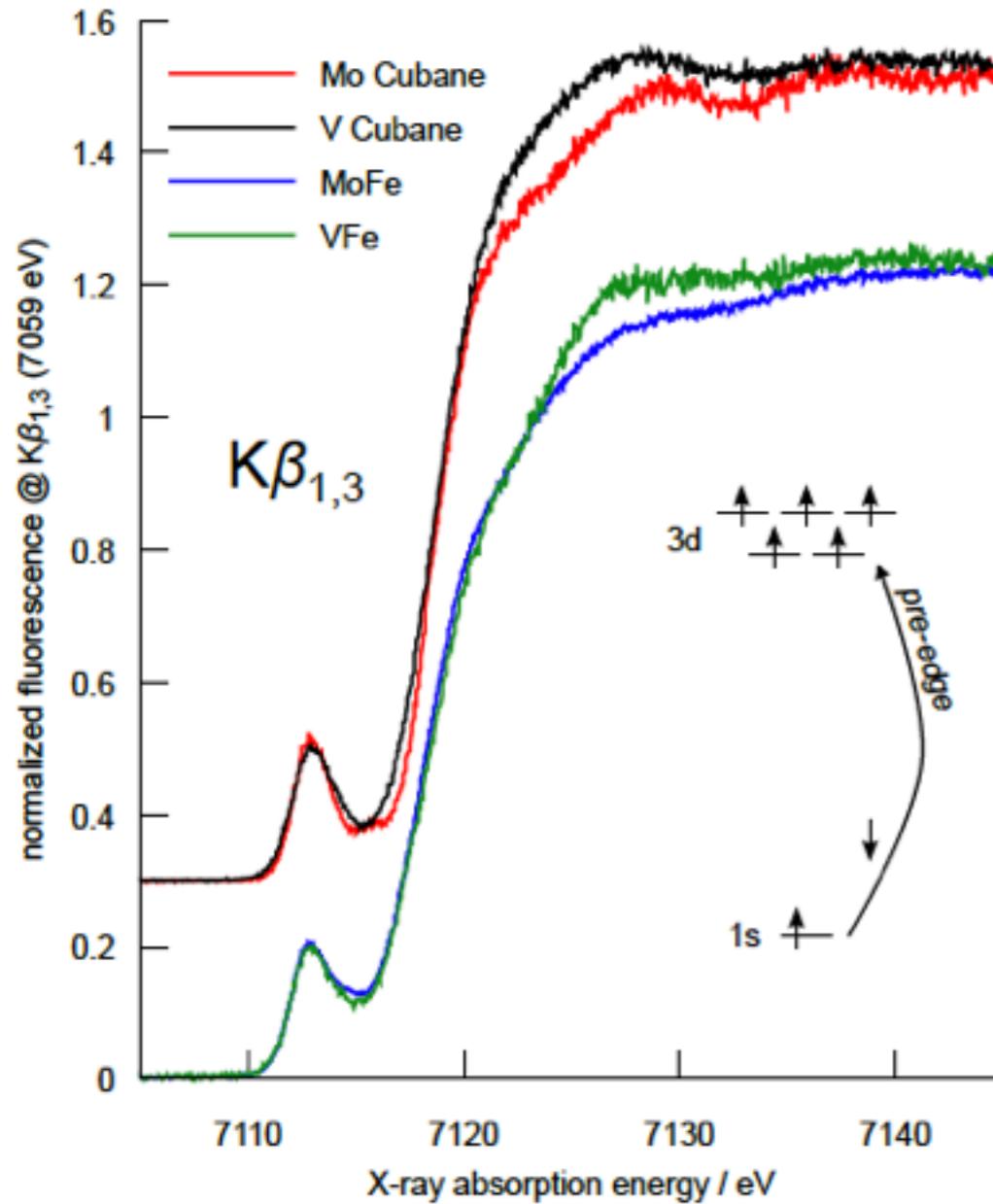
R. Bjornsson, F. A. Lima, T. Spatzl, T. Weyhermüller, P. Glatzel, E. Bill, O. Einsle, F. Neese, S. DeBeer,
Chemical Science, **2014**, *5*, 3096.

K-Beta Detected XAS: Spin Selective XAS



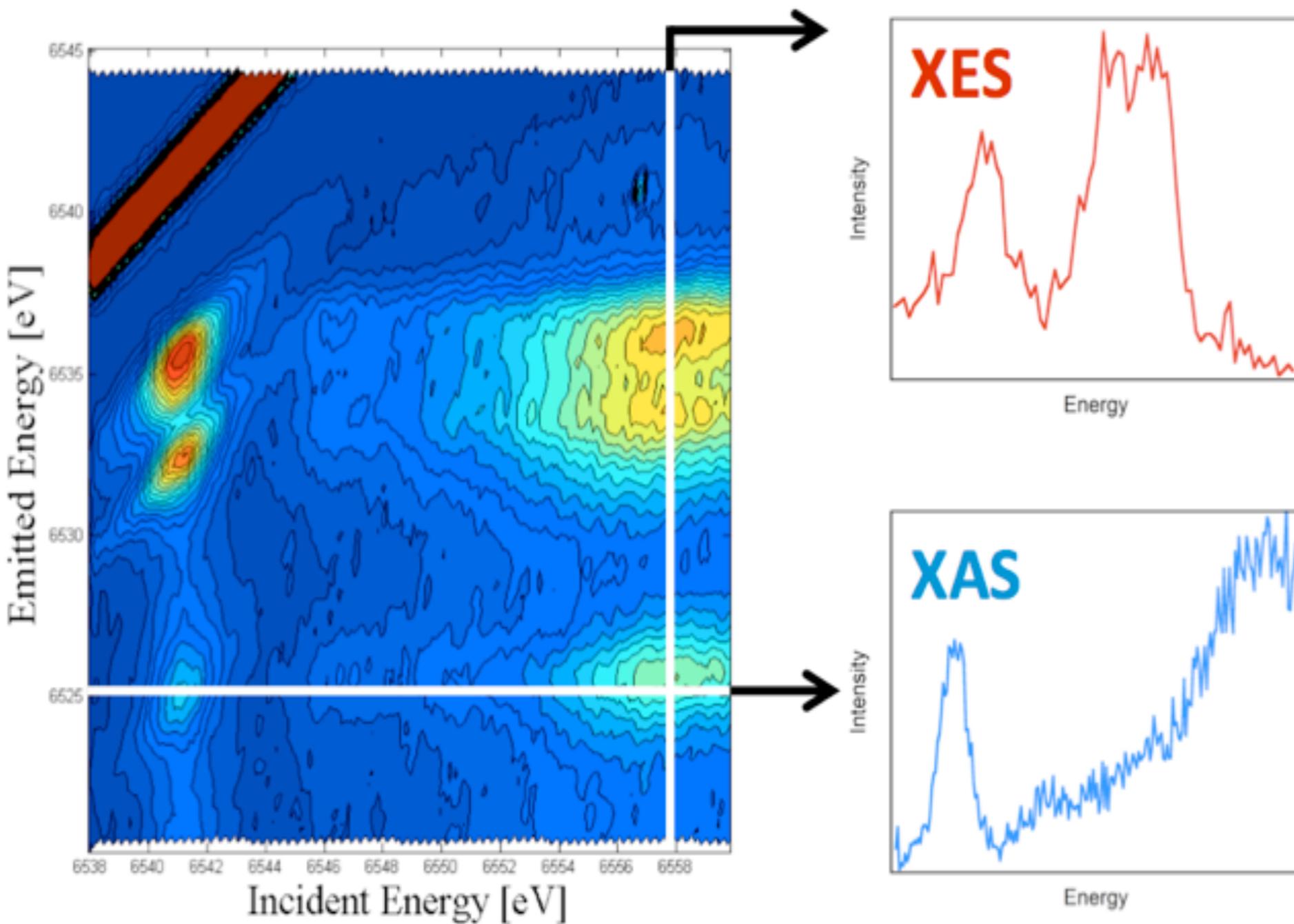
- * The K β emission line is sensitive to oxidation and spin state.
- * Allows for separation of EXAFS for atoms of different spin/oxidation state.
- * For example two different Fe sites in Prussian Blue!

K-Beta Selective XANES



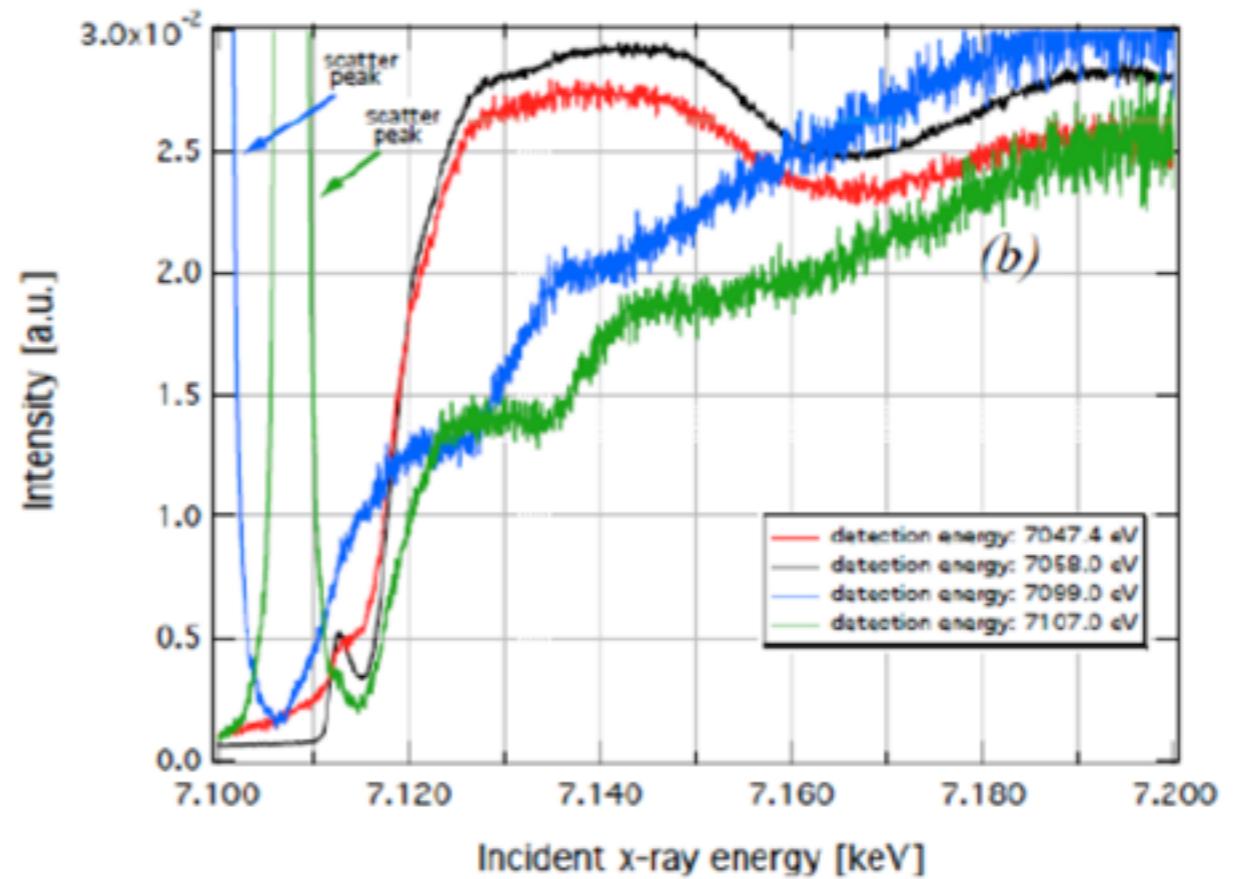
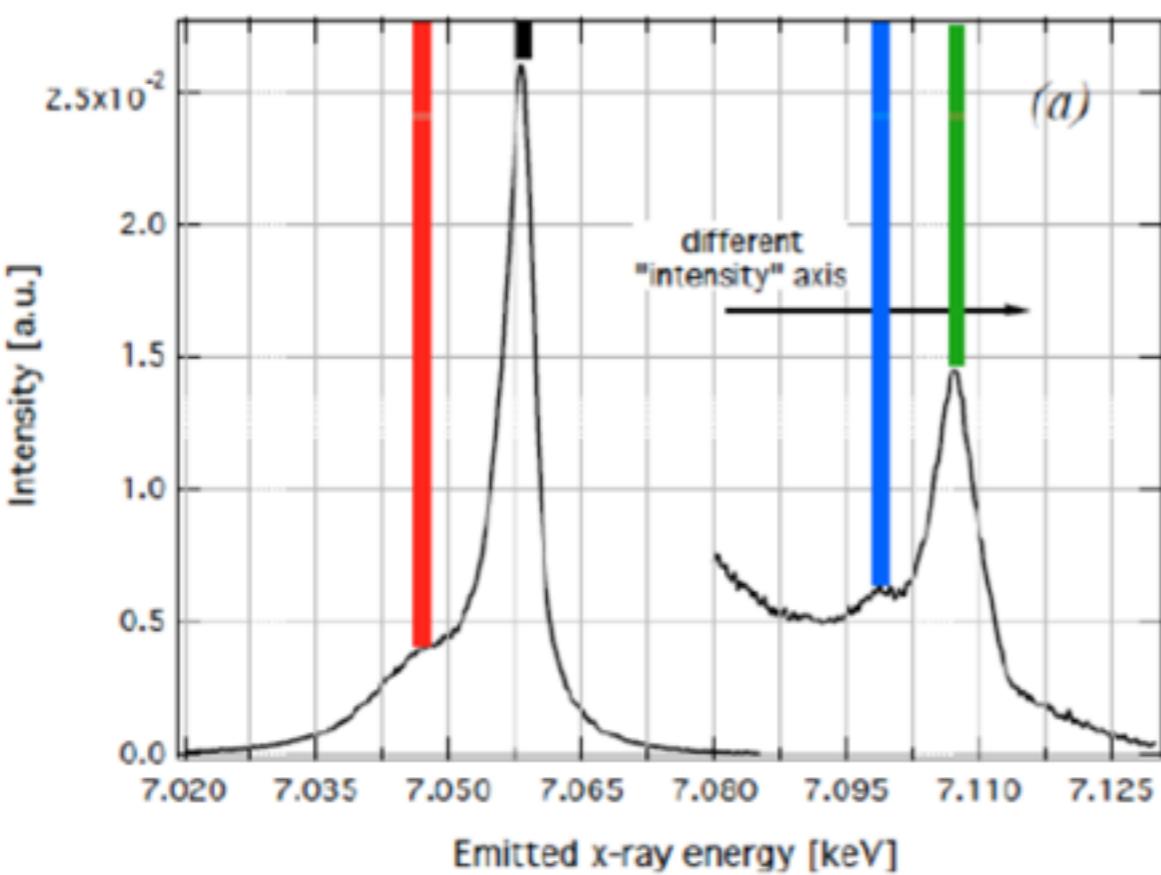
- ➊ $K\beta'$ pre-edge feature present only in N₂ases and NOT in cubanes models
- ➋ Likely reflects a significant covalent reduction of 3p-3d exchange integrals in FeMoco & FeVco relative to the cubanes

What's Next: Insights from 2D Spectroscopy?



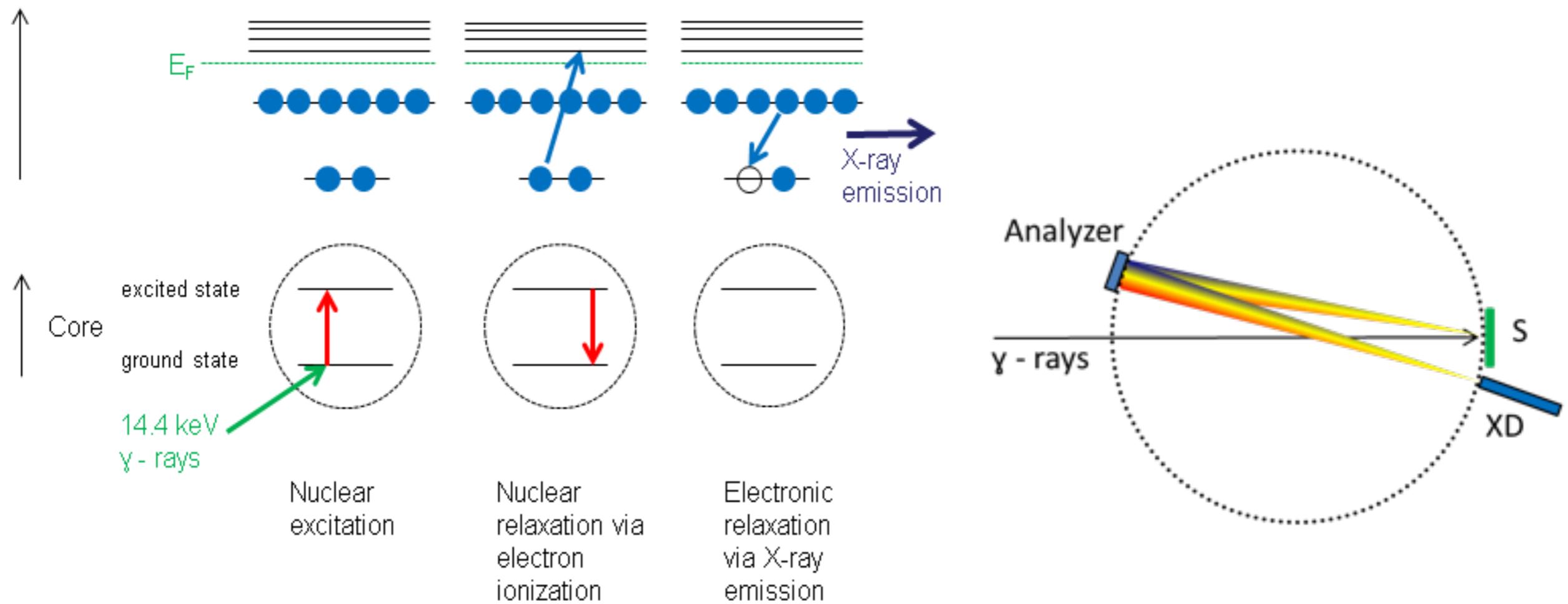
- Goal: to obtain XAS data for **a specific ligand bound to a specific absorbing metal**
- Ability to separate individual metal-ligand interactions, by differences in ligand ionization potential.
- Theory developments (Manganas/ Neese)

Valence RXES of Nitrogenase



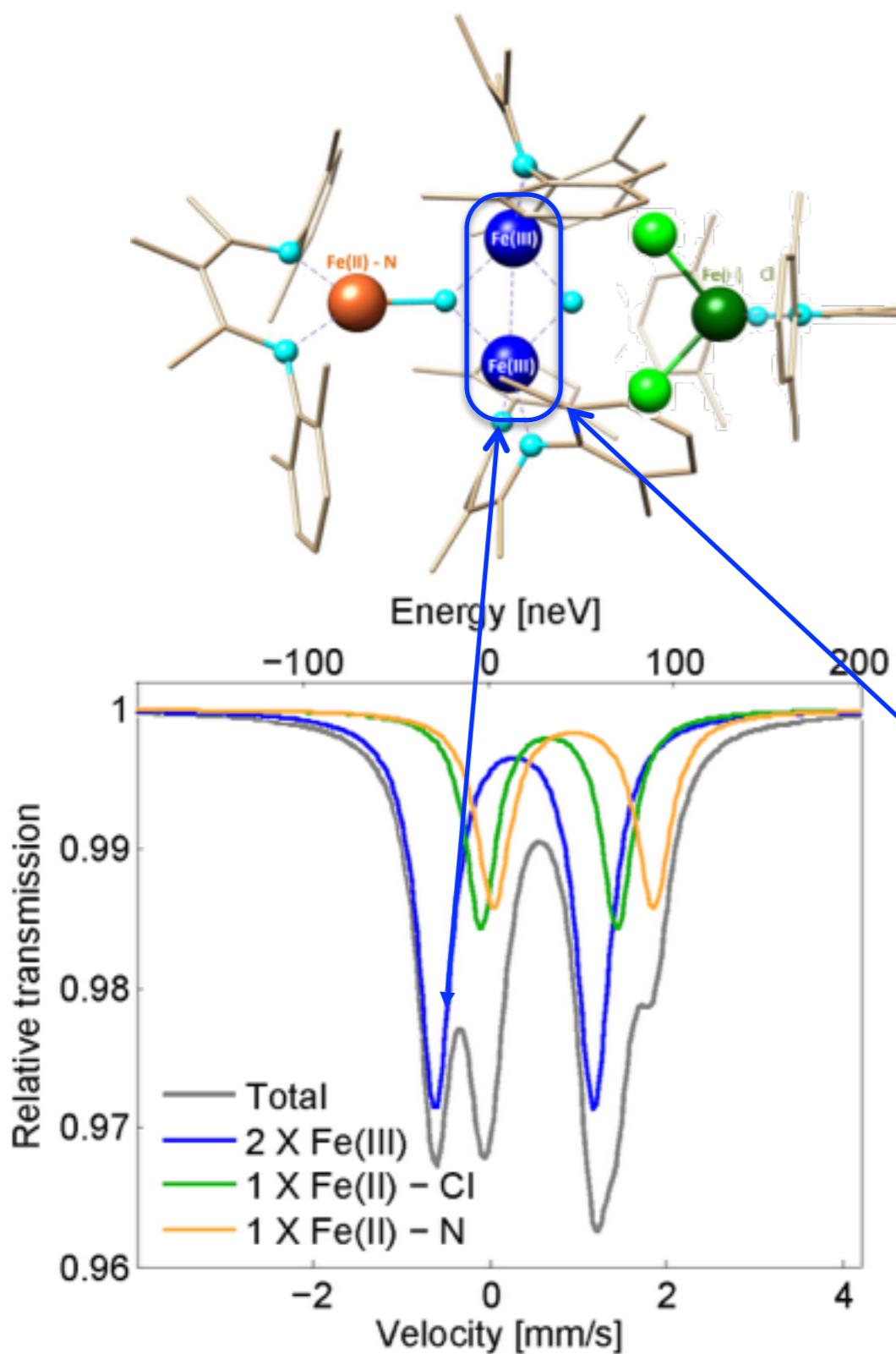
Detection of XANES from different V2C XES lines shows clear changes.
Theory developments in progress....

A Combined Mössbauer XES Instrument

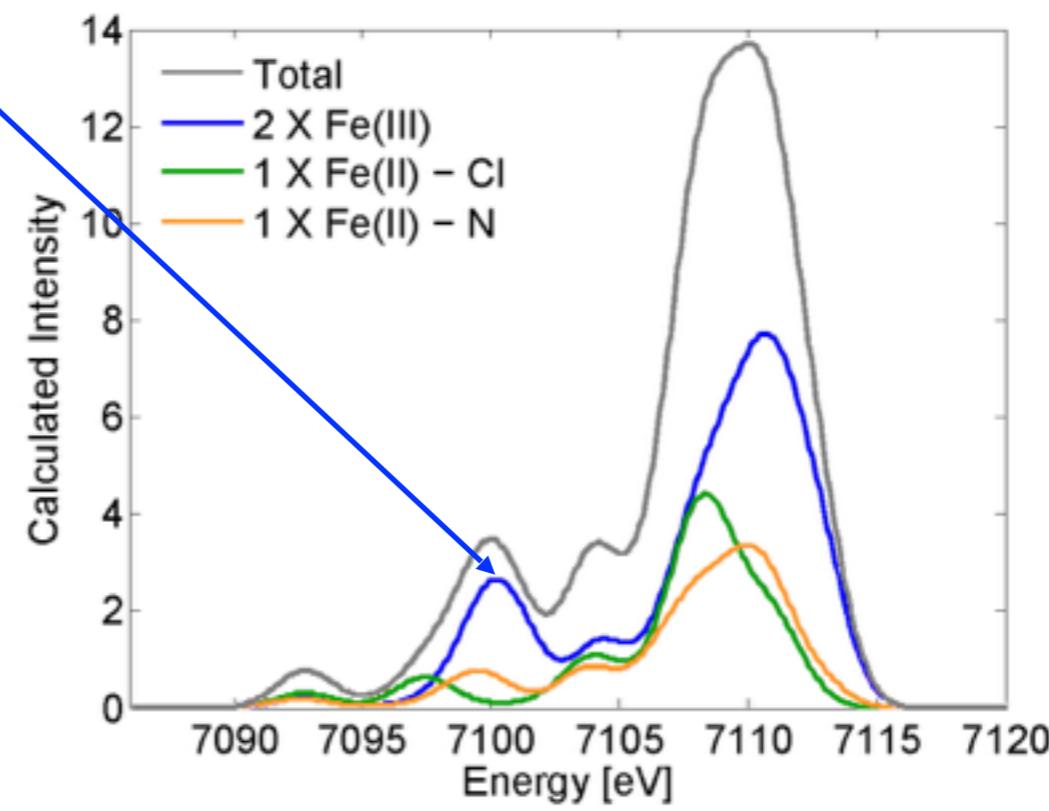


- ~90% of the nuclear excited state decay occurs through internal conversion, producing an Fe 1s core hole, which decays producing fluorescent photons

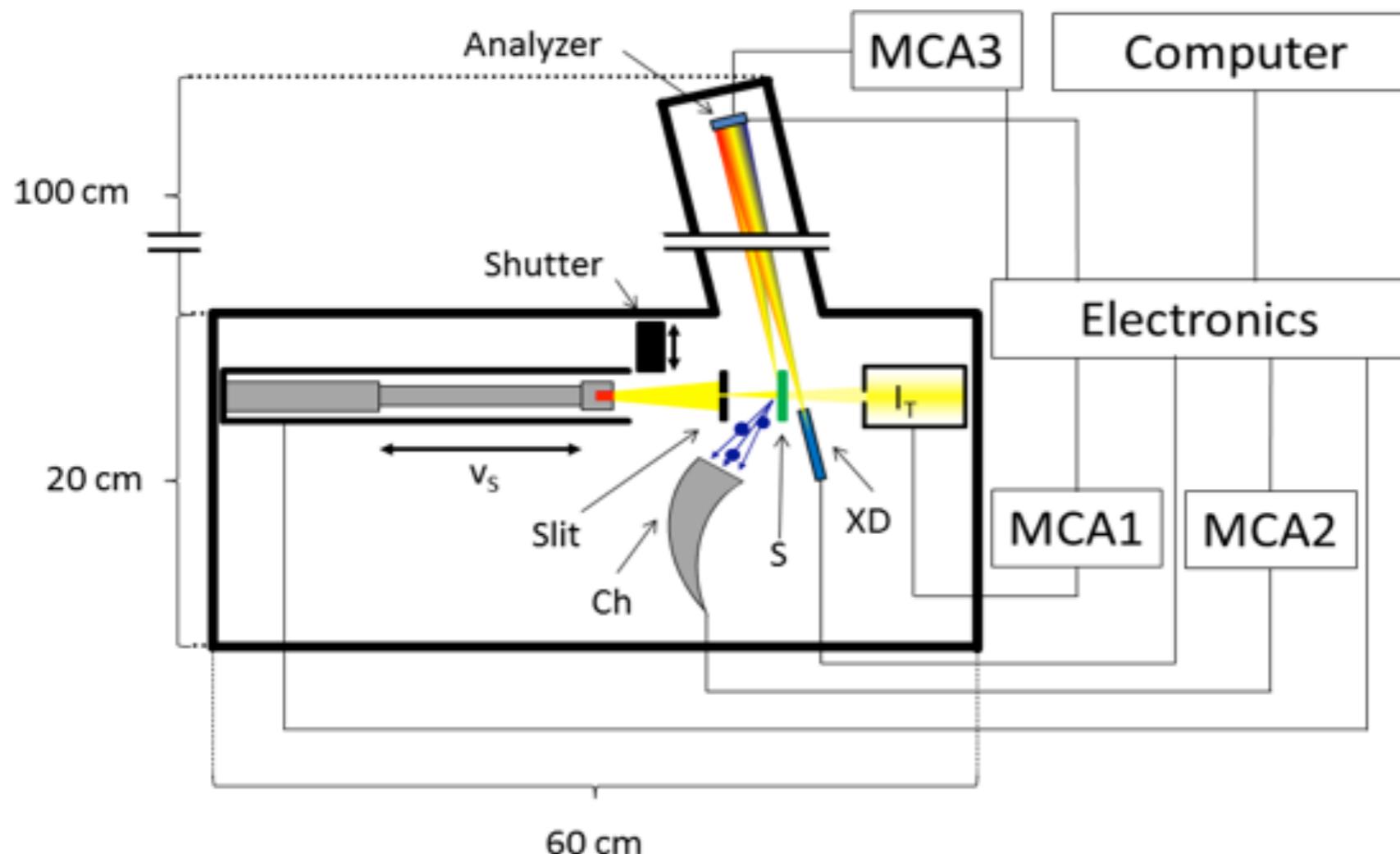
Instrumentation Developments for Novel Selectivity



- Development of a novel site selective method: a combined Mössbauer-XES experiment
- obtain VtC XES for only a **specific** Fe (based on its Mb parameters)
- utilize conversion and transmission Mb to select for surface vs. bulk

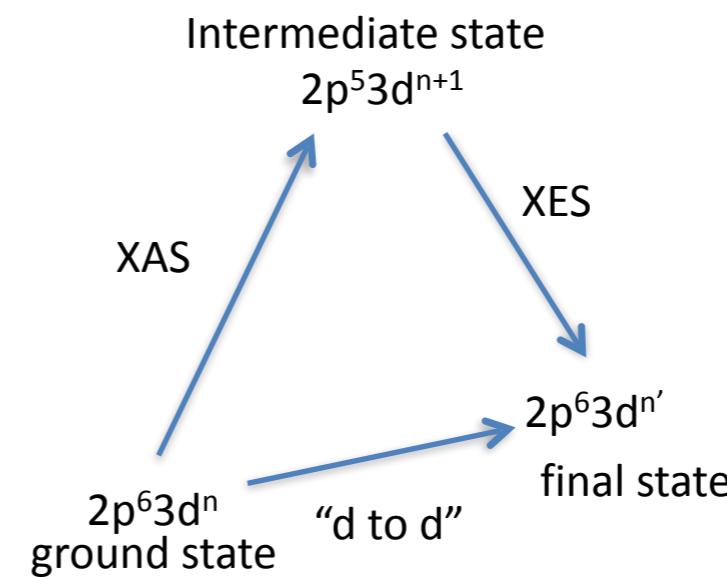
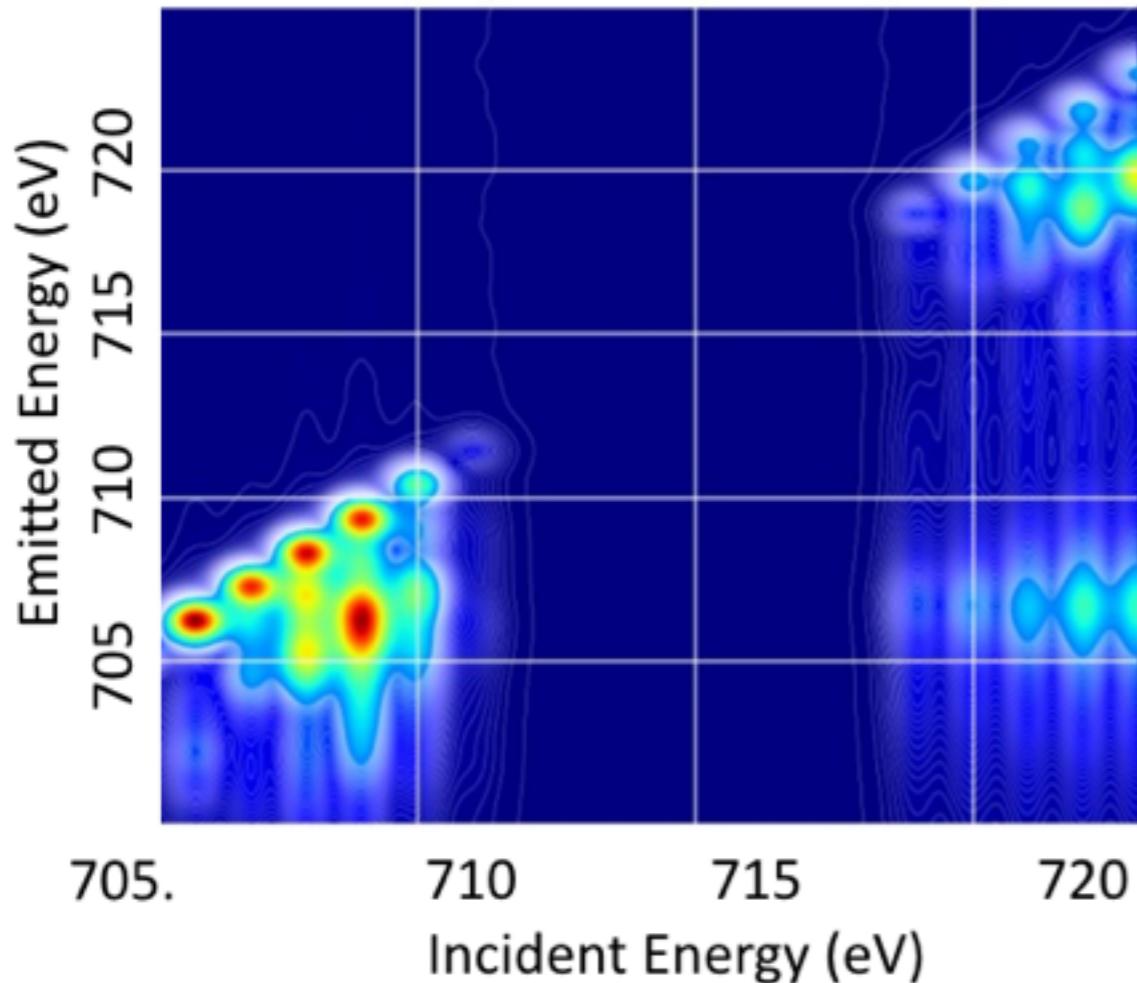


Mb-XES Instrument



- Set will allow for both transmission Mb and conversion electron Mb to be measured
- Rowland geometry will be used for XES
- Setup will provide enhanced selectivity, as well as bulk/ surface sensitivity.
- ERC Poc in progress...

2D X-ray spectroscopy: Measuring the low lying excited states



2D X-ray measurements allow for the measurement of d to d transitions, via dipole allowed excitations and de-excitations

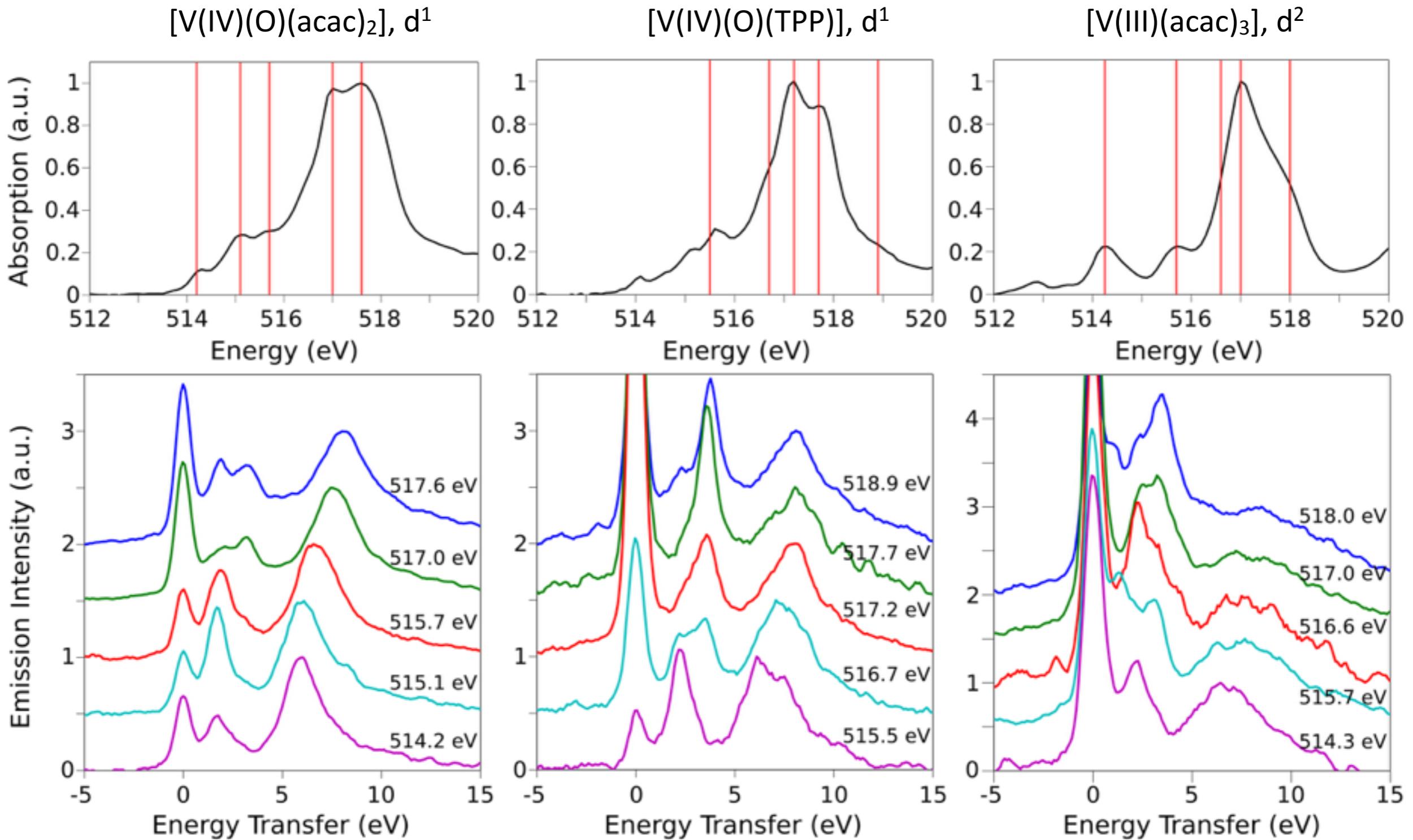
Formally forbidden transitions can be seen.

Experimental determination of the spin ladder

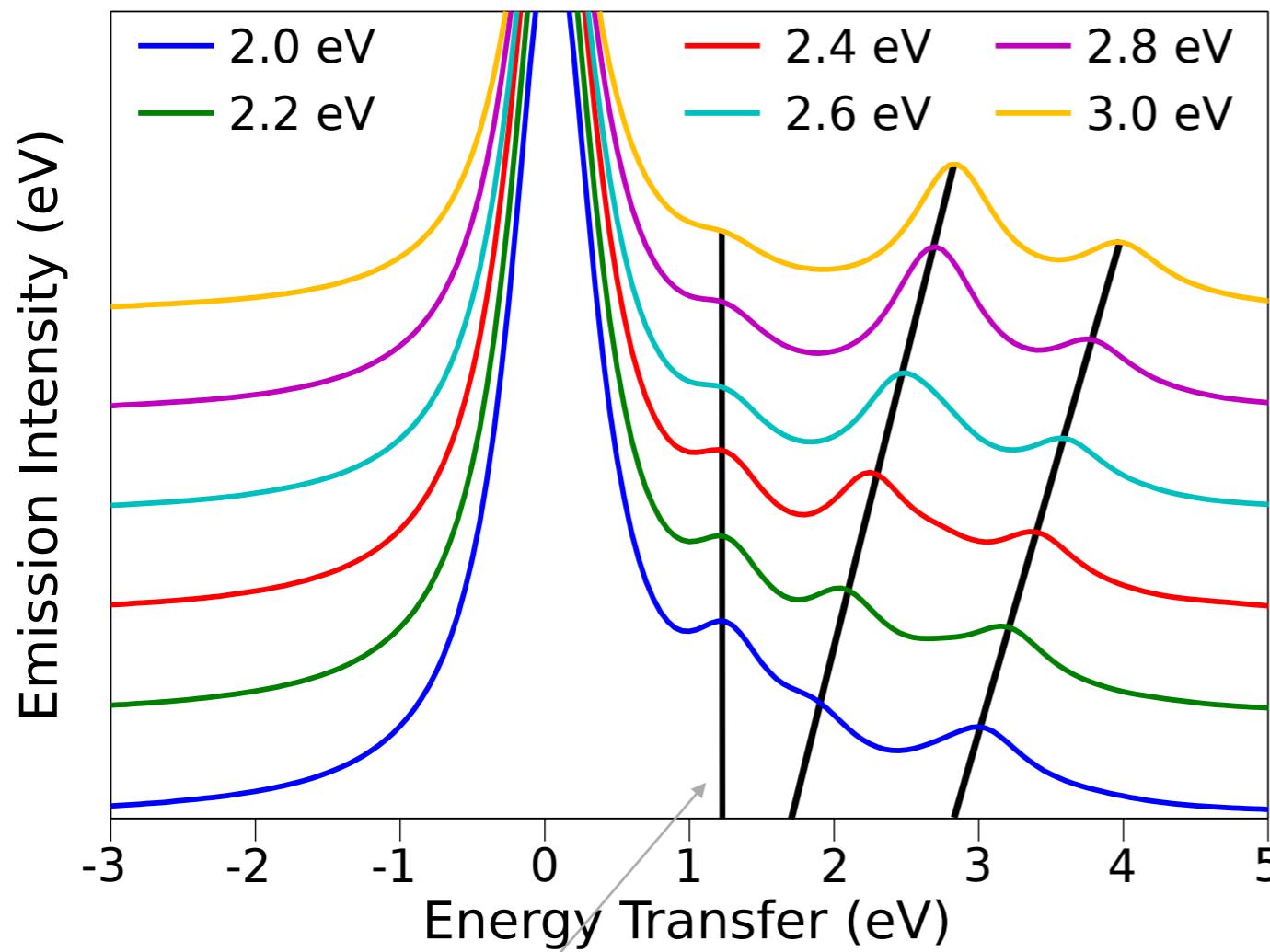


Ben van Kuiken
Anselm Hahn

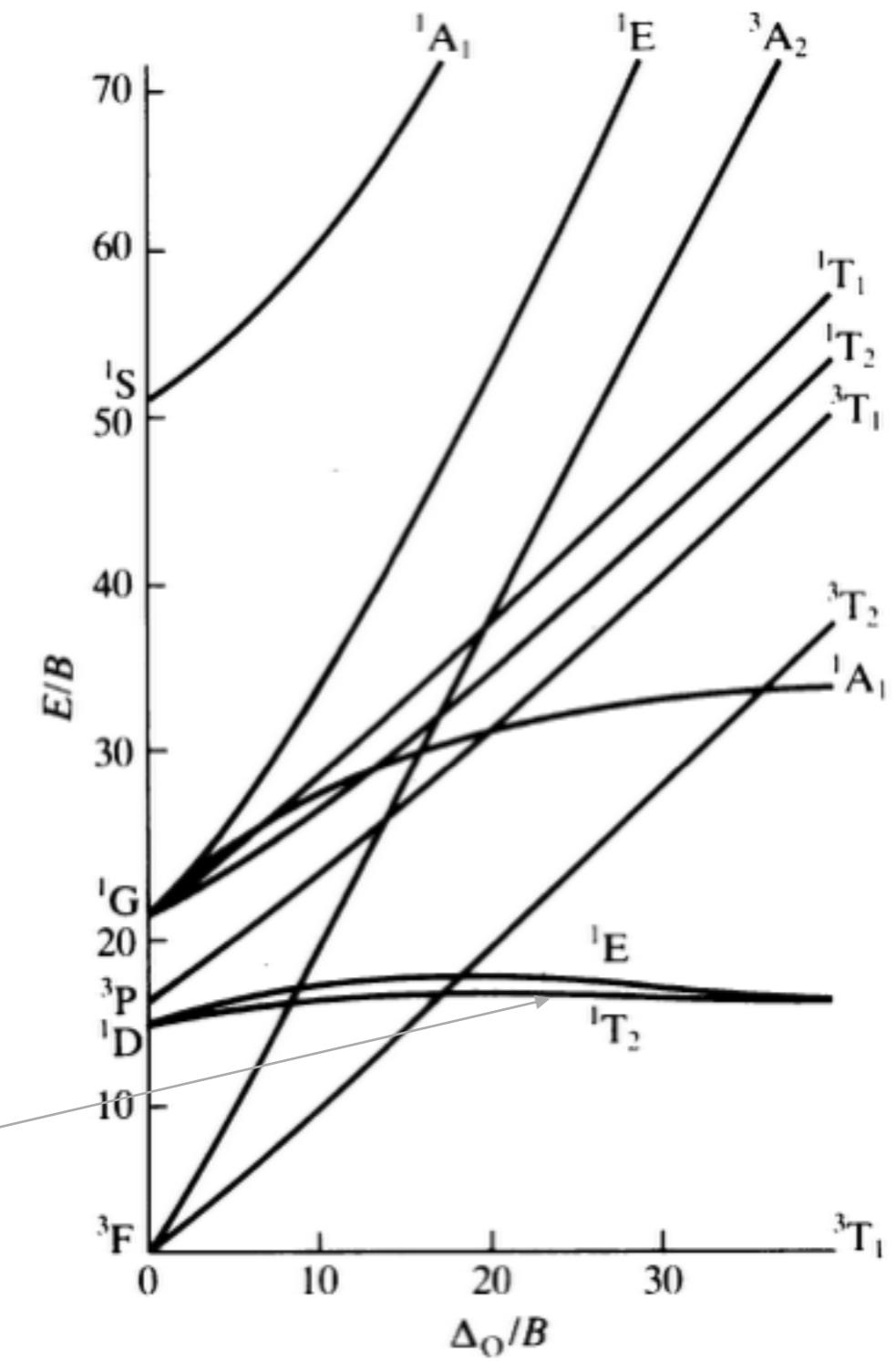
Vanadium 2p3dRIXS



Identification of Spin Forbidden Transitions



Spin Forbidden Transition
LF Independent Marker for V(III)



Iron Cluster Evolution and Functionality



Varied Structural complexity
Diverse functionality

General Assumption: Unique electronic structures enable unique functions

How does increasing complexity of FeS clusters enable varied functionality?

What is the role of the heterometal (N2ase, H2ase) in tuning the catalytic activity of these clusters?

How can advances in theory and x-ray spectroscopy bring new insights into Nature's evolved biosynthetic pathway?

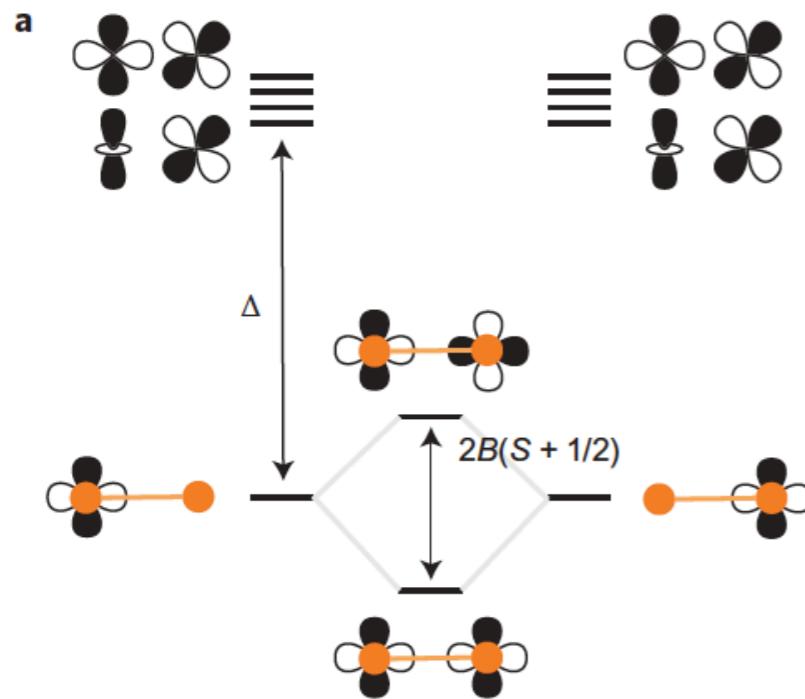
Vijay Chilkuri's talk
and Anselm Hahn's
Poster

Beyond the Heisenberg Model?

Canonical Heisenberg Double Exchange model

Predicts two low lying states for an Fe(III), Fe(II) dimer.

$$E(S) = JS(S + 1) \pm B(S + 1/2)$$



nature
chemistry

ARTICLES

PUBLISHED ONLINE: 31 AUGUST 2014 | DOI: 10.1038/NCHEM.2041

Low-energy spectrum of iron-sulfur clusters directly from many-particle quantum mechanics

Sandeep Sharma¹, Kantharuban Sivalingam², Frank Neese² and Garnet Kin-Lic Chan^{1*}



Ab initio DMRG calculations predict an order of magnitude more low lying excited states

Iron Sulfur cluster do not follow the HDE Model?! Iron Sulfur systems are the most electronically complex bioinorganic clusters.

Need **advance theory and spectroscopy** to understand the electronic structural evolution.



Acknowledgments

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Beam time: ESRF

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