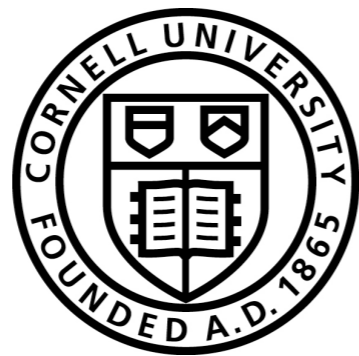


# Ligand K-edge XAS - Quantitative Applications with TDDFT

*Serena DeBeer*

*Department of Chemistry and Chemical Biology  
Cornell University*

*SSRL SMB  
Low Z XAS Summer School  
June 23, 2010*



# Outline

---

- ✓ Ligand K-edge XAS (a bit of history)
- ✓ Qualitative to more Quantitative Approaches
- ✓ TDDFT Calculation of Edges
- ✓ Applications
  - dithiolenes
  - corroles
- ✓ New Methods (XES)

# Why use Ligand K-edges?

---

## **Metal K- and L-edges**

- ✓ Oxidation state
- ✓ Ligand Field
- ✓ Geometry
- ✓ Spin State

## **Ligand K-edges**

- ✓ Probe covalency of M-L bonds
- ✓ Fundamental to reactivity, magnetic interactions, electron delocalization
- ✓ Server as a reporter for the metal site
- ✓ Both metal and ligand oxidation
- ✓ Metal and Ligand edges together provide a more complete experimental description of the electronic structure

# Ligand K- pre-edges: The Very “Qualitative” Years

PHYSICAL REVIEW B

VOLUME 25, NUMBER 12

15 JUNE 1982

Oxygen *K* near-edge fine structure: An electron-energy-loss investigation with comparisons to new theory for selected 3*d* transition-metal oxides

L. A. Grunes and R. D. Leapman\*

*School of Applied and Engineering Physics and Materials Science Center,  
Cornell University, Ithaca, New York 14853*

C. N. Wilker and R. Hoffmann

*Department of Chemistry and Materials Science Center,  
Cornell University, Ithaca, New York 14853*

A. B. Kunz

*Department of Physics and Materials Research Laboratory,  
University of Illinois, Urbana, Illinois 61801*

(Received 28 December 1981; revised manuscript received 10 March 1982)

O *K*-edge 1*s* to *p* transitions “might be expected to reflect to some extent the *d* density of states around the metal atoms as measured by the *L*<sub>2,3</sub> edges”

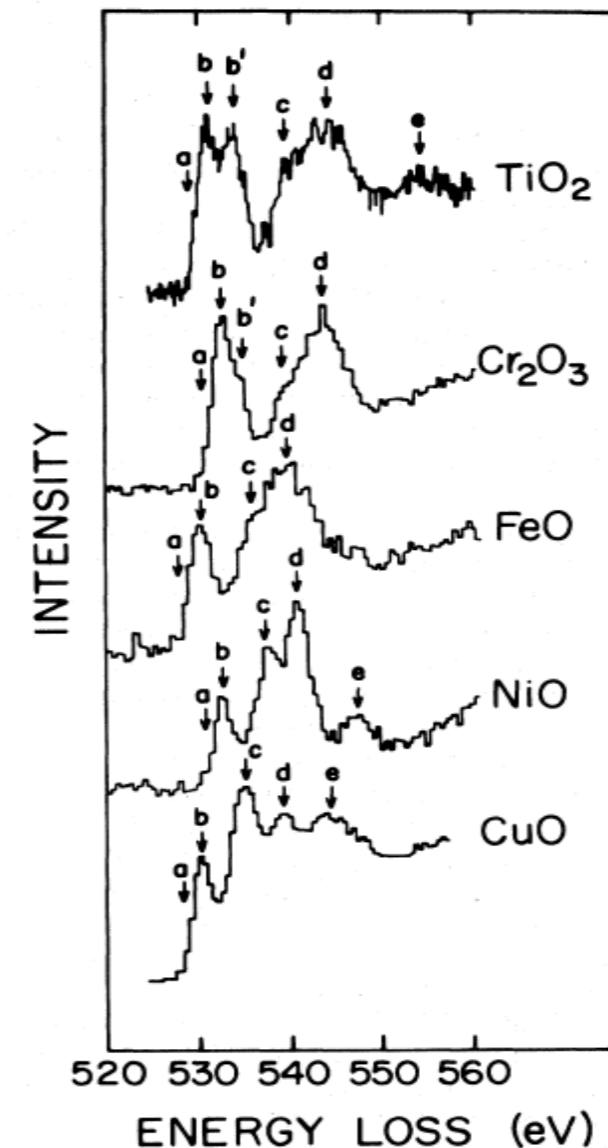


FIG. 1. O *K*-shell excitation edges measured by EELS for selected 3*d* transition-metal oxides.

# Ligand K- pre-edges: The Qualitative Years

## X-ray absorption near-edge structure of complex compounds $(\text{NH}_4)_3\text{RhCl}_6$ , $\text{K}_3\text{RuCl}_6$ , and $\text{Ru}(\text{NH}_3)_6\text{Cl}_3$

Chikara Sugiura and Michihide Kitamura  
Department of Applied Physics, Faculty of Engineering, Utsunomiya University, Utsunomiya 321, Japan  
Shinji Muramatsu  
Department of Electronic Engineering, Faculty of Engineering, Utsunomiya University, Utsunomiya 321, Japan

*Relates Cl K- pre-edge to MO picture*

PHYSICAL REVIEW B

VOLUME 37, NUMBER 18

15 JUNE 1988-II

## Core-exciton absorption in the F K absorption spectra of 3d transition-metal fluorides

S. Nakai, A. Kawata, M. Ohashi, M. Kitamura, C. Sugiura, and T. Mitsuishi  
Department of Applied Physics, Faculty of Engineering, Utsunomiya University, Utsunomiya 321, Japan

H. Maezawa  
Photon Factory, National Laboratory for High Energy Physics, Tsukuba, Ibaraki-Ken 305, Japan  
(Received 28 December 1987)

*F K- pre-edge reflects ligand 2p- metal 3d hybridization*

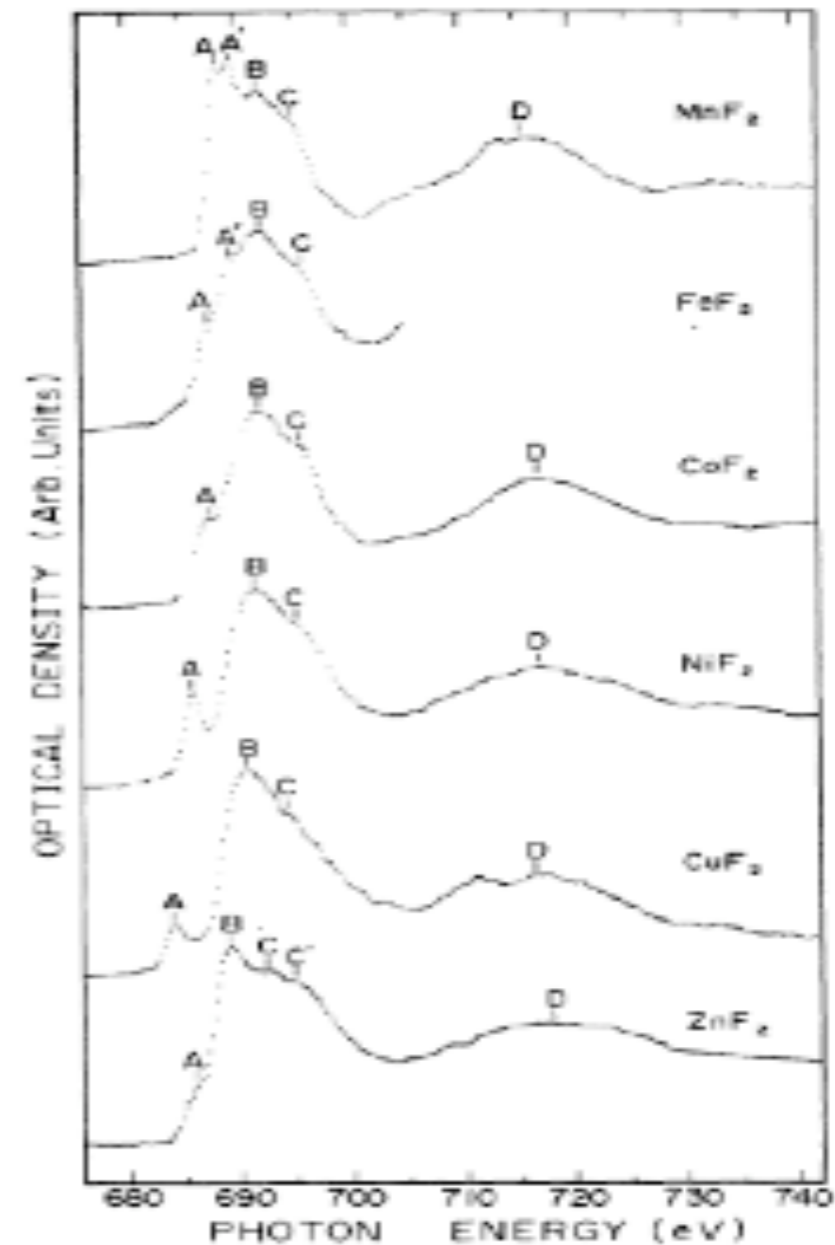
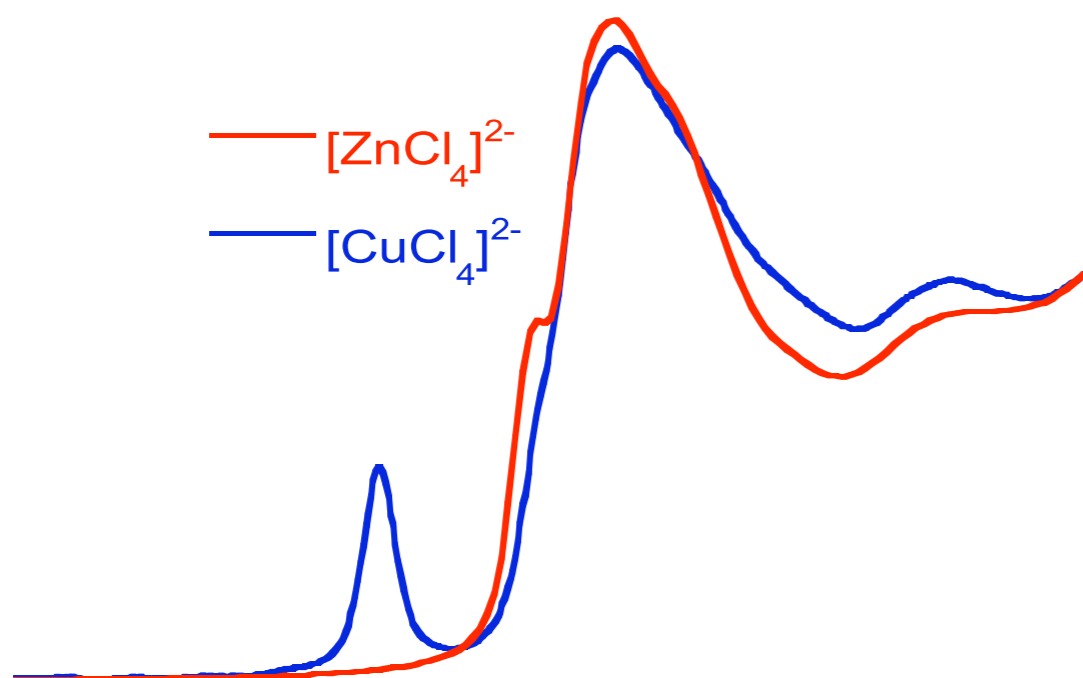


FIG. 1. Fluorine K absorption spectra of 3d transition-metal fluorides,  $\text{MnF}_2$ ,  $\text{FeF}_2$ ,  $\text{CoF}_2$ ,  $\text{NiF}_2$ ,  $\text{CuF}_2$ , and  $\text{ZnF}_2$ .

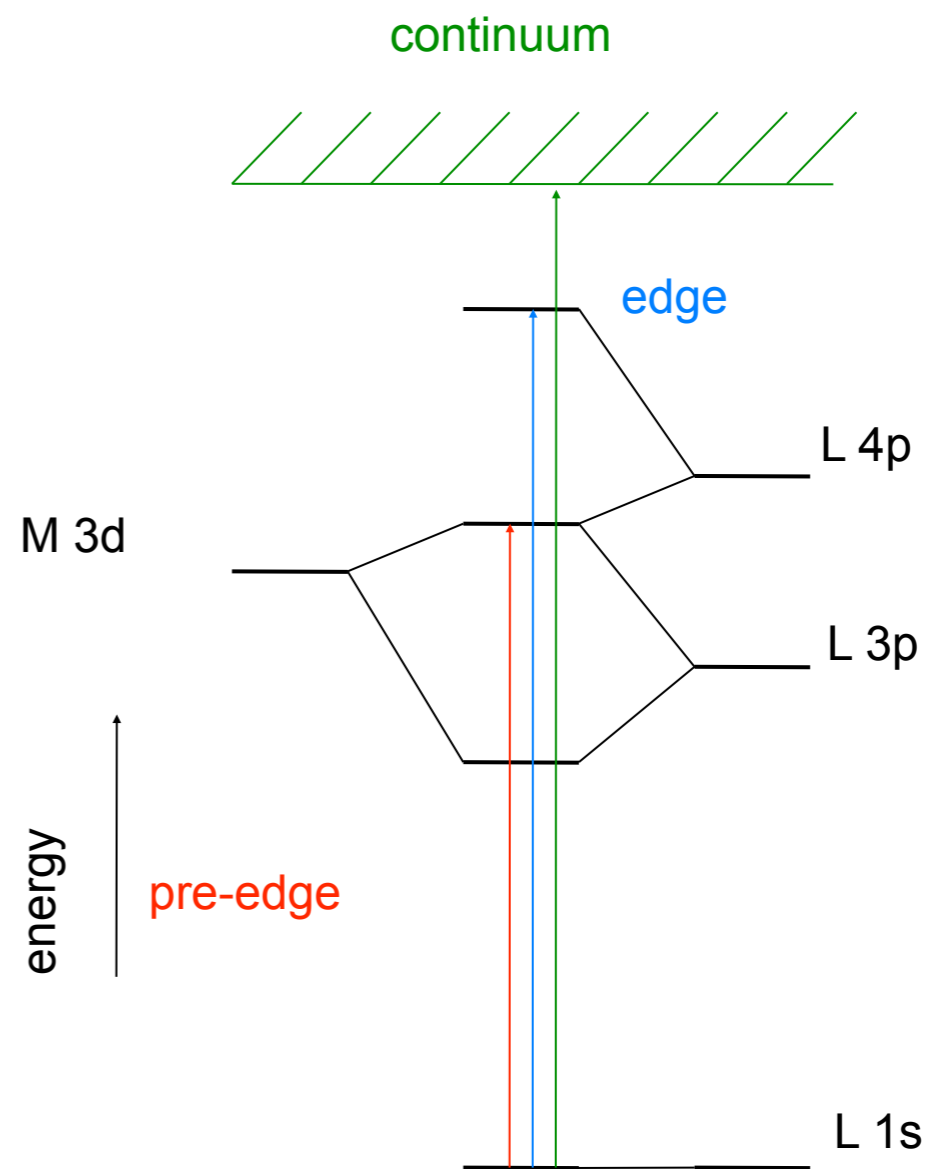
# Ligand K-edge XAS: As a Quantitative Probe of Covalency



Transitions localized on the absorbing atom → pre-edge feature due to a pure ligand transition.

Provides an experimental measure of ligand 3p character in the HOMO.

Assign intensity to covalency (based on EPR)



B. Hedman, K. O. Hodgson, E. I. Solomon, J. Am. Chem. Soc., 1990, 112, 1643.

# Correlating Ligand K- Pre-edge Intensities to Covalency

---









On a most elementary level, the intensity of the pre-edge position from a ligand 1s- into a metal d-based MO is given by:

$$I(1s \rightarrow \psi^*) = a\alpha^2$$

where  $\alpha^2$  is covalency and  $a$  is a proportionality constant – assumes the transition moment dipole integral is constant

***Is this a fair assumption?***

# The Ligand K-Edge Intensity Mechanism

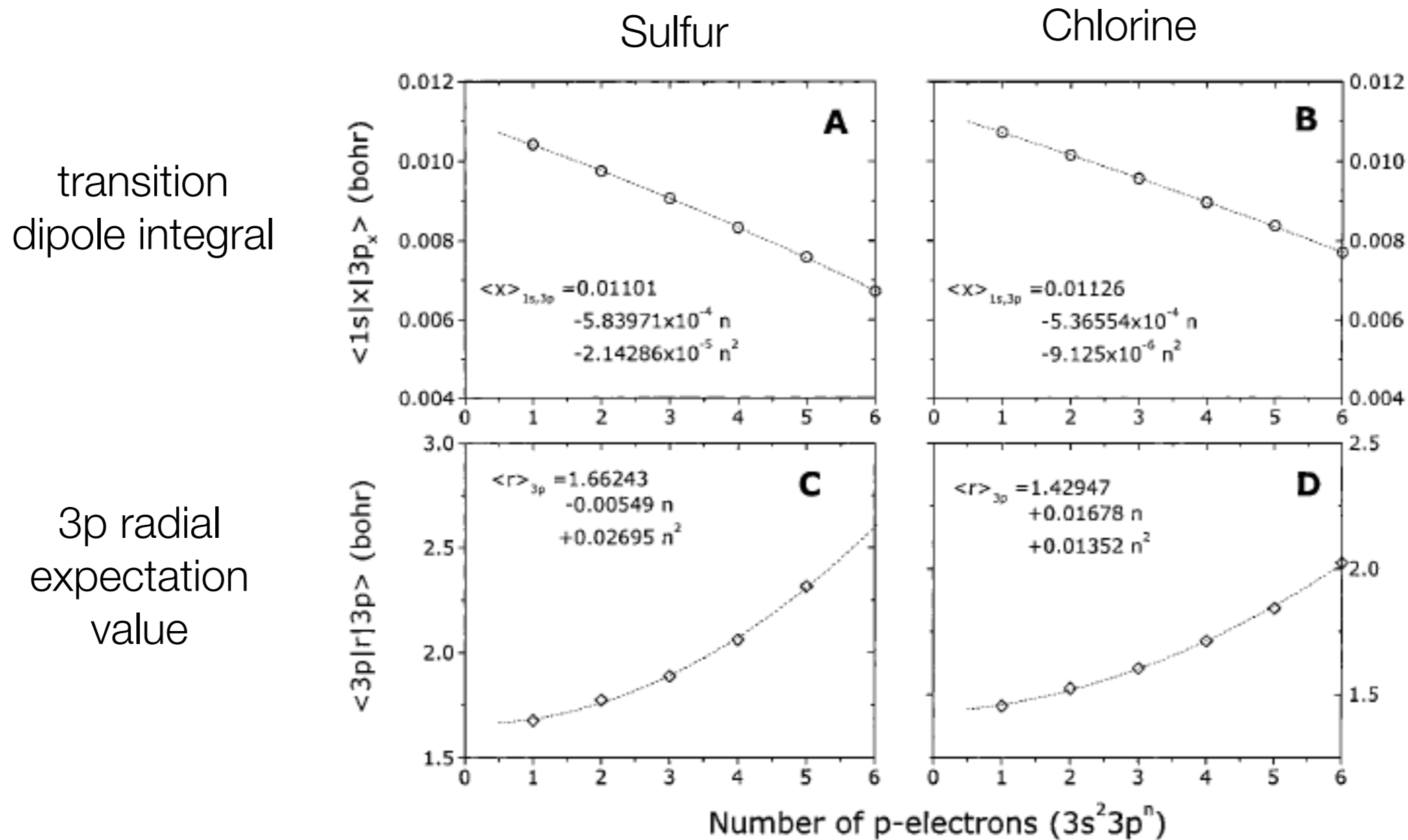
	<b>Ligand K-edge</b> <b>L—M</b>	<b>Charge-Transfer</b> <b>L—M</b>
Acceptor MO	 $(1-\alpha^2)^{1/2} M\ 3d\rangle - \alpha L\ np\rangle$	 $(1-\alpha^2)^{1/2} M\ 3d\rangle - \alpha L\ np\rangle$
Donor MO	 $ L\ 1s\rangle$	 $\alpha M\ 3d\rangle + (1-\alpha^2)^{1/2} L\ np\rangle$
Transition Density		
Transition Dipole Moment	 $\alpha\langle 1s x np\rangle$	 $\alpha(1-\alpha^2)^{1/2}R$

Neese, F.; Hedman, B.; Hodgson, K.; Solomon, El *Inorg. Chem.*, **1999**, 38, 4854-4860



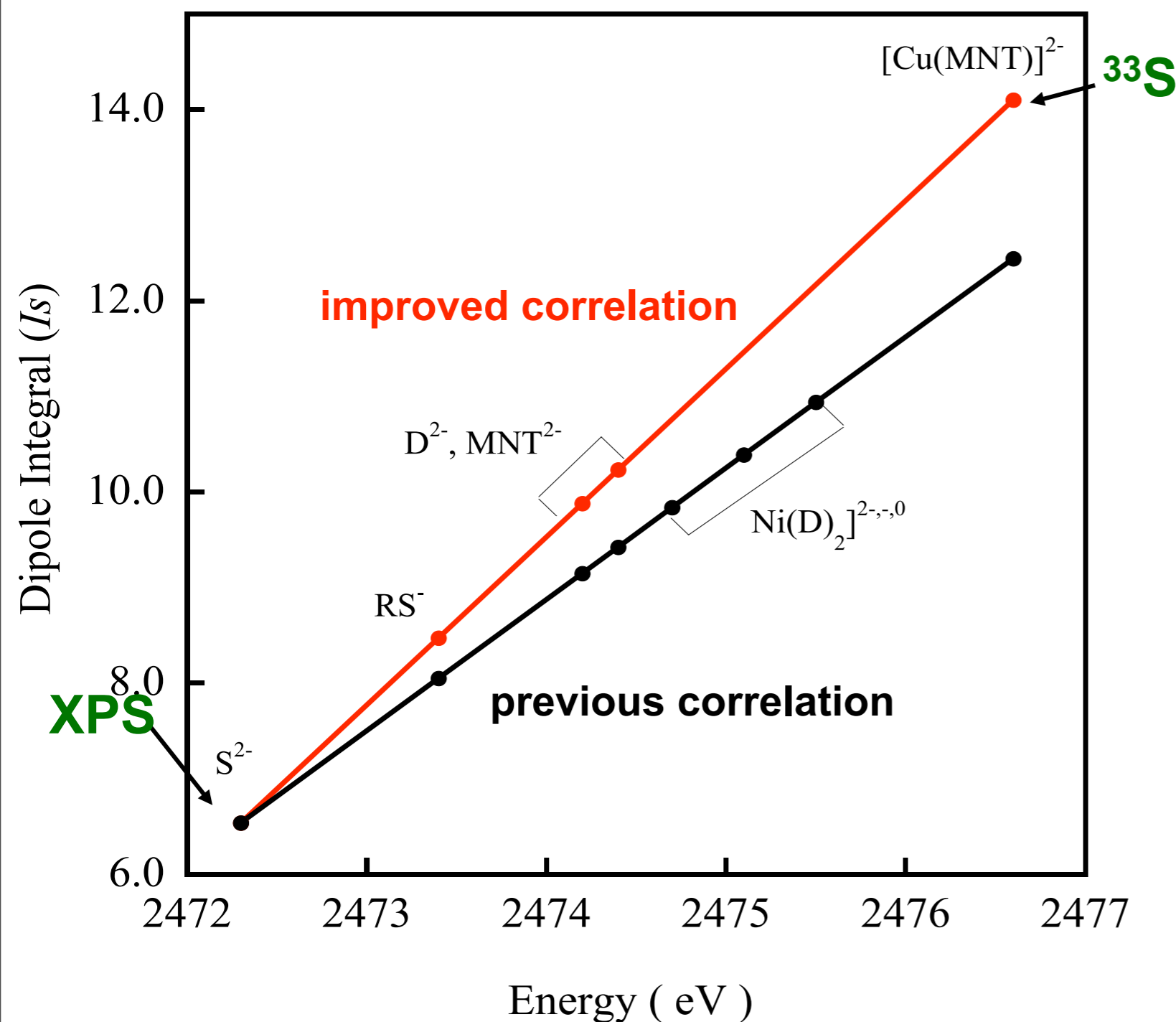
# Transition Dipole Moment

The transition dipole moment is the intrinsic intensity of a  $1s \rightarrow np$  transition.  
This depends on the radial functions of the  $1s$  and  $3p$  orbitals



F. Neese et al., Inorg. Chem., 1999, 38, 4854.

# Experimentally Estimating the Transition Dipole Moment



Use other spectroscopic methods to determine  $I(S)$

Assume Dipole Integral is linear with respect to the  $1s \rightarrow 4p$  Energy (eV)

R. Sarangi, S. DeBeer George, D. Jackson Rudd, R. K. Szilagy, X. Ribas, C. Rovira, R. H. Holm, B. Hedman, K. O. Hodgson, E. I. Solomon, J. Am. Chem. Soc., 2007, 129, 2316.

# Experimental Observable: Oscillator Strength

---

**The oscillator strength of a given transition in the pre-edge region may be factored into two contributions:**

- 1) fractional ligand character in the acceptor MO
- 2) radial transition-dipole integral  $I(S) = |\langle S1s | r | S3p \rangle|^2$

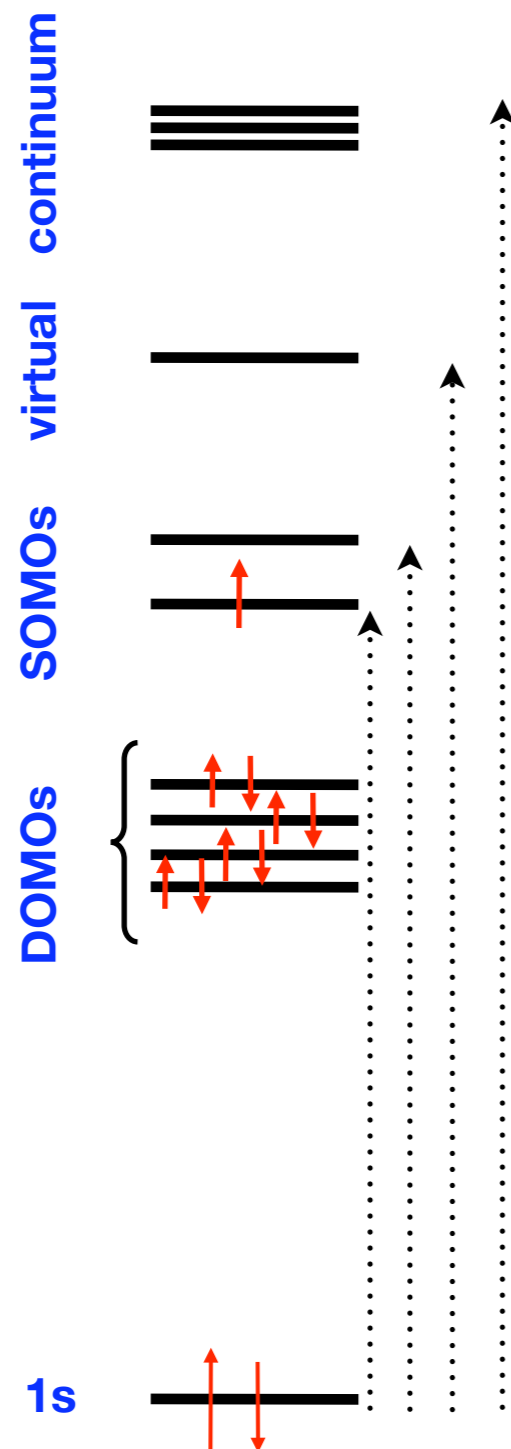
**Therefore we need to know  $I(S)$**

- 1) Experimentally estimate
- 2) Calculate the oscillator strength directly and apply the factorization of  $I(S)$  and  $\alpha^2$  after the correlation of the calculated and experimental oscillator strengths has been established

Focus on pre-edge region which readily relates to an MO-based picture

*TD-DFT Calculations: ORCA (developed by F. Neese, Bonn)*

# A Simple TD-DFT Protocol for K-Edge XAS



- ✓ Localize 1s-orbitals of symmetry equivalent S,Cl
- ✓ Include only 1s → Virtual excitations in the TD-DFT equations
- ✓ Calculate dipole and quadrupole contributions to the transition moments
- ✓ Use large basis sets on the XAS absorber atom
- ✓ Treat scalar relativistic effects through ZORA
- ✓ Compensate negative total charges through COSMO

TD-DFT:

$$\langle \Psi_0 | \vec{\mu}_{ED}^{length} | \Psi_I \rangle = \sum_{jb} (X_{jb}^I + Y_{jb}^I) \langle \psi_j | \mathbf{r} | \psi_b \rangle$$

$$\langle \Psi_0 | \vec{\mu}_{ED}^{velocity} | \Psi_I \rangle = i \sum_{jb} (X_{jb}^I + Y_{jb}^I) \langle \psi_j | \vec{\nabla} | \psi_b \rangle$$

(dipole velocity preferred on theoretical ground but in practice dipole length is more stable; for exact wavefunctions both forms would be identical)

# The Quadrupole Intensity

**Problem:** Straightforward application of the ED and MD operators:

$$\vec{\mu}_{EQ,ab} = \sum_i (\vec{r}_{i,a} \vec{r}_{i,b} - \frac{1}{3} r_i^2 \delta_{ab}) \quad \vec{\mu}_{MD,a} = \frac{1}{2} \sum_i (\vec{l}_i + 2\vec{s}_i)_a$$

Leads to results that depend (a LOT) on the choice of the coordinate origin which is unphysical!

**Solution:** (Taras Petrenko) Choose the origin that leads to the fastest convergence of the multipole expansion of the light/matter interaction. First shift the origin by **R**:

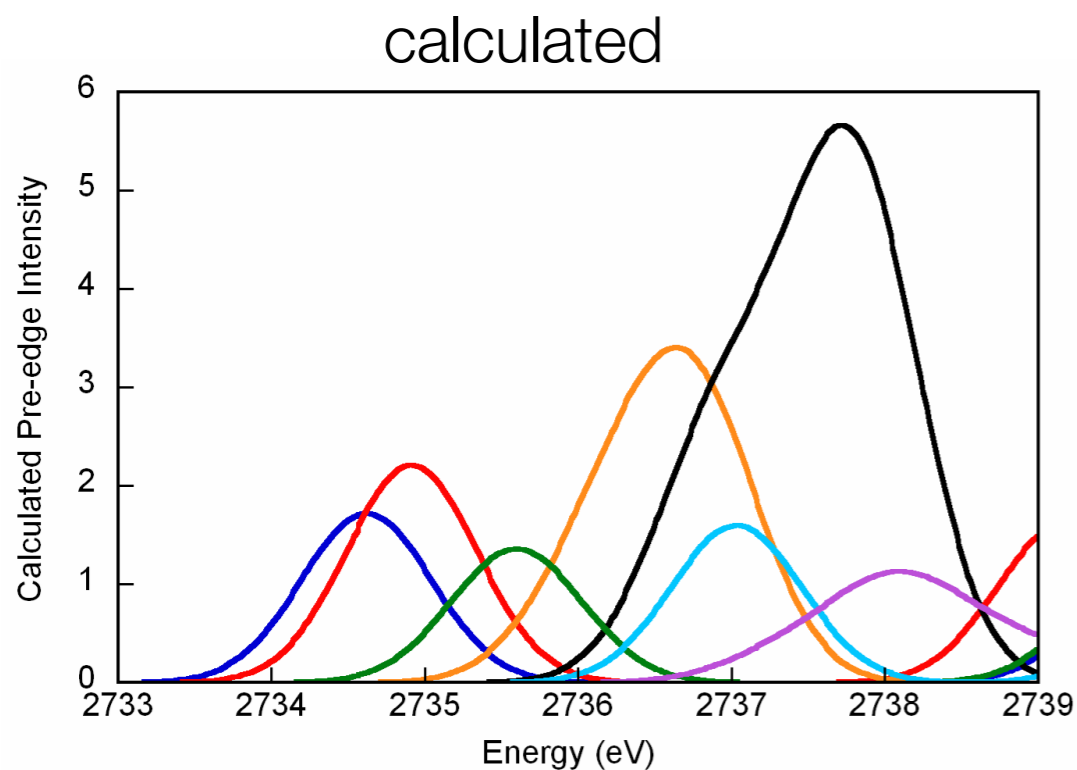
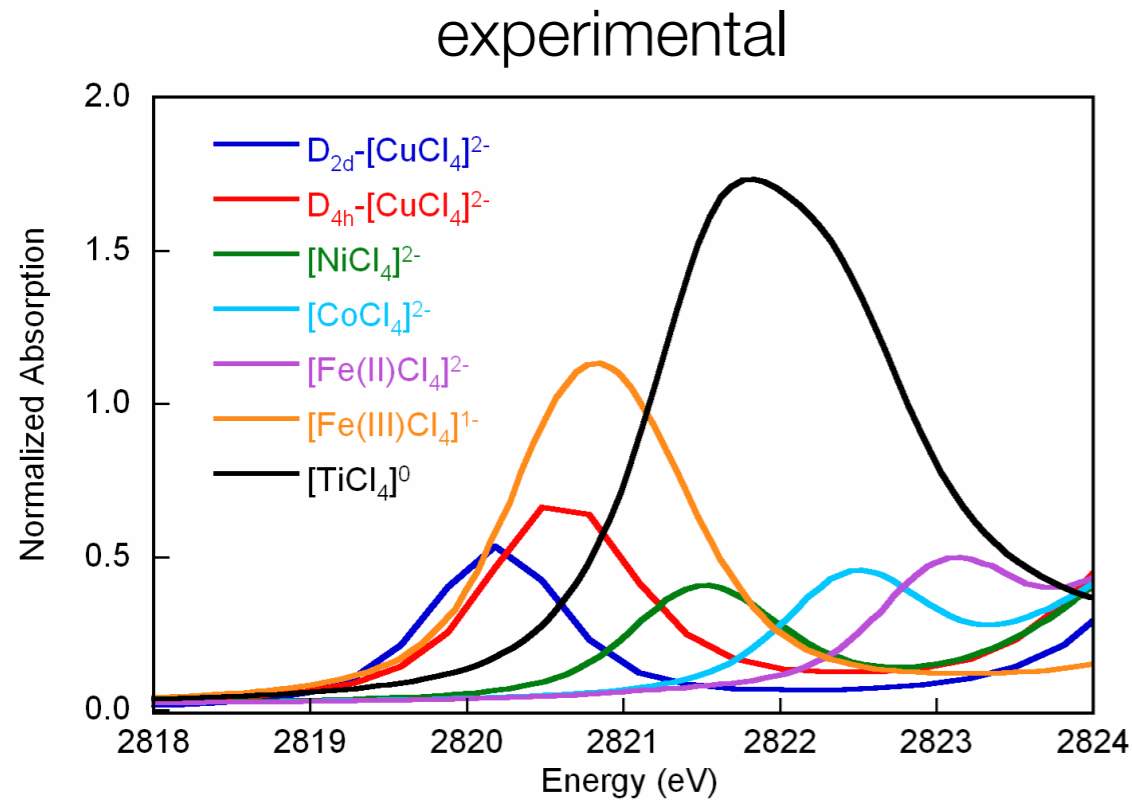
$$(Q'_{ab})_{0n} = (Q_{ab})_{0n} - R_a (D_b)_{0n} - R_b (D_a)_{0n} + \frac{2}{3} (\vec{D}_{0n} \cdot \vec{R}) \quad \vec{M}'_{0n} = \vec{M}_{0n} - \frac{i}{2} E_{0n} [\vec{R} \times \vec{D}_{0n}]$$

and then require  $\frac{\partial f_{0n}^{(1)}}{\partial \vec{R}} = \vec{0}$

Leading to:  $\hat{A}\vec{R} = \vec{C}$   $A_{ij} = \frac{8}{15} E_{0n} (\vec{D}_{0n})^2 \delta_{ij} - \frac{4}{15} E_{0n} (D_i)_{0n} (D_j)_{0n}$   $C_i = \frac{1}{5} E_{0n} \sum_j (Q_{ij})_{0n} (D_j)_{0n} - \frac{2}{3} \sum_{jk} \epsilon_{ijk} (M_j)_{0n} (D_k)_{0n}$

Solving this linear system for R gives the best possible origin. It usually nearly coincides with the X-ray absorber atom

# Cl K- pre-edge: Method Calibration



BP86  
CP(PPP): metal  
TZVP: Cl  
COSMO

Ground state DFT  
symmetry equivalent chlorine 1s orbitals  
localized

TD-DFT - allowing only for excitations from  
the localized chlorine 1s orbitals.

Relative Intensities well-reproduced

Constant energy shift 85.5 (+/- 0.3 eV)

S. E. Shadle et al., J. Am. Chem. Soc., 1995, 117, 2259.  
S. DeBeer George, P. Brant, E. I. Solomon, J. Am. Chem. Soc.,  
2005, 127, 667.  
S. DeBeer George, T. Petrenko, F. Neese, ICA, 2007

# Effect of functional, basis set, solvation & relativistics...

	For all $[\text{MCl}_4]^n$ complexes		For $[\text{MCl}_4]^{2-}$ complexes only	
Perturbation	Avg Energy Shift	Error in Norm. Intensity	Avg Energy Shift	Error in Norm. Intensity
Opt method	85.3 (0.6)	0.06	85.5 (0.3)	0.06
B3LYP	64.0 (0.6)	0.11	64.1 (0.6)	0.10
LB94	40.3 (0.8)	0.20	40.8 (0.5)	0.18
IGLO-III	86.4 (0.7)	0.09	86.8 (0.2)	0.08
TZVP	85.7 (0.9)	0.26	85.9 (0.63)	0.32
Inf DE	85.4 (0.6)	0.07	85.7 (0.2)	0.05
No solv	84.9 (0.6)	0.06	85.2 (0.3)	0.06
ZORA	61.1 (0.6)	0.06	61.0 (0.7)	0.06
DKH2	77.3 (1.2)	0.06	77.8 (1.9)	0.06

S. DeBeer George, T. Petrenko, F. Neese, ICA, 2007.

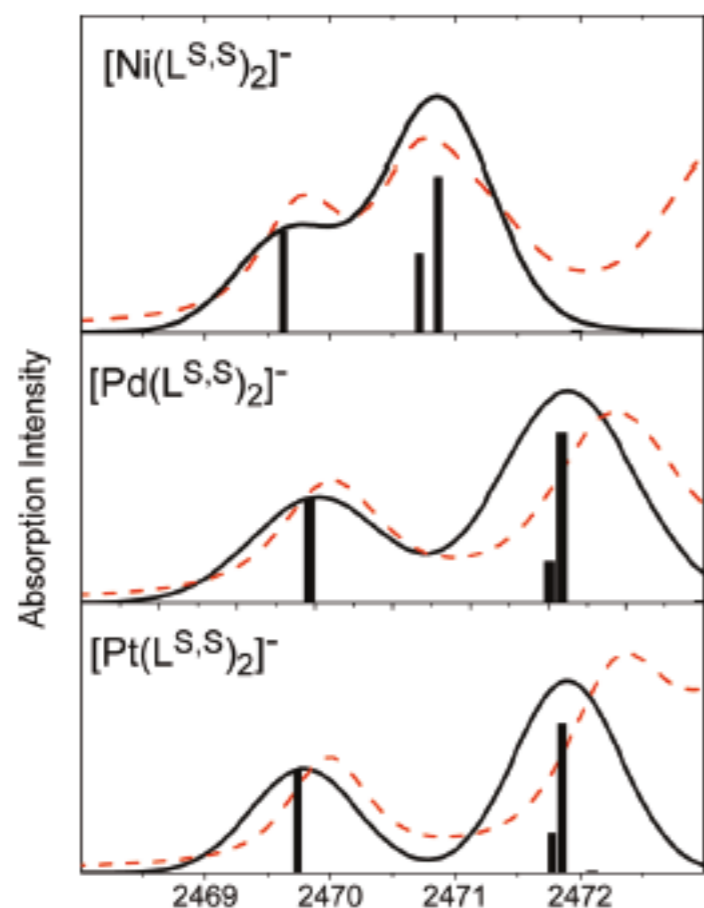
## Calibration of Scalar Relativistic Density Functional Theory for the Calculation of Sulfur K-Edge X-ray Absorption Spectra

Serena DeBeer George<sup>\*,†</sup> and Frank Neese<sup>\*,‡</sup>

<sup>†</sup>Department of Chemistry and Chemical Biology, Cornell University, Ithaca, New York 14853, and

<sup>‡</sup>Institut für Physikalische und Theoretische Chemie, Universität Bonn, D-53115 Bonn, Germany

Received November 7, 2009



**Table 1.** Calibration Data for TD-DFT-Based Calculations of S–K-Edge Absorption Spectra for Different Density Functionals ( $\Delta E$  = shift required for the transition energy;  $b$  = slope connecting oscillator strength and experimental area, i.e.,  $\text{area} = (1 \times 10^4) f_{\text{osc}}/b$ )

	$\Delta E$ (eV)	$B$
BP86 <sup>a</sup>	60.38 ± 0.12	11.44 ± 0.49
BP86 <sup>b</sup>	60.01 ± 0.11	11.49 ± 0.50
BP86 <sup>a,c</sup>	76.25 ± 0.15	12.01 ± 0.48
PBE <sup>a</sup>	61.67 ± 0.11	11.18 ± 0.55
PBE <sup>b</sup>	61.33 ± 0.12	11.40 ± 0.50
OPBE <sup>a</sup>	62.75 ± 0.12	11.15 ± 0.53
OPBE <sup>b</sup>	62.41 ± 0.13	11.28 ± 0.54
OLYP <sup>a</sup>	61.83 ± 0.12	11.26 ± 0.52
OLYP <sup>b</sup>	61.49 ± 0.12	11.34 ± 0.51
TPSS <sup>a</sup>	53.53 ± 0.13	11.25 ± 0.50
TPSS <sup>b</sup>	53.18 ± 0.13	11.28 ± 0.50
B3LYP <sup>a</sup>	40.34 ± 0.44	16.83 ± 0.57
PBE0 <sup>a</sup>	36.17 ± 0.36	18.03 ± 0.67
TPSSH <sup>a</sup>	44.14 ± 0.18	13.49 ± 0.48

<sup>a</sup>With TDA. <sup>b</sup>Full TD-DFT. <sup>c</sup>Without relativistic corrections.



# Generic ORCA Input File

---

For Sulfur K-edge calculations, the following input was used:

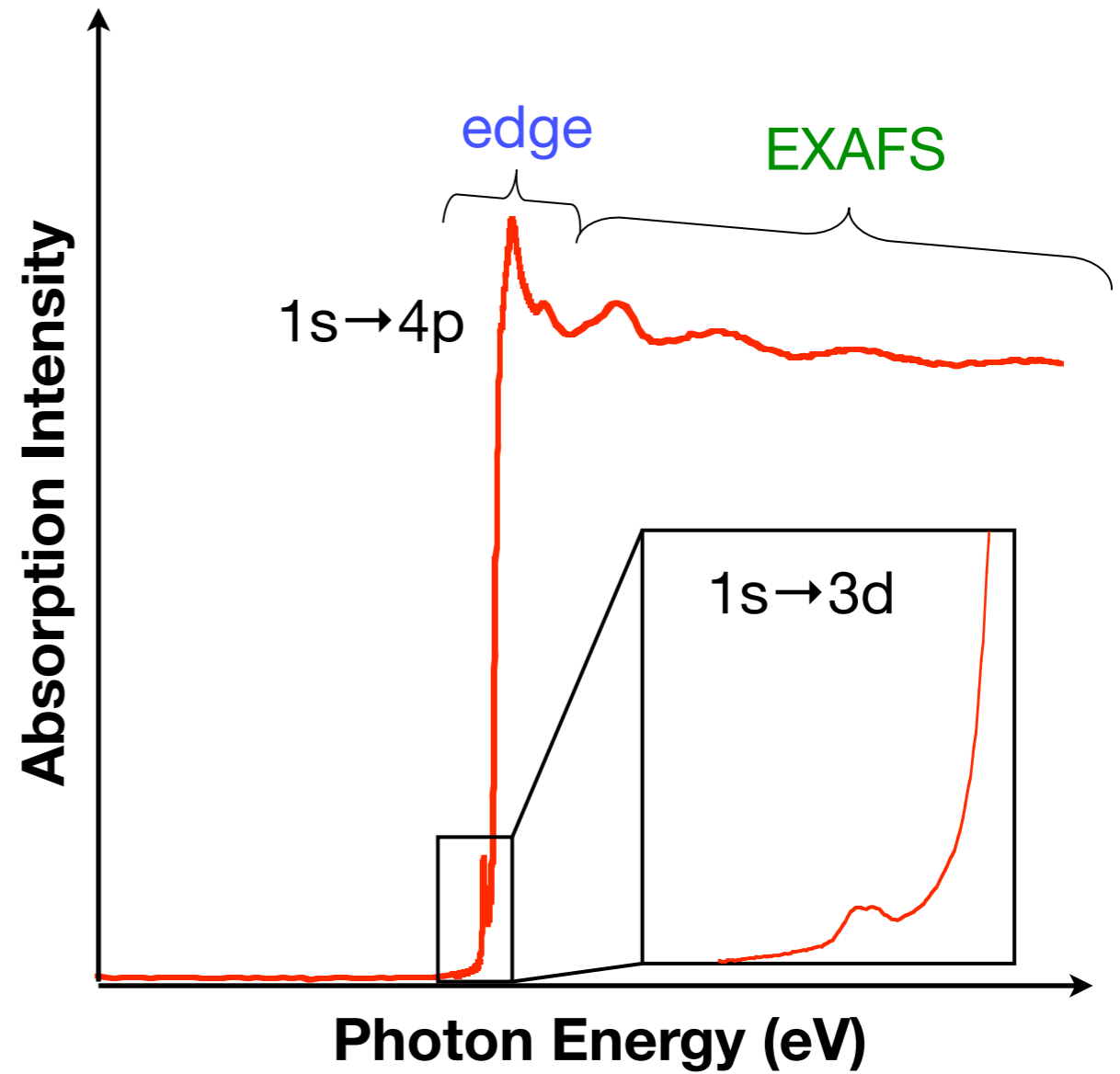
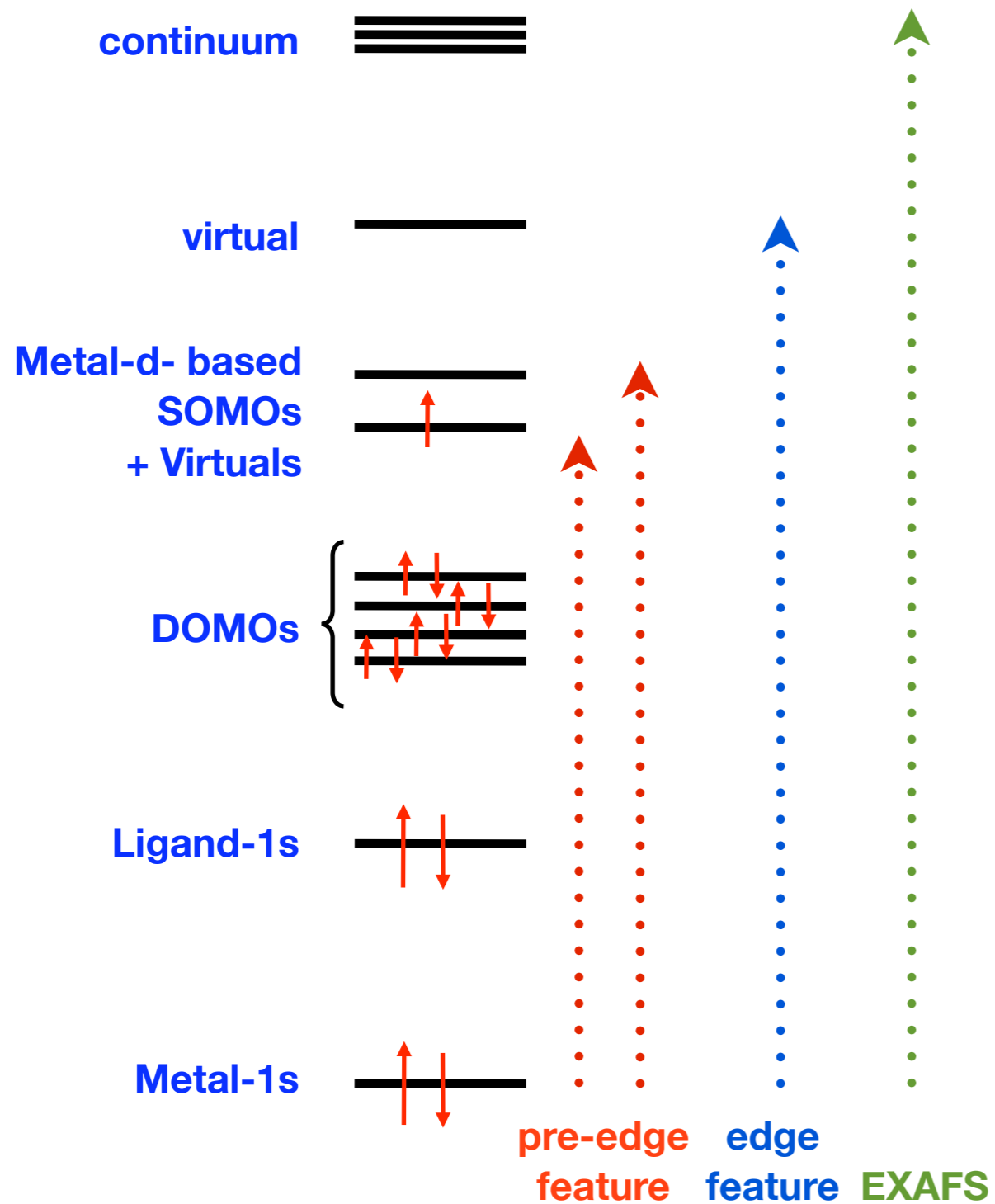
```
! SP def2-TZVP(-f) def2-TZVP/J Functional COSMO(CH2CL2) ZORA
! TightSCF Grid4 NoFinalGrid
%maxcore 1024

%tddft   NRoots      5
          MaxDim     150
          XASLoc[0] = First-S-1s, Last-S-1s
          XASLoc[1] = First-S-1s, Last-S-1s
          OrbWin[0] = First-S-1s, First-S-1s, -1, -1
          OrbWin[1] = First-S-1s, First-S-1s, -1, -1
          DoQuad true
          end

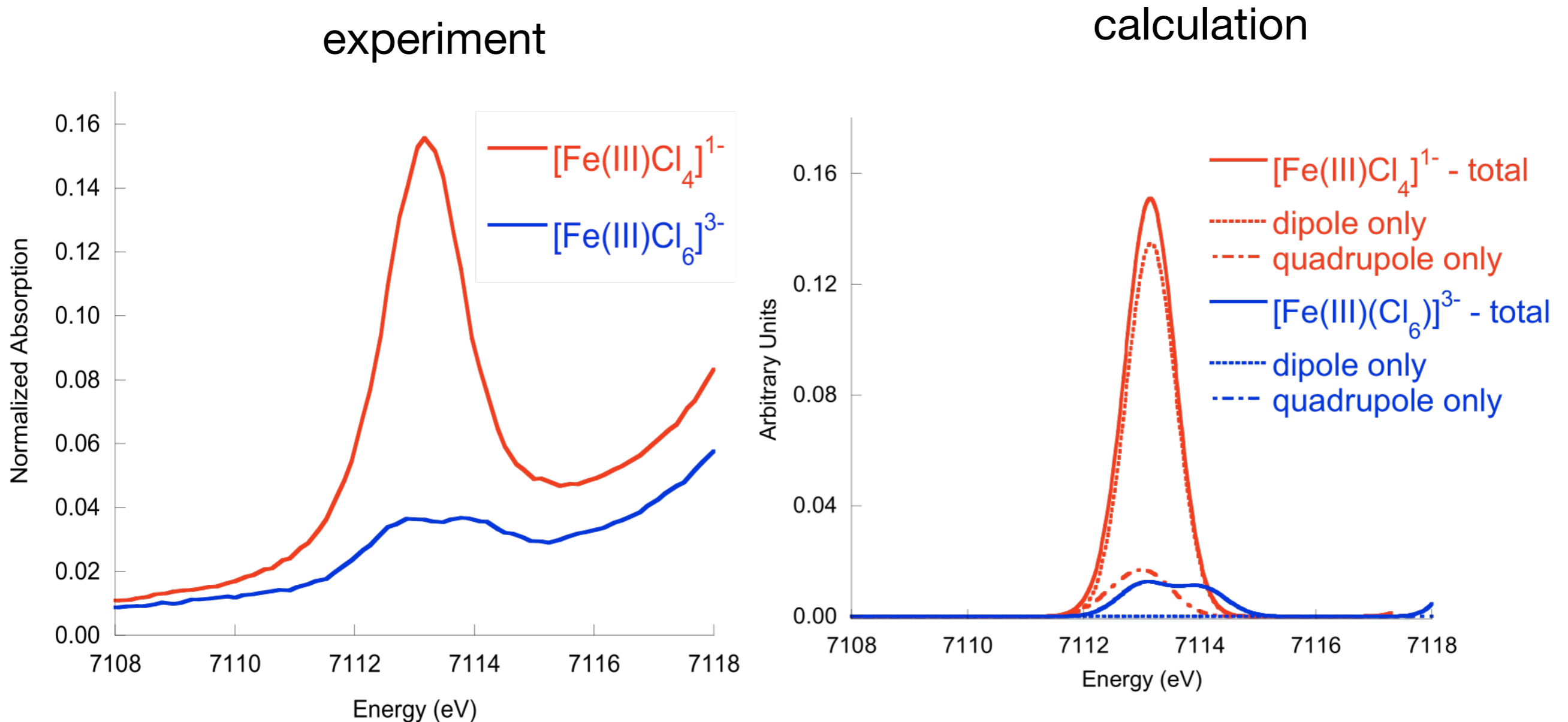
* xyz Charge Multiplicity
  (the optimized coordinates)

*
```

# Metal K-Edges



# TD-DFT with Inclusion of Quadrupole

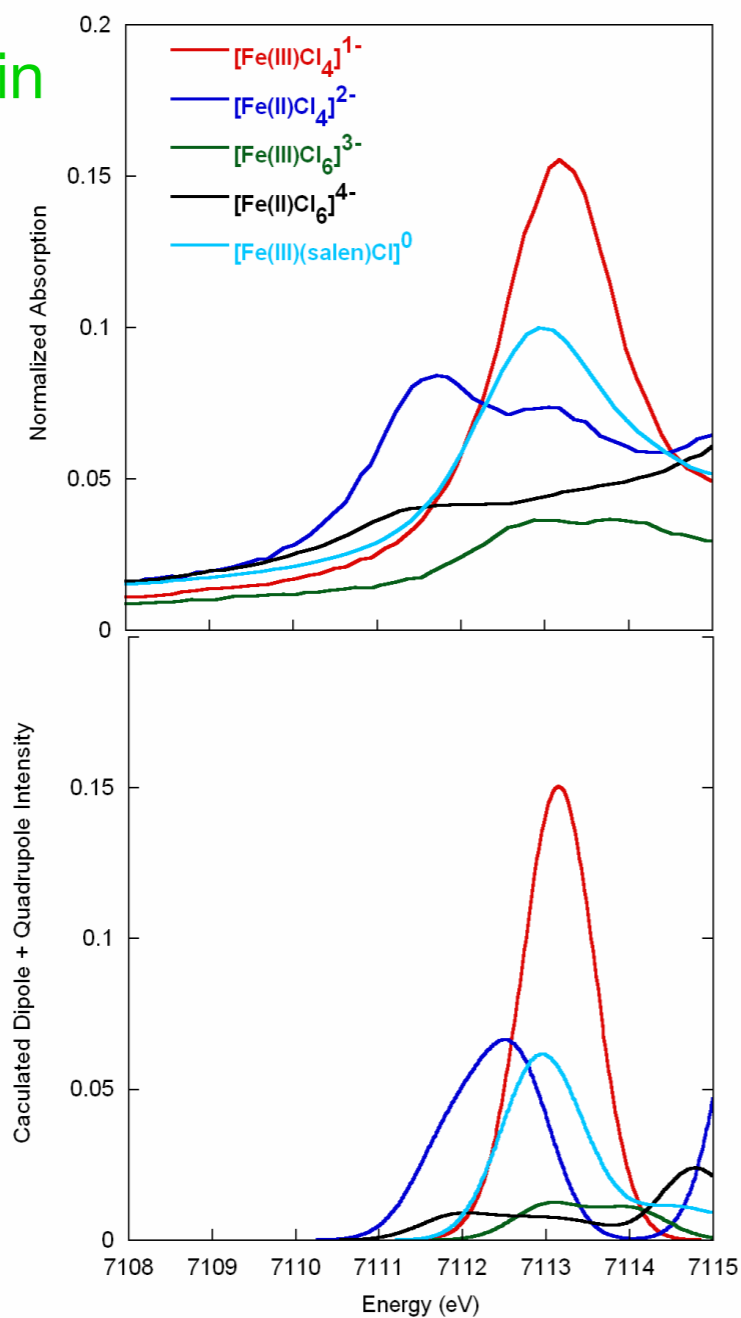


Energies and intensities are well-reproduced

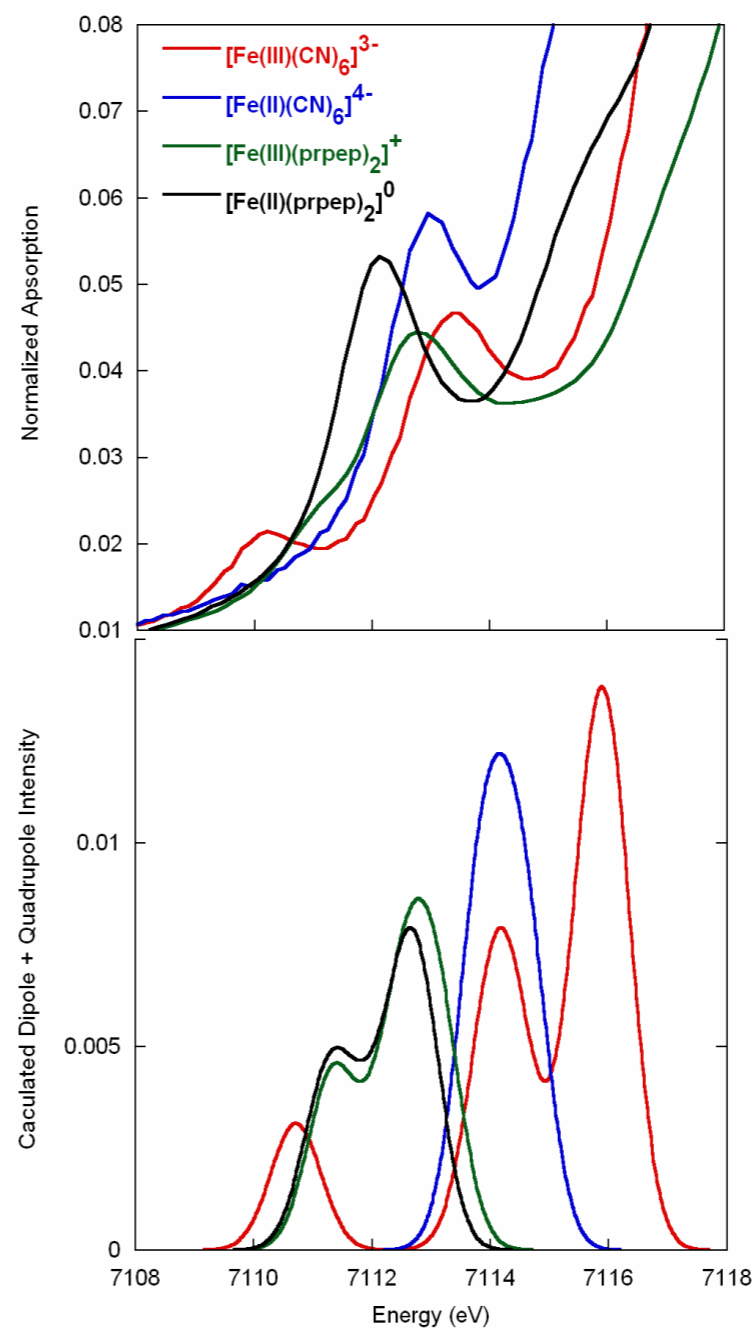
DeBeer George, S.; Petrenko, T.; Neese, F.J. Phys. Chem. A, 2008, 112, 12936.

# TD-DFT with ORCA: Theory vs Experiment

High-Spin

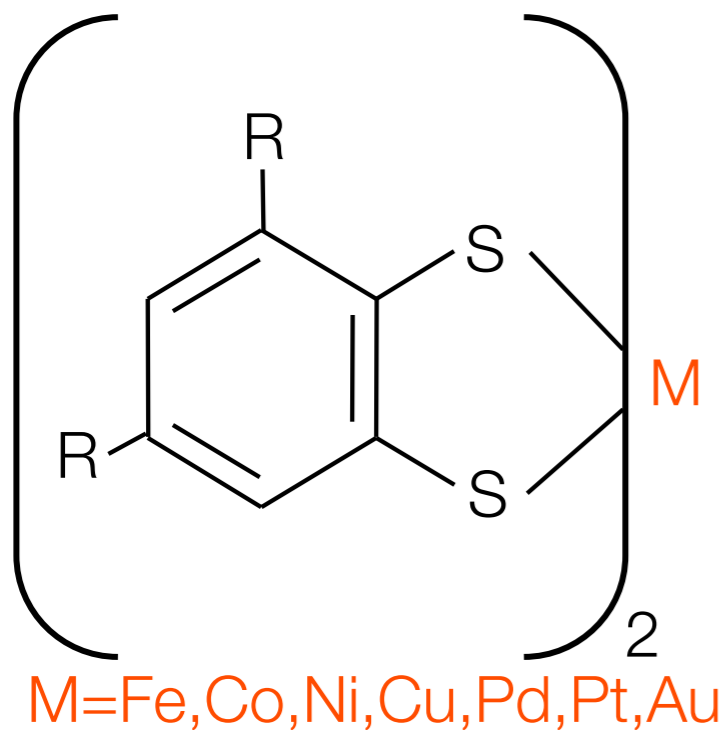
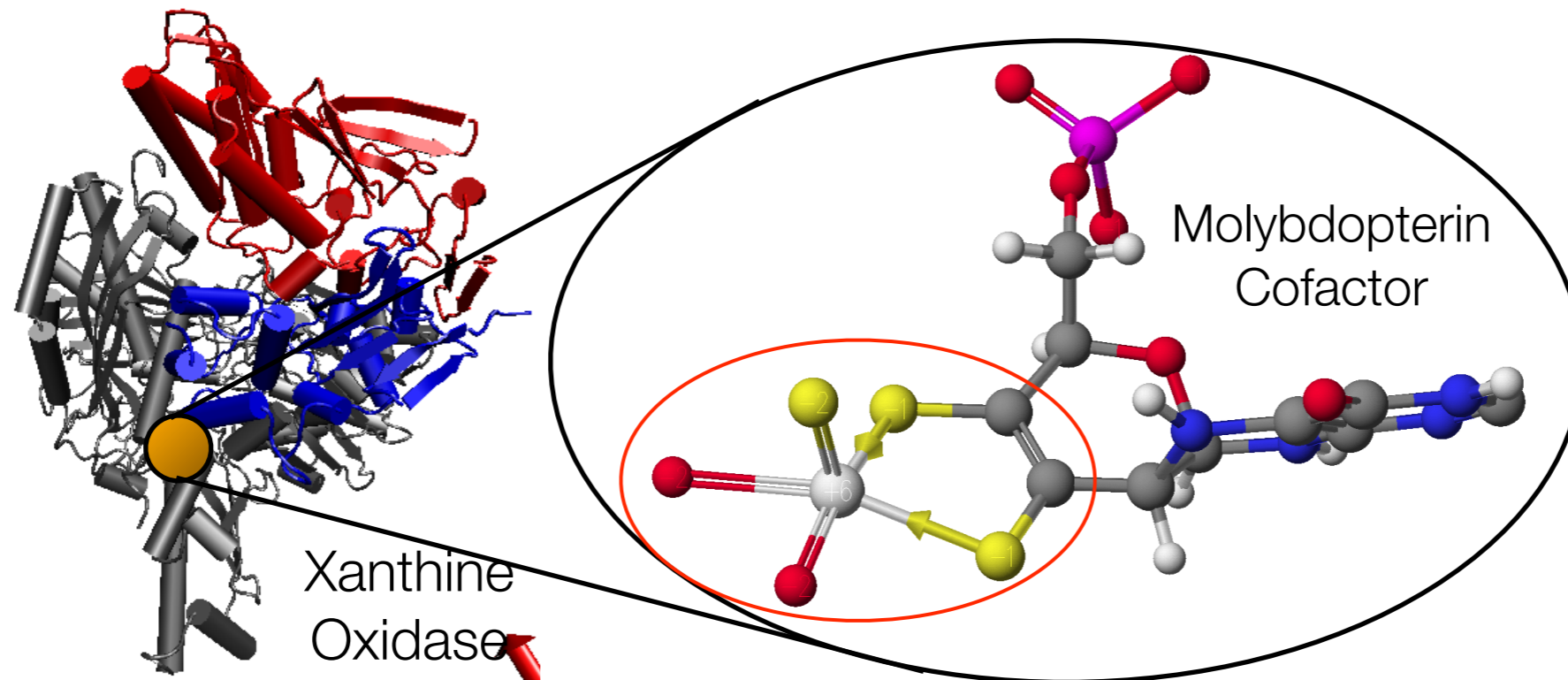


Low-Spin



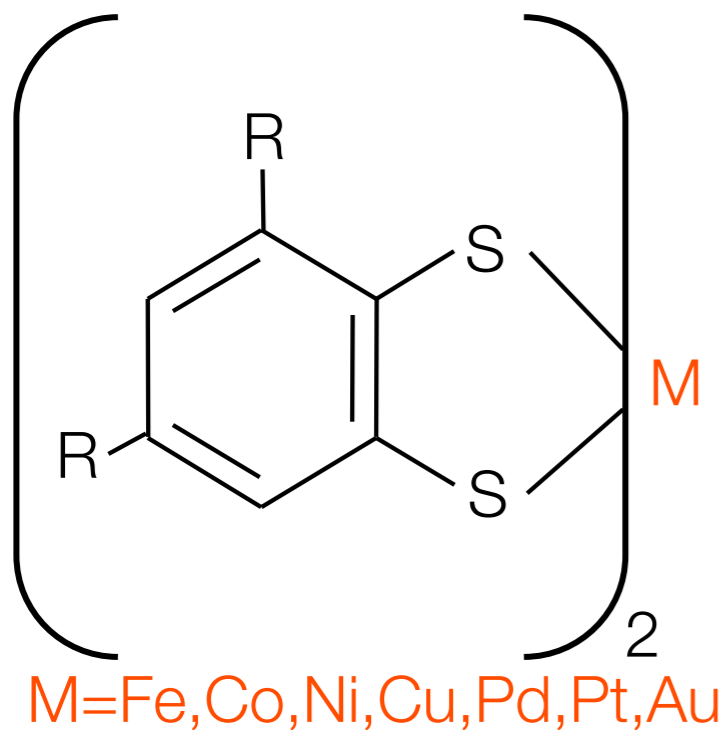
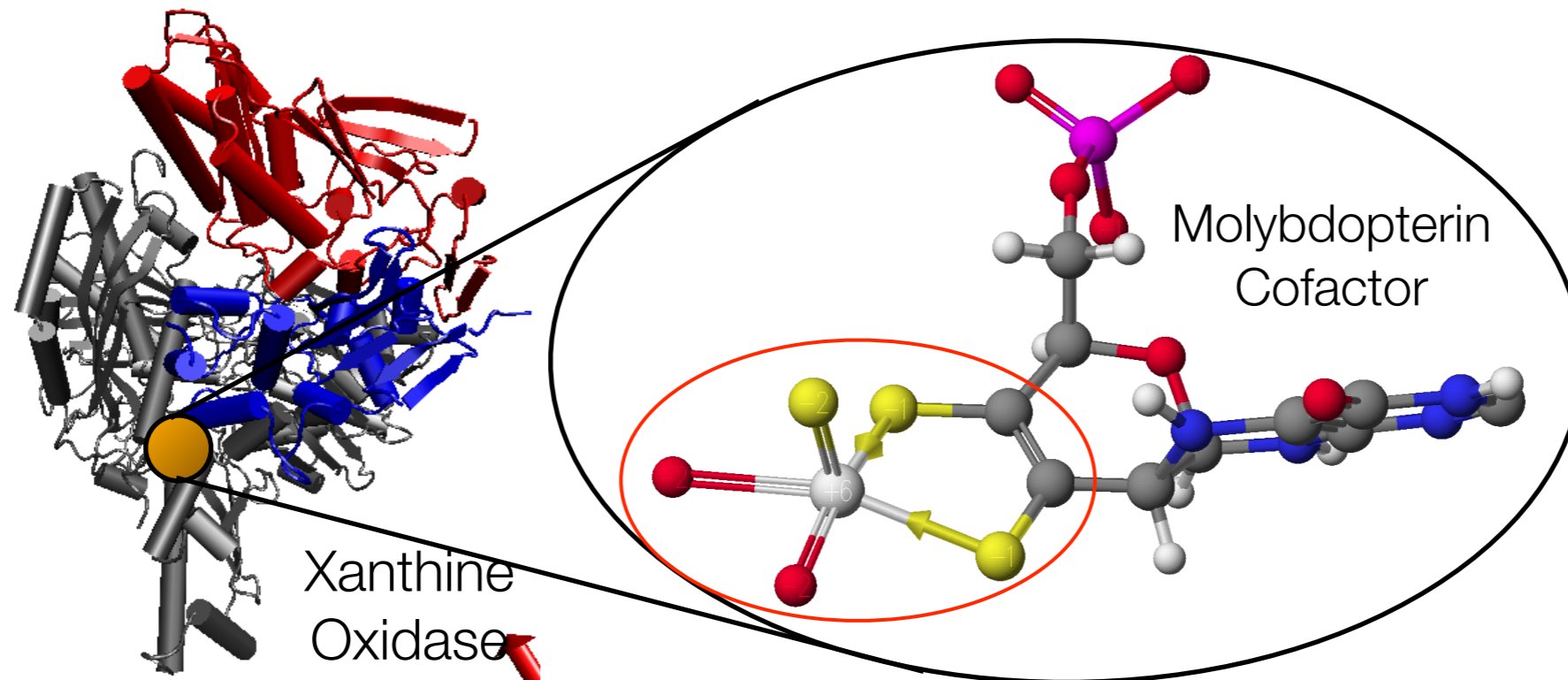
*DeBeer George, S.; Petrenko, T.; Neese, F.J. Phys. Chem. A, 2008, 112, 12936.*

# Dithiolene Complexes



- Classical coordination complexes (Holm, Maki, Gray, Stiefel, Schrauzer, Wieghart...)
- Candidate materials for nonlinear optic devices and catalysis
- Biological impact (Molybdopterines)
- Controversial electronic structure

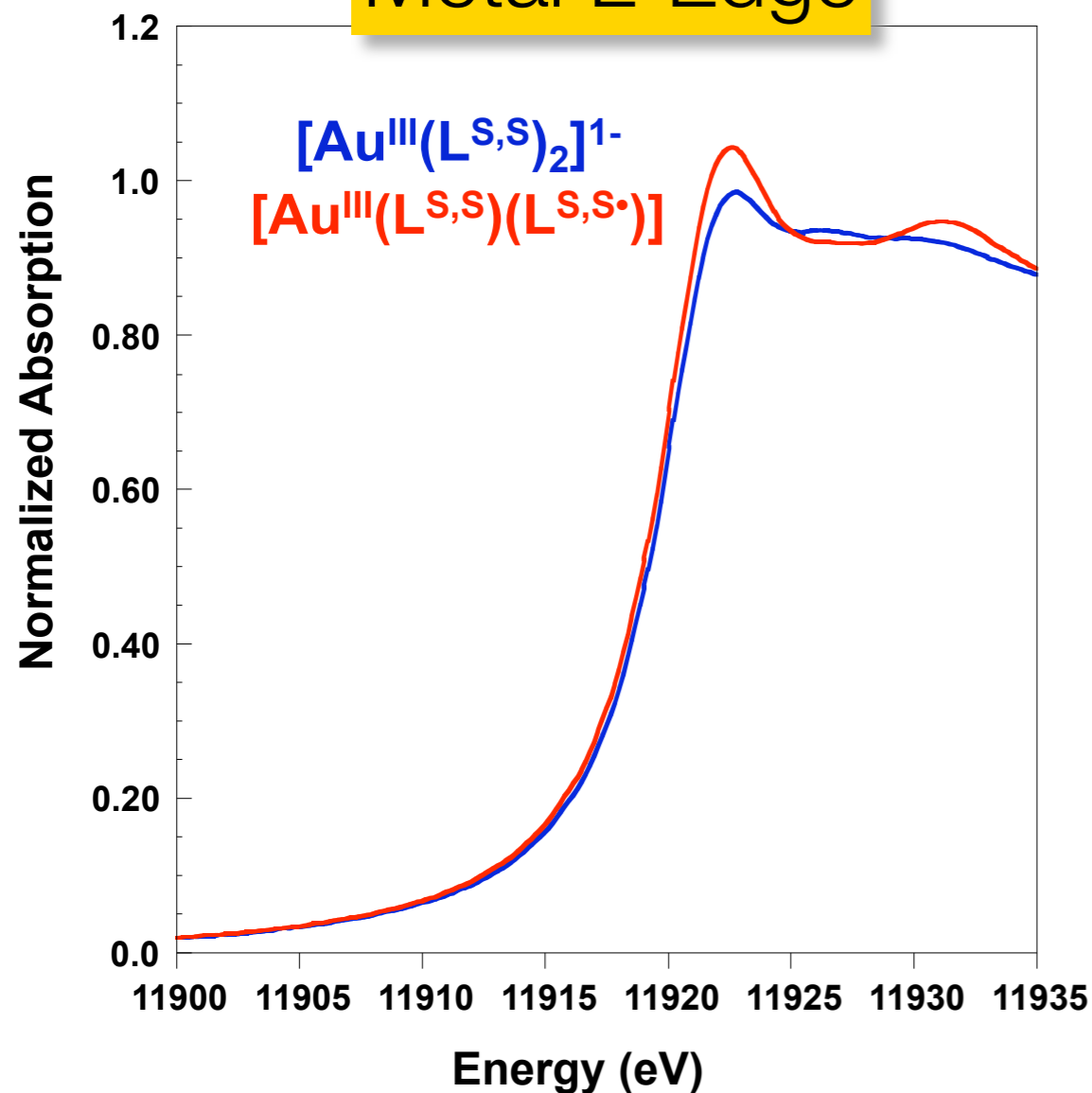
# Dithiolene Complexes



- Classical coordination complexes (Holm, Maki, Gray, Stiefel, Schrauzer, Wieghart...)
- Candidate materials for nonlinear optic devices and catalysis
- Biological impact (Molybdopterines)
- Controversial electronic structure

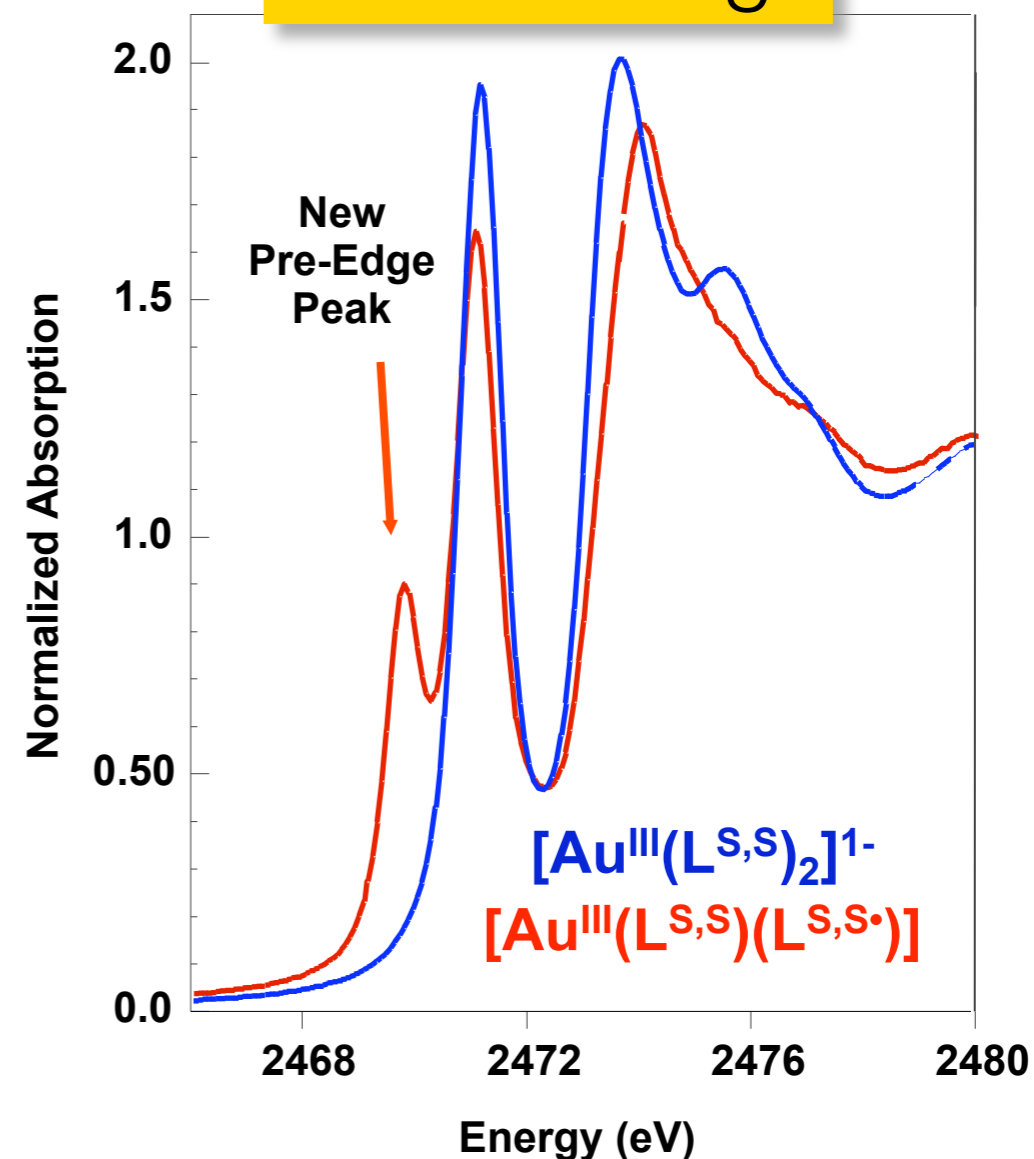
# Do dithiolene ligands contain radicals?

## Metal L-Edge



No Effect on Metal-Edge: **Ligand Centered Oxidation**

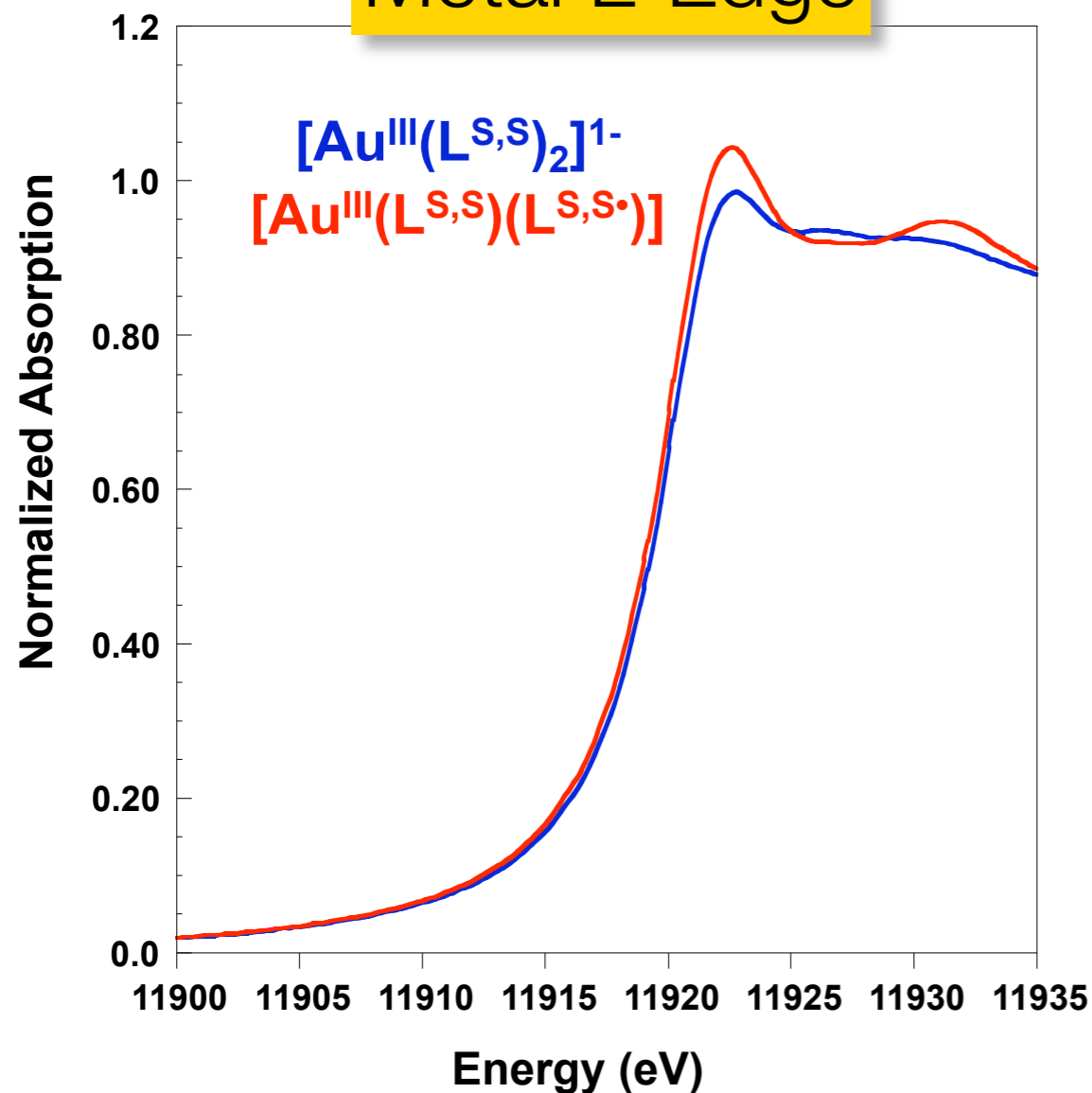
## Sulfur K-Edge



New Pre-Edge Peak: **Ligand Centered Oxidation**

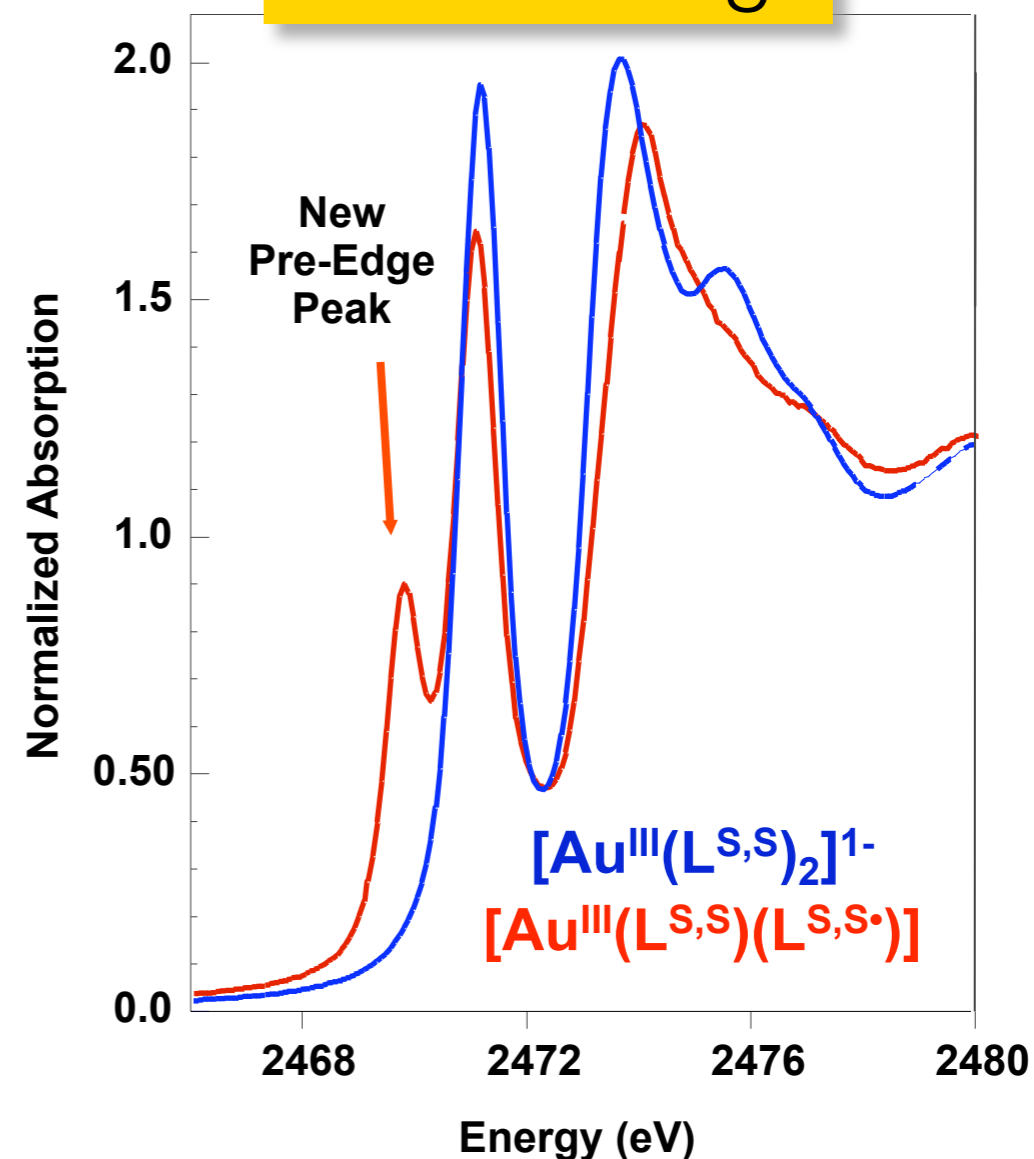
# Do dithiolene ligands contain radicals?

## Metal L-Edge



No Effect on Metal-Edge: **Ligand Centered Oxidation**

## Sulfur K-Edge



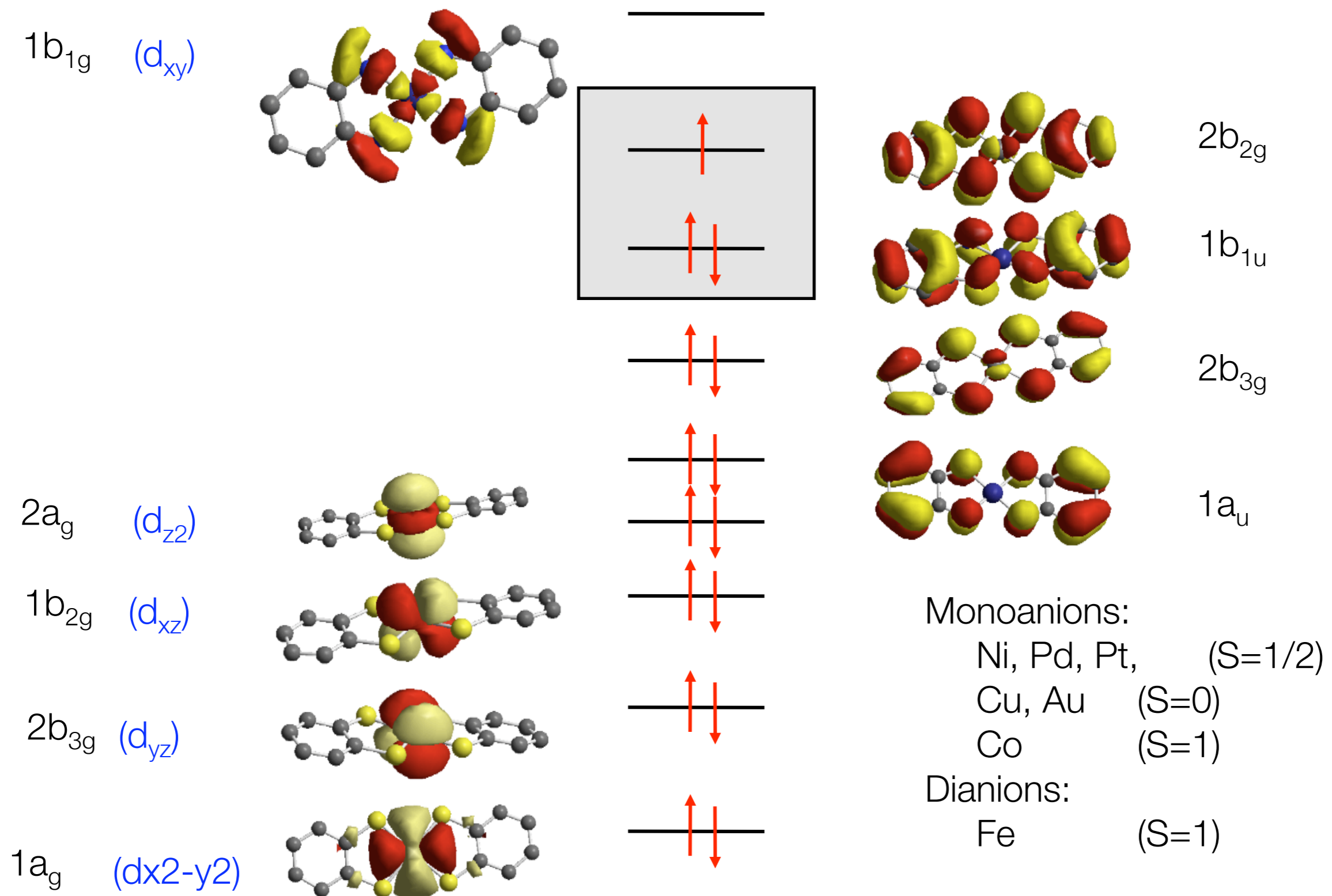
New Pre-Edge Peak: **Ligand Centered Oxidation**

**YES! ... But what determines when and how it happens?**

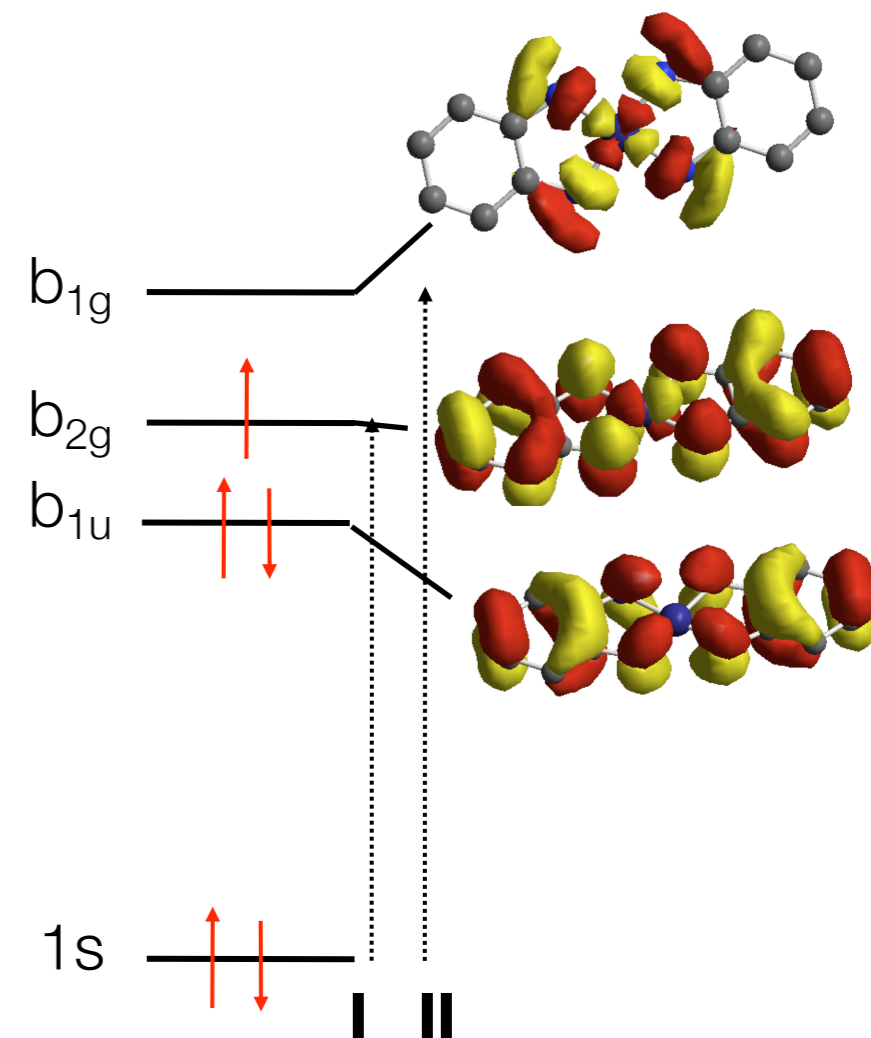
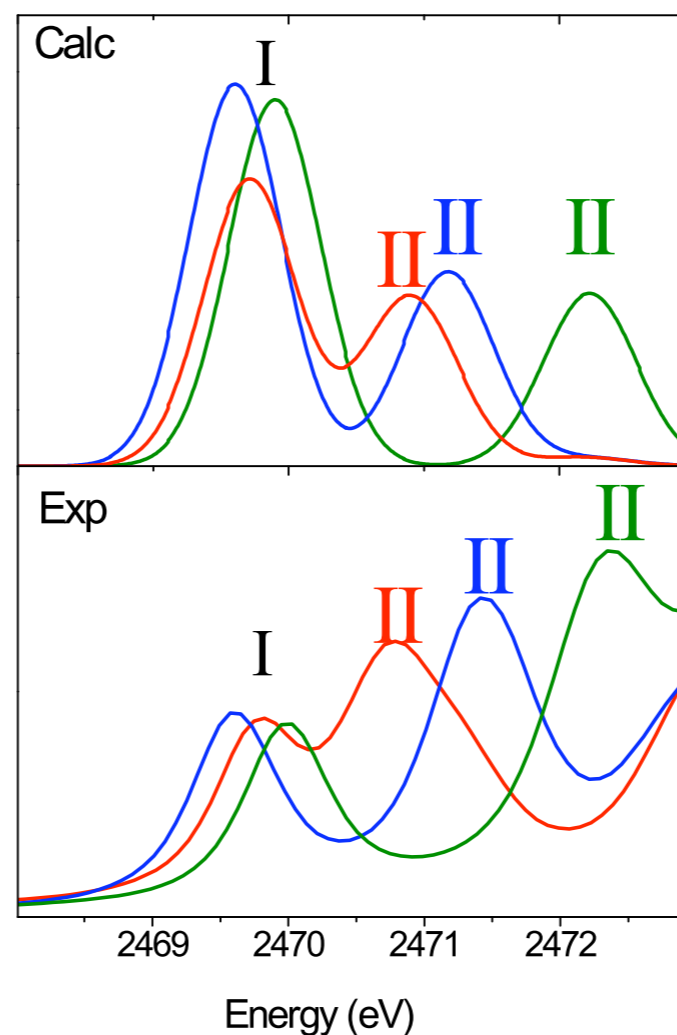
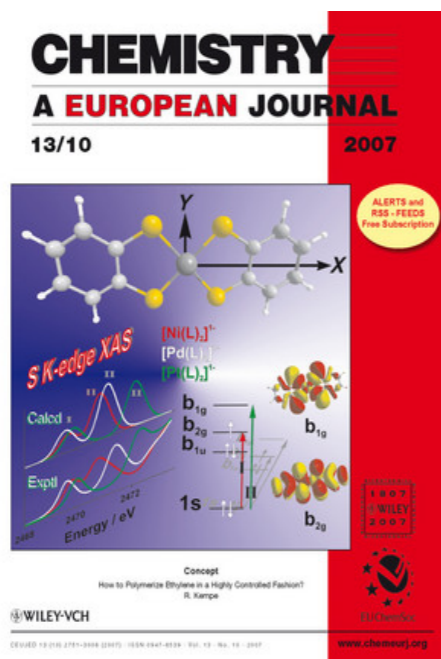
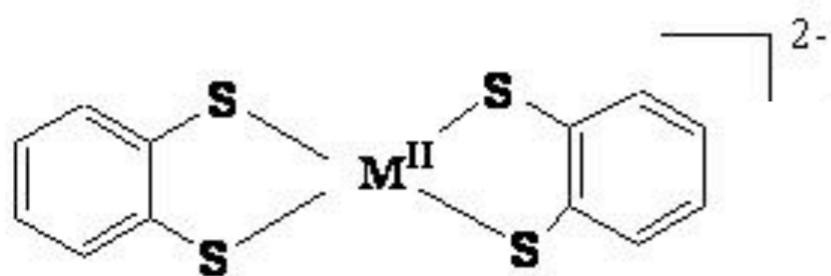
K. Ray, S. DeBeer George, E. I. Solomon, K. Wieghardt, F. Neese, Chem. Eur. J., 2007, 13, 2783.



# Electronic Structure of Square Planar $[M(L^{SS})_2]^-$



# Insights from XAS on Dithiolenes



Radical character along the series:

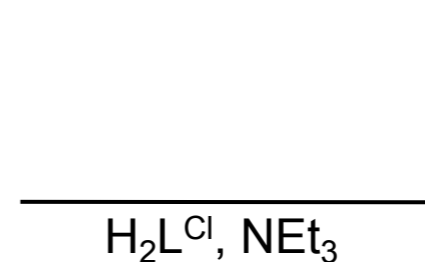
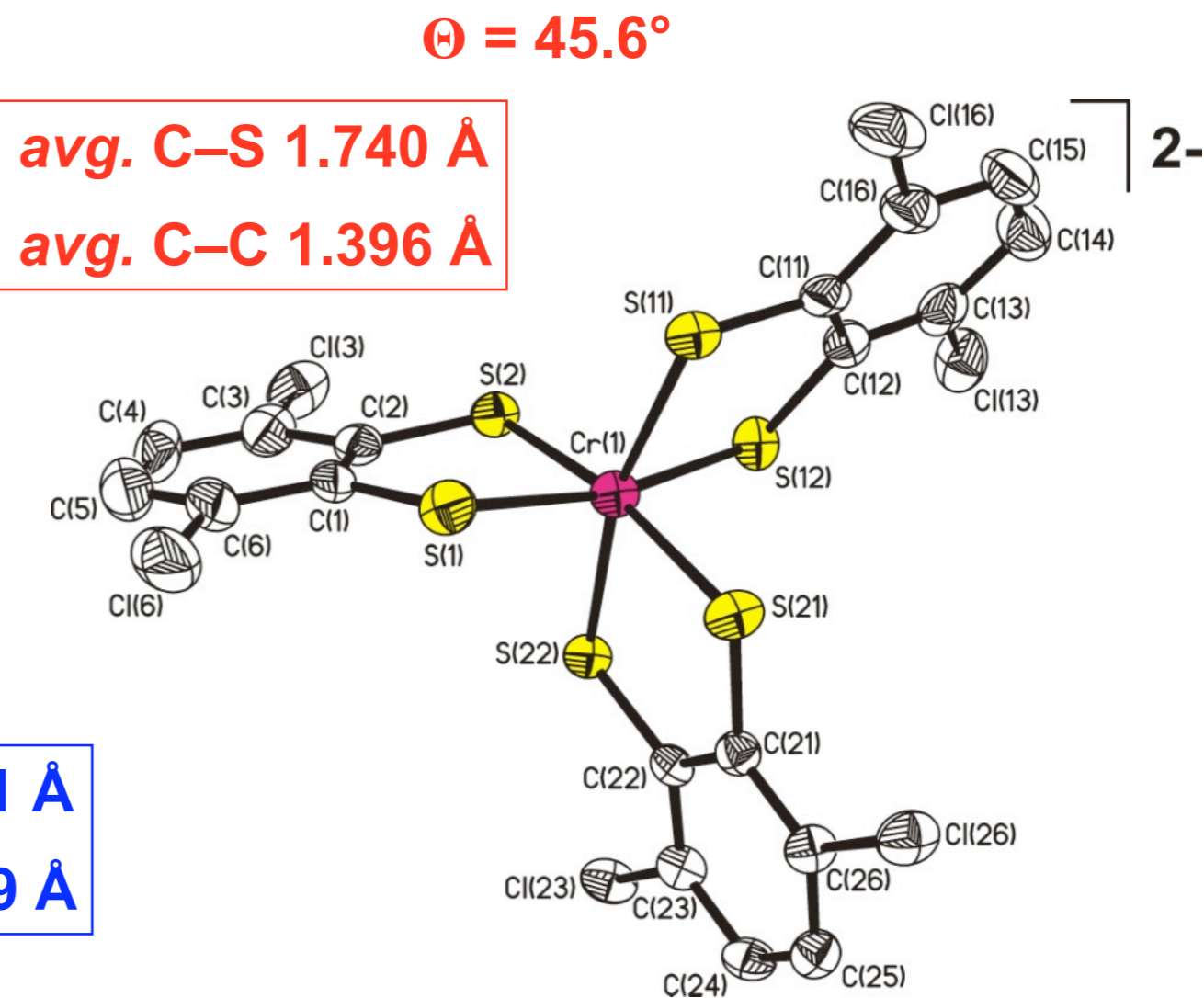
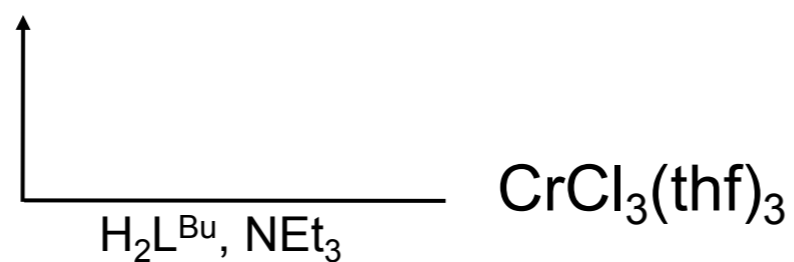
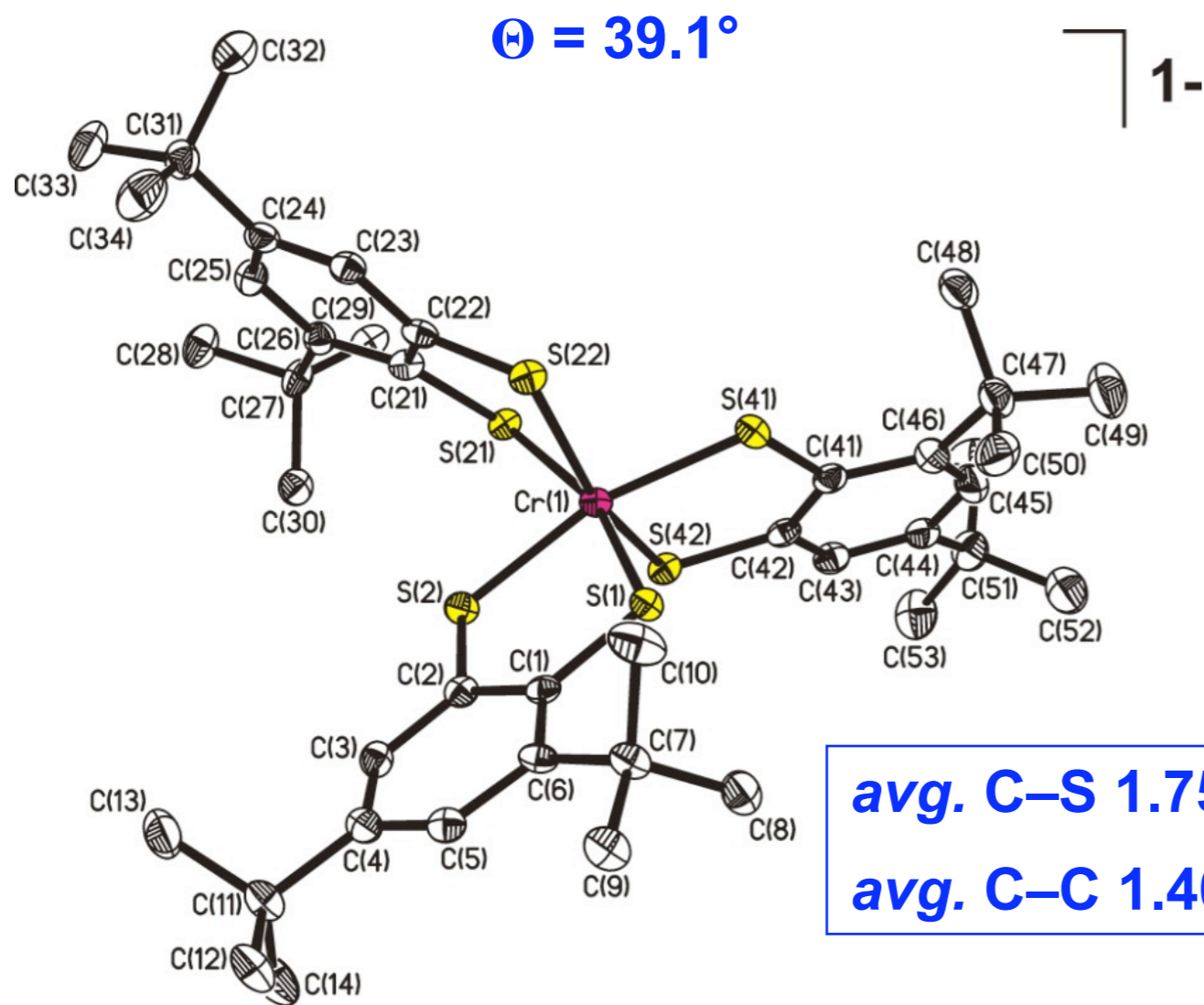


**“Innocent” ligands**

**Ambiguous**

**Ligand Radicals**

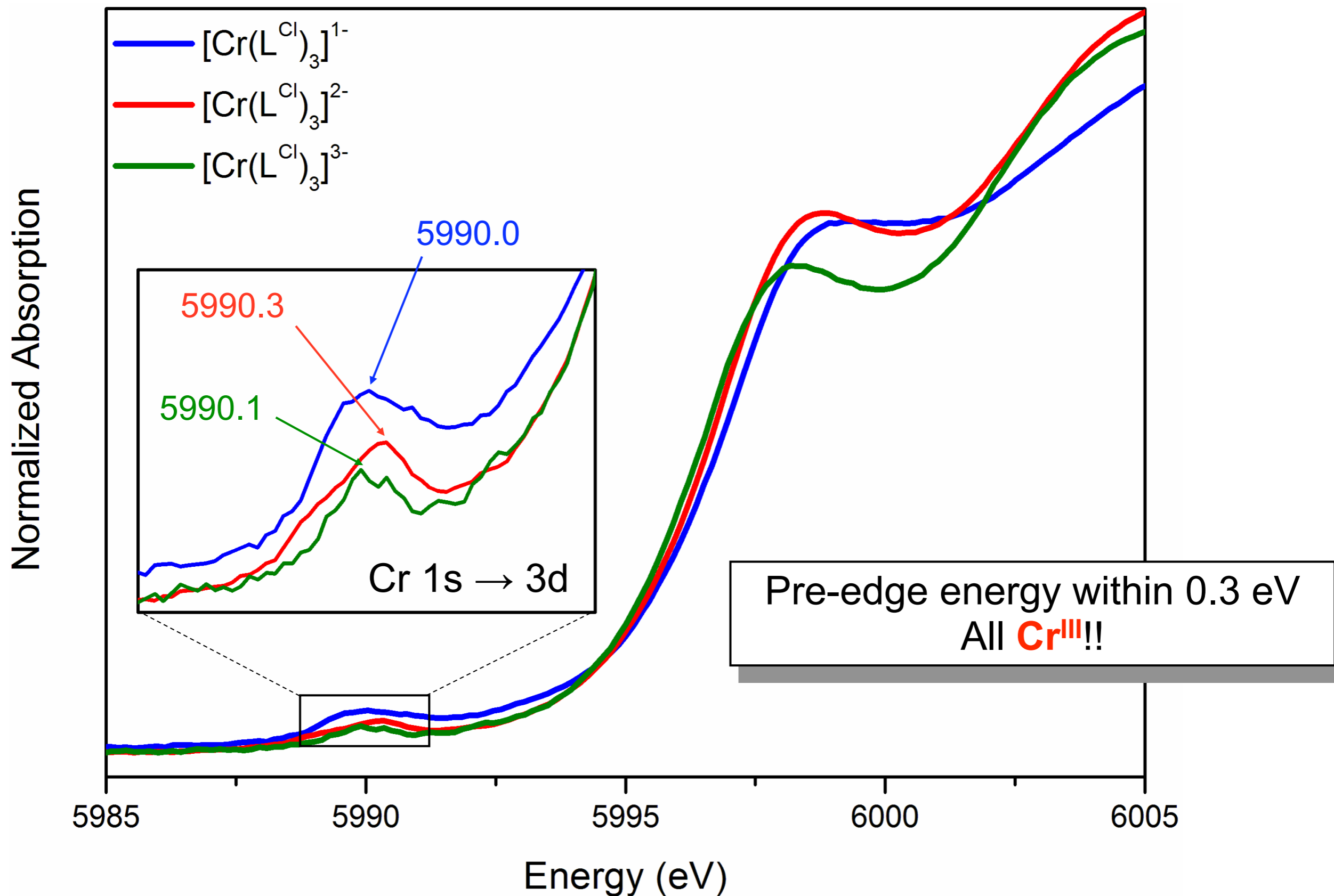
# Chromium Trisdithiolenes



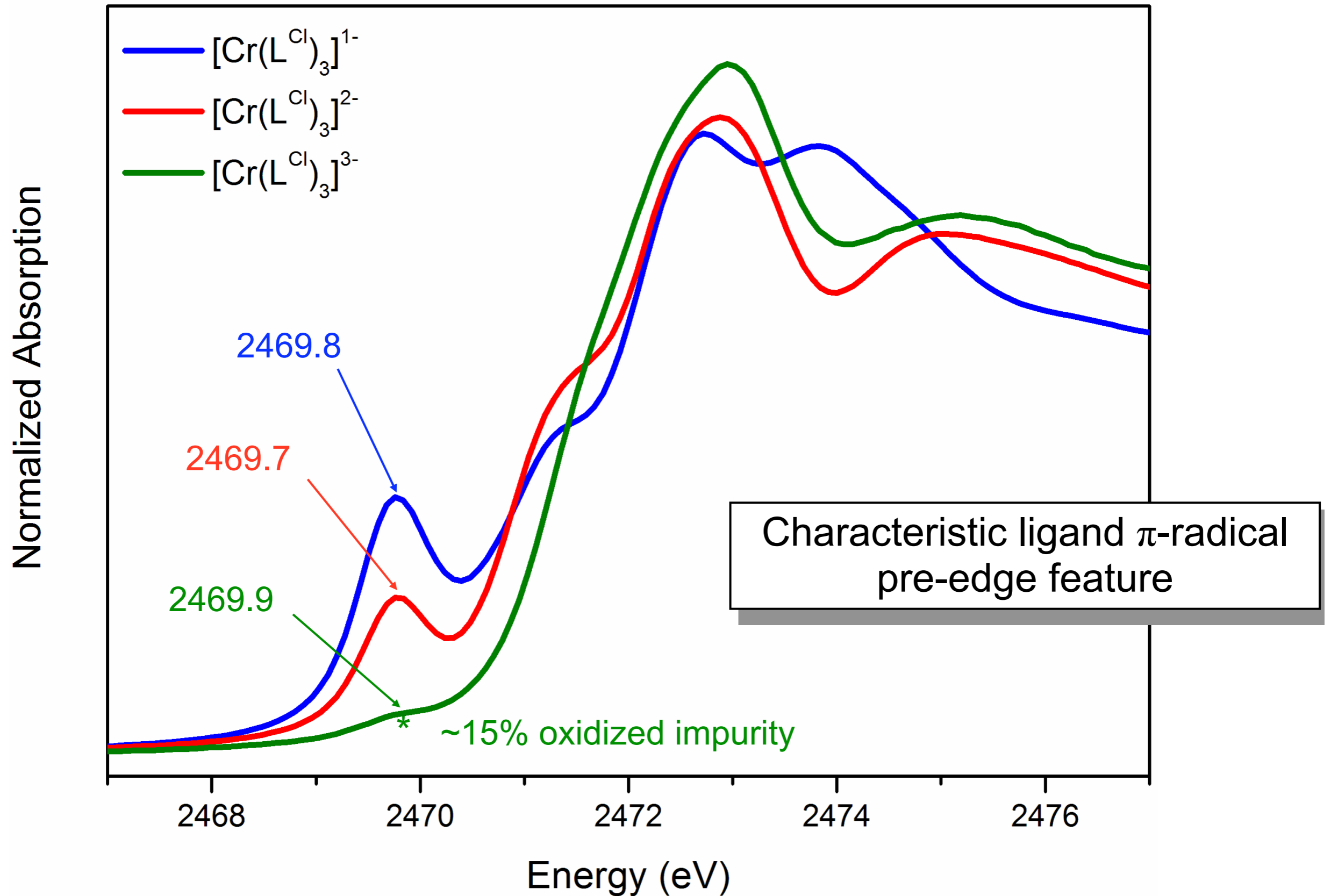
Two other structures, both octahedral:  
 $[\text{Cr}(\text{mnt})_3]^{2-} (\text{S} = 1)$  and  $[\text{Cr}(\text{mnt})_3]^{3-} (\text{S} = 3/2)$

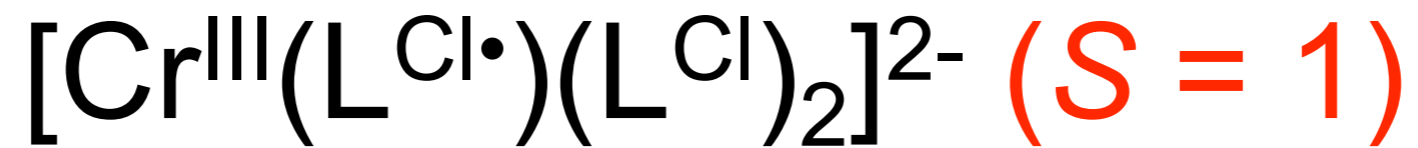
Kapre, Wieghardt et al. *Inorg. Chem.* **2007**, *46*, 7827  
 Lewis & Dance *Dalton Trans.* **2000**, 3176

# Chromium K-edge XAS

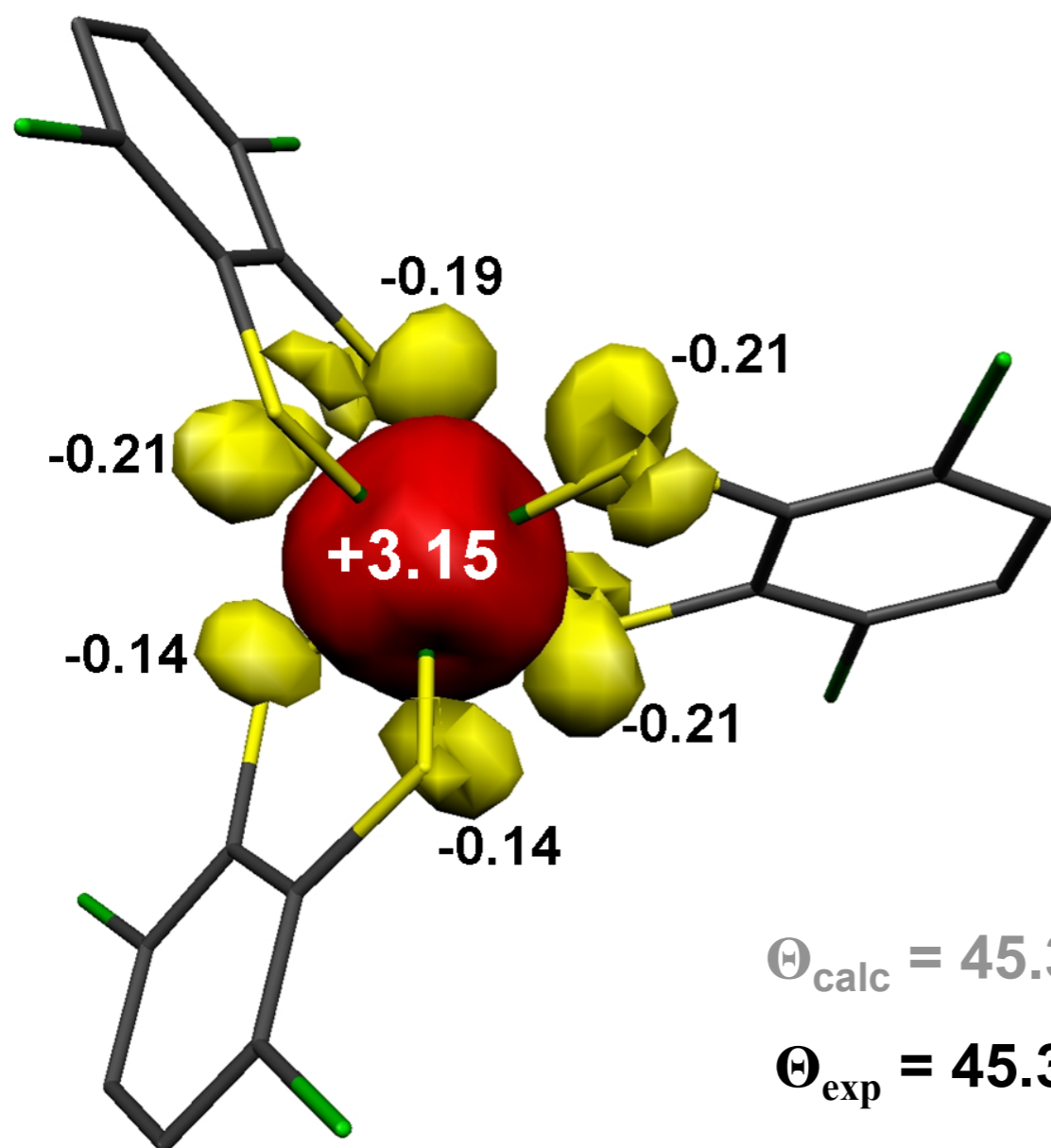


# Sulfur K-edge XAS





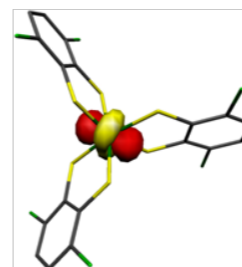
## DFT Broken Symmetry, BS(3,1)



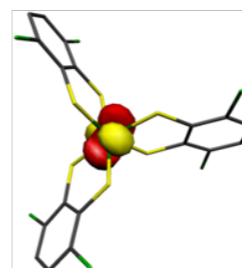
$$\Theta_{\text{calc}} = 45.3^\circ$$

$$\Theta_{\text{exp}} = 45.3^\circ$$

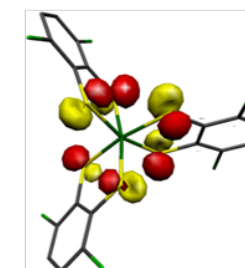
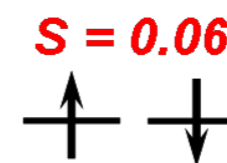
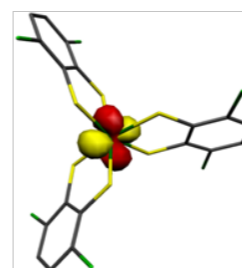
90% Cr



92% Cr

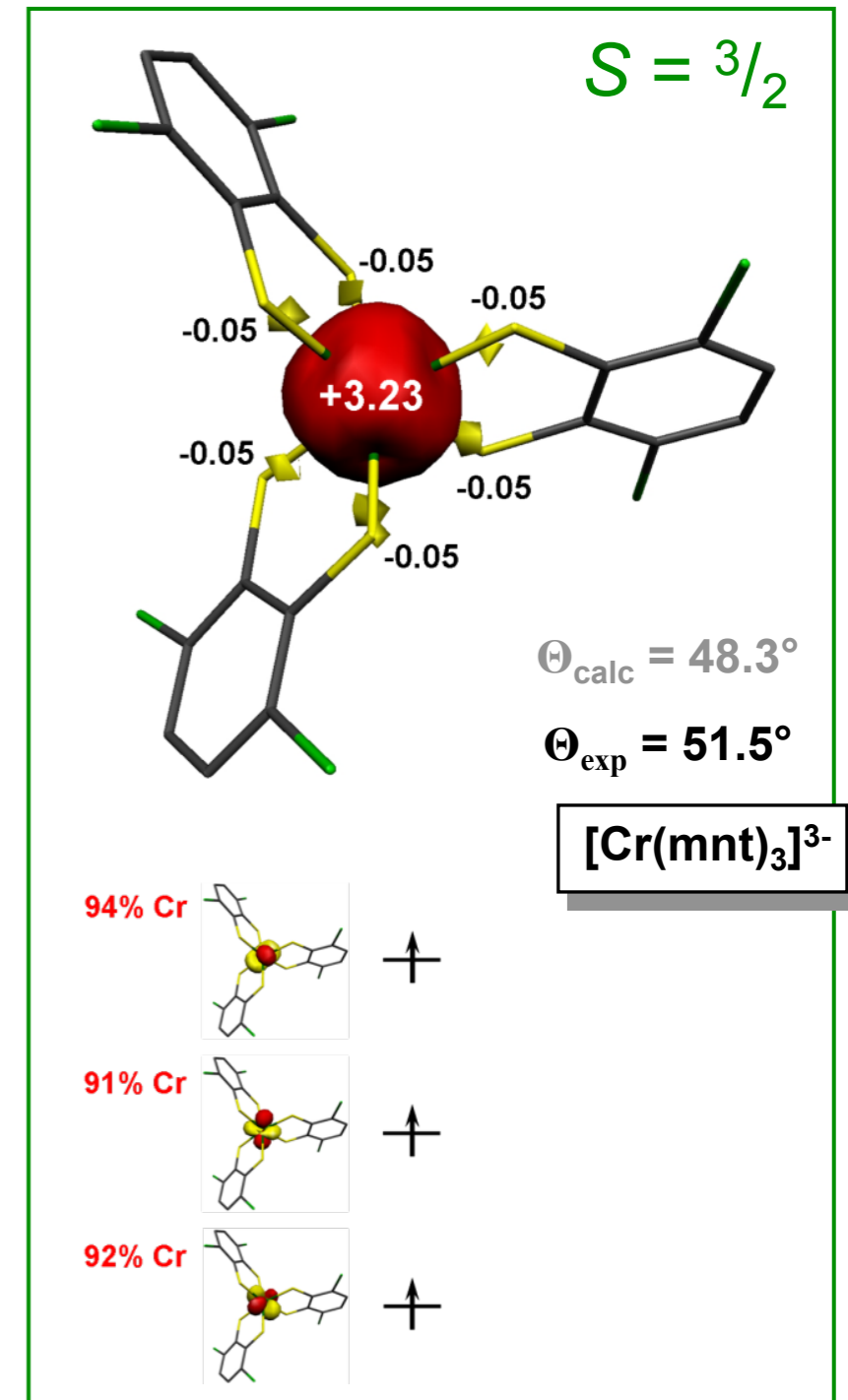
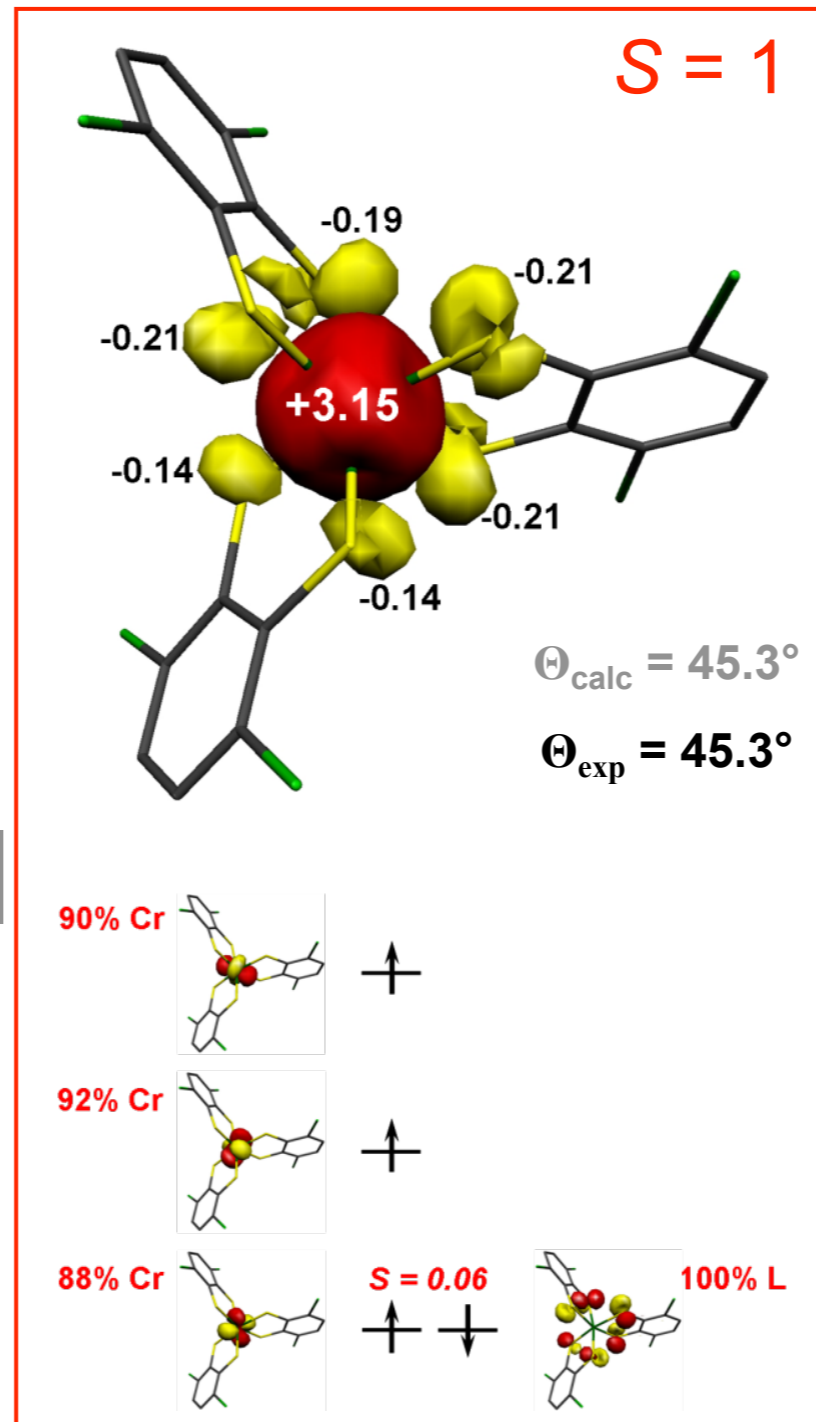
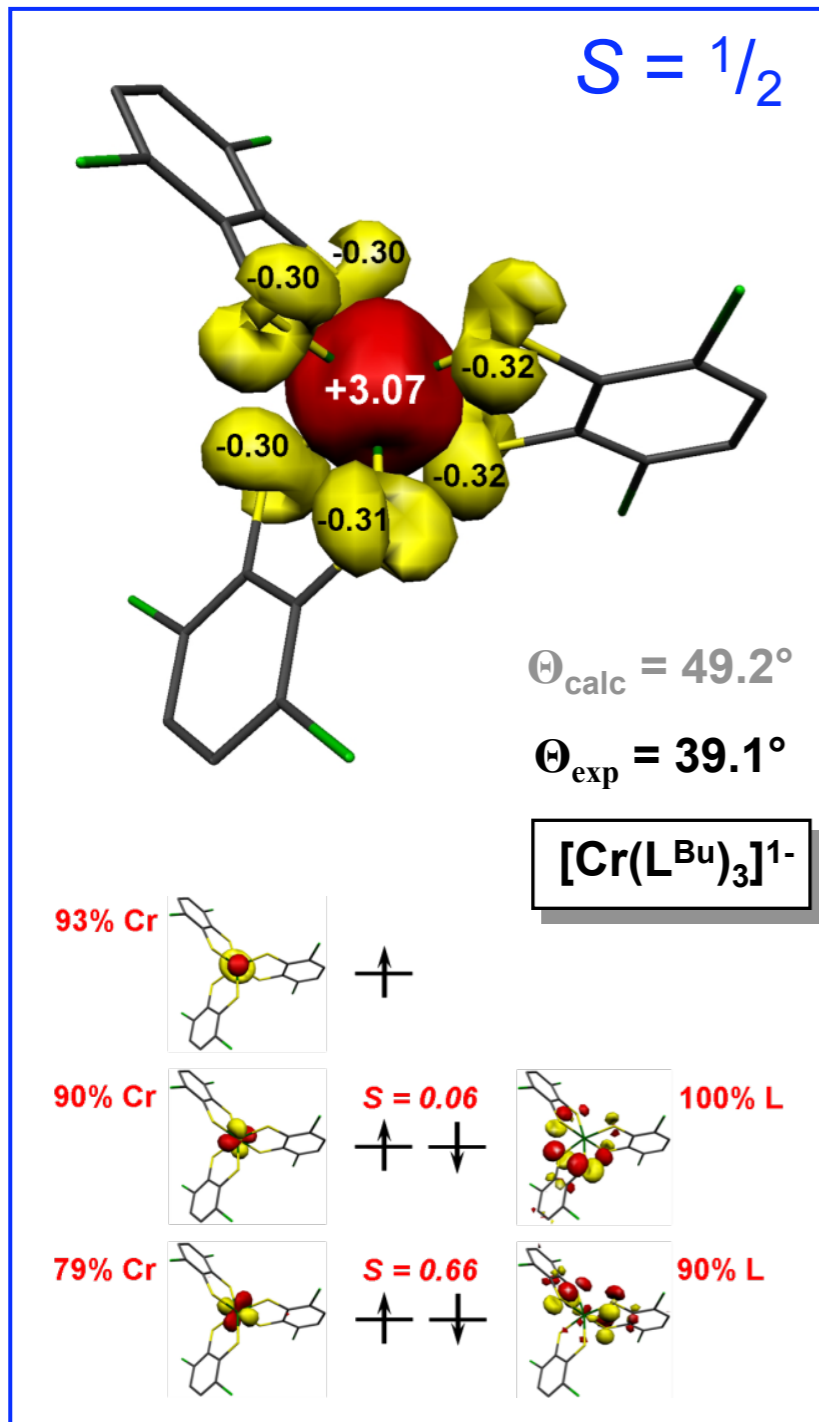
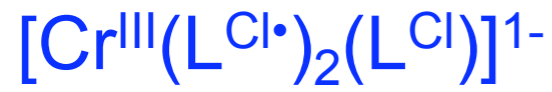


88% Cr

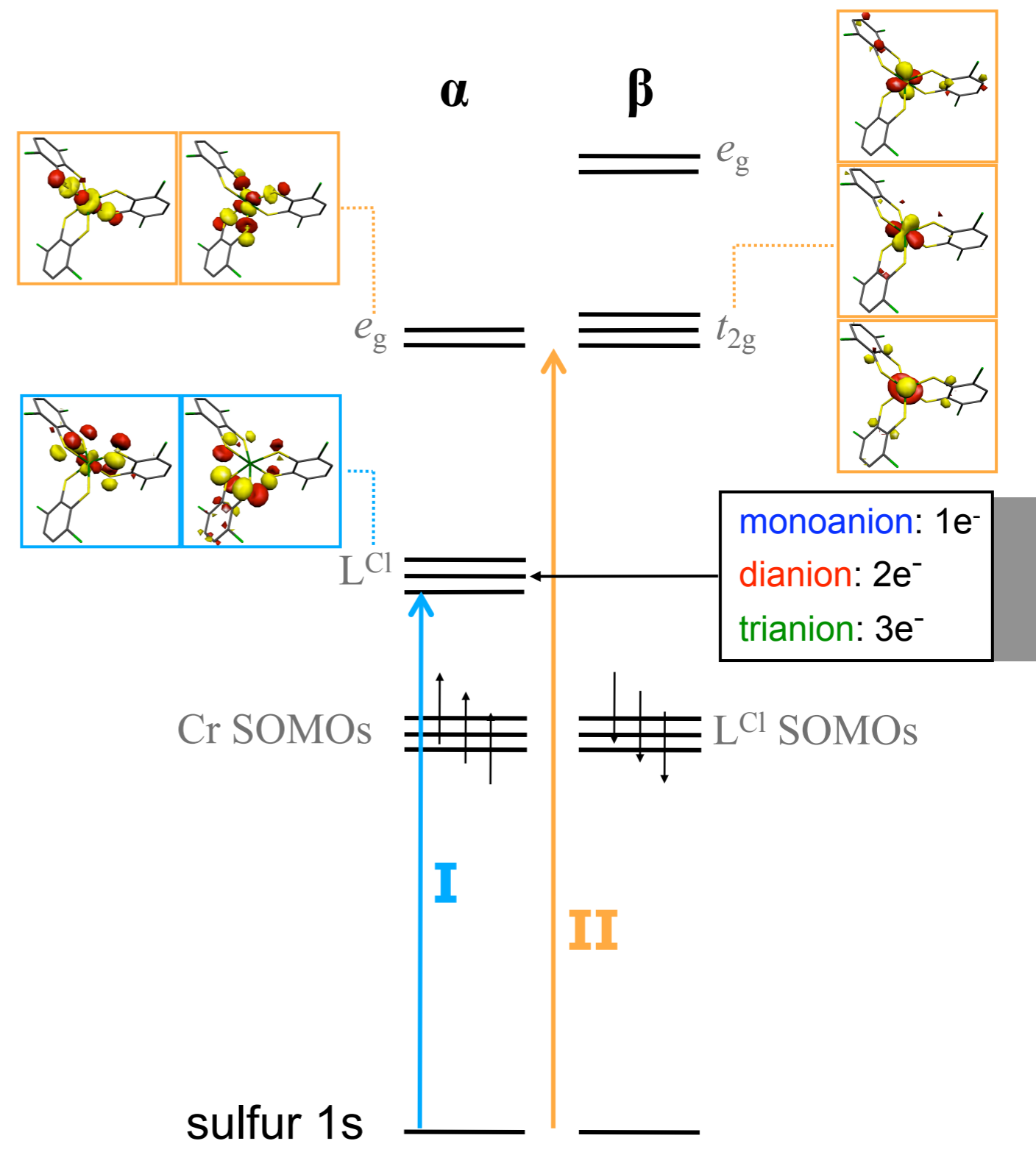
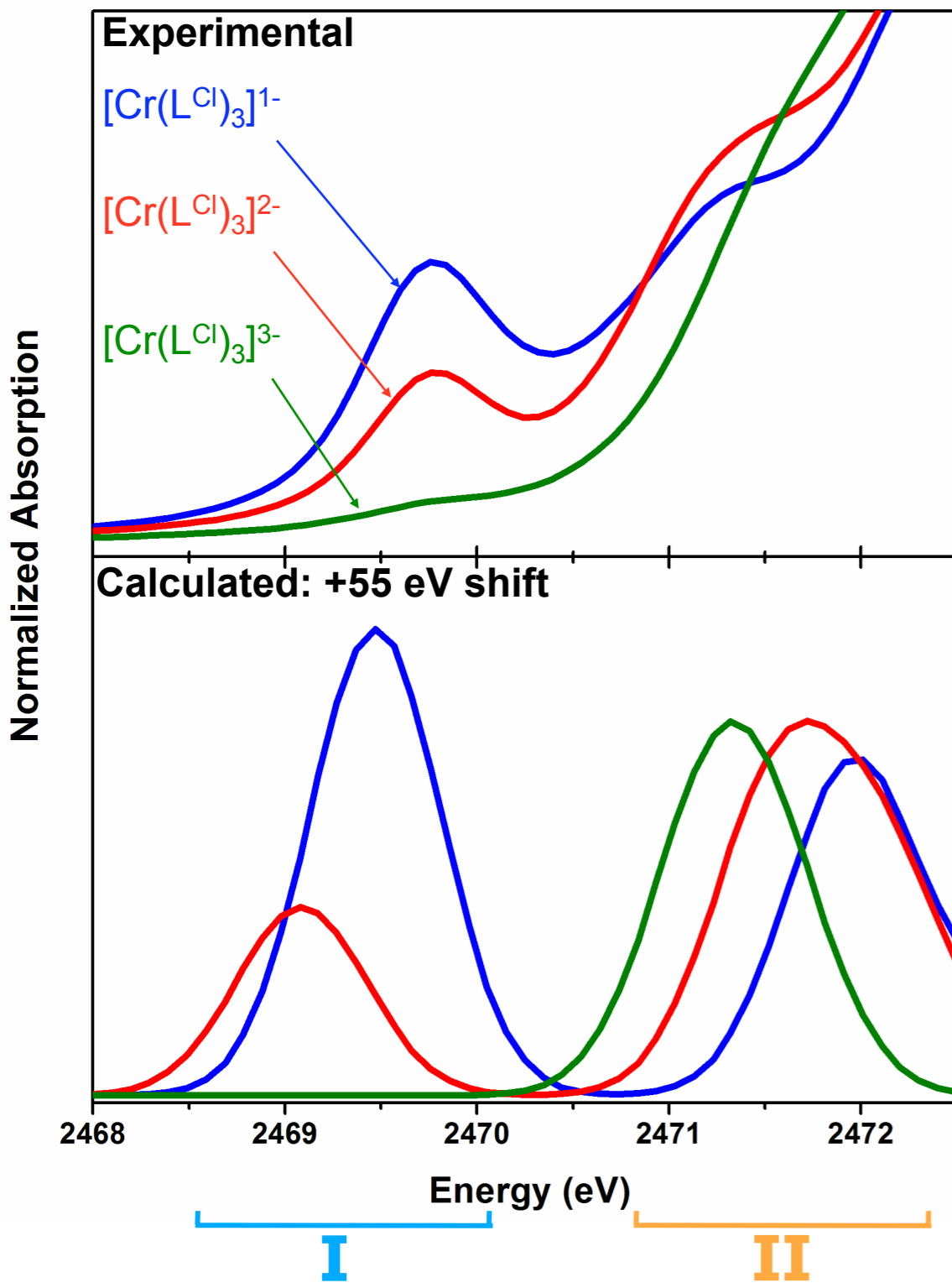


100% L

# Electronic Structure



# Time Dependent DFT

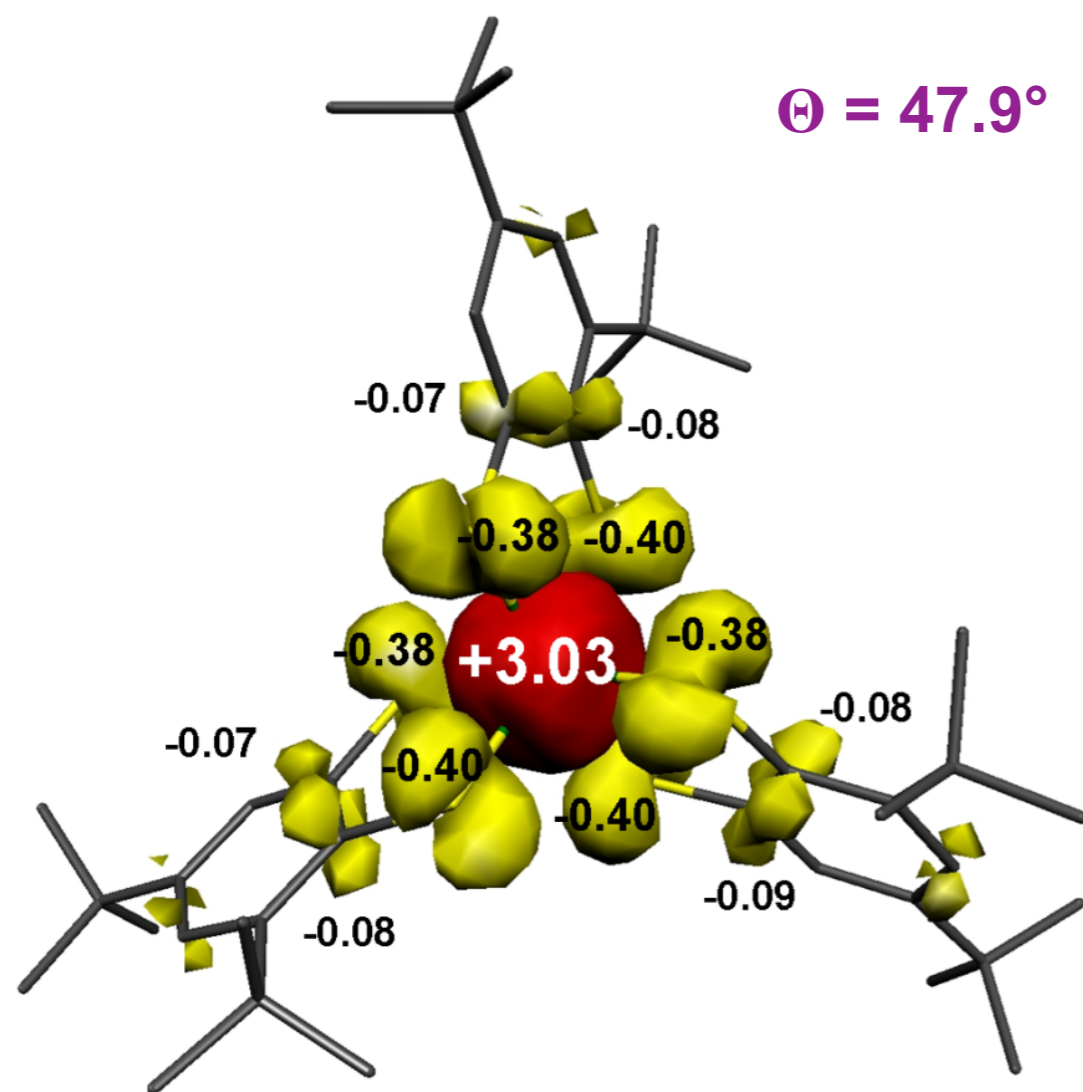


DeBeer George, Petrenko, Neese *Inorg. Chim. Acta* **2008**, 361, 965



# Neutral Complex

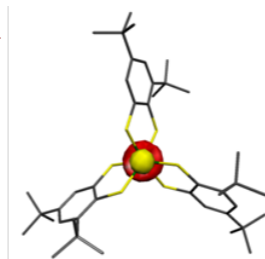
Broken symmetry DFT calculation of  $[\text{Cr}(\text{L}^{\text{Bu}})_3]$ ,  $S = 0$  – predicts octahedral geometry



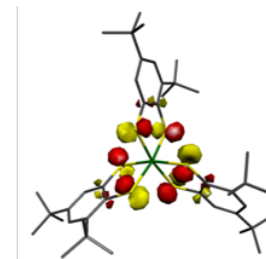
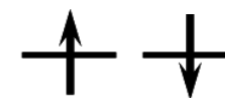
**BS(3,3)  $S = 0$**

**20 kcal mol<sup>-1</sup> lower than UKS**

**92% Cr**

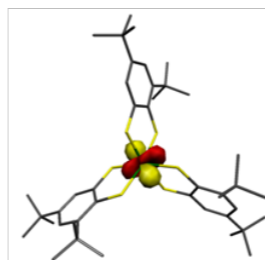


**$S = 0.009$**

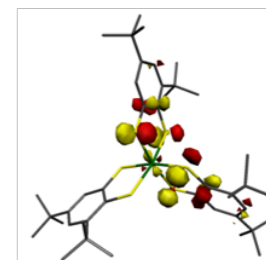
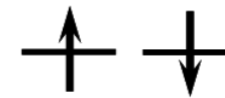


**100% L**

**85% Cr**

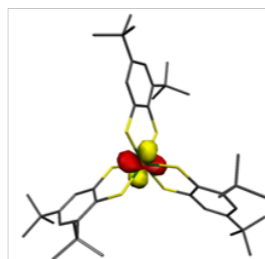


**$S = 0.56$**

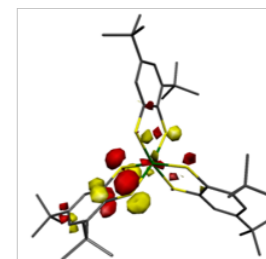
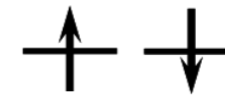


**91% L**

**85% Cr**

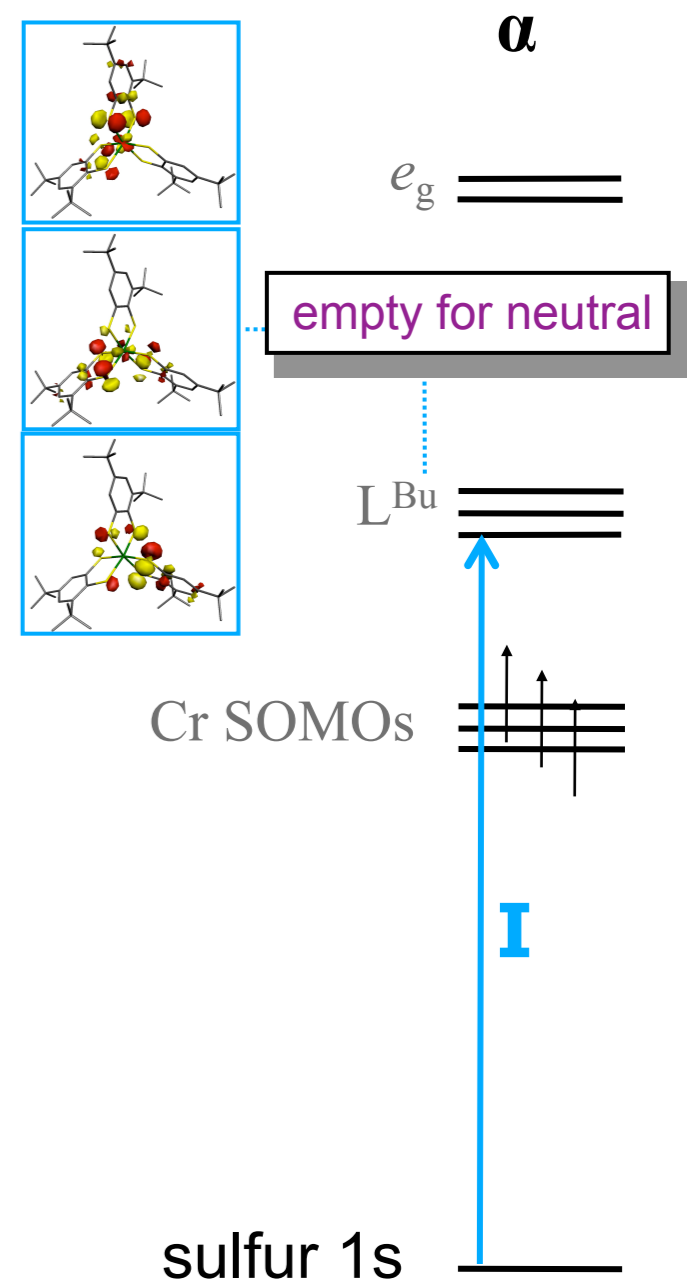
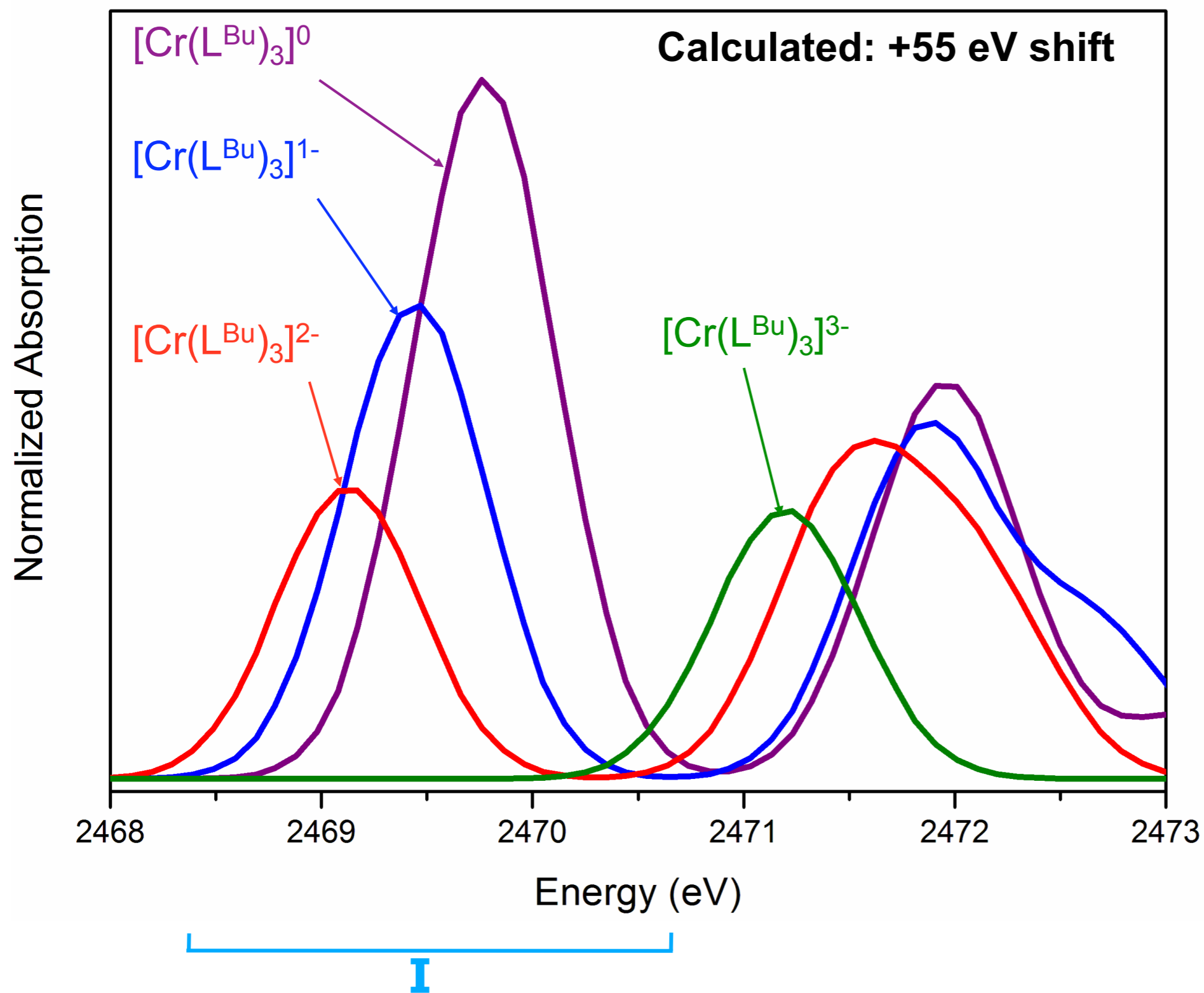


**$S = 0.56$**

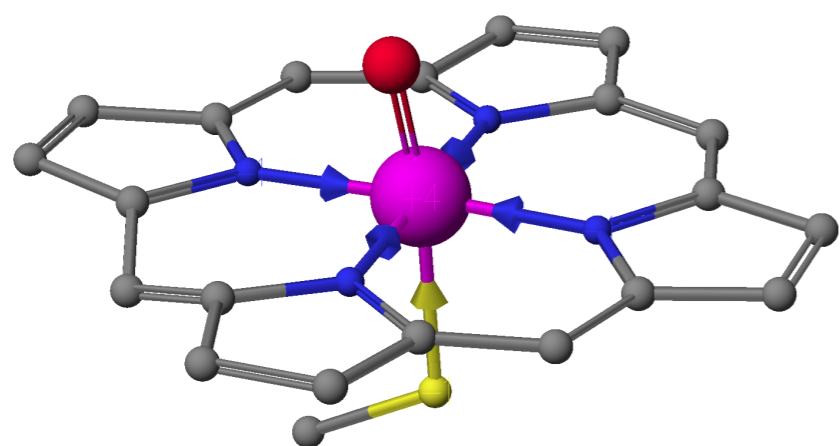


**91% L**

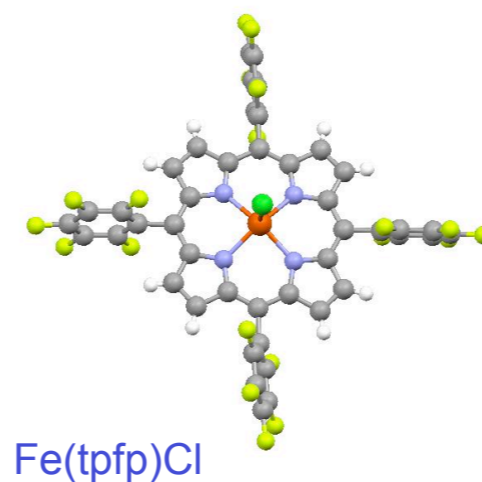
# Anticipated S K-edge



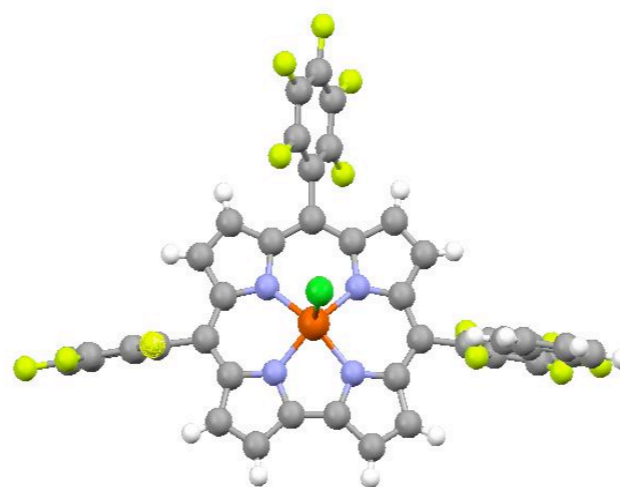
# From biological to chemical catalysis...



P450, CPO  
 $\text{RH} + \frac{1}{2}\text{O}_2 \rightarrow \text{ROH}$   
 $\text{Fe}^{\text{IV}}=\text{O}\text{P}^{\bullet+}$  (Compound I)  
 $\text{Fe}^{\text{IV}}-\text{O}/\text{OH}$  (Compound II)

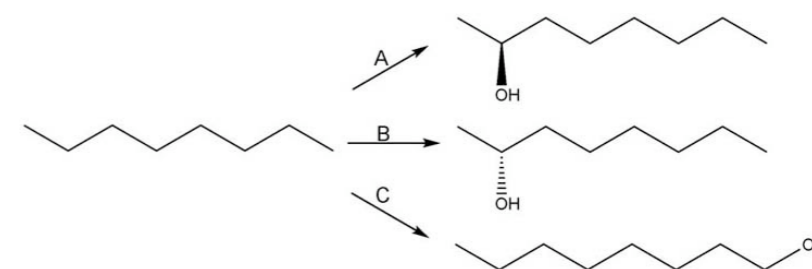


Fe(tpfp)Cl

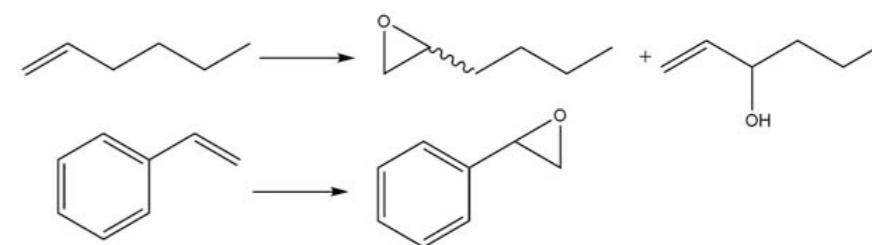


Fe(tpfc)Cl

Alkane hydroxylation:

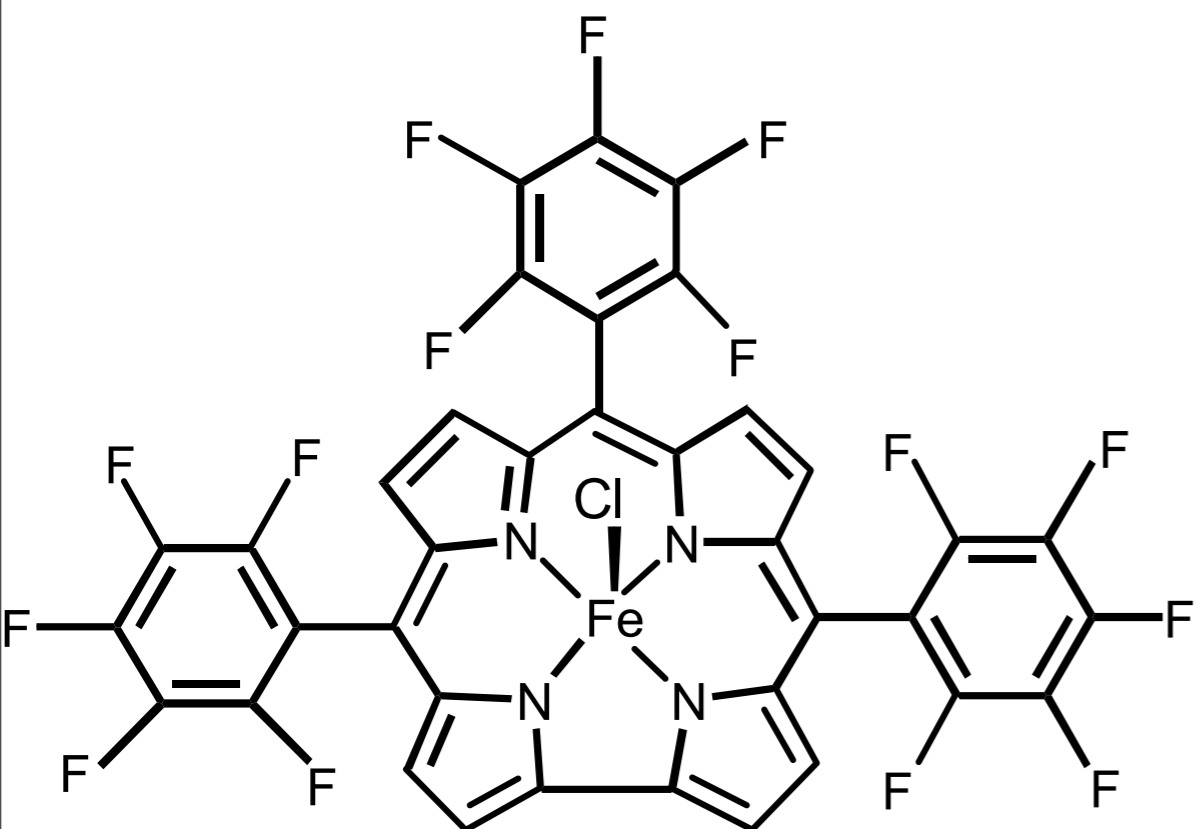


Alkene epoxidation:

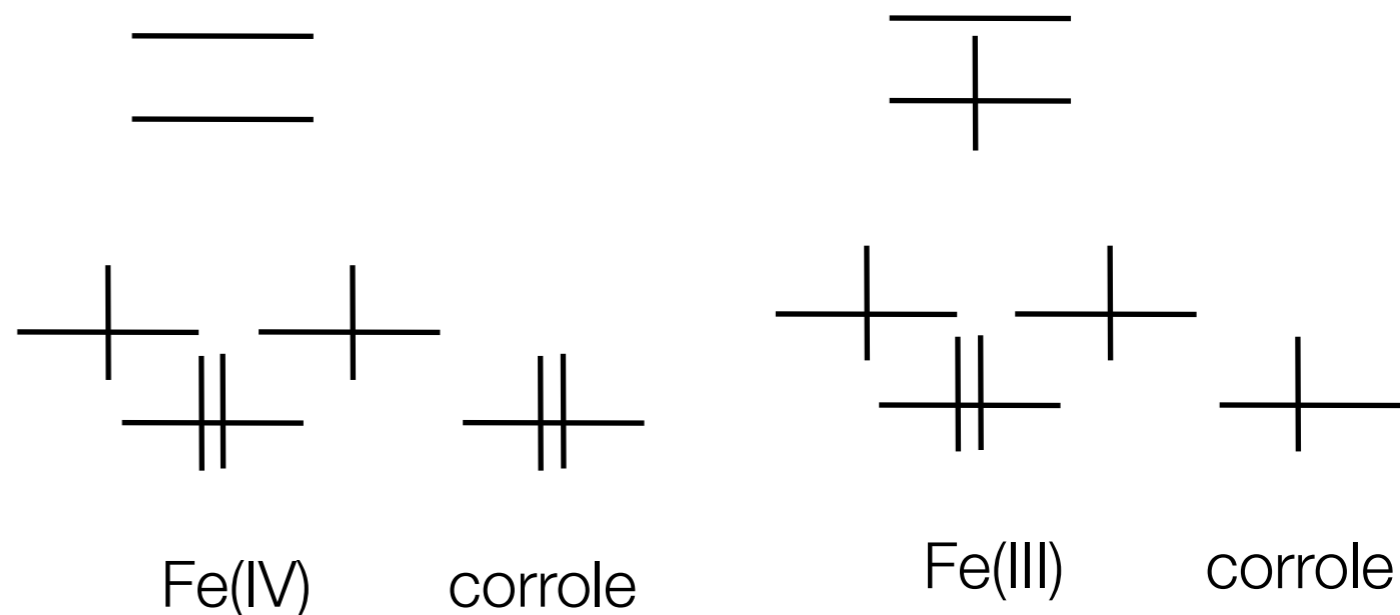


**High-valent species are invoked in catalytic mechanism**

# Corroles: Metal- or Ligand-based Oxidation?



Fe-N(cor) 1.88-1.92 Å  
 Fe-Cl 2.24 Å  
 Disp. from Fe-N4 plane 0.42 Å



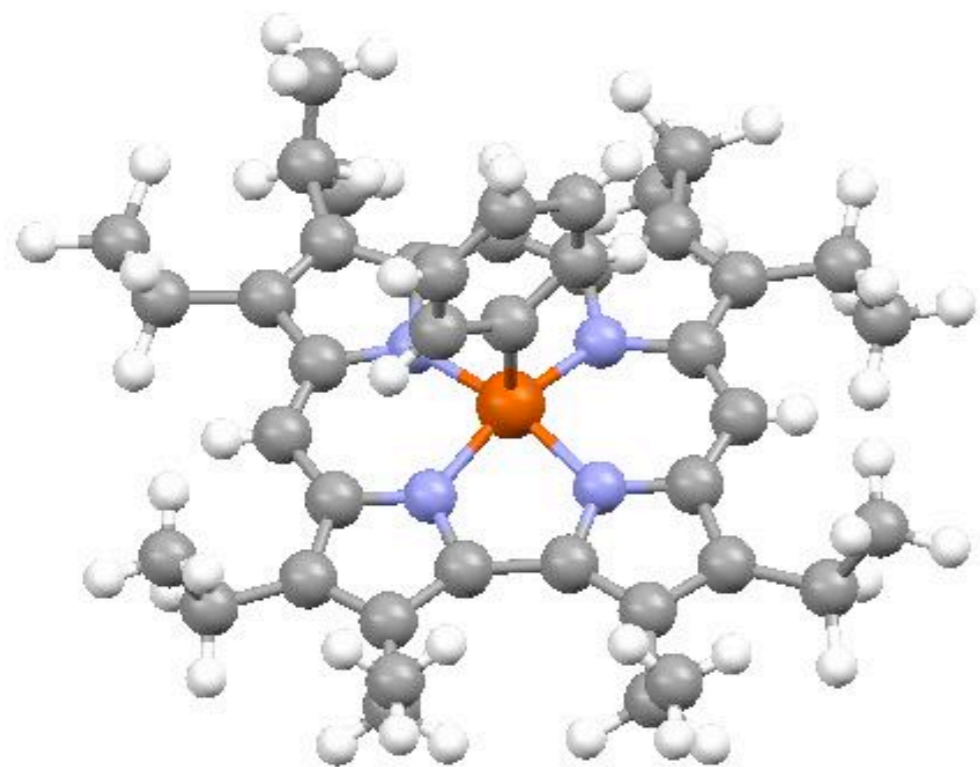
**S=1    OR    S=1= 3/2 Fe(III) – 1/2 cor•**

Mössbauer Fe(tpfc)Cl  
 $\delta = 0.19$  mm/s  
 $\Delta EQ = 2.93$  mm/s

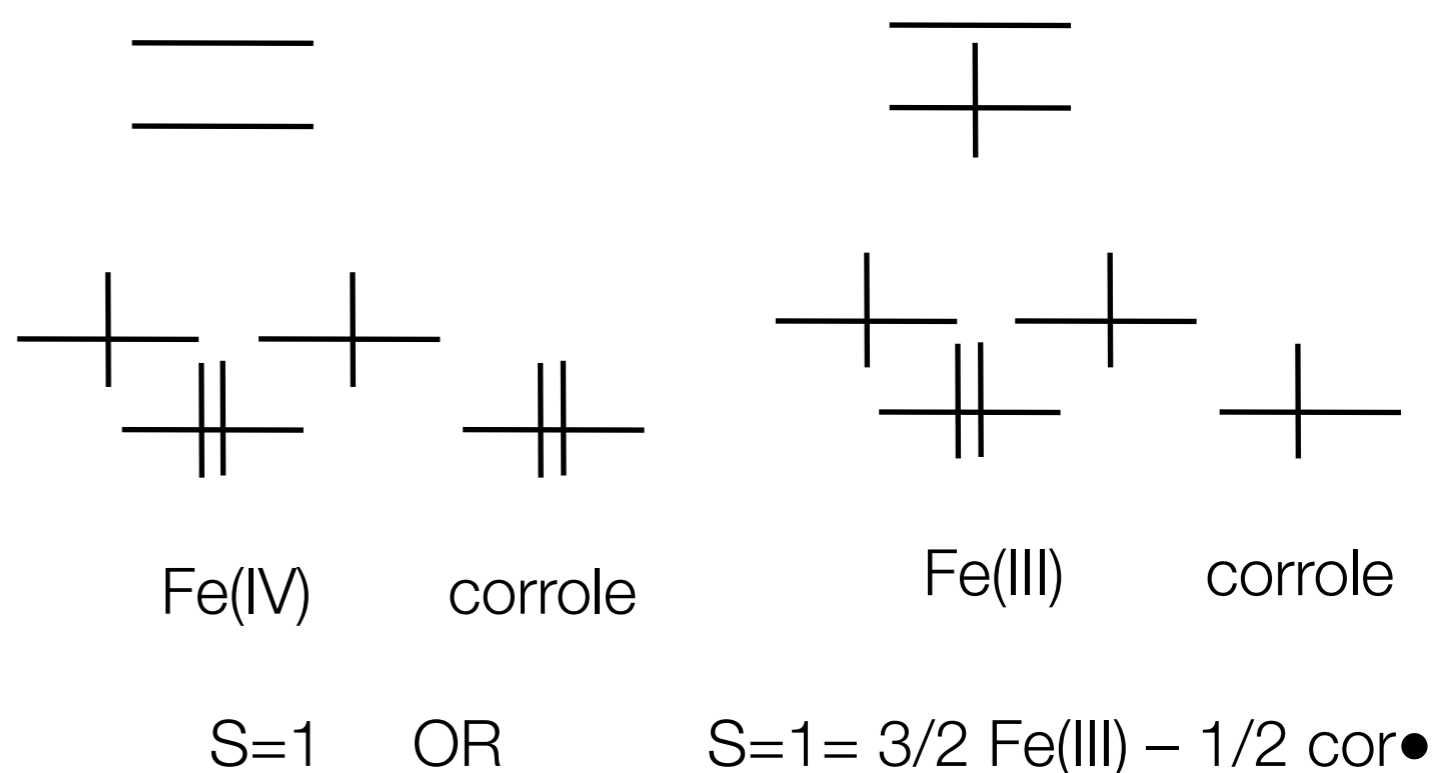
NMR – upshifted meso-H resonances suggesting large negative spin densities on carbons.

Zakharieva et al, JACS, 2002, 124, 6636.

# Corroles: Metal- or Ligand-based Oxidation?



Fe-N(cor) 1.88-1.92 Å  
 Fe-C(Ph) 1.98 Å  
 Disp. from Fe-N4 plane 0.27 Å



Mössbauer Fe(Et8C)Cl

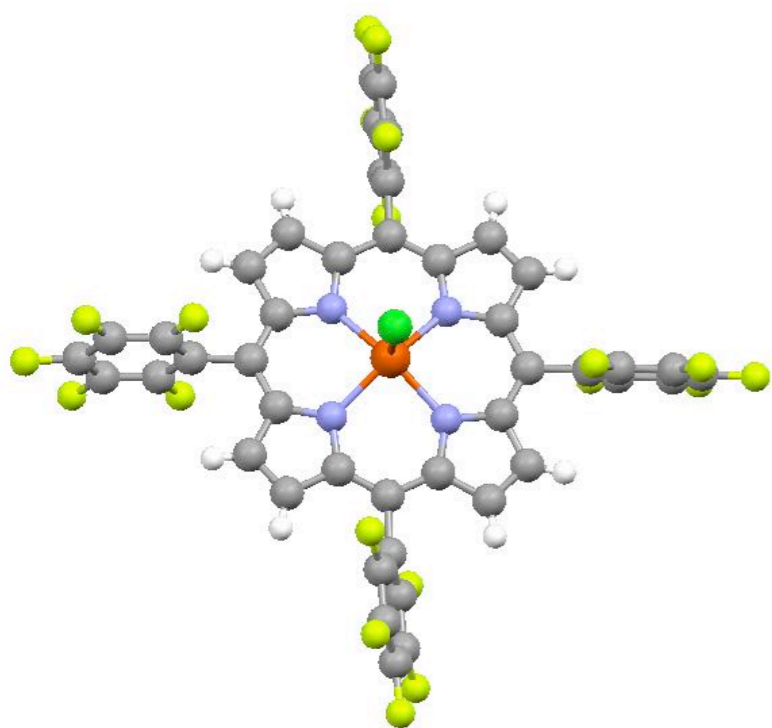
$\delta = -0.10 \text{ mm/s}$

$\Delta EQ = 2.99 \text{ mm/s}$

NMR – upshifted meso-H resonances (~1/4 of the Cl-Corr)

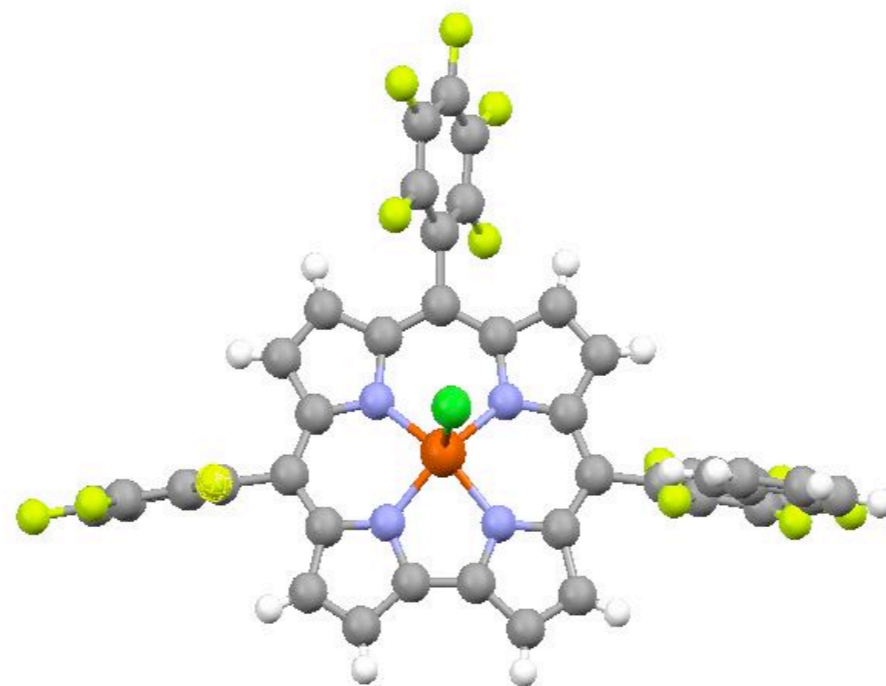
Zakharieva et al, JACS, 2002, 124, 6636.

# Porphyrin and Corrole Models



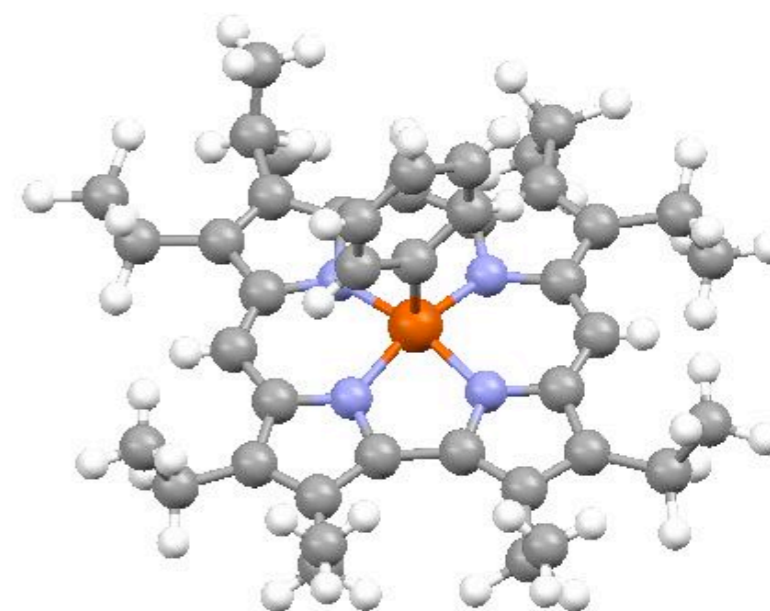
Fe(tpfp)Cl  
 $S=5/2$   
Fe(III)

Fe K-edge  
Cl K-edge  
N K-edge



Fe(tpfc)Cl  
 $S=1$   
Fe(IV) OR Fe(III)+cor\*

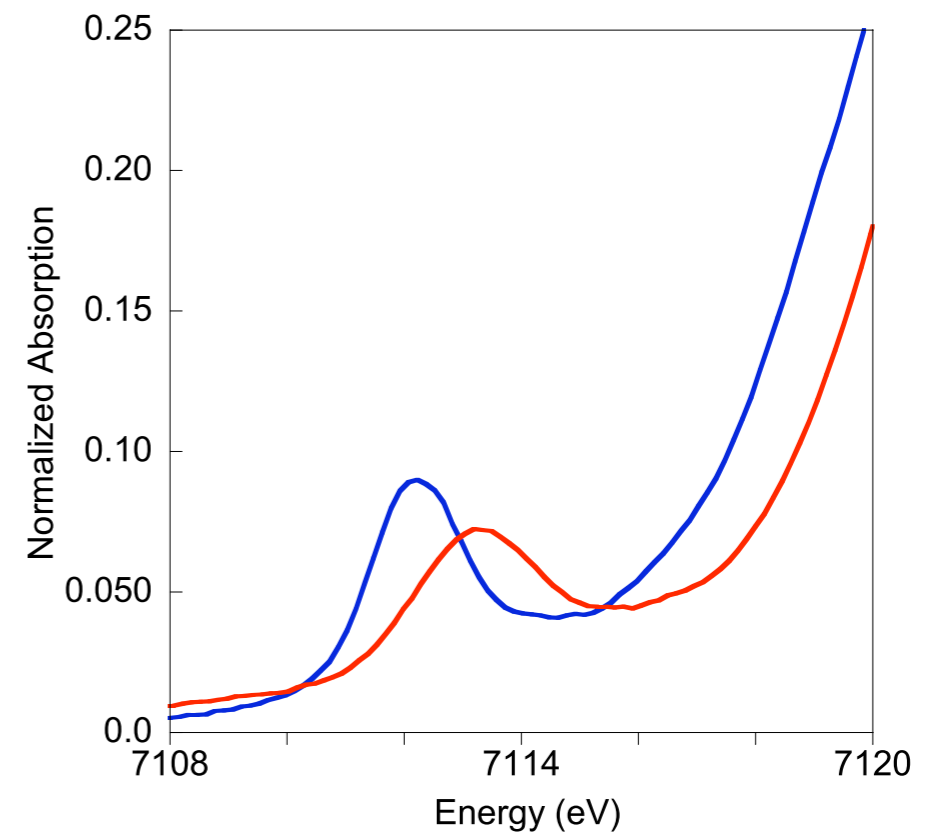
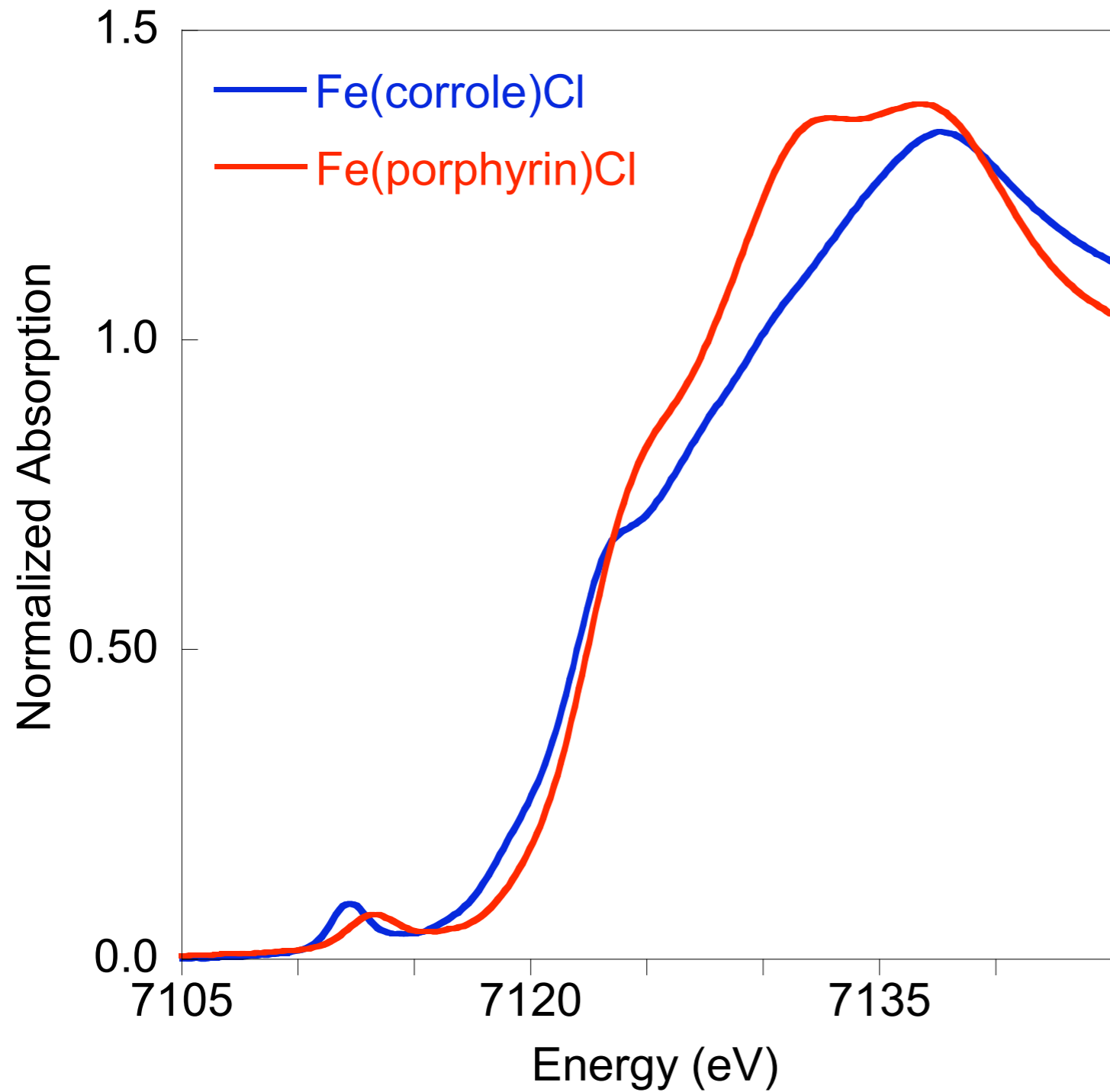
Fe K-edge  
Cl K-edge  
N K-edge



Fe(Et8-Cor)Ph  
 $S=1$   
Fe(IV)

Fe K-edge  
N K-edge

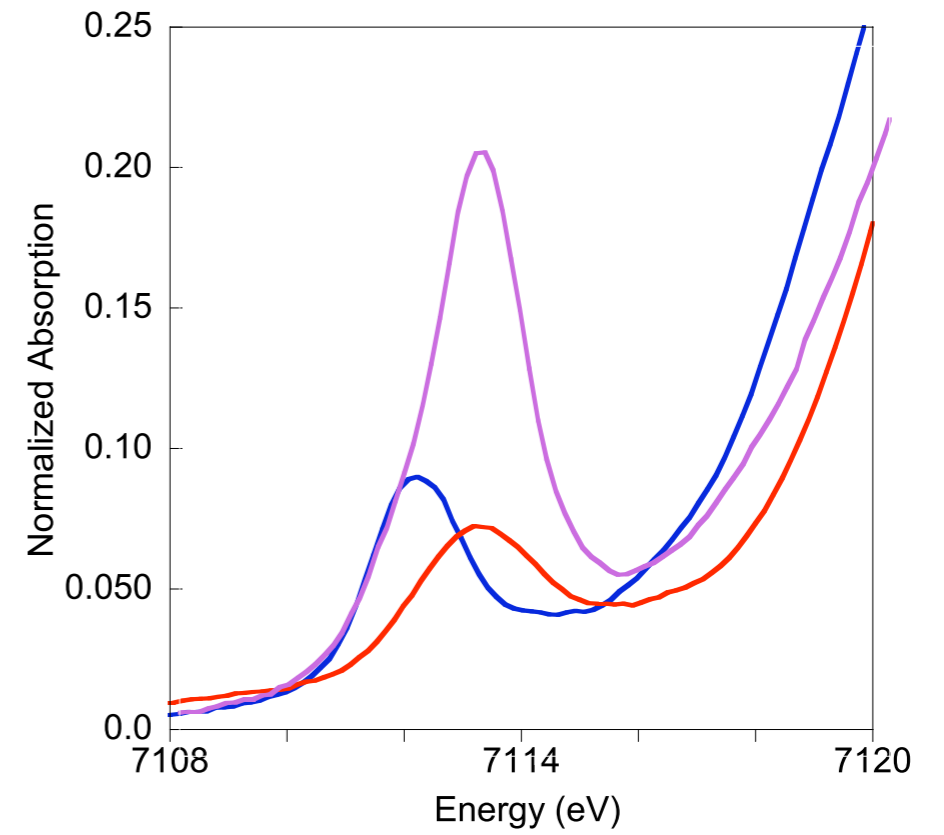
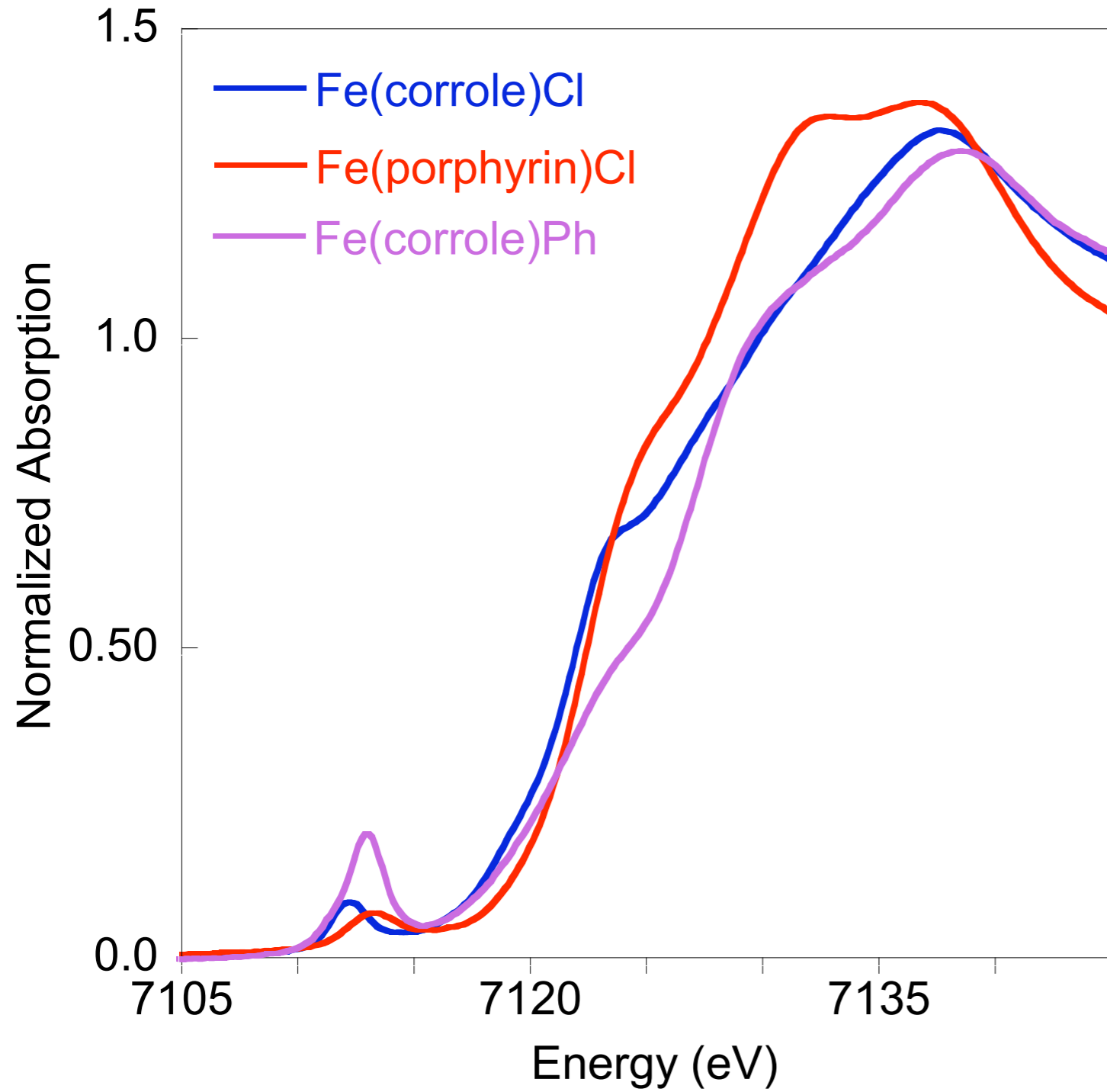
# Fe K-edge XAS



Pre-edge ~1 eV lower in Fe(corrole) Cl vs. heme (dominantly 4pz mixing)

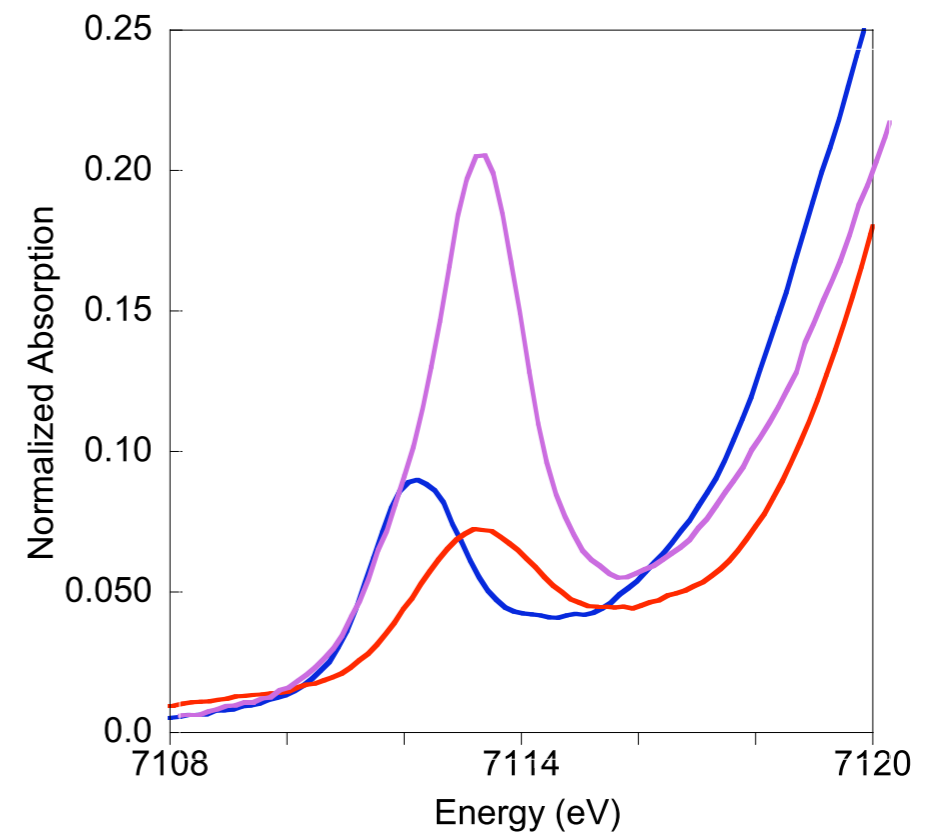
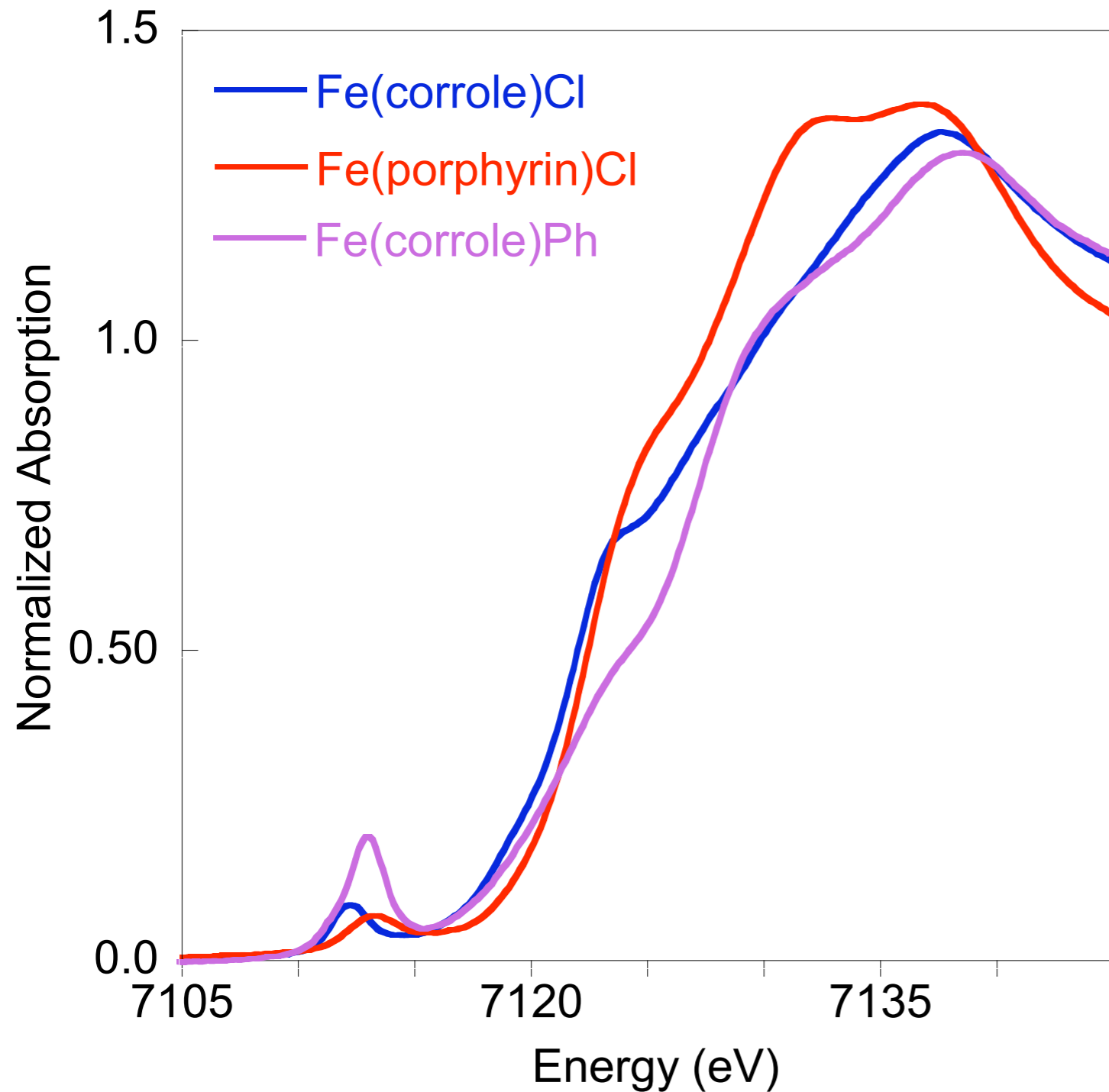
Consistent with weaker axial ligand

# Fe K-edge XAS



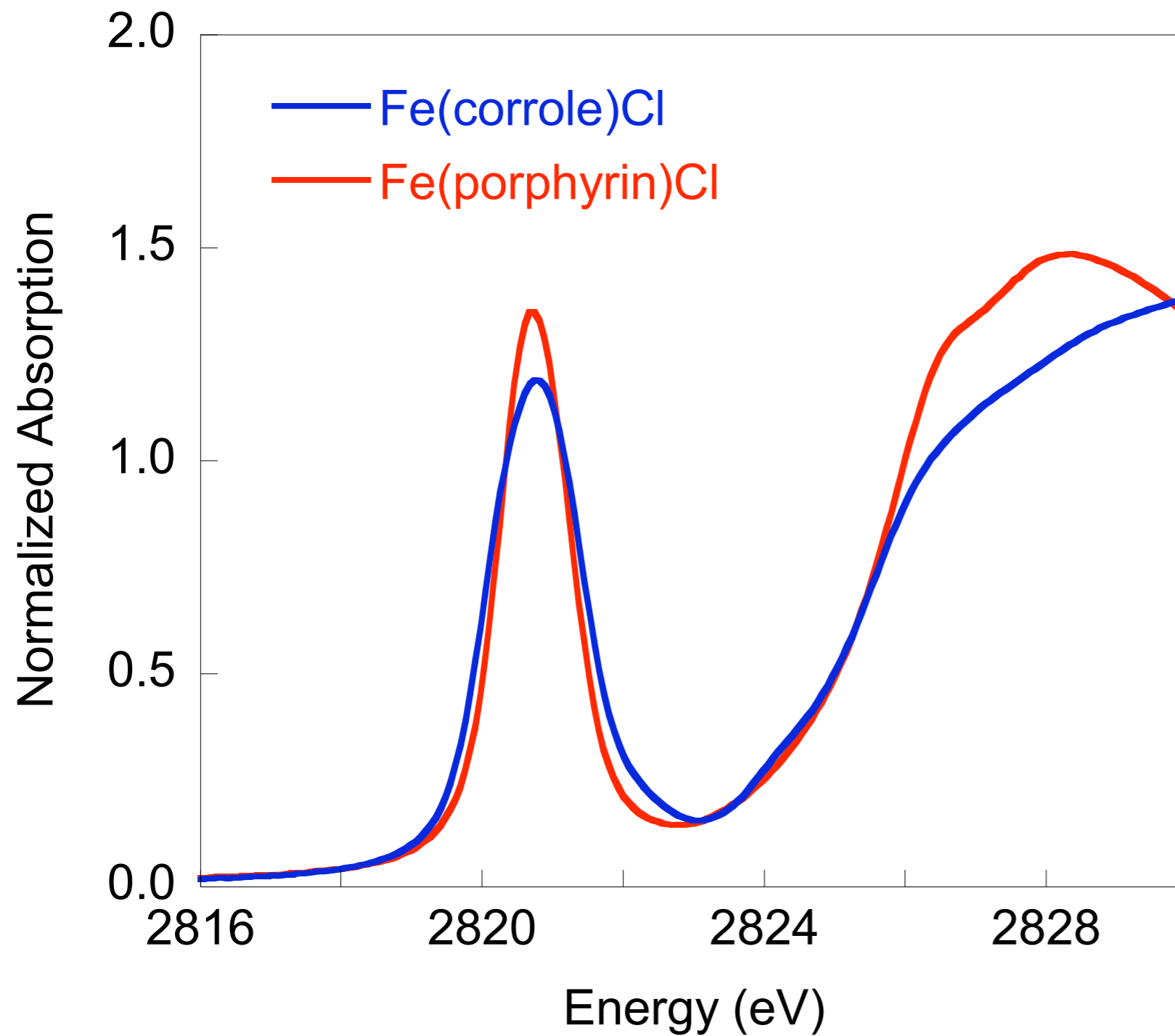


# Fe K-edge XAS



Fe(corrole)Ph rising edge and pre-edge to highest energy  
Pre-edge increased in intensity, despite (less distortion)  
Mediated by shorter Fe-C bond and a second  $d_z^2$  hole?

# Cl K-edge XAS



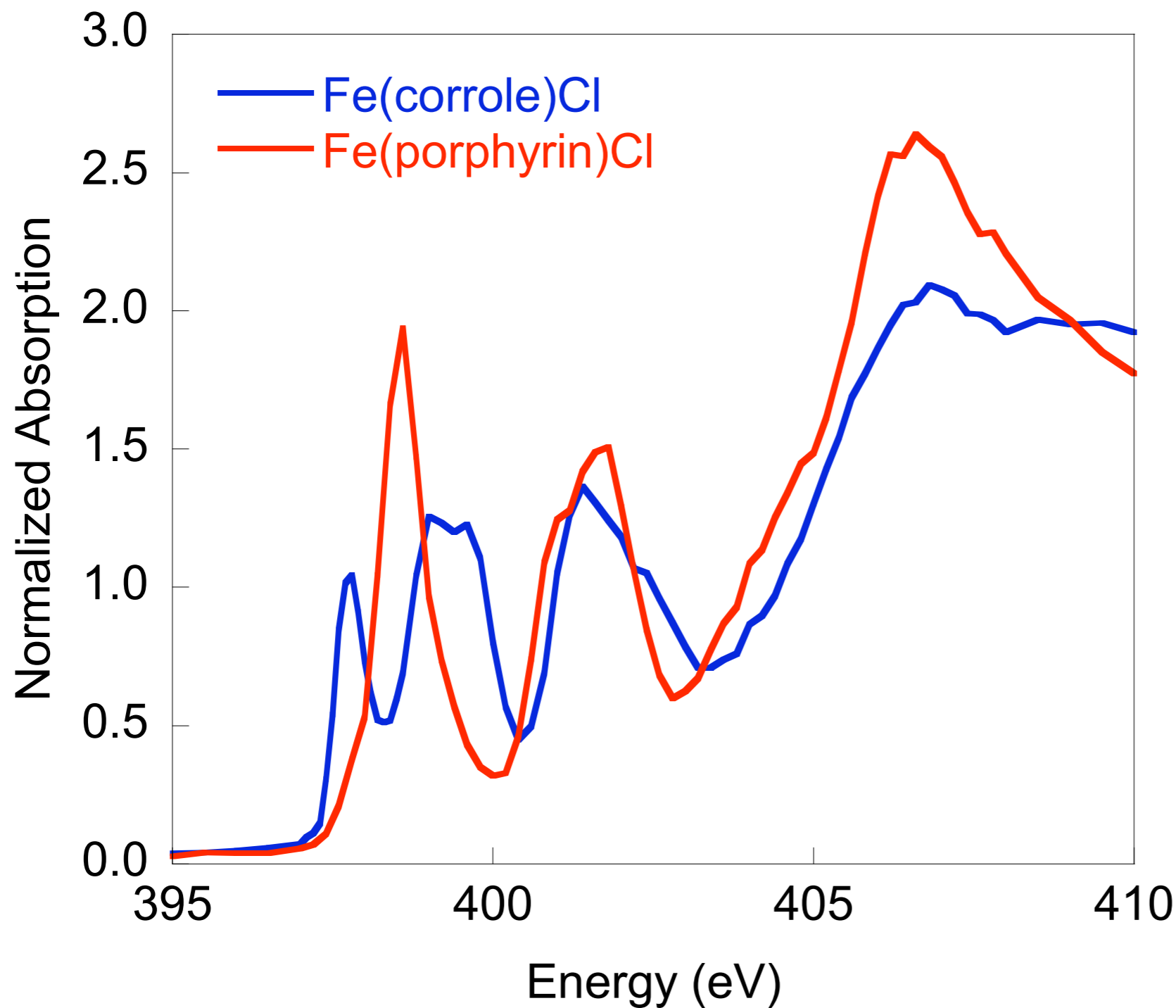
Similar Fe-Cl covalency  
(Cl contributes to  $d_{xz}$ ,  $d_{yz}$ ,  $d_{z^2}$ )

Similar effective charge on Cl

Similar d-manifold energy

Supports an  $S=3/2$  Fe(III)  
assignment for the Fe(corrole)Cl

# N K-edge XAS

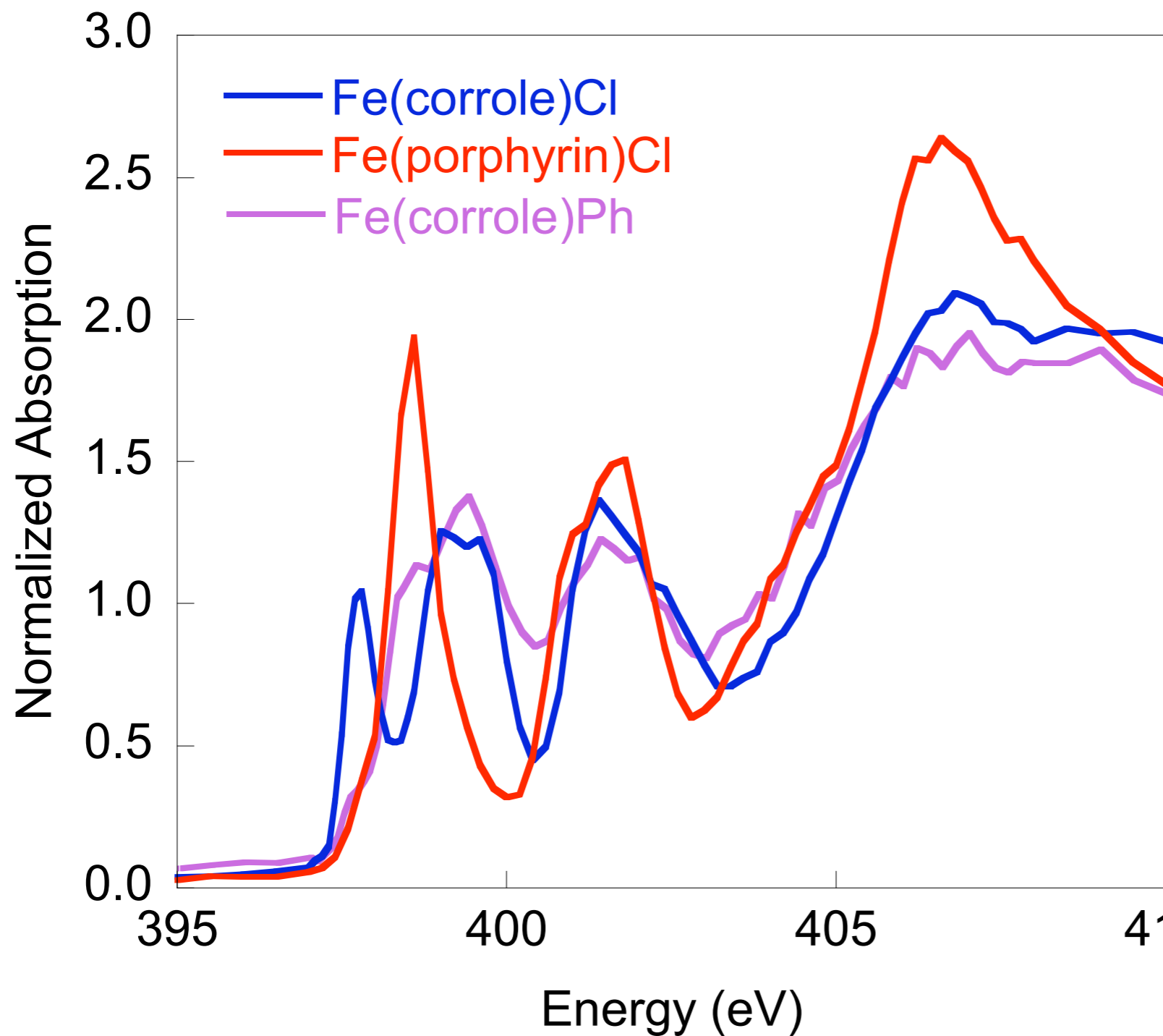


N K-edge suggests a more oxidized ligand in Fe(corrole)Cl

Low energy pre-edge feature present only in Fe(corrole)Cl

Suggests a corrole  $\pi^*$  radical in Fe(corrole)Cl

# N K-edge XAS



N K-edge suggests a more oxidized ligand in Fe(corrole)Cl

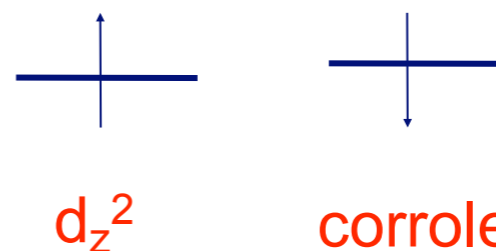
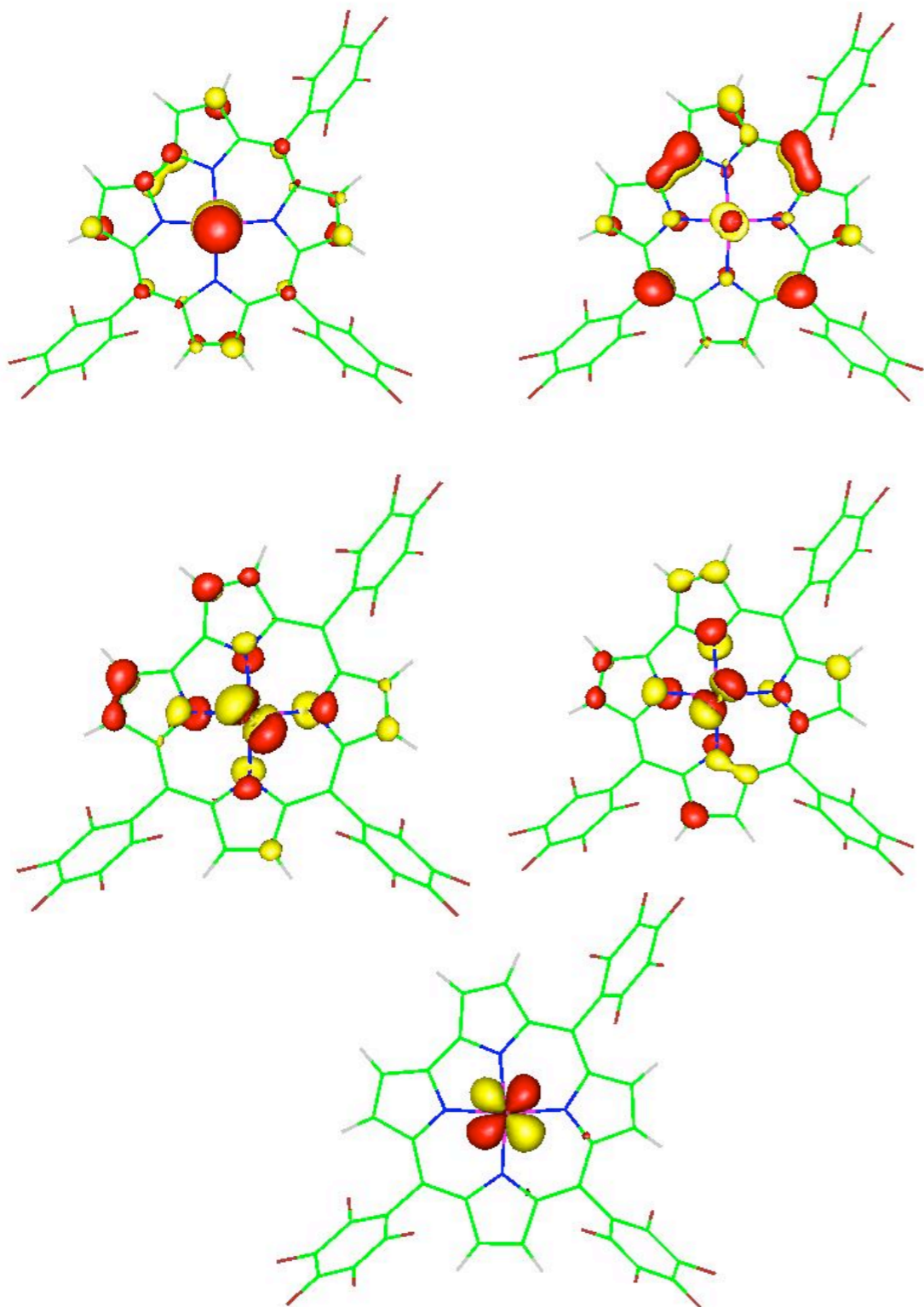
Low energy pre-edge feature present only in Fe(corrole)Cl

Suggests a corrole  $\pi^*$  radical in Fe(corrole)Cl

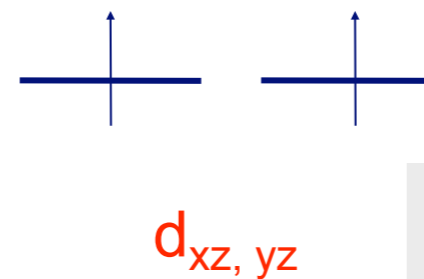
Low energy pre-edge feature is absent in Fe(corrole)Ph

Ph(Corrole) edge indicates a more reduced ligand

# Ground State DFT – Fe(corrole)Cl

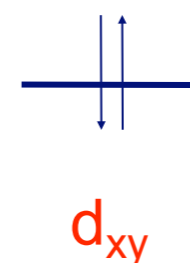


**spin coupled pair-  
Interaction between Fe- $d_z^2$  and  
corrole  $\pi$ -orbital**

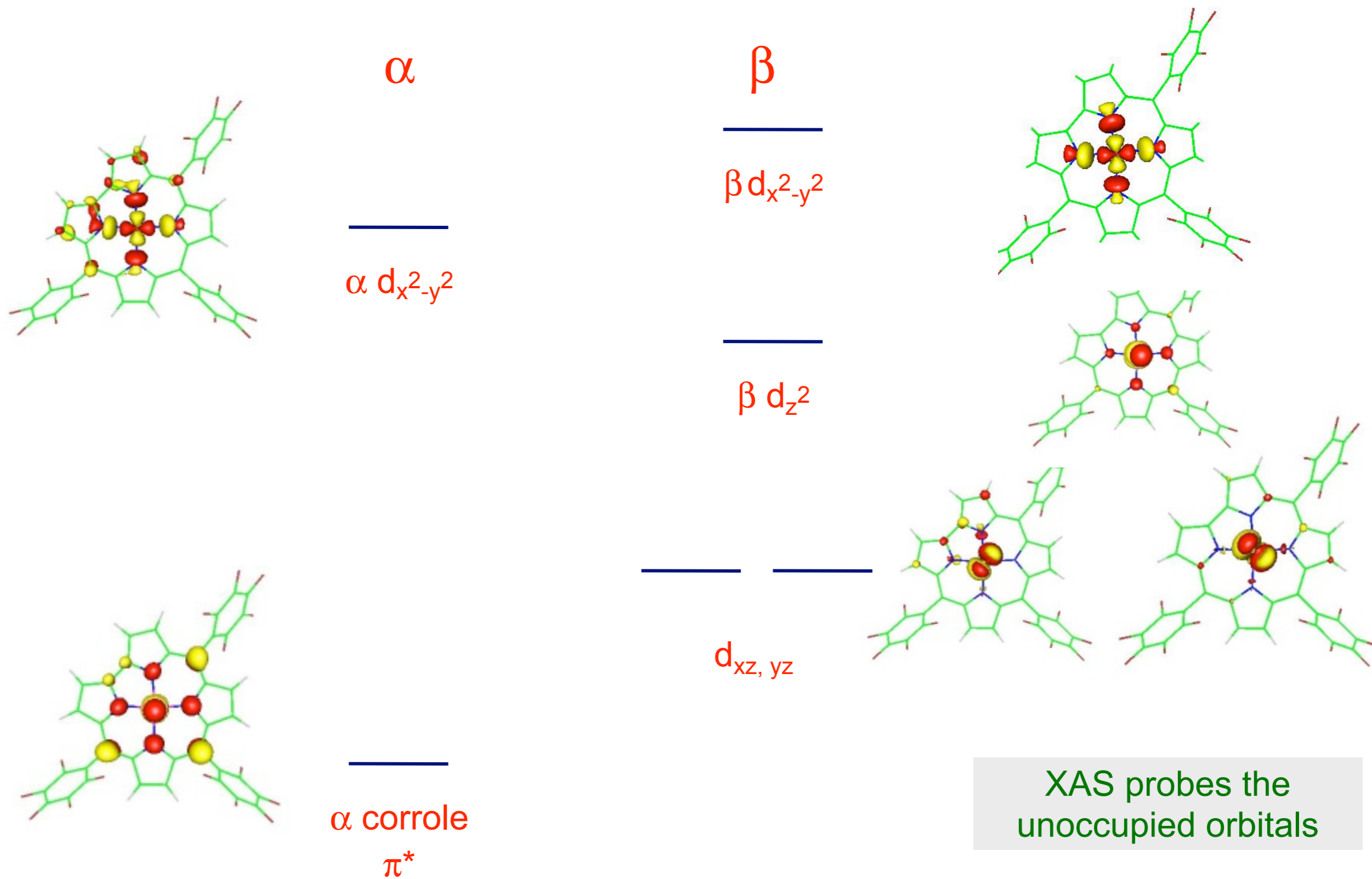


**Fe(III)  $S=3/2$  + Corr  
radical**

Consistent w/ previous  
DFT studies (Ghosh,  
Walker/Trautwein, and  
Neese)

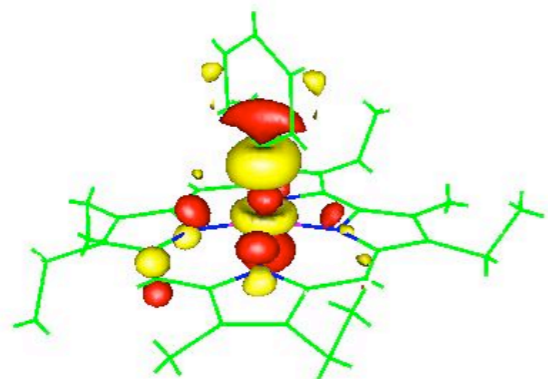


# DFT: Fe(corrole)Cl – Unoccupied Orbitals



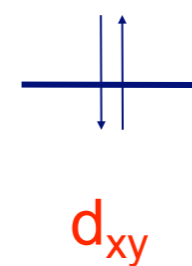
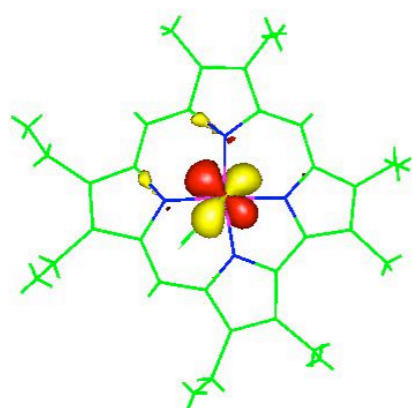
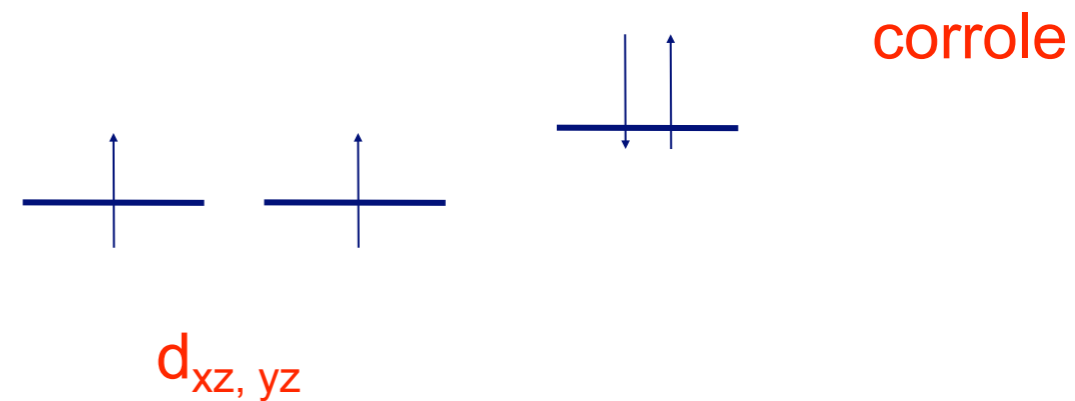
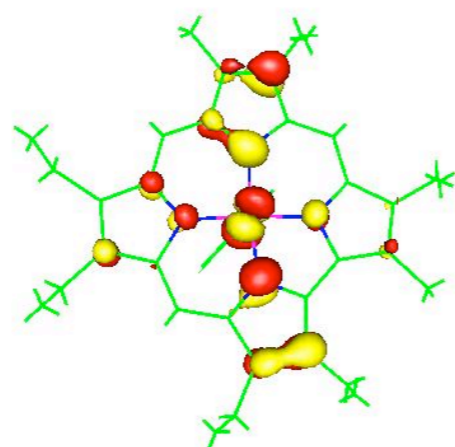
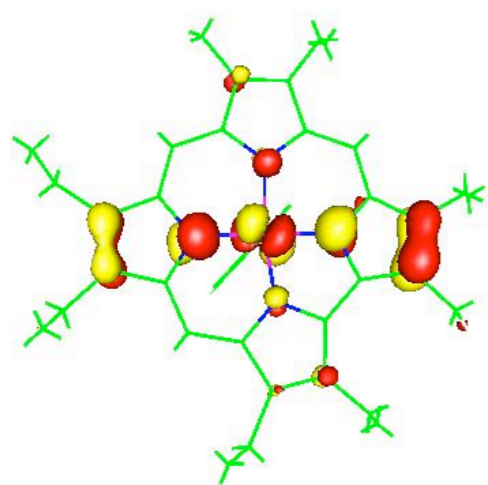
XAS probes the unoccupied orbitals

# Ground State DFT – Fe(corrole)Ph



—  $d_{z^2}$

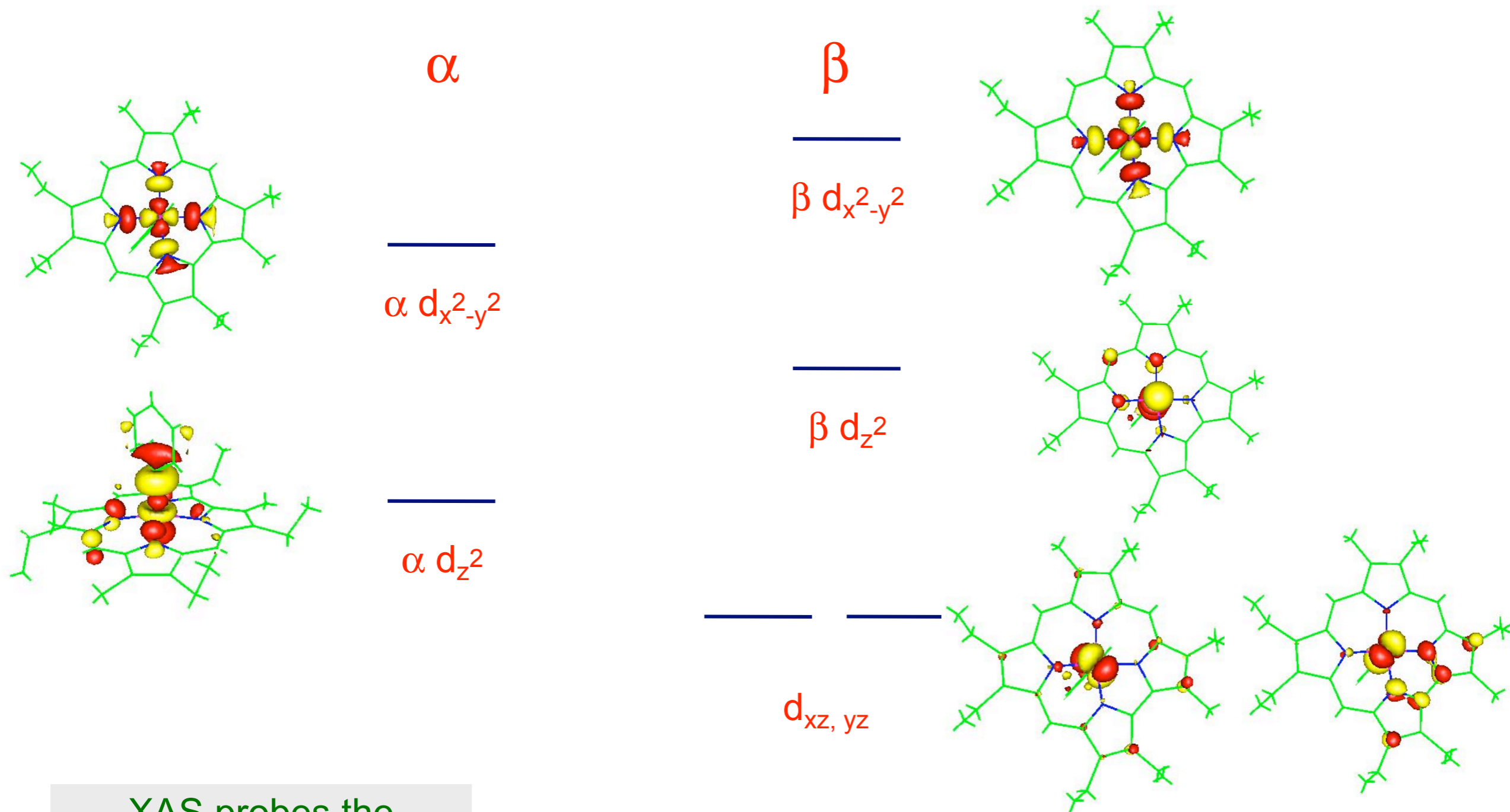
**No Broken Symmetry Solution**



**Fe(IV) S=1**

Consistent w/ previous DFT studies (Walker/ Trautwein,)

# DFT: Fe(corrole)Ph – Unoccupied Orbitals

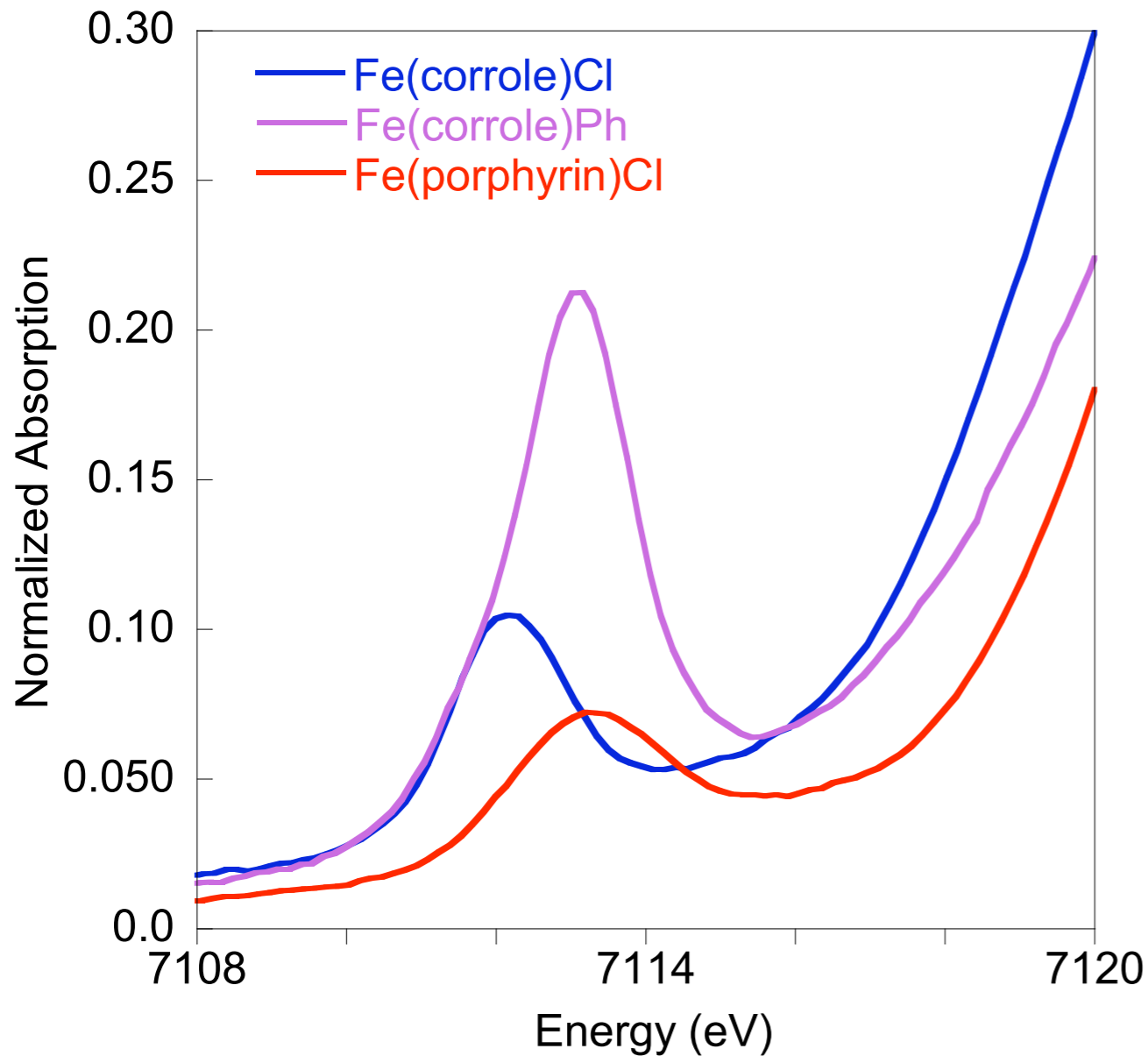


XAS probes the unoccupied orbitals

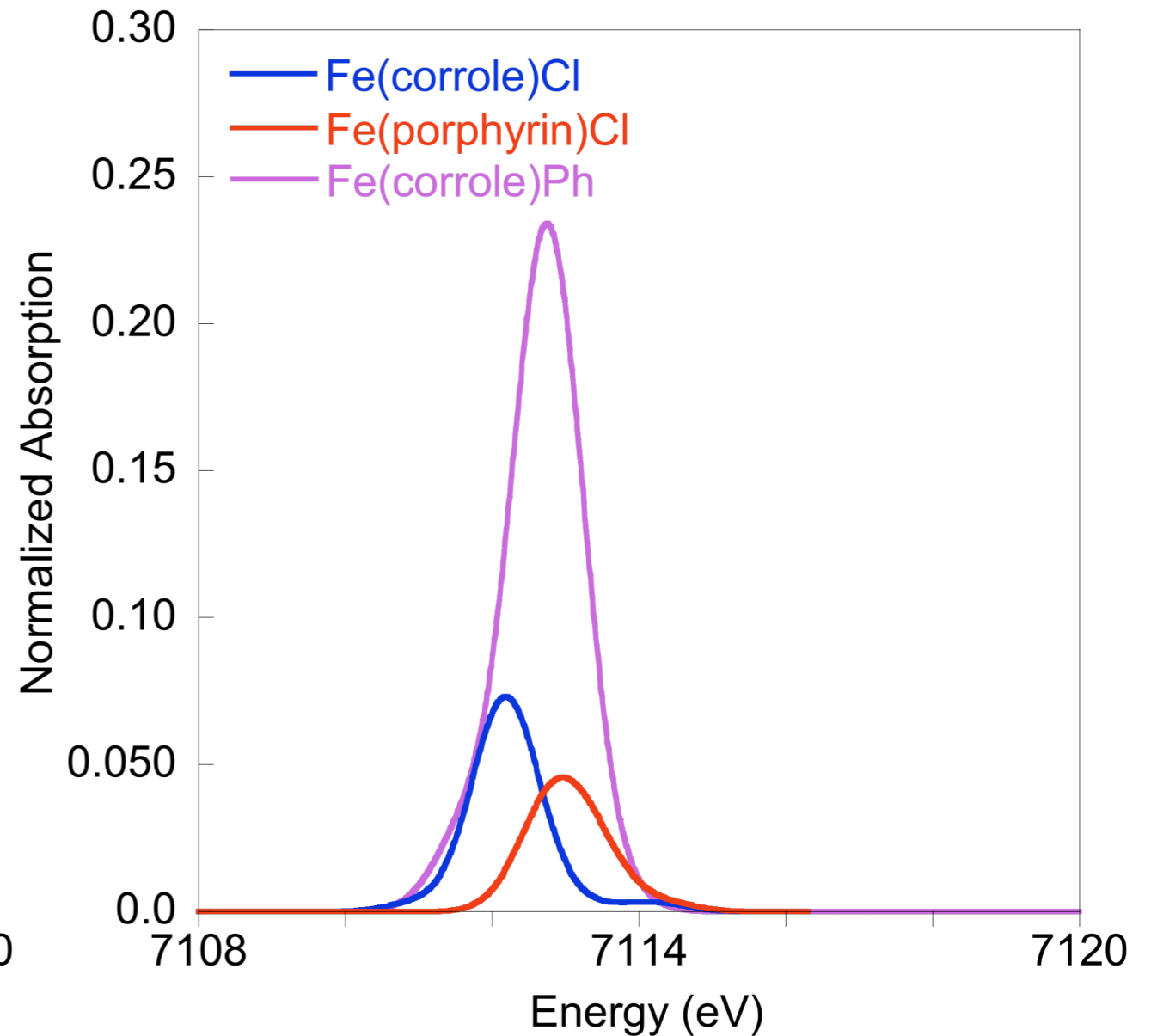


# TD-DFT: Fe K-edges

experiment



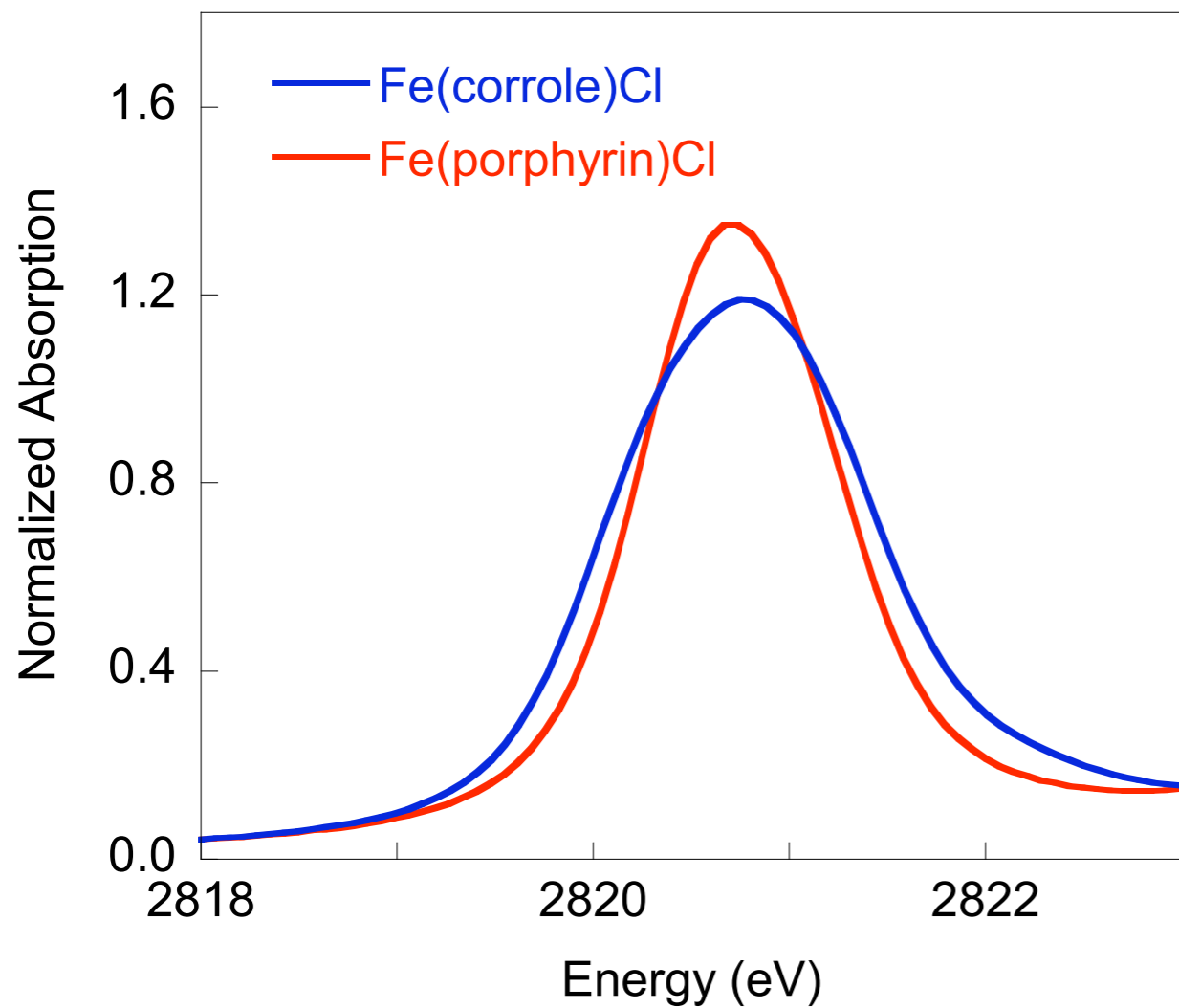
theory



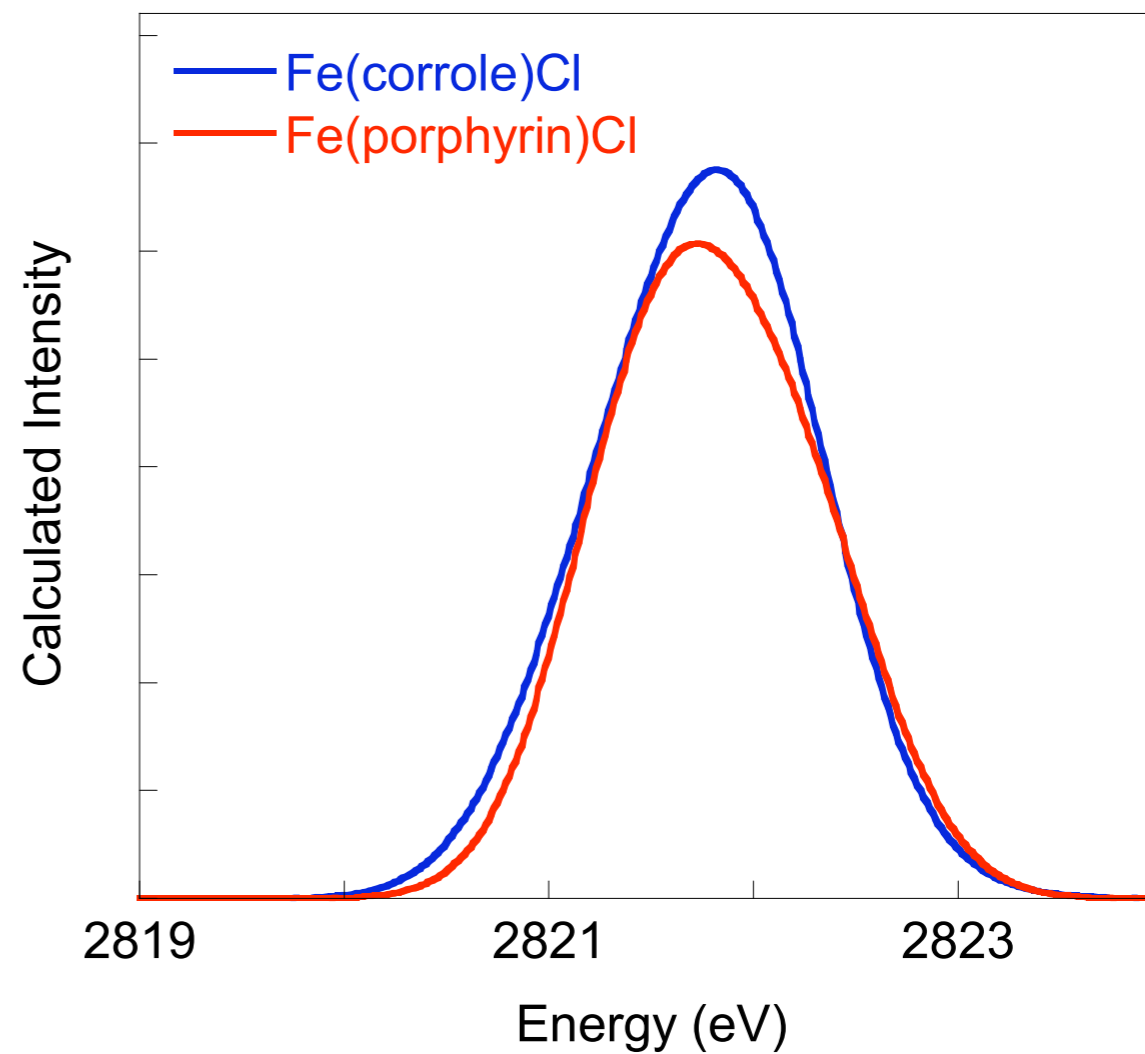
Fe K-edge energies and intensities are well-reproduced

# TD-DFT: Cl K-edges

experiment



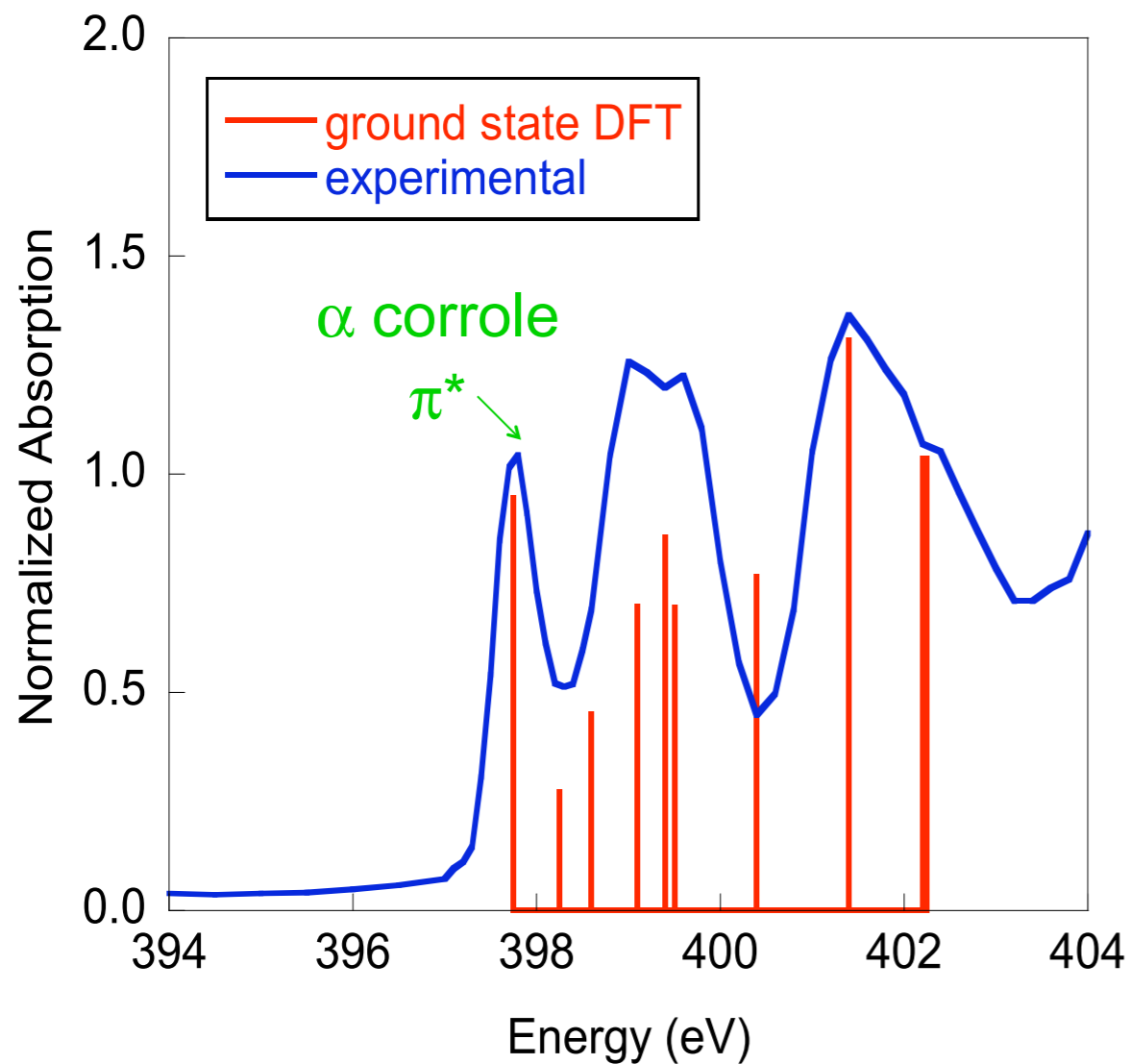
theory



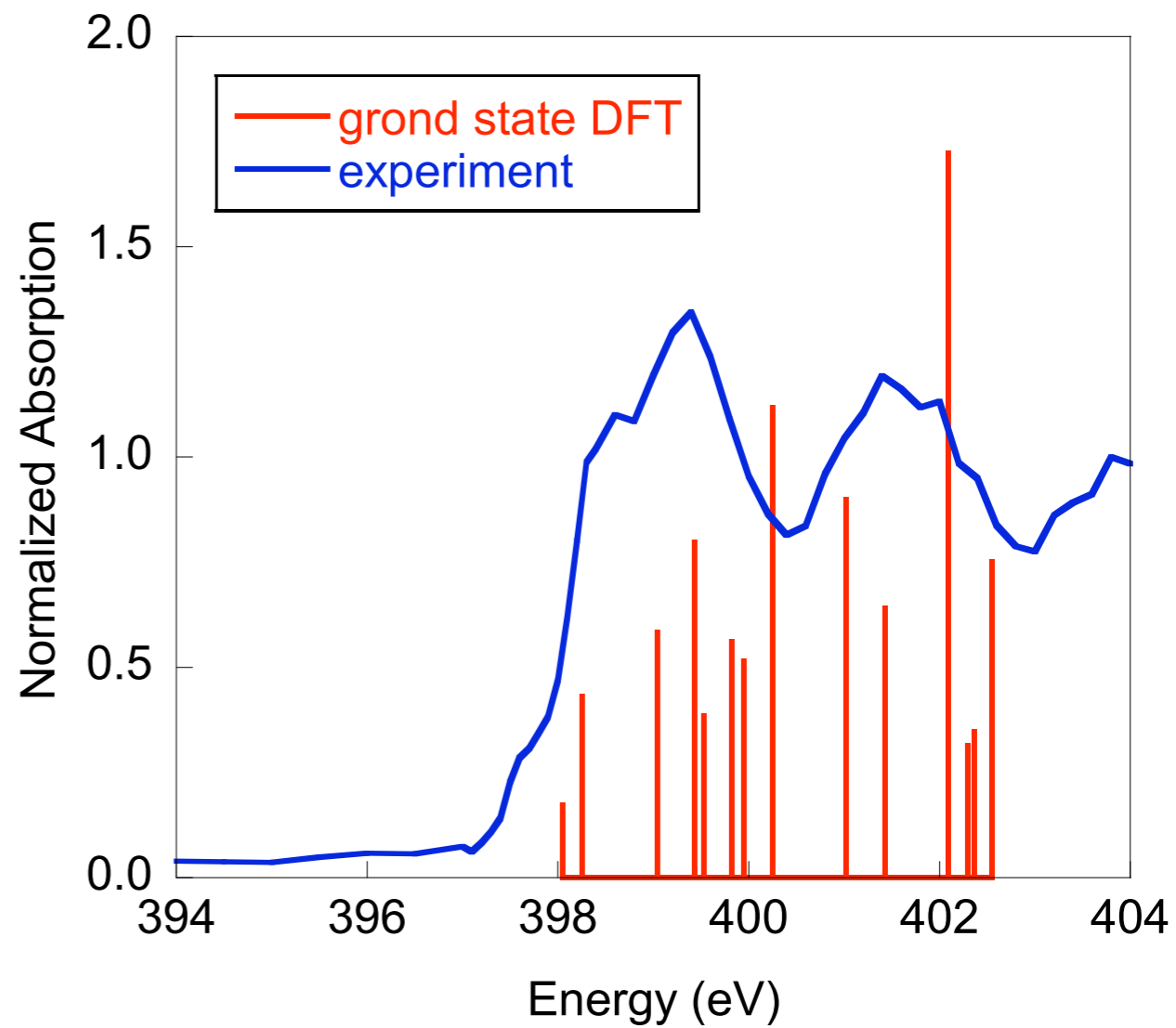
Cl K-edge energies and intensities are well-reproduced

# DFT: N K-edges

## Fe(corrole)Cl



## Fe(corrole)Ph



Ground-state DFT N 2p character show reasonable agreement

# Summary

---

- ✓ Pre-edges of ligand and metal edges are accessible using a relatively simple TDDFT approach
- ✓ Ligand and metal K-edge applications to dithiolenes have helped resolve electronic structure controversies
- ✓ Similar applications to corroles have been demonstrated

# Acknowledgments

## Group Members

**Martha Beckwith**  
**P. Chandrasekaran**  
**Nicole Lee**  
**Jennie Lin**  
**Christopher Pollock**  
**Chantal Stieber**

## Collaborators

**Frank Neese (Bonn)**  
**Taras Petrenko (Bonn)**  
**Karl Wieghardt (MPI)**  
**Stephen Sproules (MPI)**  
**Ed Solomon (Stanford)**  
**Ann Walker (Arizona)**  
**Uwe Bergmann (Stanford)**  
**Ken Finkelstein (Cornell)**

**\$ Cornell University**

**\$ ACS PRF**

**Beam time: SSRL, CHESS**