

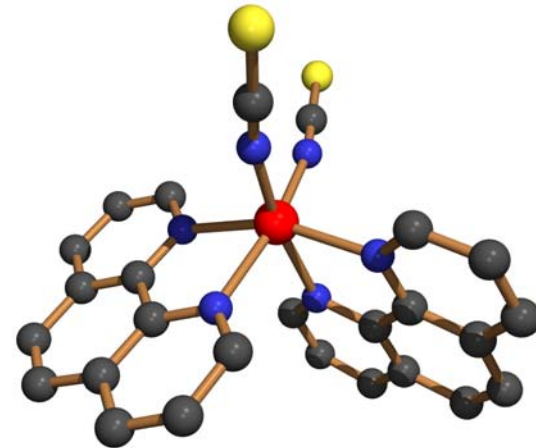
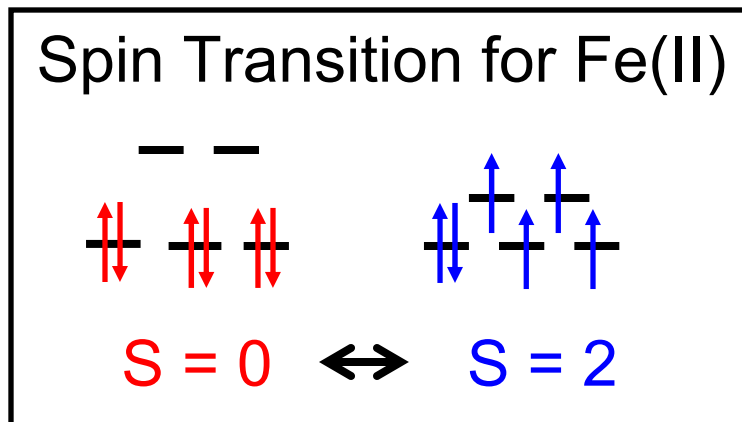
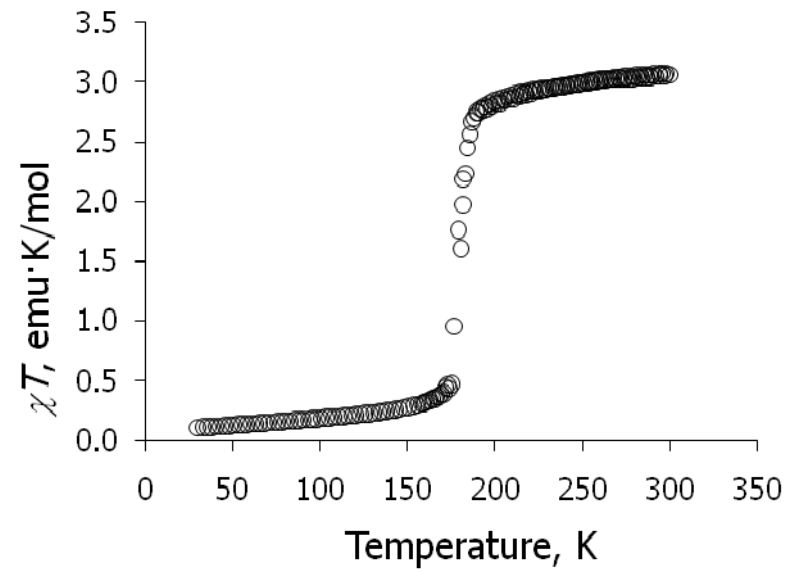
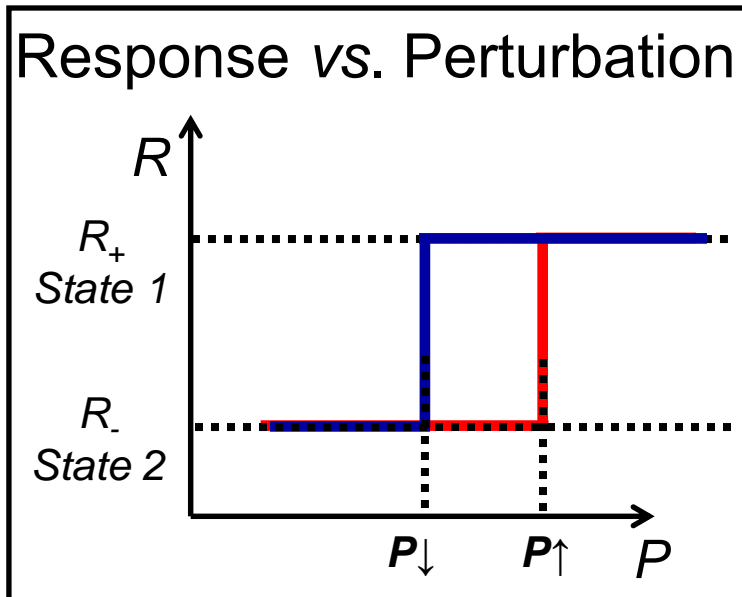
# *Mössbauer Spectroscopy Studies of Spin Transitions in Polynuclear Iron complexes*

Diaspora în cercetarea științifică și învățământul superior din România  
București, 21-24 septembrie 2010

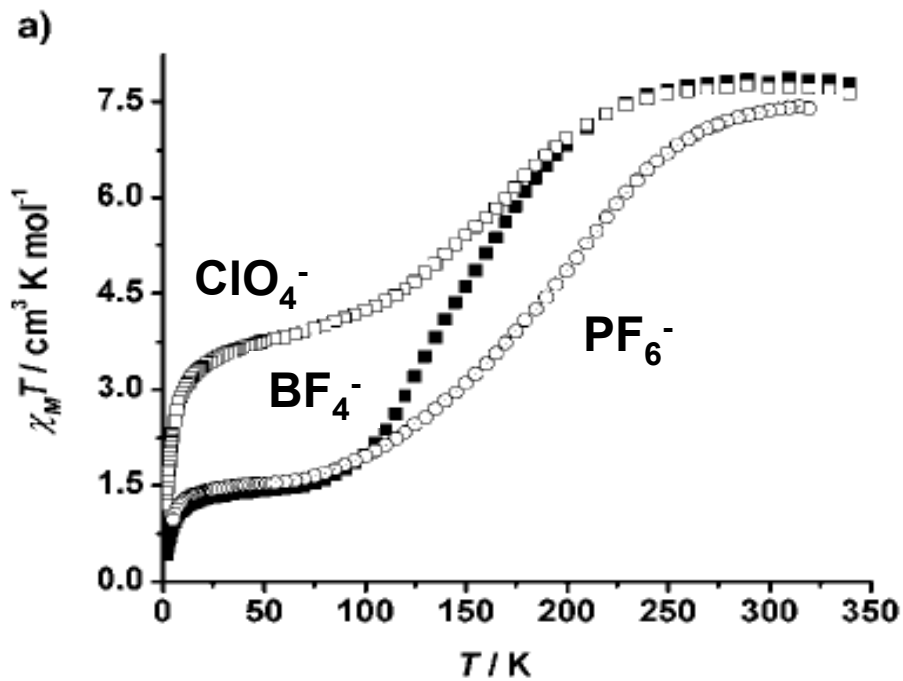
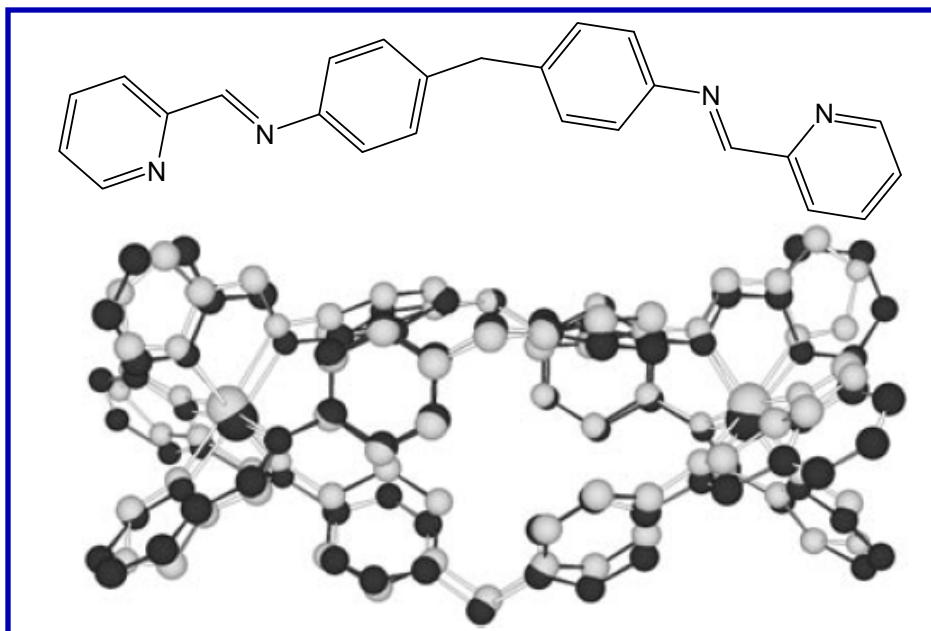
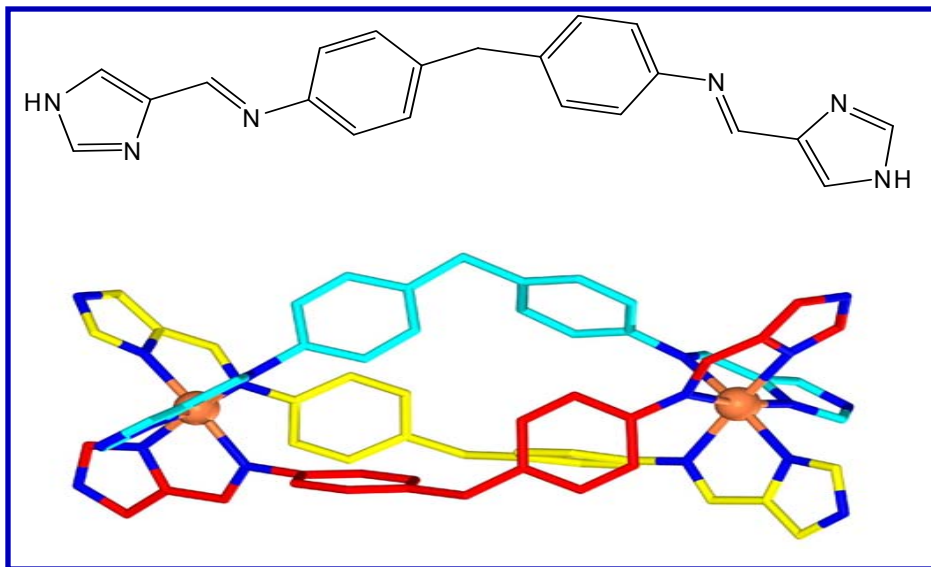
**CarnegieMellon**

# Materials with Memory

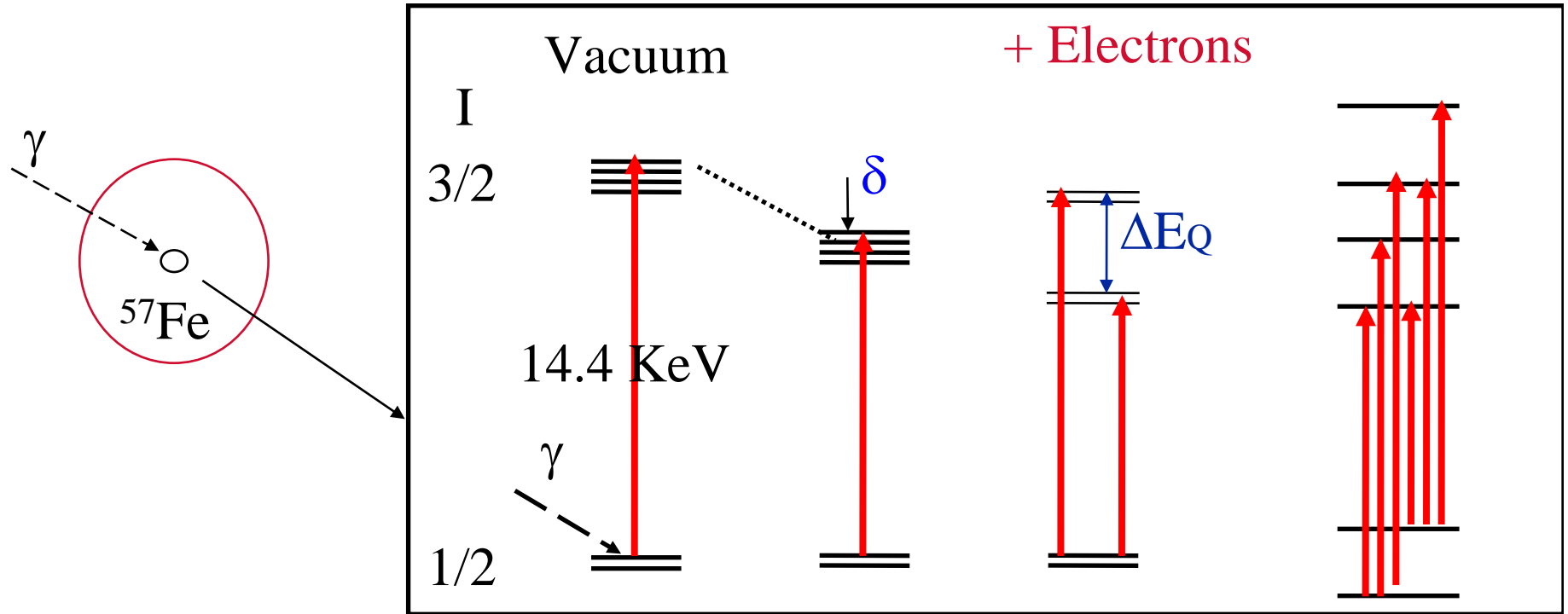
- Molecule undergoes a transition between different states with perturbation  $P$
- Transition is detectable
- Transition occurs with hysteresis



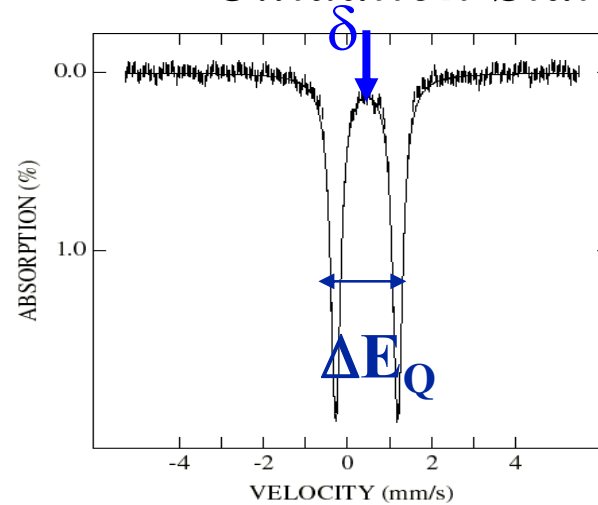
# Diiron(II) Triple Helicates $[\text{Fe}_2\text{L}_3]\text{X}_2$



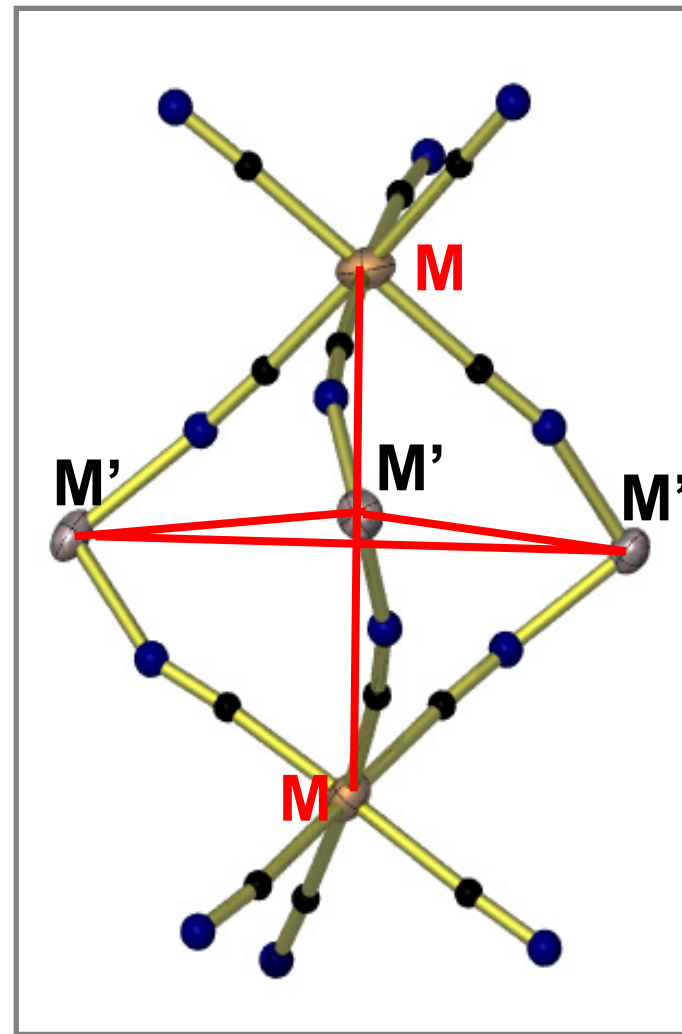
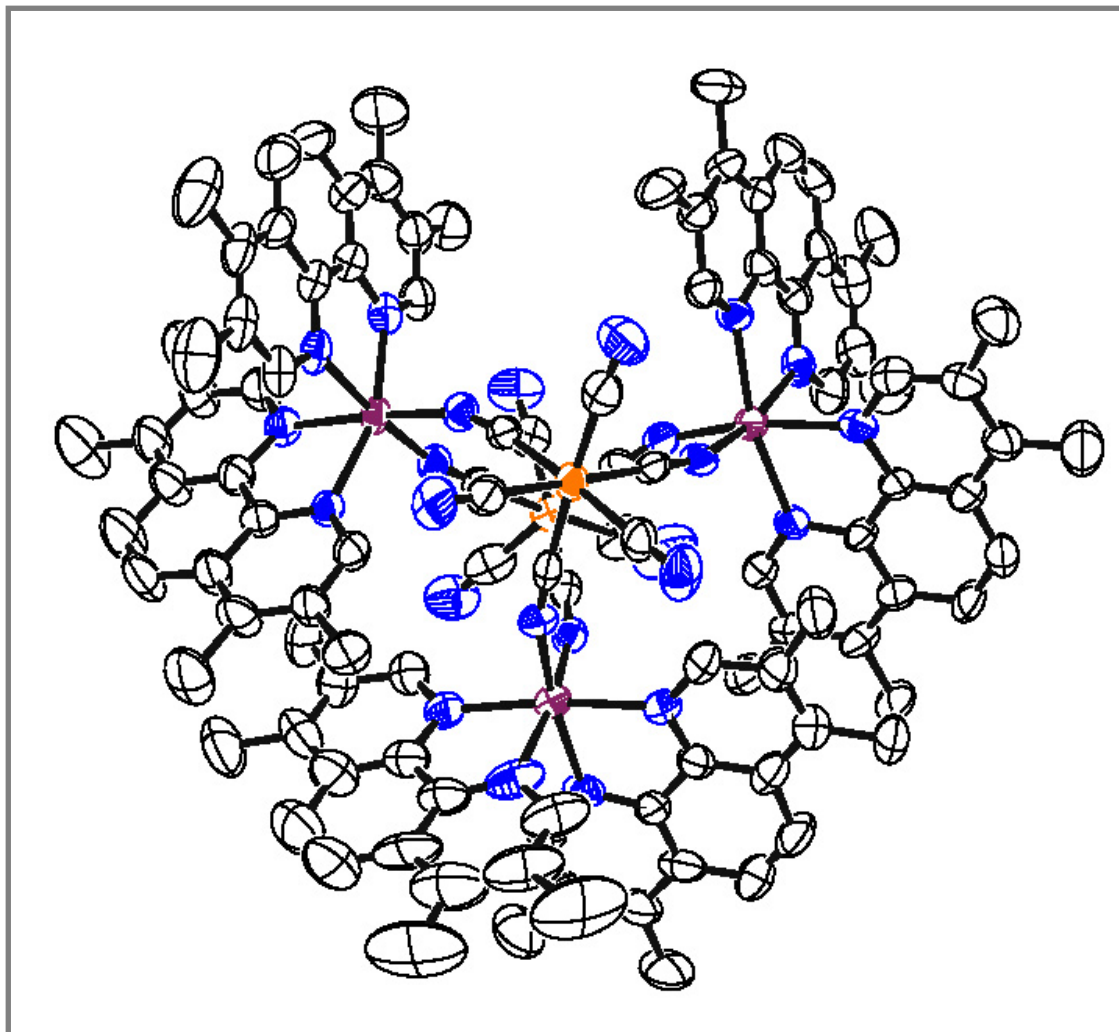
# Mössbauer Spectroscopy



*Oxidation State    Spin State*

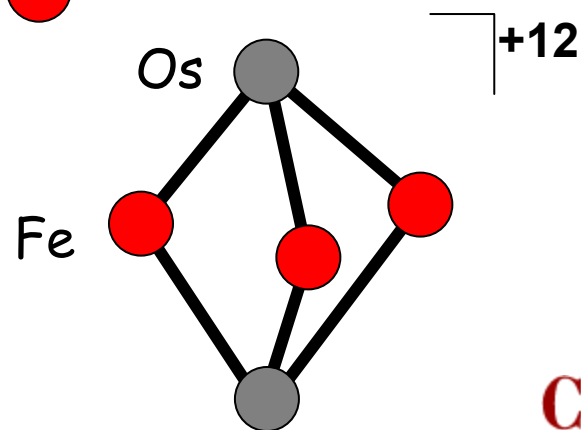
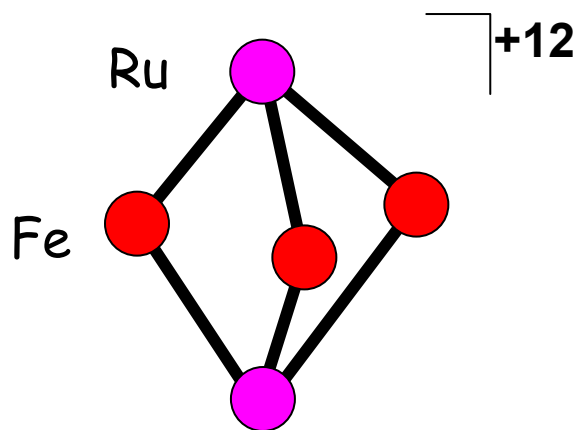
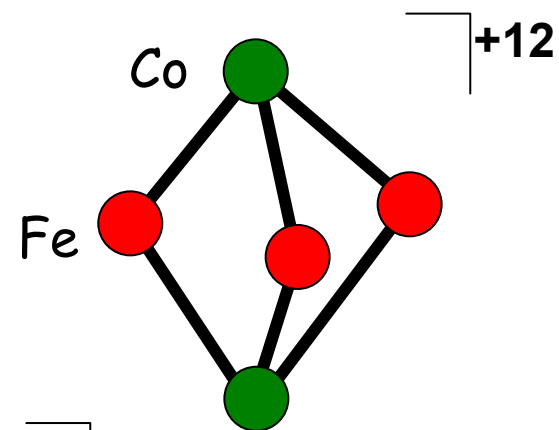
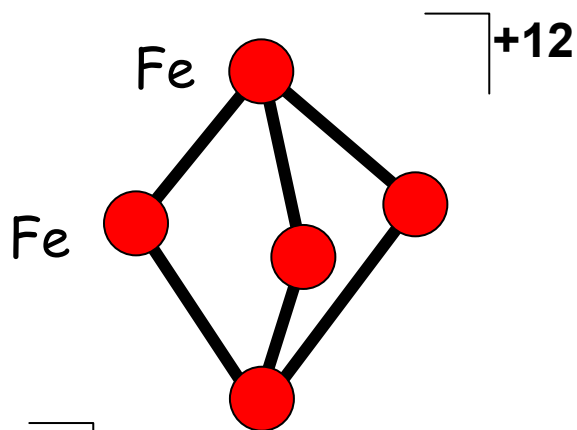
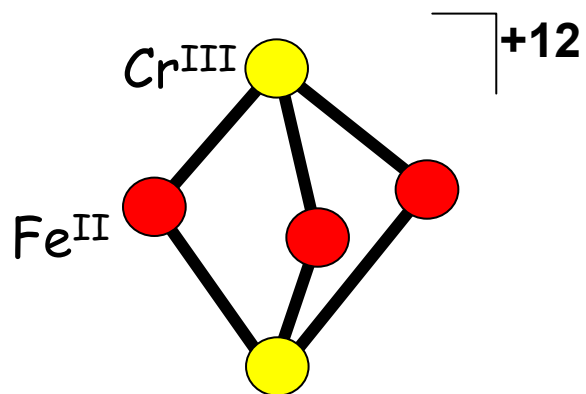
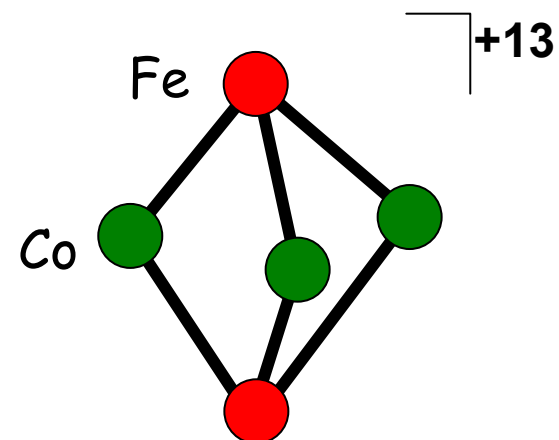
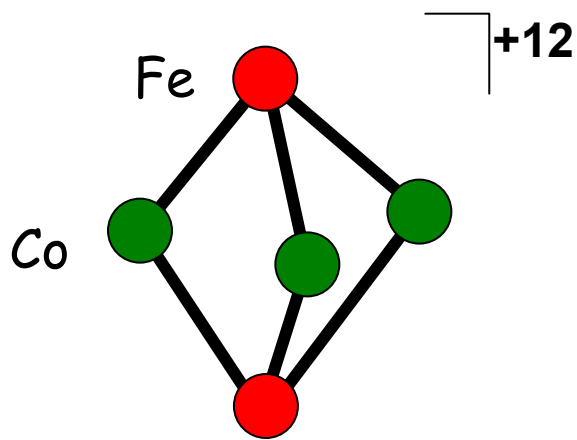
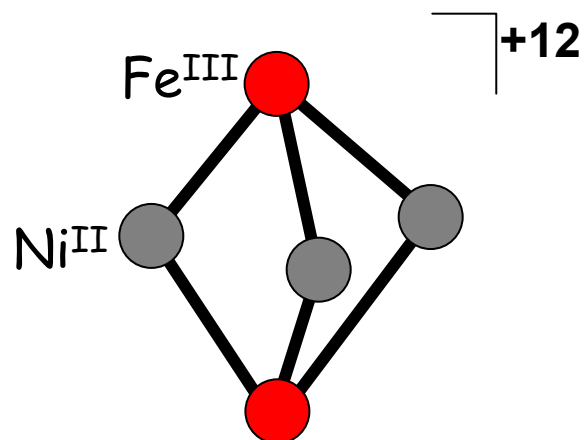


# Synthesis of Trigonal Bipyramid Co-Fe Clusters

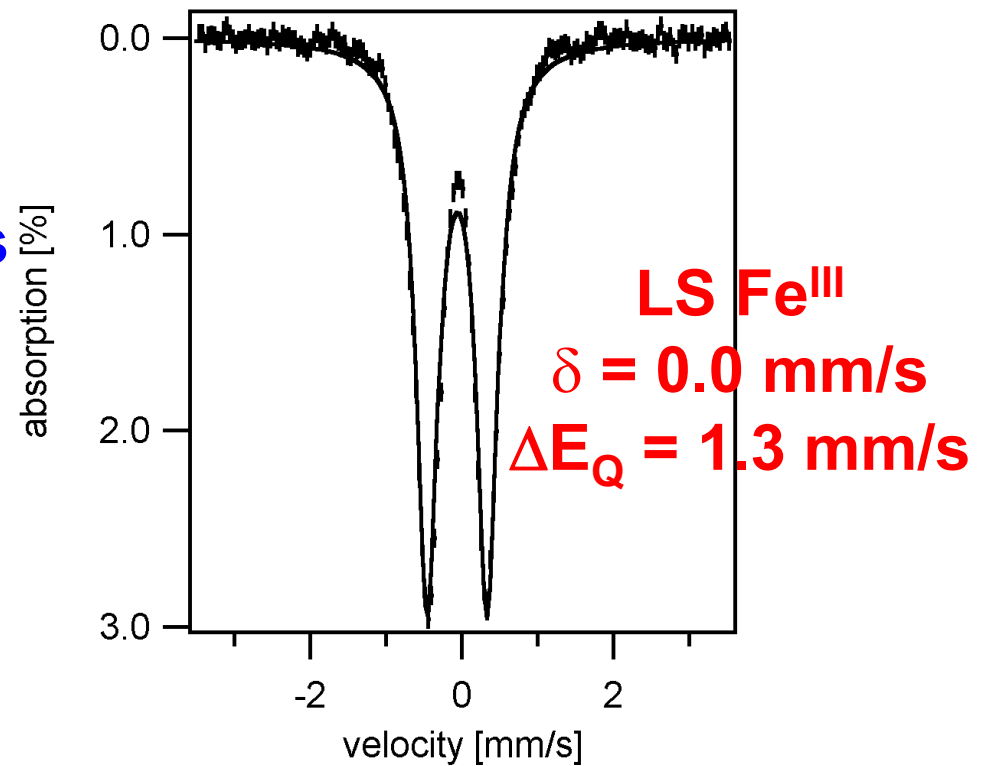
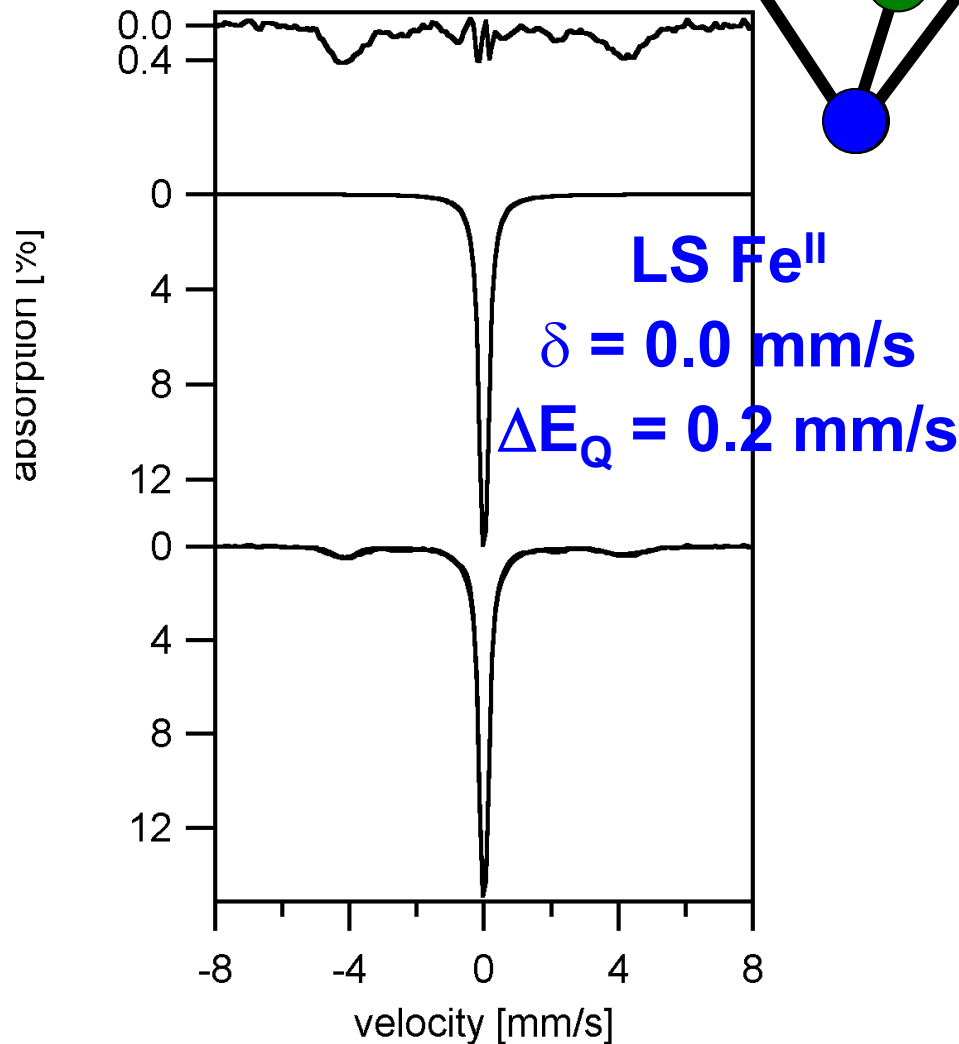
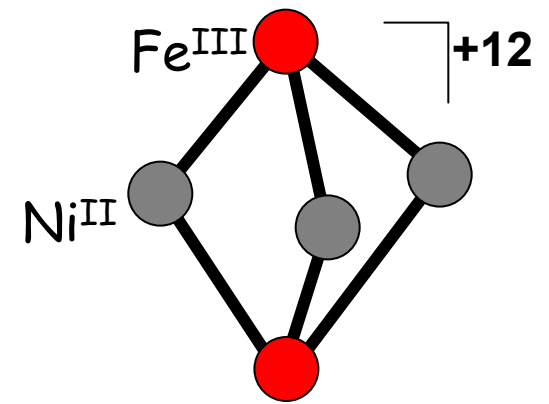
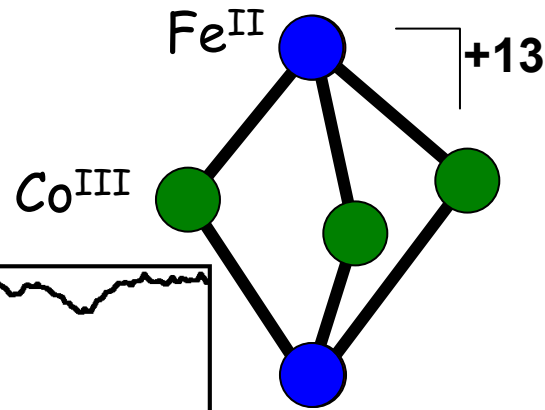


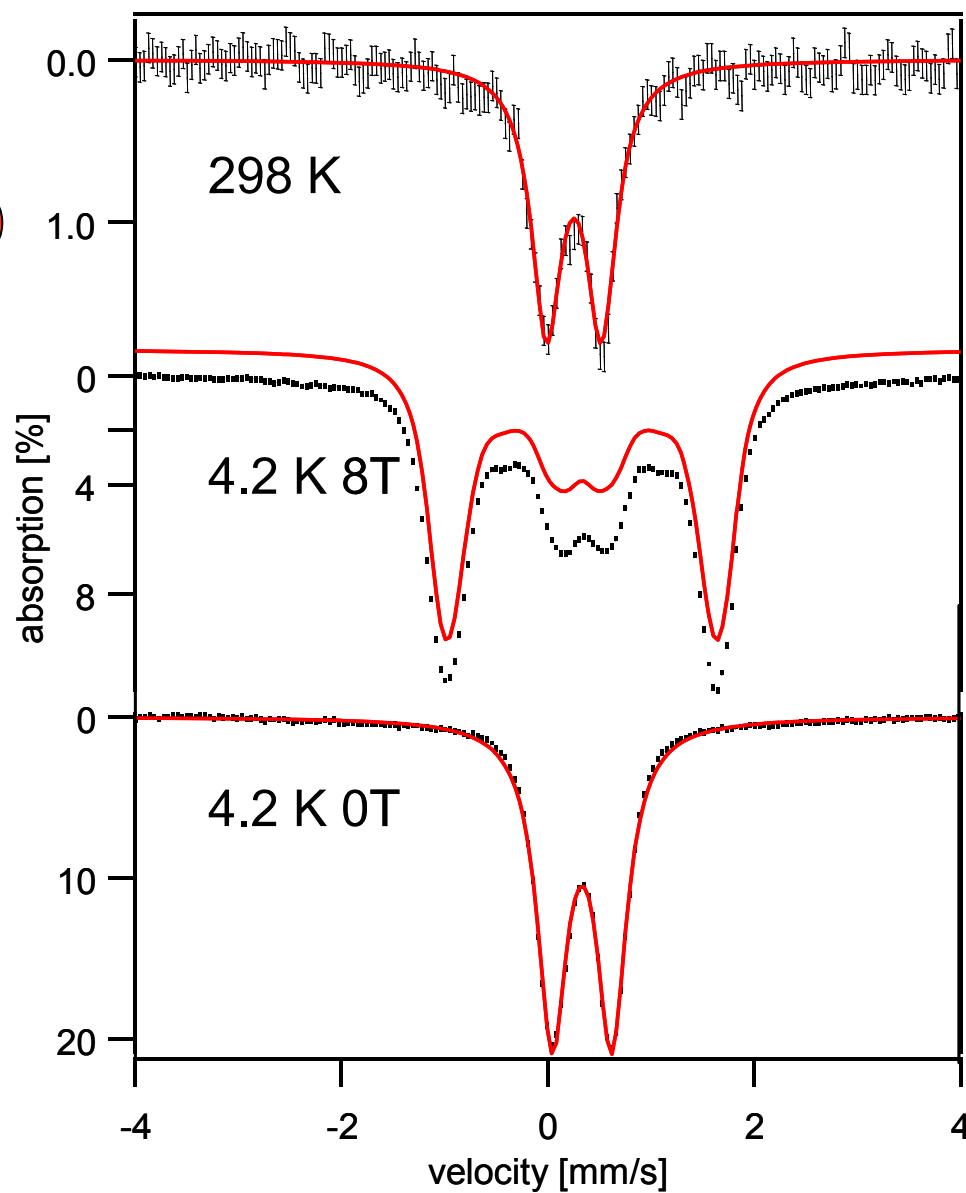
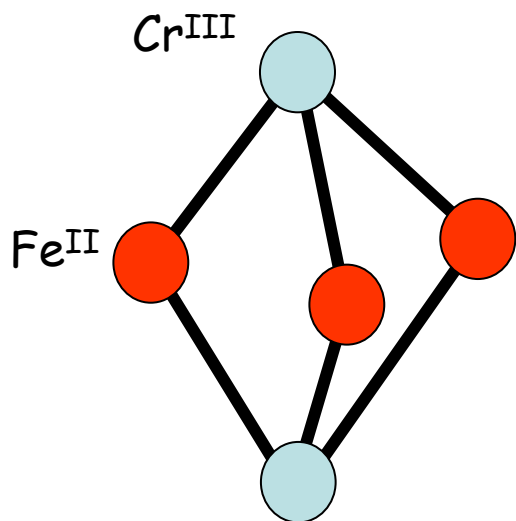
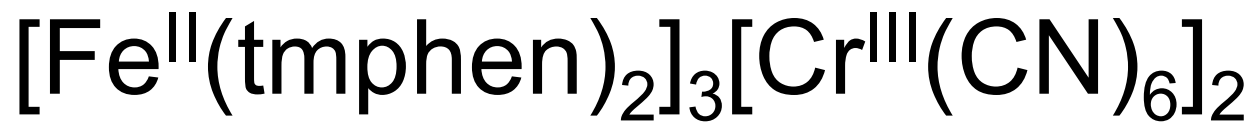
Carnegie Mellon

# Trigonal Bipyramid Clusters



# Fe Oxidation State by Mössbauer Spectroscopy



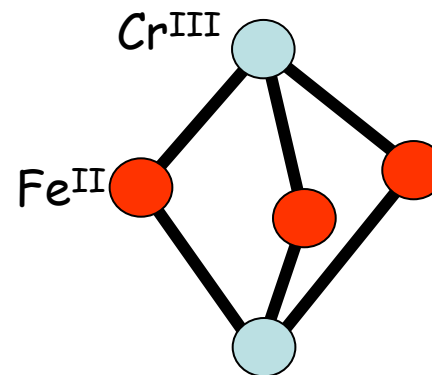
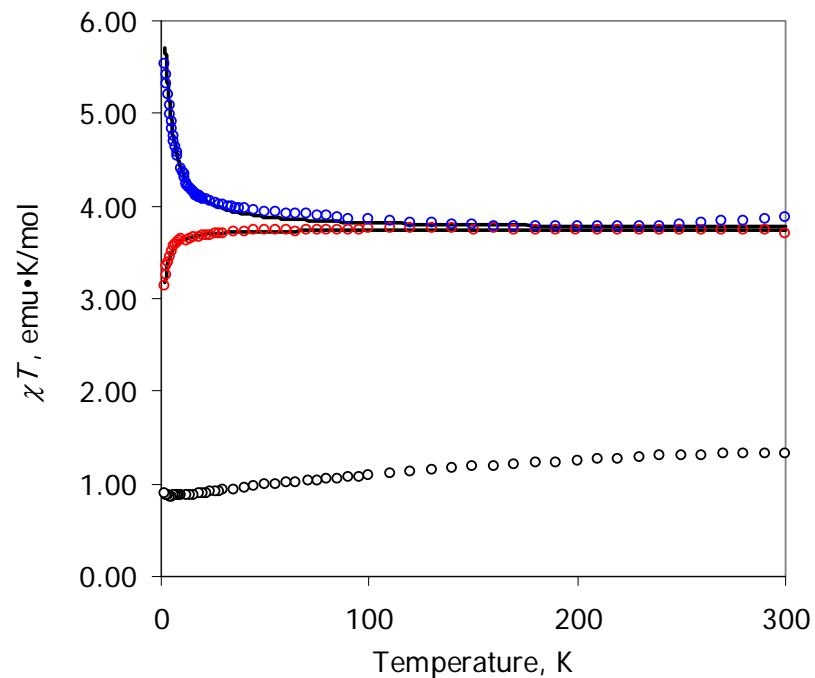


$$\delta = 0.25 \text{ mm s}^{-1}$$
$$\Delta E_Q = 0.53 \text{ mm s}^{-1}$$

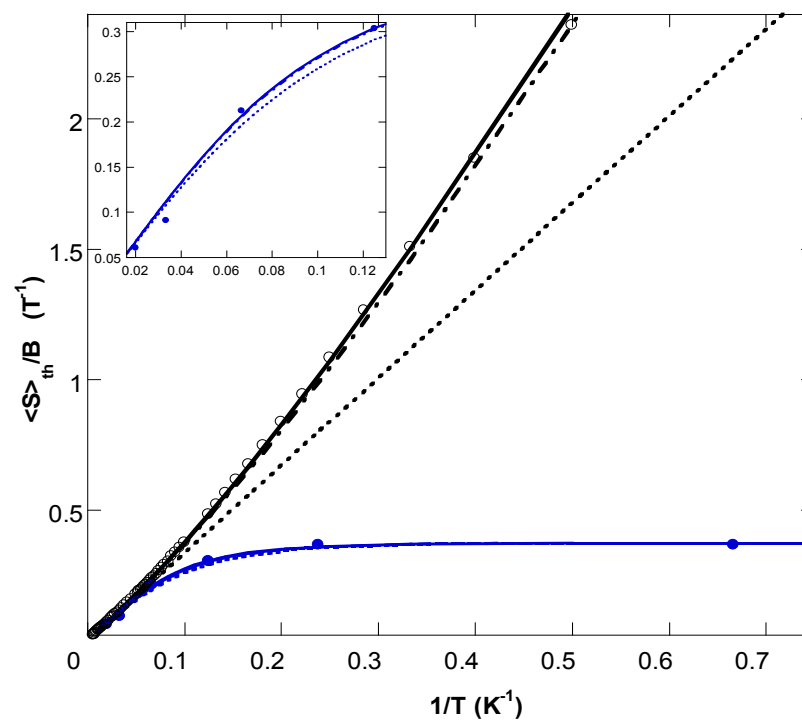
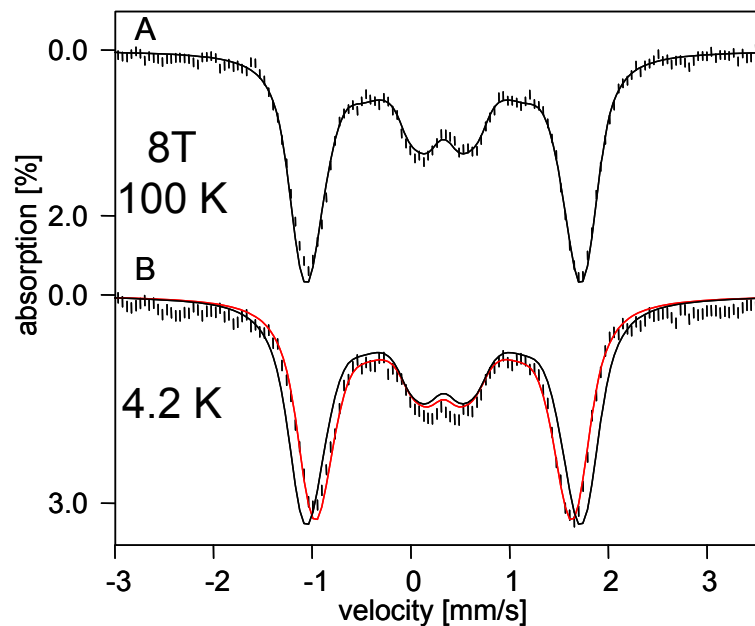
$$\delta = 0.33 \text{ mm s}^{-1}$$
$$\Delta E_Q = 0.58 \text{ mm s}^{-1}$$

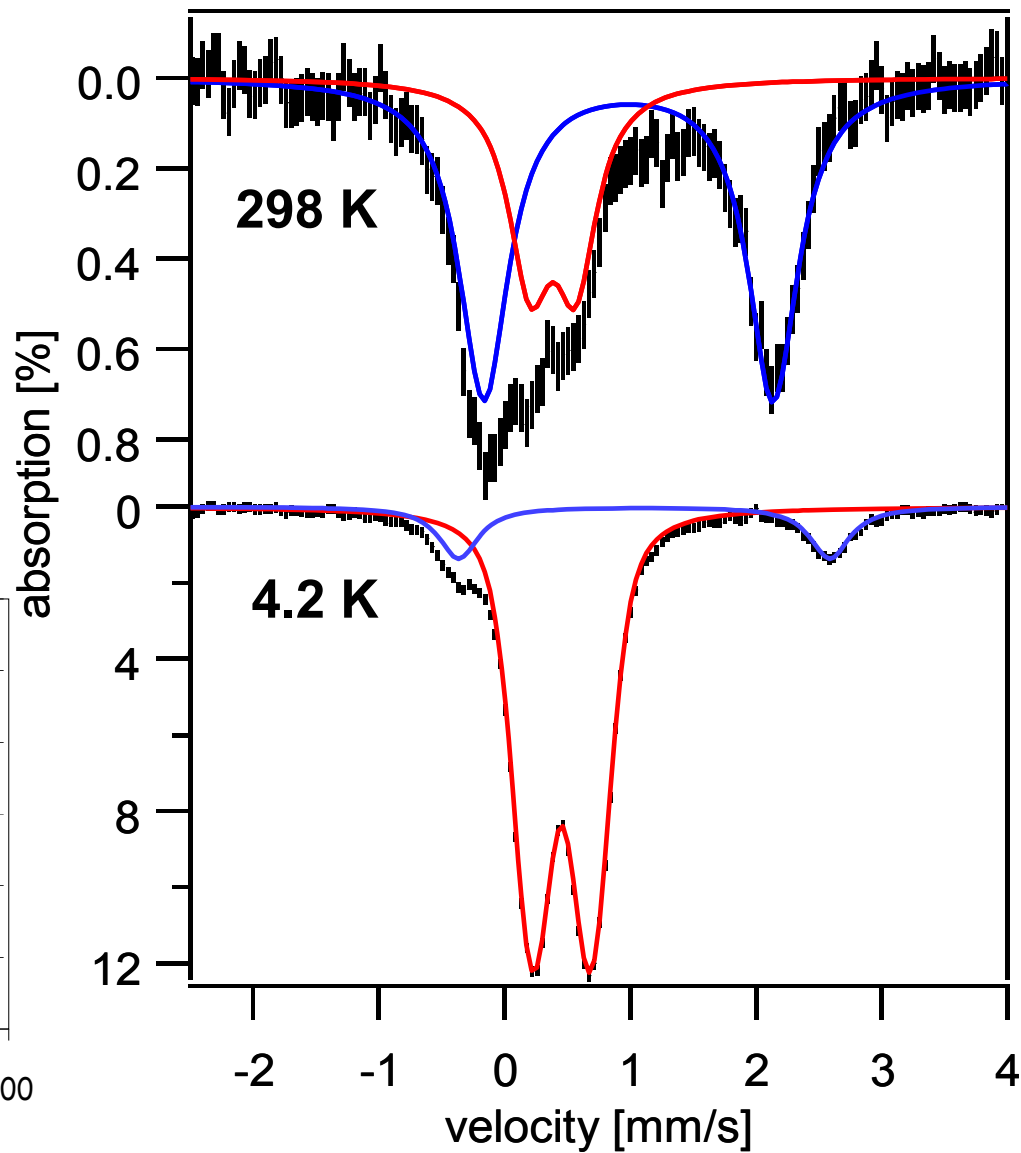
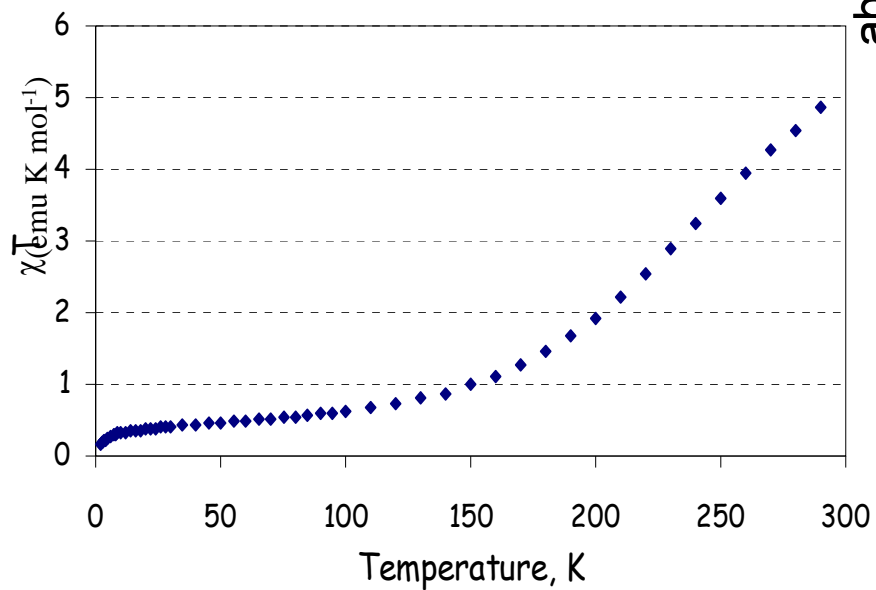
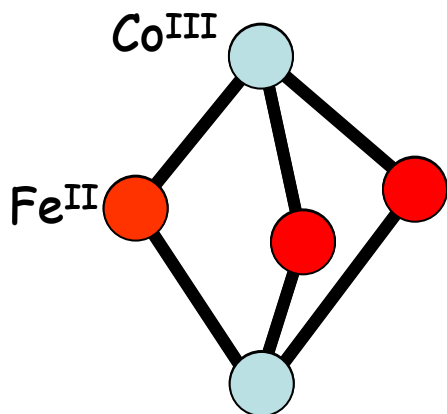
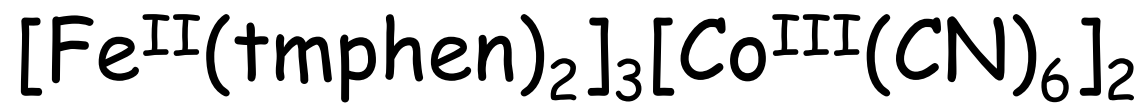


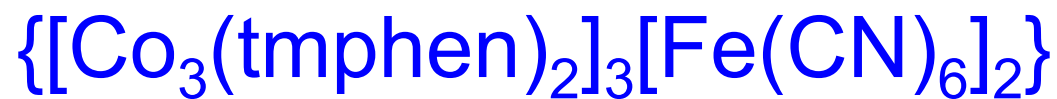
# Exchange Coupling Through NC-(LS Fe<sup>II</sup>)-CN



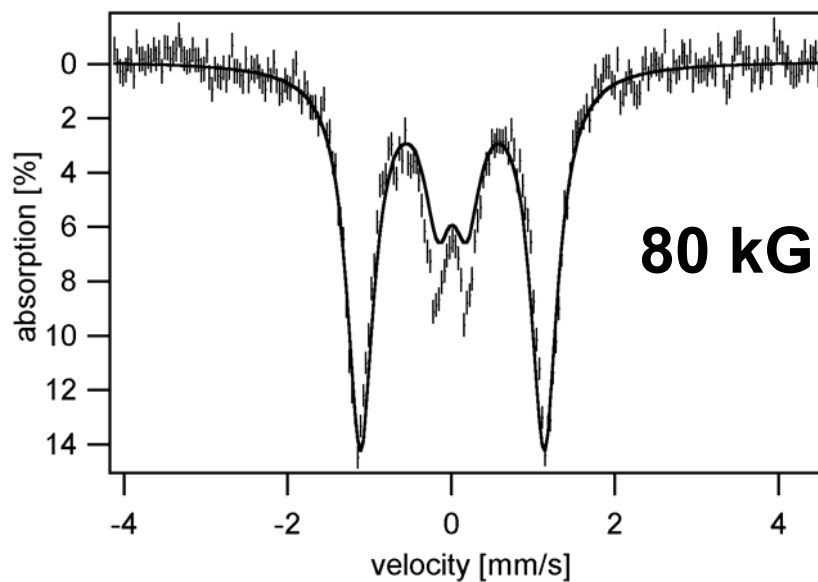
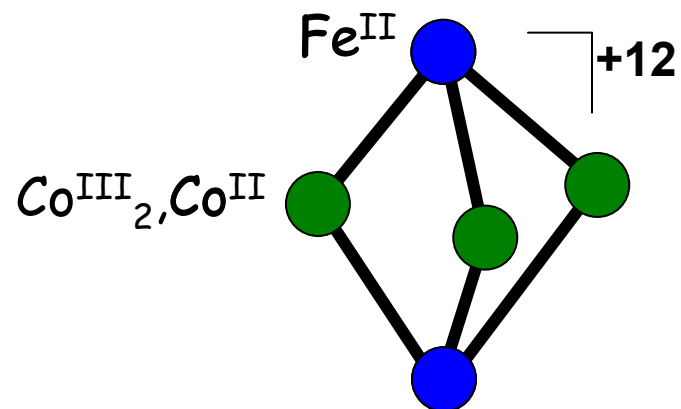
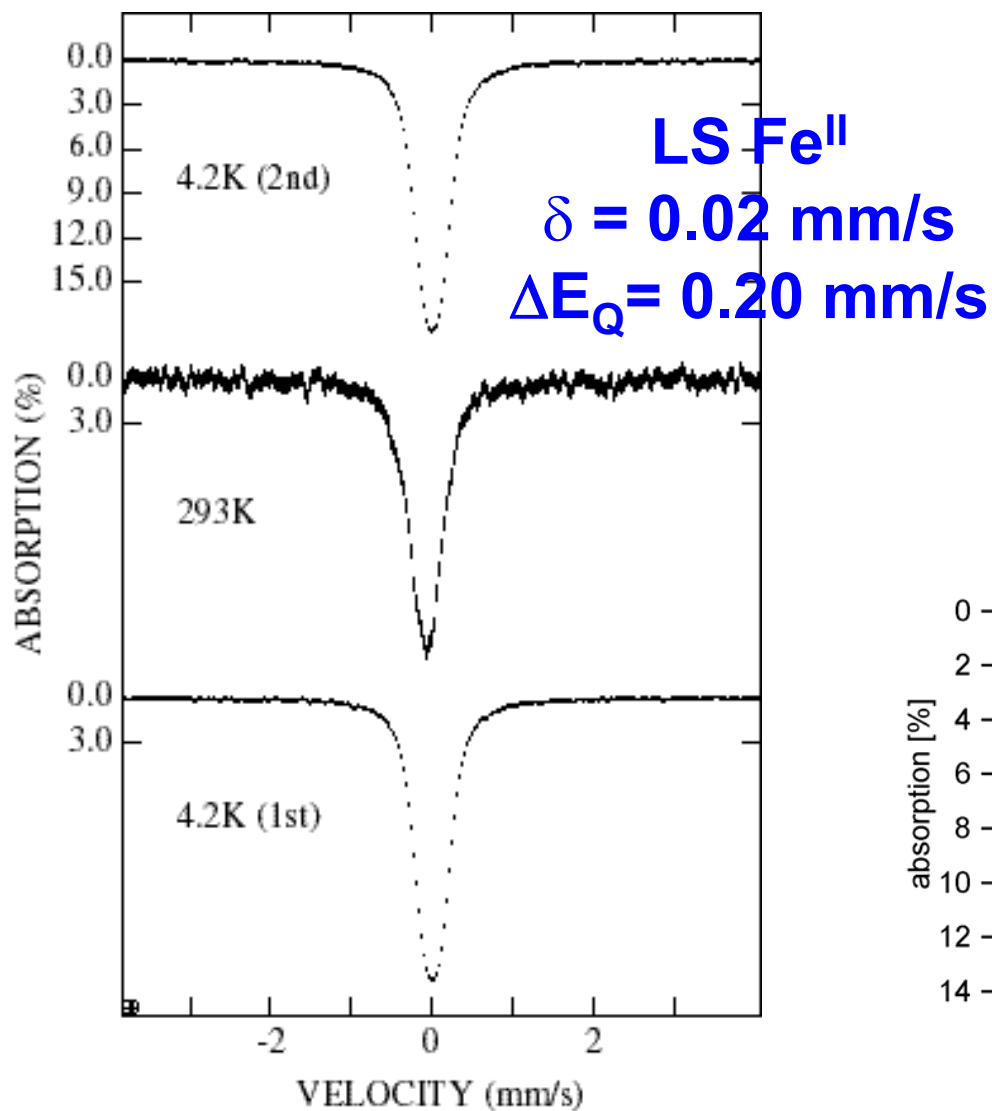
$$H = -2JS_{Cr}S_{Cr} + 2\mu_B(S_{Cr}+S_{Cr})$$



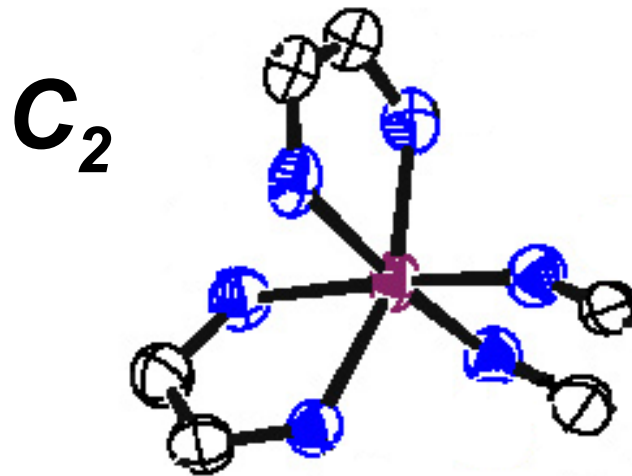
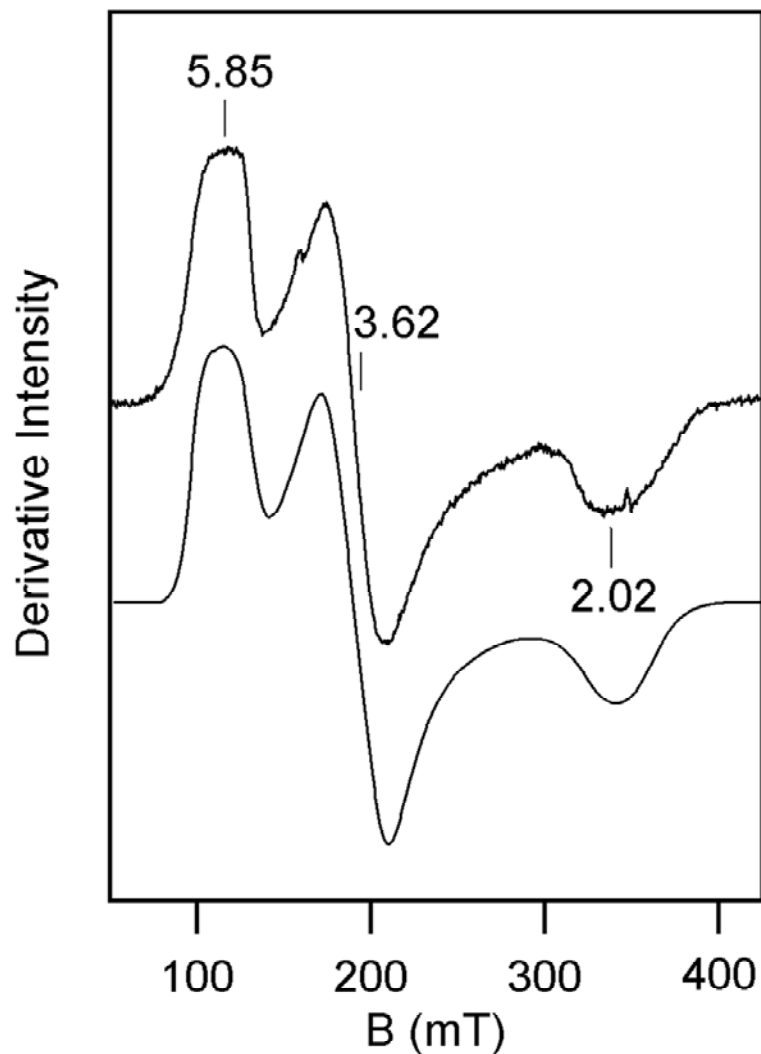




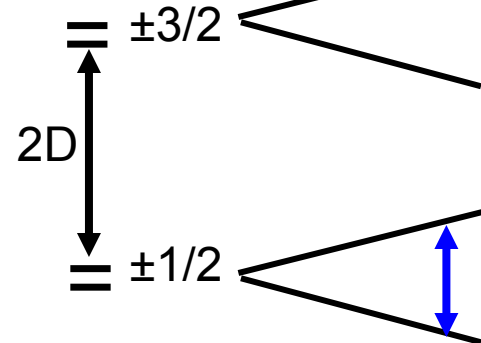
**0.45 kG**



# EPR for $\{\text{Co}^{\text{II}}\text{Co}^{\text{III}}_2\text{Fe}^{\text{II}}_2\}$ in solution



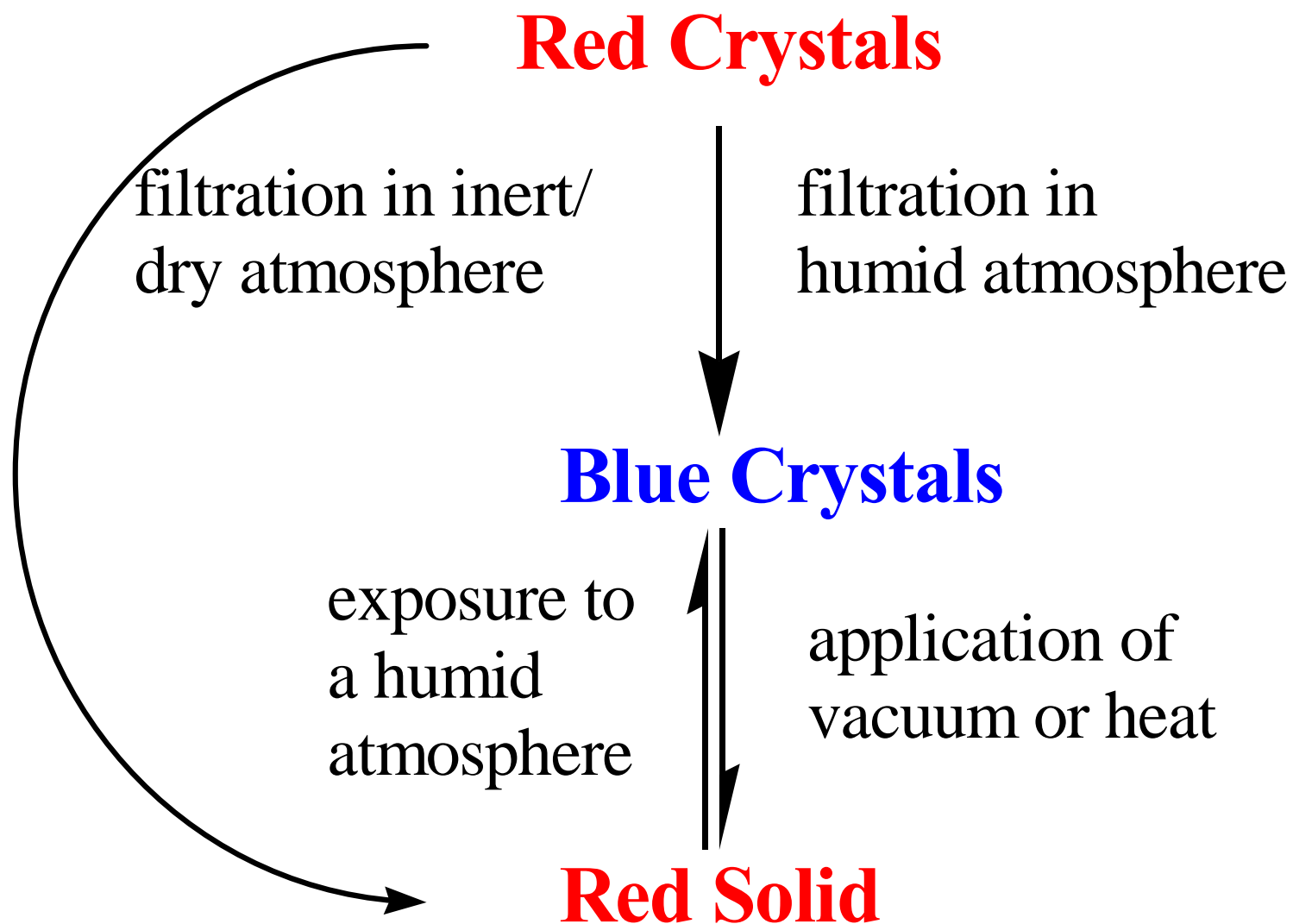
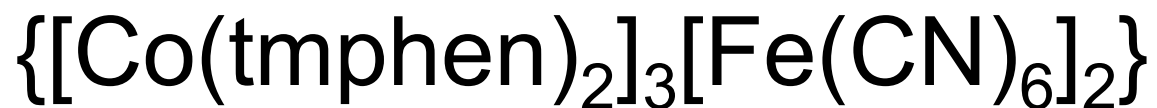
$$H = \beta S \cdot \tilde{g}_0 \cdot B + D \left( S_z^2 - \frac{5}{4} \right) + E \left( S_x^2 - S_y^2 \right) + AS \cdot I$$

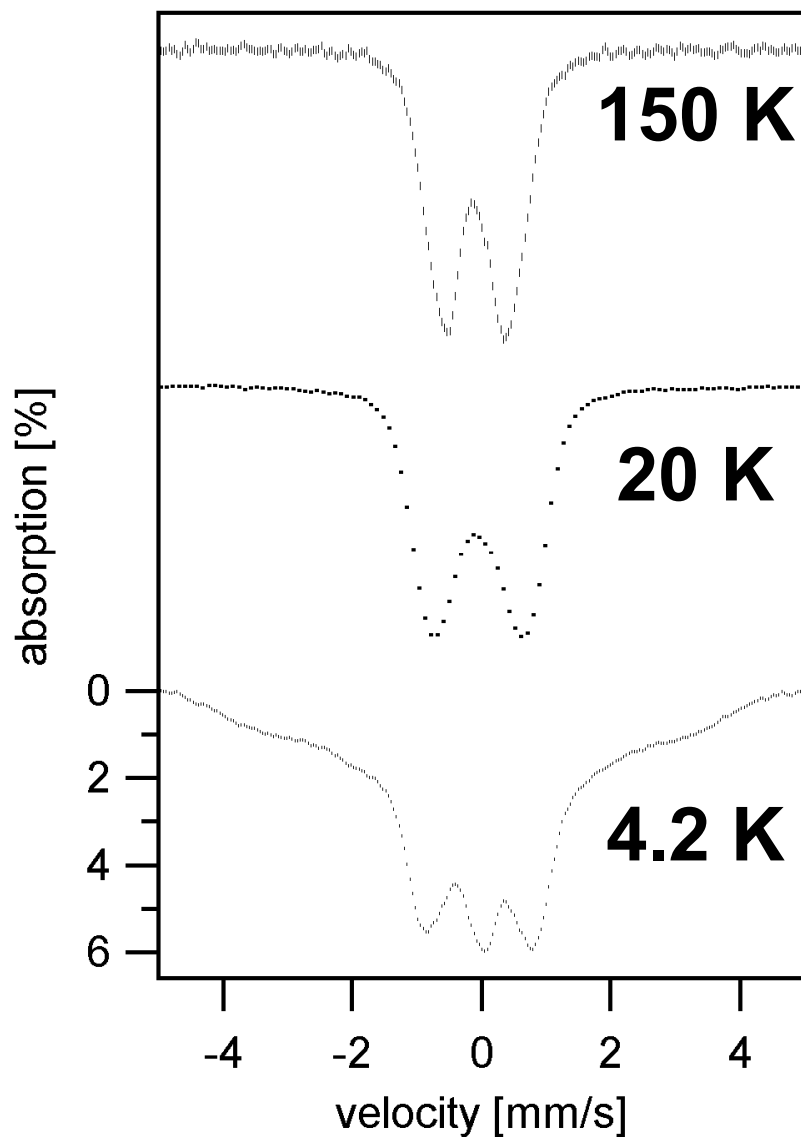
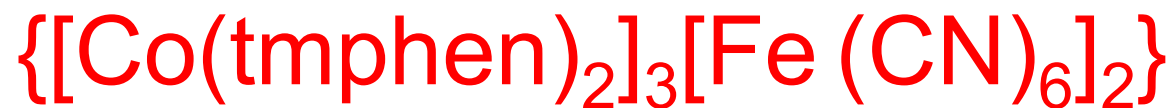


$D > 40 \text{ cm}^{-1}, E/D = 0.186$

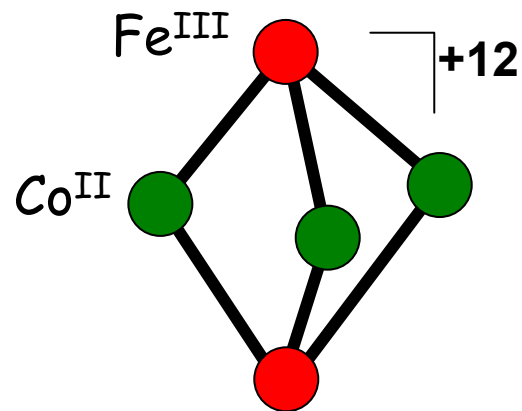
$g_x = 2.53, g_y = 2.42, g_z = 2.22$

$A_x = A_y = A_z = 147.7 \text{ G}$

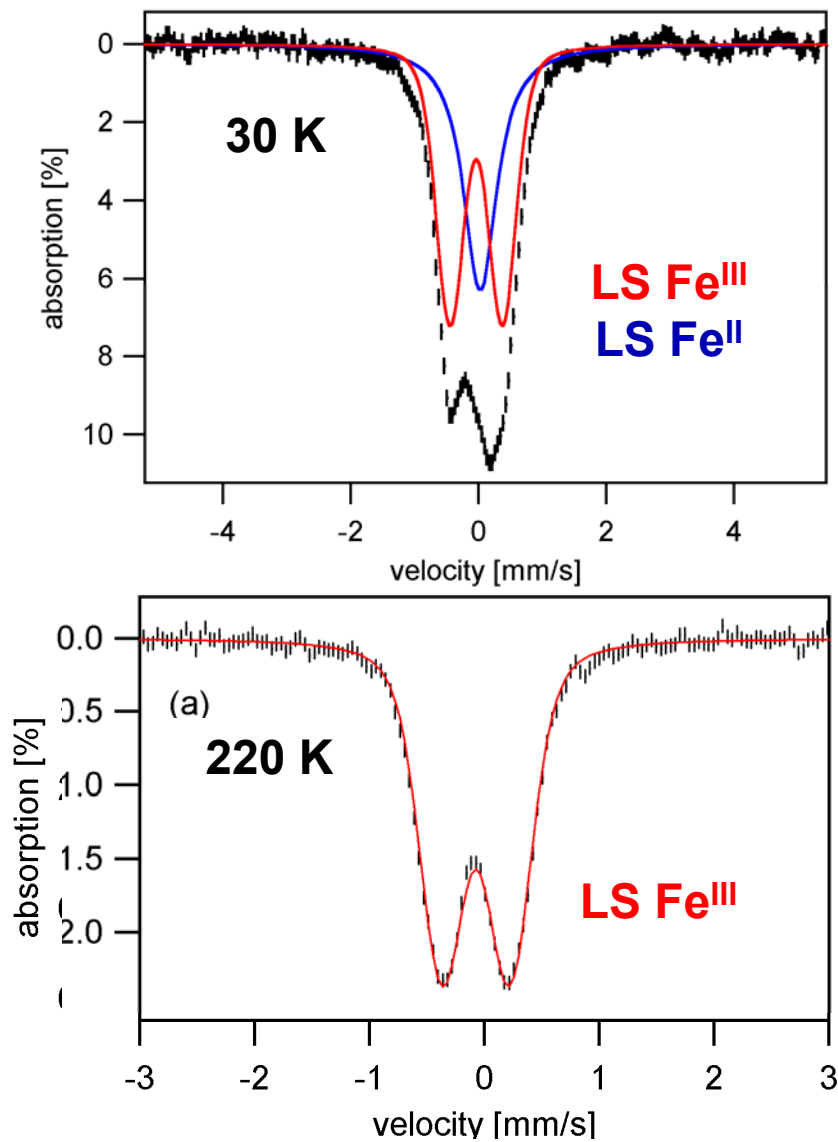
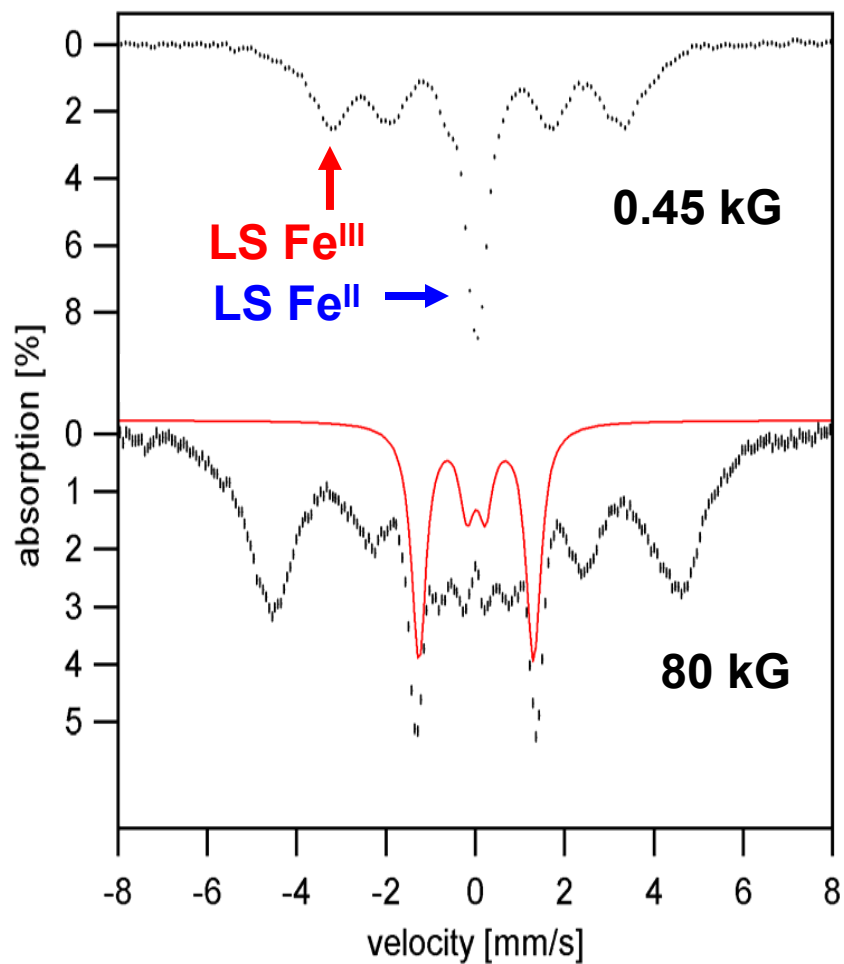




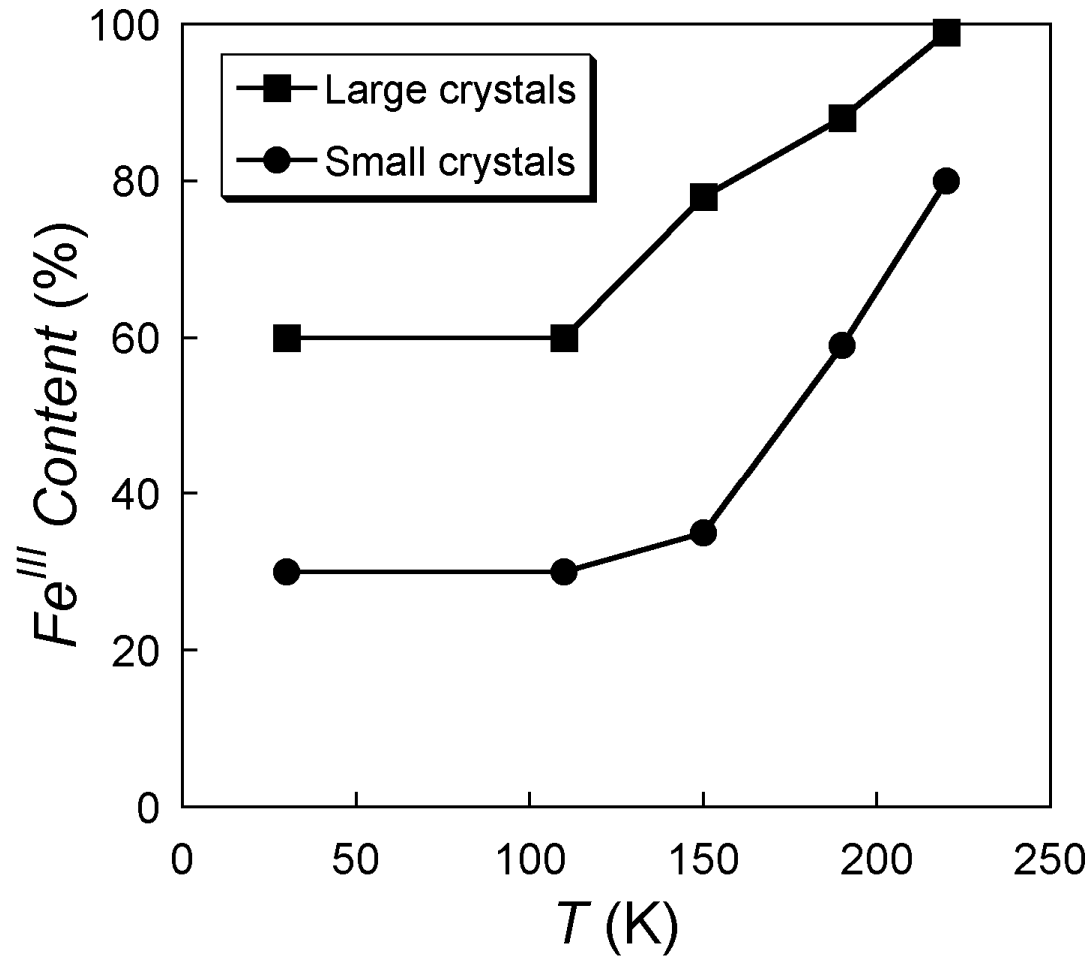
**LS Fe<sup>III</sup>**  
 **$\delta = 0.0$  mm/s**  
 **$\Delta E_Q = 1.3$  mm/s**



# Red Crystals of $\{[\text{Co}(\text{tmphen})_2]_3[\text{Fe}(\text{CN})_6]_2\}$

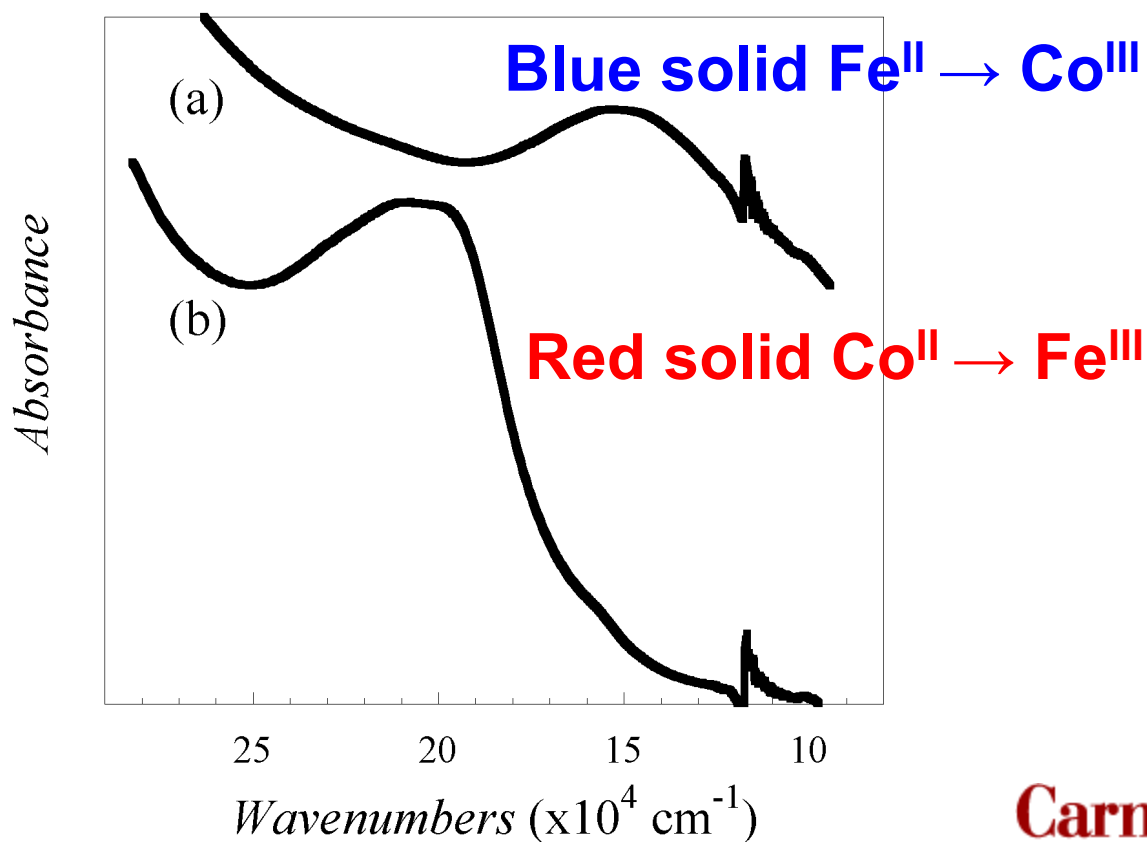
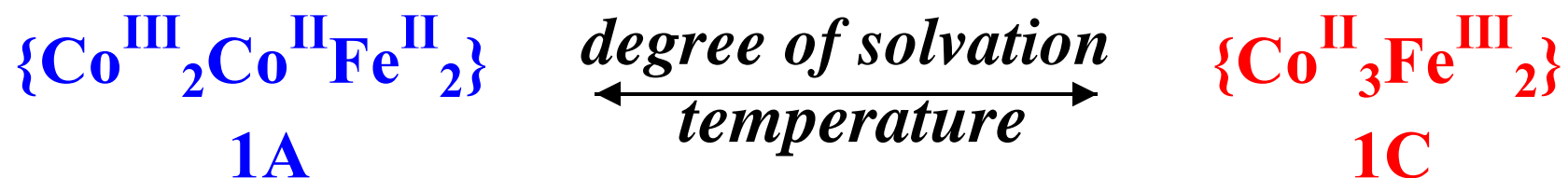


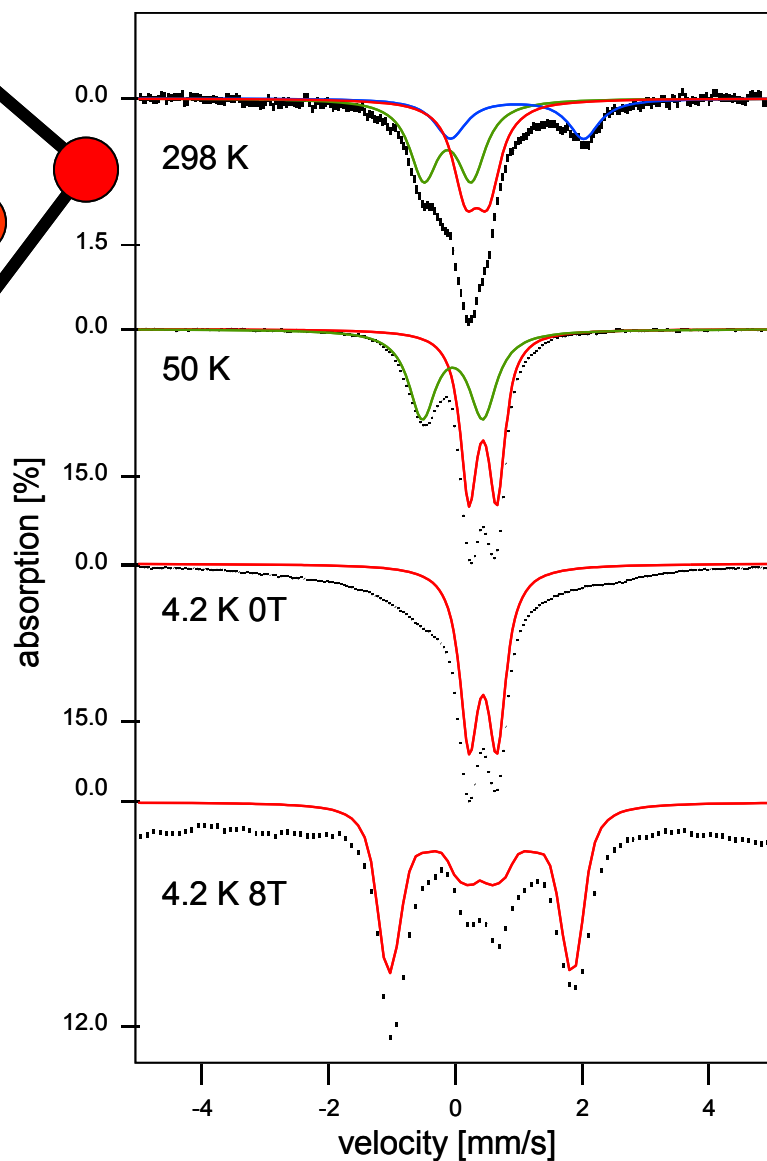
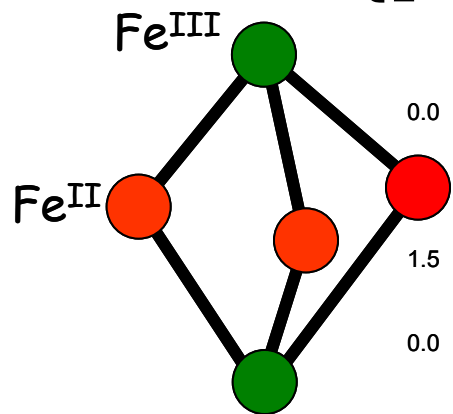
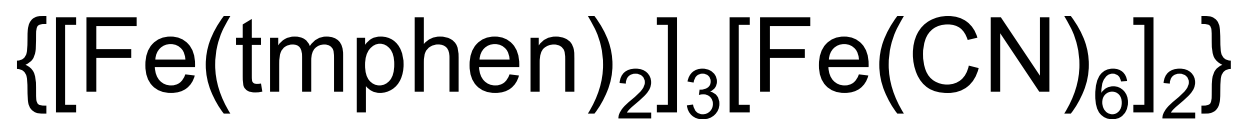
# Temperature Dependence of Fe Oxidation State





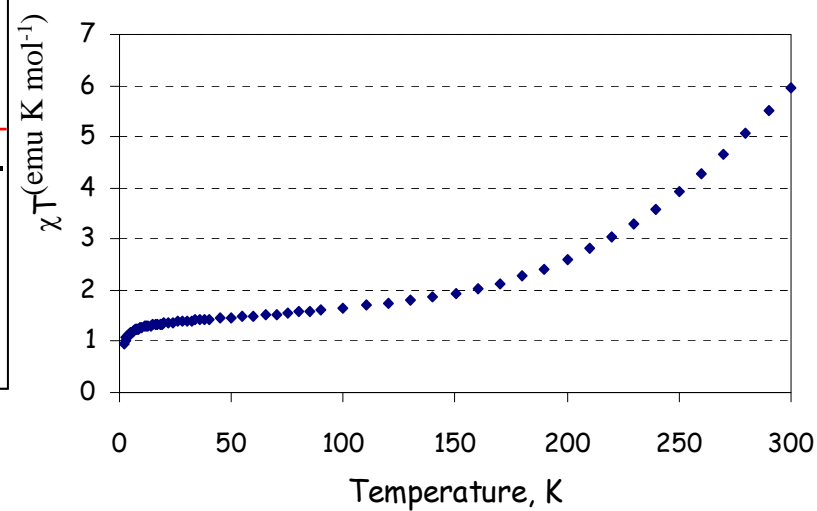
# First Charge-Transfer Induced Spin Transition in a Molecular Fe/Co Complex



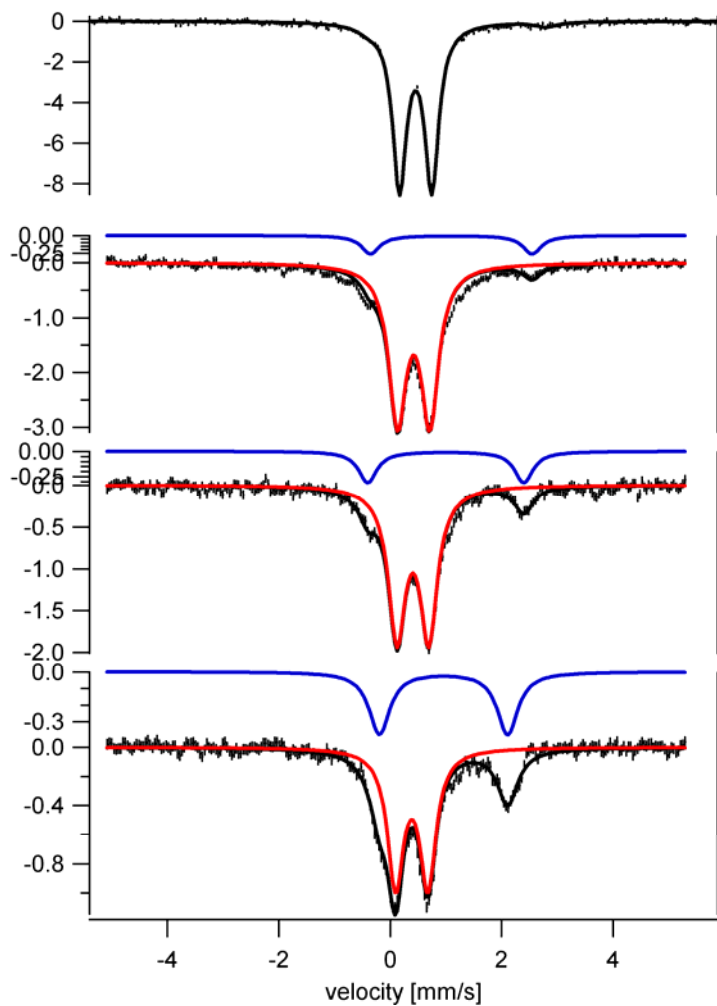


|                      | $\delta$ (mm s <sup>-1</sup> ) | $\Delta E_Q$ (mm s <sup>-1</sup> ) | %  |
|----------------------|--------------------------------|------------------------------------|----|
| LS Fe <sup>II</sup>  | 0.34                           | 0.35                               | 40 |
| HS Fe <sup>II</sup>  | 0.97                           | 2.10                               | 20 |
| LS Fe <sup>III</sup> | -0.12                          | 0.75                               | 40 |

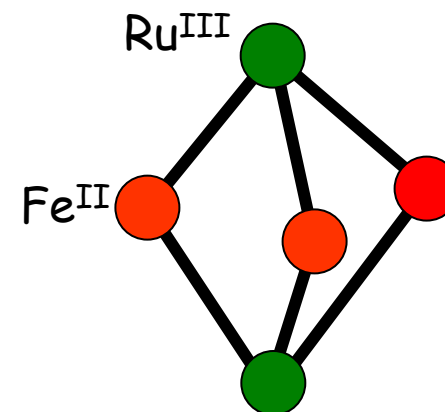
|                     | $\delta$ (mm s <sup>-1</sup> ) | $\Delta E_Q$ (mm s <sup>-1</sup> ) | %  |
|---------------------|--------------------------------|------------------------------------|----|
| LS Fe <sup>II</sup> | 0.44                           | 0.44                               | 60 |



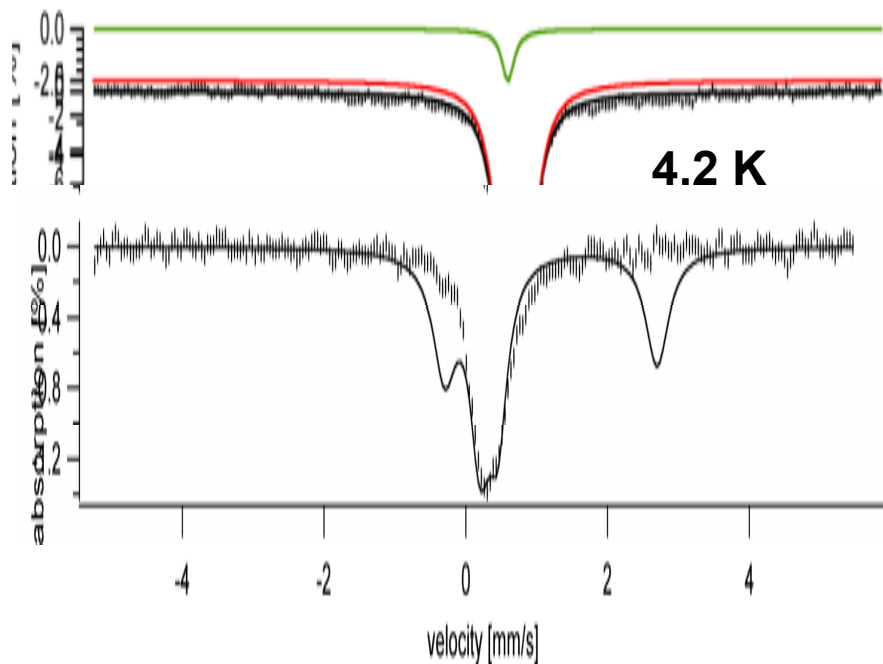
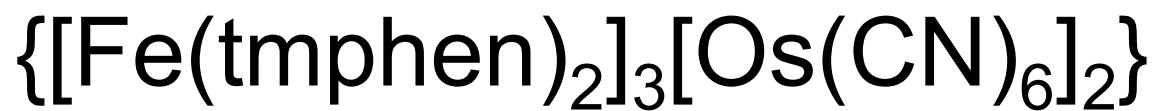
# [Fe(tmphen)<sub>2</sub>]<sub>3</sub>[Ru(CN)<sub>6</sub>]<sub>2</sub>



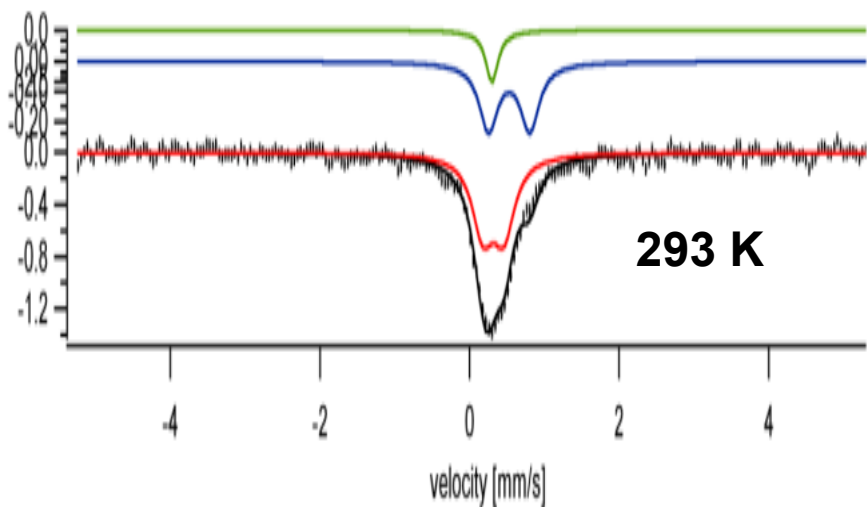
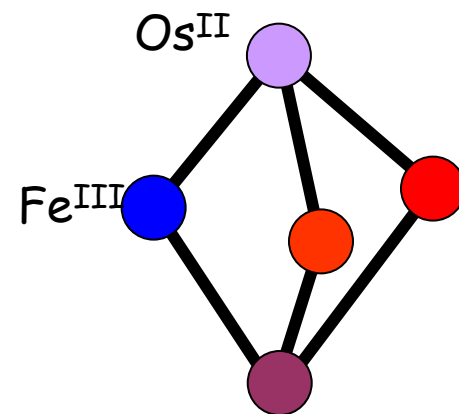
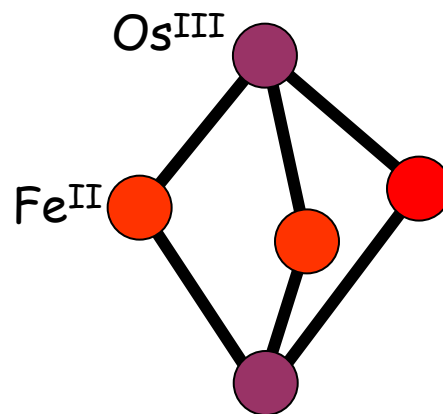
|                     | $\delta$ (mm s <sup>-1</sup> ) | $\Delta E_Q$ (mm s <sup>-1</sup> ) | %  |
|---------------------|--------------------------------|------------------------------------|----|
| LS Fe <sup>II</sup> | 0.46                           | 0.58                               | 96 |



|                     | $\delta$ (mm s <sup>-1</sup> ) | $\Delta E_Q$ (mm s <sup>-1</sup> ) | %  |
|---------------------|--------------------------------|------------------------------------|----|
| LS Fe <sup>II</sup> | 0.39                           | 0.58                               | 66 |
| HS Fe <sup>II</sup> | 0.96                           | 2.30                               | 34 |

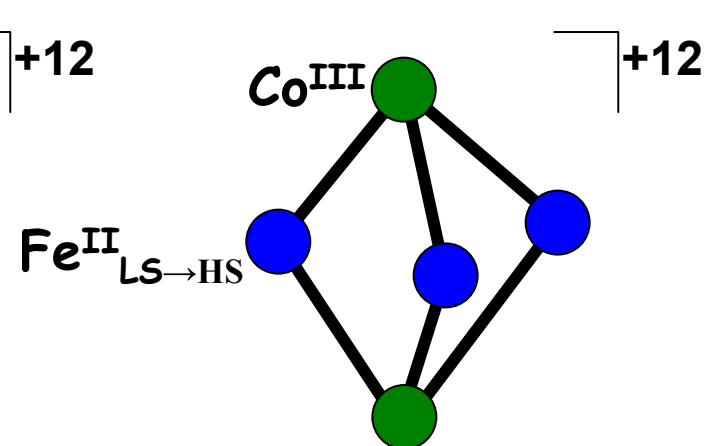
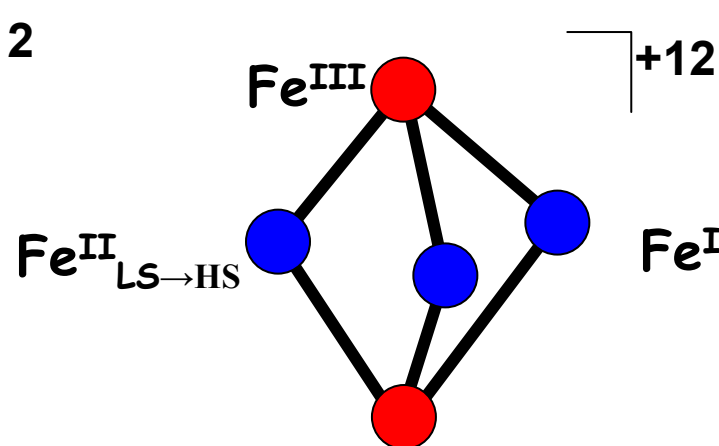
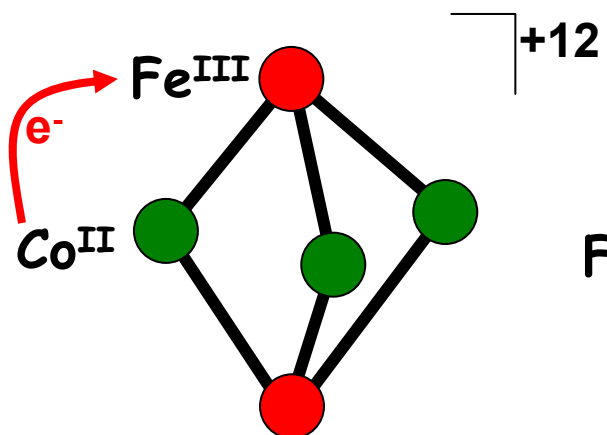
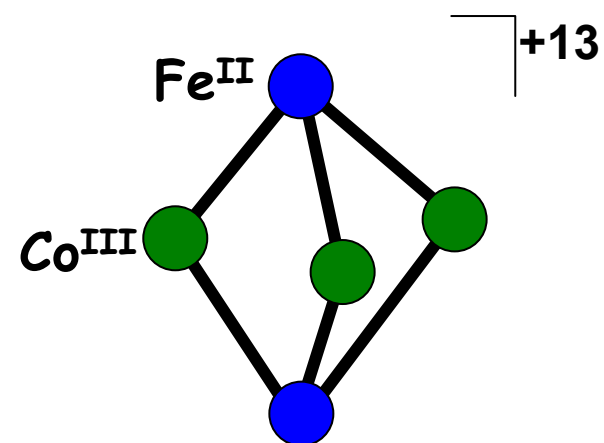
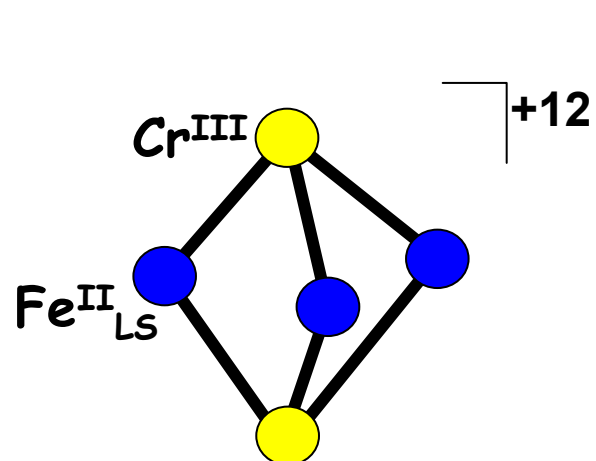
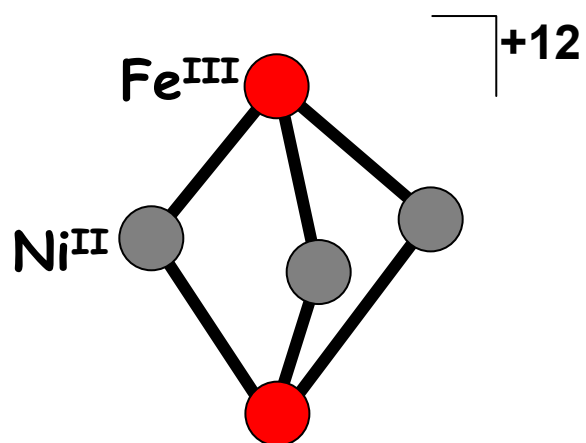


|                     | $\delta$ (mm s <sup>-1</sup> ) | $\Delta E_Q$ (mm s <sup>-1</sup> ) | %  |
|---------------------|--------------------------------|------------------------------------|----|
| LS Fe <sup>II</sup> | 0.40                           | 0.36                               | 95 |



|                      | $\delta$ (mm s <sup>-1</sup> ) | $\Delta E_Q$ (mm s <sup>-1</sup> ) | %  |
|----------------------|--------------------------------|------------------------------------|----|
| LS Fe <sup>II</sup>  | 0.32                           | 0.28                               | 66 |
| HS Fe <sup>III</sup> | 0.50                           | 0.55                               | 27 |

# Trigonal Bipyramid Clusters



# Acknowledgments

**Alina Dragulescu**  
**Meimei Chen**  
**Kurt Sweely**  
**Jon Dorando**

**Texas A&M University**

*Kim Dunbar*

Curtis Berlinguette

Mike Shatrak

Matthew Hilfiger

**Florida State University**

*Mike Shatrak*

**University of Birmingham**

*Mike Hannon*

*Floriana Tuna*

**University of Tennessee**

*Jan Musfeldt*

Tania Branzari

**Allegheny College**

*Doros Petasis*

Tanya Nocera

**Carnegie Mellon University**

*Eckard Münck*

*Mike Hendrich*



**Carnegie Mellon**