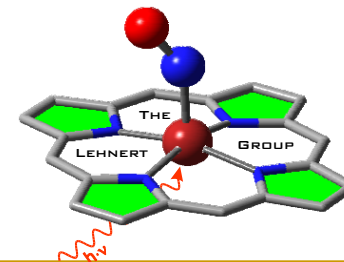**UNIVERSITY OF MICHIGAN**

**DEPARTMENT OF CHEMISTRY**

Dr. Nicolai Lehnert

Nuclear Resonance Vibrational Spectroscopy (NRVS)

# Nuclear Resonance Vibrational Spectroscopy (NRVS)

- Synchrotron-based vibrational technique
- Developed in the 1990's
  - First reported in 1970's, but proper equipment was not developed until later
- Combination of nuclear excitation and molecular vibrations
  - Uses the Mössbauer effect to excite the nucleus
  - Measures inelastic scattering of the system
  - Provides a complete set of bands that involve motion of the probed nucleus

Mössbauer Spectroscopy: Energy Source
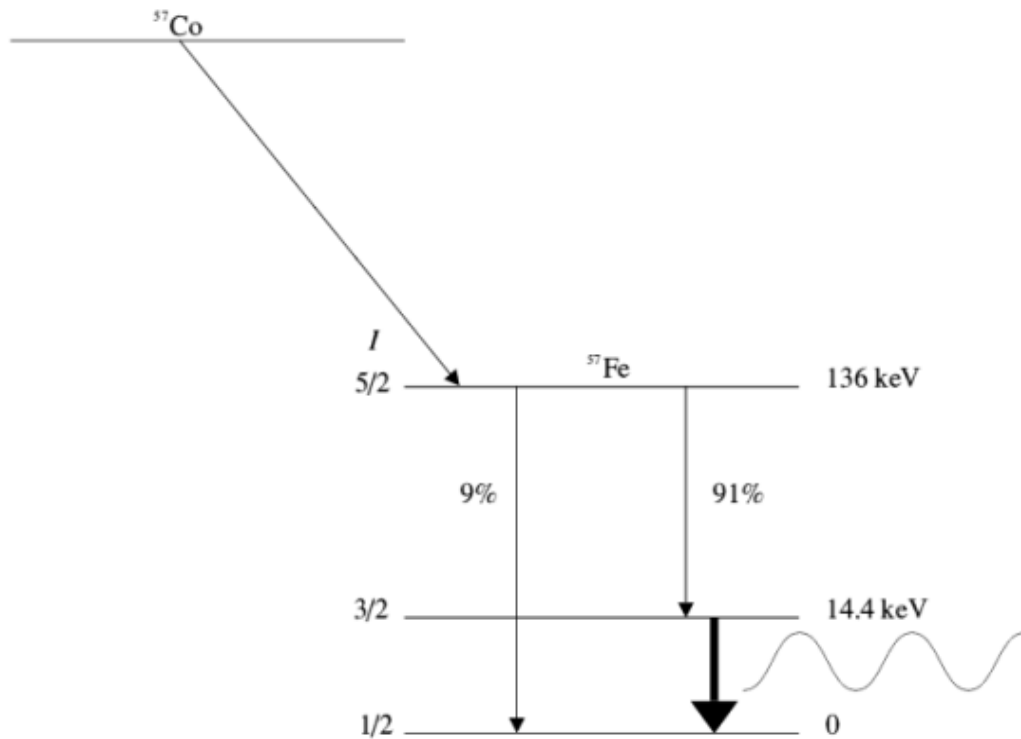
- Mössbauer dominated by internal conversion
- Source of gamma rays is a radioactive isotope of an element which decays into an excited state of the isotope under study
- Returns to the ground state by the emission of a gamma ray or electron
  - Mössbauer active isotopes must have a meta-stable excited state
- The relaxation to the ground state produces the gamma rays used in experiment

Mössbauer Spectroscopy
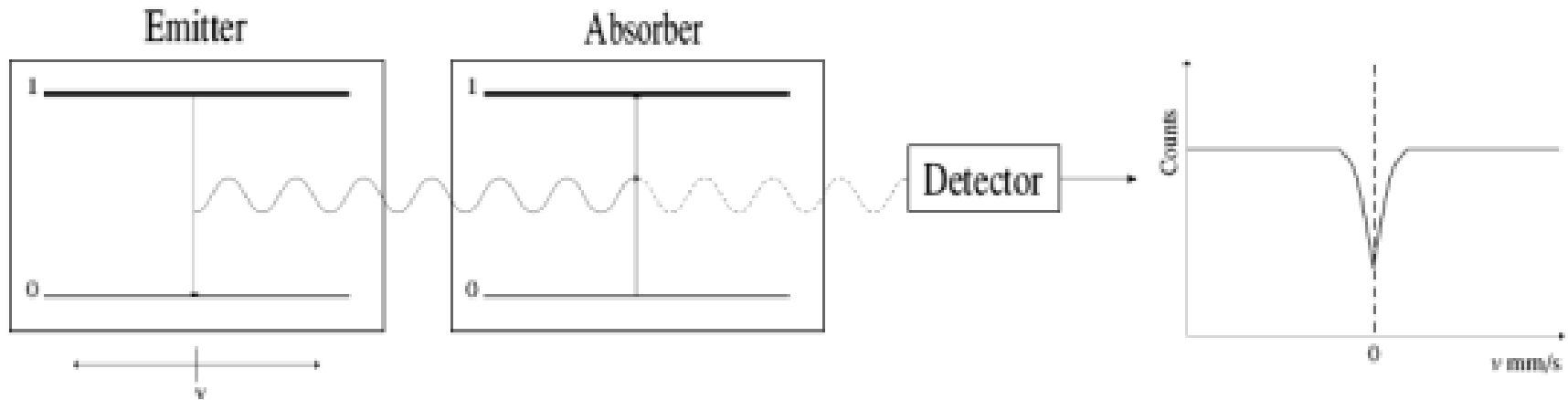
- By moving the gamma ray source a change in energy of the emitted photons is achieved using the Doppler effect
- When the energy of the modulated beam matches the difference in energy between the ground and first excited state of the absorber then the gamma rays are resonantly absorbed
- Measures transmittance so peaks appear as a decrease in counts in the spectrum

Theory of NRVS

- NRVS measures inelastic scattering of the gamma rays

- Selective for vibrations involving displacement of Mössbauer active nuclei
  - No optical selection rules apply
  - Yielding the complete set of motions involving probed nucleus

- The peaks seen are recoil-free resonance energies corresponding to vibrational quanta

- Like Raman, NRVS is a very inefficient process, so an intense gamma ray source is needed

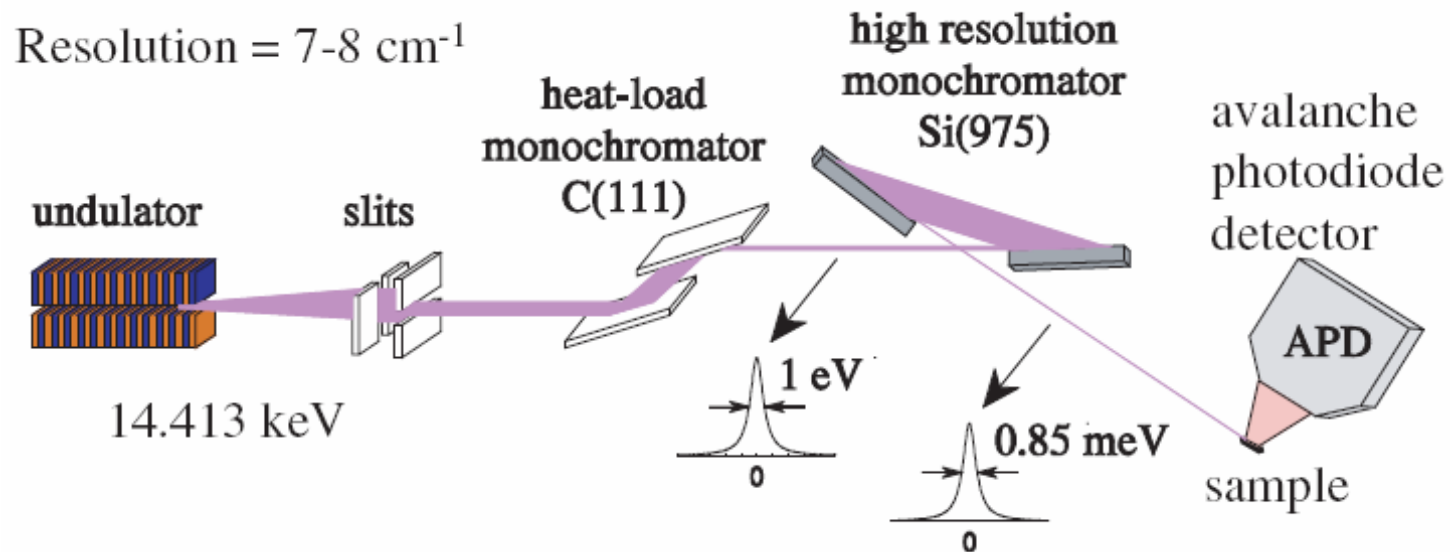# Nuclear Resonance Vibrational Spectroscopy (NRVS)

Experimental Setup

Undulator – synchrotron

- ❑ Only three 3rd generation synchrotron's in use
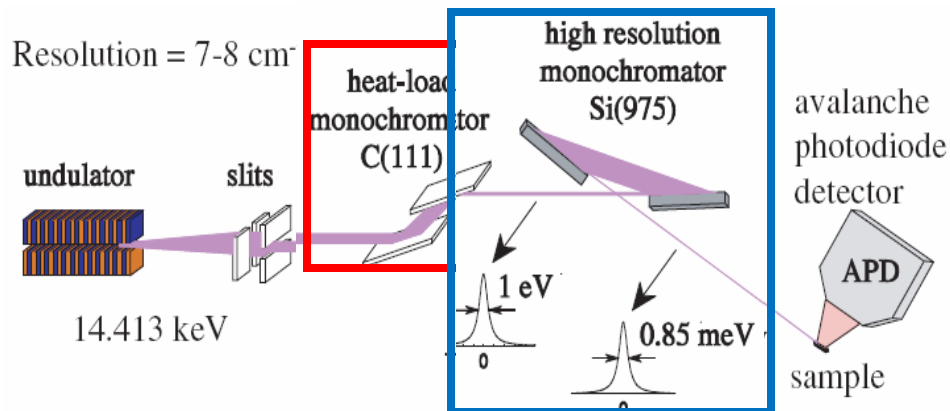
    France, USA, and Japan

Nuclear Resonance Vibrational Spectroscopy (NRVS)

NRVS Beamline

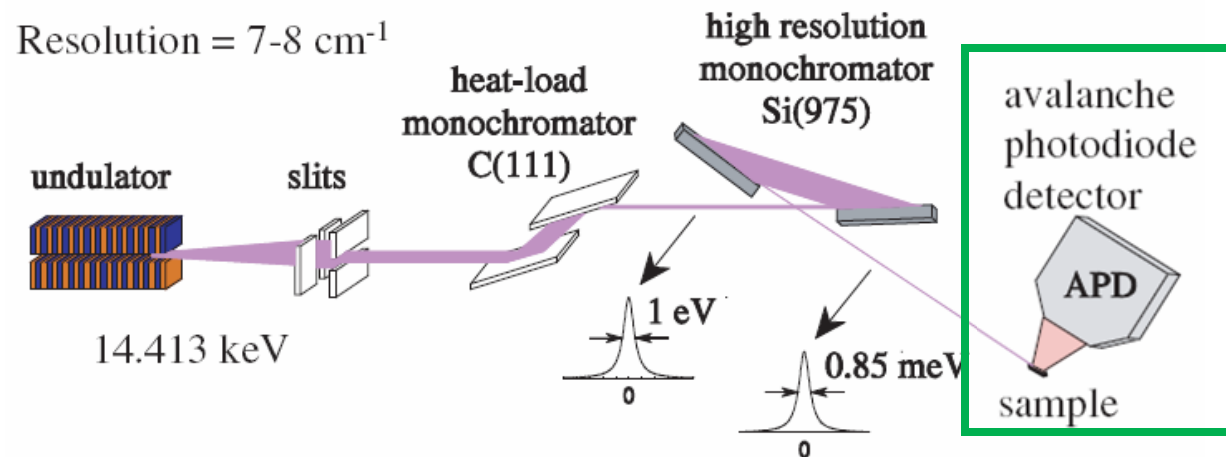'Raman' spectroscopy (inelastic scattering) on the Mössbauer line

Refining the Incident Beam

- **Heat-load Monochromator**
  - Composed of 2 crystals
    - Silicon (France, Japan)
    - Diamond (USA)
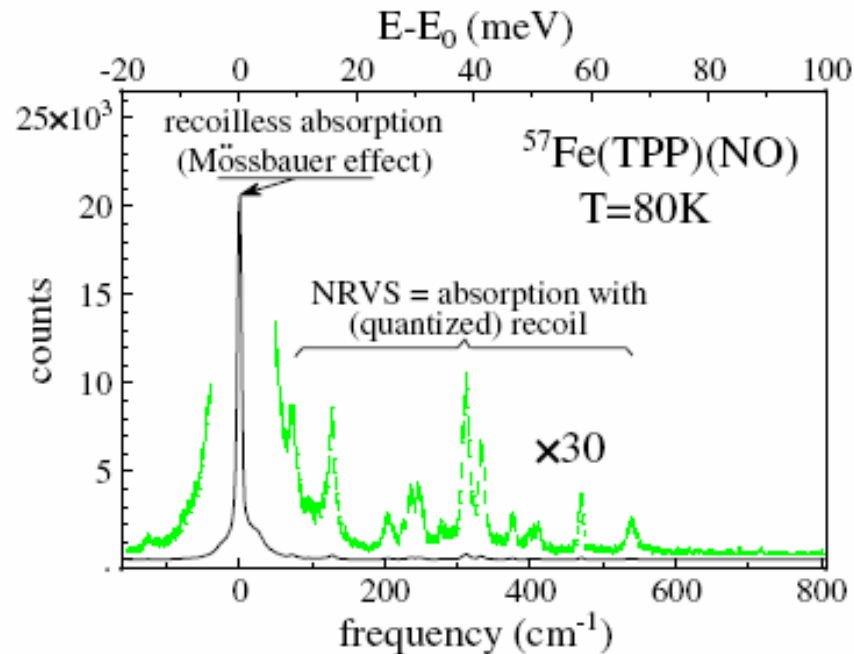 - Has to be well cooled
  - Beam is reduced to a few eV

- **High Resolution Monochromator**
  - Requires a separate crystal for each nuclei
  - Reduces the beam width to around 1meV

NRVS Theory: Sage, Sturhahn, Scheidt & coworkers, *J. Phys. Condens. Matter* **2001**, *13*, 7707

Collection of Data

Resolution = 7-8 cm⁻¹

undulator   slits   heat-load monochromator C(111)   high resolution monochromator Si(975)   avalanche photodiode detector

14.413 keV

1 eV

0.85 meV

APD

sample

- Beam grazes sample at only 6°
- Detector is located 90° from sample
  - Avoids the large amount of elastic scattering that comes off 180° from sample
- Measures the amount of counts to hit the detector

NRVS Theory: Sage, Sturhahn, Scheidt & coworkers, *J. Phys. Condens. Matter* **2001**, *13*, 7707

Example of Raw Data

- Software converts from raw intensity (photon count) to Vibrational Density of States (VDOS; see later)
- VDOS data can be used to calculate sample temperature, analogous to Stokes/Antistokes ratio in Raman spectroscopy
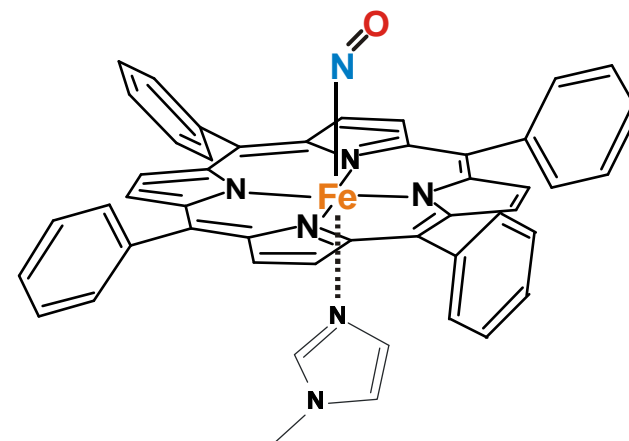
Scheidt, Sage & coworkers, *J. Inorg. Biochem.* **2005**, *99*, 60-71.

Case Study: Ferrous Heme Nitrosyls

- NO binding to deoxy Mb/Hb

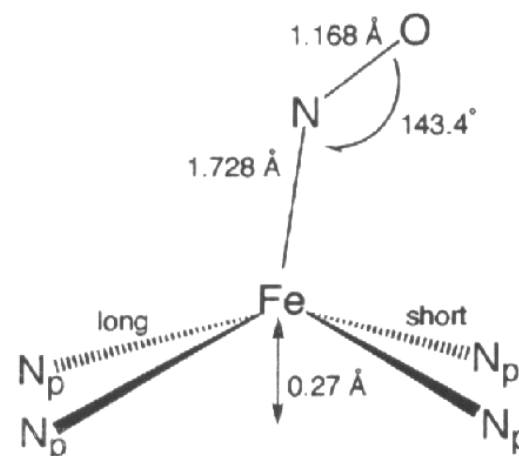 Effect of the distal hydrogen bond?
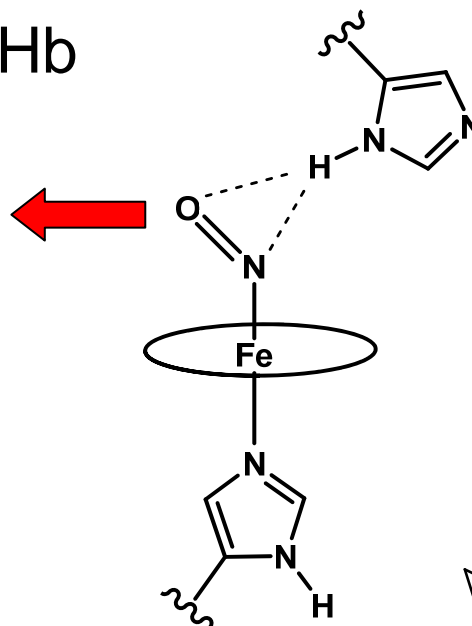
- Compare to model complex

[Fe(TPP)(MI)(NO)]
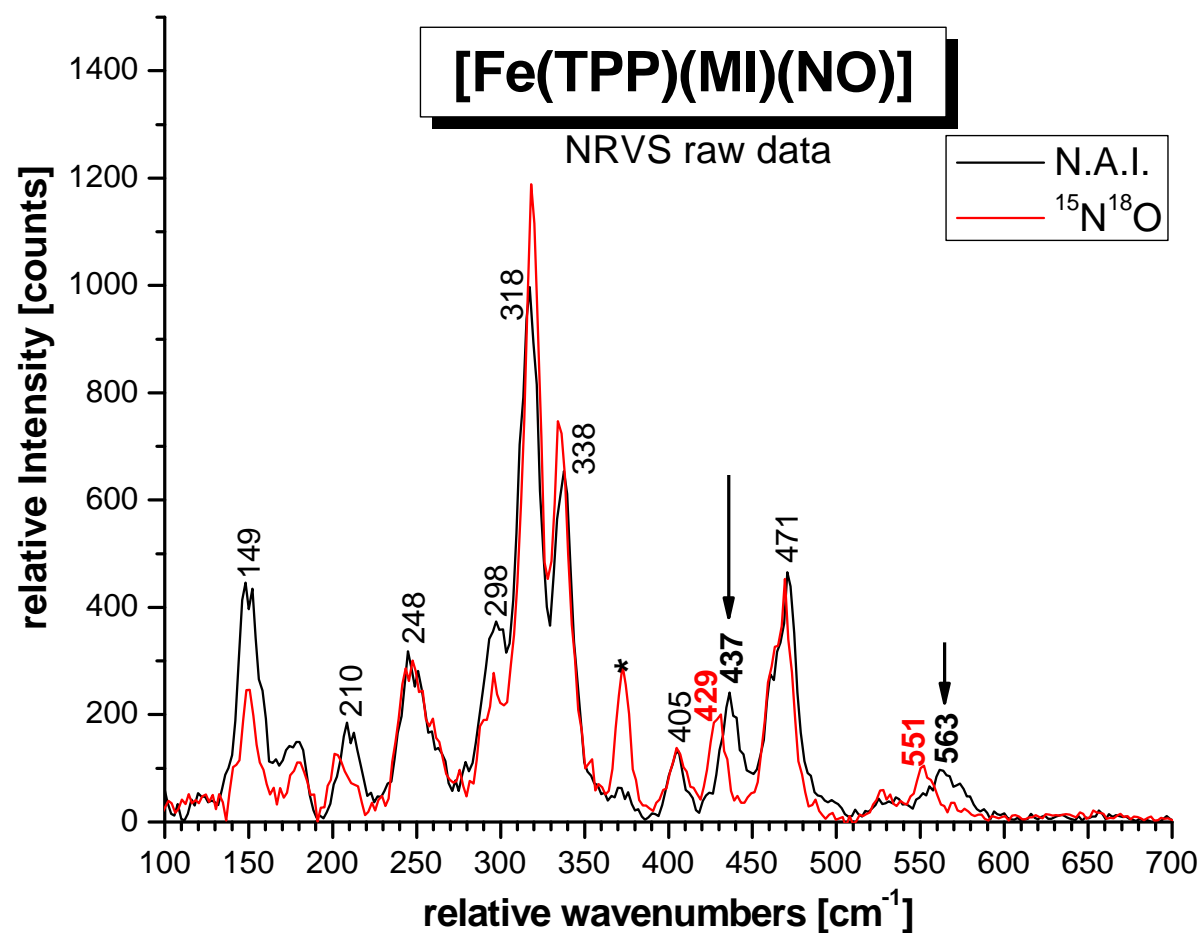
Ferrous Heme-Nitrosyls

- **Vibrational Spectroscopy: isotope labeling**
- **Important vibrations:**
  - N-O stretching
  - Fe-NO stretching
  - Fe-N-O bending

➡ Information about bond strengths, oxidation states, etc.

N. Lehnert, "Quantum Chemistry Centered Normal Coordinate Analysis (QCC-NCA): Application of NCA for the Simulation of the Vibrational Spectra of Large Molecules"; in: "Computational Inorganic and Bioinorganic Chemistry"; Solomon, E. I.; King, R. B.; Scott, R. A., Eds., The Encyclopedia of Inorganic Chemistry, John Wiley & Sons, Chichester, UK, **2009**, 123-140

NRVS on [Fe(TPP)(MI)(NO)]

Paulat, Berto, DeBeer George, Goodrich, Praneeth, Sulok & Lehnert, *Inorg. Chem.* **2008**, *47*, 11449

Vibrational Density of States (VDOS)
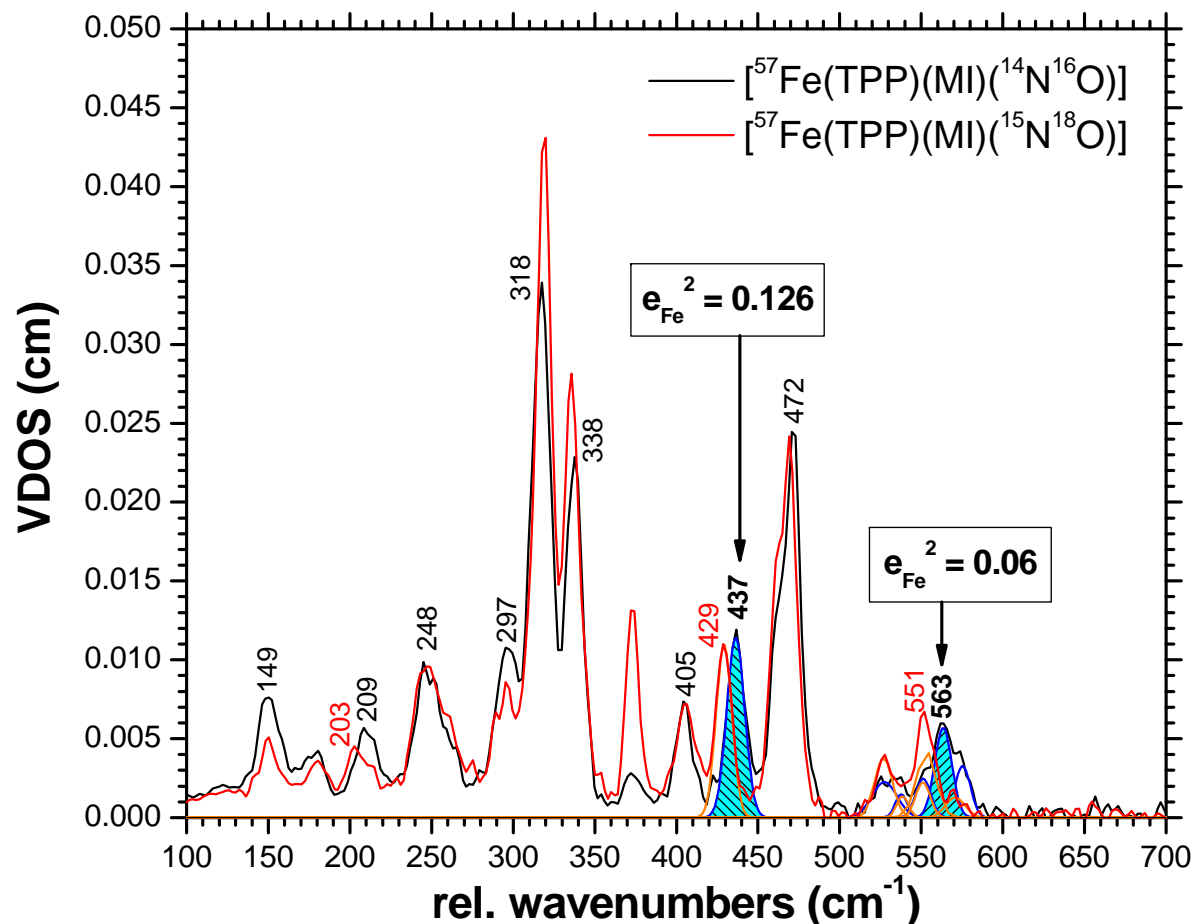
- Calculation of VDOS from NRVS raw intensity:

$$D(\widetilde{v}) = \sum_{\alpha=1}^{3N-6} e_{Fe,\alpha}^2 \cdot \Gamma(\widetilde{v} - \widetilde{v}_\alpha) \qquad \text{(total VDOS)}$$

$$D_k(\widetilde{v}) = \sum_{\alpha=1}^{3N-6} \left(\vec{k} \cdot \vec{e}_{Fe,\alpha}\right)^2 \cdot \Gamma(\widetilde{v} - \widetilde{v}_\alpha) \qquad \text{(VDOS in direction } k;\ k = x,\, y,\, z)$$

- Factors e_{Fe}^2 : amount of iron motion in a normal mode → specific property of a vibration:

$$e_{Fe}^2 = \frac{m_{Fe}\, r_{Fe}^2}{\sum_i m_i\, r_i^2}$$

Sage, Sturhahn, Scheidt & coworkers, *J. Phys. Condens. Matter* **2001**, *13*, 7707
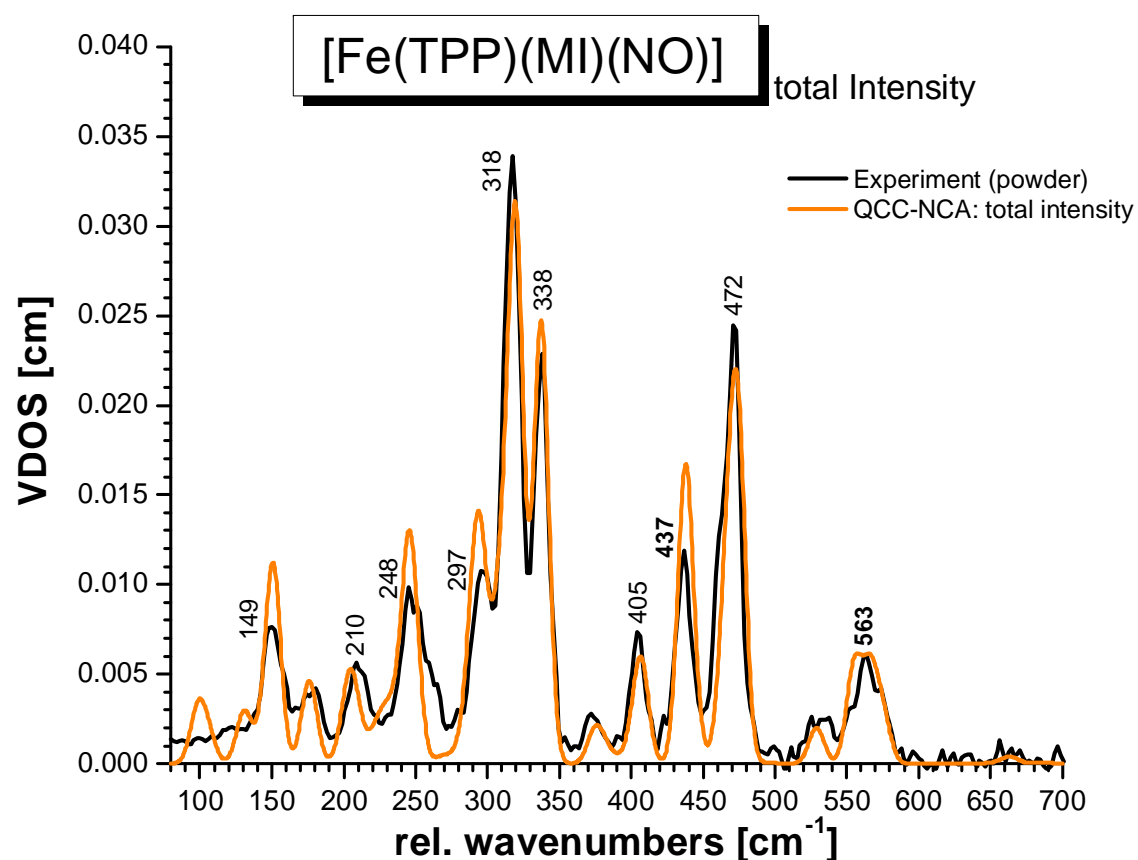
Vibrational Density of States (VDOS)

• Integrated VDOS intensity is proportional to the amount of iron motion in a normal mode
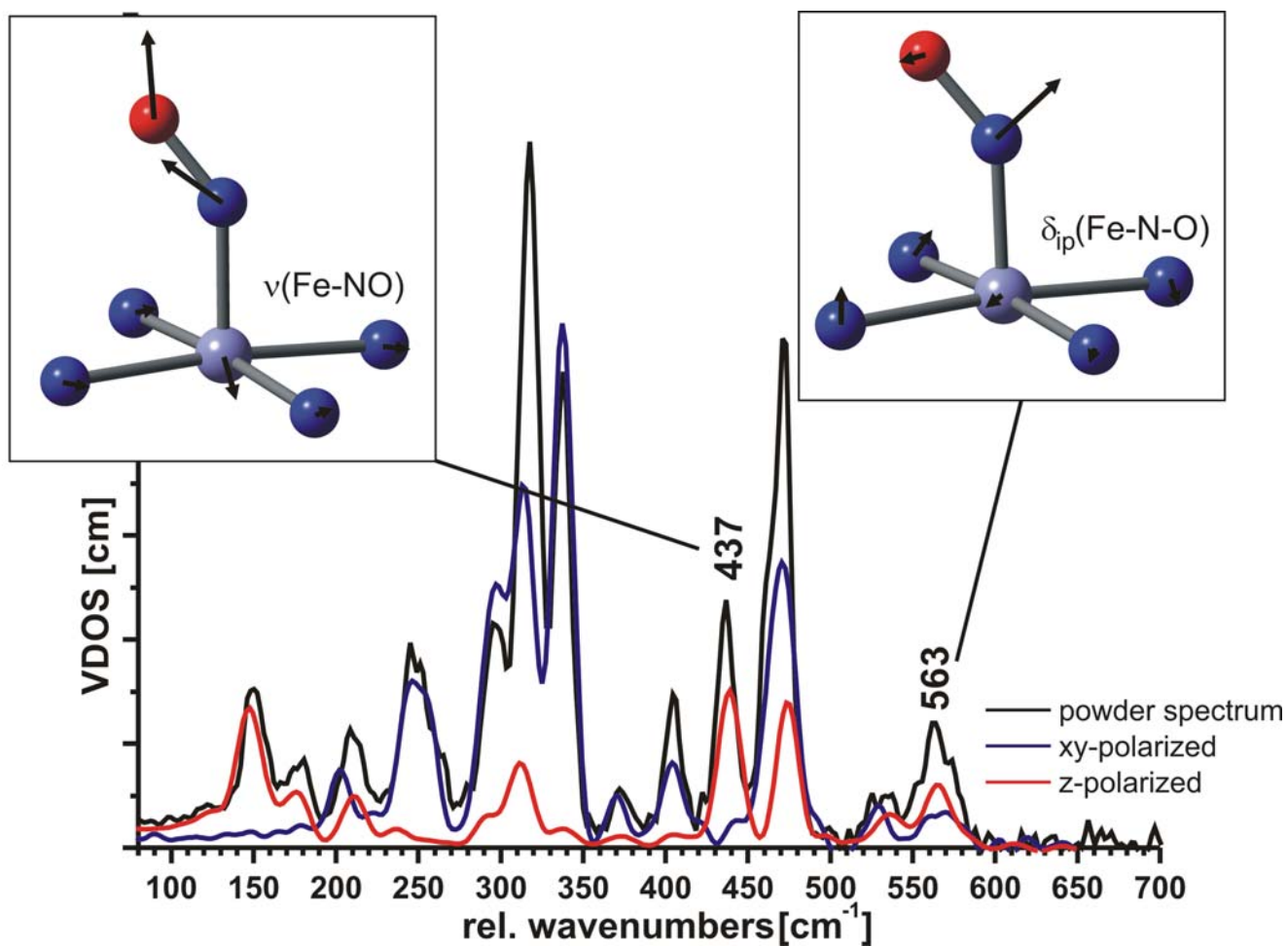• Can be simulated using normal coordinate analysis!

EXP:

$$\frac{e_{Fe}^2[563]}{e_{Fe}^2[437]} \approx 0.48$$

Paulat, Berto, DeBeer George, Goodrich, Praneeth, Sulok & Lehnert, *Inorg. Chem.* **2008**, *47*, 11449

Vibrational Analysis (NCA)

- Simulation of Data using Normal Coordinate Analysis (with some help from DFT: QCC-NCA method)

QCC-NCA: Praneeth, Näther, Peters & Lehnert, *Inorg. Chem.* **2006**, *45*, 2795

Assignment

Lehnert, Sage, Silvernail, Scheidt, Alp, Sturhahn & Zhao, *Inorg. Chem.* **2010**, *49*, 7197
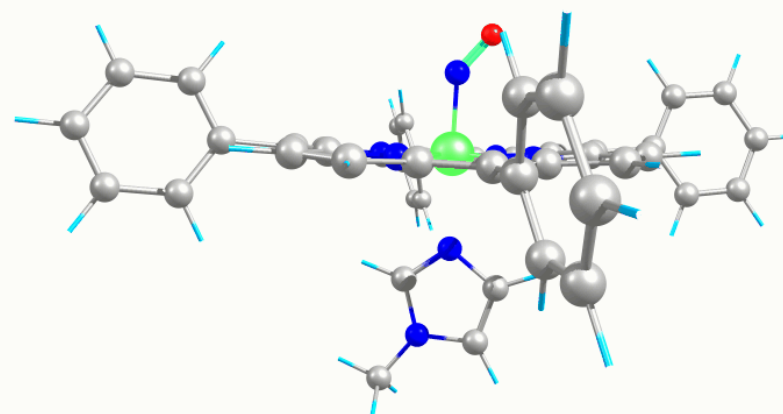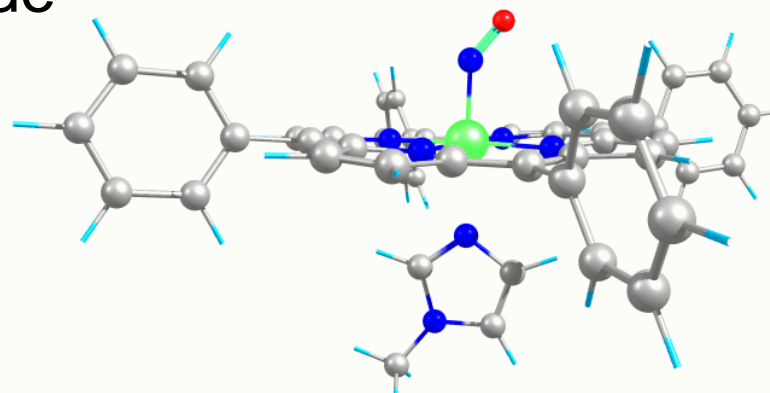
Or a bit more dynamic…

- The Fe-N-O bending mode
  (563 cm^{-1})

- The Fe-NO stretching mode
  (437 cm^{-1})

Summary

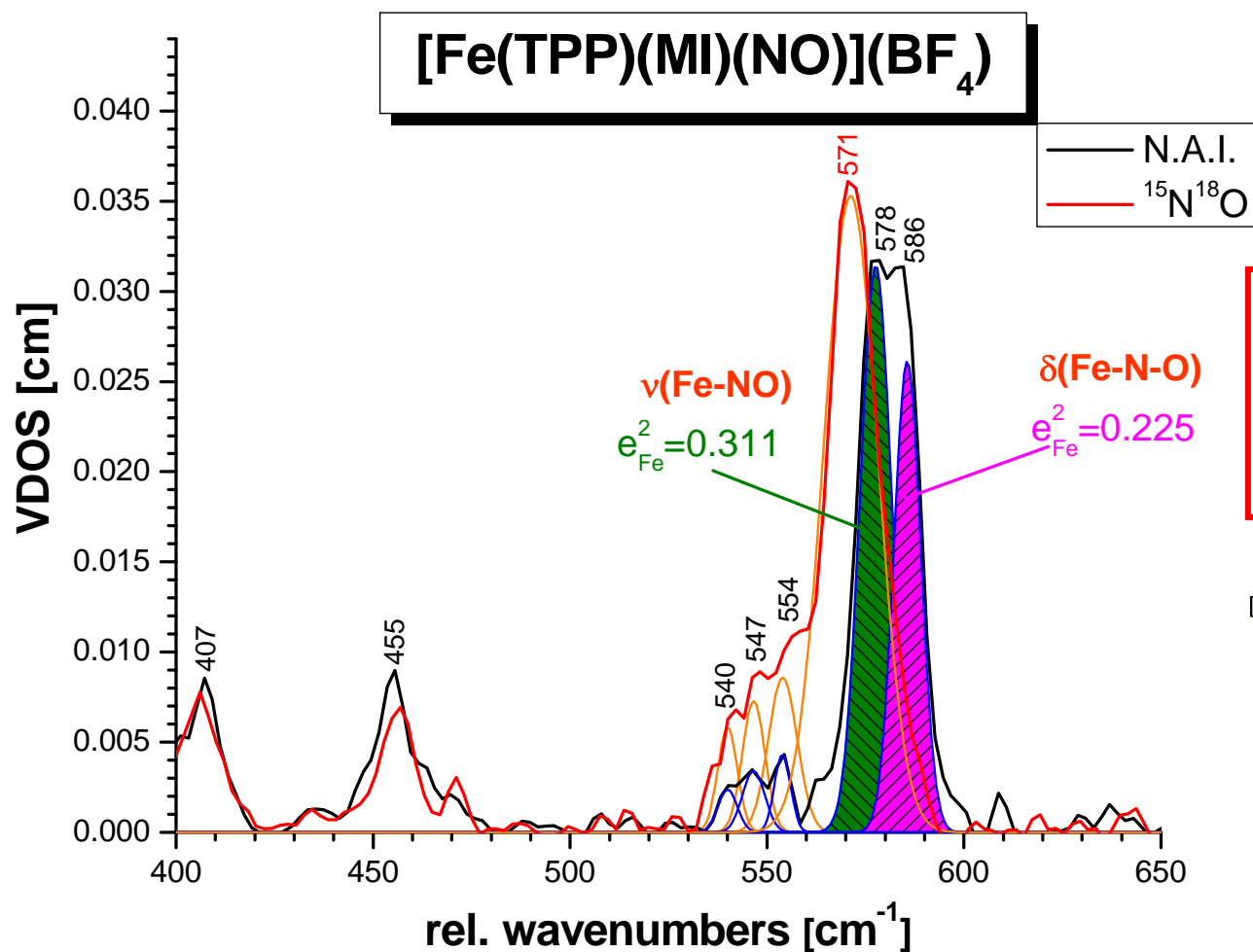- [Fe(TPP)(MI)(NO)] models hydrogen-bond free Mb mutants!

Similar Fe-NO stretching frequency in wt Mb(II)-NO and [Fe(TPP)(MI)(NO)] indicates weak effect of H-bond on Fe-NO bond!

Shift in N-O stretching frequency is due to polarization of the π/π^* orbitals of NO

Data from: Coyle, Vogel, Rush III, Kozlowski, Williams, Spiro, Dou, Ikeda-Saito, Olson & Zgierski, *Biochemistry* **2003,** 42, 4896

Lehnert, Sage, Silvernail, Scheidt, Alp, Sturhahn & Zhao, *Inorg. Chem.* **2010**, *49*, 7197

One Electron Oxidation

- NRVS on [Fe(TPP)(MI)(NO)](BF$_4$) – the analogous ferric complex
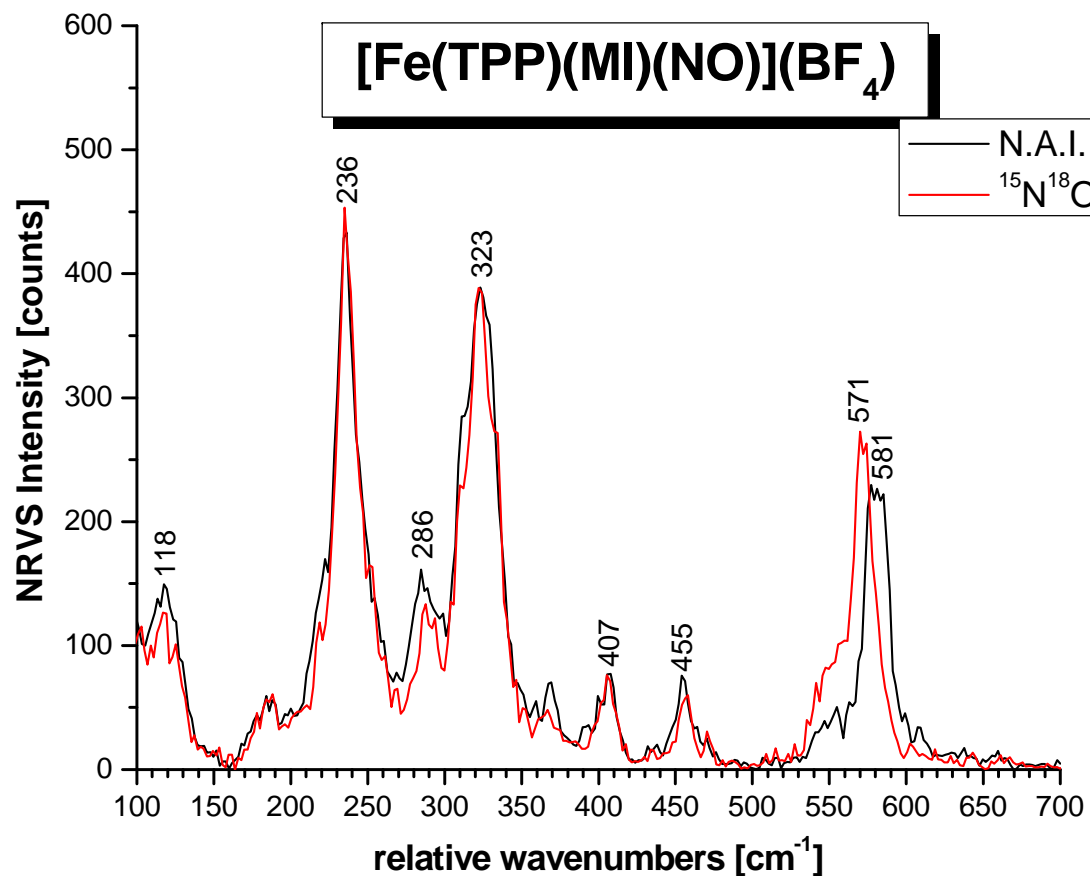
V. K. K. Praneeth, F. Paulat, T. C. Berto, S. DeBeer George, C. Näther, C. D. Sulok, N. Lehnert, *J. Am. Chem. Soc.* **2008**, *130*, 15288

NRVS on [Fe(TPP)(MI)(NO)](BF$_4$)

V. K. K. Praneeth, F. Paulat, T. C. Berto, S. DeBeer George, C. Näther, C. D. Sulok, N. Lehnert, *J. Am. Chem. Soc.* **2008**, *130*, 15288