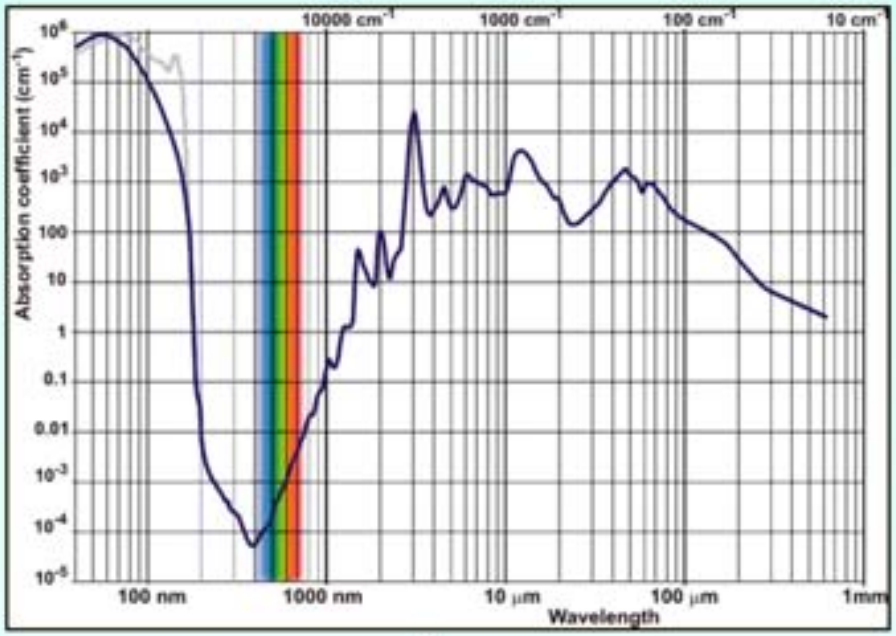
Biomolecular vibrational spectroscopy

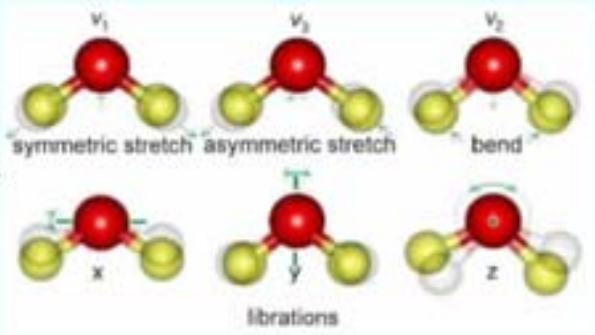
Methods in Molecular Biophysics, Spring 2010

Basics of normal mode theory
Amide vibrations in proteins
Nuclear resonance vibrational spectroscopy

Small molecule vibrational spectoscopy



Wavelength	cm^{-1}	Assignment	Wavelength[a]	cm^{-1}	Assignment
0.2 mm	50	intermolecular bend?	1470 nm	6800	$av_1 + bv_3$; a+b=2
55 μm	183.4	intermolecular stretch	1200 nm	8330	$av_1 + v_2 + bv_3$; a+b=2
25 μm	395.5	L_1, librations	970 nm	10310	$av_1 + bv_3$; a+b=3
15 μm	686.3	L_2, librations	836 nm	11960	$av_1 + v_2 + bv_3$; a+b=3
6.08 μm	1645	v_2, bend	739 nm	13530	$av_1 + bv_3$; a+b=4
4.65 μm	2150	$v_2 + L_2$	660 nm	15150	$av_1 + v_2 + bv_3$; a+b=4
3.05 μm	3277	v_3, asymmetric stretch	606 nm	16500	$av_1 + bv_3$; a+b=5 [526]
2.87 μm	3490	v_1, symmetric stretch	514 nm	19460	$av_1 + bv_3$; a+b=6 [526]
1900 nm	5260	$av_1 + v_2 + bv_3$; a+b=1	Note that a and b are integers, ≥0		

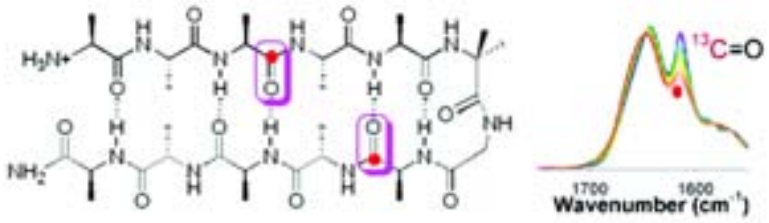


Amide vibrational spectra in proteins

Cross-Strand Coupling of a β-Hairpin Peptide Stabilized with an Aib-Gly Turn Studied Using Isotope-Edited IR Spectroscopy

Rong Huang, Vladimir Setnic#ka, Marcus A. Etienne, Joohyun Kim, Jan Kubelka, Robert P. Hammer, and Timothy A. Keiderling

J. Am. Chem. Soc., **2007**, 129 (44), 13592-13603• DOI: 10.1021/ja0736414 • Publication Date (Web): 11 October 2007



Scheme 1. Design Structure of Gellman A Peptide Showing Numbering of Individual Residues in Sequence and ^{13}C=O-Labeling Patterns (colored rectangles)

Deconvoluting complex spectra

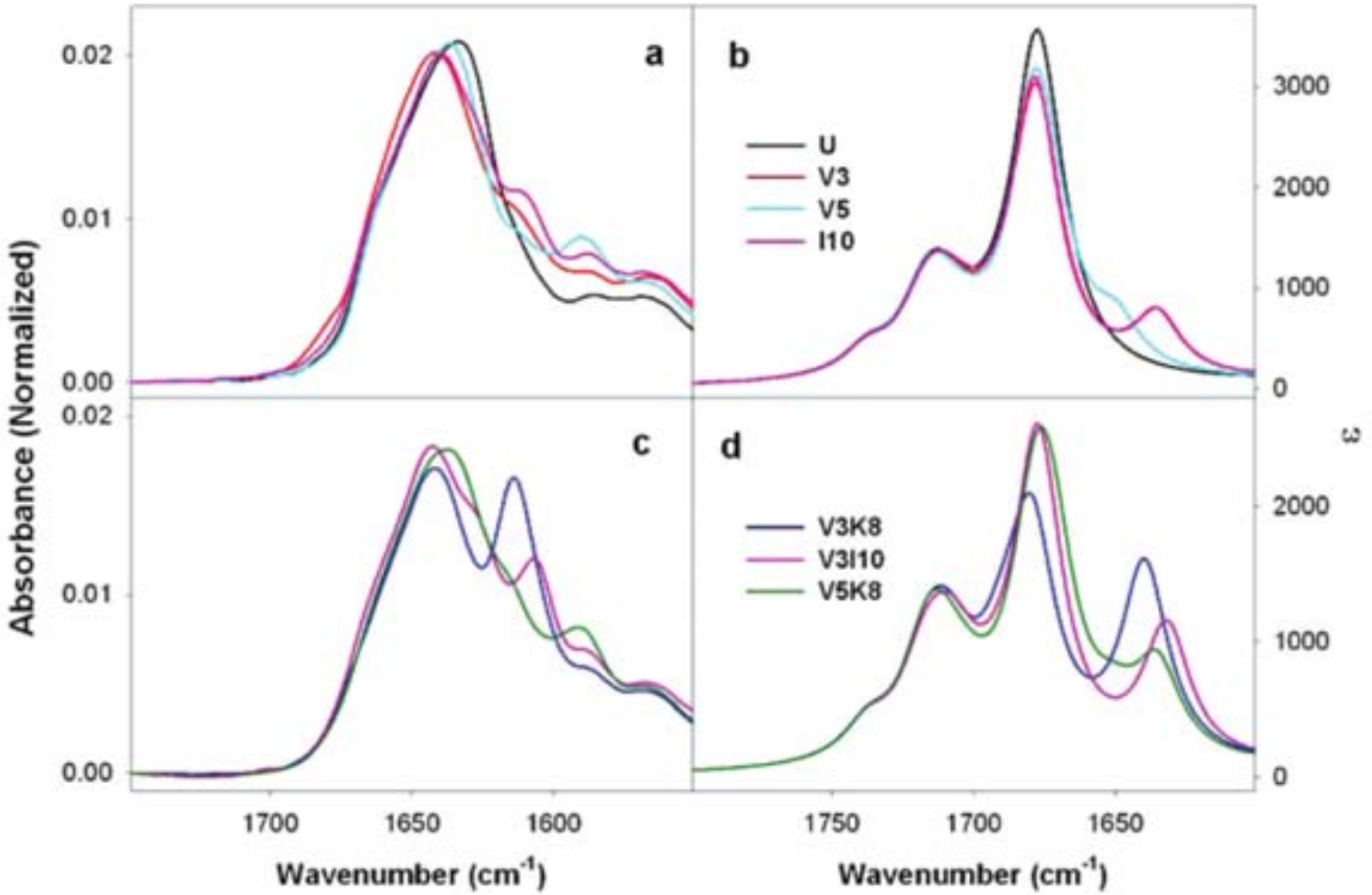


Figure 2. Experimental IR spectra of (a) the unlabeled and single-labeled hairpin peptides and (c) the double-labeled peptides. The experime were normalized to have a peak area of 1 between 1720 and 1550 cm^{-1}. The original spectra of all peptides were measured at ~23 mg/ml deuterated phosphate buffer in a 100 μm path length cell. Simulated IR spectra of Ac-A_{12}-$NHCH_3$ by transfer from shorter fragments are in unlabeled peptide compared with single-labeled peptides **A3**, **A5**, and **A10** and (d) for the double-labeled peptides **A3A8**, **A3A10**, and **A5A8**.

Deconvoluting complex spectra

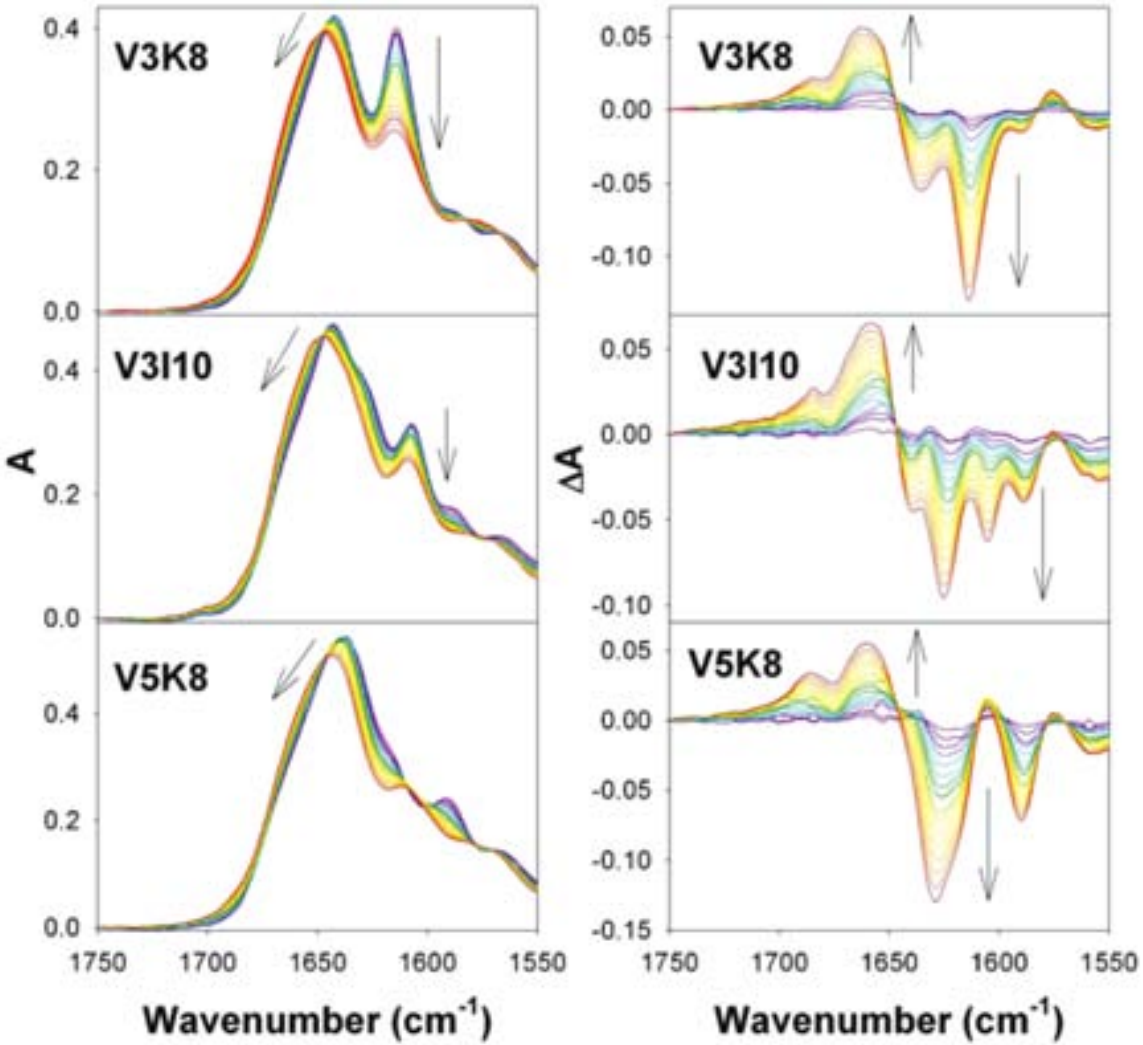


Figure 3. Original temperature-dependent IR spectra (left panels) and difference spectra (right panels) for double-labeled peptides **V3K8**, **V3I10**, and **V5K8**. All peptide concentrations were ~23 mg/mL in 20 mM deuterated phosphate buffer measured in a 100-μm path length cell. The difference spectra were taken by subtracting the spectrum at 5 °C from each spectrum at higher temperatures. In all panels the spectra are color coded for temperature, from blue at the cold (5 °C) extreme to red at the hot (95 °C) end, as suggested by the arrows.

Fitting conformational preferences

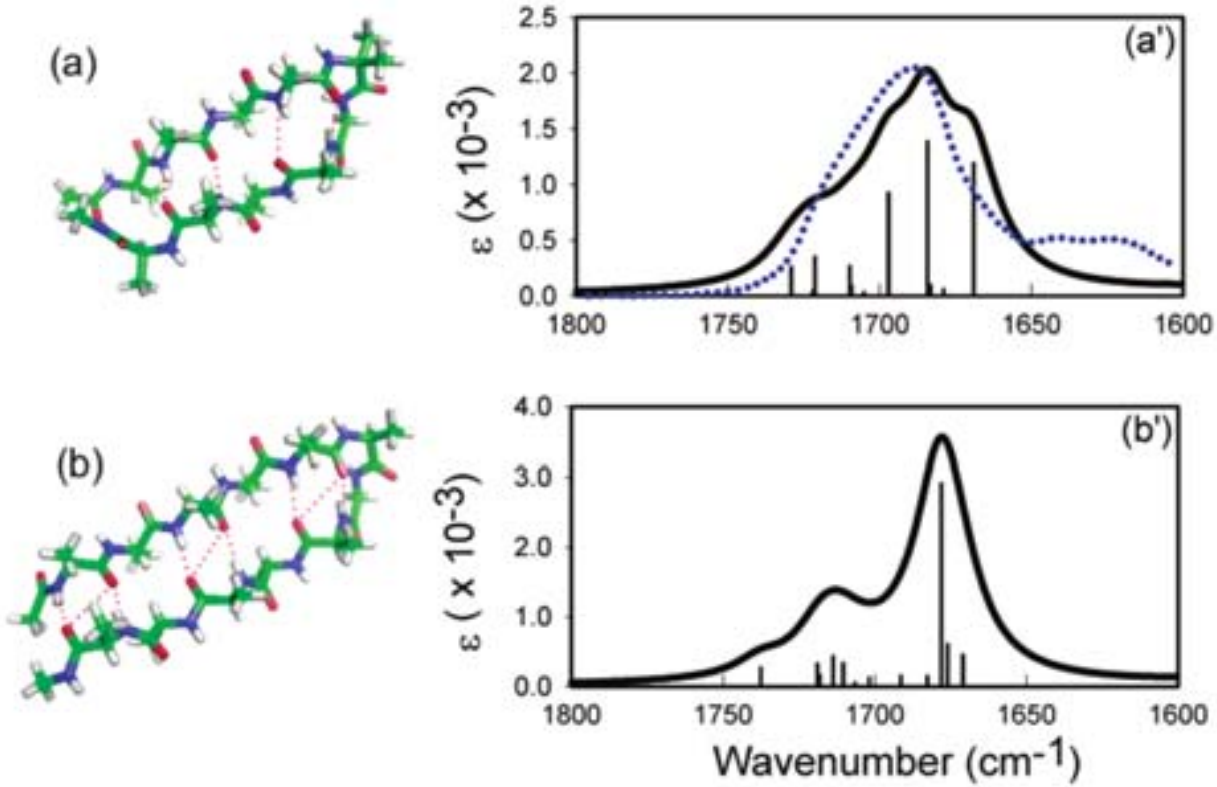


Figure 6. Amide I IR spectra for structures IV and V. Snapshot schematic of structure IV, obtained from an NMR structure, is shown in part a. Structure V, modeled from the crystal structure of 1IFC is shown in part b. The corresponding spectra are in parts a′ and b′, respectively. The experimental spectrum (low *T*) of the HBG peptide is shifted and scaled as in Figure 5 and represented as the blue, dotted spectrum in part a′.

Fitting conformational preferences

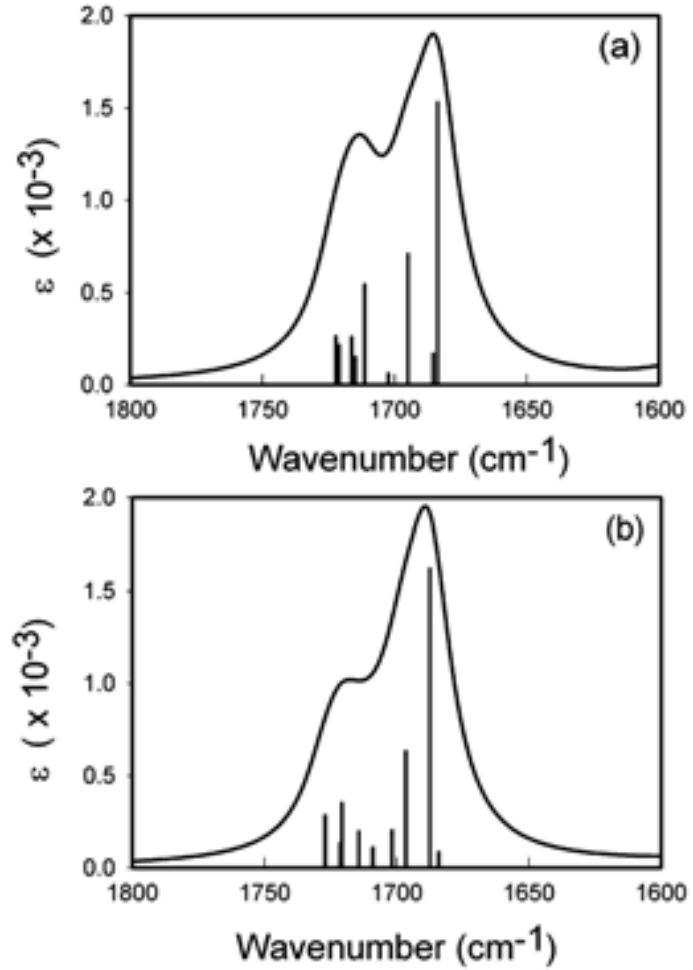
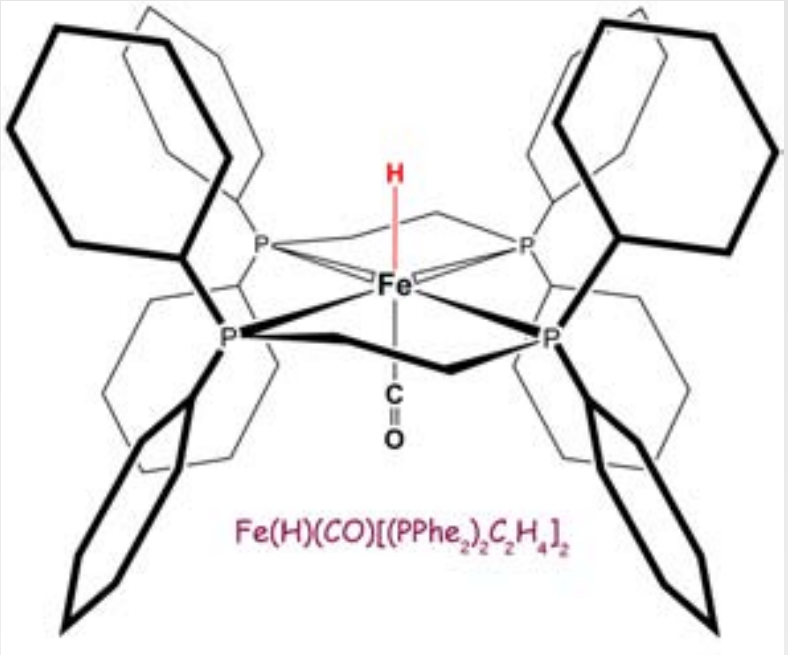
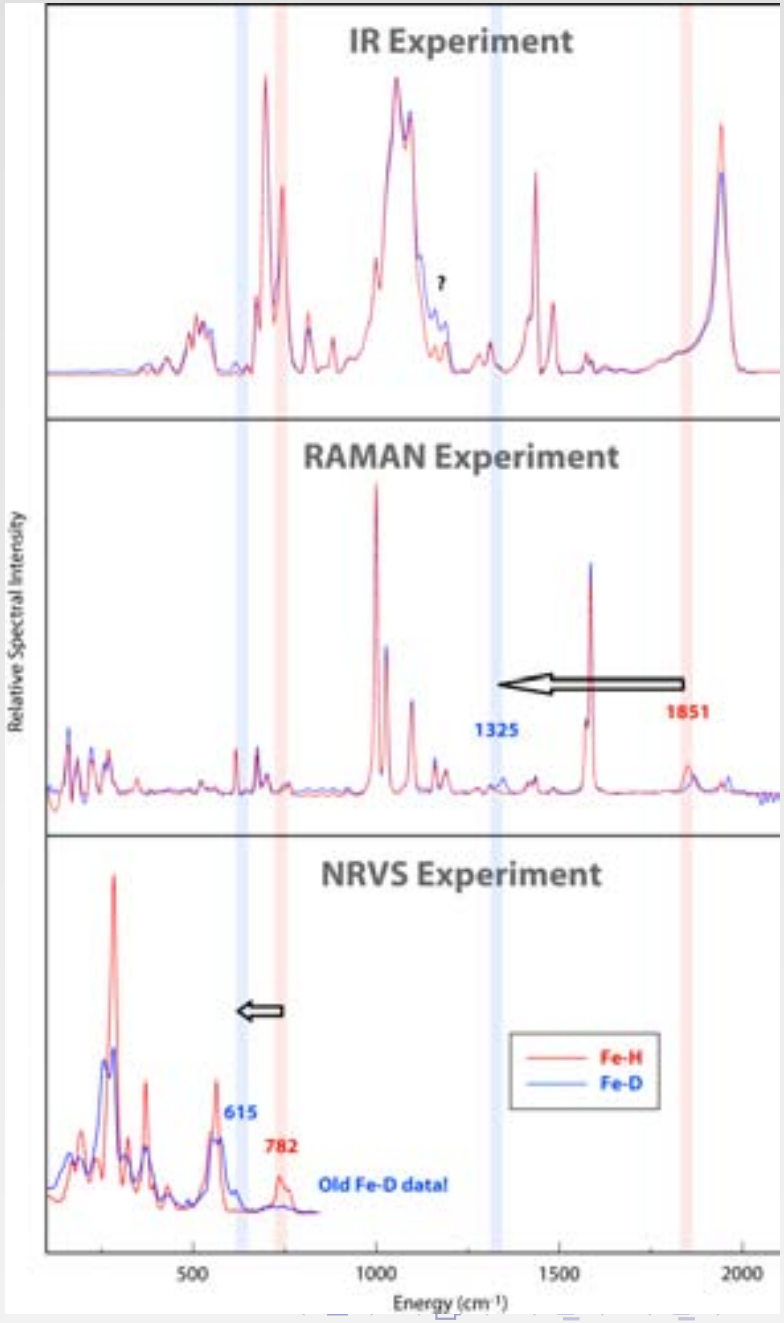


Figure 4. Amide I IR spectra of the 9-amide β-hairpin model. (a) Simulated spectra by the CSPT and (b) simulated spectra with the direct DFT.

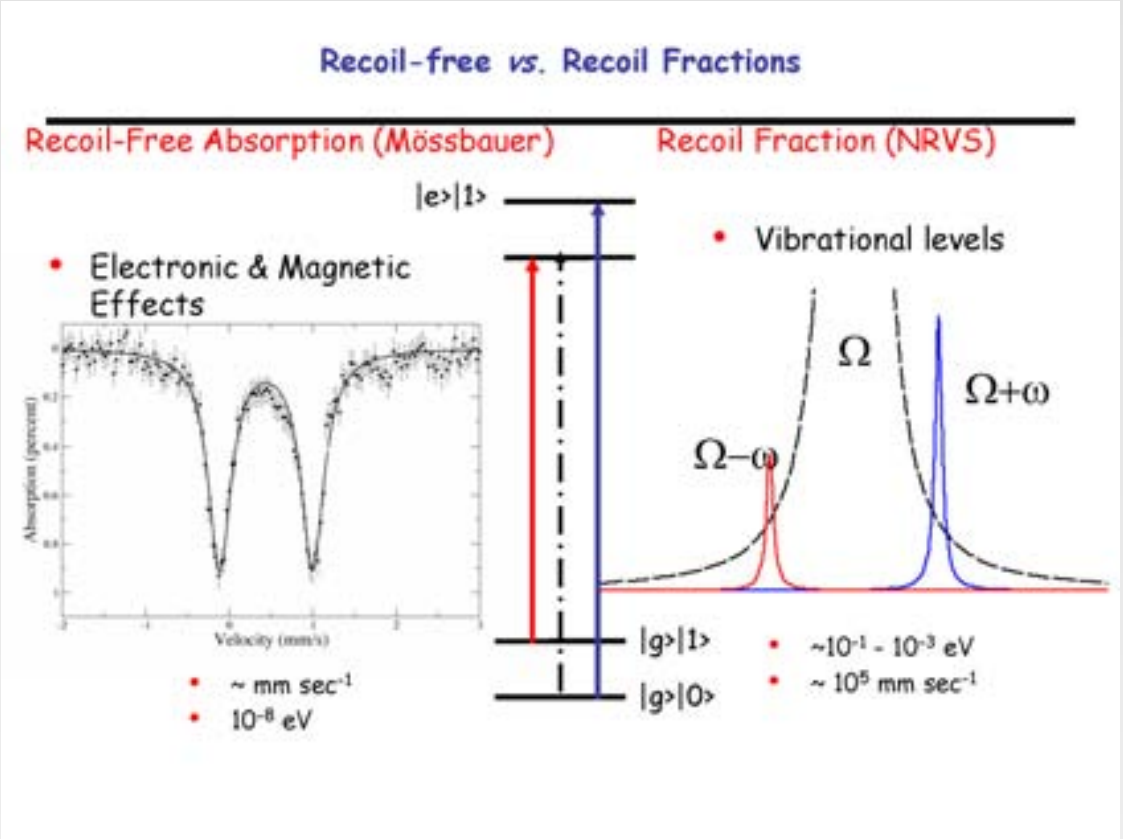
Complementary vibrational probes



cf. Guo, et al. *Inorg. Chem.* **47**: 3969, 2008

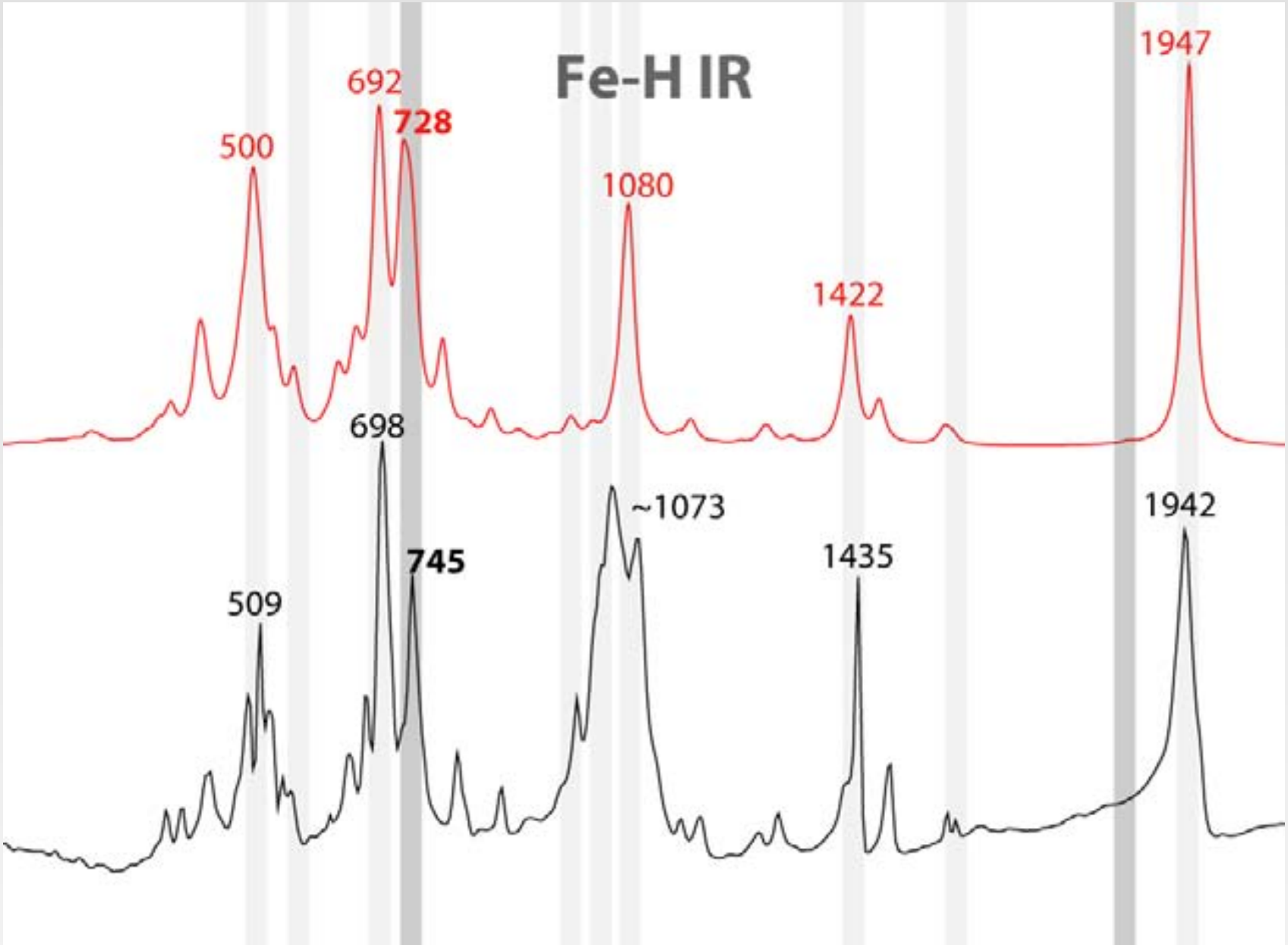


Nuclear resonance vibrational spectroscopy

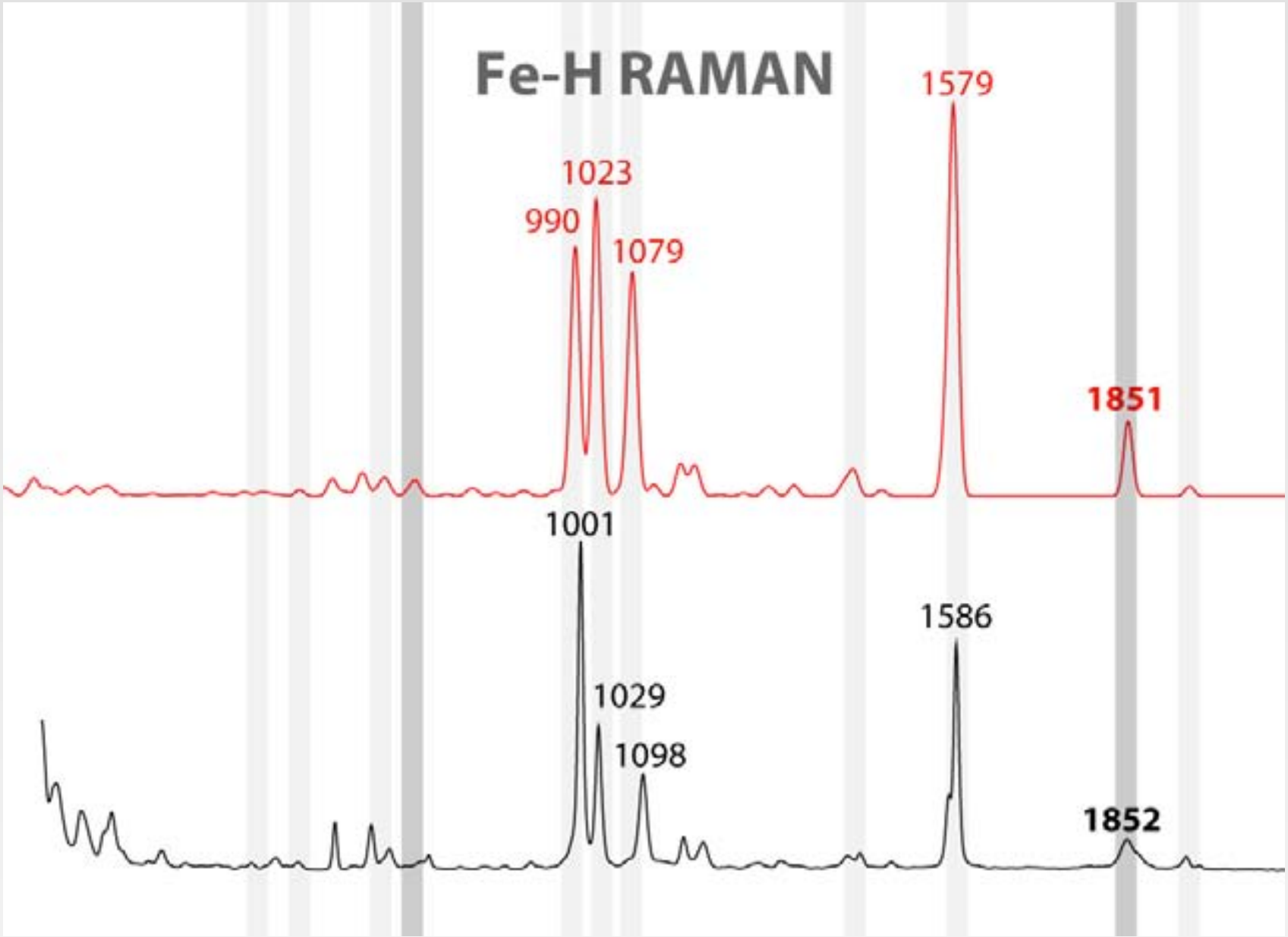


- "vibrational Mossbauer"
- only ^{57}Fe contributes (no background)
- intensity is proportion to KE in mode due to iron
- "acoustic" librational modes visible (in principle)

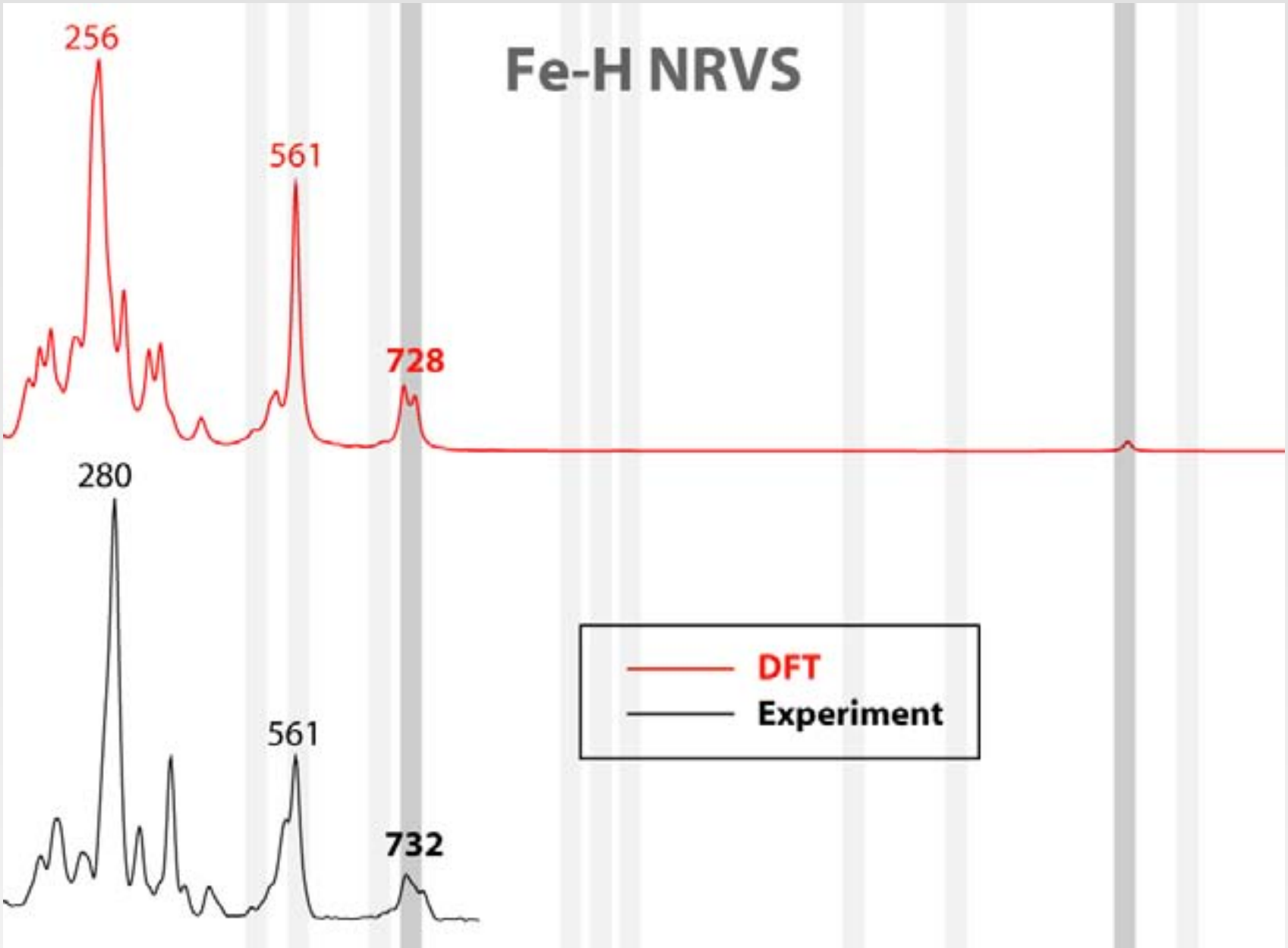
Model compound IR spectra



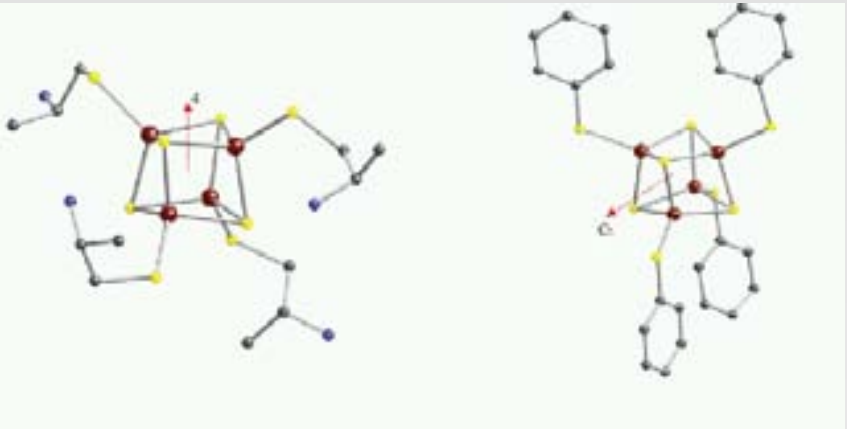
Model compound Raman spectra

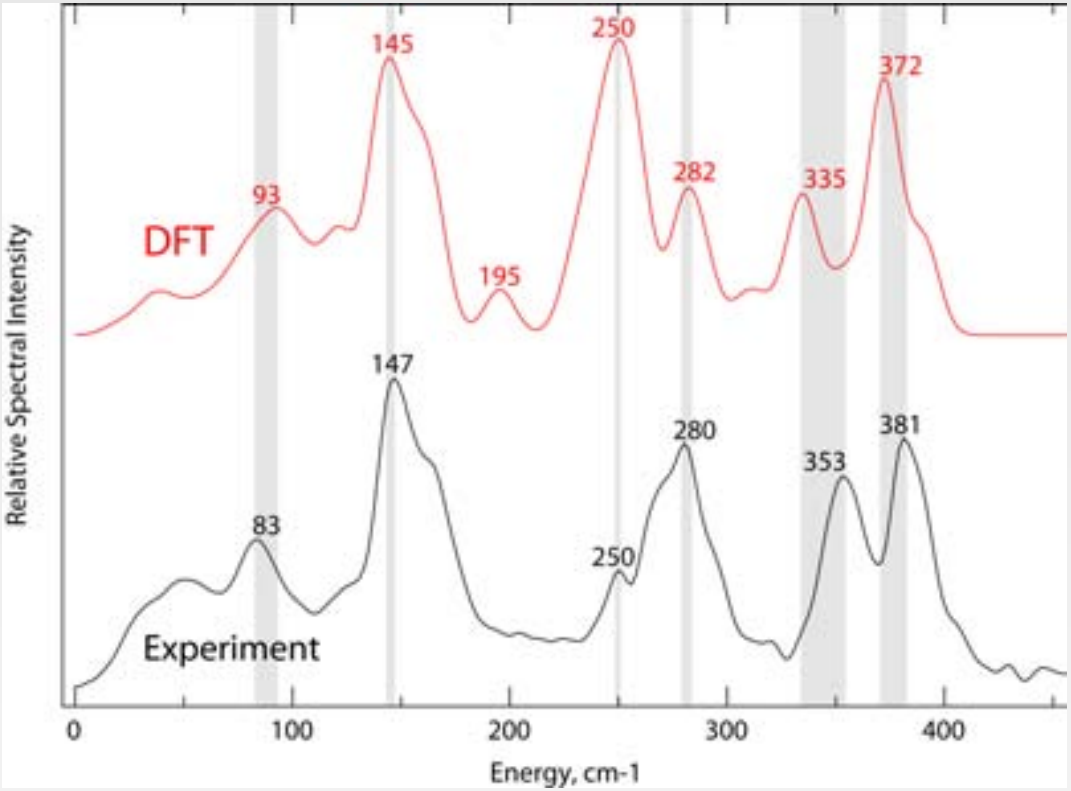


Model compound NRVS spectra



Moving to a ferrdoxin protein





Isotope shifts in the protein environment