Nuclear Resonant Vibrational Spectroscopy: A New Look at the Vibrational Spectra of [2Fe-2S] Clusters

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Iron-sulfur clusters are ubiquitous in nature. We have examined the [2Fe-2S] moiety found in Fe-only hydrogenase, ferredoxins, and Rieske type proteins via nuclear resonant vibrational spectroscopy (NRVS); an important new technique for understanding iron metalloenzymes through their vibrational spectra. It has the attribute of being element specific, as it is sensitive only to vibrations containing significant displacement of a Mössbauer type nucleus, ^{57}Fe for instance. Other techniques such as resonance Raman spectroscopy can give similar information but these often suffer from the lack of suitable optical bands or interference by fluorescent chromophores. Thus NRVS has the potential to provide information not available from any other technique .

The reduced and oxidized metalloenzymes studied have significantly different vibrational spectra (for example see figure 1), whilst similar spectra were recorded for different enzymes in the same oxidation state, i.e. the Fe(III)-Fe(III) core of the oxidized ferredoxin, Rieske type protein and the inorganic complex $[NEt_4][Fe_2S_2Cl_4]$ [**1**]. A complete normal mode analysis has been completed for [**1**][1] and is used as the starting point for solving the vibrational modes of the biological systems.

The Fe-only hydrogenase contains a unique [2Fe-2S] core and its mechanism is poorly understood. Using NRVS we have examined its vibrational spectra, and in conjunction with theoretical work, resonance Raman and IR, are attempting to elucidate it's key features such as iron oxidation states and substrate binding sites.

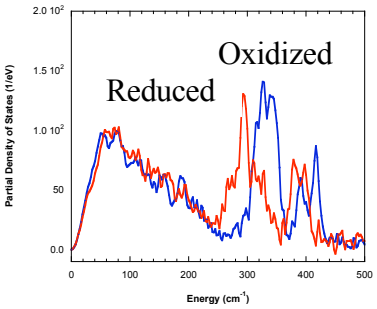

Figure 1. NRVS for [2Fe-2S] from *Aquifex aeolicus*

1. M.C. Smith, Y. Xiao, H. Wang, S.J. George, D. Coucouvanis, M. Koutmos, W. Sturhahn, E.E. Alp, J. Zhao, S.P. Cramer (2005) Normal Mode Analysis of $FeCl_4^-$ and $Fe_2S_2Cl_4^{2-}$ *via* Vibrational Mössbauer, Resonance Raman, and FT-IR Spectroscopy. Accepted for publication in *Inorg. Chem.*