X-ray MCD as a probe of Iron-Sulfur proteins magnetic structure

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Proteins containing Fe:S centers are ubiquitous in nature. These clusters play key roles in many biocatalytic processes, both as enzyme active sites and electron storage and transfer agents. Many of these clusters are paramagnetic, allowing study of their valence and spin coupling through their magnetic properties. The spin state of these coupled Fe systems is influenced by the cluster amino-acid ligands and residues in the protein pocket.

We have been measuring X-ray magnetic circular dichroism (XMCD) at Fe $L_{2,3}$-edges of [2Fe-2S] and [4Fe-4S] ferredoxins (Fd) in order to better understand the electronic and magnetic properties of these clusters. This technique is potentially a sensitive, element and site specific, probe of valence, covalence and spin structure. This is particularly true for transition metal L-edge transition (2p->3d), since the 3d unoccupied states are being accessed. The XAS and XMCD spectra measured for reduced 2Fe-2S *Aquifex aeolicus (Aa)* (S=1/2), 4Fe-4S D14C (S=1/2) and A33Y (S=3/2) variants of *Pyrococcus furiosus (PyF)* are shown in Figure 1. Initial analysis of the XMCD spectrum for *Aa* [2Fe-2S] cluster show a positive peak. This is not easily explained by simple antiferromagnetic coupling of independent Fe(II) and Fe(III) ions. Moreover the main peak of the XMCD is centered around the Fe(III) contribution. Interestingly, this changes for *PyF* [4Fe-4S] clusters, where the peak is centered around the Fe(II) contribution. Even more interesting is that the XMCD measured for A33Y variant (S=3/2) is smaller than that measured for D14C (S=1/2), which contradicts that expected for an individual spin system. The data are being interpreted using a spin Hamiltonian with the exchange coupling term explicitly included, combined with crystal field multiplet contribution of each individual ion.

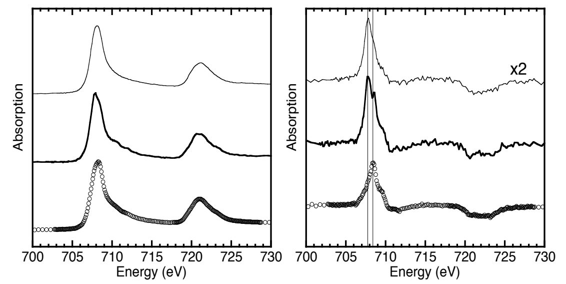

Figure 1 – XAS (left) and XMCD (right) for *Aa* 2Fe-2S (open circles), *PyF* D14C 4Fe-4S (thick line) and *PyF* A33Y 4Fe-4S (thin line). All proteins are in their reduced state. XAS spectra normalized by the peak and XMCD are in proportion to XAS.