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Nuclear Forward Scattering (NFS) on Iron-Sulfur Proteins

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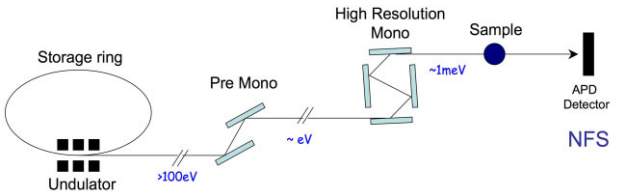
Introduction

Iron-Sulfur (Fe-S) proteins are among the most common and ancient enzymes and electron-transfer agents in nature. They play key roles in photosynthesis, respiration, and the metabolism of small molecules, such as H_2, CO and N_2. Fe-S proteins contain Fe-S clusters as active centers of the proteins, where chemical reactions happen. Conventional Mössbauer spectroscopy has achieved a great success to determine electronic structures of Fe-S clusters in Fe-S proteins [1]. Nuclear forward scattering (NFS) has been used to study minerals in earth's mantle, also it has been used to study model compounds in heme proteins [2]. Compared with conventional Mössbauer spectroscopy, instead of using radioactive sources, NFS uses synchrotron radiation to excite nuclei and monitor the decay of nuclear excited state in time domain; quantum beat pattern can be observed if the nuclear states contain nuclear hyperfine structures. NFS eliminates the contribution of radioactive source to the resolution of the spectrum, combining with long nuclear decay time observation windows, NFS could yield better spectroscopic resolution than conventional Mössbauer spectroscopy, which is important in studying complicated Fe-S proteins, such as nitrogenases and hydrogenases. Scheme 1 shows the experimental setup, Figure 1 shows the typical FeS cluster structures.

In this study, we used NFS for the first time on several Fe-S proteins under liquid N_2 and liquid He temperatures as well as magnetic field up to 7 Tesla. Nuclear decay signal has been observed up to 500 ns. Rubredoxin (Rd) and 4Fe ferredoxin (Fd) samples were provided by Prof. Mike Adams group in University of Georgia, US; 2Fe Fd sample was provided by Prof. Jacques Meyer in CEA, France, and Fe protein sample was provide by Prof. John Peters in Montana State University, US.



Scheme 1. NFS Experimental Setup

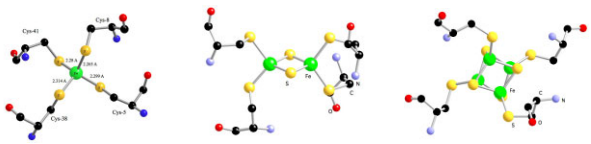


Figure 1. The Structure of Typical FeS_4 Site in Rubredoxin (left), Fe_2S_2 (middle) and Fe_4S_4 (right) Sites in Ferredoxin.

Results

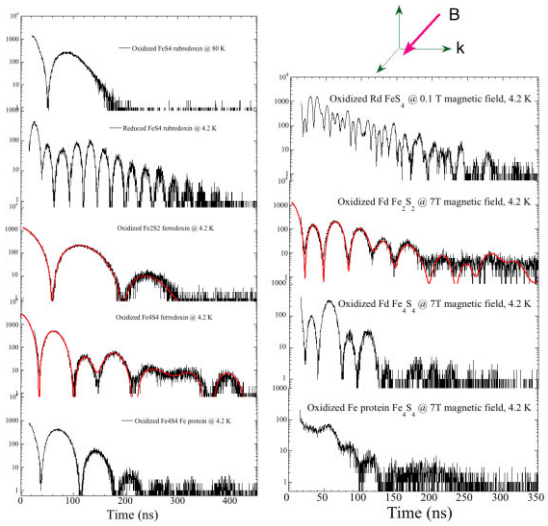


Figure 2. (a) Zero magnetic field FeS protein NFS spectra; (b)FeS protein NFS spectra with magnetic field up to 7 T at 4.2 K(Top: magnetic field direction); red solid lines showed selected fitting using CONUSS[3].

Figure 2(a) shows the zero magnetic field NFS spectra under liquid N_2 and liquid He temperature on oxidized and reduced FeS_4 cluster in Rd, oxidized Fe_2S_2 and Fe_4S_4 clusters in Fd, and oxidized Fe_4S_4 cluster in Fe protein. In this case, only quadrupole splittings of the Fe sites are showed. The different quantum beat patterns indicate different quadrupole splittings of the Fe sites in these clusters. Figure 2(b) shows the NFS spectra of oxidized Rd FeS_4 cluster under 0.1T magnetic field, oxidized Fe_2S_2 and Fe_4S_4 clusters in Fd, and oxidized Fe_4S_4 clusters in Fe protein under 7T magnetic field. The dramatic quantum beat pattern changes have been observed in all samples comparing with zero magnetic field spectra. In oxidized Rd protein, Fe site is paramagnetic at liquid He temperature; the fast quantum beat pattern is due to magnetic hyperfine splitting of the ^{57}Fe nucleus. While oxidized Fe_2S_2 and Fe_4S_4 clusters are diamagnetic, the quantum beat patterns observed are due to external magnetic field induced magnetic hyperfine splittings of ^{57}Fe nuclei. Detailed analyses are underway.

References

[1] V. Schunemann et al., Rep. Prog. Phys. 63, 263 (2000).
[2] H. Paulsen et al., Coord. Chem. Rev. 249, 255 (2005).
[3] W. Sturhahn, Hyp. Interact 125 (2000).

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