Nuclear Resonant Vibrational Spectroscopy (NRVS) of Hydrogen and Oxygen Activation by Biological Systems

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Iron-sulfur containing metalloproteins are ubiquitous in primitive organisms and hence implied in evolutionary schemes for life on Earth; thus it is unsurprising they are able to catalyze some of the simplest reactions. These include the reversible reduction of protons to dihydrogen (hydrogenases) and dinitrogen reduction (nitrogenases). This heritage has not allowed for their complete understanding.

Using the important new technique of nuclear resonant vibrational spectroscopy (NRVS), we have previously interpreted the vibrational spectra for simple iron-sulfur inorganics and proteins as well as more complicated systems such as nitrogenase.

Our most recent work at Spring-8 was to record the NRVS for a range of further iron-sulfur proteins, specifically oxidized and reduced [2Fe2S] and [4Fe4S] ferredoxins. This data, whilst important in its own right, allows us to attempt interpretation of the NRVS of a H_2 reduced Fe-only hydrogenase from *Clostridium acetylbutylicum*.

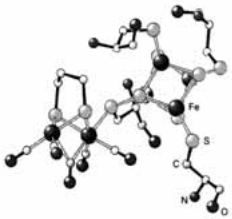

Fig 1. The active site 'H-cluster' of an Fe-only hydrogenase and it's linked [4Fe4S] cluster.

Although the element selectivity and unique selection rules of NRVS generates information that is not readily available from other techniques, the analysis of the 'H-cluster' is considerably complicated by the presence of the cysteine bridged [4Fe4S] cubane. It is anticipated that subtraction of the NRVS data for an [4Fe4S] ferredoxin from the composite Fe-only hydrogenase will allow for observation of peaks specific to the [2Fe2S] subcluster that is responsible for hydrogenase activity. We have demonstrated with the ferredoxins that Fe oxidation states can be recognized through NRVS. Application of this knowledge to the hydrogenase H-cluster may solve the debate on iron oxidations states.

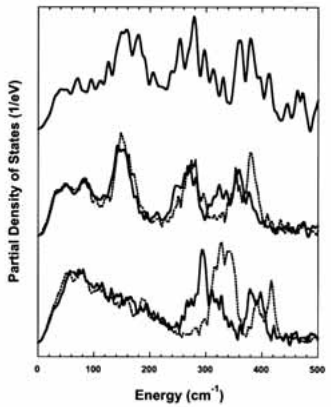

Fig 2. ^{57}Fe partial density of states for {top} H_2 reduced hydrogenase, {middle} oxidized (-) and reduced (--) [4Fe4S] ferredoxin, {bottom} oxidized (-) and reduced (--) [2Fe2S] ferredoxin.

Future studies of hydrogenase poised at reaction intermediates are planned to study the mechanism of this important enzyme.

Advancement of nuclear resonant scattering methods for the studies of local electronic and vibrational states

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Nuclear resonant scattering of synchrotron radiation is useful and effective for the studies on the dynamics and electronic states of condensed matter. One of the advantageous features of this method is that it is possible to obtain the information on the specific elements. Though it has been applied to various scientific fields, the method is not fully developed. The important purpose of this study is to develop the method for the studies of various scientific fields.

It is known that the properties of semi-conducting compounds are influenced by the impurity atoms. Therefore, the investigation on the electronic and vibrational characters of the impurity atoms is indispensable for the understanding of the thorough properties of the semi-conducting compounds. By using nuclear resonance inelastic scattering of synchrotron radiation, the observation of the motion of doped or impurity atoms is possible. We could measure the local vibrational densities of states of dilute impurity Fe atoms in Al and Cu metals [1].

In the present study, we have measured the local vibrational densities of states of impurity Fe atoms in ZnO. The energy resolution of 3.5 meV was achieved with a monochromator consisting of an asymmetric Si(5 1 1) and an asymmetric Si(9 7 5) channel-cut crystals. The delayed nuclear resonance scattering was observed with a multi-element avalanche photodiode detector. In Fig.1, the observed phonon energy spectrum of nuclear resonance scattering from Fe atoms doped in ZnO is shown. Further analysis is now in progress.

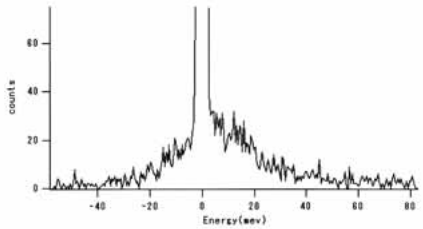

Fig.1. Phonon energy spectrum of nuclear resonance inelastic scattering from Fe atoms doped in ZnO.

[1] M. Seto, Y. Kobayashi, S. Kitao, R. Haruki, T. Mitsui, Y. Yoda, S. Nasu and S. Kikuta, Phys. Rev. B **61** (2000) 11420-11424.