

Experimental and theoretical studies of electronic structures of myoglobin

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Soft x-ray emission spectroscopy (SXES) is a new experimental tool that has been recently carried out by using high brilliant synchrotron radiation. It has been well known that SXES is very powerful for the electronic structures of transition metal compounds.

A lot of hemeproteins also contain metal ions and play important roles in living things. Myoglobin is a kind of hemeprotein and a carrier of the oxygen gas. Fe is surrounded by porphyrin and Histidine and Oxygen gas. The aim of this study is to know these electronic states of Fe directly.

The electronic states of transition metal ions play important roles for the functions of the proteins. Fe ion has 4 electronic states by 2+, 3+ valences and high and low spin states in the Myoglobin, as shown in Fig.2. Then there are 4 states. It is well known that met Mb has 3+ high spin and CN Mb has 3+ low spin. CO Mb has 2+ low spin and 2+ high spin. By changing the spin and electron valency, Myoglobin catches and releases the various gases. These electronic states have been determined by the various methods such as, magnetic method. However, there is no direct observation on the d-d transition.

We measured Fe2p-SXES on various Myoglobin. They showed complicated spectra that correspond to d-d transition. It is known that these d-d transitions should be elucidated by the ligand field theory. Then we analyze the 3d electronic state of protein using the so-called Tanabe-Sugano diagram. We can elucidate these d-d transition spectra by the Tanabe-Sugano diagram using these crystal field splitting $10Dq$ and the Racah parameter B . Furthermore, we calculated cluster calculation for Fe ion surrounded by the ligands. Fig.2 shows the schematic electronic structure of Fe²⁺ and Fe³⁺ ions.

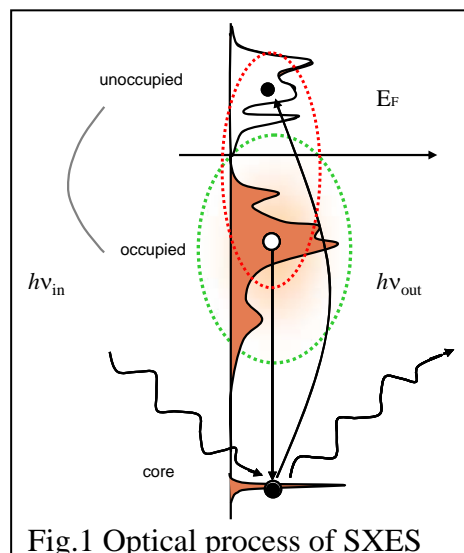


Fig.1 Optical process of SXES

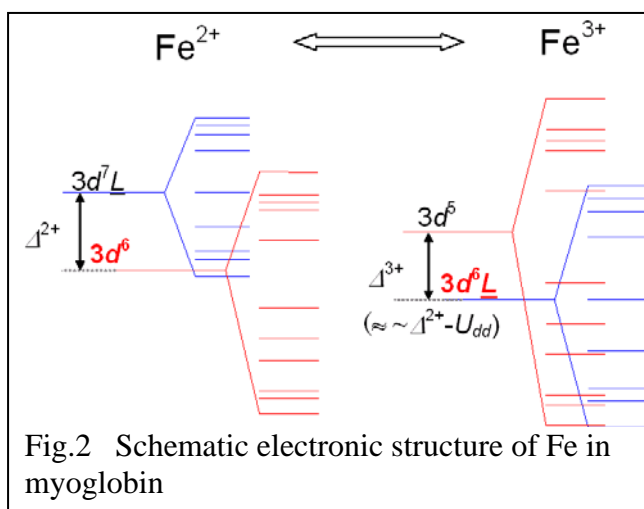


Fig.2 Schematic electronic structure of Fe in myoglobin