Electronic structure of Heme-Fe observed by soft X-ray absorption/emission spectroscopy

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Myoglobin, a hemeprotein found in cardiac- and skeletalmuscle, serves multiple biological functions based on detection, transport, release and/or binding of molecular ligands such as O_2, CO, NO, etc. Ligand binding to heme-Fe in myoglobins and its relation to functional properties have been extensively studied using structural and spectroscopy probes[1,2]. However, to date, a quantification of the energy level separation between the cationic Fe 3*d* and the anionic ligand states in aqueous myoglobins has not been possible.

Here we use resonant X-ray emission spectroscopy and model calculations to quantify the ligand: heme-Fe energy structure of aqueous myoglobins. The experiments were carried out using a high-efficiency soft X-ray emission spectrometer installed at BL17SU[3]. For reduced (Fe^{2+}) and oxidized (Fe^{3+}) states, it is found that the removal or addition of an electron primarily involves charge changes on the ligand-site, and not the Fe-site. The results indicate a finite positive/negative charge-transfer energy Δ between the heme-Fe 3*d* and ligand valence electronic states for Fe^{2+}/Fe^{3+}. Thus, the energy difference between the ligand and Fe 3*d* states ($+\Delta$ or $-\Delta$) determines the charge properties of myoglobins.

Basically this method can be applied to more complex cases where local coordination around the iron site is distorted from O_h- or D_{4h}-like symmetry. In order to analyze the electronic structure of iron complex in such lower symmetry, we have constructed ultra-high resolution soft X-ray emission spectrometer with several times better energy resolution at BL07LSU of SPring-8[4]. Combined with recently developed calculations the study will provide a reliable method for characterizing ligand-metal binding of biological systems in solution.

References

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