**Spectroscopic Insight into Electronic Structure of Ferric-Heme Proteins from Multiconfiguration QM/MM Approach**

Hemoproteins are widespread in nature, where they perform many functions, among them, one is essential, namely oxygen transport. Since the first discovery and interpretation of the binding of O2 to hemoglobin, it has been believed that the active center of heme in the most of hemoproteins is in ferrous (FeII) oxidation state. Nevertheless, ferric (FeIII) heme is also active in many hemoproteins and is generally involved in electron transport processes. Besides their importance, the nature of Fe−O2 bond in these proteins has been challenged since the first interpretation given by Pauling in 1936 [1]. Among all suggested models, Weiss model [2] with the formation of FeIII+(S=1/2)−O2−(S=1/2), which indicates a remarkable change in the oxidation state of Iron (from ferrous to ferric) upon bonding, is of highest relevance, as has been supported by experimental observations in the condensed phase [3,4] and, high-level ab initio calculations [5]. These results, in fact, have highlighted the importance of studies on ferric-heme proteins, from electronic structure point of view.

The mail goal of this project is to investigate and to reveal the effect of protein microenvironment on the electronic transitions through the comparison with gas-phase results. The Quantum Mechanical/Molecular Mechanical (QM/MM) approach implemented in COBRAMM package [6] enables us to account the effect of most important amino acids (e.g. distal His) on the electronic transitions and discriminate the intrinsic electronic properties from protein-induced ones. This study will enable us to get a deep insight on how microenvironment of protein perturbs the electronic structure of ferric heme in details. The work plan of this project will be the following:

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| --- | --- | --- | --- | --- | --- | --- |
| **Activities** | **Month** | | | | | |
| 1-2 | 3-4 | 5-6 | 7-8 | 9-10 | 11-12 |
| System preparation for QM/MM calculations. |  |  |  |  |  |  |
| Geometry optimization of the ferric-heme protein in ground and excited states. |  |  |  |  |  |  |
| Calculation of the FC electronic transitions of the interested protein. |  |  |  |  |  |  |
| Frequency calculations of the ground and excited states, then get the vibronic spectra. |  |  |  |  |  |  |
| Analyzing the data, and preparing results for the publication. |  |  |  |  |  |  |

**References:**

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