Binding of small molecules to Metalloporphyrins

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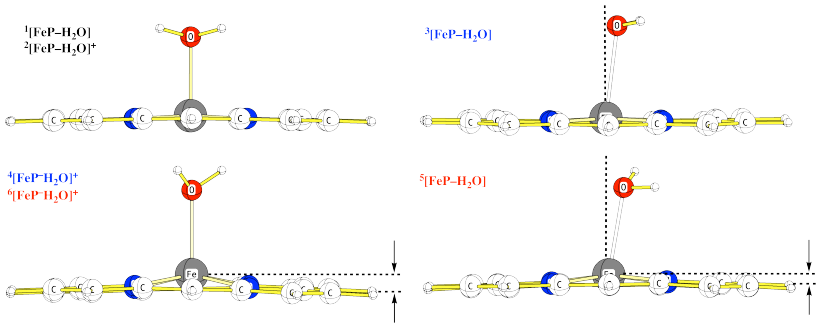
The investigation of the binding of small ligands has provided valuable insights into the relations among structure, dynamics, and function of proteins. The interaction of small molecules such as O_2, NO and CO with hemoglobin (Hb) and myoglobin (Mb) play a central role in living cells and is important for the respiration and regulation processes. For example, heme proteins (which contain iron porphyrins) serve many roles, such as O_2 storage and transport (myoglobin and hemoglobin), electron transport (cytochromes b and c), and O_2 activation and utilization (cytochrome P450 and cytochrome oxidase). Chlorophylls (which have a central magnesium ion) and pheophytins (which are metal free) are found in the photosynthetic apparatus of plants and bacteria, whereas vitamin B12 (which contains cobalt) is present in bacteria and animals.

It is thus very important and challenging to understand and predict/reproduce binding energies of these ligands reliably by quantum-chemical calculations. Additionally, the accuracy of such calculations serves as a good benchmark for the modeling of similar bioinorganic processes. Despite the increasing number of theoretical studies on this topic, the results still remain inconsistent and somewhat puzzling.



We present our computational studies involving some of the metalloporphyrins (Fe(II)P, Co(II), and others). The present investigation also explores the accuracy of several DFT methods. The geometries of MP–XO complexes and XO binding energy were found to depend very strongly on the functional and basis set used. In many cases, model systems should be described at least with a triple-ξ quality basis set.

Although relatively expensive and difficult to use, CASSCF/ CASPT2 methods often provide meaningful chemical descriptions. This, coupled with the continuing increase in computational power, suggests that the study of properties and reactions involving metalloporphyrins should be pursued with these accurate methods.

[1] T.E. Shubina. "Computational studies on properties, formation and complexation of M(II)-porphyrins», Advances in Inorganic Chemistry, vol. 62, **2010**, Chapter 7, pp. 261-300. Elsevier.

[2] T.E. Shubina and T. Clark. «CO and NO complexes of Fe(II) and Co(II) porphyrins», **2010**, *J. Coord. Chemistry,* **63 (14-16)**, 2854-2867