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Measurement of the binding energy of the heme ligand in a cooled ion trap.

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We have used a home-made experimental setup which couples an electrospray, with a cooled Paul ion trap and a time-of-flight detection. The temperature variation allows to access the thermodynamic properties of the complex and in particular the binding energy between a ligand and an organometallic compound. In my presentation I will show our results on the binding energy of iron protoporphyrin with different ligands such as O_2 , CO, H_2O,…. Indeed this system is a model for the reaction of oxygen fixation or release on a hemoprotein. The mechanism of this process has not been yet elucidated precisely. The active site of hemoglobin Heme is an Iron atom in the oxidation degree II ligated to Protoporphyrin. The nature of the iron-oxygen bond in the heme is a subject of debate since Pauling (1936) and only recently, quantum chemistry was been able to describe it. Thus, the Fe II - O_2 binding has its origin in a transfer of charge between the iron atom and oxygen. The determination of Heme-O_2 binding energies in absence of other interactions is a way to validate this hypothesis by comparison with calculations. This energy can be measured simply in the gas phase. In this presentation, I will focus on the methods developed to measure the binding energy of metal-ligand on different model system in the gas phase.The bond formation enthalpies with [O_2, CO, H_2O,…] have been derived from Van't Hoff plots of experimentally determined equilibrium constants for ligand binding reactions in the gas phase. It is the first direct determination of the binding energy iron-ligand. I will discuss the different factors and present an overview of gas phase investigation of heme-ligand binding via the Vant'Hoff equation and high level calculations. This confrontation of the experimental and theoretical results on the binding energies allows a particular insight on the Heme-Ligand properties.
As in nature, the degree of oxidation of iron plays an important role in the binding of small molecules to hemoproteins; we measured the binding energies of ferrous and feric heme with different ligand. We have also characterized the critical influence of the water molecule on the reaction of ligadation of heme.