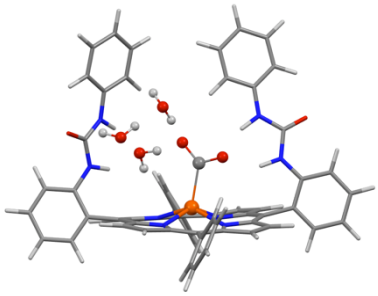
Computational study of the mechanism of CO_2 reduction at an iron porphyrin

In the context of global warming, capturing and transforming CO_2 into a higher value-added synthon has become a key challenge for chemists. Iron porphyrins, combining an abundant and non-toxic metal with a highly modulable ligand, are among the most widely used and effective catalysts for electrochemical CO_2 to CO reduction. To make them technologically applicable, a reduction of their operational energy cost, i.e. the potential at which electrocatalysis is carried out, and an enhancement of their catalytic rate is being sought.

In our lab, we have developed a series of iron porphyrins decorated with multipoint hydrogen-bonding patterns that boost CO_2 reduction. In our previous studies, we demonstrated how this second-sphere adjuvant helps enhancing the rate for CO_2 binding at the iron center. To our surprise, the best proton source donor in some cases was not usual acids such as phenol or TFE but water, a much weaker acid. We also noticed a shift of the onset potential in the presence of water. We thus suspect that second sphere interactions should also play a role by trapping and channeling water molecules near the catalytic site. In this study, we will consider several mechanistic hypotheses in order to identify the role played by water at different stage of the CO_2 reduction.



The candidate should have a good knowledge in coordination chemistry and an appetite to learn DFT calculations. He or she will also have to be very methodical and resourceful.

Note that the internship will take place at the Institut de Chimie Moléculaire et des Matériaux d'Orsay, but if the sanitary situation requires it, it can be held at a distance.

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References :

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