P1.7 DFT calculations of the spectroscopic properties (IR, NMR, UV) of supposed intermediates in the catalytic cycles

Topic and overall goal. In TP1 the goal is not simply to form oxalate from CO_2, but more importantly to understand the mechanism and the factors which influence it. Experimentally, different spectroscopic techniques will be used to obtain as much information regarding the reaction mechanism and intermediates involved as possible. To help achieve these goals computational approaches can be valuable tools. The method of choice will be mostly density functional theory (DFT) to model reaction mechanisms, but also to model spectroscopic properties of either experimentally suggested intermediates or computationally calculated ones. These calculations will be crucial for the identification of intermediates and the assignment of the corresponding spectra as well as the prediction of possible reaction paths.

Specific aims and work plan. For the purpose of this project we will opt for DFT calculations due to their good balance between accuracy and computational cost. Where necessary we will confirm our DFT results with higher level coupled cluster calculations either with CC2 or DLPNO-STEOM-CCSD(T) approaches, since the accuracy of certain functionals might not always be adequate for these systems. Furthermore, when modelling UV-Vis spectra, solvent effects can have a large influence, thus we will carry out tests to identify an appropriate way to model solvent effects. We will use either implicit solvent models or in the case of large solvent effects we will opt for explicit solvent effects using a QM-informed MM approach.[1] Furthermore, we will not focus only on the interpretation of experimental data, but also help experimental colleagues to rationally design their experiments and possible catalysts. For example, in projects P1.1 and P1.2 the aim is to harness the potential of secondary coordination sphere editing, e.g., using amine functionalities, to facilitate CO_2 binding. We will screen potential substituents and estimate which ones are most suitable to bind CO_2. Also, we will model experimentally investigated reactions and try to identify the factors which are driving the reaction. After that, we will computationally change these factors with the goal of obtaining improved reactivity.

Connection within the RTG. This PhD project will be supervised by Milica Feldt and co-supervisor Matthias Beller. Within the RTG there will be a close collaboration with Olga Bokareva (computational chemistry), Torsten Beweries (organometallic chemistry) and Angelika Brückner (operando spectroscopy).

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1   F. de Jong, M. Feldt, J. Feldt, J. N. Harvey, *Phys. Chem. Chem. Phys.* **2018**, *20*, 14537.