

## P4.2 Time-Resolved IR Spectroscopy

**Topic and overall goal.** The time-resolved infrared (TR-IR) spectroscopy will be used for unravelling the structure and character of transition metal (TM) complexes in transiently populated states. In photochemical reaction chains short lived species such as molecules in electronically excited states or energy rich ground state configurations are of particular interest to understand the underlying reaction mechanisms. However, their limited lifetime calls for methods with a high time resolution. We plan to build a vibrational spectroscopy setup with nanosecond resolution to address this point and to explore for the systems studied in TP3, the structure and dynamics of electronically excited and transient ground state TM complexes as it was demonstrated earlier.<sup>1</sup>

**Specific aims and work plan.** The aim of the PhD project is to develop a setup for time resolved FTIR (TR-FTIR) spectroscopy with a time resolution of about ten nanoseconds and to apply it for investigating the reaction dynamics in photocatalytic CO<sub>2</sub> reduction systems. In the setup, an

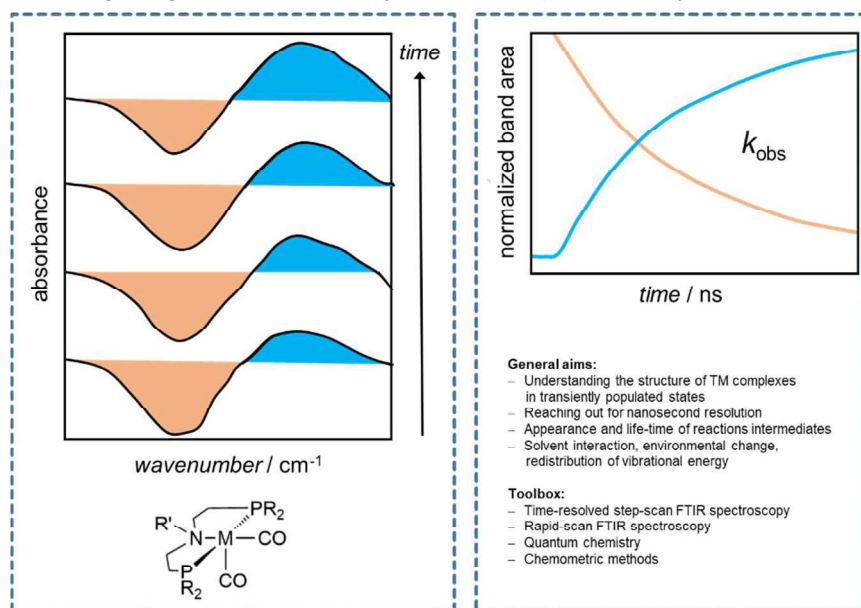


Figure P4.2. Summary of the time-resolved Fourier-transform infrared (TR-FTIR) spectroscopy.

existing step-scan FTIR spectrometer will be applied for probing while the photoexcitation, which initiates the photocatalytic reactions, will be done by a pulsed YAG laser system. The latter is equipped with a frequency doubling and tripling stage to address the absorption bands of the TM complexes. We can use so-called “reporter” ligands such as carbonyls having the advantage of a huge oscillator strength for the  $\nu(\text{CO})$  vibrations and a high sensitivity for structural changes. Accordingly, the mid-IR region is of special

interest. The time-resolved step-scan FTIR technique is applicable for investigations of TM complexes with 2 to 4 metal centers in the time interval from nanoseconds to milliseconds. It is suitable for investigations in solution, which enables us to reveal solvent effects. The evolution of the educts, longer living intermediates and products we will be measured by the rapid-scan FTIR spectroscopy available in our groups.<sup>2</sup>

**Connection within the RTG.** This PhD project will be jointly supervised by Ralf Ludwig and Stefan Lochbrunner. The data will be analyzed in collaboration with P4.3 and P4.4 to extract the reaction dynamics and the spectral signatures of specific intermediates. Together with P4.4 and P4.5 the structure sensitive IR technique will be combined with high level DFT and TDDFT calculations for providing a detailed analysis on the structural changes in the TM complexes. Furthermore, TR-FTIR is also suitable to study the processes occurring in the CO<sub>2</sub> photo release described in P4.6.

- 1 M. Zimmer, F. Rupp, P. Singer, F. Walz, F. Breher, W. Klopfer, R. Diller, M. Gerhards, *Phys. Chem. Chem. Phys.* **2015**, *17*, 14138-14144.
- 2 S. Fischer, A. Roesel, A. Kammer, E. Barsch, R. Schoch, H. Junge, M. Bauer, M. Beller, R. Ludwig, *Chem. Eur. J.* **2018**, *24*, 16052-16065.