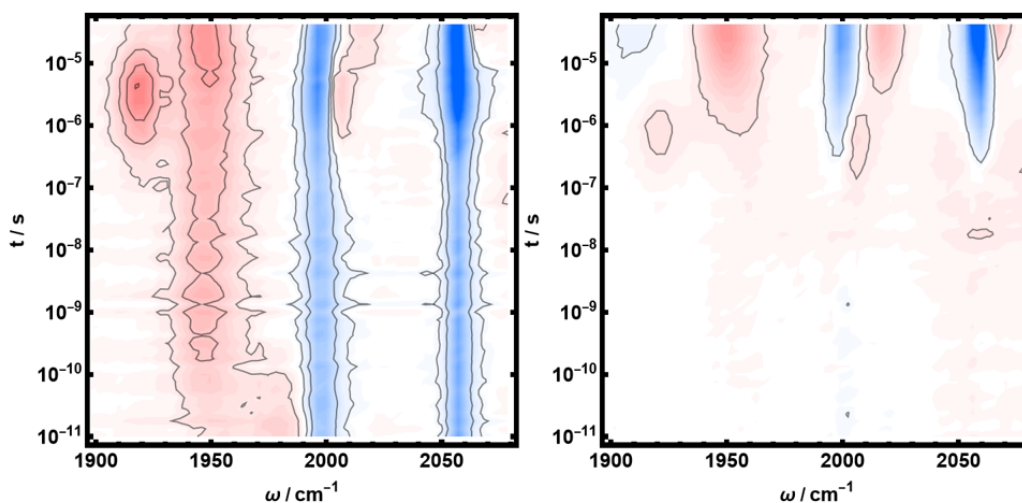


Ligand exchange kinetics in the first reduction step of CO₂ reduction catalyst: trans-(Cl)-[Ru(5,5'-dimethyl-2,2'-bipyridine)(CO)₂Cl₂]L. Tatarashvili¹, S. Aranda¹, K. Oppelt¹, P. Hamm^{1*}¹Department of Chemistry, University of Zurich, Winterthurerstrasse 190, CH-8057 Zurich, Switzerland

A significant amount of current research is dedicated to developing methods for reusing atmospheric CO₂ as a precursor in the production of valuable chemicals. Ruthenium mono- and bis(bipyridyl) dicarbonyl complexes are known as promising catalysts for electro/photo-chemical CO₂ reduction [1]. One such molecular catalyst is trans-(Cl)-[Ru(5,5'-dimethyl-2,2'-bipyridine)(CO)₂Cl₂]. To attain catalytic activity, this molecule undergoes a two-step reduction process (Ru(II) to Ru(0)). We used a simple photocatalytic system comprised of the catalyst, photosensitizer (Ru(bpy)₃Cl₂), and reductive quencher (1-Benzyl-1,4-dihydronicotinamide), and tracked the IR absorption by the carbonyls over picosecond to microsecond time range using time-resolved pump-probe spectroscopy. Since carbonyl ligands have excellent IR absorption cross-section and are sensitive to the variations of electron density on the metal, we could clearly monitor the system's evolution. Our results reveal the transient species related to the initial reduction of the catalyst and offer deeper insight into the processes leading to its activation and their associated timescales.



[1] Kuramochi, Y., Itabashi, J., Toyama, M., & Ishida, H. *ChemPhotoChem*, 2018, 2(3), 314-322.