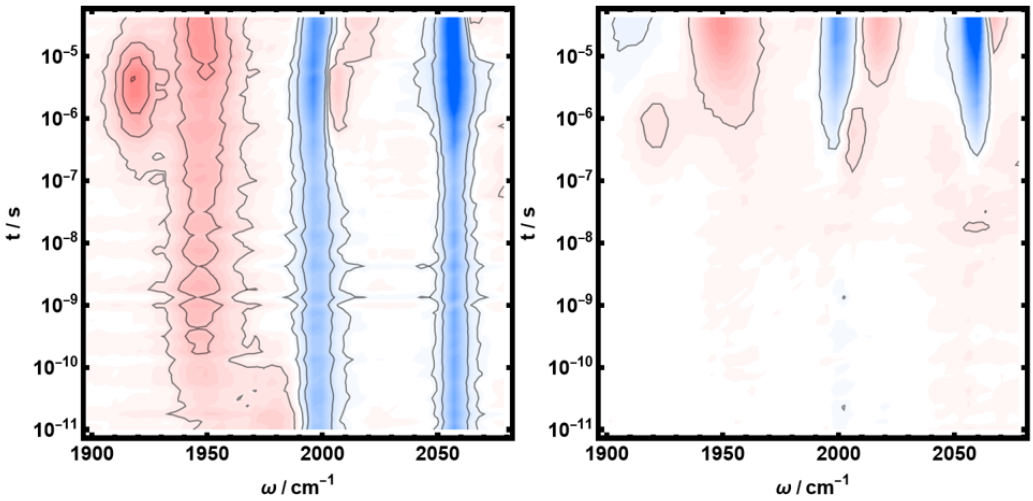
Ligand exchange kinetics in the first reduction step of CO_2 reduction catalyst: trans-(Cl)-[Ru(5,5'-dimethyl-2,2′-bipyridine)$(CO)_2Cl_2$

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A significant amount of current research is dedicated to developing methods for reusing atmospheric CO_2 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 CO_2 reduction [1]. One such molecular catalyst is trans-(Cl)-[Ru(5,5’-dimethyl-2,2′-bipyridine)$(CO)_2Cl_2$]. 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 ($Ru(bpy)_3Cl_2$), 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.