

# Photocatalysis Reaction Dynamics Probed In Operando with 2D-IR

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2D-IR can be used to track structural dynamics as well as mechanistic connectivity in functional photocatalytic reactors. Non-equilibrium 2D-IR, both transient and at steady-state reveals ultrafast intermolecular charge transfer, solvent exchange and catalyst dimerization.

Photocatalysis offers the possibility of reversing the generation of greenhouse gases while producing useful feedstocks and starting materials, consuming mainly light, which is, in principle, is plentiful. Photocatalyzed oxidation and reduction involve numerous chemical species, multiple electronic states, and one or more charge transfer processes. Although several photocatalysts have been studied using 2D-IR spectroscopy, it remains to be seen what can be learned by performing 2D-IR spectroscopy on a functional photocatalytic reactor containing all of the components required for the full photocycle.

In a series of  $\text{ReCl}(\text{N-N})(\text{CO})_3$  (N-N = diimines: phenanthroline, bipyridine and derivatives), we have used equilibrium and non-equilibrium, transient 2D-IR spectroscopy to study solvation dynamics on distinct electronic states.[1] Summarizing these findings, we find spectral diffusion of the CO stretching modes on the ground state singlet states to correlate with solvent donicity; and the photocatalytically active  $^3\text{MLCT}$  excited state exhibits roughly three-fold slower spectral diffusion than the  $\text{S}_0$  ground state, which can be understood based on the greatly reduced excited state molecular dipole moment. Overall, these results highlight the importance of the catalyst's electrostatic profile in solution.[2-3]

Functional  $\text{CO}_2$  reduction requires several species to be present in solution. First, since the net reduction of  $\text{CO}_2$  requires electrons, there must be an electron donor, typically a sacrificial reagent such as an amine (i.e. triethylamine, TEA, or triethanolamine, TEOA). Besides the sacrificial donor and the solvent, the reaction requires  $\text{CO}_2$ , all of which produce a complex heterogeneous reaction mixture, which only becomes more complex as the photocycle begins. Using 2D-IR to study solutions of TEOA in several common solvents (THF,  $\text{CH}_3\text{CN}$ , and DMSO), we identified a clear signature of preferential solvation for solvents less polar than TEOA. In particular, we observe a dynamical slowdown due to distinct solvent exchange, first observed with 2D-IR in a metal carbonyl biotin derivative.[4] Remarkably the maximum slowdown occurs at the same concentration (20% v/v TEOA in THF) known to be optimal for CO production. This finding highlights the importance of solvent exchange in the photocatalytic mechanism. Transient IR absorption provides direct evidence for ultrafast (relative to the typically assumed diffusion limit) electron transfer from the TEOA to the Re catalyst.

Our most recent results are the most relevant for functional photocatalytic systems. Using cw illumination with 405 nm laser light, we measure 2D-IR spectra at a fixed waiting time of 1 ps. We observe cross peaks between distinct chemical species, which we argue is a new mode of non-equilibrium, steady-state 2D-IR spectroscopy, which reveals the mechanistic connectivity of intermediate species in the photocycle.

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[3] L.J. Kiefer, K.J. Kubarych, *J. Phys. Chem. A*, **119**, 959-965 (2015).

[4] J.A. Dunbar, E.J. Arthur, A.M. White, K.J. Kubarych, *J. Phys. Chem. B* **119**, 6271-6279 (2015).