

Preferential Solvation: Spectral Dynamic Slowdown of a Rhenium Photocatalyst

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Equilibrium 2D IR spectroscopy was used to measure spectral diffusion of the photocatalyst $\text{Re}(\text{bpy})(\text{CO})_3\text{Cl}$ in multiple TEOA/solvent mixtures. The slowest spectral diffusion time was observed in the 20%/80% TEOA/solvent (v/v) mixture, indicating occurrence of preferential solvation.

Preferential solvation plays a significant role in the outcome of many chemical reactions by aiding in the solubility of reactant species, placing reactive solvent species in close proximity to the reactant solute, and increasing conductivity in films by clustering species together [1,2]. Specifically, in electron transfer reactions, preferential solvation can bring the Donor molecule close to the Acceptor, omitting diffusion from determining the reaction rate. In this work, preferential solvation of a sacrificial electron donor was discovered to be involved in the catalytic mechanism of a well studied photo-induced CO_2 reduction catalyst, $\text{Re}(\text{bpy})(\text{CO})_3\text{Cl}$. After a 400-nm electronic excitation to initiate the catalysis reaction, a sacrificial electron donation is required for the catalysis to proceed, and hence an electron transfer must happen. Often triethanolamine (TEOA) is used as the electron source. In this work, we find that the vibrational spectral dynamics, specifically spectral diffusion, begin to slow down as the concentration of TEOA is increased, is slowest in a ratio of 20%/80% TEOA/solvent (~ 7 ps; Fig. 1a) and then speeds up until reaching the value in the neat TEOA (~ 4 ps). The 20%/80% TEOA/solvent ratio coincides with the condition that produces maximal catalytic efficiency.

Further, UV-pump/IR-probe experiments were performed to allow for an indirect probe of the TEOA. At time delays ≥ 80 ps, a small peak is observed in the double difference spectra at 1996 cm^{-1} , the location of the singly reduced species (Fig. 1b). The early occurrence of the peak (80 ps) indicates that the TEOA is within 10 \AA of the rhenium complex, corroborating the notion of preferential solvation [3].

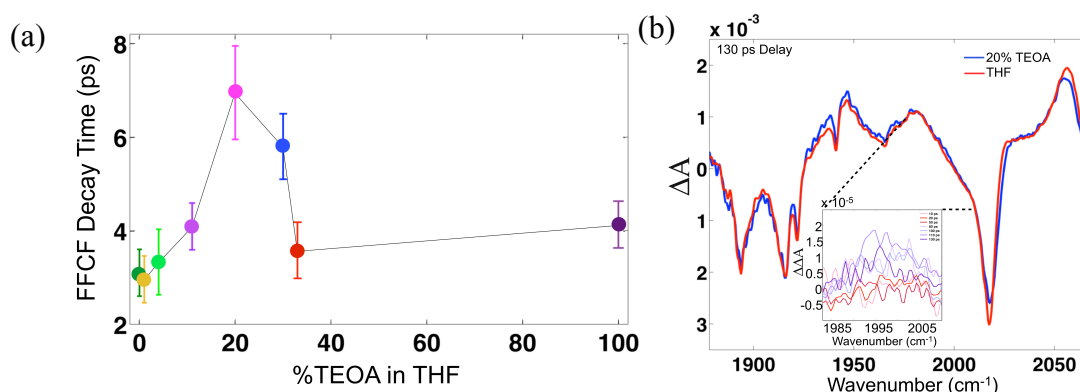


Figure 1. (a) Spectral diffusion times vs. percent triethanolamine (TEOA) in tetrahydrofuran (THF); (b) UV-Vis pump/IR probe difference spectra of $\text{Re}(\text{bpy})(\text{CO})_3\text{Cl}$ in THF (red) and 20%/80% TEOA/THF (blue) at a time delay of 130 ps. The inset shows double difference spectra between the two solvent environments at both early (red) and late (purple) waiting times of the singly reduced species.

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[2] R. Ormazabal-Toledo *et al*, J. Phys. Chem. B, **117**, 5908-5915 (2013).

[3] H. B. Gray, J. R. Winkler, Q. Rev. Biophys., **36**, 341-372 (2003).