

# Electronic Ground and Excited State Spectral Diffusion of a Photocatalyst

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**Abstract:** Equilibrium and transient 2D IR spectroscopies were used to measure spectral diffusion of the electronic ground and excited states of the photocatalyst  $\text{Re}(\text{bpy})(\text{CO})_3\text{Cl}$ . The ground state spectral diffusion decays 3 times faster than the  $^3\text{MLCT}$ .

OCIS codes: (300.0300) Spectroscopy; (260.5130) Photochemistry

## 1. Introduction

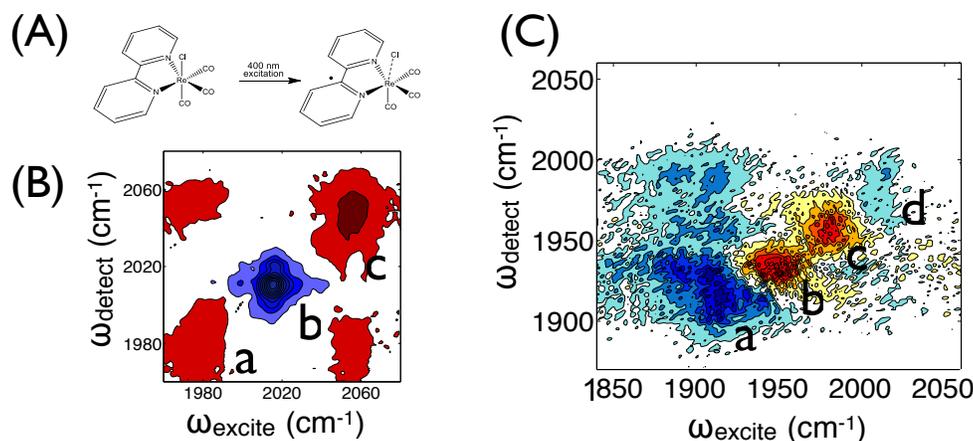
$\text{Re}(\text{bpy})(\text{CO})_3\text{Cl}$  is a well studied photo-induced  $\text{CO}_2$  reduction catalyst. It is especially popular because it is both a photosensitizer and a catalyst with high quantum yields and product selectivity [1]. The catalysis reaction is initiated by 400-nm electronic excitation into a singlet metal-to-ligand charge transfer ( $^1\text{MLCT}$ ) state. After an intersystem crossing, it relaxes to a  $^3\text{MLCT}$  state, where it remains for tens of nanoseconds. Many studies have been performed on the photophysics of the catalysis initiation, but none have reported a direct comparison of the separate equilibrated electronic states involved [2]. Measurements of vibrational spectral dynamics within the equilibrated excited state provide a probe of catalyst just as it is ready to react. In the present work, we focus on the spectral dynamics, specifically spectral diffusion, of the carbonyl stretches in the range  $1850\text{-}2100\text{ cm}^{-1}$  of both the electronic ground state and the vibrationally relaxed  $^3\text{MLCT}$  state.

## 2. Experiment and Results and Discussion

In the  $S_0$  ground electronic state, equilibrium two-dimensional infrared spectroscopy (2D IR) was used to obtain frequency-frequency correlation functions (FFCF) for the three carbonyl stretches, the  $A'(1)$  mode (in phase symmetric), the  $A''$  mode (asymmetric) and the  $A'(2)$  mode (out-of phase symmetric). We collect rephasing and nonrephasing 2D-IR spectra at multiple waiting time delays between the excitation pulse pair and the detection pulse [3]. From the peak amplitudes of both the rephasing ( $A_r$ ) and nonrephasing ( $A_n$ ) spectra at each waiting time delay we generate the inhomogeneous index (Eq. 1) which is proportional to the normalized FFCF. The FFCF is a measure of the spectral diffusion of the inhomogeneously broadened reporter modes [4].

$$I(t_2) = \frac{A_r(t_2) - A_n(t_2)}{A_r(t_2) + A_n(t_2)} \quad (1)$$

To study the  $^3\text{MLCT}$  state, we introduce a 400 nm pulse to electronically excite the photocatalyst. After tens of picoseconds, it relaxes into a quasi-equilibrated  $^3\text{MLCT}$  state which we probe using a 2D IR sequence. This technique of electronically exciting prior to the 2D IR sequence is referred to a transient 2D IR (t-2D IR). The

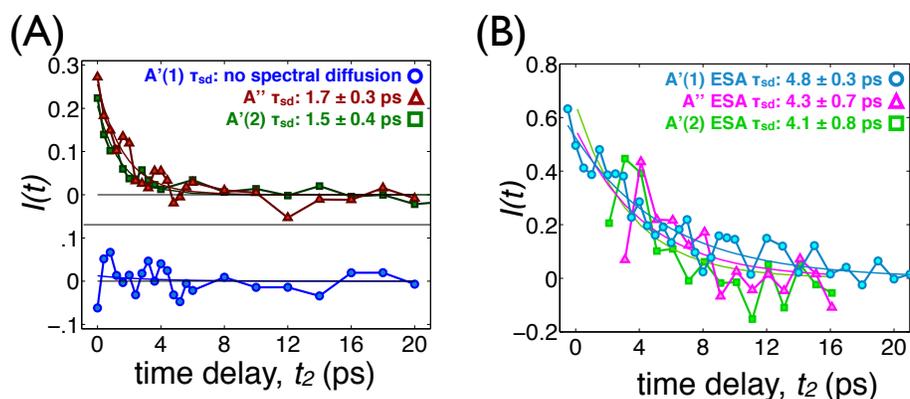


**Figure 1:** (A) Structure of  $\text{Re}(\text{bpy})(\text{CO})_3\text{Cl}$  and 400 nm excitation; (B) difference rephasing spectra, a: excited state absorption (ESA) of  $A'(2)$  mode, b: ground state bleach (GSB) of  $A'(1)$  mode, c: GSB of  $A'(1)$  mode; (C) difference rephasing spectra of lower frequency modes, a: GSB of  $A''$  mode, b: ESA of  $A''$  mode, c: ESA of  $A'(2)$  mode, d: GSB of  $A'(1)$  mode

absolute rephasing difference spectra (Fig. 1B) of the high frequency mode,  $A'(1)$ , depicts the ground state bleach (GSB) and excited state absorption (ESA), as well as the GSB for the  $A''$  mode. We also record t-2D IR spectra of the weaker low frequency  $A''$  and  $A'(1)$  modes (Fig. 1C). We report difference spectra because the introduction of the 400 nm pulse results in a non-background-free signal and we must implement a chopper.

We find an absence of inhomogeneous broadening and spectral diffusion in the totally symmetric mode in THF (Fig. 2A). This anomalous behavior has been seen in totally symmetric modes of several other metal carbonyl complexes, but we have yet to develop a full explanation of the effect. The two lower frequency modes, however, are inhomogeneously broadened and undergo spectral diffusion; both of their FFCF's decay in  $\sim 1.5$  ps (Fig. 2A).

Following electronic excitation and subsequent relaxation into the vibrationally cooled  $^3\text{MLCT}$  state, our t-2D IR measurements reveal that the high frequency mode develops a solvent sensitivity manifested as inhomogeneous broadening. In this state, all three modes exhibit spectral diffusion with a common decay time of  $\sim 4.4$  ps (Fig. 2B). Based on our quantum chemical calculations on both the ground electronic and  $^3\text{MLCT}$  states, we attribute this threefold slowdown to several origins: (1) solvent dynamics, (2) a change in the dielectric friction, and (3) a change in the molecular flexibility. Since the molecular dipole moment changes dramatically in both magnitude and direction from the ground  $S_0$  to the  $^3\text{MLCT}$  excited state, it follows that the polarizability and solvent interactions of the two states will differ. Using the permanent molecular dipole moment, we calculated the ratio of dielectric



**Figure 2:** (A) Normalized FFCF of all three carbonyl stretching modes from the equilibrium 2D IR experiment, the high frequency mode is offset to emphasize the lack of spectral diffusion; (B) normalized FFCF of all three carbonyl stretching modes from the t-2D IR experiment.

friction for the two states, which enables simple estimates of differences in solvation dynamics [5]. Though dielectric friction alone predicts a six-fold slowdown, the model is highly simplified, and there are certainly other contributions to the changes in dynamics. The change in spectral dynamics we observe in the two electronic states shows that the solute-solvent coupling is altered by charge redistribution within the molecule.

### 3. Conclusions

Since solvent fluctuations underlie the microscopic dynamics of charge transfer processes, changes in solvation structure, coupling, and dynamics throughout the photocatalytic cycle may influence selectivity, turnover number, and overall catalytic efficiency. This work shows that it is indeed possible to extract the full array of spectral dynamics (spectral diffusion, vibrational relaxation, and vibrational energy transfer) from demanding transient 2D IR experiments, and reference the observed changes to a completely characterized ground electronic state species. Future work will examine solvent-specific changes in electronic-state modulated spectral diffusion dynamics.

### 4. References

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