

Dynamics of Rhenium Photocatalysts Revealed through Ultrafast Multidimensional Spectroscopy

Published as part of the Accounts of Chemical Research special issue "Ultrafast Excited-State Processes in Inorganic Systems".

Laura M. Kiefer, John T. King,[†] and Kevin J. Kubarych*

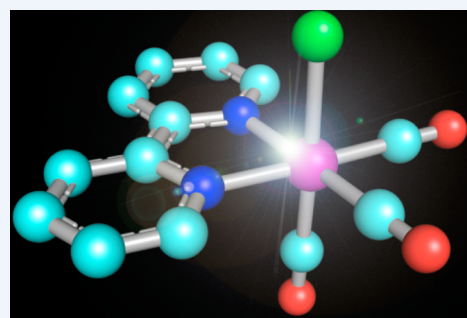
Department of Chemistry, University of Michigan, 930 N. University Ave., Ann Arbor, Michigan 48109, United States

CONSPECTUS: Rhenium catalysts have shown promise to promote carbon neutrality by reducing a prominent greenhouse gas, CO₂, to CO and other starting materials. Much research has focused on identifying intermediates in the photocatalysis mechanism as well as time scales of relevant ultrafast processes. Recent studies have implemented multidimensional spectroscopies to characterize the catalyst's ultrafast dynamics as it undergoes the many steps of its photocycle.

Two-dimensional infrared (2D-IR) spectroscopy is a powerful method to obtain molecular structure information while extracting time scales of dynamical processes with ultrafast resolution. Many observables result from 2D-IR experiments including vibrational lifetimes, intramolecular redistribution time scales, and, unique to 2D-IR, spectral diffusion, which is highly sensitive to solute–solvent interactions and motional dynamics.

Spectral diffusion, a measure of how long a vibrational mode takes to sample its frequency space due to multiple solvent configurations, has various contributing factors. Properties of the solvent, the solute's structural flexibility, and electronic properties, as well as interactions between the solvent and solute, complicate identifying the origin of the spectral diffusion. With carefully chosen experiments, however, the source of the spectral diffusion can be unveiled.

Within the context of a considerable body of previous work, here we discuss the spectral diffusion of several rhenium catalysts at multiple stages in the catalysis. These studies were performed in multiple polar liquids to aid in discovering the contributions of the solvent. We also performed electronic ground state 2D-IR and electronic excited state transient-2D-IR experiments to observe how spectral diffusion changes upon electronic excitation. Our results indicate that with the original Lehn catalyst in THF, relative to the ground state, the spectral diffusion slows by a factor of 3 in the equilibrated triplet metal-to-ligand charge transfer state. We attribute this slowdown to a decrease in dielectric friction as well as an increase in molecular flexibility. It is possible to partially simulate the charge transfer by altering the electron density moderately by adding electron donating or withdrawing substituents symmetrically to the bipyridine ligand. We find that unlike the significant electronic structure change induced by MLCT, such small substituent effects do not influence the spectral diffusion. A solvent study in THF, DMSO, and CH₃CN found there to be an explicit solvent dependence that we can correlate to the solvent donicity, which is a measure of its nucleophilicity. Future studies focused on the solvent effects on spectral diffusion in the crucial photoinitiated state can illuminate the role the solvent plays in the catalysis.



1. INTRODUCTION

The rhenium bipyridyl family of photoactivated catalysts has been widely investigated due to its varied and versatile photophysical and photochemical properties, ranging from photocatalysis to phototriggered electron donation.^{1–4} As photocatalysts, in particular, these complexes reduce CO₂ to CO and other chemical starting materials through a mechanism initiated by near-UV light absorption, proceeding through a series of steps that cycle on a millisecond time scale.⁵ There is a clear need for carbon-neutral means of removing CO₂ from the atmosphere, and a photocatalyst provides the possibility of deriving input energy from the Sun. The full mechanism of the CO₂ reduction catalysis is not known, but the initial steps have been carefully characterized by many spectroscopic techniques

including time-resolved IR, transient UV and visible absorption, and X-ray absorption.^{6–11} These studies have yielded time scales and assignments for the ultrafast dynamical processes triggered by light absorption. The early events are as follows: Absorption of ~400 nm light excites the complex to a singlet, mixed metal–ligand-charge transfer (MLCT)/ligand-to-ligand charge transfer (LLCT) state, which then intersystem crosses in a matter of tens of femtoseconds to a triplet MLCT state (³MLCT). The hot triplet state vibrationally cools within ~20 ps and survives for ~60 ns. These potential surfaces are depicted in a cartoon in Figure 1A. In the presence of a

Received: November 5, 2014

Published: April 3, 2015



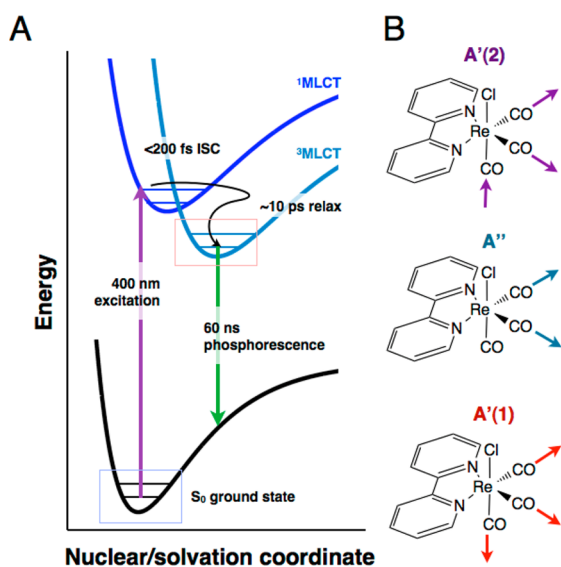


Figure 1. (A) Potential surfaces and time scales associated with the $^1\text{MLCT}$ photoexcitation of the Re catalyst followed by an intersystem crossing and relaxation into a quasi-equilibrated $^3\text{MLCT}$ state. (B) Normal modes of the three carbonyl stretches with arrows depicting the directions; $A'(2)$ is the out of phase symmetric stretch, A'' is the asymmetric stretch of the equatorial carbonyls, and $A'(1)$ is the in-phase totally symmetric stretch.

sacrificial donor, the complex is singly reduced, and the halide ligand dissociates, setting up the subsequent cascade of events that ultimately results in two-electron, two-proton reduction of CO_2 to CO or formate. Catalytic efficiencies and turnover numbers depend on solvent, halide (or pseudohalide) ligand, and substitutions on the bipyridine ring.^{5,12–15} In order to develop a complete structural and dynamical picture of the photocatalysis, researchers have turned to ultrafast spectroscopy, but even these techniques are limited by fundamental ambiguities in one-dimensional spectral line shapes that obscure direct access to the molecular dynamics and how they differ on multiple electronic excited states.

Recent advances in multidimensional spectroscopies have offered insights previously not attainable by other conventional methods, elucidating structural dynamics and solvent interactions that could aid in the understanding and performance of the catalysis. Photocatalytic oxidation and reduction inherently involves charge transfer reactions, where from the basic formulation of Marcus theory, the solvent plays a crucial role by defining the reaction coordinate through the solvent polarization.¹⁶ The solvent is responsible for two distinct but related aspects of reactivity, namely, the energetics of stabilizing species, as well as driving the molecular dynamics that guide the electronic motion. 2D-IR on the electronic excited state provides access to both of these contributions, combining the structural sensitivity with the dynamical information intrinsic to ultrafast spectroscopy. However, it has only recently become possible to apply the full suite of multidimensional observables to the electronic excited state, while comparing directly to the singlet ground state. The first catalytically relevant species visited during the cycle is the $^3\text{MLCT}$ state, which is metastable from the perspective of ultrafast spectroscopy. Hence, it is sensible to characterize this species dynamically, which can be done using 2D-IR spectroscopy of the carbonyl vibrations that serve as spectators throughout the catalysis, providing a consistent probe of molecular and electronic structural

dynamics, as well as the influence of solvation. Here we summarize the ultrafast multidimensional spectroscopy studies that have been reported on rhenium(I) photocatalysts to date, highlighting the conceptual advances made possible by using the nonlinear optical response of vibrations to probe electronic state dependent dynamics.

2. TWO-DIMENSIONAL INFRARED (2D-IR) SPECTROSCOPY OF Re(I) PHOTOCATALYSTS

Two-dimensional infrared spectroscopy (2D-IR) is analogous to 2D-NMR, but with inherent sub-picosecond time resolution, which allows direct observation of dynamics.^{17,18} The experiments can be viewed as an extension of pump–probe transient absorption, where dynamical changes become unveiled by performing multiple experiments with increasing time delays between the pump and probe pulses. In conventional IR pump–probe spectroscopy, the probe is frequency resolved, but the pump is broadband, trading frequency resolution for the short pulse's high time resolution. In contrast, a 2D-IR pulse sequence enables high frequency resolution of both the excitation and detection processes, while maintaining high time resolution during the so-called waiting time between excitation and detection.

The added information in a 2D-IR spectrum comes at a cost of the experimental complexity in generating multiple IR fields in a multibeam interferometer. Three ultrafast ($\sim 100 \text{ fs}$) IR fields, E_1 , E_2 , and E_3 , separated by delays t_1 and t_2 induce a nonlinear response in the sample, radiating a field E_s , which is detected phase sensitively in a spectrometer with a detector array (Figure 2).¹⁹ Scanning the coherence time (t_1) causes the detected signal to oscillate, and the excitation frequency axis is obtained by Fourier transforming with respect to t_1 . Though there are technical differences between experimental implementations, generally speaking, the 2D spectrum reveals structural information encoded in the relative transition dipole

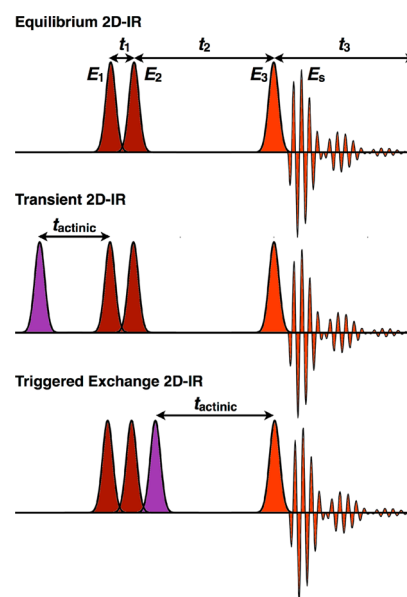


Figure 2. Pulse sequences depicting the equilibrium 2D-IR (top), transient 2D-IR (middle), and te-2D-IR (bottom) techniques, where the red pulses are the infrared pump pulses, the orange pulse is the infrared probe pulse and the purple pulse is the actinic or near-UV pulse.

moments and coupling between transitions, as well as dynamics resulting from vibrational energy transfer and relaxation, chemical exchange between different conformations,^{20,21} and spectral dynamics arising from environmental fluctuations.^{22,23} The angles between transition dipoles can be deduced by polarization dependent measurements.^{24–28} Vibrational population dynamics (energy redistribution and relaxation) are directly manifested as waiting time (t_2) dependent changes in the diagonal and cross-peak amplitudes.^{29,30} The peak shapes reveal the degree of homogeneous and inhomogeneous spectral broadening that contribute to the overall absorption line shape. The real power of 2D-IR spectroscopy is its ability to separate inhomogeneous and homogeneous broadening contributions, as well as to time resolve the loss of frequency correlation due to intermediate time scale dynamics.³¹ Condensed phase spectral bands typically have some degree of inhomogeneous broadening that arises from slight differences in local environment (i.e., solvent, surface, protein, etc.). By correlating excited and detected frequencies, the 2D spectrum will be diagonally elongated at early waiting time due to the differences in transition frequencies for the accessible microscopically distinct ensembles. As the waiting time is increased, initially excited molecules will sample all of the other available configurations, and the spectral band will diffuse through the full line shape. This stochastic equilibrium process has been denoted “spectral diffusion” in the NMR literature, and the decay of the line shape asymmetry is linked to the frequency fluctuation correlation function (FFCF), $C(t) = \langle \delta\omega(0)\delta\omega(t) \rangle$, where $\omega(t) = \langle \omega \rangle + \delta\omega(t)$.³² In metal carbonyl systems, we have shown in numerous examples that the FFCF can be directly linked to solvent dynamics in polar liquids, at the glass transition, at the protein–water interface, and at the membrane–water interface.^{33–36} The FFCF has been used to characterize many fundamentally important condensed phase systems, and we describe here how spectral diffusion can now be measured in an electronic state dependent way using transient 2D-IR spectroscopy.³⁷

The transient 2D-IR (t-2D-IR) experiment is performed by introducing an actinic, near-UV pulse prior to the equilibrium 2D-IR experiment, which then tracks the response of the excited species or the photoproducts. Because of the need to scan the coherence time long enough to obtain sufficient frequency resolution, most t-2D-IR experiments have been performed with several picosecond delays between the actinic pulse and the 2D-IR sequence. As the time delay is further increased to a point where the system is in a quasi-equilibrium, t-2D-IR measures effectively equilibrium dynamics, for example, on the electronic excited state. A notable exception is a study by Hamm et al. of a Re(I) complex where the t-2D-IR response was measured during the nonequilibrium relaxation on the MLCT excited states.³⁸ In this work, we describe the first experiments comparing equilibrated dynamics on the ground and triplet excited states and explain how they can be beneficial to understanding catalysis reactions initiated by light.

2.1. Equilibrium 2D-IR

Due to the diverse photophysical properties of the rhenium bipyridyl family of photocatalysts, considerable experimental effort has been expended to characterize the electronically excited, catalytically active state.^{1–3,7,10,39–42} In order to develop a complete framework for understanding the excited state, however, it is necessary to establish a structural and dynamical reference based on the electronic ground state. One

of the specific virtues of transient 2D-IR spectroscopy is the ability to map transient spectroscopic observations to the well-characterized equilibrium ground state, but this correspondence is only possible when the ground state has been studied in detail. Rhenium diimine carbonyl photocatalysts are particularly well suited to study with vibrational spectroscopy due to the presence of three strong IR transitions in a background free region of the spectrum. Solvent and substituents cause slight frequency shifts, but as a reference, $\text{Re}(\text{CO})_3(\text{bpy})\text{Cl}$ in tetrahydrofuran (THF) solvent has transitions at 1894 cm^{-1} [A'(2)], 1917 cm^{-1} [A''], and 2019 cm^{-1} [A'(1)], and these are delocalized over two [A''] or three [A'(2) and A'(1)] carbonyls. Despite intense interest in the electronic excited states, sparingly few studies have used 2D-IR spectroscopy to investigate the electronic ground state. Fayer et al. and Zanni et al. probed the structure and dynamics of rhenium catalysts on films with equilibrium 2D-IR.^{43,44} Zanni et al. used equilibrium 2D-IR to resolve multiple binding conformations of two rhenium dyes, $\text{Re}(\text{CO})_3(4,4'\text{-COOH-2,2'-bipyridine})\text{Cl}$ and $\text{Re}(\text{CO})_3(4\text{-COOH-2,2'-bipyridine})\text{Cl}$, bound to a semiconductor film. Though no dynamical information was extracted from the 2D measurements, they were able to establish that up to four different conformations result from the binding of the dye to the film, and when the surface has high dye coverage, coupling between the adjacent dyes is evident. Fayer et al. used 2D-IR to characterize *fac*- $\text{Re}(1,10\text{-phenanthroline})(\text{CO})_3\text{Cl}$ in solution and as a covalently linked monolayer on silica. For the monolayer case, in the presence of both solvent and air, the spectral diffusion times slowed drastically relative to bulk solution. The absence of solvent yielded the slowest spectral diffusion time scale. These variations in spectral diffusion times were attributed to differences in the available interaction mechanisms. Molecules in the monolayer were exposed to the solvent as well as other adjacent units in the monolayer, whereas the molecules in solution were only subject to fluctuations imposed by the solvent.

Recently, we observed a strict solvent dependence on the spectral diffusion times of a set of rhenium–bipyridyl molecules in polar solvents. We found that changing the electronic distribution within the molecule, by adding electron donating or withdrawing groups to the bipyridine, did not affect the spectral diffusion dynamics. The details of this experiment and a discussion of the results will be described in detail later in this Account.

2.2. Transient 2D-IR

The technique of transient multidimensional infrared spectroscopy as a method to study the rhenium photocatalyst was originally motivated by the work of Lian and co-workers who performed transient IR absorption experiments on $\text{Re}(\text{R}_2\text{-bpy})(\text{CO})_3\text{Cl}$ (R = COOH, COOEt) in multiple polar solvents. Using a visible pump (400 nm) and an infrared probe ($1820\text{--}2200\text{ cm}^{-1}$), they investigated the vibrational relaxation processes of the three carbonyl stretching modes after promotion to the electronic excited state.⁶ The resulting time-dependent solvation induced shifts in the peaks that were found to be mode dependent. The complexity of the peak shift dynamics, though similar for all three modes, made it difficult to assign the individual contributions due to solvation and vibrational relaxation. Peak narrowing, and hence low frequency mode vibrational relaxation dynamics, was determined to be solvent insensitive in the electronic excited state.

Probing vibrational modes in the electronic state naturally led to t-2D-IR studies, which offer better resolution in both structure and dynamics. The first investigations of a rhenium catalyst were by Hamm et al., who performed multidimensional nonequilibrium t-2D-IR experiments on the $\text{Re}(4,4'\text{-dimethyl-2,2'}\text{-bpy})(\text{CO})_3\text{Cl}$ in dimethyl sulfoxide (DMSO) by implementing the near-UV pulse at delay times of 1–6.5 ps prior to the infrared pulse sequence, allowing observation of the carbonyl stretching dynamics as they undergo solvation and vibrational cooling.^{38,45,46} By measuring a nonequilibrium FFCF, they observe both fast processes, which they attribute to libration, and slower processes associated with changes in the solvent packing. Hamm et al. also conducted polarization-dependent t-2D-IR experiments on the same compound, using a 20 ps time delay between the actinic and infrared pulses, concluding that they can suppress or enhance transient spectral features depending on the relative polarization angles between the near-UV and infrared.⁴⁷

Hamm and co-workers also performed a “triggered-exchange” 2D-IR experiment on the same system to label the vibrational modes before they were electronically excited.⁴⁸ In a triggered exchange sequence, the IR pulses first vibrationally excite, or label, the ground state modes, after which an actinic pulse excites the molecules electronically. The emitted signal reports the correlation between the initially excited ground state IR transition and the final excited state IR transition. Since photoinduced charge transfer in Re(I) complexes causes blue-shifted IR frequencies due to reduced back bonding, triggered-exchange (te) 2D-IR should enable a mapping of excited state vibrations to the basis of the ground state modes. In their report, they used cross-peaks in the te-2D-IR spectrum to confirm computational predictions that the lower frequency $A'(2)$ mode shifts farther in the excited electronic state than does the A'' mode (see Figure 4B).

One aspect of triggered-exchange 2D-IR in systems with multiple close-lying vibrational energy levels deserves comment. The ability to map vibrational modes between different electronic states can be limited by vibrational energy redistribution that can occur following the IR excitation of the labeling step. With too large a time delay between the labeling and the actinic excitation, intramolecular vibrational redistribution (IVR) can scramble the ground state vibrational label. In the case of the Re(I) carbonyls, we have shown that the IVR is quite rapid among all of the modes, thus somewhat diminishing the maximum possible contrast in a triggered exchange experiment.

The intrigue of photoinduced MLCT of the rhenium compound led Zanni et al. to covalently bind the rhenium dye $\text{Re}(\text{CO})_3(4\text{-COOH-2,2'}\text{-bipyridine})\text{Cl}$ to a semiconducting TiO_2 film to serve as a photoinduced electron injector.⁴⁹ The motivation of their transient and te-2D-IR experiments was to obtain structural information on the rhenium dye bound to the TiO_2 film and observe possible differences in electron ejection between conformations. The rhenium compound was found to have three distinct conformations, all of which led to an electronic excitation, but not in equal proportions. Their work shows that it is possible, using t-2D-IR, to not only observe multiple conformations of a dye on a semiconductor surface but also possibly to optimize the electron ejection dynamics by studying each conformation independently.

Recently, Weinstein et al. performed equilibrium and t-2D-IR experiments, reporting differences in the vibrational population dynamics of $\text{Re}(\text{Cl})(\text{CO})_3(4,4'\text{-diethyl-ester-2,2'}\text{-bipyridine})$ in

the electronic ground and excited states.⁵⁰ For transition metal complexes in polar solvents other than water, population dynamics tend to be most sensitive to intramolecular couplings, though we have observed solvent dependent IVR linked with solvent packing and hydrogen bonding.⁵¹ With a combination of 2D-IR and IR pump–probe spectroscopy, Weinstein et al. found mode specific population dynamics. For the high frequency $A'(1)$ mode, which is typically spectrally narrow and well-resolved, they found the vibrational relaxation in the electronic ${}^3\text{MLCT}$ state to be up to 8 times faster than that in the electronic ground state. When solvents of differing polarity were implemented, all of the modes were found to have solvent insensitive lifetimes in the electronic excited state, in contrast to the clear solvent dependence observed in the electronic ground state.

3. DIRECT COMPARISON OF GROUND AND TRIPLET STATES WITH EQUILIBRIUM AND TRANSIENT 2D-IR

While many groups focus on one particular step in the catalytic process, the goal of our current research is to characterize the spectral dynamics of known key intermediates in the CO_2 reduction catalytic mechanism, specifically the ${}^3\text{MLCT}$ state, the singly reduced species following reduction by a sacrificial electron donor, as well as the solvent-coordinated species and relatively stable intermediates such as $\text{Re}(\text{dmb})(\text{CO})_3\text{COOH}$ and $\text{Re}[(\text{dmb})(\text{CO})_3]_2(\text{CO}_2)$.^{13,52} Previous studies indicate that the catalysis is sensitive to the solvent, though it is not clear to what degree the solvent dynamics, rather than energetic stabilization, influences the catalysis. From this perspective, we began our investigations characterizing the ground state spectral dynamics of the original Lehn catalyst in multiple solvents commonly used in the reaction.⁵³ We then reported on the dynamics of the photoinitiated catalytically active, vibrationally cooled ${}^3\text{MLCT}$ state, which is a complementary approach to that taken earlier to study solvation during the relaxation process.⁵⁴ To further understand the t-2D-IR results, we performed solvent studies on several substituted Re(I) complexes having either electron donating or electron withdrawing groups attached to the bipyridyl ring.⁵⁵

Before discussing our experimental results, it is important to describe our specific experimental technique and how we obtain the FFCF. Briefly, we conduct two separate experiments for each waiting time (t_2), a rephasing (photon-echo) experiment and a non-rephasing experiment. The peak amplitude from the resulting non-rephasing 2D-IR spectrum is subtracted from the rephasing peak amplitude for each waiting time. These values are normalized by dividing by the sum of the peak amplitudes, and the result is referred to as the inhomogeneity index, $I(t_2)$.³⁷ The inhomogeneity index is proportional to the normalized FFCF [$C(t_2)$], so from here on, we will refer to the inhomogeneity index as the FFCF or $C(t_2)$. Previously published work gives a more detailed description of the experimental apparatus.⁵⁶

In the electronic ground state, we observe differences in the spectral diffusion times of the low frequency modes ($A'(2)$ and A'' ; ~ 1.4 ps, THF) and the high frequency $A'(1)$ mode (~ 2.8 ps, THF), as well as a solvent dependence. We have thus far not identified the origin of the spectral diffusion differences among the modes, but we also see this trend in CH_3CN and DMSO, as well as in other $\text{Re}(\text{bpy})(\text{CO})_3\text{Cl}$ derivatives in each of these three solvents.⁵⁵ A concentration dependence experiment, conducted in THF, determined that the FT-IR

spectrum and the ultrafast spectral diffusion times do not depend on concentration, indicating that the Re-based complexes do not aggregate. Similar lifetimes of all three carbonyl stretching modes (~ 25 ps) were observed and were obtained from the long time constant of a biexponential fit of the cross-peak amplitudes. These results form a basis with which to compare the vibrational dynamics on the $^3\text{MLCT}$ state.

Our transient 2D-IR experiments were conducted by implementing a 400 nm excitation pulse at time delays of 20, 40, and 60 ps prior to the probing 2D-IR pulse sequence, thus ensuring equilibration of the electronic excited state. For the t-2D-IR experiments, we use a chopper and report difference spectra. The results reveal very different dynamics from those exhibited by the vibrations on the electronic ground state. We observe a ~ 4.7 ps FFCF decay time for the $^3\text{MLCT}$ state that is similar for all three modes and 3-fold larger than that of the electronic ground state (~ 1.5 ps). Our vibrational lifetime results agree with those of Weinstein et al., in that they are 8 times faster in the electronic excited state (~ 3.2 ps) than in the electronic ground state (~ 25 ps), a difference that Weinstein et al. attribute partially to a higher density of states.⁵⁰

To understand the origin of such distinct dynamics, we first looked to DFT calculations to estimate the change in molecular dipole moments from the S_0 state to the $^3\text{MLCT}$ state, finding that $\mu_{S_0} = 14.1$ D and $\mu_{^3\text{MLCT}} = 5.8$ D. Following van der Zwan, Hynes, and more recently Maroncelli's treatment of dielectric friction and assuming the solvent properties do not appreciably change upon solute excitation, the ratio of the dielectric friction coefficients is equal to the ratio of the squares of the dipole moments,⁵⁷ $\mu_{S_0}^2 / \mu_{^3\text{MLCT}}^2$, which predicts a dynamical slowdown of a factor of 6. This result is promising, though not quantitative, as it qualitatively agrees with our observation of a 3-fold slowdown.

We later performed a t-2D-IR experiment on the $A'(1)$ mode of $\text{Re}(\text{CO})_3(4,4'\text{-tert-butyl-2,2'}\text{-bpy})\text{Cl}$ in THF (Figure 4D) to compare the spectral diffusion times of the unsubstituted (1) and *tert*-butyl substituted (3) compounds. The spectral diffusion in the electronic ground state (~ 3.3 ps) is faster than that in the $^3\text{MLCT}$ state (~ 4 ps), but not to the same extent as with the unsubstituted high frequency mode (S_0 , ~ 3 ps; $^3\text{MLCT}$, 4.7 ps). The more pronounced difference is in the inhomogeneity of the electronic excited state. The contribution of inhomogeneous broadening to an absorption line shape is reflected in the value of the FFCF at $t_2 = 0$, $C(0)$. For the t-2D-IR data, the extracted exponential decays are essentially the same for both $I(t_2)$ and $C(t_2)$, but since we are concerned with very small t_2 , specifically $t_2 = 0$, where the $I(t_2)$ deviates slightly from $C(t_2)$, we must compute $C(t_2 = 0) = \sin[\pi I(t_2 = 0)/2]$ to get the actual value of the intercept.³⁷ The initial value of the correlation function reports the degree to which dephasing during t_1 cannot be reversed by an echo pulse sequence. Generally speaking, the closer to 1 the initial value of the correlation function is, the more the line shape is dominated by inhomogeneous, and hence reversible, dephasing. The inhomogeneity for both 1 and 3 was found to be the same at ~ 0.1 . Upon electronic excitation, however, the inhomogeneity of the high frequency mode of 1 increases as evidenced by an intercept of 0.77 ($I(t_2 = 0) = 0.56$), while the intercept of the same mode of 3 becomes 0.97 ($I(t_2 = 0) = 0.86$) (Figure 3A,B). It remains to be determined what the origin of this pronounced increase in inhomogeneity is and how it depends on solvent.

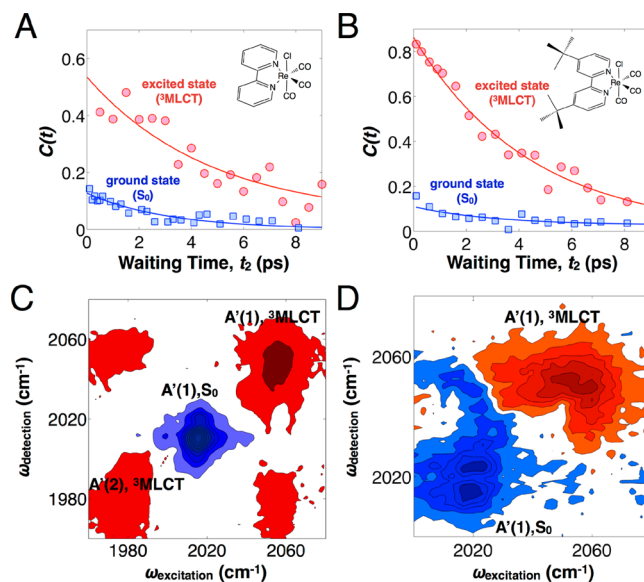


Figure 3. (A) FFCF of $\text{Re}(\text{CO})_3(\text{bpy})\text{Cl}$ in THF in the S_0 state (blue squares) and the $^3\text{MLCT}$ state (red circles). (B) FFCF of $\text{Re}(\text{CO})_3(4,4'\text{-tert-butyl-bpy})\text{Cl}$ in THF in the S_0 state (blue squares) and the $^3\text{MLCT}$ state (red circles). (C) Difference spectrum of $\text{Re}(\text{CO})_3(\text{bpy})\text{Cl}$ in THF. (D) Difference spectrum of $\text{Re}(\text{CO})_3(4,4'\text{-tert-butyl-bpy})\text{Cl}$ in THF. Portions of this figure are adapted with permission from ref 54. Copyright 2014 American Chemical Society.

Future studies using molecular dynamics simulations performed using alternatively the geometry, force field, and charges for the ground and excited state species may help to pinpoint the structural and dynamical changes associated with the charge redistribution.

The dramatic change in the local electron density of the carbonyls after the MLCT, causing the blue shifting of the carbonyl stretching modes, led us to perform experiments on a series of derivatives designed to modulate electron density on the ring.⁵⁵ Substituting the bipyridine with electron donating and electron withdrawing groups allowed us to chemically simulate to some degree the shift in charge density toward or away from the metal center, and thus from the carbonyl ligands. We synthesized $\text{Re}(\text{CO})_3(4,4'\text{-R}_2\text{-2,2'}\text{-bpy})\text{Cl}$ where $R = \text{H}$ (1), methyl (2), *tert*-butyl (3), or COOH (4) and $\text{Re}(\text{CO})_3(1,10\text{-phenanthroline})\text{Cl}$ (5) (Figure 4A) and performed electronic ground state 2D-IR experiments on all of the compounds in the solvents DMSO, THF, and CH_3CN . Figure 4B shows the linear infrared spectra of the compounds in DMSO, and Figure 4C shows the FFCF of the $A'(2)$ mode of the complexes in DMSO. Remarkably, we found no effect of the bipyridine substitutions on the 1D line shape or spectral diffusion, but a profound dependence on the solvent was discovered. The observed solvent dependence correlates with the donicity, or nucleophilic properties, of the solvent.⁵⁸ Increasing the donicity of the solvent slows the observed spectral diffusion time scale. For the $A'(2)$ mode of all five complexes, the FFCF decay times are ~ 4 ps (DMSO; Figure 4C) $> \sim 2.9$ ps (THF) $> \sim 1.4$ ps (CH_3CN); solvent donor numbers (kcal mol^{-1}), are as follows: 29.8 (DMSO) > 20.0 (THF) > 14.0 (CH_3CN).⁵⁵ That the individual substitutions on the bipyridine do not significantly alter the carbonyl solvent dynamics is unexpected but is consistent with our computational results⁵⁵ showing that while the $^3\text{MLCT}$ transition markedly alters the charges on the carbonyls, the chemical

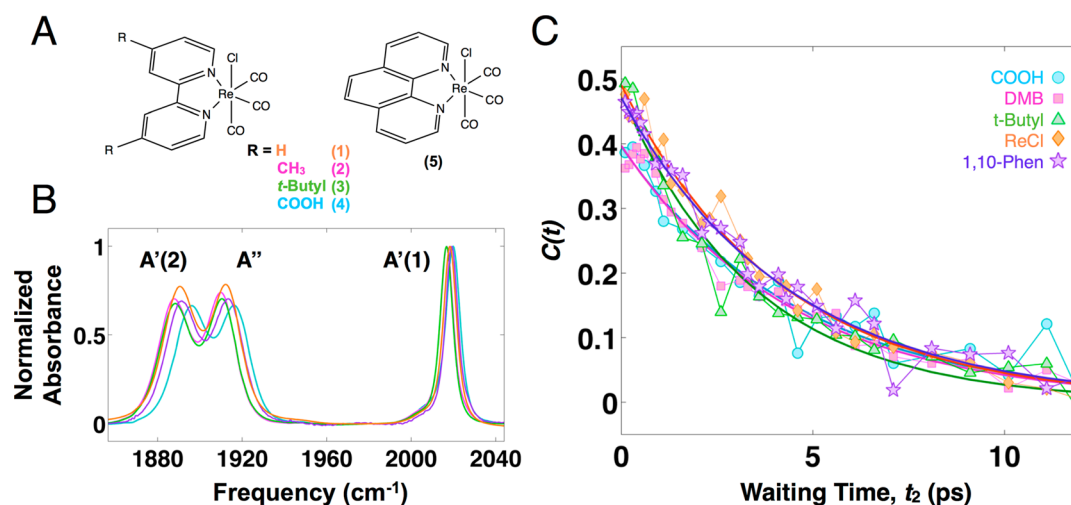


Figure 4. (A) Molecular structure of original Lehn catalyst (1) and substituents added to the bipyridine (2–5). (B) FTIR spectra of molecules 1–5 in DMSO. (C) FFCF of the A'(2) mode of 1–5 in DMSO. Figure adapted with permission from ref 55. Copyright 2015 American Chemical Society.

substitutions induce changes in partial charges only on the aromatic ligand. This finding highlights the potential pitfall in using observations made on the electronic ground state to predict excited state solvation dynamics, which are key to governing photocatalytic charge transfer processes.

4. SUMMARY AND OUTLOOK

This Account primarily focuses on the contributions that multidimensional infrared spectroscopy has made toward understanding rhenium bipyridyl photocatalysts. Two-dimensional-IR spectroscopy provides both structural and dynamical information and, when coupled with an actinic phototrigger, is capable of dissecting and comparing vibrational, spectral, and solvent dynamics on multiple electronic states. The rhenium diimine carbonyl complexes offer an ideal spectroscopic system due to the accessible and long-lived excited triplet state and the presence of very strong carbonyl IR spectator modes to track the photocatalytic cycle. The work summarized here has shown sensitivities, or lack thereof, to solvent, concentration, and substituents, as well as pronounced influences due to heterogeneous constructs such as films. In the immediate future, we can ask specific questions regarding solvation dynamics on the excited ³MLCT state, namely, are the electronic state-dependent differences in spectral diffusion solvent dependent? Since these investigations are breaking new ground, it also remains a key goal to link spectroscopy and dynamics to mechanism, performance, and design of current and next-generation carbon dioxide reduction photocatalysts. Thus, more general questions will center on the subsequent processes in the photocycle, which require two electron and two proton transfer steps. Since both proton and electron transfer occur through collective nuclear coordinates where reorganization, solvation, and polarization all contribute, how detailed a picture of charge transfer can we extract from equilibrium and transient 2D-IR spectroscopy? Can we identify transient structures, or can we resolve the stochastic interconversion between energetically similar species? Tremendous insight has been gained from 2D-IR spectroscopy of equilibrium, ground state systems, ranging from liquid water to large proteins, and we anticipate similar progress as we learn how to apply this methodology to transient states.

AUTHOR INFORMATION

Corresponding Author

*E-mail: kubarych@umich.edu.

Present Address

†Department of Materials Science and Engineering, University of Illinois, 1304 W. Green St., Urbana, IL 61801, United States.

Funding

This work has been supported by the National Science Foundation (Grants CHE-0748501 and CHE-1300239) and by the Camille & Henry Dreyfus Foundation.

Notes

The authors declare no competing financial interest.

Biographies

Laura M. Kiefer (B.S. Wayne State University, 2009) is a doctoral candidate in the Chemistry Department at the University of Michigan.

John T. King (B.S. SUNY Fredonia, 2009; Ph.D. University of Michigan, 2013) is currently doing postdoctoral research at the University of Illinois at Urbana–Champaign with Prof. Steve Granick.

Kevin J. Kubarych (Sc. B. Brown University, 1996; Ph.D. University of Toronto, Canada, 2003) is an Associate Professor of Chemistry at the University of Michigan.

REFERENCES

- (1) Takeda, H.; Koike, K.; Morimoto, T.; Inumaru, H.; Ishitani, O. Photochemistry and Photocatalysis of Rhenium(I) Diimine Complexes. In *Inorganic Photochemistry*, van Eldik, R., Stochel, G., Eds.; Advances in Inorganic Chemistry; Elsevier: Amsterdam, 2011; Vol. 63, pp 137–186.
- (2) Vlček, A. Ultrafast Excited-State Processes in Re(I) Carbonyl-Diimine Complexes: From Excitation to Photochemistry. *Top. Organomet. Chem.* **2010**, *29*, 73–114.
- (3) Kumar, A.; Sun, S.-S.; Lees, A. J. Photophysics and Photochemistry of Organometallic Rhenium Diimine Complexes. *Top. Organomet. Chem.* **2010**, *29*, 1–35.
- (4) She, C.; Guo, J.; Lian, T. Comparison of Electron Injection Dynamics from Re-Bipyridyl Complexes to TiO₂ Nanocrystalline Thin Films in Different Solvent Environments. *J. Phys. Chem. B* **2007**, *111*, 6903–6912.

- (5) Smieja, J. M.; Benson, E. E.; Kumar, B.; Grice, K. A.; Seu, C. S.; Miller, A. J. M.; Mayer, J. M.; Kubiak, C. P. Kinetic and Structural Studies, Origins of Selectivity, and Interfacial Charge Transfer in the Artificial Photosynthesis of CO. *Proc. Natl. Acad. Sci. U.S.A.* **2012**, *109*, 15646–15650.
- (6) Asbury, J. B.; Wang, Y. Q.; Lian, T. Q. Time-Dependent Vibration Stokes Shift During Solvation: Experiment and Theory. *Bull. Chem. Soc. Jpn.* **2002**, *75*, 973–983.
- (7) Liard, D. J.; Busby, M.; Matousek, P.; Towrie, M.; Vlček, A., Jr. Picosecond Relaxation of ³MLCT Excited States of [Re(Etpy)-(CO)₃(dmb)]⁺ and [Re(Cl)(CO)₃(bpy)] as Revealed by Time-Resolved Resonance Raman, UV-vis, and IR Absorption Spectroscopy. *J. Phys. Chem. A* **2004**, *108*, 2363–2369.
- (8) Cannizzo, A.; Blanco-Rodríguez, A. M.; El Nahhas, A.; Šebera, J.; Zálíš, S.; Vlček, A., Jr.; Chergui, M. Femtosecond Fluorescence and Intersystem Crossing in Rhenium(I) Carbonyl-Bipyridine Complexes. *J. Am. Chem. Soc.* **2008**, *130*, 8967–8974.
- (9) Benson, E. E.; Sampson, M. D.; Grice, K. A.; Smieja, J. M.; Froehlich, J. D.; Friebel, D.; Keith, J. A.; Carter, E. A.; Nilsson, A.; Kubiak, C. P. The Electronic States of Rhenium Bipyridyl Electrocatalysts for CO₂ Reduction as Revealed by X-ray Absorption Spectroscopy and Computational Quantum Chemistry. *Angew. Chem., Int. Ed.* **2013**, *52*, 4841–4844.
- (10) El Nahhas, A.; Consani, C.; Blanco-Rodríguez, A. M.; Lancaster, K. M.; Braem, O.; Cannizzo, A.; Towrie, M.; Clark, I. P.; Zálíš, S.; Chergui, M.; Vlček, A., Jr. Ultrafast Excited-State Dynamics of Rhenium(I) Photosensitizers [Re(Cl)(CO)₃(N,N)] and [Re-(imidazole)(CO)₃(N,N)]⁺: Diimine Effects. *Inorg. Chem.* **2011**, *50*, 2932–2943.
- (11) Dattelbaum, D. M.; Omberg, K. M.; Schoonover, J. R.; Martin, R. L.; Meyer, T. J. Application of Time-Resolved Infrared Spectroscopy to Electronic Structure in Metal-to-Ligand Charge-Transfer Excited States. *Inorg. Chem.* **2002**, *41*, 6071–6079.
- (12) Smieja, J. M.; Kubiak, C. P. Re(bipy-tBu)(CO)₃Cl-improved Catalytic Activity for Reduction of Carbon Dioxide: IR-Spectroelectrochemical and Mechanistic Studies. *Inorg. Chem.* **2010**, *49*, 9283–9289.
- (13) Hayashi, Y.; Kita, S.; Brunschwig, B. S.; Fujita, E. Involvement of a Binuclear Species with the Re-C(O)O-Re Moiety in CO₂ Reduction Catalyzed by Tricarbonyl Rhenium(I) Complexes with Diimine Ligands: Strikingly Slow Formation of the Re-Re and Re-C(O)O-Re Species from Re(dmb)(CO)₃S (dmb=4,4'-dimethyl-2,2'-bipyridine, S = solvent). *J. Am. Chem. Soc.* **2003**, *125*, 11976–11987.
- (14) Sullivan, B. P.; Meyer, T. J. Kinetics and Mechanism Of CO₂ Insertion into a Metal-Hydride Bond. A Large Solvent Effect and an Inverse Kinetic Isotope Effect. *Organometallics* **1986**, *5*, 1500–1502.
- (15) Hawecker, J.; Lehn, J. M.; Zissel, R. Efficient Photochemical Reduction of CO₂ to CO by Visible Light Irradiation of Systems containing Re(bipy)(CO)₃X or Ru(bipy)₃²⁺-Co²⁺ Combinations as Homogeneous Catalysts. *J. Chem. Soc., Chem. Commun.* **1983**, 536–538.
- (16) Barbara, P. F.; Meyer, T. J.; Ratner, M. A. Contemporary Issues in Electron Transfer Research. *J. Phys. Chem.* **1996**, *100*, 13148–13168.
- (17) Hamm, P.; Zanni, M. T. *Concepts and Methods of 2D Infrared Spectroscopy*; Cambridge University Press: New York, 2011.
- (18) Cho, M. Coherent Two-Dimensional Optical Spectroscopy. *Chem. Rev.* **2008**, *108*, 1331–1418.
- (19) Khalil, M.; Demirdoven, N.; Tokmakoff, A. Coherent 2D IR Spectroscopy: Molecular Structure and Dynamics in Solution. *J. Phys. Chem. A* **2003**, *107*, 5258–5279.
- (20) Woutersen, S.; Mu, Y.; Stock, G.; Hamm, P. Hydrogen-Bond Lifetime Measured by Time-Resolved 2D-IR Spectroscopy: N-Methylacetamide in Methanol. *Chem. Phys.* **2001**, *266*, 137–147.
- (21) Kim, Y. S.; Hochstrasser, R. M. Chemical Exchange 2D IR of Hydrogen-Bond Making and Breaking. *Proc. Natl. Acad. Sci. U.S.A.* **2005**, *102*, 11185–11190.
- (22) Zheng, J. R.; Kwak, K.; Chen, X.; Asbury, J. B.; Fayer, M. D. Formation and Dissociation of Intra-intermolecular Hydrogen-Bonded Solute-Solvent Complexes: Chemical Exchange Two-Dimensional Infrared Vibrational Echo Spectroscopy. *J. Am. Chem. Soc.* **2006**, *128*, 2977–2987.
- (23) Zheng, J.; Kwak, K.; Xie, J.; Fayer, M. D. Ultrafast Carbon-Carbon Single-Bond Rotational Isomerization in Room-Temperature Solution. *Science* **2006**, *313*, 1951–1955.
- (24) Bian, H.; Li, J.; Wen, X.; Sun, Z.; Song, J.; Zhuang, W.; Zheng, J. Mapping Molecular Conformations with Multiple-Mode Two-Dimensional Infrared Spectroscopy. *J. Phys. Chem. A* **2011**, *115*, 3357–3365.
- (25) Golonzka, O.; Khalil, M.; Demirdoven, N.; Tokmakoff, A. Coupling and Orientation Between Anharmonic Vibrations Characterized with Two-Dimensional Infrared Vibrational Echo Spectroscopy. *J. Chem. Phys.* **2001**, *115*, 10814–10828.
- (26) Woutersen, S.; Hamm, P. Structure Determination of Trialanine in Water Using Polarization Sensitive Two-Dimensional Vibrational Spectroscopy. *J. Phys. Chem. B* **2000**, *104*, 11316–11320.
- (27) Messmer, A. T.; Lippert, K. M.; Steinwand, S.; Lerch, E.-B. W.; Hof, K.; Ley, D.; Gerbig, D.; Hausmann, H.; Schreiner, P. R.; Bredenbeck, J. Two-Dimensional Infrared Spectroscopy Reveals the Structure of an Evans Auxiliary Derivative and Its SnCl₄ Lewis Acid Complex. *Chem.—Eur. J.* **2012**, *18*, 14989–14995.
- (28) Lee, K.-K.; Park, K.-H.; Park, S.; Jeon, S.-J.; Cho, M. Polarization-Angle-Scanning 2DIR Spectroscopy of Coupled Anharmonic Oscillators: A Polarization Null Angle Method. *J. Phys. Chem. B* **2011**, *115*, 5456–5464.
- (29) Bian, H.; Zhao, W.; Zheng, J. Intermolecular Vibrational Energy Exchange Directly Probed with Ultrafast Two Dimensional Infrared Spectroscopy. *J. Chem. Phys.* **2009**, *131*, No. 124501.
- (30) Kurochkin, D. V.; Naraharisetty, S. R. G.; Rubtsov, I. V. A Relaxation-Assisted 2D IR Spectroscopy Method. *Proc. Natl. Acad. Sci. U.S.A.* **2007**, *104*, 14209–14214.
- (31) Kwak, K.; Park, S.; Finkelstein, I. J.; Fayer, M. D. Frequency-Frequency Correlation Functions and Apodization in Two-Dimensional Infrared Vibrational Echo Spectroscopy: A New Approach. *J. Chem. Phys.* **2007**, *127*, No. 124503.
- (32) Klauder, J. R.; Anderson, P. W. Spectral Diffusion Decay in Spin Resonance Experiments. *Phys. Rev.* **1962**, *125*, 912–932.
- (33) King, J. T.; Baiz, C. R.; Kubarych, K. J. Solvent-Dependent Spectral Diffusion in a Hydrogen Bonded “Vibrational Aggregate”. *J. Phys. Chem. A* **2010**, *114*, 10590–10604.
- (34) King, J. T.; Kubarych, K. J. Site-Specific Coupling of Hydration Water and Protein Flexibility Studied in Solution with Ultrafast 2D-IR Spectroscopy. *J. Am. Chem. Soc.* **2012**, *134*, 18705–18712.
- (35) King, J. T.; Ross, M. R.; Kubarych, K. J. Water-Assisted Vibrational Relaxation of a Metal Carbonyl Complex Studied with Ultrafast 2D-IR. *J. Phys. Chem. B* **2012**, *116*, 3754–3759.
- (36) King, J. T.; Arthur, E. J.; Brooks, C. L., III; Kubarych, K. J. Crowding Induced Collective Hydration of Biological Macromolecules over Extended Distances. *J. Am. Chem. Soc.* **2014**, *136*, 188–194.
- (37) Roberts, S. T.; Loparo, J. J.; Tokmakoff, A. Characterization of Spectral Diffusion from Two-Dimensional Line Shapes. *J. Chem. Phys.* **2006**, *125*, No. 084502.
- (38) Bredenbeck, J.; Helbing, J.; Hamm, P. Solvation beyond the Linear Response Regime. *Phys. Rev. Lett.* **2005**, *95*, No. 082301.
- (39) Stufkens, D. J.; Vlček, A., Jr. Ligand-Dependent Excited State Behaviour of Re(I) and Ru(II) Carbonyl-Diimine Complexes. *Coord. Chem. Rev.* **1998**, *177*, 127–179.
- (40) Vlček, A., Jr.; Zálíš, S. Modeling of Charge-Transfer Transitions and Excited States in d⁶ Transition Metal Complexes by DFT Techniques. *Coord. Chem. Rev.* **2007**, *251*, 258–287.
- (41) El Nahhas, A.; Cannizzo, A.; van Mourik, F.; Blanco-Rodríguez, A. M.; Zálíš, S.; Vlček, A., Jr.; Chergui, M. Ultrafast Excited-State Dynamics of [Re(L)(CO)₃(bpy)]ⁿ Complexes: Involvement of the Solvent. *J. Phys. Chem. A* **2010**, *114*, 6361–6369.
- (42) El Nahhas, A.; van der Veen, R. M.; Penfold, T. J.; Pham, V. T.; Lima, F. A.; Abela, R.; Blanco-Rodríguez, A. M.; Zálíš, S.; Vlček, A., Jr.; Tavernelli, I.; Rothlisberger, U.; Milne, C. J.; Chergui, M. X-ray Absorption Spectroscopy of Ground and Excited Rhenium-Carbonyl

Diimine-Complexes: Evidence for a Two-Center Electron Transfer. *J. Phys. Chem. A* **2013**, *117*, 361–369.

(43) Rosenfeld, D. E.; Gengeliczki, Z.; Smith, B. J.; Stack, T. D. P.; Fayer, M. D. Structural Dynamics of a Catalytic Monolayer Probed by Ultrafast 2D IR Vibrational Echoes. *Science* **2011**, *334*, 634–639.

(44) Laaser, J. E.; Christianson, J. R.; Oudenhoven, T. A.; Joo, Y.; Gopalan, P.; Schmidt, J. R.; Zanni, M. T. Dye Self-Association Identified by Intermolecular Couplings between Vibrational Modes As Revealed by Infrared Spectroscopy, and Implications for Electron Injection. *J. Phys. Chem. C* **2014**, *118*, 5854–5861.

(45) Bredenbeck, J.; Hamm, P. Transient 2D-IR Spectroscopy: Towards a Molecular Movie. *Chimia* **2007**, *61*, 45–46.

(46) Bredenbeck, J.; Helbing, J.; Kolano, C.; Hamm, P. Ultrafast 2D-IR Spectroscopy of Transient Species. *ChemPhysChem* **2007**, *8*, 1747–1756.

(47) Bredenbeck, J.; Helbing, J.; Hamm, P. Transient Two-Dimensional Infrared Spectroscopy: Exploring the Polarization Dependence. *J. Chem. Phys.* **2004**, *121*, 5943–5957.

(48) Bredenbeck, J.; Helbing, J.; Hamm, P. Labeling Vibrations by Light: Ultrafast Transient 2D-IR Spectroscopy Tracks Vibrational Modes During Photoinduced Charge Transfer. *J. Am. Chem. Soc.* **2004**, *126*, 990–991.

(49) Xiong, W.; Laaser, J. E.; Paoprasert, P.; Franking, R. A.; Hamers, R. J.; Gopalan, P.; Zanni, M. T. Transient 2D IR Spectroscopy of Charge Injection in Dye-Sensitized Nanocrystalline Thin Films. *J. Am. Chem. Soc.* **2009**, *131*, 18040–18041.

(50) Delor, M.; Sazanovich, I. V.; Towrie, M.; Spall, S. J.; Keane, T.; Blake, A. J.; Wilson, C.; Meijer, A. J. H. M.; Weinstein, J. A. Dynamics of Ground and Excited State Vibrational Relaxation and Energy Transfer in Transition Metal Carbonyls. *J. Phys. Chem. B* **2014**, *118*, 11781–91.

(51) King, J. T.; Anna, J. M.; Kubarych, K. J. Solvent-Hindered Intramolecular Vibrational Redistribution. *Phys. Chem. Chem. Phys.* **2011**, *13*, 5579–5583.

(52) Agarwal, J.; Sanders, B. C.; Fujita, E.; Schaefer, H. F., III; Harrop, T. C.; Muckerman, J. T. Exploring the Intermediates of Photochemical CO₂ Reduction: Reaction of Re(dmb)(CO)₃COOH with CO₂. *Chem. Commun.* **2012**, *48*, 6797–6799.

(53) Hawecker, J.; Lehn, J. M.; Ziessel, R. Electrocatalytic Reduction of Carbon-Dioxide mediated by Re(bipy)(CO)₃Cl (bipy=2,2'-bipyridine). *J. Chem. Soc., Chem. Commun.* **1984**, 328–330.

(54) Kiefer, L. M.; King, J. T.; Kubarych, K. J. Equilibrium Excited State Dynamics of a Photoactivated Catalyst Measured with Ultrafast Transient 2DIR. *J. Phys. Chem. A* **2014**, *118*, 9853–9860.

(55) Kiefer, L. M.; Kubarych, K. J. Solvent-Dependent Dynamics of a Series of Rhenium Photo-Activated Catalysts. *J. Phys. Chem. A* **2015**, *119*, 959–965.

(56) Nee, M. J.; Baiz, C. R.; Anna, J. M.; McCanne, R.; Kubarych, K. J. Multilevel Vibrational Coherence Transfer and Wavepacket Dynamics Probed with Multidimensional IR Spectroscopy. *J. Chem. Phys.* **2008**, *129*, No. 084503.

(57) Maroncelli, M. Continuum Estimates of Rotational Dielectric Friction and Polar Solvation. *J. Chem. Phys.* **1997**, *106*, 1545–1555.

(58) Mayer, U.; Gutmann, V.; Gerger, W. Acceptor Number - Quantitative Empirical Parameter for Electrophilic Properties of Solvents. *Monatsh. Chem.* **1975**, *106*, 1235–1257.