

Transient 2D IR Spectroscopy of Charge Injection in Dye-Sensitized Nanocrystalline Thin Films

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Charge injection is one of the critical steps in the conversion of solar to electrical energy in dye-sensitized nanocrystalline thin films.^{1–3} Ultrafast infrared spectroscopy has emerged as a useful tool for studying this process because the ground and oxidized forms of the dye have unique vibrational frequencies and the free electrons in the semiconductor exhibit a broad electronic absorption that extends into the mid-infrared.^{4–6} The free electron absorption is particularly useful because it can be used to time-resolve the kinetics of electron injection. However, it is so intense that it obscures many vibrational features of the dye. A clear infrared spectrum of the excited dye is highly desirable, because it would help resolve multiple dye conformations that could then be used to measure their respective kinetics. Nonexponential injection kinetics is often attributed to multiple conformations, but it is difficult to distinguish this from other causes such as injection from more than one excited state.⁶

In this paper, we use nonlinear 2D IR spectroscopy to study TiO₂ nanocrystalline thin films sensitized with a Re dye (Figure 1a). We find that the free electron signal is not observed in the 2D IR spectra. Its absence allows the vibrational features of the dye to be much better resolved than with the typical IR absorption probe. We observe multiple absorption bands but no cross peaks in the 2D IR spectra, which indicates that the dyes have at least three structural conformations. Furthermore, by using a pulse sequence in which we initiate electron transfer in the middle of the infrared pulse train,⁷ we are able to assign the excited state features by correlating them to the ground state vibrational modes and determine that the three conformations have different time scales and cross sections for electron injection. 2D IR spectroscopy is proving to be very useful in disentangling overlapping structural distributions in biological and chemical physics processes,⁸ as well as organic photovoltaics.^{4,9,10} These experiments demonstrate that 2D IR probes are also a powerful means for studying photoinduced charge transfer at interfaces.

The dye that we study, referred to as Re1c, is shown in Figure 1a. The dye is synthesized by coordination of a bipyridyl linker to Re(CO)₅Cl, the details of which will be published later. It binds to the TiO₂ nanocrystalline thin films through the carboxylic acid group.¹¹ Shown in Figure 1a is the equilibrium 2D IR spectrum of Re1c over the a'(1) symmetric CO stretch region of the metal carbonyl vibrational modes. (The details of the pulse sequences used in these experiments are given in the Supporting Information (SI). The a'(2) and a'' CO modes lie outside our frequency range.) This spectrum is collected without initiating electron transfer. The spectrum exhibits three sets of diagonal peaks at $\omega_{\text{pump}} = 2020, 2030,$ and 2042 cm^{-1} with similar intensities. Re1c in solution only exhibits one set a'(1) diagonal peaks (see SI). Out-of-phase doublets appear in 2D IR spectra, with the fundamental vibrational transition appearing on the diagonal and the sequence transition shifted off the diagonal along ω_{probe} by the anharmonic shift of the vibrational

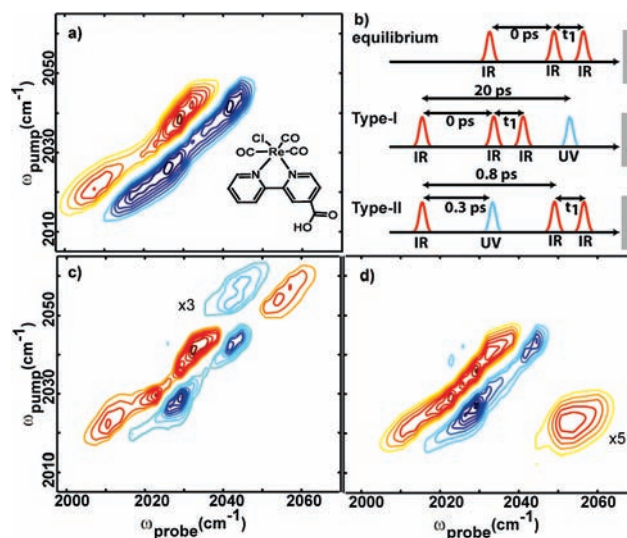


Figure 1. (a) Equilibrium 2DIR of Re1c on TiO₂. (b) Pulse sequences used to acquire 2D IR spectra. (c) Type-I and (d) Type-II transient 2D IR spectra of Re1c on TiO₂.

mode. We know that these three absorption bands correspond to three different structures and that their intensities give their relative populations for the following reasons. First, there are no cross peaks between the bands. If these three modes were located on the same molecule or caused by aggregation of multiple dyes, then we would expect the vibrational modes to be coupled, which they are not. Second, the anharmonic shifts of all three modes are similar ($\sim 10 \text{ cm}^{-1}$), which indicates a similar degree of excitonic coupling. Thus, the frequency shifts must be caused by differences in the local mode frequency of the carbonyl groups such as would arise from differences in their electrostatic environments. Third, simultaneous fits to the 2D IR and FTIR spectra indicate that the transition dipole moments of these states are the same to within the error of the fits (see SI). This fact can be deduced from the fits because FTIR spectra scale as $c|\mu|^2$ while 2D IR spectra scale as $c|\mu|^4$, where c is the concentration and μ is the vibrational transition dipole. Thus, for these three reasons, we conclude that the Re1c dye binds to the semiconductor in three different conformational states with approximately equal populations. We note that the population of the 2042 cm^{-1} state depends on the humidity of the sample.

To illustrate the advantages of using transient 2D IR spectroscopy to study electron injection, we begin by presenting a transient IR absorption experiment. Shown in Figure 2b are several transient IR spectra measured after initiating charge injection with a 400 nm ultrafast pump-pulse. Heilweil and Lian have pioneered the use of this technique for studying charge injection in dye-sensitized thin films, which provides a basis for interpretation of our spectra.^{5,12} A bleach appears around 2034 cm^{-1} with a correspond-

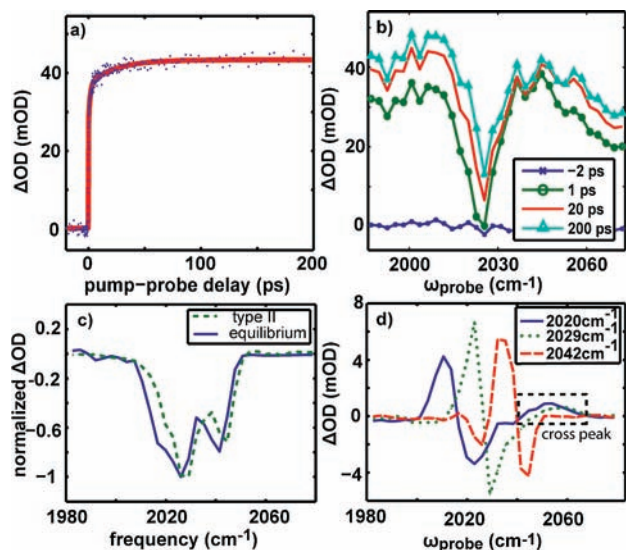


Figure 2. (a) Electron injection kinetics at 2000 cm^{-1} . (b) Transient absorption spectra of Re1c on TiO_2 . (c) Diagonal cuts through equilibrium and transient 2D IR spectra. (d) Horizontal cuts through the Type-II 2D IR spectrum.

ing new absorption at 2060 cm^{-1} . These features monitor the population change in the ground and excited electronic states of the dye, respectively. The spectra are vertically offset by the absorption of free electrons that have been injected into the semiconductor. The injection kinetics is monitored using this offset at 2000 cm^{-1} , which is shown in Figure 2a and exhibits multiexponential kinetics. The three individual absorption bands are not resolved in either the ground or excited electronic states of the transient IR spectra, largely due to the free electron offset. Thus, their respective kinetics cannot be individually resolved with transient IR spectroscopy.

Shown in Figure 1c is a transient 2D IR spectrum (Type I) of Re1C, collected 20 ps after charge injection. In this spectrum, the free electron absorption that dominates the transient IR measurements is completely absent, such that the three ground state bleach and excited state absorptions are clearly resolved. We believe that the free electron signal is absent in the 2D IR spectrum because the transition dipole strength is approximately equal for a one- or two-infrared photon process, at least at low concentrations with no multibody effects.¹³ Only anharmonic-type absorptions appear in 2D IR spectra. Thus, the free electron bleach and absorption signals cancel.

The absorptions of all three dye conformations are bleached, but only one excited state feature is observed. To better understand the origins of the excited state feature, we collected another transient 2D IR spectrum but this time placed the 400 nm excitation pulse in the middle of the 2D IR pulse sequence (Type II; Figure 1d). This pulse sequence correlates the ground state vibrational features along the pump axis with the excited state vibrational features along the probe axis.⁷ A cross peak appears in this spectrum centered at $\omega_{\text{probe}} = 2060\text{ cm}^{-1}$ and spanning from $\omega_{\text{pump}} = 2015$ to 2035 cm^{-1} , indicating that it is the two conformations with the lowest frequency absorptions that create the excited state absorption. This spectrum also reveals that the three dye conformations have different electron injection cross sections and rates, which we explain below.

Shown in Figure 2c is a slice through the diagonal of the Type-II transient 2D IR spectrum overlapped with the same slice through the equilibrium 2D IR spectrum of Figure 1a and normalized to

the strongest mode at 2030 cm^{-1} . All three features appear in the transient spectrum, indicating that all three conformations have undergone electronic excitation, but the mode at 2020 cm^{-1} is relatively less intense than the other two. Thus, the 2D IR spectra reveal that the three conformations have not all contributed equally to dye excitation. It may be that the three conformations have different electronic absorption cross sections caused by different mixings of the dye and semiconductor electronic states,¹⁴ although individual states are not resolved in the visible absorption band (not shown).

Shown in Figure 2d are slices through the transient 2D IR spectrum of Figure 1d, along the probe axis, that pass through the three ground state bleach features and any cross peaks that appear with the excited state vibrational absorption. The strongest cross peak is observed at 2020 cm^{-1} , a weaker peak at 2030 cm^{-1} , and no cross peak at 2042 cm^{-1} . Since the intensity of the cross peak primarily depends upon the population of the excited state at the time delay of the spectrum, unequal cross peak intensities indicate different electron injection rates. Thus, the three dye conformations have different electron injection rates, with the 2042 cm^{-1} mode being the fastest and the 2020 cm^{-1} mode the slowest.

2D IR spectra are presented here at only two delay times, but this technique could be used to fully resolve the kinetics of each dye conformation individually. The wavelength range could also be expanded to include the oxidized state and obtain a more complete picture of the electron transfer pathway. The usefulness of transient 2D IR spectroscopy to study charge transfer at interfaces is the ability to suppress unwanted signals, correlate vibrational modes, and time-resolve kinetics.¹⁵ These proof-of-principle experiments demonstrate some of the potential uses for 2D IR spectroscopy in studying electron transfer at molecule–semiconductor and molecule–nanoparticle interfaces.

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Supporting Information Available: Sample preparation, data collection, and analysis are described in further detail. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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