

Final Report: Vibrational Dynamics in Photoinduced Electron Transfer

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Executive Summary

The objective of this grant was to understand how molecular vibrational states (geometry distortions) are involved in photoinduced electron transfer rates of molecules. This subject is an important component of understanding how molecular absorbers of light convert that energy into charge separation. This is important because the absorption usually excites molecular vibrations in a new electronic state prior to electron transfer to other molecules or semiconductor nanoparticles, as in some types of solar cells. The speeds of charge separation and charge recombination are key parameters that require experiments such as those in this work to test the rules governing electron transfer rates. Major progress was made on this goal.

Some of the molecular structures selected for developing experimental data were bimolecular charge transfer complexes that contained metals of cobalt or vanadium. The experiments used the absorption of an ultrafast pulse of light to directly separate charges onto the two different molecular parts of the complex. The charge recombination then proceeds naturally, and one goal was to measure the speed of this recombination for different types of molecular vibrations. We used picosecond and femtosecond duration pulses with tunable colors at infrared wavelengths to directly observe vibrational states and their different rates of charge recombination (also called electron transfer). We discovered that different contact geometries in the complexes had very different electron transfer rates, and that one geometry had a significant dependence on the amount of vibration in the complex. This is the first and only measurement of such rates, and it allowed us to confirm our interpretation with a number of molecular models and test the sensitivity of electron transfer to vibrational states. This led us to develop a general theory, where we point out how molecular distortions can change the electron transfer rates to be much faster than prior theories predict. This provides a new method to predict electron transfer rates for particular conditions, and it will be important in designing new types of solar cells.

A related set of studies were also done to understand how much the environment around the active charge transfer molecules can control the speed of charge transfer. We studied different complexes with femtosecond transient absorption spectroscopy to show that solvent or components of a matrix environment can directly control ultrafast electron transfer when the environmental relaxation time response is on a similar time-scale as the natural electron transfer. Understanding such processes in both liquids and in a matrix is essential for designing new types of solar cells.

Scientific Summary

The objective of this grant was to understand how vibrational states (geometry distortions) are involved in photoinduced electron transfer rates of molecules. This subject is an important component of understanding how molecular absorbers of light convert that energy into charge separation. This is important because the absorption usually excites molecular vibrations in a new electronic state prior to electron transfer to other molecules or semiconductor nanoparticles, as in some types of solar cells. Major progress was made on this goal.

We provided the first room temperature, solution measurements of an electron transfer rate as a function of molecular vibrational state.^{2,3,6} These measurements required innovative ultrafast laser measurements with transient infrared wavelengths, and during the period of the grant we improved from 2-3 picosecond resolution to 50 femtosecond resolution.¹³ Thus far, these are the only measurements in the literature of vibrationally dependent electron transfer in solutions. We also developed electron transfer models^{8,13} and computational structural models^{7,10,14} to understand the experiments. We then generalized the treatment of vibrational properties of molecules for electron transfer or any exothermic kinetic process^{10,11}; where we discovered that proper treating of the vibrational distortion details can provide several orders of magnitude different rates than standard electron transfer models for exothermic cases. These two areas of accomplishment have created new insight into molecule based solar energy research that is being applied in many new contexts, and which will continue to be important.

A related finding was our discovery of a strong vibrational coherence in a class III mixed-valence molecule $[\text{Ru}_2(\text{TIED})\text{Cl}_4]^+$ that has two Ru metals linked by a nitrogen macrocycle.¹² This molecule is an example of how many inorganic molecules delocalize to accommodate mixed valence oxidation states and behave according to molecular orbital states. In particular, this molecule was able to have two channels of relaxation back to the ground state with no fluorescence, and the fastest channel has a strong vibrational coherence. This is once of the strongest low frequency coherences ever found, and it was due to being a promoting vibrational frequency that was part of a vibronic coupling between states. It shows for the first time that such terms are very important in molecular relaxation of inorganic molecules. Its significance is general in that many dye sensitizers in solar applications need to have charge transfer faster than such relaxation processes, and now we have a much clearer idea how vibronic coupling of low frequency molecular motions can enhance relaxation.

A more recent emphasis has been to find experimental systems that allow understanding the environmental effects on electron transfer.¹⁵⁻¹⁷ The motivation for these studies is that the molecular level structure in some solar cell designs is either liquid-like or matrix-like. Even in solid state molecular systems, there can be interfacial molecular motions that are more liquid-like than solid. The charge transfer takes place in some polarizable environment that requires environmental response, which has significant effects on rates and even pathways, as found in our earliest work.¹ We have studied charge transfer complexes both in solution and a matrix of hydrogen bonded molecules. The matrix experiments in trehalose glassy mixtures¹⁵ suggest that local solvation shells of water are important contributors to the kinetics, and models were

suggested to help understand that data. The solution studies^{16,17} have identified subpicosecond electron transfer with solvent control of the rates (crossover from a nonadiabatic to adiabatic mechanism). This experimental study on ultrafast electron transfer rates provides new insights, not previously found in other solvation studies, of electron transfer when the rate and medium relaxation are on similar time scales. The most recent data¹⁷ suggest additional theory and experiment to fully understand such effects and to allow predictions in the complex, heterogeneous structures of new types of solar cells.

Discussion of Some Specific Topics

Study of electron transfer with vibrational excitation:

The conceptual basis for studying vibrational effects on electron transfer is to find a molecular system where vibrational relaxation of some frequencies is slower than the electron transfer rates in solution at room temperature. The experimental design is to use an ionic charge transfer complex to provide solution phase stability of a structure made from two molecules; optical excitation can then directly transfer the electron and create a radical pair whose subsequent natural back electron transfer rate can be monitored as a function of vibrational state. This design requires molecules where successive quanta of vibrational population are shifted enough in frequency ($\sim 20 \text{ cm}^{-1}$) so that the decay of individual levels can be monitored by transient absorption of infrared vibration. The final result of the electron transfer can also be monitored by the vibrational populations in the ionic charge transfer pair since they are at very different frequencies. These experiments progressed from picosecond to femtosecond time scales on two complexes, and molecular modeling and electron transfer rate modeling was done to obtain insight into this phenomena.^{2-4,6-8,10-14}

The most recent charge transfer complex that was studied is $[\text{Co}(\text{Cp})_2^+|\text{V}(\text{CO})_6^-]$, where the radical pair $[\text{Co}(\text{Cp})_2|\text{V}(\text{CO})_6]$ is created by femtosecond charge-transfer excitation in the visible charge-transfer band.¹³ With transient infrared absorption spectroscopy we observe two electron-transfer components of $\sim 700 \text{ fs}$ and $\sim 5 \text{ ps}$ by transient IR with 75 fs resolution. The two ET lifetimes are attributed to the presence of two ion-pair contact geometries with absorption origins different by about $1250 \pm 350 \text{ cm}^{-1}$. The $\sim 700 \text{ fs}$ ET lifetime depends on the vibrational quantum state of the nontotally symmetric CO stretch in the $\text{V}(\text{CO})_6$ radical, where the lifetime decreases by $\sim 10\%$ for the first vibrational quantum and $\sim 45\%$ for the second quantum. There is no quantum effect for the second ion-pair geometry with a 5 ps ET lifetime. Standard ET rate models cannot explain the rate dependence for a nontotally symmetric mode, and we assign it as a breakdown of the Condon approximation. We also find that the intramolecular vibrational redistribution time (IVR) to transfer vibrational energy from the totally symmetric CO stretch to the nontotally symmetric stretch is less than 75 fs for a 1-quantum IVR process. An apparent change in the ET kinetics occurs when charge-transfer excitation wavelengths decrease from 800 and 700 nm to 620 and 555 nm. At the higher energies all quantum levels show a 200 fs rise time, which is unexpected for the zero quantum level. We assign this effect to the onset of sufficient internal vibrational energy in low-frequency vibrations to cause geometric interconversion

between energetically similar Jahn–Teller geometries in the $V(CO)_6$ radical. The rise time reflects the time for the $V(CO)_6$ radical species to assume a stable geometry by vibrational relaxation to the solvent. The hypothesis of two ion-pair geometries leading to different ET rates is supported by the transient absorbance data, where the relative amplitudes of the two rate components change with excitation frequency. Further examination of the charge-transfer band via time-dependent Raman analysis and Franck–Condon calculations confirms that two absorptions could exist under the single broad band.

Models for electron transfer in charge transfer complexes:

We have performed DFT calculations for the $V(CO)_6$ radical, the $Co(Cp)_2$ radical, and the $Co(Cp)_2|V(CO)_6$ radical pair. Primary interest was in the $V(CO)_6$ radical in both the isolated species and in the radical pair, as well as in solution.^{7-8,10,14} The most recent studies¹⁴ found several stable structures for the Jahn-Teller active 17 electron $V(CO)_6$ radical for both the isolated radical and in the radical pair. We confirmed prior studies that identified a D_{3d} structure as most stable, a D_{4h} structure at higher energies and a transition state of D_{2h} structure. We also found a new stable structure of C_{2h} geometry that is close ($\sim 130\text{ cm}^{-1}$) to the lowest energy D_{3d} structure. We calculated the relative energies of the isolated radical structures and the radical pair structures as a function of the metal-metal distance. In addition, we estimated interconversion barriers between these structures and found similar results for both the isolated radical and the radical pair. This similarity suggests that the radical pair is rapidly interconverting at room temperature in the same manner as the isolated radical. This has implications in the interpretations of ultrafast electron transfer dynamics. Specifically, a rise was observed for the radical carbonyl stretch vibration in the radical pair when the ion pair charge transfer absorption created excess vibrational energy in the radical pair. The rise time is not likely to be due to rapid geometric interconversion, but is probably due to anharmonic coupling between highly excited low frequency modes and the high frequency carbonyl stretches leading to a broadened carbonyl absorption band immediately after excitation. The observed rise time in absorption is conjectured to correlate with cooling of the low frequency vibrations to the solvent over 200 fs.

General models of vibrational distortions and electron transfer rates:

A related objective of the modeling was to examine if Franck-Condon contributions to the rate constant for ET were being over-simplified to the point of obscuring key mechanistic information.^{10,11} We have been able to show, in a *very general way* that ET in the exothermic domain requires a much better understanding of vibrations in molecules. In particular, fairly modest structural changes between electronic states can give *3 or more orders of magnitude increase in inverted region ET rates, and these effects have been totally unanticipated by prior work.* The coupling of vibrations called the Duschinsky effect is the core reason for the effect, and it had never been analyzed for consequences on ET rates. Several new effects arise from this work showing that even modest mixing of low and high frequency totally symmetric modes, as well as *non-totally symmetric modes*, are very important. This result will change our concept of absolute ET

rates and how they can be affected by molecular structure and bonding. In addition, the concept of vibrational reorganization energy needs to be redefined since it can become dependent on the mixing of vibrations in some cases.

Ultrafast Electron Transfer and Solvent Adiabaticity Effects

We studied ultrafast electron-transfer (ET) in charge transfer complexes and found solvent relaxation effects consistent with adiabatic crossover models of nonadiabatic ET.^{16,17} The complexes of either dimethyl viologen (MV) or diheptyl viologen (HV) with 4,4'-biphenol (BP) (MVBP or HVBP complexes) have identical charge transfer spectra and kinetics in ethylene glycol with ~900 fs ET decay. We assign this decay time as largely due to adiabatic control of a predicted ~40 fs nonadiabatic ET. The MVBP decay in methanol of 470 fs is reduced in mixtures having low (2-20%) concentrations of acetonitrile to as short as 330 fs; these effects are associated with faster relaxation time in methanol and its mixtures. In contrast, HVBP has much longer ET decay in methanol (730 fs) and mixture effects that only reduce its decay to 550 fs. We identify the heptyl substituent as creating major perturbations to solvent relaxation times in the methanol solvation shell of HVBP. These charge-transfer systems have reasonably well defined geometry with weak electronic coupling where the electronic transitions are not dependent on intramolecular motions. We have used a nonadiabatic ET model with several models for adiabatic crossover predictions to discuss the small variation of energy gap with solvent and the ET rates derived from adiabatic solvent control. A time correlation model of solvent relaxation was used to define the solvent relaxation times for this case of approximately zero-barrier ET.

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