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Energy Transfer Processes in Solar Energy Conversion
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M. D. Fayer
Department of Chemistry
Stanford University, Stanford, CA 94305

During the past year, we have made substantial progress in both theoretical and experimental aspects of the program. The program involves the investigation of excitation transport and electron transfer in complex systems. In the area of electron transfer, we have been studying electron back transfer following donor-acceptor photoinduced electron transfer. We are addressing this problem both theoretically and experimentally. In the area of excitation transport, we have been examining transport in solid solutions, liquid solutions, and in clustered excitation transport systems. Again, we are pursuing both experimental and theoretical approaches.

The problem of electron back transfer between photogenerated ions is of central importance in both artificial and biological solar energy conversion. Once an electron has been transferred from an optically excited donor to an acceptor, back transfer competes with the ability of the radical ions to go on to do useful chemistry. We are studying the back transfer process using picosecond transient grating experiments in conjunction with time resolved and steady state fluorescence quenching measurements. The transient grating experiment makes the back transfer process a direct experimental observable, while the fluorescence experiments allow the forward transfer to be examined. By combining the experiments, a complete picture emerges.

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We have obtained very high quality data on the donor-acceptor system, rubrene-duroquinone in sucrose-octa-acetate glass. By working in a glass, the molecules are held in fixed positions. Therefore, the theoretical analysis does not have to include molecular diffusion. Previously we had developed a theoretical description of this problem. However, it was so mathematically intractable, that it was difficult to apply. It was also not possible to extend the theory to include complex details of the problem. We have developed a new formal approach to the problem which resulted in a mathematically straight forward exact solution. The math is simple enough that we have been able to include accurately, for the first time, the influence of donor-acceptor and acceptor-acceptor excluded volume. Using this theory we have obtained very high quality fits to the experimental data over a wide range of acceptor concentrations. The theory shows that excluded volume effects are important at even relatively low concentrations, and provides accurate parameters which characterize the forward and back transfer processes.

The new theoretical approach is also making it possible to extend the theory to extremely important aspects of the electron transfer and back transfer problem. The theoretical description of experimental observables is essential to obtaining meaningful measurements. We have been able to formally include molecular diffusion into the forward and back transfer problem. Thus we will be able to move from solid solutions to liquids. We will be able to theoretically and experimentally address the extremely important problem of the competition between electron back transfer and diffusional separation of the ions. This is a central problem in solar energy conversion in

liquid solution. Previous treatments of this problem have been quite crude. The new theoretical approach is also enabling us to include the effect of solvent relaxation on electron back transfer. Again, this is an important aspect of the problem that has not been treated. When the ions are initially formed, the solvent has a configuration which is similar to that which surrounded the neutral donor and acceptor. As time goes on, the solvent structure will evolve to accommodate the charged ions. Prior to complete solvent relaxation, back transfer should be more rapid, since the solvent does not have to undergo a complete restructuring in going from ions to neutrals. Thus, the very short time behavior of the time dependent back transfer will be influenced by the nature and rate of the solvent relaxation. The theory which is under development will permit the detailed calculation of experimental observables, and therefore allow experimental investigation.

In the area of excitation transport, we have made some truly remarkable advances. In one series of experiments we have been examining excitation transport in a clustered chromophore system composed of chromophores attached randomly to a polymer chain. When the tagged chains are placed in a polymeric solid solution, each tagged chain acts as a clustered excitation transport system. Previously we had examined tagged PMMA in a PMMA host polymer solid. The samples have the form of plastic discs. In the new experiments, we have examined tagged PMMA in poly-vinylacetate (PVA). Because of unfavorable thermodynamic interactions between the PMMA and the PVA, the PMMA chains contract. This results in a smaller cluster, and the rate of excitation transport was observed to increase dramatically. Furthermore, using the

detailed statistical mechanical theory that we have developed to describe clustered systems, we were able to obtain the size of the PMMA chain when it is embedded in the PVA. The experiments and theory are quantitative with a size resolution of about one angstrom. We have also observed the the influence of microphase separation on excitation transport in this system. When the concentration of guest chains is increased in the host polymer beyond a certain point which is determined by the thermodynamic interactions of the guest and host chains, aggregation occurs. This results in microdomains rich in the chromophore containing polymer. The rate of energy transport increases dramatically as more chains are brought into the microdomains. This provides an approach for changing the rate of excitation transport without having to change the chemical nature of the tagged polymer.

In studies of the polymeric solids, we have observed, for the first time, dispersive excitation transport at room temperature and at lower temperatures close to room temperature. Dispersive transport has previously only been observed at temperatures of a few degrees Kelvin. It has generally been assumed that dispersive transport will never occur at room temperature. In a system which displays dispersive transport, the rate of excitation transport depends on the wavelength of excitation. This is in contrast to the usual situation described in terms of Forster transport theory. Basically, it has been believed that at room temperature the optical homogeneous linewidths are so wide compared to any inhomogeneous broadening, that all excitation wavelengths are equivalent. Because of the sensitivity of our experimental approach, which uses time resolved fluorescence depolarization measurements, we have observed dispersive transport. We

have also had some success in developing the first detailed statistical mechanics description of dispersive transport at high temperature (300 K). The observation of dispersive transport could have important implications in the development of useful excitation transport systems.

Finally, we have begun a series of picosecond transient grating experiments to study excitation transport among molecules randomly distributed in solution in systems in which the molecules are rotating on a time scale comparable to the time scale for excitation transport. Until now, only two limiting situations have been considered, i. e., no rotation (high viscosity solvents) or very rapid rotation (very low viscosity solvents). The Gochanour, Andersen, and Fayer theory has been shown to be an essentially perfect description in these two cases. In the no rotation case, it is necessary to average over the static set of orientations of the transitions dipoles of the molecules in obtaining the ensemble averaged Green function solution to the transport Master equation. In the rapidly rotating case, the interaction is angle averaged, and there is no angle average in the solution of the Master equation. Recently a theory has been developed by Fredrickson which describes transport in between these two limits. The difficulty is that the strength of the interaction between two molecules is changing at the same time that the transport is taking place. It requires a complex set of experiments to examine this problem. We are looking at a series of solutions which have different viscosities. We are measuring the rate of molecular rotation and the rate of excitation transport in the solutions of differing viscosity. The results will be compared to the predictions of the Fredrickson theory.

Publications Supported by the Department of Energy

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