

Energy Transfer Processes in Solar Energy Conversion

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During the past year, we have been working in three general areas: electronic excitation transport in clustered chromophore systems and other complex systems, photo-induced electron transfer and back transfer in liquid solutions in which diffusion and charge interactions are important, and the construction of a new two color dye laser system to enhance our experimental capability. In each area we have made considerable progress.

Recently we have been conducting experimental and theoretical studies of electronic excitation transport in clustered chromophore systems in which the clusters are at such high concentration that excitation transport occurs between clusters as well as on a single cluster. This is a very complex problem that is scientifically interesting and also interesting from a practical stand point. We are focusing on micelle systems and polymer systems. We have completed a detailed study of the micelle problem. The system is one that readily self-assembles. The chromophore is octadecyl rhodamine B (ODRB). This is a dye molecule with a long hydrocarbon tail. The micelles are Triton X-100. When mixed, the chromophore, which is ionic, resides on the surface of the micelle. At low micelle concentration, excitation transport occurs only on single micelles. This is a problem of excitation transport among chromophores distributed on the surface of a sphere. At high micelle concentrations, the micelles are close enough

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that excitation transfer occurs both on the initially excited micelle and between micelles. This increases the rate of transport.

Although we considered the low micelle concentration problem a number of years ago, we have made substantial advances in both experiment and theory. In our original theory, we used a second order density expansion in Laplace space. This resulted in a accurate but very complex formula. In order to compare to theory it was necessary to do a numerical inverse Laplace transform. We have now developed an equally accurate description of excitation transport for chromophores on a micelle based on a cumulant expansion with a Padé approximant. This is a very simple formula in the time domain that can be directly compared to experiment. We have studied low concentration micelles with a range of chromophores per micelle using time correlated single photon counting fluorescence depolarization measurements. This has given us a dramatic improvement in time resolution and signal to noise ratio compared to the measurements we made previously. Using the results and the new theory we are able to get quantitative agreement. The results show that at very high chromophore loading of the micelle, the chromophores are no longer randomly distributed. Because of the positive charge on the ODRB, the chromophores repel each other. We are able to determine the spatial distribution of the chromophores on the micelle surface from the details of the time dependence of the excitation transfer.

As the micelle concentration is increased, keeping the number of chromophores per micelle fixed, the time dependence of the energy transfer changes. At high micelle concentrations, transport between micelles becomes significant. This is an extremely complex theoretical

problem. We developed an approach we call the Effective Chromophore Method. It enables us to calculate the problem of excitation transport on and among micelles. We have tested the theoretical predictions by doing the high concentration micelle experiments. We examine micelle concentrations between 1% and 20%. We are able to reproduce the experimental curves almost exactly without adjustable parameters. This is an important result. It not only allows us to understand excitation transfer in micelle systems, but it proves that the theoretical method works. That will enable us to use it on other types of systems, particularly chromophores attached to polymer chains. In polymeric systems at high concentrations, microphase separation will occur. Thus excitation transport will not only occur among the chromophores on a single chain, but also among chains.

In another area of excitation transport research, we examined the temperature dependence (at and near room temperature) and wavelength dependence of excitation transport in systems of chromophores randomly distributed in solution. We recently showed that in highly viscous liquids, such as glycerol, excitation transport is dispersive, even at room temperature. This means that the standard assumption that is central to the Förster excitation transport theory does not apply. That is the optical lines are not homogeneously broadened. On the time scale of excitation transport, optical lines can be inhomogeneously broadened. However, liquids are not static, so on a long enough time scale, a chromophore will sample all transition energies in the optical line. This is called spectral diffusion. It has been observed in low temperature glasses (by the Fayer group) using techniques such as photon echoes. However, it has not previously been observed at room temperature,

and the influence of spectral diffusion on excitation transport has never be recognized.

We developed a theory that relates the rate of spectral diffusion to the wavelength dependence and temperature dependence of EET. Time resolved fluorescence depolarization measurements were used to measure EET in the systems rhodamine B (RB) in glycerol and propylene glycol as a function of wavelength and temperature from room temperature (298K) to 200K. Comparison with theory allowed us to determine the rates of the solvent fluctuations responsible for spectral diffusion for the two solvents at several temperatures. Measurements were also made of the rates of solvent relaxation about the excited RB and RB orientational relaxation. The results demonstrated that the mechanism for spectral diffusion is solvent orientational relaxation which causes the initial (time of optical excitation) dipolar field, produced by the solvent at the chromophore, to randomize. This work elucidates a fundamentally new aspect of EET.

In addition to our work on EET, we have also been studying photo-induced electron transfer and back transfer in liquid solution where diffusion of the molecules and interaction of the charged radical ions formed by electron transfer is important. We are particularly interested in the competition between electron back transfer (geminate recombination) and separation of ions by diffusion. We recently completed a study which looked at forward transfer in a relatively low viscosity solution in which diffusion of the donors and acceptors is extremely important to the kinetics of electron transfer. For the first time we were able to get quantitative agreement between experiments and theory.

The problem of back transfer is much more complex. We have just completed the full theory which includes the forward and back transfer processes with a long range transfer interaction, diffusion of the donors and acceptors, and diffusion of the ions once they are formed. The theory is good for any dielectric constant and includes the repulsion or attraction of the ions once they are formed. Previous theories have only treated the infinitely slow diffusion case and the infinitely fast diffusion case with transfer only occurring at a contact distance. We now can handle any diffusion constant. The roles of attraction (opposite charges formed) and repulsion (same sign charge on both radicals) as a function of dielectric constant are particularly dramatic. Vast changes in the yield of separated ions can occur when the dielectric constant of the medium is changed.

We have completed a moderate time resolution (150 psec) study of the back transfer process using a single color pump-probe experiment. We studied the time dependence of geminate recombination by observing the recovery of the neutral donor species. The study was done as a function of acceptor concentration in solutions for which the diffusion of the ions was of key importance. The data is in the final process of being fit at this time. This problem will be discussed further in the Research Plans section in the context of the new dual dye laser system that we are completing.

In July 1991 we received \$50,000 from DOE and a matching \$50,000 from Stanford University to upgrade our instrument for studying electron transfer. In addition Stanford invested another \$12,000 to upgrade the air conditioning and dust filtration in the laboratory. We have taken delivery of essentially all of the components, and we have

virtually finished the development of the new system. A considerable number of man hours went into this project. Because the amount of funds available was small compared to that necessary to buy a fully commercial system, we purchased major pieces, and we are building the rest. In addition, by building the system, we have been able to obtain a type of system that is not commercially available.

The new system consists of a mode-locked and Q-switched Nd:YLF laser. We bought the head and power supply and built the laser cavity. The 1 KHz repetition rate output of the YLF laser is then double in KTP to give over two watts of green (527 nm) light. This is beam split and used to pump two dye lasers. The dye lasers are entirely home built. Each is cavity dumped to produce independently tunable pulse of between 10 and 30 μ J at 1 KHz rep rate. The pulses currently are 20 psec. However, it seems clear at this point that further minor refinements will allow us to reach the design goal of 10 psec. The output of the dye lasers are directed onto a second laser table that contains the experimental setup. We are setting up to do both pump-probe experiments and transient grating experiments. One of the dye lasers runs in the visible and the other runs in the near IR. This will be used to directly detect the formation of radical cations. The experimental setup consists of a vast amount of optics and optical manipulators. In a grating experiment, three beams must be crossed in the sample. Each must have its spot size, intensity, position, time delay, and polarization controlled. We have also developed and purchase some specialized electronics for the detection of the signals. At the time of this writing, we are about one month away from having a fully functioning experimental system.

Publications Supported by the Department of Energy (Grant #DE-FG03-84ER13251)

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