

ABSTRACT

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Progress in four areas is summarized in the following:

I GEMINATE CHARGE PAIR RECOMBINATION IN HEXANE

II FAST CURRENT MEASUREMENTS RESULTING FROM EXCITATION OF CHARGE TRANSFER(CT) STATES

III MEASUREMENT OF THE DIPOLE MOMENT OF EXCITED STATES BY DC CONDUCTIVITY.

IV CHARGE SEPARATION AT MACROSCOPIC INTERFACES BETWEEN ELECTRON DONOR AND ACCEPTOR SOLIDS

In a final section, personnel who have contributed to the project during the past budget period are described.

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I GEMINATE CHARGE PAIR RECOMBINATION IN HEXANE

A manuscript describing our most recent work is almost ready for submission. The abstract of the manuscript follows:

Durene (1,2,4,5-tetramethylbenzene) dissolved in n-hexane was photoionized by 35 psec pulses at 266 nm. Transient absorption at 1064 nm arising chiefly from geminate electrons was detected and used to monitor the recombination of the electron-cation pairs produced by two-photon ionization. An excellent fit to the recombination kinetics was obtained by assuming that the distribution of initial electron-cation separations was of the form $r^2 \text{EXP} = r^2 / (2L^3) \exp(-r/L)$ with a mean radius $3L = 5.9$ nm.

My long-time collaborator in picosecond kinetics, Tom Scott, moved from Exxon to New York University this past September. I plan to visit NYU for a week or so in early December to do further studies of the recombination kinetics. One goal is to use SF₆ rather than n-perfluorohexane as electron scavenger in order to dissolve higher concentrations of scavenger at low temperature. A second is to look at the temperature dependence of the kinetics, and a third is to use a probe wavelength other than 1064 nm. We will probably use a 1.9 micrometer probe. The object of changing the analytical wavelength is to look for possible changes in the time dependence of the geminate pair absorption decay. If a difference in kinetics is observed, it will mean that the spectrum of the electron in hexane is time-dependent on the time scale of the recombination.

II FAST CURRENT MEASUREMENTS RESULTING FROM EXCITATION OF CHARGE TRANSFER(CT) STATES

This project continues to present difficulties connected with purification of phenanthrene and pyromellitic dianhydride(PMDA), the donor and acceptor, respectively, whose solid state charge transfer complex is our chief object of study. We now see unresolvably fast (<1nsec) risetimes for the photocurrent arising from the excitation of either the 1:1 solid or a sample in which the

phenanthrene is a host crystal and the PMDA a dilute guest. According to our original proposal, such a result would mean that dissociation of CT states proceeds from the initial, Franck-Condon excited state rather than from the relaxed excited state from which we observe fluorescence. This may be the case, but in the meantime (see below) we have proved that the reorientation of excited state dipoles in an electric field produces a displacement current of roughly the magnitude that we observe in the CT solids. Such a current would arise on the time-scale of a nearest neighbor electron transfer in the CT solids and thus lead to the fast current that we observe.

We ought to be able to distinguish between the "dipole current" and the dissociation current because the former is expected to decrease as the sample temperature is increased, while the later will increase. Most of the time spent on this project is devoted to sample purification in order to insure that the photocurrent measurements are as meaningful as possible.

III MEASUREMENT OF THE DIPOLE MOMENT OF EXCITED STATES BY DC CONDUCTIVITY.

We have recently succeeded in demonstrating that pulsed laser excitation of solution-phase molecules present between the electrodes of a conductivity cell gives rise to a fast dc photocurrent that is a direct measure of the change in dipole moment of the molecule upon excitation. This is an exciting result in that the method offers the possibility of direct observation of the charge displacement upon excitation in the numerous covalently-linked donor acceptor molecules that many groups are synthesizing. A manuscript describing our initial results has been submitted and its abstract follows: We report photocurrent transients arising from the pulsed laser excitation of the dipolar first excited singlet state S_1 of *trans* 4-dimethyl-amino-4'-nitrostilbene (DMANS) in toluene solution. The currents arise from rotational reorientation of DMANS dipoles with respect to the axis of an applied electric field. The method appears to offer a simple and general approach to the measurement of the change in dipole moment upon electronic excitation of a molecule.

It appears that the dipole measurement will allow direct quantitation of the extent of charge transfer in exciplex states, a question of long-standing

interest. Moreover, the method ought to allow measurement of the actual distance between "solvent separated ion pairs", objects of intense interest. A collaboration is beginning between this group and the group of Farid and Gould at Eastman Kodak in order to exploit the new method.

IV CHARGE SEPARATION AT MACROSCOPIC INTERFACES BETWEEN ELECTRON DONOR AND ACCEPTOR SOLIDS

We have just begun a collaboration with the group on Dr. C. Tang at Eastman Kodak in order to attempt to understand why charge carriers produced at a donor-acceptor interface separate into free carriers with such high efficiency. Recently, Dr. Tang showed that a photovoltaic cell that he constructed by vacuum evaporation had unusually good engineering efficiency (ca. 2%) as compared with other molecule-based solar cells. In the cell, charge carrier separation is believed to take place at the interface between a thin film donor layer and a thin acceptor layer. Dr. Tang's measurements were largely confined to cw excitation and standard IV curve recording. We hope to use pulsed laser excitation and fast current measurements to understand why carrier dissociation at the interface is so favorable.

PERSONNEL

Fuxing Hou, an associate professor in the Department of Physics, Peking University, continued on the project for a second year. Fuxing is working on the fast current measurements needed to gain mechanistic insights into the dissociation pathway of charge transfer states. She has spent most of the budget period doing chemical purification of donor and acceptor molecules.

Andrew Fusco '90 began working with me in the spring of 1989. He worked fulltime in the lab that term and then continued on part-time during his senior year. Andrew was the most self-sufficient undergrad who has ever worked with me, and he wrote a fine quality senior honors thesis that proved that absorption of UV (pump) photons by geminate electrons does not constitute a major perturbation of geminate pairs in hexane. He won a graduate fellowship from the National Science Foundation to fully fund his first three years of PhD studies. He's at Boulder, Colorado now using his fellowship to begin reseach in atmospheric science. He expects to become a

climate modeler who one day may be able to tell us just how serious the greenhouse effect is likely to become.

Steven Brown was our top chem major in the class of 1989. Steve stayed on and worked with me until August 1990 supported by the DOE grant. Steve is awesomely intelligent, but he wasn't all that confident of his laboratory abilities when he came to work. He first worked on the analysis of the picosecond transient absorption data that Sergei Smirnov and I had gathered and did such a fine job that we made him the co-author on a paper nearing submission. Then he tackled the problem of measuring excited state dipole moments. He is the first author on that submitted paper. Steve is now a first-year graduate student in the Department of Chemistry at the University of Wisconsin/Madison.

Karyn Grzeskowiak, a new graduate student in the group, worked with Steve during his final months and is already making new contributions to our method of measuring excited-state dipole moments.

Henry Spindler '92 joined the group this past September. At the end of his sophomore year last spring, Henry had a 4.0 average, 8 citations, and was a member of the heavyweight varsity crew. A citation is a sort of super A plus that a Dartmouth prof usually awards only to the top student in a course. Henry intends to try to understand a molecule-based solar battery invented by a friend of mine, Ching Tang, at Eastman Kodak. None of us understands why the cell is so efficient.

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