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Project Report for the Grant Period 10/1992 -9/1993

**Electronic and Nuclear Factors in Intramolecular Charge
and Excitation Transfer Processes**

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Research Group:

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During the first 12 months our primary efforts concentrated on the synthetic aspects of the project, as well as on the development of the necessary instrumentation. Also, as one can see above, the research group of the PI grew considerably since the submission of the original proposal. Since our original proposal contained three sub-projects we will report the progress in the same sequence.

1. Intramolecular Triplet Excitation Transfer Bands.

All necessary bichromophoric molecules have been synthesized (nearly 20 compounds, including the reference ones). The measurements aimed at the observation of the intramolecular triplet excitation transfer bands are in progress. The bands are expected to be extremely weak and thus far we were not successful at detecting them directly. However, we are observing red-shifts in the visible portion of the triplet spectra of these molecules. This leads to believe that as our skills in working in the NIR part of the transient spectrum improve, we should be able to reach our goal. We are also exploring the possibility suggested by one of the referees that the optical triplet excitation transfer is a two-photon process.

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This project has spawned an exciting and promising collaboration with Professor Donald Levy's group at the University of Chicago. It came to our attention that the spirane molecules (I, II, III) prepared for this study are perfect candidates for high-resolution molecular beam measurements of very weak electronic couplings. Indeed, we were able to show that the electronic coupling between the chromophores in the vibrational ground state of the electronically

excited states of I, II and III is exactly zero (to within 0.05 cm^{-1}), i.e., in the $\nu = 0$ vibrational state of the molecule there is no electronic communication between the two halves. Only when the molecule is excited to approximately 400 cm^{-1} above the fluorescence origin of either chromophore, the coupling between the two chromophores is turned on. This is the most elegant example of purely vibronic coupling in a relatively complex molecular system and, as far as we are aware, the only reported case involving two separate chromophores. The first part of this work has been presented at the 1993 ACS National Meeting in Chicago and at present it is being submitted for publication.

The synthetic chemistry which we have learnt during this work opened an interesting route to novell ligands for organometallic donor-acceptor systems. We have already prepared a spiro-fluorene-4,4'-diazfluorene (IV) capable of forming complexes with transition metal ions, e.g., ruthenium. We will also prepare compounds V and VI, which can serve as either electronically

isolating (V) or conducting (VI) building blocks linking two metal centers, possibly leading to new materials with interesting optical and magnetic properties.

2. Donor-Bridge-Acceptor Systems with a Tethered Ion.

Our synthetic work towards the simple form of a molecular switch (VII) has greatly accelerated since the delayed arrival of the post-doctoral associate in August of this year. We are now capable of producing large quantities (5 grams) of the 2,6-diamino-dihydroanthracene

precursor (VIII) and of the corresponding amide (IX) in crystalline form. As this report is being written the first attempts at oxidation of (IX) to the corresponding 2-amino-6-nitro-dihydroanthracene (X) are undertaken.

At this stage the full spectroscopic and kinetic characterization of X has to be performed in order to confirm that, indeed, it is a suitable model compound for the intended study. Only if the charge separated state of X will exhibit a lifetime of 10 ns or more we can proceed with the further synthesis of VII. If the lifetime of the charge separated state of X is too short, we will begin the synthesis of the alternate donor-acceptor system described in the original proposal.

Simultaneously with the synthetic work we are developing a mathematical model of intramolecular ionic diffusion which we plan to apply to our systems. In this model the ion motion is described by a separate reaction coordinate orthogonal to the "normal" dipolar solvation. This approach in principle combines the Eigen treatment of ionic solutions with the concept of two modes of solvation presented by Hynes and van der Zwan, as well as by Sumi and Marcus.

3. Depolarization of Transient Microwave Conductivity.

We now have a fully functioning time resolved microwave conductivity apparatus utilizing an NdYAG laser as the excitation source. The system is controlled by a PC computer with an efficient graphical interface and data analysis software written by us.

We have also prepared ultra-high purity *para*-amino-nitro-biphenyl (XI) and *para*-amino-nitro-terphenyl (XII):

The measurements on solutions of XI in silicon oil and in paraffin oil are currently in progress. As pointed out by some of the referees, due to severe dielectric losses measurements in polar solvents are not feasible.

We are also experimenting with immobilizing XI and XII in room temperature glasses (paraffin wax and poly-methyl-methacrylate) and measuring the transient microwave conductivity response as a function of the angle between the polarization plane of the laser beam and this of the electric field inside the microwave cavity. The results of these measurements, as much as they are interesting by themselves, are primarily intended as reference data which will aid interpretation of the measurements in viscous liquid media.

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