F I N A L R E P O R T

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

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Solvation of charge separated states in mixed solvents. The solvation of charge separated states of the probe molecules (aminonitroterphenyl and aminonitrobiphenyl) in mixed solvents has been investigated. It was found that the solvent mixtures consisting of a nonpolar principal solvent (hexane, benzene, toluene) and varying amounts of a polar co-solvent (acetonitrile, DMSO) do not behave as a homogeneous medium characterized by an average dielectric constant, but exhibit clear polar enrichment and specific solvation effects. The polar co-solvent was invariably found to concentrate in the vicinity of the probe molecule in the excited CT state, thus creating a local environment of a much higher polarity than the average, macroscopic dielectric constant would imply. The local polar enrichment effects are strongly temperature dependent and lead to large thermochromic shifts of the absorption spectra of the CT excited states. Indeed, we were able to record the largest reported thermochromic shifts of $\sim 50 \text{ cm}^{-1}/\text{K}$.

Molecular orbital symmetry in excitation and charge transfer: The now completed study of a large series of model compounds with a spiro linkage (below) has demonstrated that the concept of "symmetry forbidden" excitation transfer is valid only for near-degenerate donor-acceptor systems. As the energy gap between the donor and the acceptor increases, the perfect symmetry cancellation of the coupling becomes impossible, even if the zero-order localized wavefunctions of the donor and the acceptor are orthogonal. The donor state becomes resonant

RIGID SPIRANES WITH VARIABLE DONOR-ACCEPTOR ENERGY GAPS

with one or more vibrationally excited states of the acceptor giving rise to non-zero off diagonal elements (vibronic or Herzberg-Teller coupling). Thus the donor-acceptor coupling becomes dependent on the available density of states and the system cannot be described in terms of the standard Marcus-Jortner theory.

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Since the donor - acceptor coupling in our spiranes is vibronic some special effects, including unusual distance dependence of the excitation transfer, are expected. In order to explore these

effects we synthesized a new family of model compounds in which the symmetry of the localized orbitals has been maintained, however, both the distance and the density of the available vibrational states have been increased by the insertion of the adamantane bridge (above). Naturally, the increased distance should lead to a decrease of the purely electronic coupling element, however, the increased density of states should enhance the vibronic terms.

As it was outlined in our proposal it is of interest to investigate whether a similar density of states dependent behavior is observed in a "symmetry forbidden" triplet excitation transfer proceeding via the exchange mechanism. With this objective in mind we designed two new model compounds containing anthrone as the triplet donor and fluorene as the triplet acceptor (below). These systems are weakly exoergic, $\Delta G = 4$ kcal/mol. As it was expected on the basis

of the earlier results, the "symmetry forbidden" triplet transfer in the spirane on the left is rapid and occurs on a sub-nanosecond time scale. Evidently, the vibronic coupling is strong enough to override the zero order symmetry considerations of the electronic wavefunctions. The spirane on the right, with the adamantane bridge between the donor and the acceptor is being prepared.

Transient Raman experiments: We have completed the integration of the nanosecond time resolved transient Raman spectrometer built around the newly purchased Oriel intensified CCD camera and the existing Nd:YAG laser. The overall time resolution of the system is ~ 6 ns.

We have already recorded a number of Raman spectra of solutions of electrolytes in which the characteristic solvent vibrational frequencies are altered due to the electrostatic interaction with the ions of the salt. The efforts to obtain a resonant Raman spectrum of the charge transfer probe molecule associated with an electrolyte are continuing. Interestingly, very intense stimulated Raman scattering (a so-called "Raman laser") from the $>C=C<$ stretching mode of a twisted olefin, bi-4*H*-cyclopenta[*def*]phenanthren-4-ylidene (biphenanthrenylidene) has been also obtained. This important effect is being investigated in detail.

Publications in 1996:

Singlet Biradical → Singlet Zwitterion Optical Transition in a Twisted Olefin, P. Piotrowiak, G. Strati, S. N. Smirnov, J. M. Warman and W. Schuddeboom, *J. Am. Chem. Soc.*, **1996**, *118*, 8981.

Electrolyte Effects in Intramolecular Excitation Transfer, P. Piotrowiak, *ACS Advances in Chemistry Series*, in print.

Excited State Behavior of Twisted Olefins with Rigidly Linked and Rotationally Free Chromophores, P. Piotrowiak and G. Strati, *J. Photochem. Photobiol.*, in print.

Probing Preferential Solvation and Ion Aggregation with Charge Transfer Triplets of Aromatic Amino- Nitro- Compounds, P. Piotrowiak, R. Kobetic and T. Schatz, *J. Photochem. Photobiol.*, in print.

Intramolecular Electronic Energy Transfer in Ru(II) Diimine Donor/Pyrene Acceptor Complexes Linked by a Single C-C Bond, J. A. Simon, S. L. Curry, R. H. Schmehl, T. R. Schatz, P. Piotrowiak, X. Jin and R. Thummel, *J. Am. Chem. Soc.*, submitted.

Presentations at conferences in 1996:

The Role of MO Symmetry and the Density of States in Intramolecular Excitation Transfer Electron Donor-Acceptor Interactions Gordon Research Conference, Newport, Rhode Island, August 1996

Excited State Behavior of Twisted Olefins with Rigidly Linked and Rotationally Free Chromophores, International Meeting of Physical Chemistry, Riccione, Italy, July 1996

Probing Preferential Solvation and Ion Aggregation with Charge Transfer Triplets of Aromatic Amino- Nitro- Compounds, International Meeting of Physical Chemistry, Riccione, Italy, July 1996.

The Dependence of Intramolecular Excitation Transfer on the Molecular Orbital Symmetry and the Density of States, XX DOE Solar Photochemistry Conference, French Lick, Indiana, June 1996.

Palladium (II) Complexes with 4,5-Diazospirobifluorene and 4,4',5,5'-Tetraazobifluorenylidene, 211th National American Chemical Society Meeting, New Orleans, Louisiana, March 1996.

Preferential Solvation in Binary Solvent Mixtures, 211th National American Chemical Society Meeting, New Orleans, Louisiana, March 1996.

Singlet Biradical → Singlet Zwitterion Transition in a Twisted Olefin, 211th National American Chemical Society Meeting, New Orleans, Louisiana, March 1996.

Palladium (II) Complexes with 4,5-Diazospirobifluorene and 4,4',5,5'-Tetraazobifluorenylidene, XXVIII Mardi Gras Symposium, New Orleans, Louisiana, February 1996.

Preferential Solvation in Binary Solvent Mixtures, XXVIII Mardi Gras Symposium, New Orleans, Louisiana, February 1996.

Singlet Biradical $\rightarrow$ Singlet Zwitterion Transition in a Twisted Olefin, XXVIII Mardi Gras Symposium, New Orleans, Louisiana, February 1996.

Invited talks at universities in 1996:

Vibronic Coupling and "Symmetry Forbidden" Excitation Transfer, Department of Chemistry, University of Ferrara, Ferrara, Italy, July 1996.

Ion Pairing and MO Symmetry Effects in Charge and Excitation Transfer, Department of Chemistry, Rutgers University, New Brunswick, February 1996.

Investigations of the Role of MO Symmetry and Electrolytes in Charge Transfer Reactions, Department of Chemistry, Rutgers University, Newark, February 1996.

Molecular Orbital Symmetry and Electrolyte Effects in Intramolecular Charge Transfer, Department of Chemistry, Temple University, Philadelphia, January 1996.

Ion Association, Specific Solvation and Vibronic Coupling, Department of Chemistry, University of Texas, Austin, January 1996.