

Photochemistry

Grammaticakis-Neumann Prize Winner 1996: Prof. Matthew B. Zimmt

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The Swiss Society of Photochemistry and Photophysics has awarded the *Grammaticakis-Neumann* Prize to Prof. *Matthew B. Zimmt*, Brown University, Providence, USA. The *Grammaticakis-Neumann* Prize is awarded to young scientists for excellent research in the field of photochemistry.

Matthew Zimmt received his Ph.D. from Columbia University, New York, in 1985,

under the direction of Prof. *N. Turro*, and did postdoctoral studies with Prof. *M.D. Fayer* at Stanford University. In 1987, he was assigned Assistant Professor at Brown University in Providence, Rhode Island, where he is now Associate Professor since 1993.

The prize was attributed to *Matthew Zimmt* in recognition of his excellent contribution to the elucidation of photochemical

and photophysical processes by the use and development of original methods for spectroscopic analysis of complex molecular model compounds.

The following article contains the basic contents of the *Grammaticakis-Neumann* Lecture held by *Matthew Zimmt* on the occasion of the Prize Award Ceremony on October 1, 1996.

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Intramolecular Electron- Transfer Studies as a Function of Bridge Topology: The Importance of Solvent- Mediated Donor-Acceptor Electronic Coupling

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Abstract. The donor-acceptor electronic coupling matrix elements, $|V|$, for photoinduced, intramolecular electron-transfer (ET) reactions in one linear and three C-shaped molecules have been determined from the temperature dependence of ET rate constants. The coupling matrix element in the linear molecule was found to be solvent-independent. By contrast, the coupling matrix elements in two of the three C-shaped molecules exhibit significant solvent dependence. Donor-acceptor coupling matrix elements were calculated for the linear and C-shaped molecules in the absence and presence of solvent molecules using the generalized *Mulliken-Hush* theory. Together, the experimental and theoretical results indicate that solvent molecules, and not the covalent bridge, mediate the electronic coupling in the C-shaped molecules. Preliminary studies of ET rate constants as a function of solvent bulk are also described.

1. Introduction

Electron transfer (ET) reactions play important roles in chemistry, biology, and technology. Over the last twenty years, the chemical community has developed an increasingly sophisticated understanding of the factors that control the kinetics of these fundamental reactions. Throughout this development, *Marcus* theory [1] and its semiclassical analogs [2] provided a framework for organization of observations and for *a priori* design of molecular performance. These theories furnish descriptions of the activation free energy for ET (more generally termed a *Franck-Condon*-weighted density of states, FCWDS) in terms of intrinsic reaction barriers, the solvent (λ_s) and vibrational (λ_v) reorganization energies, and the thermodynamic driving force for reaction ($-\Delta G^\circ$). In systems involving D(onor) and A(acceptor) sites separated beyond *van der Waals* contact, the ET rate constant is often expressed as $k_{ET} = (2\pi/\hbar) |V|^2 \text{FCWDS}$, where $|V|$ is the magnitude of the electronic coupling matrix element between D and A. Many of the most interesting studies per-

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