The research supported by this AFOSR grant has involved a multi-technique (NMR, ESR, laser flash photolysis, single photon counting, photoluminescence, tailor-made syntheses, computer simulation) approach to address problems concerning the structure and dynamics of transient high energy intermediates. These techniques have been employed to investigate the behavior of these intermediates when the latter are confined to the interfacial regions of restricted reaction spaces such as micelles, zeolites, cyclodextrins, water soluble polymers, and silica. Unique information has been obtained concerning the nature of interactions between the transients as substrates bound to receptors by non-covalent bonding. This information, in turn, has been exploited to investigate situations for which the transients display extraordinary dynamic properties such as reactivity which is controlled by the application of very weak applied magnetic fields.
STABILIZATION AND CONTROL OF HIGH ENERGY INTERMEDIATES THROUGH ADSORPTION ON RESTRICTED SPACES

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September 16, 1994

Final Technical Report for the period 1 September 1991 - 31 August 1994

Prepared for

Air Force Office of Scientific Research
Building 410
Bolling Air Force Base, DC 20332
Final Technical Report

Stabilization and Control of High Energy Intermediates through Adsorption on Restricted Spaces

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I. Abstract of technical progress

The research supported by this AFOSR grant has involved a multi-technique (NMR, ESR, laser flash photolysis, single photon counting, photoluminescence, tailor-made syntheses, computer simulation) approach to address problems concerning the structure and dynamics of transient high energy intermediates. These techniques have been employed to investigate the behavior of these intermediates when the latter are confined to the interfacial regions of restricted reaction spaces such as micelles, zeolites, cyclodextrins, water soluble polymers, and silica. Unique information has been obtained concerning the nature of interactions between the transients as substrates bound to receptors by non-covalent bonding. This information, in turn, has been exploited to investigate situations for which the transients display extraordinary dynamic properties such as reactivity which is controlled by the application of very weak applied magnetic fields.

II. Status of the research effort: Significant accomplishments

This AFOSR grant produced the following significant accomplishments through 53 published manuscripts during the funding period (numbers in parentheses refer to the list of publications below):

A. The establishment of the mechanisms of a range of photophysical phenomena and photochemical reactions in restricted spaces including cyclodextrins (1, 20); zeolites (8, 11, 19, 26, 35); micelles (6, 10, 14); polymers (21, 32), starburst dendrimers (7, 42); and DNA (39, 50).

B. The establishment of the mechanisms of reactions of electronically excited states in solution. The systems investigated include acyclic ketones (18, 27, 33, 34, 40, 41, 46, 49) and cyclic ketones (2, 36).

C. The establishment of the mechanism of magnetic isotope and magnetic field effects on photochemical reactions in restricted spaces. The systems studied include magnetic isotope effects on radical pair reactions in homogeneous solution (13) and in micelles (4, 5, 12, 23, 24, 28, 44, 48); and the use of chemically induced dynamic nuclear polarization as a probe of magnetic effects (17, 43).

D. The use of steady state and time resolved electron spin resonance to investigate photoreactions in solution and in restricted spaces. The systems investigated include the use of spin probes to investigate restricted spaces (15, 22); the use of electron spin polarization to examine reaction mechanisms (29, 31, 37, 38); and the use of electron spin resonance to investigate the mechanism
of polymer stabilization by hindered amines (45), and the structure of triplet states (52, 53).

E. The use of time resolved laser flash spectroscopy to investigate the mechanism of electron transfer reactions in solution (3, 9, 51) and in restricted spaces (47).

III. Cumulative list of publications


--- Papers In Press ---


Papers Submitted for Publication


IV. List of professional personnel:

Dr. Gabriella Caminati  Ms. Shufang Niu
Dr. Naresh Ghatlia  Mr. Chung-Hsi Wu
Mr. Matthew Lipson  Mr. Zhi Liu


Ph.D. 1994 Mr. Matthew Lipson  Thesis title: “Conformational Control of the Photochemistry and Photophysics of Benzophenone and Diphenylacetone”

V. Coupling Activities

Papers presented at meetings, conferences, seminars, etc.
Year 1: September 1, 1991 to August 31, 1992
Gramatakakis Lecturer, Swiss Photochemical Society, Lausanne, Sept. 1991
Dow Distinguished Lecturer, Michigan State Univ., Oct. 1-4, 1991
Appleton Lecturer, Brown University, Nov. 18-19, 1991
Yale University, Dec. 11, 1991
Castle Lecturer, Univ. South Florida, Tampa, FL Dec. 4, 1991
University of Utah, Feb. 25, 1992
Colorado State Univ., March 18, 1992
Linus Pauling Lecturer, Oregon State Univ., March 9-13, 1992
Stanley Cristol Lecturer, Univ. Colorado, March 16, 1992
R.T. Major Lecturer, Univ. Connecticut, April 16, 1992
Lemieux Lecturer, Univ. Ottawa, May 4-6, 1992

Year 2: September 1, 1992 to August 31, 1993
Univ. No. Carolina, Chapel Hill, Sept. 25, 1992
Edward Arnett Symposium, Duke University, Sept. 26, 1992
Henry Kwivila Lecturer, SUNY Albany, October 13, 1992
Drexel University, December 2, 1992
Ramapo College, December 4, 1992
George Washington Univ., January 14, 1993
Powell Lecturer, University of Richmond, February 12, 1993
Broberg Lecturer, North Dakota State Univ., April 5-6, 1993
University of Virginia, April 23, 1993
Welch Foundation Lecturer May 5-7, 1993

Year 3: September 1, 1993 to August 31, 1994
Dow Distinguished Lecturer, University of Western Ontario, Sept. 20-22, 1993
Dauben Lecturer, Univ. Calif. at Berkeley, November 2, 1993
G.L. Closs Memorial Lecturer, November 15, 1993
University of Amsterdam, NL May 30, 1994
University of Utrecht, NL May 31, 1994
University of Delft, NL June 1, 1994
Havinga Memorial Award Lecture, Leiden, NL , June 2, 1994
Porter Medal Award Lecture, IUPAC Photochemistry Conf., Prague, Czech Republic July 22, 1994
XVth Solar Energy Conference, Interlaken, Switzerland, July 24-29, 1994
Plenary Lecturer, IIIrd Inter. Symp. on Magnetic Field and Spin Effects in Chemistry & Related Phenomena, Chicago, Sept. 26, 1994

Consultative & advisory functions to other laboratories, especially DoD labs:
Institutions, locations, dates and names of individuals involved

Year 1. The PI spoke to AFOSR research personnel at Edwards Air Force Base in California concerning the use of EPR techniques. The PI also had discussions with Dr. Frederick Hedberg (Bolling Air Force Base) on the possible use of
photochemical methods and adsorption on zeolites as a possible means of destroying hazardous chemicals.

**Year 2.** The PI had several conversations with Dr. Hedberg of AFOSR concerning the possible use of zeolites to terminate fires and as substrates for photomineralization of hazardous chemicals of interest to AFOSR. Two AASERT fellows performed summer undergraduate research in the PI’s laboratory during the summer of 1993.

**Year 3.** The PI attended a meeting at Tyndall Air Force Base, Florida on May 12 and 13, 1994 to discuss AFOSR’s mission in “Subsurface Fate & Transport in Environmental Quality.” He had numerous fruitful conversations with AFOSR researchers concerning the strategy for investigating the fate, transport, and assessment program for toxic materials. During this meeting, a number of connections were made with other PIs, in particular Dr. Howard Hanley, who will be supplying the Columbia group with clay materials and will be collaborating on neutron scattering investigations, Dr. Theodore Mill and Professor John Hassett who will be collaborating on the fate of quadracyclane adsorbed in simulated natural waters and adsorbed on clays.

On August 23, 1994 the PI met with Dr. Frederick Hedberg, Dr. Ted Mill, Professor Patrick Sullivan and Professor John Hassett at SRI’s Washington Office in Arlington, VA. At this meeting the preliminary results with quadracyclane were discussed and a priority was placed on the next series of experiments. Plans were also made to obtain from Dr. Robert Schmitt of SRI International samples of potassium dinitramide for testing in our laboratory.
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distribution in unlimited.
Joan Boggs
STINFO Program Manager

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