Inter-American Photochemical Society Newsletter

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Linda J. Johnston
Steacie Institute for Molecular Science
National Research Council
Ottawa, ON K1A 0R6
ljj@ned1.sims.nrc.ca

Vice President

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Department of Chemistry
Northwestern University
Evanston, IL 60208-3113
lewis@chem.nwu.edu

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Department of Chemistry
New Orleans, LA 70118
schmehl@mailhost.tcs.tulane.edu

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College Park, MD 20742
df37@umail.umd.edu

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University of Victoria
P.O. Box 3055
Victoria, B.C.
Canada V8W 3P6
bohne@uvic.ca

Miguel G. Neumann (South America)
Instituto de Quimica e Fisicade Sao Carlos
CP 369, Universidade de Sao Paulo
Sao Carlos, Sao Paulo CEP 13560
Brazil
neumann@iqsc.sc.usp.br

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1999 I-APS Award in Photochemistry: Doug Neckers

Professor Douglas Neckers of Bowling Green State University is the winner of the 1999 I-APS Award in Photochemistry. This Award recognizes outstanding contributions to the advancement of the photochemical and photophysical sciences during the last ten years. The nomination material notes that Doug is one of the world's leading practitioners of pure and applied photopolymerization science, with many contributions to both mechanistic studies of photoinitiation and commercial applications. His record of service to the photochemical community, particularly in the development of the Center for Photochemical Sciences at Bowling Green, is equally impressive. Please join us in honoring Doug at the next Winter Conference in Clearwater Beach in January 2000.

I-APS Fellowship: Glenn Crosby

Professor Glenn Crosby has been elected to Fellowship in the Inter-American Photochemical Society. Fellowship is awarded on the basis of lifetime scientific achievements in photochemistry or contributions to the science of photochemistry as a discipline or service to the Society. The nomination material notes that Glenn's fundamental work on the spectroscopic characterization of excited states has provided the basis for many developments in inorganic photochemistry and photophysics and their applications to device technology and energy-storage problems. Please join us in honoring Glenn at the next Winter Conference in Clearwater Beach in January 2000.

Mailing List Update

Enclosed with this issue are several sheets of mailing list updates. These are new additions since the list that was mailed with the May issue. They are not bound with the regular issue because we thought members would want to attach them to their mailing list book instead.

I-APS Electronic Distribution Lists

Electronic mail distribution lists have been created for general announcements to all I-APS members. The lists have been set up as one-way electronic mailings and are being maintained by Professor Mary Boyd at Loyola University of Chicago. If you have an announcement of interest to the general membership (e.g., postdoc openings, job postings, conference announcements), please send an e-mail message to mboyd@luc.edu and the message will be sent to the membership.

If you have not been receiving these irregular mailings or have recently changed your email address, please forward your new address to Professor Boyd so that she may get you added to the list.

Eleventh Inter-American Photochemical Society Winter Conference

Clearwater Beach, Florida
January 1-5, 2000

Co-Chairpersons

Edwin F. Hilinski	Joseph T. Hupp
Florida State University	*Northwestern University*

Information, as it becomes available, will be posted on the world-wide web. Go to the Inter-American Photochemical Society web site at <http://www.chemistry.mcmaster.ca/~iaps/>, click on "Conferences", and scroll to the entry for this meeting.

13TH INTERNATIONAL CONGRESS ON PHOTOBIOLOGY

July 1-6, 2000
Hyatt Regency San Francisco
San Francisco, California, USA

I would like to invite all IAPS members to attend the 13th International Congress on Photobioogy which will be held in San Francisco July 1-6, 2000. Photobiology 2000 is the quadrennial meeting of the AIP (Association Internationale Photobiologie) which has asked the American Society for Photobiology to be the organizer of the 13th ICP. The IAPS is one of six other photochemistry/photobiology groups are participating in Photobiology2000. The program will cover a wide range of topics. There will be several special lectures by internationally renowned scientists. The scientific program is being organized by Nancy Oleincik (Case Western Reserve University — send her your suggestions: nlo@po.cwru.edu). A comprehensive program is being designed to encourage active participation with special emphasis on emerging areas of photobioogy. As would be expected for a meeting of the 'millennium' there will be several plenary sessions as well as parallel sessions. Symposia and workshops on highly relevant and timely topics and poster sessions will be on the schedule. Please mark these dates on your calendar as there will be no other major meeting of photochemists and photobiologists in 2000. In addition to the exciting scientific program, San Francisco will offer many scenic and cultural attractions. Also, because the meeting dates include July 4th, one of the most festively celebrated US holiday, we expect there will be other interesting activities that will help to make this a memorable occasion for all participants. **Frank Gasparro, Dept. of Dermatology, Thomas Jefferson University, 233 South 10th St, Room 428, Philadelphia, PA 19107**

Glenn Arthur Crosby: Fellow of the Inter-American Photochemical Society

By David McMillin

We are happy to announce that Glenn Arthur Crosby is now a Fellow of the Inter-American Photochemical Society. Without exaggeration, Glenn's professional achievements are enormous. He was among the first to apply emission spectroscopy to the elucidation of the excited states of coordination compounds, and he has been a world leader in the development of experimental spectroscopic criteria for classifying excited states. Glenn's collective works have laid the fundamental basis for continuing developments involving the excited states of coordination compounds and their applications to device technology and energy-storage problems.

Throughout his career Glenn has worked to elucidate the nature of excited states and to relate the results to the electronic structures by using sophisticated spectroscopic methods in combination with group theory. His contributions cover the gamut of coordination chemistry. Early on, he defined the mechanism of intramolecular energy transfer in rare earth chalets, and he uncovered important deuterium isotope effects. He then did pioneering work in the area of emissive d^6 transition metal complexes involving metal-ligand charge-transfer excited states as well as d-d excited states. Later, he made important contributions in the area of ligand-ligand excited states with d^{10} metal ions.

With all these chromophores Glenn established operational criteria for identifying the nature of excited states experimentally, and he developed optical techniques and analytical methods for extracting excited state parameters from luminescence measurements. He was the first to recognize the importance of sub-77 K temperature-dependence investigations for understanding the role of spin-orbit coupling in controlling excited state properties and was also the first to show how complexes can be engineered to have desired photochemical and photophysical properties by judicious modifications of the ligands.

A long time member of the I-APS, Glenn has held Fulbright and Humboldt fellowships, and he has served on committees of the National Academy of Sciences/National Research Council and Research Corporation. He has also been one of the most influential chemistry educators in the United States and is a recipient of the ACS Award in Chemical Education.

Douglas Neckers: 1999 I-APS Award in Photochemistry

By George Hammond

I was enormously pleased to learn that Doug Neckers is the winner of the 1999 IAPS Award in Photochemistry. It is also a pleasure to recount, in condensed form, some of the highlights of the career which has led him to this richly merited recognition.

Neckers was born and grew up in western New York state. He attended Hope College, graduating in 1963. Doug is a living testimonial to the recognized excellence of undergraduate instruction, especially in chemistry, at that institution. He then did his graduate work at the University of Kansas where he worked with Earl Huyser. The work of the Huyser group at that time was focused on the chemistry of free radicals. The radicals were generally generated thermally although Neckers and Huyser found that their work led naturally into the waxing field of photochemistry. They first found that the reduction of ketones, a classical photochemical process, could be affected by radicals produced thermally.[1,2] The work was extended to study of the photoreduction of alkyl phenylglyoxates dissolved in alcohols.

Neckers then went to Harvard as a postdoctoral fellow in the late Paul Bartlett's lab. There he became irrevocably infected with the photochemical virus. At Harvard he met another postdoc, named Nick Turro, and the two collaborated in developing the photochemistry of the ketene dimers, 1,3-cyclobutane diones.[3] After Harvard, Doug returned to Hope as a member of faculty. He continued to enhance the reputation of that institution as a premiere center for undergraduate education[4] by his classroom and laboratory instruction and by his vigorous undergraduate research program. The research was predominantly in photochemistry although he also entered the field of polymer science for the first time. His interest in polymers was partly photochemical and partly light-free.

He was interested in using polymers as chemical mediators, as protective vehicles for sensitive chemical reagents[5] or as scaffolds for hearing photochemically active functional groups.[6]

In 1971 he went to the University of New Mexico where he was first able to add graduate students to his research group. He developed cross linked polymer-based photosensitizers which have the virtue of being separated from solutions in which they are suspended or as fixed beds in photochemical processes.

In 1973 Neckers moved to Bowling Green State University in the state of Ohio as Chairman of the Chemistry Department. The move had significant importance to both the University and Doug Neckers. The institution had a solid reputation as an undergraduate teaching institution and was in the initial years of a process intended to develop a research university while maintaining the quality of its undergraduate instruction. Doug has been a leader in that movement. He perceived that to develop a significant research capability it was necessary to do things differently; simple emulation of traditional research institutions would not be successful. Although many of them were truly excellent, the country and the State of Ohio already did not need more of the same. A crucial factor in creation of the "difference" at Bowling Green was funding and development of the Center for Photochemical Sciences, a unit designed to focus on a specific area of science, a contrast to the more common across the board growth in the traditional natural sciences. The Center has earned worldwide recognition, has had symbiotic coexistence with the Chemistry Department and has extended beyond the Department to include members of the faculties of Biology and Physics. Bowling Green has become a truly different university.

Concurrent with his role in institution building, Neckers has maintained a vigorous and growing program of personal research. In his research he has also chosen a "different" path. The decades of the '70s and '80s were an exciting period of growth in research on the photochemistry of small organic and inorganic small molecules and some movement into biological chemistry. Doug chose to emphasize photochemistry related to macromolecular science. His group did report interesting photochemistry of small molecules, especially photocyclo-addition reactions of acetylenic compounds[7] but their emphasis was increasingly centered on Neckers' long time interest in polymers. Three papers published in 1983 signaled what has become the dominant theme of his program - photoinitiation of vinyl polymerization. The first described peresters as photoinitiators,[8] the second dealt with sensitization of perester photolysis by benzophenone[9] and the third disclosed Doug's long term love affair with Rose Bengal and related dyes as photoinitiators.[10] He has subsequently continued study of both photoinitiation of polymerization and "small molecule" photochemistry of the initiators. The key step in most of the initiation reactions is photoinduced electron transfer. The concept had been recognized much earlier by Gerald Oster,[11] but his work with photoinitiation of polymerization by dyes and his mechanistic suggestions were ignored by most of us in the '60s. We were too infatuated by the chemical magic that could be wrought by electronic energy transfer to consider other sensitization mechanisms. Other uses had been developed by the 1980's[12] but Neckers broadened them greatly and brought valuable mechanistic understanding to guide his own work and that of others. He has published more than 50 papers reporting the work. Furthermore, the research does not adhere to any single path but branches to produce a highly informative pattern. The group has synthesized many new dyes designed to cover the visible spectral region and extending it into the near infrared. By use of these dyes they can tune the photoinitiating systems to respond to light of a wide variety of exciting wavelengths.[13] This allows assembly of polychromic photoimaging systems for tricolor photoimaging and has even pushed the excitation out of the visible and into the near IR. They have studied mechanistic details of many initiating systems including both radical (for acrylates) and cationic (for epoxides) recipes.

One of the intriguing side issues in photopolymerization was observation that fluorescence, from twisted intramolecular charge transfer fluors included in a polymerizing mixture, changes as the reaction proceeds. The

fluors are known to emit from two different excited states, one first formed on excitation and the other produced by relaxation of the first formed to a second excited state. It is not surprising that changing the properties of the medium from high fluidity to highly viscous slows the relaxation rate. However, it is surprising that careful calibration shows that there is a simple linear relationship between the degree of polymerization and relative populations of the two emitting states. The results provide a remarkably simple means for on-line determination of the degree of cure in a polymerization system.[14]

Neckers has not been content to merely develop new chemistry for others to use. He has been actively involved in real world application of the knowledge gained in his laboratory. He has been a valued consultant for industrial labs for years and has recently participated in formation of a company, Spectra Group Limited, to use photopolymerization to produce three dimensional models which faithfully translate knowledge stored in computer tomographic (CAT) scans into three dimensions.[15] The most important application at this time is medical imaging. Models of internal structures, hearts, bones, etc., can be built for the use of physicians in diagnosis and planning of surgical and other therapeutic procedures.

Finally, I mention that Doug has contributed greatly to the health and progress of photochemistry through his public services. He has served on committees and editorial boards, organized meetings and so on. *Spectrum*, the newsletter from the Center for Photochemical Sciences, is distributed to thousands of scientists around the world and holds a unique position among the multitude of scientific publications. It reports views of Doug and others on issues of the day and presents a wonderfully diverse series of reports of progress by photochemists -- a far cry from the usual institution newspaper. Finally, in 1991 Doug became one of the three editors of *Advances in Photochemistry* and now serves as the lead editor of that series.

Doug Neckers is an unusual person and an unusual scientist. He does not follow beaten tracks but creates his own itinerary. He is a paramount pure *and* applied scientist and we owe much to his dedication to the photochemical sciences.

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XVII IUPAC SYMPOSIUM ON PHOTOCHEMISTRY
July 19-24, 1998, Sitges, Spain

Lucian A. Lucia

Institute of Paper Science and Technology, Georgia Institute of Technology,

500 10th St., N.W., Atlanta, GA 30318-5794

ABSTRACT OF SYMPOSIUM

The XVII biennial IUPAC Photochemistry symposium was held in Sitges, Spain, a beach town suburb of Barcelona, from July 19-24, 1998. It was held at the Congress Center of the Meliá Gran Sitges Hotel that boasted a spectacular panoramic view of the Mediterranean Ocean. Part of the organizing committee consisted of the local chairman, Josep Font and Richard Caldwell (USA) who ceremoniously opened the program to the diverse audience of academic and industrial photochemists from Europe, Asia, and North and South America. Although the preponderance of the 390 attendants were from Europe, more than 70 were from Asia, and 26 were from the USA. The daily sessions were extremely diverse and allegedly nontopical, and consisted of 9 plenary lectures, 15 invited lectures, and 11 oral presentations over the course of five days. Two hour poster presentations were featured at the end of two of the daily sessions. Although the photochemistry sessions and posters were of high quality, the most distinguishing feature of the symposium was a personal tribute to the memory of Francesc Trull, a noteworthy Spanish photochemist. Exhibitions and tours were provided throughout the symposium, and many opportunities for personal interaction were therefore available before and after the sessions, making the symposium extremely enjoyable and well-received.

SYMPOSIUM DISCUSSION

Overview of Symposium and Presentations. The symposium was held at Sitges, a small town approximately 20 km from the metropolis of Barcelona. The town itself appears to quaintly blend into the Mediterranean seaside while maintaining a very strong and thriving summer tourist population. Walks through the town revealed an old and historic seaside town that was important for protecting Spain's northeastern coastline. Many of the attendants lodged at the Barcelona schools hostels (the University and the Autònoma) while enjoying the easily accessible underground train and busing systems that ran throughout the city and outlying suburbs.

The symposium sessions themselves were long, lasting from 9 a.m. until about 6 p.m., but the intermittent coffee breaks and long lunches were very refreshing. I will attempt to provide very brief overviews of all the talks, with particular emphasis on talks that addressed some of the themes of the symposium: Photochemistry of Single Molecules, Electronic Interactions Over Long Distances, and Microheterogeneous Photochemistry/Photocatalysis. A text version (using Adobe Acrobat Reader) of the abstract for each of the talks I overview can be found at: http://cc.uab.es/photoiupac98/abstracts98/index.html

Speakers

Bosch, Paula. "*Photopolymerization in Solid Polymeric Matrices.*" An extensive study was presented of the kinetics and mechanisms of the photopolymerization of acrylic and methacrylic monomers in polymeric matrices.

Brouwer , Fred. "*Photoinduced Charge Transfer in Rotaxanes.*" Brouwer studied macrocycles consisting of 4 N-methylpyridinium units in a "bead" around a chain that was "stoppered" by an anthracene chromophore and di-<u>tert</u>-butylbenzene. Quenching of the anthracene fluorescence by the methylpyridininium units could be inhibited by going from a less polar solvent (methylene chloride) to a more polar solvent (DMSO), presumably by interrupting the H-bonding of the "bead" and anthracene stopper.

Calzaferri, Gion. "*Transfer of Electronic Excitation Energy Between Dye Molecules in the Channels of Zeolites*." Pyronine and oxonine dyes were intercalated into zeolite L channels into linear arrays as proven by fluorescence microscopy. Calzaferri showed that the excited pyronine transferred excitation energy to the oxonine trap along a tortuous path whose inter-channel distance could be calculated.

Cassano, Alberto E. "*Quantum Yield Evaluation in Heterogeneous Photocatalytic Systems*." In heterogeneous systems, due to scattering, quantum yields are difficult to evaluate; Cassano presents an experimental procedure to obviate the inherent problems by presenting a study of the degradation quantum yields of tricholoroethylene in TiO_2.

Delaire, Jacques A. "*Photoinduced manipulations of Photochromes in Polymers: Anisotropy, Modulation of the NLO Properties and Creation of Surface Gratings*." Delaire demonstrates the reversible photoinduced NLO property changes of a photochromic crystal of N-salicylidene-4-bromo-aniline (yellow) embedded in PMMA; a photoinduced intramolecular proton transfer causes a color change (red), with both colored molecules being optically active, but with different efficiencies.

Demuth, Martin. "*An Asymmetric Induction Principle and Biomimetics with Photons*." Detailed mechanistic studies were presented describing the cascade cyclization of isoprenoid polyalkene radicals that was induced by PET. Remarkably, high asymmetric inductions were achieved by using (-)-menthone substrates in a photochemical conversion in which the site of the induced chirality was remotely located from the primary radical cation.

DeSchryver, Frans C. "*Time, Space, and Spectrally Resolved Photochemistry from Ensembles to Single Molecules*." The presentation focused on the use of scanning confocal microscopy coupled with fluorescence decay analysis and imaging as well as other scanning microscopies to obtain spectral and spatial resolution of single chromophores down to tenths of nanometers.

Fox, Marye Anne. "*Controlling Long Range Electronic Interactions*." One of two speakers chosen to honor Trull, Fox introduced several research topics, including modulation of the dynamics of electron transfer on an oligonucleotide backbone by exploiting the anisotropic orientation of the individual amide groups. Also presented was work focused on the photoisomerization of stilbene-capped organothiol surfactants on gold substrates that could be adequately demonstrated by water contact angle measurements.

Fujishima, Akira. "*Interfacial Photochemistry: Fundamentals and Applications.*" A very wide-sweeping quasi-scientific, mostly industrial lecture on the application of TiO_2 photocatalysts to many arenas in the Japanese society. Transparent coatings on glass and ceramic tiles of the photocatalysts have been developed to oxidize various air-borne pollutants; one of the modified surfaces possesses interesting anti-wetting properties.

Fukumura, Hiroshi. "*Laser-induced Molecular Transfer in Polymer Solids: Mechanism and Applications.*" Laser irradiation of anthracene-derivatized dopants in PMMA source films gave rise to a transferal of the dopants to an overlaid target film. The dopants were transferred without decomposition and *only* with laser stimulation, suggesting that the absorbed light energy was converted into thermal energy which provided the activation energy necessary to diffuse into the polymer target film.

Gassiot, Irina. "*VUV Gas-phase Photooxidation for the Treatment of Waste Water and Exhaust Gases.*" The talk reported on the photochemically initiated oxidative degradation of gas mixtures of nitrogen, oxygen, and water vapor containing up to 4000 ppm of THF. VUV irradiation of a gas phase containing molecular oxygen and water vapor generates atomic oxygen and the highly reactive hydroxyl radical, initiating oxidative reactions as typically observed in most Advanced Oxidation Processes (AOPs).

Gehlen, Marcelo H. "*Molecular Size, Solvent, and Cage Effects on Excited State Intermolecular Energy Transfer by Exchange Interaction.*" The influence of molecular size, solvent, and cage effects is presented for three different systems. For example, the size effect on the luminescence quenching is correlated to the ligand cone angle for energy transfer between Tb^{+3} and Ru(II) tetraamines with various alkyl *trans*-phosphane ligands of different size.

Griesbeck, Axel G. "*Spin-orbit Coupling Geometries in Photocycloadditions: Do They Determine the Stereochemistry of the Reaction?*" Triplet photocycloadditons of Paterno-Büchi reactions were studied with a view toward understanding the product stereoselectivities by orbital spatial orientations. Using a simple spatial distribution of the bonding orbitals, the endo, exo, and cleavage reactions could be explained, since for flexible 1,4-biradicals many conformations are responsible for facilitating intersystem crossing.

Gust, Devens. "*Mimicking Bacterial Photosynthesis.*" Remarkably, the first comment/question proceeding the lecture was delivered by James R. Bolton, who stated (paraphrased) that Gust is the first person to have successfully discovered the "holy grail" of photochemical processes. The work was wonderfully crafted and presented an overview of our understanding of charge separation in plant systems and the current work in the field, culminating in a simple and robust hydrogen shuttle system that can actually do work, i.e., convert ADP $\rightarrow$ ATP. A carotenoid-porphyrin-quinone triad molecule was successfully incorporated vectorially into the lipid bilayer of a liposome vesicle (quinone faces toward bulk, whereas carotenoid is directed toward inner volume). A charge transfer state ($C^{\bullet+}$-P-$Q^{\bullet-}$) was generated upon excitation of the porphyrin. The state can reduce a shuttle lipid-soluble quinone that is protonated at the bulk phase interface, diffuses across the bilayer interior, is reduced by the carotenoid radical cation, and releases a proton to the interior of the liposome. The proton gradient powers ATP synthase (spinach chloroplasts) to convert ADP and inorganic phosphate to ATP.

Horváth, Attila. "*Photochemistry and Photophysics of Polynuclear Species and Exciplexes of Some Ru(II) and Cu(I) Complexes.*" The photophysics and photochemistry of various Ru(II) and Cu(I) polynuclear complexes appended by diimine and halide ligands was discussed with emphasis on computer analysis (MRA and PSEQUAD) of the equilibrium species and short-lived excited species.

Keller, Richard A. "*Photochemistry and Fluorescence Emission Dynamics of Single Molecules in Solution: B-Phycoerythrin*." Photon pair correlation measurements of the fluorescence of B-phycoerythrin molecules (a collection of 34 bilin chromophores) were obtained by passing an analyte stream of molecules through picoliter detection volumes interrogated by a focused laser beam. Interestingly, the measurements indicate that the molecule behaves as a single quantum system, not as a collection of 34 independent chromophores.

Leigh, William J. "*The Photochemistry of Silacyclobutanes and Disilacyclobutanes. Reactive Intermediates in Organosilicon Chemistry.*" The study of the chemistry occurring after direct photolysis (λ = 193 or 248 nm) of 1-silacyclobutanes was presented. In the presence of nucleophiles, the presence of products (1,2-addition) consistent with a Si=C double bond reactive intermediate are observed, whereas in their absence, the silene undergoes dimerization to the disilacyclobutane.

Lemmetyinen, Helge. "*A Femtosecond Study of the Light-induced Electron Transfer in Pyropheoborbide-[60] Fullerene Dyad.*" The electron transfer dynamics of the title compound in various solvents was studied. The electron transfer was extremely efficient and facile as studied by time-resolved fluorescence and absorption spectroscopies (a 20 ps intermediate was identified).

Masuhara, Hiroshi. "*Laser-induced Single Microparticle Formation in Poly(N-isopropylacrylamide) Aqueous Solution.*" Microparticle formation dynamics as studied by a coaxially oriented IR laser and a short fluorescence excitation pulse (300 nm) into sample solutions of 9-(4-N,N-dimethylaminophenyl)phenanthrene bonded to a fluorescence probe.

Medvedev, Emile S. "*Dynamic Effects in Long-distance Biological Electron Transfer Reactions.*" Theoretical calculations were presented that exclusively related to the derivation of a general expression for electron transfer (ET) rates as a function of donor/acceptor and bridge electronic vibrations. A non-Born-Oppenheimer (BO) approach was modified for a long distance ET in terms of a mixed BO and diabatic contribution.

Meixner, Alfred J. "*Single Molecule Imaging and Spectroscopy at Room Temperature.*" An overview talk that addressed the basic principles of confocal laser microscopy and scanning near-field optical microscopy (see **DeSchryver** above) as ideal tools to identify single molecule fluorescence. Of paramount significance in the talk was the concept that various dynamic processes (e.g., reversible photobleaching) are strongly sensitive to the local chemical environment and the variation in the dynamic processes does not correlate well with behavior observed for ensemble measurements.

Monti, Sandra. "*Photochemistry of Arylpropionic Acids Containing Benzophenone-Like Chromophores in Aqueous and Cyclodextrin Environment.*" The photodegradation mechanism of ketoprofen, suprofen, and tiaprofenic acid were studied in aqueous medium and β-cyclodextrin inclusion complexes. In all systems studied, the formation of the final keto product at neutral pH was determined to involve long-lived triplet biradicals and/or ground state intermediates with enolic structure. In the cyclodextrin cavity the first electron transfer is disfavored and the photodecarboxylation of the keto substrates occurs with lower quantum yields than in aqueous media.

Muñoz, Victor. "*Kinetics and Dynamics of α-Helix and β-Structure Formation Studied by Laser T-jump*." The presentation focused on the formation and analysis of β-hairpins (a basic structural motif of folded proteins) through the use of nanosecond temperature jump, fluorescence, and statistical mechanical modeling.

Ohta, Nobuhiro. "*Electric Field Effects on Fluorescence in Photoinduced Electron Transfer Systems Doped in a Polymer Film*." The electric field (up to 1 MV/cm) was shown to increase the fluorescence of ethylcarbazole (ECZ) and dimethyl terephthalate (DMT) donor/acceptor systems in PMMA films at low ECZ concentrations. The enhancement was attributed to a field-induced inhibition of the charge recombination of the radical ion pair.

Perutz, Robin N. "*Intermediates in Transition Metal Photochemistry at the Limits of Reactivity*." The reaction intermediates generated from the photochemical dissociation of hydrogen from transition metal dihydrides were probed by time-resolved spectroscopy or matrix isolation. Principally, ultrafast IR spectroscopy is used to follow the metal complex reductive elimination that produces characterizable intermediates which react with H_2, CO, and hydrocarbons at rates up to $10^9 \, M^{-1} s^{-1}$.

Pina, Fernando. "*Photochromic Systems Based on Synthetic Flavylium Salts. Write-Lock-Read-Unlock-Erase Molecular Devices*." The photochromism of flavylium salts is investigated under pH conditions where the equilibrium is forced from one form (*cis*-chalcone) to the other (*trans*-chalcone). By the appropriate pH changes, they suggest that the molecular systems constitute the basis for write-lock-read-unlock-erase memory devices.

Richter, Christoph. "*Photochemical Application of Sunlight for Fine Chemical Synthesis*." At PSA (Plataforma Solar de Almeria, a Spanish-German center for Solar energy applications), concentrated solar light is being used for scaling up photochemical processes for water purification or for fine chemical synthesis.

Scandola, Franco. "*Photoinduced Intercomponent Processes in Supramolecular Metal Complex Assemblies*." The second speaker for the tribute to Francesco Trull, Scandola presents a very popular and burgeoning area of photochemistry, viz., the photochemistry of large arrays of tethered chromophores. Ru(II)-Rh(III) polypyridine diads bridged by poly-*p*-phenylene spacers demonstrated electron transfer (ET) from Ru → Rh whose rates decreased exponentially with distance (as the tether is changed from 1 to 3 units). Another motif of supramolecular photochemistry is pentanuclear porphyrin arrays, consisting of a central free base and four axially coordinated Ru porphyrin units. Surprisingly, despite observing energy transfer in the free solution species, the supramolecular aggregate does not display energy transfer to any appreciable extent.

Seidel, Claus M. "*Single Molecule Fluorescence Spectroscopy in Solution*." The importance and power of studying the fluorescence of single molecules was highlighted. Instead of obtaining ensemble averaging (which is what most photochemists study), the molecular and kinetic properties of individual molecules can be probed. Again, confocal fluorescence microscopy was used similar to the work demonstrated by Keller (*vide supra*).

Sundstroem, Villy. "*Femtosecond and Femtobiology of Elementary Chemical Reactions and Light-Energy Converting Processes*." General overview of the chemical dynamics of ultra-fast reactions. Elementary bond-breaking and bond-forming reactions were discussed in terms of their mechanisms as observed by ultra-fast spectroscopy.

Widengren, Jerker. "*Characterization of Anti-fading Compounds Using Fluorescence Correlation Spectroscopy*." Various photostabilizers such as n-propyl gallate, mercaptoethylamine, and ascorbic acid were used to study their effect on the photobleaching of Rhodamine 6G molecules. All studies were done using the fluorescence correlation method and showed that at low anti-fading compound concentrations, a positive impact was observed for the Rhodamine fluorescence, whereas at higher concentrations, the Rhodamine fluorescence was quenched.

Wilson, William L. "*High-Density, High-Performance Optical Storage Via Volume Holography: A Chemist's Search for the Photonics Holy Grail.*" The first of the invited lectures proved to be a cornucopia of long-standing industrial interests and fulfilled promises by a femtosecond spectroscopist by training. The angle and wavlength of laser light can be used as part of a holographic technique to multiplex information into a polymer matrix infused into vycor. All information and retrieval was done by spherical waves.

Wirz, Jakob. "*Kinetics of Proton Transfer Reactions Involving Carbon*." The very first talk of the conference was a very nice study of keto-enol tautomerization as studied by time-resolved flash photolysis. The RDS for ketonization is proton transfer from water or hydronium ions to the enols or carbon bases, and in enolization it is proton transfer from ketones as acids to water or hydroxyl ions. The intrinsic barrier for proton transfer from oxygen to carbon is 13 kcal/mol, about ten orders of magnitude less than typical acids. Interestingly, the barrier disappears during excited state prototropic reactions.

Wolff, Thomas. "*Photochemical Switching of Conductivity in Microemulsions*." The microemulsions studied were composed of aerosol-OT, isooctane, and water. When microemulsions begin as water-in-oil, an increase in the water volume causes the water regions to extend and become continuous at the "percolation" point, where conductivity changes. The above microemulsion has a percolation point at 33°C at which point the conductivity changes. By incorporating various photochemically active molecules such as acridizinium bromide, the percolation point can be increased to 43°C after photoisomerization of the chromophore. Thus, the system can be photoswitched from conductive to nonconductive (at a specific temperature) by application of UV-light.

Zhao, Jincai. "*Photocatalytic Degradation of Surfactants and Dyes at TiO$_2$-H$_2$O Interfaces*." The talk presented a very elegant study of the competitive degradation of various solutes in TiO$_2$ slurries. For example, it was found that the degradation efficiencies for solutes increased in the order anionics > non-ionics > cationics, a correlation closely matching the absorptive behaviors of the surfactants on the TiO$_2$ surface. Also, dyes in TiO$_2$ slurries can be degraded with *visible light* via excited state electron injection from the dyes into the conduction band of the semiconductor (TiO$_2$). The latter process generates a cation and superoxide (via reduction of oxygen by the conduction band of TiO$_2$) that can react with the dye cation to yield degradation products.

Symposium on Molecular and Supramolecular Photochemistry
National Meeting of the American Chemical Society

Boston, Massachusetts
August 23-28, 1998

William Jenks, Steve Fleming, Miguel Garcia-Garibay, and Vijay Kumar

Thanks to at least two years of efforts by V. Ramamurthy and several others, a four day symposium on photochemistry was held at the Boston ACS meeting in honor of the 60th birthdays of six great names in our field: Bob Liu, Doug Neckers, Jack Saltiel, Nick Turro, Pete Wagner, and Dave Whitten. Along with an astonishing 59 seminars were posters numbering in the hundreds. Attendance at the seminars was unlike anything else seen by this author for photochemistry or physical organic chemistry at an ACS meeting; it was a remarkable event and celebration.

The speakers were largely students, colleagues and close associates of the honorees, as were the session chairs. A theme of the celebration that also emerged, particularly at the speakers dinner held at the Harvard faculty club, was the presence and influence of George Hammond, who has advised or held close professional association with all six of the honorees.

In the pages that follow is a summary of the scientific content of the symposium.

Sunday's first morning session was chaired by **Tony Lamola**, and its first speaker was none other than **George Hammond**. He introduced the honorees and gave his thoughts on the current state of photochemistry and the photosciences. In particular, he urged that its practitioners not tightly split itself into overly narrow compartments. The strength and wide future of photochemistry depended on breadth and interdisciplinary approaches. **Michael Kasha** spoke next, on the topic of non-simple molecular electronic excitation. He began by speaking of the history of thought on single-photon, single molecule excitation, and the contributions of worker like Jablonski, Lewis and Dushinsky. Working his way up to more complex systems, multi-molecule and multiphoton spectroscopies were discussed, as was the relationship between Förster and Davidov models of dynamics. **Koji Nakanishi** was the third

Koji Nakanishi doing a magic trick at speakers' dinner.

speaker of the morning, giving a review of the work of his and some other laboratories in the field of visual transduction. The chiral exciton method for CD spectroscopy and its application to the rhodopsin/retinal problems was elaborated. The notion of breaking conjugation in the (heroically synthesized) retinal derivatives to get a sense of the structural distortion in the retinal Schiff base was discussed, and phoroaffinity studies to determine the location of retinal within the rhodopsin complex were reviewed. **Howard Zimmerman** closed out the session. He reviewed the importance and relevance of a number of ideas that came out of the famous 1961 sessions: his n * model, rationalization of α-cleavage, hydrogen abstraction, and α-expulsion in carbonyl chemistry. He also gave historic reviews of enone and dienone photochemistry, including the classic case of santonin. Even the meta effect and conical intersections in heterolytic photochemistry could not escape from his comprehensive look back.

The second Sunday morning session was chaired by **Ed Chandross**. Its first speaker was **Mostafa El-Sayed**, who spoke on electron-hole dynamics in semiconductor nanoparticles. After discussing some of the applications of nanoparticles, the quantum size effects on optical properties of various systems were presented. In particular, the


Mostafa El-Sayed, George Hammond and Jack Saltiel sharing the spirit of chemistry.

observation that CdS particles contain many low energy traps that lead to emission at energies lower than the nominal band gap was contrasted to CdSe, which is a "cleaner" material in that respect. Coating the surface of CdS particles with methyl viologen allowed observation of the dynamics of charge separation by the appearance of the radical cation on the sub-picosecond timescale. That the bleach recovers much faster than the viologen monocation disappears was taken as evidence that the traps serve as electron sources. Such differences in timescale were not observed for the CdSe particles with fewer traps. **Fred Lewis** discussed the work in his laboratory on probing electron transfer within DNA structures by using synthetic hairpin turns constructed with stilbene bridges. GC pairs quench the fluorescence of the stilbene by electron transfer, and AT pairs do not. In the simplest systems, approximately 50% quenching is achieved when the stilbene is separated from the GC pair by two AT pairs. Back electron transfer can also be probed. The distance dependence on the electron transfer rate, β, for the prototype system was found to be 0.64, somewhat smaller than the generally accepted value for σ-bond systems in proteins. Several new bridges that replace the stilbene, and their advantages and limitations were discussed. **Gary Schuster** then spoke about the photochemistry on DNA that he has studied, including the work they have done on damage at a distance from the sensitizer. The sensitizer is an anthraquinone derivative that can be attached to a single strand DNA oligo. Electron transfer and cleavage occurs preferentially from GG sequences. Interestingly, a sequence which contains more than one GG site along a strand will show cutting at each GG center, not just the one closest to the sensitizer. Removal of a single base or inclusion of 8-oxo-guanosine (an easily oxidized DNA base analog) does

not qualitatively affect the mix of cuts along a given strand. **Jackie Barton** closed out the Sunday morning session by reviewing the work her laboratory has done on charge transport in DNA-intercalator complexes. In particular, she distinguished between static and dynamic mechanisms of quenching in these systems, defining a "γ" distance dependence for electron transfer in addition to the traditional "β". Another special point of emphasis was the importance of distortions of the DNA conformational structure, particularly in the quality of the base stacking of the interactions, in determining the rate of electron transfer through the polymer. It was implied that some of the differences observed with different systems in this type of work could be due variations in the amount of structural distortion, as opposed to fundamental problems with the ideas of electron transfer in DNA strands.

The first part of Sunday afternoon was focused on photoinduced electron transfer processes and the second on organic photochemistry. The first session, chaired by **Dave Eaton**, opened with a presentation by **Harry Gray** on the use of electron injection triggering photochemical techniques to address questions of protein folding dynamics. The method takes advantage of differences in folding free energies in proteins possessing reduced and oxidize cofactors. It was found that hydrophobic collapse occurs within 100 microseconds after electron injection in unfolded ferricytochrome C and that the final folded state is formed within 0.1 sec. The second talk of the session was given by **Thomas Meyer** who turned gears towards electron transfer in non-biological polypetides with various donors and acceptors. In this case, molecular arrays based on simple proline derivatives bearing photoactive units were shown to displaying different helical properties where rates of electron transfer can be measured as a function of folding state. In the next talk of the session, **Marye Anne Fox** presented results on the photoelectrochemistry of dyes at the polymer/metal oxide interface. The importance of inter-particle charge transport in the formulation of electrodes and photolectrochemical cells was discussed as was the use and efficiency of layered materials. Following Marye Ann Fox's presentation on condense phase charge transport, and concluding the first afternoon session, **N.C. Yang** spoke about intramolecular electron transfer in solution and in the gas phase. In his talk he described results with silyl-linked anthracenes and anilines which had been supersonically expanded in a jet. Results were interpreted in terms of through-bond and through-space electron transfer.
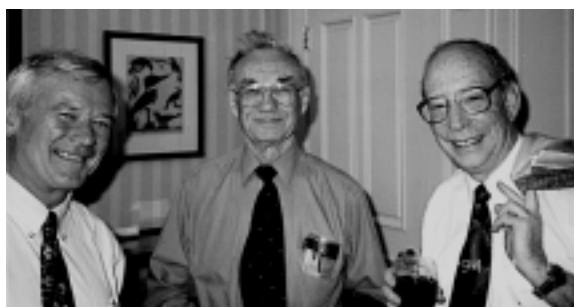
Rich Givens, Howard Zimmerman, and Harry Morrison engaging in lively conversation.

The second afternoon session, hosted by **Kurt Schaffner**, begun with a presentation by **S.C. Shim** on the photochemistry of conjugated polyalkynes and olefins. In the case of diacetylenes, it was shown that the photochemical addition of alkenes can be quite selective to give bis-carbene like adducts. Several precursors were analyzed to investigate the intermediacy of the species postulated (but I forgot what the hell he said and it is not in the damned abstract). In the second talk of the session, **Harry Morrison** presented work addressing the involvement of upper excited states in the photochemistry of indenes and thioketones in the gas phase suggesting a radical-like S2. The third talk was presented **Don Arnold** and brought us back to electron transfer-initiated chemistry. A new class of reactions, denominated "aromatic-olefin substitution nucleophile combination" was

presented and analyzed. As an example, the reaction occurs with chloromethoxyybenzene, 1,1-diphenyl ethylene and methanol as the aromatic, olefin and nucleophile. The final talk of the session was presented by **Pete Wagner**, who described a mechanism that account for the selectivity of triplet biradicals obtained by γ-hydrogen transfer in ortho-benzyl acetophenones. Wagner's proposal is based on the structure of the ortho-xylylene-related biradical and on the steric interactions that may arise upon biradical closure.

On Monday morning there were seven talks on the photochemistry of light harvesting systems and photoreceptors. The first session was chaired by **R. Srinivasan**. The opening presentation, by **T. Gillbro**, dealt with ultrafast internal conversion and energy transfer in light-harvesting carotenoid-containing complexes. In the second talk of the morning, **Y. Shihida** described studies on the structural changes and dynamics of rhodopsin, which start within the first 25 femtoseconds after excitation. The third presentation by **M. Tsuda**, centered on studies in octopus photoreceptors and addressed differences in the visual mechanism of vertebrates and invertebrates. In the final talk of the first morning session, **W.J. de Gripp** spoke about retinal analogs as probes for rhodopsin function. It was show that introduction of a methyl group near the isomerization site has a strong effect on the kinetics of the process and the importance of torsional strain was analyzed.

The second Monday morning session was chaired by **Tony Trozzolo**. Its first speaker was **Elizabeth Gaillard**, who spoke on her work on the chemical basis of macular degeneration, a light induced disease that causes loss of vision in many older individuals. The photochemical reactions that cause the build up of Human Retinal Lipofuscin, a mixture of fluorescent material, do not have to be particularly efficient, since the material can be built up over a period of many years. The main component of this mixture is a compound which has been dubbed A2E and recently synthesized independently. Gaillard presented her photophysical data on the lipofuscin and the synthetic A2E. One of the symposium's honorees, **Jack Saltiel** spoke next. He publicly introduced the application of his principal component analysis methods on the complex bacteriorhodopsin systems. As proof of concept, he showed that synthetic data from the initial ultrafast events could be analyzed properly, and he showed the progress he and his group have made in reconstructing the true absorption spectra of the several intermediates in these complex systems. The next speaker was also one of the Gang of Six, **Bob Liu**. His talk reviewed his group's work on retinyl chromophores and rhodopsin and bacteriorhodopsin analogs. Starting with various cis/trans isomers of retinal, the appearance of others is followed. The natural isomerism is a protein-directed specific isomerism that is much more complex in the absence of the "flexible lock" of the opsin protein. The heroic and completed synthesis of all the isomers of vitamin A2 was also discussed.

The first session of the Monday afternoon talks was chaired by **Kurt Deshayes**. He introduced **Rich Givens** as the first speaker. Professor Givens reported on the use of photoremovable substrates or phototriggers for biological systems. He gave a nice review of the popular o-nitrophenyl groups including the limitations of that particular functional group. As background to his recent work on biological applications of photoremovable substrates, he gave a thorough summary of the photochemistry of p-hydroxyphenacyl compounds. He also discussed the mechanistic details of the triplet photochemistry which presumably involves electron transfer and formation of a spirocyclopropanone intermediate. Applications that were presented included: brain-nerve mapping and determination of active sites with photoremovable glutamine, bradykinin photorelease, study of protein kinase A activity, and photorelease of tyrosine and glutathione. Dr. **I. Bronstein** spoke of her recent advances in the area of chemiluminescent dioxetanes. She presented an overview of the advantages that dioxetanes provide for generating excited states. Much of her recent effort has centered around developing a more effective dioxetane for biological applications. The structural variations that were reported for half-life studies included numerous aryl substituted compounds. The best aryl group for prolonged half-lives (over 300 minutes) was the m-phenyl

benzothiazole. This apparently is stabilized by intramolecular metal chelation and can provide a high light output and a constant light emission that reaches 10 hours in some cases. This particular dioxetane has a detection limit of 10-19 mol in .1 M AMP and 1 mM $MgCl_2$. **Claudia Turró**, who recently joined the faculty at Ohio State (no relation to Nick, save as a postdoc) was the third speaker. She presented her recent work on bimetallic analogues of the enediyne DNA cleaving reagents. In particular, she discussed the nature of the excited state of rhodium-rhodium complexes. The photophysics of the tetraacetate species was presented and its potential for application in DNA cleaving experiments was discussed. **Vijay Kumar** rounded out the session. Professor Kumar has recently discovered a site specific photocleaving procedure for proteins. His presentation described the use of pyrene tethered phenylalanine that binds to bovine serum albumin (BSA). The radical cation of the pyrene group can be generated by irradiating the sample in the presence of cobalt hexamine. This reactive species results in selective cleavage of BSA and lysozyme. Irradiation of pyrene itself in the presence of the proteins does not cause this photocleavage. Nor does the cobalt appear to be responsible for the site selectivity, since several different cobalt salts gave the same cleavage. The phenylalanine involvement in binding is supported by the observation that the methyl ester of the tethered amino acid and use of L-phenylalanine both gave non-selective photocleavage. The mechanism of the protein strand cleavage presumably involves hydrogen atom abstraction and oxygen addition which results in bond breaking.

Marye Ann Fox, David Schuster, and Jackie Barton enjoying dinner together.

The second section on Monday afternoon was chaired by **Andre Braun**. The first talk was given by **M. Irie**. In perhaps the single-most visually impressive talk of the whole symposium, he showed numerous examples of photochromism in single crystalline diarylethylenes. Well over 200 compounds have been studied, mostly 1,2-dithiophene substituted hexafluorocyclopentenes. Quantum yields are high, and they are among the few compounds known that exhibit photochromism as single crystals. Beautifully (and reversibly) colored crystals were illustrated. The next two talks were coupled to discuss various aspects of photochemistry in aqueous environments. **Richard Zepp** concentrated on the photoreactivity of dissolved organic material in freshwater. Organics control the absorption of near UV in coastal water; particles contribute only in minor fashion, at least down to about 300 nm. The low molecular weight products of irradiation include aldehhydes, volatile alkenes, glyoxylate, and considerable quantities of CO_2. The quantum yield of CO_2 formation as a function of wavelength of irradiation was reported — it is about two orders of magnitude higher at 280 nm than 440 nm. Oxygen also plays a key role in the degradation of the lignin. **O. Zafiriou** spoke mainly about some of the chemistry of inorganic ions in aqueous environments, their roles in generating oxidative species, e.g., hydroxyl radical, and in degradation of colored dissolved organic material. The photochemistry of nitrate and nitrite, both micromolar species, produces HO•. The concentration of

NO, a byproduct of the nitrite reaction, is correlated with light intensity in shallow waters. Iodide and bromide are both found in oceanic water. Reaction of hydroxyl and bromide leads to $Br_2^{\cdot-}$ on the microsecond timescale, and this species can result in oxidation of carbonic acid down the line.

The schedule for Tuesday morning included seven presentations with topics ranging from delocalization through sigma bonds to photophysics of proton transfer and two photon emission to biradicals and picosecond transient absoption spectroscopy. **Lisa Kelly** ran the show for the first session. The first talk, by **Josef Michl**, dealt with several aspects of electron delocalization through permethlated polysilane sigma bonds. Results were presented which suggest upper and lower length limits for excitation delocalization in polysilanes. In the second talk of the morning, **Dick Caldwell** presented new results on the controversial 1,4-cyclopropyldicarbinyl biradicals generated by gamma hydrogen transfer in cyclopropyl ketones. Results with an alpha-spiro-cyclopropyl tetralone suggest an adiabatic cyclopropyl ring opening which, at least in this case, questions the use of cyclopropyl ketones as a rigid scafolds to restrict conformational mobility of the 1,4-biradicals. In the third talk, **Dave Shuster** spoke on the photophysics several porphyrin-fullerene diads. It is expected that god absorbance in the visible along with good singlet oxygen yields will result in useful chromophores in photodynamic therapy. The second session of the morning begun with a presentation by **Laren Tolbert** on double proton transfer processess in several arenols. The increase acidity of arenols in the excited state is reflected in phototautomerization, deuterium isotope exchange, and anomalous fluorescence. Some arenols exhibits solvent-induced changes in emission that are associated with changes in microscopic proton transfer rates. Interesting results and **Dan Nocera** presented a spectroscopic analysis of a quadruply-bonded metal-metal system that can be described in terms of two weakly interacting d-orbitals that give rise to a four state model. The third talk by **Malcolm Forbes** started by describing and explaining similarities observed by TREPR on long biradicals at low temperatures and radical pairs in micelles, and went on to discuss how photochemistry is involved in the skunking of beer (Editor's note: one of the MOST important subjects of the week). In the final talk of the session, **Ed Hillinski** described a transient absoprtion picosecond studies on several all-trans-1,6-diphenyl-1,3,5-hexatriene derivatives.

Most of the Tuesday afternoon talks had to do with electron transfer. The first session was led by **George Jones**. **Samir Farid** spoke first, presenting an elegant study of the T-shaped exciplexes of pyridines with anthracenes. Experiments were designed, among other things, to show specifically that the exciplexes had this orientation. **Linda Johnston** spoke about psoralen photochemistry and the damage they can induce to DNA bases. It was pointed out that 2+2 chemistry with thymine, hydrogen abstraction, singlet oxygen, and electron transfer were all formal possibilities. The photophysics and kinetics of triplet formation, photoionization, and electron transfer reactions of representative compounds such as 8-methoxypsoralen and dimethoxycoumarin were presented. It was shown, for instance, that DNA bases can be oxidized by the radical cation of dimethoxycoumarin. **Josh Goodman**'s topic was his work on Bond Coupled Electron Transfer reactions, in which bond breaking or making is concertedly coupled with and electron transfer event. In particular, a case of Dissociative Return Electron Transfer (DRET) was outlined in which the isomerization of 1,2-diphenylcyclopropane is achieved by means of using a triplet state electron acceptor. **H. Inoue** spoke about the quenching of some ketone and quinone excited states mediated by energy flow via hydrogen bonds in the excited state. Non-radiative decay rates were much larger in protic solvents (e.g., ethanol) than either polar or non polar a-protic solvents. Studies with hyroperoxide and alcohol quenchers demonstrated that the Stern-Volmer constant increased with the available surface area of the hydrogen atom.

The second afternoon session was hosted by **Matthew Zimmt**, who was sure to let the audience know exactly what number speaker they were hearing in the symposium, which was taken with good humor by all. **Ian Gould**,

newly of Arizona State University, led off the group of speakers, reporting a study of deprotonation reactions aniline radical cations from the α-carbon. This was driven by a desire to understand the kinetics and thermodynamics of a more general set of fragmentations of radical cations. It was reported that the α-CH bond dissociation energies of variously substituted radical cations do not vary much with substitution on the aromatic ring, but that substitution designed to concentrate charge and spin on the nitrogen atom can dramatically speed up the base-induced fragmentation. **Dave Waldeck** spoke next on the intramolecular electron transfer chemistry of some large synthetic "C-clamp" donor-acceptor molecules his group has been studying in collaboration with Matthew Zimmt. Among the issues discussed were the factors that affect through bond, through space, and through solvent coupling in these molecules, and various lines of evidence for magnitudes of the couplings. **William Jenks** closed out the afternoon with a talk about physical quenching of singlet oxygen. A kinetic model was used to estimate the rate of intersystem crossing of singlet oxygen exciplexes. A series of charge transfer quenchers and their rate constants were reported. This was used to extrapolate data to weak charge transfer quenchers and show that "shortcomings" in some estimates of quenching by the electronic to vibrational energy transfer pathway may simply be because there is an additional charge transfer component.

Wednesday morning's first session was hosted by **Miguel Garcia-Garibay**, and its theme was photochemistry in constrained and solid states. **Dick Weiss** reviewed some of his work in stretched polyethylene environments. He pointed out that organic molecules tend to accumulated on the interfaces of crystalline zones of polyethylene, but that the environments are dramatically changed on stretching of the material due to a much greater orientation of the chains. Internal Paterno-Büchi reactions and photo-Fries reactions were used to probe the environments. Dramatically variable product mixtures reflected the types of motions that are easily available to the intermediates in the different environments. **John Sheffer** spoke about using crystal chirality to transfer to molecular chirality by way of photochemical transformations in the solid. A prototypical case is a derivative of dibenzobarrelene, whose crystals are chiral. Irradiation of the crystals gives the di- -methane product in high enantiomeric excess. Chiral salts can be used to make the environments in crystals asymmetric also, and screening of the counterions is practical. Several examples were discussed. **Y. Ito** also discussed photochemistry in two component crystals whose environments were asymmetric because one of the components was chiral. Chiral induction was found, for example in the dimerization of cinnamic acid by using an optically pure *trans*-1,2-diaminocyclohexane to make chiral salt crystals.

George Hefferon facilitated the second session of the morning. **Dick Schwerzel** spoke first about nanocomposite photonic polymers. Polydiacetylene was used to embed CdS particles and Z-SCAN measurements were done to measure non-linear optical properties. Capped CdS showed a negative non-linear effect, and other modifications of the CdS (e.g., particle size) could be used to modulate the effects. **Mike Sponsler** spoke of using liquid crystals to generate holographic gratings. Appropriate mixtures could be cycled a hundred thousand times, in the range that would be useful for computer displays. Simulations were done with a program originally designed to calculated interest incomes. (Business school comes through for science!) Smooth growth and decay with applied field was predicted by the model, but the observed effects were not explained by simple parameters such as viscosity. **Walter Yager**'s talk examined the use of fluorescent probes to monitor polymer initiation. Solvatochromism of dimethylaminonitrostilbenes (and related dyes) were used, as they showed solvatochromism as a function of the degree of polymerization of acrylate derivatives. Both intensity and λ_{max} were sensitive. The emission peak widths could also be monitored. Free and polymerized samples had different shapes, and gel phases showed dual emission.

The symposium wrapped up with two final sessions Wednesday afternoon. The first was hosted by **Ester Oliveros**. Its first speaker was **F. De Schryver**. He spoke of photophysical probing of dendrimer structure, and interrogation of viscosity as a function of generation. Solvent effects on dendrimer conformation could be probed with the same spectroscopic tools. It was found, for instance, that the minimum in density with respect to generation is the same place as the maximum in viscosity. Exciting advances in single dendrimer spectroscopy with confocal microscopy were also discussed. **J. Kerry Thomas** reported results on his studies of charge migration in polymer films. Two photon ionization of perylene could be used as the source for holes in the systems. Alkyl chlorides serve as outstanding electron traps and yield long lifetimes of the perylene radical cation and high charge separation yields. Evidence for "trimolecular" complexes (exterplexes) between two aromatic groups on the polymer and TCNB in charge separated states was also presented. The session was closed out by **Kirk Schanze**. He also spoke of a polymer system, this time systems designed with an antenna concept in mind. Biphenyl and bipyridal units were included in the polymer, the former transformed into Re complexes. Relatively inefficient quenching by the organometallic traps led to the conclusion that the system was probably organized as block copolymers. Synthesis of polymers by way of designed oligomeric units provided better behaved systems.

The final session of the symposium was run by **Chris Dalton**. **Paul Barbara** opened with a talk about his recent work in single molecule spectroscopy. Again, this was a polymeric system that was being studied. Much of the talk described the characteristics of single molecule spectroscopy, and their 1997 *Science* paper was referenced. Paul showed evidence of single molecule loss by sudden complete loss of intensity at a single point in space, as opposed to the stepwise loss expected if a series of "antenna" systems bleached. He also showed evidence of a thermal "repair" reaction of unknown origin. Polarization was used as evidence that the medium was not completely random coil. Fans of the Power Point presentation software will not soon forget **Doug Neckers'** talk, which immediately followed. The notion advanced was that it ought to be possible to use photopolymerization to achieve spacial and wavelength resolution with color, i.e., that three-dimensional color objects should be achievable with properly designed systems. Color flexibility and at-will polymerization are obviously the key issues. Many illustrations were given to show the work at various stages. **Doug Whitten** gave a talk on organic "gel" formation and the types of molecules that can be used as "gelators" to make these aggregates. Typical molecules had aromatic parts (e.g., anthracene), a bridge, and a liquid-crystal initiating part (e.g., cholesterol). In the best cases, only a fraction of a percent of these gellating molecules were necessary to achieve aggregation. Images of the aggregates could be taken and some of the gels could be dehydrated by half without changing the microscopic fiber appearance. Various spectroscopic probes showed that large solvent zones inside the gel were relatively "normal" despite the macroscopic appearance of the gel. The last talk of the day and of the symposium was given by **Nick Turro,** who introduced us to the world of Superdübermolecular photochemistry. Nick's talk was full of stories and fun, and then eventually worked its way back to reviewing some of the (dare we say) paradigms he has used over the years to describe/explain his work in various organized media. Zeolites of various sorts, biological polymers, and micelles all made their respective appearances in The Grand Scheme. This talk served as a marvelous bookend to accompany that at the start of the meeting four days previous given by George Hammond. By the end, we all were exhausted, but what a ride it had been.

Congratulations once again to the 1938 Six!

Recent Noteworthy Articles in the Area of Photochemistry and Photophysics

Editor's note: We are always looking for people to abstract recent exciting articles in photochemistry for the newsletter. Categories include, but are in no way limited to biochemical, organic, inorganic, and physical photochemistry. Please drop a note to William Jenks if you would like to participate.

Biochemical Photochemistry

Reported by Lisa A. Ervin, Alison Jakubek, Aric Morgan and Elizabeth R. Gaillard, Department of Chemistry and Biochemistry, Northern Illinois University

1.   "Toward Understanding Tryptophan Fluorescence in Proteins" Chen, Y.; Barkley, M.D. *Biochem.* **1998**, 37, 9976-9982.

In this article the authors report the quenching mechanisms of amino acid side chains on the fluorescence of 3-methylindole. Previously, reports of free amino acid quenching failed to take into account quenching by the alpha-amino group; therefore, the N-acetyl derivatives of amino acids were used in this study. Quenching by the N-acetyl derivatives of glycine, alanine, valine, leucine, phenylalanine, proline, hydroxyproline, serine, threonine, methionine, and arginine at neutral pH were undetectable. Fluorescence quenching by N-acetyllysine and N-acetyltyrosine appear to occur through excited state proton transfer. The other side chains studied are likely to quench through excited-state electron transfer. Bimolecular quenching in proteins are proposed to be as follows: lysine, glutamine, asparagine, and neutral histidine should be weak quenchers; neutral glutamic and aspartic acids should be moderate; tyrosine, cysteine, positively charged histidine, and cystine should be the best.

2.   "Selective Photocleavage of DNA by Anthraquinone Derivatives: Targeting the Single-Strand Region of Hairpin Structures" Henderson, P.T.; Armitage, B.; Schuster, G.B. *Biochem.* **1998**, *37*, 2991-3000.

The authors of this article studied the binding and cleavage specificity of a tetracationic anthraquinone derivative (27AQS2) on a partially self-complimentary octadecanucleotide (DNA(1), a "hairpin" structure). From the melting behavior and proton shifts seen in NMR spectra, the binding of 27AQS2 to DNA(1) was found to be complex. The anthraquinone had a slight preference for two sites: the minor groove of the AT region at the loop-stem junction and the hairpin region. Photocleavage of DNA(1) by the triplet state of 27AQS2 required alkali treatment and resulted in strong cleavage at each of the bases in the loop region and also weaker cleavage at G_5G_6 in the stem region. Three processes appear to cause cleavage. One process involves the formation of a radical cation that results in nonselective cleavage in the hairpin. A second process involves the formation of $^1O_2$ that cleaves at G_5G_6; adding Cl increases this cleavage since there is a greater concentration of unbound 27AQS2. A third process involves the migration of a radical cation in the stem region that also causes cleavage at the GG step; ethidium bromide acts as a barrier that significantly reduces this guanine cleavage. Selective cleavage of DNA hairpins may allow the determination of complex DNA or RNA structures associated with human disease.

3.   "Coupled Activation of the Donor and Acceptor side of Photosystem II during Photoactivation of the Oxygen Evolving Cluster" Rova, M.; Mamedov, F.; Magnuson ,A.; Fredriksson, P.0.; Styring, S. *Biochem.* **1998**, *37*, 11039-11045.

        Photosystem II converts solar energy into chemical energy by creating reactive species that can transfer electrons to drive ATP formation. P680 can absorb a photon and consequently transfer an electron to the primary plastiquinone (Qa), which then transfers to the secondary plastiquinone (Qb). A Mn cluster reduces oxidized P680 (P680+) thus completing the electron transport chain. The Mn cluster is photoactivated and is not fully functional until approximately one minute after the organism has been exposed to light. In the time it takes the molecule to fully synthesize the cluster many photons are absorbed. When P680 transfers an electron it forms P680+ one of the most powerful oxidizers in biological systems. This highly reactive species can cause considerable damage if there is no Mn to reduce it. The formation of the Mn cluster is approximately five times slower in the FUD 39 mutant of Chlamydomonas reinhardtii. This allows the systems that reduce the damage of the highly reactive species and electron transfer pathways to be studied more closely using fluorescence and ESR techniques.   In the presence of the herbicide DCMU, which blocks electron transfer from reduced Qa (Qa-) to Qb, back electron transfer occurs from Qa- to P680+. When the electron transfer pathway was not blocked back electron transfer did not occur and the P680+ was reduced by a nearby tyrosine residue. Another interesting observation that was made the binding affinity of Qb was affected by the formation of the Mn cluster. As the cluster was formed the binding of Qb became stronger. Therefore, back electron transfer is more likely to occur when the cluster is not fully formed.

4.   "Folding of Deoxymyoglobin Triggered by Electron Transfer" Wittung-Stafshede, P.; Malmstrom, B.G.; Winkler, J.R.; Gray, H.B. *J. Phys. Chem.* **1998**, *102*, 5599-5601.

        The mechanisms for protein folding have eluded scientists for many years. The problem in studying protein folding is that it occurs so fast that any mixing experiment is too slow to measure the intermediate steps. Protein folding may now be studied using deoxymyoglobin (deoxyMb Fe2+) and met myoglobin (metMb Fe3+). Guanidine hydrochloride (guHCl) denatures MetMb at lower concentrations than deoxyMb but the met Mb can refold upon dilution of the guHCl. NADH excited by flash photolysis can reduce met Mb to deoxyMb. At guHCl concentration of 2.5 to 3 M metMb is denatured but deoxyMb is not. Using flash photolysis to reduce the metMb to deoxyMb refolding of deoxyMb can be observed. Since the reduction can occur on a much faster time scale the structural intermediates of the protein are more easily observed.   The rate constant for refolding of deoxyMb is 5 X 10^3 s^{-1} ,which is much faster than cytochrome c refolding under similar driving force (approximately 10 kJ/mol). On the other hand, cytochrome b562 refolds at a similar rate but requires a higher driving force (approximately 25 kJ/mol).

5.   "Effect of BSA Binding on Photophysical and Photochemical Properties of Triarylmethane Dyes" Baptista, M.S.; Indig, G.L. *J. Phys. Chem. B* **1998**, *102*, 4678-4688

        Triarylmethane (TAM) dyes have been considered as agents for photodynamic therapy (PDT). The strategy involves a photosensitizing agent, light, and molecular oxygen used to generate highly reactive, cytotoxic species in situ for treatment of cancerous tissue. In these experiments, bovine serum albumin (BSA) was used as a model biological substrate, and the reactions facilitated by binding were investigated. Ethyl Violet, Crystal Violet,

and Malachite Green were the TAM dyes used, which are cationic in solution. The malachite green experienced much less efficient binding to BSA than the other TAM dyes, unable to reach sufficient binding for precise analysis of quantum yields. The singlet lifetime and intersystem crossing efficiencies of the other dyes were found to greatly increase upon protein binding. The normally used fast nonradiative transitions were curbed by the prevention of aromatic ring rotations in the BSA environment. The photoproducts of laser-induced photobleaching of protein-bound TAM dyes (Ethyl Violet triplet and semireduced radical) indicated initiation by electron or hydrogen atom transfer from the protein to the dye. Increases in yield of triplet and semireduced dye radical states caused by binding indicate that in the presence of oxygen, the reaction of primary importance comes from the interaction of the excited dye and substrate molecule (BSA), which produces damaging reactive oxygen species. The less frequent reaction becomes the direct energy transfer from excited dye to oxygen, which forms singlet oxygen. Interestingly, there was an oxygen-independent bleaching that was observed with Crystal Violet and Ethyl Violet. Therefore, photoinduced damage of the protein host proceeds in a manner that does not require oxygen, unlike typical photodynamic mechanisms. This is particularly promising for the treatment of tumors which are in hypoxic environments.

6.   "Wavelength-dependent Photoacoustic Calorimetry Study of Melanin" Forest, S.E.; Simon, J.D. *Photochem. Photobiol.* **1998**, *68*, 296-298.

Melanin, a biopolymer pigment, is a photoprotective molecule that shields skin against UV and visible radiation. The mechanism of the protection is yet unproven. Signals arising from excitation of melanin in buffered (pH 7.2) solution using short UV to visible wavelengths (264-527 nm) were monitored via photoacoustic calorimetry (PAC). Through the visible and UVA regions, extremely efficient heat transfer to solvents resulted. A transient species was detected with formation time in the subnanosecond range and decaying in hundreds of nanoseconds or longer. This transient is tentatively identified as a triplet state at 264 nm excitation. Oxygen quenching studies were performed, but data showed a quantum yield of less then 0.3 for the energy transfer using PAC. It was acknowledged that another method would better quantify the yield. The authors are currently continuing work to prove melanin's phototoxicity with short UV radiation.

7.   "Picosecond Linear Dichroism and Absorption Anisotropy of Hypocrellin: Toward a Unified Picture of the Photophysics of Hypericin and Hypocrellin" Das, K.; Smirnov, V.; Snyder, M.D.; Petrich, J.W. *J. Phys. Chem. B* **1998**, *102*, 6098-6106.

Hypericin is a naturally occurring photosensitizing dye from the wildflower St. John's wort. Hypocrellin, another naturally occurring photosensitizing dye, has similar structural characteristics. These compounds are of interest because of possible uses in photodynamic treatment of viruses (including HIV) and antitumor activity. Hypericin undergoes typical photochemical reactions involving triplet states including radical mechanisms or direct energy transfer to form singlet oxygen. The quantum yield for singlet oxygen sensitization and triplet yield of hypericin was estimated to be ~0.35 in ethanol and less in aqueous solution. An additional mechanism for hypericin activity is proton transfer, as it is known to acidify its surroundings upon absorption of light. Hypocrellin is also known to undergo proton transfer, but has very different photophysics. Time-resolved linear dichroism and anisotropy with subpicosecond resolution as well as computer simulations were employed to try to create a complete picture of excited state proton transfer in hypericin and hypocrellin. The initial step is excited state proton

transfer in both hypericin and hypocrellin. An excitation wavelength dependence was observed for hypericin kinetics, which indicates the presence of ground state tautomers. In viscous solvents hypocrellin exhibits similar initial kinetics to hypericin suggesting that hypericin and hypocrellin tautomers are very similar. No isotopic effect was observed for hypericin, nor was expected, as the O-O distance is within adiabatic limits. Hypocrellin proton transfer exhibits a strong dependence on solvent and does experience a deuterium isotope effect. Deuterium substitution may lower the ground state vibrational energy, allowing tunneling of the proton or activated crossing of a small potential energy barrier to back proton transfer. Three distinct transient components were observed for the decay of hypocrellin on time scales from 40-2000 ps. The authors attribute these three components to singlet excited states of the two ground state tautomers and a third intermediate which may also be a conformational isomer. Computer simulations based on this kinetic model were carried out. The results were found to agree with anisotropy and emission features, but absorbance features did not match quantitatively with experimental observations.

Physical Photochemistry and Photophysics

Selected and abstracted by
Jenny M. Baxter, Department of Chemistry, Florida State University, Tallahassee, Florida 32306-4390

Readers are directed to the collection of fine papers, covering a range of topics, published in a special issue of the *Journal of Physical Chemistry A* [**1998**, *102(28)*], devoted to molecular and supramolecular photochemistry, honoring six photochemists – Robert S. H. Liu, Douglas C. Neckers, Jack Saltiel, Nicholas J. Turro, Peter J. Wagner, and David G. Whitten – all of whom turned 60 years of age in 1998. Papers abstracted here were taken from sources other than this special issue.

1.   Bruchez, M., Jr.; Moronne, M.; Gin, P.; Weiss, S.; Alivisatos, A. P. "Semiconductor Nanocrystals as Fluorescent Biological Labels" *Science* **1998**, *281*, 2013-2016.

New demands on fluorescent probes in modern biology led Weiss, Alivisatos, and co-workers to prepare suitably modified semiconductor nanocrystals and to test them for use as fluorescent probes in several biological applications. The inherent properties of semiconductor nanocrystals, such as its tunability, narrow and symmetric spectrum, and resistance to photodegradation, make them ideal candidates for use in biological staining. To accomplish this, CdSe-CdS nanocrystals were coated with a layer of silica to render them soluble in water. Modification of this silica surface provides a means to control the interactions of the nanocrystals with various biological molecules.

Taking advantage of the particle-size tunability and the interaction control of the silica surface of the nanocrystals with other systems, the authors were able to label the nuclei of 3T3 mouse fibroblast cells with green-emitting fluorescent nanocrystals and use red-emitting nanocrystals to label the F-actin filaments of the same fibroblast cells. The resulting two-color fluorescence could be imaged simultaneously and showed very little photobleaching over multiple scans. These results provide a basis for envisioning a variety of uses for these nanocrystal materials.

2.   Chan, W. C. W.; Nie, S. "Quantum Dot Bioconjugates for Ultrasensitive Nonisotopic Detection" *Science* **1998**, *281*, 2016-2018.

In the paper appearing immediately after the one abstracted above, Chan and Nie describe the preparation and properties of luminescent semiconductor quantum dots (QDs) intended for use in nonisotopic detection applications involving DNA sequencing, clinical diagnostics, and fundamental molecular biology. By attaching mercaptoacetic acid to a ZnS-capped CdSe QD and covalently bonding it to a protein, the QD was made water-soluble and thus compatible with biological systems. The QD can be coupled with other biomolecules to make an ultrasensitive detector because of the ability of this probe to recognize specific analytes in biological systems. In experiments involving QDs covalently bonded to the protein transferrin, it was demonstrated that the QD could be transported into living cells. Neither the mercaptoacetic acid-modified nor the protein-conjugated QDs showed any changes in the optical properties from the original QDs.

When the photophysical properties of QDs are compared with those of organic dyes, there are several advantages to using QDs. The QDs can be tuned, by changing the particle size, from blue to red emission wavelengths; the QD conjugates have characteristically narrower fluorescence bandwidths relative to the organic dyes. Also, QDs are less susceptible to photobleaching than the organic dyes. These QD systems and the results obtained with their use should make possible the development of new, ultrasensitive biological probes.

3.   Gosztola, D.; Niemczyk, M. P.; Wasielewski, M. R. "Picosecond Molecular Switch Based on Bidirectional Inhibition of Photoinduced Electron Transfer Using Photogenerated Electric Fields" *J. Am. Chem. Soc.* **1998**, *120*, 5118-5119.

D_1 A_1 A_2 D_2
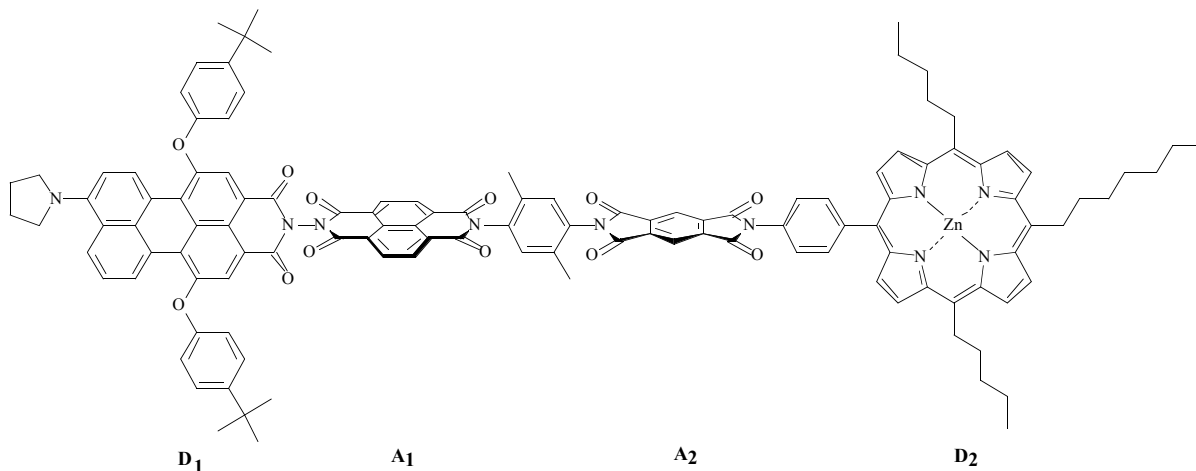
        Gosztola, Niemczyk, and Wasielewski describe studies of a D-A-A-D molecule appropriate for evaluation the effects of a photogenerated ion pair on the lifetime of another ion pair which is also prepared *via* photoinduced electron transfer. The specifically synthesized donor (D)-acceptor (A) molecule is specified above as D_1-A_1-A_2-D_2 where D_1 can be selectively excited with 645-nm laser pulses. The extinction coefficient of D_2 is 25 times greater than that of D_1 at 420 nm. The charge-separation lifetimes of the D_1^+-A_1^--dmb (dmb = 2,5-dimethylbenzene) and dmb-A_2^--D_2^+ pairs, generated from D-A reference dyads, were found to be 6.1 ps and 27 ps, respectively. The 2,5-dimethylphenyl group perpendicularly oriented to both D-A pairs serves as a spacer in D_1-A_1-A_2-D_2 to prevent electron transfer from one donor-acceptor pair to the other. It was also found that irradiation of the molecule with 645-nm, 300-nJ pulses produces D_1^+-A_1^--A_2-D_2 in 11% yield while irradiation with 420-nm, 2-μJ pulses produces D_1-A_1-A_2^--D_2^+ in 51% yield. Subtraction of spectra resulting from 645-nm pulsed excitation and from 645-nm pulsed excitation followed 10 ps later with a 420-nm pulse revealed that the initial formation of the D_1^+-A_1^- ion pair in 11% yield prevented the formation of A_2^--D_2^+ by 11% of the expected yield. The results of another experiment in which reversed arrival times of the two pulses at the sample demonstrated that the formation of A_2^--D_2^+ in 51% yield causes the concentration of D_1^+-A_1^- to be reduced by 50%. The authors conclude that the presence of one ion pair completely inhibits the formation of the other ion pair. These results demonstrate the potential use of molecules of this type as a gate and switch regulated by rapid photonic control.

4.   Adelt, M.; Devenney, M.; Meyer, T. J.; Thompson, D. W.; Treadway, J. A. "Ruthenium (II) MLCT Excited States. Stabilization toward Ligand Loss in Rigid Media" *Inorg. Chem.* **1998** *37*, 2616-2617.

        The photochemical reactivity of several polypridyl Ru(II) complexes in rigid media were investigated. Following excitation within metal-to-ligand charge-transfer (MLCT) bands and subsequent population of the dd state, these complexes can undergo rapid nonradiative decay or ligand loss. These complicating processes make less general the use of Ru^{II}(bpy) units in molecular arrays designed for energy conversion and related studies.

4-Etpy
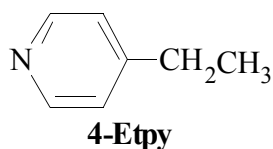
Photochemically induced ligand loss by *cis*-[Ru(bpy)$_2$(py)$_2$](PF$_6$)$_2$ in CH$_3$CN occurs within minutes. However, irradiation for 120 minutes of *cis*-[Ru(bpy)$_2$(py)$_2$](PF$_6$)$_2$ in a matrix of poly(methyl methacrylate) (PMMA) produces no significant absorption changes. While irradiation of *trans*-[Ru(bpy)$_2$(4-Etpy)$_2$](PF$_6$)$_2$ in CH$_3$CN gives *cis*-[Ru(bpy)$_2$(4-Etpy)(CH$_3$CN](PF$_6$)$_2$ within 1 minute, the same starting complex in PMMA with CH$_3$CN in the external solution undergoes only slight isomerization (demonstrating that isomerization does occur but with much lower efficiency) and no significant ligand loss after 20 minutes of irradiation. Photochemical ligand loss does occur when a coordinating anion exists: *cis*-[Ru(bpy)$_2$(py)$_2$]Cl$_2$ Ru(bpy)$_2$Cl$_2$, *hv* 20min. The stabilization of the excited states of the complexes, as also manifested by longer emission lifetimes, is achieved in PMMA relative to deaerated CH$_3$CN. For example, the average lifetime of *cis*-[Ru(bpy)$_2$(py)$_2$]$^{+*}$ is increased to 80 ns in PMMA from a lifetime of <5ns in deaerated CH$_3$CN. Stabilizations were also found to occur in another matrix – silica sol-gel monoliths. Elucidation of the reasons for the stabilization effects of rigid media is the subject of continuing studies, but possible explanations currently include an inhibition of the MLCT-dd surface crossing, a decreased reactivity of the dd states, and the ability of the rigid medium to provide an environment such that the complex experiences a cage effect which enhances the rebinding of the lost ligand to the metal.

5.   Takeshita, M.; Irie, M. "Photoresponsive Tweezers for Alkali Metal Ions. Photochromic Diarylethenes Having Two Crown Ether Moieties" *J. Org. Chem.* **1998** *63*, 6643-6649.
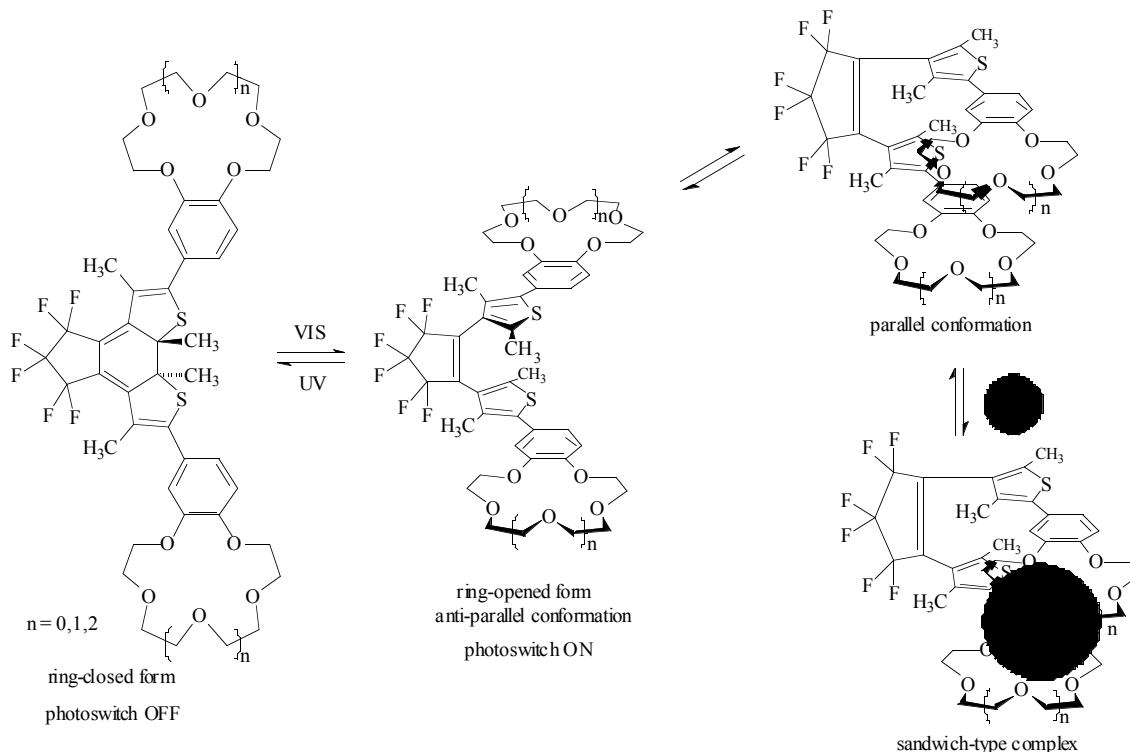
Irie and Takeshita describe the synthesis and structure of photoresponsive metal-ion–extracting tweezers having a dithienylethene photoswitch and two crown ether moieties for a binding site. As shown above for one of the series of molecules studied, the effect of light absorption, resulting in ring opening or closing, controls the ability of the molecule to trap the metal ion. The percent extraction of metal ion was measured for irradiations at 313nm and at wavelengths greater than 480nm, which have been assigned to absorption by the ring-closed and opened forms, respectively. Irradiation at 313 nm leads to a greatly lower percentage of metal-ion extraction. The decreased amount of extraction is attributed to the inability of the dithienlyethene to adopt a geometry to trap the metal ion between the two crown ethers moieties because of the ring closure initiated by UV absorption. In the ring-opened form after adoption of a parallel conformation, the formation of a sandwich-type complex involving the two crown ether groups enables the molecule to extract a metal ion with an ionic radius larger than that allowed by the ring size of one crown ether alone.

6. Steuhl, H.-M.; Klessinger M. "Excited States of Cyclic-Conjugated Anions: A Theoretical Study of the Photodecarboxylation of Cycloheptatriene and Cyclopentadiene Carboxylate Anions" *J. Chem. Soc., Perkin Trans. 2* **1998**, 2035-2038.
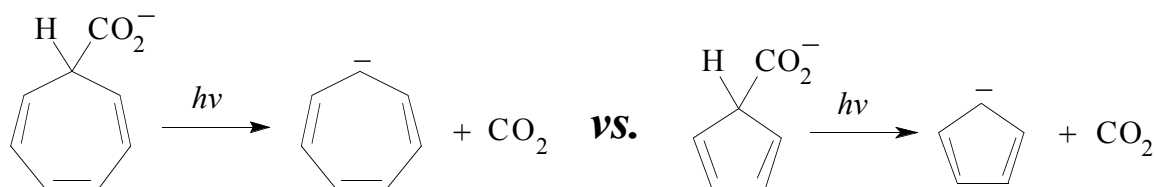
Steuhl and Klessinger use correlation diagrams, semiempirical calculations, and *ab initio* CASSCF (complete active space self consistent field) calculations to support the previously suggested experimentally derived idea that a $4n$ electron count is favored over a $4n+2$ electron count in excited states. The excited-state cycloheptatrienyl anion was previously shown to be more stable than the excited-state cyclopentadienyl anion. The authors used semiempirical calculations to obtain information about the geometries of the excited states and possible reaction paths. These results indicate that there exists a barrierless, exothermic decarboxylation of the cycloheptatriene carboxylate ion from its excited state of A" symmetry. Correlation diagrams demonstrate that the cyclopentadienyl carboxylate ion will encounter a barrier for the same reaction from its A" excited state. The results of *ab initio* calculations agree with this conclusion of the symmetry allowed formation of the cycloheptatriene anion.
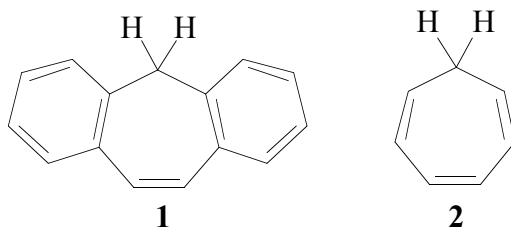
The electron count of a system can be used to consider whether the photogeneration of a conjugated cyclic anion will be allowed or forbidden by symmetry. The difference in the excited-state acidity of suberene (**1**) and cycloheptatriene (**2**), attributed to a different ordering of the excited states, is supported by the results of these calculations.

7.   Du, H.; Fuh, R.-C. A.; Li, J.; Corkan, L.A.; Lindsey, J. S. "PhotochemCAD: A Computer-Aided Design and Research Tool in Photchemistry" *Photochem. Photobiol.* **1998**, *68*, 141-142.

        In a technical and software note, Lindsey and co-workers report the development of a database for use as a research tool or a supplement to a laboratory for physical chemistry, biochemistry, or organic chemistry. The program can be run under Windows 95 and contains information, such as absorbtion and fluorescence spectra, molar absorption coefficients, and fluorescence quantum yields, for 125 photochemically relevant compounds . The program enables the user to calculate a variety of parameters including oscillator strengths, natural radiative lifetimes, transition dipole moments, and Förster energy-transfer rates. The original literature references can be accessed *via* the help feature. This software can be downloaded with a web browser directed to <http://www.kumc.edu/POL/PAPHome/Vol68/pap68sd1.html>.

Organic Photochemistry

Selected and abstracted by Loren Barnhurst, University of Denver.

1. Peterfy, K.; Garcia-Garibay, M.A., "Generation and Reactivity of a Triplet 1,4-Biradical Conformationally Trapped in a Crystalline Cyclopentanone" *J. Am. Chem. Soc.* **1998**, *120*, 4540-4541.
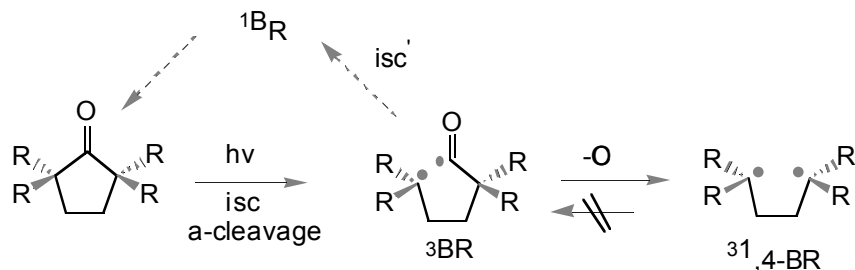
This research presents a fine example of using the crystalline solid state as a conformationally restricting medium for studying highly reactive intermediates. Studies were carried out on substituted cyclopentanones, with generation of the 1,4-biradicals following the scheme shown above. It is suggested that the 1,4-BR cannot revert to ^{3}BR and so must give cyclobutanes (cyclization) and/or olefins (cleavage) after isc to the singlet state.
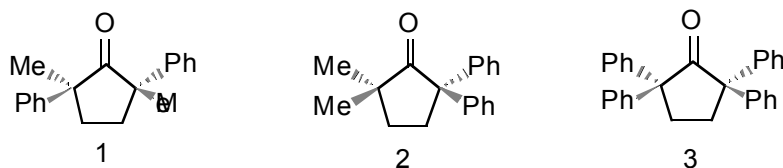
In an attempt to test the effects of different R groups, the following compounds were subjected to both solution (benzene) and solid-state photochemistry (λ>300).

In solution, all three possible reactions occurred -- disproportionation from the ^{1}BR state (for **1** and **2**), and cyclization or cleavage from the biradical (**2** and **3**). However, in the polycrystalline solid-state, **1** and **2** were completely unreacted, as a result of the suppressed disproportionation reaction and slow decarbonylation rates. Only **3** reacted, giving exclusively cyclobutane. Possible reasons proposed for this chemoselectivity include intrinsically faster cyclization rates, or environmental restrictions imposed by the solid-state, yielding the product which requires less reaction and activation volumes. Further work on the detection and characterization of these biradical intermediates is in progress.

2. Pollitt, S.K.; Schultz, P.G., "A Photochemical Switch for Controlling Protein-Protein Interactions" *Angew. Chem. Int. Ed.* **1998**, *37*, 2104-2107.

Using light as a reagent to convert molecules from the inactive to active form has proven to be quite successful, and this research adds to the versatility of this technique by expanding its usage to involve protein-protein interactions.

Using unnatural amino acid mutagenesis, an Asp38 was substituted with a *o*-nitrobenzyl ester of aspartic acid (Nb-Asp) on the p21^{ras} (ras) protein. This resulted in a photocaged interaction between itself and its

downstream effector p120-GAP (GAP=GTPase-activating protein). Mammalian proteins encoded by these ras genes function as key regulators in cell growth and differentiation, so while this caged ras protein still retains its intrinsic GTPase activity, it loses the ability to interact with p120-GAP, effectively setting a roadblock in the signal transduction pathway. This inactive form can then be converted back to the active form by irradiation with light at 355 nm, restoring 50% of the GAP-dependent GTPase activity. This approach should be applicable to other amino acids, and may provide a general method for the study of signal transduction pathways in which specific protein interactions can be identified.

3.   Dave, P.R.; Duddu, R.; Li, J.; Surapaneni, R.; Gilardi, R., "Photodimerization of N-Acetyl-2-azetine: Synthesis of syn-diazatricyclooctane and anti-diazatricyclooctane" *Tetrahedron Letters* **1998**, *39*, 5481-5484.
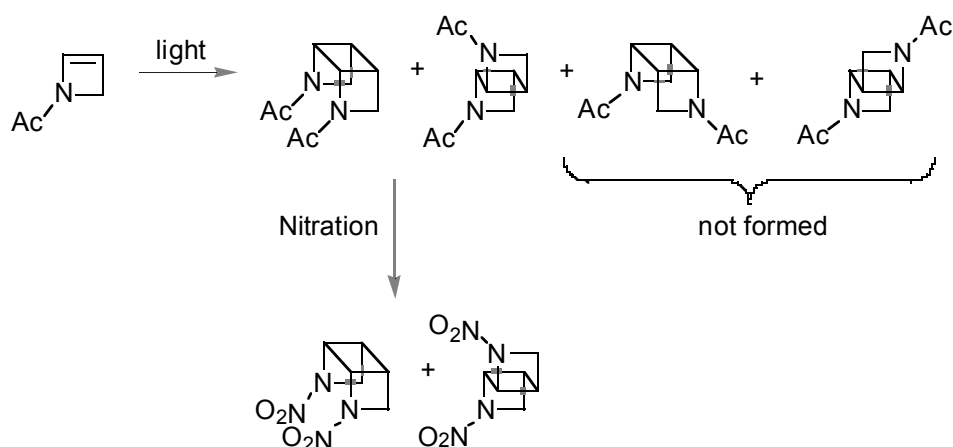
Enamides are known to undergo photochemical [1,3]-acyl shifts and engage in [2+2] photocycloadditions with ketenes, however their self-dimerization has not been previously reported.

Using a four step synthesis, readily available N-tert-butyl-3-hydroxyazetidine was converted into N-acetyl-2-azetine. After irradiation (acetone, high pressure Hg lamp, 1hr), only two of the possible four products were produced, with all the starting material being consumed. After chromatographic purification, a roughly 1:1 mixture (52% yield) of the two inseparable adducts were obtained. No other adducts were seen. To confirm the proposed structure by X-ray analysis, this mixture was then treated with trifluoroacetyl nitrate, yielding the dinitro compounds that were separable by chromatography. It was proven that only the head to head dimers were formed, paralleling the regiochemistry found in simple alkene dimerization in which electron withdrawing groups are present. Methods to produce diazacubane and higher azaladderanes are currently being pursued.

4.   Thopate, S.R.; Kulkarni, M.G.; Puranik, V.G., "The Paterno-Buchi Reaction of L-Ascorbic Acid" *Angew. Chem. Int. Ed.* **1998**, *37*, 1110-1112.

L-Ascorbic acid has been studied extensively in terms of its biological and pharmacological activity, but the organic chemistry of its functionalities has been oddly neglected (with the exception of O- and C-alkylations and

the Claisen rearrangement of its O-allyl derivatives). This compound constitutes a convenient reactive chiral olefin that is proposed to furnish chiral oxetanes through Paterno-Buchi reactions, which could be transformed further through ring-opening reactions to produce novel C-2 and C-3 branched ketosugars.
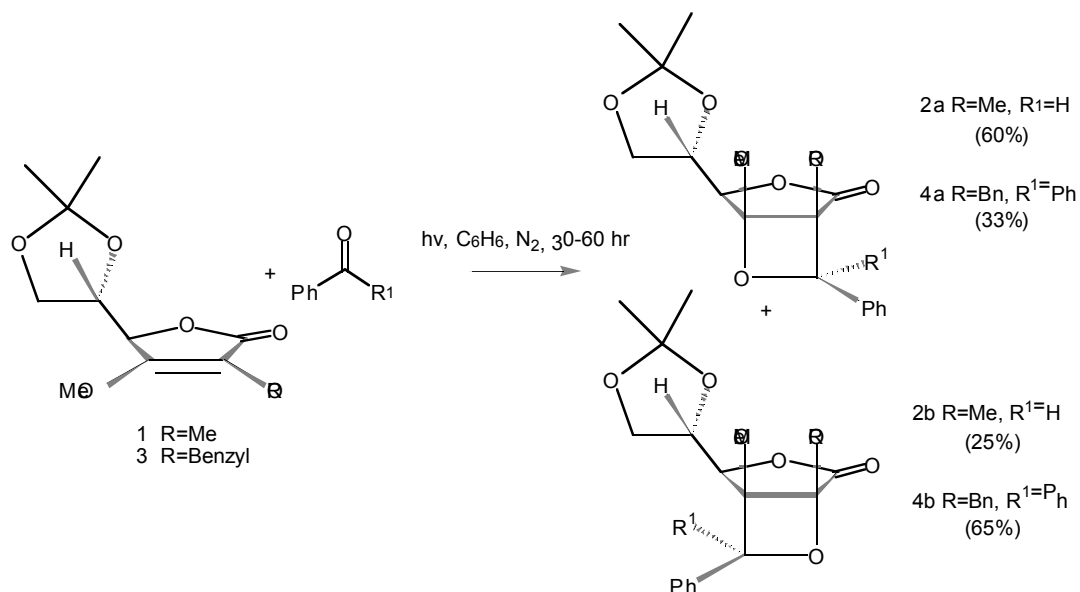
The starting material (**1**) was irradiated (C_6H_6, 125W, pyrex, 30-60 hr) in the presence of benzaldehyde, yielding the two oxetanes (**2a** and **2b**). The major product (60%) resulted from excited carbonyl attack from the less hindered face, with the aldehyde proton oriented in *endo* fashion. This structure was confirmed using X-ray crystallography. To further study the regiochemical preference, benzophenone was allowed to react with **3**, yielding **4a** and **4b**. The observed difference in regiochemical preference suggested that differing mechanisms were operative for each reaction. It was proposed that reaction with benzaldehyde occurs through a photoinduced electron transfer mechanism, while reaction with benzophenone follows a 1,4-diradical pathway. Further investigation is necessary to confirm this, however.

Finally, these oxetanes were treated with lithium aluminum hydride, leading to ring-opening and furnishing substituted ketohexoses, validating the usefulness of this method for future synthetic purposes.

The Gang of Six: Bob Liu, Doug Neckers, Jack Saltiel, Nick Turro, Pete Wagner, and Dave Whitten

Some two or three years ago, it was noted by Ramamurthy that 1938 had been a particularly auspicious year for the field of organic photochemistry, as it was the year of birth of six of our most noble compatriots. Thanks to his efforts and those of many others, a symposium was held in honor of their collective 60th birthdays in August 1998. On that occasion, I asked each of them to write some reminiscences for publication in the IAPS newsletter to mark our celebration of the same event. In the next pages are these contributions, and without further introduction, let them speak for themselves!

<div align="right">--William Jenks</div>

David Whitten, Bob Liu, Jack Saltiel, Nick Turro and Doug Neckers—Pete Wagner sent his own photo!

Playing with Excited Double Bonds. Isomeric Triplets, Upper Excited States, One-Way Isomerization & Hula-Twist

Robert Liu

University of Hawaii

The special symposium for the six 60 year-old photochemists was in reality a celebration of life, the life and career of George S. Hammond. Because of that, I would like to start out this contribution with a "story" that I read to my organic chemistry class during the last day of the year course. I called it: **Philosophy 101, The Way of Life**.

"The following is for those who think organic chemistry is the hardest course they have ever taken, almost impossible to handle or for those who are doing fine here but think some other courses are impossible to handle.

"Do you remember George Hammond? Yes, we came across him last semester when we discussed the Hammond postulate. As you know, he was my professor when I was a graduate student at Caltech, so he is your grandfather!

"A few years ago, there was a special occasion honoring his 65th birthday. All his former students and colleagues got together for a banquet in his honor. One of the gifts presented to him was a volume containing letters contributed by his former associates reminiscing their experiences with him further relating his impact on their lives. You see, at that time all his students were already professors at various universities or directors, managers or established researchers in industry, i.e., having reached a stage in life no longer afraid of admitting short-comings, especially in front of the old professor. So, we all poured our hearts out.

"You also have to realize that at that time a new graduate student had to beg his/her way into a good research group. Imagine when you didn't feel very confident of yourself, but yet you have to sell yourself into a research group, some of Nobel Prize caliber. What should you say? Perhaps, 'Please take me into your group. I promise to wash your car everyday?'

"Let me read you a few letters from this collection of letters.

"This first one says: 'We all know George's uncanny ability to see the hidden strength of his students or colleagues. (You see we had also reached the stage when we could call him George instead of Professor Hammond). His attitude of not minding the weakness but instead stressing the strength clearly worked out well for all the people associated with him. But in spite of this unique trait of his, I still cannot figure out after all these years as to what he saw in me when I asked to become a member of his research group. I was the fourth one of that year. With three ivy leaguers (close enough) preceding me, a weakling from Timbuktu (or Howard Payne College) would certainly have been rejected by any other group. But instead I became one of the original Hammond Mafia involved in a very unique period of solution photochemistry.' .... It went on and signed by .... oh, it's me.

"The second one is from a professor at Florida State University who was one year ahead of me in Caltech; so, he is your uncle. It says: 'George, the man, the scientist, was bigger than life for me when I was privileged to be in his group, and the passing of time only served to make him still bigger. How fortunate I was to have had such a teacher. Always approving, encouraging and expansive. 'Great idea. Sure do it!' That was George to me. And how exciting it was to do research in George's laboratory! In that heady atmosphere we, the students and postdocs, learned to be curious about each other's projects, and we learned to be students and teachers for each other. We were truly a research group, not just a group of researchers. Not only did George bring out the best in each of us, he also made us feel we were the best. During one of our weekly group lunches I still remember George's toast: To the best research group in the world. And, if George said it, how could it be otherwise.'

"Isn't that nice?

"The third one is from another uncle of yours, and also one year ahead of me. He is now a famous professor at Columbia University, winning all sorts of awards around the world. In his long letter, he concluded by saying: 'Personally, George has always been my hero. In particular, I have always admired George's scientific integrity and his ability to describe complicated phenomena in terms of simple ideas.' ..... 'I am proud to be part of the first and famous 'Hammond Mafia'. We are a family linked by the spirit of scientific adventure that came from our association with George. I thank him for being the 'wind beneath our wings'.'

"You see, now your uncle can fly high as an eagle that he can almost touch the sky!

"A month later Professor Hammond responded, first thanking us for the special occasion. Then he surprised us by forwarding a copy of a letter he recently sent to <u>his</u> professor. I would like to read part of that letter to you, something written by your grandfather to your great grandfather, the latter now an eighty-some retired gentleman in Massachusetts, a real Yoda. He opened the letter by saying: 'Dear Paul: Doug Neckers relayed to me your kind comments concerning the symposium. Although I wish that you could have been there in the flesh, I assure you that you were very much there in spirit. When people speak of 'the chemical family' you will forever be a presence as the real patriarch of the tribe. As I read the letters commenting on my style as a research director I realize anew the profound influence you have had on the way in which I have conducted my professional life.

"'When I arrived at Harvard I was incredibly naive and uncomfortably aware of the fact. It was an enormous reassurance to me when you accepted me as a research student. Subsequently I learned things of great value from you: the power of logical reasoning from facts, the delight that can come from creating kinetic models and using them to eliminate or support (<u>but never prove</u>) mechanisms and that science gives one lots of room for friends, but not for enemies.....'

"There, you have just heard how your grandfather described himself: incredibly naive and uncomfortably aware of the fact. (More elegantly said than "I just freaked out, blew it -- big time" -- as some of you might have put it). All these people felt one time or another totally inadequate, yet subsequently they all did fine in their own ways. So, feeling inadequate is simply the normal process of learning, the way of life. Perhaps the lesson here is that one should never take the attitude: I wish I knew half as much as he did. Well, you may say so, but you should never take it seriously. Imagine after ten generations of half as much, we might all be back in the cave!"

     *   *   *   *   *   *   *   *   *   *   *   *

When I started to do research in Hammond's group at Caltech, I was indeed incredibly naive. Fortunately, Nick Turro, Jack Saltiel and Angelo Lamola were already there. I am including Angelo with the two more senior members of the group for the simple reason that he was far ahead in research experience than the rest of us in his class. And, at that time he was already quite ready to give out directions. For a green horn like me, I was quite happy to receive suggestions from them or anybody else. To a large extent, it was the interaction with them and other members of the research group that allowed my hurried transformation from a complete novice to a full fledge member of the "Hammond Mafia".

From Nick, I learned all the basic things including how to pack a gc column. In fact, later on after Nick left for Harvard I was promoted to the post of the caretaker of the Beckman Megachrome gc, one of the few working units in the country. While I floundered in the beginning, Angelo kept on telling me to try new things on my own instead of waiting to be told what to do. So, one day I roamed around the chemical stockroom and found a bottle of isoprene. With my newly acquired gc and photochemical techniques, I irradiated a sample of the diene in the presence of benzophenone. I detected seven new peaks! A wiser man probably would have abandoned such a complex system and looked for a greener pasture. But not knowing better, I found the new result quite a nice green

pasture. In fact, with the Megachrome, I was able to separate close to gram quantities of all seven dimers. I was quite proud of myself with the quality of the NMR spectra obtained on the old Varian 60 MHz spectrometer.

At that time, Jack was completing his Saltiel plot, stilbene isomer composition versus triplet energy of sensitizers. I borrowed his idea and struggled through the rather complex mixtures of isoprene dimers and came up with a plot of percentages of C4 dimers versus sensitizer energies and submitted my first progress report to GSH. It was near the end of my first summer at Caltech. The following Monday morning George showed up in my lab with a smile on his face and proceeded to explain to me his new idea of isomeric diene triplets. I did not quite follow everything he said; but certainly I was very happy that my data generated such enthusiasm on his part. Soon, he left my lab saying that he would tell Nick about it. (You see before my isoprene work, Nick had in his hand some "unusual" butadiene dimer results where benzophenone gave a very different product mixture from that of biacetyl.) Wow, I got the news from the Cat's mouth before Nick. It certainly produced a warm feeling that I might be allowed to stay in Caltech. My mood reached a new high when in the following week, a manuscript on isomeric triplets of dienes was ready for JACS.

Of course, now it looks very odd that in that communication George Hammond, such a clear thinker, had chosen this terribly complex isoprene system to demonstrate the concept of isomeric triplets of dienes. But, the choice was not his; I was simply too fond of a system that worked for me. Later on, Nick did save the pain of the textbook writers of later years by completing the Saltiel plot of the simpler butadiene system.

One thing bothered me with the isoprene dimer work. When anthracenes were used as sensitizers, the cyclobutane dimers were inexplicably more (not by much, but the difference was real) than those from the high energy sensitizers. Soon after I joined the Central Research Department of duPont, I came across the exciting report by the group of chemists (Reid Kellogg, Peter McCartin and Dick Bennett) of the old Radiation Laboratory that described the assignment of the T_2 level of anthracene being very close to S_1. The exact position of T_2 depends on the nature of the substituents on the aromatic rings, but it was clear that intersystem crossing involved the population of T_2. It did not take long for me to associate their findings with the isoprene results by invoking T_2 sensitization and selective T_1 quenching of the cisoid triplets. But the catch was how to rule out the concept of non-vertical excitation, something made very popular by Saltiel and Hammond in their stilbene isomerization work. Fortunately, I had in my hand a set of fluorinated barrelenes which were shown to undergo triplet sensitized rearrangements. The rigid bicyclo[2.2.2]octatriene structure negates any possibility of non-vertical excitation. So with some patience, T_2-sensitization became a reality. (I used to say that the process was so inefficient that only an industrial chemist not faced with the "publish or perish" dilemma can afford to tackle the project.) Helping along the chemical study was the unique, seemingly uphill process of naphthalene phosphorescence sensitized by anthracene (I solicited the help of Reid Kellogg for this experiment). Perhaps the chemical community was getting weary of the idea of non-vertical excitation; there was virtually no resistance toward the case of T_2 sensitization, even though it was an obvious violation of the Kasha's Rule. Using chemical kinetics, we determined the lifetimes (sub-nsec) of such upper states, which later were verified by spectroscopists with the advent of more sensitive and better time-resolved instruments.

The next thirty years at Hawaii went through in a blur. The program for preparation of new stereoisomers of vitamin A started with Ramamurthy's discovery of one-way triplet sensitized isomerization of β-ionol. In spite of being a physical chemist at heart, he took up the synthetic challenge that led to many hindered 7-cis precursors of vitamin A. Strangely, it was only after successful characterization of the hindered, previously unknown 7-cis geometry and well on our way to new isomers of vitamin A, that we discovered an early paper by L. Pauling stating that such hindered 7-cis isomers were supposed to be too unstable for isolation. (I am not sure what is the moral of

this story as far as encouraging students to keep up with the literature.)   But, of course Pauling's conclusion is still valid if it is limited to comparing relative thermodynamic stability of the isomers rather than predicting their kinetic stability at room temperature.

Murthy departed in 1974 for a post-doc position with Paul de Mayo. He left with me partially separated synthetic mixtures of new 7-cis isomers of retinal. Soon after, a communication by Nakanishi appeared in which the use of 20 micron silica gel was mentioned for separation of isomers of a retinal analog. So, I packed a 7 ft "hplc" column. With that awkward setup, pure 7-cis isomers of retinal were isolated for the first time. Subsequently, after a coaching session with Allen Kropf, separation of retinal isomers on commercial columns with silica gel particles of progressively smaller sizes became a routine matter.

The program later led to all previously unknown isomers of vitamin A and A_2. These new stereoisomers allowed us to demonstrate regioselective or adiabatic isomerization, quantum chain processes and to probe for the stereospecificity of the binding site of opsin. The flexible binding site argued for possible inclusion of substituted vitamin A as the chromophore. Subsequently, many fluorinated and alkylated retinal analogs were prepared for information on specific protein-substrate interactions. Recently, we finally took up the courage to tackle the larger and more sensitive fluorinated carotenoids.

A few years ago, Al Asato prepared a series of compounds that we called "Mini-carotenes". Tomas Gillbro of Umea turned them into a wonderful set of compounds that systematically violated the Kasha's Rule -- by emitting from S_2 with varying intensity. Even azulene has played an important role in our work. Al prepared several series of highly colored azulenic retinal analogs that led to the first NIR absorbing analogs of bacteriorhodopsin and other polarized polyenes. And, Rajeev's recently prepared 1,3-difluoroazulene now has the record for high quantum yield of S_2 emission (0.20) and lifetime (9.5 ns) as claimed by our collaborator Ron Steer.

In considering conditions for regiospecific isomerization of polyenes, we came up with the "Hula-twist" model -- simultaneous twisting of a pair of adjacent double and single bonds, a process that seemingly violates the NEER Principle. We thought it could only be a high energy process taking place in a confined medium. For a while it remained as an unlikely high energy process because there were no new experimental evidence supporting the idea. It was a surprise to me that a decade later, high level calculations showed that the low energy pathway for deactivation of an excited singlet polyene, via conical intersection, followed such a two-bond twisted process (M. Olivucci *et al.*). Photoisomerization of vitamin D compounds was shown to yield "Hula-twist" products (W. Fuss) and isomerization data of exocyclic dienes suggested simultaneous two-bond twist (W. Leigh). When taken together with the early low temperature photochemical work of interconversion of S-trans,S-cis conformers of 1,3-butadiene and 1,3,5,7-octateraene (M. Squillacote & B. Kohler), there appear to be room again for this conceptually simple process (although admittedly I was guilty of being excessively optimistic in presenting the model).

In looking back, I can honestly say that when I started my job at Hawaii, I never envisioned the type of complex systems that we later worked on. The program simply evolved with the help of many capable associates. The polyene photochemical program was initiated by Yondani Butt and V. Ramamurthy. Synthetic value of this observation was subsequently realized through the effort of my long term associate, Al Asato, joined by Aravinda Kini, Dennis Mead, Achla Trehan, Rong-Liang Chen, Jin Liu and Rajeev Muthyala along the way. Hiro Matsumoto brought biochemical expertise into the group. Marlene Denny provided reliable analytical and photochemical work, Tara Mirzadegan in computer graphics, Letty Colmenares in her all around effort of bioorganic and protein NMR studies, S. Ganapathy and Bao-Wen Zhang in quantitative retinal photochemistry and Xiao-Yuan Li and Yun Zhu in spectroscopic and analog studies. It has been fun to learn with my people, and to share the fruit of their efforts

including the occasional reward of the dawning of simple explanations out of the initial, seemingly chaotic sets of data. To them I am most grateful.

Bob Liu,
October 1998

"Be A Chemist Like Uncle Jim"

Douglas Neckers
Bowling Green State University

To me one of the most interesting things about scientific research is the people that do it, who thought of, and carried out, the ideas. The artist is as important as the art so to speak.

I was born in a rural area in western New York State, went to a small, centralized school, and had the same teacher for every high school math and science course. What he lacked in sophistication, he made up for in understanding. Had he not done so, I probably would still be running a grocery store in Chautauqua County, New York. When it came time for college my family was Dutch, and Hope College was the College of the Dutch Reformed Church. So I graduated from Hope.

That I got a degree in chemistry was more fateful than reasoned. I had an uncle who was a chemist. He had gone to Hope too, and at the time he was there, only two careers Hope graduates followed upon graduation – the ministry or a teaching assistantship at some mid-western university in chemistry. My uncle didn't want to be a preacher, so he chose chemistry, went to Illinois for his degree where he studied with Wallace Caruthers, among others, and later served 37 years as Chair of the Department of Chemistry at Southern Illinois University in Carbondale.

About the only career advice my Dad gave me, save 'Go to Hope' was be a chemist like Uncle Jim and get your graduate education paid for. Don't be a musician like me. So on that basis – being a chemist like Uncle Jim because I would get my graduate education paid for --- I majored in chemistry.

I didn't warm much to smelting iron or the contact process, but essential oils, aspirin and other things of common encounter seemed more interesting. After spending a summer doing an undergraduate research project at Hope I was hooked forever.

Graduate school was a given because "somebody else would pay for it'. Gerrit van Zyl, head of chemistry at Hope for over 40 years, 'directed his boys', and van Zyl strongly pushed me to go to Ohio State. Because I knew someone else would pay for it, I began my academic business career early, and decided I could bargain. I went to Kansas because there were two Hope graduates on the staff there. And Cal, who was recruiter *par excellance* found my wife a teaching job. I never considered going as far west as California. It was too far from Chautauqua County, and Gene Van Tamelen, another Hope graduate, didn't move to Stanford until 1961 after I was already in graduate school.

Being a Jayhawk had some interesting chemical moments. I entered graduate school in the fall of 1960 with 55 other first year chemistry students, only one of whom was a foreign national! I worked for Earl Huyser who had worked for Cheves Walling so I always knew Peter Wagner. He was a Walling graduate student at the time I was with Huyser, and there was no higher calling than that – at least according to Huyser.

Cal Vander Werf moved to Hope as President in 1963. Before he left Kansas where he seriously to me again – this time to join him on the faculty at Hope. 'Van Zyl is retiring, that this would be an extraordiary opportunity for Hope and for you'. Frankly he had a lot more confidence in my ability than I did, but I was really flattered. Again being close to the roots and safe for a guy from a town of 600 people, I decided to start my teaching career at Hope. The way I figured it, young assistant professors had to do several years of laboratory work with their own hands anyway, and I might as well do it in a friendly environment as somewhere else. Though the decision was taken

mostly for the wrong reasons, and I sure didn't know what I was getting in to, those several years at Hope were very well spent – both for them and for me. Among the persons I managed to attract to Hope during those years were Shelton Wettack who is now Dean of the Faculty and Senior Vice President at Harvey Mudd; and Mike Doyle who is Vice President at Research Corporation and a Professor at the University of Arizona. It could be easily argued that Doyle has been the most successful academic chemist in the history of American liberal arts colleges.

Between VanderWerf west (Kansas) and VanderWerf midwest (Hope) came Harvard. In just a few months there, a non-extinguishable creative flame was ignited by Harvard's spark, and I discovered what a graduate degree in chemistry was worth more than 'the other guy would pay for it'. Though I worked for Paul Bartlett, it was the people in Bartlett's labs who really taught me; and none was more enthusiastic for chemistry, for his family, and for life itself was Nick Turro.

I walked in Converse labs at 7:30 AM on my first day at Harvard thinking Paul Bartlett would be as interested in my being there to post-doc, as I. There were only two people there at that hour. Nick Turro had three chromatographs running, was repairing the merri-go-round with one hand, and sealing a few vials with the other. And Roger Swigert, who often worked all night, was asleep on the floor under his desk.

Actually I knew Turro from the literature because I had read everything Hammond published. Nick could do four things at once and still talk. He talked in reverent terms of *Professor* Bartlett, and in enthusiastic terms of *George* Hammond. P. D. showed up at 8:30, told me it was the first day of classes, he had a lecture, and to come back at 2:00 PM. By that time I had talked with the wise members of Bartlett's group, the graduate students, discovered I would be assigned a problem that PD had kept going for 20 years because industry paid for it, and that – to that day – had resulted in only one publication. Folks from various Ivy League and near Ivy League places also opined that PD liked diversity. An occasional country boy from Kansas added a bit of color. And so began the first day of the rest of my life.

Nick, then as now, was the organizer. We had a basketball team and Nick was the coach. Actually we played in the law school league so I wondered a few years later how many of our opponents ended up in jail because of Watergate. Doug Applequist spent a semester during that year associating with Corey and teaching a course on small ring chemistry. From this course came conversations between Applequist and Roald Hoffmann that led, eventually, to the Woodward-Hoffmann rules. Nick, who was moonlighting on weekends with Peter Leermakers at Wesleyan developing the chemistry of tetramethylcyclobutane dione that eventually led to cyclopropanone and got him tenure at Columbia, had numerous conversations with Roald at the time too. Roald was scheduled to talk to a group of physical organic chemists on Friday, November 22, 1963 about extended Hückel theory and new calculations he had recently obtained on Harvard's new IBM 1620 computer. That was the day John Kennedy was shot in Dallas. But, after the proper moments of respect, PD and Frank Westheimer, who ran the seminars, decided there was nothing we do anyway so the seminar went on as scheduled. The next time I saw Roald was on the stage of the concert hall in Stockholm in 1981 when Tony Trozzolo and I chatted with for a minute after he received the Nobel Prize. We both recalled, vividly, the November, 1963 experience.

Nick and and Sandy invited Sue and I to join them for dinner with Doug Applequist where we chatted about chemistry at Illinois. These were the days of the 'Boston Strangler" and Sandy was, literally, petrified. I swear she had 13 independent locks on her Cambridge apartment door and only after an interview by the secret service and passing through the world's first metal detector, did a visitor gain entrance. Imagine the lab's surprise when Nick and Sandy took a job in Harlem and moved Sandy and two little girls to an apartment on Riverside Drive!

Sometime in the spring of 1964 Nick told me he had written for information about a Gordon Research Conference on Photochemistry, that he had applied to go, and been accepted. He suggested that I look into it too

which I did. I sent a letter to whomever, and Tony Trozzolo, who was the first Chairman of the first Gordon Conference on Photochemistry sent returned a note saying he'd welcome me to the Conference. Actually I knew Tony too. He had come to Kansas from Bell Labs at the invitation of Earl Huyser, my Ph. D. preceptor since they were old University of Chicago buddies. Tony communicates beautifully and told us about a problem in azo compound isomerizations. Skilled lecturers have a way of forming indelible impressions,. How many lecturers make sufficient impressions so that one remembers the contents 35 or 36 years later?

In July, Nick, Jacques Streith, who was photolyzing α-pyrone in Corey's lab on the way, he hoped, to cyclobutadiene, and I hopped in my relatively new Ford and drove to Tilton School for the 1st Gordon Conference on Photochemistry. It's hard to believe now, but photochemistry at that time was rather an aberrant bubble on much more significant field called physical organic chemistry. When I began my Ph. D. research problem at Kansas, there was only one Hammond paper – a communication in the Journal of Physical Chemistry that considered the photoreduction of benzophenone in isopropyl alcohol. Hammond's first really important papers on photochemistry appeared in the July 5, 1961 edition of J.A.C.S. At that time I was spending the summer as a Deputy Sheriff on the Lake patrol at Chautauqua Lake (political connections.) The quantum yield of benzophenone is much more sensitive to oxygen than is the quantum yield for photoreduction by benzhydrol, so this paper has received less attention that in much more famous counterpart in which Hammond first really confirmed, using steady state kinetics and the techniques available at the time, that benzophenone photoreduction can only occur through an excited state that has the characteristics of the triplet state.

But the observation is that the development of organic photochemistry was closely connected to polymer science, free radicals in solution, Walling, Kharasch, Frank Mayo, Bartlett. What Hammond exploited was the relationship between spectroscopy and the still developing theories of mechanism in organic chemistry. In the ensuing years, physical organic chemists would become as facile with excited state properties and characteristics as were their predecessors with chemical reactions in the form of the intermediates that intervened between reactants and products. The latter, parenthetically, was as much a departure in the 40's and 50's as spectroscopic relationships to mechanisms became in the hands of photoscientists.

The First Gordon Conference on Photochemistry is one of the only Gordon Conferences I've ever gone to about which I remember about mountain climbing, golf, or other diversions. It is also the only Gordon Conference I've ever gone to that I paid for myself – out of my pocket. Perhaps therein lies a lesson.

In my opinion, the 1st Gordon Conference did as much to solidify organic photochemistry as a self-standing field as anything. Trozzolo had done an excellent job assembling, except for George Hammond and Howard Zimmerman, the leaders in the then developing field. Dapper, eloquent George Porter barely mentioned flash photolysis for which he won the Nobel Prize a few years later, but talked instead about the photoreduction of Michler's ketone in cyclohexane and in isopropyl alcohol. (It photoreduces with a normal quantum yield in the former; undergoes no reaction in the latter.) At the end of his lecture George mentioned it would be interesting to see how the ammonium salt behaved because he had postulated the reason for poor photoreduction in polar solvents was the intervention of something he called a charge transfer excited state. Saul Cohen from Brandeis, Paul Bartlett's first or second graduate student, stood rather self-consciously and said, in these exact words, "We've done that". Cohen then went on to talk about some photoreduction chemistry that occurred with the ammonium salt wherein the conjugating electron donating amino group was neutralized, and suggested the idea of electron transfer/proton transfer as a route to the substituted diphenylhydroxy methyl radical in reactions of amines with benzophenone.

I was all ears during Porter's lecture but wondered, as did others, where Cohen was coming from. I was sure he couldn't be right since I had worked on aromatic ketone photoreduction at Kansas, and had tried many times to get photoreduction products from benzophenone and primary or secondary amines by irradiating them in Erlenmeyer's on the roof of Mallott Hall. In fact, the secret was to recognize that one did not need a hydrogen on the nitrogen atom to get product, and tertiary amines were much superior to alcohols as triplet reducing agents. Today only trivia buffs like Turro, Trozzolo and me remember what Porter talked about. Cohen's work, on the other hand, led to the development of amine synergists in photopolymerization wherein two-step electron transfer photoreduction leads to an α-amino radical, and this initiates an acrylate chain reaction. Just this past week I had an argument with a venture capitalist about whether photopolymerization was a $1 billion/year business or $3 billion/year.

Orville Chapman discussed his recent work on nitro compound photochemistry in alcohols. Paul de Mayo's review in the Weissburger series has pointed out that the nitro compound was, spectroscopically at least, a lot like an aromatic ketone.

An industrial guy from National Cash Resister rose with the audacity to suggest to Porter, that some of his thermochromic and photochromic compounds might illustrate one or another of Porter's obviously brilliant points (can't be not brilliant with such as beautiful accent as Sir George's). Bertleson wasn't an invited lecturer and Porter, as I recall, was anything but impressed with his industrial naivete'. Who's this guy? Silly stuff like photochromes and thermochromes being more important than the mechanism of the photoreduction of substituted benzophenones in non-polar and polar solvents?

QED #2. Today, the photochemistry of naphthospiropyrans is responsible for the singularly most profitable venture at PPG – Transitions Plastic Lenses.

Albert Weller talked about amine quenching of aromatic hydrocarbon fluorescence. Weller was a community centrist --- not an industrial upstart or a physical organic chemist trying to interlope on the community of spectroscopists and gas phase kineticists. But wow, I thought, talk about irrelevant stuff!

QED #3. How many meetings do we go to these days and not mention Rehm/Weller or Rudy Marcus?

Score – real world three --- insight of a young post-doc zero.

For the most part, though I mostly listened at lunch, dinner and in that small social room that graced Tilton those days. In the process, I met some people who would become lifelong friends – Dave Schuster, Tony Trozzolo and a couple other Bell Labs mafia, Al Padwa, Jacques Streith, Bob Bertleson, Paul Kropp, Orville Chapman, Gary Griffin, Jerry Bradshaw.

Actually I remember Turro sitting in Bradshaw's room with a copy of a manuscript from the Hammond group that had been accepted by JACS on olefin isomerizations. The last author of at least 30 listed on that now infamous, and very long, publication was J. Christopher Dalton, who was an undergraduate in George's lab at the time. Not more than 10 years later Chris became my colleague at Bowling Green and remains one of my closest friends in science and in the academy.

Hope had an enrollment of 1400 students when I began there in 1964, and it's hard to believe now, but 28 students who took the two courses I taught in the fall of 1964 joined the ranks of Ph. D.'s in chemistry and biochemistry.. Chemistry at Hope was then, as it is now, a particularly strong part of the undergraduate program at the College.

Industrial interest in my work came early. Without my knowing it, both benzophenone which I had done some organic photochemistry on as part of my thesis, and ethyl phenyl glyoxylate, which was also part of the work I did at Kansas, showed up as commercial photoinitiators for acrylate polymerization. Shortly after I started teaching at

Hope Blaine McKusick, who was a friend of Vander Werf's, invited me to DuPont for a talk. I remember talking with Jim Harris, who was working on photochemical reactions of fluorinated aldehydes, and Bob Liu who was working with him. Bob left DuPont shortly thereafter, and began the beautiful work on retinals for which he has become so properly recognized. I met Jack Saltiel first at a IUPAC meeting on Photochemistry held in Enschede, Netherlands. Jack, who was born in Greece, had gone to Greece for a visit prior to the Conference, though he was a scheduled lecturer. As luck would have it, the Greeks got in a war with somebody, probably Turkey over Cyprus, while Jack was visiting the old sod. Unfortunately for him there was a general mobilization, and he was drafted into the Greek army. Once a Greek, always a Greek as Jack told the story. Fortunately a few bribery dollars placed in the proper hands did the trick, and Jack made his lecture in Enschede as scheduled.

David Whitten is a person I've always known. I specifically remember the beautiful work, in collaboration with Tom Meyer, that introduced me to inorganic ion electron transfer. His work on monolayers seemed esoteric at the beginning until organized media became so important that there was a special ACS Symposium on the subject. David is an devoted runner. I remember him stopping at some place in Boston after a Gordon Conference so he could buy a special pair of running shoes. He gets up so early to run, that few ever seem to see him pounding the pavement.

George Hammond was always part of my professional life, though I first discovered he knew who I was in a rather strange way. Sometime in the deep dark past I got a phone call from a head hunter looking to hire a photoscientist to head up a new photoresist effort in Buffalo for Allied. "Come talk to us even if you're not that interested." So I did. Actually Buffalo had more than incidental appeal. It was close to Chautauqua County. When I told the boss I wouldn't move for less than $100,000/year to this industrial job (I was making about $30,000 at Bowling Green at the time) Allied found another. It was fortunate for me that they did. The effort folded in about 2 years when management took a different turn. But George was behind the contact and that made me feel very, very pleased.

I first met George and Eve Menger, his wife, in the bus park at the Ming Tombs near Beijing. We were both there for meetings – I for a meeting on Polymer Protected Reagents; he with a delegation visiting the Institute of Photographic Sciences in Beijing. Both groups stayed at the Friendship Hotel(s) in the center of Beijing and took sightseeing trips together. The first words out of George, the consumate teacher's, mouth were "Doug, how's Chris?".

Three years later George became a mutual colleague in a relationship that we both cherish. George, like my Uncle who mentored me early, and Cal VanderWerf from whom I learned enormously, and to whom I owe a lot, became my mentor in maturity.

George told me once "Neckers, I wish I had had someone so wise as me mentoring me when I was 55,". I envy our students who find him on their committees, and I learn from him every time he comes. When he comes to Bowling Green, there's al line outside his door just like the lines that must have been there at Iowa State, Cal Tech, Santa Cruz, and even Allied.

If there's a common trail through all of this, it's the people I've have been sincerely blessed to be around. Mentors learn to mentor from being mentored. It is a fond dream of mine to be half the mentor Jim Neckers, Cal VanderWerf and George Hammond have been to me.

The thing that struck me about Harvard when I was a student in Bartlett's lab was how interesting and genuine the people around PD were. There was a hidden spirit -- a spirit of simplicity, of honestly liking what one was doing and doing what one does because one likes it. The impression I got from that experience was that for the creative,

the energetic, the motivated, life is too much fun to be bothered with anything but crowding into every day all the fun that you can.

Over lunch in Boston Gary Schuster, Chris Dalton and I had one of many long talks about things we've had over the years. Gary, who is wonderful, for the pithy one-liner comments that clearly make him a good Dean --- "Remember guys, when you hire a faculty member, you hire the whole person."

During the Boston meeting that hidden spirit --- that same spirit of simplicity, of appreciation, of genuinness, I first experienced in Paul Bartlett's group at Harvard 35 years ago --- was clearly evident. I don't think the group assembled had ever been together, all at once, before. But what the group of photochemists, assembled by accident in the early 60's, was was a group of motivated, bright women and men going about the business of the photosciences, and appreciating one another both as individuals and for their work.

Collegiality didn't make our science, but it surely made it much more than it might have been. Along the way, those of us who were mentored by the very best learned to mentor others a little bit ourselves.

Reversible Association of Free Radicals with Benzene.
The Seed of an Idea

Jack Saltiel

Department of Chemistry

Florida State University

Tallahassee, FL 32306-4390

I take this offer to reminisce as an opportunity to tell a story that might not otherwise be told. It has to do with an irritating side reaction that led us to the study of the photooxidation of benzil and from there to the photolysis of benzoyl peroxide in the presence of oxygen. Serendipity pulled me back to the project George Hammond assigned me when I joined his research group. The demonstration that benzoyloxy radicals add reversibly to benzene brought a kind of closure to that initial free radical quest. But let me place the story into context.

Not too long ago, in my first article to this Newsletter, I described how, in 1960, I started work in George Hammond's laboratory seeking evidence for reversible formation of π-complexes between free radicals and aromatics.[1] It was George's idea and he, no doubt, could describe my project better. It concerned the thermal decomposition of benzoyl peroxide in toluene with the goal of determining quantitatively the dependence of the methylbiphenyl and bibenzyl products on the concentration of benzoyl peroxide. The formation of the methylbiphenyl would be first order in radicals if phenyl addition to toluene were irreversible, but second order in radicals if the addition were reversible and the rate determining step required a second radical to abstract a hydrogen atom from a phenyl radical/toluene complex. Bibenzyl formation, on the other hand, had to be second order in radicals, and its relative yield would increase at low radical concentrations if the phenyl radical/toluene association were freely reversible. Much data had been gathered by two graduate students and a postdoctoral fellow who had preceded me on this project. My part, the determination of the yield of bibenzyl as a function of benzoyl peroxide concentration, was soon completed, but interest in the interpretation of the data had subsided. Measurements of deuterium isotope effects by Ernest Eliel and coworkers had made a strong case for essentially irreversible addition of aryl radicals to benzene.[2,3]

How serendipity led me to the study of the isomerization of stilbene triplets and of the mechanism of stilbene photoisomerization, generally, I have already described.[1] That became my Ph.D. thesis topic during a very exciting time in George Hammond's laboratory. The paper that George wrote on this work remains one of the cornerstones of the area of cis-trans photoisomerization.[4] Though much had been learned, I was not satisfied. As I was about to leave Caltech, I asked George whether it would be alright for me to continue working on stilbene. I knew that he was of the opinion that continuing work on one's Thesis topic was not a good way to start an independent career. I was surprised, therefore, when he told me that while normally his advice would be not to do it, my case was an exception. He encouraged me to continue.

One nagging question had to do with the azulene effect on stilbene trans/cis photostationary ratios. These ratios increased with increasing azulene concentration under both triplet sensitized and direct excitation conditions and this qualitative agreement had been taken as evidence supporting common triplet intermediates in both reactions. I fear we were swayed by the then wide spread acceptance of the Förster mechanism for direct cis-trans photoisomerization.[5] The problem was that, since azulene had a shot at quenching both singlet and triplet trans excited states, its effect should have been larger on the direct than on the sensitized photoisomerization. The opposite was very much the case.

At Florida State University I assigned the problem to my first graduate student, E. Dennis Megarity. Denny's work soon established that my misgivings were justified. Without a fluorimeter, we devised a method for using a scentillation counter to evaluate the quenching of *trans*-stilbene fluorescence by azulene.[6] The results, later confirmed by a fluorimetric study,[7] showed that the azulene effect on the direct isomerization of the stilbenes was accounted for quantitatively by singlet quenching. No triplets were involved. Later, differential viscosity effects on the influence of azulene under direct and sensitized excitation conditions were more nails in the coffin of the triplet mechanism for stilbene photoisomerization.[8] The Lewis "loose-bolt" mechanism in which photoisomerization occurred following $S_1 \leftarrow S_0$ internal conversion as a hot ground state reaction again seemed possible,[9] although it had been criticized soundly on the basis of the Kassel-Rice theory.[10] Proponents of the triplet mechanism did not give it up easily and it suffered a slow demise.[11,12] One exchange in this connection that I remember vividly to this day, occurred when I first met David Whitten. I was visiting Caltech in late 1965 and David was a postdoctoral fellow in George Hammond's laboratory studying the mechanism of reactions initiated in solution by γ-rays. In front of a board in George's laboratory I was subjected to David's probing, tough questions concerning the interpretation of our scintillation counting results. David, to his credit, was one of the earliest converts to our singlet mechanism for the photoisomerization. Others waited until transient spectroscopic measurements provided direct confirmation of our conclusions.[13,14]

The Lewis mechanism deposits all the electronic energy into ground state vibrational modes and should be subject to large deuterium isotope effects so I set out to synthesize perdeuteriostilbene. The perhydrostilbene was deuterium exchanged in D_2O over platinum at 200 °C. Since exchange of the olefinic hydrogens of the trans isomer is very slow,[15] *cis*-stilbene was employed as the starting material. The exchange is accompanied by cis → trans isomerization and, as the process had to be repeated several times, the partially deuterated *trans*-stilbene was separated from side products by chromatography and converted to a cis-rich photostationary state using triplet sensitization.[16] Benzil seemed to be the sensitizer of choice as it gives photostationary states in excess of 90% *cis*-stilbene. However, for irradiations carried out in benzene under a constant stream of nitrogen bubbles, the *cis*-stilbene obtained was contaminated with a small amount of biphenyl. Pyrene, which gives a photostationary state of about 90% *cis*-stilbene, was used instead. With perdeuteriostilbene in hand, the dramatic deuterium isotope effects on the direct photoisomerization of the stilbenes that were expected for the Lewis hot ground state "loose bolt" mechanism were shown to be absent.[16] Torsional relaxation to a common twisted singlet excited state seemed the only viable alternative and the stilbene phantom singlet was born.[16]

In 1966 I assigned the problem of identifying the source of the biphenyl in the benzil irradiations to Howell C. Curtis, my third graduate student. Howell had experience in photochemical research as an undergraduate in Harry Morrison's laboratory. Photolysis of benzil in degassed benzene, $\lambda_{exc} \geq 330$ nm, gave a complex product mixture in which biphenyl and benzophenone were present in trace amounts, ~ 1% each.[17] Irradiation in benzene-C^{14} and isotopic dilution also showed that for a reaction taken to ~ 50% benzil loss, recovered benzil has ~ 1% activity incorporated. Since under nitrogen in the presence of stilbene most of the benzil survives the irradiation, biphenyl formed directly from benzil photolysis was insufficient to account for the contamination of *cis*-stilbene noted above. The source of the biphenyl in the presence of stilbene was traced to oxygen contamination of the nitrogen used in the outgassing procedure. Our attention turned to the study of the photoxidation of benzil. In the presence of air or pure oxygen the photooxidation of benzil in benzene gave biphenyl, phenyl benzoate, benzoic acid and benzoyl peroxide as major products.[18] Benzoyloxy radicals seemed likely intermediates, and a comparative study of the photolysis of benzoyl peroxide in the presence of oxygen was undertaken.

The key observation in the photolyses of benzil and benzoyl peroxide in benzene at 30 °C in the presence of oxygen was a similar strong dependence of the phenyl benzoate to biphenyl product ratio on the oxygen concentration.[19-20] As the oxygen concentration is increased the yield of phenyl benzoate increases at the expense of the yield of biphenyl. While our work was in progress a paper appeared by Tokumaru and co-workers on the photolysis of benzoyl peroxide which similarly found that the yield of phenyl benzoate increases with increasing oxygen concentration.[19] The two sets of results differed in that, in the Tokumaru study, the increase in the yield of phenyl benzoate appeared to come at the expense of benzoic acid.[19] This was the same Katsumi Tokumaru whom I came to know and admire through our mutual interest in the mechanisms of cis-trans photoisomerization of arylethenes.

The conclusion seemed inescapable. Reversible addition of benzoyloxy radicals to benzene gives an adduct radical that reacts with oxygen to give phenyl benzoate.[19-20] At low oxygen concentrations, inefficient trapping of this σ-adduct increases the importance of its dissociation and subsequent decarboxylation to phenyl radicals whose irreversible addition to benzene led to an increase in the yield of biphenyl. The mechanism is summarized in Scheme I.

**Scheme I.** The Fate of Benzoyloxy Radicals in Benzene
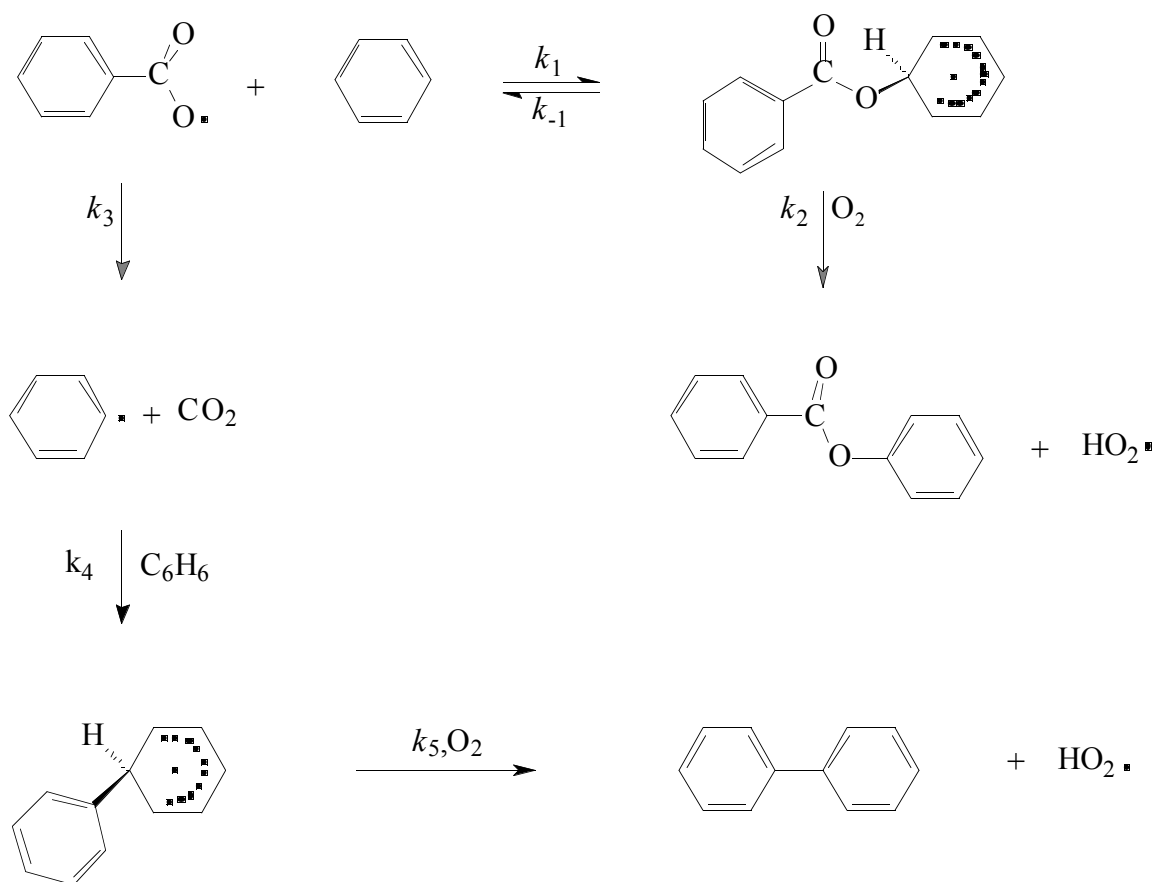
The reversible addition of a free radical to benzene that had eluded me in Hammond's laboratory was now established. Moreover, it was found, albeit for a different radical, in essentially the same system I had investigated as a graduate student. That it was probably a σ- rather than a π-adduct seemed of little consequence. Guided by Eliel's work we carried out the benzoyl peroxide photolyses in ~1:1 mixtures of benzene-d_0 and benzene-d_6.[20] The isotopic composition of the biphenyl product gave k_4^H/k_4^D = $1.2_1 \pm 0.0_6$ at 30 °C, independent of $[O_2]$ and in reasonable agreement with k_4^H/k_4^D = 1.06 obtained at a higher temperature for phenyl radicals generated from the thermal decomposition of phenylazotriphenylmethane in benzene.[3] Hydrogen abstraction from the phenylcyclohexadienyl radical by the triphenylmethyl radical gives biphenyl in the latter case.[3] In the benzoyl peroxide reaction, in the absence of O_2, an important pathway to biphenyl is the disproportionation of phenylcyclohexadienyl radicals[21] which is subject to a large deuterium isotope effect.[2] Trapping of the phenylcyclohexadienyl radicals by O_2 in our system eliminated this complication.

Cage recombination of phenyl and benzoyloxy radicals obtained from the fraction of excited benzoyl peroxide that decomposes by two bond cleavage gives phenyl benzoate in ~11% yield.[19] Upon correction of phenyl-d_0 benzoate yields for the cage product, d_0/d_5 ratios for phenyl benzoate formed from free benzoyloxy radicals are 2.3 and 3.0 for O_2- and air-saturated benzene, respectively. This requires substantial C-H bond breaking in the rate-determining step for phenyl benzoate formation confirming expectations based on Scheme I. The reason for the relatively high yields of benzoic acid was a puzzle.[2] Abstraction of hydrogen from phenylcyclohexadienyl radicals by benzoyloxy radicals was a possible source of this product, but there was the predicament of explaining "why so many ArCOO• radicals should wait around for step 4 to occur so that they can then participate in" the hydrogen abstraction step.[2] The reversibly formed benzoyloxycyclohexadienyl radical provides an answer to this dilemma.

Reversible addition of benzoyloxy radicals to benzene furnished analogy in free-radical chemistry for deactivation pathways of the triplet states of carbonyl compounds, such as benzophenone, via revertible addition to benzene[22-25] and to alkenes.[26,27] The latter addition is the first step in Schenck's mechanism for sensitized cis-trans photoisomerization,[28] a mechanism which probably applies when triplet excitation transfer to the alkene is highly exothermic.[27]

Interestingly, our results on the photooxidation of benzil also led to the conclusion that formation of a Schenck biradical is the initial step.[18]

$$^3(PhCOCOPh)^* + {}^3O_2 \longrightarrow$$

Ph—C—C—Ph

Schenck Biradical

(1)
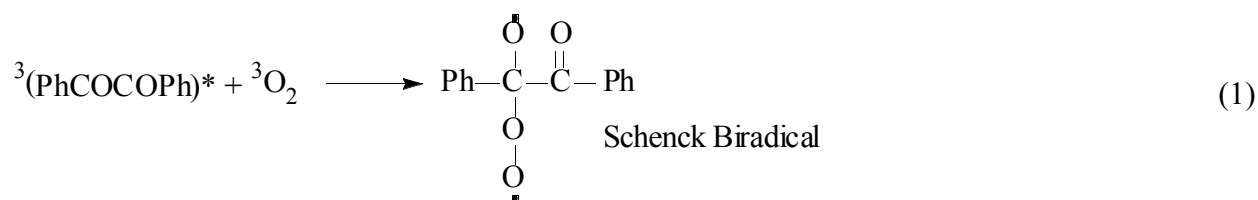
This, despite the fact that excitation transfer in this case would be exothermic. With Hammond's discovery of the crucial role of triplet excitation transfer in many photochemical reactions, many of us tended to discount Schenck biradicals as viable intermediates. Finding two systems [18,27] in which Schenck biradical formation is the dominant pathway made a considerable impression on me. What appeared to be incorrect ideas for many systems, could be correct for the right reactants. A few years later I met G. O. Schenck while visiting the Max Planck Institute in Mülheim. He told me that he was seriously ill in the hospital when my paper on alkene photoisomerization[27] appeared. His son had brought a copy to his hospital bed and this vindication of his mechanism had so cheered him up that he made a miraculous recovery.

Experience upon experience has taught me not to categorically reject ideas just because they fail to account for observations in specific systems. Schenck biradicals do not provide the universal mechanism for triplet sensitization envisioned by Schenck, but they can be the right intermediates in certain cases. The Förster mechanism does not correctly describe the photoisomerization of the stilbenes, but it is correct for other olefins, for instance, *p*-nitro-[13] and *m*-bromostilbenes[29] and certain thioindigos.[30,31] Lewis et al. could not find evidence for Olson's mechanism[32] of adiabatic cis-trans isomerization in S_1 because they searched for it in stilbene[9] where it occurs as a minor pathway.[33] Yet Olson's mechanism was resurrected nearly half a century later by Sandros, Becker and co-workers.[34] In our recent work, we have shown that the adiabatic photoisomerization pathway in S_1 can be highly conformer specific and that its contribution increases with the size of the aryl group in *cis*-ArCH=CHPh.[35] The adiabatic conversion of *cis*-stilbene triplets to *trans*-stilbene triplets[4] is consistent with Olson's mechanism, although it was several years after his proposal that the existence of triplet states in molecules was accepted. Important examples of adiabatic cis-trans isomerizations on an electronically excited potential energy surface are Tokumaru's one way photoisomerizations in the triplet state.[36] Above, I described how the reversible association of radicals with aromatics that could not be demonstrated for phenyl radicals, was demonstrated for benzoyloxy radicals. Who knows, somewhere the system may lie in wait for which Lewis' hot ground state photoisomerization mechanism will still be found.

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Skating On the Edge of the Paradigm

Nicholas J. Turro
Columbia University

Introduction

I was asked sometime ago to write a "Memoirs" piece for our Newsletters and had started to do so on several occasions, but was interrupted and kept pieces of it lying around. William Jenks finally put the strong arm on me to join in with the Gang of 6 who hit 60 this year and finally meet my obligation. I apologize for the length and hope the readers will bear with me on my reminiscence of a 40 year journey. Approaching the inevitable mid-life crises, I look forward to continuing the adventure under the direction of our muse, Chemistry, and with the companionship of Sandy, my family and a continuing group of fabulous students and colleagues.

The early days at the State Water Laboratory at Wesleyan University (summers of 1957-1960)

I started my chemical career as an analytical chemist working summers in the Connecticut State Water Laboratory at Wesleyan University. It was there that I met Peter Leermakers who was a Wesleyan student two years my senior and who also worked in the water lab during the summers when he was an undergraduate. Peter left for graduate school at Caltech in the Fall of 1958. During the summer before my senior year, Peter returned and informed me that Caltech was the place I had to go for my PhD and that I had to work for George Hammond on photochemistry! With typical respect for my elders, that's exactly what I did.

Sandy and I were married in the beginning of August, 1960 and were in Pasadena by the end of August. Peter was there waiting for us and helped us settle into the $>100^o$ Southern California temperature by inviting us to his apartment which was equipped with a wonderful swimming pool and with margaritas, so powerful that your lips began to curl as the glass of tequila approached them.

The Caltech Years in the Hammond Group (1960-1963). The Triplet State Raises Its Three Pronged Head for the First Time.

After arriving at Caltech, I spoke to a number of faculty members about research. I admired Jack Robert's work very much, but he was a big guy with a booming voice and when he looked down at me and said something like, "Turro, talk to Marjorie (Caserio) about a research problem if you want to work in my group, " he sort of scared me!! He still does (sort of, but I love him none the less!).

When I spoke to George Hammond about a research project, he mentioned that he was working on the "triplet state" (how to visualize the "three states" was a puzzle to me at the time and has remained a theme for our research group over the decades) and something about catalyzed formation of triplets by metal complexes. Three states sounded better than one to me, but I really had no idea of what this was all about and was afraid that it might be way too physical chemical-ish for me.

Metal-Complex-Catalyzed-Decomposition of Alkyl Pyruvates

My initial project was to learn if the thermolysis of methyl pyruvate could be catalyzed by paramagnetic metal complexes, the idea being that the decomposition might proceed through a triplet and that collisions with the paramagnetic species could lower the A factor and cause a catalyzed rate acceleration. There was some evidence in the literature from measurement of Arrhenius parameters that the cis-trans isomerization of ethylenes might go

through a triplet state and that certain catalysts of the cis-trans isomerization might operate by "catalyzing" formation of the triplet.

My first lab experiment was to synthesize methyl pyruvate. Eagerly I went to the library and found that an Organic Synthesis prep involving the reaction of diazomethane with pyruvic acid, which was available in the chemical stores room, should do the trick. Unfortunately, the storeroom did not stock diazomethane so I had to make some. To my amazement, diazomethane was described in the literature as a yellow gas. That sounded neat. I went to chem stores and signed out the equipment required to prepare diazomethane. I forget the details, but I remember it required a decomposition that produced this remarkable yellow gas which could then readily be distilled and collected in a cold trap.

I set up the equipment, started the reaction and everything went like gangbusters! The yellow gas came bubbling out of the round bottom flask containing the reactants and condensed into a cooled ether solvent in the collection flask. I was so proud of all this that I rushed down the hall to see if there was someone from Robert's group to whom I could show off the set-up. John Baldwin, a second year graduate student working for Jack Roberts, came and looked at the set-up, turned ashen white and raced out of the room screaming, "You should never use ground glass joints when distilling diazomethane in ether! The ground glass can cause the diazomethane to decompose uncontrollably and set off an explosion!!!" John was a real scholar and knew all this stuff. Hey, I was just a rookie; how was I to know? Anyway, the reaction worked fine as did the synthesis of methyl pyruvate, so now I could start decomposing it in the presence of the metal complexes.

Digressing just awhile, I must mention a rather spooky story that eerily connects my diazomethane story with a visit to Mülheim in October 1998. After arriving in Mülheim and enjoying Kurt (and Gertraud's) kind hospitality, we began reminiscing about the many good times we have had together since the early 60s. Later in the week I was scheduled to deliver a "Public Lecture" on "Paradigms Lost and Paradigms Found: Science Extraordinary and Science Pathological". We began discussing the make-up of the audience and the topic of fraud in science came up. At this point, Kurt told me that he had had a student whom he had suspected of faking results, and to test him, he had asked the student to synthesize diazomethane. The following day Kurt noticed that the student had set up the experiment with ground glass joints! Before any damage could occur, Kurt shut off the reaction.

Back to Caltech in the Fall of 1960. At the same time Peter Leermakers was using the same metal complexes to quench benzophenone triplets and looking for a correlation with paramagnetic properties. As it turned out, the thermolysis experiments did not show a correlation with paramagnetic properties but were a lot easier to run than photochemical quenching experiments. It turned out that the metal complexes that "catalyzed" the decomposition of methyl pyruvate were also excellent quenchers of benzophenone triplets. Pretty soon I was predicting which metal complexes would quench and which would not, in the photochemical experiments!

One of those serendipitous, career-defining events. The Friday Night Lecture Demonstration at Caltech.

After about 6 months of research on the metal complex catalyzed decomposition of methyl pyruvate, a serendipitous twist made a critical impact on my career. As an undergraduate at Wesleyan, I had discovered the luminol chemiluminescence experiment and was showing it off in the lab one day. George Hammond was about to present a "Friday demonstration lecture" to the Pasadena community and I needled him about the demonstration that he might be presenting, assuming that there would be none. George nailed me with, "Nick, why don't you show the luminol experiment. It's sort of photochemical and that's what I'm going to talk about." With a combined feeling of anxiety and excitement, I accepted. As I expected, George gave a fabulous lecture on the research that Peter, Bob Foss, Bill Baker and others had been doing on the photochemical reactions of benzophenone and his beautiful

method for demonstrating the involvement of triplets. What I didn't expect is that when he introduced my demonstration he jokingly termed me an "anti-photochemist" because my results on the catalyzed decomposition of methyl pyruvate were contrary to current paradigms about the effect of paramagnetism on photoreactivity. The demonstration went well (I still remember someone in the audience saying, "Wow! This is just like Disneyland!!!").

The Saturday Morning Experiment. The Beginning of Triplet Sensitized Photoreactions in Solution. Triplet Energy Transfer Becomes a Household Word.

On the next day, Saturday morning, I went into the lab and talked to Peter about George's comment the night before about my being an anti-photochemist. Peter had a great idea: mix up ethyl pyruvate (my project) and benzophenone and irradiate (his project) the brew and see what happens! In fact, the experiment was set up before noon and we noticed that upon irradition, bubbles of gas came streaming out. The bubbles stopped immediately when the lamp was off. Immediately, we called George at home and in minutes he was in the lab to proclaim this was a sensational result. Neither Peter nor I had much of a clue as to why he was so excited, but it was the beginning of the use of triplet energy transfer to sensitize photoreactions, and George, with his typical insight, sensed where he could go with it. (for George's recollection, see his write-up in a previous issue of the IAPS Newletter).

Little did Peter and I realize that this was the humble beginning of "triplet photosensitized photoreactions in solutions". George had obviously grasped its importance immediately and within a few weeks half the group was working on some form of photosensitized reaction. Peter and I went to work immediately on trying to photosensitize the Diels-Alder reaction of a diene with maleic anhydride.

The chemical storeroom at Caltech had a bottle labeled "purified 1,3-pentadiene", affectionately known as piperylene. That sounded pretty good so we used piperylene as the diene in an attempt to photosensitize Diels-Alder. Checking the attempted photosensitized reaction by vpc indicted no reaction of the maleic anhydride, but the piperylene appeared to isomerize. We assumed that the "purified" piperylene was *trans* and that the isomerization was *trans* to *cis*. However, we discovered that the bottle actually was PURE *cis*-piperylene. Checking into the source of the *cis*-piperylene (remember, in 1960 there was no Aldrich and students often left chemicals in the chem stores after they finished their thesis work), we found that one of Zeichmeyer's students had prepared it. The amazing thing was that the preparation involved taking a mixture of *cis* and *trans*-piperylene with maleic anhydride!! Another scholar, Zeichmeyer's student, knew that the *trans*-piperylene reacted rapidly with maleic anhydride in a Diels-Alder reaction at room temperature, but *cis*-piperylene did not react at all due to simple steric hindrance considerations! Had Peter and I known that, we probably would not have used piperylene for our photosensitizatation experiments!!

Shortly after the discovery of triplet photosensitization, Karl Kopecky showed how to produce triplet carbenes from photosensitization of diazomethane decomposition, Jack Saltiel launched the photosensitized isomerization of stilbene, John Fox did the photosensitized decomposition of azo compounds, Fred Fischer and I got involved in the norbornadiene to quadracyclene valence isomerization. Wow! This was a fabulous period of activity and excitement.

"Three Months in the Laboratory *versus* an Hour in the Library".

Two decades later, one of my great students, Matt Zimmt, would say "three months in the lab can save you an hour in the library"! In fact, it was my experience with the "scholars" at Caltech that convinced me that there was so much chemistry I did not know and that the mastery of the literature was an important professional matter. At

that point I made the decision to make "knowing" and mastering the literature a top priority. It was one of the best career decisions that I have made.

During the summers of 1961 and 1962 Sandy and I returned to Middletown, where I spent a couple of months in the library at Wesleyan just thumbing through journals and books and taking notes. I was amazed by the amount of great stuff in the literature that does not appear in the textbooks. It was clear to me that an easy way to generate a research program was just to read the older literature and follow up on interesting projects that were stalled at the time because they were technique-limited. I can still recommend this to anyone. Just go through *JACS* from 1955 to 1960 (or any five year period after the 50s) and you will find a goldmine of ideas for great projects.

Conclusion of the Caltech Years (1960-1963).

This period was one of tremendous excitement in the field of photochemistry and, scientifically, the field of mechanistic organic photochemistry was expanding in an exciting and explosive manner. What a group of colleagues! In addition to Peter, there was Angelo Lamola, Jack Saltiel, Bob Liu, Bill Herkstroeter, all of whom went on to blaze their own trails in photochemistry; Karl Kopecy, who synthesized and isolated the first 1,2-dioxetanes when he started his academic career at Alberta, was a labmate. Downstairs in Crellin Laboratory, Wilse Robinson was helping to put the ideas of molecular spectroscopy into photochemistry with postdocs like Mostafa El-Sayed.

A Year's Postdoc with Paul D. Bartlett at Harvard (1963-1964).

As I finished my Ph.D. program in May 1963, George wanted me to take a position at UCLA, but Sandy and I (and baby Cindy) wanted to return to the east coast to be closer to our families. I took a postdoc with Paul D. Bartlett, George Hammond's Ph.D. sponsor and a giant in physical organic chemistry, who was interested in applying photochemical concepts and techniques to the formation of biradicals. During the evenings and on weekends I found some time to get into the library and write a draft of mechanistic photochemistry which was to serve as the basis for a course that George Hammond recommended that I teach at DuPont. The notes for the course became "Molecular Photochemistry" published in 1965 at the same time that baby Claire arrived ("thump-thump 2").

After a delightful 12 months with Bartlett, making biradicals from addition of triplet dienes to chlorofluoroethylenes, I spent the summer of 1964 at the Dow Exploratory Research Lab in Framingham, MA working for Fred McLafferty (one of the founders of modern mass spectrometry) and a very exciting carbonium ion chemist, George Olah (who won the Nobel Prize a few years ago)!

From Triplets to Three-Membered Rings. Three's a Charm. The Cyclopropanone Years.

As the result of my literature reviews, I had become interested in the preparation of cyclopropanone, which was claimed to be an intermediate in the reaction of diazomethane and ketene at $-78\,^{\circ}C$. During that period I collaborated with Peter and Doug Neckers on the photochemistry of tetramethyl-1,3-cyclobutanedione. Why tetramethyl-1,3-cyclobutanedione you ask? Because I saw an advertisement for the molecule in *C&E News* that asked "What can tetramethyl-1,3-cyclobutanedione do for you?" It occurred to me that the photolysis of this compound might result in the loss of CO, a common process for ketones. I was ecstatic when after requesting just a small sample, I promptly received a kilogram in the mail the next week! The photolysis of tetramethyl-1,3-cyclobutanedione turned out to be rather nifty and to involve the formation of tetramethyl cyclopropanone, which

was readily trapped by alcohols and furan. This chemistry served as the basis for my proposed program when I went around job interviewing.

Since a dry box was not available, Doug and I used some polyethylene foil as a sample holder for the cyclobutandione and photolyzed the sample and then took an IR spectrum directly of the foil. We didn't see the peak we were looking for at 1810 cm^{-1} (or so), but in methanol we isolated the hemiketal of tetramethyl cyclopropanone and that was a good sign that we were on the right track.

The Columbia Era Begins (1964). A Russian Speaker Cancels. A Boldacious Joke Is Made at an Interview Seminar, and the Rest is History. (Alexander the Great).

As mentioned above, during my last year at Caltech, George Hammond wanted me to take a position at UCLA. This was a fine opportunity to join an excellent department, but Sandy and I were eager to return to the east coast and I had learned indirectly that there was an opening at Columbia University. During the Spring of 1963, I ran into Ron Breslow at the ACS meeting in Los Angeles. I asked him about the opening at Columbia and he asked me to give him a call when I was in the east and he would see what he could do. In the fall of 1963 I had an interview trip scheduled at Bell Labs and decided to try to combine it with an interview visit to Columbia. I called Ron a week before my planned visit to the New York area and he told me that a Russian speaker scheduled to give a Departmental colloquium had cancelled at the last minute and I could come to give an interview lecture and a Departmental Colloquium! Needless to say, I was very excited about this opportunity and was quite anxious to make a striking impression on the faculty. For some reason, which I no longer recall, I decided the way to do this was to warm up the audience by telling a photochemical joke at the beginning of the seminar. I guess I figured that the faculty would decide that any young rascal willing to display such chutzpah, must have what it takes to make tenure at Columbia.

The joke went something like this. The history of photochemistry extends back to antiquity. In fact, the earliest record of the use of photochemistry is attributed to the use of what we now term photochromic materials, by none other than Alexander the Great. In addition to being a military genius, Alexander was an amateur photochemist! A major reason for many of his military successes was his uncanny ability to coordinate attacks on enemy camps in broad daylight. As you can imagine, it must have been very difficult without our modern timepieces to synchronize and focus the attack of several cavalries on a target. Lore has it that Alexander figured out how to use photochemistry to signal to his generals that it was time to attack. He developed a white photochromic material which changed to a bright blue when the sun was at its peak. He impregnated this photochromic material on cloths that he distributed to his generals and instructed them to wrap the cloths around their arms and watch for the color change. At various positions, the general would wait for the color change that would signal attack and then with incredible coordination swoop down and overwhelm the enemy. The invention of this ancient military strategy is known today as "Alexander's Rag Time Band". Although it was not clear at the time exactly what impact the joke had, but by the time I returned to Cambridge, an offer to join the Columbia faculty was in my mailbox (this was all before affirmative action and the complicated interviewing system with proposals that has since developed)!

Getting Started at Columbia. Cyclopropanones and Mechanistic Organic Photochemistry and Photophysics. (ca. 1964-1970)

In the Fall of 1964 I began at Columbia as an Instructor (the last one ever hired in a science department, since they abolished the lowly position the next year). Before leaving Caltech Jack Roberts had advised me that I should

stay away from photochemistry as much as possible, because when it came time for tenure review, I would be criticized for being unimaginative and simply extending my Ph.D. work. Jack always gave me good advice, so I followed it. I decided to make a foray into synthetic chemistry employing cyclopropanones. At that time the PARADIGM of the organic community viewed cyclopropanone as impossible or an improbable target as an isolable or synthesizable species. Although I didn't use the word then, I was thrilled at the possibility of skating on the edge of the paradigm, recognizing the value of identifying and attacking problems that were good science and could also attract the community's attention at the same time.

My first graduate student, Willis Hammond, who was directed by Ron Breslow to work for me (thanks forever, Ron), showed that if one were brave enough to mix up diazomethane (remember my first experiment at Caltech?) and ketene at low temperature, one could make cyclopropanone in good yield. Bob Gagosian, John Williams, and Simon Edelson followed up these studies with some beautiful chemistry and I learned that I could perform a successful independent research program of my own. It was clear after a couple of years that tenure was a certainty because of the fabulous research productivity of the group in cyclopropanone chemistry which was good enough to write a review for *Acc. Chem.Res.* 25,1969 and in molecular photochemistry described below. At this time the power and beauty of collaborations became apparent to me. It was at this time I made a series of "French Connections". I met J. M. Conia an outstanding small ring chemist during a visit to France and we began a very fruitful collaboration on small ring chemistry. Later, colleagues such as Jean Rigaudy (aromatic endoperoxides) and Lionel Salem and Alain Devaquet (theory of photoreactions) and postdocs such as J. Pouliquen and Pierre Scribe would join the group.

I now felt that I had demonstrated my ability to execute an original research program which could attract the community's attention and so I felt released to initiate my own program in mechanistic organic photochemistry.

During the period 1963-1970 I was blessed with an incredible number of gifted graduate students and postdocs in addition to good luck. This tremendous combination served as the basis for several Ph.D. theses and put me on the map professionally. In the background we began looking at the photochemistry of ketones. Chris Dalton, a Caltech undergraduate, wanted to apply physical methods, such as fluorescence and single photon counting to investigate the photochemistry of ketones. Together with Peter Wriede and George Farrington (mechanism of the photocycloaddition of alkenes to ketones), Dave Weiss and Keith Dawes (mechanism of _-cleavage of ketones), Doug Morton, Richard Southam and Dale McDaniel (mechanism of photochemistry of cyclobutanones) and Ta-jyh Lee (photochemistry of _-diketones), by the end of the 1960s we began to build up a photochemical style which was great fun and proved to be quite effective as a paradigm for the emerging photochemical community. Postdocs such as Fred Lewis, Ed Lee-Ruff, John Williams, Dave Pond, Richard Southam and Keith Dawes taught me the value of bringing in mature, smart, well trained experts in areas about which I knew little and could learn much. Some brought in synthetic expertise, some mechanistic expertise, some computational methods, some new techniques, but all added new dimensions to the group.

Mastery of the Literature and Collaborative Research. A Systems Approach and Publication in 1978 of *Modern Molecular Photochemistry*.

At this time I learned that I needed to take a "systems" approach to operate an effective research program of the magnitude, intensity and diversity that I wanted. The only way to do it was to master the literature and work with a group that I directed and which learned from me and taught me at the same time. Collaborations within the group and within Columbia University, with collaborators from other Universities in the U.S. and abroad, in

addition to a broad knowledge of the literature were to be the roots and trunk of the program; ideas, experiments and novel results would be the "dendritic" intellectual and scientific products.

Examining the literature was tedious, so the only way to do it was to layer and leverage literature mastery with a book, and with courses in photochemistry. Thus, in 1978 "Modern Molecular Photochemistry" evolved from the notes and literature surveys maintained since the publication of "Molecular Photochemistry" in 1965 and a number of review articles in *Chemical Reviews*, *Angewandte Chemie*, *Pure and Applied Chemistry*, and *Accounts of Chemical Research.*

Thinking about Thinking. The Paradigm and Topology.

I have always been fascinated with the thinking process, how to teach and how to learn, and why it appeared that some forms of cognitive activities appear to be more effective, some more attractive, some more universal, etc. In the early 70s when I began to search for literature that discussed the cognitive aspects of teaching and learning, I discovered the teachings of Piaget, the topology of Thom, the paradigm of Kuhn, and research into the cognitive aspects of teaching and learning. I tried to incorporate these ideas in a review [*Angew. Chem.*, **25**, 882 (1986)].

In particular, the article put forward the premise that organic chemistry, the muse of all my scientific activities, seemed particularly suited to rapidly exploring, discovering, and promoting new ideas and experiments. It seemed that the reason for the success and appeal of organic chemistry to me was its qualitative, structural basis rooted in topological and geometric ideas. Coupling this idea of structure with Kuhn's concept of paradigms has provided me with a powerful intellectual engine to move from field to field by anticipating concepts and methods through topological transformation of the paradigms of one field to another.

The 1970s. Mechanistic Photochemistry Fluorishes. Forays into Chemiluminescence, Theory of Photoreactions, Photochemistry of Benzene Valence Isomers, and Micelles.

In the early 70s, another serendipitous event led to the beginning of supramolecular photochemistry at Columbia. Dick Hautala had joined the group after producing a Ph.D. thesis with Letsinger on the photochemistry of organic molecules in micelles. Because of Dick's background in micelles we decided to try some simple photophysics of aromatic molecules in micelles. Dick selected naphthalene and checked its lifetime by single photon counting. The exciting result was that he found two lifetimes, one attributable to the naphthalene "inside" a micelle and one due to naphthalene "outside" the micelle. Neil Schore synthesized an indole surfactant and showed that, not only could two lifetimes be seen, but the time resolved spectrum of the indole lumophore was different outside the micelle and inside the micelle.

At the end of the decade, Ahmed Yekta returned to Columbia as a postdoc and derived a spectacularly elegant and simple method of measuring the aggregation number of micelles from simple static quenching experiments. Together with Masayuki Aikawa, who set up our first nanosecond flash photolysis apparatus, Ahmed derived a general theory of the dynamics of probes exiting and entering micelles. The initial stages of our study of micelles was photophysical and led to a range of investigations and research skillfully performed for the next decade by Margaret Wolf Geiger, Kou-Chang Liu, Gabriella Gabor, Plato Lee, Gregor Graf, Ping-Lin Kuo and Shufang Niu.

During this same time Bill Cherry make our first foray into employing micelles as "supercages" for the photoreactions of ketones to produce geminate radical pairs. Bernard Kraeutler ended the decade by brilliantly demonstrating how radical pairs in supercages were the supramolecular systems of choice to generate huge magnetic effects on the reactivity of radical pairs. He used sunlight (on the roof of Havemeyer) and soap to separate ^{13}C from ^{12}C by photolyzing dibenzyl ketone in micelles. See *J. Am. Chem. Soc.*, **100**, 7432 (1978).

Chemiluminescent Organic Reactions and Adiabatic Photoreactions. Dioxetanes and Benzene Valence Isomers.

In the 1970s the group was immersed in the investigation of molecules which formed excited states upon thermolysis. Peter Lechtken was the first in the group to successfully synthesize and exploit dioxetanes. In one year he set up a decade of projects. A very productive and imaginative group including Hans-Christian Steinmetzer, Gary Schuster, Y. Ito and V.Ramamurthy followed Peter as the group made a lasting impact on the field of chemiluminescence. This was tremendous research power for the times and let to a productive period that was delightful in scope and science. Bill Farneth and Jeff McVey in a collaboration with George Flynn showed how IR excitation could be used to decompose dioxetanes.

Two collaborations with colleagues at Columbia, Ron Breslow and Tom Katz, brought us into investigation of the $(CH)_6$ valence isomers of benzene (Dewar benzene, benzvalene, prismane). Ramamurthy, making a second visit to the lab as a postdoc, performed a series of experiments showing how these remarkable benzene isomers could be produced from the photolysis of properly constructed azo compounds. Art Lyons found an adiabatic photoreaction of naphthalene and Carl Renner and Murthy found a number of adiabiatic reactions of benzene valence isomers.

Mechanistic Organic Photochemistry and Photophysics (1970s)

During the 1970's the group was involved in a range of investigations involving mechanistic organic photochemistry. Theron Cole, George Kavarnos and Victor Fung were involved in the investigatation of the intramolecular heavy atom effect and discovered a remarkable stereochemical aspect which was shown to be reminiscent of the Sn2 mechanism as the result of theory by A. K. Chandra. Irene Kochevar and Y. Noguchi were involved in investigations of energy transfer and quantitative features of the photochemistry of ketones. Marlis and Manfred Mirbach and Nils Harrit and Jonq Min Liu studied a range of novel photochemical and photophysical characteristics of azocompounds.

Theory of Photochemical Reactions. An Intellectual "Menage a Trois".

During July 12-18, 1970 the Third IUPAC Symposium on Photochemistry was held in St. Moritz, Switzerland. Although I did not attend that meeting, I learned of an exciting discussion or debate on the question "What is a diradical?" by two of the dominant figures in the field, George Hammond and Lionel Salem. There is a written record of the discussion that is reproduced in a previous issue of the IAPS newletter) and a second recollection in *J. Molec. Struct. (Theochem.)*, **424**, 77 (1998) dedicated to Lionel on the occasion of his 60th birthday. Although I was not present at the Hammond/Salem debate, it turned out to have a major impact on my career and my intellectual perceptions of how photochemical reactions occur, culminating in collaborations with Lionel Salem and Bill Dauben during the 1970's, a direct result of the "Diradical Debate".

At the Fourth IUPAC Symposium on Photochemistry in Baden-Baden, Germany during July 16-22, 1972, the lecture hall was very hi-tech and the audience sat two to a desk with a shared microphone available for asking questions after each lecture. I sat next to Lionel on a number of occasions and during the "organic lectures", he would gently criticize the lack of an existing discipline in the writing of organic photochemistry reaction mechanisms. He felt that "anything goes" was the rule used to explain the seemingly endless variety of reaction products being discovered in those early days of many exciting discoveries in organic photochemistry. During the Symposium, Lionel presented an outstanding lecture on diradicals (*Pure & Applied Chemistry*, **33**, 313, 1973). At the very end of the conference, Lionel, Bill Dauben and I had a beer at the hotel as we awaited transportation to the

airport. Lionel again began needling us about the lack of coherence in the mechanisms and theory of organic photochemistry. Bill and I retorted with, "Lionel, you're just the person to do something about this unfortunate state of affairs!" Lionel retorted by challenging us to join him in a venture to seek the framework of a coherent theory. German beer, with its ability to produce gemütlichkeit, had produced the atmosphere for a partnership that was to be exceedingly stimulating and informative for all three of us. The results of these discussions and correspondence led to a short note written by Lionel, "Surface Crossings in Photochemistry" (*J. Chim. Phys.*, 694, **1973**) in which he pointed out the use of a symmetry plane to classify orbitals and to serve as the basis for energy surface diagrams.

In the summer of 1973 at the Gordon Conference on Organic Photochemistry at Tilton, New Hampshire, Lionel Salem presented another outstanding lecture on diradicals emphasizing the possibilities of excited state reactions being either heterolytic of homolytic but in the context of energy surfaces. Lionel and I had an opportunity to follow up on our discussions of the theory of photoreactions, but unfortunately, Bill Dauben was unable to attend the Conference. Nevertheless, it was determined that the three of us must move forward with the sacred pledge we had made over a beer in Baden-Baden. One afternoon, while he had a strawberry shortcake and I had a hot fudge sundae, at an ice cream shop in greater downtown Tilton, Lionel wondered if some simple rules, employing the ideas of surface correlations, could be used to examine organic photoreactions, especially reactions of the ubiquious n, * excited states. To me this seemed like a very exciting possibility; at this point my topological thinking kicked in. Perhaps in the same way that organic chemists write lines and connections so profitably to describe molecules, an extension of the idea of connections could be created to describe reaction steps. For example, we speculated that there may be a relatively small number of *a priori* possibilities based on the simple notions of "perfect crossing", "perfect avoiding" and "contact" of energy surfaces. Bill was informed of this progress and it was determined that we would meet with Lionel in Orsay, just before the Vth IUPAC, which was to be held in Enschede, The Netherlands during July 21-27, 1974.

Before that meeting, there would be one other opportunity for me to meet with Lionel during the Fall of 1973 and to work with him on the preliminary aspects on the theory. By the time I arrived in Paris, he had already discovered over 20 families of surfaces types that depended on the number of radical centers. This was very exciting, but the topological simplicity I had hoped for was not apparent. We communicated the results to Bill Dauben and then prepared for our meeting in Orsay.

By the time Bill and I met Lionel in Orsay in June,1974, he had already prepared a 38 page draft which was to serve as a basis for a manuscript to be submitted to *Accounts of Chemical Research.* The first sentence of the draft was "Classification has been the dream of chemists for centuries." This sentence was one of the few things left unchanged in the final paper! During three weeks of exhilirating daily meetings and brainstorming and some fabulous French meals, we came up with the classification of photochemical reactions that appeared in the *Accounts* article (*Acc. Chem. Res*., **8**, 41, **1975**).

Lionel Salem provided the driving force in the development of this surface theory of photoreactions. In the end we all felt that we had each contributed in some significant manner to an enterprise that was worth the effort because of the pure delight of our collaborative efforts. Both Bill and I were extremely fortunate to part of a very special intellectual and scientific adventure and collaboration that comes all too infrequently in spite of good intentions.

The 1980s. Supramolecular Photochemistry, Micelles, Water Soluble Polymers, DNA, Cyclodextrins. Colloid Chemistry with an Attitude.

Although I did not recognize it at the time, I had implicitly made a commitment to continue to skate on the edge of the paradigm by embracing a program in supramolecular chemistry that would challenge the then-current paradigms in photochemistry, especially with respect to the behavior of radical pairs and the control of photochemical reactions through magnetic field effects. The basis for all this turned out to be the field of colloid chemistry to which P. Somasundaran of Columbia's School of Mines introduced me to in the mid-80s. I knew micelles were colloids, but initially didn't really appreciate the fact that their behavior was a single example of a huge family of colloidal structures that could be used to control photochemical processes. This all came about at the time I was attempting to understand the topological intellectual basis of "organic thinking" which I knew from experience was so successful. I'll have more to say about this later.

During the 1980s, John Bolt performed some beautiful work showing how Yekta's and Aikawa's theory of micellar dynamics could be used to determine the rate constants at which labeled surfactants entered and exited micelles. Aikawa and Yekta produced a very useful mathematical formulation for the extraction of rate constants and equilibrium constants from simple experiments employing steady-state or time-resolved fluorescence quenching of molecules adsorbed in micelles. Aikawa returned in the 1990s to show he still had the magic touch in the lab after his tenure as Dean in Hokkaido. He was one a a series of outstanding Japanese postdocs and visitors with whom I have been privileged to have as colleagues. In addition to those mentioned above there was T. (on/off rates of molecules adsorbed on polyions and cyclodextrins), Y. Inoue (photochemistry of cyclooctene), M. Okamoto (pressure effects on a range of photochemical reactions, together with Wen Sheng Chung), Y. Sato (photochemistry on zeolites). K. Ishiguro (CIDEP of the quadricyclene radical cation) and Yoshifumi Tanimoto (magnetic effects on reactive intermediates). Sandy and I were treated to a wonderful visit to Japan in Spring 1997 in which our former group members organized a fabulous tour of several cities and then a very special reunion dinner in Tokyo, organized by Inoue, attended by nearly every former Japanese postdoc.

A Plethora of Reactive Organic Intermediates.

The 1980s also saw the group investigate in detail a broad array of fascinating reactive intermediates such as radicals, radical pairs, biradicals, singlet oxygen, and carbenes. Titus Jenny set up our first single oxygen detector and Dave Hrovat studied the adiabatic photochemical ejection of singlet oxygen from aromatic endoperoxides. Carbenes were also a favorite topic during the 1980s with an outstanding collaboration with Bob Moss, Yuan Chan, Ian Gould, George Hefferon and Nigel Hacker. Biradicals were investigated in exquisite detail by CIDNP and magnetic effects initially by Matt Zimmt and Chuck Doubleday, followed by Jin Feng Wang and K. C. Hwang. The direct investigation of radical pairs by EPR and magnetic effects became possible at the end of the decade and is described below.

Supramolecular Photochemistry and Spin Effects on Photochemical Reactions.

During this period Ming Chow showed how the mechanism of decomposition of endoperoxides could lead to the separation of ^{17}O from ^{16}O and ^{18}O! Together with Chen-Ho Tung and Chao-jen Chung, Ming showed how the magnetic field produced by stirrer bars could change the rate of polymerization and the molecular weight of polymers by an order of magnitude!!! These were heady days when magnetic effects, formerly viewed with great suspicion in the 1970s, became commonplace when experiments were performed in the proper supramolecular

systems. Bruce Baretz, Jochen Mattay and Greg Weed executed the research that placed the supercage concepts on a firm and convincing experimental basis.

The 1980s ushered in the era of laser flash photolysis. Jed Butcher and M. Aikawa set up the first system on the 9th floor of Havemeyer in Rich Bersohn's lab. I bought an excimer laser, but shared it with Rich. When it fired to the South, the laser was the photolysis pulse for a solution flash photolysis experiment with optical detection. When it fired to the North, the laser was the photolysis pulse for a gas phase experiment with mass spectrometric detection. Ian Gould joined the group in 1981 and became my laser guru along with graduate student Matt Zimmt. Soon we returned the excimer laser to Rich Bersohn full-time and set two nanosecond flash photolysis instruments on the 7th floor of Chandler.

After acquiring a 80 MHz NMR that was being abandoned by the Department, we added NMR detection (steady state and time resolved CIDNP) and solids capability with diffuse reflection detection. Finally, we added an ESR and learned how to do time resolved CIDEP. Chuck Doubleday joined Ian and Matt to set up a series of outstanding experiments involving biradicals and various aspects of CIDNP. Together with Jin Feng Wang, Chuck demonstrated beautifully how biradical structures could be manipulated to produce enormous magnetic field effects on the lifetimes of biradicals.

Ian Gould led the group into a very fruitful collaboration on the chemistry of carbenes with Bob Moss of Rutgers and Heinz Dürr of Saarbrücken. Together with Gary Lehr, we determined a large number of rate constants for the addition of carbenes to olefins and other substrates as a function of carbene structure. In looking at the temperature dependence of the rate constants, we found a number of cases for which the value of the rate constant **decreased** as the temperature increased, corresponding to a formal **negative activation energy for reaction!** Our analysis did not attempt to formulate any new rules of chemistry, but attributed the negative temperature coefficient of the rate constants to a pre-equilibrium between carbenes and olefins (a phenomenon that was well established for excimers and exciplexes). In other words, the rate constant was not associated with a single elementary step and therefore was a composite of rate constants whose aggregate could have nearly any temperature dependence.

In 1981, Dick Bernstein, in my opinion one of the great Chemical Physicists of the century, resigned as Chairman of the Chemistry Department. I was his deputy Chairman and took over as the Chair of the Department. Perhaps the most important action of my Chairmanship was the hiring of Jackie Barton as a junior faculty member. Not only was it a great coup for the Department, but it set up an important collaboration, as Jackie taught me about DNA and we collaborated on the use of photophysical probes for the investigation of the structure and dynamics of binding of metal complexes to DNA. Thus began a wonderful and fruitful collaboration that continues to this day.

During the mid 1980s, with the arrival of Vijay Kumar, who was to replace Ian as the group's laser guru, a fabulous collaboration was initiated with Jackie Barton, then an Assistant Professor at Columbia. Vijay was the perfect person to bridge the separate disciplines of physical-organic photochemistry and DNA structure and dynamics. The original experiments were geared towards enantiomerically selective photoelectron transfer reactions between metal complexes adsorbed on DNA and eventually moved toward exploring the use of DNA as a "wire" for electron transfer.

Kartar Arora got the group started with the probe methods for investigating polymer structures by synthesizing a pyrene labeled polyacrylic acid. These experiments were important in leading to a collaboration with P. Somasundaran of the School of Mines at Columbia. Somasundaran, an expert on the adsorption of surfactants and polymers on silica and alumina particles, joined us in a collaboration investigating these systems with photophysical probes. Prem Chandar, Ken Waterman, Kevin Welsh and P. Ananth showed how the classical methods of

adsorption could be correlated with the photophysical techniques. Jin Baek Kim, Ines Pierola, and Gabriella Caminati used photophysics to investigate polymer structural changes in aqueous solutions.

The 1990s. DNA as a Wire.

As a joint postdoc with Jackie Barton, Vijay Kumar's original project was to use fluorescence probes to measure the rates of adsorption and exit of metal cations from polyions. Although we never completed this original project because of technical and chemical complications, the initial results turned out to be more exciting than the original project and eventually led to our discovery that DNA could serve as a "molecular traffic cop" for electron transfer between photoexcited ruthenium complexes and electron acceptors bound to DNA.   Among the exciting discoveries to emerge from this research was the development of a "photoluminescent light switch", a ruthenium complex that was non-emissive in water but strongly emissive when bound to DNA, and the discovery of evidence that DNA could serve as a "wire" to transport electrons from a photoexcited donor to a ground state acceptor. Evidently, this proposal was considered an affront to the community, as it resulted in a number of attacks in the literature impeaching the proposal.

After Vijay, a number of group members including Andree Kirsch-De Mesmaeker, Stefan Bossmann, Gary Jaycox, Claudia Turro and Wei Chen collaborated with Jackie's Caltech group investigating electron transfer of metal complexes adsorbed on DNA. In 1993 (*Science*, **262**, 1025) we published what I consider to be a definitive paper in which an intramolecular electron transfer from a distance of ca. 40Å occurred in ca. 1 ns. Such a fast rate of electron transfer requires the DNA to serve as a medium, like a wire, conducting electrons from excited donors to acceptors. An important point was that the efficiency is maximal when both the donor and acceptor are intercalated. The interpretation is still a matter of debate and we will see if it is eventually vindicated or not.   In *The Journal of Bioinorganic Chemistry*, 201-209 (1998) we have attempted to distinguish the science from the paradigm with respect to our proposal.

During this decade, magnetic effects on photochemical reactions fluorished. Three Russian scientists, R. Sagdeev, Kev Salikov and Yu. Molin visited Columbia in the early 1980s and made me aware of the exciting ideas and experiments abounding in A. Buchachenko's lab in Moscow and in their labs in Novosibirsk. As a result of their visit, I delved into the Russian scientific literature on "spin effects" and understood how one could employ the ideas of G. Closs for CIDNP and of Sagdeev, Buchachenko, Molin and Salikov on magnetic effects on radical pair and radical pair reactions, to search for magnetic field and magnetic isotope effects on radical pair reactions in micelles.

Their work allowed me to create a simple paradigm for myself for the ready determination of experiment after experiment that demonstated how hyperfine coupling in radical pairs and biradicals could lead to strong magnetic field and magnetic isotope effects on photoreactions: Singlet geminate radical pairs are reactive towards radical pair reactions; triplet geminate radical pairs are inert towards radical pair reactions; and the reaction of triplet geminate pairs is always a competition between intersystem crossing to form a reactive singlet pair and diffusional separation. The supercage of micelles allows exquisite control of the diffusional separation. This effect can be tuned to allow for the occurrence of large magnetic effects on the behavior of radical pairs.

Dendrimers. Polymeric Molecules Resembling Trees.

At a Gordon Conference in 1988 I met Don Tomalia who presented a spectacular lecture on dendrimers, a topic about which I knew absolutely nothing and which hit me over the head in the same way as when I discovered for the first time micelles, zeolites, cyclodextrins, liquid crystals, polyelectrolytes and DNA. Furthermore, I found

in Don another kindred spirit who shared the vision of excitement and beauty of structure and topological thinking. Our groups, made a perfect complement, since he was an outstanding synthetic chemist and wanted to find a group to characterize the new materials he was synthesizing. Immediately, topological thinking indicated that the dendrimers were objects topologically congruent with many of the systems we had been investigating for a decade with spectroscopic and photochemical probes. If this congruence were correct, our paradigm guaranteed that, with minor modification of our techniques and methodologies, we could successfully characterize dendrimers to an extent similar to that of the systems previously investigated. For a review of this research see *Acc. Chem. Res.*, **24**, 332 (1991).

Indeed, by taking the lead from the use of photoinduced electron transfer on DNA, we could immediately take the Ru systems and study the electron transfer between photoexcited Ru(II) complexes and electron acceptors. Maria Moreno-Bondi and Willie Orellana were able to show that the quenching efficiency was related to dendrimer generation and that an exciting fringe benefit was that a qualitative break in the quenching occurred around generation 3/4, exactly the place where some computer simulations by Bill Goddard had predicted. This break was confirmed by Gabriella Caminati with a pyrene fluorescence probe and then by Francesca Ottaviani with an EPR probe and by Steffen Jockusch with several absorption and fluorescence probes. K. Gopidas performed an elegant study of electron transfer on individual dendrimeric molecules. Diana Watkins showed how the probe method could be employed to investigate a range of different dendrimer structures. The research on dendrimers and DNA is now being integrated to investigate DNA/dendrimer interactions and will be extended to study DNA/dendrimer/liposome interactions as models for how dendrimers serve to assist the transfection of cells by DNA.

Putting a Spin on Radical Pair Reactions in Supercages. The Russian Invasion

At the beginning of the 1990s there was a Russian invasion of 7th floor Chandler. As mentioned above, it began with a visit by three outstanding Russian scientists, Yu. Molin, R. Sagdeev and K. Salikov, and as a result of their visit, a connection with Anatoly Buchachenko was made. The collaborative interactions with these brilliant spin experts gave me a totally different and quantitative view of what we could do with our Spin Chemistry. During this decade, magnetic effects on photochemical reactions fluorished.

The beginning of the real collaborations began with the appearance of Eugene Step and Valery Tarasov, students of Anatoly Buchackenko, on a cold day in January 1990. We met in Grandma's diner on Amsterdam Ave. where they enjoyed their first American breakfast. Next came Igor Khudyakov followed by Igor Koptyug. Over time, Anatoly made two visits to the lab.

From the association and collaborations with the Russian group, our approach to spin chemistry expanded to include time resolved EPR and comparison of theoretical models of radical pairs in micelles and experiments. Naresh Ghatlia and Valery teamed up to perform a successful series of investigations of spin chemistry as a function of micelle size. The results of these collaborations are reviewed in **Pure & Appl. Chem**., *67*, 199 (1995) and **Acc. Chem. Res**., *28*, 69 (1995).

The EPR Becomes an Important Technique in the Group. Time Resolved Measurements and CIDEP

Although the group had an EPR spectrometer since the mid 1980s, it become a powerful tool for mechanistic use when Matt Zimmt and Mark Paczckowski set it up for time resolved use allowing us to use polarized spectra (CIDEP, the EPR analogue of CIDNP) to investigate free radicals. This technique was exploited beautifully first by William Jenks who set the pattern of experiments and followed by all kinds of neat experiments by Chung Hsi (Joe) Wu, Igor Khudyakov, and Igor Koptyug . Steady state EPR and the beauty of nitroxides and their quantitative

analysis were taught to the group in a course and in the lab by Francesca Ottaviani who continues to be an important collaborator.

Photochemistry of Organic Molecules Adsorbed on Silica

Our interests in supramolecular photochemistry inevitably lead us into the solid state and silica gels were among the first host systems that we studied systematically. Chen Chih Cheng, with samples provided by Walter Mahler of DuPont, stated us off by investigating the pore size dependence of the cage effects of dibenzyl ketone. This was followed by some fascinating quantitive investigations of the diffusion of photoexcited molecules on silicas and zeolites in collaboration with Mike Drake at Exxon, and by Karen Cassidy Thompson, Rachel Leheny and Stefan Nitsche. Wen Seng (Wendy) Pan and B. Srinivas studied the adsorption of styrene onto silica by EPR and fluorescence techniques.

Modern Molecular Photochemistry in the 1990s

Although the group invested heavily in supramolecular photochemistry and photophysics in the 1990s, it maintained a healthy presence in mechanistic molecular photochemistry and photophysics. Matt Lipson, TaeHae Noh, Peter McGarry, Beatriz Ruiz-Silva, Gregory Sluggett, Ariella Evenzahav and Margaret Landis investigated a range of reactions from benzophenone cyclophanes, to olefins related to vision, to azo compounds, to the photochemical analogue of the Bergmann rearrangement to phosphorus photochemistry. Erdem Karatekin has developed a new "photocopying" system which traps living free radical polymer chains by flash producing radicals that can trap chains but not initiate polymerization of monomers.

From Boiling Stones to Smart Crystals. Much Ado About Nothing.

Zeolites are "boiling stones" (Greek *zeo*, to boil, and *lithos*, stones) that are really porous crystalline materials. They are the basis for a huge commercial market for ion exchange materials and are used in catalysis for the cracking and separation of fuels derived from crude oil. Thus, they are termed "smart" crystals. However, a key feature that determines their extraordinary chemical properties is their size/shape selectivity for absorption of small organic molecules. They are in fact "molecular sieves". The selectivity of zeolites derives from the void space or free volume of the internal surface of the crystal. Thus, the fuss over their chemistry may be said to be "much ado about *nothing*".

The zeolite story followed a familiar pattern of research for the group. After discussing the possibility of using zeolites for years, I had finally found a student, Bruce Baretz, who had the courage and initiative to try a few initial experiments. From his experiments involving the simple fluorescence measurements of pyrenealdehyde in zeolites, we found the experts who would collaborate with us to get us into the game. First there was Edith Flanigen from Union Carbide in Tarrytown, NY, who gave a "dynamite" talk on zeolites explaining essentially everything we needed to know, and who then provided us with research samples of a range of zeolites.

Armed with Edith's introduction and samples, Peter Wan initiated the first studies that demonstrated both the feasibility of doing photochemistry of DBK on zeolites and the interesting photochemistry that resulted. Chen Chih Cheng had collaborated with Walter Mahler of DuPont on the photochemistry of DBK on silica gel, and then moved into the zeolite studies. The DuPont connection expanded with Lloyd Abrams and David Corbin becoming valuable advisors. We began to feel very comfortable with our paradigm for zeolites and quickly realized that the zeolite paradigm was rich in possibilities for new photochemistry and that photochemistry could assist the understanding of both zeolite structure and how zeolites worked as molecular sieves and as catalysts. Zhenyu Zhung came in as a

graduate student and demonstrated how additives could control the chemistry of radical pairs in zeolites. Nianhe Han followed, as a student, together with Xuegong Lei, who began to discover all kinds of interesting photochemical effects in zeolites, and demonstrated, in collaboration with Jim Fehlner and Diane Hessler and Andre Braun, the remarkable selectivity in photochlorination that could be achieved for linear alkanes adsorbed in ZSM-5 zeolites. For an early review of this research see **Pure and Applied Chemistry,** *58*, l2l9 (l986).

Photochemistry of ketones in zeolites is currently fluorishing in the group. B. N. Rao discovered optically active benzoin from photolysis of benzaldehyde in cyclodextrin. From this lead and preliminary results by Nik Kaprinidis, George Lem has followed up on showing that enantiomeric selectivity can be achieved from the recombination of radical pairs in the presence of chiral inductors in zeolites; he found that magnetic field and magnetic isotope effects on radical pair recombination can be demonstrated. Xuegong Lei has discovered that reactive carbon radicals produced in zeolites can be stabilized for hours and days at room temperature. Takashi Hirano has shown that we can count the holes on the external surface of zeolites through EPR and other experiments. Fred Garces set up our solid state NMR lab, then Miguel Garcia began to show the power of the method to study the structure of zeolites. Wei Li and Sean Liu have gone on to use solid state NMR spectroscopy to investigate subtle and detailed features of the structure of zeolites and computational methods to gain insights into the structure of zeolite topology and of guests in zeolites. Collaborations involving zeolites continue to fluorish with V. Ramamurthy, John Scheffer and Y. Inoue.

Ubersupermolecular Photochemistry.

What are the paradigms for the future of research on the 7th floor of Chandler? Several trends seem apparent: first, there is a clear commitment to integrate education and research. For over a decade I've made a substantial commitment to improve undergraduate instruction in chemistry by any means possible. I've settled in on the notion that while many strategies achieve the goal of integration of education and research, strategies employing information technologies such as computers and the web are likely to be effective. For some idea of what we have been doing, the reader is invited to visit the following URLs:

http://turmac13.chem.columbia.edu/default.html (Research)

http://www.columbia.edu/itc/chemistry/chem-c3045/ (Instruction)

http://www.columbia.edu/itc/ (IT Cluster)

Next there is the issue of areas of research. It seems obvious that supramolecular chemistry is all forms will continue to thrive. In particular, materials science, biochemistry and environmental chemistry, together with computational aspects, will be important areas for the foreseeable future. Clearly supramolecular chemistry will make important contributions to each of these areas.

Finally, there is the issue of new areas or what will follow supramolecular photochemistry. I suggest that there will be an "übersupermolecular photochemistry" that employs supramolecular photochemical ideas and integrates them with the influence of static and oscillating fields on photochemical processes. Although magnetic effects due to nuclear spins and static fields have been explored over the past decade, the application of oscillating magnetic fields and static electric fields on photochemical reactions is still in its infancy. Oscillating electric fields are the domain of photochemistry, since the oscillating electric field of light is responsible for electronic and vibrational absorption and emission.

I suggest that "übersupermolecular photochemistry" will involve a conceptual framework similar to that which drives magnetic resonance, i.e., seqences of "oscillating pulses" of electric and magnetic photons and phonons that

will provide an ever-increasing level of control over photochemical reactions in space and time. For some discussions of these ideas see *J. Photochem. Photobiol. A: Chemistry*, **100**, 53 (1996).

Approaching "Senior" status offers a rich menu of exciting vistas for the photochemist. It is a happy occupation, since it continues to be an avocation as well. All the best to you out there! Sandy and I hope that all former group members and friends will visit us and send us photos for the bulletin board outside our offices.

I must finally apologize for not being able to cite the depth of the contribution of the members of the group and for the likehood that I have forgotten, inadvertantly, the important contributions of some. The riches of having such an extraordinarily large number of wonderful collaborators--teachers and students alike-- makes the task of completeness very difficult.

Sandy and I had one of the most exciting and memorable experiences of our lives at the Boston ACS meeting and reunion dinner party organized by Matt Zimmt and William Jenks. We thank all of you who were able to attend and look forward to meeting many of you who could not make it, before too long, possibly at the ACS meeting in Anaheim. The occasion of the get-together, of course, was a birthday. On such occasions it is an Italian custom to celebrate with two exhortations: "Cent'Anni!" to the birthday honoree and "Alla Famiglia!" to everyone!!!

Thirty-Something Years of Explaining Organic Chemistry to Physical Chemists: Some Random Iconoclastic Thoughts about Environmental Effects on Photochemistry

Peter Wagner

Chemistry Department
Michigan State University

For several years Murthy cajoled me to contribute a "personal" article to this newsletter; but I always demurred. I had enough trouble finding time to write "serious" papers. However the symposium in Boston honoring us six photogeezers born in 1938 leaves me with no more excuses. My only disappointment with the symposium was that the six of us did not have enough time to tell everyone about our interactions with each other and with our many wonderful fellow photoscientists. Fortunately Bill Jenks has asked us to do just that by writing essays describing our thoughts and careers, so here goes. Since this affair did involve my yet to happen birthday, I thought that a picture depicting one of my typical birthday celebrations would be appropriate.

A national League playoff game is on tonight. I love baseball, and you can sit with a Powerbook on your lap and write articles, draw drawings, plot plots, and even devise programs, without missing any action. [I just realized how lucky I am to be a Cubs fan—no need to get personally involved in these October games; just relax and enjoy the competition. Given my infatuation with the boys of fall, I cannot claim a lack of time for this assignment.

The symposium in Boston was great for several reasons. Apart from the thrill of being honored, my main sensation was the comforting knowledge that I was part of such a wide array of talents describing their diverse approaches to studying the effects of light on matter. Thus the curious title of this essay, which I shall explain.

The word "environmental" in the title is purposely misleading; it refers to the people who study photoreactions and the conditions that affect our science: *i.e.* disorganized rather than organized media. You didn't really expect me to describe the behavior of my favorite ketone in Elmer's glue, did you? Instead, I would like to reflect on personal interactions in our science, both cooperative and competitive.

When I was a graduate student, Cheves Walling impressed upon me an appreciation for the connection between the personalities of chemists and how chemical knowledge develops. For more than a century science has thrived on highly personal opinions of what presumably objective data mean, opinions that were refined as they defined new experiments. It has been competitive, just like baseball, with everyone doing his/her thing independently and the best resulting efforts winning out. Of course, you don't know which team is best unless they compete. Neither do you know which ideas and theories are best without competition. For over a decade now funding has shifted significantly from independent research to highly collaborative multidisciplinary research, with the tacit implication that individual competition is an obsolete relic of times goneby. I do not know whether this has improved productivity, but I do know that it requires teams to compete with each other just as individuals have always competed. We must accept the reality that whether we work as groups or individuals, history has taught us that we rarely reach consensus on scientific questions without input from a variety of independent researchers. So I pose a few questions: do we have enough competition in topics other than electron transfer to maintain the vitality of photochemical research; how much do present funding conditions discourage competition; and what unsolved topics of sufficient importance warrant increased competitive study?

In his introduction to the special issue of *J. Phys. Chem.* George Hammond indicated his delight that the six of us 1938-birthlings each went our own way rather than try to compete with each other. That assessment was only partially true. We are all intense competitors, as anyone knows who has played poker with Jack Saltiel and Bob Liu, golf with Doug Neckers, tennis with Nick Turro, or tried to run up Alpine hills faster than Dave Whitten, all of which I've had the pleasure of doing and occasionally winning. What George should have noted is that we have limited our more aggressive competitive spirits to games and focused our professional competition as regards each other mainly on striving to be as good as each other at doing science. I guess you could call us competitive role models for each other, sort of sibling scientists, who like a family prefer to fight with non-family members. And we all have had our share of scientific fights in the friendly competition that always arises over important topics.

In terms of success, it usually is not enough to just have had excellent Ph.D. and postdoctoral mentors, such as the polar opposite giants Cheves Walling and George Hammond that I worked with. (Actually they shared the appealing common characteristic of allowing students a good deal of autonomy.) Practically everyone has commented at one time or another that the photochemical community has established an unusually friendly and supportive social structure that allows the scientific competition to be highly cooperative and productive. As I commented after my talk in Boston, I certainly benefited early in my career from the good advice and personal attention of Paul deMayo, Bill Dauben, Srinivasan, Don Arnold, and Harold Hart; one lesson I took from these friends was to strive to be a good role model myself. (I must admit having heard that message often enough as a youth from assorted nuns and Jesuits, although I am not so sure that they had in mind getting to know our younger colleagues by staying up to 2 A.M. at Gordon conferences drinking beer with them.) I cannot continue without acknowledging my gratitude to the dozens of you other readers of these essays who have provided me (and I expect

my five co-38ers) with plenty of stimulation both friendly and scientific, all of which has made for great memories and often helped my thinking.

As I mentioned above, I do not believe we can overemphasize the importance to science of serious but friendly competition. My talk in Boston was specifically designed to exemplify how many years and different workers it can take to satisfactorily explain even a very simple photoreaction, a case of unfocused competition. So I would like to describe a few other such examples from my career.

The joint interest that N. C. Yang and I shared in the Norrish type II reaction is a good example of polite competition. A talk that N.C. gave at Columbia while I was a graduate student stirred my interest in the reaction, since he proposed that the excited carbonyl behaved like the alkoxy radicals that I was studying, by abstracting a nearby hydrogen atom to produce a biradical that could then do all the things that radical species do, such as coupling and β-cleavage. When I got to Caltech I discovered that there was disagreement among physical chemists over whether the reaction occurred from an excited singlet or triplet, although most of them preferred a concerted mechanism. Using the recent Hammond group findings on triplet energy transfer and assuming radical-like reactivity of the excited carbonyl, my study with piperylene as quencher surprised everyone by showing that both states react. N.C. and my Columbia classmate Bob Coulson then used this technology to show that the singlet reacts very inefficiently, the result which fueled Salem's seminal work on avoided crossings. Having conceded the singlet to N.C., we looked carefully at the triplet reaction to firmly establish the intermediacy of the biradical previously suggested by N.C. and to show that its major decay mode is disproportionation back to ground state reactant. So our independent competitive efforts happily blended to produce a basic paradigm for the differences between singlet and triplet reactivity, for which we both can be proud.

N.C. and I did have one real disagreement, in proposing different explanations for the reactivity of ketones whose lowest triplets are π,π^* rather than n,π^*. I went into the study entranced by the physical chemists' notion that state mixing would activate the otherwise unreactive π,π^* state, as N.C. espoused. However, our studies suggested that simple thermal equilibrium sufficiently populates the upper n,π^* state to provide the measured reactivity, the minor amount of state mixing observed spectroscopically being insufficient. Later studies by Colin Steel and Tito Scaiano strongly supported our view. If I have a pet peeve it is that so many people still cite state mixing as the major cause for chemical reactivity in such systems. There are of course plenty of other systems in which weak mixing of states can be responsible for relatively slow reactions.

Did this competition harm our relationship? Hardly. Years later NC managed to get my family into the King Tut exhibit at the Field Museum, one outcome of which was to so enhance my son Peter's interest in things ancient that he is now a curator in geology and paleantology at the same Field Museum. Not only is this great for Peter, but I have a place to stay when in Chicago for a Cubs game. My urging people to recognize the Yang reaction was scientifically justified but motivated by personal as well as professional gratitude.

This brings me to my long and delightful collaboration with Tito. Our joint interest in biradicals, especially as formed from ketones, has been what I consider the ultimate in friendly competition. You have to like a guy whose exquisite laser flash studies verify much of your early work, even if he doesn't agree on the minor details of how triplets form products. I am happy to see that what at first probably seemed like a silly spat among Tito, Dick Caldwell, and me, about the timing of intersystem crossing relative to product formation, has been taken up with great seriousness by Joe Michl, Howie Zimmerman, Charles Doubleday, Malcolm Forbes, and several other theoreticians. In science, the joy and goal of competition is not really who gets it right but that together we will eventually get it right. However, I'll still bet anyone a beer that I'm right.

I have to take this occasion to comment on my long affair with ketone photochemistry. Although my original interests were entirely mechanistic and have not disappeared, it soon became apparent that the localization of excitation on the carbonyl group makes it an excellent monitor, both spectroscopic and chemical, for all sorts of competing intramolecular reactions. Nature being the mysterious thing it is, one keeps finding new reactions and effects without really trying. So Fate (not the devil) has kept me tied to ketones. The picture (*circa* 1982) next door is simply to prove my assertion in an old Accounts paper that my editorial stint with JACS was really only practice for being a soccer referee.

That brings me back to the title. Mostafa El-Sayed and I have been good friends since my year spent on a sabbatical in his lab. Now we didn't start out talking the same language, he being a pure-bred physical chemist and I a staunch organiker.

Much of the fun of that year was our learning each other's language, especially the different phrases we used to say the same thing. The organic concept of reactivity being localized in functional groups does not sit well with the physicist's knowledge that molecular orbitals are delocalized; so when I told him a triplet carbonyl has its reactivity centered on the carbonyl oxygen he said "no, the whole molecule is excited." Of course, but the n orbital is highly localized. The small degree to which it is delocalized explains the relative efficiency of bond cleavages that people like Laurie Butler study. What is really important, however, is the degree to which physical, organic, and inorganic photochemists have learned to understand each others' lingo and thus to respect each others' unique insights into excited state behavior. Our birthyear symposium was the ultimate example of the high quality of individual research projects currently being conducted by photoscientists, on a collection of topics so diverse that it likely could not have happened twenty-five years ago. It was a celebration of individual achievements, like a great opera that lacks a sensible plot yet is replete with majestic arias. After the fun we have all returned to the real world; let the competition resume and remain friendly.

Cooking My Slides

David Whitten
Los Alamos National Laboratory

A few weeks ago William Jenks asked me if I could contribute a brief account of some personal reminiscences of the times we of the "Gang of Six" have interacted with one-another. I presume that each of us is being given a chance to write something and that perhaps this will be used as a way of checking our honesty or memory in that the same events might be reported in a different way by different people (a la "Rashomon"). We all have had many occasions to interact with each other over the many years since we started in photochemistry and of course from several different perspectives: as reviewers of each others papers and proposals, as mentors to the same students (or postdocs), socially at meetings or panels or on visits to each others institutions. Needless to say, over the years these occasions add up and lead to some interesting storytellings, as well as for some possible voids (selective or otherwise) in some of our memories.

Perhaps my longest standing interaction among the different members of the "Group of Six" is with Jack Saltiel. Although I did not know Jack while he was at Caltech, I first met him briefly when he passed through Pasadena during his postdoc at Berkeley. By that time I had heard several "Saltiel Stories".... but Jack seemed to be a reasonable and pleasant person on our first meeting. However it wasn't long before our paths crossed again. This time Jack was a reviewer of one of our early papers (although it took me a short time (one or two papers submitted on cis-trans photoisomerization) before I learned to identify him from his reviews). Many of my first reviews were negative so that was not necessarily the key; rather it was the length and detail of the reviews from Jack which led me to feel that I knew nothing about what I was writing and would probably be better off leaving photochemistry for another career. Yet each time the review ended on a positive note with an invitation to respond to all these points and then resubmit. Rather surprisingly, after receiving several of these reviews, which by now I could readily attribute to Jack, I received an invitation to visit Florida State and present a colloquium. My first visit was, on the whole, quite pleasant. However, a frightening part involved a visit to Jack's lot near an "intermittent" lake outside Tallahassee. My visit came near the end of April and during an unusually cool period for Tallahassee at that season and Jack and his group held a picnic in the waning light of day on land that was evidently usually submerged. We stayed out until well after dark and then we had to find our way back to the cars. Having lived for a short time in North Carolina, I was very concerned about encountering reptiles, particularly the much-feared venomous pit-vipers of the Southeast. Jack told me he never saw any snakes and was therefore completely unconcerned. Fortunately during the dark trek back to the cars, neither did I or anyone else. On a subsequent visit a few years later I stayed as a house-guest at Jack and Terry's new home near the same lake. He once again assured me that he and Terry almost never saw any snakes. I went for a run along the dirt road leading from their house and counted no fewer than five in a very short distance from their house. So much for Jack's vision or perhaps good fortune. On that same visit Jack had arranged for me to give two talks. I had one talk that was perhaps a little too fresh and unpracticed and another that was in somewhat better shape for an audience. Unfortunately I gave the former first; the main flaw in the talk was that I had many tables of data that had not been well-sorted or edited. Of course, Jack kindly pointed out to me that no one wishes to be assaulted with slide after slide of data that can't possibly be read or assimilated in the short time on the screen. His pointing this out is something I have remembered and greatly appreciated throughout my subsequent career and I really thank him for telling me. However, the next day when I was to be giving a talk to a larger audience and when I was actually much

better prepared, I had just begun speaking (with better slides too!) when a university police officer came running down the corridor and said, "you have to leave, we have had a bomb threat". This quickly ended my second talk. It was curious to note that Jack had briefly left the auditorium just as I had begun the talk. I wonder where he found a phone.

I had an opportunity to repay Jack's hospitality by arranging for him to visit the far North shortly after I moved to the University of Rochester. By then I had learned that Jack had never lived or even spent much time north of Texas or northern California so I arranged for him to visit the University and Kodak during mid-January. I promised him the loan of warm clothes and the adventure of a winter visit to the idyllic snowscapes of upstate New York. The weather was even more rigorous than usual and as a consequence of what he experienced during his trip I doubt whether he has ever again ventured north from Florida during the period from November-March. As I recall, he told me that he was sick for something like three weeks after returning to Florida.

Although I have interesting interactions and exchanges of visits with other members of the "Gang of Six", most have been very pleasant with no especially unusual occurrences. Sometimes, however, timing is everything. For example, I have learned that it is sometimes better to visit Bowling Green, home of Doug Neckers, at the end of a trip rather than in the beginning or middle. One occasion I rather recklessly scheduled a trip with four talks in five days involving several stops and ending in Bowling Green. Surprisingly, the travel worked and I ended up on a Friday afternoon presenting a seminar at BGSU. At that time the seminar room had a separate projection room with the slides (not transparencies!) supposedly under remote control. The first part of the talk went well, but at some stage the slides appeared to go out of focus, an occurrence which got worse with time. Eventually the slides refused to advance and finally, the last slide shown gloriously and dramatically "decomposed" before the eyes of the audience. Since this happened near the end, the event wasn't too disruptive and it was possible to complete the talk. However, upon opening the door of the projection room it was quickly apparent from the smell and smoke that something had gone terribly wrong with the projector and that many of the slides had been "cooked". On subsequent trips to Bowling Green I have used transparencies.

Having just returned from a similar marathon trip to the East, including a stop in Bowling Green, and some minor travel problems and delays, it is worth noting the wide geographic spread among the "Gang of Six". It is truly wonderful that we have been able to interact through frequent visits to each others institutions and to conferences all across the globe. This is something I don't think any of us could have foreseen 35 years ago as our careers were beginning. Although many of us studied far from our homes, the trips across country were infrequent and expensive adventures and not something we did weekly or monthly as many of us do today. The irony of it all is that it is often easier to visit Bob Liu in Hawaii, as I did a few winters ago from Rochester, than to get from Bowling Green to East Lansing or Rochester. It is also remarkable that it is sometimes easier to spend time with Jack Saltiel or Doug Neckers in Interlaken or Beijing than in more prosaic locations in the US.

One of the richest links among us (and, of course, this extends far beyond the "Gang of Six") is the co-workers who, as students, postdocs or postgraduate colleagues, have spent time or interacted closely with two or more of us through the years. These person-to-person interactions have provided a continuing basis for closeness, something we have learned well from our common friend and mentor, George Hammond. It is a consequence of these interactions and the individuals involved that the six of us have been the beneficiaries of the wonderful celebration that has lasted through most of 1998.

The University of Wisconsin's Interdepartmental Strategic Hiring Initiative in the Field of Biophotonics.

Introduction

The recent phenomenal acceleration in the rate at which new biological discoveries are made has been in large part driven by developments in instrumentation. Nowhere has this been more apparent than the recent explosion in our knowledge of the structure, dynamics and physiology of a cell obtained through the use of new optical techniques. The techniques of photon-based experimental manipulation and advanced optical imaging of live tissues define the field of biophotonics. The University of Wisconsin is proposing to hire three new faculty in this exciting new field.

Key areas of biophotonics

⟨ **Optical sectioning microscopy**. Traditionally, the internal structure of organisms was studied by cutting a specimen up into a sequence of slices and examining each cross-section under a microscope. Such a strategy is clearly not appropriate to the study of living tissue. Recently, techniques have been developed that produce "optical sections" within an intact specimen by eliminating interference from structures that are above or below the plane of focus. These techniques have enabled the three-dimensional structure of living tissues to be visualized. Together with newly developed computer algorithms, four-dimensional (three spatial dimensions plus time), animated reconstructions of fundamental biological processes such as embryology can now be obtained. The first optical sectioning technique to gain wide acceptance was confocal imaging. Recently, an exciting new optical sectioning technique has emerged from a hitherto obscure branch of spectroscopy: multiphoton fluorescence excitation. In this technique, ultrashort-pulsed (10^{-13} seconds) infrared lasers are used as illumination sources in laser-scanning microscopes. Very high photon densities excite the fluorescent probe molecules by density-dependent, multiphoton excitation events only at the point of focus. The problem of out of focus interference is therefore elegantly avoided by never generating it in the first place. Multiphoton fluorescence imaging has significant advantages over confocal imaging in that it is more benign to living specimens and can obtain images from considerably deeper within living tissue than any other method. Multiphoton imaging is a striking example of how the convergence of two advanced techniques in one discipline (the physics of ultrafast pulsed lasers and multiphoton spectroscopy) can lead to a revolutionary new tool in a quite separate discipline (the life sciences).

⟨ **Photon limited microscopy.** Many optical visualization techniques applied to the study of living tissues have to work at photon-limiting levels of signal. This has necessitated the development of advanced imaging detectors (such as cooled, charge-coupled devices) with high photon detection efficiencies and microscopes with low-loss optics. In order to make optimum use of such detectors advanced digital electronics is needed together with computer algorithms that can enhance photon-limited images.

⟨ **Fluorescent probes** have become an essential part of the armory of the research and clinical biologist. They enable the target of the probe molecule to be revealed with high selectivity (by color discrimination) and

sensitivity. The development of suitable probes for labeling DNA and RNA was one of the driving technologies for the development of automated methods of DNA sequencing.

〈 **Fluorescent probes for structure.** The use of fluorescent probes for studying the internal structure of fixed biological material (often using optical sectioning microscopy) has become a well-established technique. However, the use of fluorescent probes for studies of living specimens is more problematic. Fluorescent probes often bleach rapidly and in so doing cause toxic products to be released which damage cells. More research is needed in the field of photophysics and photochemistry in order to develop better probes for *in vivo* studies**.**

〈 **Fluorescent indicator probes** have been developed that can reveal the physiological state of a cell such as internal concentrations of selected ion or molecule species. Used in conjunction with optical sectioning microscopy, indicator probes can reveal the spatial and temporal distributions of key biological signaling molecules in live specimens.

〈 **Naturally fluorescent proteins** which were originally characterized in jellyfish have recently been cloned and genetically enhanced to improve or modify their fluorescence properties. Genes for these molecules can then be introduced into other organisms using molecular genetics techniques. Depending on the host DNA sequences to which the gene for the fluorescent protein is appended, these novel "reporter genes" can be used to reveal patterns of gene expression in a developing organism or reveal the distribution of a particular protein that has been rendered fluorescent by the appended gene. This technique is undergoing a period of explosive development at the present time. An exciting recent application has been the development of an indicator for free calcium based entirely on naturally fluorescent proteins. The gene for this indicator can be introduced into an organism by genetic transformation techniques. The dynamic changes in intracellular calcium levels within any accessible cell of this organism can then be visualized by optical sectioning.

〈 **Spectral and lifetime imaging.** The emission spectrum of a fluorescent molecule and/or its excited state lifetime often alter with changing molecular environments. Such studies used to be a relatively quiet backwater of biophysics but have recently come into prominence with the realization that these shifts in the spectral characteristics of a molecule can be used to indicate the molecular environment within a cell. The challenge is now to develop instrumentation for three-dimensional spectral and lifetime imaging to facilitate the application of these promising new techniques to studies of live tissues.

〈 **Caged bioactive probes.** A living cell is a vastly complex dynamic machine, typically 0.01 mm in diameter, that is bounded by a membrane. Recent developments in genomics are giving us information of the all the thousands of components (proteins) that go to make up this machine, yet we still have only the vaguest ideas of how this machine functions or is assembled. Aspects of cellular machinery that are beginning to be understood are the myriad signals that are used for communication both within cells and between cells. Photochemists have developed methods for inactivating signaling molecules by means of a molecular "cage". The cages are designed so that they can be released by the application of light at a particular wavelength. This novel technique is providing a unique tool that can be used to experimentally release bioactive molecules at predetermined times and places within a tissue or cell by the application of focussed beams of light of the appropriate wavelength. In this manner, an experimental biologist can at last begin to explore cellular machinery in a precise, localized way in order to determine how this machinery functions. The use of caged bioactive probes is still very much in the early tentative stages. More development is needed in the chemistry of caging. Also, there are exciting possibilities in the use of multiphoton techniques for obtaining extremely

localized release volumes that need to be developed.

〈 **Optical techniques for measurement.** The microscopic dimensions and the dynamic nature of the intracellular machinery make basic measurements of force and distance difficult to obtain. Recently two optical techniques have been developed that are beginning to be applied for molecular scale measurements with some considerable successes. The use of optical gradient field force traps in conjunction with interferometric methods has been used to measure the pico-Newton forces generated by individual molecular motors. In the second technique, use is made of the phenomenon of fluorescence resonant energy transfer to measure intermolecular distances of the order of 1 nanometer. This technique is proving very useful for revealing when two different molecules become associated within a cell (for example, as part of a signaling cascade). These two techniques provide yet more examples of the application of fairly esoteric physical optics studies to the development of powerful experimental tools for the biologist.

Need for multidisciplinary collaborations

The current possibilities and future potential for development in the field of biophotonics is huge. As has been outlined above, the currently exciting state of the field of biophotonics has arisen by the combined efforts of physicists, chemists, and molecular geneticists working together with cell, developmental and neurobiologists to produce revolutionary new tools for life-sciences research. Although the applications to pure research have been highlighted, it is likely that today's tools for the research scientist will be developed into tomorrow's tools for the clinician. Examples of this progression are already apparent in the development of methods of diagnosing connective tissue abnormalities with multiphoton imaging and the use of fluorescence lifetime methods for the clinical measurement of oxygen levels.

The cluster hire initiatives provide a unique opportunity to establish a hothouse for cultivating new developments in biophotonics at UW. The Biophotonics cluster should be truly interdisciplinary in order to be effective and will establish vital channels of communication between the traditional disciplines. It will be necessary for physicists and chemists to be aware of the challenges facing the biologist. In turn the biologists should be sufficiently fluent in the language of the physicist and chemist in order to work together productively with these disciplines in order to tackle fundamental biological problems.

Why UW is fertile ground for a Biophotonics initiative.

The lifescience research activities on the UW campus includes distinguished programs in cell, developmental and neurobiology. These basic biological sciences groups could supply the potent fuel of experimental need to a biophotonics group. In addition, there is considerable latent potential in the Physics, Chemistry and Pharmacy departments to become major contributors to core research in biophotonics. The Integrated Microscopy Resource is an NIH-funded national center for advanced microscopy techniques. The Resource will act as a focal point for a biophotonics group as it provides a center for state-of -the-art imaging technology.

Identification of research areas for new biophotonics faculty.

The following research areas have been identified as optimal for the establishment of a synergistically interacting biophotonics group:

10) A physicist with a strong track record in the application of optical techniques for biological research. This person would be based in the Physics Department but would have strong collaborations with several biology departments including the Integrated Microscopy Resource. Possible areas could be in non-linear optics, optical force-traps, molecular spectroscopy or new methods of imaging with potential biological applications, such as multiphoton, x-ray or photoelectric microscopy.

11) A photochemist/molecular biologist based in the Physiology, Chemistry, Pharmacy or Biochemistry Departments. This person could be developing new optical probes (possibly based on naturally fluorescent proteins) or new techniques for functional imaging of cells and tissues or new experimental tools based on caged molecules.

12) A biophysically-oriented cell biologist based in the Molecular Biology Laboratory (with a tenure home in the Zoology or Anatomy Departments). Such a person would be using biophotonics techniques for the study of functional aspects of the cytoskeleton. Alternatively, this person could be a biophysically-oriented neurobiologist based in the Physiology or Anatomy Departments.

13) A developmental embryologist studying a model organism with established genetics such as the mouse, zebrafish, fruit fly or nematode worm. This person would have a particular interest/need for biophotonics techniques and could have a tenure home in the Genetics Department or possibly the Anatomy or Zoology Departments but would also have strong links with the Integrated Microscopy Resource.

Structure of the biophotonics group.

It is proposed that, in the interests of fostering inter-departmental collaborations, the members of the biophotonics group will be housed within the participating departments rather than being located in one center. However, communication links within the group will be established from the beginning and continuously nurtured. The following strategies will be used to maintain the cohesion of the biophotonics group:

⟨ The group will be encouraged to apply for program project grants.
⟨ The group should establish a regular seminar series.
⟨ The group will cooperate on the teaching of biophotonics on Campus.
⟨ The Integrated Microscopy Resource will act as a focus for the group through interactions and collaborations arising through the development of optical instrumentation and imaging techniques, a common denominator for all the proposed members of the biophotonics group.

Hiring Strategy

Candidates at the assistant, associate or full professor levels will be considered. The search committee is made up of members of the participating departments.

Applications for the Biophotonics positions, including a CV and a brief research proposal, should be addressed to Pat Hansen, Laboratory of Molecular Biology, 1525 Linden Drive, Madison WI 53706.

Upcoming Meetings

An up-to-date version of this list is posted on the I-APS website (http://www.chemistry.mcmaster.ca/~iaps/index.html). Please send new meeting announcements to: wsjenks@iastate.edu and iaps@mcmaster.ca.

♦ **5TH INTERNATIONAL CONFERENCE ON SOLAR ENERGY AND APPLIED PHOTOCHEMISTRY** AND **2ND INTERNATIONAL TRAINING WORKSHOP ON ENVIRONMENTAL PHOTOCHEMISTRY**

March 30 – April 4, 1999   Cairo, Egypt

Information: Prof. Dr. M.S.A. Abdel-Mottaleb, Photoenergy Center, Faculty of Science, Ain Shams University, Abbassia, Cairo, Egypt, tel: +202 248 97 25, fax: +202 244 76 83, email: solar@photoenergy.org. The updated information at our web page http://www.photoenergy.org may be of interest to you.

♦ **FUNCTIONAL DYES 4TH INTERNATIONAL SYMPOSIUM ON FUNCTIONAL DYES SCIENCE AND TECHNOLOGY OF FUNCTIONAL *PI* ELECTRON SYSTEMS**

May 31 – June 4, 1999   Osaka, Japan

Information: Prof. Yasuhiko Shirota, Faculty of Engineering, Osaka University, Yamadaoka, Suita, Osaka, Japan 565-0871, Japan, Tel.: +81 6 879 7364, Fax: +81 6 879 7367, email: isfd@chem.eng.osaka-u.ac.jp.

♦ **13TH ISPPCC, INTERNATIONAL SYMPOSIUM ON PHOTOCHEMISTRY AND PHOTOPHYSICS OF COORDINATION COMPOUNDS**

June 26 – July 1, 1999   Isle of Lipari, Sicily, Italy

Information: Dr. Sebastiano Campagna, Dept. of Inorganic, Analytical and Physical Chemistry, University of Messina, Via Sperone, 31, I-98166 S. Agata, Messina, tel: 39 90/676 57 37, fax: +39 90/39 37 56, email: isppcc@chem.unime.it.

♦ **6TH CONGRESS OF THE INTERNATIONAL SOCIETY FOR SKIN IMAGINE**

July 4 – 6, 1999   London, England

Information: J. C. Bamber, email: hitec@rpms.ac.uk

♦ **ISES 1999 SOLAR WORLD CONGRESS**

July 4 – 9, 1999   Jerusalem, Israel

Information: ISES 1999 Solar World Congress Secretariat, P.O. Box 50006, Tel Aviv 61500, Israel, tel: +972 3/514 00 00, fax: +972 3/514 00 77, email: ises99@kenes.com

♦ **FEMTOCHEMISTRY IV 1999**

July 18 – 22, 1999   Leuven, Belgium

Information: Prof. Dr. F. C. De Schryver, K. U. Leuven, Celestijnenlaan 200F, B-3001 Heverless, Belgium, tel: +32 16/32 74 05, fax: +32 16/32 79 89, email: frans.deschryver@chem.kuleuven.ac.be

♦ **10TH IUPAC SYMPOSIUM ON ORGANO-METALLIC CHEMISTRY DIRECTED TOWARDS ORGANIC SYNTHESIS**

July 18 - 22, 1999   Versailles, France

Information: Congres Scientifiques Services (C2S), Chantal Iannarelli, 2 rue des Villarmains, B.P. 124, F-92210 Saint-Cloud, tel: 33(0)147719004, fax: 33(0)147719005, email: c2s@club-internet.fr

♦ **XIXTH INTERNATIONAL CONFERNECE ON PHOTOCHEMISTRY**

August 1 - 6, 1999   Duke University, Durham, NC, U.S.A.

Information: Prof. John D. Simon, Dept. of Chemistry, Duke University, Durham, NC 27708, email: icp99@chem.duke.edu, jds@chem.duke.edu

♦ **8TH EUROPEAN CONFERENCE ON THE SPECTROSCOPY OF BIOLOGICAL MOLECULES**

August 29 – September 2, 1999   University of Twente, Netherlands

Information: Prof. J. Greve, Univ. of Twente, POB 217, NL-7500 AE Enschede, phone: x31-53-489-3157, fax: x31-53-489-1105, email: j.greve@tn.utwente.nl

♦ **6TH INTERNATIONAL CONFERENCE ON METHODS AND APPLICATIONS OF FLUORESCENCE SPECTROSCOPY**

September 12 - 15, 1999   Paris, France

Information: MAFS6, Prof. Bernard Valeur, Conservatoire National des Artes et Metiers, 292 rue Saint-Martin, F-75141 Paris Cedex 03, tel: 33(0)140272389, fax: x33(0)140272362, email: mafs6@cnam.fr

♦ **6TH LATIN AMERICAN ENCOUNTER FOR PHOTOCHEMISTRY AND PHOTOBIOLOGY (ELAFOT-6)**

September 12 - 16, 1999   Rio de Janeiro, Brazil

Information: Prof. Ira M. Brinn, Univ. Federal do Rio de Janeiro, Brazil, email: irabrinn@iq.ufrj.br

♦ **9TH RADTECH EUROPE CONFERENCE AND EXHIBITION**

November 8 – 10, 1999   Berlin, Germany

Information: Vincentz Verlag, Schiffgraben 43, D-30175 Hannover, tel: +511/9910-271, fax: /9910-279

♦ **IXTH INTERNATIONAL SYMPOSIUM ON LUMINESCENCE SPECTROMETERY IN BIOMEDICAL AND ENVIRONMENTAL ANALYSIS. SPECTROSCOPIC AND IMAGING DETECTION TECHNIQUES**

May 15 - 17, 2000   Montpellier, France

Information: Prof. Dan A. Lerner, Univ. of Montpellier, ENSC, 8 Rue de l'Ecole Normale, F-34296 Montpellier cedex 5, tel: x33/04 6714 4323, fax: x33/04 6714 4349, email: lerner@enscm.fr

♦ **PHOTOBIOLOGY 2000: JOINT CONGRESS (AIP), ASP AND ESP MEETING**

May 31 – June 4, 2000   San Francisco, CA U.S.A.

Information: Nancy L. Oleinick, Biomedical Res Bldg 3, Case Western Reserve University, 10900 Euclid Avenue, Cleveland, OH 44106-4942, tel: +1 216/368 1117, fax: +1 216/368 1142, email: nlo@po.cwru.edu

♦ **XVIII IUPAC SYMPOSIUM ON PHOTOCHEMISTRY**

July 22 – 27, 2000   Dresden, Germany

Information: Prof. Silvia Braslavsky, Mülheim, fax: +49 208/306 39 51, email: braslavskys@mpi-muelheim.mpg.de (chairperson); Prof. Thomas Wolff, Dresden, fax: +49 351/463 33 91, email: wolff@cech01.chm.tu-dresden.de (chairman local committee).

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*Name of current advisor_____

For our information, are you currently a member of the American Society for Photobiology?   Yes   No

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___ Imaging Systems (Nonsilver) (RG)

___ Lasers (LS)

___ Macromolecular (CC)

___ Mechanistic (MP)

___ Ordered Media (OM)

___ Organometallic (CM)

___ Preparative/Synthetic (CR)

___ Polymer (CY)

___ Photochemical Kinetics (PK)

___ Spectroscopy (SP)

___ Photoemission (PE)

___ Isotope Separation (IS)

___ Photobiochemistry (BC)

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___ Photochromism (PC)

___ Photoconductivity (PN)

___ Photoelectrochemistry (PL)

___ Photoionization (PI)

___ Photolithography (PT)

___ Photomedicine (PM)

___ Photosynthesis (PS)

___ Radiation Chemistry (RC)

___ Solar Energy Utilization (SE)

___ Vision (VS)