



## **Inter-American Photochemical Society Newsletter**

Volume 24 Number 2, Fall 2001

### **Inside this issue:**

I-APS Officers .....	1
Advisory Committee Members .....	1
Letter from the President .....	2
Note from the Editor .....	3
Award Information .....	4
Symposium Honoring George S. Hammond, Jack Saltiel .....	5
XIIth Inter-American Photochemical Society Conference Report .....	10
Organic Photosensitizers to Probe Macromolecular Structure and Dynamics, Lisa A. Kelly .....	14
Celebration of Michael Kasha's 80th Birthday, Edwin F. Hilinski .....	20
Glossary of Terms in Photocatalysis and Radiocatalysis .....	22
Positions Available .....	23
Upcoming Meeting Information .....	23
Society Application Form .....	25

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# Letter from Frederick D. Lewis

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August 1, 2001

Dear Colleagues:

In my last letter to you, dated 19 October 2001, I concluded by forecasting that the coming year would be an exciting one for our Society. Events have borne this out. In the intervening nine months there have been no fewer than five photochemistry conferences in the Americas, including the highly successful 12<sup>th</sup> I-APS Conference in Córdoba, Argentina. Plans are in place for the 13<sup>th</sup> I-APS Conference to be held in Tempe, Arizona, January 2-6, 2002. Our new Secretary, Steve Fleming, and Newsletter Editor, Linda Peteanu, are in the process restructuring our membership rolls and newsletter. In cooperation with the European Photochemical Association (EPA) and Japanese Photochemical Association (JPA) we have established an Inter-Society Committee on Photochemistry (I-SCP). We are also in discussion with EPA and JPA concerning new journals sponsored by those societies.

Let me begin by thanking the co-chairs Pedro Aramendia and Miguel Garcia-Garibay and all the members of the organizing committee for the 12<sup>th</sup> I-APS Conference, particularly our local hosts Gerardo Argüello and Gustavo Argüello, for their considerable efforts in what proved to be a stimulating meeting in a most agreeable, secluded location. Pacifichem 2000 attracted many I-APS and JPA members to Honolulu for multiple large symposia. A special symposia at the San Diego ACS meeting honoring George Hammond on the occasion of his 80<sup>th</sup> birthday was organized by Carl Wamser. And Michael Kasha's friends and colleagues gathered in Tallahassee for a symposium in celebration of Michael Kasha's 80<sup>th</sup> birthday. The most recent gathering of photochemists was at the 20<sup>th</sup> Gordon Research Conference on Organic Photochemistry in New London, CT. Jack Saltiel has the distinction of having attended all five of these meetings. Society members have promised reviews of several of these conferences for this issue of the Newsletter.

Society Secretary, Steve Fleming, has undertaken the on-going task of updating our membership rolls. Last year we moved our membership renewal date to January 1. Those of you whose memberships expire at the end of this year can expect to receive dues notices from Steve during the Fall. I-APS membership is a real bargain, especially for postdocs and students. Please renew your membership and encourage your students and photochemical colleagues to become I-APS members. Several significant decisions have been made with respect to our Newsletter. At the suggestion of our new Editor, Linda Peteanu, the publication schedule has been changed from May and November to February and August. This will allow us to provide more timely announcements of meetings and society awards. The Newsletter will also be significantly reduced in size by moving the text of solicited scientific articles to our web site. Abstracts of articles will continue to appear in the Newsletter along with news and other items of interest to I-APS members. The reduction in size will significantly reduce production time and publication and mailing costs. Watch for the first issue of the reformatted Newsletter which should appear at the end of the summer both in your mailbox and on our web site.

On the international front, Dick Weiss and Cornelia Bohne are serving as I-APS representatives on the newly formed I-SCP which will represent the three societies (I-APS, EPA, JPA) in dealings with the restructured IUPAC and other issues of interest to the three societies. Last year Elsevier began publication of *J. Photochem. Photobiol. C. Reviews* under the editorial control of the JPA. Next January the Royal Society of Chemistry will begin publication of *Photochem. Photobiol. Sciences* (PPS) on behalf of the EPA and the European Society for Photobiology. I would personally encourage I-APS members to support these society-published journals as well as *Photochem. Photobiol.* which is published by the American Society for Photobiology. Support would entail submission of articles and subscription to personal and library copies. The existence of strong, society-controlled journals will benefit the international photochemistry community and may render superfluous high priced commercial journals of questionable quality.

In closing, let me encourage all society members to attend the 13<sup>th</sup> I-APS Conference in Tempe, AZ, January 2-6, 2002. Co-chairs Ian Gould and Peter Ford have assembled an impressive list of invited speakers, which can be viewed on our web site. Moreover, they guarantee flawless Arizona weather. This will be the Society's first North American meeting west of the Sewanee River and an opportunity for increased participation by colleagues in the western states. Postdocs and students are always welcome at I-APS meetings. So plan on attending — and bring a colleague or your students. I look forward to seeing you in Tempe.

Best regards,

Fred Lewis

## Note from the Editor

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With this issue, I will be taking over the editorial duties for the I-APS Newsletter from William Jenks. I first thank William for doing a great job during his tenure and for giving me a lot of help and advice. Secondly, I will describe some changes that are planned for the Newsletter and solicit your input.

The first change you may notice is that the Newsletter that you have received is considerably 'streamlined' in an effort to use space as efficiently as possible. The I-APS treasury funds, generated via modest membership dues, will be saved in the production and mailing of this reformatted Newsletter so that more money can be used in support of other important Society activities such as conferences and student travel awards. In the future, the focus of the Newsletter will be on Society news, conference announcements, and contributed summaries of recent photochemical conferences. General scientific review articles, submitted by the readership, will also be included as opportunities arise. The second upcoming change will be that some of the longer pieces will be abstracted in the Newsletter with the remaining content published on the web. Each abstract will contain an easy-to-use link to the appropriate web page. Eventually, we hope that most, if not all, of the Newsletter will be entirely web-based, saving both paper and expense.

I recognize that many of these changes may initially appear quite drastic, but I hope that the membership will grow comfortable with the print-and web format. Furthermore, I ask for your indulgence as we implement these changes because we will certainly be facing a bit of a learning curve. Please feel free to contact me with any questions and/or comments that you may have regarding the format and content of the Newsletter.

Best regards,

Linda Peteanu

# 2002 I-APS Awards and Fellowships

## 2002 I-APS Award in Photochemistry: Paul F. Barbara

Professor Paul F. Barbara of the University of Texas at Austin is the winner of the 2002 I-APS Award in Photochemistry. This Award is given in recognition of Paul's outstanding contributions to the advancement of photochemical and photophysical sciences during the last ten years. These contributions include detailed studies that use ultrafast spectroscopy, single molecule spectroscopy, and near field scanning optical microscopy and spectroscopy. As noted in the nominating materials, a hallmark of Paul's research is the use of state-of-the-art experimental strategies to investigate theoretically accessible chemical prototypes, many of which his group has introduced. Paul's descriptions of condensed phase physical and chemical phenomena are well based in fundamental principles and are well received by scientists across the range of photosciences because of Paul's ability to make the significance understandable to a broad audience.

## 2002 I-APS Fellowship: Donald R. Arnold

Donald R. Arnold, Professor Emeritus of Dalhousie University, has been elected to Fellowship in the Inter-American Photochemical Society. I-APS Fellowship in general 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 cites Don's pioneering investigations in several areas of organic photochemistry including the following: photoinduced electron-transfer reactions; exciplexes; the photochemistry of charge-transfer complexes; the captodative effect in free radicals; triplets, and radical ions; the [2 + 2] photoaddition of ketones to alkenes; the reactivity and spectroscopy of aryl- and vinylcarbenes; free radical chemistry; electrochemistry; and the photochemistry of small ring compounds such as cyclopropanes, cyclopropenes, and oxiranes. Don served as the first I-APS President (1980-83). He has been a regular participant in the I-APS Winter Conference and Gordon Research Conference on Organic Photochemistry.

## 2002 Cilento Award: Claudio D. Borsarelli

Claudio D. Borsarelli of the Universidad Nacional de Santiago del Estero, Argentina is the winner of the 2002 Cilento Award. This Award is presented to a scientist, aged 35 or younger, working in Latin America in order to encourage participation in the I-APS Winter Conference. Dr. Borsarelli is an assistant professor at the Universidad Nacional de Santiago del Estero and an assistant researcher at the Consejo de Investigaciones Científicas y Técnicas de la República Argentina (CONICET) at the university. His research interests are chemical and photochemical reactivity of natural and artificial pigments in organized media, reactions of singlet oxygen with natural pigments, photostability of pharmaceuticals, and electron-transfer and proton-transfer reactions in homogeneous and heterogeneous media.

## 2002 Closs Award: Tracy L. Morkin

Tracy L. Morkin from McMaster University is the winner of the 2002 Closs Award. The Closs Award is given to a student in recognition of high quality research that is to be presented orally at the I-APS Winter Conference. Ms. Morkin is a graduate student working with Professor William J. Leigh. She has been investigating the photochemistry of  $\nabla$ -silyl-substituted diazo compounds, diazirines, and ketenes with the ultimate goal of characterizing the reactivity of transient silenes that are formed *via* rearrangements of their precursor  $\nabla$ -silylcarbenes.

# Photochemistry Becomes More Complex: A Symposium Honoring George S. Hammond On His 80<sup>th</sup> Birthday

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Organized by Carl C. Wamser (Portland State University) and sponsored by the organic and physical chemistry divisions, this symposium was held on April 2 and 3, 2001 in San Diego, as part of the 221st National Meeting of the American Chemical Society. It was a personally and scientifically rewarding, heart-warming affair that brought to this attendee particularly strong nostalgia for the Caltech days in George Hammond's laboratory. A large appreciative audience included a fine representation of those of us who had the good fortune to be touched by George as he blazed through the different stages of his career. The Iowa State years, the Caltech years, the UC, Santa Cruz years, the Allied Chemical years, and, after his retirement, the Bowling Green, Georgetown University and now Portland State University years were all represented.

Carl Wamser (Ph.D., Caltech) opened the first afternoon session of the symposium with biographical comments about George's early years, running the family dairy farm in Auburn, Maine at 13 after his father's death and then attending nearby Bates College. The first speaker, Jay Kochi (University of Houston, Ph.D., Iowa State), prefaced his scientific lecture with a tribute to George, and his seminal contributions to physical organic chemistry and photochemistry in particular, and his ability to influence his colleagues and students at all levels. Jay spoke of George's gift of imagination, his generous intellect and his superb ability for zeroing in on the essential. A quote from Orville Chapman "George never met an idea he did not like" struck a cord with all of us who knew him. Jay knew George before his photochemistry years. He met him first as a UCLA undergraduate some 53 years ago, when George gave a substitute lecture for Saul Winstein, with whom he was a postdoctoral fellow after earning his Ph.D. with Paul Bartlett at Harvard. He was so impressed that he followed George to Iowa State, where George had a profound effect in helping assemble a dynamic group of faculty that included Ernie Wenkert, Chuck Depuy and Orville Chapman. Jay spoke of the Chinese tradition of revering, honoring, and respecting longevity, and presented George with a classical Chinese poem, that George is to have

translated in time for his 100th birthday celebration. Jay then announced the permanent establishment of the George S. Hammond Lectureship at Bates College. Former Iowa State colleagues accomplished this through contributions to George's alma mater, a wonderful gesture that touched George deeply.

The scientific part of Jay's lecture (*Charge transfer photochemistry via electron donor/acceptor organizations*) began with examples illustrating the ubiquitous, alas unheralded, involvement of colored charge transfer complexes in "garden variety" organic reactions, such as bromine addition to alkenes, electrophilic aromatic substitution and the Diels-Alder reaction. Contact ion radical pair (CIRP) intermediates, although very common, are not mentioned in Organic Chemistry textbooks. Jay reviewed incisive contributions from his own research, concentrating on those for which CIRP formation is induced by light absorption into the CT band. He emphasized the importance of including solvation energies in correlations of reaction rate constants with the electronic transition energy ( $h\nu_{CT}$ ) of the CT band. For instance, rate constants for oxymercuration of aromatic hydrocarbons show random correlation with corresponding  $h\nu_{CT}$ s but yield to a dramatically linear correlation when solvation energies are included.

**Nick Turro** (Columbia University, Ph.D. Caltech) was the second speaker. Nick was my classmate at Caltech having arrived there in the summer of 1960. He spoke of the decisively shaping influence of the late **Peter Leermakers** (Ph.D. Caltech) in bringing him to George and to Caltech, and how, on being labeled by George an "anti-photochemist" when, in a public lecture, he demonstrated for him the luminol chemiluminescence reaction, he rose to the challenge by changing research directions. Nick turned from seeking entry into triplet states thermally via transition metal ion catalysis to photochemistry and triplet photosensitization. With Peter's participation this transition immediately bore fruit in the benzophenone-photosensitized photolysis of ethyl pyruvate and launched Nick's remarkable career in photochemistry. Nick credits George for having given us

the tools to unravel photochemical mechanisms by showing how triplet sensitization could be applied generally in the unambiguous study of triplet state reactivity. Then, in the early 60s, at the dawn of modern molecular photochemistry, when each breakthrough came close on the heels of another, it was a heady atmosphere in the Hammond research group and with George's encouragement his co-workers would long maintain "photochemical highs".

Apparently, not entirely satisfied with the title of his lecture "*Supramolecular and magnetic control effects in organic photochemistry*", Nick tried "Super duper molecular photochemistry" and "Better things and better living through complexity". Supramolecular photochemistry, the study of photochemical reactions in the confining media of zeolites, cyclodextrins, micelles, and complex fluids, brings into play noncovalent interactions between substrate and environment that have a controlling influence on the outcome of photochemical reactions. Nick described the photolysis of symmetrical (ACOA) and unsymmetrical (ACOB) dibenzyl ketones in the super cage environments of zeolites. Because of different size restrictions, substrates in different locations in the zeolite (framework, holes, internal pores) behave as isomers with different relative mobility, as revealed by <sup>2</sup>H NMR measurements on strategically deuterated substrates. Conditions were described that allow control of cage products on photolysis of ACOB from 100% cage effect, CE, (AB product only) to 0% CE (statistical AA/AB/BB ratio) and to -100% CE (AA and BB products only). Enormous effects on radical lifetimes were established by transient EPR measurements (compare microseconds outside with seconds and hours within supracages). Depending on radical size, supracage size restrictions dramatically inhibit radical dimerization and favor disproportionation. In zeolites providing larger cages, cage reactions of the primary radical pairs (e.g., A/COB) could be studied and the effect of <sup>13</sup>C in the carbonyl carbon on triplet → singlet radical pair conversion and of external magnetic fields were described. At the end of this spectacular lecture Nick expressed our gratitude to George: "George we all thank you and love you for your mentoring insights, dedication, and your ability to imprint your scientific attributes on all your students and collaborators".

After a break and a chance to greet old friends, it was **Nate S. Lewis'** turn to speak. Perhaps Nate illustrates best the intricate scientific ties between many of the Symposium participants. Now a professor at Caltech, he had started out as an undergraduate there. Encouraged in 1976 by **Kent Mann**, a graduate student, he was "sucked into" the research collaboration between the **Harry Gray** and **George Hammond** groups, without knowing at the

time that that decision would have a profound effect on his future. It led him to MIT for his Ph. D. studies with **Mark Wrighton** (Florida State B. S., Caltech Ph. D.), who was the first to set the Hammond/Gray collaboration on fire, and then back to Caltech.

The title of Nate's lecture was "*Nanocrystalline titanium dioxide solar cells sensitized with ruthenium or osmium polypyridyl complexes: Photoelectrochemical studies and electron transfer dynamics*". He described the use of osmium polypyridyl complexes as sensitizers of nanoporous TiO<sub>2</sub> electrodes to solar illumination. Spectral responses of TiO<sub>2</sub> solar cells are extended to longer wavelengths with the use of Os<sup>II</sup>(H<sub>2</sub>L)<sub>2</sub>(CN)<sub>2</sub>, (where L is 4,4'-dicarboxylato-2,2'-bipyridine) or Os<sup>II</sup>(H<sub>2</sub>L)<sub>3</sub><sup>2+</sup> than with the use of Ru<sup>II</sup>(H<sub>2</sub>L)<sub>2</sub>(NCS)<sub>2</sub> and all produce very high external quantum yields for photocurrent flow. Singlet and triplet MLCT states of the ruthenium and osmium bipyridyl complexes Ru<sup>II</sup>(H<sub>2</sub>L)<sub>2</sub>(CN)<sub>2</sub>, Os<sup>II</sup>(H<sub>2</sub>L)<sub>2</sub>(CN)<sub>2</sub>, Ru<sup>II</sup>(H<sub>2</sub>L)<sub>2</sub>(NCS)<sub>2</sub> and Os<sup>II</sup>(H<sub>2</sub>L)<sub>2</sub>(NCS)<sub>2</sub> inject electrons into the semiconductor with rate constants in the 10<sup>10</sup> – 10<sup>13</sup> s<sup>-1</sup> range. The much slower rates of charge recombination decrease with increasing driving force, indicating that they fall in the Marcus inverted region. Solar cell efficiencies over 5% were achieved. Higher efficiencies may result by designing sensitizers in nanocrystalline solar cells that take advantage of the Marcus inverted region behavior of charge recombination. This augurs well, because an efficiency increase to 15% is likely to lead to commercially feasible applications.

**Tom Penner** (Caltech Ph. D.) was the first industrial speaker of the Symposium (Imaging Materials and Media, Eastman Kodak Company). In his Ph.D. studies during the late 1960s, Tom had inherited **David Whitten's** (Caltech postdoctoral) research project concerning relationships between photochemistry and radiation chemistry. The fact that Tom's presentation was co-authored by Dave Whitten is testimony to the lasting nature of research collaborations between George's co-workers. Tom spoke of George's view that the teaching of chemistry in terms of the traditional divisions presents an impediment to learning the subject. In his talk, Jay Kochi had also mentioned the Hammond/Gray paradigm of organizing the teaching of chemistry according to function: Synthesis, analysis, structure, and "the heart of chemistry" dynamics.

Tom's topic, "*Photoprocesses in ordered thin films*", concerned the design of materials for optical and photonic applications. Achieving desired performance depends, in part, on including functionality to control intermolecular interactions for large-scale organization. Chromophores that interact with light in a specified way are essential components. Systems consisting of deliberately

interactive multiple components offer opportunities and challenges for optimizing conditions to maximize performance. Energy migration in dye-polymer/clay films was described. Formation of *J*-aggregates by cyanines and other dyes incorporated in polymers allows layer-by-layer fabrication of films on anionic clays. Efficient energy transfer from dye to dye and from layer to layer produces an antenna function for harvesting light energy. The effect of increasing the number of layers is not completely understood. For instance, a case was described for which energy migration is very efficient for the first six dye layers, but further layers (up to ten total) are non-contributing. This antenna effect has practical applications in silver halide imaging. An effective absorbance of 0.15 for a monolayer of dye coating on a silver halide crystal leads to a large fraction of wasted incident light. The antenna effect of multilayer dye assemblies markedly increases light absorption efficiency in photographic films. The ordered antenna dye on the silver halide grain acts as a template for the formation of *J*-aggregates with their characteristic large absorbances.

**Dick Weiss** (Caltech postdoctoral) presented the last talk of the first session of the symposium. As a graduate student with Eugene Snyder at the University of Connecticut in the late sixties, the Woodward and Hoffmann concept of orbital symmetry conservation in electrocyclic reactions had intrigued Dick, who knew that its application to photochemical reactions was problematic. The draw of California and photochemistry, in that order, brought Dick to Caltech, armed with Eugene's advice to bet George that he could not stop smoking. Dick has enjoyed a close association with George that extended well beyond the initial two postdoctoral years. It continued through Dick's three-year appointment as an NAS Overseas Fellow at the Universidade de Sao Paulo in Brazil, a program in which George was intimately involved, and more recently, through George's highly positive association with Dick's research group at Georgetown University. He finished the introduction to his talk with two GSH quotations. The first was George's enthusiastic "Gee that's great" reaction to new results which had an exhilarating effect on students, and the second was from George's reflective side "Any scientific (or other) discipline when put into a small box will surely shrivel and die". Dick has been studying the control of photochemical reactions by polymer media. He took comfort in the fact that although the photochemistry was confined to small boxes (cages), they have flexible walls.

The title of Dick's contribution was "*Extracting fundamental (simple) photochemical and photophysical information from reactions of guest molecules in complex polymeric media*". Results were presented for the photo-

Fries reactions of 1-naphthyl esters in unstretched and stretched polyethylene. Stretching the polymer leads to a transition in structure from spherulitic organization of the crystalline portion to aligned microcrystallites and causes a decrease of mean free 'hole' volumes of 10-20 Å<sup>3</sup>. The free volume change influences the fate of caged singlet radical pairs. For instance, the ortho/para ratio of the acetylnaphthol products formed on photolysis of 1-naphthyl acetate changes from 4.2 in unstretched to 4.9 in stretched polyethylene. For the bulkier myristate, only ortho product is observed in either unstretched or stretched polyethylene. The confinement of the polymer environment prevents the relative reorientation of the initial radical pair that is required for para coupling. Decarbonylation of the initial alkanoyl radical in the cage gives a new radical pair whose fate is also influenced by the medium. The second part of the talk concerned covalent attachment of aromatic hydrocarbons to the polymer backbone via proton bombardment. According to Dick, Marshall McLuhan's 1964 aphorism, "The medium is the message", although made in a different context, aptly describes the controlling influence of polymeric media on photochemical processes, with the caveat that "To understand the message, first understand the medium" (Richard Weiss, 1984 unpublished).

**Harry Gray** (Caltech) was the first speaker of the second afternoon session on Tuesday, April 3. Harry spoke of George's enormous influence on his life, on his research career and on the inorganic and organometallic chemical community, generally. "I was a decent inorganic chemist, and then I met George", he joked. George was responsible for Harry's conversion to photochemistry and for his move from Columbia to Caltech, but when Harry turned to George and said "Thank you" he was speaking for all of us.

The title of Harry's contribution was "*Probing enzymes with photosensitizers linked to substrates*". He spoke first of the enormous barrier to electron transfer between metal ions in water due to the extremely high water reorganization energy and how the low reorganization energy of the protein medium leads to a reduced, friendly to life, barrier. For instance, electron transfer between Fe<sup>2+</sup> and Fe<sup>3+</sup>, an identity reaction, occurs within 100 ms in water at a separation of 6.5 Å but would require 10<sup>16</sup> years at a separation of 20 Å. In a protein environment electron transfer between Fe<sup>2+</sup> and Ru<sup>2+</sup> at a separation of 20 Å occurs within 0.5 μs! A series of cytochrome P450<sub>cam</sub> (P450) substrates tethered to luminescent Ru sensitizers bind the enzyme with comparable or greater affinities than those of the unmodified substrates. Ru-Fe(heme) energy transfer in the bound complex dramatically accelerates excited state decay. Analyses of luminescence decay kinetics yield dissociation constants for P-450/Ru-substrate complexes and similar Ru/Fe distances are



extracted for a variety of complexes from the energy transfer parameters. The similarity of the distances suggests a common substrate binding access channel. Confirmation of the validity of the calculated distances was obtained by x-ray crystallography of the crystal of one complex. Selective binding of the modified substrates to P450 was inferred from the luminescence kinetics in the presence of other heme proteins, indicating that such substrates could form the basis for a new class of optically detected in situ biosensors. The use of fluorinated biphenyl linkers instead of methylene chains enhances binding 100-fold.

The second speaker, **Doug Neckers** (Bowling Green) started with a tribute to George: "We honor George Hammond, the man who brought light to an organic chemistry laboratory". As a graduate student with Earl Huyser at the University of Kansas, Doug had studied thermally and photochemically induced free radical reductions of ketones. Influenced by fellow postdoctoral fellow Nick Turro in Paul Bartlett's laboratory at Harvard, he settled on photochemistry as a career. Doug was the driving force that created The Center of Photochemical Sciences at Bowling Green in 1985 and brought George there as a Senior McMaster Institute Research Fellow in 1988. Through George's frequent visits to the center, Doug has maintained a close relationship with him.

Doug spoke of his photopolymerization studies that evolved into three-dimensional imaging and photostereolithography. His 3-D photochemistry has had a significant impact on paleontology through the remarkable achievement of producing a 3-D polymer copy of the skull of a 2800-year old Egyptian mummy from the CT scan. Doug's formal contribution was on "*Photoreactions studied by step-scan transient IR spectroscopy*". He described how this technique has been applied to elucidate long-standing mechanistic questions in photochemistry. For instance, dating back to Doug's Ph.D. studies, intramolecular  $\gamma$ -H abstraction in the triplet state of alkyl phenylglyoxylates had been postulated to yield a biradical that dissociates to a ketone, derived from the alkoxy group of the ester, and 1-hydroxy-1-phenylketene as a reactive intermediate. Step-scan transient IR spectroscopy provides IR spectra in a time-window of 20 ns to 5  $\mu$ s following excitation and allows direct detection of ketene formation (400 ns rise-time) from the triplet state (389 ns decay time). The short lifetime of the biradical intermediate (15 ns) precludes its observation in the IR spectra. The ketene is trapped as the methyl mandelate when benzene or cyclohexane solutions of the phenylglyoxylates are irradiated in the presence of methanol. In another example, dating back to work carried out in collaboration with Nick Turro in Paul Bartlett's laboratory, Doug described the IR detection

of tetramethylcyclopropanone formed as a transient on photolysis of tetramethyl-1,4-cyclobutanedione.

Next was **Dave Eaton** (DuPont iTechnologies) who was George's last Caltech Ph.D. as a full Caltech resident, before George moved to Santa Cruz. In his Ph.D. work he had examined pyrazoline precursors to possible diradical intermediates that could potentially be involved in diene photorearrangements and photoisomerization, partly with **Bob Bergman** as a collaborator. After joining DuPont, Dave was able to observe George in his role as a consultant. George contributed intellectually as well as in his traditional role as cheerleader to the many technical developments involved in commercialization of photopolymer films for electronics and printing applications and in the process has gained many friends at DuPont. In fact, it was early collaborations among **Carl Wamser**, George and two DuPonters (**Cathy Chang** and **Charlie Baylor**) that led to an understanding of the exciplex nature of the interactions between benzophenone and Michler's ketone and to the commercial use of this "synergistic" photoinitiator. It was Dave's pleasure to convey DuPont's salute to George on his 80th birthday!

In his talk, "*Photochemical industry becomes complex, too*" Dave elaborated on the historical aspects of photopolymer technology, from its invention at DuPont by Louis Plambeck in the 1950's through its introduction into commercial use in the 60's and 70's. During this time the use of photopolymers revolutionized the ways that the printing process was accomplished and led, along with many other innovations, to the microelectronics revolution we have experienced over the last 40 years. Photopolymer printing plates and photoresists for the manufacture of printed wiring boards are now commonplace. New commercial laser-based systems take advantage of the digital data streams that are the backbone of our information exchange processes today. Dave concluded with predictions of uses of photopolymer materials in future optical communication network applications, as waveguide materials and optical components. The message: though photopolymers are now 50 years old, they continue to show promise for important new innovations for a long time to come. In this respect, they are just like George who continues to amaze us all after all these years.

**Jim Yardley** (Columbia Radiation Laboratory) spoke on "*Laser photochemistry: 25 years toward a fulfilled promise?*" In 1977, the lure of laser chemistry prompted Jim's move from the University of Illinois to Allied Chemical. He was there in 1978 to witness George's move to AlliedSignal, Inc. and to experience the remarkable research reorganization under his leadership.

Jim pointed out that initial attempts to develop laser activated “synthons”, starting for instance, with iron pentacarbonyl and seeking through photolysis at increasing laser intensities to form tetra- and tricarbonyl reactive intermediates, failed to yield the desired selectivity. Such initial failures, coupled with the high cost of laser photochemistry, led the scientific world to turn to “high value chemistry”: isotopic separation, pharmaceuticals, and catalysis, but again commercial viability proved elusive. Early successes were realized in the realm of semiconductor processing, including the development of new photoresist materials. Another area of laser photochemistry in which George played a crucial role at Allied concerned the development of guided wave optical devices. Through photochemistry, it is possible to define the spatial variation of refractive index within a polymeric medium and thus direct and control the propagation of light within that medium. This required the development of chromophore/polymer combinations that were not opaque in the UV. Photochemical transformations in the chromophore have yielded enormous changes in refractive index. Looking into the future, laser photochemistry holds the key for development of the next several generations of semiconductor devices through short wavelength laser lithography. Fabrication of low cost optical devices for telecommunications and for a host of data communication applications is also likely to depend on laser photochemistry. Jim concluded that the future of laser photochemistry is bright in ways not widely appreciated 25 years ago.

Fittingly, George’s wife, **Eve L. Menger** (Portland State University) gave the last scheduled talk of the Symposium. Eve’s talk “*Leitmotif from the life of a photochemist*”, liberally sprinkled with quotations from George’s talks, was a retrospective of George’s career. George’s scientific and teaching genius and his philosophy were revealed to the audience in his own words. When George left Caltech for UC, Santa Cruz in 1972, many of his friends thought he had taken leave of his senses. George had been drawn by the new challenges and the predictions that Santa Cruz was destined soon to become a UCLA or a Berkeley. As Vice Chancellor of all sciences, he had the opportunity and authority to implement his new ideas in the less rigid environment of a new place and, thus to work against artificial divisions in science and to emphasize instead its unity. After an exciting first 18 months in which several of George’s ideas were brought to fruition (some, e.g., a technical writing program, have blossomed and are still in existence), growth at Santa Cruz, and the flexibility it allowed, came to an abrupt halt. His appointment as Foreign Secretary for the National Academy of Sciences provided new

opportunities, which George whole-heartedly embraced without sacrificing his teaching commitments. George managed to keep everything going under circumstances where the “urgent takes priority over the important”. In his classes at Santa Cruz, the students’ admiration of the way he “ordered molecules around” earned him the nickname General George. Unfortunately, among the consequences of the mistaken demographic projections were the inability to continue hiring young faculty, and a continuous struggle to get existing research laboratories properly outfitted. On top of this, some colleagues were opposed to the creation of a Photochemistry Center, viewing it as an unnecessary dilution of diminished resources. When George left Santa Cruz for Allied Chemical in 1978, friends viewed the decision as beyond the pale, but the years at Allied proved exciting and productive.

George, the thinker/philosopher was revealed in excerpts from a series of remarkable speeches on topics ranging from chemical education, to chemistry in general, and to research management. According to George, the way chemistry was generally taught left much to be desired. Freshman chemistry delivered a hodgepodge of topics and organic chemistry placed a premium on the memorization of a bunch of name reactions. He advocated the restructuring of chemistry along functional lines: structural chemistry, dynamics and chemical synthesis with sensible examples of the contributions of chemistry to other sciences. This would involve the integration of, for instance, organic and inorganic chemistry and would avoid existing divisional lines with their terribly stylized traditional courses and their devastating effect on the learning of chemistry. He called for careful scrutiny of what was taught and described our current divisional system as artificial, incoherent, redundant and harmful to its most important element, the students. In a 1971 speech to the American Institute of American Engineers, George criticized the notion that teachers should motivate students. According to George, motivation comes from within. He attacked still another artificial teaching boundary by stressing that chemical science and engineering form a continuum. He called for a more inclusive, open style of teaching, while recognizing limitations imposed on teachers by their own experiences: “My own experience of open style teaching is limited—I am a product of my own experience”. In another talk he cautioned that the rapid growth of science is not reflected in what is taught. He advised that the fact that a particular topic had been included in a course for a long time was not necessarily an indication that it was basic! Furthermore, if a topic were included in a course because it was ‘basic’, one should be prepared to say to what it is basic.

# Conference Report: XII<sup>th</sup> Inter-American Photochemical Society Conference

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The XII<sup>th</sup> IAPS conference was held at the beautiful setting of Ascochinga, Córdoba, Argentina between May 20<sup>th</sup> and May 25<sup>th</sup> 2001. This was the second IAPS meeting in South America. The co-chairs of the meeting (Pedro Armendia and Miguel Garcia-Garibay), as well as the local organizers, did a superb job in putting together an excellent scientific program. On the entertainment side we all enjoyed the social activities during the week and the Argentinean hospitality.

The scientific program started on Monday morning with a lecture by A. Moore (Arizona State University, Tempe, USA) where she described the strategies for the structural design and photophysical characterization of the various components of mimetic antenna systems. She also described systems for proton transfer across membranes, where the key feature is the organization of the reaction centers in liposomes. This proton transport was then coupled to Ca<sup>2+</sup> transport. The second talk of the morning was given by F.D. Saeva (Eastman Kodak Company, Rochester, USA) who presented the behavior of electron acceptors with a  $\sigma^*$  LUMO. These compounds, which have a light absorbing chromophore and sulfonium salt moieties, lead to efficient photogeneration of protons. The session was followed by J.C. Scaiano's (University of Ottawa, Ottawa, Canada) lecture on a new fluorescent method to assess DNA damage. Dyes where the fluorescence responds to mobility restrictions were employed because they are able to discriminate between single- and double-stranded DNA. This discrimination is based on lifetime measurements and the application of this method as an analytical tool was described. The last lecture of the morning was given by C.P. Kubiak (University of California San Diego, La Jolla, USA). He spoke about the use of conductance spectroscopy, where the STM tip is brought into close contact with a monolayer of organic compounds on gold. The conductance was shown to depend on the electronic structure and length of the molecules in the monolayer. This technique can be employed to determine the energy of the HOMO level of organic molecules with respect to the Fermi level of gold.

The Monday afternoon session started with the lecture by M. R. Wasielewski (Northwestern University, Evanston, USA) on processes involving electron movements in organic nanostructures. He discussed his results on the modulation of the electronic properties of bridge molecules used as photoswitches, followed by the presentation of an assembled system, containing both an antenna and electron acceptor, where the direction of charge transport was photoswitched. L. A. Monteiro (Universidad de La Habana, La Habana, Cuba) presented theoretical studies on the photochemistry of glyoxal. He showed the various possible deactivation channels, and discussed in detail the decomposition into CO and H<sub>2</sub>. Mechanistic studies on the stereospecific ring opening of cyclobutene were the subject of W.J. Leigh's (McMaster University, Hamilton, Canada) talk. The photochemical ring opening occurs adiabatically from the Rydberg state with conrotatory stereochemistry. The reaction involves twisting and rotation. When rotation is inhibited, a  $\pi, \pi^*$  state is populated and disrotatory stereochemistry is observed. The next lecture was given by T.D.Z. Atvars (Universidade Estadual de Campinas, Campinas, Brasil) on her studies using fluorescence spectroscopy and microscopy to characterize dye-polymer interactions and to study polymer properties. Protic sites in the polymers were characterized and various relaxation processes were identified. Fluorescence microscopy was employed to study the miscibility and phase separation mechanisms of polymers. The last speaker of the afternoon's session was L.A. Bagatolli (Universidad Nacional de Córdoba, Córdoba, Argentina). He spoke about the use of two-photon excitation spectroscopy to investigate the gel-phase coexistence in membranes. The experiments were performed with single, giant unilamellar vesicles, on which images of the different microdomains were obtained. A fluorescent probe was employed that is sensitive to the state of the lipid phase. This technique was also employed to visualize protein-lipid interactions. The first poster session was held before dinner and gave everyone one more opportunity to socialize and discuss science.

The session on Tuesday morning started with F. M. Winnik's (Université de Montréal, Montréal, Canada) lecture on her use of fluorescence to characterize polymer-liposome interactions. The polymers were tagged with fluorescent probes. The interaction of cationic polymers with liposomes covered with anionic polymers showed that the anionic polymers were not removed from the surface of the liposomes when the anionic polymers contained a hydrophobic anchor. In addition, she discussed drug delivery systems that were prepared by coating liposomes with pH sensitive polymers. The next talk, by M.V. Encinas (Universidad de Santiago de Chile, Santiago, Chile), covered the characterization of new photoinitiator systems for free radical polymerization. The flavine/amine photoinitiator system was investigated with the objective of optimizing the efficiency of radical formation. In methanol, a significant amount of radicals is formed from the singlet excited state, but this channel is absent in water. S. E. Braslavsky (Max-Planck Institut für Strahlenchemie, Mülheim an der Ruhr, Germany) presented work on the application of photoacoustic spectroscopy to understand how the nature of the medium affects the volume changes in the ring opening/closing of spiropyran in water and cycloalkanes. The volume changes in water are mainly related to proton transfer, whereas electrostriction is the primary effect in cycloalkanes. The final lecture of this session was given by C. D. Borsarelli (Universidad Nacional de Santiago del Estero, Santiago del Estero, Argentina). He presented how photoacoustic spectroscopy was employed to obtain the partial volume changes of ionic species. The enthalpy and volume changes were obtained simultaneously for the quenching of  $^3[\text{Ru}(\text{bpy})_3^{2+}]^*$  by  $\text{Fe}^{3+}$  in the presence of different counterions. An expansion or contraction was observed depending on the nature of the counterions, and this effect was explained by the formation of a complex between  $\text{Fe}^{3+}$  and the counterions. In addition, he showed results on the determination of the partial molar volume for protons and for electrons in water.

The afternoon session started with the presentation of the Cilento award and the award lecture by E. Wolcan (Universidad Nacional de La Plata, La Plata, Argentina). He presented his work on the photochemistry and photophysics of Rhenium dicarbonyl compounds as monomers and when they are part of polymers. The photophysical behavior in different solvents and polymers were discussed. The results were complemented with pulse radiolysis studies to confirm the identity of the transients seen in the laser flash photolysis experiments. J. M. Riveros (Universidade de São Paulo, São Paulo, Brasil) spoke on the photodissociation of gas-phase ions. Several examples were presented where photodissociation was studied by multi-photon IR dissociation. With this

technique, the structure of isomeric ions can be distinguished. Blackbody dissociation kinetics experiments, applied to the photodissociation of acetophenone, were also discussed. The next talk was given by C.S. Foote (University of California, Los Angeles, Los Angeles, USA) on the photooxidation of guanosine and some model compounds. Mechanistic studies at low temperature were performed on model compounds in order to identify the primary products of the photooxidation reaction. Several products were observed, which were unstable. These products were characterized spectroscopically, and mechanistic possibilities were proposed. The topic of P.F. Barbara's (University of Texas, Austin, USA) lecture was the study of conjugated polymers by single molecule spectroscopy. He showed that a detailed picture of the MEH-PPV polymer structure can be obtained by studying the fluorescence behavior of a single molecule of the polymer. He proposed that MEH-PPV adopts a highly ordered collapsed conformation. The last talk of the afternoon was given by S.B. Yamaki (Universidade Estadual de Campinas, Campinas, Brasil). She described how EVA copolymers are labeled with pyrene by the photoirradiation of 1-pyrenyl-diazomethane. By comparing the photophysical properties of pyrene labeled PE and PVA, she concluded that, for EVA, the labeling occurred mainly on the PE moieties. Finally, the second poster session was held after the talks. After dinner, Michael Kasha (Florida State University, Tallahassee, USA) gave a talk entitled "Four Great Personalities of Science: G.N. Lewis, J. Franck, R.S. Mulliken and A. Szent-Gyorgyi". His recollection inspired everyone in the audience.

The Wednesday morning session started with a lecture by I.E. Kochevar (Harvard Medical School, Boston, USA) on the use of photochemistry to understand how normal oxidizing species react in biological systems. Singlet oxygen was generated close to the cell membrane by irradiating a sensitizer with an evanescent wave. Apoptosis was induced by singlet oxygen production in or near the plasma membrane, but lipid peroxidation is not involved in this process. J.R. Scheffer (University of British Columbia, Vancouver, Canada) followed with his lecture on photochemical processes in the solid state. He covered the strategies to achieve asymmetric induction in crystals, followed by a description of several reactions in the solid state that lead to unusual products. Examples included the formation of oxetanes from the reaction of cyclic ketones and 1,3 phenyl migration for acyclic ketones. The last talk of the morning was given by B.B. Craig (Spectra-Physics, Mountain View, USA) on ultrafast laser sources and their commercial applications. He described the latest laser technologies with regards to

ultrafast pulses. The afternoon was spent on an excursion through the scenic landscape of Córdoba, followed by tea. During the dinner party we were treated to a local barbeque with dancing extending through the night.

The session on Thursday morning started with a lecture by E.A. Jares-Erijman (Universidad de Buenos Aires, Buenos Aires, Argentina) on how fluorescence energy transfer processes, studied using a microscope, can be employed to evaluate molecular proximity in the nanometer range. The FRET modulation was achieved using a photochromic compound with a good fatigue resistance. In addition, time- and spectrally-resolved microscopy was performed using lanthanide chelates. M.S. Platz (Ohio State University, Columbus, USA) followed with a lecture on the photochemistry of blood products. He described his studies on photosensitized methods to inactivate bacteria and viruses in blood. The targets for the photosensitized reactions were nucleic acids, since blood products contain very little nucleic material. Riboflavin was employed for mechanistic studies using time-resolved infra-red spectroscopy and calculations.

The 2001 IAPS award was presented by Fred Lewis, the President of the Society, to M.A.J. Rodgers (Bowling Green State University, Bowling Green, USA). Mike Rodgers dedicated his award lecture to his graduate students, post docs and all young researchers who represent the future of science. He presented work on redox reactions in complexes of metalloporphyrins with native proteins or synthetic peptides. Photoinduced electron transfer was studied in complexes held together by electrostatic interactions. Several donor/acceptor pairs were used in order to change the free energy for the reactions. The results were explained by the reorganizational needs of the donor and acceptor for electron transfer to occur. Molecular dynamics were performed to relate the calculated electron transfer rate constants with the distance between acceptors and donors in the complexes. A good correlation was obtained. The last lecture of the morning was given by H.E. Toma (Universidade de São Paulo, São Paulo, Brasil). He spoke on photophysical and photochemical studies to characterize tetra-ruthenated porphyrins and porphyrazine supramolecular systems. These systems were characterized by Raman spectroscopy, luminescence spectra and electrochemical studies. The compounds described were used for several applications, such as photooxidation of DNA and electrostatic assembly of bilayers. The latter system was used as a sulfite sensor in wine.

After lunch, a lively last poster session was held. Participants enjoyed the beautiful weather as they mingled and discussed photochemistry. The afternoon session started with the presentation of the Closs award to M. Khajepour (University of Missouri-Columbia,

Columbia, USA). The award lecture dealt with the contribution of the solvent quadrupole moment to the solvent reorganization energy studied in an anthracene-dimethylamine derivative. The quenching reaction was studied in various solvents and was shown to be an activated process. In dipolar and quadrupolar solvents, the rate constant is enhanced when compared to alkanes. This difference was explained to be due to differences in the barrier crossing frequencies. G.L. Indig's (University of Wisconsin, Madison, USA) lecture was on chemical aspects of mitochondrial targeting in photochemotherapy. Instead of targeting the tumor vascular system, his approach targets tumor cells directly. The fact that the mitochondria of the tumor cell have a membrane potential that is higher than for normal cells was explored to selectively incorporate the photosensitizers in the malignant cells. The key feature is to use molecules (Crystal-Violet derivatives) that are hydrophilic enough only to partition into the tumor cells. The next lecture was given by D. Whitten (QTL Biosystems, Santa Fe, USA). He described the superquenching of fluorescent polyelectrolytes. Negatively charged fluorescent polymers are quenched much more efficiently by positively charged quenchers due to the strong, but non-specific, association of the quencher with the polymer. This type of superquenching was seen for a variety of polymers. Applications of this phenomenon to biosensors were discussed. T.J. Wallington (Ford Motor Company, USA) talked about the formation of organic aerosols during the atmospheric oxidation of toluene. These studies are related to the formation of smog in urban areas. Toluene was used as a model compound, and the mechanistic studies performed suggest that the oxidation of toluene is involved in a secondary process of smog formation. The next lecture was given by R.J. McMahon (University of Wisconsin, Madison, USA) on possible reactive intermediates, in particular carbenes, that are relevant to the chemistry of interstellar space. Numerous organic compounds have been detected in interstellar space by microwave spectroscopy. Matrix isolation experiments were described where molecules found in space have been spectroscopically detected and characterized. The last talk of the day was given by L. Otero (Universidad Nacional de Rio Cuarto, Rio Cuarto, Argentina). He described experiments on the photoelectronic effects in thin  $\text{SnO}_2$  films generated in the photoinduced charge separation in a porphyrin- $\text{C}_{60}$  dyad. This project focuses on improving the efficiency of solar cells. The synthesis and spectroscopic characterization were described and the efficiency of the photoelectric effect was evaluated.

On Friday morning, L. Kelly (University of Maryland, Baltimore County, Baltimore, USA) described the utility of dually luminescent polymers as temperature and

pressure sensors. The materials were prepared as random copolymers of aromatic hydrocarbons and dialkylaniline. The ratiometric changes in excimer to monomer luminescence as a function of temperature and applied pressure were discussed, and their utility in mapping dynamic flow and temperature fluctuations on 2D surfaces described. O. Martinez (Universidad de Buenos Aires, Buenos Aires, Argentina) presented a new form of high-resolution spectroscopy: field enhanced scanning optical microscopy or FESOM. The field enhancement to scanning optical microscopy was provided by a modulated laser. Optical images with vertical resolution of 0.1 nm were obtained, suggesting the technique may approach atomic resolution. In the next lecture, J. Toscano (Johns Hopkins University, Baltimore, USA) described how time-resolved infrared spectroscopy is used to probe organic reaction dynamics. The technique has been used to probe the mechanism of NO release upon pulsed excitation of diazeniumdiolates. Toscano showed that, by tuning the covalently attached substituents, the undesired formation of nitrosamine was minimized. In the final talk of the conference, M. de Oliveira (Universidade Estadual de Campinas, Campinas, Brasil) continued the theme of photochemical NO release. The photolysis of sodium nitroprusside or SNP produced both NO and cyanide. When the compound was irradiated in poly(ethylene glycol) matrices, the photochemical production of cyanide was inhibited and NO production was selectively favored.

# Organic Photosensitizers to Probe Macromolecular Structure and Dynamics

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Charge transfer reactions involving DNA have received a considerable amount of attention in the literature. A number of published reports have discussed the factors that control the distance dependence of electron transfer.<sup>1,2,3,4</sup> I will not attempt to engage in a discussion long-range electron transfer in DNA in this report. Instead, I wish to provide a perspective on the utility of electronically excited states as structural probes of DNA and proteins. Specifically: “What are the strategies and utilities of developing light-activated compounds to cleave DNA and proteins?” On more occasions than I would like to admit, my friends and colleagues have posed the question: “Why does everyone want to cleave DNA?” While some members of the IAPS community are aware of the relevant strategies and issues, I wish to direct this article to “non-experts” in the community. In this contribution, I will attempt to answer that question and provide a chemical basis for how to carry the reaction out. Specific challenges that lie ahead of us will be discussed. Readers are also referred to an excellent review of “photonucleases” that has recently appeared.<sup>5</sup>

Let’s start with the “why.” Knowledge of the structure of biological macromolecules is crucial to elucidating their function and modifying their reactivity (e.g. for drug design). Aside from diffraction techniques, spectroscopy (nuclear magnetic resonance, fluorescence, UV/Vis electronic, and vibrational) has long been the technique of choice to evaluate static structure and understand dynamic processes. As structures become large, crystallization becomes difficult and resolving overlapping spectroscopic transitions is challenging. An alternative approach is used in molecular biology. Genomic mapping and sequencing have been made possible using natural enzymatic agents to cleave nucleic acids and proteins. These reagents, when used as structural probes, will recognize and cut the target at a specific restriction fragment, leaving manageable fragments to be sequenced and reconstructed. The recent sequencing of the human genome is an example of this familiar to all.<sup>6</sup> Imagine a synthetic system that can mimic the action of nucleases and proteases only after being “triggered” by the absorption of a photon. When successfully developed,

activation of the structural probe can be “timed” with respect to a mixing or folding event. Suddenly, the prospect of studying dynamic processes of large, macromolecular systems unfolds

Footprinting experiments are commonly used to elucidate the protein-binding site in nucleic acid polymers. Typically, diffusible oxygen radicals that will cleave the nucleic acid at “exposed” sites are chemically produced. Hydroxyl radical-like species are most commonly used and are produced from the Fenton reaction of iron (II) with hydrogen peroxide.<sup>7</sup> While the term is often used loosely, the footprinting “reagent” should initiate DNA strand cleavage non-specifically and spontaneously. In other words, all sites should be equally viable targets, and breaking of the strand should not require the addition of post-footprinting reagents. To carry out the footprinting reaction in a time-resolved fashion, the production of the reactive species should be “turned on” at controlled times. In this way, structural dynamics involving the macromolecular complex may be obtained. In fact, it works! Such a strategy has been implemented using pulsed X-ray irradiation synchronized to a stopped-flow mixing device.<sup>8</sup> The method uses hydroxyl radicals that are produced from the radiolysis of water by pulsed X-rays from a synchrotron storage ring. Since the source is pulsed, hydroxyl radical production occurs at fixed times with respect to initiating the folding or mixing event. Although the work has shown great promise, the practical limitations of accessing pulsed X-ray sources has limited the applicability in biophysical chemistry. This is where we come in! As photochemists, we can think about strategies to design a molecule, that can be light-activated by a benchtop laser, to generate reactive and diffusible intermediates. Strategies for doing this and challenges that lie ahead are discussed in this article.

## Mechanisms of DNA Damage.

The principle pathways of DNA photocleavage involve direct interactions with the deoxyribose or base, indirect damage following energy transfer to molecular oxygen, or photogeneration of a reactive oxygen species (e.g. hydroxyl radicals). Direct interactions of the photosensitizer excited state (PS\*) with DNA may lead

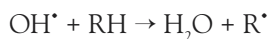
to damage following (i) hydrogen atom abstraction from deoxyribose or (ii) electron transfer from the nucleic acid base (redox-initiated damage). These are shown in Scheme 1. In the first case, spontaneous scission of the nucleic acid strand will occur. Damage will be redox-initiated if the free energy is favorable:

$$\Delta G = -[(E_{1/2}(\text{PS}^*/\text{PS}^\cdot) - (E_{1/2}(\text{B}^+/\text{B}))]$$

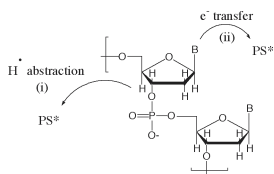
While the individual base oxidation potentials are known,<sup>9</sup> they remain undetermined in DNA, where stacking interactions and solvation will certainly play a role in modifying their values. It is, however, well-established that guanine is the most easily oxidized of all of the bases. Moreover, adjacent –GG– or –GGG– steps, are more easily oxidized, at the 5'-side, than isolated guanines. As a consequence, oxidizing equivalents that are placed on duplex DNA (e.g. by oxidizing any of the nucleobases) will migrate to a guanine trap site. Resultant strand cleavage is not spontaneous, but is induced or “visualized” upon alkali (usually hot piperidine) treatment. In summary, the two mechanisms of damage are quite different and can have different utility as structural probes. The thermal chemistry of the oxidative strand scission of nucleic acids is discussed elsewhere.<sup>10,11</sup>

#### Atom abstraction reactions.

Hydrogen atom abstraction is initiated by a variety of reactive intermediates. It is useful to consider the bond dissociation energies shown in Table 1.<sup>12</sup> Footprinting experiments are generally carried out by initiating hydrogen atom abstraction from deoxyribose. From Table 1, it is apparent that the reaction:



is driven by an exothermicity of ca. 64 kJ/mole. To time-resolve the footprinting reactions, the photochemically produced species should: (1) be produced rapidly following pulsed excitation and (ii) possess sufficient reactivity to initiate the atom abstraction event. Reports of the photoinitiated hydroxyl radical production via homolytic bond cleavage of aromatic hydroperoxides have appeared. Specifically, the utility of the hydroperoxide derivative of 1,8-naphthalimide (Shown in Figure 1) as a



Scheme 1.

“photofootprinting” reagent has been described.<sup>13</sup> Upon UV irradiation, hydroxyl radicals were formed. While hydroxyl radicals were implicated in the DNA damage, the photoinitiated damage did not target the nucleotides in a sequence-neutral fashion, as expected for hydroxyl radical damage.

Aside from hydroxyl radicals, chlorine atoms are viable reactive intermediates for initiating hydrogen atom abstraction from a H-C bond. From Table 1, it is apparent that the energetics for this process are modestly favorable. The analogous reaction with bromine or iodine atoms is energetically uphill. Armitage and Schuster have shown that UV irradiation of anthraquinone in an aqueous solution of sodium chloride induces non-selective, spontaneous cleavage of DNA.<sup>14</sup> A mechanism involving chloride oxidation by the anthraquinone triplet state, followed by hydrogen atom abstraction by free chlorine atoms, was provided. In other work, photoactivated chlorobithiozoles have been shown to effectively initiate DNA strand cleavage following C-Cl bond homolysis.<sup>15</sup>

Finally,  $n-\pi^*$  excited states are well-known to undergo hydrogen atom abstraction processes.<sup>16</sup> The similarity to alkoxy radicals is often used to explain the reactivity observed by  $n-\pi^*$  excited states.

Excited states of uranyl ( $\text{UO}_2^{2+}$ ) ion,<sup>17</sup> rhodium chelates,<sup>18</sup> cobalt(III) bleomycin,<sup>19</sup> anthraquinone derivatives,<sup>20</sup> nitro-substituted imides,<sup>21</sup> and photosensitizer-linked nitrobenzamides,<sup>22,23,24</sup> have shown to be effective at initiating hydrogen atom abstracting.

#### Nucleobase Oxidation.

As shown in Scheme 1, the direct interaction of an electronically excited state with DNA can initiate single electron transfer from a DNA nucleobase. Among the classes of molecules that have been shown to initiate DNA photooxidation are metallointercalators,<sup>25</sup> riboflavin,<sup>26</sup> imide,<sup>21,27</sup> and anthraquinone derivatives.<sup>28</sup> To date, redox-initiated cleavage has been shown to occur only at guanine-rich sites. Results from Barton’s laboratory, using metallointercalators, have indicated that the final site of damage is generally at the 5'-side of –GG– steps.<sup>25,29</sup> Computational studies have supported the hypothesis that these sites are the most readily oxidized.<sup>30</sup>

Singlet excited states of certain planar aromatic systems have been used to carry out nucleotide oxidation.<sup>31,32</sup> Since the excitation energy of singlet states

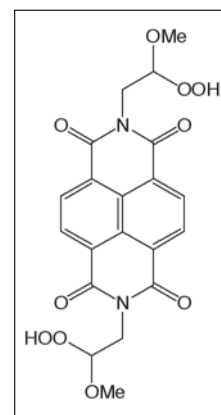


Figure 1.

Bond	Dissociation Enthalpy (kJ/mole)
H-OH	498
H-CH <sub>3</sub>	434
H-Cl	432
H-Br	366
H-I	298

Table 1.



is inherently higher than that of triplet states, singlet states are better electron acceptors. However, a major challenge in using singlet excited states is the rapid charge-recombination that “short-circuits” the redox reaction. If the lifetime of the charge-separated state is not sufficiently long to allow for thermal strand cleavage, the activity of the structural probe is substantially diminished.

In summary, the utility of chromophores that react with DNA via electron transfer is limited: (a) The structural probe is limited to targeting guanine-rich sites; (b) the strand cleavage will not occur spontaneously; and (c) the quantum yield of the process is diminished by charge recombination.

### Naphthalimide-Derived Photosensitizers for Specific and Non-Specific Damage.

Having provided an overview of the “why” and “how,” I will indulge myself by discussing the photochemistry of naphthalene derived imides and their potential utility as diverse structural probes. The naphthalene-derived imide and diimide compounds are shown in Figure 2. These compounds possess a number of desirable properties: (i) they can be readily synthesized from commercially available aromatic anhydrides; (ii) a variety of functional groups can be appended to the imide nitrogen to provide for molecular recognition; and (iii) they possess desirable and tunable redox properties that make them viable for initiating oxidative damage to DNA. It has been shown that L-lysine substituted naphthalene imides, when photolyzed in the presence of DNA, initiate oxidative damage preferentially at the 5'-side of GG steps in duplex DNA.<sup>27</sup> Saito et al. showed that thymine-selective cleavage is initiated by a nitro-substituted 1,8-naphthalimide chromophores.<sup>21</sup> Site-specific cleavage was attributed to hydrogen atom abstraction from the thymine methyl group, not to abstraction from the DNA sugar backbone or electron transfer. In other work, laser flash photolysis of a solution of the naphthalimide derivative and a duplex hexamer revealed production of the imide radical anion concomitant with the decay of the imide triplet.<sup>27</sup> The production of the radical anion was attributed to simple electron transfer to the electronically excited triplet state from a DNA nucleotide (eq 1).

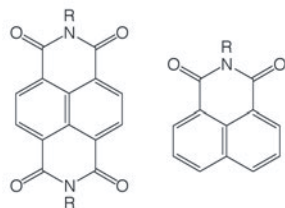
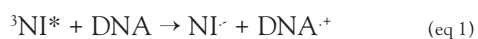
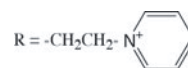


Figure 2.

The quantum yield of damage, initiated by this reaction, was small ( $< 10^{-3}$ ). Subsequent to the report by Matsugo et al., a detailed mechanistic study describing the photochemical deactivation pathways of the hydroperox-substituted naphthalene imides was published.<sup>33</sup> Both reports provided strong evidence for the production of HO. Following  $\gamma$ -hydrogen abstraction and  $-\text{O}-\text{OH}$  homolytic bond cleavage. Significantly, this latter report described a competitive and efficient triplet-state deactivation pathway (eq 2).



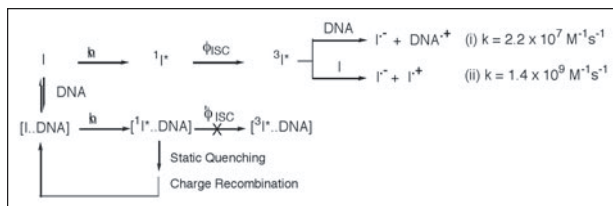
Wishing to take advantage of the redox tunability of the aromatic imides, we embarked on a detailed study of the photoinitiated redox reactions of these compounds. After characterizing the photoredox kinetics for the reactions of triplet state of these compounds with the individual nucleotides, we modified the structures to be water soluble and positively charged. The compounds shown in Figure 2 with cationic substituents R (shown below) were prepared.



The compounds bind very strongly to the anionic backbone of DNA ( $K_b = 2.5 \times 10^4 \text{ M}^{-1}$  and  $7.8 \times 10^5 \text{ M}^{-1}$  for NI and NDI, respectively). When bound, the intersystem crossing yield is significantly diminished relative to free solution ( $\Phi_{\text{ISC}} = 0.08$  and  $0.004$  for NI and NDI, respectively).<sup>34</sup> No long-lived redox products were observed on time scales longer than 30 ps. We attribute the negligible triplet-state yield and lack of redox products to the rapid “static” quenching of the singlet excited state by the nearby nucleotide bases. Since the charge recombination is rapid, no “usable” redox equivalents are produced from DNA-bound naphthalimide or naphthalendiimide. A survey of published reports reveals that, in general, the quantum yield of redox-initiated damage by cationic DNA-bound chromophores is quite low.<sup>26,32</sup>

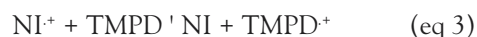
Consistent with the report by Matsugo et al., we also observed a diffusional process that resulted in the production of the naphthalimide radical anion. We initially attributed this species to the diffusional reaction of imide triplet state with DNA (process (i) in Scheme 2). Upon closer inspection and a detailed kinetic study, we found that the primary source of imide radical anions was from the bimolecular self-quenching reaction in bulk aqueous solution (process (ii) in Scheme 2 and eq 2). With the measured bimolecular rate constants for processes (i) and (ii) differing by nearly 2 orders of magnitude, the reaction of the NI triplet state with DNA

is not a viable damage pathway. After an initial reaction of despondence and talk of abandoning naphthalimide photochemistry, we suddenly realized that all is not lost. We have produced, with high quantum efficiency, an oxidizing equivalent ...  $\text{NI}^+$ . The quest for this species began.

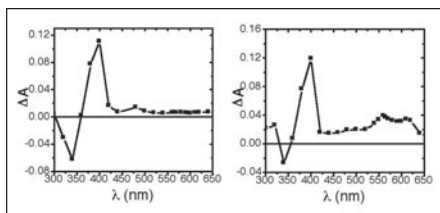


**Scheme 2.** Deactivation processes of “free” and DNA-bound naphthalimide (rate constants shown are those measured for N-(ethylpyridinium)-1,8-naphthalimide).

The radical cation of 1,8-naphthalimide is spectrally invisible in the UV and visible region and could not be directly observed. However, we have verified its production using tetramethyl-1,4-phenylenediamine (TMPD) as a radical trap:



The spectrum of  $\text{TMPD}^+$  is characterized by spectral features at 565 and 610 nm.<sup>35</sup> As shown in Figure 3, the oxidized trap is observed in the transient absorption spectrum of species produced under “self-quenching” conditions.<sup>36</sup>



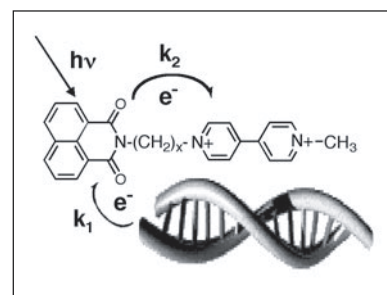
**Figure 3.** Transient absorption spectra observed 50 ms after 355 nm excitation of argon-saturated solutions of 100 mM NI (left) and 100 mM NI with 10 mM TMPD (right).

The kinetics of DNA damage were investigated under conditions where a variety of reactive intermediates were produced.<sup>36</sup> The observed rate of DNA damage was fastest when production of the radical cation was favored. In addition, preliminary data show that the damage induced by this species is not guanine-specific and is spontaneous. In summary, the self-quenching reaction that is usually deemed to be an annoyance to photochemists appears to be a viable route to the efficient production of photofootprinting reagents!

### Promising Pathways to Increasing Long-Lived Radical Yield from Singlet-State Quenching.

As discussed above, the rapid static quenching of singlet states by nearby nucleotides in DNA-bound systems often short-circuits the reaction. As a promising solution to

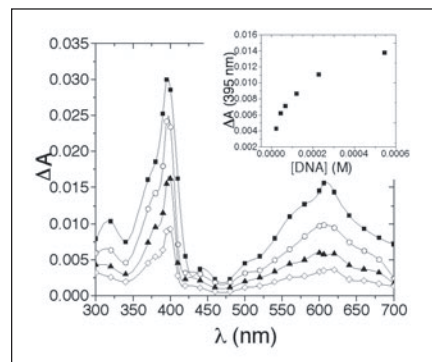
this problem, the addition of a secondary electron acceptor may increase charge separation efficiency by spatially separating the electron and hole. This “cosensitization” approach has proven effective.<sup>29,32</sup> The presence of a “secondary” electron acceptor (usually methyl viologen) has been shown to increase the yield photoredox products by a factor of 10,000.<sup>29</sup> The effect is attributed to the spatial separation of the electron and hole that slows the charge recombination. However, the enhancement generally requires large concentrations of cosensitizer to be present. In the case of our cationic naphthalimide compounds, the chromophores dissociated from DNA upon addition of the cosensitizer. Taking a lesson from photosynthetic reaction centers and artificial photosynthetic systems,<sup>37</sup> we have used a two-component donor-acceptor system to increase the yield of long-lived charge separated states, while keeping the non-covalent ground-state complex intact.<sup>38</sup> The compounds are shown in Figure 4 ( $x = 2 - 6$ ).



**Figure 4.** Schematic of NI-vio dyads to increase charge-separation yield of DNA-bound chromophores.

In aqueous solution, the singlet excited state of the 1,8-naphthalimide is rapidly quenched by electron transfer to the covalently attached viologen ( $k_2 = 1.5 \times 10^{10} \text{ s}^{-1}$  ( $x = 2$ ) –  $8.3 \times 10^7 \text{ s}^{-1}$  ( $x = 6$ )).<sup>39</sup> Charge recombination is rapid, and no redox products are observed by nanosecond laser flash. As DNA is added to the solution, viologen radical is observed in the spectrum (Figure 5), suggesting that nucleobase oxidation by the naphthalimide radical cation is competitive with charge recombination.

The yield of viologen radical increases as the addition of DNA favors formation of the associated complex. In summary, the use of



**Figure 5.** Production of bipyridinium radical cation upon 355-nm excitation of NI-vio ( $x = 4$ ) in the presence of 370  $\mu\text{M}$  calf-thymus DNA (0, 0.6, 2, and 10  $\mu\text{M}$  (decreasing  $\Delta A$ ) after the laser pulse). Inset shows the increase in the radical yield with the addition of DNA. Solutions are argon-saturated and contain 10 mM pH 7.0 phosphate buffer.

covalently attached chromophore-cosensitizer dyad systems provides a strategy for increasing the charge-separation yield as the chromophore/DNA ground-state complex is formed.

To conclude, I hope that I have provided a perspective of the biophysical applications and strategies of photoinitiating macromolecular damage. The development of a photofootprinting assay that can be time-resolved to probe dynamic processes should focus on the rapid and efficient generation of reactive intermediates. The reactive species should possess sufficient reactivity to damage all sites equivalently and spontaneously. In contrast, the one-electron oxidation of nucleotide bases will favor guanine-rich sites. Strategies for overcoming efficient charge recombination should be developed to increase the quantum efficiency of region-specific damage.

#### Acknowledgements.

We would like to thank the American Cancer Society, Maryland Division, and the National Science Foundation for support of this work.

#### References.

- Schuster, G. B. *Acc. Chem. Res.* **2000**, *33*, 253-260.  
Kan, Y. and Schuster, G. B. *J. Am. Chem. Soc.* **1999**, *121*, 11607-11614; Henderson, P. T.; Jones, D.; Hampikian, Y. K.; Schuster, G. B. *Proc. Natl. Acad. Sci.* **1999**, *96*, 8353-8358.
- Hall, D. B.; Holmlin, R. E.; Barton, J. K. *Nature* **1996**, *382*, 731-735; Núñez, M. E.; Hall, D. B.; Barton, J. K. *Chem. Biol.* **1999**, *6*, 85-97.
- R. D.; Wu, T.; Liu, X.; Letsinger, R. L.; Greenfield, S. R.; Miller, S. E.; Wasielewski, M. R. *J. Am. Chem. Soc.* **2000**, *122*, 2889-2902.
- Giese, B.; Wessley, S.; Spormann, M.; Lindemann, U.; Meggers, E.; Michel-Beyerle, M. E. *Angew. Chem. Int. Ed.* **1999**, *38*, 996-999.
- Armitage, B. *Chem. Rev.* **1998**, *98*, 1171-1200.
- Venter, et al. *Science* **2001**, 1304-1351; *Nature* **2001**, *409*, 860-921.
- Tullius, T. D.; Dombroski, B. A.; Churchill, M. E.; Kam, L. *Methods Enzymol.* **1987**, *155*, 537; Tullius, T. D.; Dombroski, B. A. *Proc. Natl. Acad. Sci. USA* **1986**, *83*, 5469; Dixon, W. J.; Hayes, J. J.; Levin, J. R.; Weidner, M. F.; Dombroski, B. A.; Tullius, T. D. *Methods Enzymol.* **1991**, *208*, 380.
- Ralston, C. Y.; Sclavi, B.; Sullivan, M.; Deras, M. L.; Woodson, S. A.; Chance, M. R.; Brenowitz, M. *Methods Enzymol.* **2000**, *317*, 353-368.
- Steenken, S. and Jovanovich, S. V. *J. Am. Chem. Soc.* **1997**, *119*, 617-618.
- Pogozelski, W. K.; Tullius, T. D. *Chem. Rev.* **1998**, *98*, 1089-1107.
- Burrows, C.; Muller, J. G. *Chem. Rev.* **1998**, *98*, 1109-1152.
- Lide, David R., Ed. (1998) CRC Handbook of Chemistry and Physics 79th Edition, pp. 9-51 CRC Press, Boca Raton, Fl.
- Matsugo, S.; Kawanishi, S.; Yamamoto, K.; Sugiyama, H.; Matsuura, T.; Saito, I. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 1351-1352.
- Armitage, B. and Schuster, G. B. *Photochem. Photobiol.* **1997**, *66*, 164-170.
- Quada, J. C., Levy, M. J and Hecht, S. M. *J. Am. Chem. Soc.* **1993**, *115*, 12171-12172.
- Turro, N. J. *Modern Molecular Photochemistry*; Benjamin/Cummings: Menlo Park, California, 1978, Chp. 10.
- Nielsen, P. E.; Hiort, C.; Sönnichsen, S. H.; Buchardt, O.; Dahl, O.; Nordèn, B. *J. Am. Chem. Soc.*, **1992**, *114*, 4967-4975.
- Sitlani, A.; Long, E. C.; Pyle, A. M.; Barton, J., K. J. *Am. Chem. Soc.* **1992**, *114*, 2303-2312;
- Chang, C. -H. Meares, C. F. *Biochemistry* **1982**, *21*, 6332-6334; Saito, I.; Morii, T.; Sugiyama, H.; Matsuura, T.; Meares, C. F.; Hecht, S. M. *J. Am. Chem. Soc.* **1989**, *111*, 2307-2308.
- Breslin, D. T.; Coury, J. E.; Anderson, J. R.; McFail-Isom, L.; Kan, Y.; Williams, L. D.; Bottomley, L. A.; Schuster, G. B. *J. Am. Chem. Soc.* **1997**, *119*, 5043-5044.
- Saito, I.; Takayama, M.; Kawanishi, S. *J. Am. Chem. Soc.* **1995**, *117*, 5590-5591.
- Nielsen, P. E.; Jeppesen, C.; Egholm, M.; Buchardt, O. *Biochemistry* **1988**, *27*, 6338-6343; Buchardt, O.; Egholm, M.; Karup, G.; Nielsen, P. E. *J. Chem. Soc., Chem. Commun.* **1987**, 1696-1697.
- Kuroda, R.; Shinomiya, M. *Biochem. Biophys. Res. Commun.* **1991**, *181*, 1266-1272.
- Karup, G.; Meldal, M.; Nielsen, P. E.; Buchardt, O. *Int. J. Pept Protein Res.* **1988**, *32*, 331.
- Hall, D. B.; Holmlin, R. E.; Barton, J. K. *Nature* **1996**, *382*, 731-735; Hall, D. B.; Barton, J. K. *J. Am. Chem. Soc.* **1997**, *119*, 5045-5046; Stemp, E. D. A.; Arkin, M. A.; Barton, J. K. *J. Am. Chem. Soc.* **1997**, *119*, 2921 - 2925.
- Ito, K.; Inoue, S.; Yamamoto, K.; Kawanishi, S. *J. Biol. Chem.* **1993**, *268*, 13221-13227.

- (27) Saito, I.; Takayama, M.; Sugiyama, H.; Nakatani, K.; Tsuchida, A.; Yamamoto, M. *J. Am. Chem. Soc.*, **1995**, *117*, 6406–6407.
- (28) Armitage, B. Yu, C.; Devadoss, C.; Schuster, G. B. *J. Am. Chem. Soc.*, **1994**, *116*, 9847–9859; Breslin, D. T.; Schuster, G. B. *J. Am. Chem. Soc.* **1996**, *118*, 2311–2319.
- (29) Barton, J. K. *Pure and Appl. Chem.* **1998**, *70*, 873–879.
- (30) Sugiyama, H. and Saito, I. *J. Am. Chem. Soc.*, **1996**, *118*, 7063–7068.
- (31) Brun, A. M.; Harriman, A. *J. Am. Chem. Soc.* **1991**, *113*, 8153–8159.
- (32) Dunn, D. A.; Lin, V. H.; Kochevar, I. E. *Biochemistry*, **1992**, *31*, 11620–11625.
- (33) Aveline, B. M.; Matsugo, S.; Redmond, R. W. *J. Am. Chem. Soc.* **1997**, *119*, 11785–11795.
- (34) Rogers, J. E.; Weiss, S. J.; Kelly, L. A. *J. Am. Chem. Soc.* **2000**, *122*, 427–436.
- (35) Worrall, D. R.; Williams, S. L.; Wilkinson, F. J. *Phys. Chem. B* **1997**, *101*, 4709–4716; Wimalasena, K.; Wimalasena, D. S. *Biochem. Biophys. Res. Comm.* **1991**, *175*, 920–927.
- (36) Rogers, J. E.; Abraham, B.; Rostkowski, A.; Kelly, L. A. *Photochem. Photobiol.* In Press.
- (37) Gust, D.; Moore, T. A.; Moore, A. L. *Acc. Chem. Res.* **2001**, *34*, 40–48.
- (38) Rogers, J. E.; Le, T. P.; Kelly, L. A. *Photochem. Photobiol.* **2001**, *73*, 223–229.
- (39) Le, T. P.; Rogers, J. E.; Kelly, L. A. *J. Phys. Chem. A* **2000**, *104*, 6778–6785.

# Celebration of Michael Kasha's 80th Birthday

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April 14, 2001 was an overcast but warm spring day in Tallahassee, Florida. Those gathered for the celebration of the 80<sup>th</sup> birthday of Michael Kasha were, however, engulfed in the bright intellectual and cultural glow generated by the events honoring Michael who was born on December 6, 1920. This celebration took the form of a rich, scientific symposium in the morning and afternoon followed by a wonderful banquet in the evening.



Photo by Jim Gattis, Florida State University

The 2001 Kasha Award Symposium and Ceremony began at 8:00 a.m. in the Turnbull Conference Center on the campus of Florida State University (FSU). The Kasha Award, which recognizes and stimulates research and promotes quality scientific writing, has been given annually since 1995 to an FSU graduate student in the Molecular Biophysics (MOB) Graduate Program. Students, who are primary authors of papers published in the past two years, are considered for the award after nomination by their major professors. This year a special award symposium was organized by the MOB graduate students and sponsored by the MOB Graduate Program, the Institute of Molecular Biophysics, and the Department of Chemistry. Over 80 scientists were present to hear the fine slate of speakers invited by the students.

After a half-hour of mixing during an energizing continental breakfast, the participants heard welcoming remarks from W. Ross Ellington, Professor and Director of the Institute of Molecular Biophysics, from Naresh Dalal, Professor and Chair of the Department of Chemistry, and from Mohammad Yousef, MOB student and Vice President of Students for the Effective Communication of Science.

The lead-off speaker was none other than the day's honored person Michael Kasha who spoke about "Auroras and Solar Protons." This topic contained once of the foci of Michael's researches, namely proton transfer. However, instead of its usual intramolecular context for Michael,

this lecture involved effects of proton transfer from the sun to the earth.

Each of the remaining guest lecturers were introduced by the MOB student who invited the speaker. Promod Mehndiratta introduced Robin M. Hochstrasser of the University of Pennsylvania. Robin, who in the past worked with Michael Kasha as a postdoctoral researcher, talked about "Infrared Analogues of NMR" and applications of this spectroscopic approach to biological processes.

A change in the original order of the program occurred when Joseph R. Lakowicz of the University of Maryland at Baltimore, who was not feeling very well, needed to present his lecture before he was forced to return to his hotel room. Debbie Kelly introduced Joseph whose talk was entitled "Radiative Decay Engineering." He presented work about the effects metal surfaces on fluorescence and described some biomedical applications of systems involving silver islands.

Elena Falvovskaia, who at the time of this symposium was a graduate student working with Michael, introduced the last speaker before lunch. Alexander P. Demchenko of the A.V. Palladin Institute of Biochemistry, Kiev, Ukraine and of the Tübitak Marmara Research Center, Turkey had been a visiting professor in Michael's laboratory. Alexander gave his lecture on a "New Generation of Fluorescence Probes for Molecular and

Cellular Research." Afterward the participants adjourned for the taking of the group photograph and for lunch.

The afternoon session convened at 1:10 p.m. when Glenn A. Crosby of Washington State University, also a past postdoctoral associate with Michael, was introduced by Cheri Hampton. "Bridging Spectroscopy and Chemistry with  $nd^6$  Metal Complexes" was the title of Glenn's talk about rhenium, rhodium, and ruthenium complexes.

Klaus Schulten of the University of Illinois at Urbana-Champaign talked about "How Nature Harvests Sunlight" after being introduced by Sanguk Kim. He described computational studies on structure and dynamics in photosynthetic systems.

The last guest speaker was Mostafa A. El-Sayed of the Georgia Institute of Technology. Mostafa was one of Michael's Ph.D. students. Mohammad Yousef introduced Mostafa whose topic was "Small is Different: Some Properties of Material Confined to Nanometer Length." He discussed the synthesis, characterization, and spectroscopic properties of gold and platinum nanoparticles.

The final event of this daylong symposium was presentation of the 2001 Kasha Award by Laura Keller, the Director of the MOB Graduate Program, to Junfeng Wang who is an MOB student working with Timothy Cross.

Throughout the day there were lively discussions of the research that was presented and fond reminiscences of time spent in Michael's laboratory and of associations with him made across Michael's broad range of interests.

The festivities associated with the evening banquet commenced with cocktails at 6:30 p.m. in the third floor dining room of the University Center Club on the campus of Florida State University. The program announced that this banquet is in celebration of the 40<sup>th</sup> anniversary of the Institute of Molecular Biophysics, the 80<sup>th</sup> birthday of Michael Kasha — its founder, and the 50<sup>th</sup> year of Michael Kasha's faculty service. It was sponsored by the Institute of Molecular Biophysics and the Department of Chemistry.

As he did for the symposium, Ross Ellington, Director of the Institute of Molecular Biophysics, provided opening remarks to the 235 people gathered from near and far for the banquet and introduced special guests.

After a very enjoyable hour and a half of dining, we were treated to a delightful 45-minute concert by Brazilian master guitarist Antonio Carlos Barbosa-Lima who played a Kasha classic guitar to perform twelve works by Villa-Lobos, Bonfá, Lecuona, Madriguera, Yasui, Gershwin, Cordero, Barrios, and Barroso.

Next, Naresh Dalal, Chair of the Department of Chemistry, gave a brief introduction of the honoree. Michael Kasha then took the stage to end the day in the manner that he began it — to give a presentation. This lecture was much less technical than the one given in the morning. It was well received by the diversity of friends, colleagues, and family who were present.

With that twinkle in his eyes and engaging smile on his face, Michael treated his audience to thirty minutes of reminiscences of personal, scientific, and artistic aspects of his life. We enjoyed it very much. Ross Ellington sent us on our ways with a few closing remarks.

The variety of interests of the speakers and participants in the symposium and of the guests at the banquet along with the range of scientific topics and artistic offerings of this celebration day reflected well Michael's Kasha's impact and the appreciation of him by his friends and associates.



Photos by Stephen Leukanech, Florida State University

# Glossary of Terms in Photocatalysis and Radiocatalysis<sup>1</sup>

## {A Preliminary Version of IUPAC's Project # 2001-036-1}

November 21, 2001

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## Glossary of Terms in Photocatalysis and Radiocatalysis

**Synopsis:** This document has two principal goals. First, it summarizes some of the issues that pertain to the complexities encountered in photocatalysis. Secondly, it presents a glossary of terms proposed to describe those phenomena, which fall under the umbrella of "photocatalysis" and "radiocatalysis". A distinction is made between the different phenomena that are related to either or both photochemistry and photocatalysis, and to radiation chemistry and radiocatalysis. Consistent definitions of terms in these areas are given. Definitions of important parameters that describe photocatalytic and radiocatalytic phenomena quantitatively are also proposed. As with the related Glossary of Terms in Photochemistry, this document is a dynamic working document, which will need to be revisited from time to time as the field progresses and new discoveries reported. Some of the terms used in photochemistry are also given here for completion, either verbatim or modified to address the issues of photocatalysis.

## Note To The Reader:

This *preliminary version* of the Glossary of Terms in Photocatalysis and Radiocatalysis is IUPAC's Project No. 2001-036-1. It is being made available to a worldwide readership through several Journals and Newsletters of photochemistry and catalysis. It is also posted on the I-APS web site. The intent of the authors is to seek the community's (at large) views, comments, and suggestions that will improve this document for ultimate submission, acceptance and publication of the final version to the appropriate Division(s) of IUPAC. The authors would sincerely appreciate it if the views, comments and suggestions would be forwarded to both senior authors at the email addresses indicated no later than June 30, 2002.

(1) People consulted during the preparation of the earlier versions of this document: Yu. Aristov (Russia), D. Bahnemann (Germany), J. Bolton (Canada), A. Cassano (Argentina), L. Koopal (The Netherlands), L. Palmisano (Italy), V.K. Ryabchuk (Russia), E. Savinov (Russia).

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