

IAPS NEWSLETTER

2006



2006

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Letter from the President

Cornelia Bohne
I-APS President (2006-08)

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August, 2006

Dear Colleagues,

I became president of the society a few days after the 17th I-APS Winter Conference held in Salvador, Brazil in June. The meeting was a great success with more than 150 participants, which included about 60 students. The informal atmosphere, leading to vibrant scientific discussions, showed how well integrated the South and North American photochemical communities are. The participation of so many young photochemists bodes well for the future of the photosciences and of the society. During the meeting the society awards were presented to Dan Nocera (I-APS award), Mohammad A. Omary (Young Investigator Award), Ryan C. White (Closs Award) and Franco M. Cabrerizo (Cilento Award). In addition, Frank and Sally Mallory were recognized as the newly elected I-APS Fellows. Congratulations to all awardees. I do want to thank Jack Saltiel and Frank Quina the co-chairs of the meeting, and José Carlos Netto-Ferreira, the chair of the local organizing committee, for the excellence of the science and the very Brazilian social program.

Further news on awards is that Howard Zimmerman and Hiroshi Masuhara were this year's winners of the Porter Medal, which were presented at the IUPAC meeting in Kyoto. The Medal, named for George Porter (Nobel Laureate), is awarded to the photochemist who, in the opinion of the Panels formed by the European Photochemistry Association, the Inter-American Photochemistry Society, and the Asian Photochemistry Association, has contributed most to the science of photochemistry. On this occasion, and unusually, the Panels have decided to award two medals.

The society has recently elected its new executive members. Kirk S. Schanze is the Vice-President and President-Elect. Phil Castellano, Hans-Peter Looock and John P. Toscano are replacing Brad Arnold, William Jenks and Mitch Winnik on the advisory board. The new newsletter editor is Igor Alabugin, who is replacing Linda A. Peteanu. The new Canadian treasurer is Glen Loppnow (replacing myself), while William Jenks (replacing Lisa A. Kelly) is the new US treasurer. The executive in Brazil also decided to invite Peter Ford, as Past-President, to be part of the executive of the society. I would like to thank all officers leaving the executive, and Peter in particular, for their hard work and leadership. Also, welcome to all new members, I am looking forward to work with you all.

One of the difficult decisions taken in the spring was the date for the next I-APS Winter Conference, which will be held at a venue in Florida. Linda A. Peteanu and John P. Toscano

have agreed to co-chair this next meeting. We decided not to have a meeting in January of 2007, because the meeting in Brazil was held in June and there are several other meeting with focus on photosciences in the next few months. The next meeting will be in early January 2008 and the location in Florida will be determined in the near future. However, we decided that the society would not cancel the nominations for the 2007 I-APS awards, and we will have presentations to award winners for 2007 and 2008 at the next meeting. Kirk Schanze is coordinating the nomination process and the deadline for the 2007 nominations is December 1. Details can be found on the I-APS webpage (<http://www.i-aps.org/>). I would like to ask you all to think and act on suitable nominations. It is important that the society recognize the achievements of our members.

One of the challenges that we encounter as a society is that, because of the great success of our field, photosciences are now relevant to many other fields of science. This poses a challenge in attracting scientists in these new fields to the society. More importantly, it actually is an opportunity to broaden the scope of the membership and I will be working with the board in a drive for new members to the society. If you have an opinion or suggestions on membership please let me know.

Best regards,



Cornelia Bohné

Letter from the Newsletter Editor

Dear Colleagues,

Very soon after taking the job as the I-APS newsletter editor, I realized how much effort had Linda Peteanu put into the newsletter. On behalf of all I-APS members, I would like to thank Linda for her dedication and hard work as the previous I-APS Newsletter Editor.

Reflecting activities and achievements of such a vibrant and diverse organization as I-APS is not a “one man job” and I am grateful to everyone who helped me in putting this issue together. My special thanks are to Silvia Braslavsky for blending skillfully the true South American spirit with insightful scientific analysis in her report on the last I-APS conference, to Andrei Kutateladze and Jai P. Mittal, for their thorough and engaging biographical essays on the 2006 Porter laureates and to 2006 I-APS awardee, Dan Nocera for sharing fascinating research findings published in this issue of the newsletter, and to Jim Pincock, Dick Weiss and Carl Wamser for sharing their memories of Don Arnold and George Hammond.

To be effective and provide you with up-to-date information, I will need your help. Please send me important news that you would like to share with other Society members. In particular, I am always looking for volunteers to cover recent conferences related to all aspects of “photosciences” such as photochemistry, photophysics and photobiology.

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2007 I-APS Awards

You are urged to submit nominations (deadline Dec. 1, 2006) for the *2007 I-APS Award in Photochemistry*, for the *2007 I-APS Young Investigator Award* and for the *I-APS Fellowships* to

Kirk S. Schanze
Chair- IAPS Awards Committee
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Procedures for nomination for these awards and for the *2007 G. Cilento Award* and the *2007 Gerhard Closs Student Award* are described in detail on the I-APS website at http://www.i-aps.org/awards_nom_procedure.html

2006 PORTER AWARDS

The Porter Medal Committee announced the winners of the 2006 Porter Medal. The Medal, named for George Porter, [Nobel Laureate], is awarded for outstanding contributions to the science of photochemistry. On this occasion, and unusually, the Panels have decided to award two medals, one each to the individuals below.

Professor Howard E. Zimmerman, University of Wisconsin, Madison, USA, one of the founders of modern organic photochemistry, who contributed over a lifetime's work to our understanding of fundamental processes in excited states.

Professor Hiroshi Masuhara, Osaka University, Japan, for his pioneering work on the integration of time and spatially resolved measurements on the emerging fields of nanosciences.

The medals were presented at the XXI'st IUPAC Symposium on Photochemistry, Kyoto, Japan, 2nd-7th April 2006.

Howard E. Zimmerman, the 2006 Porter Medal Laureate



A native of Connecticut, Howard Zimmerman graduated from Yale in 1950, with the Chittenden Award (given to the top B.S. student at Yale), majoring in chemistry with minors in math and German. His undergraduate years and research with Harry Wasserman were preceded by a tour of duty in the European theater as a tank gunner, which gave him his lecture (aka the "Sarge") voice, somewhat impaired his hearing, but most importantly made him mature and taught him not to waste time, work hard and always try to run ahead of the pack which, six decades later, is still Howard's *modus operandi*. He completed his PhD studies with English at Yale in 1953 and joined R.B. Woodward's lab as a Lilly National Research Council postdoc. In 1954 he started his independent faculty career at Northwestern University where, among other things, he published seminal papers on the stereochemistry of ketonization of enols and kinetic protonation, and introduced what is now known as the *Zimmerman-Traxler* transition state for the aldol condensation (the concept is used widely

in synthetic chemistry). It was at Northwestern where Howard's passion for theory and computations started to blossom. His early studies on carbanion rearrangements (the *Grovenstein-Zimmerman* rearrangement) and their theoretical description with MO theory, including the first organic correlation diagrams (predicting reaction allowedness), along with work of Havinga, Longuet-Higgins, Streitwieser, Daudel and others, contributed a lot to the development of new ideas in theoretical organic chemistry in the early 60's, culminating with Woodward-Hoffman's generalizations published in '65 and '66.

In 1960 Zimmerman moved his laboratory to Wisconsin where he took the experimental and theoretical mechanistic chemistry to a new and literally exciting level - the theory of photochemical reactions; initiating the lifetime work that made him a founding father of modern mechanistic organic photochemistry. Arguably, the most notable among his numerous contributions to the field are: the theoretical basis for meta electron transmission in excited states; the Möbius-Hückel concept for reaction allowedness and forbiddenness, with the Möbius counterpart of the Frost-Musulin's mnemonic; the free rotor-effect for energy dissipation of electronic excitation; polarizability predictions of organic reactions; evidence on the relative roles of conical intersections and energy barriers in photochemistry; development of quantitative theories for solid-state reactivity; and the Delta-Density Matrix method of predicting both excited and ground state reactivity. His experimental work uncovered numerous new photochemical transformations for which he provided a modern mechanistic rationale: the Type-A and Type-B rearrangements of unsaturated cyclic ketones, first synthesis of barrelene and

the mechanism of di- π -methane rearrangement, which now carries his name; the discovery of semibullvalene and its very facile tautomerism; the α,β -epoxyketone rearrangement to β -diketones and its mechanism; the triplet rearrangement of vinylcyclopropenes to cyclopentadienes; the photochemical rearrangement of cyclohexenone to vinylcyclobutanone; and the tri- π -methane rearrangement. From the early sixties Zimmerman was preaching an integrated experimental and theoretical approach to treating the reactivity of excited states. He was among very few mechanistic organic chemists who were capable of bridging the gap between rigorous quantum mechanical computations and the classical (simple and elegant) electron pushing schemes. His theoretical deductions were augmented with state of the art computations, be it the programming of PDP-11 to carry out CI matrix diagonalization in 70's, or running in-house modified Gaussian or Gamess packages to dissect spin-orbit coupling in NHO basis in the 90's.

Zimmerman has a prolific mentoring track record – 86 of his former students or postdocs went into academia and gained tenure. About the same number took industrial jobs.

His celebrated accomplishments are acknowledged with numerous awards, including the first Northeast ACS Award for Photochemistry (1971), the ACS James Flack Norris Award in Physical Organic Chemistry (1976), the Halpern Award of the New York Academy of Sciences (1980), election to the National Academy of Sciences (1980), the American Institute of Chemists Pioneering Award (1985), a Senior Alexander von Humboldt Award (1988), the Hilldale Award in the Physical Sciences from the University of Wisconsin (1990), and the Arthur C. Cope

Scholar Award of the ACS (1991).

Now the Porter award crowns this list. Still going strong, Zimmerman turns 80 this summer. Congratulations Howard!

Andrei Kutateladze,
University of Denver

Hiroshi Masuhara, the 2006 Porter Medal Laureate



Hiroshi Masuhara was born in Tokyo in 1944 and started his career in the Department of Chemistry at Tohoku University in Sendai under the supervision of Prof. Masao Koizumi, who is one of the pioneers in photochemistry in Japan. After taking the Master Course, Hiroshi moved to Professor Noboru Mataga's laboratory in Osaka University in 1968. A nanosecond ruby laser was available there which he used to measure, for the first time, the excited singlet-singlet absorption spectra of electron-donor-acceptor (EDA) complexes. His Ph.D. thesis completed in 1971 was entitled "The Electronic Structure and Dynamics of the Electron Donor Acceptor Complexes in the Excited Singlet State". This research heralded the start of the nanosecond era in Japan, which of course was followed quickly by picosecond photochemical studies. With Professor Mataga and several students, he conducted systematic studies on EDA complexes and exciplexes, and elucidated their electronic structure and dynamics.

Much of this pioneering research on electron transfer, ionic dissociation, triplet formation, and non-radiative relaxation was summarized in *Accounts Chemical Research*, 1981, 14, 312. Around 1980 Hiroshi's interest gradually shifted to molecular aggregates and polymers in solution, and then to their films and powders. The detection technique also shifted from absorption to reflectance spectroscopy, and his efforts became focused on improving the time-resolution.

In 1984 he was appointed Professor in Faculty of Textile Science and Engineering of Kyoto Institute of Technology, and there the exceptional high standard of his work and his ingenuity were recognized and ERATO (Exploratory Research of Advanced Science and Technology) Masuhara Microphoto-conversion Project was funded by Japan Science and Technology Agency for 1988-1994. Through his systematic research, Hiroshi understood that photochemistry was expanding and laser chemistry was becoming more important as a new tool which induces heating, high pressure, expansion, melting, fragmentation, and even mechanical force in addition to laser induced chemical reactions. Furthermore this tool can be conducted freely in space at arbitrary times. Hiroshi recognized the importance of interdisciplinary areas of photochemistry and understood deeply the high potential of photochemistry in modern science and technology. He and his group started to explore new photochemical and photophysical phenomena by developing time-resolved grating, scattering, and various micro/nano spectroscopies, fs-ns imaging techniques, and micro/nano manipulation and patterning methods, and several new interdisciplinary areas of molecular photoscience were initiated. Hiroshi moved to his present position as Professor in the Department of Applied Physics at Osaka University in 1991 where he continues to carry out innovative research

of the highest standard. Hiroshi Masuhara's pioneering and seminal contributions cross borders of many research fields such as materials science, physics, optics, and lately even bioscience. His seminal contributions are summarized as follows:

1. Time- and space-resolved photophysics and photochemistry of organic nanomaterials.
2. Time-resolved spectroscopy and time-resolved imaging of nonlinear photochemical processes: From laser ablation to protein crystallization.
3. Manipulation by the photon pressure of a focused laser beam: Laser trapping dynamics and laser-induced chemistry of individual nanoparticles.

For this pioneering work on the integration of time and spatially resolved measurements in the emerging fields of nanosciences, he was awarded the 2006 Porter Medal under the title of "Pioneering Laser-induced Time- and Space-resolved Micro/Nano-size Photochemistry"

Hiroshi Masuhara has contributed to the photochemistry world not only in scientific research but also as a member of associations and editorial boards and in organizing international conferences. He has worked as a member of IUPAC Photochemistry Commission (1998-2001), was the President of Japanese Photochemistry Association (2000-2001), and was largely responsible for the formation of the Asian and Oceanian Photochemistry Association of which he became the first President in 2002. He has served on the editorial boards of 13 International journals dealing with physical chemistry and photochemistry, and in 2003 he was a joint chairperson of the 21st International Conference on Photochemistry held in Nara, Japan.

Hiroshi Masuhara's scientific achievement has been recognized widely and resulted in his receiving the Japanese Photochemical Association

Award (1989), the Moet Hennessy Louis Vuitton International Prize "Science for Art" Da Vinci of Excellence (1993), the Divisional Award of Chemical Society of Japan, the Osaka Science Prize (1994), the Chemical Society of Japan Award (2006), and the Japan Spectroscopy Society Award (2006). He was also honored by being selected as a Foreign Member of the Royal Flemish Academy of Science, Literature, and Art of Belgium in 1998 and he is still serving as a Member. He has been a Guest Professor at several Universities in Europe as well as in Japan.

Hiroshi Masuhara's pioneering work has attracted many young researchers and graduate students to join his group. At present more than 40 doctors from his research group are working in relevant areas of molecular photoscience as Professors and researchers. His seminal research work has been reported in over 430 original and innovative publications and in 13 books, which he and his friends have edited and written. Hiroshi Masuhara's contribution to modern photochemistry is unparalleled and what he has brought to this field is highly innovative and of great lasting significance. In addition to his scientific excellence, he is also famous as a wonderful host, inviting foreign and domestic visiting scientists to his home. He enjoys cheerful conversation with delicious dinners, which are expertly prepared and presented by his charming wife, Nobuyo Masuhara. Every scientist who has been invited to their pleasant home for dinner will never forget their hospitality and the warm smiles. It is great pleasure for us to celebrate his 2006 Porter Medal and to wish his further successes and happiness in his coming years.

J. P. Mittal, *President of Asian and Oceanian Photochemistry Association*

2006 I-APS Awards

2006 I-APS Award in Photochemistry was awarded to Professor **Daniel G. Nocera** of the Massachusetts Institute of Technology. Daniel G. Nocera is the W. M. Keck Professor of Energy at the Massachusetts Institute of Technology.

Dan Nocera earned his B.S. at Rutgers University where he was a Henry Rutgers Scholar, obtaining a B.S. degree in 1979 with Highest Honors and a Ph.D. at California Institute of Technology in 1984 where he investigated the electron transfer reactions of biological and inorganic systems with Professor Harry Gray. He began his independent academic career in Michigan State University and moved to MIT as a Professor of Chemistry in 1997.

Nocera received the American Institute of Chemists Award upon his graduation from Rutgers University. At Caltech he was a Sun Company Fellow. Nocera has been honored as a recipient of a Dreyfus Foundation Grant for Newly Appointed Young Faculty, a Sigma Xi Junior Research Award, and he was appointed a Presidential Young Investigator and an Alfred P. Sloan Fellow. He was named a College and University Distinguished Professor in 1996 and 1997, respectively. In 2005, he was awarded the Italgas Prize and was elected to the American Academy of Arts and Sciences. He serves on the Editorial Boards of *Accounts of Chemical Research*, *Inorganic Chemistry*, *Journal of the American Chemical Society* and *Comments in Inorganic Chemistry*. He was the inaugural Editor of *Inorganic Chemistry Communications*.

Below are excerpts from the nomination of a letter written by Professor

Jim McCusker (Michigan State): "Professor Nocera has been a major force in the field of inorganic photochemistry and photophysics for nearly two decades, and I'm honored to be forwarding his nomination to you for this prestigious and well-deserved award.

After carrying out the first experiments on electron transfer in Ru-modified proteins as a graduate student with Harry Gray (experiments that are now a hallmark of research on protein electron transfer), Dan began his own career at Michigan State exploring multielectron chemistry. Nocera's research started with exquisite studies on the photophysics of quadruply bonded transition metal complexes. This early work on the $\delta\delta^*$ excited states of dinuclear Mo and Rh complexes paved the way for two of his recent and most important contributions to chemistry. One of these is what many have dubbed the first complete picture of a two-electron bond. ... An important consequence of a two-electron bond is that it should give rise to four multielectronic states (a ground state and three excited states). Other workers (e.g., F.A. Cotton and Harry Gray) had detailed three of the four requisite states for a prototypical quadruple bond, but the $\delta^*\delta^*$ excited state remained elusive. In 1999 Nocera published a communication in *J. Am. Chem. Soc.* which showed the two-photon excitation spectrum of a quadruply-bonded species; these data enabled the unambiguous identification of the $\delta^*\delta^*$ state. This difficult experiment provided the critical last piece of the experimental puzzle and represents an important contribution to our fundamental understanding of chemical bonding.

Far more significant than completing the Heitler-London picture, in my opinion, has been Nocera's exploitation of multielectronic excited states to establish new paradigms of reactivity in excited-state chemistry. Nature thrives on its ability to carry out multielectron reactions (e.g., nitrogenase, photosynthesis); in contrast, the vast majority of chemical and photochemical reactions chemists have been able to come up with are one-electron processes. Very

recently, there have been two notable developments in this area: (1) the catalytic conversion of N_2 to NH_3 by Schrock and co-workers; and (2) the catalytic photochemical production of H_2 from halohallic acid reported by Heyduk and Nocera in 2001. I was deeply impressed with this research on a number of levels. Heterogeneous systems for H_2 production are certainly known, and homogeneous systems that produce H_2 stoichiometrically have been around for at least two decades. However, Nocera has produced the first truly catalytic system for the homogeneous production of H_2 using light to drive the reaction. People have suspected that it should be possible to photocatalytically produce a fuel such as H_2 , but Nocera's work is the first to show at least one way how to do it. He has in effect opened the door, the significance of which should not be underestimated. I was no less impressed by the way in which this result built on the basic research that Nocera has carried out over the years on multielectron excited states. Of particular note is the notion of two-electron mixed-valency, a concept that Nocera developed several years ago and was able to incorporate into the design of his catalyst. This design feature proved to be the key ingredient: the production of H_2 has as its linchpin a two-electron mixedvalency in the molecular catalyst at the critical stage of catalytic turnover.

I can't think of a more appropriate way to credit Nocera's insight and scientific acumen. In short, this result represents a watershed in photochemical research. It is the culmination of years of hard work – creatively conceived and meticulously developed – that I believe will prove to be the genesis of a revitalization of this area of science in the years ahead.

The H_2 production work cited above in large part represents one half of a comprehensive effort in his group to address the water splitting problem. Recognizing that it is the oxidative part of that equation that represents the toughest hurdle, Nocera has developed compelling new systems for activating H_2O toward

$\text{O}=\text{O}$ bond formation with his “hangman” and “Pacman” porphyrins. He recently published a remarkable X-ray structure of one such porphyrin system with the H_2O molecule precariously positioned above the Fe center, in essence a snapshot for the first stage of H_2O activation. With this work, Nocera has thus turned his attention to what is arguably one of the most significant problems facing society today, namely the impending energy crisis. His combination of scientific insight and charismatic energy is helping to bring much needed visibility to this daunting but critically important area of photochemical research.

In addition to multielectron excited-state chemistry, the second major area that Nocera has pioneered is proton-coupled electron transfer, or PCET as it is now widely known. The notion that electron transfer and proton transfer can occur as coupled processes certainly did not originate with Dan Nocera. However, coming up with a chemical system that allows one to probe these reactions – and ultimately to decouple them – represents a difficult task but one whose success would impact a range of problems in both chemistry and biology. In 1992 Nocera published a paper that I believe can be regarded as ground zero for the field of mechanistic PCET. In this work, Nocera designed a donor/acceptor system consisting of a Zn porphyrin (the donor) and 3,4-dinitrobenzoic acid (the acceptor). Photoexcitation of the Zn porphyrin yields a $^1\pi\pi^*$ excited state which is then oxidized by 3,4-dinitrobenzoic acid. The dinitrobenzoic acid is hydrogen-bonded to an acid residue on the periphery of the porphyrin, thus driving electron transfer through the hydrogen bond linking the two moieties. The observation of a deuterium isotope effect of ~ 1.7 helped to establish the importance of proton transfer in the electron transfer event, but more importantly established the viability of this platform for detailed mechanistic investigations of PCET at the molecular level. Nocera then went on to expand upon this work to investigate electron transfer through salt bridges. Thanks largely to these and related efforts,

PCET is now part of the common vernacular in the field of electron transfer: many groups around the world pursuing its study both experimentally and theoretically can look to Nocera for opening up this field.

Nocera's research on hydrogen-bonded and salt-bridge systems laid the groundwork for studies of PCET in biological systems. Recently, Nocera has been making profound contributions to our understanding of the biochemistry of ribonucleotide reductase (RNR) as well as models for small-molecule activation where both proton and electron transfer are involved in catalytic oxidation processes. Again, as with his work on multielectron excited-state chemistry, Nocera has built upon fundamental studies of PCET and expanded on them to demonstrate their importance in a wide range of contexts.

The hallmark of Dan Nocera's research has always been his creativity combined with a remarkable and unparalleled vision of the broader impact of the problems he has chosen to pursue. Photochemistry and photophysics have always been at the core of his efforts, but over the years the scope of his science has extended beyond chemistry to biology and even engineering. Dan Nocera's work defines not one but two extremely important areas of chemistry. This is remarkable in and of itself, but I feel certain that even greater science is on the horizon. I can think of no one in the field of photochemistry more deserving of the I-APS Award in Photochemistry than Dan Nocera and urge the committee to recognize his outstanding contributions to our field."

2006 I-APS fellowship in recognition of lifetime scientific accomplishments and service to photochemical science was awarded to Frank and Sally Mallory. Frank Mallory is a W. Alton Jones Professor of Organic Chemistry at Bryn Mawr College. Sally Mallory is a Senior Lecturer at the University of Pennsylvania. While they

teach at different institutions, they established a highly productive collaboration conducted at Bryn Mawr which predates their marriage and continues strong for more than 40 years. They are the first team of scientists recognized by an I-APS award. A short quote from the nomination letter by Fred Lewis: "Frank and Sally have been active contributors to the photochemical literature for over 40 years. They are best known for the development of the synthetic scope of the photochemical conversion of cis-stilbenes to phenanthrenes, an exceedingly useful transformation which has become commonly known as the "Mallory Reaction."

This reaction was discovered by Frank when he was a graduate student at Caltech and studied for the first time in a systematic manner by Sally in her PhD thesis at Bryn Mawr which included about 20 carefully chosen molecules. A review co-authored by Frank and Sally twenty years later included more than two thousand examples and the scope of this very useful transformation continues to expand. In particular, Frank and Sally illustrated in their own work that the Mallory reaction provides a very convenient approach to ribbon-like polycyclic aromatic compounds.

2007 I-APS Young Investigator Award was presented to Mohammad Omary of North Texas University. Mohammad received his B.S. and M.Sc. from Yarmouk University and his Ph.D. in Physical Inorganic Chemistry from the University of Maine in 1997 working with Howard H. Patterson. In 1997-1999, he was a Faculty Fellow at Colby College. He spent the summer of 1998 as a Visiting Assistant Professor at the University of Maine. After postdoctoral research with John Fackler at Texas A&M University, 1999-2001, he started his at the University of North

Texas where he was promoted to Associate Professor in 2006. He received NSF CAREER Award in 2004.

In his nomination letter, I-APS Past President Peter Ford mentions that Mohammad “has generated an outstanding record of independent research accomplishments in studying the fundamental photochemistry and photophysics of transition metal complexes, especially the coinage metals, as well as in translating of those accomplishments into the design of new photo optical devices. He has attracted an impressive collection of collaborators and has clearly established himself as an important player in the fields of photochemistry and inorganic chemistry.”

2006 Closs Award was received by **Ryan C. White**, a graduate student at the Department of Chemistry at UNC–Chapel Hill. Brian earned his B.A. in Chemistry at University of San Diego with Mitchell Malachowski and his Ph.D. in Organic Chemistry at the University of North Carolina with Malcolm Forbes where he studied amino acid and peptide radicals and radical cations and their use as probes for aqueous microenvironments.

His advisor Malcolm Forbes writes in his nomination letter: “Ryan has been working on the oxidation of amino acids and short peptides, studying the structure, reactivity and molecular dynamics of radicals and radical cations using time-resolved electron paramagnetic resonance (TREPR) spectroscopy. He has shown diligence in pursuing this work, and it has been a pleasure to watch him evolve to become the intellectual driver of this project. ... Ryan has painstakingly put together a series of careful computer simulations to provide, for the first time, an unambiguous set of hyperfine coupling

constants and chemical shifts radical cation of methionine. It is not an exaggeration to say that this paper represents some of the best work to ever emerge from my laboratory.”

In 2005, Ryan had been awarded a 10th Anniversary Junior Scientist Fellowship from the Civilian Research and Development Foundation, allowing him to travel to Russia and to extend his studies of amino acid oxidation using time-resolved CIDNP and laser flash photolysis (LFP) techniques with our collaborators at the International Tomography Center in Novosibirsk. His was only one of 10 fellowships awarded nationally across all fields of science by the CRDF.

2006 Cilento Award was received by Franco M. Cabrerizo. Dr. Cabrerizo earned his Ph.D. degree in the research group of Dr. Alberto Capparelli in the INIFTA-Universidad Nacional de La Plata (La Plata, Argentina) working on photochemistry and photophysics of pterins. He is currently a post-doctoral fellow and as a research member of CONICET (Consejo Nacional de Investigaciones Cientificas y Tecnicas) working under the supervision of Professor Rosa Erra-Balsells at the Facultad de Ciencias Exactas y Naturales - Universidad de Buenos Aires (Buenos Aires, Argentina) where he studies chemistry and photochemistry of the desorption/ionization process in UV-MALDI ionization method. In her nomination letter, Dr. Rosa Erra-Balsells points out that “Dr. Cabrerizo is an enthusiastic and hard-working researcher with broad experience and deep knowledge of photochemistry and photophysics who fully deserves the Cilento Award.”

Photographs from the I-APS Award Session



2006 I-APS Award Winner Dan Nocera



Frank and Sally Mallory are 2006 I-APS Fellows!



I-APS President Peter Ford congratulates 2007 I-APS Young Investigator Award Winner Mohammad Omary (on the left)



Franco M. Cabrerizo (on the left) receives the Cilento Award from I-APS Vice President Cornelia Bohne



2006 Closs Award Winner Ryan C. White (on the left) shares a laugh with Jack Saltiel

Microlasers for High Gain Chemo-/Bio- Sensing on Small Length Scales

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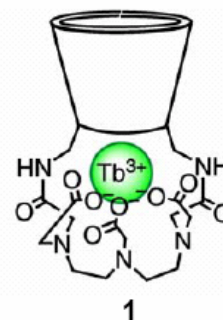
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We have sought to develop methods to enable sensing on small-length scales by combining chemosensing with optical nanoscience. The payoff of such an approach is the realization of widely distributed sensing networks that are inexpensive, easy to implement and not encumbered by the intricacies and complications posed by single molecule detection schemes. The integration of optical chemosensing with nanoscience, however, confronts a fundamental challenge. As the advancement of chemical sensing systems progresses towards small length scales, sensitivity and performance are compromised because there are simply too few sensing active sites on the micro- and nano-patterned structures to permit detection of species. We have addressed this challenge by exploring strategies to increase chemosensor response by replacing the linear, single photon response of present chemosensors with extremely nonlinear optical responses. To achieve this objective, a multi-prong approach that combines photochemistry, materials synthesis and optical science is presented in which the light emitting molecular centers of conventional optical chemosensors are substituted with a mesoscopic optical laser cavity of a Distributed Feedback (DFB) grating or spherical cavity resonator exhibiting Whispering Gallery modes (WGM). In pursuing this line of research, we wish to construct high gain sensors that can detect analytes with simple detection systems unprecedented sensitivity.

3R Chemosensing

The strategy to chemo-/bio-sensing (CBsensing) pursued in our program is the “3R” – recognize, relay, report – transduction scheme outlined in Figure 1 [1]. A noncovalent molecular recognition event at the receptor site is communicated, by physical or chemical means, to a reporter site, producing a measurable luminescent signal. We have applied the 3R approach to develop novel physical and CBsensing techniques and methods. Physical sensing by 3R is accomplished by our development of the Molecular Tagging Velocimetry (MTV) technique to measure the velocimetry of highly turbulent 3D flows [2-7]. Chemical and biological sensing by the 3R method is predicated on a rapid equilibrium between the analyte and the receptor site to afford a real-time luminescent response that varies with analyte concentration. An exemplary application is the development of a CBsensor for the detection of polyaromatic hydrocarbons (PAHs). Important design criteria included the ability to perform sensing in an aqueous environment, the generation of a luminescent signal at visible wavelengths (well shifted from the blue emission of a typical environmental background), and the appearance of the signal upon recognition of analyte (i.e., a “turn-on” CBsensor). Chemosensor **1** was developed to meet these criteria [8]. A



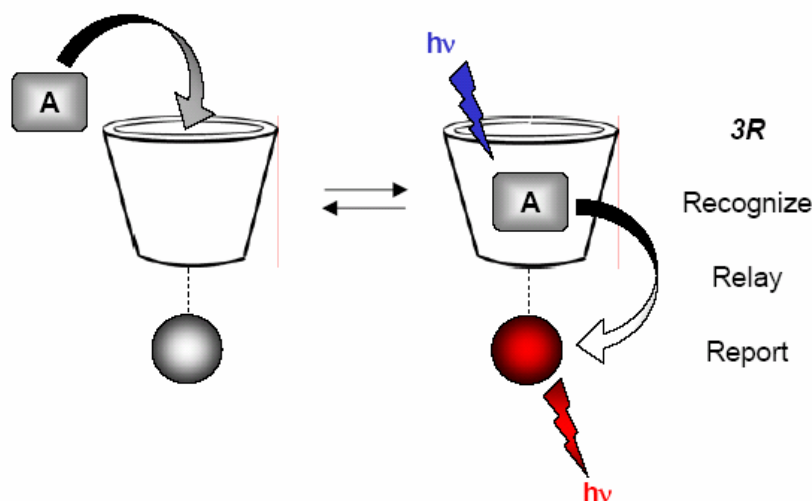


Figure 1. The 3R approach to chemosensing. A = analyte. The bucket represents a supramolecule recognition site. The relay mechanism transfers excitation energy to a light-emitting center, which provides the signal for detection.

cyclodextrin (CD) is the PAH recognition site (represented as a bucket) and a terbium (Tb^{3+}) ion is the reporting site. Molecular recognition of the aromatic hydrocarbon in the CD bucket is signaled by the appearance of green luminescence from the encrypted Tb^{3+} ion. Detailed mechanistic investigations establish signal transduction in **1** to proceed via an absorption-energy transfer-emission (AETE) mechanism in which excitation energy absorbed by the bound analyte is transferred from its long-lived triplet excited state to the Tb^{3+} reporter site [9].

Micro-Fluidic Optical Chemosensors

MicroFluidic (μF) platforms have emerged as an important technology for chemo- and bio-analytical applications [10]. The miniaturization offered by μF devices allows for the analysis of fluid samples to be performed on a chip, leading to advantages such as reduced sample volume, increased reaction speed and the possibility of massive parallelism [10,12]. We sought to combine the advantages of microfluidics with the CBsensor approach by transferring the 3R function of **1** to μF platforms.

The realization of μFOCs demanded that the supramolecule architecture of **1** be incorporated into a matrix that is compatible with lithographic patterning protocols. Accordingly, we developed methods to permit the attachment of **1** onto a thin film substrate. Of the various strategies explored, the most successful films for μFOC detection were prepared according to the method shown in Figure 2. The CD was condensed into a partially hydrolyzed tetraethylorthosilicate solution in ethanol (acid catalyzed conditions). This solution was spin-cast onto a clean, dry, quartz substrate to give gel films of thicknesses ranging from 0.2 - 0.6 μm , as determined by profilometry measurements. Squares of these sol-gel films were photo-lithographically patterned within the serpentine channel of the device shown in Figure 3. The device exhibits excellent optical response to PAHs; importantly, time-resolved kinetics measurements on the sol-gel thin films established that the same 3R mechanism observed in solution prevails in the film [13]. A 45-fold enhancement of the Tb^{3+} luminescence intensity was triggered when a 50 μM solution of biphenyl contacts the patterned microstructure. The Tb^{3+} luminescence enhancement proved to be concentration-dependent, increasing monotonically with the concentration of biphenyl. A slow response time (\sim minutes), owing to the micron thickness of the films, was a drawback of the device. Response

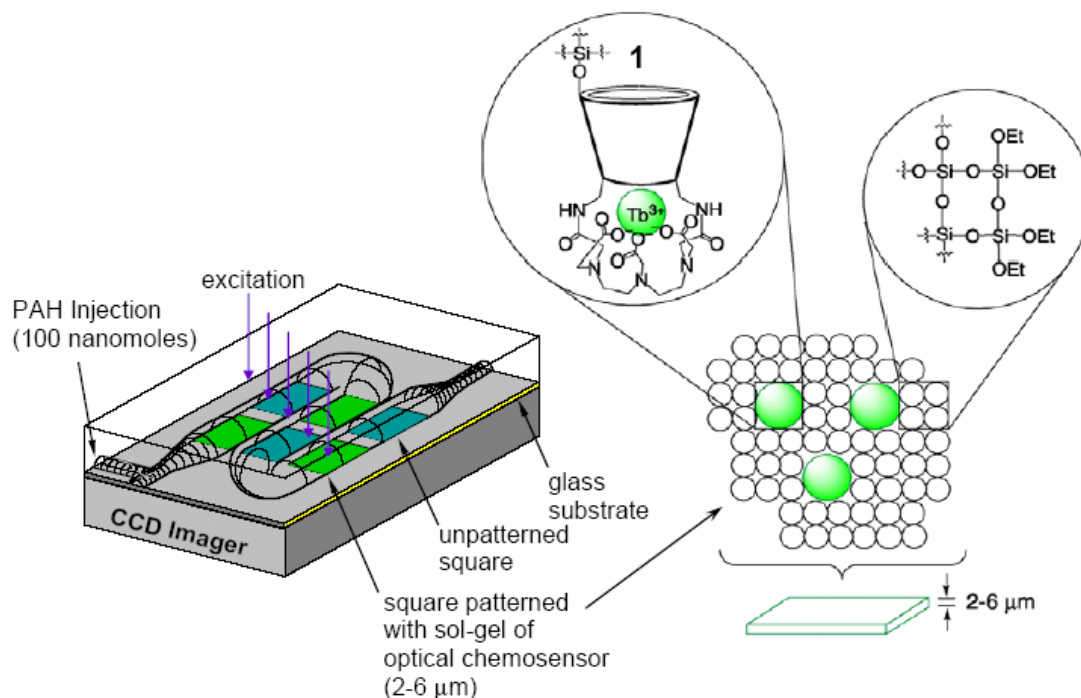


Figure 2. A microfluidic optical chemosensor based on the principles of the 3R approach.

times may be increased by decreasing the thickness of the pads but signal was eventually lost for PAH concentrations <100 nM.

The Challenge to Chemosensing on Small Length Scales

The tradeoff between signal intensity and response time of the μ FOC in Figure 2 leads to the inexorable conclusion that the implementation of CBsensing on small length scales will require new signal transduction strategies. As the number of receptor sites decreases with decreasing thickness, device sensitivity and performance is compromised because *single molecule detection – single photon generation* yields signals that are too weak to be detected. Described below is our effort to bring about the sensing advancements depicted in Figure 3 by undertaking a multi-prong approach that combines chemistry, materials and optical sciences. We have sought to overcome the paradox that nanoscience presents to optical sensing on small length scales by replacing the *linear, single photon response* of typical optical chemosensors with an *extremely nonlinear optical response of a laser cavity*. In effect, we have created a miniature version of cavity ring down spectroscopy (CRDS) and intracavity laser absorption spectroscopy (ICLAS) [14,15]. These two macroscopic techniques are related, powerful absorption techniques that obtain their sensitivity by using the very long effective cell length of a laser cavity. In brief, gaseous analytes present in the laser cavity cause a perturbation of the output. Owing to the high optical non-linearity of the cavity, trace concentrations of the gaseous analyte may be detected. We propose to emulate the ultra-sensitive detection of CRDS/ICLAS derived from the high optical non-linearities of a laser cavity – but with lasers that possess nano- to micro- meter cavities versus the meter cavities of a conventional laser. To do so, we have pursued the following strategy:

- (1) Employ nano- to micro- laser cavities with exceptionally long pathlengths afforded by exploiting nanoscience techniques.

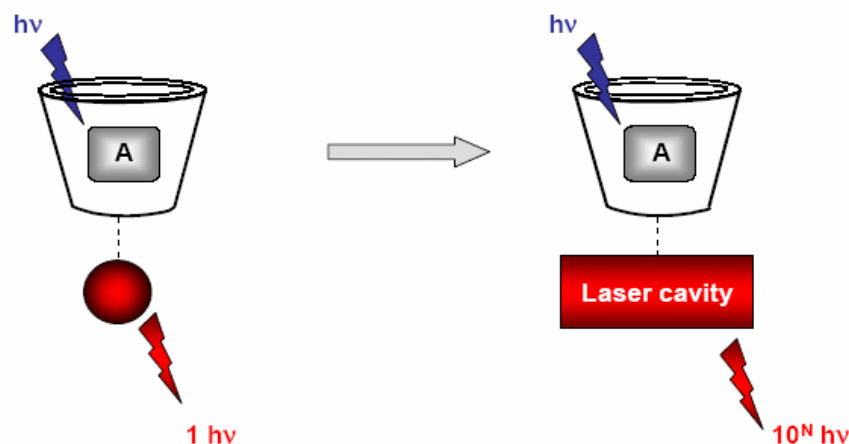


Figure 3. New design concept for 3R chemosensing. Replace single photon emitting center with a laser whose response is triggered by analyte recognition.

(2) Modify these laser cavities with receptor sites such that the optical characteristics of the laser cavities are perturbed upon recognition of a target analyte.

(3) Owing to the high nonlinearities of the optical response of the cavities, develop self-referencing transduction schemes to enable accurate measurements to be made.

We have made significant strides in the realization of (1). These advances will be described in the following section followed by a discussion of studies pertaining to (2) and (3).

Nano-/Micro- Laser Cavities for High Gain Sensing

The intensity of light can build exponentially as light propagates in a cavity with an inverted excited state population. This exponential increase in intensity is given by [16],

$$I = I_0 e^{g(\nu) \cdot z} \quad (1)$$

where I_0 is the impinging intensity, I is the intensity at some distance z into the cavity, and $g(\nu)$ is the gain coefficient given by,

$$g(\nu) = [N_u B_u(\nu) - N_l B_l(\nu)] \frac{h\nu}{c} \quad (2)$$

$N_{u(l)}$ is the upper (lower) level population and $B_{u(l)}(\nu)$ is the emission (absorption) probability at frequency ν . By separating the Einstein $B_{u(l)}$ coefficients from population inversion, Eq. (1) can be recast,

$$I = I_0 e^{\sigma(\nu) \cdot \Delta N_{ul} \cdot z} \quad (3)$$

where $\sigma(\nu)$ is the stimulated emission cross-section. The term ΔN_{ul} is related to the population inversion by $\Delta N_{ul} = [N_u - (d_u/d_l)N_l]$, including a statistical weight factor, $d_{u/l}$, which accounts for degeneracy. Eq. (3) provides an immediate inroad to sensing on small length scales. If an analyte can affect ΔN_{ul} by removing (“turn-off”) or adding (“turn-on”) energy into the cavity, then the gain coefficient will be perturbed, thus

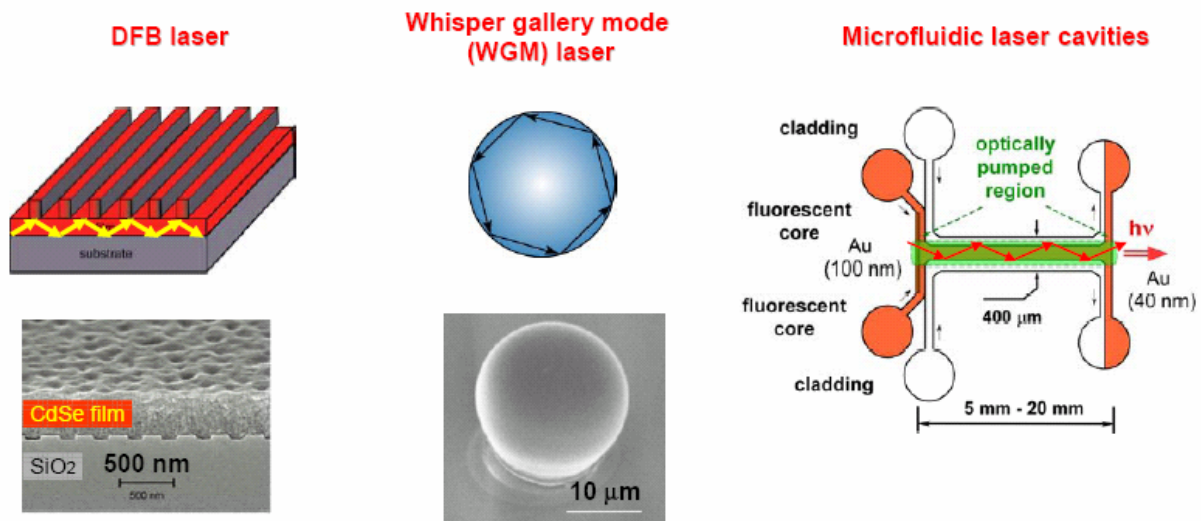


Figure 4. Three high-gain laser cavities of a: (1) distributed feedback (DFB) waveguide, (2) WGM microsphere and (3) microfluidic channel.

leading to an exponential change in the laser output. The gain coefficient can be altered by chemically functionalizing the laser structures with molecular recognition sites, where absorption of the propagating light by a specific analyte docked at the receptor site will turn the laser off when the net gain drops below threshold.

Cavity Architectures

We have incorporated these design principles described by Eqs. (1) - (3) in the three tiny lasers shown in Figure 4. Lasing in each cavity is achieved by wave-guiding light of the appropriate wavelength through the cavity of a distributed feedback (DFB) waveguide [17], a microsphere (WGM) [18], or a microfluidic Fabry-Perot channel [19]. Long pathlengths in lasers is achieved by reflection of light off a front and back mirror of a macroscopic cavity. In the DFB, the long pathlength is achieved by introducing a periodic modulation of the local refractive index along the path of light propagation. The pathlength in the spherical cavities confine light by successive total internal reflections along the concave inner surface of the sphere. This resonant increase of pathlength, or feedback, for both DFB and spherical cavities is needed to observe sharp and intense amplification of light via stimulated emission processes of Eqs. (1) - (3). The microfluidic cavity is the most classical in its design inasmuch as light propagation occurs between two gold-plated mirrors – the difference is that the laser cavity is formed within a liquid-liquid interface confined to a microfluidic channel.

For lasing to be achieved, each of the laser cavities shown in Figure 4 must meet the following characteristics:

- A sufficient refractive index mismatch between the laser cavity and environment to permit waveguiding to be achieved [20]. For the DFB and microsphere resonators, the laser cavity is fabricated from a sol-gel matrix ($n = 1.6 - 1.8$) sandwiched between air ($n = 1.0$) and a glass substrate ($n = 1.5$).
- An appropriate thickness (d) of the channel or film to permit single lasing modes to be achieved; this thickness depends on the geometry of the architecture

- A smooth surface morphology to minimize scattering at the surface of the waveguide. We have found that this feature is the most significant determinant of the quality of the laser cavity (i.e., Q-factor). In the case of the microfluidic laser, the surface is formed from the liquid-liquid interface, which is controlled by the laminar flow properties within the microchannels. In the case of the DFB and WGM microsphere lasers, the surface morphology is controlled by the composition of the sol-gel matrix. We propose new synthetic sol-gel methods to permit even smoother surfaces of the DFB and WGM microsphere lasers to be realized.

A description of the details of each of these laser cavities is presented in the following sections.

Distributed Feedback (DFB) Structures

The DFB lasing architecture comprises a slab waveguide embossed with a grating [21,22] of period (Λ) that satisfies the Bragg condition,

$$\Lambda = \frac{\lambda_B m}{2n_{\text{eff}}} \quad (4)$$

where λ_B is the Bragg wavelength that is supported by period Λ , m is the order of the grating reflection, and n_{eff} is the effective refractive index. The lasing medium must have a gain profile that is coincident with λ_B . As the propagating wave traverses the DFB grating, lasing results from the constructive feedback oscillation resulting in the stimulated emission of light.

The matrix of the DFB is composed of a $\text{SiO}_2/\text{TiO}_2$ thin film. These films were chosen because they are optically transparent, exhibit high optical homogeneity, and their surfaces may be chemically modified [23,24]. Films were synthesized via conventional acid-catalyzed hydrolysis and condensation methods of sol-gels prepared from $\text{Si}(\text{OEt})_4$ and $\text{Ti}(\text{OEt})_4$ precursors [23]. Sol-gels were spin-coated onto clean substrates (glass or Si) and thermally cured to produce thin films. The refractive index and smoothness of the films were tuned by varying the [Si]:[Ti] composition. The addition of titania to films was needed to increase the refractive index of the film and to facilitate thermal dissipation within the film (and thus minimize cracking under high light excitation fluxes). However, films containing higher titania concentrations yielded surfaces that were too rough for proper waveguiding. An exhaustive study of film compositions showed a 2:1 [Si]:[Ti] oxide composition to possess ideal properties for DFB waveguide applications. AFM and SEM measurements revealed smooth surfaces, with observed mean surface roughness (rms) of $\leq \pm 0.5$ nm; $n = 1.61$ was determined from spectroscopic ellipsometry measurements of the thin film.

Lasing from the slab waveguide will be achieved by amplified stimulated emission (ASE) of an encapsulated lumophore [25-30]. The lumophore needs to emit in spectral region that includes λ_B of Eq (4); this wavelength will be amplified in the DFB structure. In our initial studies, we introduced rhodamine 6G (R6G) at the sol-gel stage of the thin film synthesis. A single mode will propagate for film thicknesses of ~ 200 nm ($m = 0$) and ~ 800 nm ($m = 1$) for propagating wavelengths in the R6G visible region and a film of $n = 1.6$ sandwiched between $n_{\text{air}} = 1.0$ and $n_{\text{sub}} = 1.5$ [20]. Film thicknesses of 250 - 400 nm were obtained by controlling the reaction time for the acid-catalyzed cross-linking of the precursor and the speed of the film casting.

Fabrication of the DFB structures involves stamping the slab waveguide with a master grating that has a variation in period with length Λ specific to the emission wavelength of the gain material. The master DFB grating may be fabricated with 300 - 500 nm pitches by using interference lithography [31]. This lithography process involves crossing two beams from a coherent laser light source to form a grating on a

photoresist. The pitch of the grating depends on the angle between the two interfering beams. The grating period is then transferred from the photoresist using a series of reactive-ion-etch (RIE) steps, leaving a grating pattern about 50 nm deep. The Research Laboratory of Electronics at MIT has pioneered the technique of interference lithography for over 20 years [32]. Si master gratings were fabricated and preserved by subsequent transfer to a poly(dimethylsiloxane) (PDMS) stamp using standard techniques. A second order, surface emitting DFB lasing structure may be obtained by stamping the PDMS onto a freshly spin-coated thin film of the waveguide.

Our best DFB's have been obtained using CdSe nanocrystals (NCs) as the gain material [33,34]. Nanocrystals have been incorporated into a titania film that was spin-coated upon a DFB grating, and more recently, by stamping titania films. High-volume fractions can be incorporated, and the size-dependent emission of quantum-confined NCs may be exploited to generate DFB lasers that emit in the 560 - 625 nm range. As shown in Figure 5, the lasing action is very high quality, as indicated by the sharpness of the DFB lasing output. We have recently found that these devices are very stable and can be pumped by a nanosecond Nd:YAG source rather than with a femtosecond laser as demonstrated previously [34]. This increases the practicality of these systems, since the Nd:YAG excitation sources are inexpensive and much smaller in size than the ultrafast lasers.

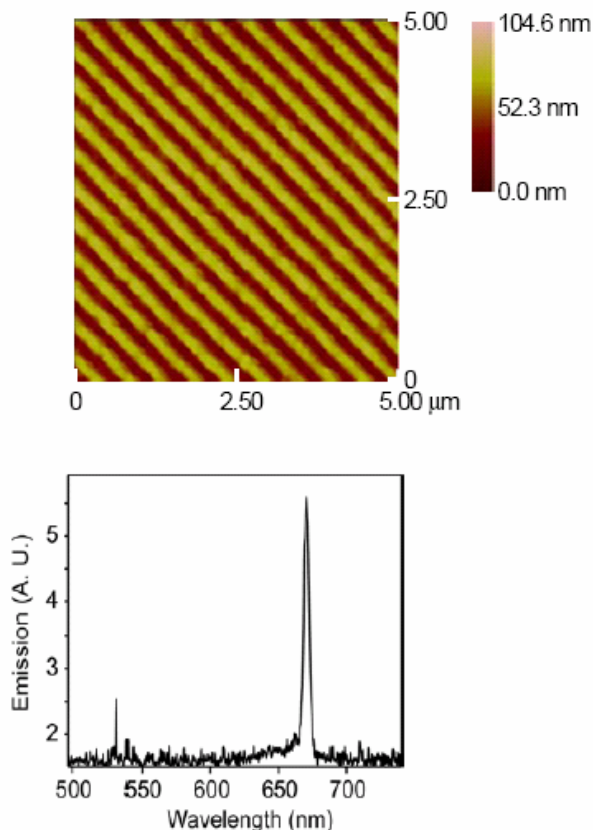


Figure 5. (Top) AFM of NCs incorporated into a thin film. The stamped grating is readily apparent. (Bottom) The emission spectrum of the NC-titania DFB laser device; the emission at 532 nm originates from the Nd: YAG source.

Whispering-Gallery Mode Spherical Resonators

Laser emission in spherical resonators is the result of light trapping in the Whispering Gallery modes (WGMs), which are formed from successive total internal reflections off the concave inner surface [35]. As light propagates in this fashion, the photonic electric field strength increases exponentially as a result of stimulated emission from an inverted population of a suitable laser gain material [36-42]. For lasing to occur, the resonator must be doped with a resilient lumophore that has gain at the resonant WGM wavelengths. Unlike the situation for DFBs, laser dyes quickly photobleach inside of a small cavity owing to exceptionally high power densities focused into the small volume of a microsphere [43]. We have overcome this problem by using semiconductor NCs, which are much more resilient under optical excitation compared to organic laser dyes. Furthermore, the NC surface may be chemically functionalized to support adhesion onto the exterior of a microcavity, such as a silica or polystyrene microsphere. Thus, a non-linear sensing scheme based upon spherical resonant cavities employing a NC gain material is particularly attractive.

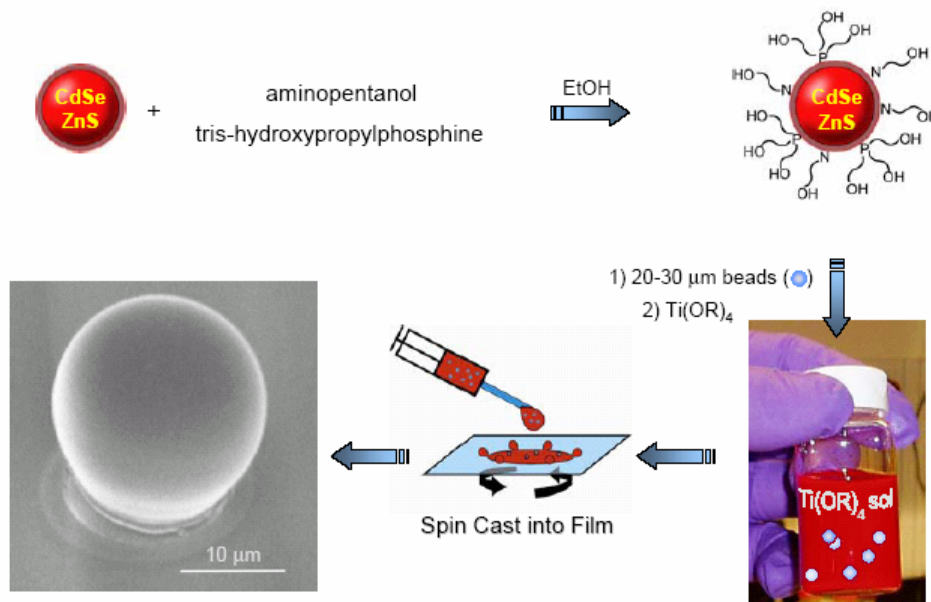


Figure 6. Facile process for making WGM lasers with CdSe nanocrystals incorporated into TiO_2 as the gain material, coating a microsphere. A SEM micrograph of a microsphere is shown.

We have developed a facile and robust method of incorporating colloiddally synthesized CdSe/CdZnS NCs onto the surface of micron-sized glass microspheres of low size dispersity [18]. The overcoating of NC/titania sol onto the 20 μm spheres produces hundreds of uniform resonators in a single spin-coating process as summarized in Figure 6. The method yields spheres possessing remarkable optical properties. The synthesis must result in the formation of monodisperse particles with a surface roughness of no more than $\lambda/8$; 44 very smooth coatings are obtained from the synthesis method.

The lasing response and optical characteristics of the NCs/microspheres are shown in Figure 7. The Q-factor of the lasing lines is very high; as observed by comparison of Figures 5 and 7, the spectral profile of the WGM microsphere output is sharper. Single-mode versus multimode lasing can be selectively achieved by adjusting the size of the microsphere template, spectral position of the gain of the NC sample, and the pump power of the laser. Our microsphere resonators are also very stable over time. Furthermore, laser emission has been observed to recover partially if a photobleached sample is left in the dark for several minutes, similar to previous observations made in fluorescence quenching studies of CdSe NCs [45]. Our method is general as we have recently achieved blue lasing from CdS/ZnS NCs as the gain material [46]. The facility and photostability of this method has made this an attractive process for developing laser cavities for biological and chemical sensing. We are currently developing technology to increase the chemical stability of NC/sol-gel films from exposure to impart specific and reversible sensitivity to chemical and biological analytes.

Microfluidic Waveguide Lasers

Recently, we were able to integrate a liquid-liquid (L^2) waveguide laser within microfluidic systems [19]. The structure of L^2 waveguides consists of laminar flow of multiple liquid streams in a single microfluidic channel in an arrangement where two streams of a low refractive index fluid, the liquid cladding, envelop

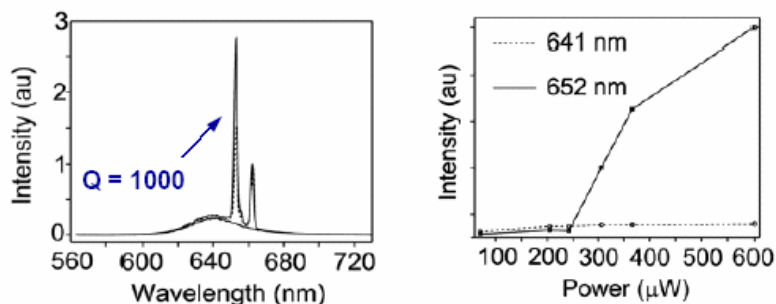
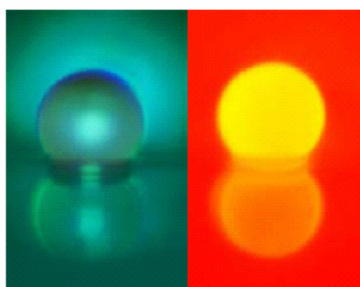


Figure 7. (Left) A 20-micron CdSe/microsphere is shown optically silent and fluorescing. Lasing begins upon pumping the CdSe NC. (Middle) Fluorescence from the CdSe (bottom trace) transforms into discrete, sharp optical resonances once the lasing threshold is crossed. (Right) Power response of the CdSe NC emission intensity, on and off resonance. The off resonance threshold shows a linear response whereas the on resonance shows a highly nonlinear increase in intensity at a threshold pump intensity.

a third stream of high refractive index, the liquid core, which contains the gain material [47,48]. The advantages to using the L^2 waveguides include control of emission wavelength, numerical aperture, absorbance, size, geometry, and modal content of the fluorescent waveguide. Changing the dye and the solvents allows for modification of the properties of the waveguide by adjusting the lasing wavelength or by modifying the refractive index contrast between the core and the cladding liquids.

The microfluidic laser (Figure 4) was fabricated using soft lithography.⁴⁹ The optically pumped region is terminated at both ends with T-junctions, which were coated with thin layers of gold, creating a Fabry-Perot optical cavity. Pressure-driven core streams containing rhodamine 640 perchlorate in methanol and pure methanol as the cladding stream flowed in from both sides of a single T-junction and down the length of the active region, forming the L^2 waveguide. Laser emission is shown in Figure 8.

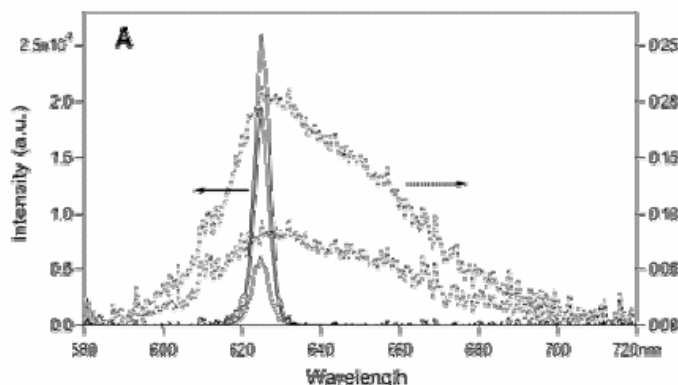


Figure 8. Emission spectra from the microfluidic L^2 waveguide at different pump powers measured on-axis (not the 10^5 difference in scale for spectra at input powers below (dashed) and above (solid) threshold).

Lasing from microfluidic waveguide gives us another platform to achieve non-linear sensing.

Implementation of microLasers for Sensing

The crucial step, depicted in Figure 4, to implement CBsensors on small-length scales, has been achieved with the construction of oxide laser cavities that can be easily produced and possess good optical characteristics. The cavity can be readily modified with receptor sites using conventional coupling synthetic methods common to surface oxide modification. The approach allows the sensing strategies in Figure 9 to be established with facility. In one case, recognition of a target molecule introduces a new loss mechanism by interfering (either by absorption or energy transfer) with the propagating lasing wavelength. When the loss of the laser cavity is greater than the gain, the laser will turn off, which is easily observed. Alternatively, the ability to produce very high Q laser cavities using standard sol-gel

chemistry on small length scales opens a new opportunity for sensing by the approach described here. The wavelength of the laser line emissions shown in Figures 7 and 9 are very sensitive to the refractive index of the gain medium. Adsorption of the CB target at the receptor site on the surface of the cavity, in principle, will alter the optical properties of the structure sufficiently to shift the lasing wavelength. Because the laser lines are very narrow, their shift in wavelength can easily be monitored. Thus sensing may now be accomplished by the “turn-off” of laser line at the frequency in absence of target analyte and “turn-on” of new laser line at the frequency for target analyte bound to the receptor site. This line of inquiry is currently under investigation for the three types of laser cavities shown in Figure 4.

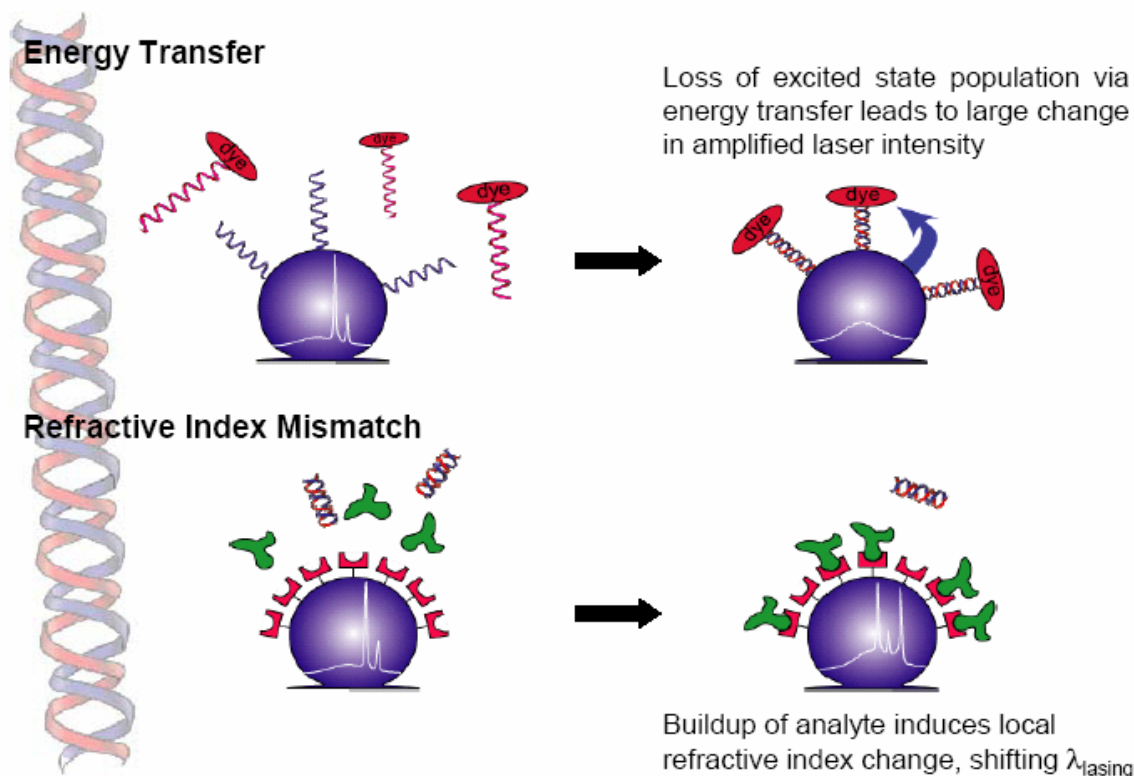


Figure 9. Two possible sensing strategies for spherical laser cavities adapted with bio-recognition sites for high gain sensing of target biomolecules.

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Reports from 2006 Photochemical Meetings

US-Brazil workshop on “The interplay of Experiment and Theory in Photochemistry” was co-sponsored by the US National Science Foundation and the Brazilian CNPq. It was co-organized by **Frank Quina** and **Jack Saltiel** and held in Salvador, Brazil on June 9-11 and was followed up by the I-APS 2006 meeting.

The morning session on June 9th was chaired by **Jack Saltiel** and started with a talk by **John Toscano** on “*Generation and Reactivity of HNO and Acyl Nitroso Species*”. John pointed out that although $^3\text{NO}^\cdot$ is bound by only ca. 0.6 kcal/mol relative to electron detachment, HNO is not expected to be easily converted to NO under biologically relevant conditions. In fact, physiological properties of NO and HNO are orthogonal and, thus, HNO has its own important role in biochemistry. Interestingly, John reported that literature pK_a of HNO changed from 4.7 to 11.4 in just a few years. One has to wonder if this is as important as global warming!

John further discussed development of photoprotected analogues of two common HNO donors, Angeli's salt and Piloty's acid. Since Piloty's acid latter can be easily derivatized, a family of photosensitive precursors to this compound is being developed. He also reported indirect generation of HNO via acyl nitroso compounds, reactivity of which was mapped with careful time-resolved IR studies. Careful kinetic analysis revealed that order of reaction of acylnitroso compounds with amines depends on whether amine is primary or secondary. The reaction is *first order* in 2° amine and second order in 1° amine. John also reported an interesting dichotomy in reactivity of acylnitroso compounds

towards amines and thiols and formation of a metastable adduct, observable on the microsecond timescale, in the latter case.

The second talk of the workshop was given by **Marcelo Henrique Gehlen** who discussed “*Dielectric friction and resonance-assisted hydrogen bond effects in photoinduced intramolecular charge transfer*” (ICT). In the first part, Marcelo analyzed the effect of solvent viscosity and polarity on the dynamics of excited state formation. He carefully addressed polarization effects, interplay of dielectric and mechanic friction as well as dynamic control in ICT and non-Marcus behavior. Effect of strong intramolecular interactions such as RAHB (Resonance-Assisted H-Bonding) on ICT dynamics were presented in the second part.

In the third talk, **Cather Simpson** discussed “*Photochemistry and photophysics of multiply bonded phosphorus systems*”. She pointed out that even though, for many years, multiple bonds between heavy main group elements were thought not to exist (the “double bond rule”), now there are hundreds of known stable multiple bonds among heavier main group elements. Cather presented results from a collaborative effort with John Protasiewicz (synthesis) that explored the photobehavior of diphosphenes with future applications as photoactive polymers in mind.

In the first part, Cather provocatively addressed fundamental aspects of electronic structure of multiple-bonded heavy element structures and pointed out that it may be that it is the first row elements such as C, N, and O that are the “special”, or “anomalous” while the heavier main group elements are “normal”. Since the “common chemical sense” that chemists developed to explain chemical and photochemical phenomena is

largely based upon studies of the lighter elements, it may not serve well for studies of systems incorporating the heavier main group elements. Cather pointed out that even though phosphorus is sometimes called the “carbon copy”, the fundamental atomic structure factors lead to dramatic differences in the relative $\pi : \sigma$ bond strength.

In the next part, Cather presented intriguing photophysical and photochemical properties of diphosphenes. Depending of the irradiation conditions and ligands on phosphorus, excitation can result in a variety of reactions, including CH bond insertion, CC bond insertion, dimerization, and photoisomerization. Alternative mechanistic hypotheses were presented and critically evaluated based on the experimental data.

Overall, as many other talks at the workshop, this work presented an impressive array of tools in perfect accord with the general theme of the workshop. The “experimental toolbox” included ultrafast transient absorption spectroscopy, ultrafast time-resolved resonance Raman spectroscopy, picosecond time resolved fluorescence spectroscopy, nanosecond transient resonance Raman spectroscopy, steady-state UV/Vis absorption and fluorescence, solvent dependence (polarity, viscosity, etc.), temperature dependence, use of sensitizers/quenchers and “a clever synthetic chemist collaborator” whereas the computational toolbox incorporated density functional theory (DFT) and time-dependent DFT, multiconfigurational *ab initio* approaches such as CASSCF, CASPT2 for both ground and excited state calculations.

On the more theoretical part of the spectrum, **Rodrigo José Corrêa** presented a talk “*Theoretical chemistry applied to organic photoreactions*” in which he analyzed H-abstraction by triplet ketones. The results were placed in a general perspective through comparison

of monoketones, diketones and t-butoxy radicals. DFT calculations (UB3LYP/6-311++G**// UB3LYP/6-31G*) of the triplet ketone phenol complex revealed significant displacement of a hydrogen atom along the H-abstraction coordinate. The reactions with α -diketones were found to be ca. 7 kcal/mol less endothermic than the respective reactions of the monoketones. These results together with the geometries obtained from the DFT calculations, Natural Bond Orbital (NBO) and Atoms-In-Molecules (AIM) analysis indicate that hydrogen abstraction for α -diketones is facilitated by the electrophilicity of the ketone rather than by the neighboring group participation of the second carbonyl group.

After an educational outline of different quantum mechanical approaches to recovering the correlation energy, **Antonio Carlos Borin** (“*Multiconfigurational quantum methods applied to the excited states of organic molecules*”) gave a detailed description of an elaborate set of computational techniques needed to obtain good spectra. In the following part of the talk, Antonio illustrated how high level theory can be applied to study photophysical properties of 2-aminopurine (2AP) – a cousin of adenine (6-aminopurine), one of the four DNA bases. Unlike adenine, which has a low fluorescence lifetime (100 fs), 2AP has excited state lifetime in the nanosecond range and is highly fluorescent. The computational analysis took into account solvent effects through sequential Monte Carlo (MC) and quantum mechanical (QM) CASSCF/CASPT2 calculations and provided a good agreement with the experimental data.

Spiridoula Matsika concluded the morning session with a talk on “*Theoretical methods for excited states and potential-energy-surface crossings as a tool to understand photochemical processes*”. After a general introduction

on how to calculate landscape of excited states and find important conical intersections, Spiridoula applied high-levels of theory to selected bases of DNA and RNA (uracil, cytosine and a related model compound 5-methyl-2-pyrimidone). The talk addressed interesting photophysical properties of DNA bases such as low fluorescence quantum yields and ultrashort excited state lifetimes and the search for efficient excitation relaxation pathways through conical intersections between the ground and the first excited state. Spiridoula reported that the differences in the photophysical behavior can be explained by the relative energies of the conical intersections. In fluorescent molecules the conical intersections are higher in energy and become less accessible, while in nonfluorescent molecules they are easily accessible. Three-state conical intersections are also present at energies close to the vertical excitation energies and may play an important role in the excited state dynamics.

In the evening session chaired by **Julio de la Fuente**, **Frank Quina** presented a talk “*Fast excited state proton transfer in anthocyanins*” devoted to the “(photo)chemistry of the colors of fruits and flowers”. Anthocyanins are pigments responsible for the color of blue flowers but also present in many fruits and berries. Sensitivity of these chromophores to their environment suggests that the “roses are red and violets are blue” as a result of differences in the local pH. Different aspects of chemistry of natural and artificial anthocyanins were presented such as reactivity towards nucleophiles, importance of hydration, tautomerization and isomerization as well as differences in acidity of such molecules in the ground and excited states.

Laura Tiemi Okano presented “*Study of the complexation of some flavones with cyclodextrins*”. Several

flavones which are important chemicals present in flowers and fruits have dual fluorescence which is sensitive to solvent polarity due to tautomerization in the excited state. Laura reported a combination of experimental and theoretical studies media-dependent photophysics of Fisetin (Fis) and 7-hydroxyflavone (7-HF). Computational studies (TD-DFT) suggest that geometries are similar in the ground and excited states but the dipole moment increases from 2.4 to 5.8 D. Interestingly β -dextrin and γ -dextrin impose dramatically different effects on the dual fluorescence of Fis. A particularly interesting observation was that of the opposite trends in the entropy and enthalpy for complexation of Fis with the two host molecules.

Teresa D. Z. Atvars presented a talk on “*Photochemistry and photophysics in polymer systems*”. After a brief discussion of photoluminescence spectroscopy of conjugated polymers, Teresa addressed the question of how to stimulate spectra for amorphous or semicrystalline polymers. Computational search for supramolecular aggregates was performed using quantum mechanical semiempirical methodologies. Results were compared with optical absorption of oligomers. Teresa also discussed photophysics and polymer relaxation processes based on experiments and results of theoretical molecular mechanics simulations. She also discussed implications of the relaxation processes on the mechanical and electroluminescence properties.

Elizabeth Gaillard talked about “*Fluorescence imaging of the human retina*.” She outlined the health problem posed by Age Related Macular Degeneration (AMD) which is the leading cause of irreversible blindness in the western world. This presentation outlined the application of photochemical principles, particularly the theory from time resolved

fluorescence spectroscopy, to the development of new non-invasive imaging technology for the human retina. The imaging technique combines a confocal scanning laser ophthalmoscope with time correlated single photon counting detection.

After an excursion to an anatomy of the eye, Elizabeth discussed why retina is uniquely situated to be imaged by visible light, provided a number of interesting facts such as enhanced autofluorescence in most macular dystrophies and discussed how fluorescent properties of the involved biological tissues were used to develop fluorescent imaging for studies of the structure of retina. Two possible origins for increased fluorescence of retina were discussed followed by description of the vision cycle and the role of ABCR Transporter Protein in the accumulation of human retinal lipofuscin. List of potential contributors to autofluorescence such as lipofuscin (A2E), melanin, FAD, NADH, elastin/collagen, AGEs and melanolipofuscin was provided to set the stage for the next part.

A number of intriguing questions were posed such as whether one can measure fluorescence from a living eye and utilize lifetime distribution analysis for determining the molecular source of fluorescence. A particularly important development will include detection of subtle metabolic changes that predate AMD and utilizing experimental techniques developed in this study for control of treatment of AMD with phototherapy agents. (SENT)

Saturday, June 10, 2006

The morning session on Saturday, June 10 was chaired by **Andrei Kutateladze** and started with a lecture by **Fred Lewis** who provided an answer to the question of "What happens when you give a DNA synthesizer and a postdoc to an organic photochemist?" in his talk on

"DNA photonics: Beyond electron transfer (and back)". Fred started with the design of capped DNA hairpins which can provide excellent control of both distance between interacting chromophores and their relative orientation. These systems can be used to study a variety of phenomena such as exciton coupling, energy transfer, hole transport and electron transport. In the first part of his talk, Fred masterfully utilized exciton coupled circular dichroism to investigate the structure of these systems. An impressive agreement between experimental and calculated CD spectra lends strong support to the structural assignments. A particularly important result was the strong angular dependence of FRET which suggests that one has to be careful in using FRET as a "molecular ruler". The fundamental studies of hole transport in DNA were outlined next. Fred stressed the importance of kinetic studies at the fast time domains and presented an intriguing finding of a crossover from tunneling to hopping in designed hairpins. Finally, new results on electron injection in DNA were presented. SENT

Igor Alabugin presented a talk on *"Photochemistry of acetylenes: From MO crossings to DNA cleavage"* where he illustrated how unique electronic properties of alkynes derived from the presence of two orthogonal π -systems can be utilized for efficient substituent control of anionic cycloaromatization reactions. He also discussed triplet cycloaddition reactions in which alkynes behave as synthetic equivalents of 1,2-bis-carbenes.

Lisa Kelly discussed *"Experimental approaches to mapping protein and DNA structure and interactions using naphthalimide photochemistry."* After a general discussion of mechanisms of DNA and protein photodamage, Lisa presented absorption, time-resolved and steady-state fluorescence spectroscopy analysis of the

interaction of functionalized naphthalimides with amino acids and proteins. It was shown that the primary photochemistry can give rise to neutral amino acid radicals, which lead to protein cross-linking. In addition, when a suitable carboxysubstituted 1,4,5,8-naphthalene diimide was used, the protein was photoaffinity labeled, presumably via the formation of a carbon-centered radical produced following intramolecular electron transfer. The results lay a foundation for the future mechanistic studies of the DNA and protein photodamage and unraveling intricate details of complicated secondary chemistry. By understanding and controlling the primary photochemistry, novel and photoactive compounds can be developed to probe macromolecular structure via cross-linking, cleavage, and photoaffinity labeling mechanisms.

Jack Saltiel presented a lecture on “*Mechanisms of cis-trans isomerization: One-Bond-Twist, Bicycle Pedal, or Hula-Twist*”. His talk illustrated the interplay of experiment and theory which is essential for understanding torsional relaxation in stilbenes, conformer-specific adiabatic photoisomerization in styrylarenes and photoisomerization in α,ω -diphenylpolyenes in solution, glassy and crystalline media. Jack pointed out a number of experimental puzzles that need to be addressed by theory, utilized spectroscopy, kinetic measurements, media effects, and, where necessary, the Ockhams’ razor to choose between mechanistic possibilities. It was concluded that reversal of single/double bond order on S0 to S1 excitation in 1,2-diarylethenes and in α,ω -diphenylpolyenes predicted by HOMO-LUMO considerations even at the Hückel MO level, account for: (i) OBT (One-Bond-Twist) in stilbenes and diphenylpolyenes, (ii) adherence to the NEER principle in polyenes and styrylarenes, (iii) adiabatic photoisomerization in styrylarenes, and

(iv) BP (Bicycle Pedal) in crystals of *cc*-DPB, ammonium *Z,Z*-muconate, and *ctc*-DPH derivatives and in *cc*-DPB in IP glass at 77 K. (2) The lowest excited Ag singlet state plays no significant role in photoisomerization. (3) S1/S2 (Ag/Bu) order is not important in DPH (4) The major radiationless decay path in stilbene vinylogues does not lead to photoisomerization and probably does not involve torsional relaxation coordinates, and (5) Fluorescence measurements alone do not reveal medium effects on torsional relaxation in vinylogues of stilbene.

In a stimulating talk entitled “*Computational Design and Characterization of a Biomimetic Photochemical Switch*”, Massimo Olivucci pointed out that more than one screwdriver is needed in a good toolbox and that new photoswitches with new geometries are desired in addition to the existing and widely used switches (e.g. azobenzene). Massimo asked whether one can develop a photoswitch that in solution mimics the behavior of retinal in rhodopsin (i.e. the superior animal retina visual pigment). The design was based on the combination of Feringas light-driven molecular motor with a constrained Schiff base. This study pushed the envelope for the development of computational technologies for excited states to new heights by successfully utilizing a hybrid quantum mechanics/molecular mechanics computational strategy based on multiconfigurational perturbation theory and complete-active-space-self-consistent-field geometry optimization. Remarkably, excitation energies were reproduced within 3 kcal/mol and both excited state and cavity charge distribution were mapped with high precision. The same computational analysis was carried out for the designed biomimetic photochemical switch. The study provided deep insight into the static and dynamics factors responsible for the color and ultrashort excited state lifetime observed for a

variety of chromophores embedded in biological and solution environments.

Jack Saltiel presided at the evening session which started with a talk by **Andrei Kutateladze** who discussed the interplay of theory in experiment in *Photoinduced fragmentations in substituted dithianes*. Andrei started with a recent progress in his laboratory in the design of externally sensitized systems that can be taken apart by photochemical irradiation. This was followed by a Stern-Volmer analysis of photophysics of triplet energy transfer, thorough mechanistic analysis of electronic structure of intermediates involved in a variety of fragmentation processes, intriguing stereoelectronic effects coupled with conformational equilibria in 1,3-dithiane systems. Interestingly, computational analysis at TD DFT and CASSCF levels suggests that the key fragmentation step in the case of amidothioxanthone may occur both from the lowest singlet and triplet states.

Andrei finished his presentation by describing two new developments: release and report experiments which described design of fragmentations that liberate highly fluorescent chromophores from non-fluorescent precursors and a system in which photochemical deprotection was designed to propagate autocatalytically like a forest fire from a selected spot on the surface of 90 micron polymeric beads. In the latter process, initial photoreaction liberated diarylketone moiety that served as a sensitizer for the photodeprotection of adjacent molecules.

In a talk on "*Optical Properties of Conjugated Organometallic Oligomers: Interplay of Experiment and Theory*", **Kirk Schanze** introduced organometallic conjugated polymers as possible new materials for optical and electronic applications which can be tuned through the variation of optical and redox properties of metal center. Kirk discussed spectroscopy of Pt-acetylide oligomers and

its dependence on the oligomer length. Theoretical and experimental work indicates that (M) $d\pi - (L)$ $p\pi$ interactions give rise to extended delocalization of ground and excited state wavefunctions and that $M \rightarrow L$ charge transfer may also play a role. The delocalization effects were examined in both the singlet and triplet excited states. Interestingly, it was found that singlet exciton is delocalized over 6 – 7 repeat units whereas triplet exciton is confined on approximately two Pt-centers. TD-DFT calculations on Pt-acetylide oligomers are consistent with experimental results and suggest that this intriguing observation parallels subtle conformational changes that gate distribution of delocalization. Rotation of a bridging Ph group in the triplet state disrupts electronic interaction between the triplet centers. The second part of the talk discussed supramolecular interaction mechanisms in designed architectures (star, helix etc) based on Pt-acetylide oligomers as building blocks. Kirk discussed the effects of triplet-triplet annihilation in "star" systems and consequences of aggregation in Pt-acetylide gelators.

Miguel Guillermo Neumann presented a lecture on "*Global polymerization rates deduced from kinetic and thermodynamic data of elementary reactions*". Miguel discussed the general kinetic scheme of polymerization processes with special attention to the photoinitiation step and a separate analysis of triplet and singlet photoreactions. The general scheme is quite complicated and involves several photochemical states and protonation/deprotonation events. After the elimination of unlikely events, the main reaction path was suggested and utilized to develop a mathematical model in which the quantum yield of radicals was given through a combination of parameters each of which could be determined experimentally. These

measurements provided an estimate of the quality of the mathematical model. Gratifyingly, a good fit between the mathematical model with the experimental data was found.

José M. Riveros gave a talk “*Vibrational photochemistry and spectroscopy of gas-phase ions: Experiment and theory*” where he discussed why gas-phase ions provide an interesting object for fundamental studies. These reactive species can be easily generated under high vacuum, steered with E and B fields and detected through MS techniques. Importantly, their electronic structures lend themselves to analysis by high level computational methods. José outlined action spectroscopy, the role of single photon induced vibrational predissociation vs. multiphoton excitation and the possibility of extracting reaction barriers and thermochemical information from experiments that involve multiphoton vibrational excitation of ions.

After discussing the instrumental details, José described experiments that probed dissociation of ruthenium bipy complexes and included dynamics and temperature dependence of these processes. Effect of charge and deuteration were analyzed as well. Finally, the master equation approach was utilized for kinetic modeling of processes. In the spirit of the workshop, these systems were analyzed computationally at ZINDO level with the subsequent refinement with B3LYP/LANL2DZ2. A potential of this technique for other interesting systems was also illustrated.

Sunday, June 11, 2006

Frank Quina presided on a morning session which started with a memorable talk “Microlasers for High Gain Chemo-/Bio- Sensing on Small Length Scales” by **Dan Nocera** (featured in a special technical article in this letter).

Jose Carlos Netto Ferreiro discussed triplet photochemistry of α -diketones in organic solvents and ionic liquids. The rates of chemical reactions are sensitive to polarity of the solvent. This effect has been interpreted in terms of conformational effects and distribution between more reactive (cisoid) and less reactive (transoid) conformations of the diketone moiety.

Marshall Newton presented a lecture entitled “*Theoretical probes of thermal and optical electron transfer: the role of electronic and nuclear degrees of freedom*”. Although a good qualitative mechanistic understanding of broad classes of ET processes (thermal and optical) is already achieved, quantitative determination and control of key energy and coupling parameters remain among the major outstanding issues. Marshall underscored the need to extend and implement current models and computational techniques to accommodate the interplay of electronic and nuclear degrees of freedom and to coordinate experimental/ theoretical/ computational efforts. In accord with the main theme of the workshop, Marshall pointed out that experiments remain vital for validation of theory whereas theory is invaluable for prediction and identification of key new experiments and formulation of design concepts.

Marshall also discussed the specific technical challenges in more detail, addressing the validity of 'separability' assumptions, timescale competition between electronic and nuclear manifolds, nuclear quantum effects, extension of the simple nonadiabatic framework (electronic tunnelling), specification of appropriate electronic 'spaces' and state representations within these spaces, state specific solute polarizability effects, medium (solvent) response and temperature dependence of enthalpic vs. entropic solvation contributions.

David Pratt presented an extraordinary educational talk on: “*High resolution spectroscopy in the gas phase: a tutorial*” which described applications of high resolution electronic spectroscopy in molecular beams. This method provides both structural and dynamical information on geometries of large molecules and how they change when they absorb UV light. This is extremely useful for elucidation of the intermolecular potential energy surfaces of a variety of supramolecular complexes and allows direct observation, in the frequency domain, of a variety of dynamical processes.

Solvent reorganization in the indole-water complex was used as an example. Studies of its spectrum in the presence of an electric field (the Stark effect) reveal how motion of the attached water molecule is coupled to the reorientation of the indole dipole moment,

produced by the absorption of light with an unprecedented structural accuracy.

Overall, it was an unusual and highly interactive talk that not only encouraged but also provoked questions from the audience. Audience participation prolonged spirited discussions well beyond the allocated 30 minutes making the last accord of the NSF workshop (and the prelude for the following I-APS conference) lasting, memorable and highly educational.

Igor Alabugin, Florida State University



17th Inter-American Photochemical Society Winter Conference June 11-16, 2006, Salvador, Bahia, Brazil

<http://www.cepema.usp.br/iaps2006/info.htm>

For the third time, the I-APS Conference was held South of Rio Grande, this time in the picturesque city of Salvador de Bahia in Brazil. In May 2001 it was held in Ascochinga, Córdoba, Argentina (**I-APS Newsletter** November 2001, <http://www.chemistry.mcmaster.ca/~iaps/iaps-newsletter-fall2001-clr.pdf>) and in May 1996 in Foz de Iguazú, Brazil (**EPA Newsl.** 57, July 1996, **I-APS Newsletter** Nov. 1996 <http://www.chemistry.mcmaster.ca/~iaps/nl-nov96/nl-nov96.html#4>).

Cornelia Bohne, **Frank Quina**, and **Jack Saltiel** wonderfully organized the Conference and the preceding US-Brazil Workshop on “The Interplay of Experiment and Theory in Photochemistry” sponsored by the US National Science Foundation and the Brazilian CNPq.

There were about 150 participants, many from Argentina, Chile, Brazil, the United States and Puerto Rico, and Canada, as well as some from Venezuela. A few Europeans from Portugal, Italy, Spain, and Germany completed the international list. More than 50% of the participants were students or young post-docs. This is a constant in these meetings and speaks well of the good health of the photochemistry field.

The Monday morning session included a Plenary Lecture by **Kirk Schanze** (Gainesville, FL) on “Conjugated Polyelectrolytes” in which the application of the amplified quenching effect to the development of biosensors was demonstrated. Several

short talks by **M.C. Simpson** (Case Western Reserve University) on “Diphosphene photochemistry”, **C. Turro** (Ohio State University) on the “Interaction of Ru(II) complexes with DNA”, **J.W. Baader** (Universidade de São Paulo) on “Inter- and intramolecular electron transfer in organic chemiluminescence”, and **M. Levitus** (Arizona State University) on “Potential sources of artifacts in single-molecule applications” (the abstracts are available on the WEB page of the Conference) showed various aspects of basic and applied photochemistry.

The I-APS awards were given during the Monday afternoon session chaired by **Peter Ford**, President of I-APS. **Dan Nocera** (W.M. Keck Professor of Energy and of Chemistry at the Massachusetts Institute of Technology, MIT) received the 2006 **I-APS Award** for his achievements in the area of Inorganic photochemistry and delivered a very comprehensive talk entitled “Powering the Planet: The Challenge for Science, Chemistry and Photochemistry in the 21st Century” during which he convinced us that it was our responsibility (as the chemists and molecular scientists) to make a big effort in fundamental molecular sciences in order to enable effective solar energy-based energy conversion (See the Preface to the Forum on Solar Energy, *Inorg. Chem.* 44, 6799-6801, 2005). The **Closs Award** was offered to **Ryan C. White** (University of North Carolina, Chapel Hill), a Gerald Closs scientific grandchild, who gave his talk on the application of various techniques (time-resolved electron paramagnetic resonance, TRPR, chemically induced dynamic nuclear polarization, CIDNP, and laser flash photolysis) to the study of amino acid derived radicals and radical cations formed upon photooxidation and photoinitiated electron transfer reactions. **Franco Cabrerizo** (Universidad de Buenos Aires) received the **Cilento Award** and delivered a lecture on the photochemistry of pterins in aqueous solutions. The **Young Investigator Award**

was received by **Mohammad A. Omary** (University of North Texas) whose talk was about “Bright, Tunable Coinage Metal Phosphors” in which he explained the efforts of his group to design efficient organic light-emitting diodes (OLEDs). **Frank B. Mallory** and **Clelia W. Mallory** were made **IAPS Fellows**. Fred Lewis offered a very interesting and warm portrait of the Mallory’s including wonderful pictures taken at various occasions over a long period of time. **Frank Mallory** then told us about the stilbene photocyclization reaction, widely used today in organic synthesis (*J. Am. Chem. Soc.* 86, 3094, 1964). This award session was really wonderful, because we learned about the evolution of photochemical knowledge over the last 50 years and also about where we should put our efforts in the future.

On Monday evening, as well as on Wednesday evening, the poster sessions with a total of 96 posters, gave the opportunity of discussing the results presented by a large number of young students and post-docs (as well as some older fellows). The sessions were well attended and the discussions as usual during these Conferences very lively.

The plenary lecture on Tuesday morning by **V. Ramamurthy** (University of Miami) on the photochemistry of organic molecules encapsulated in nanocapsules was very interesting, especially from the topological point of view. The four short talks again showed the different and creative approaches to the solution of various problems using photochemical tools, from “photolabile scaffolds for molecular recognition” by **Andrei Kutateladze** (University of Denver), the discovery of a concerted 3,3-shift of an acetate group in cinnamyl acetates by **Steven Fleming** (Brigham Young University), the time-resolved studies on higher group 14 analogues of carbenes and alkenes, *i.e.*, silylenes, germylenes, and stannylenes by **Willie**

Leigh (McMaster University), to the photophysics of artificial photosynthetic antenna-reaction center complexes presented by **Devens Gust** (Arizona State University). The Tuesday session ended at 12:00 noon for lunch followed in the afternoon by general soccer viewing (football, or futiboli en Português) enjoyed by most of the conference participants in a large hotel room in which a public viewing screen was installed. Most of the participants (Canadian and US included but with the notable exception of the Argentinians) wore the Brazilian T-shirt. Fortunately, Brazil won the game against Croacia!! In the evening we visited the wonderful Salvador and witnessed the celebrations after the game.

The Wednesday sessions started with the plenary lecture by **Massimo Olivucci** (Università di Siena) on “Computational Design and Characterization of a Bio-mimetic Photochemical Switch” in which he showed how the strategy of quantum mechanics/molecular mechanics calculations is used for the calculation (and then preparation) of optimized molecular devices with specific properties. In short lectures **Gonzalo Cosa** (McGill University) explained the “Development of new fluorescent strategies for the study of supramolecular interactions in lipid membranes” and **C. E. Crespo** (Ohio State University) showed the formation of sub-nanosecond states with significant charge transfer character upon UV excitation of vertically stacked bases in oligonucleotides and discussed how interstrand proton transfer could modulate the dynamics of these states in DNA double helices. **Alexis Aspee** (University of Ottawa) showed the development of a new methodology for the estimation of antioxidant capability of phenolic compounds in homogeneous and microheterogeneous media and **Lisa Kelly** (University of Maryland-Baltimore County) spoke about the ground- and excited-state interactions of substituted naphthalimides

and nucleic acids. **Chris Evans** (Ryerson University) told us about the development of sensor materials with fluorophore-containing cyclodextrin-based polymers. In the afternoon **David Pratt** (University of Pittsburgh) gave an impressive and theatrical plenary lecture on “High resolution electronic spectroscopy in the gas phase”. Intermolecular potential energy surfaces of weakly bound complexes between the chromophore (*e.g.*, dimethyl aminobenzonitrile) and water molecule(s) in the gas phase can be analysed. Many biologically relevant molecules, such as the amino acids, have been studied in the group of David Pratt. The influence of electric fields (Stark effect) on the high resolution spectra affords the calculation of the induced dipole moments in the excited states.

During his short talk **Glenn Loppnow** (University of Alberta) showed the possible applications of UV-resonance Raman spectra for the study of excited state dynamic behavior of pyrimidine nucleobases and **Enrique San Román** (Universidad de Buenos Aires) presented photophysical studies on dyes attached to various supporting materials. These studies are essential for the development of solid-state sensitizers, *e.g.*, for the generation of singlet molecular oxygen. **Hans-Peter Loock** (Queen’s University, Kingston) explained the use of ring-down spectroscopy with solid wave guides for the high sensitivity detection of analytes in liquids and **Carolina Aliaga** (Universidad de Santiago de Chile) showed the results of the studies on HP-136, an isobenzofuranone, proposed as an adequate antioxidant for processes of polymerization.

Miguel Neumann (Universidade de São Paulo, São Carlos) analysed in a plenary lecture the conditions required for the photoinitiation by Safranin of copolymerization of styrenesulfonate

with methyl methacrylate, or with hydroxyethyl methacrylate.

Thursday morning sessions started with a plenary lecture by **Peter Ford** (University of California, Santa Barbara) explaining the strategies developed for the efficient photoinduced delivery of NO to biological targets. An important strategy is the introduction of intramolecular antennas with large absorption coefficients. **Julio de la Fuente** (Universidad de Chile) presented in a short lecture studies on oxoisoaporphins. **Luis Arnaut** (University of Coimbra, Portugal) demonstrated the application of various techniques for the study of electron transfer reactions in supercritical CO₂ and liquid solvents. Interestingly, an ultraexothermic charge recombination process is observed at the end of the Marcus inverted region. **Mónica González** (Universidad de La Plata) explained the study of reactions of inorganic radicals at silica nanoparticles/water interfaces with microseconds flash photolysis, studies of significance for applications such as water purification by photocatalysis. **David McMillin** (Purdue University) exposed the studies on DNA interactions with cationic porphyrins and **Spiridoula Matsika** (Temple University) explained the high level *ab initio* multireference calculations on excited states of pyrimidine nucleobases in order to understand the nature of the highly efficient radiationless processes in these molecules.

On Thursday afternoon **Malcolm Forbes** (University of North Carolina at Chapel Hill) presented a plenary lecture on the results of an extensive study on the magnetic and dynamic properties of the radicals formed through Norrish I cleavage of a side chain ester group upon 248 nm excitation of acrylic polymers. Fast motion time-resolved electron paramagnetic resonance (TREPR) spectra (typically at 100 °C) led to the postulation of a dynamic effect that can be simulated using a two-site jump model for the hyperfine modulation.

Igor Alabugin (Florida State University) convinced us that alkynes are much more than alkenes with an extra π bond and showed how diaryl acetylenes in their triplet states can be used as synthetic equivalents of 1,2-bicarbenes. **Anna Krylov** (University of Southern California) introduced quantum chemical calculations of the photoelectron spectrum of the *para* benzyne anion, **Uwe Pischel** (Universidad Politécnica de Valencia) discussed the polar effects on the hydrogen transfer quenching of $n\text{-}\pi^*$ excited states by antioxidants and **Fred Lewis** reported on the femtosecond broad band pump-probe spectroscopic studies of the dynamics of charge separation and charge recombination in a series of polyaryllureas having pyrene and nitrobenzene end groups, separated by phenylenediamine bridges.

In a plenary lecture **Linda Johnston** spoke about various imaging techniques to probe nanoscale organization in membranes, such as near-field scanning optical microscopy (NSOM) which combines the high spatial resolution of atomic force microscopy with the versatility of fluorescence imaging.

The last session on Friday morning included a short talk by **Michelle Chrétien** (University of Ottawa) on the multiple ways zeolites are used as supramolecular hosts, with particular emphasis on their use in sunscreens, a plenary lecture by **Laren Tolbert** on “The strange behavior of green fluorescent protein”. Taking advantage of the group expertise in “organic superacids” they are now analysing the details of the excited state proton transfer in the class of fluorophors present in the green fluorescent protein and related proteins. Short talks were given by **Antonio Tedesco** (Universidade de São Paulo,

Ribeirão Preto) on new photosensitizers for photodynamic therapy and **Guillermo Indig** (University of Wisconsin, Milwaukee) on the strategy of mitochondrial targeting for chemo and phototherapy of neoplastic diseases. **Silvia Braslavsky** (Max Planck Institute for Bioinorganic Chemistry, Mülheim an der Ruhr) closed the Conference talking on the “Correlation between the volume change-normalized entropic terms and Marcus reorganization energy”. I have to add that I started talking when Argentina was already winning 3 to 0 against Serbia-Montenegro. During my talk Ana Moore and other prominent scientists with Argentinian soul were signaling to me (by waving their hands from the back of the room) the 4th, 5th, and 6th goals !!! We had a big laugh.... In any case, Argentina was eliminated some matches after that one by Germany....

Several speakers warmly remembered the contributions to the field of photochemistry, the wonderful human qualities and the research leading abilities of **Don Arnold** whose recent death sadly surprised many of the participants of the Conference. Sadly, another recent death noted by **Jack Saltiel** on opening the Workshop that preceded this conference, was that of George S. Hammond, regarded by many as the father of molecular photochemistry and certainly as the father of photochemistry in Brazil.

The banquet on Thursday evening was a wonderful event, with a very

colourful and exciting show including folkloric Brazilian-African dancing and the famous slaves’ dance called Capoeira. During the banquet I felt very honored by Cornelia and Frank who gave me a wonderful Brazilian stone in the name of the Latin-America photochemical community, by my doctor father (Eduardo Lissi) who spoke very warm words about me and by my former Argentinian coworkers who in the person of Pedro Aramendía presented me with a great poster portraying all the Argentinians who joined my group in Germany for various periods since 1984. I thank every one for the present and all my co-workers and colleagues during my 30 years in Germany for the great scientific and personal time we spent together.

Undoubtedly, we will all fondly remember this meeting. We learned a lot, met old friends and made new ones, enjoyed football (soccer to some) and were spoiled by the generous hospitality of our Brazilian colleagues. Thank you Cornelia, Frank and Jack for a great job.

Silvia E. Braslavsky

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Donald R. Arnold In Memoriam



Donald Robert Arnold, Professor Emeritus, Department of Chemistry, passed away at his home in Hubley, NS on May 17.

Born in 1935, Don was raised in Buffalo, New York. He received a BSc in mathematics and chemistry from Bethany College in Bethany, West Virginia, in 1957. While at Bethany, Don married Janet Price, his high school sweetheart. He received his PhD from the University of Rochester, New York, in 1961.

Don then accepted a position at the Union Carbide Research Institute in White Plains, New York, where he pioneered research in applied organic photochemistry. After a decade at Union Carbide, he was persuaded by the late Paul de Mayo to join the Photochemistry Unit at the University of Western Ontario in London, Ontario. At its peak this unit boasted seven internationally recognized faculty members in the Department of Chemistry at UWO.

In 1979, Don was attracted to Nova Scotia by Dalhousie University's offer of an Izaak Walton Killam Research Professorship. He joined an active cadre of physical organic chemists in the Department of Chemistry and proceeded to direct a strong research program of his own for the next 25 years.

Don was an internationally recognized leader in the field of organic photochemistry. His astute use of a broad range of techniques to study organic photochemical problems enabled him to bridge organic and physical photochemistry, thus contributing to the virtual elimination of this division. He showed remarkable foresight when he initiated research on photo-induced electron-transfer reactions. He wrote several classic

papers in a field on which much of the currently published literature in photochemistry is now based. His distinguished career resulted in more than 120 publications. For these contributions he was named to Dalhousie University's Alexander McLeod Chair of Chemistry in 1991.

He received numerous awards and honours including an Alfred P. Sloan Research Fellowship (1971-73), a John Simon Guggenheim Memorial Fellowship (1980-81) and the Alfred Bader Award in Organic Chemistry from the Chemical Institute of Canada (1995). He was honoured by his Alma Mater, Bethany College which an "Alumni of Distinction Award" in 2001 and in 2005 by an Honourary PhD in chemistry. He held important positions in many organizations, including President of the Inter-American Photochemical Society and Director of Organic Chemistry of the Canadian Society for Chemistry. In addition, his participation in conferences, whether as an organizer, an invited lecturer, a contributor of a talk or poster, or as one taking part in the questions, answers and comments that follow a talk, always raised the scientific level for all who attended. In 2003, the *Canadian Journal of Chemistry* published an issue in his honour with contributions from chemical colleagues and friends from all over the world.

He is survived by Janet, his wife of more than 50 years, his six children, including his son, Professor Bradley Arnold (Department of Chemistry and Biochemistry, University of Maryland Baltimore County) and their families.

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Reprinted from "DalChem News, June 2006"

George S. Hammond In Memoriam



Reprinted from *Photochem. Photobiol. Sci.*,
2006, 5, 869 - 870

The articles in this issue of *Photochemical and Photobiological Sciences* are a celebration of the legacy of our friend, mentor, and colleague, George Simms Hammond, who passed away on October 5, 2005. The contributors are members of those groups, and they span three generations of his scientific progeny. All are members of the same family, affectionately referred to as "The Hammond Mafia."

Since the time of his death, there have been several memorials, some focusing on George as a person and others concentrating on his scientific contributions.¹ A *festschrift* that appeared in 2003² includes an extensive list of his scientific accomplishments. An ongoing website is available with extensive information about George's publications, career, and hobbies, as well as contact information for students and collaborators.³

George Hammond was multidimensional in many respects. His life combined interests in theater (as an amateur actor), poker, and international affairs with (what sometimes appeared to others to be) eclectic interests even within science. Although his contributions to physical organic chemistry during the decade of the '50s and mechanistic

photochemistry, especially during the decades of the '60s and '70s, are where his long term legacy may lie, he was also very instrumental in the development of materials science as a multidisciplinary "art" form during the '70s and '80s, in educational innovation throughout his career, and in making those around him aware of the frontiers of science and challenging the dogma that bordered those frontiers.

George Hammond's life is a celebration of the macroscopic manifestation of the Heisenberg Uncertainty Principle and the American dream. He started his life on May 22, 1921 on a dairy farm in Auburn, Maine, was taught by his grandmother initially, and eventually received a BS degree from Bates College (*magna cum laude*) in 1943. His doctoral thesis at Harvard in 1947, under the mentorship of Paul D. Bartlett, focused on free-radical initiated polymerization processes and led to two of his more than 300 peer-reviewed publications.⁴ After a postdoctoral year with Saul Winstein at UCLA, he joined Iowa State University in 1948. His first article from there demonstrated his ability to use principles of physical organic chemistry to solve complicated scientific problems.⁵

The influence of Bartlett, allowing his graduate students to try new ideas, even those arousing his skepticism, had a lifelong impact on how George mentored his own students and postdoctoral fellows. He encouraged them to develop their own projects and, when presented with the ideas, usually exclaimed, "Gee, that's great!", even when he found some errors. He treated those in his group as peers; symbolically, he asked that all his students and postdocs call him "George", and those with sufficient courage and confidence did. His science was about nature *and* the people investigating nature: "It is good to have new scientific puzzles to think about and it is good to interact with the people. When I think about the matter I see that a great deal of the pleasure that I have extracted from a scientific life is actually social."⁶

He defied attempts to define who he was or where his scientific interests would lead. He changed career paths on several occasions, and he made seminal contributions in virtually each new field he entered. For instance, the “Hammond–Gray Curriculum” was considered too radical for adoption by many because the categorizations of chemistry as structure, dynamics, and synthesis deemphasized the traditional subdisciplines of physical, organic, inorganic, analytical, and biochemistry. Yet, its impact is still important in the United States and elsewhere. For instance, the program offices of the U.S. National Science Foundation are organized along lines that mirror Hammond's views. In addition, his textbook, *Organic Chemistry*, written with Donald Cram,⁷ was revolutionary because it approached the teaching of the subject according those same three major concepts—structure, dynamics, and synthesis—rather than by functional groups.

George's most famous non-photochemistry article, on the “Hammond Postulate”, was written at Iowa State in 1955.⁸ In it, he described a proposed relationship between structures of transition states and either their reactants or products, based on the relative energies of each species. Later, he mentioned that the basic concepts came to him during a dream, and he complained that the postulate had been applied in ways he never intended and then was criticized for reasons that had nothing to do with his intent. Still, the basic ideas in the paper have become an icon for structure–reactivity relationships; it is the 15th most cited article in the history of the *Journal of the American Chemical Society*.⁹

Although the first of his seminal photochemistry articles appeared in 1959,¹⁰ the year after he moved to Caltech in Pasadena, he admitted that he had tried for several years, with limited success, before making notable progress in deciphering the chemistry of excited states. The road leading to the successes of the ‘60s and ‘70s was not smooth. However, the explosion of creativity, insight, and discovery that began at Caltech

resulted in the development of modern mechanistic photochemistry.

After serving as the Chair of the Division of Chemistry and Chemical Engineering at Caltech, George moved to UC Santa Cruz as Vice-Chancellor for Natural Sciences in 1972, and he remained there until 1978. During 1974–78, he was also Foreign Secretary of the U. S. National Academy of Sciences where he was instrumental in increasing international contacts between the Academy and scientists in then Soviet block countries and in ensuring the success of a novel science and education development program with Brazil.

During various periods with Allied-Signal Corporation, from 1978 until his mandatory retirement at the end of 1987, George was Associate Director of Research, Physical & Organic Chemistry, Director of Chemical Dynamics, Energy & Chemical Process Laboratory, and Integrated Chemical Systems Laboratory, and Executive Director of Integrated Chemical Systems, Molecular & Applied Genetics, Biosciences, and Metals and Ceramics Laboratories.

In fact, George Hammond never retired spiritually, physically, or philosophically. He was affiliated with and held formal positions at Georgetown University, Portland State University, and Bowling Green State University. He continued to promote in words and deeds the interdisciplinary nature of the photosciences until the end. After listening to a particularly uninspiring oral presentation, he opined, “Any scientific (or other) discipline when put into a small rigid box will surely shrivel and die.”¹¹ In 1996, at the age of 75, he presented a plenary lecture entitled, “Where has photochemistry come in 35 years? Where is it now?”, at the I-APS Photochemistry Conference in Foz de Iguaçu, Brazil. The last sentence of the abstract for that lecture reads: “The growth and melding of all of the photochemical and optical sciences places us in a position to tackle important problems of a complexity which have made them untouchable 35 years ago.” His name

appears on 19 peer-reviewed articles that postdate his “retirement”. The last,¹² co-written with a former student and published shortly before his death, demonstrates how he was able to breathe new life into old subjects.

Many honours have been bestowed on George Hammond in formal recognition of his contributions to the field of science, especially the photosciences and science education. They include the Award in Petroleum Chemistry, the James Flack Norris Award in Physical Organic Chemistry, the Award in Chemical Education, and the Priestley and Seaborg Medals from the American Chemical Society, the E. Harris Harbison Award for Gifted Teaching by the Danforth Foundation, and honorary doctoral degrees from Wittenberg University (Ohio), University of Ghent (Belgium), Bates College (Maine), Georgetown University (Washington, DC), Bowling Green State University (Ohio), and the Weizmann Institute of Science (Israel). He also received the National Medal of Science from President Clinton in 1994 and the Othmer Gold Medal from the Chemical Heritage Foundation in 2003. He was the organizer of the first IUPAC Symposium on Photochemistry in 1964 and was an Editor of the series *Advances in Photochemistry* for many years.

Those of us who were fortunate to be able to interact extensively with George Simms Hammond know that the scientific world and the larger world outside of science have lost one of our true “luminaries”. Through this issue and what it represents, we hope to keep the spirit of George's lamp burning brightly.

Richard G. Weiss*^a and Carl C. Wamser^b

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Symposium Announcements

Annual Spring Meeting of the Materials Research Society Symposium BB: Hybrid Functional Materials for Optical Applications

Call for abstracts - Deadline Nov. 1, 2006

This symposium is focused on a wide range of materials for linear and non-linear optical applications. Contributions in the area of basic science of optical materials as well as applications are encouraged.

Invited speakers include members from the I-APS, and we anticipate that there will many talks that will be of interest to the membership of the society. Society members are encouraged to submit abstracts for presentation at the meeting. For more information see the attached flyer, abstract submission : www.mrs.org/meetings/, and/or contact kschanze@chem.ufl.edu.

Invited Speakers:

H. Agren (Royal Inst. Tech. Sweden)
U. Bunz (Ga. Tech.)
L. Dalton (U. Washington)
N. Halas (Rice U.)
A. Holmes (U. Melbourne)
J. Hupp (Northwestern U.)
R. Janssen (Eindhoven U. Tech.)
G. Meyer (Johns Hopkins)
C. Murphy (U. South Carolina)
A. Scherer (Cal. Tech.)
V. Shalaev (Purdue U.)
G. Shvets (U.T. Austin)
M. Thompson (U. Southern Calif.)
S. Tolbert (UCLA)
Y. Xia (U. Washington)
V. Yam (U. Hong Kong)

Symposium Organizers:

A. Cartwright (U. Buffalo)
A. Kohler (Potsdam)

T. M. Cooper (AFRL, Wright Patterson-AFB)
K. Schanze (U. Florida)

13th International Conference on Unconventional Photoactive Systems (UPS-13) will be held at Northwestern University, Evanston, IL, USA on August 5-9, 2007.

Northwestern University is sited on the shore of beautiful Lake Michigan approximately 15 km north of downtown Chicago.

Photoactive molecules and materials form the basis of a broad class of systems directly applicable to technological advancements in the areas of solar energy conversion, lighting, optical data processing and storage, image processing, and sensors. The purpose of this conference is to bring together investigators in these cross-cutting areas to share information on this expanding and important field.

In the past this meeting has been held most often in Europe, but traveled for the first time to Japan for UPS-12 in October, 2005. Now the meeting will be held in the United States for the first time in many years.

The conference will include the following general topics: solar energy conversion, bio-inspired photoactive systems, electroluminescence and OLEDs, nano-optics and plasmonics, single molecule spectroscopy, photonic switches, nonlinear optics, photochromic materials, and optical data storage.

Please check the Conference Website for information on the venue, conference program, invited speakers, housing options, and Registration.

The Website can be found at www.chem.northwestern.edu/~ups13

I am looking forward to welcoming you to Northwestern in August of 2007 for what promises to be an exciting conference.

Michael R. Wasielewski

Professor of Chemistry
Northwestern University



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