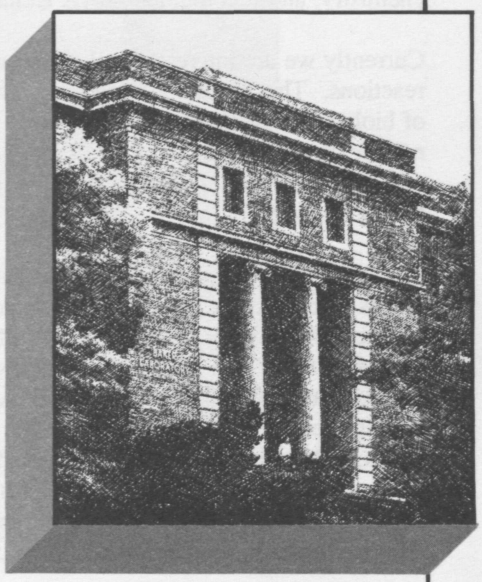
CORNELL CHEMISTRY



THE NEWSLETTER
OF THE
DEPARTMENT OF
CHEMISTRY
AND THE SOCIETY OF
CORNELL CHEMISTS

Baker Laboratory
Cornell University
Ithaca, New York
14853-1301

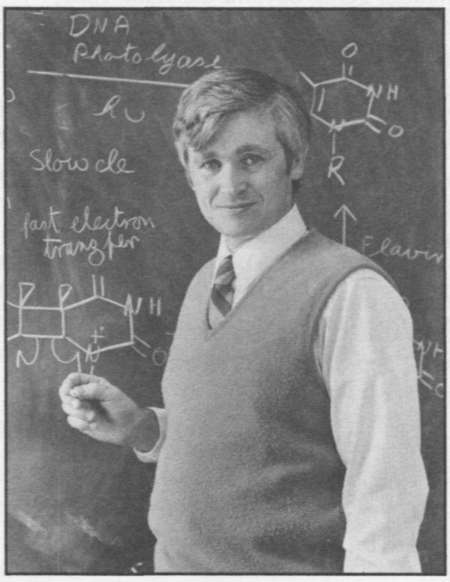
December 1986
Issue 38

JOHNSON'S WAX INITIATES CORNELL POLYMER CHEMISTRY TRAINEESHIP PROGRAM

The Johnson's Wax Fund of Racine, Wisconsin, has awarded Cornell's chemistry department a grant of $200,000 to establish a program for training graduate students for careers in polymer chemistry. The award will provide both tuition and a stipend for at least three Ph.D. students in this critical discipline of molecular science. Together with the previously announced grant by IBM Corporation of $2,000,000 for the development of research and education programs in the area of polymer and solid state chemistry, the Johnson's Wax gift will go far to revitalize an area in which Cornell has had a rich and distinguished history. That two of the largest public and privately held American companies have decided to support our endeavor so generously emphasizes the importance of polymer chemistry to the continued vigor of our nation's industries. Cornell is delighted to be playing a lead role in this endeavor; you can look forward to hearing more exciting news from us soon!

NEW FACULTY MEMBERS WELCOMED

This summer the Department was proud to welcome three new faculty members, **Tadhg Begley, Frank DiSalvo,** and **Atsuo Kuki**. Tadhg began this academic year by co-teaching Chemistry 302 with Tito Abruña, while Atsuo teamed up with Barbara Baird to teach Chem 215. Frank, meanwhile, taught Chemistry 289. All three describe their research interests in the articles below. We wish them well as they begin their Cornell Chemistry careers.



After completing his undergraduate studies at the National University of Ireland at Cork, Professor Begley carried out his Ph.D. research with P.B. Dervan at the California Institute of Technology. He then carried out one year of postdoctoral work with W. Oppolzer at the University of Geneva and two years of postdoctoral work with C.T. Walsh at the Massachusetts Institute of Technology. In July 1986 he joined the Cornell Faculty. He has been awarded a Dreyfus Foundation Young Faculty Prize for 1986-87.

There are many examples of enzyme-catalyzed reactions whose mechanisms are unknown and cannot be trivially predicted. These systems offer an exceptional opportunity to discover new organic chemistry. Mechanistic studies on such enzymes is the central theme of our research. Our strategy will involve a combination of biophysical

techniques, kinetic studies with altered substrates, protein chemistry, and recombinant DNA technology.

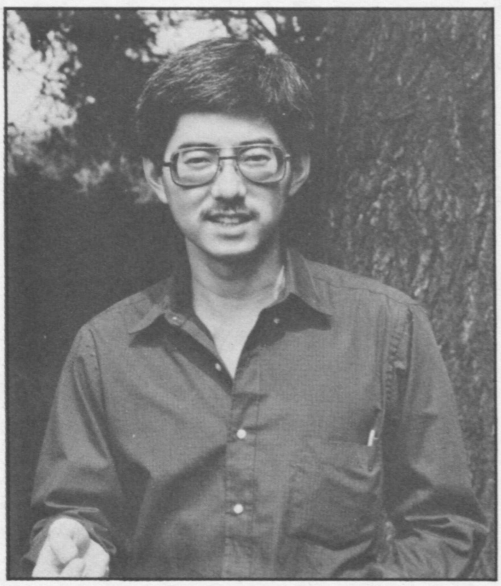
Currently we are interested in light requiring enzymatic reactions. These reactions constitute an underrepresented class of biological reactions. There are only two known examples, neither of which is understood at the mechanistic level. We will carry out studies to elucidate the mechanisms of the following systems:

a) DNA Photolyase: Irradiation of bacteria with UV light results in cell death. When these bacteria are irradiated with visible light they are brought back to life again. The biochemistry of this remarkable process has been elucidated. Ultraviolet light causes pyrimidine dimerization. These dimers are repaired by DNA photolyase which uses the energy of visible light to cleave the two unwanted C-C bonds of the dimer. This enzyme is critically important in protecting bacteria from the harmful effects of sunlight and may play a role in protecting humans against skin cancer.

b) Protochlorophyllide reductase: The final step in chlorophyllide biosynthesis in flowering plants is a light-requiring enzyme-catalyzed reduction of the D ring of protochlorophyllide. The mechanism of this important biological reaction is unknown.

We are also studying phenoxazinone synthase. Actinomycin is a chromopeptide antibiotic produced by Streptomycetes-antibioticus. It is a potent anticancer drug currently used in the treatment of choriocarcinoma, Wilm's tumors, Kaposi's sarcoma, and rhabdosarcoma. Phenoxazinone synthase catalyzes the last step in its biosynthesis. The mechanism of this complex oxidative condensation reaction is unknown.

T. Begley



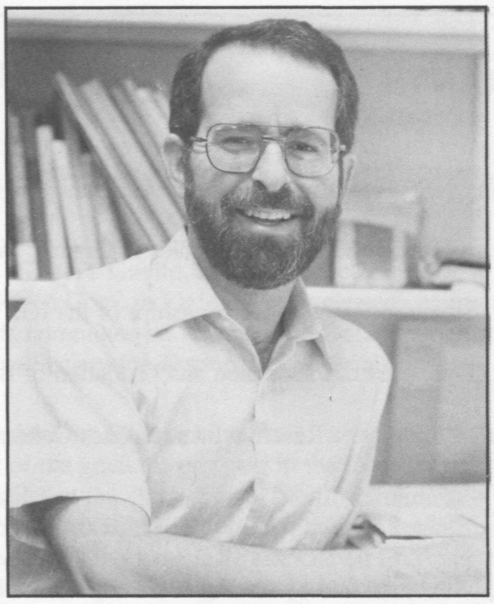
Professor Kuki came to the Department in August, 1986 from the University of Illinois, where he worked with P. Wolynes. He received his Ph.D. in 1985 from Stanford University under the direction of S.G. Boxer. He was given the NIH National Research Service Award for Individual Postdoctoral Fellows in 1985.

One of the most fundamental goals of chemistry is to understand the many body dynamics of elementary reaction processes in condensed phases, including both classical and quantum aspects. The research of our group employs a broad range of synthetic, spectroscopic, kinetic, and theoretical techniques to focus on the electronic and nuclear dynamics that control electron transfer reactivity of photo-excited states of redox centers in solution and in proteins. The challenge lies in the unravelling of the way in which the rapid rotations, vibrations, and collisions of solvent molecules conspire to influence the kinetics of rare reactive events.

Light-induced electron transfer reactions are an intriguing and important elementary reaction process. Charge transfer reactions are very strongly coupled to the solvent polarization field and its fluctuations and can provide an ideal test of emerging theories of reactions in solution, going beyond transition state theory. Our methods include nanosecond laser techniques, variable temperature and high pressure techniques to understand the role of solvent properties, and in the near future, mode-locked picosecond laser techniques.

Light-induced electron transfer is also the primary process of photosynthesis, and one which we are just beginning to understand on the molecular level. The selectivity of individual electron transfer events within photosynthetic and respiratory assemblies arises from interactions with the non-uniform structured environment of the interior of proteins. The electric fields and electronic interactions within this environment must be understood. We will synthesize structured donor/acceptor complexes as models of electron transfer proteins. Theoretical work on quantum path integral approaches to electron tunneling in structured environments is also ongoing.

A. Kuki



Professor DiSalvo came to Cornell in July, 1986 from AT&T Bell Laboratories in New Jersey, where he was Head of the Solid State and Physics of Materials Research Department. He received his Ph.D. in Applied Physics from Stanford University in 1971. From 1966 to 1969 he was an NSF Fellow. He has been a visiting professor at Stanford University and has given numerous invited lectures at universities and conferences around the world.

My interests are in the synthesis of solid state compounds with unusual structural or bonding arrangements and the subsequent measurement and understanding of their chemical and physical properties. The research by its very nature is interdisciplinary, involving concepts and techniques from chemistry, materials science and physics.

The synthetic techniques used include reactions at up to 2000° in electron beam welded metal tubes, reactions to 1150° in sealed quartz tubes, reactions under reactive or inert flowing gasses, crystal growth by chemical vapor transport or from metal or salt fluxes, and aqueous or nonaqueous solution growth. Characterization of the products is performed using methods such as X-ray diffraction, elemental analysis, electron microprobe analysis, NMR or EPR, etc. Chemical properties studied might include thermal stability, reactivity with selected substrates and topochemical solid state reactions. Physical properties such as electrical transport, magnetic susceptibility, specific heat, and UV/vis/IR transmission or reflection spectroscopy may also be examined. Phenomena observed and studied in some of these compounds include charge density wave instabilities, structural or magnetic phase transitions, superionic conductivity, intercalation reactions, and superconductivity.

As a single example, consider the compound $TlMo_3Se_3$. It consists of infinite chains of face-sharing octahedra of Mo surrounded by Se and separated by large Tl cations. The electrical properties of such pseudo-one-dimensional compounds have been of interest, but even more interesting is our observation that the individual 6 Å diameter chains can be put into solution. This is accomplished by exchanging Li for the Tl from molten LiI at 480°C, subliming off TlI. Subsequently, this solid dissolves in highly polar solvents such as DMSO, PC or NMF. Individual chains, the thinnest metallic wires ever made, can be obtained by evaporating dilute solutions. Many experiments remain to be attempted with these and similar compounds. For example, if electrical contacts can be made to one 6 Å diameter chain, the ultimate one-dimensional wire could be studied. We may also be able to prepare solutions of short, equal-length chains (say 50Å), which ought to exhibit liquid crystal-like phases but with metallic-like optical properties.

F. DiSalvo

The Society of Cornell Chemists asks you to support the cost of printing and mailing this Newsletter with your voluntary, annual dues of $10. Make your 1987 check payable to "Cornell Chemistry" and mail it to the Society of Cornell Chemists, Baker Laboratory, Department of Chemistry.

NEW GRANTS

H. D. Abruña, NSF Presidential Young Investigator Program $40,000.

A. C. Albrecht, "Basic Photoelectric Studies in Organic Condensed Phase," DHHS/NIH $136,342.

B. A. Baird, "Structure-Function Relationships of the IGE Receptor," DHHS/NIH $115,201.

S. H. Bauer, "Dynamics of Production and Oxidation of Boranes," DOD/Army $67,222.

B. K. Carpenter, "Study of Reactive Intermediates Generated by Gas-Phase Ion Neutralization," ACS-PRF $35,000.

D. B. Collum, Sloan Research Fellowship, $25,000.

J. C. Clardy, "Structural and Synthetic Studies on Marine Natural Products," SUNY Sea Grant Inst. $28,601; "Three Dimensional Structure of Gossypol," Rockefeller Foundation $3,000.

G. S. Ezra, "Large-Amplitude Motions in Molecules," NSF $58,703; Sloan Research Fellowship $25,000.

J. H. Freed, "Molecular Dynamics, Structure and Phase Transitions in Liquid-Crystalline Media: ESR Studies," NSF $106,000.

D. A. Holowka, "Interactive Structures and Dynamics of Antigen Receptors," DHHS/NIH $133,431.

F. W. McLafferty, "Chemical Agent Sensing by Tandem Mass Spectrometry." DOD/Army $60,000.

J. Meinwald, "Synthesis of Optically Pure Inhalation Anesthetics," DHHS/NIH $630,282.

G. H. Morrison, "Microcharacterization of Solid State Materials by Secondary Ion Mass Spectrometry," DOD/Navy $77,647; "Ion Microscopy in Biology and Medicine," DHHS/NIH $141,647.

G. Nemethy, "Aging: Conformational Changes of Collagen," DHHS/NIH $90,859.

Richard F. Porter, "A Study of Metastable and Hypervalent Molecules by Neutralized Ion Beam Spectroscopy," NSF $76,400.

H. A. Scheraga, "Protein Structure and Dynamics Using Nonlinear Optics," NSF $126,000.

K. H. Theopold, NSF Presidential Young Investigator, $38,000.

J. R. Wiesenfeld, "Energy Storage, Pooling and Transfer Involving Electronically Excited Mercury Atoms in Gases," GE $40,000.

FACULTY NEWS

Andreas C. Albrecht was recently awarded the Polychrome Corporation Award in Photochemistry by the New York Academy of Sciences. The award included $1000 and a certificate citing his outstanding contributions to the science of photochemistry.

Barbara A. Baird and David B. Collum have both been promoted to the rank of associate professor with indefinite tenure.

Simon H. Bauer presented a plenary lecture at the International Conference on the Chemistry of IR Lasers in Leblice, Czechoslovakia. Before the conference, he also presented a paper at the 6th International Symposium on Gas Flow, in Jerusalem, and gave a seminar at the Ben Gurion University in Beer Sheva, Israel.

Michael E. Fisher gave the Ernest W. Guptill Memorial Lecture at Dalhousie University in Halifax, Nova Scotia on October 3.

Fred W. McLafferty will receive the S.C. Lind Lectureship Award from the East Tennessee Section of the ACS in November. The award acknowledges leadership in the chemical sciences and outstanding contributions to chemistry, and honors Samuel Coleville Lind, who was an internationally known physical and radiochemist and a native of Tennessee. Dr. McLafferty is the new editor of "Accounts of Chemical Research," an ACS journal, and serves on the National Research Council's Numerical Data Advisory Board and the Panel on Chemical Research for the NRC's Board on Army Science and Technology.

Late last Spring, **Jerrold Meinwald** presented the "Beckman Lecture" at CalTech on the occasion of the dedication of the new Beckman Laboratory of Chemistry at that school. He also traveled to Europe during the summer, where he presented the *R. Martin* Lecture at the Universite Libre of Brussels, and also lectured at the Universities of Neuchatel, Fribourg, Geneva, and Bern.

William T. Miller recently traveled to Paris, France to take part in a symposium held to celebrate the centenary of the isolation of fluorine by Henri Moissan. As part of the celebration, several chemists who have done outstanding work in fluorine chemistry over the years were awarded special Moissan medals. Dr. Miller was among the group honored, and was cited for his pioneering work with fluoroolefins.

George H. Morrison was the first-ever recipient of the Eastern Analytical Symposium Award for Outstanding Achievements in the Field of Analytical Chemistry when the EAS met in New York City at the end of October.

ALUMNI NEWS

1942 **Gordon R. Finlay**, Ph.D., died December 2, 1985.

1948 **Gilbert Gavlin**, Ph.D., technical director at Safety-Kleen Corp. in Elgin, IL, was elected chairman of the standards committee on Halogenated Organic Solvents for the American Society for Testing and Materials.

1948 **Melvin D. Hurwitz**, Ph.D., a professor and director of the graduate program in the Department of Clothing and Textiles at the University of North Carolina at Greensboro, has received the Olney Medal for 1986. The Olney Medal is the American Association of Textile Chemists and Colorists' highest recognition for achievement in textile chemistry.

1949 **Sundar L. Aggarwal**, Ph.D., vice president and director of research for GenCorp., in Akron, received the Technical Contributions Award of the International Institute of Synthetic Rubber Producers at that organization's annual meeting in May. He was honored for his scientific contributions to the rubber industry, including work on new catalyst systems and solution polymerization processes.

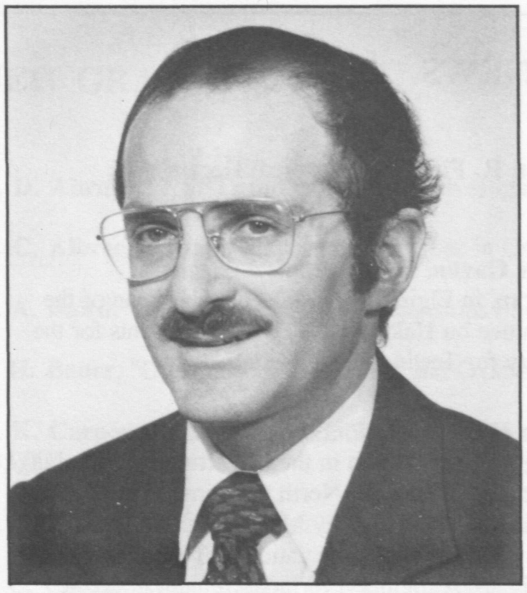
1952 **Richard Suchinsky**, B.S., M.D. SUNY Buffalo, is now director of the chemical dependence program at Northwestern Memorial Hospital in Chicago. He served for three years as chief of psychiatry at Lakeside Veterans Administration Hospital in Buffalo, New York.

1978 **Paul Lahti**, A.B., Ph.D. Yale, has joined the University of Massachusetts as assistant professor of organic chemistry.

STUDENT NEWS

Michael Eis, a graduate student in B. Carpenter's group, is one of four recipients nationwide to receive a Lilly Fellowship, sponsored by the Eli Lilly & Company Research Laboratories, from the Organic Chemistry Division of the ACS for 1986-87. He is working on the development of synthetic vaccines.

John Mitchell, '88, was awarded the 1986 ACS Regional Scholarship funded by the Connecticut General Life Insurance Company. John was nominated by the Cornell Section of the ACS because of his outstanding academic achievements.



DEBYE LECTURER

Columbia University Professor **Charles R. Cantor** spoke on gene mapping and manipulation during the Debye Lecture Series here October 7, 8 and 9. The lectures were entitled "Manipulation of Very Large DNA Molecules," "How to Make Physical Maps of Entire Genomes," and "Nucleic Acids in Tight Places."

Dr. Cantor is chairman of the Department of Genetics and Development at Columbia University Health Sciences Center, and is deputy director for biotechnology at Columbia's Comprehensive Cancer Center. His work has been devoted to molecular biology and molecular biophysics, particularly in nucleic acid research. Recently his laboratory developed a technique for fractionating chromosome-sized DNA molecules, and is using that technique to develop rapid methods for human gene mapping.

CHAIRMAN'S COLUMN

No matter if he sits at a desk with a pen and blank sheet of paper or at a microcomputer keyboard with a blank screen, composing these columns seems to have always been a difficult chore for chemistry department chairmen. In the present instance it is made doubly difficult, for late-night stints in front of a television watching first the baseball league championships and then the World Series have left this rabid Mets fan's eyes bleary and out of focus. But just as it takes three outs to complete an inning, no Chemistry Newsletter is complete without words (of wisdom and inspiration, naturally) from the chairman.

Both Earl Peters and I have greatly enjoyed the stimulating visits to industrial research labs we have made in the last several months. One common thread running through our conversations with colleagues in the business sector is the mutual desire of industrial and academic scientists to better understand each others' interests, talents, and concerns. Relatively few companies can afford to do what American universities do best, basic research, yet we have not yet found a simple mechanism to routinely identify those areas in which interactions between us are likely to be mutually most rewarding. In order to achieve that synergy of purpose in which scientists in both sectors are making optimal use of the available national intellectual and financial resources, it now seems vital that we work to open and keep active nontraditional lines of communication. It is precisely to that end that we have been arranging an ongoing series of miniconferences and workshops involving Cornell chemists and industrial scientists. We are trying to identify companies where such interactions seem to hold the most promise of being successful, but if you would like to initiate such a meeting, please don't hesitate to contact Earl or me. Our motto is, "Have slides; will travel."

By the time the next edition of *Cornell Chemistry* goes to press (or to laser printer as is more accurate), we will have more exciting news about new faculty members and even more broadly based support for the Cornell Polymer Chemistry Training Program. As always, I invite you to become part of that news by participating in our activities. Let us know what you're doing by completing the survey form in this issue. Visit us at Reunion. Take Earl to lunch.

Best wishes for a happy holiday season and a successful new year.

J.R. Wiesenfeld

Please help us maintain an accurate, up-to-date mailing list by returning this survey to **Donna Middleton, Editor, Cornell Chemistry Newsletter, Baker Laboratory, Cornell University, Ithaca, New York 14853**

Society of Cornell Chemists Survey
Fall 1986

Name:_____
Last **First** **Middle**

(If alumnus)
Year of Graduation
From Cornell:_____ **Degree(s):**_____

Faculty Advisor in Chemistry:_____

(If not alumnus)
Affiliation with Cornell Chemistry:_____

Home Address:_____

_____

_____

_____

Employer: _____

Business Address:_____

_____

_____

_____

Professional/Personal News for inclusion in the next Newsletter:

Cornell University
Baker Laboratory
Ithaca, New York 14853-1301