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Be A Chemist Like Uncle Jim*

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(Editor's Note: This is the second issue of *The Spectrum's* tribute to the six photochemists born in 1938 who were honored in Boston last August. Featured in this issue are Doug Neckers, Dave Whitten and Nick Turro.)

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

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

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

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

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

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

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

Cal VanderWerf moved to Hope as President in 1963. Before he left Kansas, he seriously recruited me again—this time to join him on the faculty at Hope. "Van Zyl is retiring and this would

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From the Executive Director

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Several things happened concurrently as I was starting to write this “From the Executive Editor”. First, two newspapers called asking for permission to reprint the last editorial I had written for *The Spectrum*. That was the one about how things had changed in the last 60 years. Next, war broke in the Balkans. Finally, Bowling Green’s email system went down—crash, bang, kaboom. When placed in the hands of a perpetual administration critic, BGNet became BGBust. Lotus Notes became about as useful as lotus petals were to scientists during the flower power days of the 60s. We were, and are, without a reliable electronic mail system at our University.

So, in a fit of frustration, I did something I never do. I read, again, what I had written in “From the Executive Editor” for the fall *Spectrum*. The sentence that caught my eye was “Maybe, just maybe, after all these years humankind has learned to live with one another and be just a little kinder and gentler ….”

As I walk around Bowling Green’s campus this spring, the magnolia trees outside my old labs bloom more beautifully than before, the spring grass turns green and dark, and the days move toward the warmth of June. As the undergraduates bounce from the University Union to class and back again, I can’t help being reminded of a similar spring 35 years ago. I was a postdoc at Harvard. My typical morning routine was to take the bus to Harvard Square and walk through Harvard Yard heading for Converse labs. The walk was always pleasant. Harvard Yard took one almost immediately away from the business of Massachusetts Avenue and the chaos around the Harvard Coop. A simple walk through that quiet got one psyched for whatever the day would bring.

Part of the routine for most of Paul Bartlett’s students was to stop by the seminar room, grab a cup of coffee, and at least glance at the front page of the *New York Times*, which always lay on the table. It didn’t occupy much of our attention at the time, but increasingly *Times* reporters were talking about a place we’d known as French Indo-China now called Vietnam. Sometime later in the summer, some PT boats were attacked in the Gulf of Tonkin. Lyndon Johnson, in a fit of tough Texas rage, sent the huge fire power of the then US Navy against North Vietnamese ports. By the end of the summer of 1964, America was headed down a path J. William Fulbright had warned us against—toward a full scale land war in southeast Asia.

The Harvard undergraduates of 1964 were less oblivious than most, but still pretty insulated. They weren’t thinking of war; they were thinking of school. Besides, none of us expected war would break out again, and so soon. Korea was still part of our memories. But it did. By the end of the spring semester of 1974, ten years later, I knew seven young men who had been killed in battle in Vietnam. I can still see the faces of some of them sitting in the back rows or front rows of the organic chemistry classes I was teaching at the time.

In these extremely good economic times in the US, have we fallen asleep? Are those politicians, like those university types who have ruined Bowling Green’s email system, to soon ruin our prosperity, disturb the domestic tranquillity, and send our sons and grandsons to war?

In the 60s none could doubt the sincerity of those who would save South Vietnam for democracy. But 35 years later, even Robert McNamara admits to try and do so was a mistake. In the 90s, none can doubt the sincerity of those who sincerely feel for the refugees of Kosevo; before that Bosnia, Croatia and the rest. But as bad as it was before, is it not worse today?

I wasn’t wrong in September, was I?

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be an extraordinary opportunity for Hope and for you." Frankly, he had a lot more confidence in my ability than I did, but I was really flattered. Being close to my roots was safe for a guy from a town of 600 people, so I decided to start my teaching career at Hope. The way I figured it, young assistant professors had to do several years of laboratory work with their own hands anyway, and I might as well do it in a friendly environment as somewhere else. Though the decision was made mostly for the wrong reasons, and I sure didn't know what I was getting in to, those several years at Hope were very well spent—both for them and for me. Among the persons I managed to attract to Hope during those years were Shelton Wettack, who is now Dean of the Faculty and Senior Vice President at Harvey Mudd, and Mike Doyle, who is Vice President at Research Corporation and a Professor at the University of Arizona. It could be easily argued that Doyle has been the most successful academic chemist in the history of American liberal arts colleges.

Between VanderWerf west (Kansas) and VanderWerf midwest (Hope) came Harvard. In just a few months there, a non-extinguishable creative flame was ignited by Harvard's spark, and I discovered that a graduate degree in chemistry was worth more than "the other guy would pay for it". Though I worked for Paul Bartlett, it was the people in Bartlett's labs who really taught me. Certainly, no one was more enthusiastic for chemistry, for his family, and for life itself than Nick Turro.

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

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

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

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

Sometime in the spring of 1964 Nick told me he had written for information about a Gordon Research Conference on Photochemistry, that he had applied to go, and been accepted. He suggested that I look into it too which I did. I sent a letter to whomever, and Tony Trozzolo, who was the first Chairman of the first Gordon Conference on Photochemistry, sent a note saying he'd welcome me to the conference. Actually I knew Tony too. He had come to Kansas from Bell Labs at the invitation of Earl Huyser, my Ph.D. preceptor, since they were old University of Chicago buddies. Tony communicates beautifully and told us about a problem in azo compound isomerizations. Skilled lecturers have a way of forming indelible impressions. How many lecturers make sufficient impressions so that one remembers the contents 35 or 36 years later?

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

The development of organic photochemistry was closely connected to polymer science, free radicals in solution, and the work of Walling, Kharasch, Frank Mayo, and Bartlett. What Hammond exploited was the relationship between spectroscopy and the still developing theories of mechanism in organic chemistry. In the ensuing years, physical organic chemists would become as facile with excited state properties and characteristics as were their predecessors with chemical reactions in the form of the intermediates that intervened between reactants and products. The latter, parenthetically, was as much a departure in the 1940s and 1950s as spectroscopic relationships to mechanisms became in the hands of photoscientists.

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

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

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

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

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

QED #1. Today, the photochemistry of naphthospiropyrans is responsible for the singularly most profitable venture at PPG—Transitions Plastic Lenses.

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

QED #2. How many meetings do we go to these days and not mention Rehm/Weller or Rudy Marcus?

Score - real world two and insight of a young postdoc zero.

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

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

Hope had an enrollment of 1,400 students when I began there in 1964, and it's hard to believe now, but 28 students who took the two courses I taught in the fall of 1964 joined the ranks of Ph.D.s in chemistry and biochemistry. Chemistry at Hope was then, as it is now, a particularly strong part of the undergraduate program at the College.

Industrial interest in my work came early. Without my knowing it, both benzophenone which I had done some organic photochemistry on as part of my thesis, and ethyl phenyl glyoxylate, which was also part of the work I did at Kansas, showed up as commercial photoinitiators for acrylate polymerization. Shortly after I started teaching at Hope, Blaine McKusick, who was a friend of VanderWerf's, invited me to DuPont for a talk. I remember talking with Jim Harris, who was working on photochemical reactions of fluorinated aldehydes, and Bob Liu who was working with him. Bob left DuPont shortly thereafter, and began the beautiful work on retinals for which he has become so properly recognized. I met Jack Saltiel first at a IUPAC meeting on photochemistry held in Enschede, Netherlands. Jack, who was born in Greece, had gone to Greece for a visit prior to the conference, though he was a scheduled lecturer. As luck would have it, the Greeks got in a war with somebody, probably Turkey over Cyprus, while Jack was visiting the old sod. Unfortunately for him, there was a general mobilization, and he was drafted into the Greek army. Once a Greek, always a Greek as Jack told the story. Fortunately, a few bribery dollars placed in the proper hands did the trick, and Jack made his lecture in Enschede as scheduled.

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

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

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

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

George told me once "Neckers, I wish I had had someone as wise as me mentoring me when I was 55." I envy our students who find him on their committees, and I learn from him every time he comes. When he comes to Bowling

Green, there's a line outside his door just like the lines that must have been there at Iowa State, Cal Tech, Santa Cruz, and even Allied.

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

The thing that struck me about Harvard when I was a student in Bartlett's lab was how interesting and genuine the people around PD were. There was a hidden spirit—a spirit of simplicity, of honestly liking what one was doing and doing what one does because one likes it. The impression I got from that experience was that for the creative, the energetic, the motivated, life is too much fun to be bothered with anything but crowding into every day all the fun that you can.

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

During the Boston meeting that hidden spirit—that same spirit of simplicity, of appreciation, of genuineness, I first experienced in Paul Bartlett's group at Harvard 35 years ago—was clearly evident. I don't think the group assembled had ever been together, all at once, before. But what the group of photochemists, assembled by accident in the early 1960s, was a group of motivated, bright women and men going about the business of the photosciences, and appreciating one another both as individuals and for their work.

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

*Reprinted with permission from *IAPS Newsletter*, November 1998, 21(2), 44-49.

The Photochemists of 1938 - AKA The Gang of Six

l-r: Dave Whitten, Bob Liu, Jack Saltiel, Peter Wagner (who dropped in for this picture), Nick Turro, and Doug Neckers

Cooking My Slides*

David Whitten, Los Alamos National Laboratory

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

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

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

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

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

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

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A New Look for *The Spectrum*

The color strip on the front page represents an updated look for *The Spectrum* based on snippets of color-enhanced results from actual research conducted in Center laboratories. From top to bottom:

Atomic force microscopy (AFM) image of negative-tone photoresist based on benzophenone ammonium borates; Conformation of diphenylamine from supersonic jet electronic spectroscopy; Micrograph of the cyanobacteria *Synechococcus* sp. PCC7942 (artistically enhanced); AFM image of spin-coated polymer film; Computer-generated model of a synthetic metalloprotein used to study electron transfer rates; AFM of polymer microspheres used in carbonless paper and color image printing; AFM image of a compact disc.

Skating on the Edge of the Paradigm*

Nicholas J. Turro, Columbia University

The Early Days at the State Water Laboratory at Wesleyan University (Summers of 1957-1960).

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

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

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

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

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

Metal-Complex-Catalyzed-Decomposition of Alkyl Pyruvates.

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

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

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

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

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

One of Those Serendipitous, Career-Defining Events. The Friday Night Lecture Demonstration at Caltech.

After about six months of research on the metal complex catalyzed decomposition of methyl pyruvate, a serendipitous twist made a critical impact on my career. As an undergraduate at Wesleyan, I had discovered the luminol chemiluminescence experiment and was showing it off in the lab one day. George Hammond was about to present a "Friday demonstration lecture" to the Pasadena community and I needled him about the demonstration that he might be presenting, assuming that there would be none. George nailed me with, "Nick, why don't you show the luminol experiment. It's sort of photochemical and that's what I'm going to talk about." With a combined feeling of anxiety and excitement, I accepted. As I expected, George gave a fabulous lecture on the research that Peter, Bob Foss, Bill Baker and others had been doing on the photochemical reactions of benzophenone and his beautiful method for demonstrating the involvement of triplets. What I didn't expect is that when he introduced my demonstration he jokingly termed me an "anti-photochemist" because my results on the catalyzed decomposition of methyl pyruvate were contrary to current paradigms about the effect of paramagnetism on photoreactivity. The demonstration went well (I still remember someone in the audience saying, "Wow! This is just like Disneyland!!!").

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

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

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

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

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

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

Two decades later, one of my great students, Matt Zimmt, would say "three months in the lab can save you an hour in the library"! In fact, it was my experience with the "scholars" at Caltech that convinced me that there was so much chemistry that I did not know and that the mastery of the literature was an important professional matter. At that point I made the decision to make "knowing" and mastering the literature a top priority. It was one of the best career decisions that I have made.

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

Conclusion of the Caltech Years (1960-1963).

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

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

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

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

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

As the result of my literature reviews, I had become interested in the preparation of cyclopropanone, which was claimed to be an intermediate in the reaction of diazomethane and ketene at –78°C. During that period I collaborated with Peter and Doug Neckers on the photochemistry of tetramethyl-1,3-cyclobutanedione. Why tetramethyl-1,3-cyclobutanedione you ask? Because I saw an advertisement for the molecule in *C&E News* that asked "What can tetramethyl-1,3-cyclobutanedione do for you?" It occurred to me that the photolysis of this compound might result in the loss of CO, a common process for ketones. I was ecstatic when I requested a small sample and promptly received a kilogram in the mail the next week! The photolysis of tetramethyl-1,3-cyclobutanedione turned out to be rather nifty and to involve the formation of tetramethyl cyclopropanone, which was readily trapped by alcohols and furan. This chemistry served as the basis for my proposed program when I went around job interviewing.

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

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

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

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

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

In the fall of 1964 I began at Columbia as an Instructor (the last one ever hired in a science department, since they abolished the lowly position the next year). Before leaving Caltech, Jack Roberts had advised me that I should stay away from photochemistry as much as possible, because when it came time for tenure review, I would be criticized for being unimaginative and simply extending my Ph.D. work. Jack always gave me good advice, so I followed it. I decided to make a foray into synthetic chemistry employing cyclopropanones. At that time the PARADIGM of the organic community viewed cyclopropanone as impossible or an improbable target as an isolable or synthesizable species. Although I didn't use the word then, I was thrilled at the possibility of skating on the edge of the paradigm, recognizing the value of identifying and attacking problems that were good science and could also attract the community's attention at the same time.

My first graduate student, Willis Hammond, who was directed by Ron Breslow to work for me (thanks forever, Ron), showed that if one were brave enough to mix up diazomethane (remember my first experiment at Caltech?) and ketene at low temperature, one could make cyclopropanone in good yield. Bob Gagosian and Simon Edelson followed up these studies with some beautiful chemistry and I learned that I could perform a successful independent research program of my own. It was clear after a couple of years that tenure was a certainty because of the fabulous research productivity of the group in cyclopropanone chemistry which was good enough to write a review for *Acc. Chem. Res.* **1969,** 2, 25, and in molecular photochemistry described below. At this time the power and beauty of collaborations became apparent to me. It was at this time I made a series of "French Connections". I met J. M. Conia an outstanding small ring chemist during a visit to France and we began a very fruitful collaboration on small ring chemistry. Later, Jean Rigaudy (aromatic endoperoxides) and Lionel Salem and Alain Devaquet (theory of photoreactions) would join the group.

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

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

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

At this time I learned that I needed to take a "systems" approach to operate an effective research program of the magnitude, intensity and diversity that I wanted. The only way to do it was to master the literature and work with a group that I directed and which learned from me and taught me at the same time. Collaborations within the group and within Columbia University, with collaborators from other Universities in the U.S. and abroad, in addition to a broad knowledge of the literature were to be the roots and trunk of the program; ideas, experiments and novel results would be the "dendritic" intellectual and scientific products.

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

Thinking about Thinking. The Paradigm and Topology.

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

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

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

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

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

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

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

In the 1970s the group was immersed in the investigations of molecules which formed excited states upon thermolysis. Peter Lechtken was the first to successfully synthesize and exploit dioxetanes in the group. In one year he set up a decade of projects. A very productive and imaginative group including Hans-Christian Steinmetzer, Gary Schuster, Y. Ito and Ramamurthy followed Peter as the group made a lasting impact on the field of chemiluminescence. This was tremendous research power for the times, and led to a productive period that was delightful in scope and science. Bill Farneth and Jeff McVey in a collaboration with George Flynn showed how IR excitation could be used to decompose dioxetanes. Two collaborations with colleagues at Columbia, Ron Breslow and Tom Katz, brought us into investigation of the $(CH)_6$ valence isomers of benzene (Dewar benzene, benzvalene, prismane). Ramamurthy, making a second visit to the lab as a postdoc, performed a series of experiments showing how these remarkable benzene isomers could be produced from the photolysis of properly constructed azo compounds. Art Lyons found an adiabatic photoreaction of naphthalene and Carl Renner and Murthy found a number of adiabatic reactions of benzene valence isomers.

Mechanistic Organic Photochemistry and Photophysics (1970s).

During the 1970s the group was involved in a range of investigations involving mechanistic organic photochemistry. Theron Cole, George Kavarnos, and Victor Fung were involved in the investigation of the intramolecular heavy atom effect and discovered a remarkable stereochemical aspect which was shown to be reminiscent of the Sn^2 mechanism as the result of theory by A. K. Chandra. Irene Kochevar and Y. Noguchi were involved in investigations of energy transfer and quantitative features of the photochemistry of ketones. Marlis and Manfred Mirbach and Nils Harrit and J. M. Liu studied a range of novel photochemical and photophysical characteristics of azo compounds.

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

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

At the Fourth IUPAC Symposium on Photochemistry in Baden-Baden, Germany, during July 16-22, 1972, the lecture hall was very hi-tech and the audience sat two to a desk with a shared microphone available for asking questions after each lecture. I sat next to Lionel on a number of occasions and during the "organic lectures", he would gently criticize the lack of an existing discipline in the writing of organic photochemistry reaction mechanisms. He felt that "anything goes" was the rule used to explain the seemingly endless variety of reaction products being discovered in those early days of many exciting discoveries in organic photochemistry. During the Symposium, Lionel presented an outstanding lecture on diradicals (*Pure & Applied Chemistry* **1973,** *33*, 313). At the very end of the conference, Lionel, Bill Dauben and I had a beer at the hotel as we awaited transportation to the airport. Lionel again began needling about the lack of coherence in the mechanisms and theory of organic photochemistry. Bill and I retorted with, "Lionel, you're just the person to do something about this unfortunate state of affairs!" Lionel retorted by challenging us to join him in a venture to seek the framework of a coherent theory. German beer, with its ability to produce Gemüchlihkeit, had produced the atmosphere for a partnership that was to be exceedingly stimulating and informative for all three of us. The results of these discussions and correspondence led to a short note written by Lionel, "Surface Crossings in Photochemistry" (*J. Chim. Phys.* **1973,** 694) in which he pointed out the use of a symmetry plane to classify orbitals and to serve as the basis for energy surface diagrams.

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

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

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

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

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

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

During the 1980s, John Bolt performed some beautiful work showing how Yekta and Aikawa's theory of micellar dynamics could be used to determine the rate constants at which labeled surfactants entered and exited micelles. Aikawa and Yekta produced a very useful mathematical formulation for the extraction of rate constants and equilibruium constants from simple experiments employing steady-state or time-resolved fluorescence quenching of molecules adsorbed in micelles. Aikawa returned in the 1990s to show he still had the touch in the lab after a stay as

Dean in Japan. He was one of a series of outstanding Japanese postdocs and visiting scientists with whom I was privileged to have as colleagues. In addition to those mentioned above there was T. Okubo (on/off rates of molecules adsorbed on polyions and cyclodextrins), Y. Inoue (photochemistry of cyclooctene), M. Okamoto (pressure effects on a range of photochemical reactions, together with W. S. Chung), Y. Sato (photochemistry on zeolites). K. Ishiguro (CIDEP of the quadricyclene radical cation) and Y. Tanimoto (magnetic effects on reactive intermediates). Sandy and I were treated to a magical week in Japan in spring of 1998 as our former group members organized a fabulous tour of several cities and then a very special party in Tokyo , organized by Inoue, where nearly every former Japanese postdoc attended.

A Plethora of Reactive Organic Intermediates.

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

Supramolecular Photochemistry and Spin Effects on Photochemical Reactions.

During this period Ming Chow showed how the mechanism of decomposition of endoperoxides could lead to the separation of ^{17}O from ^{16}O and^{18}O! Together with Chen-Ho Tung and Chao-jen Chung (the gang of three!), Ming showed how the magnetic field produced by stirrer bars could change the rate of polymerization and the molecular weight of polymers by an order of magnitude!!! These were heady days when magnetic effects, formerly viewed with great suspicion in the 1970s, became commonplace when experiments were performed in the proper supramolecular systems. Bruce Baretz, Jochen Mattay and Greg Weed executed the research that placed the supercage concepts on a firm and convincing experimental basis.

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

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

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

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

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

Kartar Arora got the group started with the probe methods for investigating polymer structures by synthesizing a pyrene labeled polyacrylic acid. These experiments were important in leading to a collaboration with P. Somasundaran of the School of Mines at Columbia. Somasundaran, an expert on the adsorption of surfactants and polymers on silica and alumina particles, joined us in a collaboration investigating these systems with photophysical probes. Prem Chandar, Ken Waterman, Kevin Welsh, and P. Ananth showed how the classical methods of adsorption could be correlated with the photophysical techniques. Jin Baek Kim, Ines Pierola and Gabriella Caminati used photophysics to investigate polymer structural changes in aqueous solutions.

The 1990s. DNA as a Wire.

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

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

Dendrimers: Polymeric Molecules Resembling Trees.

At a Gordon Conference in 1988 I met Don Tomalia who presented a spectacular lecture on dendrimers, a topic about which I knew absolutely nothing and which hit me over the head in the same way as when I discovered for the first time micelles, zeolites, cyclodextrins, liquid crystals, polyelectrolytes and DNA. Furthermore, I found in Don another kindred spirit who shared the vision of excitement and beauty of structure and topological thinking. Our groups, I thought, made a perfect complement since he was an outstanding synthetic chemist and wanted to find a group to characterize the new materials he was synthesizing. Immediately, topological thinking indicated that the dendrimers were objects topologically congruent with many of the systems we had been investigating for a decade with spectroscopic and photochemical probes. If this congruence were correct, our paradigm guaranteed that, with minor modification of our techniques and methodologies, we could successfully characterize dendrimers to an extent that was similar to that of the systems previously investigated. For a review, see *Acc. Chem. Res.* **1991**, 24, 332.

Indeed, by taking the lead from the use of photoinduced electron transfer on DNA, we could immediately take the Ru systems and study the electron transfer between photoexcited Ru(II) complexes and electron acceptors. Maria Moreno-Bondi and Willie Orellana were able to show that the quenching efficiency was related to dendrimer generation and that an exciting fringe benefit was that a qualitative break in the quenching occurred around generation 3/4, exactly the place where some computer simulations by Bill Goddard had predicted. This break was confirmed by Gabriella Caminati with a pyrene fluorescence probe and then by Francesca Ottaviani with an EPR probe and by

Steffen Jockusch with several absorption and fluorescence probes. K. Gopidas performed an elegant study of electron transfer on individual dendrimeric molecules. Diana Watkins showed how the probe method could be employed to investigate a range of different dendrimer structures. The research on dendrimers and DNA is now being integrated to investigate DNA/dendrimer interactions and will be extended to study DNA/dendrimer/liposome interactions as models for how dendrimers serve to assist the transfection of cells by DNA.

Putting a Spin on Radical Pair Reactions in Supercages.

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

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

The collaborative interactions with these brilliant spin experts gave me a totally different and quantitative view of what we could do with our spin chemistry. The beginning of the real collaborations began with the appearance of Eugene Step and Valery Tarasov, students of Anatoly Buchachenko, on a cold day in January 1990. We met in Grandma's Diner on Amsterdam Ave. where they enjoyed their first American breakfast. Next came Igor Khudyakov followed by Igor Koptyug. In the meantime, Anatoly made two visits to the lab.

From the association and collaborations with the Russian group, our approach to spin chemistry expanded to include time resolved EPR and comparison of theoretical models of radical pairs in micelles and experiments. Naresh Ghatlia and Valery teamed up to perform a successful series of investigations of spin chemistry as a function of micelle size. The results are reviewed in *Pure & Appl. Chem.* **1995**, *67*, 1999, and *Acc. Chem. Res.* **1995**, *28*, 69.

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

Although the group had an EPR since the mid 1980s, it become a powerful tool for mechanistic use when Matt Zimmt and Mark Paczkowski set it up for time resolved use. This allows us to use polarized spectra (CIDEP, the EPR analogue of CIDNP) to investigate free radicals. This technique was exploited beautifully first by William Jenks who set the pattern of experiments and was followed by all kinds of neat stuff by Chung-Hsi (Joe) Wu, Igor Khudyakov, and Igor Koptyug. Steady state EPR and the beauty of nitroxides and their quantitative analysis was taught to the group in a course and in the lab by Francesca Ottaviani who continues to be an important collaborator.

Photochemistry of Organic Molecules Adsorbed on Silica.

Our interests in supramolecular photochemistry inevitably led us into the solid state and silica gels which were among the first host systems that we studied systematically. C. C. Cheng with samples provided by Walter Mahler of DuPont started us off by investigating the pore size dependence of the cage effects of dibenzyl ketone. This was followed by some fascinating quantitative investigations of the diffusion of photoexcited molecules on silicas and zeolites in collaboration with Mike Drake of Exxon by Karen Cassidy, Rachel Leheny and Stephan Nitsche. Wendy Pan and P. Srinivas studied the adsorption of styrene onto silica by EPR and fluorescence techniques.

Modern Molecular Photochemistry in the 1990s.

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

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

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

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

Armed with Edith's introduction and samples, Peter Wan initiated the first studies that demonstrated both the feasibility of doing photochemistry of DBK on zeolites and the interesting photochemistry that resulted. Chen Chih Cheng had collaborated with Walter Mahler of DuPont on the photochemistry of DBK on silica gel, and then moved into the zeolite studies. The DuPont connection expanded with Lloyd Abrams and Dave Corbin becoming valuable advisors. We began to feel very comfortable with our paradigm for zeolites and quickly realized that the zeolite paradigm was rich in possibilities for new photochemistry and that photochemistry could assist the understanding of both zeolite structure and how zeolites worked as molecular sieves and as catalysts. Zhenyu Zhung came in as a graduate student and demonstrated how additives could control the chemistry of radical pairs in zeolites. Nianhe Han followed, as a student, together with Xuegong Lei, who began to discover all kinds of interesting photochemical effects in zeolites, and demonstrated, in collaboration with Jim Fehlner and Andre Braun, the remarkable selectivity in photochlorination that could be achieved for linear alkanes adsorbed in ZSM-5 zeolites. For an early review of this research see *Pure and Appl. Chem*. **1986**, *58*, 1219.

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

Ubersupermolecular Photochemistry.

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

http://turmac13.chem.columbia.edu/default.html (Research)
http://www.columbia.edu/itc/chemistry/chem-c3045/ (Instruction)
http://www.columbia.edu/itc/ (IT Cluster)

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

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

I suggest that "übersupermolecular photochemistry" will involve a conceptual framework similar to that which drives magnetic resonance, i.e., seqences of "oscillating pulses" of electric and magnetic photons and phonons that will provide an ever-increasing level of control over photochemical reactions in space and time. For some discussions of these ideas see *J. Photochem. Photobiol. A: Chem.* **1996**, *100*, 53.

Approaching "Senior" status offers a rich menu of exciting vistas for the photochemist. It is a happy occupation, since it continues to be an avocation as well. All the best to you out there! Sandy and I hope that all former group members and friends will visit us and send us photos that we can put on the home page for all to view and enjoy.

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

A La Famiglia!

A family is defined by a community possessing shared characteristics. There is always something special about the relationships among the members of a family. Our muse, Chemistry, has made a family of all who have spent time with Sandy and myself at Columbia. The family is connected not be the blood and shared DNA that flows in our veins, but by the ideas and memories we share as the neurons "fire" in our brains. The beauty of learning together is that it makes a family of the community of learners. We do not all think the same, but to some extent by sharing in an intellectual and social adventure, we think alike.

Sandy and I had one of the most exciting and memorable experience of our lives at the Boston meeting and reunion organized by Matt Zimmt, William Jenks and V. Ramamurthy. We thank all of you who were able to attend, and look forward to meeting many of you who could not make it. The occasion of the get-together, of course, was a birthday. On such occasions it is an Italian custom to celebrate with two exhortations: "Cent' Anni (one hundred years!) to the birthday honoree, and "A La Famiglia" (a toast to the family) to everyone!

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Angelo Lamola (l) and George Hammond (r) at the bash in Boston in August 1998.

Sandy and Nick Turro in Boston in August 1998.