10480 *J. Phys. Chem. A* **2003,** *107,* 10480−10483

Pleasures of Science with Students and Colleagues

My father was a zoologist at the University of Pennsylvania, and my mother was a physiologist at Women's Medical College in Philadelphia. Their weekends and long evenings at their desks told me that they were working even harder than I as an undergraduate chemistry major at Penn. With resolve not to be an academic, after graduation I joined a large chemical company, DuPont, as a technical representative specializing in photographic products, particularly those for the lithographic industry in Philadelphia.

Despite my enjoyment of being with masters of the industrial lithographic arts, traveling the streets of Philadelphia ultimately advised me that graduate school might lead to a better way of life. So after 2 years in Germany with the U.S. Air Force (the ROTC effect) and a year with DuPont, I found myself a University of Rochester graduate student.

My return to academics was probably preordained by my childhood exposure to science and the culture that embraced me for many summers at the Marine Biological Laboratory in Woods Hole, Massachusetts, where my parents spent their summers doing research. It was also aided by my parents' decision to send me to a local private school (The William Penn Charter School) for my high school years. Despite more important things on my mind during those times, I could appreciate the joy of intellectual achievement demonstrated by the example and the demands of outstanding teachers. That school was one of the great influences on my life.

My BA chemistry degree at the University of Pennsylvania gave me exposure to a far greater range of worlds than was available to those who followed the more narrow BS science curriculum. I recall, for example, a spellbinding hour of tribute to Albert Einstein on the day of his death by my professor of religious studies who had been his neighbor at Princeton. Economics, Shakespeare, and geography were among the more memorable diversions from science. Sociology was made a treat by a professor who later became famous for coining the acronym WASP (white anglo-saxon protestant). By far the most important aspect of my education was, however, from another Penn student, Patricia Patton. We married not long after graduation.

While a BA chemistry education is perhaps less than optimum for graduate school, the shortcomings such as only one semester of physical chemistry were easily made up with a little extra graduate work. On the other hand, the shortcomings of a BS degree are unlikely ever to be rectified. Professor Frank Buff may be surprised to learn that my appreciation of physical chemistry truly began in my first graduate school year where I sat in on his course filled with fascinating anecdotes and insights. In concert, my understanding of physical chemistry was largely derived from a tour through the course problems, mostly those of W. J. Moore's text, guided by the teaching assistant, my graduate student colleague Joe V. Michael.

My research advisor, W. A. Noyes, Jr., was a busy person. In addition to commitments with numerous chemical organizations as well as the federal government, he was at one time simultaneously editor of the *Journal of the American Chemical Society* and the *Journal of Physical Chemistry*. Accordingly, he let his students work quite independently. His approach suited me, and I prospered. Central to my success was Edmund Murad, who patiently guided the start up in my new world of experimental photochemistry as he finished his Ph.D. Among other things, I acquired respect for the Laws of Glassblowing (*First Law*: Quit while you are ahead. *Second Law*: If the *First* is inapplicable, start over again.). After a few years, the gas-phase photochemistry and photophysics of acetaldehyde excited with each of several Hg lines emerged with a reasonably unifying picture.

With two small children in the family, I arrived at Harvard with NSF and NIH fellowships for a postdoc with G. B. Kistiakowsky. My fellowship proposal concerned the photochemistry and photophysics of glyoxal vapor. Breaking from tradition, I actually did what was in the proposal. In the process, I became acquainted with a molecule that would later prove to be an ideal experimental companion for instruction about radiationless transitions, laser spectroscopy, collisional energy transfer, and crossed beam inelastic scattering.

To account for the observed CHOCHO photochemical kinetics, it was necessary to propose in the paper that three stable molecules, H_2 and two COs, were formed in a concerted step from a hot ground electronic state. I did not believe this actually happened, and like a spot on my shirt after lunch, I was hoping that no one would notice. While my hopes on that issue were fulfilled, the proposed dissociation subsequently became respectable and even acquired a name. From theoretical and experimental explorations by others, the "triple whammy" is now well characterized.

During a physical chemistry seminar I gave at Harvard concerning the photophysics of carbonyl vapors, an argument broke out between Bill Klemperer and Martin Gouterman sitting on the front row with George Kistiakowsky in between. The issue concerned the first-order and presumably collision-free intersystem crossings that were required in the mechanisms used to model the data. Bill argued that the concept was nonsense. How can an isolated quantum mechanical system prepared in one electronic state evolve into another? Martin argued that there is not necessarily a problem. In such large systems, the molecule can serve as its own heat bath. Both were correct, but that understanding was yet to come.

The carbonyl data were definitely first order but not clearly in the collision-free limit. Discussions with Kisty quickly devised a definitive test of the isolated molecule's behavior. From his work in the 1930s, Kisty knew that benzene fluorescence spectroscopy was accessible at low pressures. From my experience in the Noyes group where Hidehiko Ishikawa was studying triplet benzene−triplet biacetyl energy transfer, I knew about benzene photophysics. Thus, benzene excited with the 253.7-nm Hg line (then at 2537 Å) would be a practical system to provide an answer to the great question: When pressures are low enough for truly collision-free S_1 decay, does the S_1-S_0 fluorescence quantum yield stay below unity because triplet formation persists in the isolated molecule?

In the last 6 months of my postdoc, the glyoxal apparatus was replaced with one suited for use with low-pressure benzene. The greatest challenge in switching to a mercury-free glass vacuum system was to find practical greaseless valves. Fortunately, new valves of the type with Teflon cores now so ubiquitous made their appearance on the market just in time. With crucial help from W. R. Brennan, then a Kistiakowsky graduate student, a 0.5-m scanning spectrometer with PMT detection and a strip chart recorder was soon turning out meters

10.1021/jp031071y CCC: $25.00

of beautiful S_1-S_0 resonance fluorescence spectra from 30 mTorr of benzene excited with a bank of germicidal Hg lamps.

To see that spectrum and to follow its transformation into the "high-pressure" benzene spectrum with added cyclohexane was for me a revelation. In later years, the long affair with benzene led to many papers from our group describing the spectroscopy, the photophysics, and the vibrational relaxation in more detail than most wish to know. At that moment, however, the work led to a pretty convincing result. The low-pressure fluorescence yield was well below unity, and moreover, triplet formation was occurring in the isolated molecule regime. Clearly an isolated molecule could evolve from its initial preparation into another electronic state.

The phenomenon was real, but at that time the quantum mechanical conundrum was unresolved. With hindsight, one could embrace clues in the papers of Ian G. Ross and in a discussion of condensed-phase benzene by Wilse Robinson, two friends who have had a big influence on my scientific career. The final answer came, however, from Joshua Jortner with the famous 1968 Bixon−Jortner theory. Joshua was obviously intrigued by the statement in our paper that "a strictly intramolecular ... nonradiative transition between pure singlet and triplet stationary states is difficult to reconcile with concepts of quantum mechanics." I suspect that he subconsciously translated this phrase to read "... violates the principles of quantum mechanics." Thus it became (fortunately) a challenge he could not refuse. The Bixon−Jortner paper started a new industry with scores of papers and reviews. Their theory was given renewed impetus when the analogous phenomenon of intramolecular vibrational redistribution (IVR) became a hot topic 10 or 15 years later.

I chose Indiana University among several possibilities in part because of Walter J. Moore's influence. I never suspected how lucky I would be to be in the midst of so much additional faculty talent. They have been central to both my science and the enjoyment of my IU years. Edward J. Bair got me started by showing me how to build a microsecond flash discharge system for my first experiments, and in 1966 he designed and supervised the construction of an f/10, 1.7-m optical scanning spectrometer that has been used by almost 50 students and postdocs. George Ewing has been my "scientific advisor" for all my years at IU as well as my close friend. Collaborations and friendship with Ernest Davidson brought a new dimension to our work. His remarkable insights are inspiring.

My first IU experiment was aimed at solving the long-standing mystery of the triplet benzene lifetime. While it is seconds in the condensed phase, there were reasons to suspect that it might be orders of magnitude shorter in an isolated molecule. With a flash discharge, I hoped to measure this gas-phase lifetime by watching triplet biacetyl light up when biacetyl was excited by collision with triplet benzene. The experiment was ready to go in late winter after my fall arrival. I had worked out the shape of the signal we would see on the oscilloscope, but of course chances were slim that scope settings would be correct on first trials. But a miracle occurred. There it was. A beautiful rise and fall of emission intensity in the microseconds after the flash was perfectly displayed. Excitedly, I said to my first graduate student, "How about that!" The reply was a sleepy "hmmm". This benzene experiment ultimately prospered in the capable hands of a new graduate student, Merle Schuh. Merle has made much use of this approach with his undergraduate researchers at Davidson College.

My first research proposal was written while I was still a postdoc at Harvard in the spring of 1964 before my fall arrival at IU. V. J. Shiner, Jr., then Chairman, wrote to say it was a good proposal but do not be discouraged if NSF does not fund it. These are tough times, it's difficult to get first proposals funded, etc., etc. (Now we hear that it is still tough times, it's difficult to get our last proposals funded, etc., etc. Times are always tough on the eternal quest for the Fountain of Funding.) Fortunately, times were not irretrievably tough, and the NSF funding arrived in November.

Part of the proposal focused on triplet benzene. The rest concerned dispersed fluorescence from collision-free polyatomic molecules. This was fairly virgin territory in 1964 for molecules larger than triatomic. Technology was the great barrier even though Raman spectroscopists of the time could have done it. With the 253.7-nm Hg line from a bank of 14 30-W germicidal lamps surrounding a half-meter-long quartz cylindrical fluorescence cell, beautiful UV fluorescence spectra from benzene at pressures below 100 μTorr emerged at 1-cm^{-1} resolution. Anne Hosch White, my first successful graduate student, and I papered the hall with collision-free spectra. In the meanwhile, graduate students Helen Poland and later Larry Anderson were busy with another apparatus that isolated the 435.8-nm Hg line from germicidal lamps to study emission from biacetyl and from glyoxal, the latter providing an early example of collision-induced intersystem crossing.

These first experiments were a follow up on my postdoc research. With the theory of these nonradiative processes just emerging during my first IU years, the whole field became a hot experimental and theoretical area that persisted for more than 20 years. What good fortune to be in its midst from the beginning.

The 253.7-nm benzene spectra sparked a thirst for generating a collision-free spectrum with a tunable light source that could pump excited-state vibrational levels selected by us rather than by the caprice of atomic lines. This was before lasers, a glorious time in the lab because the equipment always worked. The tradeoff was that a lot of experiments could not be done. In politically correct parlance, one would say that we were "photon-challenged".

How could we get enough intensity with a narrow wavelength spread that could be imaged into a cell to generate detectable dispersed fluorescence at the low pressures needed to avoid gas collisions? The answer is to have graduate student M. W. Schuyler, a fearless experimental guru, arrive in your lab filled with undergraduate experience from George Pimentel's Berkeley group. Mike coupled a 500-W Xe arc with a spectrometer to provide us with microwatts of pseudo-narrow band-tunable exciting light. He used a mirror configuration adopted from high-resolution spectroscopists to multipass the exciting light and another from Raman spectroscopists to image the resulting fluorescence into another scanning spectrometer. He built a single-photon counting system to handle the dispersed fluorescence signal from a photomultiplier housed in his homemade liquid-nitrogen cooler. After all was ready, there it was, a huge signal! Unfortunately, it was all scattered exciting light. At this point, some students would say to me "*Your* experiment does not work." I've heard that more than once. Mike, on the other hand, persisted as every successful scientist must. With a reconfigured mirror arrangement, a dispersed benzene fluorescence spectrum from a single vibronic level (SVL) finally emerged. It was a series of small hills on a long baseline, but the spectroscopic signature of benzene from a single excited S_1 vibrational level was unmistakable.

This humble start opened major opportunities in spectroscopy, in photophysics, in photochemistry, and in collisional energy transfer. Prior to Mike's SVL fluorescence approach, there was no secure way to assign vibrational bands in electronic absorption spectra. We now had a tool that made most assignments absolutely unambiguous. This new SVL fluorescence technique quickly became a standard aspect of spectroscopy, particularly with the arrival of lasers and supersonic expansions.

One of the early achievements with this new tool was a refinement and serious extension by George Atkinson of the vibrational assignments of the famous S_1-S_0 benzene absorption spectrum, described in three tour-de-force papers that extend over more than 75 pages in the *Journal of Molecular Spectroscopy*. I hope that George appreciates the impressive intellectual achievement of his Ph.D. research. This work was greatly helped by the generosity of Donald A. Ramsay, who invited George to spend weeks in Don's Ottawa lab rephotographing the absorption spectrum at high resolution. It also owes much to the remarkably instructive rotational analysis of the absorption system with emphasis on Coriolis coupling presented in the classic paper by J. H. Callomon, T. M. Dunn, and I. M. Mills (*Philos. Trans. R. Soc. London, Ser. A* **259**, 499 (1966)) and to personal interactions with all three. Our absorption assignments were secured by a series of benzene SVL fluorescence studies that culminated in two 1975 *J. Am. Chem. Soc.* articles created with a big boost from the intellectual and lab expertise of Alan Knight, my first postdoc.

The ability to generate SVL fluorescence opened an area of photophysics that, in the long run, has been even more influential than the assignment of absorption spectra. In effect, it brought photophysics into the modern area by enabling chemists to study the dependence of collision-free photophysics on vibrational energy content. When lasers arrived, it quickly became a big industry.

Mike Schuyler's first benzene experiments revealed just how spectacular this vibrational dependence could be by observing the sudden cutoff of fluorescence as the excited-state vibrational energy climbed above 2800 cm^{-1}. Some fast nonradiative process became suddenly dominant at these energies. Now known as "Channel Three", that process has been the subject of scores of papers.

Our work showing this process as well as the novel SVL fluorescence spectra was first described in a 1969 meeting organized under Sydney Leach's influence outside of Paris in one of my first invited talks. It proved to be one of the most influential meetings of my career. One of the reasons was the friendship started with John Callomon, who on hearing the talk immediately pointed out that the spectroscopic signature of the fast process was also in his S_1-S_0 high-resolution benzene absorption spectra. It occurred in the loss of rotational structure from certain lifetime-broadened vibronic bands. His subsequent *Chemical Physics Letters* paper brought the existence of yet-to-be-named Channel Three to the attention of a wide audience.

Our paper first revealing the existence of this novel photophysics and with many of the first SVL fluorescence spectra is, in my heart, one of my two or three most important papers. Sadly it was almost secret stuff, being published in a special meeting supplemental issue of *Journal de Chemie Physique* that has been persistently obscure.

Our development of SVL fluorescence techniques also opened another area that persists to this day, namely, the study of single-collision state-to-state vibrational-energy transfer. Kenneth Tang's Ph.D. benzene studies of the early 1970s produced a blizzard of data that showed this energy transfer to be vibrationally state selective to a stunning degree. The finding was surprising news in chemical physics, and the qualitative Tang selection rules that account for that selectivity are still used. The experiment was adopted in other laboratories and still has an impact on our studies with crossed molecular beams and other special experimental conditions.

As is the case with many faculty, the first years are recalled with special fondness, and hence my emphasis is on these times. Bonding between graduate students and the new professor is enhanced by the fact that both are in a new world, one discovering how to do research and the other, how to establish a group in the midst of teaching and endless service work. Additionally, while not the same age, both are at least of the same generation with abundant social contacts.

In my case, these were years with many talented students, capped by the arrival of my first postdoc, Alan Knight. With equal fluency in theory, spectroscopy, and experiments, this Australian introduced us to new worlds as well as providing major advances in our ongoing projects. Alan incorporated the first tunable dye lasers into our lab along with an in-house gated detection system that was the envy of more than a few other labs. With new fluorescence cells, new imaging strategies, and improved electronics, our experimental capabilities took a leap upward. These accomplishments were matched by Alan's intellectual virtuosity that introduced us to new aspects of radiationless transitions, electronic spectroscopy, and energy transfer. They are described in many papers from our long collaboration.

He was followed by a Swiss postdoc, Berchtold Frank Rordorf, who came from UC San Diego. Frank succeeded in pumping single rotational levels in the excited electronic state of glyoxal by tuning among the modes of an argon ion laser. His pioneering study of rotational energy transfer in a nonpolar polyatomic molecule not only found huge absolute cross sections but also showed that strong state-to-state propensity rules were absent, in contrast to many observations with polar molecules. Frank left us with a mystery concerning relative line intensities in this new single rotational level fluorescence spectroscopy. They did not fit standard Hönl–London line strengths. While I was enjoying a sabbatical year at JILA in Boulder, Colorado, graduate student Gary Loge called to say in his quiet way that he had solved the mystery. It was a subtle consequence of a phenomenon previously seen only in magnetic fields (the "Hanle effect"). Unknown to me, he was working on this as a side issue to his demonstration that isolated molecule photochemistry occurred from the zero-point level of the S_1 state of glyoxal.

My sabbatical leaves have always been productive both from my own efforts away from Bloomington and especially from my group left behind without interference from me. This leave at JILA was highlighted by getting to know Carl Lineberger, David Nesbitt, who was a nonstruggling graduate student, and especially his research director Steve Leone. Back in Bloomington, Mark Seaver's graduate studies culminated in a paper showing extensive experimental support for a theory we developed to relate cross sections for various collisional processes with intermolecular potential well depths. His work did much to establish this relationship as an often-used correlation.

Postdoc R. A. Coveleskie from Illinois (Urbana) began our long affair with *p*-difluorobenzene (pDFB) by his classic spectroscopic study with SVL fluorescence. The molecule has since provided access to many new aspects of collisional and collision-free molecular dynamics. When I departed for the JILA sabbatical, he was left with a speculative problem, namely, the concept of "chemical timing" that I had conceived as a way to learn about time scales of IVR during a period when standard time-resolved laser techniques were not yet up to the task. With graduate student Dave Dolson, he demonstrated while I was away the feasibility of this new high-pressure O_2 fluorescence quenching method that enabled us to monitor picosecond events with a nanosecond laser or even a cw laser. The timing was timely, so-to-speak, since IVR had just again become a hot topic because of its role in frustrating the bond-selective dissociation of molecules pumped by IR lasers.

Chemical timing provided the first measured IVR time scales in addition to providing a pretty spectroscopic view of the process. Karl Holtzclaw finished his Ph.D. research with a tour-de-force use of chemical timing to define the IVR time scales for many vibrational energies in pDFB. He doggedly chased down a long series of possible artifacts to be sure that we got it right. Karl is the one who put the method securely on the map.

The Ph.D. work of Brad Stone showed that IVR rates were much enhanced by adding a single degree of freedom, an internal rotation, to the vibrational field. He did this by the judicious choice of *p*-fluorotoluene, a molecule in which a pDFB fluorine atom is gently replaced by a methyl group with little perturbation of ring modes. Brad's paper is among our most cited. Our work with internal rotation still continues. Graduate student Zhong-Quan Zhao, for example, has shown with an amazing compendium of fluorescence spectra (and theory) just what the internal rotation looked like in the S_1 state and why it was so effective. Quan Ju as a graduate student characterized dozens of internal rotational−vibrational level interactions in *m*-fluorotoluene. This work followed an earlier quantum mechanical treatment developed by David Moss working in his early graduate years with guidance from my colleague George Ewing. The internal rotor studies also led to a delightful series of interactions with Japanese workers, especially Mitsuo Ito and his colleagues, who were the pioneers and the experts in characterizing the internal rotational potential in the S_1 states of these aromatics.

In the midst of the IVR studies, we remained heavily involved with the state-to-state study of collisional vibrational energy transfer, particularly in the exhaustive Ph.D. study of pDFB by David Catlett. Our emphasis ultimately changed, however, to crossed molecular beams that enabled us to see both rotational and rovibrational energy transfer and to see it with detail far surpassing that of any other method. We could do this because of D. J. Krajnovich, a postdoc from Y. T. Lee's lab at UC Berkeley. To use a term in its best sense, Doug was a "great leap forward" person, one who generates a huge impact when joining a group. With unmatched experimental agility, unmatched grounding in chemical physics, an unmatched knowledge of the literature, and unmatched hard work, Doug designed and built a crossed beam machine and used it to complete an extensive study of I_2 and an even more extensive study of glyoxal. He was later joined by a talented physics student, Hong Du, who did his Ph.D. research in our group and completed separate studies of the effect of collision energy on vibrational energy transfer in iodine. Another postdoc, Miles Weida from JILA in Boulder, Colorado, worked out the theory and made the preliminary laboratory demonstrations for controlling the geometry of the collision pairs in these crossed beam experiments.

The glyoxal crossed beam inelastic scattering experiments enabled us to see the competition among literally dozens of individual rovibrational inelastic channels after pumping a selected initial rotational level within an S_1 vibrational level. This detailed view of the inelastic scattering lead to a notable finding. To a remarkable degree, the collision kinematics controlled the competition. The intermolecular potential, which is the focus of so many inelastic scattering discussions, is strictly a secondary player. Geert-Jan Kroes, while a graduate student with Rudolph Rettschnick in Amsterdam, took advantage of this characteristic and with highly approximate potentials was able to predict the competition with impressive fidelity using David Clary's fully quantal inelastic scattering algorithm.

The theoretical accounts were inspiring, and we spent time in my group discussing how best to control the collision kinematics to produce an explicit view of their influence on the channel competition. Graduate student Sam Clegg ignored my suggestions and modified the scattering chamber with his own design to yield a beautiful picture of the kinematic control of the rotationally inelastic scattering competition. He also showed that the classical picture of linear-to-angular momentum conversion developed in recent years by A. J. McCaffery is a natural and highly successful way to describe the inelastic scattering without the heavy lifting required when using carefully tailored intermolecular potentials.

Many talented group members have not been mentioned in this abbreviated account. They all have been my teachers. I cherish their accomplishments and particularly our interactions. They have been a big part of my scientific life and are in my thoughts as this is written.

Charles S. Parmenter