

Reflections on the Early Days of My Involvement in Organic Photochemistry

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The following is a highly personal account of my career in organic photochemistry, with emphasis on the early days. Although I mention a few names of individuals who had a particularly profound influence on my education and on the development of my thinking about the subject, this is in no way a complete and objective review of those aspects of photochemistry that I have dealt with, and I begin with an apology to those whose contributions have been ignored. In the same spirit, I only give a few references, mostly to exemplify particular points.

I received my education up to the Ph.D. degree in Prague, Czechoslovakia. Although it was not on a par with U.S. standards, particularly when it came to the use of up-to-date instruments, I was fortunate to have excellent and dedicated teachers. I owe an immense debt to these individuals, especially the five mentioned next. For my M.S. degree in 1961 at the Charles University, I worked in traditional physical organic chemistry: on organic reaction mechanisms and kinetics with V. Horák and on electrochemistry with P. Zuman. In my spare time, I worked in a pharmaceutical research institute with J. Kopecký on the synthesis of pyrimidines. He was also very interested in tropolones and in his free time tried to synthesize colchicine single-handedly. Of course, he had no chance against D. S. Tarbell. It is to Kopecký that I owe my long-standing interest in non-benzenoid aromatics. For my Ph.D. degree in 1965 at the Czechoslovak Academy of Sciences, I prepared a series of derivatives of non-alternant hydrocarbons, measured their various properties, and compared them with those I calculated by Hückel and PPP methods. My supervisor was an extraordinary teacher, R. Zahradník, working in a section headed by J. Koutecký. At this point, I became quite interested in the electronic spectra of organic molecules.

My first contact with photochemistry occurred in the laboratory of the first of my five outstanding post-doctoral mentors, R. S. Becker at the University of Houston, where I spent a post-doctoral year in 1965. This was also my first contact with low-temperature work. My assignment was to figure out the spectroscopy and photochromism of spiropyrans. In the process of investigating simpler models for these structures, I noticed that the irradiation of chromenes in an organic glass at 77 K produced a colored product, fairly obviously attributable to a ring-open form analogous to the colored form of spiropyrans (*J. Am. Chem. Soc.*, 1966, 88, 5931). I was immensely puzzled by the observation that the quantum yield of chromene fluorescence dropped rapidly with decreasing wavelength of excitation. I was hopelessly ignorant of what photochemistry and photophysics were already known then, but Becker had told me of Kasha's and Vavilov's laws, and something was clearly out of order. I supposed that it was at that time that I became permanently curious about the detailed nature of the processes that follow electronic excitation of an organic molecule. I tried to learn more by reading and by taking a course in descriptive organic photochemistry taught at the University of Houston by M. R. Wilcott, but became more confused than ever. For my taste, there were too many strange and mechanistically uninterpreted reactions and there was too little systematic order to feel that I had any real understanding. Some of my curiosity was satisfied by my

post-doctoral mentor, an excellent man, but a dyed-in-the-wool physical chemist, with little interest in organic reaction mechanisms, and much skepticism towards the facile state assignments found in the papers written by organic photochemists. I remember specifically his unhappiness with a young upstart, N. J. Turro, who would attribute $n\text{-}\pi^*$ and $\pi\text{-}\pi^*$ character to states of his photochemical substrates without years of prior spectroscopic scrutiny. Nevertheless, I found Turro's writings fascinating. I also had the good fortune to learn more by attending my first photochemistry conference, a Welch conference in Houston. I specifically remember being impressed by one of the masters in the field, N. C. Yang.

In 1965 the Woodward-Hoffmann rules were first published, and I was asked to present a seminar on them to the group - after all, I was the post-doc with a quantum chemical background. The connection to photochemical mechanisms was clear, but I failed to grasp the detailed mechanistic implications.

A colleague from Prague, C. Parkanyi, was spending a year with G. S. Hammond at Caltech, and arranged for me to give a seminar there. The opportunity to meet Hammond was something special, and the visit was immensely impressive, even though I only had a vague inkling of the true significance of the work he was telling me about.

I could see the merit of the formulations offered for the reactions of ketones by H. E. Zimmerman in terms of chemical structures with different labels for electrons in orbitals of different symmetry, and I became fascinated by his result on the propagation of electronic effects into the meta position in the excited state of an aromatic. I applied for a post-doctoral position with him for my second year abroad, but was turned down because I could not promise to stay for two years due to restrictions imposed by the regime in Prague, where I was determined to return. I have often wondered how different my career in photochemistry might have been if I had been accepted.

Finally, disgusted by my lack of understanding, I turned to other pursuits. I spent a few months in the laboratory of A. C. Albrecht at Cornell, learning about spectroscopy with polarized light, and then a very important year with M. J. S. Dewar at the University of Texas at Austin, synthesizing fluorinated fluoranthenes and acenaphthylenes, measuring their ^{19}F NMR spectra, and soaking up the immensely exciting atmosphere at the time when other group members, G. Klopman and N. C. Baird, worked on the development of the MINDO/1 method. In one of the group seminars, I heard for the first time about magnetic circular dichroism (MCD), and became curious about it.

I continued my interest in excited states of organic molecules, and after my return to Prague in mid-1967 began the construction of an MCD spectrometer in the group of Zahradnik. I visited Aarhus University in Denmark, where I met for the first time a future lifelong friend, E. W. Thulstrup, and his professor, J. H. Eggers, and learned about their method for the determination of transition moment directions from measurements of linear dichroism in stretched polyethylene. I also continued to study quantum chemical methods. At a summer school at Lake Balaton in Hungary and a conference at Kutná Hora near Prague, I met P. -O. Löwdin, J. Linderberg, and F. E. Harris, all of whom played an important role in my subsequent career, and many other quantum chemists.

In the spring of 1968, I became involved in Czechoslovak politics, and was one of the founding members of the "Club of Engaged Non-Party Members", later declared counter-revolutionary by the Communist party. It thus turned out to be a double blessing that I received a scholarship from Löwdin to attend his summer school on quantum chemistry in Scandinavia shortly before the Soviet-led invasion of Czechoslovakia in August of 1968. After the invasion, which occurred while I was in Norway, I hesitated only briefly. When it became clear that there would be no resistance to the attack, I decided not to return to Prague. I accepted one of the two post-doctoral offers I had from teachers at the summer school, with the

understanding that I would have a shot at the other position subsequently. Thus it came about that I spend a year at Aarhus University in Denmark with Linderberg, a theoretical chemical physicist. I was in way over my head, being totally ignorant of this specialty, Green functions, when I started, and only slightly less ignorant when I finished, but I managed to calculate and interpret the conformational dependence of the optical activity of simple disulfides using a model whose predictions appear to have survived the test of time. In my free time, mostly at night, I worked in the laboratory of Eggers and Thulstrup on linear dichroism of my fluoranthene derivatives absorbed in stretched polyethylene.

In early 1969 I attended a conference in Cambridge, where L. J. Oosterhoff's and R. Hoffmann's ideas on the course of photochemical pericyclic reactions were hotly discussed. I found this very instructive, but still had no detailed clue as to what is really going on in these processes. The most important result of the trip to Britain was that Sara Allensworth, whom I had known ever since I guided her student group in and around Prague in 1961, came from the U.S. to meet me in London, and we were married shortly thereafter in Denmark and in Austria ("doppelt genäht hält gut" - doubly sewn holds well).

In the summer of 1969 I moved to the physics department of the University of Utah to work with Harris. This was my first contact with *ab initio*, as opposed to semiempirical, quantum theory. Harris allowed me to work on my own project: interpretation of the spectra of a series of Dewar's borazaro aromatics whose absorption and emission I had measured in Becker's laboratory at the University of Houston on weekends while I worked with Dewar in Austin.

By now I had permanent resident status and was able to look for a permanent position. The apprentice years drew to a close. For my initial research project, I wished to combine my past experience in organic, physical, and theoretical chemistry. I decided to attempt the preparation of highly unstable and reactive organic molecules, such as previously unobserved non-benzenoid cyclic π -systems, by irradiation of suitable precursors in low-temperature glassy media, using the techniques I learned in Becker's laboratory. I planned to measure their UV-visible absorption and emission spectra and to interpret them using quantum chemical calculations, and to obtain chemical characterization from trapping experiments.

In this plan, photochemistry played an important role, but was primarily a tool rather than a centerpiece of investigation. The plan worked moderately well, except that with more imagination, I would have proposed to use argon matrices instead of glassy organic solvents. As it was, it was left to O. L. Chapman to introduce that important innovation into organic photochemistry soon thereafter. After that experience, I determined never again to let myself be deterred by unfamiliarity with an instrumental technique, and to specifically seek out unusual combinations of experimental tools. I believe that my more recent work on gas-phase cluster ions formed by the sputtering of frozen gases with high-energy particles, work on electron-energy loss spectroscopy of matrix-isolated species, and work on new types of Langmuir-Blodgett films built from molecular rods are some of the indirect results of that decision.

From the start, Harris intended to give me a chance to get a job in the Chemistry Department at Utah, and he put me in contact with P. D. Gardner, an outstanding organic chemist, who shared many of my interests and in effect was my next mentor. I owe him very much. I was indeed fortunate enough to get a junior faculty position in chemistry at Utah in mid-1970, in an excellent research environment with first-class colleagues, and I started the planned research program, along with work in other areas. Initially, the most important of these was the electronic spectroscopy of large molecules, where I relied mostly on linear dichroism, in which I enjoyed years of very satisfying collaboration with Thulstrup, on magnetic circular dichroism, using an instrument kindly made available by H. Eyring, and calculations. It was only later that

I became involved in additional research areas, such as frozen gas sputtering, cluster ions, and solid NMR (in collaboration with a superb colleague and friend D. M. Grant).

The first synthetic target was pleiadene, to be prepared by a photochemical disrotatory electrocyclic ring opening of the 2 + 2 adduct of benzyne to acenaphthylene. My future first post-doctoral collaborator, J. Kolc, a schoolmate from Prague, already had started to examine the benzyne addition reaction with me in Aarhus, right after he left Czechoslovakia following the invasion (as did nearly half of my schoolmates). It was quite a luxury to have a post-doc while I was still a post-doc myself! Now it came in handy that the adduct was available, as Kolc was first a post-doc in the laboratory of Becker in Houston for a year before joining me in Utah, and Becker kindly allowed him to take a look at the behavior of the pleiadene precursor before my own lab was even set up. It rapidly became clear that the photochemical ring opening takes place in the glassy matrix as planned: the first direct observation of L. F. Fieser's pleiadene succeeded (*J. Am. Chem. Soc.*, 1970, 92, 4147). This biradicaloid compound then became a source of much joy; e.g., it was the first conjugated hydrocarbon for which a predominantly doubly excited state was proven (*Chem. Phys. Lett.*, 1972, 17, 70; *J. Am. Chem. Soc.*, 1976, 98, 930; the weight of doubly excited configurations in the 2A_g state of polyenes, assigned in the same year by B. E. Kohler and B. S. Hudson, is only about one-third, but of course, these compounds are of much larger fundamental importance). This work was followed up by investigations of benzopleiadenes and related reactive non-alternant π -systems, and of various 2,3- and 1,8-naphthoquinodimethanes and o-benzoquinodimethanes, in which an outstanding post-doctoral collaborator, H. J. Dewey, played an important role. Some of this was done in collaboration with R. D. Miller, which has been one of the most pleasant and productive professional experiences of my life. I was particularly happy with the results for o-xylylene, obtained by a very gifted post-doctoral collaborator, C. R. Flynn (*J. Am. Chem. Soc.*, 1973, 95, 5802; 1974, 96, 3280). In this mostly experimental work we also introduced the definition of biradicaloid character through the occupancy numbers of natural orbitals, which still strikes me as optimal, even though I have yet to find anyone but a theoretician who would agree. I have often wondered about the possible significance of the fact that soon after finishing with me, Flynn left chemical research and to this day operates a cattle ranch in Montana.

We had our share of disappointments, too. For instance, an effort by Kolc and another old schoolmate who had escaped Czechoslovakia, V. Dvořák, to produce o-benzyne in glass isolation failed (*Tetrahedron Lett.*, 1972, 3443), while a very similar concurrent effort in Chapman's laboratory to produce it in an argon matrix succeeded. A few experiences of this type made me move away from work in glasses to work in rare gas matrices in the mid-seventies, for the study of species such as adamantene, azaadamantene, propellanes, cyclobutadiene, s-cis-butadiene, silylenes, silenes, disilenes, silanimines, silacyclopentadienes, etc., and here I must mention the name of at least one other very gifted collaborator, J. G. Radziszewski. Overall, I have enjoyed our low-temperature photochemical endeavors very much over the years, partly because they gave me an opportunity to collaborate with additional outstanding individuals such as R. West, W. T. Borden, and K. B. Wiberg, and it is only in very recent years that the production of reactive intermediates by matrix photochemistry has ceased to be the main line of research activity in my laboratory.

Returning now to 1970: two unplanned events caused me to return to the thick of mechanistic and theoretical photochemistry that I had abandoned in disgust in 1966, feeling that I understood nothing. The first was Kolc's observation, made while he was still in Houston, that the ring opening to pleiadene, which was smooth in a low temperature glass, does not occur in a room temperature solution. Now, we knew that some photochemical reactions are suppressed at low temperatures, but here we had one that was suppressed by high temperatures! The solution of the puzzle occurred to me while I was driving from a skiing trip

through a Utah blizzard, and was based on a concept I had learned about in my days with Albrecht: the reaction does not proceed from the lowest excited state, triplet or singlet, but only from a much higher energy state, reached after absorption of a second photon by the long-lived phosphorescent triplet. We soon confirmed that this was indeed the correct answer (*J. Am. Chem. Soc.*, 1970, 92, 4148; 1978, 100, 6687), but it raised more problems than it solved - isn't a disrotatory ring opening supposed to follow Woodward-Hoffmann rules and proceed in the excited state? Why the need for extra energy?

The second event was a consequence of a decision that I took right after I accepted my new position in the Utah chemistry department, not without input from Sara, who loves to travel. We shocked my new colleagues by leaving immediately for a two-month trip around the world in the summer of 1970, with the 3rd IUPAC Symposium on Photochemistry in St. Moritz, Switzerland, and the 1st International Symposium on Non-benzenoid Aromatics in Sendai, Japan, as feasible professional excuses. It turned out, fortunately, that this was an excellent thing to do, as following Sara's wishes generally is.

The St. Moritz conference had an immense impact on me. My talk on the photochemical generation of pleiadene seemed to elicit interest, and I was elated by the feeling of being accepted into the warm and friendly photochemical family. I was excited to have an opportunity to meet the famous photochemists whose work I knew from the literature and to ask them questions. I remember distinctly asking A. S. Kende what he thought the most burning issue was at the time and being told that he would love to understand the differences in the reactivity of singlets and triplets of similar electronic configuration. I remember the infinite confusion surrounding the discussions of biradicals, and my dawning realization that electron repulsion needs to be added to the simple Hückel model in order to get anywhere, i.e., that one has to go at least to what is now known as the 3×3 model. Since I was familiar with the minimum basis set description of the H_2 molecule from J. C. Slater's classic books on quantum theory, it was obvious to me how one should proceed. I had already known L. Salem, who dominated the theoretical discussions at the meeting, since he had thrown me out of his hotel room at midnight at an earlier conference at Kutná Hora in Czechoslovakia, after I was assigned to it mistakenly by the organizers late at night, when he was already in bed (he had specified explicitly that he wished to have no roommate). Fortunately, he did not recognize me in St. Moritz as the unwelcome intruder.

Subsequent travel through exotic places such as Burma, Malaya, where we nearly perished in a river accident, Sumatra, where we nearly perished in a car accident, Borneo, where we climbed the 4000 m Mount Kinabalu, etc., displaced all thought of photochemistry from my mind (Sara's recollection is different). In Sendai, I presented the pleiadene results again, this time selling them as a new non-benzenoid chemistry, and I met several individuals who became life-long friends: West, Miller, E. Vogel, and others.

After the meeting, Sara and I went to hike in the mountains of Hokkaido. However, by now my mind was saturated with travel, and like it or not, kept returning to photochemistry. Although the following may sound melodramatic, it is true: as we hiked miles over a moonscape-like volcanic area strewn with craters, deep-cut valleys, and towering peaks, I suddenly realized what I should have thought of long before: instead of thinking of my excited photochemical intermediates in terms of chemical structures and orbital pictures alone, I must think of them in terms of potential energy surfaces as well! Surely the break-down of the Born-Oppenheimer approximation for the excited molecule cannot be so complete as to invalidate a description based on a single potential energy surface at a time, and on jumps between them? An obvious thought, particularly for one with a quantum chemistry background, and a thought that theoreticians like R. S. Mulliken surely had decades earlier as they contemplated olefin isomerization. Physical chemists like Oosterhoff and Th. Förster surely had it, too. Yet, organic photochemists that I had listened to at the St.

Moritz conference did not seem to think in these terms. Perhaps some did, and I would be amazed if Salem hadn't, but most of them certainly were not using this language when talking about their reactions. There seemed to be a definite reluctance to apply the concepts of transition state theory to excited molecules, there was little understanding of what dominates the motions of nuclei in excited molecules, there was little if any talk of barriers and valleys or minima in the excited state surface, and yet this was clearly a simple way to understand it all, if it could be shown to work: initial vertical excitation landed the molecule at the S_1 surface, and subsequent motion of the wavepacket, combined with vibrational relaxation, took it down the valleys, and over the small but not the tall barriers to funnels through which return to the ground state surface took place. The Born-Oppenheimer approximation could be used everywhere except for the relatively small areas of nuclear configuration space that corresponded to "funnels" returning the excited molecules to the ground state surface. It was perfectly sensible to use the concepts of ordinary transition state theory for motion over excited state barriers. A similar description applied to triplet reactions. The electronic excitation was merely a vehicle for transporting the molecules to strange parts of their ground-state potential energy surface, from which they relaxed to often unusual products. A backwards running process, in which a ground state species climbed through a funnel to the S_1 surface, was responsible for chemiexcitation and eventually, chemiluminescence. There were no specifically photochemical processes - it was all the same photophysics that everyone was already familiar with, only the final resting minimum was different from the starting one.

I became rather poor company for the rest of the trip. Fortunately for my marriage, we were about to fly back to Salt Lake City, anyway. After my return, I modified my Hückel and PPP programs to make simple model calculations of the surfaces for pericyclic reactions, and all began to fall into place. The simple model worked. It was now clear why the formation of pleiadene required extra energy, the argument between Oosterhoff and Hoffmann became irrelevant since both were right, as the excited state minima emphasized by the former only provided a driving force for photochemical reactions when they were not made inaccessible by the barriers emphasized by the latter (*J. Am. Chem. Soc.*, 1971, 93, 523), the qualitative origin of the strange behavior of chromene that had bothered me for years became an obvious consequence of the L_b below L_a state order, etc.

I combined this "photophysical" view of the course of photochemical reactions, based on potential energy surfaces, with a qualitative quantum chemical analysis of the shapes of these surfaces: clearly, the locations of many of the barriers were predictable from correlation diagrams, and one could use the prior contributions of R. B. Woodward and R. Hoffmann, E. W. Abrahamson and H. C. Longuet-Higgins, etc., as a starting point. Equally clearly, the locations of many of the minima were predictable from correlation diagrams as well and here, Zimmerman's 1966 communication on S_0 - S_1 touching in the Hückel model of pericyclic processes represented an excellent starting point. However, it was clear that upon proper consideration of electron repulsion, the touching will be avoided, as already shown numerically in the semiempirical work of Oosterhoff. What I did not realize until ten years later - and I wish it hadn't taken me so long - was that a simple adjustment of the frontier orbital energies at the biradicaloid geometry away from degeneracy by a lowering of symmetry is all that is needed to restore the exact degeneracy of the S_0 and S_1 states and restore the touching, and I shall return to this in the final paragraphs of this article.

I was now aware of the central role played by geometries at which the S_0 - S_1 or S_0 - T_1 excitation energy is relatively low, and the excited state has a minimum (a funnel for return to S_0 , as I became fond of saying to myself), and it was also obvious that many of these geometries will be of biradicaloid character. After all, in a perfect biradical, the orbital energy difference is zero, and the non-vanishing excitation

energy is due merely to electron repulsion terms. I have therefore adapted the standard quantum chemical that the organic photochemical community did not seem to be aware of, and realized in the process a simple reason for the excited singlet's preference for "tight" biradicaloid geometries and the triplet's preference for "loose" ones. Suddenly, I knew the answer to Kende's question, at least in principle. My communication on the subject was rejected by the editors of *J. Am. Chem. Soc.*, as too speculative. This was just as well, since I subsequently discovered a paper by S. Kita and K. Fukui where a similar point had been made earlier. It is frustrating to see how few good thoughts are original! Also, the conclusions did not apply to bonds one or both of whose termini carried one or more lone pairs or a double bond (this case was beautifully analyzed soon thereafter by W. G. Dauben, Salem, and Turro in their "topicity" papers; I wish I had thought of it first).

In order to handle the prediction of barrier presence in more complicated cases of pericyclic reactions, such as the generation of pleiadene, I developed a two-step way for generating correlation diagrams. The diagram was first constructed in the presence of an imaginary insulating wall between the heart of the reaction region and the rest of the reaction domain, and in the second step the effects of wall removal were considered. This in effect offered yet another derivation of the Woodward-Hoffman rules themselves, which the world surely did not need, but it also was very effective in predicting barriers whose presence was not obvious from the standard formulation of the rules. I used this procedure first for MO correlation diagrams, but soon appreciated its utility at the level of configuration and state correlation diagrams described later by B. Bigot, A. Devaquet, and Turro, and permits an easy distinction between the "normal" and the "abnormal" HOMO - LUMO crossings whose importance had been hinted at earlier by D. R. Kearns.

By now, I felt that I had under control the three ingredients required for a qualitative model description of organic photochemical reactions: (i) motion on and between Born-Oppenheimer surfaces, (ii) understanding of the nature of electronic states at biradicaloid geometries through which the return to the ground state typically occurs, including the differences in the structural preferences of singlets and triplets, and (iii) a way of predicting the presence of excited state barriers capable of preventing the reactant from reaching these critical regions of return, applicable even in relatively complicated structures. Somewhat awed, still discouraged from my failure with the communication on singlet-triplet differences, and feeling very much a novice in the business of photochemistry, I asked some famous photochemists and photophysicists at the next photochemistry meeting I attended, the 1971 Gordon Conference in Tilton, whether this indeed was sufficiently new and important to be publishable. I was very disappointed in my discussion with Oosterhoff. He was very friendly but firmly refused to accept any generalization of the concepts from his paper on the butadiene - cyclobutene photoprocess, not even to the norbornadiene - quadricyclane interconversion, which to me was nearly identical, let alone to all ground-state "forbidden" pericyclic processes, as I was proposing. He felt a new calculation would have to be made for each type of reaction. For me, generalization was the main thing I sought, even though I realized that the minutiae of any one reaction would indeed require a separate investigation.

In contrast, Förster and Hoffmann were most encouraging, as were several organic photochemists: Hammond, P. J. Wagner, Zimmerman, who patiently listened to my views attributing excited singlet - triplet reactivity differences to different behavior of the electron repulsion terms in the simple model, and A. Lamola, who suggested that I submit the material to the journal he was editing at the time, *Molecular Photochemistry*. This turned out to be a mixed blessing: the journal was in difficulties, and the publication of my three articles on the "photophysical" model, on the "3 x 3" model, and on the stepwise derivation of

correlation diagrams was delayed for over a year (*Mol. Photochem.*, 1972, 4, 243, 257, 287 - the issue appeared only at a later date). In the meantime, the classic treatment of the 3×3 model by Salem and C. Rowland appeared and stole the thunder. Unlike my papers, it also treated the subject of intersystem crossing in biradicals. A paper by R. C. Dougherty that appeared in late 1971 and another by N. D. Epitosis in early 1972 also contained some of the points I was trying to make. Still, photochemists seemed to become aware of my work, and were asking for reviews. I presented my views at the 6th International Conference on Photochemistry in Bordeaux in 1971, the 4th IUPAC Symposium in Baden-Baden and a conference in Reading in 1972, elaborated the various aspects in a book edited by G. Klopman, another edited by H. Eyring, and provided a general summary in *Topics in Current Chemistry*, 1974, 46, 1.

At this point, I was reasonably satisfied with the general aspects of my conceptual understanding, but was vexed by many particulars. What, for instance, was the relation between the state lines drawn in organic chemists' correlation diagrams for $2 + 2$ or $4 + 4$ cycloadditions and those drawn by photophysicists for the formation of excimers from two π -systems? Or, what was the mechanism of "cross"-cycloadditions? How about triplet - triplet annihilation? And where did the surface for radical cation - radical anion recombination fit into the picture? In order to answer these and similar questions, I felt that numerical valence-bond calculations would be best, and was fortunate to find that an old friend from my post-doctoral days in Texas, R. D. Poshusta, a faculty member at Washington State University, had just the right program and was happy to collaborate. This started the next, more quantitative, stage in our work on theoretical photochemistry. Much of it was performed by an excellent German post-doc, W. Gerhartz. I felt that the way to understand $2 + 2$ processes was to perform full CI calculations on the simplest possible model, H_4 , using a minimum basis set and the valence-bond approach for ease of interpretation. Since I was unable to get any support for this project, judged by reviewers to be totally unrelated to anything in organic chemistry and far too simple to reveal anything useful about the chemistry of hydrogen as such, we had no computer time at Utah and all computations had to be performed at Pullman. This was in the pre-network days, and in fact, the Pullman computer had only just been converted from punched card input. I developed somewhat of a reputation with Poshusta's family, as I would come for a week and spend all of it in the office, hardly returning to the house to eat or sleep at all.

The effort paid off: after a while, we knew in detail not only how the neutral and charged states of the components in a $2 + 2$ process related to the states at the geometry of the excimer and that of the pericyclic minimum (funnel) along the concerted pathway, but also to their analogues along the two-step pathway. We also understood why the order of the three singlet states of the biradicaloid system varied with its geometry, where and why the 3×3 model failed to reproduce this correctly, how cross-bonding occurred via an S_0 - S_1 touching, etc. This was an immensely exciting time, when I finally resolved for myself many questions I had been asking for years. I presented the results at the Mechanisms Conference at Fort Collins, Colorado, in 1974, and was pleased to see that Salem liked them. However, I did not do well the next time; I was invited by Chapman, the organizer of the 5th IUPAC Photochemistry meeting in Enschede, in 1974, to present them there (*Pure Appl. Chem.*, 1975, 41, 507), and was very disappointed afterwards to discover that I did so in a way that was judged totally unintelligible by the participants. I may have done better at the 1974 Exciplex meeting in London, Ontario, talking to a more physically oriented audience, and I think I must have done better in the two publications (*J. Am. Chem. Soc.*, 1976, 98, 6427; 1977, 99, 4263) since R. A. Caldwell subsequently used the results to develop his equation for estimating the feasibility of a photocycloaddition. However, I could be wrong since he may have obtained them from a less technical review article that resulted from my talk at the 8th International Conference on Photochemistry at Edmonton

in 1975 (*Photochem. Photobiol.*, 1977, 25, 141), where I also proposed what I still consider to be the correct mechanism for luminol chemiluminescence. I hope I presented the material passably well as a teacher at the EPA Summer School in Louvain in 1976, but have some doubts since I was never invited back. I think I will always regret that I failed to raise any funding for the H₄ project so that it had to be abandoned after two three-dimensional subspaces of the overall six-dimensional space of our model were explored. That was the right time to explore and learn from the rest of the space.

The next few years were primarily dedicated to experimental effort. I was intrigued by the unusual, such as reactions that proceeded in upper or hot excited states, and reactions that were adiabatic, and I wanted to see how well the simple model allowed us to anticipate them. Perhaps the nicest example of this type of behavior was the photochemistry of 1,4-dewarnaphthalene, described in the dissertation of a graduate student, S. L. Wallace. This was adiabatic in the triplet state, as we had predicted earlier, and also in the singlet state, as I should have predicted earlier but did not (tilted funnel). It proceeded by tunnelling from the lowest vibrational level of S₁ at low temperatures and by thermal excitation at room temperature, it could be induced with shorter wavelength light as a hot excited state reaction at any temperature, and all of this behavior could be understood in terms of the simple model. Unfortunately, the student left before completing the last quantum yield measurement and only the portion of the results that had been obtained earlier in collaboration with N. C. Yang was published in a journal (*Chem. Phys. Lett.*, 1976, 39, 57).

In 1977, I started my dozen years of association with the IUPAC Commission on Photochemistry. This was the time of the production of the "Glossary of Terms", which involved heated debates about the definition of terms such as "biradical" and other interesting issues. I felt that the generation of this and other reports was a useful service to the photochemical community, particularly to students and beginners, and a sensible way of paying back at least a part of the debt that I owe to the community.

The post-1972 competition with Salem and his collaborators in work on organic photochemical theory resulted in interesting correspondence and turned out to be very pleasant, culminating in his visit to Utah and my stay in his laboratory in 1977, during the third and last part of my sabbatical. The French group was primarily interested in reactions of carbonyl compounds, whereas my own experimental work naturally led me to focus on pericyclic processes, so that overlap was not excessive. The second part of my sabbatical had been spent in 1976 with the ghost of G. W. Robinson in Melbourne - he had left for Lubbock before I arrived. I went there to find out whether picosecond spectroscopy could be used to observe directly molecules in "funnels". I was taken care of very well by G. R. Fleming, and at the end of my stay decided that at that time picosecond spectroscopy was a full-time avocation that I did not want to dedicate my career to, because I did not really want to give up all else I was doing. This turned out to be a correct decision at the time, since in the hands of individuals such as R. A. Mathies, the lifetimes of molecules in the pericyclic minima are now turning out to be in the femtosecond domain - the return through funnels is exceedingly rapid. In the meantime, picosecond spectroscopy has become easy, and we are now using it for the determination of rotational constants of photolabile cluster ions in the gas phase, a far cry from the direct observation of molecules in funnels, but still photochemistry.

The first part of my sabbatical in the Fall of 1976 was spent with M. Klessinger at the University of Münster in Germany, where I taught a course on the theoretical aspects of organic photochemistry. He subsequently suggested to me that he would write up the notes from my lectures for publication in a German series of textbooks dealing with physical organic chemistry that he was editing, if I agreed to review what he wrote. He did much more than write up my notes, and with relatively little effort, I eventually became a co-author on a textbook on electronic excited states of organic molecules written in the

German language! We have just completed an updated English translation, *Excited States and Photochemistry of Organic Molecules*, to be published in early 1993. In addition to photophysics and photochemistry, the textbook deals with electronic spectroscopy, including natural and magnetic optical activity.

Others had urged me to write a monograph on the theoretical aspects of organic theoretical reactions much earlier, but for some reason I always felt that the right time to do that would not arrive until reasonably reliable potential energy surfaces had been calculated for a fair number of simple organic photochemical systems, providing a completely solid basis for at least some of the qualitative arguments. The minimum-basis-set small-scale CI calculations that were feasible at the time when the basic qualitative framework was developed were really no better than semiempirical calculations in my view, and were acceptable for the generation of qualitative notions, but not capable of providing quantitative results.

Towards the end of the seventies, however, I felt that computer capabilities and *ab initio* computer programs had developed to a degree adequate for realistic calculations of selected segments of excited state hypersurfaces. I found an enthusiastic and knowledgeable coauthor in a professor at the Free University in Berlin, V. Bonacic-Koutecky, the wife of my ex-boss from Prague. She had been publishing results of high-quality *ab initio* calculations on photochemical *cis-trans* isomerization and was the person who discovered "sudden polarization" in Salem's laboratory. We found that our views on most photochemical matters, except the importance of sudden polarization, coincided (my view of the formation of bicyclic systems by cross-bonding had been biased by the H₄ calculations in favor of a covalent mechanism in which sudden polarization played no significant role). A Humboldt award permitted me to spend time in Berlin with the Kouteckys, and also in Göttingen with A. Weller and in Stuttgart with H. Kramer. Bonacic-Koutecky spent time at Utah, and the book began to take shape during the encounters. I also worked on it during other leaves, at Caltech, Stanford, Yale, Chicago, and the Technion in Haifa. It turned out that more effort went into investigation of matters that we did not really understand than into actual writing of text, and the list of joint papers grew far faster than the manuscript. I was particularly pleased by the realization that I now understood why heterocyclic ring closure and opening in species such as diphenylamines and aziridines represent a long-standing exception to the general rule that in the absence of severe geometrical constraints there are no stereospecific pericyclic processes in the triplet state, but only their non-stereospecific non-concerted analogues.

The book, entitled *Electronic Aspects of Organic Photochemistry*, finally appeared in 1990, after the publisher must have given up all hope of actually seeing it completed. Unlike the textbook written with Klessinger, it is a monograph that attempts a reasonably systematic in-depth coverage of the subject matter. I cannot resist the temptation to provide two additional excuses for the length of time taken by the writing of the book: in the first half of the 80's, I also wrote a monograph with Thulstrup on a related major research interest of mine, spectroscopy with polarized light, and in 1986, I left Utah to accept a chair at the University of Texas at Austin. Setting up laboratories there was an interminable operation that took nearly three years. By then I was tired of stirring molasses, I knew that the local style of administration and pace of life did not suit my temperament, and that I had to move again even at the expense of losing splendid friends and colleagues such as A. J. Bard, M. A. Fox, a fellow Czeck, P. Munk, and particularly, my ex-post-doctoral mentor, Dewar (who however already was in the process of being ousted by an inept administration). Although the unfortunate mistake of moving to Austin has since been wonderfully corrected by a move to Boulder, the lost time has not been recovered.

One of the numerous discoveries made during the writing of the monograph on photochemistry and written up as papers deserves mention here because of its relation to the early era discussed above. The Kouteckys and I wrote up a modern formulation of the 3x3 model of the electronic states of biradicaloids (*Angew. Chem. Internat. Ed. Engl.* 1987, 26, 170). Publishing this was a rather peculiar experience since the editor first had the manuscript translated into German, then declared the German version to be the official one, had it translated back into English and typeset, and sent us galley proofs that we hardly could recognize because of innumerable errors and misunderstandings! A full consideration of the model and the ab initio numerical results obtained earlier (*Chem. Phys. Lett.* 1984, 104, 440; *J. Am. Chem. Soc.* 1985, 107, 1765) showed how heterosymmetric symmetry-lowering perturbations can reduce the S_0 - S_1 gap in a biradicaloid species to zero, providing a ready explanation of the extremely short lifetime of molecules in funnel. The peculiar effect of such perturbations on the electronic states of biradicals had been noted a dozen years earlier by E. Evleth, but at that time I failed to draw general conclusions from it.

Our results also provided an understanding of the underlying unity in the twisting behavior of excited ordinary double bonds, charged double bonds such as protonated Schiff bases, and single bonds between a π -acceptor and a π -donor, as in TICTstates. The S_0 - S_1 touching predicted by the 3 x 3 model was confirmed by a numerical calculation on a real charged twisted double bond, and recent calculations by F. Bernardi and M. A. Robb similarly identified the S_0 - S_1 touching in several pericyclic systems. With minor modifications, the Huckel picture described by Zimmerman back in the mid-sixties is thus seen to be fundamentally correct, although of course, the situation is understood in much more detail now.

In recent years, my interests in photochemistry have shifted to silicon-containing compounds and polymers, and to gas-phase cluster ions. However, since I have now started efforts towards construction of superstructures from molecules ("molecular Tinkertoys"), I find myself returning to organic photochemistry at a supermolecular level.

As I contemplate my nearly three decades of involvement in the subject, I shake my head in disbelief at the number of obvious opportunities that I have missed over the years. Fortunately, there usually was someone else who did not miss them, and scientific progress was not hurt. Perhaps this type of realization is the main value of being asked to write a historical article about oneself.

For instance, there really is absolutely no reason why the latest formulation of the 3x3 model of biradicaloid electronic structure (*J. Mol. Struc.* 1992, 260, 299, issue in honor of C. Coulson) and of spin-orbit coupling in biradicaloids (with one- and two-electron parts of the spin-orbit coupling operator, in the process of being written up), which I immodestly consider reasonably general and definitive, could not have been written back in 1970 and 1971 when I first thought about the model, since all the simple theoretical tools needed had been long available.

In conclusion, I thank my teachers, post-doctoral mentors, and colleagues who hosted me at their institutions or collaborated with me, and particularly all the numerous post-doctoral, graduate, and undergraduate students, research associates, and sabbatical visitors who have worked in my research group over the years. I have mentioned by name only a very small fraction of these enthusiastic and dedicated individuals, nearly exclusively only those who worked with me in the early days, but it is clear that without them, hardly anything would have been accomplished in my office and laboratories. I also must mention at least one of the funding agencies that made my work on photochemistry possible over the last two decades, the National Science Foundation. Last but not least, I thank my wife, Sara, for her support, understanding, patience, and sacrifice over the years.