# Why I Love Science: A Personal Statement

I do not know when I first became interested in science. I think it was a slowly evolving process that started with my love for mathematics in high school, which was transferred to science as I realized the beauty of its application to the understanding of the world around us. I was particularly excited in a freshman chemistry course taught by Bob Rosenberg at Lawrence College, in which I discovered how simple physical models could be used to distill complex phenomena to their essential simplicity. I did not come from a scientific family. On the contrary, my mother was an artist and my father a bookbinder, which exposed me to art at a very early age. However, I have come to realize the close connection between art and science. Both artists and scientists attempt to understand the world by reducing its complexity to a few strokes of a brush or simple concepts such as Coulomb's law. So, perhaps I owe my interest in science to my artist parents.

I first became exposed to unimolecular reactions and energy flow at Wesleyan University in Connecticut where Peter Leermakers was teaching a course in physical organic chemistry, a major portion of which dealt with the then exciting new field of organic photochemistry. I followed that interest at Cornell by working on gas phase kinetics with Si Bauer, whose creative mind really inspired me. He is a master at developing simple models. As I began my independent career at UNC, I learned that creativity is also required in developing new experiments that provide clear information. Sometimes a small modification in an existing experiment provides a whole new dimension or avenue for research. The most exciting times are when you are surprised by your own discoveries. You often cannot trace the history of your thoughts. They just appear. It must be a similar experience for artists who find new ways of expressing themselves

Science is a communal effort. Most of us work in groups where we bounce ideas around and learn from each other. As professors with multiple responsibilities, we never seem to have the time to think deeply about any one topic, and thus we often depend on our students and postdocs to introduce us to new ideas and techniques. My first post-doc, Art Werner, brought his QET program to our lab, which permitted us to analyze our first measured dissociation rates in terms of the statistical theory. We of course soon learned to write our own code for calculating density and sums of states first by translating Wendell Forst's method of steepest descent into BASIC, and then using the direct count method. Don Mintz came along at the time when we were trying to understand translational energy release and were wrestling with Eph Klots's papers on this subject. Many years later, Jon Booze introduced me to the much more transparent microcanonical partitioning of energy. Jon had the wonderful, but also frustrating, habit of re-deriving everything from scratch, often in unique ways that provided great insight. Gary Willett joined our lab just as we purchased our first DEC 11/03 computer. I marveled at his agility in configuring this computer, convinced that without Gary, we would never have managed to turn it on. Our research moved into REMPI spectroscopy through the efforts of Tim Cornish who was determined to strike out on his own. He put this unfunded experiment together on a shoestring and ignored numerous suggestions until he finally made some significant discoveries. Experiences such as this have taught me to never tell a student something will not work. The point is that it may work, but for reasons that we simply have not thought about yet.

Analyzing data is an adventure in discovery and there is certainly no greater thrill than discovering something new. Liam Duffy showed us that the two-component decay rate data in our series of pentene isomers contained sufficient information to permit us to extract all of the dissociation and isomerization rate constants from the data. After that Oleg Mazyar and Paul Mayer seemed to discover two-component decay rates everywhere. Jon Booze and Karl-Michael Weitzel stared at their molecular beam PEPICO peak shapes of dimer ions sufficiently long to see that they contained a major clue about the origin of the dimer ions. Were these ions produced by photoionization of dimers, $(AB)_2 + h\nu \rightarrow (AB)_2^+$, or by dissociative photoionization of trimers, $(AB)_3 + h\nu \rightarrow (AB)_2^+ + AB$? What a thrill to have a student come to you and show you that the narrow TOF peaks are from the first process and the broad peaks with energy release are a result of dissociative photoionization. What hidden gems some data contain!

I seem to be good at raising difficult problems, but not so good at finding solutions. An example that plagued us for a long time was the following. When an aerosol particle is ionized by a high power laser pulse, you can generate millions of ions, and we know that at least some of these ions are extracted because we obtain a TOF mass spectrum. However, why should the ions be extracted at all? After all, the ionization process produces both negative and positive charges, thereby forming a stable micron sized plasma. A small applied field might separate the charges somewhat, but when you calculate the fields, you realize that 200 V/cm is orders of magnitude too small. I thought that perhaps the electrons could tunnel out of this coulomb field leaving the positive ions, which can then be extracted. However, Juri Dessiaterik showed us the correct interpretation, which is that expansion of the whole plasma into the vacuum reduces the coulomb field until it is smaller than the applied extraction field. His calculations showed that all this takes place within about 100 ns. What a simple explanation! Thank you, Juri.

We of course learn from our colleagues beyond our research group as well. I recall, Mike Bowers excitedly telling me about his transition state switching mechanism and how that could explain a conundrum in our butadiene ion rate constants. It turned out not to be the correct explanation, but his model (which is very similar to the variational transition state theory) gave us a whole new way of looking at ionic dissociations. A similarly exciting moment was experienced when Phil Johnson, on one of our DOE contractor meeting hikes in Lake Tahoe, told me about the basis of high-resolution ZEKE spectroscopy; that it was a result of field ionization of long-lived Rydberg states, and that he had just proven that with his new MATI experiment. I think the thrill one experiences at a moment like this is a result of the sudden new possibilities that open up. It reminds you that science is not dead and that there is new science out there yet to be discovered.

There are many shared moments of excitement that have enriched my scientific life. Quite early in my independent career, Terry Murray developed an electron pulsing scheme with a continuous light source that permitted us to collect threshold electrons by TOF analysis thereby eliminating the problem of hot electrons. [This same Terry came into the lab one morning to find that the quartz light source had sprung a water leak, which slowly filled the monochromator, experimental chamber, and the two diffusion pumps with water. Our security system

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had not been prepared for this disaster. He single handedly cleaned the whole system, even recuperating the Santovac5 by straining it through cheesecloth. Fortunately, I never knew about this until after I came back from a sabbatical year abroad.] With this pulsing scheme we could scan the photon monochromator and were able to get nice threshold photoelectron spectra (TPES) without hot electrons of diatomic molecules such as NO and $O_2$, although with intensities that were not at all Franck−Condon. However, when we looked at polyatomics such as benzene, COS, or $CH_3I$, the threshold electron signal filled in some 500 meV above the ionization energy, so that we observed strange peaks where we did not expect them and the threshold electron signal never went down to the baseline. I thought that this was due to some unknown defect in our experiment. A year later during my first sabbatical leave spent at the synchrotron in Orsay, Paul Guyon, Irene Nenner, and I plus some others were using the pulsed synchrotron light as a start signal for collecting threshold electrons and we were able to collect much better electron TOF distributions. We noticed the same persistence of threshold electrons in the $N_2O$ photoionization, and we immediately realized that this was a universal phenomenon and responsible for the observation of ion dissociation onsets in Franck−Condon gaps. The search for an explanation of the mechanism for threshold electron production kept Paul and me occupied in endless discussions over many years. I think Paul and I are among the very few and select people who understand (or perhaps care about) this issue.

Working at the Orsay synchrotron in the 70’s was not easy (only weekends were devoted to synchrotron radiation users at ACO). Later, when the ring became dedicated to synchrotron radiation users and life became more normal, I spent a most pleasant three weeks collecting data with Odile Dutuit. The fact that everything worked uncharacteristically well during this time permitted us to talk at length while collecting data, which as a result of Odile’s patience and her clear French improved mine considerably.

Certainly the most enjoyable scientific year of my life was in 1992, which Carol (my wife) and I spent in Montpellier, France. Our official duty as resident director of the UNC year in Montpellier involved taking care of 35 US students studying at the University of Montpellier. During this time, Bill Hase and I were working on a book on unimolecular reactions, trying to update the old Wendell Forst and Robinson and Holbrook editions that dated back to the early seventies. We arrived in our small apartment with two trunks of books and reprints and my old black and white laptop model 286 PC. I spent my days reading papers and writing down my thoughts in the tiny room that served as my office. The days were pleasantly interrupted by playing tennis at a club some 10 min walk from our apartment, our afternoon beers somewhere in downtown Montpellier, and interacting with the students or the University personnel. I will always cherish those days when I seemed to have unlimited time to read papers until I understood them. It was a heady time for unimolecular reactions. Ahmed Zewail was moving from nano to pico to femto second spectroscopy at speeds approaching that of his reactions. Other west coast groups such as Brad Moore, Curt Wittig, and Hanna Reisler were measuring rate constants of state selected reactions that seemed to provide glimpses of the transition states. Theoretical advances kept apace through the work of Bill Miller and Rainer Schinke. The task of understanding my field of unimolecular reactions was made enormously easier through my collaboration with Bill Hase, with whom I communicated via email on a daily basis. Our close contact during the two years it took to write this book developed into a close personal friendship, which we both value. During the Montpellier year, every day seemed to provide new insights into a field that I soon realized I had understood only superficially. I finally grasped, through the papers of Eph Klots and Chuck Wight, how the dissociation of a state-selected molecule (a microcanonical ensemble) can yield products with rotational distributions characterized by a temperature (a canonical ensemble). I discovered the relationship among the various forms of the variational transition state theory, or the multitude of treatments for energy partitioning among reaction products. Describing these in a coherent and unified manner was a wonderful challenge, and I hope that our efforts are helpful to others working in this field.

I feel extraordinarily lucky that I am being paid for doing what I love to do. Certainly one of the great pleasures is the constant exposure to new ideas. I had a lucky break a few years ago when Roger Miller, my colleague at UNC, and I decided to launch a new project in aerosol mass spectrometry, a field that was just beginning to take off as a result of the success of Kim Prather, Dan Murphy, and Murray Johnston. Because of its obvious environmental utility, this project attracted a group of motivated and enthusiastic students that has kept my life exciting. Two outstanding postdocs, Ephraim Woods and Geoff Smith, showed during the early stages of our project how one can do depth profiling of aerosol particles. They also interfaced a flow tube for measuring gas particle kinetics to the aerosol TOF mass spectrometer. As with many scientific efforts, we depend on others, and no one has been more generous than Doug Worsnop in providing help at various stages of our aerosol project. Science is indeed fun when we interact with others who are similarly excited about furthering our scientific understanding or thinking up new ideas. Among those fun times were several week-end brainstorming sessions with Mike White, Jim Weisshaar, and Ed Grant when we thought about new experiments that could be launched at the Advanced Light Source synchrotron, which was then under construction, or the endless discussions with Henry Rosenstock about TPEPICO over equally endless beers during the annual ASMS meetings.

Doing research is of course not all fun, and the highs one experiences when everything is working are invariably offset by the lows when nothing seems to work or new ideas seem to dry up. I recall being ready to give up on TPEPICO a few years ago because I thought we had reached the limit of what we can do and any further work seemed pretty dull. Just about that time, Bálint Sztáray, a young student from Budapest joined our lab for six months and turned everything upside down. After completing his PhD thesis in Budapest and being appointed as a professor at the Eötvös Loránd University, he returned for an extended sabbatical visit. Within a year, we were using velocity focusing to improve the electron resolution, a second electron detector to collect the hot electrons, and a reflectron to improve the mass resolution. Best of all, Bálint wrote an amazing program that permitted us to model the data in far greater detail than I had thought possible. We now have again a flourishing PEPICO program for which I am most grateful.

I cannot claim that we have made earth shaking discoveries during my 30 plus years at UNC. However, the discoveries and the surprises that constantly await us, no matter how little or big, are the elements of our work that provide such joy and satisfaction. Among those is surely observing students catch the research bug and in seeing them as excited as I am about new ideas. So, for all the wonderful years of interaction with my colleagues, including those not specifically mentioned here, I am truly grateful.

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