

THE JOURNAL OF PHYSICAL CHEMISTRY

B

© Copyright 2006 by the American Chemical Society

VOLUME 110, NUMBER 38, SEPTEMBER 28, 2006



Autobiography of Robert J. Silbey

Born and raised in a lower middle class family in Brooklyn, I was strongly influenced by the liberal atmosphere of that time and place, and still am. My father was the manager of a bottling plant on the Brooklyn docks and my mother worked at the Red Cross Headquarters in New York City. My older brother by seven years, Joel, and I shared a bedroom in our five room apartment in Flatbush. We both went to the public schools and then on to the public university system of New York City. We were clearly not rich, but our apartment was filled with books, a fact that puzzled many of my childhood friends. My father had studied chemistry at Cooper Union in Manhattan, and I am certain that my early interest in chemistry stemmed from that. I, like many young people at that time, owned a chemistry set that I used to do "experiments", which led to setting the table on fire from time to time.

I graduated from Erasmus Hall High School and then went on to City College to study chemical engineering. Within six months, I realized that I was more interested in chemistry and physics than chemical engineering, at least how it was taught back then, and decided to transfer to Brooklyn College for the

remaining three years and major in chemistry. That allowed me to become reunited with Bruce Berne, who had gone to junior high and high school with me, and was majoring in chemistry at Brooklyn College as well. We studied quantum mechanics and statistical mechanics together in a small seminar class organized by Professor Albert Levine, who had the good idea to ask us to read Pauling and Wilson and Mayer and Mayer. We read these texts, but now I can say that we really did not understand much. However, it ignited our interest and determined that we would go on to graduate school in chemistry. We both chose to go to the University of Chicago, where the excitement and intensity were exactly what we wanted. We both thrived. During my last year at Brooklyn College, I had become engaged to Susan Sorkin, and we were married the next year. She joined me at Chicago to study Political Science. We have been partners in every aspect of life for over forty years.

At Chicago, I decided to be an experimentalist and in my first year joined the research group of Clyde Hutchison. Clyde's group meetings were held on Tuesday evening and Saturday morning and were always on a stimulating theoretical topic. I

began experiments on the EPR of a ground state triplet molecule, diphenylmethylen, formed at low temperature by exciting diazo-diphenylmethane with light. My first task was to build a 1 cm microwave system to replace the 3 cm system that had been used previously and to devise a way to get the light into the dewar to illuminate the crystal of a low concentration of diazo-diphenylmethane in benzophenone that had been grown. I managed to do this by December of my second year and saw my first real signals on Christmas Eve. But, by that time I had also realized that my experimental skills were not up to the standards either Clyde or I expected (I had broken enough large dewars to be certain of that!). So, I decided to change research groups and become a theorist working with Stuart Rice. This turned out to be an inspired choice. Stuart is a wonderful research advisor, who allows his students enough freedom to flourish and gives them enough advice to make that possible. He suggested a few topics, and introduced me to a senior visitor in his group, Joshua Jortner. So began a long friendship as well as the work on the exciton states of the polyacenes that constituted my Ph.D. thesis. For the next two years, I learned a tremendous amount, largely due to the excitement of the Rice group, which included Bruce Berne, Leon Glass, Marty Vala, Aaron Bloch, Neil Kestner, and Jean Pierre Boon. In addition, we shared office space with other research groups, so Phil Pechukas, John Lekner, and I were together in one office, which led to heated discussions about many topics, not all theoretical. I should also mention that other faculty in chemistry and physics were often drawn into the discussions, including Steve Berry, John Light, Don McClure, Leo Falicov, Morrell Cohen, and Jim Phillips. The scientific ambience of the James Franck Institute at that time was the most intense and exciting that I have ever known.

After Chicago, I won an AFOSR postdoctoral fellowship that I could take anywhere, and I decided to go to the Theoretical Chemistry Institute at the University of Wisconsin where Joe Hirschfelder, Saul Epstein, and Dick Bernstein were the senior faculty. I worked with Hirschfelder on a number of problems in perturbation theory. Although it was a fun year, it convinced me that I wanted to be more connected to novel experiments rather than developing theoretical methods. This has been my mode of operation ever since.

I began interviewing for an academic job in the fall of 1965 and spent a lot of time traveling around the country. I interviewed at MIT in February, 1966, and during that interview trip, I met John Deutch who had been a Ph.D. student with Irwin Oppenheim at MIT and was at that time a postdoctoral with Bob Zwanzig. John had come back to MIT to finish up some work with Irwin and listened to my interview talk and gave me the hardest time of anyone in the question period. In spite of that (or perhaps because of it) I was offered a job and accepted an Assistant Professorship beginning in July, 1966. Deutch went off to Princeton as an Assistant Professor. We invited him back to MIT as a faculty member a few years later, and the rest is history. MIT was a wonderful place to be a young faculty member. My senior colleagues, Jim Kinsey, Irwin Oppenheim, John Ross, John Waugh, Carl Garland, and Bob Alberty were always supportive and friendly, and had a common-sense approach to academic life, or in the words of Kinsey, "they all knew where babies come from". They have been my good friends for forty years.

My first group of Ph.D. students included Morgan Grover, Paul Chalmer, John Schroeder, Christine Sloane, Shelly Rackovsky, and Ken Jordan. My first postdoctoral students were Joe Alper and Ben Scharf. We worked together on problems having

to do with electronic energy transport in solids: exciton energy levels, transport, spectral lineshapes, and phonon scattering. Over the years, I have come back to these same issues as experimental techniques improved and more can be learned about both coherent and incoherent energy transport. For my first sabbatical leave, I was invited to spend six months at the Theoretical Physics Institute of the University of Utrecht. So Susan, our two year old daughter Jessica, and I went off to the Netherlands. We had a wonderful time and our second daughter, Anna, was born in Amsterdam at the end of that stay. The scientific atmosphere in Utrecht was excellent and friendly; my research interests turned to disorder and localization in the condensed phase. Hans van Himbergen, who got his Ph.D. with John Tjon at Utrecht, came to postdoc at MIT a few years later.

Just before our leaving for the Netherlands, Ron Chance, then a graduate student at Dartmouth, and Al Prock, a Professor at Boston University on sabbatical at Dartmouth, came to see me about some experiments they were working on that seemed to show strong quenching of molecular excitations at gold surfaces. We worked together to try to come up with a model to explain the data, and saw that an idea of Hans Kuhn's, to explain the oscillations in the excited state lifetime of a molecule near a metal surface, could be improved to fit the experiment. We intuited that the quantum mechanical problem of an excited molecule near a metal surface could be modeled as an oscillating dipole near a partially conducting half space, the classical problem that Sommerfeld had solved about 75 years before. We eventually wrote and published an article in *Advances in Chemical Physics* that is still heavily cited. Ron Chance soon got his Ph.D. and went off to work on polymer physics and chemistry at Allied Chemical Corporation and later at Exxon. We remained collaborators and friends ever since (more about that later).

On my return from Europe, I worked with a succession of postdocs, Alan Gregory, Alan Gelb, and David Yarkony, on various problems in surface chemistry, vibronic coupling, and exciton-phonon interactions. Horia Metiu, who was a student working with John Ross, and Kazuo Kitahara, a Ross postdoc, also worked with me on transport. At the same time, Bob Munn (from UMIST in the UK) and I had a NATO grant together that allowed us to visit one another and to write a few more papers on electron-phonon interactions and electron and energy transport. Later on, Alex Blumen came to be a postdoc, followed in quick succession by Yossi Klafter, Reiner Wertheimer, and Rich Friesner. During those years, I had to work really hard to keep up with them, and usually failed. They taught me a tremendous amount of science. In the summer of 1976, I spent some time at Berkeley (with Bob Harris) and at IBM in San Jose (with Dietrich Haarer).

As I mentioned, Ron Chance had begun to work on polymer problems at Allied, and soon became interested in conjugated polymers, such as polyacetylene. Heeger and MacDiarmid had seen large conductivities in doped polyacetylene, and the question was how to explain this and whether it could be translated to other, more stable polymers. So Ron invited me down to Allied to talk about it. We had some ideas and the NSF was in one of its phases in which academic-industry collaborations were funded, so we applied for and received a grant allowing us to hire a postdoc. We asked Jean-Luc Brédas, a recent Ph.D. from Namur, Belgium, to join us, half at Allied and half at MIT. It was an inspired choice. Jean-Luc, Ron, and I noted that the models that were used by the physicists to study polyacetylene and other systems amounted to Hückel theory with linear electron phonon coupling. We knew we could do

as well, so we began work on polyacetylene, polyphenylenes, polyphenylene sulfide, and polyaniline. It was the beginning of a lifelong friendship and continued collaboration on the electronic states of polymers, always staying close to experiment.

In the summer of 1981, I was invited to spend a month in the lab of Jan Schmidt at Leiden University in the Netherlands. His new experimental studies of relaxation in exciton systems at low temperature were exciting and I had the fun of being in an experimental lab talking only to the experimentalists. I learned a tremendous amount, and my family enjoyed being in the Netherlands once more. Most importantly, I earned the reputation as a theorist who would work with experimentalists, so I was invited a year later to spend some time in the lab of Peter Trommsdorff at the University of Grenoble in France, then to the lab of Dietrich Haarer who had moved to the University of Bayreuth in Germany, and to the lab of Helmut Port at the University of Stuttgart. Later on, I spent a Humboldt award jointly in Bayreuth and Stuttgart.

Back in the U.S., Bob Harris and I started to think about the dynamics of optical isomers and how the environment (or bath) affects the tunneling rate. We had an intense collaboration over a few years on this subject, which turns out to be very complex, and illustrates so many aspects of the wonders of quantum mechanics.

At about the same time, Klaus Kassner, Paul Parris (postdocs), and Bret Jackson (Ph.D student) were working with me to try to understand the experiments on hole burning in low temperature glasses. My friends Dietrich Haarer, Mike Fayer, and Silvia Volker (whom I had met when visiting Leiden) were doing beautiful experiments that had us very puzzled. Why did the spectral hole widths have the temperature dependence they have? Why are they time dependent? Did the three-pulse photon echo relaxation arise from the same physics? This led us to study the two level system model in detail, and Andreas Heuer and later David Dab did lovely simulations of glasses that agreed with its basic ideas. My graduate student, Alberto Suarez, worked out many of the theoretical issues in a series of papers. Later on, Peter Neu (postdoc) and David Reichman (a Ph.D. student) worked on general issues in low temperature relaxation as well as some of the most puzzling issues that arose in the long time dynamics of spectral diffusion. Once again, I was invited to collaborate with a European experimentalist, Silvia

Volker. Understanding her elegant and powerful low temperature spectral measurements is still one of my interests. Spending time in her laboratory has kept me strongly connected to the experiments. The discovery of low temperature single molecule spectroscopy in similar systems by W. E. Moerner and Michel Orrit meant that theorists had to work hard to understand the experimental results. My students David Reichman, Frank Brown, and Younjoon Jung and postdocs Wolfgang Pfluegl, Eli Barkai, and Seogjoo Jang all contributed to our understanding of this powerful new tool.

In the early 1990s, Bob Field and I began to collaborate on understanding the highly excited vibrational states of polyatomic molecules, such as acetylene. I worked with his Ph.D. students on theoretical issues, and David Jonas and Matt Jacobson taught me much more than I could ever teach them about the behavior of hot molecules. At the same time, the non-linear optical properties of conjugated polymers became interesting and I invited Jo Zyss, a scientist at France-Telecom Research Labs, to visit MIT for the summer and help me understand the scientific issues. Manuel Joffre and David Yaron were postdocs and Theresa Kavanaugh was a Ph.D. student, all working on NLO properties. At MIT, Dick Schrock was able to synthesize well-characterized polyenes, and we collaborated with Ron Chance (now at Exxon), Jo Zyss, and Bob Cohen (MIT) to measure the properties and model them. A while later, my student Sophia Yaliraki worked on non-linear light scattering as well as the NLO properties of disordered conjugated polymers. Zyss, who is now a Professor at ENS-Cachan, and I continue to collaborate, "requiring" me to visit Paris a couple of times each year.

My scientific life has been fortunate: I have had excellent graduate students and postdoctoral students and I have been able to collaborate with world-class experimentalists who have become my close friends. My life at MIT has also been lucky: my colleagues in the department of Chemistry are friends as well as being terrific scientists and teachers. In the past few years, I have paid my dues at MIT by becoming Dean of the School of Science, a job that has few rewards. However, I have still been able to do science, because of the excellence of my students and collaborators. Finally, I have been extraordinarily fortunate in my personal life, with the unwavering support and love of my wife, Susan, and our daughters, Jessica and Anna.