Scientific Autobiography of Jack Beauchamp

I was born in 1942, the middle of three children. At the time my father worked at a magnesium plant in Henderson, NV, and my mother taught elementary school in Burbank, CA. During the war we moved to the Mojave Desert and eventually settled in Needles, CA. Although the character of the town has changed over the past 60 years, the population of Needles has remained around 5000 residents.

Growing up in a small town has advantages that I believe greatly outweigh any imagined disadvantages. We had excellent public schools supported by an involved community. Crime was minimal and doors to cars and homes were often left unlocked. As children we could walk to school and to the local theater for the Saturday matinee. Any misdeeds were reported to your parents because everybody in town knew you. The movie *American Graffiti* reminds me of my high school years in Needles.

My interest in science and engineering began at a young age with a curiosity about how things worked. Although he may at times have regretted it during my youth, my father taught me how to use tools not long after I learned to walk. I dissected any mechanical or electrical device I could scavenge and, at every opportunity, would accompany my father to the local dump site. Discarded radios were a real treasure! I also loved models and built cars, boats, airplanes, and rockets, many of my own design. To have a place to work, I built a workshop attached to the back of our house, using lumber picked out of a wash after a particularly bad flash flood one year.

By now my father operated a small store in Needles and working for him I was able to earn enough money to buy nearly every piece of electronic test equipment available from the Heathkit mail order catalog to equip my workshop. I subscribed to Popular Electronics and would eagerly await each monthly issue to see if there was an interesting circuit to build. Eventually I began designing my own circuits. Growing up with vacuum tubes, I remember paying five dollars (at a time when you could go to the movies for a quarter and a coke at the local drug store cost a nickel) for a single transistor when they became commercially available! I tried out so many circuits with this fascinating device that one of the leads broke off. I opened the case and resoldered a new connection to the pin inside.

Although the curriculum was limited by the size of the school, I had very supportive teachers that helped me to develop and pursue my interest in science and math. I think they especially enjoyed having a student who thought these subjects were fun! I was the first kid in my school to have a pocket transistor radio that I could surreptitiously listen to in class. Unfortunately, the only local radio station did not offer the rock and roll music that we all became addicted to at the time. My first exposure to “research” came when my high school chemistry and physics teacher obtained an NSF fellowship that allowed us to travel to Redlands University on weekends to learn about gas chromatography.

Growing up in the post-war years just south of where much of the early atomic bomb testing took place, I became interested in nuclear physics. After winning an essay contest on “The Importance of Scientific Progress to America”, sponsored by a local utility company, I had a great time attending the First National Youth Conference on the Atom in Atlantic City, with side trips to New York and Washington, D.C. The keynote speaker was Vice President Richard M. Nixon. This was my first airplane trip and confirmed the thought that science could be a lot of fun.

Because of its reputation in science and engineering, I applied to Caltech along with several other schools to pursue a college education. At the time Caltech interviewed all applicants and I can remember Professor of Geology Robert Sharp making a special trip to Needles to see if I was the “right stuff.” I did not realize at the time that Sharp had a real love affair with the Mojave Desert and would have made the trip even without the excuse of interviewing a potential Caltech student. As it turned out he knew my grandfather very well and we talked more about him and my grandmother’s cooking than we did my interests in science and engineering. My grandfather, Jack Mitchell, had lost a fortune in the gold mining business in Arizona in the 1920s before settling in the Providence Mountains, just north of Needles. There he developed several limestone caverns, now Mitchell’s Caverns State Park, as a tourist attraction.

I expressed an interest in both nuclear physics and electrical engineering when I entered Caltech as a freshman in 1960. Caltech at the time had a synchrotron facility that I found simultaneously impressive and intimidating. It did not seem that an individual could gain much personal satisfaction from working on a large project that involved many people. As a result, I became more interested in chemistry, particularly where electronic instrumentation was used to solve chemical problems. I found the curriculum difficult at first, because I had never had to study before coming to Caltech. I thank my parents for the work ethic and tenacity that kept me going until I caught up and the work became easier. After my freshman year I accepted a summer job at Caltech to help develop new experiments for the undergraduate chemistry labs.

Early in my second year at Caltech I was inspired by Professor John D. Roberts, who taught the introductory organic chemistry course. When I met with him to explore the possibility of undergraduate research involving the application of nuclear magnetic resonance to problems in organic chemistry, he talked with me for a few minutes and then led me into the lab where he introduced me, in a memorable encounter, to one of his graduate students, George Whitesides. Roberts issued the brusque instruction “George, teach this boy how to do research”. George gave the two of us a grimace that said, “What did I do to deserve this?” We became good friends and George was a terrific mentor who also thought science was fun.

I had a short career as an organic chemist, trying to make precursors for stable carbonium ions that were to be examined by NMR. After several failed attempts at organic synthesis that included a trip to Huntington Hospital following one mishap, Whitesides and Roberts decided I would be better off in front of a computer. My first publication involved an analysis of the NMR spectra of several methylphosphines. Following this I became interested in the theoretical aspects of NMR and developed computer programs for analyzing NMR line shapes of complex spin systems to extract kinetic parameters. By now I had succumbed to the addiction of scientific research and the pursuit of an academic career. The later interest was reinforced when Roberts asked me to teach a quarter of his graduate level NMR course during my senior year. Looking back at my undergraduate experience, I realize now how much I have

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benefited by the inspiration provided by the opportunity to learn about the excitement of chemical science at the time from people like Linus Pauling, Jack Roberts, George Hammond, Norman Davidson, Russell Pitzer, Wilse Robinson, Harden McConnell, and Sunney Chan, to name only a few.

Two factors influenced my choice of Harvard as a graduate school in 1964. Having been in southern California all of my life I wanted to experience a different environment. It snowed once in Needles in the last century, making the winter of 1948 particularly memorable. Harvard had an excellent reputation in chemical physics, and I was interested in the experimental and theoretical work of one of their young faculty, John Baldeschwieler, who at the time was examining NMR line shapes and relaxation processes using density matrix methods. John offered me a position beginning in the summer after I graduated, and by the time classes started in the fall I was well into research.

Rather than pursue my interest in NMR, I undertook an opportunity that John offered me to start a new project. This involved an examination of the effect of external electric fields on nuclear quadrupole resonance spectra. The idea was to see if one could develop interesting chemical applications of the phenomenon, in which quadrupolar nuclei are used as probes for the small shifts in electron density that accompany application of an external electrical field to a molecule. Right at the point where effects of the applied field on the spectra were observed, a loud noise would signal electrical breakdown of the sample and destruction of the probe. This was not fun! The humidity of the Boston summer contributed to these early difficulties.

Midway through my first year of graduate school Baldeschwieler announced to his research group that he would be moving to Stanford University. John indicated that he had funds that would let him purchase a new type of mass spectrometer from Varian and asked if I would be interesting in working with the instrument. He had become acquainted with Peter Llewellyn at Varian, who had led a team to develop a mass spectrometer based on ion cyclotron resonance with radio frequency detection of the ions, and John arranged for one of the first instruments to be delivered to Stanford. John was intrigued by the similarities between NMR and ICR and reasoned that ICR line shapes could be analyzed to extract information relating to ion−neutral collision dynamics. I was interested but decided to remain at Harvard another year to finish the residency requirements for a doctoral degree in chemistry. John agreed to fly me out to Stanford to perform experiments after the instrument was delivered.

What at first I perceived as a disadvantage turned out to have a silver lining in terms of broadening my scientific background. After Baldeschwieler's group departed for California, I decided to attend the group meetings of the other chemical physics groups at Harvard. These included Dudley Herschbach, Al Kwiram, E. Bright Wilson, Bill Klemperer, and George Kistiakowsky. I had the good fortune to share an office on the top floor of Prince House with a stimulating group of theoretical students, which included Bill Miller, Bill Reinhardt, and Herschel Rabitz. Not being distracted by an experimental apparatus at the time, I wrote a lengthy theoretical paper on ICR line shapes. I was particularly interested in the effect that kinetic processes, such as resonant electron transfer between isotopic rare gas ions, had on the observed ion populations and line shapes. I recall that when Baldeschwieler edited this manuscript the first thing he did was to remove his name from the title page. Fearing that he did not like the paper I asked why he did this and he responded that he did not want to feel obligated to explain it to someone else. The only comment from reviewers was that the paper seemed to lack references, so I added a few more and it was accepted for publication.

My interest in chemical dynamics was stimulated by the inspiration provided by Dudley Herschbach and his students at Harvard, which at the time included Yuan Lee. I had become acquainted with Herschbach as a teaching assistant in his upper level course on chemical dynamics. In the first lecture he announced that he needed two teaching assistants for the course. Bill Stwalley, a good friend from Caltech and now chairman of the physics department at the University of Connecticut, happened to be sitting by me at the time. We decided to volunteer, not knowing that Herschbach had a reputation for incredibly difficult homework sets with research-oriented problems. We reasoned that someone would have to do the problems correctly and we could look through the papers and make up solution keys for the homework. This proved not to be the case and Bill and I spent many hours working with Dudley in an attempt to find solutions to his "simple" exercises. At the time I had a Woodrow Wilson Teaching Fellowship, which ironically would not allow one to teach their first year of graduate school. The award stipulated that I could not receive monetary compensation for teaching, so we worked out an arrangement whereby I could have an account at the Harvard Coop, which allowed me to acquire a sizable library at the time. I believe that my career has benefited greatly from the time spent studying many of the classic chemistry texts and monographs.

After moving to Stanford in 1966 I worked with another graduate student, Les Anders, to make extensive modifications to the vacuum system and electronics of the prototype ICR instrument that Varian delivered to Stanford before it worked well enough to carry out quantitative studies of ICR line shapes to compare with our theoretical models. These studies were successful but were constantly plagued by reactions of the rare gas ions with impurities. It was not unusual to observe a large number of products resulting from competing and sequential ion−molecule reactions, many of which had never been reported before. To sort out these complex processes and extract rate constants, we developed the double resonance method in which the connections between ion populations could be easily deduced. We began to apply these methods to examine the ion chemistry of organic molecules. One of our first studies, which involved an examination of polymerization reactions in vinyl chloride, highlighted the capabilities of the double resonance method. The favorable reviewers' comments included an admonishment that we were "unnecessarily self-congratulatory" in our assessment of the experimental methodology. In addition, there were features of the experiment that made it possible to determine if a reaction was exothermic and these were exploited to develop methods to determine molecular proton affinities (gas-phase basicities) from a study of proton-transfer reactions. John Brauman and his students at Stanford later employed this experimental approach to determine gas-phase acidities of a large number of organic molecules.

Because little was known about the gas-phase ion chemistry of organic molecules at the time, we could literally run the chemical stockroom through the ICR instrument, making many exciting discoveries that rapidly filled the pages of my doctoral thesis. I had found the right toy and science was definitely fun again.

Not long after I arrived at Stanford, Baldeschwieler departed to take up a position as Deputy Science Advisor under Edward

E. David in the Nixon administration. Although he made frequent trips back to Stanford to maintain his various research efforts, I feel that I benefited from the unusual independence I had as a graduate student. As a result I have always tried not to overdirect my own students at Caltech, where I returned as a Noyes Instructor in 1967.

Caltech provided funds to purchase a specially manufactured ICR instrument from Varian and I was able to obtain substantial funding for our studies with this instrument from the Department of Energy. A memorable event occurred when the Varian engineer arrived unannounced to install the spectrometer not long after it was shipped to Caltech. Before he arrived we had already unpacked the instrument, performed some initial experiments and submitted a communication for publication! He took us to lunch and we suggested some modifications to benefit their production instrument.

The ICR mass spectrometer that Varian manufactured was never a great commercial success. The instrument was much better suited for studying ion−molecule reactions than it was for recording routine high-resolution mass spectra. The development of trapped ion cells by Bob McIver, working in John Baldeschwieler's group at Stanford, and by our group at Caltech facilitated the study of ion−molecule reaction kinetics and chemical equilibria by making it possible to follow the temporal variation of ion abundances at a fixed pressure low enough to maintain the high-resolution capabilities of the ICR method. The experiment was further improved by the development, again in analogy with NMR experiments, of Fourier transform methods by Marshall and Comisarow at the University of British Columbia in the early 1970s. With this it became possible to simultaneously detect all of the ions over a broad mass range rather than monitoring single ions with a marginal oscillator detector.

The productivity of my research group was greatly enhanced with the acquisition of a second ICR instrument funded by NSF, and our experimental efforts expanded beyond new applications of ICR during the mid 1970s. A very successful effort involved the development of a molecular beam photoelectron spectrometer to obtain high-resolution photoelectron spectra of free radicals formed by flash vacuum pyrolysis. The Franck−Condon envelope provided a snapshot of the carbonium ion dressed to look like the free radical precursor. Where adiabatic ionization potentials could be obtained, they provided an accurate connection between the thermochemistry of free radicals and their corresponding carbonium ions.

The energy crises during the late 1970s provided funds that supported fundamental investigations of chemical catalysis and organometallic chemistry. This led in our laboratory to the development of both ICR and ion beam methods for studying the kinetics and energetics of gas-phase organometallic reactions, with a particular emphasis on processes involving activation of carbon−hydrogen and carbon−carbon bonds in small unsaturated hydrocarbons by transition metal ions and complexes. We became experts on the chemistry of uranium and its compounds, which at the time had important applications in schemes for uranium isotope separation. I can recall one presentation I gave at DOE headquarters in which I proposed a complex isotope separation scheme that as a last step involved removing the US from the UN. In another study we reported the observation of UFO^+. Maybe it should not have surprised me when our DOE funding was terminated, but we were having fun.

Our studies of organometallic reactions also led to a very productive collaboration with Michael Bower's group at UC Santa Barbara in which kinetic energy release distributions were used to further characterize the mechanism and energetics of complex organometallic reactions.

The long ion residence times in the trapped ion cell made them a tempting target for photons. Our first attempt to use a high-powered YAG laser borrowed from Wilse Robinson's group to photodissociate ions resulted in a minor disaster when it blew a hole in the quartz window and vented the vacuum system! Later studies of UV ion photodissociation processes using an arc lamp were more successful. These experiments made it possible, for example, to probe the acid−base properties of molecules in excited electronic states for comparison with the ground-state properties. With some funds remaining at the end of one grant period I acquired high power pulsed and continuous wave (cw) CO_2 lasers to study the multiphoton dissociation of stored ions, for comparison with studies being conducted with neutrals in other laboratories at the time. After being told by Joshua Jortner and others that it was impossible, we discovered that multiphoton dissociation with the cw laser worked extremely well. The longer exposure of trapped ions to the laser radiation provided the required fluence levels to observe dissociation of even modest size ions, which were already in the vibrational quasicontinuum at room temperature. By measuring the photodissociation yields as a function of wavelength, "fingerprint" spectra could be obtained that permitted structural isomers to be easily distinguished. I discontinued these efforts in the early 1980s with the thought that when high powered tunable IR lasers eventually became available, we would return to pursue the many applications of this experimental methodology. Twenty years later such lasers are still not readily available. This experiment has recently had a renaissance in the photodissociation of large biopolymers to obtain sequence information.

A significant change in the direction of my research resulted from a generous gift from Arnold Beckman, which led to the construction of the Beckman Institute at Caltech, with Harry Gray as director. The Beckman Institute includes centers that emphasize the development and application of novel instrumentation and methods to solve problems in chemistry and biology. I was able to establish one of these facilities, the Resource Center for Mass Spectrometry. Funding was provided for several instruments, including a new Fourier transform ICR instrument with a 7 T superconducting magnet. This instrument could be operated with a variety of external sources, including matrix-assisted laser desorption ionization and electrospray ionization, and incorporated an octopole ion guide to transfer ions from the source to the ICR cell where they were trapped and detected. This instrument was specifically designed to investigate the properties, structures, and reaction dynamics of biological molecules in the gas phase and these studies have been a major focus of our research efforts during the past decade.

As a diversion from our work, my wife and I took up flying in 1985 and enjoyed the experience enough that we bought a Cessna 172 even before we obtained our pilot's licenses! We went on to become instrument certified and have had many memorable trips in our small plane, from fly-in Hotels in Baja California to remote airstrips in the mountains of Alaska. Flying is an endeavor where attention given to training and safety issues has enormous dividends. Because of my interest in aviation safety I agreed to chair the Committee on Commercial Aviation Security of the National Research Council in 1993. This group acts to advise the FAA on research and development involving explosives and weapons detection and passenger safety. In connection with this we worked at Caltech on new methods to sample particulates from surfaces and a variety of chemical ionization schemes for the sensitive detection of explosives. Because it was thought to be a terrorist bombing, the explosion of TWA Flight 800 after takeoff in 1996 led to formation of the White House Commission for Aviation Safety and Security, chaired by Vice President Al Gore. I spent an exciting six months serving on this commission, traveling around the world to study issues relating to aviation security and how other governments handle them. The report handed to President Clinton in February 1997, had a lot of good recommendations for both aviation safety and security. Unfortunately only a few recommendations have been implemented, and others only partially. The incidents of September 11, 2001, have brought many of the issues we addressed to the forefront again.

In addition to the fact that it is a lot of fun, I remain intensely excited about science, the thrill of new discoveries, and the opportunity for collaborations with colleagues at Caltech and elsewhere. The range of projects that my small research group is currently investigating is challenging in the breadth of subjects that it encompasses. For example, working with one of my organic colleagues, Brian Stoltz, we are synthesizing biomimetic reagents such as synthetic proteases that bind to specific sequences of amino acids of peptides in solution, are sampled using electrospray ionization, and then activated to cleave amide linkages in the gas phase.

In another collaboration, with Thomas Ahrens in geology, we have built and tested a novel impact ionization cosmic dust analyzer for use on deep space missions. We are examining the possibility that this same instrument can be used to detect trace organics in ice particles sampled in a cometary encounter. In addition, this collaboration has been recently expanded to use an orthogonal sampling time-of-flight mass spectrometer to analyze the neutral species produced from impact vaporization of minerals. This may provide some interesting clues as to global environmental changes that contributed to extinction of the dinosaurs following a massive impact. An additional collaborative space science effort, as part of a program led by Jonathan Lunine at the University of Arizona to study the organic chemistry of Titan, involves the development of novel detectors for the direct measurement of enantiomeric excesses of optically active molecules sampled from complex mixtures.

As a final illustration of our collaborative efforts, working with Richard Flagan in Chemical Engineering, a novel drift cell has been designed to investigate the evaporation and discharge dynamics of highly charged droplets formed by electrospray ionization and a range of drop-on-demand generators. Our first results with this instrument are included in this volume. These experiments have led to enough ideas to keep us busy for the next decade. It should be possible, for example, to use what I term designer droplets to lyse single cells and analyze their protein complement by an appropriate combination of the drift tube experiment modified to permit efficient collection and transfer of ions to an FT-ICR mass spectrometer for analysis. In addition, using soft sampling conditions, it is possible to transfer nanodroplets formed in the droplet discharge process, to the FT-ICR ion trap where specific solvation of ions can be examined by monitoring the kinetics of solvent evaporation processes. Studying chemical processes in these small droplets has made it possible to probe the interface between solution and gas-phase chemistry, where only a few water molecules are involved. For example, we have recently obtained evidence for the occurrence of SN_1 reactions in nanodroplets that have picked up an alkyl halide from the vapor phase.

To sum things up, science and discovery have been a lot of fun all through my life. I have a wonderful and supportive family, and I am especially indebted for the love and understanding which my wife Pat has provided during these years. In this brief scientific biography I have chosen not to mention many of the students and colleagues that have played such an important role in the research that I have been associated with over the past four decades. I have been blessed by having an enormously talented and creative group of students working in my laboratories at Caltech. Many of them have contributed research papers to this special issue and I thank them for their efforts, and for the many memorable and fun experiences we have shared together. Finally, I would be remiss if I did not acknowledge the support that I have had at Caltech, from hard working and talented staff and a sympathetic administration, which makes it easy to do great science!