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RICHARD BARRY BERNSTEIN
1923—1990

A Biographical Memoir by
JAMES L. KINSEY AND RAPHAEL D. LEVINE

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Biographical Memoir

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R. B. Bernstein

RICHARD BARRY BERNSTEIN

October 31, 1923–July 8, 1990

BY JAMES L. KINSEY AND RAPHAEL D. LEVINE

RICHARD BARRY BERNSTEIN (“Dick” to all his friends) was one of a small group of young chemists who decided in the mid- to late 1950s that the time had come to ask what really happens when a chemical reaction takes place—what is it the atoms in the molecule do during the chemical change? Chemists had produced images, sometimes very colorful and often quite useful, in order to think about chemical reactivity, but Dick and fellow members of what they were pleased to call “the lunatic fringe” wanted a science of chemical dynamics. They sought an understanding of the motion of atoms in a reaction or collision in terms of the forces that operate between them. Dick turned his attention to the task of obtaining a direct experimental characterization of these forces, which had traditionally been obtained indirectly from the bulk properties of matter. He sought a more direct route with a special emphasis on the attractive and longer-range part of the force that serves to bring molecules together.

Richard Bernstein must be regarded not only as a founding member of the experimental study of chemical dynamics but also as one who set the stage and initiated the activity in the theoretical understanding. With his characteristic

thoroughness he prepared the theoretical underpinnings needed to interpret the results of the yet to be performed experiments, including the working out of the scattering theory for treating the hard-core repulsion so characteristic of atoms and molecules. In his "subjective account" of his work,¹ published on the occasion of receiving the Robert A. Welch prize, Dick described the bringing together of all the expertise needed to do his first experiment on reactive collisions, which was published in 1965. He made many seminal contributions to both interpretive and predictive theories. He regarded theory as providing guidance for experiments,² and the fruitful synergism between experiment and theory that is characteristic of the chemical dynamics field owes much to his leadership. He was also very conscious of the need to make chemists at large familiar with the developments in his field, as is evident in his early book with R. D. Levine.³ A later updated version of this book³ reflected the rapid growth in activity by more than doubling in size.

The unique way he did science was as much a part of Dick Bernstein as the problems he chose to pursue. He had a legendary capacity for hard, concentrated work, combined with an infectious and inspiring exuberance. He brought the same bubbling enthusiasm to everything he undertook, whether it was the first trial of a marvelous new apparatus or making sure all the meticulous details were done correctly. He loved being the first to do something; yet he was most generous in his support of competitors, especially scientists in the early stages of their careers.

PERSONAL HISTORY

Dick was raised, along with his brother Kenneth, in a family that attached great importance to education, learning, scholarly accomplishment, and free inquiry. He was

born in New York City on October 31, 1923, the son of Russian immigrants. His father Simon Bernstein was a lawyer, businessman, and sometime poet. His mother Stella Grossman Bernstein created a neighborhood dress shop to help the family make ends meet; after the children were grown, she became a psychologist.

With his mother's urging and tutelage, Dick showed early promise as a musician. At age thirteen he won the New Jersey state piano competition. When he graduated from high school at the age of fifteen, he weighed the possibility of a career in music, but he decided on the study of science instead. Playing the piano continued to be something in which he took great pleasure for the rest of his life.

All of Dick's academic degrees were earned at Columbia University. In 1943 he received an A.B. degree with honors in chemistry and mathematics. His M.A. was awarded in 1946 and his Ph.D. in 1948, both in chemistry. Meanwhile, beginning in 1942, he worked on the Manhattan Project in the Synthetic Alloy Materials Laboratories at Columbia. During this period, he was inducted into the U.S. Army Corps of Engineers and was assigned for a time to a post at Oak Ridge, Tennessee. In 1945 he was transferred back to Columbia to continue Manhattan Project work. It was during that period that he met a young nurse, Norma Olivier. Their meeting was "love at first sight" on both sides and the beginning of a lifelong relationship from which Dick drew great strength. At the time, Norma was chief operating room nurse at a hospital near Columbia, and she spent a great deal of weekend time during their courtship in the laboratory where Dick was pursuing his doctoral research.

After World War II ended, Dick remained in the Army for a time. He was a participant in the first U.S. tests of fission weapons at Bikini Island in 1946. Among his reminiscences of that period was one of spending an entire af-

ternoon on the day before the first test filling bottles with seawater. He thought someone would eventually want baseline samples of ocean water before it was permanently altered by contaminants from the blast. On being told that he was probably the only person in the South Pacific who would have thought to do that, he shrugged and remarked, "there were probably hundreds of people filling bottles that day." In any event, the bottles of water survived at least to the early 1970s, at which point they were locked in a safe in the chemistry department at the University of Wisconsin.

The first Bikini test almost claimed Dick as a casualty. He was in charge of a crew installing and testing radiotelemetry instrumentation on the various islands in the Bikini atoll. The Navy provided a small boat and crew to take Dick and an Army buddy for a last test of the instruments. When it came time to head back, the Navy crew couldn't get the boat started. Neither could Dick and his friend, who turned their attention to the problem after a relaxing swim. When it became apparent that they would have to spend the night, they settled in, confident that they would be missed and sent for, even though they were beyond contact range with the parent ship. It turned out, in fact, that nobody had noted their absence, either at dinner that night or breakfast the next morning. Meanwhile, the clock was ticking on the test and the lost group was harvesting coconuts to assuage its hunger. The next morning they fashioned an SOS on the beach with cut-up underwear and, more importantly, transmitted attention-getting false radiation levels with the instruments they had been sent to check. This resulted in the arrival of a rescue launch well before the test, but the incident leaked out to the press and provided some unwelcome publicity for the Navy!

After leaving the Army, Dick settled into his Ph.D. studies at Columbia, investigating isotope separation under the su-

pervision of the late T. I. Taylor. Nineteen forty eight was a banner year; Dick completed his Ph.D., and he and Norma were married. The same year Dick began his first academic job, at the Illinois Institute of Technology. Dick and Norma remained in Chicago for five years. During that time, their son Neil and daughter Minda were born. In 1953 the University of Michigan enticed Dick away from IIT, and the family moved to Ann Arbor for a ten-year period. Daughters Beth and Julie arrived in 1956 and 1958, respectively. It was during his Michigan era that Dick began his crucial move into molecular beam studies of molecular forces and chemical reactivity. In one way or another, the rest of his career was shaped by his vision to take up this challenging new field.

The next stop in the Bernstein family odyssey was the University of Wisconsin, Madison. Another productive and exciting decade (1963-73) was spent there, the last six years as Daniells professor of chemistry. In 1968 he was elected to membership in the National Academy of Sciences while in Madison. Nineteen seventy three saw a move to the University of Texas in Austin, where Dick held the Doherty professorship with joint appointments in chemistry and physics. After a four-year period on the Texas faculty, Dick accepted an appointment to the faculty of Columbia University as Higgins professor of natural sciences in the department of chemistry. The return to his alma mater and to New York City was a source of much joy to Dick and Norma. In 1982 Dick's career took a quite bold turn when he accepted a position in industry as senior vice-president at the Occidental Research Corporation. He understood that the company intended to set up a showplace industrial laboratory, which would be the home of both applied and basic science of the very highest caliber. He set about this task with characteristic energy and enthusiasm, only to be disappointed

when the company reneged on its commitment before two years had passed. Fortunately, this setback in Dick's plans was resolved by his return to the academic community as a member of the chemistry faculty at the University of California, Los Angeles. Dick's UCLA period, from 1983 until his death, was a very happy and productive one.

In 1990, while attending a joint scientific meeting of the U. S. and Soviet academies of science in Leningrad, Dick suffered a heart attack. He recuperated for a short period in a hospital there, and was flown to Helsinki, where Norma joined him. He died there on July 8, 1990.

RESEARCH HISTORY

Dick's research career began with his Manhattan Project work. He often referred to his "zereth" publication, a book based on this research (presumably on uranium isotope separation), which remains classified. When he returned to Columbia to complete his Ph.D., he shifted his interest to enrichment of stable isotopes under the direction of T. I. Taylor. In the five years he was a faculty member at the Illinois Institute of Technology, he pursued a variety of studies on the spectra, kinetics, thermodynamic properties, and reactivity of isotopically substituted compounds. During this period he also began a long collaboration with F. F. Cleveland on the spectra of halogenated methanes and their deuterated variants. Dick's interests in isotopes and kinetics continued when he moved to the University of Michigan.

As a consultant at Oak Ridge, Dick became aware during 1953-54 of the early molecular beam scattering experiments by his friend Sheldon Datz and Datz's colleague Ellison H. Taylor. These experiments relied on Datz and Taylor's development of a remarkable surface ionization detector that could detect alkali metals and their halides with high efficiency and distinguish between them. Dick was so impressed

by this work that he decided to set up a molecular beam program of his own as early as 1955. A couple of years later, in 1957, he delivered an invited paper in Amsterdam at the International Symposium on Isotope Separation, describing a separation method based on the differential rates of reaction of isotopic variants. During the discussion of this paper, Harold Urey made a comment that was later printed as a note following Dick's paper in the proceedings: "This work is interesting from the standpoint of the velocity of chemical reactions as determined by the atomic weights, but not from the standpoint of separating isotopes. C^{13} is available in the market and can be bought in suitable concentrations." Dick was stung by this criticism and later said that it was a turning point in his scientific career. In about the same period, he was laid up with mumps and took advantage of his confinement to reflect on what he later described as "the difference between research that was significant and that which was merely interesting." He saw molecular beams and the study of molecular collisions as his route to significance and started along a path he was to follow the rest of his life.

Although he recognized from the beginning the exciting potential of molecular beams for the study of elementary chemical reactions, Dick approached the new field with his distinctive thoroughness, starting with elastic collision processes, then moving to inelastic collisions, and only progressing to reactive scattering when he had mastered its logical antecedents. The first scattering study that he took up was total scattering cross-sections—in a way, the task of determining the size of molecules. In most thinking of the time, molecular size, as far as collisional properties are concerned, was linked to a "hard-sphere" picture, with the radius determined by short-range repulsive forces. Dick realized that for energies in the range of interest to chemists

this view is wrong; it is the long-rang attractive forces that really count. Both the physical origin of that attraction (the dispersion, or London, or van der Waals force) and its consequences are best viewed in a quantum mechanical context. At the time, quantum mechanical scattering theory was in the hands of nuclear physicists and was almost totally unknown to chemists. Dick had a number of valuable insights at that point. One was that he could expect little help from the physics community, because nuclear physics at that time was very low energy physics as judged by the needs of chemical problems. This insight is still jolting at first hearing; nuclear experiments were in the MeV energy range, while chemistry is in the sub-eV range, more than six orders of magnitude lower. Bernstein's insight was that what is relevant is a dimensionless parameter $A = 2\pi\sigma/\lambda$, where σ is the scale parameter of the potential and λ is the de Broglie wavelength. λ scales as $(\text{energy})^{-1/2}$ and is thus roughly three orders of magnitude smaller in nuclear than in chemical problems. However, nuclear scales are about five orders of magnitude smaller than those of atoms (as shown by Rutherford), thus giving an A parameter that is about two orders of magnitude higher in chemistry than in nuclear physics. Nowadays heavy ion nuclear physics employs much higher energies than in the late 1950s, and the methods pioneered in chemical physics are making an appearance in nuclear physics.

Dick set out to compute cross-sections of molecules when A is large. Armed with the experimental observation from his laboratory that these were finite, he was unhampered by the mathematicians' unwillingness to discuss them for potentials with hard cores, which are typical of molecules. He was aided by another dimensionless parameter that he called B , which showed that the dimensionless mass was high and implied that molecules should be almost but not

quite classical objects. The quantum effects he saw in the computations and observed in the laboratory provided a signature of the well in the intermolecular potential energy. No one really doubted there was a well, but the experiments provided not only its direct signature but also an enumeration of the number of bound states.

From these beginning efforts on total scattering cross-sections, Dick's logical approach to molecular collisions progressed from differential cross-sections (angular distributions) for elastic collisions (in which the direction, but not the magnitude of the relative velocity changes) to the study of inelastic collisions. By using velocity-selected molecular beams to improve the energy resolution of the experiments, together with velocity analysis of the scattered atoms, Dick's research group succeeded in being among the first to observe a family of beautiful quantum interference effects in the angular distributions and to use them for very precise characterization of the underlying interatomic potentials.

At about the time of his move to Wisconsin, Dick turned his attention to the theory of inelastic scattering (collisions in which energy is exchanged between translational and internal modes). Shortly afterward, he added experimental studies of inelastic processes in crossed molecular beams. Inelastic scattering was one of the stops on Dick's road map to studying chemical reactions as collisional events. His group's early experiments on total scattering cross-sections had indicated that, even for reactive collisions, these cross-sections appeared to be accurately predicted by an equation that had been developed by Massey and Mohr for elastic collisions more than twenty years earlier. In determining the magnitude of the cross-sections, Massey and Mohr relied for their result on the dominance of long-range dispersive potentials of the form $-C_n R^{-n}$. In 1960-61 Dick made an early, seminal contribution to the theory of inelastic

scattering during his sabbatical with Sir Harrie Massey by showing why the Massey-Mohr idea worked both for elastic and inelastic (and reactive) collisions. This paper became a precursor of the phase-space theory of reactive cross-sections.

The first experimental results from the Bernstein group on inelastic scattering appeared in 1964, on rotationally inelastic scattering of D_2 by alkali metals. A couple of years later, Dick and his coworkers reported the first calculations of S-matrix elements for molecular scattering events. However, inelastic scattering did not hold his interest for long. Early in his Wisconsin era, Dick decided it was time to make an entry into the area that had always been his primary goal: reactive scattering. By this time, several other laboratories had taken up this endeavor, all of them relying on the Taylor-Datz surface ionization detector. In this flourishing "alkali age" of molecular beam reactive scattering, Dick was therefore a step behind, owing to his decision first to master non-reactive scattering. His entry into the field with the trenchant technique of combined velocity selection and velocity analysis quickly established a new "gold standard" for reactive scattering studies. Dick's group was able, for the first time in a scattering experiment, to determine directly the energy partition between translational and internal degrees of freedom in the products of an elementary chemical reaction. These data on the disposition of the available excess energy in a reaction, and similar results from a quite different (spectroscopic) technique pioneered by John Polanyi in Toronto, started Dick thinking about the role of energy in chemical reactions. Ultimately, this led, among other things, to the development with long-time collaborator R. D. Levine of surprisal analysis, a method that has now been designated an official term by the International Union of Pure and Applied Chemistry.

Dick had very early recognized the desirability of investigating stereochemical effects—the dependence of reactivity on the relative orientation of reactants. With this in mind, his laboratory constructed an apparatus that used inhomogeneous magnetic fields in a hexapole geometry to produce molecular beams of CH_3I that were oriented in space. This was used to study differences in the reactive scattering of Rb atoms with CH_3I molecules oriented with the I end versus the CH_3 end. Not surprisingly, the reaction proceeded with greater probability when the I end was presented to the reactant. Nevertheless, these experiments demonstrated the principle that steric issues were amenable to experimental study. This line of inquiry had also been taken up independently by Rice University's P. R. Brooks, whose initial publication preceded that of Bernstein by a few weeks. Dick decided to put aside his own immediate plans in this area once the initial project was completed, although his group continued to work on the production of state-selected molecular beams. This groundwork later would play a large role when he returned to stereochemistry during his Texas and UCLA periods.

Although the field of alkali metal reactions had produced a wealth of new and thought-provoking results, it was becoming clear to the leaders in this new field that this area could not be mined indefinitely. Some way of studying more general classes of reactions was required to play out the full potential of the scattering approach to chemical reactions. With this in mind, Dick decided to develop an apparatus with "universal detection." His early work in mass spectrometry served him well in the design of a detector based on ionization by electron impact, followed by mass spectrometry. This apparatus and its offspring were the vehicles for many important studies, starting at Wisconsin and continuing through the rest of Dick's career.

The beginning of the post-alkali age in the molecular beam business affords a good illustration of Dick's generosity. He was invited to speak in Oak Ridge at the 1970 Conference on Molecular Collisions, and the audience was eager to hear details of the first results from his new "universal machine." Instead, he spoke only very briefly about his group's work and then said, "Nothing else that I could speak about is as important as the recent work of Yuan Lee." Stepping aside, he turned the rest of his time over to Lee. Lee, who had just started as an assistant professor at the University of Chicago, gave a lecture on the extraordinary results that had been obtained with an apparatus he had designed with Dudley Herschbach and other colleagues in Herschbach's Harvard laboratory. Dick's instincts were not only generous, but were also prophetic. In 1986 Lee and Herschbach would share the Nobel Prize in chemistry with John Polanyi.

With his alertness to any potentiality for more incisive probing of energetic or steric effects in reactions, Dick decided soon after the appearance of high-energy lasers to try to influence the course of reactions by letting the colliding molecules absorb light the very instant they were colliding. For such an experiment to work, three beams must intersect at the same point in space: molecular beams of the two reactants and a laser beam. Getting the molecular beams to intersect properly is non-trivial. Here, however, the tightly focused laser beam also had to intersect the other two at the point of their intersections. Dick decided to begin by crossing the laser beam and the molecular beam of one of the reactants. The reaction chosen for study was that of Hg with I_2 , and so the first step was to cross the I_2 molecular beam with the laser beam. The experiment never got any further; the I_2 molecules were clearly absorbing more than one photon, because ions were being produced, and some of the molecular ions were so energetic that they were fall-

ing apart. Dick with postdoc L. Zandee had observed visible multiphoton ionization. Since Dick had a strong mass spectrometric background he immediately saw the importance of the new method for ionization. This method of quantum state-sensitive ionization has become an important technique and is currently the subject of its own Gordon conference.

When he joined the UCLA faculty, Dick continued with studies of reactive collisions, concentrating particularly on steric effects. All the earlier work on producing aligned and state-selected beams now came into use in a most productive and seminal set of studies. The study of steric effects in reaction dynamics is now a biannual international conference, the first one being held in Jerusalem in 1986⁴ and the third one, held in 1990 (organized by two former postdocs Steven Stolte and David Parker), was dedicated to Dick. The proceedings of that meeting are part of the Bernstein memorial issue brought out by the *Journal of Physical Chemistry*.⁵ UCLA has established an annual lecture series in his memory. Knowing Dick as well as we did, another spontaneous tribute he would really have cared about is that his name continues to appear as frequently as before in the citation index of the *Annual Reviews of Physical Chemistry*.

Throughout his scientific career, Dick's interests were centered on the direct observation of the effect under study. Although there is no inherent reason for it to be the case, scattering theory was typically cast in a time independent form. By the time-energy uncertainty principle we mean the energy is well defined and one gives up any time resolution. The experimentalists followed suit in ever striving for a better definition of the energy of the initial state. There are, of course, practical reasons for choosing the time independent point of view. In chemistry, unless the excitation

occurs on an ultrafast (ps or below) time scale, the initial state is practically stationary. The reason is that the natural time scale for chemical events is the typically very fast vibrational motion of the atoms. However, by the mid-1980s, laser technology could begin to produce short enough pulses for direct probing on molecular time scales, and Ahmed Zewail was able to demonstrate that he could monitor the breaking of a chemical bond in real time. By giving up energy resolution, one could monitor the real progress of a chemical reaction. What you observe and what you talk about in describing a mechanism have come together. Because quantum mechanics is complementary, the same information could be obtained indirectly by working in the energy domain, but the direct probing is, after all, direct, and this is what caught Dick's attention. He enthusiastically teamed up with Zewail to explore the potential applications⁶ in femtochemistry (a term Dick coined). Eventually he took a sabbatical as a Sherman Fairchild distinguished scholar to be at Caltech where these experiments were carried out. He liked to say he had become Zewail's postdoc in these experiments. As always, Dick believed that he should be in the lab when the real data were taken, and the time in Caltech was no exception.

When Dick Bernstein told you something, it was a good idea to listen. He was always completely candid, but he was never unkind. His demeanor was the same, whether he was speaking to a senior distinguished colleague, a young faculty member, or a graduate student. He was generous with his time and resources. While at Columbia, he once asked his department chairman to give another faculty member a raise that had been budgeted for Dick, because he thought the other person needed it more.

He maintained his energetic curiosity to the very end. When some of his colleagues visited him in the hospital in

Leningrad the day after his heart attack, he greeted them with, "I have seen my own heart beating in real time."

PRINCIPAL AWARDS AND HONORS

- 1968 Elected to membership in the National Academy of Sciences
1970 Elected a fellow of the American Academy of Arts and Sciences
1981 The American Chemical Society's Peter Debye Award in Physical Chemistry
1985 National Academy of Sciences Award in the Chemical Sciences
1986 Sherman Fairchild distinguished scholar, California Institute of Technology
1988 The American Chemical Society's Irving Langmuir Award in Chemical Physics
Honorary doctorate in science, University of Chicago
Robert A. Welch Award in Chemistry
1989 The American Chemical Society's Willard Gibbs Medal
National Medal of Science

NOTES

1. R. B. Bernstein. Molecular beams in chemistry: A subjective account. In *Welch Conference on Chemical Research XXXII: Valency*, pp. 157-97. Houston: Robert A. Welch Foundation, 1989.
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