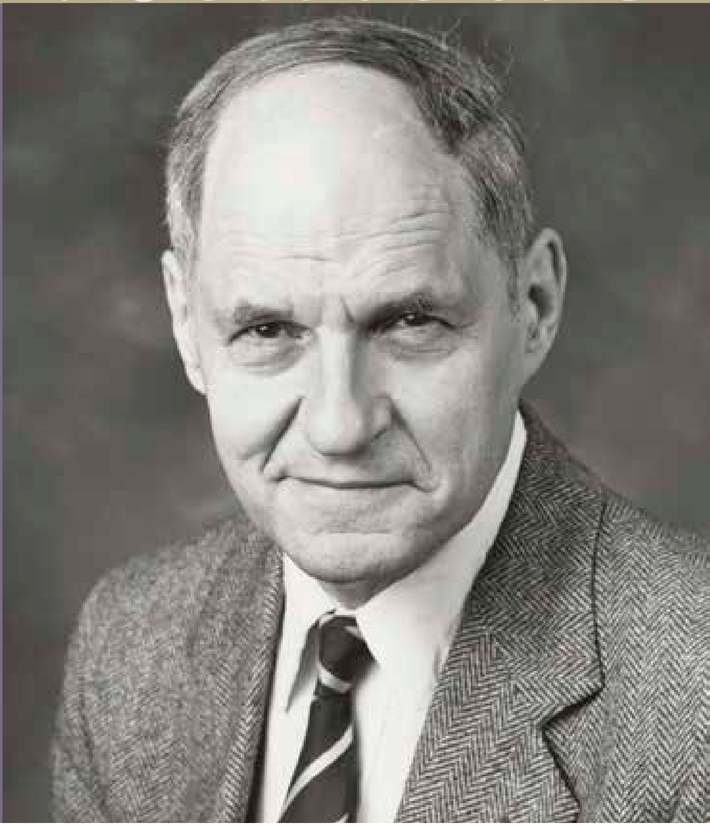
Richard Bersohn

1925–2003

BIOGRAPHICAL *Memoirs*



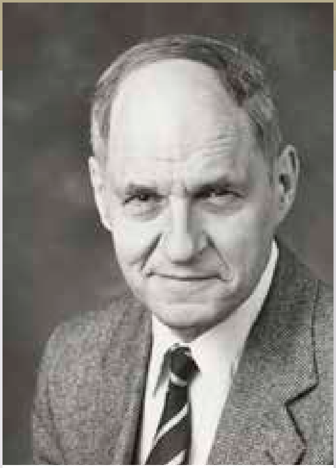
A Biographical Memoir by
Bruce J. Berne, Louis E. Brus,
George W. Flynn,
and Joshua Jortner

NATIONAL ACADEMY OF SCIENCES

RICHARD **BERSOHN**

May 13, 1925–November 18, 2003

Elected to the NAS, 1985



Richard Bersohn

By Bruce J. Berne, Louis E. Brus, George W. Flynn, and Joshua Jortner

Photograph by Joe Pineiro, courtesy Columbia University Archives.

Early life and education

Richard ("Rich") Bersohn was born in New York City and grew up on Manhattan's Upper West Side just a stone's throw from the American Museum of Natural History, a favorite childhood haunt of his. He attended the Hunter College Model School (a progressive public elementary school) and Horace Mann High School (a private preparatory school). From a young age, Rich was fascinated by science; an uncle who was a high-school chemistry teacher provided him with chemistry textbooks, and Rich's mother, herself a former mathematics teacher, cleared out a closet in their apartment and allowed him to use it as a chemistry laboratory. Early experiments resulted in the liquefaction of a friend's watch and a small fire, but Rich persevered, remaining curious, fearless, and not above a little mischief.

When preparing for his bar mitzvah, Rich began a study of the Jewish religion and the Hebrew language that continued throughout his life. An excellent student but not much of an athlete, in high school he skipped gym class for nearly a year before getting caught reading in a classroom when he was supposed to be playing tennis. ("There always seemed to be 16 places on the court, and 17 players. It just didn't seem like a good use of time," he later explained.) At first considering expulsion, the school eventually agreed to skip Rich several grades ahead, letting him graduate early.

Rich went on to the Massachusetts Institute of Technology (M.I.T.), where he enjoyed immersing himself in scientific study but chafed at the narrowness of the engineering curriculum. His favorite class at M.I.T. was on Shakespeare; his least favorite was mechanical drawing, at which he struggled. Dominance of head over hand would remain a theme throughout Rich's career—he loved beautiful ideas from many disciplines but wrestled with the machines that could help to give them form. In June 1944, having just turned 19, Rich graduated from M.I.T. with a B.S. in chemistry. His senior thesis, mentored by Avery Morton, was in the area of synthetic organic chemistry, which Rich initially found more interesting than physical chemistry.

Soon after graduation, at the height of World War II, he entered the U.S. Army and was assigned to work on the Manhattan Project, the atomic-bomb development effort based at Clinton National Laboratory (now the Oak Ridge National Laboratory). Rich was one of a group of soldiers engaged in dissolving nuclear-reactor fuel rods in nitric acid; the solution was then made basic with sodium carbonate. Rich often joked that he was chosen for this work because he was young and strong and had a B.Sc. in chemistry; he could carry the 50-pound sacks of sodium carbonate and was able to calculate how many sacks were necessary for the neutralization process. As Rich pointed out: "Not everyone on the Manhattan Project worked with Fermi, Feynman, and Bethe." Still, during that time Rich's love of physics and physical chemistry blossomed. At the end of the war, he was offered an opportunity to stay in the army for another few months in order to participate in a nuclear-bomb test on a Pacific atoll. He declined the offer, as he was eager to go on to graduate school.

His experiences in chemistry laboratory research at M.I.T. and Oak Ridge had convinced Rich that he was accident-prone—for much of his adult life he had a large scar on his hand from spilled acid— and this led him to choose a theoretical research project with physicist J. H. Van Vleck for his doctoral work.

Upon completion of his military service in 1946, and supported by the G.I. Bill and a teaching assistantship, Rich enrolled in the chemical physics Ph.D. program at Harvard University. His experiences in chemistry laboratory research at M.I.T. and Oak Ridge had convinced Rich that he was accident-prone—for much of his adult life he had a large scar on his hand from spilled acid—and this led him to choose a theoretical research project with physicist J. H. Van Vleck for his doctoral work. The initial project that Van Vleck had proposed did not pan out, but Rich became interested in some experimental results obtained by fellow students George Pake and Herb Gutowsky using the newly discovered spectroscopic phenomenon of nuclear magnetic resonance (NMR). For his thesis research, Rich calculated the line structure of solid-state NMR resonances

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and determined the fine structure of microwave rotational spectra due to the coupling between nuclear quadrupole moments and overall molecular rotation.

Upon completion of his thesis research in 1949, Rich moved from Cambridge to New York, where he had been appointed postdoctoral fellow in Columbia University's physics department to work with Willis Lamb. At this time there was great excitement in the field of quantum electrodynamics, and as part of his postdoctoral work, Rich and another graduate student (Joe Weneser) spent a couple of years calculating corrections to the Lamb shift. (Rich was later to remark that in the age of personal computers, a competent programmer using a modern [ca. 2003] device could have completed these calculations in a few days!)

Theory and experiment in chemical physics

Following his postdoctoral work, Rich snagged a faculty position in the Cornell University chemistry department, where he taught for almost a decade. His research at Cornell involved the theory of radio-frequency and microwave spectroscopy, including nuclear quadrupole resonance, NMR, and electron-spin resonance (ESR). In the period 1950–1960 he was one of the leading theoreticians in this field, having been recognized as the chief interpreter of quadrupole coupling constants and having provided the first explanation of aromatic radical nuclear hyperfine constants. In 1958, Rich spent his first sabbatical leave in Alfred Kastler's lab at the École Normale Supérieure in Paris and Saclay, where he learned about optical pumping experiments. This experience was to lead Rich back to experimental science.

Richard Bersohn in 1945, while working on the Manhattan Project at Clinton Laboratories, now Oak Ridge National Laboratory.

A formal picture taken in 1984 when Bersohn was serving as chair of the Department of Energy's Advisory Committee to the Chemistry Department at Brookhaven National Labs.

Shortly after his sabbatical leave in Kastler's lab, Rich was hired away from Cornell; he joined Columbia University's chemistry department in 1959. At the time, Columbia was home to Ben Dailey and George Frankel, leading microwave and ESR experimental spectroscopists of the day. With the addition of Rich Bersohn, Columbia achieved an impressive concentration of physical-chemistry faculty involved in measuring and interpreting constants derived from microwave spectra. Within a few years, in a trend that Rich encouraged and participated in, the department would diversify its research in experimental physical chemistry by hiring young faculty working in the areas of collision dynamics and photofragmentation using the newly developed tools of lasers and molecular beams.

In the 1960s, Rich turned to experimental work both in chemical physics and biophysical chemistry. His sabbatical year in France with Kastler had inspired him to do optical pumping of atoms with a chemical slant. Rich's interest in polarized light culminated in his celebrated and visionary photolysis mapping experiments, which earned him the title "father of modern-day molecular photofragmentation." In his classic study, cadmium dimethyl vapor held in a glass hemisphere was irradiated with polarized light from below the hemisphere, and cadmium atoms were deposited *anisotropically* on the walls of the hemisphere. When the experiment was performed without a polarizer, the cadmium was deposited *isotropically*. This result provided dramatic proof that molecules can dissociate in a short time as compared with a rotation period. In its elegance and simplicity it was one of the finest experiments ever performed in photochemistry, and it set the stage for polarized laser photofragment spectroscopy, which has yielded an astonishing wealth of information about molecular photodissociation. The photolysis mapping experiment was a forerunner of modern multidimensional product velocity mapping. Indeed, Rich's groundbreaking experiment, which occurred at the same time as the molecular-beam revolution in chemical physics, had a profound effect on the practitioners of photodynamics across the world.

Throughout the 1960s, Rich's group extended the theory of molecular photodissociation and carried out fragment angular-distribution measurements with a xenon lamp. In effect, Rich and his students did sub-picosecond experiments with a continuous-wave source by taking advantage of the short rotation period of a molecule in the gas phase. By dissociating a number of aromatic molecules with a lamp and later with a laser, they demonstrated that: 1) aryl iodides exhibited strong anisotropy in their fragment angular distribution, but aryl bromides did not; and 2) energies in excess of S_1 were usually not available as kinetic energy, showing that internal vibrational relaxation preceded dissociation. Since these early ground-breaking experiments, there have been studies on a large variety of molecules, including TlI, $CSCl_2$, H_2O_2, CH_3NO_2, CH_2IBr, CH_3I, 1, 3, 5-triazine, $Re_2(CO)_{10}$, C_2H_4S, C_6H_5CN, and C_6H_5NC.

The simplest nontrivial problem in photodissociation dynamics is that of a triatomic—and preferably one that is linear both in the ground and excited states. Rich studied the triatomics SO_2, CdI_2, and CS_2. In addition, he and Moshe Shapiro did an extensive quantum-mechanical study of the vibrational excitation of CH_3 radicals dissociated from CH_3I, approximating CH_3I as a linear triatomic XCI. He summarized these and other findings in often-quoted reviews. His pioneering work in photochemistry was not only a contribution to photochemistry but also to spectroscopy. The formerly ignored continuum states, which are so important in photodissociation, have symmetries that can be measured thanks to the creativity of Rich and his colleagues; these symmetries, together with the discrete distributions over fragment states, constituted a new spectroscopy of the continuum.

In its two-photon spectroscopic work first reported in the early 1980s, Rich's group applied laser-induced fluorescence (LIF) methods to the study of nitrogen molecules and sulfur, carbon, and iodine atoms. Before these experiments, lasers had not been used to detect nonmetallic atoms because their lowest transitions were in the vacuum ultraviolet range The use of two near-ultraviolet photons allowed for much easier detection. A first fruit of this two-photon technique was the use of LIF to determine the relative populations of iodine atoms in the lowest $^2P_{1/2}$ and $^2P_{3/2}$ states in chemical reactions and molecular photodissociation. Two-photon LIF was also used to follow the sulfur atom concentrations in the reactions

$$S(^1D) + OCS \rightarrow CO + S_2\ (a^1\Delta \text{ and } X^3\Sigma)$$

where S_2 was probed in both the $a^1\Delta$ and $X^3\Sigma$ electronic states by LIF.

Following these experiments, in the late 1980s Rich and his group turned their scientific efforts to detecting, by vacuum ultraviolet LIF, nascent hydrogen atoms from chemical reactions and molecular photodissociation. The absolute cross section for the reaction H + D_2 was measured at different energies, thus providing a normalization for the relative state-resolved cross sections measured earlier by Jim Valentini and Dick Zare. Rich's group also studied other exchange reactions, such as H + C_2D_2, C_2D_4, and SiD_4. Using this same H-atom detection method, the H atom translational energy rates and distributions were investigated for a series of aromatic methyl compounds undergoing unimolecular dissociation to form benzyl radicals and H atoms. The initial measured translational and computed vibrational temperatures of the fragments were found to be nearly the same. Photodissociation studies of CH_3OH and HDO showed that even in direct dissociations, where there is a choice, the lighter fragment is much more likely to be released. Rich and his students J. H. Park and Neil Shafer also demonstrated experimentally the evolution of the velocity distribution of hot hydrogen atoms from a near delta function at inception to the ambient Maxwell distribution. They were able to show that relaxation occurs at successively later times, after production of the H-atoms, through a series of ever-cooler Maxwell velocity distributions, which never display two maxima.

Rich is shown here with his wife Nehama (seated left), his daughters Leora and Rina (seated), and Mrs. Sandra Turro (standing) at the annual National Academy of Sciences garden party in Washington, DC, circa 1986.

Rich spent the summer of 1987 visiting the California Institute of Technology, where Ahmed Zewail had just made the first observation of real-time femtosecond-scale transient absorption of CN due to molecular bond-breaking arising from direct dissociation of ICN. In a paper written with Zewail, Rich advanced the first quantitative classical theory of this novel experiment. He used a simple exponentially repulsive function to describe the potential for this fragmentation process, which in turn yielded R(t) (the distance between the I and C atoms during dissociation) and an analytical expression for the time-dependent absorption of CN. The rise and fall of the absorption originated from the fact that the CN radical's resonance with the probing light occurs only in one region of the downward trajectory. Rich's theory provided the conceptual framework for describing the ultrafast time-dependence of absorption on the time scale of nuclear motion. Thus he added an understanding of the time-dependent behavior of photofragmentation to his repertoire of contributions to quantum-state-specific photodissociation dynamics.

Biophysics

Felix Bloch, who discovered the electronic structure of metals and NMR spectroscopy, once stated that a scientist leaves an impact provided that he or she makes not only one but *two* significant discoveries. Rich's scientific career illustrates the Bloch Principle, as he made important contributions to two very significant but distinct fields: chemical-reaction dynamics and biophysics. His experiments in biophysics stemmed from the application of the interrogation techniques of physical chemistry (i.e., magnetic resonance, fluorescence, and phosphorescence) to biomolecules. Working with Irvin Isenberg of the Marine Biological Laboratory at Woods Hole and Robert G. Shulman of Bell Laboratories during 1960–1962, Rich performed pioneering studies of the phosphorescence of DNA and of triplet energy transfer in polyadenylic acid. These studies provided a dynamic probe for monitoring structural information on the configuration of biopolymers.

Among Rich's many contributions to biophysics, his student Robert Pecora's thesis on Rayleigh light scattering serves as the theoretical basis for the modern method of determining the diffusion constants of macromolecules. Rich's group was one of the earliest to apply single-photon counting to protein fluorescence, the first to do picosecond-scale experiments on proteins, and the first to use rare-earth-ion luminescence as a protein probe. Perhaps of greatest significance was his very general demonstration that when protein molecules collide in solution they stick together and roll on each other's surfaces before separating.

His research in Israel and worldwide

Rich's strong and long-lasting collaboration with the chemistry community in Israel began in 1966 when he was invited by Aharon Katzir and Bernard Pullman to attend the Weizmann School on Biological Organization at the Molecular Level—sponsored in part by Israel's Weizmann Institute of Science—in Eilat on the Red Sea. Actually, Rich had been invited by mistake; he was asked to lecture on ESR spectroscopy of biomolecules because the organizers were very impressed by the work of *Malcolm* Bersohn, Rich's identical-twin brother, who was in that field. Nevertheless, he was delighted to rise to this challenge.

Rich ultimately established deep scientific and personal relationships with the members of the chemical physics group at Tel Aviv University, where he spent sabbatical leaves as a visiting professor in 1972, 1981, and 1986. During his visits to Tel Aviv University, Rich made valuable contributions to the Chemistry Department as a sage, perceptive colleague and as a remarkable scientist. He also delivered lectures on advances in physical chemistry to a group of bright graduate students, among them Shaul Mukamel and Yossi Klafter. With his deep relation to Jewish culture, Richard insisted at first to lecture in Hebrew, which the students referred to as “Biblical Hebrew.” The graduate students pleaded that he lecture in English and Richard kindly complied. Modest and minimalist in his tastes, during weekends in Israel he enjoyed walking long distances, including, on occasion, the 15 miles from Rehovot (where he lived) to the home of Joshua Jortner and his family in Tel Aviv. For many years Rich spent the summers holding an adjunct appointment at the Weizmann Institute in Rehovot. In 1988 he spent a few months at the Technion, the Israel Institute of Technology in Haifa, as a Distinguished Visiting Professor. On these visits his wife Nehama, whose family lived in that area, and their two daughters joined him.

The chemical physics and biophysics communities in Israel greatly benefited from Rich’s keen insights about science and its practitioners. For example, his chemical-dynamics research in collaboration with Israeli scientists was far-reaching. Rich worked with Beni Katz from Ben-Gurion University to explore the central reaction of chemical kinetics, $H+H_2$, or more precisely $H+D_2 \rightarrow HD+D$. They analyzed the kinetic-energy dependence of the reaction’s cross section in terms of the theoretical-computational work, based on trajectory calculations using the *ab initio* potential surfaces, of Israel Schechter and Raphael Levine from the Hebrew University of Jerusalem. Rich also collaborated with Moshe Shapiro from the Weizmann Institute of Science to explore the dynamics of molecular photodissociation; and while visiting Tel Aviv University, he partnered with Uzi Even on LIF spectroscopic studies of large molecules in supersonic jets; in particular, they explored heterocyclic molecules of biophysical interest and “nanocrystals” of aromatic molecules.

Rich worked with scientists from other countries as well. For example, he maintained a long collaboration with Masahiro Kawasaki, of Hokkaido University in Japan, on inversion reactions in chemical dynamics. Rich was a truly international scientist, and his deep and diverse knowledge inspired colleagues worldwide.

Later work

In the last decade of his scientific career, Rich turned his attention to reactions of $O(^3P)$ with unsaturated hydrocarbons. The reaction of O with $HC{\equiv}CH$, for example, exhibits at least two channels, which yield either CH_2+CO or $H+HCCO$. Quite remarkably, given the amount of available energy in the first reaction, CO is produced both vibrationally and rotationally cold (like an ice cube plucked from a hot oven). Such observations provide insight into the reaction mechanism, suggesting in this case a process going through a ketene-like transition state in which fragmentation takes place via repulsion along the C-C bond of CH_2CO. In the reaction of O atoms with ethylene ($O(^3P)+H_2C{=}CH_2$), one channel produces the vinoxy radical (CH_2-CHO), which is "born" with a very high level of internal energy. In a lovely demonstration of the flow of vibrational energy in a polyatomic species, Rich and his postdoctoral fellow Hongmei Su used LIF to track the initially hot vinoxy radical as it cascades down the vibrational energy ladder, finally reaching an ambient state in which all the degrees of freedom are at the same temperature.

Legacy

Rich served as professor of chemistry at Columbia University from 1959 to 2003, where he enjoyed a distinguished and fruitful scientific career—first as a theoretician and then as an experimentalist who designed simple, elegant, and *important* experiments to probe the photophysical and photochemical properties of molecules. Rich had unusually broad scientific interests in general and a deep and profound understanding of molecular science in particular. Thus his publications covered an extraordinary range of subjects, from quantum electrodynamics to applied biochemistry. Rich's first paper (on solid state NMR) appeared in 1950, and in a career that spanned more than 50 years he blanketed the field of physical chemistry with a stream of papers that provided new scientific insights and opened new research areas in radiofrequency spectroscopy, photodissociation, reaction dynamics, and biophysics.

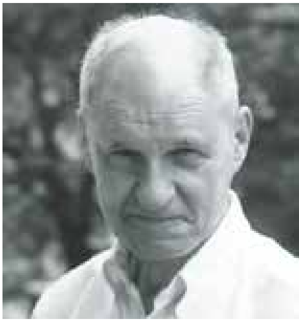
His graduate students and postdoctoral fellows knew Rich as a scientist of "the old school" who was interested in almost everything. He had been exposed to, and absorbed the culture of, outstanding scientists at M.I.T., Harvard, Cornell, and Columbia. And while Rich mentored mostly experimental Ph.D. students, his early experience as a theorist enriched their efforts and scientific development. His motivation was to understand how nature worked rather than to develop devices or patents, and he led by example rather than by giving orders. Rich believed that his job was to teach students how to think about science, recognize outstanding problems, construct a research program, and always be considering the next experimental step. Far from being a micromanager, Rich was not concerned with a student's daily productivity; he had great tolerance for allowing students to follow their own ideas and to learn from mistakes.

Richard Bersohn at Columbia University commencement exercises with Ph.D. recipient Dr. Lei Zhu, who received her doctorate in chemistry in 1992.

Because Rich was a gentle person who by nature did not criticize someone whose dedication and experimental progress seemed to be wanting, his nonconfrontational style best served those intellectually strong and independent students who normally required little supervision. And while Rich did not intrinsically love scientific apparatus—many might consider him to have been "mechanically challenged"—when designing a research program with a new student he often invested the time to dig through catalogues and figure out what to buy. Truth be told, though, he preferred to delegate this type of work to others.

Because Rich had quite broad scientific experiences, stemming from his restless curiosity and fearlessness in going into new fields, his students and postdoctoral fellows also worked on a wide range of topics, including the optical pumping of alkalis, irreversible radiationless transitions in molecules, molecular photodissociation, and gas-phase reaction kinetics. Moreover, in the 1960s Rich taught himself molecular biology and subsequently had students and collaborators working on, for example, protein structure using high-resolution NMR, Förster resonance energy transfer, and exchange-driven triplet energy transfer. In individual meetings with students, and in group sessions attended by students and postdocs, virtually no subject was off the table. Participants were sometimes thus obliged to hear and discuss issues that were interesting and potentially important but not necessarily of direct and immediate value to their projects. In this way the education of group members was often quite diversified, transcending their fields.

Members of the Columbia chemistry department remember Rich as an esteemed colleague whose wise counsel and high ethical and scientific standards enriched the department not only through his fruitful research projects but also by almost singlehandedly building its physical-chemistry component into one of the strongest in the country. He was a major influence in bringing Bruce Berne, Louis Brus, Charlie Cantor, George Flynn, and Dick Zare—all now members of the National Academy of Sciences—to Columbia.


Richard Bersohn in 2001. The photo was published in the graduate student brochure describing research activities in the Columbia University Chemistry Department.

With Rich's body of work being much admired, he too was elected to the National Academy of Sciences—in 1985. Recognition of his contributions also came in the form of the 1985 Herbert P. Broida award in chemical physics from the American Physical Society and election as a fellow of the American Academy of Arts and Sciences. He served as head of the Division of Chemical Physics of the American Physical Society in 1971 and as chairman of the Advisory Committee of the Brookhaven National Laboratory's Chemistry Department from 1981 to 1984. Rich was associate editor for chemical physics for *Physical Review Letters* from 1995 to 1998, he was chairman of his department from 1990 to 1993, and throughout his career friends and colleagues often sought his advice on matters both scientific and personal.

Rich Bersohn was a minimalist in all aspects of his life, shunning what he considered to be extraneous or venal. A wise and gentle man of the highest personal integrity, he was loved by virtually all who came to know him. Rich was one of the few people who would show up at the bedside of an ill colleague, and he was a careful listener, giving his undivided attention and, when requested, his opinion. Rich loved to tell jokes and had one for almost every occasion. We shall miss his wry smile. In the last year of his life, Rich faced his daunting illness with great courage. He continued to come to work, attend faculty meetings, and contribute to the department well beyond what anyone would have expected. He is survived by his wife Nehama, their daughters Rina and Leora, and his sons Malcolm and David.

ACKNOWLEDGEMENTS

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