Robert J. Silbey

1940–2011

BIOGRAPHICAL *Memoirs*

A Biographical Memoir by
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NATIONAL ACADEMY OF SCIENCES

ROBERT JAMES **SILBEY**

October 19, 1940–October 27, 2011

Elected to the NAS, 2003

Bob

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Robert James Silbey was born in Brooklyn, NY, the second son of Sidney and Estelle (Mintzer) Silbey. His father managed a food-processing plant on the waterfront in Brooklyn and his mother was a homemaker and Red Cross volunteer. Bob's life companion since age 15 and wife, Susan Sorkin Silbey, recalls that he spent much of his youth in pool halls, winning pocket money and worrying his mother. When asked about his father's occupation, Bob liked to say that he "worked on the docks."

Silbey's early education was in the New York City public school system. He attended Brooklyn College, from which he earned a bachelor's degree in 1961, followed by graduate study as a National Science Foundation predoctoral fellow at the University of Chicago, where in 1965 he received a Ph.D. in chemistry. He was awarded an Air Force Office of Scientific Research postdoctoral fellowship, using it to work with Joseph Hirschfelder at the University of Wisconsin for a year, and then (in 1966) he joined the faculty of the Massachusetts Institute of Technology. Silbey remained at MIT for the rest of his academic career, and he served as head of the Department of Chemistry from 1990 to 1995, director of the Center for Materials Science and Engineering from 1998 to 2000, and dean of the School of Science from 2000 to 2007.

Throughout his scientific career Silbey made brilliant contributions to condensed-matter chemistry and especially to the theories of electronic and optical properties in condensed phases. Many of his scientific peers believed he was the country's dominant chemical theorist in these fields. Silbey's research was characterized by analytical power and deep insight. One of the major hallmarks of his approach to science was to work very closely with experimentalists, both here and in Europe, and he was much sought after by experimentalists and theorists alike. He was both a "theorist's theorist," and an "experimentalist's theorist," a very rare combination.

A very large portion of Silbey's research entailed molecular crystals and other molecular aggregates. He made fundamental contributions to our understanding of electronic excitation in molecular crystals, the theory of single-molecule spectroscopy, and the theory of energy transfer; and he provided molecular-electronic interpretations of many of the nonlinear optical properties of glasses, other solids, and polymers. For the decade or so prior to his death, his work focused on energy and charge transfer in the first step of photosynthesis, which involves the capture of photons by light-harvesting pigments and the subsequent transmission of the photon's energy to structures within plant cells that convert it to chemical energy.

The thematic goals of Silbey's research program originated in the seminal contributions of his Ph.D. thesis, which dealt with the low-lying electronic excitations (the exciton spectra), as well as characterization of electron and hole transport, of crystals of the aromatic molecules benzene, naphthalene, and anthracene. Prior theoretical studies of these systems were dominated by semi-phenomenological approaches based on parameterized Hamiltonians, or analyses that represented the interaction between excited molecules only by the transition dipole-transition dipole contribution. Among other deficiencies, these analyses could not account for phenomena—the triplet exciton band structure, for example, or charge delocalization and electron and hole mobility—associated with exchange interactions.

The breakthrough reported in Silbey's doctoral work was the fully quantum calculation of the molecular interactions in the crystal using the then-best-available molecular wave functions; this advance permitted the analysis of singlet and triplet exciton band structures, singlet and triplet factor group (Davydov) energy-level splittings, estimates of electron and hole mobilities, and estimates of singlet-singlet and triplet-triplet annihilation reaction rates. As a graduate student Silbey was also involved in the first analysis of the electronic structure of ordered (isotactic) polymers. Overall, the approach used and the results reported in Silbey's thesis represented a paradigm shift that for 50 years influenced the analysis of the properties of molecular crystals.

Notwithstanding its successes, Silbey's thesis research dealt primarily with static properties of molecular crystals; even the treatments of electron and hole mobility were based on a combination of band structure and diffusive motion arguments. That is, he did not analyze the fundamental scattering, lattice distortion, and localization mechanisms

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associated with coupling of excitation and molecular motion in those crystalline systems. Addressing these omissions became one of the major topics of his subsequent research. In a series of elegant analyses, he made fundamental contributions to our understanding of the multiple consequences of interaction between electronic and vibrational excitations in molecular crystals and aggregates.

Silbey's first foray into the study of exciton-phonon coupling and its consequences, with his student M. K. Grover, developed a formal description that went far beyond previous analyses based on decoupling approximations or perturbation theory; their analysis removed strong coupling via a transformation that produces an exponential dependence of the energies and line shapes on the coupling constant. The insights thus obtained provided the foundation for further theoretical developments, as revealed in a long series of papers that dealt with topics such as exciton migration, electronic energy transfer between impurity molecules in a crystal, excitation energy trapping, and the transition between coherent and incoherent exciton motion.

Silbey further developed these ideas in his descriptions of the properties of conducting polymers. He showed how the high conductivity of conjugated polymers arose from chain distortion induced by excitations. This work provided the first quantum calculations of the soliton, polaron, and bipolaron entities that dominate the conductivity of conjugated polymers. His work, which also introduced a novel valence effective Hamiltonian method of analysis, provided the first predictions of the redox potentials of these polymers, thereby resulting in an explanation of experimental data obtained from various studies that exploited hole-burning, photon-echo, and single-molecule spectroscopies. Other of Silbey's studies investigated the nonlinear optical properties of conjugated molecules and, in collaboration with synthetic chemists, resulted in the first demonstration of the saturation of those properties with increasing chain length.

One of the major developments of experimental physical chemistry in the last two decades of the 20th century was single-molecule spectroscopy, and Silbey made major theoretical contributions to this field, in particular with regard to high-resolution spectral hole burning, photon echo, and ultra-fast optical measurements. He analyzed, using Levy statistics, the photon emission from single molecules embedded in a condensed medium and from quantum dots. In related work, he formulated a procedure, using a two-state (on-off) representation of the time trajectory of single-molecule fluorescence data, to infer the kinetics of photon emission.

Other of Silbey's efforts on single-molecule spectroscopy dealt with (1) the influence of disorder on the line shape, specifically the roles of static and dynamic interactions with the surrounding medium; and (2) in a series of landmark papers, how tunneling is affected by static and dynamic interactions with the surrounding medium. His contributions included demonstrating that the thermal properties of low-temperature glasses (the two-level model) can be used to interpret the results of hole-burning and photon-echo spectroscopic studies of single molecules.

Arguably, the technique most widely used to measure the separation between chromophores in macromolecules is Förster energy transfer. Förster originally analyzed incoherent transfer of energy from an excited donor to an acceptor molecule (or to many independent acceptor molecules) in its (or their) ground state(s). The rate of that transfer depends on the overlap of the absorption spectra of the two molecules and on the separation of the molecules. However, at low temperature, donor-acceptor energy transfer can be coherent. Silbey's reexamination of Förster energy transfer showed how low-frequency vibrations and other thermal fluctuations drove the evolution of low-temperature coherent donor-acceptor energy transfer into incoherent energy transfer at higher temperature. A distinct but not unrelated phenomenon is the modification of molecular fluorescence near a metal surface, which is a consequence of energy transfer from an excited molecule to the metal. Silbey's pioneering study of this phenomenon can be viewed as a precursor to the field of plasmonics; and his work finds current application in exploring the properties of excited molecules in microcavities and in near-field microscopy.

Melvin Calvin's work established the chemical pathway from CO_2 + H_2O to carbohydrate triggered by the first step in photosynthesis—the absorption of light by a plant. Since then, researchers have made intense efforts to unravel the complex events that immediately follow this the first step; and Silbey's contributions started with an analysis of the information content of line shapes in the spectrum of a bacterial photosynthetic complex. This was a natural extension of his earlier studies of spectral line shapes in molecular aggregates. His subsequent studies examined the coherence of the excitation transport in the photosynthetic complex, the role of fluctuations in generating the transition between coherent and incoherent excitation transport, multi-chromophoric Förster energy transfer within the photosynthetic complex, the correlation between energy and intermolecular interaction fluctuations in the photosynthetic complex, and how excitation transfer in the photosynthetic complex is optimized. The latter study led to an extraordinarily incisive analysis of the relationship between and self-consistency of the optimal fold symmetry of the chromophore rings in the photosynthetic complex and the efficiency of excitation transfer. These analyses involved development of a wide range of theoretical methods that have now become standard techniques. For example, in Silbey's work with Robert A. Harris, the researchers used a variational polaron transformation that characterizes the physical basis for reduction in efficiency of excitation energy transfer.

Silbey was elected to the National Academy of Sciences in 2003. He also was a fellow of the American Academy of Arts and Sciences, the American Association for the Advancement of Science, and the American Physical Society. He received the Max Planck Research Award of the Humboldt Foundation (jointly with Dietrich Haarer) and the J. O. Hirschfelder Prize in Theoretical Chemistry. He was a Dreyfus Foundation teacher-scholar, a Sloan Foundation fellow, and a Guggenheim Foundation fellow. He received, among other academic distinctions, honorary doctoral degrees from his alma mater, Brooklyn College of the City University of New York, and from the École Normale Supérieure in Cachan, France. He served on the boards of trustees of the McGovern Institute for Brain Research, the Gordon Research Conferences, and the Whitehead Institute for Biological Research.

At MIT, Silbey's pedagogic talent was legendary. He commanded the classroom with his passion, clarity, and repertoire of humorous stories. A consummate lecturer both at the undergraduate and graduate levels, he owned the attention of students, who invariably were mesmerized by his joy and excitement. Silbey received virtually every possible MIT teaching award, and some for curricular innovations. Among them were the School of Science Teaching Award, the Graduate Student Council Award for Teaching, and the Baker Award for Undergraduate Teaching (voted by the undergraduates); and he was named a Margaret MacVicar Faculty Fellow. Together with his colleague Bob Alberty, Silbey adapted his lectures for publication in an undergraduate textbook titled *Physical Chemistry*.[1]

Silbey's MIT research was always a distinctive one-on-one collaboration with each of his more than 65 graduate students and postdoctoral associates, for whom he was a caring mentor. He challenged them to work on problems of their own choosing and supported their interests and ingenuity with guidance, insight, and encouragement. With Silbey as an inspirational role model, many of his students have gone on to positions of leadership in academia.[2] All remember his love of science and his devotion to family and close friends as indivisible parts of his life.

In his capacity as a recognized leader among the MIT faculty, Silbey championed the work of women in science. As department chair, he instituted a research network for women in chemistry. And, after shepherding to the top level of administration the complaints of discrimination from women in the School of Science, he served on the committee that led to MIT's 1999 public confession of differential treatment of women faculty.

Many at MIT, including his scientific colleagues and the administrative leaders of the institute, attest to Silbey's skill and effectiveness as a leader. With his wit and abundant wisdom, he was the obvious person to chair committees whose work required consensus among competing factions. He could see beyond his own needs to the needs of others, and then fashion a "win-win" approach to solving political and academic problems. His collegiality made his department and university greater than the sum of its individuals, as he was so adept at weaving together the efforts of the many.

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One often finds oneself at banquets wishing to be seated next to an interesting and entertaining person. One could not wish for a better dinner partner than Bob. He would fit the bill for almost anyone and any occasion. He was a great raconteur and conversationalist, and he was deeply knowledgeable not only about science but also literature, jazz, history, and sports. He had a marvelous sense of humor and was thoroughly enjoyable to be with.

A gifted scientist and teacher and a man of great intellectual breadth, Bob was also a tremendous success in all other aspects of life. He was a nurturing parent to his daughters Jessica and Anna, who in their own successes as wives and parents, as well as in their professional lives, bear witness to his compassion and understanding. He was a loving husband to his wife Susan, a leader in her academic field (sociology), who had a wonderful sounding board in Bob for her very fertile ideas. And he was a great friend to many of his scientific colleagues and childhood companions. Bob was a happy man and truly loved his life, and what a life it was. For all of us who were privileged to know him, we only wish it had been longer.

NOTES

1. Silbey, R., R. Alberty, and M. Bawendi. 2004. *Physical chemistry*, 4th edition. Hackensack, NJ: Wiley.
2. Robert J. Silbey Memorial Website: *http://web.mit.edu/robertsilbey/*

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