Samuel I. Weissman
1912–2007

A Biographical Memoir by
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Samuel I. Weissman was a pioneer in the development of electron paramagnetic resonance (EPR), also called electron spin resonance (ESR), as a tool for exploring chemistry. His career was distinguished by his deep understanding of chemistry and physics and by his devotion to explaining their principles on a fundamental level and in simple terms. Sam’s inspiring persona infused those around him, both colleagues and students, with a similar love of science. But his most endearing trait was his quick wit and colorful sense of humor.

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Early years

After attending Chicago public schools, Sam earned a bachelor’s degree in 1933 and his doctorate in physical chemistry in 1938 from the University of Chicago. In 1941, he joined the celebrated group of G. N. Lewis at the University of California, Berkeley, to work as a National Research Fellow. Sam was studying the rare earth elements’ optical properties, which helped pave the way for lasers and resonant energy-transfer methods, while David Lipkin, who was Lewis’s research assistant, explored the rare earths’ spectroscopy and photochemistry in rigid media. Sam and Lipkin were colleagues and friends from that time on.

With the start of World War II, the two scientists began working at the Radiation Laboratory in Berkeley as part of the effort to separate the isotopes of uranium photochemically—an effort that proved unsuccessful. Meanwhile, typical of Sam’s numerous interests and his drive to explore fundamental issues, his and Lipkin’s research extended beyond
the rare earths. They also published on the “peculiar nature” of the beta phosphorescence of fluorescein in acid solution, which at that time was poorly understood.

In particular, the precise nature of the emitting excited state was not known. One speculation was that long-lived phosphorescence proceeded not by an electric dipole mechanism but by a higher-order multipole. To investigate this hypothesis, Sam and Lipkin set up the necessary experimental apparatus to observe the wide-angle interference of the long-lived phosphorescence of fluorescein. The interference diverging at different angles established that the electromagnetic radiation process of long-lived phosphorescence involves a purely electric dipole transition (Weissman and Lipkin 1942), a crucial feature in establishing the origin of the phosphorescence as the excited triplet state. World War II soon interrupted Sam’s tenure at UC Berkeley and the Radiation Laboratory. In 1943, he was recruited to work on the Manhattan Project—the endeavor in Los Alamos, New Mexico, that ultimately built the first two atomic bombs. There he worked on the implosion mechanism needed to detonate the Nagasaki bomb and on the application of a protective coating to protect the plutonium core from corrosion. As one might expect, Sam’s experience at Los Alamos had a monumental effect on his entire life.

Also in 1943, Sam married Jane Loevinger, a psychologist and intellectual peer, who became his lifelong companion.

**Washington University era**

In 1946 Sam moved to Washington University in St. Louis with five colleagues from Los Alamos—Lindsay Helmholz, Joseph Kennedy, David Lipkin, Herbert Potratz, and Arthur Wahl—and began his teaching career.

Sam also continued his research into optical spectroscopy, by examining the effects of paramagnetic ions on phosphorescence, but he soon turned to the brand new field of magnetic resonance in which he was to become a pioneer and renowned world-class expert. Sam focused his attention on EPR, which results when a substance has an unpaired electron. He carried out his pathbreaking studies in EPR using home-built spectrometers designed and fabricated by Jack Townsend, a colleague in the Washington University Department of Physics. Over the subsequent years, the contributions of the Weissman Lab were numerous.

According to Sam’s son Michael Weissman, a professor of physics at the University of Illinois at Urbana-Champaign, despite his father’s intimate knowledge of how to build an atomic bomb, during the (Sen. Joseph) McCarthy years Sam was denied security
clearance to do summer work on essentially nonmilitary magnetic resonance projects at Brookhaven National Laboratory. The most serious charge was that Sam’s mother had donated money to a collection for the Spanish Republican government. The security clearance was granted, however, by 1954.

In 1952 Sam and his colleagues G. E. Pake and J. Townsend reported the first observation of hyperfine lines in the EPR spectra of paramagnetic radicals, based on the use of Fremy’s salt (Pake, Townsend, and Weissman 1952). These hyperfine lines are caused by interaction of the spin of the unpaired electron with those of the nuclei in the molecule. The researchers used a rather primitive apparatus by today’s standards: crystals of Fremy’s salt were placed in an x-band excited wave-guide terminated by a crystal rectifier. The crystals were diamagnetic, and the three-lined hyperfine spectrum of Fremy’s salt came from the salt dissolved in the residual liquid remaining on the crystals. Beginning in 1953, Sam and colleagues Lipkin, Townsend, and Paul demonstrated that metallic sodium can react with aromatic compounds to produce anions with one unpaired electron, and that the unpaired electron is distributed over the entire aromatic “free radical” (Paul, Lipkin, and Weissman 1956; Lipkin et al. 1953).

In 1956 Sam and Harden McConnell separately published a quantum-mechanical interpretation of the isotopic hyperfine constants of π-radicals (Wertz and Bolton 1972; McConnell 1956; Weissman 1956). They proposed a simple linear relationship between the unpaired π-electron densities and the proton hyperfine splittings in π-type organic radicals. This fundamental mechanism was of great importance to the development and
testing of $\pi$-electron theories. Moreover, Sam and McConnell demonstrated how EPR could be utilized to gain information about the details of molecular structure. This effort led the way to the widespread use of nitroxide spin labels to explore structure and structural dynamics in a wide variety of materials and, especially, biological systems.

Also in the mid-'50s, Sam showed that line-broadening phenomena in EPR could be used to obtain information about the rate and mechanisms of a variety of fast chemical reactions involving free radicals. In 1954, Sam and R. L. Ward reported in a communication to the *Journal of the American Chemical Society* that certain spectral lines—those arising from the hyperfine interactions of dilute naphthalene negative ions in tetrahydrofuran solution—are broadened when excess naphthalene is added. This phenomenon was ascribed to the electron-transfer reaction between naphthalene and naphthalene negative ions. The second-order rate constant was estimated to be $1.0 \times 10^6$ M$^{-1}$sec$^{-1}$ at 30°C. Ward and Weissman’s results provided the first demonstration that the line-broadening phenomenon in EPR could be used to study rapid reaction dynamics (Ward and Weissman 1954). The two researchers published a full description of this work in 1957; their paper reported that the bimolecular rate constants between naphthalene negative ion and naphthalene vary with solvent and with the choice of positive ion. These constants lie in the range of $10^7$–$10^9$ M$^{-1}$sec$^{-1}$ (Ward and Weissman 1957).

In the case of sodium ketyl of benzophenone, the overall electron-transfer reaction is $\text{NaOC}(\text{C}_6\text{H}_5)_2 + \text{OC}(\text{C}_6\text{H}_5)_2 \rightarrow \text{OC}(\text{C}_6\text{H}_5)_2 + \text{NaOC}(\text{C}_6\text{H}_5)_2$. The question of whether this reaction proceeds by transfer of sodium atoms or by separate and uncorrelated transfers of electrons and sodium ions was answered by Adam and Weissman in 1958. The observation that the hyperfine lines collapse into four lines due to the interaction with the same sodium ion (nuclear spin 3/2) in the presence of a large amount of benzophenone clearly indicated the atom-transfer mechanism. The four lines due to the sodium nuclear spin remained unaffected because the unpaired electron traveled with the sodium atom (Adam and Weissman 1958).

In 1958, Sam made another classic contribution to EPR by recognizing the significance of the electron dipolar interaction for the observation of triplet EPR spectra, first reported by Clyde Hutchison and Billy Mangum that same year (Hutchison and Mangum 1958; Weissman 1958). Hutchison, a professor of chemistry at the University of Chicago, had been trying to detect the EPR signal of the excited triplet state of naphthalene in samples with random order. Sam explained to Clyde that in such samples, the EPR spectrum was too broad to detect (with the instrumentation available at that
time) because of the orientational dependence of the large magnetic dipole-dipole interaction between the two electrons of the excited triplet state. Hutchison then removed the random order, using single crystals of durene to host the excited triplet state of naphthalene, and he thus became the first to detect excited triplet states using EPR (Hutchison and Mangum 1958). Sam’s influence was acknowledged in this landmark publication.

In 1962, Zandstra and Weissman reported that the rate of the electron-transfer reaction is slow when ion association takes place, and that the rate in sodium naphthalenide-naphthalene in tetrahydrofuran increases with decrease of temperature. These results showed an apparent negative activation energy (Zandstra and Weissman 1962).

The electron-transfer reactions between ketyls and ketones were further investigated in detail by Hirota and Weissman. The correlation between the rate constants and the magnitudes of the sodium hyperfine splitting was noted, suggesting that the rate constant is sensitive to the ion pair structure (Hirota and Weissman 1964). Weissman extended the investigation of line-broadening phenomena to nuclear magnetic resonance (NMR). Kreilick and Weissman explored the hydrogen-transfer reaction between a 2,4,6-tris-tert-butylphenol and the corresponding phenoxy radical through the measurement of the broadening of the NMR lines; here the lifetime of the intermediate was estimated to be 1 x 10^-9 sec (Kreilick and Weissman 1962).

In 1969, Sam devised a density-matrix approach for calculating dynamic triplet line shapes (Norris and Weissman 1969). It turned out that this method is fairly general, and equivalent to the stochastic Liouville approach independently developed by R. Kubo and J. H. Freed (Freed, Bruno, and Polnaszek 1971; Kubo 1969). It is important to note that both methods can also be employed in the slow-motional regime, where conventional line-shape theories fail. These methods are thus appropriate tools for EPR/NMR spin-label studies of biological membranes, as demonstrated in numerous papers by J. H. Freed and G. Kothe.

In the early to mid-’70s Sam published a series of papers on transient and quantum effects in photoexcited triplets in the presence of a magnetic field (Felix and Weissman 1975; Levanon and Weissman 1971). However, due to limitations of the EPR instrumentation available at that time, no quantum interference effects were found in the kinetics of growth and decay of photoexcited triplet states embedded in a host single crystal. Only recently, high-time resolution EPR enabled the detection of the quantum oscillations that Sam predicted more than 30 years ago (Kothe et al. 2010). Analysis
revealed that, in contrast to a common paradigm, the nuclear spins participate in the intersystem crossing from the first excited singlet to the lowest triplet state.

In the late ’70s, Sam pioneered the development and application of transient nutation EPR. In this technique, the time evolution of the transverse electron-spin magnetization is detected in the presence of a weak microwave magnetic field. Combination of this method with pulsed laser excitation provided valuable information about short-lived paramagnetic species, including a phosphorescent quartet state (Kothe, Kim, and Weissman 1980; Kim and Weissman 1978a,b). Recent successful applications of this method involved the detection of quantum oscillations in the radical-pair intermediates of photosynthesis (Kothe et al. 1991).

Beginning in 1995, Sam and his colleagues Professor T. Lin and Dr. David Sloop at Washington University originated the development of pulsed zero-field/low-field EPR combined with fast-field switching to study the magnetic and dynamic properties of photoexcited triplet states in molecular crystals (Yang et al. 2000a,b). The scientists particularly emphasized the level anti-crossing (LAC) regions where quantum coherence effects were expected to occur. Indeed, recent studies suggest that at triplet LAC conditions, a large number of multipartite entangled quantum states can be created simply by light excitation (Kothe et al. 2010).

Respect for Sam was widespread among his colleagues. For example, in 1969, when chemist Gerhard Closs of the University of Chicago had developed a theoretical explanation for a newly discovered and strange NMR polarization phenomenon—one that manifested itself in the NMR spectrum during or immediately after certain photochemical reactions—his explanation was in serious conflict with what had already been published; the explanation already in the literature was based on the Overhauser effect and was purely physical in nature. Closs’s explanation, by contrast, relied on chemistry, in particular where a photochemical reaction occurred involving radical pairs. Before submitting a paper for publication, he wanted to see what a scientist he highly respected thought about his different treatment of the NMR polarization phenomenon, and it was clear to him who he should consult. Closs traveled to St. Louis to visit Sam, who found his colleague’s theoretical explanation new and exciting—and he approved of Closs’s explanation of the phenomenon. This gave Closs the confidence to publish his now well-known and—accepted treatment of chemically induced dynamic nuclear polarization (Closs 1969).
Sam received many national and international honors, such as honorary degrees from Washington University and the University of Siena (Italy). He was elected to the American Academy of Arts and Sciences in 1963 and to the U.S. National Academy of Sciences in 1966. In 1995, he received the International EPR/ESR Society’s Gold Medal and was appointed a fellow of the society.

Sam loved his students, and it showed. He encouraged them to work independently in their research, as he often did—doing experiments by himself, blowing glass tubes, and preparing samples on a vacuum line in his office. In the same spirit of informality and directness, his papers were always very short, describing only the essentials. Though Sam never had a large research group, a significant number of his students and associates were successful in their later careers in many countries. Promoting international friendship, Sam welcomed foreign scholars and students in his lab.

Sam became an emeritus professor in 1980. But he remained very active in science and was in the department on most days in discussions with colleagues and students. In his emeritus endeavors he had the fortunate collaboration of Professor T. Lin and Dr. David Sloop. Even until close to his death in 2007, Sam never stopped planning exceptional experiments to probe fundamental issues.

Sam the man

Sam’s passion for addressing the fundamentals extended to other areas of his life. He was a devotee of classical music and had an annual subscription to the St. Louis Symphony Orchestra and the Opera Theater of St. Louis. At home, he listened to vinyl recordings of classical music on his elaborate stereo, equipped with state-of-the-art turntable, amplifier, and speakers. “State of the art” didn’t necessarily satisfy Sam, however, and his saga of the pickup arm was a case in point. To get the ideal playback of a vinyl recording, the needle of the turntable’s pickup arm must always track on a tangent with the moving circular groove of the record. But because the pivot point of the arm is fixed to a single point away from the center of the rotating vinyl recording, and because the radii of the circular grooves are going from large to small, the needle can be tracking perfectly tangentially at only one radius—playback distortion thus occurs, to varying degrees, everywhere else. The turntable manufacturers had tried to overcome this defect by using a bent tracking arm designed to minimize the overall tracking error, but this was not good enough for Sam.
Instead, he devised a straight pickup arm that used a special low-friction sleeve bearing; with optical feedback control ensuring that the pickup arm would always be parallel to the movement of the record’s groove, whatever its radius. The only problem was that Sam’s innovation would need a straight pickup arm, not the then-standard bent arm. So he wrote to a turntable manufacturer, presented his ideas, and proposed a consequent switch to a straight arm. The company found Sam’s ideas so intriguing that it sent him a specially built straight pickup arm; in that way, he could build and enjoy his own improved turntable. Later, such a turntable was commercially produced.

Sam’s quick wit and sense of humor were well known and appreciated, and they were on display, for example, during a seminar—given by Barry Commoner, a faculty member of Washington University’s Department of Biology—on the creation of life in a test tube. At the end of his seminar someone in the audience asked Commoner how would he know if what was obtained in vitro truly qualified as “life.” He thought a moment and replied, “It would be able to reproduce itself.” At this point Sam shouted out, “How about a mule?”—which of course is alive but cannot reproduce. To Sam’s delight, much laughter emanated from the audience.

He was especially fond of telling people about his experiences during World War II at Los Alamos while on the Manhattan Project. Sam’s sense of humor came through strongly in his colorful descriptions of this critical period in history, and he particularly enjoyed recounting the adventures of the irrepressible Richard Feynman (a renowned physicist) in dealing with the project’s director, the pompous General Leslie Groves.

Sam’s sense of humor got much of its flavor from his boyhood in the 1920s and ’30s, when he lived in a Jewish neighborhood of Chicago’s South Side. A perfect example occurred when he attended a seminar at Washington University, given by a biochemist, that showed impressive data on a single enzyme isolated from a large number of different animals. His summary slide showed two columns listing the animals used. The speaker concluded that enzymes from the animals in the left column all shared certain characteristics. Likewise, the enzymes of the animals on the right also shared certain characteristics, but the two sets of characteristics differed. The biochemist asked if anyone in the audience could see some basic difference, between the animals on the left and those on the right, that might account for the disparity in their enzymes. Sam’s hand shot up immediately. “The animals on the left,” he said, “are all kosher; the animals on the right are not.”
The above glimpse into Sam’s sense of humor is too brief to be adequate. Fortunately, he provided the means to experience it directly. Sam’s 1990 memoir, titled “The Way It Was” (listed in the Selected Bibliography below), is full of laughs, and we highly recommend it.

Sam’s formidable intellect was embedded in a personality that could not have been less intimidating, and he inspired and educated students and colleagues alike, whether in the classroom or in innumerable lab or office sessions. You gained insight, but you also could have died laughing. Sam Weissman was in the great tradition of Yiddish storytellers, and his cast of characters leaped to the imagination as vividly as any in Charles Dickens’s novels.
REFERENCES


SELECTED BIBLIOGRAPHY


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