



Sam Messman

THE WAY IT WAS

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My account of the Way it Was begins with the years 1933–1941, skips the war years 1941–1945, and ends in the mid 1950s.

The first volume of the *Journal of Chemical Physics* appeared in 1933, the year of my beginning graduate work in physical chemistry at the University of Chicago. Many of the great contributors to physical chemistry—Langmuir, Debye, Lewis, Cross, Pauling, Libby, Urey, Kistiakowsky, Van Vleck, Wilson, Eyring, Mayer, Kirkwood, Hildebrand, James, and Coolidge—published in that volume. But in 1933, I had heard in my undergraduate work only of Lewis, Langmuir, and Debye.

The department, under the chairmanship of the organic chemist Julius Stieglitz, retained vestiges of Teutonic organization. The senior professor in each field had as his assistant a younger person with a nominal faculty appointment who helped run his research program and pretty much took orders from his boss. The senior physical chemist was W. D. Harkins; with his assistant David Gans he maintained active research programs in nuclear chemistry and surface chemistry, with occasional excursions into other fields, including Raman spectroscopy and synthesis of organic compounds in electrical discharges. The physical chemists not tied to Harkins were T. F. Young, T. R. Hogness, and Simon Freed, all graduates of the chemistry department at Berkeley. John Kirkwood joined the department, but departed after only one year.

In his research, Young concentrated on precision measurements of the thermodynamic properties of electrolyte solutions. I recall only one departure from his beloved heats of dilution and freezing point depressions—an imaginative attempt to measure the photoelectric properties of solutions of metals in liquid ammonia. Hogness was a pioneer in chemical applications of mass spectrometry. Several of his graduate students worked in that field, others in spectroscopy and a few other associated fields. He later turned to enzymology. Freed, fresh out of Berkeley

and work with G. N. Lewis, was the youngest and, in my view, the most imaginative member of the department. He worked on magnetism, spectroscopy of rare earth ions, and some other projects not readily categorized. His work in magnetism was concentrated on measurements of the concentration and temperature dependence of the magnetic susceptibilities of solutions of metals in liquid ammonia. He thought of the solutions as electron gases to which the recent developed theories of electrons in metals could be applied. Another conception that he hoped would be accessible to measurement was Landau's that, owing to a diamagnetic correction, the effective magnetic moment of electrons in a dilute electron gas is two thirds of a Bohr magneton.

Harry Thode, Richard Metcalf, and Nathan Sugarman did the metal ammonia work. For their measurements of the susceptibilities by the Guoy method, they had to contend with unstable solutions, an inadequate magnet, a succession of fragile and frequently broken home-built Dewar flasks necked down to fit into the narrow gap of the magnet, and a temperamental microbalance borrowed from the Universal Oil Company. Constant demands by the Universal Oil people for return of the balance were not helpful. Nevertheless, they succeeded in getting reliable measurements over a considerable range of concentrations. Freed was able to account for the data by treating the system as a gas of fermions, but his interpretation seemed not to gain wide acceptance after Pauling showed that the data could be accounted for by an equilibrium between paramagnetic monomers and diamagnetic dimers. Pauling's language was probably more appealing to chemists than Freed's, but I suspect that the two are equivalent.

I recall one magnetic measurement of Freed's that might now be considered childishly naive: the magnetic susceptibility of ethylene. (Mulliken, a member of the department of physics at the university, helped instigate the experiment.) Might not ethylene, since it is isoelectronic with dioxygen, be paramagnetic? Everyone now knows the answer.

At the time that I was hunting around for a project to work on, Freed had become interested (fascinated is probably the better word) in the high rotational speeds that could be reached with gas-driven, gas-supported rotors. He thought that new phenomena were waiting to be uncovered at the high centrifugal fields, greater than 10^6 g, that had become accessible.

I decided to take a flyer with Freed in the top-spinning business. (Harkins averred that Freed was doing secret work with spinning tops.) Probably the times had something to do with my decision. The world was in turmoil—depression in the United States, Hitler in power in Germany, the future looking bleak—so what the hell, take a chance on a long shot that probably would not pay off but might be fun for a while.

As to the results of my experiments with the spinning tops, there is little to say. I did learn how to work a lathe and a milling machine. (I built the damned things myself.) I looked for three different effects: spectroscopic shifts or splittings from a source in a high centrifugal field, rotation of the plane of polarization of linear polarized light propagating along the axis of a rotating cylinder, and development of an electrostatic potential difference between center and periphery of a rotating metallic disk ("centrifuging electrons"). The attempt to centrifuge electrons has since revealed to me the conceptual errors of which I was guilty. I calculated the free energy difference between electrons in an electron gas at the center and periphery of the disk and assumed that the corresponding electromotive force would appear as an electrostatic potential difference. As Bridgman showed in his book, *Thermodynamics of Electrical Phenomena in Metals*, it is only under special conditions (not fulfilled in my experiment) that the two are equal. The measured differences were much larger than I had calculated, I couldn't explain them, and gave up. The experiment on spectral shifts gave null results, and the one on rotation of the plane of polarization I could not do.

The department mercifully gave me a degree for a good try. I am totally amnesic about my PhD oral examination. Maybe there wasn't one.

[Two of the experiments have since been carried out successfully. R. V. Jones showed that the plane of polarization of linearly polarized light propagating along the axis of a transparent rotating cylinder is in fact turned, and Jesse Beams carried out the centrifuging of electrons. His experiment was instigated by Fairbanks' attempt to find out whether the gravitational interaction between matter and antimatter is repulsive or attractive. I don't have space to go into the connection.]

Both in physical chemistry and physics, much of the graduate students' time was spent in building apparatuses. But we did find some time for thinking. Freed, recognizing the importance of symmetry and its mathematical realization in group theory, organized a tutorial in the subject. We (Freed, Norman Davidson, George Boyd, Martin Kamen, Eugene Rosenbaum, Ruth Comroe, I, and a few others) met in the evenings to teach ourselves group theory. We studied Speiser's book on finite groups and Wigner's newly published *Gruppentheorie und Ihre Anwendung auf die Quanten Mechanik der Atomspektren*. It was great fun—all those new ideas. We finally were able to work through Bethe's 1929 paper on the splitting of levels in fields of various symmetries. It was all wondrously new to us then. Now it's old, taught, after a fashion, in undergraduate courses in inorganic chemistry.

The university was caught up in the political, philosophical, and scientific ferment of the times. Stalinists, Trotskyites, Norman Thomas socialists,

New Dealers, far right Republicans were having at each other. Professor Henry Gordon Gale, Dean of the division of physical sciences, described by the *Chicago Tribune* as a “soldier scientist,” endorsed Alf Landon for the presidency in 1936. At the physics colloquium on the day after Gale’s endorsement, almost all the graduate students and some of the faculty turned up wearing large Roosevelt buttons.

The Aristotelians, led by Mortimer Adler, were deriding modern science (not only had medicine made no progress since Galen, it had retrogressed owing to its ignoring his teachings); the scientists, led by Anton J. Carlson, responded vigorously and not too politely.

In the physical sciences, a group of operationalists, converted by Bridgman’s book, *The Logic of Modern Physics*, had become more Catholic than the pope. One of them, a graduate student in physics, confronted one of his fellow students with the question, “What are you doing?” The answer: “I’m measuring the cross section of beryllium for alphas in the alpha-n reaction.” Operationalist: “Don’t be childish. What scale readings are you making and what correlations are you finding between them?” At their next encounter, before the operationalist could repeat his question he was told, “I’m sawing this fucking piece of brass.”

But some aspects of the time were more grim than polemics over the philosophy of science. The senior machinist in the chemistry department was a Nazi. Daily at noon he read aloud to his young assistant a selection from *Mein Kampf*. I had frequent dealings with him. We got along well when the issue was how to machine the flutings in a turbine, not so well when the issue was fascism. I finally goaded him into a violent outburst. “It used to be that every Jew and Socialist could shit out his guts on Germany, but no more.”

Finding jobs, particularly for Jews, was not easy. Recruiters from the chemical companies visited the department regularly, even during the depression years. One blue eyed blond student reported that his interview with the duPont recruiter went well until he revealed that he was Jewish. The interviewer slammed down the papers that he had been filling out and exclaimed, “Damn it, you can’t tell a Jew by looking at him anymore.”

James Franck had joined the department in 1938. A naturally exuberant man, he was constantly concerned and oppressed by the Nazi atrocities in his native Germany. On the morning after Kristallnacht, he came to the laboratory distraught and ashen faced, muttered a few words in German and then left. Franck, a decorated veteran of the First World War, had no illusions about the Nazis.

Not all the responses to Nazism and war were totally grim. Roosevelt’s attempts to get the country out of the depression included provision of assistants to university laboratories. Freed was allotted Ben J. Ben (he

said that wasn't his real name; his real name couldn't be pronounced by Americans). His task, he said, was to "streamline" himself for participation in the war that the United States would soon be waging against the Nazis. He managed to distill a few solvents and wash a few dishes. Perhaps he should have been assigned to the State Department. He explained, following the Nazi-Soviet pact, that Hitler would say to Stalin, "Joe, we got pact, no? How's about you give me Ukraine (pronounced ookrayeen)?" Stalin gonna say "No, then will be invasion of Russia."

I hung on at the University of Chicago until the spring of 1941. I worked for a few months as a technician with Franck's group on a photosynthesis, and for the rest of the time with Freed on spectroscopy of rare earth ions, particularly Europium. During my stint with Franck's group, I built a photometer designed to record "rapid" (about 0.1 second) changes in fluorescence intensity from photosynthesizing leaves (spinach was the good stuff) when the composition of the atmosphere in which they were bathed was changed. The photometer included a vacuum tube amplifier. Franck was pleased with its performance but confessed, "These vacuum tubes I do not trust. Electrometers I trust."

Of the many colloquia that I attended at the University of Chicago only a few remain in my memory. (Perhaps I should use more modern language and say that I can access only a small portion of what may possibly be stored in my ROM.) I recall Pauling's talk on the entropy of ice not only for its scientific virtuosity but for his light-hearted twitting of the humorless Professor Harkins. "All of this hearkens back to—hearkens, harkins, anybody every heard that word around here?"

Another memorable colloquium was by Phipps, a report of the experiments that he had done during a sabbatical stay in Otto Stern's laboratory. He isolated one spin-selected beam from a Stern-Gerlach sorter and ran it into a second sorter whose magnetic field was rotated relative to the first. Instead of getting the expected two beams with relative intensities $\cos^2(\theta/2) \sin^2(\theta/2)$ where θ is the angle between the fields in the two sorters, he got only one beam. Analysis of the experiment revealed that the beam velocities and field gradients were such that the spins in the selected beam followed the ambient field adiabatically. The notion of adiabaticity remained murky to me until many years later when I studied Abragam's book on magnetic resonance.

In the physics department there was great, but short-lived, excitement after the colloquium in which Robert Shankland, one of A. H. Compton's students, presented the results of his experiments designed to find out whether the electron and scattered photon in Compton scattering appeared simultaneously. He set up two coincidence counters, one to detect electrons, the other photons, and recorded the dependence of coincidence

rate on relative orientation of the two counters. He found no more coincidences at the Compton angles than at the other angles and concluded that the scattered electron and photon did not appear simultaneously. Carl Eckart announced to his class in quantum mechanics that everything he had been teaching was wrong. Repetition of the experiment in other laboratories and by Shankland ultimately revealed that the scattered particles did appear simultaneously. A subtle artifact had crept into Shankland's experiment. Quantum mechanics was saved.

Finally, Carl Anderson's report on his discovery of the positron remains vivid. His data were unambiguous. There was one question over naming the new particle, and some highbrow types suggested Oreston after Electra's brother.

In 1941 I moved on to Berkeley to work as a National Research Council fellow under G. N. Lewis. I reported to Miss Kittridge, boss of the department office (and alleged by some to be boss of the department), and was directed to Lewis' laboratory. There I found him shining a flashlight on a sample cooled by liquid air in an unsilvered Dewar. He tucked the Dewar under his sport jacket and observed the afterglow. "I would say the half life is about one second, wouldn't you? And the color I maintain is yellowish green despite my associate Dr. Lipkin's stubborn insistence that it's greenish yellow." Thus my introduction to the phosphorescent state, later identified by Lewis as the triplet state.

At Berkeley, I felt for the first time that here I was where the physical chemistry that counted was being done. Lewis, Hildebrand, Latimer, Rollefson, Eastman, Olson, Bray, Gibson, Giauque, Branch, and the bright young men Pitzer, Seaborg, Kennedy, Calvin, Rubin were doing it. There was a sense of excitement and adventure that I had not experienced at Chicago. There was a most able group of graduate students, among them Gwinn, Connick, Duffield, Wilmarth, Campbell, Wahl, Brewer, Gofman, Hill, Bigeleisen. David Lipkin was Lewis' research assistant. We have been colleagues and friends ever since.

Everyone, it seemed to me, was doing important work and doing it well. Gwinn and Pitzer were completing calculations on the contributions of internal molecular rotation on thermodynamic properties. (Questions about the barrier to rotation in ethane had not yet been resolved.) Campbell, working with Hildebrand, was looking at the structure of liquid mercury by x-ray diffraction. Terrel Hill, then nominally an organic chemist, worked with Branch on relations between color and structure of organic compounds. Art Wahl, in a feat comparable to Madame Curie's extraction of radium from pitchblende, got at nuclear and chemical properties of plutonium from the few micrograms of it that he fished out of hundreds of pounds of irradiated uranyl nitrate.

I was given laboratory space in Gilman Hall in a room that had a sunlit balcony. The extraordinary resources of the laboratory (by Chicago standards) soon became apparent. I wanted to work on a phenomenon that I had stumbled across just before leaving Chicago. To photograph the absorption spectrum of an organic chelate of europium I mounted the sample close to the slit of a spectrograph and focussed the filament of a tungsten lamp on it. The light entering the spectrograph showed the expected europium absorption bands, but on the intense red background from the unfiltered light of the lamp there appeared the brighter fluorescence lines of the europium ion. The blue light of the lamp was absorbed by the ligand and the excitation transferred with high efficiency to the europium ion. To study the excitation spectrum I wanted a continuous light source, a monochromator, and a photometer. No problem—here they are. What kind of light source? Here's a heliostat. I set up the experiment on the sunlit balcony with the light produced by hot fusion 93 million miles distant.

The europium that I was using had been given to Freed by Herbert McCoy, who had devised a scheme for its separation from the other rare earths. It was rare stuff.

McCoy had served on the University of Chicago faculty from 1901 to 1911. He made fundamental observations in radioactivity and is credited with having been the first to recognize the existence of isotopes. In 1919 he became vice president of the Lindsay Light and Chemical Company. The company extracted products that it could sell from monazite, a mineral containing thorium and rare earths. The thorium went into thorium dioxide, an ingredient of Welbach mantles, the radiating element in gas lights. So McCoy had a supply of raw materials from which he extracted rare earths. He retired to Pasadena, set up a laboratory complete with laboratory bench and grand piano. He played Mozart and produced pure europium. He exploited stability of the $(4f)^7$ configuration that permitted reduction of $\text{Eu}^{3+}(4f)^6$ to $\text{Eu}^{2+}(4f)^7$, in which oxidation state it behaves like an alkaline earth and is easily separated from the other tripositive rare earth ions.

Freed had given me about 150 milligrams that I used over and over again as I prepared various chelates. McCoy was a good friend of Lewis' and turned up to visit him at a time when all my europium was in a few crystals of some chelate or other that transferred the excitation with high efficiency. In daylight the crystals glowed bright red. Lewis brought McCoy to the laboratory where I showed him the glowing crystals. "Could you use some more europium?" he asked. Before I could answer he went on, "Got a weighing bottle?" I produced one and he took from his briefcase a large bottle of pure europous carbonate—the world supply of pure

europium. He dumped about five grams into the weighing bottle, spilled a few hundred milligrams, blew them away before I could mop them up, and said "There you are." As I began an elaborate speech to thank him, Lewis returned and said, "Herbert, would you like a drink?" They disappeared into Lewis' office.

During the two years 1941–1943 that I spent in Berkeley I was privileged to witness Lewis at work. He was constantly probing in areas where he felt that new concepts were needed and was impatient with those who worked where he felt that the concepts were well established. When one of his colleagues came into the laboratory to describe yet another elaboration of an old method for measuring activity coefficients, Lewis listened with obvious annoyance and then said as the colleague was barely out of earshot, "Well, you can't stop a man from doing that sort of thing, but you certainly shouldn't pay him for it."

During my stay Lewis had as coworkers first David Lipkin, then Jacob Bigeleisen. Much of their work dealt with spectroscopy and photochemistry in rigid media. ("A rigid medium is just like a vacuum," Lewis once said, looking around for someone to have an argument with.) Lewis carried out many of the experiments himself. He seemed to enjoy working at the vacuum line. Once something went wrong, and he filled the line with an opalescent smoke that he couldn't get rid of. I diagnosed his problem. "Professor, you've filled the line with impalpable motes." He thumped me on the chest and said "Young man, did you ever palp a mote?"

In the summer of 1941, Lipkin and I, responding to the ever more ominous developments in the European war and to the growing preoccupation at Berkeley with the possibility of making nuclear explosives, tried to separate the uranium isotopes photochemically. Our attempt was provoked by a paper on the effect of nuclear spin on radiative rates in forbidden transitions. The atomic transition $^3P_0 \leftrightarrow ^1S_0$ is forbidden as a one-photon process for all multipole orders. But the 3P_0 state of the odd isotopes of mercury does radiate to 1S_0 with a lifetime of about 0.1 second owing to coupling to the nuclear spin angular momentum. We played the long shot that the long-lived (about 1 millisecond) excited state of uranyl ion might be shorter lived in $^{235}\text{UO}_2^{2+}$ than in $^{238}\text{UO}_2^{2+}$. We did not do the obvious first experiment, a direct comparison of the lifetimes (much more easily done now than then), but plunged right into a photochemical experiment—competition between photochemical reduction and fluorescence. Lipkin devised a mixture of phosphoric and hypophosphorous acids that met our requirements, but we got no isotope separation. We discovered by a tracer experiment that our chemical separation following photochemistry would have rescrambled the isotopes. We don't know to this day whether we had any isotopic enrichment in the photochemical process.

At first we had no formal connection with any organized project—we just prepared our samples and gave them to someone in the Radiation Laboratory for isotopic analysis. Later Lipkin resigned his assistantship and I my fellowship to become full time employees of the Radiation Laboratory. We worked on the chemistry of source materials for E. O. Lawrence's electromagnetic separations.

While working on isotope separation we did manage to moonlight an experiment on the phosphorescent state. There had been speculation that owing to some unspecified cause, long-lived phosphorescence proceeded not by an electric dipole mechanism but by a higher order multipole. We determined the mechanism by observation of wide angle interference of the beta phosphorescence of fluorescein—one of Lewis' favorite phosphorescences. The experiment was finished in one week; the answer, pure electric dipole. As we were setting up the experiment I managed to get beautifully bright fringes from a fluorescent source. I tried to get Lewis to look at them. At first he refused: "Every time someone asks me to look at something through an eyepiece, I don't see a damned thing." "So try already, professor." Finally, he tucked his cigar behind him, looked through the eyepiece and exclaimed, "By god, they're there."

Following the work of the war years at Berkeley and Los Alamos, Joe Kennedy, the newly appointed chairman of the chemistry department at Washington University, brought with him five of his colleagues, Helmholtz, Lipkin, Potratz, Wahl, and me. The appointments were made without benefit of advertisements in the *Journal of Higher Education* and approval by an Affirmative Action Committee.

Resuming academic work was relatively easy. We no longer had the unlimited support that we had experienced in the Manhattan Project, but we had the encouragement of the university (but not much money) and a fine group of graduate students, most of whom had worked at Los Alamos. Among the undergraduates were many veterans who had come to the university under the G.I. Bill, some older than we, and almost all with the irreverence that their years in the service had produced. I almost lost a class when I first wrote on the blackboard, $G = H - TS$. TS (tough shit in army language) did it. Thereafter, it was $G = H - ST$. It's a good thing that S and T commute.

An experience of Lipkin's in our first year at Washington University was an augury of things to come. Los Alamos volunteered financial support of his work. The university demanded substantial overhead. Overhead, what's that? It was a new concept. The university got its overhead but not as much as it had asked for.

My first project at Washington University was a study of phosphorescence. By 1943 Lewis had become convinced that the "phosphorescent

state” was a triplet state. With Calvin he then demonstrated its paramagnetism by a difficult, but straightforward, observation of its magnetic susceptibility. Phil Yuster, my first graduate student, and I demonstrated perturbation of phosphorescence by paramagnetic ions. As we were getting started on that work, Bloch and his coworkers at Stanford and Purcell at Harvard with his coworkers announced their observations of nuclear magnetic resonance in condensed phases. (Purcell emphasizes that NMR had been seen years earlier by Rabi in molecular beams.) Zavoisky’s discovery of electron paramagnetic resonance (EPR), published in 1945 in the Soviet Union, became known in the West at about the same time. With little understanding of how magnetic resonance works, I thought that EPR would be the way to look at the triplet state. The importance of NMR for chemistry was appreciated almost immediately after its discovery by a physicist, Philip Morrison. Lipkin asked him whether he wasn’t excited over this new way for measuring nuclear magnetic moments. Morrison allowed that yes, that was pretty nice, but the real use of it would be in chemistry.

I tried to arrange a summer visit to the newly established Brookhaven Laboratory for the summer of 1948. Bill Cohen had an EPR spectrometer; I would go there and look at the EPR of triplet states. It was five years before I could go to Brookhaven—a dismal but not uncommon business about clearance—and ten years before Clyde Hutchison did see the EPR of a triplet state.

As I tried to learn about magnetic resonance I realized the inadequacy of the concepts that I had used in my earlier work in optical spectroscopy. I listened to a lecture by Bloch in 1947. What’s this crossed coil business? You irradiate with one set of coils and pick up a signal with the other. Is it like resonant fluorescence? What’s all this about coherence? Spins can point up or down but not sideways as he alleges. And in Purcell’s early papers, this business about motional narrowing comes up. Fast molecular reorientations, the faster the better, produce narrowing of spectral features and improved resolution. That’s contrary to all my previous experience in optical spectroscopy, where one always tried to restrict molecular motions to improve resolution. Great new stuff to try to understand.

My entry into magnetic resonance was made easy by the arrival of George Pake at Washington University in the fall of 1948. His doctoral work, with Purcell on the NMR of a two-proton system, water, in calcium sulfate dihydrate (the “Pake Doublet”), had in it most of the ideas that were later involved in dealing with the EPR of electronic triplet states.

The vigorous research program in magnetic resonance that George Pake initiated at Washington University has grown over the years. Norberg, Conradi, and Fedders in physics, Ackerman, Schaefer, and Lin in chem-

istry are currently active in the field. Among the early advances were Lowe, Norberg, and Kessemeier's exploitation of magic angle spinning, and Lowe and Norberg's fourier transform spectroscopy. Lowe and Norberg recorded oscillatory free induction decays in the fluorine resonance of calcium fluoride. They realized that they were seeing the fourier transform of the cw spectrum. Norberg engaged an undergraduate to do the fourier transformations on a mechanical computer. I was reminded of Michelson's "harmonic analyzer" that he had used for converting his optical interferograms to frequency domain spectra.

Not long after Pake's arrival at Washington University, Professor Immanuel Estermann, then on loan to the Office of Naval Research (ONR), turned up at the University with the proposal that ONR support us in work on EPR. Perhaps a sensitive magnetometer for detection of submarines could be developed. ONR would support a few laboratories in the work. No reports or proposals—we would get together every few months and tell each other what we had been doing. We'd never had it so good.

So Pake, Jonathan Townsend, and I began work on EPR. My first observations of an EPR signal was done on a 14 MHz cw instrument designed and constructed by Nick Shuster, one of Pake's students. I prepared a polycrystalline sample of an organic free radical (tris p-nitrophenylmethyl) from starting material that Dave Lipkin had synthesized. We got a huge signal, only a few tenths of a gauss broad, at an applied field of 5.0 gauss. (I had underestimated the expected signal strength by a mere factor of 5×10^5 .) Much of the early EPR work on solid organic free radicals dealt with line breadths and g values of the pure solids. Townes had discovered that solid diphenylpicrylhydrazyl (DPPH), despite the expected dipolar breadth of several hundred gauss, had a line breadth of only one or two gauss. Van Vleck explained the phenomenon: The spin-spin exchange interaction conserves the second moment but increases the fourth moment of the spectral distribution, thus a narrow central component and broad weak wings. Studies of the solids would perhaps reveal something about the exchange interaction. One skeptic said to me "So what are you guys going to find out? Some g -values and some line breadths. Who cares?"

But we persisted. I am not sure whether it was the easy money from ONR or burning interest in exchange interactions that kept us at it. Jonathan Townsend constructed our first X-band spectrometer from a discarded mass spectrometer magnet, war surplus wave guides, and klystrons and home built electronics. (Surplus 2K25 klystrons cost less than one dollar. There were bins of them in war surplus stores.)

I tried to make a paramagnetic ionic solid in which both anions and

cations are paramagnetic. The anion was to be Fremy's ion nitrosyl-disulfonate, the cation Wurster's blue. Mixing approximately stoichiometric amounts of the two produced a solid. In my haste to look at the solid, I failed to remove the liquid that stuck to it and got a spectrum of three lines, centered close to $g = 2$ with separation 13.0 gauss between lines. We soon found that the crystals were diamagnetic and the three-lined spectrum came from the liquid that was sticking to them. It was our first hyperfine splitting in dilute liquid solution and came from the paramagnetic anion $(\text{SO}_3)_2\text{NO}^{2-}$. We put solids and triplet states aside and concentrated on our three-lined bonanza. (Jack Townsend called it our meal ticket.) At the next meeting of Estermann's group, Clyde Hutchison and I almost simultaneously informed each other "Hey, we've seen nitrogen hyperfine splitting in solutions." Clyde had looked at dilute solution of DPPH and had seen the splitting by two ^{14}N nuclei.

The happy arrangement with ONR that Estermann had managed was too good to last. The Way it Was evolved into the Way it Is: reports, proposals, grantsmanship, etc. We continued work with Fremy's salt. We found that in liquid solution the spectrum was accurately accounted for by a scalar interaction $\text{AI} \cdot \text{S}$. We measured the spectra over a range of fields from zero to several hundred gauss and found that everything fit the Breit-Rabi formula. It was astonishing, to me at least, that the same formula, properly scaled, that accounted for the magnetic field dependence of the spectra of deuterium atoms worked for an 81-electron polyatomic system tumbling about in a dense liquid, and that the only part of the hyperfine interaction that survives the buffeting in a liquid is the Fermi contact term. (Not quite true; the rest of the hyperfine interaction that is allegedly "averaged out" still affects relaxation processes. The averaging at zero field demonstrates the role of non-adiabaticity. Thus spins, owing to their gyroscopic properties, don't follow the molecular axes as the molecule tumbles.)

With improvements in sensitivity and resolution came the identification of many new radical species and the uncovering of detailed features of structure and dynamics. Our earliest observation of the EPR of triphenylmethyl in liquid solution revealed only a single line about 15 gauss broad. Even with the poor resolution then available to us, we could still see the 26 gauss ^{13}C hyperfine splitting in a sample enriched with ^{13}C in the methyl position. Howard Jarrett at duPont soon looked at triphenylmethyl in a good spectrometer that he had constructed; he got 196 lines—the complete proton hyperfine splitting was resolved. A rich lode of free radicals turned up following Dave Lipkin's suggestion that the adducts of alkali metals to aromatic hydrocarbons discovered by Scott, Walker, and Hansley in 1936 were anion-free radicals. He was right and

we, finally having equipment capable of resolving proton hyperfine splittings, had a new batch of free radicals to play with.

The origin of the Fermi contact hyperfine splittings by protons in planar aromatic radical ions (cations were soon included) was a matter of some interest for a while. The simple orbital picture of "the" odd electron occupying a pure π orbital with a node at the equilibrium position of the protons is clearly inadequate. McConnell's theory, later elaborated by others, accounts for the phenomena. To McConnell's annoyance, I pointed out that the theory had really been done in the 1930s by Fermi in his explanation of the contact interaction in a p state of thallium. The single configuration picture, with individual orbitals classified as π or σ , is simply inadequate. For odd alternate radicals such as triphenylmethyl, the question, "where is the odd electron?" clearly became inapplicable. Spin is distributed all over the molecule with alternating sign at adjacent carbon atoms. No single simple molecular orbital configuration is adequate; in the valence bond description, negative spin density turns up in the cross term of the hyperfine operator between pairs of valence bond structures.

In measuring rates of chemical processes and tracing out details of mechanisms via analysis of magnetic resonance spectra I found one of the most exciting features of the field. The earliest experiments had been done by Gutowsky & Saika and by Piette & Anderson. How do you get a rate from a continuous wave spectrum of a system at equilibrium? Does the observation disturb the equilibrium? Although the questions might now seem ridiculously naive, I worried about them nevertheless. To the question concerning disturbance of the equilibrium by the measurement, the answer is that it does. The measurement process induces coherences in the system; stochastic chemical events tend to destroy the coherences, and it's the destruction of the coherences that turn up in the spectra.

It's all pretty well illustrated by an encounter I had with the late V. V. Voevodskii, a Russian pioneer in chemical applications of EPR. He measured rates by preparing systems far off equilibrium and determining the time evolution of the composition of the mixture by EPR. He visited our laboratory during one of the periods of détente. After dinner, his Marxist zeal stimulated by capitalist Jack Daniels, he undertook to give me a lesson in dialectical materialism: "Colleague Weissman, I must tell you, in your country are the experiments static, in ours dynamic." My response: "It's OK, doc, we just take the Fourier transform."