NATIONAL ACADEMY OF SCIENCES

CLYDE ALLEN HUTCHISON JR.

1913—2005

A Biographical Memoir by

DONALD S. MCCLURE AND JACOB BIGELEISEN

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Clyde A. Hutchison Jr.

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BY DONALD S. MCCLURE AND JACOB BIGELEISEN

Beginning in the early 1950s, Clyde Hutchison Jr. explored the chemical applications of electron spin resonance (EPR), a type of spectroscopy that had just been invented and was undergoing explosive development. He was the first person to measure the electron spin resonance in the triplet states of organic molecules, thus finally confirming the triplet nature of the phosphorescent state of these molecules. He made wise choices of problems for his laboratory to work on, resulting in many firsts and a stream of well-trained and enthusiastic students. He did this with a combination of intense dedication and delightful wit that gave him a unique role in the world of physical chemistry.

Clyde was born into the family of a Methodist minister living in Alliance, Ohio, in the northeast of the state. He was followed by three siblings: sister Frances, brother Dwight, and sister Betty Lu. Their father expected each child to play at least two musical instruments and to practice at least an hour a day. Thus Clyde became an excellent pianist and organist and could sight-read any music placed before him. He played the organ in his father's church, and in later years he played the piano for the annual chemistry department Christmas party and much later for his friends in the retirement home where he lived.

Methodist ministers were subject to the church doctrine of itinerancy, and by the time Clyde was ready for high school the family was living in Plain City, Ohio, after having moved six times. This must have been a disadvantage in school and when combined with his brilliance and small stature it brought on scrapes with the local bullies. His sister recalls that he kept his dignity when these incidents happened. When he was ready for college, the family was living in the small rural town of Cedarville, Ohio, about 20 miles east of Dayton. Amazingly there were five colleges within 10 miles of each other, including Antioch, the most famous, and Cedarville college, the nearest and cheapest. Clyde took courses in Latin, religion, music, education, philosophy, and a little math and science. He graduated from Cedarville College in 1933 in the depth of the Great Depression, having taken summer courses so as to finish in three years. He had hoped to teach science courses in a high school but the only such jobs available also required him to handle the football team. This was outside of his area of expertise: He claimed to be an athletic moron; and he was smaller than any high school football player. All his college grades were “A’s” except for physical education. Failing in that career choice, he decided to apply to graduate school.

GRADUATE STUDIES

Clyde’s course of studies at Cedarville College did not prepare him for graduate work in chemistry. He had had a year of general chemistry and a year of analytical chemistry and no other courses in science by the end of his third year at Cedarville. He supplemented his education through a course in organic chemistry at Cedarville at the end of his third year and by lecture and laboratory courses in physical chemistry at Ohio State University during the 1933-1934 academic year. He began the required graduate core curriculum in chemistry at Ohio State in 1934, when he was also appointed a graduate assistant—a position he held for two years. In his last year, 1936-1937, he advanced to the position of assistant in general chemistry. During his graduate days, Clyde also took advanced courses in mathematics; there is no record of his having taken formal courses in physics or in the life sciences beyond high school.

Clyde elected to do his thesis research under the supervision of Professor Herrick L. Johnston. Johnston, as a graduate student with W. F. Giauque some five years earlier, had discovered the isotopes of oxygen, ^{17}O and ^{18}O. Following the discovery by Washburn and Urey of the electrolytic separation of deuterium from protium, Johnston measured the electrolytic separation of oxygen isotopes. Johnston was a difficult mentor. Most of his students had difficulty accommodating his volatile temperament. He was very demanding of his students and expected them to spend day and night, including weekends, in the laboratory. Clyde had but one difficulty in his relations with Johnston. In the spring of 1937, his last year of graduate work, Clyde announced to Johnston that he would not be spending the forthcoming Sunday in the laboratory. His parents along with his fiancé's parents were coming to Columbus to celebrate Clyde and Jane's engagement. Johnston warned Clyde that such action would jeopardize his professional career, but Johnston eventually adjusted to the reality of the situation.

The study Johnston had assigned to Clyde was the electrolytic separation of lithium isotopes at a mercury cathode. Since there were no mass spectrometers available to Johnston and Hutchison, they determined the isotopic ratios by gravimetric methods of a quality practiced for the accurate chemical determination of atomic weights. Aliquots of the aqueous and mercury phases were quantitatively converted to lithium fluoride (LiF). The crystals were purified and then melted and slowly recrystallized. The densities of the crystals were measured by their flotation temperatures in liquid bromoform to which small amounts of *n*-pentanol and *n*-hexanol had been added. The mixture was calibrated against water as a standard. The separation factor for lithium chloride solutions in water determined by Clyde was $\alpha = 1.055 \pm 0.005$ at room temperature. No change in the separation factor was found as a function of the amount of reaction or temperature. An identical separation factor was found for ethanol solutions. At least four other values of α had been published by the time Hutchison and Johnston's value had been published (1940). Fifteen years later workers at Oak Ridge National Laboratory published definitive equilibrium separation factors in agreement with the Johnston-Hutchison value.

Johnston and Hutchison's determination of the absolute density of LiF crystals was an order of magnitude better than any reported previously. From their density determination of LiF, the density of calcite and the lattice spacings of these two crystals, Clyde calculated the atomic weights of fluorine, and calcium from the known atomic weights of carbon and oxygen. Their value of the atomic weight of fluorine, 18.994, is to be compared with values determined from gas densities of 18.995 and 18.997. Their value for the atomic weight of calcium equal to 40.0842 ± 0.0049 is to be compared with Hoenigschmidt and Kempter's value of 40.085. We cite all of these to show the care with which Clyde did all his experimental work and the thorough analysis he made of all of his data. This is a trait we will find in all of Clyde's later work.

His personal life had advanced considerably in this period. He married Sarah Jane West of Cedarville in 1937 and their first child, Clyde III, was born the next year.

POSTDOCTORAL RESEARCH WITH HAROLD C. UREY

When Clyde completed his work for the doctorate he was awarded one of the two prestigious National Research Council Fellowships in chemistry for the year. Clyde was identified as one of the most outstanding doctoral recipients in chemistry of the year and a person who showed great promise. Clyde lived up to that expectation. He chose to utilize his fellowship to work with Harold C. Urey, the world's foremost isotope chemist of the time, at Columbia University. He, along with David W. Stewart, worked on the separation of the carbon isotopes, ^{13}C from ^{12}C, by counter current exchange between cyanide ion in aqueous solution and HCN gas. Inasmuch as HCN is extremely toxic, they kept a canary in the laboratory. If the canary was singing when they looked through the window in the laboratory door when they arrived in the morning, they knew it was safe to enter. It took two years to complete this study. During Clyde's second year he was supported by funds available to Urey from private foundations. To supply the demand for samples enriched in ^{13}C the Columbia plant was sold to the Eastman Kodak Co. in 1939.

Clyde accepted a faculty appointment at the University of Buffalo for the start of the 1939-1940 academic year. Their second child, Sarah Jane, was born in Buffalo in 1941.

SAM LABORATORY

It was not long before Clyde took a leave of absence from the University of Buffalo to respond to a call from Urey to work on the Manhattan Project at Columbia University in its SAM Laboratory. SAM was the code word for the Manhattan Project at Columbia University. The principal mission of that laboratory was to carry out the research and development of the gaseous diffusion method for the separation of the fissionable isotope, ^{235}U, from the abundant isotope, ^{238}U.

The laboratory also carried out a number of researches for the development of other isotope separation processes. Clyde never worked on the gaseous diffusion process. Urey felt a person with Clyde's abilities could be best utilized on these other programs, which included the gas centrifuge, separation of the boron isotopes, and chemical separation of the uranium isotopes. Clyde spent a year at the University of Virginia working with J. W. Beams on the separation of uranium isotopes by the countercurrent centrifuge. When primary responsibility for the development of the centrifuge was assigned to Westinghouse, Clyde returned to Columbia in 1943 and worked for a year on the boron isotope separation program. Clyde headed up the program to develop methods for the preparation of ton lots of high-purity crystalline boron of natural abundance and 50 kg lots of boron enriched in ^{10}B. After he carried out thermodynamic calculations on the feasibility of reducing boron halides with various reducing agents, Clyde chose the reduction of BCl_3 with H_2.

Early in 1944 Urey decided to revisit the possibility of chemical separation of the uranium isotopes. The success of the gaseous diffusion process was not certain. The other main enrichment process, electromagnetic separation, was experiencing serious problems. An impetus for reconsidering chemical exchange came from the theoretical predictions by Jacob Bigeleisen and Maria Goeppert-Mayer that chemical separation factors of the order of 1.001 could be realized in systems that involved changes in the bonding of the uranium atom. Clyde headed up a small group to explore such possibilities. One of the contributors to this memoir (J.B.) had the pleasure of working with Clyde during this period. Here he developed an appreciation of Clyde both as a person and as a scientist. This was a friendship that lasted for the rest of Clyde's life. The other one of us (D.S.M.) remembers the after-hours study group established by Clyde, where we studied group theory and mathematical analysis. Clyde continued these meetings for many decades, and the attendees were not only from Clyde's research group but also from various others.

UNIVERSITY OF CHICAGO

In the summer of 1945 Clyde accepted a faculty appointment at a new institute at the University of Chicago, the Institute for Nuclear Studies (now the Enrico Fermi Institute). He was to join with Harold Urey and Joseph Mayer from the Columbia University Chemistry Department and Maria Goeppert-Mayer and Willard F. Libby from the SAM Laboratory. Because of space shortage at the university itself, Clyde spent his first year at Chicago working at the Metallurgical Laboratory. There he worked on the Daniels high-temperature pile, which had beryllium oxide as a moderator. Clyde studied many of the properties of the moderator. In addition, he edited two volumes of the National Nuclear Energy Series, NNES, which covered part of the research done at SAM. One volume covered *Chemical Separation of the Uranium Isotopes.* The second volume coauthored with Martin Kilpatrick, Ellison H. Taylor, and Charles Judson covered *The Separation of the Boron Isotopes.* This was mopping-up work for the war project.

In the summer of 1946 Clyde moved to Jones Laboratory in the Department of Chemistry. Along with Norman Elliott he set up equipment to measure the magnetic susceptibilities of uranium compounds using the Gouy method. The goal was to decide where a new series of rare-earth-like elements began in the seventh row of the periodic table. Up to this time magnetic susceptibility measurements on uranium compounds had not given a clear verdict. The care with which they did this work, and especially the extended temperature range used, showed that the magnetic measurements were only consistent with a 5f series. This conclusion was confirmed a few years later in Clyde's laboratory by Gruen's measurements of the magnetic susceptibility of neptunium compounds, this time using the more sensitive Faraday balance.

Starting in the fall of 1946, Clyde taught the course in physical chemistry. His lectures were a model of clarity. Undergraduates who took the course and then went on to graduate studies in chemistry remarked that they learned more physical chemistry in Clyde's course than in their first year graduate programs.

Clyde and Jane's third child, Robert, was born in 1948 in Chicago.

Advances in electronics made during the war period were used by others to develop the new spectroscopies of electron and nuclear magnetic resonance. Clyde set up the equipment (with Clarence Arnow, who was in charge of construction and maintenance of the spectrometers for many decades), and began publishing in this field in 1949. EPR spectroscopy was then an exciting area of physical chemistry, and Clyde soon became one of its leaders. In fact, he was the first person to observe, in 1949, the electron resonance of an F-center, a favorite object of study by solid-state physicists. He and Ricardo Pastor made the first observations of electron resonance of alkali metals dissolved in liquid ammonia (1951). Then with Pastor, Kowalsky, and Wheland he made the first observation of hyperfine structure in the ESR spectrum of an organic free radical in solution, diphenyl picryl hydrazyl. Another first was the observation of the electron resonance of organic molecules in their triplet states. To sum up, this was a period in which he successfully explored the possible uses of electron spin resonance in chemistry.

Clyde presented the opening paper at a symposium on liquid ammonia in June 1953 on the work he and Ricardo Pastor were doing on alkali metals dissolved in liquid ammonia. The resonance line width was extremely narrow compared with the line widths observed in solids. This remarkable discovery was the subject of a paper by C. Kittel and J. Kaplan, who worked out a theory of the structure of liquid ammonia solutions based on Clyde's data. The four papers on this subject from Clyde's laboratory had an immediate and profound effect on the field.

Armed with this new dimension of spectroscopy, Clyde returned to the lanthanide and actinide elements. This was aided by a Guggenheim Fellowship, which supported a visit to Brebis Bleaney's laboratory at Oxford University in the 1955-1956 academic year. By measuring the hyperfine structure he was able to determine the nuclear spin and magnetic moment of ^{235}U, and in another publication the nuclear spin, the nuclear magnetic moment, and quadrupole moment of ^{233}U. Clyde wrote the review of progress in magnetic resonance for the 1956 *Annual Review of Physical Chemistry.*

The 1944 paper by Lewis and Kasha, which explained the phosphorescent states of organic molecules as the triplet states, had great impact on the community of physical chemists. But direct proof of the triplet nature of the emitting state was needed. The enhancement of the transition rate out of the metastable phosphorescent level by substituting heavy atoms showed that spin-orbit coupling was involved, a strong hint that a triplet to singlet transition was taking place. In a few cases the paramagnetism of the excited state could be measured. But Clyde wished to measure the electron spin resonance of a molecule in its phosphorescent state to see what the properties of this state would be. The solid glassy solutions of naphthalene at 77K, which phosphoresced strongly with a 2.6 sec lifetime, did not show a resonance signal. Previous optical work on oriented crystalline durene with a small percentage of naphthalene by one of us (D.S.M.) showed that the dissolved molecules were all oriented in the only two ways permitted by the durene structure, whereas in the glassy solid solutions the orientation was random. This system showed the first magnetic resonance of a phosphorescent molecule, and finally gave unambiguous proof of the triplet state hypothesis. The crystalline solid solution method was applied many times in later work in the Hutchison laboratory.

The experimental results on naphthalene were expressed in terms of a spin Hamiltonian, two parameters of which described an anisotropic zero-field splitting. This anisotropy explained why the experiments with random solid solutions failed: It simply led to a very broad line. The values of these parameters were calculated by others, assuming that the two electrons of the triplet state were coupled by a magnetic dipole-dipole interaction. The experimental results supported the calculated values. More detailed information about the triplet state came from an analysis of the proton-π-electron hyperfine coupling. All of these results neatly supported the recently developed theories of π-electron systems of Pariser, Parr, and Pople. (The papers on naphthalene were the Citation Classics of *Current Contents* for June 29, 1992).

There followed a series of papers on triplet ground state molecules oriented in single crystals. For example, a host crystal of diphenyl-diazo-methane when irradiated produces some diphenyl methylene (whose ground state was shown to be a triplet) oriented in the same way as the host molecules. Here Clyde introduced the new technique of electron-nuclear double resonance (ENDOR spectroscopy) in order to find the electron spin density distribution in the aromatic system. In a tour de force he used this and related compounds to follow the kinetics of chemical reactions in the crystalline state. In another experiment he used a biphenyl host crystal with very low concentrations of naphthalene and phenanthrene to study the mechanism of the transfer of phenanthrene triplet excitation to the naphthalene triplet level. These experiments were not easy to carry out, requiring several types of spectrometers, but were done meticulously and thoroughly. Super technician Clark Davoust made important contributions to the development of these instruments. In all, there were about 37 papers on organic systems in triplet states published between 1952 and 1981.

At the same time, his interests in the lanthanide and actinide compounds continued. Much work had already been done on the optical spectra by the 1970s and the theories of the energy levels of rare-earth ions in crystals were well developed. Clyde's 1971 paper on the spin resonance of Nd^{+3} in host crystals of $LaCl_3$ was the first to explore the application of this spectroscopy to excited states. The data from this work led to several useful comparisons of theory and experiment. There were a total of 25 papers in this general area between 1952 and 1989.

Between 1977 and 1996 there were 21 papers on determining the location of protons in molecules of biological interest. X-ray crystallography could hardly do this because of the relatively low density of the electrons in the vicinity of a hydrogen atom. ENDOR methods on the other hand could easily detect the nuclear hyperfine structure caused by H atoms. If a reference atom having a net electron spin were present in the molecule it could serve as the basis for ENDOR spectroscopy of the hydrogens. The test molecule chosen for many of these studies was lanthanum nicotinate dihydrate with a small proportion of the La atoms replaced by a rare-earth atom having an electron spin, such as neodymium. The hydrogens occurred in the waters of hydration and were involved in hydrogen bonds to nitrogens while the water oxygens were coordinated to the neodymium ion. The experiments were complex and the data analysis difficult, but hydrogen positions were found. Much of this work was done with Bleaney and his group at Oxford, where on his third visit, 1981-1982, he was appointed to the George Eastman Professorship. Clyde wrote a comprehensive article on the determination of the structure of molecules by way of resonance methods in 1992.

After reading a large number of Clyde's publications, one is impressed by the care taken with each one and how thoroughly he covered each field of investigation undertaken. There are no wasted moves in this body of work.

A UNIQUE PERSONALITY

Clyde Hutchison Jr. was a modest but self-confident individual. He was polite in all his interpersonal relationships. He never had a bad word to say about anyone. When he disagreed with you, he did so in a nonconfrontational manner. He respected confidences. Thus he never informed his wife, Jane, that their son, Clyde III, was a candidate for election to the National Academy of Sciences.

Clyde delighted in using precision to tease and tantalize. If someone, suggesting an appointment, said, "Could we meet at 5 o'clock tomorrow?" Clyde would answer, "Well, I'm usually asleep at that hour, but if that's what you would like, all right . . . (long pause) . . . Ooooh, perhaps you mean 1700 hours! Would that be right?" He insisted that the logical way to keep time was with a 24-hour day, so the clocks in his laboratory all read from 1 to 24, rather than from 1 to 12. His enemy was ambiguity.

He had lunch weekly with his graduate students, postdoctoral fellows, and a few colleagues. When he got the check at the end of the meal, he would calculate each person's pro rata share to within one cent. Clyde did not believe in dividing the bill equally. Each person took care of his own tip. When Clyde ate lunch at the Quadrangle Club with faculty members from the university, he regularly had a plain hamburger on a bun. There were no side accompaniments. This became known as a Hutchison. The reader of this memoir will note that there is no comma in Clyde's name. This is neither an error nor an oversight. This is the way Clyde wanted it. When someone, particularly an editor, wrote his name "Clyde A. Hutchison, Jr." Clyde would inform the individual that there was no comma and that he had the privilege of spelling his name. There was a lot of whimsy in Clyde. From time to time Clyde and Jane opened their home for a social evening, with good food, music, games, sparkling conversation, and much good humor. The Hutchison house on Harper Avenue was roomy and well appointed, with an eye for interesting art, and it featured Clyde's thriving collection of cacti. It was a special point that there was no TV anywhere. Clyde was much stimulated by his Chicago surroundings, and thrived in the company of the many other outstanding members of the faculty. He religiously attended seminars in many physical science disciplines.

Although Clyde was an outstanding lecturer in formal courses, in keeping with his own way of learning science, he considered formal courses at best a necessary evil. For many years he ran informal weekly study seminars that attracted students and faculty. He would choose a topic that he felt was important, usually new, something that physical chemists should know, and would then set about creating a series of reading and speaking assignments that made all the participants well educated in the new field.

Clyde was an excellent speaker and had more invitations—both foreign and domestic—than he could accept. Some of these lectureships were:

1959	Riley Lecturer, Notre Dame University
1963	Visiting professor, Department of Chemistry, Stanford University
1964	Venable Lecturer, University of North Carolina
1967	Physics lecturer and Royal Society Lecturer, University of Canterbury, Christchurch, New Zealand
1968	Lecturer, Royal Institute of Chemistry, London
1969	Visiting professor, State University of New York at Stony Brook
1970	Visiting lecturer, Weizmann Institute of Science, Rehovot, Israel
1971	Visiting professor, Pennsylvania State University
1973, 1982	Ehrenfest Lecturer, University of Leiden
1975	Visiting professor, Japan Society for the Promotion of Science
1978	Kistiakowsky Lecturer, Harvard University
1981-1982	George Eastman Professor, University of Oxford
1986	Visiting lecturer, Chinese Academy of Sciences

PROFESSIONAL ACTIVITIES

Clyde followed the family tradition of a dedication to public service. Both professional organizations and academic institutions called on him because of his leadership qualities, his good judgment, and the seriousness with which he took his commitments. At the University of Chicago he served as chairman of the Chemistry Department; he declined an invitation to be appointed dean of physical sciences because that position would take too much time from his research and teaching.

Clyde served a stint as editor of the *Journal of Chemical*

Physics, following which he served on the Editorial Board of *Annual Reviews of Physical Chemistry.* He served on the visiting committees for chemistry at Brookhaven National Laboratory, Oak Ridge National Laboratory, Massachusetts Institute of Technology, National Bureau of Standards, and the National Science Foundation. He was a long-term consultant to both the Argonne National Laboratory and Los Alamos Laboratory. Additionally, he was a member of the Board of Directors of the Ohio State University Research Foundation and a member of the evaluation panel for the Chemistry Branch of the U.S. Air Force Office of Scientific Research. He served as chairman of both the Division of Physical Chemistry of the American Chemical Society and the Division of Chemical Physics of the American Physical Society. He also served on the Council of the latter organization.

Clyde was a member of the American Chemical Society, the American Association for the Advancement of Science, a fellow of the American Physical Society, and a member of Sigma Xi. He was elected to membership in the National Academy of Sciences in 1963 and to fellowship in the American Academy of Arts and Sciences in 1968.

ACKNOWLEDGMENTS

Clyde's three children, Clyde Hutchison III, Sarah Dunn, and Robert Hutchison, and his sister, Frances Bray, each contributed importantly to this memoir. His former students John Weil, Arthur Heiss, and Ralph Weber provided technical information and anecdotes about life in the Hutchison lab.

We are also grateful to Cedarville University (formerly Cedarville College) and the Ohio State University for information about Clyde in their records. The bulk of Clyde's papers and records are held in the archives of the Regenstein

Library of the University of Chicago. We also thank Professor R. Stephen Berry for contributions about Clyde as a colleague at the University of Chicago. We also thank John Weil for his careful reading of the manuscript and many suggestions for its improvement.

HONORS

1937-1938	Postdoctoral fellow, National Research Council, Columbia University
1955-1956	J. S. Guggenheim Memorial Foundation Fellowship, Oxford University
1963	Member, National Academy of Sciences
1968	Fellow, American Academy of Arts and Sciences
1970	The Ohio State University Centennial Achievement Award
1972	Peter Debye Award in Physical Chemistry of the American Chemical Society
1972-1973	J. S. Guggenheim Memorial Foundation Fellowship, Oxford University
1981-1982	George Eastman Professor, University of Oxford

PROFESSIONAL APPOINTMENTS

1938-1939	Research associate, Columbia University
1942-1943	Manhattan District Project, University of Virginia
1943-1945	SAM Laboratories, Columbia University
1945-1946	Metallurgical Laboratory, University of Chicago

ACADEMIC APPOINTMENTS

1939-1945	Assistant professor, University of Buffalo
1945-2005	University of Chicago
1945-1948	Assistant professor, Enrico Fermi Institute
1948-1950	Assistant professor, Enrico Fermi Institute and Department of Chemistry
1950-1954	Associate professor, Enrico Fermi Institute and Department of Chemistry
1954-1963	Professor, Enrico Fermi Institute and Department of

	Chemistry
1963-1969	Carl William Eisendrath Professor, Enrico Fermi Institute and Department of Chemistry
1969-1983	Carl William Eisendrath Distinguished Service Professor, Enrico Fermi Institute and Department of Chemistry
1983-2005	Carl William Eisendrath Distinguished Service Professor Emeritus, Enrico Fermi Institute and Department of Chemistry

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