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EARLY HISTORY OF NMR AT LOS ALAMOS

by

Jasper A. Jackson

ABSTRACT

Nuclear magnetic resonance (NMR) spectroscopy has developed into an important research tool in chemistry. More recently, NMR imaging and in vivo spectroscopy promise to produce a revolution in medicine and biochemistry. Early experiments at Los Alamos led to DOE programs involving stable isotopes of importance to biology and to medicine. These events are briefly recounted.

The first nuclear magnetic resonance (NMR) experiment in which Los Alamos personnel were involved was in 1946. Rod Spence and Al Graves from Los Alamos Laboratory and Felix Bloch (codiscoverer of NMR) and Martin Packard from Stanford University measured the frequency of the NMR signal from tritium and thus derived the magnetic moment of the triton.¹

I first came to Los Alamos in June 1951, to Group GMX-5, where I worked on scintillators and photomultipliers. In 1952, I returned to school to do Raman spectroscopy on tetraethyllead on an Ethyl Corporation Fellowship. I returned to Group CMR-2 at Los Alamos to do Raman spectroscopy in the summer of 1953. The CMR-2 Raman spectrograph was not yet operational, so I worked with W. B. (Burt) Lewis on his electron spin resonance (ESR) program. I used a commercial NMR magnetometer (Pound-Watkins oscillating detector) to map the magnetic field in Lewis's 12-in. Varian magnet. In the summer of 1954, I worked with Burt Lewis to modify the NMR magnetometer for various samples, and we obtained corresponding low-resolution NMR spectra.

I returned permanently to Los Alamos in April 1956. Henry Taube, a professor from the University of Chicago, was a consultant to CMR-2 that summer, and he conceived the idea that the newly observed NMR of oxygen-17 could be used to study ionic hydration in aqueous solution if separate signals were observed from oxygen in the water of the first coordination sphere of the ion and from bulk water. Based on information supplied by Burt Lewis, Henry Taube, and the author, CMF-2 Group Leader Joe Lemons wrote a lengthy memo to Robert Fowler, the CMF Division Leader, outlining many potential applications of NMR to inorganic chemistry using the signals obtainable from many different isotopes in addition to oxygen-17. This proposal was approved by Fowler, and I was assigned to go to Varian Associates in Palo Alto, California, to attend the First Varian NMR Workshop on NMR and ESR; I also arranged for purchase and installation of the first NMR Varian model V4200 wide-line high-sensitivity spectrometer at Los Alamos. By the summer of 1957, it was installed and operating. In 1957 and 1958, we studied NMR signals (from other nuclei as well as those of oxygen-17) from many kinds of samples, but we were unsuccessful in detecting a separate signal from water in the hydration shell.

In the summer of 1959, Henry Taube made the brilliant suggestion to add a paramagnetic specie (with a short exchange time for its water of hydration) to the original aqueous solution of nonmagnetic cations. For example, to a solution of $\text{Al}(\text{ClO}_4)_3$, which showed only a single oxygen-water NMR signal, he added a dilute concentration of $\text{Co}(\text{ClO}_4)_2$. The resulting spectrum showed the oxygen-17 NMR signal in bulk water shifted downfield (and broadened). A residual peak remained at the original bulk water position, which we attributed to the relatively tightly bound water in the hydration shell of the Al^{+++} ion. This was the first reported use of a paramagnetic shift reagent.² We also saw hydration signals from Be^{+++} and Ga^{+++} ions in aqueous solution. The signal-to-noise ratio (S/N) in these solutions with oxygen of normal abundance was too small to make a quantitative measurement of the hydration number.

In work before the paramagnetic shift experiment, we had purchased (for \$1000) 1 g of water enriched in oxygen-17 to 1 per cent (compared with the normal abundance of 0.037 per cent) from the Weissman Institute of Science in

Israel, which was then the only source of enriched oxygen-17. In the summer of 1959, a meeting was held in the office of Robert D. Fowler. Present were Joe F. Lemons, Henry Taube, W. B. Lewis, and I from CMF-2; and Eugene Robinson, CMF-4 Group Leader, with B. B. McInteer and Bob Potter from CMF-4. Henry Taube and I presented our results on detecting (for the first time, by any direct instrumental technique) a distinct signal from water in the first coordination sphere of ions in solution. We said we would like to improve the S/N but we were reluctant to spend \$1000/g for oxygen-17-enriched water from Israel.

Fowler said he was very impressed by our results, and he told Robinson and McInteer that he would allow them to build a plant to produce material enriched in oxygen-17 for our NMR program. Robinson, McInteer, and Potter had previously separated tritium from hydrogen in connection with the nuclear weapons program, and they had independently proposed to build a cryogenic oxygen distillation column at DP Site (TA-21) to study certain aspects of isotope separation. By Christmas 1959, they were ready to begin separating oxygen isotopes. Their early production was enriched to about 1 per cent in oxygen-17. Production for the first few months was modest. About this time, in Switzerland, the separation factor for oxygen isotopes was discovered to be about an order of magnitude larger for distillation of liquid nitric oxide (NO) than that for liquid oxygen. Robinson, McInteer, and Potter thus modified their column for NO and began producing copious quantities of oxygen-17, oxygen-18, and nitrogen-15.

To increase the efficient use of this supply of isotopes, I began a semiweekly series of lectures to personnel in CMF-2 (and others who were interested) on the principles and practice of NMR. These were supplemented by actual "hands-on" instruction with the NMR spectrometer. By 1963, approximately half the staff members in CMF-2 were actively engaged in NMR and oxygen-17 research projects. Many pioneering papers were published by this group, which included Sherman Rabideau, W. Burton Lewis, Mohammed Alei, and Al Zeltman.

In early 1963, Eugene Robinson proposed to CMF Division Leader Fowler that CMF-4 buy its own NMR instrument. Because the one purchased by CMF-2 in

1957 was a "wide-line," low-resolution instrument, he proposed that CMF-4 be allowed to purchase one of the newly developed Varian high-resolution spectrometers. Fowler agreed that the high-resolution instrument would be a useful addition, but he directed that it be placed in CMF-2. In April 1963, I again visited Varian and arranged for purchase of a DP-60, combined high-resolution, wide-line spectrometer. This was delivered and placed in operation in the summer of 1964.

I transferred from Group CMF-2 to the Physics Division Office (P-DOR) in September 1964 to work on polarized nuclear targets.

Eugene Robinson was a very resourceful and persistent individual, and he was determined to obtain an NMR spectrometer. Group GMX-2 was involved in the study of explosive compounds and had purchased a Varian HR-60 high-resolution spectrometer for analytic studies of organic chemicals. This machine was very complex, and they had no one qualified to run it. Robinson, therefore, offered to trade it for a much simpler instrument, which he would supply, for routine analysis. By the time the Varian HR-60 was transferred to CMF-4 in 1965, it had been converted to a DP-60 dual-purpose instrument capable of both wide-line and high-resolution operation.

I attended the Gordon Conference on NMR in New Hampshire during the summer of 1963. There I met L. O. (Tom) Morgan of the Chemistry Department of the University of Texas at Austin. Several members of CMF-2 were acquainted with Tom from their association at the Metallurgical Laboratory of the University of Chicago, on the Manhattan Project during World War II. He had since begun research in NMR, and I asked him about becoming a consultant to CMF-2. He visited Los Alamos at Christmas of 1963 and arranged to visit CMF-2 in the summer of 1964. He subsequently became a regular consultant to Los Alamos and worked with members of both CMF-2 and CMF-4 (later called CNC-4 and INC-4) for many years.

In 1967, Robinson hired Eiichi Fukushima, who had recently finished his graduate work at the University of Washington (Seattle) in physics, specializing in NMR. Eiichi subsequently built a very respectable NMR program in the study of solids and in developing NMR instrumentation.

In P-DOR, I built an NMR instrument large enough to hold a 150-g rat, and in 1967 (with Wright Langham, H-4 Group Leader), I made the first in vivo NMR observations on a whole animal.

Nick Matwiyoff, who had been a summer consultant at Los Alamos, was hired by Group CMF-4 in 1968.

In 1969, Bert Tolbert (as a graduate student, he had participated in the first observation of nitrogen NMR) was on a leave of absence from his position at the University of Colorado to the Division of Biology and Medicine of the Atomic Energy Commission (AEC) in Washington, DC. He had worked with Melvin Calvin at Berkeley using carbon-14 as a radioactive tracer, and he was interested in using carbon-13 as a nonradioactive tracer. He was aware of the oxygen isotope production program at Los Alamos, which also produced nitrogen-15, and he wondered what the interest in the biological community would be if the facility's production could be expanded to produce large quantities of carbon-13. He circulated a questionnaire nationally to many research biologists and was overwhelmed by the response.

In the summer of 1969, a delegation from AEC's Division of Biology and Medicine visited Los Alamos to explore the possibility of adding carbon-13 to the production facility's output. Eugene Robinson would agree to the conversion on only one condition: that the AEC must supply CMF-4 with the latest in NMR instrumentation. This resulted in CMF-4's acquisition of a Varian XL-100 spectrometer.

With Wright Langham, I wrote a section of the carbon-13 project proposal. We proposed to establish a program for study of radiation damage to biological systems using carbon-13-labeled compounds, electron spin resonance, and electron nuclear double resonance (ENDOR). We had no leverage like Robinson had, and it was not funded, even though it was acknowledged to be a well-presented, logical addition to the program.

The isotopes of carbon, oxygen, and nitrogen (ICON) production program has been very successful, and Los Alamos is now the National Stable Isotope Resource.

The NMR program in CMF-2 continued until 1972, when support was terminated as a result of Laboratory retrenchment following cancellation of

the Rover Program. By this time, NMR had become a common laboratory tool and other groups had obtained their own instruments.

Joe Lemons died in 1965. Robert Fowler retired in 1970. Wright Langham died in the Ross Aviation crash in Albuquerque on 19 May 1972. Eugene Robinson died in June 1972. Henry Taube ^{moved to Stanford in 1961, but} continued to consult with Group CMF-2 until the early 1970s, and he received the Nobel Prize in Chemistry in 1983 for his work in electron transfer mechanisms involved in chemical reactions.

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