NUCLEAR MAGNETIC RESONANCE IN HYDRATED
CRYSTALS - POTASSIUM OXALATE
MONOHYDRATE

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NUCLEAR MAGNETIC RESONANCE IN HYDRATED
CRYSTALS - POTASSIUM OXALATE
MONOHYDRATE

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CHAPTER I

INTRODUCTION

The problem of this study was the measurement of the proton-proton separation in the water molecule of hydration in a single crystal of potassium oxalate monohydrate, \( \text{K}_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O} \). The measurement was made using nuclear magnetic resonance techniques. The experimentally determined separation was found to be \( 1.57 \pm 0.02 \, \text{Å} \).

Nuclear magnetic moments were first postulated by Pauli (6, p. 741) in 1924 in order to explain hyperfine structure in optical spectra, and the earliest measurements of nuclear spin and magnetic moments were actually made with high resolution spectroscopic equipment (4). Considerably more accurate measurements, however, were devised in the magnetic resonance molecular beam experiments of Rabi and co-workers at Columbia (3, p. 323). The resonance techniques were extended in 1946 to the study of nuclear moments in normal materials (solids, liquids, gases) simultaneously by Purcell, Torrey, and Pound at Harvard (7, p. 37) and by Bloch, Hansen, and Packard at Stanford (2, p. 127).

The nuclear magnetic resonance (NMR) methods devised by Bloch and Purcell have provided a method for studying
nuclear, atomic, molecular, and even crystalline properties of matter with relatively inexpensive equipment and in a manner which neither destroys nor damages the sample in the experimental process.

Since 1946, the NMR techniques have been employed to determine the following (1, p. 5):

1. Nuclear properties
2. Gyromagnetic ratios
3. Nuclear spin numbers
4. Nuclear magnetic moments
5. Nuclear quadrupole moments
6. Magnetic fields
7. Chemical identification and analysis
8. Diffusion constants
9. Crystal structure

This particular investigation has to do with the application of NMR techniques to a problem in crystal structure analysis, a procedure originally devised by Pake (5, p. 327), and since employed by many others (1, p. 233).
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CHAPTER II

THEORY

Basic Theory of Magnetic Resonance

Consider an isolated nucleus in a steady magnetic field, $H_0$. Consider further that the nucleus has a nuclear spin number greater than zero so that it may possess a magnetic moment. Quantum mechanics shows that the angular momentum vector has a magnitude, $[I(I + 1)]^{1/2}$ or $\frac{\hbar}{2}$ (3, p. 75), where $I$ is an integer or half-integer (spin number) characteristic of the nucleus. The only measurable values of the angular momentum vector, however, are the projections, $\hbar m$, in some quantizing direction, where $m$, the magnetic quantum number, takes any of the $(2I + 1)$ values in the series

$I, I - 1, I - 2, \ldots -(I - 2), -(I - 1), -I$.

Corresponding to the quantization of the angular momentum components, the proportional nuclear magnetic moment also has $(2I + 1)$ components, and the magnitude of the magnetic moment vector is

$$\sqrt{\frac{I + 1}{I}} \mu,$$

where $\mu$ is the maximum measurable component of the magnetic moment vector. The measurable components of the magnetic
moment vector are given by the values of $m\mu/I$, forming the series

$$\mu, (I - 1)\mu/I, \ldots -(I - 1)\mu/I, \ldots -\mu.$$ 

The energy levels of the nuclear magnet in the magnetic field, $H_0$, are given by the $(2I + 1)$ value of $-m\mu H_0/I$. Adjacent energy levels are separated by $\mu H_0/I$.

The quantum mechanical selection rules governing the allowable transitions between the nuclear spin energy levels permit only those transitions in which $m$ changes by $\pm 1$. A quantum of energy may therefore excite transitions between adjacent energy levels if the quantum has the same magnitude as the energy level spacing; i.e.,

$$h\nu_0 = \mu H_0/I,$$

where $\nu_0$ is the frequency of the electromagnetic radiation supplying the energy quantum.

In order to excite nuclear resonance transitions, it is also necessary to supply radiation with the magnetic vector circularly polarized in a plane perpendicular to the steady magnetic field. A classical argument is sufficient here. If a magnetic dipole is placed in a magnetic field, $H_0$, the dipole precesses about the direction of the applied field. The rate of precession is given by the Larmor angular frequency, $\omega_0 = \gamma H_0$, where $\gamma$ is the gyromagnetic ratio of the dipole. The addition of a small magnetic field, $H_1$, at right angles to the plane containing both $\mu$ and $H_0$ will cause the dipole
to experience a torque which tends to change the angle between $H_0$ and $\mu$. Since $\mu$ precesses about $H_0$, the small magnetic field, $H_1$, must also rotate about $H_0$ in synchronism with the precession of the dipole if the angle between $\mu$ and $H_0$ (and thus the energy) is to change steadily. If $H_1$ is out of phase with the Larmor precession frequency in any way, $H_1$ will only cause small perturbations in the orientation of $\mu$ which cancel and cause no net effect. The resonant energy absorption will only occur when the frequency of the rotating field, $2\nu$, is equal to the Larmor precession frequency, $\nu_0$. Both the quantum and the classical theories agree that the field, $H_1$, must be normal to $H_0$ and circularly polarized with a frequency exactly equal to the Larmor frequency of the dipole in $H_0$ if NMR absorption is to occur.

A linearly oscillating magnetic field can be regarded as the superposition of two counter-rotating fields. Thus, if the linearly oscillating field has magnitude $2H_1$, each of the rotating components will have magnitude $H_1$, rotating in opposite directions. Linearly polarized radiation is, thus, adequate for exciting NMR transitions. One component can follow the precession; the other will have a negligible effect (1, p. 522).

The basic conditions necessary for observing a nuclear magnetic resonance absorption may now be enumerated:

1. The nuclei must have magnetic moments different from zero;
2. A large number of the nuclei must be polarized in a large uniform magnetic field, \( H_0 \);

3. The polarized nuclei must be irradiated with a radiofrequency field polarized at right angles to \( H_0 \); and

4. The radiofrequency radiation bath must be related to the polarizing field, \( H_0 \), through the Larmor condition, \( \omega_0 = \gamma H_0 \), where \( \gamma = \frac{e}{m} \).

Magnetic Resonance in Hydrated Crystals (2)

The properties of a nuclear magnetic absorption line are greatly influenced by the magnetic environment of the absorbing nuclei. In addition to the externally applied magnetic field, \( H_0 \), a local field produced by the magnetic moments of the neighboring nuclei also contributes to the magnetic environment of any particular nucleus. This additional local field is quite small in liquid and gas samples because of the averaging effect of the random molecular motion. The nuclei in a crystal, however, are relatively fixed; the regular order of the nuclear moments in the crystalline lattice of a single crystal may well have a pronounced effect on the position, width, and shape of the NMR absorption spectrum.

The hydrogen protons in hydrated water molecules in crystals are located in closely spaced pairs (about 1.5 Å). Neighboring pairs, however, are separated by a distance almost twice as great (about 2.5 Å). Since dipole fields fall off with the inverse cube of the distance from the dipole,
the proton pairs in the waters of hydration may be considered, to a first approximation, as magnetically isolated. The local field at either proton, then, is due only to the magnetic dipole-dipole interaction with the partner proton. Classically, one expects each nuclear dipole to produce at its partner a magnetic field of a few gauss, and the effective field producing nuclear precession is simply $H_0$ plus the component of the local field in the direction of $H_0$. If $\theta$ is the angle between the steady magnetic field and the line joining the centers of the interacting nuclei, the parallel local field component varies as $(3 \cos^2 \theta - 1)$; the effective field, $H^*$, at either nucleus is given by

$$H^* = H_0 \pm \alpha (3 \cos^2 \theta - 1),$$

where the $\pm$ sign accounts for the two possible orientations of the proton magnetic moment, and $\alpha$ is an interaction field parameter to be fixed through a more rigorous quantum mechanical calculation.

In a large collection of nuclear magnetic moments with spin $I = \frac{1}{2}$, the two allowed spin orientations (parallel and anti-parallel to $H_0$) are almost equally probable because of the small energy difference in the two orientations. In a crystal containing many identically oriented proton pairs (as in the hydrates) about half the nuclei experience local fields, $- \alpha (3 \cos^2 \theta - 1)$, while the remainder experience local fields, $+ \alpha (3 \cos^2 \theta - 1)$. Thus, there are two resonance conditions in such crystals corresponding to the two external field values
\[ H_0 = \frac{\mu_0}{j} \pm \alpha(3 \cos^2 \theta - 1), \]

and two resonance absorption lines appear symmetrically displaced about \( \frac{\mu_0}{j} \) by the amount

\[ \Delta H = \pm \alpha(3 \cos^2 \theta - 1). \]

If the crystal contains more than one proton-pair orientation, a separate pair of lines occurs for each such orientation.

Since the dipole-dipole splitting of the nuclear resonance absorption depends on the relative orientation of \( H_0 \) and the line joining the dipoles, this process is most easily studied by following the resonance splitting as the crystal is rotated in the magnetic field. The angle, \( \theta \), in the line-splitting formula will only correspond to an actual angle of physical rotation of the crystal in that special case in which the proton-proton line happens to lie in the plane of rotation. If the proton-proton line makes an angle, \( \delta \), with the plane of rotation as shown in Figure 1, the line-splitting formula takes the form

\[ \Delta H = \alpha \left[ 3 \cos^2 \delta \cos^2 (\phi - \phi_0) - 1 \right], \]

where \( \phi \) is the physical angle of rotation, and \( \phi_0 \) is some reference value of \( \phi \) related to the geometry of the crystal.

If the Schrodinger equation is solved for the magnetic dipole-dipole perturbation of the nuclear Zeeman energy levels, the parameter, \( \alpha \), is found to be

\[ \alpha = \frac{3}{2} \frac{\mu}{r^3} \]

where \( \mu \) is the nuclear magnetic moment and \( r \) represents the
dipole-dipole separation. The nuclear line shifts, then takes the explicit form

\[ \Delta H = \pm \frac{3}{2r^3} \left[ 3 \cos^2 \sigma \cos^2 (\phi - \phi_0) - 1 \right]. \]
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CHAPTER III

EXPERIMENTAL DETAILS

The Signal Circuit

The experiment was performed at room temperature. The apparatus used is shown in block diagram form in Figure 2.

The sample was contained in a cylindrical coil placed with its axis perpendicular to the steady magnetic field. This coil and a tunable condenser formed a parallel tuned circuit connected to the grid of a radiofrequency oscillator. Positive feedback maintained the oscillations and caused a radiofrequency current to flow in the specimen coil. When proper adjustment of the external field, $H_0$, caused the nuclear magnetic resonance to occur, there was an absorption of radiofrequency energy. The absorption reaction on the oscillator caused the oscillation level to decrease. The steady magnetic field was modulated at 500 cps, with an amplitude of the order of a gauss. This field modulation in turn modulated the resonance absorption and likewise the oscillator level with a signal proportional to the slope of the resonance absorption curve. The oscillator signal was handled much the same as an amplitude-modulated radio signal. The radiofrequency portion was rectified, and the remaining
audio signal was passed through several stages of audio amplification.

Since the nuclear resonance signal was quite small, thermal and microphonic noise was much larger than the resonance signal. The signal-to-noise ratio was increased by passing the signal through a narrow-band amplifier tuned to the same frequency as the modulation of the steady magnetic field. Noise was further reduced by synchronously rectifying the modulation signal with a mechanical chopper, driven at the same frequency as the modulation on the steady magnetic field, and the signal was adjusted in phase so as to maximize the rectified absorption modulation signal. The chopper output was smoothed with an RC filter, selected to produce an over-all band width for the amplification system of about two cycles per second. The smoothed chopper output was recorded on a strip-chart recorder.

Circuit diagrams for the oscillator-detector and associated amplifier, the phase-shift, the 500 cps narrow-band amplifier, and the chopper circuit are shown in Figures 3 through 7. The remainder of the electronic apparatus outlined in Figure 2 was commercially manufactured. The audio oscillator was a Hewlett-Packard 202D; the strip-chart recorder was a Varian G-10; the modulation oscillator amplifier was a 25-watt Heathkit. All power for the electronic apparatus was supplied by a Lambda C-280 M-677 power supply, with the exception of the filament supply for the oscillator-detector.
The oscillator-detector filaments were heated from a 6-volt storage battery.

The Magnet

The steady magnetic field was provided by an electromagnet manufactured by Pacific Electric Motor Company, Model 12A-LI. The air-gap was 1.75 inches over 6-inch-diameter pole faces. The magnet power supply was Model HS-1050 manufactured by the Harvey-Wells Corporation. The current regulation was one part in $10^5$.

The magnetic field was swept linearly in time by varying the reference voltage in the magnet power supply. A 6-volt battery was connected through fixed resistors to a ten-turn-Micropot. The voltage taken across the Micropot was superimposed on the internal reference voltage in the power supply. The lower level of the sweep was adjusted with a variable resistance in series with the Micropot; the regular magnet-supply controls were used to adjust the upper level of the sweep. The Micropot was driven at one revolution per minute. The sweep circuitry is shown in Figure 8.

The modulating field was produced by a 25-turn coil taped to each of the magnet pole faces. The coils were driven by the Heathkit amplifier which derived its input from the Hewlett-Packard 202D signal generator.

A list of constants pertinent to the equipment and the experiment is shown below:
1. Steady Magnetic Field. . . . . . . 6.95K gauss
2. Magnet Power Supply. . . . . . . 23 amps
3. Modulating Frequency . . . . . . . 500 cps
4. Modulating Level . . . . . . . . . 1.4 gauss
5. Sweep Rate Resistor. . . . . . . . 100K ohms
6. Sweep Rate . . . . . . . . . . . . 4 gauss/inch
7. Oscillation Frequency. . . . . . . 29.6 meg. cps
8. Oscillator Filament Voltage. . . . 4.25 volts
9. Sample Coil Diameter . . . . . . . 1 inch
10. Sample Coil Length . . . . . . . 1 inch
11. Turns on Sample Coil . . . . . . . 3.5
12. Chopper Voltage. . . . . . . . . 6.1 volts
13. Chopper Time Constant. . . . . . . 0.4 second
14. Recorder Drive . . . . . . . . . 2 inch/minute

Crystal Information

The single crystal of potassium oxalate monohydrate, $\text{K}_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$, used in this experiment was grown by evaporation from a saturated solution by Professor Burl Bryant, Department of Chemistry, North Texas State University. The crystal was opaque white in the center (probably due to trapped water in the liquid phase) and clear close to the surface. The patterns of growth could be observed in the proper light (see Figures 9 and 10).

Since nothing detailed is known about the potassium oxalate crystal structure, an arbitrary axis was assumed
for future reference to the crystal. This axis system is shown in Figure 11. Actual measurements of the crystal side lengths and angles were checked by visually extrapolating the crystal surfaces with a steel rule and measuring the angles with a protractor. The results of this measurement are also shown in Figure 11. It appears that $a$ is equal to $b$ but not equal to $c$, and that $\alpha$ is equal to $\beta$ but not equal to $\gamma$.

The crystal was cut through a plane perpendicular to the ab plane so that the rotation angle would indicate the angle between the ab plane and the steady magnetic field. The cut was made by hand by holding the top surface, the smoothest, flat on the desk top and grinding one of the points of the crystal against the edge of a carborundum stone. The grinding motion was such as to make the cut perpendicular to the bisector of $\gamma$ (checked with a protractor). Figure 12 shows the results of this cut.

This crystal was mounted on the end of a glass rod with Fliobond Cement. A small section of glass tubing was mounted over the crystal to protect it from physical mishaps. The mounting is shown in Figures 13 and 14. The glass rod passed through the coil holder and a fixed protractor to a knob with a reference mark. The experimental placement located the reference mark perpendicular to the ab plane and on the side of the crystal assigned as the top. The angles, $\phi = 0$ and $\phi = \pi$,
correspond to an orientation of the reference mark perpendicular to the steady magnetic field, where \((\phi - \phi_0)\) is indicated, \(\bar{\phi}\).
CHAPTER V

EXPERIMENTAL RESULTS AND CONCLUSIONS

Before the data were recorded the sample holder without the crystal, but including some of the Pliobond Cement used to fasten the crystal in place, was located in the magnet gap and two complete sweeps of the magnetic field were made over the range within which data were to be taken in order to insure that the resonance signals were due to the crystal rather than the equipment. A false resonance was observed, but the signal-to-noise ratio was only about 1.5 (see Figure 15). This spurious resonance gave no trouble because the crystal itself was not completely dry and gave a large unshifted water resonance which was always superimposed on the false equipment signal. Neither of these resonance signals detracted from the important data, because the maximum and minimum values of \( H \) were the primary measurements in this experiment. In the final analysis, the extra signal was helpful in that it recorded the zero position of \( H \) on each data run.

A polycrystalline sample of ammonium chloride was used to calibrate the rate at which the steady magnetic field was swept. A value of five gauss peak-to-peak was used for the derivative line width (2). Five calibration
runs were made, three before the data series and two after the data series. All five calibration runs indicated a sweep rate of four gauss per inch along the data chart.

Several sample data charts, a "no crystal" chart, and an ammonium chloride calibration chart are shown in Figure 15. A complete plot of \( \Delta H \) vs \( \phi - \phi_0 \) for data taken over the range \( 0 \leq \phi - \phi_0 \leq \pi \) is shown in Figure 16.

The pertinent parameters, \( r \) and \( \sigma \), to be derived from these measurements can be extracted from the maximum and minimum values of

\[
\Delta H = \frac{3 \mu}{2r^3} \left[ 3 \cos^2 \sigma \cos^2(\phi - \phi_0) - 1 \right],
\]

which are

\[
\Delta H_{\text{min}} = - \frac{3 \mu}{2r^3}
\]

and

\[
\Delta H_{\text{max}} = \frac{3 \mu}{2r^3} (3 \cos^2 \sigma - 1).
\]

The minimum value of \( \Delta H \) is independent of the angle, \( \sigma \), so that \( r \) can be calculated directly, given that \( \mu = 1.41 \times 10^{-23} \) ergs/gauss for the proton (1). From the experimental standpoint, it is more convenient to write

\[
\frac{\Delta H_{\text{max}}}{\Delta H_{\text{min}}} = - (3 \cos^2 \sigma - 1).
\]
The following values of $\Delta H_{\text{max}}$ and $\Delta H_{\text{min}}$ are taken from Figure 16:

$$\Delta H_{\text{max}} = 10.3 \text{ gauss}$$
$$\Delta H_{\text{min}} = -5.6 \text{ gauss}$$

within the experimental error,

$$\frac{\Delta H_{\text{max}}}{\Delta H_{\text{min}}} = 2,$$

which corresponds to $\phi = 0 \text{ (or } \pi) \pm 8^\circ$. Thus, the proton-proton line lies in the plane of rotation of the crystal. Since Figure 16 shows $\Delta H_{\text{max}}$ also occurring at the initial orientation of the crystal, it follows that the proton-proton line lies in the ab plane perpendicular to the bisector of angle $\gamma$ (see Figure 11).

The average value of $r$ calculated from both $\Delta H_{\text{max}}$ and $\Delta H_{\text{min}}$ is

$$r = 1.57 \pm 0.02 \text{ Å}.$$  

This value of the proton-proton separation is typical of that found in hydrated water molecules in other substances (3, p. 925).
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REFERENCE

ANGLES

DEFINITION

Fig. 1--Reference angles - definition.
Fig. 2--Block diagram.
Fig. 3—Oscillator-detector.
Fig. 4.--A. F. amplifier.
Fig. 6—Narrow-band amplifier.
Fig. 8—Sweep rate control.
Fig. 9--Crystal, top, uncut.
ALL DIMENSIONS
IN INCHES

\[ \alpha + \theta = 40^\circ \]
\[ \gamma = 65^\circ \]

Fig. 11--Crystal lengths and angles.
Fig. 14—Crystal mounting, assembled.
Fig. 15--Sample data.
Fig. 16.-Plot of $\Delta H$ vs $(\phi - \phi_0)$, indicated by $\Phi$.
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