An electron paramagnetic resonance study of the ethylammonium-, methylammonium-, and acetamidinium-tetrachlorocuprates
by Paul Henry Amundson

A thesis submitted to the Graduate Faculty in partial fulfillment of the requirements for the degree of
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frequency of 20.39 GHz for ethylammonium-tetrachlorocuprate and 17.48 GHz for
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AN ELECTRON, PARAMAGNETIC RESONANCE STUDY OF THE ETHYLAMMONIUM, METHYLAMMONIUM, AND ACETAMIDINIUM-TETRACHLOROCUPRATES

by

PAUL HENRY AMUNDSON

A thesis submitted to the Graduate Faculty in partial fulfillment of the requirements for the degree of

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in

Physics

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Abstract

A K-band electron paramagnetic resonance spectrometer was constructed in order to determine the high and low field g-values, line shapes, and line widths for the spectra of divalent copper in ethylammonium-tetrachlorocuprate and methy lammonium-tetrachlorocuprate. The g-tensors were determined to be $g_{xx} = 2.053$, $g_{xy} = 2.067$, and $g_{zz} = 2.261$ for ethylammonium-tetrachlorocuprate and $g_{xx} = 2.054$, $g_{xy} = 2.057$, and $g_{zz} = 2.271$ for methy lammonium-tetrachlorocuprate. An exchange frequency of 20.39 GHz for ethylammonium-tetrachlorocuprate and 17.48 GHz for methy lammonium-tetrachlorocuprate was computed. Data was also taken on acetamidinium-tetrachlorocuprate to confirm earlier findings.
Chapter I: Introduction

Electron paramagnetic resonance (EPR) has been a useful tool of the spectroscopist since the first experiments of Zavoisky in 1914. The improvements in microwave equipment have given continuing impetus to the application of EPR to the solution of problems in a wide range of disciplines, including biology, chemistry, engineering and physics.

Classically, the spinning electron in a magnetic field has been compared to a spinning top precessing in the gravitational field of the earth. A simple quantum mechanical treatment will be given here. Consider the magnetic moment, \( \mathbf{\mu} = g \mathbf{s} \), associated with the spin, \( \mathbf{s} \), of an electron, where \( g \) is the spectroscopic splitting factor or Lande g-factor (2.0023 for free electrons) and \( \mathbf{\sigma} \) is the Bohr magneton (\( \mathbf{\sigma} = 0.92731 \times 10^{-20} \text{ erg/gauss} \)). Quantum mechanically, \( \mathbf{\mu} \) can assume \( 2S + 1 \) discrete orientations in a static homogeneous magnetic field, \( \mathbf{H}_0 \), according to the Zeeman interaction \( H_z = g \mathbf{\sigma} \mathbf{H}_0 \cdot \mathbf{s} \). Each of the orientations corresponds to an energy level in the system. A small perturbing magnetic field, \( \mathbf{H}_1 \), perpendicular to \( \mathbf{H}_0 \) and "rotating" about \( \mathbf{H}_0 \) with a frequency \( \nu \), provides the energy for transitions among these levels. The condition for resonant absorption is given by the following equation: \( h \nu = g \mathbf{\sigma} H_0 \), where \( h \) is Planck's constant (6.6257 \times 10^{-27} \text{ erg-s} ). The \( z \) axis is generally chosen to be along the field \( \mathbf{H}_0 \), while \( \mathbf{H}_1 \) is a small linearly oscillating field which appears to rotate in the plane perpendicular to \( \mathbf{H}_0 \). \( \mathbf{H}_1 \) can be resolved into two counter-rotating fields in the same plane. The component which rotates opposite to the Larmour precessional direction has little effect; however, the other component can be absorbed and can cause transitions. The terms for the Hamiltonian can then be written as follows: \( H_z = \)
$gS_z H_0$ and $H_{\text{pert.}} = gS_x H_1 \cos 2\pi \nu t$ where $S_z$ and $S_x$ are the $z$ and $x$ axis projections of the spin. $S_x$ can be rewritten as $S_+ + S_-$ if $S_+$ and $S_-$ are defined as follows: $S_+ = \frac{S_x + iS_y}{2}$ and $S_- = \frac{S_x - iS_y}{2}$. Let $|M\rangle$ represent a state of the system, where $M$ is the electron spin magnetic number, and operate on this set with $H_{\text{pert.}}$. It is then seen that transitions to higher and lower spin states are possible. $H_{\text{pert.}} |M\rangle = gS_x H_1 \cos 2\pi \nu t (S_+ + S_-) |M\rangle = gS_x H_1 \cos 2\pi \nu t \left[ \frac{\hbar}{2} \left( \sqrt{S(S + 1) - M(M + 1)} |M + 1\rangle + \sqrt{S(S + 1) - M(M - 1)} |M - 1\rangle \right) \right]$. The line intensity of transition probability per unit time for the state $|M - 1\rangle$ is proportional to the matrix element squared. Intensity $\sim |<M - 1|H_{\text{pert.}}|M\rangle|^2 = \frac{\hbar^2 g_s^2 \alpha^2}{4} \left[ \frac{\cos 2\pi \nu t}{2} \right]^2 |S(S + 1) - M(M - 1)|^2$. Briefly, $H_0$ splits the spin degenerate levels and $H_1$ provides the energy for transitions. Transitions take place only if the rotational frequency of $H_1$ about the $z$ axis is the same as the rotational frequency (Larmor frequency) of the magnetic moment.

In addition to the magnetic moment of the electron, many atoms have a nuclear magnetic moment which can be defined as $\mu_N = g_N \alpha N \hat{I}$, where $\hat{I}$ is the nuclear spin. The effect of this term can be considered as an interaction perturbation in the Hamiltonian and can be written as $A \hat{S} \cdot \hat{I}$, where $A$ is a constant. The nucleus of the copper atom has a spin of $3/2$ which should give a hyperfine spectrum; however, experimentally this is concealed by the spin-spin broadening of the hyperfine transition.

The electron in a crystal lattice is not free as was the case in the preceding discussion; it is constrained by various interaction and binding forces. The paramagnetic ion considered in this thesis was divalent copper ($Cu^{++}$). $Cu^{++}$ is in the iron transition group and has an electronic con-
figuration $1s^22s^22p^63s^22p^63d^9$. In solids the electronic orbital motion interacts with the crystalline electric fields and becomes decoupled from the spin. This is called quenching and is a strong mechanism in the iron group. As a result, in Cu$^{+}$ the ground state ion is only spin degenerate. The ground state is the $x^2 - y^2$ orbital. Figure One shows a schematic diagram of the energy levels of divalent copper. This figure shows that the free ion level is orbitally five-fold degenerate and two-fold spin degenerate. When the ion is placed in a cubically symmetric electric field, it splits into two energy levels, the top one of which is three-fold orbitally degenerate. The addition of a tetragonal component to the electric field further reduces the orbital degeneracy. Finally, spin orbit coupling eliminates the orbital degeneracy. Application of a magnetic field removes the spin degeneracy of all levels but is shown here only for the lowest level.

The Jahn-Teller theorem states that a crystal lattice will distort to remove as much degeneracy as possible. Kramer's theorem states that if there are an odd number of electrons in the system, no electric field can remove all the degeneracy of the states. The ground state of Cu$^{+}$ before application of the magnetic field is doubly degenerate and is split $652 \text{ cm}^{-1}$ from the nearest excited orbital state. At room temperature only a few electrons have enough energy to jump an energy gap of more than $250 \text{ cm}^{-1}$ so that there are very few electrons occupying the excited orbital levels. Therefore, the only extensively populated levels are the spin degenerate ground orbital singlet state.
Numbers on each energy level indicate orbital and spin degeneracy respectively of each level.

Figure 1. Energy level diagram for divalent copper
Chapter II: EPR of Copper Complexes.

\( \text{Cu}^{\text{II}} \) is one of the ideal ions for paramagnetic resonance since there is only one electronic transition and narrow lines can be obtained at room temperatures.

Historically, most new discoveries associated with solid state microwave spectra have been first observed in \( \text{Cu}^{\text{II}} \) salts. "The effect of exchange forces was first discovered in \( \text{CuSO}_4 \cdot 5\text{H}_2\text{O} \); the existence of hyperfine structure was first observed in a diluted copper salt; the effect of the quadrupole interaction was first noticed in the \( \text{Cu}^{\text{II}} \) hyperfine spectrum; heavy water was first used with copper Tutton salt crystals to resolve out the isotope splitting; the concept of a resonating crystal field was first introduced to account for the copper fluosilicate spectrum; and measurements on copper acetate were the first to show that two paramagnetic ions could interact strongly to form a combined system of energy levels."

Ethylammonium-tetrachlorocuprate \([\text{EATCC}, (\text{C}_2\text{H}_5\text{NH}_3)_2\text{CuCl}_4]\) and methylammonium-tetrachlorocuprate \([\text{MATCC}, (\text{CH}_3\text{NH}_3)_2\text{CuCl}_4]\) have been studied to obtain preliminary information regarding the \( g \) values, line shapes, and line widths at room temperatures.\(^9\) The present work has shown previously found \( g \) values to be incorrect because the \( g \) values tended towards Willett's for misalignment of the crystal.\(^10\) In addition, the line widths and line shapes which were determined in this work did not appear in the previous results.

The unusual "two dimensional" crystal structure found in EATCC and MATCC has stimulated interest in these and other similar crystals.
Figure Two shows an exaggerated and distorted octahedral symmetry particular to EATCC and MATCC. The axes x, y, and z are associated with the shortest to longest bonds respectively. In MATCC and EATCC, the bond lengths are $x = 2.300 \text{ Å}$, $y = 2.332 \text{ Å}$ and $z = 2.793 \text{ Å}$. In acetamidinium-tetrachlorocuprate (ACTCC, $\left[\text{CH}_3\text{C(NH}_2)_2\text{CuCl}_4\right]^+$), the x and y bond lengths are approximately equal and the z bond length is longer.

Figure Three, a. and b. points out the structure in EATCC, MATCC, and ACTCC. The broad face of the crystals is parallel to the plane of the paper in Figure Three. The z axis in a. is the long bond and in b. the z axis is perpendicular to the plane shown. The Cu$^{II}$ ions are represented as dots in both a. and b. The chlorine ions can be thought of as appearing at the end of each linear bond representation in a. and in the middle of each linear representation in b.

The data from the work on EATCC and MATCC has been used for a preliminary study of the exchange mechanism between the Cu$^{II}$ ions with Cl$^-$ as a bridge. This exchange mechanism is generally referred to as "super exchange." This data will later be used as part of a frequency dependent study of g values. ACTCC was studied to confirm the existence of a second magnetic axis in the crystal. The g values of ACTCC have been measured and are included with the results. A representative ACTCC line shape is also included.
Figure 2. Distorted Octahedral Symmetry Particular to EATCC and MATCC
Figure 3-a. Crystal Structure of EATCC, MATCC

Figure 3-b. Crystal Structure of ACTCC
Chapter III: Experimental Results

EATCC, MATCC, and ACTCC were studied with the k-band spectrometer. The maximum and minimum g values, line widths, and line shapes were taken for EATCC and MATCC. In addition, the existence of a second magnetic axis in ACTCC was confirmed with this spectrometer. This data is presented in Table I and in Figures Four through Eight. The theoretical Lorentzian and Gaussian line shapes are superimposed on the experimental line shapes of EATCC and MATCC. (It should be noted that in opposition to the usual custom, the theoretical shapes are represented as circles and crosses while the experimental data are continuous. This is because the experimental data are traced from the chart recorder output of the spectrometer.)

<table>
<thead>
<tr>
<th>Crystal</th>
<th>g min</th>
<th>g max</th>
<th>line width g min gauss</th>
<th>line width g max gauss</th>
</tr>
</thead>
<tbody>
<tr>
<td>EATCC</td>
<td>2.053</td>
<td>2.164</td>
<td>80.2</td>
<td>84.1</td>
</tr>
<tr>
<td>EATCCW</td>
<td>2.046</td>
<td>2.137</td>
<td></td>
<td></td>
</tr>
<tr>
<td>MATCC</td>
<td>2.054</td>
<td>2.169</td>
<td>94.9</td>
<td>99.4</td>
</tr>
<tr>
<td>MATCCW</td>
<td>2.046</td>
<td>2.143</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ACTCC</td>
<td>2.337 exch.</td>
<td>2.061</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ACTCC1</td>
<td>112.355 isol.</td>
<td>2.063</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

W-The data of Willett et al. on EATCC, MATCC is included for comparison.
\((C_2H_5NH_3)_2CuCl_4\)

LOW FIELD (\(g_{\text{max.}}\))

EXP. CURVE

THEOR. GAUSSIAN

THEOR. LORENTZIAN

Figure 4. EATCC
\((\text{C}_2\text{H}_5\text{NH}_3)_2\text{CuCl}_4\)

**High Field (g min)**

**Exp. Curve**

**Theor. Gaussian**

**Theor. Lorentzian**

**Figure 5.** EATCC
(CH$_3$NH$_3$)$_2$ Cu Cl$_4$

LOW FIELD (g max.)

EXP. CURVE

THEOR. GAUSSIAN

THEOR. LORENTZIAN

Figure 6, MATCG
(CH$_3$NH$_3$)$_2$CuCl$_4$

HI FIELD (g min.)

EXP. CURVE

THEOR. GAUSSIAN

THEOR. LORENTZIAN

Figure 7. MATCC
Figure 8. ACTCC
The $g$ values in MATCC and EATCC are anisotropic and are characterized by the $g$ tensor which has the principal values $g_{xx}$, $g_{yy}$, and $g_{zz}$ where the $z$ axis is the long bond axis of the distorted octahedron. Often this tensor has axial symmetry, in which case $g_{xx} = g_{yy} = g_1$ and $g_{zz} = g_\parallel$. This was the assumption made by Willett et al.\textsuperscript{11} Since the electron $g$ value is related to the Cu-Cl bond length and since $x$ is not equal to $y$ in EATCC and MATCC, it is to be expected that $g_{xx}$ would not equal $g_{yy}$. Since $g_{xx} = g_{\text{min}} = g_1$ and $\frac{1}{2}(g_{yy} + g_{zz}) = g_{\max}$, where $g_{zz} = g_\parallel$, $g_{yy}$ must be determined in order to determine $g_\parallel$. Since $x$ is related to $g_{xx}$, etc. it was thought that $g_{\max}$ must be related to $\frac{\sqrt{x^2 + z^2}}{2}$. This was confirmed by calculations with $\frac{\sqrt{x^2 + z^2}}{2}$ as related to $\frac{g_{xx} + g_{zz}}{2}$. Using a graphical solution, the data tabulated in Table II was obtained.

### TABLE II

<table>
<thead>
<tr>
<th>Crystal</th>
<th>$g_{xx} = g_1$</th>
<th>$g_{yy}$</th>
<th>$g_{zz} = g_\parallel$</th>
</tr>
</thead>
<tbody>
<tr>
<td>EATCC</td>
<td>2.053</td>
<td>2.067</td>
<td>2.261</td>
</tr>
<tr>
<td>MATCC</td>
<td>2.054</td>
<td>2.068</td>
<td>2.270</td>
</tr>
</tbody>
</table>

The data in Table II leads to the conclusion that the ratio of the square root of the bond lengths is approximately equal to the ratio of the $g$ values.

The Cu-Cl-Cu paramagnetic electron super exchange frequency has been
calculated using the following calculation from Pake: \(^3\)

\[
\omega_d^2 = \frac{\mathcal{A}}{\pi} = \left(\frac{S+1}{3} S\right) \hbar^2 \phi \frac{1}{r_{jk}} (3 \cos^2 \delta_{jk} - 1)^2,
\]

where \(S\) is the spin quantum number which is equal to \(1/2\) for \(\text{Cu}^{4+}\), \(g = 2.164\) for EATCC and 2.169 for MATCC, \(r\) is the distance between the \(\text{Cu}^{4+}\) ions and is \(5.125 \times 10^{-8}\) cm, \(\delta_{jk}\) is the angle from the \(z\) axis of a typical interior ion site \(k\) to any other interacting atom \(j\), the sum being carried out over the nearest neighbor sites only, and \(\omega_d\) is the dipolar exchange frequency.

\[
\Delta \omega_1 = \frac{\omega_e^2}{\omega_0},
\]

where \(\omega_0\) is the angular frequency half width and \(\omega_e\) is the \(\text{Cu}-\text{Cl}-\text{Cu}\) electron super exchange frequency. \(\Delta \omega_1 = \frac{\omega_e^2}{\omega_0} \Delta H_1\), where \(\Delta H_1\) is the line width in gauss at half maximum amplitude. Finally, \(\Delta H_\text{pp} = \sqrt{3} \Delta H_\text{pp}\), where \(\Delta H_\text{pp}\) is the peak to peak line width given in Table I. \(^3\)

The calculated values of \(\omega_e\) are, for EATCC and MATCC respectively, 20.39 GHz and 17.48 GHz.
Chapter IV: The Spectrometer

The Spectrometer

The k-band spectrometer constructed for this experiment is a high frequency modulation spectrometer utilizing a reflection cavity. A block diagram of the spectrometer is shown in Figure Nine. Most of the spectrometer was assembled with commercially manufactured equipment. The pieces built "in house" were the cavity, the 125 KHz modulation oscillator-amplifier, the modulation coils, the nuclear magnetic resonance (NMR) probe, and a low temperature cavity mount.

The klystron is an OKI model 24V10A which can be made to oscillate over the range 22.0 to 26.0 GHz. The klystron is mounted in a TRG model 946A oil bath mount to maintain the klystron at a stable temperature level and thus improve the frequency stability. The klystron is powered by a Narda Microline model 621A power supply with a Kepco model ABC voltage regulated klystron filament supply. The klystron frequency drift is controlled by a Teltronics model KSLP klystron stabilizer which applies a 70 KHz signal to the reflector of the klystron, phase detects the output, and provides a d.c. correction voltage to the reflector. The klystron is effectively isolated with a minimum isolation of 24 dB from any reflected microwaves by the PRD model 1209F1 isolator. The WaveLine, Inc. model 812 calibrated attenuator (0 to 40 dB) serves to reduce the effective power output of the klystron. It is necessary to have an attenuator since the klystron is a fixed power output device.

A WaveLine, Inc. model 869-20 dB cross guide coupler splits the signal from the klystron into two signals: the larger of which goes to the Ferrotec, Inc. model T380 3 port ferrite circulator and the smaller of which
Figure 9.
K BAND REFLECTION SPECTROMETER
goes to the Narda Microwave Corporation model 1068-3 db directional coupler. The signal reflected from the circulator returns to the cross guide coupler and splits, part of which returns to the attenuator and the other part of which terminates in a Waveline, Inc. model 854 matched load.

The 3 db directional coupler splits the signal from the 2 db cross guide coupler into two components, one of which goes to a Hewlett-Packard model K532A precision direct reading frequency meter, and the other of which goes to the PRD model 621A bolometer. The signal from the precision direct reading frequency meter can then be detected in a Waveline, Inc. model 816 crystal mount with a 1N26 diode. The signal from the circulator goes to the Waveline, Inc. model 883 slide screw tuner and from there to the cavity. The slide screw tuner can be thought of as a variable impedance which can be adjusted to match the impedance of the detector arm to the impedance of the cavity arm. Its effect is to tune out any standing waves in the waveguide, i.e., to reduce the power transfer along the waveguide. The reflected radiation passes through the slide screw tuner to the circulator and from there to the PRD model 621AF tuneable crystal mount, which is also equipped with a 1N26 detection diode.

The associated equipment for the spectrometer will be briefly described. A Tektronix, Inc. type 545A oscilloscope with either a type B or type E plug-in unit was used to monitor the signals from both the tuneable and fixed crystal mounts, the 125 KHz modulation and the signal from the NMR probe. The 125 KHz oscillator-amplifier was used to add a modulated component to the static magnetic field. Figures Ten and Eleven show the circuit diagrams of the oscillator-amplifier and the amplifier.
Figure 11.
125 KHz Amplifier
Channel 2
Figure 10.
125KHZ OSCILLATOR AMPLIFIER
The nuclear magnetic resonance (NMR) probe was used to determine an accurate value of the magnetic field at resonance and a Hewlett-Packard model 5246L electronic counter was utilized to determine the oscillation frequency of the NMR oscillator. The Hewlett-Packard model 200 AB audio oscillator was used to modulate the magnetic field at 400 Hz. A Princeton Applied Research Corporation model 121 lock-in amplifier/phase detector (PAR) was used to detect the absorption of energy from the microwave field in the cavity at resonance. Both a Varian model 614A-1 graphic recorder and a Hewlett-Packard model 7000 AR x-y recorder were used to record the data. A Fieldial model VFR2503 Varian field regulated magnet power supply was used to control a Varian model V-3000 electromagnet.

A variable temperature cavity mount, shown in Figure Twelve, was used at room temperature. This mount will also be used to support the cavity in low temperature dewers for possible variable temperature work. The fixed frequency cavity was designed to resonate at 2.7 GHz.

The TE₁₁ resonant mode was chosen for central positioning of the crystal in the region of maximum magnetic field and minimum interference with the electric field. As can be seen in Figure Thirteen, the perturbing magnetic field is always perpendicular to the level splitting (Zeeman) magnetic field, thus allowing the rotation of the field about the vertical axis with no loss in intensity.

The cavity used was constructed in three steps: 1. A .600 inch inner diameter hole was cut in brass stock, the outer surface of which was cut to .654 inches. 2. A .650 inch inner diameter hole was cut in low temperature plastic. 3. With the plastic piece centered in the lathe, the brass was
Figure 12. Variable Temperature Cavity Mount
Figure 13.
CYLINDRICAL $T_{E011}$ CAVITY
cooled with liquid air and forced into the plastic. The inner diameter of the brass was then machined to .650 inches and the ends of the plastic with the brass liner were faced so the length of the piece was .650 inches. A brass end plate was machined with a quarter wave choke for one end of the cavity and a copper plate with an iris hole .13 inches in diameter centered at approximately half the radius of the disc was polished for the input end. 24,000 is the theoretical maximum Q for a cavity of this design. \(^\text{17}\) The cavity has a Q of about 9,000.
Operation of the Spectrometer

The start-up procedure for the operation of the K-band spectrometer is as follows:

The power switch of the klystron supply is turned on after noting that the overload switch is on 25 ma., the grid select switch is on -300 volts, the grid voltage dial is turned all the way up, the reflector voltage dial is at about 300 volts, and the beam voltage dial is at the minimum position. The power switches of the oscilloscope, the PAR, the 125 KHz and 400 Hz oscillators, and the klystron stabilizer are all turned on. At this time the beam ready light on the klystron power supply should be lit and the beam voltage (meter value) should be increased to 2000 volts. The grid voltage should then be reduced until the beam current meter reads approximately 10 ma. (100 volts upper dial). The signal from the mod. out jack of the klystron power supply should be taken to the horizontal input of the oscilloscope. The modulator switch of the power supply should be turned to the sine wave and the amplitude dial to about 150. The horizontal display on the oscilloscope should be set on ext. x 10 and the x axis drive should be connected to the tuneable crystal detector with the variable volts/cm on 0.5. The tuneable iris, the slide screw tuner, and the tuneable detector can then be tuned for maximum signal. The klystron should then be adjusted so the cavity is in the middle of the mode. That is so the oscilloscope trace looks like the trace in Figure Fourteen.

That the dip is actually the cavity and not a spurious signal from the wave guide can be checked by moving the teflon crystal mount in and out of the cavity. If the dip in the oscilloscope is actually caused by
Figure 14. Klystron Mode with Cavity Resonance
the cavity it will move from side to side in the mode as the crystal mount is moved.

When the cavity dip is centered in the klystron mode with the crystal sample in position, the cable from the tuneable detector to the oscilloscope should be run through the klystron stabilizer and the stabilizer switched to tune. In operation, the klystron stabilizer adds a correction to the reflector voltage to control the oscillation frequency of the klystron and therefore the klystron should hold on the resonant frequency of the cavity.

The modulation output amplitude of the Narda power supply should then be decreased, maintaining the dip in the center of the signal by adjusting the reflector voltage. When the signal amplitude has been reduced by a factor of ten or so, the modulation can be turned off and the klystron stabilizer turned to reverse or normal AC lock. The reflector voltage should then be adjusted until the correction voltage goes to 0. The correction voltage should go positive or negative with or in opposite sense to the reflector dial movement. When this happens, the klystron stabilizer is locked to the cavity and the signal lead to the oscilloscope can be transferred to the sig. in jack of the PAR.

The slide screw tuner should then be tuned for maximum crystal current on the klystron stabilizer meter. The PAR should then be calibrated according to the procedure on pages III-3 and III-4 of the instruction manual. The water valves which let water flow through the electromagnet should be opened so the pressure on the dial (which reads the lower pressure) reads about 15 PSI. The master wall switch powering the electromagnet should be
turned on, the field dial control unit should be turned on and field adjusted to about 8000 gauss for warm up.

The Varian graphic recorder should be turned on (with the paper drive off). The NMR box should be turned on and the probe positioned as near to the cavity as possible. (Five turns of number 20 wire were used to make the resonant coil for proton resonance in the magnetic field range 7500 to 9000 gauss.)

The counter should be turned on and the NMR box hooked to the counter and the y axis input of the oscilloscope. The 400 Hz modulation field should be connected to the smaller wire coils in the electromagnet and to the horizontal input of the scope. The resonance signal of the NMR box looks somewhat like Figure Fifteen, with the proper amplitude 400 Hz modulation.

When the equipment is all running, the recorder is centered and the paper drive started. At that time the field dial magnet sweep is started. A reasonable sweep time for initial checkout is five minutes, with a sweep range of 1000 gauss.
Figure 15. NMR Resonance Signal
Appendix

Experimental absorption and/or experimental absorption derivative curves are generally obtained in EPR. This data usually follows the shape of the theoretical Lorentzian curve to a good approximation. Theoretical data points will be given for both Gaussian and Lorentzian absorption and absorption derivative line shapes. This numerical data can be utilized to determine whether a line shape is Gaussian or Lorentzian or neither.

The formulae for the theoretical line shapes are as follows:

Gaussian

Absorption

\[ y_g = ye^{-cx^2} \]

Absorption derivative

\[ y_g' = -2cxye^{-cx^2} \]

Lorentzian

Absorption

\[ y = \frac{y}{1 + x^2} \]

Absorption derivative

\[ y_e' = \frac{2yx}{(1 + x^2)^2} \]

where \( y \) is the amplitude, \( c \) is a constant, and \( x \) is a measure of the line width. The data in Table III is tabulated in terms of the percentage of the initial amplitude. It can be plotted on the same scale as the experimental curve or the experimental data (arbitrary scale) can be plotted against the theoretical data to determine which line shape (Lorentzian or Gaussian) gives the best fit to a straight line.
<table>
<thead>
<tr>
<th>% of maximum amplitude</th>
<th>Gaussian Absorption</th>
<th>Gaussian Absorp.</th>
<th>Gaussian Deriv.</th>
<th>Lorentzian Absorption</th>
<th>Lorentzian Absorp.</th>
<th>Lorentzian Deriv.</th>
</tr>
</thead>
<tbody>
<tr>
<td>10%</td>
<td>± 1.82</td>
<td>.06</td>
<td>2.34</td>
<td>± 3.00</td>
<td>.03</td>
<td>2.95</td>
</tr>
<tr>
<td>20%</td>
<td>± 1.52</td>
<td>.11</td>
<td>2.07</td>
<td>± 2.00</td>
<td>.06</td>
<td>2.22</td>
</tr>
<tr>
<td>30%</td>
<td>± 1.31</td>
<td>.16</td>
<td>1.88</td>
<td>± 1.53</td>
<td>.09</td>
<td>1.81</td>
</tr>
<tr>
<td>40%</td>
<td>± 1.15</td>
<td>.22</td>
<td>1.74</td>
<td>± 1.22</td>
<td>.12</td>
<td>1.58</td>
</tr>
<tr>
<td>50%</td>
<td>± 1.00</td>
<td>.27</td>
<td>1.62</td>
<td>± 1.00</td>
<td>.16</td>
<td>1.37</td>
</tr>
<tr>
<td>60%</td>
<td>± .86</td>
<td>.34</td>
<td>1.50</td>
<td>± .82</td>
<td>.20</td>
<td>1.22</td>
</tr>
<tr>
<td>70%</td>
<td>± .73</td>
<td>.41</td>
<td>1.39</td>
<td>± .66</td>
<td>.24</td>
<td>1.08</td>
</tr>
<tr>
<td>80%</td>
<td>± .57</td>
<td>.49</td>
<td>1.26</td>
<td>± .50</td>
<td>.30</td>
<td>.95</td>
</tr>
<tr>
<td>90%</td>
<td>± .32</td>
<td>.61</td>
<td>1.12</td>
<td>± .32</td>
<td>.36</td>
<td>.82</td>
</tr>
<tr>
<td>100%</td>
<td>0.00</td>
<td>.85</td>
<td>.85</td>
<td>0.00</td>
<td>.56</td>
<td>.56</td>
</tr>
</tbody>
</table>
LITERATURE CITED
Literature Cited


9. All crystals were grown by Professor Kenneth Emerson of the Montana State University Department of Chemistry.


16. Designed and constructed by Professor J. E. Drumheller.
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