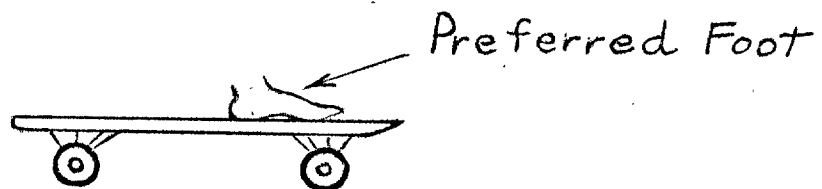
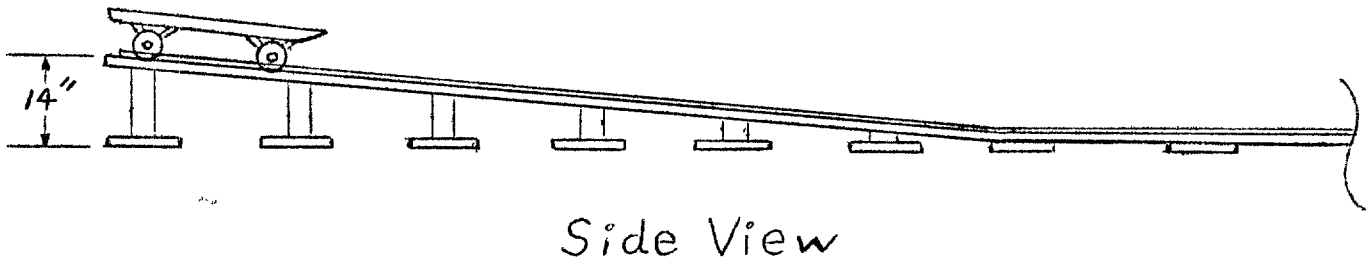
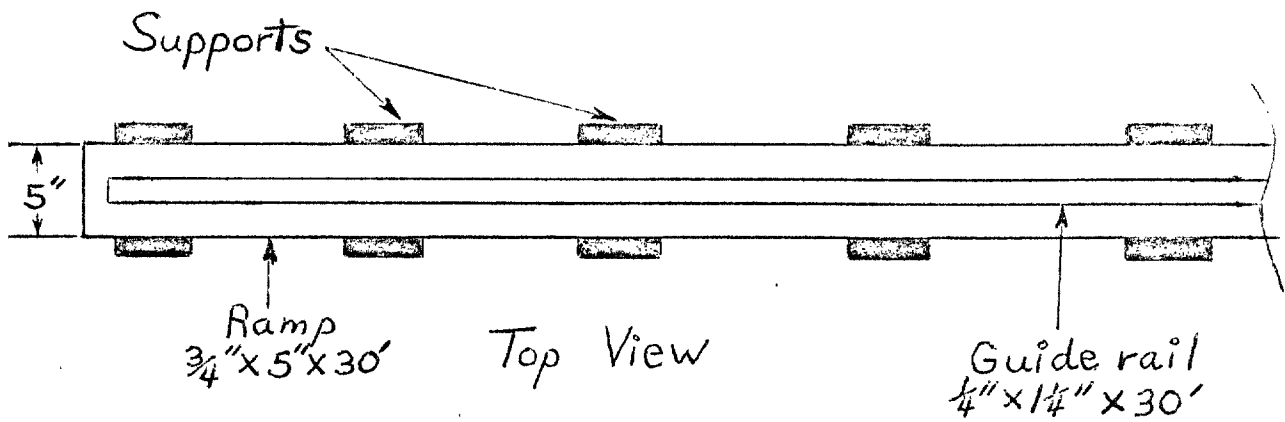


Subject	Balance on a Stationary Base Trials			Balance on a Moving Base Trials		
	1	2	3	1	2	3
18. GK	48.2	30.6	39.7	2.0	4.8	6.0
19. GR	48.0	25.1	36.2	1.5	2.8	3.4
20. TM	4.3	12.6	26.8	3.2	3.5	2.2
21. KR	7.2	14.6	22.2	2.5	3.3	4.0
22. KH	15.5	21.8	36.5	.5	1.8	1.5
23. MH	4.2	8.8	17.5	2.2	1.5	2.8
24. AA	8.5	20.6	15.8	4.5	3.2	3.8
25. BV	5.1	5.0	10.5	.8	1.0	1.4
26. DH	3.2	4.5	6.0	1.3	.6	1.5
27. DK	17.3	19.4	31.0	2.0	2.8	2.5
28. JK	15.0	21.2	35.6	3.0	4.2	5.2
29. JS	8.0	12.4	18.0	2.0	3.5	1.9
30. JB	12.0	8.5	14.8	2.1	3.2	2.8
31. DD	3.5	4.6	7.6	1.0	1.8	1.2
32. LS	9.5	18.6	25.2	5.0	6.0	4.1
33. PM	15.5	26.2	33.5	5.5	3.5	6.0
34. KM	14.0	22.3	12.5	2.2	3.4	3.8
35. BC	2.0	8.8	13.5	3.0	3.2	2.8
36. DF	2.2	5.6	12.7	2.5	1.5	2.0
37. RW	3.5	18.2	16.7	4.0	3.5	5.0
38. KC	5.5	10.8	13.6	1.5	2.0	2.5
39. JE	9.2	17.6	21.8	2.2	1.3	3.8

Subject	Balance on a Stationary Base Trials			Balance on a Moving Base Trials		
	1	2	3	1	2	3
40. CW	2.5	6.6	6.4	1.5	1.0	2.3
41. BS	4.8	10.1	15.5	2.5	1.3	3.3
42. JJ	3.2	8.2	14.5	2.0	2.4	1.8
43. TF	2.0	12.6	6.2	1.5	1.0	1.8
44. MD	12.5	19.1	21.5	4.5	2.1	4.0
45. WA	12.0	8.5	10.2	1.0	1.8	2.0
46. MF	10.5	15.1	18.4	1.5	3.5	4.9
47. MM	35.5	22.1	42.5	5.2	6.0	5.3
48. BR	3.0	14.1	16.8	5.0	2.6	3.0
49. MR	13.2	23.5	33.4	6.0	6.0	6.1
50. VL	7.5	10.6	20.6	2.0	1.5	3.0

APPENDIX D

RAMP AND SKATEBOARD



Skateboard

BIBLIOGRAPHY

Books

- Fleishman, Edwin A., The Structure and Measurement of Physical Fitness, Englewood Cliffs, New Jersey, Prentice-Hall, Inc., 1964.
- Garrett, Henry E., Statistics in Psychology and Education, 5th ed., New York, Davis McKay Company, Inc., 1958.
- Guilford, J. P., Fundamental Statistics in Psychology and Education, 4th ed., New York, McGraw-Hill Book Co., 1965.

Articles

- Bass, Ruth I., "An Analysis of the Components of Tests of Semicircular Canal Function and Static and Dynamic Balance," Research Quarterly, X (May, 1939), 33-37.
- Espenschade, Anna, "Dynamic Balance in Adolescent Boys," Research Quarterly, XXIV (October, 1953), 270-275.
- Estep, Dorothy, "Relationship of Static Equilibrium to Ability in Motor Activities," Research Quarterly, XXVIII (March, 1957), 5-15.
- Scott, Gladys, "Measurement of Kinesthesia," Research Quarterly, XXVI (October, 1955), 324-341.
- Travis, Roland, "An Experimental Analysis of Dynamic and Static Equilibrium," Journal of Experimental Psychology, XXXV (June, 1945), 216-234.

**CHLORINE NUCLEAR QUADRUPOLE RESONANCE ABSORPTION
OF 3, 4, 5, 6 - TETRACHLOROPHTHALIMIDE AND
1, 3, 6, 8 - TETRACHLOROPYRENE**

APPROVED:

Miles E. Anderson

Major Professor

John Ed Allen

Minor Professor

R. J. Bonnell, Jr.

Director of the Department of Physics

Robert B. Toulous

Dean of the Graduate School

**CHLORINE NUCLEAR QUADRUPOLE RESONANCE ABSORPTION
OF 3, 4, 5, 6 - TETRACHLOROPHTHALIMIDE AND
1, 3, 6, 8 - TETRACHLOROPYRENE**

THESIS

**Presented to the Graduate Council of the
North Texas State University in Partial
Fulfillment of the Requirements**

For the Degree of

MASTER OF SCIENCE

By

Jerry Byron Reeves, B. S.

Denton, Texas

January, 1968

TABLE OF CONTENTS

	Page
LIST OF ILLUSTRATIONS	iv
Chapter	
I. INTRODUCTION	1
II. THE THEORY OF NUCLEAR QUADRUPOLE RESONANCE	5
III. EXPERIMENTAL CONSIDERATIONS	17
Regenerative Oscillator-Detector Super-Regenerative Oscillator- Detector	
IV. RESULTS	43
3, 4, 5, 6 - Tetrachlorophthalimide 1, 3, 6, 8 - Tetrachloropyrene Recommendations	
APPENDIX	59
BIBLIOGRAPHY	72

LIST OF ILLUSTRATIONS

Figure	Page
1. Nuclear Quadrupole Energy Levels for $\eta = 0$	10
2. Regenerative Oscillator-Detector	18
3. Oscilloscope-Display Spectrometer	23
4. Lock-In Amplifier Spectrometer	24
5. Lock-In Amplifier	26
6. Resonance Absorption Signal for a Modulation Width Much Less than Width of Absorption Curve	28
7. Regenerative Spectrometer Recording of Cl^{35} Resonance Absorption Line of NaClO_3 at 77°K	31
8. Super-Regenerative Oscillator-Detector . . .	33
9. Super-Regenerative Spectrometer Recording of Cl^{35} Resonance Absorption in NaClO_3 at 77°K	38
10. Super-Regenerative Spectrometer Recording of Cl^{35} Resonance Absorption Lines of Chloranil at 77°K	40
11. 3, 4, 5, 6 - Tetrachlorophthalimide Molecule	44
12. Super-Regenerative Spectrometer Recording of Nuclear Quadrupole Absorption in 3, 4, 5, 6 - Tetrachlorophthalimide at 77°K	45

Figure	Page
13. Super-Regenerative Spectrometer Recording of Nuclear Quadrupole Absorption in 3, 4, 5, 6 - Tetrachlorophthalimide at Room Temperature with a Sweep Rate of 129 Kilohertz per Minute	46
14. Super-Regenerative Spectrometer Recording of Nuclear Quadrupole Absorption in 3, 4, 5, 6,- Tetrachlorophthalimide at Room Temperature with a Sweep Rate of 46 Kilohertz per Minute	47
15. Chloranil Molecule	50
16. Tetrachlorophthalic Acid Molecule	52
17. 1, 3, 6, 8 - Tetrachloropyrene Molecule	53
18. Nuclear Shape for Various Values of Q^*	61
19. Nuclear Orientation in the Principal Axes System of the Electric Field Gradient	63

CHAPTER I

INTRODUCTION

Many nuclei possess an electric quadrupole moment which interacts with the electric field gradient arising from the charge distribution in the vicinity of the nucleus. These interactions can be roughly divided into two categories according to their relative magnitudes. In the first category the interactions are weak and manifest themselves as perturbations to the magnetic interactions as observed in a nuclear magnetic resonance experiment. Nuclear magnetic resonance (NMR) spectra result from transitions between energy levels that arise from the interaction of an externally applied magnetic field and nuclear magnetic moments. The weak electric quadrupole interactions cause a splitting of these energy levels and perhaps a broadening or apparent loss of intensity of the resonance line (1, p. 325).

In the second category the nuclear quadrupole interactions are much stronger and are primarily responsible for the orientation energy of the nucleus. Pure quadrupole resonance experiments can then be performed in zero or very weak magnetic fields. The first successful experiment of this kind was that of Dehmelt and Kruger in 1950 in

which resonance absorption of radio-frequency energy at 27.96 MHz and 35.40 MHz in trans-dichloro-ethylene was observed (3, p. 501). The two lines were attributed to the quadrupole interaction of C^{135} and C^{137} nuclei respectively. Since that time nuclear quadrupole resonance (NQR) spectra have been observed for over thirty isotopes. Chlorine, bromine, nitrogen, arsenic, iodine, copper, antimony, and bismuth have accounted for most of the resonance lines (2, p. 1).

Nuclear quadrupole resonance spectroscopy is important in solid state physics primarily because it yields information about the nature of the electric fields in the neighborhood of a particular nucleus. This aspect will be discussed in some detail in Chapter II. Nuclear quadrupole resonance studies are also useful in several other ways, including the investigation of the nature of chemical bonds in solids, the establishment of non-equivalent sites of resonance nuclei in a crystal lattice or molecule, the analysis of the structure of crystals, the measurement of the average moments of inertia and average rotatory vibration frequencies of molecules in crystals, and the measurement of temperature with an accuracy up to 0.002°K (2, p. 2).

The experimental setup for observing NQR spectra is quite similar to that used in many nuclear magnetic resonance experiments. A radio-frequency magnetic field

of the proper frequency is applied to the sample and couples with the nuclear magnetic moment to cause changes in the nuclear orientation. Unlike nuclear magnetic resonance experiments, no external field is used in NQR studies since no appreciable electric field gradient can be produced by external means (1, p. 324). The necessary gradient is always a result of internal fields. A spectrometer used in NQR work can usually be used for NMR studies with the addition of an external magnetic field source. The observed NQR frequencies occur throughout the radio-frequency range and into the microwave region.

In this study frequency modulation was used with a regenerative spectrometer and a super-regenerative spectrometer to detect the nuclear quadrupole resonance frequencies of chlorine in two commercially available compounds, 1, 3, 6, 8 - tetrachloropyrene and 3, 4, 5, 6 - tetrachlorophthalimide. Both are aromatic organic compounds whose molecules appear to possess axial symmetry. Quadrupole resonance of chlorine nuclei has been observed in many compounds. The frequencies range from five megahertz to seventy-six megahertz, the majority occurring between twenty and forty-five megahertz (4, 5).

CHAPTER BIBLIOGRAPHY

1. Cohen, M. H. and F. Reif, "Quadrupole Effects in Nuclear Magnetic Resonance Studies of Solids," Solid State Physics, Vol. V, edited by Frederick Seitz and David Turnbull, New York, Academic Press, Inc., 1957.
2. Grechishkin, V. S. and G. B. Soifer, "Nuclear Quadrupole Resonance Instrumentation (Review)," Instrumentation and Experimental Technique, I (1964), 1-16.
3. Livingston, Ralph, "Nuclear Quadrupole Resonance," Molecular Physics, Vol. III of Methods of Experimental Physics, edited by Dudley Williams, New York, Academic Press, Inc., 1962.
4. Segal, S. L. and R. G. Barnes, Catalog of Nuclear Quadrupole Interactions and Resonance Frequencies in Solids. Part I. Elements and Inorganic Compounds, United States Atomic Energy Commission Research and Development Report, Ames, Iowa, Ames Laboratory, 1962.
5. Segal, S. L. and R. G. Barnes, Catalog of Nuclear Quadrupole Interactions and Resonance Frequencies in Solids. Part II. Halogen Resonances in Organic Compounds, United States Atomic Energy Commission Research and Development Report, Ames, Iowa, Ames Laboratory, 1965.

CHAPTER II

THE THEORY OF NUCLEAR QUADRUPOLE RESONANCE

As seen in Appendix I, the electrostatic interaction of a nucleus with its environment may be expressed as a series of k^{th} order partial derivatives of the electric potential with respect to the coordinates coupled with the 2^k order multipole moment of the nucleus ($k=0,1,2,\dots$). The electric potential is that due to all charges external to the nucleus. Because the nuclear wave function possesses definite parity, the interactions for odd values of k are zero. The monopole interaction ($k=0$) does not affect the nuclear orientation and will not be considered here. The quadrupole term is the only term of significance in the series although slight effects due to the hexadecapole (sixteen-pole, $k=4$) term have been observed (9). The nuclear quadrupole Hamiltonian has been derived in Appendix I, and in the principal axes system of the electric field gradient tensor this Hamiltonian is

$$H_Q = \frac{eQ}{2I(2I-1)} \left[V_{xx}I_x^2 + V_{yy}I_y^2 + V_{zz}I_z^2 \right] , \quad (1)$$

where e is the charge on a proton, I is the angular momentum quantum number, and I_x , I_y , I_z are quantum mechanical operators of the components of the angular momentum. The following notation is used for the partial derivatives of the electric potential V :

$$\begin{aligned} V_{xx} &= \left(\partial^2 V / \partial x^2 \right)_0 \\ V_{yy} &= \left(\partial^2 V / \partial y^2 \right)_0 \\ V_{zz} &= \left(\partial^2 V / \partial z^2 \right)_0 \end{aligned} \quad (2)$$

The zero subscript indicates that the quantity is evaluated at the origin of the coordinates, which is located at the center of mass of the nucleus. The quantity Q in equation (1) is the quantum mechanical nuclear quadrupole moment and, using Dirac notation, is given by

$$eQ = \left\langle nI(m=I) \left| e \sum_k^{\text{protons}} (3z_k'^2 - r_k^2) \right| nI(m'=I) \right\rangle, \quad (3)$$

where I is the angular momentum quantum number, m and m' are magnetic quantum numbers, and n represents all other quantum numbers needed to specify the system.

The Z' - axis is the axis along which the spin is quantized, and r_k is the position vector of the k^{th} proton with respect to the origin.

Laplace's equation,

$$V_{xx} + V_{yy} + V_{zz} = 0 \quad (4)$$

is assumed to hold at the nuclear sites, since the potential is that due to charges external to the nucleus.

Therefore, in the principal axes system only two quantities are required to specify the electric field gradient. These two quantities are usually chosen to be

$$e_q = V_{zz} \quad , \quad (5)$$

$$\eta = (V_{xx} - V_{yy})/V_{zz} \quad , \quad (6)$$

and the principal axes are labeled such that

$$|V_{xx}| \leq |V_{yy}| \leq |V_{zz}| \quad , \quad (7)$$

Thus, e_q is the principal value of the electric field gradient tensor. The quantity η is known as the asymmetry parameter. Equations (4) and (7) indicate that η ranges in value from zero to one. For $\eta = 0$ the electric field gradient is symmetric about the z - axis and

$$V_{xx} = V_{yy} = \frac{1}{2}e_q. \quad (8)$$

The asymmetry parameter is a measure of the deviation from cylindrical symmetry of the electric field gradient. For spherical symmetry $V_{xx} = V_{yy} = V_{zz} = 0$ and there is no nuclear electric quadrupole interaction.

Using equations (4), (5), and (6), one may write the quadrupole Hamiltonian as

$$H_Q = \frac{e^2 Q q}{4I(2I-1)} \left[(3I_z^2 - \hat{I}^2) + \frac{1}{2} \eta (I_+^2 + I_-^2) \right] \quad , \quad (9)$$

where \hat{I}^2 is the square of the total angular momentum operator. The operators I_+ and I_- are defined in the usual way as

$$I_{\pm} = I_x \pm iI_y \quad . \quad (10)$$

Equation (9) is a convenient form of the quadrupole Hamiltonian for finding energy levels.

The separation energy between the nuclear ground state and the first excited state of the nucleus is much larger than the nuclear orientation energy (2, p. 327). Thus, the matrix elements of concern in dealing with the quadrupole interaction are

$$\langle nIm | H_Q | nIm' \rangle . \quad (11)$$

The following equations are useful in evaluating the above matrix elements:

$$I_z^2 \psi_{Imn} = m^2 \psi_{Imn} , \quad (12)$$

$$I^2 \psi_{Imn} = I(I+1) \psi_{Imn} , \quad (13)$$

$$I_{\pm}^2 \psi_{Imn} = [(I \mp m)(I \mp m + 1)(I \mp m - 1)(I \mp m + 2)]^{\frac{1}{2}} \psi_{I(m \pm 2)n} , \quad (14)$$

where ψ_{Imn} is the nuclear wave function. The eigenvalues are given in units of \hbar^2 , where \hbar is Planck's constant divided by 2π . Using these equations one gets as the elements of the quadrupole Hamiltonian tensor:

$$H_{m'm} = \langle nIm' | H_Q | nIm \rangle . \quad (15)$$

$$\begin{aligned} H_{m'm} = & A [3m^2 - I(I+1)] \delta_{m',m} \\ & + (A \gamma / 2) [(I-m)(I+m+1)(I-m-1)(I+m+2)]^{\frac{1}{2}} \delta_{m',m+2} \\ & + (A \gamma / 2) [(I+m)(I-m+1)(I+m-1)(I-m+2)]^{\frac{1}{2}} \delta_{m',m-2} , \end{aligned} \quad (16)$$

where

$$A = \frac{e^2 Q q}{4I(2I-1)} ; \quad (17)$$

and

$$\delta_{1,j} = 1 \quad \text{for } 1 = j \quad , \quad (18)$$

$$\delta_{1,j} = 0 \quad \text{for } 1 \neq j \quad . \quad (19)$$

The energy levels may be found in the usual way by solving the secular equation

$$|\hat{H} - E \hat{1}| = 0 \quad , \quad (20)$$

where \hat{H} is the m^{th} order matrix of elements $H_{m'm}$,

$\hat{1}$ is the identity matrix, E represents the energy eigenvalues, and the parallel bars indicate the determinant of the quantity between them.

It is instructive to consider the case of a cylindrically symmetric electric field gradient ($\mathcal{N} = 0$).

The energy eigenvalues by equations (16) and (20) are then

$$E_m = A [3m^2 - I(I+1)] \quad . \quad (21)$$

The energy levels for m and $-m$ are the same. Figure 1 shows the relative spacing of the energy levels for integer and half-integer values of I . The separation between E_m and $E_{m\pm 1}$ depends on the value of m . This is in contrast to the energy levels in nuclear magnetic resonance where the energy difference between adjacent m states is the same for all values of m . For nuclei with integer spin the energy differences between adjacent m states appear in the ratios 1:3:5: ... while for half-integer spin nuclei the corresponding ratios are 1:2:3: ... If \mathcal{N} is nonzero, these ratios are more complicated.

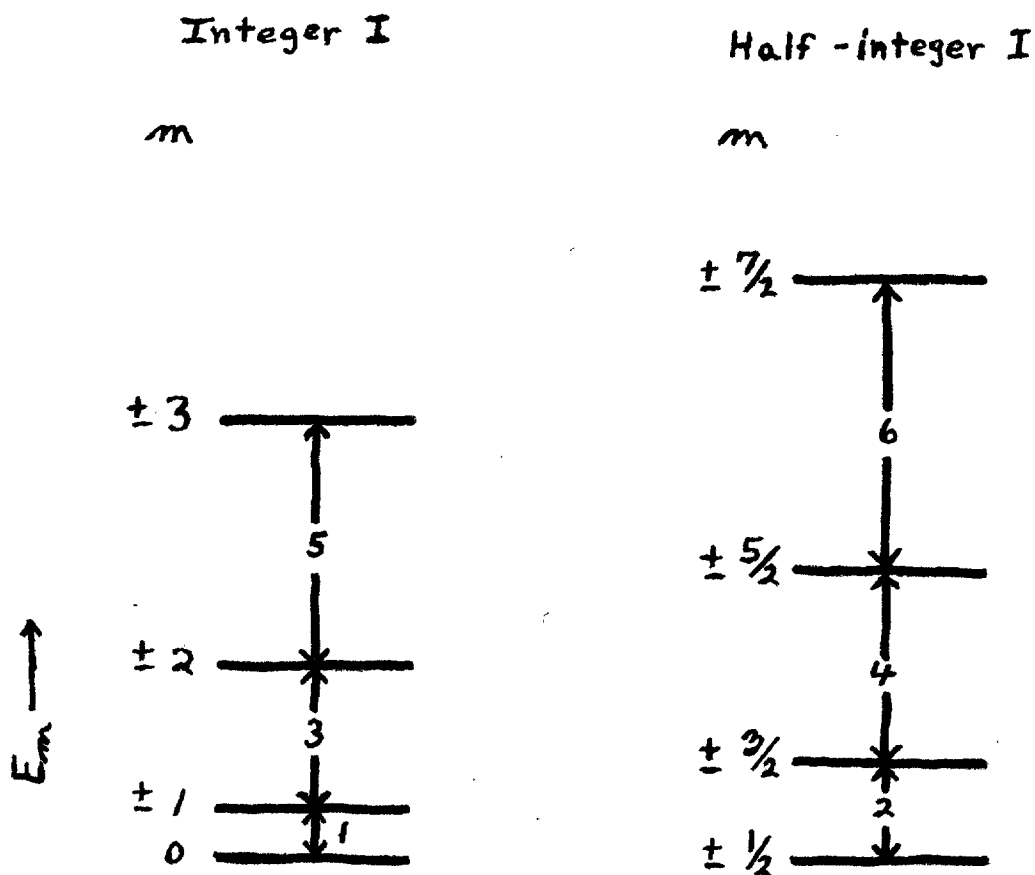


Fig. 1--Nuclear quadrupole energy levels for $\eta = 0$ in units of $\frac{3e^2Qq}{4I(2I-1)}$.

Classically for $\mathcal{N} = 0$ the spin vector of the nucleus precesses about the symmetry axis at a frequency proportional to the component of the angular momentum along the symmetry axis. For $\mathcal{N} \neq 0$ the precession may take place about the direction of strongest field gradient or about the direction of intermediate field gradient, but not about the direction of weakest field gradient (5, p. 356).

Quadrupole resonance absorption occurs only for nuclei with spin greater than a half (6, p. 8). A nucleus with $I = 0$ has a spherically symmetric charge distribution and thus no quadrupole moment exists (4, p. 113). The two possible spin orientations for $I = \frac{1}{2}$ differ only by a reversal in the spin direction. They correspond to the same effective charge distribution; thus, the electrostatic interaction does not depend on the orientation of the nucleus. Quantum mechanically the energy levels for the orientations $\pm \frac{1}{2}$ are degenerate. Since these are the only energy levels, no absorption occurs.

Chlorine, the nucleus of interest here, has a spin of three halves. Thus, m and m' in equation (16) may take on values of $3/2, 1/2, -1/2, -3/2$. Equation (20) then becomes

$$\begin{vmatrix} 3A - E & 0 & A\eta\sqrt{3} & 0 \\ 0 & -3A - E & 0 & A\eta\sqrt{3} \\ A\eta\sqrt{3} & 0 & -3A - E & 0 \\ 0 & A\eta\sqrt{3} & 0 & 3A - E \end{vmatrix} = 0 \quad . \quad (22)$$

This equation reduces to

$$E^2 - 3\eta^2 A^2 - 9A^2 = 0 \quad . \quad (23)$$

The energy levels are therefore

$$E = \pm 3A(1 + \eta^2/3)^{\frac{1}{2}} \quad . \quad (24)$$

For $I = 3/2$, A is equal to $e^2Qq/12$. The transition frequency between these two energy levels is

$$\omega = \Delta E/\hbar = (6A/\hbar)(1 + \eta^2/3)^{\frac{1}{2}} \quad , \quad (25)$$

$$= (e^2Qq/2\hbar)(1 + \eta^2/3)^{\frac{1}{2}} \quad . \quad (26)$$

Only one transition frequency exists for chlorine nuclei. The transition frequencies for other values of I may be arrived at in a similar manner.

In order to specify the electric field gradient one must find q , η , and the Eulerian angles indicating the orientation of the principal axes system with respect to the laboratory system. For half-integer spins larger than $3/2$ and for all integer spins there will exist more than one quadrupole transition frequency. (For $I = 1$ only one frequency exists if $\eta = 0$.) Using the transition frequencies obtained in a quadrupole resonance experiment one can solve two of the frequency equations simultaneously

to find e^2qQ and \mathcal{N} . The quantity e^2qQ is called the quadrupole coupling constant and is usually given in frequency units. For many nuclei Q is known and therefore q may be calculated if the coupling constant is known. The Eulerian angles may be found from Zeeman studies of a single crystal. A weak magnetic field, which eliminates the degeneracy in m states, is applied to the crystal. By observing the quadrupole resonance frequencies at various orientations of the magnetic field one can determine the directions of the principal axes of the electric field gradient (3).

For the case of $I = 3/2$ only one transition frequency exists and therefore e^2qQ and \mathcal{N} can not be calculated directly from the quadrupole resonance spectra. However, \mathcal{N} as well as the Eulerian angles may be determined from Zeeman studies of a single crystal, and the electric field gradient can be completely specified. For many chlorine compounds previous knowledge of the chemical bonding indicates that \mathcal{N} is quite small and by equation (26) the quadrupole coupling constant (in frequency units) is taken to be twice the transition frequency.

For many nuclei more than one isotope exists in nature. In chlorine compounds Cl^{35} and Cl^{37} are both found; Cl^{37} is twenty-five percent abundant. The quadrupole moments for these two nuclei are different.

In a quadrupole resonance experiment if all of the chlorine sites are equivalent, that is, if q and η are the same for all sites, two transition frequencies will be observed. The one corresponding to Cl^{35} will be three times as intense as the one corresponding to Cl^{37} . By equation (26) the ratio of the transition frequencies will be just the ratio of the quadrupole moments. For chlorine this ratio is (7, p. xlii)

$$\omega_{35} / \omega_{37} = q_{35} / q_{37} = 1.26878 \quad . \quad (27)$$

Therefore, if one of the transition frequencies is measured the other may be calculated. For some nuclei quadrupole resonance is an accurate means of finding the ratio of the quadrupole moments of two different isotopes. In molecules containing more than one chlorine atom all of the chlorine sites may not be equivalent. In this case more than one transition frequency may be found for each isotope. This information is quite useful in determining molecular structure.

Quadrupole transition frequencies are temperature dependent. Dehmelt and Kruger and later Bayer, as cited by Wang (9, p. 567), suggested that this temperature dependence was due to thermal vibrations. As molecules execute oscillations in crystals, the charge distribution in the molecules becomes distorted and the principal axes of the electric field gradient are varied causing a variation in q and η .

Bayer showed theoretically that an increase in temperature would result in a decrease in the observed quadrupole resonance frequency. The relationship is complicated and involves the components of the molecular moment of inertia tensor and the vibrational frequencies about the principal axes of the electric field gradient (3, p. 43). The thermal vibrational frequencies are large compared to the quadrupole transition frequencies and the quadrupole nuclei experience an average q and η . These averages change with a change in temperature. Because of the temperature dependence of quadrupole resonance frequencies, an NQR experiment may be used to determine temperature changes in a crystal.

CHAPTER BIBLIOGRAPHY

1. Andrew, E. R., Nuclear Magnetic Resonance, New York, Cambridge University Press, 1955.
2. Cohen, M. H. and F. Reif, "Quadrupole Effects in Nuclear Magnetic Resonance Studies of Solids," Solid State Physics, Vol. V, edited by Frederick Seitz and David Turnbull, New York, Academic Press, Inc., 1957.
3. Das, T. P. and E. L. Hahn, Nuclear Quadrupole Resonance Spectroscopy, Suppl. 1 of Solid State Physics, edited by Frederick Seitz and David Turnbull, New York, Academic Press, Inc., 1958.
4. Dehmelt, H. G., "Nuclear Quadrupole Resonance," The American Journal of Physics, XXII (January, 1954), 110-120.
5. Reich, J. C. and R. H. Good, Jr., "Discussion of Quadrupole Precession," The American Journal of Physics, XXXI (May, 1963), 356-362.
6. Ramsey, Norman F., Nuclear Moments, New York, John Wiley and Sons, Inc., 1953.
7. Segal, S. L. and R. G. Barnes, Catalog of Nuclear Quadrupole Interactions and Resonance Frequencies in Solids. Part I. Elements and Inorganic Compounds, Research and Development Report, United States Atomic Energy Commission, Ames, Iowa, Ames Laboratory, 1962.
8. Slichter, Charles P., Principles of Magnetic Resonance, New York, Harper and Row, 1963.
9. Wang, Tien-Chuan, "Pure Nuclear Quadrupole Spectra of Chlorine and Antimony Isotopes in Solids," Physical Review, XCIX (July, 1955), 566-577.

CHAPTER III

EXPERIMENTAL CONSIDERATIONS

Regenerative and super-regenerative spectrometers are most often used in the search for nuclear quadrupole resonance frequencies. A regenerative oscillator produces a continuous radio-frequency wave, whereas the super-regenerative type produces a wave whose amplitude is made to build up and decay periodically. As an aid in observing the absorption curve, frequency modulation or modulation of a weak magnetic field applied to the sample is used. Several wave forms have been tried as a means of modulating the magnetic field (4, p.6); however, square-wave modulation is apparently the most useful. In this study only frequency modulation was employed.

Regenerative Oscillator-Detector

The regenerative oscillator-detector used in this experiment was designed by Livingston (7, p. 509) and is shown in Figure 2. The sample coil and capacitors in parallel form a tuned combination in the grid circuit of the radio-frequency oscillator. The coil and capacitors are called the tank circuit and determine the operating frequency which is given by

$$\omega_0 = \sqrt{\frac{1}{LC}} \quad , \quad (1)$$

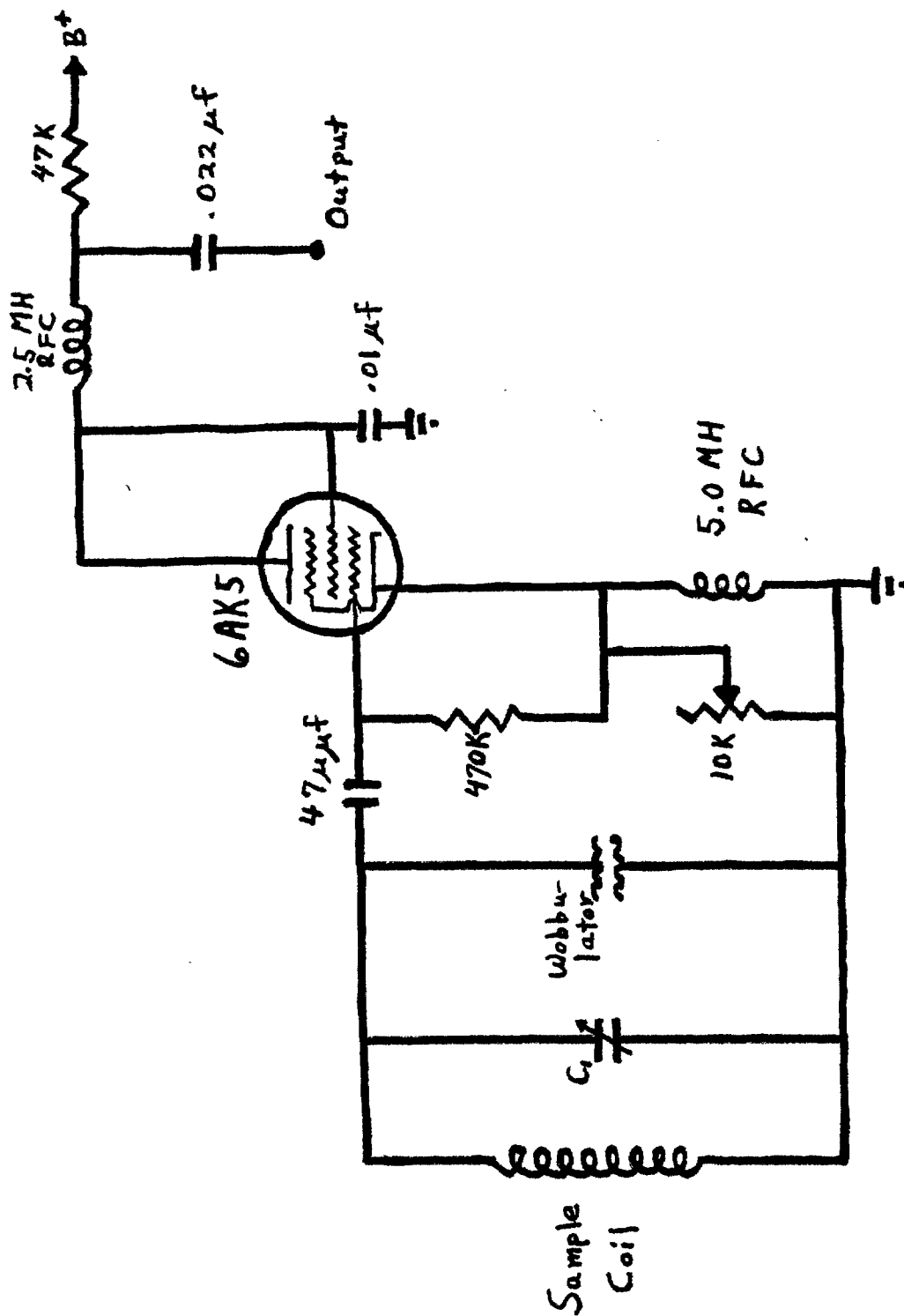


Fig. 2--Regenerative oscillator-detector

where L is the inductance of the coil in henries and C is the capacitance in farads. The radio-frequency current in the coil produces an oscillating magnetic field of the same frequency in the coil. This field couples with the nuclear magnetic moments in the sample, and if the frequency corresponds to any allowed nuclear quantum transition (magnetic dipole or electric quadrupole), then energy is absorbed.

This absorption of energy is detected in the following manner. The tube in Figure 2 serves as an amplifier which feeds back enough energy (regeneration) to the tank circuit to maintain oscillation. This regenerative amplifier may be regarded as a negative resistance in parallel with the tuned circuit (1, p.50). If this negative resistance more than compensates for the positive resistance in the circuit, oscillations are sustained. The oscillations build up until the average value of the negative resistance over a cycle is equal to the average value of the positive resistance. The impedance of the tank circuit at frequency ω_0 is given by

$$Z_0 = \frac{L}{RC} \quad , \quad (2)$$

where R is the series resistance. If resonance absorption occurs, this impedance is decreased to (3, p. 85)

$$Z_r = \frac{L}{RC} \left[\frac{1}{1 + 4\pi f QF / (\omega_0 H_1^2)} \right] \quad , \quad (3)$$

where ξ is the sample filling factor (the fraction of the radio-frequency field occupied by the sample), P is the power absorbed by the sample, ω_0 is the frequency, Q is the figure of merit of the coil given by $Q = \omega_0 L/R$, and H_1 is half the amplitude of the magnetic field produced by the radio-frequency current. Resonance absorption thus reduces the impedance by

$$Z_0 - Z_R = Z_0 \frac{4\pi Q \xi P}{\omega_0 H_1^2} \quad (4)$$

assuming P is small. As a result of this decrease in the positive resistance of the circuit the amplitude of the oscillation decreases. By monitoring the radio-frequency voltage level of the oscillator one may detect the frequencies at which absorption occurs. Modulating the frequency near resonance causes the oscillator periodically to pass back and forth through the quadrupole resonance frequency. The change in the radio-frequency voltage is repeated several times rather than just once and can be displayed on an oscilloscope or chart recorder.

A typical sample coil used in the circuit in Figure 2 was two and one-half inches long, one-half inch in diameter, and made of four turns of number fourteen bare copper wire. With a variable capacitor C_1 of 125 picofarads maximum capacitance and the above coil, the range of the oscillator was thirty to forty-eight megahertz. Frequency modulation was provided by a wobulator, a parallel-plate capacitor

whose capacitance was changed periodically by applying a sinusoidally varying voltage to an electromagnet mounted near a metallic membrane which formed one of the capacitor plates. In order to decrease the noise in the circuit the filaments of the tube were heated by a six-volt storage battery. A plate voltage of approximately 120 volts was provided by a regulated power supply. By changing the sample coil the circuit could be made to oscillate from approximately sixteen to forty-eight megahertz.

The sample coil was mounted inside a cylindrical metal shield three inches long and one and one-half inches in diameter. One end of the coil was attached to the wall of the shield while the other was connected through a hermetic seal to the center conductor of a fourteen-inch length of coaxial cable which projected down from the oscillator chassis. The outside lead of the coaxial cable was connected to the sample box and grounded to the oscillator chassis. The sample was poured into the shield container through the bottom, which could be screwed on and off; an indium O-ring was used as a seal. In this manner the entire coil was surrounded by the sample, and the holder could be lowered into a Dewar of liquid nitrogen in order to make measurements at 77°K.

Optimum detection for the regenerative oscillator occurred just past the point where oscillations commenced.

In searching for an unknown resonance the oscillator had to be frequently readjusted so that it operated near this point.

The oscillator circuit of Figure 2 was used in the two spectrometers shown in Figures 3 and 4. The spectrometer in Figure 3 was tuned to resonance by hand using a small variable capacitor in parallel with the sample coil, and the absorption curve was displayed on an oscilloscope screen. The 120 hertz modulation was provided by a Hewlett-Packard Model 202D audio oscillator. The twin-tee filters were introduced into the circuit to eliminate sixty hertz pick-up from the power lines and to filter out the spurious 120 hertz signals generated by unintentional amplitude modulation of the oscillator by the wobulator. The 120 hertz filter also removed most of the fundamental component of the absorption signals. Since the absorption was periodic, though not sinusoidal, the second and higher harmonics of the signal were passed by the filters and displayed on the oscilloscope. In this spectrometer the oscilloscope was triggered with a signal from the modulation oscillator. In order to display the entire absorption signal on the screen the amplitude of the modulation had to be larger than the width of the absorption curve, which for chlorine compounds is typically a few kilohertz. Two absorption curves were displayed on the screen, corresponding to the

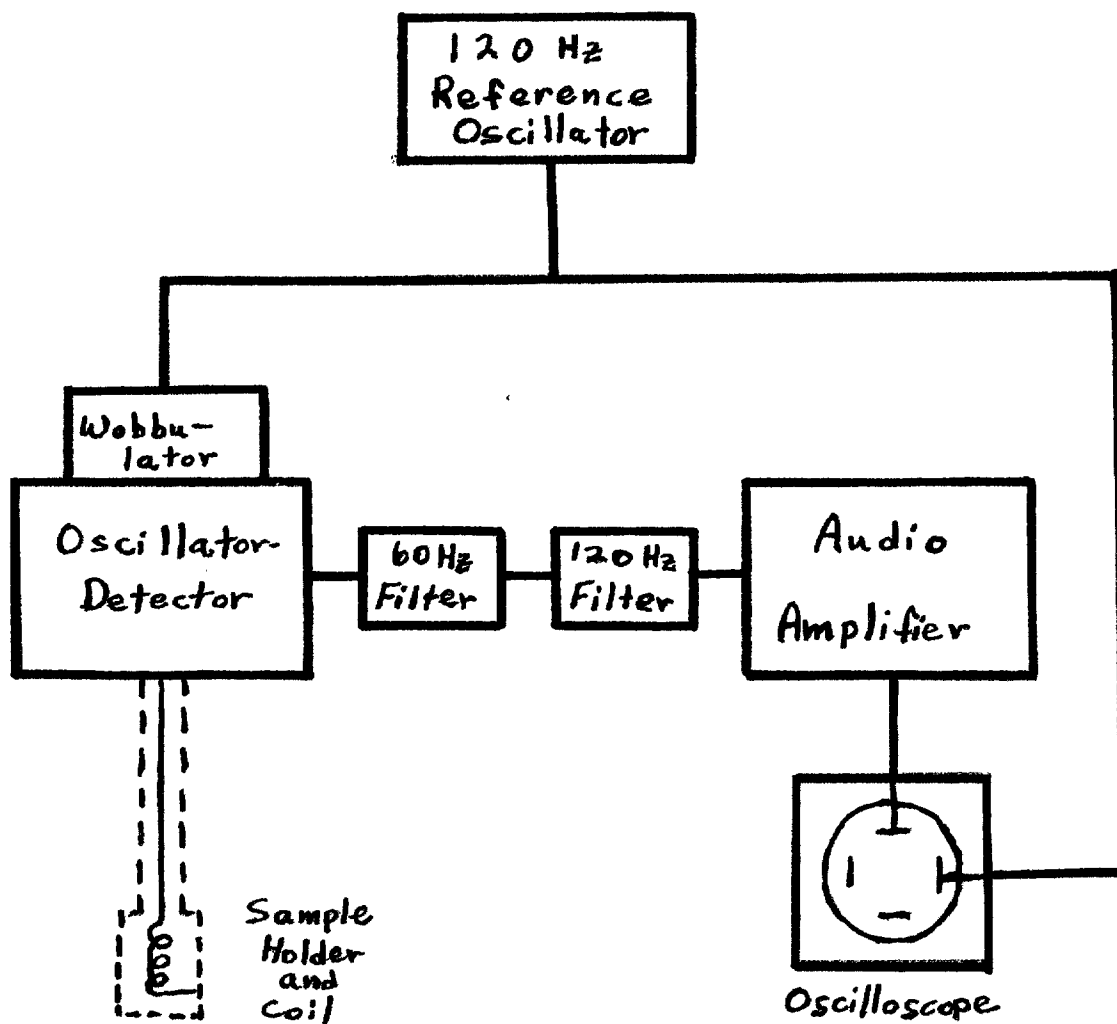


Fig. 3--Oscilloscope-display spectrometer

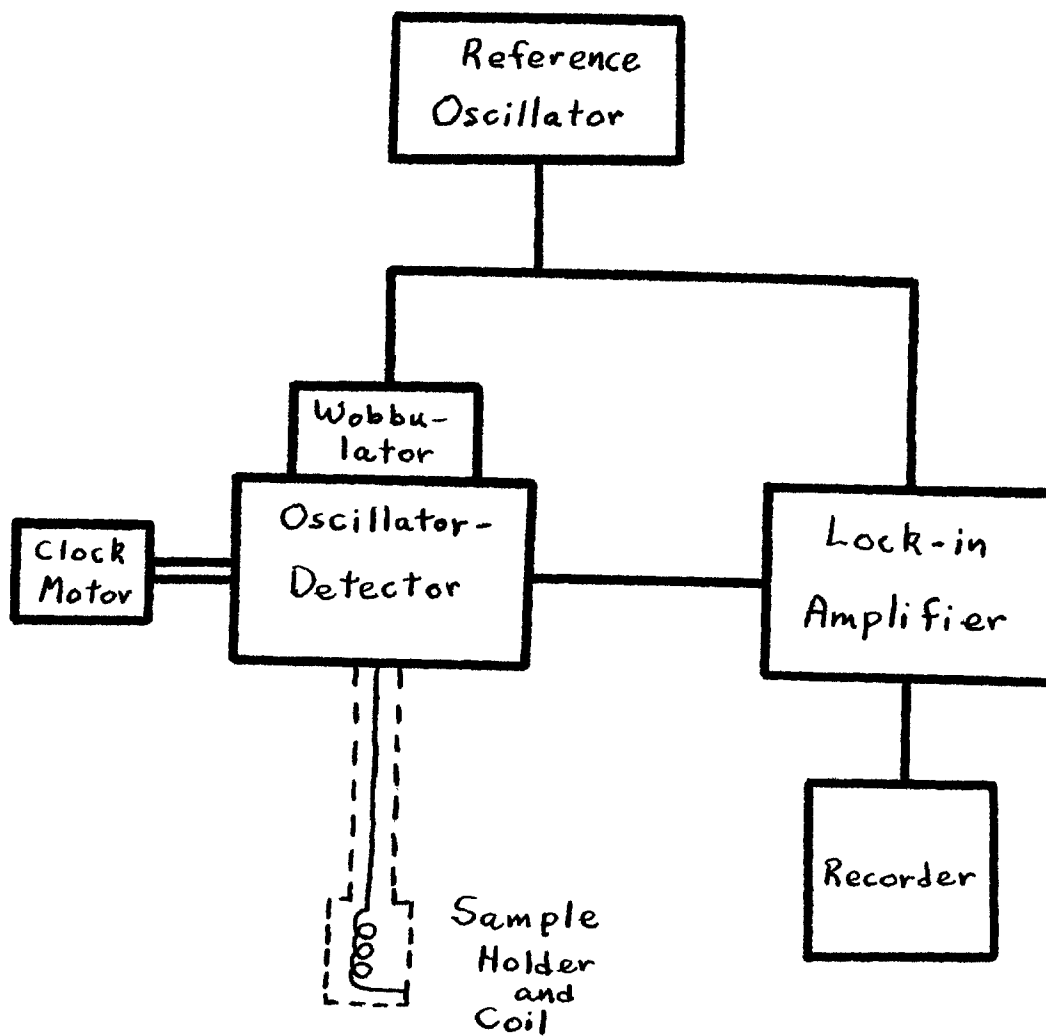


Fig. 4--Lock-in amplifier spectrometer

fact that the resonance condition was satisfied twice during each cycle of the modulation. The audio amplifier used was a Tektronix Type RM 122 and the oscilloscope was a Tektronix Type RM 564. The approximate resonance frequencies were determined by beating a Measurements Corporation Model 59 megacycle meter (grid dip meter) against the absorption oscillator. More accurate measurements were made with a Northeastern Engineering Inc. Model 14-200 frequency counter, which was coupled to the spectrometer by a small pick-up coil wound around the 6AK5 tube.

The signal-to-noise ratio was greatly improved by the use of a lock-in amplifier and recorder (Figure 4). A lock-in amplifier is a phase-sensitive detector followed by an RC low-pass filter as shown in Figure 5. A reference oscillator is used to drive the wobblator at some frequency F . The output from the reference oscillator is also fed into the reference channel of the lock-in amplifier where it passes through a phase-shifter and into the phase-sensitive detector. The output from the radio-frequency oscillator-detector is fed into the signal channel of the lock-in where it passes through an amplifier broadly tuned to F and then into the phase-sensitive detector. The phase-sensitive detector delivers an output which is proportional to the product of the amplitude of the input signal E_s and the cosine of its phase angle relative to reference

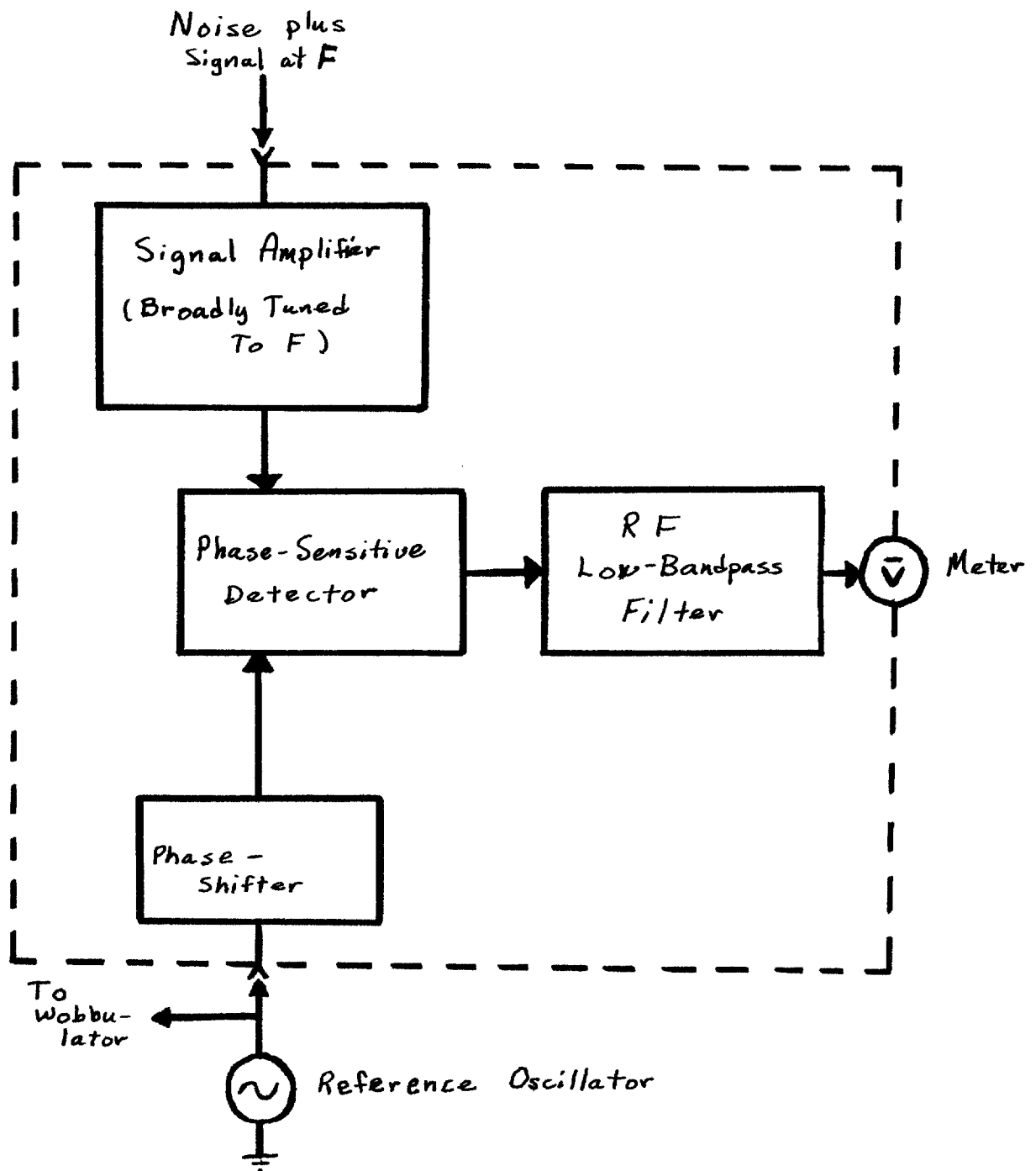


Fig. 5--Lock-in amplifier

carrier E_1 . If the signal and reference are out of phase by 90° or 270° the output from the phase-sensitive detector will be zero. If they are out of phase by 180° this output will be negative and equal in amplitude to E_2 . If a signal at a frequency F' , near F , is fed into the phase-sensitive detector, the output will be a beat frequency equal to the difference in F and F' . This beat frequency will not appear across the meter (recorder) if the resistance R and capacitance C of the low-bandpass filter are such that $2\pi RC$ is much greater than the beat period. The noise centered around F in E_2 can be considered as a random collection of carriers which beat with F in the phase-sensitive detector. This noise will cause a fluctuation of \bar{V} (the voltage output from the RC filter) about zero. Increasing the time constant RC will decrease the fluctuations of \bar{V} since this reduces the bandwidth about F to which the meter responds. The phase-shifter in Figure 5 is necessary because the phase of the absorption signal may be shifted by the wobulator, sample coil, or other parts of the oscillator-detector. An adjustment to correct the phase is made by maximizing the recorder displacement after a resonance signal is found.

In using a lock-in amplifier and recorder the width of the modulation is chosen to be somewhat less than the width of the absorption curve. See Figure 6(a). Then

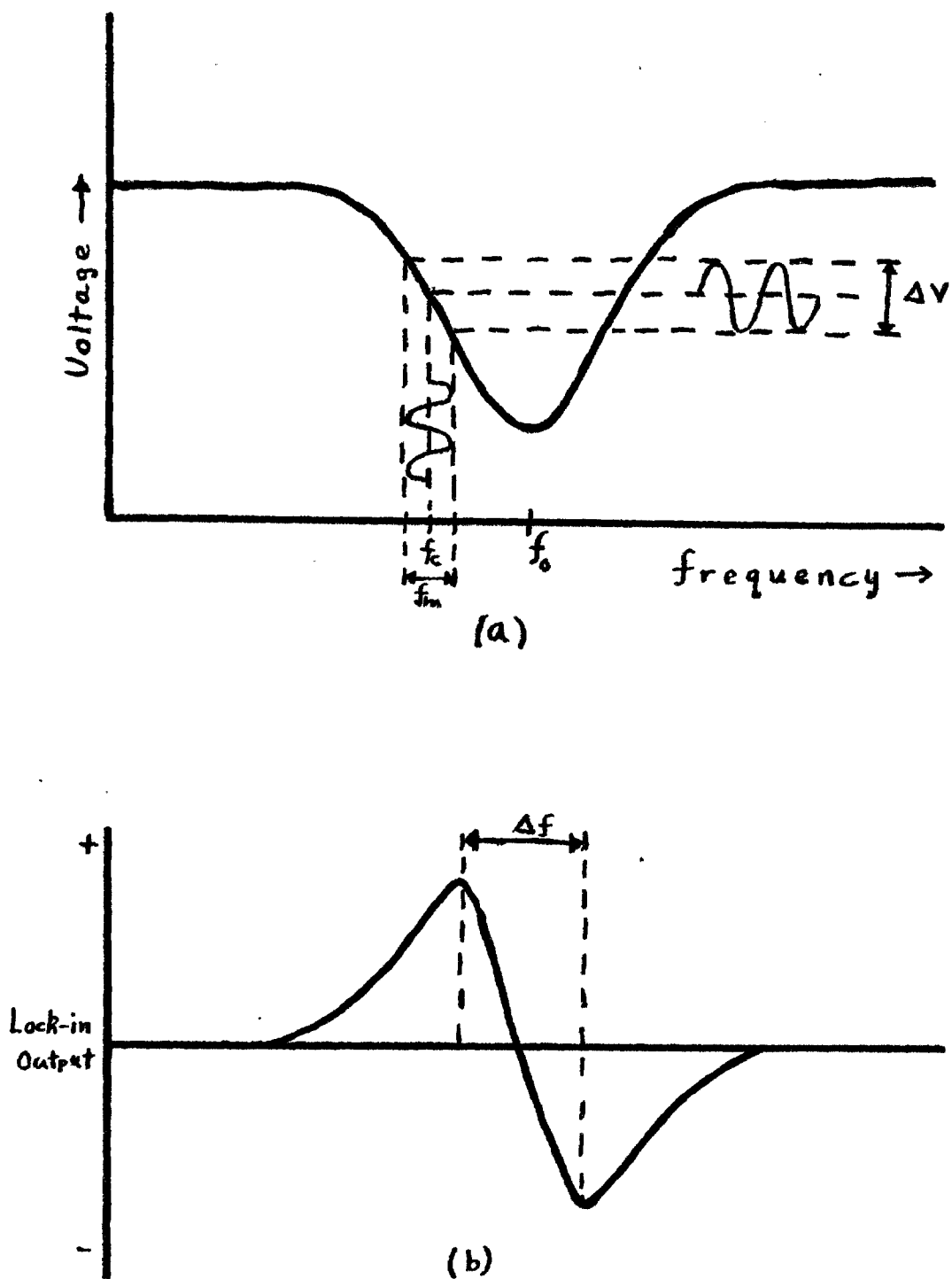


Fig. 6--Resonance absorption signal for a modulation width much less than width of absorption curve: (a) modulation derivative of absorption curve; (b) first derivative of absorption curve.

as the center frequency f_c of the oscillator-detector is slowly increased, an output voltage approximately proportional to the first derivative of the absorption curve will be fed to the recorder (Figure 6(b)). In order to get a reasonably accurate approximation to the first derivative, the modulation frequency f_m must be less than about one-sixth of the absorption curve width Δf (5, p. 28). A plot of the second derivative is provided if the frequency from the reference oscillator is doubled before it is fed into the lock-in amplifier (7, p. 512).

In the spectrometer in Figure 4 a clock motor connected to a series of gears was used to turn the tuning capacitor in the tank circuit and thereby slowly change the frequency of the oscillator. In order to record the first derivative of the absorption curve the duration of the absorption signal had to be long enough for the lock-in amplifier and recorder to respond. With a lock-in amplifier RC time constant of 0.3 seconds, the noise on the recorder was tolerable. For this time constant a signal of three seconds duration would not be distorted by the lock-in amplifier. The recorder could easily respond to such a signal. A typical line width for chlorine compounds is one kilohertz. Thus, a sweep rate of twenty kilohertz per minute would provide a signal duration of approximately three seconds. The lock-in amplifier and recorder would not display the signal if the sweep rate were greater

than approximately 200 kilohertz, even if the RC time constant were reduced to 0.03 seconds. A much slower sweep rate would result in several days being required to search the region of interest. For example, two hundred hours would be required to cover the range from twenty to forty-four megahertz if the sweep rate were two kilohertz per minute.

In this experiment three different commercial lock-in amplifiers were used at one time or another: a Princeton Applied Research Model HR-8; a Teltronics Model CA-2; and an Electronics, Missiles, and Communication, Inc. Model RJB. The Model CA-2 had a built-in reference oscillator which was used to drive the wobbulator and furnish a reference signal (usually 155 hertz) for whichever lock-in was in use. The Model HR-8 appeared to give the best signal-to-noise ratio of the three. The Model RJB had a built-in frequency doubler in the reference channel which was used to observe the second derivative of the absorption curve.

Figure 7 shows an example of an absorption curve recorded using Livingston's oscillator. The curve is the first derivative of the Cl^{35} resonance line in NaClO_3 at 77°K. For this display the plate voltage was 141 volts, the modulation frequency was 155 hertz, the voltage across the wobbulator was 0.08 volts (rms), the time constant

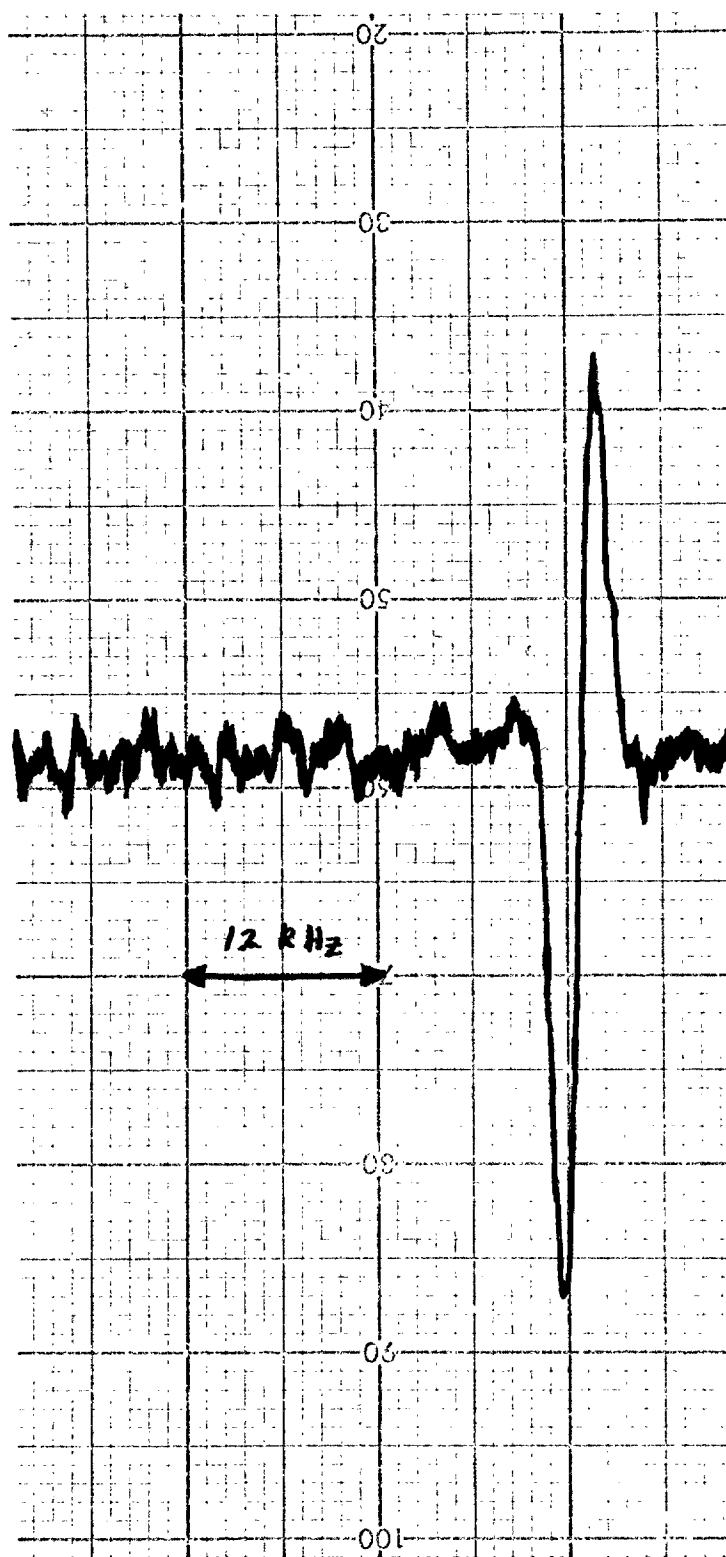


Fig. 7--Regenerative spectrometer recording of ^{135}Cl resonance absorption line of NaClO_3 at 77°K .

of the lock-in amplifier was one second, the chart speed was two inches per minute, and the sweep rate was twenty-four kilohertz per minute. The line width (the difference in frequency between maximum and minimum slope) is 2.5 kilohertz. The center of the line is 30.6325 megahertz as measured with the Northeastern frequency counter. Wang measured this frequency to be 30.630 megahertz (9). The frequency counter was calibrated using station WWV as a standard and was accurate within 300 hertz.

Super-Regenerative Oscillator-Detector

The super-regenerative oscillator-detector used in this experiment was designed by Dean (3, p. 90) and is shown in Figure 8. A super-regenerative oscillator produces a radio-frequency wave whose amplitude builds up and decays periodically. The rate at which this takes place is called the quench frequency. The quenching may be produced by an external signal injected into the oscillator grid circuit such that negative pulses appear on the grid (external quenching), or it may be caused by the proper choice of grid resistor and capacitor (internal or self-quenching). Self-quenching will occur if the RC time constant in the grid circuit (see Figure 8) is sufficiently long. Then when current is drawn on the positive half of the grid voltage cycle, the grid blocking capacitor will become charged, and ultimately the tube is

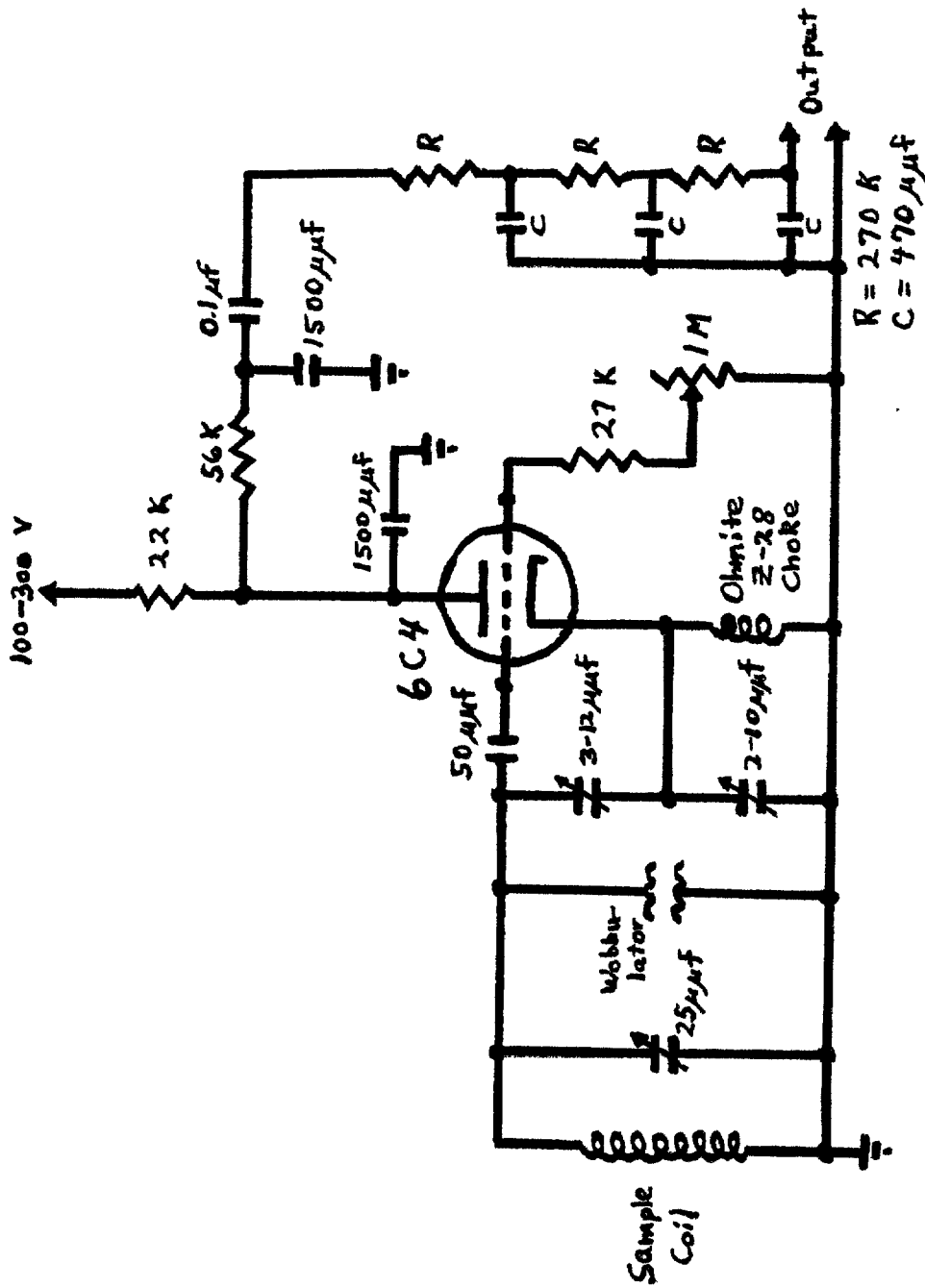


Fig. 8--Super-regenerative oscillator-detector

driven to cut off. The grid capacitor then discharges through the grid resistor, and oscillations begin again. Thus, the quench frequency for an internally quenched oscillator is determined primarily by the time constant of the grid resistor and capacitor. The variable resistor in Figure 8 is used to adjust the quench frequency from ten to eighty kilohertz.

The super-regenerative oscillator may be operated in either of two modes. In the coherent mode each pulse of radio-frequency energy starts to build up before the previous one has decayed to the noise level. In the incoherent mode each pulse starts from the noise level. Oscillators used in quadrupole resonance spectroscopy are ordinarily operated coherently for best signal-to-noise ratio.

A super-regenerative oscillator-detector is sensitive for only a short time during each quench cycle just as the radio-frequency pulse begins to grow. Two effects have been suggested as the means by which resonance absorption is detected. The first is that the absorption of energy by the sample causes a reduction in integrated pulse energy. The second effect is caused by the nuclear induction as a result of the coherent precession of the nuclei brought about by the last "on" period. If the spin-spin relaxation time T_2 (the time for individual spins to lose their

coherence as a result of their mutual interaction) is longer than the period of the quench frequency the nuclear induction signal will cause the radio-frequency burst to be initiated early. The result is an increase in the integrated pulse energy. Dean, as cited by Livingston (7, p. 515), has given evidence supporting the latter mechanism. Dean found that a spectrometer operating in an incoherent mode may begin to operate coherently when tuned to a strong resonance. He also found that very high radio-frequency amplitudes of one hundred volts or more could improve the signal-to-noise ratio of some chlorine compounds even though the sensitive period occurred at much lower voltages. Later it was discovered that an induction signal can be obtained from the same coil used to excite the resonance.

For typical chlorine compounds high (five or more volts) radio-frequency amplitude is desirable. A simple regenerative oscillator can not be operated at such levels without a large increase in noise. With a super-regenerative oscillator a large radio-frequency amplitude may be used to produce a strong induction signal which is subsequently detected at a low radio-frequency level during the sensitive period when the noise is not excessive. Thus, the signal-to-noise ratio for a super-regenerative oscillator-detector is usually greater than that of a regenerative oscillator-detector. The super-regenerative oscillator is also

usually less microphonic and can be run for longer periods of time without adjustment.

The super-regenerative oscillator has its disadvantages. The radio-frequency irradiation experienced by the sample is actually made up of many frequencies: f_c , $f_c \pm f_q$, $f_c \pm 2f_q$, $f_c \pm 3f_q$, ...etc., where f_c is the center frequency of the oscillator and f_q is the quench frequency. Some of the sidebands also are of sufficient amplitude to induce measurable resonance absorption if they happen to be equal to the resonance frequency. Thus, as the center frequency is slowly varied, several absorption curves (each separated from the next by the quench frequency) are observed for each existing resonance line. It is often difficult to decide at what frequency the resonance has occurred. If there is only one resonance line, changing the quench frequency will shift all of the absorption curves except the one due to absorption of energy at f_c . However, if two or more close-lying resonance lines exist, the several signals from each line overlap, and in most cases the spectrum becomes unintelligible. Another disadvantage of the super-regenerative oscillator is that it can not be used to study line shapes because of its complicated response.

The super-regenerative oscillator circuit of Figure 8 was also used in the spectrometers shown in Figures 3 and 4.

Figure 9 shows an example of a single resonance line detected using the super-regenerative oscillator with the lock-in spectrometer. The line is the Cl^{35} absorption curve in NaClO_3 at 77°K (see Figure 7 also). The plate voltage of the oscillator was 300 volts, the voltage across the wobulator was .09 volts (rms), the modulation frequency was 155 hertz, the recorder chart speed was two inches per minute, and the lock-in amplifier time constant was 0.1 seconds. The sweep rate was twenty-four kilohertz per minute. The quench frequency, measured on the oscilloscope by attaching a probe near the connection between the sample box and the coaxial line, was approximately thirty-seven kilohertz. The jaggedness of the curves was due to the overdamping of the recorder.

For a resonance curve in the region of thirty-eight megahertz with a modulation frequency of 155 hertz the quench frequency was set at fifty kilohertz. Thus, the period between radio-frequency pulses was short compared to T_2 which is on the order of 10^{-3} seconds for most chlorine compounds. The signal-to-noise ratio decreased as the quench frequency increased and at approximately sixty-five kilohertz the signal could no longer be detected. If the quench frequency was decreased from fifty kilohertz again the signal-to-noise decreased and at approximately thirty kilohertz the oscillator changed from coherent to

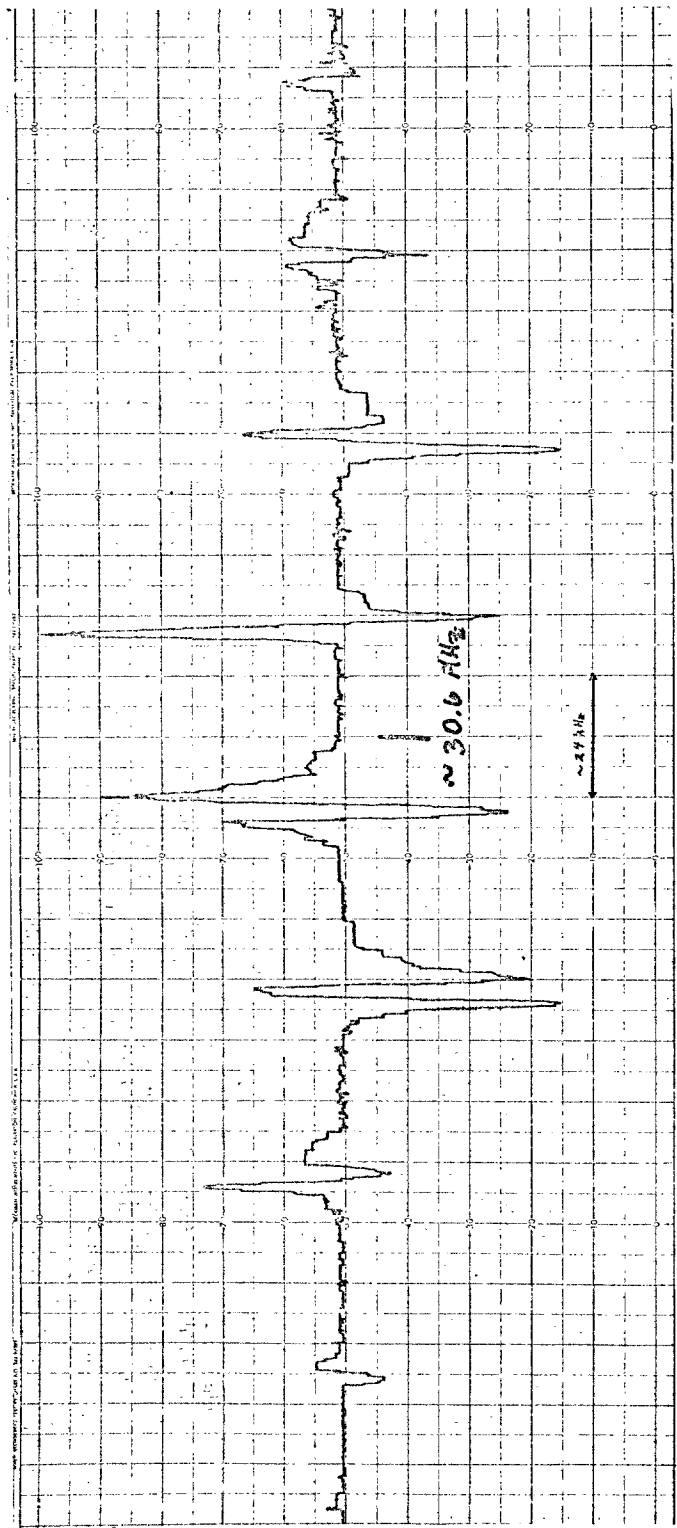


Fig. 9--Super-regenerative spectrometer recording of ^{35}Cl resonance absorption in NaClO_3 at 77°K .

incoherent operation. A filter was needed to filter out the quench frequency and is included in the circuit diagram in Figure 8.

Figure 10 shows an example of the absorption spectrum displayed when four close-lying resonance lines are present. The sample used was chlornil (2, 3, 5, 6 - tetrachloro-p-quinone), and the recording was made at 77°K. In the crystal lattice the four chlorine nuclei of each molecule are at non-equivalent sites. The four lines occur at 37.442, 37.470, 37.515, and 37.585 megahertz (2). For the recording in Figure 10 the plate voltage was 200 volts, the voltage across the webbulator was 0.08 volts (rms), the modulation frequency was 155 hertz, the chart speed was two inches per minute, the time constant was 0.1 seconds, the sweep rate was forty-two kilohertz, and the quench frequency was approximately forty-four kilohertz.

The frequency of the super-regenerative oscillator could not be measured directly with the Northeastern frequency counter since its counting period was longer than the duration of one of the radio-frequency pulses. The frequency was measured however with a Signal Corps Model BC-221-AK beat-type frequency meter loosely coupled to the oscillator by a short probe under the chassis. A grid dip meter was used to measure the approximate frequency, the BC-221 was tuned to this approximate frequency, and then the frequency meter was adjusted to zero-beat with the oscillator. If a slight change in the quench frequency

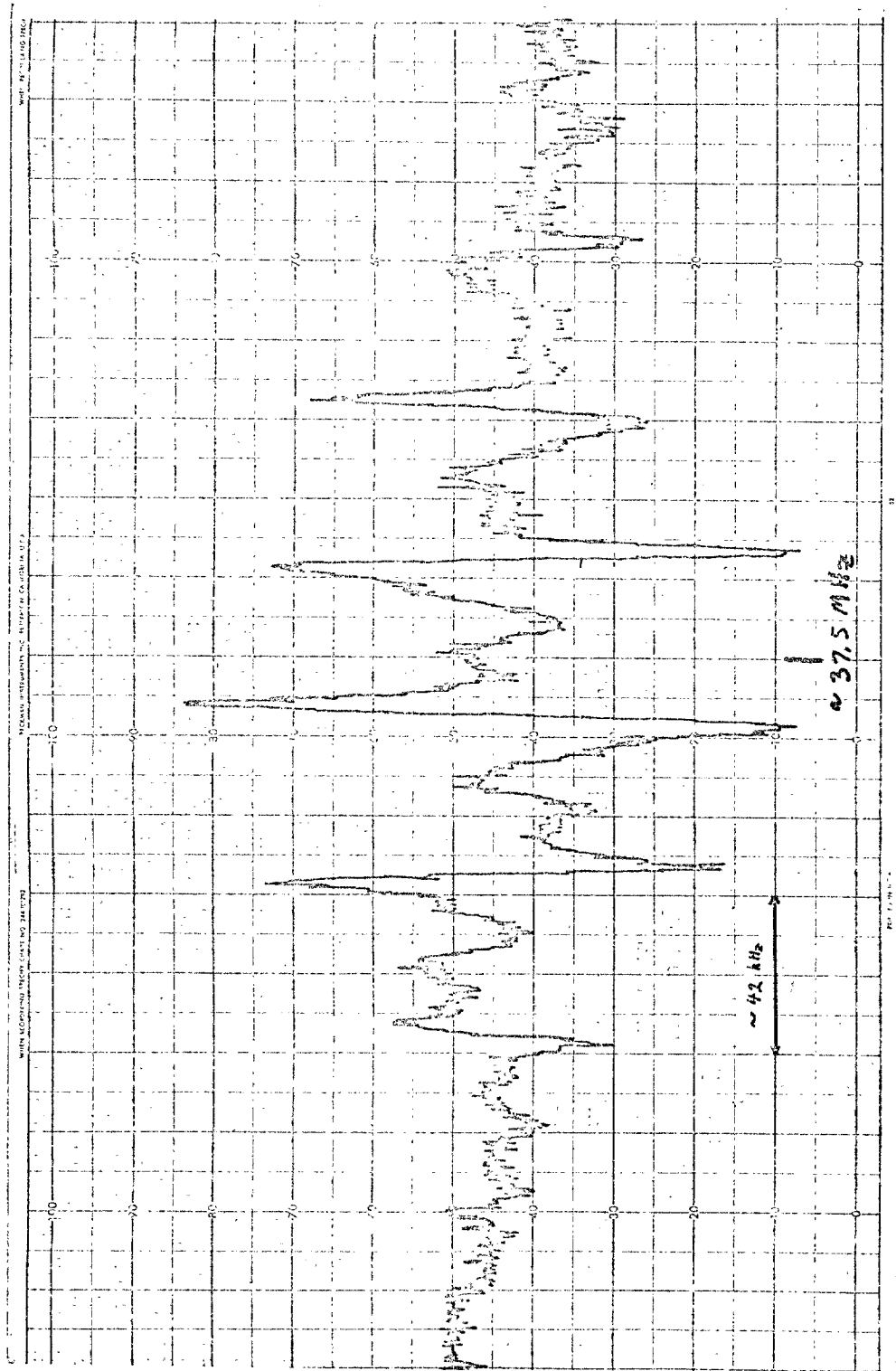


Fig. 10--Super-regenerative spectrometer recording of Cl^{35} resonance absorption lines of chloranil at 77°K.

destroyed the zero beat, the frequency meter was assumed to be tuned to one of the sidebands. When the frequency meter was tuned to the center frequency of the super-regenerative oscillator, a small change in the quench frequency produced no detuning.

Finally it might be mentioned that at times spurious signals appeared on the oscilloscope or recorder. These spurious signals arose perhaps from piezo-electric effects in the sample (6, p. 805) or electronic effects in the apparatus. A permanent bar magnet held near the sample holder was used to distinguish these spurious signals from the actual quadrupole resonance absorptions. The magnetic field eliminated the degeneracy of the m -states and caused an actual absorption curve to broaden but had no effect on the spurious signals.

CHAPTER BIBLIOGRAPHY

1. Andrew, E. R., Nuclear Magnetic Resonance, New York, Cambridge University Press, 1955.
2. Bray, P. J. and others, "Pure Quadrupole Resonance Determination of Molecular Charge Distributions. I. Substituted Quinones, Quinolines, Pyridines, Pyrimidines, and Triazines," The Journal of Chemical Physics, XXVIII (January, 1958), 99-102.
3. Das, T. P. and E. L. Hahn, Nuclear Quadrupole Resonance Spectroscopy, Suppl. 1 of Solid State Physics, edited by Frederick Seitz and David Turnbull, New York, Academic Press, Inc., 1958.
4. Grechishkin, V. S. and G. B. Soifer, "Nuclear Quadrupole Resonance Instrumentation (Review)," Instrumentation and Experimental Technique, I (1964), 1-16.
5. Instruction Manual, Model RJB Lock-in Amplifier, Mount Vernon, N. Y., Electronics, Missiles and Communications, Inc., n. d.
6. Livingston, Ralph, "Detection and Measurement of Direct Nuclear Quadrupole Transitions," Annals of the New York Academy of Sciences, LV (November, 1952), 800-807.
7. Livingston, Ralph, "Nuclear Quadrupole Resonance," Molecular Physics, Vol. III of Methods of Experimental Physics, edited by Dudley Williams, New York, Academic Press, 1962.
8. Segal, S. L. and R. G. Barnes, Catalog of Nuclear Quadrupole Interactions and Resonance Frequencies in Solids. Part II. Halogen Resonances in Organic Compounds, Research and Development Report, United States Atomic Energy Commission, Ames, Iowa, Ames Laboratory, 1965.
9. Wang, Tien-Chuan, "Pure Nuclear Quadrupole Spectra of Chlorine and Antimony Isotopes in Solids," Physical Review, XCIX (1955), 566-577.

CHAPTER IV

RESULTS

The spectrometers described in the previous chapter were constructed for the purpose of searching for the chlorine nuclear quadrupole resonance in two organic compounds which had just recently become commercially available. The two compounds were 3, 4, 5, 6 - tetrachlorophthalimide and 1, 3, 6, 8 - tetrachloropyrene. In this chapter the results of this search are discussed and some recommendations are made concerning these results.

3, 4, 5, 6 - Tetrachlorophthalimide

Approximately two hundred grams of 3, 4, 5, 6 - tetrachlorophthalimide, purchased from the Aldrich Chemical Company, were used in search for the chlorine quadrupole resonance frequencies of this compound. The 3, 4, 5, 6 - tetrachlorophthalimide molecule is shown in Figure 11 and appears to possess symmetry about a reflection plane. If the molecule is not distorted in the crystalline structure of the compound, the chlorine nuclei at sites 3 and 6 on the benzene ring should have identical environments; the same is true for the chlorine nuclei at sites 4 and 5. Thus, one would expect to observe two quadrupole resonance lines.

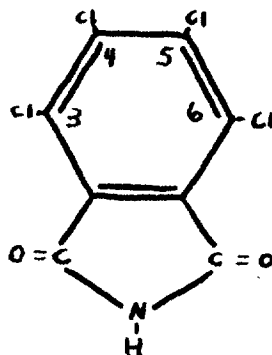


Fig. 11--3, 4, 5, 6 - Tetrachlorophthalimide molecule

Figure 12 shows the absorption curves recorded for 3, 4, 5, 6 - tetrachlorophthalimide at 77°K. Figures 13 and 14 are two displays of the curves at room temperature. All three recordings were made using the super-regenerative oscillator. For Figure 12 the plate voltage was 250 volts, the voltage across the wobulator was 0.12 volts (rms), the modulation frequency was 155 hertz, the lock-in amplifier time constant was 0.3 seconds, the recorder chart speed was two inches per minute, and the quench frequency was approximately fifty kilohertz. The center frequency of the oscillator was swept at approximately fifty-six kilohertz per minute. The center of the absorption curves shown is approximately 37.9 megahertz.

For Figure 13 the plate voltage was 150 volts, the voltage across the wobulator was 0.12 volts (rms), the modulation frequency was 155 hertz, the lock-in time constant was one second, the chart speed was two inches per minute, and the quench frequency was approximately forty-eight kilohertz. The center frequency of the

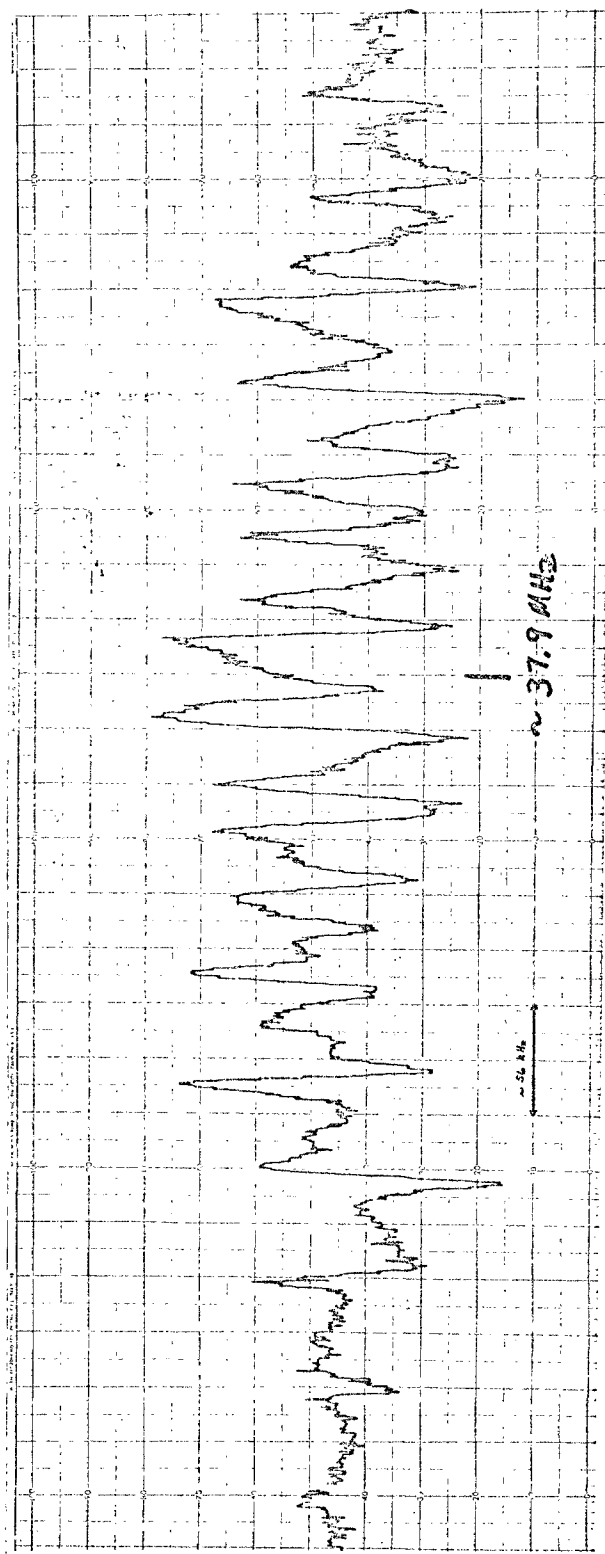


Fig. 12--Super-regenerative spectrometer recording of nuclear quadrupole absorption in 3, 4, 5, 6 - tetrachlorophthalimide at 77°K.

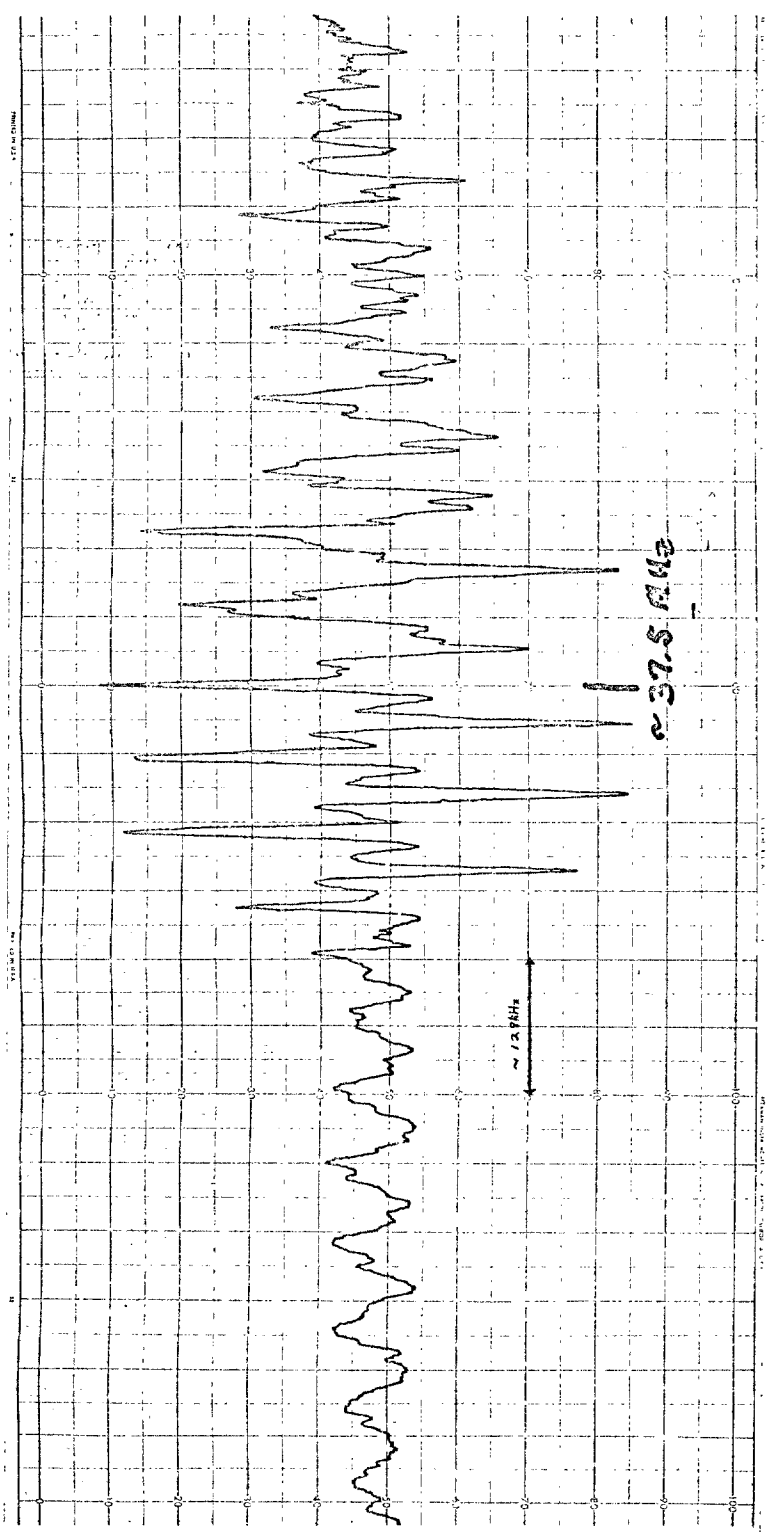


Fig. 13--Super-regenerative spectrometer recording of nuclear quadrupole absorption in 3, 4, 5, 6 - tetrachlorophthalimide at room temperature with a sweep rate of 129 kilohertz per minute.

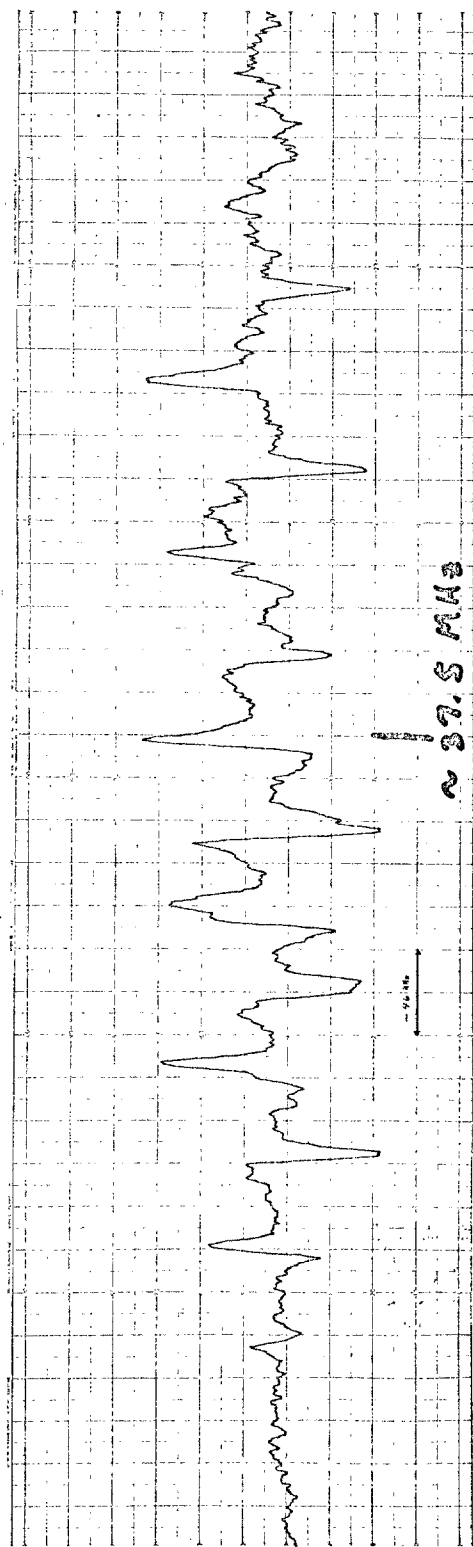


Fig. 14--Super-regenerative spectrometer recording of nuclear quadrupole absorption in 3, 4, 5, 6 - tetrachlorophthalimide at room temperature with a sweep rate of 46 kilohertz per minute.

oscillator was swept at a rate of 129 kilohertz per minute. For Figure 14 the plate voltage was 150 volts, the voltage across the wobblator was 0.12 volts (rms), the lock-in time constant was one second, the modulation frequency was 155 hertz, the chart speed was two inches per minute, the quench rate was approximately fifty kilohertz, and the frequency of the oscillator was swept at a rate of approximately forty-six kilohertz per minute. For Figures 13 and 14 the center of the absorption curves is located near 37.5 megahertz.

The rate of change of the oscillator frequency was determined by measuring the frequency at two different points with the grid dip meter and dividing the difference by the time interval between the measurements. This assumption of a linear change in frequency with respect to time is reasonable if only a small portion of the oscillator range is considered. The approximate frequencies of the absorption curves were measured with the grid dip meter, which is accurate only to a tenth of a megahertz. At room temperature and at 77°K a permanent magnet was used to verify that the recorded curves were actually due to quadrupole resonance absorption.

There is obviously more than one line present in the 3, 4, 5, 6 - tetrachlorophthalimide quadrupole resonance spectrum. It was found that the quench frequency could

be varied from approximately thirty-five to seventy-five kilohertz and the absorption curves still be observed. However, changing the quench frequency did not yield any useful information. At different quench frequencies the recording was different, but it was impossible to decide which curves had not shifted. One recording was numerically integrated, but this also failed to solve the problem as to which of the recorded curves was due to the absorption of radio-frequency energy at the center frequency of the oscillator. Apparently the lines are so closely spaced that the sidebands from one line overlap the center frequency of the other line.

The detection of the resonance absorption using the regenerative oscillator would eliminate the problem of sidebands and allow the resonance frequencies to be measured using the frequency counter. The regenerative oscillator was used to search carefully in the region near 37.9 megahertz at 77°K. No resonance absorption was detected. This was probably due to the fact that the maximum radio-frequency amplitude of the regenerative oscillator was less than two volts (rms); the optimum detection level occurred at an even lower voltage. The radio-frequency amplitude of the super-regenerative oscillator, on the other hand, was approximately fifteen volts (rms).

If the super-regenerative oscillator were used to display the absorption curves on the oscilloscope, a slight change in the quench frequency would indicate whether or not a particular curve was due to one of the sidebands. An unsuccessful attempt was made to observe the absorption curves of 3, 4, 5, 6 - tetrachlorophthalimide on the oscilloscope using the super-regenerative oscillator. However, this search was not thorough in the sense that only a few values of quench frequency and wobulator voltage were tried.

There is an indication that the apparatus used is capable of displaying the resonance lines of 3, 4, 6, 8 - tetrachlorophthalimide on the oscilloscope. In a given volume of chlorinal (see Figure 10) there are approximately 1.05 times as many chlorine nuclei as in the same volume of 3, 4, 5, 6 - tetrachlorophthalimide. Even though the chloranal molecule (Figure 15) appears to be symmetric, four resonance lines exist (1). This is apparently due to the distortion of the molecule in the crystalline

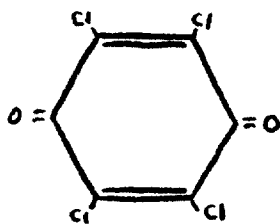


Fig. 15--Chloranal molecule

structure of the compound. If two resonance lines were present in 3, 4, 5, 6 - tetrachlorophthalimide their intensity should be approximately twice the intensity of the chloranil lines, assuming similar detection conditions in each case. The chloranil absorption lines were seen faintly on the oscilloscope. Thus, if two lines exist in 3, 4, 5, 6 - tetrachlorophthalimide, they should also be detectable. The possibility of four resonance lines, however, must not be neglected. As in the case of chloranil the crystalline structure could result in four non-equivalent sites for the chlorine nuclei. If this were true, it would be quite difficult to see the absorption curves on the scope.

At 77°K the recorded absorption curves of 3, 4, 5, 6 - tetrachlorophthalimide are centered near 37.9 megahertz, and at room temperature they are centered near 37.5 megahertz. Therefore they exhibit the expected decrease in quadrupole resonance frequency with an increase in temperature as discussed in Chapter II. The magnitude of the frequency change between these two temperatures is similar to that of other chlorine compounds (6, p. 572).

Since the ratio of the quadrupole moment of Cl^{35} to that of Cl^{37} is 1.26878 (5, p. xiii), at 77°K one would expect to observe quadrupole absorption near forty-eight megahertz three times as intense as the curves shown in Figure 12 or to observe curves near 29.9 megahertz one

third as intense. (Cl^{37} is 25 per cent abundant.) There is an indication that the absorption curves in Figures 12, 13, and 14 are due to Cl^{35} rather than to Cl^{37} . At 77°K two resonance lines due to Cl^{35} of tetrachlorophthalic acid have been observed at 38.424 and 38.140 megahertz (4). A comparison of Figures 11 and 16 shows the similarity of the two molecules. The environment of the chlorine nuclei for the two molecules would probably be similar.

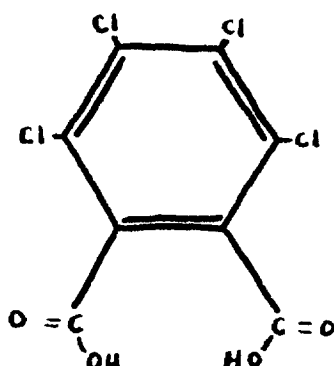


Fig. 16--Tetrachlorophthalic acid molecule

Thus, the absorption curves of 3, 4, 5, 6 - tetrachlorophthalimide at 77°K which are located near 37.9 megahertz are likely due to Cl^{35} quadrupole resonance absorption.

1, 3, 6, 8 - Tetrachloropyrene

A search for the chlorine nuclear quadrupole resonance frequencies of 1, 3, 6, 8 - tetrachloropyrene was also made. Approximately forty grams of this compound, purchased from Aldrich Chemical Company, were used. At room temperature the compound is a fine powder of very low density. Figure 17

shows the 1, 3, 6, 8 - tetrachloropyrene molecule as indicated in Aldrich Chemical Company's catalog. The molecule possesses symmetry about a reflection plane.

The search for the quadrupole resonance line (or lines) of 1, 3, 6, 8 - tetrachloropyrene proved unsuccessful. The regenerative spectrometer and super-regenerative spec-

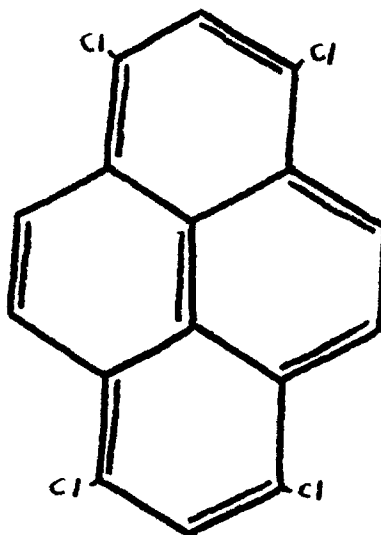


Fig. 17--1, 3, 6, 8 - tetrachloropyrene molecule

trometer were both used to search the region from eighteen megahertz to forty-eight megahertz. There are several reasons which could account for the lack of success.

The relatively small number of chlorine nuclei in the sample holder would cause the absorption curves from 1, 3, 6, 8 - tetrachloropyrene to be weak. There are approximately 6.3 times as many chlorine nuclei in a given volume of chloranil as in the same volume of 1, 3, 6, 8 - tetrachloropyrene. Since four resonance lines

exist for chloranil, the intensity of these lines should be approximately 1.6 times as great as that of a single line 1, 3, 6, 8 - tetrachloropyrene. If there were two or four lines for 1, 3, 6, 8 - tetrachloropyrene, the chloranil lines would be approximately 3.2 or 6.3 times as great respectively. Since the chloranil absorption curves could not be seen with the regenerative oscillator, it is therefore not surprising that the 1, 3, 6, 8 - tetrachloropyrene absorption curves could not be seen with this apparatus.

The super-regenerative oscillator could quite possibly be used to observe the resonance lines of 1, 3, 6, 8 - tetrachloropyrene if the modulation width, quench frequency, and radio-frequency amplitude were all adjusted properly. As can be seen from Figure 6, if the width of the modulation were too narrow, the displayed absorption curve would have a small amplitude and perhaps be lost in the noise. If the modulation width were too great, the absorption curve would be broadened and thus more easily obscured by noise. As was demonstrated in the case of 3, 4, 5, 6 - tetrachlorophthalimide, the value of the quench frequency has a pronounced effect on the amplitude of the absorption curve. For 3, 4, 5, 6 - tetrachlorophthalimide the curves could be seen best with a quench frequency of approximately fifty kilohertz. If the quench frequency were varied by

more than plus or minus twenty kilohertz, the absorption curves were lost in the noise. The proper choice of quench frequency differs for different compounds since it depends in part on the spin-spin relaxation time. The quench frequency changed slowly as the center frequency of the super-regenerative oscillator was varied. The spectrometer was run for two or three hours at a time without adjustment. During this time the quench frequency would change by ten to fifteen kilohertz.

Another explanation as to why resonance absorption in 1, 3, 6, 8 - tetrachloropyrene was not observed is that the lines occur outside the eighteen to forty-eight megahertz range. This is, however, unlikely, since by far the majority of the observed chlorine quadrupole resonance lines in organic compounds have occurred within these bounds (5). If the quadrupole resonance lines of 1, 3, 6, 8 - tetrachloropyrene are somewhat broader than the lines observed for the other chlorine compounds, their amplitude would be decreased. This also could account for the null results of the search for the resonance absorption in 1, 3, 6, 8 - tetrachloropyrene.

Recommendations

In this study a super-regenerative oscillator was used to determine that nuclear quadrupole resonance absorption in 3, 4, 5, 6 - tetrachlorophthalimide occurs near

37.9 megahertz at 77°K. The presence of sidebands made the data unintelligible. Certain things could be done to overcome this difficulty. A regenerative oscillator-detector designed by Wang (6) was modified and used by Douglass (3) to record the resonance lines in chloranil. This oscillator could possibly be used to record the quadrupole resonance lines of 3, 4, 5, 6 - tetrachlorophthalimide. The use of a regenerative oscillator-detector would eliminate the problem of sidebands and the resonance frequencies could be measured within a few hundred hertz.

A method which could eliminate several of the sidebands was suggested by Dean and Pollak (2). A circuit used to modulate slowly the quench frequency of an externally quenched super-regenerative oscillator is described. Many of the sidebands are suppressed, but the center frequency absorption is virtually unaffected. The oscillator described is similar to the super-regenerative oscillator discussed in Chapter III.

Nuclear quadrupole resonance absorption in 1, 3, 6, 8 - tetrachloropyrene was not found in the region from eighteen to forty-eight megahertz. A thorough search of this region employing several values of modulation width, quench frequency and radio-frequency amplitude using the super-regenerative oscillator might yield the desired results. The regenerative oscillator employed by Douglass (3) might also be used to search this range. If no resonance lines were found, the

search range might be broadened to include five megahertz to fifty-five megahertz.

The use of Zeeman modulation rather than frequency modulation might prove advantageous. With Zeeman modulation a magnetic field of between twenty and eighty gauss is applied to the sample and varied periodically about zero field (usually with a square-wave). For a powdered sample the resonance absorption appears only when the field is zero. The use of this modulation scheme would eliminate the amplitude modulation caused by the wobulator. A filter tuned to the modulation frequency would not be necessary in the regenerative spectrometer. With this filter in the circuit much of the desired signal is removed.

In searching for the 1, 3, 6, 8 - tetrachloropyrene quadrupole resonance absorption, one should take all possible precaution to eliminate noise in spectrometer. All of the oscillator components should be rigidly attached and the radio-frequency leads made as short as possible. All moving parts such as the tuning capacitor should be well lubricated. The electronic equipment should be shielded and free from mechanical vibration. A minimum noise level is desirable in all quadrupole resonance searches but seems especially necessary for the case of 1, 3, 6, 8 - tetrachloropyrene.

CHAPTER BIBLIOGRAPHY

1. Bray, P. J. and others, "Pure Quadrupole Resonance Determination of Molecular Charge Distributions. I. Substituted Quinones, Quinolines, Pyridines, Pyrimidines, and Triazines," The Journal of Chemical Physics, XXVII (January, 1958), 99-102.
2. Dean, C. and M. Pollak, "Suppressing Side-Band Interference in Superregenerative rf Spectrometers," The Review of Scientific Instruments, XXIX (July, 1958), 630-632.
3. Douglass, Dean C., "Quadrupole Resonance Spectrum of Chloranil and Its Hexamethyl-benzene Complex," The Journal of Chemical Physics, XXXII (1960), 1882-1883.
4. Hooper, H. O. and P. J. Bray, "Induction Studies in Several Groups of Halogen - Containing Organic Compounds by their Cl^{35} , Br^{79} , or Br^{81} Pure Quadrupole Resonance Spectra," The Journal of Chemical Physics, XXXIII (August, 1960), 334-361.
5. Segal, S. L. and R. G. Barnes, Catalog of Nuclear Quadrupole Interactions and Resonance Frequencies in Solids. Part II. Halogen Resonances in Organic Compounds, Research and Development Report, United States Atomic Energy Commission, Ames, Iowa, Ames Laboratory, 1965.
6. Wang, Tien-Chuan, "Pure Nuclear Quadrupole Spectra of Chlorine and Antimony Isotopes in Solids," Physical Review, XCIX (1955), 566-577.

APPENDIX I

THE NUCLEAR QUADRUPOLE HAMILTONIAN

Classical Derivation

Consider a nucleus of charge density ρ and atomic number Z in a region of a non-uniform electric potential V . If the center of mass of the nucleus is chosen as the origin of the coordinate system, the electrostatic interaction energy of the nucleus with the electric potential will be

$$W = \int_{\tau} \rho(\vec{r}) V d\tau \quad , \quad (1)$$

where \vec{r} is the position vector of an incremental volume $d\tau$ and τ is the volume of the nucleus. The potential will vary over the nuclear volume, but if this variation is not too great, the potential may be expanded about the origin by a Taylor series and only the first few terms considered.

$$W = \int_{\tau} \rho(\vec{r}) \left[V_0 + \sum_i x_i \left(\frac{\partial V}{\partial x_i} \right)_0 + \frac{1}{2} \sum_j \sum_k x_j x_k \left(\frac{\partial^2 V}{\partial x_j \partial x_k} \right)_0 + \dots \right] d\tau \quad (2)$$

where $i, j,$ and k go from 1 to 3 and $x_1 = x, x_2 = y, x_3 = z$. The zero subscript indicates that the quantity is evaluated at the origin. This equation becomes

$$\begin{aligned}
 W = V_0 \int_{\tau} \rho(\vec{r}) d\tau + \sum_1 (\partial V / \partial x_1)_0 \int_{\tau} \rho(\vec{r}) x_1 d\tau \\
 + \frac{1}{2} \sum_j \sum_k (\partial^2 V / \partial x_j \partial x_k)_0 \int_{\tau} \rho(\vec{r}) x_j x_k d\tau + \dots
 \end{aligned}
 \tag{3}$$

The first term of this equation yields $V_0 Z e$, where e is the magnitude of the electronic charge. This portion of the interaction energy is not affected by the nuclear orientation and will be neglected. The second integral in equation (3) is the electric dipole moment of the nucleus. Experimental evidence indicates that no electric dipole exists. This implies symmetry of the charge density such that $\rho(\vec{r}) = \rho(-\vec{r})$. The dipole term thus vanishes. The third term in the equation is the quadrupole term, which may be written out explicitly as

$$\begin{aligned}
 \frac{1}{2} \left(\frac{\partial^2 V}{\partial x^2} \right)_0 \int_{\tau} \rho x^2 d\tau + \frac{1}{2} \left(\frac{\partial^2 V}{\partial y^2} \right)_0 \int_{\tau} \rho y^2 d\tau + \frac{1}{2} \left(\frac{\partial^2 V}{\partial z^2} \right)_0 \int_{\tau} \rho z^2 d\tau \\
 + \left(\frac{\partial^2 V}{\partial x \partial y} \right)_0 \int_{\tau} \rho xy d\tau + \left(\frac{\partial^2 V}{\partial x \partial z} \right)_0 \int_{\tau} \rho xz d\tau + \left(\frac{\partial^2 V}{\partial y \partial z} \right)_0 \int_{\tau} \rho yz d\tau
 \end{aligned}
 \tag{4}$$

According to the semiclassical viewpoint in which the nucleus is spinning very rapidly about an axis, it is reasonable to assume that the nucleus has axial symmetry. If the z-axis is taken as the spin axis, the mixed terms ($\int \rho x_i x_j d\tau$, $i \neq j$) in the quadrupole expression will be zero, and since the external charges will "see" only a time average distribution, it follows that

$$\int_{\tau} \rho x^2 d\tau = \int_{\tau} \rho y^2 d\tau
 \tag{5}$$

Laplace's equation will hold at the nuclear site for the potential due to external charges.

$$\left(\frac{\partial^2 V}{\partial x^2}\right)_0 + \left(\frac{\partial^2 V}{\partial y^2}\right)_0 + \left(\frac{\partial^2 V}{\partial z^2}\right)_0 = 0 \quad (6)$$

Hence, the quadrupole portion of the interaction energy becomes

$$W_Q = \frac{1}{2} \left(\frac{\partial^2 V}{\partial x^2}\right)_0 \int_{\tau} \rho x^2 d\tau + \frac{1}{2} \left(\frac{\partial^2 V}{\partial y^2}\right)_0 \int_{\tau} \rho y^2 d\tau + \frac{1}{2} \left(\frac{\partial^2 V}{\partial z^2}\right)_0 \int_{\tau} \rho z^2 d\tau, \quad (7)$$

$$= -\frac{1}{2} \left(\frac{\partial^2 V}{\partial z^2}\right)_0 \int_{\tau} \rho x^2 d\tau + \frac{1}{2} \left(\frac{\partial^2 V}{\partial z^2}\right)_0 \int_{\tau} \rho z^2 d\tau \quad (8)$$

But

$$2 \int_{\tau} \rho x^2 d\tau = \int_{\tau} \rho x^2 d\tau + \int_{\tau} \rho y^2 d\tau = - \int_{\tau} \rho (z^2 - r^2) d\tau, \quad (9)$$

So

$$W_Q = \frac{1}{2} \left(\frac{\partial^2 V}{\partial z^2}\right)_0 \int_{\tau} \rho (3z^2 - r^2) d\tau \quad (10)$$

The quantity

$$Q^* = 1/e \int_{\tau} \rho (3z^2 - r^2) d\tau \quad (11)$$

is sometimes called the nuclear electric quadrupole moment. It is a measure of the deviation from spherical symmetry of the nucleus. As illustrated in Figure 18, if Q^* is positive, the nucleus is cigar-shaped; if Q^* is negative, the nucleus is shaped like a flattened sphere; if Q^* is zero, the nucleus is spherical.

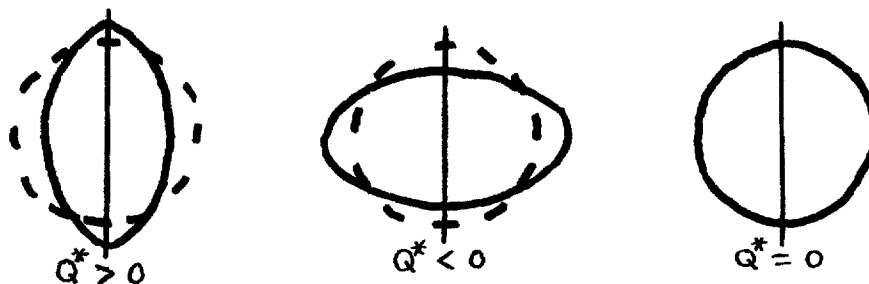


Fig. 18--Nuclear shape for various values of Q^*

Equation (10) gives the interaction energy in a coordinate system whose z-axis is along the axis of symmetry of the nucleus. Let x' , y' , z' denote the principal axes coordinate system of the electric field gradient. Figure 19 illustrates the nucleus in such a coordinate system, where the Eulerian angles θ , β , and ψ as defined by Goldstein (5, p. 107) have been used to indicate the orientation. The line of nodes is perpendicular to the plane of the z , z' axes. To find the electric field gradient in the primed coordinate system the following relationship is needed (5, p. 109).

$$\begin{bmatrix} x' \\ y' \\ z' \end{bmatrix} = \begin{bmatrix} \cos\psi\cos\beta - \cos\theta\sin\beta\sin\psi & -\sin\psi\cos\beta - \cos\theta\sin\beta\cos\psi & \sin\theta\sin\beta \\ \cos\psi\sin\beta - \cos\theta\cos\beta\sin\psi & -\sin\psi\sin\beta + \cos\theta\cos\beta\cos\psi & -\sin\theta\cos\beta \\ \sin\theta\sin\psi & \sin\theta\cos\psi & \cos\theta \end{bmatrix} \begin{bmatrix} x \\ y \\ z \end{bmatrix} \quad (12)$$

$$\begin{aligned} \frac{\partial^2 V}{\partial z^2} &= \frac{\partial^2 V}{\partial x'^2} \left(\frac{\partial x'}{\partial z} \right)^2 + \frac{\partial^2 V}{\partial y'^2} \left(\frac{\partial y'}{\partial z} \right)^2 + \frac{\partial^2 V}{\partial z'^2} \left(\frac{\partial z'}{\partial z} \right)^2 \\ &+ \frac{\partial V}{\partial x'} \frac{\partial^2 x'}{\partial z^2} + \frac{\partial V}{\partial y'} \frac{\partial^2 y'}{\partial z^2} + \frac{\partial V}{\partial z'} \frac{\partial^2 z'}{\partial z^2} \end{aligned} \quad (13)$$

By the use of equation (12), one may write equation (13) as

$$\frac{\partial^2 V}{\partial z^2} = \frac{\partial^2 V}{\partial x'^2} (\sin\theta\sin\beta)^2 + \frac{\partial^2 V}{\partial y'^2} (-\sin\theta\cos\beta)^2 + \frac{\partial^2 V}{\partial z'^2} (\cos\theta)^2 \quad (14)$$

The direction of the nuclear angular momentum \vec{I} is along the z-axis; the components of \vec{I} in the principal axes system would be

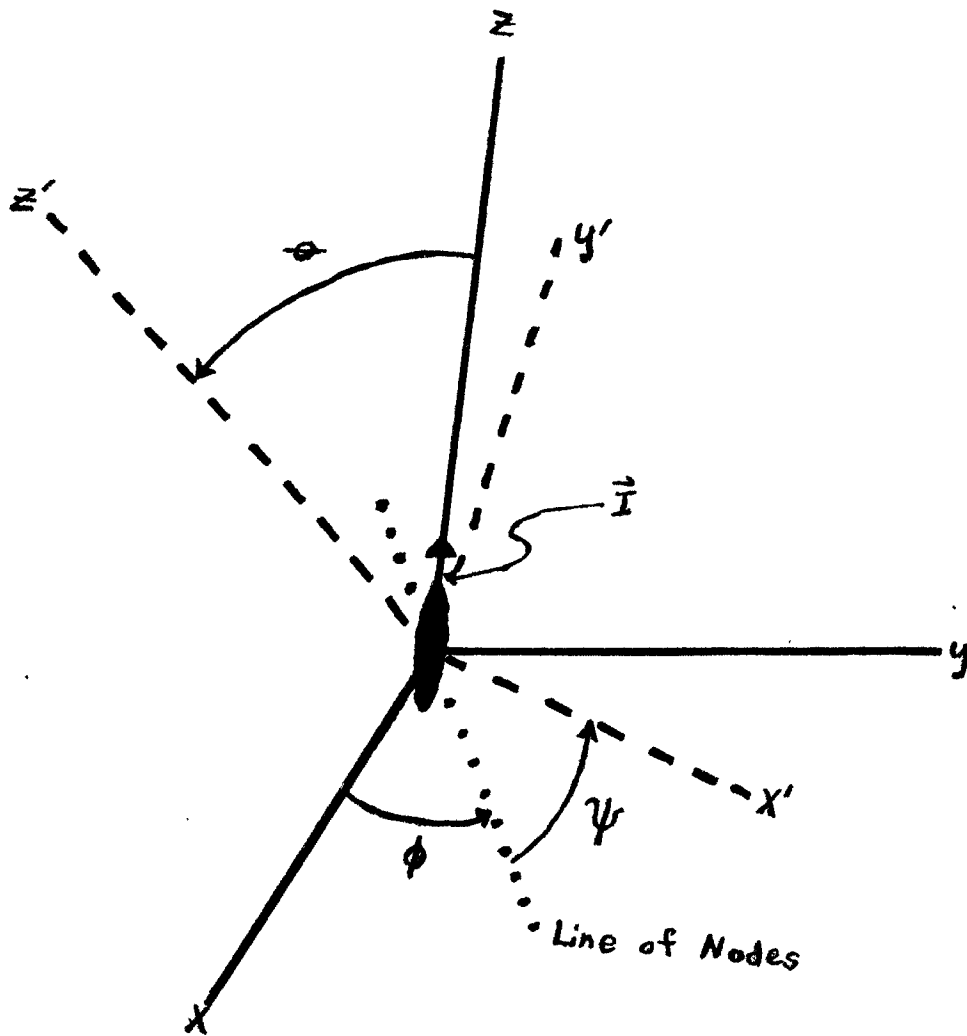


Fig. 19--Nuclear orientation in the principal axes system (primed coordinates) of the electric field gradient.

$$\begin{aligned}
 I_{x'} &= |\vec{I}| \sin \theta \sin \phi \quad , \\
 I_{y'} &= |\vec{I}| \sin \theta \cos \phi \quad , \\
 I_{z'} &= |\vec{I}| \cos \theta \quad .
 \end{aligned}
 \tag{15}$$

Equation (14) can be written as

$$\frac{\partial^2 V}{\partial z'^2} = \frac{\partial^2 V}{\partial x'^2} \frac{I_{x'}^2}{|\vec{I}|^2} + \frac{\partial^2 V}{\partial y'^2} \frac{I_{y'}^2}{|\vec{I}|^2} + \frac{\partial^2 V}{\partial z'^2} \frac{I_{z'}^2}{|\vec{I}|^2} \quad , \tag{16}$$

where $|\vec{I}|^2$ is equal to $I_{x'}^2 + I_{y'}^2 + I_{z'}^2$. Therefore, using equations (10), (11), and (16) one can write the electric quadrupole interaction Hamiltonian in the principal axes system of the electric field gradient as

$$H_Q = \frac{eQq}{4|\vec{I}|^2} \left(\frac{\partial^2 V}{\partial x'^2} \frac{I_{x'}^2}{|\vec{I}|^2} + \frac{\partial^2 V}{\partial y'^2} \frac{I_{y'}^2}{|\vec{I}|^2} + \frac{\partial^2 V}{\partial z'^2} \frac{I_{z'}^2}{|\vec{I}|^2} \right) \quad , \tag{17}$$

where the partial derivatives are evaluated at the nuclear center of mass.

Quantum Mechanical Description

Consider a nucleus of A nucleons described by the wave function $\psi_{nIm}(\vec{r}_1 \dots \vec{r}_A)$, where I is the total angular momentum quantum number, m is the magnetic quantum number indicating the orientation of the angular momentum, and n represents all other quantum numbers needed to specify the system. The separation energy between the nuclear ground state and the first excited state is large compared to the orientation energy (2, p. 327). Thus, in dealing with nuclear quadrupole interaction only matrix elements of the form

$$\langle nlm' | H_Q | nlm \rangle \quad (18)$$

need be considered.

Equation (3) of the previous section is a convenient form for the electrostatic interaction in the quantum mechanical description as well as in the classical case. However, in quantum mechanics the charge density $\rho(\vec{r})$ must be replaced by the density operator defined as

$$\rho_{op}(\vec{r}) = \sum_{k=1}^{Z'} q_k \delta(\vec{r} - \vec{r}_k) = e \sum_{k=1}^{Z'} \delta(\vec{r} - \vec{r}_k) \quad , \quad (19)$$

where e is the charge of a proton, \vec{r}_k is the position vector of the k^{th} proton with respect to an origin at the nuclear center of mass, and Z' is the atomic number of the nucleus. Equation (3) then becomes

$$\begin{aligned} W = V_0 \int_{\tau} \rho_{op}(\vec{r}) d\tau + \sum_1 \left(\frac{\partial V}{\partial x_1} \right)_0 \int_{\tau} \rho_{op}(\vec{r}) x_1 d\tau \\ + \frac{1}{2} \sum_j \sum_k \left(\frac{\partial^2 V}{\partial x_j \partial x_k} \right)_0 \int_{\tau} \rho_{op}(\vec{r}) x_j x_k d\tau + \dots \quad . \quad (20) \end{aligned}$$

The first integral in equation (20) is again the total charge of the nucleus and is not dependent upon the nuclear orientation. The second term is the dipole term, which is zero because of symmetry properties of the nucleus. Experimental evidence indicates that the nucleus has definite parity. From this fact it can be proven that the center of mass and center of charge of the nucleus coincide (8, p. 161; 7, p. 4). Hence,

$$\rho_{op}(\vec{r}) = \rho_{op}(-\vec{r}) \quad . \quad (21)$$

The dipole term goes to zero since it contains an odd function integrated over symmetric limits. The fourth term in the series (not shown in equation (20)) is zero by a similar argument.

The third term in equation (20) is the quadrupole term. It is convenient to define the quantities

$$Q_{ij} = \int_{\tau} \rho_{op}(\vec{r}) [3x_i x_j - \delta_{ij} r^2] d\tau \quad , \quad (22)$$

and

$$V_{ij} = \left(\frac{\partial^2 V}{\partial x_i \partial x_j} \right)_0 \quad . \quad (23)$$

The quadrupole term then becomes

$$W_Q = 1/6 \sum_i \sum_j V_{ij} [Q_{ij} + \int_{\tau} \delta_{ij} \rho_{op} r^2 d\tau] \quad . \quad (24)$$

Assuming that Laplace's equation holds at the nuclear site, the second term in equation (24) vanishes. Thus,

$$W_Q = 1/6 \sum_i \sum_j V_{ij} Q_{ij} \quad . \quad (25)$$

By equation (22) the quantity Q_{ij} may be written as

$$Q_{ij} = \int_{\tau} e \sum_k \delta(\vec{r} - \vec{r}_k) [3x_i x_j - \delta_{ij} r^2] d\tau \quad . \quad (26)$$

Upon integration this becomes

$$Q_{ij} = e \sum_{k=1}^Z (3x_{ik} x_{jk} - \delta_{ij} r_k^2) \quad . \quad (27)$$

The electric quadrupole Hamiltonian is

$$H_Q = 1/6 \sum_i \sum_j V_{ij} Q_{ij} \quad , \quad (28)$$

where Q_{ij} is given in equation (27).

In order to evaluate the matrix elements of the above Hamiltonian a more useful form is needed. This form can be found by the use of a theorem from quantum mechanics. The theorem applies to all second-rank tensors of, say, the form of equation (27) which are constructed in the same manner from vectors satisfying the same commutation rules with respect to \vec{I} and are symmetric and have zero trace. According to this theorem the matrix elements diagonal in I of all such tensors have the same dependence on the magnetic quantum number m (8, pp. 164-170; 7, p. 17; 2, p. 330). This is a special case of the Wigner-Eckart theorem. The components of the position vector for each nucleon and the components of the total angular momentum for each nucleon fall into a class of operators known as "class T" operators. The operators of this class all obey the same commutation rules with respect to \vec{I} .

$$\begin{aligned}
 [I_x, T_x] &= 0 & ; \\
 [I_x, T_y] &= i\hbar T_z & , \\
 [I_x, T_z] &= -i\hbar T_y & , \\
 &\text{etc.,}
 \end{aligned}
 \tag{29}$$

and

$$[\vec{I}, T^2] = 0 . \tag{30}$$

The i in the above equation is the square root of minus one. The quadrupole moment tensor as defined by equation

(22) is symmetric and has a zero trace. Therefore, the above theorem implies that the matrix elements of the quadrupole moment tensor diagonal in I may be written as

$$\langle nIm | Q_{ij} | nIm' \rangle = C \langle nIm | \left(3 \frac{I_i I_j + I_j I_i}{2} - \delta_{ij} I^2 \right) | nIm' \rangle, \quad (31)$$

where C is independent of m and m'. This equation is analogous to a more familiar one for the magnetic dipole moment vector,

$$\langle nIm | \mu_j | nIm' \rangle = C' \langle nIm | I_j | nIm' \rangle. \quad (32)$$

One can express C in terms of the matrix element for which $m = m' = I$ and $i = j = z$ as follows.

$$\langle nII | Q_{zz} | nII \rangle = C \langle nII | 3I_z^2 - I^2 | nII \rangle, \quad (33)$$

$$= C [3I^2 - I(I+1)] \quad (34)$$

$$= C I(2I - 1) \quad (35)$$

where z is the axis along which the total angular momentum is quantized. The quantity on the left in equation (33) is usually defined as eQ and Q is termed the quadrupole moment of the nucleus. Therefore,

$$eQ = CI(2I - 1) \quad (36)$$

$$C = \frac{eQ}{I(2I - 1)} \quad (37)$$

where

$$eQ = \langle nII | Q_{zz} | nII \rangle \quad (38)$$

Since the concern here is for the quadrupole Hamiltonian matrix elements for a particular I and n, equations (31)

and (37) imply that the Hamiltonian may be expressed as

$$H_Q = \frac{eQ}{6I(2I-1)} \sum_i \sum_j V_{ij} \left[3/2(I_i I_j + I_j I_i) - \delta_{ij} \hat{I}^2 \right]. \quad (39)$$

This Hamiltonian applies to an arbitrary coordinate system. If one chooses the principal axes coordinate system of the electric field gradient, the expression for the Hamiltonian may be simplified by the fact that in this system

$$V_{ij} = 0 \quad \text{for } i \neq j \quad . \quad (40)$$

Equation (39) then becomes

$$H_Q = \frac{eQ}{2I(2I-1)} \left[V_{xx} (I_x^2 - \hat{I}^2) + V_{yy} (I_y^2 - \hat{I}^2) + V_{zz} (I_z^2 - \hat{I}^2) \right]. \quad (41)$$

By Laplace's equation this reduces to

$$H_Q = \frac{eQ}{2I(2I-1)} \left[V_{xx} I_x^2 + V_{yy} I_y^2 + V_{zz} I_z^2 \right] \quad (42)$$

for the nuclear quadrupole Hamiltonian in the principal axes system of the electric field gradient.

A comparison of the Hamiltonian derived from classical considerations (equation (17)) and that derived by quantum mechanics (equation (42)) indicates that the coefficient is different. There are two reasons for this. One is that the symbol $|\hat{I}|^2$ in equation (17) is the square of the magnitude of the total angular momentum given by $|\hat{I}|^2 = I_x^2 + I_y^2 + I_z^2$. The I in equation (42) is the total angular momentum quantum number; the magnitude of the square of the

total angular momentum is given by $I(I + 1)$. The other reason for a difference in the two equations is that the definitions of the quadrupole moments in the two is different. In equation (17) Q^* has been evaluated along the x -axis for the case in which \vec{I} is along this axis. In equation (42) Q is defined for the case where the alignment of \vec{I} is taken to be that of the state $I = m$ which is not along the x -axis. According to Dehmelt (4, p. 113) the relationship between the two quadrupole moments is

$$Q^* = \frac{2(I + 1)}{2I - 1} Q \quad (43)$$

By substituting this value for Q^* and $|\vec{I}|^2 = I(I + 1)$ into equation (17) one arrives at equation (42). Thus, the classical and quantum mechanical derivations yield the same expressions for the nuclear quadrupole Hamiltonian.

APPENDIX BIBLIOGRAPHY

1. Bersohn, R., "Nuclear Electric Quadrupole Spectra in Solids," The Journal of Chemical Physics, XX (October, 1952), 1505-1509.
2. Cohen, M. H. and F. Reif, "Quadrupole Effects in Nuclear Magnetic Resonance Studies of Solids," Solid State Physics, Vol. V, edited by Frederick Seitz and David Turnbull, New York, Academic Press, Inc., 1957.
3. Dailey, B. P., "The Chemical Significance of Quadrupole Spectra," Journal of Physical Chemistry, LVII (May, 1953), 490-496.
4. Dehmelt, H. G., "Nuclear Quadrupole Resonance," The American Journal of Physics, XXII (January, 1954), 110-120.
5. Goldstein, Herbert, Classical Mechanics, Reading, Massachusetts, Addison-Wesley Publishing Company, Inc., 1950.
6. Pound, R. V., "Nuclear Electric Quadrupole Interactions in Crystals," Physical Review, LXXIX (August, 1950), 685,703.
7. Ramsey, Norman F., Nuclear Moments, New York, John Wiley and Sons, Inc., 1953.
8. Slichter, Charles P., Principles of Magnetic Resonance, New York, Harper and Row, 1963.

BIBLIOGRAPHY

Books

- Andrew, K. R., Nuclear Magnetic Resonance, New York, Cambridge University Press, 1955.
- Cohen, M. H. and F. Reif, "Quadrupole Effects in Nuclear Magnetic Resonance Studies of Solids," Solid State Physics, Vol. V, edited by Frederick Seitz and David Turnbull, New York, Academic Press, Inc., 1957.
- Das, T. P. and E. L. Hahn, Nuclear Quadrupole Resonance Spectroscopy, Suppl. 1 of Solid State Physics, edited by Frederick Seitz and David Turnbull, New York, Academic Press, Inc., 1958.
- Goldstein, Herbert, Classical Mechanics, Dallas, Addison-Wesley Publishing Company, Inc., 1950.
- Livingston, Ralph, "Nuclear Quadrupole Resonance," Molecular Physics, Vol. III of Methods of Experimental Physics, edited by Dudley Williams, New York, Academic Press, 1962.
- Ramsey, Norman F., Nuclear Moments, New York, John Wiley and Sons, Inc., 1953.
- Slichter, Charles P., Principles of Magnetic Resonance, New York, Harper and Row, 1963.

Articles

- Bersohn, R., "Nuclear Electric Quadrupole Spectra in Solids," The Journal of Chemical Physics, XX (October, 1952), 1505-1509.
- Bray, P. J. and others, "Pure Quadrupole Resonance Determination of Molecular Charge Distributions. I. Substituted Quinones, Quinolines, Pyridines, Pyrimidines, and Triazines," The Journal of Chemical Physics, XXVII (January, 1958), 99-102.

- Dailey, B. P., "The Chemical Significance of Quadrupole Spectra," Journal of Physical Chemistry, LVII (May, 1953), 490-496.
- Dean, C. and M. Pollak, "Suppressing Side-Band Interference in Superregenerative rf Spectrometers," The Review of Scientific Instruments, XXIX (July, 1958), 630-632.
- Dehmelt, H. G., "Nuclear Quadrupole Resonance," The American Journal of Physics, XXII (January, 1954), 110-120.
- Douglass, Dean C., "Quadrupole Resonance Spectrum of Chloranil and Its Hexamethyl-benzene Complex," The Journal of Chemical Physics, XXXII (1960), 1882-1883.
- Grechishkin, V. S. and G. B. Soifer, "Nuclear Quadrupole Resonance Instrumentation (Review)," Instrumentation and Experimental Technique, I (1964), 1-16.
- Hooper, H. O. and P. J. Bray, "Induction Studies in Several Groups of Halogen - Containing Organic Compounds by their Cl^{35} , Br^{79} , or Br^{81} Pure Quadrupole Resonance Spectra," The Journal of Chemical Physics, XXXIII (August, 1960), 334-361.
- Livingston, Ralph, "Detection and Measurement of Direct Nuclear Quadrupole Transitions," Annals of the New York Academy of Sciences, LV (November, 1952), 800-807.
- Pound, R. V., "Nuclear Electric Quadrupole Interactions in Crystals," Physical Review, LXXIX (August, 1950), 685-703.
- Raich, J. C. and R. H. Good, Jr., "Discussion of Quadrupole Precession," The American Journal of Physics, XXXI (May, 1963), 356-362.
- Wang, Tien-Chuan, "Pure Nuclear Quadrupole Spectra of Chlorine and Antimony Isotopes in Solids," Physical Review, XCIX (July, 1955), 566-577.

Reports

Instruction Manual, Model RJB Lock-in Amplifier, Mount Vernon, N. Y., Electronics, Missiles and Communications, Inc., n. d.

Segal, S. L. and R. G. Barnes, Catalog of Nuclear Quad-
rupole Interactions and Resonance Frequencies in
Solids. Part I. Elements and Inorganic Compounds,
United States Atomic Energy Commission Research
and Development Report, Ames, Iowa, Ames Laboratory,
1962.

Segal, S. L. and R. G. Barnes, Catalog of Nuclear Quad-
rupole Interactions and Resonance Frequencies in
Solids. Part II. Halogen Resonances in Organic
Compounds, United States Atomic Energy Commission
Research and Development Report, Ames, Iowa, Ames
Laboratory, 1965.