A NUCLEAR QUADRUPOLE RESONANCE SPECTROMETER

by

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We accept this thesis as conforming to the standard required for the degree of Master of Arts

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ABSTRACT

In conjunction with low temperature experiments on nuclear alignment and nuclear specific heat, a spectrometer has been developed in order to investigate the hyperfine structure of compounds with suitably large quadrupole coupling by the technique of Nuclear Quadrupole Resonance. The auxiliary equipment which was built in addition to an externally quenched superregenerative oscillator provided for frequency modulation and oscilloscopic display as well as Zeeman modulation and chart recorder display.

The superregenerative oscillator has a frequency range of 150 - 600 Mc./sec., which is the range required for investigation of the compounds concerned; the spectrometer has reproduced satisfactorily test signals over the range 161.5 to 332.4 Mc./sec. The test signals were obtained from the known quadrupole resonances of $^{127}$I and $^{79}$Br in SnI$_4$, I$_2$, SbBr$_3$ and Ba(BrO$_3$)$_2$.

Using the spectrometer, a search was made for resonances in a number of substances which were of interest for the nuclear alignment programme, and in which no resonances had yet been reported. In particular, we were able to make a careful investigation of the magnesium salt of para-iodo benzene sulphonate since we knew from theoretical investigations the approximate frequency at which the $^{127}$I resonance occurs. A possible explanation is given for the failure to detect any such resonance.
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INTRODUCTION

Electrostatic interaction between the nucleus and its surroundings can occur through the electric $2^l$-pole moments of the nucleus ($l = 2, 4$); the interaction of the quadrupole moment with internal electric fields is called the nuclear quadrupole coupling. The quadrupole moment is a characteristic of the particular nucleus and is a measure of the deviation of the nuclear charge distribution from spherical symmetry. The various energy levels of the nucleus which result from this quadrupole interaction correspond to various orientations of the nucleus with respect to the axis of the molecular electric field.

The work on nuclear quadrupole resonance reported in this thesis is a contribution to the problem of nuclear alignment by the mechanism first proposed by Pound (1949). The alignment takes place as a result of the hyperfine splitting produced by the interaction of the nuclear electric quadrupole moment with the internal electric field of the molecule. A crystal containing covalently bonded nuclei which have sufficiently high quadrupole coupling need only be brought into thermal equilibrium with a substance that has been cooled by adiabatic demagnetization to a temperature of a few hundredths of a degree and the majority of the nuclei will fall into the lowest hyperfine level. A nuclear orientation relative to the crystal axes will result, depending in degree on the temperature reached and the size of the quadrupole coupling.

As a consequence of this hyperfine splitting, a Schottky type anomaly in the specific heat appears at temperatures approximating $h \gamma/k$, where $\gamma$ is the frequency of transition between two hyperfine levels, and $k$ is Boltzman's constant. At these temperatures, a rearrangement of the populations of the levels takes place according to the Boltzman distribution producing a specific heat which is additional to the other contributions to the specific heat of the crystal. Thus, the hyperfine structure might be detected calori-
metrically at very low temperatures. The nuclear specific heat of iodine in
the magnesium salt of para-iodo benzene sulphonate is being investigated at
low temperatures by the group which is interested in the Pound method of
nuclear alignment.

In the study of nuclear alignment and nuclear specific heat, it is
important to have a method of investigating directly the hyperfine structure
of the compounds concerned. The technique used is Nuclear Quadrupole Resonance.

Transitions between the allowed orientations of the nucleus, I, I-1,
..... -I, produce a spectrum of frequencies \( \nu = (E|m| - E|m'|)/h \). In order
to excite these transitions between energy levels and make the spectrum observ-
able, energy must be supplied to the system at the frequency corresponding to
the splitting between them. In pure quadrupole resonance, the lines are
detected and recorded by use of an absorption spectrometer. The sample is
placed in a coil which is carrying radio frequency current. This coil forms the
tank circuit of the oscillator supplying the radio frequency power. The mag­
netic dipole moment of the nucleus interacts with the alternating magnetic field
produced in the coil, inducing a reorientation of the nuclei against the elec­
trostatic field of the molecule. The transitions which occur between energy
levels are accompanied by the macroscopic phenomena of absorption and dis­
perssion. Since the resonant frequencies involved are usually in the hundreds of
megacycles, the spectrometer was designed to have this frequency range and the
absorption and dispersion are detected by radio frequency methods.

The spectrum obtained in pure quadrupole resonance yields the product
of the principal components of the electric field gradient tensor with the
nuclear quadrupole moment. When the quadrupole system is subjected to a static
magnetic field, a Zeeman splitting of the absorption lines occurs in single
crystals. In a polycrystalline sample, the Zeeman splitting for each crystal
is different, and an external magnetic field causes the line to be smeared out
and disappear. The Zeemann splitting of the lines can be studied as a function
of the orientation of the magnetic field relative to the crystal axes in order
to determine the orientation in the crystal of the principal axes of the field gradient. The splitting of the energy levels as a function of field orientation will be calculated in the theoretical discussion for the case of spin $\frac{5}{2}$ using second order perturbation theory.

A comprehensive review of nuclear quadrupole resonance has been given by Dehmelt (1954). Many pure quadrupole resonances have been determined theoretically and experimentally by Dehmelt and Kruger; the nuclei which have been investigated and found to have quadrupole couplings in various molecules of the order of hundreds of megacycles are: iodine, bromine, arsenic, antimony, bismuth, and mercury. Kruger (1951) and Dean (1954) have developed the theory of the Zeeman effect on pure quadrupole resonance lines. Townes and Dailey (1949) have found approximate methods for the determination of the electric field gradient from a consideration of the valence electrons in the molecule.

The thesis deals mainly with the construction of the superregenerative spectrometer which was used to observe nuclear quadrupole resonances. The range covered is 150 Mc./sec. to 600 Mc./sec. Apparatus was constructed to provide either wide band oscilloscopic display or narrow band pen recorder display of the resonances.

As we expected from a spectrometer of this type, there was a great deal of trouble in obtaining satisfactory performance. However, several known signals with satisfactory signal-to-noise ratio were found with the spectrometer, and a few examples are given. A sample of the magnesium salt of para-iodo benzene sulphonate was obtained from the low temperature group and was investigated to find the $\text{I}^{127}$ resonance. The sodium salt of meta-iodo benzene sulphonate was prepared in the laboratory and investigated for the same iodine resonance. The search was made over a wide range of frequency and more carefully in the region of 280 megacycles, where the resonance is expected from theoretical calculations. A discussion is given concerning the failure to detect the resonance along with a description of the other investigations which were made in the last chapter.
CHAPTER I  THEORY

1. Energy of nuclear orientation and transition frequencies

If we take as origin the centre of the nucleus we can calculate the electrostatic energy $E = \int \rho V \, d\mathbf{r}$ of an element of charge $\rho \, d\mathbf{r}$ placed at a point of potential $V$ produced by the charges exterior to the nucleus. The potential $V$ can be expanded in a series around the origin and the energy then takes the form:

$$E = \int \rho V_0 \, d\mathbf{r} + \sum \left( \frac{\partial^2 V}{\partial x^2} \right) \rho x^2 \, d\mathbf{r} + \sum \left( \frac{\partial^2 V}{\partial x^2} \right) \rho xy \, d\mathbf{r}$$

where we have a scalar product of two tensors which represent the distribution of potential and the distribution of nuclear charge around the origin.

The elements $V_{ij}$ of the tensor which represents the electric field gradient are $\frac{\partial^2 V}{\partial i \partial j}$, where $i,j$ stand for the cartesian coordinates $x,y,z$. We can write $\frac{\partial^2 V}{\partial i \partial j}$ as the sum of two tensors, one with $V^2 V_{ij} = 0$ and the other a multiple of the unit tensor. The latter causes a shift of the centre of gravity of the energy spectrum which is independent of orientation, and therefore will be considered no further. The trace of $V_{ij}$ is then zero:

$$\frac{\partial^2 V}{\partial x^2} + \frac{\partial^2 V}{\partial y^2} + \frac{\partial^2 V}{\partial z^2} = 0$$

In the case of a potential axially symmetric about the $z$-axis, the xyz axes are principal axes of the $V_{ij}$ tensor and $\frac{\partial^2 V}{\partial z^2}$ is the largest of the principal components of the tensor. Then it follows from condition (3) that:
\[ \frac{\partial^2 V}{\partial x^2} = \frac{\partial^2 V}{\partial y^2} = \frac{1}{2} \frac{\partial^2 V}{\partial z^2} = -\frac{\rho}{2} \quad (4) \]

and \[ \frac{\partial^2 V}{\partial i\partial j} = -\frac{\partial^2 V}{\partial j\partial i} ; \quad \text{therefore,} \quad \frac{\partial^2 V}{\partial i\partial j} = 0 \quad \text{whenever} \quad i \neq j. \quad (5) \]

The distribution of charge in the nucleus is also axially symmetric, with respect to the \( z' \) axis of the nuclear coordinate system \( x'y'z' \). Therefore, \( \int \rho x'^2 \, d\mathbf{r} = \int \rho y'^2 \, d\mathbf{r} = B \), while we put \( \int \rho z'^2 \, d\mathbf{r} = A \). If the \( x \) and \( x' \) axes are allowed to fall together and if \( \theta \) is the angle between the \( z \) and \( z' \) axes,

![Diagram 1](image)

then

\[ \int \rho z^2 \, d\mathbf{r} = \int \rho (z'^2 \cos \theta - y'^2 \sin \theta)^2 \, d\mathbf{r} = A \cos^2 \theta + B \sin^2 \theta \quad (6) \]

\[ \int \rho y^2 \, d\mathbf{r} = A \sin^2 \theta + B \cos^2 \theta \quad (7) \]

\[ \int \rho z^2 \, d\mathbf{r} = B \quad (8) \]

We can now obtain from equation (2) a new expression for the energy:

\[ E_Q = \frac{1}{2} \left[ -\frac{\rho}{2} (B) - \frac{q}{2} (A \sin^2 \theta + B \cos^2 \theta) + q (A \cos^2 \theta + B \sin^2 \theta) \right] + \frac{q}{2} (A - B)(3/2 \cos^2 \theta - 1/2) \quad (9) \]

In this equation \( A - B \) can be expressed in \( z' \) and \( r \), the distance from the origin to the element of volume \( d\mathbf{r} \).

\[ A - B = \int \rho (z'^2 + y'^2 + x'^2) \, d\mathbf{r} = \frac{1}{2} \int \rho \left( \frac{3z'^2 - (z')^2 + (y')^2 + (x')^2}{2} \right) \, d\mathbf{r} \]

\[ = \frac{1}{2} \int \rho (3z'^2 - r^2) \, d\mathbf{r} \quad (10) \]

The integral, denoted by \( E_Q^* \), defines an inherent property of the nucleus called the quadrupole moment. It has the dimensions of area and is usually expressed in barns \((10^{-24} \, \text{cm}^2)\). It is positive when the nuclear charge is a
prolate spheroid and negative when the nuclear charge is an oblate spheroid. For a spherical charge distribution, \( eQ \) vanishes.

We can write down the equation for the classical quadrupole interaction energy:

\[
E_Q = \frac{1}{4} eQ^* q \left( \frac{3}{2} \cos^2 \theta - 1/2 \right) \quad (11)
\]

In order to derive the quantum-mechanical energy eigenvalues of the quadrupole system from the classical expression, we must replace \( \cos^2 \theta \) with the operator \( \hat{I}_x^2/I(I+1) \).

\[
E_Q = 1/8 \ eQ^* q \frac{3I_x^2 - I(I+1)}{I(I+1)} \quad (12)
\]

It is conventional to define \( eQ^* \) with respect to the molecular axis \( z \) rather than the nuclear axis \( z' \), and for the state \( I = I_z \). When \( Q^* \) in equation (12) is replaced by the normalized value \( Q \), then \( E_Q \) should have the value which would be obtained by putting \( \cos \theta = 1 \) in the classical expression (11).

The value

\[
Q = \frac{Q^* (2I - 1)}{2 (I + 1)} \quad (13)
\]

is the normalized quadrupole moment; this \( Q \) is used in the literature. The energy eigenvalues are now:

\[
E_m = \frac{eQq}{\hbar I (2I - 1)} \left[ 3m^2 - I(I+1) \right] \quad (14)
\]

The coefficient \( eQq \) is called the quadrupole coupling constant and is frequently expressed in megacycles \((eQq/\hbar)\).

We notice that for \( I = \frac{1}{2} \), \( [3m^2 - I(I+1)] = 0 \), and so the application of nuclear quadrupole resonance is restricted to nuclei of spin greater than \( \frac{1}{2} \).

The quadrupole moment is also zero for a nucleus of spin \( \frac{1}{2} \).

The allowed values of \( m \) are \( m = I, I-1, \ldots, -I \). When \( I \) is half integral, the energy levels are each doubly degenerate, corresponding to \( \pm m \).

When the spin is integral, there are \( I \) doubly degenerate levels and one non-degenerate level in an axially symmetric field; if the field is not axially symmetric, the levels are in general all non-degenerate. Since transitions induced by an alternating magnetic field are magnetic dipole transitions, the
The quadrupole spectrum consists of equally spaced lines. For \( I = \frac{3}{2} \), there is a single line of frequency
\[
\nu = \frac{3}{2} eQq
\]
and
\[
\nu = \frac{3}{10} eQq
\]
For \( I = \frac{7}{2} \), three lines
\[
\nu_1 = \frac{1}{11} eQq, \quad \nu_2 = \frac{1}{7} eQq, \quad \nu_3 = \frac{3}{11} eQq
\]

When the field is not axially symmetric, the parameter \( \eta = (V_{xx} - V_{yy})/q \) is used to describe the asymmetry. If \( \eta \) is small, the quadrupole resonance frequencies can be derived using perturbation theory:

For \( I = \frac{3}{2} \),
\[
\nu = \frac{3}{2} eQq (1 + \eta^2/3^{1/2})
\]

For \( I = \frac{5}{2} \),
\[
\nu_1 = \nu_2/2 (1 + 1.296 \eta^2 - 0.55 \eta^4)
\]
\[
\nu_2 = \frac{3}{10} eQq (1 - 0.2037 \eta^2 + 0.18 \eta^4)
\]

For \( I = \frac{7}{2} \),
\[
\nu_1 = \nu_2/3 (1 + 3.733 \eta^2 - 6.86 \eta^4)
\]
\[
\nu_2 = 2/3 \nu_1 (1 - 0.4667 \eta^2 + 1.82 \eta^4)
\]
\[
\nu_3 = \frac{3}{11} eQq (1 - 0.1000 \eta^2 - 0.019 \eta^4)
\]

The relative intensity of the quadrupole transition lines depends on the probabilities of transition between the different states involved. The probability of a dipole transition per unit time from a state \( m \) into a state \( m' \) or vice versa is:
\[
W_{m \leftrightarrow m'} = \frac{8 \pi^3/3 \hbar^2}{\left| (m | \overset{\rightarrow}{M} | m') \right|^2 \nu}
\]
where \( \overset{\rightarrow}{M} \) is the magnetic moment operator and \( \nu \) \( S \nu \) is the energy density of the
radiation field in a range of frequency $\delta \nu$ centred on the transition frequency $\nu$. For the quadrupole system the nuclear magnetic moment is parallel to the angular momentum $\mathbf{I}$, and so

$$|\langle m | \mathbf{I} | m' \rangle|^2 = \frac{\mu^2}{I^2} |\langle m | \mathbf{F} | m' \rangle|^2$$

Then $|\langle m | \mathbf{F} | m' \rangle|^2$ can be expressed as the sum of the squares of the matrix elements of the vector components $I_x, I_y, I_z$. Since the matrix elements for $I_x$ and $I_y$ are equal, while those for $I_z$ vanish, we obtain, remembering that $|m - m'| = 1$,

$$|\langle m | I_z | m' \rangle|^2 = \frac{\mu^2}{2I^2} [I(I+1) - m^2]$$

Combining equations (24) and (22), we finally obtain

$$W_{m \rightarrow m'} = \frac{4\pi^3 \mu^2}{3h^2 I^2} (I(I+1) - m^2) / \nu$$
2. Electronic structure of molecules and nuclear quadrupole coupling constants

In order to calculate $\frac{\partial^2 V}{\partial z^2}$, the distribution of charges in the molecule must be known. An accurate calculation requires a determination of wave functions for the electrons; an approximate calculation is made from structural considerations because $\frac{\partial^2 V}{\partial z^2} = q$ depends on a few simple parameters of bond structure. If $q$ is calculated or estimated, and the nuclear quadrupole coupling is found experimentally, the value of the nuclear quadrupole moment can be determined from

$$Q \text{ (cm.}^2) = 13.8 \times 10^{-12} \frac{eQq \text{ (mc.)}}{q \text{ (e.s.u.)}}$$

(26)

In any calculation of $q$, only the contribution of the valence shell need be considered. The effect of nuclear and electronic charges outside the valence shell in the remainder of the molecule is negligible. (One electronic charge at one angstrom contributes $10^{15}$ e.s.u.). An s-type orbit or any closed shell of electrons around the nucleus is spherically symmetric and hence gives no contribution to $q$ at the nucleus or to the variation of energy with nuclear orientation. Polarization and distortion of this closed spherical shell of electrons can occur without an appreciable effect on the value of $q$.

The largest contribution to $q$ is from the p-orbitals in the valence shell; the value of $q$ at the nucleus depends mainly on the way in which these orbitals are filled.

The shared electronic charge of a pure covalent bond can be divided equally between two atoms and $q$ can be calculated as though one electron of the shared pair existed in the atomic orbital of each atom. When bonds are partially ionic in character, the electron shell of each atom is partly closed and the coupling reduced because $q$ from the other ion is much less than that of a p-electron in the shell itself. Electrons in different atomic orbitals have widely different couplings. For this reason, hybridization of a p-state bond with an s-state bond will increase the value of $q$, while hybridization with a d-state bond will decrease the value of $q$. Resonance between different
covalent structures, which occurs in the aromatic carbon compounds, may result in an increase in $q$ and the quadrupole coupling constant.

The wave function $\psi$ for one valence electron outside a closed shell can be expanded in terms of the atomic wave functions $\psi_{nlm}$:

$$\psi = \sum_{nlm} a_{nlm} \psi_{nlm}$$ (27)

where $a_{nlm}$ is largest for lowest allowed values of $n$ and $l$, and the axis of the molecular bond is chosen as a reference direction for the magnetic quantum numbers.

Since

$$\frac{\delta^2(e/r)}{\delta z^2} = (3 \cos^2 \theta - 1) \frac{e}{r^3},$$ (28)

where $\theta$ is the azimuthal angle with respect to the bond axis, it follows that

$$\frac{\delta^2 \psi}{\delta z^2} = e \int \frac{\psi^* (3 \cos^2 \theta - 1) \psi}{r^3} d\tau$$ (29)

Inserting the series expansion for $\psi$, gathering terms, and using the simplifying notation

$$q_{nlm, n'1'm'} = \int \psi_{nlm} (3 \cos^2 \theta - 1) \psi_{n'1'm'} d\tau$$ (30)

we have:

$$\frac{\delta^2 \psi}{\delta z^2} = \sum_{nlm} |a_{nlm}|^2 q_{nlm, nlm} + \sum_{nlm, n'1'm'} a_{nlm} a_{n'1'm'} q_{nlm, n'1'm'}$$ (31)

where the quantities $q_{nlm, nlm}$ are the values of $\delta^2 \psi/\delta z^2$ for each of the atomic states and are multiplied by $|a_{nlm}|^2$, the coefficients of the respective atomic states in the molecular wave function. Except that for $l = 0$, $q_{n0m} = 0$, $q_{nlm}$ is a rapidly decreasing function of $n$ and $l$. The second sum includes only those terms for which $n \neq n'$ and $l \neq l'$, and for which $m = m'$, and either $l = l' \neq 0$ or $l = l' \pm 2$ (otherwise $q_{nlm, n'1'm'}$ would be zero).

The calculations of Townes and Dailey (1949) show that an accuracy of 10% can be obtained when the second sum of equation (31) is neglected. Then the value of $q$ due to a single valence electron is regarded as a sum of contributions $|a_{nlm}|^2 q_{nlm}$ from the various atomic states. Moreover, if the lowest
energy atomic state is a p-state, contributions from other states may be neglected.

When hydrogen-like wave functions are substituted for the $\psi_{nlm}$, the value of $q_{nlm}$ for the case of $l$ perpendicular to $z$ ($m = 0$) is

$$q_{n0} = \frac{2.24 \times 10^{15} \Delta \nu \ell (\ell + 1)}{Z' (2\ell + 1)(2\ell - 1)(2\ell + 3)} \text{ e.s.u.}$$

The fine structure splitting $\Delta \nu$ which arises from $\ell \cdot s$ coupling is known for most elements. Values of $\Delta \nu$, expressed in cm$^{-1}$, have been compiled by Moore (1949).

In the approximation in which only p-electrons are considered,

$$q = \frac{\Delta^2 \nu}{\Delta z^2} = -\left[ (N_x + N_y)\left( \frac{1}{2} q_{n,l,1} + \frac{1}{2} q_{n,l,-1} \right) + N_z q_{n,1,0} \right]$$

where $N_x$, $N_y$, and $N_z$ are the numbers of electrons in the $p_x$, $p_y$, and $p_z$ orbits respectively. Since $q_{n,l,1} = q_{n,l,-1} = -q_{n,1,0}$, then

$$q = \left[ (N_x + N_y)/2 - N_z \right] q_{n10} = U_p q_{n10}$$

where $U_p$ is the number of unbalanced p-electrons and $q_{n10}$ is the contribution per unbalanced p-electron given by $2.98 \times 10^{14} \frac{\Delta \nu}{Z'}$ e.s.u. from equation (32).

The evaluation of $U_p$ depends upon the nature of the chemical bond formed by the atom considered; this can be determined from such data as dipole moments, bond energies, bond angles, and the electronegativities of the atoms. The sign of $q$ will be negative for an excess of electrons along the $z$-axis and positive for a deficit along this axis. As an example, for a halogen atom forming a single covalent bond to complete its octet, $N_z = 1$, $N_x = N_y = 2$, and $U_p = +1$. 

3. Theory behind the method of detection

The expression for the classical quadrupole interaction energy derived in section 1 is $E_Q = \frac{1}{2} eQ (\frac{3}{2} \cos^2 \theta - \frac{1}{2})$. The dependence on the angle $\theta$ causes a torque which tends to align the nuclear and molecular axes. The nuclear spin $\vec{I}$ will respond to this torque by a precession around the z-axis. The diagram demonstrates how the components of the magnetic dipole $\mu$ and the electric quadrupole moment $eQ$ of the nucleus accompany the precession of the spin.

![Diagram 2]

One half of the nuclei precess as illustrated, the other half with $I_z$ reversed.

Although the orientation energy is determined by the nuclear quadrupole interaction with the electric field gradient, the observed transitions between energy levels are induced by the interaction of the magnetic dipole moment of the nucleus with the alternating electromagnetic field. The coupling of the electric quadrupole moment with the radiation field is too weak to induce observable transitions. The transitions are therefore magnetic dipolar and the dipole selection rule $\Delta m = \pm 1$ applies.

When the frequency of the radiation field is equal to the precession frequency of the magnetic dipole, the quadrupole system absorbs radio frequency energy from the field. Near resonance the nuclei precess with phase coherent with that of the radio frequency field. Half of the nuclei of one energy have $I_z$ reversed with respect to the $I_z$ of the other half. These two sets of nuclei precess in opposite directions, and therefore near resonance a pulsating mag-
magnetic moment is induced parallel to the radio frequency field. There is no moment perpendicular to the field because the contributions of the two 'sets of nuclei cancel. The pulsating magnetic moment \( M = (M' - jM'')e^{j\omega t} \) is not necessarily in phase with the radio frequency field \( H = H_1 e^{j\omega t} \). Its macroscopic effect can be described by the complex magnetic susceptibility

\[
\chi = \frac{M}{H} = \chi' - j\chi''
\]

(35)

where \( \chi'' \) is the susceptibility related to absorption and \( \chi' \) the susceptibility for dispersion. When the energy of the radiation field is removed, the pulsating magnetic moment decays exponentially with the spin-spin relaxation time \( T_2 \).

The pulsating magnetic moment absorbs radio frequency energy from the sample coil, and can induce a radio frequency voltage in the same coil; the absorption effect is sometimes seen alone, sometimes accompanied by the inductive effect. When absorption occurs, the impedance \( jL\omega + r \) of the sample coil becomes

\[
jL\omega [1 + \hbar\pi (\chi' - j\chi'')] + r = jL (1 + \hbar\pi \chi')\omega + (r + \hbar\pi \chi''\omega) \quad (36)
\]

and its quality factor \( Q = \frac{L\omega}{r} \) becomes such that

\[
\left( \frac{1}{Q'} \right) = \left( \frac{1}{Q} \right) + \hbar\pi \chi'' - \hbar\pi (\chi'/Q) \quad (37)
\]

If \( Q \) is sufficiently great (from 100 to 200) the expression simplifies to a term in \( \chi'' \):

\[
d(1/Q) = \hbar\pi \chi'' \rightarrow dQ = \hbar\pi \chi'' Q^2 \quad (38)
\]

The voltage which is induced by the residual magnetic moment is proportional to \( M \) and therefore to \( (\chi'^2 + \chi''^2)^{1/2} \); the inductive effect produces, in passing through the resonance, a curve resulting from the combination of absorption and dispersion terms.

The energy absorbed per cycle of the radio frequency field \( H_1 \) is
\[ \Phi \hat{H} \cdot d\hat{H} = \eta \xi \chi'' H_1^2 \sin^2 \varphi \] (39)

where \( \xi \) = filling factor of the sample coil
and \( \varphi = (H_1, z) \), the angle between the field direction and the bond axis.

The total energy absorbed for a line is proportional to

\[ \int_{-\infty}^{+\infty} \chi'\prime(F) \cdot dF, \] (40)

the area under the absorption curve \( \chi'\prime(F) \). Thus it is seen that the amount of radio frequency energy absorbed by the system of spins is measured by the variation \( dQ \) of the coefficient \( Q \) of the sample coil.
Theoretical aspects of the Zeeman effect

The quadrupole transitions take place in general between two degenerate energy states corresponding to $\pm m_z$ and $\pm (m_z + 1)$. The energy of interaction of the nuclear magnetic moment with a static magnetic field is dependent on the sign of the quantum number $m_z$; such a perturbing interaction has the effect of lifting the degeneracy of the unperturbed energy states.

The energy term is

$$E = -\gamma L \frac{\mathbf{I} \cdot \mathbf{H}}{I}$$  \hspace{1cm} (41)

where $\mathbf{H}$ = magnetic field vector of magnitude $H$.

$\mathbf{I}$ = spin vector of the nucleus

The Larmour frequency $\gamma_L$ is the frequency of nuclear precession in the field $H$, and is related by:

$$\gamma_L = \frac{\gamma L H}{I}$$  \hspace{1cm} (42)

Using equation (42), we obtain

$$E = -\gamma_L \frac{\mathbf{I} \cdot \mathbf{H}}{H}$$  \hspace{1cm} (43)

The pattern of the Zeeman effect depends upon the relative orientation of the electric field axis and the magnetic field. For a field in the $xz$ plane, the perturbation operator is

$$H' = \mathbf{L}(\theta) = -\gamma_L H I (I_x \sin \theta + I_z \cos \theta) = -\gamma_L (I_x \sin \theta + I_z \cos \theta)$$  \hspace{1cm} (44)

where $\theta = (H, z)$ is the angle between the magnetic field and the $z$-axis. For the case of spin $5/2$, the perturbation matrix is given below, where $a = -\gamma_L \sin \theta$ and $b = -\gamma_L \cos \theta$.

$$H' = \gamma L \frac{\mathbf{I}}{2}$$

$$\begin{pmatrix}
5b & \sqrt{5}a & 0 & 0 & 0 & 0 \\
\sqrt{5}a & 3b & \sqrt{6}a & 0 & 0 & 0 \\
0 & \sqrt{6}a & b & 3a & 0 & 0 \\
0 & 0 & 3a & -b & \sqrt{5}a & 0 \\
0 & 0 & 0 & \sqrt{5}a & -3b & \sqrt{5}a \\
0 & 0 & 0 & 0 & \sqrt{5}a & -5b \\
\end{pmatrix}$$  \hspace{1cm} (45)
The perturbed energies to second order in $H'$ are

$$W_m = E_m + H'_{mm} + \sum_n' \frac{|H_m n'|^2}{E_m - E_n} \quad (46)$$

where the prime on $\Sigma$ denotes the omission of the term $n = m$ from the summation, and the unperturbed energies $E_m$ are:

$$E_{\pm 5/2} = \hbar eQq, \quad E_{\pm 3/2} = -1/10 \hbar eQq, \quad E_{\pm 1/2} = -1/5 \hbar eQq \quad (47)$$

When the unperturbed state $m$ is degenerate with state $k$, equation (46) will hold only if $H'_{km}$ is zero and the degeneracy between the states $k$ and $m$ is removed in first order. This is so for $m = 5/2, k = -5/2$ and $m = 3/2, k = -3/2$. However, for $m = 1/2, k = -1/2$, $H'_{\frac{1}{2}, \frac{1}{2}} = H'_{\frac{1}{2}, -\frac{1}{2}} \neq 0$. In this case it is only necessary to diagonalize the submatrix

$$\begin{pmatrix} H_{mm} & H_{mk} \\ H_{km} & H_{kk} \end{pmatrix} \quad (48)$$

before calculating the perturbed energies. The diagonalized submatrix is

$$\begin{pmatrix} 9a^2 + b^2 & 0 \\ 0 & 9a^2 + b^2 \end{pmatrix}$$

and the perturbation operator is

$$H' = \hbar^2 \begin{pmatrix} 5b & \sqrt{5}a & 0 & 0 & 0 & 0 \\ \sqrt{5}a & 3b & \sqrt{5}a & 0 & 0 & 0 \\ 0 & \sqrt{8}a & 9a^2 + b^2 & 0 & 0 & 0 \\ 0 & 0 & 0 & \sqrt{9a^2 + b^2} & \sqrt{8}a & 0 \\ 0 & 0 & 0 & \sqrt{8}a & -3b & \sqrt{5}a \\ 0 & 0 & 0 & \sqrt{5}a & -5b \end{pmatrix} \quad (49)$$

Using equation (46), it is now possible to obtain the perturbed energies from the above matrix (49):
\[ W_{5/2} = \frac{1}{10} \text{eqq} - \frac{5}{2} \hbar \nu_L \cos \theta + \frac{25}{7} \hbar^2 \nu_L^2 \sin^2 \theta \]
\[ W_{3/2} = - \frac{1}{10} \text{eqq} - \frac{3}{2} \hbar \nu_L \cos \theta + \frac{115}{7} \hbar^2 \nu_L^2 \sin^2 \theta \]
\[ W_{1/2} = - \frac{1}{5} \text{eqq} - \frac{\hbar}{2} \nu_L \sqrt{\cos^2 \theta + 9 \sin^2 \theta} - 20 \hbar^2 \nu_L^2 \sin^2 \theta \]
\[ W_{-1/2} = - \frac{1}{5} \text{eqq} + \frac{\hbar}{2} \nu_L \sqrt{\cos^2 \theta + 9 \sin^2 \theta} - 20 \hbar^2 \nu_L^2 \sin^2 \theta \]
\[ W_{-3/2} = - \frac{1}{10} \text{eqq} + \frac{3}{2} \hbar \nu_L \cos \theta + \frac{115}{7} \hbar^2 \nu_L^2 \sin^2 \theta \]
\[ W_{-5/2} = \frac{1}{10} \text{eqq} + \frac{5}{2} \hbar \nu_L \cos \theta + \frac{25}{7} \hbar^2 \nu_L^2 \sin^2 \theta \] (50)

For the \((3/2 \leftrightarrow 1/2)\) transition we obtain the frequencies of transition:
\[ \nu_{(3/2 \leftrightarrow 1/2)} = \frac{1}{10} \text{eqq} - \frac{3}{2} \nu_L \cos \theta + \frac{\nu_L \sqrt{\cos^2 \theta + 9 \sin^2 \theta}}{2} + \frac{255}{7} \nu_L^2 \sin^2 \theta \] (eqq/h) \[ \] (51)
\[ \nu_{(-3/2 \leftrightarrow -1/2)} = \frac{1}{10} \text{eqq} - \frac{3}{2} \nu_L \cos \theta + \frac{\nu_L \sqrt{\cos^2 \theta + 9 \sin^2 \theta}}{2} + \frac{255}{7} \nu_L^2 \sin^2 \theta \] (eqq/h) \[ \] (52)

The four lines which separate in pairs from the unperturbed resonance line \( \nu_o \) are symmetrical with respect to this line and separated from it by
\[ \pm \Delta \nu = \frac{1}{2} \nu_L \left[ 3 \cos \theta - (\cos^2 \theta + 9 \sin^2 \theta)^{1/2} \right] \] (53)

for both \( \theta = \theta \) and \( \theta = \pi - \theta \). The last term in equations (51) and (52) can be neglected for fields of about 100 gauss.

There are two special cases which can be treated, for \( H \) parallel to the electric field axis and \( H \) perpndicular to the electric field axis.

**Case 1.** \( H \) parallel to the field axis: \( \theta = 0, \cos \theta = 1, \sin \theta = 0 \)
For the \((3/2 \leftrightarrow 1/2)\) transition, there will be only two lines instead of four separated by \(\Delta \nu = 2\nu_L\). For the \((5/2 \leftrightarrow 3/2)\) transition, the two perturbed lines which always appear for this transition are separated by \(\Delta \nu = 2\nu_L\). In general they are separated by \(\Delta \nu = 2\nu_L \cos \theta\).

**Case 2.** H perpendicular to the field axis: \(\theta = \pi/2\), \(\cos \theta = 0\), \(\sin \theta = 1\).

Only the state \(|m_z| = \frac{3}{2}\) is split and the \((3/2 \leftrightarrow 1/2)\) line becomes two lines separated by \(\Delta \nu = 3\nu_L\).

In a polycrystalline sample, the line is smeared out when the Zeeman splitting is greater than the line width. For \(^{127}\text{I}\) in \(\text{I}_2\), the line width is approximately 40 kc. The least splitting which occurs for any angle is \(2\nu_L\). Since \(\mu_I/I\) for the iodine nucleus is 0.8565 kc., the field necessary to cause this line to disappear completely is about 25 gauss.
CHAPTER II  The superregenerative oscillator

1. The superregenerative oscillator in theory

When oscillation conditions are established for the vacuum tube oscillator, the envelope of the oscillations rises exponentially until it is limited by non-linearities in the circuit. In a superregenerative oscillator, the vacuum tubes are switched on and off by applying a periodically varying bias to the grid; during the off period the oscillations in the circuit decay exponentially. The period length of the "quench" voltage, as it is called, is about 10 times as long as the decay time constant of the tank circuit so that the voltage across the tank circuit will be reduced to the order of thermal noise voltages before the tube is switched on again. The tube is left on long enough for the oscillations to level off at the saturation amplitude $U_{\text{max}}$. The time which is necessary for the oscillations to build up to this value depends sensitively on the minimum amplitude $U_{\text{min}}$.

If any signal is present in the tank circuit at the moment the oscillator is switched on, the oscillations build up from this rather than noise, and reach the limiting amplitude sooner than if this signal were absent. Thus the additional e.m.f. at the oscillation frequency $\Delta U$ which the signal represents can cause the time average of the oscillation amplitude to change. Any modulation of this small additional potential will appear as a change in this time average, which can be detected. The superregenerative oscillator circuit functions also as a very high gain amplifier. The smoothed output from the oscillator is a greatly amplified reproduction of the amplitudes present in the tank circuit at the start of oscillations.

The three operations, oscillation, quenching, and detection, can be performed by three separate vacuum tube circuits; or by using a class C oscillator, the same tubes can oscillate and detect. In the "self-quenching" oscillator all three functions can be performed by the same tubes.

When a sample is placed in the tank coil of the superregenerative
oscillator, the nuclei absorb energy from the tank circuit at the resonant frequency, lowering its $Q$, and causing the build up time for oscillations to be lengthened. During the period of strong oscillation following the build up, the nuclear spins precess coherently with the applied oscillations. When the oscillator is turned off, the precessing nuclei continue precessing and induce a voltage in the tank circuit which is additional to the minimum amplitude $U_{\text{min}}$ that is reached during the cut-off interval. This voltage falls off exponentially with the characteristic spin-spin relaxation time $T_2$ of the substance. The oscillations of the next quench period can start up from the voltage which the precessing nuclei induce in the tank circuit during the low oscillation interval of the previous quench cycle. This radio frequency voltage is given by

\[ \Delta U = -4\pi\chi Q \alpha U_{\text{max}} \]

where $Q$ is the quality factor of the tank circuit and $\alpha$ is a factor less than unity to account for the pulsating character of the radio frequency field exciting the nuclei.

The line shape of the absorption lines depends upon the phase relation between $\Delta U$ and $U_{\text{min}}$.

It is thus seen that the quench period must be long compared with the build up time of the oscillations and the decay time constant of the tank circuit, but not so long compared with the spin-spin relaxation time. The relaxation time must be such that the duration of the signal from the sample is comparable to the period of the quench voltage. If $T_2$ for a substance is too short, the quench frequency cannot be chosen to satisfy both these conditions, and the resonance can not be detected on the superregenerative spectrometer.

By assuming a perfect square-wave quenching voltage, Van Voorhis (1948) obtained an expression for the gain in the superregenerative oscillator circuit:

\[ G = f_q U_{\text{max}} 2L/R_T \ln \left( \frac{V_n + V_g}{V_n} \right) \]

(55)
where \( f_q \) = quench frequency

\( L \) = tank coil inductance

\( R_T \) = net series tank resistance = \( R + R_n \)

\( R \) = series loss resistance of tank circuit

\( R_n \) = negative series resistance representing the regenerator tube

\( V_n \) = noise voltage at instant that oscillations start

\( V_s \) = signal voltage at instant that oscillations start

The gain in this case can be as high as \( 10^6 \); for a sine wave quenching voltage it is higher. However, it is difficult to apply the gain law in the case of a sine wave because \( R_T \) cannot be assumed constant.

The advantages of the superregenerative oscillator are:

(i) It has a high gain with few tubes. This is important in the region 100-400 mc./sec. where radio techniques are difficult.

(ii) It develops a high radio frequency power with relatively little noise.

In the substances to be investigated there is almost no chance of saturating the resonance, so that the large output is very useful.

Its principal disadvantages are:

(i) It is sometimes tempermental and erratic and adjustment is critical.

(ii) The detection is dependent on \( T_2 \); therefore the spectrometer is limited in the substances which it can be used to investigate.
2. The superregenerative oscillator in our quadrupole spectrometer

In our spectrometer, the superregenerative oscillator uses two acorn triodes 955 in a tuned anode, tuned cathode, grounded grid push-pull circuit (see figures 1 and 2). The oscillation frequency is essentially determined by the resonant frequency of a lecher wire system in the anode circuit; the lecher wire system in the cathode circuit has a smaller effect on the frequency. However, for oscillation to take place, it is necessary that the cathode circuit be inductive at the frequency of oscillation. Proper adjustment of the oscillator is attained by proper selection of potentials applied to the electrodes of the tubes and of the quench voltage and frequency. A sinusoidal waveform was chosen for the quench. The quench oscillator is an electron coupled oscillator with frequency range 150 - 2000 kc. When lower frequencies are desired, it can be used as an amplifier and matching device for an external audio oscillator.

The lecher wire system in the anode circuit gives the oscillator its wide frequency range. It can resonate to the frequency $f$ when its effective length is equal to $(n/2 - 1/4)\lambda$ where $\lambda$ is the wave length corresponding to frequency $f$. As the length of the line is increased, sustained oscillations are obtained in successive ranges. The cathode line can usually be adjusted so that it is inductive for only one mode of oscillation. When conditions are such that two modes of oscillation are possible, usually only the lower mode is produced because the circuit losses are lowest in this situation. In some cases, however, the circuit may oscillate in both modes alternately by switching modes rapidly, slowly or irregularly. We found this effect to be a major obstacle in developing a satisfactory oscillator.

In the final circuit of the oscillator, the frequency range from 150 to 600 mc./sec. was covered in the three modes $\lambda/4$, $3\lambda/4$, and $5\lambda/4$. The oscillator was calibrated by locating measured frequencies of oscillation on coordinate axes $l_a$ and $l_c$ (the lengths of the anode line and the cathode,
FIGURE 1  JUNCTION BOX  

FIGURE 2  SUPER-REGENERATIVE OSCILLATOR
FIGURE 3 QUENCH OSCILLATOR
The Superregenerative Oscillator

Full View of the Superregenerative Oscillator

PLATE I

to follow page 22
line), and drawing the contours for each mode.

The anode lecher wire system is made of 0.120\textquotedbl{} diameter copper wires with centres spaced 1/2\textquotedbl{} apart. The sample coil, made of the same copper wire, was attached to the anode stub at the tube end of the lecher system. The coil, which had 41/2 turns of diameter 3/8\textquotedbl{}, was equivalent to about $\lambda/8$ of the line at the central frequency of the system. It is shown in the appendix that the magnetic field generated in the coil is a maximum in a $\lambda/8$ coil. The cathode line is of 1/8\textquotedbl{} diameter brass tubes which are spaced 1/2\textquotedbl{}. The heater wires are passed through the tubes to keep the heaters at the same radio frequency potential as the cathodes. A third conductor in the neutral plane of each lecher system connects the shorted end of the anode line to high tension and that of the cathode line to ground. Tuning is effected by running a phosphor-bronze shorting bar along the lecher system.

The signal is, in principle, independent of the quantity of sample, provided the filling factor of the sample coil is maximum. The filling factor $\xi$ measures the ratio between the magnetic energy contained in the volume of the sample and the total magnetic energy contained in the sample coil. In practice, for a coil solenoidal in form:

$$\xi = \frac{\text{volume of sample}}{\text{volume of solenoid}}$$

An auxiliary oscillator using a 955 tube and a lecher wire system (see figure 12) aided in the adjustment of the oscillator. The lecher wire is loosely coupled to the superregenerative oscillator to provide signals on the oscilloscope which can be improved through selection of the quench frequency and amplitude, and the various potentials applied to the electrodes of the oscillator tubes. The adjustment which is obtained in this manner should then be optimum for observation of a resonance at that particular frequency. The side bands of the spectrum have a separation equal to the
quench frequency $f_q$. The line corresponding to the centre of the spectrum is easily recognized because it is not displaced by a slight variation of $f_q$, while the side bands are displaced on the oscilloscope screen pattern.

3. A review of the various oscillators used

The first oscillator was the original design of the final circuit and used the 955 tubes. It had three modes of oscillation $\lambda/4$, $3\lambda/4$, and $5\lambda/4$ and a wide frequency range, from 160 to 700 mc./sec. We were not satisfied with the oscillator because we considered the signal-to-noise ratio obtained for known signals to be inadequate in the search for unknown signals. Minor alterations such as taking the audio frequency signal from the plates of the tubes instead of from the grids had no effect.

The tubes were replaced, first with 6J4 tubes and then with 9002 tubes. The circuit with 6J4 tubes oscillated on many more modes than the previous circuit, but unfortunately these modes overlapped. It is supposed that resonances could not be observed because of the switching from one mode to another. The only objection to the circuit using 9002 tubes was that frequencies as high as 400 mc./sec. and higher could not be obtained.

The next oscillator was an experiment in adapting the lighthouse tube to a lecher wire oscillator. The lecher wire system was of larger overall dimensions than the system of the previous oscillator. The advantages were (i) reduction of noise in the circuit due to the greater rigidity of larger diameter wires, and (ii) separation of the plate and cathode circuits due to the construction of the lighthouse tube. The main disadvantage was that, for a given length of anode stub, only a small frequency range could be covered with the lecher system.

The original circuit was reconstructed with some modifications. The third conductor was added to the lecher systems to return the direct current
from the shorted ends to the remainder of the circuit. The condenser plates for frequency modulation were placed horizontally rather than vertically as they were before. The movable plate of the condenser can be positioned using three screws placed in an equilateral triangle in the mount for the relay coil. The test signals were improved in signal-to-noise ratio. The performance of the oscillator seemed satisfactory for the search for unknown signals.
CHAPTER III  The various parts of the spectrometer

The block diagram of the superregenerative spectrometer is given in figure 4. Frequency modulation was used for wide band detection and oscillographic display; Zeeman modulation was used for narrow band detection with the phase sensitive detector and automatic recording. The various parts of the spectrometer will be described individually in this section.

1. Modulation

In nuclear magnetic resonance the magnetic field can be modulated around its value $H_0$ at the resonance; in nuclear quadrupole resonance, it is impossible to modulate the electrostatic field gradient. However, this difficulty can be avoided by using the Zeeman effect. If it is preferred to operate in the absence of any magnetic field, the radio frequency excitation can be modulated in frequency. Then a single parameter, the frequency, determines at the same time the position and shape of the quadrupole resonance lines.

Some mechanical method of frequency modulation is necessary in nuclear quadrupole resonance in view of the line widths involved. The amplitude of the frequency modulation must be variable and about 10 mc./sec. maximum. It should be about 1% of the oscillator frequency and many times the line width. A vibrating condenser operated by a relay coil at 60 c.p.s. has a maximum amplitude of vibration which provides a spread in frequency of 10 mc./sec. The vibrating condenser, shown in side view in figure 7, is connected in parallel to the tank circuit, on the anode lecher wire system. The same unit which drives the relay coil (see figure 5) provides phase control and 60 c.p.s. sweep for the oscilloscope.

For Zeeman modulation, a square wave zero-based magnetic field of about 50 gauss maximum is required. While the field is on, the resonance is smeared out by the Zeeman splitting of the levels and modulation of the signals results. It is important to use a polycrystalline sample; the method would
FIGURE 4  BLOCK DIAGRAM OF NUCLEAR QUADRUPOLE SPECTROMETER
of course not work for a single crystal. A field less than 50 gauss is ade­quate for narrow lines.

A circuit to square the output of a Hewlett-Packard audio oscillator and Helmholtz coils driven from a 10 watt Hi Fi Bell amplifier were first used to provide the square wave field; a battery and rheostat served to bias the field at zero. The coils were each 92 turns of No. 26 wire wound on a lucite former to a diameter of 5 cm. and separated by the distance $r = 2.5$ cm. The total reactance was 4 ohms which matched the output transformer of the power amplifier. A calculation gives 50 gauss as the maximum field but it is ex­pected to be less than this. The axis of centres was placed perpendicular to the direction of the axis of the sample coil.

It was soon found that we required a larger separation between coils, and since the design already made the best use of the 10 watt amplifier, another method had to be found. A power amplifier (figure 10), in which the Helmholtz coils take the place of the plate resistance of the power tube, was designed and built to replace the commercial amplifier. An automatically biased square wave field was obtained from the coils by applying to the grid of the power tube a square wave input voltage of the frequency desired for modulation. A square wave of 105 volts amplitude was obtained from a simpli­fied version of the squaring circuit, shown in figure 11. A special power pack was designed to provide $\pm 250$ volts for the plate and $-70$ volts for the grid bias of the power tube. Coils of 3400 turns of No. 33 enamelled copper wire each were wound on a lucite former with a separation of 5 cm. A frequency of 407 c.p.s. was chosen because this is the minimum frequency left unattenuated by the low frequency filter and it is not a simple multiple of the mains frequency. A square wave field would be more easily produced at lower frequen­cies because of the time constant of the coils. Because of the large induct­ance of the coils ($\sim 5$ henries), the field was measured to be only 18 gauss.

The advantages in the Zeeman method of modulation are:

(i) No previous knowledge of the line width is necessary to obtain optimum
modulation efficiency.

(ii) Response to spurious signals is greatly reduced.

There is, however, one difficulty: "pick up" of the modulation frequency is enhanced. The signal can be observed on the oscilloscope as well as on the pen recorder. The picture will show one half of the noise appearing higher on the oscilloscope than the other half.

2. Frequency sweep apparatus

In wide band search for known signals, manual variation of the frequency was used. Fine adjustment was obtained from a rotating condenser in parallel with the anode line.

During automatic recording, the speed at which the resonant frequency is swept over should be determined by:
(i) the line width of the resonant absorption
(ii) the time constant used in the detecting apparatus.

For automatic recording of signals a sweep linear with time is required. The lucite sector illustrated in figure 8, which has a radius of 6.3 cm. and an angle of 75°, was inserted between the anode lecher wires and was driven by a clock motor having a speed of 3 revolutions per hour. This arrangement gave a sweep very close to linear. However, it was useful only until the length of the anode line became too short at the higher frequencies of the oscillator.

The length of the anode line could be varied at a constant speed using a D. C. motor. The speed of a 1/10 H. P. motor was varied with a rheostat and reduced by a factor of 300 with a gear reductor (see figure 9). The worm gear and worm arrangement had a drive of 0.12 cm./min. minimum and 3.43 cm./min. maximum. Alternatively, at a right angle to this drive, a 3 foot threaded shaft produced a drive of 0.016 cm./min. minimum and 0.457 cm./min. maximum.
GLASS
LECHER WIRES

LUCITE

FIGURE 7 RELAY COIL & VIBRATOR

FIGURE 8 SHAPE OF LUCITE SECTOR

110 v DC
1000 W
FAST
SLOW

1/10 H.P MOTOR
SPEED REDUCTOR 300:1

WORM GEAR
WORM
LUCITE SPACER
STEEL ROD
BRASS CYLINDER
THREADED SHAFT

FIGURE 9 FREQUENCY SWEEP APPARATUS

to follow page 28
The lucite rod attached to the shorting bar was replaced by glass when these drives were used because the flexible lucite buckled and caused abrupt frequency changes. Connections were made from the motor shaft to the glass rod with rubber tubing. Then the drive was smooth and did not add appreciably to the noise in the circuit.

3. Filtering and Amplification

Essentially only the higher harmonics of the modulation frequency are necessary to produce a strong line on the oscilloscope. Fourier analysis of the waveform of the signal shows that the important harmonics are those whose frequencies are about $1/t$, where $t$ is the duration of the signal as the oscillator sweeps through it, usually the higher harmonics. Therefore, the unimportant lower harmonics can be removed before the last stage of amplification. A slight amplitude modulation occurs as a consequence of the 60 c.p.s. frequency modulation, which is carried by the 60 c.p.s. and 120 c.p.s. components. For these reasons, a filter was designed to attenuate frequencies below 400 c.p.s. and present infinite attenuation to the 60 c.p.s. and 120 c.p.s. components (see figure 6).

The amplitude modulated radio frequency voltage which is taken from the oscillator across the tank circuit is fed into a low pass amplifier having a gain of 9 decibels and falling off sharply at 3000 cycles. The quench frequencies used are thus removed completely. The amplifier output passes through the filter to another amplifier which has two levels of amplification, 20 and 40 decibels. The signal which is directed to the phase sensitive detector is again amplified before it reaches the Schuster circuit.

4. Phase sensitive detector, noise limiter, and d.c. amplifier

The phase sensitive detector (figure 14) is basically the Schuster
circuit described in Review of Scientific Instruments (1951). The input signal at the grid of the pentode produces a plate current \( i = g_m e \); the reference voltage applied to the grids of the switching tube 6SN7 determines through which of the two 50K plate resistors the current will travel. It alternately cuts off one half and causes the other half to conduct. The grid resistors limit the grid current and maintain the grid to cathode potential at a small positive value during the "on" period of the tube. The 2\( \mu \)fd. condensers prevent the plates of the 6SN7 from returning to H. T. during the "off" period. The "lock in" effect is obtained at high reference voltages; that is, a threshold effect is added to the intrinsic antiparasitic quality.

If \( e \), the signal voltage, and \( E \), the reference voltage, are such that \((e/E)^2 \ll 1\), the direct voltage output \( U \) is of the form

\[
U = 2k e \cos \psi
\]

where \( \psi \) is the phase difference between the two voltages and \( k \) is the gain of the detector.

The direct voltage output \( U \) from the plates of the 6SN7 tubes is fed to a d.c. amplifier through appropriate R. C. elements which limit the band pass for noise. The direct current between the plates of the 6SN7 amplifier tubes is recorded on an Esterline-Angus recording milliammeter. An overall sensitivity of 100\( \mu \)a./mv. was achieved for the detector.

The effective noise band width is approximately the reciprocal of the time constants of the R. C. elements, which were 0.5, 1.0, and 3.0 seconds. The noise band limiter does not attenuate the signal since the signal has essentially a very small frequency band width centred on \( f = 0 \), provided the frequency sweep is slow.
FIGURE 5  FREQUENCY MODULATOR

FIGURE 6  FILTER FOR VERY LOW FREQUENCIES (<400 cps)
FIGURE 10 POWER AMPLIFIER DRIVING THE HELMHOLTZ COILS
FIGURE 11  SQUARING CIRCUIT

FIGURE 12  AUXILIARY OSCILLATOR
FIGURE 13  LOW PASS AMPLIFIER

NULL FREQ.  18.6 Kc.

NULL FREQ.  7.75 Kc.
FIGURE 14

PHASE SENSITIVE DETECTOR
The Auxiliary Equipment

The Tuning System

PLATE II to follow page 30
CHAPTER IV RESULTS AND DISCUSSION

1. Performance of the spectrometer on known signals

The behavior of the oscillator was studied by testing it with samples which gave previously known resonance lines. By using various samples, we hoped to ascertain the frequency range over which the oscillator gives satisfactory performance. We also studied the effect of lowering the temperature by immersing the sample and the sample coil in a liquid air bath. A stronger signal should be expected since, by cooling the sample, we are increasing the difference in the populations of the different levels. Contrary to what was expected, we found that the signal was either decreased in strength or else could not be relocated after the cooling. It is most likely that dew or frost on the lines causes a large dielectric loss, a situation which is difficult to remedy.

About twenty different samples were prepared and tried, but resonance lines from only four of these were recorded on the Esterline-Angus. Searching for resonances in the samples which had melting points at liquid air temperatures was abandoned because of the trouble encountered whenever the oscillator coil is immersed in liquid air. The five signals in the four samples ranged in frequency from 161.5 to 332.4 Mc./sec. The data collected on each signal for critical conditions with Zeeman modulation is displayed in the table below. The signal-to-noise ratio for the same signal with frequency modulation is also given, although the conditions for resonance sometimes change slightly from one method of modulation to the other. The lucite sector was used in sweeping the frequency for the first three samples, while the tuning system shown in plate II was used in order to sweep through the I\(^{127}\) signal in I\(_2\). Photographs of the recordings are given in plates III and IV.
These signal-to-noise ratios are as good as any which have been reported by other workers, e.g. Dehmelt (1954).

2. Performance of the spectrometer on unknown signals

When the performance of the spectrometer on the test signals was found satisfactory, we decided to investigate some compounds which were of interest to the low temperature studies in connection with Pound's method of nuclear alignment, and in which no quadrupole resonances have yet been reported. The iodine atom covalently bonded to aromatic carbon atoms in iodo benzene sulphonate salts was of particular interest. Rollin and Hatton (1954) have estimated the resonant frequency of $^{127}$I in this compound to be 280 Mc./sec.; if the quadrupole coupling were this large, then the compound would be suitable in this respect for nuclear alignment.

A sample of the magnesium salt of p-iodo benzene sulphonate was obtained from the low temperature laboratory and carefully studied from about 250 to 340 Mc./sec. making adjustments in the circuit at every few megacycles.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Nucleus</th>
<th>Resonant freq. mc.</th>
<th>Quench freq. kc.</th>
<th>Quench amplitude</th>
<th>Signal-to-noise</th>
</tr>
</thead>
<tbody>
<tr>
<td>SbBr$_3$</td>
<td>Br$^{79}$</td>
<td>164.5</td>
<td>119</td>
<td>39% Eico 80% internal</td>
<td>300:1 3:1</td>
</tr>
<tr>
<td>Ba(BrO$_3$)$_2$</td>
<td>Br$^{79}$</td>
<td>174.6</td>
<td>148</td>
<td>42% Eico 50% internal</td>
<td>150:1 3:1</td>
</tr>
<tr>
<td>SnI$_4$</td>
<td>$^{127}$I</td>
<td>207.6 209.1</td>
<td>148</td>
<td>51% Eico 50% internal</td>
<td>150:1 200:1 20:1</td>
</tr>
<tr>
<td>$^3$I$_2$</td>
<td>$^{127}$I</td>
<td>332.4</td>
<td>129</td>
<td>84% Eico 80% internal</td>
<td>500:1 6:1</td>
</tr>
</tbody>
</table>
(a) $I^{127}$ in $I_2$

(b) $I^{127}$ in $SnI_4$

PLATE III

to follow page 32
(a) Br$^{79}$ in SbBr$_3$

(b) Br$^{79}$ in Ba(BrO$_3$)$_2$
In order to purify the sample, which was found to be 70% pure by chemical analysis, it was recrystallized from water. Neither the polycrystalline sample nor the small single crystals gave a resonance line with either method of modulation. Rollin investigated this substance in 1953 and did not see a line (unpublished). This result can be attributed to ionic interaction with impurities which could decrease the spin-spin relaxation time, and make the detection impossible.

Plate V shows the benzene sulphonate structure; meta-, ortho-, and para-iodo denote different substitutions of the iodine atom on the benzene ring in this structure. Since the above result with the para compound does not eliminate the possibility of an $^{127}$I resonance in the other two compounds, a sample of sodium meta-iodo benzene sulphonate was prepared in the laboratory from metanilic acid by Sandmeyer's reaction. It was investigated for a resonance over the same frequency range and again no signal was detected.

A set of complex compounds containing iodine, in which the bonds are expected to be covalent, were prepared: K$_2$HgI$_4$, K$_2$MgI$_4$, K$_2$SnI$_4$, K$_2$SnI$_4$. The reactions were: HgCl$_2$ + 2KI $\rightarrow$ HgI$_2$ followed by HgI$_2$ + 2KI $\rightarrow$ K$_2$HgI$_4$. Group theory shows that a dp$^2$s combination is possible for the tetragonal bonding in these compounds. By a consideration of the bonding orbitals and a comparison to those in the covalent I$_2$ bond, we estimated the I$^{127}$ resonance to be about 350 Mc./sec. An investigation was made in this region and also around 175 Mc./sec., but without results. The failure to observe an iodine resonance in these compounds is at least consistent with the fact that the chlorine resonance in K$_2$PtCl$_6$ cannot be seen. K$_2$PtCl$_6$ in solution is known to break up into K$^+$, Pt$^{4+}$, and Cl$^-$ ions, which suggests that the molecular complex is distorted rather than moved bodily. The resulting crystal strains may cause a spread in the values of the field gradient at the site of the iodine nucleus and broaden the line to the extent that it is unobservable. H. E. Petch and N. G. Cranna, investigating a milky sample of spodumene in this laboratory, have seen a similar effect. The quadrupole satellites of the N. M. R. line could not be found, although easily observed in other samples. Probably crystal imperfections cause a broadening of the lines as described above.
Fig. 3a. Projection of the untwinned structure of magnesium benzene sulphonate along the \( b \) axis, in the neighbourhood of a possible twin axis, the \( c \) axis of a unit cell. Hydrogen bonds between water molecules and oxygen atoms are drawn with narrow black lines unless the \( y \) co-ordinate of the oxygen atom is that shown \( \pm b \) when the line is broken. Other bonds are drawn with thicker black lines.

Table 2. Co-ordinates of atoms in the unit cell

<table>
<thead>
<tr>
<th>Atom</th>
<th>( x ) in A</th>
<th>( y ) in A</th>
<th>( z ) in A</th>
<th>( x ) in A</th>
<th>( y ) in A</th>
<th>( z ) in A</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg or Zn</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>S</td>
<td>2.37</td>
<td>2.44</td>
<td>3.60</td>
<td>2.36</td>
<td>2.44</td>
<td>3.64</td>
</tr>
<tr>
<td>O₁</td>
<td>2.30</td>
<td>0.98</td>
<td>3.60</td>
<td>2.29</td>
<td>1.02</td>
<td>3.64</td>
</tr>
<tr>
<td>O₂</td>
<td>2.11</td>
<td>3.03</td>
<td>4.85</td>
<td>1.91</td>
<td>3.03</td>
<td>4.89</td>
</tr>
<tr>
<td>O₃</td>
<td>1.73</td>
<td>3.03</td>
<td>2.46</td>
<td>1.73</td>
<td>3.03</td>
<td>2.49</td>
</tr>
<tr>
<td>(H₂O)₁</td>
<td>0.88</td>
<td>1.75</td>
<td>0.13</td>
<td>0.88</td>
<td>1.75</td>
<td>0.13</td>
</tr>
<tr>
<td>(H₂O)₂</td>
<td>1.94</td>
<td>5.60</td>
<td>1.98</td>
<td>1.93</td>
<td>5.60</td>
<td>1.98</td>
</tr>
<tr>
<td>(H₂O)₃</td>
<td>1.88</td>
<td>5.60</td>
<td>5.55</td>
<td>1.83</td>
<td>5.60</td>
<td>5.45</td>
</tr>
<tr>
<td>C₁</td>
<td>0.85</td>
<td>3.25</td>
<td>3.53</td>
<td>0.84</td>
<td>3.28</td>
<td>3.45</td>
</tr>
<tr>
<td>C₂</td>
<td>0.44</td>
<td>1.97</td>
<td>3.93</td>
<td>0.45</td>
<td>1.79</td>
<td>3.95</td>
</tr>
<tr>
<td>C₃</td>
<td>5.12</td>
<td>1.80</td>
<td>3.93</td>
<td>5.06</td>
<td>2.72</td>
<td>3.93</td>
</tr>
<tr>
<td>C₄</td>
<td>4.22</td>
<td>2.80</td>
<td>3.48</td>
<td>4.13</td>
<td>3.99</td>
<td>3.44</td>
</tr>
<tr>
<td>C₅</td>
<td>4.48</td>
<td>4.01</td>
<td>3.03</td>
<td>4.38</td>
<td>4.29</td>
<td>3.06</td>
</tr>
<tr>
<td>C₆</td>
<td>5.99</td>
<td>4.29</td>
<td>3.04</td>
<td>5.98</td>
<td>4.29</td>
<td>3.11</td>
</tr>
</tbody>
</table>

Table 2. Co-ordinates of atoms in the unit cell

Fig. 3b. Projection of the structure of magnesium benzene sulphonate along the \( b \) axis, in the neighbourhood of a twin axis. The component on the left is produced by a rotation of 180° about the \( c \) axis of the component on the right. Some bonds are shown as in Fig. 3a.
APPENDIX

Design of the sample coil for maximum field intensity

The energy stored in the magnetic field of the coil is distributed throughout the field with a density \( U = \frac{1}{2} \mu H^2 \) joules/meter. The energy density of the magnetic field can also be derived by calculating the work done in forcing the electrons of the current against the opposing electromotive force \( e = \frac{Li}{t} \).

\[
U = q.e = \frac{1}{2} i.t \times Li/t = \frac{1}{2} Li^2 \text{ joules}
\]

(57)

Diagram 3 illustrates (a) the transmission line and (b) the equivalent circuit with a coil of inductance \( L \).

For the equivalent circuit we have:

\[
V = E \sin \frac{2\pi l}{\lambda}
\]

(58)

and \( i = \frac{E \cos \frac{2\pi l}{\lambda}}{Z_0} \)

(59)

The impedance of the coil of inductance \( L \) is

\[
X = \omega L = Z_0 \tan \frac{2\pi l}{\lambda}
\]

(60)
Therefore,

\[ L = \frac{Z_0 \lambda \tan \frac{2\pi l}{\lambda}}{2\pi c} \]  

(61)

Then

\[ L_i^2 = \frac{Z_0 \lambda \tan \frac{2\pi l}{\lambda}}{2\pi c} \cdot \frac{E^2 \cos^2 \frac{2\pi l}{\lambda}}{Z_0^2} \]  

(62)

Simplifying, we find

\[ L_i^2 \propto \lambda \sin \frac{\pi l}{\lambda} \]  

(63)

Equation (63) shows:

(i) that more energy is stored in the magnetic field at the lower frequencies of oscillation.

(ii) that the quantity \( L_i^2 \) is a maximum when \( \sin \frac{\omega t l}{\lambda} = 1 \), i.e. when \( l = \lambda / 8 \).

It is thus seen that the inductance of the sample coil should be equivalent to a length \( \lambda / 8 \) of the transmission line if the field and energy density in the coil are to be maximum.
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(12) Kruger, H., Zeits. f. Phys., 130, 371 (1951)