PURE ELECTRIC QUADRUPOLE SPECTRA
IN CHLORINE COMPOUNDS

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IN CHLORINE COMPOUNDS

By

RICHARD E. MICHEL

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I. INTRODUCTION

The coulomb interaction and the quadrupole interaction are the two predominate means by which a nucleus may be coupled with a surrounding electric field. The latter type of coupling will be present, for a nucleus possessing an electric quadrupole moment, if the surrounding field has symmetry lower than cubic. The presence of such an interaction has been observed as fine structure in microwave spectroscopy[1] a nd nuclear magnetic resonance[2] investigations.

Transitions which occur directly between energy levels of the nucleus arising solely from the quadrupole interaction give rise to what is known as pure electric quadrupole spectra. The first successful observation of such transitions was made by Dehmelt and Kruger[3] in solid trans-diochlorethylene by use of an externally quenched regenerative oscillator. Soon afterwards investigations were made by Livingston[4] using a very simple self quenched super-regenerative circuit. The use of the latter circuit for the detection of pure electric quadrupole spectra forms the subject matter of this thesis. A brief review of the theory of quadrupole spectra will be presented first.

II. THE THEORY OF PURE ELECTRIC QUADRUPOLE SPECTRA

A. The Quadrupole Interaction Energy

The electric quadrupole moment of the nucleus is a measure of the non-spherical charge distribution in the nucleus. The physical picture which is commonly given to represent the quadrupole moment is a nucleus which has uniform charge density and the shape of either a prolate or an oblate spheriod. The former has a positive quadrupole moment and the latter a negative one. In either case the charge distribution is symmetric about the spin axis. From a classical electrostatic viewpoint the conception of the quadrupole interaction energy is quite straightforward. The total interaction energy of the nucleus with the surrounding charge distribution is given by:

$$E = \int V(r_n)\rho_n \, \delta\tau_n$$

Where $V(r_n)$ is the potential of the surrounding charge distribution at the element of volume $\delta\tau_n$ of the nucleus and ρ_n is the charge density of the nucleus. The expression for the potential may be expanded by a Taylor's expansion thus giving the total energy as the sum of the energy terms:

$$E = E_1 + E_2 + E_3 + \cdots$$

E_3 is then considered to be the electric quadrupole energy. The first two terms are taken as the coulomb and electric dipole interactions respectively.

While the above argument gives a fairly clear physical conception of the interaction energy, the value of E_Q used is based on quantum-mechanical considerations. This value for a field axially symmetric in the z direction is:

$$E_Q(m) = \frac{1}{4}\frac{e q_{zz} Q}{I(2I-1)}\left[3m^2 - I(I+1)\right]$$

Where I is the nuclear spin, m is the projection of I on the z axis and may take on the values $-I$ to $+I$, e is the electronic charge, q_{zz} is the field gradient evaluated at the nucleus and $e q_{zz} Q$ is the quadrupole coupling constant. Q is the nuclear electric quadrupole moment defined by:

$$eQ \equiv \int r_n^2 (3\cos^2\theta_n - 1)\rho_n \, d\tau_n$$

Where θ_n is the angle between r_n and the z axis.

There are some features of this expression which may be interpreted physically. Notice that the projection of I in the z direction appears to the second power, thus the energy expressions for $\pm m$ are the same. This should be expected since this is really a Stark splitting and is dependent only on the angle which the spin vector makes with the z axis, not its direction. Also it is seen that if $q_{zz} = 0$ then $E_Q = 0$. Since for spherical and cubic symmetry of the field $q_{zz} = 0$, no quadrupole spectra would be expected for such cases. Also for $I = 1/2$ the value of $E_Q = 0$ thus eliminating from consideration all nuclei with spin of one-half.

B. The Surrounding Electric Field

In the above expression for the quadrupole interaction energy the field considered is that arising from all surrounding charge distribution. There are two sources of the field, the valence electrons associated with the nucleus and the charges of neighboring atoms and ions. The valence electron may not be a s electron since this leads to a spherical charge distribution. Townes and Dailey[5] have calculated the relative effects of a valence p electron and an electronic charge placed 1 Å from a chlorine nucleus. The effect of the electronic charge being one-half percent of the valence electron. One of the principle causes of the small effect is the shielding of external charges by the closed shells of electrons. The valence electron which approaches the nucleus more closely is not so affected. Thus the interaction energy for a given nucleus should remain fairly constant as the nucleus is placed in different compounds. That this is so is indicated by the values of the electric quadrupole coupling constant given below:[6]

Compound	Nucleus	eQq mc
$SOCl_2$	Cl^{35}	64.18 63.78
$POCl_3$	Cl^{35}	57.96 57.88
CH_2Cl_2	Cl^{35}	71.98
$CHCl_3$	Cl^{35}	76.62 76.50
C_6H_5Cl	Cl^{35}	69.24

Although indicating a relative stability of the interaction energy this data also shows that the effect of the surrounding field is large enough for investigations to be made of these fields by use of this type of data. It is also evident that if the surrounding field were time dependent that the width of the resonance line would be too large to be observable. Thus pure electric quadrupole spectra are observed only in solids.

C. The Principle of Quadrupole Resonance

From quantum-mechanical considerations, m, the projection of the nuclear spin in the z direction, may take on only the values $-I, -I+1, ---- I-1, +I$. For a given nuclear spin there will be several values of $E_Q(m)$ which are referred to as the energy levels of the nucleus. A nucleus which possesses $E_Q(m)$ energy is said to be in the m^{th} energy state. This is physically pictured as a definite orientation of the nucleus in the electric field.

If energy is added to the nucleus it is possible to raise it from a lower state to a higher one. Not many nuclei will change their state, however, unless the energy added is exactly equal to the energy separation of the two states. This is the resonance phenomena which allows us to measure exactly the energy separation of the quadrupole splitting. In order to add energy to the nucleus use is made of the magnetic properties of the nucleus. Each nucleus has associated with it a magnetic moment, μ, which is given by:

$$|\mu| = g I \frac{eh}{4\pi Mc}$$

M is the proton mass and g is a constant called the gyromagnetic ratio which is characteristic of the nucleus. An externally applied magnetic field will interact with μ thus presenting a means of supplying energy to the nucleus.

From the Bohr relation, $\Delta E = h\nu$, a nucleus may be raised from a lower to a higher energy state when a quantum of electromagnetic radiation is absorbed. When the frequency of the radiation, ν, is such that:

$$E_Q(m) - E_Q(m') = h\nu_0$$

there will be a large amount of energy absorbed from the external field since many of the nuclei will undergo a transition. The detection of this loss of energy from the external field gives rise to the resonance absorption line. A given resonance line is identified by the frequency, ν_0, at which the absorption takes place.

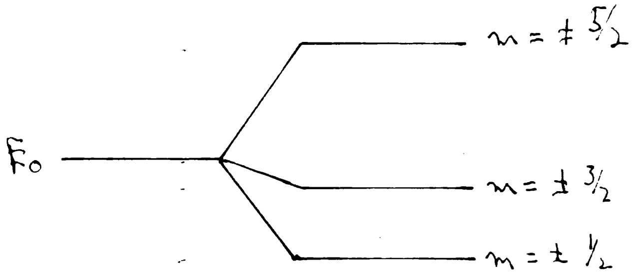
As an example consider a nucleus for which $I = 5/2$. The associated quadrupole energies are:

$$E_Q(\pm 5/2) = 5/20\,[e\,q_{zz}\,Q]$$

$$E_Q(\pm 3/2) = -1/20\,[e\,q_{zz}\,Q]$$

$$E_Q(\pm 1/2) = -4/20\,[e\,q_{zz}\,Q]$$

The energy diagram appears as:



E_0 represents the energy of the nucleus in the absence of the surrounding electric field.

We have spoken of adding electromagnetic energy to the system; however, as will be pointed out later, the energy is absorbed from the coil of an oscillating tank circuit. Since the magnetic properties of the circuit are usually associated with the coil it would seem logical to consider the transitions magnetic in nature and caused, as has been indicated, by an interaction between the oscillation external field and the magnetic moment of the nucleus. The selection rule for a magnetic dipole transition is $\Delta m = \pm 1$ so the expected spectrum would consist of two lines:

$$\nu_{5/2 \rightarrow 3/2} = 6/20 \left[e q_{zz} Q \right]$$

$$\nu_{3/2 \rightarrow 1/2} = 3/20 \left[e q_{zz} Q \right]$$

This is the spectrum observed by Dehmelt[8] for several iodine compounds.

It is well to emphasize that the nature of this transition is magnetic and is the same type of transition as is found in nuclear magnetic resonance experiments. The electric quadrupole causes the formation of the energy levels but is not concerned with the transitions between levels.

III. THE DETECTION OF PURE ELECTRIC QUADRUPCLE SPECTRA

A. The Super-Regenerative Oscillator

The circuit shown in Figure 1 is the spectrometer used in our investigations. A qualitative description of its operation will be given here; a more comprehensive discussion of the super-regenerative oscillator in resonance investigations has been given by S.I. Tahsin.[9]

A super-regenerative oscillator is a radio frequency oscillator to which an audio frequency quenching voltage is applied which causes the circuit to go into and out of oscillation. The quenching voltage may be applied externally, usually to the plate of the tube; or, as in this circuit, the components may be chosen so that intern al voltages are produced which result in a quenching action. The result of the quenching voltage is to produce a very sensitive detector since during the time when the oscillations are decaying and building up the plate current is very sensitive to any changes of energy in the tank circuit. The coil of the tank circuit furnishes an oscillating magnetic field whose frequency may be readily changed by merely tuning the tank circuit.

In order to view a resonance absorption line on an oscilloscope one further component has been added to the circuit. If the sample were placed in the tank circuit coil and the condenser tuned through the resonant frequency, ν_0, there would appear a signal on the oscilloscope as the resonance was passed; however, if the circuit was left tuned at ν_0 there would be no signal as there would be no change in the plate current. In order to observe the signal visually a

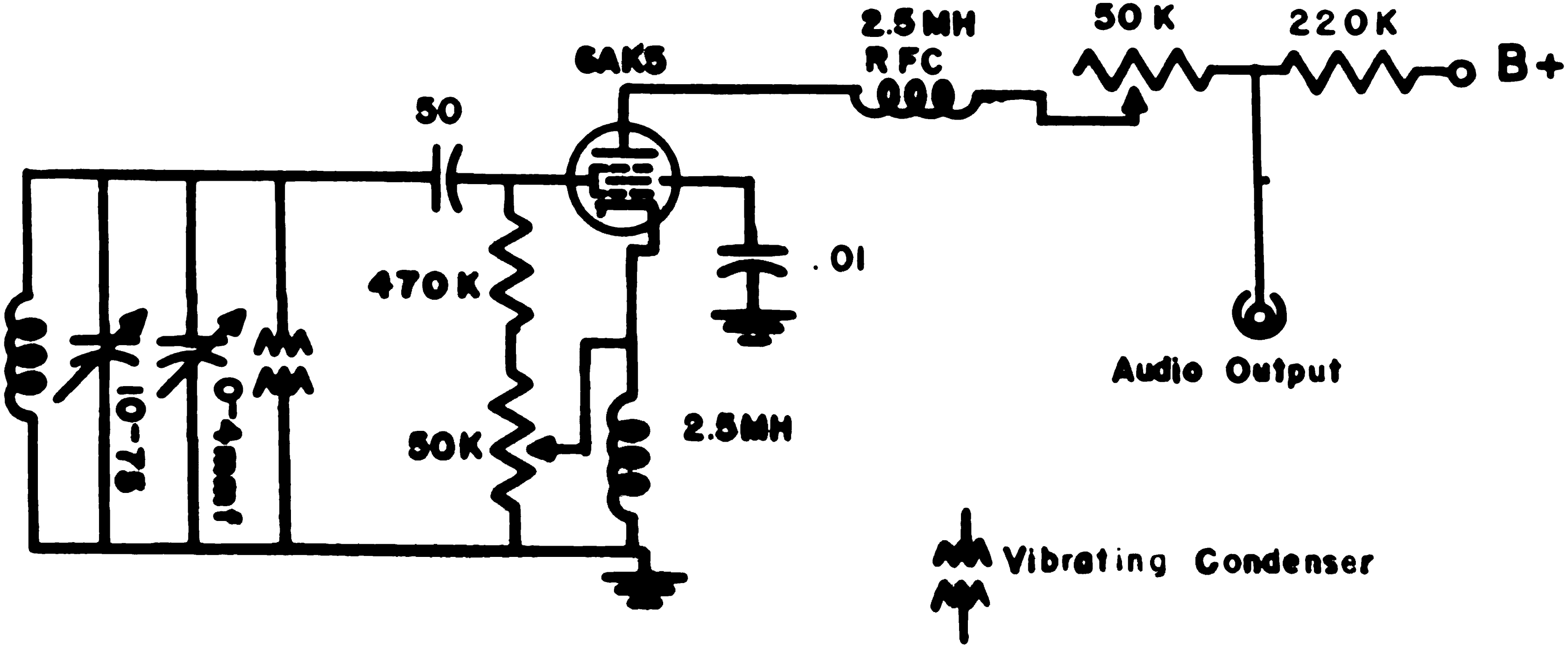


FIGURE I Super-Regenerative Oscillator

vibrating condenser has been placed in parallel with the tuning condenser. The capacitance of this condenser may be changed periodically at any low audio frequency. Thus if we tune the tank circuit to resonance and then add the periodic change of the vibrating condenser the resonance condition will be swept through periodically which will allow the absorption line to be observed visually.

The block diagram of Figure 2 shows the entire spectometer circuit. The Select-O-Ject is a commercial filter; it is used to reject the unwanted amplitude modulation which is produced as a result of the frequency modulation of the vibrating condenser. The Hewlett-Packard audio oscillator furnishes the power to drive the vibrating condenser. As the lower limit of the Select-O-Ject is 80 cps the modulating frequency has to be kept higher. The modulating frequency was normally around 120 cps.

The super-regenerative oscillator was constructed in the case which contained the vibrating condenser; the latter was taken from a Navy altimeter, RT-7/APN-1. The sample coil was made from 6-7 turns of number 58 copper wire wound on a one-half inch diameter. The coil was shielded by a one inch brass cup and was connected to the oscillator by means of a rigid coaxial line consisting of one-half inch brass pipe and number 30 brass wire approximately seven inches long. Three teflon washers were used to hold the inner conductor in place.

Later the length of the connecting line was reduced to

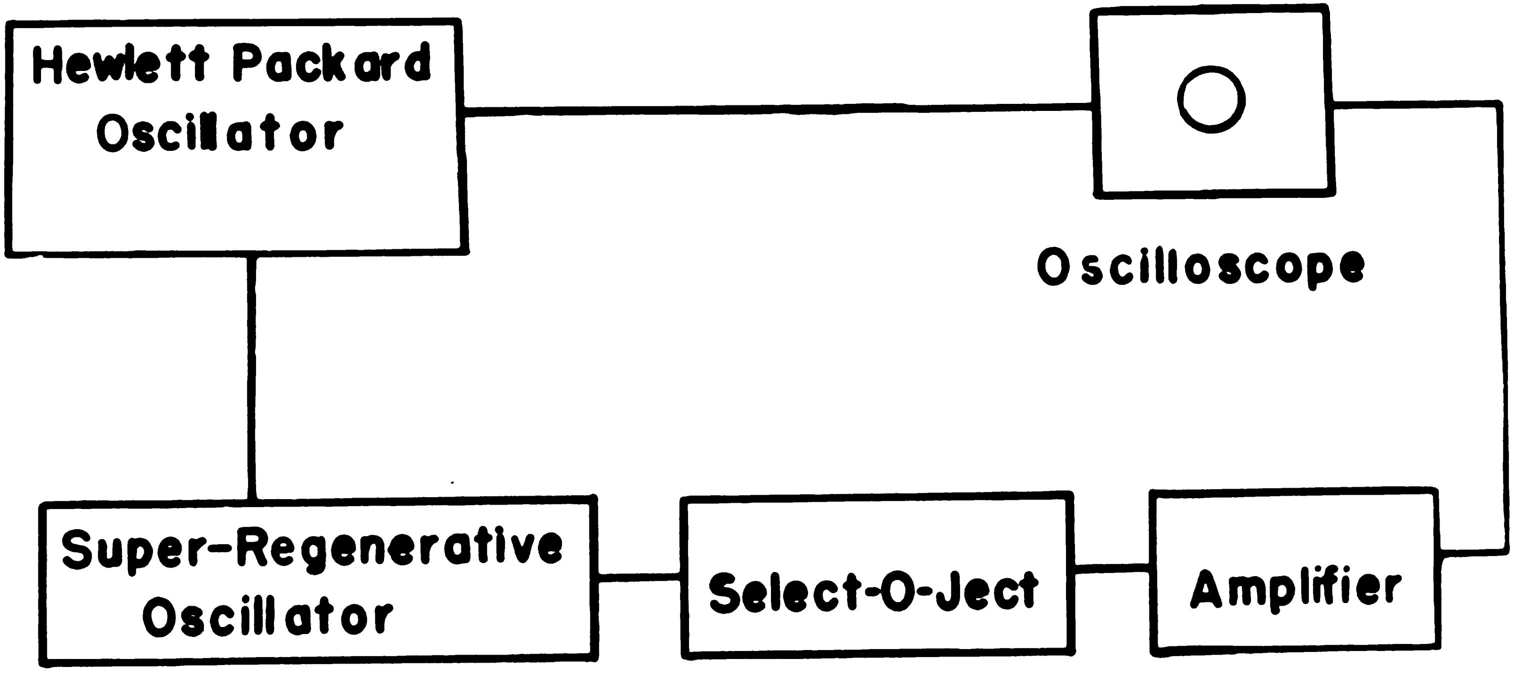


Figure 2 Block Diagram of Spectrometer

two and one-half inches so that the inductance of the tank circuit would be concentrated in the coil where the losses take place and not distributed along the coaxial line. The small vernier condenser was added to give a smoother sweep through the resonance condition.

B. Performance of the Spectrometer

To test the instrument the resonance lines associated with Cl^{35} and Cl^{37} in $CHCl_3$ were first sought as they were known to exist at:

Cl^{35}	Cl^{37}
38.3081 mc	30.1921 mc
38.2536 mc	30.1500 mc

Only one line would be expected from each nuclei since they both have a nuclear spin of three-halves. The presence of two lines has been explained[6] by considering that there are two non-equivalent positions for the Cl nucleus to take in the molecule.

The tank coil of the spectometer was immersed in a beaker of $CHCl_3$ which was then frozen by placing it in a mixture of acetone and dry ice. No results were observed. A possible reason for the negative results is that the sample was not frozen solid enough. The temperature of the freezing mixture was -77 °C and the freezing point of $CHCl_3$ is -63.5 °C. The surrounding electric field may still have had a time dependency which broadened the line width beyond the point where it could be observed. The resonance lines had been originally observed at -196 °C so liquid nitrogen was next used to freeze the sample. One of the resonance lines was observed but the tuning condenser proved too coarse to adjust carefully at resonance. Once the vernier capacitance was added both lines were observed.

In sweeping the field searching for the resonance line other signals were detected from other radio frequency oscillators in the building and even from what is thought to be a local radio station. To discriminate between the "false" signals and the quadrupole resonance the following trick was used.

Pound[2] has discussed the result of introducing a small external magnetic field to a single crystal in which a quadrupole resonance line is being observed. The result is to shift the frequency. The magnitude of the effect, however, is dependent on the angle between the magnetic and electric fields. As our sample was polycrystalline the effect of introducing a small magnetic field was to widen the line until it disappeared. Thus the quadrupole line was distinguishable from the other signals picked up by the oscillator.

The form of the observed signal as the tank circuit was tuned through resonance was unusual enough that its description is shown in Figure 3. As shown, a single line appears and splits into two lines. When ν_T , the frequency of the tank circuit without the vibrating condenser, equals ν_0 , each of the original lines is now two equally spaced lines. The signal when set at this condition proved to be smaller and less stable than when the one line was observed.

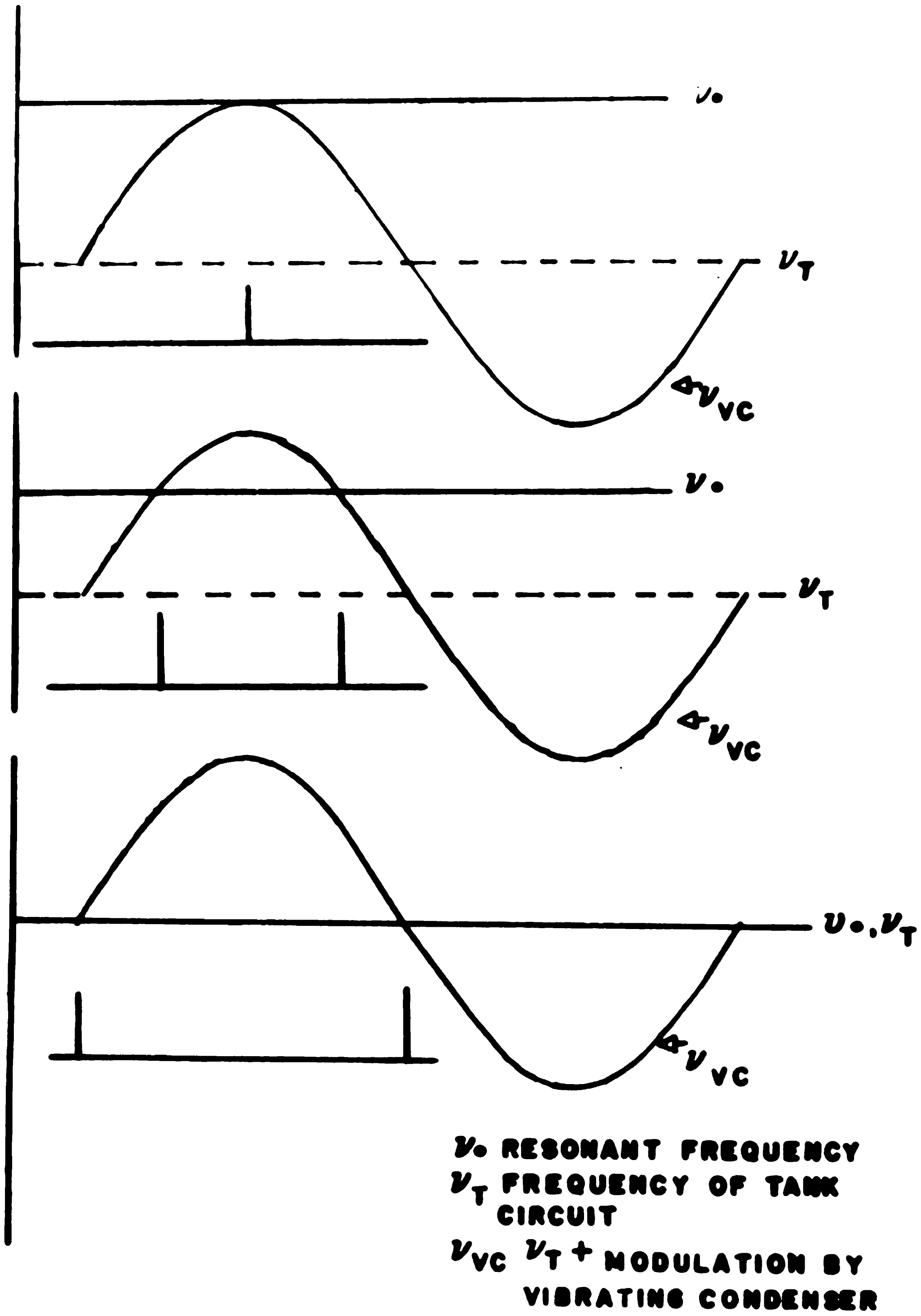

ν₀
ν_T
ν_VC
ν₀
ν_T
ν_VC
ν₀, ν_T
ν_VC
ν₀ RESONANT FREQUENCY
ν_T FREQUENCY OF TANK CIRCUIT
ν_VC ν_T + MODULATION BY VIBRATING CONDENSER

FIGURE 3

To measure the frequency of the resonance line the tank circuit was first tuned so that ν_T coincided with ν_0 . The signal of a Gertsch FM-1 frequency meter was mixed with the resonance signal. There appeared successively on the oscilloscope as the meter was tuned through the resonant frequency a series of signals which were symmetric in amplitude about a central signal. Frequency measurements were made with this central signal superimposed on the resonant line.

It was at this point that the main weakness of this type of detector came to light. The resonant frequency readings were not consistent. The reason for this lies in the very nature of the instrument. The quenching of the oscillations produces side bands which may also detect the signal. With an internally quenched oscillator the only way it might be possible to determine the frequency at which the detection is taking place is by comparing the amplitudes of the signals. In our case we were not able to do so.

Several additional compounds were checked at dry ice and acetone temperatures; the frequency being swept from 20-60 mc. No results were found in C_6H_5COCl or Aneline. $CHCl_2CHCl_2$ would not freeze with our freezing mixture although its freezing point is -43.8 °C. The metal probe perhaps conducted too much heat into the sample. $CHCl_2COOH$ conducted to such an extent that it stopped the oscillations. Finally a line was observed in solid benzyl chloride ($C_6H_5CH_2Cl$) at liquid nitrogen temperatures. The approximate position of the line being 33.6 mc.

In an attempt to repeat the experiment using benzyl chloride of only technical purity the line could not be found. Once a C.P.S. sample was used again the line was easily obtained. Although the reason why the impure sample failed to give resonance is not known it is possible that para-magnetic ions were present which had the same effect as our externally applied field.

In an attempt to measure the resonant frequency with certainty paradichlorbenzene, a solid at room temperature, was used as our sample. The vernier capacitance of the tank circuit was connected to a 1 rpm motor which was geared down 1 to 10. The main tuning condenser was set close to the resonant line and the vernier was then driven through resonance with the signal being recorded on a Millivac recorder. Preliminary work with this method indicates that the side bands of the oscillator can be detected. If so the uncertainty of the frequency measurements can be removed.
If this is done the circuit presents a very simple means by which the quadrupole spectra may be observed.

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