

#### QUADRUPOLE RESONANCE STUDIES

Thesis for the Degree of Ph. D. MICHIGAN STATE UNIVERSITY Richard Edwin Michel 1956 THESIS



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This is to certify that the

thesis entitled

Quadrupole Resonance Studies

presented by

Richard Edwin Michel

has been accepted towards fulfillment of the requirements for

<u>Ph. D</u> degree in <u>Physics</u>

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Date October 26, 1956

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## QUADRUPOLE RESONANCE STUDIES

Ву

Richard Edwin Michel

### AN ABSTRACT

Submitted to the School for Advanced Graduate Studies of Michigan State University of Agriculture and Applied Science in partial fulfillment of the requirements for the degree of

DOCTOR OF PHILOSOPHY

Department of Physics

Approved \_\_\_\_\_ Relast D. Spince -----

The quadrupole resonance of  $Cl^{35}$  has been used to study certain properties of crystals of  $p-C_6H_4Cl_2$  and  $C_{6H_5}Cl$ . The investigations of  $p-C_6H_4Cl_2$  were made at room temperature while those of  $C_{6H_5}Cl$  were made at liquid nitrogen temperature. Both resonances occur in the range of ~ 34mc. The resonances were detected by means of an internally quenched superregenerative oscillator.

The Zeeman splitting of the resonance from single crystals of  $p-C_6H_4Cl_2$  indicated that there were two directions of the C-Cl bond, separated by ~ 74°, when the crystal was in the low temperature, or  $\sim$ , phase but that there was only one direction when the crystal was in the high temperature, or  $\mathfrak{S}$ , phase. The transition temperature is ~ 32°C. The orientation of the single axis in the  $\mathfrak{S}$  phase with respect to the two in the  $\sim$  phase appeared to be either random or capable of assuming a large number of different values. Measurements of the line width of the nuclear magnetic resonance of the protons in the same samples indicated that the reorientation of the C-Cl bond during the phase transition was accompanied by a similar reorientation of the molecule as a whole.

The samples of  $C_{6}H_{5}Cl$  studied contained controlled amounts of other benzene derivatives. The addition of even .001 mole fraction of certain impurities reduced the maximum height of the signal greatly without appreciable broadening of the line. The effectiveness of the impurity in reducing the resonance was measured by the number of molecules which each impurity molecule would have to make ineffective in order to bring about the resultant loss in intensity. There appeared to be a linear relationship between the effectiveness of the impurities and the difference in volume between the impurity molecule and the  $C_{6}H_{5}Cl$  molecule. There was no observable effect due to a difference in the electric dipole moment of the impurity and resonant molecules.

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#### I. INTRODUCTION

A nucleus which possesses an electric quadrupole moment may interact with an electric field if the field is such that not all of its derivatives,  $\frac{\partial E_{x_i}}{\partial x_j}$ , vanish. The interaction energy is dependent upon the orientation of the nucleus in the electric field. The presence of such an interaction can be observed in optical,<sup>1</sup> molecular beam,<sup>2</sup> microwave<sup>3</sup> and nuclear paramagnetic<sup>4</sup> spectroscopy. In all of these cases, however, the quadrupole energy is small in comparison to other energies present in the system and manifests itself only in fine structure lines and line shapes.

The observation of spectra resulting from nuclear transitions between energy states whose separation is determined entirely by the electric quadrupole interaction was first accomplished by Dehmelt and Krüger.<sup>5</sup> The transitions observed were those of the chlorine nuclei in solid transdichloroethylene. In a series of papers<sup>6</sup> they have discussed this experiment along with similar observations of resonances of bromine, iodine and antimony nuclei.

The spectrum which is observed arises from the detection of a radio-frequency nuclear magnetic resonance absorption. That is, energy of a radio-frequency field is transferred to the nuclei by means of an interaction between the

field and the nuclear magnetic moments. The absorption of energy and the accompanying excitation of the nuclei from one energy state to another take place when the frequency of the field satisfies the condition  $v = \frac{\Delta E}{b}$  where  $\Delta E$  is the separation of the energy states. In this respect it is similar to nuclear paramagnetic resonance, the difference being the manner in which the energy states are determined. In nuclear paramagnetic resonance the energy levels are determined by the orientation of the nuclear magnetic moments in an externally applied static magnetic field. On the other hand, the quadrupole states are fixed by the interaction of the nuclear electric quadrupole moments and an electric field gradient. Furthermore, the source of the electric field is a charge distribution within the sample itself. It follows that in nuclear quadrupole resonance (NQR) the resonant frequency of a given nucleus varies from com pound to compound.

Much of the work which has been done in NQR has been concerned with attempts to use these shifts in frequency to substantiate or extend existing theories of molecular and crystalline interactions. For instance, Livingston<sup>7</sup> has observed that the quadrupole coupling constant, the product of the nuclear electric quadrupole moment and the maximum field gradient, increases regularly in the sequence of solid materials  $CH_2Cl_2$ ,  $CH Cl_3$  and  $C Cl_4$ . This behavior is in agreement with changes to be expected in the bonds within the molecule, which will be discussed later, and indicates that adjacent molecules in the solid have very little effect on the quadrupole coupling constant in molecular crystals. If the adjacent molecules did have a large effect, there would be more random behavior of the coupling constant.

In a somewhat similar vein, investigators<sup>8,9</sup> have found that there is a relation between the quadrupole coupling constant and Hamett's substituent parameter  $\sigma$ . The constant is a measure of the electron density in the molecule and thus should affect the electric field which is seen by the resonant nucleus.

In contrast to these investigations which are concerned with changes in the field gradient due to changes in molecular structure, some workers have observed variations in the spectrum when the crystal structure has been perturbed. Duchesne and Monfils<sup>10</sup> have observed the NQR of  $Cl^{35}$  in  $p - C_{6H4}Cl_2$  when small amounts  $(10^{-3} \text{ to } 10^{-2} \text{ molar concen-}$ tration) of  $p - C_{6H4}Br_2$  have been added. The two compounds form a solid solution; however, the difference in size of the two molecules should produce some strain around the impurity molecule. The investigators observed a rapid decrease of signal intensity and a broadening of the line with increasing concentration of the impurity. They did not observe a shift in the resonant frequency of the impure samples with respect to the pure sample. Dean<sup>11</sup> has reported that there is a shift in frequency for molar concentrations of

the order of one-tenth. A shift in the resonant frequency of  $Cl^{35}$  in p - C<sub>6</sub>H<sub>4</sub>Cl<sub>2</sub> has also been reported by Dautreppe and Dreyfus<sup>12</sup> when they subjected the crystal to a pressure of 900 kg/cm<sup>2</sup>. It would thus appear that even if Livingston's conclusion, that the surrounding molecules do not play a large role in determining the resonant frequency, is true, their fractional importance is large enough to be easily observed. Their exact role in the production of the field gradient, however, is still not well understood. The importance of NQR in the investigation of molecular bond structure would be greatly enhanced if these crystalline effects were better understood.

It might be mentioned at this point that, although we have discussed only the case of solid materials, pure quadrupole transitions have been observed by Sterzer and Beers<sup>13</sup> in vapors of  $CH_3I$  and  $CF_3I$ . Also Seiden<sup>14</sup> has recently proposed that it may be possible to observe such transitions in liquids which show some anisotropy.

The investigations of this thesis are restricted to solids and in particular to organic compounds containing one or more covalently bonded chlorine atoms. The resonances observed are those of  $Cl^{35}$ . There are two sections to the thesis. In the first part use is made of existing ideas concerning the electric field gradient at the nucleus to investigate a phase transition in  $p - C_{6H4Cl_2}$  known to exist

at 32°C. In the second part an attempt is made to better understand the role which the surrounding molecules play in producing the gradient at the nucleus. A discussion of the general theory applicable to both parts is given first with the more specialized discussions given in their respective sections.

### II. THEORY

A. The Pure Electric Quadrupole Energy States

The pure electric quadrupole energy states arise from an electrostatic interaction between the nuclear charge and the electric charge surrounding the nucleus. The discussion given here is merely an outline of the derivation of these energy states for the particular case of an axially symmetric electric field. A more complete discussion of the general case has been given by Pound.<sup>15</sup>

We begin by considering the total electrostatic interaction between two groups of charge, the nucleus and the surrounding charge.



The subscript "n" refers to the nucleus and the subscript "e" to the charge outside of the nucleus. In terms of the indicated quantities the electrostatic interaction is given by:  $0 \propto 0 \propto 0$ 

$$E = \int_{Y_{k}} \int_{Y_{n}} \frac{P(\underline{r}_{n}) P(\underline{r}_{e}) \partial Y_{k}}{R_{e} \left[ 1 + \left( \frac{R_{m}}{R_{e}} \right)^{2} - 2 \frac{R_{m}}{R_{e}} \cos \Theta_{k} n \right]} V_{2}$$
(1)

Since by definition  $n_n/n_k \mid$ , the denominator may be expanded in terms of Legandre polynomials.

$$E = \int_{T_{a}} \int_{T_{m}} \frac{\rho(\underline{n}_{a})\rho(\underline{n}_{a})}{\rho(\underline{n}_{a})\rho(\underline{n}_{a})} - \frac{\rho_{a}}{\rho_{a}} \frac{\rho(\omega \cdot \theta_{a})}{\rho(\omega \cdot \theta_{a})} + \frac{\rho_{a}}{\rho_{a}} \frac{\rho(\omega \cdot \theta_{a})}{\rho(\omega \cdot \theta_{a})}$$
(2)

The first term of the expansion leads to the coulomb energy which has no orientational dependence and is therefore of no interest to us. The second term leads to the electric dipole energy which vanishes for a nucleus which has a symmetrical distribution of charge. This term has been found to be zero for all nuclei so far studied. The third term leads to the quadrupole energy which is the interaction we wish to discuss. Its value is:

$$E_{Q} = \frac{1}{2} \int_{\Upsilon_{a}} \int_{\Upsilon_{m}} \frac{n_{m}}{n_{a}} \frac{\rho(\underline{r}_{m})\rho(\underline{r}_{a})}{n_{a}} (3\omega^{2}\theta_{en} - 1)\partial\Upsilon_{n}\partial\Upsilon_{e}$$
(3)

The angle  $\Theta_{n}$  may be eliminated from the problem by introducing the Cartesian coordinates through the relation

$$\underline{\Gamma}_{n} \cdot \underline{\Gamma}_{1} = \underline{\Gamma}_{n} \underline{\Gamma}_{1} \cos \Theta_{n1} = \underbrace{\Sigma}_{i} X_{ni} X_{1i}$$
This gives:
$$(4)$$

$$E_{Q} = Y_{2} \int_{Y_{1}} \int_{T_{n}} (3 \sum_{i} X_{ni} X_{ni} X_{2i} X_{2i} - R_{n}^{2} R_{2}^{2}) \frac{(n_{2})p(n_{2})Y_{2}Y_{1}}{R_{2}^{2}} (5)$$
  
It can be verified that the energy may be expressed in the following form:

$$E_{Q} = -\frac{1}{6} \sum_{i,j} Q_{ij} (\nabla \underline{E})_{ij}$$
<sup>(6)</sup>

where,

$$Q_{ij} = \int_{\gamma_n} \varrho(\underline{\sigma}_n) (3 \times_{ni} \times_{nj} - S_{ij} R_n^2) \partial \gamma_n$$
  
$$(\nabla \underline{E})_{ij} = - \int_{\gamma_n} \frac{\varrho(\underline{\sigma}_n)}{R_n^2} (3 \times_{ni} \times_{nj} - S_{ij} R_n^2) \partial \gamma_n$$

The advantage of expressing the energy in this manner is that one can investigate the contribution due to the nucleus separately from that of the surrounding charge distribution.

Considering Qi; first we see that it is a symmetric tensor, since the  $\chi_i$ 's commute, and that the sum of the diagonal terms is zero. There is a theorem<sup>16</sup> which states that if two tensors (a) are symmetric, (b) possess a zero trace and (c) are constructed in the same manner from vectors which satisfy the same commutation rules with respect to  $\underline{L}$  as  $\underline{\Lambda}$  and  $\underline{L}$ , then the matrix elements diagonal in  $\underline{I}$ of the two tensors will have the same dependence on the magnetic quantum number,  $\mathbf{w}$ . That is, if  $\overline{\chi}_i$  and  $\overline{\chi}_i^*$  are two such tensors then

$$(Im|T_{ij}|Im') = K_{i} f(m)$$
<sup>(7)</sup>

 $(I m | T_{ij}' | I m') = K_1 f(m)$ where  $K_1$  and  $K_2$  are independent of m. Since m is a measure of the orientation of the nucleus, it is f(m)which is of interest to us in NQR. We may therefore replace  $Q_{ij}$  by the following tensor:

$$Q_{ij} = C \left[ 3 \left( \underline{I} \right)_i \left( \underline{I} \right)_j - S_{ij} \left( \underline{I} \right)_j^2 \right]$$
(8)

The constant C is determined by defining the electric quad-

rupole moment, Q, in the following manner

$$Q = (II|Q_{33}|II) = C[(2I-1)I]$$
(9)

so that

$$Q_{ij} = \frac{2Q}{I(2I-i)} \begin{bmatrix} 3(\underline{I}), (\underline{J}), -S_{ij} (\underline{I})^2 \end{bmatrix}$$
(10)

The second tensor  $(\nabla \xi)_{i,i}$  is also symmetric and real so that it is possible to find a coordinate system in which it will be diagonal.<sup>17</sup> We shall assume that the coordinate system chosen originally was the correct choice.

$$(\nabla \underline{E})_{i} = -\int_{\gamma_{g}} \frac{\rho(\underline{n}_{s})(3 X_{e_{i}}^{2} - S_{ii} \overline{n}_{s}^{2}) \partial \gamma_{g} \qquad (11)$$

It is easily seen that this tensor is actually the gradient of an electric field as indicated by the symbolism. The potential arising at a point  $\underline{\wedge}$  due to the charge distribution  $\varrho(\underline{\Omega}_{i})$  is given by:

$$V = \int_{T_{A}} \frac{P(\Pi_{0})}{|\Gamma_{1} - \Gamma_{0}|} \frac{\partial T_{0}}{\partial T_{0}}$$
(12)

The second derivative of this quantity with respect to X: evaluated at n=0 results in  $(\nabla \xi)$ :. We now make the assumption that  $(\nabla \xi)$ : is constant with respect to the nuclear orientation. This simplification can not be made in investigations such as the molecular beam experiments. In these cases one is concerned with essentially free molecules, and the orientation of the nucleus certainly may have an appreciable effect on the remainder of the molecule. In the case of the NQR, however, the "remainder of the molecule" is the macroscopic crystal and we may conceivably neglect the effect of the orientation of the nucleus on such a massive object.

We further restrict the problem to the special case of an axially symmetric field gradient, that is for  $\frac{\partial E_x}{\partial x} = \frac{\partial E_y}{\partial y}$ Furthermore, since we are considering the electric field at the nucleus due to charges outside of the nucleus, the electric field must satisfy the relation  $\nabla \cdot \underline{E} = 0$ . Using these relations the Hamiltonian of the problem becomes

$$H_{q} = \frac{Q_{q}}{HI(\lambda I - 1)} \begin{bmatrix} 3(\underline{I})_{2}^{2} - \underline{I}^{2} \end{bmatrix}$$
where
$$q = \frac{\partial E_{2}}{\partial E_{2}} = \frac{\partial E_{2}}{\partial E_{2}}$$
(13)

The Hamiltonian is diagonal in m and the resulting energy states which are degenerate in  $\pm m$  are

$$E_{\pm m} = \frac{PQ}{4E(2E-1)} \begin{bmatrix} 3m^2 - E(E+1) \end{bmatrix}, \qquad (14)$$

#### B. The Electric Field Gradient

The spectrum of  $Cl^{35}$  resulting from the energy levels derived in the last section consists of a single line whose frequency is determined by the relation:

$$V_0 = \frac{a Q^{35} q}{\lambda}$$
(15)

Thus, if it is assumed that the electric quadrupole moment

of a given nucleus is independent of the nature of the compound of which it is a part, the transition frequency is a direct measure of the electric field gradient. As is evident, however, neither the value of the field gradient nor the quadrupole moment can be determined from a frequency measurement alone.

Before discussing possible sources of q and their relative importance, we can consider one aspect of the source which is entirely general. As has been mentioned before, the electric field must satisfy Laplace's equation,  $\nabla \cdot \underline{\mathbf{E}} = \mathbf{O}$ . If the symmetry of the charge distribution is cubic or spherical, the x, y and z directions will be equivalent. This requires that:

$$\frac{\partial E_x}{\partial x} = \frac{\partial E_x}{\partial x} = \frac{\partial E_z}{\partial z}$$
(16)

Taken together these two relationships require that:

$$\frac{\partial E_{x}}{\partial x} = \frac{\partial E_{y}}{\partial x} = \frac{\partial E_{z}}{\partial z} = 0$$
(17)

Therefore, for an electric quadrupole interaction to exist, the charge distribution producing the electric field must have a symmetry less than cubic.

The charge distribution is normally considered in two parts, the valence electrons associated with the nucleus in question and all other charges surrounding the nucleus. The division is made in this manner since q is primarily depen-

dent upon the valence electrons and the manner in which they are bonded. The closed shells of electrons surrounding the nucleus constitute a spherical charge distribution and therefore do not contribute to the field gradient.

For the case considered here, covalently bonded  $\operatorname{Cl}^{35}$ , the field will arise largely from the lack of one 3p electron in the valence shell. The validity of this division of the source of q may be inferred from the following comparison. The field gradient due to one electronic charge placed  $|\overline{R}^\circ|$  from the nucleus is  $|x|^{o^{16}} = \sqrt[5]{-10} = \sqrt[5]{-10}$  assuming the atom is otherwise undisturbed. It has been shown<sup>18</sup> that for the chlorine nucleus the shielding of the surrounding electrons should reduce this value to  $|x|^{o^{16}} = \sqrt[5]{-10} = \sqrt[5]{-10}$ In comparison, the observed field gradient corresponding to the resonant frequency of 35mc, which is an average value for the C-Cl<sup>35</sup> covalent bond, is  $|1\times 10|^{15} = \sqrt[5]{-10} = \sqrt[5]{-10}$ .

A further illustration of the relative contribution of the valence electrons and the external charges can be made by comparing q for the gaseous NaCl and that for a molecule in which the chlorine is covalently bonded, such as CH<sub>3</sub>Cl. In the former case the electron distribution around the chlorine nucleus is approximately spherical and the electric field gradient must be attributed to its partner ion, whereas in the second case there is no distinct charge present and q must be attributed to the asymmetrical distribution of the

chlorine electrons caused by their participation in the covalent bond. For NaCl q is known to be less than  $.17 \times 10^{15} \frac{e_{50}}{c_{10}}$ while for gaseous CH<sub>3</sub>Cl it is  $13 \times 10^{15} \frac{e_{50}}{c_{10}}$ . Thus, for a covalently bonded chlorine atom, q should be given to a good approximation by the calculation of only that portion of q which arises from the participation of the valence electron in the bond. Even if the approximation is valid, the calculation has an extremely large uncertainty in itself since the wave functions of electrons in the molecule are not known.

Townes and Dailey<sup>18</sup> have considered methods of making approximate calculations from which one can obtain at least an idea of the nature of q and in some cases an approximate value. The nature of the chemical bond between two atoms is commonly expressed in terms of a set of limiting types which are more easily visualized. Thus, for example, a bond may be said to be largely covalent with a certain percentage of ionic character and a certain percentage of double bonding. The percentage of the various parts is normally determined by fitting the available experimental evidence into a consistent pattern.

The bond we are concerned with is the C-Cl bond in chlorine derivatives of benzene, methane and ethane. In these cases it is largely a single covalent bond. A single covalent bond is visualized as a shared pair of electrons. The stabalization of the bond arises from the overlapping

of the two electron orbits. In the valence bond method the wave function for each of the electrons is expressed as a linear combination of the atomic wave functions of their respective atoms. The exact combination is chosen so as to make the bonding as strong as possible. The ground state of the atom usually makes the most important contribution with only one or two of the other states contributing to the bond to any appreciable extent. For the normal single covalent chlorine bond there is a mixture of the 3s and 3p Townes and Dailey<sup>18</sup> estimate that the character of states. this hybrid bond is 20 percent 3s and 80 percent  $3p_{z}$ . The 3pz orbital has axial symmetry about the z, or bond, direction and will produce an axially symmetric field gradient at the chlorine nucleus. The presence of the 3s character in the bond will not affect the symmetry but since the s orbit has spherical symmetry the field gradient should be reduced. To see this we can compare q for atomic chlorine where it should arise from a pure  $3p_z$  orbit to that in  $CH_3Cl$  where it arises from the s-p hybrid bond.

> Atomic chlorine  $g = 19 \times 10^{15} e_{50/c_{-3}}$ CH<sub>3</sub>Cl  $g = 13 \times 10^{15} e_{50/c_{-3}}$

There is also an ionic portion of the bond which can be determined roughly from the difference in the electronegativity of the two partner atoms. This also will not change the axial symmetry of the bond but it will reduce the value of

the gradient. It is a change in the ionic content which is assumed to account for Livingston's<sup>7</sup> results. As one adds chlorine atoms in the sequence  $CH_3Cl$ ,  $CH_2Cl_2$  and  $CHCl_3$  there is greater competition for the carbon electrons and brings about a reduction in the ionic character of the bond and an increase in the value of q and thus the resonant frequency.

In the case of the chloro-benzenes there is a contribution of about 10 percent double bonding. This is reflected in a more stable compound and in a shortening of the bond distances. The second bonding orbital is a  $p_x$  orbital where the x direction is taken normal to the plane of the benzene ring. The contribution of this orbital will destroy the axial symmetry of q. Dean<sup>19</sup> has shown that the asymmetry

 $\gamma = \underbrace{\partial E_{x}}_{\partial E_{z}}$  is  $\wedge .08$ . In the work which we do with p-C<sub>6</sub>H<sub>4</sub>Cl<sub>2</sub> the asymmetry will be neglected since the effects which we are concerned with will not be greatly changed by the small errors introduced by this assumption.

#### III. THE SPECTROMETER

One of the fortunate features of NQR is that for many cases the instrumentation necessary for the observation of the resonance is relatively simple. The circuit diagram of the instrument used for the investigations reported on in this thesis is shown in figure No. 1. It is on internally quenched superregenerative oscillator. The operation of this type of oscillator has been discussed in some detail by Whitehead.<sup>20</sup> The basic circuit is that of a pulsed oscillator. The oscillations are turned off, or quenched, due to a build-up of charge on the grid condenser. The time constant of the RC combination in the grid circuit is too long to permit the mean grid potential to adjust to the level of oscillation.

In order that the oscillator will operate effectively as a receiver the quench frequency should be between 1/100and 1/1000 of the frequency of oscillation.<sup>20</sup> The absorption frequencies we were interested in were ~ 35mc which required a quench frequency between 35 and 350kc. The quench frequency is determined to a large degree by the charging rate of the RC combination on the grid. These componets were adjusted until the quench frequency was 48kc at which time the instrument seemed to function properly. The measurement of the quench frequency was made by making use of



The Spectrometer. Fig. 1.

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the frequency spectrum of the oscillator. The periodic quenching of the oscillations produces an amplitude modulated signal which contains not only the main oscillation frequency but also frequencies which differ from it by integral multiples of the quench frequency.<sup>20</sup> A measurement of the frequency separation of these so called side band frequencies thus furnished the value of the quench frequency.

If one starts with the oscillations quenched, the growth of their peak values up to the point of steady state oscillation can be expressed by the relation  $V = V_0 e^{t/b}$ . where  $V_n$  is the voltage from which the oscillations grow and b a constant dependent upon the circuit parameters. The response of a superregenerative oscillator to a signal from an external transmitter has been studied in some detail<sup>20</sup> and is thought to occur due to the change in Vo caused by the presence of the external signal. The nature of the response depends upon whether the quenching action is interal, as in our oscillator, or is caused by the application of a periodic voltage from an external source to some point of the circuit which causes the oscillations to stop. Furthermore, if the quenching action is external, the form of the response will be dependent upon the frequency of the quench voltage. Whatever the form of the response, however, its source is still thought to be a change in the voltage level from which the periodic bursts of oscillations grow.

The response of the oscillator to the nuclear magnetic resonance and the nuclear quadrupole resonance of a sample placed in the tank coil of the oscillator still needs an explanation. It was suggested by Roberts,<sup>21</sup> who was the first to observe that a superregenerative circuit would respond to nuclear resonance, that one effect of the resonance would be a change in the value of b in the expression describing the exponential increase and decay of the oscillation. This would follow from the lowered Q of the coil due to an absorption of energy by the sample. Roberts<sup>21</sup> also suggested that in agreement with Block's<sup>22</sup> theory there should be a transient signal induced in the coil by the nuclear magnetic moments in the sample after it is subjected to the r.f. pulse of oscillation. The direct measurement of such induced voltages has been made by Hahn<sup>23</sup> for the case of nuclear resonance and by Bloom, Hahn and Herzog<sup>24</sup> for the quadrupole system. As applied to the superregenerative oscillator, this effect results in the sample acting as a signal generator. Thus the detection process should be the same as that already investigated for the response of the oscillator to an external signal.

Roberts<sup>21</sup> concluded that the latter of the two effects was the most important in the production of a nuclear resonance signal. Dean<sup>19</sup> also assumed that this was the most important process in the detection of NQR by use of a superregenerative oscillator. The argument used by Dean was

that, based upon the work of Watkins,<sup>25</sup> a pure absorption could not produce a signal with the strength and signal to noise ratio actually observed with such an oscillator. His arguments do not, apparently, apply to the oscillator which we used for our investigations. This is shown in figure No. 2 which contains the oscilloscope traces of the output of the oscillator for two different cases. (The manner in which the traces are obtained will be explained later). The first trace resulted from the pure absorption of energy from the oscillator. This was accomplished by placing a General Radio wave meter which was adjusted to the oscillation frequency close to the oscillator coil. The resulting signal certainly indicates that there is a strong response to a pure absorption by our instrument. Furthermore, the strong resemblance of this signal shape to that of the second trace which is the  $Cl^{35}$  resonance line in p-C6H4Cl<sub>2</sub> indicates that the quadrupole signal may well be determined largely by such an absorption. The observed signal shape is very similar to a mixture of the pure absorption and dispersion curves which are obtainable by use of an r.f. bridge.

Assuming that the main source of the output signal is an absorption of energy by the sample, the question still remains as to just how the output is related to this loss. Figure No. 3 shows the variation in the peak values of the r.f. oscillations and the variation of the mean grid potential as a function of time. The variation of the mean grid



(a)

(b)

Fig. 2. The response of the oscillator to (a) an absorption meter, (b) the NQR of Cl<sup>25</sup> in C<sub>6H5</sub>Cl.





potential will produce a variation in the plate voltage of the same frequency and similar shape. The output of the oscillator can then be taken to be the area of these pulses multiplied by the frequency at which they occur. There will be changes in the output corresponding to changes in the variation of the mean grid voltage.

The mean grid potential is driven negative as the oscillations increase due to a collection of electrons on the grid during the positive sweeps of the oscillations. The level of oscillations grows until the losses in the circuit prevent further growth. Meanwhile the grid potential is still decreasing due to the long time constant of the grid leak combination and starts a cumulative decrease of the oscillations. The growth of the peak values of the oscillations follows the relation  $V=V_0 e^{t/b}$ . Losses in the coil due to an absorption of energy by the sample would change the value of b and thus the rate at which the oscillations build up. This in turn would change the frequency and area of the mean grid voltage variations and thus the output.

If one assumes that the decay of the oscillations obeys the same law as the increase, then the period of the quench frequency is 2t<sub>1</sub>. The value of t<sub>1</sub> is determined by  $z_1 = b_1 g_n \frac{V_m}{V_0}$  where Vm is the maximum value of the oscillation and  $V_0$  is the voltage level from which the oscillations grow. To a first approximation the grid voltage rises as

a linear function of the time,  $V_g = ct$ . The area of the pulses of grid voltage will be  $Ag = \frac{1}{2}c(2t_1)^2$ . The output of the oscillator,  $V_1$ , will be proportional to the product of this area times the frequency of the pulses,  $1/2t_1$ ;

$$V_1 = (constant) b_1 n \frac{v_m}{V_0}$$

If we assume that any variation in  $V_0$  is negligible, the ratio of any two output voltages will be given by  $\sqrt[v]{v_1} = \frac{b_1}{b_2}$ . If none of the circuit parameters have been changed, the ratio of the b's will be proportional to the ratio of the losses due to the sample.

As a check on this idea, the maximum height of the output signal was measured for different volumes of  $C_{6}H_{5}Cl$  at the temperature of liquid nitrogen. Figure 4 shows the relation between the normalized volume and the normalized signal height. The relation is linear as is to be expected from the above discussion when one assumes the losses to be a linear function of the number of resonant nuclei. It is implicit in the discussion of some of our results that the maximum amplitude of the output signal is a linear function of the number of nuclei contributing to the resonance.

The frequency of the oscillator was varied periodically so that the condition of resonance was obtained at regular intervals of time. The resulting periodic change in the plate current due to the absorption of energy was picked up from the plate circuit by means of an audio transformer and passed through a detector circuit before being displayed on the oscillo-


Fig. 4. The dependence of the maximum signal height, S, upon the volume of the sample for  $C_{6}H_{5}Cl$ .

scope. The audio transformer passed the quench frequency without much loss; however, the time constant of the detector,  $T \sim 100 \mu$  suc, was long enough to rid the signal of the quench frequency but short enough not to effect the absorption signal appearing at a low audio frequency. The periodic appearance of the absorption signal, which allowed it to be displayed on the oscilloscope, was obtained in the following manner. The oscillator was adjusted so that its frequency was equal to the resonant frequency of the nuclei in the sample being studied. A small condenser whose capacitance could be varied periodically by the application of a small voltage was placed in parallel with the main tuning condenser of the oscillator. The small added condenser was obtained from the Navy altimeter RT-7/APN-1. A 60 cycle voltage of ~1 volt was applied to the condenser causing its capacitance to vary periodically at this rate. This in turn varied the frequency of the oscillator at this rate so that the condition of resonance was swept through periodically allowing the signal to be displayed on the oscilloscope.

It was found that by operating the heater of the 6H6 in the detector, which had its two sections in parallel, at  $\sim 3$  volts and also by operating the heater of the 675slightly under 6.3 volts the noise of the instrument could be reduced considerably without expense to the signal strength.

A measure of the sensitivity of the instrument was obtained from the fact that the smallest size sample of  $p-C_6H4Cl_2$  which gave rise to an observable signal was onetenth of a cc.

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## IV. THE PHASE TRANSITION IN p-C6H4Cl2

The observation of a phase transition in p-C6H4Cl2 has been reported by several authors. Beck and Ebbinghaus<sup>26</sup> were apparently the first to observe it. Their method was to observe a sample in a test tube as it was gradually cooled from the melt. They observed that when the sample first solidified it appeared to have intimate contact with the glass wall. During subsequent cooling the crystal became detached from the side of the test tube. The temperature at which this occurred was quite definite and was assumed to be the transition temperature of a phase change during which the sample changed volume. The transition temperature was found to be 39.5°C. Several other authors have reported observable changes in the macroscopic crystal. 27,28 The most recent of which were Danelov and Ovcienko<sup>29</sup> who observed the speed with which the interface between the two phases moved through the crystal. They concluded that the transition temperature was 30.8 °C. A different type of evidence of the phase transition was given by M. F. Vuks<sup>30</sup> when he observed a change in the Raman spectra at low and high temperatures. His determination of the transition temperature was 32 °C.

If, as it appears, the NQR absorption frequency depends upon the crystalline arrangement, there also should be a shift in it as the crystal changes phase. Such a shift has

been observed by Dean<sup>11</sup> who gives the magnitude of the shift as 27kc for Cl<sup>35</sup> at 25°C. Observations have also been made on the change in orientation of the C-Cl bond during the phase transition.<sup>31</sup> The determination of the orientation of the C-Cl bond can be made, as will be shown presently, by observing the NQR of a single crystal in the presence of a small ( $\sim$ 30 gauss) magnetic field. The results which have been obtained have not been entirely conclusive so we have attempted a further investigation along this line. We have also followed the orientation of the remainder of the molecule by means of observations made of the line width of the nuclear magnetic resonance of the hydrogen atoms situated on the sides of the benzene ring. Through a comparison of measurements in the upper phase with those in the lower phase we have attempted to determine the relation between the two phases and thus the nature of the transition itself.

Before considering the actual experimental method we will discuss the basis for the orientational determinations which have been made. We consider first the Zeeman splitting of the NQR of the chlorine nuclei and then the dipolar broadening of the nuclear magnetic reasonance of the hydrogen atoms in  $p-C_6H4Cl_2$ .

# A. Zeeman Splitting of the Nuclear

### Quadrupole Resonance

We shall consider the case of an axially symmetric field gradient and choose as our z axis the axis of symmetry. We may therefore assume that the applied magnetic field lies in the x, z phase without any loss of generality. The resulting Hamiltonian is:

(18)

$$\mathcal{H} = \mathcal{H}_{0} - \mathcal{H} + [I_{X} \text{ sin } \Theta + I_{z} \cos \Theta]$$

where  $\mathcal{H}_{0}$  is the unperturbed Hamiltonian. The matrix of the perturbation energy is not diagonal in m. The elements of interest to us are shown below. (19)

According to first order degenerate perturbation theory the correction to the  $\pm \frac{3}{2}$  levels are given directly by the corresponding diagonal elements of this matrix. To obtain the corrections of the  $\pm \frac{1}{2}$  levels we must first diagonalize the sub-matrix involving only these states. This process results in a mixing of the states  $m=\pm \frac{1}{2}$  and the resulting energy values can no longer be characterized by these states but will be called  $E_{1,2}$ . The resulting first order energy corrections for I=3/2 are thus:

$$E_{\pm \frac{3}{2}}^{(1)} = \pm \mu + \cos \Theta$$
(20)  
$$E_{\pm \frac{3}{2}}^{(1)} = \pm \mu + [4\sin^2 \Theta + \cos^2 \Theta]^{\frac{1}{2}}$$

Due to the mixing of the energy states  $m = \pm \frac{1}{2}$ , transitions are now allowed between  $(1, 2 \neq \frac{1}{2})$ .



The transition frequencies are given by  $h \mathcal{V}_{A,\Theta} = h \mathcal{V}_{Q} \pm \mathcal{M} + \mathcal{W}_{Q} \oplus \pm \mathcal{M} + \mathcal{M}_{Q} \oplus \mathcal$ 

$$\mu H \mu 2 \theta = \mu H [ 4 \sin^2 \theta + \cos^2 \theta]^{1/2}$$

$$\cos \theta = 1/\sqrt{3}$$
(22)

#### then

 $\mathcal{Y}_{c} = \mathcal{Y}_{0}$ 

The same thing will be true of  $\mathcal{J}_{\mathsf{R}}$  and  $\mathcal{J}_{\mathsf{B}}$  at  $\cos 9 = -\frac{1}{\sqrt{3}}$ . Thus if the magnetic field lies anywhere on this cone of directions about the axis of symmetry we should observe a coalescence of two of the Zeeman lines.







By use of this fact it is possible to determine the z direction in terms of coordinates fixed in the crystal. In figure No. 6  $\gamma$ ,  $\xi$ ,  $\gamma$  are the coordinates fixed in the crystal and  $\gamma' \xi'$  and  $\gamma'$  are fixed in the laboratory. The axis of the oscillator coil and crystal coincide along the 7, 7' axis. With the magnetic field fixed in the  $\gamma'$ direction the crystal is rotated about the ?,?' axis. If the z direction is such that (3 > 35) then there will be two values of X (consider only one-half the cone of directions) for which two of the Zeeman lines will coalesce. If X is set halfway between these two values the gradient should lie in the  $\gamma' \gamma'$  plane. When the magnetic field is rotated in this plane about the **S** axis there should again be two points at which the Zeeman lines coalesce and they should be  $\sim 108^{\circ}$  apart. Half-way between these two directions is the axis of the field gradient.



Fig. 6. Coordinate system for the measurement of the C-Cl direction in p-C<sub>6</sub>H<sub>4</sub>Cl<sub>2</sub>. B. Dipolar Broadening of the Nuclear Magnetic Resonance (NMR) of the Protons in p-C<sub>6</sub>H<sub>4</sub>Cl<sub>2</sub>

It was shown in the previous section how to determine the C-Cl direction in a single crystal of  $p-C_6H_4Cl_2$ . We will now indicate a method to determine the direction of the line joining the two protons on the same side of the benzene ring. If it is found that these two directions change in the same manner when the crystal undergoes the phase transition, it will be fairly certain that the molecule as a whole is undergoing the change and not just the C-Cl bond.

The line width of the protons arises from dipolar broadening due to surrounding nuclear magnetic moments. The crystal structure of  $p-C_6H_4Cl_2$  in the lower phase has been determined<sup>32</sup> and the environment of the protons based upon this work is shown in figure No. 7. There is another molecule in the unit cell which has a similar environment but a different orientation. The analysis given for the molecules shown in figure No. 7 will be equally applicable to the molecules of the other orientation. From the distances given in figure No. 7 it was thought that we should include all four protons in the group of resonant nuclei. The second moment of the line is used as a measure of the line width and is obtained from VanVleck's<sup>33</sup> treatment of the problem.



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Fig. 7. The environment of the protons in  $p-C_6H_4Cl_2$ .

VanVleck's expression for the second moment due to dipole interaction is given below in (gauss)<sup>2</sup>.

$$\left< (\Delta H)^{2} \right>_{ang} = \frac{3}{2} I (I + 1) N_{5}^{-1} g^{2} M_{6}^{2} \times \sum_{j>k} (3 \omega s^{2} \Theta_{jk} - 1)^{2} R_{jk}^{-1} (23)$$
  
+  $\frac{1}{2} N_{5}^{-1} M_{6}^{2} \sum_{j=5}^{2} I_{5} (I_{5} + 1) g_{5}^{2} (3 \omega s^{2} \Theta_{j5} - 1)^{2} R_{j5}^{-1}$ 

In the above formula g and I are the nuclear g-factor and spin for the nucleus having resonance,  $g_{i}$ ,  $I_{i}$  are the nuclear g-factors and spins of other nuclear species in the sample, rst is the length of vector connecting nuclei s and t, and  $N_{g}$  is the total number of nuclei having resonance in the sub-group considered. For our case

 $I = V_{2}$   $I_{5} = \frac{3}{2}$  $\vartheta = 5.58$   $\vartheta_{3} = \frac{55}{5}$  $N_{5} = 4$ 

We shall consider only the interactions of the protons with the nearest chlorine and the proton-proton interactions:  $H^{1}-H^{2}$ ,  $H^{2}-H^{3}$  and  $H^{3}-H^{4}$ . This gives:

$$< (\Delta H)^{2} >_{outg} = 2.45 [ (3 us^{2} \theta_{1} - 1)^{2} + .11 (3 us^{2} \theta_{2} - 1)^{2} ]$$

$$+ .008 [ (3 us^{2} \theta_{3} - 1)^{2} + (3 us^{2} \theta_{4} - 1)^{2} ]$$

Obviously the second term may be neglected with respect to the first. Within a fair degree of approximation the  $H_2-H_3$ interactions may also be neglected. This results in the line width being determined by the dipole-dipole interaction of the two protons on the same side of the benzene ring. The line width should have a minimum value at  $\Theta = (\Delta n^{-1} \frac{1}{\sqrt{3}})^{-1}$ . Thus, as long as the proton-proton and the C-Cl directions are parallel, the orientation of the magnetic field in the  $\Im, \gamma, \Upsilon$  coordinates which produce a zero splitting of Zeeman componets of the NQR of the chlorine nuclei should also produce a minimum line width of the NMR of the protons. This, of course, is based on the assumption that we can always attribute the proton line width to the dipole-dipole interaction of the two protons on the same side of the benzene ring.

#### C. The Experimental Method

<u>Crystal growth.</u> The single crystals investigated were cylinders ~10 cm long with a diameter of ~.8cm. There were no observable crystal faces to indicate crystalline structure or orientation. The crystals were grown from the melt in the following manner. A cylindrical form of the desired size was constructed from aluminum foil and glued to a piece of glass tubing which had been drawn to a very narrow tip and sealed. The form was filled with molten  $p-C_6H_4Cl_2$ (M.P. 55°C) and placed in a vertical furnace kept at approximately 75 °C. The furnace was a brass pipe two inches in diameter and one foot in length wrapped with two feet of nichrome wire and covered with asbestos insulation. The form was lowered through the furnace by means of a clock mechanism at a rate of 0.5cm per hour into a water bath immediately below the furnace. In this method, as the container is lowered from the furnace, the tip cools first and with reasonable luck a single seed crystal is formed in the very narrow tip. If the container is lowered slowly enough, all subsequent crystallization takes place on the faces of this seed and the result is that the entire sample is finally solidified into a single crystal. The aluminum foil can easily be removed leaving the crystal free from any constraining walls.

The samples were first grown in the same manner but with the form constructed entirely out of glass tubing. Since the crystals were quite fragile the glass could not be removed and the samples had to be investigated while still enclosed in this form. There was, therefore, a possibility of the rigid walls of the container exerting forces upon the crystal since there might be a change in volume during the phase transition. The data presented in this thesis was obtained from the free samples only.

<u>The phase transition.</u> It was found that most of the samples grown by the method indicated above were in the low temperature phase, the  $\propto$  phase. At least they were in the  $\propto$  phase after standing at room temperature ( $\sim 25$  °C) for a day. The phase that the crystal was in was determined originally by a comparison of the transition frequency with those given by Dean<sup>19</sup> for the two phases. Later it was possible to determine the phase from the nature of the Zeeman pattern.

Consistent results were obtained when the phase transition  $\propto \rightarrow \beta$  was induced by the following method. The crystal was warmed at ~  $30^{\circ}$ C for one-half hour in a water bath. Then the tip of the crystal was placed in water at ~  $45^{\circ}$ C until the  $\beta$  phase was observed to begin its growth. This was noted by a somewhat cloudy appearance of the  $\beta$  phase and by a sharply defined interface. The crystal was then placed in a water bath at  $\sim 34^{\circ}$ C while the (3 phase continued to grow along the crystal. If the (5 phase was allowed to grow completely throughout the crystal and if the crystal was then kept at 35°C for ten to fifteen minutes. the crystal seemed to be quite stable and would remain in the  ${f eta}$  phase for a day or two when the crystal was kept at room temperature. If, on the other hand, the  $\beta$  phase was only allowed to grow along a portion of the crystal, the  $\prec$ phase would grow back as soon as the crystal was placed at room temperature.

<u>Measurements of the molecular orientations before and</u> <u>after the phase transitions.</u> In order to make the measurements previously discussed we had to associate a fixed coordinate system with the crystal. The 7 axis was taken to be the axis of the crystal. The 3 and 7 axes were determined by clamping the crystal in a brass chuck which was attached to a disc graduated in degrees, the disc being perpendicular to the axis of the crystal. The orientation of the C-Cl direction with respect to this coordinate system

varied from crystal to crystal. We were interested, however, only in the change in orientation of this bond as the crystal underwent the phase transition. The crystal was inserted in the tank coil of the oscillator. The axes of the coil and the crystal, the  $\mathfrak{P}'$  and  $\mathfrak{P}$  axes, coincided and lay in the horizontal plane. The source of the magnetic field was a set of Helmholtz coils designed so that the magnetic field could be rotated about in the horizontal plane. The  $\mathfrak{P}'$  axis was thus taken to lie in the horizontal plane perpendicular to the  $\mathfrak{P}$ ,  $\mathfrak{P}'$  axes. With the coordinate systems thus fixed the measurements described previously were carried out to determine the C-Cl direction. Figure 8 shows the oscillator with the Helmoltz coils in place.

Once the C-Cl direction was determined it was possible to transfer the crystal to the nuclear magnetic resonance appartus with the  $\S$ ,  $\gamma$ ,  $\hat{\gamma}$  axes still fixed in the crystal. The apparatus used for this measurement is that described by Jain.<sup>34</sup> The measurements made did not determine the proton-proton direction since a rotation of the magnetic field was not possible. With the magnetic field perpendicular to the axis of the crystal, the crystal was rotated about its axis and the direction of the magnetic field in the \$  $\Upsilon$   $\rash$  coordinates was recorded for the orientation which produced minimum line widths. These orientations were compared with similar measurements for the zero splitting of the Zeeman componets of the NQR. The phase of the crystal was changed and the process repeated.



Fig. 8. The spectrometer with the Helmholtz coils in position.

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#### D. Discussion of the Results

The results of the measurements to determine the C-Cl direction in both phases of several crystals are given in Table I. Two directions were found in the  $\prec$  phase and are labeled by the subscripts "1" and "2". Only one direction was found in the  $\beta$  phase and is designated by the subscript "3". The angle  $\omega_{13}$  is the angle between the  $i^{th}$  and  $j^{th}$ axes. Figure 9 shows typical traces of the Zeeman patterns of a single crystal of  $p-C_6H_4Cl_2$ . The top trace is the pure quadrupole resonance. The middle trace shows two Zeeman lines from each molecule and the bottom trace shows the two central lines after they have coalesced. The crystal structure of p-C6H4Cl2 has been determined by Croatto, Bezzi and Bua<sup>32</sup> for the low temperature phase. Their data shows that there are two molecules to a unit cell and that the C-Cl directions of the two molecules are separated by 74.2. The average value of w<sub>12</sub> for our results is 73.9 which can be considered to be in agreement with the x-ray work. Lutz<sup>31</sup> has obtained a value of w12 of 76° 2° from the Zeeman splitting of the quadrupole resonance signal.

Table II contains the directions of the magnetic field in the  $\Im$  plane which resulted in a minimum width of the proton resonance and also those which resulted in zero splitting of the Zeeman componets of the chlorine NQR. Data are given for two crystals in both the  $\prec$  and  $\bigcirc$  phases. Although there is a very large shift in these directions

TABLE I.

THE DIRECTIONS OF THE C-CL BOND IN THE  $\sim$  AND  $\beta$  PHASES OF P-C<sub>6</sub>H<sub>4</sub>CL<sub>2</sub>

Crystal	9	Ś	5 0	วิ	( ) ( )	່ຍ	Ś	W, 3	رب ۲
Ч	86.0	162.5	35.0	23.1	74.5	78.0	273.5	88.2	46.5
8	44.5	165.5	0*617	55.0	73.6	0"911	202.0	78.8	121.2
ſ	81.5	172.5	0*†6	100.5	72.9	51.5	240.0	52.0	0.011
4	138.0	37.0	2.611	312.0	75.9	92.5	3.0	52.3	62.2
Ś	112.5	14.5	84.0	305.5	7.67	66.5	350.5	51.6	47.0
ଡେ	120.0	217.0	53.5	180.0	75.0	102.0	244.5	<b>0°</b> 69	59.0
م	135.0	172.0	87.5	236.5	74.1	99.5 137.0	142.5	43.6 17.8	94 <b>.</b> 4 91.8
2	0•62	32.0	56.5	215.5	75.5	<b>51.0</b> 87.5	117.0 257.5	79.3 133.2	6.3 131.9
8a	113.5	34.5	131.0	104.5	24.6	124.0	256.0	82.0	78.9
م	113.5	14.5	131.0	104.5	74.6	0.611	239.0	63.4	76.7
<b>9</b> a	0*66	316.5	146.0	30.0	71.3	35.0	300.0	65.3	132.8
Ą	0*66	316.5	146.0	30.0	71.3	0.67	324.0	81.5	66 <b>.</b> 8



Fig. 9. The (a) pure quadrupole signal and (b), (c) typical Zeeman splittings of it for Cl<sup>35</sup> in a single crystal of p-C<sub>6</sub>H<sub>4</sub>Cl<sub>2</sub>.



Fig. 10. The (a) maximum and (b) minimum line widths of the proton resonance in a single crystal of  $p-C_6H_{4}Cl_{2^{\bullet}}$ .

(a)

(b)

## TABLE II

COMPARISON OF POINTS OF ZERO SPLITTING (NQR) AND POINTS OF MINIMUM LINE WIDTH (NMR) FOR  $p-C_6H_4Cl_2$  WITH  $\varphi = 90^\circ$ 

Crystal	$\propto$ for Minimum Line Width	∝ for Zero Splitting
1. $\propto$ phase $\beta$ phase	164, 250, 257° 134, 205°	156 <sup>°</sup> , 247 <sup>°</sup> , 268 <sup>°</sup> 131 <sup>°</sup> , 204 <sup>°</sup>
2. ~ phase (3 phase	60°, 147° 5°, 103°	65 <sup>°</sup> , 144 <sup>°</sup> 6°, 106 <sup>°</sup>

during the phase transitions, the proton resonance and the quadrupole resonance experiments give the same data, for a given phase, within the accuracy to which the minimum line width could be determined ( $\sim 5^{\circ}$ ). Since it was found that there are two directions of the C-Cl bond in the  $\prec$  phase. there should be four points for each experiment ( $0 \leq \propto \langle | \vartheta \rangle$ ). A more detailed study of the Zeeman pattern showed that the fewer points resulted from the accidental superposition of two points. The comparison of these results can be interpreted to mean that during the phase transition there is a reorientation of the molecule as a whole and that the protonproton and C-Cl directions remain parallel. Figure 10 is a photograph of a typical oscilloscope trace of the maximum and minimum line width of the proton resonance. At its widest point the line is seen to be a badly smeared out doublet. These conclusions have been substantiated by a recent x-ray analysis of the  $\beta$  phase by Houty and Clastre.<sup>35</sup> They found that the  $\beta$  phase was a triclinic crystal with one molecule per unit cell and that the structure of the molecule was essentially unchanged from that in the ~ phase. Thus we can say quite definitely that during the phase transsition there is a reorientation of at least part of the molecules and that their reorientation is not accompanied by a distortion of the molecule.

We can increase our knowledge of the nature of the transition by determining the magnitude of the reorientation.

This should be obtainable from the values of  $W_{13}$  and  $W_{23}$ for the various crystals investigated. A comparison of these values, however, fails to show much regularity. The reorientation in crystal #1 and one part of crystal 6b, in which the upper phase was allowed to grow from both ends of the crystal, agree to within 3°. This is also true of crystal #5 and part of crystal #7 although the reorientation is there crystals differ from that in #1 and #6. The rest of the fourteen examples show completely different reorientation. This may mean that there are very many different but definite ways in which the crystal may change from the  $\propto$ to the Q structure. It may also mean that there is no definite crystallographic relationship between the two phases and that the two cases mentioned above are mere coincidences.

This lack of a very regular relationship between the two phases is further illustrated by the data obtained for the last six crystals. The data was taken for the sixth crystal in both phases and listed under 6a, the  $\bigotimes$  phase having grown throughout the crystal. The crystal was returned to the  $\propto$  phase where measurements listed under 6b were made. The orientation of the axes had changed. Perhaps a more striking result was obtained when the crystal was again raised to the  $\propto$  phase. This was done by starting the growth of the upper phase from both ends of the crystal. The result was that each end of the crystal had a single and well defined direction of the C-Cl bond but the two directions Same race

were different from one another. This same experiment was repeated for the seventh crystal with similar results. For the last two crystals the  $\mathfrak{G}$  phase was not allowed to grow completely through the crystal when measurements were taken on the G phase. As the  $\sim$  phase grew back, the C-Cl directions had their original orientations. However, when the crystals were again raised to the  $\beta$  phase the orientation of the single axis was different from the first time. In a further experiment we submerged crystals in the  $\infty$  phase in a temperature bath of ~ 40  $^{\circ}$ C at which time the  $\beta$  phase could be seen to begin its growth at a number of points in the crystals. Once the crystals were entirely in the  $\beta$  phase the Zeeman pattern of their quadrupole absorption signal was observed. It was found that the magnetic field either eliminated any observable signal or resulted in a Zeeman spectrum too complicated and weak to be analized in detail but at least indicative of several different orientations of the C-Cl direction. This last experiment can be explained by assuming that many of the centers of growth of the  $m{eta}$  phase resulted in little pieces of crystal with different orientations. That is, we can consider this experiment to be merely an extension of the case in which we allowed the (3) phase to start its growth from the two ends of crystals #6 and #7. These results seem to substantiate the views obtained from a comparison of the values of  $W_{13}$  and  $W_{23}$  that the crystallographic reorientation during the phase transition may take place in either a very large or an infinite number of ways.

There was one characteristic of the transition which appeared to be true from a visual inspection of the crystal as well as from a check of the resonant frequencies of various parts of the crystals during the time they were changing phase. The new phase grows from its source in such a manner that at no time is the entire crystal in a disordered state half way between the two phases. Instead, there is one section which has not changed its structure at all and another which has been completely changed. This was certainly substantiated by the fact that we were able to obtain normal signals, as well as Zeeman patterns, from each section of the crystal during the time that the interface between the two phases was moving along the crystal. Even the slightest irregularities in the crystal structure is sufficient to effect the signal greatly.

Another characteristic of the phase transition which appears to be definite is that, although there are many possible orientations for the new phase to take, once a center of the new phase has begun its growth all of the old phase, which is transformed as a result of the growth of this center, will undergo the same reorientation. The fact that the samples were still single crystals after they had undergone the transition requires that this be true. The results of crystal #6 and #7 further illustrates this view since, although the two sources of growth of the (3 produced sections of the crystal with different orientations, each section was a single well ordered crystal. These properties of the transition suggested a further experiment to decide if there was any relationship between the crystal orientations of the two phases. If there is no relation, then presumably the molecules of the old phase can rotate through any angle to take up the orientation of the new phase and will do so regardless of their previous orientation. The orientation of the new phase being determined by some undesignated parameters.

If the above idea is correct, it should be possible to start with a polycrystalline sample and produce a single crystal by merely causing the sample to undergo the phase transition in such a manner that it starts from only one source. The term polycrystalline would have to mean a continuous sample with different sections having various orientations. A sample composed of separate crystals would require the phase change to start anew in each crystal and thus would not produce the desired effect. A small ( $\sim 30$ gauss) magnetic field was applied to the sample to determine if it was a single crystal or polycrystalline. A single crystal will give a well defined Zeeman pattern. Each section of the polycrystal will also give a Zeeman pattern but since they have different orientations the separation of the componets will be different for each section. If the sections of the crystal with a given orientation are small enough, the application of the magnetic field "washes out" the signal. Typical results are shown in Figures 11 and 12. The pure

quadrupole resonances before and after the phase transition are shown in the first and third traces respectively. The resonances in the presence of a 30 gauss magnetic field before and after the phase transition are shown in the second and fourth traces respectively. The Zeeman lines shown in the fourth traces are taken to indicate that the sample is now a single crystal or at least contains a large section which now has a single orientation. In Figure 11 the sample was originally in the  $\sim$  phase and in Figure 12 the sample was originally in the  $\Diamond$  phase. It thus appears that either the  $\prec \rightarrow (c \ or \ the \ (b \rightarrow \prec \ transition \ can \ produce \ a \ single \ crystal \ from a \ polycrystalline \ sample. It would thus$ appear that there is no fixed relationship between the orientations of the molecules in the two phases.



Fig. 11.



Fig. 12.

### V. QUADRUPOLE RESONANCE OF IMPURE SAMPLES

The  $Cl^{35}$  resonance was observed at liquid nitrogen temperature in samples of  $C_{6}H_{5}Cl$  which contained controlled amounts of impurities. The maximum height of the resonance signal was greatly reduced by the addition of even  $10^{-3}$  molar fraction of certain impurities.

If we assume that the effect on the signal arises from strains in the crystal due to a difference in size of the impurity and resonant molecules, we can make a rough calculation of the expected change in the signal due to the presence of the impurity. According to Love<sup>36</sup>, the strain around a spherical inclusion in an elastic medium will fall off as the reciprical of the cube of the distance from the inclusion. Although such a model is only a crude approximation to our experimental situation it should at least allow us to determine the nature of the effects.

If the shift in frequency is taken to be proportional to the strain, then the resonant frequency of a nucleus at a distance r from the impurity molecule will be  $\mathcal{J} = \mathcal{J}_0 + \frac{k}{R^3}$ . We shall first consider the resulting frequency spectrum which would be expected in such a situation from an infinitely sharp line. The number of molecules lying at a distance between r and r+ dr is given by:

$$ON = \rho 4 \pi n^2 \partial n \qquad (25)$$

where e is the density of molecules. We can express dr in terms of  $\Im$  through the relation for the shift in frequency due to the strain. This gives:

$$\partial \mathbf{R} = -\frac{h \, \partial \mathbf{r}}{3(\mathbf{r} - \mathbf{r}_0)^2 n^2} \tag{26}$$

Substitution of this expression in (25) yields

$$\partial N = -\frac{4\pi}{3} \frac{\rho_{K}}{(\nu - \nu_{0})^{2}} \qquad (27)$$

$$\partial N = -\frac{K}{(\nu - \nu_{0})^{2}} \frac{\partial \nu}{\partial \nu}$$

Since for k > 0 the  $\vartheta \lor$  corresponds to a decrease in frequency when  $\vartheta N$  represents an increase in the number of molecules, the ratio is negative so that  $-\frac{\partial N}{\partial \checkmark}$  is positive. This ratio represents the number of molecules in a given frequency range which is merely the frequency distribution which we desire

$$\mathcal{N}(\mathcal{V}-\mathcal{V}_{o}) = \frac{\kappa}{(\mathcal{V}-\mathcal{V}_{o})^{2}}$$
(28)

This calculation was based upon the assumption that the effect of the impurity was strictly radial. We can consider the case of a simple angular dependence and see if there is any effect upon the nature of the results.

The above relation for the dependence of the strain is based upon the fact that the displacement of a molecule at a distance r from the impurity is proportional to  $1/r^2$ . If we now assume that the only strains which will be effective are those which arise from displacements in the Z direction, the displacements effecting the signal will be given by:

$$U_{z} = \frac{C z}{(X^{2} + y^{2} + z^{2})^{3/2}}$$
(29)

The corresponding strain in the Z direction will be given by:

$$\frac{\partial U_3}{\partial z} = \frac{C}{R^3} - \frac{3CZ^2}{R^5} = C\left(\frac{1-3\omega^2 \Theta}{R^3}\right)$$
(30)

If now the frequency shift is taken to be proportional to this strain we have:

$$\mathcal{V} = \mathcal{V}_0 + \mathcal{R}\left(\frac{1-3\omega s^2 \theta}{\Lambda^3}\right) \tag{31}$$

In this case the shift in frequency will not be all in the same direction. If we consider R>0 then:

 $(r - v_0) < 0$  for  $0 < \theta < \theta_0$   $\pi - \theta_0 < \Theta < \pi$   $\theta_0 = c_0 c_0^{-1} \frac{1}{\sqrt{3}}$ For all other values of  $\Theta$   $(v - v_0) > 0$ .

For  $0 \lt \ominus \lt - \Theta_0$  the volume included by the surface of constant frequency  $\mathcal{V} = \mathcal{V}_0 - \mathcal{C}_1$  is given by:

$$V_{1} = \int_{0}^{2\pi} \int_{0}^{T-\frac{R}{c}(\frac{1-3w^{2}}{c})} \int_{0}^{y_{3}} \int_{0}^{0} \pi^{2} \sin \theta \, \partial \theta \, dx \, du \quad (32)$$
$$= \frac{4\pi}{9 \sqrt{3}} \frac{R}{c}$$
If we take into account the remaining values of  $\theta$ , the total volume inside the surface  $\mathcal{V}_{\tau} \mathcal{V}_{0} - \mathcal{C}_{\tau}$  is given by:

$$\mathbf{V}_{*} = \frac{\Im \pi}{\Im J_{*}^{*}} \frac{R}{C}$$
(34)

with a similar expression for the volume inside the surface corresponding to the positive shift. The number of molecules between the two surfaces corresponding to  $\mathcal{V}_1 = \mathcal{V}_0 - \mathcal{C}_1$ and  $\mathcal{V}_2 = \mathcal{V}_0 - \mathcal{C}_2$  is given by:

$$\Delta N = \varrho \left( V_{\perp} - V_{i} \right)$$

$$\Delta N = \Delta V K \left( J_{i} - J_{0} \right) \left( J_{i} - J_{0} + \Delta U \right)$$
(35)

If we allow  $\Delta U$  to become small, the ratio  $\Delta N / \Delta U \rightarrow \frac{\partial N}{\partial V}$ or the frequency distribution which we desire:

$$\mathcal{N}(\mathcal{V}-\mathcal{V}_0) = \left(\frac{\mathcal{K}}{(\mathcal{V}-\mathcal{V}_0)}\right)^{-1}$$
(36)

This is the same form as for the completely radial dependence except that the frequency shift is now allowed in both directions. The effect of a strictly radial dependence would predict a shift in the average frequency of the resonance. Dean<sup>11</sup> has reported a very slight  $(6 \pm 3 \text{kc})$  shift in p-C<sub>6</sub>H<sub>4</sub>Cl<sub>2</sub> when one-tenth molar fraction of p-C<sub>6</sub>H<sub>4</sub>Br<sub>2</sub> was added. On the other hand we found no shift in the resonant frequency for the impure samples studied. Although the angular dependence chosen here may not be the correct one, it at least shows that an unshifted line is possible when some allowance is made for the anisotropy actually present in the crystal.

The fact that we observe resonances at all in the impure samples indicates that there is at least a portion of the crystal in which the frequency is not shifted greatly. For low concentrations we can surround each impurity by a sphere of radius R such that  $\frac{K}{R^3} = (V_1 - V_0) = \alpha \ll W$ , where W is the width of the original line. Since the frequency shifts in the remaining molecules lie well within the line width, we can neglect their actual dependence and assume that they give rise to an undeviated line. The total volume of the sample which is contained in the spheres of radius  $(K_{\infty})^{V_3}$  about each impurity is:

$$V_{i} = N_{i} \frac{k_{i}}{3} \pi \frac{k_{i}}{\alpha}$$

where  $N_1$  is the number of the impurity molecules. The volume outside of these regions,  $V_2$ , will be given by:

## $\mathcal{V}_{2} = V_{0} - V_{1} = N_{0} \mathcal{V}_{m} - V_{1}$

where  $N_0$  is the total number of molecules and  $V_m$  is their molar volume. The fractional value of  $V_1$  is given by:

$$\Theta = \frac{V_1}{V_0} = \frac{4}{3} \frac{\pi K}{\alpha v_m}$$
(38)

where c is the concentration of the impurity. The fraction lying outside of these volumes is given by 1-9.

If we arbitrarily apply this argument to an infinitely sharp line of height A it will result in the following shape.



Fig. 13. Broadening of an infinitely sharp line

If we apply such a broadening to a rectangular line of width 2w and height 2A, the function  $f_0$  will result in a portion of the line shape:

$$F_0 = 2 \Pi (1 - \Theta) - \omega < v < \omega$$
<sup>(39)</sup>

The contribution of f<sub>1</sub> will result in:

$$F_{1} = H\Theta \alpha \int_{-\omega}^{\nu-\alpha} \frac{\partial \nu'}{(\nu-\nu')^{2}} ; H\Theta \alpha \int_{-\omega}^{\omega} \frac{\partial \nu'}{(\nu-\nu')^{2}} (40)$$

$$-\omega + \alpha < \nu < \omega + \alpha \qquad \nu > \omega + \alpha$$

$$= H\Theta \alpha \left[ \frac{1}{\alpha} - \frac{1}{\nu_{+}\omega} \right] ; H\Theta \alpha \left[ \frac{2\omega}{\nu_{-}\omega} \right]$$





Figure 14 shows the approximate line shapes for  $\Theta = 0, \frac{1}{2}, \frac{1}{2}$ .

For 
$$V > w + \alpha$$
 or  $V < -w - \alpha$   
 $P(v) = A \theta \alpha \left[ \frac{2w}{v^2 - w} \right]$ 

$$P(v) = 2 H(1-0) + 2 H \Theta \alpha \left[\frac{1}{\alpha} + \frac{w}{v^2 - w^2}\right]$$
 (42)

given by:

Within the range  $- w + \alpha \zeta \mathcal{J} \zeta w - \alpha$  the line shape is

$$F_{1} = H \Theta \alpha \int_{\nu_{1}\alpha}^{\omega} \frac{\partial \nu'}{(\nu' - \nu)^{2}}; \quad H \Theta \alpha \int_{-\omega}^{\omega} \frac{\partial \nu'}{(\nu' - \nu)^{2}} \qquad (41)$$

$$-\omega - \alpha \langle \nu \langle \omega - \alpha \rangle \quad \nu \langle - \omega - \alpha \rangle$$

$$- H \Theta \alpha \int_{-\omega}^{\omega} \frac{d}{d} + \frac{1}{\nu - \omega} \int_{-\omega}^{\omega} \frac{d$$

The contribution of f2 will result in:

The effect of increasing the concentration of the impurity is thus to take a certain amount of absorption outside of the original line width without appreciably broadening the line as long as the concentration is low since the line width is determined in this case by the undeviated central portion.

Our results show very little broadening to the line for low concentrations although the intensity as measured by the maximum height of the signal shows a definite decrease. This can be seen in Figure 15 which shows the signal in  $C_{6H5}Cl$ for increasing concentrations of p-C\_6H4Cl<sub>2</sub>. The first trace is pure C\_6H5Cl; the second and third are the signals for . OOl7 mole fraction of impurity; the fourth and fifth are signals for .0035 mole fraction of impurity.

The fact that the intensity does decrease without great Droadening permits us to apply the following, somewhat crude Dhenomenological argument which will aid us in discussing the relative effectiveness of the various impurities. Con-Sider the impurity molecules to be distributed at random in the crystal lattice. Also let each impurity molecule so Sifect the crystal that it is surrounded by a sphere of radius R such that molecules of the sample which lie within this volume do not contribute to the resonance and those Which lie outside of the volume are unaffected by the im-Durity molecule. The probability that a given lattice position is occupied by an impurity molecule is c, where c is



Fig. 15. The Cl<sup>35</sup> quadrupole resonance in C6<sup>H5</sup>Cl with (a) .0000, (b) .0017 and (c) .0035 mole fraction of p-C6<sup>H4</sup>Cl<sub>2</sub>.



the molar fraction of the impurity. The probability that a lattice site is occupied by a resonant type molecule is given  $by(1-c)^{N}$ . This molecule will contribute to the resonance only if every site lying within a sphere of radius R surrounding it is occupied by a resonant type molecule. If there are N sites in this volume, the probability that a molecule will contribute to the resonance is  $(1 - c)^{N}$  and the signal strength, S will be given by:

$$S = S_0 (1 - c)^N$$
 (43)

where  $S_0$  is the signal strength for c = 0. Taking the logarithm of both sides gives:

$$\mathbf{S}_{\mathbf{N}} = \mathbf{N} \, \mathbf{S}_{\mathbf{N}} = \mathbf{N} \, \mathbf{S}_{\mathbf{N}} \left( 1 - \mathbf{C} \right) \tag{44}$$

For small c the logarithm on the right side may be expanded in terms of c so that:

$$\mathcal{P}_{\mathbf{N}} \approx \mathcal{P}_{\mathbf{S}_{0}} = -Nc$$
 (45)

Figures 16 and 17 are plots of  $\int s^{S/s}$ ,  $w_{1} - C$  for various impurities in C6H5Cl. At least until  $S \cong .4S_{0}$  the linear relation is quite good and the negative slope of the lines should give the number of molecules made ineffective by the Dresence of a given impurity. The deviation from a linear relation at higher concentrations may arise from the fact that as more impurity atoms are added their spheres of influence may begin to overlap, thus making their overall effectiveness diminish.

11.1.5







Fig. 17. A logarithmic plot of the maximum signal height of the  $Cl^{55}$  quadrupole signal in  $C_{6H_5}Cl$  as a function of the concentration of various impurities.

The signal strength was taken to be the ratio of the maximum signal height to noise height of the signal trace appearing on the oscilloscope. In order to obtain a permanent record as well as more accurate measurements, the traces were photographed with a Land camera and the measurements made on the photographs. Photographs of the signal from Pure samples were taken regularly in order to take into account any possible change in the operation of the oscillator over the period during which data was taken.

The purity of the C6H5Cl was Eastman Grade which was further purified by the method suggested by Vogel.<sup>37</sup> The liquid was washed with concentrated sulfuric acid until the acid came clear. It was then washed with water, sodium hydroxide and water. Finally it was dried over calcium chloride for twenty-four hours.

The impurities were added to the sample at room temperature and the sample agitated to insure a good mixture. The sample holder was a test tube with an index scratch on it to insure that the same amount of sample was used for each investigation. About 1 cc of liquid sample was used. The test tube was held in the vertical tank coil by means of a Cork washer so that the entire volume of the sample was contained within the coil. The sample and coil were immersed in a bath of liquid nitrogen until the signal stabalized. It was found that there was no further increase in the signal size or shift in frequency after three minutes. To

insure that the temperature of the sample had come to equilibrium the samples were allowed to cool from four to five minutes before the signal was recorded. The values given in Figures 16 and 17 represent the average of three to four readings at each point.

Work of this same general nature has been reported by Monfils and Grosjean.<sup>38</sup> They observed the effect of impurities on the  $Cl^{35}$  resonance in p-C<sub>6</sub>H<sub>4</sub>Cl<sub>2</sub>. The impurity molecules were of two types; those which were taken to have the same size as p-C<sub>6</sub>H<sub>4</sub>Cl<sub>2</sub> but a different electric dipole moment, and those which were taken to have the same electric dipole moment but differed in size. Their results are shown in Table III where  $V_{\pi}$  is equivalent to the N of our dis-

## TABLE III

RESULTS OF MONFILS AND GROSJEAN FOR VARIOUS IMPURITIES IN p-C6H4Cl2

_				
-	Impurity Molecule	Vr.	$(\mu_{c-q} - \mu_{c-x})^{2}(\chi   0^{36})$	( vx - va)(x 1024)
p	-chlorobromobenzene	87	0	2.1
p	- dibromobenzene	162	0	4.2
p	- bromoiodobenzene	330	0	7.8
p	- chlorophenol	135	2.59	0
p	- chlorotoluene	204	4.29	0
p /	- chloroaniline	435	9.04	0

cussion. The volume differences of the first three molecules may be obtained by associating spherical volumes with each of the Cl, Br and I atoms whose radii are equal to their respective covalent radii. The difference in volume of the molecules is then taken to be the difference in the volumes of the two atoms attached to the benzene ring. The effectiveness of the three impurities, as measured by the value of  $U_{\rm k}$ , appears to be a linear function of the difference in volume between the impurity molecule and p-C<sub>6</sub>H<sub>4</sub>Cl<sub>2</sub>. This is shown in Figure 18.

For the last three samples the size of the molecules were assumed to be equal to that of  $p-C_6H_4Cl_2$  presumably because the covalent separation of the atoms in the radicals substituted for the Cl atom is equal to the covalent radius of Cl. The value of  $\sigma_{\pi}$  for these three compounds shows a linear dependence upon the square of the dipole moment difference listed in Table III. It is not too clear, however, just how these values are obtained. For p - chlorotoluene, the moments of chlorobenzene and toluene were apparently added. For p-chloroaniline and p-chlorophenol, however, it was not possible to obtain the values given by Monfils and  $Grosjean^{38}$  by this method. If instead, one considers the total dipole moment of the molecules, the change should be equal to the value of the dipole moments of the impurities since the moment of p-C6H4Cl<sub>2</sub> is zero. For p-chlorotoluene





and p-chloroaniline the results are  $\Delta \mu = 1.93 \times 10^{-18}$  and  $\Delta \mu = 2.93 \times 10^{-18}$  respectively, which are in fair agreement with those listed by the authors. In the case of p-chlorophenol, however, the value of  $\Delta \mu = 2.27 \times 10^{-18}$  would certainly destroy any linear dependence on  $(\Delta \mu)^{1}$ .

The choice of the covalent radii and separation as a measure of the size of the radicals attached to the benzene ring seems strange since we are interested in their effect on molecules to which they are connected by weak van der Waals forces. If one treats the first three impurities in the same manner as before but uses instead the van der Waals radii, one still obtains a linear relation between change in volume and effectiveness. Their volumes are plotted in Figure 18 along with values calculated using the covalent radii.

When one considers the last three impurity molecules in the same manner, it becomes doubtful if one can consider them to be the same size as  $p-C_6H_4Cl_2$ . The van der Waals radii of all the radicals is not known, however, for the  $CH_3$  group it is 2.0 Ű as compared to 1.80 Ű for the chlorine atom. From this point of view it does not seem likely that one could obtain much information about the effect of the electric dipole moment from these impurities since at least one of them presents a change in volume also.

There are some interesting comparisons which can be made, however, between the results of Monfils and Grosjean<sup>38</sup>

and our results. The value of N for p-chlorophenol in  $p-C_6H_4Cl_2$  is the same as that for phenol in  $C_6H_5Cl_$ . There is similar agreement between the values of N for p-ClC6H4NH2 and  $p-ClC_6H_4CH_3$  in  $p-C_6H_4Cl_2$  and the respective values of N for C6H5NH2 and C6H5CH3 in C6H5Cl. The fact that impurity molecules which differ from the resonant molecule by similar structural changes have the same effectiveness is an indication that the impurity molecules in general are distributed throughout the crystal as single molecules. It is possible that they could be collected at imperfections or that groups of them could be merely caught in the crystal as it solidifies and still be quite effective. However, that two different binary mixtures would produce the same grouping or an equivalent one as far as the resonance is concerned does not seem too likely. It is even more unlikely that there should be three examples of this as we have here.

There is further support for the view that the effective impurities actually form solid solutions with the samples. To be effective in destroying the signal they certainly must be contained within the crystal. Furthermore they all possess the characteristic of having a molecular structure similar to that of the sample. While this is neither a necessary or sufficient condition for the formation of a solid solution it is fairly common. Furthermore it has been found that impurities which differ greatly in molecular structure are quite ineffective. For instance, toluene which has a value of N = 200 in C<sub>6</sub>H<sub>5</sub>Cl had a value of

 $N \approx 5$  when used in CH<sub>2</sub>Cl<sub>2</sub>. Although many impurities were added to CH<sub>2</sub>Cl<sub>2</sub> none had an N>40 except CH<sub>2</sub>I<sub>2</sub> which was the only impurity tried with a similar structure and whose N = 220. The relative effects of p, m and o-C6H4Cl<sub>2</sub> are also examples of this. It appears that m-C6H4Cl<sub>2</sub> is more effective below .001 mole fraction than for greater concentrations. This may be explained as being the limit of the solubility of the impurity in the sample. Such an explanation has been given by Monfils and Grosjean<sup>38</sup> for similar behavior of p-ClC6H4OH and p-ClC6H4NH<sub>2</sub> in p-C6H4Cl<sub>2</sub>.

Figures 16 and 17 show the plots of  $\ln \frac{1}{2}$ , versus-c for various impurities used in C6H5Cl from which the value of N was determined. Figure 19 shows a plot of the values of N versus the difference in the volume of the impurity and resonant molecule. The volume difference was calculated in the same manner as indicated previously by making use of the van der Waals radii of the substituted group.

One group of molecules,  $C_{6H_6}$ ,  $p-C_{6H_4}Br_2$ ,  $p-C_{6H_4}Cl_2$  and  $p-ClC_{6H_4}Br$  all have the same dipole moment,  $A_{H=0}$ , and thus differ from that of  $C_{6H_5}Cl$  by the same amount,  $\Delta_{H=1}N\times10^{-18}$ . Based upon the conclusion of Monfils and Grosjean<sup>38</sup> one would expect that the plot of N<sub>1</sub> versus  $\Delta V$  would be a straight line as it is, but that its intercept at  $\Delta^{V=0}$  would be ~ 150, whereas it actually appears to be ~ 0. This would seem to indicate that the effectiveness of the impurity is very low when there is no volume change, regardless of the



difference in dipole moment. This is further substantiated by the fact that the results for C6H5Br and C6H5I, both of which possess the same dipole moment as C6H5Cl ( $\mu$ =1.70A10<sup>18</sup>), lie on the line defined by the above results.

Our results indicate that in agreement with Monfils and Grosjean<sup>38</sup> there is a linear dependence between the effectiveness of the impurity in reducing the signal strength and the difference in volume of the impurity and resonant molecules. We find, however, that a difference in the dipole moment of the two molecules seems to have little if any bearing upon the effectiveness of the impurity.

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