NUCLEAR QUADRUPOLE RESONANCE STUDY OF CHARGE-TRANSFER COMPLEXES

Thests for the Degree of Ph. D. MICHIGAN STATE UNIVERSITY James Austin Ryan 1967



This is to certify that the

thesis entitled

Nuclear Quadrupole Resonance Study of Charge-Transfer Complexes

presented by

James Austin Ryan

has been accepted towards fulfillment of the requirements for

Ph.D. degree in Chemistry

Major professor

Date____December 16, 1966

O-169

ABSTRACT

NUCLEAR QUADRUPOLE RESONANCE STUDY OF CHARGE-TRANSFER COMPLEXES

by James Austin Ryan

A nuclear quadrupole resonance spectrometer of the Dean type has been constructed both for frequency and field modulation and for display of the signal either on an oscilloscope screen or, by use of a lock-in amplifier, on a recorder.

New chlorine quadrupole resonances have been found in the following charge-transfer complexes, $SbCl_5 \cdot POCl_3$, $FeCl_3 \cdot POCl_3$, $TiCl_4 \cdot 2POCl_3$ and $(TiCl_4 \cdot POCl_3)_2$. These resonances were observed both at liquid nitrogen temperature and at room temperature, although in all cases the resonances due to the chlorine nuclei of $POCl_3$ in the complex molecule disappear below room temperature. A study of the temperature dependence of the resonance due to the "axial" chlorines of the $SbCl_5$ part of $SbCl_5 \cdot POCl_3$ has been made. This study indicates a possible phase transition between $77^{\circ}K$ and $165^{\circ}K$.

An estimate of the contribution of the solid-state effect to the observed resonance frequencies has been made assuming that the partially charged atomic sites in the lattice may be replaced by point charges and that this lattice

1

2

of point charges makes the dominant contribution to the measured field gradients. A comparison of the calculated contributions of the lattice charges with the measured contributions indicated that the Sternheimer antishielding factor for chlorine is much smaller than the value previously used by other workers.

The shift in the absorption frequency of the chlorine atoms of POCl₃ in the complex, compared to their frequency in solid POCl₃ itself, was used to estimate the relative amounts of charge shifted from donor to acceptor on complex formation for the complexes studied.

The absorption frequencies due to chlorine atoms of $SbCl_5$ and $SnCl_4$ in $SbCl_5 \cdot POCl_3$ and $SnCl_4 \cdot 2POCl_3$ were used both to indicate the existence of nonequivalent bonding orbitals on the central metal atom and to estimate the total charge shifted to the central atom upon complex formation. The problems associated with the interpretation of NQR data for donor-acceptor complexes have been discussed in detail.

NUCLEAR QUADRUPOLE RESONANCE STUDY OF CHARGE-TRANSFER COMPLEXES

Ву

James Austin Ryan

A THESIS

Submitted to Michigan State University in partial fulfillment of the requirements for the degree of

DOCTOR OF PHILOSOPHY

Department of Chemistry

.

1967

I14395 GDR/57

ACKNOWLEDGMENTS

The author is deeply indebted to Professor M. T. Rogers for his guidance and encouragement during the course of this work.

He would also like to give special thanks to Dr. V. Nagarajan for his valuable advice and assistance in the construction of the NQR spectrometer and Professor R. Schwendeman for several stimulating discussions.

The experimental assistance of Mr. Michael Buckley, Mr. Russel Geyer and Mr. James Grumblatt is gratefully acknowledged.

Finally the author would like to thank the Atomic Energy Commission and the Dow Chemical Company for financial support during a part of this work.

TABLE OF CONTENTS

	raye
	1
I. THEORY AND BACKGROUND	4
Physical Theory	4
A. Absorption Frequencies	4
1) Basic Equations	4
2) Absorbtion Frequencies and .	
Selection Rules	12
B. Zeeman Splitting of Quadrupole Spectra .	18
C. The Effect of an Electric Field on an	
NQR Absorption Line	21
D. The Effect of Temperature on the NQR	
Absorption Frequency	26
E. The Effect of Internal Electric Fields	
on the NQR Frequencies	32
Chemical Interpretation of NQR Data	40
A. Atomic Field Gradients	40
B. The Townes and Dailey Theory of Mole-	
cular Field Gradients	44
C. Evaluation of the Parameters of the	- 7
Townes and Dailey Equation	57
Previous NQR Studies of Charge Transfer Com-	07
prexes	63
II. EXPERIMENTAL	70
A. The Nuclear Quadrupole Resonance Spec-	
trometer	70
1) Introduction	70
2) Superregenerative Oscillators	73
3) Modulation and the Lock-in Ampli-	
fier	82
4) Frequency Measurement	89
5) Spectrometer Operation and Problems	
in Detecting Resonances	95
6) Temperature Dependence of the 27.312	
MHz Resonance in $SbCl_5 \cdot POCl_3 \cdot \cdot \cdot$	101
B. Chemical Synthesis	101
1) Trans-dichlorobisethylenediamine	
Cobalt(III) Chloride HCl·xH ₂ O	101

	2) The Cu(I) Complexes of Some Thio-	407
	3) Mercuric Chloride Complexes	103
	and Its Derivatives	106
	5) Binary Complexes of $POCl_3$	106
	6) Ternary Complexes of POCl ₃	112
III. CALCULA FIELD G	ATION OF THE CONTRIBUTION TO THE MEASURED GRADIENT FROM CHARGES SITUATED IN THE	
LATTICE	2	114
Α.	Introduction	114
В.	Theory	118
c.	Some Details of the Modification and Use	
		123
D.	A Test of LATSUM	125
Ľ.	and Drograms DOMMER and DIAG	
	1) The First Model	126
	2) In Improved Medel	120
		131
	$(A) \mathbf{P} \mathbf{P} \mathbf{C} \mathbf{P} \mathbf{M} \mathbf{D} \mathbf{T} \mathbf{A} \mathbf{C}$	131
		104
IV. RESULTS	3	138
Α.	Assignment of Absorption Frequencies to	
	Specific Atoms in the Complexes	138
	1) $SbCl_5 \cdot POCl_3 \cdot \cdot$	138
	2) $SnCl_4 \cdot 2POCl_3 \cdot \cdot$	143
	$(\mathrm{TiCl}_4 \cdot \mathrm{POCl}_3)_2 \cdot \cdot$	144
_	4) Pure SbCl ₅	144
в.	New Resonance Frequencies and Their	440
0	Temperature Dependence	146
C.	Rounds in which No Resonances were	1 5 2
		154
Д.	1) Tabulated Results of LATSUM and	120
	ROTATE	156
	2) Comparison of the Lattice Sum Re-	
	sults Using Both the First Model	
	and the Revised Model	180
	5) DIAG Results	180

-

V. DISCUSS	ION	.87
Α.	Temperature Dependence of the Absorption Frequencies and Phase Transitions 1	187
в.	Calculation of the Point-Charge Field	03
c.	Frequency Shifts in the Complexed POCl ₃	
D.	Chlorine Atoms	200
	SbCl ₅ Upon Complex Formation	204
	2) SnCl ₄ ·2POCl ₃ \ldots \ldots \ldots 2	204 206
	3) $SbCl_5 \cdot POCl_3 \dots \dots$	211
SUMMARY		215
REFERENCES .		216
APPENDIX		223

Page

LIST OF TABLES

TABLE		Page
1.	Secular Equations for Nuclei with Half- Integral Spin	16
2.	Formulas for the Nuclear Quadrupole Resonance Frequencies	17
3.	Quadrupole Coupling Constants of Halogen Con- taining Molecules Which Have Been Measured Both in the Solid and in the Gaseous State	38
4.	NQR Data Indicating Hydrogen Bonding	39
5.	Values of $q_{n\ell 0} = \frac{\partial^2 V}{\partial Z^2}$ for Various Atomic States	42
6.	Frequency Shifts Upon Complex Formation Be- tween Br ₂ and Some Substituted Benzenes	64
7.	NQR Resonance Frequencies in Charge Transfer Complexes Compared to the Resonance Frequenc- ies in the Pure Compounds	67
8.	Physical Dimensions of the Coils Used With the High Range Oscillator	99
9.	Comparison of q and η as Calculated Both by LATSUM and by Other Authors	126
10.	Charges Used in LATSUM	131
11.	Resonance Frequencies for the Compounds Studied in This Work	148
12.	Temperature Dependence of the Most Intense Line of $SbCl_5 \cdot POCl_3 \ldots \ldots \ldots \ldots \ldots \ldots$	149
13.	Coupling Constants and Field Gradients for the Compounds Studied in This Work	150
14.	Temperature Coefficients for the Chlorine Resonances of Complexed SbCl ₅ and SnCl ₄	152

15.	Compounds in which NQR Absorptions were Missed	. 154
16-37.	LATSUM and ROTATE Results for the Complexes Studied in This Work	158-179
38.	Comparison of LATSUM Results Using the New Charges to LATSUM Results Using the Old Charges	. 181
39.	Line Splittings $ \Delta \mathbf{q} $ and "Experimental" Values	
	of γ_{∞}	. 182
40.	DIAG Results	. 184
41.	Temperature Factors for SnCl ₄ ·2POCl ₃	. 192
42.	Bond Angles (in Degrees) and Bond Lengths (in Angstroms) of POCl ₃ in Various Complexes From X-ray Investigations	. 201
43.	Electronic Charge Lost by the $POCl_3$ Chlorine Atoms Estimated from NQR Data	. 203
44.	Charge Transfer in Complexed $SnCl_4$. 210
45.	Charge Transfer in Complexed SbCl ₅	. 213

Page

LIST OF FIGURES

FIGUR	E	Page
1.	Pictorial representation of the various vectors and volume elements	4
2.	Splitting of the quadrupolar levels by a mag- netic field	19
3.	Assumed electric field direction	24
4.	Line width change with temperature for a) Hexachlorobenzene, b) 1,2,3-Trichloro- benzene	28
5.	A plot of the Sternheimer factor (γ_{∞}) versus ionic charge for helium-like ions	36
6.	Ionicity <u>versus</u> electronegativity difference according to the approximations of Pauling (#0), Gordy (60), and Townes and Dailey (44) .	62
7.	High Range (15-55 MHz) Oscillator	74
8.	Low Range (2-20(MHz) Oscillator)	75
9.	Modulation unit for the NQR spectrometer	85
10.	Block diagram of the NQR spectrometer	90
11.	The partial spectrum of $SbCl_5 \cdot POCl_3$ showing the 30.560 and the 30.616 MHz absorption lines; also shown are the quench sidebands from each line	91
12.	Definition of the angles α and β as used by ROTATE	133
13.	A molecule of SbCl ₅ ·POCl ₃	139
14.	A molecule of $SnCl_4 \cdot 2POCl_3 \cdot \cdot$	140
15.	A molecule of the dimer $[TiCl_4 \cdot 2POCl_3]_2$	141
16.	Temperature variation of the most intense $SbCl_5$ resonance of $SbCl_5 \cdot POCl_3 \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot$	151

INTRODUCTION

Although the first pure quadrupole resonance was observed in 1950 (1), as yet no extensive application of this technique has been made to chemical problems. This is not due to a lack of potential applications but rather to experimental difficulties and the fact that the theory which connects experimental results to molecular structure is not, as yet, well developed. Since the absorption frequencies measured by nuclear quadrupole resonance (NQR) spectroscopy may be interpreted in terms of migration of charge away from or toward the resonant nucleus, this method is ideally suited to the study of charge-transfer complexes.

At the beginning of this work there had been several NQR investigations (2-9) of charge-transfer complexes reported in the literature, but the results of these investigations seemed somewhat chaotic. In some cases they indicate no charge transfer while in other cases possible shifts are obscured by solid-state effects on the resonance frequency. Finally, in the cases where an unambiguous charge-transfer effect is seen in the NQR absorption frequencies, no attempt has been made to study the size of this effect in a series of charge-transfer complexes. The solid-state effects, which result in a splitting of NQR lines, have been known

1

since the beginning of NQR spectroscopy but they have never been studied in detail. The usual method for taking them into account is to take an average of the measured frequencies. Unfortunately for the study of charge-transfer complexes, this method is unsatisfactory because the splittings may be of the same order of magnitude as the chargetransfer effects.

In this work an NQR spectrometer was constructed and used to study charge-transfer complexes. The complexes studied were chosen because chemical and X-ray data indicated that strong charge transfer takes place and because they represent a chemically related series. The adducts studied are formed by a transfer of electrons from the Lewis base POCl₃ to a Lewis acid. They include [TiCl₄·POCl₃]₂, SbCl₅. **POCl₃** and **FeCl₃** · **POCl₃** which, together with the previously investigated SnCl₄·2POCl₃ (9), form a series whose charge transfer should be related to the strength of the Lewis acid involved. Furthermore, since complete X-ray data are available for SbCl₅·POCl₃, [TiCl₄·POCl₃]₂ and SnCl₄·2POCl₃, an investigation of the solid-state effects was possible. A calculation of line splitting as a function of the Sternheimer parameter was made assuming that the field gradient produced by charged ions situated in the crystal lattice dominated the charge-transfer effects. This calculation, which assumes a model that replaces the charged ions by point changes whose magnitudes are dependent on the

2

ionicity of the bonds in which the ions are involved, pushes to the limit some segments of the NQR theory. Thus results from this work may be used to evaluate this theory.

The molecular field gradients, which were obtained from the experimental absorption frequencies after allowance was made for solid-state effects, were then used to evaluate the extent of charge transfer.

I. THEORY AND BACKGROUND

Physical Theory

A. Absorption Frequencies

1) Basic Equations

The overall Hamiltonian H_{EL} describing the interaction between a charged nucleus and the surrounding electronic charge may be written as

$$H_{EL} = + \int_{V_e} \int_{V_n} \frac{\rho_e(r_e) \rho_n(r_n) dV_e dV_n}{r} , \qquad (1)$$



Figure 1. Pictorial representation of the various vectors and volume elements.

where ρ_e is charge density of the electrons external to the nucleus in the volume element dV_e at position r_e with respect to the center of the nucleus under discussion, ρ_n

is the charge density of the volume element dV_n within the nucleus at a position V_n with respect to the center of the nucleus. Also, V_n is a vector from dV_n to dV_e and Θ_{en} is the angle between r_e and r_n as shown in Figure 1. From the law of cosines

$$\frac{1}{r} = (r_e^2 + r_n^2 - 2r_e r_n \cos \theta_{en})^{-\frac{1}{2}}$$

$$= \frac{1}{r_e} (1 + (\frac{r_n}{r_e})^2 - \frac{2r_n}{r_e} \cos \theta_{en})^{-\frac{1}{2}}$$
(2)

which can be expanded in a power series in $\frac{r_n}{r_e}$ to yield

$$\frac{1}{r} = \frac{1}{r_e} \left(1 + \frac{r_n}{r_e} P_1 + \left(\frac{r_n}{r_e}\right)^2 P_2^+ \cdots \right), \quad (3)$$

where P_{l} is the Legendre polynomial of $\cos \theta_{en}$; i.e.,

$$P_{1} = \cos \theta_{en}$$

$$P_{2} = \frac{1}{2} (3\cos^{2}\theta_{en} - 1)$$

$$etc.$$
(4)

The first term of this power series corresponds to an electric monopole, the second to an electric dipole, the third to an electric quadrupole and, in general, a term in P_{ℓ} corresponds to a multipole moment of order 2^{ℓ}. We shall be concerned with the term in P_2 . In particular we are interested in the energy levels which arise due to this term. Substituting Equations 3 and 4 into 2 we obtain the equation

$$H_{\Theta} = \int_{V_e} \int_{V_n} v_n^2 \rho_n \frac{1}{2} (3 \cos^2 \Theta_{en} - 1) \rho_e(r_e) / r_e^3 dv_n dv_e$$
(5)

for the nuclear electric quadrupole interaction. This equation is valid only if $r_e > r_n$, since it is only under these conditions that the expansion (Equation 3) is valid. This restriction has the effect of excluding from our consideration electronic charge which actually penetrates the nucleus. This is not serious, however, since only s electrons have a non-zero probability of penetrating the nucleus and because of their spherical symmetry they have no interaction with the nuclear quadrupole moment. Equation 5 may be expanded in Cartesian coordinates using the relationship

$$r_{n}r_{e} \cos\theta_{en} = \sum_{i} X_{ni}X_{ei} \text{ to yield}$$

$$H_{Q} = \int_{V_{e}} \int_{V_{n}} \rho_{n}(r_{n}) \left[\frac{3}{2} \sum_{ij} X_{ni}X_{nj}X_{ei}X_{ej} - \frac{1}{2}r_{n}^{2}r_{e}^{2}\right] \qquad (6)$$

$$\times \rho_{e}(r_{e})/r_{e}^{3}dV_{n}dV_{e}.$$

However, if we define Q_{ij} and $(\nabla E)_{ij}$ by the relationships

$$Q_{ij} = \int_{V_n} \rho_n(v_n) (3x_{ni}x_{nj} - \delta_{ij}r_n^2) dV_n$$

$$= \int_{V_n} \rho_n(v_n) [3(\frac{x_{ni}x_{nj} + x_{nj}x_{ni}}{2}) - \delta_{ij}r_n^2] dV_n$$
(7)

and

$$(\nabla \mathbf{E})_{ij} = - \int_{\mathbf{V}_e} \rho_e(\mathbf{r}_e) \partial \partial \mathbf{x}_i \partial \partial \mathbf{x}_j (\frac{1}{\mathbf{r}_e}) d\mathbf{V}_e$$

$$= - \int_{\mathbf{V}_e} \rho_e(\mathbf{r}_e) / \mathbf{r}_e^5 [3\mathbf{x}_{ei}\mathbf{x}_{ej} - \delta_{ij}\mathbf{r}_e^2] d\mathbf{V}_e$$

$$(8)$$

6

$$= -\int_{\mathbf{V}_{\mathbf{e}}} \frac{\rho_{\mathbf{e}}(\mathbf{r}_{\mathbf{e}})}{\mathbf{r}_{\mathbf{e}}^{5}} \left[3\left(\frac{\mathbf{x}_{\mathbf{e}i}\mathbf{x}_{\mathbf{e}j} + \mathbf{x}_{\mathbf{e}j}\mathbf{x}_{\mathbf{e}i}}{2}\right) - \delta_{ij} \mathbf{r}_{\mathbf{e}}^{2} \right] d\mathbf{v}_{\mathbf{e}}.$$

Then,

$$H_{Q} = -\frac{1}{6} \sum_{ij} Q_{ij} (\nabla E)_{ij} = \overline{Q} : \overline{\nabla E}$$
(9)

where the double dot indicates a scalar product of two second rank tensors; this may be verified by direct expansion of Equation 9 using the first form of Equation 7 and the second form of Equation 8. Thus, we have seen that H_Q can be completely described by two tensors \overline{Q} (the quadrupole tensor) and $\overline{\nabla E}$ (the electric field-gradient tensor) whose elements Q_{ij} and $(\nabla E)_{ij}$ have been defined by Equations 7 and 8, respectively. Furthermore, the two tensors are symmetric and it can be seen by inspection of Equations 7 and 8 that both \overline{Q} and $\overline{\nabla E}$ are traceless.

Ramsey (10) has shown that the elements of the Q tensor Q_{ij} may be represented in the form

$$Q_{ij} = C[3(\frac{(I_i)(I_j) + (I_j)(I_i)}{2}) - \delta_{ij} \overset{I}{\sim}^2]$$
(10)

where I_i and I_j are components of the nuclear spin operator I and C is a constant scalar quantity. The arbitrary constant C may be expressed in terms of the scalar nuclear quadrupole moment Q which is a measure of the departure of a nucleus from the shape of a perfect sphere. By definition

$$Q \equiv \frac{1}{e} \int \rho_{n,m_{I}} = I \left[3Z_{n}^{2} - r_{n}^{2} \right] dV_{n}, \qquad (11)$$

where the subscript $m_I = I$ indicates that the integral is carried out for the nuclear state whose magnetic quantum number $m_I = I$. Q has the dimension of length squared. It is positive for a prolate spheroid and negative for an oblate spheroid. But

$$\frac{1}{e} \int \rho_{n,m_{I}} = I \left[\frac{3Z_{n}^{2} - r_{n}^{2}}{N} \right] dV_{n} \text{ is equal to the matrix element}$$

$$< I I \left| Q_{33} \right| I I > = C < I I \left| \frac{3(I_{Z})^{2} - I^{2}}{I} \right| I I >$$

$$= C \left[3I^{2} - I(I+1) \right] = C I (2I-1), \qquad (12)$$

using Equation 11. Hence,

$$Q_{ij} = \frac{eQ}{I(2I-1)} [3(\frac{I_{i}I_{j} + I_{j}I_{i}}{2}) - \delta_{ij}I^{2}].$$
(13)

It is of interest here to point out that while nuclei of spin I > 1 have non-zero quadrupole moments, nuclei of spin I = 0 and I = $\frac{1}{2}$ do not necessarily have to have a zero quadrupole moment (14). It often has been written that nuclei with I < 1 have zero quadrupole moments, this is incorrect. However, it is impossible to observe a nuclear electric multipole moment of 2^l greater than that corresponding to l = 2I. This is easy to prove. From Equations 3 and 1 we can see that insofar as the nuclear coordinates are concerned the interaction for the 2^l th moment is proportional to

$$\int_{\mathbf{v}_n} r_n \rho_n(r_n) \mathbf{P}_{\ell} d\mathbf{v}_n , \qquad (14)$$

but if ψ_n is the nuclear part of the total wave function $\Psi_{total} = \psi_e \psi_n$, Equation 14 becomes $\int_{V_n} r_n^{\ell} \psi_n^* P_{\ell} \psi_n dV_n$. However, if the angular momentum of the nucleus is I then ψ_n must be an eigenfunction corresponding to an angular momentum of I. Since r_n^{ℓ} has no angular dependence but P_{ℓ} has an eigenvalue of ℓ under operation by the angular momentum operator, $r_n^{\ell} \psi_n$ and $P_{\ell} \psi_n$ correspond to eigenfunctions with angular momentum eigenvalues of I and between I + ℓ and $|I - \ell|$, respectively. In order that Equation 14 not vanish $r_n^{\ell} \psi_n^*$ and $P_{\ell} \psi_n$ must correspond to the same eigenvalues; hence, I must lie between I + ℓ and $|I - \ell|$. This can only be true if $\ell \leq 2I$ hence for nuclei of spin I multipole interactions of order 2^{ℓ} where $\ell > 2I$ cannot take place.

Returning to the quadrupole interaction let us examine the electric field gradient tensor $\overline{\nabla E}$. The elements $(\nabla E)_{ij}$ previously given are identical to V_{ij} , where $V_{ij} = \frac{\partial^2 V}{\partial X_i \partial X_j}$, and \overline{V} is the electrostatic potential at the nucleus (the units of V_{ij} are cm⁻³). In the usual notation $X_1 = x'$, $X_2 = y'$, and $X_3 = z'$ where the primes indicate that we are not yet in the principal axis system. Since $\overline{\nabla E}$ is traceless and symmetric

 $V_{x'x'} + V_{y'y'} + V_{z'z'} = 0$ (15)

and we need specify only five elements to completely specify the tensor.

9

These elements are:

$$(\nabla E)_{0} = \frac{1}{2} V_{z'z'}$$

$$(\nabla E)_{\pm 1} = -\sqrt{\frac{1}{6}} (V_{x'z'} \pm iV_{y'z'})$$

$$(\nabla E)_{\pm 2} = \frac{1}{2\sqrt{6}} (V_{x'x'} - V_{y'y'} \pm 2V_{x'y'})$$

Any symmetric tensor may be diagonalized, this diagonalization corresponding to a transformation to the principal-axis system. The diagonalized tensor has components

$$(\nabla \mathbf{E})_{0} = \frac{1}{2} \mathbf{v}_{zz} \equiv \frac{1}{2} \mathbf{eq}$$

$$(\nabla \mathbf{E})_{\pm 1} = 0$$

$$(\nabla \mathbf{E})_{\pm 2} = \frac{1}{2\sqrt{6}} (\mathbf{v}_{xx} - \mathbf{v}_{yy}) \equiv \frac{1}{2\sqrt{6}} \eta \mathbf{eq}.$$
(16)

This corresponds to the definitions

$$q = \frac{1}{e} V_{zz} \quad \text{and} \quad (17)$$
$$\eta = (V_{xx} - V_{yy}) / V_{zz} \quad .$$

Using the convention $|V_{xx}| \leq |V_{yy}| \leq |V_{zz}|$, η may vary from 0 to 1. For $\eta = 0$, $V_{xx} = V_{yy} = -\frac{1}{2}V_{zz}$ and for $\eta = 1$, $V_{xx} = 0$ and $V_{yy} = -V_{zz}$. The first condition corresponds to cylindrical symmetry. For chlorine atoms involved in single bonds it is a very good approximation to assume cylindrical symmetry, therefore the assumption is usually made that $\eta = 0$.

An expression must now be derived which will relate the observed resonance frequencies to the quantities q and η . We proceed by writing an expression for the quadrupole energy level designated by the quantum number m, where m can take the values m = +I, I-1, ···· -I, these numbers corresponding to the allowed spin orientations in the electric field gradient. Thus, it is necessary to calculate the matrix elements $\langle m | H_Q | m' \rangle$ for the two cases of axial (η =0) and non-axial ($\eta \neq 0$) field gradients. To calculate the matrix elements we need only know the general behavior of wave functions $\psi_n(m)$ with the angular momentum squared operator \hat{I}^2 and the angular momentum operator \hat{I} , with components $\hat{I}x$, $\hat{I}y$ and $\hat{I}z$, i.e.,

$$\langle m | \hat{\mathbf{I}}_{\mathbf{z}} | m' \rangle = m\delta mm' \text{ and } \langle m | \mathbf{I}_{\mathbf{x}} \pm i \mathbf{I}_{\mathbf{y}} | m' \rangle = [(\mathbf{I} m)(\mathbf{I} + m + 1)]^{\frac{1}{2}} \delta_{m + 1, m'}$$

(18)

where **ô** is the familiar Kroneker delta. Using these relationships we can write (Equation 19) the only non-zero matrix elements (15). Since

$$H_{Q} = -\frac{1}{6} \sum_{ij}^{S} Q_{ij}(E)_{ij} = \frac{eQV_{ZZ}}{4I(2I-1)} [3I_{Z}^{2}-I^{2}] + \frac{eQ(V_{XX}-V_{YY})}{4I(2I-1)}$$

and

$$\left< m \right| H_{Q} \left| m \right> = \left< -m \right| H_{Q} \left| -m \right> = \frac{e^{2} qQ}{4I(2I-1)} \quad [3_{m}^{2} - I(I+1)] \text{ and}$$
(19)

$$\left< m \left| H_{Q} \right| m \pm 2 \right> = \left< -m \right| H_{Q} \left| -m \pm 2 \right> = \left< m \pm 2 \right| H_{Q} \left| m \right> = \left< -m \pm 2 \right| H_{Q} \left| -m \right> ; \text{ then}$$

$$E = \frac{e^{2} qQ}{4I(2I-1)} \quad \frac{\eta}{2} \quad [I(I+1) - m(m+1)]^{\frac{1}{2}} [(I+1) I - (m \pm 1) (m \pm 2)]^{\frac{1}{2}} ;$$

the quantity e^2qQ is commonly called the quadrupole coupling constant and is identical with eQq' which is another common notation since $q' \equiv eq$. For $\eta = 0$ we have only diagonal nonzero matrix elements $\langle m | H_Q | m \rangle$ and use of Equations 18 immediately yields

$$E_{m} = \langle m | H_{Q} | m \rangle = A [3m^{2} - I(I+1)]$$
(20)

where we have used the common notation $A = e^2 qQ/4I(2I-1)$. We see immediately that all levels except m = 0 are doubly degenerate. Thus, for half-integral spins there are $I + \frac{1}{2}$ energy levels and for integral spins there are I + 1 levels.

2) Absorbtion Frequencies and Selection Rules

In order to derive the selection rules it is necessary to consider a mechanism by which transitions between energy levels are produced. Although it is possible in theory to induce transitions by application of an electric field gradient, in practice this would require a field gradient which is too large to be produced in the laboratory. In order to induce an observable number of transitions, we must, therefore, turn to an oscillating magnetic field which can interact with magnetic dipoles; that is, electromagnetic radiation. The time dependent Hamiltonian representing this interaction may be written as

$$H(t) = -\gamma h(H_x I_x + H_y I_y + H_z I_z)$$
(21)

where γ is the magnetogyric ratio, h is Planck's constant, I_x , I_y and I_z are the components of the angular momentum operator and H_x , H_y and H_z are the components of the linearly polarized oscillating magnetic field. The matrix elements $\langle m | H(t) | m' \rangle^2$ will then be proportional to the transition probabilities and may be calculated with the aid of Equation 19. We then find that the transitions $\Delta m_1 = 0$ and 1 are allowed; these then are the selection rules for the case of $\eta = 0$. Furthermore, it can be shown, following the treatment of Pake (13) for the case of magnetic resonance, that maximum transition probability occurs when the Bohr condition

$$\omega = \frac{\mathbf{E}_{\mathbf{m}} + 1 - \mathbf{E}_{\mathbf{m}}}{\mathbf{h}}$$
(22)

is satisfied. We may now write, using Equations 20, an expression for ω :

$$\omega = \frac{3A}{h} (2|m|+1).$$
 (23)

There are $(I + \frac{1}{2})$ doubley degenerate energy levels for halfintegral spins and I + 1 doubly degenerate levels for integral nuclear spins. If I and m are known, which is usually the case, then e^2qQ/h (in units of MHz) may be calculated directly from the measured value of absorption frequency. If the m value is not known, and this situation may only arise for spins I > 3/2, the values of m₁ and m₂ may be uniquely determined by measuring the ratio $\frac{\omega_1}{\omega_2} = \frac{2^{1}m_1|+1}{2|m_2|+1}$.

For the case of $\eta \neq 0$ the problem of writing down expressions relating e^2qQ , η and ω becomes much more complex. Now we must also consider matrix elements of the type calculated in the second of Equations 19. This results in the mixing of the pure magnetic dipole states with states differing in m by ± 2 . Because of this the selection rules $|\Delta m| = 0, 1$ no longer hold and for values of $\eta > 0.1$ the probability for observation of transitions corresponding to $|\Delta m| = 2$ becomes quite large. Reddoch (15) has observed the ⁹³Nb(I = 9/2) resonance in NbCl₅. The observed spectrum contains lines due to transitions for which $|\Delta m| = 2$ and even $|\Delta m| = 3$. The calculated relative intensities for $\eta = 1/3$ in the transitions $|\Delta m| = 1$, $|\Delta m| = 2$ and $|\Delta m| = 3$ are, respectively, 129, 54 and 7.8. In some cases the degeneracy of the doubly degenerate levels is removed. For the case of I = 3/2 we now have to consider the matrix elements $H_{m, m\pm 2} = \langle m|H_Q|m\pm 2 \rangle$ in addition to the matrix elements $H_{mm} = \langle m|H_Q|m \rangle$; the Hamiltonian matrix now becomes

$$H_{\frac{3}{2},\frac{3}{2}} = E \qquad 0 \qquad H_{\frac{3}{2},\frac{1}{2},-\frac{1}{2}} \qquad 0$$
$$H_{\frac{1}{2},\frac{1}{2},-\frac{1}{2}$$

where $H_{\pm \frac{3}{2}, \pm \frac{3}{2}} = 3A$, $H_{\pm \frac{1}{2} \pm \frac{1}{2}} = -3A$ and $H_{\pm \frac{1}{2} \mp \frac{3}{2}} = \sqrt{3} A \eta$. This matrix may be put into the diagonal form by simply rearranging rows and columns. When this is done two submatrices are obtained along the diagonal, the first of which is

$$\begin{pmatrix} H_{\frac{3}{2}\frac{3}{2}} - E & H_{\frac{3}{2}} - \frac{1}{2} \\ H_{-\frac{1}{2}\frac{3}{2}} & H_{-\frac{1}{2}-\frac{1}{2}} - E \end{pmatrix}$$

This submatrix yields a secular equation $E^2 - 3A^2 (3 + \eta^2) = 0$, using the previously tabulated values of the matrix elements. This equation can be solved exactly to yield $E_3 = \frac{-e^2 qQ}{4} (1 + \frac{\eta^2}{3})^{\frac{1}{2}}$ and $E_{-\frac{1}{2}} = \frac{-e^2 qQ}{4} (1 + \frac{\eta^2}{3})^{\frac{1}{2}}$. Solving the second matrix gives $E_3 = E_{-\frac{3}{2}}$ and $E_{\frac{1}{2}} = E_{-\frac{1}{2}}$; thus, the mixing of the magnetic dipole states does not remove the energy level degeneracy. Using the Bohr condition one then obtains

$$\omega(\pm \frac{3}{2} \longrightarrow \pm \frac{1}{2}) = \frac{1}{2} \left(\frac{e^2 qQ}{h}\right) \left(1 + \frac{\eta^2}{3}\right)^{\frac{1}{2}}.$$
 (24)

In a similar manner the other secular equations may be derived. Except in the case of I = 1 it is not possible to obtain an analytical solution for these equations. For the case I = 1 it is found that the degeneracy of the levels is lifted; in this case two frequencies are predicted

$$\omega_{+} = \frac{3}{4} \left(\frac{e^2 q Q}{h} \right) (1 + \eta/3) \text{ and } \omega_{-} = \frac{3}{4} \left(\frac{e^2 q Q}{h} \right) (1 - \eta/3).$$

It is thus possible to obtain both η and e^2qQ from an observation of ω_+ and ω_- . It is not possible to measure both e^2qQ and η for nuclei with I = $\frac{3}{2}$ (e.g. ${}^{35}Cl, {}^{81}Br$) because only one resonance frequency is observed. As mentioned previously the assumption is made that $\eta = 0$ for chlorine resonances; from Equation 24, if $\eta = 0.1$ this assumption involves an error of about 150 kHz. This value for η is seldom exceeded even if a moderate amount of double bonding is present. The secular equations for the cases I = 3/2, 5/2, 7/2 and 9/2 are tabulated in Table 1; these are the most important values for the purposes of quadrupole resonance.

I	Secular Equation	Units of Energy
3/2	$\varepsilon^2 - 3(3 + \eta^2) = 0$	ε = Ε/Α
5/2	$\varepsilon^{3} - 7(3 + \eta^{2})\varepsilon - 2(1 - \eta^{2}) = 0$	$\varepsilon = E/2A$
7/2	$\epsilon^4 - 14(3 + \eta^2)\epsilon^2 - 64(1 - \eta^2) \epsilon$	
	+ $35(3 + \eta^2)^2 = 0$	$\varepsilon = E/3A$
9/2	$\epsilon^{5} - 11(3 + \eta^{2}) \epsilon^{3} - 44(1 - \eta^{2}) \epsilon^{2}$	
	+ $\frac{44}{3}(3 + \eta^2)^2 \varepsilon + 48(3 + \eta^2)$	
	$(1 - \eta^2) = 0$	$\varepsilon = E/6A$

Table 1. Secular Equations for Nuclei with Half-Integral Spin

Except for the cases I = 1 and I = 3/2 these equations are not analytically solvable. Various methods have been used in obtaining solutions for them. Cohen (18) has given the numerical solutions of secular equations for I = 5/2, 7/2 and 9/2 and has tabulated eigenvalues for values of η from 0 to 1.0 in steps of 0.1; Livingston and Zeldes (19) have tabulated the numerical solution for I = 5/2 in steps of 0.001; Reddoch (15) has numerically solved and tabulated results for I = 9/2 and η^2 from 0 to 1 in steps of 0.01. Numerical solution seems to be the best approach. Bersohn (17) has expanded ε in a power series in η^2 about $\eta = 0$ which is valid for low values of $\eta(\eta \leq 0.25)$. When this value for η is substituted into the Hamiltonian a perturbation treatment allows us to extract expressions for absorption frequencies in terms of η and these are presented in Table 2.

.

.

Table 2. Formulas for the Nuclear Quadrupole Resonance Frequencies

$$I = 1 \qquad \omega_{+} = \frac{3}{4} e^{2} qQ/h (1 + \eta/3)
\omega_{-} = \frac{3}{4} e^{2} qQ/h (1 - \eta/3)
I = \frac{3}{2} \omega = \frac{Y}{2} e^{2} qQ/h (1 + \eta^{2}/3)^{\frac{1}{2}}
I = \frac{5}{2} \omega_{1} = \frac{3}{200} (\frac{e^{2} qQ}{h}) (1 + 0.0926\eta^{2} - 0.634\eta^{4})
\omega_{2} = \frac{6}{200} (\frac{e^{2} qQ}{h}) (1 - 0.2037\eta^{2} + 0.162\eta^{4})
I = \frac{7}{2} \omega_{1} = \frac{1}{14} (\frac{e^{2} qQ}{h}) (1 + 50.865\eta^{2} - 101.29\eta^{4})
\omega_{2} = \frac{2}{14} (\frac{e^{2} qQ}{h}) (1 - 15.867\eta^{2} + 52.052\eta^{4})
\omega_{3} = \frac{3}{14} (\frac{e^{2} qQ}{h}) (1 - 2.8014\eta^{2} - 0.5278\eta^{4})
I = \frac{9}{2} \omega_{1} = \frac{1}{24} (\frac{e^{2} qQ}{h}) (1 + 9.0333\eta^{2} - 45.691\eta^{4})
\omega_{2} = \frac{2}{24} (\frac{e^{2} qQ}{h}) (1 - 1.3381\eta^{2} + 11.724\eta^{4})
\omega_{3} = \frac{3}{24} (\frac{e^{2} qQ}{h}) (1 - 0.1857\eta^{2} - 0.1233\eta^{4})
\omega_{4} = \frac{4}{24} (\frac{e^{2} qQ}{h}) (1 - 0.0809\eta^{2} - 0.0043\eta^{4})$$

It should be emphasized that these equations are only valid for small η and should be used with caution. Recently Alexander and Ganiel (20) have expanded the quadrupolar Hamiltonian around 1 - η and have calculated the eigenvalues and eigenfunctions of the fully asymmetric ($\eta = 1$) Hamiltonian. This expansion has certain advantages because, since their Hamiltonian changes sign upon a rotation of π , certain of the matrix elements may be set equal to zero unless both the wave functions involved in the matrix elements have the same phase

1 .: ••• • ¥. 30 1 Ś 3

factor γ under rotation of π . Comparison of their results with the exact numerical results shows that this expansion is valid in the region of η from $\eta = 1$ to about $\eta = 0.2$, thus this method slightly overlaps Bersohn's expansion. The value of the power series expansion lies in the insight which it allows into the eigenfunctions and eigenvalues of the quadrupolar Hamiltonian but it seems clear that if accurate values of η and e^2qQ are wanted from measured frequencies the numerical solutions of the secular equations should be used.

B. Zeeman Splitting of Quadrupole Spectra

If a single crystal of a material containing a quadrupolar nucleus is subjected to a weak magnetic field (of the order of 100 gauss) such that $e^2qQ \gg \gamma hH$, where γ is the magnetogyric ratio and H the magnetic field strength, it is observed that each line will be split into two or more lines. This is due to the fact that the magnetic field lifts the degeneracy of the doubly degenerate levels (Figure 2). It is observed in this case that four lines are now possible and, in fact, have been observed. No attempt will be made here to give the full theory of Zeeman splitting but the simple case of $\eta = 0$, I = 3/2 will be treated in outline. Das and Hahn (16) have treated all cases in great detail. In addition, Bersohn (17) treated spins of any value and small η and Cohen (18) has given a full treatment for half-integral spins and arbitrary η . The original study of Zeeman splitting of



Figure 2. Splitting of the quadrupolar levels by a magnetic field.

a pure quadrupole line was done by Dean (28) and his methods of analysis are for the most part still in use. As long as $e^2qQ >> \gamma hH$ we may treat the magnetic field as a perturbation. We then wish to calculate the matrix elements of the Hamiltonian $H_Q^{\prime} = H_Q + H_M$, where H_M is given by the equation

 $H_{M} = -h\gamma H(I_{z}\cos\theta + I_{x}\sin\theta\cos\phi + I_{y}\sin\theta\sin\phi),$

 Θ is the angle between the Z axis of the principal-axis system and the magnetic field direction, and ϕ is the azimuthal axis for H governed by the particular choice of X and Y for the principal-axis system. For the states of half-integral spin and m> $\frac{1}{2}$ there is essentially no mixing between states and, for example, the states $\pm 3/2$ are split apart according to the equation

•

$$\mathbf{E}_{\pm m} = \mathbf{A}[\mathbf{3}_{m^2} - \mathbf{I}(\mathbf{I} + 1)] \mp \mathbf{m}\mathbf{h}\gamma\mathbf{H}\mathbf{cos}\Theta$$

The matrix elements are not dependent on the I_x and I_y terms in H_M and hence not on ϕ ; this is because the contribution due to these terms is small and may be neglected. However, for the case of m = $\pm \frac{1}{2}$ these terms may not be neglected since this leads to a mixing of the states m = $\frac{1}{2}$ and m = $-\frac{1}{2}$. That is, two new states arise whose eigenfunctions are designated by ψ_+ and ψ_- , where $\psi_+ = C_1\psi_{\frac{1}{2}} + \psi_{-\frac{1}{2}}$ and $\psi_- = C_3\psi_{\frac{1}{2}} + C_4\psi_{-\frac{1}{2}}$. Degenerate perturbation theory then leads to energies of

$$\mathbf{E}_{\pm} = \mathbf{A} \begin{bmatrix} \frac{3}{4} - \mathbf{I}(\mathbf{I} + 1) \end{bmatrix} \mp \frac{f}{2} \text{ hyHcos}\mathbf{\Theta}$$

where

$$f = [1 + (I + \frac{1}{2}) \tan^2 \theta]^{\frac{1}{2}};$$

also,

$$\psi_{+} = \psi_{\frac{1}{2}} \sin \alpha + \psi_{-\frac{1}{2}} \cos \alpha \text{ and } \psi_{-} = \psi_{-\frac{1}{2}} \sin \alpha - \psi_{\frac{1}{2}} \cos \alpha ;$$
$$\tan \alpha = \left[\frac{f+1}{f-1}\right]^{\frac{1}{2}}$$

It is interesting to note that again we have no dependence on the azimuthal angle ϕ to the first order. From the above equations it may be shown that the frequencies of the four absorptions arising because of the level splitting are given by

$$\omega_{\alpha} = \frac{6A}{h} - \frac{3-f}{2} \gamma H \cos \theta$$
$$\omega_{\beta} = \frac{6A}{h} - \frac{3+f}{2} \gamma H \cos \theta$$

$$\omega_{\alpha}' = \frac{6A}{h} + \frac{3-f}{2} \gamma H \cos \Theta$$
$$\omega_{\beta}' = \frac{6A}{h} + \frac{3+f}{2} \gamma H \cos \Theta$$

These four lines are symmetrical about the line which appears when there is no applied homogeneous static magnetic field. It should be noted that this discussion applies only to resonance samples in the form of a single crystal. If the sample is a polycrystalline powder then we have a wide distribution of values of the angle Θ which results in a large number of lines at varying distances from the zero field line. Since the amplitude of each line is inversely proportional to the number of lines this has the effect of smearing out all lines. Therefore, Zeeman studies cannot be done on powders; however, this effect is useful in one modulation scheme.

C. <u>The Effect of an Electric Field on an</u> <u>NQR Absorption Line</u>

Bloembergen and co-workers (21-25) have observed broadening of nuclear quadrupole absorption lines upon the application of an electric field to polycrystalline and single crystal samples. Kushida and Saika (26) have also observed this effect in ⁸¹Br NQR signals in NaBrO₃. This effect is quite generally to be expected when the nucleus under investigation is located in a crystal site which lacks inversion symmetry. Dixon and Bloembergen (24,25) have investigated this effect in great detail. They present a phenomenological theory to explain the macroscopic physical interactions

21

reported in their first paper (24). They then present, in their second paper (25), microscopic theory in terms of ionic character and sp hybridization which attempts to predict the electric shift in terms of these more basic quantities.

The macroscopic theory may be understood in terms of a third-rank tensor $\overline{\overline{R}}^*$ whose elements are $R_{lmp}^* = \frac{\partial V_{mp}}{\partial E_l} = \frac{\partial V_{mp}}{\partial E_l}$ = $e \partial q_{mp} / \partial E_l^{ext}$, where $\overline{E}^{ext} = \hat{1} E_1^{ext} + \hat{j}E_2^{ext}$ = $\frac{\partial V_{mp}}{\partial E_l} = \frac{1}{2} E_l^{ext}$ $+ \hat{k}E_3^{ext}$ is the externally applied field and the V_{mp} 's have been defined previously. Thus, the perturbation in the electric field gradient components Δq_{mp} is $e\Delta q_{mp} = \sum_{l} R_{lmp}^{*}$ E_l^{ext} (25). It should be noted that R_{lmp}^* is a tensor defined at constant stress because this is the condition under which these experiments are performed. However, it is really the tensor $\overline{\overline{R}}$ defined under conditions of constant strain which we desire since strictly speaking, in Equation 25, R_{lmp}^* should be replaced by R_{lmp} . These two quantities are related by the following equation:

$$\mathbf{R}_{\ell m p}^{\star} = \mathbf{R}_{\ell m p} + \sum_{q r} \mathbf{S}_{m p q r} \mathbf{d}_{\ell q r},$$

where d_{lqr} is an element of the piezoelectric coefficient tensor and S_{mpqr} is a fourth-rank tensor (27) which relates the changes in the electric field gradient components to the induced strain components. In most materials the d_{lqr} components can be considered small and $\overline{\overline{R}}^* = \overline{\overline{R}}$; however, care must be taken with those materials which exhibit a large
piezoelectric effect. It is also assumed that $E_i^{ext} = E_i$, where E_i is the actual field which is felt by the electrons in the molecule. This is because the electron distribution in the molecule has an averaging effect on the applied field. With these assumptions the perturbed Hamiltonian representing the quadrupole interaction may be represented as

$$H_{Q}' = H_{Q} + H_{E} = [eQ/6I(2I-1)] \sum_{ik} [3/2(I_{j}I_{k} + I_{k}I_{j}) - i_{k}] \delta_{ik} I(I + 1)] [V_{jk} + \sum_{i} E_{i} R_{ijk}] .$$
(26)

From the unperturbed part of H_Q' we obtain the equation (see 22)

$$\omega^{0}(m+1 \rightarrow m) = [3e^{2}qQ/4I(2I-1)h][2|m|+1];$$

similarly,

$$= [eQ/6I(2I-1)] [3m^{2}-I(I + 1)]$$
(27)
 $x [\Delta V_{ZZ}^{E} - \frac{1}{2} (\Delta V_{XX}^{E} + \Delta V_{YY}^{E})].$

From Equation 27 we may then obtain

$$\Delta \omega^{\mathbf{E}}(\mathbf{m}+1 \rightarrow \mathbf{m}) = [eQ/(2I-1)4Ih] [2|\mathbf{m}|+1] [\sum_{i} \{R_{i33} - \frac{1}{2} \\ i \ (28) \\ (R_{i11} + R_{i22})\}].$$

Using the fact that $\overline{\overline{R}}$ is traceless, Equation 28 reduces to

$$\Delta \omega^{E}(m + 1 \rightarrow m) = [3eQ/4I(2I - 1)h] [2 | m | + 1] [E_{3}R_{333} + E_{2}R_{233} + E_{1}R_{133}] , \qquad (29)$$

where $\Delta \omega^{\mathbf{E}}$ is the electrically induced shift in resonance

ire :..: :: ----.... ::: 3 : 1 ŧχ e) • • ÷

2: 5 33 ê,

frequency. If axial symmetry holds, $R_{233} = R_{133} = 0$; therefore, $\Delta \omega^{\mathbf{E}} / \omega^{0} = \mathbf{R}_{333} \mathbf{E}_{3} / \mathbf{eq}_{\mathbf{ZE}}$, where index 3 corresponds to the z coordinate. If the sample is polycrystalline rather than a single crystal, an average must be taken over all orientations. The second moment of the line shape, which corresponds to this average, has been calculated for this case and also for the cases $\eta \neq 0$, half-integral spin, and I = 1, $\eta \neq 0$. Full details are given in the paper of Dixon and Bloembergen (24); also presented in this paper are the experimental results on a number of selected components in electric fields up to 50 kilovolts. In the second paper of this series (25) Dixon and Bloembergen present the microscopic theory in which they consider the effects of an electric field on the electronic distribution in the molecule. From consideration of several effects, they conclude that polarization of bonding electrons near the resonant nuclei is the dominant effect. Dixon has calculated the effect of an electric field on q_{zz} for a pure p bond in a diatomic molecule AB with the field applied as indicated in Figure 3.



Figure 3. Assumed electric field direction.

)ec E. eig ي. 11 - 11 .5 θχ . 13 1 • £. P: -s Because the 6-bonding orbitals are directed along the bond and the π -bonding orbitals are directed perpendicular to the bond the field has opposite effects on the 6 and π electronic distribution. For 6-bonding orbitals the change in $q_{zz}(A)$ is

$$\Delta q_{zz}(A) = - |q_{at}| \in_{0} \text{ and } \Delta q_{zz}(B) = + |q_{at}| e_{0},$$
or $|\Delta q_{zz}/q_{at}| = e E_{0} R_{B}/(2)^{\frac{1}{2}} \wedge$, where
$$(30)$$

$$\epsilon_{0} = -\langle \psi_{g} | H_{E} | \psi_{e} \rangle (\Delta_{0})^{-1} = e E_{0} R_{B} [2(1 - S_{0}^{2}) \Delta_{0}^{2}]^{-\frac{1}{2}}$$
 (31)

 $\psi_{\mathbf{g}}$ is the ground state eigenfunction of the molecule, here taken as the bonding LCAO orbital, and $\psi_{\mathbf{e}}$ is excited state eigenfunction, here taken as the antibonding LCAO orbital; $\boldsymbol{R}_{_{\boldsymbol{\mathsf{B}}}}$ is the internuclear distance. \boldsymbol{E}_{O} is the scalar value of the applied electric field, ${\bf S}_{\rm G}$ is the 6 overlap integral, ${\boldsymbol \Delta}_{\rm G}$ is the average energy separation between the ground and the excited state and eq_{at} is the field gradient due to one unbalanced p electron in the valence shell. Several approximations are involved, the most important being $\mathbf{S}_{6}^{2} = 0$ and the assumption that there is only one low-lying excited The validity of the assumptions depends on the indistate. vidual molecule but in any event the choice of a value for \triangle_{σ} is not clear-cut; Dixon has chosen, rather arbitrarily, twice the value of the bond dissociation energy for this value. For a double bond the change in the electric field gradient is calculated as

2 2 6 1) . à ţ . t

t. 2 ŧ:): 1 ġ à: •

$$\Delta q_{zz}(A) \cong \epsilon_{\pi}/2 |q_{at}|$$

$$\Delta q_{zz}(B) \cong -\epsilon_{\pi}/2 |q_{at}|,$$

with $\epsilon_{\pi} = eE_{0}R_{B}/(\Delta \pi [(1 - S_{\pi}^{2})2]^{\frac{1}{2}}).$

It is important to notice that these effects are opposite to those of Equation 20; thus, in a bond which has some double-bond character, there will be some cancellation of the effects of the electric field. This has been observed by Dixon and Bloembergen. Using both variational and perturbation approaches, they have developed equations which relate the observed broadening to the sp hybridization and ionic character of the bond; at the present time, however, these equations are too crude to yield meaningful results for the parameters. As will be discussed later e²qQ may also be expressed in terms of these quantities; thus the electric field effect gives another measurable to determine these parameters. It is clear that more work is needed on this effect.

D. <u>The Effect of Temperature on the</u> <u>NQR Absorption Frequency</u>

It is generally found that as the temperature is lowered the frequency of an NQR line increases. Studies of temperature dependence have been used to determine the temperatures at which crystalline phase transitions (28) occur and the temperature at which the barrier to internal rotation for 1.2-dichloroethane is overcome (29). These transition temperatures are recognized because of distinct breaks in

- -.... :: :e ;: : 20 • 23 . Ł 5 ê

curves of frequency <u>versus</u> temperature, the number of lines due to a particular nucleus may change due to a change in crystal structure during a phase transition. Frequently **resonance** lines which are observable at 77°K disappear or greatly decrease in amplitude when the temperature is raised; this effect is not well understood although it is generally attributed to vibrational effects. The disappearance of quadrupole lines has sometimes been attributed to crystalline phase changes and undoubtedly in some cases this is true; however, in other cases the disappearance of the line may be more realistically attributed to vibrational effects. Several compounds show an anomolous effect in that their resonance frequency increases as temperature increases. Haas and Marram (30) have recently attempted to explain this abnormal behavior in chlorine compounds in terms of two competing effects. First, there is the vibrational motion which tends to lower the frequency as the temperature is raised since this increases the amplitude of vibration with a consequent 'averaging out' of part of q_{77} . It has been found that torsional motion dominates the vibrational effect. The second effect is due to the fact that as the temperature is increased the increased bending vibrational motion tends to break down the π bonds causing an increase in the population of the $^{\tt Ch}$ lorine $2p_{\pi}$ orbitals, thus causing the absorption frequency to increase.

Bayer (31) has treated the effect of torsional motion on the quadrupole resonance frequency. Many refinements have

iee: is ' ::: fre ŧ <u>p</u>e ire :: ție fre :::: is 201 :::e Je: Fig

been introduced for this theory but only the simple theory is presented here, since the results are not used explicitly in this work. It is assumed here that the frequency of the torsional motion is much larger than the quadrupole resonance frequency and thus we need to consider only the average effect of torsional motion on the quadrupole resonance frequency. This is almost always true since vibrational motions are usually in the infra-red or Raman region with frequencies of the order of 10^{13} H₂, while quadrupole resonance frequencies are in the order of 10^8 H_z. However, if the vibrational frequencies are not much larger than the resonance frequencies a broadening of the resonance line, rather than a shift occurs and is given by the equation $\Delta \omega \, \mathbf{a} \exp(-\frac{W}{RT})$, where $\Delta \omega$ is the line width change due to rotational motion and W is the Potential barrier to rotation. Tatsuzuki (32) has studied the changes in line width with temperature in 1,2,3-trichlorobenzene and hexachlorobenzene and his results are shown in Figure 4.



a) Hexachlorobenzene, b) 1,2,3-Trichlorobenzene.

 T_a and T_b are transition temperatures after which free rotation takes place. Values for W of 6.0 \pm 0.1 kcal/mole and 12.6 \pm .2 kcal/mole have been calculated from these data for the molecules hexachlorobenzene and 1,2,3-trichlorobenzene, respectively.

Let us consider the effect of pure, very fast torsional motion on an axially symmetric electric field gradient q where the tensor, in the principal-axis system, may be written as

 $= q_{zz} \begin{pmatrix} -\frac{1}{2} & 0 & 0 \\ 0 & -\frac{1}{2} & 0 \\ 0 & 0 & 1 \end{pmatrix} .$

If a rotation of Θ about the Y principal axis occurs then

$$\begin{array}{l} = \\ q = \begin{pmatrix} \cos \theta & 0 & -\sin \theta \\ 0 & 1 & 0 \\ \sin \theta & 0 & \cos \theta \end{pmatrix} & q_{ZZ} & \begin{pmatrix} -\frac{1}{2} & 0 & 0 \\ 0 & -\frac{1}{2} & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} \cos \theta & 0 & \sin \theta \\ 0 & 1 & 0 \\ -\sin \theta & 0 & \cos \theta \end{pmatrix} \\ = q_{ZZ} & \begin{pmatrix} -\frac{1}{2}\cos^2\theta + \sin^2\theta & 0 & -\frac{3}{2}\sin\theta & \cos\theta \\ 0 & -\frac{1}{2} & 0 \\ -\frac{3}{2}\cos\theta & \sin\theta & 0 & -\frac{1}{2}\sin^2\theta + \cos^2\theta \end{pmatrix} \end{array}$$

For small values of Θ , sin $\Theta \stackrel{\sim}{=} \Theta$ and $\cos \Theta \stackrel{\sim}{=} 1$; then,

$$\mathbf{q} = \mathbf{q}_{zz} \begin{pmatrix} \frac{3}{2} \, \theta^2 - \frac{1}{2} & 0 & -\frac{3}{2} \, \theta \\ 0 & -\frac{1}{2} & 0 \\ -\frac{3}{2} \theta & 0 & 1 - \frac{3}{2} \theta^2 \end{pmatrix}$$

S17 • <u>.</u> X ż P: 51 20 5. à :: [: Since we are considering only very fast motion we are interested only in an average angle $\langle \Theta \rangle$ and, since $\langle \Theta \rangle = 0$ when Θ undergoes symmetric vibrations, we write

$$\bar{\bar{q}} = q_{zz}$$

$$\begin{vmatrix} \frac{3}{2} < \theta^2 > -\frac{1}{2} & 0 & 0 \\ 0 & -\frac{1}{2} & 0 \\ 0 & 0 & 1-\frac{3}{2} < \theta^2 > \end{vmatrix}$$

Finally, taking into account simultaneous rotations about the X axis, denoting this angle by θ_{χ} and average angular motion about the Y axis as θ_{v} we obtain

$$\bar{\bar{q}} = q_{zz}$$

$$\begin{vmatrix} \frac{3}{2} < \theta_{y}^{2} > -\frac{1}{2} & 0 & 0 \\ 0 & \frac{3}{2} < \theta_{x}^{2} > -\frac{1}{2} & 0 \\ 0 & 0 & 1 - \frac{3}{2} < \theta_{x}^{2} > -\frac{3}{2} < \theta_{y}^{2} > \\ (33) \end{vmatrix}$$

From Equation 33 we see that we must replace q_{zz}^{o} by

$$q_{zz}(T) = q_{zz}^{\circ} (1 - \frac{3}{2} < \Theta_X^2 > - \frac{3}{2} < \Theta_Y^2 >).$$

Similarly the rotational motion introduces an asymmetry parameter η given by $\eta = \frac{2}{1}(\langle \Theta_Y^2 \rangle - \langle \Theta_X^2 \rangle)$. Neglecting this small value of η we now calculate the resonance frequency as a function of temperature. If we treat the system as a rigid rotator a quantum mechanical treatment gives for the rotational (torsional) frequency v_{θ}

$$4\pi v_{\ell}^{2} < \Theta^{2} > A_{\ell} = k v_{\ell} \left[\frac{1}{2} + 1/(e^{h v_{\ell}/kT} - 1)\right], \qquad (35)$$

where k is Boltzmann's constant and A_{ℓ} is the appropriate moment of inertia. Using this equation

$$\omega(\mathbf{T}) = \omega(0) \left[1 - \frac{3}{2} h/4\pi^2 \frac{1}{A_X v_{\ell X}} \left\{\frac{1}{2} + 1/(e^{hv_{\ell X}/kT} - 1)\right\} -\frac{3}{2} h/4\pi^2 \frac{1}{A_Y v_{\ell Y}} \left\{\frac{1}{2} + 1/(e^{hv_{\ell Y}/kT} - 1)\right\}$$
(36)

and the temperature coefficient becomes

$$\frac{1}{\omega_{0}} \left(\frac{\partial \omega}{\partial \mathbf{T}} \right)_{\mathbf{V}} = -\frac{3}{2} \frac{h^{2}}{4\pi^{2}} \frac{1}{kT^{2}} \left[\frac{e^{h_{\mathcal{V}}} \ell \mathbf{X} / kT}{A_{\mathbf{X}} (e^{h_{\mathcal{V}}} \ell \mathbf{X} / \underline{kT} \ 1)^{2}} + \frac{e^{h_{\mathcal{V}}} \ell \mathbf{Y} / kT}{A_{\mathbf{Y}} (e^{h_{\mathcal{V}}} \ell \mathbf{Y} / kT \ -1)^{2}} \right]$$

$$(37)$$

But the experiments are performed under conditions of constant pressure therefore the measured temperature coefficient corresponds to $\left(\frac{\partial\omega}{\partial T}\right)_{p}$ which can be related to the theoretical temperature coefficient by the thermodynamic equation

$$\left(\frac{\partial\omega}{\partial\mathbf{T}}\right)_{\mathbf{V}} = \left(\frac{\partial\omega}{\partial\mathbf{T}}\right)_{\mathbf{P}} + \frac{\alpha}{\beta} \left(\frac{\partial\omega}{\partial\mathbf{P}}\right)_{\mathbf{T}} , \qquad (38)$$

where α is the thermal expansion coefficient and β is the compressibility. Thus, to relate theory and experiment we need to measure the effect of pressure on NQR frequency. This has been done by Kushida, Benedek and Bloembergen (33) for Cl in KClO₃ and p-dichlorobenzene and for Cu in Cu₂O and by Fuke (34) for SnI₄, As₄O₆, KBrO₃ and p-dibromobenzene. Kushida et al. (33) and McCall and Gutowsky (35) have improved the simple Bayer theory but it has not been possible to obtain quantitative agreement with experiment, probably due to the fact that rotational frequencies are temperature dependent but also because other vibrational modes besides torsional motion become important. Fuke (34) has observed this latter effect in As₄O₆.

. :..; 51. ÷ • • 2 3 22 :: . Ca 1 • 22 3 £ . 23 Ì 0 . :

2

3.

•

E. The Effect of Internal Electric Fields on the NQR Frequencies

The theory of Townes and Dailey which is discussed in the Chemical Theory section, is an attempt to interpret NQR frequencies in terms of chemical parameters. This theory is strictly true only when the individual molecules are not allowed to interact with one another, which is true only when the substances under study are in the gaseous state. Since pure quadrupole resonance experiments must be carried out on a solid, a correction should be made for the effect of the crystal lattice on the NQR frequencies. Although this adds considerable complexity to the treatment of NQR data, it has the advantage of allowing us to investigate solid-state interactions which could not otherwise be studied. Although there is no clear division among these effects an arbitrary division into three different interactions will be made in order to facilitate discussion.

(1) Direct contributions due to the effect of charges situated on neighboring atoms in the crystal lattice. This effect is proportional to r^{-3} and hence should fall off rapidly with distance. However, calculations show that some contributions are felt from atoms 60Å and even 100Å away. This contribution is enhanced in some cases and decreased in other cases, by the Sternheimer effect, which is corrected for by multiplying the calculated ionic field gradient by $1 - \gamma_{\infty}$, where γ_{∞} is called the Sternheimer factor and is positive (with a value between 0 and 1) for shielding and

negative for antishielding. The effect is due to the fact that external charges, besides having a direct contribution to the field gradient, also have an indirect effect due to a distortion of the closed shell electrons around the quadrupolar nucleus. This distortion may decrease or increase the shielding of the quadrupolar nucleus and hence is called antishielding or shielding, respectively. It could also be said that the external charges induce an electric quadrupole moment in the electron distribution around the quadrupolar nucleus. This causes a redistribution of charge in the molecule which in turn affects the electric field gradient felt by the quadrupolar nucleus. This redistribution may be such that it enhances the field gradient (antishielding) or cancels part of the field gradient (shielding). In general small cations such as Li⁺ experience shielding and large deformable anions such as Cl and Br experience antishielding. Sternheimer and others (37-42) have calculated this enhancement factor for a number of neutral atoms and ions. Unfortunately this calculation is very difficult and often two calculations for the same atom will not agree. In particular, Sternheimer has previously calculated a value of -56.6 (41) for $\gamma_{\rm co}$ of the chloride ion; however, experiment (49-54) has indicated a value of -10 as being more reasonable. Burns and Wikner (50) have pointed out that, in a solid, higher symmetry and larger internuclear distances result in pertubations of the large negative anions, and since Sternheimer used wave

s:3: 51 tie: <u>...</u> 2013 ::: in i œÌ (... ... 111 :::] i.s àS est :a] 17. 1 10.6 : i. Ple 15 30.5 àg .e às

functions which only apply strictly to atoms in the gaseous state, it follows that properties which are sensitive to this solid state effect cannot be calculated very accurately with these wave functions. Wikner and Burns (51) tried to correct this by using what they call contracted wave functions. Thev constrained the wave functions to give the correct value for the average diamagnetic susceptibility for the Cl ion in a series of compounds. Using these wave functions they calculated a value of -27.4 for $\gamma_{\rm co}$. Recently Sternheimer (55) has calculated a new value of $\gamma_{\rm co}$ for the Cl $\bar{}$ ion, taking into account second-order effects, and obtains an improved value of -45.89. He also states that the solid-state effects discussed by Burns and Wikner would decrease this value by as much as 2/3 although he did not make any quantitative estimate. Another reason for the poor agreement between the calculated and the empirical value for $\gamma_{\rm co}$ (Cl⁻) can be found in the fact that $\gamma_{\rm con}$ is sensitive to the charge on the ion. This is logical since the more polarizable an ion, the larger the antishielding. For example, in most chloro compounds the charge on the chlorine varies between zero for a chlorine in a completely covalent bond to -1 for a chlorine in a completely ionic bond. Therefore, as an ion becomes more polarizable (more ionic in the case of chlorine), it follows that the antishielding factor should become larger and, furthermore, a smooth increase is expected. The Sternheimer factor for a neutral chlorine atom has been calculated by Sternheimer (37) as +0.42 shielding. This effect is expected to be quite

----: • • • ele :t S1. (0) ii: ti 2: ¥Ì. â . 11: ſe 00 <u>31</u> + |. ... Ĵ: C: 1 fa <u>)</u>0; à::;

important. Figure 5, which is taken from a paper by Das and Bersohn (42), illustrates this point. The sharp increase in going from He° to H^{-} is especially interesting since it roughly parallels the change in going from Cl^o to Cl⁻. In this case the quadrupole moment induced in the closed shell electrons of H is such as to be highly shielding; however, it is quite likely that in a series like Cl^+ , Cl^o , Cl^- a similar curve is followed, especially since we know that γ_∞ (Cl^o) = +.42 and γ_{∞} (Cl⁻) = -45.89. Recent calculations of field gradients in ionic lattices, with the assumption that the charged nucleus may be replaced by a point charge in PrCl₃ (47) and CrCl₃ (48), have yielded reasonable answers when compared to experimental results using an antishielding factor of -10. Since these two compounds are expected to be highly ionic a value closer to -27.04 would probably be more realistic since the experimental values are for less ionic compounds. Correspondingly a lower value for compounds studied in this work is appropriate as they are more covalent than the compounds used in the "experimental" determination of the antishielding factor. Unfortunately the calculation of the contribution of point charges to the field gradient at a quadrupolar nucleus is very sensitive to the Sternheimer factor because q_{zz} (crystal) = $(1 - \gamma_{00})\phi_{zz}$, where ϕ_{zz} is the direct contribution to the field gradient from the external point charges. The large discrepancy between the calculated and the empirical factor is very disappointing and makes it



Figure 5. A plot of the Sternheimer factor (γ_{∞}) versus ionic charge for helium-like ions.

difficult to extract information from a point charge calculation.

(2) Modification of the electronic structure or molecular unit as a result of interactions with neighboring mole-The exact nature of these interactions is not well cules. understood; however, Van der Waals interactions and dipole moment interactions probably occur. The latter interaction results in a small increase in ionic character of the bond and lowers the crystal energy. Table 3 presents the quadrupole coupling constants for a number of molecules in both the gas and the solid state (45). It will be noticed that for chlorine and bromine the coupling constant decreases in going from gas to solid. This implies a gain in negative charge on the halogen atom and, hence, an increase in ionic character. For iodine in ICl and ICN the absolute magnitude of the coupling constant increases implying a gain in positive charge and, hence, an increase in ionicity since iodine has a positive charge in these two compounds.

(3) Additional bonds may occur between neighboring molecules in the solid. Examples of this are hydrogen bonding and formation of polymer-type structures in the solid. This latter behavior has been postulated to explain the NQR results for solid I_2 , Br_2 and ICN. In I_2 an examination of the crystal structure places two near neighbors each 3.54Å from one of the iodine atoms in the iodine molecule. The sum of the iodine Van der Waals distances is 4.35Å; therefore, some

.

4	seell heasured bo				
Molecule	Nucleus	e ² Qq Atomic state	e ² Qq Gas	e ² Qq Solid	Ŀ
cl ₂	35 C1	-109.74		-108.95	
CH ₃ C1	³⁵ C1	-109.74	-74.74	-68.4	
CF ₃ C1	³⁵ C1	-109.74	-78.05	-77.58	
ICI	³⁵ C1	-109.74	-82.5	-74.4	
Brz	⁷⁹ Br	796.76		765.86	0.20
СН _З Вг	⁷⁹ Br	796.76	577.0	528.9	
CF ₃ Br	⁷⁹ Br	796.76	619.0	604.0	
I_2	Izzt	-2292.71		-2156.0	0.16
CH ₃ I	1271	-2292.71	-1929.0	-1766.0	
CF ₃ I	Izzt	-2292.71	-2143.8	-2069.0	
ICI	1271	-2292.71	-2944.0	-3037.0	
ICN	Izzt	-2292.71	-2420.0	-2549.0	

Quadrupole Coupling Constants of Halogen Containing Molecules Which Have Reen Measured Both in the Solid and in the Gaseous State Table 3.

kind of partial covalent bond must be formed between adjacent iodine molecules. This type of bonding has also been postulated for some Sb and Bi compounds (45,46). Examples of hydrogen bonding were studied by Allen (57), and Bray and Ring (58). Their data are given in Table 4.

Compound	Reference	Frequencies (in MHz)			
CCl ₃ CH(OH) ₂	57	38.190, 39.429, 39.515			
$CCl_3CH(OH)(OC_2H_5)$	58	38.516, 38.705, 39.14			
CC1 ₃ COOH	57	39.967, 40.165, 40.240			

Table 4. NQR Data Indicating Hydrogen Bonding

The crystal structure of CCl₃CH(OH)₂ has been determined by Kondo and Nitta (59). They find three C-Cl bond distances of 1.79, 1.78 and 1.72A; the two longer distances are attributed to hydrogen bonding of the hydroxyl hydrogens to chlorines in near neighbors. The quadrupole resonance frequencies for this compound shows a similar grouping, two lines quite close together and one line lying over 1 MHz lower in frequency. The explanation for this is that the two chlorine atoms engaged in hydrogen bonding give rise to the two high frequency lines and the other chlorine atom accounts for the lower frequency line. The lower frequency should be taken when studying the C-Cl bond in the compound and the ::e ile ï.'! :::: the ;a::: a.j ...ee ter. exç 15 str Şec k. . e] à 23

difference between an average of the higher frequencies and the lower frequency may be interpreted in terms of a charge shift in the region between the carbon and chlorine atoms due to the formation of the hydrogen bond. This charge shift will undoubtedly affect the ionicity of the C-Cl bond and, if this is the only effect, NQR data may be used to estimate the extent of charge shift and hence the strength of the hydrogen bond. However, this charge shift may also be accompanied by a change in the sp hybridization of the Cl orbitals and this would complicate the interpretation. More data are needed for this type of compound before quantitative statements may be made. For $CCl_3CH(OH)(OC_2H_5)$ one hydrogen bond is expected and the data roughly indicate this but the situation is less clear-cut; probably the hydrogen bond is not as In trichloroacetic acid no hydrogen bonds are exstrong. pected and the data indicate that none are formed.

Chemical Interpretation of NQR Data

A. Atomic Field Gradients

Let us first consider an atom. What will be the contributions to the electric field gradient at the nucleus from the electrons of this atom? Suppose we had an electron in an atom described by the wave function $\psi_{n \ell m}$ when n is the principal quantum number, ℓ is the azimuthal quantum number and m is the magnetic quantum number. The quantum number m used here should not be confused with the nuclear spin quantum

iet: ; 22 <u>1</u>X19 If · 322 ele lig Ies £..., , . • 5 ¥3 2 1 .

,

number m used previously (it is common notation to use the letter m for both of these quantities). The operator for q_{zz} is $\hat{q}_{zz} = \frac{3\cos^2\theta - 1}{r^3}$, where θ is the angle between the z axis and r. Then, in an obvious notation,

$$q_{n\ell m} = -e \int \psi_{n\ell m} \left(\frac{3\cos^2 \Theta - 1}{r^3} \right) \psi_{n\ell m} dV .$$
 (39)

If we use this equation we can estimate the relative importance of contributions from p(l = 1), d(l = 2) and f(l = 3)electrons and also how q varies with the principal quantum number of the contributing electron. If we use hydrogenlike wave functions Equation 39 may be evaluated to give the result

$$q_{n \ell m} = \frac{2 \ell e}{2 \ell + 3} < \frac{1}{r^3} > ;$$
 (40)

furthermore,

$$\langle \frac{1}{r^3} \rangle = \frac{2 z_i^3}{n^3 a_0^3 l(l+1)(2l+1)}$$
, (41)

where \mathbf{Z}_{i} is the charge on the atom and \mathbf{a}_{0} is the Bohr radius, a constant. Combining Equations 40 and 41 we get

$$q_{n\ell m} = \frac{4 Z_{i}^{3} e}{n^{3} a_{0}^{3}(\ell + 1) (2\ell + 1) (2\ell + 3)} .$$
 (42)

Using Equation 42 for some fixed value of Z_i and n, $q_{n \ell m}$ varies in the ratio 1/30:1/105:1/252 for p, d, and f electrons, respectively. We see then that q falls off quite rapidly with ℓ . This effect is illustrated in Table 5, in which both the experimental and calculated (using Equation 42)

Electronic State	Atom ^b	Experimental Value for q _{nℓ0} x 10 ⁻¹⁵	Relative Value of q _{nℓ0} c
5p	I	-45.0	1.00
5d	Cs	-0.31	0.14
5f	Cs		0.048
6p	Cs	-3.4	0.58
6d	Cs	-0.16	0.08
6 f	Cs		0.028
7p	Cs	-1.1	0.36
7a	Cs	-0.09	0.05
2p	F	-21.0	1.00
3р	Na	-0.7	0.30
4p	Na	-0.2	0.12

Table	5.	Values	of	q _{nℓ0}	=	$\frac{\partial^2 v}{\partial^2 z^2}$	for	Various	Atomic	States ^a
-------	----	--------	----	------------------	---	---------------------------------------	-----	---------	--------	---------------------

^aC. Townes and B. Dailey, <u>J. Chem. Phys</u>., <u>17</u>, 782 (1949).

^bExperimental data are available only for these atoms.

^CObtained using Equation 42. Values are relative to 5p except for **F** and Na which are relative to 2p.

values for q for a given valence are tabulated. It can be seen that the relatively simple Equation 42 predicts intensities fairly well. In the next section we develop an equation for the ratio

$$\rho = \frac{e^2 Qq_{mol}}{e^2 Qq_{at}} , \qquad (43)$$

where $\boldsymbol{q}_{\text{mol}}$ is the molecular field gradient at the position of the quadrupolar nucleus and \boldsymbol{q}_{at} is the field gradient at an identical free atom nucleus. The values for q_{at} are obtained from the splitting of atomic spectra and also from atomic beam experiments. The atomic beam values are much more accurate. In obtaining q_{at} the Sternheimer factor must be taken into account due to the polarization of the inner electrons by valence electrons; this effect must also be considered for q_{mol} . Most chemical interpretations of NQR are given for ρ rather than e^2qQ and it has been previously assumed that taking the ratio cancels out the effect of polarization of the inner shells but for this assumption to be true $\gamma_{\rm con}$ for free chlorine atoms must equal $\gamma_{\rm con}$ for a chlorine in a covalent bond. Let us examine this assumption more closely. If the bonds of a molecule are covalent enough that the direct contribution to the field gradient from external charges may be considered to be essentially zero, then the measured coupling constant e²Qq may be considered to arise entirely from the valence p electrons of the nucleus. These electrons will certainly distort the inner electrons inducing

44

an electronic quadrupole moment characterized by a Sternheimer factor of γ_{m} '; hence, the measured coupling constant e^2qQ = $e^2q_{mol}(1 - \gamma_m)Q$. However, the free atom field gradient q_{at} also arises because of the gradient due to valence p electrons (although it is not the same as q_{mol} due to charge distortions arising from bond formation) and induces a quadrupole moment in the inner shell described by γ_{m} ". Thus, $e^2q_{a+}Q = e^2q_{a+}(1 - \gamma_{\infty})Q$, but because the same mechanism causes the inner shell distortion it is believed that $\gamma_{m}^{\prime} = \gamma_{m}^{\prime\prime}$; then $\rho = q_{mol}/q_{at}$, as desired. This is probably a good assumption. However, when there is appreciable ionic character in the bonds to chlorine (for example, in SnCl₄, HgCl₂, SbCl₅ and other similar compounds) the contribution to the field gradient due to external charges and valence electrons is expected to be more nearly equal and the measured coupling constant must be written as

where

$$\gamma_{\infty}^{i} \neq \gamma_{\infty}; e^{2}Q\phi_{zz}(1 - \gamma_{\infty})$$

 $e^{2}qQ = e^{2}Q[(q_{mol}(1 - \gamma_{\infty}) + \phi_{zz}(1 - \gamma_{\infty})]],$

must therefore be calculated and subtracted from the measured e^2Qq before ρ is calculated.

(44)

B. <u>The Townes and Dailey Theory of</u> <u>Molecular Field Gradients</u>

The following treatment is taken, in part, from Das and Hahn (8). It should be kept in mind that no completely general treatment for the molecular field gradient has been given;

the theory of Townes and Dailey was developed for the particular case of the singly bonded halogens although it may be generalized for other atoms if they are fairly electronegative. In general, however, it is better to consider each nucleus separately and test each approximation of the Townes and Dailey theory to see if it applies in the particular case. All the NOR resonances reported in this work are chlorine resonances; therefore, the original development of Townes and Dailey seems appropriate. The arguments of Townes and Dailey should be regarded as heuristic rather than rigorous. Let us consider how q_{at} of chlorine is modified when the chlorine is bonded to another chlorine in the Cl₂ molecule. The bond is not expected to have any appreciable ionic character, doublebonding or pd hybridization; however, a small amount of sp hydridization may take place. The bonds use the chlorine p_z orbitals and the direction of the z principal axis is along the chlorine-chlorine bond; cylindrical symmetry may be as-Then the electronic distribution in the valence shell sumed. of the bound chlorine atom may be described by the following four wave functions:

$$\psi_{0} = \alpha^{\frac{1}{2}} \mathbf{s} + (1 - \alpha)^{\frac{1}{2}} \mathbf{p}_{z}$$

$$\psi_{x} = \mathbf{p}_{x} \qquad \psi_{y} = \mathbf{p}_{y}$$

$$\psi_{lp} = (1 - \alpha)^{\frac{1}{2}} \mathbf{s} - \alpha^{\frac{1}{2}} \mathbf{p}_{z}$$

The measured value for q corresponds to the integral of atomic wave functions

$$q_{at} \equiv q_{n\ell m} = \int \psi^*_{n\ell 0} \left(\frac{3\cos^2 \Theta - 1}{r^3} \right) \psi_{n\ell 0} dV ;$$

m = 0

for p electrons l = 1 and we must also consider the atomic field gradients q_{nl1} and q_{nl-1} which are related to q_{nl0} by (45) $q_{nlm} = q_{nl0} [1 - \frac{3m^2}{l(l+1)}]$; thus, if $q_{nl0} = q_{at}$, $q_{nl1} = q_{nl-1} = -\frac{1}{2} q_{at}$. This means for a chlorine with one p_z electron we get V_{zz} (atomic) = q_{at} and $V_{xx} = V_{yy} = -\frac{1}{2} q_{at}$, but if the electron were in the p_x orbital then $V_{xx} = q_{at}$, $V_{yy} = -\frac{1}{2} q_{at}$ and $V_{zz} = -\frac{1}{2} q_{at}$. In order to describe the electronic state of the chlorine atom in this molecule we consider the wave functions $\psi_6, \psi_{lp}, \psi_x$ and ψ_y ; then, $q = n_6 q_6 + n_{lp} q_{lp} + n_x q_x + n_y q_y$, where n = the number of the electrons and, for example,

$$\begin{aligned} q_{6} &= \int \psi_{6}^{*} \left(\frac{3\cos^{2}\theta - 1}{r^{3}} \right) \psi_{6} \, dv \\ &= \alpha \int s^{*} \left(\frac{3\cos^{2}\theta - 1}{r^{3}} \right) \, sdv + (1 - \alpha) \int p_{z}^{*} \left(\frac{3\cos^{2}\theta - 1}{r^{3}} \right) \, p_{z} dv \\ \alpha^{\frac{1}{2}} \left(1 - \alpha \right)^{\frac{1}{2}} \int s^{*} \left(\frac{3\cos^{2}\theta - 1}{r^{3}} \right) p_{z} dv + \alpha^{\frac{1}{2}} (1 - \alpha)^{\frac{1}{2}} \int p_{z}^{*} \left(\frac{3\cos^{2}\theta - 1}{r^{3}} \right) \, sdv. \end{aligned}$$

The cross products are ignored because the atomic wave functions are orthogonal and $\int s^* (\frac{3\cos^2\theta - 1}{r^3}) s dV = 0$ because the s electrons are spherically symmetric; hence, $q_6 = (1-\alpha) \int p_z^* (\frac{3\cos^2\theta - 1}{r^3}) p_z dV = (1-\alpha) q_{at}$. Below are listed the contributions to the molecular V_{xx} , V_{yy} and V_{zz} from the various wave functions.
Orbital	Number of Electrons in the orbit	V _{xx}	V yy	Vzz
Ψ _σ	1	$-\frac{1}{2}(1-\alpha)q_{at}$	$-\frac{1}{2}(1-\alpha)q_{at}$	$(1-\alpha)q_{at}$
${}^{\psi}\mathbf{x}$	2	2g _{at}	-q _{at}	-q _{at}
${}^{\psi}\mathbf{Y}$	2	-q _{at}	^{2q} at	-q _{at}
$^{\psi}$ lp	2	-og _{at}	-og _{at}	2 og _{at}
		$\frac{1}{2}(1-\alpha)q_{at}$	$\frac{1}{2}(1-\alpha)q_{at}$	$(-1+\alpha)q_{at}$

We can see from the above that $q \equiv V_{zz} = (-1+\alpha)q_{at}$ and $\eta = 0$. If our bond had some fractional ionic character I, then the number of electrons in ψ_{δ} would be (1+I) and if the bond had some fractional double bond character \overline{T} then the number of electrons in ψ_x and ψ_y would be $(2 - \overline{T}_2)$, so $q = [(-1+\alpha) + (1-\alpha)I + \overline{T}]q_{at}$ but η still is zero.

Let us now consider a chlorine atom in a planar molecule such as a chlorobenzene, then only the p_x orbital takes part in double bond formation so that the orbital populations P become

P (6) = 1 - I P (x) = 2 - $\frac{1}{1}$ P (y) = 2 P (lp) = 2

and the field gradients become

Thus, if η can be determined for these molecules an independent determination of \mathcal{T} is possible. We now attempt to derive the above equations in a more rigorous manner. For an ICl molecule we may write an LCAO wave function

$$\psi = \frac{\psi_{C1} + i \psi_{I}}{(1 + i^{2} + 2iS)^{\frac{1}{2}}}$$
(46)

where S is the overlap integral $\int \psi_{I} \psi_{Cl} dV$ and i is relative contribution of ψ_{I} to the total wave function. The ionic character of a bond is defined as $I = \frac{1 - i^{2}}{1 + i^{2}}$ with ionic character in the bond being allowed for by the parameter i. However, if we consider the bond as being formed by the p_{Z} orbitals of I and Cl then it is known that a stronger bond will be formed if we allow some admixture of other states with the pure p_{Z} state. Energy and symmetry considerations suggest that the most likely states to mix with p_{Z} are s and $d_{Z^{2}}$ states; with this in mind we write the atomic wave functions as

$$\psi_{C1} = (1 - \alpha - \delta)^{\frac{1}{2}} p_{z}(C1) + \alpha^{\frac{1}{2}} s(C1) + \delta^{\frac{1}{2}} d_{z^{2}}(C1)$$

$$\psi_{I} = (1 - \alpha' - \delta')^{\frac{1}{2}} p_{z}(I) + (\alpha')^{\frac{1}{2}} s(I) + (\delta')^{\frac{1}{2}} d_{z^{2}}(I).$$
(47)

Four different contributions to q_{mol} at the chlorine nucleus will now be considered. They are: 1) The two electrons in the molecular orbital Equation 46; 2) The two pairs of p_x and p_y electrons on the chlorine atom; 3) The electrons which were in the $3s^2$ orbital in the free atom. These electrons were previously accounted for with $\psi_{\ell p}$ because in the molecule they are lone pair electrons; 4) The inner shell electrons.

1) The two electrons in the bonding orbital give rise to

$$q = -\int \psi^* \left(\frac{3\cos^2 \Theta - 1}{r^3} \right) \psi dV$$

= $\frac{-2}{(1 + i^2 + 2is)^2} [q_{ClCl} + i^2 q_{II} + 2iq_{ICl}] ,$

where, in an obvious notation,

$$q_{IC1} \equiv \int \psi_{I} \left(\frac{3\cos^2 \Theta - 1}{r^3} \right) \psi_{C1} \, \mathrm{d}V.$$

The term q_{II} gives the contribution of the bonding electrons to the field gradient at the chlorine nucleus when the electrons are near the iodine nucleus. Because of the $\frac{1}{r^3}$ term, q_{II} is very small and is neglected. The term q_{IC1} arises because of contributions from the overlap region. The value of q_{IC1} is certainly less than q_{C1C1} although not as small as q_{II} . Furthermore, it is multiplied by 2i where i is less than unity. If the bond which contains the chlorine nucleus is quite ionic then i is small, but in the case of IC1 Townes and Dailey estimate the ionic character as 0.25 and from this i = 0.775. Reddoch (7) has stated that for i = 1 the error involved in neglecting q_{IC1} is no more than 10%; however, he does not say how this estimate was made. Although we will neglect q_{IC1} this may not be correct for covalent compounds. If we use Equation 47 for ψ_{C1} we obtain

$$q_{C1C1} = (1 - \alpha - \delta)q_{at}(C1) + \delta q_{d_{z^2}}(C1) + 2\alpha^2 \delta^2 q_{sd_{zz}}(C1),$$

where we have neglected two cross terms which are zero because of symmetry.

2) Each of the four electrons in the p_x and p_y orbitals contributes $-\frac{1}{2}q_{at}$ to field gradient as discussed previously, giving a total of - q_{at} .

3) The two lone pair electrons contribute nothing to the atomic field gradient but in the molecule the pure s state gains some p_z character. They then contribute an amount -2α q_{at} .

4) The inner shell electrons of chlorine should contribute nothing to the field gradient but because of polarization by the valence electrons small corrections should be made to q_{at} ; however, these may be made by using a value of q_{at} which has not been corrected for polarization when we calculate the ratio $\rho = \frac{e^2 q Q}{e^2 q_{at} Q}$. This correction has been discussed, it will not suffice for $q_{d_z^2}$ and $q_{sd_z^2}$ but we are planning to neglect them so will not bother with a correction. Collecting all the contributions to the molecular field gradient q_{zz} (Cl) we write

$$q_{zz}(C1) = \frac{2}{1+i^2+2is} [q_{at}(1-\alpha-\delta) + \delta q_{d_z^2} + 2\alpha^2 \delta^2 q_{sd_z^2}].$$
(48)

In order to simplify this equation into an easily usable form, we wish to neglect $\delta q_{d_z^2}$, $\alpha^2 \delta^2 q_{sd_z^2}$ and the overlap

integral product 2is in the denominator. The term $\partial q_{d_2^2}$ may be safely neglected because both δ and $q_{d_{z^2}}$ are quite small, ô being usually less than 5%, and Table 5 shows approximately an order of magnitude decrease in the q_{at} resulting from d electrons compared to that from p electrons. The product $\alpha^2 \delta^2 q_{sd_{2}^2}$ may not so easily be neglected. There is no simple way to calculate $q_{sd_{2}}$ and no experimental values are available. Although its value is expected to be smaller than $q_{p_{\pi}} \equiv q_{at}^{1}$, $\delta^{\frac{1}{2}}$ is expected to be smaller than $\alpha^{\frac{1}{2}}$, hence the product $\alpha^2 \delta^2$ is less than α . For these reasons Townes and Dailey neglect $\alpha^2 \delta^2 p_{sd_2}$. Let us now consider the denominator of Equation 48, $(1 + i^2 + 2is)^{-1}$. A typical value for S falls in the range 1/3, hence for a molecule like Cl₂ or Br₂ where i = 1 the denominator becomes equal to [1 + 1 +2(1) $(\frac{1}{3})$] = 8/3. Therefore, according to Equation 48, for these molecules $\rho = \frac{e^2 Qq}{e^2 Qq_{a+}}$ should equal 3/4 if we neglect sp hybridization. However, the measured ρ values for these two molecules are very close to unity, which is the expected value if we neglect overlap. Gordy (60) has discussed the inclusion of S in the Townes and Dailey formulation. He argues that the overlap term is included to take into account the contribution to the molecular field gradient which comes about because of some charge migration from around the quadrupolar nucleus to the overlap region and this charge must come from the outer regions of the quadrupolar atom. Since the major contribution, to the field gradient comes from the

electronic charge close to the nucleus the effect of the overlap migration is negligible. This argument does not seem valid as it only considers the direct effect of the charge migration and does not consider indirect contributions to the molecular field gradient which must occur as a result of decreased distortion of the inner shells by the outer shells. Furthermore, the Townes and Dailey theory attributes the difference between the free atomic field gradient q_{at} and the field gradient of an atom in a chemical molecule q_{mol} entirely to the valence electrons which, of course, are the electrons which migrate into the overlap region; Gordy conveniently overlooks this point. A more reasonable argument is advanced by Das and Hahn, who refer to some calculations by Schatz of coupling constants for ³⁵Cl in the compounds HCl and CH_3Cl (61), and by Das (62) of the coupling constant for ¹¹B in some boron compounds. They find that due to a contraction of atomic orbitals on molecule formation q_{p_7} may not be strictly equal to q_{at} . This effect may be partially corrected for by neglecting the overlap integral in the denominator of Equation 48. This explanation for the consistent interpretation of NQR data with the overlap integral set equal to zero, in terms of two cancelling effects, seems more reasonable than Gordy's argument. It also suggests that we must be careful to watch for cases in which we do not get a self-cancellation of effects. After neglecting the terms just discussed Equation 48 becomes

$$q_{zz}(C1) = \left[-\frac{2(1-\alpha-\delta)}{1+i^2}q_{at} + 2(1-\alpha)q_{at}\right]$$
 (49)

which, substituting $I = \frac{1 - i^2}{1 + i^2}$ Equation 49, becomes

$$q_{zz}(C1) = [(1-\alpha+\delta-I) + I(\alpha+\delta)]q_{at}.$$
 (50)

We neglect the second order terms $I\alpha$ and $I\delta$ (although in rare cases $I\alpha$ may need to be included) to obtain

$$q_{zz}(C1) = (1-\alpha + \delta - I)q_{at}.$$
 (51)

If we wish to correct for double bonding we define a quantity \mathcal{T} as the electron density in the $p_x(\text{or } p_y)$ orbital of a free chlorine atom minus the electron density in a p_z (or p_y) orbital of a bound atom and call this quantity the fractional double bond character. The population of each p_x (or p_y) orbital is $(2-\mathcal{T}\mathcal{T})$ and $q_{p_x}(\text{Cl}) = -(\frac{1}{2}-\mathcal{T})q_{p_z}(\text{cl})$; the p_x and p_y electrons now contribute an amount $q_{\pi} = -2(1-\mathcal{T})q_{at}$ to $q_{zz}(\text{Cl})$ instead of $-2q_{at}$. Including this correction in Equation 51 gives

$$q_{zz}(C1) = (1 - \alpha + \delta - \pi - 1)q_{at}.$$
 (52)

This is commonly referred to as the Townes and Dailey equation as these two authors derived it originally and it has been used successfully in interpreting NQR data from hundreds of compounds. In a similar manner Equation 53 may be derived:

$$\mathbf{q}(\mathbf{I}) = [1 - \alpha + \delta + \mathbf{I} - \mathbf{I}] \mathbf{q}_{a+}(\mathbf{I}).$$
 (53)

Cotton and Harris (63) have recently developed an equation similar to that of Townes and Dailey but from the molecular orbital, rather than from the valence bond, formalism. These authors claim that under appropriate limiting conditions their equation reduces to the Townes and Dailey equation but they do not explicitly state these conditions. It is interesting to note that their derivation is much more general than that of Townes and Dailey, not requiring an explicit introduction of hybridization. Their proof is no more rigorous than that of Townes and Dailey, although they do attempt to provide a numerical corroboration of their most important assumption. The derivation of Cotton and Harris is given below.

It is desired to calculate the quadrupole coupling constant $e^2 Q_{\alpha} q_{\alpha}$ for a molecule which contains a quadrupolar nucleus designated by α . The wave function for the molecule may be expressed by a product wave function $\Psi = \pi \psi^k$, each ψ^k containing N^k electrons. Each molecular orbital wave function ψ^k may be expressed in the LCAO-MO approximation as:

$$\psi^{\mathbf{k}} = \sum_{i=1}^{n} c_{i}^{\mathbf{k}} \dot{\phi}_{i}$$
(54)

where n is the total number of atomic orbitals ϕ_i of the atoms in the molecule and all the ϕ_i are required to be orthogonal. The total field gradient in the molecule q_{α} may be written as $q_{\alpha} = \sum_{k} N^{k} q_{\alpha}^{\ k} + q_{\alpha}^{\ NUCL}$ where $q_{\alpha}^{\ NUCL}$ is the contribution to q_{α} from the charged nuclei of the surrounding molecule and neighboring molecules and $q_{\alpha}^{\ k}$ is defined by the equation

$$q_{\alpha}^{k} = \int \psi^{k*} \left(\frac{3\cos^2 \Theta - 1}{r^3} \right) \psi^{k} dv . \qquad (55)$$

Using Equation 54, Equation 55 becomes

$$q_{\alpha} = \sum_{k i j} \sum_{j} N^{k} c_{j}^{k} c_{j}^{k} q_{\alpha}^{ij} + q_{\alpha}^{NUCL} ; \qquad (56)$$

where

$$q_{\alpha}^{ij} = \int \phi_i^* \left(\frac{3\cos^2 \Theta - 1}{r^3} \right) \phi_i dv$$
.

Cotton and Harris then break down Equation 56 into three sums, one for each of the following types of q_{α}^{ij} :

- 1) q_{α}^{ii} , one-center integrals in which both ϕ_i are on the quadrupolar nucleus,
- 2) Two-center integrals q_{α}^{ij} and q_{α}^{jj} , where i refers to atomic orbitals centered on the quadrupolar nucleus, and
- 3) $q_{\alpha}^{j\ell}$ where neither j nor ℓ refer to atomic orbitals on the quadrupolar nucleus.

With this arbitrary grouping of terms they now write Equation 56 as

$$q_{\alpha} = \sum_{k} \mathbf{N}^{k} \left[\sum_{i} \left| \mathbf{c}_{i}^{k} \right|^{2} q_{\alpha}^{ii} + \sum_{j} \left| \mathbf{c}_{j}^{k} \right|^{2} q_{\alpha}^{jj} + \sum_{ij} \mathbf{c}_{i}^{k} \mathbf{c}_{j}^{k} \mathbf{q}_{\alpha}^{ij} + \sum_{j \ell} \sum_{j \ell} \mathbf{c}_{j}^{k} \mathbf{c}_{\ell}^{k} \mathbf{q}_{\alpha}^{j\ell} \right] + q_{\alpha}^{\text{NUCL}}$$
(57)

Equation 57 must be simplified as it would be impossible to solve this equation in its present form by any presently known methods for most molecules of any chemical interest. In order to make simplifications the following three approximations are introduced: 1) The sum over all core orbitals on atom α will be taken as a constant **P**. Although this contribution should ordinarily be zero, the Sternheimer effect will cause some contribution to q_{α} ; thus, $\sum_{i} |c_{i}^{k}|^{2} q_{\alpha}^{ii}$ becomes

$$\sum_{\mathbf{i}'} \left| \mathbf{c}_{\mathbf{i}}^{\mathbf{k}} \right|^{2} \mathbf{q}_{\alpha}^{\mathbf{i}'\mathbf{i}'} + \sum_{\mathbf{i}''} \left| \mathbf{c}_{\mathbf{i}''}^{\mathbf{k}} \right|^{2} \mathbf{q}_{\alpha}^{\mathbf{i}''\mathbf{i}''} \equiv \sum_{\mathbf{i}'} \left| \mathbf{c}_{\mathbf{i}'}^{\mathbf{k}} \right|^{2} \mathbf{q}_{\alpha}^{\mathbf{i}'\mathbf{i}'} + \mathbf{P}_{\mathbf{i}''}^{\mathbf{i}'\mathbf{i}''}$$

2) The sum over two-center integrals $q_{\alpha}^{ij''} + q_{\alpha}^{NUCL}$, where j" refers to a core orbital, will be approximated by a constant q_{α}^{CORE} which corresponds to contributions from all charged nuclei and their core electrons external to atom α . 3) The sum over all non-core two-center terms q_{α}^{ij} , plus onehalf of the sum $\sum_{i,j} C_i^{k} C_j^{iq} q_{\alpha}^{ij}$, is assumed to exactly cancel q_{α}^{Core} . Cotton and Harris attempt to justify this assumption by computing the field gradient at one chlorine atom due to the net effective charges on all atoms of PtCl₄⁻. They find, that in this case, the error made in neglecting this effect amounts to about 2.5% of the total field gradient. They do not, however, give anough details of this calculation to allow an estimate as to how good it was. 4) All three-center integrals are neglected. With these assumptions we may now write

$$q_{\alpha} = \sum_{k} N^{k} \left[\sum_{i} \left| C_{i} \right|^{k} \right|^{2} q_{\alpha}^{i'i'} + \sum_{j' > i'} C_{i'}^{k} C_{j'}^{k} q_{\alpha}^{i'j'} \right] + P.$$

Using the Mulliken-type approximation (57)

$$q_{\alpha}^{\mathbf{i}'\mathbf{j}'} = \mathbf{s}_{\mathbf{i}'\mathbf{j}'} q_{\alpha}^{\mathbf{i}'\mathbf{i}'},$$

we write

$$q_{\alpha} = \sum_{i} f_{i}, q_{\alpha}^{i'i'} + P; f_{i} = \sum_{k} N^{k} [|c_{i'}|^{2} + c_{i}^{k} \sum_{j' > i} c_{j'}^{k} s_{i'j'}],$$
(59)

where f_i , is the molecular orbital expression for the occupation of ϕ_i . When Equation 59 is multiplied by e^2Q_{α} we get

$$e^{2}Q_{\alpha}q_{\alpha} = \sum_{i} f_{i} \left[e^{2}q_{\alpha}^{i'i'}Q_{\alpha} + \frac{e^{2}Q_{\alpha}p}{\sum_{i}f_{i'}} \right] .$$
 (60)

The term in the square brackets is then replaced by $e^2 Q_{\alpha} q_{at}$, then with N^k replaced by 2-N^k (since chlorine has one hole in the p shell) we finally get

$$\rho_{\alpha} = \frac{e^{2}Q_{\alpha}q_{\alpha}}{e^{2}Q_{\alpha}q_{at}} = \sum_{i'k} \sum_{k} (2-N^{k}) \left[\left| c_{i'}^{k} \right|^{2} + \sum_{j'>i'} c_{i'}^{k} c_{j'}^{k} s_{i'j'} \right].$$
(61)

This equation has many potential advantages over that of Townes and Dailey although much more extensive computation is needed when it is employed. However, it is not yet clear whether the assumptions involved are any better than those of Townes and Dailey.

C. <u>Evaluation of the Parameters of the</u> <u>Townes and Dailey Equation</u>

From Equation 52, $\rho = (1-\alpha+\delta-I-\overline{M})$, and since we know $e^2q_{at}Q$ and may measure e^2qQ this equation may be used to interpret our experimental data in terms of bond parameters. However, we have only one measureable, ρ , and four parameters; therefore, we must estimate three of the parameters by other means in order to calculate the fourth from our experimental

data. It should be emphasized that all methods discussed in this section apply only to the interpretation of halogen NQR Townes and Dailey (65), and Gordy (66), have discussed data. approximations for obtaining these parameters. Gordv has made two approximations both of which neglect hybridization. In the first he sets α , δ and \mathcal{T} equal to zero and calculates the bond ionicity from the equation $\rho = 1 - I$. For compounds in which some double bonding is expected Gordy sets the ionicity I = $\frac{1}{2} \Delta \chi$ where $\Delta \chi$ is the difference in electronegativity between the two atoms forming the bond. He then calculates \mathcal{T} from the equation $\rho = (1 - I - \mathcal{T})$, again neglecting hybridization. Values of \mathcal{T} calculated using his second approximation are guite reasonable but his neglect of hybridization is not. For example the compound ICl has a coupling constant of 80 MHz and $e^2Qq_{a+}(C1) = 109$ MHz; no double bonding is expected in this compound hence, neglecting hybridization, about 28% ionic character is calculated. This seems much too high and it is reasonable to invoke hybridization to explain this discrepancy. Gordy's assumption of $I = \frac{1}{2}\Delta \chi$ is probably roughly correct, but it gives ionicities which are too high in the region of $\Delta \chi$ = 2. Whitehead and Jaffe (67) have used this same approximation but they use modified electronegativities. Townes and Dailey have also used two approximations, in the first dp hybridization has been neglected. This is reasonable for the halogens since the difference in energy between the p and d states is large and an upper limit of 5% probably may

je nej ic: S 202 . . ¥2 fo À. çr re Ëe . D: 5 ŧ

•

be set on dp hybridization for the halogens. They also neglect double bonding and estimate α according to the following rule: if the atom to which the halogen is bonded is less electronegative than the halogen by 0.25 units or more, then $\alpha = 0.15$, otherwise $\alpha = 0$; δ is always less than 0.05. This rule was proposed by Townes and Dailey partly from a consideration of compounds of the group V and VI "elements" where s character of the bond may be estimated from the formula

$$\alpha = \frac{\cos\phi}{1 - \cos\phi} \tag{62}$$

where ϕ is the angle between the bond in compounds where the group V and VI element is the central atom. Dailey (68) has re-examined this rule for a series of simple alkyl compounds. He finds that for halogens involved in C-Cl, C-Br or C-I bonds the factor 0.15 in the Townes and Dailey equation should be replaced by 0.136, 0.086, and 0.016, respectively. This takes into account both sp and dp hybridization. Coulson (69) has calculated that maximum overlap occurs at about 50% sp hybridization but the curve of overlap versus sp hybridization is quite flat and 25% s hybridization would not cause a large decrease in overlap. The percentage of s hybridization is governed by two competing effects, the energy needed to promote s electrons into the p orbital so that hybridization may take place and the bond energy gained by reason of additional overlap. Thus, s hybridization in the neighborhood of 25% is favored. In addition, the s hybridization of the group V and VI elements as calculated by Equation 62, varies between 10 and 25%. Finally, it is known that the amount of hybridization increases as the ionicity of a bond increases. All these facts indicate that the Townes and Dailey treatment of hybridization is quite reasonable.

When double bonding is expected to be important, Townes and Dailey use the equation

$$\mathbf{R} = \frac{a_1 R_1 + 3 a_2 R_2}{a_1 + 3 a_2} , \tag{63}$$

first derived by Pauling. In this equation R is the observed bond distance in the compound under study, R_1 is the sum of the single-bond radii for the two atoms involved in the bond, R_2 is the sum of the double-bond radii, and a_1 and a_2 are the fractional importance of the single and double bond structures, respectively. Since R_1 and R_2 have been tabulated by Pauling (70), and by Townes and Schawlow (71), and since $a_1 + a_2 = 1$, $a_2 \equiv \pi$ may be calculated if R is To correct for some anomalies observed in internuclear known. distances in fluorine compounds Schomaker and Stevenson (72) have suggested that R_1 be modified to R_1 ' by the equation $R_1' = R_1 - 0.09 \Delta \chi$, where $\Delta \chi$ is the electronegativeity difference. However, in other compounds the correction itself introduces anomalies so it is probably better to disregard it. For well defined covalent bonds, such as a C- C or C- H

bonds, Equation 63 is fairly reliable, but for bonds like Sb-Cl or P-Cl it has more qualitative than quantitative significance. Using these rules to obtain α and \mathcal{T} , Townes and Dailey have calculated the bond ionicity I in a number of compounds and have constructed a graph of ionicity versus $\Delta \chi$ from which it is possible to estimate the ionicity of any bond with the aid of a table of electronegativity. Their graph is reproduced in Figure 6, along with those of Gordy and of Pauling, for comparison. Townes and Dailey argue that their graph is more accurate than Pauling's because Pauling based his values on an incorrect interpretation of dipole moment data.

Although the Townes and Dailey equation (Equation 53) is probably quite good, and for the purposes of comparing a series of similar compounds quite reliable, their treatment loses much accuracy when the various rules are applied to evaluate the parameters in individual cases. Townes has estimated that these approximations are accurate to about 25%. Equation 61 derived by Cotton and Harris, offers certain advantages since their parameters may be calculated much more accurately than those of Townes and Dailey and thus interpretations for individual compounds will be more reliable. The best approach at present to the interpretation of the NQR data must be to interpret changes within a series of chemically related compounds as a function of the change in one specific parameter.



Figure 6. Ionicity <u>versus</u> electronegativity difference according to the approximations of Pauling (70), Gordy (60), and Townes and Dailey (44).

<u>Previous NQR Studies of Charge</u> <u>Transfer Complexes</u>

Douglass (2) was the first to study a charge-transfer complex with NQR techniques. He studied complexes formed by chloranil with several donors. The only compound in which an NQR absorption could be found was the complex of chloranil and hexamethylbenzene. If charge transfer takes place as expected from the hexamethylbenzene to the chloranil, a charge shift from the chloranil ring to the attached chlorine atoms is expected. This charge shift, by increasing the ionicity of the bonds, should decrease the ³⁵Cl NQR absorption frequency. Douglass observed a slight increase in the absorption frequency which he explains by invoking solid-state effects. In substituted benzenes the crystal splittings are about 200 kHz and Douglass points out that the frequencies which result when 200 kHz is subtracted from his measured frequencies correspond to an increase in ionicity in the C-Cl bond of chloranil in the complex. On this basis he obtains an upper limit to charge transfer. There is, however, no good reason for expecting a crystal field effect of this magnitude or even this direction. In organic complexes two types of electron donors are commonly recognized. The first is a π -donor, which donates charge from π_{-} bonds, such as carbonyl bonds, multiple bonds, etc., or donates charge from the π cloud above an aromatic ring. The second is an n-donor which donates charge from lone-pair electrons. Charge-transfer complexes formed by transfer of π -charge are known to correspond

:: :e: <u>;</u>-; Br; si: 3: <u>;</u>] •`. Da 20 ti. = Y to the weakest charge transfer (73). Moreover, charge transfer into the π -cloud of chloranil may not redistribute itself in a simple manner. Hooper (3) has studied the resonance frequencies of ³⁵Cl in a 1:1 complex of CCl₄ and p-xylene and the ⁷⁹Br NQR spectrum in CBr₄·p-xylene and Br₂·penzene. The halogen resonances in CCl₄, CBr₄ and Br₂ show only a negligible shift in frequency upon complex formation. Since the above complexes are uncomplicated by π cloud effects on the acceptors these results indicate that the charge transfer is too small to measure by this method. Duchesne et al. (4) have studied a series of charge transfer complexes between bromine and some substituted benzenes and the results are given below.

Table 6. Frequency Shifts Upon Complex Formation Between Br₂ and Some Substituted Benzenes

Compound	Br Frequency Shift (MHz)
C ₆ H ₆ ·Br ₂	+0.107
C ₆ H ₅ F·Br ₂	-0.04
C ₆ H ₅ Cl·Br ₂	-0.026
C ₆ H ₅ Br·Br ₂	-1.706

The frequency shift for the bromine in C_6H_5Br is -10.384 MHz, while the frequency shift of the Cl in C_6H_5Cl is only -0.004 MHz. These results generally support the work of Hooper and Douglass except in the case of the $C_6H_5Br \cdot Br_2$

complex. Duchesne et al. explain their results in the following manner. For the first three complexes the only mechanism for complex formation is a donation of charge from the π cloud of the ring to the bromine molecule and this type of charge transfer increases the electron population in the antibonding 4p orbitals of the Br atoms. This distribution should be spherical to a first approximation and thus have little or no effect on the Br NQR absorption frequencies. Nevertheless, if any appreciable charge transfer takes place it is puzzling that no frequency shift takes place for the chlorine frequency in chlorobenzene. In the complex $C_{BH_5}Br \cdot Br_2$, however, another type of charge transfer complex may be formed in which the bromine atom of bromobenzene may donate some charge from its lone-pair electrons to the bromine molecule. This type of complex is much stronger than a π -complex (73). Accordingly large shifts for both the bromine molecule and the bromine atom of bromobenzene are found. It is unfortunate that it was not possible to find an absorption in the complex $C_6H_5I \cdot Br_2$ as C_6H_5I is also expected to be an n-donor.

Grechishkin et al. (6) have studied the ¹²¹Sb, ³⁵Cl and ⁸¹Br resonances in a series of molecular complexes of SbCl₃ and SbBr₃ with substituted benzenes and ketones. They find only negligible shifts for the halogens (in those compounds where it was possible to find halogen resonances) and larger shifts for the antimony. These data agree well with the data previously discussed for π -complexes. Since the antimony is

the recipient of the π -charge it is logical that larger shifts are observed; however, e^2Qq_{a+} for ¹²¹Sb is about 10 times that for ³⁵Cl so the relative shift for antimony is negligible. From the above discussion it may be concluded that NQR studies have revealed only a negligible shift in the resonance frequencies for quadrupolar nuclei involved in π -type chargetransfer complexes. The probable reason for this is that such a small charge is transferred in the formation of the π -type complexes that other things obscure the effect of charge transfer on the NQR data; on the other hand, as exemplified by the C₆H₅Br·Br₂ data, n-type charge-transfer complex formation has a noticeable effect on the NQR resonance. For this reason a series of n-type charge transfer complexes formed between quinoline, pyridine and some pyridine derivatives with ICl and ICl₃ were synthesized during the present work. Unfortunately, a search on several of the compounds over a frequency region which should have contained the ³⁵Cl resonance frequencies for ICl and ICl₃ did not yield any absorptions. There is no apparent reason for this failure.

Much stronger charge transfer complexes have been studied by Dehmelt (8) and by Biedenkapp and Weiss (9). These complexes are strong enough so that they may be considered to be formed from a Lewis acid-Lewis base reaction and in these the shifts in the chlorine resonances studied averaged greater than 1 MHz. It was thought (74) that this was outside the range of frequency shifts which may be attributed to crystal

: . - -.... Ξē fr 12 Ta = As(Sn two 970 field effects. Of particular interest are the shifts in the two complexes $AsCl_3 \cdot POCl_3$ and $SnCl_4 \cdot 2POCl_3$; the chlorine resonance frequencies together with the previously measured frequencies for the pure components are given below in Table 7.

Resonance Frequencies (MHz)	Compound	Resonance Frequencies (MHz)
28.993	SnCl ₄	24.294
28.938		24.226
25.406		24.140
25.058		23.719
24.960		
30.213	$AsCl_3 \cdot POCl_3$	29.208
30.117		29.168
21.146		29.154
19.807		24.481
19.035		25.125
		24.799
	Resonance Frequencies (MHz) 28.993 28.938 25.406 25.058 24.960 30.213 30.117 21.146 19.807 19.035	Resonance Compound 28.993 SnCl4 28.938 25.406 25.058 24.960 30.213 AsCl3·POCl3 30.117 21.146 19.807 19.035

Table 7. NQR Resonance Frequencies in Charge Transfer Complexes Compared to the Resonance Frequencies in the Pure Compounds

An inspection of Table 7 reveals that each complex has two distinct groups of frequencies. The higher frequency group may be associated with the chlorine resonances of POCl₃ ni t ie I large zay k lr. W to th elect 25 1 ion: ci.lo ::10 :bse cha: CORE that form (74) 20C Ies St ti, Lea the Str Nà s

•

and the lower frequency group with those of the Lewis acid. We find that the chlorine frequencies in $SnCl_4 \cdot 2POCl_3$ have large shifts relative to the uncomplexed molecules. These may be qualitatively explained in terms of a simple model in which the charge transfer from the oxygen atom of POCla to the tin atom results, by induction, in an increase of electron density on the chlorine atoms of SnCl₄ leading to an increased ionicity in the Sn-Cl bond and a decrease in ionicity in the P-Cl bond. Thus, the NQR frequency of the chlorine atoms of SnCl₄ should decrease while that of the chlorine atoms of POCl₃ should increase as is, in fact, observed. For the AsCl₃·POCl₃ complex, only negligible changes from chlorine NQR resonance frequencies of the pure compound are observed. This may be explained on the basis that no complex, or at most only a very weak complex, is formed as indicated also by data from Raman spectroscopy (74) and from thermodynamic studies (75).

In this study we have prepared a fairly large series of POCl₃ complexes, although it has been possible to find resonances in only four of them. It was thought that the shifts in the ³⁵Cl resonance frequencies in the complex relative to those in the uncomplexed components would give a measure of the acid strengths of the Lewis acids involved in these complexes. In addition, since quite accurate X-ray structures were available for several of these complexes, it was thought that calculations of the field gradient induced

by the charged nuclei in the crystal lattice, combined with the observed splittings of the NQR lines, would yield some information on the solid state interactions in these complexes. λ. <u>Th</u> conce duce rang is đ into s s In (gua fre COM Thu Iet ba] reg had Wàs . Dec per . Down

II. EXPERIMENTAL

A. The Nuclear Quadrupole Resonance Spectrometer

1) Introduction

The problem of finding NQR absorptions is simple in concept. All that is needed is a spectrometer which produces electromagnetic radiation in the proper frequency range, and whose frequency may be varied until an absorption is detected. Since all known guadrupole resonances fall into the frequency region between 0 and 1000 MHz, we need a spectrometer which operates in the radiofrequency region. In this investigation we shall be concerned with chlorine quadrupole resonances, which are expected to fall into the frequency region 0-55 MHz; most of the NMR absorptions of commonly observed nuclei also occur in this frequency region. Thus, it is not surprising that many of the experimental methods are the same. It is not practical to use the balanced-bridge method since the frequency must be scanned, requiring that the bridge be continuously rebalanced. It had previously been thought that the nuclear induction method was unsuitable for the purpose of detecting NQR absorptions because the twofold degenercy of NQR energy levels did not permit any net nuclear induction to appear. Recently, however, it has been found that the application of magnetic

nodu. well this Spec in d They XHz resp VF-1 scog late nost of e Thes in s thr: in 1 COT the MR is the sin Pr_C reg exc.

modulation of about 30 gauss amplitude removes the degeneracy well enough so that it is possible to detect NQR resonances by this method. Hartmann et al. (76), using a Varian Wide-Line NMR Spectrometer, have recently detected chlorine NQR absorptions in bis-ethylene diamminodichlorocobalt(III) chloride·HCl·XH₂O. They detected three resonances at approximately 5, 10 and 15 MHz due to $\pm \frac{3}{2} \rightarrow \pm \frac{1}{2}$; $\pm \frac{5}{2} \rightarrow \pm \frac{3}{2}$ and $\pm \frac{7}{2} \rightarrow \pm \frac{5}{2}$ transitions, respectively, by simply tuning the variable frequency Varian VF-16 oscillator by hand and observing the output on an oscilloscope while the sample was in the probe and the field was modulated with an amplitude of about 30 gauss. However, the most common method for observing NQR absorption is by means of either marginal or supergenerative oscillator-detectors. These consist of a radiofrequency oscillator which is modified in such a way that it detects when the frequency is swept through a resonance. Marginal oscillators are in common use in wide-line NMR but superregenerative spectrometers are less commonly used because of troublesome sidebands, even though they were originally introduced by Roberts (77) for use in In NQR work, however, the superregenerative oscillator NMR. is used almost exclusively, as it is much more sensitive than the marginal oscillator. This is an important consideration since, in general, NQR lines are much weaker than NMR lines. From now on we shall confine our discussion to superregenerative oscillator-detectors as they have been used exclusively in the present work.

the si eter. nacle for s of 2/ effec quali close ratio resor effec the ana] show When ಣ t era] 11]] sati :ege Volt the -

It is of interest to examine the factors which determine the signal-to-noise ratio A_s/A_n in the output of our spectrometer. Pound (79) has calculated this ratio for the case of nuclear quadrupole resonance and found that

$$\frac{A_{s}}{A_{n}} = \frac{V_{c}^{\frac{1}{2}} Q^{\frac{1}{2}} A \int_{h^{2}N_{0}}^{h} (T_{2}^{*})^{\frac{1}{2}} \gamma v^{\frac{3}{2}} (I + m) (I - m + 1)}{2(I + 1) 16 kT(kTBF)^{\frac{1}{2}} T_{1}^{\frac{1}{2}}}$$

for single crystals; this ratio should be reduced by a factor of 2/3 if the sample is in the form of a powder. $V_{\rm C}$ is the effective volume of the resonant circuit, Q is the well-known quality factor of the resonant circuit, A is a constant very close to unity, \int is the filling factor, γ the magnetogyric ratio, N_0 the number of resonant nuclei per cc, v the resonant frequency, T₁ the relaxation time and (kTBF) an effective temperature T, bandwidth B, noise figure F for the spectrometer; T_2^* is a line width parameter roughly analogous to the spin-spin relaxation time in NMR. It may be shown (16) that the optimum signal-to-noise ratio is obtained when $\gamma^2 H_1^2 T_1 T_2^* (I + m) (I - m + 1) = 1$, where H_1 is related to the output voltage of the spectrometer. Since T₁ is generally quite small (typical values being in the range of 1 millisecond) large values for the rf voltage are needed to satisfy this equation. This is one of the reasons why superregenerative oscillators are preferred, since typical rf voltages of 20-150 volts may be developed across the coil of the tank circuit. Marginal oscillators typically only reach

about 0.5 volts, although special circuits (82) are available which can attain voltages in the range of about 20 volts.

2) Superregenerative Oscillators

In Figures 7 and 8 are given the wiring diagrams for two oscillators which were constructed during the course of this work. The first has its circuit parameters chosen so that it works well in the frequency region of 15-55 MHz while the second works well in the region of 2-20 MHz. The lowest frequency NQR line observed was that of $PrCl_3$ at 4.5 MHz and the highest was that of CCl_4 , which has its highest frequency line about 41 MHz, but the oscillators worked well as low as 2 MHz and as high as 55 MHz.

In order to make clear some of the difficulties encountered in frequency measurement we will now briefly sketch the theory of the superregenerative receiver. The distinct feature of this type of oscillator is that the oscillation is periodically dampened or quenched. Two different modes of operation may be distinguished, coherent and incoherent. In the coherent mode the next oscillation cycle is initiated before the decay of the previous cycle to noise level, while in the incoherent mode the next cycle starts from the noise level. The incoherent mode is more sensitive and most radio and radar applications of the superregenerative receiver use this mode but in our applications we require transmitting and receiving properties so use the coherent mode. Operation in the coherent








zode g one. corre two s quenc of tř ¥g + corre ītus spect band shou freg ofte atic the . Sapj ble qui is gu. .i: fr dr: le;

mode gives rise to discrete frequencies rather than a single These frequencies consist of a center frequency, which one. corresponds to the actual frequency, of the oscillator, and two series of sidebands. If v_0 designates the center frequency and $\nu_{\rm O}$ is the quench frequency, then the frequencies of the first series of sidebands correspond to the formulas ν_0 + ν_0 , ν_0 + $2\nu_0$, ν_0 + $3\nu_0$. . . , while the other series correspond to the formulas $v_0 - v_0$, $v_0 - 2v_0$, $v_0 - 3v_0$... Thus, a quadrupole resonance absorption consists of a whole spectrum of lines, one of which is v_0 and the rest are sidebands. Although in theory the amplitude of the sidebands should decrease as they are further removed from the central frequency, in practice the first upper and lower sidebands often have the same amplitude as the central band. This situation is not too bad as we may pick the central frequency of the triplets as the center frequency. However, it often happens that the first and second upper sidebands are comparable in size to the center line while the lower sidebands are quite low in intensity or vice versa and in this situation it is impossible to pick out the center band. Both this problem and that of the closely spaced doublets and triplets of NQR lines will be discussed more thoroughly in the section on frequency measurements.

The quenching action is brought about by periodically driving the voltage of the grid of the oscillator tube to a negative enough value so that current flow is stopped, there then ing (zecha CO...... usua exte tube cond Was the quer lato quer cond osci freç leve as Gue lat *e sti OSC. 10 ail(

thereby dampening the oscillations. The oscillations are then restarted by withdrawing this voltage and again allowing current to flow in the oscillator tube. There are two methods for applying this guench voltage. In the first, commonly referred to as external quenching, a periodic voltage, usually a sine wave of appropriate frequency generated by an external oscillator, is applied to the grid of the oscillator tube. It was found by running test experiments under varying conditions that the best voltage for the external frequency was in the region 4-9 volts. The higher the voltage used the higher the quench frequency that may be used but as the quench voltage is raised undesirable modulation of the oscillator output is introduced. In general, it is desirable to quench at as high a frequency as possible consistent with the condition that a small amount of noise be allowed in the oscillator output. This noise generally increases as the frequency of the oscillator increases, and to keep the noise level down the quench frequency must be continuously raised as the oscillator frequency is increased. Increasing the quench frequency also increases the coherency of the oscillations as is evident from the preceding discussion. Thus, we try to keep the quench frequency as high as possible while still allowing enough noise for the proper operation of the oscillator. Raising the voltage of the external quench introduces more noise (corresponding to more incoherency) thus allowing us to raise the quench frequency, but it also

..... çuer freq :ote exte ligi viti 20d: the OSC. in ; res ing Cur cau flc bec Cüt dec Lay pea ore ota 20the tile

introduces amplitude modulation. At low oscillator frequencies it was sometimes necessary to lower the quench frequency so much that a sharply decreased sensitivity was noted. In summary then, the voltage and frequency of the external quench are adjusted in conjunction to obtain the highest quench frequency (although not too high) consistent with the proper noise and the least amount of amplitude modulation. In the second method, called self-quenching, the oscillation is dampened by the following action. During oscillation current flows in the oscillator tube, this results in a small grid-leak current which flows through the variable resistor R_1 to ground and back to the cathode, thus completing the circuit. During its passage some of the grid-leak current is diverted to charge capacitor C₁ which in turn causes a negative potential on the grid. As more current flows the capacitor becomes more highly charged and the grid becomes more negative until current flow through the tube is cut off. The capacitor then discharges to ground through R_1 , decreasing the negative potential on the grid until current may again flow in the tube, then the whole process is repeated. The quench frequency is mostly controlled by the product of R_1 and C_1 . In the circuit of Figure 7, $R_1 = 2$ Megohm and $C_1 = 50$ pf, permitting quench frequencies in the range 20-40 kHz. This control is logical since the larger is R_1 , the more slowly is C_1 discharged to ground and hence the lower the quench frequency. Again R_1 must be continuously adjusted

as the frequency of the oscillator is changed in order to maintain the proper noise level. The advantage of selfquench is that it is slightly more sensitive than external quench. However, external quench has the advantage that it does not need to be adjusted so frequently as the oscillator frequency is changed and changing frequency does not affect the oscillator frequency; these are both significant advantages. The oscillator can only detect rf power absorption (which would indicate a nuclear absorption frequency) during the build-up of oscillation amplitude following a period in which the oscillation has been quenched. The method of detecting a resonance is to detect a slight lowering of the rf voltage at the plate of the oscillator tube. This lowering comes about in the following manner. For a selfquenched circuit, an absorption of power lowers the base voltage upon which a new oscillation cycle must start, thus it takes a longer time for the grid to reach the cut-off voltage, corresponding to a decrease in quench frequency. Since a decrease in quench frequency means fewer bursts of rf voltage at the plate in a given time, the average rf voltage at the plate decreases; this decrease is the basis for detection of the absorption. For an externally quenched frequency circuit the quench frequency is fixed but the average amplitude of the rf bursts is lowered by an absorption, which the plate sees as a drop in average rf voltage. The high-range oscillator may be operated as either a self-quenched or externallyquenched oscillator. In order to operate it with external

quench, R₁ is switched from ground to a BNC connector at which the output from the guench oscillator is injected and the value of R_1 is then decreased until self-quenching stops. Capacitors C_2 and C_3 are adjusted by experiment to obtain the most sensitive operation of the spectrometer but as a general rule if one is more open the other should be more closed. For this reason they are connected in tandem in the low-range oscillator such that as one opens the other closes. The frequency of the oscillator within a given range is varied by tuning the tank capacitor C_4 . The range of the oscillator may be changed by changing the tank coil L_1 . Typical coils allow a range of about 10 MHz. The sample to be studied is inserted directly into the tank coil and since most searches and measurements are made at liquid nitrogen temperatures some extension of this coil is needed outside the oscillator. At first this was done by means of a standard shielded cable RG-58/U but this caused problems because it introduced increased capacitance into the tank circuit. Although the problem was partially solved by using special low-capacitance cable RG-62/U this was not completely satisfactory because shielded cable was not rigid enough, the oscillator being very sensitive to vibration, and it was very inconvenient to change coils. All these problems were overcome in the following manner: A $\frac{1}{2}$ inch O.D. brass tube 6 inches long was rigidly mounted to the spectrometer chassis and fitted at the bottom with a male BNC connector. A $\frac{1}{2}$ inch

solid brass rod was then run down the middle of the tube, being careful to keep the rod and the tube electrically isolated since the tube was grounded. The end of the rod was reduced and sharpened and used as the pin in the BNC connector, the other end of the rod being connected to the side of C_4 which was above ground. The various coils were then mounted on female BNC connectors thus making coil changing quite simple and easy.

In the process of building high frequency oscillators certain good practices should be followed. It is well-known that length of leads is critical but only in certain parts of the circuit. The most critical lead lengths are the lengths of wire between resistors, capacitors, etc. and the oscillator tube. Thus, for example, a resistor which is to be connected to the tube should have its connecting wire cut off as close to the resistor body as possible, allowing only a long enough lead to insure a good solid joint; the lead on the other side of the resistor body is not important. It is also good practice to get a chassis much larger than needed and to place the oscillator tube socket in the center allowing plenty of hand room so that the elements directly attached to the tube may be squeezed in quite closely. Lead lengths in the tank circuit do not seem to be critical but they should be of heavy gauge bare wire, preferably the tin coated variety. They should not be placed close to the walls of the chassis, if possible, as the wall and the wire tend to form a capacitor.

all g
and t
sime
osci 1
all d
rect
this
ycod
call
reso
Simp
lati
lati
thr
ars
Cau
Doà
11
sig
or
a c
tea
1.
ja:

All grounds in the oscillator should be to one firm ground and the tube socket center should also be grounded to this same ground. This helps to avoid ground loops and parasitic oscillations. Finally, particular care should be taken that all components are mounted solidly and rigidly.

3) Modulation and the Lock-in Amplifier

In NMR work a resonance absorption may be detected directly by a drop in rf power at the receiver but in NQR work this drop in power is too small to be directly detected. Accordingly, a method has been adapted from radio technology called modulation. As applied to the observation of nuclear resonance absorptions the concept of modulation is quite simple. In NOR there are two types of commonly used modulation, frequency modulation and magnetic, or Zeeman, modulation. When the frequency of the oscillator is passing through resonance both types of modulation cause the rf power absorption to appear at the frequency of the modulation, thus causing a signal to appear in the oscillator output at the modulation frequency, although this signal is not necessarily in phase with the audio generator producing the modulation signal. When no absorption is taking place the modulation has no effect on the oscillator output. Thus, the appearance of a component in the oscillator output at the modulation frequency means that the frequency of the oscillator coincides with an NQR absorption frequency in the sample under study. This signal is much easier to detect than a drop in rf power.

is c iete arp] Wide thy nar Iod lin mi Thi rec con Iod lir 2-; 30(haj <u>j.</u> CO ty <u>ר</u> ÞC Se 20 73 0ŗ

In frequency modulation the frequency of the oscillator is constantly varied over a small frequency range which is determined by the amplitude of the modulation. The modulation amplitude should be determined by the width of the resonances. Wide resonances need large frequency excursions when sweeping through them; hence, large modulation amplitudes are needed; narrower lines require a smaller amplitude. Since excessive modulation amplitude tends to distort and broaden absorption lines the minimum amount of modulation should always be used. This is particularly true when using the lock-in amplifier recording technique. The frequency of modulation is another consideration. The most important consideration is that the modulation frequency must be small compared to the absorption line width. Since line widths have been observed from about 2-50 kHz, modulation frequencies generally should not exceed 300-400 Hz. It is also not advisable to use 60 cycles, or any harmonic or sub-harmonic, when using the recorder technique due to the danger of picking up line noise. Aside from this consideration many workers seem to prefer higher frequencies, typically 280 Hz, in order to avoid flicker noise but this is not a very convincing reason since flicker noise is only important for frequencies below about 10Hz. In this work several standard signals were recorded at widely varying modulation frequencies. The results showed a surprising variation in signal-to-noise ratio with modulation frequency. **Optimum modulation frequencies usually fell around 39 Hz so**

this be of lati of s pres plac para prop to i quer the of (the reg the sho Wor ste 1 ir In sta <u>g10</u> OSC üsi this modulation frequency was adopted. No explanation can be offered for the variation in signal amplitude with modulation frequency.

Although there are many schemes for frequency modulation of superregenerative oscillators the one adopted in the present work is believed to be the best. It consists of placing a 1N950 diode D_1 , which acts as a capacitor, in parallel with the tank capacitor. The diode then has the property that its capacitance varies with the voltage applied to it. Thus, if a periodic voltage is applied to D_1 the frequency of the oscillator is varied periodically. For example, the 1N950 varies in capacitance from 0-88 pf with a variation of 0-130 volts. The slope of a graph of the capacitance of the diode versus applied voltage changes in different voltage regions so the diode is biased with a d.c. voltage to bring the voltage into the region with the desired slope. Figure 9 shows the auxiliary unit used for frequency modulation in this work. It can accept either 60 Hz line voltage, which is stepped down to 6 volts rms with a filament transformer, or 1-10 rms volts of audio voltage supplied by an audio oscillator, in this case a Hewlett-Packard Function Generator Model 202A. In either case the audio frequency is supplied to an interstage transformer with a 2:1 ratio which steps up the voltage and also acts as an impedence matching device for the audio oscillator. The auxiliary unit also supplies a d.c. bias using a standard Eveready 45-volt battery.





I and di field of a n sample Thus, volta the s perio sine esser. Dodul produ direc only indu the r of a vess samp Vire þer the supp ied:

In magnetic modulation the absorption is made to appear and disappear periodically by applying a periodic magnetic field to the sample. As previously explained, the application of a magnetic field of sufficient size to a polycrystalline sample will cause the resonance to broaden out and disappear. Thus, when a square wave or half-wave rectified sine-wave voltage is applied to a Helmholtz coil or a solenoid in which the sample is placed, the resonance disappears during the onperiod and appears during the off-period. If an unrectified sine wave is applied, the situation is more complex but essentially the signal appears and disappears twice during a modulation cycle, since both positive and negative voltage produce the same magnitude magnetic field (although oppositely directed), and the broadening of NQR absorption lines depends only on the magnitude of the applied field. Accordingly, the induced frequency in the oscillator output appears at twice the modulation frequency.

Magnetic modulation in this work was applied by means of a solenoid wound in four layers around a cylindrical Dewar vessel. The sample is placed inside the Dewar vessel in the sample coil and both are immersed in liquid nitrogen. The wire was of small enough gauge to permit winding forty turns per inch over the length of three inches and the diameter of the Dewar was three inches. The sinusoidal current was supplied from the Hewlett-Packard Function Generator which was fed into a Fisher 100-watt power amplifier. This amplifier

5105 thre <u>177</u>5 . 10% In 1 sig narı we (our in t 0.2 sig banc but W15 sig lat the cen Ian Pha: tior ș bļ A Cut Setw supplies currents in the range 0.1 to several amperes rms; three amperes roughly corresponds to a field of 400 gauss rms at the center of the solenoid.

The signal-to-noise ratio for many NQR signals is so low that it may not be easily observed on the oscilloscope. In this case some device must be found which improves the signal-to-noise ratio. Abragam (78) has shown that the narrower the band width around the modulation frequency which we observe, the better the signal-to-noise ratio. Thus, if our modulation frequency is 39 Hz and we observe all signals in the output of our oscillator in the frequency range $39 \pm$ 0.1 Hz our signal-to-noise ratio will improve compared to signals observed in the range 39 ± 1 Hz. The narrower this bandwidth the more improved will be our signal-to-noise ratio but there is a practical lower limit to the bandwidth. We wish, then, to use a narrow-band amplifier to amplify only signals at the modulation frequency in the output of the oscil-The oscillator output will also contain some noise at lator. the modulation frequency at which the narrow-band amplifier is centered, but the phase of this noise will not be fixed but The signal induced by the modulation will be of fixed random. phase although not necessarily the same phase as the modulation. If we pass the output of the narrow-band amplifier into a phase-sensitive detector, then the output of the detector A_{out} is proportional to $A_{in}\cos\theta$, where θ is the phase angle between the input signal from the narrow-band amplifier and

the reà int shi 23X ser À s lev con ser dis Sir the the li àbs cha de ti ab. Un: ne(Ia <u>dia</u> fou guq

the modulation signal; the noise will then be greatly reduced. The input to the phase-sensitive detector is put into phase with the modulation by passing it through a phaseshifter circuit, the amount of phase shift being set by maximizing a strong known signal. The output of the phasesensitive detector is then rectified and fed to a recorder. A signal may be detected by noting marked changes in the level of the d.c. output to the recorder. An amplifier which consists of a narrow-band amplifier followed by a phasesensitive detector is called a lock-in amplifier. For further discussion of the lock-in amplifier see references 78-81. Since the modulation amplitude is set at only a fraction of the line-width when using a lock-in amplifier the output of the amplifier is proportional to the slope of the absorption line and a first-derivative curve is obtained instead of an absorption curve. If desired, an output proportional to the change in slope of the absorption line may be obtained by detecting at twice the modulation frequency; a second derivative of the absorption line is then obtained. This is desirable if amplitude modulation is troublesome. Also, if an unrectified sine-wave magnetic modulation is used it is necessary to detect at twice the modulation frequency. A homemade lock-in amplifier constructed according to a circuit diagram by Bolte (81) was first used in this work but it was found that there were several mistakes in the wiring diagram and even when these were corrected the amplifier never worked

reliab amplif factor lock-i report All th corde neasu obser tivel When first the : the cent is s in s Cent Càn freq tern ۵. ir_{di} reliably. A Princton Applied Research Associates Lock-in amplifier Model JB-4 is now used and has worked quite satisfactorily. No NQR spectrometer would be complete without a lock-in amplifier since approximately half of the signals reported in this work could not be observed on an oscilloscope.

Figure 10 shows a block diagram of the spectrometer. All the important parts have been discussed. A typical recorded NQR spectrum is shown in Figure 11.

4) Frequency Measurement

If the NQR absorption line whose frequency we wish to measure is a single sharp line strong enough to be easily observable on an oscilloscope, frequency measurement is relatively straightforward. The method is based on the fact that when the quench frequency is changed by an amount $\Delta\nu_{Q}$ the first upper sideband moves up in frequency by an amount $\Delta\nu_{\rm O}$, the second upper side band increases in frequency by $2 \Delta \nu_{O}$, etc., the lower sidebands similarly move to lower frequency. The center frequency, in theory at least, does not move but this is strictly true only for externally quenched oscillators; in self-quenched circuits, changing R_1 slightly does alter the central frequency and this movement of the central frequency can greatly confuse the measurement. However, once the high frequency oscillator was modified so that it could be externally quenched this uncertainty was removed. From the above discussion it is clear that the sidebands far removed from the center frequency move quite radically upon small





// // //



chang volta of al small itand some is t it i The band the the and Cnt ext sup is re] wit CSC ide siı ab; Là tr: <u>t</u>1, à

changes in the quench frequency. Without changing the quench voltage, which usually greatly alters the line shape, changes of about 5 kHz in the quench frequency may be made. Such a small change does not alter the positions of the closer sidebands on the oscilloscope screen so there is usually still some ambiguity regarding the center line. A further problem is that when an external signal is coupled to the oscillator it is received as a series of sidebands and a center band. The problem then becomes one of superimposing the central band of the external signal source upon the central line of the resonance spectrum. A useful technique is to pick out the three or four strongest lines from the external source and the sample absorption. Each sample line is then tuned onto the oscilloscope in turn and tested with each of the external source lines. Each external line is imperfectly superimposed on the absorption signal, the quench frequency is then varied and the two lines observed to see if they move relative to one another. This technique is usually successful with strong lines. However, even if the center line of the oscillator and that of the external source are correctly identified, it is very difficult to superimpose them exactly since there is a marked difference in line shape between absorption lines and those from the signal generator. This may lead to an error which has been estimated at 1 kHz from trial measurements on NaClO₃. If the NQR line is not a singlet the absorption spectrum becomes quite complex, due to overlapping of the sideband patterns. In this work the POCl₃

lines the ca specti study: solve compl est l is ju them. ments how : atter of t infa fide the from freq üse(Lea lea tha gie CSC fcl

lines in both TiCl₄·2POCl₃ and (TiCl₄·POCl₃)₂ overlapped. In the case of $(TiCl_4 \cdot POCl_3)_2$ it was possible to resolve the spectrum into three lines after a considerable time spent studying the spectrum but it has not yet been possible to resolve the spectrum of $TiCl_4 \cdot 2POCl_3$. In the case of the more complex spectra the best procedure is to pick out the strongest lines and measure their frequency by superimposing what is judged to be the center line of an external oscillator on them. The quench frequency is then changed and the measurements repeated. From a study of the results, keeping in mind how sidebands behave upon changing the quench frequencies, an attempt is then made to distinguish the number and frequencies of the center lines. Needless to say, this procedure is not infallible. In the case of $(TiCl_4 \cdot POCl_3)_2$ additional confidence in the results is gained from the agreement between the experimental results and the line multiplicity as predicted from the X-ray structure of this compound. In all cases ten frequency measurements were made for each line and an average used for the line frequency. From the precision of individual measurements of the same line, and from previous trial measurements on NaClO₃ and p-dichlorobenzene, it is believed that all frequency measurements made by the above techniques are accurate to \pm 3 kHz.

When absorption lines are too weak to be observed on the oscilloscope screen a different technique must be used. The following method was found to be the best of several methods

::: ing ati 0þ, ie ce: the lir poi si att rec lir SCC whi the Ced 007 fre Wit the <u>)</u> ± 5 . De fre ch_O;

tried. The line was first recorded repeatedly while changing oscillator settings, modulation amplitude and lock-in amplifier settings, until the best recorded spectrum was obtained. This spectrum was then studied in an attempt to determine if it was a singlet or not. The most likely center lines were then picked out and the spectrum rerun at the slow speed of 1/500 rpm and stopped on each of the likely lines in turn. An effort was made to stop at the exact zero point of the first derivative, but this was not always possible, because of a lag between the recorder and the lock-in amplifier. Furthermore, it was not possible to tell if the recorder was stopped at the correct spot. The correct center line from the external oscillator was then centered on the oscilloscope and this line was then centered on the frequency at which the oscillator was stopped by observing the output of the narrow band amplifier on another oscilloscope. The procedure was then repeated at another quench frequency and by comparison of the shifts induced by the change in quench frequency the center line was decided upon. By comparison with measurements on known compounds \pm 10 kHz is believed to be the accuracy of lines measured by this method. The precision of measurement is, however, somewhat better. Unfortunately, \pm 5 kHz was the maximum change in quench frequency which could be obtained. Since the uncertainty in measuring the quench frequency was \pm 10 kHz this allowed some ambiguity in the choice of the center line.

d C. tı Ve . s; ez :e

(ŝ

It is believed that any line whose frequency was measured on the oscilloscope is accurate to \pm 3 kHz while those measured on the chart are accurate to \pm 10 kHz. However, especially in the latter case, there is a chance that a sideband was mistakenly chosen as the center line. This possibility is inherent in all frequency measurements involving superregenerative oscillators but is often ignored by authors when assessing their possible errors.

5) <u>Spectrometer Operation and Problems in</u> <u>Detecting Resonances</u>

Searching for an NQR absorption is often frustrating and disappointing. Relatively minor things may cause the line to be missed. For example, some lines are quite sensitive to modulation while others are not. For no apparent reason some lines are quite intense while others with the same number of resonating nuclei per unit volume are quite weak. In some cases the latter phenomenon has been attributed to subtle differences in crystal structure although no one cares to go into this matter too deeply. For example, it is found that certain liquids which are rapidly cooled to liquid nitrogen temperature give no resonance signals but if they are cooled very slowly they do have resonance absorptions. This behavior is attributed to the fact that rapid cooling probably developed strains in the crystal lattice and these strains somehow erased the signal. Order-disorder phenomena also have an effect as shown by the following phenomenon observed by Dean (85): no signal was found for chlorine in p-chlorobromobenzene

but i.e se: 13 di) 0Í ce: si: WC: SO: spe at to phi li: th à. fi th e] **c**0 • ti 601 05
but when a small percentage of p-dibromobenzene was mixed with the p-chlorobromobenzene a chlorine signal appeared. The absence of absorption was explained on the basis of a certain randomness in the crystal structure of p-chlorobromobenzene due to the fact that the halogen sites have equal probability of being a bromine or a chlorine atom. When the p-dibromobenzene was added the crystal structure became more ordered since there was now a higher probability that a halogen site would contain a bromine atom. Khotsyanova (86) has explained some of his results in a similar manner. He has studied the spectrum of C_8Cl_5F which consists of 3 lines of $77^{\circ}K$, while at $195^{\circ}K$ no lines are observed. He ascribes this behavior to a crystalline phase transition to a totally disordered phase.

It is also found that impurities have an effect on NQR lines. Some types of impurities have a more marked effect than others, but all impurities tend to broaden an NQR line and lower its intensity.

Another factor which contributes to the difficulty of finding NQR lines is the wide range of frequencies at which they may occur. This difficulty is especially troublesome in elements which have a large quadrupole moment. Compounds containing these nuclei have potentially a very large absorption frequency, yet if they are involved in a highly ionic bond the absorption frequency can be quite low. An example of this is $12^{7}I$ (Q = -0.75) whose $\pm 5/2 \rightarrow \pm 3/2$ transition

ireque Portun predic but ca such a same (indeed pounds 1 Tissed This } princi pole 1 n J Lade : backs as po or, if was m oven to mi near. overn. Stadu; nitrog liquid frequency ranges from 29.5 MHz in CdI_2 to 902 MHz in ICl. Fortunately the expected frequency range for ¹²⁷I may be predicted from studies on similar ³⁵Cl containing compounds but calculated predictions have not been successful for nuclei such as ⁵⁵Mn (Q = 0.6) and ⁵⁷Co (Q is expected to be of the same order of magnitude as Q for ⁵⁵Mn) and it is difficult indeed to predict where NQR absorption will take place in compounds containing these elements.

Finally, it should be mentioned that NQR absorptions are missed in many compounds for no apparent reason whatsoever. This happens more often than is desirable and is one of the principal drawbacks to the widespread use of nuclear quadrupole resonance.

The frequency sweeps in search of unknown resonances were made so as to minimize as many of the above mentioned drawbacks as possible. First, the sample was packed as tightly as possible into a glass vial to maximize the filling factor, or, if the sample could be melted without decomposition, it was melted into the sample tube. It was then annealed in an oven overnight at a temperature just below its melting point to minimize strains. If the sample was a liquid, or a solid near its melting point at room temperature, it was precooled overnight in a refrigerator then slowly cooled to 77° K by gradually lowering it into a Dewar vessel containing liquid nitrogen which had been pretreated by adding a small amount of liquid nitrogen and allowing it to stand long enough to

establish a temperature gradient in the rest of the Dewar.

Various methods were tried for adequately sealing sample tubes which contained substances highly reactive with air. At first rubber stoppers were inserted and sealed with plastic tape. This was not successful as the corrosive samples were found to attack both the rubber and the tape. Then Nylon stoppers were machined and inserted into the glass tubes containing the sample; these were sealed in with a tape especially resistant to chemicals and the top of the tube was coated with paraffin. At first this method was successful, even though the samples attacked the tape, but repeated immersions of the sample into liquid nitrogen soon flaked off all the paraffin. The final measurements were made on samples sealed into glass tubes. This seems to be the only satisfactory way to handle corrosive samples.

In order to avoid temperature gradients, samples were kept in liquid nitrogen for half an hour prior to beginning the search. This was much longer than necessary but was a convenient time since it took this time to warm up the spectrometer and make some preliminary adjustments.

The range of a particular coil was governed by the inductance of the coil, the larger the inductance the lower the frequency range of the coil. Thus, the larger the number of turns in a coil the lower its frequency range. In order to obtain a good Q for the tank circuit these should all be of the same size and the coil should be wound neatly with

closely spaced turns. All coils used in this work were 1.5 cm in diameter. However, if too many turns were wound on a coil, the coil became quite unwieldly. Conversely, in coils intended for a high frequency the number of turns became too few causing a serious drop in rf power in the Both of these problems were solved when it was noted coil. that a coil wound with fine gauge wire always had a larger inductance than a coil with the same number of turns of heavier gauge wire. Coils with a few turns were wound with heavy gauge wire while those intended for the low range of the oscillator were wound with small diameter wire: those for intermediate ranges had their wire gauge chosen to give a convenient number of turns. Below is given a table of coil size and gauge together with the frequency range of the coil.

Number of Turns	Wire Gauge	Frequency Range in MHz
9	18	15-22
12	16	21-27
7	16	24-32
5	14	28-36
4	14	32-42
3	14	36-48

Table 8. Physical Dimensions of the Coils Used with the High Range Oscillator

pr. si sa an CO Ca is re aı U: r T. Ŀ a t The settings for the lock-in amplifier are maximized prior to the beginning of each run by use of a strong known signal. This signal should be as close to the expected sample frequency as possible.

When all is in readiness, a low frequency modulation amplitude is chosen and the frequency range provided by the coil being used is swept. This is done by means of a Holtzer-Cabot motor of 120 inch-ounce torque and 1 rpm speed which is fed to an INSCO speed reducer that may be set to provide reductions of 1:1, 2:1, 5:1, 20:1, 50:1, 100:1, 200:1, 500:1, and 1000:1. The speeds of 1/500 and 1/200 were most often If the recorder trace showed no signals, the frequency used. range was swept again with a larger modulation amplitude. This was repeated with several different modulation amplitudes. In some cases both frequency and magnetic modulation were used although frequency modulation was used most often. The noise level of the spectrometer was kept at a level which was determined through trial and error on known signals.

All frequency measurements were made with a BC-221 Frequency Meter whose frequency was then counted with a Hewlett-Packard Model 524C Electronic Counter. The direct reading on the electronic counter was compared to the corrected frequency read from the charts on the BC-221 and in all cases agreement was excellent.

01 a ť. r (2 Cā co Ξa 50. anc the so] tai for The to cer li B.

sta

6) <u>Temperature Dependence of the 27.312 MHz</u> <u>Resonance in SbCl₅·POCl₃</u>

It was decided to measure the temperature dependence of the strong ³⁵Cl line of SbCl₅ in SbCl₅·POCl₃ to see if a crystalline phase transition took place. For this purpose three slush baths were prepared to cover the temperature range from liquid nitrogen $(77^{\circ}K)$ to room temperature (297[°]K). These were carbon disulfide, ethyl acetate and carbon tetrachloride. An ice-water mixture was tried but could not be used because the mixture damped out oscillations. Each bath was made by adding about 200 cm³ of reagent to a 500 cm³ Dewar vessel and then adding liquid nitrogen in small amounts. The mixture must be vigorously stirred otherwise the two liquids quickly separate. The mixture finally solidifies and is allowed to melt until a thick slush is ob-This mixture easily holds its temperature $\pm 1^{\circ}K$ tained. for about 30 minutes, after which it must be resolidified. The samples were allowed to equilibrate with the slush baths to eliminate temperature gradients and the resonance pattern centered on the oscilloscope screen. The frequency of the line was then measured by the method given previously.

B. Chemical Syntheses

The methods for the preparation of all samples and standard compounds are given below.

1) <u>Trans-dichlorobisethylenediamine Cobalt(III)</u> <u>Chloride.HCl.xH₂O</u>

free mate 16 1 fir. ₩as nc] vol Was a d bea des of sti in jet int con lar a c cry Wit par The atm Gai

This compound was desired as a standard for the low frequency oscillator since it has ⁵⁷Co resonances at approximately 5, 10 and 15 MHz and a weak ³⁵Cl resonance at about 16 MHz. It was prepared by the method of Bailar (87). At first it was not known that the HCl occluded in the lattice was essential to observation of the ⁵⁷Co resonances so that no precautions were taken to retain the HCl which is very volatile and evaporates if the complex is air dried. When it was realized that HCl was essential the complex was dried in a desiccator over concentrated sulfuric acid with an open beaker of concentrated hydrochloric acid also inside the desiccator. The procedure is as follows: Six hundred grams of a 10% (by weight) ethylenediamine solution was added while stirring to a 2-liter flask containing 160 gms of CoCl₂·6H₂O in 500 ml of water. A vigorous stream of air from the air jets in the hood was filtered through glass wool and blown into the solution overnight. Three hundred milliters of concentrated HCl was added, the whole mixture poured into a large evaporating dish and then heated on a steam bath until a crust was formed over the surface. The bright green crystals of the complex were filtered off and quickly washed with alcohol then ether. The crystals at this point had partially turned to a dull green indicating some loss of HCl. They were then transferred to the desiccator and dried in an atmosphere of HCl gas. During the drying process they regained their bright green lustre.

t : (ł f S١ <u>d</u>(di a] ci it p. 0; 2: W W 0 ť С t)

2) The Cu(I) Complexes of Some Thiosemicarbazones

These 1:1 complexes were synthesized so that an attempt to find ⁶³Cu(I) resonances in diamagnetic compounds could be made. Thiosemicarbazones of the following ketones and aldehydes were made and complexed with CuCl:acetone, cyclohexanone, benzaldehyde, o-chlorobenzaldehyde, o-methoxybenzaldehyde and m-nitrobenzaldehyde. Each was made by reacting the corresponding ketone or aldehyde with thiosemicarbazide in a reaction quite similar to that used in forming hydrazones and oximes. The following procedure was adopted from the method of Sah and Daniels (89): 0.05 moles of thiosemicarbazide, 100 ml of water and 10 ml of glacial acetic acid were warmed on a steam bath until the thiosemicarbazide dissolved and the solution then added immediately to an alcoholic solution of the ketone or aldehyde. Usually a precipitation of the product occurred immediately but sometimes it was necessary to cool in an ice bath. The copper complexes were made as follows (Gingras et al. (88)): 0.05 moles of the thiosemicarbazone were dissolved in methanol (about 200 ml) and heated to reflux in a three-necked flask equipped with a stirring motor. To this solution was added dropwise, while stirring, 0.05 moles of CuCl dissolved in about 100 ml of ammonia solution (0.9 specific gravity). The mixture was then stirred and refluxed for an additional thirty minutes, cooled to room temperature and the complex filtered off in the form of a dark sludge ranging in color from light gray to

a dark olive green. The complexes were purified according to individual methods as recommended by Gingras. In the case of the o-methoxybenzaldehyde complex, which was not made by Gingras, the procedure for the p-methoxybenzaldehyde complex was followed. It should be mentioned that these complexes do not seem to be soluble in any of the common solvents hence recrystallization, the most reliable purification method for solids, could not be used. The purification procedures consisted of washing with various solvents and solutions. It is not known how pure these compounds are. The complexes seem to be quite stable and have been stored in plastic topped bottles for over a year without noticeable decomposition.

3) <u>Mercuric Chloride Complexes</u>

Mercuric chloride has a strong NQR absorption at about 22 MHz; hence, several complexes were made to see if the resonance line shifts upon complex formation. The preparation of $HgCl_2 \cdot (CH_3)_2 SO$ followed one of the methods of Selbin et al. (90).

Approximately 20 ml of dimethylsulfoxide was heated on a steam bath and saturated with mercuric chloride. Upon cooling transparent crystals separated. An attempt was made to recrystallize these crystals from acetone; however, an oil formed. Addition of ethyl ether followed by scratching the side of the beaker with a glass stirring rod, however, produced a white transparent precipitate of good crystalline form. The melting point as given by Selbin et al. was

3 1 ¥ Ī b 5 (; i: 0; t Wé £1 С(pł Þ ad à] ta **C**() $125-6^{\circ}C$ and the first time the complex was prepared it had a melting point of $125-6^{\circ}C$. The second time it was prepared a waxy rather than a crystalline material was obtained which, when recrystallized from ethyl ether, yielded a compound with a melting point of $77-8^{\circ}C$. Although this compound was put in a vacuum desiccator connected to a vacuum pump for several weeks no complex with a melting point $125-6^{\circ}C$ was obtained. It is suggested that this compound may be $HgCl_2 \cdot 2(CH_3)_2SO$ but no attempt was made to determine its formula because neither complex yielded an NQR resonance.

The four complexes (Pyridine)₂·HgCl₂, $(2-\text{Picoline})_2$ ·HgCl₂, (3-Picoline)₂·HgCl₂ and (4-Picoline)₂·HgCl₂ were made according to the following procedure: To a saturated ether solution of HgCl₂ the base was added and the white flocculent precipitate which appeared immediately was removed by filtration and washed 5-6 times with cold ether. It was then recrystallized from methanol, placed in a vacuum desiccator and the desiccator connected to an oil pump for several days.

Preparation of the dimer of the 1:1 complex of triphenylphosphine mercuric chloride (91). When a solution of triphenylphosphine in absolute alcohol (5.2 gms per 250 ml) was added to a solution of mercuric chloride in hot absolute alcohol (5.4 gms per 250 ml) the complex immediately precipitated in the form of glistening white scales. These were collected and dried in a vacuum desiccator.

4) <u>The Complexes of ICl with Pyridine</u> and its Derivatives

The complexes of pyridine, 3-cyanopyridine, 2-bromopyridine and quinoline with iodine monochloride were prepared with a method adapted from Meyer (92) which depends on the fact that ICl and all the organic bases are guite soluble in CCl₄ but most of the complexes are not. The method is as follows: The base and ICl were each dissolved in CCl₄ in approximate one-to-one molar ratios, the two solutions mixed together and the complex allowed to precipitate. The colors of the precipitates ranging from mustard yellow guinoline ICl to bright yellow 2-bromopyridine ICl. This precipitate was, however, mixed with some brownish red particles, also the solution remained brownish red. Evidently the complex formation does not go to completion, the reddish brown color being attributed to ICl. The original solution was decanted, fresh CCl₄ added, and the whole mixture gently warmed on a steam bath. After a time this solution was also decanted, and the process repeated until no more red particles could be observed mixed with the complex and the CCl₄ remained transparent in color. The complex was then air-dried.

5) Binary Complexes of POCl₃

Since the complexes are quite difficult to prepare, and to various extents react with moisture, no attempt will be made to give a general preparation, as has been done for the compounds previously discussed, but each preparation will be described individually. The compounds all have in common the

fact that they are hydrolyzed quite easily by the moisture in the air and every precaution must be taken to ensure as little contact as possible with the atmosphere. All operations involving extensive handling of these compounds were carried out in a dry box under nitrogen atmosphere. All reactions were carried out under an atmosphere of purified nitrogen which had been passed through a drying column. After the reaction was completed the reaction flask was quickly sealed and opened only in the dry box. The physical appearances of these compounds are quite diverse, some are low-melting waxy solids, while others are powders. It was found that the waxy solids were more stable and could be handled in the air for longer periods of time without decomposition.

The complexes SbCl₅·POCl₃, TiCl₄·2POCl₃, SnCl₄·2POCl₃ and (TiCl₄·POCl₃)₂ were all made by the same general method. Two 250 ml Erlenmeyer flasks were first flushed out with nitrogen, then about 25 ml of the acid was quickly added to the first flask and the flask was weighed again. In the case of the TiCl₄ complex, POCl₃ was then carefully weighed into the other flask on an OHAUS CENTIGRAM balance, such that the molar ratio of POCl₃ to TiCl₄ was either 2:1 or 1:1. The POCl₃ was then quickly added to the TiCl₄ and the flask again stoppered. Immediately an exothermic reaction took place and the solution became bright yellow; upon cooling the whole mass solidified. The mixture was then melted, stirred and allowed to resolidify to ensure good mixing of the

components. The solid was then completely melted and allowed to solidify except for the last few milliliters which were discarded. This process was repeated twice. The complexes were then stored in a vacuum desiccator over P_2O_5 . In the case of $SbCl_5$ and $SnCl_4$, only one complex is formed with $POCl_3$ so that a little excess reagent was added to ensure complete reaction. At first excess POCl₃ was added as recommended by Gutmann (93) but this did not work as well as excess acid, since excess acid was much easier to remove when the complex was pumped on with a vacuum pump. The SbCl₅ complex was a pale lemon yellow color, which may possibly have been due to a slight impurity of SbCl₅, while the SnCl₄ complex was colorless. BiCl₃·POCl₃ and SbCl₃·POCl₃ were also made by this method but since only a slight warming of the solution occurred, and the mixtures were cloudy liquids after cooling, there is some doubt that the complexes actually formed. Raman data show that frequencies are only shifted slightly in the mixture so the complexes are weak or nonexistent.

The preparation of 2FeCl₃·3POCl₃ and FeCl₃·POCl₃ followed a modification of the procedure of Gutmann and Baaz (94). FeCl₃ which was slightly wet was dried in the following manner. A three-necked one-liter flask was fitted with a reflux condenser whose top was closed off with a Drierite tube, a dropping funnel and a connection which allowed dry nitrogen gas to be constantly passed through the flask. This flask was flushed out for 30 minutes with dry nitrogen and about 20

qm of wet $FeCl_3$ and 100 ml of thionyl chloride was added. The mixture was refluxed on a steam bath for about three hours, until the thionyl chloride had reacted with all the water. The condenser was then put into distilling position and the excess thionyl chloride distilled off. A large excess of POCl₃ was then added to the dark black anhydrous FeCl₃ through the dropping funnel The resulting solution is a deep brownish red and was refluxed for an hour to ensure complete reaction. It was then transferred to a 250 ml Erlenmyer flask and the solution partially evaporated by use of an aspirator while warming the flask in a beaker of hot water. When the mixture was reduced to a rather viscous appearance it was transferred to the freezing compartment of a refrigerator and allowed to solidify. This process may take several weeks. The solid was allowed to warm at room temperature, at which point it remained a solid but with some drops of excess POCl₃ still adhering; these were removed by evaporation in a stream of dry nitrogen. The complex, which is a dark reddish brown spongy solid, was then transferred to a drying pistol and evacuated: the pistol was left connected to a vacuum pump until a constant weight was obtained. This latter process may also take several weeks. The complex is very easily hydrolyzed and should be handled quite carefully. Another preparation, due to Dadape and Rao (95), was tried with much less success. In this method advantage is taken of the fact that while FeCl₃ is not soluble in CCl₄ the

complex is quite soluble in hot CCl₄ and POCl₃ is quite soluble in CCl₄, hot or cold. A large excess of anhydrous \mathbf{FeCl}_3 is placed in a one-liter flask and 600 ml of dry CCl₄ is added along with 50 ml of POCl₃. The mixture is heated for an hour on the steam bath with constant stirring and the **l**iquid decanted from the remaining $FeCl_3$ and cooled in an ice bath at which point the complex precipitated and was filtered off. Perhaps some arrangement could be made to carry out these operations in a dry atmosphere and a better yield could be obtained but the only time this method was tried $m \odot st$ of the complex decomposed during the filtration step. **In** all other preparations of this complex the first method was preferred. FeCl₃·POCl₃ was made from the 2FeCl₃·3POCl₃ as follows: 2FeCl₃·3POCl₃ was placed into a drying pistol, the temperature raised to about 55° C by refluxing acetone, and the pistol connected to a vacuum pump. After several h_{Ours} the brown $2FeCl_3 \cdot 3POCl_3$ changed to greenish yellow $\mathbf{Fecl}_3 \cdot \mathbf{Pocl}_3$ by loss of \mathbf{Pocl}_3 .

The complex BCl₃·POCl₃ was made by the following pro-Cedure: A 250 ml Erlenmeyer flask was first flushed out with dry nitrogen, then cooled in a slush bath of dry ice and isopropanol. BCl₃ gas was condensed in the cooled Erlenmeyer flask and an amount of POCl₃ added such that the BCl₃ was in large excess. The very volatile excess BCl₃ was evaporated with an aspirator leaving behind a white powder. During the removal of the excess BCl₃ it was discovered that the complex

sublimes at room temperature under reduced pressure. The complex was stored in a vacuum desiccator over P_2O_5 .

The two complexes AlCl₃·POCl₃ and 2AlCl₃·3POCl₃ are probably the most difficult to prepare. Groenveld and Zuur (96) have studied the temperature versus composition diagram for the system AlCl₃: POCl₃ and they report three complexes, AlCl₃·POCl₃ (m.p. $186^{\circ}C$), AlCl₃·2POCl₃ (m.p. $164^{\circ}C$) and AlCl₃·POCl₃ (m.p. 41[°]C). They report making these compounds by sealing stoichiometric guantities of the reactants in heavy-wall glass tubes and melting the mixture. They also report making ALC1₃·POC1₃ (m.p. 186⁰C) by dissolving AlC1₃ in POC1₃ and removing the excess POCl_a with a vacuum pump. Gutmann and Baaz (94), on the other hand, on the basis of conductivity measurements find that the only possible complexes between AlCl₃ and **POC**₁₃ are AlCl₃·POCl₃ (m.p. 180° C) and 2AlCl₃·3POCl₃ (m.p.) 160° c) and do not mention a low-melting complex. It is interesting to note that Gutmann and Baaz obtain 2A1Cl₃·3POCl₃ **by** a method identical to that described by Groenveld and 2uur (96) for the preparation of AlCl₃·POCl₃. These reports are not encouraging to one who wishes to make these complexes with a minimum of fuss and bother. In all the preparations the AlCl₃ used was first purified by vacuum sublimation. In the first attempt to make these complexes AlCl₃ was dissolved in POCl_a, the mixture placed in a vacuum desiccator and Pumped on with an oil pump. A dirty white powder was obtained Whose melting point was about 50°C. This was pumped on for

Several weeks without any change. Finally the powder was transferred to a drying pistol which was heated with refluxing acetone. The melting point of the complex then started to rise as POCl₃ was removed and continued to rise until all the POCl₃ was lost. No complexes were obtained and several variations of this procedure also produced no results. In a second attempt to prepare these complexes, several thick-wall q lass tubes were obtained with sealed bottoms and constricted necks for easy sealing. The tubes were about five inches **long** with about three inches of the tube below the constriction. Approximately one gm of $AlCl_3$ was weighed into each tube and stoichiometric amounts of POCl₃ added to each tube **COrresponding to the AlCl₃: POCl₃ ratios of 1:1, 1:2 and 2:3.** The tubes were quickly dipped into liquid nitrogen to prevent reaction or vaporization of the reagents while the tube was **being sealed off with a gas-oxygen torch.** The constrictions $\mathbf{w} \mathbf{e}_{\mathbf{r}} \mathbf{e}$ wiped clean with a cotton swab and sealed. The tubes were then allowed to come to room temperature. With suitable **Preca**utions in case of an explosion each tube was heated with **a** Fisher burner until the contents melted together. These Were the samples which were used in the NQR experiments.

6) Ternary Complexes of POCl₃

In addition to the binary complexes of $POCl_3$, a number of ternary complexes were also made. $[Al(POCl_3)_6][SbCl_6]_3$ (97) Was prepared in a 3-necked 1-liter flask which was continually flushed with dry nitrogen and was equipped with a stirring

motor and dropping funnel. A 10^{-1} M solution of SbCl₅ in **POC**₁₃ was placed in the flask and a 10^{-1} M solution of AlCl₃ in POCl_a added dropwise until a ratio of 3:1 was reached. **The** resulting precipitate was filtered in a dry box and washed with dry CCl_4 . It was then transferred to a vacuum desiccator to remove any CCl_4 and $POCl_3$ remaining. A similar **procedure** was followed in preparing $[Al(POCl_3)_6]$ [FeCl₄]₃ (97), substituting FeCl₃ for SbCl₅; also the AlCl₃ was added to the solution of FeCl₃ until a color change from red to pale green occurred. K[TiCl₅·POCl₃] was made by the following **procedure:** Using the same set-up as the previous preparation, $TiCl_4$ was added dropwise to a suspension of KCl in POCl₃ until a molar ratio of 1:1 was attained. The solution was **COncentrated** in vacuo until a good crop of yellow crystals was **b**tained. The flask was then transferred to a dry box where the crystals were removed by filtration and washed with dry CCl_4 . They were then dried in a vacuum desiccator over P_2O_5 . **SbC**1₅·TiCl₄·3POCl₃ was prepared by the following procedure (98): SbCl₅ and TiCl₄ were dissolved in a 1:1 molar ratio in d_{ry} ethylene chloride and POCl₃ added in excess. The mixture **Was** concentrated under vacuum, filtered in a dry box and Washed with dry CCl₄. Finally, the resulting crystals were Sublimed in vacuo at a temperature of 180-200°C.

All solvents used in this work were dried with Drierite and then with magnesium sulphate. The solvent was then de-Canted and distilled taking only the middle cut. They were stored over Drierite.

III. CALCULATION OF THE CONTRIBUTION TO THE MEASURED FIELD GRADIENT FROM CHARGES SITUATED IN THE LATTICE

A. Introduction

As mentioned in the theoretical section, contributions to the quadrupole coupling constant may result from charges external to the molecule being investigated. These charges are situated at fixed points in the lattice and the approximation is often made of replacing these charged atoms by point charges. In order to avoid confusion in subsequent **discussions** the following definitions are made. The molecular **fi**eld gradient tensor $\overline{\overline{g}}^{mol}$ at a nuclear site is due only to electrons within the molecule and is the gradient which would be measured if the molecule was completely isolated. The \mathbf{crys} arises due to solid State effects and is a property of the crystal lattice. $\mathbf{T}\mathbf{n}$ this thesis a model has been introduced which ascribes this effect to point charges situated in the lattice; thus, the term crystal lattice field gradient will often refer to Contributions from this source. This calculation is not a simple one for several reasons. As previously mentioned a Correction must be made by use of the Sternheimer factor for the fact that the chloride ion is highly polarizable. The uncertainty in assigning a value for γ_{∞} (Cl⁻) has been

discussed. Another problem is that, for the compounds we wish to discuss, it is not certain exactly what charge to assign to each point because the compounds which are investi**qated** in this work are partially covalent. Thus, it is not **realistic** to assign the charge of the fully ionic species, but the partial charge on the ion is very difficult to determine. Sharma and Das (99) have shown in calculations on **A** $1_{2}0_{3}$, Fe₂ 0_{3} and Cr₂ 0_{3} that a rather large contribution to the electric field gradient comes about from the dipole induced in the highly polarizable $0^{2^{-}}$ ion. These contributions have been neglected in the present case partly because, since all the ions involved are much less polarizable, this contribut ion is much smaller than that expected from 0^{2-} , and partly be cause this effect would be extremely difficult to calculate **in** our case. The above three approximations introduce enough uncertainty into the actual lattice sum calculations that the **results** of the calculation should be used with caution in **quantitative** predictions. The lattice sum results are, however, guite valuable as a measure of the differences in **env**ironment of crystallographically different but chemically Similar chlorine atoms. In particular this is of value When trying to determine the relative acid strength of a series Of Lewis acids. It is important to make sure that the chlorine atoms one is using as test probes be in roughly equivalent Crystal atmospheres. An attempt is made here to get an idea of the size of the external contributions to the field

gradient. When these contributions are determined, it must be decided whether their effects overshadow chemical effects. Another reason for evaluating these sums is to explain the observed multiplicity of the NQR lines. The splittings have been attributed to chemically similar atoms in crystallographically nonequivalent lattice sites. However, few attempts have been made so far to explain even qualitatively these splittings by use of the crystal structures. Furthermore, if these crystal lattice sums could be evaluated in a more satisfactory manner, detailed information on solid state interactions would be obtained.

One final problem with these calculations should be mentioned. The calculations essentially consist of summing a function of θ and r⁻³ over various sites in the crystal lattice. This summation procedure is continued until the sum converges. In theory this convergence should be rapid because of the r⁻³ term; in practice, however, this is not found to be the case because the lattice sums are conditionally convergent rather than absolutely convergent. The usual practice is to pick a ^SPhere of arbitrary radius (usually 20-60Å) around the atom at which the lattice sum is desired and then to sum over all atoms contained within this sphere. For crystals in which the molecules are close packed, this may correspond to summing over 250,000 atoms. Even with the use of high speed computers, this procedure is very time consuming and convergence is by no means assured even for this number of atoms. An alternative

procedure is to mathematically change the conditionally convergent sum to an absolutely convergent sum. This was the method applied by DeWette (100) and DeWette and Schacher (101-102). DeWette (100) first developed his method for crystals with a fourfold or sixfold axis. The method had the disadvantage that the direction of the field gradient principal axis must be known. Jones, Barnes and Segal (103) applied **DeW**ette's method to the calculation of the field gradient in number of ionic halides. They assumed that the principal axis was along the sixfold axis. Unfortunately this is true on Ly if the atom whose field gradient is being calculated lies on the sixfold axis which is not true for several of the molecules studied by them, introducing a considerable error in these cases. In order to find the principal-axis direction it is necessary to calculate all nine components of the field gradient tensor and then diagonalize the tensor; q_{zz} will be that component of the diagonalized tensor which is largest **in** absolute magnitude. DeWette and Schacher have extended DeWette's original method so that all nine components of the field gradient tensor may be calculated for any crystal symmetry. This work is the first attempt to use this new method f_{Or} the calculation of crystal field gradients. Dickmann (104) has computerized the method of DeWette and Schacher for the purpose of calculating the electric field in a crystal due to permanent dipoles in the lattice. This program LATSUM has been obtained from Dr. Schacher and suitably modified for

the present purpose. This modification consisted of adding several subroutines, which first diagonalize the calculated tensor by rotating the axis system to the principal-axis system in order to obtain q and η . The tensor is then rotated to the principal-axis system of the molecular field gradient in order to evaluate the contribution of the crystal lattice to the measured field gradient. The main program was also modified so that the electric field gradient rather than the electric field is calculated and also so the program may be cycled for the several hundred lattice sums needed, rather than separately for each one.

B _ Theory

For the sake of completeness, a brief discussion of the **theory** involved in the calculation of the electric field **gradient** at a nucleus due to external charges situated in **a** crystal lattice will be given.

In order to calculate the full tensor Q two types of sums must be evaluated

Axial sums
$$Q_{\nu\nu} = \sum_{j} \epsilon_{j} \left(\frac{3\nu_{j}^{2} - r_{j}^{2}}{r_{j}^{5}} \right)$$
 and
Off axial sums $Q_{\nu\rho} = \sum_{j} \epsilon_{j} \rho_{j} \nu_{j} / r_{j}^{5}$ (65)

where the $Q_{\nu\rho}$ are the elements of the tensor \overline{Q} , the index j ideally runs over all the atoms in an infinite crystal, and ϵ_j is the charge at the jth atom. Both of these sums were

derived under the point-charge assumption. Previous workers, taking their cue from Bersohn (105), have aimed at the direct evaluation of these sums for all the lattice sites contained in a sphere of radius ranging from $20-100^{\circ}$ which is about the largest sphere for which this direct summation procedure is practical. However, in some cases these limits do not include enough atoms to ensure convergence. This problem can be critical as the value of the sum is usually guite small compared to individual terms since these terms are both positive and negative and the final sum is a small difference between two large terms. Although the terms fall off quite rapidly as distance from the central nucleus increases, terms quite far away from the nucleus can make significant contributions to the lattice sum. Thus, workers using this method should prove convergence of their sums but this is not easy to do and has been neglected in most cases. In our particular case a sphere 100° in diameter would contain about 400,000 atoms. Since this is too many for the CDC-3600 computer to do in a reasonable time we looked for a method which ensures faster convergence of the lattice sums.

DeWette used another approach, first evaluating the sum in each plane and then adding these sums for the complete set of planes. Each sum may then be made to converge absolutely in each plane which may be seen by considering the following simplified version of our lattice sums method:

$$\mathbf{S} = \sum_{n=1}^{\infty} f(n), \qquad (66)$$

where f(x) goes slowly to zero as $x \to \infty$ and may be infinite at x = 0. This is exactly the behavior of the general terms in our sums (65) because of the r^{-3} term. In order to ensure good convergence for (66) we introduce an auxiliary function F(x) which is finite at x = 0 and goes to zero rapidly as $x \to \infty$; now (66) may be rewritten as

$$\mathbf{s} = \sum_{n=1}^{\infty} \mathbf{f}(n) \mathbf{F}(n) + \sum_{n=1}^{\infty} \mathbf{f}(n) [1-\mathbf{F}(n)] .$$
(67)

The first sum of Equation 67 is absolutely convergent but the second is not. However, if f(x) [1-F(x)] is a smoothly varying function of x then its Fourier transform is a rapidly converging function in Fourier space. Utilizing the property that a sum of a function over a lattice in real space is equal to the sum of its Fourier transform over the reciprocal lattice in Fourier space, we can evaluate the second sum. A third condition on F(x) is that it must be such that f(x) [1-F(x)]be a smooth function at x = 0 even if $f(0) = \infty$. For the functions f(x) with which we will be concerned, it is always possible to find an auxiliary function F(x). Thus, we see from the above discussion that the sums obtained in this work may always be made absolutely convergent by introducing an auxiliary function and dividing the original sum into two parts, one being summed over the ordinary lattice and the other being summed over the reciprocal lattice. However, if f(x)is not infinite at x = 0 and is fairly smooth it is not necessary to find an auxiliary function. Instead the Fourier

transform of f(n) is taken directly and summed over the reciprocal lattice; only one sum then needs to be evaluated. Schacher and DeWette have given the necessary formulas for the evaluation of these sums and they are embodied in LATSUM. It turns out that if the sums are first evaluated in a plane the summation may be replaced by an integration. The sums are therefore not evaluated in a sphere, as in the usual practice, but in a cube. It is also more convenient to consider each atom in the unit cell separately. A lattice sum over all atoms at the equivalent position in each adjacent cell is taken, including enough adjacent cells to ensure convergence. The coordinates of the position are chosen so that the atom at which the field gradient is desired is at the origin of the unit cell. Each nonequivalent chlorine atom of the unit cell will have associated with it a total field gradient. For each total field gradient calculated, nine sums, one for each of the components of the tensors, are evaluated, multiplied by the charge of the site at which they were evaluated and added to the sum of the previous components calculated, which have also been multiplied by their respective charges. In this way an electric field gradient tensor is obtained with respect to a chosen coordinate system. The tensor is then diagonalized to transform it to the principal-axis system. The maximum contribution to the field gradient which may be obtained in this lattice can thus be obtained.

To illustrate this process consider a fully ionic molecule MCl₂ with two molecules per unit cell. Suppose further that each of the chloride ions associated with a particular M²⁺ occupies a crystallographically nonequivalent position so that the unit cell consists of two M^{2+} ions and 4 Cl⁻ ions at three nonequivalent positions. Because MCl₂ is totally ionic the measured field gradient would be expected to arise entirely from external contributions of the crystal lattice. Then, unless both nonequivalent Cl sites accidently experience identical Van der Waals forces and identical electric fields due to charges in the lattice, two quadrupole resonance absorptions would be expected. Furthermore, the difference between the two measured gradients should give some measure of the solid-state interactions which occur, since in the gas phase both of the chloride ions should be identical. In order to obtain the contribution to the field gradient from the charges in the lattice, sums at each of the nonequivalent positions must be evaluated. Designating two of the chlorines as Cl(A) and the other two as Cl(B) the whole lattice is divided into sublattices, each sublattice with a different atom from the unit cell at its corner. Since the unit cell contains six atoms there will be six sublattices; each sublattice consists of atoms of the same charge. To find the lattice sum at Cl(A) this atom is placed at (000) and the coordinates of the other five atoms with respect to this origin found. The sums are evaluated to yield a tensor at each of the six points. These

tensors are each multiplied by the proper charge and added together to yield the total field gradient at site A with respect to a chosen coordinate system. To obtain the field gradient due to external charges at site B this whole process must be repeated with one of the Cl(B) atoms at the origin. To obtain the principal values of the tensor and the relation between the principal-axis system and the chosen system, the tensors were diagonalized to give the principal values and the resulting eigenvectors gave the angular relation between the chosen axis system and the principal-axis system.

C. <u>Some Details of the Modification and</u> <u>Use of LATSUM</u>

LATSUM, as it was originally set up, calculated the contributions to an internal electric field in the crystal from the electric dipoles situated in the lattice. This was done by evaluating nine sums such as Equation 65; since the tensor system is symmetric and traceless, there are only five independent components to evaluate. The input data consist of the three unit cell lengths a, b, and c and the three angles α , β and γ for the crystal unit cell. Another card must be punched with the convergence limit and the maximum number of cells N to be summed over. The program sums over successive cells until the value contributed by the next cell is less than the convergence limit or until the number of neighbor cells summed over is equal to N. Values of N and the convergence limit should be chosen as some compromise between

speed and accuracy. If N is made large enough the sums may be made to converge to any desired accuracy but this may make the summation process too time-consuming. Values of N=20 and a convergence limit of 10^{-7} were used at first. However, it was found that some sums which were very close to the plane containing the origin of the cell did not converge so the convergence limit was changed to 10^{-5} and N set equal to 80; with these limits all sums converged satisfactorily. The final output data which the original program needed were the coordinates of the atom in the unit cell whose sublattice was to be summed over. Each sublattice then required a separate computer run which is unsatisfactory. For example, $(TiCl_4 \cdot POCl_3)_2$ has 80 atoms in the unit cell and there are seven crystallographically nonequivalent chlorine sites in the unit cell; this means that 560 sums must be performed. The first change in LATSUM, then, was to allow multiple sums to be done in one computer run. Furthermore, these sums are grouped so that all the sums for a particular lattice site are done consecutively, added, multiplied by their charge and printed out so that the contributions from different sites may be evaluated. In terms of the previous example of MCl₂ this means that the two Cl(A) contributions are added together, multiplied by -1.0 and printed. Because of this modification additional information must be supplied to LATSUM, namely, the number of sublattices, the number of nonequivalent atoms at which the field gradient is desired, the number of atoms in

the unit cell which belong to a particular nonequivalent site and the charge associated with this site.

The second change introduced was to add two subroutines which diagonalize the field gradient matrix when it is obtained for a particular site. One of these, SMDIAG, which diagonalizes a square matrix by the method of Jacobi, was kindly supplied by Professor Richard Schwendeman. In addition to these major changes in LATSUM, numerous minor changes were also made.

D. A Test of LATSUM

Before LATSUM was used on the rather complex structures involved in this work, it was desired to test it out on some simpler systems first. The two systems chosen were the low temperature form of $CrCl_3$, which was done by Morosin and Narath (48), and CdI_2 which was done by Jones et al. (103). The former was picked since it had 24 atoms in the unit cell and was the most complex previous calculation and also because a reading of the literature indicated that this calculation was done correctly. CdI_2 was chosen because it had two nonequivalent sites in the unit cell. Although Jones et al. were not correct in their choice of the principal z axis along the sixfold axis in some of their compounds, their choice was correct in this particular compound. This is verified by the fact that, with the same choice of the z axis,
our calculated tensor was very close to diagonal. The results of the LATSUM calculation are compared to those on $CrCl_3$ (which were calculated by direct summation in a sphere) and those on CdI_2 (which were done by the earlier method of DeWette) in Table 9.

Table 9. Comparison of q and η as Calculated Both by LATSUM and by Other Authors

LATSUM			M	Other Calculations	
Compound		q	η	q	η
CrCl ₃		-0.43000	0.3240	-0.42602	0.3219
CdI2	1 ⁻ (2b) ^a	-0.00380	0.1701	-0.00379	
CdI2	1 ⁻ (2a)	-0.00584	0.1108	-0.00583	

^aThe notation 2a and 2b refers to crystallographically nonequivalent iodine sites.

As can be seen the agreement is excellent. The slight difference between values of q and η for CrCl₃ is probably due to the superior convergence of LATSUM. Since the CdI₂ calculations were made using the same method (that of DeWette) and the same crystal data, it is reassuring to see such good agreement.

E. <u>The Crystal Lattice Field Gradient</u> Model and Programs ROTATE and DIAG

1) The First Model

Before a calculation of the solid-state effects could be attempted some kind of a model upon which to base the calculations had to be developed. In this case it was decided to try to explain the line splittings as due to the effect of cì. to 1 C¦ ť cì 01 2

charged ions in the crystal lattice. This effect was expected to be large for two reasons. First, the ionicity of the bonds in the complexes averages about 50% with the result that the charge on each of the sites is significant. Second, because the atoms are unusually closely packed, the density of charged sites is greatly increased compared to previous crystals on which these calculations had been tried. Thus, even though the full ionic charges were not used, significant contributions to the measured field gradients were expected. In considering only the contribution of the charged sites, contributions due to induced dipoles, dipole-dipole interactions, Van der Waals interactions and partial chemical bonds formed between the chlorines in adjacent molecules are neglected. Nevertheless, for reasons given above, this model was expected to give a good first approximation. It was further assumed for the sake of mathematical simplicity that the charged ions could be replaced by point charges. Using this model it is necessary first to assign a charge to each site. This is not easy since there are no good rules for obtaining the ionicity of bonds. The approximate relationships of Pauling (70) and of Gordy (60), involving the electronegativity, have been used to estimate the ionicity. Pauling's relation has been criticized as being based upon an incorrect interpretation of dipole moment data and Gordy's method is not really based on any experimental results. Townes and Dailey, working from quadrupole resonance data, have developed a graph of bond ionicity

versus the difference in electronegativity of the two atoms involved in the bond (71). This graph was used to assign charges to each of the chloride and oxide ions, the charges on the other atoms were then chosen to maintain charge neutrality in the molecule. It was assumed that, in the complexes, there was a single bond between the oxygen atom of POCl₃ and both the phosphorus atom and the central atom of the Lewis acid. This assumption may be justified, at least in the case of $SbCl_5 \cdot POCl_3$, by observing that the Sb-O distance in this complex is $2.18^{\circ}A$ (107) while the Sb-O distance in Sb_2O_3 is 2.27 (108). Using the charges selected as described above the calculation of the point-charge field gradients was carried out.

2) An Improved Model

After the calculation was completed it was thought that a better assignment of charge could be made if the coupling constants actually found by NQR spectroscopy for POCl₃, SbCl₅, TiCl₄ and SnCl₄ were used. According to the theory of Townes and Dailey the measured quadrupole coupling constant ratio ρ is given by $\rho = 1 - 1 - \alpha$. Using the rule of Townes and Dailey, $\alpha = 0.15$ if the difference in the electronegativities of the two atoms involved in the bond is greater than 0.25; otherwise, $\alpha = 0$. The ionicity (I) can then be calculated if the NQR resonance frequencies are known.

Since NQR data are available only for the chlorine nuclei, the charges on the phosphorus and oxygen atoms and on the

central atoms of the Lewis acids are still undetermined. If the charge on oxygen is determined, and is separated into contributions from the central atom and phosphorus, the charges on these atoms may be determined because of the charge neutrality of the molecule. The only way to do this is to use the electronegativity differences. The following procedure, explained by means of an example, was used. For a hypothetical molecule Cl-M-O, if we assume there is some linear relationship between electronegativity and bond ionicities, we may write

$$I(C1) = A \triangle \chi(MC1), \qquad (68)$$

where I(C1) is the ionicity of chlorine and $\Delta \chi(MC1)$ is the electronegativity difference between atom M and chlorine. Since $\Delta \chi(MC1)$ is known and I may be calculated from NQR data we can calculate A from Equation 68. It is reasonable to assume that the same relation will hold for the M-O bond, hence

$$I(O) = A \Delta \chi(MO) . \tag{69}$$

Using these relations the ionicity of the oxygens was calculated. In our compounds the oxygens were bonded to two atoms; therefore, using SbCl₅·POCl₃ as an example, in an obvious extension of Equation 69, $I(0) = A \triangle \chi(Sb-0) + B \triangle \chi(P-0)$, where A and B can be calculated from NQR data on SbCl₅ and POCl₃. Table 10 lists the charge assigned to each atom. For the oxygen atom in [TiCl₄·POCl₃]₂, $I(0) = A \triangle \chi(Ti-0) + B \triangle \chi(P-0)$.

In this case A was not calculated from the TiCl₄ NOR data because it was felt that these data had too large an uncorrected crystal effect because of the high ionicity of the Ti-Cl bond and the consequent low value of p. The value of A calculated from the NOR data would then be too large and, in fact, the calculated A was much larger than the A's calculated for SbCl₅, SnCl₄ and POCl₃; an average of the other A's was therefore used. In the most elegant approach this set of charges would only be the first approximation to the true charges. They would be used to refine the measured NOR data to extract the molecular field gradients. These molecular field gradients would then be used in the Townes and Dailey relations to obtain a new set of charges. This process would be repeated until self consistency was reached. However, it was felt that the model on which the calculations are based is not accurate enough to warrant this procedure. Table 10 gives the charges used in the LATSUM calculations. Since there are two kinds of chlorine atoms in the complexes, Cl(A) designates the chlorines attached to the phosphorus and Cl(B) the chlorine attached to the central atom of the Lewis acid. The LATSUM results using these charges are the ones used in further calculations. Townes (71) has estimated that the ionicity calculated using this method is within 20% of the true value.

Compound	Atom	Charge
SbC1 ₅	Sb	1.625
SbCl ₅	Cl	-0.325
SbCl ₅ .POCl ₃	Sb	2.185
SbCl ₅ .POCl ₃	C1(A)	-0.322
SbCl ₅ .POCl ₃	C1(B)	-0.325
SbCl ₅ ·POCl ₃	Ρ	1.467
SbCl ₅ ·POCl ₃	0	-1.061
$SnCl_4 \cdot 2POCl_3$	Sn	+2.806
SnCl ₄ ·2POCl ₃	C1(A)	-0.322
SnCl ₄ ·2POCl ₃	C1(B)	-0.411
SnCl ₄ ·2POCl ₃	P	+1.467
SnCl ₄ ·2POCl ₃	0	-1.082
$[TiCl_4 \cdot POCl_3]_2$	Ti	+3.952
[TiCl ₄ ·POCl ₃] ₂	C1(A)	-0.322
[TiCl ₄ ·POCl ₃] ₂	C1(B)	-0.741
[TiCl ₄ ·POCl ₃] ₂	Ρ	+1.467
[TiCl ₄ ·POCl ₃] ₂	0	-1.489

Table 10. Charges Used in LATSUM

3) <u>ROTATE</u>

LATSUM calculates a field gradient tensor due to point charges in the lattice according to a particular choice for the directions of the X, Y and Z axes. This tensor may be diagonalized by a rotation to its principal-axis system. On the other hand the molecular field gradient at a chlorine nucleus has its principal axes oriented such that the z axis is along the bond. Since we assume cylindrical symmetry for

the molecular field gradient the orientation of its X and Y axes is arbitrary. Hence, it is only necessary to rotate the Z axis of the calculated crystal lattice field gradient tensor so that it is aligned along the bond; then, since the X and Y axes of the molecular field gradient are arbitrary, the two coordinate systems will be aligned. We can then directly combine the zz component of each tensor. A computer program, ROTATE has been written which performs this rotation. **ROTATE** works in the following manner; any tensor $\overline{\overline{Q}}$ with matrix elements Q_{ij} may be rotated to any arbitrary direction by the matrix transformation $S^T Q S = Q'$ where Q' is the matrix of the rotated tensor, S is the matrix of direction cosines and $\mathbf{S}^{\mathbf{T}}$ is the transpose of S. This rotation may take place in two (or more) successive rotations if this is more convenient. If the two direction cosine matrices are represented by S_1 and S_2 then $S = S_1 S_2$ and $S^T = S_2^T S_1^T$, hence $Q' = S_2^T S_1^T Q S_1 S_2$. In this case two successive rotations are performed one in the original XY plane by an angle α and the other tipping the original Z axis by an angle β . Program ROTATE is given the coordinates of the two atoms involved in the bond and the unrotated tensor. ROTATE then calculates the bond direction relative to the Z direction of the original choice of coordinates, calculates S and S^T and performs the necessary matrix multiplication. It prints out the rotated matrix and also α , β and the bond distance as a check on the calculation. Figure 12 shows how α and β are defined with



Figure 12. Definition of the angles α and β as used by ROTATE.

D à b 1

II,

respect to the molecular bond axis Z and the axis system of the unrotated tensor X', Y' and Z', which are equivalent to the crystalline a, b and c axes, respectively, for orthorhombic symmetry. ROTATE is listed in the Appendix.

4) PROGRAM DIAG

As a first approximation, one may take the zz component of the rotated tensor and combine it directly with the measured field gradient to extract the molecular field gradient. Another more accurate method is available, however. The field gradient actually measured has principal axes slightly different from the molecular field gradient (although the molecular field gradient is expected to dominate the mea sured value) because when the rotated crystal lattice gradient tensor is added to the molecular field gradient ten sor the resulting tensor is no longer diagonal. The principal-axis orientation of the measured gradient relative to the bond direction may then be obtained by diagonalizing the resulting cumulative tensor. The largest element along the trace of the diagonalized tensor will be the experimentally measured field gradient. An asymmetry parameter η due to the solid-state effects may also be calculated from the diagonalized tensor. Ideally the solid-state effects should be the only contributors to this parameter so that the calculated η should correspond to the measured η .

At this point another complication, the Sternheimer factor, must be introduced which may increase or decrease, according

to its sign, the contribution of the crystal lattice effects. This has already been discussed but must now be taken into account. If it were known exactly this would pose no problem as we would simply multiply the calculated crystal lattice field gradient tensor by the appropriate factor. Unfortunately, for several reasons already discussed (Section I-E), the factor is not known. In addition to the previous discussion it should be noted that, although we always treat the Sternheimer factor γ_{∞} as a scalar, because it depends on the polarizability of the chlorine atom it should probably be a second rank tensor. At present it is not possible to take this into account. Or, more accurately, we assume the tensor is of the form

$$\vec{\overline{\gamma}}_{\infty} \equiv \begin{pmatrix} \gamma_{\infty} & 0 & 0 \\ 0 & \gamma_{\infty} & 0 \\ 0 & 0 & \gamma_{\infty} \end{pmatrix}$$

If we assume that the Sternheimer factor is known we can calculate the molecular field gradient from the rotated crystal lattice field gradient tensor and the measured field gradient by the following procedure. Knowing the measured field gradient we guess a molecular field gradient which we assume is cylindrically symmetric. In the axis system in which the Z axis is along the bond direction this trial molecular field gradient may be represented as a second-rank tensor of the following form

$$\bar{\bar{q}}^{\text{mol}}(\text{trial}) = \begin{pmatrix} -\frac{a}{2} & 0 & 0 \\ 0 & -\frac{a}{2} & 0 \\ 0 & 0 & a \end{pmatrix}.$$

This is then added to the rotated crystal field gradient tensor and the resulting tensor diagonalized. The absolute value of the largest element on the trace of the diagonalized tensor is then subtracted from the measured field gradient. This difference is compared to the difference calculated for the previous iteration. If it is smaller than the previous difference we are going in the proper direction and the trial field gradient is incremented by an element of the same sign and magnitude as that used in the previous iteration. If the difference is larger than that of the previous iteration the sign of the increment is changed and if the largest value of the diagonalized tensor oscillates to one side and the other of the measured value the magnitude of the increment is cut in half. This process is continued until the diagonalized tensor converges to the measured tensor. The other two values on the trace of the diagonalized tensor can be used to calculate the asymmetry parameter due to the crystal effects and the eigenvectors of the diagonalized tensor may be used to determine the relative orientations of the principal axes of the experimental field gradient. The trial field gradient is now the molecular field gradient. A computer program, **DIAG**, has been written to perform these iterations and is listed in the Appendix. The iteration procedure is repeated for a number of values of the Sternheimer factor. The method f_{Or} assigning a Sternheimer factor to a chlorine atom will be **illustrated** by an example. Consider again MCl_2 ; in the gaseous

state both chlorine atoms are equivalent, therefore their molecular field gradients are identical. Since in the solid the two chlorines have different experimental field gradients this is clearly a solid-state effect. If we know the crystal structure of MCl₂ we can apply LATSUM, ROTATE and DIAG. This results in a set of molecular field gradients as a function of the Sternheimer factor. We then pick the Sternheimer factor which makes the two molecular field gradients This procedure necessitates the assignment of identical. the correct experimental field gradients to sites A and B; however, this may usually be done from an inspection of the results of ROTATE. Also, if there is reason to believe that at least a part of the splitting between two nonequivalent sites is due to a difference in the molecular field gradient, this procedure will no longer be valid.

IV. RESULTS

A. <u>Assignment of Absorption Frequencies to</u> <u>Specific Atoms in the Complexes</u>

With the aid of chemical considerations, relative intensities and ROTATE it is possible to assign each NQR absorption to a specific chlorine atom in the molecule. Each compound will now be discussed separately. The crystal structure of $SbCl_5 \cdot POCl_3$ was determined by Lindqvist and Bränden (106) and the atomic arrangement for the complex is shown in Figure 13; each numbered chlorine atom denotes a crystallographically nonequivalent site. In a similar manner Figures 14 and 15 show the atomic arrangement for the complexes in $SnCl_4 \cdot 2POCl_3$, as found in the X-ray analysis of the crystal structure by Bränden (108), and for the complex $[TiCl_4 \cdot POCl_3]_2$ from the X-ray work of Bränden and Lindqvist (109).

1) $SbCl_5 \cdot POCl_3$

At 77° K six absorption lines are observed for this compound, two lines grouped at about 30.5 MHz, one at about 27.4 MHz, two grouped around 26 MHz and one at about 24.4 MHz. The intensities of the four lowest lines are in the approximate ratios of 2:1:1:1. From chemical considerations we expect four different resonances, one from the three POCl₃ chlorines, one from the axial chlorine atom on the SbCl₅,







Figure 14. A molecule of SnCl4.2POCl3.





one from the chlorine atom trans to the $POCl_3$ oxygen and one from the two chlorine atoms cis to the POCl₃ oxygen atom. Reference to Figure 13 shows that there are six nonequivalent chlorine atoms in this complex. As will be discussed, it is expected that charge transfer will be indicated by an increase in the resonance frequencies of the POCl₃ chlorine atoms and a decrease in the resonance frequencies of the chlorine atoms of the Lewis acid. Thus, the two absorption frequencies at about 30.5 MHz must be assigned to the POCla chlorine atoms. Furthermore, the resonance due to a chlorine atom at site 5 should be twice as intense as that due to atoms at site 4. It is observed that the higher frequency line is much less intense than the lower frequency line and the higher frequency line is therefore assigned to site 4. This assignment is confirmed by the results of the crystal lattice field gradient calculations which calculate an uncorrected q^{Crys} of +0.3 for site 4 and -0.03 for site 5 (it should be recalled that the molecular field gradients are all positive). The last four lines may be assigned to chlorine atoms bonded to antimony. The highest frequency line is unmistakably more intense than the other three lines each of which has approximately the same intensity. Therefore, this absorption is assigned to the two axial chlorine atoms (site 6). Each of the three equatorial chlorine atoms occupies a nonequivalent site so we expect three separate resonances as observed. Two of these resonances are split

by less than 300 kHz while the other resonance lies 1.6 MHz lower in frequency. Hence, the lowest frequency is assigned to the Cl at site 3, <u>trans</u> to the POCl₃ oxygen. The pointcharge calculations give an uncorrected q^{Crys} of -0.12 for site 1 and +0.3 for site 2, hence, the lower frequency is assigned to site 1 and the higher to site 2.

2) $SnCl_4 \cdot 2POCl_3$

At 77⁰K five resonances are found for this compound, which is unfortunate because Figure 15 shows seven nonequivalent chlorine sites, four for the POCl₃ chlorine atoms and three at the SnCl₄ chlorine sites. Two absorptions may be associated with the POCl₃ resonances instead of the four predicted. They were assigned to either sites 4 and 5, or 6 and 7, since these belong to different POCl₃ molecules and the most likely phase transition would be one in which the POCl₃ molecules are aligned in an equivalent manner. This point will be discussed in more detail in the discussion. The LATSUM calculations were then used to assign the measured frequency to a particular site. It is interesting to note that sites 4 and 6, which should become equivalent if the POCl₃ molecules are rotated into equivalent positions, are always assigned the higher frequency line. The resonance at highest frequency of the three which come from the SnCl₄ chlorine atoms is assigned to site 3 on the basis of intensity. Site 2 has a calculated uncorrected q^{crys} of +0.37 while g^{crys} for site 1 is +0.42; hence, the line at higher frequency of the two remaining is assigned to site 2.

3) $[TiCl_4 \cdot POCl_3]_2$

For this compound only the $POCl_3$ chlorine resonances could be observed. Three lines are measured for this compound and three nonequivalent chlorine sites (sites 5, 6 and 7) on the $POCl_3$ molecule are predicted. Hence, the NQR and X-ray results are in good agreement for this compound. Since all three resonances are about equal in intensity (also predicted from the crystal structure), we must rely on the point-charge calculations to assign the frequencies. These calculate uncorrected q^{Crys} values of -0.18, -0.09, and 0.00 for sites 5, 6 and 7, respectively. For this reason the highest frequency absorption was assigned to site 7 and the lowest to site 5.

4) Pure SbCl₅

In SbCl₅ McCall and Gutowsky (110) have observed three lines at 77° K. These lines are themselves multiplets but McCall and Gutowsky report that they seem to center about 27.88, 28.3 and 30.4. It is likely that the two closer spaced lines are associated with either the axial or the equatorial chlorine atoms and that the high frequency line is associated with the other. This spectrum was re-examined in the present work; however, it was not possible to decide whether the high frequency line or the low frequency pair was to be associated with the axial position. The only basis for this decision was the intensity ratio because, since it is believed that the molecular field gradients at the axial and equatorial

positions should differ, ROTATE results can not be used. However, the lines were too complex to yield a reliable intensity ratio. Furthermore, X-ray data on SbCl₅ (118) taken at -30° C show only two nonequivalent chlorine sites in the molecule corresponding to the axial and equatorial positions. In an effort to obtain some new information to help solve this difficulty new NQR measurements were made on SbCl₅ at -23° C; this temperature was chosen because it is quite close to the temperature at which the X-ray data were taken. The frequency region 31 MHz to 20 MHz was searched using the recording technique and two strong lines were found. These lines are quite intense and easily observable on the oscilloscope. There is no doubt that each is a single line. The two lineswere observed at frequencies of 23.114 MHz and 25.383 MHz. Furthermore a comparison of the relative intensities of the recorded signals clearly shows that the lower frequency line is less intense and the intensity ratio closely approximates 3:2. Hence, the 25.383 MHz line is assigned to the equatorial chlorine atoms while the 23.114 MHz line is assigned to axial chlorine atoms. This assignment parallels the observations of Holmes et al. (111), who found for the trigonal bipyramidal molecule PCl₄F two lines at 32.54 and 28.99. They also assigned the higher frequency line to the equatorial chlorines on the basis of intensities. It is obvious that a phase transition involving a change in the crystal structure between $77^{\circ}K$ and $250^{\circ}K$ (-23°C) has taken

place, both from the change in line multiplicity and the abrupt drop in frequency (~ 5 MHz). Working back from these results and using both the known behavior of lines which have undergone phase transitions, and the fact that the line separation at 250° K (2.3 MHz) and at 77° K (2.3 MHz) are equal, it seems quite likely that the lines centered at 30.4 MHz should be assigned to the axial position.

B. <u>New Resonance Frequencies and Their</u> <u>Temperature Dependence</u>

In this work new resonances were found in the compounds FeCl₃·POCl₃, SbCl₅·POCl₃, TiCl₄·2POCl₃, and (TiCl₄·POCl₃)₂. In addition, the room temperature frequencies were measured for $SnCl_4 \cdot 2POCl_3$. The temperature dependence of the most intense SbCl₅ line in SbCl₅.POCl₃ was also studied. The input to DIAG requires knowledge of the measured field gradients. This quantity is obtained when the measured quadrupole coupling constant is divided by $\frac{e^2Q(C1)}{b}$, where Q(C1) is the quadrupole moment of the ³⁵Cl nucleus, e is the electronic charge and h is Planck's constant; this factor has the value -2.9552×10^{6} when q is desired in units of statcoulombs per cubic Angstrom (esu/ A^3). The factor was calculated with $h = 6.627 \times 10^{-27}$, $e = 4.80 \times 10^{-10}$ and Q = -0.085. Since all the quadrupole coupling constants were negative this made all the measured field gradients positive. Although it is impossible to assign a sign to e^2qQ as measured by pure quadrupole resonance, the sign is taken to be negative for

all compounds of chlorine in which the chlorine has a charge more positive than -1. This conclusion is drawn from data on gaseous chlorine compounds measured by microwave spectroscopy where the sign of the coupling constants can be determined experimentally. The data indicate that e^2qQ becomes more negative as the chlorine becomes more positive. There is every reason to believe that the sign of the coupling constant does not change upon changing from the gaseous to the solid state. Table 11 lists the resonance frequencies of all the compounds measured in this work. Data were measured at both liquid nitrogen and room temperature for all resonances for which this was possible. All chlorine resonances which were ascribed to the POCla part of the molecules disappeared at about 200°K. Table 12 lists the results of a temperature study on the most intense line of SbCl₅ in SbCl₅. $POCl_3$. This line is listed as Cl(6) in Table 11 and has been assigned to the axial chlorines in SbCl₅ as discussed above (Section IV-A). Table 13 presents the coupling constants and the field gradients derived from the resonance frequencies. All frequencies are numbered for convenience of reference in the discussion. Figure 16 gives the data of Table 12 in graphical form.

Table 14 gives the temperature coefficients for all resonances which were observable at room temperature. These coefficients are based upon measurements at only two temperatures but only their signs and rough magnitudes are needed.

Compound	Temperature (^O K)	Frequency (in MHz)		
SbCl ₅ ·POCl ₃ ^a				
C1(1)	77	25.882		
C1(1)	297	25.370		
C1(2)	77	26.186		
CI(2)	297	25.949		
CI(3)				
C1(3)	251	24.403		
C1(4)	297			
C1(5)	77	30, 565		
c 1(5)	297			
C1(6)	77	27.327		
C1(6)	297	26.890		
SpC1 ·· 2POC1 b				
$\frac{1}{C1(1)}$	77	19.807		
C 1(1)	297	19.110		
C1(2)	77	19.035		
C1(2)	297	18.873		
C1(3)	77	21.462		
C1(3)	297	20.945		
C1(4)	77	30.213		
C1(4)	297			
		30.117		
CI(3)	291			
$(\text{TiCl}_4 \cdot \text{POCl}_3)_2$				
C1(5)	77	29.987		
C1(6)	17	30.112		
	11	30.313		
FeCl ₃ ·POCl ₃	77	30.263		
TiCl ₄ ·2POCl ₃	77 Several	lines centered		
around	d 30.1 MHz could not	be resolved.		
<u>SbCl</u> ₅				
Equatorial	77	30.4		
Axial	11	28.3		
AXIAI	11	27.88		
SbC1 ₅				
Equatorial	250	25.383		
Axial	250	23.114		
^a The number in parentheses refers to the numbered atoms in Figures 13, 14 and 15. This frequency assignment has al- ready been discussed. ^b The 77°K measurements on SnCl::2POCle are taken from				
Biedenkapp and We:	iss (9).			

Table 11. Resonance Frequencies for the Compounds Studied in This Work

^CThe 77[°]K measurements on SbCl₅ are taken from McCall and Gutowsky (116).

Temperature ([°] K)	Frequency (MHz)
77	27.327
165	27.145
190	27.118
250	26.974
297	26.890

Table 12. Temperature Dependence of the Most Intense Line of $SbCl_5 \cdot POCl_3$ (Line 6 of Table 11)

Compound	Temperature K	e ² Qq/h (MHz)	q(esu/Å ³)
SbCl ₅ ·POCl ₃			
(1)	77	-51.644	17.476
(1)	297	-50.740	17.170
(2)	77	-52.372	17.722
(2)	297	-51.898	17.562
(3)	77	-48.868	16.536
(3)	297	-48.930	16.557
(4)	77	-61.264	20.731
(5)	77	-61.130	20.686
(6)	77	-54.654	18.494
(6)	297	-53.780	18.198
$SnCl_{4} \cdot 2POCl_{3}^{a}$			
(1)	77	-39.614	13.405
(1)	297	-38.220	12.933
(2)	77	-38.070	12.882
(2)	297	-37.746	12.773
(3)	77	-42.292	14-311
(3)	297	-41.890	14.175
(4)	77	-60.426	20.447
(5)	77	-60.134	20.349
(TiCl ₄ ·POCl ₃) ₂			
(7)	77	-60.626	20.515
(6)	77	-60.224	20.400
(5)	77	-59.974	20.294
FeCl ₃ ·POCl ₃	77	-60.526	20.481
sbc1 ^b			
Axial	77	-56,18	19.011
Axial	250	-46,228	15.643
Equatorial	77	-60,8	20.574
Equatorial	250	-50.766	17.179
-			

Table 13.	Coupling	Constants	and F	field	Gradients	for	the
	Compounds	Studied :	in Thi	is Wor	:k		

 $^{a}77^{o}K$ measurements on SnCl₄·2POCl₃ by Biedenkapp and Weiss (9). $^{b}77^{o}K$ measurements on SbCl₅ by McCall and Gutowsky (110).



Compound	Atom	Temperature Coefficient (in kHz per degree)
SbCl ₅ ·POCl ₃	1	-2.3
SbCl ₅ ·POCl ₃	2	-1.1
SbCl ₅ ·POCl ₃	3	+0.14
SbCl ₅ ·POCl ₃	6	-2.0
SnCl ₄ ·2POCl ₃	1	-3.2
SnCl ₄ ·2POCl ₃	2	-0.74
SnCl ₄ ·2POCl ₃	3	-2.4

Table 14. Temperature Coefficients for the Chlorine Resonances of Complexed SbCl₅ and SnCl₄

Moreover, the Cl(6) resonance in SbCl₅·POCl₃ which was studied in more detail shows that the graph of resonance frequency versus temperature is quite linear.

C. Compounds in which No Resonances were Found

A large number of compounds were examined in the NQR spectrometer. Unfortunately, for a number of reasons, most of these failed to yield absorbances in the frequency ranges studied. It was suspected in some cases, particularly the $HgCl_2$ complexes and the POCl_3 complexes, that impurities caused the signals to be missed. It is desirable that these compounds be synthesized again and another attempt be made to find signals. Another attempt should also be made on the n-donor complexes of ICl and ICl_3 because impurities may have also caused these signals to be missed. The resonances of ICl and ICl₃ themselves are not too strong and, since it was found that the intensity of SbCl₅ and SnCl₄ resonances in their complexes was greatly reduced, it is possible that the signals in the ICl and ICl₃ complexes are too weak to be found by present methods. However, if care were taken to optimize all conditions it might be possible to find signals for these complexes. It would also be interesting to look for the nitrogen guadrupole resonances in these complexes as they have been reported for the pure pyridine derivatives. Differences in the nitrogen guadrupole coupling constants in the pure and complexed molecule could be interpreted in terms of π -electron populations. It is not known why the copper, cobalt and manganese resonances could not be found although they may not be in the frequency range of the spectrometer. Table 15 gives the compound examined, the frequency range searched and the conditions of the search for a number of compounds in which no signals could be found. In order to simplify and condense the conditions the following abbreviations have been used: fm = frequency modulation, this is followed by two numbers in parentheses. The first refers to a relative attenuation of the voltage from the modulation unit with numbers ranging from one to six, where one refers to zero attenuation, two refers to a sixth of a turn of the 10 K potentiometer which is acting as a voltage divider, three is two-sixths of a turn, etc. The second number refers

Compound	Frequency Region Searched (in MHz)	Conditions
p-C ₆ H ₄ FCl s	20-40	77 ⁰ , fm(5, .05)
(C ₆ H ₅ CH=N-NHC-NH ₂)Cu	20-40	77 ⁰ , fm(5, .02) 77 ⁰ , fm(5, .02) 77 ⁰ , fm(1, .02)
$((CH_{3}O)C_{6}H_{4}CH=N-NHC-NH_{2})$)Cu 20-40	77 ⁰ , fm(1, .02)
HgCl ₂ ·2(C ₅ H ₅ N)	17-25	297 ^o , fm(1, .05) 297 ^o , fm(5, .05) 297 ^o , fm(1, .02) 77 ^o , fm(1, .05) 77 ^o , fm(5, .05)
$HgCl_2 \cdot 2(3-CH_3C_5H_4N)$	17-25	77 ⁰ , fm(1, .05)
[(C ₆ H ₅) ₃ P·HgCl ₂] ₂	17-25	297 ⁰ (2, .05) 297 ⁰ (6, .05) 77 ⁰ (5, .05)
$HgCl_2 \cdot (CH_3)_2SO$	17-25	77 ⁰ , fm(1, .02) 77 ⁰ , fm(1, .05)
K ₃ [Co(CN) ₅ NO]	15-34 repeated a	297° , $zm(.2)$ 297° , $zm(1.0)$ 297° , $fm(1, .02)$ 297° , $fm(1, .05)$ above at 77° K
K ₃ [Co(CN) ₅ 1]	15-34	Same conditions as K ₃ [Co(CN) ₅ NO]
K ₃ [Mn(CN) ₅ NO]	15-34	Same conditions as K ₃ [Co(CN) ₅ NO]
C ₅ H ₅ N·ICl	30-45	77 ⁰ , fm
C ₉ H ₇ N·ICl	30-45	77 ⁰ , fm
C ₉ H ₇ N·ICl ₃	25-35	77 ⁰ , fm
2-BrC ₅ H ₄ N·ICl	30-45	77 ⁰ , fm
3-NCC ₅ H ₄ N·ICl	30-45	77 ⁰ , fm
SbCl ₅ .TiCl ₄ .3POCl ₃	18.5-41	77 ⁰ , fm(1 , .05) 77 ⁰ , fm(1, .02)
TiCl ₄ ·KCl·3POCl ₃	24.8-34	77 ⁰ , fm(4, .05)

Table 15. Compounds in which NQR Absorptions were Missed

Table	15	- Con	tinued
TUDIC	τU	COIL	CTITUCU

Compound	Frequency Region Searched (in MH _z)	Conditions
BCl ₃ ·POCl ₃	24.8-34	77 ⁰ , fm(4, .05)
3 Different) AlCl ₃ -POCl ₃ Complexes	24.8-34	77 ⁰ , fm(4, .05) 77 ⁰ , fm(1, .02)
BiCl ₃ ·POCl ₃	24.8-34	77 ⁰ , fm(4, .05) 77 ⁰ , fm(1, .02)
SbCl ₃ ·POCl ₃	24.8-34	77 ⁰ , fm(4, .05) 77 ⁰ , fm(1, .02)
$[A1(POCl_3)_6] [SbCl_6]_3$	24.8-34	77 ⁰ , fm(4, .05) 77 ⁰ , fm(1, .02)
$[Al(POCl_3)_6] [FeCl_4]_3$	24.8-34	77 ⁰ , fm(4, .05) 77 ⁰ , fm(1, .02)
(TiCl ₄ ·POCl ₃) ₂	3.5-10.5	77 ⁰ , fm(1, .02) 77 ⁰ , fm(1, .01)

to the reference attenuation control on the lock-in amplifier. These two settings are the only information needed to reproduce any of the modulation conditions of this experiment. Zeeman modulation is denoted by zm followed by a number in parentheses which gives the current in amperes that was passed through the modulation solenoid. The other condition given is the temperature at which the searches were conducted. Most of the searches were conducted at liquid nitrogen temperature $(77^{\circ}K)$ but others were also repeated at room temperature $(297^{\circ}K)$. It should be noted that, in addition to searching with recording techniques, visual searches were also carried out in all cases.

D. LATSUM, ROTATE, AND DIAG Results

1) Tabulated Results of LATSUM and ROTATE

In the hexagonal SbCl₅ crystal the z axis for LATSUM was chosen parallel to the sixfold axis and the x axis was chosen along the crystalline a axis. This means that the tensor for the axial chlorine atoms should be almost diagonal. This is expected since the axial chlorines almost lie on this crystal sixfold axis; for this same reason it is expected that η should be very close to zero. Both of these expectations are realized. The three complexes are orthohombic in their crystal symmetry; hence, the X, Y, Z axes of LATSUM were chosen along the crystalline a, b and c axes, respectively. LATSUM was applied to 22 nonequivalent chlorine

atoms; the results from both LATSUM and ROTATE are summarized in Tables 16-37. The numbering of the chlorine atoms refers to that used in Tables 11 and 13 and in Figures 13, 14, and 15. Each table gives the results of LATSUM and ROTATE for a single chlorine site. "Tensor" refers to the crystal field gradient tensor calculated with respect to the original choice of X, Y and Z atoms as given above. "Rotated Tensor" refers to this same tensor after it has been rotated so that its Z axis lies along the bond direction. In order to determine the principal values and the directions of the principal axes, the undiagonalized crystal field gradient tensor, as calculated with respect to the original choice of coordinates, was transformed to the principal-axis system by diagonalizing it. The eigenvector matrix for this transformation is given in the tables under the heading of "Eigenvectors." If the axes of the new coordinate system are denoted by X, Y and Z and those of the old coordinate system are denoted by X', Y', and Z', then the elements of the eigenvector matrix are the cosines of the angles between the X and X' axes, X and Y' axes, etc. The angles along the diagonal of this matrix are of special interest as these correspond to the angles between the X' and X axes, the Y' and Y axes and the Z' and Z axes, respectively. For convenience the arc cosines, rounded to the nearest degree of the elements of the eigenvector matrix, are collected in the section of the table labeled "Direction Cosine Angles." Finally, the elements on the diagonal of the diagonalized

	<u> </u>			
Tensor				
-0.4	3330	0.00011	0.00000	
0.0	00011	-0.43316	0.00000	
0.0	00000	0.00000	0.86646	
Eigenvect	ors			
1.0	00000	0.00000	0.00000	
0.0	00000	1.00000	0.0000	
0.0	00000	0.00000	1.00000	
Angles fo	or the	Direction Cos	sine (in degrees)	
0	90	90		
90	0	90		
90	90	0		
$q_{xx} = -0.$	43316	q = 0.86	646	
$q_{yy} = -0.$	43330	η = 0.00	0016	
Rotated Tensor				
-0.4	3330	0.00009	0.00000	
0.0	00009	-0.43316	0.00000	
0.0	00000	0.00000	0.86646	

Table 16. LATSUM and ROTATE Results for the SbCl₅ Axial Chlorines
Tensor			
-0.148	57	-0.00061	0.00000
-0.000	61	0.29075	0.00695
0.000	00	0.00695	-0.14125
Eigenvector	S		
1.000	000	-0.00174	0.00154
0.00177		0.99979	-0.02017
-0.001	.51	0.02018	0.99980
Angles for	the	Direction Cos	ines (in degrees)
0	90	90	
90	1	91	
90	89	1	
$q_{xx} = -0.14$	143	q = 0.29	093
$q_{yy} = -0.14$	950	η = 0.02	774
Rotated Ten	sor		
-0.141	25	-0.00872	0.00000
-0.008	372	0.29075	-0.00077
0.000	000	-0.00077	-0.14867

Table 17. LATSUM and ROTATE Results for the SbCl₅ Equatorial Chlorines

			-					
Ten	sor							
	0.11350		0.00004	4	-0.21298	5		
	0.	.0000)4	-0.15028	8	-0.00001		
	-0.	2129	98	-0.0000	1	0.03679)	
Eig	enve	ector	s					
	0.	7672	21	-0.0013	5	0.64139)	
	0.	.0000	8	1.0000	C	0.00200)	
	-0.	.6413	59	-0.0014	8	0.76721		
Ang	les	for	the	Direction	Cosir	nes (in d	egrees)	
	40)	90	50				
	90)	0	90				
	130)	90	40				
q _{xx} p	= .	-0.14	127	q = 0	.2915	5		
д ^{АА}	= -	-0.15	5028	η = Ο	.03090)		
Rot	ated	l Ter	nsor					
	0.	2709	98	0.0000	3	0.09210		
	0.	.0000)3	-0.1502	8	0.00003		
	0.	.0921	LO	0.0000	3 -	-0.12069		

Table 18. LATSUM and ROTATE Results for the SbCl₅·POCl₃ Cl(1) Chlorines

			<u></u>		
Tens	sor				
	0.2165	54	0.00000	-0.18190	
	0.000	00	-0.13559	0.00000	
	-0.1819	90	0.00000	-0.08095	
Eige	envector	cs			
	0.90361		0.00000	0.42835	
	0.000	00	1.00000	0.00000	
	-0.4283	35	0.00000	0.90361	
Ang	les for	the	Direction Cos	sines (in degrees)	
	25	90	65		
	90	0	90		
	115	90	25		
q _{vv}	= -0.13	3559	q = 0.302	277	
q _{yy}	= -0.16	6718	η = 0.108	134	
Rota	ated Ter	n s or			
	-0.1656	68	0.00000	-0.02647	
	0.00000		-0.13559	0.00000	
	-0.0264	1 7	0.00000	0.30127	

Table 19.	LATSUM and	ROTATE	Results	for	the	SbCl ₅ ·POCl ₃
	Cl(2) Chlor	ines				

Ten	sor				
	-0.00843		0.00000	0.21982	
	0.0000	00	-0.15804	0.00000	
	0.2198	32	0.00000	0.16647	
Eig	envector	s			
	0.8275	54	0.00000	0.56141	
	0.0000		1.00000	0.00000	
	-0.56141		0.00000	0.82754	
Ang	les for	the	Direction Co.	sines (in degrees)	
	34	90	56		
	90	0	90		
	124	90	34		
q, ,	= -0.15	5756	q = 0.31	560	
q _{yy}	= -0.15	5805	η = 0.00:	155	
Rot	ated Ter	nsor			
	0.2526	56	0.0000	0.16067	
	0.0000	00	-0.15804	0.00000	
	0.1606	57	0.00000	-0.09462	

•

Table 20. LATSUM and ROTATE Results for the SbCl₅·POCl₃ Cl(3) Chlorines

-					
Ten	sor				
	0.268	364	-0.00017	0.14878	
	-0.000	017	-0.13907	0.00000	
	0.148	878	0.00000	-0.12960	
Eig	envecto	ors			
	0.94897		-0.00012	-0.31537	
	-0.00034		1.00000	-0.00138	
	0.31537		0.00141	0.94897	
Ang	les for	the	Direction Co	sines (in degre	es)
	18	90	108		
	90	0	90		
	72	90	18		
q _{xx}	= -0.1	L 3 904	q = 0.31	808	
d ^{ÅÅ}	= -0.1	L790 4	η = 0.12	575	
Rot	ated Te	ensor			
	-0.176	534	-0.00006	0.03658	
	-0.000	006	-0.13904	-0.00016	
	0.036	658	-0.00016	0.31538	

·

1

Table 21. LATSUM and ROTATE Results for the SbCl₅·POCl₃ Cl(4) Chlorines

Ten	sor				
	-0.042	163	-0.19963	-0.07007	
	-0.19963		0.14861	0.13313	
	-0.070	07	0.13313	-0.10699	
Eig	envecto	ors			
	0.60394		-0.49779	0.62247	
	0.59173		0.80324	0.06824	
	-0.533	396	0.32712	0.77967	
Angles for the		r the	Direction Cos	sines (in degrees)	
	53	120	52		
	54	37	86		
	122	71	39		
q _{xx}	= -0.2	15128	q = 0.326	655	
q _{yy}	= -0.2	17527	η = 0.073	346	
Rota	ated Te	ensor			
	-0.15	674	-0.05356	-0.04667	
	-0.053	356	0.18488	0.21284	
	-0.046	667	0.21284	-0.02816	

Table 22. LATSUM and ROTATE Results for the $SbCl_5 \cdot POCl_3$ Cl(5) Chlorines

Ten	sor							
	-0.	0549	2	0.0387	9	0.00598		
	0.03879		-0.0082	9	-0.11398			
	0.	0059	8	-0.1139	8	0.06321		
Eig	enve	c tor	S					
0.52045		0.8490	3	-0.09102				
-0.70910		0.3703	6	-0.60001				
	-0.	4757	'1	0.3768	2	0.79480		
Ang	les	for	the	Direction	Cosi	nes (in d	legrees)	
	59		32	95				
	135		68	127				
	118		68	37				
q _{xx}	= -	0.03	534	$\mathbf{q} = \mathbf{C}$.1485	7		
q _{yy}	= -	0.11	322	η = C	.5242	0		
Rot	ated	Ten	sor					
	0.	0453	5	-0.0054	3	-0.11843		
	-0.	0054	3	-0.0524	1	-0.03989		
	-0.	1184	3	-0.0398	9	0.00706		

Table 23. LATSUM and ROTATE Results for the SbCl₅·POCl₃ Cl(6) Chlorines

<u></u>	<u> - Course d'Alba</u>				<u></u>
Tens	sor				
	0.15626		0.31417	0.00000	
	0.31417		0.04033	0.00000	
	0.000	00	0.00000	-0.19658	
Eige	envector	s			
	0.76858		-0.63975	0.00000	
	0.63975		0.76858	0.00000	
	0.0000		0.00000	1.00000	
Angl	les for	the	Direction Cos	sines (in degre	es)
	40	130	90		
	50	40	90		
	90	90	0		
q _{xx}	= -0.19	9658	q = 0.41	776	
ч _{уу}	= -0.22	2118	η = 0.058	389	
Rota	ated Ter	nsor			
	-0.1965	58	0.00000	0.00000	
	0.0000		-0.22028	0.02388	
	0.000	00	0.02388	0.41687	

Table 24. LATSUM and ROTATE Results for the $SnCl_4 \cdot 2POCl_3$ Cl(1) Chlorines

Tensor				
-0.1000	00	-0.19751	0.0000	
-0.197	51	0.29115	0.0000	
0.000	00	0.00000	-0.19114	
Eigenvector	rs			
0.9229	94	-0.38495	0.0000	
0.3849	95	0.92294	0.0000	
0.000	00	0.00000	1.00000	
Angles for	the	Direction Cos	sines (in degr	ees)
23	113	90		
67	23	90		
90	90	0		
$q_{xx} = -0.18$	8238	q = 0.373	353	
$q_{yy} = -0.19$	9114	η = 0.023	345	
Rotated Ter	nsor			
-0.191:	14	0.00000	0.00000	
0.000	00	-0.18173	-0.01897	
0.000	00	-0.01897	0.37288	

Table 25. LATSUM and ROTATE Results for the $SnCl_4 \cdot 2POCl_3$ Cl(2) Chlorines

-					
Ten	sor				
	-0.16016		-0.00225	0.11823	
	-0.00225		-0.20237	-0.02924	
	0.11823		-0.02924	0.36254	
Eiq	envector	cs			
5	0.95905		-0.18980	0.21024	
	0.20424		0.97770	-0.04904	
	-0.19624		0.08997	0.97642	
Ang	les for	the	Direction Co	sines (in degree	es)
	16	101	78		
	78	12	93		
	101	85	12		
a	= -0.18	3483	q = 0.38	946	
q _{yy}	= -0.20	0463	η = 0.05	084	
Rot	ated Ter	nsor			
	-0.1866	66	0.00810	0.03453	
	0.0081	10	-0.20070	0.00347	
	0.034	53	0.00347	0.38737	

Table 26. LATSUM and ROTATE Results for the $SnCl_4 \cdot 2POCl_3$ Cl(3) Chlorines

Ten	sor				
	-0.18220		0.01279	9 0.00771	
	0.01279		0.33636	6 -0.00036	
	0.00771		-0.00036	6 -0.15416	
Eig	enve	ector	s		
0.96883		0.02464	4 0.24651		
	-0.02397		0.99970	0 -0.00574	
	-0.	2465	57	-0.00035	5 0.96912
Ang	les	for	the	Direction	Cosines (in degrees)
	14	÷	89	76	
	91	-	1	90	
	104	-	90	14	
q _{vv}	= -	0.15	5220	$\mathbf{q} = 0.$.33667
q _{yy}	= -	0.18	3448	η = Ο.	.09588
Rota	ated	l Ter	nsor		
	-0.	1541	L6	-0.00769	9 -0.00068
	-0.	0076	59	-0.18025	5 -0.03425
	-0.	0006	88	-0.03425	5 0.33441

•

Table 27. LATSUM and ROTATE Results for the $SnCl_4 \cdot 2POCl_3$ Cl(4) Chlorines

Tensor				
-0.0627	71	0.06668	0.18253	
0.0666	88	-0.08149	0.12282	
0.1825	53	0.12282	0.14419	
Eigenvector	s			
0.8421	_7	-0.26375	0.47030	
0.1011	L3	0.93399	0.34269	
-0.5296	64	-0.24104	0.81325	
Angles for	the	Direction Cos	sines (in degree	s)
33	105	62		
84	21	70		
122	104	36		
$q_{xx} = -0.13$	5201	q = 0.301	_50	
$q_{yy} = -0.16$	6949	η = 0.124	31	
Rotated Ter	nsor			
-0.1652	28	0.01014	-0.01521	
0.0101	4	-0.13320	0.03352	
-0.0152	21	0.03352	0.29847	

Table 28. LATSUM and ROTATE Results for the $SnCl_4 \cdot 2POCl_3$ Cl(5) Chlorines

	C1(6)	Chlorines			
Tensor		·			
0.25	234	-0.12293	0.00000		
-0.12	293	-0.11008	-0.00000		
0.00	000	0,00000	-0.14226		
Eigenvect	ors				
0.95	5 92	0.29364	0.00000		
-0.29	364	0.95592	0.0000		
0.00	000	0.00000	1.00000		
Angles fo	r the l	Direction Co	sines (in de	grees)	
17	73	90			
107	17	90			
90	90	0			
$q_{xx} = -0.$	14226	q = 0.29	010		
$q_{yy} = -0.$	14784	η = 0.01	923		
Rotated T	ensor				
-0.14	226	0.00000	0.00000		
0.00	000	-0.14715	-0.01738		
0.00	000	-0.01738	0.28941		

Table 29. LATSUM and ROTATE Results for the $SnCl_4 \cdot 2POCl_3$ Cl(6) Chlorines

Ten	sor					
	-0.	1713	33	-0.01846	-0.02790	
	-0.	0184	1 6	-0.03017	0.25611	
	-0.	0279	90	0.25611	0.20150	
Eig	enve	ctor	s			
	0.	9979	94	0.01723	-0.06182	
	0.	0190	00	0.84070	0.54117	
	0.	0613	30	-0.54123	0.83864	
Ang	les	for	the	Direction C	cosines (in d	egrees)
	4		89	94		
	89		33	57		
	86	i	123	33		
q _{xx} p	= _	0.17	7339	q = 0.3	6882	
q _{yy}	= -	0.19	95 43	η = 0.0	5976	
Rot	ated	Ter	nsor			
	0.	2808	33	0.00467	-0.20463	
	0.	0046	57	-0.17359	0.00040	
	-0.	2046	63	0.00040	-0.10724	

Table 30. LATSUM and ROTATE Results for the SnCl₄·2POCl₃ Cl(7) Chlorines

Ten	sor				
	0.1092	13	-0.14093	0.20543	
	-0.1409	93	0.26921	0.03101	
	0.2054	43	0.03101	-0.37834	
Eig	envector	rs			
	0.747	10	-0.55866	-0.36020	
	0.5612	14	0.82054	-0.10875	
	0.3563	31	-0.12088	0.92652	
Ang	les for	the	Direction Co	osines (in degrees)	
	42	124	111		
	56	3 5	96		
	69	97	22		
q	= 0.10	125	q = -0.4	5184	
d ^{ÅÅ}	= 0.360	059	η = 0.563	154	
Rota	ated Ter	nsor			
	-0.2709	98	0.07019	-0.26537	
	0.070	19	0.35078	0.00384	
	-0.2653	37	0.00384	-0.07981	

Table 31. LATSUM and ROTATE Results for the $(TiCl_4 \cdot POCl_3)_2$ Cl(1) Chlorines

Ten	sor				
	0.565	58	-0.23411	0.09732	
	-0.234	11	-0.25465	-0.01975	
	0.097	32	-0.01975	-0.31092	
Eig	envecto	rs			
	-0.961	49	0.22749	0.15422	
	-0.254	44	0.52466	0.81240	
	0.103	90	-0.82035	0.56234	
Ang	les for	the	Direction Co	sines (in degrees)	
	16	77	81		
	105	58	36		
	84	145	56		
q _{vv}	= -0.3	1277	q = 0.63	805	
d ^{AAA}	= -0.3	2528	$\eta = 0.01$	961	
Rota	ated Te	nsor			
	-0.321	41	-0.01677	0.01959	
	-0.016	77	-0.10120	-0.39827	
	0.019	59	-0.39827	0.42262	

Table 32. LATSUM and ROTATE Results for the $(TiCl_4 \cdot POCl_3)_2$ Cl(2) Chlorines

Ten	sor			
	-0.2404	47	0.22476	0.12810
	0.2247	76	0.39100	0.37113
·	0.1281	10	0.37113	-0.15053
Eig	envector	rs		
	0.8885	56	0.27751	-0.36531
	-0.4018	39	0.85487	-0.32813
	0.2212	24	0.43838	0.87113
Ang	les for	the	Direction Co	sines (in degrees)
	27	74	111	
	114	31	109	
	77	64	29	
q _{xx} p	= -0.31	1024	q = 0.65	428
^д уу	= -0.34	4404	η = 0.05	166
Rot	ated Ter	nsor		
	-0.3256	60	-0.06738	0.07827
	-0.0673	38	-0.03637	-0.43761
	0.0782	27	-0.43761	0.36197

.

Table 33. LATSUM and ROTATE Results for the $(TiCl_4 \cdot POCl_3)_2$ Cl(3) Chlorines

Tensor				
-0.25	4 76	0.04993	-0.28331	
0.049	93	-0.28322	-0.21410	
-0.283	31	-0.21410	0.53798	
Eigenvecto	rs			
0.740	71	-0.60407	-0.29401	
0.561	73	0.79693	-0.22217	
0.368	51	-0.00060	0.92962	
Angles for	the	Direction Coa	sines (in degr	ees)
42	127	107		
56	37	103		
68	90	22		
$q_{xx} = -0.3$	2091	q = 0.678	374	
$q_{yy} = -0.3$	5784	η = 0.054	441	
Rotated Te	nsor			
-0.115	5 3	0.15127	-0.37604	
0.151	27	-0.23000	-0.29802	
-0.376	04	-0.29802	0.34544	

Table 34. LATSUM and ROTATE Results for the $(TiCl_4 \cdot POCl_3)_2$ Cl(4) Chlorines

Ten	sor				
	-0.0036	51	0.22498	0.04590	
	0.2249	98	0.11156	0.09510	
	0.0459	91	0.09510	-0.10794	
Eig	envector	cs			
	0.6847	79	0.58681	-0.43211	
	-0.6319	90	0.77350	0.04901	
	0.3630	00	0.23949	0.90049	
Ang	les for	the	Direction Co	sines (in degrees)	
	47	54	116		
	129	39	87		
	69	76	26		
q _{xx}	= -0.12	2480	q = 0.31	L68	
а ^д уу	= -0.18	3689	η = 0.19	921	
Rot	ated Ter	nsor			
	-0.0919	95	-0.11476	0.02851	
	-0.1147	75	0.26581	-0.07192	
	0.0285	51	-0.07192	-0.17385	

Table 35. LATSUM and ROTATE Results for the $(TiCl_4 \cdot POCl_3)_2$ Cl(5) Chlorines

Ten	sor				
	-0.034	96	-0.18438	-0.03693	
	-0.184	38	0.15611	0.06092	
	-0.036	93	0.06092	-0.12115	
Eig	envecto:	rs			
	0.853	74	-0.51158	0.09706	
	0.520	65	0.84133	-0.14519	
	-0.007	38	0.17448	0.98463	
Ang	les for	the	Direction Cos	sines (in degrees)	
	31	121	84		
	59	33	98		
	90	80	10		
q _{xx} p	= -0.1	3377	q = 0.280	286	
d ^{AAA}	= -0.1	4708	$\eta = 0.04$	739	
Rot	ated Te	nsor			
	-0.107	99	-0.09482	-0.03485	
	-0.094	83	0.20032	0.13726	
	-0.034	85	0.13726	-0.09233	

Table 36. LATSUM and ROTATE Results for the $(TiCl_4 \cdot POCl_3)_2$ Cl(6) Chlorines

Tensor				
-0.04414		-0.03579	0.18877	
-0.03579		-0.13273	-0.06634	
0.18877		-0.06634	0.17687	
Eigenvectors				
0.81430)	0.31223	0.48932	
-0.26073		0.94992	-0.17224	
-0.51859		0.01267	0.85493	
Angles for t	he	Direction Co	osines (in de	egrees)
3 5	72	61		
105	18	100		
121	89	31		
q _{vv} = -0.145	38	q = 0.29	9827	
$q_{yy} = -0.152$	89	$\eta = 0.02$	2518	
Rotated Tens	or			
0.08197		0.12112	0.18642	
0.12112		-0.08255	0.10273	
0.18642		0.10273	0.00058	

Table 37. LATSUM and ROTATE Results for the $(TiCl_4 \cdot POCl_3)_2$ Cl(7) Chlorines

matrix q_{xx} , q_{yy} , and $q_{zz} \equiv q$ are collected, along with the crystal field asymmetry parameter η .

2) <u>Comparison of the Lattice Sum Results Using</u> Both the First Model and the Revised Model

In order to facilitate the comparison of calculations using the charges assigned by the method of Townes and Dailey (old charges), and those using charges calculated from the NQR data (new charges), values of $q \equiv q_{ZZ}$ and η calculated using both the old charges and the new charges are collected in Table 38. As can be seen, the results are quite sensitive to the charges assigned to the sites which is a not unexpected result.

3) **DIAG Results**

In Table 39 the results of DIAG, as applied to chlorine atoms which should have identical molecular field gradients but occupy nonequivalent sites in the crystal lattice, are Thus, the difference between the two measured field qiven. gradients should be due entirely to solid state effects. The size of these effects, following our model, will be determined by the Sternheimer factor. If we write $q_{zz} = q_{zz}^{mol} + q_{zz}^{crys}$ then $\left| \Delta q_{zz}(\text{meas}) \right| = \left| q_{zz}(a) - q_{zz}(b) \right| = \left| \Delta q_{zz}^{\text{crys}} \right| = \left| q_{zz}^{\text{crys}}(a) - q_{zz}(b) \right|$ q_{zz}^{crys} (b), where q_{zz} is the measured field gradient, q_{zz}^{mol} and q_{zz}^{crys} have been defined previously, and $q_{zz}(a)$ means the field gradient at site a. Application of DIAG to the calculated and measured field gradients then allows us to estimate a Sternheimer factor. This is done by applying DIAG to the measured field gradient, using a number of different Sternheimer factors, and a series of molecular field gradients as

Using	
Results	
LATSUM	
to	
Charges	
New	
the	
Using	
Results	
LATSUM 1	S
of	arge
Comparison	the Old Cha
e 38.	
Tabl	

		01d Cha	rges	New Cha	rges
compound	ACOIII	ď	Ľ	đ	Ľ
SbC1 ₅	Cl(axial) Cl(equat)	0.91320 0.30663	0.00031 0.02775	0.86646 0.29093	0.00016 0.02774
SbC1 ₅ .POC1 ₃	c1(1) c1(2) c1(3) c1(3) c1(4) c1(5) c1(6)	0.40844 0.32386 0.33707 0.64126 0.65432 0.16092	0.0299 0.1617 0.0985 0.1166 0.0651 0.7032	0.29155 0.30277 0.31560 0.31808 0.32655 0.32655	0.03090 0.10434 0.00155 0.12575 0.07346 0.52420
snc14.2POCl ₃	c1(1) c1(2) c1(2) c1(3) c1(4) c1(5) c1(6) c1(7)	0.31648 0.26288 0.26607 0.66342 0.61709 0.58134 0.73358	0.15950 0.07783 0.09783 0.03141 0.07433 0.12137 0.06404	0.41776 0.37353 0.38946 0.33667 0.30150 0.29010 0.36882	0.05889 0.05889 0.05084 0.09588 0.12431 0.01923 0.05976
[TiCl4.POCl3]2	c1(1) c1(2) c1(3) c1(4) c1(5) c1(6) c1(7)	-0.33278 0.46274 0.51582 0.51381 0.68257 0.63089 0.65327	0.5709 0.1130 0.01351 0.14548 0.03474 0.02959 0.01664	-0.46184 0.63805 0.65428 0.67874 0.31168 0.28086 0.29827	0.56154 0.01961 0.05166 0.05441 0.19921 0.04739 0.02518

	1999 - 1999 - 1999 - 1999 - 1999 - 1999 - 1999 - 1999 - 1999 - 1999 - 1999 - 1999 - 1999 - 1990 - 1990 - 1990 -			
Compound and Atoms	Temperature (^O K)	"Experimental" ^Y ∞	∆¢ _{zz} (R ⁻³)	[∆g ^{crys}] (R ⁻³)
SbC15 · POC13				
C1(1)-C1(2)	77 297	+0.4 +0.07	0.410	0.246 0 392
c1(4) -c1(5)	22	6.0+	0.370	0.045
SnC14.2POC13				
C1(1) -C1(2)	77	-10.8	0.044	0.523
c1(1) -c1(2)	297	-2.6	0.044	0.160
C1(4) -C1(7) C1(6) -C1(7)	27	-1./ +0.75	0.397 0.397	0.098
(TiCl4.POCl3)2				
c1(7)-c1(6) c1(6)-c1(5) c1(7)-c1(5)	77 77 77	0.02	0.096 0.088 0.184	0.115 0.106 0.221

Line Splittings $\left| \Delta q \right|$ and "Experimental" Values of γ_∞ Table 39.

a function of the Sternheimer factors is obtained. Let us, as an example, consider Cl(1) and Cl(2) on $SbCl_5 \cdot POCl_3$ (see Figure 13). These two chlorine atoms are expected to have identical molecular field gradients since they both occupy equatorial positions cis to the POCl₃ oxygen atom. We compare the results of DIAG for these atoms and see that for a Sternheimer factor of +0.4 the experimental results obtained at liquid nitrogen temperatures yield the same molecular field It should be recalled that DIAG calculates a gradient. molecular field gradient with a series of trial Sternheimer factors. For a pair of chlorines which occupy nonequivalent positions in the crystal lattice, but should be identical in the isolated molecule, the "experimental" γ_{∞} is then taken as that $\gamma_{\rm co}$ which yields an identical molecular field gradient at each of the two chlorine sites. With a Sternheimer factor of +0.07 the room temperature experimental results yield an identical molecular field gradient. These, then are the "experimental" γ_{co} 's. For SnCl₄·2POCl₃ four nonequivalent positions (two on each POCl₃ molecule) are predicted for the POCl₃ chlorine atoms; however, only two resonance lines are observed. For reasons to be given in the discussion of the temperature dependence of the absorption lines, it was assumed that these two measured lines resulted from only one POCl3 molecule but it is not known whether the POCl₃ molecule containing Cl(4) and Cl(5), or that containing Cl(6) and Cl(7) gives rise to the absorption. Therefore, the DIAG results for each pair

183

Compound and Atom	Temperature (^O K)	φ _{z^z3)}	ŋcryst	X-X' (i	Y-Y' n degree	(s;	q ^{mo1} zz
SbCl5.POCl3 Cl(1) Cl(1) Cl(2) Cl(2) Cl(2) Cl(2) Cl(3) Cl(3) Cl(4) Cl(5) Cl(6) Cl(6)	297 297 297 297 297 297 297 297	-0.114 -0.114 +0.298 -0.102 -0.095 -0.102 +0.008 +0.008	0.017 0.022 0.002 0.002 0.002 0.002 0.002 0.002 0.002 0.002 0.002 0.002 0.002	0.01 0.02 0.00 0.02 0.35 3.30 3.30	00000000000000000000000000000000000000	0.00 0.00 0.00 0.00 0.00 0.00 0.00 0.0	17.544 17.544 17.276 17.244 17.276 16.605 16.605 20.693 20.693 20.693 18.490 18.191
SnCl4.2POCla C1(1) C1(1) C1(2) C1(2) C1(2) C1(3) C1(3) C1(3) C1(4) C1(4) C1(5) C1(6) C1(7)	297 297 297 297 297 77 77	+0.417 +0.417 +0.370 +0.378 +0.378 +0.388 +0.388 +0.388 +0.388 +0.388 +0.388 +0.299	0.021 0.007 0.008 0.005 0.005 0.005 0.005 0.001 0.001 0.001	$\begin{array}{c} 0.00\\ 0.00\\ 0.00\\ 25.00\\ 15.20\\ 0.0$	0.08 0.08 0.08 0.08 0.08 0.08 0.08 0.08	000000000000000000000000000000000000000	8.482 11.431 8.482 8.482 11.431 9.732 12.780 12.780 12.780 20.370 20.370
(<u>Ticl4.POCla)</u> c1(5) c1(6) c1(7)	77 77 77	-0.173 -0.092 +0.001	0.025 0.002 0.002	16.30 15.80 27.90	16.3 15.8 27.9	0.00 0.40 0.60	20.508 20.508 20.508

Table 40. DIAG Results

were applied to the experimental splitting and a separate Sternheimer factor obtained for each pair of sites. It should be remembered that the value of the calculated ϕ_{zz} is enhanced by the Sternheimer factor. That is, q_{zz}^{crys} (calculated) = $(1 - \gamma_{\infty})\phi_{zz}$, when ϕ_{zz} is the zz component of the LATSUM tensor after its coordinate system has been rotated to its final position by DIAG. As a first approximation (1 - γ_{m}) could have been obtained from the zz component of the tensor which resulted from the application of ROTATE to the results of This is a very good approximation if the rotated LATSUM. crystal field gradient tensor is nearly diagonal. DIAG essentially allows the off-diagonal elements to be taken into account so the use of DIAG becomes more important as the value of the Sternheimer factor increases. In the column of Table 39 under $\left| \Delta \phi_{\tau \tau} \right|$ is listed the difference in the calculated field gradients after the corresponding tensors have been rotated to the final coordinate system by DIAG. For purposes of comparison the measured splittings $\left| \bigtriangleup q_{zz}^{crys} \right|$ have also been in-The first column of Table 39 specifies the two atoms cluded. whose field gradients are being compared. Table 40 lists all the atoms upon which calculations have been performed. Since some atoms (for example those at sites 3 and 6 for $SbCl_5 \cdot POCl_3$) besides occupying nonequivalent sites, are also expected to differ from the other atoms in the molecule in their molecular field gradients, it is not possible to obtain a "experimental" value of $\gamma_{\rm co}$ for these sites. In these cases the values of $\gamma_{\rm co}$ obtained for chemically related sites are used when applying DIAG to the experimental frequencies measured for these lines. In Table 40 are collected the values of ϕ_{zz} (the zz components of the final rotated tensor), the values of η^{cryst} (the asymmetry parameters arising from solid state effects), and the values of q_{zz}^{mol} (the corrected molecular field gradients). In addition the angles between the axis system obtained by applying ROTATE to the results of LATSUM (X', Y', Z') and the final principal-axis system (X, Y, Z) are given for each site. All this information may be obtained from DIAG. ROTATE and DIAG have already been described (Sections III-E-3 and III-E-4).

V. DISCUSSION

A. <u>Temperature Dependence of the Absorption</u> <u>Frequencies and Phase Transitions</u>

The NQR absorption lines from these complexes show an interesting temperature dependence in that, while the POCl₃ resonances observed at a temperature of 77°K are very intense, no POCl₃ resonances are observed at room temperature. On the other hand, the resonances due to SnCl₄ and SbCl₅ in their respective complexes are observable both at liquid nitrogen temperature and at room temperature. Also, their frequencies show the normal negative temperature coefficients as listed in Table 14 except for Cl(3) in SbCl₅·POCl₃. The temperature dependence of the Cl(6) line in SbCl₅·POCl₃, was studied in more detail and is listed in Table 12 and plotted graphically in Figure 16; the plot shows a possible break indicating a phase transition between $77^{\circ}K$ and $165^{\circ}K$. Two other observations, while not directly related to temperature dependence, are also of interest. First, while the crystal structure predicts four nonequivalent sites for the chlorine atoms of POCl₃, and the crystal field gradient calculations show large differences in the gradients calculated for these sites, only two absorption frequencies are found for the chlorine atoms of $POCl_3$ in the $SnCl_4 \cdot 2POCl_3$ complex. Second, the observed splittings of the resonances attributed to POCl₃ in SbCl₅·POCl₃

187

Ľ

.

and $SnCl_4 \cdot 2POCl_3$ are much smaller than those expected from crystal field effects, while the splitting and the multiplicity of the POCl_3 lines in $[TiCl_4 \cdot POCl_3]_2$ and $TiCl_4 \cdot 2POCl_3$ are about what is expected (this point will be discussed more thoroughly in a later section).

It appears that some sort of phase transition is taking place. One possibility for the phase change would be if a change in the actual crystal structure took place. This could explain all of the observed phenomena except the line disappearance. Dean (112), and Kubo and Nakamura (113), have observed phase transitions due to a change in the crystal structure in a wide variety of organic and inorganic compounds. In all cases this phase change is accompanied by an abrupt break in the curve of resonance frequency versus temperature. If there is a change in the number of nonequivalent sites after the transition the line multiplicity will also change. However, in no case which is known to this author do the NQR absorptions completely disappear well below the melting point when the crystal undergoes a phase change which is only associated with a change in crystal structure. This observation, while not completely ruling out a change to a new crystal form as an explanation for the disappearance (fade out) of the POCl₃ lines, at least makes this explanation unattractive. It would also be difficult to explain why this new crystal form would affect only the POCl₃ chlorine resonances and not those of the SnCl₄ and SbCl₅ chlorine atoms. At least a change

in the number of nonequivalent sites in these acids may be reasonably expected if the crystal changes structure. All the data collected so far indicate that only the $POCl_3$ chlorines are involved in the phase change.

Gutowsky and McCall (111,35) have observed a fade out of the NQR signals well below the melting point in several compounds. In all of these compounds either molecular or internal reorientation is possible. Dean (28) has also observed a fade out of the chlorine resonance in CCl_3CCl_3 on warming up. Although completely free internal rotation does not seem likely in this compound because of the high barrier (116), it is quite probable that restricted rotation takes place about the C-C axis. In $C_{6}H_5CCl_3$, in which a fade out of the signal also occurs, a restricted rotation about the C_3 axis of the trichloromethyl group is possible as well as ring reorientation. NMR studies by C. Holm (115) on $p-C_6H_4(CF_3)_2$ show that both the CF₃ groups and the ring reorient in the solid. According to Gutowsky and McCall (35) a comparison of molecular models for this compound and that of C₆H₅CCl₃ indicate that such motions should also occur in the In all the complexes studied so far there is a latter. possibility of restricted rotation about the P-O bond in the POCl₃ molecule, it is therefore proposed that the phase transitions in these complexes are associated, not with a change in crystal structure, but with molecular reorientations in the solid. This restricted rotation could explain all the features

so far observed including the temperature dependence, multiplicity and anomalously small splittings. The onset of rotations is expected to be a gradual process rather than a sharp transition. As the transition temperature is approached the fraction of the molecules able to overcome the barrier to internal rotation increases. This would have an averaging effect on the crystallographically nonequivalent chlorine atoms, decreasing the splitting between the POCl₃ lines while not directly affecting the resonance frequencies of the SbCl₅ chlorine atoms. Since the chlorine atoms on the two POCl₃ molecules in SnCl₄·2POCl₃ see different environments it is likely that the barrier to rotation for each of the two POCla molecules is different. Therefore, it is quite possible that at $77^{\circ}K$ the resonances of one of the POCl₃ molecules would have already faded out. The fact that the splittings of the $POCl_3$ lines in $[TiCl_4 \cdot POCl_3]_2$ seem to follow the calculated gradients may be explained by postulating that this compound is farther from its transition temperature than the other two compounds. It is interesting to note that TiCl₄·2POCl₃ shows a very complex absorption pattern at liquid nitrogen temperature, with about 3-6 lines spread over about 300 kHz. Since TiCl₄·2POCl₃ is isostructural with SnCl₄·2POCl₃ (117) four lines are expected if the barriers to internal rotation are high enough at 77° K so that no fade out occurs for the chlorine resonances of the two POCl₃ molecules. Thus, the observed pattern may be four lines, and, if this is true, it

indicates that the transition temperature for this compound is also high. The fading out of resonances was observed by Gutowsky and McCall well below the actual temperatures of the phase transitions. The latter were known from the heat capacity and dielectric constant measurements of Rushner et al. (116). In the case of $(CH_3)_3CC1$, however, fade out occurred at the lower of two transition temperatures. Hence, the temperature at which fade out of the resonances in the complexes studied here occurs would not be expected to correlate well with the actual temperatures at which the phase transitions occur but may be expected to give a qualitative idea of the relative barrier heights. Unfortunately, since no measurements on heat capacity, dielectric constant or other physical properties which undergo an abrupt change at a phase transition, are available for the complexes studied here it is not known where their phase transitions take place and there is no way to check the conclusions drawn above at present. X-ray data, however, also suggest the possibility of restricted rotation. As shown in Table 41, the temperature factors for the X-ray scattering by the chlorine atoms of the POCl₃ molecules in SnCl₄·2POCl₃ are unusually high. A value of $3A^2$ is considered normal and anything larger than $6A^2$ is considered very large. It may be seen that, although all the temperature factors are high, those for the POCl₃ chlorine atoms (chlorine atoms 4, 5, 6, and 7) are unusually high as would be expected if the POCl₃ molecules were undergoing

191

Temperature Factor (in A^2)
3.38
6.33
5.87
4.87
4.21
4.65
5.05
4.31
7.84
6.58
7.88
7.44

Table 41. Temperature Factors for $SnCl_4 \cdot 2POCl_3$

^aC. Bränden, Acta Chem. Scand. <u>17</u>, 759 (1963).

restricted rotation around their threefold axes. Unfortunately, the temperature factors for the individual atoms are not listed but an average factor of 4.3 Å² was used for $[TiCl_4 \cdot POCl_3]_2$. Since this is only an average value it is not possible to conclude much from it, although 4.3 Å² suggests an abnormal structure. Bränden and Lindqvist have also estimated the temperature factors for SbCl₅ · POCl₃ (130). The factors for the two nonequivalent POCl₃ chlorine sites are 4.9 and 5.2 Å². These are again very large and indicate abnormal motion of the atoms. In conclusion it may be said that, although no conclusive evidence is present, the proposal
of restricted rotation explains all the available data. In this connection it would be interesting to obtain the temperature dependence of the chlorine resonances for the chlorine atoms of POCl₃ in the complexes. Such a study should include some temperatures below liquid nitrogen temperature to determine, if possible, the temperature at which the restricted rotation is "frozen out" since it seems likely that a good percentage of the POCl₃ molecules in SbCl₅·POCl₃ and SnCl₄·2POCl₃ are undergoing restricted rotation even at 77° K.

B. Calculation of the Point-Charge Field Gradient

Semin and Fedin (122) have stressed the importance of evaluating the influence of the solid-state effects on the NQR absorption frequencies. Although these effects are usually much smaller than chemical effects, this is not always true. Because of the close-packed structure of the chargetransfer complexes studied here and the moderately large fraction of ionic character in the bonds it was expected that the crystal lattice field gradient tensor \bar{q}^{crys} would be comparatively large. As previously discussed, it was assumed that the most important contribution to \bar{q}^{crys} came from the charged atoms situated in the crystal lattice. This is believed to be a good assumption since an examination of the crystal structures of these compounds show that all chlorinechlorine distances are large enough to preclude the possibility

strong intermolecular interactions and Bersohn (120) has shown that dispersive and short-range repulsive forces (Van der Waals forces) do not appreciably affect the measured field gradient. At the beginning of this work it was decided to calculate the crystal lattice field gradient $\phi_{,,}$ at each chlorine site, multiply them by the factor $1\text{-}\gamma_{\mathrm{co}},\,\mathrm{using}$ -10 (51) for $\gamma_{_{\mbox{\scriptsize CD}}}$, and use these qualitatively, if not quantitatively to estimate the importance of solid state effects. It soon became apparent, however, that such a simple interpretation of the calculated data was not possible as shown by a critical examination of the "experimental" value of $\gamma_{\rm co}$. The expected value (γ_{∞} = -10) was taken from Burns and Wikner (51) who argue that, although Sternheimer has calculated a much larger value, solid-state effects will cause this value to be greatly reduced; the value γ_{m} = -10 was deduced from ultrasonic experiments and thus is considered to be an "experimental" The quotation marks refer to the fact that no comvalue. pletely unambiguous method has yet been found to measure $\gamma_{\rm co}$. The ultrasonic experiments all were made using highly ionic alkali halides; therefore, the fact that most of the experimental values of $\gamma_{\rm co}$ measured in this work are much more shielding than -10 is not incompatible with the results of the ultrasonic experiments, since the chlorine atoms involved in the charge-transfer complexes are much less polarizable. However, the chlorine atoms of POCl₃ in SbCl₅·POCl₃ and one of the POCl₃ molecules in SnCl₄·2POCl₃ are found in our

calculations to be much more shielded than would be expected (as mentioned, γ_{∞} for a neutral chlorine is +0.46). Undoubtedly some other effect is obscuring the effect of the charged lattice sites on the field gradient of these chlorine atoms. One possible effect, restricted rotation about the P-O bond, has already been discussed and seems to be the most likely explanation. On the other hand the calculated values of γ_{∞} for [TiCl₄·POCl₃]₂ show fairly good agreement with the other calculated values of γ_{co} . In addition, the internal consistency of the values of $\gamma_{\rm cons}$ calculated for the three splittings of the POCl₃ lines in [TiCl₄·POCl₃]₂ is very satisfactory although it may be partly fortuitous. Temperature may also affect the results in other ways. Vibrational motions of the molecules containing the quadrupolar nuclei can cause a decrease in the absorption frequency due to an averaging effect. Thus the absorption frequency $\omega_{\!\!\boldsymbol{m}}$ at some temperature T can be represented as $\omega_{\rm T} = \omega_0 (1 + aT + bT^{-1})$, where ω_0 is the absorption frequency in the absence of vibrational motion in the lattice. Obviously we should compare our calculated field gradients with the corresponding values of ω_0 . However, determination of ω_0 requires points below 77°K and, at present, it is not possible to work in this temperature range in the Department of Chemistry. Another effect of the temperature is that, as the temperature is lowered, even though no phase change occurs, the positions of the atoms may be slightly shifted. Unfortunately, the point-charge fieldgradient calculations are very sensitive to changes of this

type which probably accounts for the major part of the large difference between the "measured" values of γ_{∞} at room temperature and liquid nitrogen temperature and the fact that the values of γ_{∞} at room temperature seem to be more reasonable despite the fact that the observed frequencies at room temperature are farther from ω_0 than are those at liquid nitrogen temperature. Another factor which may affect the results is the neglect of the contribution of dipolar polarization to the field gradient. This contribution is always smaller than the point-charge contribution. In our case this contribution should even be smaller because the chlorides and oxide ions, which would give the most important contribution due to this effect, are not nearly as polarizable as they are in the wholly ionic compounds in which this effect has so far been evaluated. However, this polarization may be important when we try to reproduce such small effects as the splitting of NQR lines by solid-state effects. Many authors (e.g., 105, 122, 123) have tried to account for the entire measured field gradient in ionic crystals by means of the calculated $\phi_{zz}(1 - \gamma_{\infty})$. Bersohn and Shulman (124) have strongly criticized this approach, maintaining that the pointcharge contribution has been given too much importance by using a value of γ_{∞} which is much too large. These authors claim that the largest part of the measured field gradient is due to p-electron defects on the halide ion (i.e., covalent bonding). Of course, * the effects of covalent bonding have

been included implicitly in previous calculations by permitting such large values of γ_∞ . A large value of γ_∞ implies a large amount of polarization of the charge cloud around the chlorine and, thus, is equivalent to introducing some covalent character into the bond. However, it is artificial to try to include covalent bonding in this manner. The arguments of Bersohn and Shulman are undoubtedly correct to some extent; it is certain that the value of γ_{∞} has been overestimated in many cases, the general practice being for authors to choose, from the several available values for γ_{∞} (all large), that value which most closely fits their data. However, Bersohn and Shulman may have gone too far to the other extreme. In fact, the majority of the values of $\gamma_{\rm orm}$ "measured" in this work, where other effects do not interfere, seem to lie very close to γ_{∞} = 0. Nevertheless, it seems likely that more ionic chlorine atoms will exhibit a somewhat larger $\gamma_{\rm co}$. In the one case in which the percentage covalent bonding obtained by Bersohn and Shulman was directly comparable to the percentage covalent bonding as measured by ESR the agreement is rather poor (16% for NQR as compared to 10% by ESR). Bersohn and Shulman explain this difference by reintroducing the point-charge contribution which, with $\gamma_{\rm co}$ = 0, reduces the NQR covalent bonding to 13%. One is tempted to think that a slightly larger γ_{∞} would have explained all the difference. Another effect which should be mentioned is that the Sternheimer factor is not constant as a function of distance from the nucleus. Calculations (121) show that $\gamma_{\rm CD}$ (Cl⁻) is fairly

constant after about $5a_0(2.65\text{\AA})$. In the compounds studied here most ions were more distant than 2.65 Å except the atom directly bonded to the chlorine under consideration. Although no calculations exist which give any insight into this source of error it is not thought to be important. Morosin and Narath (48) have criticized the point-charge model as applied to the nearest neighbor ions of the nucleus under investigation. Unfortunately, it is a characteristic of this type of calculation that the nearest neighbors make a most important contribution to the final value so that if the assumption of point-charges for the nearest neighbor sites is seriously in error the effect could be quite large on the calculated crystal-lattice field-gradient tensor. Although the calculations done so far have not shown that this effect is important, neither has anyone tried to apply these calculations in a consistent manner in situations which make serious demands on the accuracy of the calculations. present work is the first attempt to make stringent demands on the calculations. For this reason there are not yet enough determinations of experimental and calculated splittings available to permit comparison with the results of other Regarding the present data it may be said that the workers. calculations made so far seem to indicate that $\gamma_{\infty}^{'}$, in these only partially ionic complexes, must be given a much lower value than $\gamma_{\rm co}$ = -10 which has usually been used for more ionic structures. In particular, a value in the range 0 to -3 seems the most reasonable and a value of 0 is not too inconsistent

with the data. Very probably no single value of γ_{∞} can be used but each compound must be considered individually. A more definitive statement than this awaits more compari-Because of the uncertainty in $\gamma_{_{\mbox{CO}}}$ it is not possible sons. to use these calculations quantitatively but the calculated values of ϕ_{zz} should be reliable in a relative sense. The asymmetry parameters calculated by DIAG are quite interesting, although they are somewhat lower than those usually found for chlorine atoms in covalent bonds. These measured values of η usually fall in the range 0.05-0.1. However, the difference can easily be accounted for by the introduction of a small amount of double bonding; also, it should be noted that, in estimates which use η to give the fractional double-bond character in a bond, a serious error could be introduced by neglecting the contribution of solid-state effects to η . Some of the X-X' and Y-Y' angles of Table 40 are quite large. This is expected since ROTATE fixed the X', $\mathbf{Y}^{\prime},\ \mathbf{Z}^{\prime}$ system under the assumption that the \mathbf{X}^{\prime} and \mathbf{Y}^{\prime} directions are arbitrary. When some asymmetry is introduced into the field gradient by means of crystal effects, these directions become fixed and it is not surprising that the X' and Y' directions must be shifted to conform to the fixed directions. It is significant that the solid-state effects did not shift Z from Z' to any appreciable degree, in agreement with experiment.

C. Frequency Shifts in the Complexed POCl₃ Chlorine Atoms-

In a simple model of charge transfer we may think of a POCl₃ molecule donating electronic charge from the oxygen lone pair electrons. This donation may go so far that the P-O double bond is broken. Electronic charge is drawn from the chlorine atoms of POCl₃ toward the phosphorus atom by induction. This charge migration is reflected by an increase in the molecular field gradient at the chlorine atom of POCl₃ which is reflected in an increase in the NQR absorption frequency. In all the complexes studied so far, an increase in the absorption frequency of the $POCl_3$ chlorine atoms has been noted. It seems clear that this change in the field gradient should be attributed to inductive withdrawal of charge from chlorine by the oxygen atom of POCl₃. Until the X-ray structures of some of this type compound were done it had been postulated (93) that the charge transfer took place from one of the POCl₃ chlorines to the Lewis acid. This structure can be rejected on the basis of the NQR results.

Before a more quantitative treatment may be attempted it is necessary to evaluate the contribution of the crystal lattice to the observed shifts. An examination of the ϕ_{ZZ} values calculated for these positions shows that, if an average of the observed resonance frequencies are taken for SnCl₄·2POCl₃ and SbCl₅·POCl₃, while the highest frequency line is taken for (TiCl₄·POCl₃)₂, a shift which is fairly free from solid-state effects should be obtained. This is

especially true since there is some evidence that $\gamma_{\infty} = 0$. It should be kept in mind, however, that solid-state effects could still be large enough to cause a reordering of the acid strengths.

Badgley and Livingston (125) have studied $POCl_3$ by electron diffraction; their results, together with the results of X-ray studies on the complexes, are listed in Table 42.

Table 42. Bond Angles (in Degrees) and Bond Lengths (in Angstroms) of POCl₃ in Various Complexes From X-Fay Investigations

Bond Length or						
Bond Angle	POCl3	SbCl ₅ ·POCl ₃	$SnCl_4 \cdot 2POCl_3$	(TiCl ₄ ·POCl ₃) ₂		
P-0	1.45 <u>+</u> .05	1.46±.02	1.44 <u>+</u> .05	1.44 <u>+</u> .02		
P-Cl1	1.99 <u>+</u> .02	1.95 <u>+</u> .02	1.95 <u>+</u> .03	1.93 <u>+</u> .01		
P-Cl ₂		1.97±.02	1.93 <u>+</u> .03	1.98 <u>+</u> .0 1		
P-Cl ₃			1.89 <u>+</u> .03	1.96 <u>+</u> .01		
P-Cl ₄			2.00±.03			
Cl ₁ -P-Cl ₁	103.5	105.6	105.7	107.0		
Cl ₁ -P-Cl ₂		107.4	105.4	106.6		
Cl ₃ -P-Cl ₃			112.5	104.1		
Cl ₃ -P-Cl ₄			101.2			

The designations Cl_1 , Cl_2 , Cl_3 and Cl_4 simply designate nonequivalent chlorine atoms. It is not necessary to identify them with specific sites in the crystal lattice. An inspection of Table 42 shows that, aside from some distortion in bond lengths and bond angles, which were expected because the data were obtained for gaseous rather than solid POCl₃, the geometry of complexed POCl₃ is quite close to that of pure POCl₃. This is strong evidence that no change in π -bond character in the P-Cl bonds, and probably no great change in s hybridization at the chlorine sites, has taken place upon complex formation. Let us consider the basic equation of Townes and Dailey (Equation 52)

$$\rho = 1 - I - \alpha - \Pi + \delta ;$$

then, if we designate the ρ measured for complexed POCl₃ as ρ_1 and that for the pure POCl₃ as ρ_2 ,

$$\Delta \rho = \rho_1 - \rho_2 = -\Delta \mathbf{I} - \Delta \alpha - \Delta \mathbf{\Pi} + \Delta \delta,$$

where the other symbols have been defined previously (Section I-F). From the fact that the geometry of POCl₃ does not vary to any marked extent, the hybridization is not expected to charge very much if a small charge shift takes place, hence Δs , $\Delta \delta$ and ΔT may be set equal to zero. Then,

$$\Delta \rho = -\Delta \mathbf{I}$$

so that if ρ increases upon formation of the complex the ionicity of the P-Cl bond decreases in agreement with simple induction considerations. Dilke and Eley (126) have studied heats of formation for the reaction between benzaldehyde and a number of Lewis acids. The results are given in Table 43 along with values of ρ and ΔI for all the complexes studied in this work. The ρ values quoted are average values for SbCl₅·POCl₃ and SnCl₄·2POCl₃, the highest frequency resonance line is used for (TiCl₄·POCl₃)₂, and only one line is observed for FeCl₃·POCl₃. The compounds are arranged in order of decreasing ρ . Since ΔI is negative in all cases, ΔI values may be interpreted as providing the fraction $|\Delta I|$

Table 43. Electronic Charge Lost by the POCl₃ Chlorine Atoms Estimated from NQR Data

Compound	ρ	a ∆I	Heats of Reaction ^b kcal/mole
SbCl ₅ .POCl ₃	0.556	-0.028	21
$(TiCl_4 \cdot POCl_3)_2$	0.552	-0.024	17
FeCl ₃ .POCl ₃	0.551	-0.023	27
SnCl ₄ ·2POCl ₃	0.549	-0.021	14

^aAverage ρ for POCl₃ is 0.528 (131).

^bHeats of reaction as measured for reaction of these acids with benzaldehyde (130).

of an electronic charge which has moved from the chlorine atom to the phosphorus atom. For example, our measurements say that 0.028e of electronic charge has migrated from each chlorine atom to the phosphorus atom in $SbCl_5 \cdot POCl_3$. The ΔI values in Table 43 enable us to order the four Lewis acids

studied according to decreasing acidity, as $SbCl_5 > TiCl_4 >$ $FeCl_3 > SnCl_4$. It may be argued that, since $SnCl_4$ accepts two POCl₃ molecules, the ΔI for this compound should be doubled. This is a matter of definition but it is interesting to note in this respect that infrared studies reveal that the negative shift of the 1300 cm^{-1} P-O bond of POCl₃ upon complex formation was 95 cm⁻¹ in both $TiCl_4 \cdot 2POCl_3$ and $(TiCl_4 \cdot POCl_3)_2$ while that of $SnCl_4 \cdot 2POCl_3$ was 85 cm⁻¹ (128). The larger shift is correlated with a larger charge transfer from the P-O bond, hence, IR results predict that TiCl₄ is a stronger acid than SnCl₄ and also suggest that TiCl₄ accepts the same amount of charge from POCl₃ whether it coordinates with one or two molecules. It should be noted that the thermodynamic data disagree with the ordering of the Lewis acids proposed here. However, this is not surprising since the base used in the thermodynamic studies was benzaldehyde, and it is often found that the order of acid strength is changed when the standard base is changed. For example, infrared data and the present NQR results show that, with respect to POCl₃, TiCl₄ is a stronger acid than SnCl₄ but the reverse is true if the ordering base is $(C_{6}H_{5})_{2}PO$ (132).

D. <u>Shifts in the NQR Spectra of SnCl₄ and</u> <u>SbCl₅ Upon Complex Formation</u>

1) General Comments

Although NQR data for only two Lewis acids, involved as components of a complex, are available, it is still proper to

point out a few similarities between the spectra of the two complexed Lewis acids. The general appearance of the two spectra is quite similar, both spectra have a group of absorptions at a low frequency (two for $SnCl_4$ and three for $SbCl_5$) which are quite close together. In both cases these absorptions belong to the chlorine atoms which lie in a plane, which for SbCl₅ would correspond to the equatorial (basal) plane of the free molecule (assuming that the POCl₃ approaches SbCl₅ in the basal plane), and for SnCl₄ would correspond to a somewhat analogous plane. The other absorption line, which in SbCl₅ is due to the axial chlorine atoms, lies about 2 MHz higher in frequency than that for the basal chlorine atoms. This pattern is not due to solid-state effects as the point-charge results indicate that, if this were the case, the resonance line due to the Cl(2) chlorine atom of $SbCl_5$. **POC1**₃ would be at a higher frequency than the resonance line due to the two axial Cl(3) chlorine atoms which is contrary to observation. Furthermore, the point charge effects by themselves would put the NQR line due to Cl(1) of SnCl₄·POCl₃ higher in frequency than those due to Cl(2) and Cl(3), again contrary to observation. The available data suggest that the metal bonding orbitals directed towards the "basal" plane positions (from Sb to Cl(1), Cl(2), Cl(3) and O in SbCl₅·POCl₃ and from Sn to Cl(1), Cl(2) and the two $POCl_3$ oxygen atoms in SnCl₄[•]2POCl₃) are different from those directed towards the "axial" positions. Possibly there is some similarity between

the "basal" metal atom orbitals in the SbCl₅ complex and in the SnCl₄ complex; some similarity may also exist between the bonds to the "axial" positions in the two complexes. More data is needed to substantiate or disprove this suggestion.

2) $SnCl_4 \cdot 2POCl_3$

Livingston (127) has studied the NQR spectrum of SnCl₄ at 77° K using a regenerative oscillator. He found four very closely spaced lines whose average frequency is 24.095 MHz. All the measured frequencies for $SnCl_4 \cdot 2POCl_3$ which have been assigned in this work to the SnCl₄ molecule are lower in frequency than the average value of 24.095 MHz which he reported. This is expected if the change in frequency is due to an inductive gain of electronic charge by the $SnCl_4$ chlorine atoms when the tin atom accepts charge from the POCla oxygen atoms. The difference between the frequencies of the "basal" chlorines and the "axial" chlorines has already been interpreted to suggest a difference in the nature of the metal bonding orbitals directed towards the "axial" and "basal" positions. Van Der Doorn and Drago (129) have recently studied the bonding in the trigonal bipyramidal phosphorus(V) chlorofluorides by means of extended Hűckel calculations. They have interpreted the difference in the phosphorus bonding orbitals as a difference in the electronegativity of these orbitals. Because the equatorial bonds have a large s hybridization they are more electronegative while the more

electropositive orbitals are directed towards the axial positions. Thus, the more electronegative atoms will be in the axial positions; this assumption suffices to predict the structures of all the phosphorus chlorofluorides. Also, PCl₄F, which is thought to retain its trigonal bipyramidal structure in the solid state (PC15 does not), has been studied by NQR (111). The results show that the absorption of the axial chlorine lies about 3.5 MHz lower in frequency than the absorption of the equatorial chlorine atoms. This would be consistent with the higher ionicity of the P-Cl axial bond which is expected if the phosphorus bonds to the axial positions are more electropositive and in fact points to a quite sizeable difference in ionicity between the axial and equatorial P-Cl bonds ($\Delta I \sim 0.07$). Furthermore, measurements performed during the present work on SbCl₅ at $250^{\circ}K$ show that the axial chlorine atoms absorb at about 2.4 MHz lower in frequency than the equatorial chlorine atoms ($\Delta I \sim 0.05$). These are the only NQR measurements made on molecules which are known to retain their trigonal bipyramidal geometry in the solid-state. For the Cl(1), Cl(2), and Cl(3) NQR absorptions in SnCl₄·2POCl₃ the calculated ϕ_{22} values would group the Cl(2) and Cl(3) absorptions closely together and put the Cl(1) absorption at a somewhat higher frequency. At first glance this may seen to fit the observed pattern but two things strongly argue against accepting this assignment of lines. First, from X-ray data it is apparent that the Cl(3)

absorption should be twice as intense as the absorption due to either Cl(1) or Cl(2). The highest frequency line is noticeably more intense than the other two lines. It seems reasonable, therefore, to assign this absorption to Cl(3). Second, if Cl(1) is assigned to the highest frequency line on the basis of crystal lattice effects, in order to account for the observed splitting in terms of the calculated ϕ_{zz} values (1 - $\gamma_{\rm co}$) must be taken to be 42.0 which is quite unreasonable. It seems then that the splitting between the high frequency line and the two low frequency lines is due to a difference in the molecular field gradients at the "axial" and "basal" chlorine sites. Since it is unlikely that the s and d hybridization at the different chlorine nuclei would change very much, the difference must be accounted for by differences in ionicity and π -character of the Sn-Cl bonds. Both of these differences would arise due to nonequivalence of the tin bonding orbitals. No additional information is gained if the Sn-Cl bond lengths for the complexed SnCl₄ are studied as these seem about equal, within the standard deviations of the X-ray data. If, as a working hypothesis, we assume that the difference is entirely due to a difference in the ionicities of the two types of Sn-Cl bonds, it is possible to calculate the actual charge transferred. This is a logical extension of the idea that all the tin bonding orbitals are not equivalent, for if, as in the case of the phosphorus(V) chlorofluorides, the main difference between the

tin bonding orbitals is that one set is more electronegative than the other, it is natural to expect that the more electronegative orbitals will get a larger share of the charge transferred to the Sn from $POCl_3$. The Sn-Cl bonds which are formed with the more electronegative orbitals will then show a larger gain in ionicity and consequently the chlorine atom involved will have a lower resonance frequency. Table 44 is constructed to show this effect quantitatively. The column labeled ΔI shows the change in ionicity calculated from the equations

 $\rho = 1 - I - \alpha - 77 + \delta \text{ and}$ $\rho(\text{SnCl}_4 \cdot 2\text{POCl}_3) - \rho(\text{SnCl}_4) \equiv \Delta \rho = -\Delta I(\Delta \alpha = \Delta T = \Delta \delta = 0)$

From the definition of $\Delta \rho$ it is obvious that a positive ΔI corresponds to an increase in the ionicity of the Sn-Cl bond under consideration. The column under "corrected ΔI "(Table 44) was calculated after correcting the chlorine absorption frequencies for solid-state effects assuming $\gamma_{co} = 0$. This was done more as an indication of the error involved in neglecting solid-state effects rather than as a realistic attempt to make corrections since no X-ray data exist for SnCl₄. The chlorine resonance frequencies for SnCl₄ and SnCl₄·2POCl₃ at 77^oK were used. The total charge transferred from the uncorrected values of ΔI by taking the weighted sum 2(0.054) + 2(0.076) = 0.260e. This is a reasonable answer but it is clear that more data on SnCl₄ charge-transfer complexes of

Compound	Q	ΔΙ	$\Delta I(corrected)$
SnCl ₄	0.439		
SnCl ₄ ·2POCl ₃			
C1(3)	0.385	0.054	0.064
Cl(1) and Cl(2) ^a	0.354	0.076	0.087

Table 44. Charge Transfer in Complexed SnCl₄

^aAverage of the ρ values measured for Cl(1) and Cl(2).

.

known crystal structure must be obtained in order to confirm or deny the conclusions drawn here.

3) $SbCl_5 \cdot POCl_3$

The abnormal behavior with temperature for chlorine resonance frequencies in SbCl₅ has already been discussed in Section IV. Because there are no data available (such as values of dielectric constant as a function of temperature) which could give any information on phase changes, either for these complexes or for those of SbCl₅, the cause of this abnormal behavior is not known for certain. Although it is normal for absorption frequencies to change abruptly at a phase transition, the drop in frequency of 4.5 MHz observed for the chlorine resonance in pure SbCl₅ is distinctly abnormal (about 0.5 MHz would be normal). A phase transition would account for the observed changes but X-ray data taken at $77^{\circ}K$ along with a study of the variation of the NQR spectrum with temperature would be needed to establish whether this is the correct explanation. The very large variation in frequency strongly affects the interpretation of the observed chlorine resonances for the chlorine atoms of SbCl₅ in SbCl₅·POCl₃. If the interpretation of the NQR results for the complex are based on the data for SbCl₅ at 250° K there would be an unexplained rise in frequency for the axial chlorine atoms whereas a drop would be expected. Similarly the drops in frequency for the equatorial chlorine atoms would become smaller than expected. It would not be easy to explain these

changes, especially since the X-ray data show no dramatic changes in the bond lengths of the Sb-Cl bonds and large decreases in s hybridization and/or double bonding in the Sb-Cl bonds would be needed to explain these changes (an examination of Table 40 will show that solid-state effects cannot account for the changes). On the other hand, if we accept the NQR results at $77^{\circ}K$ and also assign the higher frequency group at 30.4 MHz to the equatorial chlorines, the results agree quite well with those found for SnCl₄. Again, the axial chlorine atoms receive a smaller charge than do the equatorial chlorine atoms. If, as expected, the complexed SbCl₅ retains some identity with the uncomplexed SbCl₅ there is every reason to believe that the Sb-Cl bonds involving Cl(1), Cl(2), and Cl(3) will be different from those involving Cl(6). Further, if the results of Van der Doorn and Drago can be extended from PCl₅ to SbCl₅, and this seems like a reasonable extension, then the basal positions should receive the largest change. Table 45 presents results similar to those of 44 using the frequencies for SbCl₅·POCl₃ and for SbCl₅ measured at liquid nitrogen temperatures. The values of ρ for the equatorial $SbCl_5$ chlorine atoms and for Cl(1) and Cl(2)of SbCl₅·POCl₃ are obtained by taking an average of the observed resonance frequencies. The column " ΔI corrected" (Table 45) gives the value of ΔI calculated after correcting the observed e^2qQ for the solid-state effects assuming $\gamma_{m} = 0$. In this case the correction is guite small. However, it should be emphasized

Compound	ρ	ΔΙ	∆I(corrected)		
SbCl ₅					
(axial)	0.512				
(equatorial)	0.554				
SbCl ₅ ·POCl ₃					
Cl(1) and Cl(2) ^a	0.474	0.080	0.083		
C1(3)	0.445	0.109	0.106		
C1(6)	0.498	0.014	0.014		

Table 45. Charge Transfer in Complexed SbCl₅

^aAverage of ρ values measured for Cl(1) and Cl(2).

that these corrected values of ΔI are probably not any better than the uncorrected values and only serve to give an idea of the error involved if the solid-state effects are neglected since there is considerable uncertainty over the value of γ_{∞} . Also, in correcting for the solid-state effects only ρ for the complex has been corrected and solid-state effects in SbCl₅ and SnCl₄ themselves have been neglected. The total charge transferred from POCl₃ to SbCl₅ may be calculated as 2(0.080) + 2(0.014) + 0.109 = 0.297e. Comparison of this result with that calculated for SnCl₄·2POCl₃ (0.260e) shows that both are about the expected magnitude and their relative magnitudes also look right. It is also interesting to note that Cl(3) receives a larger share of charge than the other basal chlorines. This is in agreement with Bränden et al. (131) who find that bonds to chlorine atoms <u>trans</u> to the donoracceptor bond are generally stronger than the bonds from the acceptor atom to other chlorine atoms.

SUMMARY

The nuclear quadrupole resonance spectra of several charge transfer complexes between POCl₃ and some Lewis acids have been obtained. The absorption frequencies have been assigned to various chlorine atoms in the complexes by comparison with X-ray data and point-charge calculations of solid-state effects.

The spectra have been interpreted in terms of charge transfer upon complex formation and the changes in the NQR absorption frequencies of the Lewis acids have been taken to indicate a nonequivalence in the bonding orbitals of the central metal atom of these acids when they are complexed with POCl₃.

REFERENCES

(1) н.	G.	Dehmelt	and	H.	Krüger,	Naturwiss.	, <u>37</u> ,	111	(1950)) .
----	------	----	---------	-----	----	---------	------------	---------------	-----	--------	-----

- (2) D. Douglass, J. Chem. Phys., <u>32</u>, 1882 (1960).
- (3) H. Hooper, J. Chem. Phys., <u>41</u>, 599 (1964).
- (4) P. Cornil, J. Duchesne, M. Read and R. Cahay, Bull. Classe Sci. Acad. Roy. Belg., <u>50</u>, 235 (1964).
- (5) V. Grechishkin and I. Kyuntsel, Fiz. Tverd. Tela, <u>5</u>, 948 (1963).
- (6) V. Grechishkin and I. Kyuntsel, Optics and Spectroscopy, <u>16</u>, 87 (1964).
- (7) V. Grechishkin and I. Kyuntsel, Soviet Physics Solid-State, <u>5</u>, 694 (1963).
- (8) H. Dehmelt, J. Chem. Phys., <u>21</u>, 380 (1953).
- (9) V. Biedenkapp and A. Weiss, Z. Naturforsch., <u>19A</u>, 1518
 (1964).
- (10) N. F. Ramsey, <u>Nuclear Moments</u> (John Wiley and Sons, Inc., New York, 1953).
- (12) C. Dean, Phys. Rev., <u>96</u>, 1053 (1954).
- (13) G. Pake, Solid State Physics, 2, 24 (1956).
- (14) C. Sharpe Cook, <u>Structure of Atomic Nuclei</u> (D. Van Nostrand Co. Inc., New York, 1964).
- (15) A. H. Reddoch, Atomic Energy Commission Report UCRL-8972, 1959.
- (16) T. Das and E. Hahn, <u>Nuclear Quadrupole Resonance Spec-</u> troscopy (Academic Press Inc., New York, 1958).
- (17) R. Bersohn, J. Chem. Phys., <u>20</u>, 1505 (1952).

- (18) M. H. Cohen, Phys. Rev., <u>96</u>, 1278 (1954).
- (19) R. Livingston and H. Zeldes, Tables of Eigenvalues for Pure Quadrupole Spectra Spin 5/2, Oak Ridge National Laboratory Report ORNL-1913, 1955.
- (20) S. Alexander and U. Ganiel, J. Chem. Phys., <u>43</u>, 4060 (1965).
- (21) D. Gill and N. Bloembergen, Phys. Rev. <u>129</u>, 2398 (1963).
- (22) J. Armstrong, N. Bloembergen, and D. Gill, Phys. Rev. Letters, 7, 11 (1961).
- (23) F. Collins and N. Bloembergen, J. Chem. Phys., <u>40</u>, 3479 (1964).
- (24) R. Dixon and N. Bloembergen, J. Chem. Phys., <u>41</u>, 1720 (1964).
- (25) R. Dixon and N. Bloembergen, J. Chem. Phys., <u>41</u>, 1739 (1964).
- (26) T. Kushida and K. Saiki, Phys. Rev. Letters, 7, 9(1961).
- (27) R. Shulman, B. Wyluda and P. Anderson, Phys. Rev., <u>107</u>, 953 (1957).
- (28) C. Dean, Thesis, Harvard University (1952).
- (29) H. Dogden and J. Ragle, J. Chem. Phys., <u>25</u>, 376 (1956).
- (30) T. Haas and E. Marram, J. Chem. Phys., <u>43</u>, 3985 (1965).
- (31) H. Bayer, Z. Physik, 130, 227 (1951).
- (32) I. Tatsuzaki, J. Phys. Soc. Japan, <u>14</u>, 578 (1959).
- (33) T. Kushida, G. Benedek and N. Bloembergen, Phys. Rev., <u>104</u>, 1364 (1956).
- (34) T. Fuke, J. Phys. Soc., Japan, <u>16</u>, 266 (1961).
- (35) H. Gutowsky and D. McCall, J. Chem. Phys., <u>32</u>, 548 (1960).
- (36) R. Sternheimer, Phys. Rev., <u>80</u>, 102 (1950).
- (37) R. Sternheimer, Phys. Rev., <u>84</u>, 244 (1951).
- (38) R. Sternheimer, Phys. Rev., <u>86</u>, 316 (1953).

- (39) R. Sternheimer, Phys. Rev., <u>95</u>, 736 (1954).
- (40) H. Foley, R. Sternheimer and S. Tycko, Phys. Rev., <u>93</u>, 734 (1954).
- (41) R. Sternheimer and H. Foley, Phys. Rev., <u>102</u>, 731 (1956).
- (42) T. Das and R. Bersohn, Phys. Rev., <u>102</u>, 733 (1956).
- (43) C. Townes, <u>Handbuch Der Physik</u> (S. Flügge editor, Springer-Verlag, Berlin, 1958), p. 429.
- (44) C. Townes and B. Dailey, Phys. Rev., 20, 35 (1952).
- (45) T. Wang, Phys. Rev., <u>99</u>, 566 (1955).
- (46) H. Robinson, Phys. Rev., <u>100</u>, 1731 (1955).
- (47) W. Hughes, C. Montgomery, W. Moulton and E. Carlson, J. Chem. Phys., <u>41</u>, 3470 (1964).
- (48) B. Morosin and A. Narath, J. Chem. Phys., <u>40</u>, 1958 (1964).
- (49) D. Jennings, W. Tantilla and O. Kraus, Phys. Rev., <u>109</u>, 1059 (1958).
- (50) D. Bolef and M. Mernes, Phys. Rev., 114, 1441 (1959).
- (51) G. Burns and E. Wikner, Phys. Rev., <u>121</u>, 155 (1961).
- (52) E. Taylor and N. Bloembergen, Phys. Rev., <u>113</u>, 431 (1959).
- (53) H. Kwamamura, E. Otsuka and K. Ishiwatari, J. Phys. Soc. Japan, <u>11</u>, 1064 (1956).
- (54) E. Otsuka and H. Kwamamura, J. Phys. Soc. Japan, <u>12</u>, 1071 (1957).
- (55) E. Otsuka, J. Phys. Soc. Japan, <u>13</u>, 1155 (1958).
- (56) R. Sternheimer, Phys. Rev., <u>146</u>, 140 (1966).
- (57) H. Allen, J. Am. Chem. Soc., <u>74</u>, 6074 (1952).
- (58) P. Bray and P. Ring, J. Chem. Phys., <u>21</u>, 2226 (1953).
- (59) S. Kondo and I. Nitta, XSen, <u>6</u>, 53 (1960).
- (60) W. Gordy, Discussions Faraday Soc., <u>19</u>, 14 (1955).
- (61) P. Schatz, J. Chem. Phys., <u>22</u>, 755 (1954).

- (62) T. Das, J. Chem. Phys., <u>26</u>, 763 (1957).
- (63) F. Cotton and C. Harris, Private Communication.
- (64) R. Mulliken, J. Chim. Phys., <u>46</u>, 497 (1949).
- (65) C. Townes and B. Dailey, J. Chem. Phys., <u>23</u>, 118 (1955).
- (66) W. Gordy, W. Smith and R. Trambarulo, <u>Microwave</u> <u>Spectroscopy</u> (Wiley, New York, 1953).
- (67) M. Whitehead and H. Jaffe, Theoret. chim. Acta, <u>1</u>, 209 (1963).
- (68) B. Dailey, J. Chem. Phys., <u>33</u>, 1641 (1960).
- (69) C. Coulsen, <u>Valence</u> (Oxford University Press, London, 1959).
- (70) L. Pauling, <u>Nature of the Chemical Bond</u> (Cornell University Press, Ithaca, New York, 3rd Ed., 1960.
- (71) C. Townes and A. Schawlow, <u>Microwave Spectroscopy</u> (McGraw-Hill, New York, 1955).
- (72) V. Schomaker and D. Stevenson, J. Am. Chem. Soc., <u>63</u>, 37 (1941).
- (73) R. Keefer and L. Andrews, <u>Molecular Complexes in Organic</u> <u>Chemistry</u> (Holden-Day, San Francisco, 1964).
- (74) P. Kinnel, Acta Chem. Scand., <u>13</u>, 1159 (1959).
- (75) I. Lindqvist, <u>Inorganic Adduct Molecules of Oxo</u> <u>Compounds</u> (I. Springer-Verlag, Berlin, 1963).
- (76) H. Hartmann, M. Fleissner and H. Sillescu, Theoret. chim. Acta 2, 63 (1964).
- (77) A. Roberts, Rev. Sci. Inst., <u>36</u>, 481 (1959).
- (78) A. Abragam, <u>The Principles of Nuclear Magnetism</u> (Oxford University Press, London, 1961).
- (79) M. Palma-Vittorelli, M. Palma and D. Palumbo, Nuovo Cimento, <u>6</u>, 1211 (1957).
- (80) R. H. Dicke, Rev. Sci. Inst. <u>17</u>, 268 (1946).
- (81) S. Bolte, Ph.D. Thesis, Michigan State Univ., 1963.

- (82) F. Robinson, J. Sci. Instr., <u>36</u>, 481 (1959).
- (83) E. Bair, <u>Introduction to Chemical Instrumentation</u> (McGraw-Hill Co., Inc., New York, 1962).
- (84) H. Malmstadt, C. Enke and E.Toren, <u>Electronics for</u> <u>Scientists</u> (W. A. Benjamin, Inc., New York, 1963).
- (85) C. Dean, J. Chem. Phys., <u>23</u>, 1734 (1955).
- (86) T. Khotsyanova, J. Struct. Chem. (USSR), <u>5</u>, 644 (1964).
- (87) J. Bailar, Jr., Inorganic Synthesis, <u>2</u>, 222 (1946).
- (88) B. Gingras, R. Hornal and C. Bayley, Can. J. Chem., <u>38</u>, 712 (1960).
- (89) P. Sah and T. Daniels, Rec. trav. chim., <u>69</u>, 1545 (1950).
- (90) Selbin, Bull and Holmes, J. Inorg. and Nuc. Chem., <u>16</u>, 219 (1961).
- (91) Evans, Mann, Peiser and Purdie, J. Chem. Soc., 1209 (1940).
- (92) W. Meyer, Ph.D. Thesis, Michigan State University, 1958.
- (93) V. Gutmann and M. Baaz, Z. Anorg. Allgem.Chem., <u>269</u>, 279 (1952).
- (94) V. Butmann and M. Baaz, Mh. Chem., <u>90</u>, 729 (1959).
 - (95) Dadape and Rao, J. Chem. Soc., <u>77</u>, 6192 (1955).
 - (96) Groenveld and Zuur, J. Inorg. Nucl. Chem., <u>8</u>, 241 (1958).
 - (97) M. Baaz, V. Gutmann, L. Hübner, F. Mairinger and T. West, Z. Anorg. Allgem. Chem., <u>311</u>, 302 (1961).
 - (98) G. Adolfsson, R. Bryntse and I. Lindqvist, Acta Chem. Scand., <u>14</u>, 949 (1960).
 - (99) R. Sharma and T. Das, J. Chem. Phys., <u>41</u>, 3581 (1964).
- (100) F. DeWette, Phys. Rev., 123, 103 (1961).
- (101) F. DeWette, Phys. Rev., <u>137</u>, A78 (1965).
- (102) F. DeWette and G. Schacher, Phys. Rev., 137, A92 (1965).
- (103) R. Barnes, S. Segal and W. Jones, J. Appl. Phys. Supplement, <u>33</u>, 296 (1962).

- (104) D. Dickmann, M.S. Thesis, U. S. Naval Postgraduate School, Monterey, Calif., 1966.
- (105) R. Bersohn, J. Chem. Phys., <u>29</u>, 326 (1958).
- (106) I. Lindqvist and C. Bränden, Acta Cryst., 12, 642 (1959).
- (107) R. Wyckoff, <u>Crystal Structures</u> (Interscience Publishers, New York, 1964), Vol. 2, p. 17.
- (108) C. Bränden, Acta Chem. Scand., <u>17</u>, 759 (1963).
- (109) C. Bränden and I. Lindqvist, Acta Chem. Scand., <u>14</u>, 726 (1960).
- (110) D. McCall and H. Gutowsky, J. Chem. Phys., <u>21</u>, 1300 (1953).
- (111) R. Holmes, R. Carter and G. Peterson, Inorg. Chem., <u>3</u>, 1748 (1964).
- (112) C. Dean and R. Pound, J. Chem. Phys., <u>20</u>, 195 (1952).
- (113) M. Kubo and D. Nakamura, <u>Advances in Inorganic Chemistry</u> (Adacemic Press, New York, 1966), Vol. 8.
- (114) Swick, Karle and Karle, J. Chem. Phys., <u>22</u>, 1242 (1952).
- (115) Unpublished results reported in reference 110.
- (116) Kushner, Crowe and Smyth, J. Am. Chem. Soc., <u>72</u>, 1091 (1950).
- (117) C. Bränden, Acta Chem. Scand., <u>16</u>, 1806 (1962).
- (118) S. Ohlberg, J. Am. Chem. Soc., <u>81</u>, 811 (1959).
- (119) G. Semin and E. Fedin, J. Struct. Chem. (USSR), <u>1</u>, 252 (1960).
- (120) R. Bersohn, J. Appl. Phys. Supplement, <u>33</u>, 286 (1962).
- (121) N. Ramsey, <u>Molecular Beams</u> (Clarendon Press, Oxford, 1956).
- (122) D. Rao and A. Narasimhamurty, Phys. Rev., <u>132</u>, 961 (1963).
- (123) J. Ramakrishna, Phil. Mag., 13, 515 (1966).
- (124) R. Bersohn and R. Shulman, J. Chem. Phys., <u>45</u>, 2298 (1966).

- (125) G. Badgley and R. Livingston, J. Am. Chem. Soc., <u>76</u>, 261 (1954).
- (126) Dilke and Eley, J. Chem. Soc., 2601 (1949).
- (127) R. Livingston, J. Phys. Chem., <u>57</u>, 496 (1953).
- (128) J. Sheldon and S. Tyree, J. Am. Chem. Soc., <u>80</u>, 4775 (1958).
- (129) P. Van Der Doorn and R. Drago, J. Am. Chem. Soc., <u>88</u>, 3255 (1966).
- (130) C. Bränden and I. Lindqvist, Acta Chem. Scand., <u>17</u>, 353 (1963).
- (131) C. Bränden, A. Hansen, Y. Hermodsson and I. Lindqvist,
 U. S. Dept. of Comm., Office Tech. Service, AD265, 316 (1961).
- (132) J. Sheldon and S. Tyree, J. Am. Chem. Soc., <u>81</u>, 2290 (1959).

APPENDIX

The computer programs ROTATE and DIAG, written during this work, have already been discussed; they are listed here along with a description of their input parameters. It should be noted that, although ROTATE is completely general, it should be used with care for any crystal whose unit cell is less symmetric than hexagonal. Also, DIAG was written for the case in which the molecular field gradient is cylindically symmetrical. The input parameters are discussed below.

1) ROTATE

NCASE-15 format gives the number of tensors to be rotated.

X1, Y1, Z1, X2, Y2, Z2 - The coordinates of the two atoms forming the bond to which the z-axis of the calculated tensor is to be rotated, X2, Y2, Z2 refer to the coordinates of the quadrupolar nucleus.

A1, A2, A3 - The crystalline unit cell a, b, c parameters. These must be in the same order as used for LATSUM.

ALPH, BET, GAM - The angles between A2 and A3, A1 and A3 and A1 and A2, respectively.

Q(I,J) - The elements of the tensor to be rotated.

The value of NCASE is only given once, the other input parameters must be repeated for each case.

2) DIAG

Q(I,J) - The elements of the rotated tensor as obtained from ROTATE.

V(I) - The first guess for the molecular field gradients on the diagonal (for example V(3) refers to q_{zz} (mol)).

ST - The starting value for $(1 - \gamma_{m})$.

VV(I) - The diagonal elements of the measured field gradient tensor. At present only VV(3) = q(exp) is used in the program.

NN - The continuation parameter, if NN = 0 the program stops, otherwise it reads the next set of Q, V, VV and ST values.

PROGRAM ROTATE DIMENSION S(3,3), ST(3,3), Q(3,3), QR(3,3), SQ(3,3)READ 15, NOASE 15 FORMAT(15)DO 14 M=1, NCASE READ 1, X1, Y1, Z1, X2, Y2, Z2 1 FORMAT(6F10.0) PRINT 2 2 FORMAT(///,*INPUT PARAMETERS*,/) PRINT 3, X1, Y1, Z1, X2, Y2, Z2 3 FORMAT (3F12.6, /, 3F12.6)READ 20, A1, A2, A3 READ 20, ALPH, BET, GAM 20 FORMAT(3F10.4)16 FORMAT(3F12.6)PRINT 16, A1, A2, A3 PRINT 16, ALPH, BET, GAM PI=ATANF(1.)*4.CONV=PI/180.AA=CONV*ALPH BB=CONV*BET G=CONV*GAM THETA = (GAM - 90.000)T=ABSF (THETA) *CONV D=ASINF(SORTF(COSF(AA) **2+COSF(BB) **2-2.*COSF(AA) *1COSF(G) * COSF(BB)) / SINF(G))X2=X2*A1 X1=X1*A1 IF (THETA) 21, 22, 22 21 Y1 = A2 * COSF(T) * Y1Y2=A2*COSF(T)*Y2GO TO 23 22 Y1 = (A2/COSF(T)) * Y1Y2 = (A2/COSF(T)) * Y223 Z1=A3*COSF(D)*Z1 Z2=A3*COSF(D)*Z2R2 = (X2 - X1) * *2 + (Y2 - Y1) * *2 + (Z2 - Z1) * *2R=SORTF(R2*)Z=Z2-Z1B = ACOSF(Z/R)**Y=Y2-Y1** $x = x^2 - x^1$ A=ATANF (Y/X)PRINT 4, A, B, R4 FORMAT (3F12.6, /) PRINT 17 17 FORMAT(/, *TENSOR*, /) DO 5 I=1,3**READ** 6, (Q(I,J), J=1, 3)

```
5 PRINT 6, (Q(I,J), J=1,3)
 6 FORMAT (3F10.5)
   S(1,1) = COSF(A) * COSF(B)
   S(1,2) = -SINF(A)
   S(1,3) = SINF(B) * COSF(A)
   S(2,1) = SINF(A) * COSF(B)
   s(2,2) = cosf(A)
   S(2,3) = SINF(A) * SINF(B)
   S(3, 1) = -SINF(B)
   s(3, 2) = 0
   S(3,3) = COSF(B)
   DO 7 I=1,3
   DO 7 J=1,3
 7 ST(I,J) = S(J,I)
   DO 8 I=1,3
   DO 8 J=1,3
   SUM=0
   DO 9 K=1,3
 9 SUM = SUM+ST(I,K) (K,J)
 8 SQ(I,J) = SUM
   DO 10 I=1,3
   DO 10 J=1,3
   SUM=0
   DO 11 K=1,3
11 SUM=SUM+SQ(I,K) * S(K,J)
10 QR(I,J) = SUM
   PRINT 18
18 FORMAT (///, *ROTATED TENSOR*, /)
   DO 12 I=1,3
12 PRINT 13, (QR(I,J), J=1, 3)
13 FORMAT(/, 3F14.6, /)
```

14 CONTINUE END

```
PROGRAM DIAG
   DIMENSION Q(3,3), V(3), VV(3), VL(3), T(3), A(3,3), VALU(3)
  1, VAL(3), QQ(3, 3)
   COMMON A, QQ, VALU, ITER, ITP
38 DO 2 I=1,3
 2 READ 1, (Q(I,J), J=1, 3)
 1 FORMAT (3F10.0)
   READ 3, (V(I), I=1, 3), ST, (VV(I), I=1, 3)
 3 FORMAT (7F10.0)
   PRINT 4
 4 FORMAT (*INPUT PARAMETERS*, //, *TRIAL QS*, /)
   PRINT 5, (V(I), I=1, 3), (VV(I), I=1, 3)
 5 FORMAT (3F15.5)
   PRINT 6, ST
 6 FORMAT (/,*ST= *,F6.3,//)
   DO 7, I=1, 3
 7 PRINT 8, (Q(I,J), J=1, 3)
 8 FORMAT (3F12.5)
   DO 37 K=1,10
   ITER=1
   ITP=0
   DO 39 I=1,3
   DO 39 J=1,3
39 QQ(I,J) = Q(I,J) * ST
   DO 12 I=1,3
12 VL(I) = V(I)
   DEL=0
   AB=100.
   KTR=0
   DELTA=0.1
10 VL(1) = VL(1) - 0.5 * DEL
   VL(2) = VL(2) - 0.5 * DEL
   VL(3) = VL(3) + DEL
   DO 13 I=1,3
13 QQ(I,I) = QQ(I,I) + VL(I)
   CALL QDIAG
   KK=4
   DO 16 I=1,3
16 T(I) = ABSF(VALU(I))
   DO 17 I=1,3
   КК=КК-1
   IF(T(1)-T(2))18, 18, 19
18 J=2
   GO TO 20
19 J=1
20 IF (T(3) - T(J)) 21, 23, 24
23 PRINT 25
```

25 **FORMAT**(//,*MISTAKE*,//)

```
GO TO 17
21 VAL(KK) = VALU(J)
   T(J) = 0.
   GO TO 17
24 VAL(KK) = VALU(3)
   T(3) = 0.
17 CONTINUE
   AA = ABSF(VAL(3)) - ABSF(VV(3))
   AA = ABSF(AA)
   IF (AA-0.001) 11, 11, 52
52 DO 60 I=1,3
60 \quad QQ(I,I) = QQ(I,I) - VL(I)
   IF (AB-AA) 15, 15, 22
15 KTR=KTR+1
28 VL(1) = VL(1) + 0.5 * DEL
    VL(2) = VL(2) + 0.5 * DEL
   VL(3) = VL(3) - DEL
   DELTA=-DELTA
   IF(KTR-3)22,22,29
29 DELTA=DELTA/2.
   DD=ABSF (DELTA) -0.0001
   IF (DD) 11, 11, 30
30 \text{ KTR}=0
22 DEL=DELTA*VL(3)
   AB=AA
   ITER=ITER+1
   IF (ITER-100) 10, 10, 11
11 DO 9 I=1,3
 9 PRINT 34, (A(I,J), J=1,3)
34 \text{ FORMAT}(//, 3F12.6)
   PRINT 36, ITER
36 FORMAT(//, 14, *)
                      ITERATIONS*,//)
   PRINT 45, (VALU(I), I=1, 3)
45 FORMAT (*TRACE ELEMENTS*, 3F12.6, /)
   PRINT 35, K, (VL(I), I=1, 3)
35 FORMAT (/, *END BLOCK*, 13, //, 3F12.6, //)
37 ST=ST+0.1
   READ 55, NN
55 FORMAT(13)
   IF (NN) 38, 56, 38
56 CONTINUE
   END
   SUBROUTINE QDIAG
   DIMENSION B(3,3), A(3,3), QQ(3,3), VALU(3)
   COMMON A, QQ, VALU, ITER, ITP
   N=3
   DO 4 I=1,3
   DO 4 J=1,3
```
```
4 A(I,J) = OQ(I,J)
    CALL SMDIAG (A, VALU, N)
    IF(ITP-ITER)1, 1, 2
  1 ITP=ITP+10
    PRINT 3, ITER, (VALU(I), I=1, 3)
  3 FORMAT(/,*ITER=*,13,4X,3F15.5)
  2 CONTINUE
    END
    SUBROUTINE SMDIAG(A, EX, N)
    DIMENSION A(3,3), T(3,3), EX(3), RI(3), RJ(3), CI(3), CJ(3)
    EPS = .00001
    LLM = 10
    LL = 1
100 DO 110 I = 1, N
    DO 105 J=1,N
105 T(I,J) = 0.0
110 T(1,I) = 1.0
120 \text{ NCNT} = 0
130 DO 350 K=2,N
    NN=N+1-K
    DO 345 I=1,NN
    J=K+I-1
    X = 2.0*A(I,J)
    IF (EPS-ABSF (X)) 150, 150, 340
150 Y = A(J,J) - A(I,I)
    IF(Y) 160,170,160
160 \mathbf{R} = \mathbf{SQRTF}(\mathbf{X} \times \mathbf{X} + \mathbf{Y} \times \mathbf{Y})
    COS = SQRTF (0.5+0.5*ABSF(Y)/R)
    SIN = ABSF(X) / (2.0*R*COS)
    IF(X/Y) 165,180,180
165 \text{ SIN} = -\text{SIN}
    GO TO 180
170 \text{ SIN} = 0.707106781186
    COS = SIN
180 MA = I+1
    DO 190 M = MA, J
190 RI(M) = A(I,M) * COS - A(M,J) * SIN
200 \text{ MA} = J+1
    DO 210 M= MA, N
    RJ(M) = A(J,M) * COS + A(I,M) * SIN
210 \text{ RI}(M) = A(I,M) * COS - A(J,M) * SIN
220 MZ = I - 1
    DO 230 M= 1,MZ
    CI(M) = A(M, I) * COS - A(M, J) * SIN
230 \text{ CJ}(M) = A(M,J) * COS + A(M,I) * SIN
240 MZ = J-1
    DO 250 M=I,MZ
250 \text{ CJ}(M) = A(M, J) * COS + A(I, M) * SIN
```

```
T1 = A(I,I)*COS*COS + A(J,J)*SIN*SIN-2.0*A(I,J)*SIN*COS
    T2 = A(I,I) + A(J,J) - T1
260 DO 270 M=1,J
    A(M,I) = CI(M)
270 A(M,J) = CJ(M)
280 \text{ MA} = I+1
    DO 290 M=MA, N
    A(I,M) = RI(M)
290 A(J,M) = RJ(M)
    A(I,I) = T1
    A(J,J) = T2
    A(I,J) = 0.0
320 DO 330 M=1,N
    T1 = T(M, I) * COS - T(M, J) * SIN
    T(M,J) = T(M,I) * SIN + T(M,J) * COS
330 T(M, I) = T1
    GO TO 345
340 \text{ NCNT} = \text{NCNT+1}
345 CONTINUE
350 CONTINUE
360 IF (N*(N-1)/2-NCNT) 370,370,400
370 DO 380 I=1,N
    EX(I) = A(I,I)
    DO 380 J=1,N
380 A(I,J) = T(I,J)
390 RETURN
400 IF(LLM-LL) 370,370,410
410 \text{ LL} = \text{LL} + 1
    GO TO 120
    END
```

