

NMR STUDIES OF  
SOME INORGANIC FLUORIDES

NMR STUDIES OF  
SOME INORGANIC FLUORIDES

By  
JOHN WILSON QUAIL, M.Sc.

A Thesis  
Submitted to the Faculty of Graduate Studies  
in Partial Fulfilment of the Requirements  
for the Degree  
Doctor of Philosophy

McMaster University

August 1963

DOCTOR OF PHILOSOPHY (1963)  
(Chemistry)

McMASTER UNIVERSITY  
Hamilton, Ontario.

TITLE: NMR Studies of Some Inorganic Fluorides

AUTHOR: John Wilson Quail, B.Sc. (University of British Columbia)  
M.Sc. (University of British Columbia)

SUPERVISOR: Professor R. J. Gillespie

NUMBER OF PAGES: vii, 93

SCOPE AND CONTENTS:

The  $F^{19}$  NMR spectrum of  $SF_4$  at  $-101^\circ C$  has been assigned as an  $A_2B_2$  type spectrum, rather than  $A_2X_2$  as previously reported.

Sulphur and boron isotope effects on  $F^{19}$  NMR spectra have been observed for the first time and a new silicon isotope effect has been measured.

An expression has been derived for the shape of the spectrum of a nucleus of spin  $I = 1/2$  spin-spin coupled to a nucleus of spin  $I = 3/2$  which is undergoing quadrupole relaxation. The derived expression is used to interpret the  $F^{19}$  spectra of  $BF_3$  and  $ClO_3F$  over a wide temperature range.

A new compound,  $IOF_5$ , has been prepared, and identified by means of its  $F^{19}$  NMR spectrum.

### ACKNOWLEDGEMENTS

The author wishes to express gratitude to Professor R.J. Gillespie who first suggested the field of study and under whose supervision the work was done.

Thanks are due to Mr. J. Bacon who imparted much of his knowledge of NMR to the author and who contributed to the interpretation of many of the results described in this thesis. Thanks are also due to Mr. R. Palme who constructed much of the glass and silica apparatus.

Finally, the author would like to thank the National Research Council of Canada for the award of a Studentship.

TABLE OF CONTENTS

	<u>Page</u>
CHAPTER I: Introduction .....	1
(A) Forward .....	1
(B) General .....	2
(C) Chemical Shifts .....	6
(D) Spin-spin Coupling .....	8
(E) Nuclear Relaxation .....	20
CHAPTER II: Experimental .....	24
CHAPTER III: Sulphur Tetrafluoride .....	26
(A) The Observed Spectrum .....	26
(B) Theoretical Treatment of the $F^{19}$ Spectrum of $SF_4$ .....	28
(C) Experimental .....	36
CHAPTER IV: Sulphur and Silicon Isotope Effects .....	37
(A) Introduction .....	37
(B) Sulphur Isotope Effects .....	37
(C) Silicon Isotope Effects .....	42
(D) Discussion .....	44
(E) Experimental .....	45
CHAPTER V: Quadrupole Relaxation for a Spin $I = 3/2$ : The $F^{19}$ NMR Spectra of $BF_3$ , $ClO_3F$ and $BrF_5$ ..	46
(A) Introduction .....	46
(B) Theory .....	47
(C) The Spectrum of Boron Trifluoride .....	52
(D) The Spectrum of Perchloryl Fluoride .....	56
(E) The Spectrum of Bromine Pentafluoride ..	62
(F) Experimental .....	65

	<u>Page</u>
CHAPTER VI: Iodine Oxide Pentafluoride .....	67
(A) Discovery .....	67
(B) Preparation .....	69
(C) Discussion .....	72
CHAPTER VII: The Tetrafluoroborate Ion .....	74
(A) Introduction .....	74
(B) Results .....	75
(C) Discussion .....	79
CHAPTER VIII: Conclusions .....	82
(A) Isotopic Shifts .....	84
(B) Quadrupole Relaxation Effects .....	85
(C) Coupling Constants .....	87

LIST OF TABLES

<u>Table</u>		<u>Page</u>
1	Basic Functions and Diagonal Matrix Elements for Two Nuclei AB	18
2	Wave Functions and Energy Levels for an AB System of Nuclei	19
3	Transition Energies and Intensities for an AB System of Nuclei	20
4	Basic Functions and Complete Matrix of Hamiltonian $\mathcal{H}_C$ for Four Nuclei $A_2B_2$	30
5	Explicit Expressions for Energy for Four Nuclei $A_2B_2$ With $J = J'$	31
6	Energies of A Transitions for Four Nuclei $A_2B_2$ With $J = J'$	34
7	Observed and Calculated Line Positions for the A Transitions in the NMR Spectrum of $SF_4$	35
8	Isotopic Shifts for Sulphur-fluorine Compounds	41
9	Isotopic Shifts and Coupling Constants for $SiF_4$ and $SiF_6^{2-}$	43
10	Line Widths of the Component Lines of the Quintet and Doublet in the $F^{19}$ NMR Spectrum of $BrF_5$	64

LIST OF FIGURES

Fig.		Page
1	Energy Levels and Transitions for AX and A <sub>2</sub> Systems of Nuclei	16
2	F <sup>19</sup> NMR Spectrum of the Low-field Half of the Resonance of SF <sub>4</sub> at - 101° C (56.4 Mc/s)	27
3	Spin-coupling Constants for Four Nuclei A <sub>2</sub> B <sub>2</sub>	28
4	F <sup>19</sup> NMR Spectra Showing S <sup>34</sup> Satellites for a) SF <sub>6</sub> , b) S <sub>2</sub> O <sub>5</sub> FCl, c) S <sub>3</sub> O <sub>8</sub> F <sub>2</sub>	40
5	Theoretical Line Shapes for the Spectra of Nuclei of Spin 1/2 Coupled to a Nucleus of Spin 3/2	53
6	F <sup>19</sup> Resonance Spectra of Liquid BF <sub>3</sub>	55
7	The Temperature Dependence of the B <sup>11</sup> $\tau$ Estimated From the F <sup>19</sup> Resonance of Liquid BF <sub>3</sub>	57
8	F <sup>19</sup> Resonance Spectra of Liquid ClO <sub>3</sub> F	59
9	Calculated Line Shape for $\eta_{35}^2 = 5.15$ , Showing the Individual Contributions of the Two Isotopes, Cl <sup>35</sup> and Cl <sup>37</sup> , and Their Sum	61
10	The Temperature Dependence of the Cl <sup>35</sup> $\tau$ Estimated From the F <sup>19</sup> Resonance of Liquid ClO <sub>3</sub> F	63
11	F <sup>19</sup> NMR Spectrum of IOF <sub>5</sub> Containing IF <sub>5</sub>	68
12	F <sup>19</sup> NMR Spectra of BF <sub>4</sub> <sup>-</sup>	76



## CHAPTER I

### INTRODUCTION

#### A. Forward

The original objective of this work was to study the stereochemistry of five-coordinate fluorides by means of nuclear magnetic resonance (NMR). As the first step in the work it was necessary to find suitable solvents for low temperature studies of fluorides. The NMR spectra of the prospective solvents showed hitherto unreported or unexplained features, including a spectrum that was attributed to a new compound. It was only natural to investigate these problems as they were recognized, and as a consequence the original objective was never attained. This thesis therefore describes and discusses the results of these essentially preliminary investigations which however turned out to be of sufficient interest to merit investigation in their own right.

The thesis deals with the  $F^{19}$  spectra of:

- 1)  $SF_4$  - an example of an  $A_2B_2$  spectrum with  $J = J'$ .
- 2) various compounds containing a S - F bond - examples of a sulphur isotope effect.
- 3)  $ClO_3F$  and  $BF_3$  - examples of quadrupole relaxation.
- 4)  $IOF_5$  - a new compound identified by NMR.
- 5)  $BF_4^-$  - an example of a variable coupling constant and a boron isotope effect.

B. General (1 - 6)

Nuclei having an even number of neutrons and an even number of protons have zero spin. With very few exceptions, all other nuclei have a spin. Nuclei with an even number of nucleons have their spin quantized in integral multiples of  $\hbar$  (= Planck's constant divided by  $2\pi$ ); nuclei with an odd number of nucleons have their spin quantized in half integral multiples of  $\hbar$ . Any nucleus with a spin  $I$  has associated with it a magnetic moment  $\mu$ . The observable values of the magnetic moment in a magnetic field are  $m\mu/I$ , where  $m$  is the magnetic quantum number and may take values

$$m = I, I-1, I-2, \dots, -I \quad (1)$$

It is convenient to define a quantity  $\gamma$ , called the magnetogyric ratio, as

$$\gamma = \mu/I\hbar \quad (2)$$

When a nucleus of spin  $I$  is placed in a magnetic field  $H_0$ , it takes one of  $2I + 1$  orientations, corresponding to the  $2I + 1$  energy levels available to the nucleus. For  $I = 1/2$  there are two energy levels available. These are separated by an energy  $E = 2\mu H_0$ . If a whole assembly of such nuclei is in thermal equilibrium with its surroundings at a temperature  $T$ , more nuclei will be in the state of lower energy than in the state of higher energy. The ratio of the populations of the two states is given by the Boltzmann factor  $\exp(2\mu H_0/kT)$ , where  $k$  is the Boltzmann constant. For the magnetic fields normally used in NMR (5,000 to 25,000 gauss) and at temperatures near room temperature, the factor  $2\mu H_0/kT$  is very small

compared to unity, and the exponential can be approximated by the first two terms of an expansion, so that the probabilities of an individual nucleus being in the upper or lower state respectively are

$$1/2(1 - \frac{\mu H_0}{kT}) \quad \text{and} \quad 1/2(1 + \frac{\mu H_0}{kT}) \quad (3)$$

For nuclei of higher spin the probability of an individual nucleus being in a state  $m$  is given by the expression

$$\frac{1}{2I + 1} (1 - \frac{m \mu H_0}{I k T}) \quad (4)$$

assuming that  $m \mu H_0 / I k T \ll 1$ .

If a nucleus of spin  $I$  is in an applied magnetic field  $H_0$  (by convention, the direction of the field is taken as the  $z$  direction in a Cartesian coordinate system) and if an oscillating magnetic field is applied in the  $x$  direction with amplitude  $2H_1$  and frequency  $\nu$ , there will be an extra term in the Hamiltonian which may be written as

$$\mathcal{H}' = 2 \gamma H_1 I_x \cos 2\pi \nu t \quad (5)$$

where  $I_x$  is the component of the nuclear spin in the  $x$  direction. This Hamiltonian can give rise to transitions between states  $m$  and  $m'$  when

$$\nu_{mm'} = \frac{|m - m'| \gamma H_0}{2\pi} \quad (6)$$

It can be shown that the probability of a transition between the two states  $m$  and  $m'$  corresponding to absorption or emission of radiation is

$$P_{m,m'} = \gamma^2 H_1^2 |(m'| I_x |m)|^2 g(\nu) \quad (7)$$

where  $(m'| I_x |m)$  is a quantum mechanical matrix element of the operator  $I_x$  between the states  $m$  and  $m'$ .  $g(\nu)$  is a line shape function which is proportional to the absorption at frequency  $\nu$ . From theory, the absorption should be infinitely sharp and  $g(\nu)$  would be a Dirac  $\delta$  function  $\delta(\nu - \nu_{mm'})$  which has a finite value only when  $\nu = \nu_{mm'}$ . In practice, it is found that various causes broaden NMR lines and  $g(\nu)$  can be thought of as a function which describes this broadening and is such that the integral of  $g(\nu)$  from  $\nu = 0$  to  $\nu = \infty$  is equal to one. If  $g(\nu)$  is not a Dirac  $\delta$  function, then Equation (7) is not rigorously correct, but it is still useful as a semi-empirical description of the absorption or emission of radiation by an assembly of identical nuclei. It is the detection of this absorption or emission of energy which is the basis of the nuclear magnetic resonance experiment.

An assembly of identical nuclei in thermal equilibrium with its surroundings (lattice), exchanges energy with its lattice, causing transitions to occur between the various spin states available to the individual nuclei, but preserving the equilibrium distribution of the assembly. This process is known as spin-lattice

relaxation. If an assembly of nuclei is not in thermal equilibrium with its surroundings, the populations of the states will tend toward the equilibrium value in an exponential manner by spin-lattice relaxation. The time constant  $T_1$ , which defines this exponential rate process is known as the spin-lattice relaxation time.

In the NMR experiment, a radio-frequency (rf) field of appropriate frequency is applied to a sample in a magnetic field. If the frequency  $\nu$  is given by  $\nu = \gamma H_0 / 2\pi$ , then transitions are stimulated in both directions between the energy levels with equal probability. If the populations of the energy levels are not the same there will be a net absorption or emission of energy. This emitted or absorbed energy is detected and amplified and becomes the NMR signal. If a very large radio frequency field is applied, sufficient transitions may be stimulated so that the relative populations of the states tend toward equality. If the populations become equal, no further net absorption of energy is possible and the sample is said to be saturated. Opposing the tendency to saturate is the relaxation process, which tends to re-establish the equilibrium populations. Thus, in order to observe the assembly of identical nuclei without appreciably altering the equilibrium, it is necessary that the intensity of the applied radio frequency field be low enough that transitions caused by the applied rf field are few compared to the number of transitions caused by spin-lattice relaxation.

There are three observables of high resolution NMR which are

of particular interest. These are chemical shifts of nuclei, spin-spin coupling constants, and relaxation times. Direct or indirect observation of these observables can give information about the composition and stereochemistry of molecules, electron distributions of molecules, chemical exchange processes, hindered rotations, and translational and rotational reorientations of individual molecules.

### C. Chemical Shifts (1 - 6)

The previous description indicates that in a given magnetic field any particular nuclear species with a magnetic moment will have its unique frequency of resonance. The actual state of affairs, fortunately, is more complex than this. If it were not, we could gain little information of chemical interest from NMR.

The frequency at which a nucleus resonates is dependent on the effective magnetic field at the site of the nucleus. This is not the same as the applied field. The applied field induces orbital motions in the electrons of the molecule containing the resonating nucleus and the motions of the electrons produce magnetic fields in the region near the electrons. In general, these induced fields oppose the applied field. The induced fields usually reduce the effective applied field at the site of a nucleus. The size of the induced fields will be proportional to the applied field. It is possible to describe the effective field at the site of a nucleus in terms of the applied magnetic field  $H_0$  and a screening constant  $\sigma$ .

$$H_{\text{eff}} = H_0(1 - \sigma) \quad (8)$$

where  $H_{\text{eff}}$  is the effective magnetic field at the site of the nucleus.

The screening constant  $\sigma$  could, in theory, be calculated from the ground and excited state electronic wave function of the molecule in which the nucleus is situated.

At a given frequency, all nuclei of the same species will resonate at the same effective field. Therefore, nuclei of the same kind but with different screening constants resonate at different applied fields.

In the NMR experiment, for reasons of convenience, the frequency of irradiation is usually kept constant and the applied magnetic field is varied ("swept") to observe the resonances of nuclei with different screening constants. In an NMR spectrum, the separation between the resonances of nuclei with different screening constants is known as a chemical shift and can be measured in units of magnetic field or frequency. We are normally concerned only with chemical shifts between nuclei of the same species. Chemical shifts are expressed in terms of a nondimensional unit  $\delta$ , defined by

$$\delta = \frac{H - H_r}{H_r} = \frac{\nu - \nu_r}{\nu_r} \quad (9)$$

where  $H$  is the resonant field of the signal being measured at a fixed frequency, and  $H_r$  is the corresponding field for a signal from a substance chosen as the reference.  $\nu$  is the resonance frequency of the signal being measured at a fixed field and  $\nu_r$  is the corresponding frequency for a second signal from a substance chosen as the reference. Because the difference  $\nu - \nu_r$  is very small compared to the magnitude of  $\nu_r$ , the fixed radio frequency (rf)  $\nu_0$  may be used in the denominator in place of  $\nu_r$ . The chemical shift  $\delta$  is usually a very small number. It is customary to multiply the value of  $\delta$  from Equation (9) by  $10^6$  and

report the chemical shift in parts per million (ppm).

For any one type of nucleus the chemical shift varies with the chemical location of the nucleus. For example, if we take the  $F^{19}$  resonance of  $F_2$  as zero, then we find the resonance of  $F^{19}$  in  $SF_6$  at + 375.6 ppm<sup>(7)</sup> the  $F^{19}$  resonance of  $CF_4$  at + 491.0 ppm<sup>(7)</sup>, and the  $F^{19}$  resonance of HF at + 625.0 ppm<sup>(7)</sup>.

Correlations of chemical shift data with electro-negativities and other chemical parameters have helped to improve our understanding and use of chemical shifts. We are unable at present to apply in detail the theory of chemical shifts due to Ramsey<sup>(8)</sup>, because of our lack of knowledge of molecular wave functions, especially in the region near the nucleus where they make the greatest contribution to the chemical shift.

#### D. Spin-spin Coupling (2,5,9,10)

When all of the nuclei with magnetic moments in a molecule are not equivalent (they may be of the same or different nuclear species) an interaction takes place between nonequivalent nuclei, causing the resonance line for each group of equivalent nuclei to be split into a multiplet of two or more components. In the cases where the splitting is small compared to the chemical shift between the lines, the splitting is found to be independent of the applied field. In such cases, called "first order" splittings, each multiplet is symmetric about its center. When the splitting is of the same order of magnitude as the chemical shift, a more complex spectrum results, the shape of which is field dependent.



The first order splitting arises from the different possible values of the total magnetic field produced at a given nucleus by the magnetic moments of neighboring nuclei. The direct magnetic dipole-dipole interaction is averaged to zero by the rapid molecular reorientations of the molecules in a fluid but an indirect effect is transmitted between magnetic nuclei by the electrons of the molecule which contains the nuclei. Consider a nucleus undergoing resonance absorption which has a single neighboring nucleus of spin  $I$  in the same molecule. The effective magnetic field at the absorbing nucleus will have one of  $2I + 1$  values, depending upon whether the magnetic quantum number  $m$  of the adjacent nucleus is  $I$ ,  $I - 1$ , or  $-I$ . The field of the neighboring nucleus either augments or decreases the applied field. For example, the deuteron spectrum of HD consists of two lines of equal intensity with a splitting of  $42.7 \text{ c/s}^{(11)}$ , corresponding to the proton having a magnetic quantum number of  $+1/2$  or  $-1/2$ . The proton spectrum consists of three lines of equal intensity with the same splitting of  $42.7 \text{ c/s}$  corresponding to the deuteron ( $I = 1$ ) having a magnetic quantum number of  $+1$ ,  $0$ , or  $-1$ . The quantity  $42.7 \text{ c/s}$  is the spin-spin coupling constant  $J_{\text{HD}}$  for HD. The quantity  $J_{\text{AX}}$  is a measure of the electron coupled spin-spin interaction between two nuclei, A and X.

When the nucleus being observed is coupled to a number  $n$  of equivalent nuclei of spin  $1/2$ , the multiplicity of lines is  $(n + 1)$ . Each of the lines corresponds to a different total magnetic quantum number. The intensities are proportional to the

probabilities for the occurrence of the various total magnetic quantum numbers.

A quantum mechanical treatment of spin-spin coupling will be in use in Chapter III in discussing the NMR spectrum of  $SF_4$ . We can think of one molecule in an assembly of identical molecules as a system of nuclear spins (a spin system). Except when  $\gamma_0 \delta \gg J$ , it is more precise to analyze the over-all energy levels of a spin system rather than just the effect of the magnetic moment of one nucleus on the magnetic field at another nucleus. Only nuclei of spin  $1/2$  for which  $I_z = \pm 1/2$  will be considered. Each nucleus with  $I_z = + 1/2$  is assigned the spin wave function  $\alpha$ ; and each with  $I_z = - 1/2$  the spin wave function  $\beta$ , where  $\alpha$  and  $\beta$  are orthogonal, normalized functions. The letters A, B, C,--- are used to denote nuclei whose chemical shifts are of similar magnitude to their spin-spin coupling constants and the letters X, Y, Z to denote nuclei whose chemical shifts from A, B, C are large compared with the corresponding spin-spin coupling constants.

The quantum mechanical treatment is based on the complete Hamiltonian

$$\mathcal{H} = \mathcal{H}^{(0)} + \mathcal{H}^{(1)} \quad (10)$$

where  $\mathcal{H}^{(0)}$  gives the sum of the interactions of the nuclei with the stationary applied field  $H_0$  and  $\mathcal{H}^{(1)}$  gives the sum of the spin-spin interactions of the pairs of nuclei.

For  $i$  nuclei

$$\mathcal{H}^{(0)} = \frac{1}{2\pi} \sum_i \gamma_i (1 - \sigma_i) H_0 I_z(i) = \sum_i \gamma_i I_z(i) \quad (11)$$

where  $\gamma_i = \frac{\gamma_i}{2\pi} (1 - \sigma_i) H_0$  c/s, and

$$\mathcal{H}^{(1)} = \sum_{i < j} J_{ij} \vec{I}(i) \cdot \vec{I}(j) \quad (12)$$

where  $\vec{I}(i)$  and  $\vec{I}(j)$  are the spin vectors of nuclei  $i$  and  $j$  and  $J_{ij}$  is the spin-spin coupling constant between nuclei  $i$  and  $j$ .

For a system of  $p$  nuclei there are a total of  $2^p$  possible states. The simplest set of functions describing this spin system is the set of  $2^p$  basic product wave functions such as

$$\psi_n = \alpha(1) \beta(2) \dots \beta(p) \quad (13)$$

If the nuclei were independent of each other, these products would be stationary state wave functions in the presence of a magnetic field. However, the spin interaction Hamiltonian  $\mathcal{H}^{(1)}$  may cause mixing between different product functions.

The Hamiltonian  $\mathcal{H}^{(0)}$  has only diagonal matrix elements with respect to the functions  $\psi_n$ , whereas  $\mathcal{H}^{(1)}$  may also have off-diagonal elements. The correct stationary-state wave functions are the linear combinations of the basic product wave functions which diagonalize the matrix of the complete Hamiltonian  $\mathcal{H}$ . The corresponding energies are solutions of the secular equation

$$|\mathcal{H}_{mn} - E \delta_{mn}| = 0 \quad (14)$$

where  $\delta_{mn} = 1$  if  $m = n$ , and  $\delta_{mn} = 0$  if  $m \neq n$

$$\mathcal{H}_{mn} = (\psi_m | \mathcal{H} | \psi_n) = \int \psi_m^* \mathcal{H} \psi_n d\tau$$

There are no off-diagonal matrix elements of the Hamiltonian between basic product functions corresponding to different values of the expectation value of the total spin component in the z direction,  $F_z$ , where

$$F_z = \sum_i I_z(i) \quad (15)$$

It can be shown<sup>(2)</sup> that the diagonal matrix elements of  $\mathcal{H}^{(1)}$  with respect to  $\psi_m$  are given by

$$(\psi_m | \mathcal{H}^{(1)} | \psi_m) = 1/4 \sum_{i < j} J_{ij} T_{ij} \quad (16)$$

where  $T_{ij} = 1$  or  $-1$  according as spins  $i$  and  $j$  are parallel or antiparallel in  $\psi_m$ . The off-diagonal elements of  $\mathcal{H}^{(1)}$  need only be considered between functions  $\psi_m$  and  $\psi_n$  with the same total spin component  $F_z$ . The matrix element is then given by

$$(\psi_m | \mathcal{H}^{(1)} | \psi_n) = 1/2 U J_{ij} \quad m \neq n \quad (17)$$

where  $U = 1$  if  $\psi_m$  differs from  $\psi_n$  by one interchange of spins  $i$  and  $j$  and is zero otherwise.

The stationary-state wave functions can be found as linear combinations of the basic product functions

$$\Phi_q = \sum_m a_{qm} \psi_m \quad q = 1, 2, \dots, 2^p \quad (18)$$

where the coefficients  $a_m$  satisfy the set of linear equations

$$\sum_n \mathcal{H}_{mn} a_{qn} = E_q a_{qm} \quad (19)$$

The absolute values of the coefficients are fixed by the normalization condition

$$\sum_m a_{qm}^* a_{qm} = 1 \quad (20)$$

The transition probability for a single nucleus was given in Equation (5). For a set of coupled nuclei the perturbing Hamiltonian is

$$\mathcal{H}' = -2H_1 M_x \cos 2\pi\nu t \quad (21)$$

where  $M_x$  is the component of the nuclear moment in the x direction

$$M_x = \hbar \sum_i \gamma_i I_x(i) \quad (22)$$

By analogy with Equation (5), the intensity of a signal arising from the transition  $q \rightarrow q'$  will be proportional to

$$\hbar^2 \left| \langle q | \sum_i \gamma_i I_x(i) | q' \rangle \right|^2 \quad (23)$$

The operator  $I_x(i)$  will have matrix elements only between two basic product functions which differ only in the spin of nucleus  $i$ . The total matrix element in Equation (21) will have a finite value only between states which differ in the value of the total spin component  $F_z$  by  $\pm 1$ . This selection rule can be

written as

$$\Delta F_z = \pm 1 \quad (24)$$

By taking advantage of the symmetry properties of molecules which have two or more equivalent nuclei we can often simplify the treatment of a spin system. This is done by describing equivalent nuclei by their basic symmetry functions rather than their basic product functions. For example, the basic product functions for two equivalent nuclei are  $\alpha\alpha$ ,  $\alpha\beta$ ,  $\beta\alpha$ , and  $\beta\beta$ . These basic products do not all belong to irreducible representations for the symmetry groups which describes the molecule containing the two equivalent nuclei. The symmetry operation which interchanges the two nuclei will transform  $\alpha\beta$  into  $\beta\alpha$ . An irreducible representation may be constructed by taking linear combinations of the simple products. Such a set is called a set of basic symmetry functions. For a set of two nuclei the basic symmetry functions are

<u>Function</u>	<u>Spin Component <math>F_z</math></u>	<u>Designation</u>
$\alpha\alpha$	1	$\underline{s}_{+1}$
$1/\sqrt{2}(\alpha\beta + \beta\alpha)$	0	$\underline{s}_0$
$1/\sqrt{2}(\alpha\beta - \beta\alpha)$	0	$\underline{a}_0$
$\beta\beta$	-1	$\underline{s}_{-1}$

The basic symmetry functions are designated by the symbol  $\underline{s}$  or  $\underline{a}$  for symmetrical or antisymmetrical and a suffix for the value of  $F_z$ . The use of basic symmetry functions allows us to reduce the

order of the secular determinants which must be solved. It can also be shown that transitions between states of different symmetry are forbidden.

For two identical nuclei (i.e. an  $A_2$  system) with zero spin-spin coupling, the  $\underline{a}_0$  and  $\underline{s}_0$  states are of equal energy. The  $\underline{s}_{+1}$  and  $\underline{s}_{-1}$  states are equal energies above and below the  $\underline{s}_0$  and  $\underline{a}_0$  states. Since there are no transitions connecting the  $\underline{a}_0$  state and since the selection rule  $\Delta F_z = \pm 1$  holds, there are only two allowed transitions,  $\underline{s}_{-1} \rightarrow \underline{s}_0$  and  $\underline{s}_0 \rightarrow \underline{s}_{+1}$ , which are of equal energy. If there is spin-spin coupling of magnitude  $J$  c/s, application of Equation (16) shows that the energy of all three symmetric energy levels is raised by  $J/4$  while the energy of the antisymmetric level is lowered by  $3J/4$ . Thus, the two allowed transitions and their energy are not changed (Fig. 1).

Consider a hypothetical molecule AX in a magnetic field. When the spin function of nucleus A changes from  $\beta$  to  $\alpha$  with an absorption of energy, this is recorded as a resonance in the NMR spectrum of A. The same is true for X. There are two A transitions, one in the presence of an  $\alpha(X)$  and one in the presence of a  $\beta(X)$ . Both transitions will have the same energy if there is no interaction between the nuclei. The same is true for the two X transitions. Having no interaction between the two nuclei corresponds to having no  $\mathcal{H}_{AC}^{(1)}$  in the Hamiltonian describing the system. If allowance is made for an interaction of the type  $J_{AX} \vec{I}(A) \cdot \vec{I}(X)$ , from Equation (16) it is found that the states having spins antiparallel are of  $J/4$  lower energy (Fig. 1).

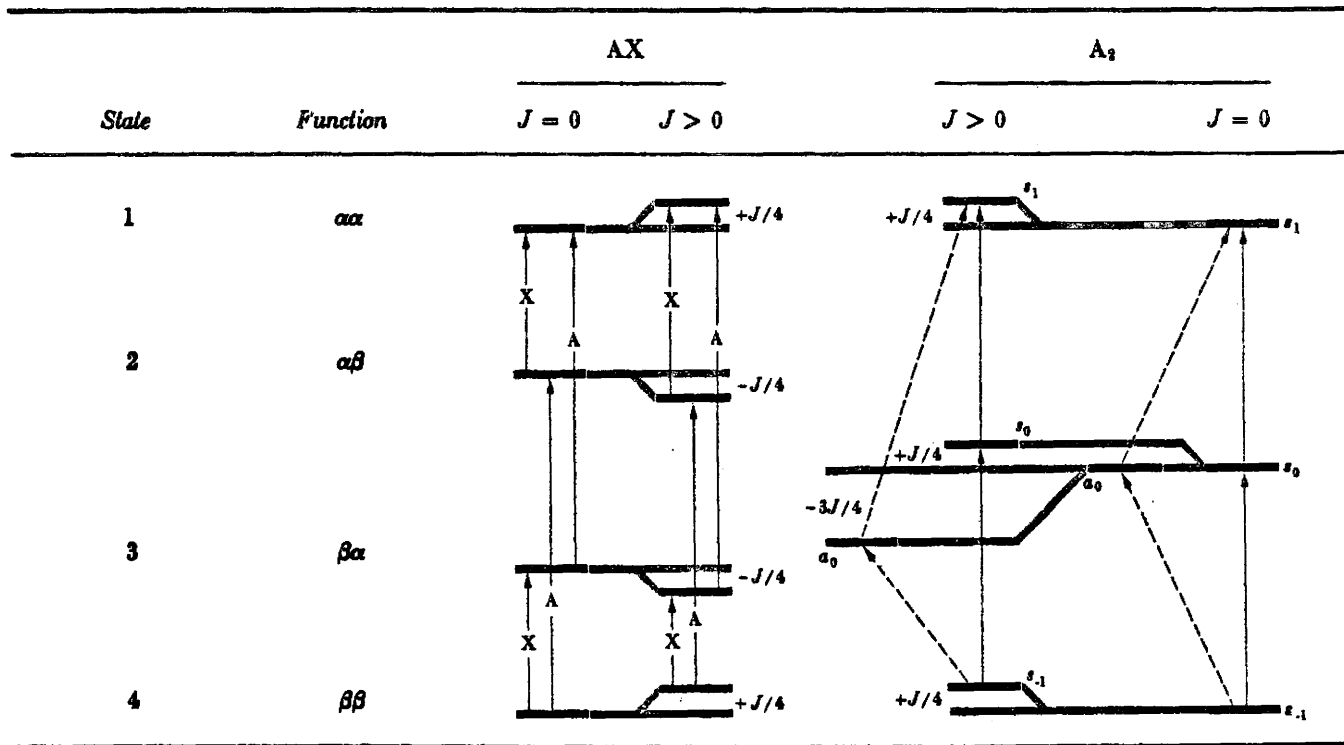


Fig. 1 Energy Levels and Transitions for AX and A<sub>2</sub> Systems of Nuclei



Spin-spin coupling decreases the energy of the transition  $4 \rightarrow 2$  by an amount  $J/2$  and increases the energy of the transition  $3 \rightarrow 1$  by an amount  $J/2$ . Instead of being degenerate, as they are when there is no spin-spin interaction, the two transitions are now found to occur at an energy  $J$  c/s apart, centered about the position of the transition with no interaction. In the same manner the two X transitions give separate lines which are also  $J$  c/s apart.

The AB system is intermediate between the  $A_2$  and the AX cases. Consider what happens to an AX system as the chemical shift between A and X is decreased and becomes of the same order as the spin-spin coupling. It becomes impossible to completely distinguish between the states  $\alpha\beta$  and  $\beta\alpha$ . The actual state of affairs can best be described by allowing for quantum mechanical mixing of the two states. The basic functions and diagonal matrix elements for two nuclei AB are given in Table 1. The diagonal matrix elements of the Hamiltonian are evaluated from the rules already given. The only nonvanishing off diagonal element is  $\mathcal{H}_{23} = \mathcal{H}_{32} = 1/2 J$ , obtained from Equation (17). Mixing occurs between  $\alpha\beta$  and  $\beta\alpha$  to give two stationary state wave functions. It is convenient to define a positive quantity  $C$  and an angle  $\theta$  ( $0 < \theta < \pi$ ) by

$$\begin{aligned} C \cos 2\theta &= 1/2 \gamma_0 \delta \\ C \sin 2\theta &= 1/2 J \\ C &= + 1/2 \left[ (\gamma_0 \delta)^2 + J^2 \right]^{1/2} \end{aligned}$$

where  $\delta = \sigma_B - \sigma_A$ , the difference in the screening constants for the two nuclei. We find that the wave functions and energy levels are as

shown in Table 2.

---

Table 1

Basic Functions and Diagonal Matrix Elements for Two Nuclei AB

n	$\psi_n$	$F_z$	$\mathcal{H}_{nn}$
1	$\alpha\alpha$	1	$\nu_0(1 - 1/2\sigma_A - 1/2\sigma_B) + 1/4 J$
2	$\alpha\beta$	0	$\nu_0(-1/2\sigma_A + 1/2\sigma_B) - 1/4 J$
3	$\beta\alpha$	0	$\nu_0(1/2\sigma_A - 1/2\sigma_B) - 1/4 J$
4	$\beta\beta$	-1	$\nu_0(-1 + 1/2\sigma_A + 1/2\sigma_B) + 1/4 J$

---

---

 Table 2

Wave Functions and Energy Levels for an AB System of Nuclei

n	$\Phi_n$	$E_n$
1	$\alpha\alpha$	$\nu_0(1 - 1/2\sigma_A - 1/2\sigma_B) + 1/4J$
2	$\cos\theta(\alpha\beta) + \sin\theta(\beta\alpha)$	$- 1/4J + C$
3	$-\sin\theta(\alpha\beta) + \cos\theta(\beta\alpha)$	$- 1/4J - C$
4	$\beta\beta$	$\nu_0(-1 + 1/2\sigma_A + 1/2\sigma_B) + 1/4J$

---

It can be seen from Table 2 that when  $\nu_0\delta$  is large compared to J, the AB case reduces to AX and that as  $\nu_0\delta$  goes to zero, the AB case reduces to  $A_2$ .

There are only four transitions allowed by the selection rule  $\Delta F_z = \pm 1$ . The relative intensities are proportional to the squares of the appropriate matrix elements of the x component of the spin,  $I_x(A) + I_x(B)$ . The transition energies (relative to the mean,  $\nu_0(1 - 1/2\sigma_A - 1/2\sigma_B)$ ) and the relative intensities are given in Table 3. It can be seen from Table 3 that the mixing of states distorts the intensities and positions of the lines relative to the simple pattern which would be expected for an AX spectrum.

Table 3Transition Energies and Intensities for an AB System of Nuclei

<u>Transition</u>	<u>Energy</u>	<u>Relative Intensity</u>
3 $\longrightarrow$ 1	$1/2 J + C$	$1 - \sin 2\theta$
4 $\longrightarrow$ 2	$- 1/2 J + C$	$1 + \sin 2\theta$
2 $\longrightarrow$ 1	$1/2 J - C$	$1 + \sin 2\theta$
4 $\longrightarrow$ 3	$- 1/2 J - C$	$1 - \sin 2\theta$

E. Nuclear Relaxation (1, 2, 5, 6, 12)

There are a number of mechanisms by which a spin system may come into thermal equilibrium with its lattice. The magnetic moment of any nucleus with spin can interact with fluctuating local magnetic fields. These fields may be due to:

1. magnetic moments of other nuclei in the same or adjacent molecules
2. spins of unpaired electrons
3. variable electronic screening of the resonating nucleus from the static field  $H_0$ .

Transitions caused by a spin-lattice interaction are similar to the radiation induced transitions of the NMR experiment. For a nucleus in a field  $H_0$  in the z direction, oscillating magnetic fields in the xy plane with frequency

$\nu_0 = \frac{\gamma H_0}{2\pi}$  will stimulate transitions between the energy levels. The frequency  $\nu_0$  can be thought of as a component of a Fourier series describing the magnetic noise caused by the three sources listed above. The field

fluctuations are caused by the random variations of the internuclear parameters

such as internuclear distances and the orientation of the internuclear vector with respect to the external magnetic field. If the fluctuating field is  $\vec{H}'(t)$ , the components  $H'_x$  and  $H'_y$  will be able to cause transitions. The interaction Hamiltonian is

$$\mathcal{H}' = \gamma \hbar \vec{I} \cdot \vec{H}'(t) \quad (25)$$

Molecular vibrations change the internuclear distances within any one molecule, but the displacements are so small and the frequencies associated with them so high that they are ineffective for nuclear relaxation. Using the theory of Brownian motion as a basis it is possible to obtain an expression for the form of the frequency distribution of a noise spectrum arising from translational and rotational motions of individual molecules, assuming that many collisions take place during the time a molecule takes to turn around or move through a distance of one molecular spacing. The frequency distribution is:

$$K(\omega) \propto \frac{2\tau_c}{1 + 4\pi^2\omega^2\tau_c^2}$$

where  $\tau_c$  is a time characteristic of the random motion called the correlation time. It is a measure of the time required for a molecular translation or reorientation.

For a nucleus of spin  $I = 1/2$  and an interaction Hamiltonian of the type in Equation (23), the theory of transition probabilities due to a fluctuating Hamiltonian <sup>(2)</sup> shows that the spin-lattice relaxation time is given by

$$1/T_1 = 2 P_{-1/2, +1/2} = 2 \gamma^2 \overline{H_x'^2} \tau_c \quad (26)$$

The result of spin-lattice relaxation is to broaden the resonance line of the nucleus which is relaxing because of uncertainties in the energies of the spin states induced by rapid transitions. The smaller  $T_1$  is, the broader the resonance line is. Under certain conditions the observed broadening is greater than that due to spin-lattice relaxation. This further broadening may be caused by variations in the irradiating field  $H_1$  (or conversely in the applied field  $H_0$ ) as seen by the resonating nucleus. Broadening of the irradiating field can be caused by magnetic dipole interactions. When the line width is larger than that due to spin-lattice relaxation, it is convenient to define another characteristic time  $T_2$ , smaller than  $T_1$ .  $T_2$  is sometimes referred to as the spin-spin relaxation time and is given by

$$T_2 = 1/2 \left[ g(\nu) \right]_{\max} \quad (27)$$

where  $g(\nu)$  is the line shape function. In liquids and gases the local magnetic fields usually average out, due to rapid rotations of the molecules. In these cases  $T_1$  and  $T_2$  become approximately equal.

A nucleus with spin  $I \geq 1$  has associated with it an electric quadrupole moment  $eQ$ . The quadrupole moment can interact with local electric fields by means of molecular reorientations. This interaction is a very efficient mechanism for nuclear relaxation and for high spin nuclei it is usually the main cause of relaxation. Since it is the electric field gradient at the site of the nucleus that interacts with the electric quadrupole moment, the effect is of an intramolecular nature. Electrical properties of other molecules have little effect on the field gradient being considered. Since

translational reorientations of a molecule do not alter the direction of the field gradients within the molecule, only rotational reorientations of the molecule need be considered. It is then convenient to define a correlation time for quadrupole relaxation,  $\tau_q$ , which is essentially a rotational correlation time.

The spectrum of a nucleus of spin  $I' = 1/2$  spin-spin coupled by an interaction  $J$  c/s to a high spin nucleus of spin  $I$  would in general consist of  $2I + 1$  lines of equal intensity and equally spaced  $J$  c/s apart, corresponding to the  $2I + 1$  possible orientations of the high spin nucleus. The interaction of the quadrupole moment with any fluctuating field gradients causes transitions to occur between the various spin states,  $m$ , of the high spin nucleus, limited by the selection rule  $\Delta m = \pm 1, \pm 2$ . If the relaxation rate increases, the components of the spectrum of  $I'$  broaden and finally merge into one line which then sharpens as the field at  $I'$  is averaged by the rapid transitions of  $I$ . At the same time the two lines in the spectrum of  $I$  will continue to broaden as the relaxation rate increases. In this case, the collapsed coupling between  $I$  and  $I'$  makes a contribution to  $T_2$  for  $I'$ .

$T_1$  for  $I$  and  $T_2$  for  $I'$  will then be closely related. The relaxation times are dependent on the rotational correlation time of the molecule, which should be temperature dependent. Thus, by temperature studies of relaxation processes, we can gain information about molecular motions in liquids.

## CHAPTER II

### EXPERIMENTAL

The nuclear magnetic resonance spectra were obtained using a Varian Associates high resolution NMR spectrometer and electromagnet. Three radio frequency units were used: 56.4 Mc/s for  $F^{19}$ , 60 Mc/s for  $H^1$  and 10.3 Mc/s for  $B^{11}$ . The spectra were calibrated using audio side bands generated with a D-890-A Muirhead Wigan decade oscillator. Peaks being measured were "bracketed" with modulation side bands from a reference peak<sup>(13)</sup>. A Varian Associates NMR integrator model V-3521 was used wherever possible. A Varian Associates model V-4340 variable temperature NMR probe was used for low and high temperature studies. A liquid air boiler was used as a source of cold gas: for high temperature studies dry nitrogen from a cylinder was heated by an electrical element. Probe temperatures were measured using a copper-constantan thermocouple and a Leeds and Northrup model 8692 temperature potentiometer. In studies where accurate temperature measurement was important, the probe was allowed about one half hour to come into equilibrium at each new temperature. The temperature was held constant within  $\pm 0.5^\circ C$  while each spectrum was recorded.

Samples were contained in 5 mm O.D. pyrex or silica tubes. All gases and liquids with appreciable vapour pressures at room temperature were distilled into the tubes and sealed under vacuum. Pyrex was preferred because of better uniformity in the tubes and ease of glass blowing and sealing. Silica was used for compounds which react readily with pyrex (such as  $IF_5$  and  $BrF_5$ ) at room temperature and for samples (such as  $SiF_4$  and  $BF_3$ ) which



were under very high pressure at room temperature. It was impossible to measure the pressure in gaseous samples but some may have been as high as 50 atmospheres.

## CHAPTER III

### SULPHUR TETRAFLUORIDE

#### A. The Observed Spectrum

The  $F^{19}$  NMR spectrum of  $SF_4$  has previously been described by Cotton, George and Waugh<sup>(14)</sup> and also by Muetterties and Phillips<sup>(15)</sup>. Both groups found the  $F^{19}$  NMR spectrum to consist of one very broad line at room temperature, due to rapid chemical exchange of the fluorines. Upon cooling the sample, these workers found that this line broadened further and then split into two peaks. At  $-100^\circ C$  each of these peaks was further resolved into a 1:2:1 triplet. This spectrum is entirely compatible with the known structure of the  $SF_4$  molecule<sup>(16)</sup>.

The symmetry of the  $SF_4$  molecule is  $C_{2v}$ . The four fluorines occupy two equatorial and two axial corners of a trigonal bipyramid around the sulphur; the fifth position being occupied by a lone pair of electrons. All of the F - S bonds are distorted away from the lone pair by lone pair-bond pair electron repulsions<sup>(17 - 19)</sup>.

The NMR spectrum can be considered as an  $A_2 X_2$  type, where the two A nuclei "see" the total spin component  $F_z$  of the two X nuclei as + 1, 0, or - 1 in the statistical ratio 1:2:1 and give a 1:2:1 triplet. The X nuclei are acted upon in the same manner by the two A nuclei. In a recent publication<sup>(20)</sup> it has been reported that the NMR spectrum of  $SF_4$  is more complex, and is actually an  $A_2 B_2$  case.

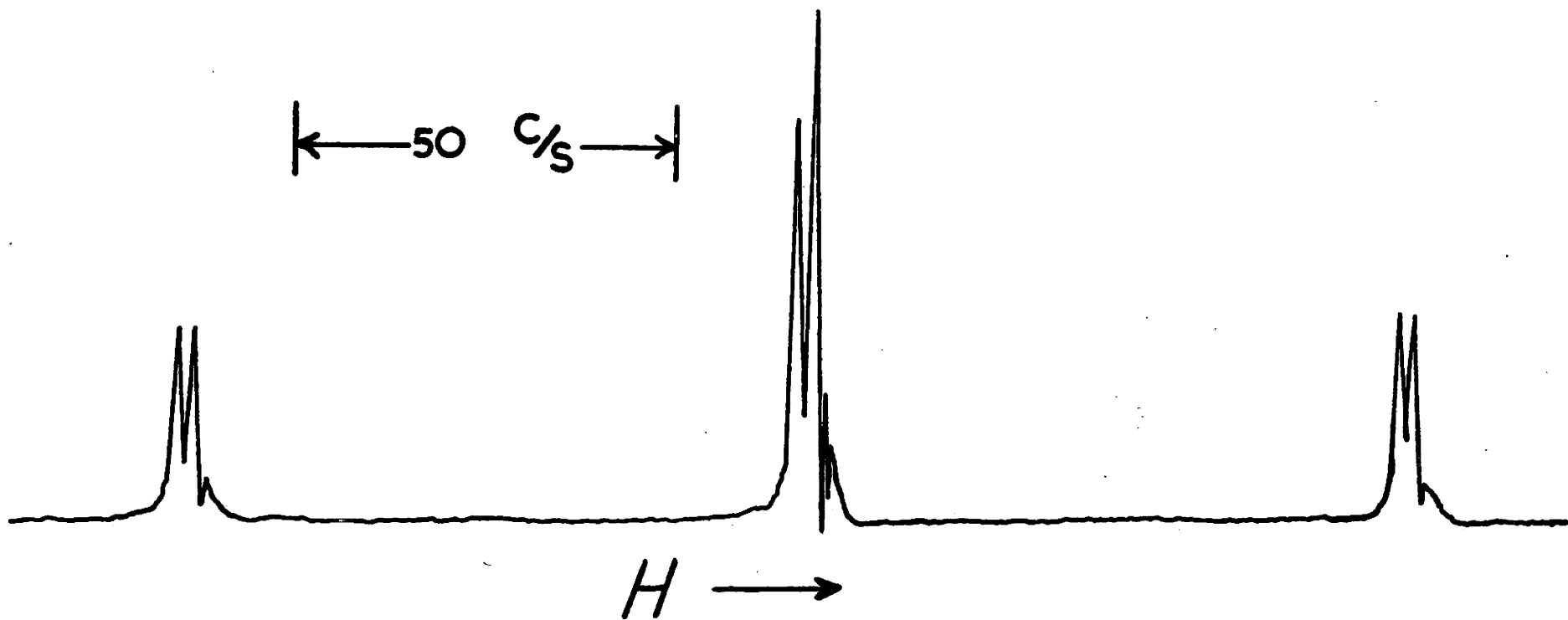


Fig. 2  $F^{19}$  NMR Spectrum of the Low-field Half of the Resonance of  $SF_4$  at  $-101^\circ C$  (56.4 Mc/s)

I observed the resolution of the  $SF_4$  spectrum into two triplets at  $-60^\circ C$ , a higher temperature than previously reported. At  $-90^\circ C$ , I observed that all of the peaks of both triplets split into doublets. The two halves of the spectrum are symmetrical about the center. The low-field half of the spectrum is reproduced in Fig. 2.

B. Theoretical Treatment of the  $F^{19}$  Spectrum of  $SF_4$

An interpretation of the observed spectrum can be achieved by treating  $SF_4$  as an  $A_2 B_2$  system. The general case of  $A_2 B_2$  has been discussed by Pople, Schneider and Bernstein<sup>(2, 21)</sup>. In general, there will be four different spin-coupling constants as shown in Fig. 3.

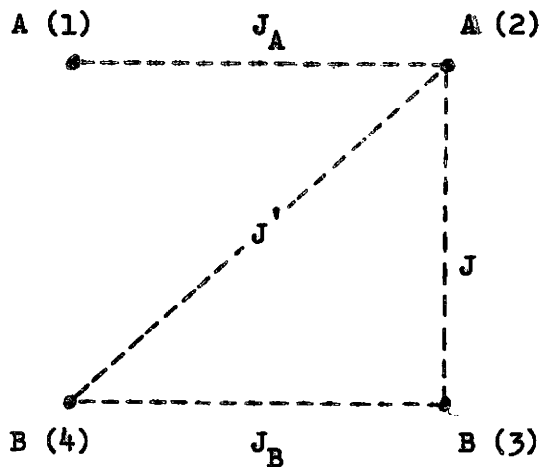


Fig. 3 Spin-coupling Constants for Four Nuclei  $A_2 B_2$

It is convenient to define the new quantities:

$$K = J_A + J_B \qquad L = J - J'$$

$$M = J_A - J_B \qquad N = J + J'$$

From a consideration of the structure of  $SF_4$  it is obvious that  $J$  must equal  $J'$ . There are no cis or trans bonds between non equivalent nuclei, only left handed and right handed bonds. If  $J = J'$ , then  $L = 0$  and  $N = 2J$ . This simplifies the complete matrix considerably by making many of the off diagonal elements equal to zero. The basic functions and complete matrix of the Hamiltonian  $\mathcal{H}_0$  for an  $A_2 B_2$  system are given by Pople, Schneider and Bernstein<sup>(2, 21)</sup> and are reproduced in Table 4. A serial notation is used for the wavefunctions. Thus  $\alpha\alpha\beta\beta$  means  $\alpha(1) \alpha(2) \beta(3) \beta(4)$ . Explicit expressions for all of the energies of the states of an  $A_2 B_2$  system, except those of the  $\underline{s}_0$  states, are given by the same authors and are reproduced in Table 5. The stationary state energies of the  $\underline{s}_0$  states are usually obtained by perturbation methods. However, in this case explicit expressions for the stationary state energies of the  $\underline{s}_0$  levels can be obtained by considering the matrix elements of the  $\underline{s}_0$  states. Since there are no non-zero off diagonal elements between the  $3 \underline{s}_0$  state and other states, the energy of the  $3 \underline{s}_0$  state remains unchanged, and the secular determinant for the  $\underline{s}_0$  states reduces to a  $3 \times 3$  determinant. The secular equation for the energies of the  $1\underline{s}_0$ ,  $2\underline{s}_0$  and  $4\underline{s}_0$  states is then

Table 4

Basic Functions and Complete Matrix of Hamiltonian  $\mathcal{H}$   
for Four Nuclei  $A_2B_2$

Function	A	B	Diagonal matrix elements†	Off-diagonal matrix elements
$0_0$	$\alpha\alpha$	$\alpha\alpha$	$\nu_A + \nu_B + \frac{1}{4}N$	
$1_{01}$	$2^{-\frac{1}{2}}(\alpha\beta + \beta\alpha)$	$\alpha\alpha$	$\nu_B$	$(1_{01} 3C 2_{01}) = \frac{1}{4}N$
$2_{01}$	$\alpha\alpha$	$2^{-\frac{1}{2}}(\alpha\beta + \beta\alpha)$	$\nu_A$	
$1_{00}$	$\beta\beta$	$\alpha\alpha$	$-\nu_A + \nu_B - \frac{1}{4}N$	$(1_{00} 3C 2_{00}) = 0$ $(2_{00} 3C 3_{00}) = \frac{1}{4}L$
$2_{00}$	$\alpha\alpha$	$\beta\beta$	$\nu_A - \nu_B - \frac{1}{4}N$	$(1_{00} 3C 3_{00}) = \frac{1}{4}L$ $(2_{00} 3C 4_{00}) = \frac{1}{4}N$
$3_{00}$	$2^{-\frac{1}{2}}(\alpha\beta - \beta\alpha)$	$2^{-\frac{1}{2}}(\alpha\beta - \beta\alpha)$	$-K$	$(1_{00} 3C 4_{00}) = \frac{1}{4}N$ $(3_{00} 3C 4_{00}) = -\frac{1}{4}L$
$4_{00}$	$2^{-\frac{1}{2}}(\alpha\beta + \beta\alpha)$	$2^{-\frac{1}{2}}(\alpha\beta + \beta\alpha)$	0	
$1_{0-1}$	$2^{-\frac{1}{2}}(\alpha\beta + \beta\alpha)$	$\beta\beta$	$-\nu_B$	$(1_{0-1} 3C 2_{0-1}) = \frac{1}{4}N$
$2_{0-1}$	$\beta\beta$	$2^{-\frac{1}{2}}(\alpha\beta + \beta\alpha)$	$-\nu_A$	
$0_{-2}$	$\beta\beta$	$\beta\beta$	$-\nu_A - \nu_B + \frac{1}{4}N$	
$1_{01}$	$2^{-\frac{1}{2}}(\alpha\beta - \beta\alpha)$	$\alpha\alpha$	$\nu_B - \frac{1}{4}K - \frac{1}{4}M$	$(1_{01} 3C 2_{01}) = -\frac{1}{4}L$
$2_{01}$	$\alpha\alpha$	$2^{-\frac{1}{2}}(\alpha\beta - \beta\alpha)$	$\nu_A - \frac{1}{4}K + \frac{1}{4}M$	
$1_{00}$	$2^{-\frac{1}{2}}(\alpha\beta + \beta\alpha)$	$2^{-\frac{1}{2}}(\alpha\beta - \beta\alpha)$	$-\frac{1}{4}K + \frac{1}{4}M$	$(1_{00} 3C 2_{00}) = -\frac{1}{4}L$
$2_{00}$	$2^{-\frac{1}{2}}(\alpha\beta - \beta\alpha)$	$2^{-\frac{1}{2}}(\alpha\beta + \beta\alpha)$	$-\frac{1}{4}K - \frac{1}{4}M$	
$1_{0-1}$	$2^{-\frac{1}{2}}(\alpha\beta - \beta\alpha)$	$\beta\beta$	$-\nu_B - \frac{1}{4}K - \frac{1}{4}M$	$(1_{0-1} 3C 2_{0-1}) = -\frac{1}{4}L$
$2_{0-1}$	$\beta\beta$	$2^{-\frac{1}{2}}(\alpha\beta - \beta\alpha)$	$-\nu_A - \frac{1}{4}K + \frac{1}{4}M$	

† For convenience,  $K/4$  is subtracted from all diagonal matrix elements. This makes no difference in calculating transition energies.

---

 Table 5

 Explicit Expressions for Energy for Four Nuclei  $A_2B_2$  With  $J = J^0$ 

<u>State</u>	<u>Energy</u>
$\underline{s}_2$	$\gamma_A + \gamma_B + 1/2 N$
$1\underline{s}_1$	$1/2(\gamma_A + \gamma_B) - 1/2 [(\gamma_0\delta)^2 + N^2]^{1/2}$
$2\underline{s}_1$	$1/2(\gamma_A + \gamma_B) + 1/2 [(\gamma_0\delta)^2 + N^2]^{1/2}$
$1\underline{s}_{-1}$	$-1/2(\gamma_A + \gamma_B) + 1/2 [(\gamma_0\delta)^2 + N^2]^{1/2}$
$2\underline{s}_{-1}$	$-1/2(\gamma_A + \gamma_B) - 1/2 [(\gamma_0\delta)^2 + N^2]^{1/2}$
$\underline{s}_{-2}$	$-(\gamma_A + \gamma_B) + 1/2 N$
$1\underline{a}_1$	$\gamma_B - 1/2 K - 1/2 M$
$2\underline{a}_1$	$\gamma_A - 1/2 K + 1/2 M$
$1\underline{a}_0$	$-1/2 K + 1/2 M$
$2\underline{a}_0$	$-1/2 K - 1/2 M$
$1\underline{a}_{-1}$	$-\gamma_B - 1/2 K - 1/2 M$
$2\underline{a}_{-1}$	$-\gamma_A - 1/2 K + 1/2 M$

---

$$\begin{vmatrix}
 \mathcal{H}_{11} - E & & 0 & & J \\
 & & & & \\
 0 & & \mathcal{H}_{22} - E & & J \\
 & & & & \\
 J & & J & & \mathcal{H}_{33} - E
 \end{vmatrix} = 0 \quad (28)$$

The solutions of this equation are of the form

$$E = k \cos \theta \quad (29)$$

$$\text{where } k = \frac{2}{\sqrt{3}} \left[ \frac{7}{3} J^2 + (\gamma_0 \delta)^2 \right]^{1/2} \quad (30)$$

$$\text{and } \cos 3\theta = \frac{\sqrt{3} J \left[ (\gamma_0 \delta)^2 - \frac{10}{9} J^2 \right]}{\left[ \frac{7}{3} J^2 + (\gamma_0 \delta)^2 \right]^{3/2}} \quad (31)$$

For any values of  $J$  and  $\gamma_0 \delta$ , three values of  $\theta$  are found which satisfy Equation (31). Substitution of these values of  $\theta$  in Equation (29) yields values for  $E(1s_0')$ ,  $E(2s_0')$  and  $E(4s_0')$ , the stationary-state energies of the corresponding wave functions.

Since the ratio  $J/\gamma_0 \delta$  for  $SF_4$  is very small, transitions giving rise to combination lines have extremely low probability and need not be considered. The remaining twenty-four transitions may be considered as two separate sets of twelve. The set of A lines is a mirror image of the set of B lines with respect to the central position,  $1/2(\gamma_A + \gamma_B)$ . From Table 6 it can be seen that the energies of the A transitions (and therefore also the B transitions) are independent of the coupling constants between equivalent nuclei and depend only on the chemical shift  $\gamma_0 \delta$  and the coupling constant  $J$ .



The frequency separation between transitions 1 and 3 of the NMR spectrum is  $2J$  and the separation between the 10, 11 transition of the A spectrum and the corresponding transition of the B spectrum is  $\gamma_0 \delta$ . The values found for  $J$  and  $\gamma_0 \delta$  at  $-101^\circ \text{C}$  are:

$$J = 76.3 \pm 0.3 \text{ c/s}$$

$$\gamma_0 \delta (56.4 \text{ Mc/s}) = 2935 \pm 10 \text{ c/s} = 52.1 \text{ ppm}$$

$$J/\gamma_0 \delta = 0.0260$$

The theoretical spectrum of  $\text{SF}_4$  was calculated using these values. Transitions 6 and 7 differ in energy by only  $2 E(4s_0')$ , which equals  $0.1 \text{ c/s}$  and were, therefore, not resolved. It may be seen in Table 7 that there is good agreement between the observed and calculated spectra.

The  $\text{F}^{19}$  NMR spectrum of  $\text{SF}_4$  is an example of second-order splitting for an extremely small value of  $J/\gamma_0 \delta$ . The reason that a second-order effect is observed in this case is that the absolute values of both  $J$  and  $\gamma_0 \delta$  are very large. The only other reported  $A_2 B_2$  spectra for which it is certain that the coupling constants between non-equivalent nuclei are equal due to the symmetry of the molecule is the  $\text{C}^{13}$  satellite spectrum of allene<sup>(22)</sup> and the  $\text{SF}_4$  portion of the spectrum of  $\text{SF}_4(\text{SO}_2\text{F})_2$ <sup>(23)</sup>. It has been suggested<sup>(24)</sup> that other NMR spectra which have previously been explained as  $A_2 B_2$  with equal coupling constants between non-equivalent nuclei ( $\beta$ -propiolactone<sup>(25)</sup>, ethyl monothiocarbonate<sup>(26)</sup>, trans-dibromocyclopropane<sup>(4)</sup>, and 2, 3 - dihydrofuran<sup>(4)</sup>) probably do not, in fact, have exactly equal coupling constants. The coupling constants for cis and trans bonds are usually different. In the above 4 cases it

Table 6

Energies of A Transitions for Four Nuclei  $A_2 B_2$  With  $J = J'$

<u>Transition</u>	<u>Energy Relative to <math>1/2(\gamma_A + \gamma_B)</math></u>
1. $1s_{-1}' \longrightarrow s_{-2}$	$J + 1/2 [(\gamma_0 \delta)^2 + 4J^2]^{1/2}$
2. $1s_0' \longrightarrow 1s_{-1}'$	$- 1/2 [(\gamma_0 \delta)^2 + 4J^2]^{1/2} - E(1s_0')$
3. $s_{-2} \longrightarrow 1s_{-1}'$	$-J + 1/2 [(\gamma_0 \delta)^2 + 4J^2]^{1/2}$
4. $1s_{-1}' \longrightarrow 2s_0'$	$E(2s_0') - 1/2 [(\gamma_0 \delta)^2 + 4J^2]^{1/2}$
5. $3s_0 \longrightarrow 2s_{-1}'$	Forbidden
6. $2s_{-1}' \longrightarrow 4s_0'$	$E(4s_0') + 1/2 [(\gamma_0 \delta)^2 + 4J^2]^{1/2}$
7. $4s_0' \longrightarrow 2s_{-1}'$	$1/2 [(\gamma_0 \delta)^2 + 4J^2]^{1/2} - E(4s_0')$
8. $2s_{-1}' \longrightarrow 3s_0$	Forbidden
9. $2a_0 \longrightarrow 2a_{-1}$	Forbidden
10. $2a_{-1} \longrightarrow 1a_0$	$1/2(\gamma_0 \delta)$
11. $1a_0 \longrightarrow 2a_{-1}$	$1/2(\gamma_0 \delta)$
12. $2a_{-1} \longrightarrow 2a_0$	Forbidden

Table 7

Observed and Calculated Line Positions for the A Transitions  
in the NMR Spectrum of SF<sub>4</sub>

Transition	Observed		Calculated	
	Line Position (c/s)	Second Order Splitting (c/s)	Line Position (c/s)	Second Order Splitting (c/s)
1	- 78.7 ± 0.6		- 78.3	
		2.0 ± 0.1		1.9
2	- 76.7 ± 0.6		- 76.4	
7	- 2.0 ± 0.1		- 2.0	
6			- 1.9	
		2.0 ± 0.1		1.9 - 2.0
10, 11	0		0	
3	74.2 ± 0.6		74.3	
		1.9 ± 0.1		1.9
4	76.1 ± 0.6		76.2	

is probably because of a limitation of resolution that effects due to  $J \neq J'$  are not observed.

### C. Experimental

The sulphur tetrafluoride used in this study was obtained from a commercial source and was contaminated with  $\text{SOF}_2$ ,  $\text{SCl}_2$  and  $\text{CH}_3\text{CN}$ . The latter two impurities and some of the  $\text{SOF}_2$  were removed by fractional distillation in a vacuum line. Due to the similarity of the boiling points of  $\text{SF}_4$  and  $\text{SOF}_2$  it was not possible to obtain samples of  $\text{SF}_4$  which were completely free from  $\text{SOF}_2$ . The oxyfluoride was usually present in a concentration of about 5%. Samples of  $\text{SF}_4$  were distilled into 5 mm O.D. silica tubes, which were sealed under vacuum.

The chemical shift was measured by the overlapping of the appropriate audio side bands from the A and B halves of the spectrum and recording the overlap pattern. Since the splitting between the multiplet peaks was known,  $\gamma_0$  could be calculated.

## CHAPTER IV

### SULPHUR AND SILICON ISOTOPE EFFECTS

#### A. Introduction

Isotope effects on the chemical shift in fluorine NMR spectra have been observed in the systems F - Si<sup>29</sup>(Si<sup>28</sup>)<sup>(27)</sup>, F - C - D(H)<sup>(28)</sup>, F - C<sup>13</sup>(C<sup>12</sup>)<sup>(29 - 34)</sup>, and F - C - C<sup>13</sup>(C<sup>12</sup>)<sup>(29 - 34)</sup>. In every case the fluorine resonance is observed at higher field when the fluorine atom is bonded directly or indirectly to the heavier nucleus. Similar, but considerably smaller, effects have been observed in proton magnetic resonance spectra<sup>(35 - 37)</sup>. The Si<sup>29</sup> - F isotopic shift was observed by Tiers<sup>(27)</sup> in the single case of the SiF<sub>6</sub><sup>2-</sup> ion and was barely large enough to be observable. Since it is considerably smaller than the C<sup>13</sup> - F isotope shift, Tiers suggested that there was a strong inverse dependence of the isotopic shift on the bond length. I have now studied another example of a Si<sup>29</sup> - F isotope effect and have observed and measured S<sup>33</sup> - F and S<sup>34</sup> - F isotope shifts for the first time.

#### B. Sulphur Isotope Effects

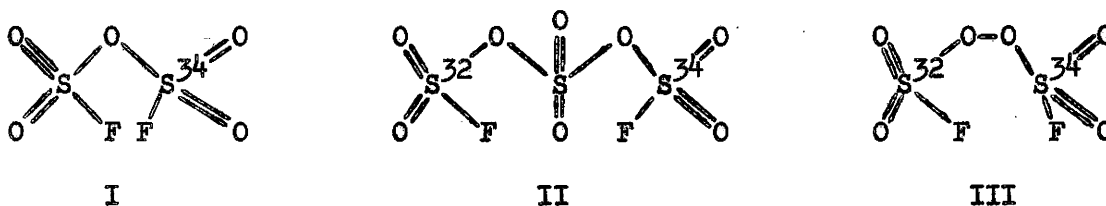
Naturally occurring sulphur consists of four stable isotopes; the generally accepted natural abundances and the nuclear spins are as follows:

$S^{32}$	95.06%	$I = 0$
$S^{33}$	0.74%	$I = 3/2$
$S^{34}$	4.18%	$I = 0$
$S^{36}$	0.0136%	$I = 0$

The only stable isotope with a nuclear spin is  $S^{33}$ , and this isotope also has an electric quadrupole moment. Electric quadrupole relaxation of the  $S^{33}$  in most compounds combined with the very low natural abundance of  $S^{33}$  makes the observation of fluorine-sulphur spin-spin coupling exceedingly unlikely except for the unique molecule sulphur hexafluoride. In this molecule the electric field gradients at the site of the  $S^{33}$  are minimized by the octahedral symmetry of the molecule and thus quadrupole relaxation is largely eliminated. Also, the presence of six equivalent fluorines in the sulphur hexafluoride molecule helps to overcome the intensity problem. The NMR spectrum of  $SF_6$  has previously been reported as a single line<sup>(15)</sup>. I have observed that in addition to the main  $S^{32} - F$  peak there are also present in the spectrum four equally spaced satellite peaks which may be attributed to fluorine on  $S^{33}$ . From the spacing of these satellite peaks and the displacement of their center from the main fluorine on  $S^{32}$  line, a coupling constant  $J_{S^{33}F} = 251.6 \pm 0.3$  c/s and an isotopic shift  $\Delta\delta_{S^{33} - S^{32}} = 0.027 \pm 0.002$  ppm were obtained.

In addition to the  $S^{33}$  satellites, a small peak approximately 5% of the area of the main peak was observed at 3 c/s to high field of the main fluorine on  $S^{32}$  signal: I assign this peak to fluorine

on  $S^{34}$ . I have observed similar peaks in the NMR spectra of many other sulphur-fluorine compounds. A few of these spectra are reproduced in Fig. 4. The isotopic shifts obtained from these observations are given in Table (8). In cases where the lines are broadened by unresolved spin-spin coupling as in  $C_6H_5SO_2F$ , or by quadrupole coupling, as in  $SO_2FCl$ , the  $S^{34}$  satellites could not be clearly resolved. Also, it was not possible to observe a clearly resolved satellite in the case of  $S_2O_5F_2$ . This is probably due to spin-spin coupling between the non-equivalent fluorines in I. This coupling should be large compared with the expected isotopic shift (compare  $SF_4(SO_3F)_2$  (23)). The resulting AB spectrum would have most of its intensity at  $\approx 1/2 \Delta\delta$  and the satellite would be very difficult to observe. In the case of  $S_3O_8F_2$  (Fig. 4) the  $S^{34}$



satellite appears to be a doublet with a splitting of approximately 0.7 c/s. This can be similarly attributed to spin-spin coupling between the non-equivalent fluorines in II. It is interesting to note that  $S_4O_{11}F_2$  and  $S_2O_5FCl$  have "normal"  $S^{34}$  satellites. In the case of  $S_2O_6F_2$  (III) the satellite is not split, presumably because of weak coupling through a peroxide bridge.

4-10501-S

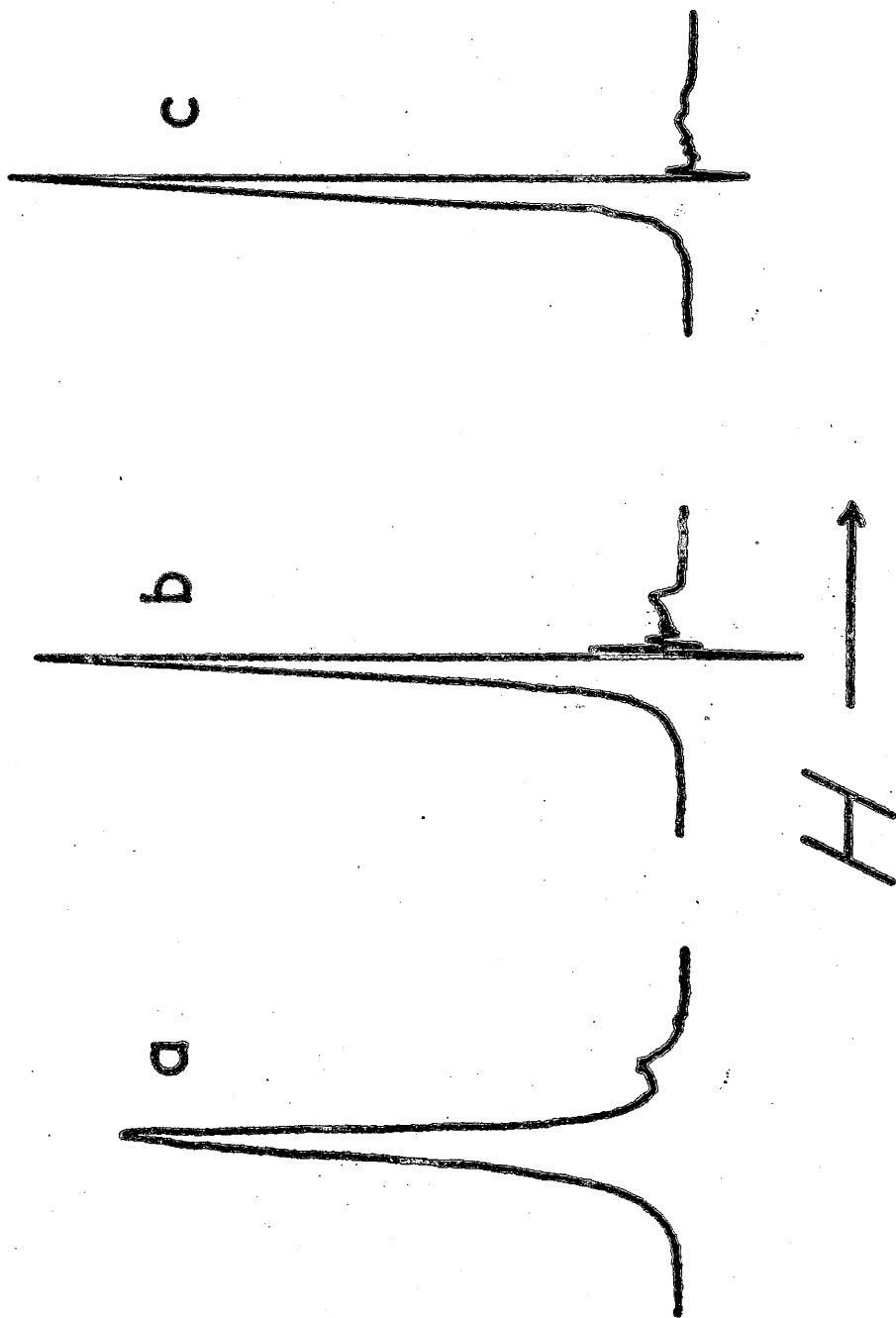


Fig. 4  $^{19}\text{F}$  NMR Spectra Showing  $^{34}\text{S}$  Satellites for a)  $\text{SF}_6$ , b)  $\text{S}_2\text{O}_5\text{FCl}$ , c)  $\text{S}_3\text{O}_8\text{F}_2$



Table 8

## Isotopic Shifts for Sulphur-fluorine Compounds

	$\Delta\delta_{S^{34} - S^{32}}$ (ppm)	<u>Number of Measurements</u>
$SF_6^*$	$0.053 \pm .004$	20
$S_2O_6F_2$	$0.033 \pm .002$	10
$HSO_3F$	$0.044 \pm .004$	16
$K^+SO_3F^-$	$0.036 \pm .004$	10
$CH_3SO_2F^\ddagger$	$0.043 \pm .004$	30
$SOF_2$	$0.053 \pm .004$	10
$SO_2F_2$	$0.048 \pm .002$	20
$S_2O_5FCl$	$0.049 \pm .003$	20
$S_3O_8F_2$	$0.050 \pm .002$	20
$S_4O_{11}F_2$	$0.050 \pm .004$	20

$$* \Delta\delta_{S^{33} - S^{32}} = 0.027 \pm 0.002 \text{ ppm}; \quad J_{S^{33}F} = 251.6 \pm 0.3 \text{ c/s}$$

$$\ddagger J_{HF} = 5.6 \pm 0.4 \text{ c/s}$$

Since most of the F on S peaks have line widths of approximately 1 c/s the tails of the F on S<sup>32</sup> and F on S<sup>34</sup> peaks overlap and tend to draw the peaks together, giving a systematic error, which means that the standard deviations quoted in Table (8) are not a completely reliable guide to the accuracy of the isotopic shifts. In the NMR spectra of all the sulphur-fluorine compounds, except SF<sub>6</sub>, the S<sup>33</sup> satellites are presumably either so broad that they cannot be observed or are completely collapsed to a single line that lies between the main peak and the S<sup>34</sup> satellite and is not resolved from the main peak.

### C. Silicon Isotope Effects

Naturally occurring silicon consists of three stable isotopes; the generally accepted natural abundances and nuclear spins are as follows:

Si <sup>28</sup>	92.18%	I = 0
Si <sup>29</sup>	4.70%	I = 1/2
Si <sup>30</sup>	3.12%	I = 0

The Si<sup>29</sup> isotopic shift and coupling constant for silicon tetrafluoride are shown in Table (9). The coupling constant is somewhat smaller than that previously reported.

In principle, a Si<sup>30</sup> satellite to the high-field side of the F on Si<sup>28</sup> peak would be expected. In the case of SiF<sub>4</sub> the shift would be probably less than 1 c/s at 56.4 Mc/s. I was unable to observe this peak, presumably because of its low intensity and very small shift.

Table 9Isotopic Shifts and Coupling Constants for  $\text{SiF}_4$  and  $\text{SiF}_6^{2-}$ 

	$J_{\text{Si}^{29}\text{F}}$	$\Delta\delta$	Number of Measurements	Reference
$\text{SiF}_4$	$169.3 \pm .2 \text{ c/s}$	$0.007 \pm .002 \text{ ppm}$	20	This work
$\text{SiF}_4$	178 c/s			15
$\text{SiF}_6^{2-}$	$108.0 \pm .1 \text{ c/s}$	$0.004 \pm .001 \text{ ppm}$	10	27
$\text{SiF}_6^{2-}$	110 c/s			15

#### D. Discussion

In all of the isotopic shifts that have been observed, the NMR signal of fluorine on a heavier nucleus is found at higher field than fluorine on a lighter nucleus of the same species. This indicates greater electronic screening of the fluorines on the heavier nucleus than on the lighter nucleus. In  $SF_6$  the  $S^{34}$  isotopic shift is twice as large as the  $S^{33}$  shift. The  $S^{33}$  isotopic shift in  $SF_6$  is approximately six times as large as the  $Si^{29}$  shift in  $SiF_6^{2-}$ . The fact that the isotopic shift in  $SiF_4$  is apparently greater than in  $SiF_6^{2-}$  is consistent with Tiers' proposal that the isotopic shift has a strong inverse dependence on the bond length ( $SiF_4$   $r = 1.58$  Å <sup>(38)</sup>,  $SiF_6^{2-}$   $r = 1.71$  Å <sup>(39)</sup>). It is evident, however, that the bond length is not the only factor involved, since the isotopic shift for  $SF_6$  ( $r = 1.58$  Å <sup>(40)</sup>) is much larger than for  $SiF_4$ . The isotopic shift for F on S varies over a much greater range than F on C. This is consistent with the fact that there is a much greater variation of bond length and bond strength for F - S bonds than for F - C bonds.

The isotopic shift could, in principle, be due to a difference in the electronic wave function arising from nucleus-electron interactions which depend upon nuclear volume and nuclear quadrupole moment, both of which differ with isotopic species. However, these interactions are small and their perturbations of the electronic wave functions occur only in the immediate vicinity of the nucleus which is changed. The fact that the isotopic shift in  $SF_6$  for  $S^{34}$  is twice that for  $S^{33}$  indicates that the quadrupole moment of  $S^{33}$  does not

contribute appreciably to the isotopic shift.

A more important way in which isotopic substitution can modify the chemical shift is by changing the dynamic state of the molecule without directly affecting the electronic wave function. The suitably averaged mean internuclear separation is changed by isotopic substitution mainly as a result of the difference in zero point vibrational amplitude. The heavier isotope has a smaller vibrational amplitude and hence polarizes the electrons of the fluorine less, causing a high field shift in the fluorine resonance. As expected on this basis,  $S^{33}$  causes a smaller isotopic shift than  $S^{34}$ . The isotopic shifts in the NMR spectra of  $H_2$ , HD and  $D_2$  have been satisfactorily accounted for on this same basis<sup>(41)</sup>.

#### E. Experimental

Commercial samples of sulphur hexafluoride and silicon tetrafluoride were distilled into the sample tubes which were sealed off under vacuum. The silicon tetrafluoride was in the gas phase at room temperature; the pressure in the tube was estimated as 10 - 40 atmospheres. The sulphur hexafluoride was in the liquid state at room temperature. A commercial sample of methanesulphonyl fluoride was used without further purification. Fluorosulphuric acid was distilled twice in a dry atmosphere.  $S_2O_5F_2$ <sup>(42, 43)</sup>,  $S_3O_8F_2$ <sup>(42, 43)</sup>,  $S_4O_{11}F_2$ <sup>(42)</sup>,  $S_2O_5FCl$ <sup>(43)</sup>,  $S_2O_6F_2$ <sup>(44)</sup>,  $SOF_2$ <sup>(45)</sup>, and  $KSO_3F$ <sup>(46)</sup>, were prepared in this laboratory by standard methods.  $SO_2F_2$  and  $SO_2FCl$  were obtained as a mixture from the Allied Chemical Corporation and were used without further purification. Except for potassium fluorosulphate which was dissolved in water, all the materials were studied as the pure liquids.

## CHAPTER V

### QUADRUPOLE RELAXATION FOR A SPIN $I = 3/2$ : The $F^{19}$ NMR

#### SPECTRA OF $BF_3$ , $ClO_3F$ AND $BrF_5$

##### A. Introduction

In general, the spectra of protons or fluorine nuclei spin-spin coupled to a nucleus of spin  $I$  (where  $I > 1/2$ ) would be expected to have a multiplet structure of  $2I + 1$  lines. Often, however, since nuclei with a spin  $I$  greater than  $1/2$  have quadrupole moments which usually couple strongly, by means of molecular reorientations, to local electric fields, relaxation of the nucleus with the quadrupole moment occurs and the multiplet structure of the  $H^1$  or  $F^{19}$  resonance is collapsed to a single line. The expected multiplet structure is therefore seen only if the high-spin nucleus has a small quadrupole moment or if the high-spin nucleus is in an environment which is highly symmetric electrically. Examples of the first case are the proton spectra of diborane<sup>(47, 48)</sup> and ammonia<sup>(49)</sup>,  $B^{11}$  and  $N^{14}$  having relatively small nuclear quadrupole moments<sup>(2)</sup>; examples of the second case are the fluorine spectrum of  $SF_6$ , discussed in the previous chapter, and the fluorine spectrum of  $MoF_6$ <sup>(15)</sup>;  $S^{33}$ ,  $Mo^{95}$  and  $Mo^{97}$  having relatively large quadrupole moments but being situated

in highly symmetric environments.

While the general cases of very slow relaxation and very rapid relaxation have been treated by various authors<sup>(5, 50, 51)</sup>, the case of an intermediate rate of relaxation which gives rise to a partially collapsed multiplet has been treated only for  $I = 1$ <sup>(5, 51)</sup>.

## B. Theory

A nucleus of spin  $I = 3/2$  in a magnetic field can exist in the states  $m = 3/2, 1/2, -1/2, -3/2$ . Pople<sup>(51)</sup> has derived a series of expressions for the transition probabilities due to quadrupole relaxation which can be summarized as follows: the probability that a nucleus in state  $m$  will undergo a one quantum transition (i.e., to state  $m \pm 1$ ) is

$$P_{m, m\pm 1} = \frac{3}{20} \frac{(2m\pm 1)^2 (I\pm m+1) (I\mp m)}{4I^2 (2I-1)^2} \left( \frac{e^2 qQ}{\hbar} \right)^2 \tau_q \quad (32)$$

and for the two quantum transition the probability is

$$P_{m, m\pm 2} = \frac{3}{20} \frac{(I\mp m) (I\mp m-1) (I\pm m+1) (I\pm m+2)}{4I^2 (2I-1)^2} \left( \frac{e^2 qQ}{\hbar} \right)^2 \tau_q \quad (33)$$

where  $e$  = the charge on an electron

$eq$  = the electric field gradient at the nucleus (assuming axial symmetry)

$eQ$  = the quadrupole moment of the nucleus

$\tau_q$  = the correlation time for molecular reorientation

and  $\frac{e^2 q Q}{\hbar}$  is the quadrupole coupling constant in radians/sec.

Transitions due to electric quadrupole moments occur only for  $\Delta m = \pm 1$  or  $\pm 2$ . For  $I = 3/2$ , it can be found from the above expressions that

$$\begin{aligned} P_{3/2, \pm 1/2} &= P_{\pm 1/2, 3/2} = P_{-3/2, \pm 1/2} = P_{\pm 1/2, -3/2} \\ &= \frac{1}{20} \left( \frac{e^2 q Q}{\hbar} \right)^2 \tau_q \end{aligned} \quad (34)$$

$$P_{3/2, -3/2} = P_{-3/2, 3/2} = P_{1/2, -1/2} = P_{-1/2, 1/2} = 0 \quad (35)$$

The inverse lifetime of each state  $m$  is given by

$$1/\tau_m = \sum_{\substack{n \\ n \neq m}} P_{m,n} \quad (36)$$

For  $I = 3/2$  we find, therefore, that

$$1/\tau_{3/2} = 1/\tau_{1/2} = 1/\tau_{-1/2} = 1/\tau_{-3/2} = 1/\tau = \frac{1}{10} \left( \frac{e^2 q Q}{\hbar} \right)^2 \tau_q \quad (37)$$

a result also obtained by Pople<sup>(51)</sup>. In the extreme narrowing case, the nuclear spin-lattice relaxation time  $T_1$ , due to quadrupole coupling for a nucleus of spin  $I = 3/2$ , can be very well approximated



from Abragam<sup>(5)</sup>, p. 314, as

$$1/T_1 = 1/10 \left( \frac{e^2 q Q}{h} \right)^2 \tau_q \quad (38)$$

At this point it is convenient to mention that frequency can be measured in either cycles per second or radians per second. It is useful to introduce the radial frequency  $\omega$  as

$$\omega = 2\pi\nu \quad (39)$$

If the quadrupole moment is small, or if the high spin nucleus is in a symmetrical environment (eq small), then  $\tau$  will be long and the spectrum of a spin 1/2 nucleus coupled to a spin 3/2 nucleus will be a quartet of equal intensities, each line corresponding to a state  $m$  of the high spin nucleus. If  $\tau_m$  is the lifetime of state  $m$ , then the line-shape function for this component of the multiplet is given<sup>(51)</sup> by

$$g_m(\omega) = \frac{2\tau_m}{1 + \tau_m^2(\omega - \omega_m)^2} \quad (40)$$

This function is proportional to the intensity at frequency  $\omega$  when the natural frequency is  $\omega_m$ . This expression is only valid if quadrupole relaxation is the only appreciable cause of broadening and if the broadening is small compared with the multiplet separation. Since the lifetime of the spin 1/2 nucleus in each of its states will be relatively long, each component of the resonance multiplet of the spin 3/2 nucleus will be broadened

by the same quadrupole mechanism. The line shape of each component of the multiplet under conditions where the relaxation times  $T_1$  and  $T_2$  are equal is (1)

$$g(\omega) = \frac{2T_1}{1 + T_1^2 (\omega - \omega_m)^2} \quad (41)$$

Abragam<sup>(5)</sup>, p. 449 and p. 504, has shown that the line shape for intermediate rates of quadrupole relaxation (assuming other relaxation mechanisms to be insignificant) is given by the expression

$$I(\omega) \propto \text{Re} [W A^{-1} \cdot \mathbf{1}], \quad (42)$$

where  $\text{Re} [ \quad ]$  denotes "the real part of". The vector  $W$  has components proportional to the a priori probabilities of the various frequencies of the multiplet, that is, to the populations of the states  $I_z = m$ .

$W$  is the vector  $\begin{bmatrix} 1 \\ \vdots \\ 1 \end{bmatrix}$

$\mathbf{1}$  is the vector  $[1, \dots, 1]$

and  $A^{-1}$  is the inverse of the complex matrix  $A$  that is defined by the relationships

$$A_{m, m} = i [(\omega_0 - \omega) + m 2\pi J] - 1/\tau_m \quad (43)$$

$$A_{m, n} = P_{m, n}, \quad m \neq n \quad (44)$$

$\omega_0$  being the center of the unperturbed multiplet and  $J$  the coupling constant in c/s. Using the previously derived relationship (Equation (37)) for  $1/\tau_m$  and expressing the transition probabilities  $P_{m, n}$  in terms of  $\tau_3$ , we obtain the following expression:

$$A = \begin{pmatrix} i [(\omega_0 - \omega) + 3\pi J] - \frac{1}{T} & \frac{1}{2T} & \frac{1}{2T} & 0 \\ \frac{1}{2T} & i [(\omega_0 - \omega) + \pi J] - \frac{1}{T} & 0 & \frac{1}{2T} \\ \frac{1}{2T} & 0 & i [(\omega_0 - \omega) - \pi J] - \frac{1}{T} & \frac{1}{2T} \\ 0 & \frac{1}{2T} & \frac{1}{2T} & i [(\omega_0 - \omega) - 3\pi J] - \frac{1}{T} \end{pmatrix}$$

Inserting the inverse of  $A$  in Equation (42) we find that the line shape is given by the expression

$$I(x) \propto \mathcal{T}f(\eta, x) \quad (45)$$

$$\text{where } f(\eta, x) = \frac{320+16\eta^2(25x^2+17) + \eta^4(80x^4+56x^2+45)}{1024x^2+64\eta^2(36x^4-20x^2+25)} \quad (46)$$

$$+16\eta^4(96x^6-160x^4+110x^2+45)$$

$$+\eta^6(256x^8-1280x^6+1888x^4-720x^2+81)$$

$$\eta = 2\pi J\tau$$

$$x = \frac{\omega - \omega_0}{2\pi J}$$

Line shapes calculated from Equation (45) with various values of  $\eta^2$  from 100 to 0.1 are shown in Fig.5. In the collapse of the quartet the outer lines move inward, but the inner lines move outward, resulting in a broad doublet-like structure at values of  $\eta^2$  near 2. Finally, the "doublet" collapses to a single line.

### C. The Spectrum of Boron Trifluoride

The  $F^{19}$  NMR spectrum of  $BF_3$  at room temperature has previously been reported by Muetterties and Phillips<sup>(15)</sup> and by Coyle and Stone<sup>(52)</sup> as a broad 1:1:1:1 quartet with  $J = 15$  c/s due to coupling of the fluorines with the 81.2% abundant  $B^{11}$ . The  $F^{19}$  on the 18.8% abundant  $B^{10}$  ( $I = 3$ ) gives some unresolved underlying structure. I have observed both the  $F^{19}$  and  $B^{11}$  NMR spectra of  $BF_3$  in the gas phase at room temperature. Since both the  $F^{19}$  1:1:1:1 quartet and the  $B^{11}$  1:3:3:1 quartet are only slightly collapsed at room temperature, the multiplet separations

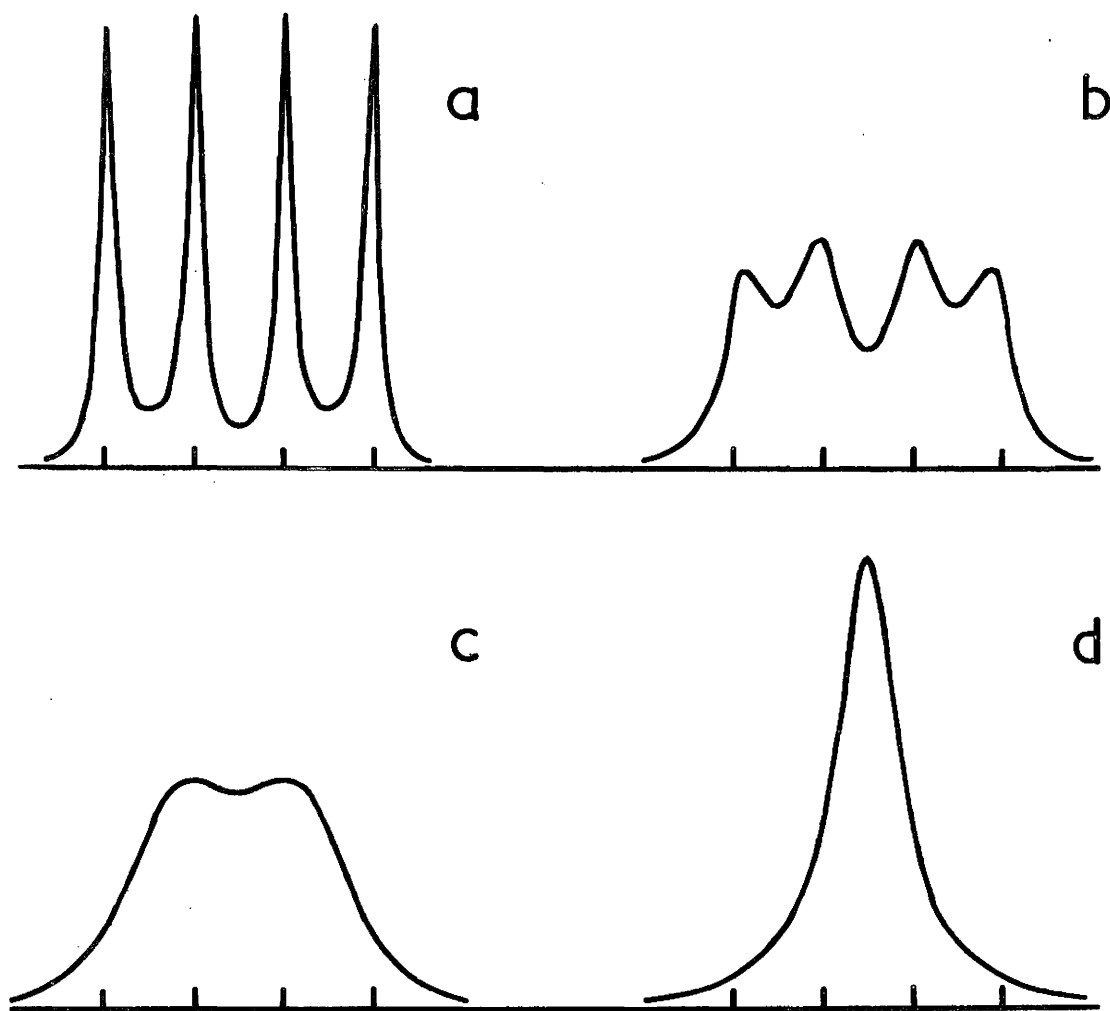


Fig. 5. Theoretical Line Shapes for the Spectra of Nuclei of Spin  $1/2$  Coupled To a Nucleus of Spin  $3/2$  According To Equation (42).  
 (a)  $\eta^2 = 100$ , (b)  $\eta^2 = 10$ , (c)  $\eta^2 = 1$ , (d)  $\eta^2 = 0.1$   
 The Vertical Lines Indicate the Positions of the Quartet In the Absence of Quadrupole Relaxation.

are taken as  $J_{B^{11}F}$ . The  $F^{19}$  resonance gives a value for  $J_{B^{11}F}$  of  $18.3 \pm 0.6$  c/s and the  $B^{11}$  resonance gives  $J_{B^{11}F} = 18.5 \pm 0.2$  c/s.

The  $BF_3$  sample used condensed to a liquid at about  $-17^\circ C$ . The  $F^{19}$  spectrum of the liquid at four lower temperatures is shown in Fig. 6. At  $-21^\circ C$  the value of  $J_{B^{11}F}$  (allowing for the partial collapse of the spectrum) was found to be  $20.0 \pm 0.5$  c/s. Since the quadrupole moment of  $B^{10}$  is three times as large as that of  $B^{11}$ , and since  $J_{B^{10}F}$  is much smaller than  $J_{B^{11}F}$  (due to the smaller magnetogyric ratio of  $B^{10}$ ), the spectrum of the fluorine on  $B^{10}$  is more collapsed than that of fluorine on  $B^{11}$ . By matching spectra calculated from Equation (45) with the experimental spectra and making due allowance for the underlying broad fluorine on  $B^{10}$  lines, I have obtained approximate values of  $\tau_q$  for temperatures in the range  $-100^\circ C$  to  $-21^\circ C$ .

If the suggestion of Moniz and Gutowsky<sup>(53)</sup> is accepted, that the reorientation is a thermally activated process described by the usual rate equation

$$\tau_q = \tau_q^0 \exp(E_a/RT), \quad (47)$$

we find from Equations (37) and (47) that a plot of  $\log \tau_q$  versus  $1/T$  should be a straight line of slope  $-E_a/2.3 R$ . The plot of the experimental data is shown in Fig. 7. The plot does not appear to be linear. Nevertheless, a straight line was drawn through the points as shown in Fig. 7. The slope of the line gave a mean activation energy of 1.4 kcal/mole.

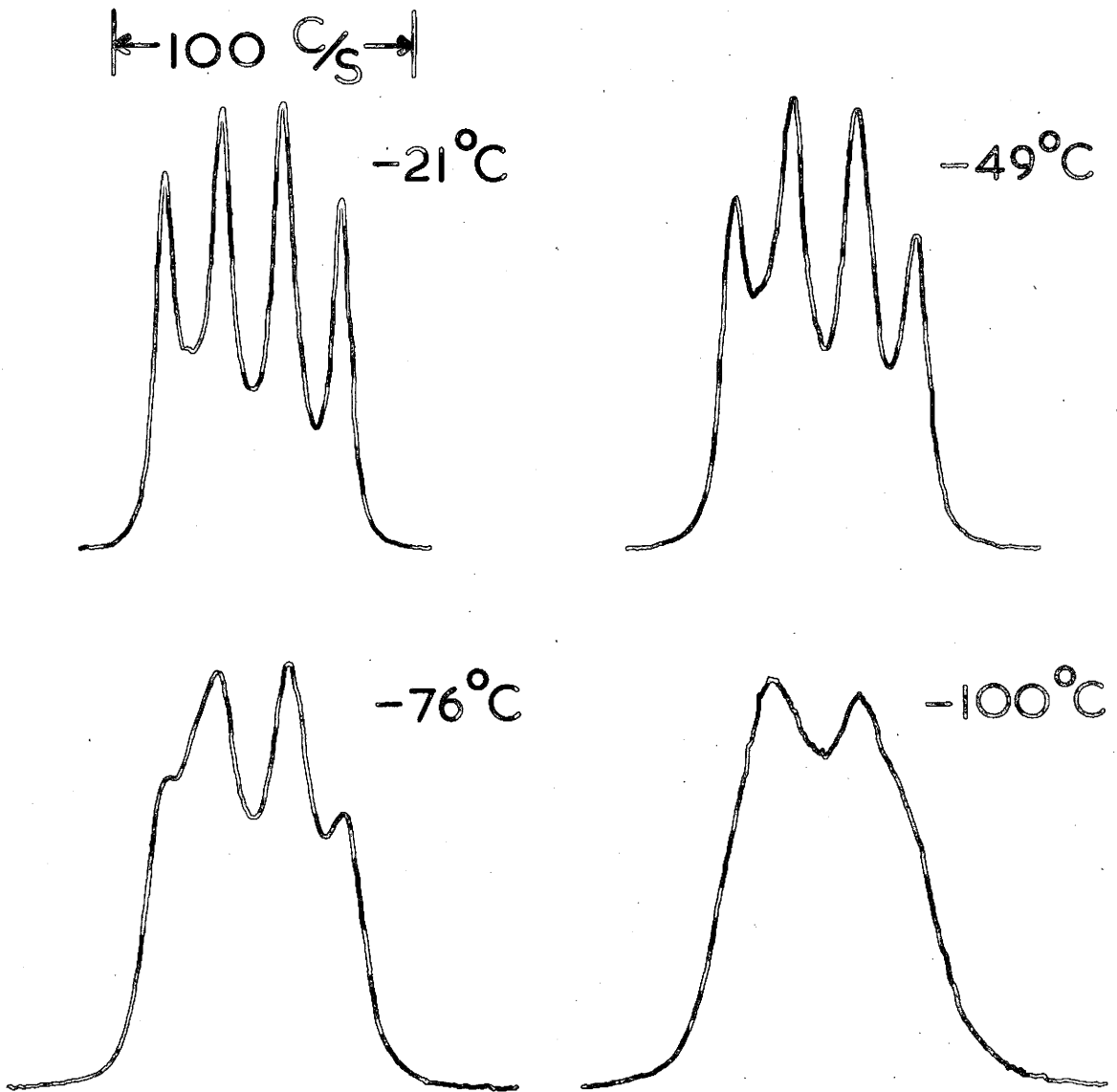


Fig. 6.  $^{19}\text{F}$  Resonance Spectra of Liquid  $\text{BF}_3$

The line widths of the  $F^{19}$  and  $B^{11}$  resonances of  $BF_3$  in the gas phase at room temperature were pressure dependent. However, for any one sample the  $F^{19}$  and  $B^{11}$  line widths were the same, as predicted by Equations (37), (38), (40) and (41).

It is clear, from the asymmetry of the  $BF_3$  spectra, that there is an isotope effect associated with the two boron isotopes. As would be expected from Chapter IV, the fluorine on  $B^{11}$  resonance occurs at slightly higher field than that of fluorine on  $B^{10}$ . The isotope effect is approximately 3 c/s at 56.4 Mc/s or approximately + 0.05 ppm.

#### D. The Spectrum of Perchloryl Fluoride

Studies of the infra-red vibrational and rotational spectra<sup>(54, 55)</sup> and the micro-wave spectrum<sup>(56)</sup> indicate that the perchloryl fluoride molecule possesses a nearly regular tetrahedral structure about the central chlorine atom, the fluorine atom being bonded directly to chlorine. The molecule possesses no observable dipole moment<sup>(57)</sup> and it is evident, therefore, that the electrical environment of the chlorine is highly symmetric: hence a slow rate of quadrupole relaxation would be expected.

The  $F^{19}$  NMR spectrum of perchloryl fluoride has previously been recorded by Brownstein<sup>(58)</sup> and by Agahigian et al.<sup>(59)</sup> at room temperature. Both authors found the  $F^{19}$  resonance at room temperature to have a broad, poorly resolved doublet-like structure. Brownstein interpreted the spectrum using a rough qualitative treatment only.



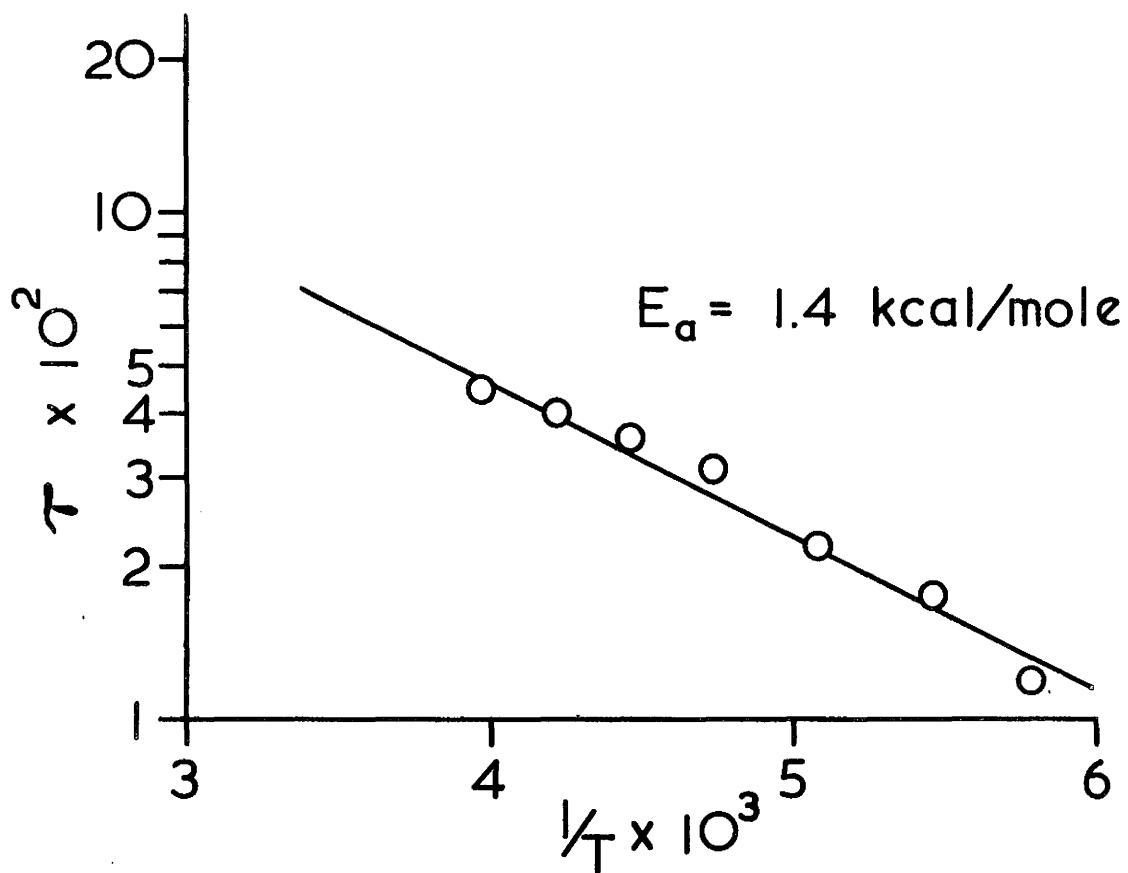


Fig. 7. The Temperature Dependence of the  $B^{11}$   $\tau$  Estimated From the  $F^{19}$  Resonance of Liquid  $BF_3$

The  $F^{19}$  NMR spectrum of perchloryl fluoride recorded at six temperatures over the range  $-131^{\circ}C$  to  $24^{\circ}C$  is shown in Fig. 8. The theory given above can be used to interpret these spectra. This task is complicated by the fact that two chlorine isotopes are present, both with spin  $3/2$ . I have therefore considered the  $ClO_3F$  spectrum as the sum of two spectra: one due to the molecule  $Cl^{35}O_3F$  and the other to the molecule  $Cl^{37}O_3F$ . The equation to describe the line shape for  $ClO_3F$  takes the form

$$I(ClO_3F) = I(Cl^{35}O_3F) + I(Cl^{37}O_3F)$$

and therefore

$$I(ClO_3F) \propto A_{35} \tau_{35} f(\eta_{35}, x_{35}) + A_{37} \tau_{37} f(\eta_{37}, x_{37})$$

where  $A_{35}$  = relative abundance of  $Cl^{35}$

$A_{37}$  = relative abundance of  $Cl^{37}$

$$\eta_{35} = 2\pi J_{35} \tau_{35}$$

$$\eta_{37} = 2\pi J_{37} \tau_{37}$$

$$x_{35} = \frac{\omega_0 - \omega}{2\pi J_{35}}$$

and  $x_{37} = \frac{\omega_0 - \omega}{2\pi J_{37}}$

Since  $\frac{J_{35}}{J_{37}} = \frac{\mu_{35}}{\mu_{37}}$  in this case, where  $\mu_{35}$  and  $\mu_{37}$  are the magnetic

moments of the Cl nuclei, it follows that

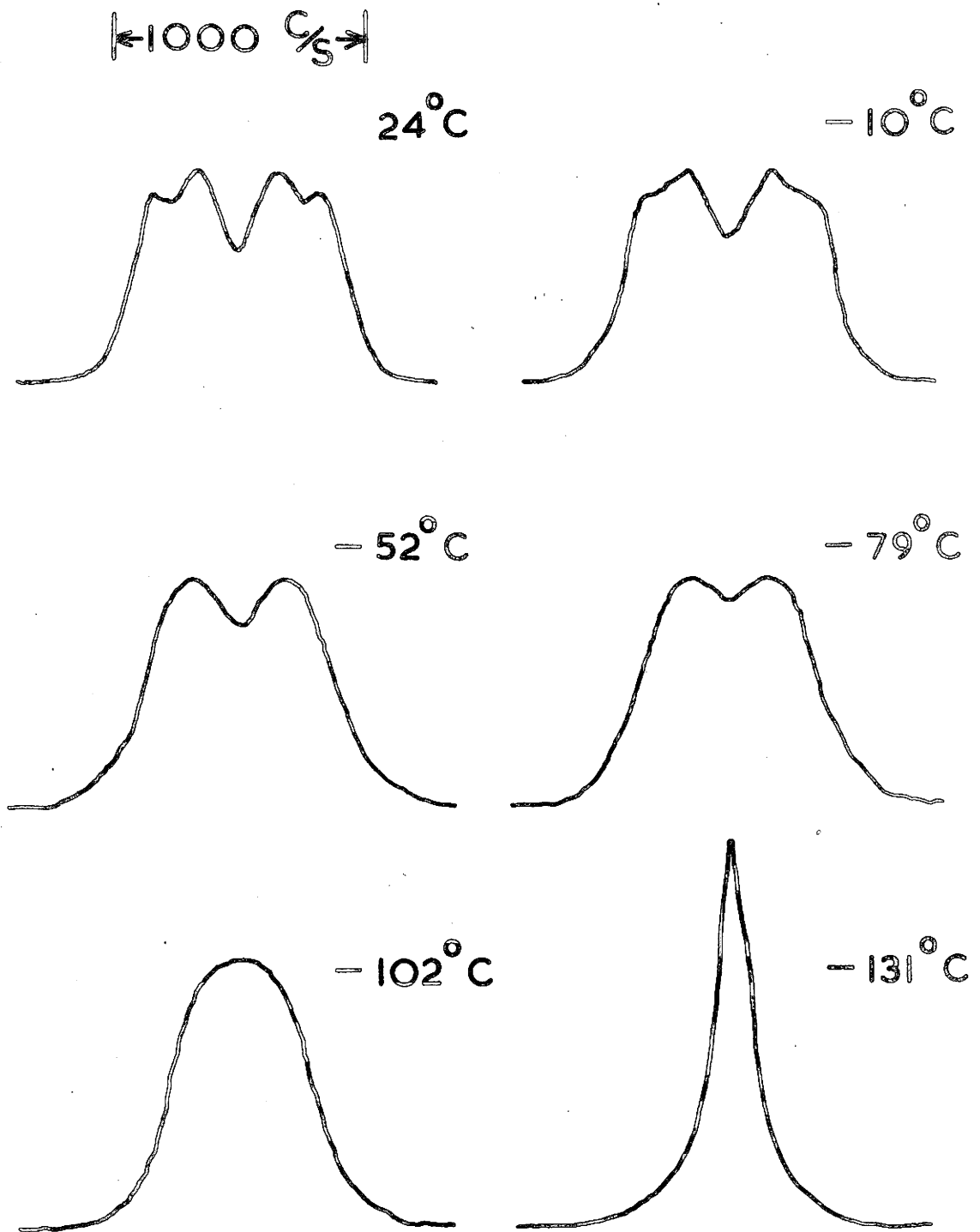


Fig. 8.  $\text{F}^{19}$  Resonance Spectra of Liquid  $\text{ClO}_3\text{F}$

$$x_{37} = \frac{\mu_{35}}{\mu_{37}} x_{35}$$

Assuming that the electrical asymmetries ( $Q$ ) and the correlation times ( $\tau$ ) are the same for both molecules, and applying Equation (37),

$$\tau_{37} = \left( \frac{Q_{35}}{Q_{37}} \right)^2 \tau_{35}$$

and

$$\eta_{37} = \frac{\mu_{37}}{\mu_{35}} \left( \frac{Q_{35}}{Q_{37}} \right)^2 \eta_{35}$$

Substituting the known values<sup>(2)</sup> for  $\mu$  and  $Q$ , the final expression for the line shape becomes

$$I(\text{ClO}_3\text{F}) \approx f(\eta_{35}, x_{35}) + .527 f(1.371\eta_{35}, 1.201x_{35}) \quad (48)$$

where  $f(\eta, x)$  is given by Equation (46).

Equation (48) was evaluated at small intervals of  $x$  over the range  $x = 0 \rightarrow x = 3.0$  for different values of  $\eta_{35}^2$ . The calculated line shape for  $\eta_{35}^2 = 5.15$ , showing the individual contributions of the two isotopes, is reproduced in Fig. 9. This was the closest fit that could be obtained for  $T = 24^\circ \text{C}$ . The splitting between the inner peaks in the experimental spectrum at this temperature was observed to be  $289 \pm 5$  c/s. From a comparison of the observed and calculated spectra a value of  $J_{\text{Cl}^{35}\text{F}} = 278 \pm 5$  c/s was obtained. Using this value and by comparing experimental and calculated spectra, values for  $\tau_{35}$  at each temperature were found.

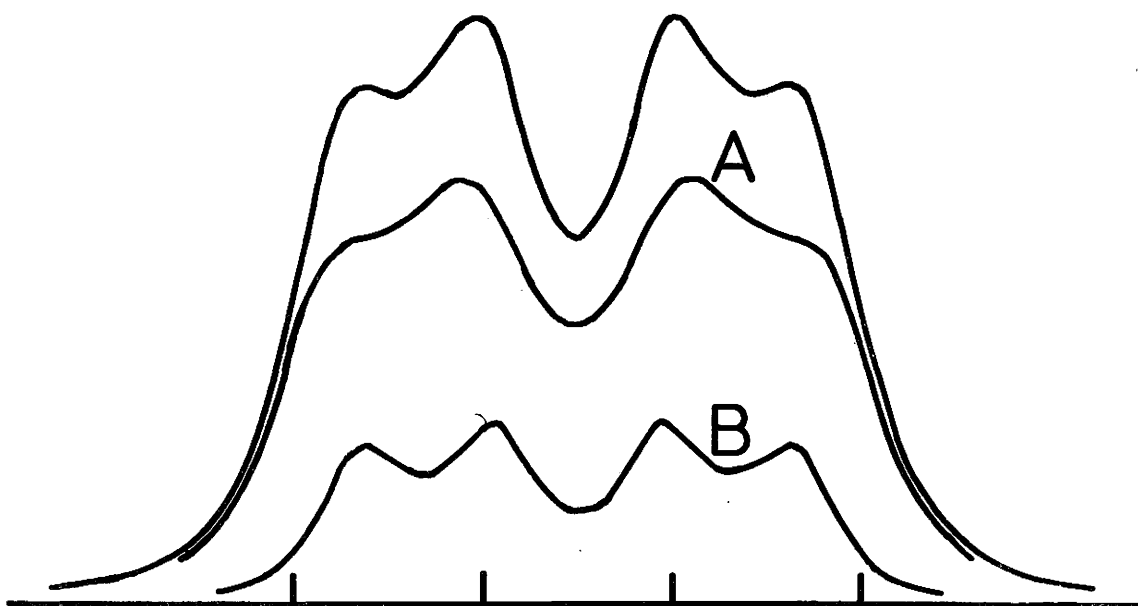


Fig. 9. Calculated Line Shape For  $\eta_{35}^2 = 5.15$ , Showing the Individual Contributions of the Two Isotopes,  $\text{Cl}^{35}$  (A) and  $\text{Cl}^{37}$  (B), and Their Sum. The Vertical Lines Indicate the Positions of the  $\text{Cl}^{35}$  Quartet in the Absence of Quadrupole Relaxation.

A plot of  $\log \tau_{35}$  versus  $1/T$  is shown in Fig. 10. It is a reasonably straight line with a slope corresponding to an activation energy of approximately 1.0 kcal/mole. This energy is less than the corresponding activation energy for any of the 12 nitrogen compounds studied by Moniz and Gutowsky<sup>(53)</sup>. Such a result is expected for perchloryl fluoride, due to the high symmetry and relatively small size of the molecule.

#### E. The Spectrum of Bromine Pentafluoride

The  $F^{19}$  NMR spectrum of bromine pentafluoride has been reported (15, 50) as a quintet and doublet in the intensity ratio 1:4. No apparent effect from the nuclear spin of the bromine was observed in the spectrum. My observations of the line widths of the components of the  $BrF_5$  multiplets, shown in Table 10, indicate that the bromine does indeed have an effect on the spectrum.

The structure of  $BrF_5$  can be thought of as an octahedron around the bromine with five of the corners occupied by fluorines and the sixth corner occupied by a lone pair of electrons. The four equatorial fluorines, which are adjacent to the lone pair, are repelled by the lone pair<sup>(17)</sup>. These four fluorine-bromine bonds are lengthened and the five fluorine atoms are all found on one side of the bromine. Spectroscopic<sup>(60, 61)</sup> and crystallographic<sup>(62)</sup> evidence has shown that the apex fluorine is closer to the bromine and more strongly bound than the four equatorial fluorines.

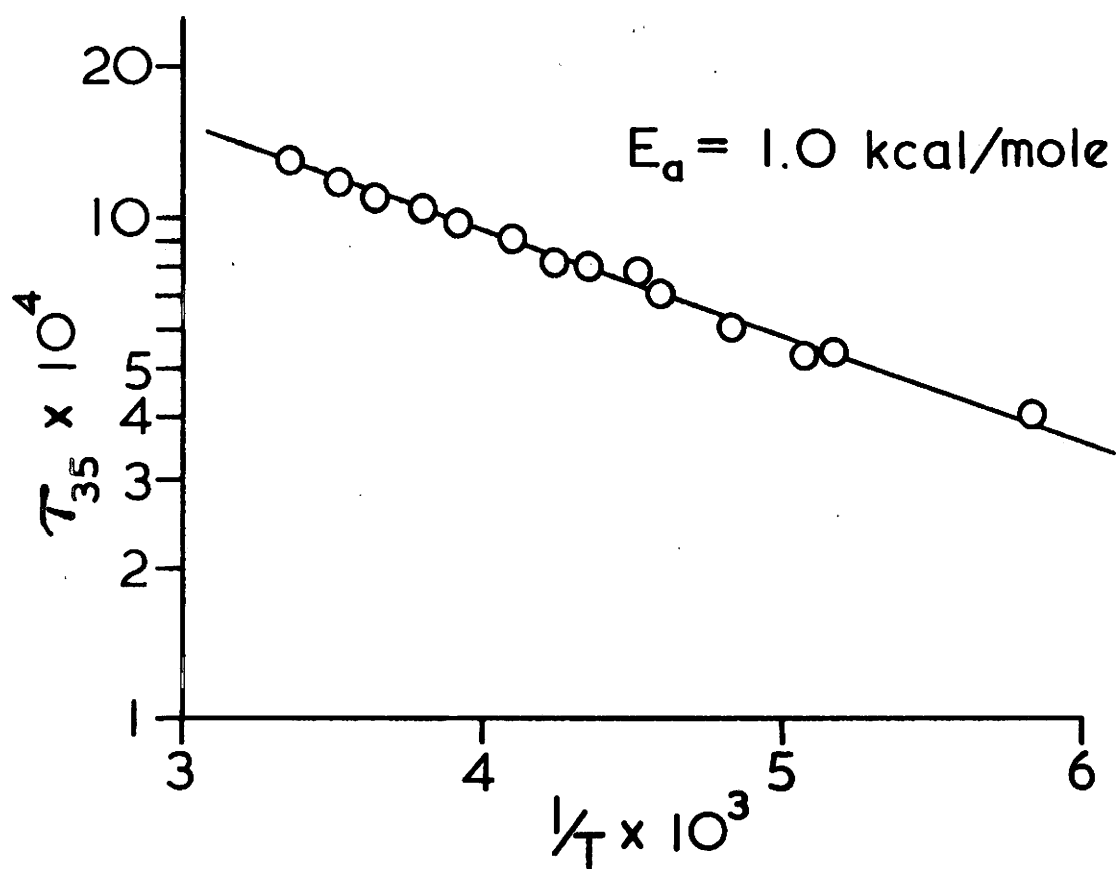


Fig. 10 The Temperature Dependence of the  $\text{Cl}^{35} \tau$  Estimated From the  $\text{F}^{19}$  Resonance of Liquid  $\text{ClO}_3\text{F}$ .

---

 Table 10

Line Widths of the Component Lines of the Quintet and Doublet  
in the  $F^{19}$  NMR Spectrum of  $BrF_5$

Temperature °C	Quintet Line Width (c/s)	Doublet Line Width (c/s)
24	30	10
0	20	2
- 29	14	2
- 43	11	2
- 60	8	2

---

Most effects which contribute to line width, except for chemical exchange and coupling with a relaxed quadrupole, would give broader lines at lower temperatures rather than sharper lines. Chemical exchange is an unlikely source of broadening, because it has been shown<sup>(63)</sup> by NMR that heating to 180° C causes no significant exchange of fluorine atoms in  $BrF_5$ . The narrowing of the resonance lines of the fluorines is consistent with a quadrupole contribution to the line width. Abragam<sup>(5)</sup>, p. 311, has derived an expression for the contribution of a relaxing quadrupole to  $T_2$  for a nucleus coupled to the quadrupole. For this case it is

$$\frac{1}{T_{2F}} = \frac{5}{4} (J_{BrF})^2 \left[ \frac{T_{1Br}}{1 + (\omega_F - \omega_{Br})^2 T_{1Br}^2} + T_{1Br} \right] \quad (49)$$



where  $\omega_F$  and  $\omega_{Br}$  are the fluorine and bromine angular resonance frequencies, respectively. For  $BrF_5$ , all factors on the right side of the equation, except  $J_{BrF}$ , are approximately the same for both equatorial and apex fluorines. If the Br - F (apex) coupling constant is larger than the Br - F (equatorial) coupling constant, as might be expected from the physical data concerning the bonds, a greater broadening contribution to the apex fluorine would be expected, and this is observed. The apparent "natural" line width of the lines of the doublet is about 2 c/s. This large line width, which is constant over an appreciable temperature range, is probably due to an isotope effect (naturally occurring bromine has two isotopes of equal abundance, both with  $I = 3/2$  and with very similar quadrupole moments) and to second order splitting of the lines.

#### F. Experimental

The boron trifluoride and bromine pentafluoride used were obtained from Matheson of Canada, Ltd., Whitby, Ontario. The gases were distilled into 5 mm O.D. silica NMR tubes on a vacuum line and sealed off under vacuum. The  $BF_3$  samples were gaseous at room temperature, but condensed to give an adequate volume of liquid for NMR studies at temperatures from  $-17^\circ C$  to  $-25^\circ C$  depending on the pressure of the sample.

Perchloryl fluoride was obtained from Pennsalt Chemicals Corporation, Philadelphia 2, Pa. The gas was distilled into 5 mm O.D. pyrex NMR tubes and the tubes sealed under vacuum. The compound

was a liquid under its own vapour pressure (about 12 atm. at 24° C). Spectra of  $\text{ClO}_2\text{F}$  were obtained with non-spinning samples, because at the high power level required to observe the  $\text{F}^{19}$  resonance (50 db below 0.5 watts) the noise induced by spinning actually decreased resolution.

The mathematical expressions for the line shapes were evaluated using a Bendix G-15 computer.

## CHAPTER VI

### IODINE OXIDE PENTAFLUORIDE

#### A. Discovery

A study of the infrared and Raman spectra<sup>(64)</sup> of  $\text{IF}_5$  has led to the conclusion that the  $\text{IF}_5$  molecule has  $C_{4v}$  symmetry and therefore, like bromine pentafluoride, has the shape of a tetragonal pyramid. The NMR spectrum of  $\text{IF}_5$ <sup>(50, 63)</sup>, like that of  $\text{BrF}_5$ , is an  $\text{AX}_4$  type, consisting of a quintet and a doublet with relative areas of 1 to 4.

During the distillation of an  $\text{IF}_5$  sample from a commercial cylinder into silica NMR tubes, considerable attack rapidly occurred on the pyrex parts of the vacuum line.  $\text{IF}_5$  attacks pyrex only on prolonged contact. The NMR tubes were sealed off and the NMR spectra obtained. At normal power levels (60 db attenuation of 0.5 watt) only the characteristic spectrum of  $\text{IF}_5$  was observed. At higher power levels (40 db attenuation of 0.5 watt) a number of broad lines appeared to the low field side of the  $\text{IF}_5$  spectrum. The lines were sharpened by lowering the sample temperature. The spectrum at  $-15^\circ\text{C}$  is shown in Fig. 11. The new spectrum is clearly of the  $\text{AB}_4$  type. The shape and intensities agree well with those calculated by Wiberg and Nist<sup>(65)</sup> for an  $\text{AB}_4$  spectrum. The approximate chemical shifts of the doublet and quintet measured from the center of the quintet in  $\text{IF}_5$  are  $-13$  ppm and  $-50$  ppm respectively. The fluorine-

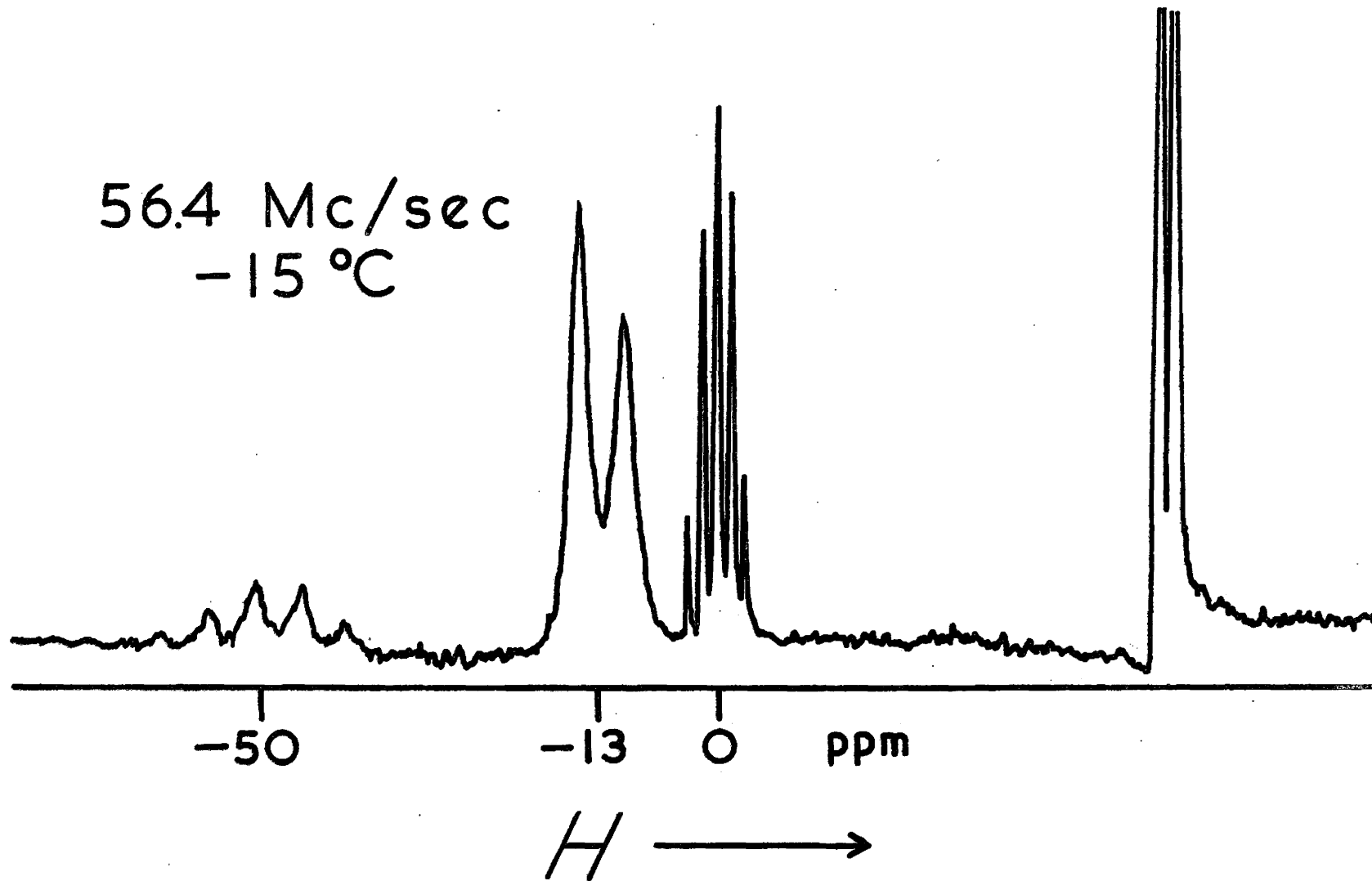


Fig. 11  $F^{19}$  NMR Spectrum of  $IOF_5$  (Low-field Peaks) Containing  $IF_5$  (High-field Peaks).  
Chemical Shifts are Measured From the Center of the  $IF_5$  Quintet.

fluorine coupling constant in the new spectrum is  $\sim 280$  c/s. The new resonance is in the fluorine on iodine region of the  $F^{19}$  NMR spectrum (between  $IF_5$  and  $IF_7^{(7)}$ ). The fact that the new substance was obtained from an  $IF_5$  sample further indicated that iodine is present in the molecule. Consideration of the new spectrum suggested that it was probably due to  $IOF_5$ , which would have an octahedral structure around the iodine with fluorines at five of the corners of the octahedron and an oxygen at the sixth corner. The large line widths (over 100 c/s at  $-15^\circ C$ ) of the components of the new spectrum, because of their temperature dependence, appear to be mainly due to quadrupole broadening rather than fluorine exchange. The  $I^{127}$  nucleus, because of its very large quadrupole moment, is usually very relaxed and does not contribute appreciably to the line widths of adjoining nuclei. For instance, the  $IF_5$  spectrum in Fig. 11 has relatively sharp lines compared to the  $IOF_5$  spectrum. In the case of  $IOF_5$  the relaxation of the iodine must be slow enough to contribute appreciably to  $T_2$  for the fluorines (Equation (49)). The iodine must be situated in a reasonably symmetric environment, which is consistent with the proposed octahedral structure.

## B. Preparation

I made a number of attempts to prepare  $IOF_5$ . The original attempt was by the ozonation of iodine pentafluoride. Ozone, in an oxygen carrier stream, was bubbled through liquid  $IF_5$  at  $25^\circ C$ . No apparent reaction took place. The sample was then distilled and

the most volatile fraction taken as an NMR sample. The NMR spectrum showed only  $\text{IF}_5$ .

The next method of preparation attempted was the fluorination of  $\text{IOF}_3$  at high temperature. The iodine oxide trifluoride was prepared by dissolving  $\text{I}_2\text{O}_5$  in  $\text{IF}_5$  (66). The reaction did not go to completion and the product obtained undoubtedly also contained  $\text{IO}_2\text{F}$  and unreacted  $\text{I}_2\text{O}_5$ . This material was placed in a nickel boat in a monel reaction tube. A mixture of fluorine and nitrogen was passed through the reaction tube and then through a line of traps made from silica. The reaction tube was surrounded by a tube furnace. The tube temperature was raised to  $300^\circ\text{C}$  and product began to collect in the silica traps, which were cooled with an alcohol-dry ice mixture. After the reaction was complete the system was flushed with dry nitrogen, the silica trap line sealed off and evacuated, and the product fractionated through the traps, using temperatures of  $-20^\circ\text{C}$ ,  $-78^\circ\text{C}$  and  $-196^\circ\text{C}$  for different sets of traps. The three different fractions were then distilled into silica NMR tubes. The NMR spectrum of the higher temperature fractions contained only the lines of the  $\text{IF}_5$  spectrum. The  $-196^\circ\text{C}$  sample contained some  $\text{IF}_5$  and also gave an extremely broad  $\text{F}^{19}$  NMR spectrum which was identified as being due to  $\text{IF}_7$  (7). No sign of the spectrum attributed to  $\text{IOF}_5$  could be found.

The silica NMR tube containing the mixture of  $\text{IF}_5$  and  $\text{IF}_7$  was heated to  $100^\circ\text{C}$  for 20 minutes. The NMR spectrum was again observed and it was found to contain the spectrum corresponding to

$\text{IOF}_5$ . The  $\text{IF}_7$  peak had decreased in intensity. A high field line, which could be attributed to  $\text{SiF}_4^{(7)}$  had also appeared. Further heating converted all of the  $\text{IF}_7$  to  $\text{IOF}_5$ , with the  $\text{SiF}_4$  line continuing to grow in intensity. A very small high field line, presumably due to a trace of  $\text{HF}$ , was also present in the spectrum.

A purer sample of  $\text{IF}_7$  was prepared by reacting  $\text{IF}_5$  with elemental fluorine. The monel tube used above was filled with silver plated copper wire as a catalyst. The fluorine was passed through a copper trap which contained  $\text{IF}_5$  and then through the monel tube. It was then led through a silica trap line and into an exhaust hood. The silica traps were cooled with liquid oxygen, rather than with liquid nitrogen, since the latter condenses elemental fluorine at atmospheric pressure while the former does not. The hazards associated with the presence of liquid fluorine in a flow system were thereby avoided. The reaction tube was heated to  $300^\circ\text{C}$  and the copper trap containing  $\text{IF}_5$  was warmed to evaporate  $\text{IF}_5$  into the  $\text{F}_2$  stream. After enough product had been collected the system was flushed with nitrogen and the silica trap line sealed off. The product was distilled through traps at  $-78^\circ$  and  $-180^\circ$ . The NMR spectrum of both fractions was obtained. The sample of lower volatility (from the  $-78^\circ\text{C}$  trap) was mostly  $\text{IF}_7$  with a small amount of  $\text{IF}_5$ . The trap at  $-180^\circ\text{C}$  showed only  $\text{IF}_7$  in the NMR spectrum.

Heating these purer samples of  $\text{IF}_7$  in their silica NMR tubes again caused the appearance of the  $\text{IOF}_5$  spectrum and the high field

line. In the sample from the  $-180^{\circ}\text{C}$  trap there was no sign of an HF line. On close observation it was noted that the high field peak had satellite peaks associated with it. The coupling constant of the satellites was measured as approximately  $170 - 180$  c/s, which corresponds very well with the known coupling constant for  $\text{Si}^{29} - \text{F}$  in  $\text{SiF}_4$  (see Table 9). The chemical shift of the high field line, measured from  $\text{IF}_5$ , differed by only 5 ppm from that expected for  $\text{SiF}_4$ . The deviations from perfect agreement could easily be due to solvent effects on the coupling constant and chemical shift.

### C. Discussion

The above results provide strong evidence that there is a reaction between  $\text{IF}_7$  and  $\text{SiO}_2$  that can be described by the following equation:



An analogous reaction is known to occur between  $\text{XeF}_6$  and  $\text{SiO}_2$  to give  $\text{XeOF}_4$  (67).

Iodine oxide pentafluoride is a colourless liquid. Preliminary studies on impure samples indicate a melting point in the range  $-10$  to  $-20^{\circ}\text{C}$ . It would be expected that the molecule is not quite a regular octahedron. The angles between the apex and equatorial fluorines should be slightly less than  $90^{\circ}$  and the angles between the oxygen atom and the equatorial fluorines slightly larger than  $90^{\circ}$  as a consequence of the greater repulsion exerted by the electrons of the IO double bond than by the electrons of the IF single bonds (17, 19).



It is noteworthy that the fluorine-fluorine spin-spin coupling constant  $J_{FF}$  of  $\sim 280$  c/s in  $\text{IOF}_5$  is considerably larger than in  $\text{IF}_5$  ( $J_{FF} = 81$  c/s<sup>(63)</sup>). A similar increase in  $J_{FF}$  is observed on passing from a S(IV) to a S(VI) compound:  $J_{FF}(\text{SF}_4) = 76.3$  c/s,  $J_{FF}(\text{SF}_4(\text{SO}_2\text{F})_2) = 156$  c/s<sup>(23)</sup>. There may be a general increase in coupling constants with increasing oxidation state of the central atom.

Only two other analogous seven-valent six-coordinate species have been reported previously; rhenium oxide pentafluoride<sup>(68)</sup> and osmium oxide pentafluoride<sup>(69)</sup>.

## CHAPTER VII

### THE TETRAFLUOROBORATE ION

#### A. Introduction

Spin-spin coupling between  $B^{11}$  and  $F^{19}$  is often observed<sup>(52, 70, 71)</sup> because of the relatively small value of the electric quadrupole moment of  $B^{11}$ . The individual multiplet components, of course, are considerably broadened by the quadrupole relaxation of the  $B^{11}$ . Spin-spin coupling of  $B^{10}$  to  $F^{19}$  has not been resolved. To observe a boron isotope effect and measure it accurately a sharp spectrum showing F -  $B^{11}$  and F -  $B^{10}$  coupling or a spectrum of F on completely relaxed boron would be required. One of the few species which might yield a sharp spectrum is the tetrafluoroborate ion,  $BF_4^-$ . The tetrahedral symmetry around the  $B^{11}$  and  $B^{10}$  should minimize quadrupole relaxation of the boron and give sharp lines in the  $F^{19}$  NMR spectrum. The  $F^{19}$  spectrum of  $BF_4^-$  has previously been reported<sup>(70)</sup> at 40 Mc/s. The value for  $J_{B^{11}F}$  was given as 4.8 c/s. Resolution was not sufficient for F -  $B^{11}$  coupling to be observed or for an isotope effect to be observed. Since the original report, an indirect reference<sup>(72)</sup> has been made to  $J_{B^{11}F}$  being approximately 2 c/s in  $BF_4^-$ . No spectra were published and no comment on the apparent discrepancy was made. Very recently, it has been recognized<sup>(73)</sup> that  $J_{B^{11}F}$  for  $BF_4^-$  is dependent upon the concentration,

the type of cation accompanying the  $\text{BF}_4^-$ , other ions in the solution, and the nature of the solvent. With solutions of  $\text{NaBF}_4$  in water the value of  $J_{\text{B}^{11}\text{F}}$  increases with concentration to a maximum of 4.8 c/s in a saturated solution. The value of  $J_{\text{B}^{11}\text{F}}$  extrapolated to infinite dilution is given as 1.1 c/s<sup>(73)</sup>.

## B. Results

A typical  $\text{F}^{19}$  NMR spectrum of  $\text{BF}_4^-$  from a solution of  $\text{NaBF}_4$  is shown in Fig. 12 (a). The coupling constant  $J_{\text{B}^{11}\text{F}}$  in this case is 2.54 c/s. Three of the peaks from F on  $\text{B}^{10}$  are resolved in the spectrum. For  $\text{B}^{10}$ ,  $I = 3$ , and therefore seven lines due to F on  $\text{B}^{10}$  should be present. The coupling constant  $J_{\text{B}^{10}\text{F}}$  in a particular chemical species can be determined by the relationship

$$\frac{J_{\text{B}^{10}\text{F}}}{J_{\text{B}^{11}\text{F}}} = \frac{\gamma_{\text{B}^{10}}}{\gamma_{\text{B}^{11}}}$$

where  $J_{\text{B}^{11}\text{F}}$  is the coupling constant between fluorine and  $\text{B}^{11}$  in the same species. The splittings between the F on  $\text{B}^{10}$  peaks were, of course, multiples of the calculated coupling constant  $J_{\text{B}^{10}\text{F}}$ . By matching the calculated F on  $\text{B}^{10}$  spectrum with the observed  $\text{F}^{19}$  spectrum of  $\text{BF}_4^-$ , it was found that only one position of the F on  $\text{B}^{10}$  spectrum would fit the observed intensities. The center of the F on  $\text{B}^{11}$  spectrum is  $0.052 \pm .003$  ppm to high field of the center of the F on  $\text{B}^{10}$  spectrum. In more dilute solutions

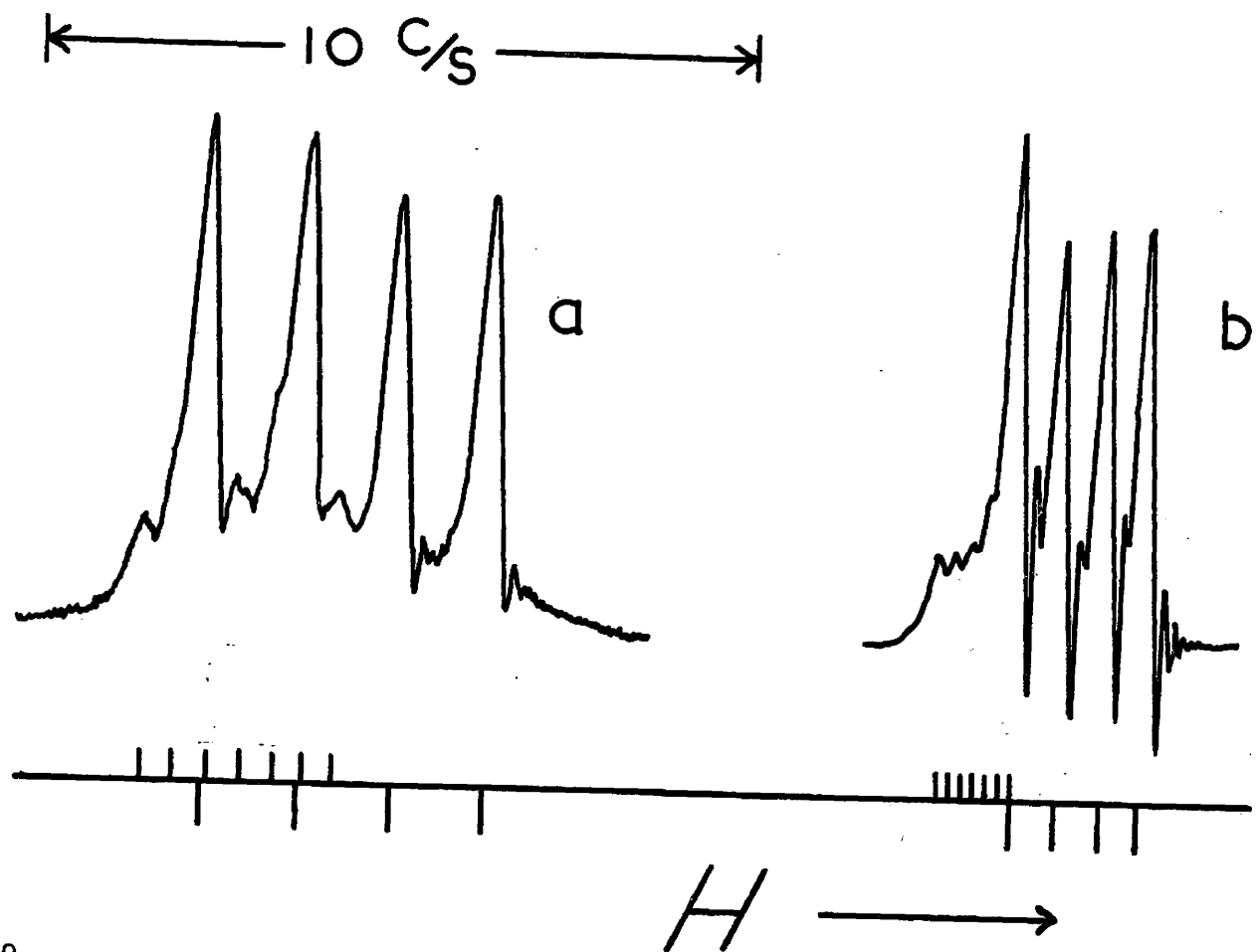


Fig. 12  $F^{19}$  NMR Spectra of  $BF_4^-$ : a)  $NaBF_4$  Solution (aqueous),  $J_{B^{11}F} = 2.5 \text{ c/s}$ , b)  $HBF_4$  Solution (aqueous),  $J_{B^{11}F} = 1.4 \text{ c/s}$ . The Vertical Lines Indicate the Positions of the Lines of the Multiplets.

of  $\text{BF}_4^-$  the coupling constant  $J_{\text{B}^{11}\text{F}}$  was smaller but the individual lines were relatively broader and no measure of an isotope effect  $\Delta\delta$  could be made.

When  $\text{BF}_3$  is bubbled into  $\text{H}_2\text{O}$  a white precipitate of  $\text{B}_2\text{O}_3$  soon appears. On further addition of  $\text{BF}_3$  the precipitate redissolves to form a clear solution. If a sample of the supernatant liquid is removed when the precipitate first appears (this solution is essentially an aqueous solution of  $\text{HBF}_4$  and  $\text{HBF}_3\text{OH}$ ) and its  $\text{F}^{19}$  NMR spectrum obtained, two peaks are found 1.8 ppm apart in the F on B portion of the spectrum. The peak at lower field has no structure and is probably due to  $\text{BF}_3\text{OH}^-$ . The other peak is a 1:1:1:1 quartet with underlying structure and extremely sharp lines, as shown in Fig. 12 (b). In this case  $J_{\text{B}^{11}\text{F}} = 1.4$  c/s. Even though  $J_{\text{B}^{10}\text{F}}$  is extremely small in this case ( $< 0.5$  c/s) four of the F on  $\text{B}^{10}$  lines are resolved and an isotope effect can be measured. The isotope effect in this instance is  $\Delta\delta = 0.050 \pm .003$  ppm.

Because  $J_{\text{BF}}$  was not constant for the  $\text{BF}_4^-$  ion, it was necessary to prove that the species under observation was actually  $\text{BF}_4^-$ . This was done by observing the  $\text{B}^{11}$  spectrum of the  $\text{BF}_4^-$  samples. In all cases where splitting was observed in the  $\text{F}^{19}$  spectrum, the  $\text{B}^{11}$  spectrum gave a 1:4:6:4:1 quintet with the same splitting as observed in the  $\text{F}^{19}$  spectrum.

Solutions with a constant concentration of  $\text{NaBF}_4$  (233 g/l) in a mixture of water and diglyme ( $\text{CH}_3\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OCH}_3$ )

varying from 100% water to 50% water - 50% diglyme were made up as NMR samples. Diglyme was chosen because it is a very good solvent for many ionic compounds and because it is completely miscible with water. The sample with 50% diglyme showed some precipitation of  $\text{NaBF}_4$  and was therefore of lower concentration. Samples with more than 50% diglyme were prepared by saturating the solution with  $\text{NaBF}_4$ . Both  $\text{F}^{19}$  and  $\text{B}^{11}$  spectra of the above solutions were obtained.

As the percentage of diglyme was increased the coupling constant decreased and the individual lines broadened, decreasing resolution. The approximate values of the coupling constant

$J_{\text{B}^{11}\text{F}}$  for this series of samples are:

100% water	3.5 c/s
10, 20, 30% diglyme	2.4 c/s
50% diglyme	1.9 c/s
70% diglyme	1.3 c/s

For samples of 90% and 100% diglyme no spin-spin coupling was observed. The  $\text{F}^{19}$  spectrum of the samples with 50% and 70% diglyme gave partially collapsed quartets, indicating that the boron was being relaxed (Chapter V). At these intermediate rates of relaxation, the broadness of the lines was too great to measure an isotope effect. In 100% diglyme solution the  $\text{F}^{19}$  spectrum of  $\text{NaBF}_4$  consisted of two single lines  $0.053 \pm .003$  ppm apart. The line at higher field was 4 times the intensity of the line at

lower field. Obviously, under these conditions the boron nucleus is completely relaxed and effectively decoupled from the fluorines. The line of higher intensity is due to F on  $B^{11}$  and the line of lower intensity is due to F on  $B^{10}$ . Dilution of the 100% diglyme saturated solution of  $NaBF_4$  with water gives a sample which has the partially collapsed quartet  $F^{19}$  spectrum described above for  $BF_4^-$  in mixtures of diglyme and water.

A very concentrated solution of  $KBF_3OH$  was prepared by the method of Ryss and Slutskaya<sup>(74)</sup>.  $KHF_2$  (0.09 moles) and  $H_3BO_3$  (0.05 moles) were dissolved in 12 mls of water. The solution was cooled with ice and filtered. The  $F^{19}$  NMR spectrum of the  $BF_3OH^-$  consisted of a 1:1:1:1 quartet that was partially collapsed due to quadrupole relaxation of the boron. The splittings between the components were not equal. Allowing for partial collapse (Chapter V) the coupling constant  $J_{B^{11}F}$  was found to be approximately 15.2 c/s. The  $B^{11}$  spectrum consisted of a 1:3:3:1 quartet on a broad underlying line which was due to some boron containing impurity (perhaps  $BF_2(OH)_2^-$ ). The coupling constant of the quartet was found to be  $J_{B^{11}F} = 15.1$  c/s. Boron-fluorine coupling was not observed for the  $BF_3OH^-$  formed in aqueous solutions of  $BF_3$  presumably because of some rapid chemical exchange process in the very acidic solution.

### C. Discussion

Certain conclusions can be arrived at from a consideration of the experimental results described above. First, there is an

isotope effect in the  $F^{19}$  NMR spectrum of  $BF_4^-$  of  $\Delta\delta = 0.050 - 0.053$  ppm. The magnitude of the isotopic shift is independent of the coupling constant between the fluorine and boron, within the accuracy of the measurements.

Second, there is an interaction between the  $BF_4^-$  ion and its solvent and/or accompanying cations. The complete collapse of the fluorine-boron coupling in  $BF_4^-$  in diglyme indicates that some interaction is destroying the tetrahedral symmetry of the  $BF_4^-$  ion. Diglyme is a basic solvent. A possible method of interaction between diglyme and  $BF_4^-$  is by electron pair donation of an oxygen of the diglyme to the boron of the  $BF_4^-$ . The resulting species with 5 - coordinate boron need have only a transient existence to result in the relaxation of the boron.

An alternative explanation is that in diglyme the  $NaBF_4$  is in the form of ion pairs. A sodium ion next to the  $BF_4^-$  ion might distort the tetrahedral ion sufficiently to cause relaxation of the boron. Sufficient information is not yet available to distinguish between the two possibilities.

Third, the existence of the  $BF_3OH^-$  ion in aqueous solution has been proven by the observation of the  $F^{19}$  and  $B^{11}$  NMR spectra of the ion. The existence of the ion in the solid state has been established. The x-ray powder photographs and infrared spectra of solid  $KBF_3OH$  and  $NaBF_3OH$  are consistent with the expected structure of the  $BF_3OH^-$  ion (75, 76). Indirect evidence for the existence of the species in aqueous solution has been reported (77).



A single NMR line with no fine structure has been attributed to  $\text{BF}_3\text{OH}^-$  or its conjugate acid<sup>(78, 79)</sup>. The results reported here indicate that under certain conditions the  $\text{BF}_3\text{OH}^-$  species has a relatively long lifetime and does not undergo any rapid chemical exchange process.

## CHAPTER VIII

### CONCLUSIONS

The use of NMR for structure determination has progressed as the technique and theory of NMR has evolved. Early experimenters were mainly concerned with the use of chemical shifts to identify and count the numbers of chemically non-equivalent nuclei of a particular element, usually H or F, as a structure confirmation. Thus, ethanol gives three peaks in the intensity ratio 1:2:3 which are naturally assigned to the hydroxyl, methylene and methyl protons in this molecule. The observation of the effects of spin-spin coupling gave much more information about the molecules being studied by showing a relationship between the different sets of equivalent nuclei. The complex high resolution spectrum of ethanol confirmed the earlier assignment. Many applications have been made in unravelling the stereochemistry of more complex molecules. Now that a considerable amount of information about chemical shifts and coupling constants for known molecules has been accumulated, structure determination by NMR is almost a routine matter.

NMR spectroscopists are turning their attention to more fundamental problems such as the interpretation of chemical shifts and spin-spin coupling constants in terms of the electronic structure of molecules and to the understanding of some of the finer details of NMR spectra such as isotope shifts, line broadening due to quadrupole relaxation and the variation of coupling constants with environment.

The interpretation of chemical shifts and spin-spin coupling in terms of electronic structures of molecules and, conversely, the

theoretical prediction of the two parameters are largely unresolved problems. There are indications that the chemical shifts will contribute information on molecular charge distribution since screening of a nucleus is accomplished by the electrons in the molecule. Couplings may be interpreted in terms of bond orders and orbital hybridizations since the spin-spin coupling is accomplished mainly by the bonding electrons. It is also likely that the study of solvent effects on NMR spectra will reveal the nature of intermolecular interactions. Because the wave functions for the hydrogen molecule are known, it has been possible to calculate the coupling constant and isotope effect for this molecule, both of which agree very well with the observed values. In the more complex molecule methane, the H-H coupling constant has been obtained to reasonable agreement with experimental results by treating the molecule as an eight electron problem in terms of the valence-bond method<sup>(80)</sup>. For H-H couplings a calculation is simple because the coupling appears to be related only to the bond order between the H's and to the Fermi contact interaction which is constant for protons bonded by s orbitals. Coupling constants involving other nuclei are more difficult to analyze because they involve contributions from an electron-dipole term and an electron-orbital term<sup>(2)</sup> which are of comparable magnitude to the contact term and may even be of opposite sign.

The work described in this thesis has not given a complete answer to any of these problems, but it has brought the eventual solution of these problems slightly nearer. Further, this work puts a few more empirical facts in the hands of workers using NMR to unravel

molecular structures. The contributions made in this thesis to the understanding of some aspects of the NMR spectra of inorganic fluorides may be summarized under three headings: isotopic shifts, quadrupole relaxation and coupling constants.

#### A. Isotopic Shifts

When we study isotopic shifts, we are studying one of the simplest forms of chemical shift. Only the mass of one nucleus is changed to cause a change in the chemical shift of the attached nucleus. The number of known isotope effects in NMR is small, but two more types, namely fluorine on sulphur and fluorine on boron, have now been recognized. The fluorine on sulphur shift was measured for ten compounds. The fluorine on boron shift was measured for the  $\text{BF}_4^-$  ion in various solvents. A boron shift was observed and estimated for the  $\text{F}^{19}$  spectrum of  $\text{BF}_3$ . With the present trend toward higher magnetic fields in NMR, more isotope effects will undoubtedly be recognized and the known isotope effects will be measured more accurately. An understanding of isotopic shifts will mean that we understand one of the many factors which contribute to overall chemical shifts. The F on  $\text{C}^{12}(\text{C}^{13})$  effect will probably yield the most information because so many examples are known, because the effect is so large, and because we have a great deal of information already about the molecules which are concerned. However, the sulphur isotope shift may be very useful because it varies very much from compound to compound. It is evident that the shape of the potential well in which a fluorine on sulphur vibrates changes very much from compound to compound. It was not possible to correlate isotope shifts in fluorine-sulphur compounds with infra-red

vibrational frequencies, however. Perhaps bond lengths would give some correlation but unfortunately very few bond lengths are known for this type of compound. The study of satellite peaks and isotope effects associated with them yields a bonus. Since the pattern of isotopic ratios and spins is essentially unique for each type of atom, a spectrum which would crudely be expected to give a single line may actually have small features which identify the atom directly connected to the resonating nucleus. Thus, the size of the small satellite in the  $F^{19}$  spectrum of  $HSO_3F$  shows that the fluorine is connected to a sulphur, and the presence of the  $S^{33}$  satellites in the  $F^{19}$  spectrum of  $SF_6$  is the most convincing evidence to show that the structure of  $SF_6$  is a perfect octahedron, as expected. Many further applications of this kind are likely to be made in the future. For example the fact that only one F in  $FSO_3F$ , fluorine fluorosulphate, is attached to S could be unambiguously confirmed by observation of the  $S^{34}$  satellite.

#### B. Quadrupole Relaxation Effects

It has long been accepted that nuclei of spin greater than  $1/2$ , except when they are located in a very symmetric environment, have no effect on the NMR spectrum of the molecule in which they are situated. No spin-spin coupling is observed because of supposedly complete quadrupole relaxation of the nucleus of spin  $> 1/2$ . Exceptions, such as boron-proton coupling in boron hydrides were thought to be the result of the small quadrupole moment of  $B^{11}$ . Recent work <sup>(81)</sup> indicates that nuclei of spin greater than  $1/2$  in very asymmetric environments still make contributions to the line widths of resonating nuclei near them. By studying the temperature dependence of  $1/T_1$  and  $1/T_2$  for both

the proton and the fluorine in  $\text{CHFCl}_2$ , Brown, Gutowsky and Shimomura<sup>(81)</sup> were able to separate the contributions to  $1/T_1$  and  $1/T_2$ . From the contribution of the Cl's they were able to obtain Cl-C-F and Cl-C-H coupling constants. The results given in Chapter V yield a Cl-F coupling constant from the  $F^{19}$  spectrum of  $\text{ClO}_3\text{F}$  and they show that the Br in  $\text{BrF}_5$  has an effect on the  $F^{19}$  spectrum of this molecule. Extension of this work on the same model used for  $\text{CHFCl}_2$  could give coupling constants for the Br-F bonds. Thus, the presence of a nucleus with a quadrupole in a molecule being studied is a further source of information about the electronic constitution of the molecule.

Other parameters which can be measured for a nucleus with a quadrupole, such as the quadrupole coupling constant and  $T_1$  give information about the field gradient at the nucleus and about the reorientations of the molecule.

The identification of  $\text{IOF}_5$  as the product of the reaction of  $\text{IF}_7$  and  $\text{SiO}_2$  shows the value of NMR information when used in only a qualitative manner. The  $\text{AB}_4$  spectrum shows the presence of five fluorines in some sort of symmetry comparable to  $\text{IF}_5$ . The magnitude of the coupling constant shows that not more than two bonds could separate the non-equivalent fluorines. The chemical shift is strong evidence that the fluorines are bonded to an iodine. The chemistry of the system showed that there was nothing present that might reduce the I(VII). The appearance of  $\text{SiF}_4$  (positively identified by its satellite peaks) indicates that oxygens are being exchanged for fluorines. The extreme broadness of the lines in the  $F^{19}$  spectrum (compared to those for  $\text{IF}_5$ ) shows that the iodine must be located

in an environment much more symmetric than the iodine in  $\text{IF}_5$ . Thus, the line widths of the spectrum and their relationship to the environmental symmetry of the iodine nucleus gives convincing argument for the predicted octahedral symmetry of the  $\text{IOF}_5$  molecule.

The identification of  $\text{IOF}_5$  by NMR shows the inherent power in this method.  $\text{IOF}_5$  was undoubtedly present in most previous samples of  $\text{IF}_7$  but was not identified because of similar physical properties. Bartlett<sup>(82)</sup> has shown that some of the lines in the infra-red spectrum of  $\text{IF}_7$  as previously reported<sup>(64)</sup> are actually due to  $\text{IOF}_5$ . The uncertainty about the existence of some of the compounds of iodine and fluorine, such as  $\text{IO}_3\text{F}$ <sup>(83)</sup> and  $\text{IF}_3$ <sup>(84)</sup>, may be removed by application of NMR.

### C. Coupling Constants

Because of the properties of the nuclei of the isotopes of many elements, no spin-spin coupling constants have been observed between a large number of elements and fluorine, even though these elements form stable covalent compounds with fluorine. The development of a complete theory of coupling constants will be facilitated by knowledge of the magnitude of as many types of coupling constants as possible. I have measured a chlorine-fluorine and a sulphur-fluorine coupling constant for the first time. I have also found that in  $\text{BF}_4^-$  the apparent  $B^{11}$ -fluorine coupling constant varies from zero to 4 cycles per second. There is also a change in the relaxation of the boron under certain conditions.

The relaxation of the boron in  $\text{BF}_4^-$  and the variable nature of the coupling "constant" in this species is an unsolved mystery at

this time. However, the recognition of this effect will alert other workers to the possibility of discovering other examples. The measurement of absolute values of parameters will always be important but the study of differential effects usually gives more insight into the problem because it isolates the parts from the overall effect and allows us to relate the effect to one variable at a time. Thus, in the case of  $\text{BF}_4^-$  where the isotope effect does not change when the coupling "constant" does change, we are seeing an effect which decreases the electron coupled nuclear spin-spin interaction without appreciably changing the shape of the potential well in which the fluorine vibrates. In some cases, because of the relaxation of the boron, it is obvious that the symmetry of the ion is being destroyed, but even in these cases the potential well of the fluorines is not appreciably changed.



## REFERENCES

1. E. R. Andrew: Nuclear Magnetic Resonance, Cambridge University Press, New York, 1955.
2. J. A. Pople, W. G. Schneider and H. J. Bernstein: High-resolution Nuclear Magnetic Resonance, McGraw-Hill, 1959.
3. J. D. Roberts: Nuclear Magnetic Resonance. Applications to Organic Chemistry, McGraw-Hill, New York, 1959.
4. L. M. Jackman: Applications of Nuclear Magnetic Resonance Spectroscopy to Organic Chemistry, Pergamon Press, New York, 1959.
5. A. Abragam: The Principles of Nuclear Magnetism, The Clarendon Press, Oxford, 1961.
6. R. E. Richards: Advances in Spectroscopy, vol II, 101, Interscience Publishers Inc., New York, 1961.
7. H. S. Gutowsky and C. J. Hoffman: J. Chem. Phys., 19, 1259 (1951).
8. N. F. Ramsey: Phys. Rev., 78, 699 (1950).
9. J. D. Roberts: An Introduction to Spin-Spin Splitting in High Resolution N.M.R. Spectra, W. A. Benjamin, Inc., New York, 1961.
10. C. N. Banwell and H. Primas: Mol. Phys., 6, 225 (1963).
11. T. F. Wimett: Phys. Rev., 91, 476 (1953).
12. N. Bloembergen: Nuclear Magnetic Relaxation, W. A. Benjamin, Inc., New York, 1961.
13. G. V. D. Tiers: J. Phys. Chem., 62, 1151 (1958).
14. F. A. Cotton, J. W. George and J. S. Waugh: J. Chem. Phys., 28, 944 (1958).
15. E. L. Muetterties and W. D. Phillips: J. Am. Chem. Soc., 81, 1084 (1959).
16. W. M. Tolles and W. D. Gwinn: J. Chem. Phys., 36, 1119 (1962).
17. R. J. Gillespie: Can. J. Chem., 39, 318 (1961).
18. R. J. Gillespie: J. Chem. Phys., 37, 2498 (1962).

19. R. J. Gillespie: *J. Chem. Ed.*, 40, 295 (1963).
20. J. Bacon, R. J. Gillespie, and J. W. Quail: *Can. J. Chem.*, 41, 1016 (1963).
21. J. A. Pople, W. G. Schneider and H. J. Bernstein: *Can. J. Chem.*, 35, 1060 (1957).
22. E. B. Whipple, J. H. Goldstein and W. E. Stewart: *J. Am. Chem. Soc.*, 81, 4761 (1959).
23. J. M. Shreeve and G. H. Cady: *J. Am. Chem. Soc.*, 83, 4521 (1961).
24. D. M. Grant and H. S. Gutowsky: *J. Chem. Phys.*, 34, 699 (1961).
25. W. A. Anderson: *Phys. Rev.*, 102, 151 (1956).
26. P. L. Corio: *Chem. Rev.*, 60, 396 (1960).
27. G. V. D. Tiers: *J. Inorg. Nucl. Chem.*, 16, 363 (1961).
28. G. V. D. Tiers: *J. Am. Chem. Soc.*, 79, 5585 (1957).
29. G. V. D. Tiers and P. C. Lauterbur: *J. Chem. Phys.*, 36, 1110 (1962).
30. G. V. D. Tiers: *J. Phys. Soc. Japan*, 15, 354 (1960).
31. G. V. D. Tiers: *J. Chem. Phys.*, 35, 2263 (1961).
32. G. V. D. Tiers: *J. Phys. Chem.*, 66, 945 (1962).
33. J. Bacon and R. J. Gillespie: *J. Chem. Phys.*, 38, 781 (1963).
34. N. Muller and D. T. Carr: *J. Phys. Chem.*, 67, 112 (1963).
35. G. V. D. Tiers: *J. Chem. Phys.*, 29, 963 (1958).
36. G. V. D. Tiers: *J. Phys. Chem.*, 64, 373 (1960).
37. H. S. Gutowsky: *J. Chem. Phys.*, 31, 1683 (1959).
38. H. Braune and P. Pinnow: *Zeit. Phys. Chem.*, B35, 239 (1937).
39. J. L. Hoard and W. B. Vincent: *J. Am. Chem. Soc.*, 62, 3126 (1940).
40. L. O. Brockway and L. Pauling: *Proc. Nat. Acad. Sci.*, 19, 68 (1933).

41. T. W. Marshall: *Mol. Phys.*, 4, 61 (1961).
42. R. J. Gillespie, J. V. Oubridge and E. A. Robinson: *Proc. Chem. Soc.*, 428 (1961).
43. R. J. Gillespie and E. A. Robinson: *Can. J. Chem.*, 39, 2179 (1961).
44. F. B. Dudley and G. H. Cady: *J. Am. Chem. Soc.*, 79, 513 (1957).
45. C. W. Tullock and D. D. Coffman: *J. Organic Chem.*, 25, 2016 (1960).
46. R. C. Thompson: Ph.D. Thesis, McMaster University (1962).
47. R. A. Ogg: *J. Chem. Phys.*, 22, 1933 (1954).
48. J. N. Shooley: *Discussions Faraday Soc.*, 19, 215 (1955).
49. R. A. Ogg and J. D. Ray: *J. Chem. Phys.*, 26, 1515 (1957).
50. H. S. Gutowsky, D. W. McCall and C. P. Slichter: *J. Chem. Phys.*, 21, 279 (1953).
51. J. A. Pople: *Mol. Phys.*, 1, 168 (1958).
52. T. D. Coyle and F. G. A. Stone: *J. Chem. Phys.*, 32, 1892 (1960).
53. W. B. Moniz and H. S. Gutowsky: *J. Chem. Phys.*, 38, 1155 (1963).
54. D. R. Lide Jr., and D. E. Mann: *J. Chem. Phys.*, 25, 1128 (1956).
55. R. P. Madden and W. S. Benedict: *J. Chem. Phys.*, 25, 594 (1956).
56. D. R. Lide Jr., and D. E. Mann: *J. Chem. Phys.*, 25, 595 (1956).
57. Booklet DC-1819. Pennsalt Chemicals Corporation, Philadelphia, Pa.
58. S. Brownstein: *Can. J. Chem.*, 38, 1597 (1960).
59. H. Agahigian, A. P. Gray and G. D. Vickers: *Can. J. Chem.*, 40, 157 (1962).
60. C. V. Stephenson and E. A. Jones: *J. Chem. Phys.*, 20, 1830 (1952).
61. R. S. McDowell and L. B. Asprey: *J. Chem. Phys.*, 37, 165 (1962).
62. R. D. Burbank and F. N. Bensey: *J. Chem. Phys.*, 27, 982 (1957).
63. E. L. Muetterties and W. D. Phillips: *J. Am. Chem. Soc.*, 79, 322 (1957).

64. R. C. Lord, M. A. Lynch, Jr., W. C. Schumb and E. J. Slowinski: J. Am. Chem. Soc., 72, 522 (1950).
65. K. B. Wiberg and B. J. Nist: Interpretation of NMR Spectra, W. A. Benjamin, Inc., New York, 1962.
66. E. E. Aynsley, R. Nichols and P. L. Robinson: J. Chem. Soc., 623 (1953).
67. C. L. Chernick, H. H. Claassen, H. H. Hyman, and J. G. Malm: "Conference on Noble Gas Compounds", Argonne National Laboratory, Argonne, Illinois, U.S.A., April 22-23, 1963.
68. E. E. Aynsley, R. D. Peacock and P. L. Robinson: J. Chem. Soc., 1623 (1950).
69. N. Bartlett, N. K. Jha and J. Trotter: Proc. Chem. Soc., 277 (1962).
70. R. D. Chambers, H. C. Clark, L. W. Reeves, and C. J. Willis: Can. J. Chem., 39, 258 (1961).
71. S. L. Stafford: Can. J. Chem., 41, 807 (1963).
72. R. D. W. Kemmitt, R. S. Milner, and D. W. A. Sharp: J. Chem. Soc., 111 (1963).
73. D. M. Grant and K. F. Kuhlmann: Private Communication.
74. I. G. Ryss and M. M. Slutskaya: Zhur. Obschei Khim., 22, 41 (1952).
75. K. C. Moss and D. W. A. Sharp: J. Inorg. Nucl. Chem., 13, 328 (1960).
76. K. C. Moss: Private Communication.
77. C. A. Wamser: J. Am. Chem. Soc., 70, 1209 (1948).
78. P. Diehl and J. Gräncher: Helvetica Physica Acta, 31, 43 (1958).
79. P. Diehl: J. Inorg. Nucl. Chem., 8, 468 (1958).
80. M. Karplus, D. H. Anderson, T. C. Farrar and H. S. Gutowsky: J. Chem. Phys., 27, 597 (1957).
81. R. J. C. Brown, H. S. Gutowsky and K. Shimomura: J. Chem. Phys., 38, 76 (1963).
82. N. Bartlett and L. E. Levchuk: In press, Proc. Chem. Soc.
83. M. Schmeisser and K. Lang: Angew. Chem., 67, 156, (1955).

84. M. Schmeisser: "Symposium on Inorganic Fluorine Chemistry", September 4 - 6, 1963, Argonne National Laboratory, Argonne, Illinois, U.S.A.