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DOCTOR OF PHILOSOPHY

of

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B.Sc., The University of British Columbia
M.Sc., The University of British Columbia

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A general broad line nuclear magnetic resonance study was made of the F spectra of WF$_6$ and the adducts IF$_7$·AsF$_5$ and SF$_4$·AsF$_5$ to determine the temperature dependence of the spectra, interpret the line shapes with respect to isotropic and anisotropic chemical shifts and identify non-equivalent fluorine sites in the compounds.

The temperature dependence of the second moment at 30 MHz indicated that rigid lattice conditions probably existed at 77°K for WF$_6$ and IF$_7$·AsF$_5$ but not for SF$_4$·AsF$_5$. The dependence indicated an nmr transition in the vicinity of 200°K for the first two compounds and one commencing below 77°K for the third. From the second moments in the vicinity of the transitions, activation energies were determined for the average motions involved.

The field dependence of the second moments of the compounds was examined, where possible, at 2, 16, 30, 40, 56.4, and 94.1 MHz at 77° and 295°K. The compound's spectra were resolved, with varying degrees of success, into components. For WF$_6$, an approximate resolution could be made into two components corresponding to the four equatorial and two axial fluorines.
in the distorted octahedron at 77\(^0\)K. The two adducts could both be resolved, especially at 295\(^0\)K or above, into components which supported the ionic formulations IF\(_6^+\)AsF\(_6^-\) and SF\(_3^+\)AsF\(_6^-\). Non-equivalent fluorine sites within individual ions could not be detected.

From the observed and estimated second moments of the resolved components above and below the transitions, the probable reorientations occurring above the transitions were suggested. The rigid lattice theoretical second moment calculations enabled suggestions to be made for the crystal structures of WF\(_6\) and SF\(_3^+\)AsF\(_6^-\) and for the bond lengths in IF\(_6^+\)AsF\(_6^-\).

For the first there had been confusion, at least here, about the space group, while the second has not yet been the subject of reported X-ray studies.

Axial symmetry of the chemical shift tensors was assumed. Then, taking account of the relative shifts between the resolved components, average values of the chemical shift anisotropies for each of WF\(_6\) and IF\(_6^+\)AsF\(_6^-\) were determined from expressions relating the field squared dependence of the second moment to those quantities.

The mean isotropic shifts of the total \(^{19}\)F spectra for each compound were measured where possible at each field at 77\(^0\) and 295\(^0\)K with respect to CF\(_3\)COOH. From those the shifts of the resolved components were calculated relative to HF. Then from the isotropic shifts and the anisotropies, the principal values of the axially symmetric shift tensors were determined.
The principal values enabled estimates to be made of I (ionic) and $\rho$ (double bond) characters, neglecting hybridization, in the M-F bonds of the hexafluoride groups. From these values a prediction was made for I and $\rho$ in the axial and equatorial bonds in PuF$_6$.

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A $^{19}$F BROAD LINE NUCLEAR MAGNETIC RESONANCE STUDY

of

$WF_6$, $IF_7$, $AsF_5$, $SF_4$, $AsF_5$

by

MATTHEW RONALD BARR
B. Sc. (Hons.), U.B.C., 1960
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A THESIS SUBMITTED IN PARTIAL FULFILMENT OF
THE REQUIREMENTS FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY

in the Department
of
Chemistry

We accept this thesis as conforming to the
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Department of Chemistry
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Date Nov. 3, 1967
Abstract

A general broad line nuclear magnetic resonance study was made of the $^{19}\text{F}$ spectra of $\text{WF}_6$ and the adducts $\text{IF}_7 \cdot \text{AsF}_5$ and $\text{SF}_4 \cdot \text{AsF}_5$ to determine the temperature dependence of the spectra, interpret the line shapes with respect to isotropic and anisotropic chemical shifts and identify non-equivalent fluorine sites in the compounds.

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The field dependence of the second moments of the compounds was examined, where possible, at 2, 16, 30, 40, 56.4, and 94.1 MHz at 77° and 295°K. The compounds' spectra were resolved, with varying degrees of success, into components. For $\text{WF}_6$ an approximate resolution could be made into two components corresponding to the four equatorial and two axial fluorines in the distorted octahedron at 77°K. The two adducts could both be resolved, especially at 295°K or above, into components which supported the ionic formulations $\text{IF}_6^+ \text{AsF}_6^-$ and $\text{SF}_3^+ \text{AsF}_6^-$. Non-equivalent fluorine sites within individual ions could not be detected.
From the observed and estimated second moments of the resolved components above and below the transitions, the probable reorientations occurring above the transitions were suggested. The rigid lattice theoretical second moment calculations enabled suggestions to be made for the crystal structures of $WF_6$ and $SF_3^+AsF_6^-$ and for the bond lengths in $If_6^+AsF_6^-$. For the first there had been confusion, at least here, about the space group, while the second has not yet been the subject of reported X-ray studies.

Axial symmetry of the chemical shift tensors was assumed. Then, taking account of the relative shifts between the resolved components, average values of the chemical shift anisotropies for each of $WF_6$ and $If_6^+AsF_6^-$ were determined from expressions relating the field squared dependence of the second moment to those quantities.

The mean isotropic shifts of the total $^{19}F$ spectra for each compound were measured where possible at each field at $77^0$ and $295^0K$ with respect to $CF_3COOH$. From those the shifts of the resolved components were calculated relative to HF. Then from the isotropic shifts and the anisotropies, the principal values of the axially symmetric shift tensors were determined. The principal values enabled estimates to be made of $I$ (ionic) and $\rho$ (double bond) characters, neglecting hybridization, in the $M-F$ bonds of the hexafluoride groups. From these values a prediction was made for $I$ and $\rho$ in the axial and equatorial bonds in $PuF_6$. 
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CHAPTER 1

INTRODUCTION

In the Fall of 1964, a joint project on the investigation of the nuclear magnetic resonance spectra of the solid addition compounds \( \text{SF}_4 \cdot \text{BF}_3 \), \( \text{SF}_4 \cdot \text{AsF}_5 \) and \( \text{IF}_7 \cdot \text{AsF}_5 \) was undertaken in collaboration with Dr. Neil Bartlett and his co-workers. Exploratory studies showed that an examination of the simpler molecule \( \text{WF}_6 \) might be helpful. In the event, it turned out that a complete interpretation of the spectra of any of these compounds was made very difficult by combined isotropic chemical shift and chemical shift anisotropy, both of which were significant, but difficult to separate from one another and from direct dipole-dipole interactions in the solids. Because of the presence in all samples of \( \text{SF}_4 \cdot \text{BF}_3 \) of a narrow, impurity line which grew as each sample aged, attention was focused on the other two adducts. It was obvious that the \( \text{AsF}_5 \) fluorines would be isotropically shifted from the fluorines in the \( \text{SF}_4 \) or \( \text{IF}_7 \) portions of the adducts. To study the effect of anisotropic shift uncomplicated by isotropic shift, a molecule, solid \( \text{WF}_6 \), in which the fluorines were expected to be equivalent, or very nearly so, was selected. Non-equivalent fluorines, however, were present in \( \text{WF}_6 \) and a search for a quantitative interpretation of the detail of the molecule's line shape ultimately occupied some two-thirds of the time involved in the research. This thesis then became a general nuclear magnetic resonance study of the fluorine
spectra of \( SF_4 \cdot AsF_5 \), \( IF_7 \cdot AsF_5 \), and solid \( \text{UF}_6 \), comprising, where possible, temperature dependence, interpretation of the line shapes with respect to isotropic and anisotropic chemical shifts, and identification of equivalent fluorine atoms.

The two \( AsF_5 \) adducts are relatively new compounds having been reported only during the last decade. In 1956, Bartlett (1) reported that \( SF_4 \) coordinated with \( AsF_5 \) in the ratio of one mole of each to form a new compound, a white solid. The following year he observed that a displacement reaction involving this adduct was a convenient method for purifying \( SF_4 \) (2). In 1958 Seel and Detmer (3) reported \( SF_4 \cdot AsF_5 \) and \( IF_6 \cdot AsF_5 \). They noted that the stable solids were a convenient form in which to store gaseous fluorocompounds such as \( SF_4 \). They also used \( IF_7 \cdot AsF_5 \) as a source of pure fluorine (4). In a longer paper in another journal (5) they discussed the compounds again and suggested an ionic formulation. In 1961, Bartlett (6) reported in greater detail on \( SF_4 \cdot AsF_5 \). Kolditz (7, 8, 9) has also reported adducts of \( AsF_5 \) which are ionic. Beaton (10) from infrared and X-ray spectra has shown that the acid-base adduct \( IF_7 \cdot AsF_5 \) is indeed the ionic salt \( IF^+ AsF^-_5 \). Tebbe and Muettterties (11) and Young and May (12) also have reported probable ionic adducts of \( AsF_5 \).

The symmetry of hexafluoride molecules has made them of interest to spectroscopists and theoreticians for many years (13 to 30). Thermodynamic values are reported in the preceding references (14, 20, 21, 26, 28) and also separately in other papers (31 to 35).
vapour phase octahedral symmetry appears well established for most hexafluorides (17, 18, 28, 30). Except for UF₆ (36) no detailed X-ray data exist for the metal hexafluorides. Since the bond lengths (37a) and X-ray results (37b) available for WF₆ do not permit determination of the symmetry of the solid, it appeared that this presented an excellent opportunity for broad line nmr. For UF₆ the X-ray data indicate below 725°C a tetragonal distortion with four short and two long bonds. Blinc et al (38) undertook a broadline nmr study of polycrystalline UF₆ in which they interpreted the ¹⁹F resonance spectrum below -30°C as a composite arising from the isotropic chemical shifts of two different fluorine sites present in a 2:1 ratio. This is in agreement with the X-ray results. The work was at an external magnetic field of 9400 gauss, at which field anisotropic chemical shift of the components could not be detected. Working at higher magnetic fields, Rigny (39) concluded that anisotropy was present. Blinc and Rigny (40) later published a joint letter on relaxation through anisotropic chemical shift in UF₆. Prior to the appearance of Rigny's thesis, work was begun on polycrystalline WF₆ in this laboratory. While the experimental results were being interpreted, Blinc et al (41) published a paper on the nmr and relaxation of hexafluoride, polycrystalline solids which included WF₆. The Blinc spectra agreed well with those obtained here and the interpretation confirmed what was already known here - that interpretation was difficult. High resolution nmr spectra of liquid MoF₆ and WF₆ have been reported by Cady (26) and
Rigny (42). In Cady's work the fluorides were also examined below the solid-solid transition (about $-8^\circ$C for both compounds) but the spectra were too broad for the lines to be observed by high resolution. In the liquid state both Cady and Rigny observed in addition to the central peak, six small satellite peaks in the $^{19}\text{F}$ spectrum of $\text{MoF}_6$ due to the $^{95, 97}\text{Mo} - ^{19}\text{F}$ coupling. For $\text{WF}_6$ Cady observed only a single, central peak. However, Rigny observed two satellites corresponding to the $^{183}\text{W} - ^{19}\text{F}$ coupling.
Since the first successful nuclear magnetic resonance experiments were reported in 1946 by Purcell, Torrey, and Pound (43) and Bloch, Hansen, and Packard (44) very many papers, reviews, and books on the phenomenon have appeared. For details of the theory one may refer to Bloembergen, Purcell, and Pound (45), reviews by Smith (46), Gutowsky (47, 48) and Pake (49), and books by Bloembergen (50), Andrew (51), Abragam (52), and Slichter (53) among others. Only information to supply a general outline of the theory is given in this section. Unless a specific reference is given, it is to be understood that acknowledgment is made to the above (especially Andrew) for the material in this chapter.

Those nuclei which do not have even mass number and atomic number have a non-zero spin angular momentum $\mathbf{I} \hbar$ and a dipolar magnetic moment $\mu = gI \hbar$ colinear with it. Prominent among these is the $^{19}F$ nucleus. The magnetic moment is also often expressed as $\mu = g\mu_0 I$ where $\mu_0$ is the nuclear magneton ($\mu_0 = \frac{e\hbar}{2mc}$) and $g$ is the nuclear $g$-factor analogous to the Lande splitting factor. In the absence of an external magnetic field the energy of a nuclear "magnet" is independent of the orientation of the magnetic moment. However, in the presence of a field $H_0$, the moment is subject to a torque $\mathbf{I} = \mu \times H_0$ which tends to align it parallel to the field.
There is an energy of interaction \( E = -\mu \cdot \mathbf{H}_0 \). If \( \mathbf{H}_0 \) is taken as the \( z \)-direction, then \( E = -\gamma I_z \mathbf{H}_0 = -m\gamma \mathbf{H}_0 \) where \( I_z \) is the component of the angular momentum vector along \( \mathbf{H}_0 \). The values of \( I_z \) or \( m \), the magnetic quantum number (the more usual symbol for the component of angular momentum) are given by the series \( I, I-1, \ldots, -(I-1), -I \). Hence for \( ^{19}F \) where \( I = \frac{1}{2} \), there are two possible orientations for the component and two possible energy levels. The selection rule for transitions between the energy levels is \( \Delta m = \pm 1 \), therefore for \( ^{19}F \) \( \Delta E = -\gamma \mathbf{H}_0 \). The frequency corresponding to an allowed transition is \( \omega_0 = 2\pi \gamma \mathbf{H}_0 = \gamma \mathbf{H}_0 \). The nuclear moment \( \mu \) precesses about the external field \( \mathbf{H}_0 \) at this frequency, the Larmor precession frequency, \( \omega_0 \). In the nuclear magnetic resonance experiment, a small, oscillating radio-frequency magnetic field \( \mathbf{H}_i \) is applied at right angles to \( \mathbf{H}_0 \). When the frequency of oscillation of \( \mathbf{H}_i \) equals \( \omega_0 \), a resonance interaction occurs which may flip the nucleus from the upper to lower or lower to upper energy level. In the usual experimental arrangement the oscillator frequency is kept fixed while the external magnetic field \( \mathbf{H}_0 \) is slowly varied to effect the resonance condition.

The above treatment for a single nucleus may be extended to a system of weakly interacting nuclei. This is an excellent approximation to the conditions in matter in bulk. At equilibrium in an external magnetic field there will be, due to a Boltzman distribution of energies, a slight excess of spins in the state
corresponding to the lower energy level for a $^{19}F$ nucleus.

There can then be a net absorption of energy by the nuclear system in an nmr experiment. This absorption produces a measurable signal which is characteristic of the system. The net absorption would cease when the populations of the two levels were equalized, but relaxation processes exist whereby the nuclei can dissipate energy to the surrounding lattice.

So far one expects an extremely narrow resonance line. In liquids this is generally realized. (There will of course be uncertainty broadening, which is fundamental to all spectral measurements.) In rigid solids, however, line widths are typically of the order of several gauss. Apart from the trivial cause of inhomogeneity in the external magnetic field, which can be reduced to a negligible value, there may exist for a spin $\frac{1}{2}$ nucleus spin-spin, dipolar, and chemical shift broadening mechanisms.

If the nuclei involved are identical, nucleus $j$ produces at nucleus $k$ a magnetic field oscillating at its Larmor frequency and a spin-spin transition involving a mutual exchange of energy may occur. This results in a broadening of the order of $H_e$ where $H_e$ is the field produced at nucleus $j$ by nucleus $k$.

In addition to spin-spin broadening, there will always be a dipolar broadening regardless of whether like or unlike nuclei are present. Each nucleus experiences the resultant effect of the external field $H_0$ and the local fields $H_r$ of all the other nuclei. The components of the local fields in the direction of $H_0$ may
increase or decrease $H_0$ with a resultant spread of resonance.

In liquids the dipolar broadening effect is removed by the rapid motional averaging of the local fields to zero, but in rigid, diamagnetic solids it is the principal contribution to line width.

Spin-spin and dipolar broadening were strikingly demonstrated by Pake (54) in a classic experiment with gypsum, CaSO$_4 \cdot 2H_2O$. Because of the $r^{-3}$ dependence of the dipole interaction, each proton in the gypsum is predominately influenced by its partner in the water molecule. Hence there are two resonance frequencies given by $H_0 = H^p \pm \mu r^{-3}(3\cos^2\Theta - 1)$ where $H^p = h\nu/2\mu$, $\mu$ is the proton moment, $r$ is the pair separation, and $\Theta$ is the angle between $H_0$ and $\mathbf{r}$ (the vector joining the two nuclei). If, as in this case, the nuclei are identical, spin-spin exchange modifies the classical picture to $H_0 = H^p \pm \frac{3}{2} \mu r^{-3}(3\cos^2\Theta - 1)$. The unit cell contains two types of protons with generally different values of $\Theta$. Depending on the orientation of a single crystal one, two, three or four of the possible resonance lines may be observed. Contributions from distant neighbours will contribute further broadening to the spectrum. If the sample is polycrystalline with the orientation of the dipole pairs isotropically distributed, a line shape function of the form

$$f(h) = \left(6\sqrt{3} \mu r^{-3}\right)^{-2} \left[1 \pm h/(\frac{3}{2} \mu r^{-3})\right]^{-\frac{1}{2}}$$

... (1)

where $h = H_0 - H^p$ and the signs are taken as plus for $-\frac{3}{2} \mu r^{-3} < h < 3\mu r^{-3}$.
and minus for \(-3\mu r^{-3} < h < \frac{3}{2} \mu r^{-3}\), can be derived (54). The polycrystalline line shape is a doublet which again is further broadened by the local fields of all other neighbours. This general line shape function will be encountered again.

The line shapes for certain three-spin and four-spin systems have been calculated, but for more general systems the task is extremely difficult and in any case the lack of detail in the spectra makes the effort of little use. Fortunately there exists a technique devised by Van Vleck whereby information can be extracted from the more complicated systems. This method and its applications will be discussed prior to describing the effect of chemical shift on line broadening.

Van Vleck (55) showed that the moments of a resonance spectrum can be readily calculated. If the normalized line shape is the function \(g(h)\) where \(h\) is the distance from the center of resonance, the \(n^{th}\) moment is \(S_n = \int_{-\infty}^{\infty} h^n g(h) dh\). All the odd-numbered moments are zero since \(g(h)\) is an even function for magnetic dipolar broadening. Van Vleck calculated second and fourth moments for the general case. For a rigid polycrystalline sample the second moment is

\[
S_2 = \frac{3}{5} I(I+1) \mu_o^2 N^{-1} \sum_{j<k} r_{jk}^{-6} + \frac{3}{10} \mu_o^2 N^{-1} \sum_{j<k} I_x (I_x + 1) g_e^2 g_f r_{jf}^{-6} \quad \ldots \quad (2)
\]

where \(I\) is the spin number of the nuclei, \(\mu_o\) is the nuclear magneton, \(g\) is the nuclear \(g\)-factor, \(N\) is the number of magnetic nuclei in the system over which the sum \(j\) is taken, and \(r_{jk}\) is the magnitude
of the vector joining nuclei j and k. The first term accounts for
dipolar broadening by those nuclei whose resonance is being ob-
served. The second term is a contribution to spectral broadening
by species of magnetic nuclei other than those at resonance. (In
\WF_6\ for example, \(^{19}\mathrm{F}\) and \(^{183}\mathrm{W}\) respectively.)

During the course of a broad line nmr investigation of a
polycrystalline solid, one normally records the magnetic resonance
spectrum over a range of temperatures varying from low (usually
liquid nitrogen temperature) up to room temperature or considerably
higher as dictated by the nature of the compound. If the lowest
temperature corresponds to a rigid lattice condition, then after
a correction for zero-point motion of the nuclei has been made \((56)\),
the observed second moment, should agree within experimental error
with the calculated rigid lattice second moment. Any discrepancy
will be due to additional motion in the crystal lattice. If the
crystal structure has not been determined a reasonable structure may
often be worked out by trial from the nmr rigid lattice second
moment. Even if rigid lattice conditions do not prevail, quite
reasonable estimates of the probable structure can be obtained by con-
sidering the effect on second moment of possible motions in the
crystal lattice. The application of second moments is also useful
in determining the positions of protons, which are difficult to
locate accurately by X-ray crystallography. Since equation (2)
involves \(r^{-6}\), a highly accurate internuclear distance \(r\) can
frequently be obtained. In single crystal spectra bond angles can be obtained in addition to bond lengths.

Motion within the lattice, whether of whole molecules or of substituent groups, contributes to a time averaging of the local fields. The averaged field is less than the steady local field for a rigid system and as motion becomes more pronounced the resonance line becomes narrower as liquid-like conditions are approached. The narrowing of the line may give evidence of molecular motion even though the frequency of reorientation may be quite small for each molecule. A potential barrier obviously exists for this motion and motion takes place when a molecule has sufficient energy to surmount the barrier. A very high barrier produces an essentially rigid structure although even then there may be rotational oscillation. In a reorientation process which can be described by a single frequency or correlation time, the temperature dependence of the correlation time, $\tau_c$, may be described by

$$\tau_c = \tau_0 \exp \left( \frac{-AE}{RT} \right) \quad \text{.............. (3)}$$

where $AE$ is the height expressed in energy per mole of the hindering potential. Then the reorientation rate, $\nu_c$, defined by

$$2\pi \nu_c \tau_c = 1$$

is

$$\nu_c = \nu_0 \exp \left( \frac{-AE}{RT} \right) \quad \text{.............. (4)}$$

The resonance line narrows when the reorientation rate becomes of the order of the frequency of the line width. Calculation of the line shape for a complicated reorienting system is of course even
more difficult than for a rigid system and again second moments are used. The change in second moment will depend on the nature of the reorientation (57). For a polycrystalline material containing a system or group undergoing a free rotation over an $n$-fold periodic potential barrier where $n \geq 3$, equation (2) becomes, for the intramolecular contribution only
\[
S_{\text{int}} = \frac{2}{3} \bar{\omega} \sum_{j,k} \sum_{l} \left( 3 \cos^2 \gamma_{jk} - 1 \right) R_{ij}^{-6}
\]
where $\gamma_{jk}$ is the angle between the internuclear vector $\mathbf{r}_{jk}$ and the axis of rotation. Each term has been reduced by the factor $\frac{1}{4} \left( 3 \cos^2 \gamma_{jk} - 1 \right)^2$. This is the reduction of only the intramolecular second moment. That for the intermolecular moment is much more complicated since $\gamma_{jk}$ varies as well. The only case in which the intermolecular contribution can be obtained simply is that for isotropic molecular reorientation of a group about its molecular center (58, 59, 60, 61). The magnetic nuclei are considered to be concentrated at the molecular centers and the distances $r_{jk}$ in equation (2) are replaced by $R_{ij}$, the center-center distance between a molecule and its $i$th nearest neighbor. The equation becomes
\[
S_{\text{int}} = \frac{3}{5} \bar{\omega} \sum_{i} \sum_{j,k} N_{i} R_{ij}^{-6} + \frac{a}{15} \sum_{i} \sum_{j,k} N_{i} \sum_{j,k} I_{jk} (l_{l} + 1) g_{l} g_{j} N_{i} R_{ij}^{-6}
\]
where $N_{i}$ is the number of resonant nuclei in the molecule, $N_{i}$ is the number of $i$th nearest neighbours and the other quantities are as before. The isotropic reorientation averages the intramolecular moment to zero and the calculated sum is the intermolecular contribution. If the reorientation is not isotropic, but about preferred
axes at random the calculation is more difficult (61, 62, 63, 64a) and the result may differ from that for isotropic reorientation by 5 to 15% (64b).

Activation energies for molecular reorientations may be derived from a log \( v_e \) versus \( 1/T \) plot of equation (4). The correlation frequency in terms of line width in gauss is (based on Gutowsky and Pake (57))

\[
v_e = \frac{\alpha \mu}{1/h} \frac{\Delta H}{\tan \left[ \frac{\pi}{2} \left( \frac{\Delta H^2 - \Delta H_A^2}{\Delta H_B^2 - \Delta H_A^2} \right) \right]}
\]

where \( \Delta H \) is the line width in the transition region, \( \Delta H_A \) is the line width above the transition, and \( \Delta H_B \) is that below the transition, \( \alpha \) is a constant of the order of unity, and \( \mu \) is the magnetic moment in nuclear magnetons. If the line shape changes during the transition, line width is not a reliable parameter (65). Since second moments are a more reliable indication of temperature effects the correlation time may be expressed according to Powles and Gutowsky (66) in terms of second moment in gauss \(^2\) as

\[
v_e = \frac{\alpha \mu}{1/h} \frac{\nu}{v_0} \tan \left[ \frac{\pi}{2} \left( \frac{S_A - S^A}{S_B - S^B} \right) \right]
\]

where \( S_2 \) is the second moment at any point in the transition region, \( S_A \) is the second moment above the region, \( S_B \) is the second moment below the region, and the other symbols are as before. Unless only a single motion is occurring these are average values of \( v_e \) and \( \Delta E \) which are obtained. Also an added uncertainty arises from the use of the line width or second moment. The intermolecular contributions to the resonance curve may vary with motion and hence with temperature in a different fashion from the intramolecular contribution. Orders
of magnitude of $\nu$ or $\Delta E$ are probably the best that can be expected. A more reliable approach is to determine correlation times from spin-lattice relaxation measurements. This is, however, not always experimentally convenient, while line widths and second moments can always be obtained. Furthermore if the motion taking place is complicated, $\nu$ and $\Delta E$ are, as noted above, average values. Comparison of the observed second moment change with that calculated on the basis of the possible motions occurring gives a more reliable picture of reorientations taking place in complicated cases. The activation energy will, however, provide supporting evidence for the occurrence of the suggested motion.

Chemical shift also contributes to nuclear magnetic resonance line-broadening. In diamagnetic molecules, the most frequent subjects for nmr experiments, the ground state has, in the absence of an external field, no resultant electronic spin or electronic orbital angular momentum (67). An external field induces an orbital motion in the electrons of a molecule which is superimposed on the electrons' motions about their nuclei. The motions constitute effective currents within the molecule which produce at the nucleus additional magnetic fields which are proportional to the external field $H_0$. The resultant field experienced by the nucleus is expressed as (52, Chap. 6; 68, Chap. 1)

$$H = H_0 (1 - \hat{\chi})$$

(9)

where $\hat{\chi}$ is a second rank tensor dependent on the electronic environment of the nucleus considered. The shift is a combination of
diamagnetic and paramagnetic shielding effects. The diamagnetic
term is essentially a Larmor precession, in the field $\mathbf{H}_0$, of the
electronic charges in the molecule about the nucleus in question;
while the paramagnetic term arises from the polarization of electron
shells by $\mathbf{H}_0$ (52, Chap. 6).

Slichter (53, p. 84) expressed the shielding after Ramsey (57)
as
$$\frac{\Delta \sigma}{2mc^2} = \frac{e^2}{2mc^2} \left( \psi_0 \left| \sum_j \left[ \mathbf{k} \left( \frac{x_j^2 + y_j^2}{r_j^3} \right) - \frac{i}{r_j^3} \frac{x_j}{r_j} \frac{\partial}{\partial x} + \frac{i}{r_j^3} \frac{y_j}{r_j} \frac{\partial}{\partial y} \right] \right| \psi_0 \right) \times \sum_n \left[ E_n - E_0 \right] \times$$
$$\left[ \left( \psi_0 \left| \hat{L}_j \right| \psi_n \right) \left( \psi_n \left| \sum_k \hat{p}_k \right| \psi_0 \right) + \left( \psi_0 \left| \sum_k \hat{L}_k \right| \psi_n \right) \left( \psi_n \left| \sum_j \hat{p}_j \right| \psi_0 \right) \right] \ldots \quad (10)$$

where $e$ is the electronic charge, $m$ the electronic mass, $c$ the speed
of light; $\psi_0$, $\psi_n$ and $E_0$, $E_n$ the wavefunctions and energies of electrons
in the ground and $n$th excited states respectively; $\hat{L}_j$ the total angular
momentum operator $\hat{A} \times \hat{p}_j$ (where $\hat{L}_j$ is the vector from the shielded
nucleus to the electron whose coordinates are $x_j$, $y_j$, $z_j$ and $\hat{p}_j$
is the linear momentum), $\hat{L}_k$ is the angular momentum operator
$$\frac{\hbar}{2} \left( x \frac{\partial}{\partial y} - y \frac{\partial}{\partial x} \right)$$
and $r_j$ is the magnitude of $\hat{L}_j$. The sums $j$ and $k$
are taken over the $N$ electrons present and the sum $n$ over the $n$
states. The two terms are of approximately equal magnitude and are
respectively the diamagnetic and the second-order paramagnetic con-
tribution. As indicated by equation (10) the diamagnetic term is a
ground state contribution. It is in fact (67), the same as Lamb's
complete expression for the diamagnetic shielding of single atoms (69).
The paramagnetic term is an excited state contribution from the magnetic fields set up by the orbital motions of the valence electrons (70). In the absence of an external static field the orbital fields have a zero average value but produce instantaneous fields of several thousand gauss at the nucleus. The applied field produces a slight polarization of these large fields and hence an appreciable shielding. Since the valence electrons are more readily polarized, the principal contribution is from them rather than from the closed shell electrons. Ramsey (67) pointed out, however, that the separation into two distinct terms is artificial and that the terms are in fact closely related.

In their discussion of fluorine chemical shifts, Saika and Slichter (70) made a division of the shift into three terms:

(a) the diamagnetic correction for the relevant atom. This is again the Lamb term. It accounts for only about 1% of the range of fluorine shifts observed.

(b) the paramagnetic correction for the relevant atom. This term is principally responsible for chemical shifts in fluorines.

(c) the contributions from electrons in other atoms. The electrons in other atoms are either in closed shells and difficult to polarize or in valence shells in which the electrons although readily polarized are still subject to a $\frac{1}{r^3}$ falling off of the interaction. The contribution from this term is therefore small.
Although term (b) is the principal contribution to the fluorine shift, in the case of electrons in a purely \( s \) state (the electrons exert a zero instantaneous orbital magnetic field at the nucleus, while \( p \) and \( d \) electrons exert large fields) the terms (a) and (c) would comprise the shift. That is, because of the spherical symmetry of an \( s \) state, the angular momentum operators make the second term of equation (10) equal to zero for a purely \( s \) state. The paramagnetic term would be zero in completely ionic \( F^- \) because of the filled \( L \) shell, and have its maximum value in covalent \( F_2 \).

Pople (68, Chap. 7) adds a fourth term to Saika and Slichter's:

(d) the contribution from interatomic currents. If it is possible for electrons to flow from one atom to another, as for example in aromatic molecules, the interatomic currents can generate additional screening.

Chemical shift broadening of the resonance line may have either isotropic or anisotropic origins or both. If a solid contains non-equivalent nuclei there will be a broadening of the resonance line due to differences in isotropic shift. If there are nuclei in non-equivalent electronic environments, Andrew (71) notes that the following additional contribution must be added to the second moment:

\[
\frac{H_0}{u} \left[ (\overline{\sigma}_1 - \overline{\sigma}_2)^2 + (\overline{\sigma}_2 - \overline{\sigma}_3)^2 + \ldots + (\overline{\sigma}_u - \overline{\sigma})^2 \right] \quad \ldots (11)
\]

where

\[
\overline{\sigma} = \frac{1}{u} \left( \overline{\sigma}_1 + \overline{\sigma}_2 + \ldots + \overline{\sigma}_u \right) \quad \ldots (12)
\]
\( \bar{\varepsilon}_u \) is the isotropic mean shift for nucleus \( u \)

where

\[
\bar{\varepsilon}_u = \frac{1}{3} \text{Tr} \varepsilon_u = \frac{1}{3} (\sigma_{xx} + \sigma_{yy} + \sigma_{zz}) \quad \cdots \quad (12a)
\]

where \( \sigma_{xx}, \sigma_{yy}, \text{ and } \sigma_{zz} \) are the principal axes of the shift tensor.

Even if a solid contains only nuclei in identical electronic environments, there may be a chemical shift contribution to line broadening. If the chemical shift tensor, \( \varepsilon \), is asymmetric, a probing external field will encounter different electronic screening depending on the molecular orientation in the field.

The investigation of chemical shift anisotropy in polycrystalline solids is based on the approach employed by Bloembergen and Rowland (72) with thallous oxide. Andrew and Tunstall (71) express the field experienced by a given nucleus in a polycrystalline solid as

\[
\mathbf{H} = H_0 \left[ 1 - (\lambda_x \sigma_{xx} + \lambda_y \sigma_{yy} + \lambda_z \sigma_{zz}) \right] \quad \cdots \quad (13)
\]

where \( \sigma_{xx}, \sigma_{yy}, \sigma_{zz} \) are again the principal axes of the shift tensor and \( \lambda_x, \lambda_y, \lambda_z \) are the direction cosines with respect to \( H_0 \). The average field experienced by all the nuclei if the crystallites in the polycrystalline sample are isotropically distributed is expressed by

\[
\mathbf{H} = H_0 \left[ 1 - \frac{1}{3} (\sigma_{xx} + \sigma_{yy} + \sigma_{zz}) \right] \quad \cdots \quad (14)
\]
For axial symmetry about the z-axis \( \lambda_3 = \cos \theta \),
\[
\sigma_{xx} = \sigma_{yy} = \sigma_z \quad \text{and} \quad \sigma_{xy} = \sigma_{yx}.
\]
and
\[
H = \tilde{H} - h
\]
where \( h = \frac{1}{3} H_0 (\epsilon_{zz} - \epsilon_{xx}) (3 \cos^2 \theta - 1) \) and where \( \tilde{H} \) and \( \tilde{H} \) are fields at nucleus

The normalized line shape is then
\[
\psi(h) = \left(2\sqrt{3}a\right)^{-1} \left(1 + \frac{h}{a}\right)^{-1/2}
\]
where \(-a \leq h \leq 2a\)
and
\[
a = \frac{1}{3} H_0 (\epsilon_{zz} - \epsilon_{xx})
\]
The function \( f(h) \) is similar in form to equation (1).

The second moment of the line shape given by equation (16)
\[
f_2(h) = \frac{4}{5} a^2 = \frac{4}{45} H_0^2 (\epsilon_{zz} - \epsilon_{xx})^2
\]
and if the dipolar broadening is described by a symmetrical, normalized line shape function \( g(h) \) then the total second moment is (71, 73)
\[
S_2 = g_2(h) + f_2(h) = g_2(h) + \frac{4}{45} H_0^2 (\epsilon_{zz} - \epsilon_{xx})^2
\]
The correct center of moments is not readily apparent in an asymmetric curve, but if first and second moments are computed about a point close to the estimated center (to minimize error) the first moment gives the center of moments directly and the second moment can be transferred to it. If the transferred second moment is plotted against \( H_0^2 \), the absolute value of the anisotropy of
chemical shift $|\sigma_n - \sigma_1|$ can be determined. The sign can be found from the direction of asymmetry of the curve. The anisotropy may be used to provide information about the type of bonding in the solid studied. The intercept of the plot will give $g_4(h)$, the dipolar second moment, and this can be used as a broadening function (gaussian usually) on equation (16) to synthesize a curve for comparison with the experimental curve. The extrapolated "dipolar moment" will of course include any field independent broadening which is present.

If both isotropic and anisotropic shifts are present the second moment equation becomes

$$S_2 = g_2(h) + f_2(h) + y_2(h)$$

$$= g_2(h) + \frac{\pi}{45} H_0 \left[ (\sigma_n - \sigma_0)^2 + \frac{h^2}{\eta} \left( (\sigma_1 - \bar{\sigma})^2 + (\sigma_2 - \bar{\sigma})^2 + \cdots + (\sigma_4 - \bar{\sigma})^2 \right) \right]$$

...(19)

Here the expressions $(\sigma_i - \bar{\sigma})$ etc. are as in equations (11) and (12) and $(\sigma_n - \sigma_1)$ is an average anisotropy for all the "isotropically" shifted resonant nuclei. Unless the various nuclei are sufficiently shifted from one another to permit a confident resolution of the curve into its components (in which case the individual $(\sigma_n - \sigma_1)$'s may be determined also) the interpretation of the resonance spectrum may be very difficult.
CHAPTER III

EXPERIMENTAL PROCEDURE

The SF\textsubscript{6} • AsF\textsubscript{5}, IF\textsubscript{7} • AsF\textsubscript{5}, and WF\textsubscript{6} samples supplied by Dr. Neil Bartlett were prepared by Dr. S.P. Beaton. Only pure SF\textsubscript{6} • AsF\textsubscript{5} and IF\textsubscript{7} • AsF\textsubscript{5} samples were used. For WF\textsubscript{6} both pure samples and samples doped with IrF\textsubscript{6} (up to one part per thousand) were run. In the latter case the paramagnetic impurity was added to shorten the spin-lattice relaxation time, reduce saturation, and improve the signal to noise ratio in the spectrum by permitting the runs to be made at higher rf field ($H_1$ field). Spectra were recorded over a two year period using several different samples of each compound. At the end of the study comparisons were made between recent samples and samples stored for more than a year. Between runs samples were stored in a dry-ice acetone bath or liquid nitrogen.

The fluorine magnetic resonance spectra of the compounds were recorded on two Varian 4250-type broad line spectrometers and on a Varian HA100 high resolution spectrometer. One of the broad line spectrometers was a DP60 with a Varian 12 inch electromagnet and a 56.4 MHz V-4311 Fixed Frequency RF Unit. The other broad line spectrometer employed a Varian 6 inch electromagnet and a 30 MHz V-4310A Fixed Frequency RF Unit and a 2-16 MHz V-4210A Variable Frequency RF Unit. The 2000 Hz sidebands of the V-3521A Integrator/
Decoupler were used to provide sweep modulation on the HA100. Since the resonance lines of the solids were very much wider than 2000 Hz, the resulting spectra were the familiar derivative signals customarily observed in broad line work. Since the normal method of calibrating the modulation amplitude of a lock-in detector by recording the derivative of a liquid line could not be used on the high resolution spectrometer, a minor problem was encountered in determining the amplitude of the modulation. However, when a liquid signal is scanned, the Integrator/Decoupler may be adjusted to give zero amplitude for the center band. Then at that point there is a known modulation index from which the modulation amplitude may be determined (74). This required adjustment of the coarse amplitude control in the interior of the instrument. It was difficult to reproduce this exact value for each series of runs without recording a tedious series of signals on a strip recorder each time. However, it was always simple to ensure that the amplitude was below the point of known amplitude which in itself was safe (about 1.2 gauss peak to peak) and that modulation broadening was absent. A more serious problem was encountered in obtaining a pure absorption derivative of the resonance signal. Balancing and phasing were quite critical and laborious. Operation on wide line diode detection with the introduction of absorption leakage was quicker and surer than phase detection. It also produced a better signal to noise ratio. Standard operating procedures were employed on the two broad line spectrometers.
The temperature dependence of the fluorine magnetic resonance spectra was studied at 30 MHz for all three compounds from 77 K to above 300 K and for a few temperatures from 173 K to 283 K at 94.1 MHz for a sample of IrF₆-doped WF₆. For low temperature runs at 30 MHz the temperature was controlled by cooled nitrogen vapour passed through a flow system which has been described by W. R. Janzen. Below about 220 K a liquid nitrogen bath was used to cool the gas. Between 220 K and room temperature a dry-ice acetone bath was used. Above room temperature, heated, compressed air was used in place of the tank nitrogen. The extremely efficient heater was of a double-pass heat exchanger type, incorporating a 600 W cylindrical heating coil, designed by W. R. Janzen for his work in this laboratory. Temperature control was approximately ±5° around 100 K and ±1° above 150 K. At 94.1 MHz the standard Varian V-4341 Variable Temperature System was used. The temperature range of this system is stated to be -60 to +200°C, but it was found that -100°C could be reached. The maximum temperature variation at the sample is ±1°C within the specified range and calibration is about ±3°C.

The H₀ field dependence of the spectrum of each compound was studied at the following temperatures and RF frequencies (H₀ field).

<table>
<thead>
<tr>
<th>Compound</th>
<th>Temperature K</th>
<th>RF Frequency MHz</th>
</tr>
</thead>
<tbody>
<tr>
<td>SF₄·AsF₅</td>
<td>295-300</td>
<td>94.1, 56.4, 40, 30</td>
</tr>
<tr>
<td></td>
<td>77</td>
<td>94.1, 56.4, 40, 30</td>
</tr>
<tr>
<td>IF₇·AsF₅</td>
<td>295-300</td>
<td>94.1, 56.4, 40, 30</td>
</tr>
<tr>
<td></td>
<td>77</td>
<td>94.1, 56.4, 40, 30</td>
</tr>
<tr>
<td>WF₆</td>
<td>173</td>
<td>94.1</td>
</tr>
<tr>
<td></td>
<td>77</td>
<td>94.1, 56.4, 40, 30</td>
</tr>
<tr>
<td></td>
<td></td>
<td>16, 2</td>
</tr>
</tbody>
</table>
For both \( \text{IF}_7 \cdot \text{AsF}_5 \) and \( \text{WF}_6 \) usable spectra could not be obtained at 77°K and 94.1 MHz due to the restriction on sample size explained below. However, a 5 mm diameter sample of \( \text{WF}_6 \) run at 173°K and 94.1 MHz using the V-4341 temperature system did produce usable spectra. For the fixed temperature work at 77°K, the samples were immersed in dewars filled with liquid nitrogen. The dewars have been described elsewhere (75, 76). The dewar (5 mm O.D.) used at 94.1 MHz in the HA100 severely restricted sample size to about 1.6 mm capillaries and had the barely sufferable disadvantage that it would hold liquid nitrogen for only four to six minutes. A dewar with a larger liquid nitrogen capacity, though of course with the same sample size restriction, was made by the Department's glassblower, Mr. Rak. This dewar held nitrogen for more than two hours but could not be removed from the probe without first taking the latter out of the magnet gap.

The samples used were all polycrystalline material, the spectra of which were independent of orientation in the magnetic field \( \mathbf{H}_0 \). Preliminary spectra were scanned up to 500 gauss on either side of resonance to establish that the resonance was confined to the region studied in expanded scale. Also, at each frequency (\( \mathbf{H}_0 \) field) preliminary spectra were run to check the rf level for saturation. The field \( \mathbf{H}_1 \) was varied over a wide range from about 0.05 mgauss to 45 mgauss. When an rf region was found where line widths remained constant as the power was lowered, forward and re-
verse scans were run to check that line shape was the same for both
directions. When an apparently satisfactory level had been found
the rf level was further reduced to ascertain that no additional
line shape changes occurred. In general, it was found that all
three steps were necessary. Since at least two chemically shifted
fluorine nuclei were present in each molecule, saturation effects
produced sometimes subtle changes in the spectra after an appar­
tently safe power level had eliminated the gross effects. Around
0.5 to 1.0 mgauss was generally a safe region, but spectra were
always checked over a range of rf power for signs of saturation.

At 77°K, the restriction placed on the sample size by the
dewars meant a poor packing factor in the receiver coil. Since
the saturation level was fairly low (H under 1.5 mgauss) by the
time the rf was reduced below saturation, the signal to noise ratio
was poor in some cases. The actual ratio varied depending on sample
and sample size, and on the RF unit used and its operating condition.
A high sweep modulation could not be used to improve the signal to
noise ratio since modulation broadening would have caused a loss
of structure which would have totally frustrated attempts to resolve
the spectra into their possible components. At the low modulation
amplitude used (approximately 0.5 gauss peak to peak), modulation
correction to the second moment was negligible, but a relatively low
signal to noise ratio had often to be tolerated. Ratios varied from
about 4:1 in some unfavourable cases at 77°K to 45:1 under good
conditions at room temperature.

No reference sample was used in the runs with variable temperature equipment or with the large dewar on the HA100, but a CF₃COOH or C₆F₆ reference was used in the H₀ field dependence runs at 77°K and 300°K. Since the purity of the CF₃COOH standard was unknown, its chemical shift relative to Freon 11 was measured at the conclusion of the experiments. The shift was +76.21 ppm.

Two sidebands were imposed on the reference's fluorine resonance with a Hewlett Packard Model 200CD Audio Oscillator. The field H₀ was scanned through one of the sidebands and, while scanning proceeded, the reference was replaced by the sample, the probe rebalanced if necessary and the spectrum recorded. The sample was then replaced by the reference and the other sideband recorded. The position of the reference resonance was taken as the midpoint between the two sidebands.

A minimum of four spectra were recorded at each temperature in the temperature dependence runs. In the H₀ field dependence runs, except at 94.1 MHz where machine time was in great demand, at least four referenced spectra were recorded at each frequency at 300°K and ten to twelve at 77°K, the temperature of greatest interest. In addition, at least a dozen non-referenced spectra were run for each sample at each frequency at 77°K and 300°K.
CHAPTER IV

RESULTS & INTERPRETATION

Programs written for the University of British Columbia's IBM 7040 computer played an extensive part in determining and evaluating the results obtained here. The programs are listed together with explanations in Appendix I.

Samples of all three of \( \text{WF}_6 \), \( \text{IF}_7 \cdot \text{AsF}_5 \), and \( \text{SF}_4 \cdot \text{AsF}_5 \) appeared quite stable when stored in dry-ice acetone or liquid nitrogen baths. There was no change exhibited between spectra of the same samples taken after more than one year of storage. Spectra of all samples of the same compound were experimentally consistent whether old or freshly supplied.

1. Results

Although samples which were doped with paramagnetic \( \text{IrF}_6 \) could be run at a higher \( r f(H_1) \) with a resultant more favorable signal to noise ratio, both pure and doped samples of \( \text{WF}_6 \) behaved identically within experimental error. Therefore no distinction is made between pure or doped samples in the results reported.

Figure 1 demonstrates the temperature dependence of the \( ^{19} \text{F} \) nmr spectra of \( \text{WF}_6 \) at 30 MHz. The absorption spectra having a common x-scale and being normalized to constant area, were
Figure 1. $WF_6$.

Temperature dependence of absorption spectra at 30 MHz.

- 77 °K
- 136 °K
- 185 °K
- 209 °K
- 262 °K
Figure 2. WF$_6$. Temperature dependence of second moment at 30 MHz
Figure 3. $WF_6^*$ Temperature dependence of line width at 30 and 94.1 MHz

- $O = 30 \text{ MHz}$
- $\Delta = 94.1 \text{ MHz}$
obtained by integration from the derivative curves using Program 2, Appendix I. Reproductions of derivative curves for temperature dependence at 30 MHz and also at 94.1 MHz are given in Appendices IIa and IIb. Figures 2 and 3 show respectively the second moment at 30 MHz (calculated with Program 1, Appendix I using the method outlined there) and the line width at 30 MHz and 94.1 MHz (between extreme maxima and minima of the derivative curve) as functions of temperature.

The second moment remains constant at 9.0±0.4 gauss$^2$ from 77°K to approximately 180°K. As seen in Figure 1, throughout this region there is an asymmetry to high field which disappears as the second moment drops between 180 and 220°K to 1.0±.05 gauss$^2$. During the transition the line changes from a slightly asymmetric derivative at 180-185°K to a symmetric derivative curve at 205 to 210°K. The second moment remains constant at 1.0 gauss$^2$ from 220 to 262°K. Beyond this region there is a sudden drop between 262 and 265°K to a value which could not be accurately measured from the derivative curve.

The behaviour of the line width at 30 MHz follows the same pattern over the temperature range. It is constant at 9.8±0.1 gauss from 77 to 180°K, dropping to 3.2±0.1 gauss by 220°K and dropping again (after remaining constant at 3.2 gauss) around 262 to 265°K to a value of 0.1 gauss as measured at 269°K. Although the line width measurement can be made between 265 and 287°K, it
is governed by the depth of modulation which was 0.1 gauss peak to peak. The spectra in this region were similar whether taken above or below the melting point of 276°K (orthorhombic to cubic crystal transition at 265.0°K, melting point at 276.4°K, and boiling point 290.3-290.7°K (20, 26)) and all had the appearance of liquid-like spectra. However, intensities were less than and lines were broader than that of a liquid signal (CF₃COOH at 298°K) in the same field. The appearance of the spectrum was really more like that of a viscous liquid within this range (265-287°K).

Variable temperature spectra at 94.1 MHz (Appendix IIb) show similar behaviour to those at 30 MHz. Line width is of the order of 12.0±0.3 gauss between 173 and 183°K. By 193°K, asymmetry is still present although it is beginning to disappear, and the line has narrowed to 11.1 gauss. Between 223 and 270°K the derivative curve is symmetrical with line width 3.1±0.1 gauss. Although line widths are plotted in Figure 3 there are not enough points to fix the transitions accurately at 94.1 MHz. The similar behaviour and identical line widths of the spectra taken at 30 MHz and 94.1 MHz in the region above the nmr transition at ~ 185-205°K indicate the absence of field dependent broadening there.

Above the melting point the 94.1 MHz spectra appear to indicate more liquid-like character than the 30 MHz spectra. This difference may be due to different temperature gradients along the samples in the two cases. In addition all 94.1 MHz spectra in the narrow line region appear to exhibit a small amount of disper-
sion which could not be balanced out. Initially it was thought this might be a low, broad peak indicating a percentage of molecules undergoing less frequent reorientation than those producing the narrow line. However, the "two components" could not be brought into phase and it was decided that the effect was probably due to the presence of a small amount of dispersion mode in the signal. Since the difficulty was not present at 30 MHz, its origin at 94.1 MHz may lie in an inability in this width region to remove completely the dispersion mode when using the Integrator to provide modulation. At temperatures below the nmr transition the 94.1 MHz spectra were quite satisfactory.

The results agree well, with one exception, with those obtained independently by Blinc (41). His second moment plot (his Figure 8) places the low temperature nmr transition at the same point as found here. His rigid lattice second moment of 9.5 gauss is course somewhat higher due to the increased anisotropy at the higher field of his experiment (9500 gauss as against 7500 gauss at 30 MHz). It is even slightly higher than the value of 9.1 gauss obtained by interpolating our results at 9500 gauss, but is certainly within the reproducibility of an nmr experiment. His line width of about 10 gauss at 7250 gauss field is the same as our value interpolated at the same field and his 3 gauss line width at \(-41^\circ C\) at 9500 gauss is again in agreement. (Blinc's line widths were estimated from his Figure 5). However his value of about
1.8 gauss$^2$ (estimated from his Figure 8) for the region above the 200°K nmr transition is significantly higher than our value of 1.0±0.05 gauss$^2$. Since the anisotropy has been averaged out in this region, the difference cannot arise from field dependent broadening. Since line widths appear the same in both studies, it is unlikely that the difference arises from saturation or modulation broadening in Blinc's spectra. The alternative that saturation narrowing exists in our spectra is discounted since great care was exercised in controlling the rf ($H_1$) level. The discrepancy may possibly lie in accurately determining the tails of the spectra. The spectra obtained here are in expanded scale and have an excellent signal to noise ratio. The second moments from them are therefore considered quite accurate. The lower second moment makes possible a slightly different interpretation of the motions occurring in this temperature region. This will be discussed later.

Figure 4 shows the field dependence of the centroid of the $WF_6$ spectrum at 77°K. The chemical shift, measured with respect to an external sample of $CF_3COOH$ at 295°K, is -255±40 ppm. Calculated relative to HF it is -380±40 ppm compared with Blinc's value of -440±20 ppm. This is not really a significant difference when the method used to obtain the shift (see Chapter III) is considered.

In Figure 2 the constant second moment from 77°K to ~180°K
Figure 4. \( \text{WF}_6 \). Chemical shift of centroid of spectrum relative to \( \text{CF}_3\text{COOH} \)

\[
\bar{\sigma} = -380 \pm 40 \text{ ppm}
\]
suggests that, except for whatever zero point motion of the atoms may be present, the $\text{WF}_6$ lattice is rigid at $77^\circ K$. The constancy of the second moment is in itself no absolute guarantee of rigidity, but as will be seen below it is supported by comparison with the calculated theoretical rigid lattice second moment. The anisotropy of the $\text{WF}_6$ spectrum can therefore be safely studied at $77^\circ K$, some 100° below the transition where motion averages out the effect. The field dependence of the average absorption curves at $77^\circ K$ is shown in Figure 5 at 2, 16, 30, 40, 56.4, and 94.1 MHz. Appendix IIc gives derivatives typical of the spectra recorded for Figure 5. The absorption curves have a common x-scale and are normalized to constant area. The 16 MHz spectra not quite consistent with the others. In contrast to $\text{UF}_6$ (38, 39, 41) there is virtually no resolution of the spectra except at 94.1 MHz. At this frequency, the spectra were actually taken at 173-175° K. However, as is apparent below, this seems to have been sufficiently into the rigid lattice region to obtain a valid spectrum. The spectra at lower frequency appear identical with Blinc's. The derivatives at 30 MHz (7500 gauss) and 40 MHz (10,000 gauss) in Appendix IIc are very similar to his 7250 and 9500 gauss spectra. As our spectra and the plot of the field dependence of the line width at $77^\circ K$ in Figure 6 indicate, there is little change in line width over the entire range of fields from 0.5 Kgauss at 2 MHz up to 23.5 Kgauss at 94.1 MHz. The change as one goes to lower frequency is really only a slight narrowing which has the effect of filling in the shoulder on the high field side
Figure 5. \(WF_6\). Field dependence of absorption spectra at 77°K

- 2 MHz
- 0.5 KG and 5G

- 16 MHz
- 4.0 KG and 5G

- 30 MHz
- 7.5 KG and 5G

- 40 MHz
- 10.0 KG and 5G

- 56.4 MHz
- 14.1 KG and 5G

- 94.1 MHz
- 23.5 KG and 5G
Figure 6. WF$_6$. Field dependence of line width at 77°K
of the spectra with scarcely any change in height. At initial stages of the investigation it was thought that saturation effects might be involved, but this was later ruled out and the effect shown to be genuine by careful checks of the rf \( (H_1) \) level.

2. Resolution attempts - Isotropic and Anisotropic Chemical Shifts

It was expected that \( \text{UF}_6 \) like \( \text{UF}\) would probably have a distorted structure at low temperatures. There would likely be four short equatorial bonds and two long axial bonds with the chemical shift tensors exhibiting axial symmetry along the bond direction. For such a molecule \( \tilde{\epsilon}_1 = \tilde{\epsilon}_2 = \tilde{\epsilon}_3 = \tilde{\epsilon}_4 = \tilde{\epsilon}_a \) and \( \tilde{\epsilon}_5 = \tilde{\epsilon}_6 = \tilde{\epsilon}_e \).

Equation (19) then becomes

\[
S_2 = \frac{1}{3} H_0^2 \left[ \frac{1}{45} (\tilde{\epsilon}_a - \tilde{\epsilon}_e)^2 + \frac{1}{45} (\tilde{\epsilon}_a - \tilde{\epsilon}_e)^2 + \frac{2}{3} (\tilde{\epsilon}_a - \tilde{\epsilon}_e)^2 \right] \tag{20}
\]

\( \tilde{\epsilon}_a \) and \( \tilde{\epsilon}_e \) correspond to the centers of zero first moment of the resolved axial and equatorial components of the total curve. The final term inside the square brackets is the relative chemical shift of the components. This equation is given with an incorrect factor of 6 instead of \( 2/3 \) before this term by Blinc (41). It is probably a typographical error since equation (20) applied to his data gives approximately his reported results for \( \text{UF}_6 \).

The averaged second moments of the spectra taken at 2, 16, 30, 40, 56.4, and 94.1 MHz were plotted against the square of the field \( (H_0) \). Figure 7 shows that, as predicted by equation (20), the plot gives a straight line. The experimental value of \( g(H) \), the zero field broadening, obtained from the intercept in Figure 7
Figure 7. \(WF_6\). Field squared dependence of second moment at \(77^\circ K\)

\[\text{TOTAL SECOND MOMENT GAUSS}^2\]

\[\text{FIELD SQUARED (H}_0^2\text{) KILOGAUSS}^2\]

\(\Delta = \text{BLINC (41)}\)
is $8.2 \pm 0.2$ gauss$^2$. This is considerably larger than the rigid lattice second moments published by Blinc (41) for other hexafluorides (4 to 5 gauss$^2$, but no value was given for WF$_6$).

Initial attempts at resolution were made prior to running the 2 and 94.1 MHz spectra. It was obvious from the lack of resolution in the 16 to 56.4 MHz spectra that an exact determination of the probable two components would be unlikely. Since the anisotropies of the components, if present, would likely be quite similar it was hoped, however, that at least a relative chemical shift and an average anisotropy could be determined. Thus began a tiresome series of resolution attempts which showed that a large variety of resolutions was possible, some promising and most plausible at one or more fields, but none of which was satisfactory over the full range.

Spectra were run at 2 MHz to determine a good approximation to the zero field line shape. The average second moment was 8.25 gauss$^2$, in splendid agreement with the 8.2 gauss$^2$ extrapolated value. The line shape was symmetrical but with little change in height or width from the shape at higher fields. When the Varian HA100 and its 23.5 k gauss field became available, spectra were run at 94.1 MHz. These spectra completed the straight line plot of second moment against field squared. The improved resolution in the spectrum gave promise that there were two components which could be separated one from the other. There was some concern that
since the spectra were run at 175 K, they might not be within the rigid lattice region, but the averaged second moment lies on the line of Figure 7 and the spectra seem valid.

Unfortunately the 94.1 MHz spectra do not clarify matters at all. They appear (see Figure 8) to define two well resolved peaks each of which is virtually symmetrical about its midpoint and whose area ratios are a quite precise 4 (low field) to 2 (high field). The chemical shift between the peaks is about 270±5 ppm. If in equation (20) the anisotropy is put equal to zero, the slope of the second moment line in Figure 7 gives a maximum value of 220±10 ppm. The agreement between the shifts is perhaps not too bad, but if the WF6 spectrum is composed of two, symmetrical, isotropically shifted peaks, the experimental curve should narrow and increase in height (if constant area is maintained) as the field is lowered. Figure 9 shows curves constructed by shifting the two components resolved at 94.1 MHz by 270 ppm at each field. As the figure indicates the constructed curves do not agree well with the experimental curves and even indicate tailing to low rather than high field. If one accepts the 220 ppm shift and resolves the 2 MHz curve into two similar components of 4:2 area ratios (Figure 9) a constructed curve can be fitted to the experimental curve at 16 and 30 MHz with quite good agreement but fails at higher fields. If a 220 ppm resolution is attempted at
Figure 8. WF$_6$. Symmetrical component reconstruction from 94.1 MHz spectra.
Figure 9. $WF_6$. Symmetrical component reconstruction from 2 MHz spectra.

Solid line experimental
Broken line constructed
94.1 MHz, the 4:2 area ratio cannot be maintained.

Prior to running the spectra at 94.1 MHz it was considered that in view of the failure to resolve the components, the chemical shift between the axial and equatorial fluorines might be so small that there were six essentially equivalent fluorines present. In this case equation (20) reduces to equation (18) and $|\sigma_{\perp}-\sigma_{\parallel}| = 345 \pm 20$ ppm. As indicated in Bloembergen (72), Andrew (71) and Abragam (52, p. 206, 220) a curve $F(H)$ may be synthesized for comparison with the experimental curve. The form of the function is

$$F(H) = \int_{-\infty}^{\infty} f(H_0-H^*)s(H-H_0)dH_0$$

(21)

where $f(H_0-H^*) = -f(h)$ as defined in equation (16), $H^*$ is the applied field at the centroid of the spectrum, $H$ is a general parameter and $H_0$ is the applied field. The asymmetries of the experimental curves tail to high field. Therefore the sign of $|\sigma_{\perp}-\sigma_{\parallel}|$ is positive.

The determination of $(\sigma_{\parallel}-\sigma_{\perp})$ defines $f(H_0-H^*)$ and for the broadening function, $S(H-H_0)$, the experimental curve at 2 MHz is used. Use of the experimental curve should provide a much better approximation to the field independent broadening than the assumption of a gaussian line shape having the extrapolated zero field second moment as has been done previously. The function was calculated using Program 3, Appendix I where it is expressed in a form suitable for computing. The constructed curves are shown in
Figure 10. Because of the relatively small anisotropy and the large (8.2 gauss) experimental broadening function, the synthesized curves are nearly symmetrical without even a hint of a shoulder. Trials showed that a reasonable approximation to the experimental line shape (up to 56.4 MHz) could be obtained by using a much smaller broadening function. This however was incompatible with the observed 2 MHz line shape. Finally the 94.1 MHz spectra were completely at variance with the concept of six like fluorines exhibiting axial symmetry of their shift tensors. The 94.1 MHz spectra show a minimum, but equation (21) cannot have a minimum within its range and non-equivalent fluorines must be present to account for the line shape. Naturally as the field is decreased the fit of synthesized to experimental curve in Figure 10 becomes progressively better from 30 MHz down until at 2 MHz it fits exactly. This at least demonstrates that the computer program works. The effectiveness of the program was further checked by its quite good fit of Rigny's (39) resolved components of UF₆.

The most probable of all possibilities was considered to be non-equivalent axial and equatorial fluorines which showed chemical shift anisotropy. However, when resolution was attempted at 94.1 MHz, the only frequency at which it was truly feasible to attempt resolution, the contours of the composite curve produced two components of area ratio 4:2, which were only very faintly asymmetrical, and had a relative shift of about 265 ppm. The shift exceeds the maximum value
Figure 10. $\text{WF}_6^+$. Asymmetrical reconstruction for 6-like fluorines.
of 220 ppm which is obtained in the absence of anisotropy. The resolution is scarcely different from the attempted resolution into symmetrical peaks. If the relative shift was kept below 220 ppm and the 4:2 area ratio still maintained, some very implausibly shaped components resulted which were disregarded. To anticipate slightly, if an average anisotropy of about 300 ppm is assumed, the relative shift must be about 105 ppm. If two similar curves of 4:2 area ratio are again constructed from the experimental 2 MHz curve then using the above anisotropies and relative shift, a fit to the experimental curve can again be made which is tolerable to 30 MHz but increasingly bad above. The computed component curves are so nearly symmetrical that even opposing their directions of asymmetry makes little change in the shape of the total curve. Indeed, the constructed curves are almost identical with those constructed in Figure 10 for the case of six like fluorines. The experimental 2 MHz broadening function is dominant in both cases.

Resolution was also attempted using opposed asymmetries as in Figure 11. The 94.1 MHz spectrum was resolved into two components - an area 4 curve at low field and tailing to high field and an area 2 curve at high field and tailing to low field. This seemed promising at 94.1, hopeful at 56.4, but clearly failing at 40 MHz, and hopeless at lower frequencies, even if the maximum 220 ppm shift was used.

In view of the above failures, non-axial symmetry of the shift tensor must also be considered possible. However separation is
Figure 11. WF₆. Resolution with opposed asymmetries

94.1 MHz

Solid line experimental
Broken line constructed

56.4 MHz

HIGH FIELD
0 5G

40 MHz
certainly not sufficient at 94.1 MHz to permit resolution of these more complicated line shapes. Attempts to do so were no better than in the preceding cases where axial symmetry was assumed.

Resolutions were also attempted with 5:1 and 3:3 area ratios of the components. They were conspicuously less successful even than the preceding attempts. There is also the possibility that there might exist more than two components. If this is the case resolution is utterly hopeless.

There is however one last attempt that can be made. If there is sufficient distortion in the molecule to permit a doublet interaction, both the minor change in line width as the field is varied and the distinct high field peak at 94.1 MHz might be explained. The doublet component must be to high field to produce the high field peak in the 94.1 MHz spectrum. One could not have a very broad doublet which might have its center of moments to low field of the centroid of the spectrum. That would make $r$, the separation between the nuclei involved impossibly small (from reference 52, p. 220, the doublet splitting in gauss is $3\mu r^{-3}$). Figures 12 and 13 show two possible resolutions at 94.1 MHz involving sets of four and two like nuclei in the components. Both resolutions, in part, produce quite plausible numbers. That in Figure 12 has two components which do not have any apparent anisotropy of chemical shift. Their isotropic shift is 220 ppm, just what is predicted by equation (20) in the absence of anisotropy. The components can be used as indicated
Figure 12. WF\textsubscript{6}. Reconstruction with doublet and symmetric singlet.
Figure 13. \( WF_6 \). Resolution with doublet and asymmetric singlet.
in the figure to construct curves whose slopes have some qualitative agreement with the experiment curves and which agreement is certainly no worse than in other attempts. The other doublet resolution, shown in Figure 13, involves a low field peak with a very strange asymmetry indeed. The relative, isotropic shift is about 115 ppm. If the low field, anisotropic component's second moment is plotted against the square of the field a value of \((\sigma_{\parallel} - \sigma_{\perp})^2 + 333\) ppm is found. Putting this value into the appropriate anisotropic term and remembering that the other anisotropic term is zero since the doublet is symmetrical, one obtains from equation (20) a relative shift of about 135 ppm. This is not bad agreement with the 115 ppm found experimentally. Obviously both of the resolutions involving doublets cannot be correct. In fact neither of them is. The doublet splitting is the same in each case. Estimated from the 94.1 MHz resolutions, it is 3 to 5 gauss giving internuclear separations of about 2.4 and 2.0 \(\AA\) respectively. In short, the internuclear distances in the doublet will be little different from those in the rest of the molecule and a distinct doublet could not be seen. This was verified using Program 4, Appendix I which is based on Abragam's doublet fitting procedure (52, p. 220). Using the parameters available from this work, the doublet could not be reproduced. There was only a rounded curve with no sign of doublet structure.

Finally it may be stated that the difficulty experienced in attempting the resolution of the WF6 spectrum can not be attributed
to electron coupling of the $^{19}$F and $^{183}$W in the solid. The contribution to the second moment from this splitting according to Gutowsky (63) is

$$S_i = \frac{1}{3} I_k (I_k + 1) \sum_{k \neq k}^L J_{2k}$$  \hspace{1cm} \text{(22)}$$

The coupling constant $J_{WF}$ measured by Rigny (42) is 43.8 Hz or 0.011 gauss. The addition to the second moment from this source will therefore be negligible.

The resolution trials are most unsatisfactory. None of the attempts gives a sure result and none is really any more plausible than any of the others. Blinc (41) seemingly encountered similar difficulty for, although he does show examples of resolved, asymmetric curves with approximate 4:2 area ratio for WF₆, he gives neither values for the anistropics obtained, nor a relative chemical shift for the components, nor a zero field second moment. From $T_1$ measurements he does give a value of $|\delta_{\text{rel}}| = 500 \pm 200$ ppm and states that this agrees within experimental error with the anisotropy determined from line width data. The range 500 to 700 ppm is clearly too high since it would give a negative value to the square of the relative chemical shift when applied to our data using equation (20). An upper limit to the average anisotropy is set by the value of 345$\pm$20 ppm obtained by assuming six like fluorines. This makes Blinc's lower limit of 300 ppm quite feasible. With our data this gives a relative shift between the components of about 105 ppm as noted earlier. It is not surprising that the curve is difficult to resolve if this is the case. Orders of magnitude are all that can be expected.
Our data give an upper limit of 220±10 ppm to the relative shift if there is zero anisotropy. The values of 300 ppm and 105 ppm for $(\delta_n - \delta_1)$ and $(\delta_4 - \delta_e)$ are of a reasonable order of magnitude therefore. They do not, unfortunately, permit accurate reconstruction of the experimental curves. Moreover, if the chemical shift anisotropy is some three times greater than the isotropic shift between the components, with both phenomena being field dependent, it is surprising that the 94.1 MHz spectra show an actual increase in resolution rather than merely a change in line shape. The doublet spectra in figure 12 really do behave qualitatively in a fashion very similar to the experimental spectra. Therefore, although it will be assumed that there are two asymmetric components of area ratio 4:2 corresponding to four equatorial and two axial fluorines at low and high field respectively, it would still be very interesting to see the $\text{WF}_6$ spectrum at 77°K and 200 MHz.

Even if an experiment were done at 200 MHz, it might not solve the resolution problem in $\text{WF}_6$, however. The attempts have all been based on the premise that if a resolution can be made at one field, the components will retain their distinct identities at other fields and using the observed chemical shift can be summed to give the experimental curves at those fields. In the case of extreme chemical shift as for one "component" arising from fluorine nuclei and another from hydrogen nuclei, there would be a clear resolution at high fields, the "components" would retain their identities at lower fields, and a "total curve" could be derived from the
"components" using the observed chemical shift. In the other extreme of identical nuclei, there will be no change arising from isotropic shift and the experimental curves can again be reproduced throughout the range of fields available. However, for the intermediate case in which similar nuclei are in components which are chemically shifted by a significant amount which is nonetheless smaller than the dipolar broadening, the component line shapes cannot be disentangled. For $\text{WF}_6$ at low fields there appear to be six essentially equivalent fluorines and at high fields two more or less distinct components with at intermediate fields a confusing mixture of the two extreme cases. The resolution attempts above have been presented in such detail mainly to emphasize one point: if resolution is not present in the experimental spectra it cannot be found by making reasonable attempts. The difficulty arises not from deficiencies in the experiment but from the nature of the interactions involved in intermediate cases of mixed isotropic and anisotropic chemical shifts.

3. Proposed Crystal Structure

A theoretical, rigid lattice second moment can be computed for comparison with the observed zero field or field independent second moment. No X-ray single crystal study of $\text{WF}_6$ has been published. The structure suggested here was based on the $\text{W}-\text{F}$ bond length of 1.833Å from Weinstock (37a) and crystal structure information in Table 1 supplied by Bartlett (37b) from a private communication from Siegel.
Table 1

Cell Parameters of UF₆

<table>
<thead>
<tr>
<th>Temperature (°K)</th>
<th>Cell Type</th>
<th>Parameters</th>
<th>ρ calc</th>
</tr>
</thead>
<tbody>
<tr>
<td>273</td>
<td>cubic</td>
<td>a=6.28 Å, V=247.7 Å³</td>
<td>3.99</td>
</tr>
<tr>
<td>253</td>
<td>orthorhombic</td>
<td>a=9.68 Å, V=434.1 Å³</td>
<td>4.56</td>
</tr>
<tr>
<td></td>
<td></td>
<td>b=8.81, c=5.09</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Z=4, space group Pnma?</td>
<td></td>
</tr>
</tbody>
</table>

Attempts to fit the four UF₆ molecules into the unit cell at 253°K produced what appeared to be unreasonable distortions and a suspicion arose that Pnma might be a transcription error for Pnma. Weinstock (77) may actually state that UF₆ is Pnma, but it is not quite clear whether he means that all the hexafluorides he discusses are Pnma or only that they are all orthorhombic. In any case it was decided to base the UF₆ second moment calculations on a Pnma structure for UF₆.

Hoarde and Stroupe (36) give the atomic coordinates, cell dimensions and bond lengths for UF₆ which are reproduced in Table 2.
Table 2

Atomic Coordinates, Cell Dimensions, and Bond Lengths of UF₆ at 298°K

<table>
<thead>
<tr>
<th></th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>U-F₁Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>U</td>
<td>0.1295</td>
<td>0.2500</td>
<td>0.081</td>
<td>-</td>
</tr>
<tr>
<td>F₁</td>
<td>0.014</td>
<td>0.093</td>
<td>0.250</td>
<td>2.01</td>
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<tr>
<td>F₂</td>
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<td>0.407</td>
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<td>2.01</td>
</tr>
<tr>
<td>F₃</td>
<td>0.246</td>
<td>0.407</td>
<td>-0.083</td>
<td>2.01</td>
</tr>
<tr>
<td>F₄</td>
<td>0.246</td>
<td>0.093</td>
<td>-0.083</td>
<td>2.01</td>
</tr>
<tr>
<td>F₅</td>
<td>0.003</td>
<td>0.250</td>
<td>-0.250</td>
<td>2.13</td>
</tr>
<tr>
<td>F₆</td>
<td>0.250</td>
<td>0.250</td>
<td>0.417</td>
<td>2.12</td>
</tr>
</tbody>
</table>

average 2.05

Orthorhombic, Pnma, Z=4, scale = 5.06
a=9.80, b=9.00, c=5.20Å

Since the ratios of the cell dimensions for WF₆ and UF₆ are approximately equal for each direction \((9.80 \sim 9.00 \sim 5.20 \sim 0.98\sim0.99)\) and Z=4 for both molecules, the same space group for both may be reasonable. The ratio of WF₆ to UF₆ cell volume is 0.95. The ratio of the respective molecular volumes computed for crude, spherical molecules including fluorine van der Waals radii is 0.82. In both cases the "spherical" volume exceeds the unit cell volume, but in the WF₆ case the excess is relatively less than in the UF₆ case. This would give the WF₆ molecule relatively more freedom to reorient and is consistent with a comparatively low temperature nmr transition at 200°K.

In computing the WF₆ structure, the coordinates of a uranium atom were chosen as a molecular origin. The atomic coordinates for the fluorine atoms in UF₆ were adjusted relative to this origin according to the following formulae to give coordinates for the
fluorine positions in WF$_6$.

(fluorine atomic coord. in WF$_6$-
origin atomic coord.) (cell dimension WF$_6$) = \frac{average U-F bond length}{average U-F bond length}

\begin{align*}
\frac{(X_{F_{WF6}} - 0.1295)(9.68)}{(X_{F_{WF6}} - 0.1295)(9.80)} &= 1.833 \\
\frac{(Y_{F_{WF6}} - 0.2500)(8.81)}{(Y_{F_{WF6}} - 0.2500)(9.00)} &= 1.833 \\
\frac{(Z_{F_{WF6}} - 0.081)(5.09)}{(Z_{F_{WF6}} - 0.081)(5.20)} &= 1.833
\end{align*}

The value $1.833\text{Å}$ given by Weinstock was taken as an approximation to the average of the possibly non-equal bond lengths in the low temperature phase of WF$_6$. The atomic coordinates for WF$_6$ calculated from equations (23) are given in Table 3.

**Table 3**

Calculated Atomic Coordinates and Bond Lengths for WF$_6$ at $253^\circ\text{K}$

<table>
<thead>
<tr>
<th></th>
<th>$x$</th>
<th>$y$</th>
<th>$z$</th>
<th>$U$-F $^\circ\text{Å}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$U$</td>
<td>0.1295</td>
<td>0.2500</td>
<td>0.0810</td>
<td>-</td>
</tr>
<tr>
<td>$F_1$</td>
<td>0.0250</td>
<td>0.1065</td>
<td>0.2354</td>
<td>1.80</td>
</tr>
<tr>
<td>$F_2$</td>
<td>0.0250</td>
<td>0.3935</td>
<td>0.2554</td>
<td>1.80</td>
</tr>
<tr>
<td>$F_3$</td>
<td>0.2349</td>
<td>0.3935</td>
<td>-0.0688</td>
<td>1.80</td>
</tr>
<tr>
<td>$F_4$</td>
<td>0.2349</td>
<td>0.1065</td>
<td>-0.0688</td>
<td>1.80</td>
</tr>
<tr>
<td>$F_5$</td>
<td>0.0150</td>
<td>0.2500</td>
<td>-0.2213</td>
<td>1.90</td>
</tr>
<tr>
<td>6</td>
<td>0.2386</td>
<td>0.2500</td>
<td>0.3879</td>
<td>1.90</td>
</tr>
</tbody>
</table>

$^\circ\text{Å}$

Orthorhombic, Pnma, $Z=4$

The positions are not of course accurate to the number of significant figures retained in this table.
Figure 14. \( \text{WF}_6 \). Proposed unit cell (along c-axis)

ATOMIC COORDINATES OF TUNGSTEN

1 \( 0.13, 0.25, 0.08 \)
2 \( -0.13, 0.75, -0.08 \)
3 \( 0.37, 0.75, 0.58 \)
4 \( 0.63, 0.25, 0.42 \)

Pnma

\[ \begin{align*}
    a &= 9.68 \text{ Å} \\
    b &= 8.81 \text{ Å} \\
    c &= 5.09 \text{ Å}
\end{align*} \]

CIRCLES INDICATE FLUORINE
Van der Waals radii
The symmetry operations of the Pnma space group give the other three positions in the unit cell. Figure 14 shows the proposed structure of WF$_6$ viewed along the c-axis.

4. Theoretical Rigid Lattice Second Moment

To provide nuclear positions for the second moment calculation a simple linear transform program (Program 5, Appendix I) was written. It translates the nuclear positions in one unit cell into positions in a block of unit cells around the original cell. In the computation of the rigid lattice theoretical second moment there is in addition to the assumption that a reasonable WF$_6$ structure at 253$^\circ$K can be derived from the UF$_6$ structure at 298$^\circ$K, the additional assumption that the results will be valid at 77$^\circ$K. The two hexalaurides are similar molecules and the temperatures at which the X-ray results are quoted are in each case rather roughly the same distance below the melting points of the respective compounds. The first is not an unreasonable approximation. The assumed WF$_6$ structure, however, is for a temperature above the nmr transition but is used at temperatures below the transition. This too is acceptable. X-ray spectroscopy and nmr spectroscopy are sensitive to different motional frequencies. As far as X-ray is concerned, the structure is essentially rigid and the nuclear positions at 253$^\circ$K may give a reasonable approximation to the positions at 77$^\circ$K if contraction of the lattice is not too great.

As will be noted later, thermodynamic evidence rules out the possibility of a crystal structure change between 77 and 253$^\circ$K (28).
Equation (2) gives the theoretical dipolar second moment for a rigid, polycrystalline solid. The first term applies to the F-F interactions, the second to the W-F interactions. The respective numerical coefficients are 316.8 and 0.27. When the 14% natural abundance of $^{183}$W, the only isotope of tungsten with a magnetic moment, is considered, the W-F factor becomes $\sim 0.04$. The contribution from W-F interactions is negligible and only F-F interactions need be summed in equation (2). The summation was carried out on the IBM 7040 using Program 6, Appendix I using the nuclear coordinates generated by Program 5 and was extended to a radius of 6Å from molecule number one (any one of the four) in the unit cell. Because of the $r^{-6}$ dependence of the second moment, it is sufficient to assume the remainder of the nuclei are uniformly distributed with known density throughout the rest of the sample (51, p. 160). If the number of nuclei between $r$ and $r+dr$ is $4\pi r^2 \rho dr$, where $\rho$ is the number of nuclei per unit volume ($Å^3$), the additional contribution is given by

$$S_{add} = \int_r^\infty (\text{numerical factor}) 4\pi r^2 \rho \frac{dr}{r^2} = (316.8) \frac{4\pi \rho}{3r^3} \quad \text{......... (24)}$$

The contributions to the total, theoretical rigid lattice dipolar second moment of 8.14 gauss$^2$ are given in Table 4.
Table 4

<table>
<thead>
<tr>
<th>Rigid Dipolar Second Moments of ( \text{WF}_6 ) at 77°K</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total Intramolecular Second Moment</td>
</tr>
<tr>
<td>Total Second Moment within 6Å</td>
</tr>
<tr>
<td>Contribution Outside 6Å</td>
</tr>
<tr>
<td>Total Theoretical Second Moment</td>
</tr>
<tr>
<td>Experimental Second Moment</td>
</tr>
</tbody>
</table>

Moderate distortion makes little difference to the second moment. The intramolecular moment calculated on the basis of six equal W-F bonds of length 1.833Å each is 4.31 gauss². The moment calculated for four short equatorial (1.80Å) and two long axial (1.90Å) bonds is 4.40 gauss² only slightly different.

The crystal structure assumed here receives some passive support from the count of internuclear interactions. The theoretical second moment program indicates that within a range of 6Å from the molecule chosen as origin, there are 152 F-F interactions. Of these, 12 interactions involve nuclei with separations of less than 2.70Å, twice the fluorine van der Waals radius. However, these interactions are all intramolecular. At least the structure has the advantage of having no intermolecular interactions less than the van der Waals radius. This of course does not say that other structures equally favourable do not exist. Considering that the structure is based on X-ray results obtained at 298°K, adjusted to 253°K, and applied at 77°K where thermal contraction might be significant, the very close agreement between theoretical and experimental second moments is
perhaps fortuitous. Nonetheless it is encouraging.

5. Reorientation in the Solid

Above the nmr transition around 180-210°K, the puzzling WF₆ line shape becomes symmetrical. Between this transition and the next around 265°K, the line width has a constant value of about 3.2 gauss at both 30 and 94.1 MHz. Clearly whatever field dependent broadening existed below 200°K, it is now averaged out. The second moment plot in figure 2 shows a drop from approximately 9 gauss² (8.2 gauss² at zero field) below the lower transition to 1.05±0.05 gauss² above the transition. Since the WF₆ molecule is approximately spherical, this drop in second moment to about 1 gauss² may be due to the onset of isotropic rotation of the molecule about its center of gravity. In this case the intramolecular second moment averages to zero and the only remaining contribution is from the intermolecular second moment (51, p. 173). For WF₆, the appropriate form of equation (6) for isotropic reorientation is

\[ S_{2, \text{iso-reor.}} = \frac{3}{4} \beta N_0 \sum_{i=1}^{N} R_i^2 \cdot (25) \]

Since this calculation concentrates the fluorine nuclei at the molecular centers, the sum is computed using Program 6 with the coordinates of the tungsten nuclei as the centers. The result corrected for nuclei at distances greater than 5A is 1.06 gauss². This is excellent agreement with the experimental value of 1.05±0.05 gauss², but Smith (64b) points out that random (non-isotropic) jumps
between equivalent positions can give a second moment different from the isotropic value by as little as 5 to 15%. Since the experimental value itself varies by 5%, it is impossible to state positively that an isotropic reorientation is taking place.

Weinstock (37a, 77) considers rotation in the solid is unlikely at the solid-solid phase transition (265 K for $\text{WF}_6$). He believes that for all the hexafluorides there is little difference between the cubic solid phase and the liquid, a belief which our results support, but that free rotation occurs in neither phase. The nmr results, however, appear to indicate a very considerable reorientation not only in the cubic phase, but also in the orthorhombic phase, some 65° below the solid-solid transition to the cubic phase. Admittedly there appears no sign of the transition in the vicinity of 200°K from thermodynamic data. The heat capacity curve for $\text{WF}_6$ is smooth with no break from 4°K to the point at which the transition to the cubic structure takes place (28). Since there is no change in thermodynamic properties, the second moment drop cannot be due to a change of crystal structure at 200°K. It must arise from reorientations which, considering the approach of the second moment to a value indistinguishable from that for isotropic reorientation, average out not only the two different fluorine sites, but also to a considerable degree the local fields as well. As Figure 14 and the count of internuclear distances in the theoretical second moment calculation demonstrate, the molecules in the $\text{WF}_6$ unit
cell interlock but do not overlap. There is clearly room for considerable restricted reorientation. Approximating the molecules as spheres of radius $3.18\text{Å} (\text{UF}_6 = 1.83 + \text{van der Waals F radius} = 1.35)$ gives a separation of $6.36\text{Å}$ between molecules for complete clearance. The separations between the centers of molecules 1, 2, 3, and 4 are 1-2, $5.68\text{Å}$; 1-3, $5.60\text{Å}$; 1-4, $5.14\text{Å}$; 2-3, $5.90\text{Å}$; 2-4, $8.92\text{Å}$; 3-4, $5.70\text{Å}$. The overlap encountered during isotropic reorientation would not be impossibly large but is rather substantial.

Weinstock's (77) evidence against a high degree of motion in the solid states of the hexafluorides is based in part on thermodynamic grounds. He gives the entropies of fusion for UF$_6$, NpF$_6$, and PuF$_6$ as $13.6$, $12.8$, and $13.7$ eu respectively. Since these values exceed Timmermans' (78) limit of $5$ eu for plastic globular compounds, he concludes that rotation below the melting point is unlikely for these hexafluorides. Cady (25) gives the entropy of fusion for UF$_6$ as $1.45$ eu. This value, which is well within the Timmermans' limit, would suggest that free rotation is possible. Weinstock points out that PtF$_6$ has an entropy of fusion of $3.2$ eu and would on this basis qualify as a plastic crystal and its solid-solid transition might be a consequence of the onset of rotation. However, the total entropy change associated with the two transitions, solid-solid and fusion, is only $7.7+3.2=10.9$ eu which is considerably less than the rotational entropy of the molecule in the vapour phase ($22.1$ eu at the fusion point). Since the $10.9$ eu total will include other as well as
rotational entropy, the total rotational entropy below the vapour phase will be even smaller than 10.9 eu. He believes that there is relatively little difference, with regard to rotation, between the cubic solid and the liquid and that free rotation does not occur in either case. Rotation at a lower transition would be even less likely then. Hence for UF₆ where the entropy of the solid-solid transition is 5.28 eu and the entropy of fusion is 1.45 eu for a total of 6.73 eu against a vapour phase rotational entropy of 21.8 eu, the same objections would apply.

However, both the 5d transition series hexafluorides, UF₆ and PtF₆, for which nmr results are available show "nmr transitions" well below their solid-solid transitions at 265⁰K and 276⁰K respectively. Blinc (41) places the UF₆ transition at about 200⁰K, as do we, and the PtF₆ transition at about 250⁰K. From equation (7) or (8) average frequencies νₕ of molecular reorientation may be obtained. From an Arrhenius-type plot of ln(νₕ) against 1/T⁰K, an activation energy for the reorientation may be determined. For the transition at 200⁰K there is an activation energy of 10.0±0.4 Kcal from second moment data and 15.0±0.9 Kcal from line width data. In accord with Powles (65), the value derived from second moment data is considered more reliable. The calculations were made using Program 7, Appendix I which was modified from Smith (79). The program gives a least squares fit to the experimental line width
data as used by Smith or to the second moment data as used here. The value 10.0 Kcal will include a slight error due to the anisotropy of the second moment, but it seems a very reasonable activation energy for molecular reorientation. It is in good agreement with the value of about 9 Kcal obtained by Blinc with $T_1$ measurements. Because of the abrupt nature of the transition at 265°K neither equation (7) nor (8) gives a meaningful activation energy for that change.

The thermodynamic and nmr results are not contradictory. The phenomena are responsive to different frequencies of reorientation. For the nmr experiment, a high degree of reorientation implies a frequency of reorientation of the order of the nmr line width, i.e. $10^4 - 10^5$ sec$^{-1}$; whereas the frequency of the reorientations must be of the order of $10^{11} - 10^{12}$ sec$^{-1}$ to affect the thermodynamic properties. It is consistent therefore for nmr to observe a transition which indicates a high degree of reorientation well below the solid-solid phase transition. Blinc's value of 1.8 gauss$^2$ above the nmr transition suggests that there may not be isotropic reorientation taking place above 200°K in $\text{WF}_6$. The value of $1.05 \pm 0.05$ gauss$^2$ obtained here suggests that as far as an nmr experiment can detect, isotropic rotation cannot be ruled out and, from the activation energy calculation, is occurring through a hindering potential barrier of 10 Kcal per mole.
The AsF₅ Adducts

In the case of the two AsF₅ adducts, there will obviously be non-equivalent fluorine nuclei present. As will be seen below, the equivalent fluorines are grouped as IF⁺ and AsF⁻ in the IF₇ • AsF₅ adduct and as SF⁺ and AsF⁻ in the SF₄ • AsF₅ adduct. There may well be non-equivalent fluorines within these groups, but there is no possibility of identifying them in a broad line nmr experiment when even the major non-equivalences are so small compared to dipolar broadening.

A. IF₇ • AsF₅

1. Results

Figure 15 shows the temperature dependence of the IF₇ • AsF₅ fluorine absorption spectrum at 30 MHz. As for the previous compound, the curves have a common x-scale and are integrated to a constant, arbitrary area from the derivatives. Reproductions of typical derivatives are given in Appendix IIIa. Figure 16 is a plot of the averaged second moments of the derivative curves. The second moment is constant at 11.6 ± 0.6 gauss² from 77°K up to about 205°K at which point the moment begins dropping until 2.1 ± 0.2 gauss² is reached at 235°K. It then remains constant up to 295°K, the highest temperature recorded. A preliminary line width study indicated no other transition from 77° to above 370°K (79a). At 77°K the spectrum tails to high field. By 174°K the spectrum appears to be approximately symmetrical and at 217°K, within the transition
Figure 15. $\text{IF}_6^{+}\text{AsF}_6^{-}$. Temperature dependence of absorption spectra at 30 MHz.
Figure 16. \( \text{IF}_6^+ \text{AsF}_6^- \). Temperature of second moment at 30 MHz.
region, it narrows and begins to tail to low field. At 295\(^{0}\)K the spectrum is much narrower and has a slight yet distinct asymmetry towards low field. As may be seen by examining the higher field spectra at 77 and 295\(^{0}\)K, this effect is indeed real. It does, however, present a distinct difficulty in deciding what is the line width between maximum and minimum on the derivative curve and for this reason no variable temperature line width plot is given.

2. Resolution into Components. Isotropic and Anisotropic Chemical Shifts

Figures 17a and 17b show the field dependence of the \(\text{IF}_7\cdot\text{AsF}_5\) absorption spectra at 300\(^{0}\) and 77\(^{0}\)K. Typical derivatives of the spectra are given in Appendices IIIb and IIIc. As Figure 17a demonstrates the spectrum at 94.1 MHz and 300\(^{0}\)K can be resolved into two quite symmetrical components. There is a comparatively broad component to low field and a narrow component at high field. The relative areas of the components are 1:1:1 and the isotropic chemical shift between them is 153±10 ppm. The components are equidistant on either side of the centroid of the total curve, which, from Figure 18, has a chemical shift of -54±8 ppm with respect to our \(\text{CF}_3\text{COOH}\) standard at 295-300\(^{0}\)K. The figure indicates that the shift of the centroid with respect to the reference at 300\(^{0}\)K is the same whether the adduct is at 77 or 300\(^{0}\)K.

The 1:1:1 ratio of the areas of the components implies that the twelve fluorines known to be present in the \(\text{IF}_7\cdot\text{AsF}_5\) adduct are
Figure 17a. $\text{IP}_6^+\text{AsF}_6^-$. Field dependence of absorption spectra at $295^\circ\text{K}$.
Figure 17b. $\text{IF}_6^+\text{AsF}_6^-$. Field dependence of absorption spectra at $77^\circ K$.
Figure 18. IF₆⁺AsF⁶⁻. Chemical shift of centroid of spectrum relative to CF₃COOH

\[ \delta = -54 \pm 8 \text{ ppm} \]

\( O = 295 \, ^\circ \text{K} \)
\( \Delta = 77 \, ^\circ \text{K} \)
arranged in two distinct groups of six fluorines each at 300°K. 
(For IF₇ and AsF₅ the ratio would have been 1.4:1). This 
supports the ionic formulation IF⁺₆ AsF⁻₆ suggested by Seel and 
Detmer (5) and confirmed by Beaton (10).

Figure 19 gives the field dependence of the line width 
at 77 and 295°K. For the 295°K spectra the slope of the plot 
is 140±25 ppm in agreement with the chemical shift determined 
from the resolved curves at 94.1 MHz. This confirms that the 
resolution does involve components which are not completely 
overlapped and which have no asymmetry. For IF⁺₆ AsF⁻₆ we may 
take \( \bar{\delta}_1 = \bar{\delta}_2 = \bar{\delta}_3 = \bar{\delta}_4 = \bar{\delta}_5 = \bar{\delta}_6 = \bar{\delta}_{As} \) and \( \bar{\delta}_7 = \bar{\delta}_8 = \bar{\delta}_9 = \bar{\delta}_{10} \) 
\( \bar{\delta}_{11} = \bar{\delta}_{12} = \bar{\delta}_1 \) where \( \bar{\delta}_{As} \) and \( \bar{\delta}_1 \) denote the mean isotropic 
shifts for fluorine atoms bonded to arsenic and iodine respec- 
tively. If, as the resolution at 94.1 MHz and Figure 19 
suggest, the asymmetry in the components is averaged out, 
equation (19) becomes

\[
S_2 = J_2(h) + \frac{H^2}{4} (\bar{\delta}_{As} - \bar{\delta}_1)^2
\]  

(26)

The relative positions of \( \bar{\delta}_{As} \) and \( \bar{\delta}_1 \) with respect to high or 
low field cannot be determined from this equation, but may be 
deduced from other considerations. It will be indicated later 
that the As-group is to high field of the I-group. From 
equation (26) and the slope of the 295°K line in Figure 20, 
which shows the field squared dependence of the second moment, 
the relative chemical shift between the components is 
\( (\bar{\delta}_{As} - \bar{\delta}_1) = 135±8 \) ppm. This is quite reasonable agreement with
Figure 19. $\text{IP}_6^+\text{AsF}_6^-$. Field dependence of line width at 77° and 295°K

○ = 295 °K
△ = 77 °K
Figure 20. $\text{IF}_6^+\text{AsF}_6^-$. Field squared dependence of second moment at $77^\circ$ and $295^\circ$K

- $\circ = 295^\circ$K
- $\Delta = 77^\circ$K
the value of 153±10 ppm from the resolution and confirms both the absence of anisotropy at 295°K and the accuracy of the resolution.

In Figure 17a, the broken curve has been constructed by shifting the two components resolved at 94.1 MHz relative to each other with a shift of 153 ppm. Although at low fields the constructed curve is taller than the experimental curve, line width is about the same and the constructed and experimental curves have very similar shapes. Evidently, in the region 235-295°K, the spectrum is composed of two distinct curves whose area ratios are a quite definite 1:1:1. From comparison of the line shapes of the components with those of the SF₄ • AsF₅ adduct, it is concluded that the tall component (second moment 0.7 gauss²) to high field is the AsF₆⁻ grouping and the short component (second moment 2.0 gauss²) to low field is the IF₆⁺ grouping. Confirmation comes from Christe et al (80), from whom a chemical shift of -126.6 ppm with respect to HF can be obtained for AsF₆⁻ in HF solution. In our work the shift of the centroid of the total IF₆⁺ AsF₆⁻ curve is -54±8 ppm with respect to CF₃COOH. The AsF₆⁻ peak is to high field and the mean shift between the components is 143±10 ppm. (The estimates of the shift range from 135±8 through 140±25, to 153±10 ppm). This places the AsF₆⁻ peak in solid IF₆⁺ AsF₆⁻ at -100±20 ppm relative to HF in fair agreement with Christe’s value. The IF₆⁺ group will be at -243±20 ppm relative to HF.

For the 77°K spectra to tail in the opposite direction to the high temperature spectra, anisotropy of chemical shift almost
certainly must be present at the lower temperature. As will be seen below when the \( \text{IF}^+ \text{AsF}^-_6 \) crystal structure is mentioned, the I-F and As-F bond lengths are quite similar. The groups are nearly identical in size and shape (there is a slight distortion in the As-group). When they are at 77°K because of the constancy of second moment between 77° and 205°K, they are both presumably rigid, they will have probably closely similar second moments of about 10.7 gauss\(^2\) each, the same value as the extrapolated zero field, dipolar second moment. This is verified below following Table 7 with the theoretical rigid lattice calculations of the second moment. (If all other factors are identical, the I-group should have a slightly greater second moment because of the greater magnitude of the F-I than the F-As interaction.) The line shapes too will be quite similar at 77°K and, in the absence of anisotropic shift, the total curve would be symmetrical. The direction of the asymmetry — to high field — gives a positive value to the anisotropies or at least to their net effect. They will almost certainly both be positive.

Figure 18 showed that the relative shift of the centroid of the total curve with respect to \( \text{CF}_3\text{COOH} \) was the same at 77° and 300°K. If we make the reasonable assumption that the relative shift between the components remains the same at both temperatures, an estimate can be made of the chemical shift anisotropy at 77°K by applying the equation

\[
\delta_1 = g_2(h) + \frac{4}{45}H_0^2\left(\overline{\delta_1} - \overline{\delta_1}\right)^2 + \frac{H_0^2}{4}\left(\overline{\delta_{\text{As}}} - \overline{\delta_1}\right)^2 \ldots (27)
\]
to the 77° line in Figure 20. From the upper limit of the relative shift of 153±10 ppm, the average shift of 143±10 ppm, and the lower limit of 135-8 ppm, average anisotropies of about 310, 333, and 355 ppm respectively are obtained. How closely the anisotropies of the individual groups approach the average value is difficult to say. The average itself appears to be of a reasonable magnitude since it is quite similar to the approximate 300 ppm for WF₆. The broken curve in Figure 17b shows curves reconstructed from two equal components of 10.7 gauss² second moment, having 333 ppm anisotropies, and with relative shift of 143 ppm. Since a gaussian broadening function has been applied to equation (16), the constructed curve is perhaps too narrow. Compared to the gaussian curve of the same second moment, the experimental zero field curve found for WF₆ was rather wider towards the top, but without such extensive wings. This would make the constructed curves in Figure 17b in somewhat better agreement with the observed shapes. However, the qualitative agreement with the experimental line shape is not bad considering the assumptions involved.

3. Crystal Structure

Beaton (10) has determined the structure of IF₆⁺ AsF₆⁻ from powder X-ray data, presumably at room temperature. His information is summarized in Table 5.
Table 5

X-Ray Powder Structure of IF₆⁺ AsF⁻₆ ~ 295°K

<table>
<thead>
<tr>
<th>Space Group</th>
<th>Pa₃ cubic</th>
<th>( a_0 = 9.4935 \pm 0.0005 \text{Å} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>atomic parameters</td>
<td></td>
<td></td>
</tr>
<tr>
<td>As in 4(a)</td>
<td>(0, 0, 0)</td>
<td></td>
</tr>
<tr>
<td>I in 4(b)</td>
<td>( \left( \frac{1}{2}, \frac{1}{2}, \frac{1}{2} \right) )</td>
<td></td>
</tr>
<tr>
<td>F in 24(d)</td>
<td>(x, y, z)</td>
<td>( x=0.0980; y=0.1377; z=-0.0489 )</td>
</tr>
<tr>
<td>F in 24(d)</td>
<td>(x, y, z)</td>
<td>( x=0.6001; y=0.5431; z=0.4411 )</td>
</tr>
</tbody>
</table>

| bond distances and angles | |
| As-F | 1.67Å* | F-As-F = 86.5° |
| I-F | 1.75Å* | F-I-F = 90° |

| intermolecular distances | |
| (3) F...F at 2.81Å | |
| (3) F...F at 2.95Å | |
| (3) F...F at 2.97Å | |
| (3) F...F at 3.04Å | |

*These distances may be too small. See text below.

Beaton points out that the bond lengths derived from his X-ray data may be rather short, the As-F length in particular. He ascribes this to his neglect of thermal motion when determining the bond lengths and suggests that such a correction might be 0.1Å or more. As evidence he cites Copeland et al \( (81) \) who found in a salt of AsF⁻₆ that the As-F bond length corrected for thermal motion was 1.77Å and uncorrected was 1.65Å. Trotter \( (82) \) considers that this appears a rather large correction for thermal
motion. However, if one arbitrarily applies a correction of 0.1Å to each of Beaton's bond lengths, both of them are still within the ranges given in the Interatomic Distances Supplement (83).

There, values of 1.71, 1.85, 1.80, and 1.83 are given for I-F bond lengths in IF₇, and 1.80±0.05Å for the As-F bond lengths in AsF₆⁻. In this last, the F-As-F angle is given as 88.3°±2.1°.

In Table 6 the first column of atomic coordinates contains Beaton's values, the second contains his coordinates adjusted for the 0.1Å increase in bond length. Only the first "molecule" in the unit cell is given, the symmetry operations will of course give the other three.

Table 6

<table>
<thead>
<tr>
<th></th>
<th>x Thermally Adjusted</th>
<th>y Thermally Adjusted</th>
<th>z Thermally Adjusted</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Beaton</td>
<td>Adjusted</td>
<td>Beaton</td>
</tr>
<tr>
<td>As</td>
<td>0.0000</td>
<td>0.0000</td>
<td>0.0000</td>
</tr>
<tr>
<td>F₁</td>
<td>0.0980</td>
<td>0.1039</td>
<td>0.1377</td>
</tr>
<tr>
<td>F₂</td>
<td>-0.0489</td>
<td>-0.0518</td>
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</tr>
<tr>
<td>F₃</td>
<td>0.1377</td>
<td>0.1460</td>
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</tr>
<tr>
<td>F₄</td>
<td>-0.0980</td>
<td>-0.1039</td>
<td>-0.1377</td>
</tr>
<tr>
<td>F₅</td>
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<td>-0.0980</td>
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<tr>
<td>F₆</td>
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</tr>
<tr>
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<td>0.6001</td>
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<td>F₁₂</td>
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<td>0.3487</td>
<td>0.5589</td>
</tr>
</tbody>
</table>

(1) "Thermally adjusted Beaton" means that the coordinate listed under "Beaton" has been increased to allow for an estimated +0.1Å thermal correction to the bond length.

(2) It is not meant to imply accuracy to four significant figures in this table.
4. Theoretical Rigid Lattice Second Moment

For \( \text{IF}_6^+ \text{AsF}_6^- \), equation (2) for the theoretical rigid lattice second moment will have a third term similar to the second. The numerical factors will be 316.8, 23.4, and 74.3 for the F-F, F-As, and F-I sums respectively. Table 7 gives the second moment contributions from calculations based both on Beaton's atomic coordinates adjusted for thermal motion and on his unadjusted coordinates. For Beaton's uncorrected values only the total second moment is shown. In calculating the second moments it has been assumed that the coordinates at 295\(^0\)K will be in reasonable approximation to those at 77\(^0\)K.

Table 7

<table>
<thead>
<tr>
<th>Rigid Lattice Second Moment Contributions to ( \text{IF}_6^+ \text{AsF}_6^- )</th>
</tr>
</thead>
<tbody>
<tr>
<td>From Beaton's adjusted coordinates</td>
</tr>
<tr>
<td>---------------------------------</td>
</tr>
<tr>
<td>( \text{IF}_6^+ \text{AsF}_6^- )</td>
</tr>
<tr>
<td>Total (including integral contributions over 6(\AA) of 0.35, 0.90, and 0.01 gauss(^2))</td>
</tr>
<tr>
<td>( \text{IF}_6^+ \text{AsF}_6^- ) INTRA</td>
</tr>
<tr>
<td>( \text{AsF}_6^- ) TOTAL (to 6(\AA))</td>
</tr>
<tr>
<td>( \text{AsF}_6^- ) INTRA</td>
</tr>
<tr>
<td>( \text{IF}_6^+ ) TOTAL (to 6(\AA))</td>
</tr>
<tr>
<td>( \text{IF}_6^+ ) INTRA</td>
</tr>
</tbody>
</table>

| From Beaton's coordinates (10) |
|---------------------------------
| \( \text{IF}_6^+ \text{AsF}_6^- \) TOTAL (including above integral contributions) | 10.68 | 0.54 | 1.34 | 12.56 |

Extrapolated Zero Field
Second Moment

Note: All contributions in this table are based on a 12-fluorine \( \text{IF}_6^+ \text{AsF}_6^- \) unit. \( N \) in equation (2) has been taken as 12 for all groups.
Zero point vibrational motion would decrease the theoretical second moment somewhat, but contraction of the crystal lattice between 295°K, where the structure was determined and 77°K where it was applied to the calculation of the theoretical moments would increase the values somewhat more. The good agreement between the theoretical second moment based on the adjusted coordinates and the zero field second moment indicates that the "thermal correction" was probably of the right order. The probable bond lengths therefore are of the same order as those listed in the Interatomic Distances Supplement as Beaton suggested, and are longer than those he reported.

The contributions of the IF$_6^+$ and AsF$_6^-$ groups to the total second moment (up to 6° radius from the center of the relevant group) are 5.01 and 5.13 gauss$^2$ respectively. Since these are based on a 12 fluorine unit, the values must be multiplied by $12/6$ to obtain the second moments the individual components would have if they could be resolved out at 77°K. This gives 10.20 and 10.44 gauss$^2$ respectively when the contribution for distant nuclei is included. Both values are in good agreement with the 10.7 gauss$^2$ assumed above for the attempted reconstruction of the experimental curves in Figure 17b.

5. Reorientations in the Solid

Above their respective nmr transitions all three of the IF$_6^+$, AsF$_6^-$, and WF$_6$ groups exhibit symmetrical spectra. Below the transition the WF$_6$ spectra exhibit asymmetry presumably both because of anisotropy of the shift tensors and because of the non-equivalent sites of the axial and equatorial fluorines in the molecule. In WF$_6$
above the transition, motions average out both the chemical shift anisotropy and the mean isotropic shift between the non-equivalent fluorines, to give a single, symmetrical line. Similar motions are likely involved above the transition in IF$_6^+$ AsF$_6^-$ which is also around 200°K. In the case of the salt, there are two symmetrical, but distinct components above the transition. Whatever motions occur can average out only the anisotropic shift and non-equivalences (if present) within each different ion. The differences between the fluorines attached to the cation and those attached to the anion are a consequence of their bonding to the respective I and As atoms and are not averaged out. The relative shift between the ions therefore remains regardless of the degree of reorientation.

With regard to the actual reorientations which are occurring above the transition, it appears that that AsF$_6^-$ is undergoing more extensive motion than the IF$_6^+$ ion. Its second moment at 295°K is about 0.7 gauss$^2$, a value quite consistent with isotropic reorientation about its center of mass. The IF$_6^+$ component, however, has a broader line and a greater second moment, 2.0 gauss$^2$. In explaining or at least rationalizing the rigid lattice line shape, we stated that both the IF$_6^+$ and AsF$_6^-$ component line shapes would probably be similar since the two ions were similar in size and geometry. This is satisfactory in the rigid lattice, but would appear true also at higher temperatures since the two groups presumably will experience and be influenced equally by the same barrier to reorientation. The more frequent reorientation exhibited at 295°K by the AsF$_6^-$ than the
IF$_6^+$ group may be a consequence of the shorter As-F bond length. About any axis of rotation, the moment of inertia of the AsF$_6^-$ ion is some 10% less than that for the IF$_6^+$ ion. This estimate was made using regular octahedra. In fact the AsF$_6^-$ octahedra are distorted (10). The compression, however, is along a $\bar{3}$ axis. The effect merely squeezes the faces of the octahedra together and the centers of mass still coincide with those of the As atoms so that the As atoms still make no contribution to the moments of inertia. Although the moment of inertia is increased for rotation about the $\bar{3}$ axis, it is reduced for rotation about an axis at right angles to the $\bar{3}$ axis along which compression occurs. Since qualitatively one expects a reorientation to occur preferentially about the axis with the least moment of inertia, then it will take place about this last axis where the moment is even less than in the undistorted case. Hence the AsF$_6^-$ ion undergoes more frequent reorientation at 295°K than the IF$_6^+$ ion.

The above view is confirmed by Das (84) who points out that the probability of transition from one potential well to the next over an n-fold barrier is

$$W = W_c + W_t$$

(28)

where $W_c$ and $W_t$ are the probabilities for classical rotation over the barrier and quantum mechanical tunneling through the barrier respectively. Since for all rotating groups other than those involving only protons $W_t$ is negligible, the probability reduces to

$$W = W_c = \frac{n}{2\pi} \left( \frac{V_0}{I_{eff}} \right)^{1/2} e^{-V_0/kT}$$

(29)
where $I_{\text{eff}}$ is the effective moment of inertia and where $V_0$, the activation energy or height of the hindering potential barrier, may be determined from equation (8). From equation (29), it is obvious that the smaller $I_{\text{eff}}$, the greater is the probability of reorientation. Hence the $\text{AsF}_6^-$ group can logically be expected to undergo more frequent reorientation than the $\text{IF}_6^+$ group at a given temperature, provided that the temperature is high enough for the motion to occur. Although the above qualitatively predicts a higher probability for $\text{AsF}_6^-$ reorientation, the actual probabilities differ by less than 10%. It may be that, contrary to the assumption above, the groups do encounter different barriers with the $\text{AsF}_6^-$ barrier to reorientation being the lesser.

The narrow $\text{AsF}_6^-$ line with its 0.7 gauss$^2$ second moment can be accounted for at 295 K by assuming isotropic reorientation of the group as noted earlier. The broader line of the $\text{IF}_6^+$ component has a second moment of 2.0 gauss$^2$, however, which is clearly much higher than the 1 gauss$^2$ value predicted for isotropic reorientation. It is too high also for reorientation at random about the symmetry axes of the octahedral group. This would have the effect that each fluoride spent 1/6 of its time at each position and would reduce the second moment to a value only slightly larger than that for isotropic reorientation (63). As noted in equation (5), reorientations about a single symmetry axis reduce each contribution to the intragroup dipolar broadening by a factor $\frac{1}{2} (3 \cos^2 \Theta_{jk} - 1)^2$ where $\Theta_{jk}$ is the angle between the internuclear vector $\Sigma_{jk}$ and the axis of rotation.
This factor holds for stepwise reorientation about an n-fold axis with \( n \geq 3 \) and for classical rotation about any axis (57). For the \( \text{IF}^+ \) ion there are two -, three -, and fourfold symmetry axes about which reorientation might occur. The intragroup second moments for \( \text{IF}^+ \) are 2.04, 2.17, and 1.93 gauss\(^2\) respectively for reorientations about the \( C_2 \), \( C_3 \), and \( C_4 \) axes. In addition to this intragroup contribution there will be an intergroup contribution. The \( \text{AsF}_6^- \) group appears to be undergoing an isotropic reorientation in which its intragroup second moment would be averaged to zero. Therefore its 0.7 gauss\(^2\) second moment is due entirely to intergroup interactions and can be used to estimate an intergroup second moment for the similar \( \text{IF}^+ \) group. This makes the total second moments of the cation 2.74, 2.87, and 2.63 gauss\(^2\) for \( C_2 \), \( C_3 \), and \( C_4 \) reorientations. All these exceed the experimental value of 2.0 gauss\(^2\) by more than 30%. The actual motion which \( \text{IF}^+ \) is undergoing must therefore be less than reorientation about octahedral axes at random but greater than reorientation about a single axis. Perhaps the motion is a combination of reorientation about one axis and simultaneous oscillation about another. This implies that different reorientational barriers may exist for the \( \text{IF}^+ \) and \( \text{AsF}_6^- \) ions.

The average activation energy for the combined motions was determined from an Arrhenius plot of equation (8) to be 19.4 Kcal per mole. This energy is very high. Because of the scatter in Figure 16 of the points just below the transition; it is possible that the change in second moment as drawn is sharper than it really is. A less
abrupt transition would have a lower activation energy. If the transition is indeed this abrupt, the activation energy found may not be valid. Instead of a change in motion within a solid phase of fixed crystal structure, the transition may mark an actual crystal transition.

\[ \text{B. } SF_4 \cdot AsF_5 \]

1. Results

Figure 21 shows the temperature dependence of the $SF_4 \cdot AsF_5$ absorption spectrum at 30 MHz. The absorption curves have the same x-scale and are integrated to a constant, arbitrary area from the derivative curves. Appendix IVa contains reproductions of the actual derivatives including some for temperatures higher than the highest value shown in Figure 21. Figure 22 is a plot of the temperature dependence of the averaged second moments at 30 MHz. The second moment does not appear to achieve a rigid lattice value by 77°C, the lowest temperature reached in the study. At 77°C the second moment is $5.9 \pm 0.3$ gauss$^2$. From that temperature it drops gradually in a smooth curve to $1.85 \pm 0.1$ gauss$^2$ around 200°C. The second moment remains constant at this value until 336°C. Throughout the region from 77 to 336°C, the 30 MHz absorption spectra are almost symmetrical, with a slight tailing to low field. Above 336°C the absorptions were so narrow that the integrated spectra were not plotted. The derivative curves in Appendix IVa show a marked increase in motion beginning at 336°C. The derivative at 320°C is similar to that at 295°C, which shows a shoulder on the low field half of the
Figure 21. $\text{SF}_2\text{AsF}_6^-$. Temperature dependence of absorption spectra at 30 MHz.
To Follow Page 69

Figure 22. SEDP - Temperature dependence of second moment at 30 MHz,
derivative. The spectra at $336^\circ$ have a very general similarity in shape and a similar second moment to those at $320^\circ$, but the shoulder has now become a narrow component. Second moment drops at $336^\circ$ to a value of about 0.1 gauss$^2$ by $342^\circ K$. Between $342^\circ$ and $373^\circ K$, the highest temperature recorded, the second moment remains constant. By $342^\circ K$ there is an almost complete resolution of the spectrum into two components with an isotropic chemical shift of 97.5 ± 5 ppm. The resolution is slightly better at $373^\circ K$, but the chemical shift is exactly the same.

Appendix IVa as noted above shows the temperature dependence of the derivative line at 30 MHz. The gradual shift of the low field shoulder towards high field changes the line shape in a manner which makes it difficult, as with IF$_6^+$ AsF$_6^-$, to define a consistent peak to peak line width from the derivative. For this reason no plot of variable temperature line width is given.

The chemical shift for the total curve with respect to CF$_3$COOH is given in Figure 23. Although it appears that there might be a temperature dependence of the shift relative to CF$_3$COOH at 300$^\circ$K, the scatter is so great that it cannot be established. The shift determined from Figure 23 is $-40 \pm 15$ ppm.

2. Resolution with Components (see Results also). Isotropic and Anisotropic Chemical Shift.

Figures 24a and b show the field dependence of the absorption spectra at 300$^\circ$K and 77$^\circ$K. Appendices IVb and IVc give the derivative curves for these spectra figure 24a demonstrates that one can make a
Figure 23. $\text{SF}_2\text{AsF}_6^-$. Chemical shift of centroid of spectrum relative to $\text{CF}_3\text{COOH}$

\[ \text{Mean Isotropic Shift (Gauss)} \]

\[ \text{Field (} H_0 \text{) (Gauss)} \]

- $\bar{\sigma} = -40 \pm 15 \text{ ppm}$
- $\bigcirc = 300 ^\circ K$
- $\bigtriangleup = 77 ^\circ K$
Figure 24a. $\text{SF}^+_3\text{AsF}_6$. Field dependence of absorption spectra at $300^\circ\text{K}$

Solid line experimental
Broken line constructed

HIGH FIELD $\rightarrow$

0 5 G

94.1 MHz

56.4 MHz
40 MHz
30 MHz
Figure 24b. $\text{SF}_3^4\text{AsF}_6^-$. Field dependence of absorption spectra at 77 K.
resolution of the curve at 300°K and 94.1 MHz. The ratio of the area under the tall, high field peak to that under the short, low field peak is 2.2:1, from which it is concluded that there are twice as many fluorines involved in the high field peak as in the low field. Hence at 300°K the SF$_4$ $\cdot$ AsF$_5$ adduct is probably the ionic salt SF$_3^+$ AsF$_6^-$ for the experimental ratio of areas under the components is greater than 6:3, not between 6:3 and 5:4. The high field component has a second moment of about 0.9 gauss$^2$ and the low field component one of 1.1 gauss$^2$. The relative chemical shift between the two components as resolved at 94.1 MHz and 300°K is 105±10 ppm in agreement with the value determined in the 30 MHz spectra at 342°K and above. The components at 300°K obtained from the resolution of the 94.1 MHz spectrum, are each symmetrical about their centers with no suggestion of asymmetry. As shown by the broken lines in Figure 24a the components, with a shift of about 100 ppm, give a reasonable reproduction of the experimental spectrum at each lower frequency investigated. From the approximate 100 ppm shift between the components and the -40±15 ppm shift of the total curve with respect to CF$_3$COOH at 300°K, the shifts of the components with respect to any standard can be determined. Relative to HF the high field component is at -107±20 ppm and the low field component at -207±20 ppm. Since the AsF$_6^-$ ion is common to both the AsF$_5$ adducts, it is undoubtedly the peak found at about -100±20 ppm in each. The cation in each adduct is then the low field component in each case.
It is also possible to make a resolution into components at 94.1 MHz and 77 K. The resolution was based on the contours of the curve and the assumption that the line shapes of the components would be roughly similar at 77 and 300 K. Two fairly symmetrical components are obtained with a relative shift of 185±20 ppm which might be "squeezed" to 160±20 ppm but no more. As indicated later even this value may be too great. The area of the taller, high field curve (AsF\textsuperscript{−}) to that of the shorter, low field curve (SF\textsuperscript{3}+) is 1.9:1, again providing support for the 2:1 area ratio required by the ionic formulation of the adduct. The AsF\textsuperscript{−} component has a second moment of 2.8 gauss\textsuperscript{2}, the SF\textsuperscript{3}+ component one of 4.7 gauss\textsuperscript{2}. Shifting the two curves appropriately gives a reasonable reproduction of the line shapes at lower frequencies as indicated by the broken curves in Figure 24b.

Figure 25 shows the field squared dependence of the second moment at 300 and 77 K. Since there was no asymmetry evident in the resolved components at either temperature, the field squared dependence of the second moment must be due entirely to the mean, isotropic chemical shift. Since $\tilde{\delta}_1 = \tilde{\delta}_2 = \tilde{\delta}_3 = \tilde{\delta}_5 = \tilde{\delta}_6 = \tilde{\delta}_7 = \tilde{\delta}_8 = \tilde{\delta}_9 = \tilde{\delta}_{As}$ where the S and As refer to the fluorine shift in SF\textsuperscript{3} and AsF\textsuperscript{−} respectively, and there is no detectable anisotropy present, equation (19) becomes

$$S_z = g_z(h) + \frac{2}{4} H_0^2 (\tilde{\delta}_{As} - \tilde{\delta}_S)^2$$

(30)

From equation (30) the 300 K line gives a value of the relative shift of 87±10 ppm in good agreement with the two other values for 295 K and
Figure 25. $\text{SF}_3\text{AsF}_6^-$: Field squared dependence of second moment at 77° and 300°K.
above. Indeed, because of the small slope of the second moment line, a change of only \( +0.2 \) gauss\(^2\) in the average second moment at 94.1 MHz would bring this shift up to about 100 ppm in even closer agreement with the values found by resolution of the spectra. From the \( 77^0K \) line on isotropic shift of \( 110\pm10 \) ppm is obtained. This agreement with the value at \( 300^0K \) confirms that there is no anisotropy at \( 77^0K \). It also suggests that the resolution at \( 77^0 \) may be in error. Although the shape of the experimental curve appears to dictate components with a shift of at least \( 160\pm20 \) ppm, in the absence of resolution in the experimental curve itself, there is certainly room for error. Probably the \( 110\pm10 \) ppm value from Figure 25 is more reliable.

3. Proposed Crystal Structure

No X-ray study is available for \( SF_3^+ AsF_6^- \). Some information is available for \( SF_4^- SbF_5^- \), enough to make a guess at the structure of \( SF_3^+ AsF_6^- \). In the absence of a rigid lattice second moment for comparison with the theoretical moment for the model, the guess must be rather tentative.

Bartlett (6) has determined a crystal structure from powder data for \( SF_4^- SbF_5^- \). The determination was not fully completed but the symmetry suggested an ionic formulation \( SF_3^+ SbF_6^- \). Muetterties (85) also suggested the ionic formulation for the adduct as the most likely of two possible structures. Bartlett's information is summarized in Table 8.
Table 8

X-Ray Data for SF\textsuperscript{+}_3 SbF\textsuperscript{-}_6 at 291°K

Simple cubic  \[ a = 5.625 \pm 0.002 \AA \]

\[ = 178 \AA^3, \ \rho_{\text{obs}} = 3.1 \pm 0.1, \ \rho_{\text{calc}} = 3.03, \ Z=1 \]

The Interatomic Distances Supplement (83) gives an Sb-F (single crystal) bond length of 1.78\AA, and in the bond length range noted earlier an As-F (powder) length of 1.80\AA. The SbF\textsuperscript{-}_6 and AsF\textsuperscript{-}_6 groups will have nearly the same symmetry and volume then and the SF\textsuperscript{+}_3 SbF\textsuperscript{-}_6 structure may be a reasonable approximation to the SF\textsuperscript{+}_3 AsF\textsuperscript{-}_6 structure. However the atomic coordinates are not known for SF\textsuperscript{+}_3 SbF\textsuperscript{-}_6 and a further approximation must be made. The AsF\textsuperscript{-}_6 groups may be placed at the corners of the simple cubic cell. They could be approximated for the purposes of a second moment calculation as spheres (86) since the orientations of the octahedra in the cell are unknown. However, Program 6 is designed to use nuclear coordinates and the (0, 0, 0) AsF\textsuperscript{-}_6 group from IF\textsuperscript{+}_6 AsF\textsuperscript{-}_6 was chosen after considerable trial and error with a model. Octahedra having this orientation were placed at the four corners of the cell. The SF\textsuperscript{+}_3 group will be in the center of the cell at \((\frac{1}{2}, \frac{1}{2}, \frac{1}{2})\), but it is unlikely (82) that the sulfur atom will be at the exact center. The group was placed so that the three fluorines were in an equilateral triangle centered on \((\frac{1}{2}, \frac{1}{2}, \frac{1}{2})\) and parallel to the a-b plane of the cell. Then the sulfur atom and its lone pair can fit along the vertical axis passing through \((\frac{1}{2}, \frac{1}{2}, \frac{1}{2})\). In the model it appeared that
the $\text{SF}_3^+$ group could rotate quite freely about the $C_3$ axis through the $S$ atom and $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$. Table 9 gives the atomic coordinates calculated for the assumed $\text{SF}_3^+ \text{AsF}_6^-$ unit cell at "291°K" and applied at 77°K. In determining the coordinates for the $\text{AsF}_6^-$ groups, As-F bond lengths of 1.77\AA, as for the previous adduct, were used. Figure 26 shows a view

<table>
<thead>
<tr>
<th>Table 9</th>
</tr>
</thead>
<tbody>
<tr>
<td>Estimated Atomic Coordinates for $\text{SF}_3^+ \text{AsF}_6^-$ at &quot;291°K&quot;</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Atom</th>
<th>x</th>
<th>y</th>
<th>z</th>
</tr>
</thead>
<tbody>
<tr>
<td>As</td>
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<td>0.0000</td>
<td>0.0000</td>
</tr>
<tr>
<td>F_1</td>
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<td>0.2464</td>
<td>-0.0874</td>
</tr>
<tr>
<td>F_2</td>
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<tr>
<td>F_3</td>
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<td>-0.0874</td>
<td>0.1754</td>
</tr>
<tr>
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<tr>
<td>F_5</td>
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<td>-0.2464</td>
</tr>
<tr>
<td>F_6</td>
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<td>0.0874</td>
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</tr>
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<td>0.5000</td>
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<tr>
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<td>F_8</td>
<td>0.7614</td>
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<tr>
<td>F_9</td>
<td>0.3693</td>
<td>0.7264</td>
<td>0.5000</td>
</tr>
</tbody>
</table>

It is not meant to imply accuracy to four significant figures.

down the a-axis for the proposed structure.


The theoretical rigid lattice second moment for $\text{SF}_3^+ \text{AsF}_6^-$ calculated by Program 6 from the above coordinates in 9.4 gauss^2. Only contributions from F-F and F-As interactions need be summed since the natural abundance of $^{33}\text{S}$, the only stable, magnetic isotope of sulfur is so low (0.74%) that F-S interactions are negligible. There are a great many assumptions involved in the calculation and no experimental value is available as a
Figure 26. $SF_3^+\text{AsF}_6^-$. Proposed unit cell (along a-axis)

- PROPOSED POSITION OF As AT CORNERS
- PROPOSED POSITION OF 'S AT $(1/2, 1/2, 1/2)$

$P 23 \ a_0 = 5.6 \text{ Å}$

CIRCLES INDICATE FLUORINE
Van der Waals radii
check. Indeed the count of internuclear distances which Program 6 can provide shows that the SF$_3^+$ ion is somewhat crowded in its assumed position. There are four SF$_3^+$ intergroup contacts with surrounding AsF$_6^-$ ions. Two are not too severe being 2.5 and 2.6 Å, but the other two are 2.2 Å well under twice the 1.35 Å fluorine van der Waals radius. Inspite of this the calculated second moment seems of a reasonable magnitude. The various contributions to the total second moment are listed in Table 10.

**Table 10**

<table>
<thead>
<tr>
<th>&quot;Rigid Lattice&quot; Second Moment Contributions to SF$_3^+$ AsF$_6^-$</th>
<th>Second Moment Gauss$^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>F-F</td>
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<tr>
<td>SF$_3^+$ AsF$_6^-$ TOTAL (including integral contribution over 6 Å of 0.31 gauss$^2$ to F-F)</td>
<td>8.80</td>
</tr>
<tr>
<td>SF$_3^+$ AsF$_6^-$ INTRA</td>
<td>4.72</td>
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<tr>
<td>AsF$_6^-$ TOTAL (to 6 Å)</td>
<td>5.96</td>
</tr>
<tr>
<td>AsF$_6^-$ INTRA</td>
<td>3.62</td>
</tr>
<tr>
<td>SF$_3^+$ TOTAL (to 6 Å)</td>
<td>2.63</td>
</tr>
<tr>
<td>SF$_3^+$ INTRA</td>
<td>0.77</td>
</tr>
</tbody>
</table>

Note: All contributions in this table are based on a 9-fluorine unit SF$_3^+$ AsF$_6^-$. N in equation (2) has been taken as 3 for all groups.

5. Reorientations in the Solid

One thing to notice in Table 10 is that total second moment for the component SF$_3^+$ curve, if it could be resolved out, is
2.64 \times \frac{9}{3} = 7.9 \text{ gauss}^2 \text{ while its intragroup second moment is only } 0.77 \times \frac{9}{3} = 2.3 \text{ gauss}^2. \text{ In determining positions in the SF}_3^+ \text{ ion, it was assumed in agreement with Bartlett (6) that because of the electron lone pair on the sulfur, the ion would have an approximately tetrahedral configuration. Therefore S-F bond lengths of 1.56 \text{ Å} (83) and F-S-F angles of } 109^\circ \text{ 28'} \text{ were used. The presence of a lone pair will repel the three bond pairs somewhat more than a bond pair (7). The bond angle will therefore be somewhat less than the tetrahedral angle. This would reduce the intra-group F-F distances of 2.59 \text{ Å} \text{ and would hence reduce the rather heavy proportion of inter } (7.9 - 2.3 = 5.6 \text{ gauss}^2) \text{ to intra-group second moment } (2.3 \text{ gauss}^2) \text{ in the SF}_3^+ \text{ ion. A position in the unit cell which tilted the ion away from its assumed position would also change the second moment. However, reducing the tetrahedral angle would reduce the effective volume of the ion and give it more freedom in the AsF}_6^- \text{ "cage" consistent with its considerable motion as low as } 77^\circ \text{ K. The most probable motion at } 77^\circ \text{ is reorientation about the C}_3 \text{ axis. The shrinkage of the ion due to the smaller bond angle would also reduce the moment of inertia about this axis and further enhance the ion's ability to reorient.}

The calculated zero field rigid lattice second moment is about 9.4 \text{ gauss}^2 \text{ yet the experimental moment at 30 MHz and } 77^\circ \text{ K, which includes a contribution from isotropic chemical shift, is only 5.9 \text{ gauss}^2. The theoretical zero field anion and cation resolved curves would have second moments of about } 6.47 \times \frac{9}{6} = 9.7 \text{ gauss}^2 \text{ and } 7.9 \text{ gauss}^2 \text{ respectively if they could be measured at their rigid lattice.}
temperature. Their actual resolved components at 77°K and 30 MHz have moments of 2.8 gauss$^2$ and 4.7 gauss$^2$. Obviously by 77°, the motion in the groups is sufficient not only to average out the anisotropy (since the components are symmetrical), but also to partially average out the dipolar interactions. By 220°K the total second moment of the experimental 30 MHz curve has fallen to about 1.9 gauss$^2$. Since there is no anisotropy in this region above the transition; the resolution into components made at 94.1 MHz and 300°K will be valid here too (there is virtually no change in line shape from 200 to 295°K at 30 MHz). The second moments are 1.1 gauss$^2$ and 0.9 gauss$^2$ for the SF$^+$ and AsF$_6^-$ ions respectively. The anion surely and the cation very likely are undergoing isotropic or near isotropic reorientation above the transition.

In the absence of a rigid lattice second moment, it is impossible to obtain a reliable activation energy for the transition. One can of course estimate a reasonable value for the experimental rigid lattice second moment at 30 MHz (at which frequency the temperature dependence studies were made) and eventually arrive at an activation energy. This was done and an energy of about 1 Kcal per mole obtained. It is of course an even cruder estimate than one normally obtains from second moment studies.

The transition between 336 and 342°K is too abrupt to give a meaningful activation energy. The value of the total second moment
is about 0.1 gauss^2 which includes the contribution from relative shift between the ions. Diffusion of the ions is probably taking place through the solid. Although the sample is rather plastic looking at 373^0K, it remains solid and does not melt even when held at that temperature for several hours.
CHAPTER V

SUMMARY AND DISCUSSION

It is difficult to obtain precise results for the three compounds studied. This is particularly so with WF₆. The most probable resolution of that compound is into two components separated by a mean isotropic shift of 105 ppm and each with an average anisotropic shift of 300 ppm. Since no accurate resolution could be made, no values were quoted for the zero field, dipolar broadening of each. From the theoretical rigid lattice second moment, the contributions of the axial and equatorial fluorines to the total second moment for the molecule are 2.71 gauss ² and 5.44 gauss ² respectively. Weighted according to the relative numbers of fluorines involved in each, they would give 8.14 gauss ² for each component if they could be resolved out. These second moments are virtually identical to the second moment of the observed zero field curve (actually at 2 MHz) which was used as a broadening function (components weighted 4:2 by area) in the attempted reconstruction based on the shifts mentioned immediately above. It was assumed that the individual line shapes would be similar to that of the total curve at zero field. The second moment, however, says nothing about line shape. Line shapes are much more difficult to predict than are second moments, which, of course, is the difficulty here.

For the two AsF₅ adducts resolution into components can be made and relative shifts determined. However, even for IPr AsF₆ only average anisotropies could be estimated for the two components. No reliable value at all could be obtained for SF₅ AsF₆ since a rigid
lattice was not found within the temperature range of the investigation.

All three of the compounds showed a transition in the second moment curve around 200°K from which activation energies of varying reliability were determined for the probable reorientations occurring. The type of reorientation was deduced from the magnitude of the change in the second moment of the total curve or resolved component.

Table 11 summarizes what are considered to be the best values obtained here for the isotropic and anisotropic shifts, second moments, transition temperatures, and possible reorientations in the solids. All these have been discussed in detail earlier.

Finally, it is possible from the anisotropic and mean isotropic chemical shifts to draw some conclusions about bond character in the hexafluoride groups. For fluorine, the principal contribution to chemical shift is from the paramagnetic term in equation (10) according to Saika and Slichter (70) and Karplus and Das (88). Following their treatment, Andrew (71) has expressed the chemical shift in terms of localized bond parameters $I, \rho$, and $s$ which are respectively the ionic character, double bond character, and degree of sp hybridization in the bond orbital. Then for a fluorine atom bonded in the z-direction, the principal values of the paramagnetic contribution to the chemical shift tensor are

$$
\sigma_x = \frac{3}{2} \sigma_0 \left[ 1 - s - I + I s + \rho_x (s + I) \right]
$$

$$
\sigma_{yy} = \frac{3}{2} \sigma_0 \left[ 1 - s - I + I s + \rho_x (s + I) \right]
$$

$$
\sigma_{zz} = \frac{3}{2} \sigma_0 \left[ \rho_x \rho_y - \rho_x \rho_y \right]
$$
### Table 11

**Summary**

<table>
<thead>
<tr>
<th>Compound or Group</th>
<th>A ppm</th>
<th>B ppm</th>
<th>C GAUSS$^2$</th>
<th>D GAUSS$^2$</th>
<th>E$_0$ K</th>
<th>F Kcal/mole</th>
<th>G</th>
</tr>
</thead>
<tbody>
<tr>
<td>WF$_6$</td>
<td>-380±40</td>
<td></td>
<td>8.25±0.2</td>
<td>1.0±0.05</td>
<td>180-210</td>
<td>10.0±0.4</td>
<td>Isotropic or near isotropic</td>
</tr>
<tr>
<td>equatorial F</td>
<td>-435±40</td>
<td>~300</td>
<td>8.14$^1$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>axial F</td>
<td>-325±40</td>
<td>~300</td>
<td>8.14$^1$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>IF$_6$ AsF$_6^-$</td>
<td>-170±8</td>
<td></td>
<td>10.7±0.2</td>
<td>2.1±0.2</td>
<td>205-235</td>
<td>19±4</td>
<td>Reorientation about one axis and simultaneous oscillation about another.</td>
</tr>
<tr>
<td>IF$_6^+$</td>
<td>-245±20</td>
<td>~333</td>
<td>10.20$^1$</td>
<td>2.0</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>AsF$_6^-$</td>
<td>-100±20</td>
<td>~333</td>
<td>10.44$^1$</td>
<td>0.7</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SF$_3$ AsF$_6^-$</td>
<td>-155±15</td>
<td></td>
<td>5.9±0.3$^2$</td>
<td>1.9±0.1</td>
<td>&lt;77-200</td>
<td>~1</td>
<td>Isotropic or near isotropic</td>
</tr>
<tr>
<td>SF$_3^+$</td>
<td>-205±20</td>
<td></td>
<td>4.7$^2$</td>
<td>1.1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>AsF$_6^-$</td>
<td>-105±20</td>
<td></td>
<td>2.8$^2$</td>
<td>0.9</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SF$_3^+$ AsF$_6^-$</td>
<td></td>
<td></td>
<td>342-373°K</td>
<td>336-342</td>
<td>0.1</td>
<td>Diffusion</td>
<td></td>
</tr>
</tbody>
</table>

---

A. Mean isotropic chemical shift to nearest 5 ppm relative to HF.

B. Anisotropy of Chemical shift ($\delta_{11} - \delta_{1}$).

C. Zero field second moment 77°K.

D. Second moment at 295°K.

E. Transition temperature range.

F. Activation energy.

G. Possible reorientation above transition temperature.

1. Calculated for theoretical, rigid lattice.

2. Not a rigid lattice.
The expressions $\rho_x$ and $\rho_y$ relate to $\pi$-bonding in the $xz$ and $yz$ planes. Such $\pi$-bonds may be formed by the overlap of the fluorine $p_x$ and $p_y$ orbitals with the $d_{xz}$ and $d_{yz}$ central atom orbitals. The chemical shift is expected to vary, according to the ionic character of the bond, from HF the most ionic down to $F_2$ the most covalent. Although hybridization could have the same effect as ionic character, Saika and Slichter neglected it because of the difficulty of making a numerical estimate. Although Andrew has taken account of hybridization, we shall follow Saika and Slichter and also Rigny (39) in ignoring it.

When hybridization is neglected, then, in the case of axial symmetry of the chemical shift tensor where $\xi_{zz} = \xi_{\perp}$ and $\xi_{xx} = \xi_{yy} = \xi_{\perp}$, equations (31) reduce to

$$\xi_{\parallel} = \frac{3}{2} \xi_0 (2 \rho - \rho^2)$$

$$\xi_{\perp} = \frac{3}{2} \xi_0 (1 - I + \rho I)$$

where $\rho_x = \rho_y = \rho$ and $\rho$ and $I$ are as above. From Karplus and Des the coefficient $\xi_0 = -863$ ppm. They point out, however, that the exact value of $\xi_0$ is not important since it does not affect the trends calculated and it is the trends, not the actual values, which are of primary significance.

The mean isotropic chemical shift may be written

$$\bar{\xi} = \frac{1}{3} Tr \xi = \frac{1}{3} (\xi_{xx} + \xi_{yy} + \xi_{zz})$$

The expressions $\rho_x$ and $\rho_y$ relate to $\pi$-bonding in the $xz$ and $yz$ planes. Such $\pi$-bonds may be formed by the overlap of the fluorine $p_x$ and $p_y$ orbitals with the $d_{xz}$ and $d_{yz}$ central atom orbitals. The chemical shift is expected to vary, according to the ionic character of the bond, from HF the most ionic down to $F_2$ the most covalent. Although hybridization could have the same effect as ionic character, Saika and Slichter neglected it because of the difficulty of making a numerical estimate. Although Andrew has taken account of hybridization, we shall follow Saika and Slichter and also Rigny (39) in ignoring it.

When hybridization is neglected, then, in the case of axial symmetry of the chemical shift tensor where $\xi_{zz} = \xi_{\perp}$ and $\xi_{xx} = \xi_{yy} = \xi_{\perp}$, equations (31) reduce to

$$\xi_{\parallel} = \frac{3}{2} \xi_0 (2 \rho - \rho^2)$$

$$\xi_{\perp} = \frac{3}{2} \xi_0 (1 - I + \rho I)$$

where $\rho_x = \rho_y = \rho$ and $\rho$ and $I$ are as above. From Karplus and Des the coefficient $\xi_0 = -863$ ppm. They point out, however, that the exact value of $\xi_0$ is not important since it does not affect the trends calculated and it is the trends, not the actual values, which are of primary significance.

The mean isotropic chemical shift may be written

$$\bar{\xi} = \frac{1}{3} Tr \xi = \frac{1}{3} (\xi_{xx} + \xi_{yy} + \xi_{zz})$$
or for axial symmetry of the shift tensor

\[ \bar{\delta} = \frac{1}{3}(2\delta_\perp + \delta_\parallel) \]  

(34)

If \( \bar{\delta} \) is measured relative to HF, then the knowledge of \( \delta_\parallel - \delta_\perp \) enables individual values of \( \delta_\parallel \) and \( \delta_\perp \) to be obtained for substitution into equations (32). Only average values of \( \delta_\parallel - \delta_\perp \) are available here, but Blinc (41) reports values of 640±50 and 670±50 for UF6 and 1300±100 and 1380±100 ppm for PtF6 for the axial and equatorial components respectively. In our case, therefore, the average anisotropies are probably good approximations to the values for the individual components. Values of \( \rho \) and \( \lambda \) for the hexafluoride groups studied here and also for UF6 are plotted in Figure 27 as a function of mean isotropic shift with respect to HF.

From Figure 27, values of \( \rho \approx 0.01 \) and \( \lambda \approx 0.8 \) can be estimated for the S-F bond in SF3+. However, Karplus and Das caution that such plots be considered only as applying to groups of similar compounds. Figure 27 will be taken only as holding for hexafluoride groups. Indeed even the value of \( \rho \) for the UF6 axial component deviates widely from the plot although the value for \( \lambda \) is in good agreement. Also neither axial nor equatorial component of PtF6 can be fitted to the plot. Both components lie far outside the range of shifts found here and give meaningless values of \( \rho \) and \( \lambda \). However, although Blinc (41) was unable to determine the anistropies of the components in PuF6, he was able to estimate mean isotropic chemical
Figure 27. Ionic and double bond character in hexafluoride groups as a function of mean isotropic chemical shift relative to $\text{HF}^*$. 

- $\circ = I$
- $\times = \rho$
shifts of -440 and -1070 ppm relative to HF for the axial and equatorial components respectively. These shifts do lie within the range of shifts in Figure 27. From the figure we can predict $\rho = 0.1, I = 0.6$ for the axial fluorine bonds and $\rho = 0.38, I = 0.03$ for the equatorial bonds.
All the programs in this appendix have been written in or adapted to Fortran IV as compatible with the University of British Columbia's IBM 7040 (now temporarily 7044) computer. Some of the programs have been tidied up slightly from the form in which they were used. However this merely involved changing notation that might have been confusing. Some quantities which really could be input as data still appear instead in the programs themselves. These are obvious, however, and can easily be changed by any one wishing to adapt the programs for his own use.
Program 1. Calculation of Experimental Second Moments from Derivative Curves.

This program is for the general case of an asymmetric derivative curve. For an asymmetric curve the second moment is

\[ SM = S - (FM)^2 \]

SM is the second moment about the centroid of the curve, \( S \) is the second moment computed about any point (taken at the estimated centroid to minimize error), and \( FM \) is the first moment computed about the same point. For the derivative curve the second moment is

\[ SM = \frac{1}{3} (\text{scale})^2 \frac{\sum x^3 y}{\sum x y} - \left( \frac{1}{2} (\text{scale}) \frac{\sum x^2 y}{\sum x y} \right)^2 - \frac{(\Delta Hm)^2}{4} \]

where \( \text{scale} = \) gauss per division. The last term in the equation for \( SM \) is Andrew's (89) correction for modulation broadening, which is one-half the peak to peak modulation. In the measurement of the experimental curves, the \( x \)-axis of the spectrum is divided into convenient, equal divisions, for which a calibration has been determined, and the corresponding \( y \) values measured in arbitrary units. The \( y \) values are written directly on computer data sheets and the remainder of the determination of the second moment is carried out by the computer.

\( N \) = the identification number of the derivative curve or TRACE
\( N1 \) = total number of data points on trace \( N \)
\( N2 \) = total number of data points on the first half of the curve including the cross-over point in the middle.
\( \text{SCALE} \) = gauss per division
\( \Delta Hm \) = peak to peak modulation
\( \text{TEMP} \) = temperature in degrees
\( IY \) = \( y \) amplitude in arbitrary units for each of the \( N1 \) equal divisions
\( SM, S, \) and \( FM \) are as described above.
It is immaterial at which end of the spectrum measurement is commenced. However to avoid confusion as to field direction in Program 2, if integrating derivatives which are only slightly asymmetric, it is recommended that a consistent policy be followed. Start always at the low field end and choose the sign of IY positive in that half of the spectrum.
SFORTRAN
C EXPERIMENTAL SECOND MOMENT
DIMENSION IY(200), C(9)
1 FORMAT (19I4, 4X)
2 FORMAT (3I4, F7.4, F6.2, F5.0, 8A6)
3 FORMAT (1X, 5HTRACE, 4X, 1HT, 5X, 1HS, 10X, 2HFM, 10X, 2HSM)
WRITE (6, 3)
4 FORMAT (1X, I5, F6.1, F9.2, 1X, F8.2, 5X, F6.2, 5X, 8A6)
5 READ (5, 2) N, N1, N2, SCALE, PMOD, TEMP, (C(I), I=1, 8)
6 READ (5, 1) (IY(I), I=1, N1)
KFM = 0
IS = 0
IA = 0
DO 10 J = 1, N1
I = J - N2
K = I * I * IY(J)
KFM = K + KFM
IS = K * I + IS
10 IA = IA + I * IY(J)
SUM = IS
A = IA
FM = KFM
FM = .5 * FM * SCALE / A
S = SCALE * SUM / (A * 3.1)
SM = S - FM * FM - 25 * PMOD * PMOD
WRITE (6, 4) N, TEMP, S, FM, SM, (C(I), I=1, 8)
GO TO 5
END
SENTRY
Program 2. **Integration of Derivative Curves to Absorption Curves.**

This program integrates the derivative curves to absorption spectra using the data punched for the second moment calculations. The integration is performed using rectangular strips which, when small enough, are sufficiently accurate for broad line nmr.

- \( \text{NMNR} = \) identification number of derivative curve
- \( N = \) total number of data points
- \( \text{SCALE} = \) gauss per division (on the derivative curve)
- \( IY = \) y amplitudes of the \( N \) points on the derivative curve

In the body of the program the \( G(I) \)'s are the amplitudes of the absorption curve at points separated one from another by the distance \( \text{SCALE} \). \( BL \) is a correction parameter applied to \( G(I) \) to ensure that \( G(I) \) approaches zero at both limits of the integration. \( Z \), the \text{DEVIATION}, gives an estimate of the accuracy of the integration. It is expressed as a percentage in terms of \( G(N) \) and \( X \) the maximum amplitude of the absorption curve. \( \text{FNORM} \) normalizes the spectra to constant arbitrary area for comparison with each other.

The punch instruction produces data for use in Program 2*. This last program outputs the data from Program 2 on an X-Y plotter.

The program was written to give a constant x-scale to all the absorption curves so that comparison could be made directly between the area-normalized curves. Since the program calls special routines which were written expressly for the computer here by the computing center staff, it cannot be used elsewhere.
PROGRAM 1

C INTEGRATION OF DERIVATIVE CURVE

DIMENSION G(100), TITLE(9), IY(100)

READ (5, 1) NMBR, N, SCALE, TITLE(I), I = 1, 9
FORMAT(A4, 14, 4X, F7.4, 6X, 9A6)
READ (5, 2) (IY(I), I = 1, N)
FORMAT(1914, 4X)

H = 0.
DO 10 I = 1, N
H = H + FLOAT(IY(I))
G(I) = H * SCALE
Z = G(N)
WRITE (6, 12) NMBR, (TITLE(I), I = 1, 9)
BL = G(N) / FLOAT(N)
DO 29 I = 1, N
29 G(I) = G(I) - FLOAT(I) * BL
X = 0
Y = 0
DO 30 I = 1, N
30 IF(G(I) .GT. X) X = G(I)
IF(Y .GT. G(I)) Y = G(I)
CONTINUE
IF(X .LT. (-Y)) X = Y
Z = Z .LT. 100. / X

DO 100 I = 1, N
AREA = 0.
AREA = AREA + G(I) * SCALE
FNORM = 1000. / AREA
DO 110 I = 1, N
110 G(I) = G(I) * FNORM
WRITE (6, 40) AREA, Z
FORMAT(70X, 5HAREA=, F10.1, 5X, 10HDEVIATION=, F10.4)
WRITE (6, 11) (G(I), I = 1, N)
WRITE (6, 11) NMBR, N, SCALE
WRITE (6, 11) N, SCALE
PUNCH (11, NMBR, N, SCALE)
FORMAT (10F8.2)
11 FORMAT (3X, A4, 10X, 9A6)
GO TO 20
END

SPECIAL
C REMEMBER LAST SPEC N, SCALE CARD MUST BE BLANK TO CALL PLOTND
DIMENSION X(100), Y(100)
CALL PLOTS
1 READ (5,2) SPEC, N, SCALE
2 FORMAT (F4.0, I4, 1X, F7.4)
3 IF (N .LE. 0) GO TO 100
4 READ (5, 4) (Y(I), I = 1, N)
5 FORMAT (10F8.2)
6 DEEX = SCALE / 2.54
7 DEEY = 0.03
8 S = FLOAT(N - 1) * DEEX
9 DO 10 I = 1, N
10 X(I) = FLOAT(I) * DEEX
11 Y(I) = Y(I) * DEEY
12 IF (Y(I) .LT. (-0.25)) Y(I) = (-0.25)
13 CALL NUMBER (5., 8., 0., SPEC, 0., -1)
14 DO 12 I = 1, N
15 CALL SYMBOL (X(I), Y(I), 0.14, 3, 0., -1)
16 CALL PLOT ((S + 2.), 0., -3)
17 GO TO 1
18 CALL PLOTND
19 STOP
20 END
Program 3. Line Shape Function $F(H)$.

This program synthesizes a curve $F(H)$ using experimentally determined values of $(\sigma_{ii} - \sigma_{jj})$ and the zero field dipolar second moment. It is written for the case of equivalent nuclei exhibiting axial symmetry of their shift tensors. If non-equivalent nuclei are present, two or more synthesized curves appropriately shifted relative to each other may be used. $F(H)$ is given by equation (21). Since the centroid of the synthesized curve will be superimposed on that of the experimental curve, $H^*$ will be identical in each case and may be chosen equal to zero for the program. Therefore

$$F(H) = \int_{-\infty}^{\infty} f(H_0)S(H-H_0)DH_0 \quad \text{.................. (A)}$$

where

$$f(H_0) = \left(1 + \frac{H_0}{\alpha} \right)^{-\frac{1}{2}} \quad \text{.................. (B)}$$

and the constant in equation (B) is omitted since the function $F(H)$ will itself be normalized in the program.

Two programs, 3a and 3b, are given below. For 3a the experimental line shape at 2 MHz has been used as the broadening function $S(H-H_0)$ and for 3b the broadening function is a gaussian function having the same second moment as the extrapolated zero field second moment. The former was used with UF$_6$ and the latter with IF$_6$ AsF$_6$.

Program 3a.

ALPHA = the "a" defined under equation (16)
SCALE = separation in gauss between the data points on the experimental broadening function (ebf.).
Program 3a Contd.

NY = the number of data points, including the centroid, on the left half of ebf.
Nfl = total number of data points on ebf.
Y(I) = an amplitude on ebf.
H and DHO = (where DHO = dHo) are as defined under equation (21).
AMP = the maximum amplitude of the experimental curve. If the curve consists of two or more components, the synthesized curve must be normalized to the area, not the height of the experimental curve.

Program 3b.

ALPHA is as for 3a.
BETA is the square root of the extrapolated zero field dipolar rigid lattice second moment.
H, DHO, and AMP are as for 3a.

Both programs output values of F(H) - labelled F(K) here - for values of H - labelled G(K) here.

Note that in the actual programs SH(H-HO) is written as SH(HO).
ANISOTROPIC FUNCTION WITH EXPERIMENTAL BROADENING FUNCTION

COMMON ALPHA, SCALE, NY, NM, Y, H, DHO

READ (5, 1) NM

READ (4*X, 13)

WRITE (6, 2) (Y(I), I=1, NM)

WRITE (10F8.1)

READ (5, 4) ALPHA, SCALE, NY, AMP

FORMAT (4*2F12.4, 4*X, 13, 4*X, F12.4)

WRITE (6, 4) ALPHA, SCALE, NY, AMP

H = -20.
DH = 0.5
DHO = 0.1

DO 11 K = 1, 80

F(K) = 0.

H = H + DH

G(K) = H

HO = ALPHA + 0.01

IF (H GT 20.) GO TO 3

DO 10 L = 1, 2000

HO = HO + DHO

IF (HO GT (2 * ALPHA)) GO TO 11

F(K) = F(K) + FH(HO) * SH(HO)

10 FMAX = F(K)

DO 20 N = 1, 80

IF (FMAX LT F(N)) FMAX = F(N)

CONTINUE

FMAX = AMP / FMAX

DO 21 N = 1, 80

F(N) = F(N) * FM + X

WRITE (6, 22) (G(K), F(K), K = 1, 80)

22 FORMAT (1*X, 2F12.4)

GO TO 3

END

Program 3a
FUNCTION FH(HO)

COMMON ALPHA, SCALE, NY, NM, Y, H, HO

DIMENSION Y(00)

FH=1.+HO/ALPHA

FH=1./SQRT(FH)

RETURN

END

FUNCTION SH(HO)

COMMON ALPHA, SCALE, NY, NM, Y, H, DHO

DIMENSION Y(100)

FEJ=FLOAT(NY)+(H-HO)/SCALE

J=FEJ

IF(J.LE.O) GO TO 110

IF(J.GE.NM) GO TO 110

BELOW=Y(J)

ABOVE=Y(J+1)

FINK=(ABOVE-BELOW)*(FEJ-FLOAT(J))

GO TO 111

110 SH=0.

GO TO 112

111 SH=BELOW+FINK

112 CONTINUE

RETURN

END
$\text{FORTRAN}

C ANISOTROPIC FUNCTION WITH GAUSSIAN BROADENING FUNCTION

DIMENSION F(100), G(100)

COMMON ALPHA, BETA, H

READ (5, 2) ALPHA, BETA, AMP

WRITE (6, 2) ALPHA, BETA

BETA = 1. / (2. * BETA * BETA)

H = -20.

DH = 0.5

DHO = 0.1

DO 11 K = 1, 80

F(K) = 0.

H = H + DH

G(K) = H

HO = -ALPHA + 0.01

IF (H.GT.20.) GO TO 1

DO 10 J = 1, 2000

HO = HO + DHO

IF (HO.GT.(2.*ALPHA)) GO TO 11

10 F(K) = F(K) + FH(HO) * SH(HO)

11 FMAX = 0.

DO 20 N = 1, 80

IF (FMAX.LT.F(N)) FMAX = F(N)

20 CONTINUE

FMAX = AMP / FMAX

DO 21 N = 1, 80

21 F(N) = F(N) * FMAX

WRITE (6, 22) (G(K), F(K), K = 1, 80)

22 FORMAT (1X, 2F12.4)

GO TO 1

END
$\text{FORTRAN}$

FUNCTION FH(HO)
COMMON ALPHA, BETA, H
FH = 1.0 + HO / ALPHA
FH = 1.0 / SQRT(FH)
RETURN
END

FUNCTION SH(HO)
COMMON ALPHA, BETA, H
SH = EXP(-(H-HO)*(H-HO)*BETA)
RETURN
END
Program 4. **Doublet Fit.**

This program is from Dr. P. Raghunathan of this Department and is based on Abragam (52, p. 220).

\[
\text{ALPHA and BETA are related by } S^2_m = \frac{4}{5} \alpha^2 + \beta^2 \text{ where } S^2_m \text{ is the second moment of the experimental curve and } \\
\alpha = \frac{3}{4} \frac{\gamma}{h} r^{-3} \text{ where } r \text{ is the estimated doublet splitting.}
\]

\( H \) is again a general field parameter.

\( X \) is the HO of Program 3 and Abragam (52, p.220).

The program puts out amplitudes, \( S^2_m \), for values, \( H \). These in the existing program (which was written for a single use and never put into "polished" form) are scaled by hand to the amplitude of the experimental curve for comparison of line shapes. Different values of \( r \) are tried until a fit is obtained.
SIBFTC
C DOUBLET FIT
DIMENSION C(14)
COMMON ALPHA,BETA,X
READ(5,22)(C(I),I=1,14)
WRITE(6,22)(C(I),I=1,14)
PRINT 10
FORMAT(1X,34HD0UBLET_LINESHAPE_FIT_ABRAGAM_P219)
READ(5,1) ALPHA,BETA
DX = 0.0125
X = 2.*ALPHA
H=0.
DO 100 I=1,1000
H= H+(40.*DX)
IF(H.EQ.ALPHA) H=(40.*DX) + H
SUM = 0.
D = -3.* ALPHA
DO 90 J= 1,14000
D = D + DX
IF(D.GT.(3.*ALPHA)) GO TO 91
T = H-D
IF(D.LT.(-ALPHA))P = FH(D)
IF(D.GT.ALPHA)P=FG(D)
IF(ABS(D).LT. ALPHA)P=FL(D)
SUM = P*SH(T)*DX+SUM
CONTINUE
WRITE(6,2) H, SUM
FORMAT(2F12.8)
1 FORMAT(1X,2H,H=F12.8,10X,5HF(H)=,F13.4)
IF(H.GT.(3.*BETA)) GO TO 101
100 CONTINUE
101 CONTINUE
GO TO 21
END
SIBFTC FHD
FUNCTION FH(D)
COMMON ALPHA,BETA,X
IF(D.LT.X)FH=0.
IF(D.GT.X)FH=(-D/ALPHA+1.)*(-0.5)
RETURN
END

SIBFTC SHT
FUNCTION SH(T)
COMMON ALPHA,BETA,X
SH = EXP(-T*T*0.5/(BETA*BETA))/(BETA*2.505)
RETURN
END

SIBFTC FLD
FUNCTION FL(D)
COMMON ALPHA,BETA,X
A = D/ALPHA
FL = (-A+1.)*(-0.5)+(A+1.)*(-0.5)
RETURN
END

SIBFTC FQD
FUNCTION FQ(D)
COMMON ALPHA,BETA,X
IF(D.GT.X)FQ=0.
IF(D.LT.X)FQ = (D+1.)*(-0.5)
RETURN
END

ENTRY
Program 5. Transformation of Coordinates.

This program generates blocks of unit cells around a cell [labelled (0, 0, 0)] from which it is desired to compute interactions. It gives the coordinates of all nuclei within the cells.

AI, BI, CI is the designation of the cell from which the program starts (not 0, 0, 0. Starting from 0, 0, 0 would give the cells in only one half of the block).

AM, BM, CM is the designation of the cell at which the program finishes.

XA, YB, ZC are the unit cell dimensions in angstroms.

XI, YI, ZI are the atomic coordinates of the nuclei in the unit cell.

NUC labels the unit cell nuclei if desired.

The punched output X, Y, Z (the A, B, C, and NUC are merely labelling) is used in Program 6 for the theoretical second moment calculation.
$\text{FORTRAN}$

C  RECTANGULAR COORDINATES

1  FORMAT(6F5.0)

3  FORMAT(3F8.4)

4  FORMAT(3F10.4,A6)

7  FORMAT(1HO)

50  FORMAT(5X,3F8.4,5X,3F5.0,A6)

READ(5,1) AI, BI, CI, AM, BM, CM

WRITE(6,1) AI, BI, CI, AM, BM, CM

READ(5,3) XA, YB, ZC

WRITE(6,3) XA, YB, ZC

READ(5,4) XI, YI, ZI, NUC

WRITE(6,4) XI, YI, ZI, NUC

A = AI

B = BI

C = CI

GO TO 100

CONTINUE

C = C + 1

IF(C.GT.CM) GO TO 11

GO TO 100

11  CONTINUE

C = CI

B = B + 1

IF(B.GT.BM) GO TO 12

GO TO 100

12  CONTINUE

C = CI

B = BI

A = A + 1

IF(A.GT.AM) GO TO 101

CONTINUE

X = (XI + A) * XA

Y = (YI + B) * YB

Z = (ZI + C) * ZC

WRITE(6,50) X, Y, Z, A, B, C, NUC

PUNCH 50, X, Y, Z, A, B, C, NUC

GO TO 10

101  CONTINUE

WRITE(6,7)

GO TO 8

END
Program 6. **Theoretical Rigid Lattice Second Moment Calculation.**

This program computes the theoretical rigid lattice second moment using the nuclear coordinates (in angstroms) generated by Program 5. It was adapted from W.R. Janzen's original program written for the IBM 1620.

LS = 1, 2. 1 instructs the computer to read in a new set of data cards and do calculations. 2 instructs it to do further calculations with the data.

RMAX = distance in angstroms up to which the sum is carried. FACT = the factor in equation (2) as is applicable. NN=DEN = N as in equation (2). NVAN = count of interactions between nuclei separated by less than the van der Waals radius. NMB = the count of interactions within the distance RMAX. NI, NM = list of data cards read in. JI, JM = is the list of parameters j in rjk in equation (2). KI, KM = is the list of parameters k in rjk in equation (2). X(I), Y(I), Z(I) are the nuclear coordinates in angstroms generated by Program 5. SM = theoretical rigid lattice second moment.
THEORETICAL SECOND MOMENT


FORMAT (1H1, 7X, 26H THEORETICAL SECOND MOMENTS, 22X, 14H PROG 4 WRJ MRB)

FORMAT (12, F3.0, F7.2, 7I5, 24H)

FORMAT (15, I5, F11.8)

FORMAT (5X, 3F8.4, 5X, 3F5.0, A6)

FORMAT (10H HOTHEO_SM =, F6.2, 8X, I5, 14H R LESS THAN, F4.1, 2H A)

WRITE (6, 55)
WRITE (6, 100)

READ (5, 74) LS, RMAX, FACT, NN, NI, NM, JI, JM, KI, KM

RMS = RMAX * RMAX
DEN = NN
J = 0
NVAN = 0
NMB = 0
SUMR = 0.0

WRITE (6, 74) LS, RMAX, FACT, NN, NI, NM, JI, JM, KI, KM
GO TO (1, 2), LS

DO 10 I = NI, NM
10 READ (5, 88) X(I), Y(I), Z(I), A(I), B(I), C(I), NUC(I)

DO 30 J = JI, JM
DO 30 K = KI, KM
IF (K.EQ.J) GO TO 30

DZ = ABS (Z(K) - Z(J))
IF (DZ.GE. RMAX) GO TO 30

DY = ABS (Y(K) - Y(J))
IF (DY.GE. RMAX) GO TO 30

DX = ABS (X(K) - X(J))
IF (DX.GE. RMAX) GO TO 30

RS = DX * DX + DY * DY + DZ * DZ
IF (RS.GE. R7.29) GO TO 40

NVAN = NVAN + 1
CONTINUE

SUMR = SUMR + 1. / (RS * RS * RS)
NMB = NMB + 1

CONTINUE
SM = (FACT / DEN) * SUMR
WRITE (6, 99) SM, NMB, RMAX
WRITE (6, 101) NVAN
GO TO 80
END
ENTRY
Program 7. Activation Energies.

This program is Smith's (79) program for the calculation of activation energies from line widths in nmr transition regions. It is listed here as adapted for the IBM 7040 by Dr. Raghunathan. It is, as noted, written for line widths as in equation (7). However it can be used without modification for second moments as in equation (8) provided $(\Delta M)^{\frac{1}{2}}$ and $\Delta M$ are used instead of $\Delta H$ and $\Delta H^2$. 
SIBFTC MOD BPP

C IF YOU DO ALL THESE CALCULATIONS BY HAND AND PLOT THEM IT IS EASIER TO
C SEE WHAT IS GOING ON.
C
C MODIFIED BPP LINE NARROWING ANALYSIS
C DIFFERS FROM ORIGINAL CASE BY INCLUSION OF TERM AG IN NUMERATOR OF
C BPP EQN PHYS REV 1948 VOL73 P679. FOR PROTONS AG=767.5
C
C THIS PROGRAM USES THE MODIFIED BPP EQN TO DERIVE THE CORRELATION
C FREQUENCY MAKES A LEAST SQUARES FIT OF LN(COR.FREQ) TO A ST. LINE
C WHEN PLOTTED VS 1/RT. DERIVES THE ACTIVATION ENERGY AND INF. TEMP.
C CORREL.FREQ. FROM THE FIT. PROGRAM THEN REVERSES THE PROCESS TO GIVE
C THEORETICAL FIT TO THE LINEWIDTH VS TEMP DATA PLOT.
C
C DEFINITIONS INPUT
C ALPHA=DATA COMMENTS E.G. NAME OF COMPOUND DATE.
C TEMP. IN DEG. KELVIN. DELTAH=LINEWIDTH (GAUSS) IN NARROWING REGION
C (LESS THAN C GREATER THAN B). C= AVG. LINEWIDTH BELOW TRANSITION.
C B= AVG. LINEWIDTH ABOVE TRANSITION. AG=PARAMETER DEPENDENT ON NUCCL
C SPECIES, >767.6 FOR H. DELMIN= MIN LINEWIDTH IN REGION OF THEORETIC
C FIT, GREATER THAN B. DELMAX=MAX. LINEWIDTH IN REGION OF THEORETIC FIT,
C LESS THAN C. DELINC=LINEWIDTH INCREMENT FOR THEORY FIT. N=NO. OF
C DATA POINTS.
C
C CALCULATED QUANTITIES OUTPUT
C CORRFREQ= DERIVED CORREL. FREQ. RECIPT=1/TEMP. XLNFREQ=LN OF CORRFREQ.
C RCPRT =1/(R*TEMP), WHERE R = 1.9869 CAL/DEG-MOLE.
C EACT = ACTIVATION ENERGY (CAL/ MOLE). FREQACT= ERROR IN SAME. FRMAX =
C INF. TEMP. CORREL. FREQ. IN THEOR. FIT. ERRFRQ=ITS ERROR. THDEL= LINE-
C WIDTH IN THEOR. FIT. THTEMP= TEMP. IN THEOR. FIT. THFRQ= CORREL. FREQ
C IN THEOR. FIT.
C
C DIMENSION TEMP(500), DELTAH(500), CORRFREQ(500), RECIPT(500),
C 1XLNFREQ(500), XSIN(500), XCOS(500), XTAN(500), RCPRT(500), ALPHA(12),
C 2THFRQ(500), THTEMP(500), THDEL(500), THSN(500), THCO(500), THTAN(500)

10 PRINT 10
15 READ (5,20) (ALPHA(I), I=1,12)
20 FORMAT (12A6)
30 WRITE (6,30) (ALPHA(I), I=1,12)
35 FORMAT (1X,12A6)
40 FORMAT (15,3F15.5)
45 READ (5,50) (TEMP(I), DELTAH(I), I=1,N)
50 FORMAT (6F12.5)
60 DO 60 I=1,N
65 XSIN(I) = SIN(1.5707*DELTAtH(I)**2-B**2)/(C**2-B**2)
XCOS(I)=COS(I*5.7077*(DELTAH(I)**2-B**2)/(C**2-B**2))
XTAN(I)=XSIN(I)/XCOS(I)
CORFRQ(I)=AG*DELTAH(I)/XTAN(I)
XLNFRQ(I)=ALOG(CORFRQ(I))
RECIPT(I)=1./TEMP(I)
RCPRT(I)=1./(1.9869*TEMP(I))

60 CONTINUE
65 WRITE(6,70).N,C,B,AG
70 FORMAT(1H0,5X,2HN=,15.5X,25HRIGID LATTICE LINEWIDTH =,F10.5,5X,20H
1NARRROD LINEWIDTH =,F10.5,5X,4HAG =,F15.5)
PRINT 80
80 FORMAT(1H0,1X,16HTEMP(DeG KELVIN),4X,16HLINEWidth(ROUsS),4X,15HCOR FRQ.(CPS),10X,6H1/TEMP,10X,13HLN(COR FRQ.),11X,4H1/RT)
WRITE(6,90) (TEMP(I),DELTAH(I),CORFRQ(I),RECIPT(I),XLNFRQ(I),
1RCPRT(I),I=1,N)
90 FORMAT(1H,2X,F12.5,8X,F12.5,7X,E14.6,9X,F10.7,9X,F12.7,9X,F10.7)
SUMX = 0.0
SUMY = 0.0
DO 200 J=1,N
SUMX = SUMX+ RCPRT(J)
SUMY = SUMY+ XLNFRQ(J)
200 CONTINUE
CALL LSQFIT(N,RCPRT,XLNFRQ,SUMX,SUMY,Q,P,STDERQ,STDERP,XAV,
1YAV,N0G0)
FROMAX = EXP(Q)
ERFRO = EXP(0)*STDERQ
EACT = (-1.)*P
EREACT= (-1.)*STDERP
WRITE (6,210)FROMAX,ERFRO,EACT,EREACT
210 FORMAT(1H0,25HCOR. FRQ. AT INF. TEMP. =,E12.5,2X,7ERROR =,E12.5,2H7CAL/MOL)
READ (5,220) DELMAX,DELMIN,DELINC
220 FORMAT(3F10.5)
NOINC= (DELMAX - DELMIN)/DELINC +0.001
NSW = NOINC+1
DO 230 K= 1,NSW
AK = K
THDEL(K)=DELMIN+(AK-1.)*DELINC
CB = C**2-B**2
THSN(K)=SIN(I.5707*(THDEL(K)**2-B**2)/CB)
THCO(K)=COS(I.5707*(THDEL(K)**2-B**2)/CB)
THTAN(K)=THSN(K)/THCO(K)
\[
\begin{align*}
\text{THFQ(K)} &= (AG \times \text{THDEL(K)}) / \text{THTAN(K)} \\
\text{THTEMP(K)} &= \text{EACT} / (1.9869 \times \text{ALOG} \left( \text{FRQMAX} / \text{THFQ(K)} \right))
\end{align*}
\]

230 CONTINUE

PRINT 240

FORMAT(1HO, 34X, 47HTHEORETICAL MODIFIED BPP LEAST SQUARES DATA FIT)
PRINT 250

FORMAT(1HO, 6X, 28HTEMPERATURE (DEGREES KELVIN), 17X, 18HLINE WIDTH(GA \text{USS}), 17X, 27HCORRELATION FREQUENCY (CPS))
WRITE(6, 260) (\text{THTEMP(K)}, \text{THDEL(K)}, \text{THFQ(K)}, K=1, N\text{W})

260 FORMAT(1H, 14X, F11.5, 30X, F10.5, Z8X, E14.6)
GO TO 15

SUBFC

SUBROUTINE LSQFIT(N, X, Y, SUMX, SUMY, B, C, STDERB, STDERC, XAV, YAV, NOGO)

DIMENSION X(500), Y(500)

IF(N-2) 1050, 1050, 1000

1000 AN = N
XAV = SUMX / AN
YAV = SUMY / AN
DIFXY = 0.
DIFXSQ = 0.

DO 1010 J = 1, N
DIFXY = DIFXY + (X(J) - XAV) * Y(J)
DIFXSQ = DIFXSQ + (X(J) - XAV)**2

1010 CONTINUE

C = DIFXY / DIFXSQ
B = YAV - C * XAV
DSQ = 0.
XSQ = 0.

DO 1020 J = 1, N
DSQ = DSQ + (B + C * X(J) - Y(J))**2
XSQ = XSQ + X(J)**2

1020 CONTINUE

Q = SQRT(DSQ / (AN-2.1))
DEE = AN * XSQ - (AN * XAV)**2
IF (DEE) 1050, 1050, 1030

1030 QOVRTD = Q / SQRT(DEE)
STDERC = QOVRTD * SQRT(AN)
STDERB = QOVRTD * SQRT(XSQ)
NOGO = 1
PRINT 1040

1040 FORMAT(1H, 52HNOGO = 1, THEREFORE LSQFIT HAS MADE A SUCCESSFUL FIT)
GO TO 1100
1050  NOGO = 2
PRINT 1060
1060  FORMAT(1H«  84HN0GO = 2, LSQFIT UNSUCCESSFUL DUE TO DEE LESS THAN 0
1R = 0, OR TO N LESS THAN OR = 2.»)
1100  RETURN
END
ENTRY
Appendix IIa. WF₆ Derivative Curves for Temperature Dependence at 30 MHz.

77 °K

136 °K

185 °K

209 °K

243 °K

261 °K

267 °K

--- modulation amplitude ---
Appendix IIb. $WF_6$ Derivative Curves for Temperature Dependence at 94.1 MHz
Appendix IIc. $WF_6$ Derivative Curves for Field Dependence at 77°K

- 115 -

$2 \text{ MHz}$

$16 \text{ MHz}$

$5G$

$R = \text{reference}$

$30 \text{ MHz}$

$40 \text{ MHz}$

$0 \text{ R}$

$5G$

$\leftrightarrow \equiv \text{ modulation amplitude}$

$56.4 \text{ MHz}$

$9.41 \text{ MHz}$

(173°K)
Appendix IIIa. \( \text{IF}_2\text{AsF}_6^- \) Derivative Curves for Temperature Dependence at 30 MHz

\[ \text{217 °K} \]

\[ \text{229 °K} \]

\[ \text{268 °K} \]

\[ \text{295 °K} \]

\[ \text{77 °K} \]

\[ \text{174 °K} \]

\[ \text{modulation amplitude} \]
Appendix IIIb. $\text{IF}_6\text{AsF}_6$ Derivative Curves for Field Dependence at $295^\circ\text{K}$

- 94.1 MHz
- 56.4 MHz
- 40 MHz
- 30 MHz

$\rightarrow$ = modulation amplitude
$R$ = reference
Appendix IVa. $\text{SF}_2\text{AsF}_6$ Derivative Curves for Temperature Dependence at 30 MHz

= modulation amplitude
Appendix IVb. $\text{SF}_3\text{AsF}_6$ Derivative Curves for Field Dependence at $300^\circ\text{K}$

<table>
<thead>
<tr>
<th>Frequency</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>94.1 MHz</td>
<td>3G to 0 R</td>
</tr>
<tr>
<td>56.4 MHz</td>
<td>3G to 0 R</td>
</tr>
<tr>
<td>40 MHz</td>
<td>3G to 0 R</td>
</tr>
<tr>
<td>30 MHz</td>
<td>3G to 0 R</td>
</tr>
</tbody>
</table>

$\leftrightarrow$ = modulation amplitude
R = reference
Appendix IVc. SF$_3^+$AsF$_6^-$ Derivative Curves for Field Dependence at 77$^\circ$K

94.1 MHz

$\leftrightarrow$ = modulation amplitude
R = reference

56.4 MHz

40 MHz

30 MHz

16 MHz
References


(37b) N. Bartlett (private communication from S. Siegel)


(55) J.H. Van Vleck, Phys. Rev. 74, 1168


(82) J. Trotter, U.B.C., private communication.


