1970

Some Aluminum-27 Nmr Studies

David Rodney Truax

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SOME ALUMINUM-27 NMR STUDIES

by

David Rodney Truax

Department of Chemistry

Submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy

Faculty of Graduate Studies
The University of Western Ontario
London, Canada.
June 1969
ABSTRACT

The $^{27}\text{Al}$ nuclear magnetic resonance spectra of the tetrahaloaluminate and mixed tetrahaloaluminate ions have been measured. The chemical shifts for the tetrahaloaluminate ions are found to be dependent upon the delocalization of electronic charge in the chemical bonds formed by the aluminum and halide ions. A semi-empirical calculation of the chemical shifts has been performed and is found to substantiate the delocalization hypothesis. The strongly electronegative character of the fluorine is also found to influence the $^{27}\text{Al}$ chemical shift in the tetrafluoroaluminate ion.

The line widths for the mixed tetrahaloaluminate complex ions are found to be symmetry dependent. The line widths of signals for complexes with the same symmetry are found to depend upon the size of the ion.

The nuclear magnetic resonance spectra of the anhydrous aluminum halides in the nonaqueous solvents, diethyl ether, nitromethane, acetonitrile, phosphoryl chloride and thionyl chloride have been obtained. The solute-solvent behaviour is interpreted in terms of a series of equilibria involving the solvent and solute. The evidence supports
the coordination model of solvent-solute behaviour rather than the solvent system concept.
ACKNOWLEDGMENTS

The author wishes to express his sincere appreciation to Dr. R.G. Kidd for his expert advice and guidance throughout the course of these studies.

The author gratefully recognizes the contributions of fellow graduate students, in particular, Mr. E.G. Bloor, Mr. M.B. Babcock, Mr. L.R. Carey and Mr. H.S. Prasad for their many helpful discussions. He would like to express his gratitude to Mr. H. Kreek for his assistance in the computer programming.

To his wife, Judy, the author expresses his most sincere thanks for her encouragement and in the preparation of this thesis.
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CHAPTER I
INTRODUCTION

A. GENERAL INTRODUCTION

Within the last decade, nuclear magnetic resonance (NMR) spectroscopy has become a very profitable tool, especially in the realm of organic chemistry where $^1\text{H}$-, $^{19}\text{F}$- and $^{13}\text{C}$-NMR have found wide application in structural determination, kinetic studies and in the investigation of the electronic constitution of molecules. However, in recent years, there has been increasing activity in the study of 'other nuclei' such as $^{17}\text{O}$, $^{27}\text{Al}$, $^{31}\text{P}$ and $^{119}\text{Sn}$ for example, which has proved a boon to the inorganic chemist in his investigation of systems normally difficult to examine.

Information has been obtained from the measurement of three quantities, the chemical shift, spin-spin coupling constants, and to a lesser extent, line shapes. The first two of these quantities, the chemical shift which represents the screening effect of the electron clouds surrounding the nucleus in question, and the second, the spin-spin coupling constant which represents the interaction with nearby nuclear spins transmitted by the bonding electrons in the molecule, can
give substantial information about the chemical and electronic environment of the nucleus under consideration. The third measurement, the signal line shape can give valuable insight into exchange effects since the resonance signal will be altered if the molecules are undergoing any rate processes. Collapse of fine structure, i.e., spin-spin splitting multiplets, or a coalescence of two uncoupled signals strongly indicates some averaging process is occurring such as intermolecular rearrangement or hindered rotation. If the nucleus under investigation possesses a quadrupole moment, then the line shape may be altered by the interaction of this moment with the electronic environment about the nucleus, and measurement of the line shape can give further structural information about the molecule being examined.

In this study, $^{27}$Al spectra have been obtained for several aluminum compounds in different solvent systems in order to elucidate what effects predominate in determining the magnitudes of the chemical shifts and the extent to which the line shape is influenced by molecular symmetry and ligand bulk. Information has also been obtained regarding the behaviour of the anhydrous aluminum halides in several donor solvents so that a secondary objective of this thesis has been to establish whether the information yielded by the spectra is sufficient to indicate a unified solvation concept for these systems.
The $^{27}$Al nucleus possesses many favourable characteristics which make it attractive for study. In Table I, several nuclei are listed along with some of these properties. Apart from having a nuclear spin (quantum number $I = 5/2$), it has a large magnetic moment which is helpful since the relative sensitivity of a nucleus to NMR detection is proportional to the cube of the magnetic moment, $\mu$, of the nucleus, at constant field strength, $H$ (i.e., $N((I + 1)/I^2)(\mu^3H^2)$).

Since $^{27}$Al is 100% abundant in nature, it may be studied without enriching the sample, an expensive process which must be done for such cases as $^{17}$O or $^2$H before meaningful results can be obtained.

Most aluminum compounds exist with aluminum in the oxidation state Al(III). In other words, there are no unpaired electrons present whose magnetic moments would interact with the nuclear magnetic moment to cause rapid relaxation and thus, produce a broadened signal or its complete absence. However, the presence of a nuclear quadrupole moment for the $^{27}$Al nucleus means that in many cases the relaxation times will be short, and saturation should not be a serious problem. But, by the same token, this same mechanism which prevents saturation may cause very short relaxation times and therefore broad signals.

In spite of the many suitable properties possessed by the $^{27}$Al nucleus, it has not been studied to any
<table>
<thead>
<tr>
<th>Isotope</th>
<th>NMR Frequency MHz, for 10 Kg Field</th>
<th>Natural Abundance %</th>
<th>Relative Sensitivity for Equal Number of Nuclei at Constant Field</th>
<th>Magnetic Moment (in multiples of the nuclear magneton)</th>
<th>Spin I (in units of h)</th>
<th>Electric Quadrupole Moment (in units of e x 10^{-24} cm^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>¹H</td>
<td>42.58</td>
<td>99.984</td>
<td>1.000</td>
<td>2.79270</td>
<td>1/2</td>
<td>-</td>
</tr>
<tr>
<td>²H</td>
<td>6.54</td>
<td>1.5 x 10^{-2}</td>
<td>9.64 x 10^{-3}</td>
<td>0.85783</td>
<td>1</td>
<td>2.77 x 10^{-3}</td>
</tr>
<tr>
<td>¹¹B</td>
<td>13.66</td>
<td>81.17</td>
<td>0.165</td>
<td>2.6880</td>
<td>3/2</td>
<td>3.55 x 10^{-3}</td>
</tr>
<tr>
<td>¹⁷O</td>
<td>5.77</td>
<td>2.7 x 10^{-2}</td>
<td>2.91 x 10^{-2}</td>
<td>- 1.8930</td>
<td>5/2</td>
<td>- 4 x 10^{-3}</td>
</tr>
<tr>
<td>¹⁹F</td>
<td>40.10</td>
<td>100</td>
<td>0.834</td>
<td>2.6273</td>
<td>1/2</td>
<td>-</td>
</tr>
<tr>
<td>²⁷Al</td>
<td>11.09</td>
<td>100</td>
<td>0.207</td>
<td>3.6385</td>
<td>5/2</td>
<td>0.149</td>
</tr>
<tr>
<td>³¹P</td>
<td>17.24</td>
<td>100</td>
<td>6.64 x 10^{-2}</td>
<td>1.1305</td>
<td>1/2</td>
<td>-</td>
</tr>
<tr>
<td>⁶⁹Ga</td>
<td>10.22</td>
<td>60.2</td>
<td>6.93 x 10^{-2}</td>
<td>2.0108</td>
<td>3/2</td>
<td>0.2318</td>
</tr>
<tr>
<td>⁷¹Ga</td>
<td>12.98</td>
<td>39.8</td>
<td>0.142</td>
<td>2.5549</td>
<td>3/2</td>
<td>0.1461</td>
</tr>
<tr>
<td>¹¹⁵In</td>
<td>9.33</td>
<td>95.84</td>
<td>0.348</td>
<td>5.5072</td>
<td>9/2</td>
<td>1.161</td>
</tr>
</tbody>
</table>

*See ref. 1.
great extent, possibly because of the nature of many important aluminum compounds — they tend to hydrolyze readily — and the expensive equipment required to obtain the spectra. Some studies have, nevertheless, been made, and the remainder of this introduction will be a review of some of the data to be found in the literature. The two studies performed upon $^{71}$Ga and $^{115}$In compounds will also be included for comparative purposes.
B. REVIEW OF THE NMR STUDIES OF THE GROUP IIIB METALS:

ALUMINUM, GALLIUM AND INDIUM.

(1) The Tetrahalometallate Ions, $\text{MX}_4^-$.

The NMR spectra of the tetrahedral complex anions, $\text{MX}_4^-$ (where $\text{X} = \text{Cl, Br, I}$) have been obtained for both gallium$^2$ and indium$^3$, but only one example, the $\text{AlCl}_4^-$ anion, has been reported for aluminum.$^4$ The chemical shift and line width data are given in Table II.

The gallium complexes were prepared and observed in acidic solution. The indium analogues were prepared in acidic solution which was then extracted with ether and the spectrum of the ethereal extract was obtained. The spectrum of $\text{AlCl}_4^-$ was ostensibly reported for a benzene solution of anhydrous aluminum chloride and sodium chloride.

These series of complexes are important in that they provide a well defined set of compounds with which to establish significant trends. For these complexes, the magnetic shielding decreases in the order $\text{MI}_4^->\text{MBr}_4^->\text{MCl}_4^-$. From a series of this type, it is hoped that some idea of the factors which are principally responsible for the magnitudes of the shifts can be determined. No adequate explanation of the trend has, as yet, been reported in the literature.

The resonance signals observed for the $\text{GaX}_4^-$ and $\text{InX}_4^-$ complexes are relatively narrower than those of other gallium and indium compounds to be discussed later in this
<table>
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<tr>
<th></th>
<th>$^{27}$Al (a)</th>
<th></th>
<th>$^{71}$Ga (b)</th>
<th></th>
<th>$^{115}$In (c)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Chemical Shifts (ppm.)</td>
<td>Line Widths (Hz.)</td>
<td>Chemical Shifts (ppm.)</td>
<td>Line Widths (Hz.)</td>
<td>Chemical Shifts (ppm.)</td>
</tr>
<tr>
<td>Cl</td>
<td>-91</td>
<td>900</td>
<td>-257</td>
<td>100</td>
<td>-440</td>
</tr>
<tr>
<td>Br</td>
<td>-</td>
<td>-</td>
<td>-127</td>
<td>100</td>
<td>-180</td>
</tr>
<tr>
<td>I</td>
<td>-</td>
<td>-</td>
<td>+450</td>
<td>100</td>
<td>+583</td>
</tr>
</tbody>
</table>

* All chemical shifts are quoted relative to the $\text{M(H}_2\text{O)}_{6}^{3+}$ ion.

(a) Ref. 4. (b) Ref. 2. (c) Ref. 3.
chapter. The tetrahedral complex anions possess cubic symmetry which implies that the electric field gradient at the nucleus is negligible. Therefore, the relaxation mechanism involving the coupling of the nuclear quadrupole moment and the electric field gradient is not available for these systems, at least to a first approximation. Consequently, these complexes will have longer spin-lattice relaxation times and give narrower resonances than those compounds with noncubic symmetry for which nonzero electric field gradients exist. A more detailed discussion of the effects of symmetry will be delayed until a later chapter.

It should be mentioned that in light of the above discussion, the line width quoted for the AlCl\textsubscript{4}⁻ ion in Table II is out of proportion to those found for the other MX\textsubscript{4}⁻ complexes in that Table. It would seem likely that it was not the AlCl\textsubscript{4}⁻ ion which was being observed.

An examination of the NMR spectra of the AlX\textsubscript{4}⁻ series to establish if they also follow the same trend in the magnetic shielding found for gallium and indium complexes would, therefore, offer a good approach towards finding an explanation of the observed order.

(2) Aqueous Solutions.

Both aluminum and gallium are amphoteric metals, possessing the ability to dissolve in acid solution to give the M(H\textsubscript{2}O)\textsubscript{6}³⁺ cation and in basic solution to yield
the $\text{M(OH)}_4^-$ anion. The $\text{In(H}_2\text{O)}_6^{3+}$ cation exists in aqueous acid solution, but in basic solution, the $\text{In(OH)}_3$ remains precipitated even in the presence of excess base.

The chemical shifts for the $\text{Al(OH)}_4^-$ and the $\text{Ga(OH)}_4^-$ complex ions relative to the $\text{Al(H}_2\text{O)}_6^{3+}$ and the $\text{Ga(H}_2\text{O)}_6^{3+}$ ions are -80 ppm., and -192 ppm., respectively. Both the $\text{Al(H}_2\text{O)}_6^{3+}$ and $\text{Al(OH)}_4^-$ ions give narrow resonances which is consistent with their cubic symmetry.\(^7^,\!^8\) The signals for the $\text{Ga(H}_2\text{O)}_6^{3+}$ and the $\text{Ga(OH)}_4^-$ ions are rather broad, 300 Hz. and 600 Hz. respectively. Aqueous indium perchlorate solutions give broad signals which sharpen upon addition of perchloric acid, but no chemical shift was indicated.\(^3\)

The broad lines observed for these gallium and indium complexes has been associated with exchange and the lowering of the molecular symmetry resulting from the effects of hydrolysis, for example,

$$\text{M(H}_2\text{O)}_6^{3+} + \text{H}_2\text{O} \rightleftharpoons \text{M(H}_2\text{O)}_5\text{(OH)}^{2+} + \text{H}_3\text{O}^+$$

Exchange effects can be seen especially well in the NMR spectra of many aqueous solutions of gallium and indium. Akitt et al.\(^2\) found that there is a critical concentration of acid for $\text{GaCl}_3 - \text{HCl}$ mixtures below which $\text{GaCl}_4^-$ is increasingly replaced by $\text{Ga(H}_2\text{O)}_6^{3+}$ and some intermediate species as marked by a displacement of the $\text{GaCl}_4^-$ signal towards the $\text{Ga(H}_2\text{O)}_6^{3+}$ signal position and a broadening of the $\text{GaCl}_4^-$ resonance. Similarly, the
GaBr$_3$ - HBr and the GaI$_3$ - HI mixtures also have their critical acid concentrations, but the tendency to form the intermediate species is less marked.

Some interesting data were obtained for indium$^3$ and can be found in Table III. The hydrolyzed species have extremely broad resonances, and they are considerably broader than the tetrachloro complexes, InX$_4^-$. There is

<table>
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<th>Solvent</th>
<th>Chemical Shifts (ppm.)</th>
<th>Line Widths (Hz.)</th>
</tr>
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<tbody>
<tr>
<td>InCl$_x$(H$<em>2$O)$</em>{6-x}$</td>
<td>H$_2$O</td>
<td>-180</td>
<td>8100</td>
</tr>
<tr>
<td>InCl$^-$</td>
<td>Et$_2$O</td>
<td>-440</td>
<td>675</td>
</tr>
<tr>
<td>InBr$^-$</td>
<td>Et$_2$O</td>
<td>-180</td>
<td>375</td>
</tr>
<tr>
<td>In(H$_2$O)$_6^{3+}$</td>
<td>H$_2$O</td>
<td>0</td>
<td>375</td>
</tr>
<tr>
<td>InBr$_x$(H$<em>2$O)$</em>{6-x}$</td>
<td>H$_2$O</td>
<td>+300</td>
<td>11,300</td>
</tr>
<tr>
<td>InI$_4^-$</td>
<td>H$_2$O</td>
<td>+578</td>
<td>1075</td>
</tr>
<tr>
<td>InI$_4^-$</td>
<td>Et$_2$O</td>
<td>+583</td>
<td>247</td>
</tr>
</tbody>
</table>

little hydrolytic interaction for the InI$_4^-$ in aqueous solution as indicated by the fact that the ratio of the line width of the complex in aqueous solution to that in ether is the same as the ratio of their viscosities. No
explanation of the anomalous shift for the $\text{InBr}_x (\text{H}_2\text{O})_{6-x}^{(3-x)+}$ was reported.

Aquated gallium and indium ions will coordinate with halide ions in solution while aluminum, with the sole exception of fluoride ions, will not. When a halide ion is added to a solution of $\text{In(ClO}_4)_3$ there is appreciable line broadening indicating complex formation with rapid exchange between the different species in solution, possibly

$$\text{In(H}_2\text{O)}_6^{3+} + \text{In(H}_2\text{O)}_5^{2+} \rightleftharpoons \text{In(H}_2\text{O)}_5^{2+} + \text{In(H}_2\text{O)}_6^{3+}$$

The $^{115}\text{In}$ chemical shift of indium nitrate solution is concentration dependent. In very dilute solutions, no shift relative to $\text{In(H}_2\text{O)}_6^{3+}$ is noted, but, as the concentration increases, the chemical shift increases 40 ppm to high field. This would imply a weak $\text{In}^{3+} - \text{NO}_3^-$ complex formation in solution.

Regardless of the concentration, the chemical shift for an indium sulphate solution is 18 ppm upfield from $\text{In(H}_2\text{O)}_6^{3+}$. At low concentration, the line is very broad, possibly indicating a rapid equilibrium such as

$$\text{In}^{3+}_{\text{aq}} + 2\text{SO}_4^{2-} \rightleftharpoons \text{InSO}_4^{+}_{\text{aq}} + \text{SO}_4^{2-} \rightleftharpoons \text{In(SO}_4)_2^{-}_{\text{aq}}.$$

Similar effects have been noted for the gallium halides. The addition of HCl to gallium perchlorate causes line broadening and a shift in line position towards the $\text{GaCl}_4^-$ ion.
The aluminum cation prefers to exist, in aqueous solution, as \( \text{Al}(\text{H}_2\text{O})_6^{3+} \) (in acid, or \( \text{Al(OH)}_4^- \) in base) and with the exception of fluoride ion, no anion was observed to produce any shift or broadening of the resonance line. When fluoride ions are added to an acidic solution containing the \( \text{Al}(\text{H}_2\text{O})_6^{3+} \) ions, there is no appreciable shift, but the resonance line is broadened appreciably, indicating some interaction of the type \(^7,^9\):

\[
\text{Al}(\text{H}_2\text{O})_6^{3+} + \text{AlF}(\text{H}_2\text{O})_5^{2+} \rightleftharpoons \text{AlF}(\text{H}_2\text{O})_5^{2+} + \text{Al}(\text{H}_2\text{O})_6^{3+}.
\]

Thus, water is not the most promising solvent in which to prepare and study the \( \text{AlX}_4^- \) ions.

(3) Non-aqueous Solutions

O'Reilly\(^7\) has obtained the spectra of the anhydrous aluminum halides in diethyl ether. The values which he found for the chemical shifts and line widths are given in Table IV. He assigned the shifts to the dimeric species, \( \text{Al}_2\text{X}_4 \), in solution on the basis of their narrow resonance lines, i.e., the dimers are 'nearly cubic' and therefore only a small electric field gradient at the nucleus might be expected. The solutions, initially colourless or pale yellow, eventually darken to a brown colour which he attributed to the formation of the etherate complex, \( \text{AlX}_3\cdot\text{OEt}_2 \).

The spectrum of the complex, \( \text{GaCl}_3\cdot\text{OEt}_2 \) was obtained by Akitt et al.\(^2\) on the pure liquid. The broad resonance
<table>
<thead>
<tr>
<th>Compound</th>
<th>Solvent</th>
<th>Chemical Shifts (ppm.)</th>
<th>Line Widths (Hz.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AlCl₃</td>
<td>Et₂O</td>
<td>-105</td>
<td>110</td>
</tr>
<tr>
<td>AlBr₃</td>
<td>Et₂O</td>
<td>-96</td>
<td>100</td>
</tr>
<tr>
<td>AlI₃</td>
<td>Et₂O</td>
<td>-39</td>
<td>88</td>
</tr>
<tr>
<td>GaCl₃·0Et₂</td>
<td>Neat</td>
<td>-137</td>
<td>Broad</td>
</tr>
<tr>
<td>AlCl₃</td>
<td>Toluene</td>
<td>-91</td>
<td>330</td>
</tr>
<tr>
<td>AlCl₃ + AlI₃</td>
<td>Toluene</td>
<td>-18</td>
<td>780</td>
</tr>
<tr>
<td>AlI₃</td>
<td>Toluene</td>
<td>+11</td>
<td>670</td>
</tr>
</tbody>
</table>

Line which they observed was attributed to the noncubic, C₃ᵥ, symmetry about the gallium nucleus.

Solutions of the anhydrous aluminum halides in toluene were studied by O'Reilly et al.⁴ They concluded that the unsymmetrical Al₂X₆·(toluene) complex was responsible for the observed shifts and line widths in Table IV. The presence of only one broad signal for the toluene solution of AlCl₃ and AlI₃ indicates that the halogens are rapidly exchanging.

(⁴) Aluminum Alkyls and their Complexes.

Initially, O'Reilly reported the chemical shifts and line widths for several aluminum alkyls in his original paper,⁷ and his results are in Table V. He concluded that the 'narrow' resonance line observed for AlMe₃ was the result of the near tetrahedral symmetry about the ²⁷Al nucleus in the dimeric Al₂Me₆ molecule. The broad line
observed for Al(i-Bu)$_3$ was interpreted as the effect of
the noncubic symmetry of the monomeric species.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Solvent</th>
<th>Chemical Shifts (ppm.)</th>
<th>Line Widths (Hz.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AlMe$_3$</td>
<td>Neat</td>
<td>-156</td>
<td>440</td>
</tr>
<tr>
<td>AlEt$_3$</td>
<td>Neat</td>
<td>-171</td>
<td>1620</td>
</tr>
<tr>
<td>Al(i-Bu)$_3$</td>
<td>Neat</td>
<td>-220</td>
<td>6000</td>
</tr>
</tbody>
</table>

Swift$^{10,11,12,13}$ and Poole$^{14}$ in their more sophisti-
cated studies of the aluminum alkyls have found that the line
widths increase with the increasing size of the alkyl group
and with increasing viscosity of the solvent. In solvents
of low viscosity, the dominant relaxation mechanism is
quadrupolar relaxation through molecular rotation, but in
solvents of high viscosity this mechanism becomes unimportant.

Several AlEt$_3$-donor complexes have been examined$^{13}$
where the donor atom is either sulphur, oxygen, or a
nitrogen atom. The chemical shifts, although crudely
measured, do show a dependence upon what donor atom is
bonded to the aluminum in the complex, decreasing in the
order $S > O > N$.

The line width is found to increase with the size of
the donor molecule, either due to an increase in the
rotational correlation time or to steric effects on the
molecular electric field gradient at the aluminum nucleus.
NMR data on the mixtures of donor molecules with AIEt$_3$ enables the donors to be arranged in order of decreasing strength towards complex formation: N > O > S. The nature of the donor atom appears to play a more important role in complex formation than do size effects. A rapid exchange between complexed and uncomplexed AIEt$_3$ occurs at room temperature.

(5) Summary.

Several important problems emerge from this literature survey. First, the magnetic shielding of the tetrahedral complex ions, MX$_4^-$, of gallium and indium lie in a series, Ml$_4^-$ > MBr$_4^-$ > MC1$_4^-$. The analogous aluminum series has not been investigated, and no theoretical explanation for the observed trend has been developed. Secondly, several authors in this survey have referred to the 'effects of symmetry on line width' argument to establish the structures of various compounds in solution. No limitations of this rule have been discussed. Similarly, no model for the effect of the size of the groups bonded to the atom in question has been developed.

In this thesis, the series of complex ions AlX$_n$Y$_m$Z$_{4-n-m}^-$ (where X, Y, Z = Cl, Br, I) will be investigated. An attempt will be made to account theoretically for the observed shifts and to define the limitations of the effects of symmetry and ligand bulk on the line width.

In order to carry out this investigation of the
above series of complex ions, nonaqueous solvents were employed. From the several attempts to prepare these anions, some valuable information on the behaviour of the aluminum halides in these solvents was obtained. Armed with this knowledge, an additional objective of this thesis will be to try and show if some solvation concept is appropriate for these solutions.
above series of complex ions, nonaqueous solvents were employed. From the several attempts to prepare these anions, some valuable information on the behaviour of the aluminum halides in these solvents was obtained. Armed with this knowledge, an additional objective of this thesis will be to try and show if some solvation concept is appropriate for these solutions.
CHAPTER II

EXPERIMENTAL PROCEDURE

A. EXPERIMENTS

(1) Purification of Solvents

Most of the solvents which were used were subject to vigorous drying procedures since the anhydrous aluminum halides are extremely susceptible to hydrolysis. In several cases, multicomponent signals were obtained which might be attributable to hydrolysis products.

Both methylene chloride and diethyl ether were stored over calcium hydride, but acetonitrile was kept over potassium hydroxide pellets.

Phosphoryl chloride was distilled prior to its use as a solvent.

Nitromethane was treated with commercial B.D.H. aluminum chloride, and it was stored in this fashion.

The remaining solvents, thionyl chloride, methylene bromide and methylene iodide, were used without further purification, i.e., the commercial grade was used.
(2) Preparation and Purification of Solutes.

All preparations were carried out under dry nitrogen in order to minimize hydrolysis. All glassware was dried in the oven or flame dried prior to its use.

Anhydrous aluminum chloride was prepared by passing dry HCl gas over aluminum turnings heated by an infra-red lamp. Excess HCl carried over the white aluminum chloride, and this crude product was then sublimed in vacuo. The sublimate was then used with no further purification.

Commercial anhydrous aluminum bromide was sublimed to give a pure white crystalline product, and it was this product which was used in the preparation of the solutions.

Anhydrous aluminum iodide was prepared by reacting iodine with excess aluminum turnings under dried CO₂ gas. The final crude product was then sublimed in vacuo. This sublimed product was used in the preparation of the solutions.

The commercial tetramethylammonium halide salts were thoroughly washed with ethanol and ether and then dried over an infra-red lamp for at least six hours.

Tetrapropylammonium iodide, (n-Pr)₄NI, was prepared from the corresponding bromide by anion exchange. An aqueous solution of the bromide salt was passed through an anion exchange column containing Dowex 1-8X, 20-50 Mesh resin. This solution was concentrated and the crystals collected. This product was then recrystallized from a methylene chloride - ethyl acetate mixture and dried over an infra-red
lamp for two to four hours.

Commercial tetrapropylammonium bromide was recrystal-
lized from a methylene chloride - ethyl acetate mixture and
dried from two to four hours over an infra-red lamp.

(3) Preparation of Solutions for NMR Spectroscopy.

Most solutions were prepared in the NMR tube in order
to reduce handling and minimize the chances of hydrolysis
during transfer processes. The general technique for the
preparation of these solutions involved the vacuum distil-
lation of the solvent onto the solute in the NMR tube which
was immersed in liquid nitrogen. Upon completion of the
distillation, the solutions were allowed to warm to room
temperature. If the solute did not readily dissolve, slight
heating was applied to coax it into solution. In most
cases, the solutions were clear, but for some, the solubility
was sufficiently low that not all of the solute dissolved
or the solvating process produced insoluble products. How-
ever, even for these cases, if enough clear solution was
available, the spectrum was obtained.

In the preparation of solutions involving the tetra-
alkylammonium salts, the salt and the appropriate aluminum
halide were mixed together prior to the distillation pro-
cess. The only exception to this was the aluminum bromide
case in which the \((n\text{-Pr})_4\text{NBr}\) was first dissolved in the
methylene chloride and the aluminum bromide dissolved in
this solution. This procedure was necessary since the mixture
of the aluminum bromide with the \((n-\text{Pr})_4\text{NBr}\) gave a melt at room temperature.

Fifteen millimeter NMR sample tubes were employed. Each was provided with a ground glass joint in order that it could be adequately sealed to exclude moisture.

(4) The NMR Spectra.

(a) Instrumentation and Measurements.

The NMR spectra in this work were obtained under high resolution conditions with the high resolution portion of a Varian model DP-60 spectrometer equipped with a model V-4311 fixed frequency oscillator operating at 15.1 MHz, with a field of approximately 13.6 k Gauss. The field was scanned using the Superstabilizer linear sweep.

The spectra were calibrated by modulating the 15.1 MHz oscillator by an audio frequency generator. Side bands were generated on either side of the reference signal or on either side of the sample signals.

Acidified aqueous aluminum nitrate was employed as the external reference. This solution was contained in a five millimeter sample tube inserted coaxially into the fifteen millimeter sample tube. All spectra were measured relative to this reference.

(b) Bulk Diamagnetic Susceptibility Corrections.

When cylindrical samples are used, it is sometimes necessary to make bulk susceptibility corrections.\(^{16,17}\) The
shifts which were measured for the various samples in this thesis were not corrected for bulk susceptibility effects for the following reasons:

(i) The chemical shifts were usually quite large (20 ppm. to 100 ppm.), and the correction would be negligible.

(ii) In the multicomponent solutions, this correction would also be negligible when comparing the chemical shifts of the various isostructural species in the same solution.

(c) The Error Limits.

On the average, six spectra were obtained for each sample; the field was scanned three times in each direction. The average chemical shift and line width was then computed from these six spectra. The error limits represent standard deviations indicating the precision of the results.

B. CALCULATIONS

(1) The Computer Programs.

Fortran IV programs were developed for the two-centre, one-electron overlap and Coulomb integrals from the results of Lofthus.\textsuperscript{18,19} Another program was then set up to calculate the shielding constant as a function of one variable. All calculations were performed on an International Business Machines 7040/44 computer maintained by the UWO Computer Centre.
CHAPTER III
RESULTS AND DISCUSSION

A. THE TETRAHALOALUMINATE IONS.

(1) The Experimental Results.

(a) The AlX₄⁻ Complexes.

In an earlier paper, mentioned briefly in the introduction, O'Reilly et al. ⁴ explained their broad NMR signal at -91 ppm, by attributing it to the AlCl₄⁻ ion. The solution was prepared by dissolving sodium chloride and aluminum chloride in benzene. This shift, however, is identical to the shift of aluminum chloride in toluene, and in addition, the signal was extremely broad (900 Hz) for an ion of cubic symmetry. This makes their assignment of this signal rather doubtful.

A more fruitful method of preparing the AlCl₄⁻ and AlBr₄⁻ ions was to dissolve the Me₄NX salt and the corresponding aluminum halide in nitromethane. ²⁰ Success was more elusive in the case of the AlI₄⁻ ion which was eventually synthesized in a methylene iodide solution of AlI₃ and (n-Pr)₄NI. Methylene iodide is not a very good solvent, and therefore, the solution was not a very concentrated one. A strong signal was, nevertheless, observed. Any attempt to
prepare the $\text{AlI}_4^-$ ion by means analogous to those used for $\text{AlCl}_4^-$ and $\text{AlBr}_4^-$ met with failure. A vigorous reaction occurred between the solutes, $\text{AlI}_3$ and $\text{Me}_4\text{NI}$, and the solvent, $\text{MeNO}_2$, and large quantities of iodine were produced. The NMR data obtained for the above three solutions can be found in Table VI.

**TABLE VI. NMR Data of the $\text{AlX}_4^-$ Complexes.**

<table>
<thead>
<tr>
<th>Complex Ion</th>
<th>Chemical Shifts (ppm.)</th>
<th>Line Widths (Hz.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{AlCl}_4^-$</td>
<td>$-101.5 \pm 0.3$</td>
<td>$39.5 \pm 7$</td>
</tr>
<tr>
<td>$\text{AlBr}_4^-$</td>
<td>$-79.7 \pm 0.4$</td>
<td>$58.1 \pm 2.8$</td>
</tr>
<tr>
<td>$\text{AlI}_4^-$</td>
<td>$+27.0 \pm 0.3$</td>
<td>$35.1 \pm 0.7$</td>
</tr>
</tbody>
</table>

(b) The Mixed Tetrahaloaluminate Ions.

An earlier attempt to prepare the $\text{AlI}_4^-$ anion in the presence of $\text{AlI}_3$ and $(\text{n-Pr})_4\text{NI}$ in methylene chloride solvent, led to some interesting and unexpected results. Five resonance lines were observed for this solution indicating five chemically distinct aluminum species in solution. A total of five resonance lines are to be expected when $\text{Cl}^-$ ions are allowed to exchange with the iodide ions of $\text{AlI}_4^-$. The chemical shift and line width data for this solution are depicted in Table VII. The signal at $-102$ ppm, was
easily identified as the \( \text{AlCl}_4^- \) ion by comparison with the shifts in Table VI. At the same time, the resonance line at +27.0 ppm. was assigned to the \( \text{AlI}_4^- \) ion on the basis of its width. The other ions were assigned by assuming that the chemical shifts decreased monotonically from +27.0 ppm. for \( \text{AlI}_4^- \) to −102 ppm. for the \( \text{AlCl}_4^- \) ion as chlorides were successively substituted for iodides.

**TABLE VII. NMR Data for the \( \text{AlI}_n\text{Cl}_4-n \) Complexes**

<table>
<thead>
<tr>
<th>Complex Ion</th>
<th>Chemical Shifts (ppm.)</th>
<th>Line Widths (Hz.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{AlI}_4^- )</td>
<td>+27.0 ± 0.2</td>
<td>23.9 ± 2.2</td>
</tr>
<tr>
<td>( \text{AlI}_3\text{Cl}^- )</td>
<td>−21.7 ± 0.4</td>
<td>46.0 ± 0.8</td>
</tr>
<tr>
<td>( \text{AlI}_2\text{Cl}_2^- )</td>
<td>−59.4 ± 0.3</td>
<td>57.6 ± 4.6</td>
</tr>
<tr>
<td>( \text{AlCl}_3^- )</td>
<td>−86.2 ± 0.3</td>
<td>42</td>
</tr>
<tr>
<td>( \text{AlCl}_4^- )</td>
<td>−102.4 ± 0.5</td>
<td>15.1 ± 0.5</td>
</tr>
</tbody>
</table>

The next spectrum which was observed was that for the solution of \( \text{AlI}_3 \) and \( (n-\text{Pr})_4\text{NI} \) in methylene bromide. Again, five signals, corresponding to the five possible \( \text{AlI}_n\text{Br}_4-n \) (\( 0 \leq n \leq 4 \)) complex ions, were observed. The resonance at −80.3 ppm., in Table VIII, was assigned to the \( \text{AlI}_4^- \) ion, and the signal at +27.0 ppm. was attributed to the \( \text{AlI}_4^- \) ion, as indicated in Table VI. The remaining three signals were assigned on the basis of the same assumption made for the interpretation of the previous spectrum.
FIGURE 1. The spectrum of $\text{AlI}_3 + (\text{n-Pr})_4\text{NI/CH}_2\text{Cl}_2$. 
The five complex ions \( \text{AlBr}_n\text{Cl}_{4-n}^- \) were prepared in a similar fashion by reacting the \( \text{AlBr}_3 \) with a solution of \((n-\text{Pr})_4\text{NBr}\) dissolved in methylene chloride. The NMR data are given in Table VIII, and illustrations of the above three spectra are depicted in Figures 1 to 3.

**TABLE VIII. The NMR Data for the (a) \( \text{AlI}_n\text{Br}_{4-n}^- \) and (b) \( \text{AlBr}_n\text{Cl}_{4-n}^- \) Complexes.**

<table>
<thead>
<tr>
<th>Complex Ion</th>
<th>Chemical Shifts (ppm.)</th>
<th>Line Widths (Hz.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a) ( \text{AlI}_4^- )</td>
<td>+26.1 ± 0.5</td>
<td>-</td>
</tr>
<tr>
<td>( \text{AlI}_3\text{Br}^- )</td>
<td>-7.4 ± 0.5</td>
<td>33.0 ± 9.8</td>
</tr>
<tr>
<td>( \text{AlI}_2\text{Br}_2^- )</td>
<td>-36.2 ± 0.4</td>
<td>31.1 ± 0.7</td>
</tr>
<tr>
<td>( \text{AlBr}_3^- )</td>
<td>-60.6 ± 0.8</td>
<td>31.1 ± 0.7</td>
</tr>
<tr>
<td>( \text{AlBr}_4^- )</td>
<td>-80.3 ± 0.6</td>
<td>20.7 ± 0.7</td>
</tr>
<tr>
<td>(b) ( \text{AlBr}_4^- )</td>
<td>-79.5 ± 0.3</td>
<td>11.5 ± 0.1</td>
</tr>
<tr>
<td>( \text{AlBr}_3\text{Cl}^- )</td>
<td>-87.2 ± 0.3</td>
<td>18.8 ± 0.6</td>
</tr>
<tr>
<td>( \text{AlBr}_2\text{Cl}_2^- )</td>
<td>-93.6 ± 0.4</td>
<td>20.7 ± 0.3</td>
</tr>
<tr>
<td>( \text{AlBrCl}_3^- )</td>
<td>-98.7 ± 0.2</td>
<td>17.4 ± 0.6</td>
</tr>
<tr>
<td>( \text{AlCl}_4^- )</td>
<td>-102.3 ± 0.3</td>
<td>-</td>
</tr>
</tbody>
</table>

An impressive spectrum containing twelve resonance lines was obtained for the methylene chloride solution of \( \text{AlI}_3 \) and \((n-\text{Pr})_4\text{NBr}\). The chemical shift and line width measurements can be found in Table IX. There are fifteen possible complex ions which can occur in this solution, and therefore, fifteen possible resonance signals which
FIGURE 2. The spectrum of $\text{AlBr}_4^-$

FIGURE 3. The spectrum of $\text{Al}_{3n}\text{Br}_4^-$.
could be observed. Only twelve lines were found.

**TABLE IX. The NMR Data of the Complexes $\text{Al}_{n}\text{Br}_m\text{Cl}_{4-n-m}$.**

<table>
<thead>
<tr>
<th>Complex Ion</th>
<th>Chemical Shifts (ppm.)</th>
<th>Line Widths (Hz.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{AlI}_4^-$</td>
<td>$+26.6 \pm 0.2$</td>
<td>$17.5 \pm 0.3$</td>
</tr>
<tr>
<td>$\text{AlI}_3\text{Br}^-$</td>
<td>$-6.2 \pm 0.2$</td>
<td>$22.8 \pm 0.3$</td>
</tr>
<tr>
<td>$\text{AlI}_3\text{Cl}^-$</td>
<td>$-21.3 \pm 0.3$</td>
<td>$-$</td>
</tr>
<tr>
<td>$\text{AlI}_2\text{Br}_2^-$</td>
<td>$-34.8 \pm 0.2$</td>
<td>$24.7 \pm 0.6$</td>
</tr>
<tr>
<td>$\text{AlI}_2\text{BrCl}^-$</td>
<td>$-47.7 \pm 0.3$</td>
<td>$42.9 \pm 1.0$</td>
</tr>
<tr>
<td>$\text{AlIBr}_3^-, \text{AlI}_2\text{Cl}_2^-$</td>
<td>$-59.2 \pm 0.4$</td>
<td>$26.3 \pm 0.4$</td>
</tr>
<tr>
<td>$\text{AlIBr}_2\text{Cl}^-$</td>
<td>$-69.3 \pm 0.6$</td>
<td>$34.8 \pm 0.5$</td>
</tr>
<tr>
<td>$\text{AlBr}_4^-, \text{AlIBrCl}_2^-$</td>
<td>$-78.6 \pm 0.7$</td>
<td>$37.2 \pm 0.9$</td>
</tr>
<tr>
<td>$\text{AlBr}_3\text{Cl}^-, \text{AlI}_2\text{Cl}_3^-$</td>
<td>$-86.7 \pm 0.9$</td>
<td>$27.3 \pm 1.8$</td>
</tr>
<tr>
<td>$\text{AlBr}_2\text{Cl}_2^-$</td>
<td>$-93.0 \pm 0.8$</td>
<td>$24.9 \pm 1.8$</td>
</tr>
<tr>
<td>$\text{AlBrCl}_3^-$</td>
<td>$-98.3 \pm 0.9$</td>
<td>$21.9 \pm 0.4$</td>
</tr>
<tr>
<td>$\text{AlCl}_4^-$</td>
<td>$-101.8 \pm 0.5$</td>
<td>$-$</td>
</tr>
</tbody>
</table>

With the aid of the assignments already made for the three previous spectra (see Tables VII and VIII), the resonances in this spectrum were identified. There were two signals at $-47.7$ ppm. and $-69.3$ ppm. which had not appeared in any previous spectra, and these were assigned on the basis of the following argument. If it is assumed that the iodide contributes a greater diamagnetic or positive shift than the bromide, and the bromide more than
FIGURE 4. The spectrum of AlI$_3$ + (n-Pr)$_4$NBr/CH$_2$Cl$_2$. 
the chloride*, then the $^{27}\text{Al}$ nuclear screening constants of the mixed halide complexes, $\text{AlI}_n\text{Br}_m\text{Cl}_{4-n-m}^-$, should lie in the order

$$\text{AlI}_2\text{BrCl}^- > \text{AlIBr}_2\text{Cl}^- > \text{AlIBrCl}_2^-.$$ 

Therefore, the signal at $-47.7$ ppm was assigned to the $\text{AlI}_2\text{BrCl}^-$ ion, and the one at $-69.3$ ppm to the $\text{AlIBr}_2\text{Cl}^-$ ion.

There still remains the $\text{AlIBrCl}_2^-$ ion to be identified. In Table IX, the line at $-78.6$ ppm is one of the broadest lines in the spectrum. This is approximately the position at which the $\text{AlBr}_4^-$ ion absorbs. However, this line is too broad to be assigned to this tetrahedral anion, and so this peak was attributed to the overlapping of the two resonance lines for $\text{AlBr}_4^-$ and $\text{AlIBrCl}_2^-$. 

This spectrum is illustrated in Figure 4.

The qualitative discussion of the above data will now be divided into two main parts; the first will deal with the chemical shift measurements, and the second will give a brief analysis of the line width data.

* This assumption is made on the basis of the order of the $^{27}\text{Al}$ screening in the pure halide complexes, i.e., $\text{AlI}_4^- > \text{AlBr}_4^- > \text{AlCl}_4^-$. 
(2) Discussion.

(a) Factors Predominant in Determining the Range of Chemical Shifts.

In Table X, the chemical shift data for the iso-electronic and isostructural series of compounds, \( \text{MX}_4 \) (where \( X = \text{Cl, Br, I} \)), of boron\(^{21} \), aluminum, gallium\(^{2} \), indium\(^{3} \) and tin\(^{22} \) are listed. The shift values from this table show that the chemical shift range increases with increasing atomic number, that is,

\[ \text{B} < \text{Al} < \text{Ga} < \text{In} < \text{Sn}. \]

This same tendency for the elements of higher atomic number to give larger chemical shifts has been noted before.\(^{23} \)

In order to arrive at a suitable explanation of this phenomenon, a rough calculation of the shielding constants will be carried out by the method of Schneider and Buckingham\(^{24} \). This discussion will also give an insight into some of the concepts involved and will provide a basis for later comments.

If an atom or a molecule is placed in a magnetic field, it acquires a diamagnetic moment by virtue of the induced orbital motion of its electrons.\(^{16} \) These moving electrons constitute effective currents within the molecule and, thereby, produce a secondary magnetic field which also acts on all the nuclei present. Since the induced currents are proportional to the applied field, \( H_0 \), the magnitude of this secondary field will also be
<table>
<thead>
<tr>
<th>X</th>
<th>(^{11}\text{B} (a))</th>
<th>(^{27}\text{Al})</th>
<th>(^{71}\text{Ga} (b))</th>
<th>(^{115}\text{In} (c))</th>
<th>(^{119}\text{Sn} (d))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl</td>
<td>-6.6</td>
<td>-102</td>
<td>-257</td>
<td>-440</td>
<td>+150</td>
</tr>
<tr>
<td>Br</td>
<td>+23.9</td>
<td>-79.7</td>
<td>-127</td>
<td>-180</td>
<td>+635</td>
</tr>
<tr>
<td>I</td>
<td>+128</td>
<td>+27.0</td>
<td>+450</td>
<td>+583</td>
<td>+1702</td>
</tr>
<tr>
<td>Range</td>
<td>135</td>
<td>130</td>
<td>707</td>
<td>1023</td>
<td>1552</td>
</tr>
</tbody>
</table>

(a) Ref. 21. (b) Ref. 2. (c) Ref. 3. (d) Ref. 22.
proportional to the applied field. Therefore, the local magnetic field, $H_{\text{loc}}$, at the position of a nucleus will be given by

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

where $\sigma$, called the shielding constant, is a nondimensional constant independent of $H_0$, but dependent on the chemical environment.

The chemical shift, $\delta$, is defined as the difference between the shielding constants, that is,

$$\delta = \sigma_s - \sigma_r = \frac{H_s - H_r}{H_r} \quad (2)$$

where $\sigma_s$ and $\sigma_r$ are the screening constants of the sample and reference respectively. $H_s$ and $H_r$ are the resonant fields for the sample and reference respectively.

The shielding constant can be written as the sum of two parts, the spherical or diamagnetic part, $\sigma_d$, and the nonspherical or paramagnetic part, $\sigma_p$, that is

$$\sigma = \sigma_d + \sigma_p \quad (3)$$

Schneider and Buckingham, in their atom-in-a-molecule model for the chemical shift, have modified Ramsey's equation to give for the diamagnetic term

$$\sigma_d = \frac{e^2}{3mc^2} \cdot \frac{Z_{\text{eff}}}{a_0 n^2}$$
\[ \sigma_d = 17.8 \times 10^{-6} \frac{Z_{\text{eff}}}{n^2} \]  \hspace{1cm} (4)

For aluminum, \( n \), the principal quantum number, is 3, \( Z_{\text{eff}} \), the effective nuclear charge, is 6.40, and \( a_0 \) is the Bohr radius.

A value of \( Z_{\text{eff}} = (Z/Z_0)^{1/2} \) was used by these authors rather than \( Z_{\text{eff}} = Z_0 = Z - s \), where \( Z \) is the nuclear charge and \( s \) is the screening constant which was evaluated by Slater's rules.\(^{26}\) This was probably because the use of \( Z_0 \) gave values of the average orbital radius, \( \langle r \rangle \), which were too large, implying that the \( Z_0 \) value is too small.

In Table XI, the values of \( \sigma_d \) for the addition of a single electron to the np shell of each atom are given. The value of \( \sigma_d = 12.7 \) ppm, for the addition of one electron to the 3p shell of aluminum cannot adequately account for the shift range of 129 ppm. Similar comments also hold for the other nuclei shown in the table.

The paramagnetic term, \( \sigma_p \), is given as

\[ \sigma_p = -\frac{e^2 \hbar^2 L(L+1)}{3m^2c^2 \Delta E} \left( \frac{1}{r^3} \right) \]  \hspace{1cm} (5)

where \( L(L+1)\hbar^2 \) is the orbital angular momentum contribution. If the atoms or ions \( M \) in the \( MX_4 \) compounds are considered to have a \( ns^1np_x^1np_y^1np_z^1 \) configuration, then \( L(L+1) = 2 \). \( \Delta E \) is an average excitation energy. The \( \langle r^{-3} \rangle \) contribution can be written as
\[ \left\langle \frac{1}{r^3} \right\rangle = \frac{Z_{\text{eff}}}{a_0 n^3 l(l + 1)(l + 1/2)} \]  

(6)

where \( l \) is the orbital angular momentum of the \( p \) orbital, i.e., \( l = 1 \). When expressions (5) and (6) are combined, the paramagnetic contribution can then be written as

\[ \sigma_p = -7.67 \times 10^{-16} \frac{Z_{\text{eff}}^3 L(L + 1)}{n^3 l(l + 1)(l + 1/2) \Delta E} \]  

(7)

Equation (7) predicts a shift of -990 ppm for aluminum which will adequately account for the observed shift range of 129 ppm. Similarly for the other elements, the shift ranges can only be explained if the paramagnetic term is the most important quantity contributing to the shielding constant. The \( \sigma_p \) values in Table XI certainly support this contention.

Since the paramagnetic term, \( \sigma_p \), is the more important contribution to the chemical shift (except for protons), it is desirable to investigate what parameters control its magnitude. There are only two factors which could appreciably influence the size of the \( \sigma_p \) term. These are the average energy, \( \Delta E \), and the mean value of \( r^{-3} \), \( \left\langle r^{-3} \right\rangle \). The latter quantity is proportional to the cube of the effective nuclear charge.

With such approximate figures in Table XI, it is difficult to specifically say which of these two quantities is predominant in determining the magnitude of the paramagnetic term. However, since the \( \left\langle r^{-3} \right\rangle \) contribution
<table>
<thead>
<tr>
<th></th>
<th>B</th>
<th>Al</th>
<th>Ga</th>
<th>In</th>
<th>Sn</th>
</tr>
</thead>
<tbody>
<tr>
<td>Z</td>
<td>5</td>
<td>13</td>
<td>31</td>
<td>49</td>
<td>50</td>
</tr>
<tr>
<td>s</td>
<td>2.75</td>
<td>9.85</td>
<td>26.35</td>
<td>44.35</td>
<td>44.35</td>
</tr>
<tr>
<td>Z₀</td>
<td>2.25</td>
<td>3.15</td>
<td>4.65</td>
<td>4.65</td>
<td>5.65</td>
</tr>
<tr>
<td>Zₑff</td>
<td>3.35</td>
<td>6.40</td>
<td>12.0</td>
<td>15.1</td>
<td>16.8</td>
</tr>
<tr>
<td>σₐ(ppm.)</td>
<td>14.9</td>
<td>12.7</td>
<td>13.3</td>
<td>10.8</td>
<td>12.0</td>
</tr>
<tr>
<td>L(L + 1)</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>ΔE (ergs)</td>
<td>5x10⁻¹²</td>
<td>5x10⁻¹²</td>
<td>5x10⁻¹²</td>
<td>5x10⁻¹²</td>
<td>5x10⁻¹²</td>
</tr>
<tr>
<td>σₚ(ppm.)</td>
<td>-480</td>
<td>-990</td>
<td>-2761</td>
<td>-2817</td>
<td>-3879</td>
</tr>
</tbody>
</table>
depends on the cube of the effective nuclear charge, then it will be sensitive to any changes in $Z_{\text{eff}}$. It does seem likely that for this series of compounds, on this evidence and the discussion to follow, that it is the $r^{-3}$ which is the controlling factor in the relative magnitudes of the $\sigma_p$ terms.

(b) The Magnetic Shielding in the AlI$_n$Br$_m$Cl$_{4-n-m}$ Series.

(i) A Simple Shift Calculation for the SnI$_n$Cl$_{4-n}$ and AlI$_n$Cl$_{4-n}$ Compounds.

The magnetic shielding for the MX$_4$ compounds decreases in the order, MI$_4 >$ MBr$_4 >$ MCl$_4$. This trend is even more strikingly illustrated for aluminum and tin by the shifts for the series of compounds, MX$_n$Y$_{4-n}$. For tin, the chemical shift was a smooth function of the composition of the complex, and the change in shift with substitution was linear for all but SnI$_n$Cl$_{4-n}$ series where a slight non-linearity was observed.

In the case of the aluminum complexes, the chemical shift is also observed to be a smooth function of the composition, but for no series of AlX$_n$Y$_{4-n}$ complexes is the change linear.

Burke and Lauterbur$^{22}$ were able to predict, with reasonable accuracy, the values of the shifts for the tin compounds by assuming that each halogen atom contributed an amount equal to one-fourth of the shift of the corresponding pure halide, SnX$_4$. Similar computations for the
aluminum analogues do not yield good agreement. Table XII contains some sample calculations for the \(\text{MI}_n\text{Cl}_{4-n}\) series of compounds. Reasonable correspondence between calculated and experimental shifts were achieved for tin, but disastrous results are obtained for aluminum.

**TABLE XII. Simple Shift Calculations for \(\text{SnI}_n\text{Cl}_{4-n}\) and \(\text{AlI}_n\text{Cl}_{4-n}\).**

<table>
<thead>
<tr>
<th>Compound</th>
<th>Sn</th>
<th>Al</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(calc.)</td>
<td>(exp.)</td>
</tr>
<tr>
<td></td>
<td>(ppm.)</td>
<td>(ppm.)</td>
</tr>
<tr>
<td>(\text{MI}_4)</td>
<td>1702</td>
<td>1702</td>
</tr>
<tr>
<td>(\text{MI}_3\text{Cl})</td>
<td>1426</td>
<td>1340</td>
</tr>
<tr>
<td>(\text{MI}_2\text{Cl}_2)</td>
<td>926</td>
<td>948</td>
</tr>
<tr>
<td>(\text{MCl}_3)</td>
<td>538</td>
<td>550</td>
</tr>
<tr>
<td>(\text{MCl}_4)</td>
<td>150</td>
<td>150</td>
</tr>
</tbody>
</table>

Can an adequate explanation be given for the observed trend in the magnetic shielding, \(\text{MI}_4 > \text{MBr}_4 > \text{MCl}_4\)? Using the atom-in-a-molecule model, the second order paramagnetic term is known to be the more important contribution to the shielding constant. The size of this term depends upon the relative magnitudes of the \(\Delta E\) and \(\langle r^{-3}\rangle\) parameters.

Experimentally, the shifts for the \(\text{AlX}_4^-\) complexes are in the order

\[ \delta_{\text{AlI}_4^-} > \delta_{\text{AlBr}_4^-} > \delta_{\text{AlCl}_4^-}. \]
If the diamagnetic term is neglected or assumed to give only a small but fixed contribution to each shift, then

\[ \sigma_{pI} > \sigma_{pBr} > \sigma_{pCl} \]  

(8)

Since \( \sigma_p \) is a negative quantity, by equation (7), the magnitude of the paramagnetic shifts will be in the order

\[ |\sigma_{pCl}| > |\sigma_{pBr}| > |\sigma_{pI}| \]  

(9)

where the relative sizes of these terms must be determined by either the \( \Delta E \) parameter, the \( \langle r^{-3} \rangle \) factor or possibly both.

(ii) The \( \Delta E \) Dependence.

Since these compounds of tin and aluminum possess no d-electrons, the lowest lying transition will be a charge transfer band in which an electron from one of the non-bonding orbitals on the halide is transferred to a vacant metal d-orbital.\textsuperscript{27} The relative ease with which the halide will lose an electron should reflect the order of the energies for these transitions. It is well known that this order is

\[ I^- > Br^- > Cl^- \]

This order can be illustrated in a number of ways, but the simplest is the order of the standard oxidation potentials. This order is \( V^0_I > V^0_{Br} > V^0_{Cl} \) as can be seen from the equations\textsuperscript{28}
\[ I^- \rightarrow \frac{1}{2}I_2 + e^-, \quad V^o_I = -0.54 \text{ volts} \]
\[ Br^- \rightarrow \frac{1}{2}Br_2 + e^-, \quad V^o_{Br} = -1.07 \text{ volts} \]
\[ Cl^- \rightarrow \frac{1}{2}Cl_2 + e^-, \quad V^o_{Cl} = -1.36 \text{ volts} \]

The more positive oxidation potential of \( I^- \) indicates that an electron is more easily removed from the iodide than the bromide which is, in turn, more easily oxidized than the chloride.

This trend in the ease with which the halide loses an electron would imply that the transition energies for charge transfer bands lie in the decreasing order \(^{29,30}\)

\[ \Delta E_{Cl} > \Delta E_{Br} > \Delta E_{I^-} \quad (10) \]

These transition series are not known for the Al\(\text{X}_4^-\) ions, but this information is known for the stannic halides. The wave lengths for the transitions in the ultraviolet are, \(^{31}\) for SnCl\(_4\) in t-BuOH, \(\lambda = 217 \text{ m}\mu\), SnBr\(_4\) in hexane, \(\lambda = \text{ca.} 235 \text{ m}\mu\), and SnI\(_4\) in t-BuOH, \(\lambda = 360, 290 \text{ m}\mu\). A similar order is also expected for the corresponding aluminum complexes.

If it is assumed that the transition energy to the first excited state is indicative of the mean excitation energy, and since \(\sigma_p\) is inversely proportional to \(\Delta E\), then the predicted order of the shifts is the reverse of the experimentally observed order in (9). Thus, the only remaining parameter which could possibly account for the
observations is the $\langle r^{-3} \rangle$ factor.

(iii) The Nephelauxetic Effect and the $\langle r^{-3} \rangle$ Dependence.

Qualitatively, these shifts can be explained on the basis of the nephelauxetic effect. This effect is a measure of the ligand's ability to expand the electron charge cloud of the metal and, thereby, reduce the interelectronic repulsion energy in the valence shell.\(^5\,^{32}\)

This effectively amounts to increasing the average electronic distance from the metal nucleus. The order of the halides in the nephelauxetic series are

$$\text{I}^- > \text{Br}^- > \text{Cl}^-.$$

The average electron-nuclear distance will lie in the same order

$$\langle r_{\text{I}} \rangle > \langle r_{\text{Br}} \rangle > \langle r_{\text{Cl}} \rangle$$

and this implies that

$$\left( \frac{1}{r_{\text{Cl}}^3} \right) > \left( \frac{1}{r_{\text{Br}}^3} \right) > \left( \frac{1}{r_{\text{I}}^3} \right).$$

This is the same order as the magnitudes of the paramagnetic terms in expression (9) and the chemical shifts.

In Part B of this chapter, an attempt to place this argument on a more quantitative basis will be made.

(c) Line Widths.

(i) General Theory of the Line Width.

The line width of a resonance signal is inversely proportional to $\tau$, the lifetime of the nucleus in the
excited spin state. The nucleus undergoing absorption of energy and the eventual transition to a lower state does not constitute a stationary system, and, therefore, the energy spread is related to the characteristic time, \( \tau \), for the rate of change of the system, by the Heisenberg uncertainty relation, \( \tau \Delta E \geq \hbar \). If the energy state, \( E \), is a stationary one, then \( \tau \) becomes infinite, and the uncertainty in the energy, or the energy spread, vanishes. If, however, the energy state is not stationary, then the energy spread is inversely proportional to the lifetime of the state, \( \tau \). If \( \tau \) is long, then \( \Delta E \) will be small, and the signal representing the absorption will be a narrow line. Conversely, if \( \tau \) is short, then the energy spread will be large and a broad resonance will be observed.

Large \( \tau \) values arise when the relaxation mechanisms which return the excited nuclei to the ground state are relatively inefficient. For nuclei with spin, \( I = 1/2 \), the only means of nuclear magnetic relaxation are the induced downwards transitions stimulated by magnetic fields oscillating at the Larmor frequency. The time constant or average lifetime of this nuclear spin-lattice relaxation process, is the spin-lattice relaxation time, \( T_1 \), which may vary from \( 10^{-3} \) to 10 seconds for liquids.\(^{17} \)

When the width is larger than due to spin-lattice relaxation, another characteristic time, \( T_2 \), smaller than \( T_1 \), is defined. \( T_2 \) is sometimes called the spin-spin
relaxation time, and it is important in determining the line widths for solids. In liquids, however, where rapid molecular rotation averages out the magnetic fields, there remains only the spin-lattice relaxation time because $T_1$ and $T_2$ become roughly equal.

If the nucleus has a spin, $I > 1/2$, it will possess an electric quadrupole moment which is a measure of the nonsphericity of the nuclear charge distribution. In addition to the relatively inefficient magnetic dipolar relaxation mechanism, these nuclei have an additional relaxation process which will shorten $T_1$ and thereby result in line broadening. In a uniform electric field, the energy of the nucleus is independent of its orientation, but if an electric field gradient is present the quadrupole moment will precess about its axis and the nuclear magnetic levels will be displaced.

Electric field gradients arise from two sources: (a) from the environment surrounding the molecule, and (b) from within a molecule along a covalent bond. The former is important for solids, but in liquids, it is averaged to zero by molecular tumbling. The latter is important for both solids and liquids.

The interaction between the electric quadrupole moment of the $^{27}$Al nucleus and an electric field gradient at the nucleus provides a facile relaxation mechanism for shortening the lifetime of the excited spin state. Shortening
the lifetime of the state increases the uncertainty in the
energy, $\Delta E$, and results in a broadened line.

Both the dipolar and quadrupolar broadening occur but
the latter is the dominant relaxation mechanism. For those
nuclei with spin, $I = 1/2$, for example $^1H$ and $^{19}F$ nuclei,
only the inefficient dipolar mechanism is operative, and
therefore, the spectra of these nuclei generally consist of
very sharp lines (of the order of 0.5 to 1 Hz.). If the
spin, $I > 1/2$, then the presence of the additional quadru-
polar relaxation mechanism will produce broader lines,
usually greater than 15 Hz. for aluminum.

The line width $\Delta \nu$ measured at one-half the peak height
can be expressed by

$$\Delta \nu = \frac{0.024}{\pi} \left( 1 + \frac{\eta_a^2}{3} \right) \left( \frac{eQ \frac{\partial^2 \nu}{\partial z^2}}{h} \right)^2 \tau_c$$

(12)

where $\frac{eQ \frac{\partial^2 \nu}{\partial z^2}}{h}$ is the quadrupole coupling constant, $\eta_a$
the asymmetry parameter of the electric field gradient,
and $\tau_c$ the correlation time. Usually $\tau_c$ can be approxima-
ted by the Debye relation

$$c = \frac{4\pi a^3 \eta}{3kT} = \frac{V_m \eta}{kT}$$

(13)

where $\eta$ is the viscosity of the solution, $a$ is a molecular
size parameter, and $V_m$ is the molar volume. $T$ is the
temperature in degrees Kelvin, and $k$ is Boltzmann's con-
stant.
Swift et al.\textsuperscript{13} and Poole\textsuperscript{14} have shown for the aluminum alkyls that the dominant relaxation mechanism is the quadrupolar one, although the viscosities of the liquids can play an important role in determining the line width. When comparing line widths of various compounds in different solvents, cognizance of the effects of the viscosity should be taken if an accurate interpretation of the results is to be made. For each $\text{AlX}_n\text{Y}_{4-n}^-$ system where each of the five anions is in the same solution, the relative effects of viscosity will be minimized. Consequently, the remaining factors contributing to the line width will be the quadrupole--electric field gradient coupling mechanism, the dipolar relaxation and the size of the ion contributing through the rotational correlation time $\tau_c$.

(ii) Effects of Symmetry on Line Width.

Several authors\textsuperscript{2,3,4,7,13} have argued that the symmetry of a molecule determines the magnitude of the electric field gradient at a particular nucleus, but never has a quantitative limit been placed upon this argument. The $\text{AlX}_n\text{Y}_{4-n}^-$ systems constitute ideal systems for investigating the role of symmetry upon the line width. In each series, there are two ions with $T_d$ symmetry, two with $C_{3v}$ and one with $C_{2v}$ symmetry. In particular, the $\text{AlI}_n\text{Cl}_{4-n}$ series of complexes will be examined since for these ions the effects are most pronounced. Also, it is the only series for which complete information is available. The
line widths for this series are shown in the following table.

TABLE XIII. Symmetry and Line Width Data for the AlI$_{n}$Cl$_{4-n}$ Series.

<table>
<thead>
<tr>
<th>Symmetry</th>
<th>Complex Ion</th>
<th>Line Widths (Hz.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>T$_{d}$</td>
<td>AlI$_{4}^{-}$</td>
<td>23.9</td>
</tr>
<tr>
<td></td>
<td>AlCl$_{4}^{-}$</td>
<td>15.1</td>
</tr>
<tr>
<td></td>
<td>AlI$_{3}$Cl$^{-}$</td>
<td>46.0</td>
</tr>
<tr>
<td>C$_{3v}$</td>
<td>AlI$<em>{2}$Cl$</em>{3}^{-}$</td>
<td>42.0</td>
</tr>
<tr>
<td>C$_{2v}$</td>
<td>AlI$<em>{2}$Cl$</em>{2}^{-}$</td>
<td>57.6</td>
</tr>
</tbody>
</table>

From this table, it can be seen that the two anions of T$_{d}$ symmetry produce the narrowest signals. The ions with C$_{3v}$ symmetry give broader signals, and the AlI$_{2}$Cl$_{2}^{-}$ complex which has the lowest symmetry, C$_{2v}$, produces the broadest resonance.

In Appendix A, it is demonstrated that the electric field experienced by the aluminum nucleus in the T$_{d}$ ions is zero. Therefore, to a first approximation, the quadrupolar relaxation mechanism is not available to these ions. The observed line widths are still too broad to result from magnetic dipolar relaxation alone. Magnetic field inhomogeneity and possibly second-order broadening resulting from anharmonic effects on the vibrational modes of the T$_{d}$ ions could account for these line widths.

Nonzero electric field gradients do exist for the ions with C$_{3v}$ and C$_{2v}$ symmetry. On the basis of the calcu-
lution performed in Appendix A, the change from \( C_{3v} \) to \( C_{2v} \) symmetry causes an increase of about 15\% in the electric field gradient at the aluminum nucleus. This does not account for all the broadening observed, and the remaining contributions to the line width may result from magnetic dipolar broadening, the effects of molecular size and viscosity on the correlation time.

(iii) The Correlation Time and Molecular Bulk.

Table XIV shows a comparison between the line widths and the size of the ions with the same symmetry.

<table>
<thead>
<tr>
<th>Symmetry</th>
<th>Complex Ion</th>
<th>( a ) (A)</th>
<th>Ratio ( a_1/a_2 )</th>
<th>Line Widths (Hz.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( T_d )</td>
<td>AlI(_4^-)</td>
<td>4.72</td>
<td>1.7</td>
<td>23.9</td>
</tr>
<tr>
<td></td>
<td>AlCl(_4^-)</td>
<td>3.94</td>
<td></td>
<td>15.1</td>
</tr>
<tr>
<td>( C_{3v} )</td>
<td>AlI(<em>3)Cl(</em>-)</td>
<td>4.53</td>
<td>1.3</td>
<td>46.0</td>
</tr>
<tr>
<td></td>
<td>AlCl(_3^-)</td>
<td>4.14</td>
<td></td>
<td>42.0</td>
</tr>
</tbody>
</table>

The values of 'a' were determined by adding the Pauling covalent radius\(^5\) of chloride or iodide ion to the corresponding Al-X bond distance.* This sum is a rough

---

* The value of 2.13 A for \( R_{\text{Cl}} \) was obtained from the X-ray measurements\(^3\)\(^4\) for the AlCl\(_4^-\) ion. No data was available for AlBr\(_4^-\) or AlI\(_4^-\). The value for \( R_{\text{Cl}} \) is, however, the average of the aluminum-terminal chlorine and aluminum-bridging chlorine distances in the dimer, Al\(_2\)Cl\(_6\).\(^3\)\(^5\) A similar average for AlBr\(_6\) and AlI\(_6\) gives the values \( R_{\text{Br}} = 2.27 \) A and \( R_I = 2.56 \) A for the AlBr\(_4^-\) and AlI\(_4^-\) ions respectively.
estimate of the radius of the $\text{AlI}_4^-$ ion. The 'a' value for
the $C_{3v}$ ions was computed by the formula

$$a = \frac{3a_x + a_y}{4}$$

(14)

where the value of $a_z$ is the a value for the pure $\text{AlZ}_4^-$ ion.

The ratio of the $a^3$ values for the $T_d$ ions more than
adequately accounts for the difference in the line widths
for these anions. Similarly, the value of 1.3 also explains
the difference in the widths for the $C_{3v}$ ions.

(3) Conclusions.

(a) Chemical Shifts.

The salient points established in the section on the
discussion of the chemical shifts are the following:
1. On the basis of the rough calculations performed in (2a),
it is clear that the paramagnetic term is the dominant con-
tribution to the $27_\text{Al}$ screening constant, and it is only this
term which can account for the large range in the observed
shifts.
2. The second order term, $\sigma_p$, is known to depend primarily
upon two quantities, an average excitation energy, $\Delta E$, and
the average $\langle r^{-3} \rangle$ value. $\Delta E$ cannot explain the observed
trend in the shifts, i.e. $\text{AlI}_4^- > \text{AlBr}_4^- > \text{AlCl}_4^-$. The
$\langle r^{-3} \rangle$ parameter, however, can explain the observed order
on the basis of the nephelauxetic effect.
3. The nonlinearity in the chemical shifts which was
observed as one iodide was exchanged for a bromide or
chloride cannot be explained on such a qualitative basis alone.

(b) Line Widths.

In section (2c) it was shown that the symmetry of the ion plays a dominant role in determining the line width. The effect of reducing the symmetry of the ion from $C_{3v}$ to $C_{2v}$ can increase the line width as much as 15%.

The line width is also dependent upon the size of the ion, the larger the ion the broader the resonance line, other things being equal.

Many of these observations in this section will be important for the discussion of the data for the aluminum halides in various solvents in Part C of this chapter.
8. SOME CHEMICAL SHIFT CALCULATIONS.

(1) Introduction.

The shielding constant, \( \sigma \), relative to the \( \text{Al}^{3+} \) ion, has been evaluated for the \( \text{AlH}_4^- \) ion in a variational calculation performed by O'Reilly.\(^7\) He has employed both valence bond and molecular orbital wave functions and has obtained values of \(-70\) and \(-75 \text{ ppm}\), respectively.

Since the chemical shift of \( \text{AlH}_4^- \), \(-106 \text{ ppm}\), was measured relative to the \( \text{Al(H}_2\text{O})_6^{3+} \) ion in aqueous solution, it is difficult to gauge the success of this calculation without the knowledge of the shielding constant for the reference. By the definition of the chemical shift,\(^16\) i.e., \( \delta = \sigma_s - \sigma_r \), the shielding constant for the reference must be positive. This does not seem particularly satisfactory in view of the importance of the negative paramagnetic term used to explain the magnitudes of the observed chemical shifts.

In this part of Chapter III, the perturbation approach will be applied, and a rough estimate of the shielding constants will be obtained for the \( \text{AlX}_4^- \) complexes using the average energy approximation of Ramsey's formula. These values will then be discussed in terms of a bonding parameter. To provide a background for this calculation, the average energy formula will be developed.
(2) Ramsey's Formula.

The simplest system for which the calculations can be performed is an atom or ion in a $^1S$ state, where there is no resultant orbital or spin angular momentum. The problem is to calculate the shielding of the nucleus due to the induced electric currents when the atom is placed in a uniform external magnetic field of intensity $H$. This field causes the whole electron system to rotate about the direction of the field, $H$, and the shielding constant, $\sigma$, is expressed by Lamb's formula $^{36}$

$$\sigma = \frac{e^2}{3mc^2} \sum \left\langle \frac{1}{r_i} \right\rangle$$  \hspace{1cm} (15)

where $r_i$ is the distance of the $i$th electron from the nucleus.

In a molecule, however, the electrons are no longer free to move in a circular fashion about the direction of the applied field, and a more complicated expression for the screening constant is obtained. Ramsey has developed, by perturbation theory techniques, a formula to calculate the screening constant for an isolated molecule. $^{25,37}$

Consider the perturbation of the energy of the system due to the joint action of $H$ and a parallel magnetic moment $\mu$ at the nucleus under consideration. The energy of the molecular system in the presence of $\mu$ and $H$ is linear in the product $\mu H$, and the terms involving this product can
be collected. They are called $W^i$. If $\sigma_\lambda$ is the desired magnetic shielding constant, and if the $W^i_\lambda$ were known, then $\sigma_\lambda$ could be evaluated from the relation

$$W^i_\lambda = \sigma_\lambda H$$  \hspace{1cm} (16)

The vector potential of the magnetic field at the point occupied by the $k$'th electron is

$$\mathbf{A}_k = \frac{1}{\hbar} (\mathbf{H} \times \mathbf{r}_k) + (\mathbf{\mu} \times \mathbf{r}_k) r_k^{-3}$$  \hspace{1cm} (17)

where $r_k$ is the distance of the $k$'th electron from the nucleus. In this case, the origin of the coordinate system is at the nucleus which is being observed.

The Hamiltonian, $\mathcal{H}$, is given by

$$\mathcal{H} = \frac{1}{2m} \sum_k \left( \mathbf{p}_k + \frac{eA}{c} \right)^2 + V$$  \hspace{1cm} (18)

where $\mathbf{p}_k$ is the linear momentum operator and $V$ is the potential energy of the interacting particles. The Hamiltonian can be rewritten as the sum of three parts by expanding equation (18) into

$$\mathcal{H} = \mathcal{H}^{(0)} + \mathcal{H}^{(1)} + \mathcal{H}^{(2)}$$  \hspace{1cm} (19)

These are

$$\mathcal{H}^{(0)} = -\sum_k \frac{\hbar^2}{2m_k} \nabla_k^2 + V$$  \hspace{1cm} (20)

$$\mathcal{H}^{(1)} = -\sum_k \frac{e}{2m_k c} (\mathbf{H} + \frac{2A}{r_k^3}) \mathbf{I} \cdot \mathbf{z}_k$$  \hspace{1cm} (21)
and

$$\mathcal{H}^{(2)} = \sum_k \frac{e^2}{8m_k c^2} (H + \frac{2}{e_k})^2 (x_k^2 + y_k^2)$$

(22)

where the magnetic moment and the field, $H$, are parallel to the $z$-axis, and $l_{z_k}$ is the $z$-component of the orbital angular momentum of the $k$'th electron.

By the usual second order perturbation theory and by selecting those terms linear in $H$,

$$\sigma_\lambda = \frac{e^2}{2mc^2} (0\lambda| \sum_k (x_k^2 + y_k^2)/r_k^3 | 0\lambda)$$

$$- \frac{e^2}{2m^2 c^2} \sum_{n\lambda} \frac{1}{(E_n - E_o)} \left\{ \left( 0\lambda | \sum_k l_{z_k} | n\lambda \right) \left( n\lambda | \sum_k \frac{l_{z_k}}{r_k^3} | 0\lambda \right) \right\}$$

$$\left( 0\lambda | \sum_k \frac{l_{z_k}}{r_k^3} | n\lambda \right) \left( n\lambda | \sum_k l_{z_k} | 0\lambda \right)$$

(23)

The wave function $|0\lambda\rangle$ is the molecular ground state function, i.e.,

$$\mathcal{H}^{(0)} |0\lambda\rangle = E_o |0\lambda\rangle$$

(24)

where the nuclei are assumed to be approximately stationary attracting centres for the electrons in an orientation specified by $\lambda$. The functions $|n\lambda\rangle$ are the excited state functions with energy eigenvalue $E_n$.

Generally speaking, the excited state wave functions and energies are not available for most systems. As a result, the $E_n - E_o$ is often approximated by the mean or average excitation energy, $\Delta E$, and the average energy
approximation of (23) is obtained\textsuperscript{38,39,40}

\[
\sigma = \frac{e^2}{3mc^2} \left( 0| \sum_k \frac{1}{r_k^*} |0 \right) - \frac{e^2}{m^2 c^2} E \left( 0| \sum_{k,k'} \frac{1_k}{r_k^*} \frac{1_{k'}}{r_{k'}^*} |0 \right) \tag{25}
\]

The first term on the right in equation (25) is called the diamagnetic shielding constant and is equivalent to the Lamb formula for atoms. The second term contributing to the shielding constant is called the paramagnetic or high frequency term. It is this term which effectively corrects for the hindrance to the free rotation of the electrons about the direction of the applied field.

(3) The Wave Functions.

(a) Molecular Orbitals.

The tetrahedral $\text{AI}X_4^-$ ions belong to the $T_d$ point group. The wave functions for these ions were obtained as linear combinations of atomic orbitals by requiring that they must transform as the irreducible representations of the $T_d$ point group.

The transformation matrices of the metal and ligand functions were obtained for the symmetry operations in the group, and the traces of these matrices were calculated. These reducible representations were then decomposed into the irreducible representations for the $\sigma$-bonding and $\pi$-bonding orbitals by standard group theoretical procedures.\textsuperscript{41,42,43} These irreducible representations are, for
the metal, $a_1$, $e$, and $2t_2$, and for the ligand orbitals, $a_1$, $e$, $t_1$ and $2t_2$.

The appropriate linear combinations of ligand orbitals which transform as the irreducible representations were obtained by projection operator techniques.\textsuperscript{42,43} The metal orbitals of corresponding symmetry were developed in a similar fashion. These functions were then normalized and orthogonalized.

The coordinate systems for the ion are illustrated in Figure 6. The metal coordinate system is right-handed, but the ligands have left-handed sets of axes with the $z$-axis of each ligand directed towards the metal nucleus. The ligand $x$- and $y$-axes are set up in such a way that the $x_1$- and $x_2$-axes will remain unchanged by a reflection in the plane containing the $z_1$- and $z_2$-axes, and that the $x_3$- and $x_4$-axes will remain unchanged by a reflection containing the $z_3$- and $z_4$-axes.

The ligand $\sigma$-bonding orbitals, the $\sigma_l$, can be the $np_{z^2}$, ns-functions or a linear combination of these (i.e., sp-type functions). The ligand $\pi$-bonding orbitals, the $\pi x_1$ and $\pi y_1$, are the $np_x$ and $np_y$ ligand functions respectively. The $\pi x_1$, $\pi y_1$, and $\sigma l$ orbitals all transform in the same way as do the $x_1$, $y_1$, $z_1$ axes of the $l$'th ligand. The ligand symmetry orbitals are tabulated in Table XV. It should be noted that the ligand nonbonding $t_1$ orbitals were ignored and, consequently, will not be found
FIGURE 5. Coordinate System for the AlX₄⁻ Ions.
<table>
<thead>
<tr>
<th>Representation</th>
<th>Metal Function</th>
<th>Ligand Function</th>
</tr>
</thead>
<tbody>
<tr>
<td>a_1</td>
<td>( \phi(3s) )</td>
<td>( \frac{1}{2}( \sigma_1+\sigma_2+\sigma_3+\sigma_4) )</td>
</tr>
<tr>
<td></td>
<td>( \phi(3p_x), \phi(3d_{yz}) )</td>
<td>( \frac{1}{2}( \sigma_1-\sigma_2+\sigma_3-\sigma_4) )</td>
</tr>
<tr>
<td>t_2</td>
<td>( \phi(3p_y), \phi(3d_{xz}) )</td>
<td>( \frac{1}{2}( \sigma_1+\sigma_2-\sigma_3-\sigma_4) )</td>
</tr>
<tr>
<td></td>
<td>( \phi(3p_z), \phi(3d_{xy}) )</td>
<td>( \frac{1}{2}( \sigma_1-\sigma_2-\sigma_3+\sigma_4) )</td>
</tr>
<tr>
<td></td>
<td>( \phi(3d_{z^2}) )</td>
<td>( \frac{1}{2}(n_x + n_x + n_x + n_x) )</td>
</tr>
<tr>
<td></td>
<td>( \phi(3d_{x^2-y^2}) )</td>
<td>( \frac{1}{2}(n_y + n_y + n_y + n_y) )</td>
</tr>
<tr>
<td></td>
<td>( \phi(3p_x), \phi(3d_{yz}) )</td>
<td>( \frac{1}{4}[n_x - n_x + n_x - n_x + \sqrt{3}(n_y - n_y + n_y - n_y)] )</td>
</tr>
<tr>
<td>e</td>
<td>( \phi(3d_{x^2-y^2}) )</td>
<td>( \frac{1}{4}[n_x - n_x + n_x - n_x + \sqrt{3}(n_y - n_y + n_y - n_y)] )</td>
</tr>
<tr>
<td></td>
<td>( \phi(3p_x), \phi(3d_{yz}) )</td>
<td>( \frac{1}{2}(n_x - n_x + n_x + n_x) )</td>
</tr>
<tr>
<td>t_2</td>
<td>( \phi(3p_y), \phi(3d_{xz}) )</td>
<td>( \frac{1}{4}[n_x - n_x - n_x + n_x + n_x - n_x + n_x - n_x + n_x - n_x] )</td>
</tr>
<tr>
<td></td>
<td>( \phi(3p_z), \phi(3d_{xy}) )</td>
<td>( -\sqrt{3}(n_y - n_y + n_y - n_y) )</td>
</tr>
</tbody>
</table>
in the table.

The metal symmetry functions are also found in Table XV. Note that there are two possible sets of metal \( t_2 \) functions for both \( \sigma \)- and \( \pi \)-bonding. Both the \( 3p_x \), \( 3p_y \) and \( 3p_z \) and the \( 3d_{xy} \), \( 3d_{xz} \) and \( 3d_{yz} \) orbitals transform in the same way, and the anion orbitals will always mix with both to form the \( \sigma \)-bonds and the \( \pi \)-bonds. \(^{41}\)

Once the ligand and metal functions were assigned to the various irreducible representations (Table XV), those metal and ligand functions belonging to the same representation were combined into one-electron molecular orbitals (MO) of the form \(^{44}\)

\[
\psi_j(\gamma,1) = N(\gamma)[\phi_j(\gamma,1) + \lambda(\gamma) \chi_j(\gamma,1)] \tag{26}
\]

for the \( i \)'th electron. \( N(\gamma) \) is the normalization constant, \( \phi_j(\gamma) \) is the metal function, \( \chi_j(\gamma) \) is the ligand function, and \( \lambda(\gamma) \) is a mixing parameter. \( \gamma \) is the irreducible representation according to which the MO transforms.

(b) The Ground State Function.

The only wave function required for the Ramsey average energy calculation is the ground state function for the ion. The total \( N \)-electron wave function is an antisymmetrized product of MO's with \( m \) spin. If

\[
\Phi_j = \psi_1(\gamma_1,1) \alpha(1) \psi_1(\gamma_1,2) \beta(2) \ldots \psi_p(\gamma_k,N) \beta(N) \tag{27}
\]

then
$$\Psi_i = a \Phi_i$$  \hspace{1cm} (28)

where $a$ is the antisymmetrizer

$$a = (N!)^{-\frac{1}{2}} \sum_p (-1)^p \mathcal{P}$$

$P$ is a permutation operator which interchanges the electrons, and $p$ is the number of interchanges. $\Psi_i$ is the wave function for the $i$'th state of the molecule. $\Psi_0$ is the ground state wave function for the system. The particular form which $\Psi_0$ will take will be decided upon in a later section.

(c) The Atomic Orbitals.

The particular form of the atomic orbitals (AO) which were used in this calculation were the Slater AO's. These functions are defined as

$$\phi(nlm) = R_{nl}(r)Y_l^m(\theta, \phi)$$

$$= N(n) r^{n-\frac{1}{2}} e^{-kr} Y_l^m(\theta, \phi)$$  \hspace{1cm} (29)

where $N(n) = (2k)^{n+\frac{1}{2}}/[\Gamma(2N + 1)]^{\frac{1}{2}}$ is the normalization constant and the $Y_l^m(\theta, \phi)$ are the well known spherical harmonic functions. The constant, $k$, is given by

$$k = \frac{Z_{\text{eff}}}{na_0}$$  \hspace{1cm} (30)

where $Z_{\text{eff}}$ is the effective nuclear charge, $n$ is an adjustable constant and $a_0$ is the Bohr radius.

Although these functions are simple in form and easy
to use, they are considerably less accurate than Hartree or Hartree-Fock orbitals. Qualitatively, they differ from the hydrogenic functions in that the radial function possesses no nodes. This leaves their usefulness suspect, especially in the region of the nucleus where precise knowledge of electronic behaviour is necessary. In spite of this criticism, however, these functions were used in hope that the qualitative aspects of the observed shifts could be evaluated.

(4) Group Overlap and Overlap Integrals.

The wave functions (26) were normalized to unity by requiring that

$$N(\gamma) = [1 + 2 \lambda(\gamma)G_1(\gamma) + \lambda^2(\gamma)]^{-\frac{1}{2}}$$  \hspace{1cm} (31)

where the $G_1(\gamma)$ are called the group overlap integrals. These integrals, defined by

$$G_1(\gamma) = (\phi_1(\gamma)|\chi_1(\gamma))$$  \hspace{1cm} (32)

are proportional to the overlap integrals $S(c_1,c_2)$. All ligand-ligand overlap was neglected in this model. The overlap integrals are defined by

$$S(c_1,c_2) = (\phi_M(c_1)|\phi_L(c_2))$$  \hspace{1cm} (33)

where $\phi_M(c_1)$ is the metal function, $\phi_L(c_2)$, a ligand wave function, and the $c_i$ specify the form of the functions. The proportionality constants were determined by group
<table>
<thead>
<tr>
<th>Group Overlap Symbol</th>
<th>Group Overlap</th>
</tr>
</thead>
<tbody>
<tr>
<td>$G_\sigma (a_1)$</td>
<td>$2S(3s\sigma, ns\sigma)$, $2S(3s\sigma, np\sigma)$</td>
</tr>
<tr>
<td>$G_{\sigma^+(t_2)}$</td>
<td>$2/\sqrt{3} S(3p\sigma, ns\sigma)$, $2/\sqrt{3} S(3d\sigma, ns\sigma)$, $2/\sqrt{3} S(3p\sigma, np\sigma)$, $2/\sqrt{3} S(3d\sigma, np\sigma)$</td>
</tr>
<tr>
<td>$G_\pi (e)$</td>
<td>$2\sqrt{2}/\sqrt{3} S(3d\pi, np\pi)$</td>
</tr>
<tr>
<td>$G_\pi (t_2)$</td>
<td>$2\sqrt{2}/\sqrt{3} S(3p\pi, np\pi)$, $-2\sqrt{2}/3 S(3d\pi, np\pi)$</td>
</tr>
</tbody>
</table>
Theoretical methods described by Ballhausen and Gray.\textsuperscript{44} The group overlaps in terms of the overlap integrals are given in Table XVII.

The overlap integrals $S(c_1,c_2)$ were calculated on the basis of the suggestions made by Lofthus.\textsuperscript{18} The two-centre overlap integrals were evaluated for the desired combinations of $s$, $p$ and $d$ orbitals for low values of $n$, from which formulae for any higher value of $n$ can be obtained by simple derivations.

The overlap integrals for the $\text{AlBr}_4^-$ ion could not be evaluated by this method directly, however, since the value of $n$ in the Slater AO is a noninteger, i.e., $n=3.7$. These integrals were found graphically by calculating the overlaps with $n = 2, 3, 4,$ and $5$ and interpolating.\textsuperscript{18}

(5) The Calculation of the Shielding Constants.

(a) The Approximations.

In addition to the use of the average energy approximation and the Slater AO's, several other assumptions were made in order to facilitate the calculation of the shielding constants for the $\text{AlX}_4^-$ ions (where $X=F$, $\text{Cl}$, $\text{Br}$ and $\text{I}$). The assumptions were the following:

1. The aluminum was assumed to use only the 3s and 3p orbitals in the $\sigma$-bonds with the halide. No 3d orbital participation was allowed.

2. No $\pi$-bonding was included in the calculation.

3. The basis set used for the ligand $\sigma$-orbitals was either
the ns- or the np\textsubscript{z} function. A linear combination, \(\alpha(\text{ns}) + (1-\alpha^2)^{1/2}(\text{np}\_z)\), could also have been employed.

4. Two values of the effective nuclear charge were used. In the evaluation of the overlap integrals, a value of

\[ Z_{\text{eff}} = Z_o = Z - s \]

was used. In the calculation of the shielding constants, values of \(Z_{\text{eff}} = (ZZ_o)^{1/2}\) were employed since this gives a better approximation of the effective nuclear charge for the heavier elements, especially in the region of the nucleus.

5. Certain integrals in the calculation of the paramagnetic term were crudely approximated or neglected since a more rigorous estimation would seem of little value in view of the above approximations. These integrals will be specified later in the section dealing with the calculation of the paramagnetic term.

6. The core electrons of the aluminum were ignored and the calculation involves only the valence electrons. Since the ultimate aim is to obtain chemical shift values, then the contribution of the core electrons will subtract out.

(b) The Diamagnetic Shielding Constant.

The diamagnetic shielding constant, \(\sigma_d\), is given by the first term on the right in equation (27), that is

\[
\sigma_d = \frac{e^2}{3mc^2} (0 | \sum_k \frac{1}{r_k} | 0)
\]  

(34)
where \( 10 \) is the ground state wave function, \( \Psi_0 \). By assumption 1, this function is given as the Slater determinant.

\[
\Psi_0 = a \Phi_0 \]

\[
= |\psi(a_1,1)\alpha(1)\psi(a_1,2)\beta(2)\psi_1(t_2,3)\alpha(3)\psi_1(t_2,4)\beta(4)
\]

\[
x\psi_2(t_2,5)\alpha(5)\psi_2(t_2,6)\beta(6)\psi_3(t_2,7)\alpha(7)\psi_3(t_2,8)\beta(8)|
\]

Substituting equation (35) into (34) and carrying out the summation, the diamagnetic contribution for the valence electrons was

\[
\sigma_d = \frac{e^2}{3mc^2} \left\{ 2(\psi(a_1)|\frac{1}{r}|\psi(a_1)) + 6(\psi(t_2)|\frac{1}{r}|\psi(t_2)) \right\} \quad (36)
\]

The integrals in (36) were calculated using the MO's of equation (26) and Table XVI. In general,

\[
(\psi(\gamma)|\frac{1}{r}|\psi(\gamma)) = N^2(\gamma) \left[ (\phi(\gamma)|\frac{1}{r}|\phi(\gamma))
\right.
\]

\[
+ 2\lambda(\gamma)(\phi(\gamma)|\frac{1}{r}|\chi(\gamma))
\]

\[
+ \frac{2}{\lambda(\gamma)}(\chi(\gamma)|\frac{1}{r}|\chi(\gamma)) \right] \quad (37)
\]

The \((\phi(\gamma)|\frac{1}{r}|\phi(\gamma))\) integrals were easily computed to be \( k/3 = 1.344 \times 10^8 \) cm\(^{-1}\). The \((\phi(\gamma)|\frac{1}{r}|\chi(\gamma))\) and the \((\chi(\gamma)|\frac{1}{r}|\chi(\gamma))\) are the resonance and coulomb integrals respectively. They are related to the molecular two-centre resonance and coulomb integrals which were evaluated by the methods described by Lofthus.\(^{19}\)

(1) Group Overlap Integrals.

In order to evaluate the normalization constant, \( N(\gamma) \), the group overlap integrals are needed. These were solved
by the methods indicated in section B(4). The numerical values for the $G(\chi)$ are given in Table XVII. In general, the group overlap integral increases from fluoride to iodide for both the ligand basis sets.

(ii) Resonance Integrals.

The resonance integrals $(\phi(\gamma)|\frac{1}{r}|\chi(\gamma))$ can be related to the molecular two-centre integrals $I_m(c_1,c_2)$. More specifically, the resonance integrals,

$$(\phi(a_1)|\frac{1}{r}|\chi(a_1)) = \begin{cases} 2I_m(3s\sigma,ns\sigma) \\ 2I_m(3s\sigma,np\sigma) \end{cases}$$

$$(\phi(t_2)|\frac{1}{r}|\chi(t_2)) = \begin{cases} (4/3)^{1/2}I_m(3p\sigma,ns\sigma) \\ (4/3)^{1/2}I_m(3p\sigma,np\sigma) \end{cases}$$

These one-electron, two-centre molecular integrals were related to overlap integrals in a very simple fashion.$^{19}$

The values of the resonance integrals is given in Table XVIII.

(iii) Coulomb Integrals.

The coulomb integrals $(\chi(\gamma)|\frac{1}{r}|\chi(\gamma))$, were also simply related to the one-electron coulomb integrals $K(c_1,c_2)$. These integrals were evaluated for the $ns\sigma$-$ns\sigma$ and $np\sigma$-$np\sigma$ combinations for all the halides from fluoride to iodide.$^{19}$ The coulomb integrals are

$$(\chi(a_1)|\frac{1}{r}|\chi(a_1)) = \begin{cases} K(ns\sigma,ns\sigma) \\ K(np\sigma,np\sigma) \end{cases}$$

$$(\chi(t_2)|\frac{1}{r}|\chi(t_2)) = \begin{cases} K(ns\sigma,ns\sigma) \\ K(np\sigma,np\sigma) \end{cases}$$
<table>
<thead>
<tr>
<th>Complex</th>
<th>Ligand s-function</th>
<th>Ligand p-function</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$G(a_1)$</td>
<td>$G(t_2)$</td>
</tr>
<tr>
<td>AlF$_4^-$</td>
<td>0.4916</td>
<td>0.4447</td>
</tr>
<tr>
<td>AlCl$_4^-$</td>
<td>0.6964</td>
<td>0.5737</td>
</tr>
<tr>
<td>AlBr$_4^-$</td>
<td>0.7296</td>
<td>0.5837</td>
</tr>
<tr>
<td>AlI$_4^-$</td>
<td>0.6862</td>
<td>0.5367</td>
</tr>
<tr>
<td></td>
<td>$I_m(3s\sigma,ns\sigma)$ (cm$^{-1}$)</td>
<td>$I_m(3s\sigma,n\rho\sigma)$ (cm$^{-1}$)</td>
</tr>
<tr>
<td>--------</td>
<td>-----------------------------------</td>
<td>--------------------------------------</td>
</tr>
<tr>
<td>$\text{AlF}_4^-$</td>
<td>3.103 x 10$^7$</td>
<td>1.754 x 10$^7$</td>
</tr>
<tr>
<td>$\text{AlCl}_4^-$</td>
<td>4.054 x 10$^7$</td>
<td>3.488 x 10$^7$</td>
</tr>
<tr>
<td>$\text{AlBr}_4^-$</td>
<td>4.180 x 10$^7$</td>
<td>3.976 x 10$^7$</td>
</tr>
<tr>
<td>$\text{AlI}_4^-$</td>
<td>3.730 x 10$^7$</td>
<td>4.007 x 10$^7$</td>
</tr>
</tbody>
</table>
The values for these integrals are shown in Table XIX, and in either case, the value of these integrals decreases as the size of the halide increases. This is reasonable in view of the fact that the aluminum-halide distance increases with the increasing size of the halide ion.

(iv) The Diamagnetic Shielding Constant.

With the values given above, the diamagnetic screening constants were computed, first, for the case where the ligand uses its ns orbitals, and secondly, where it employs the np_z orbitals for σ-bonding.

These values of \( \sigma_d \) were calculated for values of \( \lambda(a_1) = \lambda(t_2) = 1.0 \) to 2.6, and are set out in Table XX. Which shielding constant is used will ultimately be determined by the choice of the \( \lambda \) values for the different complexes. These values of \( \lambda \) will be picked by fitting the theoretical shifts to the experimental ones. A fuller discussion of these \( \lambda \) values will be given later.

(c) The Paramagnetic Shielding Constant.

The expression for the paramagnetic tensor, \( \sigma_p \), is given by the second term on the right hand side of equation (25), that is

\[
\sigma_p = - \frac{e^2}{m^2 c^2 \Delta E} (0| \sum_{k,k'} \frac{i k_i k'_i}{r^3} |0)
\]  

(40)

The average value of \( \sigma_p \) is given by

\[
\sigma_p = \sigma_{pAV} = \frac{1}{3} (\sigma_{p_{xx}} + \sigma_{p_{yy}} + \sigma_{p_{zz}})
\]  

(41)
<table>
<thead>
<tr>
<th>Complex</th>
<th>$K(n\sigma, n\sigma)$ (cm$^{-1}$)</th>
<th>$K(n\rho\sigma, n\rho\sigma)$ (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AlF$_4^-$</td>
<td>$5.682 \times 10^7$</td>
<td>$5.910 \times 10^7$</td>
</tr>
<tr>
<td>AlCl$_4^-$</td>
<td>$4.403 \times 10^7$</td>
<td>$5.084 \times 10^7$</td>
</tr>
<tr>
<td>AlBr$_4^-$</td>
<td>$4.694 \times 10^7$</td>
<td>$4.846 \times 10^7$</td>
</tr>
<tr>
<td>AlI$_4^-$</td>
<td>$3.905 \times 10^7$</td>
<td>$4.317 \times 10^7$</td>
</tr>
<tr>
<td>λ</td>
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for systems of cubic symmetry. Equation (40) can now be written as

$$\sigma_p = -\frac{e^2}{m^2 c^2 \Delta E} \sum_{k, k'} \frac{1}{r_k^3} \frac{1}{r_{k'}^3} \frac{1}{r_{k'}} \frac{1}{r_k} |c\rangle. \quad (42)$$

Substituting the wave function (35) into equation (42) and summing over the wave functions, $\sigma_p$ becomes

$$\sigma_p = -\frac{e^2}{m^2 c^2 \Delta E} \sum_{\gamma} 2 \left\{ (\psi(\gamma)| \frac{1}{r_{\gamma}^3} | \psi(\gamma)) 
- \sum_{\gamma'} (\psi(\gamma)| \frac{1}{r_{\gamma}^3} | \psi(\gamma')) (\psi(\gamma')| \frac{1}{r_{\gamma'}^3} | \psi(\gamma)) \right\}. \quad (43)$$

General expressions for the molecular integrals in (43) can be given in terms of the MO's of equation (26).

$$\langle \psi(\gamma)| \frac{1}{r_{\gamma}^3} | \psi(\gamma') \rangle = N(\gamma)N(\gamma') \left[ (\phi(\gamma)| \frac{1}{r_{\gamma}^3} | \phi(\gamma)) 
+ \lambda(\gamma)(\chi(\gamma)| \frac{1}{r_{\gamma}^3} | \chi(\gamma')) 
+ \lambda(\gamma)(\phi(\gamma)| \frac{1}{r_{\gamma}^3} | \chi(\gamma')) 
+ \lambda(\gamma)(\chi(\gamma)| \frac{1}{r_{\gamma}^3} | \phi(\gamma')) \right]. \quad (44)$$

The first integral on the right in equation (44) is easy to solve for the aluminum 3p orbitals

$$\langle \phi(\gamma)| \frac{1}{r_{\gamma}^3} | \phi(\gamma') \rangle = c \frac{k^2}{15} \quad (45)$$

only, of course, if

$$\frac{1}{r_{\gamma}^3} \phi(\gamma) = c \phi(\gamma) \quad (46)$$

holds where $c$ is a real or imaginary constant. The second and third integrals in (44) are nonzero provided that (46)
is valid for them as well, i.e.

\[
(\chi(\gamma)\frac{1}{r^3}1\phi(\gamma)) = c(\chi(\gamma)\frac{1}{r^3}1\phi(\gamma)) \quad (47)
\]

The integrals on the right were approximated by the expression \((1/R^3)G(\gamma)\) where \(R\) is the aluminum-halide distance and \(G(\gamma)\) is the group overlap integral.\(^{46}\) The fourth integral in equation (44) was neglected since the approximations, made in \(B(5a)\), precluded the effects of a more refined calculation.

The only contributions to the paramagnetic term arose from the \(t_2\) orbitals. The \(a_1\) orbitals contributed nothing.

In view of these considerations, the integrals from equation (43) were reduced to the following terms

\[
(\psi(\gamma)\frac{1}{r^3}1\psi(\gamma)) = n^2 N^2(t_2) \left[ \frac{k^3}{15} + \frac{2\lambda}{R^3}G(t_2) \right]
\]

and

\[
(\psi(\gamma)\frac{1}{r^3}1\psi(\gamma))(\psi(\gamma)\frac{1}{r^3}1\psi(\gamma)) = n^2 N^4(t_2) \left[ \frac{k^3}{15} + \frac{2\lambda}{R^3}G(t_2) \right] [1 + 2\lambda G(t_2)]
\]

The contributions from \(k^3\) and \(1/R^3\) were collected and the final expression for \(\sigma_p\) was

\[
\sigma_p = -\frac{e^2\hbar^2}{m^2 c^2 \Delta E} \left\{ c_1 k^3 + \frac{c_2}{R^3} \right\} \quad (48)
\]

where

\[
c_1 = \frac{N^2(t_2)}{5} \left[ 1 - \frac{2}{3} N^2(t_2) \left( 1 + 2\lambda G(t_2) \right) \right] \quad (49)
\]
\[ c_2 = 2 \lambda G(t_2)N^2(t_2) \left[ 1 - 2N^2(t_2)(1 + 2\lambda G(t_2)) \right] \]  \hspace{1cm} (50)

(i) The Contribution from the Metal and Ligand

The contribution of the metal to the \( \sigma_p \) term, apart from a multiplicative constant, is given by \( C_1k^3 \). The contribution from the \( 1/R^3 \) term can similarly be given by \( C_2/R^3 \). In general, the latter term is a factor of \( 10^{-3} \) smaller than the former. It is expected that the contribution of the ligand will, in general, be small compared to the metal. The precise contribution of the ligand cannot be determined in this case because of the assumptions made, and it will undoubtedly be larger than implied by this calculation.

The contribution from the ligand is negative for the smaller values of \( \lambda \).

(ii) The Average Energy, \( \Delta E \).

The paramagnetic term was computed for several values of \( \Delta E \). The final value of \( \Delta E \) was empirically selected.

Most charge transfer bands for metal complexes occur in the UV region.\(^{29,30}\) However, some do occur in the visible spectrum also. The majority of these strong absorption bands occur between 30,000 and 50,000 cm\(^{-1}\). The particular values for the \( \text{AlX}_4^- \) systems are not known, but they are probably in this region of the spectrum. The spectra for the \( \text{SnX}_4 \) compounds, for example, are 46,080 cm\(^{-1}\) and 27,780 cm\(^{-1}\) for \( \text{SnI}_4 \).
If the value of the charge transfer bands are taken as indicative of the average or mean excitation energy, then $\Delta E$ should be in this region of the energy spectrum. The value of $\Delta E$ chosen for the $\sigma_p$ term was $5 \times 10^{-12}$ ergs which corresponds to about 25,000 cm$^{-1}$ in the UV region.

(iii) The Paramagnetic Screening Constants.

The values of $\sigma_p$ were computed for $\lambda = 1.0$ to 2.6 and $\Delta E = 5 \times 10^{-12}$ ergs. They are given in Table XXI.

(d) The Shielding Constants.

The shielding constants, shown in Table XXII, were calculated from $\sigma = \sigma_d + \sigma_p$ for values of $\lambda$ ranging between 1.0 and 2.6 and an average energy $\Delta E = 5 \times 10^{-12}$ ergs.

(6) Discussion.

(a) Comparison of Theory with Experiment.

For this discussion, the empirical shifts for the $\text{AlX}_4^-$ ions will be redefined. The $\text{AlI}_4^-$ ion will be taken as the reference, and the shifts for the other tetrahalo complexes will be defined relative to it. Thus the experimental shifts become $\delta_{\text{AlI}_4^-} = 0$ ppm, $\delta_{\text{AlBr}_4^-} = -107$ ppm, and $\delta_{\text{AlCl}_4^-} = -129$ ppm.

The particular choice of the mixing parameter, $\lambda$, and the average energy, $\Delta E$, were selected to give the best fit with the data. A comparison of the theoretical shifts with experiment are given in Table XXIII. This table also gives the diamagnetic and paramagnetic contri-
<table>
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<th>p</th>
<th>s</th>
<th>Cl</th>
<th>p</th>
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boutions for the $\lambda$ parameters for both the ligand ns- and np - functions.

There is no experimental value for the chemical shift of $\text{AlF}_4^-$ available to compare with the theoretical value. The value selected here is probably a lower limit. The shift for the $\text{AlF}_4^-$ ion probably occurs around -150 ppm.

Both ligand basis sets give reasonable agreement with the experimental data. Considering the approximations which were made, the closeness of theory to experiment may be rather fortuitous.

(b) Interpretation and Criticism.

The mixing parameter, $\lambda$, in the wave function

$$\psi = N[\phi_M + \lambda \chi_L]$$

(51)

has usually been interpreted to be a measure of the 'ionicity' or 'covalent character' of the bond which the MO (51) describes.\textsuperscript{44,47} When $\lambda = 1$, a 'purely' covalent bond is the result. When $\lambda < 1$, the charge is distributed largely about the metal, but for $\lambda > 1$, the charge distribution resides mainly on the ligand. It has been argued that, generally, the M-F bonds are more ionic in character than the other metal-halide $\sigma$-bonds, and M-I $\sigma$-bonds are, in general, more covalent than the other metal-halide bonds.

Using the values of $\lambda$ in Table XXIII, the charges on the metal and ligand are then determined for the $t_2$ MO's by Mulliken's formula.\textsuperscript{48} For each MO, the charge on the metal
TABLE XXII. Shielding Constants for the AlX₄⁻ Ions.

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<th>( \lambda )</th>
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TABLE XXIII. Theoretical Shift Data for $\text{AlX}_4^-$ Systems.

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<th>$\sigma_d$ (ppm.)</th>
<th>$\sigma_p$ (ppm.)</th>
<th>$\sigma$ (ppm.)</th>
<th>$\delta$ (ppm.)</th>
<th>$\delta_{\text{exp}}$ (ppm.)</th>
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<td>-217</td>
<td>-137</td>
<td>-129</td>
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<td>$\text{AlBr}_4^-$</td>
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**Ligand p-functions**

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<th>$\sigma_p$ (ppm.)</th>
<th>$\sigma$ (ppm.)</th>
<th>$\delta$ (ppm.)</th>
<th>$\delta_{\text{exp}}$ (ppm.)</th>
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<td>-103</td>
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is given by $2N^2(t_2)(1 + \lambda G(t_2))$, and the charge on the ligand is $2N^2(t_2)(\lambda G(t_2) + \lambda^2)$. These charge distributions per $t_2$ MO are given in Table XXIV.

Regardless of which basis set is used, the trends are much the same. The charge on the halide in the $\text{AlX}_4^-$ complexes decreases from fluoride to chloride and then increases again from chloride to iodide. Presumably, there are two opposing tendencies operating: the ability of the metal to polarize the ligand charge cloud and the ability of the ligand to withhold or delocalize the charge in the bond.

In the case of the fluoride, the most electronegative halide, it is the ability of the ligand to hold its charge which accounts for the larger charge on the ligand. In the other ligands this trend to larger ligand charges arises from the increasing ability of the ligand to delocalize the charge in the MO. The decreasing charge on the ligand in the series $\text{I}^- > \text{Br}^- > \text{Cl}^-$ also substantiates the qualitative argument in terms of the nephelauxetic effect which was invoked to explain the trend in the magnetic shielding for the $\text{AlX}_4^-$ complexes.

This effect also accounts for the nonlinearity in the chemical shifts encountered in the NMR spectra of the $\text{AlI}_n\text{Br}_m\text{Cl}_{4-n-m}^-$ series. The tetrahaloborate anions also present a striking illustration of this. The chemical shift data for these complexes are given in Table
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<td>AlBr(_4^-)</td>
<td>1.5</td>
<td>0.71</td>
<td>1.29</td>
</tr>
<tr>
<td>AlI(_4^-)</td>
<td>2.4</td>
<td>0.45</td>
<td>1.55</td>
</tr>
</tbody>
</table>
XXV. This series is similar to the AlX$_4^-$ complexes as pointed out in part A of this chapter. The BF$_4^-$, however, dramatically illustrates this ability of the fluoride to withhold the charge in the bond.

TABLE XXV. The BX$_4^-$ Chemical Shift Data.

<table>
<thead>
<tr>
<th>Complex</th>
<th>Shifts (ppm.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BF$_4^-$</td>
<td>-126</td>
</tr>
<tr>
<td>BCl$_4^-$</td>
<td>-135</td>
</tr>
<tr>
<td>BBr$_4^-$</td>
<td>-99.1</td>
</tr>
<tr>
<td>BI$_4^-$</td>
<td>0</td>
</tr>
</tbody>
</table>

Similar effects have been observed in the spectra of the CH$_n$X$_4$-n series by Grant and Litchman. They carried out a valence bond calculation for the chemical shifts and observed that electron delocalization played an important role in determining the trend in shifts. Steric effects also appeared to be important in accounting for part of the nonlinearity observed for these shifts.

Just how much faith should be placed in these parameters in view of the assumptions necessary in carrying out this calculation, are uncertain. The fact that the trend is the same regardless of which basis set is used by the ligand would indicate that taking a linear combination of the ns and np$_z$ orbitals would not seriously affect
the ordering of the \( \lambda \) values.

The inclusion of \( \pi \)-bonding interactions would introduce another set of \( \lambda \) parameters which would also affect the situation. Jameson and Gutowsky\(^{23}\) have shown that the contribution from the 3d shell is less than the 3p shell of the metal. This implies that the correction to the shielding constant will not significantly alter the conclusions reached above. A more precise solution to the integrals for the ligand contribution to the paramagnetic term would also not likely affect these conclusions.

In this part, the charge delocalization and electronegativity of the ligand have shown that the qualitative explanation of the trend in magnetic shielding does in fact hold. The nonlinearity of the chemical shifts can also be accounted for by this explanation.
C. $^{27}$Al NMR STUDIES OF THE ANHYDROUS ALUMINUM HALIDES IN NONAQUEOUS MEDIA.

(1) Introduction.

In this part of Chapter III, the NMR spectra of the anhydrous aluminum halides in a number of organic and inorganic solvents will be discussed. Some of the concepts put forward in Part A of this chapter will be of importance in interpreting these spectra, especially the effects of symmetry, ligand bulk and viscosity on the line width.

Anhydrous aluminum chloride has been a popular solute for study in many solvent systems, and its most interesting chemistry occurs in nonaqueous media. Most research into these systems has involved conductivity measurements, infrared and some $^1$H NMR studies, but with the appearance of O'Reilly's papers, $^{27}$Al NMR became another important approach in the investigation of these solutions.$^{4,7}$

(2) The $\text{AlX}_3 + (\text{n-Pr})_4\text{NBr}/\text{CH}_2\text{Cl}_2$ System.

(a) Observations.

For all the solutions discussed in part A, the ratio of the aluminum halide to the tetra-alkylammonium salt was less than unity. When the ratio was greater than unity, only one signal was observed rather than the five. The chemical shift and line width data are given in Table XXVI. The position of the resonance line was constant for the three systems, but the line width was dependent upon the relative concentrations of the $(\text{n-Pr})_4\text{NBr}$ salt and aluminum halide.
<table>
<thead>
<tr>
<th>Solution</th>
<th>AlX₃ / (n-Pr)₄NBr</th>
<th>Chemical Shifts (ppm.)</th>
<th>Line Widths (Hz.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AlBr₃ + (n-Pr)₄NBr/CH₂Cl₂</td>
<td>1.0/0.68</td>
<td>-99.5 ± 0.6</td>
<td>370 ± 6</td>
</tr>
<tr>
<td>AlBr₃ + (n-Pr)₄NBr/CH₂Cl₂</td>
<td>1.0/0.85</td>
<td>-99.7 ± 0.8</td>
<td>191 ± 5</td>
</tr>
<tr>
<td>AlCl₃ + (n-Pr)₄NBr/CH₂Cl₂</td>
<td>1.0/0.93</td>
<td>-98.4 ± 0.6</td>
<td>157 ± 3</td>
</tr>
</tbody>
</table>
(b) Mechanisms.

If a rate process is occurring in solution, the NMR spectrum may be modified, and in fact, if the exchange between different chemical positions is sufficiently rapid, then a coalescence of some of the signals will be observed. For the three examples in Table XXVI, then, the observed, time averaged signal indicates rapid exchange between Al atoms in different chemical environments. When accounting for this exchange process, some mechanism for removing chloride from the solvent must be provided, and the dependence of the line width upon the relative concentration of the \((n-Pr)_4NBr\) salt and aluminum halide must be explained.

Initially it might be thought that \(Br^-\) ions could displace \(Cl^-\) ions from the solvent by a substitution process. This is unlikely, however, for two reasons. First, most of the \(Br^-\) ions in solution will react with the dimer, \(Al_2X_6\), to produce dimeric anions, \(Al_2X_6Br^-\), and monomeric anions of the type \(AlX_2Br^-\). Secondly, even should there persist some \(Br^-\) ions in solution, Hine et al. have shown that the \(S_N^2\) reactions with a halide displacing a chloride from \(CH_2Cl_2\) are very slow with rate constants of the order of \(10^{-5} \text{ mole}^{-1} \text{ sec}^{-1}\). Therefore, the exchange process is unlikely to involve any free \(Br^-\) or \(Cl^-\) ions as such.

The most suitable mechanism for exchange involves the halogen-bridged dimeric ions, \(Al_2X_nY_{7-n}^-\) and the
monomeric ions, \( \text{AlX}_{n-4}^{-n} \). An example of such a process is shown here, and it can account for the time averaged signal should the process be a rapid one. It will also explain the narrowing of the resonance line, if it is assumed that the \( \text{AlBr}_n\text{Cl}_{4-n}^{-n} \) ions do not exchange with one another. As more bromide ions are added to the solution, more monomers are produced, and the dimer anions decrease in population thereby reducing the frequency of collision and the rate of reaction. This implies, then, that the average lifetime of any one monomeric species is increased, and, as a result, the signal will be narrowed.\(^{51}\)

The mechanism whereby a chloride is transferred to the aluminum from the solvent, still has not been constructed. Since the substitution process does not yield a sufficient number of free \( \text{Cl}^- \) ions, the only remaining possibility involves the aluminum species in solution.
In the solutions in which the ratio of aluminum halide to the tetra-alkylammonium halide salt is less than one, there appears to be either no exchange, a very slow exchange or a preferential exchange. The latter warrants further elaboration.

The preferential exchange mechanism involves the excess halide ions in solution, \( \text{Br}^- \) ions for example, and the bromide ions on the aluminum. The process

\[
\text{AlBrCl}_2\text{Br}^+ + \text{Br}^- \rightleftharpoons \text{AlBrCl}_2\text{Br}^- + \text{Br}^+
\]

could be rapid or slow and since the aluminum environment remains unchanged, the spectrum remains unchanged. The side reaction in which an Al-Cl bond is broken would be energetically unfavourable* and that process would be quite slow. Corbett et al.\(^{52}\) have shown that the reactions of \( \text{AlBr}_3 \) with HCl occur quite readily at room temperature with 2/3 of the bromine atoms being replaced by chloride to form \( \text{AlBrCl}_2 \). The remaining bromide was only slowly replaced. Under similar conditions, the reverse reaction between \( \text{AlCl}_3 \) and HBr did not occur. Exchange between \( \text{AlCl}_4^- \) and Cl\(^-\) ions has been observed,\(^{53}\) and a similar exchange process is expected for \( \text{AlBr}_4^- \), \( \text{Br}^- \) and \( \text{AlI}_4^- \), I\(^-\) systems.

*The AlCl bond energy is greater than the AlBr bond energy, which is, in turn, greater than the AlI bond energy, for example, 94 kcal/mole, 79 kcal/mole and 42 kcal/mole respectively.\(^{54}\)
With the limited amount of data available, little more can be said, and no quantitative analyses of these processes are possible at present.

(3) The Results for Nonaqueous Media.
(a) Organic Solvents.

The NMR spectra for the anhydrous aluminum halides in diethyl ether, nitromethane and acetonitrile can be found in Table XXVII.

(1) The Diethyl Ether Solutions.

In his original paper on $^{27}$Al resonances, O'Reilly carried out measurements on the Al$X_3$/Et$_2$O systems and the results which he obtained were quoted in Table IV. Apart from what is probably a systematic calibration error of 5 ppm., the chemical shifts which he obtained correspond with those in Table XXVII. He attributed his 'narrow' resonances to the pseudo-tetrahedral dimers, $^{35}$Al$_2X_6$, in solution rather than the addition compounds Al$X_3$.OEt$_2$.

This assignment does not, however, appear to be particularly sound. The small structural change from Al$_2$I$_6$ to AlI$_4^-$ cannot produce such a large variation in the chemical shift, i.e., 61 ppm., in light of the smaller change in the shift of only 34 ppm. upon going from AlI$_4^-$ to AlI$_3$Br$^-$ (see Table VII). It is unlikely, then, that the dimer exists in solution, but rather it is the solvent-solute adduct, AlI$_3$.OEt$_2$, which is being observed. Similarly, the resonances at -91.7 ppm. and -100 ppm. are
<table>
<thead>
<tr>
<th>SOLUTION</th>
<th>Concentration (Wt. %)</th>
<th>Chemical Shift (ppm.)</th>
<th>Line Width (Hz.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AlCl₃/Et₂O</td>
<td>23</td>
<td>-100 ± 0.8</td>
<td>158</td>
</tr>
<tr>
<td>AlBr₃/Et₂O</td>
<td>32</td>
<td>-91.7 ± 0.5</td>
<td>130 ± 3</td>
</tr>
<tr>
<td>AlI₃/Et₂O</td>
<td>28</td>
<td>-34.0 ± 0.2</td>
<td>92.8 ± 1.2</td>
</tr>
<tr>
<td>AlCl₃/MeNO₂</td>
<td>15</td>
<td>-95.2 ± 1.0</td>
<td>208 ± 9</td>
</tr>
<tr>
<td>AlCl₃ + Me₄NCl/MeNO₂</td>
<td></td>
<td>-101.5 ± 0.3</td>
<td>39.5 ± 0.7</td>
</tr>
<tr>
<td>AlBr₃/MeNO₂</td>
<td>20</td>
<td>-82.9 ± 0.7</td>
<td>186 ± 4</td>
</tr>
<tr>
<td>AlBr₃ + Me₄NBr/MeNO₂</td>
<td></td>
<td>-79.7 ± 0.4</td>
<td>58.1 ± 2.8</td>
</tr>
<tr>
<td>AlCl₃/MeCN</td>
<td>33</td>
<td>-102.0 ± 0.1</td>
<td>19.2 ± 0.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>+20.4 ± 1.0</td>
<td>444 ± 10</td>
</tr>
<tr>
<td>AlBr₃/MeCN</td>
<td>23</td>
<td>-79.9 ± 0.6</td>
<td>34.4 ± 0.3</td>
</tr>
<tr>
<td></td>
<td></td>
<td>+21.9 ± 0.4</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td>+31.2 ± 0.4</td>
<td>-</td>
</tr>
</tbody>
</table>
assigned to the AlBr$_3$.OEt$_2$ and the AlCl$_3$.OEt$_2$ adducts respectively.

There is other evidence available to support these assignments. The existence of AlCl$_3$.OEt$_2$ in solution has been reported from Raman,$^{55}$ Infrared$^{56}$ and ultraviolet$^{57}$ studies of AlCl$_3$.OEt$_2$ solutions, and the solid adduct has been isolated.$^{56}$

(ii) The Nitromethane Solutions.

Addition compounds of the type AlX$_3$.MeNO$_2$ have been reported to exist in solutions of aluminum chloride and aluminum bromide in nitromethane.$^{56,58,59}$ The addition of AlI$_3$ to nitromethane, however, produces a vigorous oxidation of iodide to iodine.

Each solution gives rise to a relatively broad signal. The peak for the chloride solution is shifted by about 5 ppm, downfield from the AlCl$_3$.OEt$_2$ and the bromide about 9 ppm, upfield from AlBr$_3$.OEt$_2$. The line widths for these solutions are broader than for those of the corresponding ether solutions. It is likely that the structure for these compounds is the one shown below. There is some evidence
for this structure on the basis of infrared and UV studies. 56,58,59

Since both the ether adducts and the nitromethane complexes have the same structure, i.e., $C_{3v}$, then the differences in the line widths will have to be accounted for by other processes than symmetry broadening. The remaining line broadening mechanisms affect the line width through the correlation time, $\tau_c$, given by equation (13),

$$\tau_c = \frac{4na^3\eta}{3kT}$$

and by chemical exchange. The ligand bulk parameter, $a$, which effectively increases with the average size of the molecule, cannot account for such a large difference in the line width since the ether complexes are likely to be bulkier than the nitromethane adducts. If the viscosities of the solvents are indicative of the viscosities of the solutions, $\eta$, then the viscosities of the solutions are in the same ratio as the ratio of their line widths. The viscosity of nitromethane is approximately 3 times the viscosity of ether at 25°C*, and this more than adequately accounts for this difference in the line widths of the two solutions. The chemical exchange mechanism is not needed to explain the rather broad lines.

*The viscosity of nitromethane is 0.620 centipoise and that of ether is 0.222 centipoise at 25°C.
When the Me₄NX salts were added to their respective AlX₃/MeNO₂ solutions, the broad lines sharpened and the signals shifted. These new signals are assigned to the tetrahedral AlX₄⁻ ions on the basis of their narrow line widths, and in the case of the AlCl₄⁻ ion, it had already been identified in solution by means of its infrared spectrum.²⁰

(iii) The Acetonitrile Solutions.

The acetonitrile solutions provide a sharp contrast to the former ether and nitromethane solutions. The spectrum of AlCl₃ dissolved in acetonitrile consists of two lines, a very sharp line at -102 ppm. and a broad one at +20.4 ppm. The signal at -102 ppm. is due to the AlCl₄⁻ ion, a reasonable assignment in view of the previous discussion. The signal at +20.4 ppm. does however, present a more difficult interpretive problem. Popov et al.⁶² found that when AlCl₃ was dissolved in acetonitrile, chloride ions were formed as well as cations of the type AlCl₃(MeCN)₃(3-m)+ where m = 0, 1, 2, 3 and n = 1, 2, 3, 4 and possibly 5 or 6, but there was some uncertainty concerning the formation of the AlCl₄⁻ ion. Schmulbach⁶³ has shown from Raman spectra that the AlCl₄⁻ ion was indeed present in solution as well as several possible cations involving the aluminum atom. In all likelihood, these cations are the cause of the broad resonance line upfield from the reference, Al(H₂O)₆³⁺. An example of the spectrum is illustrated in Figure 6.
FIGURE 7. The AlBr$_2$/MeCN spectrum.

FIGURE 6. The AlCl$_3$/MeCN spectrum.
The AlBr$_3$/MeCN solution produces three resonance lines, a sharp signal at -79.9 ppm, which is attributed to the AlBr$_4^-$ ion, a broad resonance at +21.9 ppm, with a shoulder at +31.2 ppm. The latter two peaks can be assigned to complexes of the type AlBr$_m$(MeCN)$_n$$^{(3-m)+}$ by analogy with the chloride case. The spectrum is shown in Figure 7.

Aluminum iodide does react with acetonitrile, but a whitish-yellow insoluble product is formed. No spectrum was obtained.

(b) Inorganic Solvents.

The chemical shift and line width data for the phosphoryl chloride, thionyl chloride and sulphuryl chloride solutions is given in Table XXVIII.

(i) The Phosphoryl Chloride Solutions.

Examples of the phosphoryl chloride solution spectra are depicted in Figure 8.

Two relatively narrow resonances are observed for aluminum chloride dissolved in phosphoryl chloride. The strongest signal at -103 ppm is due to the presence of the AlCl$_4^-$ ion, and the second resonance at +21.2 ppm, which is considerably weaker than the former, is assigned to the octahedral Al(POCl$_3$)$_6^{3+}$ complex. The existence of this ion has been reported by several authors.$^{64,65,66}$

Only one signal at -102 ppm is observed for the AlBr$_3$/POCl$_3$ solution. This signal is sharp, and is,
<table>
<thead>
<tr>
<th>SOLUTIONS</th>
<th>Concentration (Wgt %)</th>
<th>Chemical Shifts (ppm)</th>
<th>Line Widths (Hz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{AlCl}_3/\text{POCl}_3$</td>
<td>7.3</td>
<td>$-102.5 \pm 0.2$</td>
<td>$9.55 \pm 0.19$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$+21.2 \pm 0.1$</td>
<td>$55.3 \pm 3.3$</td>
</tr>
<tr>
<td>$\text{AlBr}_3/\text{POCl}_3$</td>
<td>10</td>
<td>$-101.7 \pm 0.5$</td>
<td>$32.5 \pm 2.0$</td>
</tr>
<tr>
<td>$\text{AlI}_3/\text{POCl}_3$</td>
<td>16</td>
<td>$-101.3 \pm 1.2$</td>
<td>$30 \pm 1$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$+22.4 \pm 0.8$</td>
<td>$77 \pm 4$</td>
</tr>
<tr>
<td>$\text{AlCl}_3/\text{SOCI}_2$</td>
<td>19</td>
<td>$-95.2 \pm 1.0$</td>
<td>$780 \pm 25$</td>
</tr>
<tr>
<td>$\text{AlCl}_3 + \text{Me}_4\text{NCl}/\text{SOCI}_2$</td>
<td></td>
<td>$-101.8 \pm 0.5$</td>
<td>$22.0 \pm 0.2$</td>
</tr>
<tr>
<td>$\text{AlBr}_3/\text{SOCI}_2$</td>
<td>19</td>
<td>$-94.6 \pm 0.2$</td>
<td>$66.3 \pm 19$</td>
</tr>
<tr>
<td>$\text{AlBr}_3+\text{Me}_4\text{NBr}/\text{SOCI}_2$</td>
<td></td>
<td>$-101.8 \pm 0.6$</td>
<td>$21.4 \pm 0.1$</td>
</tr>
</tbody>
</table>
FIGURE 8. The $\text{AlX}_3/\text{POCl}_3$ Spectra.
undoubtedly, due to the AlCl$_4^-$ ion. This indicates that all the bromine atoms on the aluminum have been exchanged for chlorine atoms.

A similar exchange effect is observed for aluminum iodide dissolved in phosphoryl chloride. In this spectrum, there is a sharp resonance at -101 ppm, which is assigned to the AlCl$_4^-$ ion, and a second sharp, equally intense signal at +22.4 ppm, due to the Al(OPCl$_3$)$_6^{3+}$ ion as in the chloride solution. This cation would be expected to give a narrow resonance because of its cubic structure, and since it is bonded through the oxygen, it would be expected to absorb in the region close to the isostuctural Al(H$_2$O)$_6^{3+}$ ion, i.e., the reference.

(ii) The Thionyl Chloride Solutions.

Both the aluminum chloride and aluminum bromide solutions give very broad resonances at -95 ppm. The fact that both these resonances occur at the same position indicates that it is the same species absorbing in both solutions. Thus, all the bromine atoms on the aluminum have been exchanged for chlorine, as was the case with aluminum bromide in POCl$_3$. If an adduct AlCl$_3$.SOCl$_2$ is formed, its symmetry is C$_3^v$, identical to that of the AlCl$_3$.MeNO$_2$ adduct. But the signals are too broad to be accounted for by symmetry alone. Ligand bulk is unlikely to cause important differences in line width since MeNO$_2$ and SOCl$_2$ probably do not differ considerably in size.
The viscosity of SOCl₂ is 0.603 centipoise at 25°C which is similar to that for MeNO₂ (0.620 centipoise at 25°C), and if the viscosities of the solvents are indicative of the viscosities of the solutions, then this mechanism will not account for the broad lines which were observed. Exchange broadening could explain these very broad lines. Long et al. have shown by Raman spectroscopy that the solutions consist of essentially undisassociated 1:1 complex, AlCl₃·SOCl₂, in excess solvent and a 2:1 complex is also formed. The latter complex was thought to be the 1:1 complex with a loosely attached second AlCl₃ molecule. An exchange mechanism involving these species could account for these line widths.

The narrow resonance at -102 ppm. for the thionyl chloride solution of AlCl₃ and Me₄NCl is assigned to the AlCl₄⁻ ion. Infrared studies by Chatt et al. support this assignment.

When Me₄NBr was dissolved in the AlBr₃/SOCl₂ solution a sharp resonance at -102 ppm. is observed. This signal is assigned to the AlCl₄⁻ ion also.

(4) Discussion.
(a) General Background.

The subject of solvent and solute behaviour in the solvation process has been the object of numerous investigations over many years. At present, there have evolved two major theories of this process, the solvent system
concept and the coordination model.

1. The Solvent System Concept.

   The solvent system concept, based on analogy with the self-ionization of water, has been used to explain the solvation properties of many inorganic solvents. V. Gutmann,70,71,72 the major proponent of this model, has used the theory to explain the observations he has made on solutions of phosphoryl chloride. It was then extended to include a number of other inorganic solvents.

   The self-ionization of water may be written as

   \[ 2\text{H}_2\text{O} \text{ (solvent)} \rightleftharpoons \text{H}_3\text{O}^+ \text{ (acid)} + \text{OH}^- \text{ (base)} \]  

   (1)

   and the analogous equation for phosphoryl chloride is

   \[ \text{POCl}_3 \text{ (solvent)} \rightleftharpoons \text{POCl}_2^+ \text{ (acid)} + \text{Cl}^- \text{ (base)} \]

   (2)

Ferric chloride, for example, acts as an acid in this solvent and reacts as follows:

   \[ \text{FeCl}_3 + \text{POCl}_3 \rightleftharpoons \text{POCl}_2^+ + \text{FeCl}_4^- \]

   (3)

and the occurrence of the characteristic UV bands for the \( \text{FeCl}_4^- \) ion are offered as experimental evidence for this.73 There is, however, no conclusive proof for the existence of an appreciable concentration of the \( \text{POCl}_2^+ \) ion. A similar mechanism was invoked to explain the conductivity data which were observed for the \( \text{AlCl}_3 \) solutions.
Originally, the reaction

\[ \text{AlCl}_3 + \text{POCl}_3 \rightleftharpoons \text{POCl}_2^+ + \text{AlCl}_4^- \]  

was thought to account for the observed results. However, Gutmann, however, modified this approach by assuming that \( \text{AlCl}_3 \) was amphoteric in this solvent, and the reaction was

\[ 2\text{AlCl}_3 + 2\text{POCl}_3 \rightleftharpoons \text{AlCl}_2(\text{POCl}_3)_2^+ + \text{AlCl}_4^- \]  

in which \( \text{AlCl}_3 \) acts both as a \( \text{Cl}^- \) ion donor and acceptor.

(ii) The Coordination Model.

One of the major disadvantages of the solvent system concept is its inability to account for the solvation of inorganic solutes by organic solvents. In an attempt to correct this deficiency and to explain some observations of inorganic solvent behaviour which the solvent system could not account for, a secondary theory was proposed, the coordination model. R.S. Drago has written several reviews and is a strong supporter of this approach.

This model is formulated in terms of the donor or acceptor properties of the solvent molecule and its solvating ability. The solvation mechanism is set up in terms of a series of equilibria involving the solute and solvent. If \( S \) is a donor solvent, and \( MX_n \) is an acidic solute, then

\[ pS + MX_n \rightleftharpoons MS_pX_n \]
where \( MS_p X_n \) is an addition compound with all the \( X \) species coordinated.

If \( X \) is assumed to be anionic, then some or all of the \( X \) groups may be displaced by the solvent \( S \) through a series of equilibria

\[
MS_p X_n + S \rightleftharpoons MS_{p+1} X_{n-1}^+ + X^-
\]

(7)

\[
MS_{p+1} X_{n-1}^+ + S \rightleftharpoons MS_{p+2} X_{n-2}^{2+} + X^-
\]

The extent to which these reactions proceed will depend upon the solvent-solute interactions. In some systems, the addition compounds formulated in equilibrium (6) may not even exist in solution at equilibrium, but reaction (6) then represents the first step in a reaction mechanism leading to the final products. In some cases, reactions other than anionic dissociation should be considered.

The series of equilibria for aluminum chloride in a donor solvent, \( S \), will then be

\[
Al_2Cl_6 + 2S \rightleftharpoons 2AlCl_3.S
\]

(8a)

\[
AlCl_3S + S \rightleftharpoons AlCl_2S_2^+ + Cl^-
\]

(8b)

\[
AlCl_2S_2^+ + S \rightleftharpoons AlClS_3^{2+} + Cl^-
\]

(8c)

\[
AlClS_3^{2+} + S \rightleftharpoons AlCl_4^{3+} + Cl^-
\]

(8d)

\[
AlCl_4^{3+} + nS \rightleftharpoons AlCl_{4+n}^{3+}
\]

(8e)

\[
AlCl_3.S + Cl^- \rightleftharpoons AlCl_4^- + S
\]

(8f)
Several possibilities for these processes now arise. For some solvents, the series of reactions may not extend past (8a), but others may go as far as (8d) and (8f) or (8e) and (8f). In the former, only one NMR signal would be expected, whereas, in the latter solution, two signals, one for the complex cation and one for the AlCl$_4^-$ ion, are expected. If the reaction goes to completion, then the overall equation will be

$$2\text{Al}_2\text{Cl}_6 + n\text{S} \rightleftharpoons \text{AlS}_n^{3+} + 3\text{AlCl}_4^-$$  \hspace{1cm} (9)

There are two other possibilities which can arise. If all steps in the sequence (8) are established, and if the interconversions are slow, then six or more NMR signals can be expected. If, on the other hand, the rates of interconversion are rapid, then only one, broad, time averaged signal would be expected.

For the remainder of part C, the results of the previous section will be discussed in terms of the above theories in order to find which theory adequately describes or is consistent with the observed results. The solutions involving organic solvents will be discussed first, and the inorganic solvents last.

(b) The Organic Solvent Systems.

On the basis of the assignments in section 3(a), the following equations can be written:
\[
\begin{align*}
\text{Al}_2\text{Cl}_6 + 2\text{Et}_2\text{O} & \rightleftharpoons 2\text{AlCl}_3\cdot\text{OEt}_2 & (10) \\
\text{Al}_2\text{Cl}_6 + 2\text{MeNO}_2 & \rightleftharpoons 2\text{AlCl}_3\cdot\text{MeNO}_2 & (11)
\end{align*}
\]

and

\[
\frac{3}{2}\text{Al}_2\text{Cl}_6 + n\text{MeCN} \rightleftharpoons \text{AlCl(MeCN)}_{(3-m)}^+ + 2\text{AlCl}_4^- & (12)
\]

Only the one signal is observed for the ether solution, and it is assigned to the \(\text{AlCl}_3\cdot\text{OEt}_2\) species. Since ether has a low dielectric constant (4.34 at 10°C),\textsuperscript{77} it will not likely support the extensive ionization processes required for the equilibria (8), and the solvation will proceed no further than step (8a).

In contrast to ether, the other two solvents, nitromethane and acetonitrile, do possess high dielectric constants, 39 and 36 at 20°C, respectively\textsuperscript{77} and could support the dissociation mechanism (8). Acetonitrile does support the ionization process, as evidenced by the presence of the \(\text{AlCl}_4^-\) resonance in the spectrum of this solution, whereas nitromethane does not. A qualitative rationalization of this can be made in terms of the relative electron withdrawing capabilities of the two groups. The two solvent-solute adducts are shown in Figure 9.
FIGURE 9. The AlCl₃-MeNO₂ and AlCl₃-MeCN Adducts.

The electronegativities of NO₂, Cl, Br and CN, as determined by NMR methods, are 3.8, 3.2, 2.9 and 2.5 respectively. This series indicates that the NO₂ group has a greater electron withdrawing capability than the other groups in the list, and especially CN which has the lowest. In the AlCl₃-MeNO₂ adduct, if the electron withdrawal along the Al-O bond is such that charge is inductively released from the chloride to the aluminum, then the Al-Cl bond will be strengthened. This effect will be enhanced by the addition of a second MeNO₂ molecule as required by step (8b). This implies that in step (8b), the Al-Cl bond will not be broken, and the reaction will go no further than step (8a). Similar comments apply to the AlBr₃ complex with nitromethane.

Since the electronegativities of both Cl and Br are greater than the CN group, the inductive withdrawal will occur in the opposite direction for acetonitrile. This means an inductive release of charge from the aluminum to the chloride, and the Al-Cl bond will be weakened. The addition of a second MeCN molecule in step (8b) will further
weaken the Al-Cl bond sufficiently allowing it to break. Similar effects will also explain the AlBr$_3$/MeCN spectrum. This explanation also accounts for why the acetonitrile solutions go through most of the steps in the sequence (8), and the nitromethane solutions do not.

A further important point is that, once the AlCl$_4^-$ or AlBr$_4^-$ ion is formed in step (8f), there may be little inclination for the reverse reaction to take place. If the reverse reaction of step (8f) were at all important, then the resonances for these anions would be broadened and the shifts solvent dependent. However, the signals observed for AlCl$_4^-$ and AlBr$_4^-$ in various solvents are quite sharp and have constant chemical shifts. This also provides another explanation of why the reactions (8) either go to completion or stop at (8a). Once halide ions have been generated, the AlX$_4^-$ ions form and continue to do so until the system ceases to furnish further halide ions.

The broad signal observed at +20.4 ppm. for the AlCl$_3$/MeCN solution can be attributed to a rapid exchange between several possible complex cations in solution. The inter-conversions involve several complex species such as

$$\text{AlCl(MeCN)}_3^{2+}, \text{AlCl(MeCN)}_4^{2+}, \text{AlCl(MeCN)}_5^{2+} \text{ and Al(MeCN)}_6^{3+}.$$  

The spectrum of the AlBr$_3$/MeCN solution also contains a broad resonance at +21.9 ppm. as well as an additional,
sharper, but less intense one at +31.2 ppm. These resonance lines are attributed to the complex cations of the same type as discussed for the chloride example above.

(c) The Inorganic Solvent Systems.

For the inorganic solvents studied here, not only are the equilibria (8) possible, but the situation may be complicated by the additional exchange processes between the chlorides on the solvent molecule and the aluminum halides as well.

Lewis and Sowerby\textsuperscript{53} have shown from chloride ion exchange studies that aluminum chloride and phosphoryl chloride exchange only slowly at 180°C, except in the presence of free chloride ion. They have concluded that the $\text{AlCl}_4^-$ ion was not formed in the absence of ionic chloride. This does not, however, hold with the NMR evidence, and the process

$$2\text{Al}_2\text{Cl}_6 + 6\text{POCl}_3 \rightleftharpoons \text{Al(POCl}_3)_6^{3+} + 3\text{AlCl}_4^- \quad (13)$$

in which all the chloride ions on the $\text{AlCl}_4^-$ are derived from the aluminum chloride, is consistent with the exchange evidence of Lewis and Sowerby but not with their conclusion. No ionization of the solvent is necessary, and the system of equilibria (8) can provide a mechanistic pathway for the reaction. The solvent system approach which postulates the ionization of the solvent as a necessary step does not seem to account for either the NMR results nor the exchange
results.

The AlBr$_3$/POCl$_3$ solution presents the complicating features of the halide exchange process between the solvent and solute. For this solution, the spectrum probably indicates the presence of the most thermodynamically stable species in solution, the AlCl$_4^-$ ion. The exchange process is energetically favourable since the energy lost by the formation of the POCl$_2$Br

$$\text{AlBr}_3 + 3\text{POCl}_3 \rightleftharpoons \text{AlCl}_3 + 3\text{POCl}_2\text{Br}$$

(14)
molecule would be more than adequately made up by the energy gained by converting the AlBr into AlCl and completing the sequence

$$4\text{AlCl}_3 + 6\text{POCl} \rightleftharpoons 3\text{AlCl}_4^- + \text{Al(POCl}_3)_6^{3+}$$

(15)
The cation resonance was not present in the spectrum of this solution possibly because the signal was broadened beyond recognition by exchange effects.

*If the order of the heats of formation of the tetrahaloaluminate anions parallels the order for the aluminum halides, then the order of decreasing thermodynamic stability is AlCl$_4^-$ > AlBr$_4^-$ > AlI$_4^-$. The heats of formation of the aluminum halides are: $\Delta H (\text{AlCl}_3) = -166.2$ kcal./mole, $\Delta H (\text{AlBr}_3) = -125.8$ kcal./mole, and $\Delta H (\text{AlI}_3) = -75.2$ kcal./mole. The heats of formation of POCl$_3$ and POBr$_3$ are -151.0 kcal./mole and -114.6 kcal./mole respectively.
This signal reappears again, however, in the spectrum of the AlI$_3$/POCl$_3$ solution. As in the bromide solution, the iodides have been exchanged for chlorides from the solvent, and then the solvation reaction (15) has occurred. Thus, the spectrum of this solution contained two signals, one for the AlCl$_4^-$ ion and the other for the Al(OPCl$_3$)$_6^{3+}$ cation.

The signals for the thionyl chloride solutions are broadened by exchange effects, and it is difficult to know what species exist in solution. The signal could be broadened because of rapid exchange between some of the complexes postulated by mechanism (8), or a simple exchange process involving the SOCl$_2$AlCl$_3$ and SOCl$_2$·2AlCl$_3$, as implied by the Raman spectrum.

In the AlBr$_3$/SOCl$_2$ solution, the bromides have been exchanged for chlorides from the solvent. This situation is similar to the AlBr$_3$/POCl$_3$ solution. The end products are thermodynamically controlled and the most stable species in solution are formed.

This solvent system does not behave in a manner consistent with the solvent system concept which predicts the auto-ionization of the solvent and the subsequent reaction with an acid solute

$$\text{SOCl}_2 \rightleftharpoons \text{SOCl}^+ + \text{Cl}^-$$  \hspace{1cm} (16)

and

$$\text{AlCl}_3 + \text{SOCl}_2 \rightleftharpoons \text{SOCl}^+ + \text{AlCl}_4^-$$  \hspace{1cm} (17)
No sharp signal was observed at \(-102\) ppm., however, until ionic chloride was added.

(5) Conclusion.

The discussion in section (4) has pointed out the deficiencies of the solvent system concept as a model for solvation. Not only is it limited to the inorganic solvent systems, but even with them it cannot provide a suitable explanation for all the observed phenomena. The coordination model, on the other hand, does account for most of the observations and does give a reasonable mechanism of solvation for both the organic and inorganic solvents.
APPENDIX A. THE EFFECTS OF SYMMETRY ON LINE WIDTH.

The nucleus of interest, aluminum, resides at the centre of the tetrahedral complex as illustrated in Figure A1. A right-handed Cartesian coordinate system is set up with its origin at the nucleus under investigation.

Figure A1. The Coordinate System for the Al$^{n+}$ Y$^{4-n-}$ Ion.

The total electric field experienced by the nucleus will be

$$ E = \sum_i E_i $$  \hspace{1cm} (A.1)

where $E_i$ (in cgs units) is given by

$$ E_i = \frac{q_i}{r_i^3} F_i $$  \hspace{1cm} (A.2)
The vector from the nucleus to the ligand \( i \) is given by \( \mathbf{r}_i \), and the vector from ligand \( i \) to the nucleus is \( \mathbf{r}_i' = -\mathbf{r}_i \). Since \( |\mathbf{r}_1| = |\mathbf{r}_2| = |\mathbf{r}_3| = |\mathbf{r}_4| \) for a molecule with \( T_d \) symmetry, the respective \( x, y, z \) components of the vectors will be equal, and

\[
\begin{align*}
\mathbf{r}_1' &= x_1\hat{i} + y_1\hat{j} + z_1\hat{k} \\
\mathbf{r}_2' &= -x_1\hat{i} + y_1\hat{j} - z_1\hat{k} \\
\mathbf{r}_3' &= x_1\hat{i} - y_1\hat{j} - z_1\hat{k} \\
\mathbf{r}_4' &= -x_1\hat{i} - y_1\hat{j} + z_1\hat{k}.
\end{align*}
\] (A.3)

Also, the ligand charges, \( q_i \), will be identical for all the groups. Therefore, \( K \) is defined as \( q_i/r_i^3 \), and

\[
\mathbf{E}_i = K\mathbf{r}_i.
\] (A.4)

Substituting (A.4) into (A.1) gives

\[
\begin{align*}
\mathbf{E}(T_d) &= \sum_i \mathbf{E}_i = K(\mathbf{r}_1 + \mathbf{r}_2 + \mathbf{r}_3 + \mathbf{r}_4) \\
&= -K(\mathbf{r}_1' + \mathbf{r}_2' + \mathbf{r}_3' + \mathbf{r}_4') \\
&= 0.
\end{align*}
\] (A.5)

Hence, for complexes with \( T_d \) symmetry, the electric field at the nucleus will be zero. This also means that the electric field gradient at the nucleus is zero. Thus, there will be no first order broadening of the resonance line by the coupling of the nuclear quadrupole moment with the electric field gradient, and this mechanism will not
be available for cubic complexes of the type AlX$_4^-$. The symmetry of the complex will, however, become noncubic if one of the ligands is exchanged for a different one, e.g., AlX$_4^- \rightarrow$ AlX$_3Y^-$. The symmetry of this complex is now C$_{3v}$. If the position $X_1$ has been exchanged for a $Y$, then the charges will differ, i.e., $q_1 \neq q_2 = q_3 = q_4$ and the internuclear distances will no longer be equal, i.e., $|s_1| > |s_2| = |s_3| = |s_4|$ where

$$s'_1 = u_1 \hat{i} + v_1 \hat{j} + w_1 \hat{k}$$  \hspace{1cm} (A.6)

If $k' = q'_1/s'_1$ and $s_1 = -s'_1$, then

$$E(C_{3v}) = \sum_T E_T = k's_1 + K(u_2 + u_3 + u_4)$$

$$= k's_1 - K(u'_2 + u'_3 + u'_4)$$

$$= k's_1 - Kr_1$$  \hspace{1cm} (A.7)

by equation (A.3). $E(C_{3v})$ may also be written as

$$E(C_{3v}) = (kx_1 - k'u_1)\hat{i} + (ky_1 - k've_1)\hat{j} + (kz_1 - k'w_1)\hat{k}$$  \hspace{1cm} (A.8)

which gives the electric field in terms of the differences in ligand charge and components of the bond distances.

When the symmetry of the complex is further lowered to C$_{2v}$ by the exchange of another $X$ for a $Y$ ligand, i.e., AlX$_3Y^-$ to AlX$_2Y_2^-$, then the electric field will again be altered.

If $q'_1 = q'_2 \neq q_3 = q_4$ and $|s_1| = |s_2| = |s_3| = |s_4|$, then

$$E(C_{2v}) = k'(s_1 + s_2) + K(u_3 + u_4)$$  \hspace{1cm} (A.9)
where
\[ s_1 + s_2 = -(s_1^1 + s_2^1) = -2v_1 \hat{j} \]
and
\[ \mathbf{r}_3 + \mathbf{r}_4 = -(r_3^1 + r_4^1) = -(-2y_1 \hat{j}). \]
Therefore,
\[ E(C_{2v}) = 2(ky_1 - k'y_1) \hat{j}. \] (A.10)

The coordinates \( x_1, y_1, z_1 \) and \( u_1, v_1, w_1 \) can be related by a constant factor, i.e., if no bond angle distortion is assumed, i.e., \( u_1 = \sigma x_1, v_1 = \sigma y_1, w_1 = \sigma z_1 \). The electric field vectors are now modified to
\[ E(T_d) = 0 \] (A.5)
\[ E(C_{3v}) = (k-k'\sigma)x_1 \hat{i} + (k-k'\sigma)y_1 \hat{j} + (k-k'\sigma)z_1 \hat{k} \] (A.11)
\[ E(C_{2v}) = 2(k-k'\sigma)y_1 \hat{j}. \] (A.12)

The electric field gradient \( \nabla E \) is a dyadic. Carrying out the operation of \( \nabla \) on \( E \),
\[ \nabla E(T_d) = 0 \]
\[ \nabla E(C_{3v}) = (k-k'\sigma)\hat{i} \hat{i} + (k-k'\sigma)\hat{j} \hat{j} + (k-k'\sigma)\hat{k} \hat{k} \] (A.13)
\[ \nabla E(C_{2v}) = 2(k-k'\sigma)\hat{j} \hat{j} \] (A.14)

The scalar product \( |\nabla E(C_{3v})| \) is given by
\[ |\nabla E(C_{3v})| = (\nabla E(C_{3v}) \cdot \nabla E(C_{3v}))^{\frac{1}{2}} = (3)^{\frac{1}{2}} (k-k'\sigma) \] (A.15)
and similarly,
\[ |\nabla E(C_{2v})| = (\nabla E(C_{2v}) \cdot \nabla E(C_{2v}))^{\frac{1}{2}} = (4)^{\frac{1}{2}} (k-k'\sigma). \] (A.16)
If these two quantities are compared by taking their ratio, then
\[
\frac{|\nabla \mathcal{E}(C_{2v})|}{|\nabla \mathcal{E}(C_{3v})|} = \frac{[4]^{1/2}}{[3]} = 1.155 \quad (A.17)
\]

If all other contributions to the line width are equal, the line width for the \(C_{2v}\) molecule should be approximately 15.5% broader than the width for the \(C_{3v}\) molecule.
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SUMMARY

1. The magnetic shielding of the aluminum atom in the tetrahaloaluminate ions lies in the order

$$\text{AlI}_4^- > \text{AlBr}_4^- > \text{AlCl}_4^-.$$ 

This order implies that the chlorine atom generates the greatest paramagnetic shift and the iodine the least.

2. The paramagnetic term is the predominant contribution to the shielding constant for these ions. This term depends upon $\Delta E$, the average excitation energy, and the $\langle r^{-3} \rangle$ factor which gives a measure of the electron density about the nucleus.

3. The extent of the delocalization of charge in the Al-X $\sigma$-bonds is the predominant influence in determining the magnitude of the $\langle r^{-3} \rangle$ factor and, hence, the shielding constant. The order of the ability of the ligands to delocalize charge is $I^- > Br^- > Cl^- > F^-$, the order of the nephelauxetic effect. The ligand which gives the greatest delocalization of charge, $I^-$, generates the smallest paramagnetic shift, and the ligand which gives the least delocalization, $F^-$, generates the greatest paramagnetic shift. For the AlF$_4^-$ ion, the highly electronegative character of the
fluorine also is important in determining the shielding of the $^{27}$Al nucleus.

4. Ions with $T_d$ symmetry give the narrowest resonance lines. The line widths for the ions with $C_{2v}$ symmetry are about 15% broader than those for ions of $C_{3v}$ symmetry for the same $AlX_4 Y_{4-n}$ complex series. The signals for the ions of noncubic symmetry are considerably broader than those for ions with $T_d$ symmetry.

5. The nonaqueous chemistry of the anhydrous aluminum halides is best described by a series of equilibria involving the solute as described by Drago's coordination model of solvation.