REDOX AND ADDITION REACTIONS OF BINARY FLUORIDES

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by

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"There is something fascinating about science. One gets such wholesale returns of conjecture out of such a trifling investment of fact"

Mark Twain

"It is better to meet a mother bear robbed of her cubs than to meet some fool busy with a stupid project".

Proverbs, 17, 12
(Good News Bible)

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Abstract

This thesis describes the study of complexation and redox reactions of iodine pentafluoride, and redox and addition reactions of uranium hexafluoride and rhenium hexafluoride.

Solutions of IF_5 in acetonitrile and pyridine were studied using Raman, ^1H and ^{19}F n.m.r. spectroscopy. In CH_3CN solution, the I-F•••I contacts which occur in liquid IF_5, are replaced by C≡N•••I contacts as the concentration of CH_3CN increases. A large decrease in the frequency of the ν_1 band of IF_5, and small increases in the C-C and C≡N stretching frequencies of CH_3CN are observed in the Raman spectra. The results obtained suggest a maximum number of four CH_3CN molecules can co-ordinate to each IF_5. A 1:1 complex is formed between IF_5 and C_5H_5N and spectra of mixtures of the two liquids can best be explained in terms of an equilibrium between this complex and the two components. The solid 1:1 adduct, IF_5.1,4-Dioxane was prepared and characterised by elemental analysis and vibrational spectroscopy. Vibrational, and ^1H and ^{19}F n.m.r. spectra were recorded of its solutions in CH_3CN. A polymeric structure for the adduct, based on a chain-structure is suggested.

Reactions of IF_5 with metals and metal fluorides were investigated, using IF_5 or CH_3CN as solvent. Thallium metal reacts with IF_5 to form insoluble $Tl^+IF_6^-$, which readily hydrolyses to give $TlIOF_4$. Silver metal reacts with IF_5 in CH_3CN to give a viscous oil, whose spectra indicate that IF_6^- is not formed. The reaction between copper and IF_5 in CH_3CN gives a blue-white soluble solid whose composition

is variable. The product from the reaction between mercury and IF_5 is also of variable composition. Thallium (I) fluoride reacts with IF_5 in CH_3CN to give $(Tl_2)^{3+}IF_6^{3-}$ as one product. These redox reactions all involve a 2-electron reduction of I(V) to I(III), but the reaction products depend on the stability of the I(III) species towards disproportionation. The products were identified by elemental analysis and vibrational spectroscopy. The addition reactions of IF_5 with metal fluorides indicate that, in at least some instances, adduct formation is preferred to fluoride ion addition. TlF reacts with IF_5 to produce either the soluble solid $TlF.IF_5$ or the viscous liquid $TlF.3IF_5$. The latter is formed if IF_5 is present in a very large excess. CuF_2 reacts with IF_5 in CH_3CN forming the adduct $CuF_2.4CH_3CN.4IF_5$. This is a blue-green oil and was characterised by elemental analysis, ^1H and ^{19}F n.m.r., e.p.r., electronic and vibrational spectroscopy. A structure based on these data is presented.

Tungsten hexafluoride and molybdenum hexafluoride do not react with iodine in IF_5 but rhenium hexafluoride forms a stable solution containing the I_2^+ ion. This was confirmed by electronic and resonance Raman spectroscopy. No isolable product is formed. Uranium hexafluoride also forms a species containing I_2^+, but a further reaction occurs and uranium pentafluoride is obtained as a pale green precipitate. UF_5 is very soluble in CH_3CN, with which it forms an isolable 1:1 adduct, and was characterised in the solid state by vibrational spectroscopy and in solution by Raman and electronic spectroscopy.

Thallium, cadmium and copper metals are all readily oxidised by UF_6 in CH_3CN, forming soluble hexafluorouranates(V). These are isolable as the solvates $Tl(UF_6)_3.5CH_3CN$, $Cd(UF_6)_2.5CH_3CN$ and $Cu(UF_6)_2.5CH_3CN$. Electronic spectra obtained agree with the latest literature spectra. Values of vibrational frequencies obtained from vibronic couplings in electronic spectra agree well with the values from i.r. spectra. No silver compound could be isolated because of rapid solvent polymerisation caused by UF_6 in the presence of Ag.

UF_6 is reduced by CH_3CN to give UF_5, while the solvent is slowly polymerised. The increase in concentration of UF_5 with time is seen from Raman and electronic spectra, run at 30 minute intervals. ReF_6 attacks CH_3CN too rapidly to allow reactions involving excess ReF_6 to be carried out. However $Cu(ReF_6)_2.4CH_3CN.0.5IF_5$ was prepared using a mixture of IF_5 and CH_3CN as solvent.

The reduction of UF_6 by CH_3CN to give UF_5, interferes with relatively slow reactions such as F^- ion addition. HgF_2 and UF_6 in CH_3CN give $Hg(UF_6)_2.6CH_3CN$, and no U(VI) species is isolated. CuF_2 and UF_6 give a mixture of U(V) and U(VI) compounds and the equilibrium

$$UF_8^{2-} + UF_5 \rightleftharpoons UF_7^- + UF_6^-$$

is believed to exist in the reaction mixture.

$CuF_2.4CH_3CN.4IF_5$ behaves as a fluoride ion donor towards PF_5 and WF_6 in CH_3CN. The PF_6^- ion was detected in solution by ^{19}F, and ^{31}P I.N.D.O.R. n.m.r. spectroscopy, while WF_7^- was observed in both ^{19}F n.m.r. and Raman spectra. However, the reactions between $CuF_2.4CH_3CN.4IF_5$ and ReF_6 and UF_6 in IF_5 are much less straightforward. The products were not completely characterised, but fluoride ion addition is at most only a side reaction. This may indicate that UF_6 and ReF_6 are poorer F^- acceptors than PF_5 and WF_6. Another explanation is that despite the F^- ion donor properties of $CuF_2.4CH_3CN.4IF_5$ in CH_3CN, it does not behave as such in IF_5. The co-ordinated CH_3CN in $CuF_2.4CH_3CN.4IF_5$ remains unattacked, despite high concentrations of ReF_6 or UF_6 and a long period of reaction.

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INTRODUCTION

Fluorine is the most reactive of the elements and forms compounds with all others except helium, neon and argon. The range of binary compounds of fluorine is more extensive than that of any other element apart from oxygen. The chemistry of fluorine, like that of oxygen is characterised by its ability to support elements in their highest oxidation states. In this respect there are often more similarities between fluorides and oxides than between fluorides and the other halides, since this ability decreases in the order $F = O > Cl > Br > I$. This stabilisation by fluorine or oxygen can be demonstrated[1] by examining a Born-Haber cycle for a halide or oxide thermally decomposing as:

$$MX_{n+1} \rightarrow MX_n + \tfrac{1}{2}X_2$$

A Born-Haber cycle based on either an ionic or a covalent model can be used. To a first approximation, the high oxidation state compound MX_{n+1} will be thermally stable if there is a large difference in lattice energy, or total bond energy, between it and the decomposition product MX_n. This difference decreases as the radius of the halide increases, hence the stabilisation effect decreases markedly from fluoride and oxide to iodide. A good example of this stabilisation of high oxidation states by fluorine, and the decrease of the effect down the halogens can be seen from the highest oxidation states of rhenium supported by each halogen. The compounds concerned are:

ReF_7, $ReCl_5$, $ReBr_5$ and ReI_4.

Many fluorides of elements in high oxidation states such as transition metal hexafluorides are volatile and are non-conducting in the liquid phase. They cannot therefore be ionic and must be molecular with essentially covalent M-F bonds. This contrasts with many lower oxidation state fluorides which are ionic. It is important to emphasise however that there is no sharp dividing line between ionic binary fluorides and molecular ones. There is a gradation between these extremes and most binary fluorides come somewhere in between.

Fluorine is unique in being able to form binary compounds which contain a central atom in a high oxidation state and with a high co-ordination number such as 7 or 8. Although oxygen fulfils the oxidation state requirement, being divalent, it cannot maintain high co-ordination numbers.

Binary fluorides are very interesting compounds from an academic point of view as well as being extremely important industrially. They cover the whole range of chemical reactivity. CF_4 and SF_6 are almost completely unreactive because of kinetic effects arising from the complete shielding of the central atom from nucleophilic attack, and the inability of carbon and sulphur to expand their co-ordination number beyond four and six respectively. On the other hand, PtF_6 is one of the most reactive compounds known. The use of binary fluorides on a large scale started during the Manhattan Project and has steadily increased since. Some industrial uses of binary fluorides are shown in Table. 1.[2]

Table 1

Binary Fluoride	Industrial Uses
HF	Solvent, fluorinating agent, etching glass, electrolyte.
BF_3	Catalyst, e.g. in Friedel-Crafts reactions.
AlF_3	Aluminium production.
SF_4	Mild fluorinating agent.
SF_6	Electrical insulator in circuit-breakers.
ClF_3, BrF_3, BrF_5	Powerful fluorinating and oxidising agents.
CaF_2	HF production.
UF_6	Separation of ^{235}U from ^{238}U

The binary fluorides which are relevant to this work will be discussed in more detail. These are:

1) The halogen fluorides, in particular iodine pentafluoride.
2) The actinide fluorides, in particular uranium pentafluoride and uranium hexafluoride.
3) The transition metal hexafluorides, in particular rhenium hexafluoride.

The Halogen Fluorides

To date, ten halogen fluorides and eighteen ions derived from halogen fluorides have been prepared and characterised. These, together with their symmetry point groups are shown in Table 2. Two further species, bromine heptafluoride and the hexafluorochlorate(V) anion have been reported[3,4] in the patent literature but they were not characterised completely and have not been reinvestigated. They are not included in Table 2.

Table 2

Halogen Fluorides and derived ions

Chlorine	Bromine	Iodine	Symmetry
ClF	BrF	IF	$C_{\infty v}$
Cl_2F^+			C_s
ClF_2^-			$D_{\infty h}$ in $NO^+ClF_2^-$
ClF_2^+	BrF_2^+	IF_2^+	C_{2v}
ClF_3	BrF_3	IF_3	C_{2v}
ClF_4^-	BrF_4^-	IF_4^-	D_{4h}
		IF_6^{3-}	?, $<O_h$
ClF_4^+	BrF_4^+	IF_4^+	C_{2v}
ClF_5	BrF_5	IF_5	C_{4v}
	BrF_6^- (O_h?)	IF_6^- (C_{2v}?)	
ClF_6^+	BrF_6^+	IF_6^+	O_h
		IF_7	D_{5h}
		IF_8^-	?

Historical Aspects

Halogen fluorides have been known since the 19th century and early workers such as Moissan[5] carried out investigations into their physical and chemical properties as best they could with the very limited apparatus then available. Generally, early accounts tended to overestimate reactivity due to the then unsuspected presence of fluorine as an impurity. Probably the first halogen fluoride to be made was iodine pentafluoride, when in 1862, Kammerer[6] reacted silver(I) fluoride with iodine. He thought that the product was fluorine, but eight years later it was shown[7] to be a fluoride of iodine. The first bromine fluoride was discovered in 1900 when Moissan observed[8] that bromine vapour combined with fluorine at room temperature with some vigour. The identity of the product was not established until several years later when Lebeau[9] and Prideaux[10] found it to be BrF_3. The first fluoride of chlorine was discovered in 1928 when Ruff and Ascher[11] prepared ClF by heating the elements in a copper reactor at 523K and purifying by fractional distillation. Four further halogen fluorides were discovered in the period 1930-1933. On distilling crude IF_5, prepared by direct combination of the elements, Ruff and Keim[12] noted a compound of iodine and fluorine which was more volatile than the pentafluoride. Attempts to prepare this new compound by passing fluorine into IF_5 at 298K failed, but iodine heptafluoride was obtained at 543K. Chlorine trifluoride was obtained by Ruff and Krug[13] by direct combination of the elements at 100K. In 1931, Ruff and Menzel[14] prepared bromine pentafluoride by heating the trifluoride to 370K, mixing the vapour with fluorine, and heating this mixture to 470K. The preparation of bromine monofluoride has been described[14,15] but at 273K it is very unstable with respect to disproportionation to BrF_3 and Br_2. Nearly thirty years elapsed before the final three halogen fluorides were found. Schmeisser and Scharf[16] isolated iodine trifluoride as a pale yellow solid at 195K by passing a mixture of fluorine and nitrogen through a solution of iodine in trichlorofluoromethane at 195K. Chlorine pentafluoride was prepared by Smith[17] who heated a 14:1 mixture of fluorine and chlorine at $2{\cdot}53 \times 10^7$Pa to 623K for one hour. The last halogen fluoride to be isolated was iodine monofluoride. Evidence for its existence came first from its emission spectrum,[18] observed in an iodine fluorine flame. It was also reported[16] to be formed as an intermediate in the preparation of IF_3 at 195K but was not isolated pure until 1970.[19] It is a colourless solid which disproportionates at 259K to IF_5 and I_2.

It is interesting to note that the time from the identification of the first halogen fluoride, IF_5, to the isolation of the last, IF, is exactly one hundred years.

Bromine heptafluoride has been reported[3] in the patent literature but in the opinion of the author, much more work is required to prove its existence beyond doubt.

The existence of chlorine heptafluoride has been shown by Christe[20] to be extremely unlikely, at least above 195K. In a displacement reaction between $ClF_6^+PtF_6^-$ and FNO at 195K, the products were $NOPtF_6$, ClF_5 and F_2 indicating strongly the instability of "ClF_7" towards decomposition to ClF_5 and F_2, at 195K. Other new halogen fluorides would be the fluorides of astatine. By analogy with iodine, AtF_5 and AtF_7 would probably be chemically stable but the longest lived isotope of astatine, ^{210}At, has a half-life of only 8•3 hours. Since over twenty isotopes of At are known, the possibility of finding a stable one is remote, as is chance of carrying out reactions of At at other than tracer levels.

The halogen fluorides are all normally prepared by direct combination of the elements under suitable conditions of temperature and pressure. The notable exception is ClF which is more conveniently prepared by mixing equimolar amounts of ClF_3 and Cl_2 at 298K. Prior to the second world war, the seven known fluorides had been prepared only in very small quantities for academic purposes. The limitation was mainly the primitive type of fluorine cell then in use. These were unreliable and of low output and made larger scale manufacture of the halogen fluorides out of the question. However, during the war, this constriction was removed as large scale fluorine production became possible. The first really large scale plant was the one built in Germany to manufacture ClF_3 as an incendiary agent.[21] Since the end of the war, ClF_3, BrF_3 and BrF_5 have been commercially available in bulk. While fluorine generation techniques were improving, so were handling techniques. The halogen fluorides are all extremely reactive, moisture sensitive compounds and difficulties associated with their handling had also held back their large scale preparation.

Physical Properties

Some of the physical properties of those halogen fluorides which are thermally stable at room temperature are shown in Table 3.[22,23,25] BrF_3, BrF_5 and IF_5 are all associated liquids at room temperature and the specific conductance values indicate the degree of self ionisation. This is particularly pronounced in the case of BrF_3 where the specific conductance is about a thousand times higher than in IF_5, the second highest.

The bonds in the halogen fluorides are all essentially covalent although the Cl-F bond in ClF has been shown to have appreciable ionic character.[24] The structures of these compounds can all be correctly predicted using the simple Gillespie-Nyholm Valence Shell Electron Pair Repulsion theory. The structure of the trifluorides is based on a trigonal bipyramid with two equatorial sites occupied by electron lone pairs, resulting in a slightly distorted "T" shaped molecule. In ClF_3 for example, the extra repulsive forces exerted by the lone pairs causes the F_{ax}-Cl-F_{ax} angle to close slightly to 174°58'. The pentafluorides have structures based on an octahedron with one site occupied by a lone pair, resulting in a square

Table 3

Physical Property	Halogen Fluoride						
	ClF	ClF_3	ClF_5	BrF_3	BrF_5	IF_5	IF_7
Melting Point (K)	117·4	196·7	180	281·8	212·5	282·6	277·7(sub
Boiling Point (K)	173	285	259	399	314·3	373·5	279
ΔH vap. ($kJmol^{-1}$)	20·1	27·5	24·0	42·8	30·6	41·3	23·8
Trouton's Constant ($JK^{-1}mol^{-1}$)	117	96·7	92·0	107·5	97·5	110·5	-
$\Delta H_{f298}(g)$ ($kJmol^{-1}$)	-56·5	-162·8	-234·3	-255·6	-428·9	-836·8	-958·6
$\Delta G_{f298}(g)$ ($kJmol^{-1}$)	-57·7	-123·4	-145·4	-229·3	-351·5	-766·5	-838·9
Specific Conductance(l)($\Omega^{-1}m^{-1}$)	$1{\cdot}9\text{x}10^{-9}$	$4{\cdot}9\text{x}10^{-11}$	$1{\cdot}3\text{x}10^{-11}$	$8{\cdot}0\text{x}10^{-5}$	$9{\cdot}1\text{x}10^{-10}$	$5{\cdot}4\text{x}10^{-8}$	-

pyramidal structure. In this case, the extra repulsion of the lone pair has the effect of forcing the plane of the four equatorial fluorines slightly nearer the apical fluorine so that the central atom sits slightly below this plane. The structure of iodine heptafluoride has been the subject of a great deal of interest. After much controversy, the results of vibrational, n.m.r., and Mössbauer spectroscopy, electron, x-ray diffraction and molecular beam studies have shown the structure to be pentagonal bipyramidal, but non-rigid.[22,23,25]

Chemical Properties

The halogen fluorides are all reactive, moisture-sensitive compounds which must be handled in rigorously dry conditions. Although it is probably not the most important reaction of the halogen fluorides, certainly the most obvious one is hydrolysis.

Hydrolysis Reactions

The hydrolysis reactions of the halogen fluorides are of two main types. If the halogen fluoride is a strong oxidising agent then a redox reaction can occur releasing elemental oxygen, but if the fluoride is more moderate in its oxidising power, then the reaction is basically ligand exchange. The three chlorine fluorides fall into the first category although reaction products depend on starting stoichiometries. The hydrolysis reactions of the chlorine fluorides have been thoroughly investigated by Christe,[26] who observed the following reactions:

Excess chlorine fluoride

$$5ClF + 2H_2O \longrightarrow 4HF + ClO_2F + 2Cl_2$$
$$2ClF_3 + 2H_2O \longrightarrow 4HF + ClO_2F + ClF$$
$$ClF_5 + 2H_2O \longrightarrow 4HF + ClO_2F \;.$$

Excess water

$$4ClF + 2H_2O \longrightarrow 4HF + 2Cl_2 + O_2$$
$$4ClF_3 + 6H_2O \longrightarrow 12HF + 2Cl_2 + 3O_2$$
$$2ClF_5 + 5H_2O \longrightarrow 10HF + 2ClO_2 + \tfrac{1}{2}O_2$$

Although IF_5 reacts vigorously and sometimes violently with water, it does not liberate oxygen. With excess water, the reaction occurs according to :

$$IF_5 + 3H_2O \longrightarrow HIO_3 + 5HF$$

No really thorough study of the hydrolysis reactions of BrF_3, BrF_5 and IF_7 has been carried out. All three are known to react very violently. BrF_3 has been reported[22] to react yielding a mixture of HF, HBr, HOBr, Br_2 and O_2, but the reaction conditions were not stated. IF_7 has been reported[27] to give only IO_4^- and HF. The only recent study carried out concerned the hydrolysis of BrF_5 in acetonitrile at 273K. BrF_5 was found[28] to hydrolyse relatively smoothly according to $BrF_5 + 3H_2O \xrightarrow[273K]{CH_3CN} HBrO_3 + 5HF$.

Redox and Fluorination Reactions

The halogen fluorides which are thermally stable at room temperature range from very powerful to mild oxidising agents and they have been placed in the order:

$ClF_3 > BrF_5 > IF_7 > ClF > BrF_3 > IF_5$.[22]

Chlorine trifluoride is by far the most widely used oxidising agent among the halogen fluorides. It can conveniently be stored as a liquid and it rivals elemental fluorine in its oxidising properties. The most common uses of ClF_3 are in the preparation of UF_6 in particular, as well as other fluorides of metals in high oxidation states. Fluorides such as VF_5, NbF_5, TaF_5, ReF_6, MoF_6, WF_6 have all been prepared from the metals or metal oxides using ClF_3. Plutonium metal reacts to form PuF_4 which is involatile at 298K whereas uranium forms the volatile hexafluoride.[22] Reaction with ClF_3 therefore forms a good method of separating plutonium and uranium in nuclear reactor waste material. ClF_3 reacts violently with organic compounds and it has been used as the oxidising agent in rocket propellants, with such compounds as hydrazine as fuel. These compounds when mixed are hypergollic which is an additional advantage. Propellants such as $ClF_3 + N_2H_4$ have the advantage over the traditional ones such as kerosene + liquid oxygen in that cryogenic storage is not required. ClF reacts similarly to ClF_3 but less extensively and less vigorously. Metals and metal oxides are fluorinated but often with the metal in a lower oxidation state than in a similar reaction with ClF_3. ClF_5 has been used as an oxidant in rocket propellants but few of its oxidising properties are known. BrF_3 reacts in a similar way to ClF_3 but slightly less vigorously. It has been used frequently to prepare simple fluorides from metals, oxides and other compounds. Volatile fluorides such as WF_6, MoF_6 and UF_6 distil readily from the solutions in which they are formed. Non-volatile or slightly less volatile fluorides such as AuF_3, PdF_3, RhF_4, PtF_4 and BiF_5 can be obtained as residues on removal of the solvent under vacuum and at slightly elevated temperatures. The reactions between BrF_3 and 28 different oxides were studied by Emeléus and Woolf.[29] Twelve of these, CuO, B_2O_3, Tl_2O_3, SiO_2, GeO_2, TiO_2, As_2O_3, Sb_2O_3, SeO_2, VO_3, I_2O_5 and BiOCl all liberate oxygen quantitatively, Reaction with BrF_3 has been developed into a method for determining the oxygen content of metal oxides and oxygen containing salts.[30] BrF_3 reacts violently with organic compounds, including acetonitrile, but more controlled fluorinations can be carried out using halocarbons instead of the parent hydrocarbons. BrF_3 has been used in rocket propellants but it is inferior to ClF_3 in this rôle. BrF_5 is very similar to BrF_3 in its reactions though it is a more powerful oxidiser. Surprisingly, in some cases, it is reported to be less reactive. Whereas BrF_3 readily fluorinates acetonitrile,[22] Meinert and Gross report[28] that provided the acetonitrile solvent is chilled, BrF_5 is miscible without reaction. BrF_5 does not attack glass or quartz at room temperature in apparent contrast to BrF_3[22] but it is possible that this latter observation was due to HF impurity rather than the BrF_3 itself. By comparison with the halogen fluorides already mentioned, IF_5 is a mild oxidising agent. Arsenic, antimony and boron inflame on contact with liquid IF_5, molybdenum and tungsten inflame on heating. The alkali metals form passive coatings but react very violently on heating. Silver, magnesium, copper, iron and chromium are attacked only slightly. IF_5 reacts with metal oxides to form adducts rather than fluorinating them completely. Although IF_5 has been reported[31] to fluorinate the oxides of vanadium, niobium and uranium to form the volatile fluorides, this has not been verified by other workers. Aynsley, Nichols and Robinson found[81] that hot or boiling IF_5 reacted with oxides as follows:

$$V_2O_5 \longrightarrow 2VOF_3.3IOF_3$$
$$Sb_2O_5 \longrightarrow SbF_5.\ 3IO_2F$$
$$MoO_3 \longrightarrow 2MoO_3.3IF_5$$
$$WO_3 \longrightarrow WO_3.2IF_5$$
$$CrO_3 \longrightarrow CrO_2F_2$$

Since it is a milder reagent than other halogen fluorides, IF_5 has been used as a fluorinating agent in organic chemistry. Examples of organic compounds fluorinated include oximes, amines, isocyanates and hexahalobenzenes. CS_2 is also fluorinated, yielding mainly $(CF_3)_2S_2$ although some products of further fluorination such as SF_4 are also formed. IF_5 must however be treated with respect and the organic compounds selected carefully since some reactions can be extremely violent, for example the reaction with Me_2SO.[32] IF_7 is a stronger oxidant and fluorinating agent than IF_5 but its reactions with metals and metal oxides have received little attention. The reactions of IF_7 with many substances have been described by Ruff and Keim,[12] but only qualitatively.

The halogen fluorides, (other than IF_7) act as reducing agents only in reactions with extremely powerful oxidising agents such as PtF_6, KrF^+ and $Kr_2F_3{}^+$. PtF_6 oxidises the iodine fluorides to IF_7 and the chlorine fluorides to

ClF_6^+ but curiously does not oxidise the bromine fluorides beyond BrF_5. BrF_5 can be oxidised to BrF_6^+ by reaction with K_2F^+ and $Kr_2F_3^+$ compounds. Overall, it is reasonable to say that the only redox and fluorination reactions which have been thoroughly studied are those of direct industrial interest such as the fluorination of uranium oxides by ClF_3 and the use of the more reactive halogen fluorides as oxidisers in rocket propellants.

Halogen Fluorides as fluoride ion donors and acceptors,- Halogen Fluoride Cations and Anions.

As may be seen from Table 2, the halogen fluorides MF_n ($M = Cl, Br, I$, $n = 3, 5, 7$) are all capable of donation of a fluoride ion to give the cation MF_{n-1}^+. The cations ClF_6^+ and BrF_6^+ can be considered to be derivatives of the non-existent parent compounds ClF_7 and BrF_7. With these two exceptions, the cations are prepared by reacting the halogen fluoride with a strong fluoride ion acceptor such as AsF_5 or SbF_5 to give products of general formula $MF_n^+ M^1F_6^-$, $M = Cl, Br, I$, $M^1 = As, Sb$, $n = 2, 4, 6$. ClF_2^+ can also be prepared[33] by reacting PtF_6 with excess ClF_3. This reaction occurs according to :

$$3ClF_3 + 2PtF_6 \longrightarrow 2ClF_2^+PtF_6^- + ClF_5$$

if the mixture is warmed very slowly from 77 to 298K. ClF_5 reacts with AsF_5 and SbF_5 to form $ClF_4^+MF_6^-$ but does not react with BF_3.[34] BrF_3 is reported[22] to form

BrF_2^+ salts with the following anions: AuF_4^-, SnF_6^{2-}, SbF_6^-, BiF_6^-, NbF_6^-, TaF_6^-, PtF_6^{2-}, PdF_6^{2-} and RuF_6^-. The crystal structure of $BrF_2^+SbF_6^-$ has been determined.[35,36] The structure is in agreement with the ionic formulation, but there is some fluorine bridging between the bent BrF_2^+ ion and the distorted SbF_6^- octahedron. Christe and Schack concluded[37] from vibrational spectra that the complex consisted of discrete BrF_2^+ and SbF_6^- units but Carter and Aubke[38] were less certain and considered that there were strong anion-cation interactions occurring. BrF_5 reacts with SbF_5 forming $BrF_4^+Sb_2F_{11}^-$. An X-ray structure determination[39] shows that the structure consists of infinite chains of discrete BrF_4^+ and $Sb_2F_{11}^-$ ions coupled by relatively weak fluorine bridges. The Raman spectrum of this compound is also consistent[40] with discrete BrF_4^+ units. The IF_2^+ species is prepared by reacting IF_3 with AsF_5 or SbF_5 at 195K.[41] IF_4^+ salts such as $IF_4^+SbF_6^-$ have been known since 1950 and their preparation is straightforward.[42] $IF_6^+AsF_6^-$ and $IF_6^+SbF_6^-$ have been prepared from IF_7 and AsF_5 or SbF_5 The IF_6^+ ion is very close to being a regular octahedron. Its structure has been determined from Raman,[43] Mössbauer[44], broad-line[45] and high-resolution n.m.r.[46] studies. Also of octahedral symmetry are ClF_6^+ [20,47] and BrF_6^+.[48] The high-resolution n.m.r. spectra of these cations dissolved in HF are most interesting. Since the cations have O_h symmetry, the electric field gradient at the central atom is zero and so there is no nuclear quadrupolar relaxation. ^{35}Cl, ^{37}Cl, ^{79}Br, ^{81}Br and ^{127}I all have nuclear quadrupole moments and these normally prevent observation of coupling to the fluorine ligands by providing a fast relaxation process. However, ClF_6^+, BrF_6^+ and IF_6^+ provided the first good examples of spin-spin coupling involving the halogens other than fluorine.

ClF forms a 2:1 compound with either AsF_5 or BF_3 at low temperatures.[49,50] These are formulated as $Cl_2F^+AsF_6^-$ and $Cl_2F^+BF_4^-$ and contain the cation $Cl-Cl-F^+$ which has a bent structure. No 1:1 adduct has been reported, but since this would presumably contain the Cl^+ entity, its non-existence is not surprising.

The halogen fluoride cations all have structures close to those predicted by simple Gillespie-Nyholm V.S.E.P.R. theory. The situation is more complex with the halogen fluoride anions and V.S.E.P.R. theory.is inadequate in some cases where high co-ördination numbers are involved.

Fluoride ion donors such as the heavy alkali metal fluorides and NOF react with most of the halogen fluorides to add a fluoride ion. ClF forms ClF_2^- by direct reaction with an alkali metal fluoride[51] or NOF. The ClF_2^- ion apparently has the expected centrosymmetric linear structure in the NO^+ salt but is of lower symmetry in the alkali metal salts.[52] The halogen trifluorides all react with MF (M = K, Rb, Cs) to form salts containing the tetrafluorohalate(III) anion. These ions all have the expected square planar D_{4h} symmetry. ClF_3 and BrF_3 react directly at 298K with the metal fluoride[22] but the situation with IF_3

is different since at 298K it is extremely unstable with respect to disproportionation to IF_5 and iodine. IF_4^- salts of the alkali metals have been prepared by reaction of the metal fluoride with IF_3 in CH_3CN at 228K[53] or by reaction of the metal iodide with IF_5[54] or F_2.[55,56] The NO^+ salt is formed using NOF and IF_3 in CCl_3F at 195K. The reactions of IF_3 with CsCl in CH_3CN is complex.[41] The overall reaction scheme is given by:

$$6IF_3 + 6CsCl \xrightarrow{CH_3CN} 3CsIF_4 + CsIF_6 + CsICl_2 + CsICl_4$$

A further complication is that CsF and IF_3 can form, in addition to the 1:1 compound, a 3:1 complex Cs_3IF_6.[57] The vibrational spectra of the IF_6^{3-} ion have been recorded and compared to those of the IF_4^- ion.[58] The differences between the spectra of the two compounds make it unlikely that Cs_3IF_6 can be formulated as $CsIF_4.2CsF$ as has been suggested by Popov.[23] The structure of the IF_6^{3-} ion could not be determined but a regular octahedron was ruled out. BrF_5 and IF_5, but not ClF_5, react with alkali metal fluorides directly and in CH_3CN solvent, to form salts of the hexafluoro-bromate[66-68] and -iodate (V) ions. The IF_6^- ion in particular has been the subject of a great deal of investigation[44,54,59-65] but despite that, its structure is still unknown. Several possibilities have been suggested and these will be discussed later, in the light of the present work. The structure of the BrF_6^- ion is also unknown although solution work in acetonitrile using tetra-alkyl ammonium salts, indicated a D_{3d} symmetry.[69] This will also be discussed later.

The most recently discovered halogen fluoride anion is the octafluoroperiodate(VII) ion, IF_8^-. CsF and NOF were found[70] to react with IF_7 at low temperatures using NOF as solvent. The compounds were shown to be 1:1 adducts, and on the basis of vibrational spectra, they were formulated as $Cs^+IF_8^-$ and $NO^+IF_8^-$.

Molecular Complexes

The chlorine and bromine fluorides form very few molecular adducts. Clark and Sadana[71] have reported that ClF_3 reacts with CrO_3 to form $CrOF_3.0.25ClF_3$. Several salts prepared in BrF_3 solution are isolated as solvates, for example $K_2TiF_6.BrF_3$. SnF_4 is reported[72] to form solid complexes with ClF_3, BrF_3, BrF_5 and IF_5. These include $SnF_4(ClF_3)_n$, n = 0·4, 2; $SnF_4(BrF_3)_n$, n = 0·9, 1, 1·7, 2; $SnF_4 \cdot 2BrF_5$; $SnF_4(IF_5)_n$, n = 0·4, 2. ^{119}Sn Mössbauer spectra showed that the Sn-F bonds were not all equivalent. This was attributed to the existence of both terminal and bridging fluorine atoms. No complexes between organic compounds and chlorine or bromine fluorides appear to have been isolated. The iodine fluorides form a much more extensive range of molecular complexes. IF forms 1:1 complexes with pyridine, quinoline and 2,2'-bipyridine.[19] The compound IF.Pyridine was isolated and found to have a melting point of 383K, but the previously reported[73,74] adduct $IPy_2^+F^-$ was not detected. Several complexes of IF_3 with organic bases have been prepared. These include 1:1 compounds with pyridine, quinoline, pyrazine, 2,2'-bipyridine, tetrafluorophthalic anhydride, and acetonitrile as well as $IF_3.2Py$.[41,57] All complexes except those with acetonitrile and tetrafluorophthalic anhydride are thermally stable at room temperature. This contrasts with the behaviour of IF_3 itself which disproportionates to IF_5 and I_2 even below room temperature. Adduct formation is a very important part of the chemistry of IF_5. It forms thermally stable adducts with organic bases such as pyridine[66,75] and 1,4-dioxane[66,75,76] and with inorganic compounds such as XeF_2[77-80], CsF[59], MoO_3 and WO_3.[81] The adduct formation properties of IF_5 are extremely important in the work to be described and will be discussed further later.

The chemistry of the fluorides of chlorine, bromine and iodine(VII) is dominated by their reactivity; fluorination, and fluoride ion acceptance and donation being the principal reaction types. Since they are less reactive, the other iodine fluorides especially IF_5 allow adduct formation. IF_5 unlike IF and IF_3 is thermally stable at room temperature and it is unique among the halogen fluorides in its range of reactions. IF_5 has been extensively studied in the past but many aspects of its chemistry have been neglected or totally ignored. Even where much work has been done, many questions remain unanswered. As the subject of much of the work to be described, IF_5 will now be discussed in more detail.

Some Aspects of Iodine Pentafluoride

Some of the physical and thermodynamic properties of iodine pentafluoride are listed in Table 4.

Table 4

Thermodynamic and Physical Properties of IF_5[22,82]

Property	Value
Melting point ($1{\cdot}013 \times 10^5$Pa)	282.571K
Triple point	282.553 ± 0.01K
Boiling point	373.65K
Boiling point (calculated)	377.63K
Density (solid, 273.15K)	3678 ± 43 $kg.m^{-3}$
Density (liquid, 283.40K)	3263 $kg.m^{-3}$
Density (liquid, 343.96K)	3031 $kg.m^{-3}$
Enthalpy of fusion	11.222 ± 0.011 $kJmol^{-1}$
Enthalpy of vapourisation	41.3 $kJmol^{-1}$
Entropy of vapourisation	95.23 $JK^{-1}mol^{-1}$
Standard enthalpy of formation(298.15K)	-881.9 ± 1.3 $kJmol^{-1}$
Standard entropy of formation (298.15K)	-340.0 ± 0.6 $JK^{-1}mol^{-1}$
Standard free energy of formation (298.15K)	-780.6 ± 1.3 $kJmol^{-1}$
Surface tension (liquid 298.35K)	2.97×10^{-2} Nm^{-1}
Viscosity (liquid 298.65K)	$2.191 \times 10^{-3}$$kg.m^{-1}sec.^{-1}$
Dielectric constant (liquid 298.15)	36.2
Dipole moment (gas)	7.272×10^{-30}Cm
Molar refraction (gas, 302K)	$1.917 \times 10^7 m^3 mol^{-1}$
Specific conductance (liquid 298.95K)	5.4×10^{-8} $ohm^{-1}m^{-1}$

The structure of the IF_5 molecule has been established by many techniques such as electron diffraction, infrared, Raman, Mössbauer, microwave, n.m.r. and n.q.r. spectroscopy,[29] and a solid-state X-ray crystal structure determination.[83] The crystal structure determination, carried out at 193K is extremely interesting (Figure 2). There are three crystallographically distinct types of IF_5 molecules per unit cell which appear however to be chemically equivalent. The "average" IF_5 molecule is illustrated in Figure 1.

Figure 1

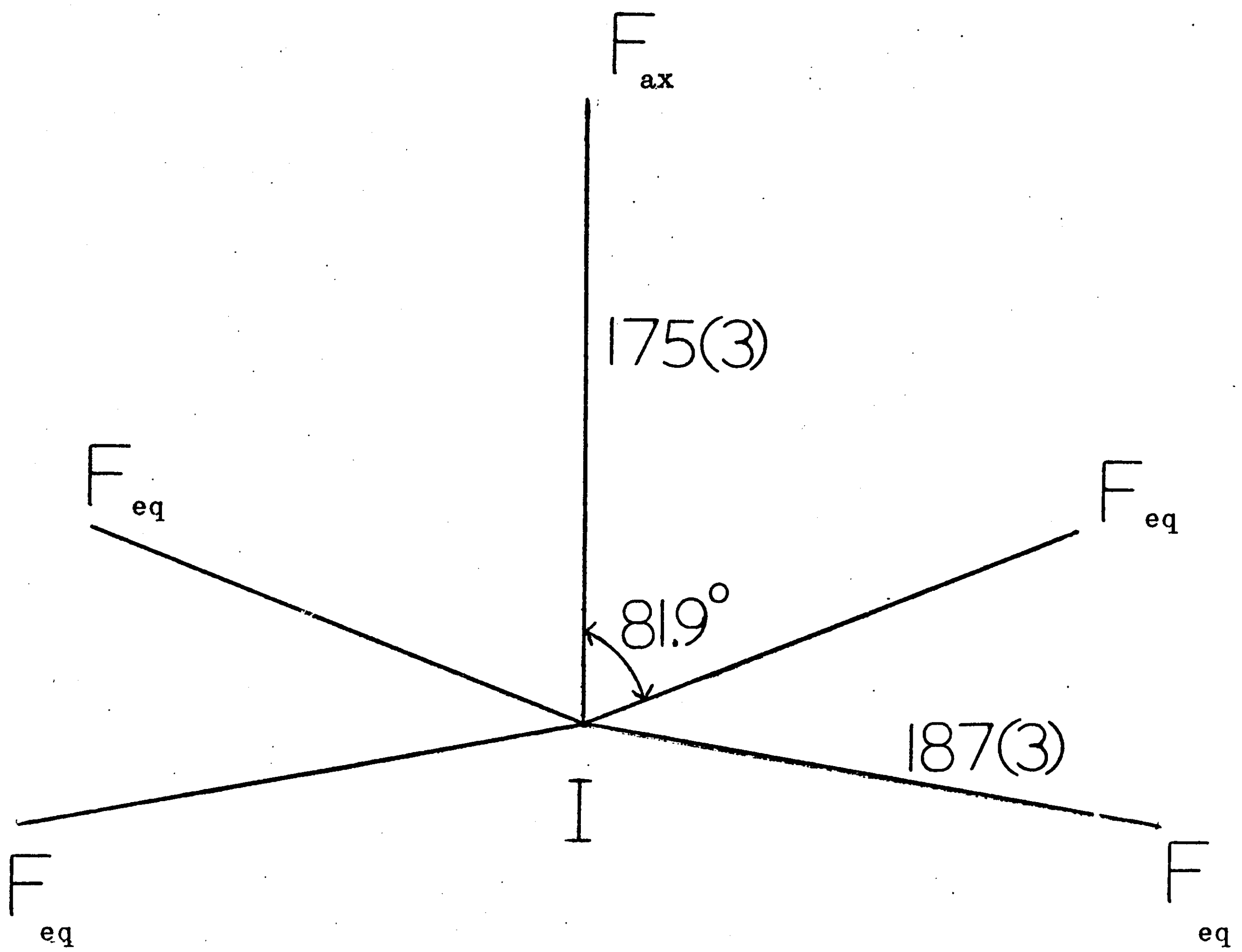
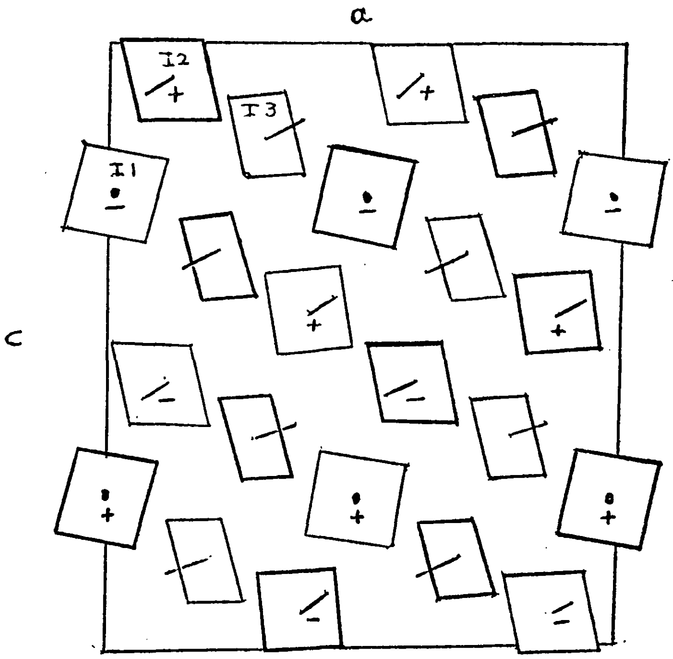


Figure 2

X-ray Crystal Structure of Solid IF$_5$ at 193K [83]



Contents of unit cell projected along b axis. Light and heavy lines designate molecules situated at heights of approximately $\frac{1}{4}$ and $\frac{3}{4}$ along the b axis respectively. Plus and minus signs indicate whether the apex of I1 and I2 pyramids projects up or down.

The most interesting feature of this structure is the existence of short polar contacts between the iodine atoms and the equatorial fluorines of neighbouring IF$_5$ molecules. The main I--F contacts have a weighted average distance of 301 ± 6 pm (sum of van der Waals radii = 350 pm) and make a weighted average angle of 36·4 ± 3·5° with the Fax-I-lone pair axis.

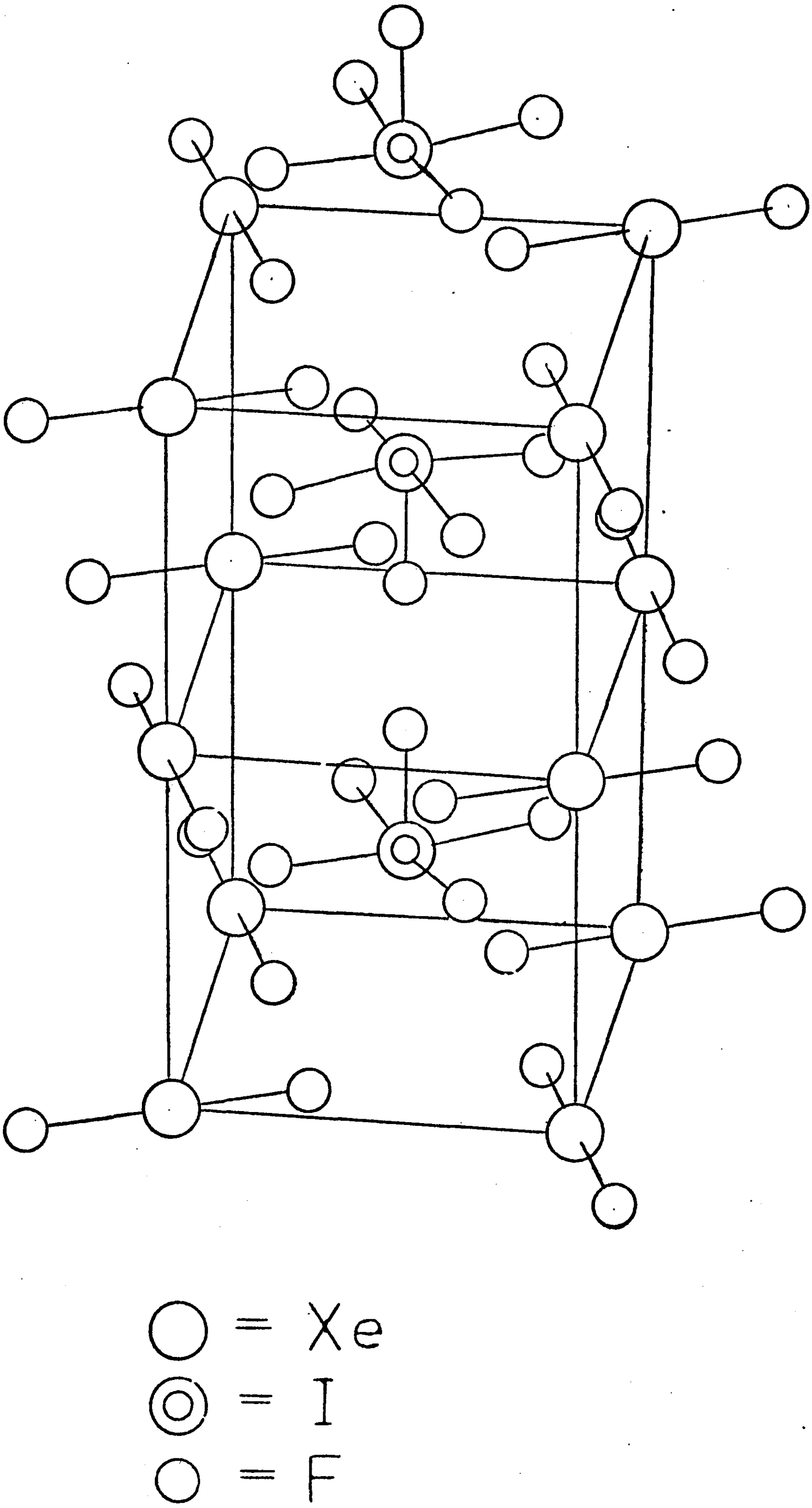
The reason that occurrence of these contacts is so interesting is as follows. Much effort has gone into attempting to add a sixth ligand to IF_5 so that the molecule would become pseudo seven-coordinate, that is, be surrounded by six ligands and a stereochemically active lone pair. The IF_6^- anion may be a good example of this but as already stated, its structure is not yet known.

The study of the stereochemistry of such a species would be very interesting, and this was one major aim of the present work. Although they are still formally pseudo six-coordinate, the IF_5 molecules in solid IF_5 are forming significantly strong contacts with each other to indicate how further bonds would occur. The I1 and I3 types of IF_5 each have four main contacts between the central iodine and neighbouring equatorial fluorine atoms, while the I2 has 2.

A somewhat similar situation exists in the case of the ideal molecular adduct $XeF_2.IF_5$ whose x-ray crystal structure is also known.[79] (Figure 3) In this case there are short contacts between the iodine atom of an IF_5 molecule and four fluorines from neighbouring XeF_2 molecules. The average length of these contacts is 314 pm and they make an angle of 41·8° with the Fax-I-lone pair axis.

Figure 3

X-ray Crystal Structure of $XeF_2.IF_5$



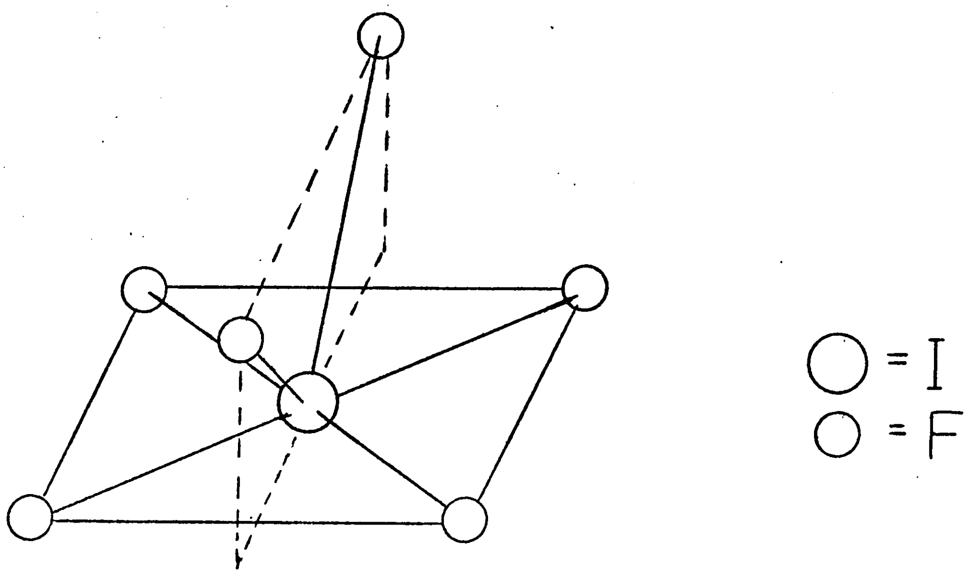
Similar contacts also occur in XeF_6 in the solid state. In the known crystalline phases of XeF_6, the molecules exist as XeF_5^+ and F^- ions.[84] The XeF_5^+ ions are both isoelectronic and isostructural with IF_5. In solid XeF_6, the XeF_5^+ ions are bridged by F^- ions to form tetrameric or hexameric rings where the bridging F^- ions make angles of about 35° with the Xe-lone pair axis. These contacts between fluorine atoms and a neighbouring iodine or xenon are believed to be purely electrostatic in nature. From E.S.C.A. studies[85] it was assumed that in XeF_5^+ ion each F ligand carries a charge of 0•3- and that the Xe atom carries a charge of 2•5+. It might therefore be expected that in IF_5, the charge distribution will be 0•3- on each F and 1•5+ on the I atom.

A knowledge of the geometry and understanding of the interactions in these structures is obviously of great help in investigating pseudo seven-coordinate derivatives of IF_5, such as the IF_6^- ion and IF_5 molecular complexes with organic bases.

The IF_6^- ion has been known since 1948 when Emeléus and Sharpe reported[86,87] the preparation of KIF_6. Subsequently, salts containing this ion have attracted considerable attention.[44,57,59-65,88,89] The vibrational spectra of alkali metal fluoride - IF_5 adducts were studied independently by four research groups.[62,63,88,89] All four groups reached the same conclusion that IF_6^- is not octahedral. However the vibrational spectra reported by the four groups differed significantly. Later it was shown[59] that IF_6^- salts were not the only product but that 1:3 adducts such as CsF.$3IF_5$ were also possible. The previous discrepancies arose from the fact that some groups had been working with 1:1 adducts, that is IF_6^- salts, whilst others were unwittingly investigating 1:3 adducts. The most systematic study of IF_6^- compounds is that published by Christe.[59] Comparison of vibrational spectra of 1:1 and 1:3 adducts shows that CsF.$3IF_5$, for example, cannot be formulated as $Cs^+IF_6^-.2IF_5$. Vibrational spectra indicated that IF_6^- is of low symmetry. In his preparations of alkali metal salts of IF_6^-, Christe combined the reactants directly whereas in their work, Meinert et al[60-64] made much use of solvents such as acetonitrile, and HF. Despite the different reaction conditions, there is fair agreement between their results and Christe's. Meinert carried out a study of the vibrational spectra of the IF_6^- ion in solution and claims on this basis that it has C_{2v} symmetry and is in a staggered conformation. (Figure 4)

<u>Figure 4</u>

<u>Structure of IF_6^- as suggested by Meinert et al</u>



The Raman spectra of IF_6^- obtained by Meinert and Christe are in good agreement, but the infrared spectra differ somewhat. Christe[59] states that IF_6^- is of low symmetry, not higher than C_{2v} but does not suggest a possible structure. One obvious way of investigating pseudo seven-coordinate species was therefore to prepare the IF_6^- ion and examine its solution spectra in more detail than had been done previously. The results of this work will be presented in Chapter 3. The problem of the structure of pseudo seven-coordinate compounds was approached from two sides. In addition to the IF_6^- ion, other obvious subjects for study were the molecular complexes of IF_5 with organic bases such as pyridine and 1,4-dioxane. A 1:1 complex between IF_5 and 1,4-dioxane was briefly reported by Scott and Bunnett[76] who found the product to be a crystalline solid which hydrolysed easily. A more extensive investigation was carried out by Rogers and Meyer[75] who reported the preparation of many interhalogen - organic base adducts. Phase diagrams of the IF_5-pyridine and IF_5-dioxane systems were shown and it was found that only 1:1 complexes were stable under conditions of reduced pressure. The ^{19}F n.m.r. spectra of IF_5 dissolved in dioxane, ethyl acetate, benzene and acetonitrile were unchanged from spectra of the neat liquid but the ^{19}F n.m.r. spectrum of IF_5-pyridine mixtures consisted of a single sharp resonance.[66] No vibrational data were available until recently, when vibrational data on IF_5.Pyridine were reported.[90] By then, the present work was nearing completion. No possible structures of IF_5.Py were suggested and the only possible structures which have been discussed are those proposed by Muetterties.[66] A large gap in the knowledge of IF_5.organic base adducts remained and it was hoped that by investigating these adducts, not only would the gap be reduced, but further information pertaining to the structures of pseudo seven-coordinate species would be obtained.

Perhaps the most wide-spread use of IF_5 is as a solvent. With a moderately long liquid range and a high dielectric constant (Table 4) it is an excellent ionising solvent and has been used in this role in reactions such as fluoride ion addition to transition metal hexafluorides.[91,92] It has also been employed as an oxidising solvent in the formation of tungsten hexafluoride according to the following reaction scheme[93]:

$$5W(CO)_6 + 6IF_5 \xrightarrow{IF_5} 5WF_6 + 3I_2 + 30CO$$

In these cases the interest of authors lay in the metal fluorides rather than in IF_5 and the reduction of the IF_5 was not investigated. The redox reactions of IF_5 have received little attention. The reactions of IF_5 and metals, metal oxides have been studied and products identified but there has been little or no attempt to follow the mechanism of the reduction of IF_5. The early reports of reactions of IF_5 have to be treated with some suspicion, for example, from Moissan's account[5] of reactions of various elements and compounds with IF_5, it is clear that in at least some of these instances he was actually using a mixture of IF_5 and residual elemental fluorine. Aynsley et al[81] reported the reaction of hot IF_5 with mercury and isolated a compound which analysed as $Hg(IF_5)_2$. The thermal and hydrolytic decompositions of this compound were studied but no investigations into its correct formulation or mechanism of formation were reported. The fact that little is known of the reduction mechanism of IF_5 is surprising for two main reasons. Firstly, its use as an oxidising solvent means workers have been studying reactions in a solvent whose own chemistry is not well understood, making unsuspected side reactions a distinct possibility. Secondly the reduction of IF_5 should be very interesting in its own right. The first step is probably a two electron reduction to I(III). I(III) compounds vary markedly in their thermal stability and ease of disproportionation to I(0) and I(V), making it difficult to predict in advance what products will be formed in the conditions used. For these reasons, it was decided that further work on IF_5 as an oxidising agent was highly desirable as well as studying pseudo seven-coordinate derivatives.

The penta- and hexa-fluorides of the Actinides

These compounds comprise the pentafluorides of protactinium, uranium and neptunium and the hexafluorides of uranium, neptunium and plutonium. PuF_5 may be known, but its isolation has not been reported in the open chemical literature.

Structures and Preparations of the pentafluorides

UF_5 is known to exist in two forms, α and β. The α form is the more stable above 423K while the β form is preferred at lower temperatures although the α form can be prepared at 298K.[94] PaF_5[95] and NpF_5[96] exist in only one form, isostructural with β-UF_5. α-UF_5 has a tetragonal cell with a = 651.2 pm and c = 446.3 pm., and has 2 molecules per unit cell. The β form has a tetragonal cell with a = 114.5 pm and c = 519.8 pm but has 8 molecules per unit cell.[97]

PaF_5 is prepared as a white crystalline solid by heating the tetrafluoride with fluorine at 973K. A colourless dihydrate can be formed by evaporating to dryness a solution of PaF_5 in concentrated aqueous HF. NpF_5 was first prepared[96] by reduction of NpF_6 by I_2 in IF_5. It is thermally stable at room temperature although slight further reduction to NpF_4 occurred. The first preparation of UF_5 was reported[98] by Ruff in 1911. Several methods for its preparation are now known; by fluorination of UF_4 by either fluorine at 423-523K[99] or gaseous UF_6, or by the reduction of UF_6 by H_2, SO_2, CO[100], $SOCl_2$[101], HBr[102] or Si/HF.[103] The reduction of UF_6 by $SOCl_2$ had previously been reported[104] to give UF_4 as the product, but this is now known to be incorrect.[101]

Properties and Reactions of the Pentafluorides

The vibrational spectra of α and β-UF_5 have been recorded and show significant differences,[106] but very few thermodynamic properties of UF_5 are known.[107] PaF_5, UF_5 and NpF_5 all react with sodium fluoride to give the isostructural Na_3MF_8 compounds.[105] The crystal structure of Na_3PaF_8 has been determined[105] and consists of a Pa atom surrounded by 8 fluorine atoms, one at each corner of a cuboid. Little is known of the chemistry of Pa and Np (V) and even the chemistry of U (V) is sparse. Selbin and Ortego have commented[108] "The chemistry of uranium is perhaps as well documented as that of any other metallic element. However the available literature on the chemistry of uranium(V)is meagre when compared to the voluminous data collected for the other oxidation states of uranium, namely the III, IV and VI oxidation states. This paucity of information is not surprising when one considers the strong tendency of U(V)to disproportionate to U (IV) and U (VI). The extreme sensitivity of U(V)compounds to atmospheric oxygen and even trace amounts of water vapour require very rigid experimental controls in their study." In the presence of water, UF_5 disproportionates and hydrolyses very readily, giving UF_4 and UO_2^{2+} compounds as products. UF_5 also disproportionates at elevated temperatures to give U_2F_9 and UF_6.[109]

UF_5 forms an interesting 1:1 adduct with XeF_6[110] which can be formed by two routes:

$$UF_5 + XeF_6 \xrightarrow{298K} UF_5.XeF_6$$

$$UF_4 + XeF_6\ (\text{excess}) \xrightarrow{298K} UF_5.1.75\ XeF_6 + UF_6 + XeF_4$$

Prolonged pumping on $UF_5 \cdot 1.75XeF_6$ yielded the 1:1 adduct. The exact formulation and structure are not yet known but an ionic formulation is thought possible.[111]

The most studied reaction of UF_5 is that of β-UF_5 with fluoride ion donors such as alkali metal fluorides. The product from such reactions is often the hexafluorouranate(V)anion, UF_6^-. Among the compounds prepared from UF_5 are:

$M^+UF_6^-$; M = NO[112], NH_4, Li, Na, K, Rb, Cs[113,114], Ag[115], $ClOF_2$[116], $(M^+)_2UF_7^{2-}$; M = NH_4, K, Rb, Cs[113]. $(M^+)_3UF_8^{3-}$; M = NH_4, Na[105], K, Rb, Cs[113], Ag[115].

These reactions involved heating the reactants directly or using anhydrous HF as solvent.

The salts $CsNpF_6$ and Rb_2NpF_7 have been prepared[117,118] by fluorination of an alkali metal fluoride - NpF_4 compound with elemental fluorine. These were the first complex fluorides of Np(V)not containing the NpO_2^+ ion. $CsNpF_6$ and $CsUF_6$ were also prepared[118] by treating a slurry of CsF and UF_4 or NpF_4 in anhydrous HF with elemental fluorine. Both $CsNpF_6$ and $CsUF_6$ could be isolated as solids, but whereas $CsUF_6$ redissolved in HF without reaction, $CsNpF_6$ immediately disproportionated to NpF_4 and NpF_6. This reflects the relative instability of Np(V)compared with U(V), and presumably Pu(V)would be even less stable towards disproportionation.

The Actinide Hexafluorides

Historical Aspects.

Uranium hexafluoride was first prepared by Ruff and Heinzelmann[119] by fluorinating uranium metal or uranium carbide with elemental fluorine. However, the compound received little attention until the second world war. UF_6 is the most volatile uranium compound[120] and is the most suitable as a feed material in gas-diffusion isotope separation plants. These are used in the isotope enrichment process which increases the relative abundance of ^{235}U from 0·7% in natural uranium to the much higher figures necessary for nuclear fission by thermal neutrons. The realisation of the potential importance of UF_6 in the early 1940's lead to the vast amount of work on the compound during the Manhattan Project. However, virtually the entire research effort of this wartime period was directed towards short-term strategic technological ends and this resulted in a very unbalanced development. A large number of the physical properties of UF_6 were determined to a high degree of accuracy but descriptive chemistry was largely ignored. This basic situation has not altered significantly since.[121] Most of the chemistry done during the Manhattan Project concerned the reduction of UF_6 to UF_4 and the adsorption of UF_6 on to alkali and alkaline earth metal fluorides. Many of the first type of reaction were done in a rather qualitative fashion[104], and have subsequently been shown to be either incorrect or at best, only partially correct.

The object of adsorbing UF_6 on metal fluorides was to see if this might be a feasible method of purifying UF_6. This goal has been achieved on a laboratory scale but the technique has not been applied industrially. The chemistry involved has been established only recently and will be discussed later. Neptunium hexafluoride was first prepared on a microgram scale and identified in 1946 by A.E. Florin.[122] The first report of its preparation and properties on a gram scale was that of Malm, Weinstock and Weaver in 1958.[123] Plutonium hexafluoride was first isolated in 1950 by fluorination of PuF_4 with F_2.[124]

Preparation and Properties of the Actinide Hexafluorides

All three hexafluorides can be formed by the action of fluorine on the tetrafluoride at high temperatures, but in the cases of NpF_6 and PuF_6, the product must be cooled rapidly in order to obtain a good yield. The temperature necessary for the fluorination of UF_4, NpF_4 and PuF_4 is 573, 773 and 973K respectively.[120] UF_6 is now prepared industrially by the following route. This is a three stage process, starting from the trioxide UO_3, which is prepared from crude U_3O_8.

1. Reduction of UO_3 to UO_2.
2. Fluorination of UO_2 by HF to give UF_4.
3. Fluorination of UF_4 by F_2 to give UF_6.

Step 3 can be carried out using the "Fluorox" process which avoids the need to handle elemental fluorine. In this process, UF_4 is oxidised by oxygen and the non-volatile by-product UO_2F_2 is recycled by reaction of HF to give UF_4.

$$UF_4 + O_2 \xrightarrow{1073K} UF_6(g) + UO_2F_2$$

The hexafluorides are all volatile solids at room temperature. Their thermal stability is in the order $UF_6 > NpF_6 > PuF_6$. $^{239}PuF_6$, suffers from radiation decomposition if stored in the solid state.

Reactions of the Hexafluorides

All three actinide hexafluorides are highly reactive and hydrolyse rapidly in moist air. The hydrolysis reaction of UF_6 has been extensively studied as it contrasts with those of the transition metal hexafluorides. The latter hydrolyse in a stepwise fashion - $MF_6 \rightarrow MOF_4 \rightarrow MO_2F_2 \rightarrow MO_3 \rightarrow MO_4^{2-}$. Ruff and Heinzelmann were the first workers to observe the reaction of UF_6 with H_2O,[125] and they reported that the reaction proceeded violently, producing UO_2F_2 and HF. There was little further study until 1967 when, in an attempt to prepare UOF_4, Otey and Le Doux[126] carried out a study involving the reaction of 100 g of water with 1000 kg of UF_6. When UF_6 and H_2O reacted in molar ratios of 1:1 and 5:1, only UO_2F_2 and HF were formed. However at a ratio of 50:1, an orange compound was formed. This analysed as $U_3O_5F_8$ and X-ray powder diffraction patterns indicated that it was a single compound. At about 681K it decomposed to UO_2F_2 and UF_6. As in the previous studies, there was no evidence for UOF_4. The first authentic sample of UOF_4 was prepared in 1972 by Wilson,[127] who reacted a slurry of UF_6 in HF with water in a controlled manner.

UOF_4, which is an orange solid, decomposes at 773K giving UO_2F_2 and UF_6. A new method has been described[129] which involves reacting UF_6 in anhydrous HF with quartz wool. The reaction between SiO_2 and HF produces H_2O which hydrolyses the UF_6.

Redox Reactions

UF_6 is a moderately strong oxidising and fluorinating agent but it is weaker than NpF_6 and much weaker than PuF_6. BrF_3 can be used as a fluorinating agent to prepare UF_6, but NpF_6 and PuF_6 both oxidise BrF_3 to BrF_5.

Salts containing the hexafluorouranate (V) ion, UF_6^- can be prepared by F^- addition to UF_5 as already described. They can also be prepared by reduction of UF_6. NO reacts with UF_6 in the gas phase producing solid $NO^+UF_6^-$.[112] Hydrazinium (+2) fluoride reacts with UF_6 in HF at 298K to give $N_2H_6(UF_6)_2$, if UF_6 is in excess, and $N_2H_6(UF_7)$ if $N_2H_6F_2$ is in excess.[130] In his review of UF_6,[121] Wilson compares the oxidising powers of UF_6 with other fluorides by examining products obtained by reaction with the same reducing agent, for example CS_2.

Table 5

The Reactions of CS_2 with some fluorinating agents.

Reactant	Products
UF_6	SF_4, $(CF_3)_2S_2$, $(CF_3)_2S_3$, SF_6, CF_4
IF_5	$(CF_3)_2S_2$, $(CF_3)_2S_3$, SF_4, CF_4
CoF_3	CF_3SF_5, SF_6, SF_4
HgF_2	$(CF_3)_2S_2$
MoF_6	$(CF_3)_2S_2$, S
$F_2(g)$	CF_4, SF_4, CSF_2, SF_6, CF_3SF_5, CF_3SF_3, S_2F_{10}, $SF_3CF_2SF_5$, $(SF_5)_2CF_2$

The conclusion drawn is that UF_6 is a mild oxidising agent, comparable to IF_5.

Fluoride ion addition reactions

Work started during the 1940's on the adsorption of UF_6 by metal fluorides. Most work was done using NaF, the first observation of adsorption of UF_6 by NaF being made in 1911.[125] The first attempt at identifying the product was made by Martin and Albers in 1946[131] who carried out the reaction of gaseous UF_6 with solid NaF and claimed Na_3UF_9 as a product. $3AgF.UF_6$, $3KF.UF_6$ and $2RbF.UF_6$ were also "discovered".[132] A typical report[133] described the condensation of UF_6 onto NaF, the mixture being left to stand at 373K for a few minutes. The excess UF_6 was then pumped off, the ratio of UF_6:NaF was determined at 1:3. It became the convention to call the complex $3NaF.UF_6$ or Na_3UF_9. Many physical and chemical properties of this "compound" were determined. It was noted that occasionally more UF_6 was absorbed than the stoichiometric amount but the implications of this observation were largely ignored. However in 1961 a most important paper appeared,[134] which reported the results of an ^{18}F exchange study of the NaF-UF_6 reaction. These results indicated strongly that the product was a 2:1 adduct, $2NaF.UF_6$, and not the 3:1 adduct as had been previously supposed. No ^{18}F exchange was observed between UF_6 and LiF, KF, CaF_2, ZrF_4 or AgF. The NaF-UF_6 system in particular was reinvestigated by Katz who showed[135] that $2NaF.UF_6$ could be prepared by adsorption of UF_6 or NaF, if the NaF had a sufficiently high surface area and had been preconditioned by adsorbing and desorbing HF a number of times. It was also found[136] that if the NaF formed by decomposition of $2NaF.UF_6$ is used, this NaF is sufficiently active for the compound $NaF.UF_6$ to be formed. The failure to observe exchange between UF_6 and other fluorides was explained by Malm et al[137], who found that KF reacted only if it were obtained from the decomposition of KHF_2, whereas the earlier work had been done using "reagent grade" fluorides. In other words, UF_6 only reacts with metal fluorides if the surface area is very high. This explains the earlier claims for $3NaF.UF_6$, since this obviously resulted from incomplete reaction. Malm et al overcame these problems by using perfluoroheptane as a dispersing agent, thus making the effective surface area of the NaF extremely high and preventing sintering. In C_7F_{16}, the NaF or KF were held as suspensions in the inert liquid and the reaction proceeded smoothly yielding $NaUF_7$. Upon heating this at 373K in vacuo, UF_6 was given off and Na_2UF_8 formed. Analogous potassium salts were prepared. $CsUF_7$ and NH_4UF_7 were prepared by reaction of the fluoride with UF_6 using ClF_3 as solvent.[138] The authors proposed a tentative scheme whereby ClF_3 acts as an ionising solvent in which intermediate species of the type $(ClF_2)_nUF_{6+n}$ are formed and these combine with the simple fluorides. NH_4UF_7 has also been prepared[139] by reacting UF_6 with a suspension of NH_4F

in tetrachloroethane. Other complexes of UF_6 now known include $N_2H_5UF_7$[140], $NOUF_7$ and NO_2UF_7.[141] Despite the progress in understanding these reactions, there is still some confusion. Malm et al reported[137] that $NaUF_7$ on heating to 373K in vacuo, produced Na_2UF_8 and UF_6 gas, and that on further heating to 573K, the Na_2UF_8 decomposed to NaF and UF_6. However, a claim to have prepared Na_3UF_9 by heating Na_2UF_8 had previously been made.[142] The decomposition of Na_2UF_8 to NaF and UF_6 at elevated temperature is, perhaps, the more feasible and the composition Na_3UF_9 could be explained by partial decomposition, i.e. $Na_3UF_9 \rightarrow Na_2UF_8 + NaF$. Some confusion also surrounds the BaF_2-UF_6 system. Most workers failed to observe any reaction between BaF_2 and UF_6 but Korinek and Peka[143] claimed that UF_6 is absorbed by BaF_2 and that the following reactions occur:

$$2UF_6.xBaF_2 \longrightarrow (UF_5)_2BaF_2 + BaF_2 + F_2$$
$$(UF_5)_2.BaF_2 \longrightarrow (UF_4)_2BaF_2 + F_2$$
$$(UF_4)_2.BaF_2 \longrightarrow 2UF_4 + BaF_2$$

The occurrence or absence of reaction between BaF_2 and UF_6 might be explained in terms of the state of the BaF_2. If it were extremely finely divided, then reaction might occur. The presence of elemental fluorine among the decomposition products is very surprising. If this proves to be correct then there is an extremely interesting consequence, namely the chemical generation of fluorine.

Since UF_6 can be prepared using HF and O_2 as the fluorinating and oxidising agents, neither requiring F_2 in its preparation, the adduct $2UF_6.XBaF_2$ can be prepared without recourse to F_2. Fluorine could therefore be generated chemically. However it is possible that in the above reactions involving the decomposition of the adducts, the uranium is reduced not through release of fluorine but by some side-reaction such as reaction with the container vessel. Similarly UF_6 has been reported to be reduced to lower oxidation state fluorides through reaction with BiF_3, FeF_3, AlF_3, SnF_4, PbF_4, ThF_4 or TiF_4. None of these fluorides could be oxidised, with the possible exception of BiF_3. However, although UF_6 reacts purely as a F^- ion acceptor towards NaF, NpF_6 and PuF_6 are both reduced in contact with the alkali metal fluoride, releasing F_2. NpF_6 reacts according to:[144]

$$3NaF(s) + NpF_6(g) \rightleftharpoons 3NaF.NpF_5(s) + \tfrac{1}{2}F_2(g)$$

PuF_6, in contact with NaF, is reduced to the +4 oxidation state. These results indicate that loss of fluorine from uranium(VI) complexes cannot be completely ruled out. This area of uranium chemistry obviously requires much further investigation.

Although the ions UF_8^{2-}, UF_7^- and UF_6^- have all been known for some time, their preparative routes are not particularly convenient. Salts of UF_8^{2-} or UF_7^- usually require high temperature gas-solid reactions using a high surface area metal fluoride, a solvent such as anhydrous HF or ClF_3 or at best an inert dispersing agent. UF_6^- salts are normally prepared by heating a metal fluoride with UF_5 or reducing UF_6 in anhydrous HF. Obviously, a simple solvent system for UF_6 enabling both fluoride ion addition and redox reactions to be carried out would be a great advantage. Acetonitrile has been shown to be an excellent solvent for tungsten and molybdenum hexafluorides[145,146] and it was considered well worthwhile attempting to extend this extremely convenient solvent to the study of UF_6. To obtain acetonitrile solutions of these ions, would aid their spectroscopic study greatly. Very little vibrational spectroscopic data were available before this study commenced although a thorough investigation of the UF_7^- and UF_8^{2-} ions appeared[147] after our study was completed. Thus the structures of these ions were completely unknown. Similarly, in the salts of UF_6^-, little vibrational data were available although their electronic spectra were known. However these were usually obtained using nujol mull samples and the extinction coefficients could not be obtained. The overall aim of this section of the work to be described was to demonstrate that acetonitrile could be used as a solvent for reactions involving UF_6 and that solution spectra could be obtained, thus giving further information on the structure of the ions.

The Transition Metal Hexafluorides

This group comprises the hexafluorides of chromium, molybdenum, technetium, ruthenium, rhodium, tungsten, rhenium, osmium, iridium and platinum. CrF_6, RuF_6, RhF_6 and PtF_6 are all thermally unstable at or above 298K. The hexafluorides are all volatile, the boiling points lying between 290•2K for WF_6 and 342•2K for PtF_6, and are all rapidly hydrolysed by traces of water.

Reactivites of the Hexafluorides

O'Donnell has investigated[148] the comparative reactivities of some hexafluorides by examining their reactions under similar conditions. It was thought for example that WF_6 and MoF_6 were both very strong oxidants and almost identical in their chemistries.[149] This belief was most probably based on the violent hydrolysis reactions of both compounds. More recently, however, it has been shown that WF_6 and MoF_6 differ considerably. O'Donnell comments that WF_6 could be classed as rather inert in reactions except hydrolysis. WF_6 does not react with carbon disulphide but MoF_6 and ReF_6 react to form $(CF_3)_2S_2$ and are reduced to the metal pentafluoride. On the basis of the reaction between CS_2 and CrF_5, CrF_6 would almost certainly oxidise CS_2 to CF_4 and SF_6. ReF_6 is readily reduced by PF_3 but WF_6 is not. By use of such comparisons, obvious trends can be observed:

1) Reactivities increase across a row, i.e.

$WF_6 < ReF_6 < OsF_6 < IrF_6 < PtF_6$

2) Reactivities decrease down a group, i.e.

$CrF_6 > MoF_6 > WF_6$

The hexafluorides cover a large range of oxidising abilities, from WF_6 which is weak, to PtF_6 which is capable of oxidising elements to their highest oxidation states such as Cl(VII) and Xe(VI). The fluorides themselves are usually reduced to the +5 state, for example MF_6^-. The very reactive hexafluorides such as IrF_6 and PtF_6 are very useful for reactions requiring extreme oxidising conditions but their great reactivity limits other studies. However, WF_6, MoF_6 and ReF_6 can undergo fluoride ion addition reactions and substitution reaction have been carried out with WF_6. Thus in a similar situation to IF_5 in the halogen fluorides, the less reactive compounds are frequently the most versatile. WF_6 has probably received most attention, followed by MoF_6 and ReF_6 and these three compounds will be discussed in a little more detail.

The hexafluorides of Tungsten, Molybdenum and Rhenium

All three compounds can be prepared by direct action of F_2 on the metal at elevated temperatures. In the case of rhenium, the product has to be heated with Re-metal at 673K to remove any ReF_7 which is also formed.[150] ReF_6 and ReF_7 are both physically and chemically similar, and it is almost certain that early work on ReF_6 was done on an ReF_6/ReF_7 mixture. WF_6 can also be prepared by halogen exchange reactions such as[151]:

$WCl_6 + 6HF \longrightarrow WF_6 + 6HCl$

$WCl_6 + 2AsF_3 \longrightarrow WF_6 + 2AsCl_3$

$WCl_6 + 3SbF_5 \longrightarrow WF_6 + 3SbF_3Cl_2$

Hexafluorometallate(V) salts are well known for all three metals. MoF_6 and ReF_6 react with NO to form $NO^+MF_6^-$ although WF_6 does not. Hexafluoromolybdate, rhenate and tungstate(V)salts are generally prepared by the reaction of an alkali metal iodide (not LiI) with the hexafluoride in liquid SO_2[150,156,157]. IF_5 can also be used as the solvent for the MoF_6 reactions. $Mo(CO)_6$, SF_4 and an alkali metal iodide heated in a bomb, also form MoF_6^- salts.[158] However it has recently been shown that acetonitrile is an excellent solvent for WF_6 and MoF_6 and that in this solvent, many metals are oxidised by the two hexafluorides which in turn are reduced to hexafluorometallate(V)species.[146] The difference in oxidising power between WF_6 and MoF_6 was reflected in the final oxidation states of the metal cations formed. The role of the CH_3CN was to solvate the metal cations. It was further shown[145] that in CH_3CN, WF_6 acts as a fluoride ion acceptor towards metal fluorides, solvated metal heptafluorotungstates(VI) being formed. Heptafluorometallate(VI) and octafluorometallate(VI) salts derived from WF_6, MoF_6 or ReF_6 are well known and preparations included:

$MF_6 + NOF \longrightarrow NOMF_7$ M = Mo[141]

$MF_6 + NOF \longrightarrow (NO)_2MF_8$ M = Re, W.[141,152]

$2KF + MF_6 \xrightarrow{IF_5} K_2MF_8$, M = W, Mo, Re[91-93,150]

$10KI + 5WF_6 + 2IF_5 \xrightarrow{IF_5} 5K_2WF_8 + 6I_2$ [93]

$10KI + 5W(CO)_6 + 8IF_5 \xrightarrow{IF_5} 5K_2WF_8 + 9I_2 + 30CO$ [93]

$M + M'F \xrightarrow{BrF_3} M'_2MF_8$, M = W, Mo; M' = K, Rb, Cs [153]

$2M'I + 2WF_6 + IFr \xrightarrow{IF_5} 2M'WF_7 + IF_3 + I_2$, M' = K,Rb,Cs [92]

$2NaF + MF_6 \xrightarrow{433-627K} Na_2MF_8$ or M = W or Mo

$NaF + MF_6 \xrightarrow{433-627K} NaMF_7$ Reaction depends on type of NaF. [135]

$M'F + MF_6 \xrightarrow{IF_5} M'MF_7$ M = W, Mo, Re; M' = Rb, Cs [91-93]

$2MF + ReF_6 \longrightarrow M_2ReF_8$ M = K, Rb, Cs. [154,155]

In the preparation of salts containing the ions WF_6^-, MoF_6^- and WF_7^-, there is a strong contrast between the preparations using IF_5 or liquid SO_2 as solvents or a high temperature gas-solid reaction, and the new preparations using CH_3CN as solvent. In the latter case, reaction conditions are very mild, the solvent is extremely easy to handle and it promotes reactions which most probably would not occur in a less powerful coordinating solvent such as IF_5. Another great advantage is that the products are soluble, thus allowing solution spectra to be recorded. This is very useful in structure elucidation. With the advantages of this solvent, it was hoped that the chemistry of ReF_6 could be investigated in CH_3CN.

The extension of the use of CH_3CN to study the behaviour of ReF_6 and UF_6 in that solvent was, in part, aimed at obtaining a valid comparison between the chemistry of the hexafluorides of:

1) Tungsten
2) Molybdenum, the element above tungsten in the periodic table.
3) Rhenium, the next element to tungsten in the 5d transition series.
4) Uranium, the actinide element most closely resembling tungsten.

This would therefore give a good indication of change in going up a group, along a row, and going from a d-block metal to an f-block metal.

Overall, therefore, this work concerns the study of a high oxidation state fluoride of:

1) A p-block element; iodine
2) A d-block element; rhenium
3) An f-block element; uranium

CHAPTER ONE

EXPERIMENTAL TECHNIQUES

Experimental Techniques

During the course of this work, considerable use was made of physical techniques, particularly spectroscopy. While it is unnecessary to discuss at length routine procedures such as infrared spectroscopy, some general remarks on the techniques and their experimental aspects may be useful.

Infrared Spectroscopy

A molecular vibration is infrared active if there is a change in dipole during the vibration. Modes of vibration which are i.r. inactive are often Raman active, thus i.r. and Raman spectra complement each other.

The number, position and intensity of i.r. bands, together with similar data from Raman spectra are extremely useful in structure determination.

Samples for i.r. spectra were prepared as thin films, if the substances were liquid, or as nujol mulls, if the materials were solid. These were run between AgCl plates in the region 4000-350cm^{-1} or between Si plates in the region 350-200cm^{-1}. Samples were prepared in an inert atmosphere box where the water content was <10 p.p.m. The spectra were recorded on a Perkin-Elmer PE577 spectrophotometer, and were calibrated using a polystyrene film. Frequencies quoted are to ± 5cm^{-1}.

Raman and Resonance Raman Spectroscopy

A normal Raman spectrum is obtained by using an exciting line whose frequency is such that it is not absorbed strongly by the sample. If the sample is coloured, then the colour of the light beam is chosen to be as close as possible to that of the sample. In resonance Raman, however, the opposite is the case and this can lead to greatly enhanced band intensities. In Raman spectroscopy, the frequency of the scattered light is analysed. Occasionally, a photon is scattered inelastically by a molecule and a frequency change is observed corresponding to a molecular transition. This transition may be rotational, vibrational, translational or electronic but vibrational transitions are usually the ones of most interest. Resonance enhancement of Raman bands occurs when the energy of the incident light approaches that of an electronic transition. If the photon is actually absorbed and re-emitted, the process is fluorescence. In liquids, this process almost always occurs in a broad spectral band, whereas Raman bands are sharp. For this reason, fluorescence can often obscure Raman spectra. The total intensity of a Raman band for randomly orientated molecules is given by[159]

$$I = \frac{2^7\pi^5}{3^2c^4} \quad I_o\nu_s^{\,4} \sum_{i,j} |\alpha_{ij}|^2 \qquad (1)$$

where I_o = intensity of incident light

ν_s = frequency of scattered light

α_{ij} = element of the scattering tensor.

From perturbation theory;

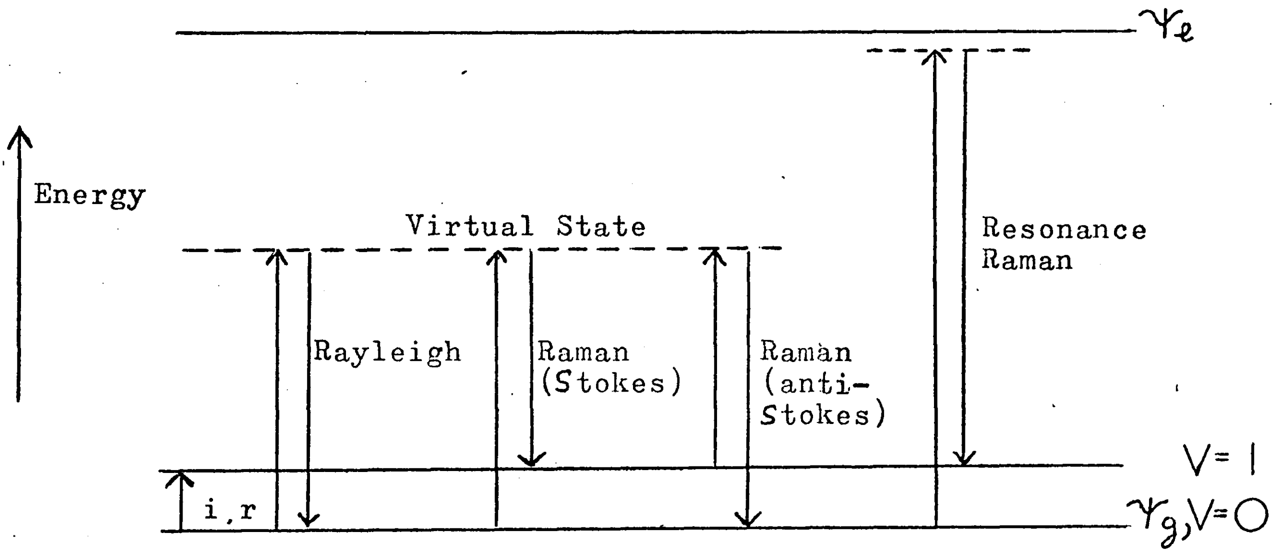
$$(\alpha_{ij})_{mn} = \frac{1}{h} \sum_{e} \left[\frac{(M_j)_{me}\ (M_i)_{en}}{\nu_e - \nu_0} + \frac{(M_i)_{me}\ (M_j)_{en}}{\nu_e + \nu_s} \right] \qquad (2)$$

where: m and n are initial and final states of the molecule, e is an excited state, the summation being over all excited states, $(M_j)_{me}$ and $(M_i)_{en}$ are electric dipole transition moments along the directions j and i from m to e and from e to n, ν_e is the frequency of the transition from m to e, ν_0 and ν_s are the frequencies of the incident and scattered photons respectively.

In the non-resonance region, i.e. in the normal Raman effect, $\nu_0 \ll \nu_e$ and α_{ij} is independent of the exciting frequency. As ν_0 approaches ν_e, $\nu_e - \nu_0$ becomes small, hence the first term on the right hand side of equation (2) becomes very large, subjecting α_{ij} to preresonance enhancement. When $\nu_e - \nu_0$ becomes very small, (it is prevented from becoming zero by the inclusion of a damping constant to allow for a finite electronic line width) then one element in the summation, corresponding to the resonant electronic transition, assuming that the transition moments are sizeable, dominates all others. When $\nu_0 \gg \nu_e$, the resonance enhancement again diminishes. The situation can be represented diagramatically. (Figure 5)

Figure 5

Light Scattering Processes



Samples, both solid and liquid, were prepared in dried pyrex capillaries either in an inert atmosphere box or in vacuo. These tubes were then sealed off in vacuo. The spectra were recorded on a Spex Ramalog instrument employing either a Kr^+ or Ar^+ ion laser source. Spectra were calibrated using the ν_1 band of pure CCl_4 at 459cm^{-1}, and are accurate to ± 2cm^{-1}.

Nuclear Magnetic Resonance Spectroscopy

Proton n.m.r. spectroscopy has been a familiar technique for many years, especially in organic chemistry. However, interest in the study of n.m.r. using other nuclei has been increasing markedly, especially since the advent of Fourier-transform spectrometers. The nucleus examined most frequently in this work was ^{19}F and this will be briefly discussed, in comparison with ^{1}H. ^{19}F is 100% abundant and like ^{1}H, has a spin quantum number of ½. ^{19}F also has a similar gyromagnetic ratio and its sensitivity is 0·83 times that of ^{1}H. In addition, the resonant frequencies of the two nuclei are similar. If the ^{1}H frequency is 60MHz, then the equivalent ^{19}F frequency is 56·4MHz. ^{19}F n.m.r. spectroscopy therefore shares many of the advantages of ^{1}H n.m.r. spectroscopy. It also has one additional advantage. Like most magnetic nuclei other than ^{1}H, the range of chemical shifts is very large, about 1000 ppm , compared with 15 for protons. This is advantageous since, normally, the chemical shift is very much larger than any coupling constant and so a first-order spectrum is obtained A disadvantage however is the instrumentation involved to cover the extra frequency ranges. ^{19}F coupling constants are also larger than equivalent ^{1}H ones but are still small compared to the chemical shifts. The compound most studied by n.m.r. in this work was IF_5. Although ^{19}F, having a spin quantum number of ½ does not have a quadrupole moment, ^{127}I has a spin of $\frac{5}{2}$ and does possess a quadrupole moment. However, the rate of quadrupolar relaxation of iodine in IF_5 is large compared with coupling between iodine and fluorine, and so the spectrum shows no evidence of ^{19}F-^{127}I coupling.

Samples were prepared in 5mm precision n.m.r. tubes which were sealed off in vacuo before running. For ^{19}F samples, CCl_3F was used as the reference, internally whenever possible. External $(CH_3)_4Si$, (T.M.S.) was used as a ^{1}H

reference. Chemicals shifts are reported as positive to low field. The spectra were recorded on a JEOL C-60HL spectrometer operating at a frequency of 60MHz for ^1H and 56•4MHz for ^{19}F. For greatest accuracy, chemical shifts were measured from the smallest possible scan width which used the external lock facility.

Typical errors are:

270 ppm scan ± 10 ppm (no lock facility)

90 ppm scan ± 1 ppm

18 ppm scan ± 0•2ppm

9 ppm scan ± 0•1ppm

Electron Paramagnetic Resonance Spectroscopy

The basic principles behind e.p.r. spectroscopy are very similar to those of n.m.r. The spin quantum number of an unpaired electron, m_s, has a value of $\pm \frac{1}{2}$. These states are normally degenerate but in the presence of a magnetic field, the degeneracy is lifted and transitions can occur between the two states. The energy, E, of the transition is given by $E = h\nu = g\beta H_o$ where

h = Planck's constant

ν = frequency of radiation

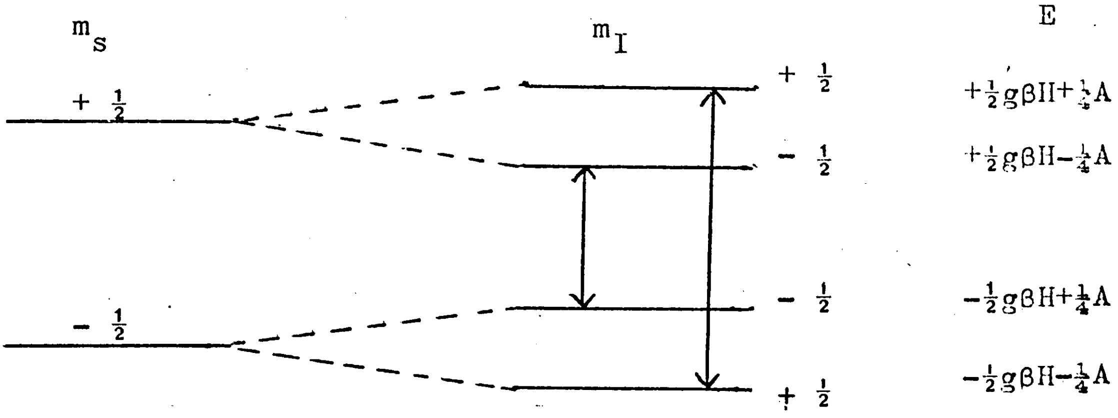
β = Bohr magneton

H_o = field strength

g = Landé g-factor

"g" is a tensor quantity and has a value of 2•0023 for a free electron. In general, the magnitude of g depends on the orientation of the molecule containing the unpaired electron, with respect to the magnetic field. If the paramagnetic radical or ion is situated in a perfectly cubic site, e. g. at the centre of a regular octahedron or tetrahedron, g is independent of orientation and is said to be isotropic. If the symmetry is lowered, g becomes anisotropic. The z-axis direction is defined to be coincident with the highest-fold rotation axis. The g_z value is equivalent to $g^{\parallel}$, that is the g value obtained with the z-axis parallel to the external magnetic field. In a tetragonal site, $g_x = g_y = g^{\perp}$. If a system has axial symmetry, and θ = angle between z-axis and the magnetic field, then $g^2 = g^{\parallel 2} \cos^2 \theta + g^{\perp 2} \sin^2 \theta$. E.p.r. spectra are normally presented by the first derivative of the absorption. When an unpaired electron is close to a nucleus with spin I, an interaction takes place which causes the absorption signal to be split into $2nI + 1$ components, analogous to the n.m.r. case. An unpaired electron whose m_s value is $+\frac{1}{2}$ coupling with a nucleus ($I = \frac{1}{2}$) whose m_I value is $-\frac{1}{2}$ will be a lower energy interaction than that between an electron and nucleus with $m_s = +\frac{1}{2}$ and $m_I = +\frac{1}{2}$ or $m_s = -\frac{1}{2}$ and $m_I = -\frac{1}{2}$ respectively. The following diagram (Figure 6) shows the splitting of the e.p.r. signal into two through interactions with a nucleus, $I = \frac{1}{2}$.

Figure 6



The energy of each level is given by $E = g\beta m_s H + Am_s m_I$ where A = hyperfine coupling constant. The selection rules are $\Delta m_s = \pm 1$, $\Delta m_I = 0$. In the spectrum, the energies for each transition are $g\beta H \pm \frac{1}{2}A$, therefore the separation of the peaks is A. A can be measured from the splitting, and g can be found from the mid-point of the signal, from the formula $h\nu = g\beta H$. h, ν and β are constants, and H is shown on the spectrum. E.p.r. spectroscopy is a very sensitive technique, giving information about the environment of an atom with an unpaired electron, such as in an organic radical or a transition metal ion. E.p.r. spectra of systems with more than one unpaired electron present can be recorded, but their interpretation is extremely difficult because of their complexity.

Samples were prepared in "spectrosil" quartz sample tubes, which were then sealed off in vacuo. Spectra of solids and solutions frozen as glasses, were recorded at 77K, on a Decca X3 spectrometer fitted with a Newport 11 inch magnet.

Electronic Absorption Spectroscopy

This form of spectroscopy involves the study of the transitions of an electron in a molecule, or in a transition metal ion. The frequency of radiation necessary to effect such transitions is such that transition metal ions can absorb in the u.v., visible or near-i.r. parts of the spectrum. The following selection rules are relevant :

1) Transitions in which the number of unpaired electrons changes in going from the ground to excited state are referred to as "spin" or "multiplicity" forbidden.

2) Transitions within a given set of p, d or f orbitals i.e. those which only involve a redistribution of electrons in the given sub-shell, are "Laporte" forbidden.

As a result of the Laporte rule, pure d-d transitions are forbidden and so many complexes would be colourless except for the following:

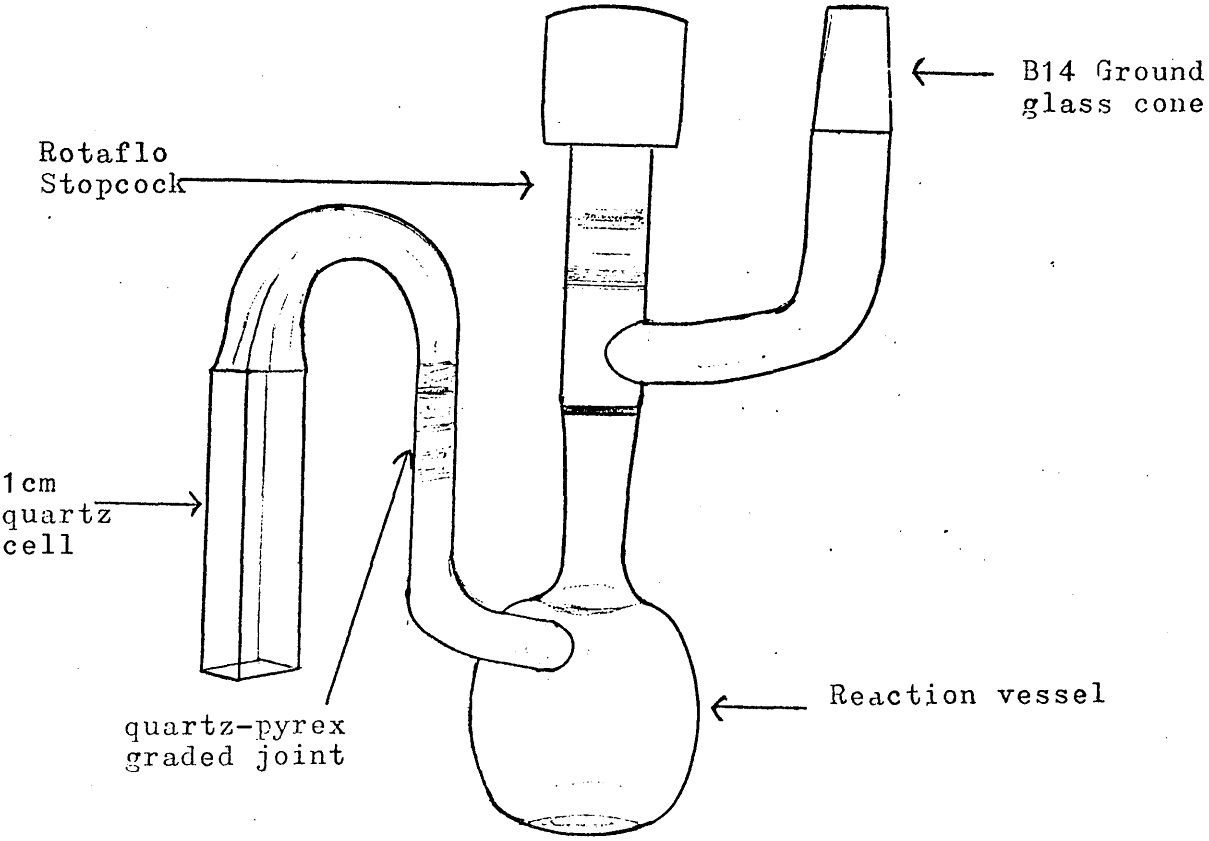
a) If the ion does not have perfect O_h symmetry but is distorted so that the centre of symmetry is destroyed, hybridisation of orbitals e.g. p and d can occur and the transition occurs between d levels with different amounts of p character. The intensity is roughly proportional to the extent of mixing and $\mathcal{E}$, the extinction coefficient is often in the range 20 to 50.

b) A complex with O_h symmetry can absorb light by the following mechanism. In the course of the normal vibrations of an octahedral complex, some of the molecules are slightly distorted from O_h symmetry at any given time.

The d and p orbitals mix in the unsymmetrical configuration and a very low intensity transition is observed ($\varepsilon = 5$ to 25). These transitions are said to be vibronically allowed and the effect is described as vibronic coupling. This is important in metal ions with an unfilled d or f shell, such as UF_6^- ($5f^1$) and this will be discussed later. Electronic absorption spectroscopy is a very powerful tool and can give much information about structure and ligand field parameters.

Samples were usually prepared in a 1cm quartz cell specially designed for air sensitive samples (Figure 7). Reactions could be carried out as usual in the reaction vessel, the solution decanted into the cell and the spectrum run, all in the complete absence of air or moisture. Some spectra of a neat oil were recorded between quartz plates.

Figure 7

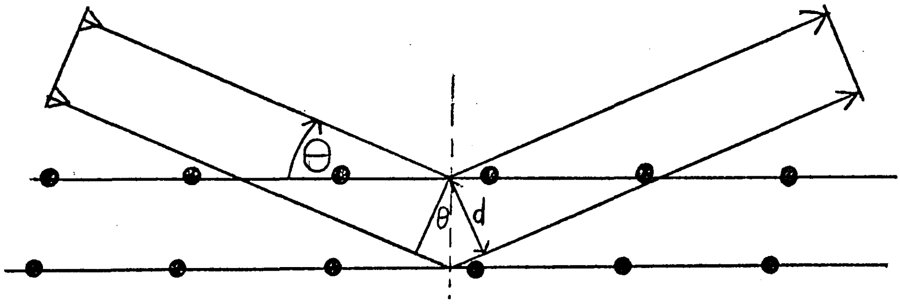


Spectra were recorded on either a Pye-Unicam SP800 or SP700C spectrophotometer, covering the ranges 850-210nm and 54,000-4,200cm^{-1} respectively. Frequencies are quoted to ± 100cm^{-1}.

X-ray Powder Diffraction

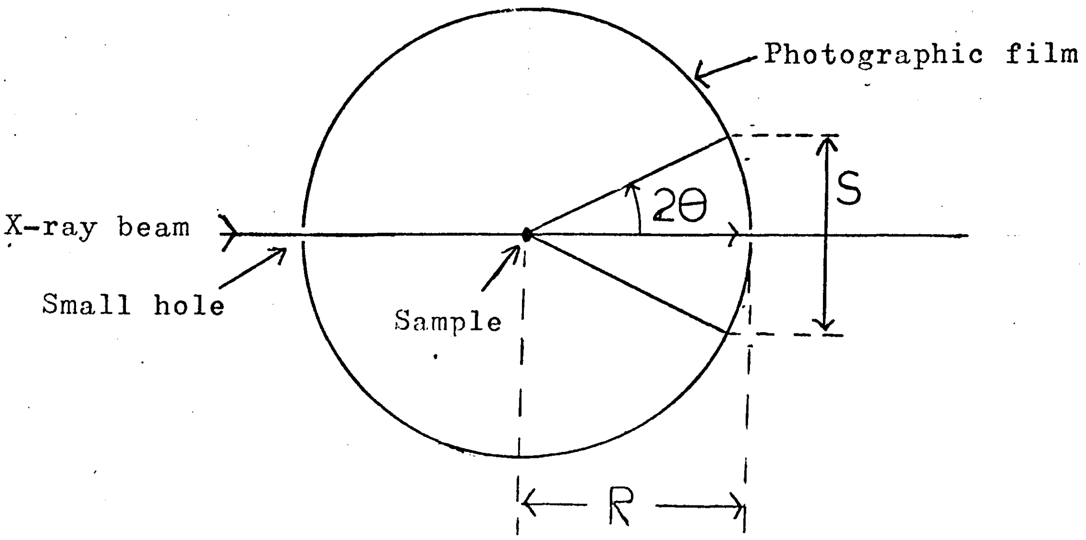
A paraxial beam of monochromatic x-rays striking a crystal lattice will be scattered. The Bragg equation, $n\lambda = 2d \sin \theta$, (where n is an integer, λ is the wavelength of the radiation and θ and d are as shown in Figure 8), gives the condition for scattering in phase.

Figure 8



In an x-ray powder photograph experiment, the arrangement is normally as shown in Figure 9.

Figure 9



In a polycrystalline powder, each tiny crystal is in a different orientation. Among these grains, many are so orientated that a particular set of planes (h, k, l) makes the appropriate glancing angle θ for that plane, with the x-ray beam. Such grains reflect x-rays, making an angle 2 θ with the x-ray beam. The locus of directions making an angle 2 θ with a given direction is a cone of opening angle 4 θ. The scattered radiation then makes a series of concentric arcs on the film, each arc corresponding to a different plane. The diameter of these arcs, S, is then measured, and θ can be found from $S = R.4\theta$, where R is the radius of the film, i.e. sample to film distance, and θ is expressed in radians. From each value of θ, each value of d can be determined. If the crystal is of high symmetry, then it is a routine procedure to determine the h, k, l values corresponding to each d and so the unit cell dimensions can be obtained. Even if this indexing is not possible, the values of d are unique to that one compound and this feature makes x-ray powder photography an excellent "finger-printing" technique.

The samples were prepared in 0•5 mm o.d. "Lindemann" glass capillaries which had been pre-dried by sustained pumping. The capillaries were loaded in an inert atmosphere box, and the end sealed with plasticine. Co Kα radiation (wavelength = 179•02 pm) and Fe filter were used.

^{18}F Exchange

Apart from the 100% naturally occurring isotope ^{19}F, ^{18}F is the only isotope of fluorine with a sufficiently long half-life, ca. 6,600 seconds, for use as a tracer. ^{18}F which is a $2{\cdot}643 \times 10^{-19}$ J, β^+ emitter is normally prepared by the neutron irradiation of Li_2CO_3 according to:

$^6Li(n,\alpha)t$; $^{16}O(t,n)^{18}F$.[160] Labelled CsF is prepared as follows:

$$Li_2CO_3 \xrightarrow[\text{irradiation}]{\text{neutron}} Li\,^{18}F \xrightarrow[\text{distil}]{50\%\ H_2SO_4} H^{18}F$$

$$H^{18}F \xrightarrow[273K]{CsOH(aq)} Cs\,^{18}F_{(aq)} \xrightarrow[\text{neutralise, dry}]{\text{dil. HF}} Cs^{18}F$$

When this CsF is used to label a highly reactive fluoride such as UF_6 directly, some hydrolysis usually occurs. If there is a sufficient difference in volatility between the fluoride to be labelled and BF_3, the latter is used as an intermediate. BF_3 is, by comparison to UF_6, reasonably stable to hydrolysis and can be labelled by $Cs^{18}F$ and then used to label the reactive fluoride without causing hydrolysis.

The results of exchange reactions are normally expressed in terms of "f", the fraction exchanged. f is defined by:

$$f = \frac{A_1}{A_1+A_2} \Big/ \frac{n_1m_1}{n_1m_1+n_2m_2}$$

where

A(disintegrations sec^{-1}) = activity after exchange.

m(mmol) = amount of species with n exchangeable fluorines.

1,2 = initially inactive and active species respectively.

The neutron irradiation was carried out at the Scottish Universities Research Reactor, East Kilbride. Samples for counting were prepared in pyrex ampoules, and activities were determined using a NaI well scintillation counter. (Ekco Instruments).

Analysis

Samples for elemental analysis were sealed in pyrex tubes in vacuo. Analyses were carried out by A.Bernhardt, Elbach, West Germany.

Conventional high vacuum techniques, using a Pyrex glass vacuum line were used throughout this work. An "Edwards High Vacuum" two-stage rotary oil pump and "Jencons" mercury diffusion pump arranged in series provided a vacuum of better than 10^{-2} Pa. Standard glass joints were greased with Edwards High Vacuum Silicone or Voltalef Kel-F grease, or waxed with 3M Kel-F wax. P.T.F.E./glass stopcocks (Quickfit Rotaflo or West Glass Corporation) were used when required. All glassware was "flamed-out" before use. Reactions were carried out in pyrex vessels fitted with Rotaflo stopcocks. Sidearms carrying Raman, n.m.r., e.p.r. or analysis tubes were fitted when required. Manipulations involving involatile compounds were carried out in the nitrogen atmosphere of a Lintott inert atmosphere box in which the concentrations of water and oxygen were kept below 10p.p.m.

CHAPTER TWO

REACTIONS OF IODINE PENTAFLUORIDE WITH ORGANIC BASES

Reactions of Iodine Pentafluoride with Organic Bases

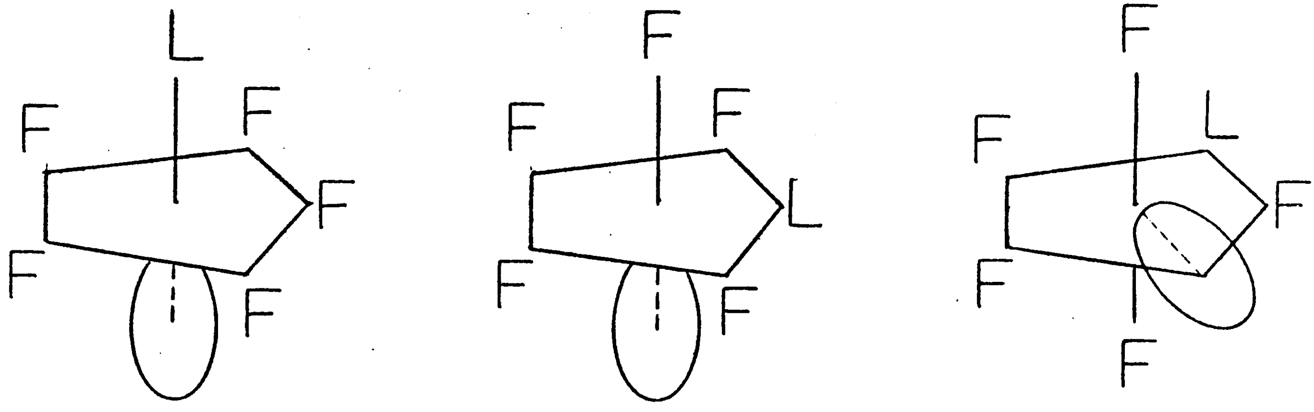
Introduction

Iodine pentafluoride is known to form complexes with organic bases such as dioxane and pyridine.[66,75,76] ^{19}F n.m.r. data were obtained, as were phase diagrams for the IF_5-1,4-dioxane and IF_5-pyridine systems. No vibrational spectroscopic results were determined and the geometry of each complex is unknown. The stereochemistry of these complexes is of great interest, since the iodine atom could be pseudo seven-coordinate. Since the study of pseudo 7-coordinate species was one of the main aims of this work, it was felt that a vibrational spectroscopic study of these complexes would be very important.

A 1:1 complex of IF_5 with 1,4-dioxane was briefly reported by Scott and Bunnett[76] who found that the product was a colourless crystalline solid. This compound hydrolysed easily, and on slow warming decomposed above 357K. On immediate contact with a hot heating-block, however, it did not decompose below 385K. A much more extensive investigation was carried out by Rogers and Meyer[75] who prepared many interhalogen-organic base adducts. Among these were adducts of IF_5 with 1,4-dioxane, pyridine, 2-fluoropyridine, trifluoroacetic anhydride, 2-methylpyrazine, quinoline, diethyl ether, isopropyl ether, pyrazine and ethylene oxide. Several of these were, however, stable only at low temperature. Phase diagrams, (temperature Vs concentration of IF_5) were presented for the systems IF_5-1,4-dioxane and IF_5-pyridine although much is of the form of an interpolation rather than actual experimental results.

There was a maximum in the dioxane-IF_5 curve corresponding to a composition of IF_5:dioxane = 2:1 as well as 1:1 but it was not certain whether this was a true maximum or a peritectic point. The 2:1 adduct dissociated into the 1:1 adduct and IF_5 under conditions of reduced pressure. Measurements of apparent dipole moments, molar polarisations, and molar refractions were made for the complexes dissolved in either benzene or carbon tetrachloride. The ^{19}F n.m.r. spectrum of IF_5 dissolved in dioxane, ethyl acetate, benzene or acetonitrile was reported to be very similar to that of the neat liquid, whereas in pyridine the spectrum was a single sharp resonance.[66] Muetterties examined the following three possible structures of $IF_5{\cdot}C_5H_5N$ in the light of these n.m.r. data. (L = C_5H_5N)

Figure 10



A (C_{5v}) B (C_s, σ_d) C (C_1)

A single-line ^{19}F n.m.r. spectrum is consistent with structure A, but neither structures B nor C can be ruled out because of the possibility of rapid fluorine exchange.

During the course of the work to be described, Lehmann, Naumann and Schmeisser[90] reported the Raman, i.r. and n.m.r. spectra of $IF_5.C_5H_5N$. This compound was examined in the course of investigating the adducts $IX.IF_5.2C_5H_5N$. (X = F, Cl, Br) These complexes of general formula $IX.IF_5.2C_5H_5N$ were found to be adducts between $IX.C_5H_5N$ and $IF_5.C_5H_5N$ with covalent I-F-I bridges. The compound previously reported as $IF_3.C_5H_5N$[41] was found to be $IF.IF_5.2C_5H_5N$. The ^{19}F n.m.r. spectrum of $IF_5.C_5H_5N$ was found to consist of a single signal, in agreement with previous work.[66] No possible structures for the adduct were discussed.

There have been no reports of extensive studies of IF_5 with nitriles, despite the fact that nitriles are known to be good co-ordinating solvents. It was therefore considered well worthwhile investigating the IF_5-CH_3CN system, in addition to carrying out a thorough spectroscopic study of known adducts.

Results and Discussion

I Liquid Iodine Pentafluoride

Iodine pentafluoride belongs to the C_{4v} point group, and group theory predicts that there should be six bands active in both the i.r. and Raman spectra and a further three active only in the Raman spectra. The nine Raman bands comprise:

$\nu_1(A_1)(ax)$, $\nu_2(A_1)(s,eq)$, $\nu_3(A_1)(\pi)$, $\nu_4(B_1)(as,eq)$ $\nu_5(B_1)(\pi)$, $\nu_6(B_2)(\delta,eq)$, $\nu_7(E)(as,eq)$, $\nu_8(E)(\delta,eq)$, where

ax = $I - F_{axial}$ vibration
eq = $I - F_{equatorial}$ vibration
s = symmetric vibration
as = asymmetric vibration
π = out-of-plane bending vibration
δ = deformation vibration

The Raman spectrum of liquid IF_5 was first recorded by Lord et al in 1950[161] who observed the expected nine lines and assigned them (Table 6). This work was repeated by Begun et al[162] who also investigated BrF_5, ClF_5 and $XeOF_4$. Several discrepancies between the two IF_5 spectra were noted and different assignments were made. Lord et al reported two strongly polarised lines at 693 and 710cm^{-1} whereas Begun et al found only one at 698cm^{-1} and concluded that if there were two bands, the separation must be less than 8cm^{-1}. Further investigations by Gillespie and Clase.[163], Selig and Holzman,[164] and Alexander and Beattie[165] have confirmed the presence of two polarised bands in the 700cm^{-1} region. These latter investigations were in general agreement except for the assignment of the two bands at approximately 700cm^{-1}. The problem arises through the

Table 6

Raman Spectra of IF_5 - frequencies (cm^{-1}) and assignments

Lord et al[161]	Begun et al[162]	Gillespie Clase[163]	Selig Holzman[164]	Alexander Beattie[165]	This Work	Gas Phase
192(2)E	189(0+)ν_9E	191(1)ν_9E	191 ν_9E	191 w	191 (1)	200 w
			218 "Polymer"			
275(7)B_1	273(2)$\nu_6 B_2$	275(4)$\nu_6 B_2$	275 $\nu_6 B_2$	274 m	274 (4)	274 w
317(6)pA_1	315(1)p$\nu_3 A_1$	316(2)p$\nu_3 A_1$	316p $\nu_3 A_1$	316 mp	317 (4)p	318 mp
375(7)E	374(2)ν_8E	376(4)ν_8E	375 ν_8E	375 m	375 (4)	370 w
572(10)pB_2	575(8)$\nu_4 B_1$	574(12)$\nu_4 B_1$	578 $\nu_4 B_1$	575 s	581 (17)	602 sh
	593(10)p$\nu_2 A_1$	598(11)p$\nu_2 A_1$	600p$\nu_2 A_1$	598 sp	597(16)p	614 vs p
605(9)B_1						
		635(0)ν_7E		630 vw sh	635 (0)	631 sh
693(8)pA_1		694(9)p $\nu_1 + 2\nu_9+\nu_3$	697p"polymer"	697 sp	700 (16)p	
	698(6)p$\nu_1 A_1$					
710(8)pA_1		705(9)p	705$\nu_1 A_1$	705 sp	708(16)p	710 sp

Figures in parentheses refer to relative intensities

s = strong, m = medium, w = weak, vs = very strong, vs = very weak, p = polarised.

All samples were liquid unless otherwise stated.

presence of three polarised bands in the stretching region of the spectrum although group theory predicts only two. Gillespie and Clase[163] assigned the doublet to a Fermi resonance between ν_1 and the ternary combination $2\nu_9 + \nu_3$. Selig and Holzman[164] put forward a different argument, based on the gas phase spectrum which has only one band in the region of controversy. (at 710cm^{-1}) They noted that as the temperature of the liquid was increased, the lower frequency component of the doublet gradually disappeared. They suggested that in the spectrum of the liquid, the band at 705cm^{-1} is ν_1 and the lower frequency band is a "polymer band" arising from association in the liquid phase. They also observed a weak band at 218cm^{-1} in the liquid spectrum although this was not observed by other workers either before or since. This band was tentatively assigned as another polymer band. Although no subsequent workers have commented on this assignment, 218cm^{-1} is the stretching frequency of molecular iodine dissolved in IF_5. As IF_5 is often difficult to obtain completely free of iodine, which absorbs intensely in the Raman spectrum, the author feels that this 218cm^{-1} band observed by Selig and Holzman is almost certainly due to a trace of iodine in the IF_5. Alexander and Beattie[165] discussed the two possible explanations for the occurrence of the extra band near 700cm^{-1}, in the light of the gas phase, high temperature liquid phase, and solution spectra (in C_6F_6). The choice of C_6F_6 as a solvent is a little surprising since it is a very poor Raman solvent with several intense absorptions in the same regions as IF_5, thus masking some IF_5 bands. However, the overall conclusion was that the band just below 700cm^{-1}, is due to the fact that IF_5 is an associated liquid.[166] By analogy with $XeF_2.IF_5$[29] and solid IF_5,[83] (Figures 2 and 3), this association probably occurs via an $I-F_{eq}$---I interaction with donation occurring between the lone pair axis and the plane of four equatorial fluorine atoms. If this assumption is correct then in a solvent such as C_6F_6 all the IF_5 molecules could be represented by $D \longrightarrow IF_5$. The solution spectrum in fact shows a single narrow band near 700cm^{-1} and therefore the authors felt that this was justification for their argument. The results of the present work agree in general with the "associated liquid" interpretation of Alexander and Beattie, which is a development of the argument put forward by Selig and Holzman.

II Iodine Pentafluoride and Acetonitrile

Tungsten hexafluoride is miscible in all proportions with acetonitrile at 298K without reaction. The Raman and n.m.r. spectra of mixtures of the two liquids indicate very little solvent effect. This lack of change of position in any of the bands or peaks indicates that there is no significant solvent-solute interaction occurring.

Iodine pentafluoride is miscible in all proportions with CH_3CN and Raman and n.m.r. spectra show no changes in number or intensities of bands or peaks, with one exception. However, unlike the WF_6 - CH_3CN system, IF_5 and CH_3CN exhibit a solvent effect in their spectra. The Raman data for a series of IF_5 - CH_3CN mixtures are shown in Table 7, and in graphical form as Figure 11.

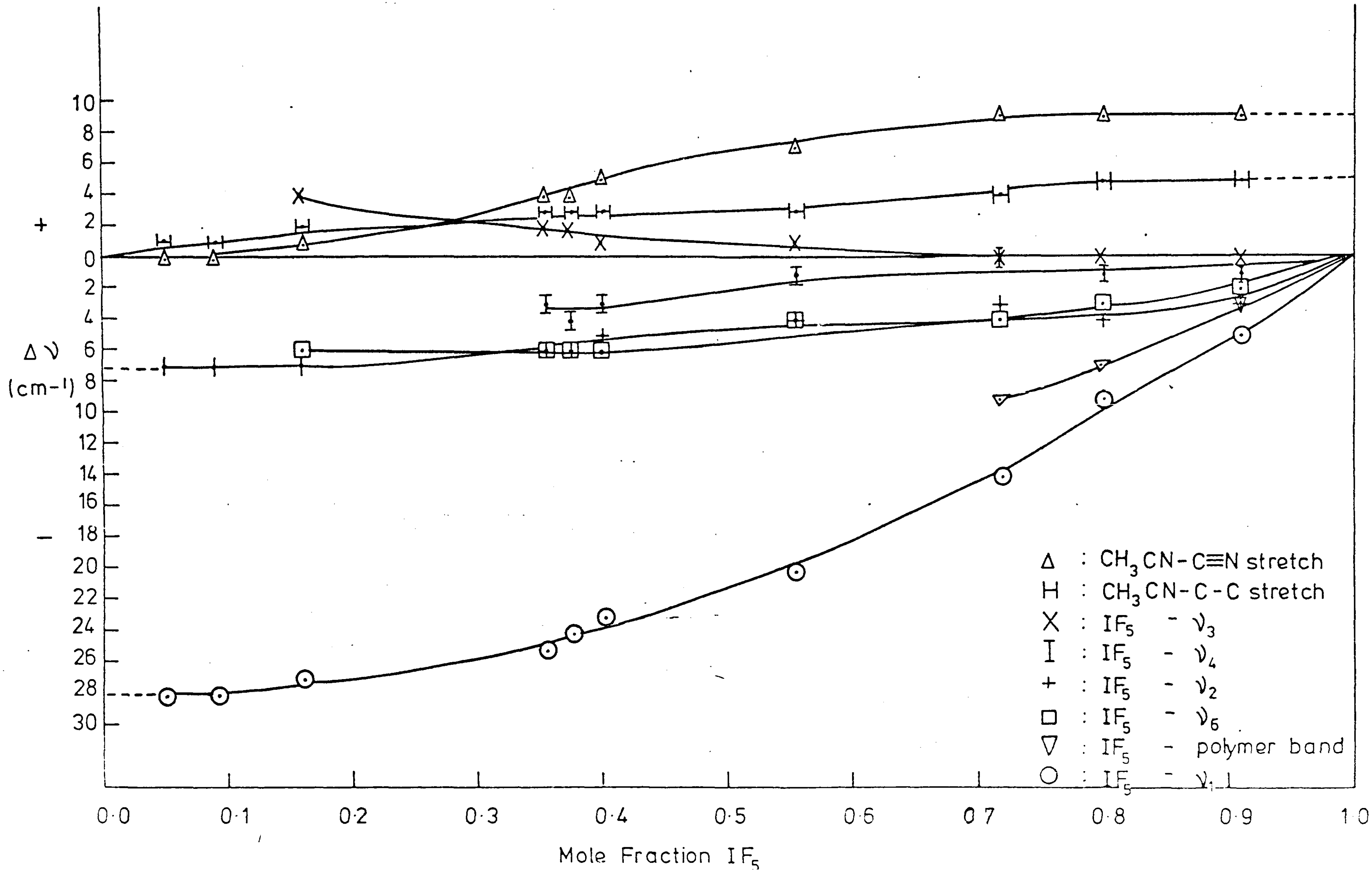
Table 7

Raman Bands of IF_5 - CH_3CN Mixtures

Mole Fraction (IF_5)			Bands (IF_5)(cm^{-1})				Bands (CH_3CN)(cm^{-1})	
	ν_1	"Polymer"	ν_2	ν_4	ν_3	ν_6	νC-C	νC≡N
1·00	708	700	596	581	317	274	-	-
0·91	703	697	593	580	317	272	925	2269
0·80	699	693	592	580	317	271	925	2269
0·72	694	691	593	581	317	270	924	2269
0·56	688	-	592	580	318	270	923	2267
0·40	685	-	592	578	318	268	923	2265
0·37	684	-	590	577	319	268	923	2264
0·35	683	-	590	578	319	268	923	2264
0·16	681	-	589	-	321	268	922	2261
0·09	680	-	589	-	-	-	921	2260
0·05	680	-	589	-	-	-	921	2260
0·00	-	-	-	-	-	-	920	2260

Figure 1.1

Change in Frequency of Raman Bands of IF_5 and CH_3 CN ($\Delta\nu$, cm^{-1}) Vs Concentration (Mole Fraction IF_5)

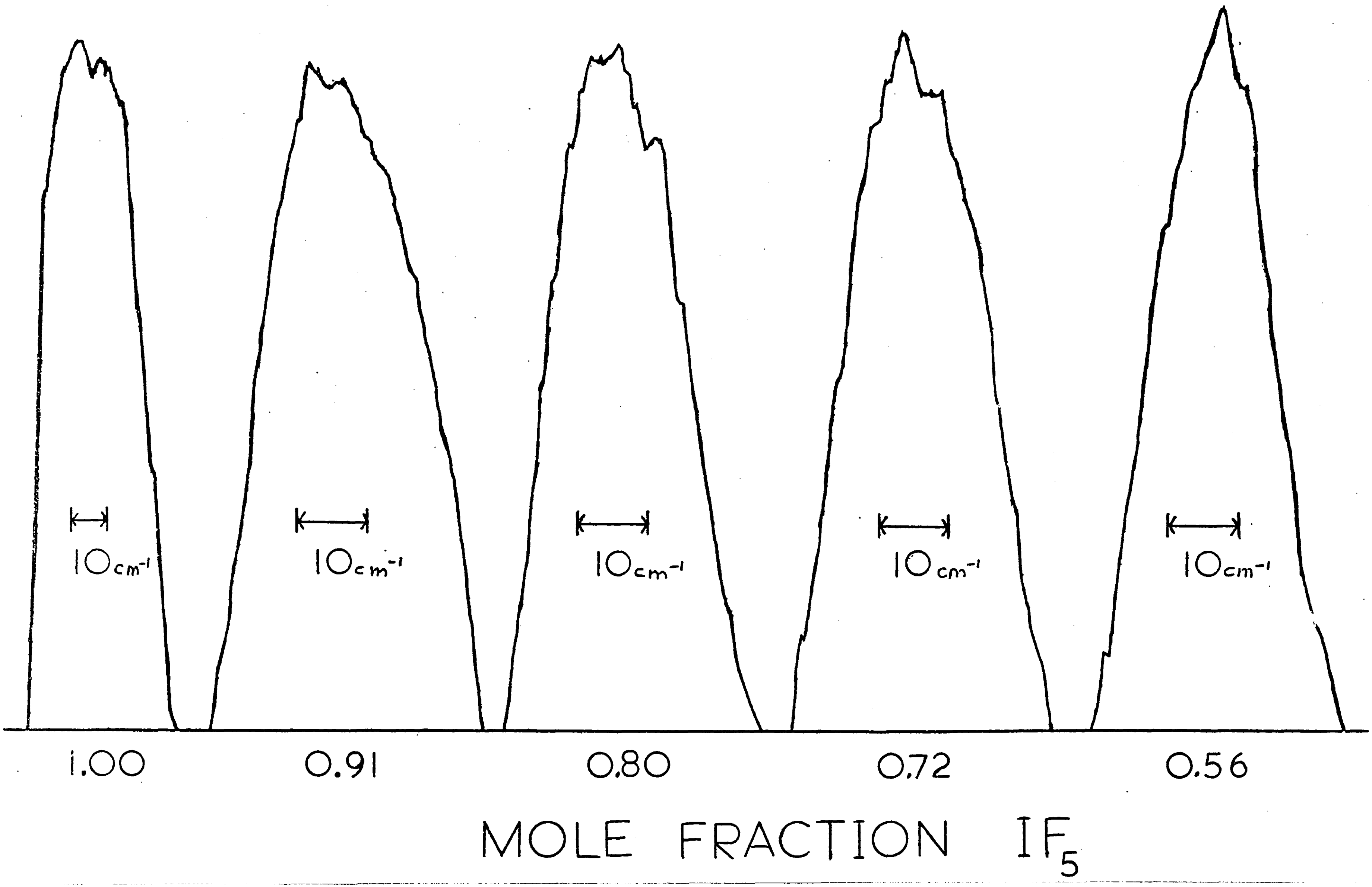


On increasing the CH_3CN concentration, the ν_2, ν_4 and ν_6 bands of IF_5 (all I-F$_{equatorial}$ vibrations) shift to slightly lower frequencies, whereas ν_3 (π mode) increases slightly in frequency. The major change involves the I-F$_{axial}$ stretch, ν_1. The frequency of this band drops by up to 28cm^{-1}. Another highly significant feature is the increase in frequency of both the C-C and C≡N stretches in CH_3CN as the IF_5 concentration increases. This is characteristic of CH_3CN when the nitrogen atom σ-coordinates to an acid which cannot undergo π back bonding.[167] With a high CH_3CN concentration, the frequency of the I-F$_{axial}$ stretch is most strongly affected while at high IF_5 concentrations, the CH_3CN stretching vibrations behave as though coordination was occurring. The graph of the change in frequency of the ν_1 mode of IF_5 against concentration (Figure 11) is reasonably smooth and no discontinuities are observed. IF_5 is known from viscosity, surface tension and heat capacity measurements[166] to be an associated liquid, probably involving interactions of the type I-F---I. The effects observed in the Raman spectra of IF_5 - CH_3CN mixtures can be explained by the occurrence of a process involving the gradual replacement of IF_5 molecules round one particular IF_5 by CH_3CN molecules. In other words, the I-F---I interactions are being replaced by C≡N---I interactions. The intermolecular contacts in IF_5 most probably result from electrostatic attraction between the positively charged iodine and the negatively charged fluorine atoms on neighbouring

IF_5 molecules. The nitrogen atom in acetonitrile carries a partial negative charge so that an electrostatic interaction between the iodine atom in IF_5 and the nitrogen atom in CH_3CN might be anticipated. Short intermolecular contacts of the type $I\cdots\cdot F_{eq}-I$ or $I\cdots F-Xe$ are a significant feature of the crystal structures of solid IF_5[83] and $XeF_2\cdot IF_5$[79]. In the former, intermolecular I-F contacts as short as 303 pm occur while in the latter, the minimum $I\cdots F-Xe$ distance is reported to be 314·2pm. For comparison, the sum of the van der Waals radii of iodine and fluorine is 350pm. Similar electrostatic intermolecular interactions are believed to cause the association of IF_5 molecules in the liquid phase and hence give rise to the so-called "polymer band" in the Raman spectrum of liquid IF_5. On addition of CH_3CN, this band decreases in intensity and disappears altogether when the mole fraction of IF_5 is less than 0·7, leaving a symmetric peak due to ν_1. (Figure 12) The frequency of ν_1 reaches the minimum value when the mole fraction of $IF_5 \sim 0{\cdot}2$, that is a ratio of $IF_5 : CH_3CN = 1:4$. From the crystal structure of IF_5[83], it is known that most of the IF_5 molecules have closest contacts with four other IF_5 molecules. The graph of change in frequency of ν_1 versus concentration is consistent with this, if it is assumed that the structure of IF_5 in the liquid state is similar to that of the solid, with each IF_5 associated with four others. Thus when the concentration of IF_5 is reduced to the point where there are four CH_3CN molecules to every IF_5, then each IF_5 is completely solvated by acetonitrile,

Figure 12

ν_1 AND POLYMER BANDS OF IF_5 IN CH_3CN

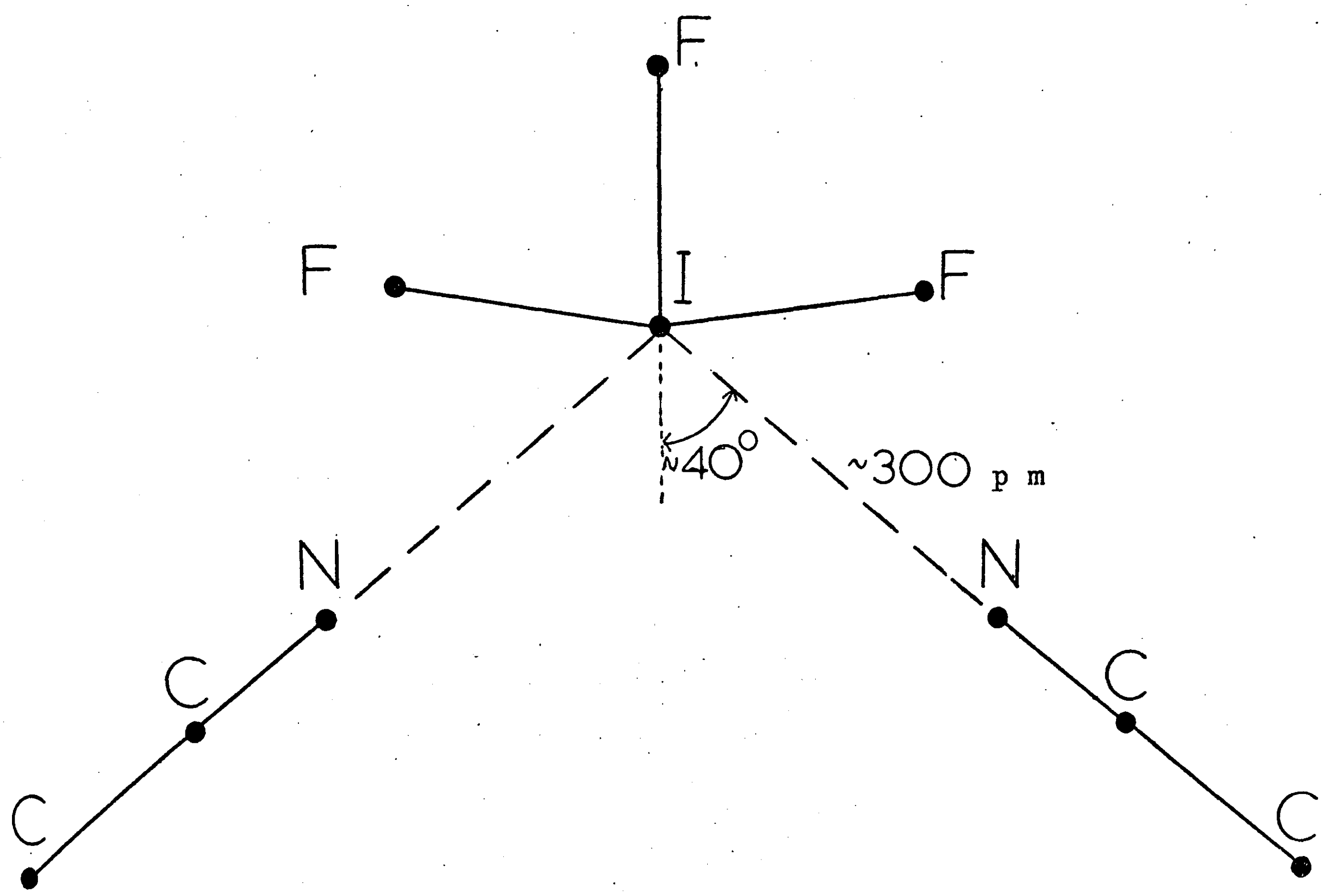


and any extra solvent will have little effect. It would have been interesting to observe the effect of dilution on ν_8, the I-F$_{axial}$ bending vibration. Unfortunately, this band is weak and is swamped by the C-C bending vibration of CH_3CN whose frequency is less than 5cm^{-1} different from ν_8.

Solvent effects in the IF_5 - CH_3CN system are also observed in ^1H and ^{19}F n.m.r. spectra. The ^{19}F n.m.r. spectrum of IF_5 with CCl_3F as internal reference shows a doublet at +11•2ppm and a quintet at +59•8ppm of relative intensity 4:1 and J_{F-F} = 84Hz. A solution of IF_5 in CH_3CN (mole fraction IF_5 = 0•27) also referenced internally shows a very similar doublet and quintet. The coupling constant, J_{F-F} = 84Hz but there is a solvent shift with the doublet moving 5•7ppm upfield to +5•5ppm and the quintet moving 6•5ppm upfield to +53•3ppm. This indicates that the interaction between IF_5 and CH_3CN has a slightly greater effect on the axial fluorine than on the equatorial fluorines. The ^1H spectrum of CH_3CN shows a sharp singlet at +1•80ppm, whereas the IF_5 - CH_3CN mixture shows a sharp singlet at +2•04ppm. The effect of interaction on the ^1H spectrum is therefore to move the $\underline{CH_3}$ group resonance 0•24 ppm downfield. This is consistent with the concept of electron donation from the nitrogen to the iodine, thus lowering electron density in the nitrile group. The methyl group, which is slightly electron repelling, would then increase its contribution to the nitrile carbon, resulting in a deshielding of the methyl protons. It should be emphasised at this point that although these interactions are strong enough to cause solvent shifts in both Raman and n.m.r. spectra, they are too weak to cause any alteration to the symmetry of the molecules involved. The spectra of the solutions are still consistent with a C_{4v} structure for IF_5.[83] It has been found that in solid IF_5, the primary interactions between fluorine atoms and iodine atoms of neighbouring molecules make a weighted average angle of 36·4° with the F_{axial}-I-lone pair axis[83] (Figure 2). The structure of $XeF_2 \cdot IF_5$[79] (Figure 3) consists of layers of IF_5 molecules, each layer separated by a layer of XeF_2 molecules. The IF_5 molecules are stacked in columns, base to base and apex to apex. Where superimposed IF_5 molecules, in adjacent layers, are base to base, the sandwiched XeF_2 molecules orientate to make short I···F-Xe contacts. However, the XeF_2 molecules are orientated away from the IF_5 molecules when they are apex to apex. This arrangement implies that the iodine atom, which bears an appreciable positive charge, is effectively shielded by the fluorine ligands but not by the lone pair. The angle between the Xe-F····I interaction and the I-lone pair axis is calculated by the present writer, from the distances given, to be 41·8°. Each iodine forms contacts with a fluorine on each of four XeF_2 molecules. By analogy with $XeF_2 \cdot IF_5$ and solid IF_5, it seems reasonable to assume that at least four acetonitrile molecules could coordinate with an IF_5 molecule. Figure 13 is a two-dimensional representation of a possible coordination arrangement. If each IF_5 molecule in a dilute solution in CH_3CN is fully solvated by four CH_3CN molecules, either in a staggered or eclipsed conformation, the C_{4v} symmetry of the IF_5 molecule

Figure 13

Possible Co-ordination Arrangements between IF_5 and CH_3CN



1mm ≡ 5pm

Only side view shown for clarity.

will be maintained. However at higher concentrations of IF_5 this would not be possible. More likely is the situation where the CH_3CN ligands are very labile and exchange of CH_3CN molecules is fast. There could also be rapid rotation of the IF_5 molecules about the I-lone pair axis. The overall result would be that the time-averaged structure will be that of IF_5 with acetonitriles forming a "cone" round the lone pair, thus preserving the C_{4v} symmetry of IF_5 at all concentrations. It seems reasonable to imagine that the N•••I contacts are similar to the $I-F_{eq}\cdots I$ and $Xe-F\cdots I$ contacts in solid IF_5 and $XeF_2 \cdot IF_5$ respectively. Despite the strong spectroscopic evidence for interaction between IF_5 and CH_3CN, no complex is isolable at room temperature.

III Iodine Pentafluoride and 1,4-Dioxane

IF_5 and 1,4-dioxane react at room temperature to form a white solid. The ratio of $IF_5 : C_4H_8O_2$ was shown to be 1:1 by elemental analysis and by weighing reactants and product. The melting point was found to be 351K, in fair agreement with the literature value of 357K.[76] The complex was found to be only slightly soluble in $C_4H_8O_2$, moderately soluble in IF_5 and very soluble in CH_3CN. However, solutions in IF_5 are thermally unstable at 298K and soon show signs of reaction. Iodine and HF are among the decomposition products. $IF_5 \cdot C_4H_8O_2$ can, however, be recrystallised very conveniently from CH_3CN solution. Vibrational spectra of the recrystallised solid show no evidence of residual CH_3CN. X-ray powder data for the adduct are presented in the appendix.

Vibrational spectra of the solid adduct and solution Raman spectra are shown in Table 8. The IF_5 bands in the spectra of the solid indicate that the C_{4v} symmetry of IF_5 is probably retained. The two ring stretching frequencies observed in the Raman and i.r. spectra of the adduct show little change from those of pure liquid $C_4H_8O_2$ [168]. The most interesting feature of the Raman spectrum of the solid is the band at ca 594cm^{-1}. This has been tentatively assigned as IF_5 ν_7 (E) with a large shift to lower frequency. This band is difficult to observe in the spectrum of IF_5 itself and there is no obvious explanation for the increase in intensity. The Raman spectra of $IF_5{\cdot}C_4H_8O_2$ dissolved in CH_3CN are unfortunately very poor. The spectra, especially that of the concentrated sample, are dominated by a very steeply rising base-line, indicating strong fluorescence, and only a few weak, broad bands can be observed. This rules out the possibility of obtaining useful polarisation data. The ^{19}F n.m.r. spectrum of $IF_5{\cdot}C_4H_8O_2$ in CH_3CN shows a doublet at +5•2ppm, J_{F-F} = 84Hz and a quintet at +55•0ppm, J_{F-F} = 84Hz. This spectrum is very similar to that of an IF_5-CH_3CN mixture. Whether this indicates little or no perturbation of the IF_5 in $IF_5{\cdot}C_4H_8O_2$, or merely that in solution the adduct dissociates into IF_5 and $C_4H_8O_2$ is unknown. The ^1H n.m.r. spectrum shows resonances at +1•9ppm (CH_3CN) and +3•5ppm ($C_4H_8O_2$). Both are sharp singlets. This suggests that all the protons in $C_4H_8O_2$ are equivalent but exchange processes cannot be ruled out. A dilute solution of $IF_5{\cdot}C_4H_8O_2$ in IF_5 was prepared and its ^1H spectrum obtained before serious decomposition occurred. This shows a single

Table 8

Vibrational Spectra of $IF_5.C_4H_8O_2$ (cm^{-1})

Raman					I.r.	
Solid (1)	Solid (2)	Solid (Recryst)	Solution 1 (CH_3CN)	Solution 2 (CH_3CN)	Solid (Recryst)	Assignments
144 (2)		141 (2)	139 (1)			I-O?
198 (0+)						IF_5 ν_9
274 (1)	272 (2)	272 (1)				IF_5 ν_6
325 (0+)	322 (0+)					IF_5 ν_3
	386 (1)	379 (0+)				IF_5 ν_8
			378 (5)	382 (2)		CH_3CN
562 (4)	562 (8)	561 (3)		570 (0+)	560 vs, br	IF_5 ν_4
580 (5)	578 (14)	579 (5)	588 (2)	588 (3)		IF_5 ν_2
595 (2)	594 (5)	592 (2)				IF_5 ν_7
					630 sh	IF_5?
672 (11)	671 (19)	669 (9)	680 (3)	681 (4)		IF_5 ν_1
836 (3)	835 (7)	832 (2)	834 (1)	837 (2)	837 s	$C_4H_8O_2$ ring str.
					860 vs	$C_4H_8O_2$ ν_{27}
					880 sh	$C_4H_8O_2$

Table 8 (cont'd)

Solid (1)	Solid (2)	Solid (Recryst)	Solution 1 (CH_3CN)	Solution 2 (CH_3CN)	Solid (Recryst)	Assignments
			921 (8)	925 (2)		CH_3CN
1020 (1)	1020 (2)	1018 (1)				$C_4H_8O_2$ ring str.
					1040 w	$C_4H_8O_2$ ν_{25}
					1075 s	$C_4H_8O_2$ ν_{26}
					1100 s	$C_4H_8O_2$ ν_{17}
					1255 s	$C_4H_8O_2$ ν_{15}
					1290 s	$C_4H_8O_2$ ν_{24}

Figures in parentheses indicate relative intensities; s = strong, w = weak etc.

Solution Raman spectrum 1 : dilute solution

Solution Raman spectrum 2 : concentrated solution (3·27 molal) signal at +4·2ppm. Most probably either the protons are all equivalent or intramolecular exchange is occurring. The energy barrier for the ring inversion process in 1,4-dioxane is small, 40·6kJmol^{-1} at 177K, but on complexation the situation could change completely. If the O•••I contacts occur in a similar manner to the F•••I and N•••I contacts already described, then it is obvious that on complexation, the chain form will be preferred because of steric reasons (Figure 14). There will be repulsion between the equatorial fluorine atom and the oxygen atom (B) when the dioxane molecule is in the boat conformation. These lone pair-lone pair repulsions could eliminate the possibility of proton exchange <u>via</u> a chair→boat→chair interconversion. The simplest explanation for the single ^{1}H n.m.r. signal is that all the protons are equivalent. This however could only be the case if the dioxane molecules are coordinating at each end. The simplest structure which appears to fit the vibrational and n.m.r. data is a "chain" structure comprising alternate IF_5 and $C_4H_8O_2$ molecules as shown in Figure 15. In this structure, the dioxane molecules retain their C_{2h} symmetry. The IF_5 molecules probably retain their C_{4v} symmetry but this could be lowered without affecting the n.m.r. spectrum at all and merely causing small effects in the Raman spectrum. With the situation where the E modes are all weak, and good polarisation data are not available, it was not possible to determine the exact structure. The suggested structure consisting of chains, might be capable of close packing and this is consistent with the adduct being a solid at room temperature.

Figure 14

Co-ordination of IF_5 to Dioxane in chair and boat conformations

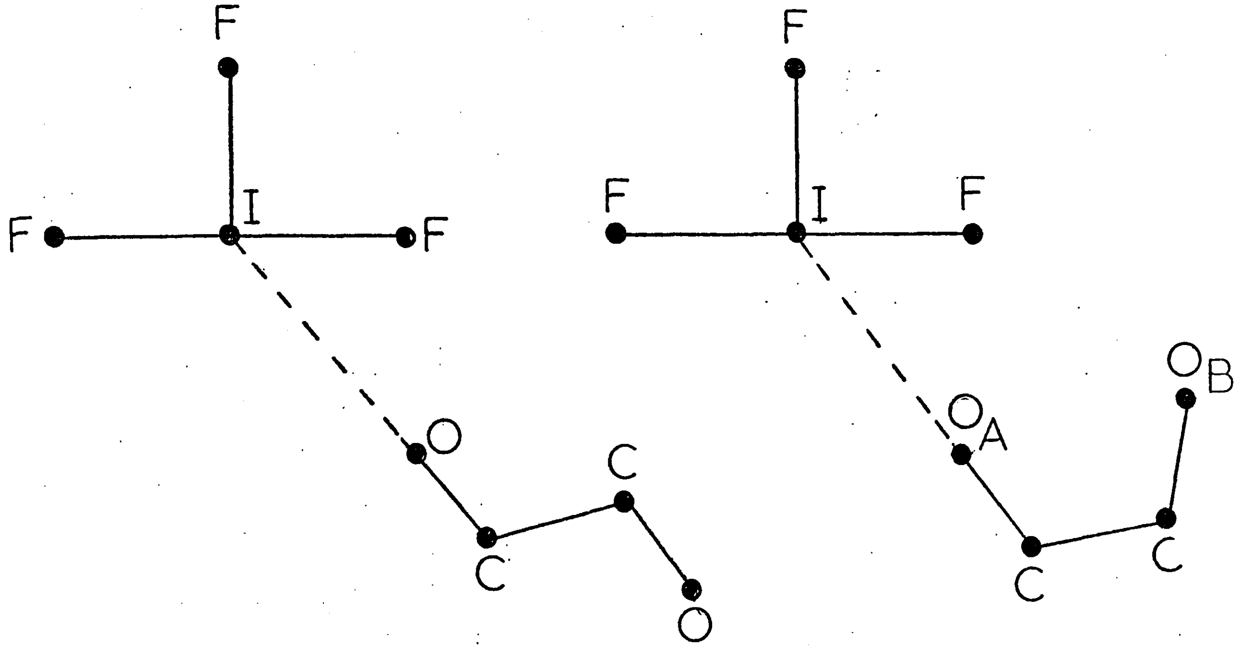
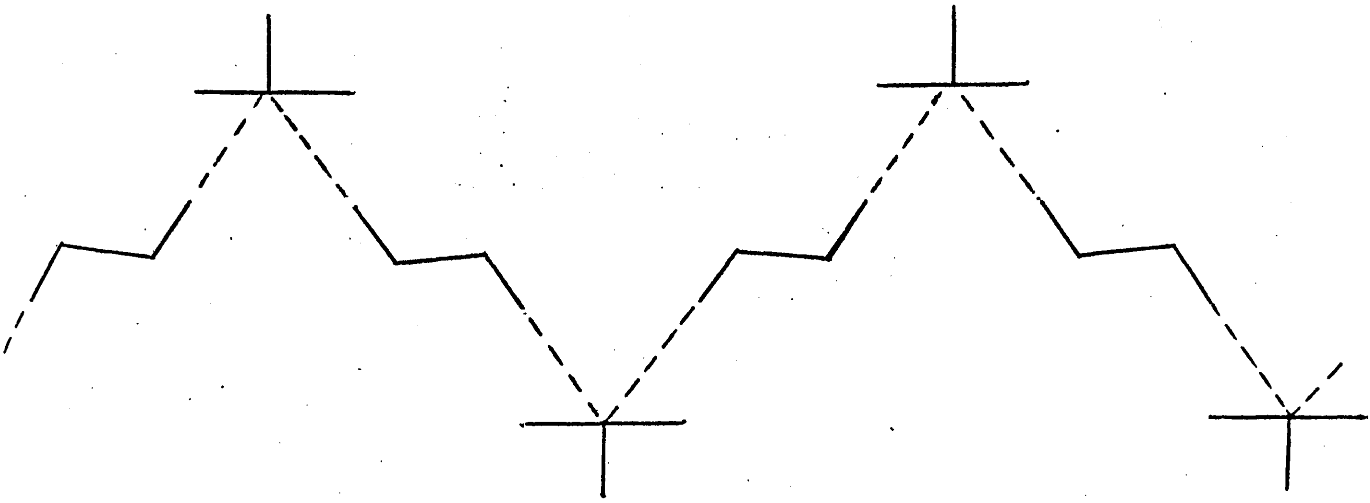


Figure 15

Possible Structure of $IF_5.C_4H_8O_2$



IV. Iodine Pentafluoride and Pyridine

Iodine pentafluoride and pyridine are miscible in all proportions, but unlike IF_5-CH_3CN mixtures, IF_5-C_5H_5N mixtures are not thermally stable at room temperature indefinitely. Decomposition takes place over a period of several days, iodine being one product. The Raman, ^1H, and ^{19}F n.m.r. spectra were recorded of IF_5-C_5H_5N mixtures. (Tables 9,10) The IF_5-C_5H_5N system is quite unlike the IF_5-CH_3CN system. Lehmann et al have shown[90] that a 1:1 complex between IF_5 and CH_3CN can be isolated. The Raman spectrum of the 1:1 adduct as reported[90], is in good agreement with the spectra of the mixtures. The Raman spectrum of the isolated adduct is most interesting. The highest frequency IF_5 band is shifted down to 650cm^{-1}, nearly 60cm^{-1} from that of pure IF_5. Another interesting feature is the small number of bands assignable to IF_5. There are only six and this is surprising since the spectrum of liquid IF_5 comprises nine bands including the polymer band. The four low frequency bands in the spectrum of $IF_5 \cdot C_5H_5N$ can be correlated with ν_3, ν_6, ν_8 and ν_9 in IF_5 but there are only two bands in the I-F stretching region, at 650 and 565cm^{-1}. One explanation might be that as a result of reasonably strong co-ordination between the iodine and nitrogen atoms, not only is the I-F$_{axial}$ bond weakened and the value of ν_1 reduced but the symmetric and asymmetric I-F$_{equatorial}$ stretches coincide. This seems feasible since they are only 15cm^{-1} apart in IF_5. Coincidence or extensive overlap of ν_2 and ν_4 is a possible explanation for the presence of only two stretching frequencies. Two possible structures for $IF_5 \cdot C_5H_5N$ are shown in Figure 16. These are based on the interactions known to occur in

Table 9

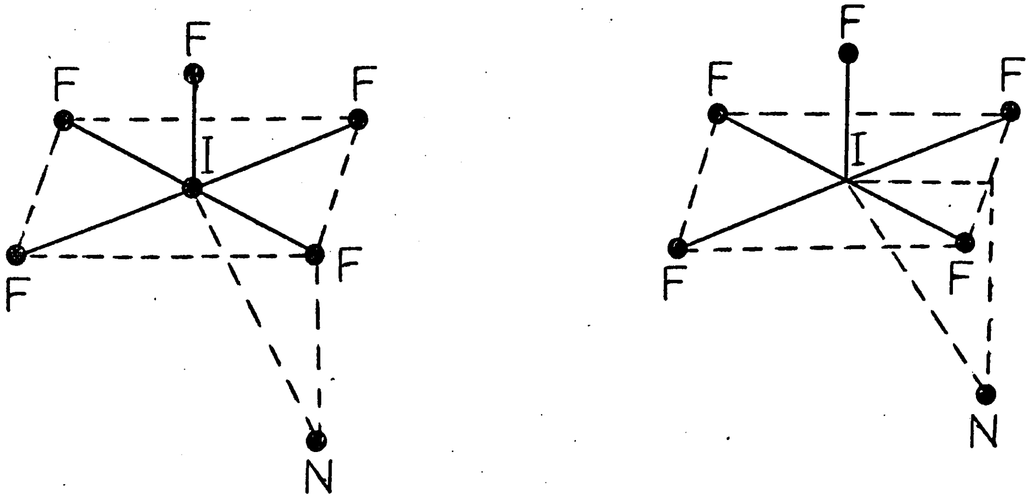
N.M.R. data on IF_5 - C_5H_5N mixtures

Mole Fraction IF_5	^{19}F (int. CCl_3F)	^1H (ext. C_5H_5N)
0·27	+14ppm	+0·17 (ortho) +0·37 (meta) +0·38 (para)
0·50*	+10·9ppm (in CH_3CN)	-
0·72	+19ppm	+0·48 (ortho) +0·88 (meta) +0·93 (para)

* data from reference 90

Figure 16

Possible Structures of $IF_5.C_5H_5N$



$C_s(\sigma_v)$ $C_s(\sigma_d)$

Table 10

Raman bands of IF_5 - C_5H_5N mixtures (cm^{-1})

Mole Fraction IF_5	C_5H_5N	C_5H_5N	C_5H_5N	IF_5	IF_5	IF_5	IF_5	IF_5	IF_5	IF_5	IF_5	IF_5	IF_5
0·00	1033(7)	993(10)	-	-	-	-	-	-	-	-	-	-	-
0·26	1036(9)	994(3)	1003(6)	-	-	652(6)	-	-	566(4)	370(0+)	-	270(0+)	-
0·50*	-	-	-	-	-	650(10)	-	-	565(7)	380(0·3)	315(0·4)	280(0·5)	190(0+)
0·70	1036(10)	-	1004(4)	697(8)	675(8)	644(2)	597(6)	580(6)	-	372(1)	317(1)	271(1)	172(1)†
0·81	1036(8)	-	1004(4)	699(7)	685(6)	644(1)	597(7)	580(7)	-	371(1)	314(1)	271(1)	173(0+)
1·00	-	-	-	708	700	-	597	581	-	375	317	274	191

* data from reference 90

† tentatively assigned as ν(I-N)

More detailed assignments are made in the text.

$XeF_2 \cdot IF_5$[79] and in solid IF_5.[83] The C_s (σd) structure is similar to structure B proposed by Muetterties (Figure 10), except that the four equatorial fluorines are not coplanar with the nitrogen atom. The two structures are of similar symmetries so the vibrational spectra would also be similar. The selection rules for the two structures differ slightly from those of the C_{4v} structure for IF_5 and from each other. A correlation table for $C_{4v} \rightarrow C_{s(\sigma v)} \rightarrow C_{s(\sigma d)}$ is presented as table 11.

In theory, the Raman spectrum should distinguish between the three possibilities. However, the E modes in the adduct spectrum are very weak. All the E modes except ν_8 are very weak even in liquid IF_5. The fact that these E modes lose their degeneracy as the symmetry is lowered is not of much use. The only other criteria upon which to determine the structure would be the polarisations of ν_4 or ν_6. (ν_5 is never observed in Raman spectra of IF_5). Unfortunately, ν_6, like the E modes, is very weak and ν_4 is complicated by the possible coincidence of bands mentioned earlier. In their work on the adduct, Lehmann et al[90] do not present any polarisation data. The ^{19}F n.m.r. spectrum of the adduct is a single line. This means that either all the fluorines are equivalent or, more likely, the pyridine molecules are promoting fast exchange between the fluorines. Work with R_fIF_4 compounds has shown[169] that C_5H_5N promotes fluorine exchange much more readily than CH_3CN. There is good evidence to suggest that the C_5H_5N molecules are relatively strongly co-ordinated to the IF_5 molecules in the 1:1 complex. When C_5H_5N is added to IF_5, the gradual change in Raman frequencies which occurs on addition of

Table 11

Correlation Table - $C_{4v} \rightarrow C_s$[183]

IF_5 (gas phase), C_{4v}		$\longrightarrow$ $C_{s(\sigma v)}$	$\longrightarrow$ $C_{s(\sigma d)}$
ν_1; R, ir, pol,	a_1	a'	a'
ν_2; R, ir, pol,	a_1	a'	a'
ν_3; R, ir, pol,	a_1	a'	a'
ν_4; R, depol,	b_1	a'	a"
ν_5; R, depol,	b_1	a'	a"
ν_6; R, depol,	b_2	a"	a'
ν_7; R, ir, depol,	e	a' + a"	a' + a"
ν_8; R, ir, depol,	e	a' + a"	a' + a"
ν_9; R, ir, depol	e	a' + a"	a' + a"

a' = polarised, a" = depolarised

CH_3CN to IF_5, is not observed. The changes can be better explained in terms of the formation of a 1:1 complex in solution. The Raman spectrum of a dilute solution of IF_5 in C_5H_5N is consistent with this since it shows the bands due to the 1:1 complex as well as the excess pyridine. Similarly, when IF_5 is in excess, bands due to the complex and IF_5 solvent are seen. The IF_5 solvent bands are slightly shifted and there is one especially interesting feature of this spectrum. There are four bands between 580 and 700cm^{-1}, all except the one of lowest frequency are polarised. This situation is very similar to pure liquid IF_5. The bands at 580 and 597cm^{-1} change little in frequency over the range of concentration mole fraction IF_5 = 1•00 -0•70, and are assigned as ν_4 and ν_2 respectively. The frequency of the highest band drops from 708 to 697cm^{-1} and is assigned as ν_1. The remaining band decreases in frequency from 700 to 675cm^{-1}. This band is believed to be the polymer band but it behaves very differently on addition of C_5H_5N as compared with CH_3CN. In the latter case, it merely becomes less and less intense with increasing dilution of IF_5, consistent with the break-up of IF_5 "clusters". In the case of C_5H_5N however, the frequency drops markedly (more than ν_1) but the intensity varies little. It only disappears when there is no remaining uncomplexed IF_5. This suggests that on addition of a small amount of C_5H_5N to IF_5, each C_5H_5N molecule attaches itself to one particular IF_5 molecule, and while IF_5 is in excess, it remains an associated liquid and the polymer band is observed in its Raman spectrum. Further evidence for the relatively strong co-ordination between IF_5 and C_5H_5N comes from the

Raman spectrum of a mixture of IF_5, C_5H_5N and CH_3CN. The mole fractions of the components were, $IF_5 = 0{\cdot}08$, $C_5H_5N = 0{\cdot}18$ and $CH_3CN = 0{\cdot}74$. The details of the spectrum are shown in Table 12.

The overall conclusion from this experiment is that IF_5 complexes to C_5H_5N in preference to CH_3CN. The identity of the band at 662cm^{-1} is not clear. Possibly it is an I-F band of $IF_5.C_5H_5N$, solvent shifted by CH_3CN, but it certainly does not arise from uncomplexed IF_5 in CH_3CN as the frequency is nearly 20cm^{-1} too low. Bearing in mind the apparent strength of the I-N interaction in $IF_5.C_5H_5N$ and the change in the stretching region of the Raman spectrum of the adduct, the most likely structure is $C_s(\sigma d)$ (Figure 16). The fact that $IF_5.C_5H_5N$ is a liquid whereas $IF_5.C_4H_8O_2$ is solid is believed to be due to the difference in the denticity of the organic ligand. C_5H_5N is monodentate and $IF_5.C_5H_5N$ is likely to be monomeric but $C_4H_8O_2$ is bidentate and can form chains which could result in a compound which is solid at room temperature.

Conclusions

The following conclusions are drawn from this work:

1. IF_5 is an associated liquid and the extra stretching frequency band in the Raman is due to this association.
2. On addition of CH_3CN to IF_5, the F•••I-F contacts are replaced by C≡N•••I-F contacts up to a maximum of _ca_ four CH_3CN molecules per IF_5. This prevents the association of IF_5 molecules, resulting in the disappearance of the polymer band. The N•••I interactions are believed to be similar to the F•••I interactions in $XeF_2.IF_5$ and solid IF_5. CH_3CN

does not form an isolable complex with IF_5.

3. $C_4H_8O_2$ forms a solid 1:1 adduct with IF_5, the spectra of which indicate retention of C_{2h} and C_{4v} symmetries for $C_4H_8O_2$ and IF_5 respectively. The adduct can be recrystallised from CH_3CN, and $C_4H_8O_2$ is not displaced. A structure based on chains is suggested.

4. C_5H_5N forms a liquid 1:1 adduct with IF_5. The Raman spectra of IF_5-C_5H_5N mixtures can best be interpreted in terms of $IF_5.C_5H_5N$ in solution in either IF_5 or C_5H_5N. C_5H_5N molecules appear to co-ordinate to one particular IF_5 molecule, and excess IF_5 remains as an associated liquid. CH_3CN does not displace C_5H_5N from $IF_5.C_5H_5N$. A monomeric structure of symmetry $C_2(\sigma d)$ is the most likely.

Table 12

Frequency (cm^{-1})	Intensity	Assignment
2302	0+	CH_3CN, combination band
2262	7	C≡N stretch
1036	10	C_5H_5N ring stretch
1032	14	C_5H_5N
1002	12	C_5H_5N complexed
994	11	C_5H_5N ring stretch
922	7	CH_3CN, C-C stretch
662	12	$IF_5 \cdot C_5H_5N$?
654	13	I-F stretch in $IF_5 \cdot C_5H_5N$
568	10	I-F stretch in $IF_5.C_5H_5N$
380	6	CH_3CN
318	0+	$IF_5.C_5H_5N$
272	0+	$IF_5.C_5H_5N$

Experimental

Chemicals

IF_5 (Fluorochem Ltd.), was purified by trap to trap distillation at 298K over NaF to remove HF, shaken with Hg to remove I_2 and stored over Hg. CH_3CN (Koch-Light Ltd.) was purified by multiple refluxing over P_2O_5 and was stored over activated Linde 4A molecular sieves. C_5H_5N and $C_4H_8O_2$ (B D.H. Analar), were purified by trap to trap distillation and stored over sodium.

Experimental Procedure

All samples were prepared using a conventional high vacuum system, rigorous precautions being taken to exclude moisture. IF_5 was found to react very slowly with Kel-F grease, becoming contaminated with iodine. Use of Kel-F wax solved the problem. IF_5 and CH_3CN or C_5H_5N mixtures were prepared by distilling IF_5 into a weighed, flamed-out Raman or n.m.r. tube, fitted with a Rotaflo stopcock. The tube was removed and reweighed, before distillation of the organic base. The tube was again weighed, the contents frozen at 77K and the sample sealed in vacuo. The concentrations were calculated from the weight differences ($\pm 10^{-4}$g). Typical amounts used were 0·05 - 0·5 mmoles, for Raman spectra and ca 1-4 mmoles for n.m.r. spectra.

At room temperature, IF_5 and $C_4H_8O_2$ formed a pale grey or white solid. This was prepared by distilling excess $C_4H_8O_2$ on to IF_5, shaking the reaction vessel, and pumping to remove the excess $C_4H_8O_2$. Careful weighing of reactants and product indicated a ratio of IF_5 : $C_4H_8O_2$ = 1 : 1.1. Further proof of the composition of the adduct was obtained from elemental analysis. Found; C:15•6, H:2•6, F:30•8, I:41•0, O: (by difference) 10•1%. $C_4H_8F_5IO_2$ requires C:15•5, H:2•6, F:30•7, I:41•0, O:10•3%. $IF_5.C_4H_8O_2$ on recrystallisation from CH_3CN yielded a white solid which did not contain residual CH_3CN. Samples for spectroscopy were prepared by reacting IF_5 and $C_4H_8O_2$, isolating the product which was then recrystallised in CH_3CN. This solid was then transferred to a weighed Raman or n.m.r. tube in a dry box and the solvent distilled. The tube was reweighed and finally the solution frozen and the tube sealed off in vacuo.

CHAPTER THREE

REACTIONS OF IODINE PENTAFLUORIDE WITH METALS AND METAL FLUORIDES

Reactions of Iodine Pentafluoride with Metals and Metal Fluorides

Introduction

The reactions of IF_5 with metals were investigated by Moissan[5], who described the reactions with arsenic, antimony, the alkali metals (in particular sodium), magnesium, iron and silver. As and Sb reacted quickly at room temperature releasing iodine. A piece of freshly cut Na immediately formed a passive coating, as did the other alkali metals. However, on melting the sodium pellet in IF_5, a violent and sometimes explosive reaction occurred. Mg, Fe and Ag were unaffected by IF_5 even up to 373K. In 1953, Aynsley, Nichols, and Robinson studied the reactions of IF_5 with Ag, Hg and Cd. In agreement with Moissan, no reaction was observed between IF_5 and Ag. However Cd formed cadmium fluoride and iodine was liberated. Mercury developed a thin film of white solid on its surface after standing at 298K for 24 hours. However on heating the IF_5 to its boiling point and refluxing for 5 hours, all the Hg was converted into a dense white solid. The excess liquid was removed and the solid became pale brown in colour after heating. This was thought to be due to the presence of a little free iodine as contaminant. The solid analysed as $F_{10}HgI_2$ and was formulated as $Hg(IF_5)_2$. No substantial evidence for this formulation was presented. The compound turned red on exposure to air, hydrolysed slowly in water though very rapidly in aqueous NaOH giving a solution containing fluoride and iodate ions. The mercury was precipitated quantitatively as the yellow oxide.

The solid was soluble in alcohol but insoluble in chloroform which it coloured faintly purple, indicating a small amount of free iodine.

It has been stated[22] that molybdenum and tungsten inflame in hot IF_5 but that chromium and copper are attacked only slightly. Few other reactions between IF_5 and metals have been studied. In most cases, the exact products are uncertain and nothing of the mechanism of the reactions is known although Stein[22] suggests the following reaction scheme for the slight reaction between Cu or Ni and IF_5.

$$M(s) + IF_5(g) \longrightarrow MF_2(s) + IF_3(g)$$

$$M(s) + IF_3(g) \longrightarrow MF_2(s) + IF(g)$$

No evidence for these reactions is presented however.

A recent short study of the reactions between Hg, Ag and IF_5 was undertaken.[170] This work involved a spectroscopic investigation of the products obtained from reactions between IF_5 and each metal using both IF_5 and CH_3CN as solvents. The results, together with those from the present work will be discussed later.

Much more work has been carried out on reactions between IF_5 and metal fluorides than on IF_5 and metals. The main incentive for this is the interest surrounding the IF_6^- ion. At one time, the IF_6^- ion was thought to be polymorphic. There was much controversy over vibrational spectra until it was found that two products could be formed from the reaction between CsF and IF_5, namely $CsIF_6$ and $CsF{\cdot}3IF_5$.[59] Two main routes have been found to IF_6^- compounds. The method used by most workers is to heat a metal fluoride such as CsF with excess IF_5 in a metal bomb. However, Meinert and co-workers have reported the preparation of several IF_6^-

compounds by using CH_3CN as solvent. Christe[59] and Meinert[63] have shown that the highest possible symmetry for IF_6^- would be C_{2v}. Christe does not propose a structure but two possibilities are discussed by Meinert (Figure 4). Although the most common reactions of IF_5 with fluorides are fluoride ion addition (IF_6^-) and donation e.g. $IF_4^+ AsF_6^-$, the discovery of $CsF.3IF_5$ showed that adduct formation is also possible. The precise formulation of $CsF.3IF_5$ is not known but vibrational spectra rule out the simple IF_6^- ion.

The aim of this section of the work was to study the redox reactions between IF_5 and metals, to attempt to rationalise the various aspects of the reactions between IF_5 and metal fluorides, and to investigate the IF_6^- ion.

Results and Discussion

I Reaction of Thallium with IF_5

Thallium metal reacts with IF_5 over a period of 24 hours at 298K. A white precipitate and iodine are the products. The solid analyses as F_6ITl and the equation for the reaction is:

$$10Tl + 12IF_5 \longrightarrow 10TlIF_6 + I_2$$

The compound $TlIF_6$ can be isolated by removal of I_2 and excess IF_5 but is very unstable to hydrolysis. In this respect, it is much less stable than IF_5. $TlIF_6$ reacts with water to give HF and a white precipitate but does not release iodine. This is good evidence that the iodine is present as I(V), since I(III) compounds disproportionate in water to give a mixture of I_2 and I(V).[171]

$TlIF_6$ was found to be insoluble in IF_5, CH_3CN or a mixture of the two solvents. The insolubility of the compound in these media prevented solution spectra being obtained and the extreme instability to hydrolysis was a problem in obtaining spectra of the solid. I.r. spectra were recorded but show only very broad bands in the I-F region due to hydrolysis products. A Raman spectrum of the solid shows a band which corresponds to the most intense band in the spectrum of IF_6^-, and most of the others can be assigned as IOF_4^- bands. (Table 13). The assighments are made by comparison with the IOF_4^- data reported by Milne and Moffett[200], which was published after this work was completed. The sample of $TlIF_6$ showed signs of decomposition in the laser beam of the Raman spectrophotometer. On the

Figure 17

Raman Spectrum of Product from Tl+IF$_5$ Reaction

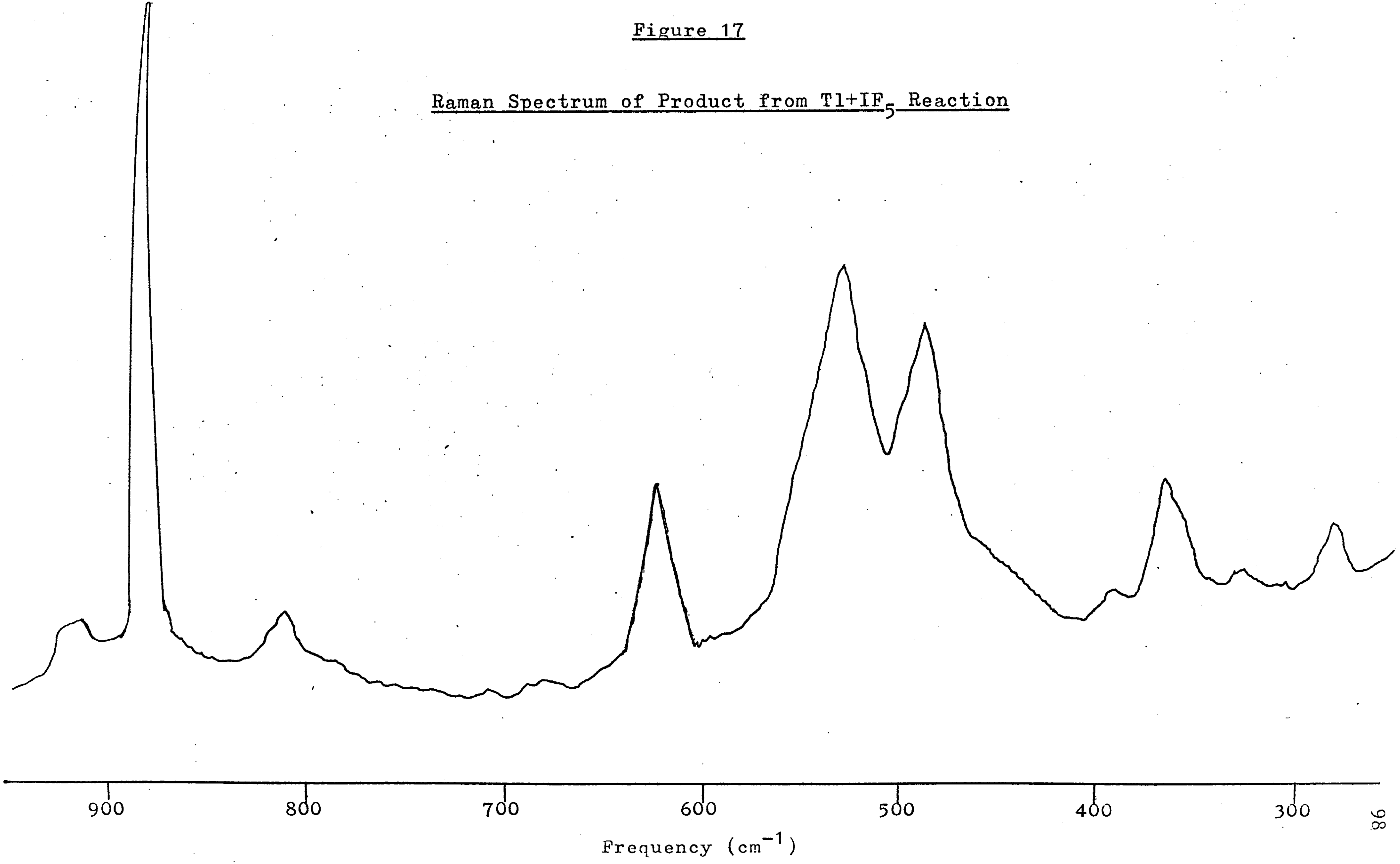


Table 13

Vibrational data on product from $Tl+IF_5$ reaction

Raman (cm^{-1})	I.r. (cm^{-1})	Assignments[1]
200 (0+)		IOF_4^-, ν_6
280 (1)		IOF_4^-, ν_3
325 (0+)		$IO_2F_2^-$
370 (2)		IOF_4^-, ν_8
385 (0+)		
485 (6)	475 s, br	IOF_4^-, ν_4 and ν_7
530 (7)	550 sh	IOF_4^-, ν_2
620 (4)	620 sh	IF_6^-
	730 s	IO_3^-
876 (14)	870 vs	IOF_4^-, ν_1

[1] IOF_4^- assignments from reference 200.

basis of the Raman data, the solid is formulated as Tl^+ IF_6^-.

The reaction between Tl and IF_5 presumably proceeds as follows:

$$Tl \longrightarrow Tl^+ + e^-$$
$$IF_5 + 2e^- \longrightarrow IF_3 + 2F^-$$
$$IF_5 + F^- \longrightarrow IF_6^-$$
$$5IF_3 \longrightarrow 3IF_5 + I_2$$

Overall: $10Tl + 12IF_5 \longrightarrow 10TlIF_6 + I_2$

This reaction makes an interesting comparison with those of AsF_5 with Mn, Cu, Ni; and SbF_5 with Mn, Fe and Ni in liquid SO_2.[172,173] As a typical example, excess Cu reacts with AsF_5 according to:

$$2Cu + 3AsF_5 \xrightarrow[298K]{SO_2} 2Cu^+AsF_6^- + AsF_3$$

Excess AsF_5 leads to the formation of Cu(II) $(AsF_6)_2$

These results are extremely important as they closely resemble the proposed reaction scheme for the reaction of Tl and IF_5. AsF_5 and SbF_5 undergo a 2 electron reduction to the trifluoride, plus fluoride ions which combine with other pentafluoride molecules. This is proposed in the reaction of Tl with IF_5, but in this case the trifluoride is extremely unstable to disproportionation and the products are IF_6^- and I_2, rather than IF_6^- and IF_3.

Despite the fact that Tl^+ is soluble in CH_3CN (as $TlWF_6$)[196] and IF_6^- is also soluble[61] (as $NR_4^+IF_6^-$, R = Me, Et), $TlIF_6$ is insoluble. The alkali metal salts of IF_6^- are also insoluble. The salts which are soluble in acetonitrile are those which have very large cations, tetramethyl and tetraethyl ammonium cations. The lattice energy in these salts will therefore be much less than with metal cations and the solvation energy is large enough to overcome this.

II Reaction of Thallium(I) Fluoride with IF_5

Thallium(I) fluoride dissolves very slowly in a large excess of IF_5 to give a clear solution. On removal of excess IF_5, a white solid is left. Weight differences indicate that the solid has a $TlF:IF_5$ ratio of 1:1. This was confirmed by elemental analysis which agrees well with the formula $TlIF_6$. If the starting ratio of $IF_5:TlF$ is very large, (greater than 24:1) then a very viscous, colourless liquid can be isolated. Weight differences correspond to a composition $TlF.3IF_5$. No authentic Raman spectra of the white solid were obtained, due to serious decomposition in the laser beam although six different exciting lines were tried. The Raman spectrum of $TlIOF_4$ was obtained on each occasion, and this is believed to be the major decomposition product. X-ray powder data on the white solid (Appendix) are very similar to those obtained from $Tl^+IF_6^-$ (from $Tl+IF_5$) and both are believed to be due to $TlIOF_4$.

Raman and ^{19}F n.m.r. spectra of $TlF+IF_5$ reaction mixtures were run and show only peaks due to IF_5. A 0.5M solution of $TlF.IF_5$ in IF_5 was prepared and its ^{19}F n.m.r. spectrum recorded. This also shows only signals due to IF_5. This spectrum is well resolved and the parts of the spectrum where IF_6^- peaks have been reported were scanned very carefully but no other signals were observed. Since the concentration of the compound was high enough to detect signals, it is believed that this is consistent with $TlF.IF_5$ rather than $Tl^+IF_6^-$. Other evidence which supports this is the absence of IF_6^- bands in solution Raman spectra and, the solubility of the compound in IF_5. The solubility is much larger than is the case for $Tl^+IF_6^-$. $TlF.IF_5$ is insoluble in CH_3CN.

The viscous liquid $TlF.3IF_5$ after pumping at 298K under very high vacuum, slowly loses weight until the composition is close to $TlF.2IF_5$, at which stage the compound is still liquid. Addition of CH_3CN followed by overnight shaking gives a white solid beneath a colourless liquid. On hydrolysis, the white solid yields iodine, indicating that I(III) is present.

III Reaction of Thallium(I) Fluoride with IF_5 in the presence of CH_3CN

TlF also reacts with IF_5 in the presence of CH_3CN, however the reaction takes a completely different course. CH_3CN is an excellent solvating agent for soft metal cations, especially those with a d^{10} configuration where back-bonding interactions occur.[174] Ions such as Cu(I) and Tl(III) are therefore particularly stabilised by CH_3CN. Cu(I) and Cu(II) salts can both be prepared easily in CH_3CN whereas in water Cu(I) is extremely unstable to disproportionation to Cu(0) and Cu(II). The presence of acetonitrile affects redox potentials and, for example, by stabilising ions such as Tl(III), the potential of the $Tl^+ \rightleftharpoons Tl^{3+} + 2e^-$ system is reduced, making Tl(III) more accessible. The $TlF+IF_5$

reaction illustrates this point well. Without CH_3CN, the reaction is simply one of adduct formation. However, with CH_3CN present, a redox reaction occurs. TlF reacts slowly with an IF_5-CH_3CN mixture to give an insoluble white solid and a trace of iodine. The solid analyses as F_6ITl_2. On hydrolysis, iodine is liberated indicating the presence of I(III) Raman spectra of the solid show a strong band at ca 465cm^{-1} but none at a higher frequency. This band agrees reasonably well with the most intense band in the Raman spectrum of Cs_3IF_6[58] which is believed to contain the hexafluoroiodate (III) anion. (Table 14). On this basis, Tl_2IF_6 is formulated as $Tl(I)_3$ Tl(III) $(I(III)F_6)_2$. The i.r. spectrum shows a very strong broad band at 460cm^{-1} and a weak band at 370cm^{-1} which are in reasonable agreement with Cs_3IF_6.[58] A band at 610cm^{-1} is attributed to residual IF_5 and some bands due to hydrolysis products are also observed. The occurrence of a band at ca 460cm^{-1} in both the Raman and i.r. spectra rule out the possibility that the IF_5^{3-} ion has O_h symmetry. The possible presence of the IF_4^- ion in Tl_2IF_6 can be ruled out from the Raman spectra which show only one band, whereas in $CsIF_4$, there are two bands of similar intensity. (Figure 18).

The exact nature of the cation is not known, but the "Tl_2^{3+}" entity occurs in some thallium halides. These have the empirical formula Tl_2X_3 (X = Cl or Br) and are known to exist[177] as 3Tl(I), Tl(III), $(X^-)_6$. On this basis, the most likely composition of the "Tl_2^{3+}" unit in Tl_2IF_6 is 3Tl(I) + Tl(III). The compound should then be written $Tl_4(IF_6)_2$ but it will be referred to as Tl_2IF_6.

Table 14

Vibrational data on Tl_2IF_6 and Cs_3IF_6

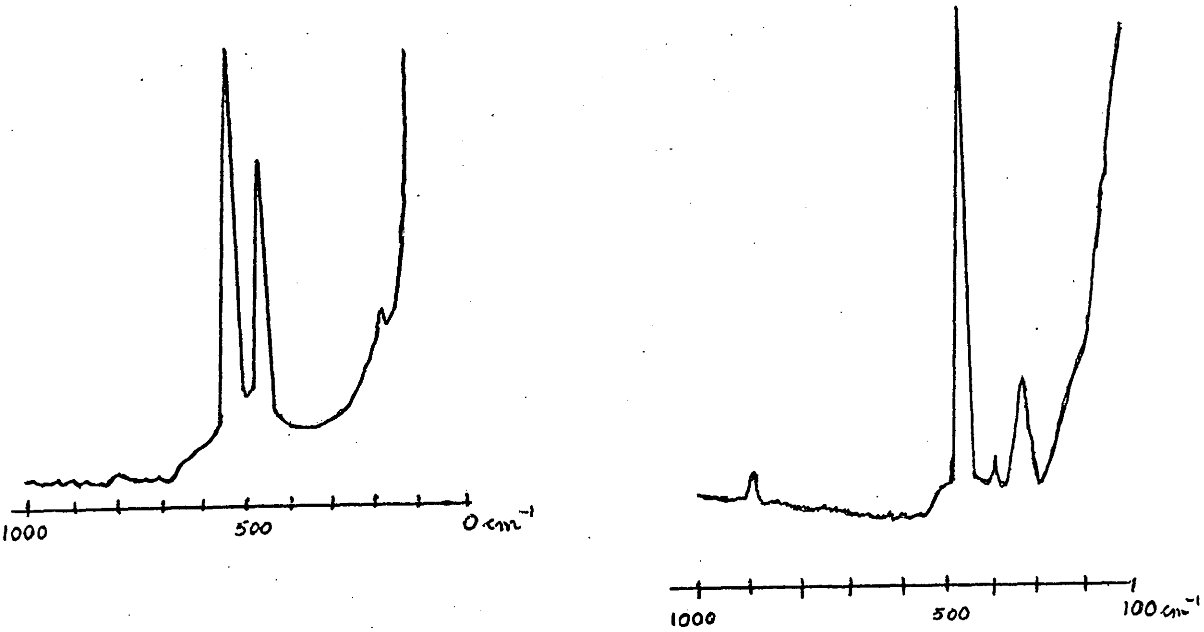
Tl_2IF_6[1]		Cs_3IF_6[2]	
Raman (cm^{-1})	I.r. (cm^{-1})	Raman (cm^{-1})	I.r. (cm^{-1})
		225 (0+)	225 w
		255 (0+)	255 w
	370 w	345 (2)	345 m
		405 (0+)	405 s
468 vs	460 vs, br	480 (9)	480 vs
	940 sh (CH_3CN)		
	2280 w (CH_3CN)		

1 Data from this work

2 Data from reference 58

Figure 18

Raman Spectra of $CsIF_4$ and Cs_3IF_6[58]



$CsIF_4$ Cs_3IF_6

Tl_2IF_6 cannot be the only product from the reaction, and TlF_3 may also be formed. No direct evidence of its formation was found but if it formed a soluble complex with IF_5 and CH_3CN then it would have been decanted off the solid Tl_2IF_6. The presence of unreacted TlF prevented isolation of any soluble species. The most likely reaction scheme is believed to be:

$$5TlF + 2IF_5 \xrightarrow{CH_3CN} Tl_4(IF_6)_2 + (TlF_3)$$

The presence of a small amount of residual CH_3CN in Tl_2IF_6 was detected by elemental analysis and i.r. spectroscopy. In this reaction the IF_5 is being reduced to an I(III) species which is stable to disproportionation, unlike the I(III) compound produced in the Tl and IF_5 system. Possibly this stability is due to the fact that the compound is solid, and is stabilised by its lattice energy.

Since TlF_3 is proposed as a possible product from the $TlF + IF_5 + CH_3CN$ reaction, the behaviour of the trifluoride in the mixed solvent system was investigated.

IV Reaction of Thallium(III) Fluoride with IF_5 in the presence of CH_3CN

This reaction does not go to completion and TlF_3 is still present, but on removal of solvent, a viscous, involatile, colourless liquid is left, in addition to unreacted TlF_3. The ^{19}F n.m.r. spectrum of this liquid shows only a doublet and quintet, very similar to the spectrum of pure IF_5. The i.r. spectrum also shows bands attributable to IF_5 and CH_3CN, with others due to hydrolysis products. (Table 15) The Raman spectrum of the liquid is less easy to explain. Bands due to IF_5 and CH_3CN are present and are easily identified, but in the lower frequency region there are six bands which cannot be assigned with certainty. The most intense of these bands occurs at $345cm^{-1}$, the others occurring at 321, 305, 270 and 240 cm^{-1}. Some of these bands may be due to Tl-F vibrations.

The vibrational and n.m.r. spectroscopic data overall strongly suggest that the liquid is a molecular adduct between TlF_3, IF_5 and CH_3CN. This therefore explains the non-isolation of TlF_3 in the $TlF + IF_5 + CH_3CN$ reaction.

V Reaction of Mercury with IF_5

This reaction was investigated by Paolini[170] in an attempt to characterise $Hg(IF_5)_2$, the product claimed by Aynsley et al.[81] A white solid was isolated whose Raman spectrum shows 15 bands, all below $500cm^{-1}$. The band at

Table 15

Vibrational Data on product from reaction of TlF_3 with IF_5 in CH_3CN

Raman (cm^{-1})	I.r. (cm^{-1})	Assignment
215 (1)		I_2
240 (3)		
270 (4)		
305 (0+)		
321 (1)		
345 (15)		Tl-F?
375 (0+)	375 w	IF_5/CH_3CN
570 (2)	570 w	IF_5 ν_4
585 (3)	600 s, br	IF_5 ν_2
690 (5)	685 m	IF_5 ν_1
	750 w	IO_3^-
	870 s	IOF_4^-
	930 m	CH_3CN
	1035 s	
1330 (1)		
	1370 s	
	1430 s, br	
1610 (0+)		
1902 (3)		
2258 (0+)	2260 w	CH_3CN
2300 (0+)	2280 w	CH_3CN
2325 (0+)	2300 w	CH_3CN

377 cm^{-1} was especially intense. The i.r. spectrum shows a main absorption at ca 500 cm^{-1}. These vibrational data suggest that the iodine is present as I(III). Elemental analysis gave the composition of the white solid as $Hg_3I_2F_6$. No distinct product could be identified and the reaction scheme remained unknown. This reaction was reinvestigated by the present author.

Hg reacts slowly with IF_5 at 298K yielding, initially traces of Hg_2I_2 but then very much larger amounts of an insoluble white solid which analysed as $HgIF_3$. A second sample analysed as $HgIF_6$. The product from this reaction was hydrolysed and iodine was released, indicating the presence of I(III). KI solution was added, the iodine extracted and the amount determined. The amount of iodine released on addition of I^- depends on the oxidation state of the positive iodine. The percentage of iodine in the sample was calculated to be 19•8% if all iodine present as I(V), 29•5% if I(III) and 59•1% if I(I). The previous elemental analyses had given %I as 26•05, 28•58 and 32•47% and therefore the figure based on the assumption that the iodine is present mainly as I(III) seems the most reasonable. This substantiates the conclusions drawn from the Raman spectra obtained by Paolini.[170] The Raman spectra do not show bands assignable to either IF_4^- or IF_6^{3-} ions but suggest I(III).

The IF_5 is almost certainly reduced to an I(III) species by the usual two electron reduction step. The difference between the Hg-IF_5 reaction and the two redox reactions already discussed is that the degree of disporportionation of the I(III) compound is neither complete, such as with $Tl+IF_5$, nor negligible, such as in the $TlF+IF_5+CH_3CN$ case. With the $Hg+IF_5$ system the amount of disproportionation appears to be variable, This causes the product isolated to be a mixture, which makes the results of elemental analysis of little value. If I(III) disproportionates to give I_2 as a product, then Hg_2I_2 and HgI_2 will be formed since mercury reacts very much faster with iodine in IF_5 than with IF_5 itself. To determine whether the iodides of mercury were possible products, each was shaken with IF_5. Hg_2I_2 shows no signs of reaction after a week, but HgI_2 reacts over the same period producing iodine and a pink-coloured solid. These results mean that Hg_2I_2 produced in the $Hg-IF_5$ reaction would remain as a product, but HgI_2 reacts further, and the amount present would depend on the duration of the experiment.

Occasionally during the reaction between Hg and IF_5, a yellow solid is deposited on the walls of the reaction vessel. This material produces a different Raman spectrum from the main solid product and shows an intense band at 151 cm^{-1}, assigned as an Hg-Hg stretch, as well as eight weaker bands all below 400cm^{-1}. Three of these are assigned as Hg_2F_2 bands.[178] Overall, in the $Hg-IF_5$ system, the main reaction is believed to be reduction of the IF_5 by mercury to given an I(III) species, as in previous redox reactions.

The I(III) compound then partially disproportionates to I_2 and IF_5 and side reactions occur such as

$$2Hg + I_2 \longrightarrow Hg_2I_2$$

$$Hg + I_2 \longrightarrow HgI_2$$

$$Hg + HgI_2 \longrightarrow Hg_2I_2$$

$$HgI_2 + IF_5 \longrightarrow Hg_2F_2\ ? + I_2 + ?$$

These side-reactions therefore complicate what is probably a relatively straightforward redox reaction.

Aynsley et al[81] studied this reaction at 373K but unless it is markedly different at the higher temperature, their results are misleadingly simple and the analysis HgI_2F_{10} is probably fortüitous.

VI Reaction of Silver with IF_5

In contrast to previous workers[22], Paolini reported[170] that silver is attacked by IF_5 but in the present work, no evidence for such a reaction was obtained.

VII Reaction of Silver with IF_5 in the presence of CH_3CN

Silver metal dissolves slowly in an IF_5-CH_3CN mixture, releasing elemental iodine. Removal of iodine, excess IF_5 and CH_3CN in vacuo leaves a colourless viscous liquid. A yellow-brown solid can be obtained but only after a long period of pumping at 323K.

A Raman spectrum of the viscous liquid obtained after pumping for one hour, shows only bands due to IF_5 and CH_3CN. A second spectrum of the liquid after a further two hours pumping also shows only bands due to IF_5 and CH_3CN but in this spectrum the IF_5 bands are relatively weaker than those of CH_3CN, indicating preferential loss of IF_5. ^{19}F n.m.r. spectra of reaction mixtures show only a broad signal at + 14 ppm. (Several reaction mixtures were used to show that the broad signal was not due to a small amount of HF causing exchange). The ^{19}F n.m.r. spectrum of the viscous liquid shows an even broader signal at + 14 ppm, the width of the signal at half height being 900 Hz. The chemical shift of this peak is the weighted average of the two IF_5 peaks, and indicates fast exchange between the fluorine atoms. The ^1H n.m.r. spectrum of the reaction mixture shows a very sharp singlet at +2·33 ppm due to CH_3CN but the ^1H n.m.r. spectrum of the viscous liquid shows a much broader peak at +2·63 ppm. The broadening of the ^{19}F and ^1H n.m.r. spectra of the viscous liquid could be due to the presence of paramagnetic Ag(II) ions, but this is unlikely since it would be surprising if Ag(II) could co-exist in solution with I_2.

An i.r. spectrum was run of the solid produced by warming the liquid to 323K in vacuo. It shows bands consistent with IF_5 but these may have been due to residual liquid IF_5 since the solid could not be obtained powdery but was still "mushy". No Raman spectrum of the solid could be obtained because of decomposition of the sample in the laser beam. (The solid, being pale brown, absorbed all exciting lines used). On hydrolysis of a sample of the solid, no iodine was liberated. This indicates that no I(III) is present. On the basis of the data obtained, the liquid is believed to be a molecular adduct between IF_5, CH_3CN and AgF. A possible reaction scheme is:

$$Ag \longrightarrow Ag(I) + e^-$$

$$IF_5 + 2e^- \longrightarrow IF_3 + 2F^-$$

$$5IF_3 \longrightarrow 3IF_5 + I_2$$

Overall:

$$10Ag + (m + 2)\ IF_5 + (n)\ CH_3CN \rightarrow 10AgF(IF_5)_m(CH_3CN)_n + I_2$$

In this reaction, disproportionation of the I(III) species is complete.

Meinert and co-workers have reported that AgF reacts with IF_5 in CH_3CN to form[61] $Ag^+IF_6^-$. However no evidence for the presence of IF_6^- was obtained in this work.

VIII Reaction of Gold with IF_5 in the presence of CH_3CN

No evidence of a reaction between Au and IF_5 in CH_3CN was obtained after 10 days shaking.

IX Reaction of Copper with IF_5

Copper metal reacts extremely slowly with IF_5. After several days shaking, a very fine suspension of solid particles and a trace of iodine are present. On removal of the IF_5 and iodine, unreacted copper and a very small amount of a brown solid are isolated. The quantity of solid product is too small to obtain even a Raman spectrum. On addition of CH_3CN, a yellow solution is obtained, which suggests that the solid contains Cu(I). To obtain a yield large enough to investigate would require weeks of shaking the reactants, and for this reason, the reaction was not investigated further.

X Reaction of Copper with IF_5 in the presence of CH_3CN

Copper reacts rapidly with an IF_5-CH_3CN mixture, completely dissolving when IF_5 is present in excess. Iodine is formed. Removal of excess solvents and iodine leaves a very pale blue, powdery solid. The solid decomposes rapidly in the laser beam of the Raman spectrophotometer and the spectra show only iodine and other decomposition products. I.r. spectra show bands due to I(V)-F and I(III)-F as well as others which cannot be assigned. A Raman spectrum of the solid redissolved in CH_3CN shows bands due to IF_5, I_2

and I(III)-F. Four separate samples from different reactions were analysed. In each reaction, the amount of IF_5 present was at least ten times the amount of copper. The samples analysed as:

1) $CuIF_6 \cdot CH_3CN$
2) Cu_3IF_{12}
3) $Cu_2I_3F_{18}$
4) Cu_2IF_5

The Cu:I:F ratios are all very close to integral, which strongly suggests that these are not mixtures. Samples 2, 3 and 4 also contain very small amounts of C, H, and N but these do not correspond to C_2H_3N. The analysis of the second sample, Cu_3IF_{12} suggests that either one Cu is present as Cu(III), some iodine is present as I(VII) or the small amount of C, H and N is in the form of a cation. None of these is likely and the analytical result is thought to be in error. The remaining three results can only be explained by invoking a situation similar to that in the Hg + IF_5 reaction, which involves a variable degree of disproportionation of the I(III) produced.

In the first sample, a possible explanation is

$$Cu + IF_5 \longrightarrow Cu^{2+} + IF_3 + 2F^-$$
$$\tfrac{1}{2}IF_3 + {}^3/2F^- \longrightarrow \tfrac{1}{2}IF_6{}^{3-}$$
$$\tfrac{1}{2}IF_3 \longrightarrow {}^1/10I_2 + {}^3/10IF_5$$

Half the IF_3 disproportionates and the product is

$$Cu^{2+} + \tfrac{1}{2}IF_6{}^{3-} + \tfrac{1}{2}F^- + \tfrac{1}{2}IF_5$$
$$Cu(II)_2\ (IF_6{}^{3-}).F.IF_5 \quad = \quad 2(CuIF_6)$$

In the third case:

$$2Cu + 2IF_5 \longrightarrow 2Cu^{2+} + 2IF_3 + 4F^-$$
$$\tfrac{1}{2}IF_3 + {}^3/2F^- \longrightarrow \tfrac{1}{2}IF_6{}^{3-}$$
$${}^3/2IF_3 \longrightarrow {}^3/10I_2 + {}^9/10IF_5$$

Three-quarters of the IF_3 disproportionates and the product is

$2Cu^{2+} + \frac{1}{2}IF_6{}^{3-} + {}^5/2F^- + {}^5/2\ IF_5$

$Cu(II)_4\ (IF_6)^{3-}\ F_5.5IF_5 = 2(Cu_2I_3F_{18})$

In the fourth case:

$Cu + IF_5 \longrightarrow Cu^{2+} + IF_3 + 2F^-$

$IF_3 + F^- \longrightarrow IF_4{}^-$

$Cu + Cu^{2+} \longrightarrow 2Cu^+$

No IF_3 disproportionates and product is

$Cu(I)_2.IF_4.F = Cu_2IF_5$

Concentrated solutions of the solid in CH_3CN were prepared and ^{19}F n.m.r. spectra recorded. No signals were observed and this is attributed to the presence of paramagnetic Cu(II) ions. A large sample of the solid was prepared in an attempt to record the ^{63}Cu n.q.r. spectrum. No signal was obtained however. Samples of the solid yield iodine on hydrolysis indicating the presence of I(III). The situation in this reaction is thought to be similar to that in the $Hg + IF_5$ system in that the I(III) compound disproportionates to a varying degree.

The main conclusion drawn from the redox reactions of IF_5 is that they all involve a 2 electron reduction step to an I(III) species. The final products however are governed by the behaviour of this I(III) species. In some cases disproportionation is complete, e.g. $Tl + IF_5$, whereas in others it is negligible, e.g. $TlF + IF_5 + CH_3CN$. However in cases such as $Hg + IF_5$ or $Cu + IF_5 + CH_3CN$ the disproportionation appears to occur to a variable degree and the reaction products are inconsistent.

XI Reaction of Copper(II) Fluoride with IF_5 in the presence of CH_3CN

CuF_2 does not react with IF_5 alone and is insoluble in CH_3CN. However, CuF_2 reacts very slowly with a mixture of the two solvents at 298K. Decanting the solution, followed by removal of excess solvents in vacuo leaves a very viscous, involatile blue-green oil. Pumping on this oil does not produce a solid product.

Raman spectra of the reaction mixture are very similar to those of IF_5 + CH_3CN mixtures. The ^{19}F n.m.r. spectrum shows only a doublet and quintet due to IF_5. The ^1H n.m.r. spectrum shows only a sharp singlet assigned to CH_3CN. (Table 16). Electronic spectra display the Cu(II) d-d band at <u>ca</u> 13,000 cm^{-1}, typical of Cu(II) in CH_3CN. Similar spectra are obtained when the oil is redissolved in CH_3CN, although the fine structure in the ^{19}F n.m.r. spectrum is lost. Raman spectra of the neat oil contain only bands due to IF_5 and CH_3CN. (Figure 19). I.r. spectra of the oil contain bands due to IF_5 and CH_3CN as well as one at 275 cm^{-1}. This may be a Cu-F or Cu-N vibration.

^{19}F n.m.r. spectra show a broad signal 3 ppm downfield from CCl_3F and a much weaker broad signal 50 ppm downfield, assigned to IF_5. No ^1H n.m.r. signal is observed in any spectrum of the neat oil. These results indicate that the CH_3CN molecules must be very close to the paramagnetic Cu(II) ions and the IF_5 molecules further away but still close enough for the spin-spin coupling to be destroyed. Raman spectra suggest however that the symmetry of the IF_5 and CH_3CN molecules has not been perturbed, implying that the oil is some form of molecular adduct. Samples of the oil were

Table 16

N.M.R. Data on $CuF_2.4CH_3CN.4IF_5$

Sample: Reaction Mixture

Nucleus	Signal	Chemical shift(ppm)	Coupling Constant (Hz)
^{19}F	Doublet (X_4)	+ 5 (±1)	85 ±3
	Quintet (A)	+53 (±1)	85 ±3
^{1}H	Sharp Singlet	+1·1(±0·05)	-

Sample: Neat Oil

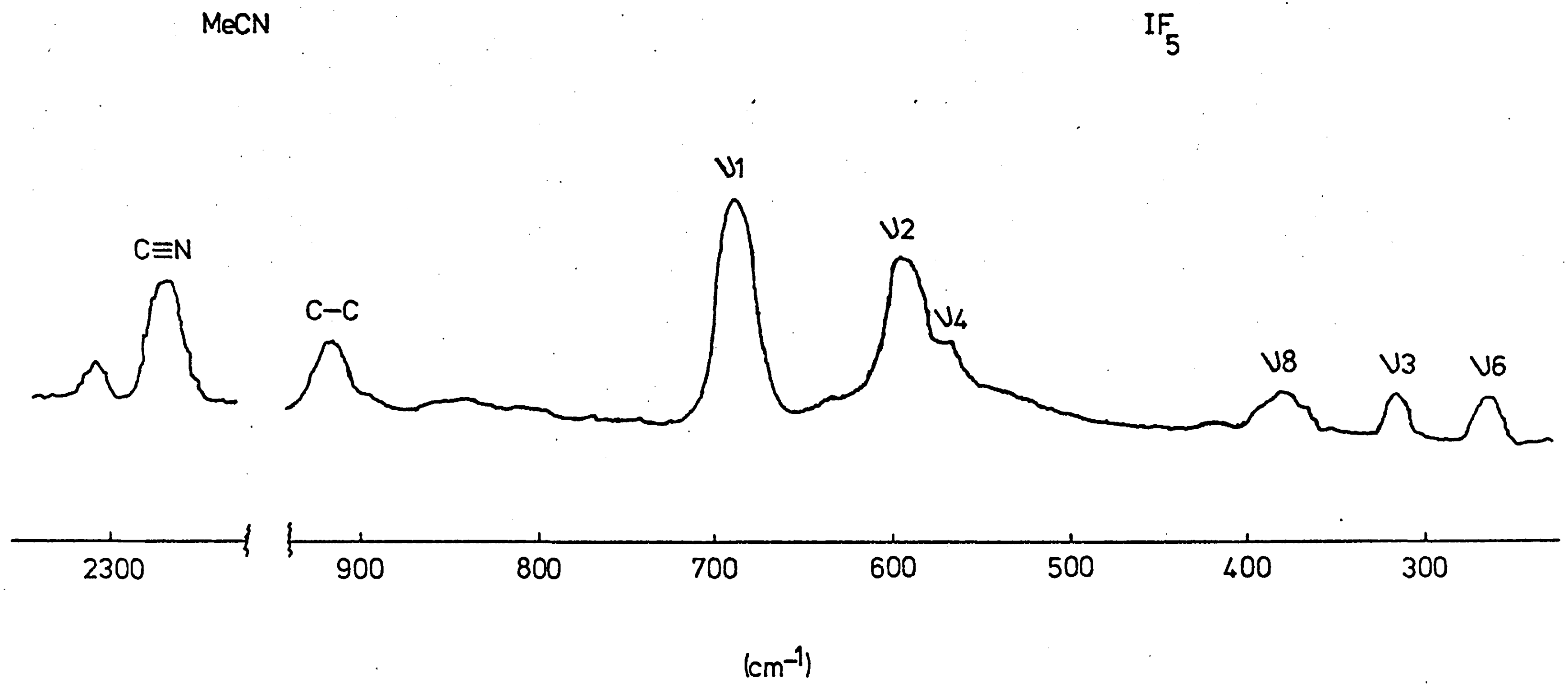
Nucleus	Signal	Chemical shift (ppm)
^{19}F	Broad peak	+ 3 (±2)
	Very broad peak	+50 (±3)
^{1}H	No signal observed	-

Sample: Oil redissolved in CH_3CN

Nucleus	Signal	Chemical shift (ppm)
^{19}F	Broad peak	+ 4 (±2)
	Very broad peak	+51 (±3)
^{1}H	Broad peak	+1·0 (±0·1)

Figure 19

Raman Spectrum of $CuF_2.4CH_3CN.4IF_5$



analysed and results agree well with the empirical formula $CuF_{12}I_4C_8H_{12}N_4$. The compound is therefore formulated as $CuF_2.4CH_3CN.4IF_5$.

E.p.r. spectra were recorded at 77K. (Figure 20). These spectra comprise two main signals, a weak one to low field and an intense signal to higher field. This is very characteristic of an axially symmetric system. The z-axis is taken as principal axis, thus making the z direction the parallel ($\|$) direction and the xy plane the perpendicular ($\perp$) direction.

$I^{63}Cu = I^{65}Cu = {}^3/2$ (and $\mu\ {}^{63}Cu \approx \mu^{65}Cu$)

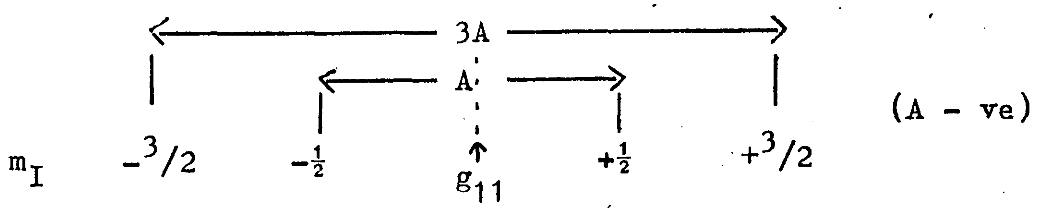
where I = nuclear spin quantum number and μ = magnetic moment.

$m_I = +{}^3/2, +\frac{1}{2}, -\frac{1}{2}, -{}^3/2.$

$E_{11} = g_{11}\ \beta_e\ m_sH_o + Am_sm_I$ + 2nd order terms

If the field is in the 11, i.e. z direction, then a quartet results. (Figure 21)

Figure 21



$\Delta E = h\nu = g_{11}\beta_eH_o$

h, β, H_o and ν are all known.

Hence g_{11} and A can be found

If the field is in the perpendicular direction: see Figure 22.

However the spectra were obtained from samples frozen as glasses, so that adduct molecules are all randomly orientated with respect to the external magnetic field. The relative intensity of the two signals is therefore

Figure 20

EPR Spectrum of $CuF_2.4CH_3CN.4IF_5$

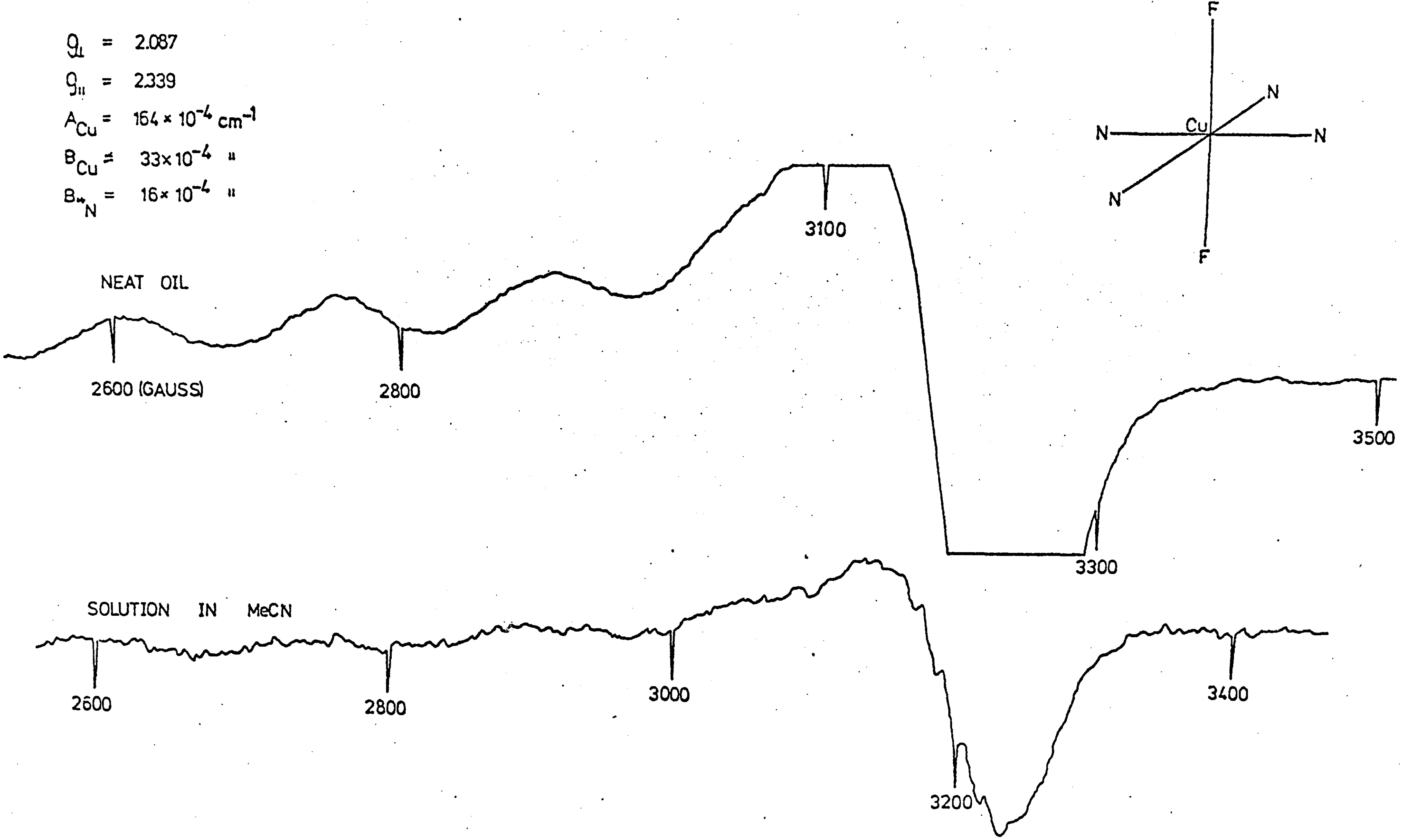
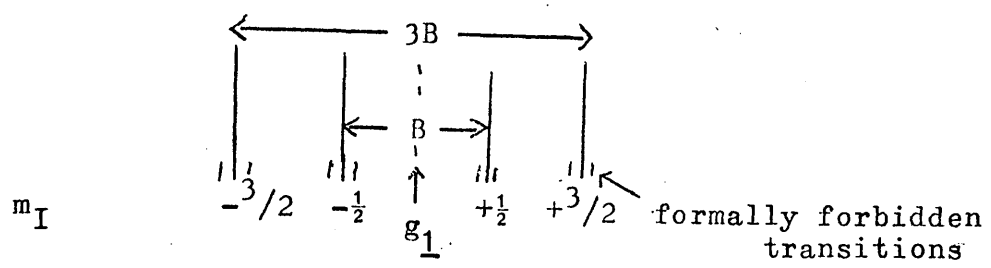


Figure 22



$$E_\perp = g_\perp \beta_e m_s H_o + B m_s m_I + \text{2nd order terms.}$$

proportional to the probability of the z-axis of the molecule being orientated parallel or perpendicular to the field. There will be many more molecules with the z axis ⊥ to the field than ∥, so the ⊥ signal is the more intense. (Figure 23).

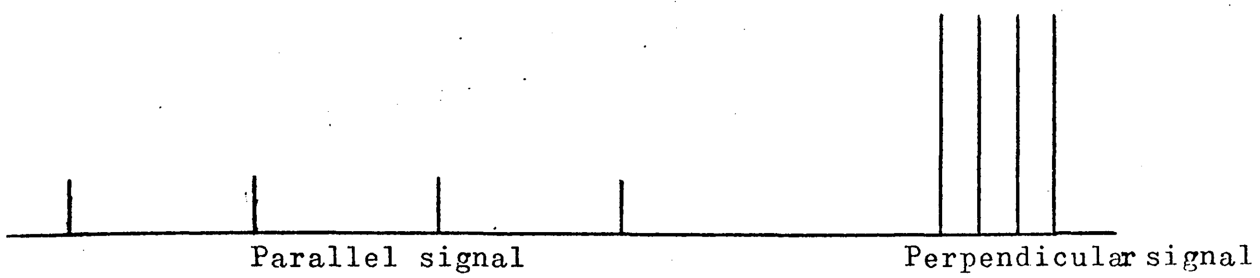
This "theoretical" spectrum fits the observed spectrum closely and shows that $CuF_2.4CH_3CN.4IF_5$ possesses local axial symmetry. However the perpendicular signal could not be resolved into its 4 components and an upper limit only can be given for B.

One striking feature of the two spectra shown is that despite the great difference in concentration, (>100x), the spectra are very similar, indicating retention of structure and strongly suggesting that the adduct is monomeric. Additional fine structure can be observed on the perpendicular signal of the dilute solution. At least five small peaks can be observed, which rules out allowed Cu hyperfine interaction. These could be due to formally forbidden Cu hyperfine interactions but the writer feels that they are more likely to be due to superhyperfine interaction between the unpaired electron and the four nitrogen atoms in the

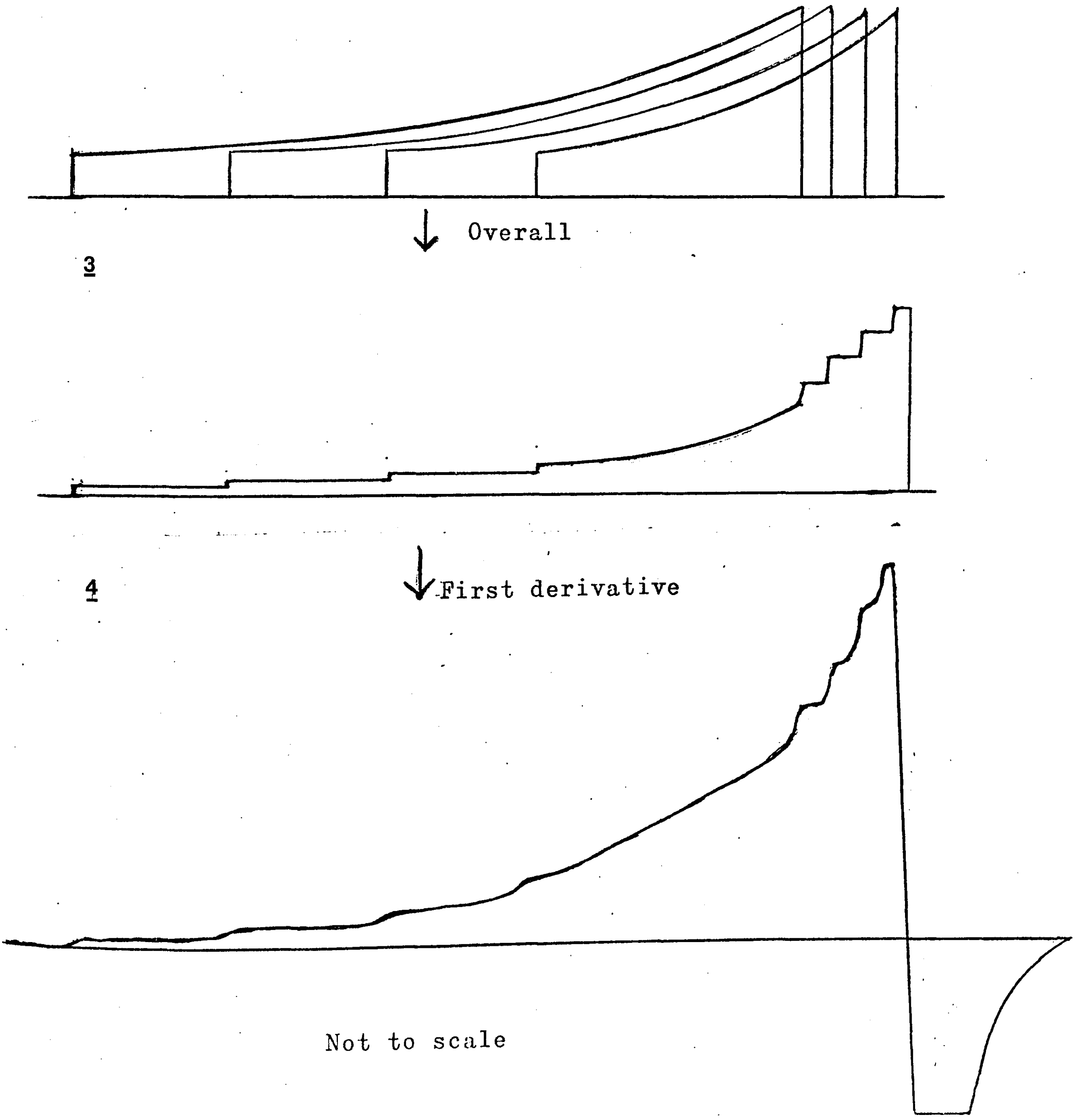
Figure 23

Derivation of e.p.r. spectrum of Cu(II) in an axially symmetric environment.

1 All molecules || or ⊥ to magnetic field.



2 Molecules randomly Orientated



Not to scale

in the acetonitrile molecules. Four equivalent ^{14}N atoms, (I = 1), coupling to an unpaired electron would split the e.p.r. signal into a nonet, the signals being of relative intensity 1:4:10:16:19:16:10:4:1. It is not surprising therefore that the four outermost peaks are not observed. The value of the peak separation corresponds to $1{\cdot}6\times10^{-3}cm^{-1}$ which is similar to known $B_{^{14}N}$ values.[181] One method of verifying that the fine structure is due to superhyperfine interaction between the ^{14}N nuclei and the unpaired electron would be to use acetonitrile labelled with ^{15}N which has a spin quantum number of $\frac{1}{2}$. If the fine structure is altered then this would be very good evidence for the presence of hyperfine interactions involving the nitrogen nuclei, and not the copper nucleus.

The results of the e.p.r. study are summarised in Table 17. The e.p.r. spectra are consistent with the unpaired electron being mainly in the $d_{x^2-y^2}$ orbital which is the expected situation for a Cu(II) ion in a tetragonally elongated octahedron. (Figure 24)

The electronic spectrum (d-d band centred at $13{,}000cm^{-1}$ with a shoulder at <u>ca</u> $10{,}600cm^{-1}$) resembles closely the spectrum of Cu(II) solvated by acetonitrile (λ max = $13{,}320$ cm^{-1})[180] but differs from that of Cu(II) surrounded by fluoride ions (peaks at 10,400 and $11{,}300cm^{-1}$).[191] The spectrum is consistent with the Cu(II) ion being at the centre of a tetragonally elongated octahedron, but not a regular octahedron. If the latter were true, the spectrum

Table 17

E.P.R. Data on $CuF_2 \cdot 4CH_3CN \cdot 4IF_5$. (77K)

Sample: Neat Oil

$g_{\underline{1}} = 2{\cdot}087 \pm 0{\cdot}002$

$g_{11} = 2{\cdot}339 \pm 0{\cdot}002$

$A = 16{\cdot}4 \pm 0{\cdot}4 \times 10^{-3}cm^{-1}$

Sample: Solution in CH_3CN, approximately 5% by volume

$g_{\underline{1}} = 2{\cdot}083 \pm 0{\cdot}002$

$g_{11} = 2{\cdot}345 \pm 0{\cdot}002$

$A = 16{\cdot}2 \pm 0{\cdot}4 \times 10^{-3}cm^{-1}$

$B \leq 3{\cdot}3 \pm 0{\cdot}3 \times 10^{-3}cm^{-1}$

Sample: Solution in CH_3CN, approximately 0·5% by volume

$g_{\underline{1}} = 2{\cdot}082 \pm 0{\cdot}002$

$B \leq 3{\cdot}0 \pm 0{\cdot}3 \times 10^{-3}cm^{-1}$

$B_{^{14}N} = 1{\cdot}6 \pm 0{\cdot}2 \times 10^{-3}cm^{-1}$

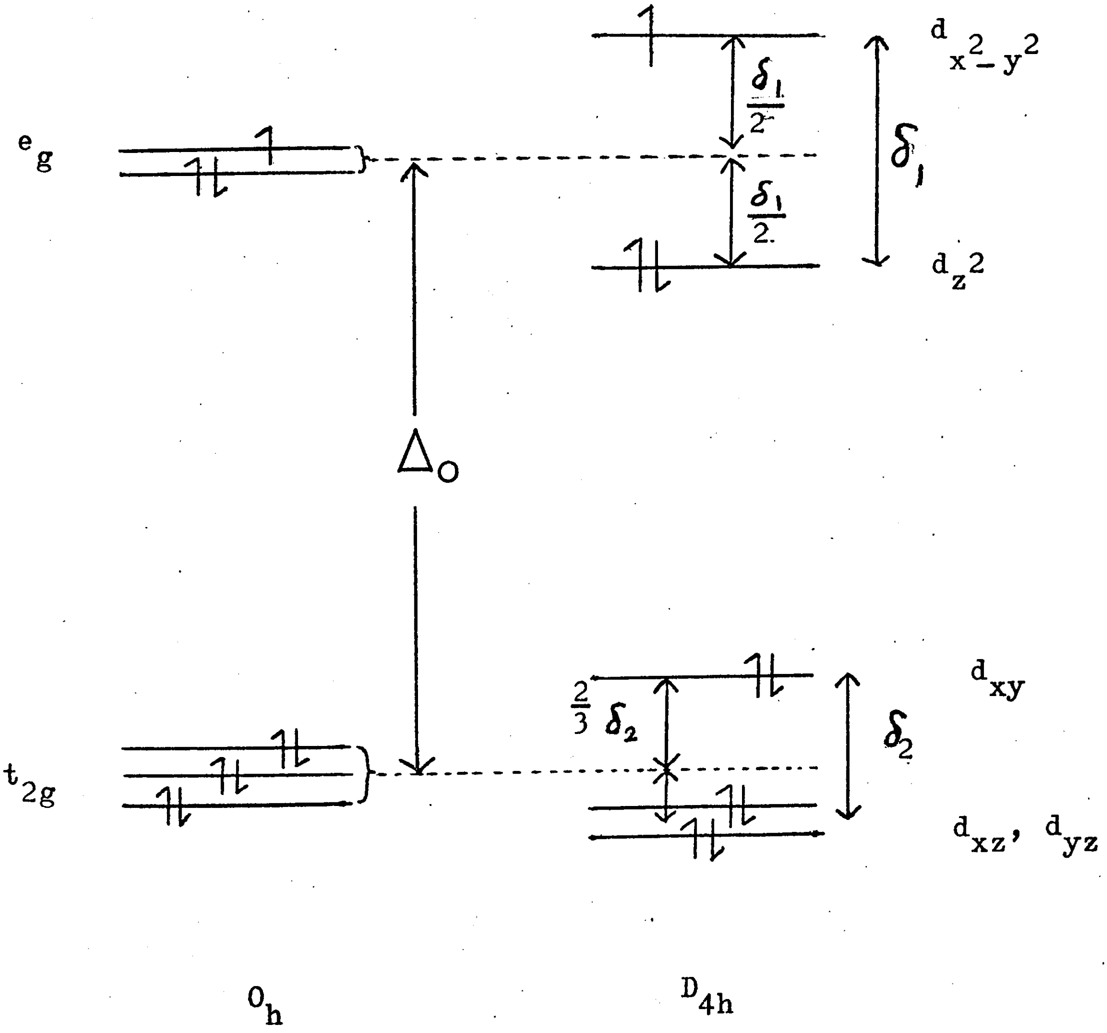
would be a single symmetric peak, corresponding to the $t_{2g} \longrightarrow e_g$ transition. If two trans ligands are further from the metal ion than the other four, three transitions are then allowed. (Figure 24). These bands are very broad and considerable overlapping takes place, resulting in an asymmetric peak.

The adduct dissolved in CH_3CN gives a green-blue solution but in IF_5 the colour is a much stronger blue. It was found however that the d-d band remains centred on 13,000 ± 100 cm^{-1} whether the adduct is neat, dissolved in CH_3CN or in IF_5. The change in colour observed is caused by variation in position of a very intense ligand-metal charge transfer band. In IF_5 solution, this band is almost entirely in the ultraviolet. However in the neat adduct and in CH_3CN solution, the band has a very long "tail", This extends well into the blue end of the visible region, while the Cu(II) ion absorbs in the red end, resulting in a green solution. On the other hand, in IF_5, only the copper absorbs in the visible region.

Combining the spectroscopic and analytical data on $CuF_2.4CH_3CN.4IF_5$ results in the conclusion that the most probable structure for this adduct is that shown in Figure 25. The Cu(II) ion is surrounded by two fluoride ions trans to each other and a square plane of four acetonitrile molecules, resulting in a tetragonally distorted octahedron as an "inner co-ordination sphere" for the copper ion. The four IF_5 molecules are assumed to take up positions where each is at the corner of a tetrahedron. F-I•••F-Cu contacts similar to those previously described are envisaged. The frequency of the C≡N stretch of the acetonitrile molecules is higher than it is in free CH_3CN (2266 instead of 2260cm^{-1}) but it is

Figure 24

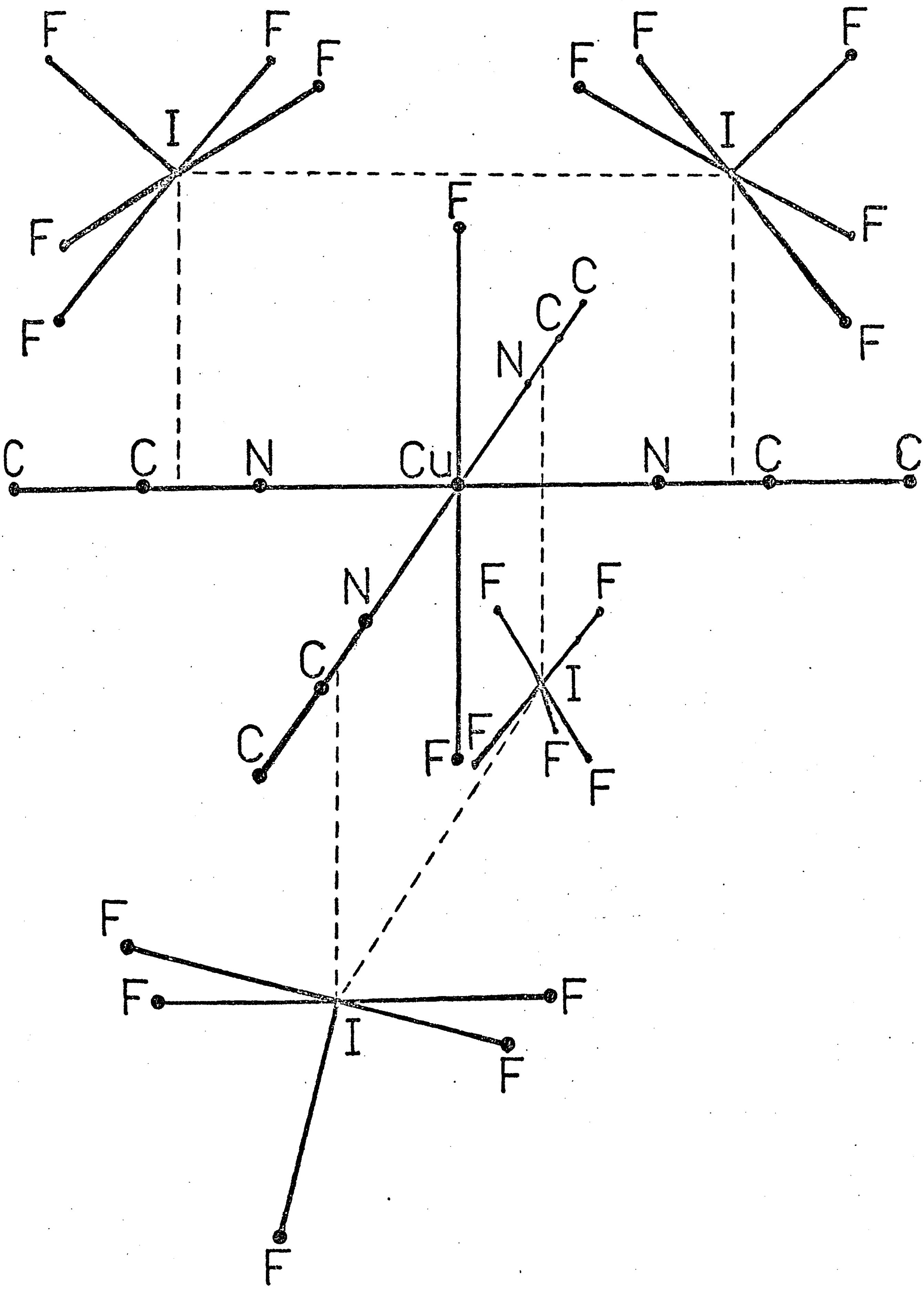
Splittings of a d^9 system caused by elongation of an octahedron along one axis (z)



Not to Scale

Figure 25

Structure of $CuF_2.4CH_3CN.4IF_5$



lower than is often found when CH_3CN co-ordinates to Cu(II).[167] The cause may be an interaction between the π electrons in the C≡N bond and the positively charged iodine atom. This would be opposite in effect to the normal σ donation of CH_3CN which increases the C≡N stretching frequency.[182] If CH_3CN molecules are involved in σ interaction with the copper ion and π interactions with an iodine atom, then the resulting effect on the C≡N stretching frequency might well be a small increase rather than the large increase normally observed. Because of the possibility of π electron interaction between the acetonitrile and IF_5 molecules, the latter are tentatively placed in an eclipsed rather than a staggered conformation.

Although the IF_5 cannot be removed by pumping at room temperature, it can be removed through reaction. Copper metal was added to a solution of the adduct in CH_3CN in order to see if it reacted with the co-ordinated IF_5 or reduced the Cu(II) ion to Cu(I). The reaction proceeded rapidly with the release of iodine. It was therefore assumed that a reaction was proceeding between Cu and IF_5, similar to that previously described. Further reactions of the adduct will be discussed later in chapter 6.

The main conclusion from the reactions of metal fluorides with IF_5 is that in at least some cases, adduct formation is preferred to fluoride ion addition. For example, despite the fact that CuF_2 in CH_3CN is a good fluoride ion donor to WF_6, under the same conditions, IF_5 forms a molecular adduct instead of an IF_6^- compound.

Ideal molecular adducts such as $XeF_2.IF_5$ (and almost certainly $CuF_2.4CH_3CN.4IF_5$) contain short polar contacts ca 300 pm long, between the iodine atoms and neighbouring fluorine atoms. It is proposed that ideal molecular adducts, and the IF_6^- ion are two opposite extremes of a range of compounds involving I•••F contacts with non-ideal adducts in between. A good example of a non-ideal adduct would be $CsF.3IF_5$.[59] The vibrational spectra of this compound show that the IF_5 molecules are being perturbed to a greater extent than in $XeF_2.IF_5$. No fewer than fourteen bands in the Raman spectrum and ten i.r. bands are reported. These include many coincidences. These data suggest low symmetry for the adduct. However, comparison of the Raman spectra of $CsF.3IF_5$ and liquid IF_5 show some possible correlations. (Table 18). The apparent splitting of an IF_5 E mode indicates lower symmetry for the IF_5 molecules in the adduct. There are other weak bands present and the adduct is most probably of C_s symmetry. The I•••F contacts in this case are probably much shorter than 300 pm but longer than the I-F bond length in IF_6^-. This would lead to significant perturbation of the IF_5 molecules destroying the C_{4v} symmetry, but without the formation of formal I-F bonds.

The distinction between such non-ideal molecular adducts and IF_6^- salts is not a clear one. There is almost certainly a gradation between the two extreme cases of ideal molecular adduct and IF_6^-, depending on the length of the I•••F contact. One way of looking at the IF_6^- ion would

Table 18

Raman data, and possible correlations for $CsF.3IF_5$

$CsF.3IF_5$[1]	IF_5 (liquid)[2]	
Frequency (cm^{-1})	Frequency (cm^{-1})	Assignment (IF_5, C_{4v})
157 (1·5)		
186 (0·2)	191 (1)	ν_9 (E)
231 (0·2)		
271 (0·9)	274 (4)	ν_6 (B_2)
319 (0·4)	317 (4)	ν_3 (A_1)
367 (0·3) 382 (0·5)	375 (4)	ν_8 (E)
543 (3·0)	581 (17)	ν_4 (B_1)
557 (0+)		
568 (0+)		
585 (sh)		
593 (5·3)	597 (16)	ν_2 (A_1)
635 (0+)	635 (0)	ν_7 (E)
	700 (16)	'Polymer'
674 (10)	708 (16)	ν_1 (A_1)

1. Ref. 59.
2. Values from this work, assignments from ref. 164.

Figures in parentheses refer to relative intensities.

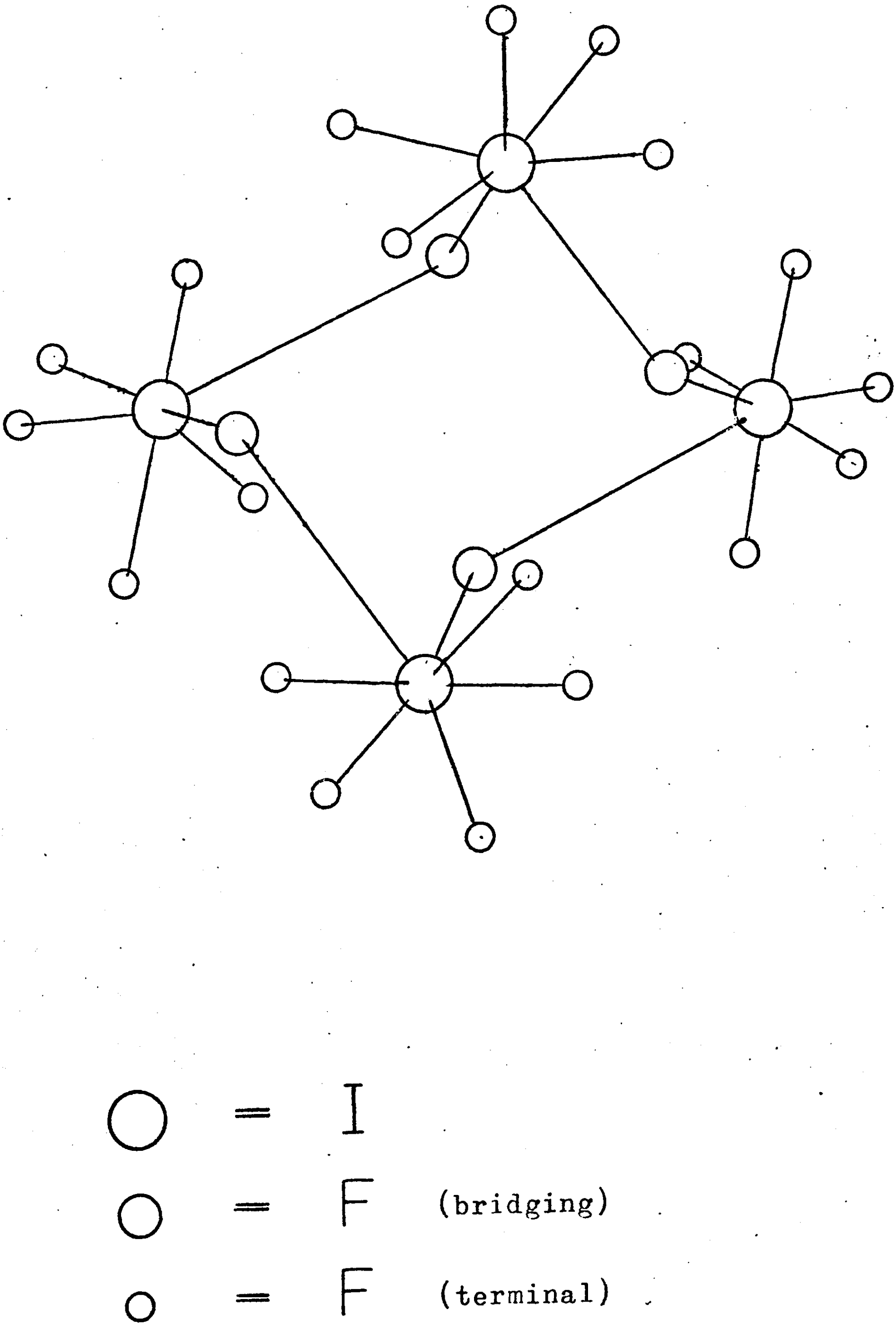
be therefore to consider it as the example where the I•••F interaction is so short that it has become similar to the length of a typical I-F covalent bond. Christe[59] has shown that the structure of $CsIF_6$ is not simple. The unit cell contains 18 "molecules" and the symmetry cannot be higher than C_{2v} for the IF_6^- ion. This latter conclusion was also reached by Meinert et al[63] who proposed a possible structure. (Figure 4). Meinert[69] proposes that the lone pair on the iodine is stereochemically active whereas it is much less active in BrF_6^-. D_{3d} symmetry is suggested for BrF_6^-.[69] However in these arguments it has been assumed that the IF_6^- ion is monomeric, although the isoelectronic species XeF_6 is known to be tautomeric in the solid and liquid states.[84,201] XeF_6 exists as tetramers and hexamers and is based on the association of XeF_5^+ and F^- ions. XeF_5^+ is isoelectric and isostructural with IF_5 and the F-Xe•••F contacts in solid XeF_6 are very similar to the F-I-F interactions previously discussed. The structures of BrF_6^- and IF_6^- ions have been compared frequently but it is considered by the author that an XeF_6-IF_6^- comparison is more meaningful, since bromine is considerably smaller than iodine whereas xenon is similar in size. The fact that XeF_5^+ and IF_5 are both isoelectronic and isostructural suggests that XeF_6 and IF_6^- might well have the same shape. An XeF_6 tetramer consists of four XeF_5^+ ions bridged by F^- ions. Each Xe has a short contact with one bridging F^- and a longer contact with the second. Burbank and Jones[84] state that "the term 'bridging' is used in the sense of an electrostatic interaction stronger than a Van der Waals contact". This statement reinforces the suggestion made earlier that IF_6^- could be considered as being the extreme case of F-I•••F interactions where the I•••F contact was very short. The bond lengths in solid XeF_6 illustrate this well. They are:

$Xe{\cdots}F_{apical}$ = 183 pm
$Xe{\cdots}F_{basal}$ = 184 pm
$Xe{\cdots}F_{bridging}$ = 223 pm (short contact)
$Xe{\cdots}F_{bridging}$ = 260 pm (longer contact)
(Sum of Van der Waals radii = 300 pm)

If IF_6^- is isostructural with solid XeF_6 tetramers (Figure 26) then each "IF_6" unit would have C_s (σ_d) symmetry while the whole tetramer would have C_2 symmetry. There would almost certainly be minor distortions to accommodate the cations but the suggested structure could easily give rise to the known spectra. The exact structure of the IF_6^- ion will remain unknown until an x-ray crystal structure determination is carried out. In the meantime, however, the present writer feels that a polymeric structure similar to that of solid XeF_6 is more likely tobe correct than the monomeric structure proposed by Meinert.

Figure 26

Suggested structure of IF_6^- ion, based on known structure of solid XeF_6 (cubic)



Experimental

Chemicals used were as follows (Table 19).

Table 19

Compound	Source	Purity
Ag		
Au		
Cu		
CuF_2	Ozark Mahoning	99•5%
Hg	F.W. Berk and Co.	
Hg_2I_2	F.W. Berk and Co.	
HgI_2	W. Jarvie and Co.	
Tl	B.D.H.	99•999%
TlF	Alfa	98•95%
TlF_3	Cerac Pure	99•9%
CCl_3F	B.D.H.	
CH_3CN	Koch Light	99•9%
IF_5	Fluorochem Limited	98%

IF_5 and CH_3CN were purified as previously described in chapter 2. CCl_3F was dried over activated Linde 4A molecular sieves and stored over molecular sieves. The metals were scraped free of oxide coating in an inert atmosphere box with a blade (for Tl) or abrasive paper (Cu and Ag). The other materials were used as received.

I Reaction of Tl with IF_5

Tl (<u>ca</u> 0·3g., 1·5 mmol) and IF_5 (<u>ca</u> 5g., 22mmol) reacted over a period of 24 hours, producing a white solid and elemental iodine. The reaction did not go to completion. $TlIF_6$ was obtained as a powdery white solid after removal of the I_2 and excess IF_5 in vacuo. Excess Tl was removed in an inert atmosphere box. In a typical reaction, 0·77 mmol of Tl were used and 0·78 mmol $TlIF_6$ formed. The reaction stoichiometry

$$10Tl + 12IF_5 \longrightarrow 10TlIF_6 + I_2$$

was confirmed by removal of the I_2 and IF_5, extracting the iodine with $CHCl_3$ (after hydrolysing the IF_5) and titrating it against standard sodium thiosulphate.

Amount of $TlIF_6$	produced	=	0·50 mmol
amount of I_2	expected	=	0·050 mmol
amount of I_2	obtained	=	0·045 mmol

Hydrolysis of $TlIF_6$, followed by the addition of KI solution and titration of the iodine produced, resulted in only half the expected amount of iodine. Despite precautions such as extraction of the I_2 using $CHCl_3$, a black precipitate was always formed. TlI is known to react with I_2 to give black Tl_3I_4[177] and it is believed that a similar side reaction was occurring between the Tl^+ ions and either I^- or I_2, reducing the amount of iodine released.

One sample of the white solid product analysed as:

F: 25·6, I: 28·2%; F_6ITl requires F: 25·6, I: 28·5%.

However a second sample from a different reaction gave

F: 18·4, I: 30·9%; F_4IOTl requires F: 18·0, I: 30·0%.

Vibrational spectroscopic data are shown in Table 13, and the spectrum is shown in Figure 17.

If the Tl+IF_5 reaction was allowed to continue over a period of several days, the white solid often redissolved. This may have been due to partial hydrolysis, and the resulting $TlIOF_4$ being soluble in IF_5. X-ray powder diffraction data on the white solid are shown in the appendix. The solid is believed to be $TlIOF_4$.

II The reaction of TlF with IF_5

TlF dissolved after shaking for 24 hours in a large excess of IF_5 (TlF:IF_5 = 1 : 21•2) producing a colourless solution. Removal of excess IF_5 gave a white solid, the weight of which indicated a TlF:IF_5 ratio of 1:1•06. A 1:1 stoichiometry was confirmed by elemental analysis. Found F: 25•4, I: 28•8%. F_6ITl requires F: 25•6, I: 28•5%.

A second sample from another reaction analysed as F: 18•8, I: 31•4%. F_4IOTl requires F: 18•0, I: 30•0%. X-ray powder diffraction data on the product from TlF+IF_5 (Appendix) gave a very similar pattern to that from Tl+IF_5, and is also believed to be $TlIOF_4$.

A mixture of TlF and IF_5 (TlF:IF_5 = 1:25) after removal of excess IF_5 gave as product a very viscous, colourless liquid whose weight indicated a composition TlF. 2.8IF_5. Pumping on this compound for over ten hours produced an even more viscous liquid which corresponded to a composition TlF.1•8IF_5. No solid could be obtained.

Raman spectra of the solid 1:1 adduct showed bands at 280, 310, 370, 385, 482, 522 and 874 cm^{-1}. These are assignable to $TlIOF_4$ but the sample showed signs of decomposition.

A 0•49M solution of $TlF \cdot IF_5$ in IF_5 was prepared. The ^{19}F n.m.r. spectrum showed only the doublet and quintet of IF_5. A Raman spectrum of a similar solution contained bands at 191, 274, 316, 376, 582, 697 and 707 cm^{-1}. These are all attributable to IF_5. $TlF.IF_5$ was insoluble in CH_3CN but $TlF.1.8IF_5$ reacted, forming a white solid. On hydrolysis, this solid released I_2, indicating the presence of I(III).

III The reaction of TlF and IF_5 in CH_3CN

This reaction proceeded slowly to give a very finely divided white solid, unchanged TlF and a trace of iodine. The fine white solid was separated from the much coarser TlF by swirling the reaction mixture, decanting the liquid and solid suspension into a sidearm and allowing the solid to settle. The liquid was then decanted back. Remaining volatiles were removed by vacuum distillation, leaving as product, a white powdery solid which occasionally contained some very small black specks which could not be identified. Two separate samples were prepared and analysed. (Table 20).

To demonstrate the presence of iodine in the I(III) state, a sample of the solid was hydrolysed and KI added. Unfortunately the side-reaction involving Tl^+ occurred and no result was obtained.

Table 20

	C	H	N	I	F	Tl (by difference)
Sample 1	0·8	0·1	0·5	19·4	17·0	62·3
Sample 2	0·6	0·2	0·6	18·9	17·0	62·8
Required for $Tl_2IF_6\cdot0\cdot2CH_3CN$	0·8	0·2	0·5	19·3	17·3	62·0

Vibrational data on Tl_2IF_6 and Cs_3IF_6 are given in Table 14.

IV Reaction of TlF_3 with IF_5 in CH_3CN

After 48 hours shaking, followed by removal of excess IF_5 and CH_3CN, a colourless viscous liquid was obtained. The reaction did not go to completion and unchanged TlF_3 was left. The liquid remained unaltered after 24 hours pumping. The ^{19}F n.m.r. spectrum of this liquid showed only the IF_5 doublet and quintet. Vibrational data are given in Table 15.

V Reaction of Hg with IF_5

Hg reacted slowly with IF_5 and Hg_2I_2 was the first product to be observed, although it was present in small amounts. After 24 hours shaking, much larger quantities of a pale grey solid were present. This was separated from unreacted Hg by decanting it, along with IF_5, into a sidearm and distilling back the IF_5. Two samples of the solid were analysed with the following results:

Found	F: 14·6,	Hg: 52·0,	I: 32·5%
Hg.IF_3 requires	F: 14·8,	Hg: 52·2,	I: 33·0%
Found	F: 25·4,	Hg: 45·4,	I: 28·6%
$HgIF_6$ requires	F: 25·8,	Hg: 45·4,	I: 28·8%

A Raman spectrum of the yellow solid deposited on the reaction vessel walls showed bands at 110(0+), 151(20) (Hg-Hg), 175(0+), 188(1) (Hg_2F_2) 200(0+), (Hg_2F_2), 266(0+), 287(0+), 323(0+), and 389 cm^{-1}(0+) (Hg_2F_2). Brick red HgI_2 reacted with IF_5 producing I_2 and a light pink-brown solid. This analysed as F: 8·0, Hg: 40·5, I: 51·3%. F_2HgI_2 requires F: 7·7, Hg: 40·7, I: 51·6%. The iodine released was titrated against $Na_2S_2O_3$ and a ratio of HgI_2 used :I_2 released = 1:1·05 was found.

VII The Reaction of Ag with IF_5 in CH_3CN

Ag foil and IF_5 did not react but on distilling CH_3CN into the reaction vessel, I_2 was observed. After shaking overnight, all the Ag had dissolved. Distillation resulted in loss of excess CH_3CN, IF_5 and I_2 leaving a colourless liquid. The Raman spectrum showed bands at 194(0+), 278(3), 330(2), 382(3), 390(3), 570(6), 598(11), 697(17), and 937(2)cm^{-1}. These were all assignable to IF_5 or CH_3CN. Prolonged pumping on this liquid produced an even more viscous liquid and a 'wet' solid. The Raman spectrum of this liquid contained bands at 195(0+), 277(2), 333(1·5), 384(1·5), 390(3), 570(4), 593(7), 692(13), 942cm^{-1}(2·5). The IF_5 bands are relatively weaker than the CH_3CN bands as compared with the earlier spectrum. An i.r. spectrum of the wet solid showed bands at 3020w, 2950m, 2310s, 2290s, 1440s, 1420 sbr, 1370s, 1225m, 1030s, 940w, 805w, 740vs, 600vs br, 500cm^{-1}w, consistent with IF_5, CH_3CN as well as hydrolysis products.

X The Reaction of Cu with IF_5 in CH_3CN

This reaction went to completion within ten minutes. Removal of excess solvents and iodine lead to the isolation of a pale blue-white solid without the intermediate formation of a viscous liquid. Analysis of a sample of the product from four different reactions gave:

<u>Sample 1</u> Found C: 6·7, H: 1·1, N: 3·8, Cu: 18·6, F: 32·7,
I: 36·6%

CuF_6I,C_2H_3N requires C: 6·9, H: 0·9, N: 4·1, Cu: 18·4,
F: 33·0, I: 36·8%.

<u>Sample 2</u> Found C: 4·1, H: 1·0, N: 4·3, Cu: 31·2, F: 37·3,
I: 20·8%

$Cu_3F_{12}I$,1·5C_2H_3N requires C: 5·9, H: 0·7, N: 3·5, Cu: 31·4,
F: 37·6, I: 20·9%.

<u>Sample 3</u> Found C: 5·2, H: 1·4, N: 4·2, Cu: 13·2, F: 36·0,
I: 39·8%

$Cu_2F_{18}I_3$,2·5C_2H_3N requires C: 6·3, H: 0·8, N: 3·7, Cu: 13·3,
F: 35·9, I: 40·0%

<u>Sample 4</u> Found C: 4·9, H: 0·7, N: 2·0, Cu: 33·6, F: 25·1,
I: 33·6%

Cu_2F_5I,0·75C_2H_3N requires C: 4·8, H: 0·6, N: 2·6, Cu: 33·5,
F: 25·1, I: 33·5%

An i.r. spectrum of the solid from one of these reactions showed bands at 735s (IO_3^-), 680s, 590vs br (I(V)-F), 475m (I(III)-F), 405w, and 375cm^{-1}w. Samples decomposed rapidly in the laser beam of the Raman spectrophotometer and the following was the best spectrum that could be obtained: 400-500vs (I(III)-F), 625w (IF_6^-?), 690vw(IF_5), 780 br, 830s br, 905m (I=O), 935cm^{-1}w(CH_3CN). On two occasions resonance Raman spectra of I_2 were obtained with peaks at 217, 431, 643, 854, and 1066cm^{-1}. Solutions of the solid in CH_3CN (blue in colour) produced Raman bands at 220(5), 280(1), 371(4), 385(4), 470(1, br), 595(1), 683(1) and 926cm^{-1}(6). The band at 470cm^{-1} was probably I(III)-F and the others could be assigned to IF_5 and CH_3CN. In common with several other reactions, no Raman spectrum of the reaction mixture could be obtained because of the high concentration of iodine present.

XI The Reaction of CuF_2 with IF_5 in CH_3CN

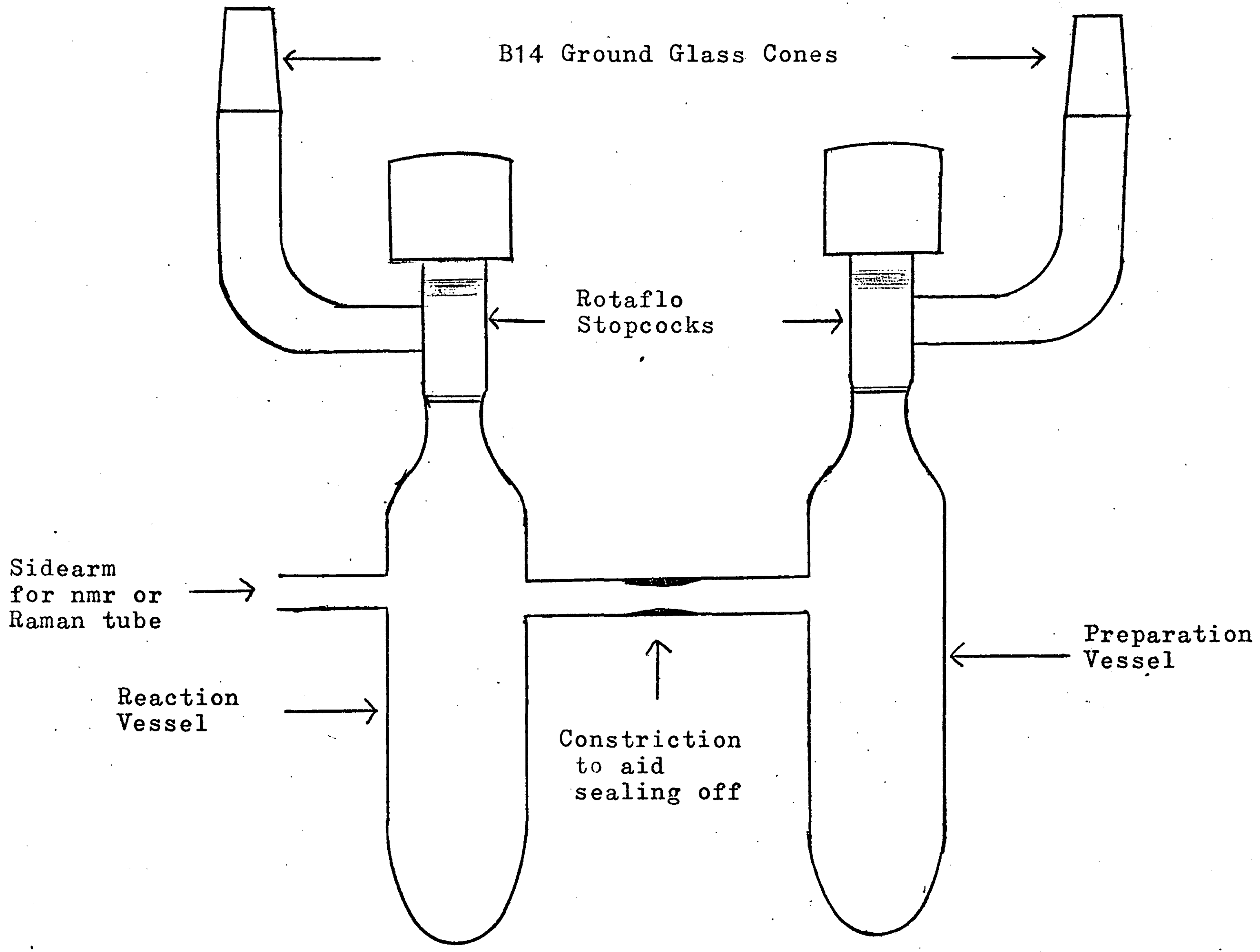
This reaction was extremely slow and required shaking for about a week to obtain a reasonable yield. In order to separate the product oil from unreacted CuF_2, a two-compartment vessel was used. (Figure 27). The reaction was carried out in one half and the adduct solution decanted into the other half. The excess solvents were then back-distilled into the reaction vessel part, which was subsequently sealed off. The isolated adduct was then redissolved in CH_3CN before decanting into sidearms for spectra or analysis since the neat oil was much too viscous to be tipped into tubes. The solvent was then removed, leaving the adduct behind. The results of analyses of two samples were:

Found C: 8·2, H: 1·2, N: 4·7, Cu: 5·6, F: 35·9, I: 44·0%
C: 8·4, H: 1·0, N: 4·8, Cu: 5·3, F: 36·0, I: 44·3%

$CuF_{22}I_4C_8H_{12}N_4$ requires C: 8·3, H: 1·0, N: 4·9, Cu: 5·5, F: 36·2, I: 44·0%.

Figure 27

Double Reaction Vessel



Raman spectra of the neat adduct showed bands at 291(1), 319(1), 376(1), 387(0·8), 576(2·5), 592(4·5), 687(6), 923(1), 2266(3·5), 2310cm^{-1}(1) and i.r. bands occurred at 600 s br, 540 br, 300 m and 275 cm^{-1}sh (Si plates), and 2940 w br, 2300 m, 2260 m, 1365 w br, 1020 m, 910 m, 680 s, 600 s br, 550 br (AgCl plates).

The following electronic absorption spectral data were obtained:

Neat adduct (thin film between quartz plates):

Charge transfer band tail down to 19,000cm^{-1}, d-d band centred at 13,000cm^{-1}.

Solution in CH_3CN (1cm cell)

Charge transfer band tail down to 19,000cm^{-1}, d-d band centred at 13,000cm^{-1}, with a very weak shoulder at 10,600 ±500cm^{-1}.

Solution in IF_5 (1cm cell)

Charge transfer band tail down to 25,000cm^{-1}, d-d band centred at 13,000cm^{-1}, with a very weak shoulder at 9,500 ±500cm^{-1}.

CHAPTER FOUR

REACTIONS OF METAL HEXAFLUORIDES WITH IODINE IN IODINE PENTAFLUORIDE

Reactions of Metal Hexafluorides with Iodine in Iodine Pentafluoride

Introduction

Reactions with a specific reducing agent such as carbon disulphide[148] or iodine[184] have been used to obtain qualitative comparisons among the oxidising properties of metal hexafluorides. The latter study involved heating I_2 and the metal hexafluoride in a bomb at 373 - 473K for 1 - 10 hours. WF_6 and MoF_6 did not react whereas UF_6 oxidised I_2 to IF_5 and was itself reduced to U_2F_9. PuF_6 was found to oxidise not only I_2, but also Br_2 and Cl_2.

Iodine dissolved in IF_5 has been used as a reducing agent in the preparations of the pentafluorides of technetium[185], osmium[186,187] and neptunium[96] from the respective hexafluorides.

The objectives of this work were to examine the reactions of I_2 in IF_5 at 298K, with the hexafluorides of molybdenum, tungsten, rhenium and uranium, compare their oxidising powers in this solvent, and characterise the reaction products.

Results and Discussion

Iodine in Iodine Pentafluoride with Tungsten or Molybdenum Hexafluoride

Electronic spectra of the chocolate-brown solutions of I_2 in IF_5 show bands at ca 310 and 490 nm and an intense charge-transfer band below 225 nm. Addition of either WF_6 or MoF_6 does not affect the 490 nm band although the charge-transfer band now starts at ca 350 nm. Even after several hours shaking, there is no evidence of reaction. This is in agreement with previous work[184] carried out at elevated temperatures in the absence of a solvent.

Iodine in Iodine Pentafluoride with Rhenium Hexafluoride

ReF_6 reacts rapidly with iodine, and a spectacular colour change occurs with the formation of a bright blue solution. Blue solutions are known to be formed when I_2 is dissolved in strong acids such as oleum or fluorosulphuric[188,189] and they are reported to occur when I_2 in IF_5 is treated with MF_5(M=Sb,P,As,Nb,Ta)[190] or when IF_5 is contaminated with traces of iodine and moisture.[192] A blue colour is sometimes observed during the preparation of IF_5 from the elements, but is discharged under conditions of even the slightest excess of fluorine. This colour was originally believed to be due to IF_3[81] but later reports claimed that it arose from the iodine cation I^+.[192] However Gillespie et al[188] showed that the colour formed when I_2 is dissolved in HSO_3F is due to the I_2^+ ion. They characterised this species in HSO_3F, and from the similarity of electronic spectra, the blue colour in IF_5 is now known to arise from I_2^+.

Electronic and Raman spectra of the $ReF_6 + I_2$ in IF_5 system were obtained and these are entirely consistent with the presence of the I_2^+ ion in solution. The electronic spectral data are shown in Table 21, and the spectrum is shown together with that of I_2 in Figure 28.

The Raman spectra of a solution of I_2^+ using 488.0 nm and 647.1 nm laser excitation are shown in Figure 29 and Table 22. These spectra demonstrate the resonance Raman effect extremely well since 647.1 nm lies very close to λ_{max} for I_2^+. (Figure 28). The resonance Raman spectrum is in excellent agreement with those obtained for I_2^+ in other media.[194] The stretching frequency of I_2^+ is 238 cm^{-1} which is 20 cm^{-1} higher than that in I_2. This is consistent with the removal of an antibonding electron on going from I_2 to I_2^+ (Figure 30).

The reaction between I_2 and ReF_6 in IF_5 is believed to be:

$$I_2 + ReF_6 \rightleftharpoons I_2^+ \; ReF_6^-$$

A Raman spectrum was obtained which shows bands due to ReF_6, I_2^+ and I_2, suggesting an equilibrium. No direct evidence for the presence of ReF_6^- was found but the stretching frequency of this anion is 703 cm^{-1},[193] so this would not be observed because of the ν_1 and polymer bands of IF_5. In the hope of observing a band due to ReF_6^-, WF_6 was used as a solvent. However no reaction was observed. This probably reflects the low dielectric constant of WF_6 and means that ReF_6 only oxidises I_2 at 298K in the presence of an ionising solvent such as IF_5.

Table 21

Electronic Spectra of the I_2^+ Ion

† This Work	† Aynsley et al[192]	* Gillespie et al[188]	Assignments[190]
λ_{max}(nm)	λ_{max}(nm)	λ_{max}(nm)	
418	418	410	$^2\pi_{\frac{3}{2}}(g) \rightarrow \Sigma(u)$
512	508	490	$^2\pi_{\frac{3}{2}}(g) \rightarrow {}^2\pi_{\frac{1}{2}}(u)$
637	641	640	$^2\pi_{\frac{3}{2}}(g) \rightarrow {}^2\pi_{\frac{3}{2}}(u)$

† in IF_5 solution

* in HSO_3F solution

Figure 28

Electronic Spectra of I_2 and I_2^+ in IF_5

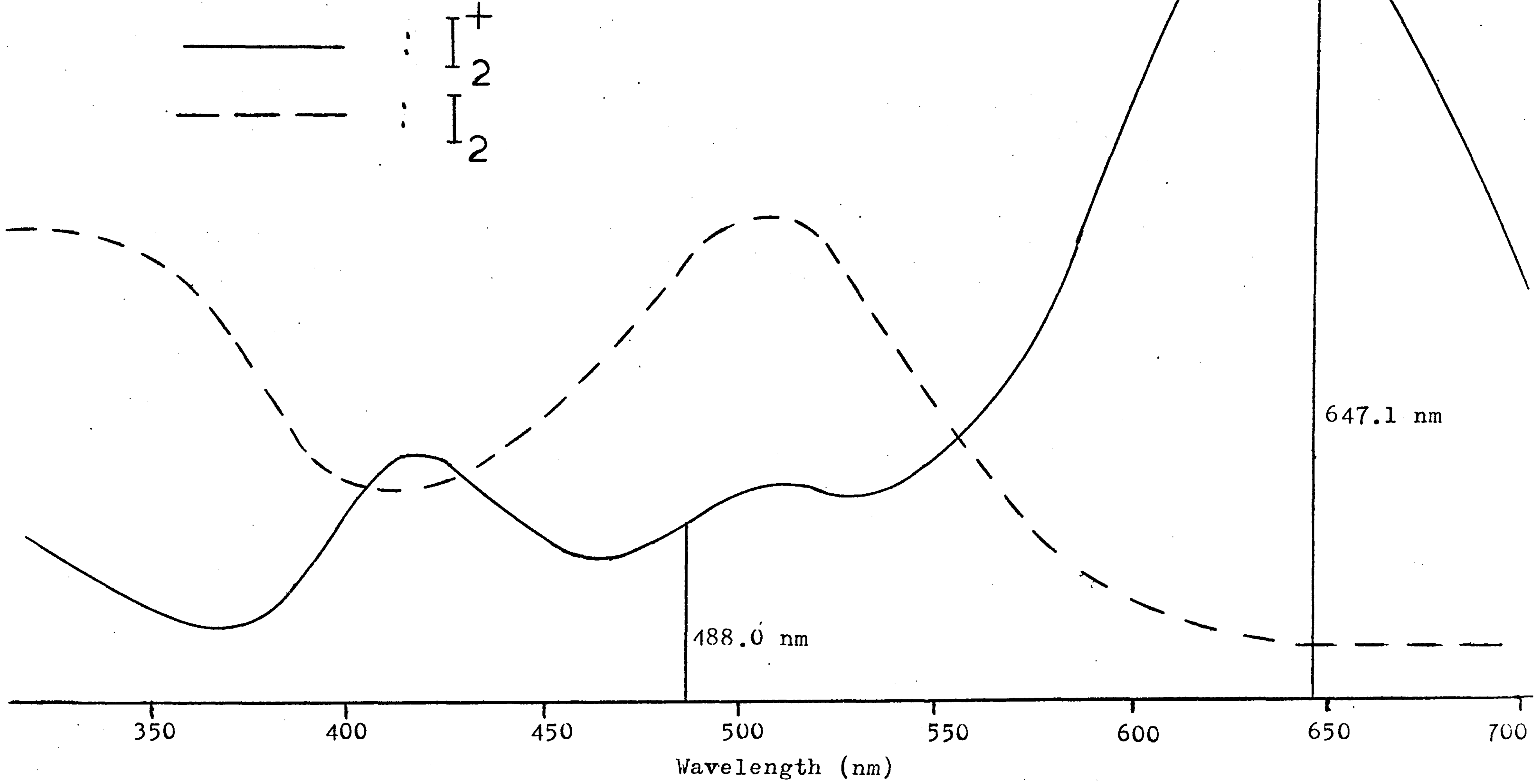


Figure 29

Raman and Resonance Raman Spectra of I_2^+ in IF_5

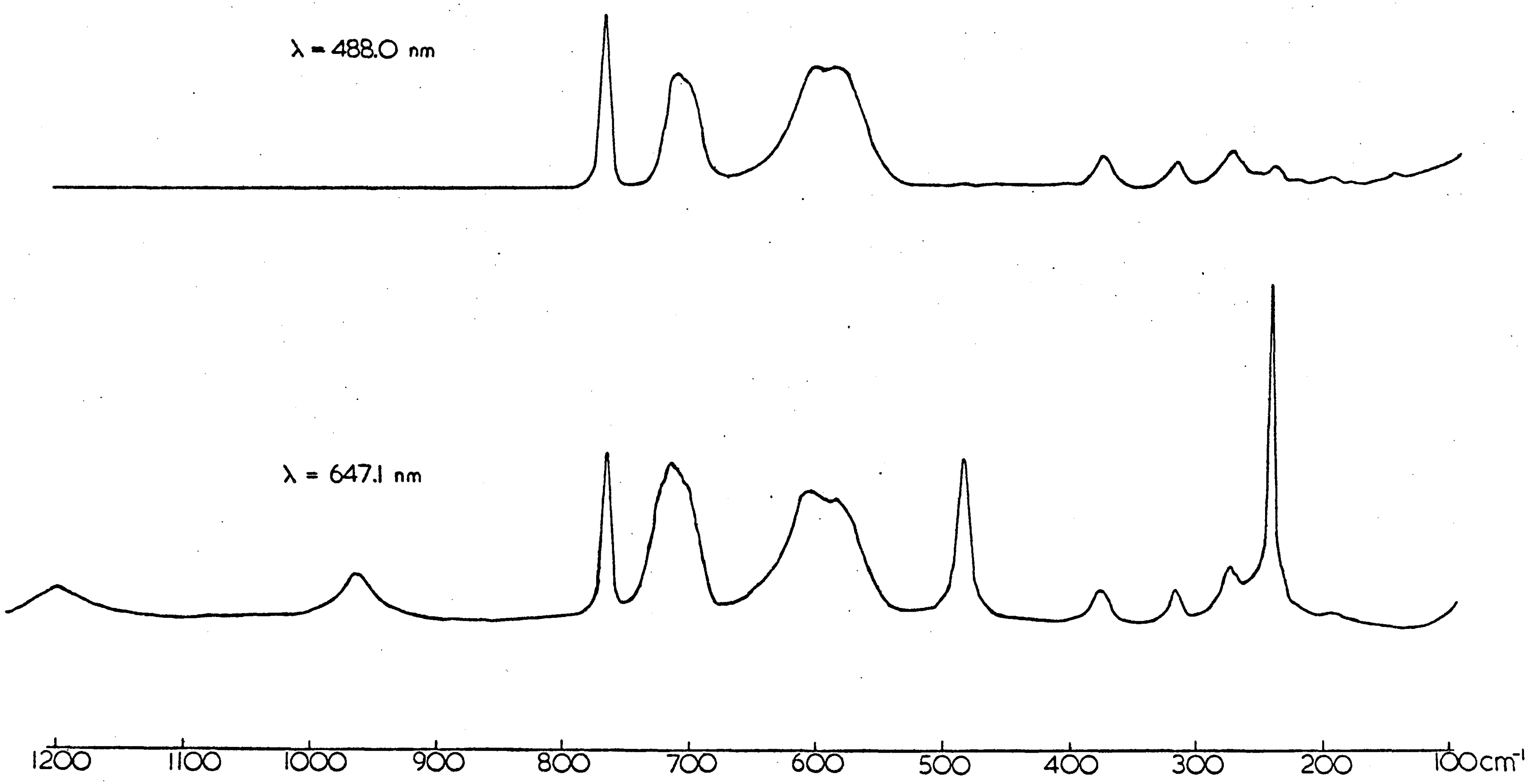


Table 22

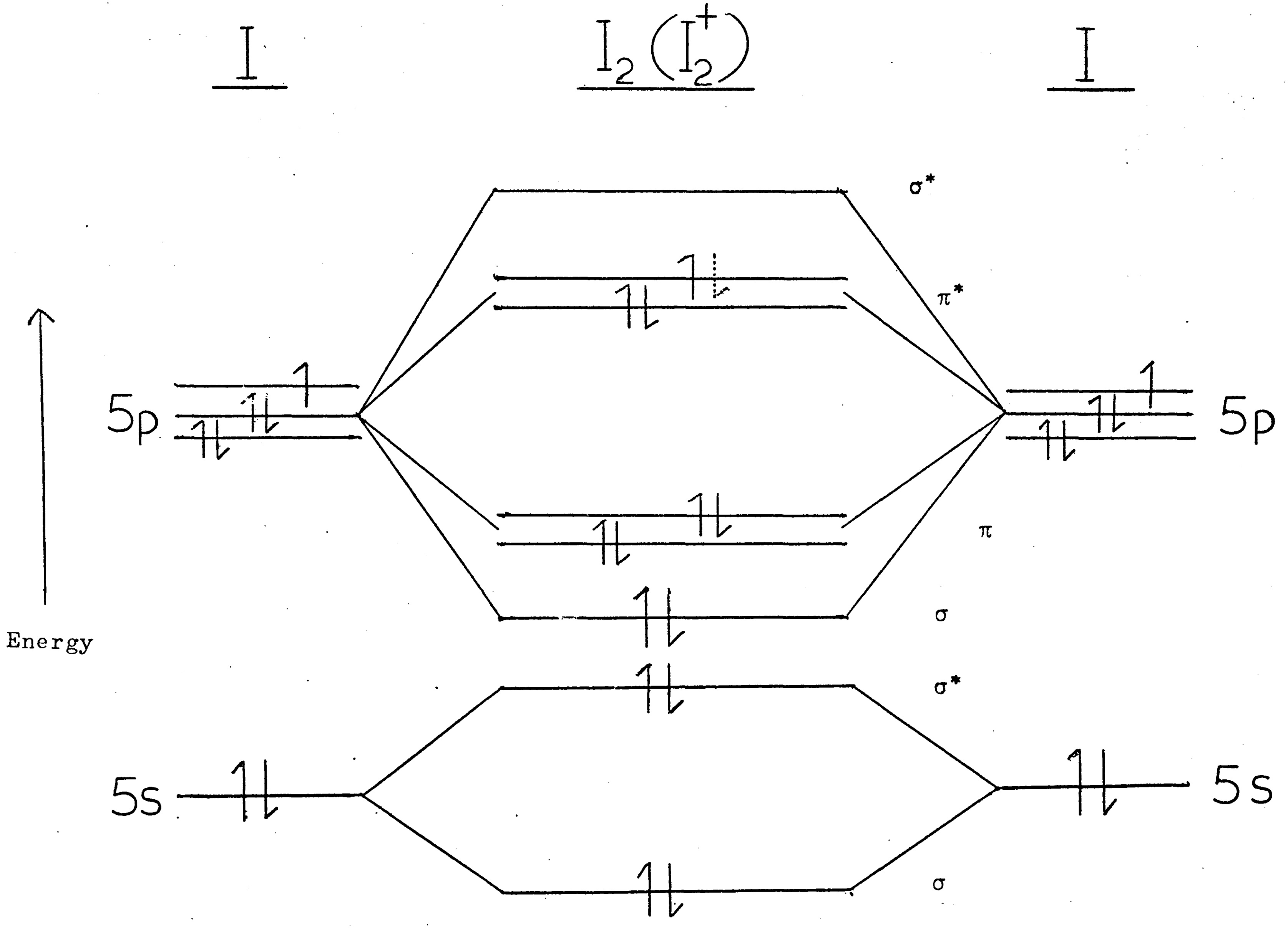
Raman Data on $I_2 + ReF_6$ in IF_5

Exciting Line Frequency (nm)

647.1		488.0		
Frequency(cm^{-1})	Rel.Int.	Frequency(cm^{-1})	Rel.Int.	Assignment
194	0+	193	0+	IF_5 ν_9
238	17	238	1	νI_2^+
270	1.5	271	1.5	IF_5 ν_6
314	1.5	315	1	IF_5 ν_3
370	1.5	372	1.5	IF_5 ν_8
477	8			$2\nu I_2^+$
578	6	578	6	IF_5 ν_4
597	6	597	6	IF_5 ν_2
698	7	698	6	IF_5"polymer"
706	8	706	6	IF_5 ν_1
712	sh.			$3\nu I_2^+$
756	8	756	9	ReF_6 ν_1
953	2			$4\nu I_2^+$
1189	1.5			$5\nu I_2^+$

Figure 30

Simplified Molecular Orbital Diagram for $I_2^{(+)}$



No product is isolable from an $ReF_6 + I_2 + IF_5$ mixture, all materials being volatile at room temperature. On freezing mixtures to 77K, the colour sometimes remains blue but on other occasions it reverts to brown and a yellow ring of ReF_6 is observed above the frozen solvent.

I_2^+ has been reported[195] to dimerise to the brick-red coloured I_4^{2+} ion on cooling. However, on no occasion was this observed. IF_5 solutions of I_2^+ in sealed tubes appear to be stable over a period of several weeks at 298K.

Iodine in Iodine Pentafluoride with Uranium Hexafluoride

UF_6 and I_2 react immediately at 298K and the solution assumes the deep blue colour noted previously. Electronic spectra confirm the presence of I_2^+ in solution. In this reaction however, the colour fades over a period of a few minutes and a very fine pale green precipitate appears. If the ratio of $UF_6:I_2$ is large, e.g. 20:1, then after an hour, the liquid is colourless and a pale green insoluble solid is present at the bottom of the reaction vessel. This can be isolated very easily by removal of the excess IF_5 and UF_6 in vacuo, the solid being completely involatile at 298K.

The solid was identified as UF_5 by elemental analysis. By recording the weight of I_2 consumed and UF_5 formed, the stoichiometric ratio of $I_2:UF_5$ was found to be 1:10. This strongly supports the equation:

$$10UF_6 + I_2 \longrightarrow 10UF_5 + 2IF_5$$

which is analogous to the reaction of TcF_6 with I_2 in IF_5.[185] This is also consistent with the high temperature reaction between UF_6 and I_2 which produces U_2F_9 and IF_5.[184] UF_5 is known to disproportionate at elevated temperatures giving U_2F_9 and UF_6.[196] No direct evidence for the formation of IF_5 was obtained since this was present as the solvent.

The oxidation of I_2 may proceed as follows:

$$I_2 + UF_6 \longrightarrow I_2^+ + UF_6^-$$

$$I_2^+ + UF_6^- \longrightarrow "I_2F" + UF_5$$

$$"I_2F" + 9UF_6 \longrightarrow 2IF_5 + 9UF_5$$

The reason that UF_6 oxidises I_2 beyond I_2^+ whereas ReF_6 does not, could be either that U(VI) is a stronger oxidising agent in IF_5 than is Re(VI), or that UF_6^- is a stronger F^- ion donor than ReF_6^-, so that UF_5 forms more readily than ReF_5.

Several routes to UF_5 are known and these include reduction of UF_6 by H_2, SO_2, CO[100] with uv radiation, $SOCl_2$[101], Si/HF[103], and HBr.[102] The last mentioned is now much used, since UF_5 can be prepared on a continuous basis but a disadvantage is that Br_2 and HF are also formed. For small-scale laboratory preparations, the use of I_2 in IF_5 is much more convenient. Despite the use of I_2 in IF_5 as a reducing agent in the preparation of TcF_5[185], OsF_5[187] and NpF_5[96], its use in preparing UF_5 has not been previously reported. The vibrational spectra of UF_5 were recorded and the results are shown in Table 23. The data obtained from previous studies by Jacob[106] and Asprey and Paine[103] are included for comparison.

The spectra of UF_5 obtained in the present work agree with the data for β-UF_5 better than that for α-UF_5. However X-ray powder diffraction data (appendix) fit neither those

Table 23

Vibrational Spectra of UF_5 (cm^{-1})

This Work		Jacob				Asprey and Paine	
		α-UF_5		β-UF_5		β-UF_5	
Raman	I.r.†	Raman	I.r.†	Raman	I.r.†	Raman	I.r.*
		223(m)					
						280(m)	
					308(w)		
	400(sh)		398(s)		390(vs,br)		405(s,sh)
492(0+)							
		503(m)					
	520(s)				512(m)		508(s)
	575(vs,br)		580(s,br)		573(s)		567(s)
					605(sh)		
604(1)						610(s)	
615(2)		628(s)		614		623(s)	623(s,sh)

† nujol mull, * powder at 77K

obtained for β-UF_5 nor α-UF_5.[97] This may indicate the existence of a third form of UF_5 or that the sample hydrolysed during the recording of the photograph.

UF_5 is soluble in acetonitrile giving a pale green solution which is stable at 298K, both thermally and to disproportionation. Removal of solvent in vacuo leaves a bulky solid, similar in colour to UF_5. Weight differences indicate that the solid is a 1:1 adduct, $UF_5.CH_3CN$.

A Raman spectrum of UF_5 in CH_3CN shows bands at 611 (2) and 602 cm^{-1} (1), both strongly polarised, in addition to CH_3CN vibrations. This spectrum is very similar to those of UF_5 solid. An i.r. spectrum of $UF_5.CH_3CN$ has bands at 530 vs,br, and 350 cm^{-1} m,br, as well as bands due to coordinated acetonitrile. This spectrum differs from the i.r. spectrum of solid UF_5 (Table 23). The vibrational data are not sufficient to allow a detailed comparison between UF_5 and $UF_5.CH_3CN$. The Raman spectra suggest that their symmetries are very similar but differences are detected in the i.r. spectra. β-UF_5 has a much distorted pentagonal bipyramidal structure in the solid state,[97] but the structure of the isolated UF_5 molecule is not yet known although it is believed to be of C_{4v} symmetry.[197] The possible structure of UF_5 in CH_3CN will be discussed further in Chapter 5. UF_5 and $UF_5.CH_3CN$ can also be distinguished using X-ray powder diffraction data, since those for $UF_5.CH_3CN$ (Appendix) differ completely from those for UF_5.

The electronic absorption spectrum of UF_5 in CH_3CN was recorded. (Figure 31, Table 24). This spectrum will be discussed more fully in the section on the UF_6^- ion in

Figure 31

Electronic Spectrum of UF_5 in CH_3CN

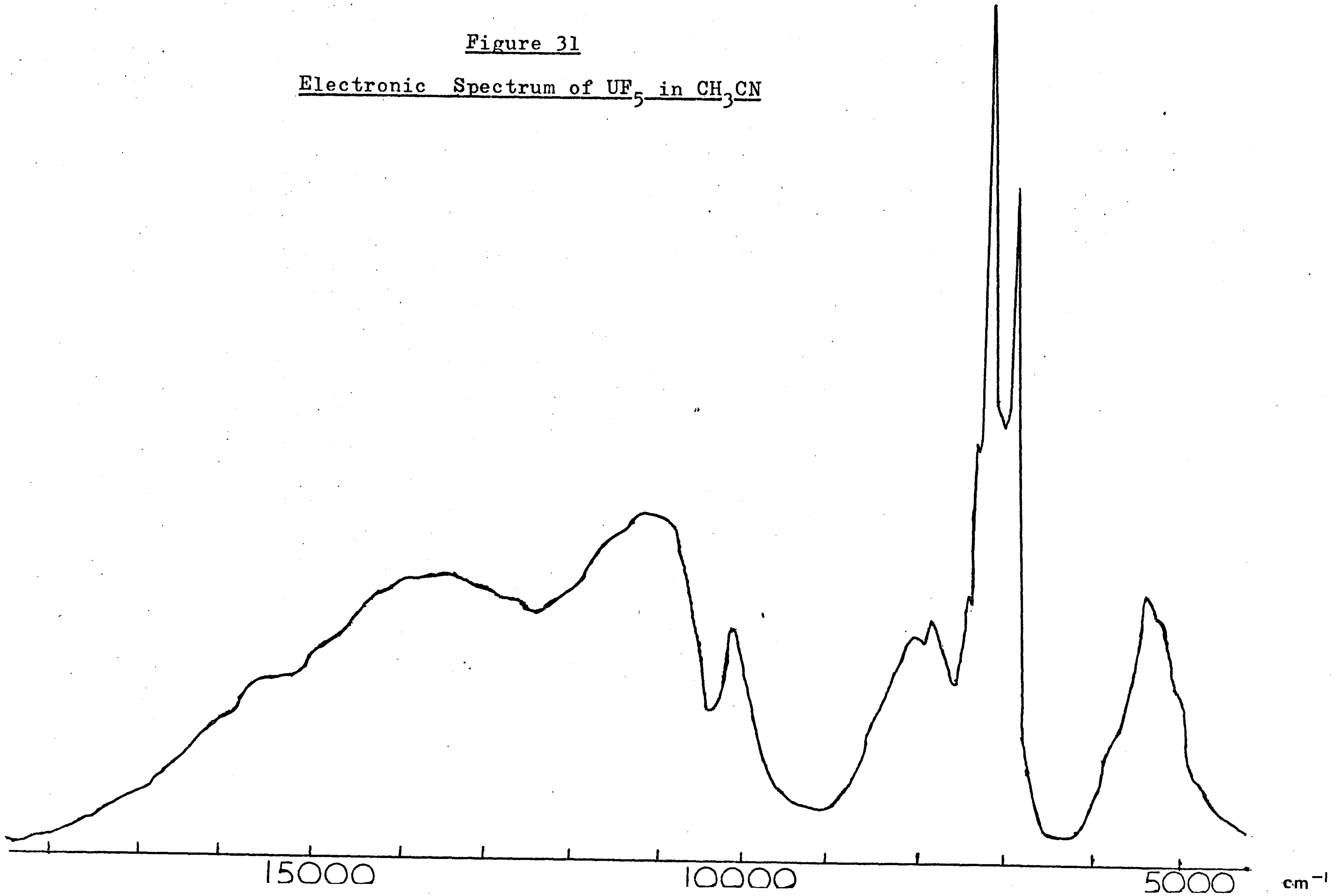


Table 24

Electronic Absorption Data for UF_5 in CH_3CN

Sample 1		Sample 2	
Frequency (cm^{-1})	Relative Intensity	Frequency (cm^{-1})	Relative Intensity
(16100)	24	(16170)	45
(15350)	32	(15510)	70
13620	52	13590	110
11150	65	11070	132
10150	42	10130	80
(8170)	40	(8100)	75
7900	43	7910	89
(7510)	46	(7510)	99
(7310)	78		
7210	166	7200	278
6910	130	6900	270
5380	52	5390	118
(5120)	32	(5130)	78

Parentheses indicate shoulders

Chapter 5. There are many similarities between the spectra of UF_5 and UF_6^- in CH_3CN but there are significant differences between the spectrum of UF_5 in CH_3CN recorded in this work and that of UF_5 in HF.[198] This may just be a reflection of the different nature of the two solvents. In CH_3CN, UF_5 will be coordinated by acetonitrile molecules which may affect the symmetry.

Good evidence for the existence of UF_5 in solution is obtained from the reaction between UF_5 and TlF in CH_3CN. An electronic spectrum recorded after a few minutes reaction is in excellent agreement with those of authentic UF_6^- salts in CH_3CN. The product from this reaction may well be $Tl(I)UF_6$. UF_6 oxidises Tl(I) to Tl(III) in CH_3CN (Chapter 5), but UF_5 may not be a sufficiently strong oxidising agent to do this. For example, UF_5 in CH_3CN does not react with iodine.

Metal Hexafluorides with Bromine in Iodine Pentafluoride

None of the four metal hexafluorides investigated in this work reacts with bromine in IF_5. Electronic spectra indicate no alteration in the bromine absorption bands.

The overall conclusions are that ReF_6 and UF_6 are stronger oxidising agents towards I_2 in IF_5 than WF_6 or MoF_6. In this respect, either UF_6 is a stronger oxidising agent than ReF_6 or UF_6^- is a better F^- ion donor than ReF_6^-. The reaction between I_2 and UF_6 in IF_5 is a very convenient route for the small scale preparation of UF_5. I_2^+ is not observed in the $I_2 + NpF_6$ reaction[96] and this is attributed to the greater oxidising power of NpF_6 resulting in a faster reaction.

Experimental

The reagents used were as follows:

Reagent	Source	Purity
WF_6	Fluorochem	99%
MoF_6	Fluorochem	
ReF_6	Fluorochem	
UF_6	Gift from U.K.A.E.A.	
I_2	B.D.H.	Analar grade
Br_2	Hopkin and Williams	Analar grade

IF_5, TlF and CH_3CN were used as described in Chapters 2 and 3. WF_6 and MoF_6 were purified by fractional distillation in vacuo and stored over NaF. ReF_6 and UF_6 were freshly purified for each reaction by double vacuum sublimation from NaF which had been pre-dried by pumping at 420K for 12 hours. I_2 was dried by triple vacuum sublimation. Br_2 was purified by refluxing with P_2O_5, followed by fractional distillation in vacuo. Spectra were obtained by distilling IF_5 into the Raman tube or u.v. cell (described in Chapter 1, Figure 7) followed by I_2 and the metal hexafluoride. In the case of ReF_6, the blue colour of I_2^+ formed as soon as the IF_5 melted and was stable indefinitely. However with UF_6, the electronic spectrum had to be run immediately the colour formed, since it faded within a few minutes. These spectra were poorly resolved by comparison with those from the I_2 + ReF_6 reaction since UF_5 was steadily precipitating from solution. Only the band at ca 640 nm was distinct.

To prepare a typical sample of UF_5, IF_5 (ca 3g, 13 mmol), I_2 (9.1 mg, 35.8 μmol) and UF_6 (ca 0.2g, 0.6 mmol) were distilled into a reaction vessel and shaken for an hour. Excess UF_6 and IF_5 were removed in vacuo, leaving UF_5 (0.1166g, 0.35 mmol). This gave a ratio of I_2:UF_5 = 1:9.8. The solid analysed as F:28.5, U:71.3%, F_5U requires F:28.5, U:71.5%.

UF_5 was handled very easily in an inert-atmosphere box and its solutions in CH_3CN gave no indication of disproportionation. On hydrolysis, the pale green solution became light green and a precipitate formed. This indicated rapid disproportionation to U(IV) and U(VI).

CHAPTER FIVE

REDOX REACTIONS IN ACETONITRILE, REACTIONS OF URANIUM AND RHENIUM HEXAFLUORIDE WITH METALS

Redox Reactions in Acetonitrile

Reactions of Uranium and Rhenium Hexafluorides with Metals

Introduction

The preparations of hexafluorouranates (V) and hexafluororhenates (V) have previously involved the use of solvents such as liquid SO_2 or HF, high temperature conditions or gas phase reactions.[112-116,130,150,157]

Since acetonitrile is such a good solvent for MoF_6 and WF_6[146], it was considered most important to see if the advantages of this very convenient solvent system could be extended to the more reactive hexafluorides of uranium and rhenium.

CH_3CN is especially good at solvating ions such as Cu(I), Cu(II), Tl(I) and Tl(III) and therefore p and d block metals were used in this study. Ions such as Cu(II) have an additional advantage since physical techniques such as electronic absorption and e.p.r. spectroscopy are available.

A further aim was to obtain good vibrational spectroscopic data on the hexafluorouranate (V) ions. Previous workers have reported values for most of the vibrational modes of UF_6^-, but these differ considerably as is shown in Table 25.

Table 25

Reported Vibration Frequencies of the UF_6^- Ion

Vibration	Frequency (cm^{-1})	Reference	Source	
ν_1	628	130	$NOUF_6$	(a)
ν_1	506	202	$CsUF_6$	(b)
ν_3	551	112	MUF_6	(c)
ν_3	526	130	MUF_6	(c)
ν_3	503	202	$CsUF_6$	(b)
ν_3	525	203	Ph_4AsUF_6	(b)
ν_4	150	202	$CsUF_6$	(b)
ν_4	170	203	Ph_4AsUF_6	(b)
ν_5	145	202	$CsUF_6$	(b)
ν_6	100	202	$CsUF_6$	(b)
ν_6	129	203	Ph_4AsUF_6	(b)

(a) = Raman spectrum of HF solution

(b) = From vibronic fine structure in electronic spectrum

(c) = I.r. spectra

Results and Discussion

I Oxidation of Metals by Uranium Hexafluoride in Acetonitrile

Copper, cadmium and thallium metals are all readily oxidised by UF_6 in CH_3CN at 298K. The reactions are complete within 30 minutes, yielding a blue-green solution in the case of copper, or very pale green solutions in the reactions of Cd or Tl. Removal of the solvent leaves a blue-green (Cu) or pale green powdery solid. The analyses of these solids (Table 32) are in excellent agreement with the compositions $Cu(UF_6)_2.5CH_3CN$, $Cd(UF_6)_2.5CH_3CN$, and $Tl(UF_6)_3.5CH_3CN$ respectively.

Raman spectra of the solutions show a strongly polarised band at 613 cm^{-1}, and a much weaker band at 194 cm^{-1} as well as solvent peaks. Spectra of the Cu and Tl salts run at 77K also display bands at 613 and 194 cm^{-1}. I.r. spectral data are shown in Table 26.

The i.r. spectra strongly suggest the presence of two types of CH_3CN molecules in the Cu(II) salts, but not in the Cd(II) or Tl(III) compounds. Cu(II) salts isolated from CH_3CN solution, often contain 5 molecules of CH_3CN per Cu(II) ion. Examples include $Cu(WF_6)_2.5CH_3CN$,[146] $Cu(WF_7)_2.5CH_3CN$,[145] and $Cu(MoF_6).5CH_3CN$.[146] It is probable that each Cu(II) ion is closely associated with four CH_3CN molecules and the two anions, with the fifth CH_3CN molecule being further away. This would be analogous to $CuSO_4.5H_2O$, which consists of an aggregate of sulphate and $Cu(H_2O)_4$ groups with the fifth water molecule occupying a hole in the structure.[213]

Table 26

I.R. Spectra of UF_6^- Compounds

Compound	Frequency (cm^{-1})	Assignments
$Cu(UF_6)_2.5CH_3CN$	2330 sh	CH_3CN combination band and two C≡N stretches.
	2310 m	
	2285 w	
	945 m	CH_3CN C-C stretch
	935 sh	C-C stretch
	725 m	U-O?
	520 vs,br	U-F stretch,$UF_6^-\nu_3$
$Cd(UF_6)_2.5CH_3CN$	2320 m	CH_3CN combination band,
	2290 s	C≡N stretch
	940 m	C-C stretch
	720 m	U-O ?
	520 vs	U-F stretch,$UF_6^-\nu_3$
$Tl(UF_6)_3.5CH_3CN$	2320 sh	CH_3CN combination band
	2295 s	C≡N stretch
	945 s	C-C stretch
	725 m	U-O ?
	520 vs,vbr	U-F stretch,$UF_6^-\nu_3$
	†145 m	U-F,$UF_6^-\nu_4$

† Obtained from a spectrum of the far-i.r. The other salts were not investigated in this region.

Electronic absorption spectra of solutions of the Tl and Cu compounds were obtained (Figures 32, 33 and Table 27). The spectrum of the Tl compound is in good agreement with published spectra of salts containing the UF_6^- ion.[202,203] (Table 28). The Cu compound displays similar f-f bands but these appear as very weak shoulders on the much more intense Cu(II) d-d band.

On the basis of the vibrational and electronic spectra, these compounds are formulated as $Cu(II)(UF_6)_2.5CH_3CN$, $Cd(II)(UF_6)_2.5CH_3CN$ and $Tl(III)(UF_6)_3.5CH_3CN$, all containing the UF_6^- ion.

The results of an ^{18}F exchange study between $Cu(UF_6)_2.5CH_3CN$ and labelled UF_6 indicate that exchange is complete within 30 minutes. The count rate for the solid $Cu(UF_6)_2.5CH_3CN$ is however, even higher than that expected for complete exchange. The reason for this will be discussed later.

An e.p.r. spectrum of $Tl(UF_6)_3.5CH_3CN$ at 77K shows no signal. This suggests that the symmetry of the UF_6^- ion is close to O_h. E.p.r. studies have shown[204] that the degree of distortion of the UF_6^- ion depends on the cation.

An f^1 ion in an octahedral environment such as U(V) in UF_6^-, should give rise to four electronic transitions in its absorption spectrum.

The ^2F term is split into $^2F_{\frac{5}{2}}$ and $^2F_{\frac{7}{2}}$ through spin-orbit coupling, making J half-integral for the $5f^1$ system. ($J=\frac{5}{2}$ and $\frac{7}{2}$), It is therefore necessary to use double group representations.[205] The characters for the new operations of the double group must be obtained for the reducible

Figure 32

Electronic Spectrum of $Tl(UF_6)_3.5CH_3CN$ in CH_3CN

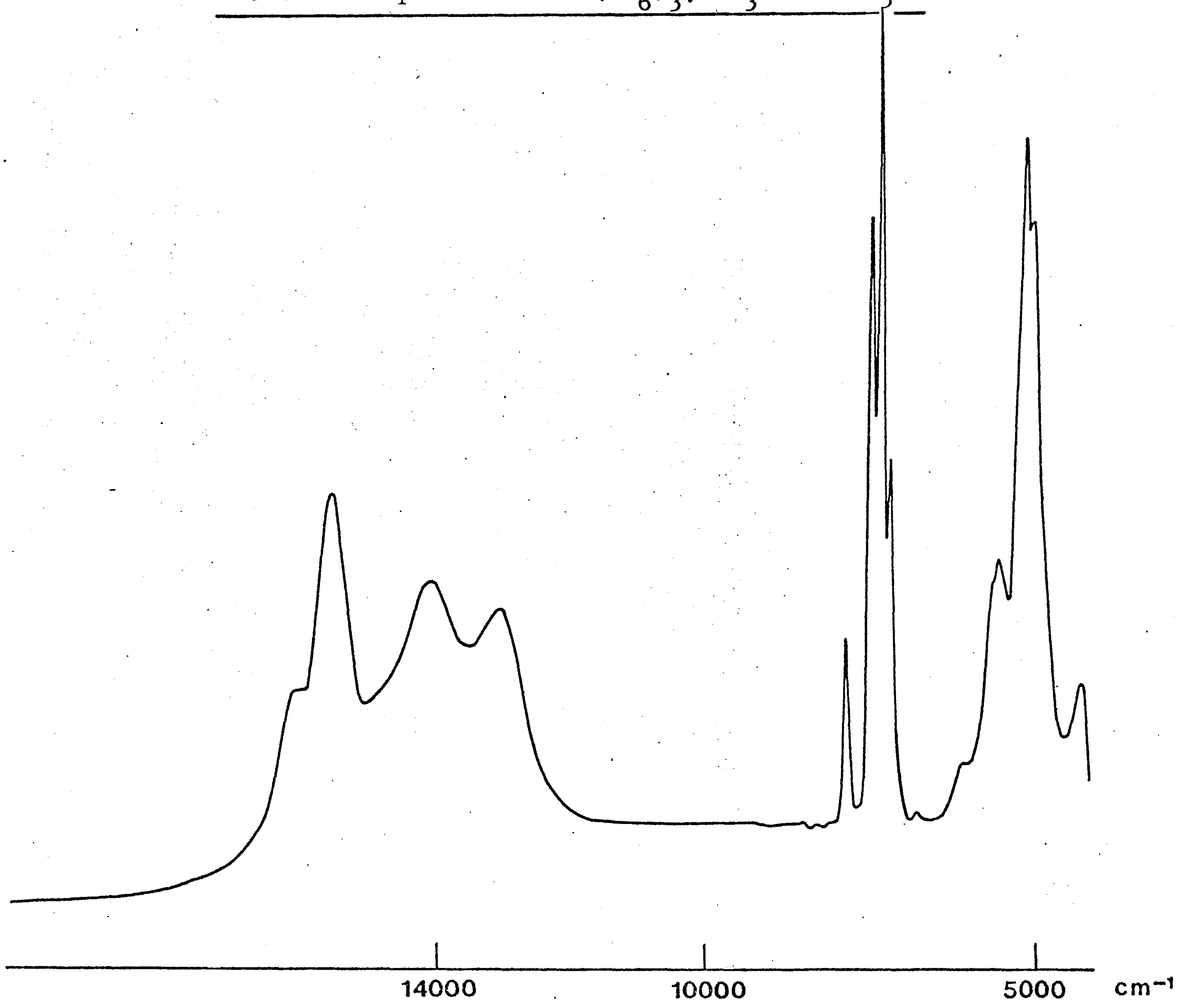


Figure 33

Electronic Spectrum of $Cu(UF_6)_2.5CH_3CN$ in CH_3CN

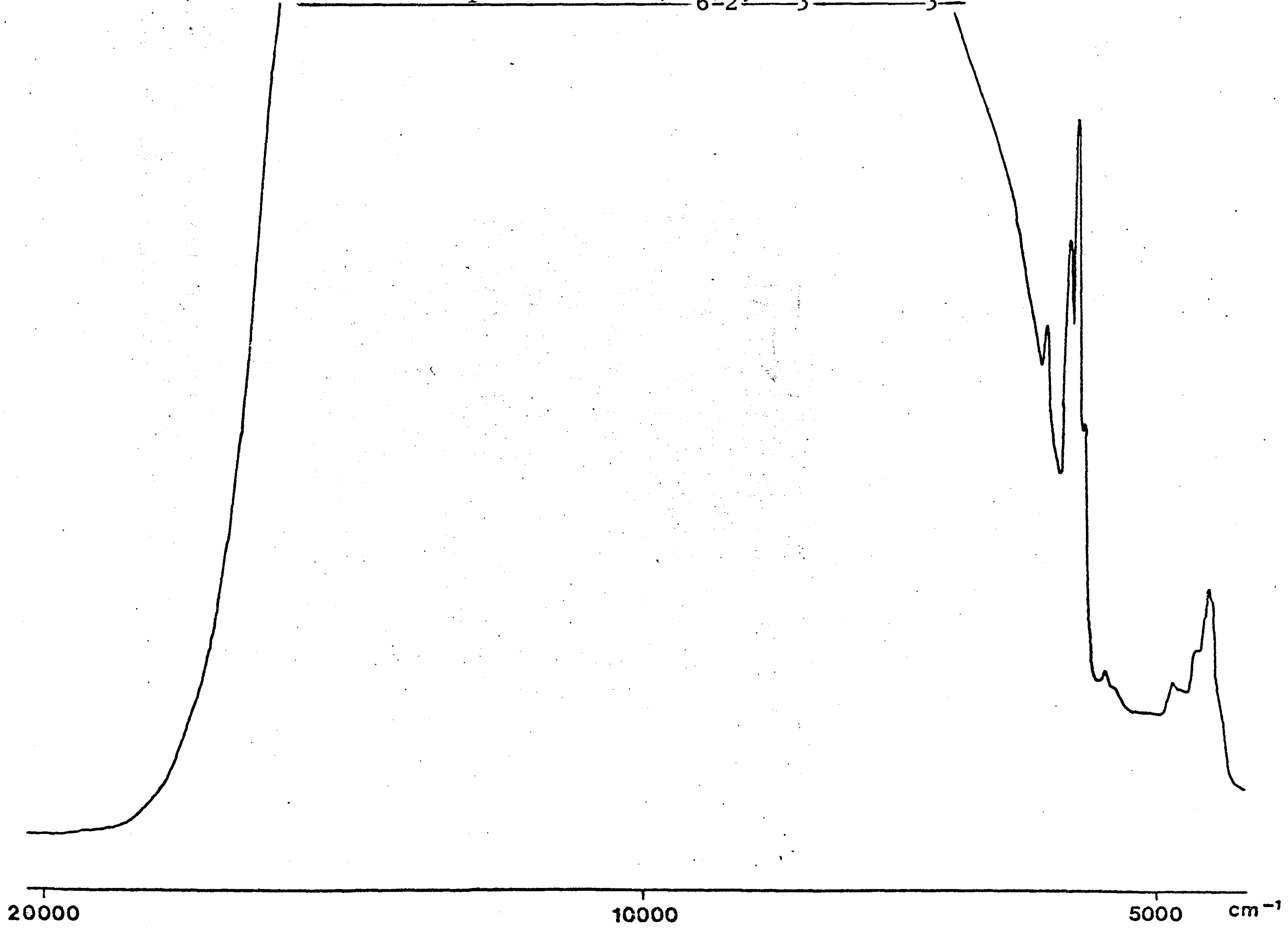


Table 27

Electronic Spectrum of $Tl(UF_6)_3$ in CH_3CN

$\nu(cm^{-1})$	ε(molal)	Electronic Transition	$\Delta\nu(cm^{-1})$	I.r.	Vibrational Mode
(16150)	0.4	$\Gamma_7 \longrightarrow \Gamma_6$			
15650	0.7				
14175	0.4	$\Gamma_7 \longrightarrow \Gamma_8'$			
13175	0.4				
7950	0.3		525	520	ν_3
7580	1.0		155	145	ν_4
7425	1.4	$\Gamma_7 \longrightarrow \Gamma_7'$	Pure Electronic		
7290	0.6		135		ν_4
6900	0.02		525		ν_3
6190	0.1	$\Gamma_7 \longrightarrow \Gamma_8$			
(5775)	0.4				
5680	0.5				
5240	1.1				
(5230)	0.9				
5175	1.2				
5115	1.0				
(4360)	0.2				

Parentheses indicate shoulders.

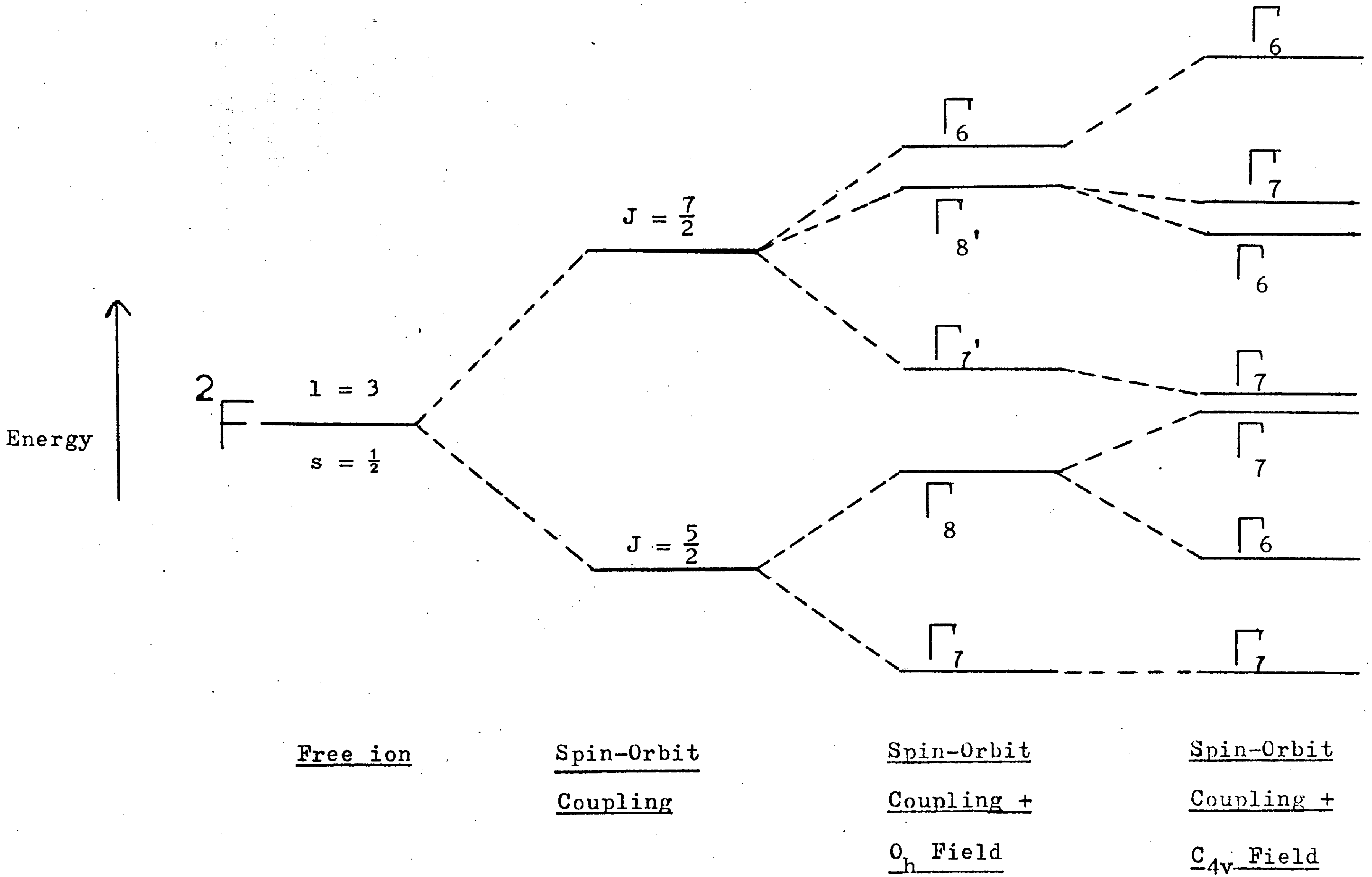
Error in frequencies = ±20 cm^{-1}

$Cu(UF_6)_2$ spectrum shows only the most intense f-f bands.

For comparison, ε(molal) Cu(II) d-d = 25.4

Figure 34

Energy level Diagram of an f' Species



representations $\Gamma_{\frac{5}{2}}$ and $\Gamma_{\frac{7}{2}}$. The irreducible states belonging to these representations are the levels which arise from the splitting of the $^2F_{\frac{5}{2}}$ and $^2F_{\frac{7}{2}}$ terms in octahedral symmetry. The results of applying an octahedral field to the terms $^2F_{\frac{5}{2}}$ and $^2F_{\frac{7}{2}}$ are:

$$\Gamma_{\frac{5}{2}} \longrightarrow \Gamma_7 + \Gamma_8 \quad \text{and}$$

$$\Gamma_{\frac{7}{2}} \longrightarrow \Gamma_6 + \Gamma_7' + \Gamma_8'$$

Γ_6, Γ_7 and Γ_7' are doubly degenerate (Kramer's Doublets) and Γ_8 and Γ_8' are quadruply degenerate. The ordering of these energy levels is determined by solving the appropriate wave equations. This results in the energy level diagram shown in Figure 34, and the transitions are:

$\Gamma_7 \longrightarrow \Gamma_8$, $\Gamma_7 \longrightarrow \Gamma_7'$, $\Gamma_7 \longrightarrow \Gamma_8'$ and $\Gamma_7 \longrightarrow \Gamma_6$.

However it is obvious from the spectrum of the UF_6^- ion, that rather than four bands being present, there are in fact four groups of bands. This is because of "vibronic coupling" in which an electronic transition is accompanied by a change in vibrational state. In perfect O_h symmetry the pure electronic bands are forbidden as electric dipole transitions and only the vibronic transitions are observed. However in the UF_6^- ion, since it is slightly distorted, at least one electronic transition is observed. Greater distortion from O_h, e.g. to C_{4v} would lead to the splitting of the two non-

Kramer degenerate levels, Γ_8 and Γ_8', hence further transitions would occur. This will be discussed later.

One important feature of vibronic coupling is that odd vibrational modes, in this case $2T_{1u}(\nu_3$ and $\nu_4)$, and $T_{2u}(\nu_6)$ are predicted to couple much more strongly with the electronic transitions than the even modes, $A_{1g}(\nu_1)$, $E_g(\nu_2)$ and $T_{2g}(\nu_5)$. This can be explained in simple terms by the following argument. If, during a vibration, the centre of symmetry of the octahedron were destroyed, then during the period of that vibration, electronic transitions would be formally allowed. Hence simultaneous electronic and vibrational transitions could occur. The destruction of the centre of symmetry in the octahedron does occur during the $\nu_3(T_{1u})$, $\nu_4(T_{1u})$ and $\nu_6(T_{2u})$ modes, i.e. the odd modes. By contrast, the totally symmetry stretch $\nu_1(A_{1g})$ can couple to give bands of very low intensity.[212] It is therefore a misnomer to call the u.v.-visible-near i.r. spectra "electronic" spectra as they comprise almost entirely vibronic bands but the word electronic will be used to avoid confusion.

The electronic absorption spectrum of $CsUF_6$ was recorded and discussed in detail by Reisfeld and Crosby.[202] Ryan[203] gave a similar account of $Ph_4As\ UF_6$. The two sets of data were similar but the authors differed over some assignments. (Table 28). The sample of $CsUF_6$ used by Reisfeld and Crosby apparently contained some U(IV). Because of this they ignored several bands at ca 16000 cm^{-1}. Among these bands however were two genuine U(V) peaks. They also believed that pure electronic bands would be very weak, and in the group of sharp bands at ca 7400 cm^{-1}, assigned the very weak, lowest

Table 28

Electronic Spectroscopic Data for UF_6^- Compounds

Reisfeld and Crosby[a] Frequency (cm^{-1})	Ryan[b] Frequency (cm^{-1})	Assignment
14245	16130	$\Gamma_7 \longrightarrow \Gamma_6$
	15630	
12705	14120	$\Gamma_7 \longrightarrow \Gamma_8'$
	13070	
	7905	
	7553	
6928	7513	$\Gamma_7 \longrightarrow \Gamma_7'$
	7386	
	7246	
	6849	
4587	_ca_ 5200	$\Gamma_7 \longrightarrow \Gamma_8$

a Experimental electronic levels assigned from observed absorptions and deduced vibrational frequencies. Spectrum (Fluorolube mull of $CsUF_6$ at 75K) contains _ca_ 30 bands in this region (Refence 202).

b Ph_4AsUF_6 in CH_3CN solution. (Reference 203).

energy band to this transition. Ryan, however assigned the strong central, narrow peak to this transition, since there were other bands equally spaced at higher and lower energies, consistent with vibronic coupling to the pure electronic transition.

The results of the present work are in good agreement with those of Ryan and only differ in the value of ν_4. The assignments used in Table 27 are those of Ryan. The values of ν_3 and ν_4 obtained from i.r. spectra are shown for comparison. The vibrational data obtained in the present study are summarised in Table 29.

The value of ν_1 is in good agreement with the value of 618 cm^{-1} reported very recently,[193] for $NO^+UF_6^-$.

In the present work, the reactions were always carried out using excess metal. This was to prevent any attack on solvent by excess UF_6. One interesting difference between the reactions of UF_6 in CH_3CN and those of WF_6 and MoF_6 is apparent. WF_6 and MoF_6 react with Cu in CH_3CN to form Cu(II) hexafluorometallate (V) salts if the metal hexafluoride is in excess, but the Cu(I) salt is formed if the reverse is true.

This is not the case with UF_6 however. Despite the presence of excess metal, the cation is always found in the higher oxidation state, e.g. Cu(II), Tl(III). To confirm this, UF_6 and a large excess of Cu were shaken for 4 days. The product analysed as pure Cu(II). The reason for this is not clear. The formation of Cu(I) salts of WF_6^- and MoF_6^- proceeds via Cu(II) which is slowly reduced by the metal. This process would be expected to be independent of the identity of the anion, but this is clearly not always correct.

Table 29

Vibrational Data on UF_6^- Ion

Frequency (cm^{-1})	Mode	Source
613±2	ν_1	Raman spectra of solutions and solid
525±20	ν_3	Splitting of $\Gamma_7 \longrightarrow \Gamma_7'$ electronic transition
520±5	ν_3	I.r. spectrum of solid
145±20	ν_4	Splitting of $\Gamma_7 \longrightarrow \Gamma_7'$ electronic transition
145±5	ν_4	Far i.r. spectrum
194±2	ν_5	Raman spectra of solutions and solid

The value of ν_1 is in good agreement with the value of 618 cm^{-1} reported very recently,[193] for $NO^+UF_6^-$.

These observations may indicate the occurrence of cation-anion interaction in UF_6^- solutions which are absent in similar systems.

Overall, the reaction of UF_6 in CH_3CN with Cu, Cd or Tl is an extremely convenient route to hexafluorouranate (V) species. The reactions involve a solvent which is easy to handle, mild conditions and a short reaction time at 298K. The products obtained are soluble, which allows solution spectra to be recorded, and are easily handled in an inert atmosphere box.

II Reduction of Uranium Hexafluoride by Acetonitrile

At 298K, UF_6 polymerises acetonitrile over a period of several hours, the time taken depending on the concentration. The presence of silver metal accelerates the reaction dramatically. A brown colour, believed to be due to polymerised CH_3CN forms within minutes, even at 243K. The cause may be a catalytic effect of Ag ions or severe local heating due to a strongly exothermic reaction between Ag and UF_6. The solvent polymerisation prevented the isolation of a silver hexafluorouranate species.

The much slower polymerisation caused by UF_6 itself was followed by observing the ^1H n.m.r. signal of CH_3CN over a period of twelve hours. The peak width at half-height increased from 5 to 250Hz as the solution gradually darkened and solidified.

Electronic spectra of a UF_6 solution in CH_3CN, run every 30 minutes, show a gradual increase in the intensity of f-f bands as a U(V) species forms. After two hours reaction, the spectrum (Table 30) is very similar to those obtained by dissolving UF_5 in CH_3CN (Table 24). The reduction of UF_6 to UF_5 by CH_3CN is confirmed by Raman spectra which show the increase in intensity of a band at 615 cm^{-1} as the reaction proceeds. The solution is pale green after two hours but is dark brown after a further four hours. Fluorination and polymerisation of CH_3CN are believed to accompany the reduction of UF_6.

Attempts to prepare the heptafluorouranate (VI) species $Hg(UF_7)_2$ and $TlUF_7$, by reacting HgF_2 or TlF with UF_6 in CH_3CN were unsuccessful. Instead, $Hg(UF_6)_2.6CH_3CN$ and $Tl(UF_6)_3.5CH_3CN$ are formed. Initially, this reduction was thought to be due to the presence of traces of water in the CH_3CN.[206] However the following reaction schemes are now believed to be a better explanation:

$$UF_6 \xrightarrow{CH_3CN} UF_5 + F^{\cdot} \qquad (1)$$

$$2UF_5 + HgF_2 \longrightarrow Hg(UF_6)_2 \qquad (2)$$

$$UF_6 \xrightarrow{CH_3CN} UF_5 + F^{\cdot} \qquad (1)$$

$$Tl(I)F + 2UF_6 \longrightarrow Tl(III) + 2UF_6^- + F^- \qquad (3)$$

$$F^- + UF_5 \longrightarrow UF_6^- \qquad (4)$$

Reactions (2) and (4) are probably slow by comparison with the redox reactions (1) and (3). The fluoride ion addition is therefore to a uranium (V) rather than a uranium (VI) species.

Table 30

Electronic Spectrum of UF_5 from Reduction of UF_6 by CH_3CN

Frequency (cm^{-1}) ±50 cm^{-1}	Relative Intensity
(16150)	25
(15550)	41
13700	58
11070	68
10090	53
(8080)	45
7900	56
(7500)	71
(7280)	135
7190	230
6900	158
5300	72
(5070)	52

Parentheses indicate shoulders

UF_6 reacts much more quickly with metals such as Cu, Cd and Tl than with CH_3CN, and no UF_5 was detected during the preparations of the hexafluorouranates (V) of these metals.

The electronic spectrum of UF_5 in CH_3CN will now be discussed briefly. This has been left until now, in order that the UF_6^- spectrum might be discussed first.

Since UF_5 forms a 1:1 complex with CH_3CN, it is probably of C_{4v} symmetry in CH_3CN, with one molecule of CH_3CN co-ordinating to the uranium. This would lift the quadruple degeneracies of Γ_8 and Γ_8' energy levels in going from $O_h \longrightarrow C_{4v}$, leaving four doubly degenerate levels,and would also raise the Γ_6 level. (Figure 34). This effect can be seen by examining the spectrum of the UOF_5^{2-} ion.[207] (Table 31).

However, as is shown in Figure 31, the spectrum of UF_5 in CH_3CN is not of this form. The spectrum consists of four main groups of bands clustered at ca 15800, 12400, 7200 and 5200 cm^{-1}, and is similar to that of UF_6^-. (Figure 32). The peak at ca 10,150 may be due to an impurity since it remains in the spectrum of UF_6^- when TlF is added to the UF_5 solution. These spectra therefore suggest that the environments around the uranium atoms in $UF_5.CH_3CN$ and UF_6^- are similar, but the uranium atom in UOF_5^{2-} is in a different environment. This is consistent with the observation that there is very little difference between the electronic spectra of Cu(II) surrounded by CH_3CN and $Cu(II).(F^-)_2.(CH_3CN)_4$ (Chapter 3). Further confirmation comes from the electronic spectrum of $UCl_5.OCClCClCCl_2$. This is similar to the spectrum

Table 31

Electronic Spectrum of $(Et_4N)_2$ UOF_5

Frequency (cm^{-1})	Assignment in D_4 symmetry[a]
18660	$\Gamma_7 \longrightarrow \Gamma_6\ (\Gamma_6)$
12420	$\Gamma_7 \longrightarrow \Gamma_7\ (\Gamma_8')$
11448	$\Gamma_7 \longrightarrow \Gamma_6\ (\Gamma_8')$
6837	$\Gamma_7 \longrightarrow \Gamma_7\ (\Gamma_7')$
6792	$\Gamma_7 \longrightarrow \Gamma_7\ (\Gamma_8)$
2380	$\Gamma_7 \longrightarrow \Gamma_6\ (\Gamma_8)$

[a] The symbol in parentheses represents the irreducible representation of the O_h molecular species UF_6^-.

of UCl_6^-, but differs[208] from that of $UOCl_5^{2-}$. The major difference between the spectra of UCl_6^- and $UF_5.L$ is the size of the splitting of the Γ_8' level. This splitting is 540, and 825 cm^{-1} respectively.

By analogy, the broad bands at ca 13,600 and 11,100 cm^{-1} in the spectrum of UF_5 are assigned to $\Gamma_7 \rightarrow \Gamma_8'$. This splitting of 2,500 cm^{-1} compares with 1,000 cm^{-1} in the spectrum of UF_6^-. No peak in the $\Gamma_7 \longrightarrow \Gamma_7'$ group in the UF_5 spectrum can be definitely assigned as the pure electronic band, since none of the splittings can be correlated with vibrational data.

However in HF solution, the electronic spectra of UF_5 and UF_6^- differ considerably.[198]

III Oxidation of Copper by Rhenium Hexafluoride

Acetonitrile is attacked very much more rapidly by ReF_6 than it is by UF_6. At 298K, polymerisation occurs within a few minutes. The techniques employed to study the oxidation of metals by WF_6, MoF_6[146] or UF_6 in CH_3CN are unsatisfactory with ReF_6. It is possible to prepare salts such as $Cu(I)ReF_6$ and $Tl(I)ReF_6$ by using large quantities of the metal, adding ReF_6 in very small increments, and by keeping the reaction vessel cooled.[209] However, even with these precautions, small amounts of polymer are usually isolated with the hexafluororhenate. While this is not an especially serious problem with some spectroscopic techniques, it means that Raman spectra are very difficult to obtain. Since obtaining good vibrational data was one objective, a method was therefore sought which would prohibit polymerisation, and allow ReF_6 to be present in excess.

ReF_6 does not react with copper in IF_5, despite the fact that the dielectric constants of IF_5 and CH_3CN are similar. The excellent coordinating properties of CH_3CN are presumably required. With this in mind, ReF_6 and Cu were reacted in a mixture of the two solvents, IF_5 being the bulk solvent, and CH_3CN present only in sufficient quantities to solvate the copper ions. ReF_6 was present in excess, despite which the solid isolated was only slightly contaminated by polymer. The solid analyses reasonably well as Cu(II) $(ReF_6)_2.4CH_3CN.0.5IF_5$. This was the first time a reaction involving excess ReF_6 and CH_3CN had been successful. Further work is undoubtedly needed on this solvent system, to optimise the $IF_5:CH_3CN$ ratio. However mixtures of IF_5 and CH_3CN are potentially useful solvents for reactions with materials too reactive to be handled in CH_3CN alone. The products obtained should allow a thorough spectroscopic study, including Raman spectroscopy, to be carried out.

The conclusions from this section of the present work are as follows.

CH_3CN is a good solvent for UF_6 providing that the reaction of UF_6 is fast, e.g. oxidation of metals. If the intended reaction is slow, e.g. fluoride ion addition to UF_6 by HgF_2, reduction of UF_6 by the solvent occurs to give UF_5.

Spectroscopic data on the UF_6^- ion are in good agreement with those of Ryan.[203]

CH_3CN is not a good general solvent for ReF_6, but solvent attack can be minimised by using IF_5-CH_3CN mixtures.

Experimental

Chemicals

Cd metal (Koch-Light 99.9999%) was scraped free of oxide in an inert atmosphere box. HgF_2, (Roc/Ric, 99%) was stored in a glove box and used as received. Other materials were purified as described in Chapters 2 - 4.

I UF_6 + Metals

In a typical reaction, Cu(0.1251g, 2.0 mmol) was placed in a flamed-out reaction vessel in an inert atmosphere box. After evacuation, CH_3CN, (ca. 1.5g, 40 mmol) was distilled in, followed by UF_6 (0.44g, 1.9 mmol). On warming to room temperature, the solution was yellow in colour, but rapidly became blue-green. After shaking for a period of 30 minutes to an hour, the acetonitrile was removed in vacuo, leaving a blue-green solid and unreacted Cu. 0.0666g (1.0 mmol) Cu reacted and this is consistent with the anticipated stoichiometry of $Cu:UF_6 = 1:2$.

The reactions with Cd and Tl metals were carried out in exactly the same manner. For example, Tl (0.3601g, 1.76 mmol) was reacted with UF_6 (ca 0.95g, 2.7 mmol) in 3.9g CH_3CN.

On removal of excess CH_3CN, $Tl(UF_6)_3.5CH_3CN$ was obtained as a pale green solid, as well as 0.1871g (0.92 mmol) unreacted Tl. 0.84 mmol Tl had reacted with 2.7 mmol UF_6 which is in reasonable agreement with the elemental analysis.

When the metal present was silver, the acetonitrile began to polymerise as soon as it melted, and a very dark brown

Table 32

Analyses of the Hexafluorouranate (V) Salts

Found (calculated) %

Compound	F	M	U	C	H	N
$Cu(UF_6)_2.5CH_3CN^a$	23.2 (23.4)	6.4 (6.5)	49.0 (48.9)	12.1 (12.3)	1.5 (1.6)	7.0 (7.2)
$Cu(UF_6)_2.5CH_3CN^b$	23.2 (23.4)	6.4 (6.5)	48.6 (48.9)	12.4 (12.3)	1.5 (1.6)	7.4 (7.2)
$Cd(UF_6)_2.5CH_3CN$	22.3 (22.3)	10.8 (11.0)	46.6 (46.6)	11.8 (11.8)	1.6 (1.5)	6.7 (6.8)
$Tl(UF_6)_3.5CH_3CN^c$	23.1 (23.3)	-	49.1 (48.7)	8.3 (8.2)	1.0 (1.0)	3.7 (4.8).
$Tl(UF_6)_3.5CH_3CN^d$	23.3 (23.3)	-	48.9 (48.7)	8.4 (8.2)	1.0 (1.0)	3.7 (4.8)
$Hg(UF_6)_2.6CH_3CN^e$	18.9 (19.8)	16.6 (17.4)	40.2 (41.4)	11.0 (12.5)	1.4 (1.6)	-

a Product from reaction of one hour duration

b Product from reaction of four days duration

c From Tl + UF_6 reaction

d From TlF + UF_6 reaction

e From HgF_2 + UF_6 reaction

solution resulted. Attempts to isolate the silver compound by distillation and redissolving were unsuccessful, since the polymer formed was moderately soluble in the remaining CH_3CN.

The far-i.r. spectrum of $Tl(UF_6)_3.5CH_3CN$ was obtained using a Beckman-RIIC FS 720 Far-i.r. Fourier Transform spectrophotometer with an FTC100 computer. The sample was a nujol mull between Ge plates.

In the ^{18}F exchange experiment, $Cs^{18}F$ was used to label BF_3 which in turn was used to label UF_6. Labelled UF_6 (0.0826g, 0.235 mmol) was added to a solution of $Cu(UF_6)_2.5CH_3CN$ (0.1400g, 0.144 mmol) in CH_3CN. This mixture was allowed to stand at 299K for 30 minutes, after which time the volatile material (UF_6 and CH_3CN) was removed from the involatile $Cu(UF_6)_2.5CH_3CN$ and both were counted.

Counts from volatile materials=744 counts $mmol^{-1}$ sec^{-1}

Counts from involatile materials=1332 counts $mmol^{-1}sec^{-1}$

These results indicated complete exchange, as well as partial reduction of volatile UF_6 to involatile UF_5.

II Reduction of UF_6 by CH_3CN

CH_3CN and UF_6 were distilled into a 1 cm cell (Figure 7), and a Raman tube. Spectra were run immediately the solutions warmed to room temperature. Electronic spectra were then run every 30 minutes for two hours. The f-f bands gradually increased in intensity with time, as is shown by the growth of the band at 7190 cm^{-1}.

t (minutes)	0	30	60	90	120
Relative Intensity	16	25	36	54	99

The spectra were in good agreement with those obtained previously (Chapter 4) for UF_5 in CH_3CN. The spectrum obtained after 120 minutes is shown in Table 30.

Raman spectra were run after 2, 3 and 5 hours:

t=0 :	665(1)	647(8)	635(3)	615(1)		503(1.5)
t=2 :	663(1)	647(7)	635(3)	614(1.8)		504(1.5)
t=3 :	666(1)	647(8)	635(3.5)	616(3)	608(1.2)	504(1.5)
t=5 :	No spectrum because of polymerisation					

III ReF_6 + Copper

IF_5 (*ca* 8g, 36 mmol) and CH_3CN (*ca* 0.1g, 2.5 mmol) were distilled into a reaction vessel containing Cu (0.02g, 0.3 mmol). The solvents were allowed to melt in order to mix before the addition of ReF_6. Very little polymerisation occurred. ReF_6 must be in excess or remaining Cu reacts with IF_5. The solid product analysed as:

Cu: 7.1, F : 26.5, I : 7.2, C : 10.7, H : 1.3, N : 6.1%

$Cu(ReF_6)_2\ 4C_2H_3N\ 0.5\ IF_5$ requires:

Cu : 6.8, F : 29.3, I : 6.8, C : 10.2, H : 1.3, N : 6.0%

CHAPTER SIX

FLUORIDE ION ADDITION REACTIONS. REACTIONS OF COPPER(II) FLUORIDE WITH URANIUM HEXAFLUORIDE, AND COPPER(II) FLUORIDE TETRAKIS-(ACETONITRILE) TETRAKIS-(IODINE PENTAFLUORIDE) WITH PHOSPHORUS PENTAFLUORIDE, TUNGSTEN HEXAFLUORIDE, RHENIUM HEXAFLUORIDE, AND URANIUM HEXAFLUORIDE.

Fluoride Ion Addition Reactions

Reactions of Copper(II) Fluoride with Uranium Hexafluoride, and Copper(II) Fluoride tetrakis-(Acetonitrile) tetrakis-(Iodine Pentafluoride) with Phosphorus Pentafluoride, Tungsten Hexafluoride, Rhenium Hexafluoride and Uranium Hexafluoride.

Introduction

Part of the work described in this chapter is an extension of that described in Chapter 5, and is a study of fluoride ion addition reactions of UF_6 in CH_3CN.

ReF_6 attacks CH_3CN too rapidly for hepta- and octa-fluororhenate(VI) compounds to be isolated. IF_5 was examined as an alternative solvent for these preparations.

The main objective was to prepare MF_7^- and MF_8^{2-} compounds (M = U, Re), and record their vibrational spectra. No thorough investigation of the vibrational spectra of these compounds had previously been reported. However, after the present work on UF_6 had been completed and the work on ReF_6 started, detailed accounts of the vibrational spectra of hepta- and octa-fluorouranates(VI)[147] and rhenates(VI)[92] appeared.

Results and Discussion

I Reaction of Copper(II) Fluoride with Uranium Hexafluoride in Acetonitrile

CuF_2 reacts with UF_6 over a period of 1 to 2 hours at 298K, forming a blue-green solution. Removal of solvent leaves a blue-green solid. However, the results obtained indicate that two main reactions are occurring. These are fluoride ion addition to UF_6 and reduction of UF_6, this latter reaction being analogous to the $HgF_2 + UF_6$ reaction discussed in Chapter 5.

The elemental analysis of one sample indicates a composition close to $CuF_2.(UF_6)_2.5CH_3CN$, and the weight of CuF_2 used compared with the weight of product obtained also gives a ratio of $CuF_2 : UF_6 = 1 : 2$. A Raman spectrum of the reaction mixture shows a strongly polarised band at 594cm^{-1} and an i.r. spectrum of the solid product shows bands at 450 w, 505 s, br, and 530cm^{-1}, s, br. Since there were no vibrational data on UF_7^- or UF_8^{2-} ions available for comparison, these results were believed to be consistent with the formation of $Cu(UF_7)_2.5CH_3CN$.[206]

With other samples, Raman and electronic absorption spectra show the presence of UF_6^-.

These spectra are very similar to those obtained from the reaction between Cu and UF_6 in CH_3CN. (Chapter 5).

Subsequently, Bougon et al published[147] the results of a thorough investigation of vibrational spectra of $M(UF_7)$ and M_2UF_8 (M = Cs, NO). These show that the most intense band in the Raman spectrum of UF_7^- and UF_8^{2-} compounds occurs at <u>ca</u> 625cm^{-1} and 590cm^{-1} respectively. This suggests that the 594cm^{-1} band observed much earlier in the present work is due to UF_8^{2-} rather than UF_7^-. The i.r. data obtained by Bougon et al[147] and in this work are shown in Table 33. The i.r. data from the present work are inconclusive.

The bands at 530 and 505cm^{-1} may be due to either UF_7^- or UF_8^{2-}, and the weak band at 450cm^{-1} is insufficient to make a definite assignment although it suggests the presence of UF_7^-.

An ^{18}F exchange study carried out by Dr. R.T. Poole indicates complete exchange occurring between "$Cu(UF_7)_2$" and labelled UF_6, within 15 minutes. If the compound is $Cu(UF_7)_2$, then the value of "f" is 1·0255, whereas if the compound is $Cu(UF_8)_2$, then f = 1·115. However the technique does not differentiate between pure $Cu(UF_7)_2$ and a mixture whose overall composition is CuU_2F_{14}.

It is believed that the following reactions occur in the CuF_2 + UF_6 in CH_3CN system.

$$UF_6 + F^- \longrightarrow UF_7^-\,(solv) \qquad \underline{1}$$

$$UF_{7(solv)}^- + F^- \longrightarrow UF_8^{2-}\,(solv) \qquad \underline{2}$$

$$UF_6 \longrightarrow UF_{5(solv)} + \text{solvent fluorination} \qquad \underline{3}$$

$$UF_{5(solv)} + F^- \longrightarrow UF_6^-\,(solv) \qquad \underline{4}$$

The reactions are probably linked by an equilibrium such as:

$$UF_8^{2-} + UF_5 \rightleftharpoons UF_7^- + UF_6^- \qquad \underline{5}$$

It is interesting to compare this equilibrium with that found in the reaction between Cu and WF_6 in CH_3CN.[211]

Table 33

Infrared Data on Hepta- and Octa-Fluorouranates(VI).

Octafluorouranates(VI)[a]

Cs_2UF_8	$(NO)_2UF_8$
586 w	590 sh
578 w	
	534 sh
508 s	510 s
	498 sh
464 sh	

Heptafluorouranates(VI)[a]

C_5UF_7	$NOUF_7$
618 vw	624 vw
605 m	604 m
540 sh	540 sh
507 s	508 s
450 sh	450 sh
	420 vw

Product from CuF_2+UF_6 in CH_3CN
530 s br
505 s br
450 w

Frequencies in cm^{-1}

[a] Data from reference 147

This is:

$$WF_7^- + "WF_5" \rightleftharpoons WF_6 + WF_6^-$$

The occurrence of this equilibrium supports the concept that equilibria such as equation 5 occur in the reaction between CuF_2 and UF_6 in CH_3CN.

The product isolated from this reaction is most probably a mixture containing UF_6^-, UF_7^- and UF_8^{2-}. If UF_6 is present in a large excess, UF_5 will also be included. The exact composition of the mixture probably depends on factors such as the concentration of UF_6 and particle size of the CuF_2. High UF_6 concentration and large CuF_2 particle size would probably increase the amount of $Cu(UF_6)_2$ formed.

The main conclusion drawn is that although CH_3CN is a good solvent for copper[206] and alkali metal[210] heptafluorouranates(VI), it is not a good medium for carrying out their preparations. This is because the fluoride ion addition reaction is not sufficiently fast with respect to reduction by the solvent.

II Reaction of Copper(II) Fluoride tetrakis-(Acetonitrile) tetrakis-(Iodine Pentafluoride) with Phosphorus Pentafluoride and Tungsten Hexafluoride in Acetonitrile and with Rhenium Hexafluoride and Uranium Hexafluoride in Iodine Pentafluoride.

Since CH_3CN is not a suitable solvent for fluoride ion addition reactions to either ReF_6 or UF_6, IF_5 was considered as an alternative solvent. However no reaction occurs between CuF_2 and ReF_6 in IF_5. UF_6 was not investigated. IF_5 and CH_3CN have similar dielectric constants but CH_3CN is a much better co-ordinating solvent.

It was hoped that a reaction would occur if $CuF_2.4CH_3CN.4IF_5$ were used in place of CuF_2. This compound has the advantages that the Cu(II) ion is already co-ordinated, and unlike CuF_2, it is soluble in CH_3CN and IF_5. It was not known if this molecular adduct would function as a fluoride ion donor. This was determined by reacting it in CH_3CN with the known F^- ion acceptors PF_5 and WF_6, since the PF_6^- and WF_7^- ions are both well known, and easily detected.

PF_5 reacts with a blue-green solution of $CuF_2.4CH_3CN.4IF_5$ in CH_3CN, producing a green solution. A ^{19}F n.m.r. spectrum shows a quintet at +52 ppm and a doublet at +4 ppm, J_{F-F} = 90 Hz., assigned to IF_5. A doublet at -73 ppm, J_{P-F} = 695 Hz. is also observed. The ^{19}F n.m.r. data for the PF_6^- ion in the literature are δ = -72 ppm, J_{P-F} = 710Hz.[214] A ^{31}P I.N.D.O.R. spectrum was run and this shows a septet (Figure 35), J_{P-F} = 720 ± 40 Hz. This confirms the presence of the PF_6^- ion.

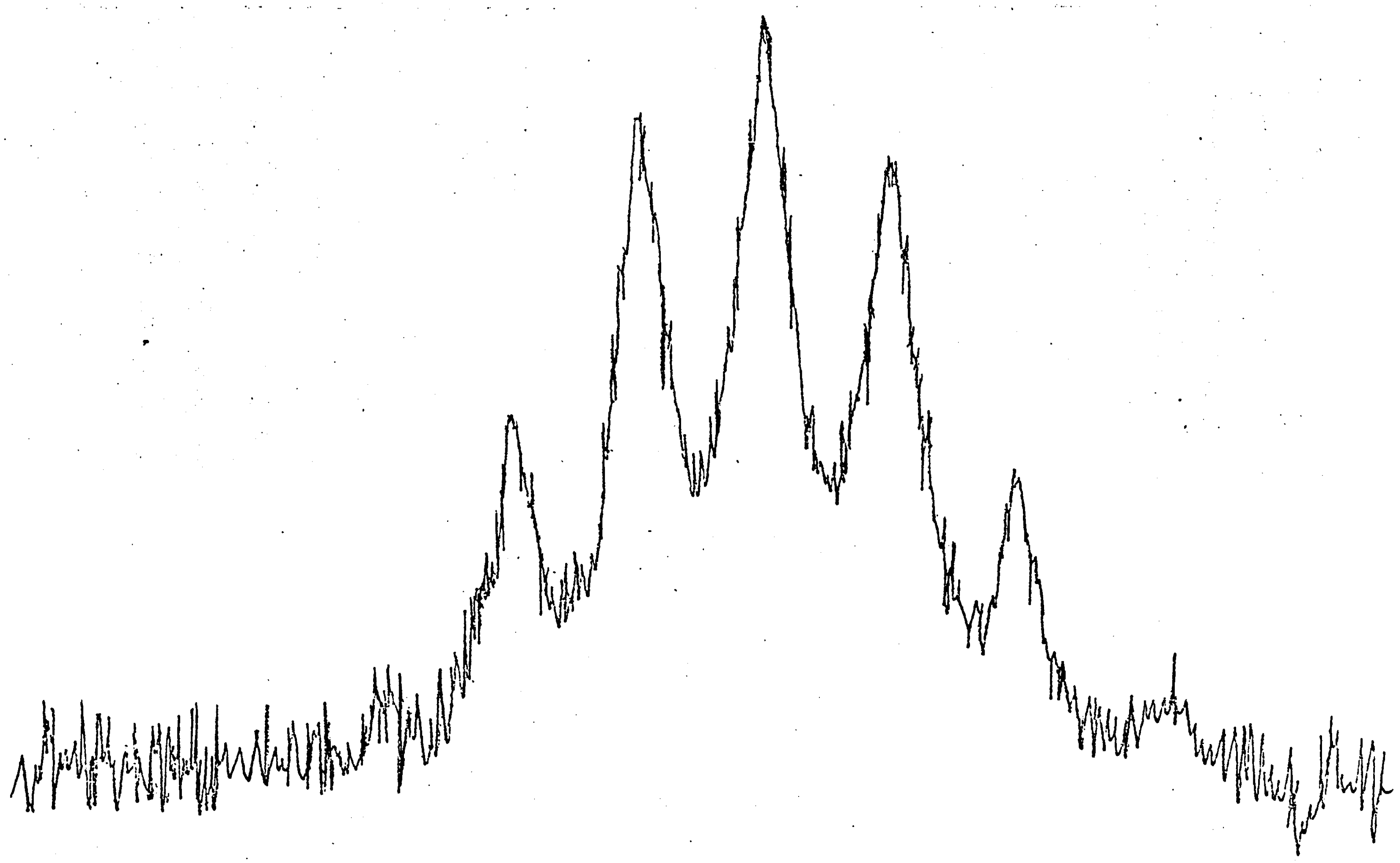
An interesting feature of the ^{19}F n.m.r. spectrum is the observation of F-F coupling in the IF_5 signals. This is not observed in spectra of CH_3CN solutions of $CuF_2.4CH_3CN$ $4IF_5$ and suggests that the IF_5 molecules are no longer under the influence of the paramagnetic Cu(II) ion, and that the adduct is no longer intact. The reaction is believed to be:

$$CuF_2.4CH_3CN.4IF_5 + 2PF_5 \xrightarrow{CH_3CN} Cu(PF_6)_2.5CH_3CN + 4IF_5$$

Figure 35

^{31}P I.N.D.O.R. SPECTRUM OF $PF_5 + CuF_2.4CH_3CN.4IF_5$

REACTION MIXTURE



The reaction of $CuF_2.4CH_3CN.4IF_5$ with WF_6 in CH_3CN is very similar. A ^{19}F n.m.r. spectrum shows the doublet and quintet characteristic of IF_5, as well as a peak at +66 ppm due to WOF_4 and a broad peak 7 ppm upfield from external WF_6. This latter peak is assigned as WF_7^- rapidly exchanging F^- ions with WF_6. A Raman spectrum of a sample of reaction mixture shows bands due to IF_5, CH_3CN and a band at 710cm^{-1} which is in good agreement with the reported[145] frequency of 705cm^{-1} for WF_7^-.

$CuF_2.4CH_3CN.4IF_5$ therefore acts as an F^- ion donor towards PF_5 and WF_6 in CH_3CN solution.

When $CuF_2.4CH_3CN.4IF_5$ is dissolved in IF_5 and ReF_6 added, a dark green solution is formed. There is no further colour change after 12 hours shaking. Removal of volatile material in vacuo leaves a sticky blue-black solid. This solid analyses as $CuF_{31}I_{3.7}Re_3C_{12}H_{18}N_6$, and dissolves readily in CH_3CN forming a deep blue-green solution. A Raman spectrum of the solution shows bands due to IF_5 and CH_3CN as well as one at 670cm^{-1}. This band cannot be assigned with certainty, but it may be due to ReF_7^-. An i.r. spectrum of the solid was run, and the data are shown in Table 34.

An interesting feature of this spectrum is the presence of co-ordinated CH_3CN, unattacked by ReF_6 despite the high concentration of the latter, and a long reaction time. The shoulder at 950cm^{-1}, assigned to a second C-C stretching frequency, suggests the presence of two types of CH_3CN molecules. The very broad band at <u>ca</u> 600cm^{-1} is not very informative and probably arises mainly from IF_5

Table 34

I.r. Spectrum of Product from Reaction between $CuF_2.4CH_3CN.4IF_5$ and ReF_6 in IF_5 (Thin film)

Frequency (cm^{-1})	Possible Assignments	
3010 w	CH_3CN	C-H stretch
2945 m	CH_3CN	C-H stretch
2320 sh	CH_3CN	Combination Band
2300 s	CH_3CN	C≡N stretch
1720 w, br		
1405 s, br	CH_3CN	C-H bend
1365 s	CH_3CN	C-H bend
1300 w		
1070 sh	Re-O	
1035 s, br	CH_3CN	CH_3 rock
1010 m, sh	Re-O	
960 s	CH_3CN	C-C stretch
950 sh	CH_3CN	C-C stretch
785 w		
705 sh	ReF_6	
695 sh	IF_5	
600 Vs, Vbr	IF_5, ReF_7^-	
465 w		
400 sh		

with perhaps ReF_7^- also. The results of the elemental analysis are probably best expressed by the formulation: $CuRe_3F_{12}.6CH_3CN.3.7IF_5$. The presence of six CH_3CN molecules can only be explained by assuming that residual CH_3CN remained from the preparation of $CuF_2.4CH_3CN.4IF_5$.

UF_6 reacts rapidly with $CuF_2.4CH_3CN.4IF_5$ in IF_5 and a bright yellow-green solid precipitates. This solid analyses as $CuF_{27}I_2U_3C_8H_{12}N_4$. Samples decompose in the laser beam of the Raman spectrophotometer, however one spectrum shows bands at 625, 870 and 910cm^{-1}. (Other spectra show only a steeply rising baseline). The first of these bands is tentatively assigned as UF_7^- while the others are believed to be decomposition products. An i.r. spectrum was recorded and the data are presented in Table 35.

The vibrational data therefore suggest the presence of two types of acetonitrile, as well as molecular IF_5, UF_7^- and perhaps UF_6. These data are not sufficient for an exact formulation to be made but $CuU_3F_{17}.2IF_5.4CH_3CN$ is believed to be correct.

The reactions of $CuF_2.4CH_3CN.4IF_5$, with ReF_6 and UF_6 in IF_5 are not simple F^- ion addition reactions yielding heptafluoro or octafluorometallate(VI) ions. These species are probably present, but only to a small extent. The products are most likely to be mainly adducts. This suggests that either ReF_6 and UF_6 are poorer F^- ion acceptors than PF_5 or WF_6, or that although $CuF_2.4CH_3CN.4IF_5$ behaves as an F^- ion donor in CH_3CN, it does not in IF_5. The products obtained, however, are most interesting and deserve to be thoroughly characterised. Of particular interest are

Table 35

I.r. Spectrum of Product from Reaction between $CuF_2.4CH_3CN.4IF_5$ and UF_6 in IF_5. (Nujol Mull)

Frequency (cm^{-1})	Possible Assignment	
2320 sh	CH_3CN	Combination band
2300 m	CH_3CN	C≡N stretch
1295 vw		
1080 w		
1025 m	CH_3CN	CH_3 rock
1015 sh		
960 s	CH_3CN	C–C stretch
950 s	CH_3CN	C–C stretch
825 w		
720 w		
685 m	IF_5	
645 sh		
605 Vs	IF_5, UF_6?	
530 Vs	UF_7^- ?	
505 w	UF_7^- ?	
470 m	UF_7^- ?	
400 sh		

the facts that there are two types of CH_3CN molecule present, despite the parent compound $CuF_2.4CH_3CN.4IF_5$ having only one, and that the fluorine content of these compounds is lower than expected. Hydrolysis is a possible explanation in the case of the rhenium compound since the element Re was not analysed directly and therefore a small oxygen content in the compound would not be detected by the analysis results. However the analysis of the uranium compound totalled 99•9% and therefore hydrolysis can be ruled out. Further investigation of these compounds is obviously required.

Experimental

Chemicals

Phosphorus pentafluoride (Fluorochem Ltd) contained HF as an impurity. This was removed by trap to trap distillation over NaF. PF_5 was stored over NaF at 77K. Other materials were purified as described in previous chapters. $CuF_2.4CH_3CN.4IF_5$ was prepared as described in Chapter 3 using a double flask, one half for the preparation and the other for the subsequent reaction. (Figure 27)

I $CuF_2 + UF_6$ in CH_3CN

CuF_2 (0·0144g.; 0·14mmol), reacted overnight with UF_6 (0·1778g., 0·51mmol) in CH_3CN (1·0072g). Removal of excess UF_6 and CH_3CN left a blue-green solid (0·1468g) which analysed as $CuF_2(UF_6)_2.5CH_3CN$.

Found: Cu: 6·2, F: 24·9, U: 44·5, C: 12·6, H: 1·7, N: 4·0%.

$CuF_{14}U_2C_{10}H_{15}N_5$ requires Cu: 6·3, F: 26·3, U: 47·1, C: 11·9, H: 15, N: 6·9%.

Atomic ratios included Cu: F = 1:13·5, Cu: U = 1:1·9 and U: F = 1:7·02. The sample of reaction mixture, which showed a Raman band at 594cm^{-1}, was sealed off in vacuo after 30 minutes shaking.

Samples of reaction mixtures from other reactions showed a Raman band at 613cm^{-1} and their electronic spectra were very similar to that of $Cu(UF_6)_2$ in CH_3CN (Figure 33).

The ^{18}F exchange study (Table 36) was performed by Dr. R.T. Poole, using a freshly isolated sample of reaction product. UF_6 was labelled as described in Chapter 5.

No Raman spectrum of any sample of solid product could be obtained because of decomposition in the laser beam.

Table 36

^{18}F Exchange between U^*F_6 and "$CuU_2F_{14}.5CH_3CN$" in CH_3CN

m mols $CuU_2F_{14}C_{10}H_{15}N_5$	m mols U^*F_6	% mass balance	Counts/100 sec [Corrected A_1]	Counts/100 sec [Corrected A_2]	Radiochemical Balance %	f	Time (minutes)
0·3984	1·5238	99·2	207023 [212250]	329784 [334000]	103·1	1·0255 ± 0·0026	15

T = 293·0 ±0·1K

Data obtained by Dr. R.T. Poole

IIa Reaction of $CuF_2.4CH_3CN.4IF_5$ with PF_5

$CuF_2.4CH_3CN.4IF_5$ (ca 0·1mmol) was dissolved in CH_3CN and PF_5 (0·2mmol) added. PF_5 was measured by allowing the solid at 77K to warm and expand into a calibrated vessel, the pressure being measured on a mercury manometer. The reaction vessel was shaken overnight and a sample of reaction mixture in an n.m.r. tube sealed off.

IIb Reaction of $CuF_2.4CH_3CN.4IF_5$ with WF_6

WF_6 (ca 0·5mmol) was added to a CH_3CN solution of $CuF_2.4CH_3CN.4IF_5$ (ca 0·2mmol) and the mixture shaken for six hours. A sample of this mixture was sealed off in an n.m.r. tube. A similar reaction was carried out and a sample for a Raman spectrum obtained.

IIc Reaction of $CuF_2.4CH_3CN.4IF_5$ with ReF_6

$CuF_2.4CH_3CN.4IF_5$ (ca 0·2mmol) dissolved in IF_5, was reacted with excess ReF_6. On removal of excess IF_5 and ReF_6 a very sticky blue-black solid was obtained which analysed as:

	Cu	F	I	Re (by difference)	C	H	N
Found %	: 3·4	31·0	25·2	28·4	7·1	1·1	4·0
$CuF_{30.5}I_{3.7}Re_3C_{12}H_{18}N_6$ requires %	: 3·3	30·3	24·5	29·1	7·5	0·9	4·4

The solid was found to be extremely moisture sensitive, but dissolved readily in CH_3CN without reaction.

IId Reaction of $CuF_2.4CH_3CN.4IF_5$ with UF_6

On addition of UF_6 to an IF_5 solution of $CuF_2.4CH_3CN.4IF_5$, a yellow-green precipitate appeared as soon as the mixture melted. The excess UF_6 and IF_5 were removed in vacuo and a powdery solid isolated, whose colour can be best described as "L.N.E.R. Apple Green". This analysed as:

		Cu	F	I	U	C	H	N
Found %	:	3·7	29·7	14·6	41·9	5·8	0·9	3·2
$CuF_{27}I_2U_3C_8H_{12}N_4$ requires	:	3·7	30·0	14·9	41·8	5·6	0·7	3·3

A sample of this solid decomposed in the laser beam of the Raman spectrophotometer, despite the use of several different excitation frequencies, including 457·9, 476·5, 488·0 and 514·5nm.

APPENDIX

X-ray Powder Data

IF_5.1,4-Dioxane

$\sin^2\theta$	d	Intensity
0•0196	6•394	vs
0•0230	5•901	s
0•0268	5•465	m
0•0314	5•054	vs
0•0452	4•210	vs
0•0498	4•009	m
0•0612	3•618	s
0•0685	3•419	m
0•0909	2•969	s
0•1221	2•562	w
0•1305	2•478	w
0•1349	2•437	vw
0•1502	2•310	vw
0•1667	2•192	w
0•2147	1•932	w
0•2248	1•888	vw
0•2350	1•846	w
0•2542	1•775	w
0•2676	1•730	vw

$TlIOF_4$ from $Tl+IF_5$ reaction

$\sin^2\theta$	d	Intensity
0·0413	4·405	vw
0·0516	3·941	m
0·0585	3·700	s
0·0663	3·475	vs
0·0714	3·350	w
0·0811	3·142	vw
0·0865	3·045	m
0·0929	2·936	m
0·1474	2·332	m
0·1549	2·275	m
0·1606	2·233	m
0·1690	2·177	m
0·1796	2·112	s
0·1881	2·064	w
0·1949	2·027	vw
0·2015	1·994	s
0·2197	1·910	s
0·2519	1·783	w
0·2618	1·749	m
0·2859	1·674	vw
0·2994	1·635	w
0·3580	1·496	w
0·3676	1·476	w

$TlIOF_4$ from TlF + IF_5 reaction

$\sin^2\theta$	d	Intensity
0·0489	4·048	w
0·0589	3·687	m
0·0663	3·475	s
0·0867	3·039	w
0·0919	2·952	w
0·1464	2·339	w
0·1539	2·282	w
0·1609	2·231	w
0·1684	2·182	w
0·1793	2·114	m
0·2008	1·997	m
0·2193	1·911	m
0·2500	1·790	vw
0·2610	1·752	w
0·3563	1·500	vw
0·3685	1·475	vw

UF_5

$\sin^2\theta$	d	Intensity
0·0133	7·757	vw
0·0274	5·409	vw
0·0387	4·548	s
0·0461	4·169	s
0·0533	3·877	m
0·0594	3·675	vw
0·0710	3·360	m
0·0989	2·847	m
0·1281	2·500	vw
0·1530	2·289	vw
0·1736	2·148	vw
0·1970	2·016	w
0·2086	1·960	w
0·2215	1·902	w
0·2325	1·857	vw

$UF_5.CH_3CN$

$\sin^2\theta$	d	Intensity
0•0309	5•092	vw
0•0379	4•597	s
0•0474	4•112	vs
0•0882	3•014	s
0•1198	2•586	m
0•1331	2•453	w
0•1894	2•057	vw
0•2029	1•987	vw
0•2219	1•900	s
0•2477	1•799	vw

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