

**INORGANIC FLUORINE CHEMISTRY; LOW-TEMPERATURE
FLUORINATION OF THE MAIN GROUP ELEMENTS AND SOME
METAL FLUORIDES**

A thesis presented for the degree of

DOCTOR OF PHILOSOPHY

in the

Faculty of Science

by

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Dedicated to my parents,

wife and daughter

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Statement

The experimental work described in this thesis has been carried out by the author in the Department of Chemistry of the University of Leicester between October 1986 and March 1990. The work has not been submitted, for any other degree at this or any other university

date:

signed: 
M.N. Al-Mulki

Abstract

The U.V. and laser induced photolysis of noble-gas/fluorine mixtures have been studied at -196°C . The U.V. photolysis of krypton/fluorine and xenon/fluorine mixtures for 12h gives approximately a 30% yield of KrF_2 and XeF_2 respectively. Whilst photolysis with an argon ion laser gives comparable yields after only 30 minutes. Two temperature dependent phases of KrF_2 were observed. Laser photolysis of oxygen/fluorine mixtures at -196°C gives O_4F_2 and O_2F_2 and of UF_5/F_2 mixtures gives UF_6 .

The photolysis of noble-gas /fluorine mixtures with added Lewis acids were also examined. A 1:1:2 mixture of fluorine, krypton and MF_5 (M= As, Sb, I), photolysed at -196°C using either U.V. or argon ion laser radiation also gives KrF_2 . There is no evidence of reaction with MF_5 at -196°C . Warming of the resultant mixtures affords $\text{Kr}_2\text{F}_3^+\text{SbF}_6^-$, α - and β - $\text{KrF}^+\text{Sb}_2\text{F}_{11}^-$, α - $\text{KrF}^+\text{AsF}_6^-$, $\text{KrF}^+\text{As}_2\text{F}_{11}^-$ and $\text{KrF}_2.n\text{IF}_5$ (n=1-3) at various temperatures which have been identified by Raman Spectroscopy.

Investigations of reactions involving fluorine atoms, produced from elemental fluorine by the catalytic method, were made. Reactions involving krypton/fluorine and xenon/fluorine mixtures gave KrF_2 , XeF_2 and XeF_4 respectively.

Also in this work an attempt was made to prepare a possible (Xe-I) containing species by the reaction between $\text{Xe}_2^+\text{Sb}_2\text{F}_{11}^-$ with iodine. Further investigations need to be carried out to clarify the results obtained.

LIST OF CONTENTS

CHAPTER ONE	The history, preparation and properties of KrF ₂ and its chemistry	
1.1	Introduction	1
1.2	Physical properties of KrF ₂	7
1.2.1	Physical properties and thermodynamic data	7
1.2.2	Infrared and Raman spectroscopy	10
1.2.3	Mass spectrometry	13
1.2.4	NMR spectroscopy	13
1.2.5	Photoelectron spectroscopy	16
1.2.6	Crystal and molecular structure determined by diffraction methods	16
1.2.7	Molecular orbital calculations	18
1.2.8	Other data	19
1.3	Chemistry of KrF ₂	21
1.3.1	Lewis adducts of KrF ₂ - their preparation	21
1.3.2	Lewis adducts of KrF ₂ - spectroscopic data	26
1.3.2a	¹⁹ F NMR spectroscopy	26
1.3.2b	Raman spectroscopy	29
1.3.3	Oxidizing power of KrF ₂ and its adducts	32
CHAPTER TWO	The reaction of some noble gases with liquid fluorine at -196°C using U.V. photolysis	36
2.1	Introduction	37

2.2	The preparation of KrF_2	37
2.3	A new solid state form of KrF_2	39
2.3.1	Discussion	45
2.4	The U.V. photolysis of F_2/Ar mixtures at -196°C (Attempt to prepare ArF_2)	47
2.4.1	Raman spectroscopy	47
2.4.2	Mass spectrometry	48
2.4.3	Reaction of the product of the photolysis of Ar/F_2 mixture with KI	48
2.4.4	Conclusion	50
CHAPTER THREE	The reaction of Kr/F_2 mixture with some Lewis acids using U.V. photolysis at -196°C	51
3.1	Introduction	52
3.2	The reaction of Kr/F_2 mixture with SbF_5 using U.V. photolysis at -196°C	52
3.2.1	The preparative method	52
3.2.2	Raman data	53
3.2.2a	Raman spectrum at -196°C	53
3.2.2b	Raman spectrum at -95°C	55
3.2.2c	Raman spectrum at -25°C	55
3.2.2d	The identification of two forms of $\text{KrF}^+\text{Sb}_2\text{F}_{11}^-$	60
3.2.2e	The observation of a new adduct $[\text{xKrF}_2.\text{KrF}]^+\text{Sb}_2\text{F}_{11}^-$	61
3.3	The reaction of Kr/F_2 mixture with AsF_5 using U.V. photolysis	65
3.3.1	The preparation of $\alpha\text{-KrF}^+\text{AsF}_6^-$	65
3.3.2	The observation of a new KrF_2 adduct	

	with AsF ₅	70
3.3.2a	The preparation of KrF ⁺ As ₂ F ₁₁ ⁻	70
3.3.2b	Raman spectrum at -30°C	70
3.3.2c	Discussion	75
3.4	The reaction of α- and β-KrF ⁺ Sb ₂ F ₁₁ ⁻ mixture with O ₂ gas	76

CHAPTER FOUR Laser photolysis reactions in liquid

	fluorine	78
4.1	Introduction	79
4.2	Experimental procedure	79
4.3	The reactions	80
4.3.1a	The laser photolysis of a Kr/F ₂ mixture at -196°C	80
4.3.1b	The prolonged laser photolysis of an KrF ₂ /F ₂ mixture at -196°C ; an attempt to prepare higher fluorides of krypton	82
4.3.2	The laser photolysis of a Kr/F ₂ mixture with IF ₅ at -196°C	83
4.3.3a	The preparation of a new KrF ₂ adduct with IF ₅	83
4.3.3b	The laser photolysis of an IF ₅ /F ₂ mixture at -196°C	84
4.3.4	The laser photolysis of a Xe/nF ₂ mixture at -196°C	88
4.3.4a	The preparation of XeF ₂ using laser photolysis	88
4.3.4b	The laser photolysis of a XeF ₂ /F ₂ mixture at -196°C	88
4.3.5	The laser photolysis of an O ₂ /F ₂ mixture	

	at -196°C	89
4.3.5a	The preparation of O_4F_2 using laser photolysis	89
4.3.5b	The laser photolysis of an $\text{O}_4\text{F}_2/\text{F}_2$ mixture -196°C	91
4.3.6a	The laser photolysis of an F_2/Ar mixture at -196°C	91
4.3.6b	The laser photolysis of an $\text{SbF}_5/\text{Ar}/\text{F}_2$ mixture at -196°C	94
4.3.6c	The laser photolysis of an $\text{O}_2/\text{Ar}/\text{F}_2$ mixture at -196°C	95
4.3.7	The laser photolysis of a $\beta\text{-UF}_5/\text{F}_2$ mixture at -196°C	96
4.3.8	The laser photolysis of a N_2/F_2 mixture at -196°C	98
4.3.9	The laser photolysis of an OsF_6/F_2 mixture at -196°C	100
4.3.10a	The laser photolysis of a RuF_5/F_2 mixture at -196°C	101
4.3.10b	The laser photolysis of a $\text{Kr}/\text{F}_2/\text{RuF}_5$ mixture at -196°C	101
4.3.11	The laser photolysis of CsF/F_2 mixture at -196°C	104
4.4	Discussion	107
4.5	Conclusion	108

CHAPTER FIVE	Preliminary work on the use of the hot wire method for producing fluorine atoms for reaction	109
5.1	Introduction	110

5.2	Reactor designs	113
5.2.1	The Pyrex reactor	115
5.2.2	The metal reactor	115
5.3	The reactions (glass reactor)	118
5.3.1	Attempts to prepare KrF_2	118
5.4	The reactions (metal reactor)	119
5.4.1	The preparation of KrF_2	119
5.4.2	Attempt to prepare " KrF_4 "	120
5.4.3	The synthesis of XeF_2	121
5.4.4	The synthesis of XeF_4	122
5.4.5	Attempts to prepare XeF_6	122
5.4.6	Attempts to prepare " ArF_2 "	124
5.4.7	The hot wire reaction between OsF_6 and F_2	126
5.5	Discussion	127
CHAPTER SIX	Attempts to prepare a (Xe-I) containing species	128
6.1	Introduction	129
6.2	The preparation of $\text{XeF}^+\text{Sb}_2\text{F}_{11}^-$	129
6.3	The preparation of $\text{Xe}_2^+\text{Sb}_2\text{F}_{11}^-$	130
6.4	The reaction of $\text{Xe}_2^+\text{Sb}_2\text{F}_{11}^-/\text{XeF}^+\text{Sb}_2\text{F}_{11}^-$ mixture with I_2	134
6.5	The reaction of $\text{Xe}_2^+\text{Sb}_2\text{F}_{11}^-/\text{XeF}^+\text{Sb}_2\text{F}_{11}^-$ mixture with I_2 with xenon gas involved	134
6.5.1	The effect of SbF_5 on the reaction	137
6.6	Discussion	139
6.7	Conclusion	140
CHAPTER SEVEN	Experimental	141
7.1	Preparative techniques	142

7.2	Vacuum systems, reaction vessels and flow system	143
7.2.1	Vacuum line	143
7.2.2	Reaction vessels	146
7.2.3	Flow line	147
7.3	Characterisation of products	147
7.3.1	Infrared spectroscopy	147
7.3.2	Raman spectroscopy	150
7.3.3	Mass spectrometer	150
7.3.4	Electron spin resonance spectroscopy	153
7.3.5	Ultraviolet spectroscopy	153
7.4	Chemicals, sources and purification	153
7.4.1	Starting materials	153
7.4.2	Solvents	154

REFERENCES		155
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Abbreviations

O.D Optical density

H_{subl} Enthalpy of sublimation

H_f Standard enthalpy of freezing

p,q,r Rotational splitting in optical spectra

s- strong, m- medium, w- weak, br- broad, vs- very strong

Ng Noble gas

Chapter one

The history, preparation and properties of KrF_2 and its chemistry

1.1 Introduction:

Following the discovery of the noble gases between 1894 and 1906, several early attempts to prepare noble gas halides were made.¹⁻⁷ Argon was the first element to be used. In 1895, Ramsay supplied Moissan, the discoverer of fluorine, with a sample of argon gas in order that he should attempt to prepare a fluoride.¹ However, Moissan was unsuccessful.² Later, in 1932, efforts were made to induce krypton/bromine and krypton/chlorine mixtures to react. An electrical discharge was passed through mixtures of krypton with either bromine or chlorine but no evidence of compound formation was detected.^{3,4} Even when fluorine, which is thermodynamically the most likely halogen to form a krypton halide, was used, no clear positive results were obtained.⁵ In 1933 Pauling suggested,⁶ from considerations of ionic radii, that XeF_6 , KrF_6 , and perxenates should be preparable, and at his instigation an attempt was made to synthesize xenon fluoride. The attempt failed.⁷

The first successful synthesis of a noble gas compound was achieved in 1962 when Bartlett obtained an orange brown solid from the reaction of platinum

hexafluoride vapour with xenon gas in a glass container. He formulated the compound, $\text{Xe}^+\text{PtF}_6^-$.⁸ This discovery provided the impetus for noble-gas compounds, including compounds of krypton.

In 1963 KrF_4 was said to have been prepared⁹ by passing an electric discharge through a 1:2 mixture of krypton and fluorine at low temperature (-183°C) and pressure (20mmHg). A colourless crystalline solid was obtained which sublimed at temperatures below 0°C , had a vapour pressure of 125 mmHg at 25°C and could be handled in dry Pyrex glass or Kel-F (polychlorotrifluoroethylene) containers. At -78°C the compound could be stored for several months in Kel-F without decomposition. The formula, KrF_4 , was suggested on the basis of the fluorine analysis carried out by reaction with mercury. The fluorine was estimated gravimetrically as mercury fluoride ($\text{Hg}_2\text{F}_2 + \text{HgF}_2$) and the krypton as krypton gas. It was also reported that no krypton fluorides were obtained when a mixture of the gases was either heated in a nickel reactor at 500°C or subjected to U.V. irradiation at -60°C . The report also indicated that krypton did not react with RuF_6 or PtF_6 , which are known to be strong fluorinating agents.⁹

Although the formulation KrF_4 appeared to be correct on the basis of theoretical calculation of chemical shielding constants in a ^{19}F NMR study by Brown and Verdier,¹⁰ additional physical data on

samples of KrF_4 later showed it to be KrF_2 .¹¹

Krypton difluoride is the only well-documented stable fluoride of krypton. It was first characterized by Turner and Pimentel using the matrix isolation technique.¹² A matrix of fluorine, krypton and argon in molar ratio 1:70:220 was slowly deposited on to a caesium iodide window kept at 20K. A focused light beam from a mercury discharge lamp was used to irradiate the sample. After 3 hours the infrared spectrum showed sharp absorptions at 580cm^{-1} and 236cm^{-1} . These bands were interpreted as being due to the two fundamental modes of a linear KrF_2 molecule. However, the experiment did not produce an isolable compound. In later spectroscopic investigations of the KrF_2 molecule others also used the matrix isolation technique.^{13,14}

Mackenzie reported a preparation of KrF_2 in larger amounts by irradiation of a krypton and fluorine mixture in a 1.5MeV electron beam at -150°C . The white crystalline compound obtained was reported to be unstable above -30°C .¹⁵ In another report from the same laboratory KrF_2 was also prepared when mixtures of krypton and fluorine were subjected to a 10MeV proton beam with a current of 5mA from a cyclotron.¹⁶ Approximately 1g of the compound was produced after one hour of irradiation at -140°C . Attempts to prepare KrF_4 using different ratios of krypton/fluorine gas mixtures were also made but

without success . Mixtures of solid KrF_2 and liquid fluorine at -196°C bombarded with 10MeV protons, also failed to yield KrF_4 .¹⁶

In the same year, Streng and Streng reported that a white crystalline compound has formed as a result of exposing low-pressure mixtures of krypton and fluorine or krypton and oxygen difluoride to sunlight for 5 weeks in Pyrex bulbs. The white crystalline product was condensed onto a cold finger cooled with dry-ice.¹⁷ The presence of one atom of noble gas to two atoms of fluorine was determined by estimating the fluorine as mercury fluorides and measuring the volume of noble gas produced. The amount of solid produced was very small , only a maximum of 100mg being obtained . An identical investigation of this reaction by Holloway at the same time showed that the yield could not be increased and spectroscopic data for the white compound proved it to be XeF_2 .¹⁸ The reason for the extremely small yields was explained by the presence of small amounts of xenon impurity in the krypton gas used.¹⁸

The successful preparation of krypton difluoride in large usable quantities was made in 1964, by Schreiner et al.¹⁹ who passed an electric discharge through a krypton/fluorine mixture at -183°C and an approximate pressure of 20mmHg ; a similar method to that originally reported for the preparation of " KrF_4 " . The rate of production of KrF_2

was 0.25 gh^{-1} . The compound was characterized as KrF_2 by chemical analysis and infrared and ^{19}F NMR spectroscopy. Mass spectrometry showed the presence of the ions, KrF^+ and Kr^+ , only.²⁰

From 1966 to 1969 patents were obtained for the production of KrF_2 by high-frequency electrical discharge on mixtures of krypton with fluoro-carbons, such as CF_2Cl_2 in quartz apparatus.²¹ A similar yield is obtained to that by electrical discharge of gaseous mixtures of krypton and fluorine. Xenon difluoride can also be prepared by this route, and it has been suggested that the method might be used as a suitable method for the separation of the two noble gases, because of the different physical properties of KrF_2 and XeF_2 .²¹

In 1975, colourless crystals of KrF_2 were also prepared in high yields by Slivnik *et al.*²² using the U.V. irradiation of a mixture of liquid fluorine and solid krypton at -196°C for 48 hours. Howard and Andrews,¹³ in a similar experiment, have shown that condensed gaseous mixtures subjected to argon laser and mercury arc photolysis also result in the photoproduction of KrF_2 . This was established by observation of the Raman active vibration of KrF_2 in solution.¹³

In 1976, Russian workers prepared KrF_2 in high yield by subjecting krypton/fluorine mixtures to

a hot wire at 600–700°C in a reactor with walls cooled to -196°C. The wire acts as a thermal generator of atomic fluorine and these atoms attack the krypton condensed on the inner surfaces of the reactor walls to form KrF_2 .²³

1.2 Physical Properties of KrF_2 :

1.2.1 Physical Properties and Thermodynamic data :

Krypton difluoride is a colourless crystalline solid which sublimes below -30°C.¹⁹ The vapour pressure of the solid is about 29 mmHg at 0 °C and in excess of 70 mmHg at 15°C.^{24,25} These data clearly indicate that it is possible to sublime the compound in a good vacuum.²⁵ In 1970, more detailed studies yielded a vapour pressure equation for KrF_2 ²⁶ [equation i] which corresponds almost exactly with that published earlier for the sample reported to be KrF_4 [equation ii].⁹:-

$$\log_{10} P^a = 8.814 - (2000/T^C) \text{ ----- (i)}$$

$$\log_{10} P^a = 8.531 - (1930/T^C) \text{ ----- (ii)}$$

Thermodynamic data for KrF_2 were obtained from measurements of the heat of decomposition for the

gaseous compound at different temperatures using the drop-calorimeter method.²⁵ These data along with other thermodynamic parameters are reported in Table 1.1

Thermodynamic data in Kcal mol ⁻¹				
$\Delta H_{\text{subl.}}$	$-E_1$ (av.)	H_f (KrF ₂ g)	E (Kr—F)	Ref.
9.9±1	14.2	14.4±0.8	11.7	24, 25
9.2±0.8				26
		15.52	10.67	27

Table 1.1 : Thermodynamic data for KrF₂

1.2.2 Infrared and Raman Spectroscopy :

The infrared and Raman spectra of KrF_2 show that krypton difluoride, like xenon difluoride, is a linear symmetrical molecule. The data in Table 1.2 show the absorptions observed and assignments made from a number of different studies of both the solid and the vapour phase.

Claassen and co-workers published estimates of the force constants which are : $f_x=0.21$, $f_r=2.46$, $f_{rr}=-0.20$ mdyn/Å.²⁸ The Kr-F bond length has been estimated to be 1.9 Å in gaseous krypton difluoride. The negative bond-bond interaction constant, f_{rr} , is an indication of the low thermodynamic stability of KrF_2 , and was explained by Coulson²⁹ who suggested that the magnitude and sign of f_{rr} are related to the distribution of the negative charge in the molecule and the ionization potential of the noble gas atom. A greater weight towards a non-bonding structure rather than an ionic one in a resonance description gives rise to a negative sign.

The Raman spectrum of krypton difluoride is strange because of the absence of a Fermi resonance interaction between ν_3 and $2\nu_2$, there being no sign of the overtone of the bending mode. In comparison with CO_2 , which is a structurally similar molecule to KrF_2 ,

the overtone of the bending mode is expected to be strongly coupled to the symmetric stretching fundamental through Fermi resonance . In 1967, Reichman and Overend discussed this absence.³⁰

A measurement of the ν_3 infrared active band of $^{86}\text{KrF}_2$ in the gas phase at 590cm^{-1} , to a resolution of 0.08 cm^{-1} , has been conducted.³¹ It is clear that KrF_2 is a linear molecule and the rotational fine structure indicates that the two fluorines are symmetrically equivalent. The data leads to two probable sets of constants from which values of the bond length can be calculated . The most probable value is $r_\sigma = 1.875 \pm 0.002 \text{ \AA}$.

The mean amplitudes of vibration and thermodynamic functions of KrF_2 , are considered in a paper by Nagajan.³²

Preparations	Matrix isolation U.V. Photolysis	1.5 MeV electron beam irradiation	Electrical discharge	Matrix isolation and laser irradiation	Ass ^{nt}
Absorption in cm ⁻¹	236(s)		232.6(v) [p,q,r]		ν_2 IR
			449(v) 462(s)	452(s)	ν_1 R
	580(s)	582(v) 597(v) [p,r]	580 596 } 588(v) [p,r]		ν_3 IR
			1032(v) w		$\nu_1 + \nu_3$
Reference	12	16	28	13	

s= solid; v= vapour; p,q,r= rotational splitting .

Table 1.2: Infrared and Raman spectroscopic data for KrF₂

1.2.3 Mass spectrometry:

Soon after the discovery of KrF_2 mass spectrometric examination of the compound showed the presence of only the KrF^+ and Kr^+ ions.²⁰ Even after a further six years had elapsed mass spectrometric studies had still not provided evidence for the parent ion, KrF_2^+ , and it was suggested that this was due to its ready decomposition.³³ A later time of flight mass spectrometric study by Falconar et al. demonstrated that KrF_2 exists in the vapour phase as a monomer.³⁴

A photoionization mass spectrum of KrF_2 gave a value of $+15.5 \pm 2$ Kcal mole⁻¹ for ΔH°_p which leads to an average Kr-F bond energy of 0.46 eV. This data agrees with that from thermodynamic studies (see section 1.2.1). The dissociation energy for KrF_2 was estimated as ≥ 1.53 eV from the appearance potential data.²⁷

1.2.4 NMR Spectroscopy :

At room temperature KrF_2 dissolves in anhydrous HF allowing the ¹⁹F NMR spectrum to be studied. Only one peak is obtained indicating the equivalence of the two fluorines in the KrF_2 molecule in solution. Unlike XeF_2 , there is no evidence of exchange between the KrF_2 fluorines and those of HF up to room temperature.¹⁹ Chemical shifts relative to fluorine for two concentrations of KrF_2 in HF at 0°C were reported by

Schreiner et al.¹⁹ These data agree well with values calculated on the basis that the bonding in KrF_2 is similar to that in XeF_2 .³⁵ This was confirmed by the later experimental work of Gillespie and Schrobilgen³⁶ and further supported by the theoretical value published by Mason (Table 1.3).³⁷

References		19	10	36	37
Chemical shifts	Temp. c°	0	R.T.	26	
relative	(ppm)	-41 ^a			
	Experimental		-44	-55.6 ^c	
CFCl ₃	in anhyd. HF	-53 ^b			
	(ppm)	-59	-81		-50
	Theor.	[-287]			
Ionicity	I (Expt.)	0.468			
values	I (Theor.)	0.45[0.29]			
	Proposed				
	structure	KrF ₂ [KrF ₄]	KrF ₄ ?	KrF ₂	KrF ₂

All Chemical shifts relative to CFCl₃

a- Concentration 4.6 moles /1000 g. HF

b- Concentration 16.4 moles /1000 g. HF

c- Concentration 0.22 M in HF

Table 1.3 ¹⁹F NMR spectroscopic data for KrF₂

1.2.5 Photoelectron Spectroscopy :

He-I and He-II radiation high resolution photoelectron spectra have been obtained for KrF_2 .³⁸ The valence-level photoelectron spectrum indicates a great similarity of orbital energies and an identical molecular orbital ordering to that in XeF_2 .³⁹ Broad bands at 22 and 23 eV have been obtained from a He-II photoelectron spectrum, and assigned to the $7\sigma_g$ orbital transitions.⁴⁰

In another paper,⁴¹ KrF_2 was obtained by the excitation of a mixture of krypton gas and BF_3 with microwave radiation, and the ultraviolet emission spectrum for the sample showed bands at 2485 and 2220 Å, which correlate poorly with those associated with KrF_2 .

1.2.6 Crystal and Molecular Structure Determined by Diffraction Methods :

In 1964, a report by Siegel and Gebert on an X-ray structure analysis of KrF_2 indicated that the crystal symmetry of KrF_2 differs from that of XeF_2 .⁴² The KrF_2 unit cell appeared to be primitive, whereas XeF_2 is body-centred. Single-crystal oscillation and Weissenberg patterns indicated tetragonal symmetry with $a = 6.533$ Å and $c = 5.831$ Å. The X-ray density was 3.24 g/cm^3 . A later single-crystal structure determination,⁴³ confirmed the tetragonal structure (space group $P4_2/mnm$), and showed the presence of two linear molecules per unit cell aligned in

planes perpendicular to the tetragonal axes , (Figure 1.1). The alignment alternates by 90° between successive planes. The Kr—F bond distance is $1.89 \pm 0.2 \text{ \AA}$.

The structure of KrF_2 in the vapour was investigated by electron diffraction in 1967.⁴⁴ The electron diffraction patterns were recorded using a 40 KeV beam scattered by the vapour from a sample purported to be KrF_4 . The well-defined patterns were analysed by conventional procedures and found to be produced by KrF_2 contaminated with SiF_4 . The symmetry of the difluoride was established as $D_{\infty h}$, and a value of $1.899 \pm 0.10 \text{ \AA}$ for the Kr—F bond length obtained. Values of the Kr-F bond length measured by a variety of techniques in the solid and vapour states are compared in Table 1.4 .

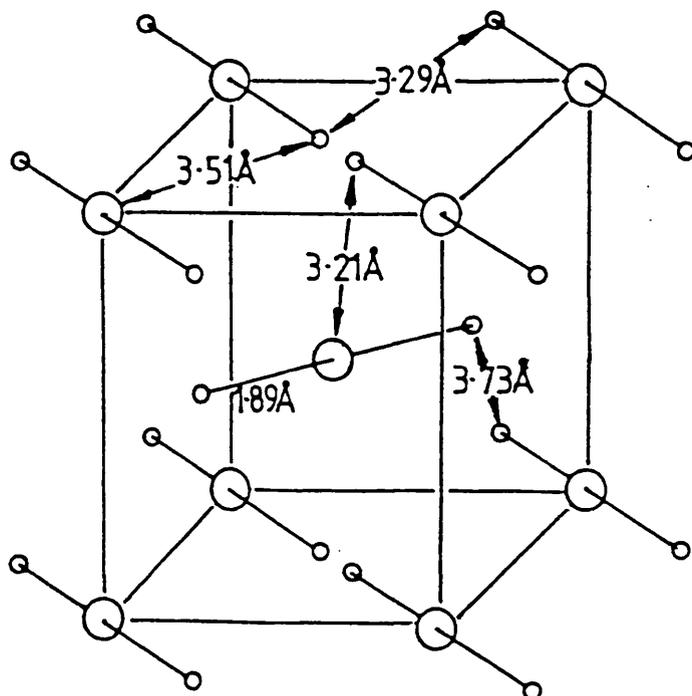


Fig. 1.1 Cell Dimensions of KrF_2

1.2.7 Molecular Orbital Calculations :

A substantial amount of work has been reported concerning the molecular orbital and electronic structure of the compounds, of the noble gases . A comprehensive discussion of papers on this subject has been published in two Russian reviews.^{45,46}

In 1970, ab initio calculations by Collins⁴⁷ and Catton⁴⁸ and their co-workers, showed that the krypton 4d orbitals must be included in calculations in order to give an adequate description of bonding . The inclusion of 5s and 5p orbitals had little effect.⁴⁷ In another study Collins published contour maps of the valence shell molecular orbitals.⁴⁹ The one-electron orbital energies were then compared with photoelectron spectroscopic data,³⁸ and showed a lack of agreement ,which indicates that the existing ab initio calculations are not of sufficiently high accuracy to say whether or not 4d orbitals are important in the bonding.³⁸

Bagus et al. also used ab initio calculations , which confirmed the linear symmetric configuration and gave a Kr—F distance of 1.907 Å and a dissociation energy of 0.39 eV.⁵⁰ These data suggested that the Kr—F bond is ionic in character near the equilibrium distance but becomes covalent at larger separations. This model was also suggested by Coulson (see section 1.2.2).²⁹ In 1977 Shimanouchi published tables of calculated molecular vibration frequencies.⁵¹

1.2.8 Other Data :

The decomposition rate of KrF_2 for temperatures between 50 and 100°C has been investigated,⁵² and has been shown to occur via a homogeneous monomolecular first order reaction. The rate constant is $2 \times 10^{12} \exp(-23800/RT) \text{sec}^{-1}$. The reaction is of a heterogeneous nature below 50°C and depends on the surface area of the reactor.

Investigation of the thermal decomposition under jet conditions,⁵³ has led to a suggestion that it goes by a radical chain process.⁵⁴

A number of papers has been published containing calculations associated with possible molecular structures for KrF_4 .⁵⁵ Covalent radii have been used to predict a Kr—F bond length of 1.77Å for KrF_4 (c.f. 1.81Å for KrF_2).⁵⁶ A bond length of 1.84Å has been calculated for KrF_4 on the basis of correlation of electronegativity with covalency, assuming 2-electron bonds.⁵⁷ In another paper, bond energies and electronic structure were considered and, by using The LCAO method, the Kr—F distance in KrF_4 was calculated as 2.1Å for a molecule of D_{4h} symmetry.⁵⁸

Kr—F bond length, r_o^a	Source	Ref.
1.9 ± 0.1^b	I.R. and Raman	28
1.889 ± 0.010^b	Electron diffraction	44
1.875 ± 0.002^b	I.R. rotational fine structure	31
1.907^c	M.O. calculations	50
1.81^c	Covalent radii	56
1.89 ± 0.02^d	Crystal structure	43

a- In Å

b- Vapour phase data

c- Calculated

d- Solid phase data

Table 1.4 Bond length data for KrF_2

1.3 Chemistry of KrF₂ :

Krypton chemistry is more limited than that of xenon because of the higher first ionization energy and smaller size of krypton, and the greater fluorinating ability and the relative instability of its difluoride. Also, krypton compounds exist only in oxidation state 2, early reports on the preparation of KrF₄ having not been confirmed, whereas xenon compounds exist in oxidation states 2, 4, 6 and 8, and the fluorides XeF₂, XeF₄ and XeF₆ are well known. The basic chemistry of KrF₂ is similar to that of XeF₂ in its reaction with Lewis acids, and adducts with similar formulations to the xenon difluoride compounds are obtained.

Attempts at investigation of the solution chemistry, in water, have not led to a clear-cut result. However, the low temperature reaction of KrF₂ with H₂O appears to yield (KrO)_n.¹⁸

Recently Schrobilgen has identified the first examples of Krypton bonded to an element other than fluorine in the synthesis of the (RC=N-Kr-F)⁺ cation (R = H, CF₃, C₂F₅, n-C₃F₇).⁵⁹

1.3.1 Lewis Adducts of KrF₂ - Their preparation :

The first adducts of KrF₂ to be prepared were reported by Selig and Peacock in 1964 from the reaction of

KrF_2 and SbF_5 at -20°C .⁶⁰ A white crystalline solid was produced analysis of which suggested the formula $\text{KrF}_2 \cdot 2\text{SbF}_5$. The compound is more stable than KrF_2 decomposing above 30°C to give SbF_5 , Kr and F_2 . In acidic or basic solution, the hydrolysis of the compound gave krypton, oxygen and some fluorine monoxide. Organic compounds reacted explosively with the adduct. Preliminary work showed that AsF_5 also combined with KrF_2 at -78°C to form a complex less stable than $\text{KrF}_2 \cdot 2\text{SbF}_5$.⁶¹

Between 1964 and 1971 no other papers in this area were published but in 1971 McKee et al. suggested that the compound prepared by Selig and Peacock could be described as a salt, $\text{KrF}^+\text{Sb}_2\text{F}_{11}^-$.⁶¹ A stretching frequency ν ($\text{Kr}-\text{F}^+$), at 626 cm^{-1} was shown to be in very good agreement with Schaefer's theoretical prediction of 620 cm^{-1} .⁶² In the same year, Pruskov et al., reported the preparation of the compounds $2\text{KrF}_2 \cdot \text{MF}_4$ ($\text{M}=\text{Ti}, \text{Sn}$), $\text{KrF}_2 \cdot \text{MF}_5$ ($\text{M}=\text{Sb}, \text{Ta}$) and $\text{KrF}_2 \cdot 2\text{MF}_5$ ($\text{M}=\text{Sb}, \text{Ta}, \text{Nb}$), from a solution of KrF_2 and the metal fluoride in anhydrous HF or BrF_5 .⁶³ The characterization was made on the basis of very poor infrared spectra. In another paper, the same authors reported the isolation of the solid product $\text{KrF}_2 \cdot \text{SbF}_5$ from the binary system $\text{KrF}_2/\text{SbF}_5$ and claimed that $\text{KrF}_2 \cdot 2\text{SbF}_5$ was the only product from the ternary system $\text{KrF}_2/\text{SbF}_5/\text{BrF}_5$.⁶⁴ A phase diagram was also constructed showing the limited solubility of KrF_2 in BrF_5 .

A paper by Gillespie and Schrobilgen,⁶⁵ attributed a considerable temperature dependence of the

^{19}F NMR chemical shift of KrF_2 in BrF_5 to the equilibrium [equation iii]:



In 1978, Russian workers reported a new synthesis of the adduct $\text{KrF}^+\text{SbF}_6^-$ by creating a plasma from the glow discharge of a mixture of krypton, fluorine and antimony pentafluoride.⁶⁶ The compound was identified by infrared spectroscopy.

In 1973, Frlec and Holloway prepared and characterized the compounds $\text{KrF}_2 \cdot \text{TaF}_5$, $\text{KrF}_2 \cdot 2\text{MF}_5$ ($\text{M}=\text{Ta}, \text{Nb}$) by Raman spectroscopy.⁶⁷ The compounds were synthesized in BrF_5 solution at low temperature. Good evidence for $\text{KrF}_2 \cdot \text{SbF}_5$ was also presented. Both $\text{KrF}_2 \cdot 2\text{TaF}_5$ and $\text{KrF}_2 \cdot 2\text{NbF}_5$ are thermally much less stable than $\text{KrF}_2 \cdot 2\text{SbF}_5$. They also showed that the trend in the change of the stretching frequency, $\nu(\text{Kr}-\text{F})$, and hence the degree of ionic character and bond length in these adducts, is the same as that for the analogous XeF^+ compounds.

In a later paper, Frlec and Holloway reported that thermal decomposition studies produced evidence for new adducts which were formulated as $[\text{xKrF}_2 \cdot \text{KrF}]^+ \cdot \text{Ta}_2\text{F}_{11}^-$ and $[\text{xKrF}_2 \cdot \text{KrF}]^+ \cdot \text{Nb}_2\text{F}_{11}^-$ (where x is probably equal to 1). The additional KrF_2 units appeared to be weakly associated with the cationic parts of the adducts.⁶⁸ The same authors also reported Raman spectroscopic evidence for the compounds $\text{KrF}_2 \cdot \text{SbF}_5$ and $2\text{KrF}_2 \cdot \text{SbF}_5$ which indicated that

the bonding in the adducts has contributions from the salt-like formulations.⁶⁹ Evidence was also presented for a compound consisting of a $\text{KrF}^+\text{SbF}_6^-$ -like species with associated KrF_2 which was given the formulation $[\text{xKrF}_2.\text{KrF}]^+\text{SbF}_6^-$ ($\text{x}=1$). The adduct, $2\text{KrF}_2.\text{SbF}_5$, was produced from the reaction of KrF_2 with SbF_5 in BrF_5 solution at -40°C .

At the same time Gillespie and Schrobilgen reported similar compounds characterized by both ^{19}F NMR and Raman spectroscopy.³⁶ They also confirmed that adducts of KrF_2 with AsF_5 , SbF_5 , and PtF_6 have considerable ionic character and the formulations $\text{KrF}^+\text{MF}_6^-$ ($\text{M}=\text{As}, \text{Sb}, \text{Pt}$) $\text{KrF}^+\text{Sb}_2\text{F}_{11}^-$, $\text{Kr}_2\text{F}_3^+\text{MF}_6^-$ ($\text{M}=\text{As}, \text{Sb}$) and $\text{Kr}_2\text{F}_3^+\text{MF}_6^-.n\text{KrF}_2$ ($\text{M}=\text{As}, \text{Sb}$ and $n>2$) were used to describe them. The $\text{KrF}^+\text{AsF}_6^-$ adduct had both high and low temperature phases. In the case of SbF_5 adducts, this work confirmed that of Frlec and Holloway. A ^{19}F NMR spectroscopic study of the compounds revealed the presence of the KrF^+ and Kr_2F_3^+ ions in solution.^{70,36}

In 1975, a short communication by Zemva *et al.* suggested that the reaction of KrF_2 with VF_5 produced the adduct $\text{KrF}_2.\text{VF}_5$.⁷¹ Since the vapour pressure of the product was similar to that of the starting material, the compound was not isolated. Infrared spectra showed that $\text{KrF}_2.\text{VF}_5$ existed in the system and was similar to the analogous $\text{XeF}_2.\text{VF}_5$ adduct.

In the same year, Holloway and Schrobilgen

reported that the reaction of KrF_2 with gold powder in HF at 20°C produced a light yellow solid,⁷² the Raman spectrum of which showed that it had a composition consistent with the formulation $\text{KrF}^+\text{AuF}_6^-$. Later, Yeh reported the preparation of another adduct of KrF_2 with AuF_5 ,⁷³ by reaction of KrF_2 with AuF_5 in HF. The Raman spectrum suggested the formula $\text{Kr}_2\text{F}_3^+\text{AuF}_6^-$.

Gillespie and Schrobilgen reported the preparation of a KrF_2 adduct with BiF_5 ,⁷⁴ by reaction of KrF_2 with BiF_5 in anhydrous HF. Following a brief warming and mixing at room temperature a fine white solid was obtained. The nature of the adduct was established as $\text{KrF}^+\text{BiF}_6^-$ by low temperature Raman spectroscopy.

Selig and co-workers, made an attempt to interduce KrF_2 into a graphite lattice which resulted in the formation of an intercalation compound.⁷⁵ It appeared that the reaction of graphite was a balance between oxidative fluorination and intercalation with fluorination most likely dominant at the edges and internal defects.

In 1978, Klimov and co-workers reported the isolation of a 1:1 complex of KrF_2 with XeF_6 as a colourless crystal described as $\text{KrF}_2 \cdot \text{XeF}_6$.⁷⁶ The molecular nature of complex was established by infrared spectroscopy.

In 1981, Holloway and Schrobilgen reported the preparation and characterization of KrF_2 adducts with

MoOF_4 and WOF_4 ,^{77,78} by the reaction of KrF_2 with MOF_4 ($\text{M}=\text{Mo},\text{W}$) in SO_2ClF solution at low temperature. The ^{19}F NMR spectra of $\text{KrF}_2 \cdot n\text{MOF}_4$ ($n=1-3$) and $\text{KrF}_2 \cdot \text{WOF}_4$ in solution showed that they are best formulated as essentially covalent structures containing $\text{Kr}-\text{F}-\text{M}$ bridges and mononuclear or polynuclear metal oxide fluoride moieties. Raman spectra of the solid $\text{KrF}_2 \cdot \text{MOF}_4$ ($\text{M}=\text{Mo},\text{W}$) adducts have been compared with those of the analogous xenon compounds and have been interpreted in terms of covalent fluorine-bridged structures.

Recently Christe and co-workers reported the preparation of a KrF_2 adduct with CrOF_4 , by reaction of KrF_2 with CrOF_4 to form a purple solid which was described as $\text{KrF}_2 \cdot \text{CrOF}_4$.⁷⁹ The nature of the adduct was established by low temperature infrared, Raman and ^{19}F NMR spectroscopy.

1.3.2 Lewis Adducts of KrF_2 - Spectroscopic Data :

The bulk of spectroscopic data for the adducts appears in four papers.^{68,70,78,79} This consists mainly of Raman and ^{19}F NMR data. The data presented in these papers gives a detailed view of the molecular structures of the compounds in the solid state and in solution, and parallels with the structures of the xenon analogues have been drawn.

1.3.2a ^{19}F NMR Spectroscopy :

The ^{19}F NMR spectroscopic data is summarised in Table 1.5.⁷⁰ The KrF^+ ion was investigated by adding a solution of KrF_2 in anhydrous HF to an excess of SbF_5 . A new singlet to high field of KrF_2 was obtained and the magnitude of the shift is analogous to that observed when XeF_2 is ionized to XeF^+ suggesting the presence of KrF^+ in solution.⁷⁰ Solutions of the AsF_5 and SbF_5 adducts in mole ratio 2:1, KrF_2 to MF_5 in BrF_5 , gave identical AX_2 spectra at low temperatures. These were assigned to the V-shaped fluorine bridged structure similar to that established for Xe_2F_3^+ by X-ray crystallography.⁸⁰ The relatively large coupling constant, 329 Hz, is also similar to that observed for Xe_2F_3^+ . Although Raman spectra of solids derived from reactions involving large excesses of KrF_2 indicated the presence of weakly associated $n\text{KrF}_2 \cdot [\text{Kr}_2\text{F}_3]^+$ species⁷⁰, no evidence for interaction between KrF_2 and Kr_2F_3^+ in solution was indicated by the ^{19}F NMR spectra.

The ^{19}F NMR spectra of solutions of MoOF_4 or WOF_4 with KrF_2 in SOClF have been studied.⁷⁸ Large coupling constants were observed ($J_{\text{F}-\text{F}}=314-327$), which are similar in magnitude to those reported for Kr_2F_3^+ ($J_{\text{F}-\text{F}}=357$)⁷⁰ and $\text{XeF}_2 \cdot n\text{MOF}_4$ ($\text{M}=\text{Mo}, \text{W}; n=1-4$) ($J_{\text{F}-\text{F}}=258-275\text{ppm}$).⁸¹ Those for other fluoro- and oxyfluoro-compounds of xenon are much smaller ($J_{\text{F}-\text{F}}=103-176\text{ppm}$).⁸² This difference is thought to be due to the $\text{F}-\text{Ng}-\text{F}$ angle being $\sim 180^\circ$ in Ng_2F_3^+ and $\text{NgF}_2 \cdot n\text{MOF}_4$ but $\sim 90^\circ$ in the other cations.

Solute	Solvent	Temp.	J_{ff} Hz		Chemical Shifts (ppm) ^a					
			BrF_5	Ng_2F_3^+	Ng_2F_3^+	NgF^+	NgF_2	Anion	Solvent	
M conc. Krf_2 (0.22)	HF	26					-55.6			199.2
Krf_2 (0.80)	BrF_5	27	75				-77.7			A -275.9 X ₄ -139.0
		-50	75				-67.9			A -272.6 X ₄ -135.5
Krf_2 (0.22) Sbf_5 (4.96)	HF	-40			22.6				92 ^b	
									119 ^b	Sbf_5
								139 ^b		192.4
								124 ^b	Sbf_6^-	
$\text{Krf}_3^+\text{Sbf}_6^-$ (~0.5)	BrF_5	-65	347	A -18.8 X ₂ -73.4				118		-156 ^c
$\text{Krf}_3^+\text{Asf}_6^-$ (~0.5)	BrF_5	-65	347	A -19.0 X ₂ -73.8						-150 ^d
Krf_2 (~1.5) Sbf_5 (~0.5)	BrF_5	-65	75	351	A -19.2 X ₂ -73.6			120		A -276.4 X ₄ -136.8
Krf_2 (~1.5) Sbf_5 (~0.5)	BrF_5	-65	75	351	A -19.0 X ₂ -73.6			123		A -276.9 X ₄ -137.0

- a- Relative to CFCl_3
b- The spectrum is similar to that reported for high concentrations of Sbf_5 dissolved in HF.
c- Axial and equatorial fluorine environments of BrF_5 collapsed into a single broad exchange averaged peak.
d- The peak represents Asf_6^- and fluorine environments undergoing rapid fluorine exchange.

Table 1.5 ¹⁹F NMR Parameters for Lewis acid adducts of Krf_2 .

1.3.2b Raman spectroscopy :

The Raman and infrared frequencies observed for the krypton fluoride adducts can be assigned in terms of ionic formulations $[\text{KrF}]^+[\text{M}_2\text{F}_{11}]^-$, $[\text{KrF}]^+[\text{MF}_6]^-$ and $[\text{Kr}_2\text{F}_3]^+[\text{MF}_6]^-$. However, both Kr---F and M---F bridging stretches and F—Kr---F bending modes are evident in the spectra and this evidence of covalent contributions to the bonding is further supported by assignment of the anion modes for $[\text{MF}_6]^-$ in $[\text{KrF}]^+[\text{MF}_6]^-$ on the basis of C_{4v} rather than O_h symmetry. The spectra of $[\text{KrF}]^+$ and $[\text{Kr}_2\text{F}_3]^+$ are summarized in Table 1.6 .

The $[\text{Kr-F}]^+$ stretching constant is lower than that for $[\text{Xe-F}]^+$ and estimates of the bond length suggest a value of $\sim 1.8 \text{ \AA}$ for the bond in the $[\text{Kr-F}]^+$ cation.

Raman spectra of $[\text{Kr}_2\text{F}_3]^+$ are similar to those of $[\text{Xe}_2\text{F}_3]^+$ but there are additional bands in the krypton spectra which have no equivalents in those of $[\text{Xe}_2\text{F}_3]^+$. This data has been interpreted in terms of $[\text{Kr}_2\text{F}_3]^+$ being unsymmetrical (See Figure 1.2) in contrast to $[\text{Xe}_2\text{F}_3]^+$ which is thought to be regular.

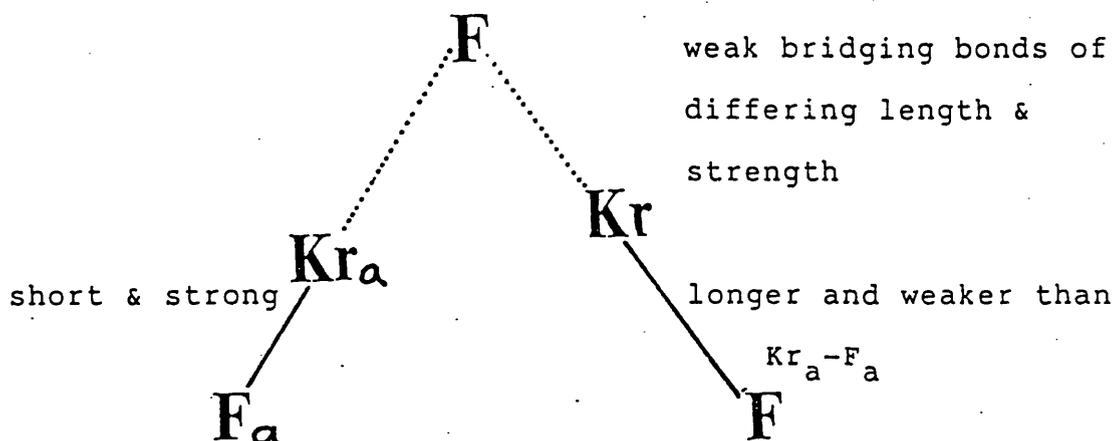


Figure 1.2

Another interpretation is that the cation might be regarded as a distorted KrF_2 molecule fluorine bridged to a $[\text{KrF}]^+$ cation (see Figure 1.3).

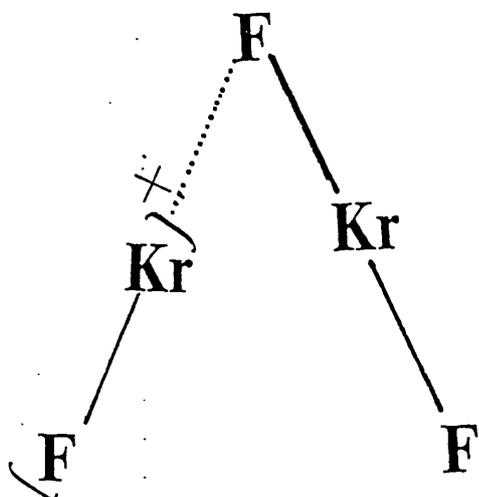


Figure 1.3

Lewis acid	Refs.	2X:1	1X:1	1+X:2	1:1	1:2
SbF ₅	68		623, 619		621, 618	627, 619
	70	599	603, 594		619, 615	624
AsF ₅	70	[610, 600] 594			σ- 607, 596 β- 619, 615	
TaF ₅	68			613	603.5, 599	609, 600
NbF ₅	68			596		[613, 606] 597
PF ₆	70				606, 599	
AuF ₅	72					
	73			597		
BiF ₅	74				610, 604 600	
MoF ₄	77, 78				566, 579	
WOF ₄	77, 78				571, 581	

X = nK₂F₂

Table 1.6 Raman stretching frequencies (cm⁻¹) for Lewis adducts of K₂F₂

Definitive characterization will only be possible if a crystal structure is done.

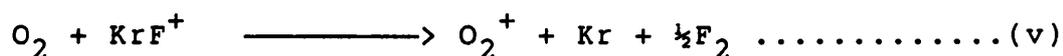
Addition of more KrF_2 to $[\text{Kr}_2\text{F}_3]^+$ adducts produces other adducts of interest. Raman spectra of the compounds suggest further interaction of KrF_2 with the cation to give $[\text{xKrF}_2.\text{Kr}_2\text{F}_3]^+$. It has also been suggested that the thermal decomposition of tantalum and niobium fluoride adducts of $[\text{Kr}_2\text{F}_3]^+$ gives rise to species containing $[\text{xKrF}_2.\text{KrF}]^+$ (where x is probably equal to 1). It is also clear that the associated KrF_2 is only weakly bound to the cation.

1.3.3 Oxidizing power of KrF_2 and its adducts :

In 1971, Prusakhov and Sokholov reported that KrF_2 reacts with BrF_3 , ClF_3 and IF_5 at room temperature to yield higher fluorides.⁶³ In accordance with the expected high value of the electron affinity of KrF^+ , the cation has also proved to be a very strong oxidizer. For example McKee and co-workers have shown that IF_5 is oxidized to IF_6^+ by KrF^+ .⁶¹

The same group have also reported that the reaction of $\text{KrF}^+\text{Sb}_2\text{F}_{11}^-$ with XeOF_4 leads to the cation, XeOF_5^+ .⁸³ Detailed analysis of the Raman data has later shown this to be incorrect. An identical experiment carried out by Holloway and Schrobilgen, established by Raman and ^{19}F NMR analysis that the isolated product is

probably $[\text{XeOF}_4.\text{XeF}_5]^+\text{SbF}_6^-$.⁷² The presence of $\text{O}_2^+\text{SbF}_6^-$ was also indicated. The reaction scheme may be summarised in the following two equations [equations (iv) and (v)]:



Later, in 1977, Liebman published a paper suggesting a possible mechanism for this reaction.⁸⁴ He proposed that the XeOF_5^- produced in the reaction was subject to nucleophilic attack by XeOF_4 to form an intermediate, XeO_2F_5^+ . This intermediate is attacked by XeF_4 to give O_2 and XeF_5^+ .

In the paper published by Frlec and Holloway on the adducts of KrF_2 ,⁶⁷ the authors showed that, at room temperature, the fluoride will oxidize iodine to IF_7 and xenon to XeF_6 . Gillespie and Schrobilgen have shown that Kr_2F_3^+ adducts are even more powerful oxidative fluorinating agents which react with BrF_5 to give BrF_6^+ salts.³⁷ Solutions of some of these adducts appear to be corrosive even towards Kel-F and FEP.

Preparation and isolation of the new high oxidation state transition metal fluoride, AuF_5 , by reaction of the metal with KrF_2 has also been carried out. The adduct $\text{KrF}^+\text{AuF}_6^-$ is formed initially and this

thermally decomposes to yield an orange powder which was shown to have the formula $\text{AuF}_{4.98}$ by chemical analysis.⁷²

Artyukhov et al. have investigated the reaction of KrF_2 and NF_3 in the presence of several Lewis acids.⁸⁵ Reactions in HF with SbF_5 , NbF_5 , PF_5 , TiF_4 and BF_3 are reported to give $\text{NF}_4 \cdot \text{SbF}_6$, $\text{NF}_4 \cdot \text{NbF}_6$, $\text{NF}_4 \cdot \text{PF}_6$, $(\text{NF}_4)_2 \cdot \text{TiF}_6$ and $\text{NF}_4 \cdot \text{BF}_4$.

Soviet authors Drobyshevskii et al.⁸⁶⁻⁸⁸ have reported that the ambient-temperature or lower temperature fluorination of the oxides and tetrafluorides of uranium, neptunium and americium and the oxyfluorides of neptunium with KrF_2 in bromine pentafluoride or anhydrous HF give the respective hexafluorides. German workers have briefly mentioned the generation of UF_6 by reaction of UF_4 with KrF_2 .⁸⁹ Peacock and Edelstein reported the fluorination of NpOF_4 to NpF_6 by KrF_2 in anhydrous HF.⁹⁰ Recently, Asprey et al. reported the oxidation of low-valent uranium, neptunium and plutonium compounds to the respective hexafluorides by reaction with KrF_2 at ambient or lower temperature.³⁵

In 1982, Braun et al.⁹¹ have reported the oxidation of PuF_3 to PuF_4 by KrF_2 at room temperature or lower.

In 1984, Russian workers reported the reaction between KrF_2 and MO_2 ($\text{M}=\text{Ce}, \text{Pr}, \text{Tb}$) in 2:1 and 3:1 molar ratios to give MF_4 . At the ratio 1:1 compounds were formed

with a formula close to MOF_2 .⁹² In the same year Bougon et al. reported the reaction of KrF_2 with AgF_2 to produce AgF_3 .⁹³ The compound has been characterized by using X-ray powder patterns, infrared and Raman spectra.

Chapter two

The reaction of some noble gases with liquid fluorine at $-196\text{ }^{\circ}\text{C}$ using U.V. photolysis

Chapter two

The reaction of some noble gases with liquid fluorine at -196°C using U.V. photolysis

2.1 Introduction

The preparation of KrF_2 by the U.V. photolysis of krypton in liquid fluorine was first carried out by Slivnik and his co-workers.²² This reaction has been reinvestigated in detail and attempts have been made to prepare an argon fluoride using a similar approach.

2.2 The preparation of KrF_2

The method used to prepare KrF_2 was similar to that used by Slivnik et al.²² The light sources used were medium pressure mercury lamps the filaments being arranged vertically in a ring around the reactor (Figure 2.1). Irradiation at 350nm was used. Initially, experiments were tried in Pyrex, quartz and F.E.P. reactors. However, under the severe conditions of the reactions both Pyrex and quartz gave rise to the production of silicon tetrafluoride. The FEP reactor exhibited little evidence of fluorination and so this material was chosen as the reactor material for subsequent investigations.

The initial $\text{F}_2:\text{Kr}$ ratio used was 2:1. In a typical reaction krypton (1.5mmol) was condensed from the manifold into the pre-fluorinated FEP reactor at -196°C (liquid

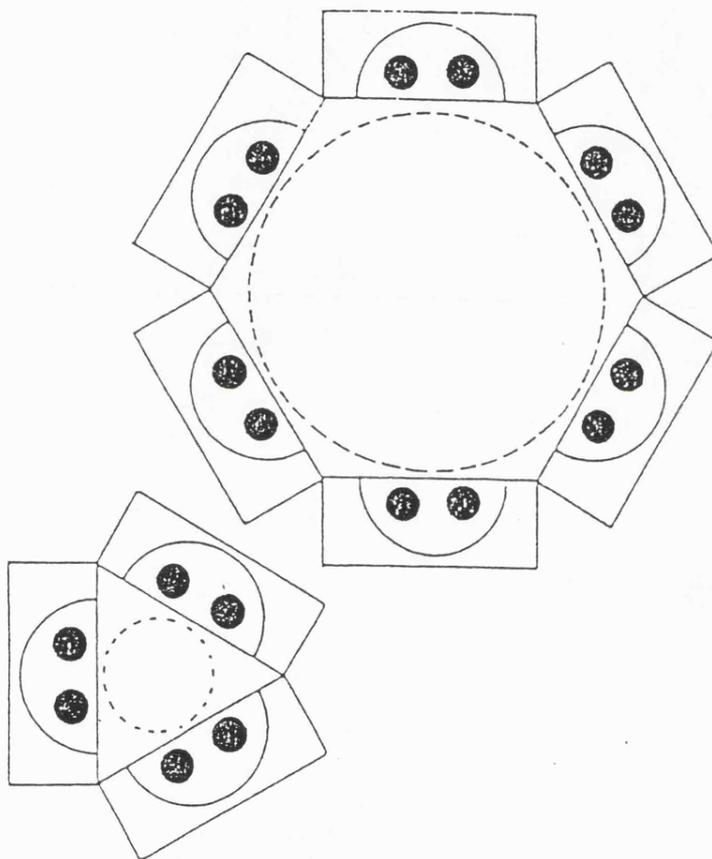


Figure 2.1

The U.V. light sources with the filaments in a ring arrangement

nitrogen temperature) and then fluorine (3mmol) was condensed on top at -196°C . The solid krypton is partly soluble in liquid fluorine at this temperature. The U.V. irradiation was carried out for 8 hours. When the photolysis was complete, a white compound was observed in the bottom of the reactor. The reactor was pumped at -196°C to remove unreacted fluorine and, when no measurable pressure remained, the reaction vessel was warmed to liquid oxygen temperature (-183°C) for the removal of unreacted krypton. Finally the reactor was warmed to dry-ice temperature (-78°C) and pumped to remove remaining impurities such as oxygen fluorides. The Raman spectrum of the residual white compound was measured at -196°C using the exciting frequency, 488nm (Kr-Ne laser). This showed a sharp peak at 464cm^{-1} , comparable to that at 462.6cm^{-1} attributed to the compound KrF_2 (Figure 2.2).²⁸

The yield of KrF_2 produced using this method was ~30% of the starting material after 8 hours.

2.3 A new solid state form of KrF_2 :

During the process of measuring the Raman spectrum of KrF_2 samples prepared by the above method it was observed that, after leaving the sample at -30°C for 20 minutes, a change in the Raman spectrum was observed. The peak at 464cm^{-1} disappeared and two new peaks at 470 and 471cm^{-1} were observed (Figure 2.3). When the scan was repeated the intensity of the two peaks decreased and, at the third scan the two peaks became very small. By

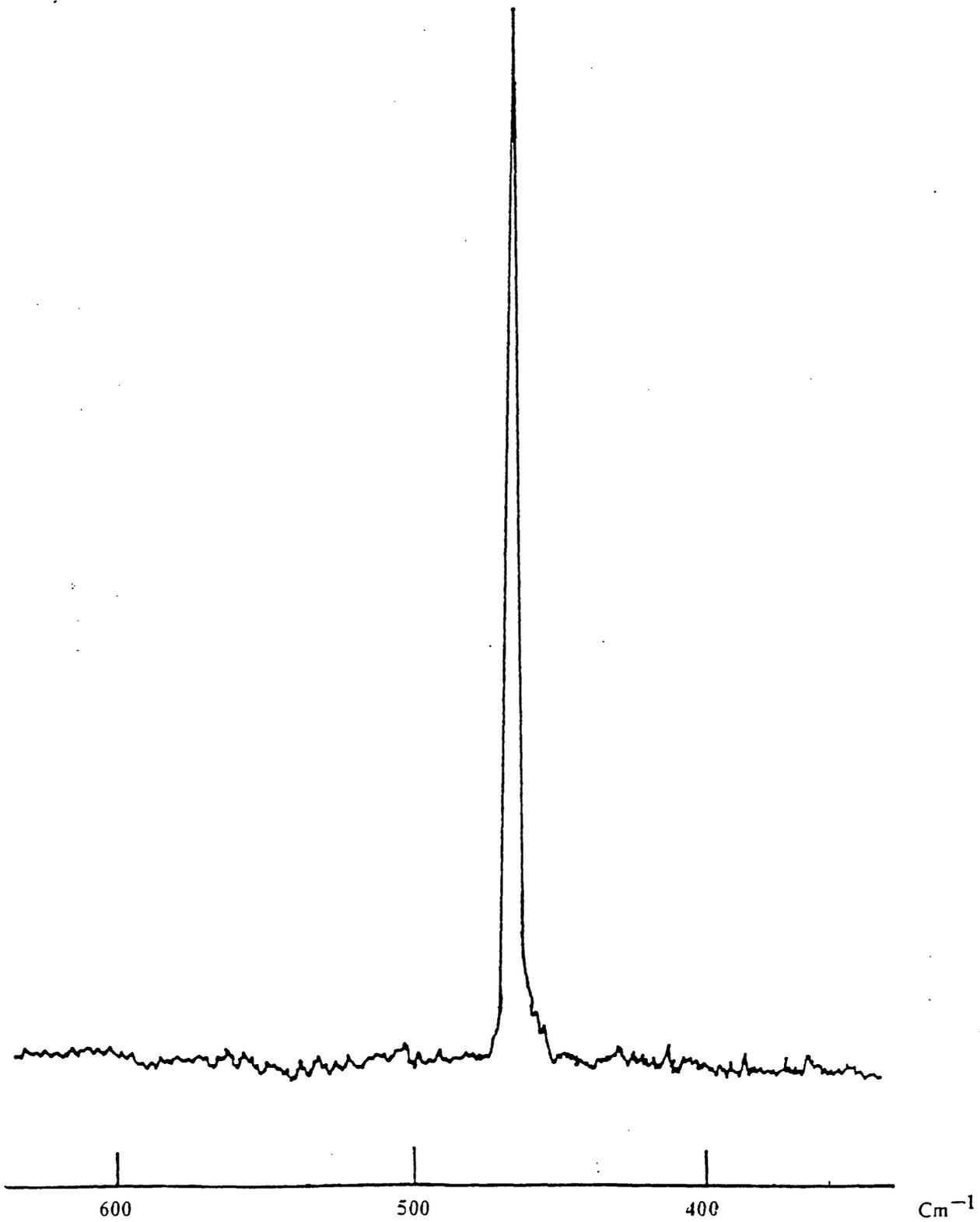


Figure 2.2 The Raman Spectrum of $\alpha\text{-KrF}_2$ at -196°C

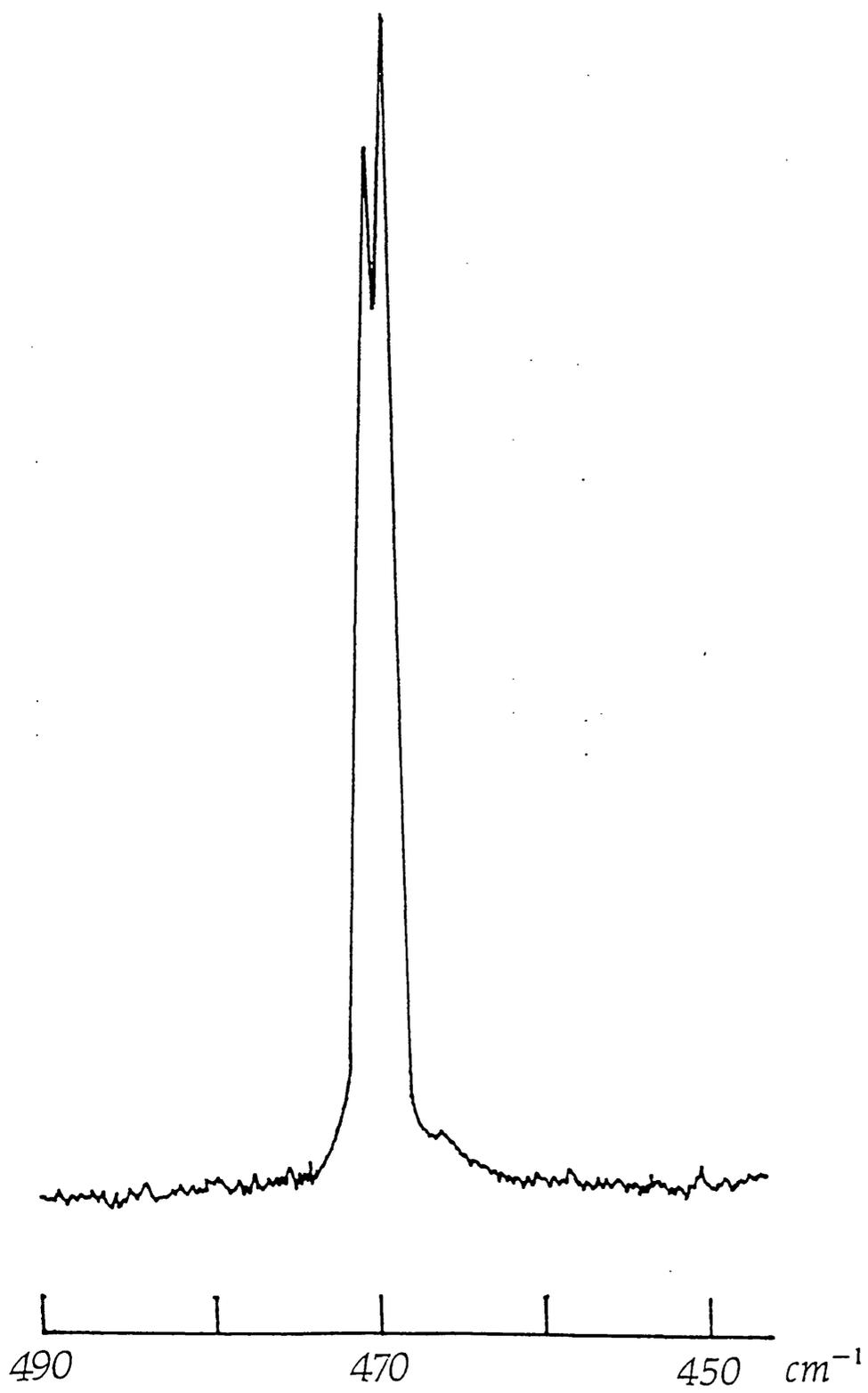


Figure 2.3 The Raman Spectrum of $\beta\text{-KrF}_2$ at -30°C

rotating the sample tube by $\sim 45^\circ$ and recording the Raman spectra again the two peaks were again observed. However, repeated scanning resulted in the same decrease in peak intensity. It was assumed that this could be explained by the laser beam creating a heating effect on the reflection spot on the sample tube which resulted in the compound subliming gradually from the irradiated spot, or that decomposition had occurred.

The two new peaks were also observed together with the peak due to KrF_2 in the Raman spectrum of a KrF_2 sample warmed to room temperature and then left at $\sim -78^\circ\text{C}$ for 24 hours.

At first, it was believed that the new peaks might be due to the presence of a new krypton fluoride, but re-measurement of the Raman spectrum of the sample at -196°C showed only the characteristic peak for KrF_2 at 464cm^{-1} . This suggested that KrF_2 was undergoing a temperature-dependent phase change. Further evidence to support this hypothesis was obtained by warming the KrF_2 sample to -30°C for 20 minutes and quenching the sample in liquid nitrogen (-196°C). The Raman spectrum for the sample was then recorded at -196°C every 5 minutes for 20 minutes. The first spectrum exhibited strong intensities for the peaks at 470 and 471cm^{-1} compared to the peak at 464cm^{-1} . In the second and third spectra however, the intensities of the peaks at 470 and 471cm^{-1} were decreased while the intensity of the peak at 464cm^{-1} increased. In the fourth scan the peaks at 470 and 471cm^{-1} had

disappeared and a sharp single peak at 464cm^{-1} remained (Figure 2.4). We have thus concluded that KrF_2 exists in two different crystallographic modifications and we have designated the low temperature (-196°C) phase $\alpha\text{-KrF}_2$ and the higher temperature (-78°C) phase $\beta\text{-KrF}_2$.

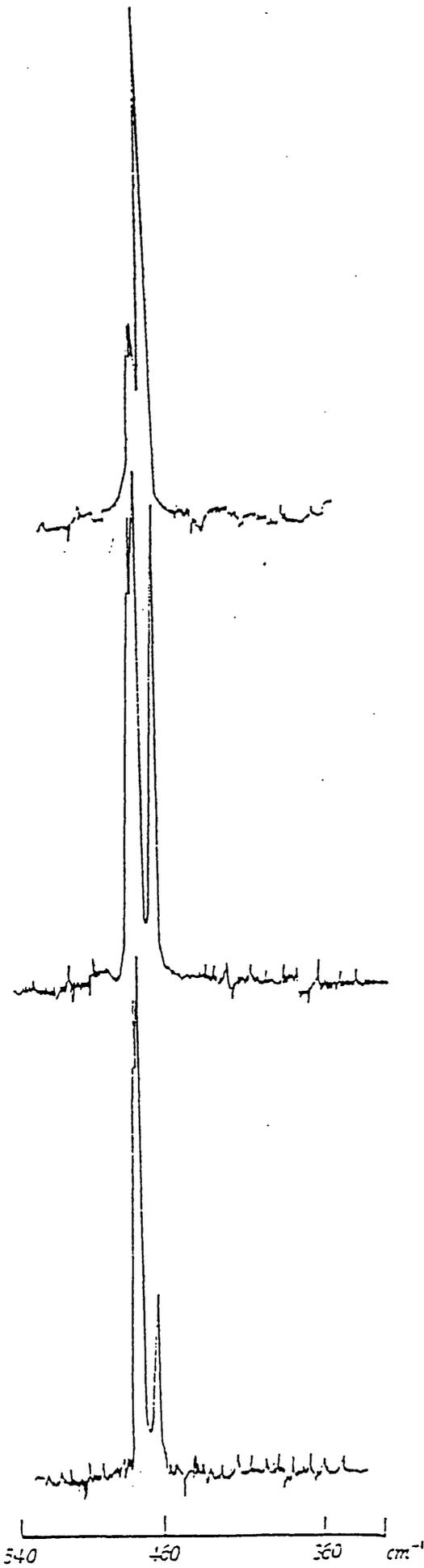


Figure 2.4 The Raman Spectrum of α - and β - KrF_2 at -196°C

Showing the conversion from β to α form.

2.3.1 Discussion :

The Raman spectrum (recorded at -196°C) of the white solid from the krypton/fluorine photolysis shows unequivocally that this is the same material as that described by Claassen *et al*²⁸ from electric discharge experiments and we obtain ~30% yield of KrF_2 after 8 hours photolysis. The single Raman active Kr-F stretch at 463.5cm^{-1} is comparable to the single Xe-F stretch at 500cm^{-1} for XeF_2 . However, on warming the sample to room temperature and cooling the sample at -78°C the Raman spectrum for KrF_2 changes. The peak at 464cm^{-1} decreases in intensity and additional peaks at 470 and 471cm^{-1} are observed. At first, it was believed that these might be assignable to a new krypton fluoride, but the absence of the peaks in the Raman spectrum at -196°C and the fact that their appearance is reversible with respect to temperature suggests that KrF_2 undergoes a phase change around -80°C .

The temperature-dependent phase change is of considerable interest. The x-ray crystal structure of KrF_2 at -78°C has been reported.⁴³ The molecule crystallises in the tetragonal space $P4_2/mnm$ with two linear KrF_2 molecules per unit cell aligned in planes perpendicular to the tetragonal axis. A factor group analysis for this crystal has been reported incorrectly⁹⁴ and Table 2.1 gives the correct factor-group analysis together with that for crystalline XeF_2 ⁹⁵ for comparison.

Table 2.1 Factor-Group Analyses for Crystalline Krf_2 and XeF_2 *

Krf_2 (D_{4h}^{14} , $Z^1 = 2$) ^a						XeF_2 (D_{2h}^{17} , $Z^1 = 1$)				
D_{4h}^b	N_T^b	T_A	T	R	v_i	N_T	T_A	T	R	v_i
A_{1g}	1	-	-	-	1	1	-	-	-	1
A_{2g}	1	-	-	1	-	-	-	-	-	-
B_{1g}	1	-	-	1	-	-	-	-	-	-
B_{2g}	1	-	-	-	1	-	-	-	-	-
E_g	1	-	-	1	-	1	-	-	1	-
A_{1u}	-	-	-	-	-	-	-	-	-	-
A_{2u}	2	1	-	-	1	2	1	-	-	1
B_{1u}	2	-	1	-	1	-	-	-	-	-
B_{2u}	-	-	-	-	-	-	-	-	-	-
E_u	4	1	1	-	2	2	1	-	-	1

a Z^1 = Number of molecules in primitive cell.

b N_T = Total number of modes of primitive cell; T_A = acoustic modes;

T = optic branch translatory modes; R = rotatory modes; v_i = internal modes of molecules.

* Prepared with the assistance of Dr. D. M. Adams

As can be seen the Σ_g^+ Raman active stretch for gaseous, monomeric $D_{\infty h}$ KrF_2 splits into two bands ($A_{1g} + B_{2g}$) in space group $P4_2/mnm$. This contrasts with that for XeF_2 for which only one band is predicted .

When these predicted splittings are compared with our Raman data, it is clear that Falconer *et al*⁴³ solved the x-ray crystal structure of β - KrF_2 . Furthermore, the simplicity of the Raman spectrum at $-196^\circ C$ and its similarity to that of XeF_2 suggests that α - KrF_2 probably crystallizes in the same space group as XeF_2 .

2.4 The U.V. photolysis of F_2/Ar mixtures at $-196^\circ C$ (Attempt to prepare ArF_2)

In an attempt to prepare ArF_2 by a similar route to that used to make KrF_2 , the reaction of argon with liquid fluorine was investigated. Fluorine (1.5 mmol) and argon (1.5 mmol) were condensed from a metal manifold into a pre-passivated FEP reactor (6 cm³ total volume) at $-196^\circ C$. The mixture was photolysed for 13 hours. Traces of a white solid were obtained in the bottom of the reactor. The reactor was pumped at $-196^\circ C$ and $-183^\circ C$ to remove unreacted fluorine and argon respectively. Careful examination of the white residual solid showed that this decomposes at $\sim -140^\circ C$.

2.4.1 Raman Spectroscopy :

The Raman spectrum of the white solid (traces)

condensed onto the inner wall of the FEP reactor at -196°C showed a peak at 580 cm^{-1} along with other peaks due to the FEP reactor (Figure 2.5). It seemed at first that the peak at 580 cm^{-1} might be assigned to an argon fluoride, but the Raman spectrum of the reactor at -100°C showed that the peak at 580 cm^{-1} was still present. This suggested that the peak may be due to a product from the fluorination of FEP. However, since the photolysis of krypton dissolved in liquid fluorine does not produce the same product this suggest that it may result from fluorination by a more powerful fluorinating agent than KrF_2

2.4.2 Mass Spectrometry :

The mass spectrum of the white solid showed the Ar^+ ion. Since the sample had been pumped at -183°C no unreacted argon should be present. The observed Ar^+ ion may, therefore, be due to an argon fluoride which decomposes to argon and fluorine before reaching the ionisation chamber of the mass spectrometer.

2.4.3 Reaction of the product of the photolysis of Ar/F_2 mixture with KI :

In order to test for the presence of fluorine in the white solid which resulted from the U.V. photolysis of Ar/F_2 mixture at -196°C , a U-shape FEP reactor with two Teflon valves at each end was made. After photolysing an Ar/F_2 mixture in the reactor it was pumped at -196°C and

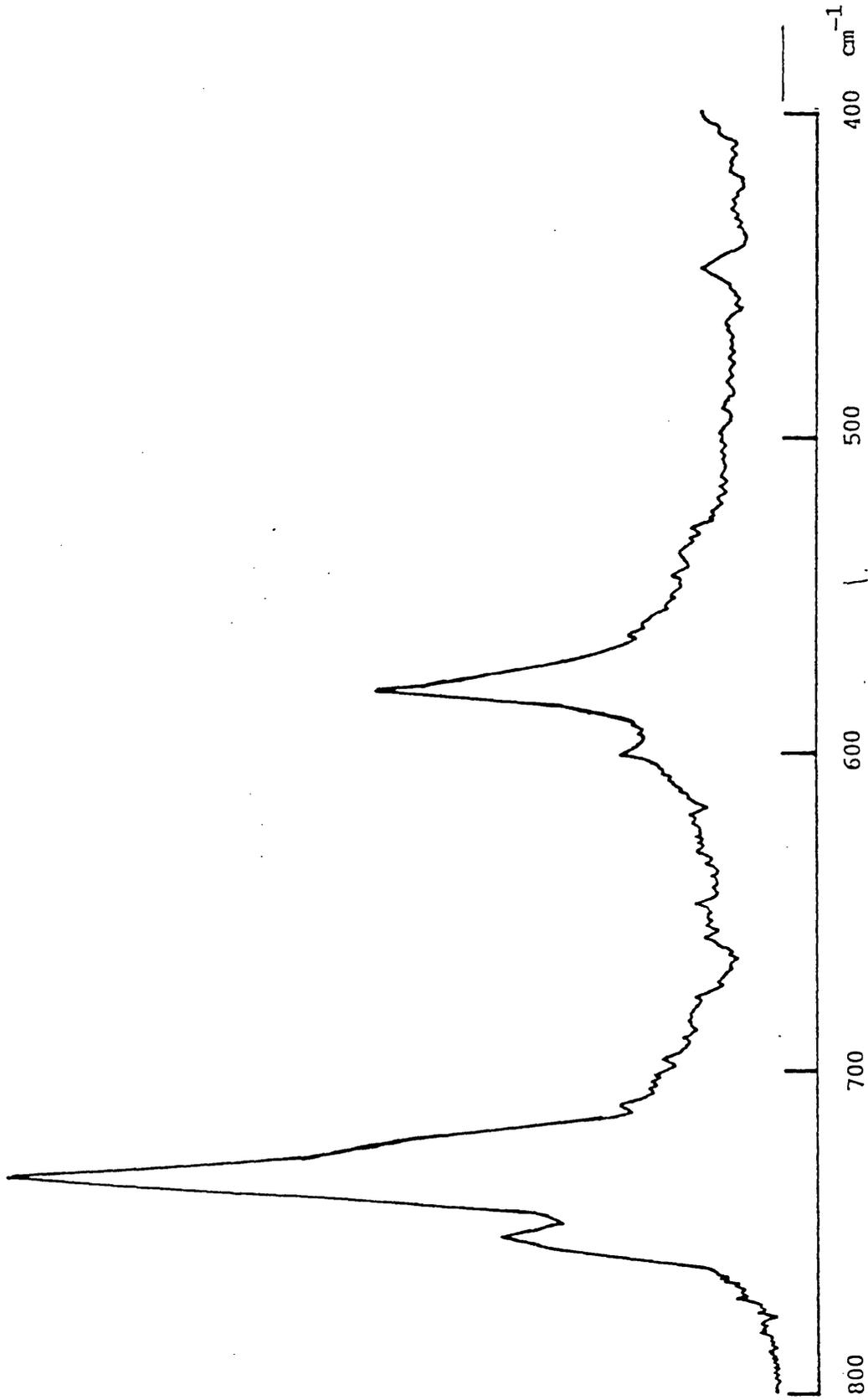


Figure 2.5 The Raman Spectrum of FEP Reactor Following

U.V. Photolysis of Ar/F₂(L) Mixture at -196°C

at -183°C to remove unreacted fluorine and argon respectively until there was no residual pressure. The reactor was warmed to R.T. in order to decompose the white product and a flow pressure of nitrogen carrier gas was passed through one end of the reactor with the other end connected to a bubbler containing KI solution. The colourless KI solution changed to brown as the bubbling process progressed which indicated the presence of fluorine in the decomposition product of the white solid.

2.4.4 Conclusion :

The evidence provided by mass spectrometry suggested that an argon compound may be formed in small yield by the U.V. photolysis of Ar/F_2 mixture at -196°C . This was further supported by the observation that elemental fluorine is also a decomposition product of the thermolysis of the white compound. Definitive characterization, however, will only be possible if unambiguous vibrational spectroscopic evidence can be obtained on a larger product sample.

Chapter three

The reaction of Kr/F₂ mixture with some Lewis acids using U.V. photolysis at -196 °C

Chapter three

The reaction of Kr/F₂ mixture with some Lewis acids using U.V. photolysis at -196°C

3.1 Introduction :

The bulk of information about SbF₅ and AsF₅ adducts with KrF₂ appears in three papers^{60,68,70} (see chapter 1).

The reactions of AsF₅ and SbF₅ with Kr/F₂ mixtures were carried out to see if SbF₅ adducts of KrF₂ could be prepared directly by reaction of krypton, fluorine and SbF₅ or AsF₅ in a similar way to that used earlier (see 2.1) to prepare KrF₂. In the case of the reactions involving AsF₅ we were also interested to know whether it was possible to prepare KrF⁺As₂F₁₁⁻ under these conditions.

3.2 The reaction of Kr/F₂ mixture with SbF₅ using U.V. photolysis at -196°C :

3.2.1 The preparative method :

As in the preparation of KrF₂ (see 2.2) the light sources used were medium wavelength mercury lamps, the filaments being arranged in a circle round the reactor. Radiation of 350nm wavelength and an FEP reactor were again

employed.

The FEP reactor and the vacuum manifold were pumped to high vacuum (10^{-4}) for 8 hours with periodic heating to remove adsorbed moisture, and were then seasoned several times with elemental fluorine. The apparatus with the manifold were then re-evacuated. A small amount of SbF_5 (0.15g, 0.7mmol) was condensed into the FEP reactor at -78°C , and Kr (1.5 mmol) and F_2 (1.5 mmol) were condensed on top at -196°C . The mixture was irradiated for 17 hours at -196°C . After photolysis was finished the reactor was pumped at -196°C and at -183°C to remove unreacted fluorine and krypton respectively. A white solid was obtained and the Raman spectrum was recorded at -196°C and then at various temperatures up to -25°C .

3.2.2 Raman data :

3.2.2a Raman spectrum at -196°C :

The Raman spectrum of the white solid was recorded at -196°C and it showed strong peaks at 464, 673 and 718cm^{-1} . The peak at 464cm^{-1} was attributed to $\alpha\text{-KrF}_2$ and the peaks at 673 and 718cm^{-1} coincided with data for unreacted SbF_5 .⁹⁶ Identical data were also obtained from the Raman spectrum of the sample at -120°C (Figure 3.1). This suggests that SbF_5 does not react with either liquid fluorine or KrF_2 at -196°C , nor does it react with KrF_2 at -120°C .

* = FEP peak

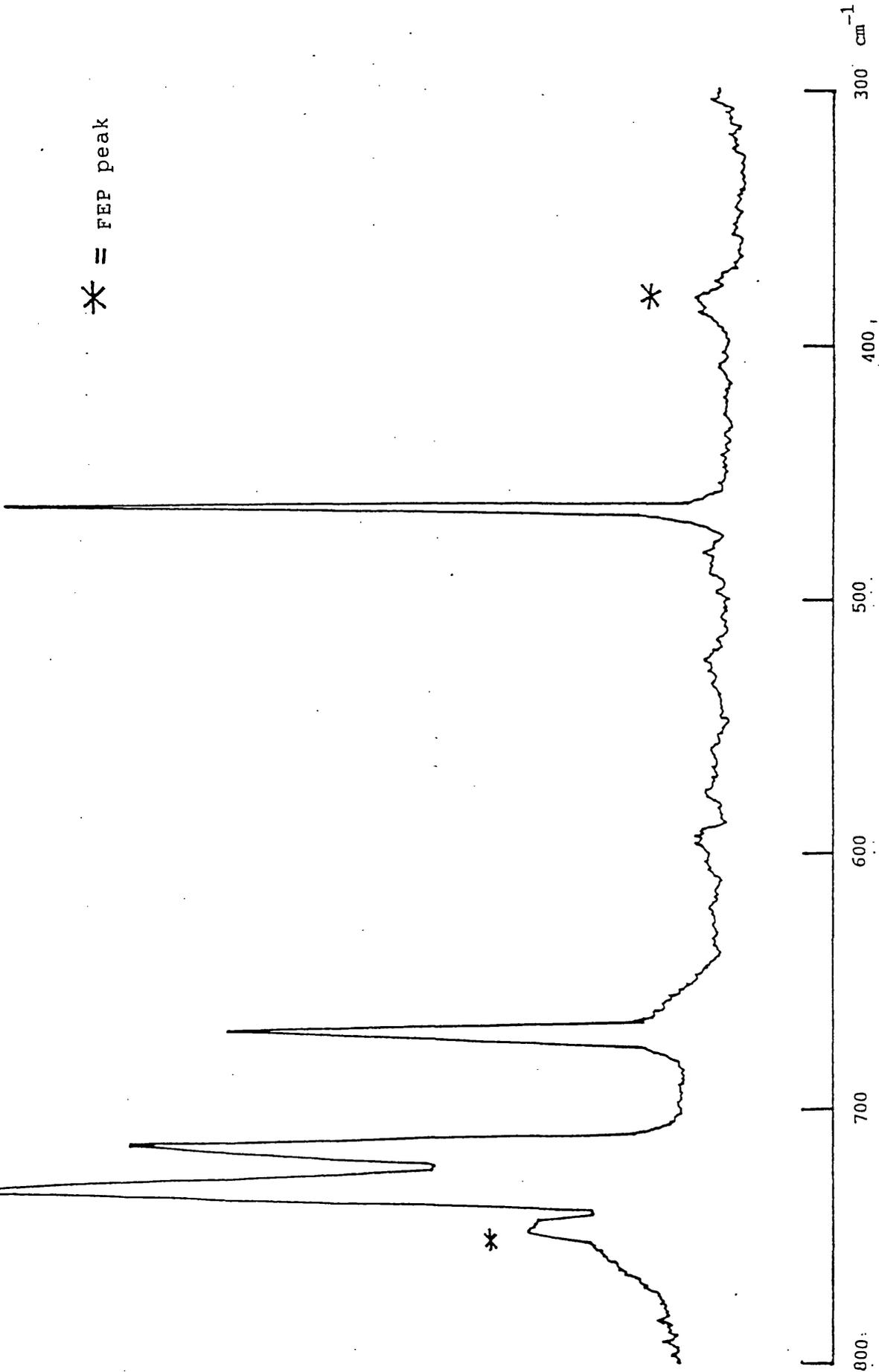


Figure 3.1 The Raman Spectrum of α - KrF_2 with unreacted

SbF_5 at -196°C

3.2.2b Raman spectrum at -95°C :

The same sample (3.2.2a) was warmed to $\sim -95^\circ\text{C}$ for ~ 30 minutes, The Raman spectrum of the white solid was recorded at -95°C and showed strong peaks at 464, 606 and 595cm^{-1} (see Figure 3.2) . The peak at 464cm^{-1} indicated the presence of $\alpha\text{-KrF}_2$, while the peaks at 606 and 595cm^{-1} could be assigned to the Kr_2F_3^+ cation.⁶⁴ Weaker peaks between 640 and 700cm^{-1} were assigned to SbF_6^- (Table 3.1) and peaks assigned to unreacted SbF_5 were also observed. Thus it appears that KrF_2 reacts with SbF_5 at $\sim -95^\circ\text{C}$ to produce the adduct $\text{Kr}_2\text{F}_3^+\text{SbF}_6^-$. This is interesting since $\text{KrF}^+\text{Sb}_2\text{F}_{11}^-$ is the first product observed from the reaction of KrF_2 with SbF_5 at room temperature.^{60,70}

3.2.2c Raman spectrum at -25°C :

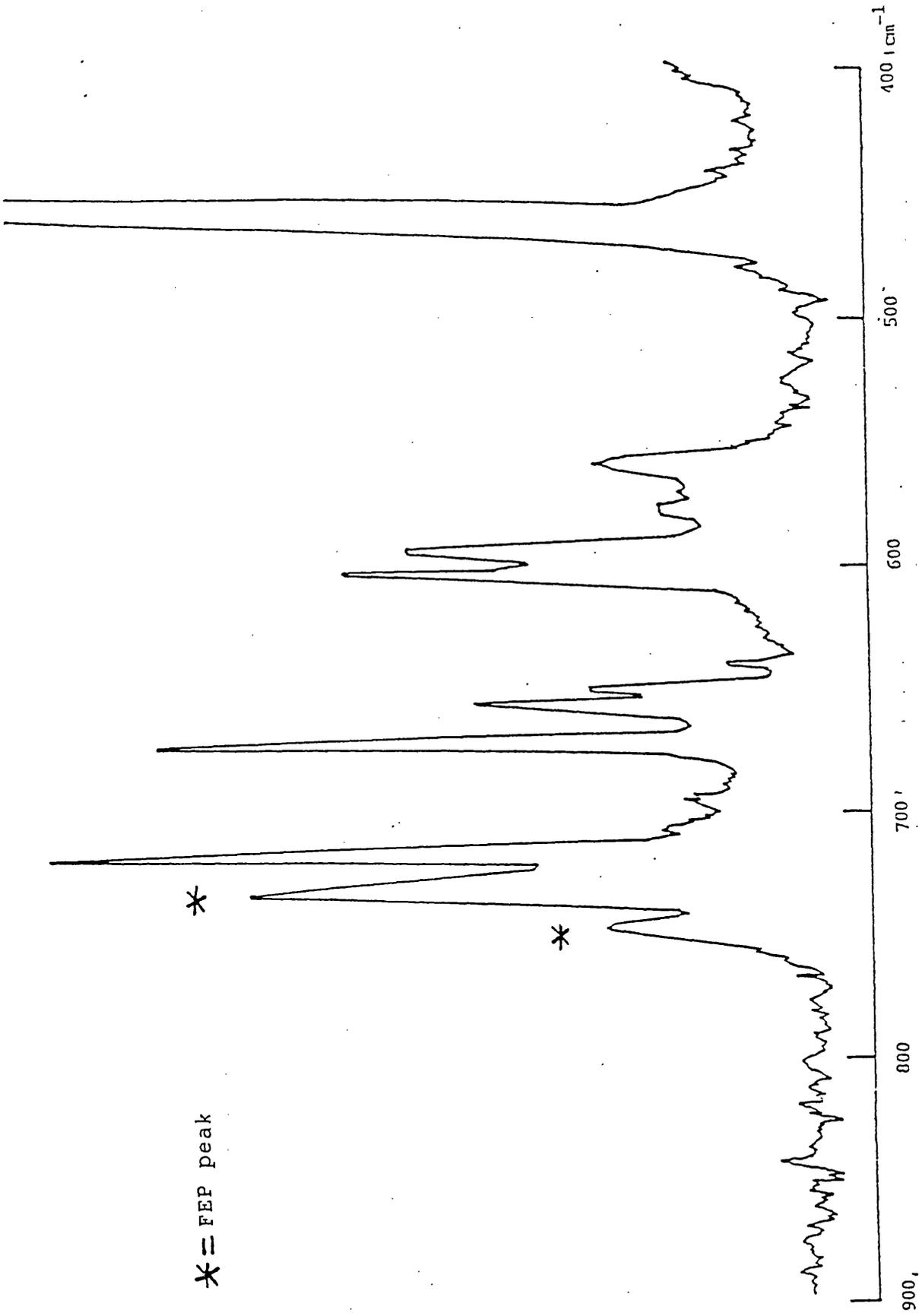
The sample from (3.2.2b) was warmed to -25°C for one hour and at this temperature the Raman spectra for the white solid was recorded. This showed a strong peak at 627cm^{-1} and weaker peaks at 620, 694, 680, 672, 654, 523 and 482cm^{-1} (Table 3.2). The spectrum is in good agreement with that reported for $\text{KrF}^+\text{Sb}_2\text{F}_{11}^-$ by Frlec and Holloway.⁶⁸ Weak peaks at 673 and 718cm^{-1} were also observed indicating the presence of a small traces of unreacted SbF_5 . Thus on warming the reactor to -25°C , SbF_5 reacts further with $\text{Kr}_2\text{F}_3^+\text{SbF}_6^-$ and KrF_2 to form the adduct $\text{KrF}^+\text{Sb}_2\text{F}_{11}^-$ (Figure 3.3).

<u>Observed (cm⁻¹)</u>		<u>Assignments</u>
606 (100)	γ	
595 (91)	⊥	Kr ₂ F ₃ ⁺
565 (8)		
559 (43)	⊥	
658 (45)	γ	
652 (42)	⊥	SbF ₆ ⁻
645 (9)		
565 (8)	⊥	
673 (S)		SbF ₅
718 (S)		
463 (VS)		KrF ₂

**Table 3.1 The Raman Frequencies (cm⁻¹) and Assignments
for (Kr₂F₃⁺ SbF₆⁻) at -95°C .**

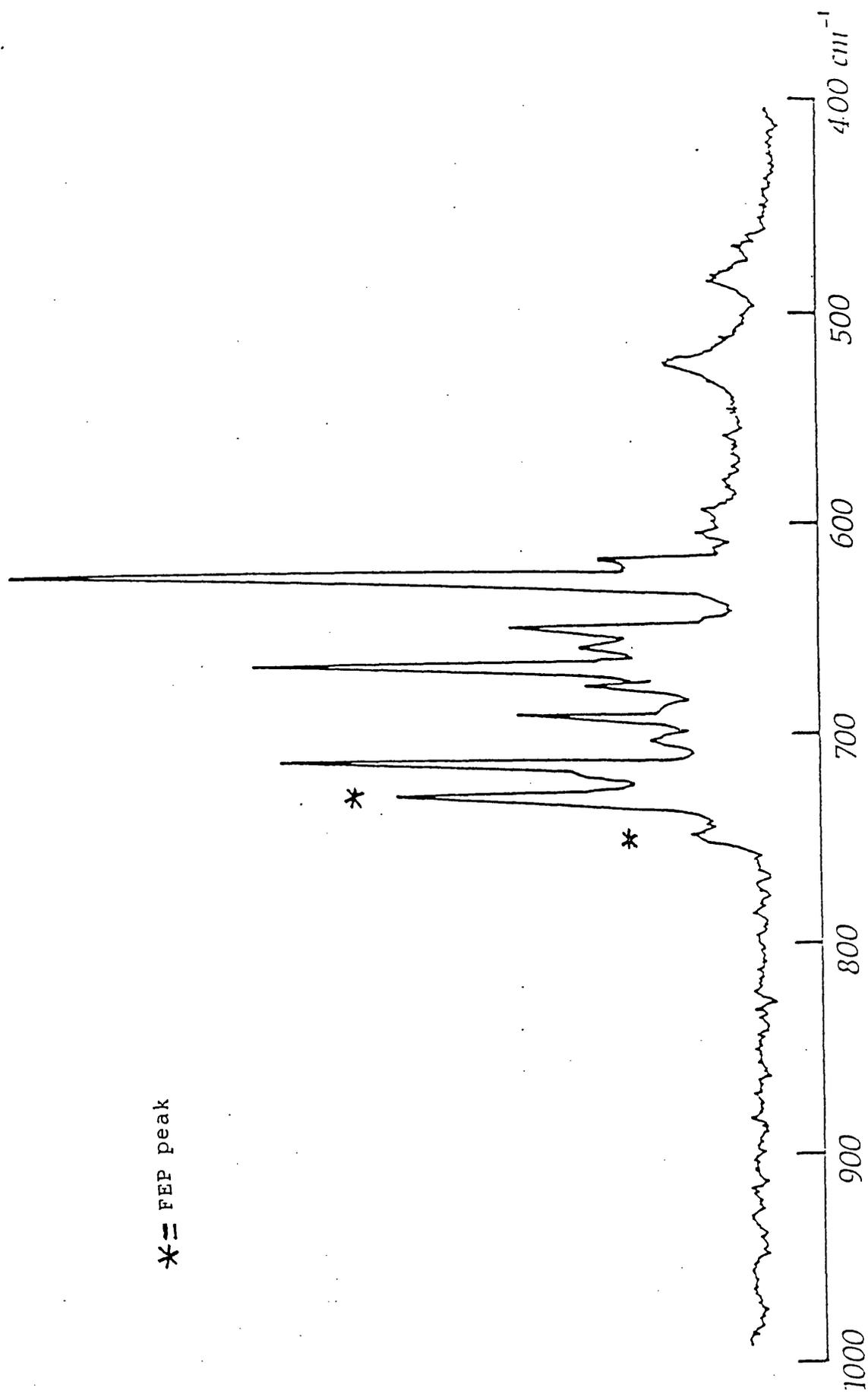
<u>Observed</u>		<u>Assignments</u>
627 (100)		
620 (20)		KrF ⁺
694 (30)	γ	
680 (16)		
672 (13)	†	Sb ₂ F ₁₁ ⁻
654 (30)		
523 (13)		
482 (10)	↓	

Table 3.2 The Raman Frequencies (cm⁻¹) and Assignments
for α KrF⁺Sb₂F₁₁⁻ at -25°C .



* = FEP peak

Figure 3.2 The Raman Spectrum of $\text{Kr}_2\text{F}_3\text{SbF}_6^-$ at -95°C



* = FEP peak

Figure 3.3 The Raman Spectrum of $\alpha\text{-KrF}^+\text{Sb}_2\text{F}_{11}^-$ at -25°C

3.2.2d The identification of two forms of $\text{KrF}^+\text{Sb}_2\text{F}_{11}^-$:

In the literature there is a disagreement regarding the Raman spectrum of $\text{KrF}^+\text{Sb}_2\text{F}_{11}^-$. Two peaks at 620 and 627cm^{-1} were reported for the Kr-F stretch by Frlec and Holloway,⁶⁸ while only one peak at 624cm^{-1} was reported for the same stretch by Gillespie and Schrobilgen.⁷⁰ This apparent inconsistency is explained by the following experiment :-

An additional quantity of krypton and fluorine in a 1:1 ratio was condensed on to the product from the reaction described in (3.2.2c), and U.V. photolysis at -196°C was repeated for 8 hours. When the photolysis was finished the unreacted F_2 and Kr were removed as described previously. A white solid was obtained and the Raman spectra at -196°C showed the presence of KrF_2 which does not react with $\text{KrF}^+\text{Sb}_2\text{F}_{11}^-$ or with SbF_5 at -196°C . As the sample warmed the Raman spectra was recorded at various temperatures. The peaks due to $\text{KrF}^+\text{Sb}_2\text{F}_{11}^-$ did not change but, at $\sim -90^\circ\text{C}$ peaks due to $\text{Kr}_2\text{F}_3^+\text{SbF}_6^-$ appeared again along with those of $\text{KrF}^+\text{Sb}_2\text{F}_{11}^-$ confirming that KrF_2 reacts initially with SbF_5 at this temperature to yield the 2:1 adduct.

With warming the sample further to -10°C the peaks due to the 2:1 adduct decreased in intensity while those due to the 1:2 adduct increased along with a number of other new peaks (Table 3.3). It appears that the new peaks correlate with the most intense peaks in the Raman spectra of $\text{KrF}^+\text{Sb}_2\text{F}_{11}^-$ reported by Gillespie and Schrobilgen.⁷⁰

Therefore, it appears that, as in the case of KrF_2 (see 2.2) and $\text{KrF}^+\text{AsF}_6^-$,⁶⁵ there are two crystalline modifications (α - and β -) of $\text{KrF}^+\text{Sb}_2\text{F}_{11}^-$. These may be related in a thermal equilibrium but have been seen together for the first time only in these variable low-temperature Raman experiments (Figure 3.4).

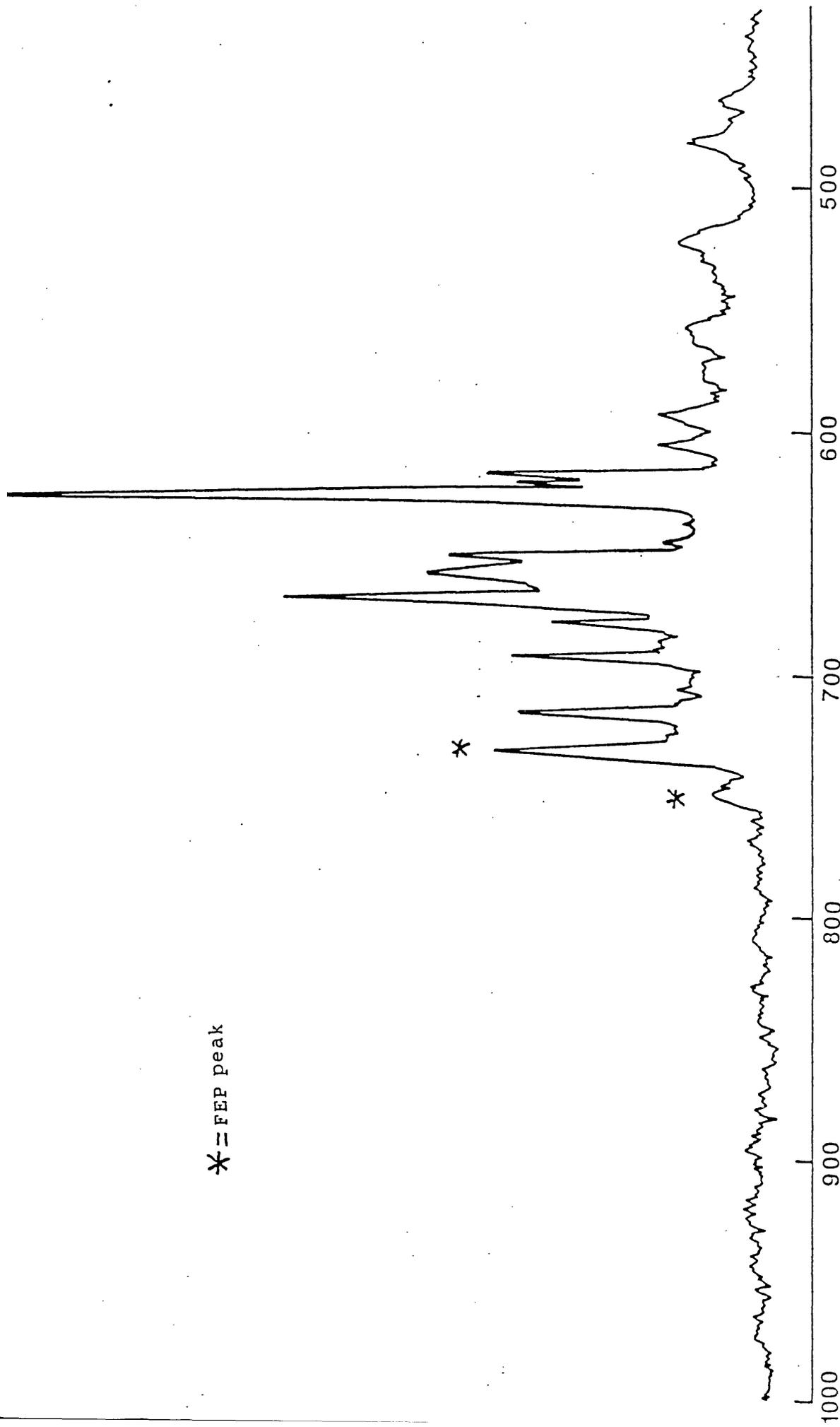
3.2.2e The observation of a new adduct $[\text{xKrF}_2 \cdot \text{KrF}]^+\text{Sb}_2\text{F}_{11}^-$:

The only KrF_2 adducts of the type $[\text{KrF}_2 \cdot \text{KrF}]^+\text{M}_2\text{F}_{11}^-$ were reported with NbF_5 and TaF_5 .⁶⁸ The experiment below provided evidence for a similar KrF_2 adduct with SbF_5 .

A mixture with a ratio of $1\text{F}_2:1\text{Kr}$ was condensed onto a sample of the α - and β - $\text{KrF}^+\text{Sb}_2\text{F}_{11}^-$ mixture from (3.2.2d) at -196°C and U.V. photolysis was carried out for 8 hours. When the photolysis was finished the reactor was pumped at -196°C and -183°C to remove unreacted fluorine and krypton respectively. The Raman spectra of the sample was recorded at -196°C and showed the characteristic peak at 464cm^{-1} for KrF_2 along with the peaks due to the two forms of $\text{KrF}^+\text{Sb}_2\text{F}_{11}^-$. The sample was warmed to -30°C and the Raman spectrum for the sample recorded at this temperature. This showed all the peaks due to α - and β - $\text{KrF}^+\text{Sb}_2\text{F}_{11}^-$, a peak at 633cm^{-1} , and a weaker peak at 573cm^{-1} (Figure 3.5) which may be attributed to loosely associated KrF_2 . This can reasonably be expected to be associated with the cation. In the event of this type of association occurring there should be partial donation of

Observed	Frlec & Holloway ⁶⁷	Gillespie & Schrobilgen ⁶⁹	Assignment
<u>cm</u> ⁻¹	<u>cm</u> ⁻¹	<u>cm</u> ⁻¹	
627 (100)	627 (100)		γ
624 (18)		624 (100)	┆ KrF ⁺
620 (21)	619 (20)		
			┆
694 (30)	694 (30)		γ
680 (16)	680 (18)		
677 (3)		675 (15)	
672 (13)	672 (11)		
654 (30)	653 (27)		
648 (6)		648 (26)	┆ Sb ₂ F ₁₁ ⁻
523 (13)	524 (8)	591 (10)	
482 (10)	483 (5)		
			┆

Table 3.3 The Raman Frequencies (cm^{-1}) and Assignments for KrF^+ $\text{Sb}_2\text{F}_{11}^-$ α and β .



* = FEP peak

Figure 3.4 The Raman Spectrum of α - and β - $\text{KrF}^+\text{Sb}_2\text{F}_{11}^-$

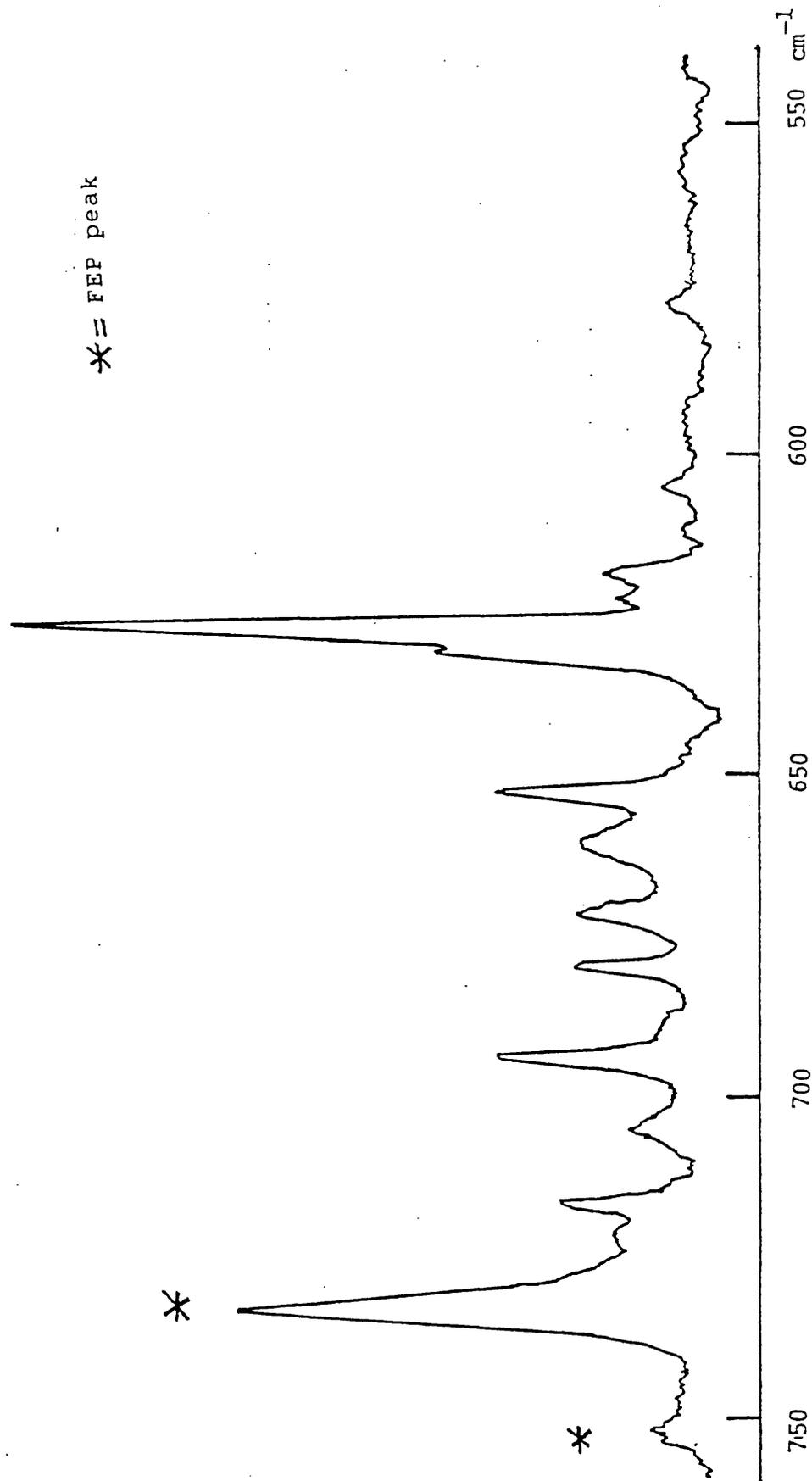


Figure 3.5 The Raman Spectrum of $[\text{xKrF}_2 \cdot \text{KrF}]^+ \text{Sb}_2\text{F}_{11}^-$ and α - and β - $[\text{KrF}]^+ \text{Sb}_2\text{F}_{11}^-$

electron density to the cationic part of the adduct which should be evidenced by a slight drop in the value of the frequency $\nu(\text{Kr}-\text{F})$. Such a reduction was, in fact, observed (see Table 3.4).

3.3 The reaction of Kr/F_2 mixture with AsF_5 using U.V. photolysis :

3.3.1 The preparation of $\alpha\text{-KrF}_2^+\text{AsF}_6^-$:

AsF_5 (0.8mmol) was condensed into a Pyrex reactor at -196°C and argon (1.5mmol) and fluorine (1.5mmol) were condensed onto the solid AsF_5 at -196°C (liquid nitrogen temperature). The reaction was carried out by irradiating the mixture for 9 hours at -196°C using U.V. photolysis. When the photolysis was finished a white solid was obtained in the bottom of the reactor. The reactor was pumped first at -196°C and then at -183°C to remove unreacted fluorine and krypton respectively. The Raman spectrum of the white solid was recorded at -196°C . This showed strong peaks at 464 and 740cm^{-1} and weaker peaks at 638 and 812cm^{-1} , the peak at 464cm^{-1} due to unreacted KrF_2 . The other peaks are all associated with unreacted AsF_5 .⁹⁷ Identical spectra were obtained at -78°C which suggests that AsF_5 does not react with either F_2 at -196°C or KrF_2 at temperatures up to -78°C .

After warming to -40°C for about 30 minutes the Raman spectra of the white solid was recorded at -196°C . This showed (Table 3.5), a spectrum typical of

$\alpha\text{-KrF}^+\text{AsF}_6^-$,⁷⁰ along with a small peak at 464cm^{-1} indicative of the presence of small amounts of unreacted KrF_2 (Figure 3.6). No evidence was found for a 2:1 adduct comparable to $\text{Kr}_2\text{F}_3^+\text{SbF}_6^-$.

Observed	Frlec & Holloway ⁶⁷	
$[\text{xKrF}_2 \cdot \text{KrF}]^+$ $[\text{Sb}_2\text{F}_{11}]^-$	$[\text{xKrF}_2 \cdot \text{KrF}]^+$ $[\text{Ta}_2\text{F}_{11}]^-$	$[\text{xKrF}_2 \cdot \text{KrF}]^+$ $[\text{Nb}_2\text{F}_{11}]^-$
633 (30)	613 (41)	596 (100)
573 (5)	575 (17)	571 (52)
	564 (9)	541 (9)
	571 (20)	535 (14)
	539 (6)	

Table 3.4 The Raman Frequencies (cm^{-1}) and Assignments for $[\text{xKrF}_2 \cdot \text{KrF}]^+[\text{Sb}_2\text{F}_{11}]^-$.

<u>Observed</u>	<u>Assignments</u>
604 (100)	Kr-F
612 (100)	
712 (11)	AsF_6^-
421 (13)	
385 (7)	

Table 3.5 The Raman Frequencies (cm^{-1}) and Assignments
for $\alpha\text{-KrF}^+ \text{AsF}_6^-$

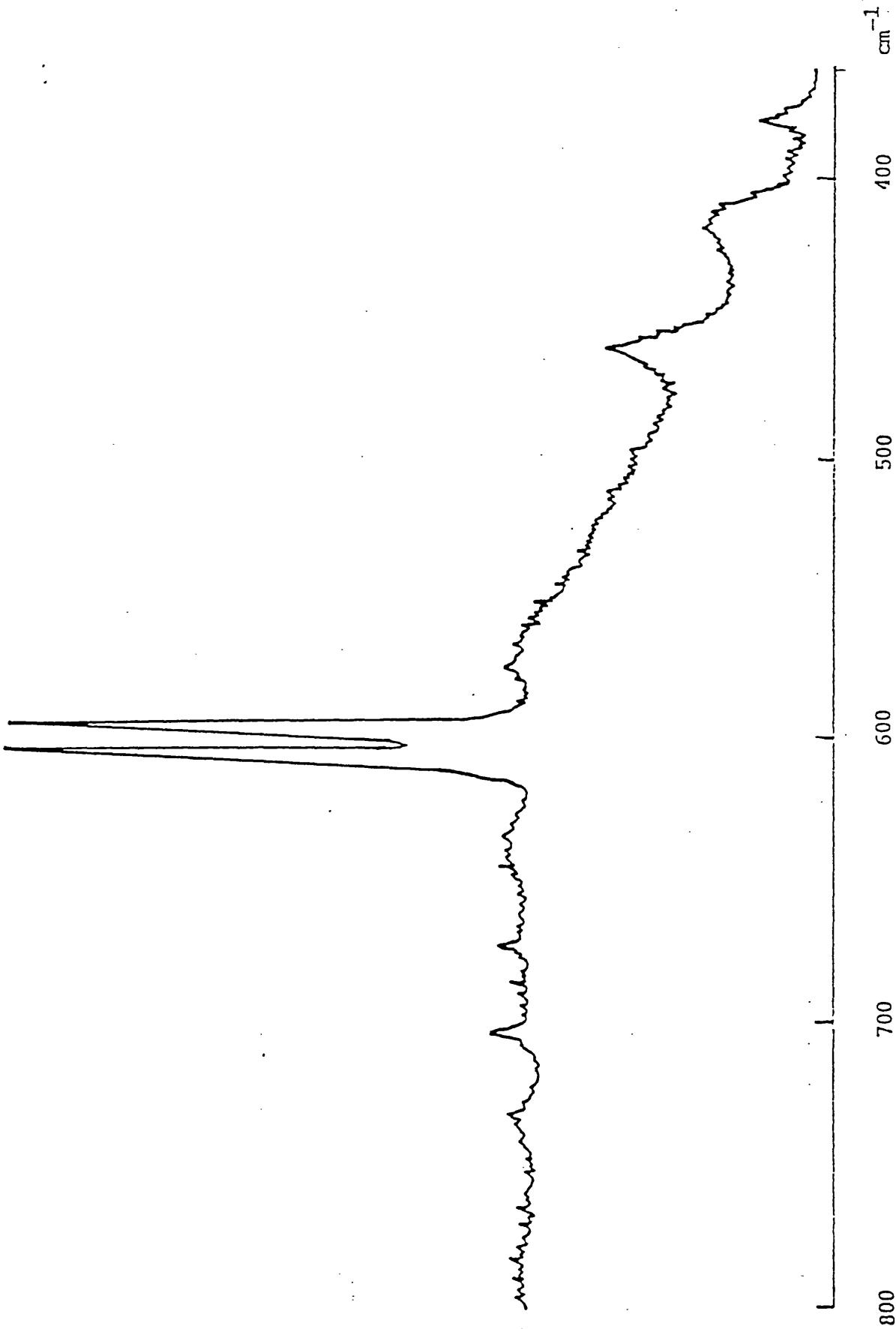


Figure 3.6 The Raman Spectrum of $\alpha\text{-KrF}_7\text{AsF}_6^-$ at -196°C

3.3.2 The observation of a new KrF_2 adduct with AsF_5 :

There is no mention in the literature about a 1:2 adduct of KrF_2 with AsF_5 . This adduct is the most common KrF_2 adduct with Lewis acids such as SbF_5 ,^{60,68,70} TaF_5 and NbF_5 .⁶⁹ Whilst there are few observations of the $\text{As}_2\text{F}_{11}^-$ ion and it is generally agreed that this anion is of limited stability. A series of experiments was therefore made to investigate the possibility of preparing a KrF_2 adduct with AsF_5 of the type $\text{KrF}_2 \cdot 2\text{AsF}_5$.

3.3.2a The preparation of $\text{KrF}^+\text{As}_2\text{F}_{11}^-$:

AsF_5 , F_2 and Kr were condensed into a reactor as described previously (3.3.1). With a ratio of 3:1:1, $\text{AsF}_5:\text{F}_2:\text{Kr}$, after 8 hours of U.V. photolysis and subsequent pumping at -196°C and -183°C to remove unreacted fluorine and krypton respectively, a white solid was obtained. A Raman examination of the product of the reaction at -45°C indicated the presence of $\alpha\text{-KrF}^+\text{AsF}_6^-$ and an excess of unreacted AsF_5 .

3.3.2b The Raman spectrum at -30°C :

When the mixture was warmed to -30°C the Raman spectrum of the sample at this temperature showed a sharp decrease in intensity of the peaks due to $\alpha\text{-KrF}^+\text{AsF}_6^-$ and a number of new peaks at 737, 692 and 566cm^{-1} (Figure 3.7) appeared. The peak at 737cm^{-1} was attributed to free AsF_5 .⁹⁷ The weaker peak at 692cm^{-1} is comparable to that at

697cm^{-1} for the polyanion $\text{As}_2\text{F}_{11}^-$ in $\text{Na}^+\text{As}_2\text{F}_{11}^-$,⁹⁸ while the peak at 566cm^{-1} can be related to the stretching vibration associated with KrF^+ .

When the reactor containing the above solid was recharged with a 1:1 ratio of fluorine and krypton at -196°C and subjected to U.V. photolysis for a further 8 hours and the unreacted fluorine and krypton removed as previously, the Raman spectra for the sample at -78°C showed the presence of KrF_2 . The reactor was then warmed to -45°C and the Raman spectra at this temperature confirmed the formation of the 1:1 adduct along with the new peaks observed earlier. The reactor was warmed further to -30°C for 30 minutes and the Raman spectrum at -196°C showed traces of the peaks due to the 1:1 adduct, decreased intensity in the peak due to free AsF_5 and an increase in intensity of the peaks at 692 and 566cm^{-1} . Further new small peaks at 676 , 711 , 647 , 373 , 285 and 798cm^{-1} were observed (Figure 3.7).

The same process of adding a Kr/F_2 mixture and irradiating it at -196°C in the presence of the initial product and subsequent removal of unreacted F_2 and Kr and warming the product to -45°C and -30°C was repeated. The Raman spectrum of the final product showed dominance of the peaks due to $\text{KrF}^+\text{As}_2\text{F}_{11}^-$ and the disappearance of the peaks associated with $\alpha\text{-KrF}^+\text{AsF}_6^-$. However, the small peak at 736cm^{-1} due to free AsF_5 was still evident (Figure 3.8).

Table 3.6 shows the increasing yield of the

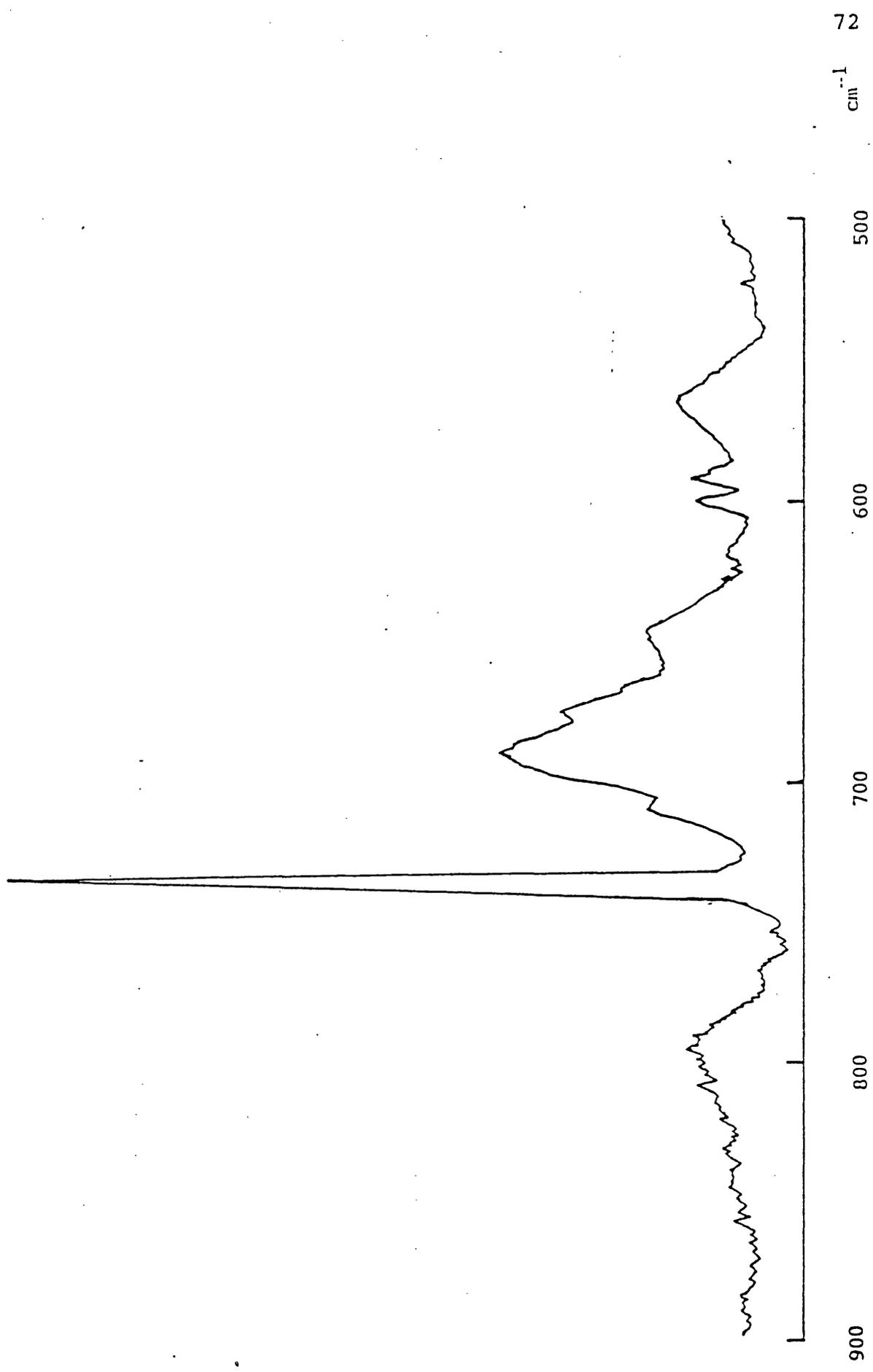


Figure 3.7 The Raman Spectrum of $\text{KrfAs}_2\text{F}_{11}^+$ and (Free) AsF_5 at -196°C

Observed		Assignments	
$\text{KrF}^+ \text{As}_2\text{F}_{11}^-$			
566 (8)	570 (28)	570 (41)	γ
		566 (26)	$\vdash \text{KrF}^+$
282 (7)	282 (9)	286 (10)	\downarrow
798 b	$+\text{KrF}_2$ 798 b	$+\text{KrF}_2$ 798 (vb)	γ
711 (3)	-----> 711 (4)	-----> 711 (10)	
692 (22)	692 (90)	692 (100)	
676 (6)	680 (14)	680 (18)	$\vdash \text{As}_2\text{F}_{11}^-$
647 (5)	647 (7)		
373 (10)	373 (20)	373 (62)	
		540 (6)b	
		490 (10)	\downarrow
734 (100)	734 (100)	734 (7)	AsF_5

Table 3.6 The Raman Frequencies (cm^{-1}) and Assignments for $\text{KrF}^+ \text{As}_2\text{F}_{11}^-$.

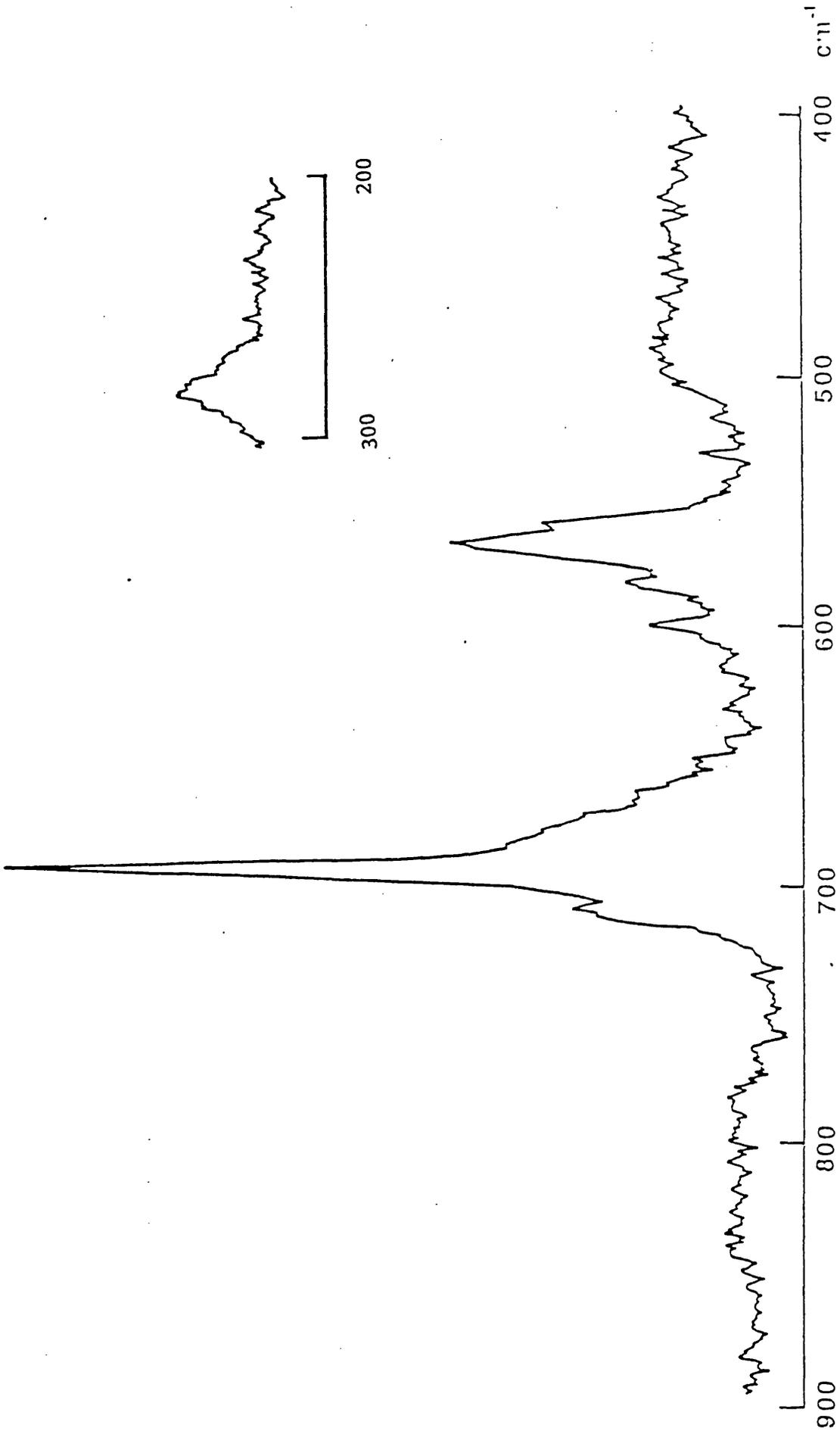
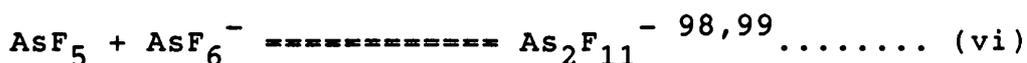


Figure 3.8 The Raman Spectrum of K_2F_7 at -196°C

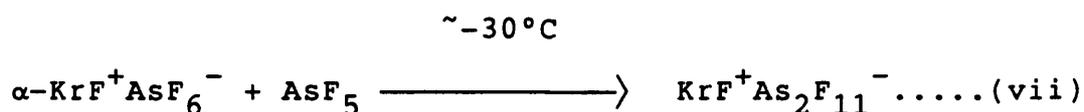
$\text{KrF}^+\text{As}_2\text{F}_{11}^-$ with the addition of KrF_2 .

3.3.2c Discussion :

In the literature the formation of $\text{As}_2\text{F}_{11}^-$ was described as follows :



In the case of the adduct $\text{KrF}^+\text{As}_2\text{F}_{11}^-$, evidence obtained from Raman spectra at various temperatures suggests that $\text{KrF}^+\text{As}_2\text{F}_{11}^-$ is formed by reaction between $\alpha\text{-KrF}^+\text{AsF}_6^-$ and AsF_5 below $\sim -30^\circ\text{C}$ and, at this temperature AsF_5 evaporates to the gas phase leaving solid $\text{KrF}^+\text{As}_2\text{F}_{11}^-$ in the presence of a small quantity of liquid AsF_5 (Figure 3.8). Since the equilibrium mentioned above only exists in solution it may not apply in our system and, indeed the Raman spectrum of the final product showed no evidence of the parent species ($\text{KrF}^+\text{AsF}_6^-$, AsF_5). However, the spectrum showed peaks which could be assigned to $\text{KrF}^+\text{As}_2\text{F}_{11}^-$ by comparison with the Raman spectra of α - and β - $\text{KrF}^+\text{Sb}_2\text{F}_{11}^-$ and with the Raman spectra of $\text{Na}^+\text{As}_2\text{F}_{11}^-$. Therefore the formation of $\text{KrF}^+\text{As}_2\text{F}_{11}^-$ could be described in terms of the reaction :-



3.4 The reaction of α - and β - $\text{KrF}^+\text{Sb}_2\text{F}_{11}^-$ mixture with O_2 gas :

A sample of a mixture of α - and β - $\text{KrF}^+\text{Sb}_2\text{F}_{11}^-$ (~1mmol) was prepared as described in (3.2) in a 6mm FEP reactor. This was kept at -196°C , and (0.3mmol) of O_2 gas was admitted. The Raman spectrum for the sample was recorded at -196°C and it showed no sign of reaction between O_2 and the adduct. When the sample was warmed to 0°C , however, and the Raman spectra for the product was recorded at this temperature complete collapse of the peaks due to α - and β - $\text{KrF}^+\text{Sb}_2\text{F}_{11}^-$ was observed and new peaks were obtained which are in good agreement with the Raman spectrum of $\text{O}_2^+\text{Sb}_2\text{F}_{11}^-$.¹⁰⁰ (Figure 3.9)

This reaction, therefore, shows the powerful oxidative fluorinating ability of KrF^+ -containing adducts even at temperatures below room temperature and it confirms earlier observations.⁷⁰

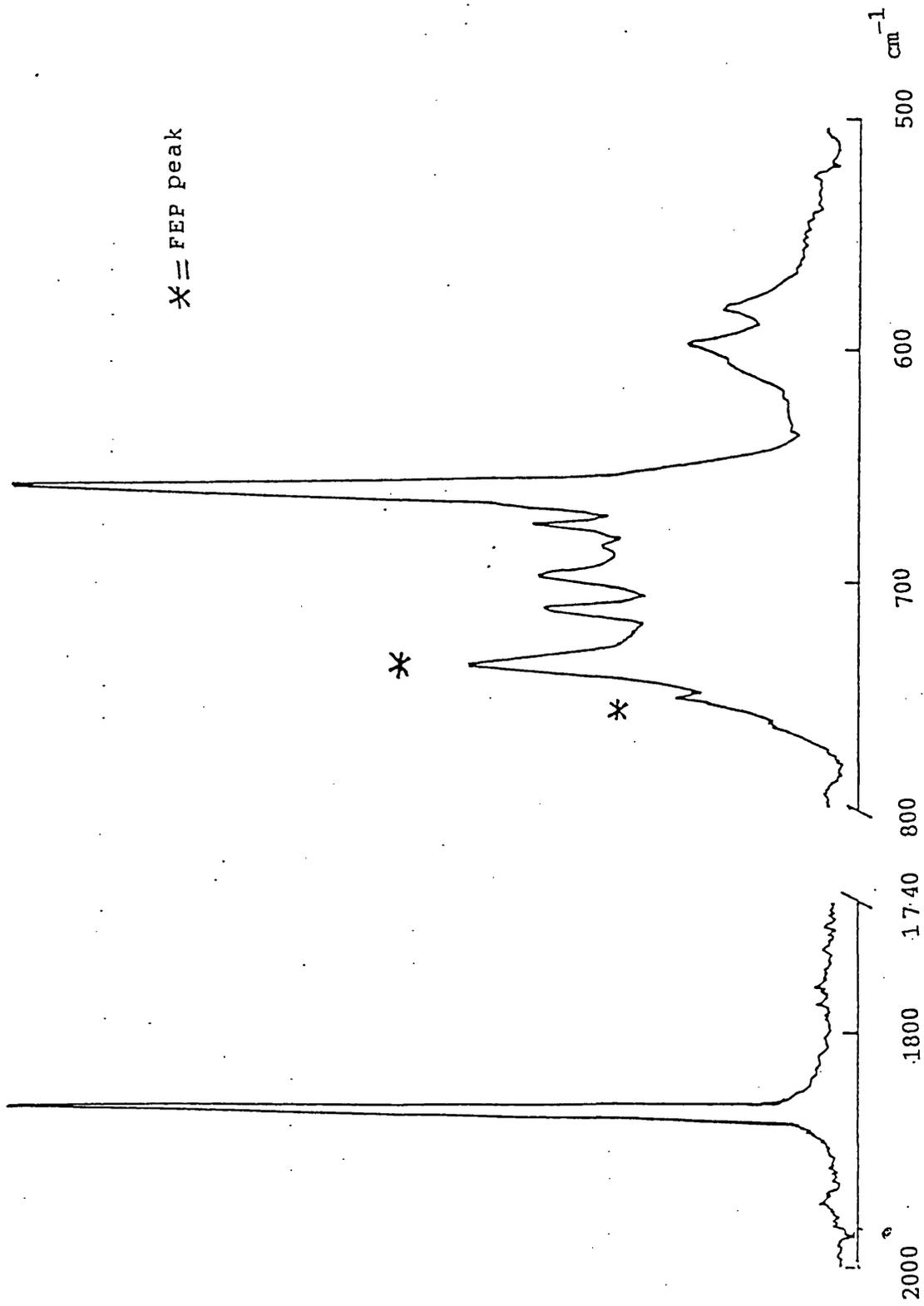


Figure 3.9 The Raman Spectrum of $\text{O}_2^+ \text{Sb}_2\text{F}_{11}^-$

Chapter four

Laser photolysis reactions in liquid fluorine

Chapter four

Laser photolysis reactions in liquid fluorine

4.1 Introduction :

The only report on the use of laser photolysis for inducing reactions of noble gases is that by Hoard and Andrews ¹³ in which they photolysed fluorine in krypton and xenon matrices at -259°C to yield matrix isolated KrF_2 and XeF_2 respectively. In the light of the observation that U.V. photolysis reactions of krypton and xenon dissolved in liquid fluorine at -196°C readily afford the same noble gas fluorides ^{22,101} the following work was carried out in order to see if the range of reactions in liquid fluorine could be extended by the use of more powerful laser radiation.

4.2 Experimental procedure :

All reactions were carried out in pre-fluorinated F.E.P. reactors which were connected to an all-metal vacuum manifold via P.T.F.E. valves. Solid reagents were weighed and loaded into these reactors in an inert-atmosphere dry box, while volatile reagents and fluorine were charged into the reactors at -196°C via a nickel and stainless steel vacuum manifold. Stoichiometries were maintained such that an approximate three-fold excess of fluorine was added as a solvent for the reactions, except for the reactions with

oxygen where 2:1 and 1:1 ratios of $O_2:F_2$ were employed.

In each case, after charging the reactor, the mixture was photolysed at $-196^\circ C$ in an unsilvered Pyrex Dewar vessel for between 30 minutes and 10 hours using the blue 488nm line of a Coherent Radiation Laboratories Model 52 argon ion laser. After photolysis, Raman spectra were recorded for the product dissolved in liquid fluorine, when the product had sufficient solubility, or on the solid product at $-196^\circ C$ after the removal of unreacted fluorine.

4.3 The reactions :

4.3.1a The laser photolysis of a Kr/F_2 mixture at $-196^\circ C$:

Krypton gas (1.5mmol) was condensed into an F.E.P. reactor at $-196^\circ C$, and a three-fold excess of fluorine gas was added at the same temperature. The krypton was partly dissolved in liquid fluorine but some remained undissolved as a white solid. The mixture was subjected to laser irradiation (0.8 - 0.9W) at $-196^\circ C$. As soon as the photolysis was begun the liquid fluorine started to boil because of the heating effect created by the laser beam. After 15 minutes of photolysis the laser power was lowered to 0.3W and the Raman spectrum was recorded for the sample in liquid fluorine. This showed the characteristic peak at 464cm^{-1} for $\alpha\text{-KrF}_2$ (2.3) along with weaker peaks at 466 and 468cm^{-1} (Figure 4.1a). The laser power was increased to 0.8W and photolysis was resumed for a further 15 minutes. When the photolysis ceased the Raman spectra

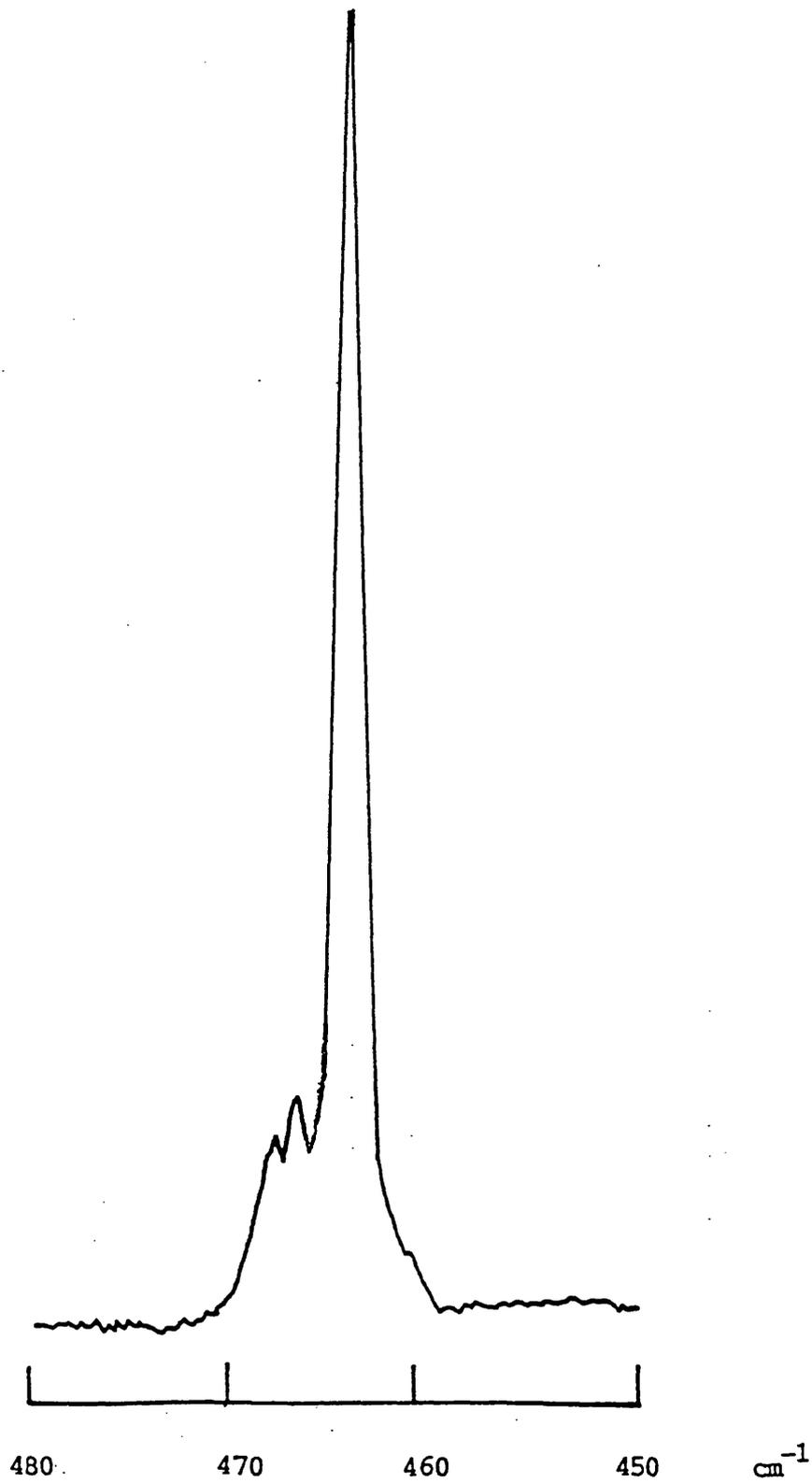


Figure 4.1a The Raman Spectrum of α -KrF₂ in liquid Fluorine at -196°C

was recorded for the product in liquid fluorine and showed the same bands as recorded previously but with a relatively more intense peak at 464cm^{-1} while the intensity of the two peaks at 466 and 468cm^{-1} did not change. The two peaks could be due to either a short lived species such as those illustrated in Figure 4.1b.



Figure 4.1b Some expected short lived species

or they could be due to Fermi resonance, in the sense that some of $\alpha\text{-KrF}_2$ could be dissolved in liquid fluorine. In that case f_{rr} will be expected to increase and may give rise to Fermi resonance. The yield of KrF_2 after 30 minutes of laser photolysis indicated that about 28% of the krypton used had been converted.

4.3.1b The prolonged laser photolysis of KrF_2/F_2 mixture at -196°C ; an attempt to prepare higher fluorides of krypton :

A further (4.5 mmol) of fluorine was added to the KrF_2 sample obtained in the initial photolysis (4.3.1a) at -196°C in the F.E.P. reactor and the mixture was again irradiated with the laser at -196°C for up to 8 hours. When

the irradiation was terminated, a Raman spectrum for the sample was recorded at -196°C in liquid fluorine and showed no change from the $\alpha\text{-KrF}_2$ spectra obtained previously (4.3.1a). This suggests that $\alpha\text{-KrF}_2$ does not react further with liquid fluorine under the conditions described.

4.3.2 The laser photolysis of a Kr/F₂ mixture with IF₅ at -196°C :

At room temperature, KrF_2 reacts with IF_5 or I_2 to produce IF_7 .^{63,67} It is also reported to form the following equilibrium with BrF_5 :



On the other hand XeF_2 is reported to react with IF_5 to produce the adduct $\text{XeF}_2 \cdot \text{IF}_5$,¹⁰² It seemed likely that failure to observe a KrF_2 adduct with IF_5 may be due to the powerful fluorinating ability of KrF_2 at room temperature and that a laser photolysis reaction of a Kr/F_2 mixture with IF_5 at -196°C might offer the possibility of observing a krypton compound analogous to the $\text{XeF}_2 \cdot \text{IF}_5$ adduct at low temperature. The experiment described below was designed to test this idea.

4.3.3a The preparation of a new KrF₂ adduct with IF₅ :

Iodine pentafluoride (4.5mmol) was condensed into an F.E.P. reactor at -196°C , krypton (1.5mmol) and fluorine (4.5mmol) were condensed on top of the IF_5 at the same

temperature to give a ratio of $3\text{IF}_5:1\text{Kr}:3\text{F}_2$. The mixture was subjected to laser photolysis for 1 hour at -196°C , after which the Raman spectrum of the mixture was recorded at -196°C . This showed peaks due to unreacted IF_5 ¹⁰³ together with the characteristic peaks of $\alpha\text{-KrF}_2$ (Figure 4.2). This suggested that IF_5 does not react with either KrF_2 or F_2 at -196°C even when laser photolysis is employed.

The reactor was pumped at -196°C and -183°C to remove unreacted fluorine and krypton respectively, and the sample was warmed to -78°C and the Raman spectrum for it was recorded at this temperature. This showed a number of new peaks in the region between 500 and 700cm^{-1} (Figure 4.3). These new peaks can be attributed to an adduct $\text{KrF}_2 \cdot n\text{IF}_5$ ($n = 1-3$) on the basis of the comparability of the spectrum to that of $\text{CsF} \cdot 3\text{IF}_5$ ¹⁰⁴ (Table 4.1).

4.3.3b The laser photolysis of a IF_5/F_2 mixture at -196°C :

Iodine pentafluoride (1.5mmol) was condensed in an F.E.P. reactor at -78°C and a three fold excess of fluorine was condensed on top at -196°C . The mixture was irradiated with a laser for 8 hours. When the irradiation was stopped a Raman spectrum was recorded at -196°C in liquid fluorine and showed a characteristic spectrum of IF_5 at low temperature¹⁰³ and a peak at 894cm^{-1} due to fluorine.¹⁰⁵ This suggests that IF_5 does not react with fluorine at this temperature when laser photolysis was employed.

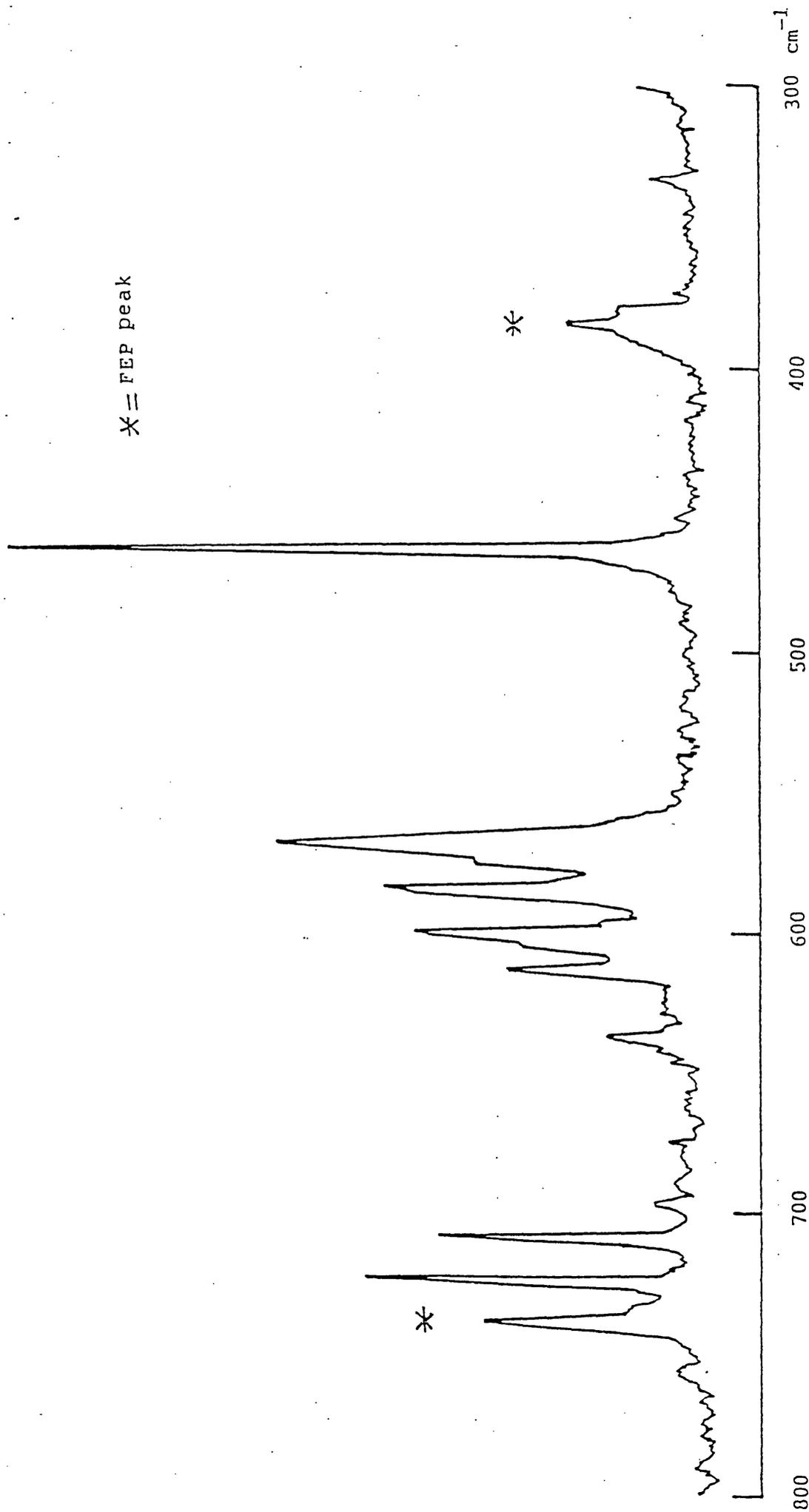


Figure 4.2 The Raman Spectrum of α - KrF_2 with unreacted IF_5 at -196°C

* = FEP peak

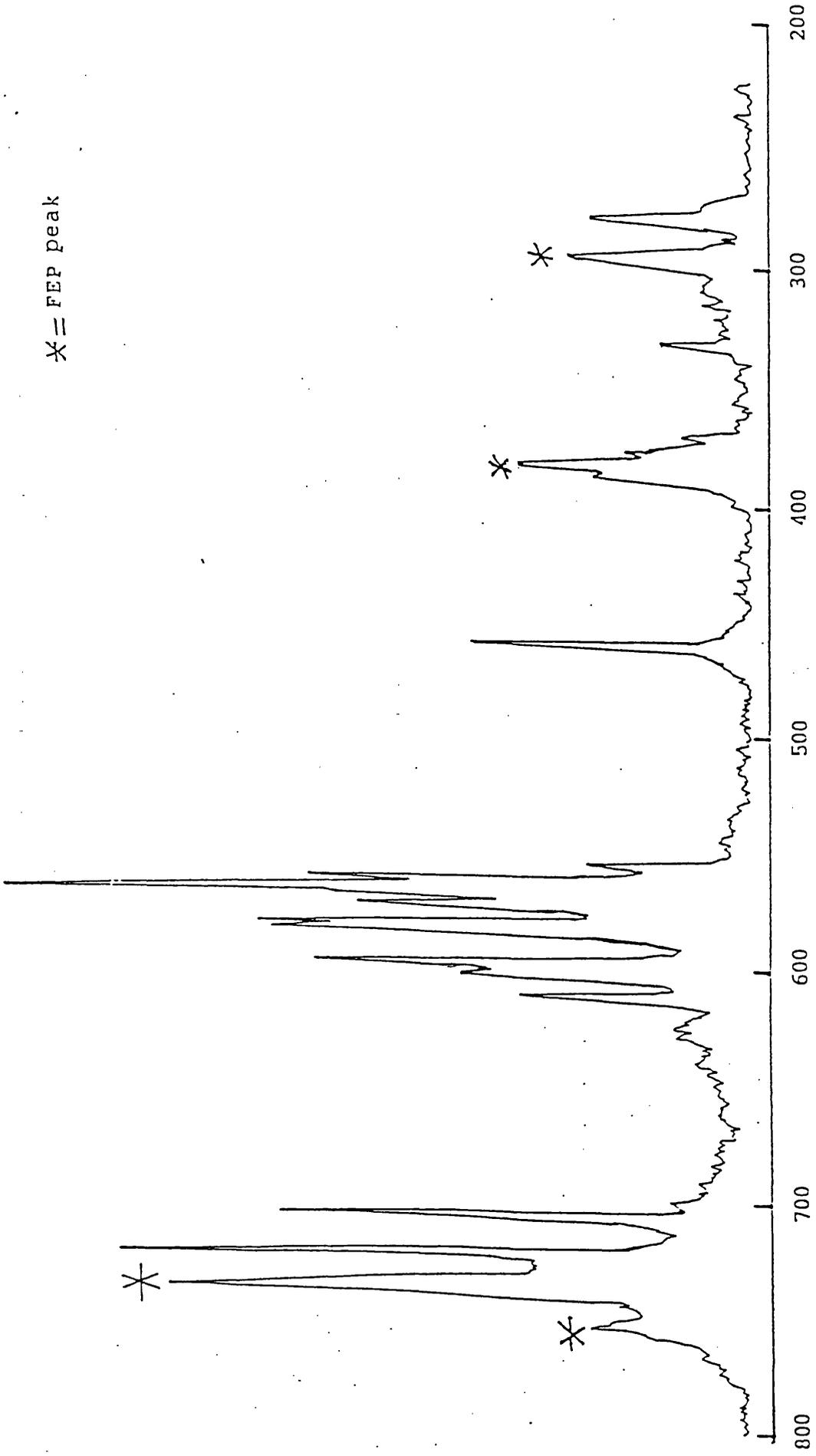


Figure 4.3 The Raman Spectrum of $\text{KrF}_2 \cdot n\text{HF}_5$ ($n=1-3$)

$\text{KrF}_2 \cdot n\text{IF}_5^a$	$\text{CsF} \cdot 3\text{IF}_5$	$\text{XeF}_2 \cdot \text{IF}_5$
		211 (3)
278 (22)	271 (9)	273 (5)
330 (10)		329 (2)
370 (4)	367 (3)	
376 (6)	382 (5)	385 (7)
553 (25)	543 (30)	
559 (51)	557 (2)	
563 (100)		
568 (43)	568 (2)	
578 (58)		578 (80)
582 (57)	585 (sh)	
594 (49)	593 (53)	
610 (33)		607 (85)
640 (5)	635 (3)	
	674 (100)	
709 (57)		691 (81)
720 (80)		
		495 (100) XeF_2
460 (38) KrF_2		

a: n = 1-3

Table 4.1 The Raman Frequencies (cm^{-1}) for $\text{KrF}_2 \cdot n\text{IF}_5$ in comparison with Raman frequencies of $\text{CsF} \cdot 3\text{IF}_5$ and $\text{XeF}_2 \cdot \text{IF}_5$.

4.3.4 The laser photolysis of a Xe/nF₂ mixture at -196°C :

The laser photolysis of a Xe/F₂ mixture was carried out to investigate the possibility of preparing xenon fluorides (XeF₂, XeF₄, XeF₆) in view of the effectiveness of laser irradiation as a means of preparing KrF₂ compared with the more familiar U.V. photolysis method (2.2).

4.3.4a The preparation of XeF₂ using laser photolysis :

Xenon gas (1.5mmol) was condensed into an F.E.P. reactor at -196°C, a two fold excess of fluorine was condensed on top at the same temperature. The xenon was partly dissolved in the liquid fluorine. The mixture was irradiated with laser light for 20 minutes at -196°C. When the photolysis was terminated the sample was pumped at -196°C to remove unreacted fluorine. The Raman spectrum of the solid sample was recorded at -196°C and showed a very intense peak at 499cm⁻¹ which could be attributed to XeF₂.¹⁰⁶ The yield of the XeF₂ produced after 20 minutes was approximately 99% of the xenon gas used.

4.3.4b The laser photolysis of a XeF₂/F₂ mixture at -196°C:

Further fluorine (4.5mmol) was condensed on top of the XeF₂ sample mentioned above (4.3.4a) at -196°C. The mixture was photolysed by the laser for up to 10 hours. When the photolysis ceased, a Raman spectrum of the sample was recorded at -196°C and showed no changes from that obtained for XeF₂ itself. This implies that XeF₂ does not

react with fluorine under the conditions mentioned.

4.3.5 The laser photolysis of an O_2/F_2 mixture at $-196^\circ C$:

Following the initial successes mentioned above, laser photolysis of oxygen/fluorine mixtures at $-196^\circ C$ was studied in order to investigate the possibility of the preparation of oxygen fluorides (O_2F_2 , O_4F_2 , OF_2 , O_2F), and if successful, to examine the sequence of reaction products.

4.3.5a The preparation of O_4F_2 using laser photolysis :

Oxygen (1.5mmol) was condensed into an F.E.P. reactor at $-196^\circ C$, then fluorine (4.5mmol) was condensed on top at the same temperature to afford a green-yellow solution which was irradiated with the laser for 30 minutes at $-196^\circ C$. When the photolysis was terminated, a deep red solid which partly dissolved in liquid fluorine was observed. The deep colour prohibited its characterisation by Raman spectroscopy, however, the E.S.R spectrum of the dilute solution of the deep red product in diamagnetic carbon tetrafluoride, CF_4 , was obtained at $-196^\circ C$ and this showed a broad-band signal with a g value of 2.0034. Upon warming this sample to $-183^\circ C$ for 30 minutes and then re-cooling to $-196^\circ C$ the E.S.R spectrum changed from the single broad-band signal to a sharp doublet with a g value of 2.0059 characteristic of the FOO^* radical.¹⁰⁷ After 10 minutes, the doublet signal collapsed to the same broad-band signal mentioned previously (Figure 4.4), which

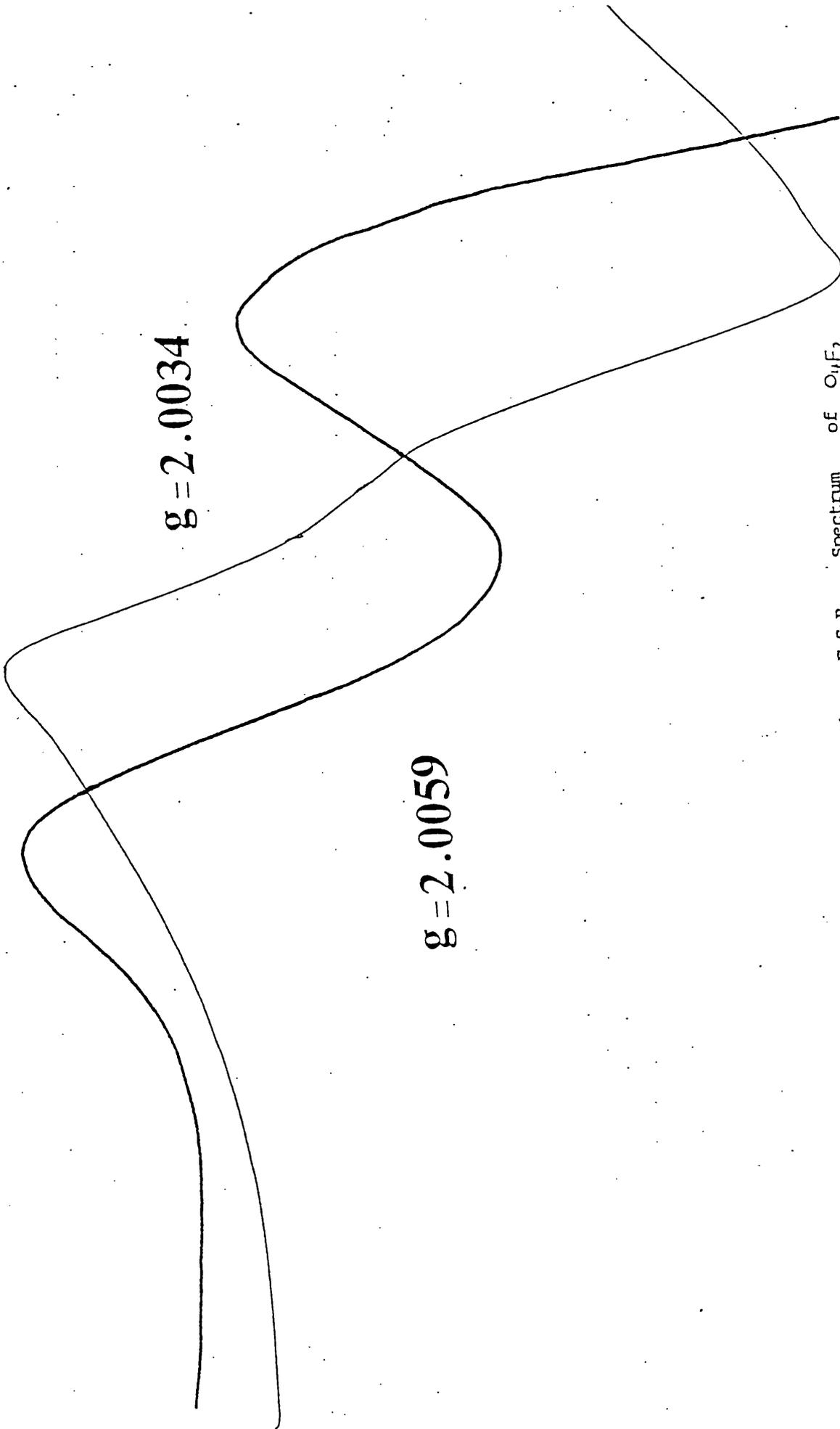


Figure 4.4 The E.S.R. Spectrum of O_1F_2

is characteristic of O_4F_2 .¹⁰⁸

4.3.5b The laser photolysis of an O_4F_2/F_2 mixture at $-196^\circ C$

A sample of O_4F_2 was prepared using laser photolysis of an O_2/F_2 mixture in an F.E.P. reactor at $-196^\circ C$ (4.3.5a). A further quantity (1.6mmol) of fluorine was added to the sample. After charging the reactor, the mixture was irradiated with the laser at $-196^\circ C$ for 8 hours in an unsilvered vessel. When the photolysis was stopped, a yellow solid was obtained in the bottom of the reactor which is insoluble in liquid fluorine. The Raman spectrum of the product was recorded at $-196^\circ C$ in liquid fluorine (Figure 4.5), and showed the characteristic peaks of O_2F_2 ,¹⁰⁹ together with other peaks due to the F.E.P. reactor and elemental fluorine ($892cm^{-1}$) (Table 4.2). Irradiation for a further 8 hours was carried out and the Raman spectrum of the irradiated sample was recorded at $-196^\circ C$. This showed no change from the previously recorded spectra of O_2F_2 , which suggests that liquid fluorine does not react with O_2F_2 under the conditions mentioned.

4.3.6a The laser photolysis of an F_2/Ar mixture at $-196^\circ C$:

Following the results obtained from the U.V. photolysis of an Ar/F_2 mixture at $-196^\circ C$ (2.3), and the relatively high yield of KrF_2 obtained by laser photolysis compared to that obtained by U.V. photolysis, the laser photolysis of Ar/F_2 mixtures at $-196^\circ C$ was investigated in order to provide additional information about the nature

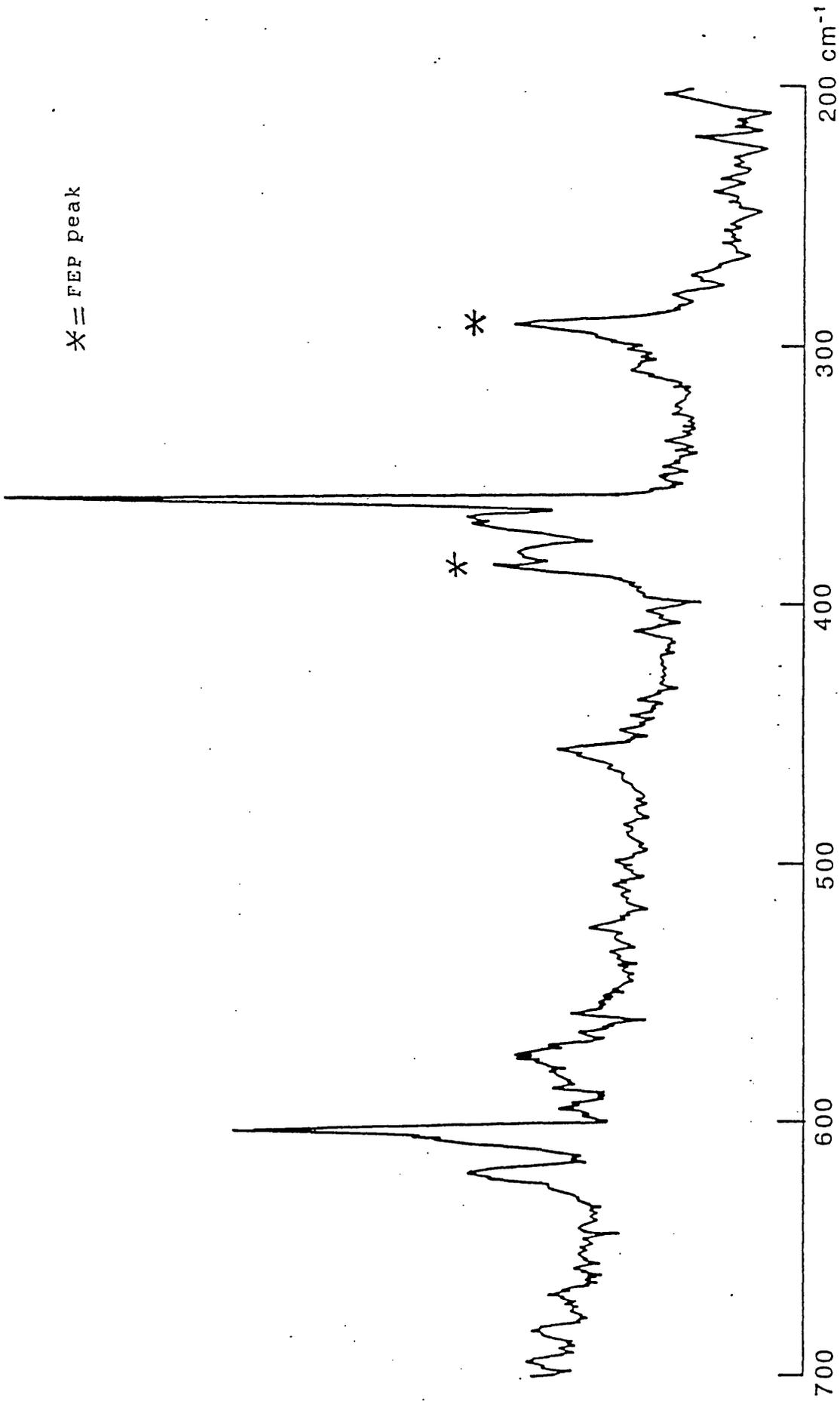


Figure 4.5 The Raman Spectrum of O_2F_2 in liquid Fluorine
at -196°C

cm ⁻¹	Intensity	Assignment
360	(100)	
370	(25)	ν_3
459	(14)	ν_5
607	(57)	ν_1
622	(22)	ν_4
892	F ₂	F ₂

Table 4.2 The Raman Frequencies (cm⁻¹) and Assignments
for O₂F₂

of the Ar/liquid fluorine reaction system.

At -196°C , an F.E.P. reactor was charged with argon (1.6mmol) and fluorine (3.2mmol) respectively, the argon was dissolved in liquid fluorine and the solution was photolysed with a laser at -196°C for up to 8 hours. When the photolysis was terminated, traces of a white solid were obtained. The reactor was pumped at -196°C and -183°C to remove unreacted fluorine and argon respectively and the Raman spectrum of the sample was recorded at -196°C . This showed a peak at 580cm^{-1} which is similar to that obtained in the reaction of argon and fluorine under U.V. irradiation (2.3) which could be due to fluorinated F.E.P. However, the mass spectrum of the decomposed sample showed the presence of the Ar^+ ion, which suggests that argon might be a component of the decomposition products of the white solid, while a positive KI test for the decomposition products suggest the presence of fluorine. These results are similar to those obtained by U.V. photolysis (2.3), and again, support the suggestion of possible formation of an argon containing fluoride.

4.3.6b The laser photolysis of an $\text{SbF}_5/\text{Ar}/\text{F}_2$ mixture at -196°C :

The laser photolysis of a $\text{SbF}_5/\text{Ar}/\text{F}_2$ mixture was carried out in order to investigate the possibility of forming ArF_2 adducts with SbF_5 should the white solid mentioned in 4.3.6a be an argon-fluoride species. If so

then this might be stabilised by reaction with a Lewis acid, such as SbF_5 , in much the same way that KrF_2 is stabilised by the formation of the $\text{KrF}^+\text{SbF}_6^-$ species (3.2).

SbF_5 (0.7 mmol) was condensed into an F.E.P. reactor at -78°C and argon (0.7 mmol) and fluorine (1.5mmol) were condensed on top at -196°C . The mixture was subjected to laser photolysis for 8 hours at -196°C . When the photolysis was terminated, a white solid was obtained. The reactor was pumped at -196°C and -183°C to remove unreacted fluorine and argon respectively. The Raman spectrum of the sample was recorded at -196°C and showed peaks at 673, 718 and 580cm^{-1} along with the characteristic peaks assigned with F.E.P. The peaks at 673 and 718cm^{-1} were attributed to the unreacted SbF_5 ,⁹⁶ and the peak at 580cm^{-1} may be due to fluorinated F.E.P. which always seems to appear with the U.V. or laser photolysis of Ar/F_2 mixtures. When the sample was warmed carefully to -140 , -100 , -80 , -40 and 0°C and the Raman spectrum recorded at each temperature, the spectrum showed no change from that previously recorded. At $\sim -100^\circ\text{C}$ a pressure was observed in the reactor which may suggest that the white solid mentioned in 4.3.6a decomposes without reacting with SbF_5 .

4.3.6c The laser photolysis of an $\text{O}_2/\text{Ar}/\text{F}_2$ mixture at -196°C :

The gases argon, oxygen and fluorine were condensed into an F.E.P. reactor at -196°C in a ratio of 1:0.1:2 respectively. The mixture was irradiated with the laser for

8 hours at -196°C . When the photolysis ceased a white-yellow solid was obtained in the bottom of the reactor. The reactor was pumped at -196°C to remove unreacted fluorine and oxygen and then at -183°C to remove unreacted argon. The Raman spectrum of the sample was recorded at -196°C and it showed a characteristic spectrum for O_2F_2 ,¹⁰⁹ together with an additional unassignable strong peak at 547cm^{-1} which decreased in intensity with time. A peak at 580cm^{-1} was also obtained (Figure 4.6). The sample was then warmed to $\sim -130^{\circ}\text{C}$. At this temperature the white-yellow solid evaporated. When the reactor was re-cooled to -196°C and the Raman spectrum of the yellow solid which condensed was recorded, it showed the previously mentioned spectrum of O_2F_2 along with the peak at 580cm^{-1} . No peak at 547cm^{-1} was obtained which suggests that the material responsible for the peak at 547cm^{-1} does not react with O_2F_2 or O_2 under the conditions mentioned and also that it decomposed.

4.3.7 The laser photolysis of a $\beta\text{-UF}_5/\text{F}_2$ mixture at -196°C

An F.E.P. reactor was pumped to high vacuum (10^{-4}mmHg) and seasoned with elemental fluorine several times and re-evacuated. The reactor was taken to a dry-box and charged with $\beta\text{-UF}_5$ (0.7g, 1.6mmol) and then re-connected to the manifold and re-evacuated. Fluorine (3.2mmol) was condensed into the reactor at -196°C . Solid $\beta\text{-UF}_5$ is partly soluble in liquid fluorine and dissolved to give a light-green solution over a green solid. The

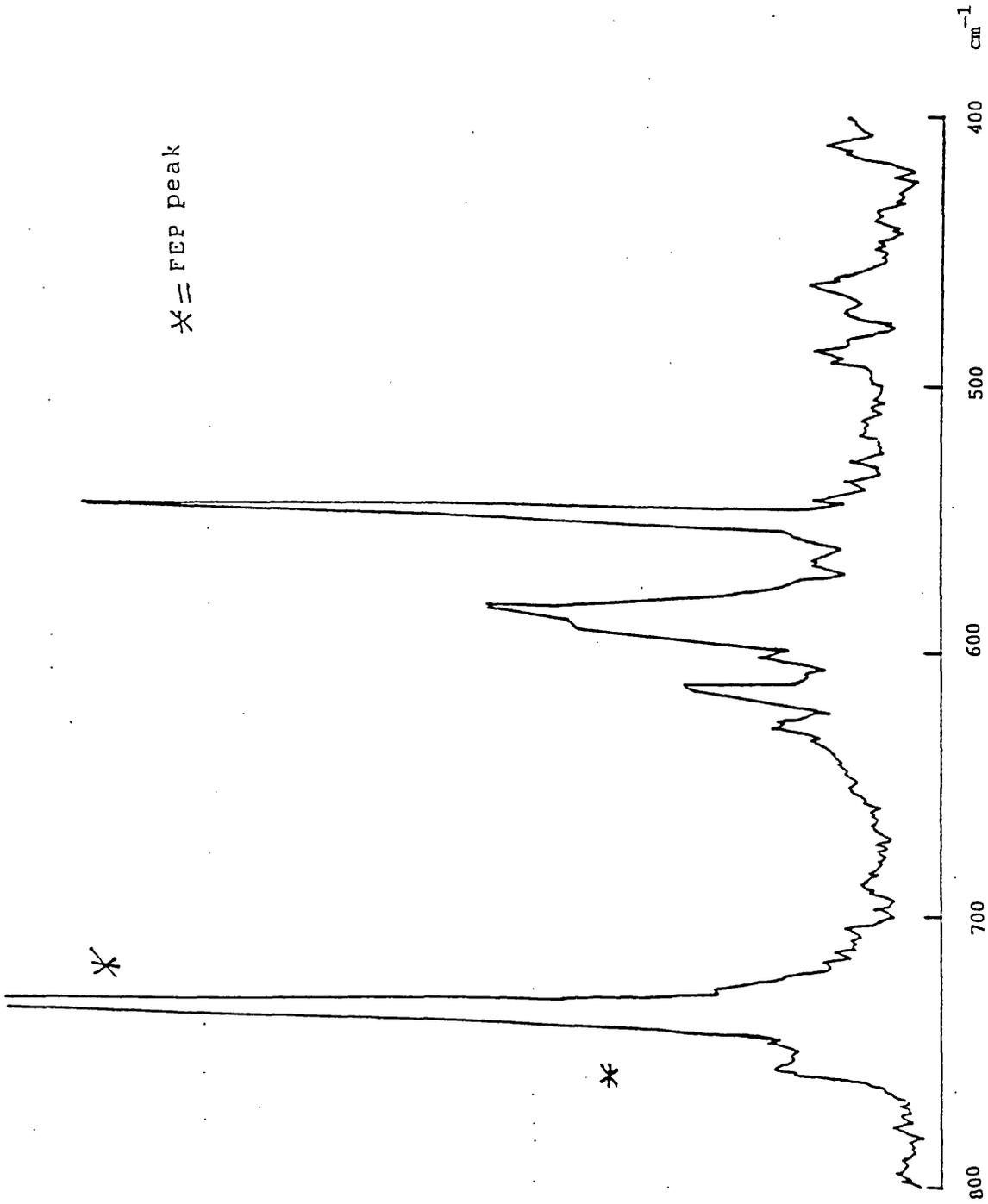


Figure 4.6 The Raman Spectrum of the product of the laser photolysis of $\text{Ar/O}_2/\text{F}_2(\text{r.l.})$ mixture at -196°C

mixture was irradiated with the laser for 30 minutes at -196°C , when the irradiation was terminated, a white solid was obtained. The reactor was pumped at -196°C to remove unreacted fluorine.

The Raman spectrum of the white solid was recorded at $\sim -80^{\circ}\text{C}$ and showed a strong peak at 666cm^{-1} and weaker peaks at 532 and 201cm^{-1} (Figure 4.7), These peaks are comparable to peaks at 667, 533 and 202cm^{-1} obtained from UF_6 .^{110,112}

The mass spectrum for the white product was recorded and showed UF_6^+ , UF_5^+ , UF_4^+ , UF_3^+ , UF_2^+ , UF^+ and U^+ ions confirming the formation of UF_6 .

The UF_6 product may be obtained in 100% (1.6mmol) yield after only 30 minutes of laser photolysis of $\beta\text{-UF}_5$ since all of the product sublimed from the reactor to a can cooled at -196°C .

4.3.8 The laser photolysis of a N_2/F_2 mixture at -196°C :

Fluorine (3.2mmol) and nitrogen (1.6mmol) were condensed respectively into an F.E.P. reactor at -196°C . Two liquid layers were obtained, a colourless one on top which was assumed to be liquid nitrogen and yellow one on the bottom which was thought to be liquid fluorine. By shaking the reactor the two layers were mixed, affording a light yellow solution which, with time, went back to two layers. it appears therefore that liquid fluorine

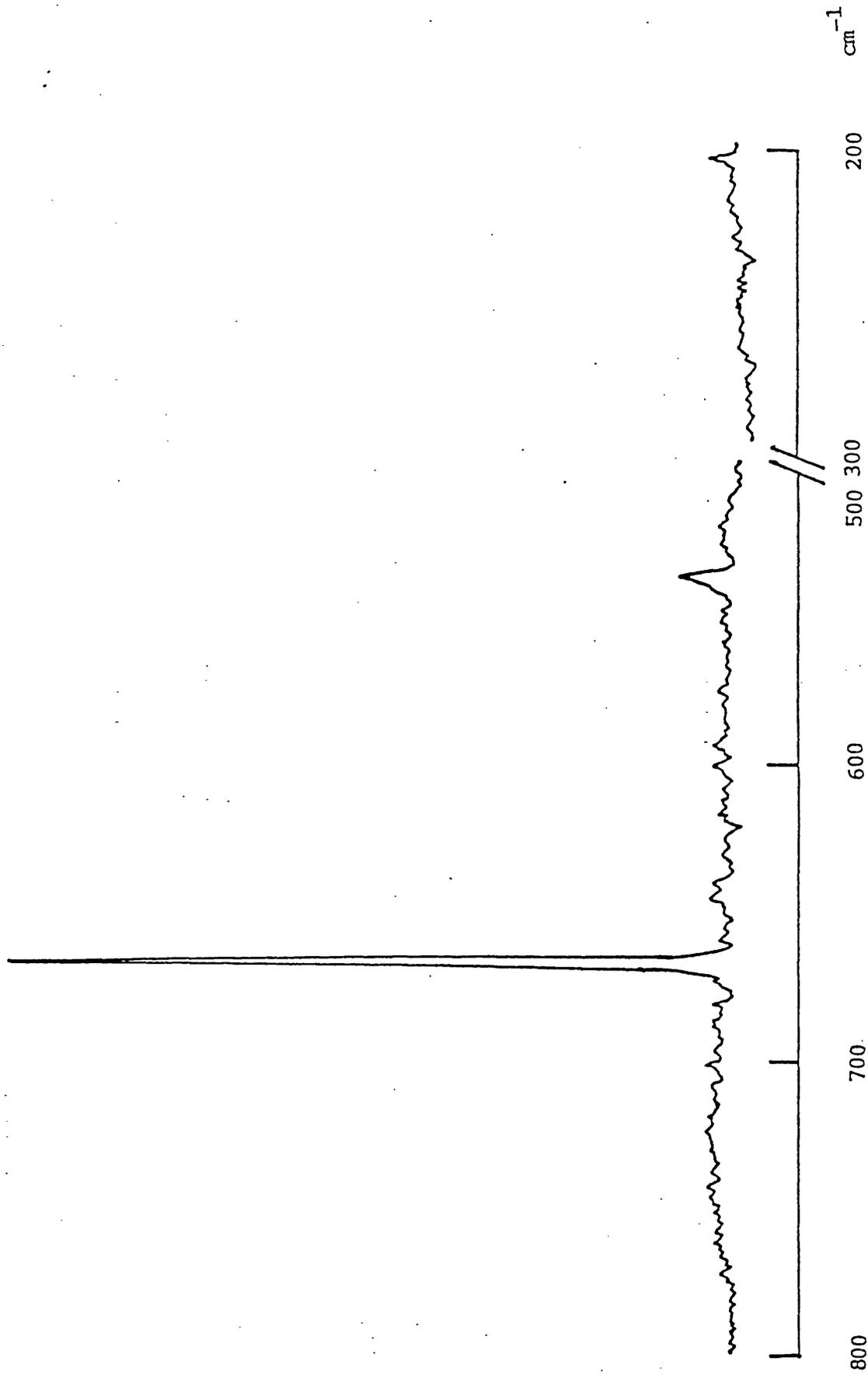


Figure 4.7 The Raman Spectrum of UF_6 at -196°C

does not mix with liquid nitrogen. The two layers of liquid were subjected to laser irradiation for 1, 3 and 8 hours at -196°C with the laser beam positioned at the interface between the two layers. When the irradiation ceased no solid product was obtained, even when ratios of 2:1, 3:1, 1:3 and 1:4 $\text{N}_2:\text{F}_2$ were used. This suggests that liquid fluorine does not react with liquid nitrogen under the conditions outlined.

4.3.9 The laser photolysis of an OsF_6/F_2 mixture at -196°C

The laser photolysis of osmium hexafluoride in liquid fluorine was carried out to investigate the possibility of obtaining higher fluorides of osmium such as OsF_7 or OsF_8 .

OsF_6 (1.5mmol) was condensed into a Pyrex reactor at -196°C . A three fold excess of fluorine was condensed on top at the same temperature. The solid OsF_6 did not dissolve in the liquid fluorine at -196°C . The mixture was photolysed by laser irradiation for up to 8 hours at -196°C and, when the photolysis was ceased the reactor was pumped at -196°C to remove unreacted fluorine. The Raman spectrum of the sample was recorded at -196°C and it showed a strong peak at 734cm^{-1} which is comparable to a peak at 731cm^{-1} reported for OsF_6 .¹¹¹ A small peak at 798cm^{-1} was obtained which could be attributed to the presence of a small amount of SiF_4 ¹⁰⁵ resulting from fluorination of the reactor. The Raman spectrum suggested that osmium hexafluoride does not react with fluorine under the conditions mentioned.

4.3.10a The laser photolysis of a RuF₅/F₂ mixture at -196°C

A dry and fluorinated Pyrex reactor was charged with powdered RuF₅ (1.7mmol) in a dry-box. The reactor was connected to a vacuum manifold and evacuated and a three fold excess of fluorine was condensed into the reactor at -196°C. The RuF₅ did not dissolve in liquid fluorine. The mixture was photolysed using laser irradiation for up to 8 hours. When the photolysis was finished the unreacted fluorine was pumped at -196°C. The Raman spectrum of the residual green solid was recorded at -196°C (Figure 4.8) and showed a spectrum comparable with that for RuF₅,¹¹³ (Table 4.3) which suggests that RuF₅ does not react with fluorine under the conditions mentioned.

4.3.10b The laser photolysis of a Kr/F₂/RuF₅ mixture at -196°C :

A Pyrex reactor was charged with RuF₅ in the same way as that described earlier (4.3.10a). Krypton (1.6mmol) and fluorine (3.2mmol) were condensed into the reactor at -196°C, the mixture was irradiated with the laser at -196°C for one hour, when the photolysis ceased the reactor was pumped at -196°C and -183°C to remove unreacted fluorine and krypton respectively. The Raman spectrum of the sample was recorded at -196°C and showed a peak at 464cm⁻¹ due to α-KrF₂ along with the peaks due to unreacted RuF₅.¹¹³ The mixture was warmed to different temperatures up to room temperature, and the Raman spectrum was recorded at each temperature. The spectra showed no changes from the

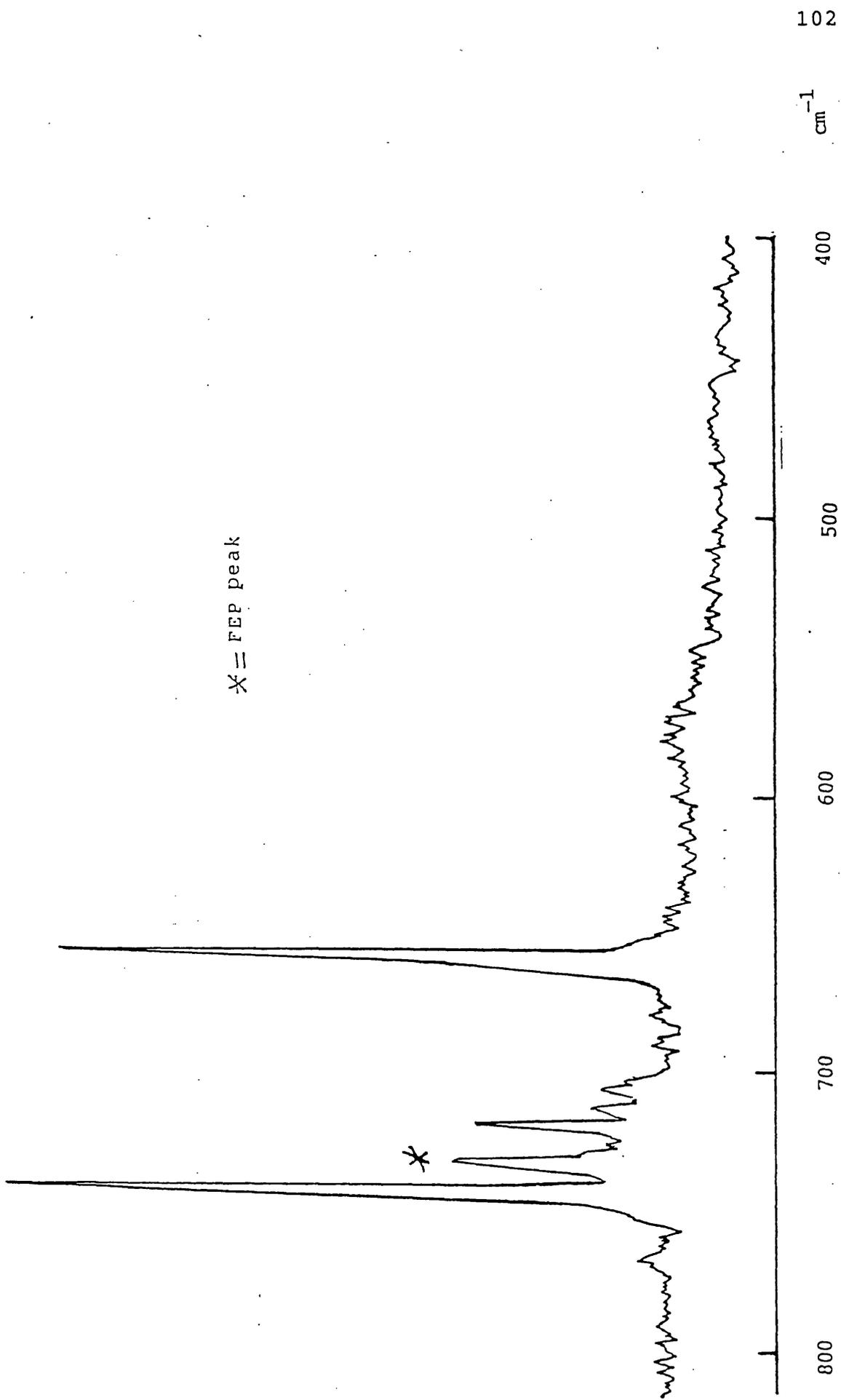


Figure 4.8 The Raman Spectrum of RuF₅

RuF_5		NbF_5^{96}	
Raman	I.R	Raman	I.R
Observed			
664 (91)	515 s,br	656 m	514
706 (8)	580 m,br	668 w	661
714 (11)	655 m	716 vs	688
728 (25)	705 s	752 w	
748 (100)	735 m,sh	766vvs	734

Table 4.3 The Raman and I.R frequencies of RuF_5 and NbF_5

spectra mentioned previously. However, at $\sim -30^\circ\text{C}$ the single peak for $\alpha\text{-KrF}_2$ changed to two weak peaks due to formation of $\beta\text{-KrF}_2$ (2.3). At $\sim -20^\circ\text{C}$ the two peaks due to $\beta\text{-KrF}_2$ decrease in intensity and at R.T the two peaks disappeared. Apart from the phase change for KrF_2 , the Raman spectrum for RuF_5 did not change from the one obtained previously which suggests that KrF_2 does not react with RuF_5 under the conditions mentioned. However, since XeF_2 reacts with RuF_5 to form adducts like $\text{XeF}^+\text{RuF}_6^-$, $\text{XeF}^+\text{Ru}_2\text{F}_{11}^-$ and $\text{Xe}_2\text{F}_3^+\text{RuF}_6^-$ ^{114,115} at room temperature, it seems likely that KrF_2 might behave similarly under these conditions.

4.3.11 The laser photolysis of a CsF/F₂ mixture at -196°C

The laser photolysis of a CsF/F_2 mixture was conducted to investigate the possibility of obtaining higher fluorides of caesium such as " CsF_3 ".

A Pyrex reactor was pumped to high vacuum with periodic heating to remove moisture and was seasoned with elemental fluorine several times and re-evacuated. The reactor was charged with CsF powder in a dry box and was re-connected to the vacuum manifold and re-evacuated. A two fold excess of fluorine was condensed into the reactor at -196°C . The CsF did not dissolve in the liquid fluorine. The mixture was irradiated with the laser for up to 8 hours. A Raman spectrum of the irradiated sample was recorded in liquid fluorine at -196°C and showed a strong peak at 892cm^{-1} which can be assigned to fluorine. The spectrum also exhibited an unassignable peak at 347cm^{-1} and

a weaker peak at 354cm^{-1} , which is comparable to the peak at 353cm^{-1} reported for CsF^{116}

After the unreacted fluorine was removed from the reactor by pumping at -196°C , the Raman spectrum of the solid at -196°C was recorded and showed only the peaks at 347 and 354cm^{-1} (Figure 4.9). The sample was warmed to -140°C for 10 minutes and re-cooled to -196°C and the Raman spectra was again recorded at -196°C and showed a weak peak at 354cm^{-1} . No peak at 347cm^{-1} was observed. When the reactor was connected to the line, a small pressure (14mmHg) was observed at -196°C . The Raman data may suggest that CsF reacts with liquid fluorine at -196°C under laser irradiation and the Raman peak at 347cm^{-1} may possibly be due to a higher caesium fluoride than CsF which decomposes at $\sim -140^\circ\text{C}$. However, it would be reasonable to expect that, were CsF_3 to be formed the Cs-F bond stretching frequency would be lower than that of the observed unexplained band (347cm^{-1}). The origin of the absorption at 347cm^{-1} , therefore, is not clearly accounted for.

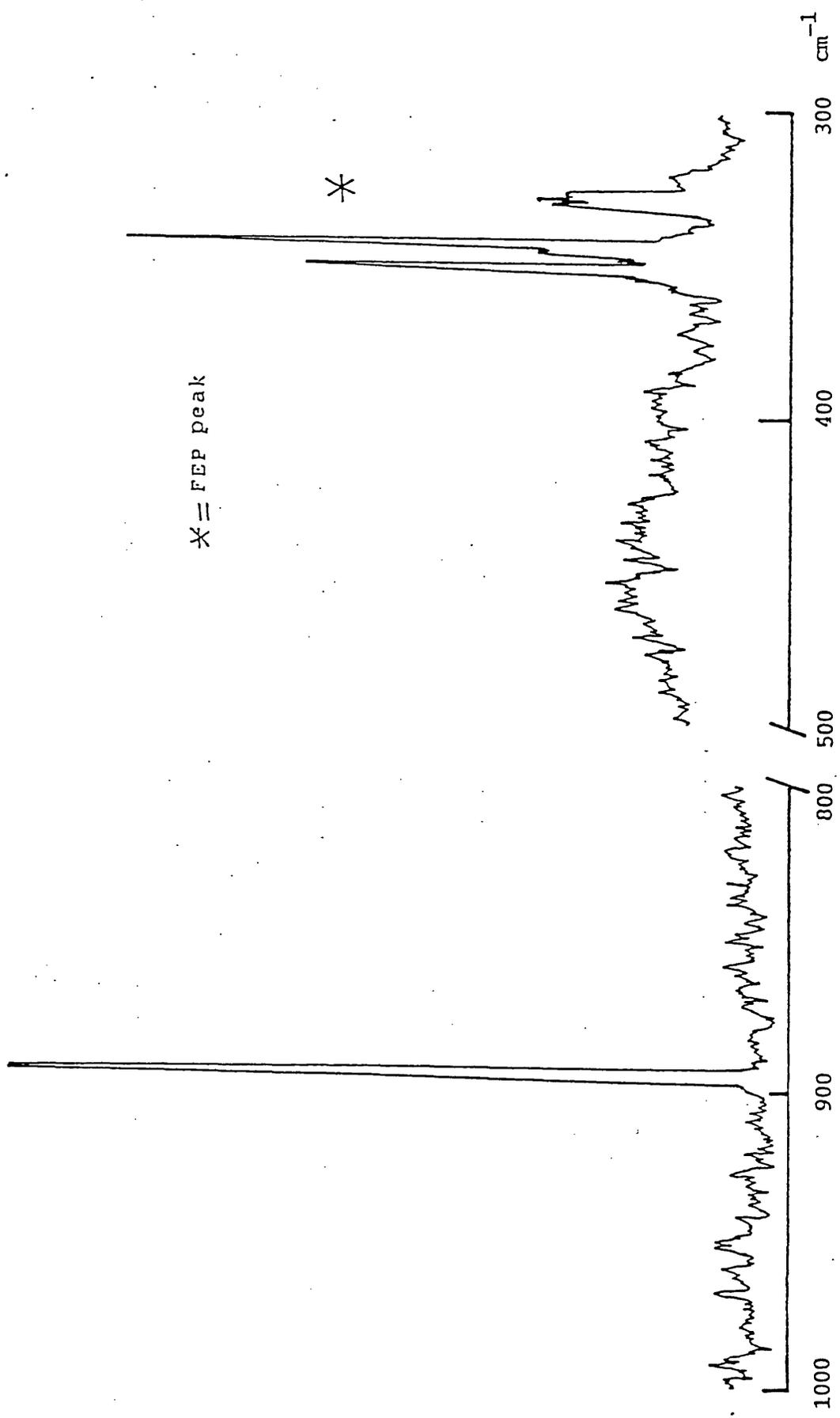


Figure 4.9 The Raman Spectrum of the product of the laser photolysis of CsF in Liquid Fluorine at -196°C

4.4 Discussion

The absorption spectrum of fluorine indicates that photolysis at 488 nm will readily cleave the F-F bond, and so it is expected that all the reactions described in this chapter involve fluorine radicals. However, reactions appear only to occur when the substrate is dissolved in liquid fluorine. The compounds IF_5 , RuF_5 , OsF_6 and O_2F_2 apparently have virtually no solubility in liquid fluorine at -196°C and we observe no evidence of fluorination occurring. On the other hand, O_2 , O_4F_2 , Kr, Xe and $\beta\text{-UF}_5$ are all soluble in liquid fluorine and undergo oxidative fluorination reactions very rapidly under laser photolysis. Substrate solubility is clearly not the only significant criterion for reaction since KrF_2 , XeF_2 , N_2 and Ar are all partially soluble in liquid fluorine but do not undergo oxidative fluorination under laser photolysis at -196°C . In the case of KrF_2 , XeF_2 , and N_2 this may be due to a kinetic effect resulting from the very low reaction temperature. The stability of XeF_4 , XeF_6 , N_2F_2 and N_2F_4 at room temperature certainly supports this. For argon we observe a small amount of turbidity during the photolysis which may be due to the formation of transient ArF_2 . However, the predicted limited thermodynamic stability of ArF_2 ¹¹⁷ may preclude its isolation at -196°C .

4.5 Conclusion

Laser photolysis gives rise to oxidative fluorination of some reagents dissolved in liquid fluorine. However, the technique, as described, has little applicability for reagents insoluble in liquid fluorine at -196°C .

Chapter five

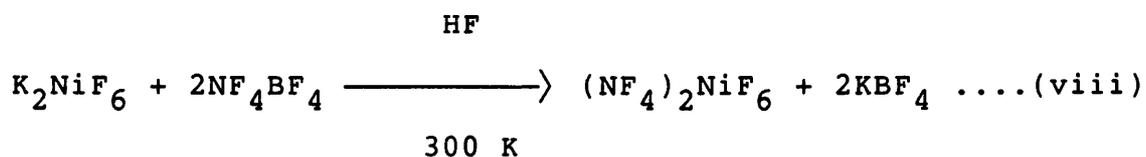
Preliminary work on the use of the "hot wire" method for producing fluorine atoms for reaction

Chapter five

Preliminary work on the use of the "hot wire" method for producing fluorine atoms for reaction

5.1 Introduction :

By the beginning of 1970 preparative fluorine chemistry had reached a stage when further achievements seemed hardly probable, especially in the field of synthesis of new high-valent forms of chemical elements. The classic method of synthesis using molecular fluorine seemed practically exhausted and incapable of yielding less stable compounds such as KrF_2 , O_2F_2 , NiF_3 and PdF_6 . even at very high temperatures and pressures, and with large excesses of fluorine. At that time, the exchange method for the synthesis of complex fluorine-containing species in non-aqueous solvents,¹¹⁸ for example (equation viii):



also had very limited possibilities because of technological difficulties and the difficulty of obtaining substances of high purity. This created a need for the development of new low-temperature methods of chemical synthesis of fluorine-containing compounds, which might

give the possibility of obtaining thermodynamically and thermally unstable compounds under mild conditions.

By 1976, a number of methods had been developed to prepare thermally unstable compounds such as O_2F_2 and KrF_2 , using low-temperature, non-equilibrium methods such as electrical discharge, ionization and U.V. photolysis to generate atomic fluorine^{19,22,23}. Thermally generated atomic fluorine was not used because molecular fluorine is not significantly dissociated until 500 - 600°C is reached. At such temperatures thermally unstable compounds could not exist. However, in 1976, Soviet workers reported the preparation of KrF_2 using catalytic-thermal generation of atomic fluorine from molecular fluorine.²³ The required non-equilibrium conditions in the reaction system using thermally generated atomic fluorine were attained by creating separated zones for the dissociation of molecular fluorine and the low-temperature reaction of the atomic fluorine so produced. The transfer of atomic fluorine to the reaction zone was provided by diffusion.

Russian workers demonstrated the new synthetic method by using it to prepare KrF_2 . The preparation of KrF_2 was carried out in a reactor whose walls were cooled with liquid nitrogen (-196°C) (Figure 5.1), and coated with solid krypton. Atomic fluorine was generated by heating the surface of a nickel catalyst within the reactor at 600 - 700°C. It was claimed that KrF_2 could be prepared at a rate of 6g/h using this method.²³

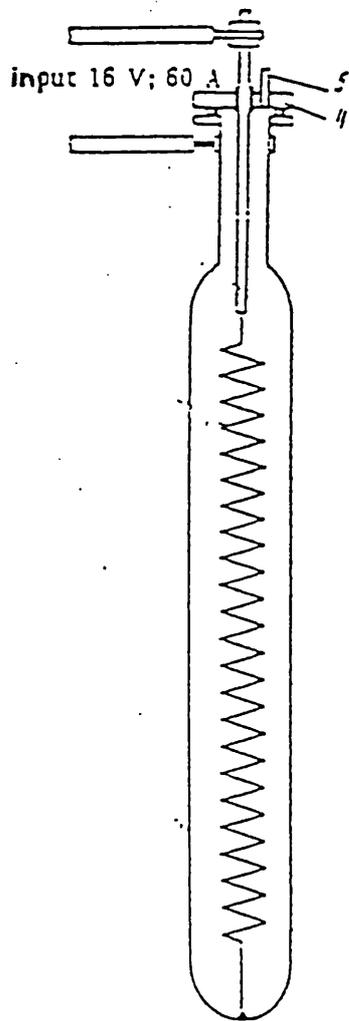


Figure 5.1 The Hot Wire Reactor (Soviet Design)

An unrefereed Russian review claims to have used this low-temperature method not only to synthesise KrF_2 but also for reactions of atomic fluorine with nitrogen oxides (NO , NO_2), halogen fluorides (ClF , ClF_3 , IF_5) and some compounds of transition elements (ReF_6 , OsF_6). These reactions were reported to be studied under similar conditions to those for the synthesis of krypton difluoride and it was claimed that the products of the reactions are higher fluorides of the appropriate elements (NOF_3 , NO_2F , ClF_5 , IF_7 , ReF_7 , OsF_7).¹²⁰ Part of this work was repeated in this chapter unsuccessfully (see 5.4.2). Recently, American workers have reported an improved design (Figure 5.2) of the Soviet Hot Wire reactor with the ability to produce KrF_2 in an average yield of 1.5g/h.¹¹⁹ In 1990, the same laboratory reported the preparation of XeF_6 from reaction between fluorine and xenon in a 20:1 ratio.¹²¹

The following work was carried out to investigate the use of the Hot Wire method and the possibility of extending its use by attempting to prepare either existing thermally unstable compounds such as (O_2F_2 and N_2F_2), and by trying to produce theoretical compounds such as ArF_2 or OsF_8 .

5.2 Reactor designs :

In this work two reactor designs were tried, one in Pyrex and one in stainless steel.

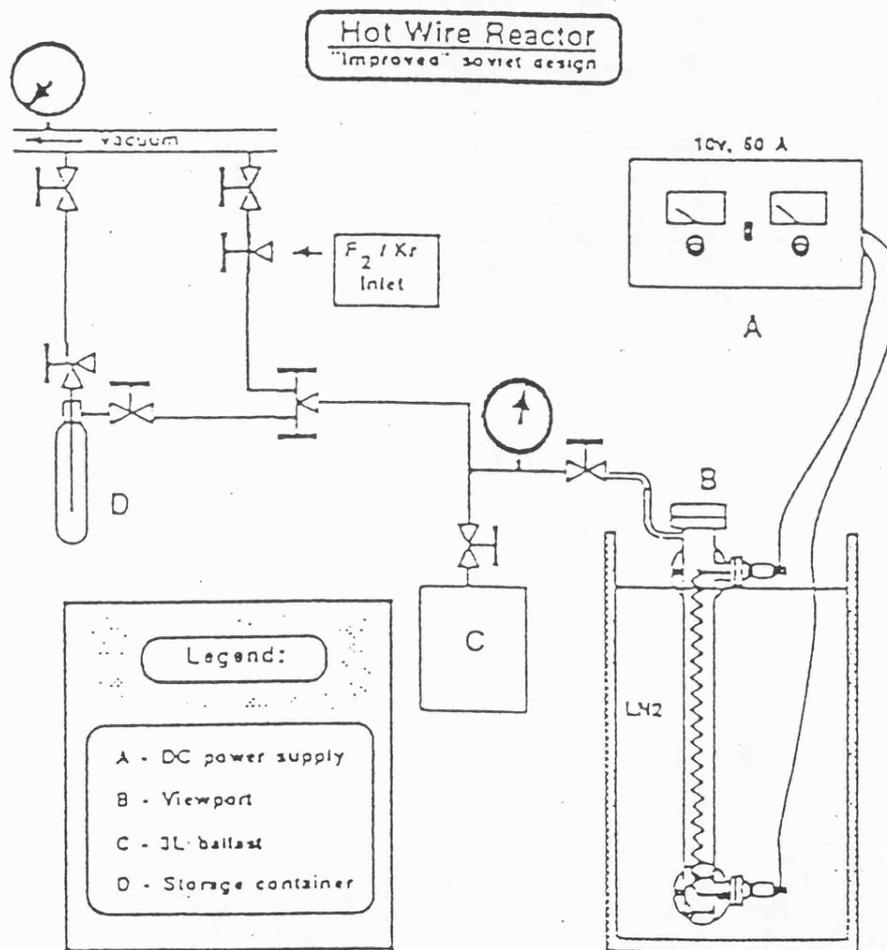


Figure 5.2 The Hot Wire Reactor (American Design)

5.2.1 The Pyrex reactor :

A Pyrex reactor was produced as shown in (Figure 5.3). The volume of the vessel was 372cm^3 . The top was fitted with a Young greaseless valve and a central Quickfit joint (B24) into which was inserted a nickel coiled wire heater. A seal was formed between the reactor body and the heater by a B24 Quickfit socket sealed with Kel-F grease. To improve thermal contact and increase surface area ten undulations or ribs were formed on the side of the reactor. On the bottom of the reactor a $3/8$ " diameter break-seal vessel was connected to collect the product and allow Raman spectroscopic and E.S.R analysis of the products. The distance between the wire and the inner walls was 1.5 - 2.5cm.

5.2.2 The metal reactor :

A stainless steel reactor was produced as shown in (Figure 5.4). The volume of the vessel was 500cm^3 . The top was fitted with a Hoke valve and a central Quickfit stainless steel joint (B24) into which was inserted the nickel coiled wire heater. A seal was formed by a B24 Quickfit socket sealed with Kel-F grease. To improve thermal contact, fins were welded to the outside wall of reactor. A $1/4$ " diameter break-seal vessel was connected to the bottom of the reactor by a glass to metal seal in

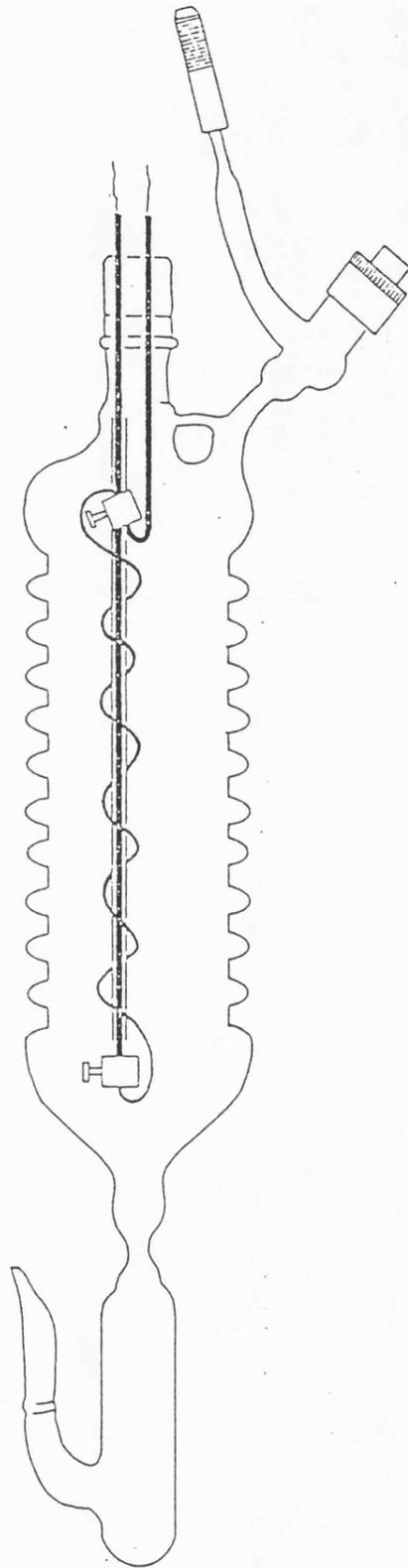


Figure 5.3 The Glass Reactor

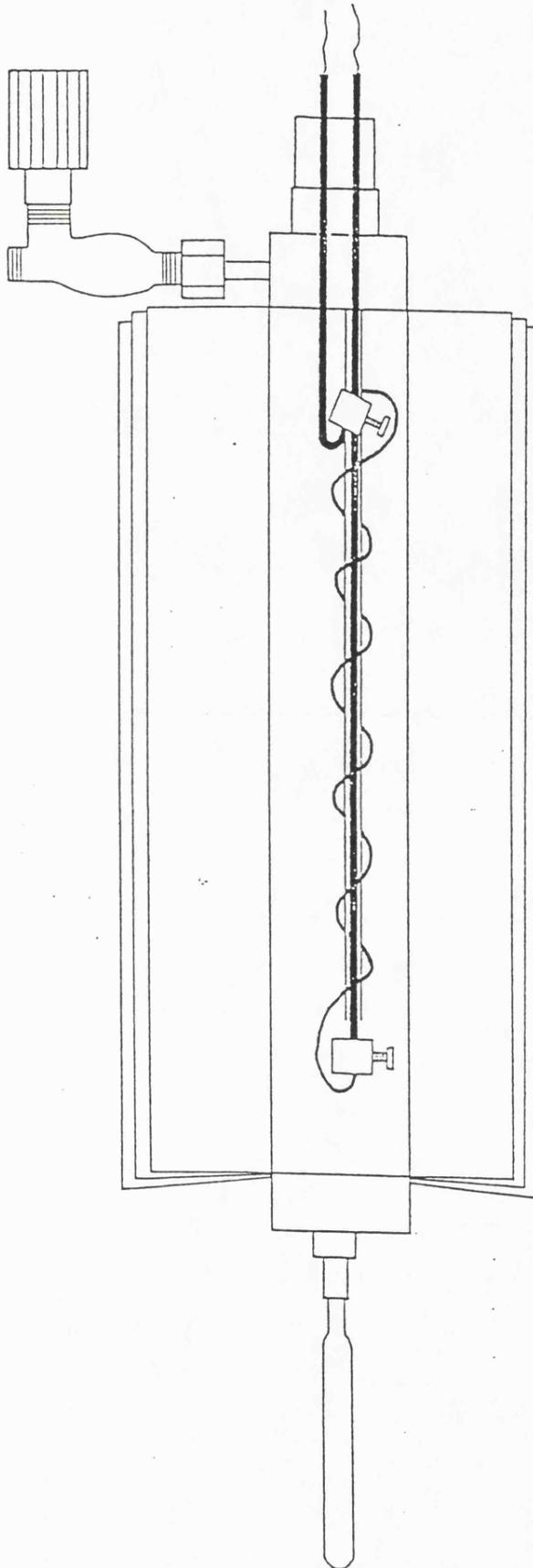


Figure 5.4 The Metal Reactor

order to collect the products and allow Raman spectroscopic analysis and E.S.R analysis of the products to be carried out. The distance between the wire and the inner walls was 2cm. In both the Pyrex and the metal reactors the filament was heated to ~ 700°C by a d.c. power supply.

5.3 The reactions (glass reactor) :

5.3.1 Attempts to prepare KrF_2 :

The glass reactor was pumped to high vacuum (10^{-4} mmHg) for several hours and was then filled with 240mmHg of elemental fluorine. The reactor was cooled to -196°C and the wire was heated to 700°C for 30 minutes to ensure that the reactor was fully fluorinated. The reactor was pumped free of fluorine and then warmed to room temperature and pumped to high vacuum before use.

At -196°C , krypton gas (15 mmol) was condensed onto the walls of the reactor in 5mmol aliquots to ensure that the krypton was evenly distributed along the complete length of the reactor as a thin coating. A two fold excess of fluorine was then introduced in batches (5mmol per batch). Following the addition of the krypton and fluorine the power was turned on and the wire was heated to 700°C for one hour. After this time the power was turned off and the reactor was pumped at -196°C to remove unreacted fluorine. The liquid nitrogen Dewar was then lowered to the level of the collection tube vessel at the bottom and

the reactor was allowed to warm up so that the product could be sublimed to the bottom of the reactor. A large amount of white solid was obtained in the break-seal vessel.

A Raman spectrum of the solid was recorded at -196°C and it showed a single peak at 799cm^{-1} which is comparable to that at 800cm^{-1} reported for SiF_4 .¹²² No peak was obtained for KrF_2 .

The experiment was repeated three times with the same results. The failure of the method to produce the intended KrF_2 when the Pyrex reactor was used is likely to be because most of the atomic fluorine produced attacked the material of the reactor instead of reacting with krypton. The use of a glass reactor was therefore shown to be inappropriate and a metal reactor similar to the American one was built.

5.4 The reactions (metal reactor) :

5.4.1 The preparation of KrF_2 :

The metal reactor was pumped to high vacuum (10^{-4} mmHg) for several hours and then it was filled with 300 mmHg of elemental fluorine and the wire heated to 700°C for 30 minutes and re-evacuated. This process was repeated three times. Krypton gas (15 mmol) was condensed onto the walls of the reactor at -196°C in 5 mmol aliquots to ensure that the krypton was evenly distributed along the length

of the reactor as a thin coating. A two fold excess of fluorine was introduced in batches (5mmol per batch). Following the addition of the krypton and fluorine the power was turned on and the wire was heated to 700°C for one hour.

When the time was up the power was turned off and the reactor was pumped at -196°C to remove unreacted fluorine and the liquid nitrogen Dewar was lowered to allow the body of the reactor to warm up. However, the bottom of the reactor was kept cold so that the product could be sublimed to the bottom of the reactor. A white solid was obtained in the break-seal vessel. Before closure the vessel was warmed to -78°C to remove unreacted krypton.

A Raman spectrum of the white solid was recorded at -196°C and it showed a strong peak at 464cm^{-1} which is comparable to that at 462.6cm^{-1} reported for KrF_2 ²⁸ ($\alpha\text{-KrF}_2$, see 2.3), and also showed a weak peak at 799cm^{-1} due to SiF_4 .¹²²

5.4.2 Attempt to prepare " KrF_4 " :

After pumping the reactor to high vacuum (while keeping the bottom of the reactor cooled at -196°C) , the prepared sample of KrF_2 (5.4.1) was sublimed onto the walls of the reactor by cooling the body of the reactor to -78°C by forming a jacket of dry ice around the reactor's fins and warming the break-seal vessel containing the KrF_2

to room temperature. When all the KrF_2 sample was sublimed onto the walls the dry ice jacket was removed and the reactor was cooled quickly to -196°C . The power was then turned on and the nickel wire was heated to 700°C . Fluorine (15mmol) was introduced into the reactor in batches (5mmol per batch) over one hour.

When the time was up, the power was turned off and the body of the reactor was tapped to knock down any thermally unstable product (KrF_4 ?) as the liquid nitrogen Dewar was lowered. This resulted in the product falling and subliming to the bottom of the reactor. A white solid was obtained in the collection vessel at the bottom of the reactor.

A Raman spectrum of the product was recorded at -196°C and it showed a strong peak at 464cm^{-1} which can be assigned to $\alpha\text{-KrF}_2$ and a weaker peak at 799cm^{-1} which could be attributed to SiF_4 .¹²² This presumably formed by attack of fluorine on the quartz insulation tube on the nickel wire. No other peaks were obtained which suggests that atomic fluorine does not react with KrF_2 under the conditions used.

5.4.3 The synthesis of XeF_2 :

After seasoning the reactor with elemental fluorine as in 5.4.1 xenon (15 mmol) was condensed onto the walls of the reactor at -196°C in 5mmol aliquots as for the krypton difluoride synthesis and the same experimental

procedure was adopted. After one hour the power was turned off and the reactor was pumped at -196°C to remove unreacted fluorine. The product of the reaction was collected as a white solid as in the case of the krypton reaction. A Raman spectrum of the solid was recorded at -196°C and it showed a sharp peak at 499cm^{-1} which is comparable with that reported for XeF_2 .¹⁰⁶

5.4.4 The synthesis of XeF_4 :

Xenon (15mmol) was condensed onto the walls of the reactor at -196°C in 5mmol aliquots as in experiments described above. The wire was again brought up to operating temperature and a four-fold excess of fluorine was introduced into the reactor in batches (5mmol per batch) over two hours. After the power was turned off the reactor was pumped at -196°C to remove unreacted fluorine. The liquid nitrogen Dewar was lowered and the white solid product was collected as in the earlier experiments.

A Raman spectrum of the solid was recorded at -196°C and showed sharp peaks at 499, 504, 545 and a weaker peak at 444cm^{-1} (Figure 5.5) . The peak at 499cm^{-1} is due to XeF_2 , while the peaks at 444, 504 and 545cm^{-1} can be assigned to XeF_4 .¹²³

5.4.5 Attempts to prepare XeF_6 :

In an effort to prepare xenon hexafluoride the XeF_4 experiment (5.4.4) was repeated but with a ten-fold excess

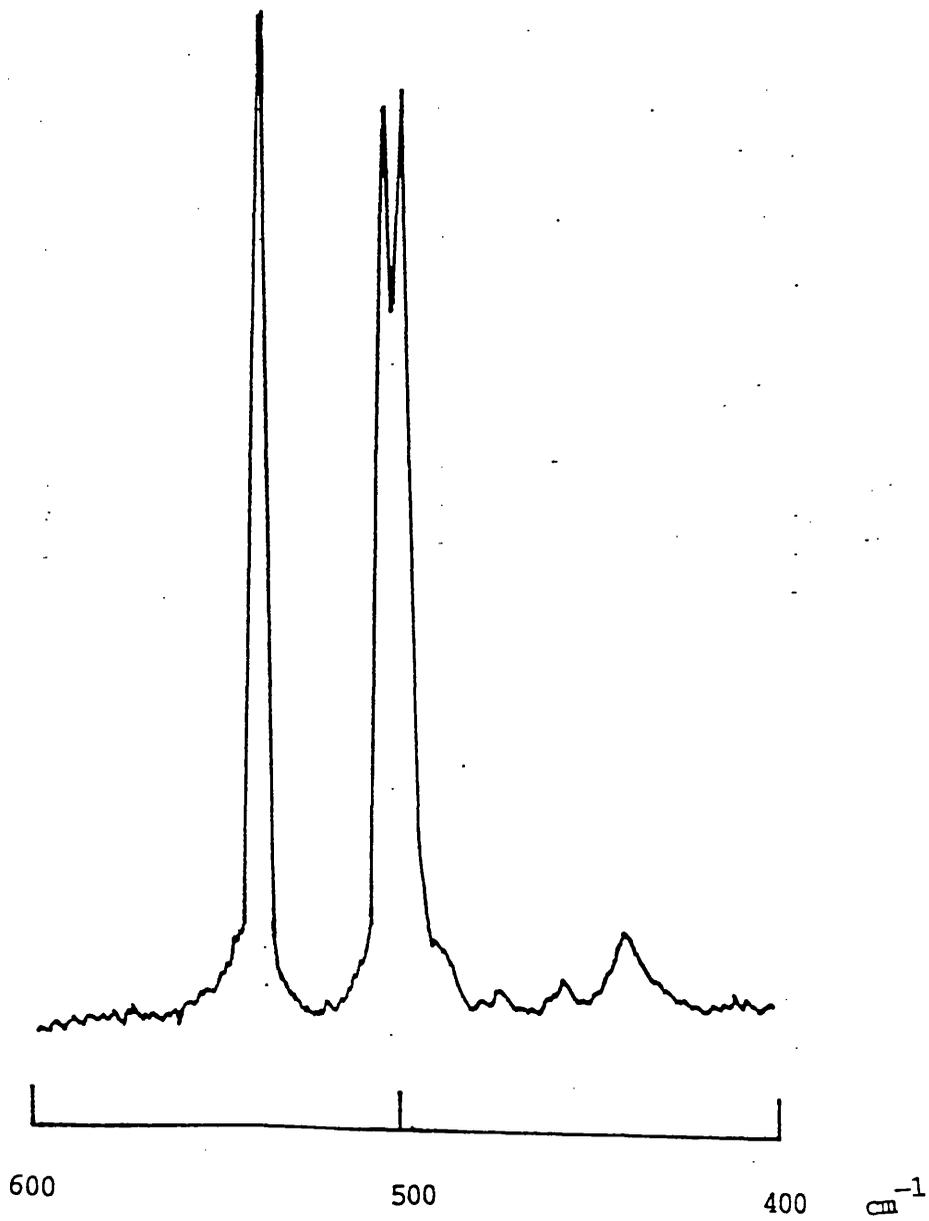


Figure 5.5 The Raman Spectrum of XeF₄/XeF₂ mixture at -78°C

of fluorine introduced over three hours. A Raman spectrum of the sample obtained was recorded at -196°C and it showed a sharp peak at 633cm^{-1} and a weaker peak at 440cm^{-1} (Figure 5.6) which are both unassignable at this point. A peak at 799cm^{-1} was also observed which is due to SiF_4 .¹²² No other peaks were obtained. When the sample was allowed to warm to $\sim -45^{\circ}\text{C}$ it changed to a colourless liquid with a vapour pressure of $\sim 110\text{mmHg}$. No satisfactory explanation for the above observations has been produced so far and the experiment clearly deserves closer examination. Unfortunately, lack of time has prevented further study but it may well be that XeF_6 and/or XeF_4 is produced and that this may have reacted with components of the reactor on warming. The peak at 633cm^{-1} is in the correct region for an XeF_3^+ cation.

5.4.6 Attempts to prepare " ArF_2 " :

Following the successes outlined above, the reaction between argon and fluorine was investigated in the belief that argon fluoride compounds such as ArF_2 might be produced.

Argon (10mmol) was condensed onto the walls of the reactor at -196°C in 5mmol aliquots as for the krypton and xenon experiments and a three-fold excess of fluorine was introduced into the reactor in batches (5mmol per batch) over two hours. Similar collection procedures were adopted as described previously and a white solid product was obtained in the collection vessel. A Raman spectrum of the

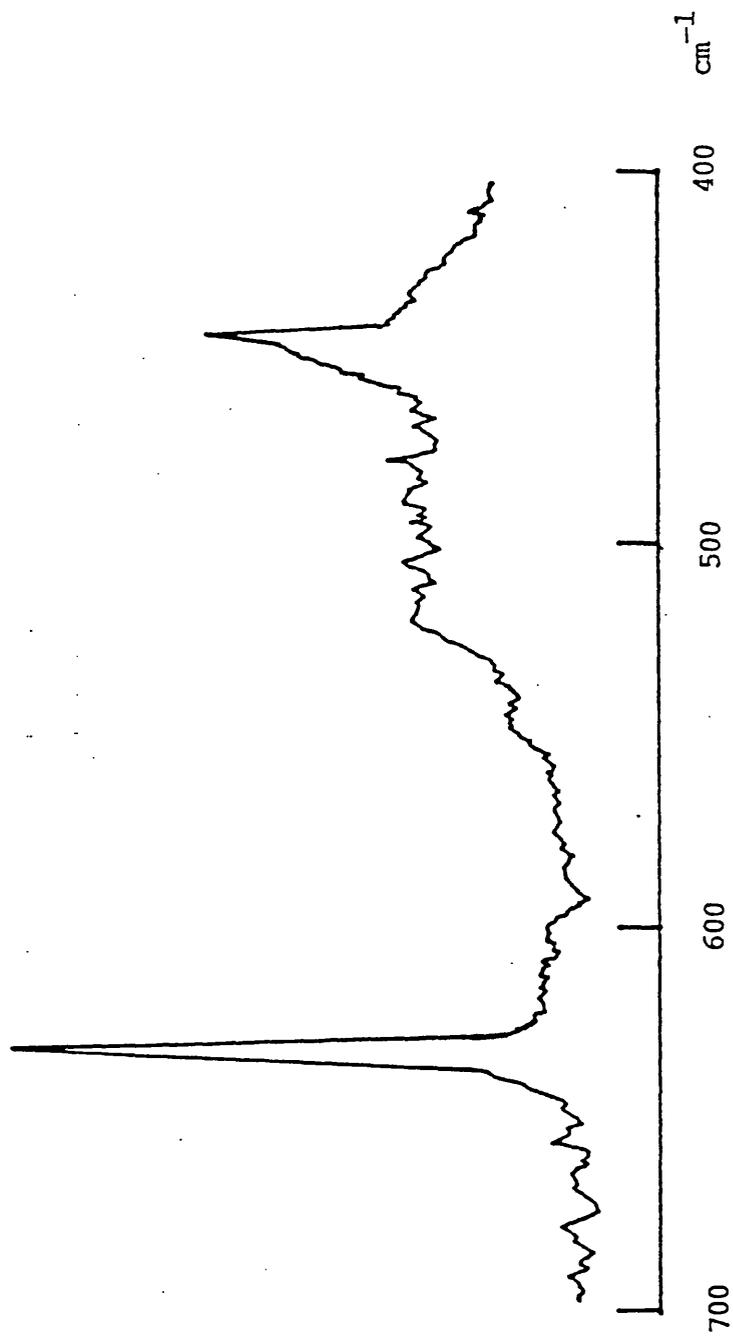


Figure 5.6 The Raman Spectrum of the product of the hot wire reaction between xenon and five fold excess of fluorine at -196°C

white solid was recorded at -196°C and this showed a single peak at 799cm^{-1} due to SiF_4 ¹²² This is almost certainly a result of reaction between atomic fluorine and the quartz insulation tube on the wire heating element. No other peaks were obtained which suggests that atomic fluorine does not react with argon under the conditions used.

5.4.7 The hot wire reaction between OsF_6 and F_2 :

In an attempt to prepare higher fluorides of osmium such as OsF_7 or OsF_8 an attempt was made to induce reaction between OsF_6 and F_2 using the hot wire method.

Osmium hexafluoride (10mmol) was condensed onto the walls of the reactor at -196°C in 5mmol aliquots to ensure that the compound was evenly distributed along the complete length of the reactor as a thin coating. the power was turned on and the wire was heated to 700°C . A two-fold excess of fluorine was introduced into the reactor in batches (5mmol per batch) over one hour. After this time, the power was turned off and the reactor was pumped to remove unreacted fluorine. The liquid nitrogen Dewar was lowered gradually to the bottom of the reactor to allow the product to sublime to the collection vessel at the bottom of the reactor. A yellow solid was obtained.

The Raman spectrum of the sample was recorded at -196°C and it showed a single sharp peak at 733cm^{-1} which

was due to unreacted OsF_6 .¹¹¹ This result is not in accord with the work published by Soviet workers in which they claimed to have prepared OsF_7 using the hot wire method.¹²⁰

5.5 Discussion :

The hot wire method is an effective method for thermal production of atomic fluorine. It was found that in order to produce KrF_2 , XeF_2 and XeF_4 the reactor should be very-well fluorinated and a large excess of fluorine should be used.

Chapter six

Attempts to prepare a (Xe-I) containing species

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6.1 Introduction :

In addition to the xenon fluorine bond, xenon also forms bonds with oxygen, nitrogen and carbon,¹²⁴ and most interestingly it can also form a bond with another xenon atom as in the cation Xe_2^+ in the adduct $\text{Xe}_2^+\text{Sb}_2\text{F}_{11}^-$.^{125,126}

The adduct $\text{Xe}_2^+\text{Sb}_2\text{F}_{11}^-$ is the principal product of the reaction of xenon gas with xenon (II) in antimony pentafluoride solution. The bright green paramagnetic ion is characterised by its Raman, U.V-visible and E.S.R. spectra, and it has been shown to be formed as an intermediate product in reactions of elemental xenon with dioxygenyl salts.^{125,126}

The dioxenon cation, Xe_2^+ , is isoelectronic with XeI , and therefore, a reaction between a $\text{Xe}_2^+\text{Sb}_2\text{F}_{11}^-/\text{XeF}^+\text{Sb}_2\text{F}_{11}^-$ mixture and I_2 was investigated to test the possibility of forming XeI or an XeI adduct.

6.2 The preparation of $\text{XeF}^+\text{Sb}_2\text{F}_{11}^-$:

XeF_2 was prepared by photolysis of a F_2/Xe mixture at room temperature in a Pyrex bulb by a method similar to

that reported earlier.¹²⁷ A sample of XeF_2 (0.05g, 0.3mmol) was transferred to a quartz U.V. cell at -78°C and a three fold excess of SbF_5 was condensed on top. The mixture was warmed up to room temperature and, within a few minutes, a green solution was formed which contained a pale yellow solid, the unreacted SbF_5 was removed carefully by transferring it to a Pyrex vessel cooled to -78°C .

The Raman spectrum of the solid was recorded at room temperature and showed the characteristic spectrum for $\text{XeF}^+\text{Sb}_2\text{F}_{11}^-$ (Figure 6.1).¹²⁸ A single peak at 289nm was observed in the U.V-visible spectrum for a solution of the yellow solid in SbF_5 which is comparable to that at 287nm reported for $\text{XeF}^+\text{Sb}_2\text{F}_{11}^-$ (Figure 6.2).¹²⁶

6.3 The preparation of $\text{Xe}_2^+\text{Sb}_2\text{F}_{11}^-$:

A pressure of 1 atmosphere of xenon gas was added to a sample of $\text{XeF}^+\text{Sb}_2\text{F}_{11}^-$ in the presence of traces of SbF_5 for 40 minutes in a quartz U.V. cell at room temperature. After this time the yellow colour of the $\text{XeF}^+\text{Sb}_2\text{F}_{11}^-$ had changed gradually to give a bright yellow-green colour. The U.V-visible spectrum of the product was recorded at room temperature and showed peaks at 336 and 710 nm (Figure 6.3), along with a peak at 289 nm which was observed earlier for $\text{XeF}^+\text{Sb}_2\text{F}_{11}^-$. The peaks at 336 and 710 nm are comparable to peaks reported for the Xe_2^+ cation.^{125,126} The spectrum suggests, therefore, that the product was a mixture of $\text{Xe}_2^+\text{Sb}_2\text{F}_{11}^-$ and $\text{XeF}^+\text{Sb}_2\text{F}_{11}^-$.

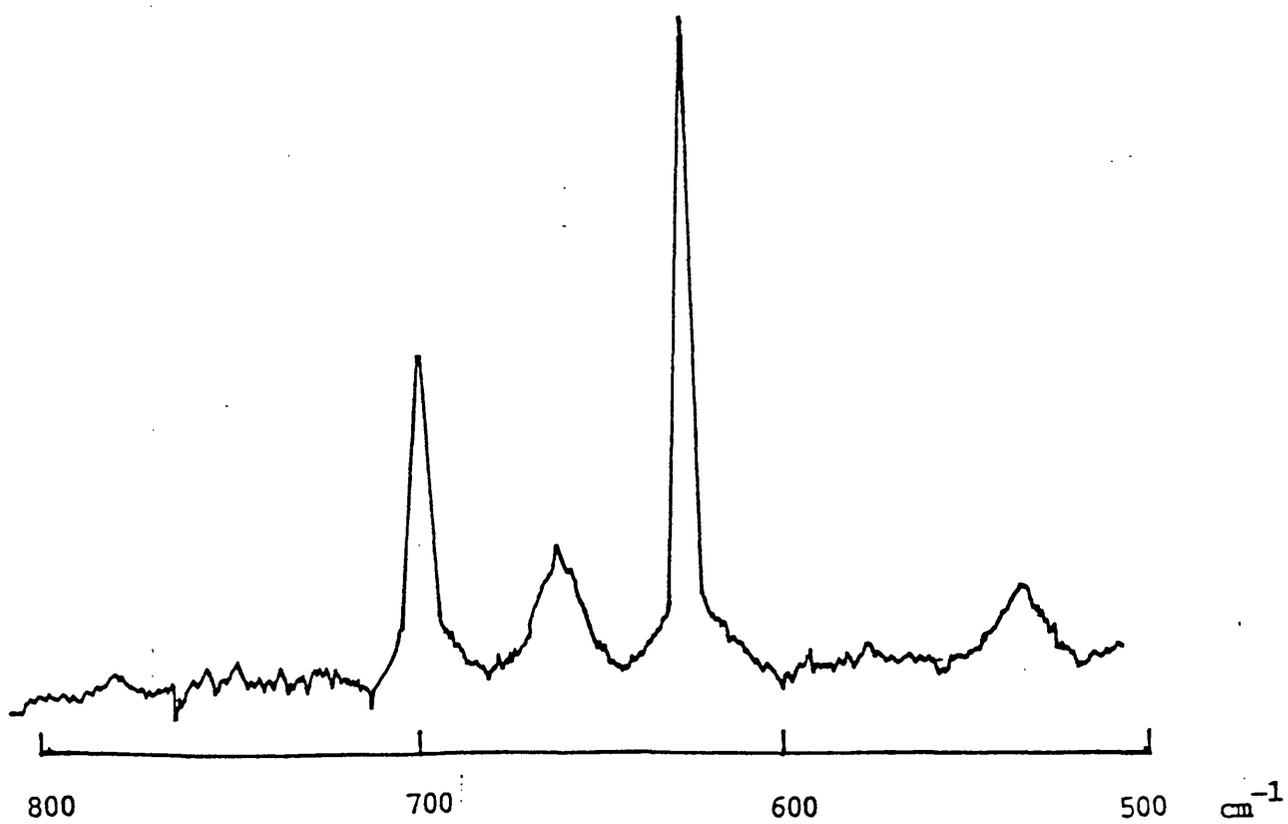


Figure 6.1 The Raman Spectrum of $\text{XeF}^+\text{Sb}_2\text{F}_{11}^-$

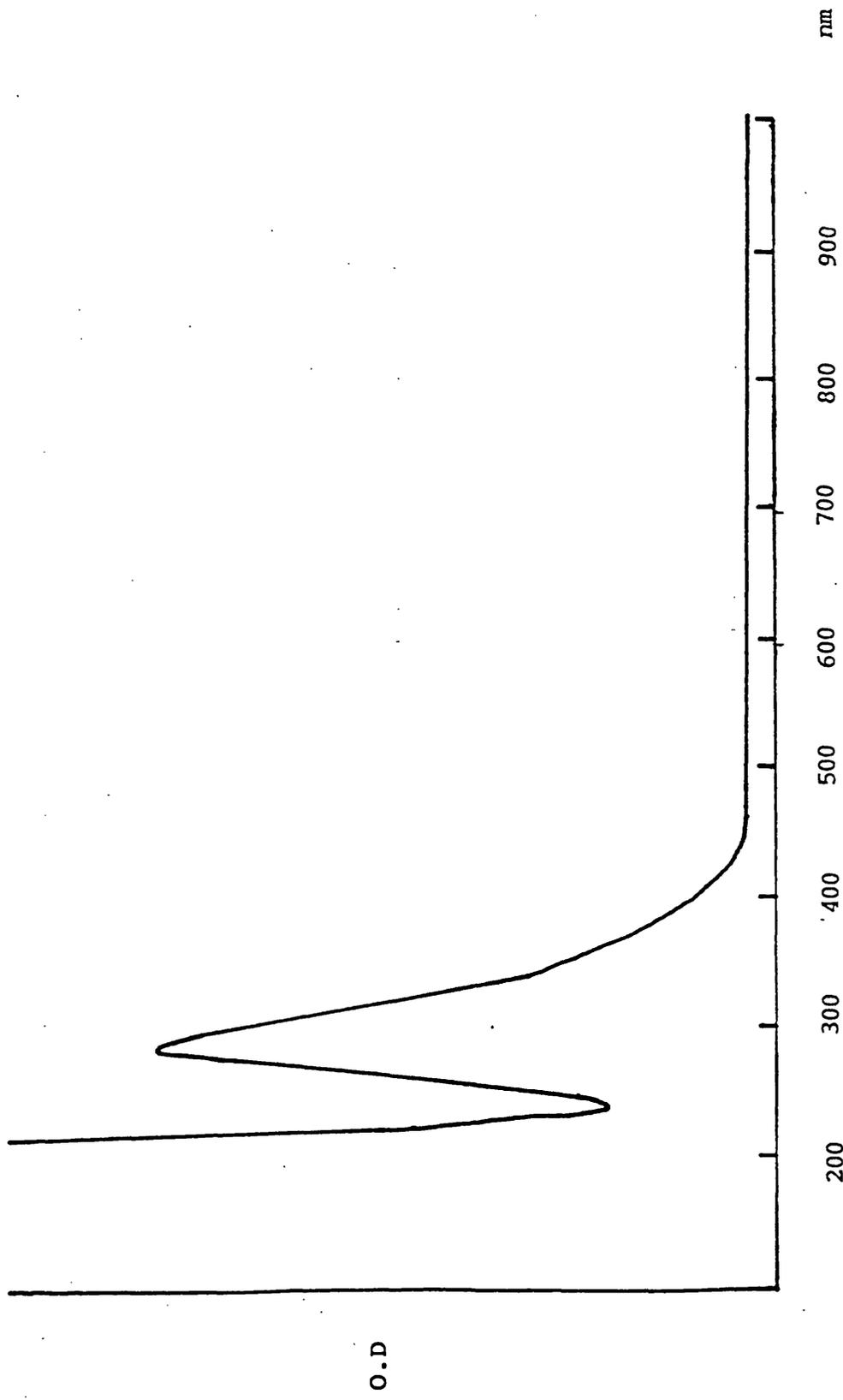


Figure 6.2 The U.V-Vis. Spectrum of $\text{XeF}^+\text{Sb}_2\text{F}_{11}^-$

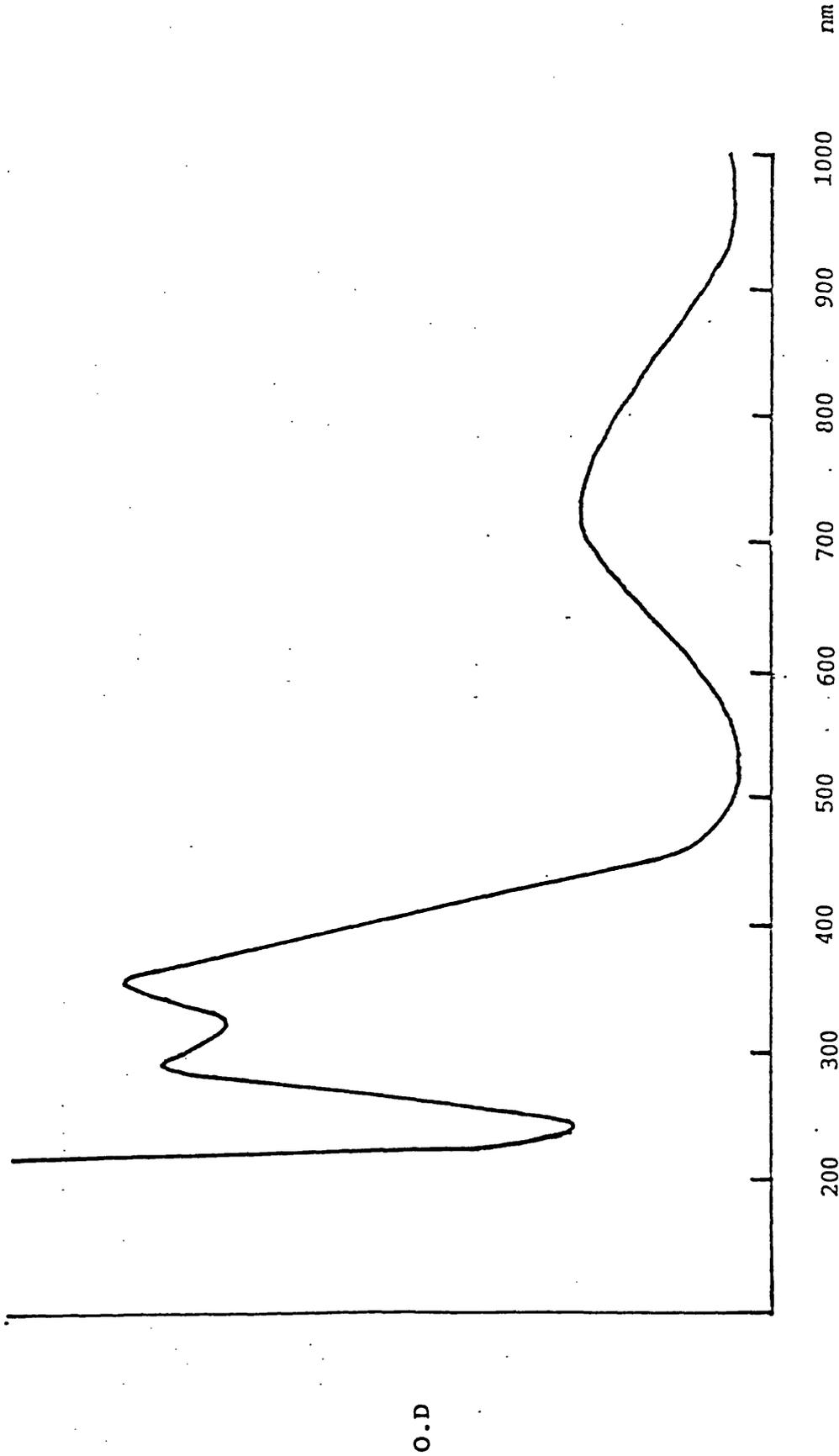


Figure 6.3 The U.V-Vis. Spectrum of $\text{Xe}_2^+\text{Sb}_2\text{F}_{11}^-$

6.4 The reaction of $\text{Xe}_2^+\text{Sb}_2\text{F}_{11}^-/\text{XeF}^+\text{Sb}_2\text{F}_{11}^-$ mixture with I_2 :

The reaction of $\text{Xe}_2^+\text{Sb}_2\text{F}_{11}^-/\text{XeF}^+\text{Sb}_2\text{F}_{11}^-$ was carried out in a glass apparatus similar to that shown in Figure 6.4. The apparatus was pumped to high vacuum with periodic heating to remove moisture. It was then seasoned with elemental fluorine several times and re-evacuated.

The apparatus was placed in a dry-box and the U.V. cell (Figure 6.4) was loaded with $\text{Xe}_2^+\text{Sb}_2\text{F}_{11}^-/\text{XeF}^+\text{Sb}_2\text{F}_{11}^-$ mixture. The apparatus was then connected to a vacuum manifold, the U.V. cell was cooled to -78°C and the apparatus was pumped to a good vacuum. Iodine vapour was transferred to the U.V. cell at -78°C under static vacuum. The brown I_2 was condensed above the yellow-green mixture but no reaction was observed at this temperature. The U.V. cell was then warmed gradually to room temperature. At $\sim 10^\circ\text{C}$ the brown colour of I_2 changed to a blue oily material which covered the inner walls of the U.V. cell. The U.V-visible spectrum of the product was recorded at room temperature and showed a peak at 640 nm (Figure 6.5) which is characteristic for the cation, I_2^{+129} .

6.5 The reaction of $\text{Xe}_2^+\text{Sb}_2\text{F}_{11}^-/\text{XeF}^+\text{Sb}_2\text{F}_{11}^-$ mixture with I_2 with xenon gas involved :

Some of the yellow-green $\text{Xe}_2^+\text{Sb}_2\text{F}_{11}^-/\text{XeF}^+\text{Sb}_2\text{F}_{11}^-$

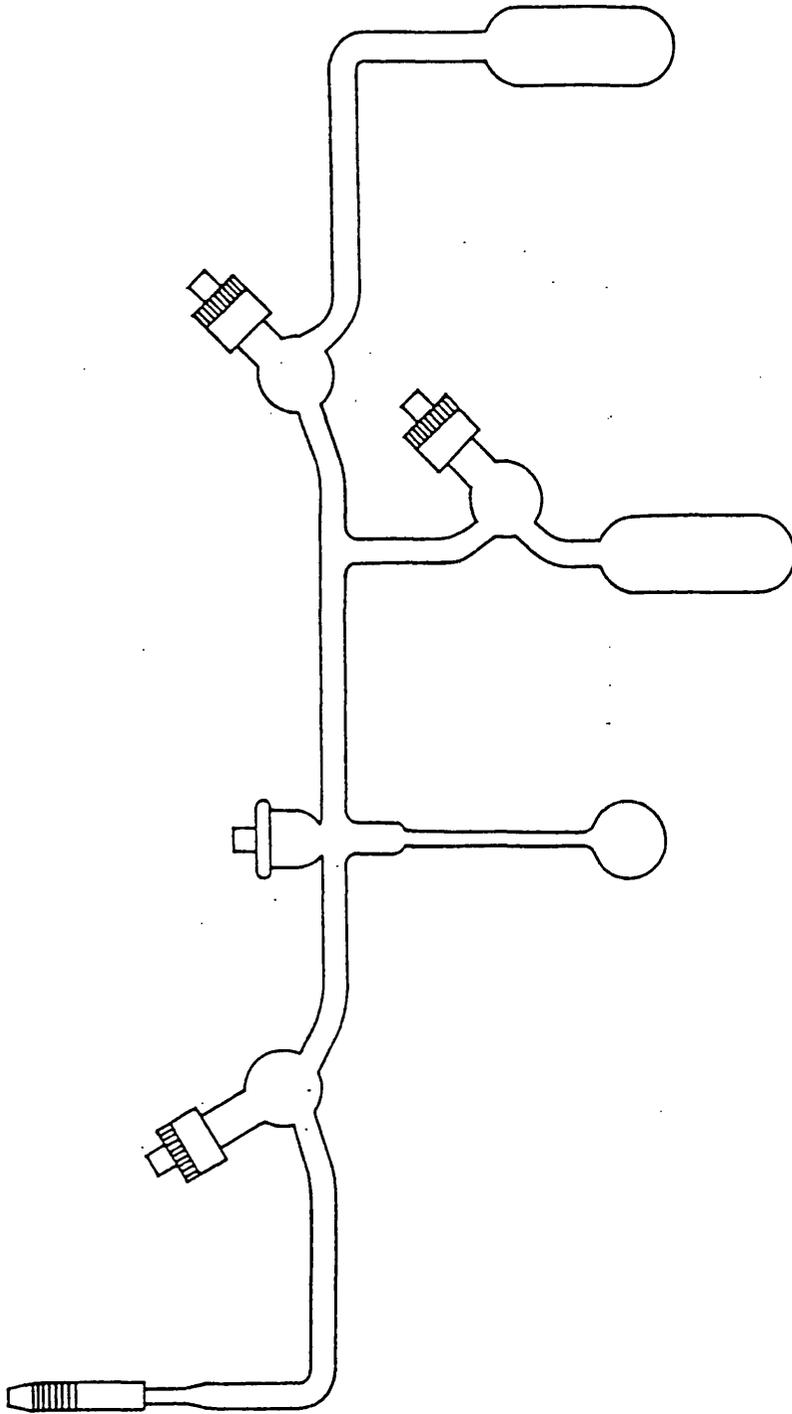


Figure 6.4 Apparatus used to attempt to prepare (Xe-I) containing species

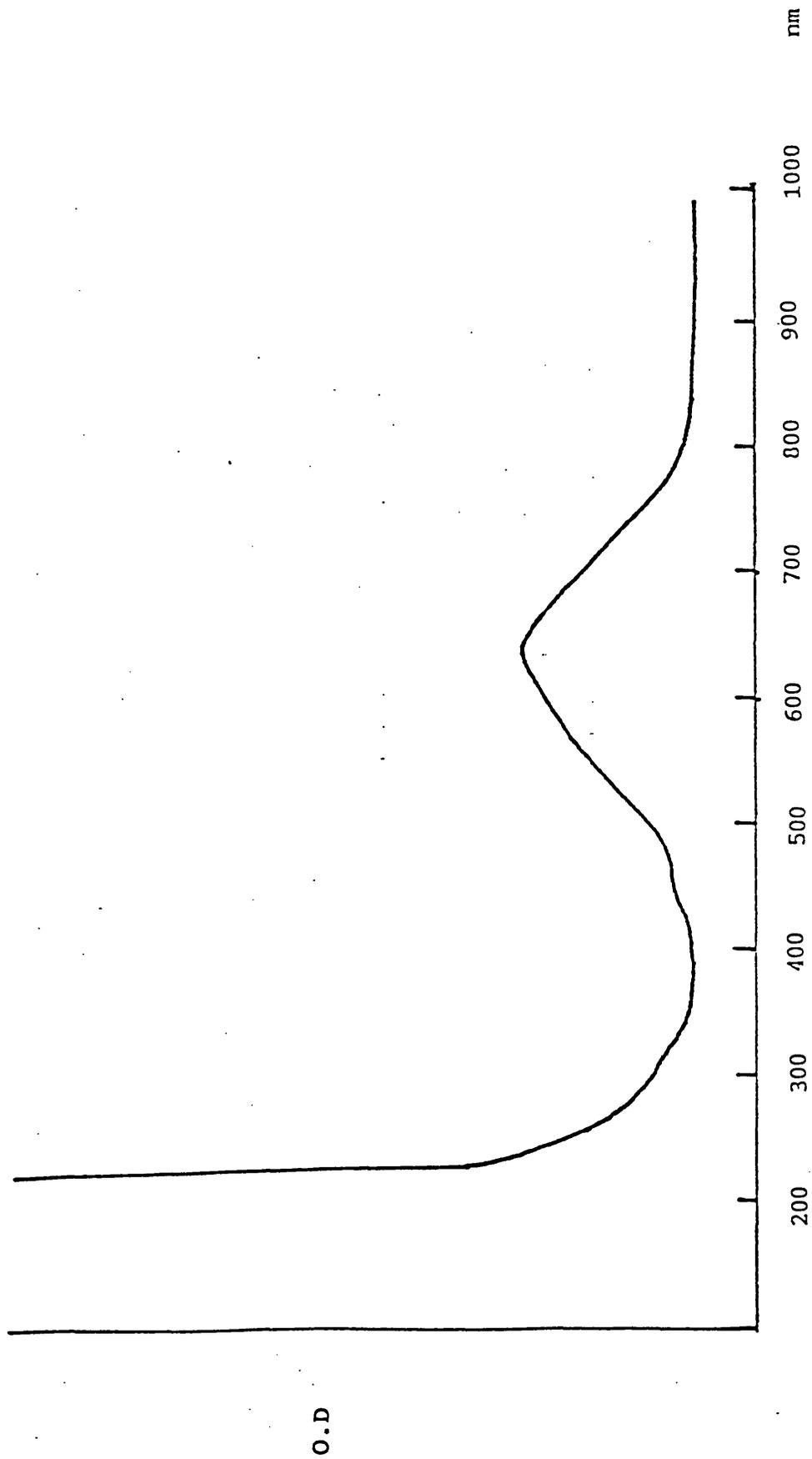


Figure 6.5 The U.V.-vis. Spectrum of $I_2 + Sb_2F_{11}^-$

mixture was loaded into a U.V. cell as described previously. A pressure of 500 mmHg of xenon gas was admitted to the mixture for 40 minutes at room temperature and the colour of the mixture changed gradually from yellow-green to bright green which indicated that more $\text{Xe}_2^+\text{Sb}_2\text{F}_{11}^-$ was formed. The apparatus was then pumped for a short time to remove unreacted xenon gas. Iodine vapour was transferred to the U.V. cell at -78°C and was condensed above the green mixture. No reaction was observed. When the sample was warmed to $\sim 0^\circ\text{C}$ the bright green colour changed to dark green. A small amount of SbF_5 was added as a solvent and the U.V-visible spectrum of the product in SbF_5 was recorded at room temperature. This showed peaks at 673, 710 and 336 nm (Figure 6.6), since Xe_2^+ has peaks at 710 and 336 nm,^{125,126} the additional peak at 673 nm suggests either that the entire spectrum is due to a new species which is not Xe_2^+ or that a new species is produced in addition to Xe_2^+ . This could be a Xe-I containing species. The sample was left at room temperature for 20 days, the dark green colour changed to blue and the U.V-visible spectrum recorded at room temperature, showed the distinctive I_2^+ peak at 640 nm.¹²⁹

6.5.1 The effect of SbF_5 on the reaction :

When the reaction described in 6.5 was repeated in the presence of a large excess of SbF_5 as a solvent the bright green colour of Xe_2^+ was changed to dark green by warming to $\sim 0^\circ\text{C}$ in presence of I_2 for just a few minutes it then changed to blue which was shown to be $\text{I}_2^+\text{Sb}_2\text{F}_{11}^-$

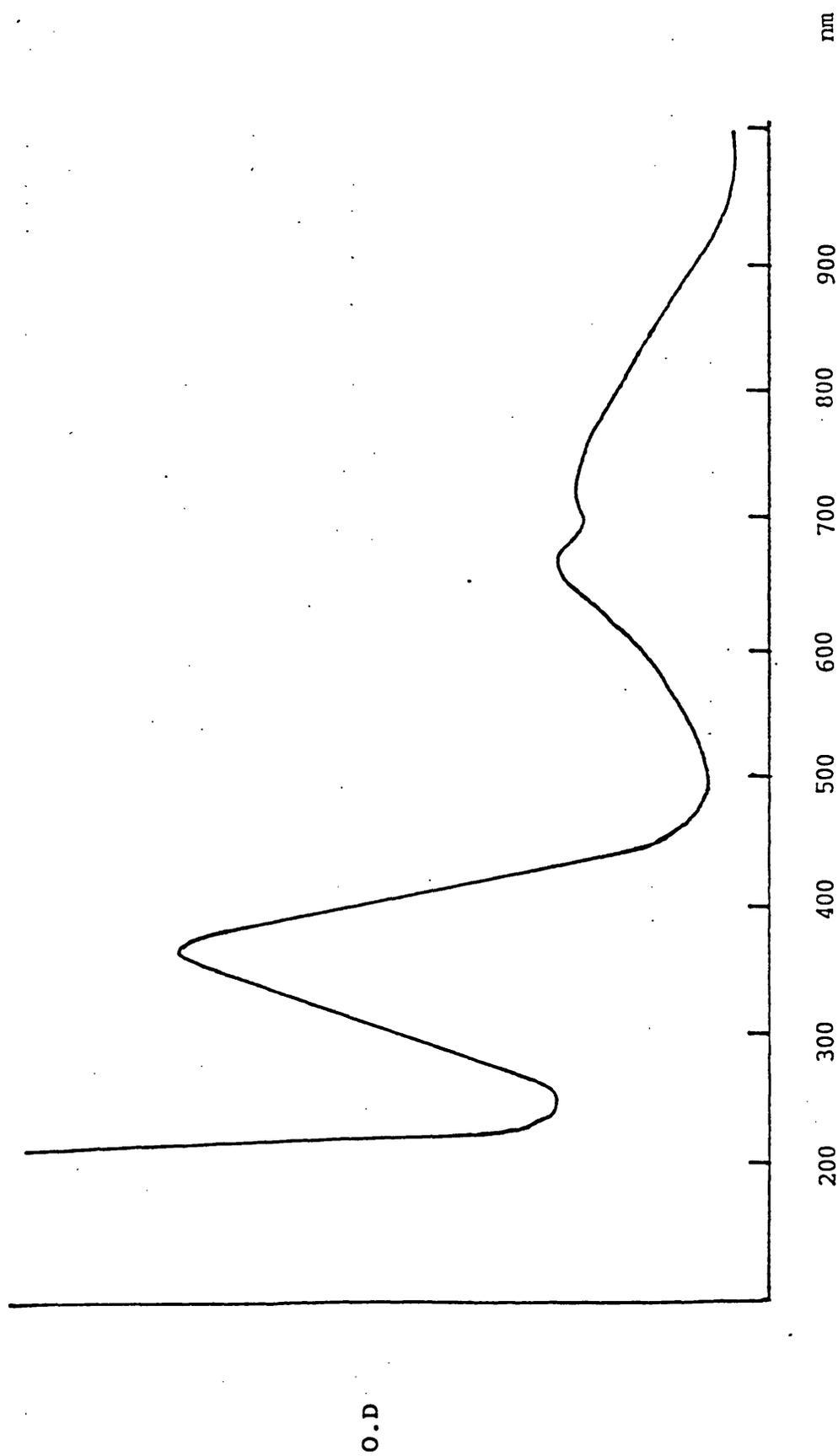
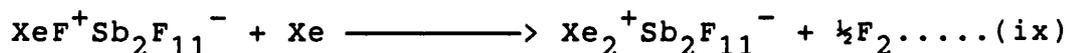


Figure 6.6 The U.V-Vis. Spectrum of the dark-green product of reaction between I_2 and $Xe_2^{+}Sb_2F_{11}^{-}$

by U.V-visible characterisation.

6.6 Discussion :

The reaction of $\text{Xe}_2^+\text{Sb}_2\text{F}_{11}^- / \text{XeF}^+\text{Sb}_2\text{F}_{11}^-$ mixture with I_2 in 6.4 could be explained in terms of the oxidation of I_2 by the yellow $\text{XeF}^+\text{Sb}_2\text{F}_{11}^-$ at $\sim -10^\circ\text{C}$ to yield a blue oily material which at room temperature was shown to be $\text{I}_2^+\text{Sb}_2\text{F}_{11}^-$ from its U.V-visible spectrum. Hence a reaction between I_2 and $\text{Xe}_2^+\text{Sb}_2\text{F}_{11}^-$ did not occur. However, when xenon gas was admitted to the $\text{Xe}_2^+\text{Sb}_2\text{F}_{11}^- / \text{XeF}^+\text{Sb}_2\text{F}_{11}^-$ mixture in 6.5 most of XeF^+ was changed to Xe_2^+ :¹²⁵



Therefore, this procedure provided a better chance for I_2 to react with $\text{Xe}_2^+\text{Sb}_2\text{F}_{11}^-$, which at $\sim 0^\circ\text{C}$ yielded a dark green coloured product which could be either a Xe-I containing species or a mixture of $\text{Xe}_2^+\text{Sb}_2\text{F}_{11}^-$ (green) and $\text{I}_2^+\text{Sb}_2\text{F}_{11}^-$ (blue). It appeared that the former is more likely since the U.V-visible spectrum of the dark-green product showed a peak which did not appear in the spectra of either $\text{Xe}_2^+\text{Sb}_2\text{F}_{11}^-$ or $\text{I}_2^+\text{Sb}_2\text{F}_{11}^-$.

The excess of SbF_5 in the sample forbade the reaction between I_2 and $\text{Xe}_2^+\text{Sb}_2\text{F}_{11}^-$ since excess SbF_5 oxidises I_2 to I_2^+ .¹³⁰

6.7 Conclusion :

The reaction of $\text{Xe}_2^+\text{Sb}_2\text{F}_{11}^-$ with I_2 at $\sim 0^\circ\text{C}$ produces a dark green solid the U.V-visible spectra of which suggests the possible presence of a species with a "Xe-I" bond.

Chapter seven

Experimental

Chapter seven

Experimental

7.1 Preparative techniques :

Some of the starting materials and the majority of the compounds prepared and studied in this thesis are air and moisture sensitive and require handling under high vacuum or inert atmospheres to prevent decomposition. Metal, glass and fluoroplastic containers were used as reaction and storage vessels. Before use, metal reactors were heated to 300-400°C, pumped to 10^{-4} mmHg, hydrogenated, seasoned with fluorine and re-evacuated. All glass vessels were heated to ~ 300°C and pumped for several hours, seasoned with fluorine and pumped to high vacuum and all fluoroplastic vessels were pumped to 10^{-4} mmHg, seasoned with fluorine and re-evacuated.

Volatile air sensitive materials were transferred in metal or glass vacuum systems using either static vacuum conditions with a suitable temperature gradient, or dynamic vacuum. Involatile materials were manipulated in a dry box (Vacuum Atmospheres Co., VAC NE 42-2 Dri-lab). Oxygen and water was removed from the atmosphere in the dry box by circulation through columns of manganese oxide and molecular sieves. When transferring or weighing small quantities of powders in

the dry box the sample and apparatus were exposed to a 4mci ^{210}Po α -emitter [Type PDV1, Radiochemical Center Amersham, Bucks.] to eliminate static electricity. Weighings accurate to ± 0.1 mg were performed in the dry box with a Sartorius balance [model 1601 MP8]. Powdered samples were weighed in small glass boats prior to loading into the reaction vessels. Weighing for mass balance calculations was carried out on a laboratory balance [Stanton Unimatic CL 41].

Samples not required for immediate use were sealed under vacuum in glass ampoules. Volatile samples were stored in nickel cans fitted with Hoke bellows valves [Model 4171 M2B]. Thermally unstable samples were stored at -196°C in a cryostat [British oxygen Co. Ltd] or at -78°C in solid carbon dioxide.

7.2 Vacuum systems, reaction vessels and flow system :

Vacuum lines were used to prepare all of the compounds studied, except the compound SbF_5 which was prepared in a flow line at atmospheric pressure.

7.2.1 Vacuum line :

The vacuum line consisted of a metal manifold with high and low vacuum facilities which formed the basic system (Figure 7.1). this was constructed from $3/8$ " o.d, $1/8$ " i.d. nickel tubing [H. Wiggin & Co. Hereford] and argon welded "U" traps (25cm^3 capacity). The manifold

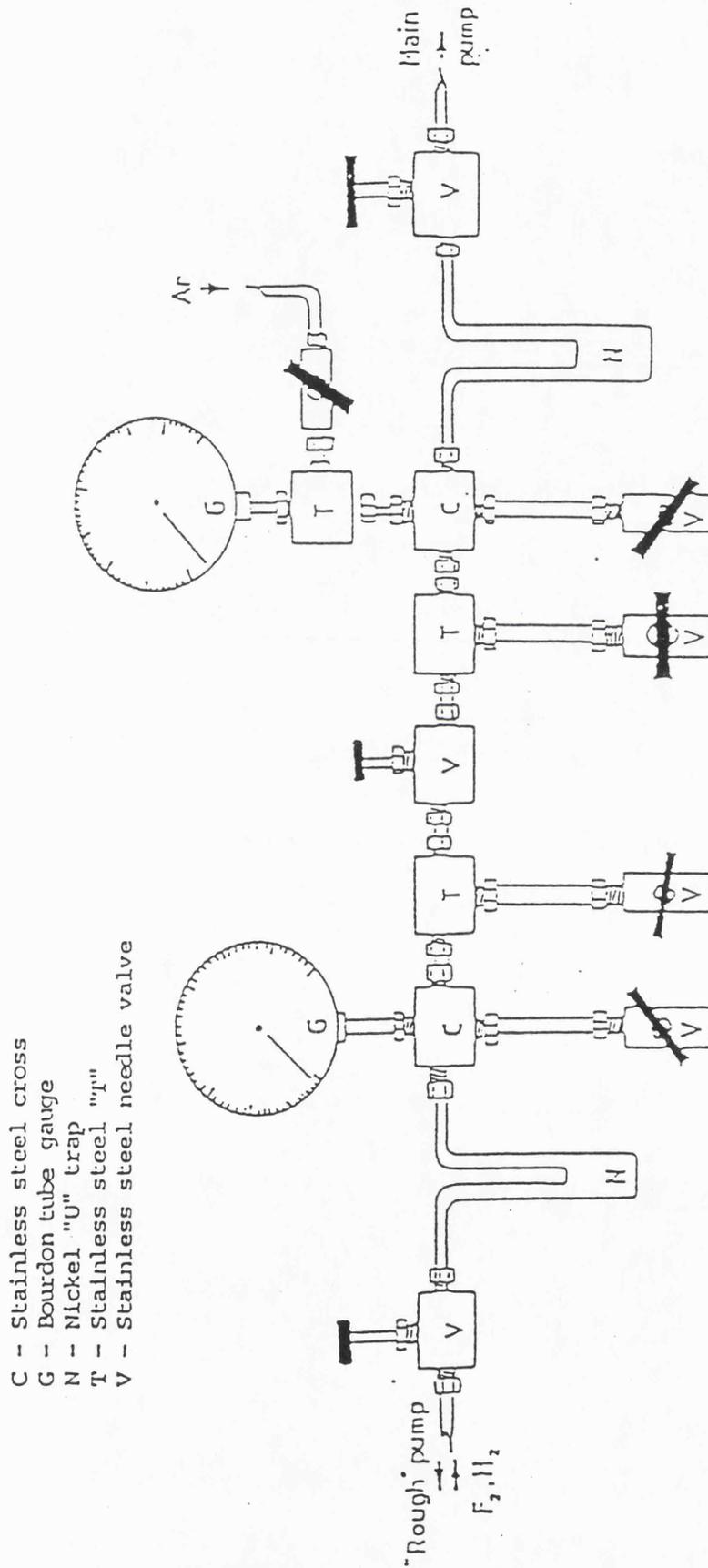


Figure 7.1 The Basic High Vacuum Manifold

was completed with AE-30 series hard drawn stainless steel needle valves, crosses and tees [Autoclaves Engineers Inc. Erie, Pennsylvania, USA.].

The low vacuum system (10^{-2} mmHg) consisted of a single stage rotary pump [Model PSR/2, NGN Ltd., Accrington, Lancashire] with a large metal trap filled with soda lime (5-10 mesh) between the pump and the manifold. This chemical trap collected fluorine or volatile fluorides exhausted from the manifold. The low-vacuum system served to remove large quantities of gases before opening the manifold to the high vacuum system.

The high vacuum (10^{-4} mmHg) was maintained by a single stage rotary pump which was connected to the manifold via a mercury diffusion pump and liquid nitrogen cold trap (-196°C). A facility for admission of argon directly into the manifold, from a cylinder, was provided and fluorine was introduced to the line from welded nickel cans (1dm^3 capacity) fitted with AE-30 stainless steel needle valves.

Manifold pressures in the range +1 to -1 atmosphere (0-1500mmHg) were measured using a stainless steel Bourdon tube gauge [type 1F/66Z, Budenberge Gauge Co. Ltd., Broadheath, Greater Manchester]. The vacuum was monitored using a cold-cathode Penning gauge [Model 2A, Edwards High Vacuum Ltd., Crawley, West Sussex], capable of measuring pressures in the range 10^{-2} to 10^{-6} mmHg.

Leaks in the manifold and in constructed reaction systems were located with a helium leak detector [Edwards High Vacuum Ltd., Mass Spectrometer Leak Detector Model LT 104].

7.2.2 Reaction vessels :

A variety of metal, fluoroplastic, Pyrex or silica reaction vessels could be attached to the vacuum line. Glass reaction systems were designed and fabricated as required and were attached to the manifold via a 1/4" o.d. glass to 1/4" o.d. stainless steel tubing connector machined to an Autoclave Engineers AE-30 series fitting, by Chemcon Teflon connectors [Type STD/4 E1P, Production Techniques Ltd., Fleet, Hampshire] using Teflon compression unions. Greaseless glass valves [Quickfit 'Rotoflo' type TF2/13 and TF6/13 or J. Young, Scientific Glassware Ltd., Acton, London] fitted with Teflon stems were used where glass systems were employed or, alternatively, glass reaction vessels were fitted with Chemcon Teflon needle valves [Type STD/VC 4/P].

1/4" or 3/8" o.d. F.E.P. tubes with the bottom sealed were used as reactors. These were connected to the manifold via Chemcon Teflon needle valves [Type STD/VC 4/P].

7.2.3 Flow line :

The flow line consisted of a metal manifold with a low vacuum facility (Figure 7.2). It was constructed of 3/8" o.d., 1/8" i.d. nickel and stainless steel pipe, stainless steel needle valves, crosses, tees and elbows [Autoclave Engineers Inc., Erie, Pennsylvania, USA].

A vacuum was obtained using a single stage rotary pump [Model PSR/2, NGN Ltd., Accrington, Lancashire], with a large metal trap filled with soda lime (5-10 mesh) between the pump and the manifold which is used to collect fluorine or volatile fluorides exhausted from the manifold. Facilities for the admission of nitrogen, hydrogen and fluorine from cylinders were provided. Reactions were performed in a silica reaction tube and products were collected in Pyrex traps (Figure 7.3).

7.3 Characterisation of products :

7.3.1 Infrared spectroscopy :

A Perkin Elmer 580B spectrometer was used to obtain infrared spectra. Gas phase spectra were obtained using a 10cm path-length copper cell, fitted with AgCl windows ($4000-400\text{cm}^{-1}$), which could be attached directly to the main manifold. Teflon gaskets provided an air tight seal between the windows and the cell body.

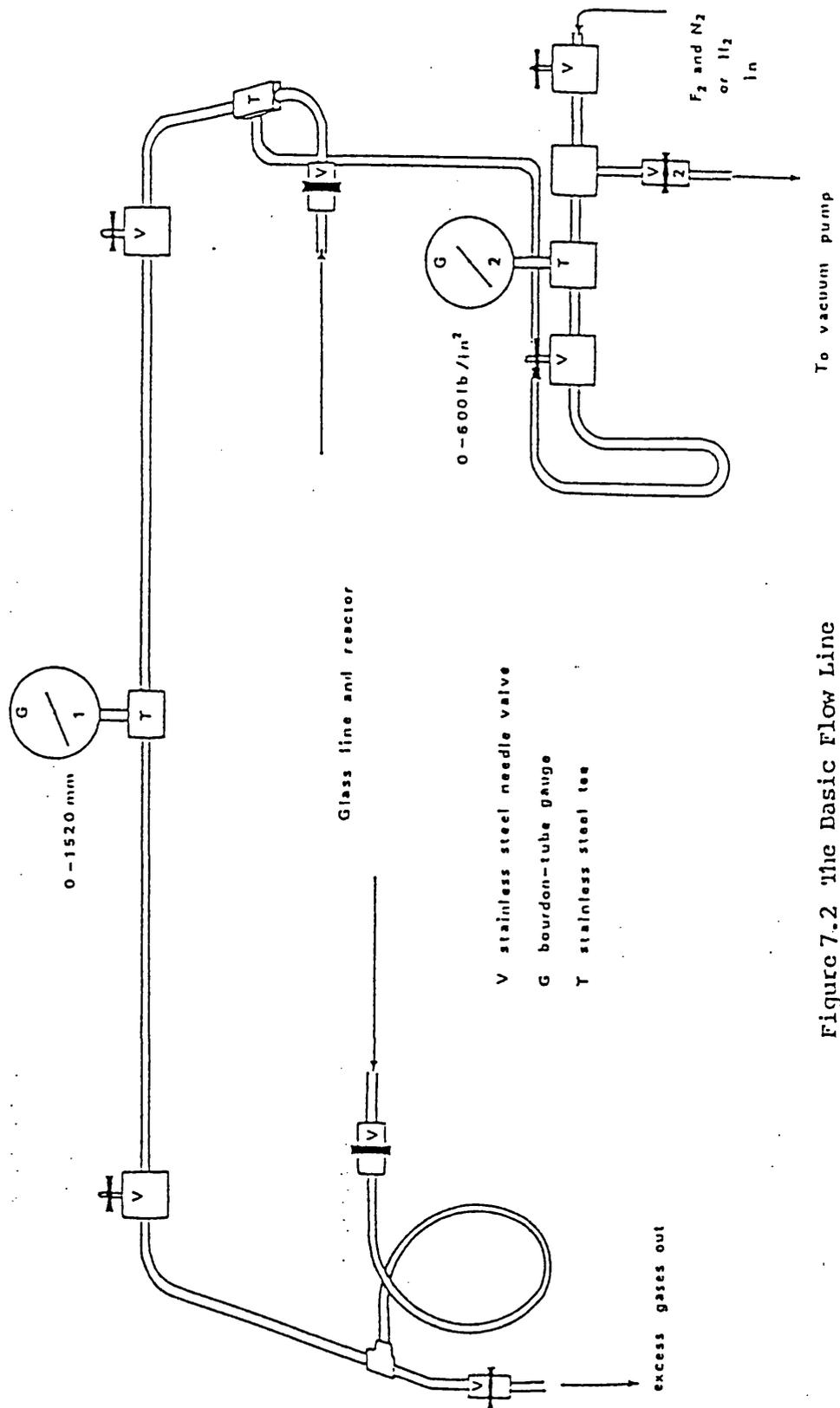


Figure 7.2 The Basic Flow Line

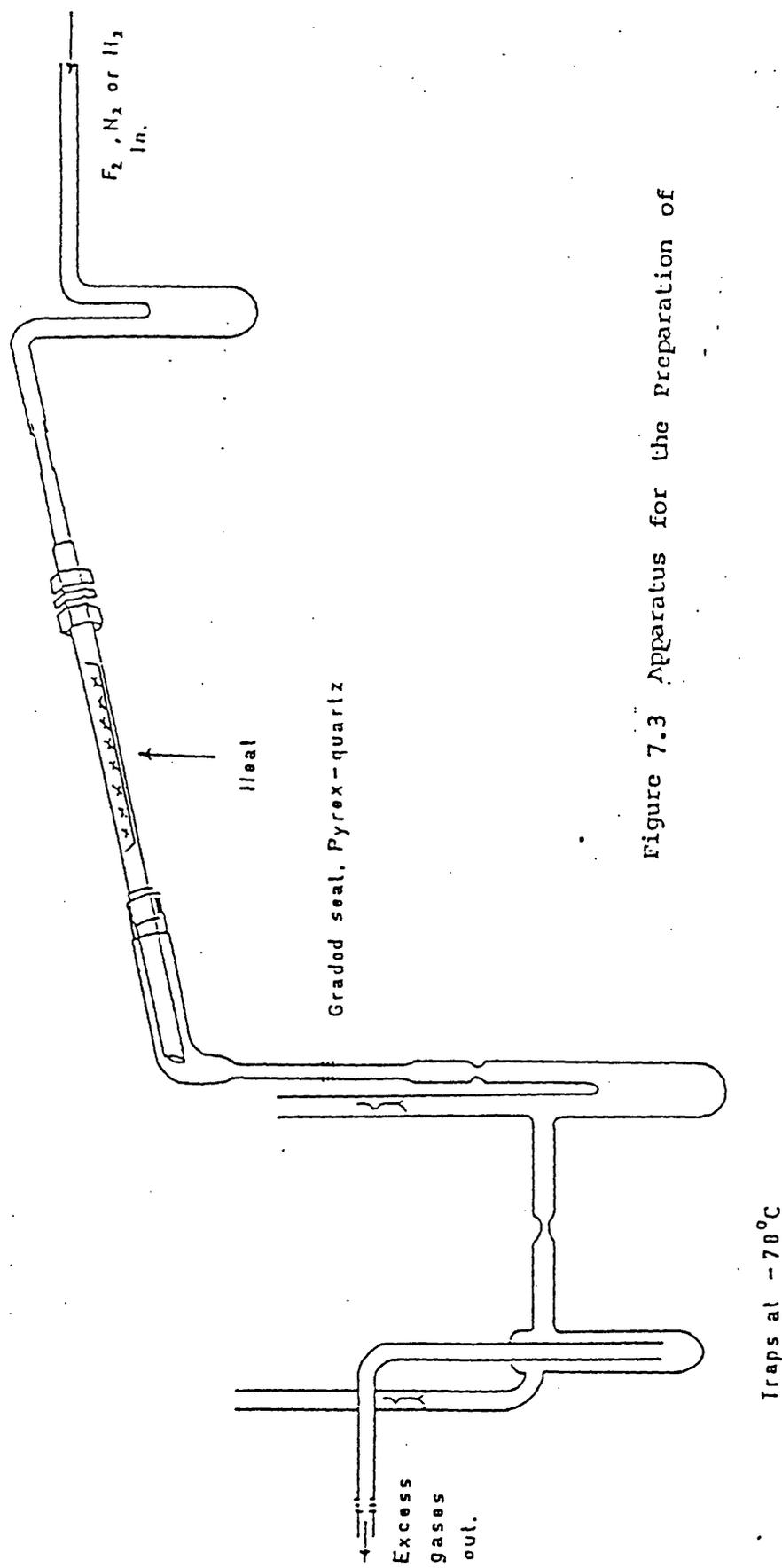


Figure 7.3 Apparatus for the Preparation of

7.3.2 Raman spectroscopy :

Raman spectra were recorded with a Coderg T800 spectrometer, with a 250 mW Ar⁺ laser [Model 52, coherent Radiation Laboratories] which provided 5145Å (green) and 4880Å (blue) radiation.

Solid and volatile samples were contained in 3/8" o.d. Pyrex or F.E.P. tubes. Those which were likely to decompose in the beam or were not stable at R.T. were run at liquid nitrogen temperature using an unsilvered Dewar. In the event of studying the spectra at different low temperatures a special cooler was used (figure 7.4), This was cooled by passing cold nitrogen vapour boiled off from liquid nitrogen in a larger Dewar over the samples in a vacuum jacket. The temperature was monitored with a copper-constantan thermocouple. Adjustment of the nitrogen flow rate allowed control of the temperature (as low as -110°C) to be used.

7.3.3 Mass spectrometry :

Mass spectra were recorded on a V. G. Micromass 16B instrument, the samples being introduced directly into the ionising chamber. The volatile samples were admitted through a pre-seasoned copper pipe with a Teflon insulation tip (Figure 7.5). In order to minimise decomposition of the sample during passage through the mass spectrometer, the entire system was pre-seasoned by flushing with small amounts of fluorine.

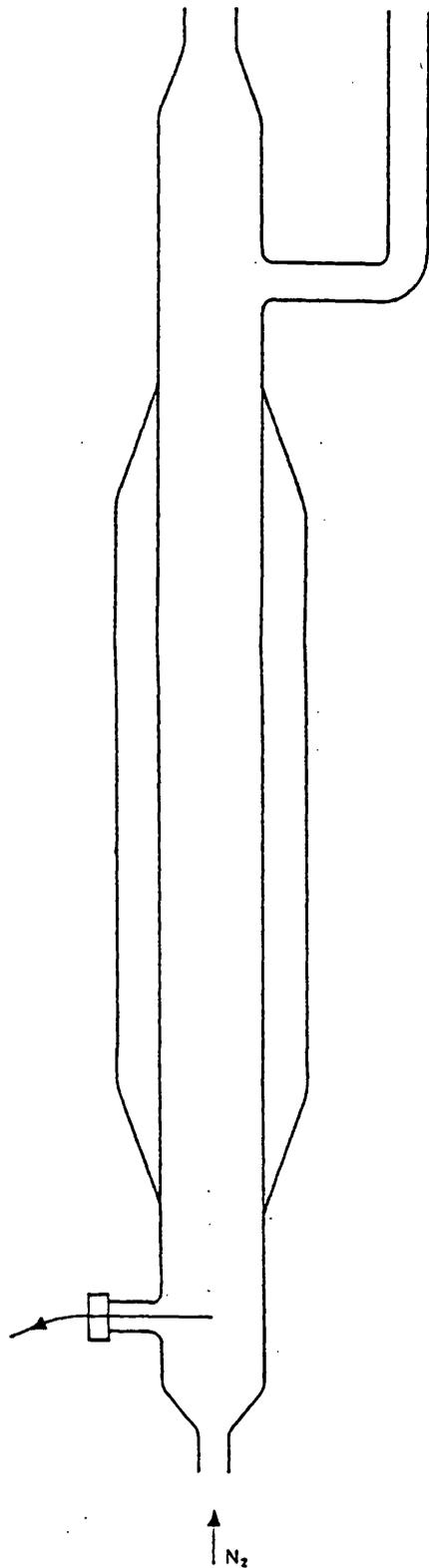


Figure 7.4 Cooler used to obtain variable low temperatures in Raman spectroscopy

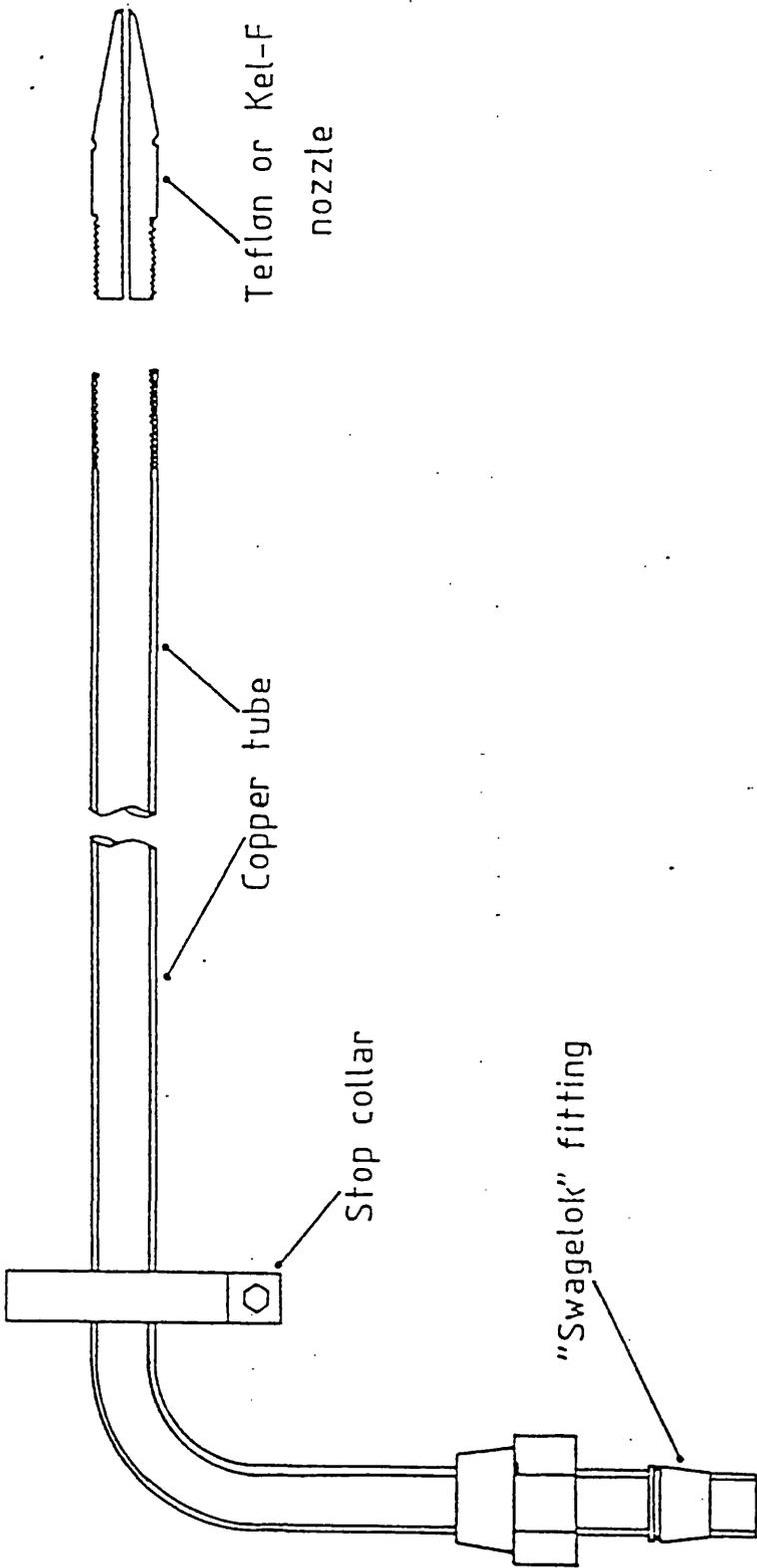


Figure 7.5 Gas and Liquid Inlet System for Mass Spectrometer

7.3.4 Electron spin resonance spectroscopy :

E.S.R. spectra were recorded on a Bruker ER 200D instrument. Samples for E.S.R. analysis were contained in capillaries drawn from 1/4" od F.E.P. tubing. The spectra were indexed using 2,2-diphenyl 1-picrylhydrazyl (DPPH).

7.3.5 Ultraviolet spectroscopy :

U.V-Visible spectra were recorded on a Shimadzu U.V-160 which is capable of measuring wavelength over a range of 900nm (200-1100nm) with a wavelength accuracy of ± 0.5 nm.

7.4 Chemicals, Sources and purifications :

7.4.1 Starting materials :

Fluorine : [99.8% purity, Matheson Gas Products]; for use on the manifold was used without purification from the cylinder. For safety and convenience the gas was transferred to welded nickel cans (1dm^3 capacity) when used on the vacuum line.

Krypton : BOC Special Gas Division, Deer Park Road, London.

Xenon : BOC Special Gas Division.

- Argon : BOC Special Gas Division.
- Nitrogen : BOC Special Gas Division.
- Iodine : [Aldrich Chemical Co. Ltd.];
purified by vacuum distillation.
- Antimony : BDH laboratory reagents, BDH
Chemical Ltd., Poole, England.
- Arsenic : BDH laboratory reagents, BDH
Chemical Ltd., Poole, England.
- Osmium : Johnson Matthey Chem. Ltd.
- Ruthenium : Johnson Matthey Chem. Ltd.

Iodine pentafluoride : [Ozark Mahoning]; was vacuum distilled from the cylinder into a 3/4" Kel-F tube. To remove traces of iodine approximately 400 mmHg of fluorine was distilled on to the IF₅ and agitated for several hours, periodically more fluorine was added to replace that used during conversion of iodine to iodine pentafluoride. Reaction was known to be complete, when the tube contained a colourless liquid, this was pure iodine pentafluoride.

7.4.2 Solvents

Carbon tetrafluoride : [Aldrich Chemical Co.]

Ltd.],[99.95%].

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