Spectroscopic Studies on the Higher Binary Fluorides of Chromium : CrF_4, CrF_5, and CrF_6, both in the Solid State and Isolated in Inert Gas Matrices†

Eric G. Hope, Peter J. Jones, William Levason,* J. Steven Ogden,* Mahmoud Tajik, and Jeremy W. Turff
Department of Chemistry, The University, Southampton SO9 5NH

Pure samples of CrF_4, CrF_5, and CrF_6, together with the related salts $CsCrF_6$ and Cs_2CrF_6, have been prepared, and a number of spectroscopic measurements made. In particular, the solid state i.r. and u.v.–visible spectra of CrF_4 and CrF_5 indicate fluorine-bridged polymeric structures, whilst $CsCrF_6$ and Cs_2CrF_6 contain essentially discrete CrF_6 units. Matrix isolation studies on CrF_4 and CrF_6 lead to the identification of molecular CrF_4 (T_d) and CrF_6 (O_h) which are characterised by intense i.r. bands at 784.3 and 763.2 cm^{-1} respectively (argon matrices); the vaporisation of CrF_5 is shown to yield CrF_4 + CrF_6 by disproportionation. The u.v.–visible spectrum of CrF_6 contains prominent charge-transfer bands at *ca.* 38 450 and *ca.* 26 700 cm^{-1}.

Five binary fluorides of chromium have been reported,[1] namely CrF_2, CrF_3, CrF_4, CrF_5, and CrF_6, of which only the first two have been studied in detail. The three higher fluorides are very difficult to obtain in even a reasonably pure state, and their corrosive nature has in general hampered investigations,[2–9] although some spectroscopic data have been reported.[10–13] However, for CrF_6, the extreme conditions of the literature synthesis[3] and its reported thermal instability (decomposing $\geqslant$ *ca.* 150 K), have essentially precluded all studies.

As an extension of our earlier work on the synthesis and characterisation of chromium oxohalides ($CrOCl_3$,[14] $CrOF_3$,[15] $CrOF_4$,[16] and CrO_2F_2[17]) we have recently completed detailed i.r. and u.v.–visible studies on CrF_4, CrF_5, and CrF_6 both in the solid state and also using matrix isolation techniques. A preliminary account of our work on CrF_6 has been the subject of a recent communication;[18] this present paper discusses in detail the synthesis and spectroscopic results obtained for all three higher binary fluorides, and for the related salts $CsCrF_6$ and Cs_2CrF_6.

Experimental

The preparation of the higher chromium fluorides has generally involved the fluorination of either chromium powder, CrF_3, or CrO_3 using both flow and static methods. We have explored both these methods, and attempted a large number of syntheses under a wide variety of conditions. Relatively few of these yielded pure materials,‡ as the conditions necessary for preparation proved to be rather critical. Elemental analyses were performed using standard reagents as described previously.[15]

Synthesis of CrF_4.—Chromium tetrafluoride was made by static fluorination of CrF_3, and also by a flow method from chromium powder and fluorine similar to that described by Clark and Sadana.[9] This latter route proved to be more satisfactory, and in a typical preparation, powdered electrolytic grade chromium (4 mmol) was placed in a nickel boat inside a copper tube and heated to 350 °C for 30 min in a stream of fluorine. After cooling in a stream of argon, the apparatus was transferred to a dry-box, and dark green CrF_4 removed (Found: Cr, 47.7; F, 52.1. Calc. for CrF_4: Cr, 47.7; F, 52.3%).

Synthesis of CrF_5.—Samples of dark red CrF_5 were most conveniently prepared by static fluorination of CrF_3 using a procedure similar to that described by Slivnik and Zemva.[7] In a typical preparation, CrF_3 (Cerac) (15 mmol) was loaded into a Monel autoclave (300 cm^3) in a dry-box, and after evacuation, F_2 was admitted to a pressure of 30 atm. After heating at 350 °C for 2 h, the autoclave was cooled to room temperature. The excess F_2 was pumped out, and the autoclave evacuated to 10^{-1} Torr for several hours. The autoclave was subsequently opened in a dry-box and sticky red CrF_5 was removed from the lid (Found: Cr, 35.3; F, 64.6. Calc. for CrF_5; Cr, 35.4; F, 64.6%).

Synthesis of CrF_6.—The original preparation of CrF_6 described by Glemser *et al.*[3] involved the static fluorination of chromium powder under extreme conditions (350 atm F_2, 400 °C). Our samples of CrF_6 were obtained under somewhat milder conditions by the static fluorination of CrO_3 in a pre-fluorinated Monel autoclave fitted with a water-cooled lid.

The course of this reaction proved to be very dependent upon temperature and pressure. Under moderate F_2 pressures (*ca.* 4 atm) the principal product at 120 °C (24 h) was found to be CrO_2F_2, whilst at *ca.* 140 °C (72 h) a mixture of CrO_2F_2 and $CrOF_4$ was obtained. At *ca.* 200 °C (72 h), increasing amounts of CrF_5 appeared and this is consistent with a mechanism involving the stepwise substitution of oxygen by fluorine to give CrF_6, followed by thermal decomposition to CrF_5. It therefore seemed likely that at lower temperatures and higher fluorine pressures this reaction might yield CrF_6.

In a typical preparation of CrF_6, the Monel autoclave (300 cm^3) was loaded in a dry-box with powdered CrO_3 (25 mmol) and, after evacuation, was filled with F_2 to *ca.* 25 atm. The autoclave was then heated to 170 °C for 72 h and allowed to cool, first to room temperature, and subsequently to −63 °C, where it was evacuated to remove the more volatile contents. After warming to room temperature, the autoclave was opened in a dry-box and found to contain deep red CrF_5 on the water-cooled lid, and volatile, lemon-yellow[3] CrF_6 on the walls. This latter product decomposed only slowly (a few days) to CrF_5 when stored in the autoclave, but samples transferred to pre-fluorinated steel containers decomposed within a few hours. Both glass and silica were rapidly attacked by CrF_6 at room temperature, and its hydrolysis reactions were spectacular. In particular, it reacted instantly in air producing an orange smoke, and violently in water to give a greenish yellow solution.

This reactivity and thermal instability precluded a complete analysis, but after hydrolysis the resulting solution gave an

† *Non-S.I. units employed:* atm = 101 325 Pa, Torr = 133 Pa, dyn = 10^{-5} N.

‡ Purity was estimated by a combination of elemental analysis and spectroscopic studies: analysis alone is an imperfect guide in this area.[19]

elemental ratio Cr:F of typically 1:5.7, thus confirming that the yellow material was CrF_6.

The success of this preparation under much less extreme conditions than those previously reported[3] is almost certainly due to the ease with which the volatile intermediate oxofluorides can exchange oxygen for fluorine. In the direct fluorination of elemental chromium, it is probable that the lower (solid) fluorides are somewhat inert and that much higher temperatures are required for the reaction to proceed to completion. As a result, much higher F_2 pressures will be needed to prevent decomposition to CrF_5.

Matrix Isolation Studies.—The general features of our matrix isolation apparatus have been described elsewhere.[20] In these present studies, samples of CrF_4, CrF_5, and $CsCrF_6$ were vaporised from stainless-steel or Monel tubes at relatively low temperatures, and the vapours co-condensed with an excess of nitrogen or argon matrix gas (B.O.C. 99.999%) onto an optically transparent window cooled to *ca.* 12 K.

Samples of matrix-isolated CrF_6 were obtained by simultaneous deposition of a CrF_6–matrix gas mixture and a flow of pure matrix gas. In a typical experiment, the autoclave containing a sample of freshly prepared CrF_6 was cooled to *ca.* −10 °C and rapidly pumped out to remove residual volatile impurities. Nitrogen or argon gas was then admitted to atmospheric pressure, and the autoclave connected to the matrix equipment *via* a stainless-steel spray-on line.

There are no reliable vapour pressure data for CrF_6, but we estimate that this procedure resulted in a room-temperature CrF_6–matrix gas mixture of *ca.* 1:10. This sample was subsequently co-condensed with an excess of pure inert matrix gas to ensure good isolation. During deposition, the autoclave was at room temperature, but the stainless-steel spray-on line between the autoclave valve and the cryostat could be heated or cooled to investigate the possible thermal decomposition of CrF_6.

I.r. spectra were recorded using CsI optics in conjunction with Perkin-Elmer instruments, models 225 and 983G, whilst u.v.–visible spectra were obtained from a Perkin-Elmer 554 instrument, using LiF optics.

Results and Discussion

Solid State Studies.—Chromium tetrafluoride. This compound is reportedly amorphous,[2,9] but by analogy with some other transition-metal tetrahalides,[21] it seems probable that its structure is based on edge-sharing CrF_6 octahedra. This would result in an i.r. spectrum characterised by both terminal and bridging Cr–F stretching modes, and a u.v.–visible spectrum which should show similarities to a d^2 ion in an O_h environment.

The i.r. spectrum of solid CrF_4 (Nujol mull) shows strong absorptions in the regions 830—750 cm^{-1} (ν_{Cr-F} terminal) and 550—490 cm^{-1} (ν_{Cr-F} bridge) and also at *ca.* 290 cm^{-1} (δ_{Cr-F}). The diffuse reflectance spectrum of the solid contains a very broad, intense absorption at 35 000—40 000 cm^{-1}, strong bands at 21 000 and 28 000 cm^{-1}, and weak features at 12 350 and 13 500 cm^{-1}. Using the conventional ligand-field approach for a d^2 ion in O_h symmetry,[22] we assign the most intense features of this spectrum as follows: 21 000 $[^3T_{1g}(F) \rightarrow {}^3T_{2g}]$, 28 000 $[^3T_{1g}(F) \rightarrow {}^3T_{1g}(P)]$, 35 000—40 000 cm^{-1} (F→Cr charge transfer). This assignment yields values: $Dq = 2\,200 \pm 100$ cm^{-1}, $B' = 550 \pm 100$ cm^{-1}, and taking $B(Cr^{4+})$[22] as 1 039 cm^{-1}, a value for β of 0.52. The third spin-allowed band $[^3T_{1g}(F) \rightarrow {}^3A_{2g}]$ is predicted to lie at *ca.* 44 000 cm^{-1}. Although the actual symmetry will be lower than O_h, there was no evidence of band splitting. The ligand-field parameters obtained from this analysis compare favourably with those found in the related ion $[MnF_6]^{2-}$, for which $Dq = 2\,175$ cm^{-1} and $\beta = 0.56$.[22] The remaining very weak features at 12 350 and 13 500 cm^{-1} are assigned as spin-forbidden transitions to singlet states.

Chromium pentafluoride. Pure CrF_5 is hydrolysed rapidly in air, and violently in water to give a solution containing Cr^{III} and Cr^{VI} species. It inflames ammonia and most organic materials on contact, and is a very strong fluorinating agent.[8] I.r. and Raman studies on the *liquid*[11] indicate a fluorine-bridged octahedral structure, and in particular, i.r. bands have been reported at 820—650, 580—400, and *ca.* 250 cm^{-1}. Preliminary *X*-ray data are available for the solid,[4] but there are no published u.v.–visible or i.r. studies in this phase.

We have obtained an i.r. spectrum of solid CrF_5, pressed between plastic discs, which shows broad intense absorptions at 830—750, 600—450, and *ca.* 300 cm^{-1}, and assign these as ν_{Cr-F} (terminal), ν_{Cr-F} (bridge), and δ_{FCrF} modes respectively. The diffuse reflectance u.v.–visible spectrum contained bands at 22 400, 26 000, and 37 000 cm^{-1}, and these are interpreted in terms of a d^1 species in a low-symmetry environment. In particular, we assign the two lowest bands to the (split) $^2T_{2g} \rightarrow {}^2E_g$ transition in O_h symmetry and this leads to a value of *ca.* 2 400 cm^{-1} for the parameter *Dq*. The broad absorption at 37 000 cm^{-1} is then assigned as the lowest F→Cr charge transfer (c.t.) band. These assignments result in reasonable agreement with the *Dq* value for CrF_4 (2 200 cm^{-1}, see above) and with a prediction of 36 000 ± 2 000 cm^{-1} for the position of the c.t. band based on the optical electronegativity model.[23]

$CsCrF_6$ *and* Cs_2CrF_6. Spectroscopic data on Cr^V and Cr^{IV} compounds are very limited, and we therefore prepared small amounts of these materials, using literature methods,[8,24] for comparative purposes. Both were found to show a single, very broad, intense absorption in the i.r. spectrum at *ca.* 600 ($CsCrF_6$) and *ca.* 580 cm^{-1} (Cs_2CrF_6), in good agreement with the literature,[8,24] and these features are assigned to terminal Cr–F stretching modes in the essentially discrete anions $[CrF_6]^-$ and $[CrF_6]^{2-}$. The diffuse reflectance spectrum of $CsCrF_6$ shows bands at *ca.* 21 100 (sh), 24 150, and 30 000—43 000 cm^{-1}. The two lower energy features are assigned as the $^2B_{2g} \rightarrow {}^2A_{1g}$ and $^2B_{2g} \rightarrow {}^2B_{1g}$ transitions in the Jahn–Teller distorted anion (D_{4h}), whilst the higher energy absorption is F→Cr c.t. These features are thus very similar to those observed for CrF_5.

Our samples of Cs_2CrF_6 showed a diffuse reflectance spectrum similar to that published for Rb_2CrF_6.[24] An intense F→Cr c.t. band was observed in the region 30 000—40 000 cm^{-1}, and weaker *d–d* transitions noted at 20 700 and 29 400 cm^{-1}. An analysis of these data similar to that described above for CrF_4 gives $Dq = 2\,125 \pm 100$ cm^{-1}, with $B' = 580 \pm 100$ cm^{-1}, and $\beta = 0.56$.

E.S.R. Studies.—Intense e.s.r. signals were observed from powdered samples of CrF_5 and $CsCrF_6$. At −196 °C, CrF_5 gave a broad, asymmetric, structureless feature centred at *g ca.* 2.0, whilst $CsCrF_6$ gave a single line at $g = 1.93$.

Matrix Isolation I.R. Studies.—Matrix isolation studies on CrF_4, CrF_5, and CrF_6 were carried out in an attempt to characterise their products of vaporisation. The only previous reports* on vapour species from these systems were a series of mass-spectrometric/electric deflection observations[6,12,13] and the publication by Glemser and co-workers[10] of a (complex) i.r. spectrum obtained by condensing CrF_6 vapour onto a CsBr

* *Note added in proof*: An electron diffraction study has recently been reported (E. J. Jacob, L. Hedberg, K. Hedberg, H. Davis, and G. L. Gard, *J. Phys. Chem.*, 1984, **88**, 1935) on the vapour species produced by heating CrF_5 to *ca.* 80 °C. The scattering curve is interpreted in terms of manomeric CrF_5 with C_{2v} symmetry.

Table 1. Selected spectroscopic data for fluorides of Cr, Mo, and W

	CrF_4		CrF_5		Cs_2CrF_6
	solid	Ar matrix	solid	liquid[a]	solid
Principal i.r. bands (cm^{-1})	830—750	784.3	830—750	820—650	*ca.* 580
	550—490	—	600—450	580—400	
	ca. 290	303	*ca.* 300	*ca.* 250	
Stretching constant[b]		4.76			
Principal u.v.–visible bands (cm^{-1})	35 000—40 000	32 700	37 000		30 000—40 000
	28 000	22 000 (sh)	26 000		29 400
	21 000		22 400		20 700
	13 500				
	12 350				

	$CsCrF_6$ solid	CrF_6 N_2 matrix	MoF_6 gas[c]	WF_6 gas[c]
Principal i.r. bands (cm^{-1})	*ca.* 600	758.9	741	711
			—	—
			262	258
Stretching constant[c]		3.86—3.92	4.38	4.71
Principal u.v.–visible bands (cm^{-1})	30 000—43 000	38 450	57 500	69 350
	24 150	31 250	52 750	63 100—66 700
	21 100 (sh)	26 700	47 600	58 350

[a] From ref. 11. [b] The value tabulated is for the diagonal *F*-matrix element (mdyn $Å^{-1}$) for the i.r.-active stretching mode. [c] From refs. 26 and 31.

Table 2. Observed[a] and calculated vibration frequencies (cm^{-1}) for matrix-isolated CrF_4 and CrF_6

(*i*) CrF_4	Observed (Ar)	Calculated[b]	Assignment[c]		Observed (N_2)	Assignment[d]	
	789.5	789.4	^{50}Cr		796.0	^{50}Cr	
	788.2	—	S		790.6	^{52}Cr	B_2(?)
	786.6	—	S		788.0	^{53}Cr	
	784.3	784.3	^{52}Cr		785.7	^{54}Cr	
	783.0	—	S	T_2	780.7	^{50}Cr	
	781.8	781.9	^{53}Cr		778.5	^{52}Cr	E(?)
	780.5	—	S		776.4	^{53}Cr	
	779.5	779.5	^{54}Cr			^{54}Cr	
	778.3	—	S				
	303	303	(T_2 bend)		304	('T_2' bend)	

(*ii*) CrF_6	Observed (Ar)	Assignment		Observed (N_2)	Calculated[e] I	Calculated[e] II	Assignment	
	769.6	^{50}Cr		765.3	765.3	765.3	^{50}Cr	
	763.2	^{52}Cr	T_{1u}	758.9	758.9	758.9	^{52}Cr	T_{1u}
	760.0	^{53}Cr		755.8	755.9	755.9	^{53}Cr	
	757.1	^{54}Cr		753.0	752.9	753.0	^{54}Cr	
	—	—		—	250	300	(T_{1u})	

[a] Frequency accuracy ± 0.3 cm^{-1}. [b] Assuming force constants F_{33}, F_{34}, and F_{44} of 4.76, 0.20, and 0.31 mdyn $Å^{-1}$. [c] Bands denoted S are assigned to CrF_4 molecules trapped on minor sites. [d] Assuming a distortion to D_{2d} symmetry. [e] Assuming force constants f_{33}, f_{34}, and f_{44}: I, 3.86, 0.16, and 0.19; II, 3.92, 0.23, and 0.27 mdyn $Å^{-1}$.

window cooled to -180 °C. As a result of preliminary studies on these binary systems, we also became interested in the vaporisation of the salt $CsCrF_6$. Both CrF_4 and CrF_5 are polymeric in their condensed phases, whilst $CsCrF_6$ almost certainly contains discrete $[CrF_6]^-$ units. Its thermal decomposition might therefore provide a simple route to monomeric CrF_5.

The matrix i.r. spectra obtained from these systems all showed intense absorptions in the Cr–F stretching region (600—850 cm^{-1}) and the region down to 200 cm^{-1} was also routinely scanned in a search for bending modes. In view of the reactivity of these systems towards hydrolysis, the spectral region 1 100—1 000 cm^{-1} was also examined in detail for evidence of $\nu_{Cr=O}$ bands. Both $CrOF_4$ and CrO_2F_2 are potential contaminants, and would be volatile at the temperatures employed in these vaporisations.

Another general feature of these spectra was the occurrence of weak satellite peaks accompanying the most intense absorptions. These arise from the natural distribution of chromium isotopes (^{50}Cr, 4.5; ^{52}Cr, 83.8; ^{53}Cr, 9.4; ^{54}Cr, 2.3%) and in addition to revealing vibrational motion involving one atom of chromium, this pattern may also be used quantitatively

as a preliminary indication of structure. The isotope shifts associated with i.r.-active Cr–F stretching modes are, in general, angle dependent. Thus for the antisymmetric stretch of a linear F–Cr–F unit, such as would be found in octahedral CrF_6 or square-planar CrF_4, an overall ^{50}Cr–^{54}Cr separation of *ca.* 12.4 cm^{-1} at 760 cm^{-1} can be estimated, whilst for tetrahedral CrF_4, this separation will be only *ca.* 9.6 cm^{-1}.

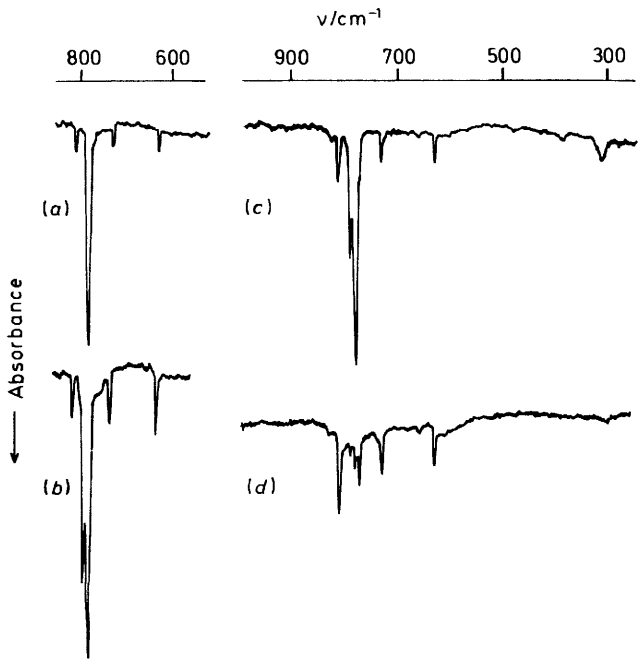

Figure 1. I.r. matrix spectra obtained from (*a*) CrF_4 (Ar), (*b*) CrF_4 (N_2), and (*c*) $CsCrF_6$ (N_2) before diffusion; (*d*) as (*c*), after diffusion

A considerable number of experiments were carried out on these systems employing argon and nitrogen as matrix gases, and the vaporisation of CrF_5 was also studied in a krypton matrix. However, only seven of these need to be discussed in any detail, and the numerical results from these experiments are summarised in Tables 1 and 2.

CrF_4 *and* $CsCrF_6$. When samples of CrF_4 were heated to *ca.* 110—120 °C, and the vapours condensed in an argon matrix, the i.r. spectrum was typically found to contain an intense absorption centred at 784.3 cm^{-1} together with weaker features at 810, 730, 632, and 303 cm^{-1}. Variations in deposition conditions indicated that the bands at 784.3 and 303 cm^{-1} were due to a single species which predominated in more dilute matrices, whilst the remaining three features were more prominent in concentrated matrices. Figure 1(*a*) shows a typical spectrum obtained in the Cr–F stretching region. In nitrogen matrices, a similar pattern of weaker bands was observed (812, 730, 629, and 304 cm^{-1}), but the most intense feature now appeared as a doublet with components at 790.6 and 780.7 cm^{-1} [Figure 1(*b*)].

Figure 1(*c*) shows the nitrogen matrix spectrum obtained from the vaporisation of $CsCrF_6$ at *ca.* 220 °C. This spectrum is essentially identical to that obtained from CrF_4, and controlled diffusion studies confirmed the isolation of two different species. When the deposit shown in Figure 1(*c*) was warmed to *ca.* 25 K, there was a rapid decrease in the intensity of the 790.6/780.7 cm^{-1} doublet, and of the lower frequency feature at 304 cm^{-1}, but the features at 812, 730, and 629 cm^{-1} all increased in intensity. At the same time, a new band at 772 cm^{-1} emerged from the shoulder of the lower frequency component of the doublet. Figure 1(*d*) shows the extent of these spectral changes.

It would therefore appear that CrF_4 and $CsCrF_6$ yield essentially the same matrix isolation i.r. spectra, and that behaviour characteristic of a monomer ⟶ polymer reaction occurs on diffusion. We therefore provisionally assign the intense doublet observed in nitrogen matrices (790.6/780.7 cm^{-1})

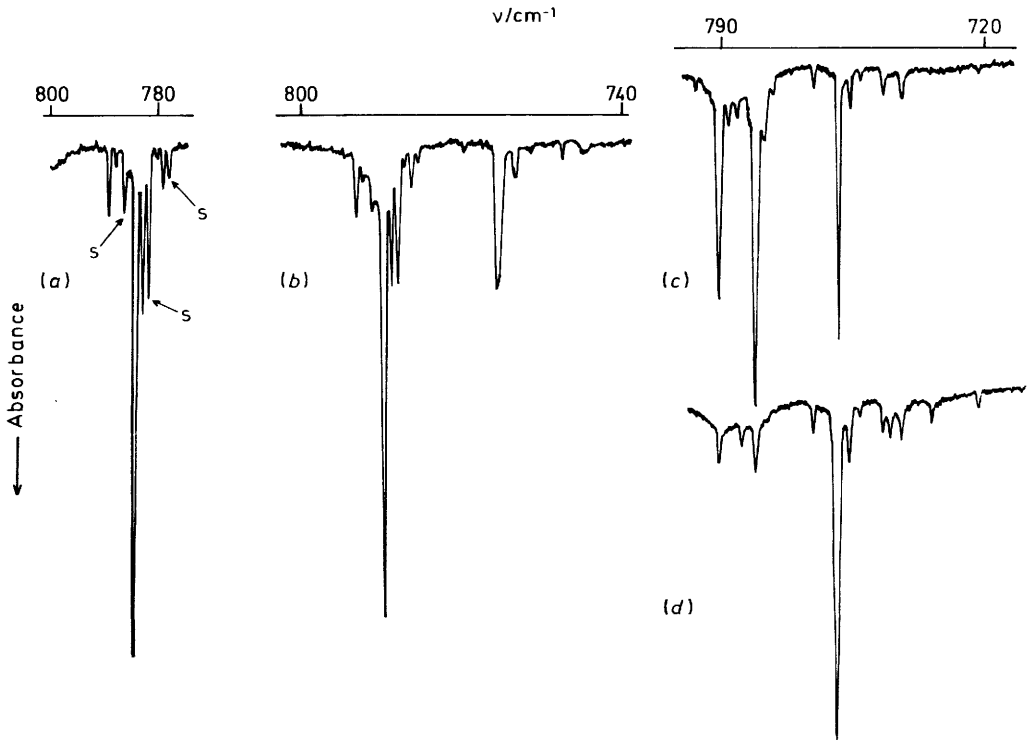

Figure 2. Higher resolution i.r. spectra of principal features obtained from (*a*) CrF_4 (Ar), (*b*) CrF_5 (Ar), (*c*) CrF_5 (N_2), (*d*) CrF_6 (N_2)

and its accompanying band at 304 cm^{-1} to monomeric CrF_4, and propose the same assignment for the corresponding argon matrix features at 784.3 and 303 cm^{-1}.

Figure 2(*a*) shows the argon matrix band at 784.3 cm^{-1} under higher resolution. At least seven sharp components may be distinguished, and this pattern is clearly more complex than would be expected for the natural distribution of CrF_4 isotopomers. However, it is evident that the most intense component at 784.3 cm^{-1} must correspond to a species containing ^{52}Cr (83.8% abundant), and on the basis of their intensities and *relative* spacings from this band, the weaker peaks at 789.5, 781.8, and 779.5 cm^{-1} are assigned to the isotopomers $^{50}CrF_4$, $^{53}CrF_4$, and $^{54}CrF_4$. The magnitude of the ^{50}Cr–^{54}Cr separation (10.0 cm^{-1}) indicates a tetrahedral rather than a square-planar structure. The additional bands at 788.2, 786.6, 783.0, 780.5, and 778.3 cm^{-1} (denoted S) are attributed to CrF_4 molecules trapped on other sites.

Tetrahedral CrF_4 would be expected to have a $^3A_2$ ground state, and should not show any static Jahn–Teller distortion. For a T_d MX_4 species, $\Gamma_{vib} = A_1 + E + 2T_2$. The absorptions at 784.3 and 303 cm^{-1} are thus assigned as the T_2 stretch and T_2 bend respectively, and this assignment is supported by an analysis of the isotope pattern for the stretch.

The secular equations for these T_2 modes are summarised in the Appendix, and it is evident that three independent force-constant parameters are required for their solution. Using the $^{52}CrF_4$ argon matrix absorptions at 784.3 and 303 cm^{-1}, it is found that the observed isotope pattern is reproduced to within experimental error by taking values of 4.76, 0.31, and 0.20 mdyne $Å^{-1}$ for F_{33}, F_{44}, and F_{34} respectively (Table 2).

In nitrogen matrices, the most intense feature from CrF_4 vaporisation is a doublet at 790.6/780.7 cm^{-1}. This doublet could arise from (T_d) CrF_4 trapped on two different sites, but estimates of the intensity ratio of these bands suggest an alternative explanation. Experimentally, it is found that these bands have a constant intensity ratio very close to 1:2, and this could arise from a splitting of the T_2 degeneracy into, for example, $A_1 + E$ in C_{3v} symmetry, or $B_2 + E$ in D_{2d}. A similar lifting of degeneracy has been noted for other species isolated in nitrogen matrices.[16,20] In principle, these two possible explanations for the doublet may be distinguished by a consideration of the isotope structure on each component. Although these isotope patterns overlap in the region 780—790 cm^{-1} [Figure 2(*b*)] the ^{50}Cr–^{52}Cr shift for the higher frequency component, and the ^{52}Cr–^{54}Cr shift for the lower component can be measured to within ± 0.2 cm^{-1}.

As indicated earlier, these shifts are angle dependent, but for T_d isotopomers trapped in similar sites, they should be almost identical. In argon matrices, where one site predominates, values of 5.2 and 4.8 cm^{-1} (both ± 0.2 cm^{-1}) are obtained for the ^{50}Cr–^{52}Cr and ^{52}Cr–^{54}Cr shifts respectively. In nitrogen matrices, the ^{50}Cr–^{52}Cr shift for the higher frequency component is 5.4 cm^{-1}, whilst the ^{52}Cr–^{54}Cr shift for the more intense lower frequency component is only 4.6 cm^{-1}. This difference is outside experimental error, and thus indicates an *angle* distortion from T_d symmetry and hence a lifting of the T_2 degeneracy. In particular, a simple analysis analogous to that described for molecular K_2CrO_4[25] shows that both the *ca.* 1:2 intensity ratio and the differing isotope shifts are consistent with a distortion to D_{2d} symmetry in which the B_2 and E components lie at 790.6 and 780.7 cm^{-1} respectively.

CrF_5 *and* CrF_6. Samples of CrF_5 yielded vapour species at considerably lower temperatures than were necessary for CrF_4, and Figure 2(*b*) shows part of an argon matrix spectrum obtained from a CrF_5 sample at *ca.* 55 °C. It is evident that the most prominent band centred at 784.3 cm^{-1} is very similar to the multiplet previously assigned to CrF_4, the only significant differences being the lower relative intensities of those absorptions (denoted S) attributed to $^{52}CrF_4$ molecules trapped on minor sites. However in addition to these CrF_4 absorptions, this spectrum also shows a prominent new band at 763.2 cm^{-1}.

A typical nitrogen matrix spectrum obtained from CrF_5 is shown in Figure 2(*c*). The two intense bands at 790.6 and 780.7 cm^{-1} are due to CrF_4, and the spectrum also exhibits an intense absorption at 758.9 cm^{-1}. This clearly shows the characteristic chromium isotope pattern, and corresponds to the argon matrix absorption at 763.2 cm^{-1} in Figure 2(*b*). The weak bands at *ca.* 746.6 and 741.8 cm^{-1} are due to $CrOF_4$[16] and this deposit also showed weak features at 1 027.7 cm^{-1} ($CrOF_4$) and at 304 cm^{-1} (CrF_4).

Figure 2(*d*) shows the same spectral region after codeposition of a CrF_6–N_2 mixture with an excess of nitrogen. The band at 758.9 cm^{-1} is now the most prominent feature, and this spectrum shows traces of CrO_2F_2, $CrOF_4$, and CrF_4 together with new weak bands at *ca.* 745 and 734 cm^{-1}. However, despite a careful search in the low-frequency region, there was no obvious bending mode which could be associated with the intense absorption at 758.9 cm^{-1}. In argon matrices, the spectrum obtained from CrF_6–Ar mixtures was qualitatively similar to that from CrF_5 [Figure 2(*b*)] but the band at 763.2 cm^{-1} was relatively more intense.

Finally, one experiment was carried out in which CrF_5 was vaporised and co-condensed in a krypton matrix. Spectral quality was poorer than in argon or nitrogen, but the principal (^{52}Cr) absorptions of CrF_4 and $CrOF_4$ were found at 786.2 and 747 cm^{-1} respectively, and a prominent doublet (intensity ratio 1:2) was noted at 762/758.2 cm^{-1}.

The spectra obtained from CrF_5 and CrF_6 thus all show absorption due to CrF_4, but the most significant new feature is an intense absorption at *ca.* 760 cm^{-1}. This band shows isotope structure consistent with the motion of one atom of chromium, and it is the only prominent feature observed from samples of CrF_6 [Figure 2(*d*)]. The ^{50}Cr–^{54}Cr frequency shift of *ca.* 12.4 cm^{-1} (Table 2) indicates a linear F–Cr–F unit, and it is therefore assigned as the T_{1u} stretching mode in octahedral CrF_6. The related species MoF_6 and WF_6 are known to possess O_h symmetry, and have T_{1u} stretching modes at 741 and 711 cm^{-1} respectively.[26]

In addition to showing a single T_{1u} stretching mode, the i.r. spectrum of CrF_6 should contain one T_{1u} bending mode. This bending mode is found at 262 cm^{-1} in MoF_6 and at 258 cm^{-1} in WF_6, and we therefore expect the bend in CrF_6 to lie in the frequency region 250—300 cm^{-1}. As was the case for CrF_4, the secular equations for the i.r.-active modes in CrF_6 require three force-constant parameters for their solution (see Appendix). In the absence of an experimental value for the bend we therefore selected arbitrary values of 250, 275, and 300 cm^{-1} and calculated three sets of force constants which gave a satisfactory fit for the isotope structure on the stretching mode. Two of these sets are included in Table 2. In view of this additional assumption inherent in the CrF_6 analysis, it would be unwise to treat these force constants too seriously, but it is significant that the stretching constant f_{33} is relatively insensitive to the uncertainty in the position of the bending mode. In addition, this parameter, which represents $f_r - f_{rr}$ in a valence force field, is significantly lower than the analogous parameter in MoF_6 and WF_6 (see Table 1). This difference points to a relatively weak bond in CrF_6 and is consistent with low thermal stability and high reactivity.

Matrix Isolation Ultraviolet–Visible Studies on CrF_4 *and* CrF_6.—U.v.–visible spectra were obtained from samples of CrF_4 and CrF_6 using argon as a matrix gas, and employing deposition conditions similar to those described in the i.r. studies. Chromium tetrafluoride samples gave spectra which consisted of an intense c.t. band at *ca.* 32 700 cm^{-1} with a long

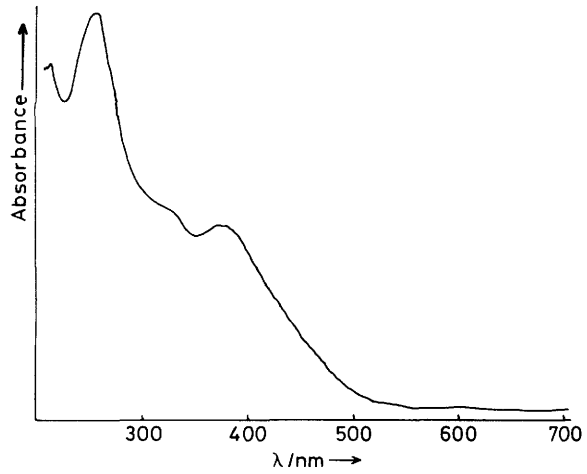

Figure 3. U.v.–visible spectrum of CrF_6 isolated in an argon matrix

tail into the visible region. After extended deposition, a weak shoulder became apparent at *ca.* 22 000 cm^{-1}, but no additional well defined features were detected.

For a d^2 ion in T_d symmetry, three spin-allowed *d–d* bands are expected. In order of increasing energy, these are $^3A_2 \rightarrow {}^3T_2(F)$ (ν_1), $^3A_2 \rightarrow {}^3T_1(F)$ (ν_2), and $^3A_2 \rightarrow {}^3T_1(P)$ (ν_3). The lowest of these corresponds to $10Dq$, and using the value of 22 000 cm^{-1} for this parameter in *solid* (O_h) CrF_4, we estimate that ν_1 for molecular CrF_4 will occur at *ca.* 9 500 cm^{-1} and thus lie below the limit of our spectrometer. It is possible that the shoulder at 22 000 cm^{-1} corresponds to ν_3 [*cf.* ν_3 in $Cr(OBu^t)_4$ at 25 000 cm^{-1}][27] but if so, we would expect to see ν_2 at *ca.* 13 000—15 000 cm^{-1}.

It would therefore seem likely that in comparison with the intense band at 32 700 cm^{-1}, the absorption coefficients of the *d–d* bands are very small, and that they are masked by the low-energy tail. We also note that some difficulty has been encountered in the assignment of the *d–d* spectra of tetrahedral Cr^{IV} compounds.[28,29]

The u.v.–visible spectrum of CrF_6 in argon is shown in Figure 3. Sample deposition was conducted in a similar way to the i.r. studies, except that the spray-on tube was cooled to *ca.* −20 °C to minimise the formation of impurities during deposition. The spectrum consists of three main bands at *ca.* 38 450, 31 250 (sh), and 26 700 cm^{-1}, with a long tail into the visible region. The transition at 26 700 cm^{-1} is of comparable energy to the lowest F→Cr c.t. band in $CrOF_4$ (27 000 cm^{-1})[16] and is consistent with the predictions of the optical electronegativity model.[23]

A more detailed assignment may, however, be made by comparison with the spectra of MoF_6 and WF_6.[30,31] For an O_h MF_6 molecule, the c.t. bands $\pi(F) \rightarrow Cr(t_{2g})$ are, in order of increasing energy,[31] $t_{1g} \rightarrow t_{2g}$, $t_{1u} \rightarrow t_{2g}$, and $t_{2u} \rightarrow t_{2g}$, and these provide a basis for assigning the three observed transitions. In WF_6, these transitions lie at *ca.* 58 350, *ca.* 63 100—66 700, and *ca.* 69 350 cm^{-1} whilst in MoF_6 they occur at *ca.* 47 600, *ca.* 52 750, and *ca.* 57 500 cm^{-1}.[31] A further bathochromic shift of *ca.* 20 000 cm^{-1} between Mo and Cr would therefore account for the observed CrF_6 transitions. An alternative possibility is that some of the CrF_6 transitions arise from $\pi(F) \rightarrow Cr(e_g)$ charge transfer. However, it seems unlikely that the t_{2g}–e_g separation in CrF_6 is less than *ca.* 25 000 cm^{-1}, as $10Dq$ in solid CrF_5 is *ca.* 24 000 cm^{-1}, and this set of c.t. bands is therefore expected at much higher energy (> *ca.* 50 000 cm^{-1}). We therefore assign the CrF_6 c.t. bands as $\pi(F) \rightarrow Cr(t_{2g})$ transitions (Table 1).

Several of the absorptions in the gas-phase spectra of MoF_6 and WF_6 show clearly resolved vibrational progressions which have been correlated with A_{1g}(M–F) stretches.[31] Our spectra of CrF_6 in argon matrices showed little evidence of structure, but using second-derivative recording, a partially resolved progression of *ca.* 530 cm^{-1} could be discerned on the lowest energy band (*ca.* 26 700 cm^{-1}). The estimated value[26] for the A_{1g} stretch in the ground state is *ca.* 720 cm^{-1}.

Thermal Stability of CrF_6 *and* CrF_5: *Additional Observations.*—Although the principal vapour species obtained from samples of CrF_6 appears to be molecular CrF_6, with some CrF_4, CrO_2F_2, and $CrOF_4$ impurity, prolonged deposition sometimes produced two weak bands at *ca.* 734 and *ca.* 745 cm^{-1} [see Figure 2(*d*)] which did not correlate with any other known chromium fluoride species. The same bands were also occasionally observed after prolonged deposition from CrF_5 samples, and although they were never sufficiently intense for a chromium isotope pattern to be observed, it is possible that they could be fundamentals of molecular CrF_5.

In their initial studies on the stability of CrF_6, Glemser and co-workers[3,10] noted that solid CrF_6 readily decomposed into (solid) $CrF_5 + F_2$, and we also noted a colour change from yellow to red, consistent with this reaction, when solid samples of CrF_6 were stored in the dry-box for short periods.

Although the matrix i.r. spectra obtained from samples of CrF_5 appear to indicate complete disproportionation to CrF_4 and CrF_6, it is possible that molecular CrF_5 could be formed in the stepwise thermal decomposition of molecular CrF_6. In order to test this, a sequence of spectra was run in which the stainless-steel tube between the autoclave and the cryostat was slowly heated to *ca.* 100 °C during a CrF_6 deposition. Simultaneous monitoring of the i.r. spectrum over the region 820—700 cm^{-1} clearly showed that as the temperature of the tube was raised the CrF_6 band ceased to grow. However, this change was accompanied not by an increase in the bands at 734 and 745 cm^{-1}, but the rapid growth of CrF_4 monomer and polymer features.

We therefore conclude that the principal decomposition product of molecular CrF_6 is CrF_4, and this would perhaps account for the complexity of Glemser's i.r. spectrum[10] of 'solid CrF_6'. The disproportionation of CrF_5 at low pressures is similar to that found for WF_5,[32] and could account for certain anomalies found in connection with the mass-spectrometric data obtained for CrF_5.

As indicated earlier, samples of CrF_5 have been studied by mass spectrometry[6] and by molecular beam electric deflection.[13] At 25 °C, the relative intensities of the ion currents due to $[CrF_5]^+$, $[CrF_4]^+$, $[CrF_3]^+$, $[CrF_2]^+$, $[CrF]^+$, and Cr^+ were found to be 0.048, 1.00, 0.85, 0.25, 0.32, and 0.38 respectively, whilst at 90 °C the relative intensities of the first four of these were 0.026, 0.52, 1.0, and 0.5.[13] No evidence for polymeric species was found from these studies, and in the absence of any other information, the authors regarded all these ions as arising essentially from molecular CrF_5. However, they noted that the relative abundances of these ions were unusual, and suggested that contamination by CrF_4, or possibly disproportionation, might account for this. Nevertheless, they regarded CrF_5 as the only neutral precursor for $[CrF_5]^+$ and concluded on the basis of a small refocussing effect,[13] that CrF_5 did not have D_{3h} symmetry.

If our conclusions regarding the vaporisation of CrF_5 are correct, it is evident that CrF_6 is the most likely neutral precursor for $[CrF_5]^+$. Either disproportionation, or the thermal decomposition of CrF_6 could then account for the anomalous proportions of $[CrF_4]^+$ and $[CrF_3]^+$ ions. The refocussing effect observed for $[CrF_5]^+$ could arise from a vibrationally induced dipole in (O_h) CrF_6, and although early studies on other transition-metal hexafluorides have not shown this effect,[33] thermally accessible polar states have been invoked

to account for the refocussing behaviour observed for CrF_4 and TiF_4.[13]

Appendix

Vibrational analyses for CrF_4 (T_d) and CrF_6 (O_h) were based on secular equations derived using the Wilson matrix method.[34]

For CrF_4, suitable symmetry co-ordinates for the T_2 modes are: $S_3 = \frac{1}{2}(R_1 + R_2 - R_3 - R_4)$ and $S_4 = \frac{R}{\sqrt{2}}(\theta_{12} - \theta_{34})$ where R_1 is the Cr–F(1) bond, and θ_{12} is the F(1)–Cr–F(2) angle. The corresponding G-matrix elements are then: $G_{33} = \frac{1}{M_F} + \frac{4}{3M_{Cr}}$, $G_{44} = \frac{2}{M_F} + \frac{16}{3M_{Cr}}$, with $G_{34} = G_{43} = -\frac{8}{3M_{Cr}}$. The F-matrix elements F_{33}, F_{44} and F_{34} ($= F_{43}$) were evaluated directly.

In the case of CrF_6, with F(1) and F(2) *trans* the symmetry co-ordinates $s_3 = \frac{1}{\sqrt{2}}(r_1 - r_2)$ and $s_4 = \frac{r}{2\sqrt{2}}(\theta_{13} + \theta_{14} + \theta_{15} + \theta_{16} - \theta_{23} - \theta_{24} - \theta_{25} - \theta_{26})$ for the T_{1u} modes lead to the elements $g_{33} = \frac{1}{M_F} + \frac{2}{M_{Cr}}$, $g_{44} = \frac{2}{M_F} + \frac{8}{M_{Cr}}$, and $g_{34} = g_{43} = -\frac{4}{M_{Cr}}$.

The force constants f_{33}, f_{44}, and f_{34} were again evaluated directly, and it is worth noting, for comparative purposes, that $f_{33} = f_r - f_{rr}$ and $F_{33} = F_R - F_{RR}$.

The vibrational analysis of XY_6 (O_h) species has a chequered history[35–38] but these expressions are identical to those obtained by Claassen,[39] and are believed to be correct.

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