# Characterisation of Chromium(VI) Oxide Tetrafluoride, $CrOF_4$, and Caesium Pentafluoro-oxochromate(VI) $Cs[CrOF_5]$ †

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The title compounds have been characterised by elemental analyses, i.r. and u.v.–visible spectroscopy, and some of their reactions are described. Matrix isolation studies on $CrOF_4$ show characteristic i.r. absorptions at 1 027.7 and 746.3,741.6 $cm^{-1}$ in nitrogen matrices, which are assigned as the $A_1$ (Cr=O) and $E$(Cr–F) modes respectively of the $C_{4v}$ monomer. Chromium isotope fine structure and relative intensity estimates suggest a bond angle of *ca.* 106° for OCrF. The electronic spectrum of matrix-isolated $CrOF_4$ shows prominent charge-transfer bands at 40 000 and 27 000 $cm^{-1}$.

There appear to be only two reports in the literature concerning the chemistry of chromium oxide tetrafluoride, $CrOF_4$. In the first of these, Edwards[1] describes some physicochemical properties and preliminary $X$-ray data, whilst a second paper[2] includes vapour pressure and mass spectrometric data, and describes its controlled synthesis from $CrO_3$ and $F_2$. By comparison with the structural and spectroscopic data available[3–6] for $WOF_4$ and $MoOF_4$, very little is therefore known about the lightest member of this triad, and $CrOF_4$ is also unique among first-row transition-metal complexes in being the only example of a neutral $MOX_4$ species.

This paper describes i.r. and u.v.–visible studies on $CrOF_4$ both as a solid and as a monomeric species isolated in low-temperature inert-gas matrices. In addition, some of its chemical reactions are described, including the preparation of $Cs[CrOF_5]$.

## Experimental

*Techniques.*—The physical measurements and analyses of solid samples of $CrOF_4$ and $Cs[CrOF_5]$ described herein were carried out using standard procedures outlined elsewhere,[7] but special care was found to be necessary in the handling of $CrOF_4$. This compound reacts rapidly with dry Pyrex or silica, and all manipulations were carried out using Monel or stainless steel containers in a nitrogen-filled glove box ($H_2O \leqslant 5$ p.p.m.).

The general features of our matrix-isolation apparatus have been described previously.[6] In this present work, samples of $CrOF_4$ were vaporised at temperatures of 40—50 °C from a Monel ampoule fitted with a Monel Hoke valve (polytetrafluoroethylene seating). Co-condensation with the matrix gas ($N_2$ or Ar, BOC 99.999%) took place over periods of up to 30 min, and spectra were subsequently obtained using the Perkin-Elmer instruments 225 (i.r.) and 554 (u.v.–visible).

## Results and Discussion

*Synthesis and Properties of* $CrOF_4$.—Our samples of $CrOF_4$ were prepared by a method similar to that described by Edwards *et al.*[2] which involves the static fluorination of $CrO_3$. In a typical preparation, dried and powdered $CrO_3$ (2.5 g) was loaded into a 300-$cm^3$ Monel autoclave which was then filled with fluorine to *ca.* 4 atm. The autoclave was then heated to 140 °C (±5 °C) for *ca.* 72 h, whilst maintaining efficient water cooling on the lid. A large number of syntheses were carried out in which reaction conditions (temperature, stoicheiometries, heating time, with or without cooling the lid) were varied systematically. We found that the conditions described above gave a mixture of $CrO_2F_2$ and $CrOF_4$, with yields of the latter typically being *ca.* 25%. Although operating at higher temperatures increased the yield of $CrOF_4$, contamination of the latter with $CrF_5$ often occurred. These two products are difficult to separate owing to their very similar vapour pressures,[2] whilst $CrO_2F_2$ is considerably more volatile, and is easily removed.

When the reaction was complete the autoclave was cooled to room temperature, and the volatile materials ($F_2$ + $CrO_2F_2$) removed. The autoclave was then opened in a dry box and the dark red $CrOF_4$ scraped from the lid and stored in stainless steel containers (Found: Cr, 35.9; F, 53.2. Calc. for $CrOF_4$: Cr, 36.1; F, 52.8%).

$CrOF_4$ hydrolyses rapidly in air and reacts vigorously with water, whilst '880' ammonia and ethanol inflame on contact with the solid. Immediate reaction also takes place with acetone, acetonitrile, and dimethyl sulphoxide. Gentle warming with S, Se, Si, or red P results in ignition, but $I_2$ is fluorinated without flame. However, $CrOF_4$ neither reacts with nor dissolves in $CCl_4$ or $CFCl_3$. The reactivity of $CrOF_4$ as a strong fluorinating/oxidising agent appears to be intermediate between that of $CrOF_3$[7] and $CrF_5$,[8] and as expected,[9] it is much more reactive than $MoOF_4$ or $WOF_4$. When an excess of $BCl_3$ was condensed onto $CrOF_4$ at −196 °C and the mixture then allowed to warm to room temperature, a very dark red solution was produced which, after removal of boron halides, yielded $CrOCl_3$[10] and some $CrO_2Cl_2$. There was no evidence for the formation of $CrOCl_4$. A similar sequence with $BBr_3$ resulted in only a limited reaction, and after removal of the $BBr_3$, the bulk of the $CrOF_4$ appeared unchanged. This was possibly due to an impervious coating of (insoluble) $CrBr_3$ which prevented further reaction. However, on warming the '$CrOF_4$ residue' to *ca.* 60 °C, ignition occurred.

*Infrared Studies on* $CrOF_4$.—Infrared spectra were obtained from powdered samples of $CrOF_4$ pressed between plastic plates, from mulls using sodium-dried Nujol (which reacts only slowly), and in low-temperature inert-gas matrices. The solid phase powder and mull spectra showed a medium intensity band at 1 020 $cm^{-1}$, assigned as ν(Cr=O), and several broad bands at 760—690,670 (Cr–F terminal), and *ca.* 500 $cm^{-1}$ (Cr–F bridging). These spectra indicate a fluorine-bridged polymer structure for the solid, and this is also suggested by the (unpublished) $X$-ray data.[1]

Spectra of matrix-isolated $CrOF_4$ were obtained in both

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† *Non-S.I. units employed:* atm = 101 325 N $m^{-2}$, dyn = $10^{-5}$ N.

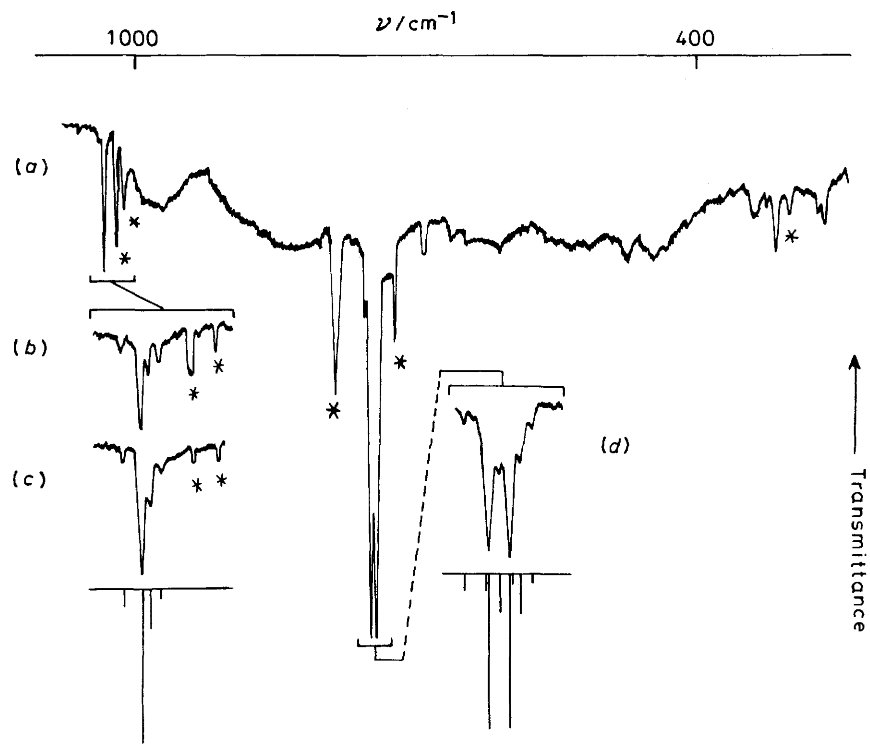

**Figure 1.** I.r. spectra of $CrOF_4$ isolated in nitrogen matrices. (*a*) Low-resolution scan, 1 050—250 cm$^{-1}$. (*b*) High-resolution scan of region 1 040—1 000 cm$^{-1}$. (*c*) As (*b*), but after rapid deposition. (*d*) High-resolution scan of region 760—730 cm$^{-1}$. Bands denoted (*) are due to $CrO_2F_2$

argon and nitrogen, but although the band positions were similar in the two matrices, nitrogen proved to be superior as regards the resolution of chromium isotope fine structure, and thus all frequencies refer to nitrogen matrices unless otherwise stated. Throughout these studies, variable amounts of $CrO_2F_2$ were noted[11] in virtually all i.r. spectra, despite extensive pumping to remove this more volatile impurity prior to deposition. Its presence is believed to arise from partial hydrolysis of $CrOF_4$ during deposition and this probably occurs by contact with those parts of the metal 'spray-on' system which could not be adequately pre-fluorinated. This explanation is supported by the observation that under conditions of *fairly rapid* 'spray on' (*ca.* 10 min) the proportion of $CrO_2F_2$ could be minimised.

Figure 1(*a*) shows a typical nitrogen-matrix i.r. spectrum (1 050—250 cm$^{-1}$) obtained from a sample of $CrOF_4$ under normal, slow deposition conditions. Three prominent absorptions may be identified in the terminal ν(Cr=O) region. These are found at 1 027.7, 1 013.9, and 1 006.7 cm$^{-1}$, whilst in the ν(Cr–F) region there are strong bands at 784.8 and 721.7 cm$^{-1}$, an intense doublet at 746.3,741.6 cm$^{-1}$, and a much weaker feature at 686 cm$^{-1}$. The bending region below 400 cm$^{-1}$ shows weak features at 320.2, 306, 276.5, and 270.5 cm$^{-1}$.

Figure 1(*b*) and (*c*) shows higher resolution studies of the spectral region 1 040—1 000 cm$^{-1}$ under conditions of slow and rapid deposition respectively. The two bands at 1 013.9 and 1 006.7 cm$^{-1}$, with their attendant fine structure are known to be the $B_1$ and $A_1$ Cr=O stretching modes respectively of matrix-isolated $CrO_2F_2$,[11] and we assign the higher frequency multiplet centred at 1 027.7 cm$^{-1}$ to $CrOF_4$. This band shows a well resolved chromium isotope pattern, and can only be due to a terminal Cr=O vibration. Comparison between these two spectra clearly shows that under more rapid deposition conditions, the proportion of $CrOF_4$ is significantly greater, albeit with some deterioration in spectral quality.

The Cr–F stretching region between 600 and 800 cm$^{-1}$ shows three prominent features: an intense doublet at 746.3,741.6 cm$^{-1}$, and additional absorptions at 784.8 and 721.7 cm$^{-1}$. These two latter bands are due to $CrO_2F_2$,[11] and variation of deposition conditions reveals a correlation between the intensity of the doublet and that of the Cr=O band at 1 027.7 cm$^{-1}$. The 746.3,741.6 cm$^{-1}$ doublet is therefore assigned to $CrOF_4$ and this is supported by the presence of chromium isotope structure on both components, when examined under high resolution [Figure 1(*d*)]. This spectral region also shows a much weaker band at 686 cm$^{-1}$ which appears to be associated with the doublet, and is therefore also assigned to $CrOF_4$.

In the bending region, the absorption at 306 cm$^{-1}$ corresponds closely to the $\nu_4$ fundamental in $CrO_2F_2$ (304 cm$^{-1}$) and it showed a variable intensity ratio with respect to the features at 320.2, 276.5, and 270.5 cm$^{-1}$. These latter bands are provisionally assigned as fundamentals of $CrOF_4$, although because of their comparative weakness in relation to the feature at 1 027.7 cm$^{-1}$, this assignment remains tentative.

*Spectral Interpretation.*—In our earlier paper[6] on matrix-isolated $WOF_4$ and $MoOF_4$, the i.r. spectra were shown to be consistent with the (known) square-pyramidal geometry ($C_{4v}$), and it was possible to assign the observed bands to specific fundamental modes by comparison with earlier gas-phase data. For molecular $CrOF_4$ there are no previous spectroscopic or structural data, but there is sufficient correspondence between the spectra observed here and those obtained for $MoOF_4$ and $WOF_4$ first to propose a similar $C_{4v}$ structure for $CrOF_4$, and secondly to suggest a vibrational assignment. Both these assumptions may be tested by a detailed analysis of the chromium isotope shifts.

For this $C_{4v}$ geometry, $\Gamma_{vib.} = 3A_1 + 2B_1 + B_2 + 3E$, of which $\Gamma_{Cr=O} = A_1$, $\Gamma_{Cr-F} = A_1 + B_1 + E$, and $\Gamma_{bend} = A_1 + B_1 + B_2 + 2E$. I.r. activity is vested only in the $A_1$ and

**Table 1.** I.r.-active fundamentals (cm$^{-1}$) for $CrOF_4$, $MoOF_4$, and $WOF_4$ isolated in low-temperature nitrogen matrices

| $CrOF_4$[a] | $MoOF_4$[b] | $WOF_4$[b] | Assignment |
|---|---|---|---|
| 1 027.7 | 1 050 | 1 050 | $\nu_1$ ($A_1$) |
| 686 | 714 | 726 | $\nu_2$ ($A_1$) |
| 276.5 | 267 | 254 | $\nu_3$ ($A_1$) |
| 746.3,741.6 | 708 | 686 | $\nu_7$ ($E$) |
| 320.2 | 309,304 | 309,304 | $\nu_8$ ($E$) |
| 270.5 | 238 | 236 | $\nu_9$ ($E$) |

[a] This work; $^{52}Cr$ isotopes. [b] Ref. 6; centre of isotope pattern.

$E$ modes, and so only six fundamentals are expected to be observed. Table 1 compares the positions of the i.r.-active fundamentals in $WOF_4$ and $MoOF_4$ with the bands assigned here to $CrOF_4$. In the stretching region, $\nu_1$(Cr=O) is unequivocal, and we assign both components of the 746.3,741.6 cm$^{-1}$ doublet to the degenerate Cr–F $E$ mode $\nu_7$. Not only is this expected to be the most intense Cr–F stretching mode in the i.r., but the doublet is characteristic of a slight lifting of degeneracy which has previously[6] been noted in nitrogen-matrix spectra. In argon matrices, a single broad band is observed centred at 744 cm$^{-1}$. The remaining weak feature observed in this region at 686 cm$^{-1}$ is tentatively assigned as the $A_1$(Cr–F) stretch, $\nu_2$. Although this mode lies above $\nu_7(E)$ in $WOF_4$ and $MoOF_4$ (see Table 1) there are good reasons for it appearing *below* $\nu_7$ when the central atom mass is relatively light. The weak bending modes cannot be assigned as readily, but the frequency ordering $\nu_8(E) > \nu_3(A_1) > \nu_9(E)$ is found for both $WOF_4$ and $MoOF_4$, with little apparent dependence on central atom mass, and we propose corresponding assignments for the features at 320.2, 276.5, and 270.5 cm$^{-1}$.

It is evident from these results that the stretching modes in $CrOF_4$ are reasonably well separated from the bending modes, and if one assumes that stretch–bend coupling may be neglected, it is then possible to use the chromium isotope data from the stretching modes to estimate the one independent bond-angle parameter in the $C_{4v}$ pyramid. Force constant parameters which simulate the observed isotope shifts may then be extracted. A similar approach has been used with reasonable success in the vibrational analyses of closely related species such as molecular $CrO_2F_2$, $CrOCl_3$, and $K_2[CrO_4]$.[10–12]

The Appendix summarises the $F$ and $G$ matrix elements relevant to this problem for a general $XYZ_4$ molecule. In the special case where XYZ = 90°, these expressions are identical to those derived by Begun *et al.*[13] The secular equations resulting from these matrix elements take the form of a quadratic for the $A_1$ modes, but for the single $E$ mode we have equation (i). This equation leads directly to θ (and hence β)

$$\lambda_7 = 4\pi^2\nu_7{}^2 = (F_r - F_{rr'})(1/M_F + 2\sin^2\theta/M_{Cr}) \quad \text{(i)}$$

when frequency data for two different isotopic species are available.

However, this particular mode in $CrOF_4$ is split into an equal doublet in our nitrogen-matrix studies. This must reflect a small departure from ideal $C_{4v}$ symmetry which might arise either from slight differences within the sets of symmetry-related bond angles, or between the Cr–F bonds themselves. In the latter case, the two components of the $E$ mode $\lambda_{7a}$ and $\lambda_{7b}$ can be regarded as arising from two secular equations which have identical $G$ matrix terms, but slightly different force constants $F_{77a}$ and $F_{77b}$. If this assumption is correct for the origin of the splitting, the isotope fine structure on each component of the doublet should yield the same value for β, and this can be tested experimentally.

**Table 2.** Observed and calculated frequencies (cm$^{-1}$) for $CrOF_4$ isotopic species in nitrogen matrices

| Observed[a] | Calculated[b] | Assignment | |
|---|---|---|---|
| 1 033.0 | 1 033.0 | $^{50}Cr$ | $\nu_1$ |
| 1 027.7 | 1 027.7 | $^{52}Cr$ | |
| 1 025.2 | 1 025.2 | $^{53}Cr$ | |
| 1 022.7 | 1 022.7 | $^{54}Cr$ | |
| | 687.0 | $^{50}Cr$ | $\nu_2$ |
| 686 | 686.0 | $^{52}Cr$ | |
| | 685.5 | $^{53}Cr$ | |
| | 685.0 | $^{54}Cr$ | |
| 751.9 | 751.9 | $^{50}Cr$ | $\nu_{7a}$ |
| 746.3 | 746.3 | $^{52}Cr$ | |
| 743.7 | 743.6 | $^{53}Cr$ | |
| (overlapped) | 740.9 | $^{54}Cr$ | |
| (overlapped) | 747.3 | $^{50}Cr$ | $\nu_{7b}$ |
| 741.6 | 741.6 | $^{52}Cr$ | |
| 739.1 | 738.9 | $^{53}Cr$ | |
| 736.5 | 736.3 | $^{54}Cr$ | |

[a] Frequency accuracy ±0.4 cm$^{-1}$. Components of split $E$ mode ($\nu_7$) tabulated and assigned separately. [b] Assuming OCrF = 112°, and $F$-matrix elements $F_{11}$ = 7.58, $F_{22}$ = 4.59, $F_{12}$ = 0.4, $F_{77a}$ = 3.82, and $F_{77b}$ = 3.78 mdyn Å$^{-1}$ respectively.

The line diagram accompanying Figure 1(*d*) shows the calculated chromium isotope pattern for the split $E$ mode assuming a uniform value of β = 112° and equal FCrF angles. The numerical data are summarised in Table 2, and the agreement is clearly satisfactory. A difference of *ca.* 1% between the parameters $F_{77a}$ and $F_{77b}$ is sufficient to produce the basic doublet, and the isotope structure on each component is consistent with a single value of β.

When this value is substituted into the $A_1$ secular equations, the isotope pattern for the Cr=O mode may be obtained, and the line diagram accompanying Figure 1(*c*) summarises this calculation. Here, however, there is no independent check, as the observed spectrum may be fitted almost exactly with an appropriate choice of interaction constant $F_{12}$. However, the value of this parameter and of the diagonal Cr=O and Cr–F constants $F_{11}$, $F_{22}$, and $F_{77}$ are all very reasonable, and similar to those found in $CrO_2F_2$. The numerical data are included in Table 2.

This analysis therefore supports the $C_{4v}$ model proposed for $CrOF_4$, and provides an estimate of *ca.* 112° for the angle OCrF. All other models, including the $C_{3v}$ trigonal bipyramid, would be expected to show a more complex pattern of bands in the Cr–F stretching region and are therefore discounted. Molecular $CrOF_4$ thus appears to be isostructural with the species $MoOF_4$ and $WOF_4$. However, for the latter two species, electron-diffraction studies have shown that the angles β are very similar, with values 104 and 105° respectively,[3,4] and it is worth examining briefly whether our estimate of 112° for $CrOF_4$ is realistic.

The most important source of systematic error in the above treatment is probably the neglect of anharmonicity. The secular equation used to estimate β is essentially the same as has been used for non-linear triatomics, where it is known[14] that the neglect of anharmonicity leads to a systematic error in bond angle. In our analysis of $CrOF_4$, this error is such that the derived value of β will be an *upper limit*,[14] and the error may be as large as 5 or 6°. In addition, one can estimate error limits of *ca.* ±4° arising directly from uncertainties in the measured isotope frequencies, and we anticipate a small error arising from the neglect of coupling with the bending modes. In view of these uncertainties, we believe that a more realistic value for β is *ca.* 106 ± 6°.

Finally, there is one independent check which may be made on this estimate which involves our band assignments. It is evident from Figure 1(*a*) that the feature at 686 cm$^{-1}$ assigned as $\nu_2(A_1$, Cr–F) is very much weaker than the 746.3,741.6 cm$^{-1}$ doublet $\nu_7$. The intensity ratio is difficult to estimate, but is *ca.* 1:50. If it is assumed that the Cr–F stretching modes are only weakly coupled to the remaining molecular vibrations then application of the bond dipole model for i.r. intensities[15] allows the relative intensities of these modes to be predicted *via* the

$$\frac{I_E}{I_{A_1}} = \tan^2\theta\left(\frac{1}{M_F} + \frac{2\sin^2\theta}{M_{Cr}}\right)\Bigg/\left(\frac{1}{M_F} + \frac{4\cos^2\theta}{M_{Cr}}\right) \quad \text{(ii)}$$

expression (ii). This approach has been used with some success in interpreting relative band intensities for several matrix-isolated molecules[16,17] and substitution here of $\theta$ values in the range 68—80° ($\beta = 106 \pm 6°$) leads to an expected intensity ratio of between 8:1 and 55:1.

*U.v.–Visible Studies on* $CrOF_4$.—The diffuse-reflectance spectrum of $CrOF_4$ was obtained from a sample of the solid, diluted with $BaSO_4$, and exhibited broad bands with rather ill defined maxima at *ca.* 40 000, *ca.* 27 000, and *ca.* 21 000 cm$^{-1}$, together with a long tail on the low-energy side of this last band. There are no SCF-$X\alpha$-SW molecular orbital calculations on this compound, and in attempting an assignment, we have therefore relied on the optical electronegativity ($\chi_{opt.}$) model.[18] This approach has given reasonable predictions of the lowest-energy ligand⟶metal charge-transfer (c.t.) bands in related molecules.[6,16,19] No data on five- or six-co-ordinate $Cr^{VI}$ are available in the literature, but $\chi_{opt.}$ for four-co-ordinate $Cr^{VI}$ has been reported[18] as 2.3 and one would anticipate higher co-ordination to result in values of $\chi_{opt.}$ in the range 2.8—2.9.[18] Using this estimate, and taking $\chi_{opt.}$ for $F^-$ and $O^{2-}$ to be 3.9 and 3.6 respectively, we obtain predictions of the *lowest* energy O⟶Cr and F⟶Cr c.t. bands as *ca.* 21 000 and *ca.* 30 000 cm$^{-1}$ respectively. Realistic error limits would be *ca.* ±2 000 cm$^{-1}$, and these predictions thus provide tentative assignments for the experimentally observed bands at *ca.* 21 000 and *ca.* 27 000 cm$^{-1}$.

The electronic spectrum of molecular $CrOF_4$ isolated in a nitrogen matrix under conditions of rapid deposition is shown in Figure 2, and consists of major absorptions centred at 40 000 and 27 000 cm$^{-1}$, with a much weaker, broad feature at *ca.* 22 000 cm$^{-1}$ which has a low-energy tail.

The electronic spectrum[20] of $CrO_2F_2$ shows a strong band at *ca.* 21 000 cm$^{-1}$ and a weaker feature at *ca.* 29 000 cm$^{-1}$, and it would appear that this possible impurity does not contribute significantly to the spectrum in Figure 2. This conclusion is supported by the fact that i.r. spectra obtained from the same sample before and after these u.v.–visible studies revealed only small amounts of $CrO_2F_2$.

The $CrOF_4$ u.v.–visible spectrum is similar in profile to those previously obtained[6] for $MoOF_4$ and $WOF_4$, but as expected, the absorptions occur at significantly lower energies. The optical electronegativity model outlined above suggests assignments for the features at 22 000 and 27 000 cm$^{-1}$ as O⟶Cr and F⟶Cr c.t. respectively, and for the latter band, this is supported by (partially resolved) vibrational fine structure. Using 2nd derivative recording, the band at 27 000 cm$^{-1}$ is seen to contain a single progression of 615 ± 70 cm$^{-1}$ (Figure 2) which can be correlated with the ground state $A_1$ (Cr–F) mode tentatively identified at 686 cm$^{-1}$. No progressions were evident on the band at 40 000 cm$^{-1}$, but the remaining feature at 22 000 cm$^{-1}$ and the low-energy tail showed evidence of some structure. However, this could not be convincingly resolved even with derivative spectroscopy, although it appeared that at least two overlapping progressions were present.

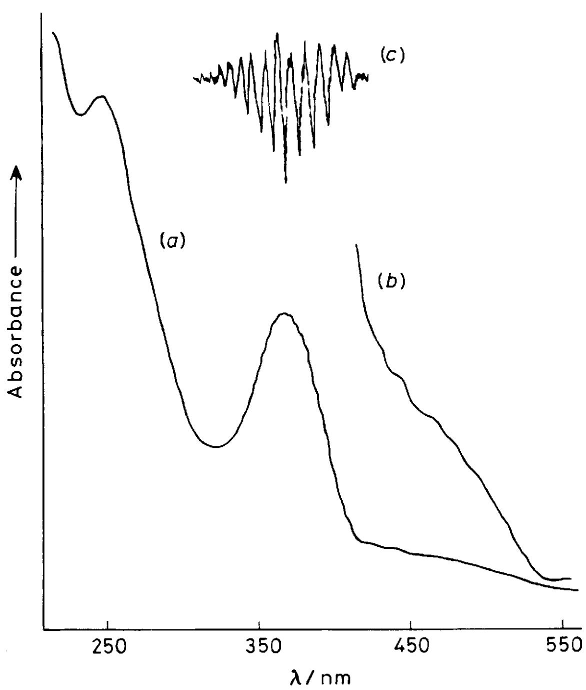

**Figure 2.** U.v.–visible spectra of $CrOF_4$ isolated in nitrogen matrices. (*a*) Survey spectrum, 230—550 nm. (*b*) Thicker deposit, 400—550 nm. (*c*) 2nd derivative spectrum, 300—420 nm

*Synthesis and Characterisation of* Cs[$CrOF_5$].—Several attempts were made to prepare Cs[$CrOF_5$] by heating mixtures of $CrOF_4$ and CsF *in vacuo* in a Monel container. These were largely unsuccessful, as much of the $CrOF_4$ sublimed onto cooler parts of the container, but this separation of reactants could be prevented by working under a pressure of 1 atm $N_2$. In a typical reaction, dry CsF (0.48 g, 3.2 mmol) and $CrOF_4$ (0.5 g, 3.5 mmol) were intimately mixed in a dry box, and placed in a 20-cm$^3$ Monel container fitted with a Hoke valve. The container was filled with dry $N_2$ to 1 atm, and then heated to 100 °C for 1 h, with occasional shaking. After cooling to room temperature, the container was opened in a dry box, and an orange-brown solid scraped off the base.

This material had the composition expected for Cs[$CrOF_5$] (Found: Cr, 17.6; F, 31.9. Calc. for $CsCrOF_5$: Cr, 17.6; F, 32.0%). It reacted with water to give a yellow solution, and although hydrolysing rapidly in air, appeared to be stable for long periods when sealed in glass ampoules. A Nujol mull spectrum of the product showed a moderately intense i.r. band at 955 cm$^{-1}$, which is assigned as ν(Cr=O), and an intense, broad absorption in the range 650—720 cm$^{-1}$ assigned as terminal ν(Cr–F). The diffuse-reflectance u.v.–visible spectrum was not well defined, but was similar in profile to that of $CrOF_4$.

These spectra suggest that in Cs[$CrOF_5$], the anion is six-co-ordinate, with no fluorine bridging. In contrast, Cs[$CrOF_4$] shows both terminal and bridging ν(Cr–F) i.r. absorptions.[7]

## Conclusions

This work demonstrates that $CrOF_4$ can readily be prepared and that despite its reactivity, it can be satisfactorily

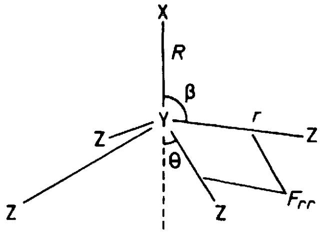

**Figure 3.** Parameters used to define geometry of $CrOF_4$ ($C_{4v}$)

characterised by i.r. and u.v.–visible spectroscopy. In particular, the matrix-isolated monomer is shown to have $C_{4v}$ geometry, whilst the i.r. spectrum of the solid suggests a fluorine-bridged polymer. $CrOF_4$ is a vigorous fluorinating agent, and in addition to its reactions with a variety of common reagents, it has been employed in the first synthesis and characterisation of $Cs[CrOF_5]$.

## Appendix

The parameters used in the vibrational analysis of $CrOF_4$ are defined in Figure 3. Using the internal co-ordinates $R$ and $r$, the following $F$ and $G$ matrix elements may be derived[15] for the stretching modes.

$$A_1 \quad G_{11} = \frac{1}{M_X} + \frac{1}{M_Y};\ G_{22} = \frac{1}{M_Z} + \frac{4\cos^2\theta}{M_Y};$$

$$G_{12} = G_{21} = \frac{-2\cos\theta}{M_Y}$$

$$F_{11} = F_R;\ F_{22} = F_r + F_{rr'} + 2F_{rr};\ F_{12} = F_{21} = 2F_{Rr}$$

$$B_1 \quad G_{44} = \frac{1}{M_Z};\ F_{44} = F_r + F_{rr'} - 2F_{rr}$$

$$E \quad G_{77} = \frac{1}{M_Z} + \frac{2\sin^2\theta}{M_Y};\ F_{77} = F_r - F_{rr'}$$

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