On the Vibrational Assignment and Bond Angles in Chromyl Fluoride

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Gas-phase Raman and matrix i.r. spectra are reported for CrO_2F_2. An unambiguous vibrational assignment has been made for the stretching modes, and the bond angles estimated as O–Cr–O 102.5 and F–Cr–F 124°. The differences in structural patterns between transition-metal and main-group oxyhalides are emphasized and discussed.

VALENCE-SHELL ELECTRON-PAIR REPULSION (VSEPR) theory[1] has been widely used to rationalize the structures of compounds of the *p*-block elements, although it is by no means the only useful approach.[2] It is attractive in that its success is achieved with a small number of simple postulates, and the number of failures {notably $[InCl_5]^{2-}$, $N(SiH_3)_3$, and $[TeCl_6]^{2-}$} is small.[3-5] However, it does not appear to be applicable to derivatives of the transition metals even when the element is exhibiting the group oxidation state. This observation is just one indication of the profound chemical and structural differences between main-group (*p*-block) and analogous transition elements. Interesting examples include C_{2v} SOF_4,[6] but C_{4v} WOF_4,[7] and it is noteworthy that although WOF_4 and ReO_2F_3[8] are readily obtained as monomers, both $TeOF_4$[9] and IO_2F_3[10] form strong oxygen-bridged dimers.

We have been concerned with the molecular shapes and structures of formally analogous compounds of the non-transition and transition elements and have noticed that some important properties of CrO_2F_2 are in dispute. Investigations of its structure by electron diffraction[11] and by microwave spectroscopy[12] have led to grossly different values for the bond angles, and the vibrational assignment proposed several years ago by Stammreich *et al.*[13] (on the basis of data acquired by Hobbs[14]) has recently been challenged.[15] As a prelude to a detailed study of the fluorescence spectrum of CrO_2F_2,[16] we have examined the gas-phase Raman spectrum and matrix i.r. spectrum of this molecule. Our results demonstrate that the vibrational assignment of Stammreich *et al.*[13] was substantially correct, and, furthermore, provide an independent estimate of the bond angles, based on i.r. frequency shifts associated with the naturally occurring chromium isotopes.

EXPERIMENTAL

Chromyl fluoride was prepared from the reaction between IF_5 and CrO_3 at 100 °C,[17] purified by repeated distillation in a metal vacuum system, and stored in a Monel vessel. It is a volatile solid, subliming at 29.6 °C to give an orange vapour. The electronic absorption spectrum shows a prominent band at *ca.* 21 000 cm^{-1}, and it is known to be photochemically unstable, particularly to shorter wavelength radiation. Our Raman spectra of the vapour were obtained using a Monel cell fitted with sapphire windows. Although irradiation with the yellow line of a krypton laser led to rapid decomposition, excitation with the red 647.1 nm line produced only minor spectral changes with time. Raman spectra were recorded using a modified Spex 1401 monochromator. Infrared spectra of matrix-isolated species were obtained using a Perkin-Elmer 225 spectrometer (calibrated with suitable lines in the spectra of water vapour, carbon dioxide, and ammonia) together with an Air Products Displex system to obtain cryogenic temperatures.

RESULTS AND DISCUSSION

There are nine fundamental vibrations for the C_{2v} molecule CrO_2F_2, of which four may reasonably be described as stretching motions. The a_1 modes are ν_1 (Cr–O stretch) and ν_2 (Cr–F stretch) and following the convention[14] that the CrO_2 residue defines the σ_{xz} plane, the antisymmetric stretching modes are then ν_6 (b_1 Cr–O stretch) and ν_8 (b_2 Cr–F stretch). Stammreich *et al.*[13] using Hobbs' gas-phase i.r. data,[14] assigned the stretching modes as follows: ν_1 1 006, ν_2 727, ν_6 1 016, and ν_8 789 cm^{-1}. Recently[15] *liquid*-phase Raman studies have been reported on CrO_2F_2, and the following features detected in the stretching region: 1 045 (ρ_p 0.93), 995 (ρ_p 0.36), 770 (ρ_p 0.67), and 708 cm^{-1} (ρ_p 0.16). On the basis of these observations, it was suggested[15] that a medium-intensity band found at 1 057 cm^{-1}, and assigned as a *combination* band in the original gas-phase i.r. study, should be reassigned as ν_6, leaving the very strong feature at 1 016 cm^{-1} to be explained either as a combination band or as unresolved rotational fine structure. The unusual value $\rho_p = 0.93$ observed for the band at 1 045 cm^{-1} was not discussed.

From our gas-phase Raman spectra we were able to locate unambiguously two a_1 stretching modes at 1 007 and 728 cm^{-1}, both in excellent agreement with the i.r. data.[14] In this Raman work, ρ_p values of *ca.* 0.1 were obtained for both bands. The frequency agreement with the corresponding Raman bands in the liquid (995 and 708 cm^{-1}) is acceptable in view of the change of phase, but the reported[15] value of $\rho_p = 0.36$ for the feature in the liquid spectrum at 995 cm^{-1} is appreciably higher than our gas phase result.†

When CrO_2F_2 was isolated in a nitrogen matrix at 10 K the i.r. spectrum showed four prominent peaks in the stretching region. Under high resolution each band was seen to consist of four components due to the various chromium isotopes present in natural abundance: ^{50}Cr 4.3, ^{52}Cr 83.8, ^{53}Cr 9.6, and ^{54}Cr 2.4%. For $^{52}CrO_2F_2$ we observed absorptions at 1 013.9, 1 006.7, 784.8, and

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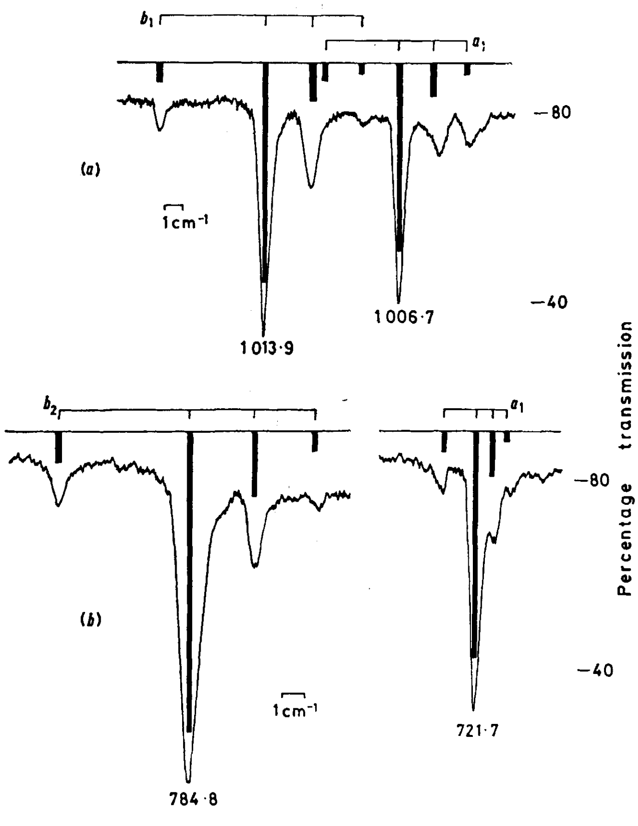
† It should be noted that the liquid Raman results do not readily allow one to dismiss the possibility that polymers may be present.

721.7 cm^{-1}, all within 5 cm^{-1} of the gas-phase fundamentals reported by Hobbs.[14] A typical nitrogen-matrix spectrum of these four bands, recorded with a resolution of *ca.* 0.4 cm^{-1}, is shown in the Figure. Argon-matrix spectra were qualitatively similar but of poorer quality. Both the gas-phase Raman and the matrix i.r. data are therefore in accord with the original assignments for the stretching modes by Stammereich, and the danger inherent in making inferences on properties of monomeric species from vibrational data of condensed phases is emphasized.

High-resolution Matrix I.r. Spectrum.—The frequency shifts resulting from isotopic substitution are influenced both by the molecular force field and by bond angles and masses in the associated *G* matrix. A rigorous determination of the complete force field is not yet possible, since it contains 17 independent elements even in the harmonic approximation, while the number of independent frequencies is much smaller than this. Since the frequency of the highest bending mode is less than half that of the lowest stretching mode, we have chosen to assume that the stretching and bending modes may be separated. In this approximation, the five general valence stretching constants are varied so as to reproduce all the isotopic stretching frequencies. The main advantage of this approach is that estimates of the O–Cr–O and F–Cr–F bond angles may be derived directly from measurement of the isotopic shifts of the b_1 and b_2 stretching modes, respectively, using the equation for the antisymmetric stretching mode of a C_{2v} XY_2 triatomic unit.[18] Here



Observed and calculated i.r. spectra (cm^{-1}) for the Cr–O (*a*) and Cr–F (*b*) modes of CrO_2F_2 isolated (*ca.* 1 : 1 000) in a nitrogen matrix at *ca.* 12 K

$$\lambda = 4\pi^2\nu^2 = (F_r - F_{rr})\left(\frac{1}{M_Y} + \frac{2\sin^2\theta}{M_X}\right)$$

M_X and M_Y represent the masses of atoms X and Y, F_r and F_{rr} the principal and interaction stretching force constants, and 2θ the bond angle Y–X–Y. Applying this equation to the CrO_2 and CrF_2 units in chromyl fluoride, we calculated the bond angles to be O–Cr–O 102.5 and F–Cr–F 124°, using the ^{50}Cr–^{52}Cr isotopic shifts.

In the Table, the experimental frequencies are compared with those calculated for the four isotopic species, using the above bond angles and the force constants listed, while the line diagram accompanying the Figure shows the frequency and intensity fit for the components of each fundamental, taking into account the natural abundance of the various chromium isotopes. The spectral fit is within our estimated frequency uncertainty.

Stretching fundamentals (cm^{-1}) of CrO_2F_2

Observed					
I.r. gas	Raman gas	I.r. N_2 matrix	Calculated[a]	Assignment	
			1 010.6	^{50}Cr–O	a_1
1 006	1 007	1 006.7	1 006.7	^{52}Cr–O	
		1 004.6	$1\,004.8_5$	^{53}Cr–O	
		1 003.1	1 003.1	^{54}Cr–O	
		723.2	723.0_5	^{50}Cr–F	a_1
727	728	721.7	721.7	^{52}Cr–F	
		720.8	721.0_5	^{53}Cr–F	
		720.2	720.4	^{54}Cr–F	
		1 019.4	1 019.4	^{50}Cr–O	b_1
1 016		1 013.9	1 013.9	^{52}Cr–O	
		1 011.4	1 011.3	^{53}Cr–O	
		1 008.6	1 008.8	^{54}Cr–O	
		790.5	790.5	^{50}Cr–F	b_2
789		784.8	784.8	^{52}Cr–F	
		782.0	782.1	^{53}Cr–F	
		779.4	779.5	^{54}Cr–F	

[a] Calculations based on force constants $F_{Cr-O} = 7.429$, $F_{Cr-O,Cr-O} = 0.382$, $F_{Cr-F} = 4.774$, $F_{Cr-F,Cr-F} = 0.384$, $F_{Cr-O,Cr-F} = 0.390$ mdyn Å^{-1} and assuming O–Cr–O = 102.5° and F–Cr–F = 124°.

It is difficult to give a realistic estimate of the overall uncertainty in our bond-angle values, since the contribution from systematic errors may be at least as great as that from random effects. A change in the ^{50}Cr–^{52}Cr isotopic shift of only 0.2 cm^{-1} leads to changes of *ca.* 3.5° for O–Cr–O and *ca.* 6.5° for F–Cr–F; we are confident, however, that the experimental uncertainty in the frequency *shifts* is less than 0.2 cm^{-1}. Two of the approximations involved in the normal-co-ordinate analysis already outlined might be expected to lower the reliability of our bond-angle estimates. The neglect of anharmonicity has been shown [19] to lead to an upper limit for the bond angle in a triatomic unit if isotopic substitution is carried out at the central atom. There will also be a small error arising from our assumption of the 'high frequency' separation of stretching and bending modes.

We are not aware of a sufficient number of cases in which bond angles derived by this method have been calibrated against values determined by reliable diffraction or spectroscopic techniques for us to be able to assess how serious this approximation might be, but we feel that our derived bond angles for CrO_2F_2 are unlikely to differ by more than 10° from the true values. The estimates of 102.5° for O–Cr–O and 124° for F–Cr–F are pleasingly close to the electron-diffraction results[11] of 102.1° (1σ 0.4°) and 118.9° (1σ 0.5°) respectively, and may thus be taken not only as a confirmation of these latter, but also as an indication that the results of the microwave investigation[12] (O–Cr–O 110° and F–Cr–F 98°) are erroneous.

Bond Angles in CrO_2F_2 *and* SO_2F_2.—By applying the VSEPR principle that formal double bonds require a greater proportion of the co-ordination sphere round a central atom than do single bonds,[1] one can readily account for the observation that in SO_2F_2 the angle O–S–O (= 124.0°) is significantly greater than F–S–F (= 96.1°).[20] Our work described here on CrO_2F_2 supports the results of the electron-diffraction investigation[11] which gives O–Cr–O as 102.1° and F–Cr–F as 118.9°, *i.e.* these angles are quite different from the values predicted using the above principles. A similar contrast between transition-metal and main-group (*p*-block) compounds may be noted in other pairs of related molecules, such as VOF_3[21] (F–V–F 111.3°) and POF_3[22] (F–P–F 101.3°), $VOCl_3$[23] (Cl–V–Cl 111.3°) and $POCl_3$[22] (Cl–P–Cl 103.3°), or MnO_3F[24] (O–Mn–O 110.5°) and ClO_3F[25] (O–Cl–O 116.6°); it appears that terminal bonds to oxygen from transition metals are less sterically demanding than those from main-group elements. It is tempting to correlate this difference in bonding patterns with the ready accessibility of *d* orbitals for transition elements. However, in the absence of reliable quantum-mechanical calculations, we feel such a step to be unwarranted, and turn instead to two very simple models which might be used to account for the difference between CrO_2F_2 and SO_2F_2.

Ab initio calculations have been mentioned[26] which predict the net atomic charges in CrO_2F_2 to be +2.1 on Cr, −0.39 on O, and −0.62 on F but +0.69 on S, −0.09 on O, and −0.26 on F in SO_2F_2. The entirely plausible contention that the bonding in CrO_2F_2 has much greater ionic character than that in SO_2F_2 is supported not only by those figures but also by the available force-constant data, which although not yet rigorously determined are adequate for present purposes. Approximate values for the bending force constants in mdyn Å rad^{-2} * are F_{OSO} 1.83, F_{FSF} 1.33 in SO_2F_2,[27] but only F_{OCrO} 1.19 and F_{FCrF} 0.32 in CrO_2F_2.[28] It has been suggested[11] that the unexpectedly large F–Cr–F angle in CrO_2F_2 is caused chiefly by electrostatic repulsions between F atoms, and the following very crude calculations show that this idea may well have some merit. If the net atomic charges already mentioned are assumed to be localized on the atoms, and the Cr–F bond length considered fixed at 1.74 Å,[11] the reduction in electrostatic potential energy due solely to the F ··· F interaction as the F–Cr–F angle is relaxed from a 'natural' value (*cf.* SO_2F_2) of *ca.* 100 to 120° is *ca.* 22.2 kJ mol^{-1}. This energy change is roughly twice that required to shrink the F–Cr–F angle from 120° to the same reference state of 100°, if we assume the other angles and the experimental harmonic bending force constant to remain unchanged throughout the operation. The corresponding energy changes in SO_2F_2 are quite different; the lower net atomic charges reduce the electrostatic interaction by roughly 75% while the angle bending force constant is about four times as great. While dissection of the total molecular energy in this way is clearly naive, the numerical values are suggestive, at least for the cases of CrO_2F_2 and SO_2F_2.

A second point of comparison between the structures of CrO_2F_2 and SO_2F_2 may be relevant. The combination of longer M–O bonds and a narrower O–M–O angle in CrO_2F_2 than in SO_2F_2 leads to remarkably similar O ··· O distances of 2.46 Å (CrO_2F_2) and 2.48 Å (SO_2F_2). Although this one observation proves little by itself, it is consistent with a large body of circumstantial evidence[29] which supports the idea[30] that *non-bonded repulsions* are of great significance in determining molecular shapes, even in cases where the atoms carry very low net charges.

Conclusions.—The initial conclusion which may be drawn from this work is that the original vibrational assignment made by Stammreich for vapour-phase CrO_2F_2 is substantially correct, and that the recent reassignment suggested by Brown *et al.*[15] on the basis of liquid-Raman work is in error. Secondly, the chromium-isotope frequency shifts obtained here from the high-resolution matrix i.r. spectrum are consistent with O–Cr–O and F–Cr–F bond angles of *ca.* 102.5 and *ca.* 124° respectively. These estimates are close to the electron-diffraction values of 102.1 and 118.9°, and thus provide independent evidence that the structural parameters obtained from the electron diffraction study are to be preferred to the different values suggested by microwave spectroscopy. Finally, the relatively small O–Cr–O angle is in keeping with related bond-angle data for other transition-metal oxyhalides.

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* Throughout this paper: 1 dyn = 10^{-5}N.

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