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Gas-Phase Molecular Structure of Chromium Oxytetrafluoride, $CrOF_4$

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An electron-diffraction study of gaseous $CrOF_4$ at 42–45 °C has been carried out. The structure analysis was based on r_α distance models; the approximate quadratic force field required by this approach was adjusted to fit the observed IR frequencies and estimated for the unobserved Raman-active modes. The diffraction data are consistent with a molecule of C_{4v} symmetry, but small deviations from that symmetry cannot be ruled out. With the assumption of C_{4v} symmetry the principal distances (r_g), bond angles ($\angle_\alpha$), and rms amplitudes of vibration (l) with estimated 2σ uncertainties are $r(\mathrm{Cr{=}O}) = 1.547\ (4)$ Å, $r(\mathrm{Cr{-}F}) = 1.730\ (2)$ Å, $\angle\mathrm{O{=}Cr{-}F} = 104.0\ (3)°$, $\angle\mathrm{F{-}Cr{-}F} = 86.7\ (1)°$, $l(\mathrm{Cr{=}O}) = 0.041\ (4)$ Å, $l(\mathrm{Cr{-}F}) = 0.056\ (3)$ Å, $l(\mathrm{O{\cdot}F}) = 0.095\ (8)$ Å, $l(\mathrm{F{\cdot}F}) = 0.084\ (6)$ Å, and $l(\mathrm{F{\cdot\cdot}F}) = 0.087\ (12)$ Å. The structure is compared with those of other group 6 five-coordinate molecules.

Introduction

The gas-phase structures of the oxytetrahalides of the group 6 metals molybdenum and tungsten have received considerable attention in recent years. One of the more interesting questions has been the symmetries of the molecules. Early spectroscopic work[1] on $MoOF_4$ and WOF_4, for example, led to the suggestion of C_{2v} symmetry for both. Later, gas-phase IR data[2] as well as IR and Raman data in several phases and in matrix isolation[3,4] were interpreted to favor C_{4v} symmetry. Electron-diffraction results for $MoOF_4$[5] and WOF_4[6] are consistent with C_{4v} symmetry, but very small distortions from that symmetry could not have been detected by this method.

It is surprising that little is known about the structure of gaseous $CrOF_4$, the homologous compound of the remaining group 6 metal, apart from a suggestion that the molecule has C_{4v} symmetry based on analysis of the IR and UV–visible spectra.[7] The proposal is interesting because the structure of the corresponding main-group compound, SOF_4, is that of a distorted trigonal bipyramid with the oxygen in an equatorial site (C_{2v} symmetry).[8] Details of the structure of $CrOF_4$ are obviously also of interest, and we decided to undertake an electron-diffraction investigation of the molecule.

Experimental Section

The sample of $CrOF_4$ was made at the University of Idaho as follows.

Apparatus. Volatile materials were manipulated in Monel/nickel vacuum lines equipped with Whitey stainless-steel valves and Swagelock fittings. A Hoke Monel container (150 mL) and Kel-F tube (Zeus) fitted with Whitey valves were used as reaction vessels. The vacuum lines and other hardware employed were passivated with ClF. Nonvolatile hygroscopic solids were handled in an inert-atmosphere box. Infrared spectra were recorded on a Perkin-Elmer Model 1710 Fourier transform spectrometer. Spectra of solids were obtained with samples pressed between AgBr disks. Spectra of gases were obtained by using a metal cell of 6 cm path length equipped with AgCl windows.

Materials. CrO_2F_2 was prepared according to a literature method.[9] COF_2 (PCR) and F_2 (Matheson) were used as received. CsF (Aldrich) was dried in an oven maintained at 160 °C.

Preparation of $CrOF_4$. The following preparation has not been reported heretofore. About 1.0 mg of dry, powdered CsF was introduced into a passivated 150-mL Monel vessel in the drybox. The vessel was connected to a metal vacuum line and evacuated. Then, 10 mmol of CrO_2F_2 and 54 mmol of F_2 were introduced at −196 °C. The vessel was allowed to warm to ambient temperature and then heated at 200 °C for 62 h in a tube furnace with the valve end of the vessel cooled by circulating tap water. After the reaction, the vessel was cooled to ambient temperature and finally to −196 °C where the excess F_2 was removed under dynamic vacuum via a soda lime trap. All the other volatile compounds were removed at −60 °C. The yield of $CrOF_4$ was 1.3 g (9.0 mmol, 90%). The dark red $CrOF_4$ was characterized by its vibrational spectrum, its melting point, and its vapor pressure.[10]

Diffraction Experiments. Electron-diffraction photographs were made in the Oregon State apparatus under the following operating conditions: nominal nozzle-to-plate distances, 750 and 300 mm (long and middle camera); nozzle-tip temperature, 42–45 °C; r^3 sector; exposure times, 100–110 s (long camera) and 120 s (middle camera); nominal electron wavelength, 0.057 Å (calibrated against gaseous CO_2 ($r_a(\mathrm{C{=}O}) = 1.1646$ Å, $r_a(\mathrm{O{\cdot\cdot}O}) = 2.3244$ Å); beam current, 0.42–0.49 μA; ambient pressure in the diffraction chamber during run, 1.2×10^{-6} Torr (long camera) and 1.4×10^{-6} Torr (middle camera); 8 × 10 in Kodak lantern slide (medium contrast) plates; development with nitrogen burst agitation, 11 min in D-19 developer diluted 1:1.

Three plates made at the long distance were selected for analysis, but due to shortage of sample only one could be made at the middle camera distance. This plate was of excellent quality, however, and was traced repeatedly to minimize random photometric errors. Procedures by which the total scattered intensities (s^4I_t) were obtained and the backgrounds removed to obtain the molecular intensities (sI_m) were as previously described.[8b,11] Elastic and inelastic electron scattering amplitudes for all calculations were obtained from tables.[12] The data ranges were $2.00 \le s/\text{Å} \le 13.75$ (long camera distance) and $7.00 \le s/\text{Å} \le 33.50$ (middle camera distance) with a data interval Δs equal to 0.25 Å^{-1} ($s = 4\pi\lambda^{-1} \sin\theta$; 2θ is the scattering angle). Curves of the total scattered intensity data are shown in Figure 1; these data, the final backgrounds, and the molecular intensity averages are available as supplementary material.

Structure Analysis

The experimental radial distribution curve shown in Figure 2 was calculated in the usual way from a composite of the two average molecular intensity curves multiplied by $Z_{Cr}Z_F(A_{Cr}A_F)^{-1} \exp(-0.0025s^2)$. Theoretical intensity data were used for the unobserved or uncertain region $s < 2.00$ Å^{-1}. The three peaks were found to be consistent with a molecule of C_{4v} symmetry having $\angle\mathrm{O{=}Cr{-}F} \simeq 105°$.

Shrinkage Corrections. It was thought best to specify models of the $CrOF_4$ molecule in terms of the geometrically consistent r_α set of distances in order to remove the effects of vibrational averaging ("shrinkage"). Calculation of the corrections[13] necessary for conversion of these distances to the r_a type compatible with the diffraction data requires a suitable quadratic force field. For C_{4v}-symmetry $CrOF_4$, nine vibrational modes ($3A_1$ and 3E) are IR and Raman active and three ($2B_1$ and $1B_2$) are only Raman active. The IR-active modes have been assigned,[7] but the Raman spectrum of the gas has apparently not been investigated. Any force field is accordingly highly arbitrary, and although one has

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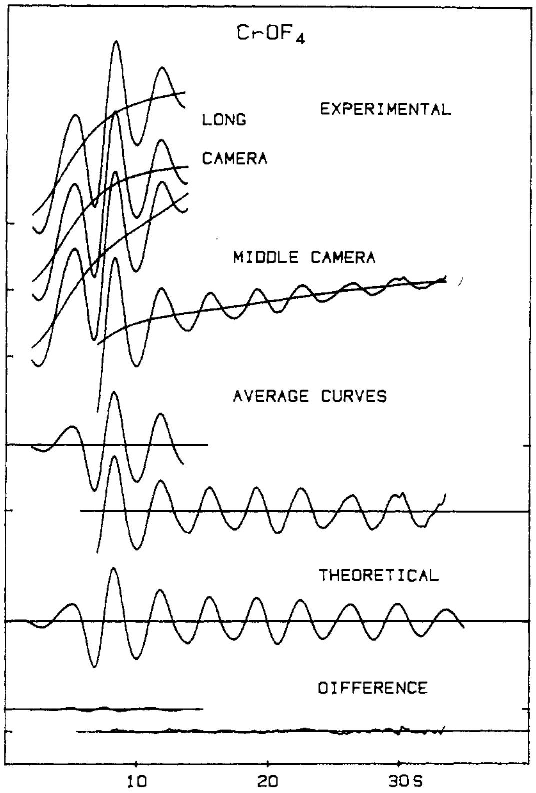

Figure 1. Intensity curves. The s^4I_t curves from each plate are shown superimposed on the final backgrounds and are magnified 4 times relative to the backgrounds (bkgd). The average curves are $s[s^4I_t - \text{bkgd}]$. The difference curves are experimental minus theoretical for model A.

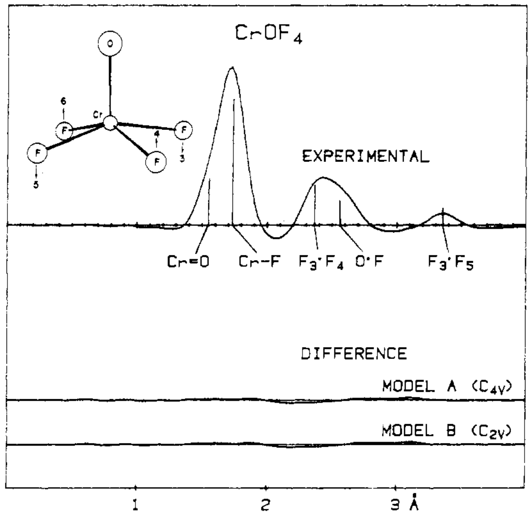

Figure 2. Radial distribution curves. The experimental curve was calculated from a composite of the average curves of Figure 1 with addition of theoretical data from model A for $s < 2.00$ Å^{-1} and with the convergence factor B equal to 0.0025 Å. The difference curves are the experimental minus the theoretical. The diagram shows the distortion of the C_{4v} model to form the C_{2v} model.

been reported,[14] we preferred to deduce a force field based in part on more extensive data[7] from several isotopes of chromium. Our force field was adjusted to fit the observed frequencies to within 1 cm^{-1}, after which values consistent these were adopted for the force constants of the B_1 and B_2 blocks. Tests showed that the desired distance corrections and mean amplitudes of vibration were not very sensitive to reasonable variation in the values of the force constants. The force field and symmetry coordinates are given in the supplementary material.

Table I. Parameter Values for Models of $CrOF_4$ (r/Å, $\angle_\alpha$/deg)[a]

	model A (C_{4v})	model B (C_{2v})	model C (C_{2v})
Parameters Used To Define the Geometry			
Cr=O[b,c]	1.543 (4)	1.544 (5)	1.543 (4)
⟨Cr—F⟩[b-d]	1.725 (2)	1.724 (3)	1.725 (2)
Δr(Cr—F)[c,d]	[0]	−0.034 (169)	−0.009 (35)
⟨∠O=Cr—F⟩[b-d]	104.0 (3)	104.1 (3)	104.2 (3)
Δ∠O=Cr—F[c,d]	[0]	3.7 (71)	[6.0]
Other Parameters			
∠O=Cr—F_3	104.0 (3)	105.9 (37)	107.2 (3)
∠O=Cr—F_4		102.2 (34)	101.2 (3)
∠F_3—Cr—F_4	86.7 (1)	86.7 (2)	86.7 (1)
∠F_3—Cr—F_5	152.1 (5)	148.2 (74)	145.6 (6)
∠F_4—Cr—F_6		155.5 (69)	157.6 (6)
R[e]	0.0632	0.0637	0.0638

[a] Quantities in parentheses are estimated 2σ. [b] Parameters for model A. [c] Parameters for models B and C. [d] See text for definitions. [e] $R = [\sum_i w_i\Delta_i^2/\sum_i w_i(s_iI_i(\text{obsd}))^2]^{1/2}$ where $\Delta = s_iI_i(\text{obsd}) - s_iI_i(\text{calcd})$.

Refinement of Trial Structures. The refinements were carried out by least-squares methods based on intensity functions.[15] Theoretical $sI_m(s)$ values calculated from models of the molecule were fit to two data sets: the average of the data obtained from all plates made at the long camera distance and the average of the data made from four traces of the single plate made at the middle camera distance. Although the preliminary results were completely consistent with C_{4v} symmetry for the molecule, we decided to establish the extent to which the molecule could deviate from C_{4v} symmetry without worsening the quality of fit to the diffraction data; accordingly models of C_{2v} symmetry were also investigated. For C_{4v} symmetry the parameters (r_α space) were r(Cr=O), r(Cr—F), ∠(O=Cr—F), and the vibrational amplitudes l corresponding to the five different interatomic distances. For C_{2v} symmetry they were r(Cr=O), ⟨r(Cr—F)⟩, Δ(Cr—F) = r(Cr—F_3) − r(Cr—F_4), ⟨∠(O=Cr—F)⟩, Δ∠(O=Cr—F) = ∠(O=Cr—F_3) − ∠(O=Cr—F_4), and eight amplitudes l. Refinement of all geometrical and vibrational parameters for the C_{4v} model converged quickly. Because of the good fit provided by this model, it was expected that the C_{2v} models would lead to little or no improvement and, further, that the resulting parameter values with their estimated uncertainties would encompass the results for the C_{4v} model. This turned out to be the case: although refinement of the C_{2v} structure was achieved (the shrinkage corrections were assumed to be equal to those calculated for the C_{4v} model and some of the l's had to be refined in groups), the uncertainties associated with the parameter values were very large. In an attempt to meet better the objectives set for tests of the C_{2v} model, we next carried out a series of refinements in which the parameter Δ∠(O=Cr—F) was not allowed to refine, but instead was stepped through the range 0–8° at 2° invervals. It was found that this parameter could be as large as 6° without significantly worsening the fit.

Results. The final results of our refinements are summarized in Tables I and II. Model A represents the best fit obtained for a molecule of C_{4v} symmetry, and model B the best for a molecule of C_{2v} symmetry when all geometrical parameters were allowed to refine independently. Model C is similar to B, but shows more directly the extent to which deviation from C_{4v} is tolerable. It was found that all C_{2v} models similar to model C with |Δ∠O=Cr—F| < 8° gave fits about as good as that from model A, but judged from the relatively large values of the quality-of-fit factor R that they yielded, the fits from models with |Δ∠O=Cr—F| ≥ 8° were unacceptable. We take model A as the best representation of the structure, but deviations from C_{4v} symmetry as large as those found in model C cannot be ruled out. The correlation matrix for model A is given in Table III. The intensity curve and intensity–difference curves for model A are seen in Figure 1; differences of radial distribution curves for models A and B are seen in Figure 2.

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Table II. Interatomic Distances and Vibrational Amplitudes for Models of $CrOF_4$ (r/Å, l/Å)[a]

	model A (C_{4v})					model B (C_{2v})		model C (C_{2v})	
	r_α	r_g[b]	r_a[b]	l_{obsd}	l_{calcd}	r_α	l_{obsd}	r_α	l_{obsd}
Cr=O	1.543 (4)	1.547	1.546	0.041 (4)	0.037	1.544 (5)	0.043 (7)	1.543 (5)	0.041 (5)
Cr—F_3	1.725 (2)	1.730	1.728	0.056 (3)		1.741 (9)	0.053 (41)	1.721 (7)	0.056 (3)
Cr—F_4					0.044	1.707 (8)	0.053	1.729 (7)	0.056
O·F_3	2.578 (6)	2.581	2.577	0.095 (8)	0.089	2.625 (37)	0.083 (31)	2.648 (9)	0.066 (15)
O·F_4					0.089	2.533 (31)	0.083	2.516 (8)	0.066
F_3·F_4	2.367 (4)	2.375	2.373	0.084 (6)	0.087	2.366 (4)	0.085 (7)	2.369 (4)	0.083 (7)
F_3·F_5	3.348 (5)	3.350	3.347	0.087 (12)	0.071	3.35 (22)	0.088 (44)	3.266 (13)	0.072 (27)
F_4·F_6					0.071	3.34 (20)	0.088	3.402 (14)	0.072

[a] Quantities in parentheses are estimated 2σ. [b] $r_g = r_\alpha + \delta r + K$; $r_a = r_g - l^2/r$. δr and K are respectively centrifugal distortion and perpendicular amplitude corrections.

Table III. Correlation Matrix (×100) for Parameters of $CrOF_4$[b]

param no.	param type	σ_{LS}[a]	r_1	r_2	r_3	r_4	r_5	l_6	l_7	l_8	l_9	l_{10}	$\angle_{11}$	$\angle_{12}$
1	r(Cr=O)	0.14	100	28	29	50	50	1	−57	−7	−13	−6	−40	40
2	r(Cr—F)	0.040		100	46	41	41	32	−8	2	5	3	11	−11
3	r(O·F)	0.17			100	−45	−45	14	−5	−10	−7	5	75	−75
4	r(F·F)	0.11				100	100	10	−35	6	3	−6	−87	87
5	r(F··F)	0.15					100	10	−35	6	3	−6	−87	87
6	l(Cr=O)	0.13						100	9	<1	4	3	7	−7
7	l(CR—F)	0.06							100	13	21	11	34	−34
8	l(O·F)	0.24								100	53	7	−6	6
9	l(F·F)	0.17									100	4	<1	<1
10	l(F··F)	0.42										100	8	−8
11	∠O=Cr—F	9.7											100	−100
12	∠F—Cr—F	4.5												100

[a] Standard deviations from least squares. [b] Units: distances (r) and amplitudes (l) in Å; angles (∠) in degrees.

Discussion

Although our diffraction data do not rule out C_{2v}-type structures for $CrOF_4$, there is no reason to believe that the equilibrium symmetry is not C_{4v}; acceptable models of the former comprise relatively small distortions of the latter, as is seen in the similar values of the defining parameters (Table I). The model differences are marked by distance splittings of only a few hundredths of an angstrom (Table II), usually accompanied by decreases in the values of the corresponding vibrational amplitudes. The well-known consequence of such a combination of parameter changes is a similar intensity distribution for the resulting models.

There are some interesting comparisons to be made between the structures of $CrOF_4$ and CrO_2F_2, both d^0 complexes. The Cr—F bond length in $CrOF_4$ is about the same as in CrO_2F_2[16] (r_g = 1.720 (2) Å), but the Cr=O distance is 0.03 Å shorter. These observations may be rationalized as follows. The greater number of strongly electronegative atoms in $CrOF_4$ are expected to shorten all distances slightly relative to those in CrO_2F_2. However, because the nonbonding F·F distance is much smaller (by about 0.48 Å) in $CrOF_4$, the fluorine atoms experience greater mutual repulsion that is partially relieved by elongation of the Cr–F bonds. The two effects tend to cancel and result in a Cr–F bond length similar to that in CrO_2F_2. (The still shorter bond length in CrF_4, a molecule of T_d symmetry, r_g = 1.706 (2) Å,[17] is consistent with these arguments.)

The bonding by the chromium atoms in $CrOF_4$ and CrO_2F_2 is also similar, judged by the similar empirical total bond orders in the two molecules. These may be estimated from the formula[18] $D(1) - D(n) = 0.71 \log n$. With use of Pauling's single bond radii (Cr = 1.26 Å,[19] O = 0.74 Å, F = 0.72 Å), n(Cr=O), n(Cr—F), and n(total) are respectively calculated to be 3.4, 1.7, and 10.2 in $CrOF_4$; the corresponding values in CrO_2F_2 are 3.1, 1.8, and 9.6.[20]

It is noteworthy that the angle Y=M—X in five-coordinate transition-metal compounds is remarkably constant irrespective of ligand size or metal identity. Thus, in WOF_4,[6] $WOCl_4$,[21] WSF_4,[22] $WSCl_4$,[23] $WSeF_4$,[24] $WSeCl_4$,[23] $MoOF_4$,[25] and $MoOCl_4$[21] this angle has an average value of 104.0° with a standard deviation of 0.8°. Our measurement of this angle in $CrOF_4$ is exactly the average for the other compounds.

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Registry No. $CrOF_4$, 57414-29-6.

Supplementary Material Available: Table IV, giving symmetry coordinates, symmetrized force constants, and observed and calculated wave numbers, and Tables V–VII, giving total scattered intensities from each plate, the calculated backgrounds, and the averaged intensities from each camera distance (6 pages). Ordering information is given on any current masthead page.

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