Molecular Structure of Chromium Tetrafluoride in the Gas Phase

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Hedberg, L., Hedberg, K., Gard, G.L. and Udeaja, J.O., 1988. Molecular Structure of Chromium Tetrafluoride in the Gas Phase. – Acta Chem. Scand., Ser. A 42: 318–323.

The molecular structure of gaseous chromium tetrafluoride at 195–220 °C has been studied by electron diffraction. The diffraction patterns are completely consistent with a molecule of tetrahedral (T_d) symmetry having a bond length r_g = 1.706(2) Å. The rms amplitudes of vibration were measured to be l(Cr–F) = 0.051(3) Å and l(F···F) = 0.124(9) Å. Refinement of the two distances without regard to symmetry restrictions led to a shrinkage of 0.009(9) Å, i.e., the F···F distance is measured to be slightly shorter than that predicted from the Cr–F distance with the assumption of T_d symmetry. The parameter-value uncertainties in parentheses are estimated 2σ.

Dedicated to Professor Otto Bastiansen on his 70th birthday

A part of our work on the structures of inorganic molecules in the gas phase has been concerned with compounds of the first transition-group metals. Among the compounds examined have been some four- and five-coordinate chromium compounds with very electronegative ligands: CrO_2Cl_2,[1] CrO_2F_2[2] and CrF_5.[3] The chromyl halides have distorted tetrahedral structures (symmetry C_{2v}), the most interesting aspects of which are the relative values of the O=Cr=O and X–Cr–X bond angles; in each case the latter are greater than the former, a violation of Gillespie's rules.[4] Chromium pentafluoride has a distorted trigonal bipyramidal structure that, on the *average,* appears to be C_{2v}. The origin of this presumably lies in a Jahn-Teller[5] effect that arises from the d^1 electron configuration of the Cr^{5+} ion; for nominal D_{3h} molecular symmetry the odd electron would lie in an e'' orbital, and under these circumstances the Jahn-Teller theorem predicts distortion to lower symmetry with accompanying removal of the degeneracy.

The differences and similarities between CrF_4 and the molecules just mentioned also make the structure of CrF_4, a d^2 complex, of considerable interest. The following is account of our electron-diffraction investigation.

Experimental

The sample of CrF_4 was prepared after the method reported by Christe *et al.*,[6] which is based on the following reactions:

$$CrF_3 + F_2 \xrightarrow{270\text{–}303^\circ} CrF_5 \quad (1)$$

$$CrF_5 + Cl_2 \xrightarrow{183^\circ} CrF_4 + (ClF, ClF_3). \quad (2)$$

Anhydrous CrF_3 (ROC/RIC Chemical) was dried prior to use. High purity Cl_2 (Matheson) was used as received. In a 100 ml Monel vessel containing stainless steel ball bearings and equipped with a Whitey stainless steel valve, 32.0 mmol of pre-dried CrF_3 and 156 mmol of F_2 were placed. After shaking for 29 h at 270–303 °C the remaining F_2 was removed at −196 °C. 32.0 mmol of CrF_5 (100 % yield based on CrF_3) was formed [eqn. (1)].

To the 32.0 mmol of CrF_5 obtained as above and placed in a Monel vessel, 16.0 mmol of Cl_2 was added. The mixture was heated at 183 °C for 22 h with shaking at 15 min intervals. Removal of volatile materials at room temperature left behind 31.8 mmol of CrF_4 [yield 99 %, eqn. (2)]. The infrared spectrum of this solid agreed with that reported for CrF_4.[6] The CrF_4 product was transferred in a dry-box to a 100 ml quartz vessel equipped with a Teflon stopcock. The CrF_4 was sublimed *in vacuo* at 185–190 °C. The bluish sublimed product was transferred to pre-dried copper storage vessels for use in the diffraction experiments.

The diffraction experiments were made with the Oregon State apparatus using an r^3 sector and Kodak projector slide plates, medium contrast; the temperature of the nozzle tip was 195–220 °C. Other parameters of the experiment were as follows. Nominal electron wavelength, 0.057 Å [calibrated against CO_2, $r_a(C{=}O)$ = 1.1646 Å; $r_a(O\cdots O)$ = 2.3244 Å]; nozzle-to-plate distances, 750 mm (long camera) and 300 mm (middle camera); ambient apparatus pressure during sample run-in, $1.4–2.1\times10^{-6}$ torr; exposure times, 120–210 s; development, 10 min in D-19 developer diluted 1:1. Mottling of some of the plates occurred, but as on other occasions,[7] the problem was solved by allowing the exposed plates to stand in air for 24 h before development. Two plates from the long camera distance and three from the middle distance were selected for analysis. Data in the ranges $2.00 \leq s/Å \leq 13.75$ (long camera) and $6.00 \leq s/Å \leq 33.75$ ($s = 4\pi\lambda^{-1}\sin\theta$) were obtained. Procedures for extracting the total scattered intensities [$s^4I_t(s)$], backgrounds, and molecular intensities [$sI_m(s)$] have been described.[8,9] Electron scattering amplitudes and phases for all calculations were taken from tables.[§] Curves of the intensities and backgrounds are shown in Fig. 1; the corresponding data are available in supplementary material available from the authors upon request.

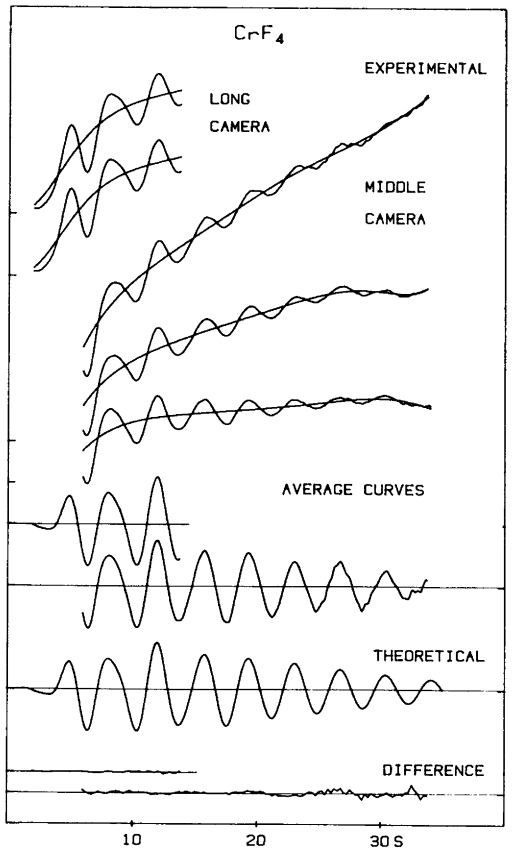

Fig. 1. Intensity curves. The $s^4I_t(s)$ curves from each plate are shown superimposed on the final backgrounds and are magnified 2.5 times relative to the backgrounds. The theoretical curve is for model A of Table 1. The difference curves are experimental minus theoretical.

Structure analysis

Radial distribution curves were calculated from composites of the average intensity curves (Fig. 1) after multiplication by $Z_{Cr}Z_F(A_{Cr}A_F)^{-1}\exp(-0.0025s^2)$, and after attaching data from theoretical curves for the unobserved or uncertain region $s \leq 1.75$ Å^{-1}. Peaks of the radial distribution curves (the final one is shown in Fig. 2) were found at positions that correspond to distances in a tetrahedral molecule.

If one assumes T_d symmetry for the CrF_4 molecule, the complete structure is defined by a single distance parameter and two vibrational amplitude parameters. To obtain the most accurate distance values with this symmetry assumption, the effects of vibrational averaging ("shrinkage")[11] must be properly taken into account.

[§]For elastic amplitudes and phases, see Ref. 10a; for inelastic amplitudes, see Ref. 10b.

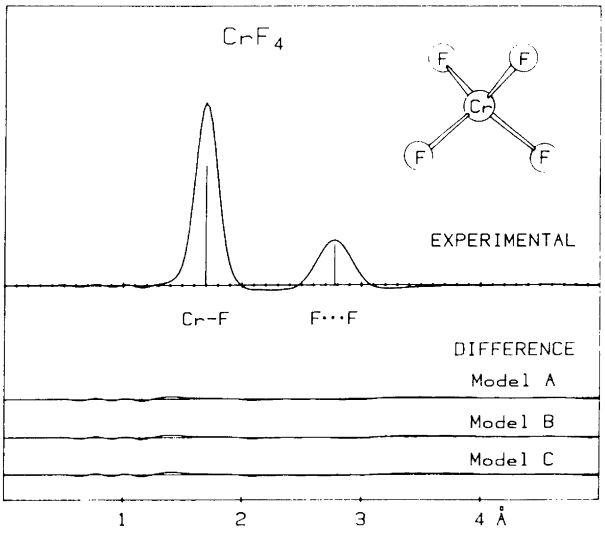

Fig. 2. Radial distribution curves. The experimental curve was calculated from a composite of the average curves of Fig. 1 with addition of theoretical data from model A for $s \leq 1.75$ Å^{-1}.

Shrinkage is usually estimated from calculations based on vibrational force fields that have either been fitted to spectroscopic data for the molecule in question or adopted from other, similar molecules. For CrF_4 the normal modes of vibration are found in the species $\Gamma = a_1 + e + 2f_2$. The published vibrational wavenumbers appear to be limited to the two f_2 modes, i.e. an asymmetric stretch and a bend, seen in the infrared.[6] We first chose a set of force constants that reproduced these values exactly. Values for the a_1 and e constants were then estimated by scaling the F_2 constants by ratios for the corresponding stretching and bending constants in TiF_4.[12] This force field for the molecule, while not unreasonable, is obviously completely arbitrary (at least for the a_1 and e species), but the desired shrinkage corrections in CrF_4 were not expected to be very sensitive to it.[+] The force constant values are $F_{11} = 6.178$ aJ Å^{-2} (a_1 species); $F_{22} = 0.794$ aJ rad^{-2} (e); $F_{33} = 4.762$ aJ Å^{-2}, $F_{44} = 0.901$ aJ rad^{-2}, and $F_{34} = 0.347$ aJ Å^{-1} rad^{-1} (f_2). The calculated wavenumbers (equal to those observed for the f_2 species) are 743 cm^{-1} (a_1), 271 cm^{-1} (e), 784 cm^{-1} (f_2) and 303 cm^{-1} (f_2). The vibrational corrections corresponding to the force field can be deduced from the distance values for models A and B in Table 1.

In the case of five-atom molecules of T_d symmetry there is an attractive alternative approach. The two types of distances in these molecules are widely separated in magnitude, and accordingly their values and the associated amplitudes of vibration are essentially uncorrelated. Refinement of such structures may then be carried out without regard to the equilibrium molecular symmetry, i.e., in terms of the four independent parameters – the two distances and the two amplitudes. The deviation of the measured distance ratio from that defined by tetrahedral symmetry provides an *experimental* estimate of the shrinkage.

We refined the CrF_4 structure in terms of three models. Models A and B resulted from least-squares fits[14] of theoretical intensity curves in which two r_α-type distances were made to conform to T_d symmetry for the molecule (i.e., one geometrical parameter). Although two amplitude parameters were refined in each case, model A incorporated the *observed* amplitude values for the conversion from r_g to r_a ($r_a = r_g - l^2/2$) and model B the *calculated* values. Model C resulted from refinement of two r_a-type distances (and the two vibrational amplitudes) as independent pa-

[+]The differences between the corrections (K and δr) obtained from force fields based on ratios from different tetrahedral molecules (for methane, see Ref. 13a; for SiF_4, see Ref. 13b; for TiF_4, see Ref. 12) were less than 0.001 Å. Differences between calculated amplitudes of vibration from these force fields were less than 0.005 Å.

Table 1. Distances (r/Å) and vibrational amplitudes (l/Å) for CrF_4.[a]

Parameter	r_α[b]	r_g[b]	r_a[b]	l_{obs}	l_{cal}
Model A (T_d symmetry)[c]					
Cr–F	1.701(2)	1.706	1.704	0.051(3)	0.0434
F···F	2.778(3)	2.782	2.776	0.124(9)	0.0903
δ(F···F)[d]		0.004	0.007		
R[e]	0.0758				
Model B (T_d symmetry)[f]					
Cr–F	1.701(2)	1.705	1.704	0.051(3)	0.0434
F···F	2.778(3)	2.781	2.778	0.124(9)	0.0903
δ(F···F)[d]		0.004	0.005		
R[e]	0.0758				
Model C (two independent distances)[g]					
Cr–F			1.704(2)	0.051(3)	
F···F			2.774(10)	0.124(9)	
δ(F···F)[h]			0.009(9)		
R[e]			0.0757		

[a]Values in parentheses are 2σ uncertainties and include estimates of systematic error and correlation. Uncertainties for r_α, r_g and r_a are expected to be similar. [b]$r_g = r_\alpha + K + \delta_r$; $r_a = r_g - l^2/r$. The perpendicular amplitude corrections K, the centrifugal distortions δr, and the l_{calc} were calculated from the force field mentioned in the text. [c]Model described in terms of r_α. Experimental l's used for interconversion of distance types. [d]Calculated shrinkage. [e]$R = \{\Sigma_i w_i \Delta_i^2 / \Sigma_i w_i [s_i l_i(\text{obs})]^2\}^{1/2}$, where $\Delta_i = s_i l_i$ (obs) – $s_i l_i$(calc). [f]Model described in terms of r_α. Calculated l's used for interconversion of distance types. [g]Model with no geometrical constraints. [h]Observed shrinkage.

rameters. The results for all models are given in Table 1 and the correlation matrices in Table 2.

Discussion of results

We note first that there is no significant difference in the values of the structural parameters obtained from the three models of the CrF_4 molecule. Each model is thus an appropriate expression of our final results, but of the two with imposed T_d symmetry we prefer model A slightly because it incorporates more of the experimental information (the observed amplitudes) in the $r_\alpha \rightarrow r_a$ conversion.

The Cr–F bond length in CrF_4 is slightly shorter than the average value in CrF_5 [r_a = 1.712(2) Å].[3] This result is mildly surprising because the effect of increased fluorine substitution, first observed by Brockway[15] in the series of methyl fluorides, and found as well in the sulfur fluorides [SF_6: r_a = 1.5622(7) Å;[16a,*] SF_4: $\langle r_a \rangle$ = 1.595(3) Å;[17] SF_2: r_{av} = 1.59208(8) Å][18] is to decrease the average fluorine bond distance. The bond length in CrF_4 is also shorter than that in CrO_2F_2[1] [r_a =

Table 2. Correlation matrices (×100) for parameters of CrF_4.

	$\sigma_{LS}\times100$[a]	r_1	r_2	l_3	l_4
Model A[b]					
1. r(Cr–F)	0.041	100	100	<1	2
2. r(F···F)	0.067		100	<1	2
3. l(Cr–F)	0.058			100	18
4. l(F···F)	0.25				100
Model C					
1. r(Cr–F)	0.042	100	−1	<1	3
2. r(F···F)	0.33		100	3	−1
3. l(Cr–F)	0.058			100	18
4. l(F···F)	0.25				100

[a]In Å; standard deviations from least-squares refinements. [b]Correlation matrix for model B essentially identical.

*A value of r_g = 1.561(2) Å is listed in Ref. 16b.

1.716(2) Å], whereas in the analogous sulfur pair the shorter distance is found in SO_2F_2 [r_a = 1.530(2) Å].[19]

We have noted[3] that, according to well-known bond order, bond length criteria, the Cr–F bonds in CrO_2F_2 as well as the Cr–Cl bonds in CrO_2Cl_2 may be interpreted as nearly pure single bonds and the Cr=O bonds are nearly pure double bonds. Inasmuch as the Cr–F bond lengths differ only slightly in d^0 CrO_2X_2, d^1 CrF_5, and d^2 CrF_4, it follows that the total bond order realized by the Cr atoms in these compounds increases linearly with the number of d electrons formally involved with the ligands.

The data of Table 1 suggest that shrinkage in CrF_4 is apparently measurable at only a marginal level of significance: based on the r_a bond length for model C, the value of the F···F distance predicted from the tetrahedral bond angle [2*r*sin (109.47/2)] is about 0.009 Å greater than the measured value. If the tabulated uncertainty is used to estimate the precision of the shrinkage measurement, however, the tabulated uncertainty for F···F should probably be a little smaller. The reason is that this uncertainty contains an estimate of the effect of possible errors in scale parameters, such as wavelength and camera distance, calculated as being independent of similar possible errors in the measurement of the Cr–F distance. As is seen from Table 2, however, for a CrF_4 molecule of T_d symmetry the two distances are completely correlated; there is in fact only a single molecular size parameter. Since the results for all models were obtained from the same data set, uncertainties in molecular size due to possible errors in scale parameters should be similar. Our estimate of uncertainties arising from possible errors in scale parameters is about 0.001 Å, which leads to a shrinkage measurement of 0.009(9) Å.

The amplitudes of vibration in CrF_4 are observed to be substantially larger than the calculated ones. Since the latter are derived from an approximate force field, one for which the frequencies for the a_1 and e species are unobserved, it could be supposed that the force field is badly in error. Investigation shows that no reasonable changes in the a_1 and e force constants can bring about agreement between the observed and calculated amplitudes. At 0.901 aJ rad^{-2} the magnitude of the bending constant in the f_2 species (F_{44}) seems large, but is the smallest possible value consistent with the observed frequencies. Arbitrary smaller values bring about much better agreement for l(F···F) and correspondingly much poorer agreement for the f_2 frequencies. We believe the vibrational spectra of CrF_4 need further investigation.

Acknowledgements. This work was supported by the National Science Foundation under grant CHE84-11165 to Oregon State University, and by the Petroleum Research Fund under a grant to Portland State University. L.H. and K.H. are immeasurably indebted to our good friend Otto Bastiansen. Without circumstances made possible by him, our respective careers as well as our personal lives would have been vastly different.

Supplementary material available: Tables of the total scattered intensities from each place, the calculated backgrounds from each plate, and the averaged molecular intensities for each camera distance.

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Received February 16, 1988.