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Gas-Phase Structure of Chlorine Trifluoride Oxide, ClF_3O

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The molecular structure of ClF_3O has been studied by gas electron diffraction. A distorted trigonal bipyramid with the following geometric parameters (r_α values) was obtained: Cl=O = 1.405 (3) Å, $Cl-F_e$ = 1.603 (4) Å, $Cl-F_a$ = 1.713 (3) Å, $\angle F_eClO$ = 108.9 (0.9)°, $\angle F_aClF_e$ = 87.9 (1.2)°, and $\angle F_aClO$ = 94.7 (2.0)°. Steric repulsion effects in equatorial and axial directions for the double bond and the lone electron pair of chlorine are discussed. The position of the lone pair was derived from ab initio calculations.

Introduction

Chlorine trifluoride oxide was independently discovered in 1965 at Rocketdyne[1] and 1970 at Saclay.[2] No structural data have been published for this interesting compound, except for its vibrational[2,3] and ^{19}F[1,4] and ^{17}O[5] NMR spectra, which were in agreement with a pseudo-trigonal-bipyramidal structure of symmetry C_s. In this structure, two fluorines occupy the axial positions and one fluorine, one oxygen, and one sterically active free valence electron pair occupy the equatorial positions. It was recently proposed[6] that free valence electron pairs and π bonds can result in directional repulsion effects for trigonal-bipyramidal molecules. Since ClF_3O possesses both a free valence electron pair and a π bond, a knowledge of its exact molecular structure was of great interest. In this paper, the results of a structure determination of ClF_3O by gas-phase electron diffraction are given in support of the previously proposed[6] directional repulsion effects.

Experimental Section

The sample of ClF_3O used for this study was prepared by low-temperature fluorination of $ClONO_2$ using a previously described method.[1] The sample was purified by fractional condensation, followed by complexation with KF and controlled vacuum pyrolysis of the resulting $KClF_4O$ adduct.[7] The product showed no impurities detectable by vibrational and NMR spectroscopy[1-4] and was handled exclusively in well-passivated (with ClF_3) Teflon–stainless steel equipment.

The electron diffraction intensities were recorded with a Balzer diffractograph KD-G2[8] at two camera distances (50 and 25 cm) and an accelerating voltage of about 60 kV. The nozzle temperature was 10 °C, and the sample was kept at −35 °C. The camera pressure never exceeded 1×10^{-5} torr during the experiment (throughout this paper 1 Å = 100 pm, 1 torr = 101.325/760 kPa). The electron wavelength was determined from ZnO diffraction patterns. s ranges ($s = (4\pi/\lambda)\sin(\theta/2)$, λ = electron wavelength, θ = scattering angle) of 1.4–17 $Å^{-1}$ and 8–35 $Å^{-1}$, for the two camera distances, were covered in the experiment. For each camera distance two plates were selected and the intensity data were evaluated in the usual way.[9] The averaged molecular intensities were measured in steps of $\Delta s = 0.2$ $Å^{-1}$.

Results and Discussion

Structure Analysis. The observed molecular intensities are given in Figure 1. A preliminary geometric model was derived from the radial distribution function (Figure 2) and then refined by a least-squares analysis based on the molecular intensities. A diagonal-weight matrix was used,[9] and theoretical intensities were calculated with the scattering amplitudes and phases of Haase.[10] The only geometric constraint was an assumed C_s symmetry. The ratios between the vibrational amplitudes of the bonded distances and of some nonbonded distances were constrained to the spectroscopic values (see Table I). Parallel vibrational amplitudes and harmonic vibrational corrections $\Delta r = r_a - r_\alpha$ (Table I) were calculated from the force field of ref 3 with the program NORCOR.[11] Two correlation coefficients had values larger than

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Table I. Results of the Electron Diffraction Experiment and Spectroscopic Calculations

(a) Geometric Parameters (r_α Values) (Å and Deg)[a]

Cl=O	1.405 (3)	$\angle F_aClF_e$	87.9 (1.2)
$Cl-F_e$	1.603 (4)	$\angle F_aClO$	94.7 (2.0)
$Cl-F_a$	1.713 (3)	$\angle F_aClF_a$[b]	170.5 (4.1)
$\angle F_eClO$	108.9 (0.9)		

(b) Vibrational Amplitudes from Electron Diffraction and Spectroscopic Data and Harmonic Vibrational Corrections (Å)

	vibrational amplitudes: ed	vibrational amplitudes: spectr	$r_a - r_\alpha$
Cl=O	0.032 (7)[c]	0.036	0.0010
$Cl-F_e$	0.041 (7)[c]	0.047	0.0001
$Cl-F_a$	0.048 (7)[c]	0.053	0.0010
$F_e\cdots O$	0.066 (6)[c]	0.065	−0.0008
$F_a\cdots O$	0.073 (6)[c]	0.072	0.0000
$F_a\cdots F_e$	0.079 (6)[c]	0.078	−0.0007
$F_a\cdots F_a$	0.061 (10)	0.067	−0.0010

(c) Agreement Factors for Both Camera Distances (%)
$R_{50} = 5.2$ $R_{25} = 7.0$

[a] See text for estimated uncertainties. [b] Dependent parameter. [c] Ratio constrained to the spectroscopic value.

Table II. Atomic Net Charges, Dipole Moment, and Overlap Populations for ClF_3O

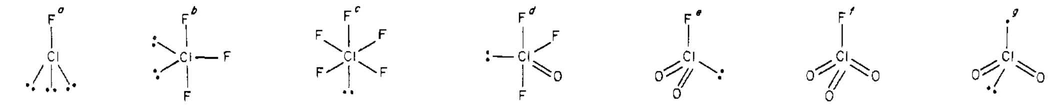
	net charge		overlap pop., au
Cl	1.76+	$Cl-F_e$	0.092
F_e	0.31−	$Cl-F_a$	0.070
F_a	0.46−	Cl=O, π_e	0.103
O	0.53−	π_a	0.091

μ^a = 1.74 D

[a] See Figure 3 for the direction of dipole moment.

(1) Pilipovich, D.; Lindahl, C. B.; Schack, C. J.; Wilson, R. D.; Christe, K. O. *Inorg. Chem.* **1972**, *11*, 2189.
(2) Bougon, R.; Isabey, J.; Plurien, P. *C. R. Hebd. Seances Acad. Sci., Ser. C* **1970**, *271*, 1366.
(3) Christe, K. O.; Curtis, E. C. *Inorg. Chem.* **1972**, *11*, 2196.
(4) Alexandre, M.; Rigny, P. *Can. J. Chem.* **1974**, *52*, 3676.
(5) Virlet, J.; Tantot, G. *Chem. Phys. Lett.* **1976**, *44*, 296.
(6) Christe, K. O.; Oberhammer, H. *Inorg. Chem.* **1981**, *20*, 296.
(7) Christe, K. O.; Schack, C. J. *Adv. Inorg. Chem. Radiochem.* **1976**, *18*, 319.
(8) Oberhammer, H. In *Mol. Struct. Diffr. Methods* **1976**, *4*, 24.
(9) Oberhammer, H.; Gombler, W.; Willner, H. *J. Mol. Struct.* **1981**, *70*, 273.
(10) Haase, J. A. *Z. Naturforsch., A* **1970**, *25A*, 936.
(11) Christen, D. *J. Mol. Struct.* **1978**, *48*, 101.

Table III. Geometric Parameters of Some Chlorine-Fluorine-Oxygen Compounds (Å and Deg)



	[a]	[b]	[c]	[d]	[e]	[f]	[g]
Cl–F	1.628	1.598 (5)	1.571 (14)	1.603 (4)	1.697 (3)	1.619 (4)	
$Cl–F_a$		1.698 (5)	1.669 (15)	1.713 (3)			
Cl=O				1.405 (3)	1.418 (2)	1.404 (2)	1.475 (3)
$\angle F_eClF_a$		87.5 (5)	86.0 (15)	87.9 (12)			
$\angle F_aClF_a$		175.0 (7)		170.5 (41)			
				108.9 (9)[h]			
∠OClF				94.7 (20)[i]	101.7 (1)	100.8 (8)	
∠OClO					115.2 (1)	116.6 (5)	117.7 (17)

[a] r_e values from ref 19. [b] r_0 values from ref 20. [c] r_a values from ref 21. [d] r_α values from this work. [e] r_0 values from ref 22. [f] r_a values from ref 23. [g] r_a values from ref 24. [h] $\angle O{=}Cl{-}F_e$. [i] $\angle O{=}Cl{-}F_a$.

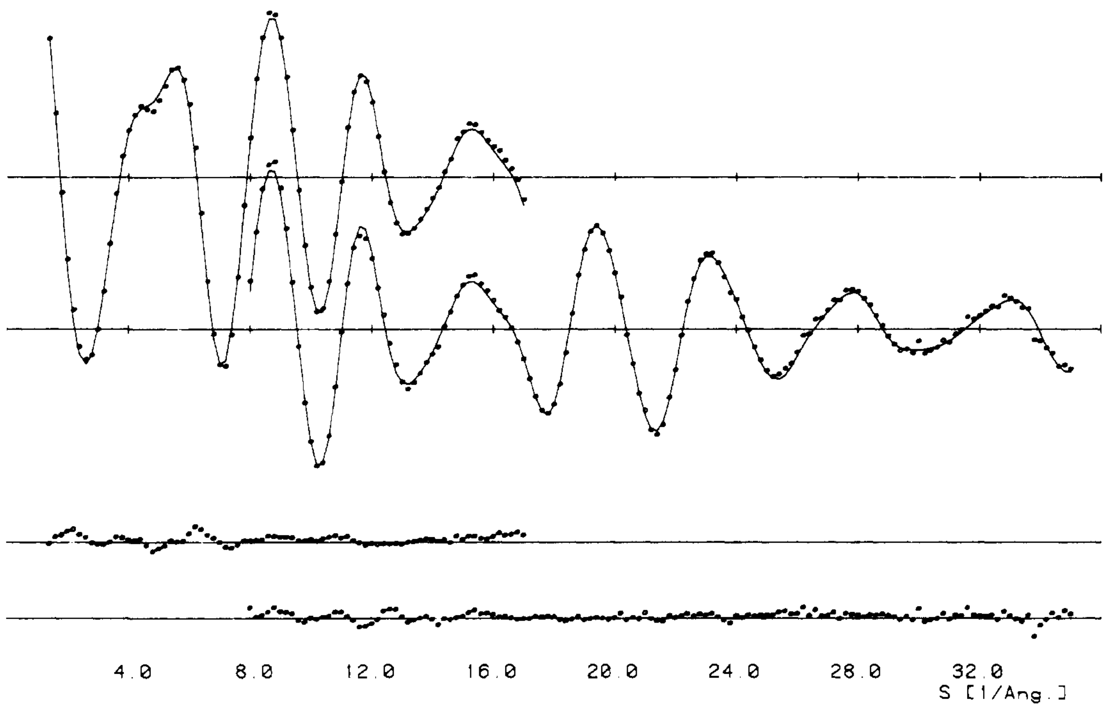


Figure 1. Experimental (points) and calculated (—) molecular intensities and differences.

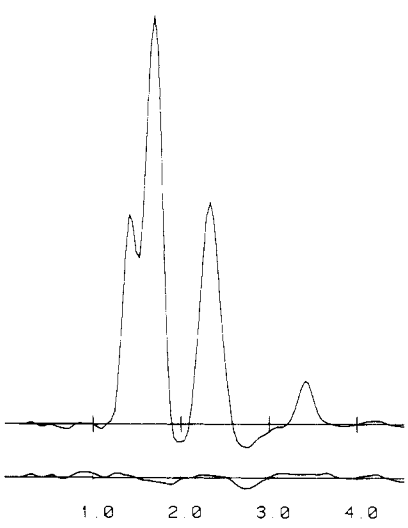


Figure 2. Experimental radial distribution function and difference curve.

0.5: $[\angle F_aClF_e/\angle F_aClO] = 0.88$ and $[l(\text{bonded})/l(F_a \cdots F_a)] = 0.61$. The results of the least-squares analysis are summarized in Table I. Estimated uncertainties are 3σ values, and a possible scale error of 0.1% is included for bonded distances.

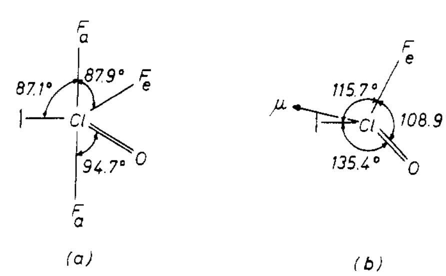


Figure 3. Bond angles in axial (a) and equatorial (b) directions.

Ab Initio Calculations. The molecular wave function at the experimental geometry was calculated with the program TEXAS.[12] For second-row atoms, 4-21 basis sets[13] were used, and for chlorine, a 3-3-21 basis set,[14] supplemented by d functions,[12] was used. The position of the chlorine lone electron pair (Figure 3) was obtained by transformation to localized orbitals, using Boys' criterion.[15] Atomic net charges and

(12) Pulay, P. *Theor. Chim. Acta* **1979**, *50*, 299.
(13) Pulay, P.; Fogarasi, G.; Pang, F.; Bogg, J. E. *J. Am. Chem. Soc.* **1979**, *101*, 2550.
(14) Oberhammer, H.; Bogg, J. E. *J. Mol. Struct.* **1979**, *55*, 283.
(15) Boys, S. F. In "Quantum Theory of Atoms, Molecules, and the Solid State"; Löwdin, P. O., Ed.; Academic, Press: New York, 1966.

overlap populations (Table II) were derived by a Mulliken population analysis.[16]

Molecular Structure of ClF_3O. Chlorine trifluoride oxide is a distorted-trigonal-bipyramidal molecule with three different ligands in the equatorial plane: a single bond, a double bond, and a lone valence electron pair. The angles (Figure 3) between the axial bonds and the double bond are larger (by about 7°) than the angles between the axial bonds and the single bond or the lone electron pair; i.e., the axial fluorine atoms are bent away from the double bond into the sector between the single bond and the lone electron pair. This demonstrates that in the axial direction the steric repulsion of the double bond is larger than the repulsion from either the lone pair or the single bond. The angles in the equatorial plane, however, indicate that in the equatorial direction the repulsion by the lone pair is largest, followed by the double bond, with the single bond being smallest. This directional repulsion effect of double bonds, which has been pointed out previously,[6] correlates well with the different populations of the π-bond orbitals in the axial and the equatorial planes.[17] For ClF_3O, these populations (Table II) are almost equal.

The observed bond distances ($Cl{=}O$ = 1.405 Å, $Cl{-}F_e$ = 1.603 Å, $Cl{-}F_a$ = 1.713 Å) agree well with previous estimates ($Cl{=}O$ = 1.42 Å, $Cl{-}F_e$ = 1.62 Å, $Cl{-}F_a$ = 1.72 Å)[3] derived from the observed vibrational spectra and a comparison with related molecules. They confirm the conclusions, previously reached from the results of a normal-coordinate analysis,[3] that the chlorine–oxygen bond has double-bond character and that the axial Cl–F bond is significantly weaker than the equatorial one. These results support a previously outlined bonding scheme assuming mainly sp^2 hybridization for the bonding of the three equatorial ligands (ClF, ClO σ bond, and free valence electron pair) and the use of a chlorine p orbital for the bonding of the two axial fluorines by means of a semiionic three-center–four-electron bond pair.[3,7,18]

A comparison of the bond lengths in ClF_3O with those in closely related molecules (see Table III) also correlates well with the conclusions previously derived from force field computations.[3,7,18] These computations had shown that, if the bonds are separated according to the two possible types (i.e., mainly covalent and mainly semiionic 3c–4e), the bond strength within each type increases with increasing formal oxidation state of the central atom and decreases with increasing oxygen substitution. The first effect is due to an increase in the effective electronegativity of the central atom with increasing oxidation state. This increase causes the electronegativities of the central atom and the ligands to become more similar and therefore the bonds to become more covalent. The second effect is caused by oxygen being less electronegative than fluorine, thereby releasing electron density to the molecule and increasing the ionicity of the Cl–F bonds.[7,18] Although the previous force field computations clearly reflected these trends, the uncertainties in force constants, obtained from an underdetermined force field, were rather large and certainly are not as precise as the more reliable bond length measurements from this study.

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(16) Mulliken, R. S. *J. Chem. Phys.* **1955**, *23*, 1833.
(17) Oberhammer, H.; Bogg, J. E. *Mol. Struct.* **1979**, *56*, 107.

(18) Christe, K. O. *Plenary Main Sect. Lect. Int. Congr. Pure Appl. Chem., 24th* **1974**, *4*, 115.
(19) Gilbert, D. A.; Roberts, A.; Griswold, P. A. *Phys. Rev.* **1949**, *76*, 1726L.
(20) Smith, D. F. *J. Chem. Phys.* **1953**, *21*, 609.
(21) Altman, A. B.; Miakshin, I. N.; Sukhoverklov, V. F.; Romanov, G. V.; Spiridonov, V. P. *Dokl. Akad. Nauk SSSR* **1978**, *241*, 360.
(22) Parent, C. R.; Gerry, M. C. L. *J. Mol. Spectrosc.* **1974**, *49*, 343.
(23) Clark, A. H.; Beagley, B.; Cruickshank, D. W. J. *J. Chem. Soc. A* **1970**, 872.
(24) Clark, A. H.; Beagley, B. *J. Chem. Soc. A* **1970**, 46.

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Molecular Structures of Phosphorus Compounds. 10. Conformations and Structures of (Trifluoromethyl)fluorophosphoranes, $(CF_3)_nPF_{5-n}$ (n = 1, 2, 3), in the Gas Phase

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The molecular structures of CF_3PF_4, $(CF_3)_2PF_3$, and $(CF_3)_3PF_2$ have been studied by gas electron diffraction. For CF_3PF_4 a mixture of two conformers with equatorial (60 ± 10%) and axial CF_3 groups is found. In $(CF_3)_2PF_3$ both CF_3 groups occupy axial positions, while in $(CF_3)_3PF_2$ all three CF_3 groups occupy equatorial positions. Geometric parameters and vibrational amplitudes are given in the paper. The electron diffraction results are discussed in connection with earlier experimental studies, and an attempt is made to rationalize these results.

Introduction

The basic trigonal-bipyramidal framework of pentacoordinate phosphorus compounds with monofunctional substitutents has been confirmed by various experiments such as NMR, infrared, and microwave spectroscopy and X-ray or electron diffraction. Less certain is the location of various substituents in axial or equatorial positions. The initially suggested "electronegativity rule",[2] according to which more electronegative substituents prefer axial positions, has since been modified by the concept of "apicophilicity".[3] The following "apicophilicity" series, which indicates the relative tendency to occupy axial positions, has been suggested:[4,5]

$$F > Cl, Br > CF_3 > OR, SR, NR_2, R$$

Discrepancies exist in this series, which is based on NMR data and other experiments, when Cl and CF_3 groups compete for

(1) (a) Universität Tübingen. (b) Technische Hochschule, Darmstadt.
(2) (a) R. J. Gillespie and R. S. Nyholm, *Chem. Soc. Rev.*, **11**, 339 (1975); R. J. Gillespie, *Can. J. Chem.*, **38**, 818 (1960); R. J. Gillespie, *J. Chem. Educ.*, **47**, 18 (1970). (b) E. L. Muetterties, W. Mahler, and R. Schmutzler, *Inorg. Chem.*, **2**, 613 (1963).
(3) I. Ugi, D. Marquarding, H. Klusacek, P. Gillespie, and F. Ramirez, *Acc. Chem. Res.*, **4**, 288 (1971).
(4) R. G. Cavell, D. D. Poulin, K. I. The, and A. J. Tomlinson, *J. Chem. Soc. Chem. Commun.*, 19 (1974).
(5) R. G. Cavell, J. A. Gibson, and K. I. The, *J. Am. Chem. Soc.*, **99**, 7841 (1977).

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