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Chlorine Trifluoride Oxide. VI. The Tetrafluoroxychlorate(V) Anion, ClF_4O^- . Vibrational Spectra and Force Constants

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The infrared and Raman spectra of $\text{Cs}^+\text{ClF}_4\text{O}^-$ and $\text{Rb}^+\text{ClF}_4\text{O}^-$ have been recorded. Nine fundamental vibrations have been observed consistent with a C_{4v} structure analogous to that of XeF_4O and ClF_5 . An assignment of the fundamental vibrations is proposed and a modified valence force field has been calculated. The bonding in ClF_4O^- is best described by a mainly covalent $\text{Cl}=\text{O}$ double bond and two semiionic three-center, four-electron p-p σ $\text{Cl}-\text{F}$ bond pairs.

Introduction

ClF_3O forms adducts¹ with strong Lewis acids and bases. In this paper, we present proof for the structure of the ClF_3O -Lewis base complexes.

Experimental Section

The materials, apparatus, and the preparation of $\text{Rb}^+\text{ClF}_4\text{O}^-$ and $\text{Cs}^+\text{ClF}_4\text{O}^-$ have previously been described.¹ The infrared and Raman spectra were recorded as previously reported.²

Results and Discussion

Vibrational Spectra.—Figures 1 and 2 show the vibrational spectra of solid $\text{Rb}^+\text{ClF}_4\text{O}^-$ and $\text{Cs}^+\text{ClF}_4\text{O}^-$, respectively. Table I lists the observed frequencies. For comparison, the values reported for ClF_4^- ³ and ClF_5 ^{4,5} are included. Since ClF_4O^- and ClF_4^- are pseudo-isoelectronic with XeOF_4 and XeF_4 , respectively, the values reported for the latter two molecules^{4,6} are also listed.

Comparison with the known structures of isoelectronic ClF_5 ⁴ and pseudo-isoelectronic XeOF_4 ⁶ suggests for ClF_4O^- symmetry C_{4v} . For this point group, the nine normal modes of vibration are classified as $(3A_1 + 2B_1 + B_2 + 3E)$. Of these, all nine modes are Raman active, while only the three A_1 and the three E modes are infrared active. However, for the related compounds listed in Table I, the antisymmetric XF_4 out-of-plane deformation mode is either inactive for point group D_{4h} or of such low intensity for point group C_{4v} that it has not been observed. Further complications might be expected due to the fact that we are not dealing with the isolated ClF_4O^- ion but with a solid in which the ClF_4O^- ions might occupy lattice sites having a symmetry lower than C_{4v} . This site symmetry lowering might particularly influence the doubly degenerate E modes and cause their splitting into two components. The observation of seven or eight Raman bands (assuming two of the three E modes to split into their degenerate components), with two of them having none and one of them having only a very weak counterpart in the infrared spectrum, is consistent with the above considerations.

The assignments for ClF_4O^- were made by com-

parison with the known spectra of ClF_4^- ,³ ClF_5 ,^{4,5} XeF_4 ,^{6,7} and XeOF_4 .⁴ The band at about 1200 cm^{-1} occurs at a frequency much too high for any $\text{Cl}-\text{F}$ fundamental vibration and, hence, is assigned to the $\text{Cl}=\text{O}$ stretching vibration, $\nu_1(A_1)$. The shoulder on the lower frequency side of the 1200-cm^{-1} band is due to the ^{37}Cl isotope. The strongest Raman band, at about 460 cm^{-1} , should belong to the totally symmetric ClF_4 stretching vibration, $\nu_2(A_1)$. Similarly, the strongest infrared band at about 580 cm^{-1} should be due to the antisymmetric ClF_4 stretching vibration, $\nu_7(E)$, which is split into its two degenerate components. The second strongest Raman band at about 350 cm^{-1} obviously should represent the symmetric out-of-phase ClF_4 stretching mode $\nu_4(B_1)$. The frequencies and relative intensities of $\nu_2(A_1)$ and $\nu_4(B_1)$ of ClF_4O^- are in good agreement with those reported³ for ClF_4^- .

The remaining five modes are deformation modes. The $\text{O}=\text{ClF}_4$ deformation mode, $\nu_8(E)$, involves mainly a motion of the double-bonded oxygen and, hence, should have the highest frequency. It is assigned to the band at about 400 cm^{-1} , assuming again a splitting into its degenerate components. By analogy with the related molecules listed in Table I, the antisymmetric in-plane ClF_4 deformation mode should have the lowest frequency and is therefore assigned to the band at about 210 cm^{-1} . For the remaining three modes, we are left with only two frequencies. Since the antisymmetric out-of-plane XF_4 deformation mode, $\nu_5(B_1)$, has not been observed for any of the compounds given in Table I, it is assumed to be the unobserved mode. There are two frequencies at about 340 and 280 cm^{-1} left for assignment to the ClF_4 umbrella deformation, $\nu_3(A_1)$, and the ClF_4 scissoring mode, $\nu_6(B_2)$. These two modes can easily be distinguished based upon their relative infrared intensities. The ν_3 mode should be of high intensity, whereas ν_6 should ideally be only Raman active. Consequently, the bands at 340 and 280 cm^{-1} are assigned to $\nu_3(A_1)$ and $\nu_6(B_2)$, respectively. The frequencies of $\nu_3(A_1)$ and $\nu_4(B_1)$ almost coincide. The possibility that for $\text{Rb}^+\text{ClF}_4\text{O}^-$ the 339-cm^{-1} infrared band is the counterpart of the 350-cm^{-1} Raman band is not likely owing to its high relative intensity and the relatively large frequency difference of 11 cm^{-1} . Comparison of the ClF_4^- frequencies with those of ClF_4O^- and ClF_5 involving only the approximately square-planar ClF_4 part reveals the following trend. The ClF_4O^- anion has the lowest frequencies, ClF_4^- is inter-

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TABLE I
VIBRATIONAL SPECTRA OF $\text{Rb}^+\text{ClF}_4\text{O}^-$ AND $\text{Cs}^+\text{ClF}_4\text{O}^-$ AND THEIR ASSIGNMENT COMPARED WITH THOSE OF ClF_4^- , ClF_5 , XeOF_4 , AND XeF_4

Observed frequencies, cm^{-1} , and relative intensities												Assignment for XZF_4 in point group	Type of vibration
$\text{Rb}^+\text{ClF}_4\text{O}^-$		$\text{Cs}^+\text{ClF}_4\text{O}^-$		ClF_4^- ^a		ClF_5 ^b		XeOF_4 ^b		XeF_4 ^{c,d}			
Ir	Raman	Ir	Raman	Ir	Raman	Ir	Raman	Ir	Raman	Ir	Raman	C_{4v}	
1216 s	1211 (0.6)	1201 s	1203 (0.6)			722 m	709 (3)	926 s	920 (2)			A ₁ ν_1	ν XZ
462 w	461 (10)	457 w	456 (10)		505 (10)	541 m	538 (1)	576 m	567 (10)		543 (10)	ν_2	ν_{sym} in-phase XF_4
339 s	[350] ^e	339 s	[345] ^e	425 m		493 s	480 (10)	294 s	285 (0+)	291 s		ν_3	δ_{sym} out-of-plane XF_4
	350 (4.3)		345 (4)		417 (10)		480 (10)		527 (4)		502 (8)	B ₁ ν_4	ν_{sym} out-of-phase XF_4
					288 (1)		[346] ^e		[230]			ν_5	δ_{asym} out-of-plane XF_4
							375 (1)		233 (1)		235 (0+)	B ₂ ν_6	δ_{sym} in-plane XF_4
283 vw	285 (0.4)	280 vw	283 (0.4)			732 vs		608 vs		586 vs		E	ν_{asym} XF_4
600	599 (0.1)	600	593 (0.2)	500-680									
550	557 (0.4)	560	564 (0.3)	vs, br									
415	416 (1.4)	415	416 (1.4)			482 s	[480]	361 s	365 (2)			ν_8	δ ZXF
394	395 (0.1)	396	397 (0.1)			302 s	296 (0.4)		161 (0+)	[250]		ν_9	δ_{asym} in-plane XF_4
	213 (0.6)		204 (0.7)										

^a Reference 3. ^b References 4 and 5. ^c Reference 6. ^d Reference 7. ^e Frequency values listed in brackets were not observed directly. They were either obscured by stronger bands in the same region or estimated from combination bands or force constant calculations.

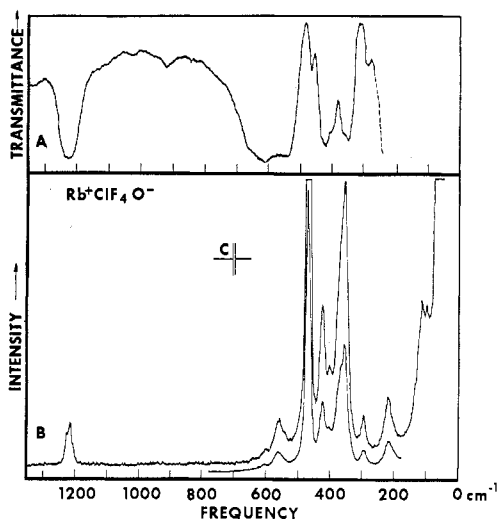


Figure 1.—Vibrational spectrum of solid $\text{Rb}^+\text{ClF}_4\text{O}^-$: (A) infrared spectrum as AgBr disk; (B) Raman spectrum at two different recorder voltages, exciting line 4880 Å; C indicates spectral slit width.

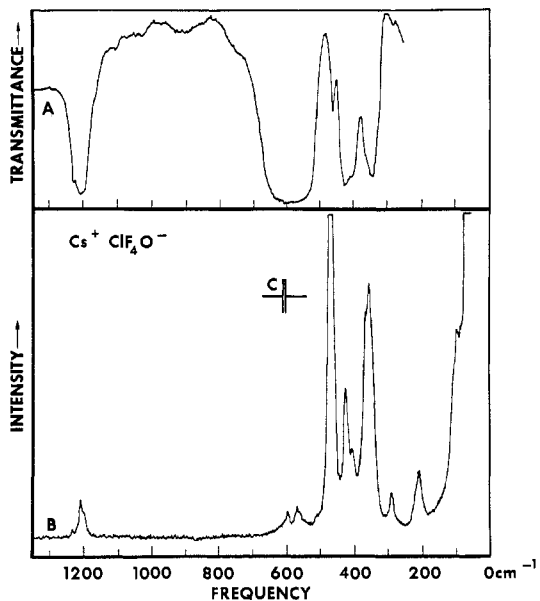


Figure 2.—Vibrational spectrum of solid $\text{Cs}^+\text{ClF}_4\text{O}^-$: (A) infrared spectrum as AgBr disk; (B) Raman spectrum, exciting line 4880 Å; C indicates spectral slit width.

mediate, and ClF_5 exhibits the highest frequencies. This is not surprising, since ClF_4O^- possesses, in addition to a bond-weakening formal negative charge, an oxygen ligand. The pronounced weakening effect on Cl-F bonds upon oxygen substitution has previously been discussed in detail for ClO_2F_2 ⁸ and, hence, will not be reiterated.

The difference in the vibrational spectra of ClF_4O^- and isoelectronic XeOF_4 can be rationalized in the following way. The two symmetric XF_4 stretching modes do not involve a motion of the central atom. Hence, no mass effect of the central atom is expected, and XeOF_4 with the stronger X-F bond shows the higher frequencies for these two modes. For the anti-symmetric XF_4 stretching mode, the frequencies become similar for XeOF_4 and ClF_4O^- due to a pronounced mass effect. The deformation modes of XeOF_4 all show lower frequencies than the corresponding modes of ClF_4O^- . This is due to the increased size of the central atom in XeOF_4 which facilitates angle deformations. For ClF_4O^- , an overlap of the range of stretching and deformation vibrations occurs. This unusual overlap has previously been recognized and discussed³ for the structurally related ClF_4^- anion and requires relatively weak Cl-F bonds and a small central atom. Furthermore, a comparison between the pairs ClF_4O^- - ClF_4^- and XeOF_4 - XeF_4 shows for the chlorine fluoride stretching modes a frequency decrease from ClF_4^- toward ClF_4O^- , whereas for the xenon fluorides the trend is reversed. This is due to the difference in the electronegativity of the central atoms. In the case of the xenon compounds, the addition of an oxygen ligand (which is more electronegative than xenon) to xenon results in a slight further electron-density withdrawal from xenon. This increases the effective electronegativity of xenon and makes it more similar to that of fluorine, thus increasing the contribution of covalent bonding to the Xe-F bond. In the case of chlorine fluorides, the multivalent chlorine atom is more electronegative than oxygen. Hence, oxygen addition lowers the effective electronegativity of chlorine, thus causing an increase in the polarity of the Cl-F bond. This effect of oxygen substitution has been observed for the following related pairs:

$\text{ClF}_3\text{-ClF}_3\text{O}$,² $\text{ClF}_2^-\text{-ClF}_2\text{O}_2^-$,⁸ ClF-ClFO_2 ,⁸ and $\text{ClF}_2^+\text{-ClF}_2\text{O}^+$,⁹ and, hence, appears to be quite general. This interpretation assuming a reversed polarity of the X=O bond in chlorine oxyfluorides and XeOF_4 is further supported by the observed ¹⁹F nmr shifts. Thus, the fluorine ligands in XeF_4 are more shielded than those in XeOF_4 , whereas the fluorine ligand in FClO_2 is less shielded than that in FClO_3 .¹⁰

Force Constants and Bonding.—The potential and kinetic energy metrics for the tetrafluoroxychlorate anion were computed by a machine method.¹¹ The geometry was assumed to be that of an ideal square-pyramid with $D(\text{Cl-O}) = 1.42 \text{ \AA}$, based on a correlation between stretching frequency and bond length,¹² and with $r(\text{Cl-F}) = 1.75 \text{ \AA}$, which is somewhat longer than the long bonds in ClF_3 .¹³ The bond angles, α and β , are defined as $\angle\text{O-Cl-F}$ and $\angle\text{F-Cl-F}$, respectively, and were assumed to be 90° .

The force constants were found by trial and error with the aid of a computer, requiring exact fit between the observed and computed frequencies. The results are given in Table II. The values shown for the inter-

TABLE II
FORCE CONSTANTS OF ClF_4O^- ^a

f_R	9.13		
f_r	1.79	$f'_{\beta\beta}$	0.29
f_β	1.33	$f'_{\alpha\alpha}$	0.08
f_α	0.61	$f_{r\beta}$	0.15
f_{rr}	0.25	$f'_{r\beta}$	-0.15
f'_{rr}	0.04		

^a Stretching force constants in mdyn/\AA and deformation force constants in mdyn \AA/radian^2 .

action constants, while not unique, were the simplest set that would give an exact fit. Since the force constants are underdetermined, a statistically meaningful uncertainty estimate cannot be made. Numerical experiments showed that assuming different interaction constants, and constraining them to plausible values, would result in valence force constants differing from these shown by less than 0.2. These estimated uncertainties are felt to be conservative. The potential energy distribution for this force field is shown in Table III.

The two constants of greatest interest are the stretching force constants. The value of 9.13 mdyn/\AA found for the Cl=O stretching force constant, f_R , is within the range expected for a covalent Cl=O double bond. For example, values of 9.37, 9.07, and 8.3 mdyn/\AA were found for the chlorine oxyfluorides, ClF_3O ,² ClO_2F ,¹⁴ and ClO_2F_2^- ,⁸ respectively. The fact that the value of f_R in ClF_4O^- is slightly lower than that in ClF_3O can be explained by the negative charge

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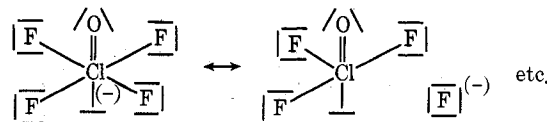
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TABLE III
POTENTIAL ENERGY DISTRIBUTION^a FOR ClF_4O^-

Assignment	Frequency, cm^{-1}	Potential energy distribution
$A_1 \nu_1$	1203	$0.98f_R$
ν_2	456	$0.77f_r + 0.21f_{rr}$
ν_3	339	$0.80f_\beta + 0.17f'_{\beta\beta}$
$B_1 \nu_4$	345	$1.34f_r - 0.37f_{rr}$
ν_5	(218) ^b	$0.82f_\beta + 0.17f'_{\beta\beta}$
$B_2 \nu_6$	283	$0.89f_\alpha + 0.11f'_{\alpha\alpha}$
$E \nu_7$	578	$0.97f_r + 0.17f_\beta$
ν_8	406	$1.11f_\beta$
ν_9	204	$1.04f_\alpha - 0.13f'_{\alpha\alpha}$

^a Only the more important terms are given. ^b Computed frequency.

on the central atom in ClF_4O^- . The low value of 1.78 mdyn/\AA obtained for the Cl-F valence force constant, f_r , is similar to that of 1.6 mdyn/\AA obtained for ClO_2F_2^- .⁸ These low values are due to the formal negative charge and oxygen substitution (see above). The negligible change in the Cl-O order (when compared with normal Cl=O double bonds), coupled with a pronounced decrease in the Cl-F bond order, implies that the negative charge in ClF_4O^- is, to a large extent, located on the fluorine ligands and not on the chlorine central atom or oxygen atom.



The pseudo-octahedral C_{4v} structure of ClF_4O^- could be explained by two different bond models: (1) an sp^3d^2 hybridization of the valence electrons of chlorine resulting in mainly covalent Cl-F bonds and (2) a model¹⁵⁻¹⁸ involving mainly two delocalized p-electron pairs of the chlorine atom for the formation of two semi-ionic three-center, four-electron p-p σ bonds with the four fluorine atoms. Mainly covalent sp hybridization is assumed for the Cl-O σ bond and the free electron pair. For model 1, we would expect for the Cl-F valence force constant a value in the range $2.8\text{-}3.6 \text{ mdyn/\AA}$. For model 2, f_r should be between 1.6 and 2.5 mdyn/\AA . The value of 1.78 \AA observed for the Cl-F stretching force constant in ClF_4O^- strongly favors model 2.

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