$NiIn_2Cl_8(g)$, the hypothesis that equilibrium 17 does not depend on L seems to be supported by the nickel complexes (Table II).

If we calculate $K(17)$ at, e.g., 900 K using the thermodynamic functions of Table II, we find that the values differ by less than 1 order of magnitude (Table VI) and that $K_{NiAl_2Cl_8} > K_{NiGa_2Cl_8} > K_{NiIn_2Cl_8}$. This, however, does not imply that the partial pressure of the gaseous nickel complexes in an ampule containing solid nickel chloride and identical amounts of LCl_3 is proportional to these equilibrium constants. To illustrate the relative stability of NiL_2Cl_8, it is better to compare the reactions $NiCl_2(s) + 2LCl_3(g) = NiL_2Cl_8(g)$, which show that the stability of $NiL_2Cl_8(g)$ is roughly proportional to the dimerization energy of $LCl_3(g)$. The same trend is observed for the formation of $NiLCl_5(g)$. This is expected if the approximations discussed in the context of eq 15 and 16 are valid. The relative amounts of nickel carried into the gas phase under "reasonable" experimental condition are shown in Figure 5.

Schäfer[21] and Dewing[1] proposed that the thermodynamics of reaction 17 should be similar ($\Delta H = 50 \pm 8$ kJ mol^{-1}, $\Delta S = 46 \pm 13$ J mol^{-1} K^{-1}) for all M which have octahedral coordination in the solid MCl_2 as well as in the gaseous complex. While the enthalpies of formation of the cobalt complexes fit into this scheme, the enthalpies of the nickel complexes do not—they are too positive (Table II). Within Schäfer and Dewing's concept this would be understandable if the coordination number of the nickel was smaller in the gas than in the solid. This, however, is contradicted by the UV-visible spectrum, which is essentially that of a $NiCl_6$ chromophore[10] with only a small—if any—contribution from a tetrahedral $NiCl_4$ center. Although we have no proposition for reconciling the low stability of the $NiL_2Cl_8(g)$ complexes with the structure derived from their optical spectrum, we consider it worth mentioning that $NiCl_2$ has by far the highest melting point (1000 °C) of all the isostructural chlorides ($CdCl_2$-type) for which equilibrium 17 has been studied (e.g., $MnCl_2$, 650 °C; $CoCl_2$, 740 °C). The structural stability which is responsible for the high melting point of $NiCl_2$ evidently also is against its "evaporation" by equilibrium 17.

The results of the present investigation of the stability of $NiAlCl_5(g)$, $NiAl_2Cl_8(g)$, $NiGaCl_5(g)$, and $NiGa_2Cl_8(g)$ are largely consistent with the ideas about the correlation between stability and structure of gaseous complexes. This agreement with the general aspects of a larger experimental body of gaseous complexes is considered as an additional element of support for our results.

Acknowledgment. The authors thank Dr. C. Daul and J. Kuenlin for computer assistance. The project has been supported by the Swiss National Science Foundation, Grant No. 2.654-0.80.

Note Added in Proof. While this paper was in press, a paper dealing with the stability of $NiAl_2Cl_8(g)$ and $NiAl_3Cl_{11}(g)$ has been published by W. Lenhard and H. Schäfer, *Z. Anorg. Allg. Chem.*, **482**, 167 (1981).

Registry No. $NiCl_2$, 7718-54-9; $AlCl_3$, 7446-70-0; $GaCl_3$, 13450-90-3; $NiAlCl_5$, 81315-93-7; $NiGaCl_5$, 66143-12-2; $NiAl_2Cl_8$, 40556-06-7; $NiGa_2Cl_8$, 66594-41-0; Al_2Cl_6, 13845-12-0; Ga_2Cl_6, 15654-66-7.

Contribution from Rocketdyne, a Division of Rockwell International Corporation,
Canoga Park, California 91304

Fluorine Perchlorate. Vibrational Spectra, Force Field, and Thermodynamic Properties

KARL O. CHRISTE* and E. C. CURTIS

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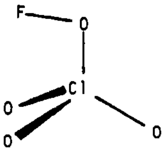
Infrared spectra of gaseous, solid, and matrix-isolated ClO_3OF and Raman spectra of liquid ClO_3OF are reported. All 12 fundamental vibrations expected for the covalent perchlorate structure of symmetry C_s were observed and assigned. A modified valence force field was computed for ClO_3OF by using the observed ^{35}Cl–^{37}Cl isotopic shifts, symmetry relations between the A′ and the A″ block, and the off-diagonal symmetry force constants of the closely related $FClO_3$ molecule as constraints. Previous assignments for ClO_3OCl, ClO_3OBr, ClO_3OCF_3, Cl_2O_7, and Cl_2O_7 are revised. The ^{19}F NMR spectrum of ClO_3OF was recorded, and thermodynamic properties were computed in the range 0–2000 K.



Introduction

Fluorine perchlorate (or perchloryl hypofluorite) was probably first prepared[1] in 1929 by Fichter and Brunner by the fluorination of dilute $HClO_4$ with F_2 but was incorrectly identified. The first positive identification of ClO_3OF was reported[2] in 1947 by Rohrback and Cady, who obtained the compound from the reaction of F_2 with concentrated perchloric acid. They reported that ClO_3OF consistently exploded when frozen.

In view of its explosive nature, it is not surprising that very few papers dealing with ClO_3OF have been published since then. In 1962, Agahigian and coworkers reported[3] the ^{19}F NMR spectrum of ClO_3OF in $CFCl_3$ and four infrared absorptions of the gas. The same four infrared bands have also been observed in a study[4] at United Technology Corp. in which the heat of hydrolysis was measured for ClO_3OF. Macheteau and Gillardeau studied[5] the thermal decomposition of ClO_3OF

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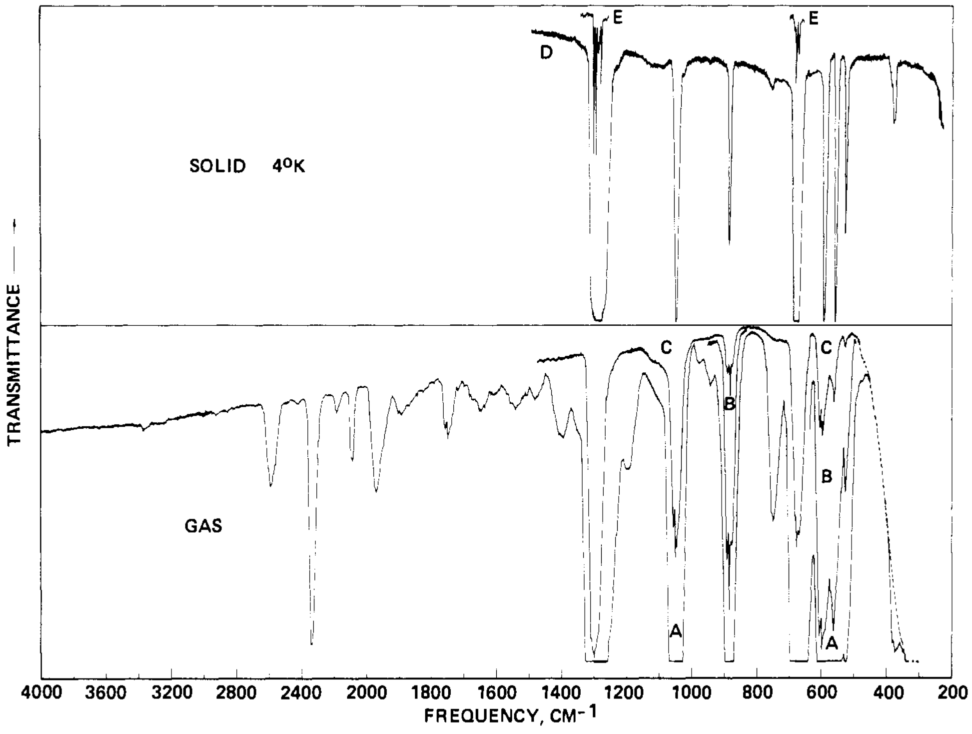

Figure 1. Traces A, B, and C: infrared spectra of gaseous ClO_3OF recorded in a 5-cm path length cell at pressures of 1000, 100, and 10 torr, respectively. The broken line indicates background absorption by the AgCl windows. Traces D and E: infrared spectra of neat and Ne matrix-isolated ClO_3OF, respectively, recorded at 4 K with CsI windows.

and confirmed the four infrared bands previously reported.[3,4] Small amounts of ClO_3OF have been reeported to form as byproducts in the reactions of F_2 with metal perchlorates[4,6,7] and Cl_2O_6.[8] Force constants have been predicted[9] for ClO_3OF by Witt and Hammaker using the four published infrared frequencies, estimating the missing frequencies from the known ClO_3OCl data[10] and transferring five internal force constants from ClO_3OCl to ClO_3OF. It was recently found that very pure ClO_3OF could be obtained in high yield by the thermal decomposition of NF_4ClO_4.[11] The ClO_3OF, prepared in this manner, could be manipulated and repeatedly frozen without explosions.[12] In view of this improved synthesis and the paucity of previous data on ClO_3OF, a better characterization of this compound was undertaken.

Experimental Section

Caution! Although no explosions were incurred during the present study, the original reports[2] of Rohrback and Cady indicate that ClO_3OF is a highly sensitive and powerful explosive. It should be handled only in small quantities and with proper safety precautions.

Fluorine perchlorate was prepared by thermal decomposition of NF_4ClO_4[11,13] at ambient temperature and was purified by fractional condensation in a well-passivated (with ClF_3) stainless steel–Teflon FEP vacuum system. Fluorine perchlorate was found to pass slowly through a −126 °C trap but to stop in a colder trap. The only impurity detectable in the infrared spectrum of the gas at 1000 mm pressure was a trace of $FClO_2$.

Infrared spectra were recorded on a Perkin-Elmer Model 283 spectrometer, which was calibrated by comparison with standard gas calibration points.[14,15] The reported frequencies and isotopic shifts are believed to be accurate to ±2 and ±0.1 cm^{-1}, respectively. Gas spectra were recorded with use of a Teflon cell of 5-cm path length equipped with a Teflon PFA valve (Fluoroware Inc.) and AgCl windows. The spectra of neat and matrix-isolated ClO_3OF were recorded at 4 K with use of an Air Products Model ACL3 helium refrigerator equipped with CsI windows. Research grade N_2 or Ne (Matheson) was used as the matrix in a mole ratio of 1000:1.

The Raman spectra were recorded on a Cary Model 83 spectrometer using the 4880-Å exciting line with a Claassen filter for the elimination of plasma lines.[16] Polarization measurements were carried out by method VIII, as described[16] by Claassen et al. A flamed-out 4-mm o.d. quartz tube was used as a sample container in the transverse excitation–transverse viewing mode. It was cooled to −100 °C in an apparatus similar to that[17] described by Miller and Harney.

The ^{19}F NMR spectrum of ClO_3OF in HF solution was recorded at 84.6 MHz on a Varian Model EM390 spectrometer equipped with a variable-temperature probe. Chemical shifts were determined relative to external $CFCl_3$ with positive shifts being downfield from $CFCl_3$.

Results and Discussion

Properties of ClO_3OF. Fluorine perchlorate is colorless as a gas and a liquid and white as a solid. It was found to be stable at room temperature in either Teflon or passivated steel containers and to be the most stable member of the series ClO_3OF, ClO_3OCl, ClO_3OBr. Contrary to the original report of Rohrback and Cady,[2] explosions were not incurred on either freezing or melting ClO_3OF. Since Rohrback and Cady had prepared their sample of ClO_3OF by fluorination of $HClO_4$, a small amount of the latter could have caused their samples to be more sensitive.[18]

The ^{19}F NMR chemical shift of ClO_3OF has been reported[3] to be 225.9 ppm downfield from $CFCl_3$. However, since the

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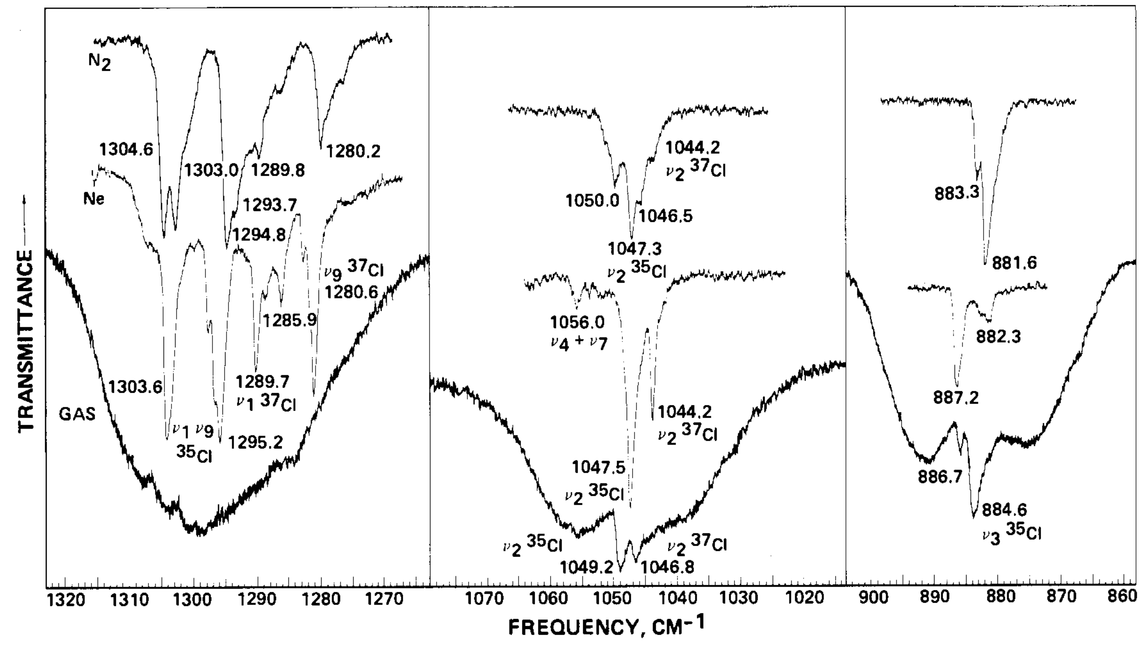


Figure 2. Infrared spectra of N_2 and Ne matrix-isolated and of gaseous ClO_3OF recorded with 20-fold scale expansion under higher resolution conditions.

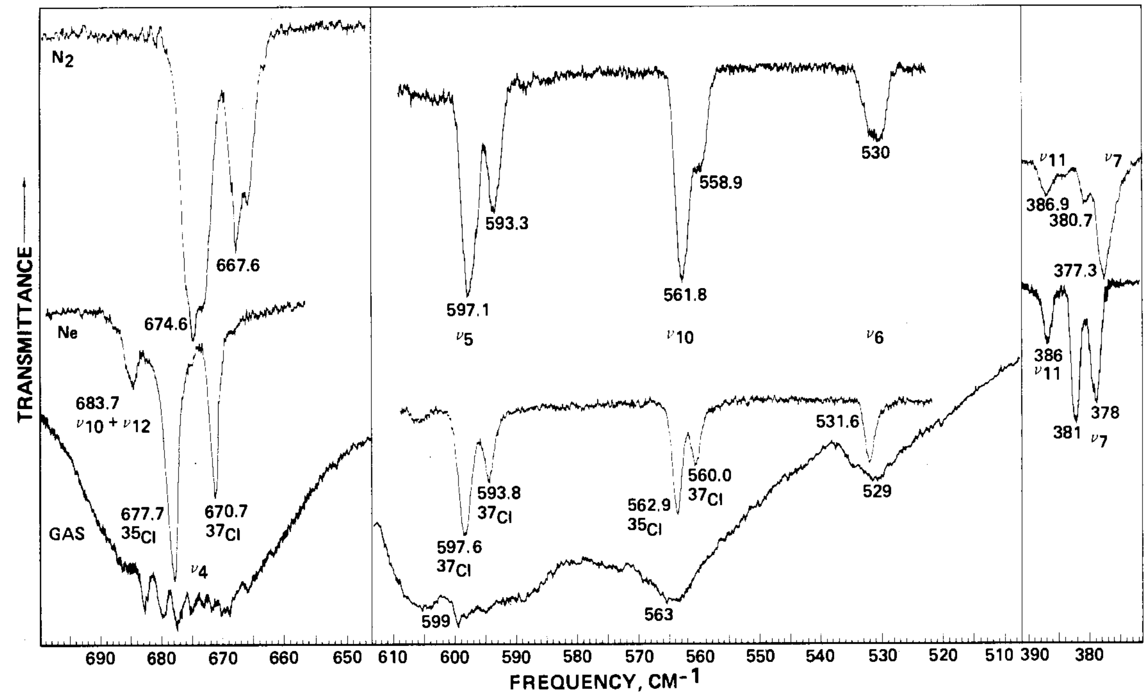
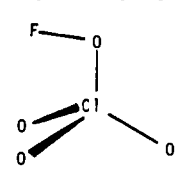


Figure 3. See caption of Figure 2.

shift for $FClO_3$, reported in the same paper, is in error by about 35 ppm,[19] we have redetermined the shift for ClO_3OF. In HF solution, a single line, 219.4 ppm downfield from external $CFCl_3$, was observed, in fair agreement with the previously reported[3] value of 225.9 ppm.

Vibrational Spectra. The infrared spectra of ClO_3OF were recorded for the gas, and for the neat and the neon- and nitrogen-matrix-isolated solid (see Figures 1–3). The Raman spectra of liquid ClO_3OF, recorded at −100 °C, are given in Figure 4. The observed frequencies and their assignments are summarized in Table I. The four infrared bands previously reported[3-5] for gaseous ClO_3OF agree well with our results.

Assignments. By analogy with closely related molecules, such as CF_3OF,[20,21] fluorine perchlorate should possess a staggered structure of symmetry C_s.



The 12 fundamental vibrations expected for ClO_3OF of symmetry C_s can be classified as 8 A′ and 4 A″, where all modes are allowed in both the infrared and the Raman spectra. In

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Table I. Vibrational Spectra of ClO_3OF

obsd freq, cm^{-1}, and intens							
infrared				Raman			
gas	N_2 matrix	Ne matrix	solid	liquid	HF soln	assignt in point group C_s	
2588 vw						1302 + 1295 = 2597	$\nu_1 + \nu_9$ (A'')
						2 × 1295 = 2590	$2\nu_9$ (A'')
2335 w						1295 + 1049 = 2344	$\nu_9 + \nu_2$ (A'')
2183 vvw						1302 + 885 = 2187	$\nu_1 + \nu_3$ (A')
						1295 + 885 = 2180	$\nu_9 + \nu_3$ (A'')
2092 vw						2 × 1049 = 2098	$2\nu_2$ (A')
1968 vw						1295 + 677 = 1972	$\nu_9 + \nu_4$ (A'')
1891 vvw						1295 + 599 = 1894	$\nu_9 + \nu_5$ (A'')
1749 vw						2 × 885 = 1770	$2\nu_3$ (A')
1670 vvw, sh						1295 + 379 = 1674	$\nu_9 + \nu_7$ (A'')
1645 vvw						1049 + 599 = 1648	$\nu_2 + \nu_5$ (A')
1610 vvw, sh						1049 + 563 = 1612	$\nu_2 + \nu_{10}$ (A'')
1555 vvw, sh						885 + 677 = 1562	$\nu_3 + \nu_4$ (A')
1538 vvw						1302 + 230 = 1532	$\nu_1 + \nu_8$ (A')
1480 vvw						885 + 599 = 1484	$\nu_3 + \nu_5$ (A')
1394 vvw						563 + 559 + 230 = 1392	$\nu_5 + \nu_{10} + \nu_8$ (A'')
1345 vvw, sh						2 × 677 = 1354	$2\nu_4$ (A')
		1307 sh					
	1304.6 vs	1303.6 vw	1284 vs	1289 (0.3) br	1289 (0.3)		ν_1 (A') ^{35}Cl
	1303.0 vs	1302 sh				2 × 386 + 529 = 1301	$2\nu_{11} + \nu_6$ (A')
	1301.8 sh	1297.4 mw					
	1294.8 vs	1296.1 mw	1284 vs	1289 (0.3) br	1289 (0.3)		ν_9 (A'') ^{35}Cl
	1293.7 sh	1295.2 vs					
1299 vs	1289.8 m	1289.7 m					ν_1 (A') ^{37}Cl
		1288.4 mw					
	1286.4 m	1285.9 mw				2 × 378 + 529 = 1285	$2\nu_7 + \nu_6$ (A')
		1281.6 w					ν_9 (A'') ^{37}Cl
	1280.2 ms	1280.6 ms					
	1276 sh						
1195 vw						2 × 599 = 1198	$2\nu_5$ (A')
		1063 w				2 × 529 = 1058	$2\nu_6$ (A')
	1055 vw	1056.0 w				678 + 379 = 1057	$\nu_4 + \nu_7$ (A') ^{35}Cl
	1051.2 sh					671 + 379 = 1050	$\nu_4 + \nu_7$ (A') ^{37}Cl
	1050.0 mw						
1049.2 s	1047.3 ms	1047.5 ms	1042 ms	1044 (10) p	1045 (10)		ν_2 (A') ^{35}Cl
	1046.5 mw						
1046.8 ms	1044.2 mw	1044.2 m					ν_2 (A') ^{37}Cl
975 vvw						599 + 379 = 978	$\nu_5 + \nu_7$ (A')
943 vvw						563 + 379 = 942	$\nu_{10} + \nu_7$ (A'')
886.7 w	883.3 mw	882.3 mw				2 × 379 + 127 = 885	$2\nu_7 + \nu_{12}$ (A'')
884.6 mw	881.6 m	887.2 m	879 m	882 (4.3) p	882 (1.9)		ν_3 (A')
751 w			750 w			2 × 379 = 758	$2\nu_7$ (A')
		683.7 mw				563 + 127 = 690	$\nu_{10} + \nu_{12}$ (A')
682.1							
679.2							
676.8							
674.6 s	674.6	677.7 s	669 s	670 (2.8) p	670 (1.5)		ν_4 (A') ^{35}Cl
672.3	667.6 ms	670.7 ms					ν_4 (A') ^{37}Cl
671.0							
668							
599 mw	597.1 ms	597.6 ms	595 ms	596 (0.8) dp			ν_5 (A') ^{35}Cl
	593.3 m	593.8 m					ν_5 (A') ^{37}Cl
563 mw	561.8 ms	562.9 ms	558 ms	559 (0.8) dp			ν_{10} (A'') ^{35}Cl
	558.9 m	560.0 m					ν_{10} (A'') ^{37}Cl
529 w	530 m	531.6 m	529 m	528 (4.4) p	528 (1.8)		ν_6 (A')
	386.9 w	386 w					
			383 sh	382 sh, dp	382 sh		ν_{11} (A'') and $3\nu_{12}$ (A'')
378 w	380.7 w	381 mw				3 × 127 = 381	
	377.3 mw	378 mw	377 mw	377 (8.9) p	377 (4.7)		ν_7 (A')
				230 (1.4) p	232 (0.8)		ν_8 (A')
				127 (0.6) dp			ν_{12} (A'')

the Raman spectrum, the A′ modes can be either polarized or depolarized, while the A″ modes should all be depolarized. An approximate description of all 12 modes is given in Table II.

By comparison with the known spectra of the related molecules ClO_3OCl,[10] ClO_3OBr,[10] ClO_3OH,[22] ClO_3OD,[22] $O_3ClOClO_3$,[9,23,24] CF_3OClO_3,[25] $FClO_3$,[26-30] $FOSO_2F$,[31-33] and CF_3OF,[34-39] the assignments for most fundamental vibrations of ClO_3OF (see Table II) are straightforward. Additional

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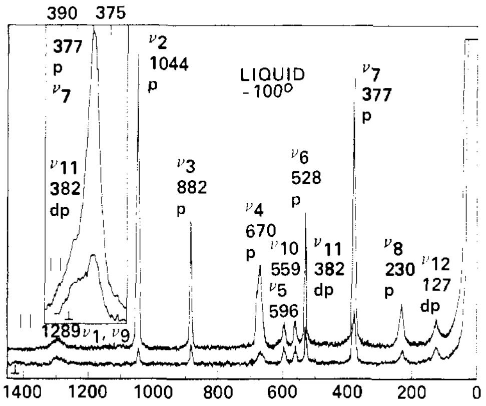

Figure 4. Raman spectra of liquid ClO_3OF in a 4-mm quartz tube recorded at −100 °C with parallel and perpendicular polarization. The insert shows the 377-cm^{-1} band recorded with scale expansion.

support for these assignments comes from the observed $^{35}Cl-^{37}Cl$ isotopic shifts (chlorine has two naturally occurring isotopes, ^{35}Cl and ^{37}Cl, with an abundance ratio of 3:1), from the normal-coordinate analysis (see below), and from the Raman polarization data. Consequently, only the less straightforward assignments will be discussed.

The two antisymmetric ClO_3 stretching modes, $\nu_1(A')$ and $\nu_9(A'')$, are almost degenerate and therefore could be observed as separate bands only in the matrix spectra at about 1303 and 1295 cm^{-1}. In the Ne matrix, the ^{37}Cl satellite of the 1303.6-cm^{-1} fundamental at 1289.7 cm^{-1} appears to be in Fermi resonance with the A′ combination band ($2\nu_7 + \nu_6$) at 1285.9 cm^{-1}. Because Fermi resonance is possible only between vibrations belonging to the same symmetry species, the 1303.6-cm^{-1} band is tentatively assigned to the A′ mode. The additional smaller splittings observed for the 1295-cm^{-1} band in the Ne matrix and for the other bands in the N_2 matrix are attributed to matrix site effects. The Raman polarization data for the 1289-cm^{-1} band were inconclusive due to the great line width, low intensity, and low degree of polarization and therefore were not useful for distinguishing between the A′ and the A″ fundamental.

The frequencies of the two ClO_3 rocking modes, $\nu_7(A')$ and $\nu_{11}(A'')$, almost coincide and are readily assigned on the basis of their Raman polarization ratios (see Figure 4). The splitting of $\nu_{11}(A'')$ (see Figure 3) into two components in the matrix-isolated infrared spectra is attributed to Fermi resonance with $3\nu_{12}(A'')$.

The symmetric (umbrella) ClO_3 deformation mode, $\nu_5(A')$, and the two antisymmetric ClO_3 deformation modes, $\nu_{10}(A'')$ and $\nu_6(A')$, are assigned to the three fundamentals observed at about 599, 563, and 529 cm^{-1}, respectively. The assignment of the 599-cm^{-1} fundamental to $\nu_5(A')$ is established by the

Table II. Vibrational Spectra of ClO_3OF Compared to Those of Closely Related Molecules

assignt for ClO_3OF in point group C_s		approx description of mode for ClO_3OF	obsd freq, cm^{-1}							
			$FClO_3$[a]	ClO_3OH[b]	ClO_3OD[b]	ClO_3OF	ClO_3OCl[c]	$O_3ClOClO_3$[d]	ClO_3OBr[c]	CF_3OF[e]
A′	ν_1	$\nu_{asym}(ClO_3)$ }	1314 (15.8)[f]	1326 1201	1282	1302 (14.5)[f]	1287 (15)[f]	1300	1279	1222
	ν_2	$\nu_{sym}(ClO_3)$	1062 (3.05)	1048	1050	1049 (3.3)	1040	1060, 1025	1039	1294
	ν_3	$\nu(O-F)$		3553	2624	885 (~0)	749 (3.8)	} 704, 698	683	882
	ν_4	$\nu(Cl-O)$	717 (10.0)	726	725	677 (7.0)	646 (8.5)		648	947
	ν_5	$\delta_{umbrella}(ClO_3)$	549 (0.89)	582	587	599 (3.8)	580 (2.5)	600	572	678
	ν_6	$\delta_{asym}ClO_3$ (α)	589 (3.1)	555	555	529 (~1)	511 (<1.5)	521, 512	509	585
	ν_7	$\delta_{in\text{-}plane}(ClO_3$ rock) (β)	405 (0.2)	421	420	379 (<1)	355	430, 283	387	429
	ν_8	$\delta_{in\text{-}plane}(Cl-O-F)$ }		1326 1201	930	230	198	154		278
A″	ν_9	$\nu_{asym}(ClO_3)$	1314 (15.8)	1263	1282	1295 (14.6)	1271 (15)	1300	1262	1261
	ν_{10}	$\delta_{asym}(ClO_3)$ (α)	589 (3.1)	582	577	563 (2.9)	561 (2.5)	571, 567	566	607
	ν_{11}	$\delta_{out\text{-}of\text{-}plane}(ClO_3$ rock (β)	405 (0.2)	421	420	385 (<1)	382 (<1)	490, 272	387	431
	ν_{12}	$\tau(Cl-OX)$		306		127	92			127

[a] References 28–30. [b] Reference 22; ν_1 and ν_8 of ClO_3OH are strongly coupled and best described as antisymmetric (1326) and symmetric (1200) combination of the corresponding symmetry coordinates. [c] Reference 10. [d] Reference 9, but with revised assignment for ν_5, ν_6, and ν_7. [e] References 34–38; it should be noted that for the A′ block of CF_3OF the mode description is inaccurate due to strong mixing.[38] [f] $^{35}Cl-^{37}Cl$ isotopic shifts.

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Table III. Symmetry Force Constants,[a] Observed and Calculated Frequencies, and $^{35}Cl-^{37}Cl$ Shifts and Potential Energy Distribution[b] of ClO_3OF

assignt		freq, cm^{-1}		Cl isotopic shift, cm^{-1}		symmetry force constants		potential energy distribution
		obsd	calcd	obsd	calcd			
A′	ν_1	1302	1303	14.5	15.7	$F_{11} = f_r - f_{rr}$	9.53	97 (1)
	ν_2	1049	1049	3.3	3.3	$F_{22} = f_r + 2f_{rr}$	9.49	97 (2)
	ν_3	885	885	<1	0.1	$F_{33} = f_D$	3.51	84 (3) + 10 (7)
	ν_4	677	677	7.0	7.0	$F_{44} = f_R$	2.38	52 (4) + 41 (5) + 9 (8) + 6 (6) − 20 (45)
	ν_5	599	599	3.8	3.8	$F_{55} = 0.65f_\beta + 0.35f_\alpha + 1.30f_{\beta\beta} + 0.70f_{\alpha\alpha} - 1.91f_{\alpha\beta'} - 0.95f_{\alpha\beta}$	2.38	54 (5) + 20 (6) + 8 (8)
	ν_6	529	529	~1	1.2	$F_{66} = f_\alpha - f_{\alpha\alpha}$	1.62	63 (6) + 28 (4) + 7 (8) + 4 (5) − 9 (46) + 5 (45)
	ν_7	379	379	<1	0.7	$F_{77} = f_\beta - f_{\beta\beta}$	1.54	69 (7) + 13 (3) + 10 (6) + 7 (4) + 5 (8) − 6 (67)
	ν_8	230	230		0.3	$F_{88} = f_\gamma$	0.99	66 (8) + 18 (7) + 15 (4)
A″	ν_9	1295	1295	14.6	15.1	$F_{99} = f_r - f_{rr}$	9.53	99 (9)
	ν_{10}	563	563	2.9	2.9	$F_{10,10} = f_\alpha - f_{\alpha\alpha}$	1.55	80 (10) + 8 (11) + 7 (10,11)
	ν_{11}	385	385		0.3	$F_{11,11} = f_\beta - f_{\beta\beta}$	1.21	94 (11) + 18 (10) − 12 (10,11)
	ν_{12}	127				$F_{12,12} = f_\tau$		
						$F_{16} = -F_{9,10} = f_{r\alpha'} - f_{r\alpha}$	−0.27	
						$F_{17} = F_{9,11} = f_{r\beta} - f_{r\beta'}$	0.35	
						$F_{24} = 3^{1/2}f_{rR}$	0.16	
						$F_{25} = 0.81f_{r\beta} - 1.18f_{r\alpha} + 1.61f_{r\beta'} - 0.59f_{r\alpha'}$	0	
						$F_{45} = 1.39f_{R\beta} - 1.02f_{R\alpha}$	0.51	
						$F_{46} = f_{R\alpha}$	0.218	
						$F_{67} = -F_{10,11} = f_{\alpha\beta'} - f_{\alpha\beta}$	−0.2	

[a] Stretching constants in mdyn/Å, deformation constants in mdyn Å/rad², and stretch-bend interaction constants in mdyn/rad. Although identical explicit F terms are given for F_{11}, F_{66}, F_{77} and F_{99}, $F_{10,10}$, $F_{11,11}$, respectively, it must be kept in mind that the corresponding A′ and A″ force constants are similar, but not identical (see text for explanation). [b] Contributions of less than 5% to the PED are not listed.

observed PQR band contour in the infrared spectrum of the gas, by its large $^{35}Cl-^{37}Cl$ isotopic shift, and, in particular, by the results from the normal-coordinate analysis (see below). By analogy with CF_3OF,[35] ClO_3OF is an accidental symmetric top with Cl and F lying on the axis of the smallest moment of inertia (I_A) and rotational constants of $A = 0.181$, $B = 0.0932$, and $C = 0.0931$ cm^{-1}. Therefore, the band contours for ClO_3OF are expected to be analogous of those of CF_3OF for which the PQR band contour of the umbrella deformation mode is well established. By analogy with $FClO_3$[30] and ClO_3OCl,[10] the Cl–O single bond stretching and the ClO_3 umbrella deformation mode in ClO_3OF are expected to exhibit a total of about 11 cm^{-1} in $^{35}Cl-^{37}Cl$ isotopic shift whose distribution between the two modes is governed by their degree of coupling. The assumption of a total isotopic shift of about 11 cm^{-1} for these two modes was supported by a large number of different force fields. As long as plausible interaction terms were used, this total isotopic shift remained close to 11 cm^{-1}. In ClO_3OF, the Cl isotopic shift of the Cl–O stretching mode is only 7.0 cm^{-1}, thus requiring a Cl shift of about 4 cm^{-1} for the ClO_3 umbrella deformation mode. This condition is met by the 599-cm^{-1} fundamental ($\Delta\nu = 3.8$cm^{-1}) but not by that at 529 cm^{-1} ($\Delta\nu \approx 1$ cm^{-1}). Furthermore, the normal-coordinate analysis strongly preferred a Cl isotopic shift of about 3.0 cm^{-1} for ν_{10}(A″) and could accommodate a 3.8- or 1-cm^{-1} shift only with unreasonable off-diagonal symmetry force constants. Also, the potential energy distributions of all physically meaningful force fields, obtained with the different possible assignments, insisted on 599 cm^{-1} belonging to the A′ block and being the umbrella deformation mode. With the 599-cm^{-1} fundamental being firmly assigned to the umbrella deformation mode, assignments for ν_6(A′) and ν_{10}(A″) are unambiguous on the basis of the Raman polarization data.

The frequency of 127 cm^{-1} for the Cl–OF torsional mode in ClO_3OF is in excellent agreement with that[36,39] found for the closely related CF_3OF molecule and confirmed by microwave spectroscopy.[21] Since the reduced moment of inertia for internal rotation $(I_A)_r$ of CF_3OF and ClO_3OF should be comparable, the potential barrier to internal rotation in ClO_3OF is expected to be similar to that of CF_3OF (about 4 kcal mol^{-1}).[20,39] The remaining assignments for ClO_3OF are all unambiguous and require no further comment.

Only minor frequency shifts were observed for ClO_3OF when going from the gas to the liquid and the solid. This indicates little or no association in the condensed phases.

Comparison of the ClO_3OF Assignments with Those of Similar Molecules. In Table II, the assignments for ClO_3OF are compared to those of similar molecules. The general agreement between the different compounds is excellent and permitted improvement of some of the previous assignments. For example, the assignments previously proposed for the antisymmetric (A′) and the symmetric ClO_3 deformation modes of ClO_3OCl,[10] ClO_3OBr,[10] and Cl_2O_7[9] should be reversed and the assignments for ClO_3OCF_3 should be revised to conform with those of ClO_3OF.

For CF_3OF, we propose to exchange the previous assignments[38] for the symmetric and antisymmetric CF_3 stretching modes in species A′. The CF_3 modes in CF_3OF are almost identical with those in CF_3ONF_2. Raman polarization data recently obtained in our laboratory for CF_3ONF_2 established beyond doubt that the highest CF_3 fundamental represents the symmetric stretching mode.

Chlorine Isotopic Shifts. The $^{35}Cl-^{37}Cl$ isotopic shifts observed for ClO_3OF are summarized in Table III. In view of the importance of these shifts for the force field computation, factors influencing some of these shifts will be briefly discussed. Whereas ν_5, ν_9, and ν_{10} are essentially undisturbed, some of the other bands appear to be influenced by effects such as Fermi resonance with combination bands.

For ν_1, resonance between $(2\nu_7 + \nu_6)$ ^{37}Cl and ν_1 ^{37}Cl most likely shifts the latter to higher frequency and decreases its relative intensity and the apparent $^{35}Cl-^{37}Cl$ separation of ν_1's. Using a weighted average of the 1285.9- and 1289.7-cm^{-1} bands for the frequency of ν_1 ^{37}Cl results in a Cl isotopic shift of abut 14.5 cm^{-1}, similar to that (14.6 cm^{-1}) observed for the almost degenerate ν_9(A″) fundamental.

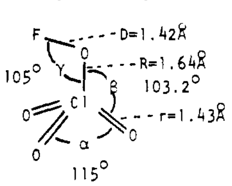
For ν_2 a discrepancy exists between the matrix isolation and the gas-phase data. Whereas two Q branches with a frequency separation of 2.4 cm^{-1} were observed in the gas-phase spectrum, the matrix isolation data show that in the Ne and N_2

matrices the isotopic shifts are 3.3 cm^{-1}. Two combination bands, ($\nu_4 + \nu_7$) and $2\nu_6$, occur in this region and were indeed observed in the matrix spectra. However, since in the Ne matrix they occur on the high-frequency side of ν_2 and are of low relative intensity, the larger isotopic shift in the matrix spectrum cannot be attributed to Fermi resonance effects. Since in the closely related $FClO_3$ molecule the Cl isotopic shift of this highly characteristic symmetric ClO_3 stretching mode is 3.05 cm^{-1},[30] we prefer the matrix shift value for ν_2 of ClO_3OF. The second Q branch, observed in the infrared spectrum of the gas, might be due to other effects such as hot bands.

The O–F stretching mode, ν_3(A′), shows a splitting of about 5 cm^{-1} in the Ne-matrix spectrum, but in the N_2-matrix and gas-phase spectra the satellite band is shifted to the high-frequency side of ν_3 and therefore is attributed to the combination band ($2\nu_7 + \nu_{12}$).

Normal-Coordinate Analysis. The normal-coordinate analysis of ClO_3OF presented a particular challenge because previous force field computations for the closely related ClO_3OX (X = Cl, Br, ClO_3),[9,10] CF_3OX (X = F, Cl),[34,38,41] and FSO_2OF[33] molecules revealed difficulties in reproducing the experimental frequencies and resulted in extensive mixing of symmetry coordinates for many of the A′ modes. Because of the highly underdetermined nature of these force fields, the mere reproduction of the observed frequencies does not necessarily result in a meaningful force field or even support a certain assignment. In order to avoid most of these drawbacks, we have used for our normal-coordinate analysis of ClO_3OF the following additional constraints: (i) $^{35}Cl-^{37}Cl$ isotopic shifts, (ii) symmetry relations between the A′ and A″ block, and (iii) transfer of many force constants, particularly off-diagonal symmetry force contants from the closely related $FClO_3$ molecule to ClO_3OF. For this purpose, it became necessary to determine first a reliable general valence force field for $FClO_3$ from a combination of Cl isotopic shifts, Coriolis constants, and ab initio force constant calculations.[30] Using this well-established $FClO_3$ force field both as a starting point for the ClO_3OF computations and as a criterion for judging the plausibility of the resulting force field, we determined a force field that met all our criteria.

For the computation of the ClO_3OF force field, the vibrational frequencies, Cl isotopic shifts, and assignments of Tables II and III were used. The required potential and kinetic energy metrics were computed by a machine method[42] using the following geometry, estimated from a comparison with the related molecules $FClO_3$,[43] ClO_3OH,[44] and CF_3OF.[20,21]



The symmetry coordinates used were the same as those given in ref 38, except that the numbering is different and the redundant coordinate was made exactly orthogonal to the other coordinates by the Gram–Schmidt process. Analytical expressions for the symmetry force constants are given in Table III. The off-diagonal symmetry force constants were adjusted by trial and error and then kept fixed during adjustment of the diagonal symmetry force constants by a least-squares method to reproduce the observed frequencies and isotopic shifts. Due to the symmetry relations between the A′ and the A″ block ($F_{11} = F_{99}$, $F_{66} = F_{10,10}$, $F_{77} = F_{11,11}$, $F_{16} = -F_{9,10}$, $F_{17} = F_{9,11}$, and $F_{67} = -F_{10,11}$), both blocks were refined simultaneously. Due to its low frequency and weak coupling with other modes, the torsional mode ν_{12} was omitted for the analysis.

Table IV. Comparison of Internal Force Constants[a] of ClO_3OF with Those of $FClO_3$

	ClO_3OF	$FClO_3$		ClO_3OF	$FClO_3$
f_r	9.52	9.76	$f_\beta - f_{\beta\beta}$	1.54 (A′)	1.49
f_{rr}	−0.01	0.07		1.21 (A″)	
f_{rR}	0.09	0.08	$f_{r\alpha} - f_{r\alpha'}$	0.27	−0.29[b]
$f_\alpha - f_{\alpha\alpha}$	1.62 (A′)	1.53	$f_{r\beta} - f_{r\beta'}$	0.35	−0.33[b]
	1.55 (A″)		$f_{\alpha\beta} - f_{\alpha\beta'}$	0.2	0.26

[a] For dimensions of force constants see footnote *a* of Table III. [b] The different signs in these force constants are caused by the different signs in the symmetry coordinates used for the two computations and therefore have no physical meaning.

With use of this method and the $FClO_3$ force field as a starting solution (supplemented by appropriate estimates for the O–F group), the A′–A″ symmetry constaint was at first fully enforced. Although a close duplication of the observed frequencies and isotopic shifts was possible, the resulting force field and potential energy distribution were unsatisfactory. For satisfactory force field solutions, the computed frequency of ν_7 was always too low and that of ν_{11} too high. This suggested that the two ClO_3 rocking modes, ν_7(A′) and ν_{11}(A″), are not completely degenerate, and therefore the $F_{77} = F_{11,11}$ constraint was removed. Removal of this constraint significantly improved that force field, but again the results suggested that removal of the $F_{66} = F_{10,10}$ constraint would significantly benefit the force field. In this manner, a very satisfactory force field (see Table III) was obtained that exactly duplicated the observed frequencies and isotopic shifts and contained force constants for the ClO_3 part of the molecule, which are very similar to those of $FClO_3$[30] (see Table IV). Removal of the $F_{11} = F_{99}$ constraints was shown to be unnecessary since it did not change the values of F_{11} and F_{99}. The only minor deviation between observed and computed isotopic shifts exists for ν_1 and ν_9; however, it must be kept in mind (i) that the shift of ν_1 is disturbed by Fermi resonance effects (see above) and (ii) that anharmonicity corrections[45] for these large shifts would be of the same magnitude as the observed deviations.

The force field of ClO_3OF, given in Table III, contains, in addition to the interaction terms transferred from $FClO_3$, only one relatively small (F_{46} = 0.22 mdyn rad^{-1}) off-diagonal symmetry force constant. This is not surprising in view of the near degeneracy of the $-OClO_3$ modes. if these modes were completely degenerate, ν_1, ν_6, and ν_7 would belong to species E and ν_2, ν_4, and ν_5 to species A_1 of the corresponding C_{3v} symmetry molecule and, therefore, no interaction force constants between the two species would be allowed. In the case of near degeneracy of these modes, as in ClO_3OF, the interaction force constants between the two groups can be nonzero because they both belong now to species A′. However, their numerical values should be very small or zero, as can be shown by semiquantitative arguments.

The fact that the symmetry constraints between the A′ and the A″ block are not strictly valid is not surprising. As expected, the two ClO_3 rocking modes are the least degenerate (22% difference). Because the O–F group is situated in the symmetry plane of the molecule, the in-plane rocking motion requires a significantly higher force than the corresponding out-of-plane motion. For the antisymmetric ClO_3 deformation

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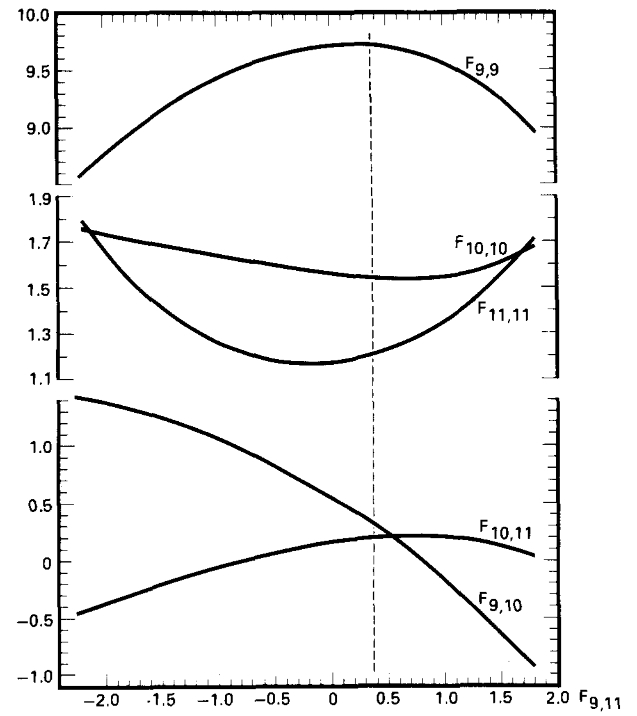

Figure 5. Solution range of the A″ block symmetry force constants of ClO_3OF computed from the chlorine isotopic data and plotted as a function of $F_{9,11}$. The units are identical with those given in Table III. The broken line indicates the preferred force field.

constants the difference between A′ and A″ values amounts to only 4% and for the antisymmetric ClO_3 stretching modes it is zero. In view of the very near degeneracy of the antisymmetric ClO_3 stretching and deformation modes, it is not surprising the symmetry constraint imposed on the corresponding off-diagonal symmetry force constants worked well for our force field. In this connection, it should be pointed out that the expected, albeit small, tilt angle of the Cl–O bond away from the threefold axis of the ClO_3 group should cause a small difference between the A′ and A″ force constants. However, in the absence of exact structural data for ClO_3OF, the tilt angle was assumed to be zero in this study.

To obtain a better feel for the possible variation in the force constant values of ClO_3OF, we calculated the range of possible solutions for the A″ block which is shown in Figure 5. Since five independent frequency values were available from the isotopic data for the computation of six symmetry force constants, five force constants were calculated as a function of the sixth one, in this case $F_{9,11}$. As can be seen from Figure 5, limitation of the off-diagonal force constants to reasonable values places rather narrow limits on the more important diagonal terms. The force field selected from the simultaneous A′–A″ refinement is given by the broken line and is analogous to the $FClO_3$ E block force field.[30] The differences in the signs of some of the off-diagonal force constants between $FClO_3$ and ClO_3OF are caused by the different signs in the symmetry coordinates used for the two computations and therefore have no physical meaning.

The potential energy distribution for ClO_3OF is given in Table III. It shows that the approximate mode descriptions used in Table II are appropriate. The largest amount of mixing was observed for ν_4, which, by analogy with ν_2 of $FClO_3$,[30] is an antisymmetric combination of S_4 (Cl–O stretch) and S_5 ($\delta_s(ClO_3)$).

In order to test the possibility of interchanging the assignments of ν_5, ν_6, and ν_{10}, we computed force fields for all possible assignments, which led to the conclusions stated in the discussion of the assignments.

Table V. Thermodynamic Properties of ClO_3OF

T, K	$C_p°$, cal/(mol deg)	$(H°_T - H°_0)$, kcal/mol	$-(F°_T - H°_0)/T$, cal/(mol deg)	$S°_T$, eu
0	0	0	0	0
100	9.438	0.831	50.106	58.411
200	14.097	2.003	56.334	66.347
298.15	18.111	3.592	60.712	72.761
300	18.176	3.626	60.787	72.873
400	21.166	5.601	64.532	78.535
500	23.289	7.830	67.840	83.500
600	24.789	10.238	70.823	87.886
700	25.861	12.774	73.545	91.793
800	26.641	15.401	76.049	95.299
900	27.221	18.095	78.367	98.472
1000	27.660	20.840	80.524	101.364
1100	28.000	23.624	82.541	104.017
1200	28.266	26.438	84.434	106.465
1300	28.480	29.275	86.217	108.736
1400	28.652	32.132	87.902	110.854
1500	28.794	35.005	89.499	112.835
1600	28.911	37.890	91.016	114.697
1700	29.010	40.786	92.461	116.453
1800	29.093	43.692	93.841	118.114
1900	29.164	46.605	95.160	119.689
2000	29.225	49.524	96.424	121.186

Thermodynamic Properties. The thermodynamic properties of ClO_3OF were computed with the molecular geometry given above and the vibrational frequencies of Table II, with the assumption of an ideal gas at 1 atm pressure and use of the harmonic-oscillator, rigid-rotor approximation.[46] These properties for the range 0–2000 K are given in Table V.

Conclusions. The observed spectra of ClO_3OF agree well with a covalent perchlorate structure of symmetry C_s. All 12 fundamental vibrations were observed and assigned. The assignments were confirmed by a normal-coordinate analysis using Cl isotopic shifts, symmetry relations between the A′ and A″ block, and force constants transferred from $FClO_3$, as constraints. The resulting force field exactly duplicates the experimental data, retains the most important force constant features of $FClO_3$, and results in a characteristic potential energy distribution, thus demonstrating the usefulness of these constraints for the determination of a reliable force field. A comparison of the A′ and A″ block force constants shows that the two ClO_3 rocking modes significantly differ, whereas the two antisymmetric ClO_3 deformation modes are almost degenerate and the two antisymmetric ClO_3 stretching modes are completely degenerate. This is not obvious from the observed frequencies, which due to a different degree of mixing in A′ and A″ are very similar for the two rocking modes but are significantly different for the two antisymmetric ClO_3 deformations. The force constants of the ClO_3 group of ClO_3OF are very similar to those of $FClO_3$ but, as expected from the replacement of F by the somewhat less electronegative –OF group, are slightly lowered.

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Registry No. ClO_3OF, 10049-03-3.

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