posed readily by using electrical analogs to reaction rates.[20,21] The alternate mechanisms make use as well of eq 18 and 19 and are then composed of the following

$$\mathrm{Cr(V)} + \mathrm{IrCl_6}^{3-} \underset{k_8}{\overset{k_7}{\rightleftharpoons}} {}^*\mathrm{Cr(V)} + \mathrm{IrCl_6}^{3-} \tag{18}$$

$${}^*\mathrm{Cr(V)} \xrightarrow{k_9} {}^{**}\mathrm{Cr(V)} \tag{19}$$

sequences of steps: eq 13, 14, 19, 15, 17, and 11, with $a = k_3k_9K_1'/(k_4 + k_9)$, $d = k_3k_5K_1'/(k_4 + k_9)$, and $c = k_5/(k_4 + k_9)$; eq 13, 18, 19, 16, 17, and 11, with $a = k_6K_1'$, $b = k_7K_1'$, and $c = k_8/k_9$; eq 13, 18, 14, 19, 17, and 11, with $a = k_3k_9K_1'/(k_4 + k_9)$, $d = k_7k_9K_1'/(k_4 + k_9)$, and $c = k_8/(k_4 + k_9)$. Although no previous study of Cr(VI) oxidations has yielded a rate equation which demands the existence of more than one form of Cr(V), it does not seem unreasonable to propose forms of Cr(V) with different states of coordination. Known compounds of Cr(V) are four-coordinate and of Cr(IV) are six-coordinate. On this basis, it has been proposed that the change in coordination number accompanying the reduction of Cr(VI) occurs at the Cr(V)–Cr(IV) step.[17] Although certain reducing agents may aid in changing the coordination number of chromium,[1,2] it should be possible for the adjustments in the coordination sphere of chromium to occur either before or after reduction to Cr(IV).

Various other possibilities for the interpretation of eq 2 and 4 were considered without success—*e.g.*, the term first order in $[\mathrm{IrCl_6}^{3-}]$ was assumed to arise from a reaction between two different oxidation states of chromium or from a disproportionation of Cr(V) or Cr(IV),[22] but a rate equation of the correct form could not be derived. Attempts were also made to attribute the observed variation in the order of $[\mathrm{IrCl_6}^{3-}]$ to medium effects by making Harned's rule type corrections,[23] but the correct functional dependence was not obeyed so it appears that a true mechanistic effect is involved.

The products of the reaction were found to consist entirely of Cr^{3+} and $\mathrm{IrCl_6}^{2-}$, with no evidence for a binuclear complex $\mathrm{CrIrCl_6}^+$ or for transfer of Cl^- from Ir to Cr. The absence of either of these effects precludes the classification of the reaction as inner or outer sphere. A binuclear complex may have been formed if it decomposed sufficiently rapidly with Cr–Cl bond breaking. A related binuclear complex $\mathrm{CrIrCl_6}$ containing Ir(III) decomposes within a few seconds with Ir–Cl bond breaking.[24] Since $\mathrm{IrCl_6}^{2-}$ aquates more slowly than $\mathrm{IrCl_6}^{3-}$,[5,25] a $\mathrm{Cr^{III}}$–$\mathrm{Ir^{IV}}$ binuclear complex should decompose more slowly than $\mathrm{CrIrCl_6}$, but even an order of magnitude difference in rates would still result in complete decomposition during the time of our experiments. Further, since CrCl^{2+} aquates more rapidly than $\mathrm{IrCl_6}^{2-}$,[25,26] the decomposition would be expected to occur with Cr–Cl bond breaking, and no evidence for a binuclear complex is likely to appear. Thus the identity of the products is consistent with either an inner-sphere or an outer-sphere reaction, and this reaction may possibly be of the "reverse ligand-transfer" type as was expected for reasons discussed in the Introduction. This system now provides an example of a reaction with a substitution-inert reducing agent in which the second step is rate-determining, indicating that previous explanations[1,2] for the identity of the rate-determining step were probably overly simplified. However, it does not appear to be possible at this time to advance an alternate explanation.

Acknowledgment.—Partial support of this work by the Advanced Research Projects Agency and by the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged.

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[21] J. P. Birk, *J. Chem. Educ.*, **47**, 805 (1970).

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[23] R. A. Robinson and R. H. Stokes, "Electrolyte Solutions," 2nd ed, Butterworths, London, 1965, Chapter 15.

[24] A. G. Sykes and R. N. F. Thorneley, *J. Chem. Soc. A*, 232 (1970).

[25] M. R. Martinez, Ph.D. Thesis, University of California, Los Angeles, Calif., 1958; quoted in ref 5.

[26] T. W. Swaddle and E. L. King, *Inorg. Chem.*, **4**, 532 (1965).

CONTRIBUTION FROM ROCKETDYNE, A DIVISION OF NORTH AMERICAN ROCKWELL CORPORATION,
CANOGA PARK, CALIFORNIA 91304

Halogen Perchlorates. Vibrational Spectra

BY KARL O. CHRISTE,* CARL J. SCHACK, AND E. C. CURTIS

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The infrared spectra of gaseous, solid, and matrix-isolated $\mathrm{ClOClO_3}$ and the Raman spectrum of liquid $\mathrm{ClOClO_3}$ have been measured. All 12 fundamentals expected for symmetry C_s were observed and assigned. The infrared spectra of gaseous and matrix-isolated $\mathrm{BrOClO_3}$ have also been recorded. Some vibrational force constants and the thermodynamic properties have been computed.

Introduction

Recently, the existence of the two novel halogen oxides, $\mathrm{ClOClO_3}$ and $\mathrm{BrOClO_3}$, has been discovered.[1,2] Their chemical and physical properties[1,2] were in accordance with covalent halogen perchlorate structures. In this paper we wish to present spectroscopic data supporting these suggested structures.

Experimental Section

The preparation, purification, and handling of $\mathrm{ClOClO_3}$ and $\mathrm{BrOClO_3}$ have been reported elsewhere.[1,2] The apparatus used

[1] C. J. Schack and D. Pilipovich, *Inorg. Chem.*, **9**, 1387 (1970).

[2] C. J. Schack, K. O. Christe, D. Pilipovich, and R. D. Wilson, *ibid.*, **10**, 1078 (1971).

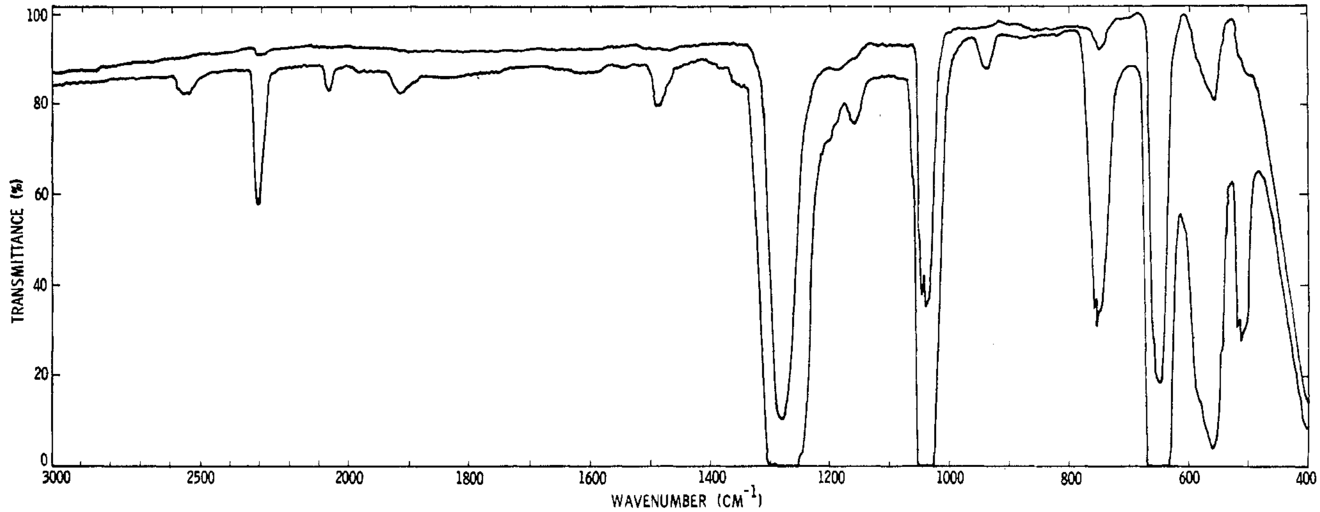

Figure 1.—Infrared spectrum of $ClOClO_3$ at 180 and 8 mm pressure (5-cm path length).

for the low-temperature matrix isolation and infrared spectroscopic studies has previously been described.[2,3] The low-temperature infrared spectrum of solid $ClOClO_3$ was recorded by condensing the sample on the cold (−196°) internal AgCl window of a conventional low-temperature cell. The Raman spectra of liquid $ClOClO_3$ were obtained using Kel-F or Teflon FEP capillaries in the transverse viewing–transverse excitation mode. The capillaries were cooled (−20 to −80°) by a stream of cold gaseous N_2. The intense light from the exciting laser beam (1.3 W at 5145 Å) tended partially to decompose the sample causing gas evolution, thus rendering the recording of spectra difficult. However, reproducible spectra could be obtained by rapidly scanning the spectrum by hand. Under these conditions no lines could be detected due to Cl_2O_7[4,5] which is the major decomposition product in the photolysis of $ClOClO_3$.[1] The Raman instrument used in this study has previously been described.[6]

Results and Discussion

Caution! Halogen perchlorates are shock sensitive[1] *and should be handled with proper safety precautions.*

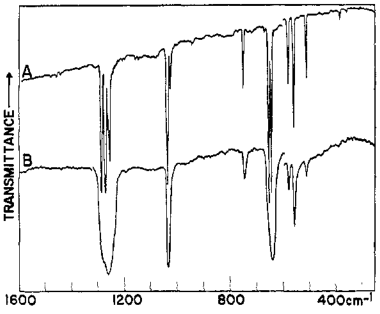

Figure 2.—Infrared spectrum of solid $ClOClO_3$: trace A, 8.2 μmol of sample in Ar matrix (mole ratio = 800) at 4°K; trace B, crystalline solid.

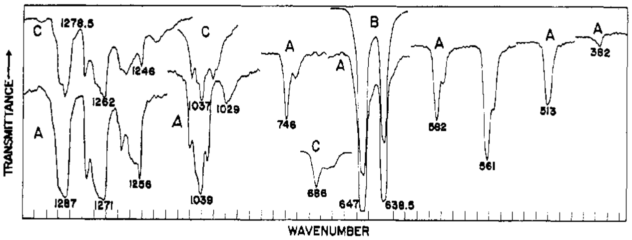

Figure 3.—Infrared spectra of matrix-isolated $ClOClO_3$ and $BrOClO_3$ at 4°K under high-resolution conditions and tenfold scale expansion (1 scale unit = 5 cm^{-1}): trace A, $ClOClO_3$ sample of Figure 2A; trace B, 4.6 μmol of $ClOClO_3$ in Ar matrix (mole ratio = 400); trace C, 2.5 μmol of $BrOClO_3$ in Ar matrix (mole ratio = 400).

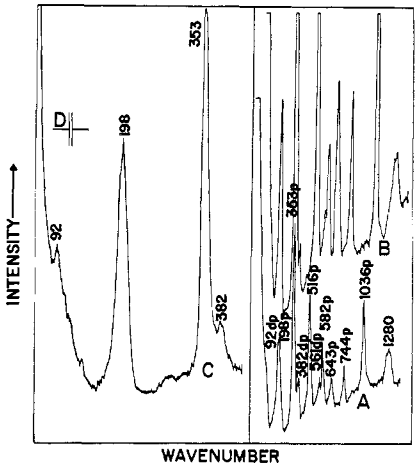

Figure 4.—Raman spectrum of liquid $ClOClO_3$ at −40°. Traces A and B scanned manually; trace C automatically: traces B and C, incident polarization perpendicular; trace A, incident polarization parallel; D, spectral slit width.

Figure 1 shows the infrared spectrum of gaseous $ClOClO_3$. The infrared spectra of solid and matrix-isolated $ClOClO_3$ are given in Figure 2. Since chlorine has two natural isotopes (^{35}Cl and ^{37}Cl in a 3:1 mole ratio), the spectra of matrix-isolated species were recorded at 10-fold scale expansion under high-resolution conditions (see Figure 3) to determine the isotopic shifts. Figure 4 shows the Raman spectrum of liquid $ClOClO_3$. Figure 5 shows the infrared spectrum of gaseous and matrix-isolated $BrOClO_3$. The observed frequencies are listed in Table I.

The recording of the vibrational spectra of $ClOClO_3$ and $BrOClO_3$ presented several experimental challenges since these two halogen perchlorates are shock and light sensitive, thermally unstable (they decompose at or below ambient temperature), and highly reactive[1,2] (they attack infrared windows such as AgCl causing formation of $AgClO_4$ and Cl_2). Consequently, numer-

(3) K. O. Christe and D. Pilipovich, *J. Amer. Chem. Soc.*, **93**, 51 (1971).

(4) R. Savoie and P. Giguère, *Can. J. Chem.*, **40**, 991 (1962).

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TABLE I

VIBRATIONAL SPECTRA OF $ClOClO_3$ AND $BrOClO_3$

Obsd freq, cm^{-1}						
$ClOClO_3$				$BrOClO_3$		Assignment in point group C_s
Infrared			Raman	Infrared		
Gas	Matrix	Solid	Liquid	Gas	Matrix	
2570 vw						$2\nu_1$
2322 w		2290 w		2300 w		$\nu_1 + \nu_2$, $\nu_9 + \nu_2$
2090 vw		2070 vw				$2\nu_2$
1934 vw						$\nu_1 + \nu_4$
1500 vw						$2\nu_3$
	1289 sh				1280 sh	B^{35}
	1287 vs				1278.5 vs	$\nu_1(^{35}Cl)$ (A′)
	1278 m				1270.5 m	C^{35}
	1274 sh				1265 sh	B^{37}
	1272 sh				1263 sh	$\nu_1(^{37}Cl)$ (A′)
1283 vs	1271 vs	1278 sh	1280 mw	1275 vs	1262 vs	$\nu_9(^{35}Cl)$ (A″)
	1264 mw	1259 vs			1256 sh	C^{37}
	1258 sh	1239 sh			1252 m	D
	1256 m				1246 mw	$\nu_9(^{37}Cl)$ (A″)
					1240 w	
	1044 m				1041 m	
1040 s, PQR	1039 s	1031 vs	1036 vs, p	1039 s	1037 s	ν_2 (A′) and $2\nu_6$
	1036.5 m				1033 m	
	1029 m					
749 mw, PQR	746 m					
	742 mw	743 m	744 ms, p	683 m	686 m	ν_3 (A′)
646 vs	647 vs	635 vs	643 ms, p	648 s	651 vs	ν_4 (A′)
	638.5 vs				643 s	
580 sh	582 m	580 m	582 m, p		572 mw	ν_5 (A′)
	579.5 mw					
561 m	561 ms	558 ms	561 w, dp	570 ms	566 m	ν_{10} (A″)
	558.5 m					
511 mw, PQR	513 m	512 m	516 s, p	509 m	516 m	ν_6 (A′)
	512 sh					
	382 w	384 vw	382 w, dp		387 vw	ν_{11} (A″)
	355 vw	360 vw	353 vs, p			ν_7 (A′)
			198 ms, p			ν_8 (A′)
			92 w, dp			ν_{12} (A″)

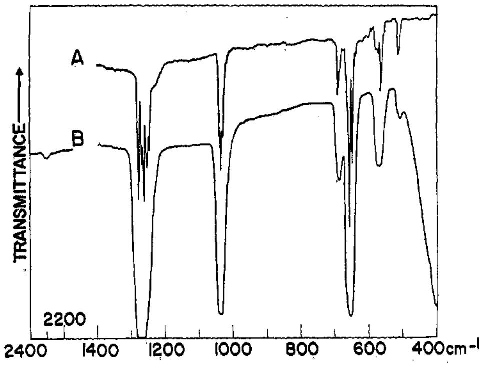
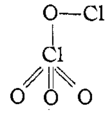


Figure 5.—Infrared spectrum of $BrOClO_3$: trace A, 2.5 μmol of sample in Ar matrix (mole ratio = 400) at 4°K; trace B, gas at 20 mm pressure (5-cm path length).

ous spectra had to be recorded under varying experimental conditions to be able to eliminate bands due to decomposition products.

For a chlorine oxide, having the empirical formula Cl_2O_4, many possible structures can be written. However, the number of observed fundamentals (eight polarized and four depolarized ones), the resemblance between the spectrum of Cl_2O_4 and those of $BrClO_4$, $HOClO_3$,[7] $O_3ClOClO_3$,[4,5] $FClO_3$,[8] $FOClO_3$,[9] and $ClOSO_2F$[10] (see Table II), and its chemical and physical properties[1] can only be explained in terms of the following covalent perchlorate structure of symmetry C_s



For a six-atom molecule of symmetry C_s, a total of 12 fundamentals is expected. Of these, 8 belong to species A′ and should be polarized, and 4 belong to species A″ and should be depolarized. Indeed, three lines (at 561, 382, and 92 cm^{-1}) appear to be depolarized and a fourth one (at 1280 cm^{-1}) may contain a depolarized component. Hence, these four fundamentals are assigned to the four A″ modes. Of these four, the highest and lowest frequency bands can be readily assigned to the antisymmetric ClO_3 stretch and the –O–Cl torsion, respectively. Since the antisymmetric ClO_3 deformation mode should be of higher frequency and infrared intensity than the ClO_2 torsional mode, it is assigned to the 561-cm^{-1} band.

Of the 8 A′ modes, the antisymmetric and symmetric ClO_3 stretches should have the highest frequencies since they involve double bonds. Consequently they are assigned to the bands at 1287 and 1040 cm^{-1}, respectively. The coincidence of the A′ and A″ antisymmetric ClO_3 stretching modes at about 1280 cm^{-1} is supported by the splitting of this band into two intense components in the spectrum of matrix-isolated $ClOClO_3$. Furthermore, the computation of the frequencies of the fundamentals from estimated force constants results in almost identical frequency values for ν_1 and ν_9. The observed ^{35}Cl and ^{37}Cl isotope

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(7) P. A. Giguere and R. Savoie, *Can. J. Chem.*, **40**, 495 (1962).

(8) H. H. Claassen and E. H. Appelman, *Inorg. Chem.*, **9**, 622 (1970).

(9) H. Agahigian, A. P. Gray and G. D. Vickers, *Can. J. Chem.*, **40**, 157 (1962).

(10) K. O. Christe, C. J. Schack, and E. C. Curtis, *Spectrochim. Acta, Sect. A*, **26**, 2367 (1970).

TABLE II

FUNDAMENTAL VIBRATIONS OF HALOGEN PERCHLORATES COMPARED TO THOSE OF SIMILAR MOLECULES

Obsd freq, cm^{-1}							Assignment in point group C_s	Approx description of vibration for YOXO$_2$Z
ClOSO$_2$F[a]	FOClO$_3$[b]	ClOClO$_3$	BrOClO$_3$	HOClO$_3$[c]	O$_3$ClOClO$_3$[d]	FClO$_3$[e]		
1248	1298	1287	1279	1263	1313, 1300	1314	A′ ν_1	$\nu_{as}(XO_2Z)$
855	1049	1040	1039	1050	1060, 1024	1062	ν_2	$\nu_s(XO_2Z)$
703	885	749	683	3560	698, 704		ν_3	$\nu(O–Y)$
831	666	646	648	725		716	ν_4	$\nu(X–O)$
572		580	572	563	598, 571	573	ν_5	$\delta_{sciss}(XO_2)$
486		511	509	519	521, 512	549	ν_6	$\delta_{umbrella}(XO_2Z)$
364		355	[278][f]	402	283, 272	414	ν_7	δ_{rock}
<250		198	[159][f]	1200	154		ν_8	$\delta(XOY)$
1481	1298	1271	1262	1326	1300	1314	A″ ν_9	$\nu_{as}(XO_2Z)$
532		561	566	579	567	573	ν_{10}	$\delta_{as}(XO_2Z)$
390		382	387	430	495, 283	414	ν_{11}	Torsion XO$_2$
<250		92		310			ν_{12}	Torsion O–Y

[a] K. O. Christe, C. J. Schack, and E. C. Curtis, *Spectrochim. Acta, Sect. A*, **26,** 2367 (1970). [b] H. Agahigian, A. P. Gray, and G. D. Vickers, *Can. J. Chem.*, **40,** 157 (1962). [c] P. A. Giguere and R. Savoie, *ibid.*, **40,** 495 (1962). [d] J. D. Witt and R. M. Hammaker, *Chem. Commun.*, 667 (1970), and private communication. [e] H. H. Claassen and E. H. Appelman, *Inorg. Chem.*, **9,** 622 (1970). [f] Computed values.

splittings (see below) confirm these assignments. The complexity of the bands in the 1280- and 1040-cm^{-1} region renders the assignment to individual bands somewhat uncertain. However, in the matrix spectra of both ClOClO$_3$ and BrOClO$_3$ a similar pattern of band pairs was observed. The splitting of each pair is about 15 cm^{-1} and the components have a relative intensity of approximately 3:1. The two most intense pairs were chosen to be due to ν_1 and ν_9, respectively. The remaining band pairs (marked by B–D in Table I) might be caused by possible Fermi resonance of ν_1 and ν_2 with $2\nu_4$, respectively, and/or matrix site splittings. The bands at 749 and 646 cm^{-1} should represent the two remaining stretching modes of species A′. Comparison between the spectra of ClOClO$_3$ and BrOClO$_3$ shows that the 749-cm^{-1} band is shifted to 683 cm^{-1} in BrOClO$_3$ whereas the 646-cm^{-1} band exhibits practically no frequency shift. Consequently, the 749 cm^{-1} must be due to the –O–Hal stretching mode and 646 cm^{-1} represents the O$_3$Cl–O stretch.

There are four frequencies (580, 511, 355, and 198 cm^{-1}) left for assignment to the four deformational modes in species A′. Of these, the Cl–O–Cl deformation should have the lowest, and the rocking mode, the second lowest frequency. Consequently, they are assigned to 198 and 355 cm^{-1}, respectively. The two remaining frequencies belong to the ClO$_2$ scissoring and the ClO$_3$ umbrella deformational modes. Of these two, the umbrella mode should have the higher relative intensity in the Raman spectrum. Furthermore, force constant arguments (see below) favor a higher frequency value for the scissoring mode. This is due to the fact that the scissoring mode involves mainly an angle change between two double bonds, whereas the umbrella mode involves also a change of the angle between the single and double bonds. Consequently, the 580-cm^{-1} band is assigned to the scissoring, and the 511-cm^{-1} band, to the umbrella mode. This assignment agrees well with that made for FClO$_3$.[8,11]

Additional support for the above given assignments can be obtained from the observed band contours of gaseous ClOClO$_3$ (see Figure 1). Thus, the bands at 1040, 749, and 511 cm^{-1}, assigned to the A′ modes, ν_2, ν_3, and ν_6, respectively, exhibit a PQR structure close to that expected for parallel bands of an almost symmetric-top molecule.

The vibrational spectrum of BrOClO$_3$ is not as complete as that of ClOClO$_3$ owing to the lack of Raman data. However, nine out of the expected twelve fundamentals were observed. Eight out of the nine observed fundamentals of BrOClO$_3$ show frequencies almost identical with those of ClOClO$_3$ and, hence, were assigned by analogy. The ninth mode exhibits a shift to a lower frequency and is assigned to the O–Br stretching vibration. The magnitude of the shift agrees well with that predicted assuming the O–Br bond strength to be comparable to that of the O–Cl bond and taking the different mass into consideration. Comparison of the vibrational spectra of ClOClO$_3$ and BrOClO$_3$ with those of HOClO$_3$,[7] O$_3$ClOClO$_3$,[4,5] FClO$_3$,[8] FOClO$_3$,[9] and ClOSO$_2$F[10] (see Table II) shows excellent agreement.

Normal-Coordinated Analysis.—The potential and kinetic energy metrics for chlorine and bromine perchlorates were evaluated by a machine method.[12] An assumed geometry was used, with the perchlorate group taken the same as in perchloric acid.[13,14] The remaining parameters, the O–Cl and O–Br bond lengths and the Cl–O–Hal bond angle, were taken to be 1.63 and 1.85 Å and 110°, respectively, based on a comparison with related molecules.[15]

The force constants were adjusted by trial and error with the aid of a time-sharing computer to give a reasonably close fit between the computed frequencies and those reported in Table II. The results obtained for the force constants are $f_{Cl=O} = 8.8$, $f_{Cl-O} = f_{O-Cl} = f_{O-Br} = 2.65$, $f_{O=Cl=O} = 1.9$, $f_{Cl-O-Cl} = 1.4$, and $f_{O=Cl-O} = 1.1$, with the units for the stretching constants being millidynes per ångström and for the bending constants being millidynes per angström per square radian. The bending coordinates were weighted by unit (1 Å) distance. The only significant interactions found were $f_{Cl-O,O=Cl-O}$, which has a value about 0.2 mdyn/(Å radian), and $f_{Cl-O,O-Cl} = f_{Cl-O,O-Br} = 0.35$ mdyn/Å. The isotope shifts were computed using these force constants and are reported in Table III. A somewhat better frequency fit was obtained with slightly different force constants and additional interaction constants with small numerical values, but they were not used here because they are underdetermined

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(11) D. R. Lide and D. E. Mann, *J. Chem. Phys.*, **25**, 1128 (1956).

(12) E. C. Curtis, Rocketdyne Report R6768, Oct 1966.

(13) A. H. Clark, B. Beagley, and D. W. J. Cruickshank, *Chem. Commun.*, 14 (1968).

(14) A. H. Clark, B. Beagley, D. W. J. Cruickshank, and T. G. Hewitt, *J. Chem. Soc. A*, 1613 (1970).

(15) L. E. Sutton, *Chem. Soc., Spec. Publ.*, **No. 18** (1965).

TABLE III

COMPARISON BETWEEN OBSERVED AND CALCULATED $^{35}Cl-^{37}Cl$ ISOTOPIC SHIFTS OF $HalOClO_3$

Normal mode		Isotopic shift (cm^{-1}) and rel abund		
		Calcd		Obsd
A′	ν_1	0, 16.2	3:1	0, 15[a,b]
	ν_2	0, 4.8	3:1	0, 4.6[b]
	ν_3	0, 0.5, 3.1, 3.6	9:3:3:1	0, 3.8[a]
	ν_4	0, 0.5, 4.5, 4.9	9:3:3:1	0, 8.5
	ν_5	0, 1.8	3:1	0, 2.1[a]
	ν_6	0, 0.3, 3.0, 3.3	9:3:3:1	<1.5[a]
	ν_7	0, 1.0, 2.8, 3.9	9:3:3:1	Not obsd
	ν_8	0, 0.3, 2.5, 2.8	9:3:3:1	Not obsd
A″	ν_9	0, 15.8	3:1	0, 15[a,b]
	ν_{10}	0, 1.7	3:1	0, 2.5[a,b]
	ν_{11}	0, 0.9	3:1	<1

[a] For $ClOClO_3$. [b] For $BrOClO_3$.

and not particularly transferable between the two perchlorates. The computed potential energy distribution for chlorine perchlorate is given in Table IV.

TABLE IV

POTENTIAL ENERGY DISTRIBUTION FOR CHLORINE PERCHLORATE[a]

A′	ν_1	1287	$0.91f_{\mathrm{Cl=O}}$
	ν_2	1040	$0.94f_{\mathrm{Cl=O}}$
	ν_3	749	$0.58f_{\mathrm{O-Cl'}} + 0.20f_{\mathrm{ClO-O-Cl'}} + 0.15f_{\mathrm{O=Cl-O}}$
	ν_4	646	$0.78f_{\mathrm{Cl-O}} + 0.16f_{\mathrm{O-Cl'}} - 0.10f_{\mathrm{Cl-O,O=Cl-O}} + 0.10f_{\mathrm{O=Cl=O}} - 0.10f_{\mathrm{Cl-O,O-Cl'}}$
	ν_5	580	$0.92f_{\mathrm{O=Cl=O}}$
	ν_6	511	$0.44f_{\mathrm{O=Cl=O}} + 0.33f_{\mathrm{O=Cl-O}} + 0.10f_{\mathrm{Cl-O-Cl}}$
	ν_7	355	$0.60f_{\mathrm{O=Cl-O}} + 0.21f_{\mathrm{O-Cl'}}$
	ν_8	198	$0.60f_{\mathrm{Cl-O-Cl'}} + 0.25f_{\mathrm{O=Cl-O}}$
A″	ν_9	1271	$0.94f_{\mathrm{Cl=O}}$
	ν_{10}	561	$0.99f_{\mathrm{O=Cl=O}}$
	ν_{11}	382	$1.05f_{\mathrm{O=Cl-O}}$

[a] The results do not add up to unity since the less important terms are not shown.

The results for bromine perchlorate were very similar.

Further attempts to refine the force constants using both the usual least-squares methods and the reparameterization method[16] were unsuccessful. This appears to be due to mixing of ν_7 and ν_8. The problem was investigated at some length by varying the interaction constants with the time-sharing computer until we became convinced that any reasonable set of harmonic force constants that fit the other frequencies in the A′ block could not fit ν_7. The same problem occurred with two other molecules with similar geometry, CF_3OF[17] and $ClOSO_2F$.[10]

The failure of the force constants to duplicate the observed $^{35}Cl-^{37}Cl$ isotope splittings for all modes suggests that the chosen valence force field might be too simple. In particular, the frequency shift of 8.5 cm^{-1} observed for ν_4 is about twice that calculated. Since ν_1 is the only mode in the A′ block having an isotope splitting larger than 5 cm^{-1}, mixing between ν_1 and ν_4 is indicated, though difficult to rationalize due to the great dissimilarity of the force constants involved.

Thermodynamic Properties.—The thermodynamic properties for chlorine and bromine perchlorate were computed for the ideal gas using the rigid-rotor harmonic oscillator approximation.[18,19] The vibrational frequencies used were those of Table II. The rotational constants computed from the geometry assumed above were $A = 5636$, $B = 1821$, and $C = 1808$ Mc for chlorine perchlorate and $A = 5626$, $B = 1155$, and $C = 1150$ Mc for bromine perchlorate. The reduced moment of inertia[19] was 24 Gc for chlorine perchlorate and 18 Gc for bromine perchlorate. The thermodynamic properties are given in Tables V and VI.

TABLE V

COMPUTED THERMODYNAMIC PROPERTIES FOR $ClOClO_3$

T, °K	$C_p°$, cal deg^{-1} mol^{-1}	$H° - H°_0$, kcal mol^{-1}	$-(F° - H°_0)/T$, cal deg^{-1} mol^{-1}	S_0, cal deg^{-1} mol^{-1}
0	0	0	0	0
100	11.451	0.938	51.985	61.362
200	16.471	2.333	59.166	70.829
298.15	20.563	4.161	64.256	78.211
300	20.628	4.199	64.343	78.339
400	23.572	6.418	68.658	84.701
500	25.623	8.883	72.428	90.195
600	27.058	11.522	75.799	95.001
700	28.077	14.281	78.852	99.253
800	28.816	17.128	81.643	103.053
900	29.363	20.038	84.216	106.481
1000	29.778	22.996	86.601	109.597
1100	30.097	25.991	88.823	112.450
1200	30.348	29.013	90.903	115.080
1300	30.549	32.059	92.857	117.518
1400	30.711	35.122	94.701	119.788
1500	30.844	38.200	96.445	121.911
1600	30.954	41.290	98.099	123.905
1700	31.046	44.390	99.673	125.785
1800	31.124	47.498	101.174	127.502
1900	31.191	50.614	102.607	129.246
2000	31.248	53.736	103.980	130.848

TABLE VI

COMPUTED THERMODYNAMIC PROPERTIES FOR $BrOClO_3$[a]

T	$C_p°$, cal deg^{-1} mol^{-1}	$H° - H°_0$, kcal mol^{-1}	$-(F° - H°_0)/T$, cal deg^{-1} mol^{-1}	S_0, cal deg^{-1} mol^{-1}
0	0	0	0	0
100	12.042	0.972	53.975	63.692
200	16.926	2.420	61.434	73.533
298.15	20.898	4.286	66.697	81.073
300	20.961	4.325	66.786	81.202
400	23.819	6.572	71.217	87.649
500	25.809	9.060	75.071	93.191
600	27.202	11.715	78.503	98.027
700	28.190	14.487	81.603	102.299
800	28.907	17.344	84.433	106.112
900	29.438	20.262	87.036	109.549
1000	29.840	23.227	89.446	112.672
1100	30.149	26.227	91.689	115.532
1200	30.393	29.254	93.787	118.166
1300	30.587	32.304	95.757	120.606
1400	30.744	35.371	97.614	122.879
1500	30.873	38.452	99.370	125.005
1600	30.980	41.545	101.035	127.001
1700	31.069	44.647	102.619	128.882
1800	31.145	47.758	104.128	130.660
1900	31.209	50.876	105.569	132.345
2000	31.265	54.000	106.948	133.948

[a] Units are identical with those of Table V.

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