The Rotational Spectrum and Molecular Structure of Chlorine Chlorate

R. R. Friedl, M. Birk[1], J. J. Oh[2] and E. A. Cohen

Jet Propulsion Laboratory
California Institute of Technology
Pasadena, CA 91109

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Running head: Spectrum *and* Structure of $ClOClO_2$

Address for proofs: E. A. Cohen
                  Rm. 183 301
                  Jet Propulsion Laboratory
                  California Institute of Technology
                  4800 Oak Grove Drive
                  Pasadena, CA 91109

ABSTRACT

Cl_2O_3 has been identified as a product of the ClO + OClO + M reaction at 220K using submillimeter spectroscopy of the reaction products in a flowing gas mixture. 'J']} (., spectra of all four Cl isotopic species have been observed in the 41 5 436 GHz region. Selected transitions have also been measured at frequencies down to 209 GHz. The rotational and centrifugal distortion constants have been determined for all four species. The quadrupole splittings have been fitted for the main species. Structural parameters similar to those of other chlorine oxides have been derived from the rotational constants. These and the quadrupole coupling constants are consistent with those expected from a chlorine chlorate structure with no planes of symmetry. Structures which satisfy the requirement inferred from published infrared data that the the Cl-O bonds are shorter than those in OClO all must have long single bonds between the ClO and OClO portions of the molecule.
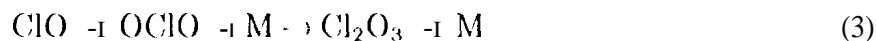
INTRODUCTION

The recent recognition of the role of chlorine in Antarctic ozone destruction has motivated a number of experimental and *ab initio* studies of the ClO self reaction. A primary focus of many of these studies has been the characterization of the reaction products under stratospheric temperature and pressure conditions. Although a dimer having a peroxide structure *(1)* has been identified as a major product of the low temperature three body reaction,

$$ClO + ClO + M \rightarrow ClOOCl + M \tag{1}$$
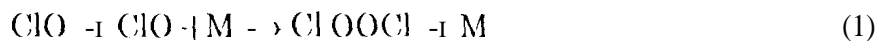
there continues to be speculation about the importance of the chloryl chloride, $ClClO_2$, and unsymmetric straight chain, $ClOClO$, isomers *(2-4)*. Spectroscopic evidence for the alternate isomers has been obtained using the reaction

$$Cl + OClO \rightarrow 2ClO \tag{2}$$

as the source of ClO. Interpretation of data obtained in these Cl/OClO reaction systems has been complicated, however, by processes which form higher oxides of chlorine. For example, the infrared and ultraviolet absorptions previously attributed to $ClOClO$ have been recently reinterpreted by Hayman and Cox *(5)* as belonging to Cl_2O_3. Formation of Cl_2O_3 in these mixtures is presumably due to the reaction

$$ClO + OClO + M \rightarrow Cl_2O_3 + M \tag{3}$$

which competes with ClO dimerization and apparently is favored at low temperature and high OClO concentration. Production of Cl_2O_4 has also been observed in OClO static photolysis experiments *(6,7)*. The mechanism for formation of this species remains uncertain but may involve further reactions of Cl_2O_3.

In the present study we have examined the products of the Cl + OClO reaction system at 220 K using millimeter spectroscopy. In addition to transitions corresponding to ClO and ClOOCl, many new, highly resolved, product spectral features have been observed and

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assigned to the main isotopic species of a compound whose rotational constants are consistent with a chlorine chlorate structure. Subsequent assignment of the two singly substituted species as well as the disubstituted species have confirmed the presence of two chlorines and have allowed the determination of some structural parameters. The production of ClOOCl in this reaction system is observed to be much lower than in a system using $Cl_2O + Cl$ as the ClO source, even when the initial ClO concentrations are similar. In this report we summarize the spectroscopic data that we have obtained both in terms of the structure of Cl_2O_3 and in terms of the relative rates of reactions 1 and 3.

EXPERIMENTAL DESCRIPTION

The basic spectrometer - flow reactor setup is similar to that described by Birk, *et al.(1)* Several enhancements were added, however. Whereas previously only the reactor was temperature controlled, for this experiment the absorption cell and the reactor were maintained at the same temperature. The sample cell also was fitted with insulated, recessed Teflon windows to keep the observing region more uniformly cold over its entire length. The millimeter waves were passed through a polarizer, traversed the sample cell, reflected off a rooftop reflector back through the sample and were then reflected into the detector. The total path for the double pass measures 1.8 m.

The analog signal from the lock-in amplifier was passed with minimal time constant to a voltage to frequency converter followed by a counter. The total number of counts per point was stored in a desk top computer. Since there is negligible time constant distortion of spectral features using this scheme, features recorded during the initial search for spectra were used without the need for remeasurement. All data in the 400 GHz region were recorded with a point spacing of 120 kHz and a dwell time of 220ms per point of which the final 200 ms were used to record counts.

The region between 415 and 436 GHz was covered nearly completely by a number of individual sweeps of between 50 and 200 MHz in length. Master files containing all the data in

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proper sequence were then generated for both the reaction mixture and the OClO reference. New features were readily identified and measured. For the purposes of this paper, peak finding routines were not used for most measurements. In general, the frequencies reported represent cursor positions for line maxima obtained during visual comparison of reaction and reference spectra. It is expected that these are within one data point of the true line center for most features. This assumption seems to be borne out by the rms of the fits. The measurements are adequate for the determination of very precise rotational constants. Peak finding routines were used for quadrupole split lines, measurements of individual lines at lower frequencies, and for checking the accuracy of transitions in the 40(I GHz region. The positions of some transitions partially obscured by OClO features were accurately measured after subtraction of the reference spectrum.

For the initial product surveys, Cl + OClO reaction conditions were chosen to maximize the expected yield of Cl_2O_3. Towards this goal OClO concentrations within the reactor were kept significantly higher than those of atomic chlorine in order to insure complete conversion of Cl to ClO and ClO k) Cl_2O_3. One possible complication was competition from the ClO self reaction (Reaction I). In the Cl/OClO chemical system the relative yields of Cl_2O_3 and ClOOCl are proportional to the ratio of $k_1[ClO]$ to $k_3[OClO]$ since

$$\frac{[Cl_2O_3]}{[Cl_2O_2]} = \frac{k_3[ClO][OClO]}{k_1[ClO][ClO]} = \frac{k_3[OClO]}{k_1[ClO]}$$

Rate constant values have been obtained recently by Sander, et al. (8) and Trolier, et al. (9) for Reaction 1 in the temperature range 200 to 250 K and by Parr, et al. (10) at 226 K and Burkholder, et al. (11) over the range 200 - 260 K for reaction 3. Based on the literature kinetics data we estimate that the value of k_3/k_1 at the experimental temperature of 223 K is approximately 6. Accordingly, the use of initial ratios greater than 5 for [OClO]/[Cl] was predicted to suppress chlorine peroxide production as well as to greatly reduce residual ClO levels. This prediction was borne out by the fact that features attributed to Cl_2O_3 showed no growth for OClO/Cl ratios greater than 5.

Atomic chlorine was generated using a microwave discharge in molecular chlorine which was flowing into the reactor through a 2mm id. thick walled quartz capillary tube. Maximum Cl concentrations obtainable in the chemical reactor were on the order of $3 \times 10^{15} \cdot cm^{-3}$. Chlorine dioxide was generated *in situ* by passage of molecular chlorine through a 2.5 cm diameter U-tube trap find to a height of approximately 20 cm with sodium chlorite and glass beads. Gas flow rates and pressures inside the trap were regulated by two fine-control needle valves located up and downstream of the trap, respectively. The trap was located inside a protective box in case of explosive decomposition of the OClO.

The experimental pressure and residence times employed for the initial part of this study were similar to those employed previously for ClOOCl. 'J'eta] pressures were approximately 3 to 0.05 Torr in the reactor and absorption cell, respectively. One second residence times were maintained in both regions. During later measurements of quadrupole splittings it was found that Cl_2O_3 could be produced at very low pressures (<0.0] 'J'err) directly in the absorption cell. This low pressure production is consistent with the kinetics data reported by Parr, *et* (1/.(10), and Burkholder, *et* (/1.(11).

<center>SPECTRA AND ANALYSIS</center>

The experimental reaction product spectra contain numerous new lines as well as those due to HOCl and ClO. ClOOCl transitions may be present in some scans, but they are very weak. Cl_2O and $HClO_4$ features are absent. In addition to transitions eventually assigned to Cl_2O_3, there are a significant number of weaker features which have not been identified.

Although there are no published *ab initio* structures for Cl_2O_3, Hayman and Cox *(5)* suggested previously that chlorine chlorate, $ClOClO_2$, is its most probable form. This configuration of the molecule is shown in Fig. 1. Preliminary structural parameters were estimated from those of related compounds and a series of rotational constant calculations were carried out as a function of dihedral angle. The estimated parameters are listed in Table 1 and the results of the calculation are plotted in Fig. 2. The dihedral angle is that

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between l_{12} and the one of the double bonds (1-2-35 in Fig.1.) It can be seen that while the A rotational constant is quite sensitive to the choice of dihedral angle, B and C have a limited range of likely values.

In the 415 436 GHz range o f the initial search one expects strong perpendicular ' R branches of the type J -{ 1 ← J; K_a -| 1 ← K_a with no asymmetry splitting at the highest values of K_a. These would have a characteristic spacing of $\approx (B + C)$. The searched region was chosen to be large enough to contain at least one branch origin ($J = K_a$). The μ_a parallel transitions in this region have J values of ≈ 100. Lower frequency observation s subsequently showed that they should be very weak and unobservable under the conditions of the 400 (;117 Seal'cll .

The transitions of the new species were q u i t e strong and several branches with approximately the correct spacing, were quickly identified by visual inspection of the plotted spectrum. After an initial fit yielded rotational constants for the main isotopic species, rotational constants for both 1110110 ^{37}Cl species were estimated from a molecular structure consistent with the normal species constants. Transitions were again readily assigned. Finally, the substitution coordinates were used to predict the rotational constants of the disubstituted molecule. Its transitions were found very close to their predicted values and their assignment was straightforward. The approximate 9:3:3:1 intensity ratio for the spectra assigned to the normal, both monosubstituted, and disubst ituted species indicated that the assignment was correct. Confirmation o f the fact that spectra had been properly assigned to the mono-substituted species was obt ained by observing the quadrupole splittings of several lower J transitions at lower frequen cies, thus eliminating the possibility that these spectra arise from low lying excited vibrational states.

Almost all the transitions used for fitting the spectrum have μ_c selection rules. Some lower frequency μ_a transitions of the main species were meas ured using signal averaging and included in the final fits. Some scans were taken at higher sensitivity and disclosed weak

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features at frequencies predicted for μ_b transitions. The presence of a b component of the dipole moment eliminates structures with a plane of symmetry from consideration. Both μ_a and μ_b type transitions were found to be at least a factor of ten weaker than μ_c transitions of corresponding strength per unit dipole. The values of both μ_a and μ_b thus must be less than $1/3$ that of μ_c.

Table II shows the transitions used to obtain the rotational and centrifugal distortion constants shown in Table III. These are used in the determination of structural parameters discussed below. The Hamiltonian is a Watson S reduction in a P representation.

$$\hat{H} = A\hat{P}_a^2 + B\hat{P}_b^2 + C\hat{P}_c^2$$
$$- D_J\hat{P}^4 - D_{JK}\hat{P}_a^2\hat{P}^2 - D_K\hat{P}_a^4 + d_1\hat{P}^2(\hat{P}_+^2 + \hat{P}_-^2) + d_2(\hat{P}_+^4 + \hat{P}_-^4)$$
$$+ H_J\hat{P}^6 + H_{JK}\hat{P}^4\hat{P}_a^2 + H_{KJ}\hat{P}^2\hat{P}_a^4 + H_K\hat{P}_a^6$$
$$+ h_1\hat{P}^4(\hat{P}_+^2 + \hat{P}_-^2) + h_2\hat{P}^2(\hat{P}_+^4 + \hat{P}_-^4) + h_3(\hat{P}_+^6 + \hat{P}_-^6)$$
$$+ L_{JJKK}\hat{P}^4\hat{P}_a^4 + L_{JKKK}\hat{P}^2\hat{P}_a^6 + L_K\hat{P}_a^8$$

with

$$\hat{P}_+ = \hat{P}_b + i\hat{P}_c$$
$$\hat{P}_- = \hat{P}_b - i\hat{P}_c$$

For the singly substituted species, it was found that the coefficients of terms with sixth and higher powers of angular momenta could be fixed to those of the main species with no significant deterioration in the quality of the fit. The quartic constants of the doubly substituted species, when determined independently, were within their own uncertainties of those calculated from those of the singly substituted species by assuming that the effects of

the Cl substitutions were additive. The final fit was carried out simultaneously on all the isotopic species using a common set of sextic and octic parameters and quartic terms for the disubstituted species subject to the condition

$$D(37 - 37) = D(37 - 35) + D(35 - 37) - D(35 - 35),$$

where D is any quartic constant.

Quadrupole splitting has been observed for a number of transitions at relatively high J for the main species and several transitions for the singly substituted ^{37}Cl species. Only the main species splittings have been fit ted. The substituted species are used to distinguish between the chlorines. For the transitions observed, the sixteen strongest components occurred in groups that gave the appearance of doublets, triplets or quartets symmetrically arranged about the unperturbed line center. The best measured of these were used to determine the diagonal components of the quadrupole tensors. These are listed in Table IV and the derived constants are in Table V. Terms off diagonal in J were neglected. There is no sign information available in the data set, but this can be inferred from quadrupole couplings in related compounds. Two such examples are also listed in Table V and will be discussed further in the following section.

It has not yet been possible to assign torsional or other vibrational satellites for any of the Cl_2O_3 species nor has it been possible to identify a pattern of lines attributable to another molecular conformation. None of the unassigned transitions appear to be as strong as those of the mono ^{37}Cl species. The strongest unassigned transitions are about a factor of seven weaker than st rong Cl_2O_3 transitions in their vicinity. A torsional frequency of ≈ 100 cm^{-1} would give rise to satellites considerably stronger than transitions from the singly substituted species. It seems unlikely that the stronger excited state transitions are all obscured by the rich OClO and Cl_2O_3 spectra or occur in regions of low sensitivity. Burkholder, et al., (11) find discrepancies in their analyses of kinetic and thermochemical data which they take

as an indication that the entropy Of Cl_2O_3 is not calculated correctly from the rotational constants reported here, *ab initio* vibrational frequencies provided to them by Hehre, and the assumption of rigid rotor behavior. While this may be a result of significant non-rigidity, it is not possible from these rotational data alone to determine if the torsional frequency is high or if torsion - rotation perturbations make the satellites difficult to identify. Although Cl_2O_3 is weakly bound, the results of Ref. 11 make it seem unlikely that the molecule dissociates when the torsional mode is excited. More experimental work is required to assign excited states and to identify, or eliminate the possibility of other conformers.

MOLECULAR STRUCTURE

Although the derived rotational and quadrupole coupling constants provide strong evidence that the assigned species have a chlorine chlorate configuration, individual structural parameters cannot be determined unambiguously from the available rotational data alone. Certain assumptions about some of the molecular parameters must be made. These are based on molecular parameters of related compounds and on published Cl_2O_3 vibrational spectra.

The positions of the chlorine atoms are easily determined by the substitution method. These are given in Table V]. It is found that both atoms have very small b coordinates, and that the terminal Cl atom has a small c coordinate as well. The c coordinate for the end Cl is small and imaginary when derived from the rotational constants of the two molecules with a central ^{35}Cl. This is probably the result of small vibrational effects and is not uncommon for atoms near a principal axis. It should be noted that the magnitude of the c coordinate is about the same as the b coordinates and provides a measure of the uncertainty in determining the small coordinates in this molecule. The Cl-Cl distance is well determined and is slightly larger than in Cl_2O, 2.87Å versus 2.80Å. It suggests strongly, without< the need of any assumptions, that the molecule contains a Cl-O-Cl group. This distance may also be compared to the 1.99Å bond length in Cl_2 and the 3.33Å Cl-Cl distance

in ClOOCl. Although it is possible to obtain a suitably short Cl- Cl distance in a molecule containing a ClOOCl group by postulating a small Cl-O-O-Cl dihedral angle, such structures are incompatible with the derived substitution coordinates for the Cl atoms.

For the general non-planar asymmetric rotor $N - 3$ isotopic substitutions are required to determine the molecular structure. Although it may seem that the substitution of each of the two chlorines would provide enough information for a complete structural determination, that is not the case for this particular molecule. The presence of a triangle of O atoms leads to an ambiguity in the structural determination which can be uniquely solved only by isotopic substitution of at least one of the O atoms. If the triangle were equilateral, its rotation about its center in the plane of the oxygen atoms would not change the molecular moments of inertia. Although this is not the case, the moments of inertia are not very sensitive to the orientation of the O_3 triangle and acceptable fits to all the rotational constants can be found for a large number of molecular geometries. In the absence of oxygen substitution, the position of the oxygens must be constrained for the structure calculation. This can be done by fixing the terminal Cl O bond distance, l_{12}, to a convenient value close to those in other compounds. It was found that the terminal Cl O bond length had little effect on the structure of the remainder of the molecule except for the Cl-O-Cl and dihedral angles.

The small c coordinate for the end Cl and the small b coordinates for both Cl atoms lead to additional ambiguities in the structural determination. In addition to the usual problems associated with the determinations of small coordinates caused by vibrational effects, the relative signs of the small coordinates cannot be determined without further assumptions about the structure. There is a range of structures in the vicinity of four distinct minima obtained by fitting the planar moments of inertia which adequately reproduce the moments of inertia for all the observed isotopic species. The four minima correspond to the four unique choices for the relative signs of the small coordinates. The molecular parameters for each minimum are given in Table VII. The parameters have been calculated for outer single bond

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lengths of .673 and .705Å which span the range of bond lengths from $ClONO_2$ (14) to ClOOCl (1). This illustrates the small effect of the assumed bond length on the remainder of the structure. The relative sign of the b coordinates of the Cl atoms is determined by the inner single bond length, l_{23} which has a strong inverse correlation with the lengths of the Cl=O bonds. The b coordinates are the same sign for a minima with a long l_{23}. The relative sign of the c coordinates is a function of dihedral angle. The signs are the same for l_{123}, near 50°. All of the structures near the minima have skew chlorine chlorate geometries, but some are more compatible with published spectroscopic and structural data for this and related molecules. A preferred molecular configuration may be selected by applying additional constraints based on these data.

The fits seem to require that both the O-Cl=O angles and the Cl=O double bonds be somewhat different from one another. However, these parameters are strongly correlated with each other. Although Cl_2O_3 has no symmetry, fits to the planar moments for which the double bonds are constrained to be equal to each other have about the same standard deviations as fits for $FClO_2$ (12,15). Since the correlations preclude a reliable determination of the individual double bond lengths, and since its seems reasonable that they be approximately of equal length, the assumption has been made that the double bonds lengths are identical. The O-Cl=O angles cannot be simultaneously treated as identical without a significant deterioration of the quality of the fit. The net result is that the departure of the ClO_3 group from C_s symmetry is assumed to be entirely the result of a tilt of the O=Cl=O group with respect to the Cl-O bond. The condition that the double bond lengths be the same causes the minima in the vicinity of Fit 1 and 4 in Table VII to be very broad and shallow. The minimum in the vicinity of Fit 4 disappears entirely as l_{12} is increased from 1.673 to 1.705 Å. The minima in the vicinity of Fits 2 and 3 remain sharp and distinct. The parameters at these new minima are given in Table VIII. Note that once again the structural parameters depend only slightly upon the value to which l_{12} has been fixed.

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Infrared studies indicate that the Cl= () stretching frequencies are higher than those of OClO but less than those Of $FClO_2$ *(7, 11, 15)*. Stretching frequencies Of bonds between identical atoms are often an indication of bond strength and length with higher frequencies associated with stronger shorter bonds. In the present case the stretching frequencies are taken as an indication that the double bond lengths are less than those of OClO but greater than those of $FClO_2$ *(2)*. Therefore, the double bond lengths are restricted to the range 1.42- 1.47Å *(11,16)*. The sharp minimum in this range is Fit 3a, although structures with slightly different parameters near this minimum adequately reproduce the planar moments. A series of structure in the vicinity of Fits 1 a and 3a with the outer Cl-() bond fixed at 1.705Å and the double bonds varied from 1.42! to 1.47Å are given in Table 1X. The variation of these parameters with l_{12} may be estimated from Table V]] 1. Structural parameters of OClO and $FClO_2$ are shown for comparison. Structures in the vicinity Of Fits 2a and 4a are rejected Im.cause Of the long Cl= O bonds.

The structures in the vicinity Of Fit 1a are not unreasonable, but all have O= Cl= () angles less than $FClO_2$ and an average O= Cl- o angle greater than F ClO_2. The strut.tums near the sharper minimum 3a are the only ones which simultaneously can have both Cl= O bond lengths and O= Cl= () angles between those Of $FClO_2$ and OClO. In addition, their O-Cl= () and Cl- ()- Cl angles are reasonable when compared with the F- Cl= 0 angle in $FClO_2$ and the Cl- 0- X angles in ClOCl and ClOOCl. Because Of the better fit and the greater similarity Of the structural parameters with those Of related compounds, it is believed that the true structure is close to that that determined by Fit 3a.

The structures listed all have long inner Cl- () single bonds, l_{23}. This is consistent with the fact that Cl_2O_3 is easily dissociated into ClO and OClO and the fact that $FClO_2$ has a long F- Cl bond. The structures near Fit 3a all have the 1- 2 bond almost irons to the 3 4 double bond. Fig. 1 is drawn to represent these stru ctures.

The quadrupole coupling constants are also consistent with the derived molecular struc.-

tures in Table IX and with the assumption that l_{12} is a typical Cl-O single bond. As was shown in Table IV, the components for the Cl in $ClONO_2$ are very close to those of the end Cl in $ClOClO_2$. This is in agreement with the determination of the molecular geometry which shows that the Cl-O-Cl plane is only slightly out of the principal ab plane and that the projection of the molecule in that plane has a configuration similar to the planar $ClONO_2$. It is also an indication that the outer chlorines have similar environments in both molecules, a condition which is implied by the assumptions about l_{12}.

The comparison of the $FClO_2$ Cl quadrupole constants with those of the central Cl shows that both atoms have a similar chemical environment. The chlorate portion of Cl_2O_3 has only a slightly different orientation with respect to the c principal axis than dots $FClO_2$ to its c axis and the values for the χ_{cc}'s are quite close. Some of the differences in the values of χ_{aa} and χ_{bb} can be accounted for by rotation about the c axis. Parent and Gerry estimate the change in p electron population at the Cl atom in OClO upon formation of $FClO_2$. They conclude that there is a shift of 0.64 of an electronic charge toward the F atom. It appears that the ClO group is about as effective in withdrawing charge from OClO as is a fluorine atom.

CONCLUSIONS

The millimeter spectrum of an isomer of Cl_2O_3 has been identified for the first time. The rotational constants, quadrupole coupling constants, the derived Cl coordinates, and selection rules show unambiguously that the observed molecule has a chlorine chlorate structure with no planes of symmetry. One must be careful not to over interpret the structural details. There remain correlations among the molecular parameters which can be resolved with this type of experiment only by substitution of at least one of the O atoms. The structural determinations have required some assumptions and consequently the individual parameters are not precise. However, it has been possible to find a small range of structures which are consistent with not only all the experimental data reported here, but also with structural

parameters of related compounds, and previous low resolution 11{ and UV spectroscopic investigations of gas phase Cl_2O_3. The main features of these structures are Cl= () bond lengths between those of OClO and $FClO_2$, a long single bond between the ClO and OClO moities of the molecule, and a nearly planar *trans* Cl- O Cl= () portion of the molecule. This study dots not eliminate the possible existence of other forms of Cl_2O_3.

ACKNOWLEDGMENTS

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Footnotes

1, Present address: Deutsche Forschungsanst alt für Luft und Raumfahrt, W-8031 Oberp-faffenhofen, Germany.

2. Present address: Department of Chemistry, Sookmyung Women's University, Seoul 140-742, Korea.

Figure Captions

Figure 1. Chlorine chlorate configuration of Cl_2O_3.

Figure 2. Estimated Cl_2O_3 rotational constants as a function of Cl–O–Cl=O dihedral angle. The angle is defined as zero when the terminal Cl–O bond is *cis* to one of the Cl=O bonds. The left hand side of the plot represents a C_s configuration in which the terminal Cl–O bond is *cis* to the bisector of the O=Cl=O angle.

Figure 1. Chlorine Chlorate Configuration of Cl_2O_3.
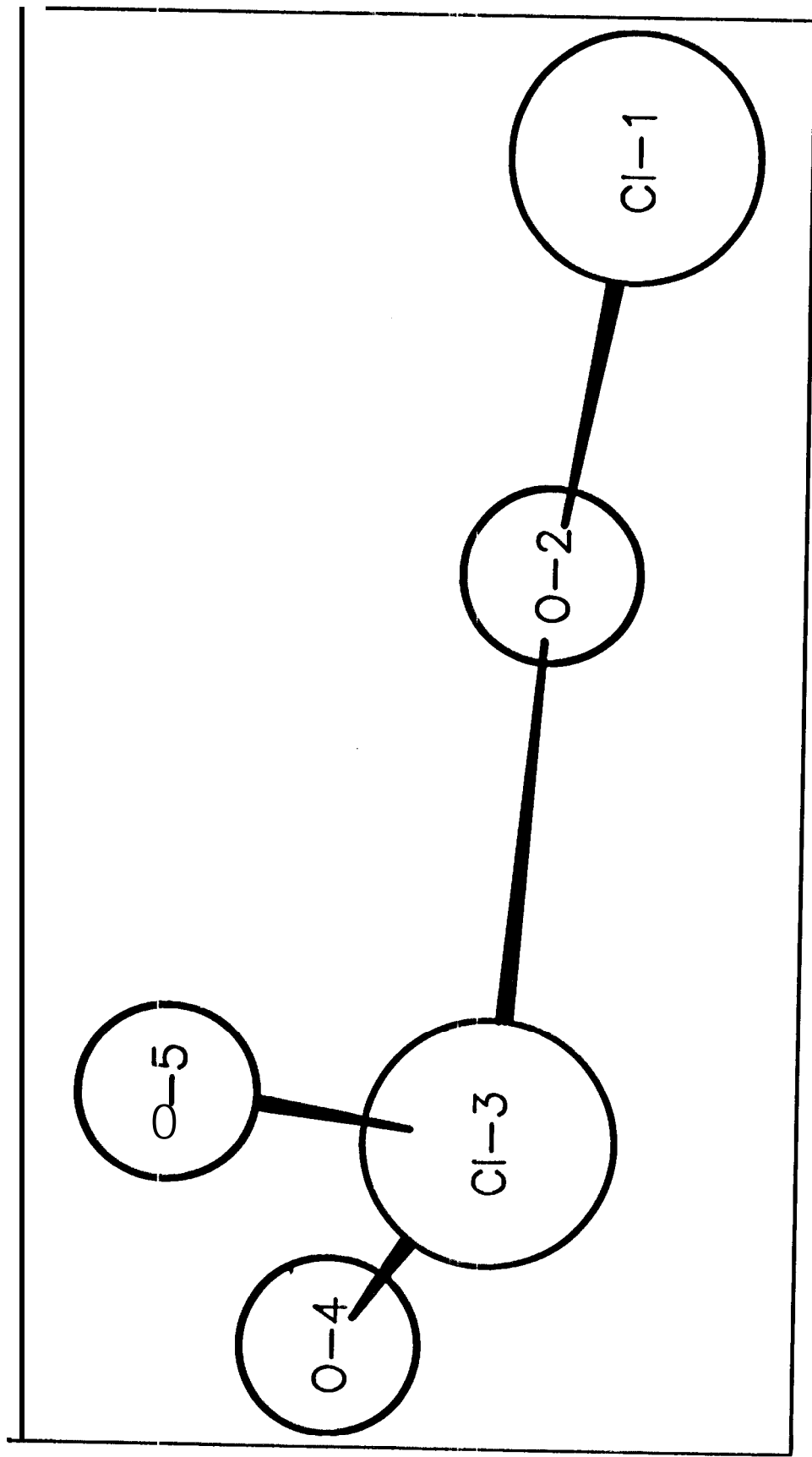
Figure z.   Rotational Constants vs Dihedral Angle.

A.

B

C

−50   0   50   100

Cl−O−Cl=O Dihedral Angle

Rotational Constants in GHz

2000   4000   6000   8000
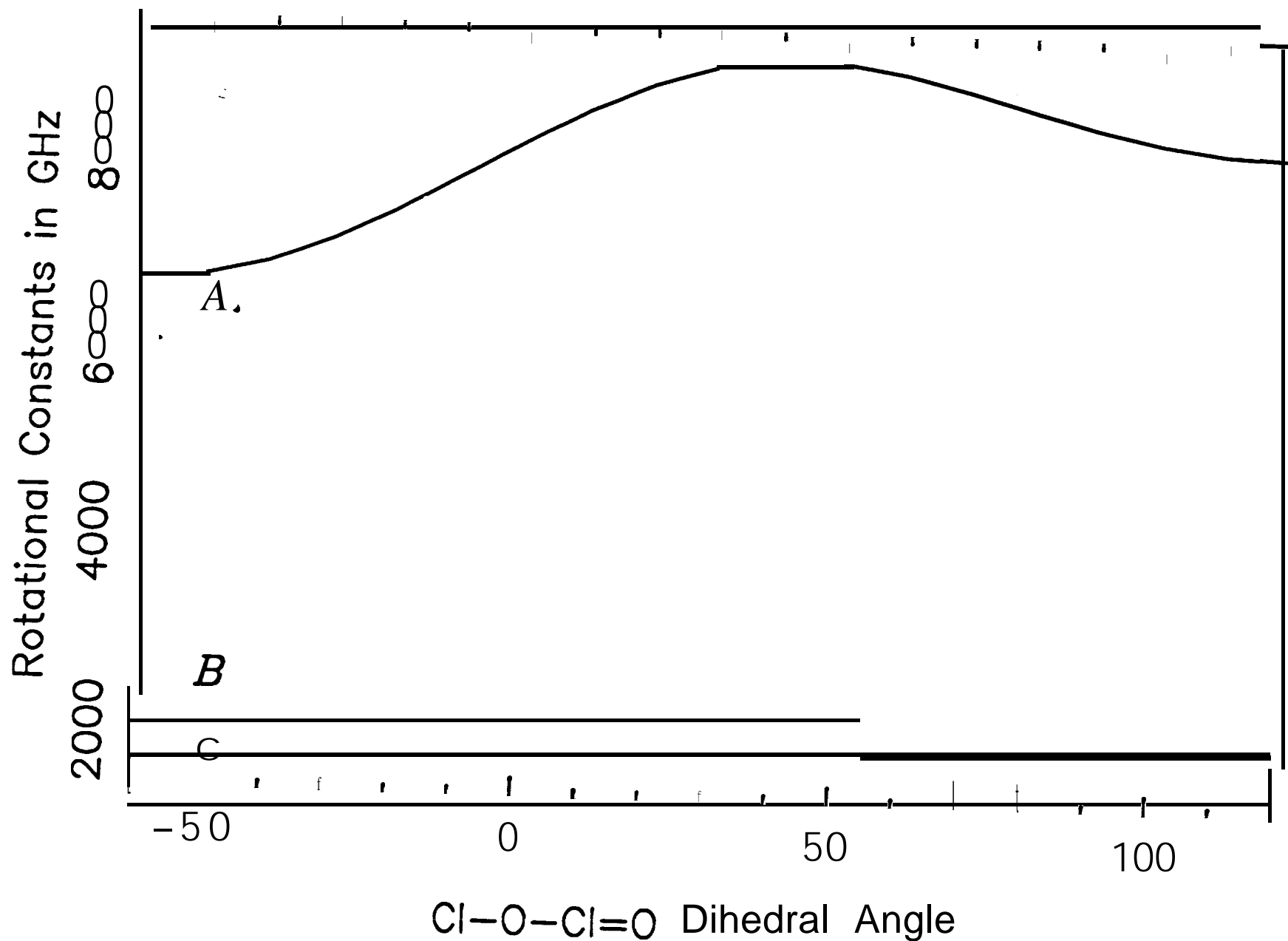
Table 1. Parameters for Estimating Rotational Constants

Parameter	Estimated Value	Reference Molecule
l Cl(1)-O(2)	1.705 Å	ClOOCl[a]
∠Cl(1)-O(2)-Cl(3)	110.0°	ClOOCl
∠O(2)-Cl(3)-O(4)	101.7°	FClO$_2$[b]
l Cl(3)=O(4)	1.445 Å	FClO$_2$ and OClO[b] average
∠O(5)=Cl(3)=O(4)	116.4°	FClO$_2$ and OClO average
l O(2)-Cl(3)	1.775 Å	0.07Å longer than normal single bond.[b]

a Reference 1.

b From Table 1X of Reference 12.

TABLE II. Fitted Transitions

		³⁵Cl₂O₃		³⁵ClO³⁷ClO₂		³⁷ClO³⁵ClO₂		³⁷Cl₂O₃	
$15_{15,0}$	$14_{14,0}$	252080.005	-0.03	...		252004.829	0.01?	...	
$16_{12,5}$	$151],5$	215875.411	−0.05?	215015.913	0.081	...			
$19_{11,9}$ ←	$]8_{10,9}$	214134.596	--0.02	...		...			
$22_{10,12}$ ←	$21_{9,12}$	212347.859	0.07?	...		...			
$22_{10,13}$	$21_{9,13}$	212347.859	0.07!	...		...			
$22_{13,10}$	$21_{12,10}$	252478.972	--0.04"	...		...			
$23_{10,13}$	$229,13$	...		215230.399	0.026	214759.272	0.089	...	
$23_{10,14}$ ←	$229,14$	...		215230.399	0.025	214759.272	0.088		
$25_{25,0}$ ←	$24_{24,0}$	424253,107	0.07?	422672.587	-0.010	424162.867	0.104	422582.467	-0.118
$26_{25,1}$ ←	$25_{24,1}$	...		426503.802	0.078	...		426307.722	0.022
$27_{24,3}$	$26_{23,3}$	418632.835	--0.01?	417035,708	−0.000	4]8226.515	0.032	416629.028	0.000
$27_{25,2}$	$26_{24,2}$	431967.594	- 0.05?	430333.842	-0.020	431665.674	-0.092	430031.994	0.128
$28_{24,4}$ ←	$27_{23,4}$	422489.947	-0.041	...		421977,883	0.043	420353.4G7	-0.061
$28_{25,3}$	$27_{24,3}$	435823.433	0.01?	434162.945	- 0.035	435415.841	0.048	...	
$29_{11,19}$ ←	$28_{10,19}$	252672.664	- 0.03?	...		...		...	
$29_{24,5}$	$2823,5$	...		..		...		424076.947	- 0.067
$30_{8,22}$	$297,22$	...		214484.894	0,084	...		...	
$30_{8,23}$	$297,23$	215603.682	0.044	214550.819	−0,02]	...		...	
$30_{23,7}$	$2922,7$	416868.595	0.184			416040.188	0.008	...	
$30_{24,6}$ ←	$2923,6$	430200.954	-0.01?	428523.78G	-0.09]	429477.474	0.058	...	
$31_{23,8}$ ←	$3022,8$	420723.283	-0.092	419056.315	0.03?	419789.515	0.005		
$31_{24,7}$ ←	$3023,7$	434054.841	0.110	432350.994	-0.028	433225.505	--0.049		
$32_{20,12}$ ←	$31_{19,12}$	...		...		383217.968	-0.137	...	
$32_{23,9}$ ←	$31_{22,9}$	424576.987	--0.099	422883.427	0.033	423537.667	0.011	...	
$32_{24,8}$	$31_{23,8}$	...		...				435241.121	0.130
$33_{23,10}$	$3222,10$	..		...		...		425562.666	0.011
$34_{22,12}$ ←	$3321,12$	418949.947	0.06?	417239.635	-0.080	417594.787	-0.065	415882.628	-0.010
$34_{23,11}$ ←	$3322,11$	432280.554	0.03?	...		431030.154	-04034	...	
$357,28$	$346,28$	215751.152	- 0.00?	...		...		...	
$35_{22,13}$	$3421,13$	422800.267	- 0.03?	...		421339.843	-0.131	419601.043	--0.007
$35_{23,12}$ ←	$3422,12$	...		...		434774.513	0.043	432998.921	-0.187
$365,32$ ←	$354,32$	214889.294	-0.00?	213128.079	0.011	...		...	
$366,31$ ..	$355,31$	215643.370	−0.03?	2]4181.371	-0.039	...		...	
$3622,14$ ..	$3521,14$	...		...		425083.506	−0.120	423318.067	0.042
$372],16$ ..	$3620,16$	417163.747	-0.15[	415411.041	-0.0]1	415388.924	0.025	...	
$3722,15$ ..	$3621,15$	...		428706.786	0.071	428825.754	0.011	...	
$3732,6$ ..	$3731,6$	420401.587	0.10?	..		...		...	
$38_{21,17}$ ..	$3720,17$	...		419230.267	-0.027	419129.755	0.077	...	
$38_{22,16}$ ..	$3721,16$	434341.793	--0.00?	432525.834	0.059	432566.273	0.018	430747.554	0.152
$3918,21$ −.	$38.7,.]$	...		383122.251	-0.114	...		...	
$3921,18$	$3820,18$	...		...		...		42105S1.7G3	-0.055
$3932,8$	$3931,8$	420318.307	0.081	...		...		...	
$10_{8,33}$	$397,33$	251983.343	0.014	...		...		...	
$10_{20,20}$	$3919,20$	415356.188	0.008	...		...		...	
$10_{21,19}$	$3920,19$	428694.786	−0.047	...		...		424770.426	0.014
$10_{32,9}$	$40_{31,9}$	120274.255	-0.104	...		..		...	
$1_{20,21}$	$40_{19,21}$	419194.747	0.016	417373.867	0.135	416897.875	0.007	415072.908	- 0.011
$1_{21,20}$	$40_{20,20}$	132534.354	0.028	430676.274	0,035	...		...	
$1_{32,10}$	$41_{31,10}$	120228.835	-0.124	...		...		...	
$12_{6,36}$ ←	$41_{5,36}$	...		...		214379.668	-0.013	...	
$12_{12,30}$ ←	$41_{11,30}$			313922.244	--0,023	...		...	
$12_{12,31}$	$4111,31$			313922.244	-0.230	...		...	
$12_{20,22}$ ←	$41_{19,22}$	123030.787	--0.015	421183.723	0.025	120630.067	0.060	118778.755	0. (12G
$12_{21,21}$	$41_{20,21}$	120182.155	0.161	...		134073.881	- 0,029	...	
$1322,11$	$42_{31,11}$	...		...		...		122482.147	−0.073
$13_{20,23}$	$42_{19,23}$	...		...		...		...	
$14_{19,25}$	$4318,25$	...		115478.181	−0.026	...		426183,282	- 0.006
$14_{20,24}$	$4319,24$	421164.403	-0.00?	428795.946	0.030	418352.155	-0.011	416459.756	-0.021
$15_{19,26}$	$4418,26$	...		4]9277.184	−0.041	431811.762	0.064	429881.802	-0.020
$15_{20,25}$	$4419,25$	420031.363	.-0.001	432597.833	-0.091	...		...	
$15_{32,14}$ ←	4531.14	424985.826	0.030	423073.082	0.128	422071.123	0.003	420152.875	0. 062
$16_{19,27}$	$4518,27$	...		...		435533.585	- 0.054	...	
$16_{20,26}$	$4519,X$	419977.823	0.027			...		...	
$1632,15$ ←	$4631,15$	433317,233	--0.074	...		425786.946	0.093	...	
$16_{3,14}$ ←	$4632,14$	428803.674	0.040	417300.883	-0.000	4IGO10.0G8	-0.039	...	
$17_{19,28}$	$4618,28$	419225.707	--0.018	430653.91]	-0.000	429499.194	-0.027	...	
$18_{18,30}$ ←	$47_{17,30}$	132617.753	-0.007	...		...		...	
$18_{19,29}$	$47_{18,29}$	119865.307	-0.094	421079.083	− 0.047	...		...	
$1832,17$	$4S31,17$	123028.987	-0.052	...		419712. 955	- 0.018	117756.235	-0.071
$19_{18,31}$	$48,7,3]$	...		434438. 817	-0. 000	133?08. 105	0.030	...	
$19_{18,31}$ ←	$48]7,3]$	...				...		...	
$19_{19,30}$	$4818,30$	119806. 495	-0.005			123411.547	-0.038	121429.843	0.174
$1932,18$	$4931,18$					...		134892,353	0.095
$0]8,32$	$4917,32$	1330"84.181	0.007			...		...	
$0]9,3]$	$4918,31$	417168.427	-0.022	115209.908	-0.088	...		...	
$0_{33,18}$	$5032,18$	130621.314	0.025	128621.706	0.029	...		125098.866	0.144
$1_{17,34}$	$50]6,34$	120944.443	0.005	118961.827	- 0.009	117241.723	0.074	115250.588	− 0.005
$1_{18,33}$ ←	$50_{17,33}$	134409.833	0.053			130795.194	-0.078	128763.306	0.032
$2_{17,35}$ ←	$51_{16,35}$	419618.443	-0.078			...		...	
$2_{18,34}$	$5117,34$	432956.621	--0.106			...		...	
$2_{32,21}$ ←	$52_{31,21}$	24714.026	0.036	122707.507	0.062	120914.563	0.032	118898.947	-0.170
$2_{33,20}$	$52_{32,20}$					...		132422,994	-0.132
$3_{17,36}$ ←	$52_{16,36}$	19551.963	--0.004	...		...		...	
$3_{18,35}$	$52_{17,35}$	32890.143	-0.014	...		...			
$332,22$ ←	$5331,22$	11276.326	− 0.010	...		...			
$333,21$	$5332,21$	13028.521	0.003	...		...			
$47,48$	$537,47$	11302,862	− 0.176	...		...			
$48,47$	$538,46$	11302.862	0.003	...		...		.	
$413,41$	$5313,40$	28476.866	0.059	126446.562	0.000				
$413,42$	$5313,41$								
$4,7,77$	$531,6,37$								

TABLE 11. Fitted Transitions (continued)

		"—=ci;cz"—		'-' −35~,<}37(:1(~~		^{37}ClO^{35}ClO$_2$		^{37}Cl$_2$ 0 3	
55₁₆,₃₉	54₁₅,₃	418648.915	−0.00	...		...			
55₁₇,₃₈	54₁₆,₃	432232.554	−0.02	...		...			
55₃₂,₂₄	553[:	419412.835	0.06	...		...			
55₃₃,₂₃	55₃₂,₂	432751.073	−0.05	...		...			
56₁₆,₄₀	55₁₅,₄	422373.907	0.12	...		18217.875	0.03	416176.148	0.019
56]7,39	55₁₆,₃₉	...		433903.913	−0.03	31895.906	−0.07	429808.602	−0.102
56₃₃,₂₄	56₃₂,₅₄	432678.473	−0.12	...		...			
57₃,₅₄	563,53	212771.595	0.05	...		...		..	
574,54	56₄,₅₃	212770.620	0.00	...		...		...	
57₁₆,₄₁	56₁₅,₄₁	4213089.202	0,03	424036.867	0.01	...			
57₃₂,₂₆	57₃₁,₂₆	419265.187	0.02	...		...			
57₃₃,₂₅	57₃₂,₂₅	432604.073	0.08	...		...		...	
58₁₅,₄₃	57₁₄,₄₃	415997.228	0.07	...		...		...	
58]5,44	57₁₄,₄₄	415997.228	−0.02	...		...		...	
58₁₆,₄₂	57₁₅,₄₂	...		...		...		42337'2.547	−0.02₄
5832,27	5 8₃₁,₂ 7	419187.9(I7	−0.18	...		...		...	
5915,44	5 8₁,₄ ₄	419651.035	0.11	4 7611.227	0.16	...		...	
59]5,45	5 8₁,₄ ₅	41'3651.035	−0.04	4 7611.227	0.03			...	
59₁₆,₄₃	58₁₅,₄₃	433489.673	−0.00	...		..		...	
608,52	59₇,₅₂	317403.276	0.01!	...		..		...	
6015,45	59₁₄,₄₅	423290.827	0.11	421231,723	0.06	..		416669.995	0.12₅
60₁₅,₄₆	59]4,4 G	423290.827	−0.14'	421231.723	−0.15			416669.995	0.03₅
60₁₆,₄₄	59]5,44	...		435057.52]	0.00	3266 073	0.081	130533.594	0.02(
60₃₃,₂₈	6 0₃₂,₂₈	432367.554	0.19₂	...		..		...	
61₁₅,₄₆	60]4,4 G	...		...		..		120196.675	0.06₉
61₁₅,₄₇	60]4,47	...		...		..		120196.675	−0.073
61₁₆,₄₅	60₁₅,₄₅	...		...		..		134099.681	−0.07.!
6132,30	61₃₁,₃₀	418943.347	0.08₅	...		..		...	
62₁₄,₄₈	61₁₃,₄₈	416245.868	−0.02₈	...		..		...	
62₁₄,₄₉	61₁₃,₄₉	416254.988	−0.05₇	...		...			
62₁₅,₄₇	61₁₄,₄₇	430525.674	0.271	...		25824.866	0.11'	..	
62₁₅,₄₈	61₁₄,₄₈	430525.674	−0.37(	...		25824.8GG	−0.16₂	..	
6232,31	62₃₁,₃₁	418857.007	0.05:	...		...		...	
6 3₁,₄,₄₉	62₁₃,₄₉	419755.435	−0.011	417720.355	0.04!	15014.788	0.05!	...	
6314,50	62₁₃,₅₀	...		417731.515	−0.07'	15021.028	−0.06₅	...	
6315,48	62₁₄,₄₈	434118.665	−0.02₂	132005.874	0.30:	29343.746	0.20₆	...	
6315,49	62₁₄,₄₉	434119.625	−0.06₉	432005.874	−0.51:	29343.746	−0.22!	...	
6333,31	63₃₂,₃₁	432110.754	0.16₀	...		...		...	
64₁₄,₅₀	63]3,5()	423240.307	−0.03[	121192.963	0.00₇	...		116367.476	0.032
64₁₄,₅₁	63₁₃,₅₁	4232G0.587	0.034	121209.643	−0.02₅	18451.875	−0.03[	116375.156	−0.039
65₁₄,₅₁	64]3,5]	...		...		21848.283	0.071	...	
65₁₄,₅₂	64₁₃,₅₂	...		124664.946	−0.011	...		...	
65₁₇,₄₈	6516,5[	...		214885.845	−0.06₂	...		...	
6517,49	6 5]₆,₄₉	...		214885.845	−0.04:	...		...	
65₃₂,₃₄	653].34	418583.275	0.028	...		...		...	
66₃,₆₃	65₂,₆₃	417619.147	−0.017	...		...		...	
66₄,₆₃	65₃,₆₃	417619.147	−0.095	...		...		...	
66₁₄,₅₂	65]3,5 ₂	430128.234	0.049	...		...		23129.787	−0.119
66₁₄,₅₃	65]3,53	430171.434	0.041	...		...		23146.587	−0.043
6632,3s,	66₃₁,₃₅	418486.795	−0.116	...		...			
67₂,₆₅	66,,65	429446.154	−0.014	...		...			
67₃,₆₄	66₂,₆₄	424170.067	0.094	...		...			
G73,65	66₂,₆₅	429446.154	−0.016	...		...		...	
67₄,₆₄	66₃,₆₄	424170.067	0.040	...		...		...	
67]3,54	66₁₂,₅₄	417723.355	0.014	...		...		...	
G7₁₃,₅₅	6 6₁₂,₅₅	418303.555	−0.070	16315.708	0.017	...		...	
67₁₄,₅₃	6613,53	433526.393	0.076	31451.354	0.071	...		...	
67₁₄,₅₄	66]3,54	433588.793	0.044	...		...		...	
67₁₂,₅₀	67₁₆,₅₂	214700.026	−0.018	14270.791	0.001	...		...	
67₁₇,₅₁	67₁₆,₅₁	2]4700.026	0.024	'14270.791	0.034	...		...	
67₃₂,₃₆	673].₃₆	418387.795	−0.144	...		...		...	
68₁₃,₅₅	67₁₂,₅₅	...		...		6253.308	0.004	...	
G8₁₃,₅₆	67₁₂,₅₆	421580.563	0.039	19581.363	0.069	6666.995	0.136	...	
68₁₄,₅₄	6713.54	.		34809.673	0.026	...			
G8₁₇,₅₁	68₁₆,₅₃	214358.876	−0.016	...		...		...	
68,7,5₂	68₁₆,₅₂	214358.876	0.052	...		...		...	
69₆,₆₄	68₅,₆₄	424952.706	−0.086	...		...		...	
69₇,₆₃	68₆,₆₃	417484.987	−0.030	...		...		...	
69₁₃,₅₆	68₁₂,₅₆	423754.747	−0.118	21904.323	−0.053	9301.907	−0.122	...	
69₁₃,₅₇	68₁₂,₅₇	...		22826.067	0.037	9868.787	−0.032	...	
69₁₄,₅₆	68₁₃,₅₆	...		...		...		433138.841	0.135
70₆,₆₄	695,64	424095.187	0.0G3	...		...		...	
70₇,₆₄	69₆,₆₄	424190.347	0.120	...		...		...	
70₁₃,₅₈	69₁₂,₅₈	...		26053.442	−0.134	...		...	
71₁₂,₆₀	70₁₁,₆₀	416647.916	0.080	...		...		...	
71₁₃,₅₈	70₁₂,₅₈	4293G0.30G	−0.011	...		...		...	
71₁₃,₅₉	70₁₂,₅₉	...		29268.914	0.116	6209.922	−0.104	...	
72₁₂,₆₁	71₁₁,₆₁	420266.275	−0.064	18011.475	0.006	...		...	
72₁₃,₆₀	71₁₂,₆₀	434544.881	−0.011	32478.074	0.140	9355.986	0.080	...	
73₁,,63	72₁₀,₆₃	416821.272	−0.016	...		...		...	
7312,62	72₁₁,₆₂	423992.107	−0.011	21649.683	0.027	...		...	
7313,61	72₁₂,₆₁	...		...		2491.644	0.056	...	
74 10,65	73₉,₆₅	425148.404	−0.092	...		...		...	
74₁₁,₆₄	73₁₀,₆₄	421937.323	0.013	...		...		...	
7412,63	7311,63	...		25400.666	−0.10G	421098.523	−0.068	...	
7413,61	7312,61	...		35100.962	−0.055	...		...	
7512,64	7411.,34	...		...		124682.826	0.029	...	
76₁₁,₆₆	75₁₀,₆₆	432740.873	−0.022	...		...		...	
78₁₀,₆₈	779,68	421930.238	−0.024	...		...		...	
80₁₁,₆₉	79₁₀,₆₉	415112.521	0.040	...		...		...	
82₁₂,₇₀	8111,70	422317.507	0.027	...		...		...	

Table 111. Rotational Constants

Parameter	$^{35}ClO^{35}ClO_2$	$^{35}ClO^{37}ClO_2$	$^{37}ClO^{35}ClO_2$	$^{37}ClO^{37}ClO_2$
A/MHz	8629.1968(44)	8597.0701(65)	8628.4417(64)	8596.3222(91)
B/MHz	2106.40979(200)	2089.93166(262)	2044.34739(290)	2027.8504(44)
C/MHz	1776.12211(242)	1765.6250(36)	1731.7612(83)	1721.0860(92)
D_K/kHz	1.6055(122)	1.5925(1 27)	1.8711 (142)	. . .[b]
D_{JK}/kHz	6.5344(45)	6.4329(46)	6.2956(50)	. . .[b]
D_J/kHz	0.47403(47)	0.46752(47)	0.45302(59)	, . .[b]
d_1/kHz	--0.081808(293)	- 0.078775(3(15)	-0.07611(42)	. . .[b]
d_2/kHz	−0.020749(141)	- 0.019779(155)	- 0.018948(185)	. . .[b]
H_K/Hz	0.2100(152)	. . .[a]	. . .[a]	, . .[a]
H_{KJ}/Hz	−0.2110(44)	. . .[a]	. . .[a]	. . .[a]
H_{JK}/Hz	−0.00305(83)	. . .[a]	. . .[a]	. . .[a]
H_J/Hz	---0.000212(39)	. . .[a]	. . .[a]	. . .[a]
h_1/Hz $\times 10^4$	- 0.25(51)	. . .[a]	. . .[a]	. . .[a]
h_2/Hz $\times 10^4$	−0.16(35)	. . .[a]	. . .[a]	. . .[a]
h_3/Hz $\times 10^4$	0.1092(228)	. . .[a]	. . .[a]	. . .[a]
L_K/Hz $\times 10^4$	0 . 3 1 7 (6 6)	. . .[a]	. . .[a]	. . .[a]
L_{JKKK}/Hz $\times 10^4$	−0.2635(207)	. . .[a]	. . .[a]	. . .[a]
L_{JJKK}/Hz $\times 10^5$	---0.127(52)	. . .[a]	. . .[a]	. . .[a]

[a] Fixed to $^{35}ClO^{35}ClO_2$ values.

[b] Fixed as described in the text.

'Jable IV. Fitted Quadruple Splittings

Transition	Calc. Freq.	splitting	O-C		Transition	Calc. Freq.	Splitting[a]	() - C
$36_{5,32} - 35_{4,32}$	214889,295	2.198(80)	−0.009		$80_{11,69} - 79_{10,69}$	415112381	1.800(80)	0.031
		3.216(80)	0.011				3.600(80)	0.060
		5.352(80)	-0.061		$65_{2,63} - 64_{1,63}$	416379.364[b]	1.800(80)	0.079
$41_{6,35} - 40_{5,35}$	215007.825	0.940(80)	0.077		$65_{3,63} - 64_{2,63}$	416379.367b	2.520(80)	0.037
		1.050(80)	-0.148				4,200(80)	-0.004
		2.066(80)	0.005		$53_{32,22} - 53_{31,22}$	419551.968	1.335(80)	0.127
$36_{6,31} - 35_{5,31}]$	215643.407	1.358(80)	0.00{}		$52_{32,20} - 52_{31,22}$	419618.522	1.330(80)	0.089
		2.678(80)	- 0.021		$49_{32,18} - 49_{31,18}$	419806.501	1.497(80)	0.054
$35_{7,28} - 34_{6,28}$	215751.158	0,905(100)	0.134		$48_{32,16} - 48_{31,18}$	419865.401	1.510(80)	0.037
		2.006(100)	0.065		$41_{32,10} - 41_{31,10}$	420228.860	2,002(80)	--0.016
		2.857(100)	0.143		$40_{32,8} - 40_{31,10}$	420274.359	2.147(80)	--0,019
$22_{13,10} - 21_{12,10}$	252479.140	0.368(40)	0.019		$37_{32,5} - 37_{31,7}$	420401.482	2.640(80)	0.166
		1.173(40)	--0.044		$78_{10,68} - 77_{9,68}$	421930.262	1.988(80)	-0.089
		1.539(40)	--0.026				3.409(80)	---0.004
$60_{8,52} - 59_{7,52}$	317403,257	1.990(80)	0.013				5.469(80)	-0.021
		3.208(80)	-0.003		$81_{11,70} - 80_{10,70}$	422695,305	1.523(80)	--0.032
		5.182(80)	- 0,006				2.582(80)	0.037
							4.047(80)	- 0.052

[a] Measured from lowest frequency feature.

[b] Blended.

Table V. Chlorine Quadrupole Coupling Constants

	*$ClOClO_2$	$ClONO_2$[a]	ClO^*ClO_2	$FClO_2$[b]
χ_{aa}	$-74.1(9)$	$-83.9(3)$	$-22.6(12)$	$-34.75(13)$
χ_{bb}	$14.5(6)$	$18.8(10)$	$-24.0(7)$	$-17.08(13)$
χ_{cc}	$59.6(6)$	$65.1(11)$	$46.6(7)$	$51.82(16)$

[a] Reference 12.
[b] Reference 13.

Table VI. Chlorine substitution coordinates

	$^{35}Cl_2O_3$ reference			$^{37}Cl_2O_3$ reference		
	d	b	c	d	b	c
*ClOClO$_2$	1.9258	0.0522	0.0037i	1.9095	0.0470	0.0147
ClO*ClO$_2$	0.9251	0.0694	0.3278	0.9423	0.0662	0.3203

Table VII. Molecular Parameters with Fixed Outer Cl- O Bond length

Fit	l_{12}	l_{23}	l_{34}	l_{35}	$\angle_{123}$	$\angle_{235}$	$\angle_{234}$	$\angle_{435}$	$\angle_{1235}$
1	1.705	1.758	1.470	1.424	112.33	109.40	99.94	112.97	31.75
	1.673	1.755	1.474	1.424	114.10	109.G8	99.62	113,02	32.35
	RMS = 0.00172 amu·Å²								
2	1.705	1.598	1.529	1.536	121.26	101.30	103.30	118.22	30.17
	1.673	1.598	1.530	1.534	123.25	101.22	103.39	118.20	30.81
	RMS = 0.00157 amu·Å²								
3	1.705	1.812	1.409	1.455	109.19	104,71	98.05	114.62	49.81
	1.673	1.809	1.415	1.453	110.80	104.99	97.64	114.76	51,02
	RMS = 0.00024 amu·Å²								
4	1.705	1.665	1.475	1.554	116.74	97.02	101.10	120.07	49.58
	1.673	1.666	1.481	1.546	118.47	96.94	101.13	120.12	51.00
	RMS = 0,00029 amu·Å²								

Bon lengths in Å, angles in degrees.

'liable V]]]. Molecular Parameters with Identical Cl=O Bond Lengths

Fit	l_{12}	l_{23}	l_{34}	$\angle_{123}$	$\angle_{235}$	$\angle_{234}$	$\angle_{435}$	$\angle_{1235}$	RMS
1a	1.705	1.738	1.457	113.3	108.6	101.5	112.6	31.2	0.00215
	1.673	1.736	1.458	115,1	108.9	101.2	112.5	31,8	0,00220
2a	1.705	1.602	1.531	121.0	101.5	103.1	118.3	30.2	0.00159
	1.673	1.596	1.533	123.4	101.1	103.5	118.2	30.8	0.00158
3a	1.705	1.825	1.427	108.6	105.3	96.7	114.7	49.7	0.00156
	1.673	1.819	1.430	110.4	105.4	96.6	114.9	51.0	0.00129
4a	1.705				110 minimum				
	1.673	1.702	1.497	116.5	98.7	99.1	119.8	50.1	0.00229

Units are given in Table VII. Fit 3a is preferred as discussed in the text.

Table IX. Structural Parameters as a Function of Cl=O Bond Length.[a]

l_{34}	l_{23}	$\angle_{123}$	$\angle_{235}$	$\angle_{234}$	$\angle_{435}$	$\angle_{1235}$	RMS
Structures near Fit 3a							
1.420	1.836	108.1	105.9	96.4	114.3	50.2	0.0017
1.430	1.820	108.8	105.0	96.9	114.9	49.5	0.0016
1.440	1.804	109.6	104.1	97.3	115.6	49.0	0.0018
1.450	1.788	110.4	103.2	97.6	116.3	48.7	0.0021
1.460	1.771	111.2	102.3	98.0	117.0	48.5	0.0024
1.470	1.754	112.1	101,4	98.2	117.8	48.4	0.0026
Structures near Fit 1 a							
1.420	1.797	110.5	112.4	99.7	109.9	33.0	0.0039
1.430	1.781	111.2	111.3	100.3	110.6	32.4	0.0030
1.440	1.765	112.0	110.3	100.8	111.3	31.9	0.0025
1.450	1.749	112.8	109.3	101.2	112.1	31.4	0.0022
1.460	1.733	113.6	108.3	101.6	112.8	31.1	0.0022
1.470	1.716	114.5	107.3	101.9	**113.6**	30.8	0.0022

Parameters of Related Molecules

Molecule	l_{Cl-O}	$l_{Cl=O}$	$\angle_{ClOX}$	$Lo._{Cl=O}$	$\angle_{O=Cl-X}$
ClOOCl[b]	1,704		110.1		
ClOCl[c]	1.700		110.9		
ClONO$_2$[d]	1.673		113.0		
OClO[e]		1.471		117.5	
FClO$_2$[f]		1.420		115.3	101.8

[a] $l_{12} = 1.705$Å. Units are given in Table V]]. Preferred structures are scar Fit 3a.
[b] Ref. (1), [c] Ref. (1 7), [d] Ref. (14), [e] Ref. (18), [f] Ref. (16).