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Submillimeter Spectrum and Structure of Chloryl Chloride, $ClClO_2$

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The submillimeter spectrum of $ClClO_2$ has been observed between 365 and 398 GHz in a flowing system as a product of the $FClO_2 + HCl$ reaction. Absorptions of three isotopomers, $^{35}Cl^{35}ClO_2$, $^{37}Cl^{35}ClO_2$, and $^{35}Cl^{37}ClO_2$, have been assigned. Rotational and centrifugal distortion constants have been determined and structural parameters derived. The data are compared with those from a matrix-isolation study, *ab initio* calculations, and related molecules.

Introduction

Chlorine oxides are among the most important molecules to participate in the catalytic ozone destruction. About a decade ago, a catalytic cycle involving the dimerization of ClO to ClOOCl was proposed as having a key role in the formation of the Antarctic ozone hole. The ClOClO form of Cl_2O_2 was thought not to contribute to net ozone loss.[1] Initial *ab initio* calculations suggested three Cl_2O_2 isomers, dichlorine peroxide, ClOOCl, chloryl chloride, $ClClO_2$, and chlorine chlorite, ClOClO, to be thermodynamically stable under stratospheric conditions.[2] More sophisticated calculations indicate that ClOOCl and $ClClO_2$ differ in their heat of formation by less than the suggested uncertainties of ~8 kJ mol^{-1} and are approximately 40 kJ mol^{-1} more stable than ClOClO.[3]

Both ClOOCl and $ClClO_2$ have been directly observed in the gas phase as relatively long-lived species.[4,5] The molecular structure of the peroxide has been determined from its rotational spectrum,[4] and the harmonic force field has been derived from its IR spectrum and centrifugal distortion constants.[6] The harmonic force field and a preliminary structure of $ClClO_2$ have been derived from its IR spectra in inert gas matrices[7] and in the gas phase.[5] ClOClO has not been observed directly in the gas phase although evidence has been presented for its formation as a transient product of the ClO self-reaction.[5,8]

More recently $ClClO_2$ was observed in the ClO self-reaction on ice[9] and in the photochemistry of OClO in and on ice, respectively.[10,11] In a photoionization study on products of the ClO dimerization in the gas phase evidence was found for the formation of another Cl_2O_2 isomer besides ClOOCl.[12] These findings have raised the question of the importance of the different Cl_2O_2 isomers in the ClO dimerization and of the role of $ClClO_2$ in stratospheric chemistry in general.

As part of a program to provide a millimeter and submillimeter spectroscopic data base of potentially important upper atmospheric molecules and to determine molecular properties which may influence chemical behavior, we have studied the rotational spectrum of $ClClO_2$. This Letter reports an analysis of the spectra of three isotopomers between 365 and 398 GHz, the spectroscopic constants, and the derived structural parameters. Work is in progress on further measurements of hyperfine patterns to determine the quadrupole coupling constants of both Cl nuclei. Since *ab initio* calculations are often used to determine thermochemical properties of molecules, the structural information reported here will provide an important reference point for such calculations. It is also of interest to compare the structure with that deduced from a matrix IR study since the reliability of the latter is often difficult to assess.

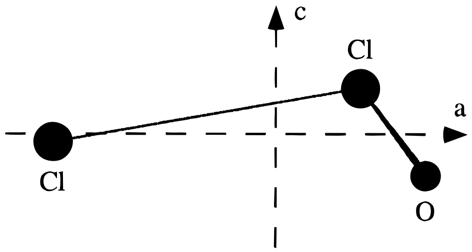

Figure 1. Projection of the $ClClO_2$ molecule into the *ac*-plane.

Experimental Details

$ClClO_2$ was prepared *in situ* by the reaction of $FClO_2$ with HCl. $FClO_2$ was prepared from ClF_3 (Spectra Gases) and $NaClO_3$. A commercial sample of HCl (Spectra Gases, 99.995%) was used. Conditions for $ClClO_2$ production were optimized by first observing the UV spectrum of the reaction products in the millimeter sample cell. At ~255 K about 10−30% of the total pressure was due to $ClClO_2$ when $FClO_2$ was mixed with about stoichiometric amounts of HCl in a ~1 m long, 2.5 cm i.d. prereactor at pressures of 10−30 Pa, and the products were expanded through a ~1.5 mm pinhole into the 1 m long, 5 cm i.d. absorption cell. The pumping speed was low to minimize the amount of chemicals used. It was adjusted so that a pressure inside the cell was in the 1 Pa range, suitable for submillimeter spectroscopy.

The spectrometer is essentially identical to that described by Friedl *et al.*[13] The entire region between 378.5 and 395.0 was scanned. Additional measurements were made outside this range in order to extend and confirm the initial assignments of R-branch series having the same K_a. Lines of unreacted $FClO_2$ and of OClO, a decomposition product of $ClClO_2$ and a hydrolysis product of $FClO_2$, were eliminated from consideration by comparison with reference spectra and calculated line positions.

Results

Initial predictions of the rotational spectrum of $ClClO_2$ were made using the structure from ref 7 together with the quartic distortion constants derived from the harmonic force field. The

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TABLE 1: Spectroscopic Constants[a] (MHz) of Chloryl Chloride, $ClClO_2$

parameter	$^{35}Cl^{35}ClO_2$	$^{37}Cl^{35}ClO_2$	$^{35}Cl^{37}ClO_2$	parameter	$^{35}Cl^{35}ClO_2$	$^{37}Cl^{35}ClO_2$	$^{35}Cl^{37}ClO_2$
A	9450.9218 (98)	9449.8443 (396)	9414.6640 (99)	$\delta_J \times 10^3$	0.3842 (4)	0.3537 (13)	0.3754 (6)
B	3588.0617 (62)	3469.5738 (229)	3565.0887 (94)	$\delta_K \times 10^3$	6.1348 (43)	5.8911 (130)	6.0322 (58)
C	2787.9468 (79)	2715.9436 (232)	2777.2698 (123)	$\Phi_{JK} \times 10^7$	0.113 (22)	b	b
$\Delta_J \times 10^3$	1.7603 (13)	1.6600 (35)	1.7350 (19)	$\Phi_{KJ} \times 10^7$	0.221 (74)	b	b
$\Delta_{JK} \times 10^3$	6.5029 (38)	6.2313 (125)	6.4457 (46)	$\Phi_K \times 10^7$	−0.283 (63)	b	b
$\Delta_K \times 10^3$	−1.2229 (147)	−0.8188 (463)	−1.2450 (147)	$\phi_K \times 10^7$	1.837 (223)	b	b

[a] Numbers in parentheses are 1 standard deviation in units of the least significant figures. Watson's A reduction in the representation I^r was used. [b] Common constants for all three isotopomers.

TABLE 2: Structural Parameters (pm, deg) of $ClClO_2$ and Related Molecules

	$ClClO_2$, exptl		$ClClO_2$, *ab initio*				$FClO_2$[e]	OClO[f]
	gas phase[a]	matrix[b]	MP2/6-31G*[c]	MP2/TZ2P[d]	MP2/TZ2Pf[d]	CCSD(T)/TZ2P[d]	exptl, gas phase	
r(XCl)	219.78 (23)	222. (6)	245.9	233.4	226.9	227.9	169.43	
r(ClO)	143.60 (12)	144.0 (5)	146.9	145.1	144.2	146.8	142.03	146.98
∠(XClO)	104.06 (14)	103.5 (10)	104.2	103.9	103.8	104.1	101.81	
∠(OClO)	115.05 (15)	116.0 (5)	116.7	115.6	115.0	114.9	115.25	117.40

[a] r_o structure, this work. [b] Reference 7. [c] Reference 2. [d] Reference 3. [e] r_0 structure, ref 14. [f] r_e structure, ref 15.

pyramidal $ClClO_2$ is an asymmetric prolate top, $\kappa = -0.7598$ for $^{35}Cl^{35}ClO_2$. It has C_s symmetry with dipole components along the a- and c-axes, as shown in Figure 1. In the region searched, the strongest features in the spectrum are expected to be high K_a c-type R-branches. Because $A - (B + C)/2 \approx B + C$, each R-branch has its origin in the vicinity of the third member of the branch with one lower K_a. At high K_a this leads to some clustering of the stronger transitions and facilitates the identification of different series once one has been identified.

Initially a series of strong, partially resolved doublets with spacings of approximately the estimated value of $B + C$ was identified and eventually extended to six consecutive members. Comparison with predicted spectra and some trial fits quickly led to the correct assignment of the $J'' = 24-29$ members of the $K_a'' = 16$ ^rR branch and the identification of further transitions. Because of higher quantum numbers, large uncertainties, and a possibly small value for μ_a, the a-dipole transitions have not yet been unambiguously assigned. Most of the observed lines showed small effects of quadrupole coupling due to the two Cl nuclei, generally in the form of doublets. The centers of the patterns were used in fitting the spectra. The quadrupole analysis will appear in a subsequent paper. Rotational, quartic, and some sextic centrifugal distortion constants have been determined. Because not all of the sextic distortion constants were determinable by the present data, the final values of the molecular constants may lie outside the quoted uncertainties. For the rotational and quartic distortion constants as well as for the derived structure these effects are expected to be small.

A preliminary structure was derived from the rotational constants of $^{35}Cl^{35}ClO_2$ and an estimate of r(ClO) in order to predict rotational constants of $^{37}Cl^{35}ClO_2$ and $^{35}Cl^{37}ClO_2$. Quartic distortion constants were estimated from the harmonic force field.[7] Sextic constants were taken from the main isotopomer. Some lines were found for both isotopomers within a few megahertz of the predictions enabeling further transitions to be assigned. Although the number of observed transitions was smaller for the less abundant isotopomers than for $^{35}Cl^{35}ClO_2$, rotational and quartic distortion constants could be determined precisely.

The spectroscopic constants from a combined fit of all three isotopomers are given in Table 1. The principal planar moments were used to derive a ground state effective, r_0, structure which is given in Table 2. The uncertainties quoted are those derived from the standard deviation of the fit. Because of vibrational effects inherent in r_0 structure determinations, parameters determined from a different set of isotopomers may lie outside the quoted uncertainties. Matrix and *ab initio* data as well as those for the related $FClO_2$ and OClO molecules are also included.

Discussion

The structural parameters obtained in the matrix study agree well with the present, more precise gas phase values (Table 2). At the MP2/6-31G* level the ClCl distance is poorly predicted, and the remaining parameters are in reasonable agreement with the experiment. MP2 calculations employing much larger basis sets yielded more reasonable values for r(ClCl), with the other values also in better agreement. The highest level coupled cluster structure calculation published obtained a better ClCl distance than the MP2 calculation with the same basis set with the remaining constants of similar quality.

It should be mentioned that the MP2/6-31G* method is frequently used to estimate thermodynamic properties. It predicted $ClClO_2$ to be higher in energy than ClOOCl by about 100 kJ mol^{-1},[2] whereas calculations with larger basis sets predict the difference to be *ca.* 4 ± 8 kJ mol^{-1}.[3]

To our knowledge, $ClClO_2$ constitutes the first determination of a bonding ClCl distance with one of the Cl atoms bonded to more than one atom. For both $ClClO_2$ and $FClO_2$ the XCl bond is longer than that in the respective XCl molecule. However, for $FClO_2$ the difference is about 7 pm,[14,16] while for $ClClO_2$ it is ∼20 pm.[17] The larger XClO bond angle in $ClClO_2$ compared to $FClO_2$ may be due to the steric effect of the larger Cl atom.

As has been pointed out earlier,[7] the substitution of an electronegative atom at the Cl atom of OClO lowers the electron density in antibonding orbitals, thus shortening the ClO bond length. Since F is more electronegative than Cl, its effect is larger. The substitution also reduces the OClO angle, but the electronegativity seems to have little effect on the magnitude of reduction, since the OClO angles are the same in $ClClO_2$ and $FClO_2$ within experimental uncertainties.

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