

Infra-red absorption spectrum of gaseous chloryl fluoride (FClO_2)

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Abstract—The infrared spectrum of gaseous chloryl fluoride has been investigated in the region between 2.5 and 25 μ at pressures from ca. 1 mm Hg to ca. 1 atm at room temperature.

The strong bands located at 1265, 1104, 627 and 542 cm^{-1} have been assigned to four of the six fundamental vibrations expected for a pyramidal tetratomic molecule pertaining to the C_s point group.

The other two bands could not be detected but they were tentatively located at 405 and 349 cm^{-1} .

A correlation of the chloryl fluoride spectrum with spectra of related molecules and ions has been useful to the assignment of the bands.

INTRODUCTION

Chloryl fluoride was obtained by SCHMITZ and SCHUMACHER [1] in the thermal reaction between fluorine and chlorine dioxide. Its infrared absorption spectrum in the sodium chloride region at low gas pressure has been published by SMITH *et al.* [2], although BURKE and SMITH had reported in 1956, at the Columbus Symposium of Molecular Structure and Spectra, that two weak bands which were observed by CLAASSEN *et al.* [3] in the infrared absorption spectrum of impure chlorine trifluoride, were due to the presence of chloryl fluoride.

SMITH *et al.* obtained the spectrum for analytical purposes employing a 10-cm path length cell and silver chloride windows. They have reported only two bands which were centered at 7.94 and 9.06 μ (1260 and 1104 cm^{-1} , respectively).

The aim of the present work is to extend the range of the spectrum covering as well as the potassium bromide region and employing pressures of the substance as high as 1 atm at room temperature.

EXPERIMENTAL

Chloryl fluoride was prepared by reaction between gaseous fluorine diluted with dry nitrogen and liquid chlorine dioxide at temperature between -50 and -55°C , according to the method described by SICRE and SCHUMACHER [4], in an all quartz apparatus. The substance was then purified by distilling it at low temperature and pressure and finally collected in a quartz storage trap kept at liquid air or dry-ice temperature. The trap was closed by an aluminium valve, provided with nickel needle and Teflon seat and gaskets.

The substance, which was originally colorless, very slowly took a yellow tinge due to a reaction with the quartz walls of the trap.

[1] H. SCHMITZ and H. J. SCHUMACHER, *Z. Anorg. Allgem. Chem.* **249**, 238 (1942).

[2] E. A. SMITH, F. C. STEINBACH and K. E. BEN, U.S. Atomic Energy Commission GAT-T-687 (1959).

[3] H. CLAASSEN, B. WEINSTOCK and J. G. MALM, *J. Chem. Phys.* **28**, 285 (1958).

[4] J. E. SICRE and H. J. SCHUMACHER, *Z. Anorg. Allgem. Chem.* **286**, 232 (1956).

The trap was connected with a manifold to a Bodenstein manometer and a female standard tapered joint, all made of quartz, and to the vacuum line, through another aluminium valve.

The ca. 10-cm path length cell was made of quartz tubing and had a lateral inlet tube closed by a tap ending in a male ST joint.

The flat ends of the cell were optically polished. Windows were attached to them with Halocarbon grease. This lubricant was also employed for tap and joint. A metallic mounting was used to assemble the cell and to fit it into the 221 Perkin-Elmer infrared spectrometer. As a reference, commercial cells adequately diaphragmated have been used.

Spectra were somewhat distorted in the regions of carbon dioxide and water absorption due to the unavoidable difference in path length of the cells used. This caused some uncertainty in the location and shape of the absorption bands in a region where chloryl fluoride has only overtone and combination bands.

Rock salt and potassium bromine windows withstood satisfactorily chloryl fluoride when humidity was excluded; consequently, blank spectra made before and after measurements agreed well. Nevertheless window bands slowly developed which obliged us to repolish the windows periodically.

Spectra were obtained at room temperature, chloryl fluoride being thermally stable at that temperature even at pressures as high as one atmosphere [5].

Fluorine was used to eliminate any chlorine dioxide, as it has been suggested by SMITH *et al.* [2]. It was prepared by electrolysis of potassium bifluoride and purified by flowing through sodium fluoride packed towers and a trap cooled at liquid air temperature, to be finally stored in a copper container. It was transparent in the region covered by the spectrophotometer.

It is worthwhile mentioning that chlorine dioxide formation in the absence of fluorine is dubious. According to SMITH *et al.* [2] the intensity ratio of the bands located at 1260 and 1104 cm^{-1} if lower than 100:43 would give an indication of the presence of chlorine dioxide. The ratio we found was always lower in spite of the addition of fluorine. No chlorine dioxide colour could ever be observed, even in the absence of fluorine.

The absorption cell was highly evacuated before the filling operation, specially when it had been previously disassembled. The storage trap was evacuated each time for a short while at dry ice temperature to eliminate volatile impurities.

Fluorine was added to the cell before or after chloryl fluoride, according to the circumstances. The pressure ratio of fluorine to chloryl fluoride was changed from 0 to 1.

Preliminary spectra showed spurious bands which could be distinguished from true chloryl fluoride bands because they weakened and even disappeared after successive evacuations of the storage trap cooled at -78°C . Among the very weak remaining bands stood the resolved *Q* branch of HF-monomer band [6] and the strongest band of silicon tetrafluoride [7]. Unavoidable traces of the latter due to

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[6] A. M. BUSWELL, R. T. MAYCOCK and W. H. RODEBUSH, *J. Chem. Phys.* **8**, 362 (1940).

[7] E. A. JONES, J. S. KIRBY-SMITH, P. J. H. WOLTZ and A. H. NIELSEN, *J. Chem. Phys.* **19**, 242 (1951).

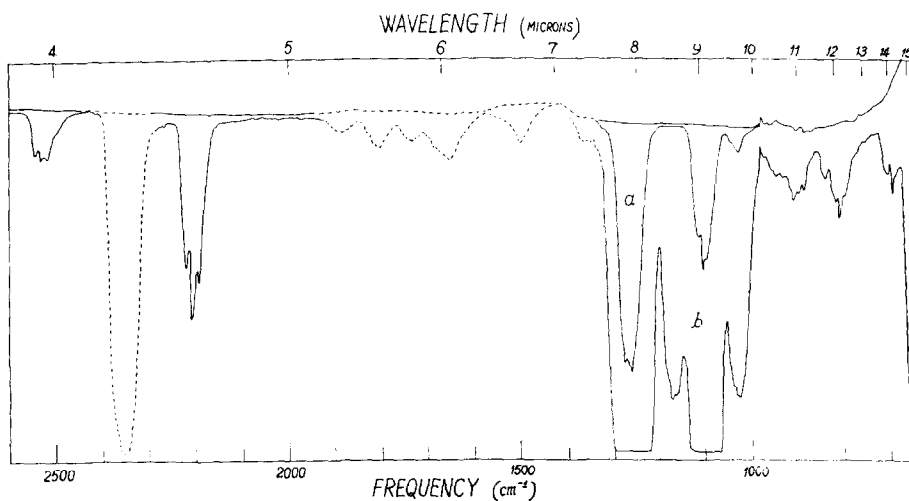


Fig. 1. Infrared absorption spectra of gaseous FClO_2 in the sodium chloride region. (a) 6 mm Hg of FClO_2 + 12 mm Hg of F_2 ; (b) 661 mm Hg of FClO_2 + 158 mm Hg of F_2 .

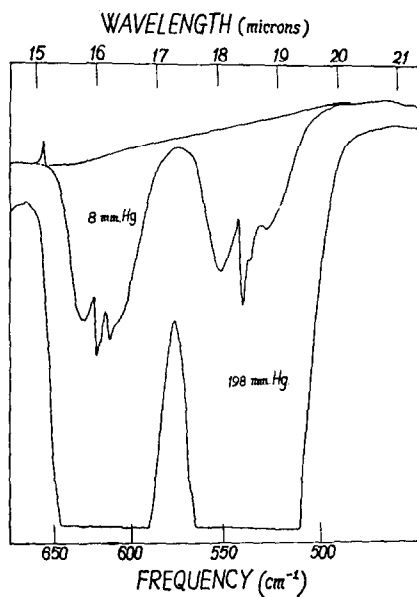


Fig. 2. Infrared absorption spectra of FClO_2 in the potassium bromide region.

slow attack of cell walls and windows by highly pressurized chloryl fluoride alone or mixed with fluorine, caused a serious interference in the region near 400 cm^{-1} , just where chloryl fluoride could have a fundamental band of low intensity. Silicon tetrafluoride band at 1031 cm^{-1} also distorted the envelope of a combination band.

Figs. 1 and 2 reproduce infrared absorption spectra recorded at different pressures with the spectrometer set to obtain the highest resolution. Dotted lines are drawn where band envelopes are somewhat distorted by atmospheric absorption.

Table 1. Infrared spectrum of gaseous FClO_2

Frequency	Intensity	Assignment
(349)	?	$\nu_6 (a'')$?
(405)	?	$\nu_4 (a')$?
533		P
ca. 540 sh		$\left. \begin{array}{l} P \\ Q \\ R \end{array} \right\} \text{FCl}^{37}\text{O}_2?$
542	s	Q
567		R
ca. 610		P
619		$\left. \begin{array}{l} P \\ Q \\ R \end{array} \right\} \text{FCl}^{37}\text{O}_2?$
625 sh		Q
627	s	R
639		P
690		Q
698	w	R
708		$2 \times (349) = 698 (A')$
ca. 799		P
810	w	Q
818		R
910	w	$2 \times (405) = 810 (A')$
1026	m	$(349) + 542 = 891 (A'')$
1030 sh		$(405) + 627 = 1032 (A')$
1096		$(+ \text{impurity SiF}_4?)$
1104	s	P
1112		Q
1162		R
1172	m	$\nu_1 (a')$
1259	vs	$542 + 627 = 1169 (A')$
1270		$\nu_5 (a'')$
ca. 1501	w	$(405) + 1104 = 1509 (A')$
		$(+ \text{impurity?})$
ca. 1654	w	$542 + 1104 = 1646 (A')$
ca. 1730	vw	$627 + 1104 = 1731 (A')$
1806	w	$542 + 1264 = 1806 (A'')$
1814		
ca. 1884	vw	$627 + 1264 = 1891 (A'')$
2194		P
2209	m	Q
2218		R
ca. 2351	m	$2 \times 1104 = 2208 (A')$
2518		P
2530	w	Q
2541		R
		$2 \times 1264 = 2528 (A')$

Table 1 gives frequencies, intensities and interpretation of the bands. The spectrometer was calibrated with polystyrene, water, carbon dioxide and silicon tetrafluoride bands.

DISCUSSION

Chloryl fluoride molecule should be a slightly deformed trigonal pyramid with the free electron pair of chlorine placed at its apex and fluorine and oxygen atoms at the other corners. Such a molecule must belong to symmetry group C_s , and have six fundamental infrared active vibrations.

By comparison with thionyl fluoride molecule [8], the four symmetric vibrations (a') could be described as the F—Cl stretching and one of the Cl—O stretchings, an angular deformation and another one in which the OClO angle increases while the OClF' one decreases. The asymmetric vibrations (a'') would be the other Cl—O stretching and a deformation of the pyramid.

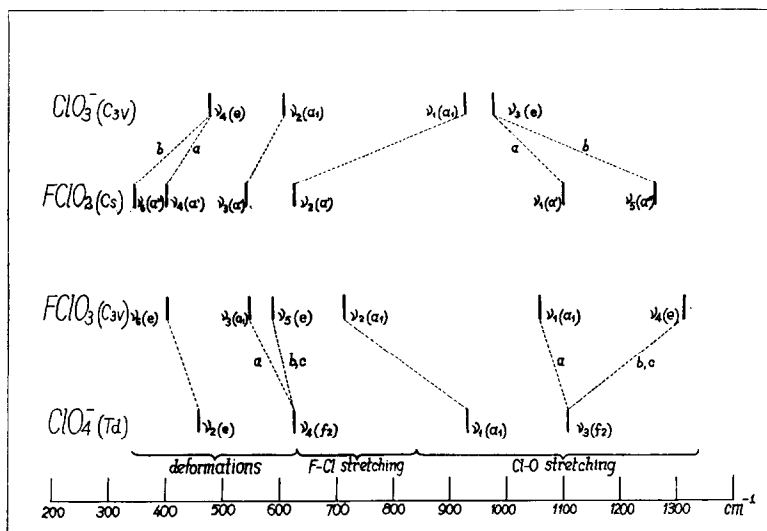


Fig. 3. Spectral correlations between FCLO_2 and related molecules.

Considering that masses, diameters and electronegativities of fluorine and oxygen atoms are little different, chloryl fluoride molecule could be taken as a nearly symmetric top which should originate parallel (a') and perpendicular (a'') bands in spite of some hybrid character.

In the region of the spectrum studied there are only four intense bands which could be assigned to fundamental vibrations due to their positions and intensities. They are located at 1265, 1104, 627 and 542 cm^{-1} . At least one of the other two fundamental bands would be beyond the region covered by the spectrometer, and the other one would be just where silicon tetrafluoride also strongly absorbs. Nevertheless it is possible to estimate the location of both bands through their supposed overtones and combinations.

The comparison of the spectrum of chloryl fluoride with spectra of perchloryl fluoride [9], fluorine perchlorate [10], chlorate and perchlorate ions [11] and even

[8] J. K. O'LOANE and M. K. WILSON, *J. Chem. Phys.* **23**, 1313 (1955).

[9] D. R. LIDE, JR. and D. E. MANN, *J. Chem. Phys.* **25**, 1128 (1956); R. P. MADDEN and W. S. BENEDICT, *Ibid.* **25**, 594 (1956); F. X. POWELL and E. R. LIPPINCOTT, *Ibid.* **32**, 1883 (1960); J. L. DUNLAP and E. A. JONES, *Spectroscopia Mol.* **9**, 32 (1960); *Chem. Abstr.* **54**, 13859b (1960).

[10] H. AGAHIGIAN, A. P. GRAY and P. D. WICKERS, *Can. J. Chem.* **40**, 157 (1962).

[11] E. L. WAGNER, *J. Chem. Phys.* **37**, 751 (1962).

with molecules such as thionyl fluoride [8] and phosphorus trifluoride [12] have been useful in the assignments of bands.

Cl—O stretching vibrations of chloryl fluoride could thus be assigned to the bands centered at 1265 and 1104 cm^{-1} . As it is shown in Fig. 3 both bands are originated in the splitting of the degenerate band $\nu_3(E)$ of chlorate ion (C_{3v}) when it is formally transformed into chloryl fluoride (C_s). By comparison with the above mentioned substances and with others containing also the Cl—O bond, such as chlorine dioxide [13], dichlorine heptoxide [14], perchloric acid [15] and chlorite ion [11], the band of higher frequency and intensity could be associated with the Cl—O asymmetric stretching (ν_5) and that of low frequency with the Cl—O symmetric stretching vibrations (ν_1).

Contours of both bands are very likely distorted by first overtones of ν_2 ($2 \times 627 \text{ cm}^{-1}$) and ν_3 ($2 \times 542 \text{ cm}^{-1}$) and also by weak bands due to impurities located in

Table 2. Average Cl—O stretching frequencies of some related molecules

Compound	Cl—O stret. freq.	Reference	Weighted average
ClO^-	713	[11]	713
ClO_2^-	844, 797	[11]	821
ClO_3^-	982(2), 930	[11]	965
ClO_2	1127, 965	[11]	1046
ClO_4^-	1110(3), 932	[11]	1065
FClO_2	1265, 1104	(This paper)	1184
Cl_2O_7	(1294, 1280?, 1272 1260, 1057, 1034	[14]	1199
HClO_4	1326, 1263, 1050	[15]	1213
FClO_4	1298(2), 1049	[10]	1215
FClO_3	1315(2), 1061	[9]	1230

the neighborhood. In spite of ν_5 not being clearly resolved, PQR branches of ν_1 are clear enough to substantiate the present classification.

As can be seen in Table 2, the mean frequency of Cl—O stretching vibration in chloryl fluoride is not far from those of other molecules containing the same bond. Figures are not all equal as predicts the Average Rule [16] but they show a trend which is explainable by an increasing amount of π bonding between chlorine and oxygen atoms [11]. Mean values for chloryl and perchloryl fluorides are higher than the ones of chlorine oxides and oxianions possibly due to a strong inductive effect of the fluorine atoms increasing the multiplicity of the Cl—O bond.

In both fluorine containing derivatives a higher number of oxygen atoms determines also on its part a stronger bond since the mean Cl—O stretching frequency in perchloryl fluoride is 46 cm^{-1} higher than in chloryl fluoride. The difference in bond strength is also reflected in the activation energies for the thermal decomposition of the fluorides in gaseous phase, a monomolecular reaction which in both

[12] M. K. WILSON and S. R. POLO, *J. Chem. Phys.* **20**, 1716 (1952).

[13] K. HEDBERG, *J. Chem. Phys.* **19**, 509 (1951).

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[15] P. A. GIGUÈRE and R. SAVOIE, *Can. J. Chem.* **40**, 495 (1962).

[16] W. J. LEHMANN, *J. Mol. Spectrosc.* **7**, 261 (1961).

cases apparently begins with the rupture of the Cl—O bond. The activation energy is 13 kcal/mol greater in perchloryl fluoride [17] than in chloryl fluoride [5].

The strong band located at 627 cm^{-1} has been assigned to the F—Cl stretching vibration (ν_2). Its complex envelope suggests the presence of the corresponding band of the isotopically related molecule $\text{FCl}^{37}\text{O}_2$. The distortion observed on the left side of the right branch could thus be due to the Q -branch of the band originated by the Cl^{37} species. Unless the Cl^{37} Q -branch would unlikely be the shoulder at ca. 625 cm^{-1} , the isotopic shift would be ca. 10 cm^{-1} such as in the perchloryl fluoride molecule.

The F—Cl stretching frequency would therefore be lower in chloryl fluoride (627 cm^{-1}) than in perchloryl fluoride (715 cm^{-1}) probably due to the above mentioned inductive effect of oxygen atoms. Likewise, in the following pairs of molecules the more oxygenated exhibits the larger X—F stretching frequency: (a) nitrosyl fluoride [18] and nitryl fluoride [19], (b) thionyl fluoride [8] and sulphuryl fluoride [20] and (c) phosphorus trifluoride [12] and phosphoryl fluoride [21].

The F—Cl stretching vibration (a') of chloryl fluoride molecule could be derived from the symmetric stretching of chlorate ion (a_1), located at 930 cm^{-1} . A comparable shift is produced in going from perchloryl fluoride (715 cm^{-1}) to perchlorate ion (932 cm^{-1}).

The fourth band which has been assigned as a fundamental is the strong one placed at 542 cm^{-1} showing at least three distinct branches. As this band would be originated by a symmetric deformation of the pyramid, it could be related to the band of chlorate ion observed at 610 cm^{-1} (ν_2). A similar deformation band is observed in perchloryl fluoride spectrum at 549 cm^{-1} (ν_3) which has to be related with the symmetric component (ν_{4a}) of the triple degenerated band of perchlorate ion (f_2) located at 626 cm^{-1} .

The shoulder on the low frequency side of the Q branch of this band could be due to the $\text{FCl}^{37}\text{O}_2$ molecule because according to the Teller—Redlich rule the separation between the Q branches of both species isotopically related could be ca. 2 cm^{-1} , if for the F—Cl band is accepted to be ca. 10 cm^{-1} .

To complete the set of fundamental bands expected for the chloryl fluoride molecule we are forced to estimate the position of the last two bands. One of them is probably located in the neighborhood of 400 cm^{-1} where silicon tetrafluoride strongly absorbs, interfering with the expected band, which should be of low intensity such as in thionyl fluoride and others. Hence its position could be estimated at 405 cm^{-1} because it would explain the bands at 810 cm^{-1} ($2 \times \nu_4$), ca. 1026 ($\nu_2 + \nu_4$) and 1501 ($\nu_1 + \nu_4$).

Finally, by exclusion the band at 698 cm^{-1} could be taken as the first overtone of a fundamental band which would be located at ca. 349 cm^{-1} . This band is useful to explain also the weak band at 910 cm^{-1} ($\nu_6 + \nu_3$). Pyramidal tetratomic molecules such as thionyl fluoride and phosphorus trifluoride have their deformation

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[19] R. E. DODD, J. A. ROLFE and L. A. WOODWARD, *Trans. Faraday Soc.* **52**, 145 (1956).

[20] W. D. PERKINS and M. K. WILSON, *J. Chem. Phys.* **20**, 1791 (1952).

[21] H. S. GUTOWSKY and A. D. LIEHRS, *J. Chem. Phys.* **20**, 1652 (1952).

bands of lowest energy at frequencies not very far from that postulated for ν_6 of chloryl fluoride.

The last two fundamental bands of chloryl fluoride could be related to the $\nu_4(e)$ band at 479 cm^{-1} of chlorate ion. The lower symmetry of chloryl fluoride molecule splits that band into a symmetric and an asymmetric one.

We are tentatively assigning the band which would be located at 405 cm^{-1} to the a' species and the one at ca. 349 cm^{-1} to the a'' species by comparison with the assignments made for thionyl fluoride molecule.

All other bands of medium and low intensity observed in the spectrum of chloryl fluoride could be reasonably assigned to overtones and combinations of bands taken as fundamentals. Shapes of many of them are somewhat distorted as could be seen in Fig. 1 due perhaps to interference of traces of impurities or atmospheric bands.

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