

Matrix Infrared Spectrum and Vibrational Analysis of the FClO Intermediate

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Abstract: Photolysis of argon matrix samples containing ClF and O₃ with 2200–3600-Å radiation produced new absorptions at 1038, 593, and 315 cm⁻¹ which were assigned to the new FClO intermediate species. Secondary reactions produced the known FClO₂ molecule. The observed chlorine and oxygen isotopic frequencies and band intensities identified isolated F–Cl and Cl–O stretching modes which defined the F–Cl–O structural arrangement.

Perchloryl fluoride, FClO₃, and chloryl fluoride, FClO₂, are well known chlorine oxyfluorides whose infrared spectra have been completely characterized.² However, the first intermediate in the oxidation of ClF to FClO₂ and FClO₃, namely FClO, has not heretofore been reported.

The analogous chlorine species, Cl–ClO, has been produced in matrix isolation experiments by mercury arc photolysis of Cl₂O and Cl₂–O₃ matrix samples^{3,4} and by 4880-Å laser photolysis of Cl₂O matrix samples.⁵ Infrared and Raman spectra of Cl–ClO indicated a weak Cl–Cl bond and a strong Cl–O bond.^{3,5} It is of interest to characterize the F–ClO species for spectroscopic, chemical bonding, and mechanistic reasons.

Here follows a detailed matrix isolation study of oxygen atom matrix reactions with ClF provided by *in situ* photolysis of O₃–ClF matrix samples.

Experimental Section

The cryogenic refrigeration system and vacuum vessel used at Virginia has been described earlier.⁶ Chlorine monofluoride and ozone samples diluted in argon were codeposited onto a 15°K CsI window from separate stainless steel manifolds. Chlorine monofluoride (Ozark-Mahoning) was used directly in a thoroughly passivated (ClF overnight) stainless steel vacuum system. Isotopic ozone samples, ¹⁶O₃, ^{16,18}O₃, ¹⁸O₃, were prepared by tesla coil discharge of O₂ gas (55% ¹⁸O, 99.5% ¹⁸O, Miles Laboratories) in a Pyrex finger immersed in liquid nitrogen. Ozone was outgassed and diluted with argon in a stainless steel vacuum system.⁷

In the experiments at Virginia, Ar:ClF = 50:1 and Ar:O₃ = 50:1 samples were codeposited for 14 hr at rates of just under 1 mmol/hr for the ClF sample and slightly more than 1 mmol/hr for the ozone sample. Samples were subjected to periods of mercury arc photolysis using a BH-6 high-pressure mercury arc (General Electric) focussed by a quartz lens system through a 5-cm saturated CoSO₄–NiSO₄ filter (passes 2200–3600 Å). Infrared spectra were recorded in the 200–1600-cm⁻¹ range during and after sample deposition on a Beckman IR-12 filter-grating spectrophotometer. Expanded scale scans at 8 cm⁻¹/min were recorded before, during, and after photolysis studies. Frequency accuracy was ±0.5 cm⁻¹.

The Texaco experiments employed a liquid helium cold cell which has been described previously.⁸ Approximately 14 mmol of each gas blend was deposited at 4°K over a 90-min period. Photolysis

light was directed through a 5-cm cell containing 100 g of NiSO₄/l. of H₂O and a 1-cm cell containing 100 g of cumene/l. of isooctane (passes 2750–3600 Å). Spectra were recorded on a Beckman IR-9 from 400 to 1600 cm⁻¹.

Results

A matrix sample of chlorine monofluoride (Ar/ClF = 50) was deposited at 15°K. The infrared spectra exhibited a complicated structure at 770–740 cm⁻¹ for ClF and weak bands near 1260, 1100, 620, and 530 cm⁻¹ for FClO₂ produced from the reaction of trace impurities with ClF. An expanded scale scan revealed sharp bands at 770.2 and 762.7 cm⁻¹ for ³⁵ClF and ³⁷ClF; weaker site splittings were noted at 767 and 760 cm⁻¹. A prominent feature at 749.8 cm⁻¹ displayed matrix site splittings at 753 and 756 cm⁻¹.

In krypton matrix experiments, the ClF doublet was observed at 763.6 and 756.5 cm⁻¹ with much weaker site splittings at 753.8 and 746.6 cm⁻¹ than in the present argon matrix experiments. Xenon matrix–ClF samples produced the sharp 3:1 doublet at 751.9 and 745.1 cm⁻¹ without any observable side bands or matrix splittings. These data suggest that the side band in argon and krypton matrices is due to ClF aggregates.

Matrix samples of chlorine monofluoride, Ar/ClF = 50, and ozone, Ar/O₃ = 50, were codeposited at 15°K for 14 hr. The initial spectrum showed the intense ν_3 band of O₃ at 1039.5 cm⁻¹ with weaker side bands at 1032 and 1026 cm⁻¹ and the 770- and 763-cm⁻¹ ClF bands with 754- and 756-cm⁻¹ side bands. Sample photolysis with 2200–3600-Å mercury arc radiation for periods totaling 25 min reduced the O₃ and ClF band intensities, destroyed the O₃ side band at 1026 cm⁻¹ and the ClF side bands at 754 and 756 cm⁻¹, and produced a number of new spectral features. Intense new bands at 1265, 1105, 621, and 545 with chlorine isotopic counterparts at 1252, 1098, 613, and 542 cm⁻¹ and weak new bands at 385 and 367 cm⁻¹ are due to FClO₂.^{2b} The 962- and 945-cm⁻¹ doublet (0.10 OD, optical density) of ClClO and the 823-cm⁻¹ band (0.02 OD) of OF₂ were observed^{3,5,8} along with a new chlorine isotopic doublet at 733.8 cm⁻¹ (0.30 OD) and 727.6 cm⁻¹ (0.10 OD). Of most interest, a new, very intense chlorine isotopic doublet was observed at 593.5 and 588.0 cm⁻¹ (completely absorbing) and a sharp band at 315.0 cm⁻¹ (0.20 OD).

Experiments were performed at 4°K with ClF and ozone isotopic samples of natural 0.2, 67, 80, and 99.5% oxygen-18 enrichment. Photolysis with 2750–3600-Å

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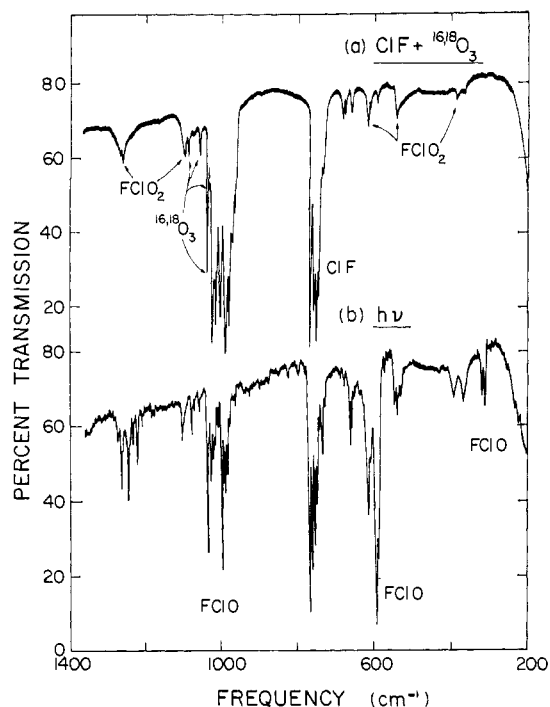


Figure 1. Infrared spectra, 200–1400 cm^{-1} , of a matrix sample codeposited at 15°K from separate Ar/ClF = 50 and Ar/ $^{16,18}\text{O}_3$ = 50 (55% oxygen-18) mixtures: (a) 14-hr sample deposition; (b) same sample after 2200–3600-Å photolysis for 40 min.

light produced a doublet at 593 and 587 cm^{-1} (0.40 OD) with $^{16}\text{O}_3$ which shifted to 592 and 586 cm^{-1} (0.40 OD) with $^{18}\text{O}_3$ while ozone and ClF side bands were destroyed. In the 67 and 80% oxygen-18 ozone samples, new bands appeared after photolysis at 997 and 988 cm^{-1} within the isotopic ozone ν_3 bands. The 99.5% oxygen-18 enriched ozone experiment removed interference from oxygen-16 containing isotopic ozones and these bands were clearly observed as a doublet at 997.7 and 988.3 cm^{-1} .

In order to observe the oxygen-16 isotopic counterpart of the new 998- cm^{-1} feature, which is predicted at 1038 cm^{-1} , the $^{16}\text{O}_3$ isotope, which absorbs strongly at 1038–1040 cm^{-1} , must be kept to a minimum, and ozone must be destroyed by photolysis. Accordingly, an experiment was conducted with ClF and 55% oxygen-18 enriched ozone; samples were deposited slowly at 15°K for 14 hr. Figure 1 illustrates the 200–1400- cm^{-1} spectrum before and after 2200–3600-Å photolysis, which is sufficient to photodecompose ozone. The initial spectrum shows the intense ν_3 multiplet of the six isotopic ozone species, weak bands at 1091 and 1061 cm^{-1} due to ν_1 of the 16–16–18 and 18–18–16 isotopes and the ν_2 bands at 682 and 688 cm^{-1} of these same isotopic species.⁷ The intense ClF doublet with side bands is evident. Weak bands due to CO_2 at 664 cm^{-1} and FClO_2 at 1265, 1105, 621, 546, and 385 cm^{-1} are present, along with a trace (0.03 OD) of the new 593- cm^{-1} band produced by precursor reaction, ozone decomposition, or Nernst glower photolysis. The mercury arc photolysis was conducted in six stages, which are defined in Table I; expanded scale spectra were recorded after each photolysis. Intensities of the new absorptions are listed in Table I following each photolysis; photometric accuracy for comparison of band intensities is limited by the great intensity of the 593-

Table I. Absorptions (cm^{-1}) Produced by Mercury Arc Photolysis of a 15°K Matrix Sample Codeposited from Separate Ar/ClF = 50 and Ar/ $^{16,18}\text{O}_3$ = 50 Mixtures (55% Oxygen-18)

Photolysis ^a	Absorptions produced by photolysis ^b							
	593	587	1038	1029	999	990	315	307
Background	0.03							
(1) 20 min A	0.15	0.05	<i>c</i>		0.15			
(2) 1 min B	0.50	0.17	0.40		0.40		0.03	0.03
(3) 2 min B	1.2	0.40	0.55	<i>c</i>	0.55	<i>c</i>	0.06	0.06
(4) 20 min B	1.5	0.50	0.58	0.20	0.65	0.25	0.08	0.08
(5) 17 min B	1.5	0.55	0.60	0.20	0.64	0.25	0.09	0.09
(6) 10 min C	0.70	0.30	0.30	0.10	0.32	0.13	0.05	0.05

^a Filters: A, Pyrex plus saturated NiSO_4 , CoSO_4 aqueous solution, transmits (2900–3600 Å); B, saturated NiSO_4 , CoSO_4 , transmits (2200–3600 Å); C, water, transmits (2200–10,000 Å). ^b Intensity in optical density units. ^c Observed as shoulder on isotopic ozone band.

cm^{-1} feature and the overlapping of O_3 bands with the 1038- and 999- cm^{-1} absorptions. Photolysis 1 produced the 593- and 588- cm^{-1} doublet and the 999- cm^{-1} feature which falls between the isotopic ozone ν_3 bands; the 1038- cm^{-1} feature was present as a shoulder on the 1039.6- cm^{-1} ν_3 $^{16}\text{O}_3$ band. Photodecomposition of ozone in photolysis 2 was evidenced by pronounced growth of the bands of interest listed in Table I with only 1 min of irradiation; the 1039.6- cm^{-1} ozone band and the new 1038.0- cm^{-1} feature appeared as a partially resolved doublet. Photolysis 3 produced growth of the 1038- and 999- cm^{-1} bands, destruction of the isotopic ozone bands, and the appearance of shoulders at 1029 and 990 cm^{-1} and weak new bands at 315 and 307 cm^{-1} . Irradiations 4 and 5 produced little growth in the new bands of interest, but more importantly, considerable ozone photodecomposition was effected. It appears that a steady state was reached in the maximum yield of a new photolysis product with a minimum of ozone remaining; trace b of Figure 1 shows the entire spectrum. Note the triplet bands at 1265, 1248, and 1224 cm^{-1} (with chlorine isotopic splittings at 1252, 1235, and 1211 cm^{-1}), 1106, 1081, and 1061 cm^{-1} , and 546, 539, and 529 cm^{-1} and an unresolved band at 616 cm^{-1} indicating two equivalent oxygen atoms and a single chlorine atom for FClO_2 . Also present are the 385- and 367- cm^{-1} FClO_2 bands. The new 734- and 728- cm^{-1} doublet showed no measurable oxygen isotopic shift.

Figure 2 illustrates expanded scale scans of the new bands of interest, which are required to do justice to the spectrum. Two sharp doublets appeared at 1038.0 and 1029.0 and 999.2 and 990.1 cm^{-1} in place of the photolyzed isotopic ozone bands, traces of which still remain. The intense doublet at 593.5 and 587.5 cm^{-1} is clearly resolved as is the weaker doublet at 315.2 and 307.0 cm^{-1} . Table I shows that the new bands were halved by the complete visible photolysis, indicating a photosensitive nature for the new species.

Discussion

We are interested in the identification, structure, and vibrational analysis of the new molecular species observed here.

FClO Identification. The new isotopic absorptions reported in Table I grew together with irradiation capable of photolyzing ozone; they decreased in unison when exposed to visible photolysis. Hence, we conclude that the Table I bands are due to isotopic absorptions of a single new molecular species.

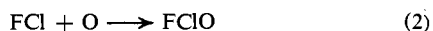
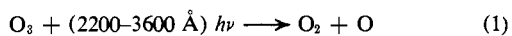
The pair of doublets, shown at the left of Figure 2, exhibited chlorine and oxygen isotopic shifts appropriate for an isolated Cl-O stretching mode; the band intensities are consistent with the single chlorine-single oxygen atom stoichiometry. The chlorine isotopic frequency ratios $1029.0:1038.0 = 0.9913$ and $990.1:999.2 = 0.9909$ are in excellent agreement with the calculated values, 0.9915 and 0.9908, respectively. Likewise, the oxygen isotopic frequency ratios $999.2:1038.0 = 0.9626$ and $990.1:1029.0 = 0.9622$ are in excellent agreement with the calculated ratios, 0.9610 and 0.9604, respectively, with the expected small anharmonic difference.

The intense 593.5- and 587.5- cm^{-1} doublet exhibits the 3:1 intensity ratio expected for a single chlorine atom vibration. The frequency ratio, $587.5:593.5 = 0.9899$, is in excellent agreement with the value calculated for an isolated F-Cl vibrational mode, 0.9904. The observation of a 1- cm^{-1} shift in this intense doublet when $^{16}\text{O}_3$ was replaced by $^{18}\text{O}_3$ indicates the incorporation of oxygen in the molecule and the lack of major participation of oxygen in the mode responsible for the 593- cm^{-1} absorption.

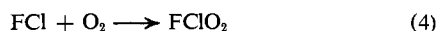
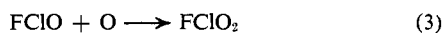
The sharp doublet at 315.2 and 307.0 cm^{-1} on the right side of Figure 2 clearly arises from a vibrational motion of a single oxygen atom species. Chlorine isotopic splittings within this band were not resolved.

The 1038- cm^{-1} band is assigned to ν_1 , the Cl-O mode, of the FCIO intermediate species. The 593- cm^{-1} absorption is assigned to ν_2 , the F-Cl stretch, and the 315- cm^{-1} band is attributed to ν_3 , the F-Cl-O bending mode. The isotopic shifts identify F-Cl and Cl-O bond stretching modes which indicate the structural arrangement F-Cl-O.

There is evidence for the photolysis of the ozone side band at 1026 cm^{-1} and the 754, 756 cm^{-1} ClF side bands with 2900-3600-Å radiation, which does not photolyze ozone. This suggests that a complex species $\text{FCl}\cdots\text{O}_3$ may exist which photolyzes to give FCIO and O_2 . However, Table I shows that the major yield of the FCIO species required ozone photolyzing radiation. The reaction sequence 1 and 2 is therefore primarily



responsible for the production of FCIO. The oxygen atom diffused from the site of its photoproduction and reacted with FCl. There is no evidence for insertion forming the isomeric F-O-Cl species. If F-O-Cl could be formed, it probably would photoisomerize to F-Cl-O, based on the photolysis behavior of Cl-O-Cl.^{3,5} The growth of triplet bands due to $\text{FCl}^{16,18}\text{O}_2$ in Figure 1 indicates that reaction 3, or perhaps reaction 4, is responsible for FCIO_2 production in the 15°K



experiments. It is perhaps noteworthy that no FCIO_2 was observed in the 4°K experiments. No FCIO_3 was detected in any of these experiments.

The new chlorine isotopic doublet at 733.8 and 727.6 cm^{-1} exhibits a 3:1 intensity ratio appropriate for a molecular species containing a single chlorine atom. The vibrational mode does not involve oxygen since no measurable oxygen isotopic shift was observed. This

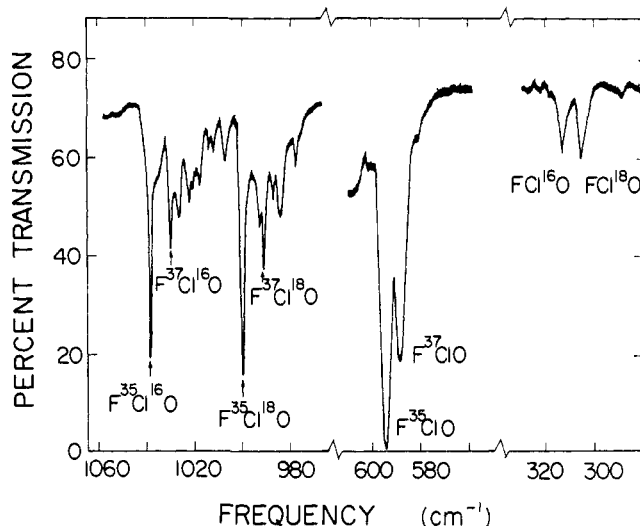
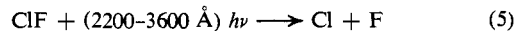
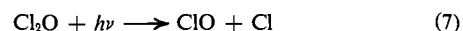


Figure 2. Expanded scale infrared spectra of the FCIO fundamentals using natural isotopic FCl and 55% oxygen-18 enriched ozone as reagents.

doublet was observed along with another band at 611 cm^{-1} following photolysis of $\text{F}_2/\text{Cl}_2/\text{O}/\text{Ar}$ samples at 4°K; the bands were not observed in photolyzed $\text{F}_2/\text{Cl}_2/\text{Ar}$ samples.⁹ The most intense absorption of the ClF_2 free radical¹⁰ has been reported at 578 cm^{-1} . The most likely assignment for the 733- and 727- cm^{-1} doublet consistent with the two above synthetic routes is the species F_2ClO . Its synthesis could arise from



in the ClF/O_3 studies or from



in the $\text{F}_2/\text{Cl}_2/\text{O}$ photolysis experiments.⁹ The 733- and 727- cm^{-1} doublet is tentatively assigned to the anti-symmetric F-Cl stretching mode of the intermediate species F_2ClO . The F_3ClO molecule has been studied very recently; the antisymmetric F-Cl stretching mode was observed at 652 cm^{-1} in solid nitrogen,¹¹ lending some support to the above tentative identification of F_2ClO .

Vibrational Analysis of FCIO

A normal coordinate analysis was performed for FCIO using the 12 isotopic frequencies given in Table II. The calculations utilized the Wilson FG matrix method¹² and the Schachtschneider Programs GMAT and FADJ. Bond distances, F-Cl = 1.80 Å and Cl-O = 1.57 Å, were estimated from bond length-force constant relationships¹³ based on preliminary force constant estimates. A F-Cl-O bond angle of 120° was used in the calculations; small changes ($\pm 20^\circ$) in this estimate will have little effect on the calculations.

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Table II. Observed and Calculated Frequencies (cm^{-1}) for the FCIO Species^a

Isotope	Assignment	Obsd	Calcd ^b
F ³⁵ Cl ¹⁶ O	ν_1	1038.0	1038.3
	ν_2	593.5	593.9
	ν_3	315.2	316.0
F ³⁷ Cl ¹⁶ O	ν_1	1029.0	1028.9
	ν_2	587.5	588.4
	ν_3	315.2	313.8
F ³⁵ Cl ¹⁸ O	ν_1	999.2	999.5
	ν_2	593.5	592.6
	ν_3	307.0	308.3
F ³⁷ Cl ¹⁸ O	ν_1	990.1	989.6
	ν_2	587.5	587.1
	ν_3	307.0	306.2

Potential function ^c	Potential energy distribution ^d		
	ν_1	ν_2	ν_3
$F_{\text{Cl-O}} = 6.85 \text{ mdyn/\AA}$	97.8 ^e	1.5	0.6
$F_{\text{Cl-F}} = 2.59 \text{ mdyn/\AA}$	1.9	94.6	3.6
$F_{\text{F-Cl-O}} = 0.92 \text{ (mdyn \AA)/rad}^2$	0.3	3.9	95.8

^a Vibrational potential function and potential energy distribution.

^b Average difference between calculated and observed frequencies, $\Delta\nu = 0.7 \text{ cm}^{-1}$. ^c Interaction force constants held at zero. ^d For F³⁵Cl¹⁸O isotope. ^e Interpretation: ν_1 is 97.8% Cl-O bond stretching in character.

Several calculations were performed with various combinations of interaction force constants in addition to the principal force constants. The simplest potential function, with zero off-diagonal force constant values, produced very good agreement between calculated and observed frequencies. The force constants are listed in Table II, where the calculated and observed frequencies are compared.

The potential energy distribution listed in Table II indicates that each FCIO fundamental frequency depends primarily upon a single diagonal force constant. The three FCIO modes are well described by the internal coordinates, FCl and ClO bond stretching, and FCIO valence angle bending.

The ClO force constant for FCIO (6.85 mdyn/\AA) is higher than the ClO force constants in ClClO (5.94 mdyn/\AA)⁵ and the ClO radical (4.66 mdyn/\AA)⁵. The F-Cl force constant for FCIO (2.59 mdyn/\AA) is smaller

than the value for ClF (770 cm^{-1} , 4.29 mdyn/\AA). The F-Cl-O bending force constant ($0.92 \text{ (mdyn \AA)/rad}^2$) is higher than the ClClO bending force constant ($0.78 \text{ (mdyn \AA)/rad}^2$)⁵.

Bonding in FCIO

The intermediate species FCIO is analogous to the chlorine species ClClO. The F-Cl bond in FCIO is weaker than the FCl diatomic bond, whereas the ClO bond in FCIO is stronger than the ClO diatomic bond.

The Spratley-Pimentel ($p-\pi^*$) bonding picture¹⁴ for F-NO and Cl-NO is satisfactory for the F-ClO and Cl-ClO species with the very important difference that the lower electronegativity of ClO relative to F, as compared to the electronegativity of NO relative to F, requires that antibonding electron density be removed from ClO by F since the Cl-O frequency is increased upon the bonding of an F atom to ClO. The opposite charge transfer occurs for F-NO; the NO frequency is lowered upon bonding of F to NO.

Conclusion

Photolysis of argon matrix samples containing ClF and O₃ with 2200-3600-Å mercury arc radiation produced the new intermediate species FCIO from oxygen atom matrix reactions with ClF. Secondary reactions yielded the known FCIO₂ species. The isotopic frequencies and intensities identified isolated F-Cl and Cl-O stretching modes which defined the F-Cl-O structural arrangement. The Cl-O frequency in FCIO is higher than the ClO free radical fundamental, which suggests that the more electronegative F atom removes antibonding electron density from the less electronegative ClO species.

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