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# Atmospheric Cryochemistry: Oxygen Atom Reaction with the Fluorocarbon Freon 11 in Matrices. FTIR Spectra of Isolated COFCI and COFCI:Cl<sub>2</sub> Complex in Solid Argon

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Fourier transform infrared spectroscopy has been employed to investigate the reaction of CFCl<sub>3</sub> (Freon 11) with atomic oxygen in argon and oxygen matrices at 12 K. Ozone was employed as a photolytic oxygen atom source. The results indicate that the only primary reaction product is COFCI when the oxygen atom is in an excited state. No intermediate was observed. Upon thermal annealing after photolysis, diffusion through the matrix leads to the efficient formation of COFCI:Cl<sub>2</sub> aggregates. The spectra obtained after irradiation in various experimental series (isotopic ozone, wavelength dependence, product growth curves) are analyzed and have been interpreted from vibrational spectra of normal and isotopically substituted COFCl isolated in argon and from vibrational spectra of their molecular complexes with Cl<sub>2</sub> embedded in argon. Fermi resonance doublets in the  $\nu_{C=0}$  stretching region are observed mainly for the C<sup>18</sup>OFCl species and the C<sup>16</sup>OFCl-Cl<sub>2</sub> complex.

#### Introduction

The fluorocarbons F-11 (CCl<sub>3</sub>F) and F-12 (CCl<sub>2</sub>F<sub>2</sub>) are the two most abundant species of the anthropogenically produced halocarbons in the atmosphere.<sup>1</sup> Both species may influence the equilibrium concentration of stratospheric ozone<sup>2</sup> and the radiative budget of the earth.<sup>3,4</sup> There has been speculation about oxidation of halogenated compounds in the troposphere that can remove the halocarbons before they can reach the stratosphere. The fluorocarbons are considered inert, but since their lifetime is very long,<sup>5</sup> a combination of many very slow processes can have a significant effect on the global budgets and hence on reducing the potential of these compounds for destroying the stratospheric ozone. In the present work, the matrix-isolation technique has been used in conjunction with FTIR spectroscopy to identify the products for the photolysis of ozone in the presence of CFCl<sub>3</sub>. In the troposphere ( $\lambda > 290$  nm), ozone production occurs either via the photodissociation of NO<sub>2</sub> into NO and O followed by the recombination of O with  $O_2^{6,7}$  or via carbon monoxide and hydrocarbon oxidation with  $NO_x$  species (NO + NO<sub>2</sub>) acting as a catalyst.<sup>8</sup> The reaction presently studied in a matrix between CFCl<sub>3</sub> and atomic oxygen differs from that known in the stratosphere where CFCl<sub>3</sub> is photolyzed by short-wavelength ultraviolet radiation and then can be removed by reaction with O(1D) according to eq 1 in a first step.<sup>9</sup>

$$CF_{x}Cl_{\nu} + h\nu(O^{1}D) \rightarrow CF_{x}Cl_{\nu-1} + ClO$$
(1)

The irradiation domain used in our experiments for inducing in situ the O<sub>3</sub> photodissociation cannot release the chlorine atom from UV photolysis of CFCl<sub>3</sub>.

#### **Experimental Section**

The studies were conducted using a closed-cycle helium refrigerator (Air Products Model 202A). Modification of the device allowed us to place the matrix sample in the beam path of the spectrophotometer through a CsI window or situate in the perpendicular direction the matrix sample in front of the photolysis source through a quartz window. Mixtures of CFCl<sub>3</sub>/Ar (typically M/R = 1/500 and ozone/argon (typically M/R = 1/200) were deposited from separate inlets onto a gold mirror cooled at 12 K. Deposition time and rate were approximately 1 h and 5 mmol·h<sup>-1</sup>, respectively. Infrared spectra were recorded by reflection after deposition and also after each photolysis on a Bruker IRF 113V in the 4000–400-cm<sup>-1</sup> spectral region, at a resolution of 0.5 cm<sup>-1</sup> (200 scans) with a frequency accuracy of  $\pm 0.1$  cm<sup>-1</sup>.

Samples were irradiated with a 90-W medium-pressure mercury lamp (Philips 93136) in combination with Schott and 10-cm water filters which exposed the samples to the following wavelength ranges: 330-800, 260-800, and full arc 240-800 nm.

CFCl<sub>3</sub> (from Merck Schurhardt) were degassed by freeze-thaw cycles and pumping at 77 K before matrix samples were prepared. Ozone was synthesized by Tesla coil discharge of O<sub>2</sub> gas in a Pyrex finger immersed in liquid nitrogen. Diluted ozone samples were immediately used. Argon and oxygen were commercially obtained with a purity of greater than 99% and also used without further purification. The <sup>18</sup>O content of the enriched oxygen obtained from CEA was 50%. COFCI was prepared from a gas mixture of CFCl<sub>3</sub> and ozone in a quartz bulb which was irradiated by the medium-pressure mercury lamp for 12 h. Oxygen was removed by vacuum pumping at 77 K, and then COFCl was vacuum distillated several times at 190 K.



Figure 1. Overall FTIR spectrum of  $CFCl_3-O_3$  in argon at 10 K ( $CFCl_3/O_3/Ar = 1/3/800$ ): (a) before irradiation and after deposition; (b) after 17 h of irradiation with an unfiltered medium-pressure mercury lame.

## Results

Before the reaction products of CFCl<sub>3</sub> with atomic oxygen generated by  $O_3$  photolysis in situ were investigated, three different types of experiments were performed: (i) the first set consisted of blank experiments conducted on both reagents alone in argon; (ii) the second set examined the IR spectra of the possible products of the codeposition of CFCl<sub>3</sub>/Ar samples with the O<sub>3</sub>/Ar sample; (iii) the third set was devoted to the investigation of products resulting from the thermal reaction between O<sub>3</sub> and CFCl<sub>3</sub> premixed in the same bulb in argon.

(i) Several studies have been devoted to the spectra of natural ozone in the gas phase<sup>10,11</sup> and argon matrix;<sup>12-14</sup> our spectra were consistent with the earlier measurements. The infrared strengths of the three vibrational bands of CFCl<sub>3</sub> in "the atmospheric window" between 8 and 16  $\mu$ m have been measured in the gas phase at 296 K.<sup>15</sup> In matrices (argon), CFCl<sub>3</sub> spectra with natural isopotomers (C<sup>35</sup>Cl<sub>3</sub>F 42.87%, C<sup>35</sup>Cl<sub>2</sub><sup>37</sup>ClF 41.96%, C<sup>35</sup>Cl<sup>37</sup>Cl<sub>2</sub>F 13.69%, C<sup>37</sup>Cl<sub>3</sub>F 1.49%) have been studied in great detail in the 1300–500-cm<sup>-1</sup> region by King.<sup>16</sup> The bands observed in this work were in good agreement with those previously reported. An additional spectrum of CFCl<sub>3</sub> with oxygen in argon (CFCl<sub>3</sub>/O<sub>2</sub>/Ar = 1/3/800) was also recorded and then irradiated in situ for 20 h with the medium-pressure mercury lamp. The resultant spectrum was virtually identical with that obtained before irradiation and with that of the CFCl<sub>3</sub>/Ar sample.

(ii) When CFCl<sub>3</sub> (CFCl<sub>3</sub>/Ar 1/2000) was codeposited with O<sub>3</sub> (O<sub>3</sub>/Ar 1/150), no new bands were observed in the  $\nu_{CF}$  and  $\nu_{CCl}$  stretching regions, showing no evidence for interaction between CFCl<sub>3</sub> and O<sub>3</sub>.

(iii) As expected, the spectrum of a premixed  $CFCl_3/O_3$  mixture showed only the infrared absorption of  $O_3$  and  $CFCl_3$ . Evidence for any thermal reaction products was absent.

(1) Product Absorptions after Full Irradiation.  $CFCl_3/^{16}O_3/Ar$ . Matrices containing  $CFCl_3/^{16}O_3/Ar$  in the ratio of 1/2/800 were photolyzed with the full light of the mercury lamp for several hours. Analysis of the sample after 15 h of irradiation time revealed a depletion of the  $CFCl_3$  concentration of 20% and growth of a number of new absorptions. Figure 1 shows a survey spectrum in the range 2000-500 cm<sup>-1</sup>, while Figure 2 shows the key spectral ranges of 1900-1700, 1150-1000, and 800-700 cm<sup>-1</sup> at different times. The frequencies and relative intensities of the absorptions which appeared on photolysis of the sample are summarized in the first column of Table I.

The major product bands were three doublets at 1865.2–1862.5, 1083.2–1081.7, (which appeared between the  $\nu_5 + \nu_6$  bands of the CFCl<sub>3</sub> parent molecule), and 761.9–759.7 cm<sup>-1</sup>. Several other weaker bands were also observed in the same region: the  $\nu_{CO}$  region (1838.1, 1832.7, and 1828.1 cm<sup>-1</sup>), the  $\nu_{CF}$  region (1100.6, 1098.3, 1094.9, and 1074.7 cm<sup>-1</sup>), and the  $\nu_{CCI}$  region (768.5 cm<sup>-1</sup>) with additional features at 848.4, 847.1, and 840.4 cm<sup>-1</sup> in shouldering of the  $\nu_{CCI}$  region of CFCl<sub>3</sub> and at 666.3 cm<sup>-1</sup>. Examination of major product intensity vs photolysis time indicated



Figure 2. Evolution of the spectrum of a  $CFCl_3/O_3/Ar$  sample (1/3/800) with the time of irradiation (medium-pressure mercury lamp) in the 1875–1820-, 1110–1070-, and 775–750-cm<sup>-1</sup> spectral regions. Irradiation time: (a) 0, (b) 3.5 h, (c) 9 h, (d) 17 h.

TABLE I: Vibrational Frequencies  $(cm^{-1})$  and Intensities of Product Absorptions That Appear upon Medium-Pressure Mercury Lamp Photolysis of the CFCl<sub>3</sub>/O<sub>3</sub>/Ar Mixture  $(1/2/800)^a$ 

$CFCl_3 + {}^{16}O_3{}^b$					
before annealing		after annealing		$CFCl_3 + {}^{16-18}O_3{}^c$ before annealing	
ν	OD		OD	ν	assignment
1869.0	sh	d		1813.6	
1867.8	sh	d			
1865.8	sh		0.05	1810.9	
1865.2	0.47	d	vvw	1809.7	FClCOAr $(\nu_2)$
1863.2	VVW	i	0.27		$FClCO···Cl_2(\nu_1 + \nu_4)$
1862.5	0.27	d	vvw		FClCO····Cl $(\nu_2)$
1841.5	sh	1	sh		
1840.0	sh	1	0.51	1806.4	
1838.9	sh	1	sh		$FClCO···Cl_2(\nu_2)$
1838.1	0.125	1	0.3	1805.0	
1835.7	sh	1	sh		
1832./	0.04	a		1000.0	
1830.9	0.007	a		1830.0	FCICO $(v_1 + v_4)$
1828.1	0.01	0 1222		1828./	
		1332	w		$FCICO····Cl_2(2\nu_6)$
1100 4	0.045	: 1105	0.05		
1000.0	0.045	1	0.10		$\Gamma(U_{2})_{H}(\nu_{4})$
1096.5	0.05	1006.2	0.50		
1004 0	0.12	1090.2	03	1002.0	$\mathbf{FC}(\mathbf{C}) = \mathbf{C}(\mathbf{u})$
1074.5	0.12	1093.0	0.5	1092.9	$\Gamma C C C C C L_2 (\nu_4)$
		1003.8			
1083.2	0.10	d			
1081 7	0.17	ă		1078.1	FC)CO (".)
1074.7	sh	đ		10/011	10100 (14)
848.4	sh	đ			
847.1	sh	-	sh		not identified
840.4	sh		sh		
768.5	0.01	i		754.2	
766.9	vw	i	0.11	753.4	$FC[CO-C]_{2}(y_{1})$
764.9	vw	i		751.2	
762.7	sh	d		748.6	
761.9	0.10	d	0.02	747.8	FCICO $(v_1)$
760.5	sh	d		746.5	
759.7	0.06	d	0.01	745.8	
666.3	vvw	i	0.06		$FClCO-Cl_2(v_6)$
659.9	vvw	d			FClCO (v <sub>6</sub> )

 $^{a}$ i = increase, d = decrease or disappear, sh = shoulder, vvw = very very weak.  $^{b}$  Photolysis time: 16 h.  $^{c}$  Photolysis time: 4 h. The new bands are only reported.

three distinct growth behaviors as illustrated in Figure 3 for the 1865.2-, 1862.5-, and 1838.1-cm<sup>-1</sup> bands. The product band at 1862.5 cm<sup>-1</sup> grows rapidly and approaches a constant value after nearly all the ozone is depleted. In contrast, the 1865.2-cm<sup>-1</sup> band has a sigmoidal contour with non-zero slope at short times and continues to increase after ozone depletion. The 1838.1-cm<sup>-1</sup> band also has sigmoidal character at short times but grows to a constant value (at a long time like the 1862.5-cm<sup>-1</sup> feature). The 759.7-cm<sup>-1</sup> band grew in concert with the 1862.2-cm<sup>-1</sup> band, whereas the 761.9-cm<sup>-1</sup> line grew in concert with the 1865.2-cm<sup>-1</sup> band, showing respectively their properties at the same product. The overlapping of the 1083.2–1081.7-cm<sup>-1</sup> features with the parent molecule absorptions prevented meaningful measurements of their



Figure 3. Product growth curves in the C=O stretching region,  $(1880-1800 \text{ cm}^{-1})$  during photolysis with the medium-pressure mercury lamp (CFCl<sub>3</sub>/O<sub>3</sub>/Ar 1/3/800). For comparison, the ozone decay curve is indicated by the dotted line.



Figure 4. Infrared spectrum of (a) a sample of  $CFCl_3/^{16-18}O_3/Ar = 1/4/4000$  and (b) a sample of  $CFCl_3/^{16-18}O_3/Ar = 1/2/1000$  in the 1870–1800- and 780–700-cm<sup>-1</sup> regions after irradiation at 12 K with the medium-pressure mercury lamp. Irradiation time: (a) 3.5 h (b) 3 h.

optical densities. Experimental curves relative to the 1862.5- and 1838.1-cm<sup>-1</sup> growth were well fitted by the first-order relationship  $A_{\infty}(1 - e^{-kt})$ , where the quantity  $A_{\infty}$  is the optical density of the asymptotic limit of the curves. In a given experiment, the relative rate coefficient k was found to be similar (2.5 × 10<sup>-3</sup> mn<sup>-1</sup>) to the rate coefficient of the ozone depletion.

CFCl<sub>3</sub>/<sup>18</sup>O<sub>3</sub>, <sup>16</sup>O<sub>3</sub>/Ar. Isotopic ozone substitution was carried out to help in the identification of the photoproducts. The <sup>18</sup>O composition was 50% 18-enriched ozone. As illustrated in Figure 4b, notable behavior was displayed by the bands in the  $\nu_{C=0}$  region. It appeared as a triplet absorption, one corresponding to pure <sup>16</sup>O<sub>3</sub> and two weaker structured others having nearly the same intensity. In the 750-cm<sup>-1</sup> region, the 763-760-cm<sup>-1</sup> features were resolved into a doublet of equal intensity but with a surprisingly strong shift for an expected C-Cl mode. Bands at 1083 cm<sup>-1</sup> were slightly shifted, and features at 848.4, 847.1, and 840.4 cm<sup>-1</sup> were not sensitive to <sup>18</sup>O, indicating that they cannot be assigned to the ClO radical.<sup>17</sup> Other experiments performed with weaker concentrations of the parent molecules (CFCl<sub>3</sub>/O<sub>3</sub>/Ar 1/4/4000) showed the same behavior (Figure 4a). The triplet absorption observed in the 1850-cm<sup>-1</sup> region could suggest the existence of some products containing two equivalent oxygen atoms. However, the location of the multiplet and the relative intensities of its components (2/1/1) are not in agreement with this assumption for which relative intensities of components are expected of 1/2/1. This anomalous behavior can be explained by Fermi resonances as discussed later.

(2) Wavelength-Dependent Photolysis. A series of experiments involving in situ photolysis of  $CFCl_3/O_3/Ar$  matrix samples were performed at the following wavelengths:  $\lambda > 320$  nm and  $\lambda > 270$  nm. Formation of the previously described photoproduct bands was not observed upon irradiation above 320 nm. At this wavelength domain, the primary process is the production of  $O(^{3}P)$  and  $O_2$ .<sup>18</sup> Thus, as expected, atomic oxygen in the triplet P state is not sufficiently reactive. Irradiation performed in the 280-800-nm domain led to the same products previously observed with



Figure 5. Comparison of the photolyzed matrix spectrum (a) after irradiation at 12 K (medium-pressure mercury lamp) and (b) after annealing at 35 K and then recording at 12 K for samples of normal and isotopically substituted ozone. Bottom:  $CFCl_3/O_3/Ar = 1/3/800$ . Top:  $CFCl_3/^{16-18}O_3/Ar = 1/2/1000$  ( $^{18}O$  enrichment = 50%).

full irradiation but with a different yield distribution of the two components of the three doublets in the 1850-, 1080-, and 750-cm<sup>-1</sup> regions; the site distribution of the photoproducts bands was found to be independent of the amount of sample.

(3) Matrix Effect. One photolysis experiment was performed in an oxygen matrix. Photolysis in an oxygen matrix can allow identification of radical species from formation of new products obtained by reacting radicals with oxygen during the photolytic process. Irradiation of a CFCl<sub>3</sub>/O<sub>3</sub>/O<sub>2</sub> (1/3/1000) mixture with the medium-pressure mercury lamp led to the same photoproduct bands observed in the argon matrix with only a weak frequency shift (~1 cm<sup>-1</sup>) upon the higher component of the different doublets in the  $\nu_{C-O}$  and  $\nu_{C-Cl}$  regions. These results indicate that no radical species was isolated in the matrix cage after irradiation.

(4) Annealing of the Photolyzed Argon Matrix. Important changes were observed in the three key regions after warm up at 35 K of a photolyzed CFCl<sub>3</sub>/O<sub>3</sub>/Ar mixture. A first group of bands at 1869.0, 1867.8, 1865.2, 1862.5, 1832.7, 1828.1, 1083.2–1081.7, 1074.7, 761.9, and 759.7 cm<sup>-1</sup> strongly diminished, indicating that they may belong to the same species. On the contrary, a second group of weaker bands at 1863.2, 1838.9, 1100.6, 1094.9, 768.5, 766.9–764.9, 666.3 cm<sup>-1</sup> grew strongly with, in some cases, several components. Lastly, two new bands appeared at 1332 and 1105 cm<sup>-1</sup>, whereas shoulders at about 840 cm<sup>-1</sup> remained nearly unchanged. Typical spectra are displayed in Figure 5 for experiments with both natural and isotopic ozone. The observed effects are reported in column 2 of Table I.

### Discussion

If we take into account that the rigid matrix environment has the capacity to inhibit the separation of migration of photoproducts from their site, the previously described results suggest the formation of more than one photoproduct, with vibrational bands falling in the same region. However, when the photoprocess involves atom detachment, the atoms can escape their argon cage, 19,20 and some molecule group can likely be complexed to other products. In consequence, assignments are more difficult and separate studies of each assumed species are needed. In this way, we have undertaken studies of the vibrational spectra of C<sup>16</sup>OFCl and C<sup>18</sup>OFCl isolated in an argon matrix with, in addition, the vibrational identification of their complexes with the  $Cl_2$  molecule. From the results, we discuss the complexity of the spectrum obtained after irradiation of a CFCl<sub>3</sub>/O<sub>3</sub>/Ar mixture and the different behaviors observed with isotopic ozone and after annealing.

(1) Infrared Spectrum of C<sup>16</sup>OFCl and C<sup>18</sup>OFCl. Carbonyl chlorofluoride is an asymmetric rotor whose structure has been determined from an electron diffraction study<sup>21</sup> and microwave spectroscopy.<sup>22</sup> Since it has  $C_s$  symmetry, the symmetry coordinates transform as 5A' + A''. The fundamental frequencies

TABLE II: Frequencies (cm<sup>-1</sup>) of the Major Infrared Bands of C<sup>16</sup>OFCl and C<sup>16</sup>OFCl in the Gas Phase, CO<sub>2</sub> Matrix, and Argon Matrix<sup>a</sup>

mode	gas	CO <sub>2</sub> matrix <sup>b</sup>	Ar matrix <sup>c</sup>	C <sup>18</sup> OFCl Ar matrix <sup>c</sup>	
	776 <sup>d</sup>				
$v_1$ ( $v_{CCI}$ )	764.2 (Cl <sup>35</sup> )e	766.2	760.2 (0.2)	746.2 (0.19)	
	762.2 (Cl <sup>37</sup> )		758.3 (0.08)	744.15 (0.08)	
$v_2 (v_{C=0})$	1876	1858.2	1863.3 (0.88)	1807.2 (0.43)	
2 ( 0-0/			. ,	1806.5 (0.22)	
$\nu_1(\delta_s)$	501		497.0		
$\nu_4 (\nu_{C-F})$	1095	1088.0	1082.7 (1)	1080.1 (1)	
νς (δ.)	415		417.2		
			414.6		
$\nu_6(\gamma)$	667		661.1	657	
243	1004				
204	2182		2155.8	2150.3	
216	1327		1319.2	1318.4	
$v_1 + v_2$	2634		2622.9		
$\nu_1 + \nu_4$	1847		1830.1 (0.16)	1830.0 (0.43)	
			1827.8 (0.06)	1829.0 (0.18)	
$v_2 + v_4$	2958		2934.7		
$v_3 + v_6$	1165		1149.9		

<sup>a</sup>Relative intensities are indicated in parentheses. <sup>b</sup>Reference 25. <sup>c</sup>This work. <sup>d</sup>Reference 23. <sup>c</sup>Reference 22.

and a number of overtone and combination frequencies observed in the infrared spectrum of C<sup>16</sup>OFCl in the gas phase have been reported by Nielsen et al.<sup>23</sup> and Brown et al.<sup>24</sup> Very recently, Wilson et al. identified some infrared absorption features of matrix-isolated C<sup>16</sup>OFCl in CO<sub>2</sub> in order to measure the mixing ratio of COFCl near the tropopause.<sup>25</sup> No information about the spectrum of isotopic C<sup>18</sup>OFCl has been reported.

Representative spectra of C<sup>16</sup>OFCl in argon matrices (M/R = 1000) at 10 K are shown in Figure 6a. Table II summarizes the observed frequencies along with the gas-phase results and the values measured in a CO<sub>2</sub> matrix. Three sharp bands at 1863.3, 1830.1, and 1827.8 cm<sup>-1</sup> with a relative intensity ratio of 1/0.2/0.15 were observed in the  $\nu_{C=0}$  stretching region of the natural compound. These bands can be assigned as a weak Fermi resonance between the  $\nu_{C=0}$  band and the  $\nu_2 + \nu_{4^{35}Cl}$ - $^{37}Cl$  combination band. Such a resonance has been invoked to explain, in the gas phase, the observed close pair at 1876–1847 cm<sup>-1</sup> in the  $\nu_{CO}$  region. If the anharmonic terms are ignored, the approximate nonresonance frequency of the  $\nu_1 + \nu_4$  mode could be calculated as 1842 cm<sup>-1</sup>. Unfortunately, it was not possible to obtain the corresponding one for  $\nu_2$  because the overtone  $2\nu_2$  was not identified.

Two important observations can be made after the isotopic oxygen substitution in the carbonyl chlorofluoride when the ratio of the concentrations of  $C^{16}OFCl$  and  $C^{18}OFCl$  is close to 1:1 (Figure 6b):

(i) The two absorptions of equal intensity observed at 760.2 and 746.2 cm<sup>-1</sup> in the  $\nu_1$  region suggest a strong coupling between  $\nu_{CO}$  and  $\nu_{CCI}$  and could explain the observed splitting, 1807.2-1806.5 cm<sup>-1</sup>, of the  $\nu_{CIB}$  band.

(ii) In the  $\nu_{CO}$  region, the two bands at 1863.3 and 1807.2 cm<sup>-1</sup> centered on the pure  $\nu_{C^{16}O}$  and  $\nu_{C^{16}O}$  peak locations did not show the same intensity as expected; an enhancement of the intensity of the  $\nu_1 + \nu_4$  combination previously observed at 1830 cm<sup>-1</sup> in



Figure 6. FTIR spectrum of (a)  $C^{16}OFCl/Ar = 1/1000$  and (b)  $C^{16}O-FCl + C^{18}OFCl/Ar = 1/1000$  in the  $\nu_{C=0}$ ,  $\nu_{CF}$ , and  $\nu_{CCl}$  spectral regions.

the pure C<sup>16</sup>OFCl spectrum appeared, leading to a relative ratio at 1863/1830/1807 cm<sup>-1</sup> of 1/0.5/0.5. This behavior can be explained by a Fermi resonance between  $\nu_{C^{18}O}$  and the  $\nu_1 + \nu_4$ combination of C<sup>18</sup>OFCl calculated at 1826.3 cm<sup>-1</sup>; the two modes involved in the resonance are shifted, and the  $\nu_1 + \nu_4$  combination of C<sup>18</sup>OFCl falls at a frequency in coincidence with the frequency of the  $\nu_1 + \nu_4$  combination of C<sup>16</sup>OFCl.

(2) Identification of COFCI/Cl<sub>2</sub> Complexes in the Argon Matrix. (a)  $C^{16}OFCI + CI_2$ . The infrared spectrum of the deposited COFCl and Cl<sub>2</sub> mixture in argon at high dilution in both dopants (COFCl/Cl<sub>2</sub>/Ar 2/1/2000) exhibited new absorptions at 1840.0, 1095.5, and 767.2 cm<sup>-1</sup> belonging to the C<sup>16</sup>OFCl/Cl<sub>2</sub> complex and assigned to the  $\nu_2$ ,  $\nu_1$ , and  $\nu_3$  modes of the COFCl submolecule. At higher Cl<sub>2</sub> concentrations (COFCl/Cl<sub>2</sub>/Ar 1/2/1000), these bands increased in intensity with a structure in multiplets, whereas the isolated COFCl bands disappeared. In the  $\nu_{CO}$  region, there appeared a relative broad band at 1863.2 cm<sup>-1</sup>, in coincidence with the  $\nu_{CO}$  mode of the unperturbed COFCI which kept a constant relative intensity ratio with the 1840.0-cm<sup>-1</sup> band. The Cl<sub>2</sub> submolecule, which is allowed by symmetry, was characterized by a triplet at 546.5, 538.5, and 531.0 cm<sup>-1</sup> due to the <sup>37</sup>Cl<sup>35</sup>Cl shift, with a ratio of intensities of the components close to 9/6/1. From the Raman spectrum of chlorine isolated in argon,<sup>26</sup> a red shift (7.5 cm<sup>-1</sup>) in  $\nu_{Cl-Cl}$  was observed, caused by interaction with the C=O group. The origin of the 1863-cm<sup>-1</sup> band correlated to the 1840-cm<sup>-1</sup> band can be explained by a Fermi resonance in the 1:1 complex but with a relatively different position of the levels  $v_2$  and  $v_1 + v_4$  in the complex than in the COFCI parent molecule. The 1863-cm<sup>-1</sup> band is assigned to the mixed  $v_1 + v_4$ mode calculated at 1863 cm<sup>-1</sup>, whereas the 1840-cm<sup>-1</sup> band corresponds to the mixed perturbed  $\nu_{CO}$  mode. The resonance interaction explains the abnormally strong shift observed for the  $\nu_{\rm CO}$  band (13%) in the complex compared to the shift observed in the  $Cl_2CO/Cl_2$  complex (0.2%).<sup>2</sup>

(b) C<sup>18</sup>OFCl + Cl<sub>2</sub>. Upon isotopic substitution in the COFCl molecule, the product absorptions of the 1:1 complex, FClC= <sup>18</sup>O/Cl<sub>2</sub>, were observed at 1806.8-1806.0, 1092.2, and 753 cm<sup>-1</sup>. In this case, the resonance interaction between  $\nu_2$  and  $\nu_1 + \nu_4$  at 1837 cm<sup>-1</sup> seems removed, and the  $\nu_{CO}$  band falls nearly in co-incidence with the mixed  $\nu_{Cl<sup>3</sup>O}$  band of the parent molecule.

An overall summary of the observed bands is listed in Table III.

(3) UV Photodissociation of COFCl in the Argon Matrix. In order to check on the relative contribution of various possible atomic detachment processes in the photolysis of COFCl, pho-

TABLE III: Comparison between Frequencies (cm<sup>-1</sup>) of COFCI Uncomplexed and Complexed by Cl<sub>2</sub>

-	•	• •				
mode		FClC <sup>16</sup> O	FClC <sup>16</sup> O····Cl <sub>2</sub>	FClC <sup>18</sup> O	FClC <sup>18</sup> O····Cl <sub>2</sub>	
$\nu_1(\nu_{\rm CCl})$		760.2	767.2-765.9 (sh)	746.2	752.9-751.7	
		759.5	765.3	744.15	750.9	
			1841.2 (sh)		1808.7-1808.0	
$\nu_2 (\nu_{C=0})$	Farmi	1863.3	1840.0	1807.2-1806.5	1806.8-1806.0	
	rermi		1838.7-1838.0			
$v_1 + v_4$	resonance	1830.1		1830.0		
		1827.8	1863.2	1829.0	1837	
$\nu_4 (\nu_{\rm C-F})$		1082.7	1095.5	1080.1	1092.9-1092.2-1091.3	
			1094.7 (sh)-1093.8 (sh)			
$\nu_6(\gamma)$		661.1	666.5	657.0	661.9	
$2\nu_6$		1319.2	1332.0	1318.4	1324.2	

tochemical studies of the COFCI/Ar (1/1000) mixture were carried out with the medium-pressure mercury lamp. No photoproduct bands were identified. In particular, although it would be anticipated that the C-Cl band would undergo photolytic rupture, the CFO radical was not observed,<sup>28</sup> suggesting that the produced molecular fragments recombine within the matrix cage.

(4) Reaction of the O(<sup>1</sup>D) Atom with CFCl<sub>3</sub>. Comparison of the vibrational frequencies recorded for isolated COFCl and the COFCl/Cl<sub>2</sub> complex in argon matrix reveals that the reaction between CFCl<sub>3</sub> and atomic oxygen in the singlet D state gave only COFCl as the photoproduct:

$$CFCl_3 + O(^1D) \rightarrow COFCl + 2Cl$$

In the matrix cage or in adjacent sites, some COFCI molecules are complexed by  $Cl_2$  species and are at the origin of the weak bands observed after irradiation, which grew strongly after annealing. Thus, except for one or two weak absorptions, it has been possible to assign all the features appearing in the spectra after irradiation or annealation to the COFCl and COFCl/Cl<sub>2</sub> products as summarized in Table I. The particular behavior observed with isotopic ozone is explained by a Fermi resonance in the C<sup>18</sup>OFCl molecule and by some coincidences of frequencies between C<sup>16</sup>-OFCl and C<sup>18</sup>OFCl.

The major infrared absorptions of COFCl produced after photolysis of the  $CFCl_3 + O_3$  mixture appeared as doublets, and the measured relative intensities for the splitting of the bands were found to be dependent on the photolysis wavelength. This behavior was not observed with directly deposited COFCI and could be explained by the existence of two different environments of the COFCl photoproduct due to the escape of atomic Cl from its argon matrix cage when photolysis energy exceeded that required to effect dissociation of the guest. Such a phenomenon explained in terms of "localized annealing process of the matrix lattice" has been previously recognized and discussed by Clemitshaw and Sodeau<sup>29</sup> in their study of photolysis of the  $CF_3X$  compounds (X = I, Br, NO), which produces a range of "proximity radicals". Thus, in our spectra, the lower component of each doublet (1862.5-759.7 cm<sup>-1</sup>) can be assigned to the FCIC=O...Cl proximity species, whereas the higher component (1865.2-761.9 cm<sup>-1</sup>) can correspond to the vibrational modes of FClCO--Ar in which the CO bands is less perturbed.

The mechanism by which the COFCl primary product is obtained cannot be postulated in the absence of detected intermediates. However, direct F and Cl abstractions by atomic oxygen are ruled out since FO<sup>30,31</sup> and ClO<sup>17</sup> were not identified. The COFCI molecule must originate from an highly unstable species formed either by a direct attack of the oxygen atom upon the carbon atom or by the insertion of an oxygen atom inside the CCl bond. Bond cleavages of the intermediate species lead to COFCl. Formation of FCO followed by recombination of FCO and Cl in the matrix cage seems unlikely. No trace of FCO was observed even after a long irradiation time, and the growth of the 1862-cm<sup>-1</sup> product band with time (Figure 3) gives no evidence of an induction period.

The results obtained in this work show that Freon 11 is not an inert compound since it can react with an excited-state oxygen atom,  $O(^{1}D)$ . However it is less reactive than  $CHCl_{3}^{32}$  and CBrCl<sub>3</sub><sup>26</sup> which lead to phosgene by reaction with oxygen atoms even in the triplet P state. Traces of COFCl in the troposphere (<4 pptv) could originate from the reaction of  $O_3$  and CFCl<sub>3</sub> if the kinetic rate of the reaction is greater than that for the deactivation of O(<sup>1</sup>D) by air  $(k^{298K} = 2.9 \ 10^{-11} \ \text{cm}^3 \ \text{mol}^{-1} \ \text{s}^{-1})^{.33}$ 

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Registry No. CFCl<sub>3</sub>, 75-69-4; O<sub>3</sub>, 10028-15-6; COFCl, 353-49-1; C<sup>18</sup>FCl, 143238-43-1; Cl<sub>2</sub>, 7782-50-5; O, 17778-80-2.

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