

# Vibrational Spectra and Normal Coordinate Analysis of CF<sub>3</sub>OF and CF<sub>3</sub>OCl

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The IR spectra (1400 cm<sup>-1</sup> to 160 cm<sup>-1</sup>) of the gases at ambient temperature and the Raman spectra (below 1400 cm<sup>-1</sup>) of the liquids near -196 °C are reported for CF<sub>3</sub>OF and CF<sub>3</sub>OCl. All fundamentals are assigned under C<sub>s</sub> symmetry and the results of a normal coordinate analysis are presented. The assignments of Smardzewski and Fox are adopted with one exception for both CF<sub>3</sub>OF and CF<sub>3</sub>OCl: the CF<sub>3</sub> rock of A' symmetry is assigned near 430 cm<sup>-1</sup> and the two bands between 200 cm<sup>-1</sup> and 300 cm<sup>-1</sup> are assigned to an A' fundamental, involving CF<sub>3</sub> rocking and COX bending and a Δν = 2 transition in the CF<sub>3</sub> torsion. An extra band at 548 cm<sup>-1</sup> in the Raman spectrum of liquid CF<sub>3</sub>OCl near -196 °C is assigned to a CF<sub>3</sub>OCl⋯Cl<sub>2</sub> complex. The values of the force constants *d*(OX) for CF<sub>3</sub>OX molecules are suggested to be near those for X<sub>2</sub>O molecules. More than half the normal modes of A' symmetry show extensive mixing of symmetry coordinates. In some of these cases the symmetry coordinate for which the normal mode is named is the largest but not the dominant contributor to the potential energy distribution, while in others this symmetry coordinate is not even the largest contributor to the potential energy distribution. No normal modes of A' symmetry are present in which ν(CO), δ<sub>s</sub>(CF<sub>3</sub>), δ(COX), or ρ(CF<sub>3</sub>) symmetry coordinates are dominant, and the mode conventionally labeled as ν(CO) should be labeled as ν<sub>s</sub>(CF<sub>3</sub>). For the remaining A' normal modes and all the A'' normal modes, the symmetry coordinate for which the normal mode is named is dominant in the potential energy distribution.

## INTRODUCTION

Trifluoromethyl hypofluorite, CF<sub>3</sub>OF, is an important reagent in the synthesis of organic and inorganic fluorine compounds.<sup>1</sup> Trifluoromethyl hypochlorite, CF<sub>3</sub>OCl, is the first member of the chloroxy perfluoroalkane series and molecules known to readily undergo free radical reactions form derivatives of CF<sub>3</sub>OCl in which the CF<sub>3</sub>O group is retained.<sup>2</sup> CF<sub>3</sub>OF has been studied by IR and Raman spectroscopy,<sup>3,4</sup> electron diffraction<sup>5</sup> and microwave spectroscopy.<sup>6</sup> The preparation, identification and characterization of CF<sub>3</sub>OCl included IR spectra only.<sup>2,7</sup> More recently, Raman spectra of both CF<sub>3</sub>OF and CF<sub>3</sub>OCl diluted in argon matrices at 8 K and of gaseous CF<sub>3</sub>OF at ambient temperature have been reported.<sup>8</sup>

As a prelude to investigations of the structure of the CF<sub>3</sub>OOX series (X = H, D, F, Cl) by vibrational spectroscopy,<sup>9</sup> electron diffraction<sup>10</sup> and microwave spectroscopy,<sup>11</sup> we reinvestigated the IR and Raman spectra of CF<sub>3</sub>OF and CF<sub>3</sub>OCl. While this work was in progress, the contribution by Smardzewski and Fox<sup>8</sup> appeared and complemented our results. Considerations about Δν = 2 transitions in the CF<sub>3</sub> rotor<sup>12,13</sup> analogous to the CH<sub>3</sub> rotor<sup>14,15,16</sup> have arisen and the final results are being reported separately.<sup>17</sup> Concurrently, our work with the CF<sub>3</sub>OOX series has been completed<sup>18</sup> and is

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being reported separately.<sup>19</sup> The present paper summarizes our complete results<sup>20</sup> for the assignments and normal coordinate analysis of CF<sub>3</sub>OF and CF<sub>3</sub>OCl.

## EXPERIMENTAL

CF<sub>3</sub>OF and CF<sub>3</sub>OCl were prepared at Kansas State University by the cesium fluoride catalyzed addition of F<sub>2</sub> and ClF, respectively, to COF<sub>2</sub>.<sup>21</sup> Purification was normally by vacuum line distillation. CF<sub>3</sub>OF was contaminated with CF<sub>2</sub>(OF)<sub>2</sub> whose separation required low temperature gas chromatography.

Mid-IR spectra (4000–160 cm<sup>-1</sup>) of the gases were recorded at Kansas State University with a Perkin-Elmer Model 180 IR spectrophotometer. Cells of 10 cm path length with AgCl windows and 15 cm path length with polyethylene windows were used in the regions 4000–400 cm<sup>-1</sup> and 650–160 cm<sup>-1</sup>, respectively.

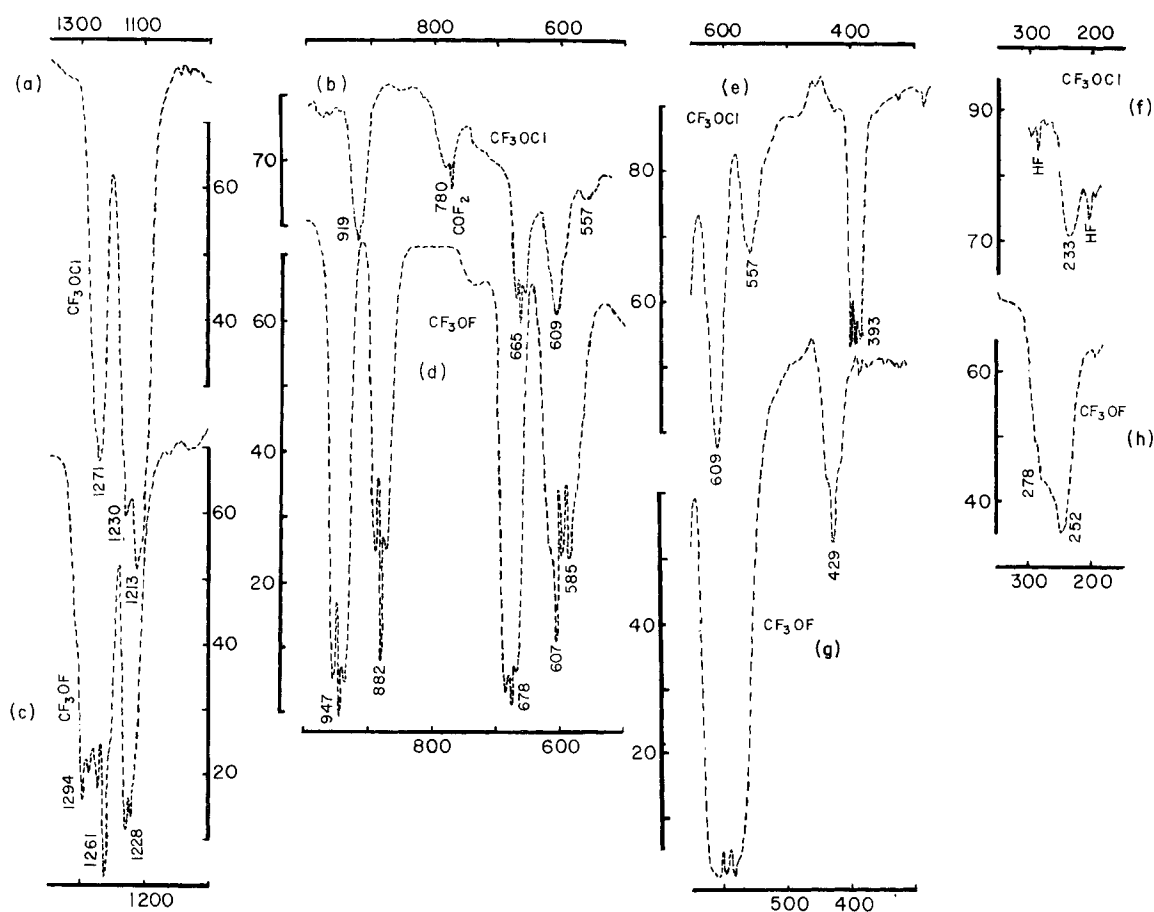
Raman spectra of the liquids were recorded at Kansas State University in a low temperature cell similar in design to that of Brown *et al.*<sup>22</sup> with the coolant bath at -196 °C (liquid N<sub>2</sub>) using a JASCO R-300 Laser Raman spectrophotometer. The 514.5 nm line of a Spectra Physics Model 164-00 argon ion laser was used with power levels at the laser in the range 100–300 mW. Depolarization ratios were determined by method IV of Claassen *et al.*<sup>23</sup> Their *f* has not been determined for the JASCO R-300; however, known depolarized bands gave depolarization ratios between 0.75 and 0.89.

Raman spectra of liquid CF<sub>3</sub>OCl were also recorded at Allied Chemical Company using a Spex Ramalog system and low temperature cell and the 514.5 nm line of a Coherent Radiation argon ion laser.

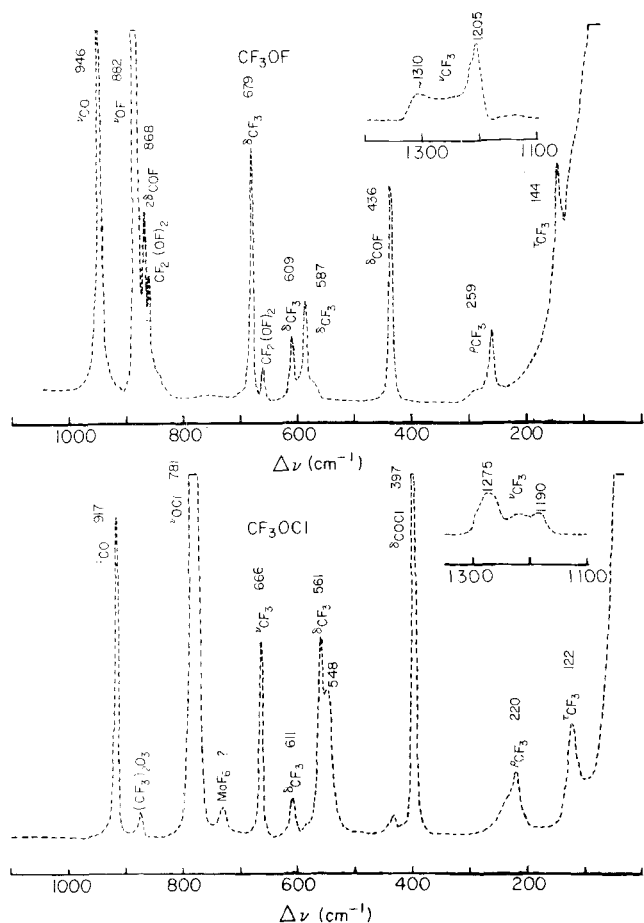
## SPECTRAL RESULTS

The IR and Raman spectra below 1400 cm<sup>-1</sup> are shown in Figs 1 and 2, respectively. The frequencies are listed in Table 1 along with the complementary data of Smardzewski and Fox.<sup>8</sup> In general, our IR data for CF<sub>3</sub>OF agree well with those of Wilt and Jones.<sup>4</sup> However, between 300 and 200 cm<sup>-1</sup> our spectra show peaks 25–28 cm<sup>-1</sup> higher in frequency but with similar band shapes. Since our IR and Raman data are self-consistent and in good agreement with the Raman data of Smardzewski and Fox for both CF<sub>3</sub>OF and CF<sub>3</sub>OCl, we conclude that the IR data of Wilt and Jones for CF<sub>3</sub>OF below 300 cm<sup>-1</sup> are in error for reasons unknown. Our IR data for CF<sub>3</sub>OCl above 500 cm<sup>-1</sup> are similar to the results of Schack and Maya<sup>2</sup> with our sample appearing to be of higher purity.

The assignments shown in Table 1 are those of Smardzewski and Fox<sup>8</sup> with the exception of one of the CF<sub>3</sub> rocking modes. We are in complete agreement with their reversal of the CO and OF stretching mode assignments of Wilt and Jones. Initially we had assumed, as do Smardzewski and Fox, that the two CF<sub>3</sub> rocking modes would lie between 200 and 300 cm<sup>-1</sup>. However, our normal coordinate analysis places the two CF<sub>3</sub> rocking modes far apart with the one in the A'' symmetry block being in the surprisingly high frequency range of 400–500 cm<sup>-1</sup>. The lowest frequency bands in the Raman spectra of both compounds initially seemed high to us for the CF<sub>3</sub> torsion and we suggested they might be  $\Delta\nu = 2$  transitions<sup>12,13</sup> analogous to CH<sub>3</sub> torsions.<sup>14–16</sup> However, the microwave work of Buckley and Weber<sup>6</sup> strongly supports the assignments of  $\Delta\nu = 1$  transitions being responsible for these bands. Vibrational satellite lines having 0.4 times the intensity of the ground state lines at 194 K in the microwave spectrum of gaseous CF<sub>3</sub>OF<sup>6</sup> are in good agreement with a population ratio of 0.39 if the  $\nu = 1$  state in the torsional mode is 127 cm<sup>-1</sup> above the  $\nu = 0$  state (using the gas phase Raman frequency of Smardzewski and Fox<sup>8</sup> of 127 cm<sup>-1</sup> from Table 1 for the 0 → 1 transition in the CF<sub>3</sub> torsion).



**Figure 1.** IR spectra (1400–160 cm<sup>-1</sup>) of gaseous CF<sub>3</sub>OF and CF<sub>3</sub>OCl at ambient temperature. Spectra (a), (b), (e) and (f) are CF<sub>3</sub>OCl and spectra (c), (d), (g) and (h) are CF<sub>3</sub>OF. Spectra (a), (b), (c) and (d) are from a 10 cm cell with AgCl windows. Spectra (e), (f), (g) and (h) are from a 15 cm cell with polyethylene windows. Gas pressures are as follows: (a) 3 torr; (b) 65 torr; (c) 3 torr; (d) 161 torr; (e) 100 torr; (f) 140 torr; (g) 438 torr; (h) 438 torr. The mid-point of the doublet whose more intense component is labeled 1228 cm<sup>-1</sup> in (c) is at 1222 cm<sup>-1</sup> and the latter frequency is listed in Table 1. The band at 393 cm<sup>-1</sup> in (e) has a contribution from the Q branch of the degenerate deformation of SiF<sub>4</sub> present as an impurity and in higher resolution expanded scale spectra the SiF<sub>4</sub> Q branch is clearly resolved.



**Figure 2.** Raman spectra (below  $1400\text{ cm}^{-1}$ ) of liquid  $\text{CF}_3\text{OF}$  and  $\text{CF}_3\text{OCl}$  near  $-196^\circ\text{C}$ . The  $\text{CF}_3\text{OF}$  sample contains a small amount of  $\text{CF}_2(\text{OF})_2$ . The  $\text{CF}_3\text{OCl}$  sample is believed to contain a small amount of  $\text{Cl}_2$  held as a  $\text{CF}_3\text{OCl}\cdots\text{Cl}_2$  complex.

If the band at  $127\text{ cm}^{-1}$  were due to a  $0 \rightarrow 2$  transition, then the  $0 \rightarrow 1$  transition would be  $65\text{ cm}^{-1}$  giving a population ratio of 0.62 at 194 K. Consequently, the two overlapping bands between 200 and  $300\text{ cm}^{-1}$  may be interpreted as the  $\text{CF}_3$  rock in the  $A'$  symmetry block and  $2\tau(\text{CF}_3)A'$  (i.e. a  $\Delta\nu = 2$  transition in the  $\text{CF}_3$  torsion). A detailed investigation of the Raman spectrum of gaseous  $\text{CF}_3\text{OF}$  under higher resolution confirms this suggestion and is being reported separately.<sup>17</sup>

When the IR band of gaseous  $\text{CF}_3\text{OF}$  with a  $Q$  branch at  $429\text{ cm}^{-1}$  in Fig. 1 is recorded with abscissa expansion and higher resolution a shoulder at  $431\text{ cm}^{-1}$  is seen on the  $Q$  branch. The corresponding liquid Raman band at  $436\text{ cm}^{-1}$  is polarized and so belongs in the  $A'$  symmetry block; however, the presence of a weak depolarized band a few  $\text{cm}^{-1}$  away can neither be confirmed nor denied by the appearance of the Raman spectrum of the liquid. The Raman spectra of Smardzewski and Fox<sup>8,24</sup> for  $\text{CF}_3\text{OF}$  in an argon matrix show a single band at  $433\text{ cm}^{-1}$  whose width is comparable to that of other bands in the argon matrix. In our opinion their Raman spectra can neither confirm nor deny the possible presence of two fundamentals separated by several  $\text{cm}^{-1}$ . Initially we had not tried to interpret the shoulder at  $431\text{ cm}^{-1}$ . However, we now adopt the suggestion of our normal coordinate analysis and assign  $431\text{ cm}^{-1}$  as the  $\text{CF}_3$  rocking mode in the  $A''$  symmetry block.

Our Raman data for liquid  $\text{CF}_3\text{OCl}$  show a very weak band at  $430\text{ cm}^{-1}$  in every spectrum where the sensitivity is high enough to record the  $611\text{ cm}^{-1}$  band which is the weakest Raman band previously assigned to a fundamental. Since the IR baseline is not flat in this region due to problems with exact compensation of polyethylene sheets placed in the reference beam, it is difficult to tell whether or not a very weak IR band may be present at  $430\text{ cm}^{-1}$ . Here, also, we now adopt the suggestion of our normal coordinate analysis and assign  $430\text{ cm}^{-1}$  as the  $\text{CF}_3$  rocking mode in the  $A''$  symmetry block.

Initially our sample of  $\text{CF}_3\text{OCl}$  contained a large amount of chlorine, and the band in  $\text{CF}_3\text{OCl}$  listed at  $561\text{ cm}^{-1}$  in Table 1 for the Raman spectrum of the liquid was only visible as a small shoulder on the intense band due to the dissolved chlorine. Purification of the  $\text{CF}_3\text{OCl}$  sample gave the Raman spectrum shown in Fig. 2. The band at  $548\text{ cm}^{-1}$  in Fig. 2 does not appear in the IR spectrum of gaseous  $\text{CF}_3\text{OCl}$ . Smardzewski and Fox<sup>8,24</sup> observe extra bands in the Raman spectrum of  $\text{CF}_3\text{OCl}$  in an argon matrix at  $547$  and  $539\text{ cm}^{-1}$  with relative intensities of 9 and 10 respectively. Our band at  $548\text{ cm}^{-1}$  in the Raman spectrum of liquid  $\text{CF}_3\text{OCl}$  appears upon abscissa expansion and higher resolution to consist of two overlapping bands of equal intensity at about  $551$  and  $545\text{ cm}^{-1}$ . Since all the  $\text{CF}_3\text{OCl}$  fundamentals are reasonably accounted for, the band(s) at  $548\text{ cm}^{-1}$  must be either a non-fundamental of  $\text{CF}_3\text{OCl}$  or an impurity.

The assignment to a difference band is reasonable on a frequency basis but not on the basis of intensity and polarization. Using liquid Raman frequencies,  $\delta_s(\text{CF}_3)A' - \tau(\text{CF}_3)A'' = 666 - 122 = 544\text{ cm}^{-1}$  in good agreement with  $548\text{ cm}^{-1}$ . However, the transition from ( $\nu_{12} = 1$  all other  $\nu_i = 0$ , an  $A''$  state) to ( $\nu_5 = 1$ , all other  $\nu_i = 0$ , an  $A'$  state) is a non-totally symmetric transition and should be depolarized. The  $548\text{ cm}^{-1}$  band is polarized. The population of ( $\nu_{12} = 1$ , all other  $\nu_i = 0$ ) is 10–17% of that of (all  $\nu_i = 0$ ) for  $\nu_{12} = \tau(\text{CF}_3)A'' = 122\text{ cm}^{-1}$  between 77 and 100 K (estimated range of sample temperature with liquid  $\text{N}_2$  in the coolant bath of the low temperature cell). The fact that the  $548\text{ cm}^{-1}$  band has 80% of the intensity of the  $\delta_{as}(\text{CF}_3)A'$  fundamental at  $561\text{ cm}^{-1}$  is difficult to explain for a non-fundamental with no apparent Fermi resonance possibilities and such an unfavorable Boltzmann population ratio. On both the intensity and polarization basis we feel that the  $548\text{ cm}^{-1}$  band must be due to a species other than  $\text{CF}_3\text{OCl}$ .

Possible impurities in the  $\text{ClF}$  used to prepare  $\text{CF}_3\text{OCl}$  by addition to  $\text{COF}_2$  are  $\text{ClF}_5$  and  $\text{ClF}_3$ . However, the Raman spectra of liquid  $\text{ClF}_5$ <sup>25</sup> and liquid  $\text{ClF}_3$ <sup>26</sup> are such that both compounds would be detected by intense bands well separated from any of the  $\text{CF}_3\text{OCl}$  bands in Fig. 2.

For the case of  $\text{CF}_3\text{OF}$  prepared by the addition of  $\text{F}_2$  to  $\text{COF}_2$ ,  $\text{CO}_2$  impurity in the  $\text{COF}_2$  leads to the production of some  $\text{CF}_2(\text{OF})_2$ . By analogy the addition of  $\text{ClF}$  to  $\text{CO}_2$  might lead to a variety of materials of the general formula  $\text{CF}_w\text{Cl}_x(\text{OF})_y(\text{OCl})_z$ . Here  $w, x, y, z$  may have values 0, 1 or 2 in various combinations subject to the restrictions that  $(w + x) = 2$  and  $(y + z) = 2$ . For compounds with C—Cl bonds ( $x \neq 0$ ) and for compounds with O—F bonds ( $y \neq 0$ ), Raman bands

**Table 1. IR and Raman data<sup>a,b</sup> below 1400 cm<sup>-1</sup> and assignment of fundamentals for CF<sub>3</sub>OF and CF<sub>3</sub>OCl**

CF <sub>3</sub> OF								CF <sub>3</sub> OCl							
IR <sup>c</sup> gas		gas <sup>d</sup>	Raman liquid		Ar matrix <sup>d</sup>		IR <sup>c</sup> gas	vs liquid	Raman		Ar matrix <sup>d</sup>		Assignment <sup>e</sup>		
1294	vs	1300	1310	1	?	1288	5	1271	vs	1275	3	0.60	1269	17	$\nu_{as}(\text{CF}_3)A'$
		↓ w, br													
1261	vs	1250				1250	7	1230	vs				1221	8	$\nu_{as}(\text{CF}_3)A''$
1222	vs	1219 w	1205	3	0.45	1211	14	1213	vs	1190	2	0.66	1200	3	$\nu_s(\text{CF}_3)A'$
947	Q s	945 m	946	16	0.49	945	54	919	Q m	917	26	0.46	920	28	$\nu(\text{CO})A'$
882	Q m	881 vs	882	100	0.03	883	100	780	w	781	100	0.12	783	100	$\nu(\text{OX})A'$
		864 vw	868	8	0.04	871	7								$2\delta(\text{COF})A'$
													776	24	$\nu(\text{O}^{37}\text{Cl})A'$
678	Q s	675 w	679	12	0.35	678	24	665	Q m	666	15	0.38	663	30	$\delta_s(\text{CF}_3)A'$
607	m	606 w, sh	609	3	0.85	606	9	609	m	611	3	0.76	609	15	$\delta_{as}(\text{CF}_3)A''$
585	m	581 w	587	5	0.43	582	9	557	w	561	14	0.26	558	28	$\delta_{as}(\text{CF}_3)A'$
										548	12		547	9	CF <sub>3</sub> OCl...Cl <sub>2</sub>
													539	10	
431	sh vw									430	1	?			$\rho(\text{CF}_3)A''$
429	Q vw	429 m	436	10	0.32	433	34	393	Q m	397	41	0.27	398	62	$\delta(\text{COX})A'$
278	vw	272 w	259	3	0.52	256	16	233	vw	220	4	0.47	239	5	$\rho(\text{CF}_3)A'$
252	vw	246 w	285 sh?	?	?			220 sh??	~235 sh?	?	?	?			$2\tau(\text{CF}_3)A'$
		127 w, br	144	5	0.86					122	6	0.81			$\tau(\text{CF}_3)A''$

<sup>a</sup> All observed frequencies are in cm<sup>-1</sup>. Abbreviations used are: w, weak; m, medium; s, strong; vw, very weak; vs, very strong; sh, shoulder; br, broad.

<sup>b</sup> Raman data are listed as frequency in cm<sup>-1</sup> first and relative intensity second. For all spectra but those of gases, relative intensity is on a scale where the most intense band is 100. For the spectra of liquids the third entry is depolarization ratio measured by method IV of Claassen *et al.*<sup>23</sup> These numbers are really  $R$  rather than  $\rho_s$  in the notation of Table 1 of Claassen *et al.* since  $f$  has not been measured on the JASCO R-300. Known depolarized bands gave  $R$  values in the range 0.75 to 0.89 on the JASCO R-300 between 200 cm<sup>-1</sup> and 3000 cm<sup>-1</sup> Raman shift from the 514.5 nm argon ion laser line.

<sup>c</sup> The notation Q designates the Q branch frequency for bands having PQR structure as follows: CF<sub>3</sub>OF 938, 947, 956; 874, 882, 890; 670, 678, 688; ~420, 429, 439. CF<sub>3</sub>OCl 915, 919, 923; 659, 665, 671; 386, 393, 399.

<sup>d</sup> Data is from Smardzewski and Fox.<sup>8,24</sup>

<sup>e</sup> The word descriptions for these symbols shown in Table 3 are used to name the normal modes. These normal mode names may be classified as reasonable or misleading by inspection of the potential energy distribution in Table 5 using the following criterion: the appropriate symmetry coordinate makes by far the largest contribution to the potential energy distribution. By that criterion, all four modes in the A'' block but less than half the modes in the A' block have reasonable names.<sup>45-48</sup> Based on the potential energy distributions in Table 5, the following tabulation provides complicated but reasonable symbols for the A' modes in question next to the numbers and symbols from Table 3.

Table 3	CF <sub>3</sub> OF	CF <sub>3</sub> OCl
1 $\nu_{as}(\text{CF}_3)A'$		
2 $\nu_s(\text{CF}_3)A'$	$\nu(\text{CO})A' + \delta_s(\text{CF}_3)A' + \nu_s(\text{CF}_3)A'$	$\nu(\text{CO})A' + \delta_s(\text{CF}_3)A' + \nu_s(\text{CF}_3)A'$
3 $\nu(\text{CO})A'$	$\nu_s(\text{CF}_3)A'$	$\nu_s(\text{CF}_3)A'$
4 $\nu(\text{OX})A'$		$\nu(\text{OCl})A' + \delta(\text{COCl})A' + \rho(\text{CF}_3)A'$
5 $\delta_s(\text{CF}_3)A'$	$\delta_s(\text{CF}_3)A' + \delta(\text{COF})A' + \nu(\text{OF})A' + \nu(\text{CO})A'$	$\delta_s(\text{CF}_3)A' + \nu(\text{CO})A' + \nu(\text{OCl})A' + \delta(\text{COCl})A'$
6 $\delta_{as}(\text{CF}_3)A'$		
7 $\delta(\text{COX})A'$	$\rho(\text{CF}_3)A' + \delta_{as}(\text{CF}_3)A' + \delta(\text{COF})A'$	$\rho(\text{CF}_3)A' + \nu(\text{OCl})A' + \delta_{as}(\text{CF}_3)A'$
8 $\rho(\text{CF}_3)A'$	$\rho(\text{CF}_3)A' + \delta(\text{COF})A'$	$\delta(\text{COCl})A' + \rho(\text{CF}_3)A'$
9 $\nu_{as}(\text{CF}_3)A''$		
10 $\delta_{as}(\text{CF}_3)A''$		
11 $\rho(\text{CF}_3)A''$		
12 $\tau(\text{CF}_3)A''$		

should be present that are well separated from any of the CF<sub>3</sub>OCl bands in Fig. 2. One that might be less easily detected is CF<sub>2</sub>(OCl)<sub>2</sub>. It is possible to estimate the frequencies for CF<sub>2</sub>(OCl)<sub>2</sub> from those of CF<sub>3</sub>OCl by using differences between CF<sub>3</sub>OF and CF<sub>2</sub>(OF)<sub>2</sub> frequencies. These estimates suggest that CF<sub>2</sub>(OCl)<sub>2</sub> might have a strong band at 548 cm<sup>-1</sup> but not no traces of other bands in addition to those in Fig. 2.

An additional possibility is further reaction of CF<sub>3</sub>OCl to form CF<sub>3</sub>OClF<sub>2</sub>. The CF<sub>3</sub>O fragments of both CF<sub>3</sub>OCl and CF<sub>3</sub>OClF<sub>2</sub> might have indistinguishable spectra and differentiation would depend on vibrations of the ClF<sub>2</sub> fragment. Since ClF<sub>3</sub> has a ClF stretching mode at 529 cm<sup>-1</sup> (gas phase with liquid at lower frequency), the ClF<sub>2</sub> fragment of CF<sub>3</sub>OClF<sub>2</sub> could

be responsible for the 548 cm<sup>-1</sup> band. However, it is difficult to believe that the remaining modes of the ClF<sub>2</sub> fragment would not produce additional bands in Fig. 2.

We attribute the 548 cm<sup>-1</sup> band to the stretching of the Cl—Cl bond of a complex of CF<sub>3</sub>OCl with molecular chlorine. Chlorine dissolved in CF<sub>3</sub>OCl would be expected to give three bands for <sup>35</sup>Cl<sub>2</sub>, <sup>35</sup>Cl<sup>37</sup>Cl and <sup>37</sup>Cl<sub>2</sub> near 545 cm<sup>-1</sup>. Liquid chlorine in our low temperature cell with liquid nitrogen in the bath gave bands at 547, 540 and 533 cm<sup>-1</sup> in the intensity ratio 6.5:4.5:1 (theoretical 9:6:1). Condensation of chlorine into a CF<sub>3</sub>OCl sample of purity similar to Fig. 2 gave bands at 552 and 544 cm<sup>-1</sup> and a possible shoulder at 537 cm<sup>-1</sup>. The 548 cm<sup>-1</sup> band in CF<sub>3</sub>OCl does not appear to be due to chlorine in the same environment as pure liquid

**Table 2. The possible arrangements of chlorine isotopes**

No.	Mass arrangement CF <sub>3</sub> OCl...Cl—Cl			Relative abundance
1	35	35	35	27
2	35	35	37	9
3	35	37	35	9
4	35	37	37	3
5	37	35	35	9
6	37	35	37	3
7	37	37	35	3
8	37	37	37	1

chlorine or excess chlorine in CF<sub>3</sub>OCl. However, it would be possible for CF<sub>3</sub>OCl to form a complex with chlorine of sufficient strength that is not possible to remove all the chlorine from CF<sub>3</sub>OCl by our purification procedure. Then the 548 cm<sup>-1</sup> band could be due to the stretching of the Cl—Cl bond in a CF<sub>3</sub>OCl...Cl—Cl complex.

A complex via the chlorine atom of CF<sub>3</sub>OCl, analogous to X<sub>3</sub><sup>-</sup> halide complex ions such as I<sub>3</sub><sup>-</sup>, would have eight possible isotopic chlorine modifications. The eight possible arrangements of chlorine isotopes and their relative abundances are as shown in Table 2.

The effect of the mass of the chlorine atom in CF<sub>3</sub>OCl on the frequency for stretching the Cl—Cl bond from Cl<sub>2</sub> in the complex depends on the strength of the complex. The limit for a weak complex could be three bands due to three degenerate sets as follows: 1 and 5 of relative intensity 36; 2, 3, 6 and 7 of relative intensity 24; and 4 and 8 of relative intensity 4. As complex strength increases these degeneracies would be broken as the mass of the chlorine atom in CF<sub>3</sub>OCl begins to influence the frequency. A reasonable strong complex extreme would be where the vibration is still best treated as a perturbed diatomic molecules stretching rather than a three body problem with antisymmetric and symmetric skeletal stretching and skeletal bending. However, the degeneracies are broken and the eight frequencies might tend to group into the following four bands: 1 of relative intensity 27; 2, 3 and 5 of relative intensity 27; 4, 6 and 7 of relative intensity 9; and 8 of relative intensity 1.

For the weak complex extreme, the third band probably would not be observed as it is too weak, so a higher frequency band 1.5 times as intense as a lower frequency band is to be expected. For the strong complex extreme the fourth band would definitely be too weak to observe and the extent of overlap of the other three bands is uncertain. A likely result would be that the third band of intensity 9 would overlap the second band of intensity 27 to give a single asymmetric band or a band with a low frequency shoulder. This superposition would result in a lower frequency band with relative intensity 27 (or more from overlap of the third band) and a higher frequency band of relative intensity 27 (from complex 1). Then two resolvable bands seem reasonable for the range of complex strengths suggested. The higher frequency band would be expected to be from 1.5 times as intense to slightly less intense than the lower frequency band depending on the strength of the complex.

Thus, superposition of spectra of these eight complexes for plausible strengths of the complex could provide two resolvable bands with the higher frequency

band being from 1.5 times as intense to slightly less intense than the lower frequency band. Formation of a CF<sub>3</sub>OCl...Cl—Cl complex could account for a band at 548 cm<sup>-1</sup> in the Raman spectrum of liquid CF<sub>3</sub>OCl appearing to consist of two overlapping bands of about equal intensity at 551 and 545 cm<sup>-1</sup>. The observation by Smardzewski and Fox<sup>8</sup> of bands at 547 and 539 cm<sup>-1</sup> of relative intensities 9 and 10, respectively, in the Raman spectrum of CF<sub>3</sub>OCl in an Ar matrix is also consistent. Although the CF<sub>3</sub>OCl in Ar sample is intended to contain isolated molecules, experience in other systems suggests that the Ar:CF<sub>3</sub>OCl ratio of 100 is too low to insure isolated molecules since ratios >10<sup>4</sup> may be necessary in some cases to ensure really isolated molecules. The conditions of a liquid near 77 K and an Ar matrix at 8 K should favor complex formation<sup>27</sup> and the improved resolution in the Ar matrix is reasonable. Thus, a CF<sub>3</sub>OCl...Cl—Cl complex provides a simple explanation and is proposed as the most likely origin of the 548 cm<sup>-1</sup> band.

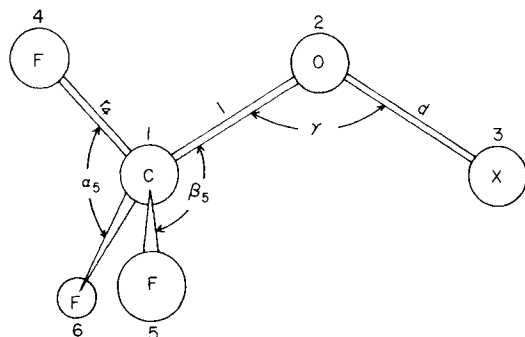
## NORMAL COORDINATE ANALYSIS

The Wilson FG-matrix method<sup>28</sup> was used with the computer programs written by Schachtschneider.<sup>29</sup> The G matrices were calculated from the electron diffraction structure for CF<sub>3</sub>OF<sup>5,30</sup> and reasonable assumptions for the structure of CF<sub>3</sub>OCl.<sup>30</sup> Symmetrization was accomplished using the symmetry coordinates listed in Table 3 generated from the internal coordinates in Fig. 3.

**Table 3. Symmetry coordinates for CF<sub>3</sub>OX molecules of C<sub>3v</sub> symmetry**

A' symmetry	
Antisymmetric CF <sub>3</sub> stretch, $\nu_{as}(\text{CF}_3)A'$	$S_1 = \sqrt{6}^{-1}(2\Delta r_4 - \Delta r_5 - \Delta r_6)$
Symmetric CF <sub>3</sub> stretch, $\nu_s(\text{CF}_3)A'$	$S_2 = \sqrt{3}^{-1}(\Delta r_4 + \Delta r_5 + \Delta r_6)$
CO stretch $\nu(\text{CO})A'$ ,	$S_3 = \Delta l$
OX stretch $\nu(\text{OX})A'$ ,	$S_4 = \Delta d$
Symmetric CF <sub>3</sub> deformation, $\delta_s(\text{CF}_3)A'$	$S_5 = \sqrt{6}^{-1}(\Delta\alpha_4 + \Delta\alpha_5 + \Delta\alpha_6 - \Delta\beta_4 - \Delta\beta_5 - \Delta\beta_6)$
Antisymmetric CF <sub>3</sub> deformation, $\delta_{as}(\text{CF}_3)A'$	$S_6 = \sqrt{6}^{-1}(2\Delta\alpha_4 - \Delta\alpha_5 - \Delta\alpha_6)$
COX bend, $\delta(\text{COX})A'$	$S_7 = \Delta\gamma$
CF <sub>3</sub> rock, $\rho(\text{CF}_3)A'$	$S_8 = \sqrt{6}^{-1}(2\Delta\beta_4 - \Delta\beta_5 - \Delta\beta_6)$
Redundant	$S_0^o = \sqrt{6}^{-1}(\Delta\alpha_4 + \Delta\alpha_5 + \Delta\alpha_6 + \Delta\beta_4 + \Delta\beta_5 + \Delta\beta_6)$
A'' symmetry	
Antisymmetric CF <sub>3</sub> stretch, $\nu_{as}(\text{CF}_3)A''$	$S_9 = \sqrt{2}^{-1}(\Delta r_5 - \Delta r_6)$
Antisymmetric CF <sub>3</sub> deformation, $\delta_{as}(\text{CF}_3)A''$	$S_{10} = \sqrt{2}^{-1}(\Delta\alpha_5 - \Delta\alpha_6)$
CF <sub>3</sub> rock, $\rho(\text{CF}_3)A''$	$S_{11} = \sqrt{2}^{-1}(\Delta\beta_5 - \Delta\beta_6)$
CF <sub>3</sub> torsion, $\tau(\text{CF}_3)A''$	$S_{12} = \Delta\tau$

<sup>a</sup> These coordinates are correct for tetrahedral C<sub>3v</sub> angles. However, they may be used for the non-tetrahedral angle case since the redundancy is removed during the diagonalization of the G matrix.



**Figure 3.** Internal coordinates for CF<sub>3</sub>OX molecules. *C<sub>s</sub>* symmetry is assumed with F, C, O and X atoms in the same plane.

The simple molecules F<sub>2</sub>O,<sup>32</sup> Cl<sub>2</sub>O,<sup>33</sup> CF<sub>3</sub>H<sup>34</sup> and CF<sub>4</sub><sup>35</sup> were used to establish a reasonable range of force constant values for CF<sub>3</sub>OF and CF<sub>3</sub>OCl. Force constant values within this range that were consistent with bond strengths of CF<sub>3</sub>OF and CF<sub>3</sub>OCl implied by their chemical reactions are shown in Table 4 where force constants based on internal coordinates are listed. The internal coordinate F matrix follows from the list of force constants in Table 4.<sup>36</sup> The potential energy distributions using symmetry force constants based on the symmetry coordinates in Table 3 and the internal coordinate force constant values in Table 4 are in Table 5 along with a comparison of calculated and observed frequencies.

Improvement of the frequency fit for CF<sub>3</sub>OCl to that for CF<sub>3</sub>OF requires a higher OCl stretching constant, *d*(OCl), near the value for *d*(OF) in CF<sub>3</sub>OF or alteration of some off diagonal force constants. The force constant values in Table 4 are consistent with the chemical behavior of CF<sub>3</sub>OF and CF<sub>3</sub>OCl and the force constant values in the following molecules related to CF<sub>3</sub>OF and CF<sub>3</sub>OCl, respectively: HOF,<sup>37</sup> F<sub>2</sub>O<sup>32</sup> and ClO<sub>3</sub>OF,<sup>38</sup> and HOCl,<sup>37</sup> Cl<sub>2</sub>O,<sup>33</sup> ClO<sub>3</sub>OCl<sup>39</sup> and ClO<sub>3</sub>OClO<sub>3</sub>.<sup>38</sup> The available data favors values of *d*(OX) in these CF<sub>3</sub>OX compounds close to those of the corresponding X<sub>2</sub>O compounds.

CF<sub>3</sub>OF is thermally stable in an IR cell at room temperature and the gas phase Raman spectrum can be obtained at room temperature using Ar<sup>+</sup> laser radiation. CF<sub>3</sub>OCl is stable at room temperature only under scrupulously dry, inert conditions. Photolytic decomposition of CF<sub>3</sub>OCl is quite rapid and the decomposition products are consistent with a two step reaction path involving the two radicals CF<sub>3</sub> and Cl<sup>2</sup>. In our work CF<sub>3</sub>OCl began to decompose during the recording of its IR spectrum at ambient temperature. Smardzewski and Fox<sup>8</sup> report that CF<sub>3</sub>OCl photolyzed almost immediately during their attempt to record its gas phase Raman spectrum at room temperature using Ar<sup>+</sup> laser radiation. Since this behavior suggests that the OF bond in CF<sub>3</sub>OF is stronger than the OCl bond in CF<sub>3</sub>OCl, similar values of *d*(OF) and *d*(OCl) are considered unlikely.

Values of *d*(OF) in mdyne Å<sup>-1</sup> are 4.27, 3.95 and 3.56 for HOF,<sup>37</sup> F<sub>2</sub>O<sup>32</sup> and ClO<sub>3</sub>OF,<sup>38</sup> respectively. Noble and Pimentel<sup>40</sup> have suggested that *d*(OF) is larger in HOF than in F<sub>2</sub>O because the electronegativity of the F atom weakens the OH bond and strengthens the OF bond by attraction of electron density out of the OH

**Table 4.** Internal coordinate force constants<sup>a,b</sup> for CF<sub>3</sub>OF and CF<sub>3</sub>OCl

Force constant <sup>c</sup>	CF <sub>3</sub> OF	CF <sub>3</sub> OCl
<i>r</i>	6.950	6.950
<i>l</i>	5.200	5.200
<i>d</i>	3.850	2.800
<i>α</i>	2.000	2.050
<i>β</i>	1.200	1.150
<i>γ</i>	1.800	1.700
<i>τ</i>	0.0167	0.0161
<i>rr</i>	0.900	0.900
<i>rl</i>	0.850	0.900
<i>ld</i>	1.000	0.300
<i>rα</i> (opp.)	0.120	0.120
<i>rα'</i> (adj.)	0.910	0.910
<i>rbeta</i> (adj.)	0.750	0.700
<i>rbeta'</i> (opp.)	0.100	0.100
<i>lα</i>	0.200	0.200
<i>lβ</i>	0.600	0.600
<i>lγ</i>	0.000	0.100
<i>dγ</i>	0.250	0.100
<i>αα</i>	0.300	0.350
<i>αβ</i> (opp.)	0.000	0.000
<i>αβ'</i> (adj.)	0.150	0.150
<i>ββ</i>	0.100	0.100

<sup>a</sup> Stretching constants in units of millidynes per angstrom. Stretch-bend interaction constants in units of millidynes per radian. Bending and torsion constants in units of millidyne angstrom per square radian.

<sup>b</sup> See Fig. 3 for definition of these internal coordinates.

<sup>c</sup> For torsions  $\nu_n$  (kcal mol<sup>-1</sup> rad<sup>-2</sup>) = 287.9*n*<sup>-2</sup>  $\tau$  (mdyne Å rad<sup>-2</sup> molecule<sup>-1</sup>). For the CF<sub>3</sub> torsion *n* = 3 but the GMAT program<sup>29</sup> has already taken into account *n* = 3 so *n* = 1 must be used on the right hand side of the equation to give  $\nu_3$  = 287.9 $\tau$ . For a program not taking *n* = 3 into account, the proper  $\tau$  value would be a factor of 9 (*n*<sup>2</sup> for *n* = 3) greater than the one in this table. See Ref. 17 and Ref. 18 Appendix B for further discussion.

bond into the OF bond. For such a change competition it seems reasonable that the CF<sub>3</sub> group of electronegativity 3.3 to 3.4<sup>41</sup> would be better able to compete with the F atom for electron density over the CF<sub>3</sub>OF frame than the H atom would with the F atom over the HOF frame. Thus, an upper limit for *d*(OF) in CF<sub>3</sub>OF might be expected to be smaller than in HOF and near to F<sub>2</sub>O. The *d*(OF) value of 3.56 in ClO<sub>3</sub>OF where the ClO<sub>3</sub> group has an electronegativity of 3.25 to 3.4<sup>42</sup> represents a reasonable lower limit. The value *d*(OF) = 3.85 in Table 4 is near the middle of the range from 3.56 to about 4.00 and close to the value for F<sub>2</sub>O.

Values of *d*(OCl) in mdyne Å<sup>-1</sup> are 3.68, 2.75, 2.65 and 3.09 for HOCl,<sup>37</sup> Cl<sub>2</sub>O,<sup>33</sup> ClO<sub>3</sub>OCl<sup>39</sup> and ClO<sub>3</sub>OClO<sub>3</sub>,<sup>38</sup> respectively. The electronegativity argument of Noble and Pimentel can be applied to HOCl, Cl<sub>2</sub>O and CF<sub>3</sub>OCl. Then, *d*(OCl) in CF<sub>3</sub>OCl should be lower than in HOCl but now the CF<sub>3</sub> group is more electronegative than the Cl atom (3.3–3.4 compared to 3.0), rather than being less electronegative than the F atom in CF<sub>3</sub>OF. The *d*(OCl) value of 2.65 in ClO<sub>3</sub>OCl, where the ClO<sub>3</sub> group has an electronegativity of 3.25 to 3.4, represents a reasonable lower limit. The *d*(OCl) values of 3.09 in ClO<sub>3</sub>OClO<sub>3</sub> as a normal ClO single bond gives a reasonable upper limit. The value *d*(OCl) = 2.80 in Table 4 is near the middle of the range from 2.65 to 3.09 and close to the value for Cl<sub>2</sub>O.

**Table 5. Potential energy distribution<sup>a</sup> for CF<sub>3</sub>OX (X = F, Cl) and comparison of calculated and observed frequencies<sup>b</sup>**

		A' symmetry															
<i>i</i>		1		2		3		4		5		6		7		8	
X		F	Cl	F	Cl	F	Cl	F	Cl	F	Cl	F	Cl	F	Cl	F	Cl
$\nu_i$ calc (cm <sup>-1</sup> )		1321	1309	1214	1208	941	935	883	774	674	658	589	571	420	348	267	217
$\nu_i$ obs (cm <sup>-1</sup> )		1294	1271	1222	1213	947	919	882	780	678	665	585	557	429	393	278	233
<i>i</i>	$F_i$																
1	<i>r-rr</i>	76	89	17	5	5				6							
2	<i>r+2rr</i>			38	41	60	65			6	5						
3	<i>l</i>	12	5	54	67	8	16	18		11	15			5		6	
4	<i>d</i>					7		76	51	12	9		8	8	30		
5	*	5		38	46			5		36	48		12	5	10	6	
6	$\alpha-\alpha\alpha$	16	18									12	5	10	6		
7	$\gamma$	11	9			8		5	22	17	8		61	73	24	12	
8	$\beta-\beta\beta$	10	10					7	14					29	38	58	44

$$* = \{(\alpha + \beta)/2 + \alpha\alpha + \beta\beta - \alpha\beta - 2\alpha\beta'\}$$

		A'' symmetry							
<i>i</i>		9		10		11		12	
X		F	Cl	F	Cl	F	Cl	F	Cl
$\nu_i$ calc (cm <sup>-1</sup> )		1256	1262	616	613	429	422	128	108
$\nu_i$ obs (cm <sup>-1</sup> )		1261	1230	607	609	431	430	127	108
<i>i</i>	$F_i$								
9	<i>r-rr</i>	105	104	8	8				
10	$\alpha-\alpha\alpha$	20	20	55	57	31	30		
11	$\beta-\beta\beta$	12	11	15	13	76	77		5
12	$\tau$							96	96

<sup>a</sup> The numbers in the table give the contributions to the potential energy of the various diagonal elements of the symmetrized F matrix ( $100 L_{kk}^2 F_{kk}/\lambda_i$ ). Numbering of the symmetrized force constants,  $F_i$ , and the normal mode frequencies,  $\nu_i$  are identical to the numbering of the symmetry coordinates in Table 3. The expression for each symmetrized force constant,  $F_i$ , in terms of the force constants in Table 4 is included in the table. Contributions of less than 5% are not included in the table. The sum of the entries in each column will be 100 when positive contributions from diagonal elements of less than 5% and both positive and negative contributions from off diagonal elements are included.

<sup>b</sup> The frequencies for CF<sub>3</sub>OF are from gas phase IR spectra (Table 1) except for the CF<sub>3</sub> torsion which is from the gas phase Raman spectra of Smardzewski and Fox.<sup>8,24</sup> The frequencies for CF<sub>3</sub>OCl are from gas phase IR spectra (Table 1) with two exceptions: 430 cm<sup>-1</sup> from the Raman spectrum of the liquid and 108 cm<sup>-1</sup> estimated as the Raman frequency of the liquid less 12% which is the percentage decrease from the liquid frequency to the gas frequency for the CF<sub>3</sub> torsion in CF<sub>3</sub>OF.

The potential energy distributions in Table 5 show that extensive mixing of the symmetry coordinates in Table 3 occurs in some of the normal modes<sup>43</sup> as might be expected for molecules with atoms of similar masses. Potential energy distributions based on internal coordinates and the corresponding force constants in Table 4 are available elsewhere.<sup>44</sup> Using either potential energy distribution, five modes, all in the A' block under C<sub>s</sub> symmetry, differ somewhat between CF<sub>3</sub>OF and CF<sub>3</sub>OCl; they are  $\nu_s(\text{CF}_3)A'$ ,  $\nu(\text{OX})A'$ ,  $\delta_s(\text{CF}_3)A'$ ,  $\delta(\text{COX})A'$ ,  $\rho(\text{CF}_3)A'$ . The normal mode symbols used in Table 1, based on the symbols of the symmetry coordinates in Table 3, may be classified as reasonable or misleading depending upon whether or not the following criterion is met: the appropriate symmetry coordinate makes the dominant contribution<sup>45</sup> to the potential energy distribution. By that criterion, all four modes in the A'' block but less than half the modes in the A' block have reasonable symbols in Table 1.<sup>46</sup> The normal modes whose symbols in Table 1 are misleading are in two categories: those where the symmetry coordinate for which the mode is named makes the largest but not the dominant contribution<sup>47</sup> and those where another symmetry coordinate makes the largest contribution.<sup>48</sup> Inspection of Table 5 suggests several changes<sup>49</sup> for the

normal mode symbols in Table 1, with the result that the simple symbols  $\nu(\text{CO})A'$ ,  $\delta_s(\text{CF}_3)A'$ ,  $\delta(\text{COX})A'$  and  $\rho(\text{CF}_3)A'$  will no longer occur in the A' block, and the mode conventionally labeled as  $\nu(\text{CO})A'$  becomes  $\nu_s(\text{CF}_3)A'$ .

The acceptance of the view stated previously that values of  $d(\text{OX})$  in CF<sub>3</sub>OX compounds are close to  $d(\text{OX})$  in the corresponding X<sub>2</sub>O compounds supports the acceptance of the force constant values in Table 4 and the potential energy distribution in Table 5 as reasonable. Although a normal coordinate analysis should not normally be said to confirm an assignment absolutely, the results are useful for suggesting alternatives and reasonable conclusions from contradictory data. Here the result that a CF<sub>3</sub> rocking frequency of A'' symmetry should be above 400 cm<sup>-1</sup> led to the recognition that one of two bands between 200 and 300 cm<sup>-1</sup> could be  $2\tau(\text{CF}_3)A'$  and prompted our detailed investigation of the CF<sub>3</sub> torsion.<sup>17</sup> The reversal of the CO stretching and OF stretching assignment of Wilt and Jones for CF<sub>3</sub>OF by Smardzewski and Fox<sup>8</sup> is supported, although the name CO stretching is misleading.<sup>48,49</sup> For CF<sub>3</sub> compounds of C<sub>s</sub> symmetry the assignment of one of the bands in the 1150–1350 cm<sup>-1</sup> region to the antisymmetric CF<sub>3</sub> stretch of A'' symmetry is often

ambiguous. Our results here for CF<sub>3</sub>OX compounds and elsewhere for the CF<sub>3</sub>OOX series<sup>18</sup> suggest that the intermediate frequency of the three bands between 1150 and 1350 cm<sup>-1</sup> belongs in the A'' block.

## SUMMARY

1. The reassignment of  $\nu(\text{OF})A'$  in CF<sub>3</sub>OF by Smardzewski and Fox is consistent with our normal coordinate analysis.
2. For both CF<sub>3</sub>OF and CF<sub>3</sub>OCl,  $\rho(\text{CF}_3)A''$  is assigned near 430 cm<sup>-1</sup> and the two bands between 200 cm<sup>-1</sup> and 300 cm<sup>-1</sup> are assigned to a fundamental involving both  $\rho(\text{COX})A'$  and  $\delta(\text{COX})A'$  and to a  $\Delta\nu = 2$  transition in  $\tau(\text{CF}_3)A''$ .
3. An extra band at 548 cm<sup>-1</sup> in the Raman spectrum of liquid CF<sub>3</sub>OCl is assigned to a CF<sub>3</sub>OCl...Cl<sub>2</sub> complex.
4. The force constants  $d(\text{OX})$  for CF<sub>3</sub>OX molecules

are suggested to be near in value to  $d(\text{OX})$  for X<sub>2</sub>O molecules.

5. More than half the normal modes of A' symmetry show extensive mixing of symmetry coordinates.
6. For some normal modes of A' symmetry, the symmetry coordinate for which the normal mode is named is the largest but not the dominant contributor to the potential energy distribution.<sup>47</sup>
7. For other normal modes of A' symmetry, the symmetry coordinate for which the mode is named is not even the largest contributor to the potential energy distribution.<sup>48</sup>
8. No normal modes of A' symmetry are present in which  $\nu(\text{CO})A'$ ,  $\delta_s(\text{CF}_3)A'$ ,  $\delta(\text{COX})A'$ , or  $\rho(\text{CF}_3)A'$  symmetry coordinates are dominant.
9. The normal mode conventionally labeled as  $\nu(\text{CO})A'$  should be labeled as  $\nu_s(\text{CF}_3)A'$ .
10. For the remaining A' normal modes and all the A'' normal modes, the symmetry coordinate for which the normal mode is named is dominant in the potential energy distribution.

## NOTES AND REFERENCES

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27. Since low temperature should favor complex formation, the complex is probably not present in the gaseous CF<sub>3</sub>OCl at room temperature. Even if the complex were present in the gas it would probably be too weak to cause the IR inactive stretching of gaseous Cl<sub>2</sub> to become observable in the IR spectrum of the gaseous complex. Thus, the absence of a 548 cm<sup>-1</sup> band in the IR spectrum of gaseous CF<sub>3</sub>OCl at room temperature is consistent with the presence of a weak CF<sub>3</sub>OCl...Cl—Cl complex at low temperature.
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30. For CF<sub>3</sub>OX the structural parameters are the CF, CO and OX bond lengths and the five angles: FCF angle or  $\alpha$ , tilt angle or  $\beta$ , COX angle or  $\gamma$ , the angle each CF bond makes with the C<sub>3</sub> axis of the CF<sub>3</sub> group or  $\delta$ , and the FCO angle for the F atom in the FCOX plane or  $\theta$ . Specification of  $\alpha$  and  $\beta$  fixes the angles  $\delta$  and  $\theta$  since only two of the four angles  $\alpha$ ,  $\beta$ ,  $\delta$  and  $\theta$  are independent. The angle of tilt,  $\beta$ , is in the FCOX plane between the C<sub>3</sub> axis of the CF<sub>3</sub> group and the C—O bond. For a positive angle of tilt the F atom in the FCOX plane is closer to the O atom than are the two out-of-plane F atoms. The following structural parameters were used for both CF<sub>3</sub>OF and CF<sub>3</sub>OCl: R(C—F) = 1.319 Å, R(C—O) = 1.395 Å,  $\alpha = 109.4^\circ$ ,  $\beta = 4.1^\circ$ ,  $\delta = 70.5^\circ$ ,  $\theta = 105.4^\circ$ . For CF<sub>3</sub>OF, R(O—F) = 1.421 Å, and  $\gamma = 104.8^\circ$ . For CF<sub>3</sub>OCl, R(O—Cl) = 1.70° and  $\gamma = 112.8^\circ$ . These two parameters were estimated by comparison of CF<sub>3</sub>OF with F<sub>2</sub>O<sup>31</sup> and F<sub>2</sub>O<sup>31</sup> with Cl<sub>2</sub>O<sup>31</sup>. Since the OF bonds in CF<sub>3</sub>OF and F<sub>2</sub>O differ by only about 0.01 Å, the O—Cl bond length from Cl<sub>2</sub>O is used for CF<sub>3</sub>OCl. Since the Cl—O—Cl angle in Cl<sub>2</sub>O is 8° larger than the F—O—F angle in F<sub>2</sub>O, the Cl—O—Cl angle in CF<sub>3</sub>OCl is taken as 8° larger than the C—O—F angle in CF<sub>3</sub>OF. The principal moments of inertia for CF<sub>3</sub>OF in amu-Å<sup>2</sup> are 89.6, 164.6 and 166.0 and the asymmetry parameter is -0.98. The principal moments of inertia for CF<sub>3</sub>OCl in amu-Å<sup>2</sup> are 89.6, 254.9 and 256.4 and the asymmetry parameter is -0.99. The  $\alpha$ ,  $\beta$ ,  $\gamma$  and  $\delta$  used in this note are defined in Fig. 1 of Ref. 5 and do not correspond to the angles defined in our Fig. 3 in all cases.



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44. See Table 15 in Ref. 18.
45. A symmetry coordinate is classified as making the dominant contribution to a column in Table 5 if the corresponding entry is greater than 67% of the sum of the entries in that column or if the corresponding entry is a factor of 4 or more larger than the next largest entry in that column.
46. The normal modes in the  $A'$  block that have reasonable symbols in Table 1 are:  $\text{CF}_3\text{OF}$ ,  $\nu_{\text{as}}(\text{CF}_3)A'$ ,  $\nu(\text{OF})A'$  and  $\delta_{\text{as}}(\text{CF}_3)A'$ ;  $\text{CF}_3\text{OCl}$ ,  $\nu_{\text{as}}(\text{CF}_3)A'$  and  $\delta_{\text{as}}(\text{CF}_3)A'$ .
47. The normal mode symbols where the symmetry coordinate for which the normal modes is named makes the largest but not the dominant contribution are:  $\text{CF}_3\text{OF}$ ,  $\delta_{\text{s}}(\text{CF}_3)A'$ , and  $\rho(\text{CF}_3)A'$ ;  $\text{CF}_3\text{OCl}$ ,  $\nu(\text{OCl})A'$  and  $\delta_{\text{s}}(\text{CF}_3)A'$ .
48. The normal mode symbols where another symmetry coordinate makes the largest contribution are:  $\text{CF}_3\text{OF}$ ,  $\nu_{\text{s}}(\text{CF}_3)A'$ ,  $\nu(\text{CO})A'$  and  $\delta(\text{COF})A'$ ;  $\text{CF}_3\text{OCl}$ ,  $\nu_{\text{s}}(\text{CF}_3)A'$ ,  $\nu(\text{CO})A'$ ;  $\delta(\text{COCl})A'$  and  $\rho(\text{CF}_3)A'$ .
49. See Table 1, footnote e.

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