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Vibrational Analysis of the Ground States of Trifluoroacetyl Fluoride and Trifluoroacetyl Chloride

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The vibrational frequencies, normal modes of vibration, and force constants of CF_3COF and CF_3COCl are calculated using the MP2/6-31G(d′) method. Our calculations agree with those of Pacansky et al. in showing that the values of the ν_6, ν_7, ν_8, ν_{12}, and ν_{13} experimental frequencies of CF_3COF need to be reassigned. Our calculations also show that the same experimental frequencies in CF_3COCl need to be reassigned. The calculated force constants are improved by fitting them to the reassigned experimental vibrations. The simple descriptions of vibrational motion previously given are shown to be inaccurate for most vibrations.

I. Introduction

Trifluoroacetyl fluoride (CF_3COF) and trifluoroacetyl chloride (CF_3COCl) are stable compounds that are formed by the degradation of hydrofluorocarbons (HFCs) and hydrochlorfluorocarbons (HCFCs) in the troposphere.[1] The replacement of the chlorofluorocarbons by HFCs and HCFCs in air conditioners, for foam blowing, and as cleaning solvents has sparked recent interest in determining the properties of CF_3COF and CF_3COCl. Francisco and Williams[2] have investigated the vibrational spectrum of CF_3COF and CF_3COCl. Pacansky et al.[3] and Ottavianelli et al.[4] have studied the vibrational spectrum of CF_3COF. In a separate paper, Ottavianelli et al.[5] calculated the vibrational spectrum of CF_3COCl.

In the 1960s and 1970s, several spectroscopists[6−10] investigated the vibrations of CF_3COF and CF_3COCl. After some initial controversy, these spectroscopic papers agreed on the assignments of vibrational bands to a′ and a″ symmetries of the C_s point group.

Ottavianelli et al.'s[4,5] calculations of the vibrational spectra of CF_3COF and CF_3COCl agreed with the spectroscopic assignments. However, Franscisco and Williams'[2] calculations showed that the ν_7(a′) and ν_{13}(a″) vibrations in CF_3COF were most likely misassigned by the experimental work.[7−9] Pacansky et al., using higher level calculations, found that the ν_6(a′) and ν_{13}(a″) vibrations in CF_3COF had been misassigned.

In this paper, we show that the ν_6(a′) and ν_{13}(a″) vibrations in CF_3COCl need to be reassigned in the experimental work.[6,9,10] Since three calculations[2−4] on the vibrational assignments of CF_3COF do not agree, we have also examined the vibrational assignments of CF_3COF.

We have calculated ab initio force fields for both molecules with second-order, Moller−Plesset perturbation theory (MP2). Using the revised experimental frequencies, we have refined these force fields.

We were curious about the different descriptions of molecular motion that were assigned to vibrations. In many cases, experimentalists disagree on the motion that gives rise to a particular vibration. We investigated the vibrational motions of CF_3COF and CF_3COCl in detail and found that, in some cases, none of the motions assigned to a vibration by different experimentalists agree with the motions formed from the calculated normal modes.

II. Ab Initio Calculations

A. Computational Methods. Figure 1 is a scheme of the CF_3COF and CF_3COCl molecules in their ground-state equilibrium geometries. Our calculations show that the oxygen, carbons, fluorine 5, and fluorine 4 (chlorine 4) all lie in a plane in CF_3COF (CF_3COCl). Fluorine 6 and fluorine 7 are mirror images of each other through this plane. Thus, the molecules have C_s symmetry in their $1^1A'$ ground states.

All geometries and frequencies were calculated with the Gaussian 94 program.[11] Geometries were optimized with both the Hartree−Fock (HF) and MP2[12] methods using a 6-31G(d) basis.[13] Later it was found that the 6-31G(d′) basis[14] which contains optimized polarization functions for fluorine yielded frequencies that were in better agreement with the experimental ones for fluorine compounds; the MP2 calculations were repeated with this basis.

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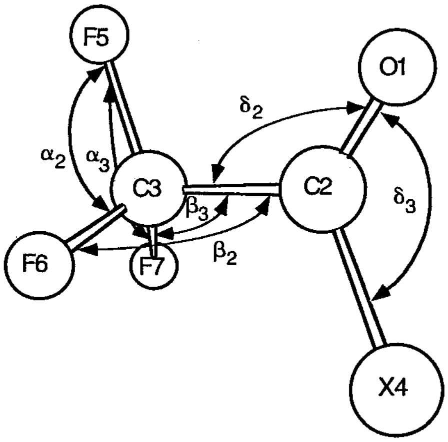

Figure 1. Equilibrium geometry for the $1^1A'$ ground state of CF$_3$COX (X = F, Cl). Some of the angles used in defining internal symmetry coordinates are shown.

The equilibrium geometries of both molecules were determined using analytic gradients,[15] and the frequencies and intensities calculated with analytic second derivatives.[16,17] The calculations of the frequencies provide the force fields,[18] and the normal modes of vibration characterized by a set of atom displacement vectors in Cartesian coordinates.

B. Geometries. Table 1 shows the geometries calculated with the MP2/6-31G(d′) method compared with the experimental geometries determined by Boulet[19] and Brake et al.,[20] both using electron diffraction. Of course, the experimental geometries are averaged over the range of motions the molecules are executing during the experiment, while the calculated equilibrium geometries are frozen in space. Thus, one does not expect exact agreement even with perfect experiments and perfect calculations.

In Table 1 and succeeding tables, the notation ∠A−B−C/D−E−F denotes the dihedral angle between the planes formed by atoms A−B−C and atoms D−E−F. The experimental and calculated angles are in good agreement. The r(C2−C3) bond length in CF$_3$COF, the r(C2−Cl4) bond length in CF$_3$COCl, and the r(C3−C5) and r(C3−F6,F7) bond lengths in both molecules are in good agreement. The calculated r(C2−O1) bond length is longer than the experimental in both molecules. The calculated r(C2−C3) bond length is shorter than the experimental in CF$_3$COCl. The calculated r(C2−F4) bond length is longer than the experimental in CF$_3$COF. If the experimental geometries are accurate, one might expect that the discrepancies in calculated bond lengths would also show as discrepancies in any vibrations dominated by changes in these bonds.

In addition to our MP2 results, we used different levels of theory in order to compare to previous calculations. The geometries of both molecules calculated with different levels of theory are compared in Table 2. The numbers before the slash are for CF$_3$COCl, and the numbers after, for CF$_3$COF. The geometries of Ottavianelli et al.[4,5] (first column) agree almost exactly with the geometries of Francisco and Williams[2] (column 2), as they should since both use the HF/3-21G method. Our MP2/6-31G(d) (column 4) geometry for CF$_3$COF agrees almost exactly with one determined by Pacansky et al.[3] who also used the MP2/6-31G(d) method. The differences between our MP2/6-31G(d) and MP2/6-31G(d′) geometries are small (<0.01 Å for bond lengths), but the MP2/6-31G(d′) bond lengths are closer to the experimental values for almost every change.

As can be seen from column 3, adding a polarization function to the 3-21G basis and including some of the correlation energy by the MP2 method increases all of the bond lengths from those of HF/3-21G method except the r(C2−Cl4) bond length which decreases. There are only small changes in the angles. Columns 4 and 5 show that going to a better basis in MP2 decreases all the bond lengths. There is also a significant decrease in the ∠C3−C2−O1 for both molecules and a significant increase in the ∠C3−C2−Cl4 for CF$_3$COCl. The MP2/6-31G(d) carbon−fluorine bond lengths are all in good agreement with those from the HF/3-21G method, while the r(C2−O1) and r(C2−C3) bond lengths are longer and the r(C2−Cl4) bond length is significantly shorter than those of the HF/3-21G method. Again, these differences can be expected to show up in any vibrations dominated by these bonds.

C. Frequencies and Infrared Intensities. Table 3 shows the frequencies calculated at different levels of molecular orbital theory. Ottavianelli et al.[4,5] (column 1) and Francisco and Williams[2] (column 2) used the same calculational method (HF/3-21G), but there are significant differences in the frequencies they calculated. One reason might be that Ottavianelli et al. used numerical differentiation of analytic gradients to obtain frequencies, while Francisco and Williams were able to use analytic second derivatives. Analytic calculation of frequencies does not have the problems of numerical noise, choice of step size, and convergence difficulties that numerical methods are plagued with.

Even with this difference, some of the assignments of frequencies by Ottavianelli et al. are hard to understand. Their set of frequencies (column 1) for ν_{13} is an excellent match with the ν_8 set of Francisco and Williams (column 2). Frequency ν_5 for CF$_3$COCl in column 1 is an excellent match with ν_{12} for CF$_3$COCl in column 2. For CF$_3$COF, ν_6 in column 1 is a good match with ν_{12} in column 2. Close examination of column 1 shows that if the ν_{13} set is moved to ν_8, ν_5 for CF$_3$COCl is moved to ν_{12}, and ν_6 for CF$_3$COF is moved to ν_{12}, then ν_5, ν_6, ν_7, ν_8, ν_{12}, and ν_{13} are in much better agreement with the frequencies in column 2.

TABLE 1: Comparison of Geometries of CF$_3$COF and CF$_3$COCl from ab Initio Calculations with Those from Experiments (Distances in Angstroms, Angles in Degrees)

	CF$_3$COF			CF$_3$COCl	
	MP2/6-31G(d′)[a]	exptl[b]	exptl[c]	MP2/6-31G(d′)[a]	exptl[b]
r(C2−O1)	1.187	1.171 ± 0.01	1.158 ± 0.007	1.192	1.180 ± 0.02
r(C2−C3)	1.537	1.544 ± 0.015	1.525 ± 0.006	1.548	1.569 ± 0.02
r(C2−X4)[d]	1.338	1.315 ± 0.007	1.324 ± 0.002	1.756	1.750 ± 0.005
r(C3−F5)	1.327	1.330 ± 0.02	1.324 ± 0.002	1.327	1.330 ± 0.005
r(C3−F6,F7)	1.336	1.330 ± 0.02	1.324 ± 0.002	1.334	1.330 ± 0.005
∠C3−C2−O1 (δ_2)	126.6°	131 ± 3	129 ± 2	123.7	126 ± 3
∠C3−C2−X4 (δ_1)[d]	108.9°	108 ± 2	109.6 ± 0.5	111.9	109 ± 3
∠C2−C3−F5 (β_1)	110.2°	109 ± 1	109.6 ± 0.5	109.5	109 ± 1
∠C2−C3−F6,F7 (β_2,β_3)	109.7°	109 ± 1	109.6 ± 0.5	110.1	109 ± 1

[a] This work. [b] Reference 19. [c] Reference 20. [d] X = F, Cl

TABLE 2: Comparison of Geometries for Both Molecules among Different Levels of Calculation[e]

	CF_3COCl/CF_3COF				
	HF/3-21G[a]	HF/3-21G[b]	MP2/3-21G(d)[b]	MP2/6-31G(d)[c]	MP2/6-31G(d′)[c]
r(C2−O1)	1.176/1.175	1.175/1.175	1.244/1.213	1.201/1.193	1.192/1.187
r(C2−C3)	1.516/1.507	1.516/1.508	1.540/1.528	1.539/1.527	1.548/1.537
r(C2−X4)[d]	1.828/1.338	1.830/1.339	1.780/1.380	1.749/1.345	1.756/1.338
r(C3−F5)	1.338/1.334	1.339/1.335	1.367/1.366	1.335/1.333	1.327/1.327
r(C3−F6,F7)	1.338/1.342	1.337/1.342	1.369/1.371	1.343/1.342	1.334/1.336
∠C3−C2−O1 (δ_2)	125.8/127.0	125.8/127.1	125.4/128.1	123.2/126.8	123.7/126.6
∠C3−C2-X4 (δ_1)[d]	110.3/109.5	110.3/109.4	108.7/108.3	112.2/108.7	111.9/108.9
∠C2−C3−F5 (β_1)	109.7/109.4	109.5/109.7	108.9/110.3	109.7/110.3	109.5/110.2
∠C2−C3−F6,F7 (β_2,β_3)	110.3/110.7	110.1/110.0	110.3/110.3	110.1/109.6	110.1/109.7
∠C3−C2−O1/C3−C2-X4[d]	180/180	180/180	180/180	180/180	180/180
∠C3−C2−O1/C3−C2−F5	0/0	0/0	0/0	0/0	0/0
∠C3−C2−Cl4/C2−C3−F6	60/59.55	60/60	60/60	60/59.65	59.99/59.68
∠C3−C2−Cl4/C2−C3−F7	−60/−59.55	−60/−60	−60/−60	−60/−59.65	−59.99/−59.68

[a] Reference 5 for CF_3COCl, and ref 4 for CF_3COF. [b] Reference 2. [c] This work. [d] X = Cl,F. [e] The number before the slash is for CF_3COCl; the number after the slash is for CF_3COF. All bond lengths are in angstroms and angles are in degrees.

TABLE 3: Comparison of Vibrational Frequencies for Both Molecules among Different Levels of Calculation[d]

	CF_3COCl/CF_3COF				
mode	HF/3-21G[a]	HF/3-21G[b]	MP2/3-21G(d)[b]	MP2/6-31G(d)[c]	MP2/6-31G(d′)[c]
a′					
ν_1	2024/2092	2023/2094	1683/1791	1836/1934	1857/1941
ν_2	1447/1456	1451/1454	1315/1314	1340/1403	1322/1388
ν_3	1361/1444	1360/1449	1234/1297	1300/1311	1295/1303
ν_4	959/1249	961/1246	887/1126	960/1137	951/1128
ν_5	*768*/896	757/850	703/771	749/816	757/816
ν_6	759/*834*	607/724	567/661	587/685	596/697
ν_7	609/758	510/620	483/575	522/595	526/604
ν_8	510/608	421/451	391/414	404/425	408/431
ν_9	343/394	344/403	331/375	345/390	346/393
ν_{10}	204/191	203/226	197/211	201/227	200/229
a″					
ν_{11}	1425/1409	1420/1408	1283/1275	1262/1260	1258/1251
ν_{12}	531/539	763/826	703/742	708/764	717/775
ν_{13}	*421/449*	525/533	488/495	504/512	520/526
ν_{14}	250/263	251/248	231/227	234/237	235/240
ν_{15}	67/157	50/46	41/39	43/47	42/45

[a] Reference 5 for CF_3COCl and ref 4 for CF_3COF. [b] Reference 2. [c] This work. [d] The number before the slash is for CF_3COCl; the number after the slash is for CF_3COF. All values are in cm^{-1}. Questionable assignments are in italic type.

However the normal mode for the ν_{13} vibration has a″ symmetry, while the ν_5 normal mode for CF_3COCl and the ν_6 normal mode for CF_3COF have a′ symmetry. Examination of the normal modes should clearly distinguish the a′ frequencies from the a″ frequencies. Perhaps Ottavianelli et al. did not have the normal modes for examination and were influenced by the experimental assignments.

The HF/3-21G frequencies in column 1 are consistently larger than the MP2 frequencies. The MP2/3-21G frequencies are consistently smaller than the MP2/6-31G(d) and MP2/6-31G(d′) frequencies. Our MP2/6-31G(d) frequencies agree almost exactly with the MP2/6-31G(d) frequencies calculated by Pacansky et al.[3] The MP2/6-31G(d) frequencies and MP2/6-31G(d′) frequencies have small differences, but, as Table 4 will show, the MP2/6-31G(d′) frequencies are closer to the experimental ones.

The MP2/6-31G(d′) frequencies and infrared intensities are compared with experimental ones in Table 4. On the basis of their MP2/3-21G(d) frequencies for CF_3COF, Francisco and Williams[2] decided that the 692 cm^{-1}(ν_7) and 426 cm^{-1}(ν_{13}) vibrations in column 3 were misassigned in the experimental work of Berney.[8] They reassigned the 692 cm^{-1} vibration as ν_{13} which has a normal mode symmetry of a″ and the 426 cm^{-1} vibration as ν_8 which has a normal mode symmetry of a′. Pacansky et al.[3] based on their much better MP2/6-31G(d) frequencies, assigned the 760 cm^{-1} vibration in their experimental spectrum (column 2) as ν_{12} and assigned their 692 cm^{-1} vibration as ν_6. Our calculations agree with the assignment of the 692 cm^{-1} vibration as ν_6, the 595 cm^{-1} vibration as ν_7, the 426 cm^{-1} vibration as ν_8, the 761 cm^{-1} vibration as ν_{12}, and the 519 cm^{-1} vibration as ν_{13}. The rest of the frequencies in column 3 agree very well with the MP2/6-31G(d′) frequencies (column 1) when these changes are made.

Because of the inaccuracy of their MP2/3-21G(d) frequencies for CF_3COCl, Francisco and Williams could not determine if any experimental frequencies should be reassigned. Our MP2/6-31G(d′) frequencies for CF_3COCl (column 4) show that some experimentally determined vibrations in columns 5 and 6 should be reassigned. The 583 cm^{-1} vibration in columns 5 and 6 should be assigned as ν_6, the 511 cm^{-1} vibration should be assigned as ν_7, the 390 cm^{-1} vibration in column 5 (411 cm^{-1} vibration in column 6) should be reassigned as ν_8, the 703 cm^{-1} should be assigned as ν_{12}, and the 517 cm^{-1} vibration should be assigned as ν_{13}. These reassignments are very similar to the reassignments done for CF_3COF. After these changes are made to the experimental frequencies in columns 5 and 6, the experimental frequencies are in excellent agreement with the MP2/6-31G(d′) frequencies (column 4). The ratios of the experimental frequencies after reassignments to the MP2/6-31G(d′) frequencies vary from 0.96 to 1.07. Furthermore, the infrared intensity calculated for ν_8 in column 4 agrees much

TABLE 4: Comparison of Calculated and Experimental Frequencies and Infrared Intensities[f]

	CF_3COF			CF_3COCl		
mode	MP2/6-31G(d′)[a]	exptl[b]	exptl[c]	MP2/6-31G(d′)[a]	exptl[d]	exptl[e]
a′						
ν_1	1941 (168)	1897 (48)	1899 (s)	1857 (225)	1811 (vs)	1821
ν_2	1388 (96)	1334 (30)	1340 (m)	1322 (98)	1284 (s)	1284
ν_3	1303 (321)	1253 (86)	1254 (vs)	1295 (253)	1240 (vs)	1240
ν_4	1128 (291)	1098 (80)	1099 (vs)	951 (291)	937 (vs)	933
ν_5	816 (7)	805 (6)	806 (w)	757 (72)	750 (s)	750
ν_6	697 (47)	692	*761 (m)*	596 (8)	*703 (m)*	*703*
ν_7	604 (2)		692 (m)	526 (19)	583 (m)	583
ν_8	431 (2)		595 (w)	408 (0.2)	511 (ms)	511
ν_9	393 (0.1)		390 (w)	346 (3)	334 (m)	334
ν_{10}	229 (4)		228 (mw)	200 (2)	198 (mw)	198
a″						
ν_{11}	1251 (295)	1200 (75)	1214 (vs)	1258 (291)	1202 (vvs)	1202
ν_{12}	775 (14)	760 (14)	519 (m)	717 (4)	517 (ms)	517
ν_{13}	526 (8)		*426 (w)*	520 (7)	*390 (mw)*	*411*
ν_{14}	240 (6)		242 (m)	235 (4)	234 (m)	234
ν_{15}	45 (0.6)		50	42 (0.5)		45

[a] This work [b] Reference 3. [c] Reference 8. [d] Reference 6. [e] Reference 10. [f] The intensities are in parentheses in the table. The frequencies are in units of cm^{-1}, and the intensities are in km/mol. Questionable assignments are in italic type.

better with the infrared intensity of the reassigned 390 cm^{-1} band in column 5.

The infrared intensities appear as the numbers or letters in parentheses in Table 4. The infrared intensities determined with the MP2/6-31G(d′) method are in qualitative agreement with the intensities noted by Berney[6,8] after the vibrations are reassigned. In Berney's notation, "vs" stands for "very strong", "vvs" for "very, very strong", "s" for "strong", "m" for "medium", "ms" for "medium strong", "w" for "weak", and "mw" for "medium weak". For CF_3COF, the MP2/6-31G(d′) intensities are about a factor of 3.5 higher than the intensities measured by Pacansky et al.[3] Other investigators[21,22] have found that intensities calculated with the MP2/6-31G(d) method are generally 1.5 to 2 times larger than but in qualitative agreement with the experimental ones.

The infrared spectrum of CF_3COCl and CF_3COF consists of broad bands. It is difficult to determine the symmetry of the weaker bands in these molecules. Berney[6,8] used Raman spectra to assist him in determining the symmetries of the vibrations. The scattered light should be polarized if it comes from an a′ vibration and depolarized if it comes from an a″ vibration. For CF_3COCl, he determined that the 390 cm^{-1} was depolarized but the infrared band had a PQR structure that indicates it is of a′ symmetry.[6] Thus, there was an ambiguity about what symmetry should be assigned to the 390 cm^{-1} band. The 703 cm^{-1} band was extremely weak in the Raman spectrum making it difficult to determine the polarization. Berney decided on a′ symmetry for this band assuming it occurred with ν_{12} as a pair of CF_3 asymmetric deformations. As will be shown in section IV, it can be misleading to assign simple motions to the vibrations of these molecules.

In CF_3COF, Berney[8] measured the depolarization ratios of the Raman spectrum; the sampling geometry indicated that the depolarization ratio should be greater than or equal to 0.75 for a depolarized line (a″ symmetry). He assigned the 426 cm^{-1} to a″ symmetry on the basis of a 0.72 depolarization ratio. There is some ambiguity in this designation since the 692 cm^{-1} Raman band was assigned a′ symmetry with a depolarization ratio of 0.63. The 761 cm^{-1} band appears in the Raman spectrum as one of two very weak overlapping bands at 770 and 758 cm^{-1}.[8] Berney chose the 770 cm^{-1} with a depolarization ratio of 0.15 to be the 761 cm^{-1} band and thus to have a′ symmetry. He assigned the 758 cm^{-1} band as a combination of the ν_{10} and ν_{12} bands, both of a″ symmetry. The ambiguity in the 761 cm^{-1} band assignment is in deciding which of these two weak bands in the Raman spectrum represents it.

TABLE 5: Descriptions of Vibrational Motions by Different Experimentalists[a]

	CF_3COCl/CF_3COF		
mode	exptl frequency	ref 9	ref 8
η_1	1821/1897	CO str./CO str.	CO str./CO str.
η_2	1284/1334	CF_3 str./CF_3 str.	CF_3 str./CF str.
η_3	1240/1253	FCF_2 str./FCF_2 str.	FCF_2 str./FCF_2 str.
η_4	933/1098	CCCl str.(oop)/CF str.	CC str./CF_3str.
η_5	750/805	CF_3 def./CC str.	CCl str./CC str.
η_6	583/692	CCO def./OCF def.	FCF_2 def./CF_3 def.
η_7	511/595	FCF_2 def./CF_3 def.	OCCl def./OCF def.
η_8	411/426	CCCl str.(ip)/FCF_2 def.	CF_3 def./FCF_2 def.
η_9	334/390	antigear rock/antigear rock	rock/rock
η_{10}	198/228	gear rock/gear rock	CF_3 rock/CF_3 rock
η_{11}	1202/1200	CF_2 str./CF_2 str.	CF_2 str./CF_2 str.
η_{12}	703/761	CF_2 def./CF_2 def.	OCCl wag/CF_2 def.
η_{13}	517/519	antigear wag/antigear wag	CF_2 def./OCF wag
η_{14}	234/242	gear wag/gear wag	CF_3 wag/CF_3 wag
η_{15}	45/50	CF_3 torsion/CF_3 torsion	CF_3 torsion/CF_3 torsion

[a] The number before the slash is for CF_3COCl; the number after the slash is for CF_3COF. Frequencies are in cm^{-1}, and some assignments are modified as described in the text.

The purpose of the above discussion is to illustrate the problems that may arise in making symmetry assignments from infrared or Raman spectra. Calculations at a suitable level of molecular orbital theory can be of assistance in assigning vibrations since the normal modes yield an unambiguous identification of the symmetries of the vibrations.

In section II.A., the idea was presented that differences in bond lengths may result in differences in vibrational frequencies. The reasoning is that a shorter bond length implies a stronger force constant which indicates a larger vibrational frequency if the vibration depends primarily on that bond. This idea is examined below based on the data in Tables 2 and 3.

Table 5 shows the descriptions for vibrational motions of CF_3COCl and CF_3COF presented by Berney and Cormier[10] and Redington.[9] Both investigators describe the ν_1 vibration as a CO stretch. In Table 2, $r_3(C2-O1) > r_4(C2-O1) > r_5(C2-O1) > r_2(C2-O1)$ for both CF_3COCl and CF_3COF, where the subscript denotes the column in Table 2. If our reasoning is correct and the description is accurate, then $\nu_1(3) < \nu_1(4) <$

TABLE 6: Symmetry Coordinates Used for Refining the Force Fields of CF_3COF and CF_3COCl

symmetry	definition	description
a′		
	$S_1 = r(C2{-}O1)$	CO stretch
	$S_2 = r(C2{-}X4)^a$	CX stretch[a]
	$S_3 = r(C2{-}C3)$	CC stretch
	$S_4 = r(C3{-}F5)$	CF stretch
	$S_5 = r(C3{-}F6) + r(C3{-}F7)$	CF_2 stretch
	$S_6 = \angle C3{-}C2\text{-}X4^a$	CCX bend[a]
	$S_7 = (\delta_2{-}\delta_3)^b$	CO wag
	$S_8 = \angle C2{-}C3{-}F5$	CF deformation
	$S_9 = (-\alpha_2 - \alpha_3 + \beta_2 + \beta_3)^c$	CF_2 wag
	$S_{10} = \angle F6{-}C3{-}F7$	CF_2 bend
a″		
	$S_{11} = r(C3{-}F6) + r(C3{-}F7)$	CF_2 stretch
	$S_{12} = (\alpha_2 - \alpha_3 + \beta_2 - \beta_3)^c$	CF_2 twist
	$S_{13} = (\alpha_2 - \alpha_3 - \beta_2 + \beta_3)^c$	CF_2 rock
	$S_{14} = \angle C3 - C2 - X4/C3 - C2 - 01^a$	CO wag
	$S_{15} = (\tau_1 + \tau_2 + \tau_3)^d$	CF_3 torsion

[a] X = F, Cl. [b] $\delta_2 = \angle C3{-}C2{-}O1$, $\delta_3 = \angle O1{-}C2{-}X4$, where X = F, Cl. [c] $\alpha_2 = \angle F5{-}C3{-}F7$, $\alpha_3 = \angle F5{-}C3{-}F6$, $\beta_2 = \angle C2{-}C3{-}F6$, $\beta_3 = \angle C2{-}C3{-}F7$. [d] $\tau_1 = \angle O1{-}C2{-}C3{-}F5$, $\tau_2 = \angle O1{-}C2{-}C3{-}F6$, $\tau_3 = \angle O1{-}C2{-}C3{-}F7$.

$\nu_1(5) < \nu_1(2)$ where the number in parentheses denotes the column in Table 3. Examination of Table 3 shows that this is the case, lending credence to the vibration being caused by the CO bond stretching and contracting. However, this is the only case where this simple model agrees with the experimental descriptions. Vibrations described as arising from simple motions such as the CC stretch (ν_4 for CF_3COCl, ν_5 for CF_3COF), CF stretch (ν_5 for CF_3COF), and CCl stretch (ν_5 for CF_3COCl) do not even approximately fit this model. While the model may be naive, it does cast doubt on the simple descriptions of vibrational motion in Table 5.

III. Refinement of Force Fields

The frequencies are calculated using the harmonic approximation. The observed frequencies include anharmonic effects that are not accounted for in the calculations. Furthermore, the observed frequencies may be perturbed by Fermi resonances. The MP2/6-31G(d′) harmonic frequencies are in excellent agreement with the observed anharmonic ones with the largest deviation being 4%. The large amplitude ν_{15} frequency, that has a deviation of 7% for CF_3COCl and 11% for CF_3COF, is not included in this analysis. Since the observed value for ν_{15} is 45 cm^{-1} for CF_3COCl, the 7% discrepancy is only 3 cm^{-1}; for CF_3COF, ν_{15} is 50 cm^{-1} so the discrepancy is 5 cm^{-1}. The agreement between calculated harmonic and observed frequencies indicates that anharmonic effects are small in CF_3COF and CF_3COCl or there is a fortuitous cancellation of errors in the calculations.

As shown in Table 4, the largest differences between the harmonic and observed frequencies is ν_2 with 54 cm^{-1} and ν_3 with 50 cm^{-1} for CF_3COF, and ν_3 with 55 cm^{-1} and ν_2 with 38 cm in CF_3COCl. These differences are large enough to indicate that the calculated force field may not be useful for spectroscopic purposes. Therefore, the force field was improved by using the calculated force field and geometry and the experimental frequencies in a program developed by Schachtschneider[23] and refined by Dempsey.[24]

Table 6 shows the internal symmetry coordinates used for refining the force field calculated with Gaussian 94. Some of the angles used in these symmetry coordinates are shown in Figure 1. The calculated equilibrium geometry and symmetry coordinates were used as input to form the $\underline{\underline{B}}'$ matrix which relates the symmetry coordinates, $\underline{S}$, and the Cartesian coordinates, $\underline{X}$ by

$$\underline{S} = \underline{\underline{B}}'\,\underline{X} \qquad (1)$$

and the $\underline{\underline{G}}$ matrix defined by

$$\underline{\underline{G}} = \underline{\underline{B}}'\underline{\underline{M}}^{-1}(\underline{\underline{B}}')^T \qquad (2)$$

where $\underline{\underline{M}}$ is a $3N \times 3N$ diagonal matrix with the mass of each of the N atoms appearing three consecutive times on the diagonal.[25] To convert the force constants in Cartesian coordinates, $\underline{\underline{F}}_x$, that were calculated in Gaussian 94 to force constants in symmetry coordinates, $\underline{\underline{F}}$, a square matrix is required. The $3N \times 3N$ matrix $\underline{\underline{B}}$ is formed by adding the six Eckart conditions to $\underline{\underline{B}}'$. The force constant matrix in symmetry coordinates is[18]

$$\underline{\underline{F}} = (\underline{\underline{B}}^T)\underline{\underline{F}}_x\underline{\underline{B}}^{-1} \qquad (3)$$

The experimental frequencies, the $\underline{\underline{F}}$ and $\underline{\underline{G}}$ matrices, and a vector, $\underline{\varphi}$, of 17 scaling factors were used as input to adjust the force constants in $\underline{\underline{F}}$ to determine the best least-squares fit to the experimental frequencies. The vector $\underline{\varphi}$ is composed of one scaling factor for each diagonal force constant, a scaling factor for the off-diagonal a′ force constants, and a scaling factor for the off-diagonal a″ force constants. Since there are only 15 experimental frequencies to fit, the off-diagonal scaling factors were set to a reasonable value; the program was allowed to adjust the diagonal scaling factors until the root-mean-square (rms) error was no longer decreasing. One of the off-diagonal scaling factors was then adjusted by trial and error until the rms error was decreasing again. When the improvement halted, the other off-diagonal scaling factor was adjusted. This procedure was continued until no further improvement in rms error occurred.

When no further improvement was obtainable for CF_3COCl, the rms error between the refined and experimental frequencies was 8.45 cm^{-1}. For CF_3COF, the rms error was 7.81 cm^{-1} when no further improvement in the least-squares fit could be obtained. The scale factors, sf2, in Tables7 and 8 are the final φ values for the diagonal force constants for CF_3COF and CF_3COCl, respectively.

The improved frequencies and diagonal force constants are shown in Tables 7 and 8. Table 9 shows the a′ off-diagonal force constants for CF_3COCl and CF_3COF, and Table 10 shows the a″ off-diagonal force constants. For both molecules, ν_2 is the vibration that has the largest disagreement with its experimental values. This raises the possibility that the ν_2 vibrations are perturbed in the experimental spectra. It is noteworthy that the 511 and 517 cm^{-1} experimental vibrations of CF_3COCl have two of the largest changes in force constants as indicated by scale factor 2 in Table 7. Berney[6] declared these two vibrations as the hardest to assign symmetry. It is possible that the assignment of these two frequencies should be reversed, but there is not enough evidence to revise them at this time.

Tables11 and 12 show the percentages of the most important symmetry coordinates that appear in each normal mode for the a′ and a″ modes, respectively. The symmetry coordinates shown in boldface are the ones influenced by the F4 or Cl4 atom. The numbers in parentheses are for the refined normal modes and

TABLE 7: Comparison of Gaussian 94, Modified Experimental, and Refined Frequencies and G94 and Refined Diagonal Force Constants^g

	CF_3COF							
	ν					diagonal force constants		
mode	G94^a	exptl	refined^a	$\Delta\nu^d$	sf1^e	G94^a	refined^a	sf2^f
a′								
1	1941	1897^b	1897	0	0.98	15.05	14.50	0.96
2	1388	1334^b	1357	−23	0.96	6.11	5.12	0.84
3	1303	1253^b	1249	4	0.96	4.44	4.35	0.98
4	1128	1098^b	1080	18	0.97	7.02	6.12	0.87
5	816	805^b	800	5	0.99	7.48	8.05	1.08
6	697	692^c	689	3	0.99	1.47	1.41	0.96
7	604	595^c	593	2	0.99	1.06	1.10	1.04
8	431	426^c	426	0	0.99	1.51	1.46	0.97
9	393	390^c	390	0	0.99	1.65	1.57	0.95
10	229	228^c	225	3	1.0	1.86	1.80	0.97
a″								
11	1251	1200^b	1200	0	0.96	5.94	5.69	0.96
12	775	761^c	761	0	0.98	1.08	1.23	1.14
13	526	519^c	519	0	0.99	1.36	1.11	0.82
14	240	242^c	241	1	1.01	0.502	0.492	0.98
15	45	50^c	50	0	1.11	0.0148	0.0170	1.15

[a] This work. [b] Reference 3. [c] Reference 8. [d] $\Delta\nu = \nu(\text{exp}) - \nu(\text{refined})$. [e] sf1 = ν(exp)/ν(G94). [f] sf2 = fc(refined)/fc(G94). [g] Frequencies are in cm^{-1} and force constants are in mdyn/A.

TABLE 8: Comparison of Gaussian 94, Modified Experimental, and Refined Frequencies and G94 and Refined Diagonal Force Constants^f

	CF_3COCl							
	ν					diagonal force constants		
mode	G94^a	exptl^b	refined^a	$\Delta\nu^c$	sf1^d	G94^a	refined^a	sf2^e
a′								
1	1857	1821	1821	0	0.98	14.22	13.54	0.95
2	1322	1284	1310	−26	0.97	3.28	2.69	0.82
3	1295	1240	1225	15	0.96	4.19	3.41	0.81
4	951	933	933	0	0.98	6.97	5.14	0.74
5	757	750	739	11	0.99	7.49	7.48	1.00
6	596	583	579	4	0.98	1.47	1.42	0.97
7	526	511	507	4	0.97	1.01	1.19	1.18
8	408	411	405	6	1.01	1.55	1.48	0.95
9	346	334	333	1	0.97	1.70	1.64	0.96
10	200	198	197	1	0.99	1.85	2.13	1.15
a″								
11	1258	1202	1202	0	0.96	5.97	5.72	0.96
12	717	703	703	0	0.98	1.11	1.28	1.15
13	520	517	517	0	0.99	1.37	1.07	0.78
14	235	234	234	0	1.00	0.499	0.501	1.00
15	42	45	45	0	1.07	0.0213	0.0226	1.06

[a] This work. [b] Reference 10. [c] $\Delta\nu = \nu(\text{exp}) - \nu(\text{refined})$. [d] sf1 = ν(exp)/ν(G94). [e] sf2 = fc(refined)/fc(G94). [f] All frequencies are in cm^{-1}, and force constants are in mdyn/A.

the numbers without parentheses are for the Gaussian 94 normal modes. A positive percentage means the bond is stretching or the angle is increasing, while a negative percentage means the bond is contracting or the angle is decreasing from the equilibrium positions.

Examination of Tables 11 and 12 shows that, with the exceptions of η_1, η_{11}, and η_{15}, the normal modes involve both the CF_3 and OCF or OCCl parts of the molecules in the vibrational motion. The η_1 mode is dominated by the CO stretch, but the CC stretch and CCX(X = F,Cl) bend also are part of the motion.

One might expect, that for those modes in which the motion of the F4 or Cl4 atom was important, the percentages would be much different between the symmetry modes involving F4 or Cl4. Only in the η_5, η_7, η_8, η_{10}, η_{12}, η_{13}, and η_{14} modes is this true. For CF_3COCl, the CCl stretch is a major component of η_7; however, the CF4 stretch is not important in CF_3COF, a major difference for η_7 in these two molecules. In η_{12}, η_{13}, and η_{14}, the magnitudes of the out-of-plane OCX wag (X = Cl,F) are the same, but the wags are in different directions in CF_3COCl and CF_3COF.

Surprisingly, there are major differences between CF_3COCl and CF_3COF in the amount of S_4 (in-plane CF5 stretch), S_5 (symmetric CF_2 stretch), S_8 (in-plane CF5 deformation), S_9 (symmetric CF_2 wag), and S_{10} (symmetric CF_2 bend) involved in all the a′ normal modes with the exception of η_1. In other words, in any a′ normal mode in which the CF_3 moiety has significant motion, there are major differences in the CF_3 motions between CF_3COCl and CF_3COF. One might expect just the opposite since the CF_3 moiety is further away from the F4 or Cl4 atom than any other part of these molecules.

IV. Description of Vibrational Motions

Table 5 shows the description of CF_3COF and CF_3COCl vibrations by two different researchers. These are brief labels that are supposed to describe the dominant part of the vibrational motion. Section II.C. indicated that the differences in bond lengths and frequencies calculated at different levels of theory do not correlate with the descriptions in Table 5. Tables 11 and 12 show that more is involved in the vibrational motions than the brief descriptions in Table 5.

To describe the vibrational motion in more detail, we put the Gaussian 94 center-of-mass displacement vectors for the normal modes of CF_3COF and CF_3COCl into HyperChem[26] and animated the vibrations. It was a revelation to see these molecules move in their different vibrational modes. The motions of the modes in HyperChem correspond to the displacement vectors from Gaussian 94; however, it is much more meaningful to "see" the vibration than it is to attempt to visualize the motion by looking at displacement vectors.

Unfortunately, we cannot reproduce the animations in a paper. Instead Figures 2 and 3 show the motion of some of the vibrational modes represented by the molecules in three positions for the a′ modes and two positions for the a″ modes. The molecule with white, labeled atoms is at the equilibrium position; the molecule with speckled atoms and solid bonds is at one extreme of its normal mode vibration as determined by the Gaussian 94 displacement vectors; the molecule with striped atoms and dashed bonds is at the other extreme. For the a″ modes, only the equilibrium position and one extreme of the vibration is shown since the diagrams became too confusing with three positions shown. Figures 2 and 3 were made with a drawing program using the Gaussian 94 data as input. The positions of the molecules in the figures agree with the animated motions in HyperChem.

Figures 2 and 3 show some of the normal mode vibrations that illuminate the similarities and differences between the CF_3COCl and CF_3COF motions; these figures also show that these vibrational motion are much more complicated than the simple descriptions given in Table 5. Figures and descriptions for the remaining vibrational motions can be found in the Supporting Information.

Figure 2 shows the η_4, η_5, and η_6 a′ modes. The view is perpendicular to the mirror plane with the F7 atom always eclipsed by the F6 atom. Figure 3 shows the η_{11}, η_{12}, and η_{13} a″ modes. The view is parallel to the mirror plane, with the F4(Cl4), C2, and O1 atoms being closer to the viewer with the C3 atom being eclipsed by the C2 atom and the F5 atom being

TABLE 9: Off-Diagonal Force Constants for the a′ Modes of CF_3COCl and CF_3COF after Refinement[a]

	CF_3COCl (CF_3COF)								
a′	2	3	4	5	6	7	8	9	10
1	0.839 (1.144)	0.333 (0.322)	.039 (0.069)	0.060 (0.120)	−0.389 (−0.509)	0.036 (−0.053)	−0.118 (−0.125)	0.076 (0.136)	0.009 (−0.004)
2		0.121 (0.231)	.062 (0.081)	0.152 (0.209)	0.246 (0.358)	−0.282 (−0.392)	0.091 (0.189)	0.045 (−0.009)	−0.058 (−0.083)
3			.199 (0.248)	0.327 (0.397)	0.163 (0.229)	0.165 (0.181)	0.217 (0.266)	0.262 (0.249)	−0.072 (−0.092)
4				0.867 (1.08)	0.165 (0.234)	−0.058 (−0.049)	0.211 (0.282)	−0.534 (−0.635)	−0.254 (−0.314)
5					−0.068 (−0.080)	0.118 (0.153)	−0.382 (−0.459)	−0.009 (0.023)	0.359 (0.425)
6						0.055 (0.225)	0.062 (0.167)	0.037 (−0.028)	0.011 (0.001)
7							0.003 (−0.010)	0.067 (0.087)	−0.027 (−0.035)
8								0.121 (0.185)	0.048 (0.056)
9									0.046 (0.035)

[a] The numbers in parentheses are for CF_3COF. The units are mdyn/A.

TABLE 10: Off-Diagonal Force Constants for the a″ Modes of CF_3COCl and CF_3COF after Refinement[a]

	CF_3COCl (CF_3COF)			
a″	12	13	14	15
11	−0.026 (−0.011)	−0.838 (−0.855)	−0.089 (0.110)	−0.006 (−0.011)
12		0.291 (0.299)	0.004 (0.047)	0.041 (−0.018)
13			0.031 (−0.062)	−0.041 (−0.027)
14				0.048 (−0.037)

[a] The numbers in parentheses are for CF_3COF. The units are mdyn/A.

eclipsed by the O1 atom in the equilibrium position. Atoms F6 and F7 appear on each side of the mirror plane.

There may be some question as to whether the calculated normal modes give us an accurate depiction of the actual vibrational dynamics since the figures show the normal modes for harmonic vibrations, whereas the observed vibrations are anharmonic. However, Tables 7 and 8 show that the values of MP2/6-31G(d′) harmonic frequencies are almost the same as the values for the observed frequencies, indicating that anharmonic corrections may be very small. Tables 11 and 12 show that refining the Gaussian 94 harmonic force constants to fit the observed anharmonic frequencies does not introduce many changes into the motion of the normal modes. Thus, for small-amplitude vibrations, the motions shown in Figures 2 and 3 should be a reliable approximation to the true vibrational motions.

In the paragraphs below, we describe the motions of the normal modes shown in Figures 2 and 3. The numeral associated with an atom will be dropped whenever there is no confusion over which atom in a molecule is indicated, e.g., we refer to the CO bond instead of the C2−O1 bond. Whenever, the descriptions of Berney and Cormier[10] and Redington[9] are referred to, we are referring to the data in Table 5.

Normal Modes for ν_4. The motion of the C2 atom is dominant in this mode as depicted in Figure 2. The C2 atom moves diagonally up and left toward the F5 equilibrium position or diagonally down and right toward the F4(Cl4) atom. The C3 atom has a small motion in phase with the C2 atom, resulting in only small changes in the CC bond. The major changes are the CF4 (CCl4) stretch and the CO wag. There is a small symmetric CF_3 stretch that is out-of-phase with the CF4 (CCl4) stretch. The motion of the C2 atom and the CF_3 stretch causes changes in the CCF5 bend and the CF_2 wag.

Berney and Cormier[10] described the η_4 mode in CF_3COCl as an out-of-phase CCCl stretch. This description is correct in that there is a small CC stretch that occurs when the CCl4 bond contracts. However, the CO wag and the CF_3 motions are more important than the CC stretch. They described the motion in CF_3COF as a CF4 stretch which is correct but misses the CO wag and CF_3 motions.

Redington[9] described the CF_3COCl motion as a CC stretch which is not important here. He described the CF_3COF motion as a CF_3 stretch which is also small in this mode. The vibrational motions of CF_3COCl and CF_3COF are similar in this mode, and the difference between chlorine and fluoride in the CCl4 or CF4 stretch shows up as a 150−170 cm^{-1} difference in their frequencies.

Normal Modes for ν_5. In this mode, there is a qualitative difference in the motions of the CF_3COCl and CF_3COF molecules as shown in Figure 2. This mode could be called a breathing mode in CF_3COF since all the bonds stretch and contract in phase. In CF_3COCl, the C2 atom moves up and down instead of back and forth so the CC stretch is smaller than in CF_3COF as shown in Table 11. The chlorine atom moves very little, but the up and down motion of C2 produces a CCl4 stretching motion. The oxygen atom moves up and down in phase with C2 so the CO bond does not change much. The CF_3 motions are similar in the two molecules. The simultaneous stretching of all bonds produces a much larger CCF4 bend in CF_3COF than CCCl4 bend in CF_3OCl as shown in Table 11.

Berney and Cormier[10] identified this mode as the CF_3 deformation in CF_3COCl. The CF_3 deformation is also called an umbrella mode in which all the CCFJ angles ($J = 5, 6, 7$) increase and decrease simultaneously. This certainly occurs as is reflected in Table 11, but they miss the CCl4 stretch and CF_3 stretch which are also significant. They describe the CF_3COF motion as a CC stretch which misses all the other stretching motions and changes in angles.

Redington[9] describes the CF_3COCl motion as a CCl4 stretch

TABLE 11: Percentages of the Most Important Symmetry Coordinates Appearing in Each Normal Mode of a′ Symmetry[a]

		symmetry modes[b] [%CF_3COCl/%CF_3COF]									
normal mode	ν(cm^{-1}) CF_3COCl/CF_3COF	S_1	**S_2**	S_3	S_4	S_5	**S_6**	S_7	S_8	S_9	S_{10}
η_1	1857/1941 (1821/1897)	35/32 (35/32)		−15/−15 (−14/−15)			**21/22** **(21/22)**				
η_2	1322/1389 (1310/1357)			18/19 (15/19)		3/−8 (−19/−9)		−16/−19 (−18/−18)		−29/−22 (−18/−21)	2/8 (21/9)
η_3	1295/1304 (1225/1249)				15/20 (16/20)	−19/−14 (−4/−14)		1/5 (18/7)	−18/−14 (−6/−14)	2/14 (24/16)	21/17 (5/16)
η_4	951/1128 (933/1080)		**17/18** **(17/19)**					34/26 (34/28)	−12/−16 (−9/−15)	−3/−11 (−11/−11)	
η_5	757/816 (739/800)		**11/11** **(7/13)**	6/14 (8/14)		10/13 (12/12)	**−5/−11** **(−5/−12)**	17/−13 (12/−10)	−17/−9 (−17/−11)	−17/−11 (−15/−10)	12/6 (16/8)
η_6	596/697 (579/689)						**−18/−14** **(−16/−14)**	−7/−30 (−8/−28)		29/20 (29/21)	17/−9 (19/−9)
η_7	526/604 (507/593)		**−23/3** **(−23/4)**				**15/16** **(19/16)**	17/−9 (10/−11)		−3/−21 (−5/−20)	24/−23 (19/−23)
η_8	408/431 (405/426)		**11/3** **(17/3)**				**9/21** **(8/20)**	−30/−20 (−27/−21)	9/19 (7/17)		23/29 (17/31)
η_9	346/393 (333/390)			10/18 (13/17)				24/26 (18/23)	31/19 (33/20)	3/18 (3/20)	
η_{10}	200/229 (197/225)						**40/30** **(41/27)**	−9/−19 (−7/−17)	−25/−28 (−25/−31)	16/15 (16/16)	

[a] The numbers without parentheses are for the Gaussian 94 normal modes, and the numbers in parentheses are for the refined normal modes. The numbers before the slash are for CF_3COCl, and the numbers after the slash are for CF_3COF. [b] S_1, CO stretch; S_2, CX stretch; S_3, CC stretch; S_4, in-plane CF stretch; S_5, symmetric CF_2 stretch; S_6, CCX bend; S_7, in-plane CO wag; S_8, in-plane CF deformation; S_9, symmetric CF_2 wag; S_{10}, symmetric CF_2 bend; X = Cl, F.

TABLE 12: Percentages of the Most Important Symmetry Coordinates Appearing in Each Normal Mode of a″ Symmetry[a]

	Symmetry Modes[b] [%CF_3COCl/%CF_3COF]					
normal mode	ν(cm^{-1}) CF_3COCl/CF_3COF	S_{11}	S_{12}	S_{13}	**S_{14}**	S_{15}
η_{11}	1258/1251 (1202/1200)	30/28 (31/29)		33/31 (33/31)		−19/−21 (−19/−21)
η_{12}	717/775 (703/761)			−14/−11 (−13/−11)	**−35/36** **(−35/36)**	41/42 (42/42)
η_{13}	520/526 (517/519)		27/27 (34/32)	18/23 (29/28)	**−24/22** **(−15/17)**	29/24 (18/18)
η_{14}	235/240 (234/241)		21/25 (18/22)		**28/−28** **(27/−28)**	−35/−29 (−34/−29)
η_{15}	42/45 (45/50)		−4/−3 (−4/−2)		**−6/5** **(−5/5)**	85/88 (85/89)

[a] The numbers without parentheses are for the Gaussian 94 normal modes, and the numbers in parentheses are for the refined normal modes. The numbers before the slash are for CF_3COCl and the numbers after the slash are for CF_3COF. [b] S_{11}, asymmetric CF_2 stretch; S_{12}, asymmetric CF_2 twist; S_{13}, asymmetric CF_2 rock; S_{14}, out-of-plane OCX wag (X = Cl, F); S_{15}, CF_3 torsion.

which describes the portion missed by Berney and Cormier but leaves out the CF_3 deformation correctly described by them. Redington commits the same error as Berney and Cormier in describing the CF_3COF motion as a CC stretch.

Normal Modes for ν_6. Figure 2 shows that there are qualitative differences between CF_3COCl and CF_3COF in this mode. The CF_3COF motion can be described as an out-of-phase OCF4 scissors motion and a CF_3 umbrella motion such that the umbrella is opening when the scissors is closing and vice versa. However, to a great extent, these motions are caused by the C3 and C2 atoms moving in phase right and left keeping the CC bond distance fixed.

In CF_3COCl, the OCCl4 motion is similar to the OCF4 motion, but the C3 atom does not move right and left; instead, it moves almost vertically up and down. Thus, the CF_3 umbrella motion does not occur. The motions of the CF_3 moiety are more complicated. This is reflected in Table 11 by S_{10}, the CF_2 bend, being in different directions in CF_3COCl and CF_3COF.

For this mode, Berney and Cormier[10] correctly describe some of the motions of the OCCl4 (OCF4) moiety while neglecting the CF_3 moiety; Redington[9] goes to the opposite extreme correctly describing some of the CF_3 moiety's motions. Berney and Cormier call the CF_3COCl motion a CCO bend and the CF_3COF motion an OCF bend. Besides missing the CF_3 motions, they only describe half the OCCl4 (OCF4) motions since the CCO bend and OCCl4 (OCF4) bend are important in both molecules. Redington is correct in that a F6−C3−F7 scissors motion (FCF$_2$ deformation) occurs in CF_3COCl and a CF_3 umbrella motion in CF_3COF, but he misses all of the OCCl4 (OCF4) motions.

Normal Modes for ν_{11}. This is the first of the a″ modes. As shown in Figure 3, this mode is dominated by the large-amplitude motion of the C3 atom out of the mirror plane in both molecules. The motion of C3 creates an asymmetric CF_2 stretch and changes in the α_i and β_i angles (i = 1, 2, 3) producing a CF_2 rock and CF_3 torsion as shown in Table 12.

Both Berney and Cormier and Redington describe the motions in both molecules as asymmetric CF_2 stretches which is largely correct. Since it is the C3 atom that has the large-amplitude motion with the F6 and F7 atoms barely moving, their descriptions do not recognize the CF_2 rocks and CF_3 torsions that are also important.

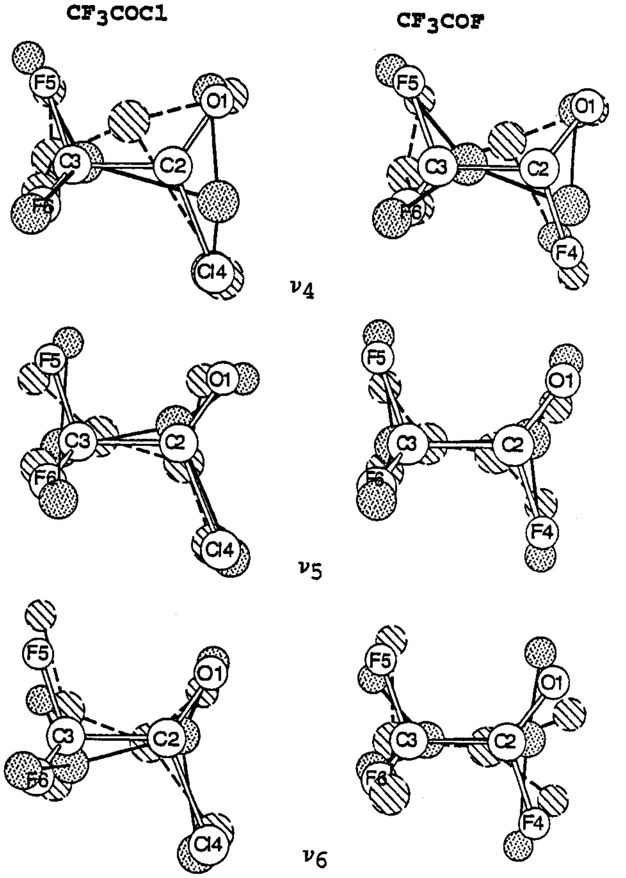

Figure 2. Freeze frames of the ν_4, ν_5, and ν_6 vibrational motions of CF_3COCl and CF_3COF. The molecule with labeled atoms and cylindrical bonds is at the equilibrium geometry in each diagram. The molecule with speckled atoms and solid bonds is at one extreme of the vibrational motion; the molecule with striped atoms and dashed bonds is at the other extreme of vibrational motion.

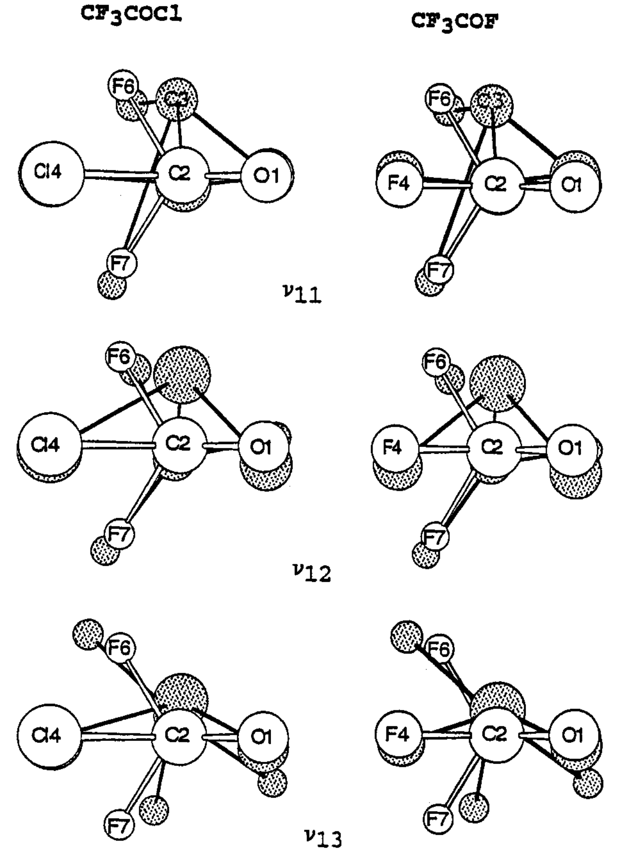

Figure 3. Freeze frames of the ν_{11}, ν_{12}, and ν_{13} vibrational motions of CF_3COCl and CF_3COF. The perspective is changed from that of Figure 2 so that the axis along the C2−C3 bond is into the paper and the molecule is rotated 90° clockwise around this axis. The molecule with labeled atoms and cylindrical bonds is at the equilibrium geometry. The molecule with speckled atoms and solid bonds is at one extreme of the vibrational motion.

Normal Modes for ν_{12}. Figure 3 shows that this mode is essentially the same in both molecules. The C2 atom has a large out-of-plane motion that dominates the mode. This is reflected in Table 12 by the large OCF4 (OCCl4) wag (S_{14}) shown. The OCCl4 wag has a different sign from the OCF4 wag in Table 12 because the F6 and F7 atom motions have opposite phases in CF_3COCl and CF_3COF. Since the F6 and F7 atom motions are small, this is not important. The large motion of C2 produces large changes in the τ_2 and τ_3 dihedral angles and, thus, a large CF_3 torsion.

Berney and Cormier described both the CF_3COCl and CF_3COF motions as CF_2 deformations. There are CF_2 rocks (S_{13}) in both molecules, but these motions are small. Redington comes closer to the correct description for CF_3COCl by calling it an OCCl deformation. This description would be completely accurate if it were the O and Cl atoms moving out of plane. Instead, it is the C2 atom moving out of plane, so his description misses the large CF_3 torsion.

Normal Modes for ν_{13}. Figure 3 shows that these modes are very similar in both molecules. Both the C2 and C3 atoms move out of plane but with smaller amplitudes than in the η_{12} mode. The motion of the C2 atom eclipses the motion of the C3 atom. In addition, the F5, F6, and F7 atoms have large motions. When the C2 and C3 atoms move up, the F7−C3−F5 angle decreases in both molecules.

Table 12 shows that the OCF4 wag (S_{14}) has a different phase than the OCCl4 wag. Figure 3 shows this as a subtle effect. When the C2 and C3 atoms are up in CF_3COCl, the F6 atom is behind its equilibrium position and the F7 atom is in front. In CF_3COF, when the C2 and C3 atoms are up, the F6 atom is in front of its equilibrium position and the F7 atom is behind.

Berney and Cormier[10] describe the motions in both molecules as antigear wags. We assume they mean that when the OCF4(OCCl4) angle is decreasing the F5−C3−F6(F7) angle is decreasing. However, Figure 3 shows that just the opposite occurs. In their nomenclature, describing the motions as gear wags would be more accurate, but this description misses the large CF_2 twist that occurs.

Redington[9] describes the CF_3COCl motion as an asymmetric CF_2 deformation. This description misses the OCCl wag, the CF_2 twist, and the CF_3 torsion that occurs. He describes the CF_3COF motion as an OCF4 wag. This motion is important in this mode, but his description does not cover the CF_2 and CF_3 motions.

V. Conclusions

Our work agrees with that of Pacansky et al. in showing that the $\nu_6(a')$, $\nu_7(a')$, $\nu_8(a')$, $\nu_{12}(a'')$, and $\nu_{13}(a'')$ experimental frequencies in CF_3COF need to be reassigned.[7−9] We show for the first time that the $\nu_6(a')$, $\nu_7(a')$, $\nu_8(a')$, $\nu_{12}(a'')$, and $\nu_{13}(a'')$ experimental frequencies in CF_3COCl also need to be reassigned.[6,9,10] When the experimental frequencies are reassigned, the agreement with MP2/6-31G(d′) calculated frequencies is excellent. The differences between the calculated harmonic frequencies and the experimental anharmonic frequencies in both molecules are less than 5% except for the extremely small torsion frequencies (ν_{15}).

The force constants determined with the MP2/6-31G(d′) method were refined by fitting them to the reassigned experimental frequencies using internal symmetry coordinates. The normal modes of vibration for both the originally calculated force constants and the refined force constants show that none of the symmetry coordinates are dominant in a particular vibration except for the ν_{15} (torsion) vibration.

The descriptions of the vibrations given by experimentalists[9,10] were checked by animating the calculated normal modes of vibration using HyperChem.[26] The animations revealed that most of the vibrations were much more complicated than the simple descriptions previously given. Very few of the experimental descriptions were accurate. In most vibrations, both the CF_3 and OCF4 (OCCl4) moieties were participants.

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Supporting Information Available: Figures 1S−4S show the ν_1−ν_3, ν_7, and ν_8, ν_9 and ν_{10}, and ν_{14} and ν_{15} vibrational motions, respectively, and descriptions of the motions and a summary are also included. This information is available free of charge via the Internet at http://pubs.acs.org.

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