

IR Spectra and Vibrational Modes of the Hydrofluoroethers CF_3OCH_3 , $\text{CF}_3\text{OCF}_2\text{H}$, and $\text{CF}_3\text{OCF}_2\text{CF}_2\text{H}$ and Corresponding Alkanes CF_3CH_3 , $\text{CF}_3\text{CF}_2\text{H}$, and $\text{CF}_3\text{CF}_2\text{CF}_2\text{H}$

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Abstract: The structures and IR spectra of CF_3OCH_3 , $\text{CF}_3\text{OCF}_2\text{H}$, and $\text{CF}_3\text{OCF}_2\text{CF}_2\text{H}$ and corresponding alkanes CF_3CH_3 , $\text{CF}_3\text{CF}_2\text{H}$, and $\text{CF}_3\text{CF}_2\text{CF}_2\text{H}$ have been calculated using the B3LYP method with a 6-311G(2d,2p) basis set. The calculated IR spectra are consistent with, and provide additional confidence in, the available experimental data.

Keywords: Density functional theory, infrared spectroscopy, IR spectra, global warming, CFC replacements.

INTRODUCTION

The use of chlorofluorocarbons (CFCs) and Halons as refrigerant or heat transfer fluids leads to their emission into the atmosphere where they contribute to stratospheric ozone depletion [1, 2]. Over the past 10-20 years there has been an international effort to replace these compounds with environmentally acceptable alternatives. Hydrofluoroethers (HFEs) are one class of replacement compounds. These compounds do not contain chlorine or bromine and do not contribute to stratospheric ozone destruction [3]. Young *et al.* [3] have noted that the "atmospheric window" or range of infrared (IR) wavelengths that can easily escape the atmosphere is between 750 and 1250 cm^{-1} and that typical C-O and C-F vibrational stretching modes absorb in this range. The atmospheric lifetime of fluorinated ethers can be relatively long [3] with lifetimes increasing with the degree of fluorination [4,5] allowing longer times for these compounds to absorb radiation and contribute to radiative forcing of climate change.

The Global Warming Potential (GWP) of a fluorinated ether thus depends on its radiative forcing value, which is a function of its infrared spectrum, and upon its atmospheric lifetime [6-8]. Computational studies have predicted the IR spectra of several fluorinated ethers and provided estimates of radiative forcings [7-10]. Information on lifetimes has come from several recent kinetics experiments [4,11-13]. Lifetime estimates may also be based on computational studies of thermodynamic properties [7,14].

The relationship between the molecular structure of fluorinated ethers and their ability to absorb radiation has been a subject of recent study. Recent work by Young *et al.* [5] has developed a quantitative relationship between molecular structure and radiative efficiency. Good and Francisco [7] studied the theoretical IR spectra of the compounds CHF_2OCF_3 (E125), $\text{CHF}_2\text{OCHF}_2$ (E134), and CH_3OCF_3 (E143A) as determined by intensive *ab initio*

electronic structure calculations; their observations indicated that absorption of IR within the "atmospheric window" would occur for the compounds they studied, and that further, increases in the degree of fluorine substitution increased the quantity of absorption within the window wavelengths.

The work of Francisco does not specifically address the impact of the inclusion of the O atom upon absorptions in the window- i.e., it does not consider spectrum of the ether in comparison to that of the analogous alkane (where "analogous" means the alkane that would be obtained by removing an oxygen atom from the ether formula). Fluorinated alkanes, or hydrofluorocarbons (HFCs), are believed to have even longer lifetimes than HFEs [9,11-14]. Though some concerns exist about their presence as pollutants in the troposphere [15], HFCs are currently used as CFC replacements [7,15]. It has been postulated that HFEs have a lower global warming potential than the HFCs they would replace [7]. Assessment of the relative global warming potential of HFCs and HFEs requires knowledge of atmospheric lifetimes and the infrared absorption characteristics of both.

In this work, we present for comparison the computed structures and IR spectra of several fluorinated ethers and their analogous alkanes in the gas phase. IR spectra are compared to experimental data; T.J. Wallington of Ford Motor Company has provided experimental IR absorption spectra of fluorinated ethers and analogous alkanes to our group. The collection of the experimental data is described and spectra for these compounds are presented in several recent publications [16-18].

The following section describes our computations. Then our results section displays and compares the experimental and theoretical spectra. The results section also includes our predictions on the structure and relative energies of the conformers of these compounds, and data on the nuclear motions associated with each vibrational mode. In the conclusions section, this latter information is discussed with respect to the computed intensity of the modes.

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Table 1. Calculated Vibrational Mode Data for CF₃OCH₃. Frequency (cm⁻¹), Intensity (KM/mol) and Irreducible Representation ("Irrep") of Each Mode are Displayed

Point group	C _s		
Mode	Frequency (cm ⁻¹)	Intensity (KM/mole)	Irrep
1	102.8455	2.3416	A''
2	169.2162	2.6189	A''
3	270.8083	4.5735	A'
4	428.1435	0.2067	A''
5	443.3161	5.3928	A'
6	580.8619	7.6788	A'
7	608.4573	1.4520	A''
8	656.0349	0.4211	A'
9	838.2863	8.3070	A'
10	1069.3876	33.1635	A'
11	1144.8144	341.6713	A''
12	1177.7678	159.5930	A'
13	1180.1872	4.1002	A''
14	1249.8973	190.9129	A'
15	1291.1719	521.2602	A'
16	1492.6496	28.5025	A'
17	1499.7863	4.1599	A''
18	1511.0472	19.9171	A'
19	3057.6750	24.8581	A'
20	3129.0874	16.3197	A''
21	3167.1768	9.4001	A'

Table 2. Calculated Vibrational Mode Data for CF₃CH₃. Frequency (cm⁻¹), Intensity (KM/mol) and Irreducible Representation ("Irrep") of Each Mode are Displayed

Point group	C _{3v}		
Mode	Frequency (cm ⁻¹)	Intensity (KM/mole)	Irrep
1	215.3777	0.0000	A ₂
2	360.4157	0.5636	E
3	360.4180	0.5632	E
4	532.1031	0.6164	E
5	532.1048	0.6172	E
6	592.9739	20.0174	A ₁
7	825.9967	4.5571	A ₁
8	967.8262	63.2752	E
9	967.8436	63.2423	E
10	1229.7347	214.6035	E
11	1229.7972	214.6176	E
12	1281.9552	163.7336	A ₁
13	1428.9812	77.6058	A ₁
14	1486.9411	0.5006	E
15	1486.9421	0.5009	E
16	3074.6659	0.6521	A ₁
17	3153.7227	5.3224	E
18	3153.7259	5.3201	E

Table 3. Calculated Vibrational Mode Data for CF₃OCF₂H Conformers. Frequency (cm⁻¹), Intensity (KM/mol) and Irreducible Representation ("Irrep") of Each Mode are Displayed

Point group	Conformer 1			Conformer 2		
	C ₁			C ₁		
	Mode	Frequency (cm ⁻¹)	Intensity (KM/mol)	Irrep	Frequency (cm ⁻¹)	Intensity (KM/mol)
1	34.6328	0.5847	*C ₁ *	29.0592	1.2676	*C ₁ *
2	116.9270	0.9667		72.4722	0.1758	
3	185.1446	0.2109		192.5289	2.3800	
4	348.1465	0.2830		352.4635	0.1220	
5	357.2944	0.2016		372.0863	0.5131	
6	502.5844	0.1456		455.6153	3.9255	
7	516.1444	3.9617		514.0684	2.9585	
8	580.2568	3.7716		585.4060	8.9714	
9	598.7415	17.5815		613.0644	3.7122	
10	634.7807	8.9575		655.2620	6.2636	
11	808.6871	27.5459		717.9024	12.8965	
12	840.6765	13.4829		907.2831	78.0883	
13	1081.5008	189.7208		1091.2452	285.9720	
14	1113.3428	137.1986		1121.3989	104.3745	
15	1144.0875	250.8496		1159.1950	236.2846	
16	1206.5129	433.4465		1182.7357	442.1670	
17	1218.8824	415.1468		1231.5262	373.4783	
18	1271.9252	408.6371		1300.4974	384.2171	
19	1381.1138	32.4193		1390.0975	45.4571	
20	1426.1840	41.6729		1428.7996	8.2197	
21	3151.4961	21.3588		3130.1854	17.8326	

Table 4. Calculated Vibrational Mode Data for CF₃CF₂H. Frequency (cm⁻¹), Intensity (KM/mol) and Irreducible Representation ("Irrep") of Each Mode are Displayed

Point group	C _s		
Mode	Frequency (cm ⁻¹)	Intensity (KM/mole)	Irrep
1	64.6182	0.7848	A''
2	205.8253	2.2851	A''
3	239.2363	3.6431	A'
4	357.4182	0.0477	A'
5	410.3050	0.8440	A''
6	513.0201	6.9090	A'
7	570.7500	13.2191	A'
8	575.2809	0.4977	A''
9	716.6621	31.8403	A'
10	862.9864	45.9991	A'
11	1134.3085	98.6785	A''
12	1136.8769	130.4402	A'
13	1187.6755	195.6044	A'
14	1204.9731	360.2865	A''
15	1306.2303	145.4710	A'
16	1373.4765	7.1873	A''
17	1438.7735	0.7726	A'
18	3100.2398	19.7938	A'

Table 5. Calculated Vibrational Mode Data for CF₃OCF₂CF₂H Conformers. Frequency (cm⁻¹), Intensity (KM/mole) and Irreducible Representation ("Irrep") of Each Mode are Displayed

	Conformer 1			Conformer 2		
Point group	C ₁			C ₁		
Mode	Frequency (cm ⁻¹)	Intensity (KM/mole)	Irrep	Frequency (cm ⁻¹)	Intensity (KM/mole)	Irrep
1	35.0326	0.1627	*C ₁ *	35.5712	0.0272	*C ₁ *
2	59.0553	0.7184		66.4939	1.1493	
3	88.1468	0.0834		91.0391	0.2070	
4	133.4210	0.7372		135.2615	0.6394	
5	211.0256	1.2143		206.3622	1.0889	
6	247.1508	2.0882		214.4308	2.1579	
7	312.9975	1.4489		334.9857	0.1717	
8	341.3613	0.8573		345.8128	0.3043	
9	354.4157	1.0326		364.1107	0.2116	
10	425.4664	1.3823		452.7500	0.1105	
11	505.8179	4.2338		520.6574	5.5810	
12	531.4008	0.9212		546.9576	6.8792	
13	557.0270	14.1182		560.1589	7.9298	
14	608.6853	5.5255		586.2555	55.9488	
15	638.9984	2.6682		630.2814	3.4643	
16	677.2749	13.7477		647.4391	7.9746	
17	790.5566	59.0787		760.7335	38.6658	
18	851.2707	22.6810		829.2702	2.4953	
19	907.0643	40.5334		964.4617	2.1461	
20	1111.6405	249.1341		1110.9638	329.8109	
21	1138.0969	80.5685		1133.4036	30.0983	
22	1148.0569	453.8026		1138.4121	132.2048	
23	1155.9705	167.5193		1160.3459	192.6040	
24	1216.6582	132.7238		1221.3180	519.8325	
25	1229.2760	488.4415		1229.9909	423.9226	
26	1254.6516	285.6867		1268.5272	508.1193	
27	1328.2648	308.9304		1310.0708	53.2860	
28	1375.2470	10.5269		1373.4133	9.5562	
29	1431.5737	3.3987		1436.2635	7.2735	
30	3102.3219	16.9444		3097.2670	18.5014	

Table 6. Calculated Vibrational Mode Data for CF₃CF₂CF₂H Conformers. Frequency (cm⁻¹), Intensity (KM/mol) and Irreducible Representation ("Irrep") of Each Mode are Displayed

	Conformer 1			Conformer 2		
Point group	C _s			C ₁		
Mode	Frequency (cm ⁻¹)	Intensity (KM/mol)	Irrep	Frequency (cm ⁻¹)	Intensity (KM/mol)	Irrep
1	18.7521	0.3215	A''	43.8475	0.8176	*C ₁ *
2	94.3642	1.2037	A''	77.9294	0.4598	
3	159.5023	0.3154	A'	151.9656	1.0026	
4	211.3936	2.4294	A''	215.9412	3.5457	
5	217.2527	0.1772	A''	237.8643	2.1502	
6	276.0926	4.1858	A'	270.5530	1.1637	
7	331.6876	0.0131	A'	316.9001	0.4931	
8	365.1800	0.3698	A''	344.9278	0.0551	
9	369.0100	0.3138	A'	382.2249	0.7719	
10	498.1578	0.7277	A''	448.0799	3.2599	
11	516.3121	15.3319	A'	518.5032	10.8155	
12	555.5813	10.4475	A'	568.2713	2.9386	
13	596.0115	0.5057	A''	584.9568	4.3081	
14	607.6390	45.4794	A'	635.0028	7.2967	
15	701.5329	31.8089	A'	738.0897	37.2824	
16	773.5069	2.8535	A'	831.6396	52.0026	
17	1109.7708	68.6179	A'	1031.9058	194.0983	
18	1130.9818	46.4719	A''	1126.1856	59.6210	
19	1138.5059	147.9003	A'	1138.0923	71.7179	
20	1174.2100	150.0782	A''	1168.6061	136.7032	
21	1199.6784	244.5615	A'	1203.8594	294.2338	
22	1225.0681	385.0124	A''	1225.5769	264.8343	
23	1236.2790	70.4915	A'	1266.8306	113.9035	
24	1333.3357	85.5642	A'	1346.3336	46.8223	
25	1369.1067	16.5306	A''	1385.3947	19.0368	
26	1434.8419	3.4370	A'	1419.7105	18.2302	
27	3087.5365	18.4544	A'	3107.6426	14.4095	

The spectrum of CF₃OCF₂H displays the experimental IR cross sections and calculated spectra for both conformers. Weighting is assigned to the computed absorbances of the conformers by multiplying each by its relative fraction as determined by calculation of the Boltzmann ratio of the conformers at 298 K; i.e., we first compute the ratio of molecules in conformer 1 to conformer 2, N₁/N₂, by

$$N_1/N_2 = \exp[-(E_1 - E_2)/kT]$$

where E₁ - E₂ is the energy difference between conformer 1 and 2, k is the Boltzmann constant, and T is 298 K, a

temperature value equal or close to the temperature at which experiments were performed [18]. This ratio is then converted into relative fractions. This calculation assigns a fraction of 0.1516 to conformer 1 and 0.8484 to conformer 2.

Computations predict the small experimental peak at 907 cm⁻¹ as arising from a mode in conformer 2, and experiment and calculation both place a group of peaks between 1080 cm⁻¹ and 1450 cm⁻¹, with contributions from modes from both conformers. The observed peak at 1300 cm⁻¹ seems to correspond to a mode in conformer 2, and a small observed

Fig. (6). Arrow projections of the three brightest vibrational modes of CF_3OCH_3 and both conformers of $\text{CF}_3\text{OCF}_2\text{H}$.

[22]. The larger the change in the dipole caused by a vibrational motion, the more intense the IR peak corresponding to that mode is expected to be. In the case of the ethers studied in this work, the most intense vibrational modes are uniformly associated with motions which serve to distort carbon-oxygen bonds within the ether, making the bonds alternately longer and shorter as the mode oscillates. Fig. (6) displays vector projections for the three brightest modes of CF_3OCH_3 and the conformers of $\text{CF}_3\text{OCF}_2\text{H}$; Fig. (7) displays the three brightest modes for $\text{CF}_3\text{OCF}_2\text{CF}_2\text{H}$. The two figures illustrate the C-O bond distortions associated with the brightest modes of the ethers.

CONCLUSION

Computations have determined the gas-phase IR spectra of several fluorinated ethers and their analogous alkanes, and these spectra have been compared to experimental measurements. The theoretical spectra reproduce the essential features of each of the measured absorption spectra. The good agreement between experiment and theory, both in terms of wavenumber location and relative intensities of peaks, suggests that the B3LYP/6-311G(2d,2p) calculations correctly describe the motions of each molecule associated with each vibrational mode. Examination of the vibrational modes and the corresponding nuclear motions clearly

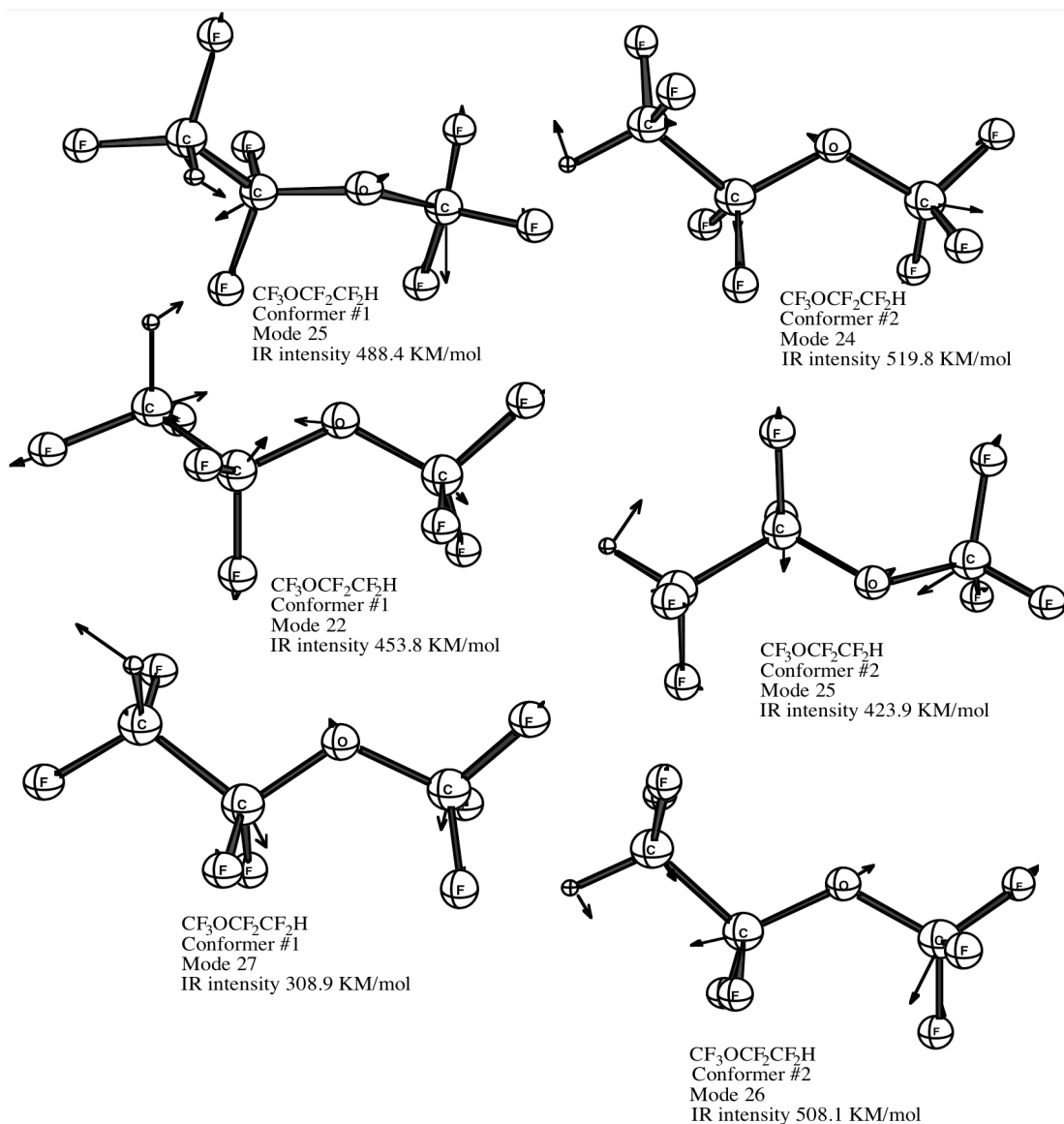


Fig. (7). Arrow projections of the three brightest vibrational modes of both conformers of CF₃OCF₂CF₂H.

indicates that the IR spectrum of each fluorinated ether studied has very intense peaks arising from modes involving distortion of carbon-oxygen bonds. The spectrum of each ether has more peaks, and brighter peaks, than that of its analogous alkane. This result may be true for a comparison of any fluorinated ether and its alkane.

While this study clearly shows that any given atmospheric concentration of fluorinated ethers would contribute more to global warming than the corresponding alkane. This study does not address other relevant issues such as the reactivity, fate, and relative atmospheric lifetimes of fluorinated ethers and alkanes, which must be considered for evaluation of the global warming impact of these compounds.

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