The Vibrational Spectra and Normal Coordinate Analysis of 3,3,3-Trifluoropropene and Hexafluoropropene

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The infrared spectra of 3,3,3-trifluoropropene and hexafluoropropene were studied in the vapour phase and in solution between 4000 and 40 cm^{-1}. Raman spectra of the compounds as vapours and liquids were recorded and polarization data obtained.

The spectra of both molecules are interpreted in terms of C_s symmetry. Complete vibrational assignments, including the torsional mode, are presented, based upon infrared and Raman vapour contours, Raman polarization measurements and the results of a normal coordinate analysis.

Introduction

The title compounds 3,3,3-trifluoropropene (TFP) and hexafluoropropene (HFP) are important intermediates for preparing fluorinated polymers. The molecular structure of TFP has been studied by microwave [1, 2] and electron diffraction [3] methods. An electron diffraction study of HFP [4] suggested that the $F_2C=CFC$ skeleton is twisted 40°, but a subsequent microwave investigation [5] confirmed that the skeleton is planar as expected. A very recent new electron diffraction study [6] reconfirmed the planar skeleton for HFP. Various physical studies including photodissociation [7], calculation of fluorine-fluorine NMR coupling constants [8], measurements [9] and calculations [10] of core level binding energies and calculations of charge distributions [11] have recently been reported for HFP.

The vibrational spectra for these molecules have only been incompletely studied. Thus, the infrared spectrum of TFP in the middle infrared region was reported by Crowder and Smyrl [12] (later referred to as CS). Their tentative assignments were hampered by the complete lack of Raman spectra and polarization measurements in particular. A very careful infrared and Raman study of HFP was published by Nielsen, Claassen and Smith [13] (NCS) more than 25 years ago. Since their infrared region was restricted by their KRS-5 optics and the Raman polarization data were uncertain, their assignments are in need of revision. No normal coordinate analyses have to our knowledge been reported for either TFP or HFP.

We therefore decided to reinvestigate the infrared and Raman spectra of TFP and HFP, including accurate Raman polarization measurements in the vapour and in the liquid state. Moreover, far infrared spectra were recorded by means of a 5 m long path length cell in order to find the unobserved torsional frequencies. The assignments were checked by a normal coordinate analysis in which fairly similar force fields were adopted for both molecules.

Experimental

The samples were commercial products from PCR, Inc. Their purities were checked by gas chromatography at dry ice temperature, and they were studied without purification.

The infrared spectra were recorded in the region 4000 – 180 cm^{-1} with a Perker-Elmer model 180 spectrometer. Below 400 cm^{-1} a Polytec FIR 30 far infrared interferometer was employed, using beamsplitters of Mylar of thicknesses 12 and 25 μ. Standard vapour cells of 10 cm path length and windows of KBr and polyethylene were used above 180 cm^{-1}. A 5 m copper tube with polyethylene windows connected with the interferometer functioned as a vapour cell for the far infrared region below 300 cm^{-1}. Additional infrared spectra of TFP and HFP in CCl_4 and CS_2 solutions were obtained.

The Raman spectra were recorded with a Coderg model T 800 spectrometer, excited by a Spectra Physics model 170-03 argon ion laser, using the

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5145 and 4880 Å lines. The liquids were studied in sealed ampoules under pressure, with less than 100 mW laser power. The vapours were filled to ca. 600 torr pressure in a cube-shaped vapour cell of stainless steel, using 4 – 10 watts of laser power. Careful polarization measurements of the vapours and liquids were made by measuring spectra with the electric vector of the scattered radiation parallel and perpendicular to that of the exciting light. A polarization scrambler was placed before the entrance slit of the spectrometer.

The infrared vapour spectrum of TFP is shown in Fig. 1 (corresponding curves for HFP are given by NCS [13]) while the Raman spectra of TFP and HFP as vapours are given in Figs. 2 and 3, respectively. Lists of the observed wave numbers for the

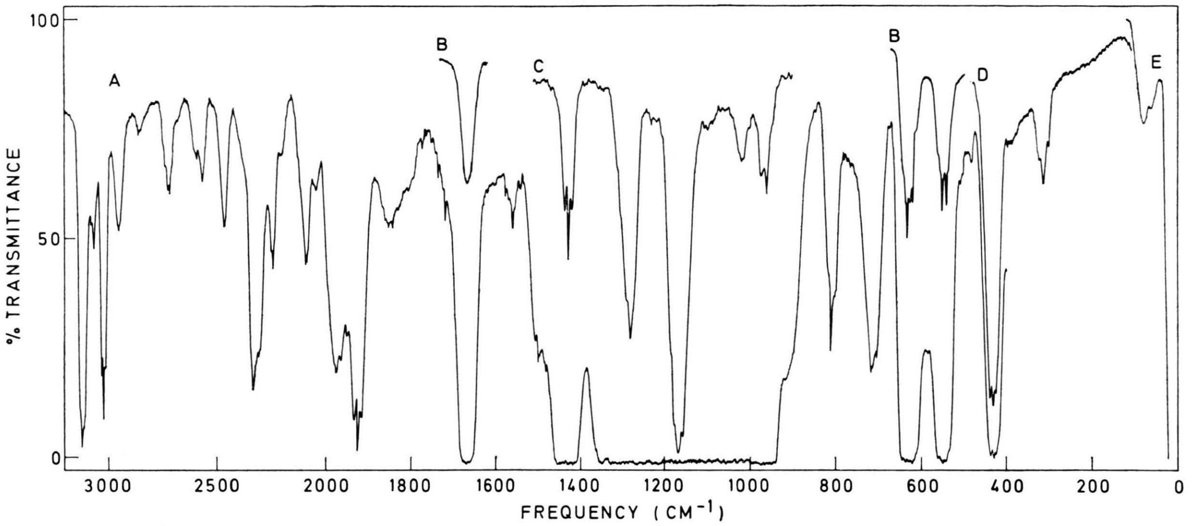

Fig. 1. The infrared vapour spectrum of 3,3,3-trifluoropropene (TFP) at ambient temperature: A) 10 cm path, KBr windows, 200 torr; B) 10 cm path, KBr windows, 50 torr; C) 10 cm path, KBr windows, 15 torr; D) 10 cm path, polyethylene windows, 150 torr; E) 5 m path, polyethylene windows, 50 torr.

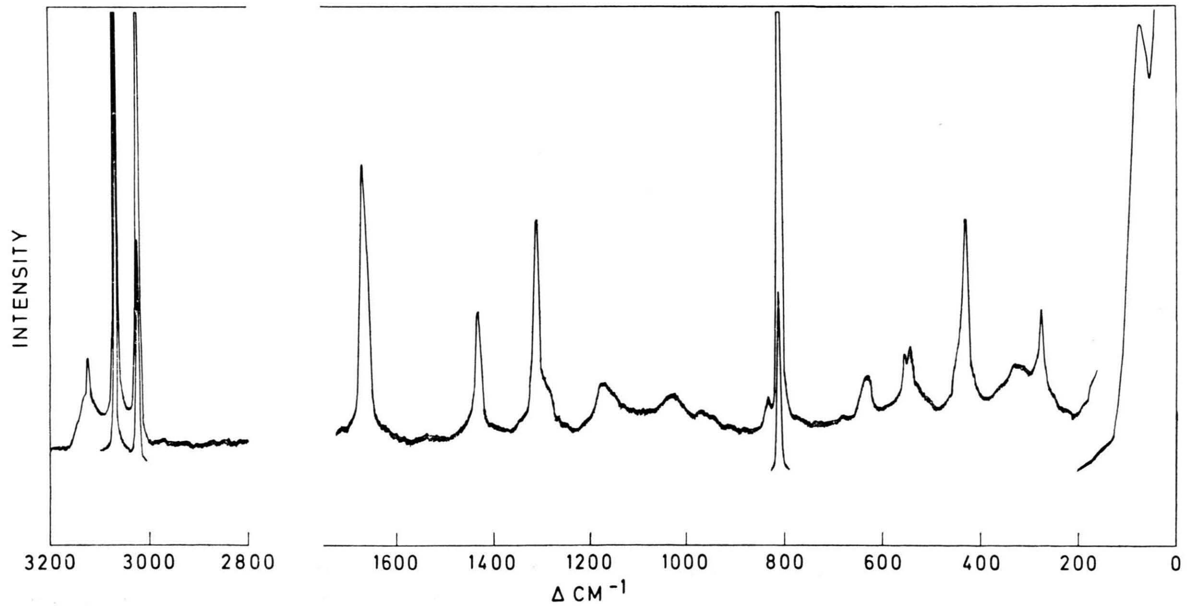

Fig. 2. The Raman spectrum of 3,3,3-trifluoropropene (TFP) at ambient temperature, ca. 5 watt of 5145 Å radiation.

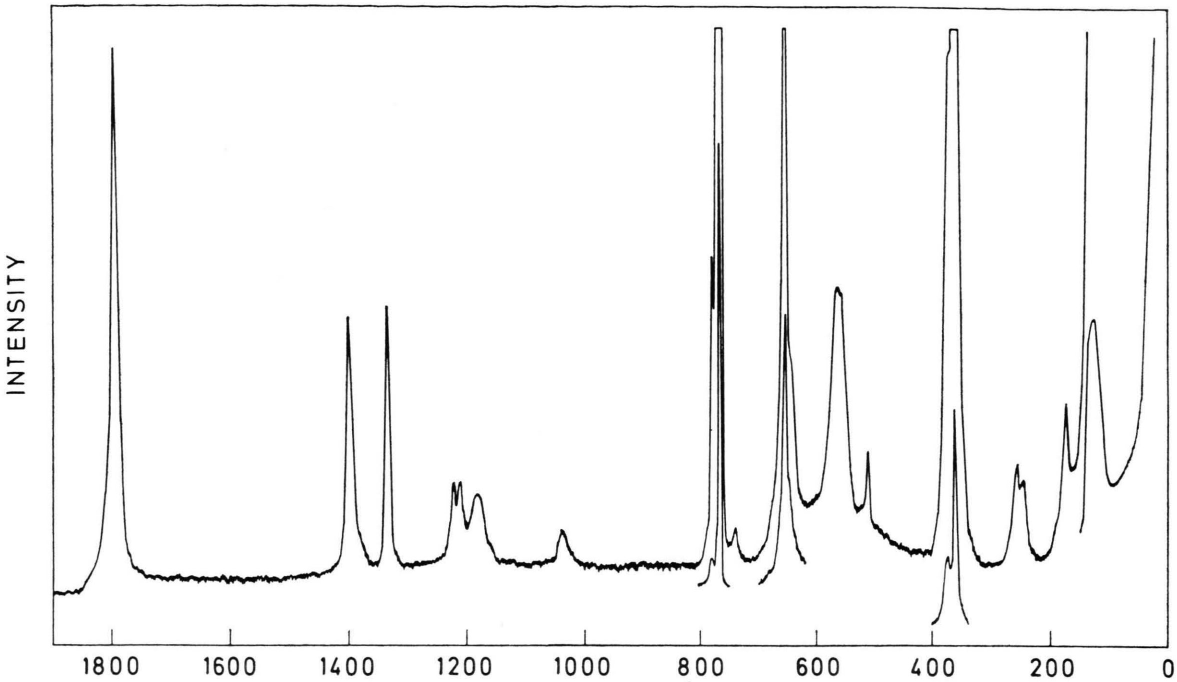

Fig. 3. The Raman spectrum of Hexafluoropropene (HFP) at ambient temperature, 5 – 10 watt of 5145 Å radiation.

infrared and Raman bands are presented in Tables 1 (TFP) and 3 (HFP). The assigned fundamentals for the two compounds are compared with the calculated frequencies in Tables 2 and 4. Finally, the force constants employed in the normal coordinate analyses of both compounds are listed in Table 6.

Spectral Interpretation

The structural data reported for TFP [1 – 3] and HFP [5, 6] leave no doubt about planar skeletons of both molecules. Therefore, it seems safe to conclude that both molecules belong to point group C_s for which the 21 fundamentals divide themselves into 14 of species $\mathbf{a}'$ and 7 of species $\mathbf{a}''$. The lowest and intermediate axes of inertia lie in the symmetry plane for both molecules [2, 5]. Therefore, the $\mathbf{a}'$ fundamentals should have infrared vapour contours being **A/B** hybrids, while the $\mathbf{a}''$ modes should have C-type contours. However, as apparent from Fig. 1 regarding TFP and the figures given by NCS [13] for HFP, the infrared contours are frequently ill defined although some distinct **C**-type bands were prominent and could immediately be correlated with $\mathbf{a}''$ fundamentals. Conclusive evidence for species $\mathbf{a}'$ or $\mathbf{a}''$ could for practically all the modes be extracted from the Raman spectra. Most of the Raman bands gave clear-cut polarization ratios both in the vapour phase and in the liquid state spectra and the vapour bands of species $\mathbf{a}'$ had prominent **Q**-branches.

Finally, the results of the normal coordinate analyses were of great help for the assignments and gave important clues regarding overlapping $\mathbf{a}'$ and $\mathbf{a}''$ modes.

3,3,3-Trifluoropropene

The fundamental frequencies listed in Table 2 appear quite certain on the basis of the available infrared and Raman data and the results of the force constant calculations. Interpretations reported by CS [12] were based upon mid-infrared data alone and comparison with the corresponding vinyl trifluorosilane spectrum. As apparent from Table 2, two of our fundamentals (ν_{14} and ν_{21}) which were particularly prominent in the Raman spectra were not observed previously [12]. In addition, our

Table 1. Vibrational Spectral Data [a] for 3,3,3-Trifluoropropene.

Infrared			Raman			Interpretation
Vapour		Solution	Vapour		Liquid	
3130 m [b] 3123 s 3118 s 3110 m	B	3110	3137 m 3127 s 3115 m	P	3127 s, P	ν_1 a′
3075 w 3066 m 3058 w	A		3070 vs, P		3066 vs, P	ν_2 a′
3031 s 3023 s 3015 s	A	3010	3026 vs, P		3021 vs, P	ν_3 a′
					2968 w	
2954 w					2946 vw	
					2865 w	
2858 w					2859 vw	
2343 m 2330 s 2305 s	B				2332 vw	
2250 w 2241 m 2229 w	C					
1988 m 1975 m 1965 m	A					
1933 s 1923 s 1916 s	A	1925				
1678 s 1670 s 1659 s		1659	1671 vs, P		1662 vs, P	ν_4 a′
			1668 1665 1662			hot bands
					1645 m	
					1635 m	
					1615 vw, P	
1507 m 1499 m 1490 m	A					
1440 vs 1431 vs 1423 vs	A	1426 vs	1458 w 1434 s 1415 w	P	1432 s, P	ν_5 a′
1350 s		1348 w				
1316 s 1307 s	B	1304 s	1312 vs, P		1311 vs, P	ν_6 a′
1295 vs 1284 vs 1274 vs	A C	1277 vs	1295 m		1285 m, P	ν_7 a′
1230 s		1215				
1187 vs 1182 vs		1165	1180 m, P		1169 s, P	ν_8 a′
1170 vs 1159 vs		1138	1160 m, D		1143 s, D	ν_{15} a″
1096 m		1095 w				
1020 vs, C		1011 s	1030 w, br		1017 m, D	ν_{16} a″
978 vs		974 s	968 w		972 m, P	ν_9 a′
963 vs 950 s	C	962 s			960 vw	ν_{17} a″
			834 vw			
818 m 809 m 801 m	A?		812 vs, P		808 vs, P	ν_{10} a′
730 w 716 m 705 m 695 w					708 vw,D?	ν_{18} a″
650 s 645 s 634 s 628 s 621 s 613 s		630 m	637 m, P		636 m, P	ν_{11} a′
562 s 552 vs			555 s, P		547 s, P	ν_{12} a′
542 vs 536 s			541 s		521 m, D	ν_{19} a″
437 vs 431 vs 425 vs 418 vs	A/B		450 w 430 vs 415 w	P	431 vs, P	ν_{13} a′
327 w 317 w			320 s, D		312 s, D	ν_{20} a″
275 vw?			276 vs, P		275 vs, P	ν_{14} a′
60 [c] vw			70 s, D		83 s, D	ν_{21} a″

[a] Weak infrared bands outside the fundamental region have been omitted.

[b] Abbreviations: s, strong; m, medium; w, weak; v, very; P, polarized; D, depolarized; A, B and C denote infrared vapour contours.

[c] Estimated to 88 ± 25 cm^{-1} from microwave spectra [2].

Raman polarization measurements made it clear that a number of CS′ fundamentals were assigned to the opposite symmetry species. For the sake of brevity, we shall restrict our discussions mainly to the instances in which we have changed their assignments.

Since the 1284 cm^{-1} infrared vapour contour could be either **A** or **C**, the band might be attributed to species **a**″. However, the Raman band is definitely polarized and should therefore be ν_7 of species **a**′ involving mainly CF$_3$ stretch. The bands with complex infrared vapour contours around 1170 cm^{-1} appear as two distinct vapour bands 20 cm^{-1} apart in Raman. Since one is polarized and the other depolarized they have been assigned as the **a**′ and **a**″ CF$_3$ stretching modes ν_8 and ν_{15}. The 1020 cm^{-1} infrared band has a **C**-type contour with a prominent **Q**-branch, and was assigned as ν_{16} since the Raman

Table 2. Fundamental Frequencies of 3,3,3-trifluoropropene.

Observed [a]		Calculated [b]	CS [c]	Approximate motion (Vibrational energy distribution (%))
Infrared	Raman			
			a′	
3120	3127	3120	3124	ν_1 CH_2 asym str (98)
3066	3070	3066	3067	ν_2 CH str (94)
3023	3026	3023	3024	ν_3 CH_2 sym str (95)
1670	1671	1670	1669	ν_4 C=C str (54)
1431	1434	1435	1443	ν_5 CH_2 scissor (34), CCH (29), CC (25)
1311	1312	1313	1306	ν_6 CCH def (34), CCH_2 (19)
1284	1295	1285	1173	ν_7 CF_3 str (25), C=C (19), CCH_2 (16)
1185	1180	1175	1173	ν_8 CF_3 str (98)
978	968	978	1024	ν_9 CH_2 rock (106)
809	812	809	811	ν_{10} C–C str (18), CF_3 (39), CCH_2 (33)
634	637	640	718	ν_{11} CCC def (29), FCF (20), CCH_2 (17)
552	555	543	552	ν_{12} CF_3 def (75)
428	430	426	431	ν_{13} CF_3 def (32), CC (26), CCF (26)
275	276	259	318	ν_{14} CF_3 rock (87), CCC (21)
			a″	
1165	1160	1173	1286	ν_{15} CF_3 str (117)
1020	1030	1022	980	ν_{16} CH_2 wag (56), twist (31)
963	960 *	961	964	ν_{17} CH_2 twist (62), CH_2 wag (36)
710	708 *	707	635	ν_{18} CH trans wag (56)
542	541	549	552	ν_{19} CF_3 def (80)
322	320	332	318	ν_{20} CF_3 rock (97)
60	70	60	—	ν_{21} CF_3 torsion (96)

[a] Vapour phase values, except when fitted with an asterisk (* liquid state).

[b] For force field, see Table 6.

[c] Assignment according to Crowder and Smyrl [12], infrared vapour phase.

counterpart appeared depolarized. The 978 cm^{-1} band with uncertain contours, had a polarized Raman counterpart and was assigned as ν_9.

Although the infrared vapour contour around 710 cm^{-1} looks more like **B** than **C**, and the very weak Raman band had an uncertain polarization ratio, we have tentatively assigned the band to ν_{18} in excellent agreement with the calculated value. On the other hand the Raman vapour band at 637 cm^{-1} was polarized and with a sharp Q-branch it was assigned as ν_{11}, also in contradiction to CS' proposal [12]. The corresponding infrared vapour band had very complex features, probably as a result of Fermi resonance between the fundamental and $2\,\nu_{20}$ and $\nu_{19}+\nu_{21}$.

CS have assigned an infrared band at 552 cm^{-1} to coinciding **a′** and **a″** modes. Our Raman spectra strongly support this conclusion since two bands were observed, separated by 14 cm^{-1} in the vapour and 26 cm^{-1} in the liquid spectra. The high frequency band was polarized and assigned as ν_{12}, the low frequency band was depolarized and therefore attributed to the **a″** fundamental ν_{19}. The strong Raman vapour band at 320 cm^{-1} has the appearance of an **a″** mode and is furthermore depolarized. Although the corresponding infrared vapour band has no prominent Q-branch the bands are assigned as ν_{20} rather than ν_{14} [12].

A very intense Raman vapour band at 276 cm^{-1} was definitely polarized and therefore assigned as ν_{14}, whereas the infrared counterpart was extremely weak. Similar intensity relations were found for the bands around 70 cm^{-1} apparently connected with the CF_3 torsional mode. The infrared band around 60 cm^{-1} was very weak even in a 5 meter path length cell and showed no fine structure with 0.5 cm^{-1} resolution. In the Raman spectra a strong, broad, depolarized band was observed at 70 cm^{-1} in the vapour and at 83 cm^{-1} in the liquid spectrum. No rotational fine structure or hot band progressions were detected in the Raman vapour spectrum with the slit widths (6 – 2 cm^{-1}) used. Moreover, no higher harmonics of ν_{21} were found in the Raman spectra, as frequently reported by Durig and coworkers [14, 15] for comparable systems. The agreement with the value of 88 ± 25 cm^{-1} estimated from the microwave spectra [2] is satisfactory. Using the program ONETOP [19] and the structural parameters of Table 5, the torsional barrier in TFP was calculated as $V_3 = 535$ cm^{-1} (equal to 1530 cal/mol) when the absorption maximum was assigned to the $v=0 \rightarrow 1$, $v=1 \rightarrow 2$ and the $v=2 \rightarrow 3$ transitions.

The breadth of the vapour bands observed in infrared as well as in Raman, suggests that many excited states are populated. Since the anharmonicity is reasonably small the hot band progression is not resolved in the spectra.

Hexafluoropropene

The experimental infrared and Raman frequencies of Table 3 support the remarkably accurate work published by NCS [13] more than 25 years ago, in which also Raman vapour data were included. However, with photographic registration their polarization measurements were in several cases uncertain, leading to apparently wrong assignments. Also, their

Table 3. Vibrational Spectral Data [a] for Hexafluoropropene.

Infrared			Raman			Interpretation
Vapour		Solution	Vapour		Liquid	
2604 w [b]					2606 vw	
2250 w					2255 vw	
2100 w					2108 vw	
2049 vw					2053 vw	
1880 w 1868 s 1855 w		1866				
1796 vs		1788	1795 vs, P		1795 vs, P	ν_1 a'
1766 m					1780 m 1767 vw	
1407 s 1401 vs 1395 vs 1386 s	B	1391	1402 vs, P		1398 vs, P	ν_2 a'
1337 vs 1330 vs	B	1325	1334 vs, P		1332 vs, P	ν_3 a'
					1300 vw, P	
1216 vs 1209 vs	B	1199	1222 m 1211 m	P	1220 m, P	ν_4 a'
1185 s 1178 vs 1172 s	C	1159	1181 m, D		1165 m, D	ν_{15} a''
1120 s 1113 s	B	1112	1124 vw, P		1120 vw, P	ν_5 a'
1041 vs 1036 vs 1030 vs	A	1029	1036 w, P		1030 w, P	ν_6 a'
903 vw					900 vw, P	
					785 vw	
			774 m		775 m, P	
771 vs 766 vs 761 vs	A	766	767 vs, P		767 vs, P	ν_7 a'
			742 vw		744 w, P	
					722 vw, P	
658 vs 654 vs 650 vs	A	651	664 m 655 vs 648 m	P	655 vs, P	ν_8 a'
		648 m	642 w		648 m, D	ν_{16} a''
608 vw 601 vw			603 vw		603 w, P?	ν_9 a'
568 vw 559 vw 549 vw	C		564 s 555 s	D	564 vs, D	ν_{17} a''
518 s 512 s 506 s	A	512	519 m 512 s	P	513 s, P	ν_{10} a'
487 vw						
466 m 461 s 456 m	C	460	460 vw		461 w, D	ν_{18} a''
377 m		373	373 s, P		371 s, P	ν_{11} a'
365 m 356 m		363	360 vs, P		362 vs, P	ν_{12} a'
289 m					290 vw, P	ν_{13} a'

Table 3 (continued).

Infrared			Raman			Interpretation
Vapour		Solution	Vapour		Liquid	
255 s 248 w	C	251	257 s 242 s	D	251 s, D	ν_{19} a''
178 w 171 m 165 w	A	171	171 m, P		172 m, P	ν_{14} a'
126 w, C			130 s 122 s	D	133 s, D	ν_{20} a''
60 vw [c]					80 vw	ν_{21} a''

[a] Weak infrared bounds outside the fundamental region were reported by NCS[13] and have been omitted. — N_2-matrix isolation spectra, which will be discussed in a subsequent paper, show no frequency deviations except for ν_{15}.

[c] Estimated to 30 ± 15 cm^{-1} from microwave spectra [5].

Table 4. Fundamental Frequencies of Hexafluoropropene.

Observed [a]		Calc. [b]	NCS [c]		Approximate motion (Vibrational Energy Distribution (%))
Infrared	Raman				
			a'		
1796	1795	1782	1797	ν_1	C=C str (80), CF_2 (15)
1398	1401	1412	1399	ν_2	CF_2 asym str (100)
1334	1334	1332	1333	ν_3	CF str (59), CC (30)
1212	1216	1210	1211	ν_4	CF_3 str (111)
1117	1124	1144	1122	ν_5	CF_3 str (25), CC (26), CF_2 (24)
1036	1036	1009	1037	ν_6	CF_2 sym str (39), CF_3 (35)
766	767	758	767	ν_7	C—C str (1), CF_3 (27), CF_2 (20)
654	655	658	655	ν_8	CF_3 def (8), CCF_2 (43), CCF (23)
604	603	590	609	ν_9	CF_3 def (52), CF_3 (10)
512	512	517	559	ν_{10}	CF_2 scissor (54), CF_3 def (23)
377	373	379	513	ν_{11}	CF_3 rock (41), CF_2 rock (53)
365	360	351	364	ν_{12}	CF_2 rock (49), CF_3 rock (21)
289	290 *	284	250	ν_{13}	CCF bend (35), CC (25)
171	171	162	134	ν_{14}	CCC def (82), CF_3 rock (25)
			a''		
1178	1181	1179	1179	ν_{15}	CF_3 str (120)
648 *	648 *	649	559	ν_{16}	CF_2 wag (59)
559	559	574	462	ν_{17}	CF_3 def (67)
461	460	444	369	ν_{18}	CF_3 rock (66), CF_2 wag (21)
255	250	255	250	ν_{19}	CF_2 twist (88)
126	126	126	171	ν_{20}	CF wag (73)
60	80 *	60	94	ν_{21}	CF_3 torsion (100)

[a] Vapour phase values, except when fitted with an asterisk (* liquid state).

[b] For Force Field, see Table 6.

[c] Assignment according to Nielsen et al. [13], infrared vapour phase.

infrared measurements were limited to the region above 300 cm^{-1} by the transmission of their KRS-5 optics. Revised Raman polarization measurements obtained in the vapour phase have previously been obtained by Harvey and Nelson [16] and the existence of four definitely depolarized bands advanced as an argument for a planar $F_2C=CFC$ skeleton.

Our assigned fundamentals, listed in Table 4, are compared with the calculated frequencies and with the earlier assignments [13]. Only the cases in which we have revised NCS′ interpretations [13] will be briefly commented.

Overlapping the intense infrared and Raman bands around 654 cm^{-1} we have observed shoulders at 648 cm^{-1} in the liquid state spectra. Since the latter Raman band was depolarized, it is assigned as ν_{16} in good agreement with the results of the normal coordinate calculations. NCS assigned the bands around 560 cm^{-1} to overlapping **a**′ and **a**″ fundamentals ν_{10} and ν_{16}. Our data strongly suggest only one fundamental in this region. Since the weak infrared band at 559 cm^{-1} had a C-type contour and the intense Raman band seemed depolarized, we have assigned them to the **a**″ mode ν_{17}. The close lying pair at 373 and 360 cm^{-1} (Raman vapour) were assigned by NCS [13] as **a**″ and **a**′ fundamentals, respectively. However, both bands are definitely polarized and should therefore be assigned as **a**′ modes (ν_{11} and ν_{12}) supported by the normal coordinate analysis.

A medium intense infrared band at 289 cm^{-1} (outside NCS′ region) had a very weak and apparently polarized Raman counterpart and was assigned as ν_{13}. NCS were forced to assume overlapping **a**′ and **a**″ fundamentals around 250 cm^{-1}, while this band should in our opinion be attributed to ν_{19} only. The infrared vapour contours and Raman polarization measurements both reveal that the bands around 171 and 126 cm^{-1} should be **a**′ and **a**″ modes, respectively, whereas NCS have made the opposite assignments [13].

A very weak infrared vapour band was observed at 60 cm^{-1} while no other absorptions bands were detected above 30 cm^{-1}. An extremely weak Raman band of the liquid was detected at 80 cm^{-1} for which no polarization ratio could be obtained. In spite of many attempts with varying slits, laser power and exciting laser lines no corresponding Raman band was detected in the vapour phase. Since the Rayleigh background was quite low the experimental conditions should be favourable for observing the vapour band. NCS, however, reported Raman bands at 94 cm^{-1} (vapour) and 84 cm^{-1} (liquid) and assigned [13] them to the torsional mode ν_{21}. It seems ironic that the present Raman technique involving a 10 watts laser, triple monochromator, cooled detector and photon counting should not match the nearly 30 years old facilities [13] including a Toronto lamp, glass prism spectrograph and photographic recording.

In infrared, the low intensity of the 60 cm^{-1} band has apparently, prevented earlier observations [17]. Our experiments indicate that the infrared intensities of ν_{21} are of comparable magnitude for TFP and HFP. In Raman, however, the intensity was at least 100 times larger for TFP, revealing very different polarizability terms for the CF_3 torsional motion in the two compounds. In the series CF_3-CH_2X ($X=I$, Br, Cl, F) Lopata and Durig [18] reported very intense and broad Raman bands connected with the torsional modes, in agreement with the present data for TFP, but in contradiction to the results for HFP. The present value for ν_{21} will give an estimated barrier height [19] equal to $V_3=1235\ cm^{-1}$.

An estimated value of $30\pm15\ cm^{-1}$ for the torsional mode in HFP was derived from the microwave spectra [5], but this value seems definitely to be too low in view of the present results. The recent electron diffraction study of Lowrey et al. [6] suggested that the CF_3 group in HFP was not freely rotating although their barrier height was estimated to be as low as 425 cm^{-1} (1500 cal/mol). However the introduction of a V_6 term in addition to V_3 will tend to reconcile the present estimated potential parameters with those obtained from electron diffraction [6, 25].

Force Field Calculations

The normal coordinate calculations were carried out using valence type force constants in a basis of mass-weighted cartesian coordinates [20]. Several factors added to complicate these calculations. Most important was the lack of data (21 measured frequencies per compound compared to 133 different elements in a general harmonic force field) and the strong mixing of internal vibrational modes, which resulted in highly significant contributions to the

Jacobian matrix from several interaction constants. This mixing was also responsible for drastic changes in the vibrational energy distribution (approximate motion) upon minute changes of the interaction constants. Thus a "reasonable" energy distribution was used as an extra criterium to decide the goodness of a fit.

We expected the structure (and the involved force constants) of the two trifluoromethyl groups to be similar. Therefore new r_0-structures were calculated, especially since the published MW-structure for TFP is a conglomerate of structural parameters obtained from electron diffraction (r_g), Kraitchman calculations (r_s) and fit to rotational constants (r_0) [2], and since new diffractional data for HFP have just been published [6]. For TFP, the rotational constants for different isotopic species were corrected (in A) to yield the same pseudoinertial defect as for the parent species. The obtained rotational constants were employed to obtain a fit of the structure using the program GEOM [21] and fixing the fluoromethyl group at CF = 1.334 Å and FCF = 108.0°. For HFP all the three =CF distances were additionally set equal to 1.325 Å.

It was necessary to introduce a tilt of the trifluoromethyl group in TFP to reconcile rotational constants of different isotopic species [2]; for HFP this tilt was neglected. The resulting structural parameters for TFP and HFP are collected in Table 5. The assignment and force field for the parent compound of TFP, ethylene, is well established [22]. Calculations using a modified force field almost identical to the appropriate part of the force field for TFP gave a reasonably good fit and yielded similar numerical values for the two molecules.

Table 5. Structural parameters for 3,3,3-Trifluoropropene (TFP) and Hexafluoropropene (HFP) (dist. in Å, angles in deg).

	TFP	HFP
C=C	1.315	1.322
C−C	1.514	1.510
C−F	1.334 *	1.334 *
$=C-X_{cis}^{a}$	1.071	
$=C-X_{trans}$	1.072	1.325 *
$=C-X_{gem}$	1.099	
$C=C-X_{cis}$	119.5	126.2
$C=C-X_{trans}$	121.3	125.0
$C=C-X_{gem}$	122.0	125.0
C=C−C	124.8	125.5
F−C−F	108.0 *	108.0 *
tilt	1.0 *	0.0 *

[a] cis, trans and gem relative to CF_3-group.
* fixed during the least squares fit.

The assignment of tetrafluoro ethylene is much less certain [23, 24]. A modified valence force field was fitted to the data of Nielsen et al. [23] as part of this work. The force constants for tetrafluoro ethylene are apparently not directly transferable to HFP, although the discrepancy can be caused by the simplyfying assumptions incorporated into the force field of HFP to be described below.

The least amount of mixing among the internal modes was found in TFP, therefore a force field for this molecule was first determined.

3,3,3-trifluoropropene

In order to keep the number of force constants as low as possible, the two vinyl hydrogen atoms opposite the fluoromethyl group were treated as equivalent and the force constants involving the third hydrogen atom were restricted to values close to those involving the other two.

Moreover, the three fluorine atoms were considered equivalent. The **a′** frequencies were calculated after several attempts were made to define the most meaningful interaction constants, required to obtain a good fit. The assignment posed no problem, i. e. the vibrational energy distribution corresponded to the assignment given above.

The **a″** frequencies, however, were easily fitted, but the vibrational energy distribution fluctuated wildly. Only the introduction of an interaction constant twist/H-wag stabilized the fit. This is probably reasonable since both internal coordinates result principally in a movement of the third hydrogen atom perpendicular to the plane of the heavy atom, thus they will very easily couple.

Hexafluoropropene

The **a″** vibrations did not cause any problems and the interaction constant twist/F-wag was not necessary, apparently because the $C-CF_3$ part participates more in the fibration relative to CF and thus decouple the two internal modes. Besides the simplifications introduced for TFP, the C = C − C and the C = C − F in plane bend were considered equivalent for the geminal, trans and cis deformation interactions.

Table 6. Force fields for 3,3,3-Trifluoropropene (TFP), Ethylene, Hexafluoropropene (HFP) and Tetrafluoroethylene (stretch in mdyn/Å, bend in mdynÅ/rad^2 and stretch/bend in mdyn/rad).

Group *	Type	TFP	Ethylene	HFP	Tetrafluoro-ethylene
$C=C$	stretch	7.882	8.893	7.882	8.471
$C-C$		4.543		3.790	
$C-F$		6.207		6.189	
$=C-X_2$		5.133	5.56	7.460	7.313
$=C-X$		5.096		7.400	
$C=C-C$	in plane bend	1.966		1.985	
$C-C-F$		0.910		1.143	
$C=C-X_2$		0.893	1.004	2.141	2.145
$C=C-X$		0.976		2.056	
$F-C-F$		1.725		1.786	
twist	out of plane bend	0.674	0.546	0.969	0.593
torsion		0.025		0.120	
X_2 wag		0.245	0.261	0.451	0.343
X wag		0.327		0.107	
	interactions				
$C=C-X/C=C-X$ gem		0.415	0.441	0.934	1.270
$C-F/C-F$		0.671		0.677	
$C-F/F-C-F$		0.584		0.689	
$C-F/C-C-F$		0.894		0.747	
$C-C/C-F$		0.475		1.047	
$C-C/C=C-X$		−0.316			
$=C-X/=C-X$ gem		0.035	0.058	−0.550	0.580
twist/X wag		0.111			
$C=C/C=C-X$			0.266		
$C=C/C-X_2$			0.125		
$C=C-X/C=C-X$ trans			0.085	0.156	0.182
$C=C-X/C=C-X$ cis				0.351	0.240
$C-X/C=C-X'$				−1.129	−0.814
wag/wag			0.041		

* TFP: X=H, HFP: X=F.

The vibrational energy distribution for the CF_3-deformation and the C − C stretch are very unfavourable. Other quite similar force fields gave much better correspondance with the assignment but then failed for the CF-stretches. Undoubtedly, the inclusion of more interaction constants would result in a more reasonable vibrational energy distribution.

Including the simplifying assumptions, 23 force constants were needed to fit the spectrum, forcing us to keep at least 3 terms constant during the iteration procedure.

The force constants are collected in Table 6 and as apparent most of the physically significant stretching and bending constants which can be compared are quite similar for TFP and HFP. An exception is represented by the torsional constant which was much higher for HFP as a consequence of our experimental results. As mentioned above the agreement between the corresponding force constants in TFP and ethylene is quite good, whereas larger discrepancies were observed between those of HFP compared to tetrafluoro ethylene.

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[1] I. A. Mukhtarov and V. A. Kuliev, Izv. Akad. Nauk. Azerb. SSR **1970**, 146.

[2] S. Saito and F. Makino, Bull. Chem. Soc. Japan **47**, 1863 (1974).

[3] I. Tokue, T. Fukuyama, and K. Kuchitsu, J. Mol. Struct. **17**, 207 (1973).

[4] S. H. Bauer and C. H. Chang, Abstract of Papers of the 161st Meeting of the American Chemical Society, Los Angeles, California, 28 March 1971, paper Phys. 14.

[5] E. J. Jacob and D. R. Lide, J. Chem. Phys. **59**, 5877 (1973).

[6] A. H. Lowry, C. George, P. D. Antonio, and J. Karle, J. Mol. Structure **53,** 189 (1979).

[7] B. S. Freiser and J. L. Beauchamp, J. Am. Chem. Soc. **96,** 6260 (1974).

[8] K. Hirao, N. Nakatsuji, and H. Kato, J. Am. Chem. Soc. **95,** 31 (1973); J. Hilton and L. H. Sutcliffe, J. Magn. Resonance **14,** 241 (1974).

[9] D. W. Davis, M. S. Banna, and D. A. Shirley, J. Chem. Phys. **60,** 237 (1974).

[10] W. L. Jolly and A. A. Bakke, J. Am. Chem. Soc. **98,** 6500 (1976).

[11] M. A. Landau, A. V. Fokin, and A. S. Kabankin, Zh. Strukt. Khim. **15,** 327 (1974).

[12] G. A. Crowder and N. Smyrl, J. Chem. Phys. **53,** 4102 (1970).

[13] J. R. Nielsen, H. H. Claassen, and D. C. Smith, J. Chem. Phys. **20,** 1916 (1952).

[14] J. R. Durig, W. E. Bucy, L. A. Carreira, and C. J. Wurrey, J. Chem. Phys. **60,** 1754 (1974).

[15] J. R. Durig, W. E. Bucy, and C. J. Wurrey, J. Chem. Phys. **60,** 3293 (1974).

[16] A. B. Harvey and L. Y. Nelson, J. Chem. Phys. **55,** 4145 (1971).

[17] K. R. Roos, Ph. D. Thesis, Dept. of Chemistry, MIT, Cambridge, Mass. USA, 1964.

[18] A. D. Lopata and J. R. Durig, J. Raman Spectrosc. **6,** 61 (1977).

[19] A. Bauder and H. H. Günthard, J. Mol. Spectry. **60,** 290 (1976).

[20] D. Christen, J. Mol. Structure **48,** 101 (1978).

[21] P. Nösberger, A. Bauder, and H. H. Günthard, Chem. Phys. **1,** 418 (1973).

[22] J. L. Duncan, D. C. McKean, and P. D. Mallinson, J. Mol. Spectry. **45,** 221 (1973).

[23] D. C. Smith, J. R. Nielsen, and H. H. Claassen, J. Chem. Phys. **18,** 326 (1950); J. R. Nielsen, H. H. Claassen, and D. C. Smith, J. Chem. Phys. **18,** 812 (1950).

[24] Y. Morino, K. Kuchitsu, and T. Shimanouchi, J. Chem. Phys. **20,** 726 (1952).

[25] Discussed in Paper A 48, EUCMOS, Frankfurt 1979.