# Vibrational spectra and normal coordinate analysis of CF<sub>3</sub> compounds. The trifluoromethylgermanes $(CF_3)_2GeH_{2-n}D_n$ and $(CF_3)_3GeH_{1-n}D_n$

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Abstract—The gas phase i.r. and liquid phase Raman spectra of  $(CF_3)_2GeH_2$ ,  $(CF_3)_2GeH_2$ ,  $(CF_3)_2GeH_2$ ,  $(CF_3)_2GeH_2$ ,  $(CF_3)_3GeH$  and  $(CF_3)_3GeD$  are reported and assigned. Force constants have been calculated yielding f(GeC) 2.25/2.27, f(GeH) 2.743/2.762 and f(CF) 5.75/5.82 N cm<sup>-1</sup> for  $(CF_3)_2GeH_2$  and  $(CF_3)_3GeH$ , respectively. Bonding parameters are discussed with respect to related molecules.

#### INTRODUCTION

Recently we have reported the vibrational spectra of trifluoromethylgermanes,  $CF_3GeH_{3-n}D_n[1]$ . This study extends the investigations to the di- and tri-CF<sub>3</sub>-substituted germanes which also complement the previously investigated series of trifluoromethyl(halo)germanes, (CF<sub>3</sub>)<sub>2</sub>GeX<sub>2</sub>[2] and  $(CF_3)_3GeX[3]$  (X = F, Cl, Br, I). In all cases considerable weakening of the Ge-C bond with respect to the methyl analogues was deduced. Within the series bond strengths increased smoothly with increasing electronegativity of the atoms or groups attached to germanium, the CF<sub>3</sub> group behaving very similar to a bromine or chlorine atom. The combined investigation of all trifluoromethylgermanes including all possible deuterated species allows a detailed analysis of the spectra yielding much more reliable force constants than would be obtained from the investigation of any single compound.

# **EXPERIMENTAL**

 $(CF_3)_2GeH_2$  and  $(CF_3)_3GeH$  were obtained from the reaction of  $(CF_3)_2GeI_2$  and  $(CF_3)_3GeI[4]$ , respectively, with NaBH<sub>4</sub> in aqueous phosphoric acid. The deuterated materials (95% isotopic purity) were prepared employing all deuterated reagents, while  $(CF_3)_2GeHD$ , contaminated with 24% of the D<sub>2</sub> and 2% of the H<sub>2</sub> compound, was obtained utilizing NaBD<sub>4</sub> and H<sub>3</sub>PO<sub>4</sub>. Details of this reaction will be described elsewhere [5]. The samples were purified by g.l.c. using 8 m × 6 mm SE-30 columns on a Varian 3700 gas chromatograph. The purity of the samples was checked by <sup>1</sup>H and <sup>19</sup>F NMR spectroscopy (Varian EM 390).

Raman spectra were recorded on liquid samples sealed in 1 mm i.d. capillaries employing a Cary 82 spectrometer with Kr<sup>+</sup> excitation at 647.1 nm, 200 mW at the sample. Typical slit widths were 2–3 cm<sup>-1</sup>, wavenumber accuracy  $\pm 1$  cm<sup>-1</sup>. Depolarization states are estimated. The Raman spectra were also recorded at -196°C on glassy samples employing slit widths <2 cm<sup>-1</sup>. Deviations from the frequencies listed in Tables 2 and 3 were <5 cm<sup>-1</sup>. Infrared spectra were obtained on gaseous samples in 10 cm gas cells fitted with KBr, polyethylene or TPX windows. For 4000-180 cm<sup>-1</sup> a Perkin-Elmer 580B spectrometer, wavenumber accuracy  $\pm 1$  cm<sup>-1</sup>, resolution  $2 \text{ cm}^{-1}$ , as well as a Nicolet 7199 FT spectrometer (4000–400 cm<sup>-1</sup>) at a resolution of  $1 \text{ cm}^{-1}$  were utilized. The pressures were varied from 1 to 300 mbar. The region from 400 to 50 cm<sup>-1</sup> was investigated with a Nicolet 8000 vacuum spectrometer.

#### VIBRATIONAL ANALYSIS

To a first approximation the spectra of the molecules (CF<sub>3</sub>)<sub>2</sub>GeH<sub>2</sub> and (CF<sub>3</sub>)<sub>3</sub>GeH can be analyzed assuming the highest possible symmetry,  $C_{2v}$  and  $C_{3v}$ , respectively. The distribution of the fundamentals, their notation and their symmetry properties are given in Table 1. From the electron diffraction study of  $(CF_3)_4Ge[6]$  it is known that the barriers to the rotation of the CF<sub>3</sub> groups are very low with an estimated torsional force constant of 0.04 N cm<sup>-1</sup>. Furthermore, fluorinefluorine interactions suggest that twisted conformers may be slightly favoured which could result in low i.r. intensity for the "forbidden" a2 fundamentals. The observed i.r. and Raman spectra and their assignments are listed in Tables 2 and 3, polarization Raman while the spectra of (CF<sub>3</sub>)<sub>2</sub>GeH<sub>2</sub> and (CF<sub>3</sub>)<sub>3</sub>GeH are shown by Figs. 1 and 2, respectively.

The spectra may be separated into  $GeH_n$  and  $CF_3$  vibrations, the latter exhibiting H/D isotope shifts of less than 5 cm<sup>-1</sup> if no specific coupling is involved. The CF<sub>3</sub>Ge part resembles the corresponding features of the spectra of  $(CF_3)_2GeX_2[2]$  and  $(CF_3)_3GeX[3]$  with characteristic frequency regions:

$\nu(CF_3)$	$1100-1200 \text{ cm}^{-1}$
$\delta_{\rm S}({\rm CF}_3)$	<i>ca.</i> 730 cm <sup><math>-1</math></sup>
$\delta_{\rm as}({\rm CF}_3)$	<i>ca.</i> 520 cm <sup><math>-1</math></sup>
$\rho(CF_3)$ and $\nu(GeC)$	$200-300 \text{ cm}^{-1}$ .

Major vibrational couplings will occur for  $\rho(CF_3)$ and  $\nu(GeC)[2, 3]$  and between  $\delta_{as}(CF_3)$  and  $\delta(HGeC)$  as in  $CF_3Ge(H, D)_3[1]$ .

		(CF <sub>3</sub> ) <sub>2</sub> (	$GeH_{2}(\underline{C}_{2v})^{a}$	(CF <sub>5</sub> ),	GeH(C3v)		
	<u>a</u> ,(i.r./Rap)	<u>a</u> (Ra)	<u>b</u> 1(i.r./Ra)	<u>b</u> 2(i.r./Ra)	<u>a</u> 1(i.r./Raj	p) <u>a_2(-)</u>	<u>e</u> (i.r./Ra)
vas CF;	<b>ب</b> ر	¥10	$v_{1.5}$	V <sub>21</sub>	ν <sub>1</sub>	ν <sub>s</sub>	V13, V1+
∨ <sub>s</sub> CF₃	ν <sub>2</sub>			V2 2	ν <sub>2</sub>		V15
$\delta_{as}$ CF <sub>3</sub>	$v_3$	$v_{1 1}$	V1 6	V <sub>23</sub>	$v_5$	V1 o	$v_{16}, v_{17}$
δ <sub>S</sub> CF <sub>5</sub>	∨.			V2 4	V.		V <sub>18</sub>
ρ CF <b>,</b>	ν,	$\nabla_{1, \eta}$	V1 7	V2 5	v,	V1 1	V19, V20
ν GeCn	∨ <sub>6</sub>			V <sub>26</sub>	$\nabla_6$		V <sub>2 1</sub>
∨ GeH	$\nu_7$		V1 B		V.7		
δ GeCn	Va				ve		V2 2
δ GeH <sub>2</sub>	$\vee_9$						
δ CGeH		V1 3	والأ	V <sub>27</sub>			V <sub>23</sub>
τ		V1.4	¥20			V12	V2.4

Table 1. Distribution and notation of vibrational fundamentals

<sup>a</sup>For (CF<sub>3</sub>)<sub>2</sub>GeHD ( $C_s$ ):  $a_1, b_1 \rightarrow a', a_2, b_2 \rightarrow a''$ .

# $(CF_3)_2Ge(H, D)_2$

The CF stretching region clearly differs from that of  $(CF_3)_2GeX_2[2]$  in that four well-separated i.r. absorptions are observed. The highest coincides with a polarized Raman line and is assigned to  $\nu_2$ . The Raman spectrum shows a second distinct peak at 1168 cm<sup>-1</sup> coinciding again with an i.r. band which is attributed to the second  $\nu_s(CF_3)$ component,  $\nu_{22}$ . The  $\nu_{as}(CF_3)$  bands presumably occur in two groups,  $\nu_1/\nu_{15}$  at 1136 cm<sup>-1</sup> and  $\nu_{10}/\nu_{21}$ around 1110 cm<sup>-1</sup>. In the Raman spectrum these modes give rise to a very broad, weak feature which extends from *ca.* 1070 cm<sup>-1</sup> to the peaks of  $\nu_2$  and  $\nu_{22}$ .

As in all CF<sub>3</sub> compounds a strong polarized Raman line is characteristic for  $\delta_s(CF_3)$ ,  $\nu_4$ . Due to the presence of the strong GeH<sub>2</sub> wagging mode at 720 cm<sup>-1</sup>, the corresponding i.r. band is not detected in (CF<sub>3</sub>)<sub>2</sub>GeH<sub>2</sub>, whereas it is clearly present at 730 cm<sup>-1</sup> in the D<sub>2</sub> species. In the i.r. spectrum of the mono-deuterated compound  $\nu_4$  appears as a shoulder of an absorption at 724 cm<sup>-1</sup> which is ascribed to  $\nu_{24}$  and which obviously has gained intensity by mixing with the strong absorption at 688 cm<sup>-1</sup>.

The  $\delta_{as}(CF_3)$  fundamentals display an interesting vibrational coupling. The  $a_1$  component does not interact significantly with other modes and is ascribed to the weak Raman band around  $530 \text{ cm}^{-1}$ , which becomes clearly visible in the low-temperature spectrum. The relatively strong i.r. band of  $(CF_3)_2GeH_2$  at  $548 \text{ cm}^{-1}$  must be assigned to  $v_{16}$ , which is blue-shifted by mixing with  $v_{19}$  at  $454 \text{ cm}^{-1}$ . The large isotope shift of  $v_{19}$ will remove the coupling for the deuteride. For this species, however, strong mixing with 1:1 sharing of intensities occurs for the  $b_2$  modes  $v_{23}$ and  $v_{27}$  at 494 and 541 cm<sup>-1</sup>. In  $(CF_3)_2GeH_2$ ,  $v_{27}$  is too far away to interact, and thus  $v_{23}$  is assigned at  $516 \text{ cm}^{-1}$ . A similar situation holds for the  $a_2$  mode  $\nu_{16}$  which is assigned to the Raman band at 510 cm<sup>-1</sup>, which, however, disappears from this position in the deuteride due to mixing with  $\nu_{13}$  at 445 cm<sup>-1</sup>. The mixed HD species will exhibit less pronounced coupling patterns. The strongest interaction occurs for the *a*" component ( $\nu_{11}$ ) causing a slight blue-shift of the main Raman band to 535 cm<sup>-1</sup>.

As in (CF<sub>3</sub>)<sub>2</sub>GeX<sub>2</sub>[2] extensive coupling determines the  $\nu$ (GeC) and  $\rho$ (CF<sub>3</sub>) modes. The  $a_1$  pair is easily recognized as polarized Raman lines at 315 and  $250 \text{ cm}^{-1}$ . The second pair of  $b_2$  symmetry,  $\nu_{as}$ (GeC) at 324 cm<sup>-1</sup> and  $\nu_{25}$  at 203 cm<sup>-1</sup>, interacts much less, only small H/D shifts being observed. The  $a_2$  mode  $v_{12}$  is expected close to  $v_{25}$  and is assigned to the almost coincident, very weak depolarized Raman line at 206 cm<sup>-1</sup>, which exhibits, however, an isotope shift differing distinctly from that of  $\nu_{25}$ . No direct evidence is found for  $v_{17}$ . Due to coupling with  $v_{19}$ , the  $b_1$  rocking modes should show marked H/D shifts. An overtone with such an isotope shift is observed at 1410 cm<sup>-1</sup> which could originate from a combination with a CF stretch.

The GeH(D) stretches exhibit distinct i.r. band contours, type C with a rather broad Q branch for  $v_{18}$ , and type B with PQQR structure for  $v_7$ . The average values of  $\nu_7$  and  $\nu_{18}$  match well the frequencies of the isolated GeH and GeD stretches in (CF<sub>3</sub>)<sub>2</sub>GeHD. Especially the asymmetric stretches experience large phase shifts, the Raman frequencies being blue-shifted by 10 cm<sup>-1</sup>. The skeletal deformations are very similar to those of GeH<sub>2</sub>Br<sub>2</sub> and GeD<sub>2</sub>Br<sub>2</sub>[7], major differences only being caused by interactions with  $\delta_{as}(CF_3)$  modes (see above). A slight deviation from  $C_{2v}$  symmetry is indicated by the i.r. activity of the  $a_2$  band,  $\nu_{13}$ , which gains considerable intensity when the symmetry is lowered to  $C_s$  in the mixed HD species.

(C3	,),GeH,	(c)	,),GeHD	(CF	'3)2GeD2	
i.r.(gas)	Raman(liq.)	i.r.(gas)	Raman(liq.)	i.r.(gas)	Raman(liq.)	Assignment <sup>a</sup>
75 WD	79 m	75 wb	78 w	75 wb	78 w	
203 w		200 w		197 w		V25
	206 vw				205 vw	V12
248 vw	250 vsp	248 vw	250 vsp	248 vw	250 vsp	V.6
	315 sv		314 sp		313 sp	
324 s	323 sh	322 s	321 sh	321 s	320 sh	
454 m	458 w	399 w	405 vw	375 m	378 w	¥19
		468 m	465 w	445 w	446 m	$v_{13}(D_2)$
(508 sh)	510 w		-	494 s	495 vw	v23 (D2)
516 w (530 sh)	530 100	516 w	535 wh		532 vw	۵ <sub>as</sub> CF <sub>3</sub> <sup>C</sup>
548 w	550 w	*p				(7)
				541 S	74⊥₩	$v_{27}(u_2)$
644 vw	652 m				a. a	V13
				607 m <b>-s</b>	606 m	ν <sub>9</sub> (D <sub>2</sub> )
673 w		672 sh		673 w		
720 s	720 w	688 <b>s</b>	688 w			V27
	728 sp	724 m. <sup>C</sup>	727 sp	730 m	727 sp	V4 , V2 4
846 m-s	843 mp	753 <b>m</b> -s	752 wp			٧ <sub>9</sub>
		797 vw		802 vw		v <sub>8</sub> +v₂⊾
		877 100		850 VW 877 VW		v <sub>e</sub> +v <sub>p</sub>
916 vw		922 vw		921 w		V24/, V27 + V25
974 <b>v</b> w		977 vw		977 VW		V24/V27+V6
998 WW 1054 W		1055 w		1053 w		V1 - Vn
1106 5		1105 s		1105 s		V.,
1111		1110 m-s		111C m-s		V1 o
1136 18	1120 vwb	1135 ve	1120 vsb	1135 VS	1120 vwb	
1150 va	1169 10	1167 ve	1167 w	1167 45	1167 ч	N
1106 -	1100 *	110/ 03	1105 00	1106 0	110/ wp	*22
1196 s	1192 WD	1196 5	1192 #b	1363 1	1124 <b>#</b> Þ	ν2 Α.δ. (CE.)
1205 W 1298 VW		1298 W		1202 ₩		s as (0r)
1332 w		1329 w		1327 W		V1 + V2 5
1371 W 1410 VW		1398 vw		1392 vw		$\left(v_{1}+v_{1}\right)^{C}$
1450 vw		1450 vwb		1450 vw		v1 + v 5
1487 VW 1522 VW		1487 VW		1487 VW		$v_{5} + v_{22}$
1)22 **				1539(P)	1544 sp	$v_{\pi}(D_{\pi})$
		1550 8	1545 sn	1543(R)"	23 · · · · · · · · · · · · · · · · · · ·	· / · - 2 /
		1))03	1)40.35	1559 s	1570 w	ν <sub>18</sub> (D <sub>2</sub> )
1570 vw						v <sub>4</sub> +v <sub>9</sub>
1645 VW 1675 VW		1640 sh 1665 wwb		1638 VW 1670 VW		$v(CF_{\star})+b$ (CF_{\star})
10/5 **		1725 vwb		1719 vw		as
1782 vw		1835 v∾		1838 vr		V13 +V15
1856 W		1855 w		1856 w		V4 +V13
1896 vw		1895 vw		1895 vw		V. +V22
1924 VW 2042 VW		1924 VW		1920 VW		V2 + V2 + V2 + V6
2143(P)						
2147(R) <sup>m</sup>	2150 sp					v7
2161 s	2170 w	2153 s	2160 тр			V18
2224 m		2223 m		2222 m		2v1 D
2252 w		2250 w 2274 w		2248 W 2272 W		V10 +V19
2295 w		2293 w		2292 🖌		V1 +V22
2331 m		2331 m		2331 m		2422
2389 w		∠228 m 2390 w		2008 m 2390 w		200
2594 vw		2550 vw				
2695 vw		2680 vw				V7 +V1 6
2804 WW 2858 WW		2830 vw				V13 TV18 V= TV==
2994 w		2894 vw				Vg +V18
3280 vw		3285 VW		2674 vw 2754 vw		$v_7 + v_{15}$
VW UCCC		wvt;⊷رىر		3064 w		$2v_{7}(D_{2})$

Table 2. Infrared gas and Raman liquid frequencies of (CF<sub>3</sub>)<sub>2</sub>Ge(H, D)<sub>2</sub> [cm<sup>-1</sup>]

<sup>8</sup>Unless otherwise quoted the assignment is given for  $(CF_3)_2GeH_2$ . <sup>b</sup>Overlapped by strong  $GeD_2$  band. <sup>c</sup>See text.

#### $(CF_3)_3Ge(H, D)$

The  $(CF_3)_3Ge$  part of the spectra is very similar to those of other  $(CF_3)_3GeX$  derivatives[3] with only minor deviations due to the light mass of hydrogen. The CF<sub>3</sub> stretch region is characterized by four i.r. bands, whereas the Raman spectrum shows a polarized line  $(\nu_2)$  and a broad feature extending from 1100 to 1200 cm<sup>-1</sup>. The strongest i.r. absorption at 1167 cm<sup>-1</sup> which corresponds to the maximum of the Raman band is assigned to  $\nu_{14}$ . The Raman band contains a shoulder at *ca*. 1180 cm<sup>-1</sup> which might originate from  $\nu_{15}$ . As in ref. [3] the bands at 1131 and 1155 cm<sup>-1</sup> are ascribed to  $\nu_{13}$  and  $\nu_{1}$ , respectively. The  $a_2$  mode,  $\nu_{10}$ , is not observed directly. The combinations and overtones, however, suggest a value of *ca*. 1110 cm<sup>-1</sup>. Similar to (CF<sub>3</sub>)<sub>2</sub>GeH<sub>2</sub> and CF<sub>3</sub>GeH<sub>3</sub>[1], upon deuteration one set of the degenerate  $\delta_{as}$ 

(CF, )	(CF, ), GeH (CF, ), GeD			
i.r. (gas)	Raman (liq.)	i.r. (gas)	Raman (liq.)	Assignment <sup>a</sup>
73 sh	75 m	72 sh	74 m	v <sub>a a</sub>
82 mb		80 mb		∨ <sub>8</sub>
20 <b>2 m</b>	205 vw	199 m		¥1 g
238 w	241 vsp	238 w	241 vsp	vé
251 vw	253 m	251 vw	252 m	V20
323 в	320 mp	322 s	318 wp	V3
343 vs	341 m	340 vs	338 w	V2 1
		375 w		
		470 s	468 w	∨ <sub>23</sub> (D)
512 m	515 vw			ν <sub>1 6</sub>
525 sh	527 w		532 w	V17
		537 m	539 vw	ν <sub>16</sub> (D)
539 w		675 mb		V19 +V21
597 w		607 w		$v_{20} + v_{21}$
667 w				V5 +V21
6 <b>79 vs</b>	676 m			V <sub>23</sub>
731.5 m	731 sp	774 -	730 sp	V.
755 m		γ <b>5</b> 4 μ		¥18
760 W 930 W		930 w		$v_3 + v_7$ $v_4 + v_{19}$
975 vw		974 vw		$v_1 + v_2$
1050 W 1077 m		1073 m		$\nu_{a} + \nu_{p}$
1131 s		1131 s		V13
1155 s		1154 s		V1
1167 vs	1160 wb	1166 vs	1160 wb	V1.
	ca.1180 sh	c	a,1180 sh	¥15
1206 s	1205 vwp	1206 <b>s</b>	1205 vwp	Vz
1242 m		1240 sh		V1 + + V2 g
1256 m		1260 m		v5 +v4
1337 m		1334 m		$v_{13} + v_{19}$
1409 w		1407 w		$v_1 \mathbf{A} + v_1 \mathbf{p}$ $v_2 + v_1 \mathbf{p}$
1452.45		1420 sh		V1 + + V20
1452 sn 1464 w		1464 w		$v_{13} + v_{21}$
1509 vw		1507 vw		V1 4 + V2 1
		1556 s (PQR)	) 1562 wp	ע <sub>7</sub> (D)
1640 vwsh		1638 vw		
1690 sh		1685 sh		$v(CF_3) + b_{as}(CF_3)$
1735 vwb		1735 VW		No. + No
1841 W 1862 W		1862 w		$v_1 + v_1$
1877 w 1897 w		1874 w		$v_{i} + v_{i}$
1939 vw		1939 w		$v_2 + v_4$
		2019 vw		V7 +V2 5
2160.5 s(P	2R) 2168 mp			<b>∨</b> 7
2241 m		2240 m 2272 m		
2300 m		2300 m		21
2320 sh		2320 sh		241
2369 m 2409 m		2369 m 2409 ww		V2+V1+ 2N-
2478 vw				$v_3 + v_7$
		2606 vw 2760 vw		ν <sub>7</sub> +ν <sub>1 +</sub> ν <sub>2</sub> +ν <sub>2</sub>
2826 w		2,00		$v_7 + v_{23}$
		3078 vw		227
3310 vw				$v_7 + v_1$
5060 VW				

Table 3. Infrared gas and Raman liquid phase frequencies of  $(CF_3)_3Ge(H, D)$  [cm<sup>-1</sup>]

"Unless otherwise quoted the assignment is given for (CF<sub>3</sub>)<sub>3</sub>GeH.

modes is shifted from 512 to  $537 \text{ cm}^{-1}$  by interaction with the GeH rocking vibration,  $\nu_{23}$ , which decreases from 679 to  $470 \text{ cm}^{-1}$ . The Raman band at *ca*. 527 cm<sup>-1</sup> presumably contains both the  $a_1$ and the second *e* set, which experiences a small blue-shift in the deuteride. The two degenerate  $\rho(CF_3)$  modes are clearly detected as i.r.  $(\nu_{19})$  and depolarized Raman bands  $(\nu_{20})$ . As in all  $(CF_3)_n$ Ge compounds, the  $a_1$  component is strongly coupled to the  $\nu_s(GeC)$  stretch, both appearing as polarized Raman lines. All these modes are hardly effected by deuteration because the e species are separated by more than 200 cm<sup>-1</sup> from the closest H dependent vibration ( $\nu_{23}$ ) whereas the  $a_1$  vibrations are influenced by the small mass difference only. The  $\nu_{as}$ (GeC<sub>3</sub>) mode at 340 cm<sup>-1</sup> will involve small contributions from  $\nu_{23}$  in the deuteride resulting in an isotope shift of 3 cm<sup>-1</sup>. The GeC<sub>3</sub> deformations are observed at ca. 80 cm<sup>-1</sup>. Following the normal coordinate analysis the main i.r. absorption is attributed to  $\nu_8$ , whereas the low-energy shoulder coinciding with the Raman band is assigned to  $\nu_{22}$ .



Fig. 1. Raman polarization spectrum of (CF<sub>3</sub>)<sub>2</sub>GeH<sub>2</sub>.



Fig. 2. Raman polarization spectrum of (CF<sub>3</sub>)<sub>3</sub>GeH.

The torsions are expected in the region below  $50 \text{ cm}^{-1}$  which was not investigated.

The only i.r. absorption exhibiting a pronounced PQR structure is found for the Ge-H(D) stretch,  $\nu_7$ , the calculated value (8.9 cm<sup>-1</sup>) being in good agreement with the experimental value of 9 cm<sup>-1</sup>. As in (CF<sub>3</sub>)<sub>2</sub>GeH<sub>2</sub> the liquid phase (Raman) frequency is significantly higher than the gas phase value.

## NORMAL COORDINATE ANALYSIS

Since structural data are not available, the

geometrical parameters were those employed for  $CF_3GeH_3[1]$  with tetrahedral angles at the Ge atom. The input force field was transferred from  $CF_3GeH_3$  and  $(CF_3)_2GeX_2[2]$ , and refined for all isotopic frequencies simultaneously[9]. Interaction constants of the  $CF_3$  groups were fixed at the same or similar values. Interactions between different  $CF_3$  groups were limited to non-zero elements f(FCGe/F'C'Ge).

As a consequence of the idealized geometry, anharmonicities (e.g. GeH) and the artificial limi-

tation of non-zero elements of the force field, the calculations were not expected to match all vibrational patterns exactly. For example, the splitting of the CF stretches is reproduced only qualitatively because all CF bonds were assumed to be equal and no interactions beyond those used in CF<sub>3</sub>GeH<sub>3</sub> were taken into account. Calculated and experimental fundamentals are listed in Tables 4 and 5 for  $(CF_3)_2Ge(H, D)_2$  and  $(CF_3)_3Ge(H, D)$ , respectively. A selection of the final force constants is given in Table 6. In general, the potential energy distribution is very similar to that given for  $CF_3GeH_3[1]$ , including typical coupling patterns like the interactions of FCF and CGeH deformations.

# DISCUSSION

To a good approximation the vibrational spectra of trifluoromethylgermanes may be considered to consist of rather independant CF<sub>3</sub> and skeletal modes, the latter being almost identical to those of bromogermanes,  $Br_nGeH_{4-n}$  [7,8]. The only significant interaction between these modes is found for the  $\delta$ (CGeH) and  $\delta_{as}$ (CF<sub>3</sub>) coordinates, especially in the deuterated species. In contrast to the vibrations of methylgermanes [11], which possess nearly uncoupled fundamentals, bond strengths are not directly related to frequency values but rather can only be divined by a detailed normal coordinate analysis. This is especially true for the evaluation of the GeC bond strength if more than one  $CF_3$  groups are present because the GeC stretches strongly mix with the rocking coordinates of the same symmetry.

In general, the force constants found for the series  $(CF_3)_n GeH_{4-n}$  are consistent with the trends observed for the corresponding trifluoromethylgermanium halides, (CF<sub>3</sub>)<sub>n</sub>GeX<sub>4</sub> <sub>n</sub>[3]. The GeC force constants,  $2.25 \pm 0.04$  N cm<sup>-1</sup>, are clearly lower than those of their methyl counterparts,  $(CH_3)_n GeH_{4-n}$ , which are calculated to be 2.68 ±  $0.04 \text{ N cm}^{-1}[12, 13]$ . Whereas increasing methyl substitution decreases the weighted average frequencies  $\nu$ (GeC) slightly from 598 to 592 cm<sup>-1</sup>, f(GeC) increases from 2.21 to 2.30 N cm<sup>-1</sup> in the series  $CF_3GeH_3[1]$  to  $(CF_3)_4Ge[14]$  (Table 6). The bond strengthening effect of the electron withdrawing CF<sub>3</sub> group is also felt by all other bonds; e.g., f(CF) increases by ca. 0.15 N cm<sup>-1</sup>. Throughout the hydride series a rather high interaction constant f(CF/CF) of ca. 0.94 N cm<sup>-1</sup> is calculated, which previously [3] was attributed to

Table	4. Calculated	and.	experimental	vibrational	frequencies	of
			$(CF_3)_2GeH_nD_2$	- n		

		(CF3	) <sub>z</sub> GeH <sub>z</sub>	(CF3	) <sub>2</sub> GeHD	(CF,	) <sub>2</sub> GeD <sub>2</sub>
γ۲	, <u>k</u> =	calc.	exp.	calc.	exp.	calc.	exp.
<u>a</u> 1	1	1135	1136	1135	1135	1134	1135
	2	1191	1196	1191	1196	1191	1196
	3	532	530	532	(535)	532	(532)
	4	728	728	728	727	728	727
	5	314	315	312	314	310	313
	6	249	250	249	250	249	250
	7	2156	2145	2164	2153	1533	1541
	8	79	79	78	78	78	78
	9	846	846	751	753	608	607
₫₂	10	1115	(1111)	1114	(1110)	1111	(1110)
	11	508	510	538	(535)	534	(532)
	12	208	206	508		207	<b>2</b> 05
	13	651	652	466	468	444	445
	14	29		29		29	
<u>b</u> ₁	15	1129	1136	1129	1135	1127	1135
	16	547	548	534	(535)	532	(532)
	17	257		243		231	
	18	2168	2161	1541	1550	1551	1559
	19	453	454	400	399	376	375
	20	36		36		36	
<u>b</u> 2	21	1114	1106	1114	1105	1108	1105
	22	1169	1168	1169	1167	1169	1167
	23	513	516	512	516	493	494
	24	725		722	724	722	
	25	200	203	199	200	197	197
	26	324	324	322	322	321	321
	27	716	720	690	688	551	541

		(CF3	),GeH	(CF3	),GeD
Ň	<u>κ, κ</u> =	calc.	exp.	calc.	exp.
<u>a</u> 1	1	1139	1155	1139	1154
	2	1207	1206	1207	1206
	3	528		528	
	4	729	731	729	730
	5	323	323	322	322
	6	242	241	242	241
	7	2172	2161	1547	1556
	8	81	82	81	80
a2	9	1111		1111	
-	10	518		518	
	11	216		216	
	12	28		28	
e	13	1133	1131	1128	1131
	14	1136	1167	1136	1166
	15	1178	(1180)	1177	(1180)
	16	513	512	539	537
	17	526	527	529	532
	18	721	735	721	734
	19	202	202	199	199
	20	253	253	253	252
	21	345	343	340	340
	22	75	75	75	74
	23	678	679	471	470
	24	30		30	

Table 5. Calculated and experimental vibrational frequencies of (CF<sub>3</sub>)<sub>3</sub>GeH and (CF<sub>3</sub>)<sub>3</sub>GeD

the lack of  $\pi$ -backdonation of the X (= H or CF<sub>3</sub>) substituent.

The best picture of the GeH bond is drawn from the isolated GeH stretch frequencies of the species  $(CF_3)_nGeHD_{3-n}$  which increase from 2112.5 cm<sup>-1</sup> in GeHD<sub>3</sub>[8] to 2136 cm<sup>-1</sup> in CF<sub>3</sub>GeHD<sub>2</sub>, 2153 cm<sup>-1</sup> in (CF<sub>3</sub>)<sub>2</sub>GeHD and 2160.5 cm<sup>-1</sup> in (CF<sub>3</sub>)<sub>3</sub>GeH. In contradistinction, the averaged GeH frequencies drop from 2080 to 2045 cm<sup>-1</sup> in the analogous methyl series. This large range suggests that the GeH stretches, which are essentially

undisturbed, may be used as a sensitive probe for substitutional effects. Force constant calculations on trifluoromethylgermanium halides have shown that  $CF_3/X$  (X = Cl or Br) substitution scarcely influences either the GeC or the GeX bond while replacement of a CF<sub>3</sub> group by fluorine was found to strengthen both bonds. The GeH bonds, however, do not follow this pattern. In trifluoromethylgermanes all GeH stretch frequencies clearly exceed those of the corresponding chlorides  $Cl_nGeH_{4-n}$  ( $\nu_{av}GeH_3Cl_2125.9[8]$ ,  $\nu_{av}$ GeH<sub>2</sub>Cl<sub>2</sub> 2142.5[15],  $\nu$ GeHCl<sub>3</sub> 2155.7 cm<sup>-1</sup>[16]). In  $CF_3GeHD_2$ ,  $\nu(GeH)$  even occurs at a higher energy than  $v_{av}$  (GeH) in GeH<sub>3</sub>F (2128.0 cm<sup>-1</sup>[8]). Similarly, almost the same values are observed for  $(CF_3)_3$ GeH and  $(CF_3)_2$ FGeH (2162 cm<sup>-1</sup>[17]). This data may be rationalized in terms of a basic difference between a CF<sub>3</sub> group and a halide. While halides are capable of  $\pi$ -backbonding, the  $CF_3$  group will not reduce a positive charge on the central atom effectively. Considering CF<sub>3</sub>/F substitution the higher inductive  $\sigma$ -effect of fluorine is cancelled or even overridden by  $\pi$ -electron back donation as is indicated by the comparison of CF<sub>3</sub>GeH<sub>3</sub> and FGeH<sub>3</sub>. Since hydrogen will not participate in  $\pi$ -bonding, this case is expected to display an extreme CF<sub>3</sub>/F substitutional effect; consequently a "normal", but still very small GeH frequency shift, is observed for the pair (CF<sub>3</sub>)<sub>3</sub>GeH/(CF<sub>3</sub>)<sub>2</sub>FGeH. In molecules with competing fluorines such as  $F_2GeH_2$  ( $\nu(GeH)$ ) 2164.5 cm<sup>-1</sup>[17]), the amount of backbonding per bond is lower and the total inductive effect of the fluorines apparently dominates. From another point of view, which does not necessarily make use of  $\pi$ -bonding, the electron distribution may be estimated utilizing the electronegativity equalization procedure (EESOP[18]). Taking the electronegativity  $\chi$  in terms of partial charges  $\delta$ , ( $\chi$  =  $(a + b\delta)$ , the basic difference between CF, and F is implied by the factor  $b = d\chi/d\delta$  which is larger for

(n-1-4)					
<u><u>f</u></u>	CF3GeH3[1]	$(CF_3)_2 GeH_2$	(CF3 )3 CeH	(CF,),Ge[14]	
GeC	2.211	2,25	2,27	2.30	
GeH	2,700	2.743	2.762		
CF	5.698	5.75	5.82	5.86	
α	1.736	1.70	1.72	1.52 °	
β	0.652	0.71	0.68	0.70 <sup>C</sup>	
۲	0.419	0.40	~		
δ	0.456	0.44	0.42		
£		0.565	0.54	0.48 0	
*	0.04	0.04	0.04		
GeC/GeC		0.12	0.12	0.11	
CF/CF	0.937	0.94	0:93	0.96	
GeC/CF	0.068	0.07	0.07	0.06	

Table 6. Selected [10] inner force constants  $[N \text{ cm}^{-1}]$  of  $(CF_3)_n \text{GeH}_{4-n}$ 

<sup>a</sup>Scaled to 100 pm. <sup>b</sup> $\alpha$  = FCF,  $\beta$  = FCGe,  $\gamma$  = HGeH,  $\delta$  = HGeC,  $\epsilon$  = CGeC,  $\tau$  = torsion. <sup>c</sup>f<sub>2</sub> symmetry force constants.

 
 Table 7. EESOP<sup>a</sup> calculated partial charges of fluoro- and trifluoromethylgermanes

	<sup>8</sup> Ge	٥ <sub>H</sub>	<sup>5</sup> <sub>F</sub> ∕ <sup>8</sup> CF <sub>3</sub>	v(GeH)[cm <sup>-1</sup> ]
CF, GeH, FGeH,	0.020	0.081	-0.263 -0.233	2136 2128
(CF <sub>3</sub> ) <sub>2</sub> GeH <sub>2</sub> F <sub>2</sub> GeH <sub>2</sub>	0.094 0.117	0.120 0.132	-0.167 -0.191	2153 2164,5
(СF <sub>3</sub> ) <sub>3</sub> GeH (СF <sub>3</sub> ) <sub>2</sub> FGeH F <sub>3</sub> GeH	0.147 0.165 0.236	0.148 0.158 0.195	-0.098 -0.172/-0.075 -0.144	2160.5 2162

<sup>a</sup> $\chi_{CF_3} = 9.6 + 5.32 \quad \delta_{CF_3}[19], \quad \chi_{Ge} = 8.07 + 6.82 \quad \delta_{Ge}, \quad \chi_F = 12.18 + 17.36 \quad \delta_{F}, \quad \chi_H = 7.17 + 12.85 \quad \delta_H[18].$ 

the fluorine atom (Table 7); that is, the four atoms of the CF<sub>3</sub> group accommodate charges much easier than a single fluorine atom does. The partial charges given in Table 7 were calculated employing the values for  $\chi_{CF_1}$  which was derived from ESCA data on trifluoromethylgermanium halides[19]. In accordance with the GeH stretch frequencies the calculations indicate that the positive charges on Ge or H are higher in CF<sub>3</sub>GeH<sub>3</sub> than in FGeH<sub>3</sub> whereas the opposite is true for (CF<sub>3</sub>)<sub>2</sub>GeH<sub>2</sub> and F<sub>2</sub>GeH<sub>2</sub>. Similarly, slightly higher charges are calculated for (CF<sub>3</sub>)<sub>2</sub>FGeH than for (CF<sub>3</sub>)<sub>3</sub>GeH.

In general, the conclusions based on the vibrational spectra are reinforced by the analysis of the photoelectron spectra [20] in that both core and valence levels become more stabilized upon increasing  $CF_3$  substitution while a relative destabilization with respect to their methyl analogues is deduced for the orbitals mainly associated with GeC bonding.

#### REFERENCES

- [1] R. EUJEN and H. BÜRGER, Spectrochimica Acta 37A, 1029 (1981).
- [2] H. BÜRGER and R. EUJEN, Spectrochimica Acta 31A, 1955 (1975).
- [3] R. EUJEN and H. BÜRGER, Spectrochimica Acta 35A, 549 (1979).
- [4] R. J. LAGOW, R. EUJEN, L. L. GERCHMAN and J. A. MORRISON, J. Am. Chem. Soc. 100, 1722 (1978).

- [5] R. EUJEN and R. MELLIES, to be published.
- [6] H. OBERHAMMER and R. EUJEN, J. Mol. Struct. 51, 211 (1979).
- [7] J. E. DRAKE and C. RIDDLE, J. Chem. Soc. A 2114 (1969).
- [8] T. SHIMANOUCHI, J. Phys. Chem. Ref. Data 1, 210 (1972).
- [9] D. CHRISTEN, J. Mol. Struct. 48, 101 (1978).
- [10] The complete force fields may be obtained from the first author.
- [11] D. F. VAN DE VONDEL and G. P. VAN DER KELEN, Bull. Soc. Chim. Belges 74, 467 (1965).
- [12] K. HASSLER, Diplomarbeit, T. H. GRAZ, (1974); S. BIEDERMANN, H. BÜRGER, K. HASSLER and F. HÖFLER, Monatshefte f. Chem. 111, 703 and 715 (1980).
- [13] GeC force constants of  $(CH_3)_nGeH_{4-n}$  (n = 1-3)were derived by extrapolation from  $(CH_3)_4Ge$  using weighted average GeC stretch frequencies.
- [14] R. EUJEN and H. BÜRGER, Spectrochimica Acta 35A, 541 (1979).
- [15] J. E. DRAKE, C. RIDDLE and D. E. ROGERS, J. Chem. Soc. A 910 (1969).
- [16] A. RUOFF, H. BÜRGER, S. BIEDERMANN and J. CICHON, Spectrochimica Acta 30A, 1647 (1974).
- [17] R. EUJEN, unpublished data.
- [18] J. E. HUHEEY, Inorganic Chemistry, p. 162. Harper and Row, New York (1978). J. E. DRAKE, C. RIDDLE, H. E. HENDERSON and B. GLAVINCEVSKI, Can. J. Chem. 54, 3876 (1976).
- [19] J. E. DRAKE, R. EUJEN and K. GORZELSKA, *Inorg. Chem.* to be published.
- [20] J. E. DRAKE, K. GORZELSKA and R. EUJEN, J. Electr. Spectrosc. Rel. Phenom. (In press).