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Vibrational Spectra and Normal Coordinate Calculations for Trimethylgermane

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Vibrational spectra of $(CH_3)_3GeH$, $(CH_3)_3GeD$, $(CD_3)_3GeH$, and $(CD_3)_3GeD$ were obtained. Assignments for all the fundamentals except internal torsions were made by assuming the C_{3v} molecular symmetry. Normal coordinate calculations were carried out to confirm the assignments.

In our previous paper,[1] we reported on a study of vibrational spectra and normal coordinate calculations for trimethylsilane. The study has now been extended to trimethylgermane. Although numerous vibrational studies on trimethylsilane have been reported,[2] only a limited number have been reported on trimethylgermane[3–6] and most of them relate to substituent effects on the GeH stretching mode. As far as we know, study on the assignment of all the active fundamentals has been made only by Van de Vondel and Van der Kelen.[6] They made also normal coordinate calculations with no data of isotopic compounds available by assuming the methyl group as a point mass. In the paper[1] on trimethylsilane, it was pointed out that the methyl rock, the SiH bend, and the asymmetric SiC_3 stretch are fairly strongly coupled with one another. Since it may highly be expected that a similar vibrational coupling will be operative also in the case of trimethylgermane, it seems inadequate to make the calculation by assuming that the methyl group is a point mass. In this paper, we will report vibrational spectra of trimethylgermane and its deuterated analogues and results of normal coordinate calculations on these compounds carried out without assuming the methyl group as a point mass.

Experimental

$(CH_3)_3GeH$ and $(CH_3)_3GeD$ were prepared by reduction of $(CH_3)_3GeI$ with $LiAlH_4$ and $LiAlD_4$, respectively. $(CH_3)_3GeI$ was prepared through a reaction of tetramethylgermane with I_2 in a sealed tube at 50 °C. The crude trimethylgermane was purified by vacuum distillation with a conventional vacuum line. $(CD_3)_3GeH$ and $(CD_3)_3GeD$ were prepared similarly to $(CH_3)_3GeH$ and $(CH_3)_3GeD$, respectively, by using $(CD_3)_4Ge$ instead of $(CH_3)_4Ge$. The purity of the compounds was checked by their infrared spectra in the gas phase.

Infrared spectra (4000—300 cm^{-1}) and far-infrared spectra (400—80 cm^{-1}) were recorded on a Hitachi 345 spectrophotometer and on a Hitachi FIS-III spectrophotometer, respectively, in the gas phase and with solid films at liquid nitrogen temperature.

Raman spectra were recorded with liquids in capillary tubes on a JEOL JRS-S1 Raman spectrophotometer equipped with a 50 mW NEC GLG 5800 He-Ne laser.

Results and Vibrational Assignments

If each methyl group in a molecule is staggered to both the Ge–H bond and the adjacent Ge–C bonds, the molecule will have a C_{3v} symmetry. On this assumption the 36 normal vibrations are made distributed as $8A_1+4A_2+12E$. The A_1 and E modes are active in infrared and Raman spectra but the A_2 modes inactive in both.

Symmetry coordinates have been classified, according to the description of the modes of methyl group and of the skeletons in the molecules, as given in Table 1, where the numbering of the symmetry coordinates is the same as that for the corresponding coordinates for trimethylsilane.[1] Figures 1 and 2 show the infrared spectra in the gas phase and the Raman spectra in the liquid phase, respectively. Tables 2—5 list the observed fundamental frequencies.

By taking into consideration the isotopic shift and polarization of Raman bands as well as data for related compounds,[7–9] assignments for the methyl stretches and the GeH and GeD stretches may easily be made.

There should be five methyl deformations. Asymmetric deformations bonded to a metal atom are usually relatively weak and broad, and their positions in spectra do not markedly shift with change in the nature of the metal atom, whereas symmetric methyl deformations usually give relatively strong and sharp bands and exhibit slight shifts with change in the nature of the metal atom.[10] For $(CH_3)_3GeH$ and $(CH_3)_3GeD$ the asymmetric deformations are observed at *ca.* 1410 cm^{-1}. Upon deuteration of the methyl groups, these shift to *ca.* 1040 cm^{-1}. The symmetric deformations are observed at *ca.* 1250 cm^{-1} for $(CH_3)_3GeH$ and $(CH_3)_3GeD$ and at *ca.* 970 cm^{-1} for $(CD_3)_3GeH$ and $(CD_3)_3GeD$.

Three methyl rocks, two GeC_3 stretches, and a GeH or GeD bend are expected to appear in the

Table 1. Description of the symmetry coordinates for trimethylgermane[a)]

Vibrational mode	Coordinate A_1	A_2	E
Stretching $(CH_3)_a$ or $(CD_3)_a$	S_1	S_9	S_{13}, S_{14}
Stretching $(CH_3)_s$ or $(CD_3)_s$	S_2		S_{15}
Stretching (GeH) or (GeD)	S_3		
Deformation $(CH_3)_a$ or $(CD_3)_a$	S_4	S_{10}	S_{16}, S_{17}
Deformation $(CH_3)_s$ or $(CD_3)_s$	S_5		S_{18}
Rocking (CH_3) or (CD_3)	S_6	S_{11}	S_{19}, S_{20}
Bending (GeH) or (GeD)			S_{21}
Stretching (GeC_3)	S_7		S_{22}
Deformation (GeC_3)	S_8		S_{23}
Torsion		S_{12}	S_{24}

a) Abbreviations used: a, asymmetric; s, symmetric.

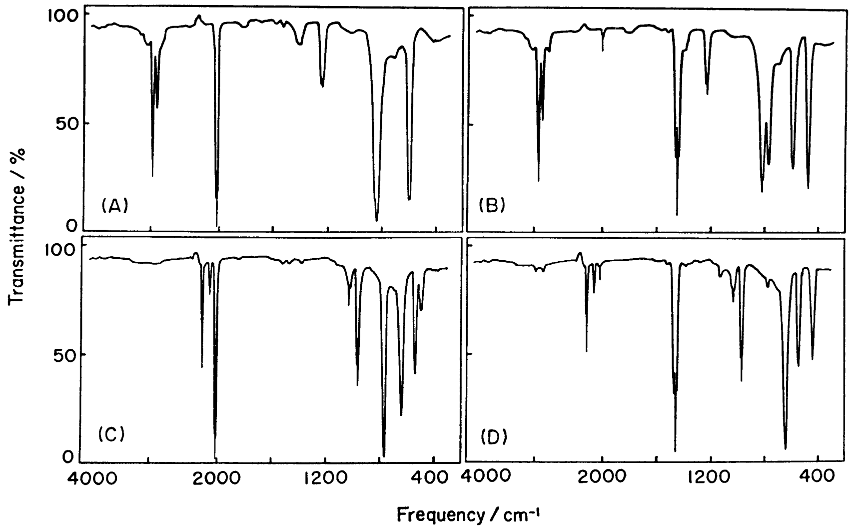

Fig. 1. Infrared spectra of $(CH_3)_3GeH$ (A), $(CH_3)_3GeD$ (B), $(CD_3)_3GeH$ (C), and $(CD_3)_3GeD$ (D) in the gas phase.

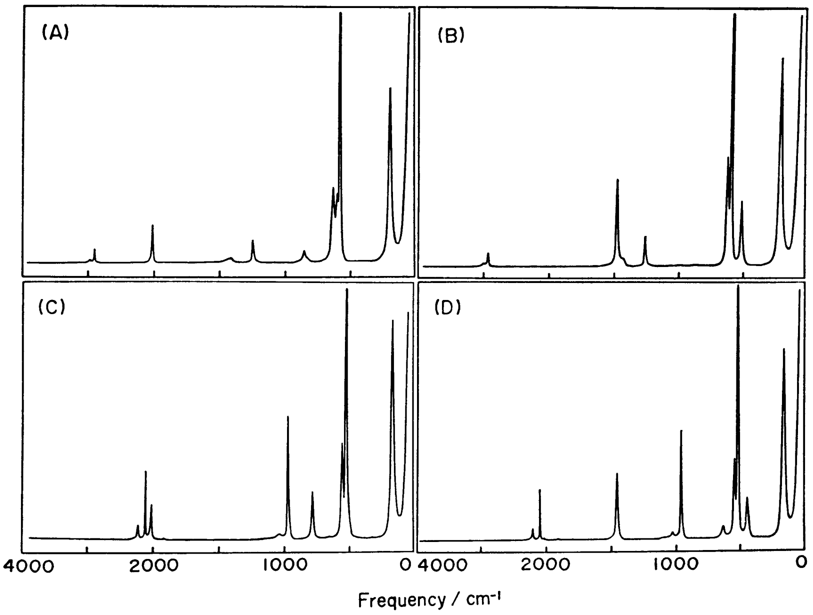

Fig. 2. Raman spectra of $(CH_3)_3GeH$ (A), $(CH_3)_3GeD$ (B), $(CD_3)_3GeH$ (C), and $(CD_3)_3GeD$ (D) in the liquid.

range 900—400 cm^{-1}. Of these vibrations the A_1 GeC_3 stretching mode should give an intense polarized Raman band. Therefore, the Raman bands at *ca.* 550 cm^{-1} for $(CH_3)_3GeH$ and $(CH_3)_3GeD$ may undoubtedly be assigned to this mode. Upon deuteration of methyl groups these shift to 520 cm^{-1}. A_1 methyl rocking frequencies are expected to be approximately identical with each other for $(CH_3)_3GeH$ and $(CH_3)_3GeD$ and for $(CD_3)_3GeH$ and $(CD_3)_3GeD$, since it is also the case with trimethylsilane (850 cm^{-1} for $(CH_3)_3SiH$ and 847 cm^{-1} for $(CH_3)_3SiD$; 704 cm^{-1} for $(CD_3)_3SiH$ and 705 cm^{-1} for $(CD_3)_3SiD$).1) On this basis, to this mode we have assigned the Raman bands at 830 cm^{-1} for $(CH_3)_3GeH$ and $(CH_3)_3GeD$ and at *ca.* 650 cm^{-1} for $(CD_3)_3GeH$ and $(CD_3)_3GeD$. However, these Raman bands are only partly polarized. This suggests that there are some other vibrations in the E class coinciding on these bands. The most probable candidate is the E methyl rock, since the same accidental degeneracy is found in the A_1 and E methyl rocks in $(CH_3)_3GeCl$,7) $(CH_3)_3GeCF_3$,9) and $(CH_3)_3GeGeH_3$.11)

The remaining bands observed in the range 900—400 cm^{-1} may be considered to be the vibrations due to the E modes but it is not easy to assign these bands. However, the 480 cm^{-1} band in $(CH_3)_3GeD$ and the 780 cm^{-1} one in $(CD_3)_3GeH$ are probably due to the GeD and GeH bends, respectively, since no corresponding Raman bands are observed for $(CH_3)_3GeH$ or $(CD_3)_3GeD$ in the same region. Assignment of the other bands is impossible without the aid of normal coordinate calculations.

The two GeC_3 deformation modes (A_1 and E) should be expected in the region below 300 cm^{-1},

TABLE 2. OBSERVED AND CALCULATED FREQUENCIES (cm^{-1}) FOR $(CH_3)_3GeH$

No.	Infrared gas	Raman liquid	Calcd	PED
1	2982	2982	2986	$100S_1$
2	2922	2913	2914	$99S_2$
3	2040	2036	2041	$100S_3$
4	1426	1419	1425	$97S_4$
5	1246	1247	1250	$85S_5$, $10S_2$
6	833	830	830	$95S_6$
7	571*	573	578	$98S_7$
8	187	189	188	$77S_8$, $23S_6$
13	2982	2982	2987	$77S_{13}$, $23S_{14}$
14	2982	2982	2986	$77S_{14}$, $23S_{13}$
15	2922	2913	2914	$99S_{15}$
16	1426	1419	1425	$90S_{16}$
17	1426	1419	1425	$88S_{17}$
18	1246	1247	1251	$86S_{18}$, $10S_{15}$
19	624*	626	627	$44S_{19}$, $43S_{21}$, $12S_{22}$
20	833	830	834	$89S_{20}$
21	850*	850	852	$45S_{21}$, $43S_{19}$
22	592	597	604	$79S_{22}$, $12S_{21}$
23	187	189	188	$99S_{23}$

* The frequency is taken from the solid state spectrum.

TABLE 3. OBSERVED AND CALCULATED FREQUENCIES (cm^{-1}) FOR $(CH_3)_3GeD$

No.	Infrared gas	Raman liquid	Calcd	PED
1	2982	2982	2986	$100S_1$
2	2920	2913	2914	$99S_2$
3	1470	1467	1454	$100S_3$
4	1410	1420	1425	$97S_4$
5	1248	1249	1250	$85S_5$, $10S_2$
6	833	830	829	$95S_6$
7	570*	574	578	$98S_7$
8	187	190	187	$77S_8$, $23S_6$
13	2982	2982	2987	$76S_{13}$, $24S_{14}$
14	2982	2982	2987	$76S_{14}$, $24S_{13}$
15	2920	2913	2914	$99S_{15}$
16	1410	1420	1424	$91S_{16}$
17	1410	1420	1425	$89S_{17}$
18	1248	1249	1251	$86S_{18}$, $10S_{15}$
19	787	785	783	$85S_{19}$, $10S_{21}$
20	833	830	836	$94S_{20}$
21	490	490	486	$78S_{21}$, $20S_{19}$
22	603	606	610	$94S_{22}$
23	187	190	188	$99S_{23}$

* See the footnote in Table 2.

However, only one band is observed in the infrared and Raman spectra for each isotopic compound below 300 cm^{-1}. It may be considered that these two vibrations coincide with each other in the present compounds, since in $(CH_3)_3GeCl$ the A_1 and E GeC_3 deformation modes are observed in the Raman spectra as two closely positioned bands at 193 and 185 cm^{-1}.[7)]

TABLE 4. OBSERVED AND CALCULATED FREQUENCIES (cm^{-1}) FOR $(CD_3)_3GeH$

No.	Infrared gas	Raman liquid	Calcd	PED
1	2236	2232	2227	$99S_1$
2	2129	2123	2121	$97S_2$
3	2041	2032	2041	$100S_3$
4	1043	1038	1030	$98S_4$
5	976	969	966	$75S_5$, $13S_2$, $12S_7$
6	654	650	649	$90S_6$
7	520*	520	515	$88S_7$
8	160	163	163	$73S_8$, $27S_6$
13	2236	2232	2225	$52S_{13}$, $47S_{14}$
14	2236	2232	2226	$52S_{14}$, $47S_{13}$
15	2129	2123	2121	$97S_{15}$
16	1043	1038	1031	$83S_{16}$, $15S_{17}$
17	1043	1038	1029	$82S_{17}$, $15S_{16}$
18	976	969	965	$75S_{18}$, $13S_{15}$
19	511	500	505	$76S_{19}$, $23S_{21}$
20	654	650	633	$90S_{20}$
21	787	780	780	$89S_{21}$, $10S_{19}$
22	552	553	548	$86S_{22}$
23	160	163	166	$97S_{23}$

* See the footnote in Table 2.

TABLE 5. OBSERVED AND CALCULATED FREQUENCIES (cm^{-1}) FOR $(CD_3)_3GeD$

No.	Infrared gas	Raman liquid	Calcd	PED
1	2235	2232	2227	$99S_1$
2	2128	2122	2121	$97S_2$
3	1468	1463	1454	$100S_3$
4	1038	1037	1030	$98S_4$
5	976	969	966	$75S_5$, $13S_2$, $12S_7$
6	649	646	649	$90S_6$
7	520*	520	514	$88S_7$
8	161	163	163	$73S_8$, $27S_6$
13	2235	2232	2225	$56S_{13}$, $43S_{14}$
14	2235	2232	2226	$56S_{14}$, $43S_{13}$
15	2128	2122	2121	$97S_{15}$
16	1038	1037	1031	$82S_{16}$, $16S_{17}$
17	1038	1037	1029	$81S_{17}$, $16S_{16}$
18	976	969	965	$75S_{18}$, $13S_{15}$
19	649	646	646	$27S_{19}$, $34S_{20}$, $27S_{21}$
20	635*	646	626	$65S_{20}$, $20S_{21}$, $12S_{21}$
21	447	448	444	$55S_{21}$, $44S_{19}$
22	550	551	546	$81S_{22}$
23	161	163	166	$97S_{23}$

* See the footnote in Table 2.

Normal Coordinate Calculations and Discussion

Normal coordinate calculations were carried out by Wilson's GF-matrix method on an ACOS 77/900 computer at the Computer Center, Tohoku University, the iterative least-squares procedure being used in the usual way. The G matrix was calculated by use of the molecular parameters determined from microwave study[12] (r(Ge–H)=0.1532 nm, r(Ge–C)=0.1947 nm, r(C–H)=0.1905 nm, ∠C–Ge–C=109.6°) and by assuming a tetrahedral angle around carbon atoms. In the calculations the observed frequencies were weighted by $(1/\lambda)$. The torsional mode was neglected in the E class.

A least-squares refinement was carried out in terms of symmetry force constants which had been fitted simultaneously to the observed frequencies for the four isotopic species. This refinement was carried out in the same manner as with the acetonitrile-borane adduct[13] and trimethylsilane.[1] The calculated frequencies have an average error of 0.39% for A_1 vibrations and 0.59% for E vibrations. The sum of the weighted squares of errors $\Sigma(\lambda_{\text{obsd}}-\lambda_{\text{calcd}})^2/\lambda_{\text{obsd}}$ was 1.7×10^{-3} for A_1 vibrations and 3.2×10^{-3} for E vibrations. The symmetry force constants, together with the uncertainty ranges from the last cycle in the least-squares refinement, are given in Table 6.

TABLE 6. SYMMETRY FORCE CONSTANTS FOR TRIMETHYLGERMANE[a)]

	Constant	σ		Constant	σ
F_1	4.739	0.011	F_{13}	4.754	0.014
F_2	4.715	0.055	F_{14}	4.743	0.014
F_3	2.439	0.008	F_{15}	4.718	0.062
F_4	0.527	0.003	F_{16}	0.527	0.003
F_5	0.510	0.016	F_{17}	0.522	0.003
F_6	0.415	0.017	F_{18}	0.512	0.018
F_7	2.803	0.041	F_{19}	0.381	0.007
F_8	0.620	0.070	F_{20}	0.479	0.005
			F_{21}	0.482	0.007
$F_{2,5}$	−0.388	0.067	F_{22}	2.596	0.040
$F_{5,7}$	−0.145	0.032	F_{23}	0.457	0.018
$F_{6,8}$	−0.216	0.045			
			$F_{15,18}$	−0.388	0.076
			$F_{18,22}$	−0.144	0.033
			$F_{19,21}$	0.102	0.004
			$F_{21,22}$	0.016	0.026

a) The stretching force constants are given in 10^2 N m^{-1}, the deformation force constants in 10^{-18} N m rad^{-2}, and the stretching-deformation interaction constants in 10^{-8} N rad^{-1}. The subscript number i in F_i corresponds with that in S_i in Table 1.

TABLE 7. COMPARISON OF FORCE CONSTANTS (10^2 N m^{-1}), BOND DISTANCES (nm), AND BOND ANGLES (°)

	f(Ge-CH$_3$)	r(Ge-CH$_3$)	(CH$_3$-Ge-CH$_3$)
$(CH_3)_3GeCN$	2.83[8)]	0.1930±0.0006[15)]	114.8±0.1[15)]
$(CH_3)_3GeCl$	2.69[7)]	0.1940±0.0003[16)]	112.8±0.5[16)]
$(CH_3)_3GeH$	2.67[a)]	0.1947±0.0006[12)]	109.6±0.2[12)]
$(CH_3)_4Ge$	2.65[14)]	0.1945±0.0003[17)]	109.5[17)]

a) Present work.

Potential energy distributions also are given in Tables 2—5. It is clear from these tables that the methyl rocks (S_{19} and S_{20}) and the GeH or GeD bend (S_{21}) are strongly coupled with each other.

The valence force constant of the Ge–CH$_3$ bond, derived from the symmetry force constants, is given in Table 7, together with those of the related compounds. The Ge–CH$_3$ bond distances and CH$_3$–Ge–CH$_3$ angles, determined by the microwave and electron diffraction study, are included for each compound in Table 7. The Ge–CH$_3$ force constant for the present compound is nearly equal to those for $(CH_3)_4Ge$ and $(CH_3)_3GeCl$ and slightly smaller than that for $(CH_3)_3GeCN$. This is in agreement with what might be expected from the Ge–CH$_3$ bond distances and CH$_3$–Ge–CH$_3$ bond angles.

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