Vibrational Spectra and Normal Coordinate Calculations for Trimethylstannane

Yoshika Imai* and Koyo Aida
Department of Engineering Science, Faculty of Engineering, Tohoku University, Sendai 980
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The infrared and Raman spectra of trimethylstannane and its deuterated analogues were obtained. Assignments for all the fundamentals except internal torsions were made and normal coordinate calculations were carried out to confirm the proposed assignments.

Our previous studies[1,2] have concerned with the reexamination of the vibrational spectra for $(CH_3)_3MH$ (M=Si, Ge). This work extends the studies to trimethylstannane. The vibrational spectra of trimethylstannane have been reported by previous authors,[3,4] but there are some discrepancies in the vibrational assignments. For example, Dillard and May[3] have assigned an infrared band at *ca.* 670 cm^{-1} for $(CH_3)_3SnH$ to the SnH bending vibration, while Kriegsmann and Pischtschan[4] have assigned a band at *ca.* 540 cm^{-1} to this vibration.

Kriegsmann and Pischtschan have calculated the force constants, assuming the methyl groups as a point mass. Our previous studies revealed that for trimethylsilane and trimethylgermane the methyl rocking, the MH bending, and the degenerate MC_3 stretching vibrations are fairly strongly coupled with one another. Since a similar vibrational coupling will be encountered in the case of the present compound, it seems inadequate to make the calculation by assuming that the methyl groups is a point mass.

In this paper we will report the vibrational spectra of trimethylstannane including its three deuterated analogues and the results on normal coordinate calculations without assuming the methyl groups as a point mass.

Experimental

Trimethylstannane and its deuterated analogues were prepared by reacting $(CH_3)_3SnCl$ or $(CD_3)_3SnCl$ with $LiAlH_4$ or $LiAlD_4$ in dibutyl ether. The crude compounds were purified by trap-to-trap fractionations by using a conventional vacuum line. The purity of the compounds was checked by their gas-phase infrared spectra. $(CH_3)_3SnCl$ and $(CD_3)_3SnCl$ were prepared by the reaction of $SnCl_4$ with $(CH_3)_4Sn$ and $(CD_3)_4Sn$, respectively. $(CH_3)_4Sn$ and $(CD_3)_4Sn$ were prepared by reacting $SnCl_4$ with $(CH_3)_2Zn$ and $(CD_3)_2Zn$, respectively, in sealed glass tubes and purified by trap-to-trap fractionations under vacuum. Dimethylzinc and its deuterated analogue were prepared by a method described in the literature.[5]

The infrared spectra were recorded on a Hitachi 345 spectrophotometer (4000—300 cm^{-1}) and on a Hitachi FIS-III spectrophotometer (400—30 cm^{-1}) in the gas phase and in the solid state at liquid nitrogen temperature.

Raman spectra were recorded on a JEOL-JRS-S1 Raman spectrophotometer equipped with a 50 mW NEC GLG 5800 He-Ne laser in the liquid state. Qualitative polarizations were also obtained.

Results and Vibrational Assignments

Since each methyl group of trimethylstannane is staggered with respect to the Sn–H bond,[6] the molecule has a C_{3v} molecular symmetry. Under this symmetry, its normal vibrations distribute as $8A_1+4A_2+12E$, where the A_1 and E modes are infrared and Raman active while the A_2 mode is inactive in both. Symmetry coordinates have been classified, according to the description of the modes, as given in Table 1, where the numbering of the symmetry coordinates is the same as those for the corresponding coordinates for trimethylsilane[1] and trimethylgermane.[2] Infrared spectra of trimethylstannane and its deuterated analogues in the gas phase are shown in Fig. 1. The Raman spectra

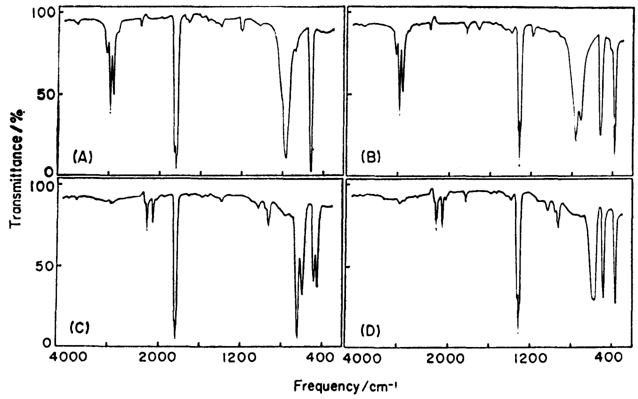

Fig. 1. Infrared spectra of $(CH_3)_3SnH$ (A), $(CH_3)_3SnD$ (B), $(CD_3)_3SnH$ (C), and $(CD_3)_3SnD$ (D) in the gas phase.

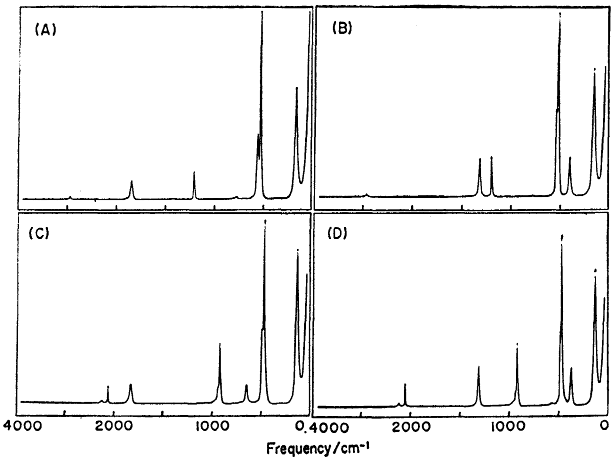

Fig. 2. Raman spectra of $(CH_3)_3SnH$ (A), $(CH_3)_3SnD$ (B), $(CD_3)_3SnH$ (C), and $(CD_3)_3SnD$ (D) in the liquid.

TABLE 1. DESCRIPTION OF THE SYMMETRY COORDINATES FOR TRIMETHYLSTANNANE[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 (SnH) or (SnD)	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 (SnH) or (SnD)			S_{21}
Stretching (SnC_3)	S_7		S_{22}
Deformation (SnC_3)	S_8		S_{23}
Torsion		S_{12}	S_{24}

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

TABLE 2. OBSERVED AND CALCULATED FREQUENCIES(cm^{-1}) FOR $(CH_3)_3SnH$

No.	Infrared Gas	Raman Liquid	Calcd	Potential energy distribution
1	2974	2984	2990	$100S_1$
2	2903	2911	2915	$99S_2$
3	1843	1835	1841	$100S_3$
4	1407	1415	1417	$97S_4$
5	1203	1200	1201	$87S_5$ $10S_2$
6	764	761	772	$97S_6$
7	521[a)]	515	518	$100S_7$
8	144	150	149	$82S_8$ $18S_6$
13	2974	2984	2988	$100S_{13}$
14	2974	2984	2993	$100S_{14}$
15	2903	2911	2915	$99S_{15}$
16	1407	1415	1417	$76S_{16}$ $21S_{17}$
17	1407	1415	1417	$76S_{17}$ $21S_{16}$
18	1203	1200	1201	$87S_{18}$ $10S_{15}$
19	764	761	785	$84S_{19}$ $14S_{21}$
20	746[a)]		748	$96S_{20}$
21	547[a)]	544	548	$44S_{21}$ $40S_{22}$ $16S_{19}$
22	514		512	$48S_{22}$ $41S_{21}$ $11S_{19}$
23	144	150	149	$99S_{23}$

a) The frequency is taken from the solid state spectrum.

TABLE 3. OBSERVED AND CALCULATED FREQUENCIES (cm^{-1}) FOR $(CH_3)_3SnD$

No.	Infrared Gas	Raman Liquid	Calcd	Potential energy distribution
1	2974	2985	2990	$100S_1$
2	2911	2917	2915	$99S_2$
3	1325	1317	1308	$100S_3$
4	1407	1420	1417	$97S_4$
5	1203	1199	1201	$87S_5$ $10S_2$
6	774	785	772	$97S_6$
7	518[a)]	515	518	$100S_7$
8	144	148	149	$82S_8$ $18S_6$
13	2974	2985	2988	$100S_{13}$
14	2974	2985	2993	$100S_{14}$
15	2911	2917	2915	$99S_{15}$
16	1407	1420	1417	$73S_{16}$ $24S_{17}$
17	1407	1420	1417	$73S_{17}$ $24S_{16}$
18	1203	1199	1201	$87S_{18}$ $10S_{15}$
19	774	785	763	$95S_{19}$
20	728		748	$96S_{20}$
21	392	396	391	$85S_{21}$ $13S_{19}$
22	533	529	532	$97S_{22}$
23	144	148	149	$99S_{23}$

a) See the footnote in Table 2.

TABLE 4. OBSERVED AND CALCULATED FREQUENCIES (cm^{-1}) FOR $(CD_3)_3SnH$

No.	Infrared Gas	Raman Liquid	Calcd	Potential energy distribution
1	2238	2236	2228	$100S_1$
2	2125	2120	2119	$97S_2$
3	1842	1833	1841	$100S_3$
4	1037	1040	1025	$98S_4$
5	933	922	920	$78S_5$ $13S_2$
6	601		590	$94S_6$
7	472[a)]	470	467	$94S_7$
8	124	131	131	$79S_8$ $21S_6$
13	2238	2236	2226	$98S_{13}$
14	2238	2236	2229	$98S_{14}$
15	2125	2120	2119	$97S_{15}$
16	1037	1040	1024	$68S_{16}$ $31S_{17}$
17	1037	1040	1025	$67S_{17}$ $31S_{16}$
18	933	922	920	$78S_{18}$ $13S_{15}$
19	454	450	465	$34S_{19}$ $35S_{21}$ $29S_{22}$
20	601		559	$95S_{20}$
21	651	654	653	$60S_{21}$ $38S_{19}$
22	493	488	487	$50S_{22}$ $31S_{19}$ $14S_{21}$
23	124	131	132	$99S_{23}$

a) See the footnote in Table 2.

in the liquid are shown in Fig. 2. Observed fundamental frequencies are listed in Tables 2—4.

The asymmetric and symmetric CH_3 stretches were observed at *ca.* 2980 and *ca.* 2900 cm^{-1}, respectively, for $(CH_3)_3SnH$ and $(CH_3)_3SnD$. For $(CD_3)_3SnH$ and $(CD_3)_3SnD$, these modes were observed at *ca.* 2240 and *ca.* 2120 cm^{-1}.

Polarized Raman bands at *ca.* 1850 cm^{-1} for $(CH_3)_3SnH$ and $(CD_3)_3SnH$ are assigned to the SnH stretching vibration. Upon deuteration of the SnH group, these bands shift to *ca.* 1300 cm^{-1} for $(CH_3)_3SnD$ and $(CD_3)_3SnD$. The corresponding infrared band of each compound in the gas phase has a definite PQR band contour.

Weak infrared bands at *ca.* 1400 cm^{-1} for $(CH_3)_3SnH$ and $(CH_3)_3SnD$ are assigned to the asymmetric methyl deformation. The corresponding Raman bands are broad and very weak. Therefore, their frequencies are fairly indefinite. Upon deuteration of the methyl groups these bands shift to *ca.* 1040 cm^{-1} for $(CD_3)_3SnH$ and $(CD_3)_3SnD$.

For $(CH_3)_3SnH$ and $(CH_3)_3SnD$, weak infrared bands at *ca.* 1200 cm^{-1} are assigned to the symmetric methyl deformation and the correspinding Raman bands are polarized. These bands shift to *ca.* 920 cm^{-1} for $(CD_3)_3$-

TABLE 5. OBSERVED AND CALCULATED FREQUENCIES (cm^{-1}) FOR $(CD_3)_3SnD$

No.	Infrared Gas	Raman Liquid	Calcd	Potential energy distribution
1	2238	2235	2228	$99S_1$
2	2124	2120	2119	$97S_2$
3	1324	1317	1308	$100S_3$
4	1040	1035	1025	$98S_4$
5	932	922	920	$78S_5$ $13S_2$
6	584		590	$94S_6$
7	471[a]	471	467	$94S_7$
8	124	130	131	$79S_8$ $21S_6$
13	2238	2235	2226	$98S_{13}$
14	2238	2235	2229	$98S_{14}$
15	2124	2120	2119	$97S_{15}$
16	1040	1035	1024	$68S_{16}$ $31S_{17}$
17	1040	1035	1025	$67S_{17}$ $31S_{16}$
18	932	922	920	$78S_{18}$ $13S_{15}$
19	584		588	$83S_{19}$ $14S_{21}$
20	567	570	559	$95S_{20}$
21	375	378	374	$74S_{21}$ $23S_{19}$
22	489	487	482	$89S_{22}$
23	124	130	132	$99S_{23}$

a) See the footnote in Table 2.

SnH and $(CD_3)_3SnD$ upon deuteration of the methyl groups.

Three methyl rocking, two SnC_3 stretching and one SnH or SnD bending vibrations are expected to appear in the region 900—300 cm^{-1}. Raman bands at *ca.* 510 cm^{-1} for $(CH_3)_3SnH$ and $(CH_3)_3SnD$ are strong and polarized. Upon deuteration of the methyl groups these bands shift to *ca.* 480 cm^{-1} for $(CD_3)_3SnH$ and $(CD_3)_3SnD$. Therefore, they are evidently assigned to the A_1 SnC_3 stretching mode. The infrared band due to this mode is weak and could not be observed in the gas phase owing to the obscuration of strong neighbouring bands. However, in the solid state this is clearly observed as a sharp band for each isotopic analogue except for $(CH_3)_3SnH$. For $(CH_3)_3SnH$ three bands were observed at 547, 521, and 512 cm^{-1} in the solid infrared spectrum. The 512 cm^{-1} band is very strong while the 547 cm^{-1} and the 521 cm^{-1} bands are weak and the 521 cm^{-1} band is observed as a shoulder of the 512 cm^{-1} band. Considering its frequency and intensity, we assigned the shoulder to the A_1 SnC_3 stretching mode. Of the 547 cm^{-1} and the 512 cm^{-1} bands, one band should be due to the SnH bending mode and another due to the E SnC_3 stretching mode. Dillard and May have assigned an infrared band at *ca.* 670 cm^{-1} for $(CH_3)_3SnH$ to the SnH bedning mode. We also observed the very weak band at the same position. However, since its intensity was decreased by repeating purification of the compound, it was concluded that this band is due to some other species than trimethylstannane. For $(CH_3)_3SnD$ two bands at *ca.* 530 and *ca.* 390 cm^{-1} were assigned to the E SnC_3 stretching and the SnD bending vibrations, respectively. The 530 cm^{-1} band shifts to *ca.* 490 cm^{-1} for $(CD_3)_3SnH$ and $(CD_3)_3SnD$ upon deuteration of the methyl groups. A strong infrared band at *ca.* 650 cm^{-1} for $(CD_3)_3SnH$ was assigned to the SnH bending, since no corresponding band was observed in the same region for $(CD_3)_3SnD$.

Since the A_1 methyl rocking frequencies are approximately identical with each other for $(CH_3)_3MH$ and $(CH_3)_3MD$ and for $(CD_3)_3MH$ and $(CD_3)_3MD$ (M=Si, Ge),[1,2] we assigned infrared bands at *ca.* 770 cm^{-1} for $(CH_3)_3SnH$ and $(CH_3)_3SnD$, and at *ca.* 480 cm^{-1} for $(CD_3)_3SnH$ and $(CD_3)_3SnD$ to the A_1 methyl rock. For trimethylsilane and trimethylgermane the band due to this mode coincides with that due to one of the E modes. Therefore, it may be considered that the same accidental degeneracy is encountered in trimethylstannane. Assignments of the remaining E modes which appear in the range 900—300 cm^{-1} is impossible without the aid of normal coordinate calculations.

The two skeletal deformation modes should be expected in the region below 300 cm^{-1}. However, only one band is observed in the Raman spectrum for each isotopic compound below 300 cm^{-1}. Since the corresponding infrared band is observed as two closely bands in the solid state and the same modes coincide with each other for $(CH_3)_3SnCF_3$ and $(CD_3)_3SnCF_3$,[7] we assigned bands at *ca.* 150 cm^{-1} for $(CH_3)_3SnH$ and $(CH_3)_3SnD$ and at *ca.* 130 cm^{-1} for $(CD_3)_3SnH$ and $(CD_3)_3SnD$ to the A_1 and E skeletal deformations.

One methyl torsional mode should be expected. However, no band ascribable to this mode was observed in both the infrared and Raman spectra for each isotopic compound.

Normal Coordinate Calculations and Discussion

Normal coordinate calculations were carried out on an ACOS 77/900 computer at the Computer Center,

TABLE 6. SYMMETRY FORCE CONSTANTS FOR TRIMETHYLSTANNANE[a]

	Constant	σ		Constant	σ
F_1	4.754	0.013	F_{13}	4.750	0.157
F_2	4.723	0.067	F_{14}	4.766	0.157
F_3	1.994	0.009	F_{15}	4.722	0.099
F_4	0.512	0.003	F_{16}	0.511	0.006
F_5	0.471	0.019	F_{17}	0.510	0.006
F_6	0.378	0.019	F_{18}	0.471	0.028
F_7	2.270	0.039	F_{19}	0.381	0.010
F_8	0.453	0.082	F_{20}	0.384	0.006
			F_{21}	0.371	0.013
$F_{2,5}$	−0.385	0.084	F_{22}	2.133	0.057
$F_{5,7}$	−0.152	0.039	F_{23}	0.371	0.028
$F_{6,8}$	−0.158	0.069			
			$F_{15,18}$	−0.388	0.122
			$F_{18,22}$	−0.140	0.056
			$F_{19,21}$	0.088	0.009
			$F_{21,22}$	−0.029	0.023

a) The stretching force constants are given in 10^2 N m^{-1}, the defor mation 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 ($10\ N^2\ m^{-1}$)

	f(Sn–C)	f(Sn–H)
$(CH_3)_4Sn$	2.19[10]	
$(CH_3)_3SnH$	2.18[a]	1.99[a]
$(CH_3)_3SnCl$	2.12[4]	
CH_3SnH_3	2.12[11]	2.23[b]
SnH_4		2.27[b]

a) This work. b) The force constant was calculated from the symmetry force constants reported in the earier papers.[11,12]

Tohoku University, by using the interactive least-squares procedure. G-matrix was calculated by use of the structural parameters from the electron-diffraction study[6] and by assuming a tetrahedral angle around carbon atoms; r(Sn–H) = 0.1705 nm, r(Sn–C) = 0.2147 nm, r(C–H) = 0.1086 nm, ∠C–Sn–C = 107.5°. The torsional mode of the methyl groups was neglected in the E class.

The least-squares refinement was carried out in the same manner as with the acetonitrile-borane adducts,[8] trimethylsilane,[1] and trimethylgermane.[2] The calculated frequencies have an average error of 0.42% for A_1 vibrations and 0.76% for E vibrations. The sum for the weighted squares of errors $\sum(\lambda_{obsd}-\lambda_{calcd})^2/\lambda_{obsd}$ was 2.0×10^{-3} for A_1 vibrations and 7.7×10^{-3} for E vibrations. The symmetry force constants from the last cycle in the least-squares refinements are given in Table 6, together with their uncertainties.

Potential energy distributions are also given in Tables 1—4. These show that one of the E methyl rocks, the SnH bend, and the SnC_3 stretch in the E class for $(CH_3)_3SnH$ and $(CD_3)_3SnD$ are strongly coupled with each other.

The Sn–C and Sn–H valence force constants derived from the symmetry force constants are compared with those of the related compounds in Table 7. The Sn–C force constants are almost the same in these compounds. However, the Sn–H force constants seem to decrease slightly with increasing the number of methyl groups attached to a tin atom. This trend is quite similar to that found for the Si–H force constants of methylsilanes.[9]

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