

Vibrational Spectra and Normal Coordinate Calculations for Trimethylstannane

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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 $(\text{CH}_3)_3\text{MH}$ ($\text{M}=\text{Si}, \text{Ge}$). 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 May³⁾ have assigned an infrared band at *ca.* 670 cm^{-1} for $(\text{CH}_3)_3\text{SnH}$ to the SnH bending vibration, while Kriegsmann and Pischtschan⁴⁾ 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 $(\text{CH}_3)_3\text{SnCl}$ or $(\text{CD}_3)_3\text{SnCl}$ 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. $(\text{CH}_3)_3\text{SnCl}$ and $(\text{CD}_3)_3\text{SnCl}$ were prepared by the reaction of SnCl_4 with $(\text{CH}_3)_4\text{Sn}$ and $(\text{CD}_3)_4\text{Sn}$, respectively. $(\text{CH}_3)_4\text{Sn}$ and $(\text{CD}_3)_4\text{Sn}$ were prepared by reacting SnCl_4 with $(\text{CH}_3)_2\text{Zn}$ and $(\text{CD}_3)_2\text{Zn}$, 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 ($4000\text{--}300\text{ cm}^{-1}$) and on a Hitachi FIS-III spectrophotometer ($400\text{--}30\text{ cm}^{-1}$) 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 $8\text{A}_1 + 4\text{A}_2 + 12\text{E}$, 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 trimethylsilane¹⁾ and trimethylgermane.²⁾ Infrared spectra of trimethylstannane and its deuterated analogues in the gas phase are shown in Fig. 1. The Raman spectra

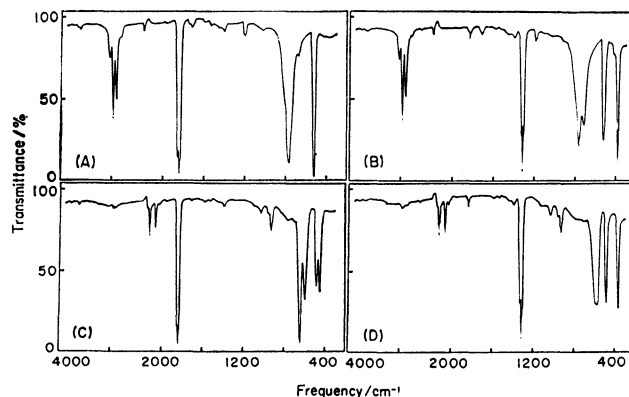


Fig. 1. Infrared spectra of $(\text{CH}_3)_3\text{SnH}$ (A), $(\text{CH}_3)_3\text{SnD}$ (B), $(\text{CD}_3)_3\text{SnH}$ (C), and $(\text{CD}_3)_3\text{SnD}$ (D) in the gas phase.

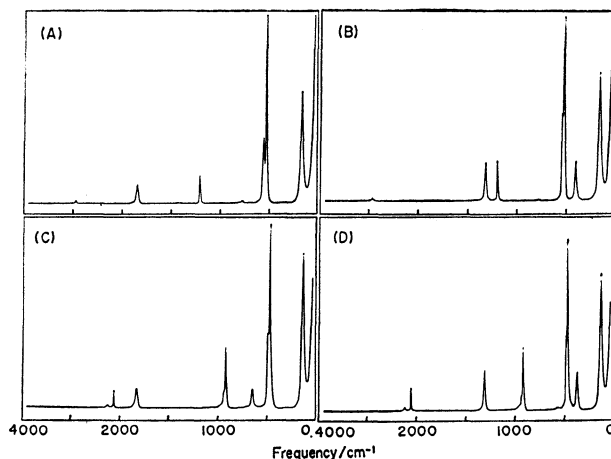


Fig. 2. Raman spectra of $(\text{CH}_3)_3\text{SnH}$ (A), $(\text{CH}_3)_3\text{SnD}$ (B), $(\text{CD}_3)_3\text{SnH}$ (C), and $(\text{CD}_3)_3\text{SnD}$ (D) in the liquid.

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 (CH₃)₃SnH

No.	Infrared	Raman	Calcd	Potential energy distribution
	Gas	Liquid		
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.

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

The asymmetric and symmetric CH₃ stretches were observed at *ca.* 2980 and *ca.* 2900 cm⁻¹, respectively, for (CH₃)₃SnH and (CH₃)₃SnD. For (CD₃)₃SnH and (CD₃)₃SnD, these modes were observed at *ca.* 2240 and *ca.* 2120 cm⁻¹.

Polarized Raman bands at *ca.* 1850 cm⁻¹ for (CH₃)₃SnH and (CD₃)₃SnH are assigned to the SnH stretching vibration. Upon deuteration of the SnH group, these bands shift to *ca.* 1300 cm⁻¹ for (CH₃)₃SnD and (CD₃)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 (CH₃)₃SnH and (CH₃)₃SnD are assigned to the asymmetric methyl deformation. The corresponding Raman bands are

TABLE 3. OBSERVED AND CALCULATED FREQUENCIES (cm⁻¹) FOR (CH₃)₃SnD

No.	Infrared	Raman	Calcd	Potential energy distribution
	Gas	Liquid		
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 (CD₃)₃SnH

No.	Infrared	Raman	Calcd	Potential energy distribution
	Gas	Liquid		
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.

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 (CD₃)₃SnH and (CD₃)₃SnD.

For (CH₃)₃SnH and (CH₃)₃SnD, weak infrared bands at *ca.* 1200 cm⁻¹ are assigned to the symmetric methyl deformation and the corresponding Raman bands are polarized. These bands shift to *ca.* 920 cm⁻¹ for (CD₃)₃SnH and (CD₃)₃SnD.

TABLE 5. OBSERVED AND CALCULATED FREQUENCIES (cm^{-1}) FOR $(\text{CD}_3)_3\text{SnD}$

No.	Infrared	Raman	Calcd	Potential energy distribution
	Gas	Liquid		
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 $(\text{CD}_3)_3\text{SnD}$ 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 $(\text{CH}_3)_3\text{SnH}$ and $(\text{CH}_3)_3\text{SnD}$ are strong and polarized. Upon deuteration of the methyl groups these bands shift to *ca.* 480 cm^{-1} for $(\text{CD}_3)_3\text{SnH}$ and $(\text{CD}_3)_3\text{SnD}$. 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 $(\text{CH}_3)_3\text{SnH}$. For $(\text{CH}_3)_3\text{SnH}$ 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 $(\text{CH}_3)_3\text{SnH}$ to the SnH bending 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 $(\text{CH}_3)_3\text{SnD}$ 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 $(\text{CD}_3)_3\text{SnH}$ and $(\text{CD}_3)_3\text{SnD}$ upon deuteration of the methyl groups. A strong

infrared band at *ca.* 650 cm^{-1} for $(\text{CD}_3)_3\text{SnH}$ was assigned to the SnH bending, since no corresponding band was observed in the same region for $(\text{CD}_3)_3\text{SnD}$.

Since the A_1 methyl rocking frequencies are approximately identical with each other for $(\text{CH}_3)_3\text{MH}$ and $(\text{CH}_3)_3\text{MD}$ and for $(\text{CD}_3)_3\text{MH}$ and $(\text{CD}_3)_3\text{MD}$ ($M=\text{Si}, \text{Ge}$),^{1,2)} we assigned infrared bands at *ca.* 770 cm^{-1} for $(\text{CH}_3)_3\text{SnH}$ and $(\text{CH}_3)_3\text{SnD}$, and at *ca.* 480 cm^{-1} for $(\text{CD}_3)_3\text{SnH}$ and $(\text{CD}_3)_3\text{SnD}$ 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 $(\text{CH}_3)_3\text{SnCF}_3$ and $(\text{CD}_3)_3\text{SnCF}_3$,⁷⁾ we assigned bands at *ca.* 150 cm^{-1} for $(\text{CH}_3)_3\text{SnH}$ and $(\text{CH}_3)_3\text{SnD}$ and at *ca.* 130 cm^{-1} for $(\text{CD}_3)_3\text{SnH}$ and $(\text{CD}_3)_3\text{SnD}$ 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 deformation force constants in $10^{-18} \text{ N m rad}^{-2}$, and the stretching-deformation interaction constants in $10^{-8} \text{ N rad}^{-1}$. The subscript number i in F_i corresponds with that in S_i in Table 1.

TABLE 7. COMPARISON OF FORCE CONSTANTS ($10 \text{ N}^2 \text{ m}^{-1}$)

	$f(\text{Sn-C})$	$f(\text{Sn-H})$
$(\text{CH}_3)_4\text{Sn}$	2.19 ¹⁰⁾	
$(\text{CH}_3)_3\text{SnH}$	2.18 ^{a)}	1.99 ^{a)}
$(\text{CH}_3)_3\text{SnCl}$	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 earlier 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 study⁶⁾ and by assuming a tetrahedral angle around carbon atoms; $r(\text{Sn-H})=0.1705 \text{ nm}$, $r(\text{Sn-C})=0.2147 \text{ nm}$, $r(\text{C-H})=0.1086 \text{ nm}$, $\angle\text{C-Sn-C}=107.5^\circ$. 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 $\sum(\lambda_{\text{obsd}} - \lambda_{\text{calcd}})^2 / \lambda_{\text{obsd}}$ 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 $(\text{CH}_3)_3\text{SnH}$ and $(\text{CD}_3)_3\text{SnD}$ 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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