Vibrational Spectra and Normal Coordinate Calculations for Trimethylsilane

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Synopsis. Vibrational spectra of trimethylsilane-d_0, -d_1, -d_9, and -d_{10} have been obtained. Assignments for all the fundamentals have been made assuming C_{3v} molecular symmetry. Normal coordinate calculations have been carried out to confirm the assignments.

The vibrational studies of trimethylsilane have been made extensively.[1] For instance, Ball *et al.*[2] have reported the vibrational spectra of $(CH_3)_3SiH$ and $(CH_3)_3SiD$, and based on their data, Tenisheva *et al.*[3] have carried out the normal coordinate calculations. From these studies, it was found that there is a considerable coupling between the SiH bending and the methyl rocking vibrations, thus remaining some ambiguities in these assignments. Therefore, it is desirable to obtain the vibrational spectra of its methyl-d_9 homologues, $(CD_3)_3SiH$ and $(CD_3)_3SiD$, and to achieve the normal coordinate calculations using the data of these four isotopic species.

Experimental

The compounds were prepared by reduction of bromotrimethylsilane-d_0 or -d_9 with $LiAlH_4$ or $LiAlD_4$ and purified by vacuum distillation.

Infrared spectra (4000—300 cm^{-1}) were obtained on a Hitachi 345 spectrophotometer in the gas phase and in the solid films at liquid nitrogen temperature. Far-infrared spectra (400—80 cm^{-1}) were recorded on a Hitachi FIS-III spectrophotometer in the solid films at liquid nitrogen temperature. Raman spectra were recorded in the liquid state on a JEOL JRS S-1 laser Raman spectrophotometer equipped with a 50 mW NEC GLS 5800 He–Ne laser. Qualitative polarizations were also measured.

Results and Discussion

With C_{3v} symmetry, 24 normal vibrations are expected to distribute as $8A_1+4A_2+12E$. The A_1 and E modes are both infrared and Raman active, and the A_2 modes are inactive in both spectra. The observed frequencies for $(CD_3)_3SiH$ and $(CD_3)_3SiD$ are listed in Table 1. Those for $(CH_3)_3SiH$ and $(CH_3)_3SiD$ are nearly equal with those given by the previous authors.[2] The Raman spectra below 1000 cm^{-1} are shown in Fig. 1.

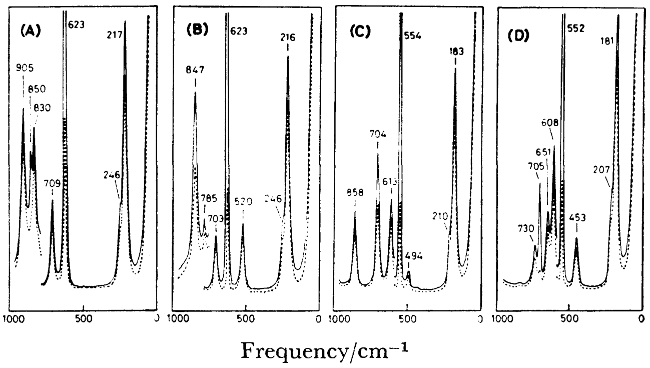

Fig. 1. Raman spectra of (A) $(CH_3)_3SiH$, (B) $(CH_3)_3$-SiD, (C) $(CD_3)_3SiH$, and (D) $(CD_3)_3SiD$. Solid line; parallel polarization, broken line; crossed polarization.

Table 1. Observed and calculated frequencies (cm^{-1}) for $(CD_3)_3SiH$ and $(CD_3)_3SiD$[a)]

	No.	$(CD_3)_3SiH$			$(CD_3)_3SiD$		
		Obsd	Calcd	PED	Obsd	Calcd	PED
A_1	1	2218	2213	$99S_1$	2217	2213	$99S_1$
	2	2119	2117	$90S_2$	2119	2118	$96S_2$
	3	2119	2126	$95S_3$	1544	1533	$100S_3$
	4	1038	1029	$98S_4$	1035	1029	$98S_4$
	5	992	988	$70S_5$ $15S_7$ $15S_2$	990	988	$71S_5$ $15S_7$ $15S_2$
	6	704	708	$66S_6$ $14S_7$ $15S_8$	705	703	$65S_6$ $13S_7$ $15S_8$
	7	554	546	$73S_7$ $12S_5$ $15S_6$	552	545	$74S_7$ $12S_5$ $14S_6$
	8	183	183	$62S_8$ $37S_6$	181	182	$62S_8$ $37S_6$
E	13	2218	2211	$64S_{13}$ $35S_{14}$	2217	2210	$68S_{13}$ $31S_{14}$
	14	2218	2212	$64S_{14}$ $35S_{13}$	2217	2212	$68S_{14}$ $31S_{13}$
	15	2119	2116	$97S_{15}$	2119	2117	$97S_{15}$
	16	1038	1029	$77S_{16}$ $22S_{17}$	1035	1029	$73S_{16}$ $25S_{17}$
	17	1038	1028	$76S_{17}$ $22S_{16}$	1035	1028	$73S_{17}$ $25S_{16}$
	18	992	986	$65S_{18}$ $14S_{15}$ $21S_{22}$	990	986	$65S_{18}$ $14S_{15}$ $21S_{22}$
	19	494	490	$79S_{19}$ $19S_{21}$	453	452	$59S_{19}$ $40S_{21}$
	20	613	591	$64S_{20}$ $27S_{22}$	608	590	$61S_{20}$ $31S_{22}$
	21	858	857	$90S_{21}$	651	648	$40S_{21}$ $19S_{20}$ $26S_{19}$
	22	704	700	$41S_{22}$ $31S_{20}$ $19S_{18}$	730	728	$33S_{22}$ $22S_{21}$ $20S_{20}$ $13S_{18}$
	23	210	213	$93S_{23}$	207	212	$92S_{23}$

a) The subscript number i in S_i corresponds with that in F_i given in Table 2.

Table 2. Symmetry force constants and their uncertainties for trimethylsilane[a)]

A$_1$ species				E species			
Mode			σ	Mode			σ
$\nu(CH_3)$	F_1	4.674	0.011	$\nu(CH_3)$	F_{13}	4.683	0.033
$\nu(CH_3)$	F_2	4.657	0.055	$\nu(CH_3)$	F_{14}	4.679	0.033
$\nu(SiH)$	F_3	2.584	0.009	$\nu(CH_3)$	F_{15}	4.664	0.077
$\delta(CH_3)$	F_4	0.527	0.003	$\delta(CH_3)$	F_{16}	0.525	0.005
$\delta(CH_3)$	F_5	0.524	0.016	$\delta(CH_3)$	F_{17}	0.520	0.005
$\rho(CH_3)$	F_6	0.359	0.016	$\delta(CH_3)$	F_{18}	0.499	0.022
$\nu(SiC_3)$	F_7	3.222	0.050	$\rho(CH_3)$	F_{19}	0.351	0.010
$\delta(SiC_3)$	F_8	0.731	0.065	$\rho(CH_3)$	F_{20}	0.459	0.008
				$\delta(SiH)$	F_{21}	0.549	0.012
	$F_{2,5}$	−0.414	0.064	$\nu(SiC_3)$	F_{22}	2.843	0.063
	$F_{5,7}$	−0.132	0.029	$\delta(SiC_3)$	F_{23}	0.620	0.025
	$F_{6,8}$	−0.275	0.023				
					$F_{15,18}$	−0.410	0.090
					$F_{18,22}$	−0.086	0.028
					$F_{19,21}$	0.113	0.006
					$F_{20,22}$	0.149	0.039

a) The stretching force constants are given in mdyn/Å, the deformation force constants in mdyn·Å, the stretching-deformation interaction constants in mdyn.

The observed spectra and the assignments for $(CH_3)_3SiH$ and $(CH_3)_3SiD$ are almost identical with those given by the previous authors.[2)] However, a discrepancy is found in the assignments for the methyl rocking vibrations. They have reported two Raman bands at 853 and 831 cm^{-1}, of which the latter was assigned to the A$_1$ mode from the polarization measurements. In agreement in frequency with their results, we have observed two bands at 850 and 830 cm^{-1}, but the former band, not the latter, is found to be polarized (Fig. 1. (A)). Therefore, the band at 850 cm^{-1} should be assigned to the A$_1$ methyl rocking mode and the latter to the E mode. This mis-assignments were probably caused by the fact that the polarization measurements were difficult in a photographic method with a Hg-arc as an excitation, especially in the case of closely separated bands.

For $(CD_3)_3SiH$ and $(CD_3)_3SiD$, the assignments can be easily made except the range between 1000 and 400 cm^{-1}. In the case of $(CD_3)_3SiD$, two polarized Raman bands are observed at 705 and 552 cm^{-1} in this region (Fig. 1. (D)) and can be assigned to the CD_3 rock(A$_1$) and to the SiC_3 stretch(A$_1$), respectively. These bands are observed nearly at the same frequencies in $(CD_3)_3SiH$, but the band at 704 cm^{-1} is now only partly polarized (Fig. 1. (C)). This suggests that some vibrations other than the CD_3 rock(A$_1$) coincide on this band. The most probable candidate is the asymmetric SiC_3 stretch, for this mode has been observed at *ca.* 700 cm^{-1} in $(CD_3)_3SiX$.[4)] This asymmetric SiC_3 stretch is found at 730 cm^{-1} in $(CD_3)_3SiD$.

The Raman band at 858 cm^{-1} in $(CD_3)_3SiH$ can be assigned to the SiH bending vibration, for it disappears in $(CD_3)_3SiD$. However, as a considerable coupling is expected between this mode and the methyl rock, the exact assignments can only be made with the aid of the normal coordinate calculations.

The normal coordinate calculations were carried out by Wilson's GF-matrix method on an ACOS 77/900 computer at the Computer Center, Tohoku University, using the iterative least-squares procedure in the usual manner. The G matrix was calculated by use of the molecular parameters determined from microwave study.[5)] The least-squares refinement[6)] was carried out in terms of the symmetry force constants, which were fitted to the Raman frequencies observed in the liquid, for the four isotopes simultaneously. The torsional mode was neglected in the E class. The symmetry force constants, together with uncertainties from the last cycle are given in Table 2. The average errors were 0.41 and 0.66% for the A$_1$ and E vibrations, respectively. The sum of the weighted squares of errors $\Sigma(\lambda_{obsd}-\lambda_{calcd})^2/\lambda_{obsd}$ was 1.8×10^{-3} for the A$_1$ and 4.9×10^{-3} for the E vibrations. The potential energy distributions are also given in Table 1.

The results of the calculations clearly indicate that the methyl rock, the SiH bending and the asymmetric SiC_3 stretch strongly couple with each other, especially in $(CD_3)_3SiD$.

The valuence force constant f(Si–C), derived from the symmetry force constants, is 2.97 mdyn/Å. This value is equal to that of CH_3SiH_3(2.97 mdyn/Å)[7)] and is slightly larger than that of $(CH_3)_4Si$(2.88 mdyn/Å).[8)] This is in agreement with what might be expected from their Si–C bond lengths; 1.868 Å in $(CH_3)_3SiH$,[5)] 1.867 Å in CH_3SiH_3,[9)] and 1.875 Å in $(CH_3)_4Si$.[10)]

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