BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 46, 2044—2052 (1973)

Vibrational Assignments of Ethylmethylsilane

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(Received December 12, 1972)

The infrared spectra of ethylmethylsilane, $CH_3CH_2SiH_2CH_3$, its deuterated species, $CH_3CH_2SiD_2CH_3$, and a mixture of $CH_3CH_2SiHDCH_3$, $CH_3CH_2SiH_2CH_3$, and $CH_3CH_2SiD_2CH_3$ have been measured in the gaseous, liquid, and crystalline states. The Raman spectrum of ethylmethylsilane has also been measured in the liquid state. Vibrational assignments have been made in relation to the rotational isomerism, on the basis of a modified Urey-Bradley force field, in which the force constants have been transferred from those for dimethylsilane and ethylsilane. The conclusion regarding the molecular forms of the rotational isomers, which has been obtained from the experimental evidence of the SiHD deformation vibrations for an asymmetrically-deuterated species, $CH_3CH_2SiHDCH_3$, can be considered to be also supported by the present results of the normal vibration calculations.

In previous notes, we have reported the existence of the rotational isomers in ethylmethylsilane[1] and have determined the molecular forms of the isomers from the SiHD deformation vibrations for the asymmetrically-deuterated species, $CH_3CH_2SiHDCH_3$, experimentally.[2] In the present paper, we will deal with the molecular forms of the isomers and with the vibrational assignments based on the normal vibration calculation using a modified Urey-Bradley force field.

Experimental

The samples of ethylmethylsilane and its deuterated species were prepared by the method of making CH_3CH_2MgBr react with CH_3SiCl_3 in ethylether and by reducing the resultant $CH_3CH_2SiCl_2CH_3$ with $LiAlH_4$, $LiAlD_4$, or an equimolar

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[1] M. Hayashi, K. Ohno, and H. Murata, This Bulletin, **45**, 298 (1972).

[2] M. Hayashi, K. Ohno, and H. Murata, *ibid.*, **46**, 684 (1973).

mixture of $LiAlH_4$ and $LiAlD_4$ in *n*-butylether.[3] The purities of the samples of $CH_3CH_2SiH_2CH_3$ and $CH_3CH_2SiD_2CH_3$ were found to be better than 95% by a study of the infrared spectra and the gas chromatograph. Though the sample prepared using the mixture of $LiAlH_4$ and $LiAlD_4$ was a mixture of $CH_3CH_2SiHDCH_3$, $CH_3CH_2SiH_2CH_3$, and $CH_3CH_2SiD_2CH_3$, it was used in the measurements without further attempts at isolation.

The infrared spectra in the region from 200 to 4000 cm^{-1} were recorded on a Perkin-Elmer instrument (model 621) using conventional techniques.[1,2] The Raman spectrum in the liquid state was measured with a JEOL Raman spectrometer.

Rotational Isomerism

The observed infrared and Raman spectra of ethylmethylsilane, $CH_3CH_2SiH_2CH_3$, are given in Table 1. The infrared spectra of its deuterated species, $CH_3CH_2SiD_2CH_3$, and the mixture of $CH_3CH_2SiHDCH_3$, $CH_3CH_2SiH_2CH_3$, and $CH_3CH_2SiD_2CH_3$ are also given in Tables 2 and 3. As has been reported in the previous notes,[1,2] from a comparison of the spectra in the gaseous and liquid states with those in the crystalline state in the region from 300 to 950 cm^{-1}, definite evidence of the rotational isomers is obtained, as is shown in Fig. 1; that is, some of the bands existing in both the gaseous and liquid states disappear in the crystalline state. On the other hand, the existence of the isomers cannot be concluded from the spectra in the region from 950 to 1500 cm^{-1} alone, since the infrared spectra in the liquid and crystalline states are not so much different.

Normal Vibration Calculation

A normal vibration calculation based on a modified Urey-Bradley force field was carried out, with the force constants being transferred from those for dimethylsilane and ethylsilane,[4] except the force constant of

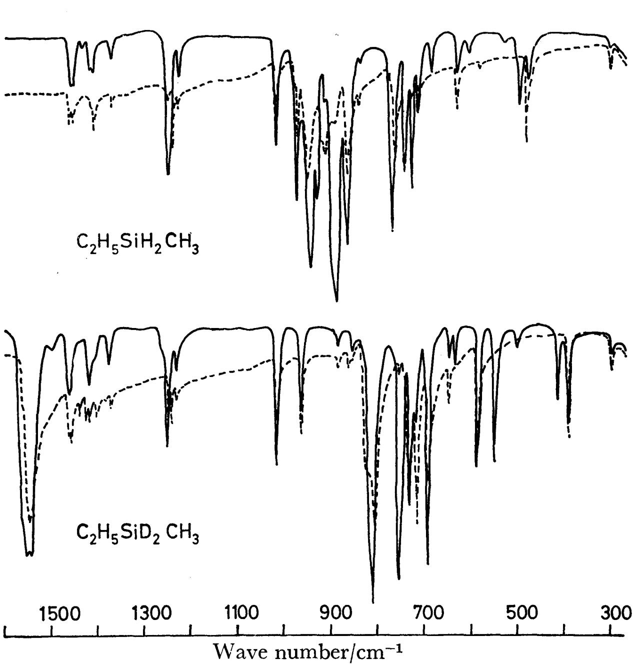

Fig. 1. The infrared spectra of ethylmethylsilane and its deuterated species, ——: in the liquid state (19 °C), ------: in the crystalline state.

Table 1. Infrared and raman spectra of $CH_3CH_2SiH_2CH_3$[a] (cm^{-1})

Infrared						Raman		Assignment
Gas	Int.	Liquid	Int.	Crystal	Int.	Liquid	Int.	
2972	s							
2966	s			2962	m	2961	m	C–H str. T,G
2962 sh	s	2950	s	2950	s			
						2939	m	
2926 b	s	2928	w	2928	w	2930 sh	m	
		2913	w	2914	m	2911	s	
2896	m							
2890		2891	w	2895	m	2899	s	
2882		2870	m	2870	w	2880	s	
		2800	vw	2800	vw			
2150	vs							SiH_2 str. T,G
2146	vs							
2139	vs	2126	vs	2126	vs	2137	vs	
1463	w	1462 sh	m	1463	m	1463	s	CCH_3 asym. def. (A′,A″) T,G
1455	w	1455 sh	m	1455	m			
1444	w							
		1437	vw			1437 sh	m	
1431 sh	w							CH_2 sci., $SiCH_3$ asym. def. (A′, A″) T,G
1420		1422 sh	m	1418	vw	1423	m	
1414		1413 sh	m	1410	m			
1385	w	1377	w	1373	w			CCH_3 sym. def. T,G
1351 b	vw							
						1298	w	

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3) F. S. Kipping, *Proc. Chem. Soc.*, **20**, 15 (1904); W. Dilthey, *Ber.*, **37**, 319 (1904); A. E. Finholt, A. C. Bond, Jr., and H. I. Schlesinger, *J. Amer. Chem. Soc.*, **69**, 1199 (1947).

4) K. Ohno, M. Hayashi, and H. Murata, *J. Sci. Hiroshima Univ., Ser A*, **36**, 121 (1972).

Infrared						Raman		Assignment
Gas	Int.	Liquid	Int.	Crystal	Int.	Liquid	Int.	
1266 1261 1255	m	1251	s	1250	w	1254	m	$SiCH_3$ sym. def. T,G
				1244	m			
1227	w	1230	m	1230	w	1228	m	CH_2 wag., CH_2 twist. T,G
						1122	vw	
1031 1023 1016	m	1021	s	1021	m	1022	m	C–C str. T,G
983 977 969	s	977	s	981 sh 975	vw m	971	m	CCH_3 rock. (A′,A″) T,G
958 952 945	vs	946	vs	952	s	953	m	SiH_2 sci. T
		933	s	—				SiH_2 sci. G
		914	vw	915 b	m			
908 900 892	vs	890	vs	—				SiH_2 wag. G
873	m	868	s	869	s			SiH_2 wag. T
		840	vw	841	vw	842	w	$SiCH_3$ rock. (A″) T,G
772	m	770	s	765	s	772	vw	CH_2 rock. T
740 730 723	m	743 730	s s	746 —	s	741	w	$SiCH_3$ rock. (A′) T $SiCH_3$ rock. (A′) G, CH_2 rock. G
715	m	715	m	719	m	714	m	C–Si str. T
690	w	687	m	—		686	m	C–Si str. G
639 sh	w	630	m	630	m	628	vs	C–Si str. T
619	w							
		606	w	—				C–Si str. G
		577	vw	580	w	590	m	SiH_2 twist. T
		530	w	—				
492	w	498	m			500	vw	SiH_2 rock. G
482 sh	w	480	m	480	m			SiH_2 rock. T
						331	vw	
294 sh	w	301	vw	301	w	298	m	C–C–Si bend. T
280	w							
215 ?	vvw					216 ?	vw	CCH_3 torsion T,G
						200 ?	vw	
170 ?	vvw					167	w	C–Si–C bend. T
87 ?	w							CH_2–SiH_2 torsion T,G

a) Int.=intensity; s, m, w=strong, medium, weak; v=very; b=broad; sh=shoulder; T=*trans* isomer; and G=*gauche* isomer.

Table 2. Infrared spectra of $CH_3CH_2SiD_2CH_3$[a] (cm^{-1})

Infrared						Assignment
Gas	Int.	Liquid	Int.	Crystal	Int.	
2972	s					
2966	s			2964	w	C–H str. T,G
		2951	vs	2951	m	
2927 b	m	2932	m	2932	w	
		2916	m	2916	w	
2905	m					
2898 2889 2882	m	2893 2874	m s	2896 2871	w w	
		2828	vvw	2825	vw	

Infrared						Assignment
Gas	Int.	Liquid	Int.	Crystal	Int.	
1561	vs	1561 sh	s	1562 sh	m	Si–D str. T,G
1556 b	vs	1552	vs	1549	vs	
		1542	vs			
		1499	vw	1504 sh	w	
1473	w					
1466	w	1463	m	1463	m	CCH_3 asym. def. (A′, A″) T,G
1458 b	w	1458 sh	m	1458	m	
		1437	vw	1440	w	
1427				1427	w	CH_2 sci., $SiCH_3$ asym. def. (A′, A″) T,G
1417	w	1419	m	1418	w	
1410 sh		1408	w	1403	w	
				1386	vw	
		1378	m	1373	w	CCH_3 sym. def. T,G
1263		1263	w			
1261	m	1251	s	1250	m	$SiCH_3$ sym. def. T,G
1256						
				1243	m	
		1232	m	1230	w	CH_2 wag., CH_2 twist. T,G
1026						
1018	m	1015	s	1014	s	C–C str. T,G
1010						
966	m	963	s	960	s	CCH_3 rock. (A′, A″) T,G
		893	vw	896	vw	
		883	w	885	w	
867	vw			863	w	
		852	w	857	w	
820 b	s			822 sh	s	
812	s	810	vs	814 sh	s	$SiCH_3$ rock. (A′, A″) T,G
				805	vs	
762 b						
755 b	s	753	vs	—		CH_2 rock. G
749 b		730	vs	732	vs	CH_2 rock. T
743	s					
741	s					
723	s	719	s	716	vs	C–Si str. T,G
719						
701						
695	m	691	vs	691	vs	SiD_2 sci. T,G
688						
653	w	644	w	646	m	C–Si str. T
643						
		633	w	—		C–Si str. G
592						
585	m	584	s	587	s	SiD_2 wag. T
578						
554						
547	m	548	s	—		SiD_2 wag. G
541						
498	w	501	w	—		SiD_2 twist. G
422 sh						
412	m	414	s	—		SiD_2 rock. G
402 sh						
393	m	390	s	390	s	SiD_2 rock. T
380 sh						
		294	m	294	m	C–C–Si bend. T

a) See a) of Table 1.

TABLE 3. INFRARED SPECTRA OF THE MIXTURE OF $CH_3CH_2SiHDCH_3$, $CH_3CH_2SiH_2CH_3$ ($-d_0$), AND $CH_3CH_2SiD_2CH_3$ ($-d_2$)[a)] (cm^{-1})

Infrared[b)]				Assignment
Liquid	Int.	Crystal	Int.	
893 sh	s			
890 sh	s	888 sh	s	$-d_0$
879	s	876	s	$-d_0$
862 sh	vs	866	s	$-d_0$
856 sh	vs	852 b	vs	SiHD sci. T, G
849	vs			$SiCH_3$ rock. T,G
808	vs	809	vs	$-d_2$
796	s	798	s	$SiCH_3$ rock. T,G
766	vs	765	s	CH_2 rock. T, $-d_0$
748	vs	748	vs	CH_2 rock. G, $-d_2$
740 sh	s	740	s	CH_2 rock. G, $-d_0$
726	s	726	s	C–Si str. T, G, $-d_2$
716	s	714	s	C–Si str. G, $-d_0$, $-d_2$
687	s	689	s	$-d_0$, $-d_2$
677	m	678	s	SiH def. T, G
640	w	640	w	C–Si str. T
624	m	625	m	$-d_0$
666	w	—		C–Si str. G
578	m	578	m	$-d_2$
543	m	—		$-d_2$
519	w	—		SiD def. G
508 sh	w	—		SiD def. G
495	m	486	m	SiD def. T, $-d_0$
477	w	477	m	$-d_0$
443	m	—		SiHD rock. G
434	m	—		SiHD rock. G
		422	m	SiHD rock. T
413	m	—		$-d_2$
390	w	391	w	$-d_2$
293	vw	294	vw	C–C–Si bend.

a) The vibrational assignments are only described for $CH_3CH_2SiHDCH_3$. See also a) of Table 1.
b) The spectra were not measured in the region from 900 to 4000 cm^{-1}.

F(C·C·Si), which was adjusted in order to reproduce the observed C–C–Si bending vibration.

The Urey-Bradley force field was modified as follows: 1) the internal rotation force constants for CH_3–C, CH_2–Si, and Si–CH_3 groups were assumed to be the calculated values from the barrier heights of 3.49, 1.24, and 1.24 kcal/mol respectively; 2) the *trans* and *gauche* coupling constants between the CH_3 and SiH_2 groups, between the CH_2 and SiH_2 groups, and between the Si–C–H bendings and the C–Si–C bending were added, and these values were transferred from dimethylsilane and ethylsilane, and 3) the C–H bond interaction constant was added in order to reproduce the observed C–H stretching frequencies.

The bond lengths used in the calculation were the values transferred from those for methylsilane and ethylsilane.[5)] All of the valency angles were assumed to be tetrahedral.

The force constants and the observed and calculated frequencies of ethylmethylsilane are given in Tables 4—7. Since the adjustment was made only for F(C·C·Si), while the other transferred force constants were fixed at the original values, relatively larger differences were found between the observed and calculated frequencies of some of the hydrogen deformation modes. However, the results of the calculation were considered still to be valid for the assignments of the observed spectra.

From the calculated potential energy distributions, considerably larger mixings of the modes were found in the following pairs of modes: 1) the CH_2 scissoring and CCH_3 symmetric deformation, 2) the SiH_2 wagging and $SiCH_3$ rocking, 3) the CH_2 rocking and SiH_2 twisting for $CH_3CH_2SiH_2CH_3$, 4) the CH_2 scissoring and CCH_3 symmetric deformation, and 5) the C–Si stretching and SiD_2 scissoring for $CH_3CH_2SiD_2CH_3$. The localization of the CH_2 rocking mode for the

TABLE 4. FORCE CONSTANTS FOR ETHYLMETHYLSILANE[a)]

K(C–H), CCH_3	4.297	κ (CCH_3)	0.029
K(C–H), CH_2	4.297	κ (CH_2)	−0.040
K(C–H), $SiCH_3$	4.403	κ (SiH_2)	0.104
K(Si–H)	2.462	κ ($SiCH_3$)	0.014
K(C–C)	2.400	*Y*(C–C)	0.109
K(Si–C)	1.991	*Y*(C–Si)	0.039
H(C–C–H), CCH_3	0.164	*F*(C · C · H), CCH_3	0.470
H(H–C–H), CCH_3	0.370	*F*(H · C · H), CCH_3	0.200
H(C–C–Si)	0.087	*F*(C · C · Si)	0.540[b)]
H(Si–C–H), CH_2	0.123	*F*(Si · C · H), CH_2	0.271
H(C–C–H), CH_2	0.278	*F*(C · C · H), CH_2	0.540
H(H–C–H), CH_2	0.331	*F*(H · C · H), CH_2	0.200
H(C–Si–C)	0.133	*F*(C · Si · C)	0.040
H(C–Si–H)	0.092	*F*(C · Si · H)	0.149
H(H–Si–H)	0.180	*F*(H · Si · H)	0.041
H(Si–C–H), $SiCH_3$	0.102	*F*(Si · C · H), $SiCH_3$	0.271
H(H–C–H), $SiCH_3$	0.349	*F*(H · C · H), $SiCH_3$	0.200
t(CH_2, SiH_2)[c)]	0.072	*t*(SiH_2 $SiCH_3$)[c)]	0.057
t(Si–C–H, C–Si–C)[c)]	0.030	*p*(C–H)	−0.084

a) The units of the force constants are in mdyn/Å for stretching, *K*; bending, *H*; repulsion, *F*; and bond interaction, *p*; and in mdyn·Å for intramolecular tension, κ; internal rotation, *Y*; and *trans* coupling, *t*. Force constants were transferred from dimethylsilane and ethylsilane.
b) The value was adjusted in order to reproduce the observed C–C–Si bending frequency.
c) *Gauche* coupling constants were assumed to be $g=-0.5t$.

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5) M. Hayashi and C. Matsumura, This Bulletin, **45**,732 (1972).

TABLE 5. OBSERVED AND CALCULATED FREQUENCIES FOR $CH_3CH_2SiH_2CH_3$ (cm^{-1})

	No.	*Trans* form		*Gauche* form		P.E.D.[a)]
		Obsd	Calcd	Obsd	Calcd	
A′	ν_1	2950	2965	*A* 2950	2965	CCH_3 asym. str.
	ν_2	2950	2964	2950	1964	$SiCH_3$ asym. str.
	ν_3	2928	2933	2928	2933	CH_2 sym. str.
	ν_4	2913	2901	2913	2901	$SiCH_3$ sym. str.
	ν_5	2870	2900	2870	2900	CCH_3 sym. str.
	ν_6	2126	2148	2126	2148	SiH_2 sym. str.
	ν_7	1462	1461	1462	1461	CCH_3 asym. def.
	ν_8	1422	1429	1422	1429	CH_2 sci.
	ν_9	1413	1413	1413	1413	$SiCH_3$ asym. def.
	ν_{10}	1377	1377	1377	1377	CCH_3 sym. def.
	ν_{11}	1251	1254	1251	1254	$SiCH_3$ sym. def.
	ν_{12}	1230	1189	1230	1188	CH_2 wag.
	ν_{13}	1021	1021	1021	1022	C–C str.
	ν_{14}	977	965	977	965	CCH_3 rock.
	ν_{15}	946	948	933	945	SiH_2 sci.
	ν_{16}	868	865	890	865	SiH_2 wag.
	ν_{17}	743	760	730	745	$SiCH_3$ rock.
	ν_{18}	715	714	687	711	C–Si str.
	ν_{19}	630	656	606	644	C–Si str.
	ν_{20}	301	301	—	317	C–C–Si bend.
	ν_{21}	167	186	—	187	C–Si–C bend.
A″	ν_{22}	2950	2975	*A* 2950	2975	CH_2 antisym. str.
	ν_{23}	2950	2964	2950	2964	CCH_3 asym. str.
	ν_{24}	2950	2959	2950	2959	$SiCH_3$ asym. str.
	ν_{25}	2126	2148	2126	2148	SiH_2 antisym. str.
	ν_{26}	1455	1458	1455	1458	CCH_3 asym. def.
	ν_{27}	1413	1413	1413	1413	$SiCH_3$ asym. def.
	ν_{28}	1230	1244	1230	1248	CH_2 twist.
	ν_{29}	977	975	977	968	CCH_3 rock.
	ν_{30}	840	840	840	840	$SiCH_3$ rock.
	ν_{31}	770	790	730	758	CH_2 rock.
	ν_{32}	577	594	—	622	SiH_2 twist.
	ν_{33}	480	487	498	498	SiH_2 rock.
	ν_{34}	215	243	—	250	C–CH_3 torsion
	ν_{35}	—	147	—	144	Si–CH_3 torsion
	ν_{36}	87	65	—	67	CH_2–SiH_2 torsion

a) Only the predominant symmetry coordinates are shown.

TABLE 6. OBSERVED AND CALCULATED FREQUENCIES FOR $CH_3CH_2SiD_2CH_3$ (cm^{-1})

	No.	*Trans* form		*Gauche* form		P.E.D.[a)]
		Obsd	Calcd	Obsd	Calcd	
A′	ν_1	2951	2965	*A* 2951	2965	CCH_3 asym. str.
	ν_2	2951	2964	2951	2964	$SiCH_3$ asym. str.
	ν_3	2932	2933	2932	2933	CH_2 sym. str.
	ν_4	2916	2901	2916	2901	$SiCH_3$ sym. str.
	ν_5	2874	2900	2874	2900	CCH_3 sym. str.
	ν_6	1542	1537	1542	1537	SiD_2 sym. str.
	ν_7	1463	1461	1463	1461	CCH_3 asym. def.
	ν_8	1419	1428	1419	1429	CH_2 sci.
	ν_9	1408	1413	1408	1413	$SiCH_3$ asym. def.
	ν_{10}	1378	1377	1378	1377	CCH_3 sym. def.
	ν_{11}	1251	1254	1251	1254	$SiCH_3$ sym. def.
	ν_{12}	1232	1189	1232	1188	CH_2 wag.
	ν_{13}	1015	1020	1015	1020	C–C str.
	ν_{14}	963	964	963	964	CCH_3 rock.
	ν_{15}	810	819	810	818	$SiCH_3$ rock.
	ν_{16}	719	731	719	721	C–Si str.
	ν_{17}	691	698	691	688	SiD_2 sci.
	ν_{18}	644	638	633	629	C–Si_2 str.
	ν_{19}	584	579	548	572	SiD_2 wag.
	ν_{20}	294	297	—	305	C–C–Si bend.
	ν_{21}	—	184	—	186	C–Si–C bend.
A″	ν_{22}	2951	2975	*A* 2951	2975	CH_2 antisym. str.
	ν_{23}	2951	2964	2951	2964	CCH_3 asym. str.
	ν_{24}	2951	2959	2951	2959	$SiCH_3$ asym. str.
	ν_{25}	1552	1552	1552	1552	SiD_2 antisym. str.
	ν_{26}	1458	1458	1458	1458	CCH_3 asym. def.
	ν_{27}	1408	1413	1408	1413	$SiCH_3$ asym. def.
	ν_{28}	1232	1243	1232	1247	CH_2 twist.
	ν_{29}	963	971	963	963	CCH_3 rock.
	ν_{30}	810	816	810	816	$SiCH_3$ rock.
	ν_{31}	730	761	753	750	CH_2 rock.
	ν_{32}	—	451	501	464	SiD_2 twist.
	ν_{33}	390	392	414	406	SiD_2 rock.
	ν_{34}	—	239	—	246	C–CH_3 torsion
	ν_{35}	—	146	—	144	Si–CH_3 torsion
	ν_{36}	—	64	—	65	CH_2–SiD_2 torsion

a) See a) of Table 5.

gauche form was worse than that for the *trans* form.

For the SiHD deformation modes of $SiHDCl_2$ and $(CH_3)_2SiHD$, it was found that the SiHD wagging and twisting modes should be more properly called the SiH and SiD deformation modes respectively, while the SiHD scissoring and rocking modes keep their original modes.[4)] In $CH_3CH_2SiHDCH_3$, the situation was nearly the same as in $SiHDCl_2$ and $(CH_3)_2SiHD$ for the SiHD rocking and SiD deformation modes, while the SiHD scissoring and SiH deformation modes were different and were considerably mixed with the C–Si stretching, CH_2 rocking, and $SiCH_3$ rocking modes.

Molecular Forms and Vibrational Assignments

The infrared spectra of ethylmethylsilane in the region from 1000 to 1500 cm^{-1} are not much different in the liquid and crystalline states; also, they are close to the superposition of the spectra of ethylsilane and methylsilane. The results of the calculations indicate that, as the coupling between the ethyl and methyl groups seems to be negligible, the calculated frequencies for the *trans* and *gauche* forms are essentially identical with each other. Therefore, the assignments of the observed spectra in this region can easily be obtained from the reported assignments for ethylsilane and methylsilane, without regard to the rotational isomerism.

On the other hand, it can be expected from the calculation that spectra sensitive to the molecular forms of the isomers exist in the region from 650 to 1000 cm^{-1}. Actually, in this region, ten infrared bands are observed in the liquid state for $CH_3CH_2SiH_2CH_3$, while four of them disappear in the crystalline state. For $CH_3CH_2SiD_2CH_3$, six infrared bands are observed in the liquid state; one of them disappears in the

TABLE 7. OBSERVED AND CALCULATED FREQUENCIES FOR $CH_3CH_2SiHDCH_3$[a] (cm^{-1})

	No.	*Trans* form		*Gauche* form (G)[b]		*Gauche* form (G')[c]		P.E.D.[d]
		Obsd	Calcd	Obsd	Calcd	Obsd	Calcd	
A	ν_{21}	—	974	—	965	—	965	CCH_3 rock.
	ν_{22}	—	965	—	964	—	964	CCH_3 rock.
	ν_{23}	856	857	856	858	856	857	SiHD sci.
	ν_{24}	849	843	849	844	849	838	$SiCH_3$ rock.
	ν_{25}	796	810	796	811	796	810	$SiCH_3$ rock.
	ν_{26}	766	776	740	739	748	754	CH_2 rock.
	ν_{27}	726	732	726	736	716	721	C–Si str.
	ν_{28}	677	689	677	682	677	699	SiH def.
	ν_{29}	640	654	616	642	616	642	C–Si str.
	ν_{30}	486	489	519	503	508	496	SiD def.
	ν_{31}	422	422	443	438	434	430	SiHD rock.
	ν_{32}	293	299	—	307	—	315	C–C–Si bend.
	ν_{33}	—	241	—	248	—	248	C–CH_3 torsion
	ν_{34}	—	185	—	187	—	186	C–Si–C bend.
	ν_{35}	—	146	—	144	—	144	Si–CH_3 torsion
	ν_{36}	—	65	—	66	—	66	CH_2–SiHD torsion

a) The calculated frequencies for the other vibrations are omitted in the Table.
b) The CCH_3 group occupies the *trans* position to the deuterium of the SiHD group.
c) The CCH_3 group occupies the *trans* position to the hydrogen of the SiHD group.
d) Only the predominant symmetry coordinates are shown.

crystalline state.

For $CH_3CH_2SiH_2CH_3$, the strong infrared band at 977 cm^{-1} and the pairs of strong bands around 940 and around 879 cm^{-1} are easily assigned to the CCH_3 rocking, SiH_2 scissoring, and SiH_2 wagging modes respectively, since the band at 940 cm^{-1} and the pair of bands around 879 cm^{-1} are not observed for $CH_3CH_2SiD_2CH_3$, and since the CCH_3 rocking modes are observed at 979 cm^{-1} for ethylsilane, and the SiH_2 scissoring and wagging modes are observed at 959 and 919 cm^{-1} for dimethylsilane.

There are a weak infrared band at 840 cm^{-1}, a strong band at 770 cm^{-1}, and two pairs of strong bands around 736 cm^{-1} and around 700 cm^{-1}, which correspond to the weak Raman bands at 842, 772, and 741 cm^{-1} and two medium bands around 700 cm^{-1} respectively, while the lower-frequency infrared bands of the two pairs disappear in the crystalline state.

On the basis of a comparison of the spectra with those for methylsilane, ethylsilane, and dimethylsilane, they can be assigned to the CH_2 rocking, $SiCH_3$ rocking of the A′ and A″ species, and asymmetric C–Si stretching modes. That is, since the averaged frequency of the observed $SiCH_3$ rocking modes of the A_1 and B_1 species for dimethylsilane is about 780 cm^{-1}, either the band at 770 cm^{-1} or the pair of the bands around 736 cm^{-1} may be the $SiCH_3$ rocking modes of the A′ species for both the *trans* and *gauche* isomers, while the weak band at 840 cm^{-1} can be assigned to the $SiCH_3$ rocking modes of the A″ species for both isomers, since the averaged frequency of the $SiCH_3$ rocking modes of the A_2 and B_2 species for dimethylsilane is about 840 cm^{-1}. On the other hand, since the CH_2 rocking mode is found at 764 cm^{-1} for ethylsilane, the CH_2 rocking mode can also be expected in this region for the $SiCH_3$ rocking mode.

As the calculated frequencies of the CH_2 rocking mode are 790 cm^{-1} for the *trans* form and 758 cm^{-1} for the *gauche* form, while those of the $SiCH_3$ rocking mode are 760 and 745 cm^{-1}, the band at 770 cm^{-1} can be assigned to the CH_2 rocking mode for the *trans* isomer, the higher frequency band (743 cm^{-1}) of the pair can be assigned to the $SiCH_3$ rocking mode for the *trans* isomer, and the lower-frequency band (730 cm^{-1}) of the pair can be regarded as the overlapping band of the $SiCH_3$ rocking and CH_2 rocking modes for the *gauche* isomer.

The pair around 700 cm^{-1} can be easily assigned to the asymmetric C–Si stretching mode for the *trans* and *gauche* isomers, since the mode is to be expected in the range of 695—805 cm^{-1}, as has already been pointed out by Janz and Mikawa,[6] and since the corresponding mode can be found at 728 cm^{-1} for dimethylsilane.

For $CH_3CH_2SiD_2CH_3$, three independent infrared bands at 810, 719, and 691 cm^{-1} and a pair of strong bands around 742 cm^{-1} are observed in the liquid state, while the higher-frequency band of the pair disappears in the crystalline state.

Since the $SiCH_3$ rocking modes are found around 800 cm^{-1} for the analogous deuterated molecules such as dimethylsilane, the band at 810 cm^{-1}, which shows a complicated pattern in the crystalline state, may be assigned to the overlapping band of the $SiCH_3$ rocking modes of the A′ and A″ species.

Although the above assignments seem questionable at first glance from the fact that the corresponding modes of the A′ and A″ species for $CH_3CH_2SiH_2CH_3$ are greatly separated from each other, it may be understood that the $SiCH_3$ rocking modes of the A′ species at 743 and 730 cm^{-1} for $CH_3CH_2SiH_2CH_3$ are pushed down by the SiH_2 wagging modes at 868 and 890 cm^{-1}, since the calculation shows that the larger mode mixing

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[6] G. J. Janz and Y. Mikawa, This Bulletin, **34**, 1495 (1961).

is found between these modes, while the $SiCH_3$ rocking modes of the A″ species at 840 cm^{-1} stay at the original frequency. On the other hand, for $CH_3CH_2SiD_2CH_3$, both of the two $SiCH_3$ rocking modes, belonging to the A′ and A″ species, exist in the 800—830 cm^{-1} region, outside the influence of the SiD_2 hydrogen deformation modes which exist in the far lower frequency region, as the calculations indicate.

From the results of the calculations and the comparison of the spectra for $CH_3CH_2SiD_2CH_3$ with those for $CH_3CH_2SiH_2CH_3$, the pair of the bands around 742 cm^{-1} and the two bands at 719 and 691 cm^{-1} can be assigned to the CH_2 rocking, C–Si asymmetric stretching, and SiD_2 scissoring modes respectively.

It is noticeable that the CH_2 rocking mode for the *trans* isomer has a higher frequency than that for the *gauche* isomer for $CH_3CH_2SiH_2CH_3$, while they are the reverse in frequency for $CH_3CH_2SiD_2CH_3$. This is understandable for the following reasons, obtained by an examination of the calculated potential energy distributions.

First of all, for the *trans* form, from the symmetry the coupling is possible between the modes belonging to the same species. Therefore, the CH_2 rocking mode for the *trans* form is pushed up by the SiH_2 twisting mode for $CH_3CH_2SiH_2CH_3$, while the corresponding mode stays at the unaffected frequency for $CH_3CH_2SiD_2CH_3$ since the SiD_2 twisting mode goes to a far lower frequency.

However, for the *gauche* form, as the molecular symmetry is lowered, coupling is possible between all of the modes. For $CH_3CH_2SiH_2CH_3$, the CH_2 rocking mode, which is influenced by the SiH_2 twisting mode, is also affected by the $SiCH_3$ rocking mode corresponding to that of the A′ species for the *trans* form, which may be at a slightly higher frequency than the unaffected frequency for the CH_2 rocking mode. Therefore, as the pushing-up effect of the SiH_2 twisting mode may be cancelled by the pushing-down effect of the $SiCH_3$ rocking mode, the CH_2 rocking mode can be found around the unaffected frequency. For $CH_3CH_2SiD_2CH_3$, though the $SiCH_3$ rocking mode in question exists at a higher frequency with a diminishing influence on the CH_2 rocking mode, the SiD_2 scissoring and C–Si stretching modes corresponding to those of the A′ species for the *trans* form appear anew at the lower frequencies and push the CH_2 rocking mode up to a higher frequency.

Therefore, the CH_2 rocking mode for the *gauche* form is found at a lower frequency than that for the *trans* form for $CH_3CH_2SiH_2CH_3$, while it is found at a higher frequency than that for the *trans* form for $CH_3CH_2SiD_2CH_3$.

In the region from 350 to 650 cm^{-1}, two pairs of the bands for $CH_3CH_2SiH_2CH_3$ and three pairs of the bands for $CH_3CH_2SiD_2CH_3$ are observed in the liquid state. Since the symmetric C–Si stretching mode is found at 659 cm^{-1} for dimethylsilane, the pairs around 620 and 638 cm^{-1} can be assigned to the symmetric C–Si stretching modes for $CH_3CH_2SiH_2CH_3$ and $CH_3CH_2SiD_2CH_3$ respectively, while the lower-frequency bands in each pair vanish in the crystalline state and belong to the *gauche* isomers.[7]

The SiH_2 and SiD_2 twisting modes can be expected to be very weak bands, since the corresponding band is infrared-inactive because of the symmetry for dimethylsilane. Therefore, another pair of bands, that around 490 cm^{-1} for $CH_3CH_2SiH_2CH_3$ can easily be assigned to the SiH_2 rocking mode; this pair corresponds to the pair around 402 cm^{-1} for $CH_3CH_2SiD_2CH_3$.

The pair around 566 cm^{-1} for $CH_3CH_2SiD_2CH_3$ can be assigned to the SiD_2 wagging mode. As for the SiH_2 and SiD_2 twisting modes, there are no distinct pairs of bands except for the very weak bands in the region expected from the calculations.

For $CH_3CH_2SiH_2CH_3$, a weak band at 577 cm^{-1}, which is found in both the liquid and crystalline states and which corresponds to a medium Raman band at 590 cm^{-1}, may be assigned to the SiH_2 twisting mode for the *trans* isomer, while the mode for the *gauche* isomer cannot be found in the expected region around 620 cm^{-1} where the bands assigned to the C–Si stretching mode are also present.

For $CH_3CH_2SiD_2CH_3$, the weak band at 501 cm^{-1}, existing only in the liquid state, may be assigned to the SiD_2 twisting mode for the *gauche* isomer, while the mode for the *trans* isomer cannot be found in the expected region (around 450 cm^{-1}).

In the region below 350 cm^{-1}, two skeletal bending and three torsional modes are expected. The Raman bands at 298 and 167 cm^{-1} in the liquid state, and the infrared bands at 301 cm^{-1} in the crystalline state and at about 170 cm^{-1} in the gaseous state, are observed for $CH_3CH_2SiH_2CH_3$. These bands may be assigned to the C–C–Si and C–Si–C bending modes for the *trans* isomer.

In Table 3, the observed and calculated frequencies fot the mixture of $CH_3CH_2SiHDCH_3$, $CH_3CH_2SiH_2CH_3$, and $CH_3CH_2SiD_2CH_3$ are shown as a basis for finding the vibrational assignments for $CH_3CH_2SiHDCH_3$, especially in the range from 250 to 900 cm^{-1}, where the bands sensitive to the molecular forms of

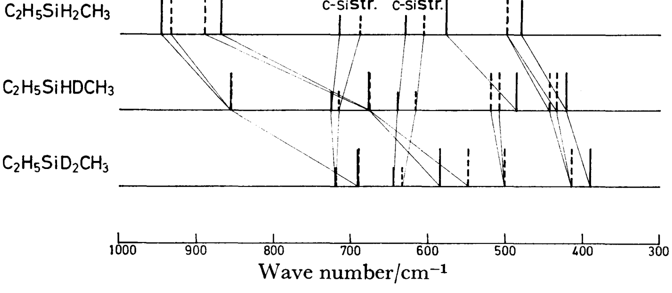

Fig. 2. Observed frequencies for the SiH_2, SiD_2, SiHD deformation modes and the C–Si stretching mode. ——: the spectra which persist in the crystalline state. ·········: the spectra which disappear in the crystalline state.

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[7] In the previous note (Ref. 1), the pair around 620 cm^{-1} for $CH_3CH_2SiH_2CH_3$ has been erroneously assigned to the SiH_2 wagging mode from the reported assignments for dimethylsilane given by Ball *et al.* (D. F. Ball, P. L. Goggin, D. C. McKean, and L. A. Woodward, *Spectrochim. Acta*, **16**, 1358 (1960).) However, the normal vibration calculation indicates the present assignment is correct for both dimethylsilane and ethylmethylsilane.

the isomers can be expected to exist. A comparison of the spectra of the mixture with the other species easily leads to the vibrational assignments for CH_3CH_2-$SiHDCH_3$ in this region. The correlation of the spectra for the three isotopic species is found to be excellent, as is shown in Fig. 2, where only the SiH_2 hydrogen deformation and C–Si stretching modes are shown. The results of the normal vibration calculations also prove the correctness of the present assignments, as is shown in Table 7.

So far, the vibrational assignments have been made without any impropriety on the assumption of the co-existence of the *trans* and *gauche* isomers in the gaseous and liquid states. In general, the calculated frequencies can be considered to reproduce the observed frequencies well, though most of the force constants are transferred from those for other, similar molecules without any adjustments. Therefore, the co-existence and the molecular forms of the isomers can be regarded as also proved by the present normal vibration calculations.

The authors wish to express their thanks to Professor Tatsuo Miyazawa of Osaka University and to the staff of his research group for allowing us to use their instruments and for their technical assistance.