Normal Vibrations and Calculated Thermodynamic Properties of Methyltrichlorosilane

By Kazuhiro SHIMIZU and Hiromu MURATA

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Methylchlorosilane is the simplest of those methylchlorosilanes which are both industrially important and theoretically interesting. The infrared and the Raman spectrum of this compound have been reported by several investigators[1-5]. But the normal vibrational frequencies have been calculated and assigned only by a method in which a methyl group is regarded as one particle. Therefore, the vibrational frequencies accompanied by the motion of hydrogen atoms have been excluded from the calculations, and the coupling between the skeletal vibrations and the characteristic modes of the methyl group has been ignored. To make all the normal modes clear, it is necessary that the vibrations of hydrogen atoms are taken into account. In this paper, the fundamental frequencies are calculated and assigned, their normal modes are determined, and the thermodynamic properties are calculated.

Normal Coordinate Treatment. — In methyltrichlorosilane, there are two symmetrical groups, CH_3 and $SiCl_3$. Because of the interaction between the CH_3 and the $SiCl_3$ group, the internal rotation is restricted, and it is more correct in the present consideration to treat the relative movement of CH_3 and $SiCl_3$ as torsional oscillation rather than as free internal rotation. This molecule belongs to the point group C_{3v} whether the groups have staggered or eclipsed forms. According to the group theory, it is clearly shown that this molecule has twelve fundamental frequencies of which five belong to species a_1, one to species a_2, and six to species e. All vibrations except the a_2 torsional mode are both infrared and Raman active. If this molecule has the torsional angle about the Si—C axis, it belongs to the point group C_3. The species a_1 and a_2 of the point group C_{3v} correspond to the species a of the point group C_3. Previous work by Collins and Nielsen[6] shows a normal coordinate treatment of the staggered configuration of methyltrifluorosilane having a structure similar to methyltrichlorosilane. But, in this investigation, at first, we undertake to make an attempt to carry out a normal coordinate treatment with an arbitrary torsional angle, and, next, to calculate the normal vibrational frequencies of the point group C_{3v} molecule for which the torsional angle θ is 0° in the eclipsed from, and 180° in the staggered form. We do not calculate the a_2 mode which is both infrared and Raman inactive. A normal coordinate treatment was carried out using the Wilson FG matrix method[7]. The F matrix elements were formed from the force constants in a Urey-Bradley force field[8].

The various bond distances, the interbond angles, and the distances between nonbonded atoms used to determine the internal coordinates are shown in Fig. 1. From the internal coordinates the following orthonormal symmetry coordinates were found; for the a vibrations,

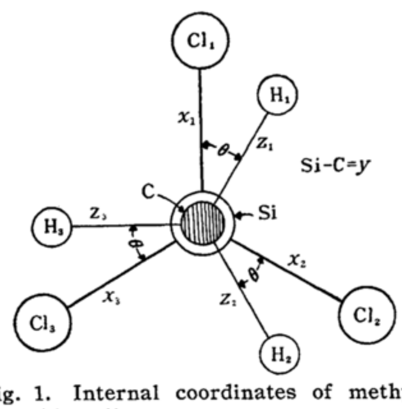

Fig. 1. Internal coordinates of methyltrichlorosilane.

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6) R. L. Collins and J. R. Nielsen, ibid., **23**, 351 (1955).
7) E. B. Wilson, Jr., ibid., **7**, 1047 (1939); **9**, 76 (1941).
8) T. Shimanouchi, ibid., **17**, 245, 734, 848 (1949).

$R_1=\Delta(z_1+z_2+z_3)/\sqrt{3}$

$R_2=\Delta(z_1y+z_2y+z_3y-z_1z_2-z_1z_3-z_2z_3)/\sqrt{6}$

$R_3=\Delta y$

$R_4=\Delta(x_1+x_2+x_3)/\sqrt{3}$

$R_5=\Delta(x_1y+x_2y+x_3y$
$\quad -x_1x_2-x_1x_3-x_2x_3)/\sqrt{6}$

and for the e vibrations

$R_{6a}=\Delta(2z_1-z_2-z_3)/\sqrt{6}$

$R_{7a}=\Delta(2z_2z_3-z_1z_3-z_1z_2)/\sqrt{6}$

$R_{8a}=\Delta(2z_1y-z_2y-z_3y)/\sqrt{6}$

$R_{9a}=\Delta(2x_1-x_2-x_3)/\sqrt{6}$

$R_{10a}=\Delta(2x_1y-x_2y-x_3y)/\sqrt{6}$

$R_{11a}=\Delta(2x_2x_3-x_1x_3-x_1x_2)/\sqrt{6}$

The numbering of these coordinates corresponds to the numbering of the fundamentals in Table II.

From the coefficients of the symmetry coordinates and the potential constants of a Urey-Bradley force field, one gets the following F matix elements:
for the a vibrations,

$F_{11}=K_z+4s^2{}_{zz}F_{zz}+s^2{}_{zy}F_{yz}+t^2{}_{zy}F'{}_{yz}$

$F_{12}=[(t_{yz}s_{zy}F_{yz}+t_{zy}s_{yz}F'{}_{yz})y$
$\quad -2t_{zz}s_{zz}(F_{zz}+F'{}_{zz})z]/\sqrt{2}$

$F_{13}=\sqrt{3}(s_{yz}s_{zy}F_{yz}-t_{yz}t_{zy}F'{}_{yz})$

$F_{22}=(H_{yz}+t_{yz}t_{zy}F_{yz}-s_{yz}s_{zy}F'{}_{yz})yz/2$
$\quad +(H_{zz}+t^2{}_{zz}F_{zz}-s^2{}_{zz}F'{}_{zz})z^2/2+3\sqrt{2}\kappa'/4$

$F_{23}=\sqrt{6}(t_{zy}s_{yz}F_{yz}+t_{yz}s_{zy}F'{}_{yz})z/2$

$F_{33}=K_y+3(s^2{}_{yx}F_{xy}+t^2{}_{yx}F'{}_{xy})$
$\quad +3(s^2{}_{yz}F_{yz}+t^2{}_{yz}F'{}_{yz})$

$F_{34}=\sqrt{3}(s_{xy}s_{yx}F_{xy}-t_{xy}t_{yx}F'{}_{xy})$

$F_{35}=\sqrt{6}(t_{xy}s_{yx}F_{xy}+t_{yx}s_{xy}F'{}_{xy})x/2$

$F_{44}=K_x+4s^2{}_{xx}F_{xx}+s^2{}_{xy}F_{xy}+t^2{}_{xy}F'{}_{xy}$

$F_{45}=[(t_{yx}s_{xy}F_{xy}+t_{xy}s_{yx}F'{}_{xy})y$
$\quad -2t_{xx}s_{xx}(F_{xx}+F'{}_{xx})x]/\sqrt{2}$

$F_{55}=(H_{xx}+t^2{}_{xx}F_{xx}-s_{xx}F'{}_{xx})x^2/2$
$\quad +(H_{xy}+t_{xy}t_{yx}F_{xy}-s_{xy}s_{yx}F'{}_{xy})xy/2$
$\quad +3\sqrt{2}\kappa/4$

$F_{14}=F_{15}=F_{24}=F_{25}=0$

for the e vibrations

$F_{66}=K_z+s^2{}_{zz}F_{zz}+3t^2{}_{zz}F'{}_{zz}+s^2{}_{zy}F_{yz}+t^2{}_{zy}F'{}_{yz}$

$F_{67}=-t_{zz}s_{zz}(F_{zz}+F'{}_{zz})z$

$F_{68}=(t_{yz}s_{zy}F_{yz}+t_{zy}s_{yz}F'{}_{yz})y$

$F_{77}=(H_{zz}+t^2{}_{zz}F_{zz}-s^2{}_{zz}F'{}_{zz})z^2+\sqrt{2}\kappa'/4$

$F_{78}=-\kappa'/\sqrt{2}$

$F_{88}=(H_{yz}+t_{yz}t_{zy}F_{yz}-s_{yz}s_{zy}F'{}_{yz})yz+\sqrt{2}\kappa'/4$

$F_{99}=K_x+s^2{}_{xx}F_{xx}+3t^2{}_{xx}F'{}_{xx}+s^2{}_{xy}F_{xy}+t^2{}_{xy}F'{}_{xy}$

$F_{910}=(t_{yx}s_{xy}F_{xy}+t_{xy}s_{yx}F'{}_{xy})y$

$F_{911}=-t_{xx}s_{xx}(F_{xx}+F'{}_{xx})x$

$F_{1010}=(H_{xy}+t_{yx}t_{xy}F_{xy}-s_{xy}s_{yx}F'{}_{xy})xy+\sqrt{2}\kappa/4$

$F_{1011}=-\kappa/\sqrt{2}$

$F_{1111}=(H_{xx}+t^2{}_{xx}F_{xx}-s^2{}_{xx}F'{}_{xx})x^2+\sqrt{2}\kappa/4$

and

$F_{69}=F_{610}=F_{611}=F_{79}=F_{710}=F_{711}=F_{89}=F_{810}$
$\quad =F_{811}=0$

where the following abbreviations are adopted:

$s_{zz}=4z/3q_{zz}$ $\qquad t_{zz}=2\sqrt{2}z/3q_{zz}$

$s_{zy}=(3z+y)/3q_{yz}$ $\qquad t_{zy}=2\sqrt{2}y/3q_{yz}$

$s_{yz}=(3y+z)/3q_{yz}$ $\qquad t_{yz}=2\sqrt{2}z/3q_{yz}$

$s_{yx}=(3y+x)/3q_{xy}$ $\qquad t_{yx}=2\sqrt{2}x/3q_{xy}$

$s_{xy}=(3x+y)/3q_{xy}$ $\qquad t_{xy}=2\sqrt{2}y/3q_{xy}$

$s_{xx}=4x/3q_{xx}$ $\qquad t_{xx}=2\sqrt{2}x/3q_{xx}$

and the symbols used for the equilibrium values of the interatomic distances are x=Si—Cl, y=Si—C, z=C—H, q_{xx}=Cl···Cl, q_{xy}=C···Cl, q_{yz}=Si···H and q_{zz}=H···H.

The G matrix elements are obtained by use of the table of Decius[9]. In terms of the abbreviations ρ_x, ρ_y and ρ_z for the reciprocals of the Si—Cl, Si—C and C—H bond lengths, respectively, and μ_x, μ_y, μ_c and μ_h for the reciprocals of the atomic masses of the Cl, Si, C and H, the following G matrix elements are found, assuming all angles to be tetrahedral:
for the a vibrations,

$G_{11}=\mu_h+\mu_c/3$

$G_{12}=4\rho_z\mu_c/3$

$G_{13}=-\mu_c/\sqrt{3}$

$G_{22}=2(\mu_h+8\mu_c/3)\rho^2{}_z$

$G_{23}=-4\rho_z\mu_c/\sqrt{3}$

$G_{33}=\mu_y+\mu_c$

$G_{34}=-\mu_y/\sqrt{3}$

$G_{35}=-4\rho_x\mu_y/\sqrt{3}$

$G_{44}=\mu_x+\mu_y/3$

$G_{45}=4\rho_x\mu_y/3$

$G_{55}=2(\mu_x+8\mu_y/3)\rho^2{}_x$

$G_{14}=G_{15}=G_{24}=G_{25}=0,$

for the e vibrations,

$G_{66}=\mu_h+4\mu_c/3$

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9) J. C. Decius, ibid., **16**, 1025 (1948).

$G_{67}=4\sqrt{2}\,\rho_z\mu_c/3$

$G_{68}=-\sqrt{2}\,(3\rho_y+\rho_z)\,\mu_c/3$

$G_{610}=\sqrt{2}\,\rho_y\mu_c\cos\theta$

$G_{77}=(8\mu_c/3+5\mu_h/2)\,\rho^2_z$

$G_{78}=-2(3\rho_y+\rho_z)\,\rho_z\mu_c/3+\rho^2_z\mu_h/2$

$G_{710}=2\rho_y\rho_z\mu_c\cos\theta$

$G_{88}=3\rho^2_y\mu_y/2+(3\rho_y+\rho_z)^2\mu_c/6+\rho^2_z\mu_h$

$G_{89}=\sqrt{2}\,\rho_y\mu_y\cos\theta$

$G_{810}=-\,[(3\rho_y+\rho_x)\,\mu_y$
$\quad+(3\rho_y+\rho_z)\,\mu_c]\,\rho_y\cos\theta/2$

$G_{811}=2\rho_x\rho_y\mu_y\cos\theta$

$G_{99}=\mu_x+4\mu_y/3$

$G_{910}=-\sqrt{2}\,(3\rho_y+\rho_x)\,\mu_y/3$

$G_{911}=4\sqrt{2}\,\rho_x\mu_y/3$

$G_{1010}=\rho^2_x\mu_x+(3\rho_y+\rho_x)^3\mu_y/6+3\rho^3_y\mu_c/2$

$G_{1011}=\rho^2_x\mu_x/2-2(3\rho_y+\rho_x)\,\rho_x\mu_y/3$

$G_{1111}=(5\mu_x/2+8\mu_y/3)\,\rho^2_x$

$G_{69}=G_{611}=G_{79}=G_{711}=0$

Since the repulsive force constants between non-bonded atoms are ignored, the F matrix elements of an eclipsed configuration are equal to those of a staggered one. Also, as shown in the G matrix elements, the different point between an eclipsed and a staggered configuration is only the change of the signs of G_{610}, G_{710}, G_{89}, G_{810} and G_{811} elements. However, the calculated values of GF for both the configurations are equivalent.

The C—H stretching vibrations were split off by the method of Wilson. The molecular constants and the potential constants used are listed in Table I. As an aid in determining some of the potential constants, K_x, K_y, K_z, H_{xx}, H_{xy}, H_{zz}, F_{xx}, F_{xy}, F_{zz} and κ, the results from previous investigations of methane[8] and the skeletal vibrations of this molecule[2] were used. But for K_y, a slightly lower value was adopted. We gave -0.05 md/A to the value of κ', taking into consideration the corresponding constants found for methane, monochloromethane, monofluoromethane and methyl alchohol. The values of H_{yz} and F_{yz} were selected so as to give the good agreement with the observed fundamentals. The values of F' are assumed to be $-0.1\,F$.

TABLE I
MOLECULAR AND POTENTIAL CONSTANTS OF METHYLTRICHLOROSILANE

Bond distance and angle	Potential constants (md/A) Type	
x=Si—Cl	K_x(Si—Cl)	2.59
=2.021 A	K_y(Si—C)	2.72
y=Si—C	K_z(C—H)	4.63
=1.876 A	H_{xx}(Cl—Si—Cl)	0.059
z=C—H	H_{xy}(Cl—Si—C)	0.035
=1.093 A	H_{yz}(Si—C—H)	0.20
all angles	H_{zz}(H—C—H)	0.40
=tetrahedral	F_{xx}(Cl···Cl)	0.29
	F_{xy}(Cl···C)	0.162
	F_{yz}(Si···H)	0.13
	F_{zz}(H···H)	0.10
	κ($CSiCl_3$)	0.17 A^2
	κ'($SiCH_3$)	-0.05 A^2

Normal Frequencies.—A normal coordinate treatment of the skeletal vibrations which assumed the methyl group to be one particle was carried out by Goubeau et al.[1] and Shimanouchi et al.[2]. The calculated frequencies of all the normal vibrations are in good agreement with the observed, if the assignment of these frequencies is made adequately as shown in Table II. In it, the results of previous investigations are listed together for comparison.

The L matrices, whose components give the modes of vibrations and the potential energy distribution for each normal vibration were calculated. They are shown in Tables III and IV. Since the ν_1 and ν_6 are considered to have almost pure C—H streching frequencies, their L mairices and potential energy distributions are omitted.

Judging from the values of the contribution of each symmetry coordinate to the normal coordinates Q_{10} and Q_{11} in Table III and the distribution of potential energy in the symmetry coordinates for the normal frequencies ν_{10} and ν_{11} in Table IV, it is reasonable to designate the frequencies 229 cm^{-1} and 164 cm^{-1} respectively as "$SiCl_3$ rocking" and "$SiCl_3$ non-symmetric deformation". Thus, the classification given in Table II is reasonable.

As shown in Tables III and IV, the skeletal vibrations and the vibrations accompanied by the motion of hydrogen atoms are separated to a considerable extent. Therefore, the calculated values of the skeletal vibrations are expected to be in good agreement with their corresponding observed values.

Internal Rotation.—The torsional vibration belongs to the species a_2 and is both infrared and Raman inactive. The frequency can be calculated if the height of the potential barrier hindering the internal rotation is known. However, the

TABLE II

RAMAN AND INFRARED DATA, PROBABLE VALUES OF THE OBSERVED FUNDAMENTALS, CALCULATED WAVE NUMBERS, AND ASSIGNMENTS FOR METHYLTRICHLOROSILANE

Type	Mode of vibration	G.S.W.[a]	S.T.M.[b]	B.D.[c]	M.[d]	S.[e]	calc.	obs.
a_1	ν_1(CH_3 sym. str.)	—	—	2915	—	2923	2928	2923
	ν_2(CH_3 sym. def.)	—	—	1271	—	1271	1274	1271
	ν_3(Si—C str.)	758	761	764	760	764	760	764
	ν_4(Si—Cl sym. str.)	450	450	457	450	458	449	458
	ν_5($SiCl_3$ sym. def.)	228	229	—	230	229	228	229
e	ν_6(CH_3 nonsym. str.)	—	—	2977	—	2990	2980	2990
	ν_7(CH_3 nonsym. def.)	—	—	1416	—	1417	1431	1417
	ν_8(CH_3 rocking)	—	—	807	—	804	843	804
	ν_9(Si—Cl nonsym. str.)	569	576	578	575	577	597	577
	ν_{10}($SiCl_3$ rocking)	351	229	—	230	164	227	229
	ν_{11}($SiCl_3$ nonsym. def.)	162	164	—	165	229	165	164

a Goubeau, Siebert and Winterwerb, reference 1;
b Shimanouchi, Tsuchiya and Mikawa, reference 2;
c Burnelle and Duchesene, reference 3;
d Murata, reference 4;
e Smith, reference 5.

TABLE III

L MATRICES OF THE NORMAL VIBRATIONS OF METHYLTRICHLOROSILANE

a_1 vibrations,

	Q_2	Q_3	Q_4	Q_5
R_2(CH_3 sym. def.)	1.41	0.17	0.03	0.01
R_3(Si—C str.)	−0.16	0.30	0.04	0.01
R_4(Si—Cl sym. str.)	0.01	−0.09	0.18	−0.01
R_5($SiCl_3$ sym. def.)	0.01	−0.14	0.07	0.19

e vibrations,

	Q_7	Q_8	Q_9	Q_{10}	Q_{11}
R_7(CH_3 nonsym. def.)	1.47	−0.27	−0.03	0.01	0.00
R_8(CH_3 rocking)	0.36	0.88	0.12	−0.02	−0.01
R_9(Si—Cl nonsym. str.)	−0.01	−0.06	0.27	0.02	0.00
R_{10}($SiCl_3$ rocking)	−0.03	0.11	−0.12	0.16	0.10
R_{11}($SiCl_3$ nonsym. def.)	0.00	−0.04	0.12	−0.09	0.13

TABLE IV

POTENTIAL ENERGY DISTRIBUTION $F_{ii}L_{ia}^2/\lambda_a$ FOR THE NORMAL VIBRATIONS OF METHYLTRICHLOROSILANE

a_1 vibrations,

	ν_2	ν_3	ν_4	ν_4
R_2(CH_3 sym. def.)	0.96	0.03	0.00	0.00
R_3(Si—C str.)	0.08	0.89	0.04	0.01
R_4(Si—Cl sym. str.)	0.00	0.07	0.94	0.01
R_5($SiCl_3$ sym. def.)	0.00	0.04	0.03	0.96

e vibrations,

	ν_7	ν_8	ν_9	ν_{10}	ν_{11}
R_7(CH_3 nonsym. def.)	0.92	0.08	0.00	0.01	0.00
R_8(CH_3 rocking)	0.06	0.90	0.03	0.01	0.00
R_9(Si—Cl nonsym. str.)	0.00	0.02	0.98	0.04	0.00
R_{10}($SiCl_3$ rocking)	0.00	0.01	0.04	0.55	0.40
R_{11}($SiCl_3$ nonsym. def.)	0.00	0.00	0.05	0.23	0.79

question as to the potential hill has not been definitely settled. Here, the potential barrier of monomethylsilane, methyltrichlorosilane and methyltrifluorosilane are compared with the values of ethane, 1, 1, 1-trichloroethane and 1, 1, 1-trifluoroethane, respectively. The heights of ethane[10], 1, 1, 1-trichloroethane[11] and 1, 1, 1-trifluoroethane[12] are respectively 2.875±0.125 kcal/mole, 2.97 kcal/mole and 3.25±0.40 kcal/mole. That is to say, the value of 1, 1, 1-trichloroethane is found between the value of ethane and of 1, 1, 1-trifluoroethane. On the other hand, the value of monomethylsilane[13] and of methyltrifluorosilane[14] are respectively 1.314±0.229 kcal/mole and 1.20 ±0.16 kcal/mole. Thus it seems that the height of the potential barrier of methyltrichlorosilane is 1.30±0.25 kcal/mole.

TABLE V

HEAT CAPACITY, ENTROPY, FREE ENERGY, AND HEAT CONTENT OF METHYLTRICHLOROSILANE FOR THE IDEAL GASEOUS STATE AT 1 ATOMS PRESSURE (cal. deg.$^{-1}$ mol.$^{-1}$)

T°K		$\frac{(H^0-E^0_0)}{T}$	$-\frac{(F^0-E^0_0)}{T}$	S^0	C^0_p
	torsional:	0.58	0.26	0.84	1.39
100	other:	9.71	51.47	61.18	13.28
	total:	10.29	51.73	62.02	14.67
		1.32	1.23	2.55	1.89
273.15		15.03	63.61	78.64	22.27
		16.35	64.84	81.19	24.16
		1.36	1.35	2.71	1.90
298.15		15.66	64.96	80.62	22.98
		17.02	66.31	83.33	24.88
		1.37	1.35	2.72	1.90
300		15.70	65.05	80.75	23.15
		17.07	66.40	83.47	25.05
		1.51	1.77	3.28	1.94
400		17.94	69.89	87.83	26.11
		19.45	71.66	91.11	28.05
		1.60	2.12	3.72	1.96
500		19.82	74.10	93.92	28.41
		21.42	76.22	97.64	30.37
		1.66	2.42	4.08	1.97
600		21.40	77.85	99.25	30.19
		23.06	80.27	103.33	32.16
		1.70	2.67	4.37	1.97
700		22.76	81.32	104.08	31.66
		24.46	83.99	108.45	33.63
		1.74	2.90	4.64	1.97
800		23.95	84.37	108.32	32.85
		25.69	87.27	112.96	34.82
		1.76	3.11	4.87	1.98
900		25.00	87.25	112.25	33.88
		26.76	90.36	117.12	35.86
		1.78	3.29	5.07	1.98
1000		25.93	89.93	115.86	34.76
		27.71	93.22	120.93	36.74

In the present investigation, the usual $V=V_0\ (1-\cos 3\theta)/2$ is adopted as the form of the potential barrier. In this formula, V_0 is the height of the potential barrier and θ is the torsional angle. The torsional frequency can now be obtained from V_0. The calculated value 147±15 cm^{-1} is believed to be not far from the real torsional frequency.

Thermodynamic Properties.—The probable values of the wave numbers of the normal frequencies given in Table II were used to calculate values of the heat content, free energy, entropy and heat capacity for the ideal gaseous state at 1 atoms pressure (rigid rotator, harmonic oscillator approximation). The bond distances and the interbond angles given in Table I were used to calculate the product of the principal moments of inertia, using the Hirschfelder formula[15]. The value obtained was $I_aI_bI_b=1.48102\times 10^{-112}$ gm^3 cm^6. The molecular weight used was 149.496 and the symmetry number was 3. In Table V, the contributions of the torsional frequency and the others (translational, rotational and vibrational except torsinal) are listed separately to facilitate revision of the table, if and when a better way is found to calculate the contribution for the former.

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Osaka Municipal Technical Research Institute, Kita-ku, Osaka

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