Vibrational Spectra of Methyltrimethoxysilane

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(Received August 26, 1959)

The group frequency assignments have already been given for the infrared spectra of methyltrimethoxysilane and its higher homologues in the rock salt region[1]. This paper contains the Raman spectrum of methyltrimethoxysilane, the assignment of the observed frequencies and the calculation of the frequencies and the modes of the skeletal vibration. In the calculation a methyl group was regarded as one particle.

The normal coordinate treatment was carried out by the Wilson FG matrix method[2] with a Urey-Bradley potential function. The normal vibration has not yet been calculated for any $YM(XZ)_3$ type molecule.

Experimental

Material.—The preparation and the physical constants of methyltrimethoxysilane used in the present work have already been reported elsewhere[3].

Raman Spectrum.—The Raman spectrum has been obtained by a Yūki-gōsei Raman spectrograph. The observed frequencies are shown in Table II together with the infrared and the calculated frequencies.

Normal Coordinate Treatment

For the convenience of the calculation, it has been assumed that the molecule belongs to the point group C_{3v} and has the structure shown in Fig. 1, in which a C–Si–O–C plane and an O–Si–O plane including the same Si–O bond are assumed to have an interplaner angle of 120°. According to the group theory, this molecule has twelve skeletal vibrations, five of a_1, one of a_2 and six of e species. One of the six skeletal vibrations of the species e is the torsional oscillation of the (Si–)OCH_3 group*. All vibrations except the a_2 torsional mode are active both in infrared and Raman spectra.

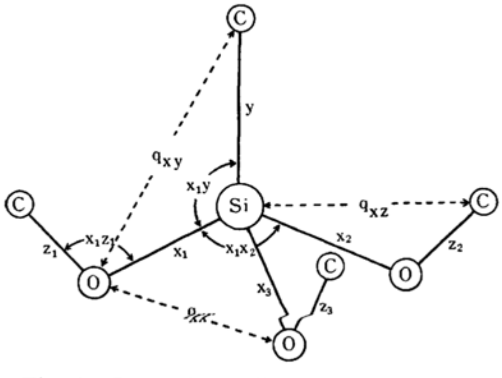

Fig. 1. Internal coordinates of the skeletal of methyltrimethoxysilane.

From the internal coordinates (Fig. 1), the following orthonormal symmetry coordinates have been found:

for the a_1 vibrations,

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

$$R_2=\Delta y$$

$$R_3=\Delta(x_1+x_2+x_3)/\sqrt{3}$$

$$R_4=\Delta(x_1x_2+x_1x_3+x_2x_3-x_1y-x_2y-x_3y)/\sqrt{6}$$

$$R_5=\Delta(x_1z_1+x_2z_2+x_3z_3)/\sqrt{3}$$

and for the e vibrations,

$$R_{7a}=\Delta(2z_1-z_2-z_3)/\sqrt{6}$$

$$R_{8a}=\Delta(2x_1-x_2-x_3)/\sqrt{6}$$

$$R_{10a}=\Delta(2x_1z_1-x_2z_2-x_3z_3)/\sqrt{6}$$

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

$$R_{12a}=\Delta(2x_1y-x_2y-x_3y)/\sqrt{6}$$

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

From the coefficients of the symmetry coordinates and the potential constants in a Urey-Bradley force field[4], the F matrix elements are obtained as follow:

for the a_1 vibrations,

$$F_{11}=K_z+s_{zx}^2F_{xz}+t_{zx}^2F_{xz}'$$

$$F_{13}=s_{xz}s_{zx}F_{xz}-t_{xz}t_{zx}F_{xz}'$$

$$F_{15}=(s_{zx}t_{xz}F_{xz}+s_{xz}t_{zx}F_{xz}')x$$

$$F_{22}=K_y+3s_{yx}^2F_{xy}+3t_{yx}^2F_{xy}'$$

$$F_{23}=\sqrt{3}\,(s_{xy}s_{yx}F_{xy}-t_{xy}t_{yx}F_{xy}')$$

$$F_{24}=-\sqrt{3/2}(s_{yx}t_{xy}F_{xy}+s_{xy}t_{yx}F_{xy}')x$$

$$F_{33}=K_x+4s_{xx}^2F_{xx}+s_{xy}^2F_{xy}+s_{xz}^2F_{xz}+t_{xy}^2F_{xy}'+t_{xz}^2F_{xz}'$$

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1) T. Tanaka, This Bulletin, **31**, 762 (1958).

2) E. B. Wilson, Jr., *J. Chem. Phys.*, **7**, 1047 (1939); **9**, 76 (1941).

3) T. Tanaka, A. Tasaka, R. Ōkawara and T. Watase, *Technol. Repts. Osaka Univ.*, **7**, 193 (1957).

* It represents the methoxy group attached to the silicon atom.

4) T. Shimanouchi, *J. Chem. Phys.*, **17**, 245, 734, 848 (1949).

$$F_{34}=\sqrt{2}\,s_{xx}t_{xx}(F_{xx}+F_{xx}')x-(s_{xy}t_{yx}F_{xy}$$
$$+s_{yx}t_{xy}F_{xy}')y/\sqrt{2}$$
$$F_{35}=(s_{xz}t_{zx}F_{xz}+s_{zx}t_{xz}F_{xz}')z$$
$$F_{44}=(H_{xx}+t_{xx}F_{xx}-s_{xx}^2F_{xx}')x^2/2$$
$$+(H_{xy}+t_{xy}t_{yx}F_{xy}-s_{xy}s_{yx}F_{xy}')xy/2$$
$$+3\kappa/\sqrt{8}$$
$$F_{55}=(H_{xz}+t_{xz}t_{zx}F_{xz}-s_{xz}s_{zx}F_{xz}')xz$$
$$F_{12}=F_{14}=F_{25}=F_{45}=0$$

and for the e vibrations,

$$F_{77}=K_z+s_{zx}^2F_{xz}+t_{zx}^2F_{xz}'$$
$$F_{78}=s_{xz}s_{zx}F_{xz}-t_{xz}t_{zx}F_{xz}'$$
$$F_{710}=(s_{zx}t_{xz}F_{xz}+s_{xz}t_{zx}F_{xz}')x$$
$$F_{88}=K_x+s_{xx}^2F_{xx}+s_{xy}^2F_{xy}+s_{xz}^2F_{xz}+3t_{xx}^2F_{xx}'$$
$$+t_{xy}^2F_{xy}'+t_{xz}^2F_{xz}'$$
$$F_{810}=(s_{xz}t_{zx}F_{xz}+s_{zx}t_{xz}F_{xz}')z$$
$$F_{811}=s_{xx}t_{xx}(F_{xx}+F_{xx}')x/2$$
$$F_{812}=(s_{xy}t_{yx}F_{xy}+s_{yx}t_{xy}F_{xy}')y$$
$$F_{1010}=(H_{xz}+t_{xz}t_{zx}F_{xz}-s_{xz}s_{zx}F_{xz}')xz$$
$$F_{1111}=(H_{xx}+t_{xx}^2F_{xx}-s_{xx}^2F_{xx}')x^2+\kappa/\sqrt{8}$$
$$F_{1112}=\sqrt{2}\,\kappa/4$$
$$F_{1212}=(H_{xy}+t_{xy}t_{yx}F_{xy}-s_{xy}s_{yx}F_{xy}')xy$$
$$+\kappa/\sqrt{8}$$
$$F_{711}=F_{712}=F_{1011}=F_{1012}=0$$

where the following abbreviations have been adopted:

$$s_{xx}=4x/3q_{xx} \qquad t_{xx}=\sqrt{8}\,x/3q_{xx}$$
$$s_{xy}=(3x+y)/3q_{xy} \qquad t_{xy}=\sqrt{8}\,y/3q_{xy}$$
$$s_{yx}=(3y+x)/3q_{xy} \qquad t_{yx}=\sqrt{8}\,x/3q_{xy}$$
$$s_{xz}=(x-z\cos\theta)/q_{xz} \qquad t_{xz}=z\cos\theta/q_{xz}$$
$$s_{zx}=(z-x\cos\theta)/q_{xz} \qquad t_{zx}=x\cos\theta/q_{xz},$$

and the symbols used for the equilibrium values of the interatomic distances and of the interbond angles are x=Si–O, y=Si–C, z=O–C, q_{xx}=O···O, q_{xy}=O···C, q_{xz}=Si···C and $\theta=\angle$SiOC.

The G matrix elements are obtained by the use of the table of Decius[5] and the method of Crawford[6]. Using the notations ρ_x, ρ_y and ρ_z for the reciprocals of Si–O, Si–C and O–C bond lengths, and μ_{Si}, μ_{O} and μ_{C} for the reciprocals of the masses of silicon and oxygen atoms and methyl group, respectively, the following G matrix elements have been obtained:
for the a_1 vibrations,

$$G_{11}=\mu_{\mathrm{O}}+\mu_{\mathrm{C}}$$
$$G_{13}=\mu_{\mathrm{O}}\cos\theta$$
$$G_{14}=-\sqrt{2}\,\rho_x\mu_{\mathrm{O}}\sin\theta$$
$$G_{15}=-\rho_x\mu_{\mathrm{O}}\sin\theta$$
$$G_{22}=\mu_{\mathrm{Si}}+\mu_{\mathrm{C}}$$
$$G_{23}=-\mu_{\mathrm{Si}}/\sqrt{3}$$
$$G_{24}=4\rho_x\mu_{\mathrm{Si}}/\sqrt{3}$$
$$G_{25}=\sqrt{8/3}\,\rho_x\mu_{\mathrm{Si}}$$
$$G_{33}=\mu_{\mathrm{Si}}/3+\mu_{\mathrm{O}}$$
$$G_{34}=-4\rho_x\mu_{\mathrm{Si}}/3$$
$$G_{35}=-\sqrt{8}\,\rho_x\mu_{\mathrm{Si}}/3-\rho_z\mu_{\mathrm{O}}\sin\theta$$
$$G_{44}=2\rho_x^2(8\mu_{\mathrm{Si}}/3+\mu_{\mathrm{O}})$$
$$G_{45}=8\sqrt{2}\,\rho_x^2\mu_{\mathrm{Si}}/3+\sqrt{2}\,\rho_x(\rho_x-\rho_z\cos\theta)\ \mu_0$$
$$G_{55}=8\rho_x^2\mu_{\mathrm{Si}}/3+\rho_z^2\mu_{\mathrm{C}}+(\rho_x^2+\rho_z^2$$
$$-2\rho_x\rho_z\cos\theta)\mu_{\mathrm{O}}$$
$$G_{12}=0$$

and for the e vibrations,

$$G_{77}=\mu_{\mathrm{O}}+\mu_{\mathrm{C}}$$
$$G_{78}=\mu_{\mathrm{O}}\cos\theta$$
$$G_{710}=-\rho_x\mu_{\mathrm{O}}\sin\theta$$
$$G_{711}=-\rho_x\mu_{\mathrm{O}}\sin\theta/4$$
$$G_{712}=\rho_x\mu_{\mathrm{O}}\sin\theta$$
$$G_{88}=4\mu_{\mathrm{Si}}/3+\mu_{\mathrm{O}}$$
$$G_{810}=\sqrt{2}\,\rho_x\mu_{\mathrm{Si}}/3-\rho_z\mu_{\mathrm{O}}\sin\theta$$
$$G_{811}=-\sqrt{8}\,\rho_x\mu_{\mathrm{Si}}/3$$
$$G_{812}=-\sqrt{2}\,(\rho_x/3+\rho_y)\mu_{\mathrm{Si}}$$
$$G_{1010}=\rho_x^2\mu_{\mathrm{Si}}/6+\rho_z^2\mu_{\mathrm{C}}+(\rho_x^2+\rho_z^2$$
$$-2\rho_x\rho_z\cos\theta)\mu_{\mathrm{O}}$$
$$G_{1011}=-\rho_x^2\mu_{\mathrm{Si}}/3+\rho_x(\rho_x-\rho_z\cos\theta)\mu_{\mathrm{O}}/4$$
$$G_{1012}=-\rho_x(\rho_x+3\rho_y)\mu_{\mathrm{Si}}/6-\rho_x(\rho_x$$
$$-\rho_z\cos\theta)\mu_{\mathrm{O}}$$

TABLE I. MOLECULAR AND POTENTIAL CONSTANTS OF METHYLTRIMETHOXYSILANE

Bond distance and angle	Potential constants	
	Type	md·Å
x=Si-O		
=1.64 Å[a]	K_x(Si-O)	3.25
y=Si-C	K_y(Si-CH$_3$)	3.03
=1.888 Å[b]	K_z(O-CH$_3$)	4.88
z=O-C	H_{xx}(O-Si-O)	0.13
=1.42 Å[a]	H_{xy}(O-Si-CH$_3$)	0.12
∠O-Si-O	H_{xz}(Si-O-CH$_3$)	0.22
=∠O-Si-C	F_{xx}(O···O)	0.13
=109°28′	F_{xy}(O···CH$_3$)	0.08
∠Si-O-C	F_{xz}(Si···CH$_3$)	0.21
=113°[a]	κ	0.25

a) Values in tetramethoxysilane, Si(OCH$_3$)$_4$; M. Yokoi, This Bulletin, **30**, 100 (1957).
b) Value in tetramethylsilane, Si(CH$_3$)$_4$; W. F. Sheehan, Jr. and V. Schomaker, *J. Am. Chem. Soc.*, **74**, 3956 (1952).

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5) J. C. Decius, ibid., **16**, 1025 (1948).
6) B. Crawford, ibid., **21**, 1108 (1953).

TABLE II. RAMAN AND INFRARED DATA, CALCULATED WAVE NUMBERS AND THE ASSIGNMENT FOR METHYLTRIMETHOXYSILANE

ν. Obsvd.		ν. Calcd.	Assignment	Mode of vibration
Raman	Infrared			
150(0b)		165	$\nu_5(a_1)$	SiOC and $CSiO_3$ sym. def.
174(2b)		171	$\nu_{12}(e)$	SiO_3 rocking
268(3bb)		286	$\nu_{11}(e)$	SiO_3 nonsym. def.
336(0)		325	$\nu_4(a_1)$	$CSiO_3$ and SiOC sym. def.
374(0)		371	$\nu_{10}(e)$	SiOC nonsym. def.
425(3b)		—	$\nu_9(e)$	SiOC nonsym. torsion
628(7)		627	$\nu_3(a_1)$	Si-O sym. str.
748(2)		782	$\nu_8(e)$	Si-O nonsym. str.
800(3)	790(m)	829	$\nu_2(a_1)$	Si-C str.
860(3b)	845(m)			(Si-)CH_3 rocking
1072(6)	1089(s)	1069	$\nu_7(e)$	C-O nonsym. str.
		1073	$\nu_1(a_1)$	C-O sym. str.
	1110(sh)			
1148(4)				(O-)CH_3 rocking
	1192(m)			
1270(4)	1267(m)			(Si-)CH_3 and (O-)CH_3 def.
	1402(vw)			
1430(3)				
1461(4b)	1459(w)			
	2333(b)			
2795(1)	2825(m)			(Si-)CH_3 and (O-)CH_3 str.
2915(5)	2931(m)			
2954(5b)	2953(sh)			
2990(5b)				

$$G_{1111}=\rho_x^2(8\mu_{Si}/3+5\mu_O/2)$$
$$G_{1112}=\rho_x(\rho_x/3+\rho_y)\mu_{Si}-\rho_x^2\mu_O/4$$
$$G_{1212}=(\rho_x+3\rho_y)^2\mu_{Si}/6+\rho_x^2\mu_O+3\rho_y^2\mu_C/2$$

The geometrical and the potential constants used in the calculation are listed in Table I. As an aid in determining these potential constants, excepting H_{xz} and F_{xz}, the results in the previous investigations on tetramethylsilane[7], methoxychlorosilanes[8] and diethylether[9] have been used. However, somewhat lower and higher values for K_x and K_z, compared with the corresponding values in methoxychlorosilanes and diethylether, respectively, have been adopted, to obtain better agreement between the observed and the calculated frequencies. The value of K_z adopted here is rather close to that previously obtained in dichloromethylether[10]. The mean value of $H(CH_3\text{-}Si\text{-}CH_3)$ in $Si(CH_3)_4$[7] and H_{xx} in this paper, and that of $F(CH_3\cdots CH_3)$ and F_{xx} have been used as H_{xy} and F_{xy}, respectively. The value of κ has been derived by means of the proportional allotment from the intramolecular tension of silicon tetrahedron in $Si(CH_3)_4$[7] and that in $Si(OCH_3)_4$[8]. The values of H_{xz} and F_{xz} have been selected so as to give good agreement between the calculated and observed ones. Finally, the value of F' has been assumed to be equal to $-F/10$ by the usual way.

Assignment of Observed Frequencies

From the F and G matrix elements given above, the fundamental frequencies have been calculated by the use of the molecular and the potential constants listed in Table I, and the results are shown in Table II, together with the observed wave numbers of the Raman and the infrared bands. The skeletal vibrations have been assigned by the calculation of the potential energy distribution in the symmetry coordinates, and also the hydrogen vibrations have been tentatively assigned.

The L matrices and the distribution of potential energy in symmetry coordinates have been calculated for the skeletal normal modes; the results are shown in Table III and IV, respectively.

The calculated frequencies of the skeletal vibrations are in good agreement with their corresponding observed values, except for the Raman line at 425 cm^{-1}. This line may be classified as the (Si-)OCH_3 torsional oscillation of e species. As shown in Table IV some of

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7) T. Shimanouchi, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **74**, 266 (1953).

8) H. Murata, ibid., **77**, 893 (1956).

9) M. Hayashi, ibid., **78**, 222 (1957).

10) Y. Morino and M. Katayama, *Reports of Research Institute of Radiation Chemistry, The University of Tokyo* (*Fukusyaken-hôkoku*), **4**, 1 (1947).

TABLE III. THE L MATRICES OF THE SKELETAL NORMAL VIBRATIONS OF METHYLTRIMETHOXYSILANE

a_1 Vibrations

	Q_1	Q_2	Q_3	Q_4	Q_5
R_1(C-O sym. str.)	1.13	0.05	0.08	−0.07	−0.01
R_2(Si-C str.)	0.00	−0.85	0.54	0.07	0.01
R_3(Si-O sym. str.)	−0.29	0.58	0.55	−0.15	0.03
R_4($CSiO_3$ sym. def.)	−0.44	−0.73	−0.13	−0.57	−0.32
R_5(SiOC sym. def.)	−0.27	−0.81	−0.56	−0.53	0.33

e Vibrations

	Q_7	Q_8	Q_{10}	Q_{11}	Q_{12}
R_7(C-O nonsym. str.)	1.11	−0.23	−0.03	−0.02	−0.01
R_8(Si-O nonsym. str.)	−0.42	−0.96	−0.07	−0.03	0.02
R_{10}(SiOC nonsym. def.)	−0.25	0.44	0.77	−0.29	0.24
R_{11}(SiO_3 nonsym. def.)	−0.03	0.26	−0.42	−0.85	−0.13
R_{12}(SiO_3 rocking)	0.39	0.23	−0.66	0.11	0.48

TABLE IV. POTENTIAL ENERGY DISTRIBUTION $F_{ii}L_{ia}^2/\lambda_a$ FOR THE NORMAL VIBRATION OF SKELETAL IN METHYLTRIMETHOXYSILANE

a_1 Vibrations

	ν_1	ν_2	ν_3	ν_4	ν_5
R_1(C-O sym. str.)	0.94	0.00	0.01	0.04	0.01
R_2(Si-C str.)	0.00	0.57	0.40	0.03	0.00
R_3(Si-O sym. str.)	0.04	0.31	0.49	0.14	0.02
R_4($CSiO_3$ sym. def.)	0.02	0.09	0.01	0.39	0.49
R_5(SiOC sym. def.)	0.00	0.11	0.09	0.32	0.48

e Vibrations

	ν_7	ν_8	ν_{10}	ν_{11}	ν_{12}
R_7(C-O nonsym. str.)	0.91	0.07	0.01	0.00	0.00
R_8(Si-O nonsym. str.)	0.09	0.90	0.03	0.01	0.01
R_{10}(SiOC nonsym. def.)	0.00	0.03	0.51	0.12	0.23
R_{11}(SiO_3 nonsym. def.)	0.00	0.01	0.13	0.87	0.05
R_{12}(SiO_3 rocking)	0.01	0.01	0.30	0.01	0.74

the symmetry coordinates of totally symmetric species are related to several normal modes to a considerable extent; the R_2 and R_3 coordinates to both modes of ν_2 and ν_3, and the R_4 and R_5 coordinates to both modes of ν_4 and ν_5. Especially, in the latter case, the symmetrical deformation of the $CSiO_3$ group and that of the SiOC groups have their equal share in the potential energy of the ν_4 normal mode, and also of the ν_5 mode.

The author wishes to express his sincere thanks to Professor T. Watase of this University, and Dr. H. Murata and Dr. K. Shimizu of Osaka Municipal Technical Research Institute for much valuable discussion.

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