Vibrational Spectra of Triethylfluorosilane

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One of the present authors has previously reported on the normal vibrations of methyltrimethoxysilane, $CH_3Si(OCH_3)_3$,[1] in which the methyl groups were treated as one particle. The vibrational spectra of this molecule can be explained by assuming the point group C_{3v} for the molecular symmetry. Triethylhalogenosilanes, $(C_2H_5)_3SiX$ (X=halogen atoms), can be treated as $YM(XZ)_3$-type molecules with regard to their skeletal vibrations in the same way as methyltrimethoxysilne.

Among triethylhalogenosilanes, the Raman spectrum has been obtained previously only for triethylchlorosilane. Tentative assignments have been made for this compound.[2] The present paper will report on the infrared and the Raman spectra of triethylfluorosilane and a normal coordinate treatment for the skeletal modes by Wilson's ***FG*** matrix method[3] using a simple Urey-Bradley potential function.

Experimental

Material.—Triethylfluorosilane was prepared by the reaction of triethylchlorosilane with hydrofluoric acid (a 46% aqueous solution) in a copper flask.[4] A sample for measuring the infrared and Raman spectra was purified by two fractional distillations through a Stedman column (about 25 plates); b. p. 110°C/760 mmHg, n_D^{25} 1.3895; (lit. b. p. 109°C/730 mmHg, n_D^{25} 1.3900[4]).

Spectra.—The infrared spectrum of the neat liquid sample was recorded using a Reitz infrared spectrophotometer equipped with an NaCl or KBr prism. The Raman spectrum was measured by the photographic method using a Japan Yūki-gōsei Raman Spectrograph. The observed and calculated frequencies are shown together in Table III.

Normal Coordinate Treatment

It has been assumed that the molecule belongs to the point group C_{3v} and has the structure shown in Fig. 1, in which an F–Si–C–C plane and a C–Si–C plane, including the same Si–C bond, has an interplanar angle of 120°. This molecule has twelve skeletal vibrations; five of A_1 species, one of A_2 species, and six of E species. One of the six skeletal vibrations of the E species is the torsional oscillation of the $Si–CH_2–CH_3$ group. All vibrations except the A_2 torsional mode are active in both the infrared and the Raman spectra. The $Si–CH_2–CH_3$ torsional vibration of the E species could not, however, be observed in the present experiment. This may be due to the weak intensity of this band, which may appear in the region lower than 100 cm^{-1}, where any weak band is difficult to measure with the spectrograph used here. For this reason, the $Si–CH_2–CH_3$ torsional oscillation of the E species has not been considered in the normal coordinate treatment.

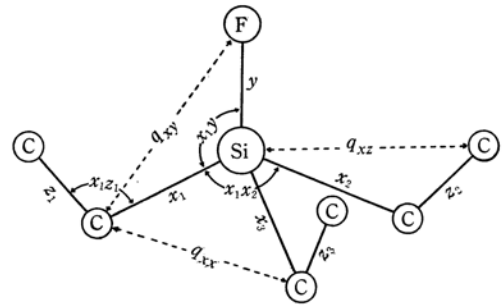

Fig. 1. Internal coordinates of the skeletal modes of triethylfluorosilane.

The orthonormal symmetry coordinates are shown in Table I. The numbering of these symmetry coordinates corresponds to that of the fundamentals in Table III.

The types of ***F*** matrix elements in the simple Urey-Bradley force field are the same as those reported earlier for methyltrimethoxysilane,[1] in which ∠Si–O–C was represented by a general angle of θ. In the present molecule, the corresponding angle of Si–C–C is tetrahedral. The ***G*** matrix elements used previously for methyltrimethoxysilane[1] were also used, changing the masses of the atoms or groups concerned and replacing θ with a tetrahedral angle.

At first we adopted the force constants transferred or estimated from those obtained

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1) T. Tanaka, This Bulletin, 33, 446 (1960).
2) H. Murata, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zassi*), 73, 465 (1952).
3) E. B. Wilson, Jr., *J. Chem. Phys.*, 7, 1047 (1939); 9, 76 (1941).
4) N. S. Marans, L. H. Sommer and F. C. Whitmore, *J. Am. Chem. Soc.*, 73, 5127 (1951).

TABLE I. INTERNAL SYMMETRY COORDINATES OF TRIETHYLFLUOROSILANE

	$S_1=\Delta(z_1+z_2+z_3)/\sqrt{3}$	C-C sym. str.
	$S_2=\Delta y$	Si-F str.
A_1	$S_3=\Delta(x_1+x_2+x^3)/\sqrt{3}$	Si-C sym. str.
	$S_4=\Delta(x_1z_1+x_2z_2+x_3z_3)/\sqrt{3}$	Si-C-C sym. def.
	$S_5=\Delta(x_1x_2+x_1x_3+x_2x_3-x_1y-x_2y-x_3y)/\sqrt{6}$	$FSiC_3$ sym. def.
A_2	S_6	Si-C-C torsion
	$S_7=\Delta(2z_1-z_2-z_3)/\sqrt{6}$	C-C deg. str.
	$S_8=\Delta(2x_1-x_2-x_3)/\sqrt{6}$	Si-C deg. str.
E	$S_9=\Delta(2x_1z_1-x_2z_2-x_3z_3)/\sqrt{6}$	Si-C-C deg. def.
	$S_{10}=\Delta(2x_1x_2-x_1x_3-x_2x_3)/\sqrt{6}$	SiC_3 deg. def.
	$S_{11}=\Delta(2x_1y-x_2y-x_3y)/\sqrt{6}$	Si-F def.
	S_{12}	Si-C-C deg. torsion

TABLE II. MOLECULAR AND POTENTIAL CONSTANTS OF TRIETHYLFLUOROSILANE

Bond distances and bond angles

$x=r(\text{Si-C})=1.89$ Å[5]
$y=r(\text{Si-F})=1.57$ Å[5]
$z=r(\text{C-C})=1.54$ Å

$\angle$C-Si-C, $\angle$C-Si-F, $\angle$Si-C-C $=109°28'$

Potential constants	
Type	md./Å
$K_x(\text{Si-CH}_2)$	2.70
$K_y(\text{Si-F})$	4.10
$K_z(\text{CH}_2\text{-CH}_3)$	4.00
$H_{xx}(\text{CH}_2\text{-Si-CH}_2)$	0.13
$H_{xy}(\text{CH}_2\text{-Si-F})$	0.15
$H_{xz}(\text{Si-CH}_2\text{-CH}_3)$	0.15
$F_{xx}(\text{CH}_2\cdots\text{CH}_2)$	0.04
$F_{xy}(\text{CH}_2\cdots\text{F})$	0.22
$F_{xz}(\text{Si}\cdots\text{CH}_3)$	0.25
$\kappa(C_3SiF)$	$0.10\times$ Å^2

TABLE III. RAMAN AND INFRARED DATA, CALCULATED WAVE NUMBERS AND THE ASSIGNMENT FOR TRIETHYLFLUOROSILANE

ν. Obs. Raman	Infrared	ν. Calcd.	Assignment	Modes of vibration*
131(0)		150	$\nu_5(A_1)$	$FSiC_3$ sym. def. + Si-C-C sym. def.
241(3b)		195	$\nu_{11}(E)$	Si-F def. + Si-C-C deg. def.
279(1b)		258	$\nu_{10}(E)$	SiC_3 deg. def.
297(2b)		286	$\nu_4(A_1)$	Si-C-C sym. def. + $FSiC_3$ sym. def.
377(0)		371	$\nu_9(E)$	Si-C-C deg. def. + Si-F def.
571(10)	577(vw)	638	$\nu_3(A_1)$	Si-C sym. str. ?
587(9)	587(vw)			
679(1b)	679(w)			(Si-)CH_2 rocking
737(3)	742(vs)	752	$\nu_8(E)$	Si-C deg. str.
835(1)	834(vs)	849	$\nu_2(A_1)$	Si-F str.
980(3)	984(w)	998	$\nu_1(A_1)$	C-C sym. str.
991(1)				
	1005(sh)			
1011(2)	1016(s)	999	$\nu_7(E)$	C-C deg. str.
1242(3)	1244(m)			(C-)CH_3 rocking
1304(3)				(Si-)CH_2 wagging
1380(2)	1383(sh)			(C-)CH_3 sym. def.
1418(4)	1419(m)			(Si-)CH_2 scissors
1468(6b)	1467(m)			(C-)CH_3 deg. def.
2885(10b)				
2912(7)	2913(s)			(Si-)CH_2 str.
2940(6)				(C-)CH_3 str.
2966(7)	2981(sh)			

* (Si-)CH_2 and (C-)CH_3 represent the methylene group attached to silicon and methyl group attached to carbon, respectively.

5) R. L. Gunton, J. F. Ollon and H. N. Rexroad, *J. Chem. Phys.*, 22, 1942 (1954).

in many related compounds which had previously been studied on the basis of a simple Urey-Bradley force field;[6] the values of F' in the $\boldsymbol{F}$ matrix elements were assumed to be equal to $-F/10$. These trial force constants were then modified so as to give a good agreement between the observed and the calculated frequencies. The molecular parameters and final potential constants used in the calculation are shown in Table II.

The value of K_x(Si–F) used in the present calculations is considerably smaller than that of tetrafluorosilane.[6] This may reflect the tendency for the bond distance of Si–F bond to increase as the number of fluorine atoms attached to silicon decreases; 1.54, 1.565, 1.577 and 1.595 Å for SiF_4, $HSiF_3$, H_2SiF_2 and H_3SiF respectively.[7] The tendency of a bond-stretching force constant is quite similar to that for Si–O bond, whose stretching force constant in methylmethoxysilanes, $(CH_3)_nSi(OCH_3)_{4-n}$, ($n=0-3$), decreases with the number of oxygen atoms attached to silicon, as has been described previously by one of the present authors.[8] The other potential constants in Table II seem reasonable considering those in related compounds.

Results and Assignment

The calculated frequencies are shown in Table III, together with the observed wave numbers of the infrared and Raman spectra. The calculated wave numbers of ν_{10} and ν_{11} are considerably lower than the observed values. This seems to be due to the neglect of the Si–CH_2–CH_3 torsional oscillation of E species in the normal coordinate treatment. The $\boldsymbol{L}$ matrices and the distribution of potential energy in symmetry coordinates have been calculated for the skeletal normal modes; the results are shown in Tables IV and V respectively. The skeletal vibrations have been assigned on the basis of the potential energy distribution in the symmetry coordinates; also, the hydrogen vibrations have been tentatively assigned.

The most characteristic line in the Raman spectrum of triethylfluorosilane is the strong doublet observed at 571 and 587 cm^{-1}. The corresponding bands in the infrared spectrum are very weak. This doublet can be assigned to the symmetric-stretching vibration of Si–C bonds on the basis of the intensities of the infrared and Raman spectra, although the observed wave numbers are somewhat lower than the calculated values. There are no corresponding doublets in the vibrational spectra of triethylchlorosilane,[2] methyltrimethoxysilane,[1] and triethyltinchloride,[9] which are considered to have a symmetry similar to that of the present molecule. It is not clear from the present work why the doublet appears for the symmetric-stretching vibration of the Si–C bond in this molecule.

As is shown in Table V, the Si–C–C symmetric deformation and $FSiC_3$ symmetric deformation modes of the A_1 species, and the Si–C–C degenerate deformation and Si–F deformation modes of the E species, are coupled with each other considerably. This coupling behavior is similar to that found for methyltrimethoxysilane.[1] However, the symmetric-stretching mode of the Si–C bonds is not so coupled with the Si–F stretching mode as with the vibrational coupling between Si–C and

Table IV. The $\boldsymbol{L}$ matrices of the skeletal normal vibrations of triethylfluorosilane

A_1 Vibrations

	Q_1	Q_2	Q_3	Q_4	Q_5
S_1	+1.17	+0.02	+0.08	−0.06	−0.02
S_2	0.00	−0.89	+0.31	+0.04	0.00
S_3	−0.27	+0.47	+0.72	−0.15	+0.01
S_4	−0.27	−0.60	−0.67	−0.50	+0.29
S_5	−0.43	−0.59	−0.23	−0.50	−0.32

E Vibrations

	Q_7	Q_8	Q_9	Q_{10}	Q_{11}
S_7	+1.15	−0.23	+0.04	−0.01	−0.01
S_8	−0.41	−1.01	−0.01	−0.03	+0.01
S_9	−0.25	+0.45	+0.73	−0.14	+0.37
S_{10}	−0.04	+0.21	−0.21	−0.82	−0.08
S_{11}	+0.39	+0.26	−0.70	+0.07	+0.40

Table V. Potential energy distribution $F_{ii}L_{ia}^2/\lambda_a$ for the skeletal normal vibrations of triethylfluorosilane

A_1 Vibrations

	ν_1	ν_2	ν_3	ν_4	ν_5
S_1	0.96	0.00	0.01	0.03	0.01
S_2	0.00	0.82	0.18	0.02	0.00
S_3	0.03	0.16	0.67	0.16	0.00
S_4	0.00	0.06	0.13	0.38	0.44
S_5	0.02	0.05	0.01	0.37	0.55

E Vibrations

	ν_7	ν_8	ν_9	ν_{10}	ν_{11}
S_7	0.93	0.06	0.01	0.00	0.00
S_8	0.08	0.93	0.00	0.00	0.00
S_9	0.00	0.04	0.48	0.04	0.45
S_{10}	0.00	0.00	0.03	0.95	0.02
S_{11}	0.00	0.00	0.45	0.01	0.52

6) T. Shimanouchi, ibid., **17**, 245, 743, 848 (1949); *J. Chem. Soc., Japan, Pure Chem. Sec.* (*Nippon Kagaku Zassi*), **74**, 266 (1953).
7) E. A. V. Ebsworth, "Volatile Silicon Compounds," Pergamon Press, Oxford (1963), p. 56.
8) T. Tanaka, This Bulletin, **34**, 1752 (1961).
9) T. Tanaka, to be published.

Si–O stretching modes in methyltrimethoxysilane.[1] This is because the vibrational frequency of the stretching vibration of the Si–F bond is not so close to that of Si–C bonds in triethylfluorosilane.

Summary

The infrared and the Raman spectra of triethylfluorosilane have been measured, and the normal vibrations for the skeletal modes have been calculated by Wilson's ***FG*** matrix method, using a simple Urey-Bradley force field and assuming point group C_{3v} for the molecular symmetry. The skeletal vibrations have been assigned quantitatively on the basis of the normal coordinate treatment, and the hydrogen vibrations have been tentatively assigned. The vibrational spectra of this molecule have also been discussed in comparison with those of triethylchlorosilane and methyltrimethoxysilane.

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