MOLECULAR
SPECTROSCOPY

IR Absorption Band Contours of Methyltrifluorosilane: Calculation and Comparison with Experiment

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Abstract—The **IR** spectrum of methyltrifluorosilane is measured in the range 220-3500 cm^{-1}. Both the equilibrium configuration of the molecule and its vibrational frequencies are calculated quantum chemically. Using the rotational and Coriolis constants obtained in these calculations, the contours of the rotational bands in the **IR** spectrum are numerically modeled. A comparison between the calculated and the experimental spectra made it possible to refine the frequencies of the fundamental vibrations of the molecule and determine the isotope shifts of the fundamental Si-F vibration with respect to the stable isotopes of silicon. © *2005 Pleiades Publishing, Inc.*

INTRODUCTION

Recently, interest in studying the IR-induced multiphoton dissociation of silicon compounds has increased [1-6]. Largely, this is associated with the possibilities of applying materials of isotopically pure silicon in electronics [7, 8]. The isotopically selective dissociation of silicon compounds under the action of IR lasers can lay the foundations for separation of silicon isotopes [5]. At the present stage, investigations in this field are concentrated on the search for compounds most suitable for isotopically selective dissociation.

The goal of this paper was to study the IR-induced multiphoton dissociation of methyltrifluorosilane. For this purpose, information on the frequencies of the normal vibrations of both ordinary and isotopically substituted molecules is necessary.

Previously, the IR spectrum of SiF_3CH_3 was studied in [9] and then, repeatedly, in [10]. In both cases, the rotational structure of the absorption bands was unresolved and the vibrational frequencies were determined from the maxima of the absorption band contours in the IR spectrum. Upon analysis of rotationally unresolved spectra, it is pertinent to compare an experimentally observed band contour with the calculated one. This may help in determining more precisely the frequencies of vibrations, as well as in finding the frequencies of overlapped bands. In particular, this can be useful in determining isotope shifts from spectra whose isotopic structure is unresolved.

In this study, we remeasured the IR spectrum of S1F3CH3 in the range 220-3500 cm^{-1}, performed quantum-chemical calculations of the vibrational frequencies, and numerically modeled the rotational contours of the absorption bands. The rotational constants of the methyltrifluorosilane molecule necessary for the modeling were obtained from the quantum-chemical calcu-lations. A comparison between the calculated and the experimental spectra made it possible to refine the frequencies of the vibrations, as well as to determine the isotope shifts of the Si-F stretching vibration.

EXPERIMENT

Methyltrifluorosilane was synthesized from the reaction of methyltrichlorosilane with SbF_3. The reaction yield exceeded 80%. The synthesized SiF_3CH_3 was purified in a low-temperature rectification column. The purity of the gas was checked by mass spectrometry and IR spectroscopy. The main impurity was SiF_4, whose content (determined from the IR band at 1032 cm^{-1}) did not exceed 0.3%.

In the ranges 450-3500 and 220-500 cm^{-1}, the IR spectra were recorded on Vector-22 and IFS66/V Fourier spectrometers (Bruker), respectively. The resolution of the former instrument amounted to 1 cm^{-1}. On the IFS66/V Fourier spectrometer, the spectra were recorded with a resolution of 0.15 cm^{-1} and then numerically smoothed to reduce the resolution to about 1 cm^{-1}. In the range 450-3500 cm^{-1}, the spectra were recorded in a cell with KBr windows, while, in the range 220-500 cm^{-1}, a cell with KRS-5 windows was used. In all the cases, the cell length amounted to 18 cm. The pressure of SiF_3CH_3 was equal to 3, 5, and 27 Torr.

CALCULATIONS

The equilibrium geometrical configuration and vibrational frequencies of the methyltrifluorosilane molecule were calculated using the B3LYP/6-31G** quantum-chemical method [11], which, as has been shown in numerous studies, provides fairly accurate

values of vibrational frequencies. The Gaussian 98 software package [12] was used in the calculations.

The shape of the rotational branches of the vibrational bands was calculated by summation of the contributions from each rotational level. The SiF_3CH_3 molecule is a symmetric top, and its rotational levels are described by the momentum J and the projection K of the momentum onto the molecule axis. The population of a rotational level was found from the Boltzmann distribution,

$$n(J, K) = (2J + 1)\exp(-E_0^{\text{rot}}(J, K)/kT)/Z^{\text{rot}}, \quad (1)$$

where

$$E_0^{\text{rot}} = B_0 J(J + 1) + (A_0 - B_0)K^2, \quad (2)$$

A_0 and B_0 are the rotational constants of the molecule in the ground vibrational state, and Z^{rot} is the rotational statistical sum. The parallel vibrational bands obey the selection rules $J \longrightarrow J, J \pm 1; K \longrightarrow K$.

The frequencies ν_i and intensities I_i of the rotational lines in the $P, Q,$ and R branches were calculated according to the following formulas [13]:

$$\nu_P(J, K) = \nu_0 + (E_1^{\text{rot}}(J - 1, K) - E_0^{\text{rot}}(J, K)),$$
$$I_P(J, K) = \frac{J^2 - K^2}{3J(2J + 1)}, \quad (3)$$

for the P branch,

$$\nu_Q(J, K) = \nu_0 + (E_1^{\text{rot}}(J, K) - E_0^{\text{rot}}(J, K)),$$
$$I_Q(J, K) = \frac{K^2}{3J(J + 1)}, \quad (4)$$

for the Q branch, and

$$\nu_R(J, K) = \nu_0 + (E_1^{\text{rot}}(J + 1, K) - E_0^{\text{rot}}(J, K)),$$
$$I_R(J, K) = \frac{(J + 1)^2 - K^2}{3(J + 1)(2J + 1)}, \quad (5)$$

for the R branch.

The shape of the rotational branches was found by summation of the contributions from all the rotational lines,

$$A(\nu) = \sum_{J, K} n(J, K)[F(\nu - \nu_P(J, K))I_P(J, K) \\ + F(\nu - \nu_Q(J, K))I_Q(J, K) \\ + F(\nu - \nu_R(J, K))I_R(J, K)]. \quad (6)$$

Here, $F(\Delta\nu)$ is the shape of an individual rotational line, which, for all the rotational lines, was defined as a Gaussian contour of the same width.

We also performed calculations in which the term $-DJ(J + 1)^2$ (the centrifugal correction) was added to the rotational energy (2). For the constant $D = 0.25 \times$

10^{-6} cm^{-1} [14], typical for such molecules, the calculation showed that the effect of the additional term on the band contour of the rotational branch is negligibly small.

For the perpendicular bands, corresponding to doubly degenerate vibrations, the excited state is characterized by an additional quantum number $l = \pm 1$, which determines the projection of the vibrational momentum onto the molecule axis. The formula for the rotational energy in the excited state of the molecule has the form

$$E_1^{\text{rot}}(J, K, l) = B_1 J(J + 1) + (A - B)K^2 + 2Al\zeta_i K, \quad (7)$$

where ζ_i is the Coriolis constant.

The formulas for the frequencies ν_i and the intensities I_i of the rotational lines of a perpendicular band have the form [13]

$$\nu_P(J, K) = \nu_0 + (E_1^{\text{rot}}(J - 1, K \pm 1, \pm 1) - E_0^{\text{rot}}(J, K)),$$
$$I_P(J, K) = \frac{(J \mp K)(J \mp K - 1)}{12J(2J + 1)}, \quad (8)$$

for the P branch,

$$\nu_Q(J, K) = \nu_0 + (E_1^{\text{rot}}(J, K \pm 1, \pm 1) - E_0^{\text{rot}}(J, K)),$$
$$I_Q(J, K) = \frac{J(J + 1) - K(K \pm 1)}{12J(J + 1)}, \quad (9)$$

for the Q branch, and

$$\nu_R(J, K) = \nu_0 + (E_1^{\text{rot}}(J + 1, K \pm 1, \pm 1) - E_0^{\text{rot}}(J, K)),$$
$$I_R(J, K) = \frac{(J \pm K + 1)(J \pm K + 2)}{12(J + 1)(2J + 1)}, \quad (10)$$

for the R branch.

The contour of the absorption band was found by summation of the contributions from all the rotational lines using a formula similar to (6) but with an additional summation over $l = \pm 1$.

In these calculations, the rotational constants of the molecule in the ground state A_0 and B_0 were calculated using the program Gaussian 98. The rotational constants of the molecule in the excited vibrational state A_1 and B_1 were varied within a small range from A_0 and B_0 so as to improve the agreement between the calculated and the observed band contours.

The program Gaussian 98 cannot calculate the Coriolis constants ζ_i for degenerate vibrations. However, it is capable of calculating the vectors of atomic displacements corresponding to the normal vibrations of the molecule, based on which one can calculate the Coriolis constants. These constants were calculated by the following formula:

$$\zeta_i = \frac{\sum m_i(x_i^{II} y_i^{I} - x_i^{I} y_i^{II})}{\sqrt{\sum m_i((x_i^{I})^2 + (y_i^{I})^2 + (z_i^{I})^2)}\sqrt{\sum m_i((x_i^{II})^2 + (y_i^{II})^2 + (z_i^{II})^2)}}, \tag{11}$$

where $(x_i^{I}, y_i^{I}, z_i^{I})$ and $(x_i^{II}, y_i^{II}, z_i^{II})$ are the vectors of the displacements of the ith atom corresponding to the two components of the doubly degenerate vibration (the molecule axis coincides with the z axis) and m_i is the mass of the ith atom.

Formula (11) can be derived from the general expression for the matrix obtained in [15, 16]. Another way to derive this formula consists of using the definition of the constant ζ_i as an average value of the projection of the vibrational momentum upon simultaneous excitation of both components of the degenerate vibration [17]. The phases of the components of the degenerate vibration differ by 90°, with the atoms themselves moving in a circle,

$$\begin{pmatrix} x_i(t) \\ y_i(t) \\ z_i(t) \end{pmatrix} = \begin{pmatrix} x_i^{I} \\ y_i^{I} \\ z_i^{I} \end{pmatrix} \sin(\omega_i t) + \begin{pmatrix} x_i^{II} \\ y_i^{II} \\ z_i^{II} \end{pmatrix} \cos(\omega_i t). \tag{12}$$

If one finds the average kinetic energy T and the projection of the momentum L_z for this motion, the Coriolis constant can be calculated by the formula

$$\zeta_i = \frac{\langle L_z \rangle / \hbar}{2\langle T \rangle / \hbar \omega_i}. \tag{13}$$

Applying some algebra to (13), we can obtain formula (11).

To check the possibility of obtaining the Coriolis constant with the help of the program Gaussian 98, we calculated this constant for the doubly degenerate Si-F stretching vibration of the molecule SiF_3H. We found that $\zeta = 0.642.$ The experimental value of this constant determined from the spectra with the resolved rotational structure is equal to 0.5927 [18].

RESULTS

The S1F3CH3 molecule has five vibrations of the A_1 symmetry, one vibration of the A^2 symmetry, and six doubly degenerate vibrations belonging to the E symmetry. Table 1 lists the geometrical parameters of this molecule calculated by the B3LYP/6-31G** method. In the ground vibrational state, the rotational constants are equal to $A^0 = 0.131$ cm^{-1} and $B^0 = 0.1208$ cm^{-1}. The experimentally determined value of the latter rotational constant is $B^0 = 0.1239$ cm^{-1} [19]. The calculated frequencies of different vibrations are given in the third column of Table 2. The fifth column of this table shows

the Coriolis constants calculated by formula (11) for doubly degenerate vibrations.

The A_1 Vibrations

The five totally symmetric vibrations of the SiF_3CH_3 molecule, arranged in increasing order of their frequencies, are as follows: the SiF_3 deformation, the Si-C stretching, the Si-F stretching, the CH_3 deformation, and the C-H stretching modes. All these modes are IR active; however, the CH stretching vibrations are not observed in the absorption spectrum due to their very small intensities.

The SiF_3 deformation vibrations. Figure 1 shows a fragment of the IR spectrum containing the band of the SiF_3 deformation vibrations, located at 390 cm^{-1}. The solid line is the numerical modeling of the rotational branches. Upon fitting, both the frequency of vibrations ν^0 and the rotational constants in the excited vibrational state, more exactly, the differences between these constants and those in the ground state,

$$dA = A_0 - A_1, \quad dB = B_0 - B_1,$$

were varied.

The differences between the rotational constants in the ground and excited states manifest themselves primarily as different widths of the P and R branches. Therefore, the parameters dA and dB were chosen such that the ratio between the calculated widths of the P and R branches would coincide with the experimentally determined ratio of these widths. A fairly good agreement with the experimental spectrum was obtained at $dA \approx dB \approx 0.0003$–0.0008 cm^{-1}. In this case, the shape of the rotational branches proved to be rather insensitive to whether the rotational constant A or B is varied.

In these calculations, the width of each individual rotational line was assumed to be equal to 1 cm^{-1}, which corresponds to the spectral resolution of the experimental spectrum. As is seen from the figure, the

Table 1. Geometric parameters of the SiF_3CH_3 molecule calculated by the B3LYP/6-31G** method

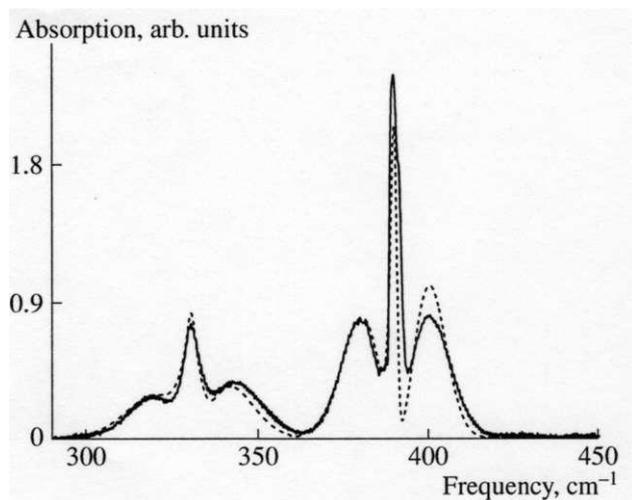| Structural element	Calculation	Experiment [19]
R (Si–C), Å	1.8433	1.812
R (C–H), Å	1.0937	1.081
R (Si–F), Å	1.596	1.574
$\angle$(H–C–Si), deg	110.7349	111.02
$\angle$(F–Si–C), deg	111.5802	112.33

Fig. **1.** Absorption bands of methyltrifluorosilane (at a pressure of 5.1 Torr) in the range 300–450 cm⁻¹. The solid line corresponds to the experimental spectrum, while the dashed line represents the numerical modeling.

calculation predicts well the widths of the rotational branches and qualitatively describes their shapes. However, no precise quantitative description of the shape of the rotational contour was obtained by varying *dA* and *dB*. The differences between the experimental and the calculated contours point to the existence of additional sources of broadening that are not taken into account in the calculations.

The Si-C and Si-F stretching and CH₃ deformation vibrations. Fragments of the **IR** spectrum with the

bands corresponding to these vibrations are shown at the top of Fig. 2. At the bottom of this figure, the results of the numerical modeling of the shape of the *R* branches are presented. It is seen from this figure that the calculated curves reproduce well the basic features of the experimental spectra; however, one can see that, in this case, there also exist sources of additional broadening. It is likely that the most probable reason for the additional broadening of the experimental spectra is hot bands. The methyltrifluorosilane molecule has several low-frequency vibrations (at 142 and 212 cm⁻¹), and the vibrational levels corresponding to these frequencies are populated at room temperature. The absorption spectrum of excited molecules can be shifted with respect to the spectrum of unexcited molecules, which manifests itself as an additional broadening.

The *R* branch of the C-H deformation vibrations has a specific feature at 1292 cm⁻¹. This feature may be the *Q* branch of the combination band of the stretching and deformation vibrations of the SiF₃ group (901.9 + 390.5 = 1292.4 cm⁻¹).

The E Vibrations

The doubly degenerate vibrations of the SiF₃CH₃ molecule, arranged in increasing order of their frequencies, are as follows: the SiF₃ rocking, the SiF₃ deformation, the CH₃ rocking, and the C-H stretching modes. The frequency of one of these vibrations, the SiF₃ rocking mode, is outside the transmission range of the KRS-5 windows. The absorption bands corresponding to the

Table 2. Experimental and B3LYP/6-31G** calculated frequencies of vibrations of the SiF₃CH₃ molecule

Symmetry	Vibration	B3LYP/6-31G**			Experiment	
		frequency, cm⁻¹	relative intensity	Coriolis constant	data from [9]	this study
					frequency, cm⁻¹	
	CH₃-str	3062.0	0.0006		-	-
	CH₃-deform	1340.8	43.3		1285	1285.1
	SiF₃-str	902.3	170		781	901.9
	Si-C-str	685.8	4.29		700	701.6
	SiF₃-deform	376.4	61.1		390	390.5
A_2	SiF₃-CH₃-tors	142	0		-	-
E	CH₃-str	3145.4	2.77	0.316	2994	2997
	CH₃-deform	1476.1	3.86	0.577	1412	1418? 1420?
	SiF₃-str	1008.9	201	0.271	982	981.8
	CH₃-rock	814.8	3.79	0.439	900	781
	SiF₃-deform	322.4	14.9	0.31	332	331
	SiF₃-rock	212.1	0.023	0.316	-	-

Note: str, stretching; deform, deformation; tors, torsional; rock, rocking.

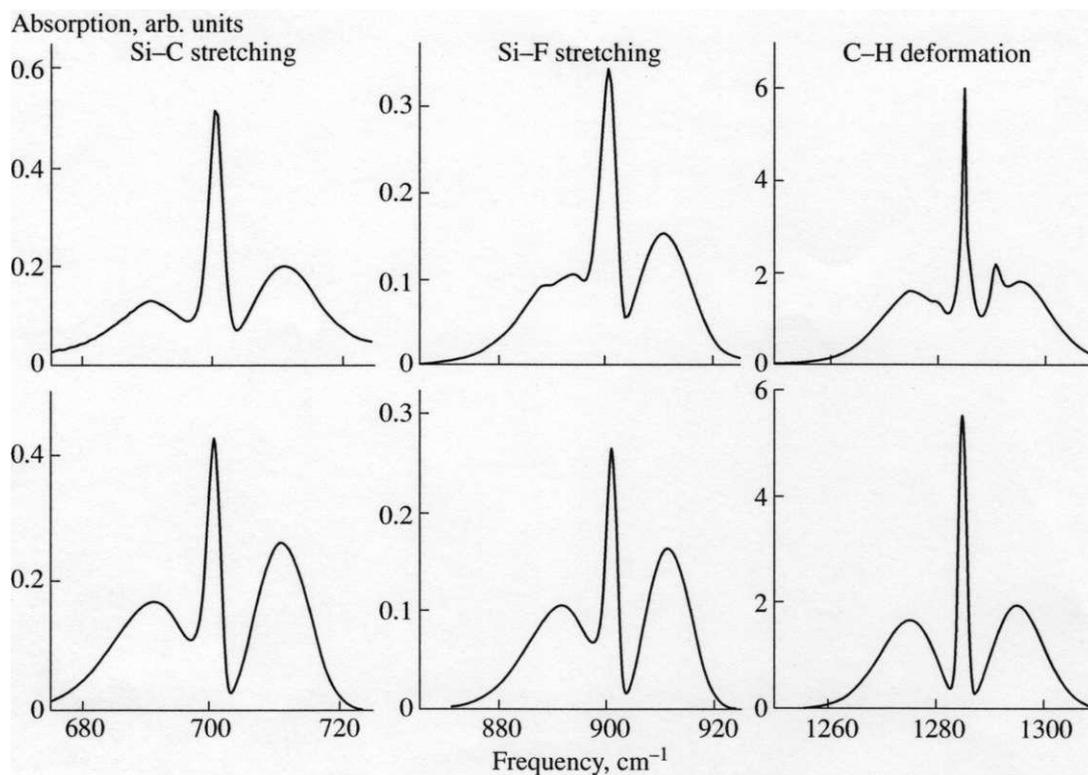**Fig. 2.** Experimental (top) and calculated (bottom) parallel absorption bands in the IR spectrum of SiF_3CH_3. The spectral ranges of the Si-C stretching and C-H deformation vibrations were measured at a pressure of 27 Torr, while the range of the Si-F stretching vibrations was recorded at a pressure of 3 Torr.

remaining vibrations were observed in the experimental spectrum. They are shown in Figs. 1 and 3.

The SiF₃ deformation vibrations. The band corresponding to this mode is observed at 331 cm⁻¹ (Fig. 1). The Coriolis constant for this vibration is comparatively large, 0.439, which determines the shape of the contour, with the *P, Q,* and *R* branches being partially merged.

The CH₃ rocking vibrations. The band corresponding to this vibration is observed at 781 cm⁻¹ (Fig. 3). The calculation of the rotational branches using the Coriolis constant 0.2713 describes well the shape of the experimental spectrum. Note that the experimental spectrum in this range contains a weak unidentified band centered at 805 cm⁻¹.

The Si-F stretching vibrations. The band corresponding to this mode is observed at 982 cm⁻¹ (Fig. 3). The contour of this band is affected most by the Coriolis interaction. It is impossible to distinguish the P, *Q,* and *R* branches in the experimental spectrum. In general, the calculated and experimental contours are similar; however, the smaller scale features are not reproduced.

The CH₃ deformation vibrations. For this mode, the quantum-chemical calculations predict a low-intensity band at 1470 cm⁻¹. In the spectrum recorded at a high pressure of SiF_3CH_3, a band of a complex shape is observed in the range 1380-1440 cm⁻¹. This band can be considered as a result of superposition of the P, *Q,* and *R* branches of several bands of comparable intensities, centered at 1400.5, 1418, and 1420 cm⁻¹. In [9], the band at 1400.5 cm⁻¹ was identified as an overtone of the Si-C stretching vibration at 701.6 cm⁻¹. One of the remaining bands, 1418 or 1420 cm⁻¹, belongs to the CH₃ deformation mode.

The C-H stretching vibrations. The band corresponding to this mode is observed at 2997 cm⁻¹ (Fig. 3). The Coriolis constant of this vibration is small, $\zeta = 0.051$; therefore, the band has clearly pronounced *P, Q,* and *R* branches. Comparison between the calculated and the experimental band contours shows again that there is an additional source of broadening of the experimental spectrum that was not considered in the calculations.

Isotope Shifts

In the experimental spectrum, the band of the symmetric stretching vibrations at 902 cm⁻¹ shows two specific features located at frequencies somewhat smaller than those of the *Q* branch. The positions of these features correspond to the positions expected for the *Q* branches in the spectra of molecules containing sili-
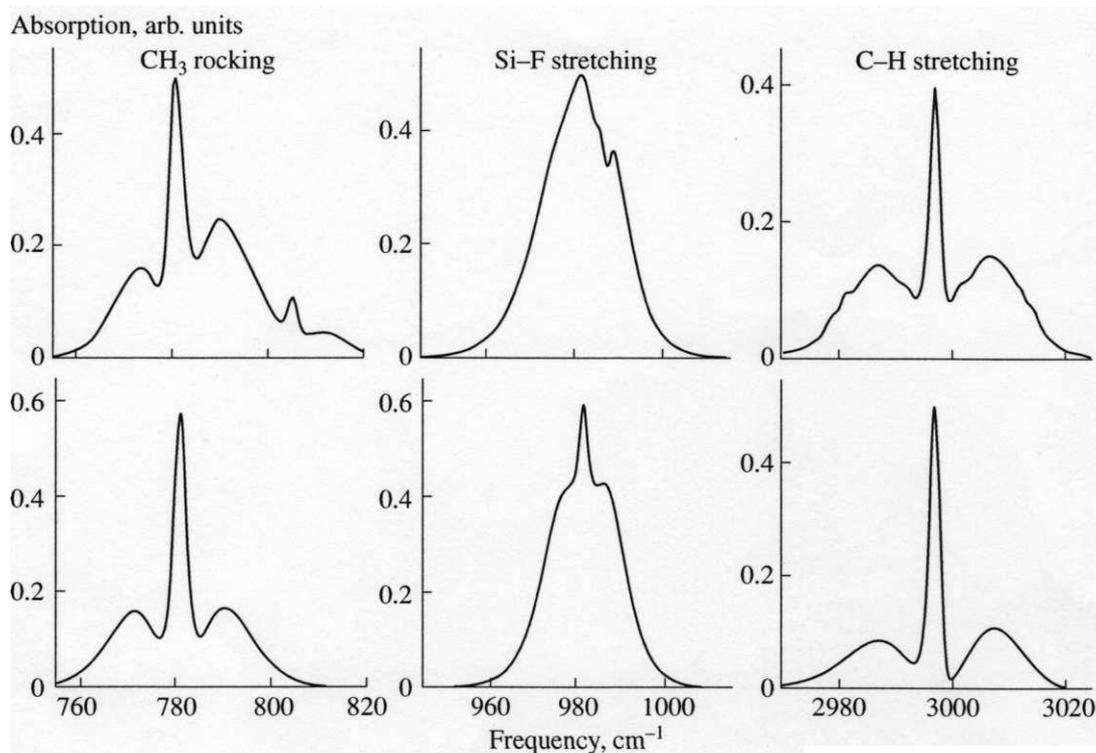
Fig. **3,** Experimental (top) and calculated (bottom) perpendicular absorption bands in the IR spectrum of SiF₃CH₃. The spectral ranges of the CH₃ rocking and C-H stretching vibrations were measured at a pressure of 27 Torr, while the range of the Si-F stretching vibrations was recorded at a pressure of 3 Torr.

con isotopes ^{29}Si and ^{30}Si. Figure 4 depicts a fragment of the spectrum containing these features. The solid line represents the experimental spectrum, while the dashed line shows the band contour calculated taking into
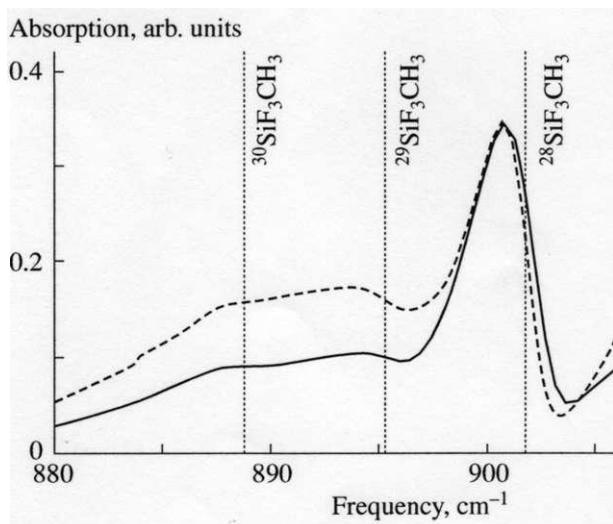

Fig. **4.** The isotopic structure of the Si-F stretching vibrations in the range near 900 cm^{-1}. The vertical lines indicate the frequencies of the 0-0 transitions.

account the natural abundance ratio of the silicon isotopes ^{29}Si and ^{30}Si. The frequencies of the vibrational transitions in molecules containing ^{29}Si and ^{30}Si were selected such that the spectral positions of the calculated and the observed features were the same. As was noted, the calculation does not reproduce well the relative intensities of the P and Q branches. Since the spectral features are assumed to be determined by the Q branches of isotope-containing molecules, the scale factor for the calculated curve was chosen such that the intensities of the Q branches coincided.

The isotope shifts of the frequency of the Si-F stretching vibration determined in this way amounted to 6.6 and 13.2 cm^{-1} for ^{29}Si- and ^{30}Si-containing molecules, respectively. The isotope shifts for this and other vibrations calculated by the B3LYP/6-31G** method are presented in Table 3. As follows from the calculations, the isotope shifts are appreciable only for the Si-F vibrations. For the Si-F symmetric stretching vibration, the calculation reproduces well the experimentally observed shifts. The contour of the doubly degenerate vibration shows no sharp features; therefore, the frequencies of this vibration in isotope-containing molecules are unavailable.

The isotope shift of the Si-F stretching vibrations is fairly large: upon replacement of ^{28}Si with ^{29}Si, it amounts to 6.6 cm^{-1} for the symmetric vibration and

Table 3. The isotope shifts of the vibrational frequencies of the SiF_3CH_3 molecule calculated by the B3LYP/6-31G** method

Symmetry	Vibration	Frequency, cm^{-1}	Frequency shift (cm^{-1}) for ^{29}Si	Frequency shift (cm^{-1}) for ^{30}Si
	CH_3-str	3062.0	0	0.01
	CH_3-deform	1340.8	0.11	0.21
	SiF_3-str	902.3	6.87 (6.6)	13.25 (13.2)
	Si-C-str	685.8	0.88	1.75
	SiF_3-deform	376.4	1.35	2.66
A_2		142	0	0
E	CH_3-str	3145.4	0	0
	CH_3-deform	1476.1	0.03	0.06
	SiF_3-str	1008.9	8.86	17.16
	CH_3-rock	814.8	0.03	0.06
	SiF_3-deform	322.4	1.01	2
	SiF_3-rock	212.1	0.11	0.22

Note: The experimentally measured shifts for the Si-F vibration near 900 cm are shown in the parentheses.

8.86 cm^{-1} for the doubly degenerate vibration. This fact and the large intensity of IR bands near 10 μm make methyltrifluorosilane promising for multiphoton excitation selective with respect to the silicon isotopes and for dissociation under the action of a CO_2 laser.

REFERENCES

1. J. L. Lyman and S. D. Rockwood, J. Appl. Phys. **47,** 595 (1976).
2. N. K. Serdyuk, E. N. Chesnokov, and V. N. Panfllov, React. Kinet. Catal. Lett. **17,** 19 (1981).
3. M. Kamioka, S. Arai, Y. Ishikawa, *et aL,* Chem. Phys. Lett. **119,** 357 (1985).
4. M. Kamioka, Y. Ishikawa, H. Kaetsu, *et al,* J. Phys. Chem. **90,** 5727 (1986).
5. H. Suzuki, H. Araki, and T. Noda, J. Jpn. Inst. Met. **61,** 145 (1997).
6. J. L. Lyman, B. E. Newman, T. Noda, and H. Suzuki, J. Phys. Chem. A **103,** 4227 (1999).
7. W. S. Capinski, H. J. Maris, E. Bauser, *et al.*, Appl. Phys. Lett. **71,** 2109 (1997).
8. K. Takyu, K. M. Itoh, K. Oka, *et al,* Jpn. J. Appl. Phys. **38,** 1493 (1999).
9. R. L. Collins and J. R. Nielsen, J. Chem. Phys. **23,** 351 (1955).
10. A. J. Clark and J. E. Drake, Spectrochim. Acta A **37,** 391 (1981).
11. C. Lee, W. Yang, and R. G. Parr, Phys. Rev. B **37,** 785 (1988).
12. M. J. Frisch, G. W. Trucks, H. B. Schlegel, *et al, Gaussian 98, Revision A.6-A11* (Gaussian, Pittsburgh PA, 2001).
13. U. Flaiger, *Structure and Dynamics of Molecules* (Mir, Moscow, 1982), Vol. 1 [in Russian].
14. L. Margules, J. Cosleou, R. Bocquet, *etal.,J.* Mol. Spectrosc. **196,** 175 (1999).
15. J. H. Meal and S. R. Polo, J. Chem. Phys. **24,** 1119 (1956).
16. J. H. Meal and S. R. Polo, J. Chem. Phys. **24,** 1126 (1956).
17. G. Herzberg, *Molecular Spectra and Molecular Structure* (Van Nostrand, New York, 1945; Inostrannaya Literatura, Moscow, 1947).
18. M. Gnida, L. Margules, J. Cosleou, *et al,* J. Mol. Spectrosc. **200,** 40 (2000).
19. J. R. Durig, Y. S. Li, and C. C. Tong, J. Mol. Struct. **14,** 255 (1972).

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