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Microwave spectroscopic study of the SiF₃ radical: Spin-rotation interaction and molecular structure

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The trifluorosilyl radical has been produced by glow discharge in hexafluorodisilane in a free space cell. The rotational spectrum of the radical has been measured from the 330 ($N=22-21$) GHz region down to the 90 ($N=6-5$) and 75 ($N=5-4$) GHz regions. In the lower N transitions the $K=1$ hyperfine components showed a distinct splitting. From the splitting of the $K=1$ lines it was concluded that the spin-rotation interaction constant of trifluorosilyl radical has a positive sign, which is different from that of trifluoromethyl. This difference is discussed in terms of the electronic states. The simplified discussion based on the Mulliken-Walsh diagram of the energy level is used to rationalize the difference in the sign of the interaction constants in the two radicals. The Si-F bond length is determined from the rotational constant B_0 to be 1.565 Å when the bond angle F-Si-F is assumed to be 109.9° deduced in the matrix infrared spectroscopy. The spin density on the fluorine atoms is derived from the hyperfine coupling constants. The obtained molecular structure is compared with those of related molecules.

I. INTRODUCTION

Microwave spectroscopy has extensively been applied to the observation of rotational spectra of many diatomic and polyatomic free radicals. However, symmetric top radicals have rarely been the subject of the high-resolution spectroscopy. The only symmetric top free radicals studied with pure microwave spectroscopy are CF₃,¹ CH₃O,² and CH₃S.³ The SiF₃ radical, which is a silicon analog of the CF₃ radical, is not extensively studied with any spectroscopic techniques.

Milligan *et al.* trapped HSiF₃ in a low temperature matrix of Ar, N₂, and CO and photolyzed it by using ultraviolet light.⁴ The photolysis products were studied with infrared spectroscopic technique. They observed four vibrational bands and concluded that the SiF₃ radical, which was produced by hydrogen atom abstraction, was pyramidal in the above matrices and that the angle between the C₃ molecular symmetry axis and the Si-F bond was about 71°. Infrared absorption spectra of SiF₃⁻ and SiF₃⁺ as well as SiF₃ were also observed, when a mixture of Ne and SiF₄ was codeposited at approximately 5 K with a beam of discharged neon atoms.⁵ ESR spectra of SiF₃ in inert matrices⁶ and crystals^{7,8} were observed and yielded hyperfine interaction constants, including an isotropic and anisotropic part.

On the other hand, it is still not clear whether SiF₃ exists in a discharge system which involves fluorine and silicon. The structure of gaseous SiF₃ radical is almost unknown. Broad chemiluminescence in the reaction of F atom with silicon was ascribed to the emission from SiF₃ produced in the gas phase.⁹ Dispersed fluorescence from photoexcitation of SiF₄ around 95 nm was attributed to SiF₃ according to the energy constraint.¹⁰ Both emission spectra showed no structures in their envelopes. Wang *et al.*¹¹ discharged SiF₄ with

microwave and observed emission spectrum with vibrational structures between 2100 and 2600 Å, which they assigned to ²B₁-X²A₁ transition of SiF₃. This band system was recently shown to come from SiF₂ on the basis of the measurement of the lifetime of the emitting species¹² and the analysis of long progressions involving the bending frequency.¹³

The mid-infrared LMR spectrum of the reaction products between SiF₃H and F was reported.¹⁴ The assignment of the spectrum to SiF₃ radical was based on the chemical information upon the appearance and disappearance of the spectrum with various precursors. The spectrum was not analyzed at all.

Discharge of SiF₄ is the subject of recent experimental studies, which show the unambiguous evidence for the existence of the radical in the gas phase. Weibel *et al.*¹⁵ produced molecular beams of active species including SiF₃ which were focused by an electrostatic hexapole. From the focusing behavior and the trajectory calculation they estimated the dipole moment of the trifluorosilyl radical to be 1.2±0.1 D. Biehl *et al.* observed the fluorescence from SiF₄ excited by tunable vacuum-UV radiation from a synchrotron source.¹² They showed that the excitation in the range 13-15 eV gave rise to SiF₃ emission. No rotationally resolved spectra have so far been reported in any wavelength regions.

Fluorosilicon and fluorocarbon radicals are supposed to play important roles in the chemical vapor deposition and the plasma etching process, but it is still uncertain which molecules are desorbed from the silicon surface. Many theoretical investigations have recently been carried out to derive chemical and thermochemical properties of small silicon and fluorine containing molecules including SiF₃.¹⁶⁻¹⁹ Such properties are important to the understanding of the indus-

trial processes during microcircuit fabrication.

Among compounds containing both silicon and fluorine, stable SiF_4 and transient SiF and SiF_2 molecules have extensively been studied spectroscopically and their precise molecular constants have been determined. On the other hand, little work is done on the spectroscopy of SiF_3 . This paper presents the first observation and rotational characterization of SiF_3 by microwave spectroscopy. We assigned the hyperfine components to derive molecular constants including the fine and hyperfine interaction constants. The spin-rotation interaction constant of SiF_3 is in strong contrast with that of CF_3 and the difference will be discussed in terms of the electronic states of both radicals. From the observed molecular constants structural parameters were derived, which were also compared and discussed with those of related molecules.

II. EXPERIMENT

We used a source-modulated microwave spectrometer with a glow discharge cell which was under control of a personal computer. The Pyrex cell, 2 m in length and 90 mm in diameter, was cooled with liquid nitrogen, which flowed through a copper tube soldered onto a thin copper plate that covered the cell. Submillimeter-wave source was a multiplier (trippler or quadrupler) produced by Millitech and driven by millimeter-wave OKI klystrons. In the millimeter wave region the output of klystrons were directly introduced into the cell. A photoconductive InSb detector QMC IFV2, which worked at the temperature of 4.2 K, was used.

The first search was carried out in 1983 at Institute for Molecular Science.²⁰ The structure of the SiF_3 radical was predicted by So with an *ab initio* molecular orbital method.²¹ His result was $r(\text{Si}-\text{F}) = 1.530 \text{ \AA}$ and $\angle \text{FSiF} = 108.86^\circ$. The bond angle was nearly equal to the value estimated by Milligan *et al.*⁴ in their matrix infrared spectroscopic study, 109.9° . The bond length $r(\text{Si}-\text{F})$ was considerably short in comparison with that for the related molecule HSiF_3 , $1.562 \text{ \AA}$.

On the basis of the rotational constant calculated from the above molecular structure we searched for the $N = 10-9$ transition in the 150 GHz region, limited by the multiplier available then. The experimental conditions were transferred from those for CF_3 ,¹ with substitution of SiF_4 for CF_4 . An absorption line of SiF_2 was observed under the similar conditions of low discharge current, and the formation of HSiF_3 was confirmed, when H_2 was simultaneously introduced into the cell. Thus it was supposed that discharge in SiF_4 would yield SiF_3 in the system. However, between 153 and 159 GHz there were no paramagnetic lines observed, although the typical K -pattern of a symmetric top from HSiF_3 was observed.

Since no paramagnetic lines were observed in the predicted frequency region in spite of the probable formation of SiF_3 as an intermediate, we thought that the assumed rotational constant was not appropriate. We compared the structure of SiF_n ($n = 1-4$) with one another and found that there might exist a nearly linear relation between the bond length $r(\text{SiF})$ and the number of fluorine atoms n in the molecule. This yielded the Si-F bond length for SiF_3 radical to be about $1.571 \text{ \AA}$, which was not far from that in HSiF_3 and

seemed reasonable. This bond length and the bond angle from infrared spectroscopy gave the rotational constant for SiF_3 to be $7457 \pm 90 \text{ MHz}$, with the uncertainty estimated from those of the bond length ($0.01 \text{ \AA}$) and the bond angle (1°).

We thought Si_2F_6 (also commercially available) to be a better precursor than SiF_4 because of a weak Si-Si bond. The melting point of Si_2F_6 is -18.6°C and the boiling point is -18.9°C . It exists as liquid only in a narrow temperature range, but has appreciable vapor pressure in condensed phase. Thus we cooled the cell to about -20°C .

The spectrum of the radical was searched for in the 300 GHz region where the sensitivity of the spectrometer with a frequency multiplier used was high and the spectral intensity was also supposed to be high. After confirming that the HSiF_3 molecule was produced when Si_2F_6 was weakly glow-discharged (discharge current of 5 mA), we carefully searched for the absorption lines on CRO near $328 \pm 5 \text{ GHz}$, where $N = 22-21$ rotational transitions should appear. Suddenly above 330 GHz many paramagnetic lines appeared on CRO. These lines extended towards the upper frequency side with decreasing intensity. They were supposed to be lines of an oblate symmetric top, which usually had a negative centrifugal distortion constant D_{NK} and showed a K -pattern like the observed one.

For a radical with a single odd electron the spin-rotation interaction produces two sets of the K -structure, the separation of which primarily depends on the spin-rotation interaction constant ϵ_{bb} . The 330 GHz spectrum showed such a duplicate structure of the K -pattern. Thus this spectrum was consistent with that of an oblate symmetric top radical with a central Si atom accompanied by three heavy F atoms.

These lines were used to optimize the experimental conditions. The pressure of Si_2F_6 was around 200–300 mTorr at the inlet of the cell, discharge current was 30 mA and the cell temperature was set to -110°C , which was considerably lower than the melting point of Si_2F_6 . We accumulated 50 times of observation (5 cycles/s) and observed about 80 absorption lines in the frequency region between 329 960 and 330 170 MHz. A tentative assignment of these paramagnetic lines as the $N = 22-21$ rotational transition enabled us to predict higher and lower rotational transitions.

To confirm the assignment we turned to another rotational transition. The frequency estimated for $N = 24-23$ fell around 359 992 MHz, where paramagnetic lines were observed. The paramagnetic spectrum was heavily disturbed by the spectrum of a diamagnetic symmetric top molecule, HSiF_3 . We tuned then the microwave frequency to the 375 GHz region to search for $N = 25-24$ and observed paramagnetic lines from 374 818 MHz up to around 375 150 MHz. The transitions $N = 21-20$ and $23-22$ were subsequently observed. Thus it was certain that we detected the spectrum of the symmetric top radical SiF_3 .

We have thus at an earliest stage observed more than 300 lines in the frequency regions above 300 GHz. As

N'	J'	F'	$-$	N''	J''	F''	K	Obs. Freq.	$\sigma - c^a$	N'	J'	F'	$-$	N''	J''	F''	K	Obs. Freq.	$\sigma - c^a$
5	4.5	3		4	3.5	2	0	75071.901	-0.055			7				6	3	90121.881	0.018
		6				5	0	75075.454	0.003		5.5	5			4.5	4	4	90068.426	-0.006
		5				4	0	75081.987	-0.010			6				5	4	90095.706	0.185 ^b
		4				3	0	75088.185	-0.069		6.5	6			5.5	5	4	90122.683	0.033
	5.5	4			4.5	3	0	75088.892	-0.036			7				6	4	90122.683	0.060
		5				4	0	75091.953	-0.042		5.5	5			4.5	4	5	90060.109	-0.028
		7				6	0	75102.055	-0.003			6				5	5	90099.094	0.125 ^b
	4.5	4			3.5	3	1	75068.799	-0.030		6.5	7			5.5	6	5	90125.345	0.102 ^b
		5				4	1	75078.992	0.434 ^b	7	6.5	5		6	5.5	4	0	105097.271	-0.035
	5.5	5			4.5	4	1	75095.101	0.432 ^b			8				7	0	105102.084	0.007
		6				5	-1	75102.882	0.015			7				6	0	105108.102	-0.027
		6				5	1	75104.138	0.036			6				5	0	105114.278	0.003
	4.5	4			3.5	3	2	75062.070	-0.021		7.5	6			6.5	5	0	105115.129	-0.019
		5				4	2	75078.992	-0.067 ^b			7				6	0	105119.780	0.107 ^b
	5.5	5			4.5	4	2	75098.838	0.091 ^b			8				7	0	105123.560	-0.019
		6				5	2	75104.138	-0.028			9				8	0	105130.527	0.026
	4.5	4			3.5	3	3	75075.454	0.420 ^b		6.5	6			5.5	5	-1	105094.963	-0.023
		5				4	3	75077.607	0.095 ^b			6				5	1	105096.184	-0.036
		6				5	3	75077.607	-0.045 ^b			7				6	1	105104.240	0.183 ^b
	5.5	7			4.5	6	3	75095.752	0.006		7.5	7			6.5	6	1	105123.560	-0.294 ^b
		4				3	3	75099.785	-0.049 ^b			8				7	-1	105131.182	0.021
		5				4	3	75105.165	0.040			8				7	1	105131.970	0.116 ^b
		6				5	3	75114.647	0.036		6.5	6			5.5	5	2	105094.103	-0.019
	4.5	5			3.5	4	4	75082.613	-0.104 ^b			7				6	2	105104.634	-0.047
	5.5	5			4.5	4	4	75113.664	0.286 ^b		7.5	7			6.5	6	2	105125.987	0.052
6	5.5	4		5	4.5	3	0	90084.981	-0.019			8				7	2	105132.498	0.000
		7				6	0	90089.463	0.013		6.5	5			5.5	4	3	105086.339	-0.024
		6				5	0	90095.706	-0.048			8							

^bNot included in the least-squares analysis.

described below in the Analysis, it became necessary to observe spectra with low J in the correspondingly low frequency regions. A part of the spectra was measured with another spectrometer of the same type.²² Finally, we observed the $N=5-4$ transition in the 75 GHz region. The observation of this transition was possible using a spectrometer of improved sensitivity as a result of the introduction of a more sensitive InSb detector.²³

are listed in Table I. The line frequencies other than listed in Table I are deposited.²⁴

III. ANALYSIS

The analysis of the spectrum was carried out by using Hamiltonian, $H = H_{\text{rot}} + H_{\text{sr}} + H_{\text{hfs}}$, where H_{rot} is the symmetric top rotational Hamiltonian with centrifugal distortion corrections, H_{sr} is the spin-rotation interaction Hamiltonian, and H_{hfs} is the magnetic hyperfine Hamiltonian for three

fluorine nuclei with $I=1/2$. This Hamiltonian is the same as that used for CF_3 (Ref. 1) which has the same electronic ground state 2A_1 . The basis function used is the Hund's case (b) wave function $|N, K, S, J, \Gamma, I_0, F, M_F\rangle$ with $J=N+S$ and $F=J+I_0$ ($I_0=I_1+I_2+I_3$). The nuclear spin functions have the symmetry species Γ , which are A_1 and $E_{\pm}$ symmetry according to $K=3n$ ($I_0=3/2$) and $K\neq 3n$ ($I_0=1/2$), respectively. The Hamiltonian matrix was diagonalized numerically. Initial values of the hyperfine parameters were taken from those for CF_3 .

As usual in the spectrum of an oblate symmetric top molecule the K -pattern of the observed spectrum tails towards the higher frequency. The spin-rotation interaction produces a pair of K -patterns which are separated by the magnitude of the spin-rotation interaction constant ϵ_{bb} . Accordingly the spectrum becomes congested when the higher frequency K -pattern overlapped the lower frequency K -pattern (see Fig. 1). The existence of the fictive nuclear spin I_0 further splits rotational lines into hyperfine multiplet of various separation according to the value of I_0 .

The rotational spectrum of a symmetric top displays lines of different K with the mutual separation proportional to $2D_{NK}(N+1)(2K+1)$ and with decreasing intensity according to the increasing K -numbering. As described above, for a doublet radical this K -pattern is shown twice and if the spin-rotation interaction constant is comparable to the shift caused by higher K , the second pattern overlaps the weaker lines belonging to the first pattern. The observation of line crowdedness of the spectrum in 300 GHz regions lead to the approximate ϵ_{bb} value of around 30 MHz. In the high N transitions, the low-frequency part of the spectrum was more or less uniquely identified. The assignment of K to each absorption line was not easily accomplished, however. Linear combinations of the transition frequencies of particular K yield a limited number of molecular constants, ϵ_{bb} , ϵ_{cc} , T_{aa} , and D_{NK} .¹ Endo *et al.* selected the proper lines of CF_3 for $K=1$ and 2 among the observed $N=6-5$ lines by using a simple computer program. This method of selecting lines of a certain K was not successful in the analysis of the rotational spectrum of SiF_3 in the submillimeter region (300 GHz region) because of probable overlap of lines or disturbance by neighboring lines. Thus we had to trust on the pattern of the line distribution. The influence of a small change in each molecular constant on the line frequencies was carefully studied and the constants were adjusted step by step. This set of the molecular parameters could roughly explain the general characteristics of the spectrum, but could not reproduce some of the lines beyond experimental uncertainty. Several calculated lines appeared at the frequency regions where there were no observed lines.

This necessitated the observation of the rotational transitions in the low frequency regions. Subsequent observation with another spectrometer²² down to 105 GHz still did not allow the unique K assignment. With an improved spectrometer²³ further two rotational transitions in the 90 and 75 GHz regions were observed. This observation brought about a considerable development in the analysis. In the lower frequency transitions more lines seemed to have appeared than expected for the rotational transition. The possi-

FIG. 1. Spectrum of the SiF_3 radical in the 330 GHz region. The low-frequency part of the rotational transition $N=22-21$ is shown. The overlapping region of the two K -patterns separated by the spin-rotation interaction constant ϵ_{bb} is seen.

bility of the inversion motion in this molecule was ruled out as a result of *ab initio* calculations, which gave a barrier to inversion of 56.5 kcal/mol.²⁵ In the lower frequency side of the transition, the K assignment was possible for two consecutive rotational transitions, only if it was assumed that the lines for $K=1$ appeared as a wide distinct doublet (see Fig. 2). When the center frequency of the doublet lines was used, the K -pattern on the low-frequency side agreed with the calculated one. In CF_3 the splitting of $K=1$ lines was observed for the highest and lowest F hyperfine components and the splitting of the lines on the high frequency side was larger than that on the low frequency side. However, in the SiF_3 radical, the splitting was found larger on the low-frequency side. This demanded the reconsideration of the previous assignment of fine structure. In order for the splitting in the $K=1$ hyperfine components to be explained, the spin-rotation interaction constant ϵ_{bb} had to be positive and thus had different sign from that in CF_3 .

The molecular constants of SiF_3 were determined by a least-squares fit to the eight rotational transitions between $N=5-4$ and $22-21$. The standard deviation of the fit was 34 kHz. Table II lists the molecular constants obtained.

IV. RESULTS AND DISCUSSION

The present study is the first definite observation of the high-resolution spectrum of the trifluorosilyl radical in the

FIG. 2. The transition of SiF_3 radical in the 90 GHz region. The lines are assigned from the left to $K=2, 1, 1$, and 0. The $K=1$ transition is clearly split into two lines.

TABLE II. Molecular constants of SiF₃ and CF₃.^a

	SiF ₃	CF ₃ ^b
B_0 /MHz	7509.08299(92)	10900.9118(21)
D_N /MHz	0.009966(11)	0.013882(35)
D_{NK} /MHz	-0.0171121(56)	-0.02343(7)
D_K /MHz	0.0055(fixed)	
H_N /Hz	0.165(36)	
H_{NK} /Hz	-0.1806(70)	
H_{KN} /Hz	0.228(12)	
Φ_N /mHz	-0.127(35)	
ε_{bb} /MHz	36.0224(69)	-36.500(17)
ε_{cc} /MHz	4.810(22)	3.35(6)
a_F /MHz	386.83(24)	408.5(6)
T_{cc} /MHz	115.390(46)	320.01(8)
$ T_{aa}-T_{bb} $ /MHz	117.7(20)	40.1(20)

^aValues in parentheses are one standard deviation in unit of the last digit.^bReference 1.

gas phase. The molecular constants derived in the present study and listed in Table II were determined by using the Hamiltonian for a symmetric top radical in the doublet electronic state. This unambiguously establishes the symmetry of the electronic ground state as 2A_1 .

Assuming the bond angle from the matrix infrared study we obtain the Si-F bond length to be 1.565(3) Å, where the uncertainty is estimated from the supposed uncertainty (1°) of the bond angle. Molecular structure of the related fluorine-containing species are compared in Table III. For SiF_n the bond length between the silicon and fluorine atoms becomes longer as the number of fluorine atoms decreases, whereas for the carbon compounds the opposite tendency is observed. It is interesting that the structure of the XF₃ radical resembles that of HXF₃ from which a hydrogen atom is removed. This means that elimination of the hydrogen atom of HSiF₃ does not significantly disturb the molecular orbitals of the remaining part, i.e., SiF₃. This picture is approximately consistent with the small degree of delocalization of the unpaired electron from the silicon atom to the fluorine atoms, as described below. Milligan *et al.*⁴ suggested the same picture based on the close correspondence between the vibrational spectrum observed for SiF₃ and that of the SiF₃ part in HSiF₃.

The molecular constants of SiF₃ are compared with those of CF₃ in Table II. The constants are similar in many points. However, the most interesting point in the SiF₃ molecule will be the different sign of the spin-rotation interaction constant ε_{bb} from that of the very similar CF₃ radical. This must reflect the difference in the manifold of electronic

states. As Curl showed,²⁶ the spin-rotation interaction constant is closely related to the wave functions of the excited electronic states and given by the following expression:

$$\varepsilon_{bb} = \sum_n \frac{4A_{SO}\langle 0|L_b|n\rangle\langle n|BL_b|0\rangle k}{E_n - E_0},$$

where $k=1$ or -1 according to an electron added to or subtracted from the closed level in the excited state n . Since the angular momentum L_b belongs to the E species and the ground state symmetry is A_1 , the relevant excited states for ε_{bb} belong to the e symmetry. The electronic states of XY₃ molecules are discussed by Walsh²⁷ and later by Buenker and Peyerimhoff.²⁸ These authors gave a diagram, in which the approximate sequence of the orbital energies and their change with the XYX angle were shown. The trifluorosilyl radical will take a pyramidal form as the present observation of the rotational spectrum has confirmed. Methyl and trifluoromethyl radicals have both negative spin-rotation interaction constant ε_{bb} .^{1,30,31} This means that if a single excited electronic state is responsible for the interaction, the promotion of an electron from fully occupied doubly degenerate e state to a vacant totally symmetric a_1 orbital ($k=-1$) is necessary in the interacting excited state of CH₃ [(1e')⁴(1a₂')²→(1e')³(1a₂')³] and CF₃ [(5e)⁴(6a₁)²→(5e)³(6a₁)³]. In SiF₃, however, the excitation from the highest occupied totally symmetric orbital to a degenerate orbital (8a₁→7e) is occurring so that the spin-rotation interaction constant in SiF₃ has the sign opposite to that in CF₃. This information would be useful to a discussion on the electronic spectrum of SiF₃.

Isotropic electron spin resonance spectrum of the trifluorosilyl radical was measured in a SF₆ matrix. The isotropic hyperfine parameter for fluorine in a SF₆ matrix at -175 °C was obtained to be 136 G or 382.8 MHz.⁶ The three fluorine atoms on the SiF₃ radical at 77 K (-196 °C) in an irradiated single crystal of SiF₄ were also equivalent and the isotropic part of the hyperfine interaction was 134.1 G or 375.7 MHz.⁷ Fluorine Fermi contact interaction constant in the present study, 386.83 MHz, is in good agreement with the ESR results. This corresponds to the s -character of 0.7% at fluorine nucleus. The gas phase value is slightly larger than the matrix value. This trend was also observed in the case of CF₃ and it is probably a result of matrix interactions.

The dipole-dipole interaction constant T_{cc} in this radical is about half of the interaction constant in CF₃. The difference between the principal values T_{aa} and T_{bb} has been determined from the doublet splitting of the hyperfine compo-

TABLE III. Comparison of the structure of fluorosilicon and fluorocarbon.^a

	$r_e(\text{Si-F})/\text{\AA}$	$\theta(\text{FSiF})/^\circ$	Ref.		$r_e(\text{C-F})/\text{\AA}$	$\theta(\text{FCF})/^\circ$	Ref.
SiF ₄	1.5540		32	CF ₄	1.3193		36
SiF ₃ H	1.5624(1)	110.64(3)	33	CF ₃ H	1.328	108.6(3)	37
SiF ₃	1.565	109.94 ^b	This work	CF ₃	1.318(2)	110.8(4)	38
SiF ₂	1.5901(1)	100.77(2)	34	CF ₂	1.300	104.94	39,40
SiF	1.601018(3)		35	CF	1.271977(17)		41

^aValues in parentheses are one standard deviation in units of the last digit.^bFixed. Reference 4.

nents for $K=1$. Since the splittings in SiF_3 were larger than those of CF_3 , the difference $|T_{aa} - T_{bb}|$ was 3 times as large as the anisotropy in CF_3 . The dipole-dipole interaction tensor is transformed from the principal axis system of inertia to the principal axis of the hyperfine interaction. This transformation is accomplished by the rotation of the axis around the b -axis through the angle between the plane perpendicular to the molecular symmetry axis and the Si-F bond, 19° . This yields the value of T_{ac} , which is not determined experimentally. From these values the principal components, T_{zz} and T_{xx} , are calculated. These principal values were decomposed into a sum of two axially symmetric parts. The spin densities on the SiF_3 radical was calculated from these hyperfine coupling constant of ^{19}F . When $T_{aa} - T_{bb}$ is assumed to be negative, T_{aa} and T_{bb} are calculated to be -118.7 MHz and 1.16 MHz, respectively. In this case the spin density amounts to 9.2% on a fluorine atom. This value agrees with that from the ESR spectroscopy of SiF_3 in a γ -irradiated single crystal of SiF_4 . Partition of the unpaired electron between p orbitals of the fluorine atom is slightly different from that in a single crystal. Positive value of $T_{aa} - T_{bb}$ as in CF_3 leads to spin density inconsistent with that derived from ESR spectroscopy for an irradiated single crystal of SiF_4 .

The present observation of the rotational spectrum of SiF_3 confirms that SiF_3 has a well-defined potential minimum in the electronic ground state. Lack of the fine structure in the electronic emission spectrum of SiF_3 mentioned in the Introduction will thus imply that a dissociative excited state is concerned with the electronic transition. A similar explanation was proposed for the nonstructured band of CF_3 in the visible region.²⁹

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