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# Microwave spectroscopic study of the $SiF_3$ 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 $CF_3$,[1] $CH_3O$,[2] and $CH_3S$.[3] The $SiF_3$ radical, which is a silicon analog of the $CF_3$ radical, is not extensively studied with any spectroscopic techniques.

Milligan *et al.* trapped $HSiF_3$ in a low temperature matrix of Ar, $N_2$, 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 $SiF_3$ radical, which was produced by hydrogen atom abstraction, was pyramidal in the above matrices and that the angle between the $C_3$ molecular symmetry axis and the Si–F bond was about 71°. Infrared absorption spectra of $SiF_3^-$ and $SiF_3^+$ as well as $SiF_3$ were also observed, when a mixture of Ne and $SiF_4$ was codeposited at approximately 5 K with a beam of discharged neon atoms.[5] ESR spectra of $SiF_3$ in inert matrices[6] 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 $SiF_3$ exists in a discharge system which involves fluorine and silicon. The structure of gaseous $SiF_3$ radical is almost unknown. Broad chemiluminescence in the reaction of F atom with silicon was ascribed to the emission from $SiF_3$ produced in the gas phase.[9] Dispersed fluorescence from photoexcitation of $SiF_4$ around 95 nm was attributed to $SiF_3$ according to the energy constraint.[10] Both emission spectra showed no structures in their envelopes. Wang *et al.*[11] discharged $SiF_4$ with microwave and observed emission spectrum with vibrational structures between 2100 and 2600 Å, which they assigned to $^2B_1-X\,^2A_1$ transition of $SiF_3$. This band system was recently shown to come from $SiF_2$ on the basis of the measurement of the lifetime of the emitting species[12] and the analysis of long progressions involving the bending frequency.[13]

The mid-infrared LMR spectrum of the reaction products between $SiF_3H$ and F was reported.[14] The assignment of the spectrum to $SiF_3$ 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 $SiF_4$ 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 $SiF_3$ 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 $SiF_4$ 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 $SiF_3$ 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 $SiF_3$.[16–19] Such properties are important to the understanding of the industrial 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 (tripler 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 IFI/2, 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 $r(\text{Si–F})=1.530$ Å and $\angle\text{FSiF}=108.86°$. 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 $r(\text{Si–F})$ was considerably short in comparison with that for the related molecule $HSiF_3$, 1.562 Å.

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 Å, 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 $7457\pm90$ MHz, with the uncertainty estimated from those of the bond length (0.01 Å) 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 $328\pm5$ 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 $\varepsilon_{bb}$. 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

TABLE I. Observed transitions of $SiF_3$ in units of MHz.

| $N'$ | $J'$ | $F'$ | – | $N''$ | $J''$ | $F''$ | $K$ | Obs. Freq. | $o-c$[a] |
|---|---|---|---|---|---|---|---|---|---|
| 5 | 4.5 | 3 | | 4 | 3.5 | 2 | 0 | 75071.901 | −0.055 |
| | | 6 | | | | 5 | 0 | 75075.454 | 0.003 |
| | | 5 | | | | 4 | 0 | 75081.987 | −0.010 |
| | | 4 | | | | 3 | 0 | 75088.185 | −0.069 |
| | 5.5 | 4 | | | 4.5 | 3 | 0 | 75088.892 | −0.036 |
| | | 5 | | | | 4 | 0 | 75091.953 | −0.042 |
| | | 7 | | | | 6 | 0 | 75102.055 | −0.003 |
| | 4.5 | 4 | | | 3.5 | 3 | 1 | 75068.799 | −0.030 |
| | | 5 | | | | 4 | 1 | 75078.992 | 0.434[b] |
| | 5.5 | 5 | | | 4.5 | 4 | 1 | 75095.101 | 0.432[b] |
| | | 6 | | | | 5 | −1 | 75102.882 | 0.015 |
| | | 6 | | | | 5 | 1 | 75104.138 | 0.036 |
| | 4.5 | 4 | | | 3.5 | 3 | 2 | 75062.070 | −0.021 |
| | | 5 | | | | 4 | 2 | 75078.992 | −0.067[b] |
| | 5.5 | 5 | | | 4.5 | 4 | 2 | 75098.838 | 0.091[b] |
| | | 6 | | | | 5 | 2 | 75104.138 | −0.028 |
| | 4.5 | 4 | | | 3.5 | 3 | 3 | 75075.454 | 0.420[b] |
| | | 5 | | | | 4 | 3 | 75077.607 | 0.095[b] |
| | | 6 | | | | 5 | 3 | 75077.607 | −0.045[b] |
| | 5.5 | 7 | | | 4.5 | 6 | 3 | 75095.752 | 0.006 |
| | | 4 | | | | 3 | 3 | 75099.785 | −0.049[b] |
| | | 5 | | | | 4 | 3 | 75105.165 | 0.040 |
| | | 6 | | | | 5 | 3 | 75114.647 | 0.036 |
| | 4.5 | 5 | | | 3.5 | 4 | 4 | 75082.613 | −0.104[b] |
| | 5.5 | 5 | | | 4.5 | 4 | 4 | 75113.664 | 0.286[b] |
| 6 | 5.5 | 4 | | 5 | 4.5 | 3 | 0 | 90084.981 | −0.019 |
| | | 7 | | | | 6 | 0 | 90089.463 | 0.013 |
| | | 6 | | | | 5 | 0 | 90095.706 | −0.048 |
| | | 5 | | | | 4 | 0 | 90101.410 | −0.041 |
| | 6.5 | 5 | | | 5.5 | 4 | 0 | 90102.796 | −0.026 |
| | | 6 | | | | 5 | 0 | 90106.322 | 0.007 |
| | | 7 | | | | 6 | 0 | 90109.576 | 0.011 |
| | | 8 | | | | 7 | 0 | 90117.074 | −0.003 |
| | 5.5 | 5 | | | 4.5 | 4 | −1 | 90081.392 | −0.040 |
| | | 5 | | | | 4 | 1 | 90083.198 | −0.018 |
| | | 6 | | | | 5 | 1 | 90092.440 | 0.481[b] |
| | 6.5 | 6 | | | 5.5 | 5 | 1 | 90109.576 | 0.338[b] |
| | | 7 | | | | 6 | 1 | 90117.840 | 0.040 |
| | | 7 | | | | 6 | −1 | 90118.713 | 0.007 |
| | 5.5 | 5 | | | 4.5 | 4 | 2 | 90079.508 | −0.031 |
| | | 6 | | | | 5 | 2 | 90092.440 | −0.067 |
| | 6.5 | 6 | | | 5.5 | 5 | 2 | 90112.706 | 0.078 |
| | | 7 | | | | 6 | 2 | 90119.124 | −0.003 |
| | 5.5 | 4 | | | 4.5 | 3 | 3 | 90065.592 | −0.017 |
| | | 7 | | | | 6 | 3 | 90091.487 | −0.003 |
| | | 6 | | | | 5 | 3 | 90093.937 | −0.005 |
| | | 5 | | | | 4 | 3 | 90097.617 | −0.001 |
| | 6.5 | 5 | | | 5.5 | 4 | 3 | 90109.234 | −0.017 |
| | | 8 | | | | 7 | 3 | 90114.615 | 0.050 |
| | | 6 | | | | 5 | 3 | 90115.966 | 0.020 |
| | | 7 | | | | 6 | 3 | 90121.881 | 0.018 |
| | 5.5 | 5 | | | 4.5 | 4 | 4 | 90068.426 | −0.006 |
| | | 6 | | | | 5 | 4 | 90095.706 | 0.185[b] |
| | 6.5 | 6 | | | 5.5 | 5 | 4 | 90122.683 | 0.033 |
| | | 7 | | | | 6 | 4 | 90122.683 | 0.060 |
| | 5.5 | 5 | | | 4.5 | 4 | 5 | 90060.109 | −0.028 |
| | | 6 | | | | 5 | 5 | 90099.094 | 0.125[b] |
| | 6.5 | 7 | | | 5.5 | 6 | 5 | 90125.345 | 0.102[b] |
| 7 | 6.5 | 5 | | 6 | 5.5 | 4 | 0 | 105097.271 | −0.035 |
| | | 8 | | | | 7 | 0 | 105102.084 | 0.007 |
| | | 7 | | | | 6 | 0 | 105108.102 | −0.027 |
| | | 6 | | | | 5 | 0 | 105114.278 | 0.003 |
| | 7.5 | 6 | | | 6.5 | 5 | 0 | 105115.129 | −0.019 |
| | | 7 | | | | 6 | 0 | 105119.780 | 0.107[b] |
| | | 8 | | | | 7 | 0 | 105123.560 | −0.019 |
| | | 9 | | | | 8 | 0 | 105130.527 | 0.026 |
| | 6.5 | 6 | | | 5.5 | 5 | −1 | 105094.963 | −0.023 |
| | | 6 | | | | 5 | 1 | 105096.184 | −0.036 |
| | | 7 | | | | 6 | 1 | 105104.240 | 0.183[b] |
| | 7.5 | 7 | | | 6.5 | 6 | 1 | 105123.560 | −0.294[b] |
| | | 8 | | | | 7 | −1 | 105131.182 | 0.021 |
| | | 8 | | | | 7 | 1 | 105131.970 | 0.116[b] |
| | 6.5 | 6 | | | 5.5 | 5 | 2 | 105094.103 | −0.019 |
| | | 7 | | | | 6 | 2 | 105104.634 | −0.047 |
| | 7.5 | 7 | | | 6.5 | 6 | 2 | 105125.987 | 0.052 |
| | | 8 | | | | 7 | 2 | 105132.498 | 0.000 |
| | 6.5 | 5 | | | 5.5 | 4 | 3 | 105086.339 | −0.024 |
| | | 8 | | | | 7 | 3 | 105104.240 | −0.005 |
| | | 7 | | | | 6 | 3 | 105108.102 | 0.188[b] |
| | | 6 | | | | 5 | 3 | 105113.949 | −0.012 |
| | 7.5 | 6 | | | 6.5 | 5 | 3 | 105119.780 | −0.103[b] |
| | | 7 | | | | 6 | 3 | 105127.128 | 0.014 |
| | | 9 | | | | 8 | 3 | 105130.098 | 0.008 |
| | | 8 | | | | 7 | 3 | 105131.970 | −0.057 |
| | 6.5 | 6 | | | 5.5 | 5 | 4 | 105088.234 | 0.019 |
| | | 7 | | | | 6 | 4 | 105107.636 | 0.003 |
| | 7.5 | 7 | | | 6.5 | 6 | 4 | 105133.802 | 0.002 |
| | | 8 | | | | 7 | 4 | 105136.480 | 0.021 |
| | 6.5 | 6 | | | 5.5 | 5 | 5 | 105083.801 | 0.001 |
| | | 7 | | | | 6 | 5 | 105110.493 | 0.023 |
| | 7.5 | 7 | | | 6.5 | 6 | 5 | 105139.062 | −0.008 |
| | | 8 | | | | 7 | 5 | 105139.485 | 0.056 |
| | 6.5 | 5 | | | 5.5 | 4 | 6 | 105053.854 | 0.081 |
| | | 8 | | | | 7 | 6 | 105111.096 | 0.021 |
| | | 7 | | | | 6 | 6 | 105111.096 | −0.052[b] |
| | 7.5 | 9 | | | 6.5 | 8 | 6 | 105128.897 | 0.041 |
| | | 6 | | | | 5 | 6 | 105145.982 | 0.017 |
| | | 7 | | | | 6 | 6 | 105145.982 | 0.423[b] |
| | | 8 | | | | 7 | 6 | 105157.096 | 0.046 |

[a] Observed minus calculated transition frequencies.
[b] Not 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]

Rotational transitions observed between 75 and 105 GHz 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, $H=H_{\mathrm{rot}}+H_{\mathrm{sr}}+H_{\mathrm{hfs}}$, where $H_{\mathrm{rot}}$ is the symmetric top rotational Hamiltonian with centrifugal distortion corrections, $H_{\mathrm{sr}}$ is the spin-rotation interaction Hamiltonian, and $H_{\mathrm{hfs}}$ 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 $\mathbf{J}=\mathbf{N}+\mathbf{S}$ and $\mathbf{F}=\mathbf{J}+\mathbf{I}_0(\mathbf{I}_0=\mathbf{I}_1+\mathbf{I}_2+\mathbf{I}_3)$. The nuclear spin functions have the symmetry species $\Gamma$, 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 $\varepsilon_{bb}$. 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 $\varepsilon_{bb}$ 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, $\varepsilon_{bb}$, $\varepsilon_{cc}$, $T_{aa}$, 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 spectrometer[22] down to 105 GHz still did not allow the unique $K$ assignment. With an improved spectrometer[23] 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 possibility 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 $\varepsilon_{bb}$ had to be positive and thus had different sign from that in $CF_3$.

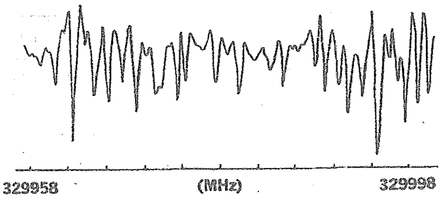

FIG. 1. Spectrum of the $SiF_3$ radical in the 330 GHz region. The low-frequency part of the rotational transition $N=22-21$ is shown. The overlapping region of the two $K$-patterns separated by the spin-rotation interaction constant $\varepsilon_{bb}$ is seen.

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

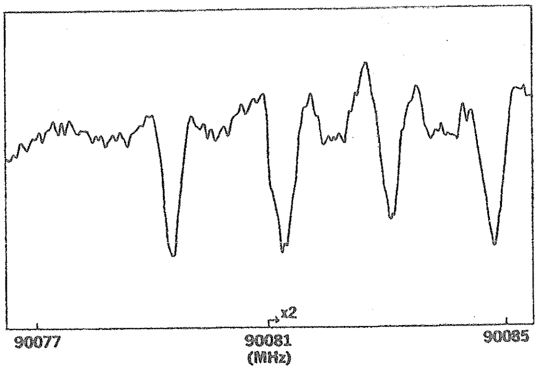

FIG. 2. The transition of $SiF_3$ radical in the 90 GHz region. The lines are assigned from the left to $K=2,1,1$, and 0. The $K=1$ transition is clearly split into two lines.

TABLE II. Molecular constants of $SiF_3$ and $CF_3$. [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) | |
| $\Phi_N$/mHz | −0.127(35) | |
| $\varepsilon_{bb}$/MHz | 36.0224(69) | −36.500(17) |
| $\varepsilon_{cc}$/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) |

[a] Values in parentheses are one standard deviation in unit of the last digit.
[b] Reference 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 $XF_3$ radical resembles that of $HXF_3$ from which a hydrogen atom is removed. This means that elimination of the hydrogen atom of $HSiF_3$ does not significantly disturb the molecular orbitals of the remaining part, i.e., $SiF_3$. 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 $SiF_3$ and that of the $SiF_3$ part in $HSiF_3$.

The molecular constants of $SiF_3$ are compared with those of $CF_3$ in Table II. The constants are similar in many points. However, the most interesting point in the $SiF_3$ molecule will be the different sign of the spin-rotation interaction constant $\varepsilon_{bb}$ from that of the very similar $CF_3$ 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:

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

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 $\varepsilon_{bb}$ belong to the $e$ symmetry. The electronic states of $XY_3$ molecules are discussed by Walsh[27] 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 $\varepsilon_{bb}$.[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 $CH_3$ $[(1e')^4(1a_2'')\rightarrow(1e')^3(1a_2'')^2]$ and $CF_3$ $[(5e)^4(6a_1)\rightarrow(5e)^3(6a_1)^2]$. In $SiF_3$, however, the excitation from the highest occupied totally symmetric orbital to a degenerate orbital $(8a_1\rightarrow 7e)$ is occurring so that the spin-rotation interaction constant in $SiF_3$ has the sign opposite to that in $CF_3$. This information would be useful to a discussion on the electronic spectrum of $SiF_3$.

Isotropic electron spin resonance spectrum of the trifluorosilyl radical was measured in a $SF_6$ matrix. The isotropic hyperfine parameter for fluorine in a $SF_6$ matrix at −175 °C was obtained to be 136 G or 382.8 MHz.[6] The three fluorine atoms on the $SiF_3$ radical at 77 K (−196 °C) in an irradiated single crystal of $SiF_4$ 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 $CF_3$ 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 $CF_3$. 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]

| | $r_e$(Si–F)/Å | $\theta$(FSiF)/° | Ref. | | $r_e$(C–F)/Å | $\theta$(FCF)/° | Ref. |
|---|---|---|---|---|---|---|---|
| $SiF_4$ | 1.5540 | | 32 | $CF_4$ | 1.3193 | | 36 |
| $SiF_3H$ | 1.5624(1) | 110.64(3) | 33 | $CF_3H$ | 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 |

[a] Values in parentheses are one standard deviation in units of the last digit.
[b] Fixed. 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 $\gamma$-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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