Microwave Spectroscopic Study of the SiF Radical

MITSUTOSHI TANIMOTO

Sagami Chemical Research Center, Nishi-Ohnuma 4-4-1, Sagamihara, Kanagawa 229, Japan

AND

SHUJI SAITO, YASUKI ENDO, AND EIZI HIROTA

Institute for Molecular Science, Okazaki 444, Japan

The microwave spectrum of the SiF radical was observed in both ${}^{2}\Pi_{1/2}$ and ${}^{2}\Pi_{3/2}$ of the ground vibronic state. The SiF radical was produced by a dc discharge either in a SiF₄/SiH₄ mixture or in a transient molecule SiF₂ generated by the reaction of SiF₄ with heated solid silicon. The latter gave twice as intense a spectrum. A least-squares fit to the observed spectrum showed the rotational constant and the centrifugal distortion constant to be 17 350.2752(63) and 0.03188(13) MHz, respectively, with three standard errors in parentheses applying to the last digits of the constants. The lambda-doubling parameter p_0 was found to be negative, -87.67 MHz, indicating that the ${}^{2}\Sigma^{+}$ excited state contributions dominate over those of ${}^{2}\Sigma^{-}$. All four hyperfine coupling constants *a*, *b*, *c*, and *d* were determined and were employed to discuss the unpaired-electron spin and orbital distributions in the SiF radical.

INTRODUCTION

Spectroscopy of the SiF radical has long been attracting much interest in various fields. This molecule has been detected in stellar atmospheres (1) and has been suspected to be a constituent of the solar atmosphere (2). According to a recent experiment (3) SiF may constitute a chemical laser oscillating in its electronic transition. Electronic spectroscopy has been carried out extensively, as compiled by Huber and Herzberg (4). For the electronic ground state $X^2 \Pi_r$ Martin and Merer (5) have reported the rotational constant, the Λ -doubling constant, the spin-orbit interaction constant, and its centrifugal distortion parameter (A_J) determined by an analysis of the $a^4 \Sigma^- \rightarrow X^2 \Pi_r$ transition at 3360 Å. Houbrechts *et al.* (6-10) have investigated a few other electronic transitions and have derived molecular constants in the ground $X^2 \Pi$ state and in many excited electronic states.

On the other hand, no spectroscopic investigations of SiF have been reported in the infrared, far-infrared, and microwave regions, and thus the hyperfine interaction constants have not been determined. These constants will allow us to elucidate the electronic structure of the molecule. In the present paper we report the first microwave study of the SiF radical in both ${}^{2}\Pi_{1/2}$ and ${}^{2}\Pi_{3/2}$ spin states in the ground vibronic state, including the determination of all four hyperfine coupling constants.

TANIMOTO ET AL.

EXPERIMENTAL DETAILS

An initial search for the SiF microwave spectrum was carried out at the Sagami Chemical Research Center using a Stark-modulated spectrometer with a parallelplate cell. The SiF radical was generated by a microwave discharge in SiF₄ induced in a side arm about 15 cm upstream the cell. No paramagnetic absorption lines were observed; the lifetime of the SiF radical seems to be too short to observe its spectra with this type of spectrometer. Subsequent observations of rotational spectra of SiF were done at the Institute for Molecular Science using a source-frequency modulation spectrometer with a 3.5-m-long glow discharge cell (11).

The SiF radical was initially generated by a glow discharge in SiF₄, as reported by Martin and Merer (5). This reaction system produces quite a large amount of SiF₂, and because SiF was suspected to be formed from or simultaneously with SiF₂, the $8_{18}-7_{07}$ transition of SiF₂ at 121 382 MHz was employed to optimize the reaction condition. The line increased the intensity with the dc discharge current up to 200 mA, but beyond this limit the discharge caused pulse noises in the detecting system, making the search for the spectra difficult. The best condition was attained at the dc discharge current of 100 mA with SiF₄ of 30 mTorr as measured at the outlet of the cell.

Searching for the ${}^{2}\Pi_{3/2}$, $J = 7/2 \leftarrow 5/2$ transition of SiF was started around 121 800 MHz, where the sensitivity of the spectrometer was high. Martin and Merer's rotational constant (5) was used to predict the transition frequency, but because no information had been available on the hyperfine structure the region of ± 90 MHz from the predicted frequency was scanned carefully; a frequency region 4 MHz wide was covered in one time and the absorption signal was accumulated 800 times to maintain the sensitivity high. Two paramagnetic lines were thus observed which were separated by about 39 MHz, and when the hyperfine contributions were subtracted using a preliminary set of hyperfine constants, the observed frequency was found to be close to the predicted value.

Using the two lines the experimental conditions were further optimized. Addition of helium as a buffer gas decreased the discharge current at the same voltage and decreased the signal intensity. An addition of a small amount of silane, on the other hand, increased the signal intensity nearly twice, but not as much as in the case of CF (12), for which the signal intensity was found to be much increased by adding CH₃F to CF₄. The optimum partial pressures of SiF₄ and SiH₄ were 15 and 2 mTorr, respectively. The dc discharge current was typically about 100 mA.

After the experimental conditions were optimized, the same $J = 7/2 \leftarrow 5/2$ transition of ${}^{2}\Pi_{1/2}$ was searched for. Because the spin-orbit coupling constant A of SiF is only 160 cm⁻¹, ${}^{2}\Pi_{1/2}$ lines were also expected to show Zeeman effects. Because A is positive, ${}^{2}\Pi_{1/2}$ transitions are stronger than ${}^{2}\Pi_{3/2}$ transitions, even if split by Λ -type doubling. The Λ -type splitting was found to be of some use in making assignments for ${}^{2}\Pi_{1/2}$ lines. Figure 1 shows the $J = 9/2 \leftarrow 7/2$, $e, F = 5 \leftarrow 4$ transition as an example of the ${}^{2}\Pi_{1/2}$ spectra; it is seen that the line exhibits observable Zeeman effect at the magnetic field of 24 G.

Transitions of J smaller than $7/2 \leftarrow 5/2$ were too weak to be observed. We thus tried to find a more efficient method for generating SiF. A glow discharge in SiF₂



FIG. 1. The $J = 9/2 \leftarrow 7/2$, $e, F = 5 \leftarrow 4$ transition of SiF in ${}^{2}\Pi_{1/2}$, generated by a dc discharge in a mixture of 17 mTorr SiF₄ and 1.5 mTorr SiH₄. The lower trace shows that the line has sizeable Zeeman effect for a magnetic field of 24 G.

was first tested. However, SiF_2 produced by a microwave discharge outside the cell gave absorption signals that were too weak to be used for optimizing conditions; they were not visible on an oscilloscope. It has been known (13) that SiF_2 is efficiently formed by passing low-pressure SiF_4 gas over solid silicon at high temperature. This method was applied; silicon powder was loaded inside a quartz tube of 20 mm o.d. which was connected to a 1-m-long glow discharge absorption cell and was heated by an electrical furnace placed about 23 cm apart from the cell. The temperature of the quartz tube was monitored by a thermocouple gauge. The SiF_4 gas of about 30 mTorr in the cell flowed through the quartz tube heated to $1050^{\circ}C$. Strong absorptions of SiF_2 were observed, and when the discharge was induced in the cell with a current of 21 mA their intensities were decreased to about one-tenth, while SiF lines became stronger. Care had to be taken to keep the vacuum line including the cell tight to air leakage, because even a small amount of air weakened the absorption signals of both SiF and SiF₂. The experimental condition could be adjusted so that the SiF signal became twice as strong as that observed for the SiF_4/SiH_4 system.

In this way we observed transitions from $J = 5/2 \leftarrow 3/2$ up to $J = 11/2 \leftarrow 9/2$ for both the ${}^{2}\Pi_{1/2}$ and ${}^{2}\Pi_{3/2}$ states. The lowest transition $J = 3/2 \leftarrow 1/2$ of ${}^{2}\Pi_{1/2}$ expected to appear at 51.8 GHz was too weak to be observed. The observed transition frequencies are listed in Table I with the assignment.

ANALYSIS

The Hamiltonian used in analyzing the observed spectra is given by

$$\mathbf{H} = \mathbf{H}_{rso} + \mathbf{H}_{hfs} \tag{1}$$

where H_{rso} includes the rotational, spin-orbit coupling, Λ -type doubling, and spinrotation Hamiltonians and H_{hfs} denotes the hyperfine Hamiltonian. The basis function used is a symmetry-adapted Hund's case (a) function given by

$$|{}^{2}\Pi_{\Omega}J\pm\rangle = [|J\Omega S\Sigma\Lambda\rangle \pm (-1)^{J-S}|J-\Omega S-\Sigma-\Lambda\rangle]/\sqrt{2}.$$
 (2)

TABLE I	
---------	--

	² _Π _{1/2}			² ₁ 3/2		
J' - J"	F' - F"	obs	0-c	F' - F"	obs	0-c
5/2 - 3/2	3-2e 2-1e	86 459.373 86 483.839	-0.027	3 - 2 e,f 2 - 1 e,f	87 045.295 87 128.310	-0.006 -0.014
	3 - 2 f 2 - 1 f	86 379.504 86 417.393	0.046 -0.007			
7/2 - 5/2	4 - 3 e 3 - 2 e	121 034.687 121 046.708	0.013 0.002	4 - 3 e,f 3 - 2 e,f	121 881.600 121 920.542	-0.009 0.045
	4 - 3 f 3 - 2 f	120 950.449 120 966.976	0.020 0.000			
9/2 - 7/2	5 - 4 e 4 - 3 e	155 603.834 155 610.973	0.010 0.030	5 - 4 e,f 4 - 3 e,f	156 709.125 156 731.965	0.003 -0.057
	5 - 4 f 4 - 3 f	155 517.701 155 526.976	-0.083 -0.004			
11/2 - 9/2	6 - 5 e 5 - 4 e	190 168.268 190 172.914	-0.020 -0.011	6 - 5 e,f 5 - 4 e,f	191 530.747 191 545.997	0.001 0.030
	6 - 5 f 5 - 4 f	190 081.495 190 087.235	0.040 -0.004			

Observed Transition Frequencies of the SiF Radical in $X^2\Pi_r$ (MHz)

The matrix elements of H_{rso} and H_{hfs} have been given by Endo *et al.* (14). (It is to be noted that the \pm sign of Eqs. (4) and (6) and the \mp sign of Eq. (8) of Ref. (14) need to be replaced by \mp and \pm , respectively.) The parity of the Λ -doublet was chosen such that the hyperfine coupling constant d was positive (15). The energy matrix thus constructed, which includes the $\Delta J = 0$ and ± 1 matrix elements of H_{hfs}, was numerically diagonalized. The spin-orbit coupling constant A_0 was fixed to the value (161.88 cm⁻¹) of Ref. (5), and the spin-rotation coupling constant γ_0 was neglected because of its correlation with A_J pointed out by Brown and Watson (16). As discussed by Endo et al. (14), A_J , γ_0 , and p_0^* and also B_0 and q_0^* cannot be separated from one another. Therefore, both p_0^* and q_0^* were fixed to zero in the present analysis. Since A-type doubling was not resolved in the ${}^{2}\Pi_{3/2}$ state, the q_{0} constant obtained must be regarded as an effective constant; it involves the contribution of a higherorder term called $p_{\rm J}$ (17). The fitting of the ${}^{2}\Pi_{3/2}$ spectra was made using the averages of the calculated A-doublet frequencies. It was found that $p_0 + 2q_0$ and q_0 , rather than p_0 and q_0 , were better determined, presumably because of the correlation between the two parameters. The standard deviation of the fit is 27 kHz, which is of the same order of magnitude as the frequency measurement error. The molecular constants thus determined are listed in Tables II and III, and the transition frequencies calculated using these constants are compared with the observed values in Table I.

DISCUSSION

Table II includes molecular constants previously derived from electronic spectra (5, 8) to be compared with the present results. Martin and Merer's constants (5) agree remarkably well with the present values. It is to be noted that they did not discriminate between p_0 and p_0^* and also between q_0 and q_0^* . Therefore, their B and A_J constants

TAB	LE	П
-----	----	---

Molecular Constants of the SiF Radical in the $X^2\Pi_r$ State (MHz)^a

	Present study ^b	Martin, Merer ^C	Houbrechts et al. ^d		
B ₀	17 350.275 2(63)	17 350.1(15)	17 358.3(54)		
D	0.031 88(13)	0.032 1(6)	0.033 9(10)		
A,T	1.630 6(42)	1.829(90)	3.96(18)		
p ₀ +2q ₀	-90.19(17)	-89.6(54)	-52(14)		
q	-1.26(29)	-0.31(calcd)			
a. Values in parentheses denote three standard deviations and					
apply	apply to the last digits of the constants.				
b. A. is	A_{0} is fixed to 161.88 cm ⁻¹ [Ref. (5)].				

c. Ref. (5). In this work $p_0 = p_0^*$ and $q_0 = q_0^*$ were assumed.

d. From the $B \rightarrow X$ 0-0 band [Ref. (8)].

need to be corrected, but the p constant remains to be almost unaffected. Their p constant corresponds to $p_0 + 2q_0$ of the present paper. On the other hand, results of Houbrechts et al. (8) show discrepancies that exceed their experimental uncertainties. However, when the B_e and α_e constants listed in Table 3 of Ref. (8) are employed, B_0 is calculated to be 17 349.0(72) MHz, which agrees better with the present value than that directly obtained from the 0-0 band does. The D_e constant given in the same table is also closer to the present result.

Because p_0 is found to be negative, it receives more contributions from ${}^{2}\Sigma^{+}$ excited electronic states than ${}^{2}\Sigma^{-}$. If the observed p_0 constant is explained by one ${}^{2}\Sigma^{+}$ state, this state must be located at 125 000 cm⁻¹ above the ground state, provided that the pure precession hypothesis holds. This excitation energy is certainly much larger than those of the known low-lying ${}^{2}\Sigma^{+}$ states, $A^{2}\Sigma^{+}$ (22 858.3 cm⁻¹) (18) and $B^{2}\Sigma^{+}$ (34 561.57 cm⁻¹) (8). Although only one ${}^{2}\Sigma^{-}$ state ($D^{2}\Sigma^{-}$ (6)) has so far been identified, the p_0 constant determined is more reasonably interpreted in terms of contributions of both

TABLE III

Hyperfine Interaction Constants of the SiF Radical in the $X^2 II_r$ State (MHz)^a

a+(b+c)/2	288.26(45)
a-(b+c)/2	336.4(11)
b	127(16)
d	359.0(33)
a	312,35(60) ^b
с	-175(16) ^b

 Values in parentheses denote three standard deviations and apply to the last digits of the constants.

b. Calculated from experimentally determinable parameters.



FIG. 2. A typical absorption line of ${}^{2}\Pi_{3/2}$ SiF: $J = 9/2 \leftarrow 7/2$, $F = 5 \leftarrow 4$. The line is broadened because of incomplete A-doublet splitting.

 ${}^{2}\Sigma^{+}$ and ${}^{2}\Sigma^{-}$, which are cancelled by each other to some extent, resulting in the small negative Λ -doubling constant.

The observed q_0 constant does not satisfy a relation $q_0 = p_0 B_0 / A_0$ which the pure precession hypothesis predicts. This is understandable, because all the observed ${}^2\Pi_{3/2}$ transitions are not split by the Λ -type doubling, making the determination of q_0 difficult, as noted above. As shown by an example of Fig. 2, high J lines of the ${}^2\Pi_{3/2}$ state are broad presumably because of incomplete Λ -type splitting.

The observed hyperfine coupling constants listed in Table III were used to calculate the expectation values for the unpaired-electron orbital and spin distributions, which are reproduced in Table IV. The orbital average $\langle 1/r^3 \rangle_0$ is close to the spin average $\langle 1/r^3 \rangle_s$, the former being only 4% larger than the latter. A comparison of the observed value of $g_N g_e \beta_N \beta \langle 1/r^3 \rangle_s$, 300.7 MHz, with the corresponding value (3800 MHz (19)) of the fluorine atom in the ground ²P state gives the spin density on the fluorine atom to be about 8% in SiF, which represents the extent of delocalization of the unpaired electron from the silicon to the fluorine atom. This value is about half of that in the CF radical (12). The observed ratios of $\langle 1/r^3 \rangle_s: \langle (3 \cos^2 \chi - 1)/r^3 \rangle_s:$ $\langle \sin^2 \chi/r^3 \rangle_s$ are 1:-0.39:0.80, which agree very well with those 1:-0.4:0.8 calculated for a pure p_{π} orbital of the fluorine atom. The Fermi term of SiF, 68.3 MHz, is also close to one-half of the value of CF (12), as in the case of the spin density.

A parallel relation pointed out in Ref. (14) between the spin density and the Fermi term of fluorine-containing radicals, FSO, SF, and CF, holds also for SiF, as shown in Table V; both the Fermi term and the spin density of SiF are very close to those of FSO. It may be interesting to see whether the correlation between the spin density and the spin-orbit coupling constant which was shown to hold for carbon monohalide radicals (20) is applicable to SiF. When the spin-orbit coupling constants of 145.7 and -269.3 cm^{-1} are used, respectively, for the Si and F atoms, the value 161.88

TABLE IV

Distribution of the Unpaired Electron in SiF (MHz)^s

$2 g_N \beta_N \beta < 1/r^3 >_o$	312.35(60)
g _N g _{e^βN^{β<1/r³>s}}	300.7(60)
$g_N g_e \beta_N \beta < (3 \cos^2 \chi - 1) / r^3 >_s$	-117(10)
g _N g _e β _N β <sin<sup>2χ/r³>_s</sin<sup>	239.3(22)
$g_N g_e \beta_N \beta < (8\pi/3) \psi^2(0) >_s$	68(16)

a. See Footnote a of Table III.

TABLE V	
---------	--

Fermi Contact Term and Spin Density on the F Atom

	Radical	a _F (MHz)	Spin Density (%)
	SiF	68	7.9	
	FSO ^a	67	7.8	
	SF ^b	105	13	
	CF^{C}	151	18	
a.	Y. Endo, S. Sa Phys. 74, 1568	ito, and E. -1579 (1981)	Hirota, J. Chem.	
b.	Ref. (<u>12</u>).			
c.	Ref. (10).			

 cm^{-1} obtained for the SiF radical (5) gives the spin density on the F atom to be 11.8%, which may be compared with 8% calculated from the hyperfine coupling constants.

ACKNOWLEDGMENTS

The authors express their gratitude to Professor Yonezo Morino for invaluable advice and encouragement throughout the course of the present work and to Professor Anthony J. Merer for clarifying the energy level structure of the ${}^{2}\Pi$ state. One of the authors (M.T.) is grateful to the Institute for Molecular Science for the support by the Joint Studies Program 1981–1982.

RECEIVED: March 31, 1983

REFERENCES

- 1. D. N. DAVIS, Astrophys. J. 106, 28-75 (1947).
- 2. A. SCHADEE, 26th Intern. Astron. Union Symp., Utrecht, Netherlands, 92 (1964) cited in P. A. O'HARE AND A. C. WAHL, J. Chem. Phys. 55, 666-676 (1971).
- 3. G. R. BRADBURN, R. A. ARMSTRONG, AND S. J. DAVIS, Opt. Eng. 19, 66-70 (1980).
- 4. K. P. HUBER AND G. HERZBERG, "Molecular Spectra and Molecular Structure IV. Constants of Diatomic Molecules," Van Nostrand, New York, 1979.
- 5. R. W. MARTIN AND A. J. MERER, Canad. J. Phys. 51, 634-643 (1973).
- 6. Y. HOUBRECHTS, I. DUBOIS, AND H. BREDOHL, J. Phys. B 12, 2137-2141 (1979).
- H. BREDOHL, I. DUBOIS, AND Y. HOUBRECHTS, 21st Int. Astrophys. Sym. Spectres Mol. Simples Lab. Astrophys., Commun. Colloq. Int. Astrophys., 21st 1977, pp. 318-322 (published 1980).
- 8. Y. HOUBRECHTS, I. DUBOIS, AND H. BREDOHL, J. Phys. B 13, 3369-3373 (1980).
- 9. Y. HOUBRECHTS, I. DUBOIS, AND H. BREDOHL, J. Phys. B 15, 603-611 (1982).
- 10. Y. HOUBRECHTS, I. DUBOIS, AND H. BREDOHL, J. Phys. B 15, 4551-4560 (1982).
- 11. Y. ENDO, S. SAITO, AND E. HIROTA, J. Chem. Phys. 75, 4379-4384 (1981).
- 12. S. SAITO, Y. ENDO, M. TAKAMI, AND E. HIROTA, J. Chem. Phys. 78, 116-120 (1983).
- 13. V. M. RAO, R. F. CURL, JR., P. L. TIMMS, AND J. L. MARGRAVE, J. Chem. Phys. 43, 2557-2558 (1965).
- 14. Y. ENDO, S. SAITO, AND E. HIROTA, J. Mol. Spectrosc. 92, 443-450 (1982).
- 15. T. AMANO, S. SAITO, E. HIROTA, AND Y. MORINO, J. Mol. Spectrosc. 32, 97-107 (1969).
- 16. J. M. BROWN AND J. K. G. WATSON, J. Mol. Spectrosc. 65, 65-74 (1977).
- 17. K. KAWAGUCHI, S. SAITO, AND E. HIROTA, J. Chem. Phys., in press.
- 18. J. W. C. JOHNS AND R. F. BARROW, Proc. Phys. Soc. London Sect. A 71, 476-484 (1958).
- 19. J. S. M. HARVEY, Proc. R. Soc. Ser. A 285, 581-596 (1965).
- 20. R. N. DIXON AND H. W. KROTO, Trans. Faraday Soc. 22, 1484-1489 (1963).