INFRARED DIODE LASER SPECTROSCOPY OF THE SiF^+ ION

Yasunobu AKIYAMA, Keiichi TANAKA and Takehiko TANAKA

Department of Chemistry, Faculty of Science, Kyushu University 33, Hakozaki, Higashiku, Fukuoka 812, Japan

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The infrared diode laser spectrum of the SiF^+ ion generated in a SiF_4 plasma has been observed. Twenty-one and ten lines in the R and P branches, respectively, of the fundamental band and three R branch lines in the $v=2\leftarrow1$ hot band were recorded using the hollow cathode discharge modulation technique. A sharp decrease of the intensity caused by the magnetic field, which is characteristic of ion lines, was observed. The band origins are 1040.4833 ± 0.0006 and 1030.5908 ± 0.0005 cm^{-1} for the fundamental and hot bands, respectively, from which $\omega_e=1050.3757\pm0.0013$ cm^{-1} and $\omega_ex_e=4.9462\pm0.0004$ cm^{-1} are derived. The rotational constants for the ground and first excited vibrational states are 0.637010 ± 0.000015 and 0.632311 ± 0.000015 cm^{-1}, respectively, and the centrifugal distortion constant in the ground state is $(0.9466\pm0.0046)\times10^{-6}$ cm^{-1}. The equilibrium bond length is $r_e=1.52652\pm0.00008$ Å.

1. Introduction

Transient molecules in fluorine containing discharge plasmas reacting with silicon substrate are of considerable interest in connection with plasma etching and sputtering processes [1–5]. The SiF^+ ion is among the species which may be produced abundantly in such plasmas. However, this species lacked spectroscopic data in any frequency region until very recently, by sharp contrast with the SiF radical, which has been extensively studied by microwave [6], infrared [7], and visible and ultraviolet [8] spectroscopies.

Recently, Robbe [9] and Karna and Grein [10] carried out ab initio calculations with configuration interaction for SiF^+. These calculations predict that there are only two strongly bound electronic states in the low-energy region, i.e. the ground $^1\Sigma^+$ state and the lowest $^3\Pi$ state. The transition between these states is not expected to give intense emission. In the case of a non-emitting species, for which the laser-induced fluorescence (LIF) technique is inapplicable, infrared spectroscopy in the ground electronic state seems useful for its detection in plasmas. Molecular constants of SiF^+ including the rotational constant and harmonic vibrational frequency have been predicted for the X $^1\Sigma^+$ and 1 $^3\Pi$ states [10].

In the present paper, we report infrared diode laser spectroscopy of the SiF^+ ion generated in a glow discharge of SiF_4. The spectrum was recorded by the hollow cathode discharge modulation method using a multireflection absorption cell. The magnetic field effect on the ion lines, i.e. a sharp decrease of the intensity, was observed, to discriminate them from the lines of neutral species.

After we completed the measurement and analysis, we learned that Petrmichl, Peterson and Woods [11] have published a microwave study on the SiF^+ ion.

2. Experimental details

The present experiment was performed with an infrared diode laser spectrometer newly constructed at Kyushu University. A Spectra Physics diode laser (SP5615) was used as a light source. Details of the spectrometer will be described in a separate paper [7], in which detection of the SiF radical in a glow discharge of SiF_4 will be reported.

The discharge cell used for the present measurement is shown in fig. 1. A 103 cm long Pyrex glass tube with a diameter of 50 mm contained a 50 cm long stainless-steel cylinder with a diameter of 45 mm

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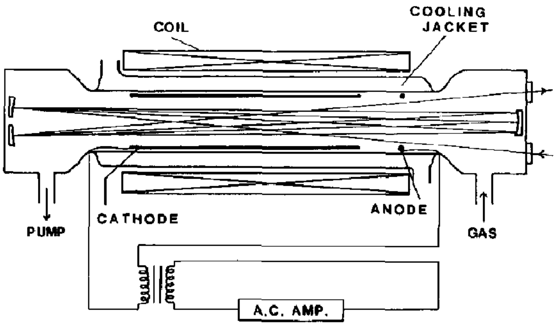

Fig. 1. Schematic diagram of the hollow cathode discharge cell. A 3 kHz ac high voltage stepped up by a transformer is applied between the electrodes to produce a glow discharge. The three concave mirrors form a White-type multireflection optical path. The solenoid coil is used to check the magnetic field effect on the ion lines.

as a hollow cathode and a 45 mm diameter ring made of 2 mm diameter stainless-steel wire as an anode. The gap between the electrodes was about 20 cm. ac high voltage of several kHz generated by a 1.4 kW amplifier and stepped up by a transformer (1:30) was applied between the electrodes to produce a glow discharge. The hollow cathode discharge cell works as a rectifier [12], and discharge occurs only in half cycles when the cathode is negative relative to the anode, modulating the concentration of discharge products in the cell. The ion lines were detected by a phase-sensitive detector (PSD) operating at the frequency of the high voltage for discharge.

A cooling jacket surrounded the cell, through which acetone at the dry ice temperature was circulated. Resin-coated copper wire of 2 mm diameter was wound in three layers around the cooling jacket. A dc current up to 50 A was fed to the solenoid to produce an axial magnetic field for the check of the magnetic field effect characteristic to ion lines [13,14].

The discharge cell was incorporated with a White-type multireflection optical path formed by three concave mirrors of 50 cm focal length. The laser beam traveled ten round trips, yielding an effective path length of 20 m, and was focused onto a HgCdTe detector. The absorption cell was evacuated by a high-speed mechanical booster pump backed up by a rotary pump. The observed wavenumbers were calibrated using the lines of CD_3F [15], CH_3Cl [16], and allene (C_3H_4) [17] as reference, and a vacuum spaced etalon as an interpolation device. The PSD outputs for the ion lines, reference lines, and etalon fringes were accumulated in a microcomputer.

3. Observed spectra and analysis

The SiF^+ ion was produced directly in the absorption cell in the glow discharge of SiF_4. Pure SiF_4 was used and the optimum pressure was about 80 mTorr as measured at the inlet to the absorption cell. Mixing of He or Ar did not appreciably improve the signal-to-noise ratio, although the signal intensity slightly increased. Addition of H_2 by about 100 mTorr did not enhance the line intensity, in contrast with the case of the CF^+ ion [18]. The signal strength increased with the discharge current until it was saturated at about 800 mA peak-to-peak, at which most measurements were carried out. The optimum frequency for the discharge modulation was 2.84 kHz. Higher frequencies around 10 kHz were also tested resulting in a slightly better signal to noise ratio. However, the discharge was rather unstable with occasional spiky noises. The intensity of the ion signals was not much affected by the change of the cell temperature from 0 to $-78\,^\circ C$.

Thirty-one lines in the R and P branches of the fundamental band and three lines in the R branch of the $v=2\leftarrow1$ hot band for the normal species were observed in the frequency range 973–1094 cm^{-1}. Several lines for the less abundant isotopic species, $^{29}SiF^+$ (4.7%) and $^{30}SiF^+$ (3.1%), were also observed. However, no exhaustive search has been attempted for the transitions in the hot band or those for the isotopic species.

The R(2)–R(51) and P(31)–P(45) transitions were assigned for the $^{28}SiF^+$ fundamental band. Observation of the low-J P-branch lines in the range of 998–1040 cm^{-1} was prevented by the very intense ν_3 band of SiF_4, which totally absorbed infrared radiation in this region. However, in the other ranges, the SiF^+ lines were easily discriminated from crowded SiF_4 lines, because, by virtue of the discharge modulation, the two kinds of lines were recorded with opposite signs as shown in fig. 2, corresponding to production and destruction of SiF^+ and SiF_4, respectively, by the discharge. Fig. 3 shows

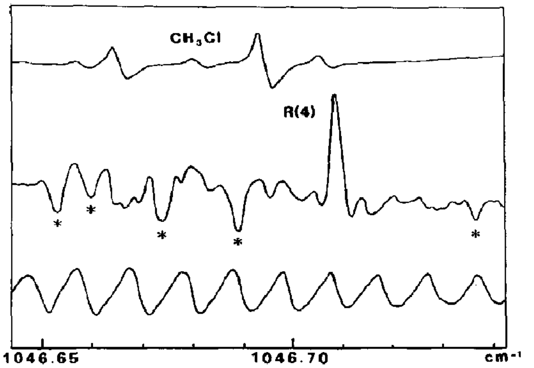

Fig. 2. Observed spectrum for the R(4) line of the SiF^+ ion. The SiF_4 lines (asterisked) are observed with signs opposite to that for the ion line. The spectrum of CH_3Cl (top) and the etalon fringe (bottom) were used for the wavenumber calibration.

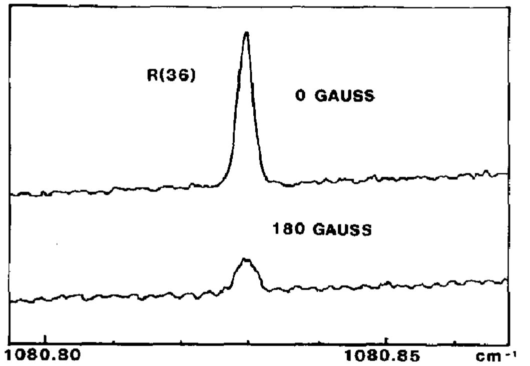

Fig. 3. Magnetic field effect on the R(36) line of SiF^+. The spectrum was observed by discharge modulation with 800 mA p–p current.

a typical trace for the R(36) line of the normal species. The signal-to-noise ratio was fairly high, e.g. about 100 for the strongest lines of the normal species.

When a dc magnetic field of about 180 G was applied along the axis of the cell, the line intensity decreased to about one fifth, as shown in the lower trace of fig. 3, and at about 220 G the ion lines almost disappeared. However, the lines for the neutral species, SiF_4, hardly lost their intensities. The magnetic field effect on the observed lines strongly supports that the newly identified species is an ion.

Spectra of the SiF and SiF_2 radicals in the 800–950 cm^{-1} range were also observed in the glow discharge of SiF_4 using the present hollow cathode absorption cell. These spectra were nearly as intense as those observed in our previous experiment with a positive column cell [7]. The hollow cathode cell did not enhance the signal intensity appreciably. On the contrary, the SiF^+ lines were only observed with the hollow cathode cell, but not with the positive column cell.

Table 1 lists the observed SiF^+ lines with their assignments. The measured wavenumbers are accurate to 0.0005 cm^{-1}. These wavenumbers were least-squares fitted to the energy formula for a diatomic molecule in the $^1\Sigma$ electronic state,

$$E_{v,J}=E_v+B_vJ(J+1)-D_vJ^2(J+1)^2\,, \qquad (1)$$

where v and J denote vibrational and rotational quantum numbers, respectively. The optimized molecular constants are listed in table 2. The standard deviation of the fit was about 0.0005 cm^{-1}, consistent with the experimental accuracy. The three lines observed at 1053.8919, 1073.2816, and 1074.1448 cm^{-1} were assigned to R(19), R(39), and R(40) transitions in the $v=2\leftarrow1$ hot band. From these lines, the hot band origin was determined to be 1030.5908 ± 0.0005 cm^{-1}, where all other constants were fixed at the values given by the present diode laser spectroscopy and the microwave study [11]. The observed spectra for the less abundant isotopic species have not been analyzed.

4. Discussion

The rotational assignments for the vibration–rotation band of a $^1\Sigma$ diatomic molecule may be unambiguously determined by confirming a missing line at the band origin. In diode laser spectroscopy, however, this method is often hampered by the discontinuous frequency coverage of the diode, which was unfortunately the case in the present study. The assignment in table 1, which turned out to be correct, was made based on the following relation among the equilibrium rotational constant B_e, centrifugal distortion constant D_e, and the harmonic frequency ω_e,

$$D_e=4B_e^3/\omega_e^2\,. \qquad (2)$$

Table 1
Observed spectrum (in cm^{-1}) of SiF^+ in the X $^1\Sigma^+$ state

Transition	Observed	Obs. – calc. [a]	Transition	Observed	Obs. – calc. [a]
$v=1\leftarrow0$ band					
P(45)	974.2028	–2	R(10)	1053.8727	5
P(44)	975.8675	3	R(14)	1058.4535	–3
P(42)	979.1705	–1	R(17)	1061.7875	6
P(40)	982.4404	0	R(21)	1066.0938	–6
P(39)	984.0629	3	R(23)	1068.1901	11 [c]
P(38)	985.6759	–5	R(25)	1070.2433	–6
P(36)	988.8790	6	R(28)	1073.2516	2
P(35)	990.4666	–1	R(29)	1074.2341	3
P(33)	993.6166	–7	R(32)	1077.1210	2
P(31)	996.7342	–6	R(33)	1078.0627	–2
			R(36)	1080.8286	1
R(2)	1044.2485	–3 [b]	R(37)	1081.7295	–4
R(3)	1045.4855	4	R(41)	1085.2329	–4
R(4)	1046.7112	–7	R(42)	1086.0838	4
R(6)	1049.1367	–3	R(46)	1089.3808	1
R(7)	1050.3350	–2	R(51)	1093.2679	0
$v=2\leftarrow1$ band					
R(19)	1053.8919	0	R(40)	1074.1448	–3
R(39)	1073.2816	3			

[a] Observed minus calculated frequency in 10^{-4} cm^{-1}. [b] Not included in the analysis. [c] Less weighted in the analysis.

Table 2
Molecular constants of SiF^+ in the X $^1\Sigma^+$ state [a]

Constant	Ground	$v=1$
B_v (cm^{-1})	0.637010(15)	0.632311(15)
D_v (10^{-6} cm^{-1})	0.9466(46)	0.9442(44)
ν_0 ($v=1$–0) (cm^{-1})	1040.48328(61)	
ν_0 ($v=2$–1) (cm^{-1})	1030.59082(46)	

[a] Figures in parentheses are three standard deviations in units of the last digit.

With a tentative rotational assignment, the least-squares fit yields the rotational and centrifugal distortion constants in the ground and first excited vibrational states, from which B_e and D_e may be derived. The fit also yields the fundamental band origin, from which we may derive ω_e if the $\omega_e x_e$ constant is assumed. In an early stage of the analysis, we estimated $\omega_e x_e = 5.34$ cm^{-1}, which was sufficiently accurate, from the corresponding values of SiF [19] and SiO [20]. For the correct rotational assignment, the centrifugal distortion constant calculated according to eq. (2) should agree with the D_e value derived from the fit. The assignment in table 1 gives a satisfactory agreement between the calculated value 28.38 kHz and the value derived from the fit, 28.41±0.22 kHz. However, if we change the assignment so that the J numbers of the R branch transitions in table 1 are decreased or increased by unity, less satisfactory results are obtained: the calculated value 27.68 kHz compared with 28.34±0.22 kHz derived from the fit for the former case, and the calculated value 29.06 kHz compared with 28.48±0.22 kHz derived from the fit for the latter case.

Rotational constants determined by microwave spectroscopy [11], which are now available, confirm the present assignment more definitely, because they are consistent with the values obtained in the present study (table 2). A different assignment would have resulted in a large discrepancy.

The molecular constants of the SiF^+ ion obtained in the present study are compared in table 3 with those for SiF [7,19] and SiO [20], the latter being isoelectronic with SiF^+. The results of the ab initio calculations [9,10] are also included for comparison. The harmonic frequency $\omega_e = 1050.3757 \pm 0.0013$ cm^{-1} and the harmonic constant $\omega_e x_e = 4.9462 \pm 0.0004$ cm^{-1} were derived from the ob-

Table 3
Equilibrium molecular constants of SiF^+ in the $X\ ^1\Sigma^+$ state [a]

Constant	SiF^+		SiF [7,19]	SiO [20]
	present	ab initio [10]		
B_e (cm^{-1})	0.639360(23)	0.6261	0.581241(2)	0.7267526(4)
α_e (cm^{-1})	0.004699(21)	0.0012	0.004997(4)	0.0050379(5)
$10^6 D_e$ (cm^{-1})	0.9477(73)		1.0625(75)	0.9923(58)
r_e (Å)	1.52652(8)	1.543	1.601019(3)	1.5097371(4)
ω_e (cm^{-1})	1050.3757(13)	1114.4	875.20(10)	1241.5430(15)
$\omega_e x_e$ (cm^{-1})	4.9462(4)		4.735(45)	5.9739(8)
$10^2 k_e$ (N/m)	7.35519(2)		4.8986(11)	9.24225(2)

[a] Figures in parentheses are three standard deviations in units of the last digit.

served band origins. The equilibrium bond length r_e of the SiF^+ ion is 1.52652 ± 0.00008 Å, which is shorter by 0.0745 Å than that for SiF, but longer by 0.0168 Å than that for SiO. The quadratic force constant of SiF^+, $k_e = 7.355$ mdyn/Å, is larger by 50% and smaller by 20%, respectively, than those of SiF and SiO. Removement of an unpaired electron from an anti-bonding π orbital of SiF to form the SiF^+ ion strengthens the Si–F bond resulting in the shorter bond length and the greater force constant. The SiF^+ ion has a slightly weaker bond than that of isoelectronic SiO.

The ab initio calculation by Karna and Grein [10] gave a vibrational frequency higher by about 6% and a bond length longer by about 0.016 Å than the present experimental values.

Petrmichl et al. [11] observed the microwave spectra of SiF^+ in vibrational states up to $v = 15$ for the normal species, and up to $v = 4$ and $v = 3$ for the $^{29}SiF^+$ and $^{30}SiF^+$ species, respectively. They obtained accurate mass-independent Dunham coefficients. The molecular constants derived from these coefficients agree satisfactorily well with those determined in the present work. The present diode-laser study gave very accurate values of the harmonic frequency and the $\omega_e x_e$ constant, which are also consistent with the values derived from the microwave results, $\omega_e = 1050.74 \pm 0.20$ cm^{-1} and $\omega_e x_e = 5.03 \pm 0.20$ cm^{-1} [11].

The hollow cathode discharge modulation method was successfully applied to the detection of SiF^+ in the glow discharge of SiF_4 by infrared diode laser spectroscopy. The magnetic field effect on the SiF^+ lines was clearly demonstrated, which was similar to that observed for H_3^+ [13], HCO^+ [14], CF^+ [18], CO_2^+ [21], etc.

In situ spacially resolved detection of the SiF^+ ion in the plasma etching and sputtering processes by infrared spectroscopy may be practicable by the use of the present spectral data.

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