Experimental Determination of the Structure of SiF$_2$ in Its Excited Triplet State

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Abstract: Laser-induced phosphorescence excitation spectra of SiF$_2$ in the gas phase have been obtained by the pyrolysis jet technique. Vibrational analysis gives a value of $v'_2 = 278.2$ cm^{-1} and ground state vibrational frequencies in good agreement with literature values. The 0^0_0 band at 380 nm has been recorded with sufficient resolution to observe most of the rotational structure. Rotational analysis establishes that the upper state has $^3B_1$ symmetry with an r_0 structure of r(SiF) $= 1.586 \pm 0.001$ Å and $\angle$(FSiF) $= 113.1 \pm 0.1°$. The upper state spin constants and spin splittings are small, as expected for a nonlinear molecule composed of light atoms. Analysis of the intensity distribution among the rotational branches in the 0^0_0 band shows that the triplet—singlet transition gains its intensity primarily by spin—orbit coupling with excited $^1B_2$ states. A nonradiative decay channel opens up for excited state vibrational energies in excess of two quanta in the bending mode.

Introduction

The divalent compounds of group IVA elements have received considerable experimental and theoretical attention over the last three decades. In particular, the triatomic carbenes, silylenes, and germylenes have been extensively studied[1-5] owing to their importance as intermediates in a large variety of reactions. With the important exception of methylene (CH$_2$), the triatomic carbenes, silylenes, and germylenes have singlet ground states. Extensive theoretical calculations have shown that such species have a relatively low-lying first excited electronic state of triplet multiplicity, formed by promotion of a σ-type electron to an unoccupied pπ-type orbital. The same electron promotion can also form the corresponding first excited singlet state, which lies above the triplet state. The ground state to first excited singlet state transitions of many of these species have been thoroughly studied, as they are spin-allowed and usually quite intense. In contrast, the electronic transitions from the ground singlet state to the excited triplet state are spin-forbidden and generally very weak. Consequently, experimental studies of the excited triplet states are rare and usually only provide information about the excited state vibrational energy levels. To our knowledge, rotationally resolved triplet—singlet spectra of the carbenes, silylenes, or germylenes have not been previously reported, and the excited triplet state geometries have not been experimentally determined.

In recent years, we have shown that it is possible to obtain supersonic expansion-cooled laser-induced phosphorescence

(LIP) spectra of the triplet—singlet transitions of GeF$_2$[6] and GeCl$_2$.[7] Unfortunately, the large moments of inertia and the plethora of naturally abundant germanium isotopes precluded the observation of resolved rotational structure in these molecules. The stability of the germylene species, the enhancement of the singlet—triplet transition strength by spin—orbit effects, and a ground state to triplet state energy gap favorable for laser excitation all contributed to the success of these studies. Similar experiments with the carbenes are less feasible, because few of the transitions occur in the visible and the transition strengths are likely to be too weak for direct excitation. However, in the present work we have succeeded in recording the jet-cooled laser-induced phosphorescence spectrum of difluorosilylene, due to its relative stability and our ability to produce it in high yield.

There is a voluminous literature on the chemical and physical properties of difluorosilylene (silicon difluoride, SiF$_2$).[8] It is readily prepared in a flow system by the reaction of SiF$_4$ with hot silicon[9] or by pyrolysis of hexafluorodisilane.[10] SiF$_2$ prepared by these methods has a much longer gas-phase lifetime and is much less reactive than the triatomic carbenes. It has been shown to be a versatile reagent that reacts with organic and inorganic compounds to produce a wide variety of unique and interesting products. Most importantly, SiF$_2$ has been shown to be an intermediate in a variety of semiconductor fabrication processes,[11-14] which has fueled continued interest in its properties.

There have been extensive spectroscopic studies of the ground and first excited singlet states of SiF$_2$. Analyses of the

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microwave[15−18] and infrared[19,20] absorption spectra have established the equilibrium ground state geometry and molecular constants for the excited vibrational states of the fundamentals. The transition to the first excited singlet state at 227 nm has been studied by absorption[21,22] and emission[23] techniques, providing detailed information about the excited state symmetry, geometry, and vibrational frequencies. Electronic excitation results in a small increase (0.011 Å) in the SiF bond length and a large (15.1°) increase in the bond angle.

The triplet−singlet transition is much less well-known. In 1970, Rao[24] reported a low-resolution emission spectrum in the 418−365-nm region obtained from an electric discharge through SiF$_4$. The vibrational structure was analyzed, showing that the lower state was the ground state. An upper state bending frequency of 277 cm^{-1} and an electronic state separation of 26 310 cm^{-1} were obtained and the band system was assigned as involving the first excited triplet state. In later work, Lin and co-workers[25] observed the direct triplet−singlet transition by resonance enhanced multiphoton ionization (REMPI) methods, confirming the assignments from the emission spectrum.

There have been a few theoretical predictions of the properties of the first excited triplet state of SiF$_2$.[26−29] The most recent and detailed of these[29] obtained an adiabatic excitation energy of 3.01 eV, compared to Rao's experimental value of 3.26 eV, with a bond length of 1.586 Å and a bond angle of 113.1°. All of the available calculations suggest that the triplet−singlet transition occurs around 380 nm, the excited state is of $^3B_1$ symmetry, and the bond angle increases substantially on excitation.

Experimental Section

Two methods of producing SiF$_2$ and observing laser-induced phosphorescence were attempted. The first was conducted without jet cooling and involved flowing the products of the reaction of SiF$_4$ with elemental silicon at 1200 °C through a vacuum chamber at low pressures (20−60 mTorr). Low-resolution, rotationally congested LIP spectra of SiF$_2$ were successfully observed under these conditions. Subsequently, jet-cooled spectra were obtained using the pyrolysis jet technique previously described.[30] Briefly, Si$_2$F$_6$, cooled to −78 °C to decrease its vapor pressure, was seeded in 1.0−1.5 atm of argon, passed through a pyrolysis zone heated to 750 °C, and expanded into vacuum through a 300-μm nozzle.

Laser-induced emission spectra were obtained by exciting the products of the high-temperature reactions with the beam from a pulsed, tunable dye laser (Lumonics Hyperdye-500, line width 0.1 cm^{-1}). The resulting emission was imaged through appropriate cutoff filters onto the photocathode of an EMI 9816QB photomultiplier. The pulsed signals were processed with gated integrators. Low-resolution room

Table 1. Experimental and *ab Initio* Values for the Ground and Excited State Geometric Parameters and Vibrational Frequencies of SiF$_2$

	ground state		triplet ($^3B_1$) state		singlet ($^1A_1$) state	
	expt	theory[a]	expt	theory[a]	expt[b]	theory[a]
r(SiF)	1.5901[c]	1.599	1.586(1)[d]	1.586	1.601	1.611
∠(FSiF)	100.77	101.0	113.1(1)[d]	113.1	115.9	115.5
ν_1 (sym str)	855.01[e]	834		886		828
ν_2 (bend)	343.1[f]	359	278.2[f]	288	250	253
ν_3 (asym str)	870.40[e]	880		1030		979

[a] MRSDCI *ab initio* calculations, ref 29. Bond lengths in Å, angles in deg, vibrational frequencies in cm^{-1}. [b] High-resolution absorption spectrum, ref 22. [c] Equilibrium structure, ref 17. [d] Effective (r_0) structure, this work. [e] Gas-phase IR, ref 19. [f] Harmonic vibrational frequency, this work.

temperature and jet-cooled spectra, digitized at 0.2 cm^{-1} intervals, were wavelength calibrated with optogalvanic lines from various neon- and argon-filled hollow cathode lamps. High-resolution jet-cooled spectra were obtained in 5−10-cm^{-1} segments by angle tuning an etalon within the cavity of a dye laser (Lambda Physik FL 3002E). The spectra were digitized at 0.003-cm^{-1} intervals and calibrated to an accuracy of ±0.005 cm^{-1} using the Raman shifting technique described elsewhere.[31] The laser-induced emission spectra and calibration lines were digitized and recorded simultaneously on a data acquisition system of our own design.[32]

Hexafluorodisilane was prepared by the fluorination of hexachlorodisilane by reaction with either ZnF$_2$[33] or SbF$_3$.[34] The latter method proved more efficient and involved freezing 10 g of Si$_2$Cl$_6$ under vacuum with liquid nitrogen on the surface of 200 g of thoroughly dried SbF$_3$. The container was sealed and allowed to warm to room temperature. The volatile products were trap-to-trap distilled, leaving essentially pure Si$_2$F$_6$ as a white solid at −131 °C.

Results and Analysis

A. Vibrational Structure. Difluorosilylene is a bent molecule of C_{2v} symmetry with three nondegenerate normal modes of vibration. The known experimental values for the vibrational frequencies and geometric parameters of SiF$_2$ in the ground and lowest excited states and the corresponding *ab initio* predictions are summarized in Table 1. As expected by comparisons with the trends on excitation to the first excited singlet states of various carbenes and silylenes, SiF$_2$ is predicted to undergo a large increase in bond angle (12°) on excitation, with only a small decrease in the bond length. Franck−Condon considerations suggest that the T$_1$ ← S$_0$ spectrum should exhibit pronounced progressions in the excited state bending mode.

Preliminary experiments without jet-cooling using the conventional high-temperature reaction of SiF$_4$ with silicon[9] as a source of SiF$_2$ showed that it is possible to observe the LIP spectrum of SiF$_2$ at modest pressures. Figure 1 illustrates a typical spectrum scanned over the range of one laser dye, showing two broad bands with extensive unresolved rotational structure. These features have maxima at 26 320 and 26 598 cm^{-1}, in agreement with the emission band head measurements of the 0^0_0 and 2^1_0 bands assigned by Rao.[24] The rotational congestion is relieved by jet-cooling, resulting in the spectrum shown in Figure 2. The most prominent progression in the spectrum involves an interval of about 278 cm^{-1}, readily assigned as the upper state bending frequency (ν'_2). It is important to note that the upper state bending progression shows an abrupt decrease in intensity above two quanta of ν'_2, as shown

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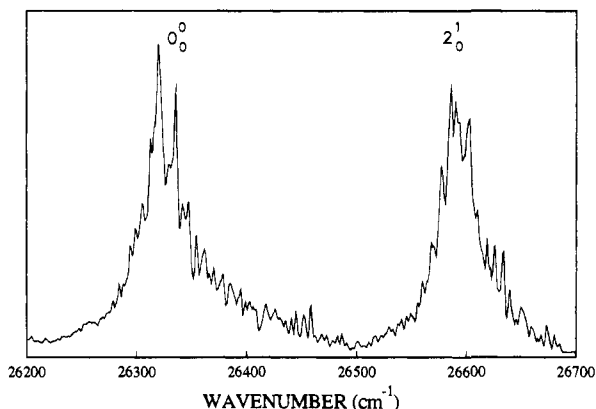(29) Cai, Z. L.; Bai, J. L. *Chem. Phys.* **1993**, *178*, 215.

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Figure 1. Low-resolution room temperature laser-induced phosphorescence excitation spectrum of SiF_2. The spectrum is uncorrected for variations in laser power across the tuning range. SiF_2 was generated in a flow system by the reaction of SiF_4 with elemental silicon at 1200 °C.
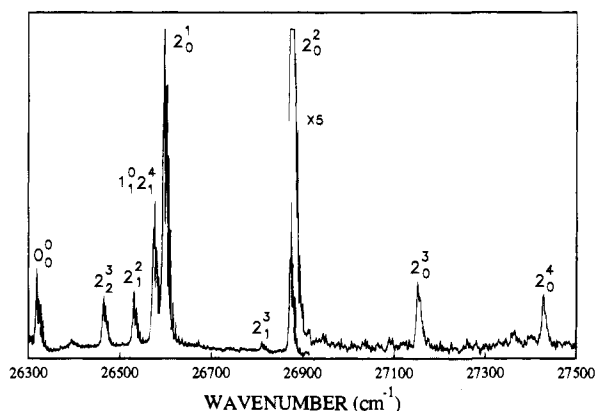
Figure 2. Low-resolution, jet-cooled LIP spectrum of SiF_2, obtained by pyrolysis of Si_2F_6. The spectra were obtained over the tuning range of two laser dyes and are uncorrected for variations in laser intensity. Note the change of scale at about 26 900 cm^{-1}; the 2_0^3 and 2_0^4 bands are much weaker than the other cold bands in the spectrum.

in Figure 2. It proved quite difficult to observe the 2_0^3 and 2_0^4 bands, and we were unsuccessful in recording any bands to shorter wavelengths. A substantial number of weaker bands in the spectrum are found to differ from the most prominent features by an interval of ca. 345 cm^{-1}, which is the ground state bending frequency.[21,22] The weaker bands are then "hot" bands, originating from excited vibrational levels in the ground state owing to the high source temperature in the pyrolysis jet. An additional set of hot bands was identified involving ground state excitation of a quantum of the symmetric SiF stretching mode ($v_1 = 855$ cm^{-1}) . We were unable to identify any intervals in the spectrum as involving the excited state symmetric stretching mode (v_1'). The vibrational assignments are summarized in Table 2, along with the calculated values obtained by fitting the observed band maxima to the anharmonic expression[35]

$$\bar{\nu} = T_{00} + \omega_2^0 v_2' + x_{22}^0 v_2'^2 - (\omega_1^{0''} v_1'' + \omega_2^{0''} v_2'' + x_{12}^{0''} v_1'' v_2'') \quad (1)$$

As expected, the observed band maxima can be fit with only moderate fidelity to such an expression, since we do not have precise band origins or sharp band heads in the spectra and the

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Table 2. Vibrational Assignments and Band Maxima of the Observed Vibronic Bands of the $T_1 \leftarrow S_0$ Band System of SiF_2

assign	band max^a	obs − calc^b
$1_1^0 2_1^3$	25960	0.8
2_1^0	25976	−0.4
$1_1^0 2_1^4$	26236	−0.5
2_1^1	26254	−0.5
$1_1^0 2_0^3$	26301	1.3
0_0^0	26320	0.5
2_2^3	26465	−1.8
2_1^2	26532	−0.3
$1_1^0 2_0^4$	26576	−1.0
2_0^1	26598	0.4
2_1^3	26812	2.2
2_0^2	26875	−0.4
2_1^4	27090	2.9
2_0^3	27152	−0.9
2_0^4	27429	−1.2

^{a} All values in cm^{-1}. Very weak unassigned features were observed at 26 394 and 27 364 (2_1^5?) cm^{-1}. ^{b} Calculated values using eq 1 and the constants $T_{00} = 26319.5(11)$, $\omega_2^{0'} = 278.2(11)$, $\omega_1^{0''} = 853.2(14)$, $\omega_2^{0''} = 343.09(76)$, $x_{22}^{0'} = -0.13(26)$, $x_{12}^{0''} = -2.6(18)$. The values in parentheses are standard errors of 1σ.
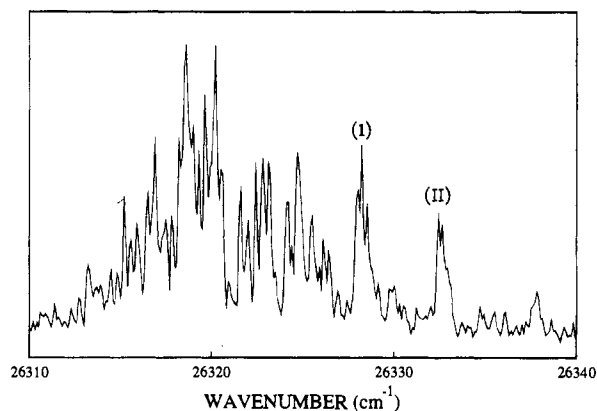
Figure 3. Partially rotationally resolved spectrum of the 0_0^0 band of the $\tilde{a}^3B_1 - \tilde{X}^1A_1$ transition of SiF_2. The labels (**I**) and (**II**) refer to certain unresolved rotational branches, as discussed in the text.

unresolved rotational structure contributes to uncertainty in locating the maxima. However, the resulting constants (Table 2) are reasonable and reproduce the observed positions of the low-resolution vibronic bands to about the experimental precision.

B. Rotational Structure. Even at moderate resolution, the SiF_2 bands show clear rotational subband structure, as illustrated for the 0_0^0 band in Figure 3. The partially resolved features labeled (**I**) and (**II**) are reminiscent of the R-form ($\Delta K_a = +1$) R branches seen in the S_1-S_0 jet-cooled spectra of the triatomic carbenes such as CCl_2[36] and $CClF$.[37] We were able to record the jet-cooled 0_0^0 band at sufficiently high resolution to resolve most of the rotational structure. The band is complicated, even at the estimated temperature of 6 K, as might be expected for a triplet−singlet transition. The rotational analysis of this band proved to be the most challenging aspect of this work and provided the most information about the excited triplet state.

In the ground state, SiF_2 is a bent planar asymmetric top with the b rotational axis bisecting the FSiF angle, the a axis in the molecular plane perpendicular to the b axis, and the c axis is perpendicular to the molecular plane. *Ab initio* calculations[27-29]

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and the analysis of the singlet—singlet transition of SiF_2 at higher energies[19] all suggest that the first excited triplet state should be of B_1 symmetry. As SiF_2 is a nonlinear molecule composed of relatively light atoms, we anticipate that the effect of the unpaired electron spins on the energy levels will be fairly small, analogous to Hund's case *(b)* in diatomic molecules. This expectation has been found to be true for most asymmetric top molecules whose triplet—singlet spectra have been rotationally analyzed, including formaldehyde,[38] thioformaldehyde,[38] sulfur dioxide,[39] and glyoxal.[40]

In the triplet state, the electron spin angular momentum couples weakly to the principal inertial axes, yielding three closely spaced spin levels for most rotational states. Four quantum numbers, J, N, K_a and K_c, are necessary to describe the energy levels. N is the quantum number for the total rotational angular momentum, which excludes spin, and is analogous to J in the ground state. J is the quantum number for the total angular momentum (rotational plus electron spin) and takes the values $N - S$, N, and $N + S$, where the triplet state spin angular momentum quantum number $S = 1$. The three components of the same N but different J are usually labeled F_1 [$J = N + 1$], F_2 [$J = N$], and F_3 [$J = N - 1$]. K_a and K_c are the usual quantum labels for the energy levels of an asymmetric top.

Raynes[41] has demonstrated how the energy levels of an asymmetric top molecule in a triplet state can be calculated in a form suitable for the analysis of spectra. For molecules of orthorhombic symmetry (C_{2v}, D_{2d}, and D_{2h}), the energies depend on the rotational constants A, B, and C, which are related to the moments of inertia in the usual fashion, and on a set of five spin constants α, β, a_0, a, and b, along with the usual centrifugal distortion constants Δ_K, δ_K, etc. The spin constants α and β describe the electron spin—spin interaction and higher-order spin—orbit effects, while a_0, a, and b account for the spin—molecular rotation interaction. In the absence of molecular rotation, as would be the case for a triplet state molecule isolated in a matrix, α and β are directly related to the D and E spin constants determined from zero-field splittings in electron spin resonance experiments.

Hougen[42] has shown that only the direct product of the vibronic species of the combining singlet and triplet states ($^3\Gamma_{ev} \times {}^1\Gamma_{ev}$) needs to be considered in determining the rotational selection rules of triplet—singlet transitions in near symmetric top molecules with small spin splittings. In this case, we have $B_1 \times A_1 = B_1$, which leads to the selection rule $\Delta K_a = \pm 1$ along with the general selection rules $\Delta J = 0$, ± 1 and $\Delta N = 0$, ± 1, ± 2, resulting in various O-, P-, Q-, R-, and S-form branches. The rotational branches are designated by the notation $^{\Delta K_a \Delta N}\Delta J_{Fi}(J'', K''_a)$. The resulting spectrum is analogous to a C-type singlet-singlet band with additional O- and S-form branches, as discussed in more detail by Brand, *et al.*[43] in their analysis of the triplet—singlet spectrum of sulfur dioxide.

Although forbidden by the $\Delta S = 0$ selection rule, triplet—singlet transitions acquire intensity by mixing of the triplet state spin—vibronic wave functions with other singlet states of the same symmetry through spin—orbit interactions. The transition moment integral for the triplet—singlet transition is

$$\mu = \langle {}^3\Gamma_{ev} \times \Gamma_{spin} | \hat{M} | {}^1\Gamma_{ev} \rangle \qquad (2)$$

where $^3\Gamma_{ev}$ is the vibronic symmetry of the triplet state spatial wave function, Γ_{spin} is the symmetry of the triplet spin function, $\hat{M}$ is the transition dipole moment operator, and $^1\Gamma_{ev}$ is the vibronic symmetry of the ground state. For SiF_2, the three triplet spin functions have symmetries A_2, B_1, and B_2 and the transition moment integral (eq 2) is nonvanishing for two of the triplet spin functions

$$\mu_a = \langle {}^3B_1 \times A_2 | \hat{M}_a | {}^1A_1 \rangle \qquad (3)$$

and

$$\mu_b = \langle {}^3B_1 \times B_1 | \hat{M}_b | {}^1A_1 \rangle \qquad (4)$$

where $\hat{M}_a$ and $\hat{M}_b$ are the transition dipoles oriented along the a and b rotational axes (y and z Cartesian axes), respectively. In this case, Hougen has shown[42] that the rotational line intensities are functions of the rotational quantum numbers of the singlet state and combinations of the two independent transition moments which can take on any real values. The μ_a and μ_b transition moments are nonvanishing for mixing of the triplet state wave functions with singlet states of B_2 and A_1 electronic symmetry, respectively. In SiF_2, the rotational line intensities are also affected by nuclear statistical weights associated with the two identical fluorine nuclei, leading to an expected 3:1 intensity alternation in many of the rotational branches.

With the above considerations in mind, we proceeded with the rotational analysis of the 0_0^0 band of SiF_2. First, the ground state constants were redetermined by least-squares fitting of Watson's A reduction of the asymmetric top rotational Hamiltonian in the I^r representation to the 75 microwave transitions reported by Rao and Curl.[16] Then, using a graphical computer program of our own design,[44] we first calculated an approximate spectrum using the known ground state rotational constants, estimates of the upper state rotational constants from an *ab initio* prediction of the geometry,[29] the spin constants and transition moments obtained experimentally for SO_2,[39] and an estimated rotational temperature of 6 K. This trial spectrum matched the general features of the SiF_2 spectrum surprisingly well, allowing us to make initial assignments of the stronger rotational lines. The high wavenumber end of the spectrum showed simple rotational branch structure with partially resolved spin splittings, as illustrated in Figure 4. The individual rotational lines in the previously unresolved branches (I) and (II) shown in Figure 3 are readily distinguished in the high-resolution spectra of Figure 4. In each case, the pairs of lines labeled **A**, **B** and **C**, **D** are transitions from the same lower state rotational level to different spin components of the same upper state rotational level. Their energy separation is the spin splitting. In most of the spectrum, the spin splittings were barely resolved, as expected for small spin effects in the excited state. The analysis was complicated by extensive overlap of the individual transitions and the 3:1 intensity alternation which made it difficult to follow the branches. It was found that the observed rotational structure was entirely consistent with that expected for the triplet—singlet bands of SiF_2, both in terms of the operative selection rules and the relative intensities of the various lines.

Once a set of initial assignments was made, the upper state rotational and spin constants were refined by least-squares minimization of the sum of the squares of the observed minus calculated transition wavenumbers, keeping the ground state constants fixed. By boot-strapping up from our initial assign-

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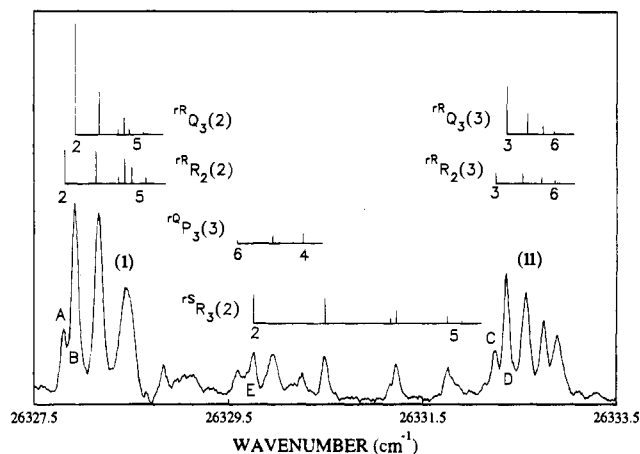(39) Hallin, K. E. J.; Hamada, Y.; Merer, A. J. *Can. J. Phys.* **1976**, *54*, 2118.

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Figure 4. A portion of the high-resolution LIF spectrum of the 0_0^0 band of SiF_2, showing the rotational assignments and calculated line positions and intensities. The branch notation is $\Delta K \Delta N \Delta J_{Fi}(K_a'')$ and the numbers below the vertical lines denote the lower state J. The labels **A, B, C, D, E, (I),** and **(II)** refer to particular features discussed in the text.

Table 3. Molecular Constants (cm⁻¹) for the Lowest Vibrational Levels of the Ground and First Excited Triplet States of SiF_2

	ground ($\tilde{X}^1A_1$) state[a]	triplet ($\tilde{a}^3B_1$) state[b]
A	1.020759(10)	1.36743(46)
B	0.2943172(31)	0.25324(48)
C	0.2278284(24)	0.21338(43)
$10^4\Delta_K$	0.1909(14)	0.0[c]
$10^5\Delta_{JK}$	−0.309(34)	0.0[c]
$10^7\Delta_J$	0.34(36)	0.0[c]
$10^6\delta_K$	0.68(14)	0.0[c]
$10^6\delta_J$	0.1169(46)	0.0[c]
10^9H_K	0.192(80)	0.0[c]
α		0.0473(55)
β		0.090(16)
T_0		26319.478(6)

[a] From a fit of 75 microwave transitions from ref 16. [b] From a fit of 181 assignments of the 0_0^0 band, standard deviation = 0.014 cm⁻¹. [c] Constant fixed in least-squares fitting.

ments, we found that most of the strong rotational transitions could be fit using only A, B, C, α, and the band origin T_0, which is the energy difference between the two vibronic states. However, it was necessary to include β in order to fit those transitions with upper state $K_a = 1$, as indicated by the spin-splitting expressions derived by Raynes.[41] Attempts were made to vary the other spin constants and some of the centrifugal distortion constants, but these were poorly determined and did not significantly improve the fit. The final standard deviation of fit for 181 assigned transitions was 0.014 cm⁻¹, about as good as could be expected for our experimental resolution and the extensive blending of transitions in the spectrum. The molecular constants for the ground and excited states are presented in Table 3.

Although only the wavenumbers of the assigned transitions were least-squares fit, we used calculated spectra including intensities at all stages of the analysis to ensure the validity of the assignments. For intensity calculations, it was necessary to estimate the rotational temperature and the relative values of the two transition moments, μ_a and μ_b. The rotational temperature was obtained from the jet expansion conditions and our experience with other pyrolysis jet spectra to be about 6 K. The transition moments were evaluated by a judicious choice of rotational lines in the spectrum and consideration of the rotational line intensity expressions given by Hougen.[42] The $^{rR}Q_3(2,2)$ and $^{rS}R_3(2,2)$ rotational transitions (lines **A** and **E** in
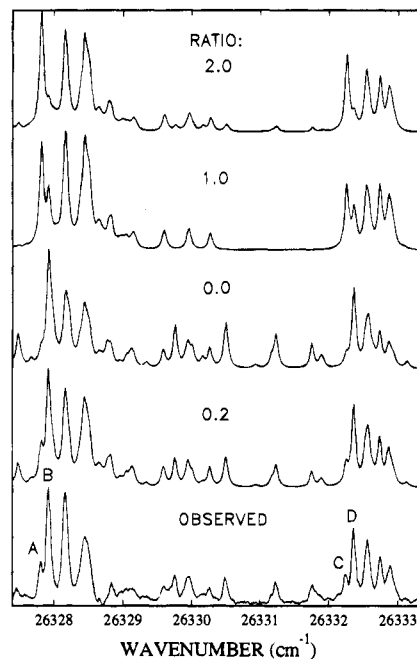
Figure 5. A comparison of calculated and observed spectra as a function of the ratio of transition moments μ_b/μ_a. Note the pronounced intensity variation of the pairs of lines **A, B** and **C, D** with changes in the ratio of the transition moments.

Figure 4) have the following calculated relative intensities:

$$\text{intensity (line } \mathbf{A}) = 0.625(2\mu_a)^2 \qquad (5)$$

$$\text{intensity (line } \mathbf{E}) = 0.417(\mu_b - \mu_a)^2 \qquad (6)$$

where the numerical factors are calculated for lower state $J = 2$ and $K = 2$ and the Boltzmann factors can be neglected since the lower state is the same for both lines. Experimentally, line **A** is 3.9 times stronger than line **E**. Since the intensity of the weaker line **E** is governed by the *difference* of the transition moments, it follows that the moments cannot have opposite signs. Otherwise, the intensity of **E** is calculated to be comparable or greater than that of **A**. The calculated rotational structure is very sensitive to the ratio of transition moments, as illustrated in Figure 5. Note that the relative intensities of the spin-split pairs of lines **A, B** and **C, D** are dramatically altered by changes in the ratio of transition moments. The optimum value obtained from simulations throughout the spectrum was $\mu_b/\mu_a = 0.2 \pm 0.05$.

The most stringent test of the intensity calculations is in the low wavenumber half of the band, where the overlap of rotational transitions is greatest. As shown in Figure 6, the agreement between the observed and calculated contours is quite acceptable. In most cases, even weak features in the calculated spectrum, often consisting of two or more overlapping transitions, can be found in the observed spectrum.

Discussion

The r_0 structure for the triplet state of SiF_2, calculated from I_a and I_b, is $r(SiF) = 1.586 \pm 0.001$ Å and $\angle(FSiF) = 113.1 \pm 0.1°$. This result is identical to the r_e structure prediction obtained by Cai and Bai[29] by means of multireference single and double excitation calculations with a double-ζ plus polarization basis set. Clearly, *ab initio* theory gives a good description of the excited triplet state of difluorosilylene.

All of the available data are consistent with assigning the 380 nm band system of SiF_2 to the $\tilde{a}^3B_1–\tilde{X}^1A_1$ electronic

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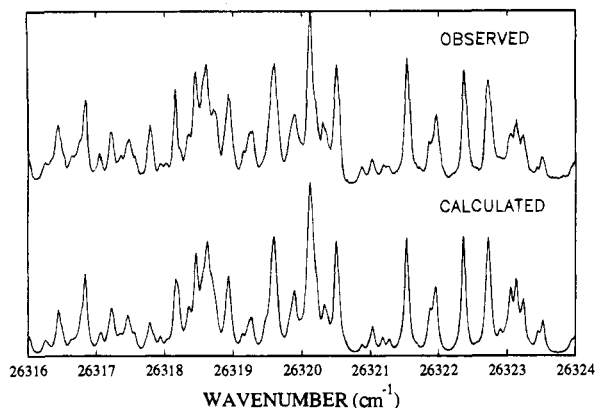
Figure 6. A comparison of the observed and calculated spectra for the low wavenumber end of the 0_0^0 band of the $\tilde{a}^3B_1 - \tilde{X}^1A_1$ system of SiF_2. The spectrum was calculated with a rotational temperature of 6 K and $\mu_b/\mu_a = 0.20$.

transition. The electronic excitation energy is 26 319.478 cm^{-1}, compared to *ab initio* values of 25 700[27] and 24 300[29] cm^{-1}. The experimental spectrum shows spin splittings in the upper state, and obeys $\Delta K_a = \pm 1$, $\Delta K_c = 0$, ± 2 selection rules, proving that the transition is $^3B_1-^1A_1$. Since the experimentally determined excited state geometry and bending frequency agree so well with theory (Table 1), we can conclude with certainty that the upper state is $\tilde{a}^3B_1$.

The ratio of the transition moments determined experimentally $(\mu_b/\mu_a = 0.20 \pm 0.05)$ is similar to that of SO_2 $(0.12 \pm 0.04)^{[39]}$ and means that spin—orbit coupling with excited states of $^1B_2$ symmetry predominates. A strong electric dipole allowed electronic transition has been observed at 62 214 cm^{-1} (161 nm),[45,46] in agreement with *ab initio* predictions for the $^1B_2-\tilde{X}^1A_1$ electronic transition.[29] The weaker μ_b transition moment comes from mixing with $^1A_1$ excited states, which are predicted to be much higher in energy,[26] and have not been observed experimentally. Because the mixing of the triplet state with other excited singlet states is inversely proportional to the energy difference between the two states, it is likely that mixing with the $^1B_2$ (π,π^*) state at 161 nm is largely responsible for the strength of the triplet—singlet transition in SiF_2.

The spin constants α and β obtained from the rotational analysis of the 0_0^0 band can be related to the zero-field splittings one would normally obtain from an ESR spectrum of triplet state molecules frozen in a rigid matrix. The interaction of an unpaired electron with the magnetic fields associated with its own orbital motion (spin-orbit interaction), with the magnetic fields created by the orbital motion of the other electrons (spin—other-orbit interaction), and the direct magnetic dipole—dipole interactions between unpaired electron spins (spin-spin interac-

tion) lead to the splitting of the triplet state into three nondegenerate, spin components in the nonrotating molecule. In ESR spectroscopy the spin Hamiltonian is

$$\hat{H} = g\beta_e S \cdot H + DS_Z^2 + E(S_X^2 - S_Y^2) \qquad (7)$$

which at zero field depends only on the parameters D and E. Furthermore, these parameters give the relative energies of the three spin components as $D + E$, $D - E$, and 0. For orthorhombic molecules, D and E can be related to the gas-phase parameters of Table 3 by $\alpha = D/3$ and $\beta = E$, giving SiF_2 triplet state relative energies of 0.232, 0.052, and 0.0 cm^{-1}. The zero-field splittings of the triplet state spin components obtained in this way are relatively small, as expected for nonlinear molecules composed of light atoms and consistent with case *(b)* coupling in the excited state.

The $\tilde{a}^3B_1-\tilde{X}^1A_1$ band systems of $GeF_2^{[6]}$ and $GeCl_2^{[7]}$ show long progressions in the excited state bending mode, as expected for molecules whose bond angles change substantially on excitation. Similar behavior would be expected for the corresponding SiF_2 absorption spectrum, but the LIP spectrum exhibits an abrupt decease in intensity beyond the 2_0^2 band, with the 2_0^3 and 2_0^4 bands showing up only very weakly. A nonradiative decay channel must open up at excited state vibrational energies between two (555 cm^{-1}) and three (832 cm^{-1}) quanta of the bending mode. As the triplet state is very much lower than the energy of any possible dissociation products,[47] the ground state must be involved in the abrupt decrease in the phosphorescence yield.

Conclusion

We have observed the rotationally resolved triplet—singlet electronic transition of SiF_2 for the first time. Analysis of both the wavenumbers and intensities of the rotational transitions in the 0_0^0 band shows that the upper state is the $\tilde{a}^3B_1$ state, as predicted for many years by *ab initio* calculations. The upper state r_0 structure is $r(SiF) = 1.586 \pm 0.001$ Å and $\angle(FSiF) = 113.1 \pm 0.1°$, showing a slight (0.004 Å) decrease in the bond length and a large (12.1°) increase in the bond angle on excitation. The spin constants and spin splittings of the upper state are small, as expected for case *(b)* coupling. A nonradiative process dominates the excited state decay for levels above two quanta in the bending mode.

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