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A theoretical study of the electronic spectroscopy of the SiF₃ radical

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Abstract

A recent vacuum-UV fluorescence spectrum of SiF₄ [H. Biehl, K.J. Boyle, D.P. Seccombe, D.M. Smith, R.P. Tuckett, K.R. Yoxall, H. Baumgärtel, H.W. Jochims, J. Chem. Phys. 107 (1997) 720] has yielded information about the decay of electronically excited states of neutral fragments and the parent molecular cation. Emission in the visible region (λ > 380 nm) has been observed for an excitation energy of 13.0 eV with a lifetime of 3.9 ns, but the emitter was not assigned. Ab initio CASSCF calculations show that the observed emission is due to the A ¹A₁→X ¹A₁ transition in the SiF₃ radical. The experimental lifetime, however, is too short to be attributed to this radiative process. We suggest that the lifetime is dominated by rapid internal conversion of SiF₃ A ¹A₁ into high vibrational levels of the ground state. © 2001 Elsevier Science B.V. All rights reserved.

1. Introduction

The plasma etching of silicon wafers by fluorine-containing gases (e.g. CF₄) is an important technological process in the fabrication of micro-electronic devices. Etching proceeds by the formation of gas-phase products through ion-stimulated reaction between the wafer surface and reactive species generated by a radio-frequency discharge. The glow from such plasmas is due to emission from electronically excited species such as free radicals and molecular ions, and it is now established that the SiF₂ molecule plays an important role in the etching process [1,2]. SiF₂ has a well-established electronic spectrum, but the electronic spectroscopy of the SiF₃ radical is very poorly understood. Because no unambiguous optical sensor has been established, it is not clear if this radical plays any role in the fluorine-assisted etching of silicon.

The SiF₃ radical has pyramidal geometry, belonging to the C₃ᵥ symmetry point group. Despite its non-zero dipole moment, it is only recently that the microwave spectrum of this radical has been recorded [3]. All the observed transitions were a-type with ΔKₐ = 0. A unique geometry could not therefore be determined, but the B rotational constant was found to be 0.2505 cm⁻¹. No gas-phase infrared vibrational spectrum of SiF₃ has been reported. In the ab initio work reported in this Letter, we use an Si–F bond length of 1.59 Å and an F–Si–F bond angle of 108° for the electronic ground state [4] as the starting point for our calculations.

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There have been three reports of emission from SiF$_3$ in the UV/visible electronic region of the spectrum, but none has any high-resolution content. First, a broad band ($\lambda_{\text{peak}} = 632$ nm, f.w.h.m. = 240 nm) was observed in the red region of the visible from the reaction of F atoms with a single-crystal Si sample [1,2]. Second, Suto et al. [5] dispersed the emission induced from SiF$_4$ and SiF$_3$H [6], both photoexcited with fixed-wavelength vacuum-UV line sources between 90 and 100 nm. Two broad and unstructured bands, spanning the ranges 290–340 and 400–800 nm, were observed. They commented that these spectra showed some similarities with those of the CF$_3$ radical where discrete UV and unstructured visible bands are well characterised [7]. Third, undispersed emission in the range 380–ca. 650 nm was observed by one of us when SiF$_4$ was excited by tunable vacuum-UV radiation from a synchrotron source [8]. This emission was only observed in the range of excitation energies 12.4–13.6 eV, with a maximum at 13.0 eV and a threshold of 12.4 ± 0.1 eV. The excited state of SiF$_4$ populated at 13.0 eV is either a (3t$_2$)$^{-1}$3s or (1t$_1$)$^{-1}$3p Rydberg state [8]. This experiment confirmed data from an earlier synchrotron study with SiF$_4$ by Suto et al. [9] who, whilst not definitively assigning the emitter, determined the fluorescence cross section of the induced emission at 13.0 eV to be $5 \times 10^{-19}$ cm$^2$. Using the single-bunch, pulsed mode of the synchrotron, one of us has measured the lifetime of this visible emission to be $3.9 \pm 0.7$ ns [8].

In all cases, the strongest reason for assigning the visible emission band to the SiF$_3$ radical is not spectroscopic, but thermochemical. Using the enthalpies of formation of SiF$_3$ determined from a guided ion beam study of Fisher et al. [10], the ground states of SiF$_2$ and SiF are calculated to lie as high as 10.08 and 16.98 eV above the ground state of SiF$_4$, assuming the other dissociation products are F$_2$ and F$_2$ + F, respectively. Emission down to 400 nm (or 3.1 eV) is not compatible with either species being the emitter since the threshold energy of the emission is as low as 12.4 eV. The ground state of SiF$_3$, however, is calculated to lie much lower at 7.18 eV above the ground state of SiF$_4$ [8,10], so both the UV and visible emissions observed by Suto et al. [5] are energetically allowed for excitation energies in the range 12.4–13.6 eV. Unlike CF$_3$ [11], however, there have been no ab initio calculations on the energies and radiative lifetimes of excited states of SiF$_3$ to confirm these assignments. This Letter reports such calculations. We show that excited states of this radical do lie at energies consistent with the observations of Suto et al. [5] and Biehl et al. [8]. However, we calculate that the radiative lifetime of the upper state of an allowed electronic transition in any region of the visible spectrum, 400–800 nm, cannot be as low as 3.9 ns.

2. Results

We compute the energies of the low-lying states of SiF$_3$ at the CASSCF level [12–15] in the aug-cc-pVTZ basis of Dunning [16,17]. The calculations are performed using an Si–F bond length of 1.59 Å [4]. That is, for simplicity we assume that the bond length in excited states of SiF$_3$ is unchanged from its ground-state value. Eight doubly occupied core orbitals were frozen, these being the 1s orbitals of each fluorine, and the 1s, 2s and 2p orbitals of Si. A total of 8 a$_1$, 1 a$_2$ and 8 e orbitals formed the closed-shell part of the calculation, and the occupied space consisted of 11 a$_1$, 6 a$_2$ and 12 e orbitals. Fig. 1 shows the variation of energy of the lowest few states of SiF$_3$ with respect to bond

![Fig. 1. CASSCF energies of the lowest electronic states of SiF$_3$ as a function of the F–Si–F angle, $\theta$, calculated with a fixed Si–F bond length of 1.59 Å. The energy scales are relative to the minimum in the X $^2$A$_1$ potential curve of SiF$_3$ (left-hand scale) or to the ground state of SiF$_4$ (right-hand scale).](image)
angle in the range $106^\circ \leq \theta \leq 120^\circ$. At a bond angle of 116°, the leading configurations of the five lowest electronic states are

\[ \cdots (6e)^4 (1a_2)^2 (8a_1) \frac{1}{2} \tilde{X}^2{A}_1, \]
\[ \cdots (6e)^4 (1a_2)^2 (9a_1) \frac{1}{2} \tilde{A}^2{A}_1, \]
\[ \cdots (6e)^4 (1a_2)^2 (7e) \frac{1}{2} \tilde{B}^2{E}, \]
\[ \cdots (6e)^4 (1a_2)^2 (10a_1) \frac{1}{2} \tilde{C}^2{A}_1, \text{ and} \]
\[ \cdots (6e)^4 (1a_2)^2 (2a_2) \frac{1}{2} \tilde{D}^2{A}_2. \]

The observed spectroscopy is dominated by the two lowest energy states, $\tilde{X}$ and $\tilde{A}$, both of $^2A_1$ symmetry. The thermochemical dissociation energy of SiF$_3$, $\tilde{X}^2{A}_1 + F$ lies 7.18 eV above the ground state of SiF$_4$ [8,10]. With the excitation energy set at 13.0 eV, the remaining 5.82 eV is partitioned between translational energy of the two photofragments and rovibrational energy of SiF$_3$. The only accessible electronically excited state of SiF$_3$ is $\tilde{A}^2{A}_1$, and at this energy the $\tilde{A}^2{A}_1$ state lies ca. 5.3 eV above the ground state (corresponding to a bond angle of ca. 115.3°; see Fig. 1). Thus we might expect to see an emission band extending from ca. 5.3 to 0.9 eV or 230–1360 nm (Table 1); the lower-energy threshold is determined by the smallest gap between the $\tilde{A}$ and $\tilde{X}$ states which pertains at planarity (Fig. 1). The experiments of Suto et al. [5] and Biehl et al. [8] cannot detect the predicted high-wavelength region due to the insensitivity of photomultiplier tubes above ca. 800 nm. The predicted low-wavelength threshold of 230 nm assumes that all the excess energy after fragmentation is taken up by rovibronic energy of SiF$_3$, especially in the $v_2$ vibrational bending mode. The observed band, however, occurs in the range 400–800 nm [5], suggesting that fragmentation of SiF$_3^*$ yields fragments with ca. 2 eV in translational energy or in the stretching modes of SiF$_3$.

The CASSCF transition moment for SiF$_3$ $\tilde{A}^2{A}_1$–$\tilde{X}^2{A}_1$ varies smoothly over the range of F–Si–F bond angles pertinent to this problem, ca. 115–120° (Fig. 1), with values increasing smoothly from 0.4 to 1.4 a.u. as the bond angle increases (Table 1). The radiative lifetime of SiF$_3$ $\tilde{A}^2{A}_1$ corresponding to the experimentally observed range of emission wavelengths, 400–800 nm, is then calculated to be in the range 80–190 ns. Even for emission at the predicted low-wavelength threshold of 5.3 eV or 230 nm, the lifetime is calculated to be as high as 30 ns (Table 1). These lifetimes are between 8 to 50 times greater than the experimental lifetime of 3.9 ns [8]. The radiative lifetime is inversely proportional to the cube of the energy separation between the two states, and to the square of the transition moment. We do not expect higher levels of theory to change the transition moments or the $\tilde{A}$–$\tilde{X}$ energy separation to any significant extent. Indeed, such theory is likely to decrease the energy separation between

| $\theta$(F–Si–F) | $\Delta E$ (eV) | $\lambda$ (nm) | $|R_e|$ (a.u.) | $\tau$ (ns) |
|-----------------|----------------|--------------|--------------|-----------|
| 115             | 5.47           | 227          | 0.44         | 29        |
| 115.3°          | 5.30           | 234          | 0.45         | 30        |
| 116             | 4.93           | 251          | 0.47         | 35        |
| 117             | 4.29           | 289          | 0.51         | 46        |
| 118             | 3.50           | 354          | 0.57         | 66        |
| 118.4°          | 3.10           | 400          | 0.63         | 78        |
| 119             | 2.47           | 502          | 0.73         | 120       |
| 119.6°          | 1.55           | 800          | 1.14         | 194       |
| 120             | 0.91           | 1362         | 1.43         | 615       |

*a* Corresponds to the bond angle at which the $\tilde{A}^2{A}_1$ state of SiF$_3$ lies 13.0 eV above the ground state of SiF$_4$.

*b* Corresponds to the bond angle at which the separation between the $\tilde{A}^2{A}_1$ and $\tilde{X}^2{A}_1$ states of SiF$_3$ corresponds to a photon of wavelength 400 nm.

*c* Corresponds to the bond angle at which the separation between the $\tilde{A}^2{A}_1$ and $\tilde{X}^2{A}_1$ states of SiF$_3$ corresponds to a photon of wavelength 800 nm.
the $\tilde{\Lambda}$ and $\tilde{X}$ states for a given value of the bond angle, thereby increasing the calculated lifetime.

The $\tilde{\Lambda} \, ^2A_1$ state of SiF$_3$ must therefore be depopulated by some mechanism other than the transition observed through fluorescence in the range 400–800 nm. This alternative mechanism cannot be attributed to a UV electronic transition in SiF$_3$, since at the lowest wavelength at which emission is possible, 230 nm, the calculated radiative lifetime is as high as 30 ns. Furthermore, no band was observed in the spectra of Biehl et al. around this wavelength (see Fig. 2 of [8]). Suto et al. [5] have observed a UV spectrum in the range 290–340 nm when SiF$_4$ was photodissociated at an excitation energy of 13 eV. However, this band is centered at ca. 310 nm, and there is good evidence that this is the bound-to-free $D \, ^2A_1$–$\tilde{\Lambda} \, ^2T_2$ transition of SiF$_4^+$ arising from second-order radiation at 26 eV [8].

We conclude that the visible emission observed by Suto et al. [5] and Biehl et al. [8] when SiF$_4$ is photoexcited at 13.0 eV is due to the $\tilde{\Lambda} \, ^2A_1$–$\tilde{X} \, ^2A_1$ radiative transition of SiF$_3$, but the observed lifetime must be dominated by a faster, competing non-radiative process. This is similar to the situation in the $\tilde{a} \, ^3B_1$ state of SiF$_2$ produced in the same set of experiments by photodissociation of SiF$_4$ at 15.9 eV [8], where a fast decay component of 2.6 ± 0.4 ns was measured. This was interpreted to be the lifetime for inter-system crossing from high vibrational levels of the $\tilde{a} \, ^3B_1$ state into its electronic ground state, and not the radiative lifetime of spin-forbidden $\tilde{a} \, ^3B_1$–$\tilde{X} \, ^1A_1$ phosphorescence. For SiF$_3$, $\tilde{\Lambda} \, ^2A_1$, the most likely non-radiative process is internal conversion into high vibrational levels of the electronic ground state. We tentatively suggest that this mechanism is responsible for the low measured lifetime of SiF$_3^+.$

3. Conclusions

We have performed CASSCF calculations on the low-lying states of the SiF$_3$ radical. We conclude that fluorescence in the range 400–800 nm observed by both Suto et al. [5] and Biehl et al. [8] following fragmentation of the $(3t_2)^{-1}3s$ or $(1t_1)^{-1}3p$ Rydberg state of SiF$_4$ at 13.0 eV arises from the $\tilde{\Lambda} \, ^2A_1$–$\tilde{X} \, ^2A_1$ transition of SiF$_3$. The observed lifetime of 3.9 ns is probably dominated by rapid internal conversion of SiF$_3$, $\tilde{\Lambda} \, ^2A_1$ into high vibrational levels of the electronic ground state. The fluorescence quantum yield of the $\tilde{\Lambda} \, ^2A_1$ state of SiF$_3$, defined by $k_{\text{rad}}/(k_{\text{rad}} + k_{\text{non-rad}})$ where $k_{\text{rad}}$ and $k_{\text{non-rad}}$ are its first-order rate constants for radiative and non-radiative decay, must therefore be much less than unity.

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References

[15] MOLPRO is a package of ab initio programs written by H.-J. Werner, P.J. Knowles, with contributions from R.D. Amos, et al.