STUDIES AND *AB INITIO* CALCULATIONS ON THE CHARACTERISTICS OF THE C STATE OF SF$_2$

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SF$_2$ radicals were generated by a pulsed dc discharge in a gas beam of SF$_2$ and Ar. The (2+1) resonance-enhanced multiphoton ionization (REMPI) excitation spectrum of SF$_2$ radical was obtained between 330 and 365 nm. The SF$^+$ cation signals were also observed in the same wavelength range. *Ab initio* calculations show that the C state is a predissociative state with Rydberg characteristics. The REMPI spectrum is assigned to a two-photon resonant excitation of the SF$_2$ radical (the B^{1}B$_1$ and C^{1}A$_1$ states). Potential energy curves of excited states of the SF$_2$ radical obtained by *ab initio* calculations suggest that SF$^+$ cations originate from the ionization of SF fragments yielded from the dissociation of the C state.

1. Introduction

There is considerable interest in SF$_2$ radicals because of their great importance in semiconductor manufacturing. It is believed that SF$_2$ radicals play a significant role in plasma etching by SF$_6$ and O$_2$ mixtures.[1–4] Previously, the spectrum of the ground state (X^{1}A$_1$) of SF$_2$ has been extensively investigated by various high-resolution spectroscopy methods.[5–10] Earlier information on the excited states of SF$_2$ radical was obtained from chemiluminescence and emission spectra.[11,12] The 4s (B^{1}B$_1$) and 4p (E^{1}B$_1$) Rydberg states of SF$_2$ have been identified by the pioneering resonance-enhanced multiphoton ionization (REMPI) work of Hudgens' group.[13] More detailed investigations of the electronic band systems of SF$_2$ have been performed by the REMPI spectroscopy.[14–16] Several theoretical investigations have also been made to identify the equilibrium geometries, excitation energies and vibrational frequencies of the ground state and lower excited states of the SF$_2$ radical.[17–22]

Although there are several studies of the C state,[13,14,16] there is still no definite assignment due to the complexity of its excitation spectrum. Furthermore, there is a contradiction about the main electronic configuration of the C state. Hudgens' group[13] assigned it ^{1}A$_2$ symmetry, while Z. L. Cai's calculation[22] suggested to be ^{1}B$_2$. In addition, dissociation of the SF$_2$ radical has been observed near the B and C states. Therefore, it is our aim in this study to clarify the nature of the C state and the most probable dissociation mechanism.

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In the present study, we reinvestigate the (2+1) REMPI excitation spectrum of the SF_2 radical between 330 and 365 nm. *Ab initio* calculations are also used to obtain the optimized geometries and energies of the ground state and several excited states of SF_2. The nature of the B and C states is clarified by computation. Furthermore, the main electronic configuration and symmetry of the states are also determined. In order to qualitatively study the dissociation processes, further *ab initio* calculations on potential energy curves of the ground and excited states of the SF_2 radical have been done.

2.   Experiment and Computation

2.1.   *Experiment*

The experimental apparatus consists of a radical generation source, a pulsed Nd:YAG-pumped frequency-doubled dye laser, a time-of-flight mass spectrometer and a computer data acquisition system. It has been described in detail elsewhere.[14−16]

SF_2 radicals were generated by a pulsed dc electronic discharge in a molecular beam of gas mixture SF_6/Ar (1:1). The stagnation pressure was about 2 atm. The light source was a dye laser (Lumonics: HT500) pumped by a Nd:YAG laser (Spectral Physics: GCR-170). The dye laser output was frequency-doubled with a doubler (Lumonics: HT1000) and focused by a f 30 cm lens into the photoionization zone. The ion signals were detected by a time-of-flight mass spectrometer, amplified by an amplifier (NF Electron Corp: BX231A), and recorded with a computer acquisition system.

The REMPI excitation spectra were obtained by measuring the ion signals as a function of excitation laser wavelength. The spectral intensity was normalized using the dye laser intensity.

2.2.   *Computation*

All *ab initio* calculations were carried out using GAUSSIAN 98 programs.[23] The Dunning basis set cc-PVTZ was initially used as defined in GAUSSIAN. To take into account the possibility of diffuse electronic distributions in these lowest excited states, the basis set was supplemented with one s-type and one p-type function on sulfur atom. The exponents of those diffuse Rydberg-type functions were taken from Ref. 24: 0.023 for 4s and 0.020 for 4p. The

augmented basis set is refined to cc-PVTZ+ in the following sections.

The equilibrium geometry of the ground state of SF_2 was calculated at the HF and MP2 level of theory. Optimized geometries and energies of several excited states of SF_2 were obtained at the single-excitation configuration interaction (CIS) level. Since there was not valuable experimental ionization potential of SF, we obtained it using the G2 method, which was confirmed to be accurate enough for many radical and small molecules.[25]

The dissociative potential energy curves of ground state and several excited states of the SF_2 radical were calculated using the HF and CIS methods, respectively. In the vertical excitation potential energy calculations, the ground state equilibrium parameters were used.

3.   Results and Analysis

3.1.   Ab initio *calculations*

3.1.1.   *Geometries and excited energies of the SF_2 radical*

The optimized geometries, *ab initio* harmonic vibrational frequencies (scaled by 0.893), and energies of the ground state and several excited states of the SF_2 radical are listed in Table 1. These parameters from other theoretical and experimental studies are also summarized in Table 1. The calculated vibrational frequencies are consistent with the previous theoretical and experimental results. However, because of the fact that the CIS method is a simple approximation and neglects the electron correction, there are moderate differences in the band origins between the present results and experimental data. The theoretical results are used for assignment, which is assumed not to influence our conclusions.

As shown in Table 1, the calculated core geometries of the B^1B_1 and C^1A_1 states, $R_{S-F} = 1.498$ Å, $\theta = 98.40°$ and $R_{S-F} = 1.481$ Å, $\theta = 100.28°$, are very similar to those of the X^2B_1 cation core, $R_{S-F} = 1.481$ Å, $\theta = 100.73°$.[26] The calculated vibrational frequencies ($\omega_1 = 949$ and 974 cm^{-1}, $\omega_2 = 378$ and 360 cm^{-1}) are in excellent agreement with our experimental values ($\omega_1 = 989$ and 970 cm^{-1}, $\omega_2 = 383$ and 379 cm^{-1}), which are also very close to that of the cation ($\omega_1 = 935$ cm^{-1}).[26] Moreover, it is found that the diffuse of 4s Rydberg orbital

Table 1. Optimized geometries, harmonic vibrational frequencies and adiabatic excited energies of the ground and several excited states for the SF_2 radical.[a]

State	R_{S-F} (Å)	θ_{F-S-F} (°)	ω_1 (cm^{-1})	ω_2 (cm^{-1})	ω_3 (cm^{-1})	ΔE (eV)
X^1A_1						
HF/cc-PVTZ+[b]	1.565	97.42	844	359	816	0.00
MP2/cc-PVTZ+[b]	1.602	98.73				0.00
HF/6-31G*R(s,p)[c]	1.587	97.92	844	342	830	0.00
CISD/6-31G*[c]	1.621	99.02				0.00
MRCISD/DZ+P[d]	1.599	98.85	850	362	819	0.00
Exp[e]	1.589	98.3	832	358	804	0.00
A^1B_1						
CIS/cc-PVTZ+[b]	1.644	179.85	642	88	578	2.91
HF/6-31G*R(s,p)[c]	1.654	159.40	608	249	694	2.77
CISD/6-31G*[c]	1.632	157.33				2.43
MRCISD/DZ+P[d]	1.661	161.05	602	242	869	2.29
Exp[f]				243 ± 6		2.25
$^1A_2$						
CIS/cc-PVTZ+[b]	1.620	83.06	749	388	491	3.42
HF/6-31G*R(s,p)[c]	1.641	82.38	759	475	377	3.37
CISD/6-31G*[c]	1.661	82.80				3.33
MRCISD/DZ+P[d]	1.645	82.78	707	457	620	3.32
B^1B_1						
CIS/cc-PVTZ+[b]	1.498	98.40	949	378	752	7.07
Exp[g,h]			991 ± 12[g]	361 ± 24[g]		6.75[g]
			989 ± 22[h]	383 ± 21[h]		6.75[h]
C^1A_1						
CIS/cc-PVTZ+[b]	1.481	100.28	974	360	812	7.98
Exp[h]			970 ± 21	379 ± 19		7.10
X^2B_1 (SF_2^+)						
HF/cc-PVTZ+[b]	1.481	100.73	992	414	982	9.08
MP2/cc-PVTZ+[b]	1.516	101.80				9.86
Exp[i]			935 ± 40			10.08

[a]Vibrational frequencies were scaled by a factor of 0.893. [b]The present *ab initio* calculations.
[c]Reference 21. [d]Reference 22. [e]References 5, 6, 8. [f]Reference 11. [g]Reference 13.
[h]The present experimental results. [i]Reference 26.

has a severe effect on calculations of these states. Therefore, the B and C states exhibit Rydberg characteristics.

The present calculated adiabatic excitation energies are 7.07 eV for the B state and 7.98 eV for the C state, respectively. They are somewhat larger than the corresponding experimental values, 6.75 eV and 7.10 eV, due to simple approximation in the CIS method. In our study, the main electron configuration near the equilibrium geometry of the B state is $(1a_2)^2(8a_1)^2(5b_2)^2(3b_1)^1(4sa_1)^1$

with $^1B_1$ symmetry, while that of the C state is $(1a_2)^2(8a_1)^2(5b_2)^2(3b_1)^1(4b_1)^1$ with $^1A_1$ symmetry.

Compared to previous theoretical studies, there is disagreement in the main electron configuration of the C state. Hudgens' group[13] have assigned it as $(1a_2)^2(8a_1)^2(5b_2)^2(3b_1)^1(6b_2)^1$ with $^1A_2$ symmetry, since they have considered just the following four states: $(1a_2)^2(8a_1)^2(5b_2)^2(3b_1)^1(6b_2)^1$, $(1a_2)^2(8a_1)^1(5b_2)^2(3b_1)^2(9a_1)^1$, $(1a_2)^2(8a_1)^2(5b_2)^1(3b_1)^2(9a_1)^1$ and $(1a_2)^1(8a_1)^2(5b_2)^2(3b_1)^2(9a_1)^1$. Their assumption excludes excitations to the higher vacant

molecular orbitals. All theoretical studies including our result show that the adiabatic excitation energy for $^1A_2$ state is only about 3.35 eV, which is far lower than the experimental value, about 7.10 eV. On the other hand, the C state should be a $^1B_2$ with $(1a_2)^2(8a_1)^1(5b_2)^2(3b_1)^2(6b_2)^1$ configuration, as Z. L. Cai suggested.[22] However, we note that in his calculations, the diffuse electronic distribution in the excited states have not been taken into account. In fact, the B and C states have the Rydberg characteristics as indicated above. Therefore, we believe that the present calculations are more accurate than previous studies.

3.1.2.   *Potential energy curves*

The potential energy curves of the ground state and several excited states of SF_2 radical are plotted in Fig. 1. The geometry parameters were fixed on the experimental values of the ground state, except the asymmetry stretch coordinate. As shown in Fig. 1, the ground X^1A_1 and the excited B^1B_1 states are bonding states, which is consistent with experimental results. It is very interesting to find that the C^1A_1 state is a predissociative state. Furthermore, configuration interaction expansion coefficients for excitation of $3b_1$ to $4b_1$ are slightly decreasing with the asymmetry stretch coordinate increasing. Especially,

near R_{S-F} 1.9 Å, a crossing can occur due to interaction between the C state and an upper repulse excited state $^1A'$, so that the C state has changed from a valence bonding state to a predissociative state.

3.2.   *Experimental results and discussion*

3.2.1.   *REMPI excitation spectrum of the SF_2 radical between 325 and 365 nm*

The vibrationally resolved REMPI excitation spectrum of the SF_2 radical is shown in Fig. 2. According to the adiabatic ionization potential $[IP_a(SF_2) = 10.08$ eV], at least three photons need to be absorbed to ionize SF_2 radicals between 330 and 365 nm. The excitation spectrum can be assigned a two-photon resonant transition from the ground state to the B^1B_1 (4s) Rydberg state and C state, referring to previous REMPI spectra.[13]

The band positions, assignments and spacing observed in the REMPI spectrum are presented in Table 2. Line positions relative to band origins correspond to vibrational energy level separations. The present vibrational band positions and frequency internals are in good agreement with those observed by Hudgens' group.[13]
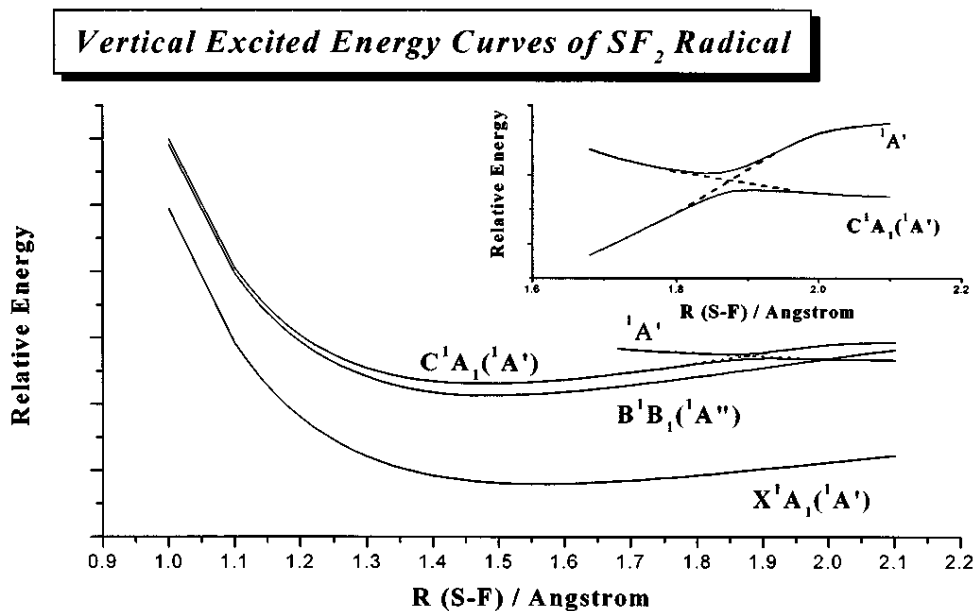

Fig. 1.   Vertical excitation potential energy curves of the ground state and several excited states of the SF_2 radical.
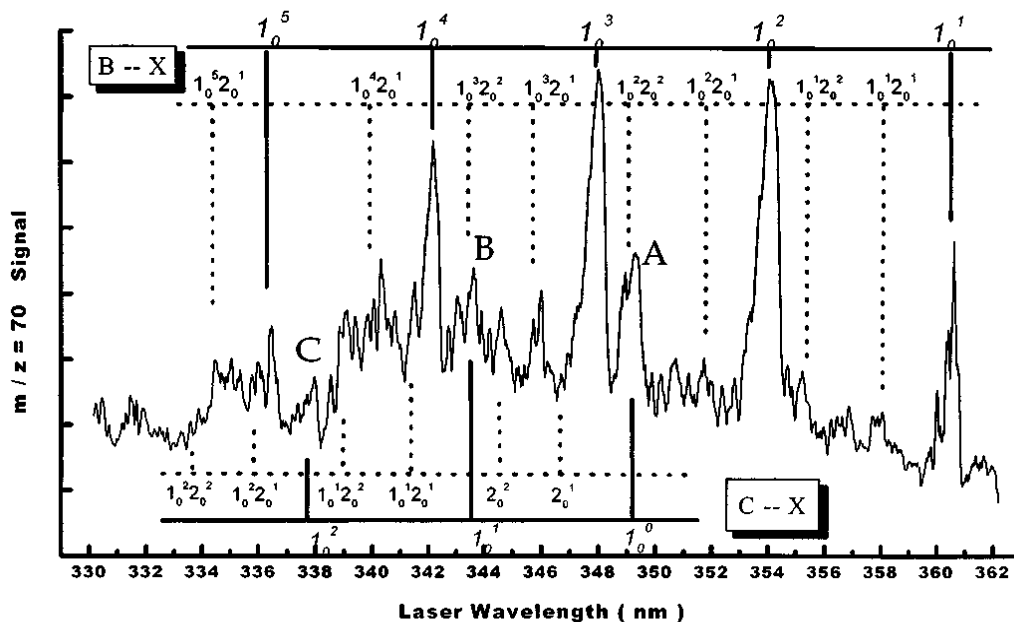
Fig. 2.   Vibrationally resolved (2+1) REMPI excitation spectrum of the SF_2 radical between 325 and 365 nm.
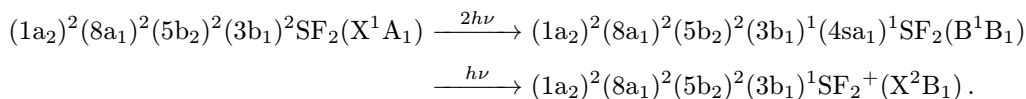
Table 2.   Band positions, assignments and spacing observed in the (2+1) REMPI excitation spectrum of the SF_2 radical between 325 and 365 nm.

Assignment	Band position λ (nm)	State energy (cm^{-1})	ω_1 (cm^{-1})	ω_2 (cm^{-1})
B^1B_1				
1_0^1	360.60	55463		
$1_0^1 2_0^1$	358.08	55853		390
$1_0^1 2_0^2$	355.46	56265		412
1_0^2	354.07	56486	1023	
$1_0^2 2_0^1$	351.73	56862	1009	376
$1_0^2 2_0^2$	349.20	57274	1009	412
1_0^3	348.00	57471	995	
$1_0^3 2_0^1$	345.72	57850	988	379
$1_0^3 2_0^2$	343.50	58224	950	374
1_0^4	342.17	58450	979	
$1_0^4 2_0^1$	340.05	58814	964	364
1_0^5	336.46	59442	992	
$1_0^5 2_0^1$	334.46	59798	984	356
C^1A_1				
0_0^0	349.29	57259		
2_0^1	346.97	57642		383
2_0^2	344.55	57983		341
1_0^1	343.62	58204	945	
$1_0^1 2_0^1$	341.37	58587	945	383
$1_0^1 2_0^2$	339.09	58981	998	394
1_0^2	337.95	59180	976	
$1_0^2 2_0^1$	335.74	59570	983	390
$1_0^2 2_0^2$	333.60	59952	971	382

According to our experimental and *ab initio* results, it is reasonable to assign the stronger intensity band A to the band origin of the C state, $v_{00} = 57259$ cm^{-1} (7.10 eV). As shown in Table 2, the vibrational frequencies $\omega_1 989\pm22$ cm^{-1} and $\omega_2 383\pm 21$ cm^{-1} are close to those of the X^{2}B$_1$ cation core. Obviously, no Rydberg state is suitable to be assigned this state, which suggests that the C state is just a valence state with Rydberg characteristics.

3.2.2.   *The dissociation mechanism of SF$_2$ radicals*

In the present experiment, SF$^+$ ion signals can also be observed in the same wavelength range. The trace of it began at about 350 nm, close to the band origin of the C state. The ion intensity increases steadily between 350 and 330 nm, with a maximum near 340 nm, a profile which follows the intensity of the C state spectrum. It suggests that dissociation processes maybe occur near the C state of SF$_2$ radical. Figure 3 shows the REMPI excitation spectrum of m/z 70 (SF$_2^+$) and 51 (SF$^+$) signals between 330 and 370 nm.

Both experimental and theoretical studies show that the B^{1}B$_1$ state of the SF$_2$ radical is a bonding state. The probable excitation and ionization mechanisms of the state can be described as the following:

$$(1a_2)^2(8a_1)^2(5b_2)^2(3b_1)^2 SF_2(X^1A_1) \xrightarrow{2h\nu} (1a_2)^2(8a_1)^2(5b_2)^2(3b_1)^1(4sa_1)^1 SF_2(B^1B_1)$$

$$\xrightarrow{h\nu} (1a_2)^2(8a_1)^2(5b_2)^2(3b_1)^1 SF_2^+(X^2B_1).$$

Ab initio calculation suggests that the X^{2}B$_1$ cation core is also a bonding state. Therefore, SF$^+$ ion signals are impossible to be originated from the B state of the SF$_2$ radicals. As we expect, the m/z 51 REMPI profile does not emulate any features associated with the B state in Fig. 3.

As described above, the C state of SF$_2$ radical is a predissociative state. Therefore, the excitation, dissociation and ionization processes of the state probably occur through three steps. The SF$_2$ radical is excited to the C state by the
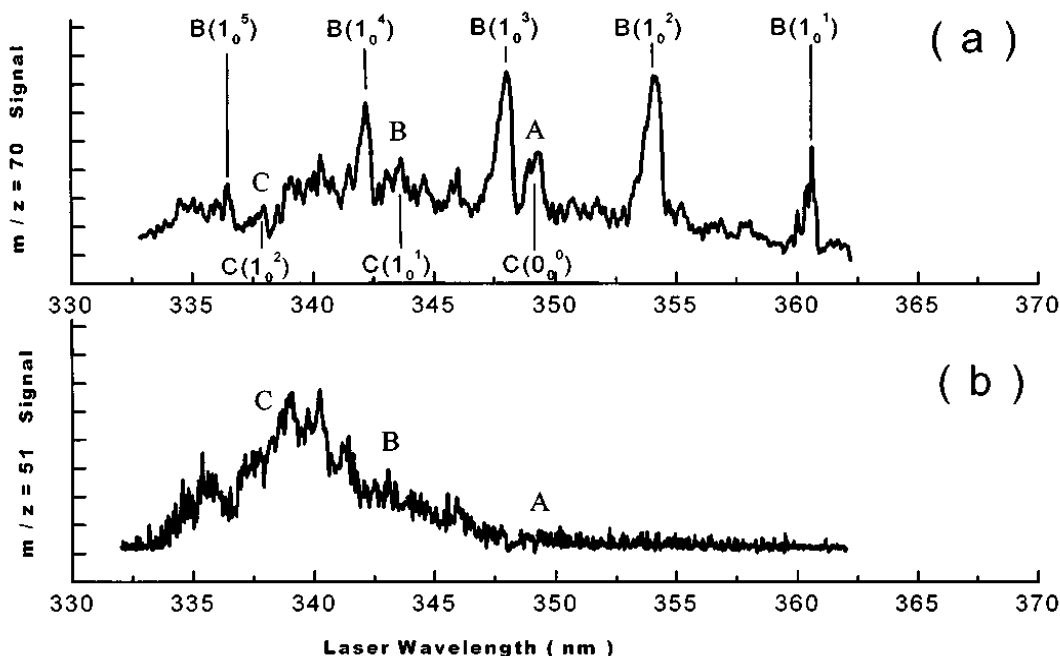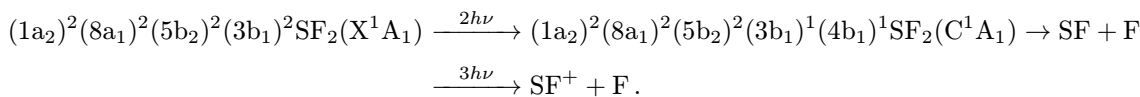

Fig. 3.   Composite (2+1) REMPI excitation spectrum between 330 and 365 nm, carried by (a) FS$_2^+$ (m/z 70) and (b) SF$^+$ (m/z 51).

two photon resonance transition, then dissociates to SF fragment, which could be ionized. The calculated ionization potential of SF is 11.41 eV at the G2 level, which suggest that the neutral SF fragment needs to absorb further three photons to be ionized. This assumed mechanism is in good agreement with the experiment. The total excitation, dissociation and ionization processes could be described as the following:

$$(1a_2)^2(8a_1)^2(5b_2)^2(3b_1)^2SF_2(X^1A_1) \xrightarrow{2h\nu} (1a_2)^2(8a_1)^2(5b_2)^2(3b_1)^1(4b_1)^1SF_2(C^1A_1) \rightarrow SF + F$$

$$\xrightarrow{3h\nu} SF^+ + F .$$

4. Conclusions

In this study, the (2+1) REMPI excitation spectroscopy of the SF_2 radical between 330 and 365 nm was reinvestigated. *Ab initio* calculations are used to obtain the optimized geometries and energies of several excited states of SF_2. Theoretical results show that the B state is a bonding Rydberg state, and the C state is a predissociate state with Rydberg characteristic. The probable main electronic configuration and symmetry of the C state is $(1a_2)^2(8a_1)^2$ $(5b_2)^2(3b_1)^1(4b_1)^1$ with $^1A_1$ symmetry. According to the computation results, we obtain an assignment of the REMPI excitation spectrum of SF_2 radicals. In order to qualitatively investigate the dissociation mechanism, more *ab initio* calculations on potential energy curves of the ground and excited states of the SF_2 radical have also been done. Results suggest that SF^+ cation originate from ionization of SF fragment yielded from dissociation of the C state.

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