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Study on the resonance-enhanced multiphoton ionization of the 4s and \tilde{C} states of SF₂ radicals

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Abstract

SF₂ radicals were generated by using a pulsed dc discharge in a mixture of SF₆/Ar. The (2+1) resonance-enhanced multiphoton ionization (REMPI) spectroscopy of SF₂ radical was observed between 320 and 365 nm. The analysis shows that the observed spectra can be assigned as the resonant excitation of the SF₂ radical (the 4s Rydberg state and \tilde{C} state). The spectroscopic parameters ω'_1 and ω'_2 were obtained. We also clarified the dissociative characteristics of the \tilde{C} state and inferred the mechanism of dissociation. © 2000 Elsevier Science B.V. All rights reserved.

1. Introduction

There is considerable interest in the SF₂ radical because of its potential importance in semiconductor manufacturing. It has been proved that SF₂ radicals play a significant role in plasma etching by SF₆/O₂ [1–4]. Previously, many effects have been made to study the ground state of SF₂ radical and its cation [5–10]. However, spectroscopic and structural information on the excited electronic states of the neutral SF₂ radical are relatively limited. Glinski et al. [11] observed an emission spectrum from 550 nm to the infrared region in the gas-phase reaction of F₂ with CS₂, and assigned it to transition of the SF₂ ($\tilde{A} \leftarrow \tilde{X}$) system (the electronic state origin $T_0 \sim 18\,200\text{ cm}^{-1}$). Johnson and Hudgens [12] observed the REMPI excitation spectra of the SF₂ radical

between 330 and 370 nm, which were assigned as the two-photon resonance of the 4s Rydberg state (\tilde{B}^1B_1) and the valence state (\tilde{C}) of the SF₂ radical from the ground electronic state. The band origin and the vibrational frequencies of the \tilde{B} state were obtained. However, the \tilde{C} state was not assigned because of complications in the spectrum. More recently, we [13] have investigated the electronic band systems of the SF₂ radical between 240 and 370 nm by (2+1) REMPI spectroscopy. The band origin (ν_{00}) and vibrational frequencies [$\omega'_1(a_1, \text{sym, str})$, $\omega'_2(a_1, \text{bend})$] of the $\tilde{B}^1B_1(4s)$ Rydberg state have been obtained.

In this paper, we generated SF₂ radicals by a pulsed dc discharge in a supersonic beam of SF₆/Ar (1:1). In order to reduce the interference of non-resonant MPI signals, we used a 30 cm lens instead of a 6 cm lens. Thus, we obtained a clearer REMPI excitation spectra of SF₂ radical between 320 and 365 nm. The band origin, the quantum defect and the

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spectrum of SF₂ radicals between 320 and 365 nm. Since the SF₂ radical production probability is improved, and a 30 cm lens is used instead of the original 6 cm lens to reduce the interference of non-resonant MPI signals with too large laser intensity, we can obtain clearer excitation spectra. The adiabatic ionization potential (IPa(SF₂)=10.08 eV) has been measured by gas-phase photoelectric spectroscopy [15]. In the region between 320 and 365 nm, at least three photons need to be absorbed in order to make SF₂ (\tilde{X}^1A_1) radicals ionize. Referring to the REMPI spectra of the 4s Rydberg state observed by Johnson and Hudgens [12], the spectra can be attributed to a two-photon resonant transition from the ground state to 4s (\tilde{B}^1B_1) Rydberg state and \tilde{C} state. Unfortunately, laser wavelengths larger than

365 nm are not accessible because we have no available frequency-doubled crystal. Accordingly, the band origin of \tilde{B} (4s) state is not measured in this account.

Table 1 summarises the band position, assignments and spacing observed in the REMPI spectrum of SF₂ radical between 320 and 365 nm. The vibrational band positions and frequency internals presented here agree with those observed by Johnson and Hudgens [12]. A vibrational analysis of the \tilde{B} (4s) Rydberg state observed here gives the spectroscopic values: $\omega'_1(a_1, \text{sym, str})=981(34) \text{ cm}^{-1}$, $\omega'_2(a_1, \text{bend})=373(26) \text{ cm}^{-1}$. The $\omega'_1(a_1, \text{sym, str})$ of the \tilde{B} state is similar to the vibrational frequency of the \tilde{X}^2B_1 cation, $\omega_1=935(40) \text{ cm}^{-1}$ [15]. This similarity suggests that the \tilde{B} state is a Rydberg state

Table 1

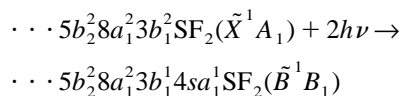
Band positions, assignments, and spacings observed in the (2+1) REMPI spectrum of SF₂ radical between 325 and 361 nm

Assign-ment	Band pos. (λ_{air}), nm	State energy cm^{-1}	Energy rel. to $4s(1^1_0)$, cm^{-1}	Energy rel. to $\tilde{C}(0^0_0)$, cm^{-1}	ω'_1 band interval, cm^{-1}	ω'_2 band interval, cm^{-1}
$\tilde{B} \leftarrow \tilde{X}$						
1^1_0	360.61	55 462	0	–	–	–
1^1_2	358.08	55 853	391	–	–	391
1^1_2	355.36	56 281	819	–	–	410
1^2_0	354.10	56 481	1019	–	1019	–
1^2_2	351.70	56 867	1405	–	1014	386
1^2_0	349.25	57 266	1804	–	985	399
1^3_0	347.97	57 476	2014	–	995	–
1^3_2	345.80	57 837	2375	–	970	361
1^3_2	343.60	58 207	2745	–	941	370
1^4_0	342.17	58 450	2988	–	974	–
1^4_2	340.26	58 779	3317	–	942	329
1^4_2	338.28	59 123	3661	–	916	344
1^5_0	336.48	59 439	3978	–	990	–
1^5_2	334.43	59 803	4341	–	1024	363
1^6_0	330.88	60 445	4983	–	1005	–
$\tilde{C} \leftarrow \tilde{X}$						
0^0_0	349.22	57 270	–	0	–	–
2^1_0	347.09	57 622	–	352	–	352
2^2_0	344.93	57 983	–	713	–	361
1^1_0	343.59	58 209	–	939	939	–
1^1_2	341.46	58 572	–	1302	950	363
1^1_2	339.12	58 976	–	1706	993	404
1^2_0	338.01	59 170	–	1900	961	–
1^2_2	335.96	59 531	–	2261	959	361
1^2_2	333.87	59 904	–	2634	928	373
1^3_0	332.18	60 208	–	2938	1038	–
1^3_2	330.42	60 529	–	3259	998	321
1^4_0	326.66	61 226	–	3956	1018	–

that possesses a \tilde{X}^2B_1 cation core. The type of Rydberg orbital involved in this electronic state is determined by solving the Rydberg formula

$$h\nu_{00}(\text{cm}^{-1}) = \text{IPa} - 109\,373/(n - \delta)^2$$

where ν_{00} is the electronic state origin, IPa is the adiabatic ionization potential in cm^{-1} (for SF_2 , IPa = $81\,301\text{ cm}^{-1}$ [15]), n is the principal quantum number, and δ is the quantum defect. For a sulfur-centered Rydberg orbital, the δ values of the ns , np , nd and nf Rydberg state should lie near 2.0, 1.6, 0.08, and 0.06, respectively [16]. The only reasonable solution gives the principal quantum number of $n=4$ and the quantum defect of $\delta=1.98$. The solution for the \tilde{B} state corresponds to the 4s Rydberg state. Thus, the spectral features arise from the two-photon excitation



$\text{SF}_2(\tilde{B}^1B_1(4s))$ radicals can ionize after absorbing one laser photon. The overall ionization mechanism occurs through a (2+1) REMPI mechanism. Johnson and Hudgens [12] assigned the band origin position of the \tilde{C} state to about 350 nm. Generally, for an excitation transition from C_{2v} symmetry to C_{2v} symmetry, the Franck–Condon factor of band origin is the maximum. Thus, we assign the stronger intensity band (A) to band origin of the \tilde{C} state. Calculation can derive the band origin of 3p, 4p and 3d Rydberg state to be about $25\,313\text{ cm}^{-1}$, $62\,249\text{ cm}^{-1}$ and $68\,431\text{ cm}^{-1}$. Obviously, the \tilde{C} state ($\nu_{00}=57\,270\text{ cm}^{-1}$) is not a Rydberg state. According to the similarity of the vibrational frequency between the \tilde{C} state and 4s Rydberg state, both states have the same \tilde{X}^2B_1 cation core. So, we believe that there is a strong interference between the two states. The \tilde{C} state is a valence state with Rydberg character.

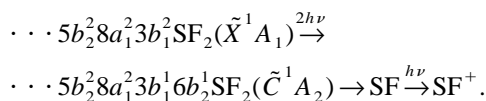
3.2. Discussion on dissociative characteristics of SF_2 radical between 330 and 350 nm

We also measured the SF^+ ($m/z=51$) REMPI signal. The trace of this signal began at 350 nm, steadily grew in intensity between 350 and 330 nm,

reached its maximum at 340 nm, and followed the trace of the m/z 70 REMPI signal intensity associated with the $\tilde{C} \leftarrow \tilde{X}^1A_1$ band system. Fig. 2 shows the REMPI spectrum of m/z 70 and 51 signals in the wavelength range of 330–350 nm.

Johnson and Hudgens [12] discussed the configuration and symmetry of the \tilde{C} state, and gave the probable mechanism–REMPID processes. In this view, the m/z 70 signal would occur through a (2+1) REMPI mechanism, and subsequent photon absorption by SF_2^+ causes photofragmentation and generates the m/z 51 signal. Our experimental result shows that the m/z 51 REMPI trace does not emulate any feature associated with the $B(4s)$ Rydberg state. Though the energy levels of the \tilde{C} state and 4s Rydberg state are very near, the 4s 1_0^n ($n=3, 4, 5$) band is absent from the SF^+ ($m/z=51$) trace. According to Hudgens' conclusion, the SF_2^+ signal originated from the \tilde{B} and \tilde{C} states would have the same cation core (\tilde{X}^2B_1). The m/z 51 signal should be able to derive from both the \tilde{B} state and \tilde{C} state. But the result does not support the REMPID mechanism.

We think that the m/z 51 signal may originate from the REMPID processes. That is, the $\tilde{C}(^1A_2)$ state derives from the ground state by two-photon resonant excitation, then dissociates to the neutral SF radical, which can ionize after absorbing one laser photon:



Since there are possibilities of occurrence by the (2+2) and (2+3) REMPI mechanism, more detailed spectroscopic information of the valence state mentioned above needs to be made clear.

4. Conclusion

The SF_2 radical was generated by the pulsed dc discharge in a supersonic beam of mixture gas. The (2+1) REMPI spectra of the SF_2 radical were obtained between 320 and 365 nm. The vibrational assignment of the 4s Rydberg state and \tilde{C} state gave the vibrational frequency [$\omega'_1(a_1, \text{sym}, \text{str})$ and

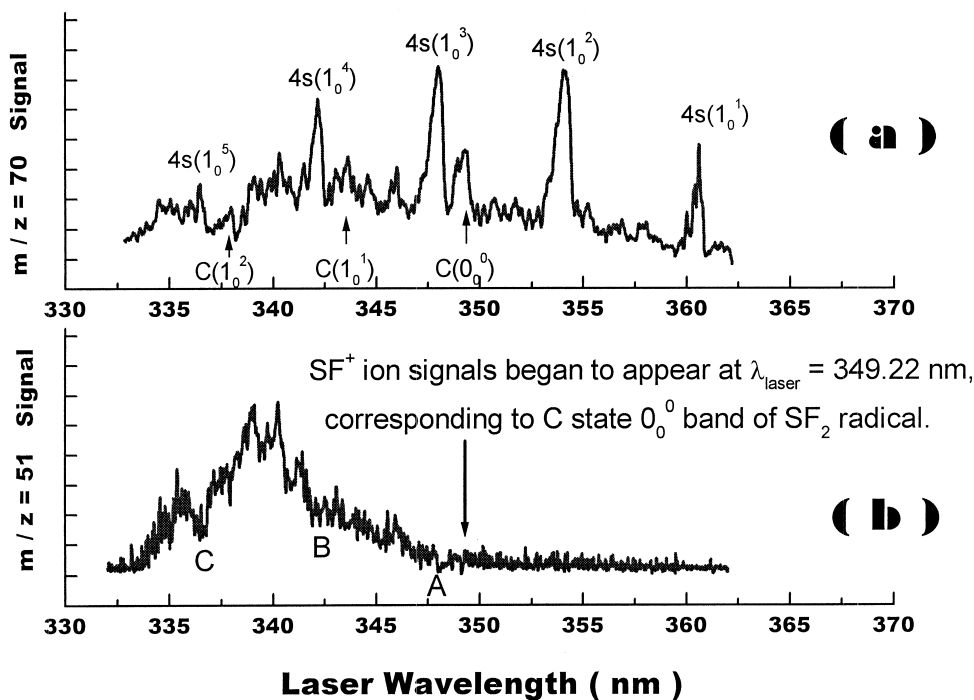


Fig. 2. Composite (2+1) REMPI excitation spectra between 330 and 365 nm, which were carried by (a) SF_2^+ ($m/z=70$), (b) SF^+ ($m/z=51$).

$\omega_2'(a_1, \text{ bend})$]. Also, we discussed and clarified the dissociative characteristics of the \tilde{C} state.

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