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Koichiro Mitsuke, Shinzo Suzuki, Takashi Imamura, and Inosuke Koyano

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Negative-ion mass spectrometric study of ion-pair formation in the vacuum ultraviolet. III. $SF_6 \rightarrow F^- + SF_5^+$

Koichiro Mitsuke

Department of Chemistry, College of Arts and Sciences, The University of Tokyo, Komaba, Meguro-ku, Tokyo 153, Japan

Shinzo Suzuki,^{a)} Takashi Imamura, and Inosuke Koyano^{b)} Institute for Molecular Science, Myodaiji, Okazaki 444, Japan

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Ion-pair formation from photoexcitation of SF_6 has been studied by negative-ion mass spectrometry using synchrotron radiation in the 11.27-31.0 eV photon energy range. Negative ions F^- , SF_6^- , and SF_5^- have been observed. The appearance energy of the F^- ion is about 1 eV higher than the thermochemical threshold for the formation of the pair of the ground state ions $F^{-}({}^{1}S_{o})$ and $SF_{5}^{+}(\tilde{X}{}^{1}A_{1})$. The peak features observed in the F^{-} efficiency curve are interpreted as resulting from transitions to neutral excited states with the ${}^{1}T_{1\mu}$ symmetry which effectively couple with ion-pair states through avoided potential surface crossings. The peaks assigned to diffuse Rydberg states are distinctively enhanced in the F⁻ efficiency curve, probably because of large transition probabilities from the dissociative Rydberg states to the ion-pair states. In contrast, the excited states of valence type autoionize in a short period and have quite small branching to the ion-pair channel. Consequently, the corresponding peaks are markedly suppressed in the F⁻ spectrum. Assignments of the peak features in the previous photoabsorption spectra are also performed by using the term values for related Rydberg and virtual valence orbitals. Other negative ions observed, SF_6^- and SF_5^- , are produced by resonance capture of low energy electrons emitted by photoionization of the parent molecules, and are not of major concern of the present study.

I. INTRODUCTION

Photoexcitation of sulfur hexafluoride in the vacuum ultraviolet (VUV) has received much attention in the past three decades, since this molecule shows a typical molecular shape resonance.^{1,2} Dehmer and co-workers^{2,3} suggest on the basis of x-ray absorption spectra⁴⁻⁶ that an outgoing excited electron experiences a high potential barrier in highly symmetric molecules containing the most electronegative ligands. This barrier divides the potential for an electron along the radial distance into two regions, an inner well and an outer well, as illustrated in Fig. 1. The resonance peaks observed in the x-ray and VUV absorption spectra⁴⁻¹⁰ of SF_6 have been interpreted as intravalence transitions to the inner-well virtual orbitals, the wave functions of which have large amplitude inside the barrier.^{2,7,10,11} Several resonance peaks are considered to result from transitions to quasibound states buried in the ionization continuum (shape resonances). The excited electron is trapped temporarily by the barrier above the ionization threshold. Evidence for the intravalence transitions has also been provided from electron energy loss spectra,¹¹⁻¹⁴ and the partial ionization cross section curves measured bv photoelectron spectroscopy.^{3,15-19} Theoretical calculations indicate that the resonances originate from the interference between wave functions of the excited electrons which have large ampli-

^{b)} Present address: Department of Material Science, Himeji Institute of Technology, 2167 Shosha, Himeji, 671-22, Japan.

tude at the central sulfur atom and those of the electrons scattered by the surrounding fluorine atoms.²⁰

The conclusive assignments of the VUV absorption structures have not, however, been given for SF_6 , since there are so many possible combinations of an initial occupied orbital and a final virtual orbital. Additional difficulty arises



FIG. 1. Schematic representation of the effective potential acting on an excited electron of SF_6 . Broken lines indicate vacant virtual orbitals, and full lines occupied valence orbitals.

^{a)} Present address: Department of Chemistry, Tokyo Metropolitan University, Fukazawa, Setagaya-ku, Tokyo 158, Japan.

from the fact that some of the peak features are attributed to transitions to diffuse Rydberg orbitals expanding over a shallow outer well region (see Fig. 1). It is widely accepted that such transitions have small oscillator strengths due to small overlaps between the inner-well valence orbitals and the outer-well Rydberg orbitals.^{11,21} Nevertheless, several authors have assigned peaks below the first ionization potential to the Rydberg states.^{10,15,22}

In the present paper, we report the ion-pair formation induced by the photoexcitation of SF_6 ,

$$SF_6 + h\nu \rightarrow SF_6^{**} \rightarrow F^- + SF_k^+ + (5-k)F \quad (k \leq 5).$$
 (1)

We have recently shown that measurement of the photodissociation efficiency curves of negative ions produced from N_2O , OCS, and CO_2 can be used to investigate their neutral excited states (doorway states).^{23,24} It has been found that almost all features in these efficiency curves are assigned to the excited valence states or Rydberg states which predissociate into the ion-pair states. The cross section for the ionpair formation is generally determined by the configuration coupling between the doorway state and the ion-pair state. This coupling is quite sensitive to the properties of the excited state, such as the shape of the potential surface and the spatial extent of the excited state orbital.²³⁻²⁵ It is therefore expected that examination of the F⁻ efficiency curve may provide useful information to identify the excited states which yield the resonance peaks in the photoabsorption spectra of SF_6 .

II. EXPERIMENTAL

The negative-ion efficiency curves are measured at the UVSOR synchrotron radiation facility in Okazaki. The apparatus and details of the procedure are described elsewhere.^{23,26} Neat sample gas is expanded from an orifice of 50 μ m diameter. The stagnation pressure and nozzle temperature are 760 ± 50 Torr and 298 ± 3 K, respectively. The pressure in the chamber is monitored by a cold cathode Pirani gauge and kept constant at 1.0×10^{-4} Torr by regulating the gas flow through a needle valve upstream of the nozzle. Commercial high purity SF₆ gas (Kanto Denka, 99.99%) pure) is used without further purification. A central portion of the free jet is sampled by a skimmer and allowed to intersect at 90° with the monochromatized photon beam. The dispersed light from the normal incidence monochromator with 3.0 m focal length is focused by a toroidal mirror onto the photoionization region. Negative ions formed are extracted coaxially with the molecular beam and focused using an ion lens system. The ions are mass analyzed by a quadrupole mass filter mounted in a differentially pumped chamber and are detected by a channel electron multiplier. Ion signal is processed using a fast amplifier/discriminator and a standard CAMAC pulse counting system. Incident photon intensity is monitored by a sodium salicylate phosphor/photomultiplier combination. The efficiency curves for the negative ions produced by photoirradiation are obtained by plotting the ion signal counts divided by photon counts as a function of photon wavelength. The curves are taken by fixing the mass-to-charge ratio m/z at the highest intensity position in each ion peak. The step of the wavelength scan and

the signal accumulation time at each wavelength are typically 1 Å and 30 s, respectively. All efficiency curves reported in this paper are measured with the wavelength resolution of 0.8 Å. The calibration of the wavelength is made in reference to the sharp Rydberg peak at 504.4 \pm 0.3 Å first reported by Codling.²⁷

III. RESULTS

A. Negative ion formation from SF₆

The negative-ion mass spectrum of SF_6 consists of F^- , SF_6^- and SF_5^- . The count rates of SF_6^- and SF_5^- are an order of magnitude lower than that of F^- . As shown in Fig. 2, the peak positions in the efficiency curves of SF_6^- are found to be in agreement with those in He I and He II photoelectron spectra of SF_6 .²⁸⁻³¹ Hence, SF_6^- may be taken as produced by the following two-step mechanism: photoionization (or dissociative photoionization) of the SF_6 molecules and the resonance capture of a slow photoelectron by SF_6 as represented by

$$SF_6 + h\nu \rightarrow SF_k^+ + (6-k)F + e^- \quad (k \leq 5),$$
 (2)

$$SF_6 + e^- \to SF_6^-. \tag{3a}$$

It is well known that SF_6 captures thermal and subthermal electrons with a large attachment cross section $(2 \times 10^{-14} \text{ cm}^2 \text{ at } 40 \text{ meV}^{32})$. The relative intensities of the peaks in the SF_6^- efficiency curve, however, differ from those in the reported photoelectron spectra. Measurements of the threshold photoelectron yield would be necessary to interpret the present efficiency curve of SF_6^- . SF_5^- is also likely to be produced by dissociative attachment of the slow photoelectrons:

$$\mathbf{SF}_6 + e^- \to \mathbf{SF}_5^- + \mathbf{F}. \tag{3b}$$

The efficiency curve of F^- in Fig. 3 is in marked contrast with those of SF_6^- and SF_5^- . The same spectrum is plotted in Fig. 4(a) as a function of the photon energy. The



FIG. 2. Ionization efficiency curve of SF_6^- produced from SF_6 taken at a wavelength resolution (FWHM) of 0.8 Å and wavelength intervals of 1 Å. Arrows mark vertical ionization potentials for SF_6^+ formed by removal of an electron from various valence orbitals (Ref. 28).



FIG. 3. Photodissociation efficiency curve of F^- produced from SF₆ plotted as a function of the photon wavelength. The curve is taken at a wavelength resolution (FWHM) of 0.8 Å and wavelength intervals of 1 Å.



FIG. 4. Comparison among (a) photodissociation efficiency curve of F^- produced from SF₆, (b) photoabsorption cross section curves (Refs. 8–10), and (c) high resolution electron energy loss spectrum (Ref. 11).

appearance energy of F⁻ is determined from the onset energy of feature F 1 to be 12.98 \pm 0.03 eV (955 \pm 2Å). We have carefully searched the ion signal counts down to the wavelength of 1100 Å (11.27 eV), with no F⁻ signals being observed below the 12.98 eV onset. The upper limit of the thermochemical threshold for the F⁻ (${}^{1}S_{g}$) ion can be evaluated to be 11.92 eV from the onset of photoionization (see Sec. III B)^{33,34} for SF₅⁺ ($\tilde{X} {}^{1}A_{1}$) + F(${}^{2}P_{u}$) + e^{-} , 15.32 eV, and the electron affinity of the F atom, 3.399 \pm 0.003 eV.³⁵ This upper limit is about 1 eV lower than our experimental F⁻ appearance energy, implying that the Franck–Condon region of the ion-pair state lies about 1 eV higher than the dissociation limit of F⁻ (${}^{1}S_{g}$) + SF₅⁺ ($\tilde{X} {}^{1}A_{1}$).

The F⁻ spectrum is composed of peak features labeled F 1-F9. All features except F8 have been observed in photoabsorption spectra^{8-10,27} and electron energy loss spectra.¹¹⁻¹³ The total photoabsorption cross section curves of SF₆ molecule measured by Blechschmidt *et al.*,⁸ Lee *et al.*,⁹ and Sasanuma *et al.*¹⁰ are shown in Fig. 4(b). Figure 4(c) shows the electron energy loss spectrum reported by Sze and Brion.¹¹ The most striking difference between the curves in Figs. 4(a) and 4(b) is that feature F11, the highest peak in the absorption spectrum, is completely absent in the F⁻ efficiency curve. Instead, feature F8 is identified in the F⁻ curve. A series of sharp peaks observed at 505, 482, and 474 Å which were first reported by Codling,²⁷ are assigned to the npt_{1u} (n = 4-6) Rydberg series converging to the SF₆⁺ [(5 a_{1g})⁻¹ \tilde{F}^2A_{1g}] state.

The cross section for process (1) with k = 5 at the maximum position of feature F2 (867 Å, 14.3 eV) is estimated to be $(7 \pm 2) \times 10^{-21}$ cm² from a comparison between the count rate of F⁻ produced by process (1) and that of O⁻ produced by

$$O_2 + h\nu \to O^- + O^+.$$
 (4)

Here, the cross section of $\sim 2 \times 10^{-19}$ cm² at 716.35 Å for process (4) is derived from the data given by Dehmer and Chupka.³⁶ The quantum yield for process (1) is then obtained to be $(1.9 \pm 0.5) \times 10^{-4}$ at 867 Å from the total photoabsorption cross section⁸ for SF₆, 3.6×10^{-17} cm².

B. Positive ion formation from SF₆

Photoionization efficiency curves of the positive ions from SF₆ are measured for the purpose of comparison. In the mass spectrum, only fragment ions SF_k⁺ ($k \le 5$) are observed. Figure 5 shows the efficiency curves of SF₅⁺ and SF₃⁺, both of which exhibit a large peak at ~535 Å. This peak probably has the same origin as feature F11 at 534 Å (23.2 eV) in Fig. 4(b). In the case of SF₅⁺, weak "window" resonances assignable to the npt_{1u} "Codling" Rydberg series²⁷ converging to the SF₆⁺ [($5a_{1g}$) $^{-1}\tilde{F}$ $^{2}A_{1g}$] state can be identified on the higher energy side of this peak. The appearance energy of SF₅⁺ is 809.5 ± 2 Å (15.32 ± 0.04 eV), in good agreement³⁷ with the results of Dibeler and Walker³³ and Berkowitz *et al.*³⁴ Below 15.32 eV, we cannot detect any signals of SF₅⁺ produced by the ion-pair formation process (1), undoubtedly because of much lower quantum yield for process (1) than that for the photoionization process (2).

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FIG. 5. Photoionization efficiency curves of SF_5^+ (upper panel) and SF_3^+ (lower panel) produced from SF_6 taken at a wavelength resolution (FWHM) of 0.8 Å and wavelength intervals of 1 Å. Ionization thresholds for the ground and excited ionic states of SF_6^+ are indicated.

Several onsets can be clearly observed in the SF₅⁺ efficiency curve, corresponding to the adiabatic ionization potentials for the SF₆⁺ ionic states:²⁸ $(1t_{1g})^{-1}\tilde{X}^2T_{1g}$ $(I_P^a = 15.5 \text{ eV or}$ 800 Å), $(5t_{1u})^{-1}\tilde{A}^2T_{1u}$ and $(1t_{2u})^{-1}\tilde{B}^2T_{2u}$ $(I_P^a = 16.62 \text{ eV or 746 Å})$, and $(3e_g)^{-1}\tilde{C}^2E_g(I_P^a = 18.0 \text{ eV or 689 Å})$.

The appearance energy of SF_3^+ (18.79 ± 0.14 eV or 660 ± 5 Å) is in fair agreement with the reported value.³⁴ The SF_3^+ efficiency curve gradually rises above I_P^a for SF_6^+ [(1 t_{2g})⁻¹ \tilde{D}^2T_{2g}] of 19.245 eV²⁸ (644 Å). As pointed out by Berkowitz,³⁴ this ion mainly arises from the dissociative \tilde{D}^2T_{2g} state.

IV. DISCUSSION

A. Assignment of the features in the ${\rm F}^-$ efficiency curve

Most of the peak features in the F^- efficiency curve can be observed in the VUV absorption spectra⁸⁻¹⁰ and electron energy loss spectra¹¹⁻¹³ of SF₆. Obviously, the ion-pair formation proceeds via the neutral excited states formed by the photoabsorption, because the resonance peaks in Figs. 4(b) and 4(c) have been assigned as resulting from excitation of a valence electron into a virtual unoccupied orbital. In the vicinity of the electronegative fluorine atoms, the potential that an electron experiences has a barrier and is separated into inner and outer well regions,^{1,2} since the electron is prohibited from moving freely in the space where the wave functions of the occupied nonbonding orbitals centered on the fluorine atoms have appreciable amplitude. As a result, compact valence molecular orbitals are localized in the innerwell region, whereas the diffuse wave functions of Rydberg orbitals may have large amplitude near the outer-well region. Overlap of occupied valence orbitals with inner-well virtual valence orbitals would then be much larger than that with outer-well Rydberg orbitals. This suggests that the valence–valence transitions yield much intense peaks in the absorption spectrum of SF₆ compared to other polyatomic molecules.

As discussed below, the identification of the resonance peaks is rather confusing and yet in dispute, partly because of uncertainty in the orbital energies for the virtual orbitals. Sasanuma et al.¹⁰ have interpreted the peaks in their photoabsorption spectrum as resonances originating from intravalence transitions from seven occupied outer valence orbitals to four unoccupied virtual orbitals $6a_{1g}$ (-8.2 eV), $6t_{1u}$ (-3.0 eV), $2t_{2g}$ (+2.8 eV), and $4e_g$ (+15.3 eV). They used the orbital energies given in the parentheses taken from x-ray absorption spectra⁵ near the sulfur 2p edge of SF_6 . The excitation energies were thus calculated as the energy differences between the initial and final orbitals (oneelectron approximation). Their assignments obtained in this manner (listed in Table I) do not seem to be very convincing, since the energies for the virtual orbitals are shifted by \sim 3–3.5 eV toward higher energies in going from inner-shell to valence-shell spectra due to different screening effects (viz. smaller antishielding effect in the valence excitation).^{3,11,16,38} Taking this point into account together with the fact that a resonance occurs at about 23 eV in the partial photoionization cross section curve for the formation of the SF_6^+ [$(5t_{1u})^{-1}\widetilde{A}^2T_{1u}$] ionic state, Dehmer *et al.*³ have ascribed feature F11 of Fig. 4(b) to the $5t_{1u} \rightarrow 2t_{2g}$ transition.

Sze and Brion¹¹ have measured high resolution electron energy loss spectra (HREELS) of inner shell and valence shell of SF₆, which are essentially identical with the corresponding photoabsorption spectra. They determined the term values [= - (orbital energies)] for the Rydberg orbitals 4s-6s, and 4p. In addition, they proposed, by investigating the HREELS near the sulfur 2p edge, a larger term value for the virtual 6t_{1u} orbital than that reported previously.^{2,5} Using the revised term values, assignments listed in Table I have been made for the observed features in the valence-shell HREELS in Fig. 4(c).

We make assignments for features F1-F12 in Figs. 4(a)-4(c) as summarized in Table I, assuming that the term values for transitions terminating at the same virtual orbitals are almost constant irrespective of the particular initial valence orbital.¹¹ Several transitions are chosen and so checked that the term values for the final orbital may nearly accord with those proposed by Sze and Brion.¹¹ The final assignments are essentially in agreement with those by Sze and Brion.¹¹ We calculate the term value T_f by the equation

$$T_f = -E_{h\nu} - E_i,\tag{5}$$

where the orbital energy E_i of occupied valence orbitals are taken from the vertical ionization potentials determined by photoelectron spectroscopy²⁸ and are listed in Table II. The

TABLE I. Summary of the observed features in the F^- photodissociation efficiency curve of SF₆, photoabsorption spectrum of SF₆ (Ref. 10), and electron energy loss spectrum of SF₆ (Ref. 11). Photon energies and term values for transitions to the virtual orbitals are in eV.

		This work	Sasanuma et al.°		Sze and Brion ^d		
Feature	Photon energy ^a	Assignment	Term value ^b	Assignment	Term value	Assignment	Term value
F 1	13.2	$1t_{1g} \rightarrow 4p$	2.5	$4t_{1u} \rightarrow 6a_{1g}$	9.4	$1t_{1g} \rightarrow 4p$	2.5
F2	14.3	$\begin{cases} 5t_{1u} \rightarrow 4s \\ 3e_{g} \rightarrow 6t_{1u} \end{cases}$	2.6 4.4	e		$\begin{cases} 5t_{1u} \to 4s \\ 3e_g \to 6t_{1u} \end{cases}$	3.0 4.4
F3	14.6	$1t_{1g} \rightarrow 5p$	1.1	e		$5t_{1u} \rightarrow 4p$	2.3
F4	15.7	$\begin{cases} 5t_{1u} \rightarrow 5s \\ 1t_{2g} \rightarrow 6t_{1u} \end{cases}$	1.2 4.1	$3e_g \rightarrow 6t_{1u}$	3.0	$1t_{2g} \rightarrow 6t_{1u}$	3.9-4.3
F5	17.0	$4t_{1\mu} \rightarrow 6a_{1g}$	5.7	$1t_{2g} \rightarrow 6t_{1u}$	2.8	$4t_{1u} \rightarrow 6a_{1g}$	5.9
<i>F</i> 6	19.6	$4t_{1u} \rightarrow 4s$	3.1	$5t_{1\mu} \rightarrow 2t_{2g}$	- 2.9	$4t_{1u} \rightarrow 4s$	3.1
F7	21.2	$4t_{1u} \rightarrow 5s$	1.5			$\begin{cases} 4t_{1u} \rightarrow 5s \\ 1t_{1g} \rightarrow 2t_{2g} \end{cases}$	2.0 - 5.2
F 8	22.1	$\begin{cases} 5t_{1u} \rightarrow 2t_{2g} \\ 4t_{v} \rightarrow ns (n \ge 6) \end{cases}$	- 5.2 0.6				
	(24.6	$5a_{1a} \rightarrow 4p$	2.4			$5a_{1a} \rightarrow 4p$	2.4
F9	25.7	$5a_{1g} \rightarrow 5p$	1.3			$5a_{1e} \rightarrow 5p$	1.2
	26.2	$5a_{1g} \rightarrow 6p$	0.8				
F 10 ^f	11.52 ^d	$\begin{cases} 1t_{1g} \to 6t_{1u} \\ 5t_{1u} \to 6a_{1g} \end{cases}$	4.2 5.4	e		$\begin{cases} 1t_{1g} \rightarrow 6t_{1u} \\ 5t_{1u} \rightarrow 6a_{1g} \end{cases}$	4.2 5.5
F 11 ^f	23.2 ^d	$\begin{cases} 5a_{1g} \rightarrow 6t_{1u} \\ (5t_{1u} \rightarrow 2t_{2g}) \end{cases}$	3.8 - 6.3	$5a_{1g} \rightarrow 6t_{1u}$	3.8	$\begin{cases} 5a_{ig} \rightarrow 6t_{1u} \\ 5t_{1u} \rightarrow 2t_{2g} \end{cases}$	3.8 - 6.2
<i>F</i> 12 ^f	28.3 ^d	$4t_{1u} \rightarrow 2t_{2g}$	- 5.6	$1t_{2u} + 5a_{1g}$ $\rightarrow 6a_{1g} + 6a_{1g}$	•••	$4t_{1u} \rightarrow 2t_{2g}$	5.4

^a The energies for features F1-F9 are estimated from the peak maximum positions in the F⁻ efficiency curve.

^b Calculated by using Eq. (5) in the text. The vertical ionization potentials for the ionic states of SF₆ are taken from the He I and He II photoelectron spectra reported by Karlsson *et al.* (Ref. 28) as listed in Table II.

^c Reference 10.

^dReference 11.

^e Rydberg series converging to the 16.15 eV limit (Ref. 22).

^fNot observed in the F⁻ efficiency curve.

order of the occupied valence orbitals is that adopted by Dehmer *et al.*³ Recent discrete-variational $X\alpha$ calculations²⁰ certify this order. Table II compiles the T_f values for transitions to different final orbitals.

The most significant conclusion drawn by comparing the F^- spectrum with the absorption spectra is that the peaks assigned to transitions to outer-well Rydberg orbitals are stronger than those assigned to transitions to inner-well virtual valence orbitals. This trend can most clearly be seen as a marked depression of features F4, F5, F10, F11, and F12, which are observed most eminently in Figs. 4(b) and 4(c). In contrast, the enhancement of the peaks arising from valence-Rydberg transitions is recognized in the $5a_{1g} \rightarrow npt_{1u}$ (feature F9) and $4t_{1u} \rightarrow nsa_{1g}$ (features F6 and

FABLE II. Orbital energies of the occupied	valence orbitals and term values for	r transitions from the valence orbitals	s to the virtual orbitals (in eV).
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	- Orbital - energy ^a	Final virtual orbital							
W-lawse		Inner-well orbital		Outer-well orbital					
orbital		$6a_{1g}$	6t 1 u	2t _{2g}	4 <i>s</i>	5 <i>s</i>	4 <i>p</i>	5 <i>p</i>	6 <i>p</i>
1t _{1p}	- 15.67		4.2				2.5	1.1	•••
$5t_{1u}$	- 16.93	5.4		- 5.2	2.6	1.2	•••		•••
$1t_{2u}$									
$3e_{g}$	- 18.66	•••	4.4	•••	•••		•••		•••
$1t_{2g}$	- 19.76	•••	4.1	•••	•••		•••	•••	•••
$4t_{1u}$	- 22.7	5.7		5.6	3.1	1.5	•••	•••	•••
$5a_{1g}$	- 27.0	•••	3.8		•••		2.4	1.3	0.8

^a Orbital energy of the initial (occupied) valence orbital is assumed to be equal to $-I_p$ for SF₆⁺ formed by removal of an electron from the orbital. Vertical ionization potential I_p is derived from Ref. 28.

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F7) transitions. As stated before, these transitions are considered to have small oscillator strengths in the photoabsorption process due to small overlap between the inner-well valence orbitals and the outer-well Rydberg orbitals. Conceivably, the optically allowed Rydberg states with the symmetry of ${}^{1}T_{1u}$ may interact strongly with the ion pair continuum. When one S-F bond stretches, the ${}^{1}T_{1u}$ Rydberg state of the O_h symmetry is resolved into ${}^{1}A_1 + {}^{1}E$ species in the C_{4v} point group (see Sec. IV B). Subsequent avoided surface crossings with F ${}^{-}({}^{1}S_{g}) + SF_{5}^{+}({}^{1}A_{1} \text{ or } {}^{1}E)$ potentials may produce F⁻ ions.

Features F1 and F2 in Fig. 4(a) are attributed to $1t_{1g} \rightarrow 4p$ and $5t_{1u} \rightarrow 4s$, respectively. The ratio of the intensities of features F2 and F1, I_2/I_1 , is 2-3 times as high as that in the absorption spectra or HREELS. The reason for this is discussed in Sec. IV B. According to Sze and Brion assignment,¹¹ the peak due to the $3e_g \rightarrow 6t_{1u}$ transitions may overlap with that due to the $5t_{1\mu} \rightarrow 4s$ transitions to form feature F2. In the F^- spectrum, however, the former transitions are considered to be almost suppressed just like other intravalence transitions. The marked enhancement of transitions to the outer-well Rydberg orbitals in the F^- efficiency curve implies that the $1t_{1g} \rightarrow 5p$ resonance is the origin responsible for feature F3. Similarly, the $5t_{1\mu} \rightarrow 5s$ transitions may have some contribution to feature F4 in the F^- spectrum. These valence-Rydberg transitions, $1t_{1g} \rightarrow np$ (features F1 and F3) and $5t_{1\mu} \rightarrow ns$ (features F2 and F4), can give rise to optically allowed ${}^{1}T_{1\mu}$ Rydberg states.

Feature F 11 has the highest intensity in Fig. 4(b) as well as in the efficiency curves of SF_5^+ and SF_3^+ in Fig. 5. Sze and Brion¹¹ and Ferrett et al.¹⁸ have proposed that this feature is associated with the $5a_{1g} \rightarrow 6t_{1u}$ and/or $5t_{1u} \rightarrow 2t_{2g}$ resonance(s). From the nature of the wave functions, we adopt the former transitions for feature F11. Ab initio calculations³⁹ predict that the bonding orbital $5a_{1g}$ and the nonbonding orbital $6t_{1u}$ correlate with the 3s and 3p orbitals, respectively, of the central sulfur atom. On the other hand, the 5t_{1u} and 2t_{2g} orbitals arise from the fluorine $2p\pi$ orbitals and the sulfur 3d orbitals, respectively. Thus, the intrava-Pence transitions $5a_{1g} \rightarrow 6t_{1u}$ are expected to have larger oscillator strength on account of larger overlap of the wave functions than the $5t_{1u} \rightarrow 2t_{2g}$ transitions. In the energetical sense, both resonances may accidentally occur at the same excitation energy to form feature F11. However, it seems unlikely that the two resonances, $5t_{1u} \rightarrow 2t_{2g}$ and $5a_{1g} \rightarrow 6t_{1u}$, simultaneously disappear in the F^- spectrum.

Feature F8 has not previously been noticed either in absorption spectra or in HREELS, mainly owing to overlapping of the intense $5a_{1g} \rightarrow 6t_{1u}$ peak (feature F11) in this wavelength region. We adopt the transition to the shape resonance state $5t_{1u} \rightarrow 2t_{2g}$ as the most probable one responsible for feature F8, since the value of T_f for the $2t_{2g}$ state obtained by Eq. (5) (-5.2 eV) is in good agreement with the value proposed previously.¹¹ Spectral features associated with the valence-Rydberg transitions $4t_{1u} \rightarrow ns(n \ge 6)$ would exist near 560 Å. Actually, the 4s and 5s Rydberg states converging to SF₆⁺ (\tilde{E}^2T_{1u}) are observed as features F6 and F7 at lower photon energies. Nevertheless, feature F8 probably results from the $5t_{1u} \rightarrow 2t_{2g}$ transitions, since the peak height of feature F 8 is much higher than that expected from the oscillator strengths for the $4t_{1u} \rightarrow ns$ transitions, which have a $1/n^3$ dependence on the principal quantum number.⁴⁰

B. Potential surface crossings between the Rydberg and ion-pair states

The F^- photodissociation efficiency curve shows that the outer-well Rydberg states couple effectively with the ionpair state. These couplings can be understood in terms of the potential surface crossings occurring during the course of stretching of the SF_5 -F bond. In what follows, we consider the Rydberg states converging to the ground and first excited states of the SF_6^+ ion from this point of view. The relevant potential surfaces are schematically shown in Fig. 6. Using this diagram, we discuss why the intensity ratio I_2/I_1 of features F^2 and F^1 in the F^- efficiency curve is larger than that in the absorption spectrum or HREELS [Figs. 4(b) and 4(c)].

Stretching of an SF₅-F bond in the SF₆ molecule reduces its symmetry from O_h to C_{4v} . Removal of the degeneracy of T_{1e} and T_{1u} states in the former symmetry gives rise to E and A_2 states, and E and A_1 states, respectively. Concerning the ionic state, the ${}^{2}E$ component originating from the ground state SF₆⁺ ($\tilde{X}^2 T_{1g}$) and the 2A_1 component originating from the first excited state SF_6^+ (\tilde{A}^2T_{1u}) correlate to the same dissociation limit, $SF_5^+(\tilde{X}^1A_1) + F({}^2P_u)$, as shown in Fig. 6. We check this correlation of the electronic states by examining the orbital correlation diagram between valence molecular orbitals of SF_6 and $SF_5 + F$ obtained by *ab initio* calculations.³⁹ It should be noted that the accessible Franck-Condon regions for these SF_6^+ states lie well above the dissociation limit of 15.32 eV, corresponding to much smaller adiabatic ionization potential of SF₅ ($\sim 10.17 \text{ eV}^{41}$) than that of SF₆ (~15.5 eV²⁸). This explains negligibly



FIG. 6. Schematic potential diagram of the ground and first excited states of SF_6^+ , the two Rydberg states converging to the SF_6^+ states, and the ion-pair ground state. Photoexcitation of $SF_6(\tilde{X} \, {}^1A_{1g})$ in the O_h symmetry to the Rydberg states is followed by dissociation into a pair of a ground state F atom and a Rydberg-state radical SF_5^{**} in the C_{4v} symmetry. Conversion to the ion-pair potential can occur at the points of avoided surface crossing.

small amount of SF_6^+ ions produced by photoionization of SF_6 (see Sec. III B).^{13,33,34,42-44}

As to the neutral excited states of relevance, we have to consider two types of Rydberg states with the optically allowed ${}^{1}T_{1u}$ symmetry for a given nominal principal quantum number *n*: the lower state converging to $SF_{6}^{+}(\tilde{X} {}^{2}T_{1g})$ and expressed as $1t_{1g} \rightarrow npt_{1u} {}^{1}T_{1u}$, and the higher state converging to $SF_{6}^{+}(\tilde{A} {}^{2}T_{1u})$ and expressed as $5t_{1u} \rightarrow nsa_{1g} {}^{1}T_{1u}$. These are denoted by $V(\tilde{X})$ and $V(\tilde{A})$, respectively.

The ${}^{1}A_{1}$ component of the V(X) state correlates to the dissociation limit producing a pair of a ground F atom and a radical in a p-type Rydberg state, $SF_5^{**}(npe^{-2}E)$. At a certain distance $R = R_x(\tilde{X})$, this ${}^{1}A_1$ potential intersects the ${}^{1}A_{1}$ ion-pair potential that dissociates into $\mathbf{F}^{-}({}^{1}S_{g}) + \mathbf{SF}_{5}^{+}(\widetilde{X}{}^{1}A_{1})$. The system can be converted from the covalent potential to the ion-pair potential through the avoided surface crossing. Thus, feature F1 at 13.2 eV in the F⁻ efficiency curve can be explained as resulting from photoexcitation to the $V(\hat{X})$ state of n = 4 followed by a switchover to the ion-pair potential. On the other hand, the ${}^{1}A_{1}$ component of the V(A) state correlates with a pair of a ground state F atom and a radical in an s-type Rydberg state, $SF_5^{**}(nsa_1^2A_1).$ Decay channel of $\mathbf{F}^{-}({}^{1}S_{g})$ + SF₅⁺ ($\tilde{X}^{1}A_{1}$) is also accessible by photoexcitation to the V(A) state through the subsequent avoided surface crossing with the ion-pair potential at $R = R_x(\widetilde{A})$. The energy of the peak of feature F2, 14.3 eV, thus reflects the vertical excitation energy to the V(A) potential of n = 4.

The diabatic dissociation limit of the $V(\tilde{X})$ potential $F({}^{2}P_{u}) + SF_{5}^{**}(4pe {}^{2}E)$, lies several tenths eV above that of the $V(\tilde{A})$ potential, $F({}^{2}P_{u}) + SF_{5}^{**}(4sa_{1}{}^{2}A_{1})$, since the quantum defect of the *p*-type Rydberg state is generally smaller than that of the *s*-type Rydberg state. If the Rydberg electron has no essential effect on the bonding of the SF_{5}^{+} ion core, each ${}^{1}A_{1}$ Rydberg potential should be parallel to the corresponding ionic potential. Hence, we can make rough estimates of about 12.8 eV for the energies of the two $F({}^{2}P_{u}) + SF_{5}^{**}$ dissociation limits as indicated in Fig. 6.

With these potential relations in mind, we now discuss the ratio I_2/I_1 . The probability P_x that the system remains on the adiabatic surface to form the ion pair may be approximated by the one-dimensional Landau–Zener formula⁴⁵

$$P_x = 1 - \exp[-\pi^2 \Delta E^2 / hv |\Delta F|].$$
(6)

Here, ΔE is the energy gap between the two adiabatic potentials at the avoided surface crossing point R_x , v the radial velocity at R_x , and $|\Delta F|$ the absolute value of the difference in slopes between the diabatic potentials at R_x . Since $|\Delta F|$ at $R = R_x(\tilde{X})$ is larger than that at $R = R_x(\tilde{A})$ as is evident from Fig. 6, P_x for the $V(\tilde{X})$ to ion-pair transition is smaller than P_x for the $V(\tilde{A})$ to ion-pair transition. This would rationalize the larger intensity ratio I_2/I_1 in Fig. 4(a) than those observed in Figs. 4(b) and 4(c). It is possible that the ion-pair state formed from $V(\tilde{A})$ via the avoided surface crossing at $R = R_x(\tilde{A})$ undergoes the second avoided surface crossing at $R = R_x(\tilde{X})$ and the system is converted to the $V(\tilde{X})$ state. However, the probability for the second switchover may be rather small, because the ~ 1 eV potential energy difference between the two avoided crossing points has been transformed to the kinetic energy for flying apart and accordingly v at $R = R_x(\tilde{X})$ may be much higher than that at $R = R_x(\tilde{A})$.

Analogous avoided surface crossings with high transition probabilities would occur between the ion-pair potentials and the Rydberg states converging to higher excited states of SF_6^+ , if the two potentials intersect each other on their repulsive walls (i.e., small $|\Delta F|$) at relatively short separation (i.e., low v). Such situations appear to be always realized in the Rydberg states of SF₆. First, the ground and excited SF₆⁺ ions treated in the present study are known to be unstable^{13,33,34,43} with respect to dissociation into SF_k⁺ + (6 - k)F + e⁻, and so should be the concomitant Rydberg states with respect to dissociation into SF_k^{**} + (6 - k)F. Second, the dissociation limit for the ionpair state F⁻(¹S_g) + SF_k⁺ + (5 - k)F lies at least 0.3 eV below the limit for the Rydberg states because of the large electron affinity of the fluorine atom.

Dissociation of Rydberg molecules is often discussed in terms of the ion core model.⁴⁰ When a molecule AB is excited to a Rydberg state AB^{**}, the ion core starts to dissociate into $A + B^+$ with the Rydberg electron either remaining bound to B^+ or following neither A nor B^+ . The former case leads to $A + B^{**}$ and the latter to $A + B^+ + e^-$. The investigation reported here suggests that the Rydberg electron can behave yet in another way: remaining bound to A to form $A^- + B^+$.

In the F^- efficiency curve, we have observed pronounced depression of the resonance peaks assigned to the inner-well valence state of SF₆, such as the $5a_{1g} \rightarrow 6t_{1u}$ resonance (feature F11). This result gives strong evidence that the autoionization or radiative decay of the inner-well state must occur much faster than the dissociation processes involving the conversion to the ion-pair states through avoided surface crossings.

V. SUMMARY

The photodissociation efficiency curve of F^- from SF_6 has been obtained in order to study the ion-pair formation induced by the photoexcitation of SF_6 . All of the observed features are identified as resonance peaks resulting from excitation of a valance electron into a virtual unoccupied orbital. Neutral excited states thus formed are subsequently converted to ion-pair states through avoided potential surface crossings. Assignments of the peaks have been made in such a way that the term values for the virtual orbitals estimated from the energies of the resonance peaks are consistent with the values reported previously.¹¹ It is clearly observed that transitions to directly dissociating Rydberg states give much stronger peak intensity than transitions to excited states of valence type.

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