



Negative ion mass spectrometric study of ionpair formation in the vacuum ultraviolet. II. OCS \rightarrow S-+CO+, O-+CS+, and CO2 \rightarrow O-+CO+

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Negative-ion mass spectrometric study of ion-pair formation in the vacuum ultraviolet. II. $OCS \rightarrow S^- + CO^+$, $O^- + CS^+$, and $CO_2 \rightarrow O^- + CO^+$

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Ion-pair formation from photoexcitation of OCS and CO₂ has been studied by negative-ion mass spectrometry using synchrotron radiation in the 15-35 eV photon energy range. Negative ions S⁻ and O⁻ from OCS and O⁻ from CO₂ have been observed. The lowest onset energy in the photodissociation efficiency curve for each ion is in good agreement with the thermochemical threshold for the formation of the negative ion in the ground ${}^{2}P_{u}$ state and its counterpart positive ion in the ground ${}^{2}\Sigma^{+}$ state. There exist series of peaks with medium intensities in the efficiency curves of S^- from OCS and O^- from CO₂; they are identified as resulting from predissociation of the Rydberg states converging to OCS⁺ ($\tilde{B}^{2}\Sigma^{+}$) and CO_2^+ ($\tilde{C}^2\Sigma_g^+$), respectively. Broad peaks are observed at 18.4 eV (~675 Å) in the efficiency curves for both S⁻ and O⁻ produced from OCS. Predissociation of the excited valence state formed by the intravalence $9\sigma \rightarrow 10\sigma$ transition is considered to mainly contribute to these features. In addition, a broadband feature is present in the wavelength range of 400-620 Å in the O^- efficiency curve. The most likely candidate for the corresponding doorway state is the two-electron excited state involving simultaneous $9\sigma \rightarrow 10\sigma$ and $3\pi \rightarrow 4\pi$ transitions. In the case of the O⁻ efficiency curve from CO₂, two maxima observed at 21.4 (580 Å) and 23.0 eV (538 Å) are explained as resulting from the $3\sigma_u \rightarrow 5\sigma_g$ transition forming an excited valence state which effectively couples to the ion-pair continuum.

I. INTRODUCTION

In the photon energy range of 10-50 eV, photoionization and photodissociation of molecules often proceed via neutral superexcited states (doorway states) of two different types:¹⁻⁹ Rydberg states converging to various ionic states, and the excited valence states formed by the promotion of a valence electron into a virtual valence orbital (π^* or σ^*). The resonance-like peaks assigned to the members of Rydberg series are detected by a variety of experimental methods such as photoabsorption spectroscopy,^{2-4,7} photoionization mass spectrometry,^{2-4,9} fluorescence excitation spectroscopy,^{3,5} (threshold) photoelectron spectroscopy,^{2-5,7,8} and dipole (e,2e) spectroscopy.^{4,6} Several authors have studied the decay channels for these Rydberg states which are embedded in ionization and dissociation continua.^{2,3,5} Bound Rydberg states undergo autoionization into the ground and excited ions or predissociation into neutral fragments through coupling with the continua by configuration interactions.¹ In contrast, less knowledge has been accumulated for the excited valence states, mainly due to lack of data on their excitation energies and the transition oscillator strengths.⁵ The excited valence states may also decay via autoionization and predissociation, though their dynamic behaviors are not fully elucidated.

One of the most common relaxation pathways for these doorway states is predissociation into ion pairs of the type

$$AB + h\nu \rightarrow A^{-} + B^{+}, \qquad (1)$$

since many ion-pair states lie 10–50 eV above the neutral ground state of a molecule. $^{10-17}$ The cross section for process

(1) is considered to be resonantly enhanced when an ionpair continuum couples strongly with the discrete Rydberg states. In fact, electronic predissociation of the Rydberg states gives rise to a series of intense peaks in the efficiency curve of the A^- ion: O^- from O_2 ,^{12,13} O^- from NO,¹³ $O^$ and C^- from CO,¹³ and O^- from N₂O.¹⁷ Assuming analogous coupling between excited valence states and an ion-pair continuum, one can expect similar resonances occurring at the excitation energies for the valence states. If this is the case, the efficiency curve of A^- should provide useful information on intravalence transitions to unoccupied virtual orbitals of the molecule AB.

The main purpose of the present work is to study the ion-pair formation process induced by photoabsorption of typical triatomic molecules OCS and CO₂ with particular attention to the properties of the doorway neutral excited states. For OCS and CO₂, the measurements of the cross sections for photoabsorption,¹⁸⁻²⁵ partial ionic photofragmentation,^{11,25-30} and partial photoionization^{20,31-34} have been the subject of many previous investigations. Their Rydberg states have been observed in photoabsorption spectra,^{18,19,21-24} photoionization efficiency curves,^{11,26,28,29} partial photoionization cross-section curves,^{32,34} threshold electron spectra,³⁵ electron energy-loss spectra,³⁶ and fluorescence excitation spectra.³⁷⁻³⁹ The decay pathways for the Rydberg states converging to $OCS^+(\tilde{B}^2\Sigma^+)$ and CO_2^+ ($\tilde{C}^2\Sigma_a^+$) have been discussed by Nenner *et al.*⁵ and Hubin-Franskin et al.,32 respectively. Concerning the intravalence excitations, prominent peaks have been found near the threshold energy region in the partial photoionization

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cross-section curves for OCS⁺ ($\tilde{C} \, {}^{2}\Sigma^{+}$) and CO₂⁺ ($\tilde{B} \, {}^{2}\Sigma_{u}^{+}$) by dipole $(e,2e)^{20,33}$ and synchrotron radiation photoelectron spectroscopy.³⁴ Langhoff and co-workers have performed single-channel static-exchange calculations of the virtual orbital energies of OCS and CO₂ and the associated transition oscillator strengths.^{40,41} They have shown that intravalence excitations to low-lying antibonding orbitals (σ^{*} or π^{*}) characterize the shapes of the measured ionization cross-section curves. On the other hand, no efforts have been made to detect the negative ions produced from OCS and CO₂ by ion-pair formation, probably due to very low intensities, so that there is no data concerning the interaction between the neutral photoexcited states and the ion-pair continuum.

As mentioned in a previous paper,¹⁷ our negative-ion mass spectrometer operates in high detection efficiencies with high signal-to-noise ratios, owing to the high photon flux over a wide vacuum ultraviolet (vuv) range available with synchrotron radiation. The present paper reports the measurements of photodissociation efficiency curves for negative ions produced by the processes

$$OCS + h\nu \rightarrow S^- + CO^+, \qquad (2)$$

$$OCS + hv \to O^- + CS^+, \tag{3}$$

$$\mathrm{CO}_2 + h\nu \to \mathrm{O}^- + \mathrm{CO}^+. \tag{4}$$

The efficiency curves are found to clearly exhibit the resonance-like structures assignable to the transitions to both Rydberg and excited valence states of the parent molecules, representing sharp contrast with the photoionization efficiency curves for positive ions in which uniform backgrounds due to direct ionization more or less smear the resonance structure. It is also proved that predissociation of the excited valence states whose electronic configurations correlate consistently with those of the ion-pair states plays a major role in the negative-ion efficiency curves.

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.^{17,42} Neat sample gas is expanded from an orifice of 50 μ m diameter. The stagnation pressure and nozzle temperature are 500 \pm 50 Torr and 298 \pm 3 K, respectively. The pressure in the chamber is monitored by a cold cathode Pirani gauge and kept constant at 1.1×10^{-4} Torr by regulating the gas flow through a needle valve upstream of the nozzle. Commercial high-purity gases are used without further purification (OCS, Matheson, 97.5% pure; CO₂, Nihon Sanso, 99.99% pure). A central portion of the beam 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 ion produced by photodissociation 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 0.5–1 Å and 30–60 s, respectively. All efficiency curves reported in this paper are measured with the wavelength resolution of 0.8 Å, corresponding to the widths of the entrance and exit slits of 200 μ m.

III. RESULTS

A. S⁻ formation from OCS

The mass spectrum of OCS consists of S⁻ and O⁻ ions. The intensities of other ions such as C⁻ and CS⁻ are below our detection limit. The photodissociation efficiency curve for the formation of S⁻ from OCS is shown in Fig. 1(a). Energies of the various dissociation limits and the adiabatic ionization potentials of OCS are listed in Table I for use in the following discussion. The appearance energy of S⁻ determined in the present study is $15.10 \pm 0.04 \text{ eV}$ (821 ± 2 Å), in excellent agreement with the thermochemical threshold for the formation of S⁻(²P_u) + CO⁺($\tilde{X}^{2}\Sigma^{+}$), $15.09 \pm 0.05 \text{ eV}$ ($821.6 \pm 2.7 \text{ Å}$), which is calculated from the C-S bond dissociation energy of the OCS molecule, 3.16



FIG. 1. Photodissociation efficiency curves for S⁻ and O⁻ produced from OCS taken at a wavelength resolution (FWHM) of 0.8 Å and wavelength intervals of 1 Å. The vertical lines indicate the ionization limits for the vibrational ground states of OCS⁺ (\tilde{B} and \tilde{C}) and the thermochemical thresholds for the formation of S⁻(${}^{2}P_{u}$) + CO⁺(\tilde{X} , \tilde{A} , and \tilde{B}), O⁻(${}^{2}P_{u}$) + CS⁺(\tilde{X} , \tilde{A} , and \tilde{B}), S⁻(${}^{2}P_{u}$) + C⁺(${}^{2}P_{u}$) + O(${}^{3}P_{g}$), and O⁻(${}^{2}P_{u}$) + C(${}^{3}P_{g}$) + S⁺(${}^{4}S_{u}$).

Key*	Energy (eV)	Species	Symmetry	References
I _P	11.174	$OCS^+[\tilde{X}^2\Pi(0,0,0)]$	² П	Ref. 48
D	13.52	$S^+({}^4S_u) + CO(\tilde{X}{}^1\Sigma^+)$	⁴ Σ	b,c
I_P	15.075	$OCS^+[\tilde{A}^2\Pi(0,0,0)]$	² Π	Ref. 48
D_	15.10 (15.09) ^d	$\mathbb{S}^{-}(^{2}P_{u})+\mathrm{CO}^{+}(\widetilde{X}^{2}\Sigma^{+})$	$^{1,3}\Sigma^+, ^{1,3}\Pi$	Present work
D	15.36	$S^+(^2D_u) + CO(\tilde{X}^{\dagger}\Sigma^+)$	$^{2}\Sigma^{-},^{2}\Pi,^{2}\Delta$	b,c
Ip	16.041	OCS ⁺ [$\tilde{B}^{2}\Sigma^{+}(0,0,0)$]	$2\Sigma^{+}$	Ref. 48
D	16.56	$S^+({}^2P_u) + CO(\widetilde{X}{}^1\Sigma^+)$	${}^{2}\Sigma^{+},{}^{2}\Pi$	b,c
D_{-}	17.08 (16.72) ^d	$\mathbf{O}^{-}(^{2}P_{u}) + \mathbf{C}\mathbf{S}^{+}(\tilde{X}^{2}\Sigma^{+})$	$^{1.3}\Sigma^{+}, ^{1.3}\Pi$	Present work
D	17.17	$S(^{3}P_{g}) + CO^{+}(\tilde{X}^{2}\Sigma^{+})$	^{2,4} ∑ ⁻ , ^{2,4} ∏	b, Ref.44
D_{-}	17.63	$\mathbf{S}^{-}(\tilde{\mathbf{P}}_{u}) + \mathbf{CO}^{+}(\tilde{\mathbf{A}}^{2}\Pi)$	$^{1,3}\Sigma^+, ^{1,3}\Sigma^-, ^{1,3}\Pi, ^{1,3}\Delta$	b, Refs. 45 and 46
Ip	17.958	$OCS^+[\tilde{C}^2\Sigma^+(0,0,0)]$	$^{2}\Sigma^{+}$	Ref. 48
D	18.18	$O({}^{3}P_{g}) + CS^{+}(\tilde{X}^{2}\Sigma^{+})$	^{2,4} Σ ⁻ , ^{2,4} Π	b, Ref. 52
D_{-}	18.18	$O^{-}(\tilde{P}_{u}) + CS^{+}(\tilde{A}^{2}\Pi)$	$^{1.3}\Sigma^+, ^{1.3}\Sigma^-, ^{1.3}\Pi, ^{1.3}\Delta$	b, Refs. 12 and 52
D	18.32	$S(^{1}D_{g}) + CO^{+}(\tilde{X}^{2}\Sigma^{+})$	$^{2}\Sigma^{+},^{2}\Pi,^{2}\Delta$	b,c, Ref. 44
D	19.70	$S({}^{3}P_{R}) + CO^{+}(\tilde{A} {}^{2}\Pi)$	$^{2,4}\Sigma^{+},^{2,4}\Sigma^{-},^{2,4}\Pi,^{2,4}\Delta$	b, Ref. 45
D	19.64	$O({}^{3}P_{g}) + CS^{+}(\tilde{A}^{2}\Pi)$	$^{2,4}\Sigma^+, ^{2,4}\Sigma^-, ^{2,4}\Pi, ^{2,4}\Delta$	b, Ref. 52
D	20.15	$O(^{1}D_{g}) + CS^{+}(\tilde{\chi}^{2}\Sigma^{+})$	$^{2}\Sigma^{+},^{2}\Pi,^{2}\Delta$	b,c Ref. 52
D	20.47	$O^+({}^4S_u) + CS(\tilde{X}^+\Sigma^+)$	$4\Sigma^{-}$	b,c
D_	20.76	$S^{-}(^{2}P_{u}) + CO^{+}(\dot{B}^{2}\Sigma^{+})$	$^{1.3}\Sigma^+, ^{1.3}\Pi$	b, Refs. 45 and 46
D_{-}	21.23	$O^{-}({}^{2}P_{u}) + CS^{+}(\tilde{B}^{2}\Sigma^{+})$	^{1,3} Σ ⁺ , ^{1,3} Π	b, Refs. 12 and 52
D_{-}	23.15	$O^{-}({}^{2}P_{u}) + C({}^{3}P_{g}) + S^{+}({}^{4}S_{u})$		b,c, Ref. 12
D_{-}	23.44	$S^{-}({}^{2}P_{u}) + C^{+}({}^{2}P_{u}) + O({}^{3}P_{g})$		b,c, Ref. 46
D_{-}	24.05	$O^{-}({}^{2}P_{u}) + C^{+}({}^{2}P_{u}) + S({}^{3}P_{z})$		b,c, Ref. 12
D _	25.79	$S^{-}({}^{2}P_{u}) + C({}^{3}P_{g}) + O^{+}({}^{4}S_{u})$		b,c, Ref. 46

TABLE I. Adiabatic ionization potentials and the dissociation limits of OCS. All energies are measured with respect to the neutral ground state OCS $[\tilde{X} \, {}^{1}\Sigma^{+}(0,0,0)]$.

^a The symbols I_P , D, and D_- , refer to the adiabatic ionization potential, the limit for the dissociative ionization, and the limit for the ion-pair formation.

^b Bond dissociation energies used for the energy calculations are 3.16 eV for D_0^0 (S–CO) (Ref. 43), 6.85 eV for D_0^0 (O–CS) (Ref. 51), and 11.092 eV for D_0^0 (C–O) (Ref. 61).

^c The atomic energy levels of neutrals and ions are taken from Moore's table [C. E. Moore, *Atomic Energy Levels*, Natl. Stand. Ref. Data Ser., Natl. Bur. Stand. (U.S. GPO, Washington, D.C., 1970), Vol. 34]. ^d See the text.

eV,^{26,43} adiabatic ionization potential for CO⁺ ($\tilde{X}^2 \Sigma^+$), 14.01 eV,^{28,44,45} and the electron affinity of the sulfur atom, 2.0772 \pm 0.0005 eV.⁴⁶

The efficiency curve of S⁻ comprises two distinct features, the maximum intensity positions of which are at ~770(16.1 eV, feature F1) and ~675 Å (18.4 eV, feature F2). Feature F1 is made up of several peaks assigned to the Rydberg states R_B converging to the OCS⁺ ($\tilde{B}^2\Sigma^+$) state. This part of the spectrum recorded with the better statistics is shown in Fig. 2. Our assignments of the observed peaks to the $nd\sigma$ ¹ Σ^+ (series IV) and $ns\sigma$ ¹ Σ^+ (series V) states are summarized in Table II. The agreement with the existing experimental results is seen to be excellent.^{18,26,35,36,47} Among the members of the $np\sigma$ ¹ Σ^+ series (series III), only the 5 $p\sigma$ peak is identifiable. Other higher members are probably hidden in the stronger $nd\sigma$ peaks.

Feature F2 extends over the wavelength range of 600– 730 Å and its integrated intensity is five times as large as that of feature F1. The peak maximum energy is no more than about 0.4 eV higher than the ionization threshold for OCS⁺ $[\tilde{C}^{2}\Sigma^{+}(0,0,0)]$, 17.958 eV (690.42 Å).⁴⁸ We can, however, observe no resonance peaks or dips for the Rydberg states R_{C} converging to the $\tilde{C}^{2}\Sigma^{+}$ state (series VII and IX), which have been reported by photoabsorption spectroscopy,^{18,21} the photoionization²⁶ and electron-impact ionization⁴⁹ mass spectrometry, and the electron-impact energyloss spectroscopy.³⁶ The larger integrated intensity of



FIG. 2. Photodissociation efficiency curve for S^- produced from OCS near the adiabatic ionization potential for OCS⁺($\tilde{B}^2\Sigma^+$). The spectrum is taken at a wavelength resolution (FWHM) of 0.8 Å and wavelength intervals of 1 Å. The positions of the Rydberg states identified by Leclerc *et al.* (Ref. 36) are indicated. The nominal principal quantum numbers are defined by Eqs. (4)–(6) of Ref. 36.

TABLE II. Wavelengths for Rydberg series converging to $OCS^+[\tilde{B}\,^2\Sigma^+(0,0,0)]$ observed in the S⁻ efficiency curve. All of the Rydberg series have the $^1\Sigma^+$ symmetry.

Wavelength (Å)		Designation ^a		
Present work	Leclerc et al. ^b	Series III	Series IV	Series V
818	818.7			5so
810	809.5	5 <i>p</i> \sigma		
806	806.0		$5d\sigma$	
802	801.2			$6s\sigma$
795	795.2	(6po)	$6d\sigma$	
793	792.4	-		7s♂ ^c
790	788.8		7do	
787	787.1			$8s\sigma$
785	785		$8d\sigma$	

^a We follow the assignments made by Leclerc et al. (Ref. 36).

^b Reference 36.

^c Appears as the shoulder of the 6do peak.

feature F2 than that of feature F1 may exclude the possibility of the R_c states as the principal contributor to feature F2, since the Franck-Condon factors between OCS $(\tilde{X} \ \Sigma^+)$ and OCS⁺ $(\tilde{C} \ \Sigma^+)$ are less favorable than those between OCS $(\tilde{X} \ \Sigma^+)$ and OCS⁺ $(\tilde{B} \ \Sigma^+)$.^{48,50} We, therefore, conclude that predissociation from some neutral excited states other than the R_c Rydberg states gives rise to feature F2. The nature of these states will be discussed in Sec. IV C. Weak fine structures are superimposed on the envelope of feature F2, for instance at 682, 696, and 710 Å. Their identity must await studies with smaller statistical errors than available here.

The S⁻ efficiency curve shows no marked *step up* at the threshold energies for other energetically accessible ion-pair states, S⁻(²P_u) + CO⁺(\tilde{A} ²\Pi) (17.63 eV or 703.4 Å) and S⁻(²P_u) + CO⁺(\tilde{B} ² Σ ⁺) (20.76 eV or 597.4 Å) (see Table I). In several experimental runs, we can identify an additional weak peak centered at about 500 Å. The onset energy for this peak appears to nearly be in accord with the thermochemical threshold for the formation of S⁻(²P_u) + C⁺(²P_u) + O(³P_k), 23.44 eV or 529 Å (see Table I).

The cross section for process (2) at 675 Å is estimated to be $(2.1 \pm 1) \times 10^{-21}$ cm² from a comparison between the count rate of O⁻ produced by process (2) and that of O⁻ produced by

$$O_2 + h\nu \rightarrow O^- + O^+. \tag{5}$$

Here, the cross section of $\sim 2 \times 10^{-19}$ cm² at 716.35 Å for process (5) is derived from the data given by Dehmer and Chupka.¹² The quantum yield for process (2) is then obtained to be $(4.6 \pm 2) \times 10^{-5}$ at 675 Å from the total photoabsorption cross section for OCS, 4.6×10^{-17} cm².²⁰

B. O⁻ formation from OCS

The photodissociation efficiency curve for O⁻ produced from OCS behaves in quite a different manner from that for S⁻ as shown in Fig. 1. The appearance energy of O⁻ is determined by a linear extraporation of the 710–725 Å portion of the curve to be 17.08 ± 0.09 eV (726 ± 4 Å). This value is slightly higher than the thermochemical threshold for the formation of $O^{-}({}^{2}P_{u}) + CS^{+}(\tilde{X}\,{}^{2}\Sigma^{+})$, 16.72 \pm 0.3 eV (742 \pm 13 Å), calculated from the C–O bond dissociation energy of the OCS molecule, 6.85 eV,⁵¹ adiabatic ionization potential for CS⁺($\tilde{X}\,{}^{2}\Sigma^{+}$), 11.33 \pm 0.01 eV,^{52,53} and the electron affinity of the oxygen atom, 1.462 \pm 0.003 eV.¹² This discrepancy may be due to the uncertainty in locating the threshold for the slowly rising yield curve.

The most intense peak at ~ 675 Å in the O⁻ efficiency curve (feature F3) is in accord in shape with feature F2 in the S^- curve. This suggests that the same doorway state(s) is (are) involved in the formation processes of both S⁻ and O^- in this wavelength region (see Sec. IV C). The O^- curve shows a band with a slowly increasing ion yield from ~ 610 to \sim 540 Å (feature F4). We have applied a deconvolution procedure to the O⁻ efficiency curve to determine the precise onset of feature F4, assuming that the overlapping feature F 3 originates from the same doorway state(s) as feature F2. The onset energy thus obtained, 20.0 eV (620 Å), is considerably lower than the thermochemical threshold for the ion-pair channel $O^{-}({}^{2}P_{\mu}) + CS^{+}(\tilde{B}{}^{2}\Sigma^{+}), 21.23 \text{ eV or}$ 584 Å (Table I). We, therefore, conclude that the opening of this ion-pair channel does not account for feature F4; instead, photoexcitation to a neutral resonance state is considered to give rise to this feature (see Sec. IV C). In the midway of feature F4, a reproducible peak is observed at 589-590 Å. This peak can be explained as arising by predissociation from the Rydberg state converging to an inner-valence electron excited ionic state.

A sharp onset occurring at 537 Å (23.09 eV, feature F5) corresponds to the photodissociation to two fragment ions and a neutral atom, $O^{-}({}^{2}P_{u}) + S^{+}({}^{4}S_{u}) + C({}^{3}P_{g})$ (the estimated thermochemical threshold = 23.15 eV or 536 Å). On the other hand, the origin of the weak onset observed at ~495 Å is not yet clear. This feature may possibly be related to photodissociation to $O^{-}({}^{2}P_{u}) + C^{+}({}^{2}P_{u}) + S({}^{3}P_{g})$ (the estimated thermochemical threshold = 24.05 eV or 516 Å).

The cross section and the quantum yield for process (3)



FIG. 3. Photodissociation efficiency curve for O⁻ produced from CO₂ taken at a wavelength resolution (FWHM) of 0.8 Å and wavelength intervals of 1 Å. The vertical lines indicate the ionization limits for the vibrational ground states of CO₂⁺ (\tilde{B} and \tilde{C}) and the thermochemical thresholds for the formation of O⁻(${}^{2}P_{u}$) + CO⁺(\tilde{X} , \tilde{A} , and \tilde{B}), O⁻(${}^{2}P_{u}$) + C⁺(${}^{2}P_{u}$) + O(${}^{3}P_{g}$), and O⁻(${}^{2}P_{u}$) + C(${}^{3}P_{g}$) + O⁺(${}^{4}S_{u}$).

at 675 Å are estimated to be $(2.2 \pm 1) \times 10^{-21}$ cm² and $(4.7 \pm 2) \times 10^{-5}$, respectively, according to the procedure discussed in Sec. III A.

C. O⁻ formation from CO₂

In the mass spectra of negative ions from CO_2 , only O⁻ ions are detected in the wavelength range of 300-1000 Å. The photodissociation efficiency curves for O^- in the range of 350–710 Å and near the onset energy region are shown in Figs. 3 and 4, respectively. The onset energy observed at 17.990 ± 0.025 eV (689.2 ± 1 Å) agrees well with the thermochemical threshold for the formation of $O^{-}({}^{2}P_{u})$ $+ CO^+ (X^2 \Sigma^+)$, 18.004 $\pm 0.025 \text{ eV}$ (688.7 $\pm 1 \text{ Å}$), which is deduced from the adiabatic ionization threshold for $CO^+(\tilde{X}^2\Sigma^+) + O({}^{3}P_{g}) + e^-$, 19.466 eV,²⁸ and the electron affinity of the oxygen atom, 1.462 ± 0.003 eV.¹² The sharp peak at 687 Å is considered to result from predissociation of Rydberg states converging to CO_2^+ [$\tilde{B}^2\Sigma_{\mu}^+$ (0,0,0)], since there exist a number of high n Rydberg states having either the ${}^{1}\Sigma_{\mu}^{+}$ or ${}^{1}\Pi_{\mu}$ symmetry slightly below the CO_2^+ [$\tilde{B}^2\Sigma_u^+(0,0,0)$] ionization limit of 18.077 eV (685.87 Å).50

The peaks observed at 645–683 Å in Fig. 4 (feature F6) can be assigned to Rydberg series converging to $CO_2^+ [\tilde{C}^2 \Sigma_g^+ (0,0,0)]$: the $np\sigma_u^{-1} \Sigma_u^+$ series and the much weaker $nd\pi_g^{-1}\Pi_g$ series (optically forbidden states). It is likely that the $np\sigma_u$ Rydberg states preferentially predissociate into the ${}^{1}\Sigma_u^+$ ion-pair state which asymptotically correlates to $O^-({}^{2}P_u) + CO^+(\tilde{X}\,{}^{2}\Sigma^+)$. The assignments for the observed Rydberg states are given in Table III.

The efficiency curve for O⁻ gradually rises with the increase of the photon energy above ~20 eV (620 Å), and makes two broad maxima overlap each other (feature F7); their peak energies are 21.4 ± 0.2 (580 ± 5 Å) and 23.0 ± 0.2 eV (538 ± 5 Å). In Sec. IV D, we will see that the contribution of intravalence photoexcitations accounts for this feature. After passing through a flat region below 510 Å, the curve shows a steep onset occurring at 26.38 ± 0.11 eV (470 ± 2 A) and a less clear onset at 28.70 ± 0.2 eV

npo_i,

nditte



c²Σ,

(0,0,0)

FIG. 4. Photodissociation efficiency curve for O⁻ produced from CO₂ near the adiabatic ionization potential for CO₂⁺ (\tilde{C} ² Σ_{g}^{+}). The spectrum is taken at a wavelength resolution (FWHM) of 0.8 Å and wavelength intervals of 1 Å. The positions of the Rydberg states identified by McCulloh (Ref. 28) are indicated. The nominal principal quantum numbers are defined by Eqs. (8) and (9) of Ref. 22.

TABLE III. Wavelengths for Rydberg series converging to CO_2^+ [$\tilde{C}^2\Sigma_g^+(0,0,0)$] observed in the O⁻ efficiency curve. The $np\sigma_u$ and $nd\pi_g$ series have the $^1\Sigma_u^+$ and $^1\Pi_g$ symmetry, respectively.

Wavelength (Å)		Designation ^a		
Present work	McCulloh ^b	"Absorption" series	"Weak absorption" series ^c	
683	682.9	3ро,		
669	669.2		$4d\pi_a$	
664	664.2	4 <i>pσ</i> ,,	•	
658	658		$5d\pi_{\pi}$	
655	655.5	5pσ"	8	
652	652.2		$6d\pi_a$	
650-651	650.9	6po.,	8	
647–648	648.0	7ρσ.		
645-646	•••	8pou		

^a We follow the assignments made by Tanaka et al. (Ref. 22).

^bReference 28.

^c Dipole transitions to the $nd\pi_{g}$ series are optically forbidden.

 $(432 \pm 3 \text{ Å})$. The related dissociation limits and the adiabatic ionization potentials of CO₂ are summarized in Table IV. The observed onsets are in good agreement with the thermochemical thresholds for the formation of $O^{-}(^{2}P_{u})$ $+ C^{+}(^{2}P_{u}) + O(^{3}P_{g})$ (26.34 \pm 0.04 eV or 471 Å) and $O^{-}(^{2}P_{u}) + O^{+}(^{4}S_{u}) + C(^{3}P_{g})$ (28.70 \pm 0.04 eV or 432 Å), respectively. No marked increase in the O⁻ intensity is found both at the threshold for the formation of $O^{-}(^{2}P_{u})$ $+ CO^{+}(\tilde{A} ^{2}\Pi)$ (20.54 \pm 0.02 eV or 604 \pm 1 Å) and at that of $O^{-}(^{2}P_{u}) + CO^{+}(\tilde{B} ^{2}\Sigma^{+})$ (23.66 \pm 0.02 eV or 524 \pm 1 Å). The O⁻ efficiency curve smoothly fades out below 400 Å.

The cross section and the quantum yield for process (4) at 538 Å are estimated to be $(4.4 \pm 2) \times 10^{-21}$ cm² and $(1.3 \pm 0.6) \times 10^{-4}$, respectively (see Sec. III A). In this estimation, the value of 3.4×10^{-17} cm² is adopted as the total photoabsorption cross section for CO₂ measured by Lee *et al.*²⁴

IV. DISSCUSSION

A. Rydberg states converging to OCS⁺[$\tilde{B}^{2}\Sigma^{+}(0,0,0)$] (feature *F*1)

The photodissociation efficiency curve for S⁻ produced from OCS shows the peaks assigned to the R_B Rydberg states with ${}^{1}\Sigma^{+}$ symmetry (Fig. 2 and Table II). This finding provides tangible evidence that the ${}^{1}\Sigma^{+}$ ion-pair potential intersects the R_B potentials near their minima at about 15.10 eV (= the appearance energy of S⁻) above the ground state.

Various decay processes have so far been proposed for the R_B Rydberg states formed by photoexcitation.^{5,35} Because of favorable Franck–Condon factors, a portion of OCS molecules in the R_B Rydberg states eject electrons with energies of $E_{h\nu} - I_p(\tilde{X})$ to produce the vibrational ground state of OCS⁺($\tilde{X}^2\Pi$) by electronic autoionization (path 1). Here, $E_{h\nu}$ is the photon energy, $I_p(\tilde{X})$ the adiabatic ionization potential for OCS⁺[$\tilde{X}^2\Pi(0,0,0)$], 11.174 eV.⁴⁸ If the excitation energies of the R_B states are higher than the ioni-

TABLE IV. Adiabatic ionization potentials and the dissociation limits of CO₂. All energies are measured with respect to the neutral ground state CO₂ [\tilde{X} ⁺ Σ_{s}^{+} (0,0,0)].

Keyª	Energy (eV)	Species	Symmetry	References
Ip	13.778	$CO_{2}^{+}[\tilde{X}^{2}\Pi_{g}(0,0,0)]$	² Π _g	Ref. 50
I_P	17.314	CO_2^+ [$\tilde{A}^2\Pi_{\mu}(0,0,0)$]	² Π,	Ref. 50
D_	17.990 (18.004) ⁶	$\mathrm{O}^-({}^2P_u) + \mathrm{CO}^+(\tilde{X}{}^2\Sigma^+)$	$^{1,3}\Sigma^+, ^{1,3}\Pi$	Present work
I_P	18.077	$\operatorname{CO}_{2}^{+}\left[\tilde{B}^{2}\Sigma_{\mu}^{+}(0,0,0)\right]$	$2\Sigma_{\mu}$	Ref. 50
D	19.071	$O^+({}^4S_{\mu}) + CO(\tilde{X}{}^1\Sigma^+)$	⁴ Σ	Ref. 28
I_P	19.394	$\operatorname{CO}_{2}^{+} \left[\widetilde{C}^{2} \Sigma_{g}^{+} (0,0,0) \right]$	$^{2}\Sigma_{g}$	Ref. 50
D	19.466	$O({}^{3}P_{g}) + CO^{+}(\tilde{X}^{2}\Sigma^{+})$	$^{2,4}\Sigma^{-},^{2,4}\Pi$	Ref. 28
D_{-}	20.54	$O^{-}(\tilde{P}_{\mu}) + CO^{+}(\tilde{A}^{2}\Pi)$	^{1,3} Σ ⁺ , ^{1,3} Σ ⁻ , ^{1,3} Π, ^{1,3} Δ	c, Refs. 12 and 45
D	21.43	$O({}^{1}D_{\mu}) + CO^{+}(\tilde{X}^{2}\Sigma^{+})$	$^{2}\Sigma^{+},^{2}\Pi,^{2}\Delta$	c,d, Ref. 44
D	22.00	$O({}^{3}P_{g}) + CO^{+}(\widetilde{A}{}^{2}\Pi)$	^{2,4} Σ ⁺ , ^{2,4} Σ ⁻ , ^{2,4} Π, ^{2,4} Δ	c, Ref. 45
D	22.40	$O^+(^2D_u) + CO(\tilde{X}^1\Sigma^+)$	² Σ ⁻ , ² Π, ² Δ	c,d
D_{-}	23.66	$O^{-}(^{2}P_{u}) + CO^{+}(\tilde{B}^{2}\Sigma^{+})$	$^{1,3}\Sigma^+, ^{1,3}\Pi$	c, Refs. 12 and 45
D	25.13	$O({}^{3}P_{*}) + CO^{+}(\tilde{B}{}^{2}\Sigma^{+})$	^{2,4} Σ ^{-,2,4} Π	c, Ref. 45
D_{-}	26.34	$O^{-}({}^{2}P_{\mu}) + C^{+}({}^{2}P_{\mu}) + O({}^{3}P_{\mu})$	-	c,d, Ref. 12
D_	28.70	$O^{-}({}^{2}P_{u}) + C({}^{3}P_{g}) + O^{+}({}^{4}S_{u})$	·	c,d, Ref. 12

^a The symbols I_P , D, and D_- refer to the adiabatic ionization potential, the limit for the dissociative ionization, and the limit for the ion-pair formation.

^bSee the text.

^c Bond dissociation energies used for the energy calculations are 5.453 eV for D_0^0 (O–CO) (Ref. 28) and 11.092 eV for D_0^0 (C–O) (Ref. 61).

^d The atomic energy levels of neutrals and ions are taken from Moore's table (see footnote c of Table I).

zation potential for OCS⁺ [\tilde{A} ² Π (0,0,0)], 15.08 eV,⁴⁸ they can also autoionize into the vibrationally ground or excited $A^{2}\Pi$ states (path 2). The ionic states thus formed may subsequently predissociate via the dissociative states,³⁵ finally forming $S^+({}^4S_{\mu}) + CO(\tilde{X}{}^1\Sigma^+) + e^-$ and $S^+({}^2D_{\mu})$ $+ \operatorname{CO}(\widetilde{X}^{1}\Sigma^{+}) + e^{-}$. On the other hand, the fluorescence excitation spectra of OCS show that the R_{R} states undergo predissociation into neutral fragments via a repulsive valence state D which correlates with a pair of the ground and electronically excited fragments (path 3).5,37 The electronic autoionization of the D state by the interaction with an ionization continuum generates the vibrationally ground and excited states of OCS⁺ ($\tilde{X}^{2}\Pi$) (path 4). Moreover, the photoelectron energy distribution curves suggest that the Rydberg states R_X converging to the vibrationally excited $OCS^+(\tilde{X}^2\Pi)$ state are formed through the avoided surface crossing from the D state, and that subsequent vibrational autoionization of R_X produces highly vibrationally excited OCS⁺ ($\tilde{X}^2\Pi$) (path 5) by ejecting very low-energy electrons ("resonant" autoionization). It has become apparent from the present S⁻ efficiency curves that another decay channel for the R_B states exists, i.e., predissociation into the ${}^{1}\Sigma^{+}$ ion-pair state (path 6).

An alternative mechanism for the formation of the ionpair state in this region would be the initial conversion of the R_B states to a neutral repulsive state D followed by another conversion from the D state to an ion-pair state via an avoided surface crossing. According to the absorption and ionization yield measurements, ¹⁹ the rate of the predissociation of the R_B states via the D state is comparable with that of the electronic autoionization (paths 1 and 2).^{5,37} The autoionization lifetime is estimated to be shorter than 5×10^{-14} s from the widths of the autoionization peaks in the photoionization efficiency curve.²⁶ This implies that the conversion to the *D* state takes place in a time much shorter than the period of a vibration $(10^{-12}-10^{-13} \text{ s})$.

B. Rydberg states converging to CO_2^+ [$\tilde{C}^2\Sigma_g^+(0,0,0)$] (feature *F*6)

Three Rydberg series converging to CO_2^+ [$\tilde{C}^2\Sigma_e^+$ (0,0,0)] have been observed in photoabsorption spectra,^{22,24} photoionization efficiency curves of CO₂⁺ produced from CO₂,^{28,29} and a partial ionization cross-section curve for CO₂⁺ ($\tilde{B}^{2}\Sigma_{\mu}^{+}$).³² By using synchrotron radiation photoelectron spectroscopy, Hubin-Franskin et al.³² have found that the Rydberg states R_c converging to $\operatorname{CO}_2^+(\widetilde{C}\,^2\Sigma_g^+)$ decay mainly to the $\operatorname{CO}_2^+(\widetilde{B}\,^2\Sigma_u^+)$ state and, to a lesser extent, to the CO_2^+ ($\tilde{X}^2\Pi_g$) state. In all cases, the $np\sigma_{\mu}$ and $nd\pi_{g}$ resonances make asymmetrical peaks $(|q| \approx 2)$, whereas each of the $np\pi_{\nu}$ resonances makes a striking dip ($|q| \approx 0$). The small |q| value for the $np\pi_u$ states and their preferential decay to the ionic \tilde{B} state suggest that they strongly couple with the CO_2^+ ($\tilde{B}^2\Sigma_u^+$) + $\epsilon\pi_g$ continuum with a large matrix element of the dipole transition moment $|\langle \psi_E | T | \phi_i \rangle|$. Here, q is the profile index that characterizes the natural line shape for resonance transition to the neutral superexcited state, and ϕ_i and ψ_E denote the neutral ground $CO_2(X^1\Sigma_g^+)$ state and the unperturbed autoionization continuum of CO_2^+ ($\tilde{B}^2\Sigma_u^+$), respectively.¹

In contrast, no resonance peaks assignable to the $np\pi_u$ series are observed in the O⁻ efficiency curve in Fig. 4. Con-



FIG. 5. Orbital correlation diagrams between (a) OCS and $CO^+(\tilde{\chi}^2\Sigma^+) + S^-(^2P_u)$ and (b) OCS and $CS^+(\tilde{\chi}^2\Sigma^+) + O^-(^2P_u)$. The approximate binding energies for occupied and vacant orbitals are taken from data of photoelectron spectra (Refs. 45, 48, and 52) and results of *ab initio* calculations (this work), respectively.

ceivably, the couplings of the $np\pi_u$ states with the dissociative continua are weaker than those with the ionization continua.

C. Doorway states for the S⁻ and O⁻ formation from OCS (features F2–F4)

Features F2 and F3 observed at 18.4 eV in the efficiency curves for S⁻ and O⁻, respectively, may be ascribed to predissociation of the same doorway state, judging from the identical spectrum profiles. One candidate for this state might be the Rydberg state(s) converging to the OCS⁺ state(s) lying higher than the OCS⁺ [$\tilde{C}^2\Sigma^+(0,0,0)$] state, i.e., the ionic state(s) resulting from the removal of an innervalence electron. However, this possibility can be ruled out for the following reasons.

The symmetry adapted cluster-configuration interaction (SAC-CI) calculations by Nakatsuji⁵⁴ including threeand four-electron excitations have shown that the satellite peaks related to the ionizations of the inner-valence 7σ electron of OCS appear at 24.23, 25.68, and 26.13 eV with medium intensities. In these peaks, one or two extra valence electrons are promoted to low-lying antibonding valence orbitals accompanying the 7σ ionization. His spectrum is in fair agreement with those experimentally obtained by He II photoelectron spectroscopy for chemical analysis (ESCA)],⁵⁶ and binary and dipole (*e*,2*e*) electron impact spectroscopy.²⁰ For example, Potts and Williams⁵⁵ and Allan *et al.*⁵⁶ have observed a peak at 23.56 and 23.4 eV, respectively, corresponding to the theoretical 24.23 eV peak.⁵⁴

The energy difference between features F2/F3 and the 23.56 eV satellite⁵⁵ is more than 5 eV, so that it is highly unlikely that these features arise from predissociation of the

Rydberg state(s) converging to the latter satellite ionic state. Even if the Rydberg series is of the *nso* type, the excitation energy for the first member is estimated to be larger than 19.36 eV (640.4 Å) from the generally accepted lower limit, 1.8, of the effective principal quantum number.⁵⁷ Furthermore, the absence of any noticeable peaks in the wavelength range of 450–600 Å gives us reasonable evidence for little configuration coupling between the ion-pair state and the Rydberg states converging to the excited OCS⁺ satellites lying above 20 eV. Therefore, we have to resort to other types of excited states, such as the excited valence state, for a reasonable assignment of features F2-F4.

A number of excited valence states are indeed known to exist in the excitation energy range of 10-30 eV, although only a little is known about the energy levels and the transition oscillator strengths. Here, we will investigate the electronic configurations of possible doorway states by examining the orbital correlation between OCS and $S^- + CO^+$ as well as OCS and $O^- + CS^+$. The ground state of OCS (core)14 has the electronic configuration of $(6\sigma)^2(7\sigma)^2(8\sigma)^2(9\sigma)^2(2\pi)^4(3\pi)^4(4\pi)^0(10\sigma)^0(11\sigma)^0.$ Figure 5(a) shows a correlation diagram between valence molecular orbitals of OCS and $S^- + CO^+$ obtained by 4-31G ab initio calculations. The orbital energy of the antibonding 10σ decreases with the increase of the C-S bond length and asymptotically correlates with the σ -type 3p orbital of the S^- atom. The remaining two 3p orbitals evolve into the degenerate 3π orbitals of OCS. On the other hand, the occupied valence orbitals 5 σ , 1 π , and 4 σ of CO⁺ correlate with the 9σ , 2π , and 8σ orbitals of OCS, respectively. Thus, the diagram reveals that the $S^{-}({}^{2}P_{\mu}) + CO^{+}(\tilde{X}{}^{2}\Sigma^{+})$ ionpair state is produced most efficiently by predissociation of the valence excited state with the electronic configuration of ... $(8\sigma)^2(9\sigma)^1(2\pi)^4(3\pi)^4(4\pi)^0(10\sigma)^1(11\sigma)^0$. This is because the CO⁺ $(\tilde{X}^2\Sigma^+)$ state has the $(5\sigma)^{-1}$ single-hole configuration which correlates with the $(9\sigma)^{-1}$ single-hole configuration of OCS⁺.

Sheehy and Langhoff⁴⁰ have obtained single-channel static-exchange virtual orbital energies and oscillator strengths for intravalence transitions in OCS by performing minimal-basis-set SCF calculations. From their results, the promotion of the 9σ electron to the antibonding 10σ orbital occurs around the ionization threshold for the OCS⁺ ($\tilde{B}^{2}\Sigma^{+}$) state with a large oscillator strength. The strong peak observed at ~18 eV in the partial ionization cross-section curve for OCS⁺ ($\tilde{C}^{2}\Sigma^{+}$) by dipole (*e*,2*e*) experiments²⁰ has then been interpreted tentatively as the autoionization from the $9\sigma \rightarrow 10\sigma$ resonance state.⁴⁰ This experimental and theoretical evidence leads to the conclusion that intravalence $9\sigma \rightarrow 10\sigma$ excitation is responsible for feature F2 at ~18.4 eV.

We can also gain the same insight into the features appearing in the O⁻ efficiency curve from the orbital correlation diagram between molecular orbitals of OCS and those of O⁻ + CS⁺ [Fig. 5(b)]. Since one of the degenerate 2p orbitals of O⁻ and the highest occupied 7 σ orbital of CS⁺ correlate with the 10 σ and 9 σ orbitals of OCS, respectively, the electronic configuration ...(8σ)²(9σ)¹(2π)⁴(3π)⁴(4π)⁰(10σ)¹(11σ)⁰ should also couple strongly with the ion-pair state O⁻($^{2}P_{u}$) + CS⁺($\tilde{X}^{2}\Sigma^{+}$). In fact, the same feature (feature F3) as feature F2 appears in the O⁻ curve, as stated in Sec. III B.

Feature F4 may also be related to the resonance state formed by intravalence transitions in OCS. The correlation diagram in Fig. 5(b) indicates that the excited states produced by the $3\pi \rightarrow 10\sigma$ or $8\sigma \rightarrow 10\sigma$ transition can strongly correlate with the $O^{-}({}^{2}P_{\mu}) + CS^{+}(\tilde{A}{}^{2}\Pi)$ or the $O^{-}({}^{2}P_{\mu})$ + CS⁺ ($\tilde{B}^{2}\Sigma^{+}$) ion-pair continua, respectively. However, the calculated transition oscillator strengths for these transitions are two orders of magnitude smaller than that for the $9\sigma \rightarrow 10\sigma$ transition.⁴⁰ A more plausible explanation for feature F4 is that it originates from the two-electron excited state ... $(8\sigma)^2(9\sigma)^1(2\pi)^4(3\pi)^3(4\pi)^1(10\sigma)^1(11\sigma)^0$ for the following two reasons. First, the $3\pi \rightarrow 4\pi$ transition has the largest oscillator strength in the outer-valence shell spectrum⁴⁰ and occurs far below the ionization threshold for the OCS⁺ ($\tilde{X}^2\Pi$) state (11.174 eV)⁴⁸ probably because of the channel-coupling effects.⁴⁰ Second, on the basis of the correlation diagrams in Fig. 5, the electronic configuration of this two-electron excited state can correlate with the exit channel of $O^- + CS^+$, but not with the $S^- + CO^+$ channel. This marked difference reasonably explains another experimental finding, i.e., the absence in the S^- efficiency curve of the feature corresponding to feature F4.

D. Doorway states for the O^- formation from CO_2 (feature F 7)

Similarly to the case of OCS, the origin of feature F7 in the efficiency curve of O⁻ from CO₂ can be interpreted in two ways: (1) predissociation of the first and/or second member(s) of the Rydberg series converging to an ionic state lying higher than CO₂⁺ ($\tilde{C}^2\Sigma_g^+$), and (2) predissociation of an excited valence state into O⁻($^2P_{\mu}$)

+ CO⁺ ($\tilde{X}^2 \Sigma^+$) and/or O⁻ (${}^2P_{\mu}$) + CO⁺ ($\tilde{A}^2 \Pi$).

The excited ionic states of CO₂ have been extensively studied: experimentally by ESCA,⁵⁶ far UV synchrotron ra-diation photoelectron spectroscopy,^{34,58} He II photoelectron spectroscopy,⁵⁵ and dipole (e,2e) energy-loss spectroscopy,³³ and theoretically by coupled electron pair approximation (CEPA) and multireference single and double configuration interaction (MRSD-CI) calculations.^{41,59} Roy et al.⁵⁸ have reported ten CO₂⁺ satellites in the 22-45-eV binding energy region in their 45-eV photoelectron spectra. Each of the satellites corresponds to an ionic state with multipleexcited configurations. The ground state of CO₂ has the electronic configuration of $(\text{core})^6 (3\sigma_g)^2 (2\sigma_u)^2 (4\sigma_g)^2$ $(3\sigma_{\mu})^{2}(1\pi_{\mu})^{4}(1\pi_{g})^{4}(2\pi_{\mu})^{0}(5\sigma_{g})^{0}$. Below 30 eV, the most prominent band has been asssigned to the $3^{2}\Pi_{\mu}$ state which has the vertical ionization energy of 27.3 eV;58 this band has also been detected near this energy by other groups. 34,55,56 Ab initio SCF-CI calculations show that the $3^{2}\Pi_{u}$ state is the satellite of the $(1\pi_u)^{-1}$ CO₂⁺ ($\widetilde{A}^2\Pi_u$) state.⁵⁸

If the quantum defect δ of 1.2 or smaller is assumed for the $ns\sigma_g^{-1}\Pi_u$ Rydberg states converging to the $3^{-2}\Pi_u$ state (see Sec. IV C), the peak of the first member of this series, i.e., $3s\sigma_g$, appears at an energy higher than 23.10 eV (wavelength shorter than 537 Å). This value estimated for the excitation energy, probably giving the lower limit, is close to the peak maximum at 23.0 eV (538 Å) in feature F7 (see Fig. 3). Nevertheless, it is unlikely that transitions to the $3s\sigma_g$ Rydberg state give rise to feature F7, judging from the absence of any structure assignable to the second member of the series, $4s\sigma_g$, expected at approximately 485 Å (25.6 eV). The quantum defect for other optically allowed Rydberg series $(nd\sigma_g^{-1}\Pi_u, nd\pi_g^{-1}\Sigma_u^+, and nd\delta_g^{-1}\Pi_u)$ is generally smaller than that for the s-type series, and, hence, the d-type Rydberg series cannot be responsible for feature F7.

In order to search for more plausible doorway states yielding the observed peaks, we again check up on the correlation diagram between molecular orbitals of CO₂ and $O^- + CO^+$ as illustrated in Fig. 6. The degenerate 2p orbitals of O⁻ correlate with the antibonding $5\sigma_g$ and the nonbonding $1\pi_{p}$ orbitals of CO₂, whereas the outer-valence 5σ , 1π , and 4σ orbitals of CO⁺ correlate with the $3\sigma_u$, $1\pi_u$, and $4\sigma_g$ orbitals of CO₂, respectively. Therefore, the ion pair $O^{-}({}^{2}P_{u}) + CO^{+}(\tilde{X}{}^{2}\Sigma^{+})$ is considered to be produced most efficiently from the excited state with the electronic configuration of ... $(4\sigma_g)^2 (3\sigma_u)^1 (1\pi_u)^4 (1\pi_g)^4 (2\pi_u)^0$ $(5\sigma_{g})^{1}$, because CO⁺ ($\tilde{X}^{2}\Sigma^{+}$) arises from the ionization of the 5σ electron of CO. Indeed, the static-exchange calculations by Padial et al.41 and Lucchese et al.59 show that the intravalence transition $3\sigma_u \rightarrow 5\sigma_g$ has a considerable oscillator strength and gives an intense resonance-like peak in the partial photoionization cross-section curve for the CO_2^+ ($\tilde{B}^2\Sigma_u^+$) state at ~ 19 and 22–23 eV, respectively. The corresponding peaks have actually been observed at 20-21 eV in the cross-section curves measured by dipole (e,2e)experiments,³³ synchrotron photoelectron spectroscopy,³⁴ and fluorescence excitation spectroscopy.⁶⁰ Hence, it is highly probable, on the theoretical grounds, that feature F7in the present O⁻ efficiency curve predominantly originates

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FIG. 6. Orbital correlation diagram between CO_2 and $CO^+(\tilde{X}^2\Sigma^+) + O^-(^2P_u)$. The approximate binding energies for occupied and vacant orbitals are taken from data of photoelectron spectra (Refs. 45 and 50) and results of *ab initio* calculations (this work), respectively.

from the predissociation of the excited valence state formed by the $3\sigma_u \rightarrow 5\sigma_g$ transition. At photon energies higher than 25 eV, two-electron excited valence states may also have some contribution to the O⁻ efficiency curve.

Another interpretation for feature F7 might be that the $1\pi_u$ electron is promoted to the $5\sigma_g$ orbital and the excited state thus formed predissociates via the ion-pair state correlating with $O^-({}^2P_u) + CO^+(\tilde{A} {}^2\Pi)$ (thermochemical threshold = 20.54 eV, see Table IV). Strong coupling between these states is expected because of the orbital correlation between $1\pi_u$ of CO_2 and 1π of CO^+ (see Fig. 6). The $1\pi_u \rightarrow 5\sigma_g$ transition is, however, known to occur a few eV below the ionization threshold⁵⁰ of 17.31 eV for the $CO_2^+(\tilde{A} {}^2\Pi_u)$ state.⁴¹ It then seems to be less probable for this intravalence excited state to decay into any ion pairs.

Note added in proof: In the text, the weak onset at ~ 495 Å (25.0 eV) in the efficiency curve for O^- from OCS is considered to be related to photodissociation to $O^{-}({}^{2}P_{\mu})$ $+ C^+ ({}^2P_u) + S({}^3P_g)$. After the submission of this paper, we have measured the efficiency curve for O⁻ from SO₂, and clearly observed two onsets with an energy separation of 1.85 eV, corresponding to the dissociation channels of $O^{-}({}^{2}P_{u}) + S^{+}({}^{4}S_{u}) + O({}^{3}P_{g}) \text{ and } O^{-}({}^{2}P_{u}) + S^{+}({}^{2}D_{u})$ + O(${}^{3}P_{g}$). This observation suggests that the 495 Å onset in Fig. 1(b) can be assigned as resulting from photodissociation to $O^{-}({}^{2}P_{u}) + S^{+}({}^{2}D_{u}) + C({}^{3}P_{g})$ rather than to $O^{-}(^{2}P_{u}) + C^{+}(^{2}P_{u}) + S(^{3}P_{g})$, since this onset lies 1.9 eV above the sharp onset for the $O^{-}({}^{2}P_{u}) + S^{4}({}^{4}S_{u})$ + C(${}^{3}P_{g}$) channel (feature F 5). Similarly, the shoulder observed at 385 Å in the efficiency curve for O^- from CO_2 (Fig. 3) probably results from photodissociation to $O^{-}(^{2}P_{u}) + O^{+}(^{2}D_{u}) + C(^{3}P_{g})$ (the estimated thermochemical threshold = 32.03 eV or 387 Å).

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