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Photodissociation Efficiency Spectroscopy Study of the Rydberg Excited Ion-Pair States of Carbon Dioxide *

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Photodissociation efficiency spectrum of anionic oxygen atom produced via ion-pair dissociations of carbon dioxide is recorded by means of the synchrotron radiation excitation (XUV photon energy 17.40–20.00 eV). The present spectrum is assigned as the Rydberg-like excited ion-pair states, i.e., Tanaka-Ogawa and Henning series, $\tilde{C}^2\Sigma_g^+$ (CO_2^+) vibrational ground-state and excitation series. Three Rydberg series, $np\sigma_u$, $np\pi_u$, and nf_u, converging to $\tilde{C}^2\Sigma_g^+(0,0,0)$, show the higher cross sections.

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Ion-pair dissociation as one of the most common relaxation pathways for the superexcited states of a molecule can be resonantly enhanced when the ion-pair continuum couples strongly with the discrete Rydberg states.[1−3] For the ion-pair dissociation, $AB + h\nu \rightarrow A^+ + B^-$, the efficiency curve of the anionic product B^- can clearly exhibit the resonance structures that are shaper or distinctly different from the photoionization efficiency curves for the positive ions. Such spectral character helps us to have insights into the electron excitations to both Rydberg and valence excited states of the parent molecules. In our previous work,[4] we demonstrated the feasibility of experimental study on the ion-pair dissociation dynamics by means of the Hefei synchrotron radiation source, and successfully recorded the ion-pair anion efficiency spectrum (IPAES) for $CO_2 + h\nu \rightarrow CO^+ + O^-$ in the extreme ultraviolet (XUV) energy 19.70–22.24 eV. The IPAES is generally in agreement with the spectrum obtained by Mistuke *et al.*[3] On the basis of our Hartree–Fock calculations, the transitions of the valence excitations were used to make the assignments to the IPAES.[4] According to the work of Mistuke *et al.*,[3] the fine structures in the PIAES at the photon energy lower than 19.40 eV were assigned to two Rydberg series converging to CO_2^+ $[\tilde{C}^2\Sigma_g^+(0,0,0)]$. However, in our previous work we failed in recording the spectrum in this energy range due to the low signals.[4] In this Letter, we re-examine the IPAES in the XUV energy range 17.40–20.00 eV, and give a new set of assignments. This work is accomplished owing to a improvement of the reflectron time-of-flight mass spectrometer (RTOFMS) and the recent achievements on the photoexcitation of CO_2.[5,6]

The experimental apparatus used in this work has been described in detail in our previous work.[4,7] In the reaction chamber, the RTOFMS is set perpendicularly to the XUV light and molecular beam (MB). The skimmer of the supersonic MB is about 5 cm far from the reaction point, which leads to the difficulty of the alignments of RTOFMS, XUV light, and MB, as well as the low intensity of MB at the reaction area. Thus, the anionic signals were seriously reduced by the poor alignment and the low intensity of MB in our previous work.[4] Here we modify the first three lenses and the sample input system. As shown in Fig. 1, the gaseous sample CO_2 (purity $\geq 99.99\%$) is introduced by a thin stainless tube inserted between lenses 1 and 2, and a pin hole with diameter 0.5 mm of the stainless tube is 1–2 mm far from the XUV beam. Since the diffuse MB and XUV synchrotron radiation are continuous, a dc voltage about −1.45 V is added on lens 1, then the up-pushed anions are accelerated by the pulsed voltage −165 V (width 1.5–2.0 μs) on lens 2. The residual part of RTOFMS is similar to the one described previously.[4,7] The present experiment is carried out at the Atomic and Molecular Physics endstation of the National Synchrotron Radiation Laboratory at Hefei.

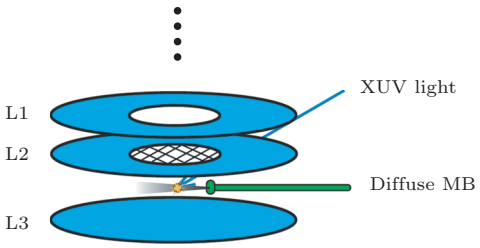


Fig. 1. Modifications of the RTOFMS.

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According to the PIAES recorded by Mistuke *et al.*,[3] the highest cross sections in the energy range 17.40–20.00 eV are only about one third of those at 21.00 eV. In most cases of the ion-pair dissociations, the extremely low cross sections seriously hinder the extensive experimental studies. Here the anionic detection sensitivity is enhanced, thus the modified RTOFMS enable us to record the PIAES as shown in Fig. 2. This spectrum is similar to that recorded by Mistuke *et al.*,[3] although some weak peaks show the different intensities. It is more important that the identification of the spectrum in the photon energy 18.10–19.40 eV has been controversial for almost half a century since Tanaka *et al.* reported the photoabsorption spectrum of CO_2 in 1960.[8] McCulloh observed that there are Rydberg series converging to the ionization threshold, 19.39 eV, of $\tilde{C}^2\Sigma_g^+$ (CO_2^+).[9] This threshold was further determined to be 19.3944 eV by the following experiments.[10,11] Tanaka *et al.* named three Rydberg series (converging to $\tilde{C}^2\Sigma_g^+$) as a, w, and e, according to their strong and weak absorption profiles and emission profile.[8] In fact, different resonance shapes in the photoabsorption spectra imply different couplings of the various channels, exhibiting the different Fano profiles.[12] Therefore, the e series in the photoabsorption spectrum[8] are the real absorption lines. Unfortunately such misleading "emission" caused that this set of Rydberg states were ruled out by Mistuke *et al.* in the assignments to the PIAES.[3] Another problem is that Mistuke *et al.* assigned the weak Rydberg series as the optically forbidden states $nd\pi_g\,{}^1\Pi_g$.[3] The optically forbidden states usually lead to extremely low intensity or disappearing in the photoabsorption spectra. It is unreasonable that the ion-pair dissociations are assigned with the optically forbidden states because the cross sections of the ion-pair dissociations are much smaller than the photoabsorptions.

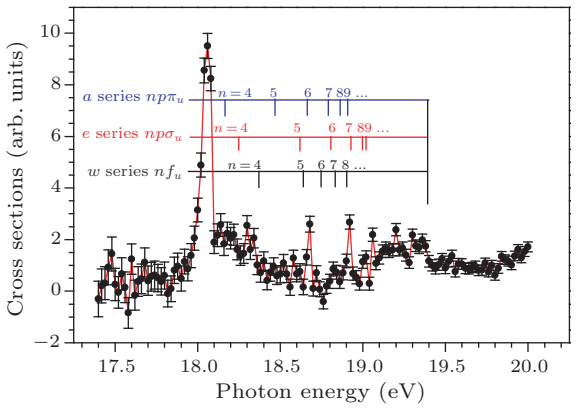


Fig. 2. Photodissociation efficiency curve for O^- produced from CO_2 near the ionization threshold of CO_2^+ $\tilde{C}\,{}^2\Sigma_g^+(0,0,0)$.

The previous theoretical works[13,14] indicated that the a series corresponded to $np\pi_u\,{}^1\Pi_u$, with a quantum defect 0.65 and the e series corresponded to $np\sigma_u\,{}^1\Sigma_u^+$, with a quantum defect 0.55. The w series were proposed to be nf_u, with a quantum defect 0.01, by Fridh *et al.*[15] The above assignments have been adopted in a recent study on the photoionization and photoabsorption of CO_2.[6] All of them are the dipole-allowed transitions, thus used in the assignments to the present IPAES. As shown in Fig. 2, the principle quantum numbers of the a series ($np\pi_u\,{}^1\Pi_u$) start from 4, while Mistuke *et al.*[3] assigned them as $np\,\sigma_u\,{}^1\Sigma_u^+$ ($n = 3, 4, 5, \ldots$). In general, the a series ($np\,\pi_u\,{}^1\Pi_u$) shows the strongest intensity, while the w series (nf_u) is the weakest. The energies of these Rydberg series converging to the vibrational ground-state $\tilde{C}^2\Sigma_g^+(0,0,0)$ (here estimated to be 19.39 eV) are listed in Table 1.

Table 1. Energies for Rydberg series converging to $\tilde{C}\,{}^2\Sigma_g^+(0,0,0)$ observed in the O^- efficiency curve.

Energy (eV)		Assignment		
This work	Tanaka *et al.*[3]	a series	e series	w series
18.21	18.16	$4\pi_u$		
18.30	18.26			$4f_u$
18.60	18.54		$4p\sigma_u$	
18.67	18.67	$5p\pi_u$		
18.72	18.72		$5p\sigma_u$	
18.89	18.85			$5f_u$
18.91	18.91	$6p\pi_u$		
18.92	18.93		$6p\sigma_u$	
19.02	19.01			$6f_u$
19.03	19.05	$7p\pi_u$		
19.07	19.07		$7p\sigma_u$	
19.12	19.11			$7f_u$
19.13	19.14	$8p\pi_u$		
19.15	19.15		$8p\sigma_u$	
19.19	19.18			$8f_u$
19.20	19.20	$9p\pi_u$		
19.20	19.20		$9p\sigma_u$	

The highest peak at 18.06 eV presents the threshold about 18.02 eV for the ion-pair dissociation CO_2 $(\tilde{X}) \rightarrow O^-(^2P_u) + CO^+(\tilde{X})$.[3] The left-hand spectrum in the lower energy range (less than 18.00 eV) can be assigned as the Tanaka–Ogawa series and Henning diffuse and sharp series.[5] In 1995, Shaw *et al.* assigned the right-hand spectrum (energy > 19.40 eV) as two Rydberg series, ns and nd, converging to the $\tilde{C}\,{}^2\Sigma_g^+(1,0,1)$ state.[5] However, their recent fluorescence spectra suggested that the different vibrationally excited states of $\tilde{C}\,{}^2\Sigma_g^+$ may be involved in this energy range.[6] These vibronically induced Rydberg series are remarkable in the fluorescence spectra,[6] but they are very weak, even structureless in the PIAES. The above Rydberg series both at the higher and the lower energies are scarcely coupled with the ion-pair dissociations. Only three Rydberg series ($np\pi_u$, $np\sigma_u$, and nf_u) converging to $\tilde{C}\,{}^2\Sigma_g^+(0,0,0)$ strongly couple with the ion-pair dissociations, indicating the distinct peaks in the PIAES.

In summary, the efficiency to detect the anions produced through photoexciation ion-pair dissociations is enhanced by the modifications to our home-made RTOFMS. This improvement enables us to success-

fully record the IPAES (O^- anion) of CO_2 in the photon energy range 17.40–20.00 eV, which exhibits the clear Rydberg series converging to the ionization state $\tilde{C}\,^2\Sigma_g^+(0,0,0)$. This implies that these Rydberg states strongly couple with the ion-pair dissociation channels. The spectral assignments given by Mistuke *et al.*[3] are not corrected, and a new set of assignments to the PIAES, namely, $np\,\pi_u$, $np\,\sigma_u$, and nf_u, obtained in this work, are made on the basis of the recent literature.[5,6]

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