

Branching Ratio Measurements of the Predissociation of $^{12}\text{C}^{16}\text{O}$ by Time-Slice Velocity-Map Ion Imaging in the Energy Region from 106 250 to 107 800 cm^{-1}

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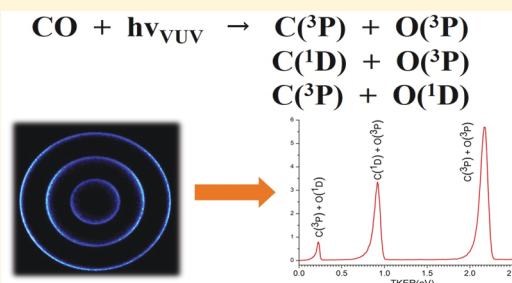
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ABSTRACT: Photodissociation of CO is a fundamental chemical mechanism for mass-independent oxygen isotope fractionation in the early Solar System. Branching ratios of photodissociation channels for individual bands quantitatively yield the trapping efficiencies of atomic oxygen resulting into oxides. We measured the branching ratios for the spin-forbidden and spin-allowed photodissociation channels of $^{12}\text{C}^{16}\text{O}$ in the vacuum ultraviolet (VUV) photon energy region from 106 250 to 107 800 cm^{-1} using the VUV laser time-slice velocity-map imaging photoion technique. The excitations to four $^1\Pi$ bands and three $^1\Sigma^+$ bands of $^{12}\text{C}^{16}\text{O}$ were identified and investigated. The branching ratios for the product channels $\text{C}(^3\text{P}) + \text{O}(^3\text{P})$, $\text{C}(^1\text{D}) + \text{O}(^3\text{P})$, and $\text{C}(^3\text{P}) + \text{O}(^1\text{D})$ of these predissociative states strongly depend on the electronic and vibrational states of CO being excited. By plotting the branching ratio of the spin-forbidden dissociation channels versus the excitation energy from 102 500 to 110 500 cm^{-1} that has been measured so far, the global pattern of the $^1\Pi$ – $^3\Pi$ interaction that plays a key role in the predissociation of CO is revealed and discussed.



1. INTRODUCTION

Carbon monoxide, as the second most abundant known molecule after H_2 in the interstellar medium,^{1,2} carries ~50% of the oxygen budget in the solar nebula.³ Photodissociation of CO by the vacuum ultraviolet (VUV) radiation during the formation of the Solar Nebula played a critical role in the evolution of oxygen isotopic compositions.^{4–7} Oxygen displays significant isotopic heterogeneity among early Solar System objects found in primitive meteoritic components and planetary materials with both ^{16}O -rich and ^{16}O -poor reservoirs of equal $^{17}\text{O}/^{18}\text{O}$ ratio.⁴ The equal abundance of the heavy isotopes of oxygen is the most notable example of mass-independent fractionation in the solar nebula,^{5–7} while the vast majority of the elements have mass-dependent fractionation. The carbon monoxide self-shielding (COSS) theory, which involves the detailed predissociation dynamics of CO in the VUV region, was proposed to explain the observed oxygen isotope anomalies.^{8–12} The model focuses on the photochemical isotopic effects of major volatile species CO and tracks a parcel of dust and gas with an initially homogeneous oxygen isotopic composition. When the parcel of materials in a molecular cloud or protoplanetary disk is subjected to VUV radiation from an external source of a nearby star, photo-

dissociation of CO occurs. Given the different column densities and energies of predissociative states of isotopologues of C^{16}O , C^{17}O , and C^{18}O , isotope-specific VUV attenuation (“self-shielding”) occurs on the edge of molecular clouds or protoplanetary disks. Because the C^{16}O dominates the composition of CO in the molecular clouds, the VUV radiation at the wavelengths that are absorbed by C^{16}O is much more attenuated with a long path length of CO than at the wavelengths absorbed by C^{17}O and C^{18}O . As a result of this isotope-specific attenuation, the VUV with a rescaled spectrum generates $^{17,18}\text{O}$ -rich atomic oxygen by predissociating CO. The highly reactive $^{17,18}\text{O}$ -rich atomic oxygen would rapidly react with H_2 molecules to form $^{17,18}\text{O}$ -enriched H_2O , appearing as water-ice mantles on silicate dust grains.^{9,10}

Recent laboratory measurements of the solar wind collected by the Genesis mission showed that both heavy isotopes of oxygen are depleted in the Sun relative to that in the Earth and other terrestrial planetary materials by ~7%,¹³ and the heavy isotope of nitrogen is depleted in the Sun by 40%.¹⁴ These

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observations collectively lend strong support for the COSS model and the isotopic N_2 self-shielding (N_2SS) in the molecular cloud. The interesting observation here is that, although the cosmic abundance of CO is 7 times more than that of N_2 in the solar nebula,^{15,16} ^{15}N is found to be ~ 7 times more enriched than ^{17}O and ^{18}O in planetary materials relative to the Sun.^{13,14} Clayton proposed the first explanation to this difference in the heavy isotope enrichment for nitrogen compared to oxygen.¹⁷ It was proposed to be attributable to the difference in chemical reactivity of the product atoms formed in different electronic states by the photodissociation of CO and N_2 . The differences in chemical reactivity of the photofragment atoms to H_2 relative to other available species can influence their subsequent trapping efficiencies. By using the branching ratio of CO photodissociation measured recently in our lab,^{18–20} and that of N_2 photodissociation measured previously by Cosby and co-workers,^{21–23} we calculated the trapping yield of O and N in the solar system and qualitatively explain the above difference in isotope compositions between O and N.²⁴ We recently reported the detailed branching ratio measurements for the VUV photodissociation of CO in the energy regions of 108 000–110 500^{18,19} and 102 500–106 300 cm^{-1} .²⁰ In this work, we completed the branching ratio measurement in the energy gap from 106 300 to 108 000 cm^{-1} using the same method.

Besides the applications to the cosmochemical theories, the branching ratio measurement can also provide important information for understanding the detailed predissociation dynamics of CO. A comparison between the two isoelectronic molecules N_2 and CO made by Huber²⁵ pointed out that the interactions between different electronic states of CO, especially the Π – Π type, are still largely unknown compared with N_2 , because the absence of g/u symmetry adds a great deal of complexity to CO. For N_2 , the shapes of the $^3\Pi$ potential energy surfaces and their interactions with various $^1\Pi$ states determine the overall pattern of dependence of the branching ratio on the excitation energy, while the similar $^1\Pi$ – $^3\Pi$ interactions for CO, which determine the branching ratio into the triplet spin-forbidden dissociation channels, have not been completely mapped out yet. A recent theoretical study by Lefebvre-Brion et al. has tried to plot all the low-lying $^1\Pi$ and $^3\Pi$ states,²⁶ and a comparison with our branching ratio measurement has helped them refine the coupling constants between different electronic states, which indicates that branching ratio measurements can reveal the most detailed information on the predissociation dynamics of CO.²⁷

2. EXPERIMENT

The experimental methods including the time-slice velocity-map ion imaging (TS-VMI) system and the tunable VUV laser source used in the present study were described in the previous work.^{28,29} Briefly, a pulsed molecular beam of pure CO is produced by supersonic expansion through an Evan-Lavie pulsed valve (EL-5–2004) with a nozzle diameter of 0.2 mm operating at a stagnation pressure of 50 psi and 30 Hz and collimated by two conical skimmers. The molecular beam is perpendicularly intersected by the VUV laser beam. The nascent C atoms produced from the photodissociation of CO are directly photoionized by the same VUV laser beam. The resulting C^+ ions are extracted and focused by the VMI ion optics onto a microchannel plate (MCP) detector. The electrons ejected from the MCP detector by ion impact are

accelerated onto a phosphor screen to form an image that is recorded by a CCD camera.

To generate the VUV laser source, we used Xe in the form of a gas jet as the nonlinear four-wave mixing medium. The UV wavelength is fixed at 222.568 nm (ω_1) that is resonant with the two-photon transition of Xe: $(5p)^5(^2P_{1/2})6p^2[1/2](J=0) \leftarrow (5p)^6(^1S_0)$ at 89 860.018 cm^{-1} . The visible laser wavelength (ω_2) is scanned from 555 to 610 nm so that the sum-frequency ($2\omega_1 + \omega_2$) VUV laser has a range of 106 250–107 800 cm^{-1} (13.175–13.366 eV). In this experiment, the CO molecule is excited to each of the rovibronic states by the absorption of a sum-frequency VUV photon ($2\omega_1 + \omega_2$) and undergoes predissociation to produce carbon atoms in the 3P and 1D states. The carbon atoms thus produced are photoionized by absorbing another VUV photon ($2\omega_1 + \omega_2$) within the same VUV laser pulse, which is set at energy above the ionization threshold of carbon atoms at 90 883.84 cm^{-1} .

To acquire the C^+ photofragment excitation (PHOFEX) spectra of CO, we gated on the C^+ ion peak in the time-of-flight (TOF) mass spectrum using a Boxcar data acquisition system (Stanford Research System, SR250) and scan the VUV spectrum from 106 250 to 107 800 cm^{-1} . The C^+ PHOFEX spectra provided information about transition energy of VUV to individual predissociation state of CO for us to investigate the branching ratios for the product channels $C(^3P) + O(^3P)$, $C(^1D) + O(^3P)$, and $C(^3P) + O(^1D)$. The TS-VMI image was used to measure the branching ratios between different dissociation pathways. In this experiment, the VUV photon energy is fixed at a particular (E' , v' , J') state of CO, and the TS-VMI image is collected by applying a 40 ns high voltage pulse (negative) to the front MCP when C^+ ions arrive. The C photofragments with different recoil velocities produced from different dissociation channels can be distinguished in the TS-VMI images. The total kinetic energy release (TKER) spectra converted from TS-VMI image showing different C^+ number distribution peaked at thresholds corresponding to dissociation channels are used to obtain the branching ratios.

3. RESULTS

In this work, TS-VMI images of the carbon ion (C^+) were taken for each CO predissociation band from 106 250 to 107 800 cm^{-1} , to complement our previous branching ratio measurements for $^{12}C^{16}O$ predissociation in the energy regions of 108 000–110 500^{18,19} and 102 500–106 300 cm^{-1} .²⁰ The TS-VMI images were converted to TKER spectra to identify the three dissociation channels: $C(^3P) + O(^3P)$, $C(^1D) + O(^3P)$, and $C(^3P) + O(^1D)$. Their branching ratios were measured by integrating the areas under the corresponding peaks in the TKER spectra and then calibrating the areas with the corresponding photoionization cross sections of $C(^3P)$ and $C(^1D)$.

A. $^1\Pi$ Bands. Since 2011, we reported on the C^+ PHOFEX spectra and the branching ratios in the predissociation for nine $^1\Pi$ bands at 109 565; 109 018; 108,014; 106 251; 105 442; 104 576; 103 272; 103 212; 102 807 cm^{-1} .^{18–20} These nine bands and their upper states were listed as #7A: $^1\Pi$ ($v' = 0$), #9A: $^1\Pi$ ($v' = 2$), #12: $W(3s\sigma)$ $^1\Pi$ ($v' = 3$), and #18: $W(3s\sigma)$ $^1\Pi$ ($v' = 2$), #20: $L(4p\pi)$ $^1\Pi$ ($v' = 1$), #22: $W(3s\sigma)$ $^1\Pi$ ($v' = 1$), #25: $L(4p\pi)$ $^1\Pi$ ($v' = 0$), #26: $L'(3d\pi)$ $^1\Pi$ ($v' = 1$), #28: $W(3s\sigma)$ $^1\Pi$ ($v' = 0$), respectively, following the numbering by Eidelsberg and Rostas.³⁰ To complete the branching ratio measurement for all CO photodissociation bands in the energy

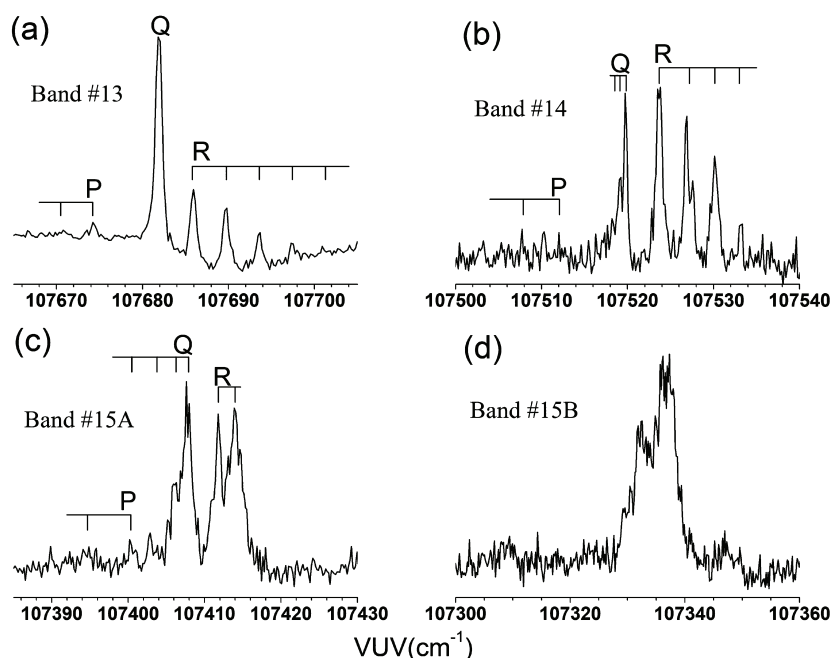


Figure 1. Carbon ion PHOFEX spectra for the four $^1\Pi$ bands of $^{12}\text{C}^{16}\text{O}$: (a) band #13 with upper state $^1\Pi(v'=2)$, (b) band #14 with upper state $^1\Pi(v'=2)$, (c) band #15A with upper state $^1\Pi(v'=0)$, and (d) band #15B with upper state $(5p\pi)^1\Pi(v'=0)$. The relative intensities of these bands were not normalized to the corresponding VUV laser intensities.

Table 1. Predissociation Branching Ratios of the CO Bands from 106 250 to 107 800 cm^{-1} Measured in the Present Work

band ^a	upper state	VUV (nm) (cm^{-1})		rotation lines	$\text{C}(^3\text{P})+\text{O}(^1\text{D})$, %	$\text{C}(^1\text{D})+\text{O}(^3\text{P})$, %	$\text{C}(^3\text{P})+\text{O}(^3\text{P})$, %
13	$^1\Pi(v'=2)$	92.855	107 693.5	R(2)	5.0 ± 0.3	35.3 ± 0.4	59.6 ± 0.7
		92.859	107 689.7	R(1)	5.3 ± 0.1	38.9 ± 0.4	55.8 ± 0.3
		92.862	107 685.9	R(0)	5.8 ± 0.1	39.8 ± 0.2	54.4 ± 0.1
		92.866	107 682.0	Q	5.4 ± 0.2	38.1 ± 0.3	56.5 ± 0.4
		92.997	107 530.2	R(2)	7.9 ± 0.9	64.5 ± 0.8	27.6 ± 0.1
14	$(4p\pi)^1\Pi(v'=2)$	93.000	107 527.2	R(1)	7.9 ± 0.4	65.6 ± 0.1	26.5 ± 0.3
		93.003	107 523.6	R(0)	7.9 ± 0.2	65.6 ± 0.6	26.4 ± 0.5
		93.006	107 519.8	Q	7.70 ± 0.03	64.6 ± 0.4	27.8 ± 0.4
		93.098	107 414.0	R(1)	11.5 ± 0.2	35.0 ± 3.2	53.5 ± 3.3
15A	$^1\Pi(v'=0)$	93.100	107 411.8	R(0)	15.0 ± 0.7	41.7 ± 0.7	43.3 ± 1.4
		93.103	107 407.8	Q(1) (+Q(2))	14.3 ± 0.3	43.8 ± 0.7	41.9 ± 1.0
		93.105	107 403.5	Q(3)	14.0 ± 0.1	42.7 ± 1.1	43.2 ± 1.0
		93.165	107 336.7		4 ± 2	24 ± 8	72 ± 10
15B	$(5p\pi)^1\Pi(v'=0)$	93.297	107 184.3	R(1)	1.0 ± 0.3	9.2 ± 0.1	89.8 ± 0.4
15C	$(5p\sigma)^1\Sigma^+(v'=0)$	93.302	107 179.0	R(0)	0.80 ± 0.01	9.2 ± 0.2	90.0 ± 0.2
		93.309	107 170.7	P(1)	0.20 ± 0.02	2.2 ± 0.1	97.6 ± 0.1
		93.312	107 167.6	P(2)	0.80 ± 0.08	9.3 ± 0.2	89.9 ± 0.3
		93.558	106 885.5		3.3 ± 0.7	20.1 ± 0.4	76.6 ± 1.0
16	$^1\Sigma^+(v'=2)$	93.989	106 395.4		<1	<1	100
17	$I'(5s\sigma)^1\Sigma^+(v'=0)$						

^aNumbering follows by Eidelsberg and Rostas.³⁰

range of astrophysical interest, we measured four more $^1\Pi$ bands in this range besides those bands mentioned above. These four $^1\Pi$ bands locate at 107 682, 107 520, 107 403, and 107 336 cm^{-1} ; their band numbering and corresponding upper states were listed as #13: $^1\Pi(v'=2)$, #14: $^1\Pi(v'=2)$, #15A: $^1\Pi(v'=0)$, and #15B: $(5p\pi)^1\Pi(v'=0)$, respectively.

These four $^1\Pi$ bands have been observed in the absorption and photoionization spectra of $^{12}\text{C}^{16}\text{O}$ previously.^{30–34} Reports by Ubachs and Eikema et al. provided great details on the band origins ν_0 , the rotational constants B , the centrifugal distortion constants D , the Λ -doubling parameters, predissociation lifetimes of these bands.^{31,32} These constants were used to

assign the vibronic states in our PHOFEX spectra of $^{12}\text{C}^{16}\text{O}$ (Figure 1). A clear perturbation was found in the absorption spectrum of $^{12}\text{C}^{16}\text{O}$ in the excited state $^1\Pi(v'=2)$ of the band #13 at $\sim 107 750 \text{ cm}^{-1}$, which is a clear indication of an accidental resonance.³² This perturbation leads to an extremely rapid predissociation. Eikema et al. suggested that such a perturbation may be induced by an interaction with a vibronic state, possibly a $^1\Delta$ state with the origin at 107 710 cm^{-1} or a $^1\Pi$ state with the origin at 107 706 cm^{-1} .³² The analysis of absorption spectra of $^{12}\text{C}^{16}\text{O}$ from 106 400 to 107 560 cm^{-1} also showed fast predissociation rates of $(0.8\text{--}3.5) \times 10^{11} \text{ s}^{-1}$

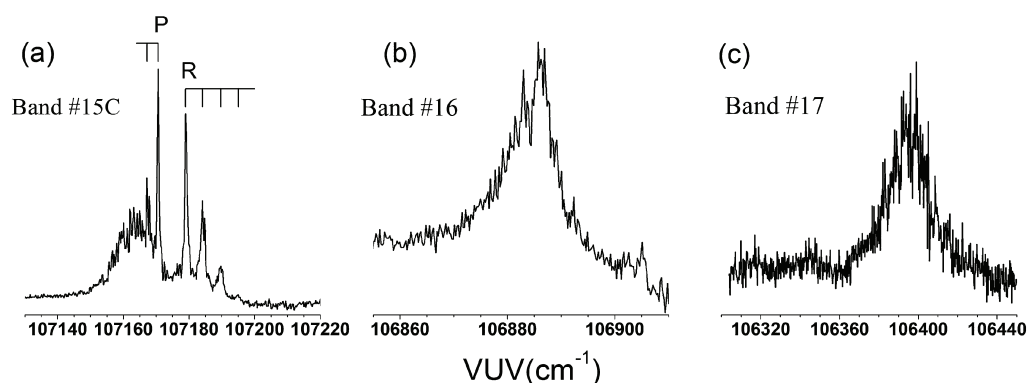


Figure 2. Carbon ion PHOFEX spectra for the three $1\Sigma^+$ bands of $^{12}\text{C}^{16}\text{O}$: (a) band #15C with upper state $(5p\sigma)1\Sigma^+(v'=0)$, (b) band #16 with upper state $1\Sigma^+(v'=2)$, (c) band #17 with upper state $I'(5s\sigma)1\Sigma^+(v'=0)$. The relative intensities of these bands were not normalized to the corresponding VUV laser intensities.

for the excited states $(4p\pi)1\Pi(v'=2)$ of band #14, $1\Pi(v'=0)$ of band #15A and $(5p\sigma)1\Pi(v'=0)$ of band #15B.^{33,34}

We observed these same bands in the C^+ PHOFEX spectra of CO in supersonic molecular beam with a rotational temperature much lower than the absorption experiments by Eidelsberg et al.^{33,34} (Figure 1). These photofragment spectra provided direct evidence for the strong predissociation behavior of these four 1Π bands. To measure the branching ratios of the 1Π bands, we tuned the VUV laser at the Q branch of each band and obtained the TS-VMI images by detecting C^+ ions. Examples of the TS-VMI images and the corresponding TKER spectra for the Q branch of the band #15A at $107\,407.8\text{ cm}^{-1}$ with the upper state of $1\Pi(v'=0)$ was shown in our recent ApJ paper.²⁴ The branching ratios of the three dissociation channels $\text{C}(^3\text{P}) + \text{O}(^1\text{D})$, $\text{C}(^1\text{D}) + \text{O}(^3\text{P})$, and $\text{C}(^3\text{P}) + \text{O}(^3\text{P})$ for CO upper states $1\Pi(v'=2)$ of band #13, $1\Pi(v'=2)$ of band #14, $1\Pi(v'=0)$ of band #15A, and $(5p\sigma)1\Pi(v'=0)$ of band #15B are listed in Table 1. The percentages for the triplet spin-forbidden dissociation channels for the three bands are equivalent to or larger than the spin-allowed dissociation channel. At band #14, $\sim 8\%$ CO dissociated to $\text{C}(^3\text{P}) + \text{O}(^1\text{D})$, while 65% dissociated to the $\text{C}(^1\text{D}) + \text{O}(^3\text{P})$ channel. The sum of the branching ratios of these two spin-forbidden dissociation channels is much larger than the 27% branching ratio of the spin-allowed $\text{C}(^3\text{P}) + \text{O}(^3\text{P})$ channel.

B. $1\Sigma^+$ Bands. Previously, we reported the branching ratios in the predissociation for eight $1\Sigma^+$ bands at $109\,480$, $109\,448$, $109\,173$, $108\,371$, $108\,151$, $105\,676$, $103\,691$, and $103\,054\text{ cm}^{-1}$.^{18–20} These eight bands and their upper states were listed as #7B: $(5p\sigma)1\Sigma^+(v'=1)$, #7D: $1\Sigma^+(v'=2)$, #8B: $(6p\sigma)1\Sigma^+(v'=0)$, #10: $(5d\sigma)1\Sigma^+(v'=0)$, #11: $1\Sigma^+(v'=1)$, #19: $(4d\sigma)1\Sigma^+(v'=0)$, #24: $J(4s\sigma)1\Sigma^+(v'=1)$ and #27: $\text{K}(4p\sigma)1\Sigma^+(v'=0)$, respectively.³⁰ To complete the branching ratio measurement for all the $1\Sigma^+$ bands that leads to predissociation in the energy region of astrophysical interest, we investigated three more $1\Sigma^+$ bands; their band numbering and corresponding upper states were listed as #15C: $(5p\sigma)1\Sigma^+(v'=0)$, #16: $1\Sigma^+(v'=2)$, #17: $I'(5s\sigma)1\Sigma^+(v'=0)$ located at $107\,174$, $106\,876$, and $106\,388\text{ cm}^{-1}$, respectively.

These three $1\Sigma^+$ bands have been observed in the absorption and photoionization spectra of $^{12}\text{C}^{16}\text{O}$ previously.^{30–34} These studies provided great details on the band origins ν_0 , the rotational constants B , the centrifugal distortion constants D , predissociation lifetimes of these bands. An anomalously large B constant of 2.24 cm^{-1} was obtained for band #15C by

Eikema et al.³² The B constant of band #16 was measured to be 2.92 cm^{-1} , and band #17 was noted diffuse by Eidelsberg et al.³⁰ It was an indication of perturbation by other states. The CO photoabsorption spectrum of the #15C: $(5p\sigma)1\Sigma^+(v'=0)$ from $107\,190$ to $107\,160\text{ cm}^{-1}$ clearly illustrated the consistency between line broadening effect and loss of intensity observed in $1 + 1'$ photoionization via a predissociative state. On the basis of this photoabsorption spectrum, Eikema et al. suggested that the photodissociation rate of the #15C: $(5p\sigma)1\Sigma^+(v'=0)$ band is J -dependent.³² The calculated values for the predissociation rates are $k_p(J=0) = (3.4 \pm 2.0) \times 10^{10}\text{ s}^{-1}$ and $k_p(J=1) = (1.8 \pm 0.5) \times 10^{11}\text{ s}^{-1}$.³² As a direct observation of the predissociation process, our photofragment spectrum of #15C: $(5p\sigma)1\Sigma^+(v'=0)$ captured the carbon atoms generated from the predissociation of CO (Figure 2a). The photofragment spectra of the upper state $1\Sigma^+(v'=2)$ of band #16 and $I'(5s\sigma)1\Sigma^+(v'=0)$ of band #17 are very diffuse and broad (Figure 2b,c), which also indicated a strong dissociation character. Because of the broadening effect, the rotational states of these two bands could not be resolved.

To measure the branching ratios of the three $1\Sigma^+$ bands discussed above, we parked the VUV laser at P(0) line of the band #15C with the upper state of $(5p\sigma)1\Sigma^+(v'=0)$, and at the intensity maximum of band #16 (with the upper state $1\Sigma^+(v'=2)$), band #17 (with the upper state $I'(5s\sigma)1\Sigma^+(v'=0)$), and obtained the time-slice velocity-map ion images by detecting C^+ ions. The branching ratios of the three dissociation channels $\text{C}(^3\text{P}) + \text{O}(^1\text{D})$, $\text{C}(^1\text{D}) + \text{O}(^3\text{P})$, and $\text{C}(^3\text{P}) + \text{O}(^3\text{P})$ for CO excited states $(5p\sigma)1\Sigma^+(v'=0)$, $1\Sigma^+(v'=2)$, and $I'(5s\sigma)1\Sigma^+(v'=0)$ are listed in Table 1. Different from the four 1Π bands discussed in the previous session, the vast majority of CO predissociation was conducted through the spin-allowed channel $\text{C}(^3\text{P}) + \text{O}(^3\text{P})$. The branching ratios of the $\text{C}(^3\text{P}) + \text{O}(^3\text{P})$ channel are $\sim 90\%$, 77% , and 100% for CO excited states $(5p\sigma)1\Sigma^+(v'=0)$, $1\Sigma^+(v'=2)$, and $I'(5s\sigma)1\Sigma^+(v'=0)$, respectively. The branching ratios of the spin-forbidden dissociation channel $\text{C}(^3\text{P}) + \text{O}(^1\text{D})$ are only $\sim 1\%$, 3% , and 0 , respectively. These $1\Sigma^+ - 1\Sigma^+$ transitions do not have sufficient contribution to the generation of excited oxygen atoms $\text{O}(^1\text{D})$. Together with our previous branching ratio measurements, we observed that $1\Sigma^+$ bands of CO have higher branching ratios into the $\text{C}(^3\text{P}) + \text{O}(^3\text{P})$ channel and lower branching ratios into $\text{C}(^3\text{P}) + \text{O}(^1\text{D})$ and $\text{C}(^1\text{D}) + \text{O}(^3\text{P})$ channels in the energy range investigated, compared to the 1Π bands at adjacent energy levels. A table that summarizes

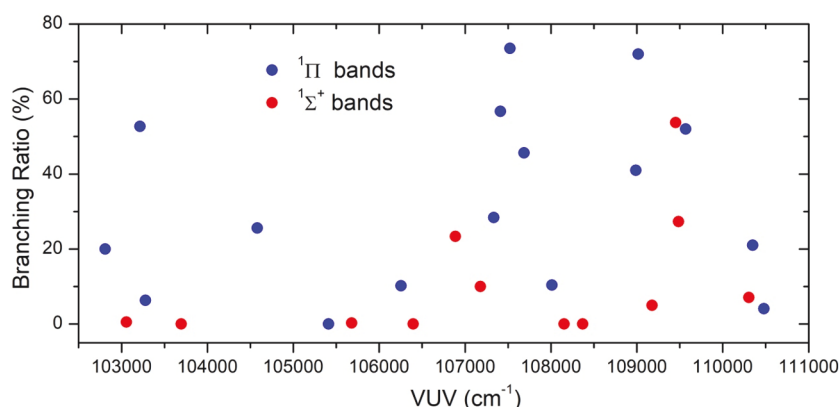


Figure 3. Branching ratio for the sum of the two triplet spin-forbidden dissociation channels $\{[C(^3P) + O(^1D)] + [C(^1D) + O(^3P)]\}$ of $^{12}C^{16}O$ in the energy range from 102 500 to 111 000 cm^{-1} . (red) $^1\Sigma^+$ and (blue) $^1\Pi$ bands.

the branching ratios of all the 33 CO predissociation bands can be found in our recent ApJ paper.²⁴

4. DISCUSSION AND CONCLUSION

In our previous discussion,²⁰ we identified three different pathways for the predissociation of $^{12}C^{16}O$: Pathway I involves with the well-known $D^1\Sigma^+$ state, which correlates to the lowest dissociation channel $C(^3P) + O(^3P)$; Pathway II is through a repulsive $^1\Pi$ state, which also correlates to the lowest dissociation channel $C(^3P) + O(^3P)$; Pathway III is through coupling to an intermediate $^1\Pi$ state, then further to repulsive $^3\Pi$ states (or through direct coupling with a $^3\Pi$ state without the intermediate step) that dissociates into the two triplet spin-forbidden channels. This is consistent with the conclusions by Cacciani et al. when investigating the predissociation dynamics of the $(4p\pi)$ $L^1\Pi$ ($v' = 0$) band of $^{12}C^{16}O$,³⁵ except for the accidental local perturbations, which usually happens at relatively high rotational levels. For the four $^1\Pi$ bands that are investigated in the present work, the rotational structure of the band #15B cannot be resolved due to the fast predissociation process; the other three all show well- or partially resolved rotational patterns. From the branching ratio data as presented in Table 1, both of the e-parity and f-parity states of the three $^1\Pi$ bands, #13: $^1\Pi(v' = 2)$, #14: $^1\Pi(v' = 2)$, and #15A: $^1\Pi(v' = 0)$, predissociate, and their branching ratios do not depend on the parity within the experimental uncertainties. This is clear indication that a valence state with $^1\Pi$ characteristics that correlates to the lowest dissociation channel $C(^3P) + O(^3P)$ must be involved (Pathway II) in the predissociation of the above three $^1\Pi$ bands. Considering the fact that all the four $^1\Pi$ bands dissociate into the triplet spin-forbidden channels with significant amount, the Pathway III, which proceeds through a $^3\Pi$ state, must be involved, while, because of the very cold rotational temperature of the supersonic molecular beam used in the current experiment, we were not able to measure the branching ratios for higher rotational levels. This prevents us from doing a reliable rotational dependence analysis of the branching ratio of these $^1\Pi$ bands, and thus it is uncertain at the current stage to claim if the $D^1\Sigma^+$ state (Pathway I) has been involved or not in the predissociation process of these four $^1\Pi$ bands. For the three $^1\Sigma^+$ bands investigated in the present work, only #15C: $(5p\sigma)^1\Sigma^+(v' = 0)$ has resolved rotational structures; the other two only show a single broad peak as seen in Figure 2. Both of the bands #15C and #16 predissociate into the triplet spin-

forbidden channels; thus, Pathway III should be present, while this is not the case for the band #17, since it does not dissociate into the triplet spin-forbidden channels. Because of the same reason as for the $^1\Pi$ bands, it is not clear if one of Pathway I and II is involved or both of them are involved. To confirm if the $D^1\Sigma^+$ state plays a role in the predissociation of these highly excited Rydberg states of $^{12}C^{16}O$, we need measure the branching ratio at higher rotational levels, probably with a hotter supersonic molecular beam.

So far, we finished measuring the branching ratios for most of the relatively strong absorption bands in the energy region between 102 500 and 110 500 cm^{-1} for $^{12}C^{16}O$.^{18,19,20} These branching ratio data are astrophysically important and have been applied to explain the anomalous oxygen isotope composition of the solar nebula revealed recently by the NASA's Genesis mission.^{13,24} Besides its importance in the astrophysical perspective, CO together with the isoelectronic molecule N_2 have served as benchmark systems for studying the photodissociation dynamics of diatomic molecules. Compared with N_2 , which has been well-studied, CO has much more complicated mutual interactions between different electronic states due to the absence of g/u symmetry as pointed out by Huber 20 years ago.³⁶ Thanks to a series of photodissociation branching ratio measurements by Cosby and co-workers^{21–23} and recently by Jackson and co-workers,³⁷ together with the theoretical work by Lewis et al.,^{38,39} the pattern of the branching ratio dependence on the excitation energy for the dissociation of N_2 can be qualitatively explained by the structures of the three lowest adiabatic $^3\Pi$ states and their interactions with singlet states. For CO, a global pattern for the branching ratio into the spin-forbidden channel similar to that of N_2 has not so far been built; this is supposed to be the key to understand the detailed predissociation dynamics of CO, especially the structures of the $^3\Pi$ band system correlating to the triplet spin-forbidden channels as has been well-established in the case of N_2 .

In Figure 3, we plot the sum of branching ratios of the two triplet spin-forbidden channels $\{[C(^3P) + O(^1D)] + [C(^1D) + O(^3P)]\}$ as a function of the excitation energy for all the $^1\Pi$ (blue dots) and $^1\Sigma^+$ (red dots) bands in the energy range of 102 500–110 500 cm^{-1} that were measured so far. We know that the directly photoexcited singlet states cannot correlate with triplet dissociation channels directly; thus, spin-orbit interaction with certain triplet states, mostly with $^3\Pi$ characteristics, must play a role.⁴⁰ As seen in Figure 3, most

of the $^1\Pi$ bands dissociate into the two triplet channels with significant amount, and the dependence of the branching ratio on the excitation energy reveals a much more complicated pattern compared with that of N_2 . There are at least four energy points where strong $^1\Pi$ – $^3\Pi$ interactions should be present, which causes intensive predissociation into the triplet channels; these four points are at $\sim 103\,000$, $104\,500$, $107\,500$, and $109\,400\text{ cm}^{-1}$ as shown in Figure 3. Lefebvre-Brion et al. have recently calculated all the potential curves of $^1\Pi$ and $^3\Pi$ states of CO below $120\,000\text{ cm}^{-1}$ and their mutual interactions at relatively low excitation energy. On the basis of this they reproduced the branching ratio by ab initial calculation for the $W(3s\sigma)$ $^1\Pi$ ($v' = 1$) band that we measured before.^{26,27} The good agreement between the calculated result and our experimental measurements confirms that $^1\Pi$ – $^3\Pi$ interactions play important roles in the process of predissociation of CO into the triplet channels, and the overall pattern of energy dependence of the branching ratio for the triplet channels as shown in Figure 3 should guide theoreticians to further investigate the strong $^1\Pi$ – $^3\Pi$ interactions, which are the key to understanding the predissociation dynamics of CO. Compared with the $^1\Pi$ bands, most of the $^1\Sigma^+$ bands do not dissociate into the triplet channels significantly. This is probably due to the very weak direct interaction between $^1\Sigma^+$ and $^3\Pi$ states. $^1\Sigma^+$ states can couple with a $^1\Pi$ state first and then dissociate into the triplet channels through the relatively strong $^1\Pi$ – $^3\Pi$ interactions. A typical example is the $K(4p\sigma)^1\Sigma^+(v' = 0)$ band that was carefully studied by us before.²⁰ Several $^1\Sigma^+$ bands near $107\,000$ and $109\,400\text{ cm}^{-1}$ dissociate into the triplet channels with significant amount as shown in Figure 3; this is very possibly due to the strong interactions between the $^1\Sigma^+$ states and the $^1\Pi$ states nearby, which strongly couple with $^3\Pi$ states. The strong interactions between $^1\Sigma^+$ states and $^1\Pi$ states in these two energy regions have been analyzed and confirmed by Eidelsberg et al. using absorption and photoionization methods.³³

In summary, this work reports the branching ratio measurements for the photodissociation of four $^1\Pi$ bands and three $^1\Sigma^+$ bands of $^{12}C^{16}O$ in the energy range from $106\,250$ to $107\,800\text{ cm}^{-1}$. The branching ratio measurements shed light on the CO predissociation mechanisms over the energy region of interest. The branching ratio measurements supported the prediction of trapping yields of atomic oxygen and nitrogen by H_2 in the early solar nebula made in our recent paper.²⁴ The pattern of the energy dependence of branching ratio into the triplet spin-forbidden dissociation channels indicates much more complicated $^1\Pi$ – $^3\Pi$ interactions for CO compared with N_2 , and this should stimulate and guide further theoretical studies on the photodissociation dynamics of CO.

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