Photodissociation branching ratios of $^{13}\text{C}^{16}\text{O}$ and $^{12}\text{C}^{18}\text{O}$ in the vacuum ultraviolet region from 107 800 to 109 700 cm^{-1}

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ABSTRACT

In this study, we present C^+ ion photofragment spectroscopic studies and photodissociation branching ratio measurements for two CO isotopologs, $^{13}\text{C}^{16}\text{O}$ and $^{12}\text{C}^{18}\text{O}$, in the vacuum ultraviolet (VUV) region from 107 800 cm^{-1} (92.76 nm) to 109 700 cm^{-1} (91.16 nm) using a time-slice velocity-map imaging setup and a tunable VUV laser radiation source generated by the two-photon resonance-enhanced four-wave mixing technique. Several absorption bands of $^{12}\text{C}^{16}\text{O}$ in the above energy region are reinvestigated up to higher rotational levels compared with previous studies. The results are compared among $^{12}\text{C}^{16}\text{O}$, $^{13}\text{C}^{16}\text{O}$, and $^{12}\text{C}^{18}\text{O}$ on a state-by-state basis, and the photodissociation branching ratios for channels $\text{C}(^1\text{D}) + \text{O}(^3\text{P})$, and $\text{C}(^3\text{P}) + \text{O}(^1\text{D})$ are dramatically changed for most of the absorption bands due to the substitutions of ^{12}C by ^{13}C and ^{16}O by ^{18}O . The branching ratios of $^{13}\text{C}^{16}\text{O}$ and $^{12}\text{C}^{18}\text{O}$ are close to each other due to their similar reduced masses. The strong and selective isotope effects obtained here not only provide useful information for understanding the complicated predissociation dynamics of CO, but are also important for developing a comprehensive photochemical model for explaining the C and O isotope heterogeneities as observed in the Solar System.

Key words. astrochemistry – molecular data – Sun: UV radiation – ISM: molecules – ISM: kinematics and dynamics – photon-dominated region

1. Introduction

Carbon monoxide (CO) is the second most abundant molecular species in the interstellar medium after hydrogen (H_2) and one of the most studied molecules in the fields of astronomy and astrophysics (Bally & Langer 1982; van Dishoeck & Black 1988; Yan et al. 2000; Bertoldi et al. 2003). An intriguing model known as CO “self-shielding” has been proposed for interpreting the abnormal oxygen isotopic compositions as observed in the early Solar System materials (Clayton 2002; Yurimoto & Kuramoto 2004; Lyons & Young 2005). Early self-shielding models only considered the “shielding” effect caused by the isotope dependent absorption peak positions and the large difference of column densities between $^{12}\text{C}^{16}\text{O}$ and other rare CO isotopologs.

However, other important photochemical properties, such as oscillator strengths and predissociation rates, were not considered to be isotope dependent in the early models. Recently, Chakraborty et al. (2008) measured the oxygen isotopic fractionation associated with CO photodissociation at different VUV wavelengths and in different experimental conditions. These latter authors found that the abundance ratios between ^{17}O and ^{18}O are strongly wavelength dependent with various values other than 1, which is thought to be contrary to early self-shielding models. This conclusion was immediately questioned by several other researchers (Federman & Young 2009; Lyons et al. 2009; Yin et al. 2009). Visser et al. (2009) updated the early model of van Dishoeck & Black (1988) using new accurate spectroscopic data from the literature, and concluded that CO “self-shielding” is very important, while other isotope-dependent

properties besides the absorption line positions need to be taken into account. The anomalous O isotope distributions observed in the Solar System are believed to be mainly caused by the CO self-shielding effect, while other important isotope-dependent photolysis properties of CO also play important roles, such as photo-absorption cross sections, oscillator strengths, and predissociation rates.

Whole spectroscopic studies have been devoted to characterizing the molecular parameters of all CO isotopologs so that the astronomical observations can be better interpreted and to further improve the photochemical modeling (Eidelsberg & Rostas 1990; Eidelsberg et al. 1991, 1992, 2004, 2006, 2012, 2014, 2017; Eikema et al. 1994; Ubachs et al. 1994; Stark et al. 2014; Lemaire et al. 2018), but very few studies have discussed the subsequent “trapping reactions” following the VUV photodestruction process of CO (Clayton 2011; Shi et al. 2017; Lyons et al. 2018). Recently, Lyons et al. (2018) reanalyzed the ATMOS FTS data and found that the heavy C isotope (^{13}C) is also depleted in the Sun compared with that in the Earth and other planetary objects. These latter authors considered a variety of reactions and estimated the chemical loss timescales of the most relevant species to evaluate the possible chemical pathways for several carbon species in the solar nebula. In their model, the reaction between excited $\text{C}(^1\text{D})$ atoms and H_2 is several orders of magnitude faster than any other reaction, which may play an important role in sequestering the isotope fractionation results formed in the photodissociation process. To quantitatively verify the roles played by the excited $\text{C}(^1\text{D})$ and $\text{O}(^1\text{D})$ atoms, accurate determination of the branching ratios in the photodissociation processes of all CO isotopologs is highly desired.

Since 2011, significant progress has been made toward systematically determining the quantum state populations of the atomic photodissociation products of $^{12}\text{C}^{16}\text{O}$ and its isotopologs using a time-slice velocity-map imaging (TSVMI) setup and a tunable VUV laser radiation source produced by the two-photon resonance-enhanced four-wave mixing scheme. Jackson, Ng, Gao, and coworkers (Gao et al. 2011, 2012, 2013; Shi et al. 2018; Jiang et al. 2019a; Chi et al. 2020a) measured and documented all strong $^{12}\text{C}^{16}\text{O}$ absorption bands in the VUV region from $102\,807\text{ cm}^{-1}$ (97.27 nm) to $109\,700\text{ cm}^{-1}$ (91.16 nm) that are of astrophysical importance as listed in Table 1 by Visser et al. (2009). Collectively, these findings show that the photodissociation products are formed not only in the ground state, but also in the excited states in substantial amounts. The photodissociation branching ratios are strongly quantum-state dependent. Recently, Gao and coworkers (Jiang et al. 2019b, 2020; Chi et al. 2020b) measured the photodissociation branching ratios of $^{13}\text{C}^{16}\text{O}$ in the VUV region from $102\,807\text{ cm}^{-1}$ (97.27 nm) to $107\,685\text{ cm}^{-1}$ (92.87 nm), which are found to be dramatically different from those of $^{12}\text{C}^{16}\text{O}$. This strong and selective isotope effect on the photodissociation branching ratio is important for future quantitative photochemical modeling.

In the present work, we continue to measure the photodissociation branching ratios of $^{13}\text{C}^{16}\text{O}$ in the higher energy range from $107\,800\text{ cm}^{-1}$ (92.76 nm) to $109\,700\text{ cm}^{-1}$ (91.16 nm) with the same experimental method, and those of $^{12}\text{C}^{18}\text{O}$ are also measured for the first time in the same energy range. To compare with $^{13}\text{C}^{16}\text{O}$ and $^{12}\text{C}^{18}\text{O}$, several absorption bands of $^{12}\text{C}^{16}\text{O}$ in the titled energy region are reinvestigated up to higher rotational levels. The C^+ ion photofragment spectra and the corresponding photodissociation branching ratios of $^{13}\text{C}^{16}\text{O}$ and $^{12}\text{C}^{18}\text{O}$ are similar to each other due to their similar reduced masses, while both of them are dramatically different from that of $^{12}\text{C}^{16}\text{O}$. This is important not only for any relevant astrophysical applications, but also for understanding the complicated predissociation dynamics of CO.

2. Experimental method

The experimental setup and the data-collection procedure used in the current study have been described in detail before, which consists of a TSVMI component and a tunable VUV laser radiation source (Qi et al. 2018; Jiang et al. 2019a,b). Briefly, a pulsed supersonic molecular beam of different pure CO isotopologs (Yuan-Hua in China, $^{12}\text{C}^{16}\text{O} > 99.9\%$; Cambridge Isotope, $^{13}\text{C}^{16}\text{O}$, $^{13}\text{C} > 99\%$, $^{18}\text{O} < 5\%$; Linde Gas North America LLC, $^{13}\text{C}^{16}\text{O}$, $^{13}\text{C} > 99\%$, $^{18}\text{O} < 5\%$; Sigma-Aldrich, $^{12}\text{C}^{18}\text{O} > 95\%$, $^{18}\text{O} > 99\%$) is generated by a general valve (Parker, Series 9) with a nozzle diameter of 0.5 mm operating at the stagnation pressure of 30 psi and repetition rate of 10 Hz. The molecular beam passes through two conical skimmers (both with diameter of 2 mm) and perpendicularly intersects with the tunable VUV beam in the photodissociation/photoionization (PD/PI) region of the TSVMI setup. CO molecules absorb a single sum-frequency VUV photon to be excited to specific quantum states, and then undergo predissociation to form C and O atoms in the ^3P and ^1D states. The nascent C atoms thus produced are directly photoionized by absorbing a second sum-frequency VUV photon in the same laser pulse. The 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.

The tunable VUV laser radiation used in the current study is produced by the two-photon resonance-enhanced four-wave mixing scheme with the pulsed Xe gas as the nonlinear medium. The third harmonic output of a Nd:YAG laser (Quanta-Ray, Pro-270-10E) operating at 10 Hz is used to pump two dye lasers (Sirah, Cobra-Stretch) at the same time. The first dye laser is frequency doubled to generate UV laser (ω_1), which is fixed at 222.568 nm to be resonant with the two-photon transition of Xe: $(5p)^5(^2\text{P}_{1/2})6p^2[1/2](J=0) \leftarrow (5p)^6\ ^1\text{S}_0$ at $89\,860.015\text{ cm}^{-1}$. The second dye laser is used to generate the visible laser beam (ω_2), which is tuned from 504 to 557 nm. The UV (ω_1) and visible (ω_2) laser beams are combined through a dichroic mirror, and then focused into a T-shape channel by two plano-convex lenses both with $f = 600\text{ mm}$. The Xe gas is pulsed into the T-shape channel by a second general valve (Parker, Series 9) when the two laser beams arrive. A four-wave mixing process occurs in the T-shape channel for generating the tunable sum-frequency VUV laser radiation ($2\omega_1 + \omega_2$) from $107\,800\text{ cm}^{-1}$ to $109\,700\text{ cm}^{-1}$ as used in the current experiment. The difference-frequency VUV ($2\omega_1 - \omega_2$) is also generated and enters the PD/PI region together with the UV (ω_1), visible (ω_2), and sum-frequency VUV ($2\omega_1 + \omega_2$) laser beams.

In this study, we gate and integrate on the C^+ ion peak in the time-of-flight (TOF) mass spectra while scanning the VUV photon energy from $107\,800\text{ cm}^{-1}$ to $109\,700\text{ cm}^{-1}$ to acquire the C^+ ion photofragment spectra, which help us identify the vibronic states and rotational levels of $^{13}\text{C}^{16}\text{O}$ and $^{12}\text{C}^{18}\text{O}$ that are being studied. The VUV photon energy is then fixed at a specific rovibronic level and the corresponding TSVMI image is collected. The three dissociation channels $\text{C}(^3\text{P}) + \text{O}(^3\text{P})$, $\text{C}(^1\text{D}) + \text{O}(^3\text{P})$ and $\text{C}(^3\text{P}) + \text{O}(^1\text{D})$ can be distinguished in the TSVMI images by their different kinetic energy releases. The branching ratios into the three channels can be deduced by integrating the corresponding peaks in the total kinetic energy release (TKER) spectra converted from the TSVMI images after normalization with respect to the photoionization cross sections of $\text{C}(^3\text{P})$ and $\text{C}(^1\text{D})$, respectively. In this study, the photodissociation branching ratios (or percentages) for channels $\text{C}(^3\text{P}) + \text{O}(^3\text{P})$, $\text{C}(^1\text{D}) + \text{O}(^3\text{P})$ and $\text{C}(^3\text{P}) + \text{O}(^1\text{D})$ are defined as $[\text{C}(^3\text{P}) + \text{O}(^3\text{P})] / \{[\text{C}(^3\text{P}) + \text{O}(^3\text{P})] + [\text{C}(^1\text{D}) + \text{O}(^3\text{P})] + [\text{C}(^3\text{P}) + \text{O}(^1\text{D})]\} \times 100\%$, $[\text{C}(^1\text{D}) + \text{O}(^3\text{P})] / \{[\text{C}(^3\text{P}) + \text{O}(^3\text{P})] + [\text{C}(^1\text{D}) + \text{O}(^3\text{P})] + [\text{C}(^3\text{P}) + \text{O}(^1\text{D})]\} \times 100\%$ and $[\text{C}(^3\text{P}) + \text{O}(^1\text{D})] / \{[\text{C}(^3\text{P}) + \text{O}(^3\text{P})] + [\text{C}(^1\text{D}) + \text{O}(^3\text{P})] + [\text{C}(^3\text{P}) + \text{O}(^1\text{D})]\} \times 100\%$, respectively, where the square brackets represent the photoionization cross section corrected peak intensities of the corresponding photodissociation channels in the TKER spectra.

3. Results and discussion

The C^+ ion photofragment spectra produced from the predissociation of $^{13}\text{C}^{16}\text{O}$ and $^{12}\text{C}^{18}\text{O}$ in the VUV photon energy region from $107\,800\text{ cm}^{-1}$ (92.76 nm) to $109\,700\text{ cm}^{-1}$ (91.16 nm) are shown in Figs. 1–4. The assignments of peak positions and rotational quantum levels are based on the previous spectroscopic studies by Eidelsberg & Rostas (1990), Eidelsberg et al. (1991, 2004) and Casey (1978). Total kinetic energy release (TKER) spectra are converted from the time-slice velocity-map ion (TSVMI) images and the kinetic energies of each peak in TKER spectra are used to distinguish the three lowest dissociation channels, namely $\text{C}(^3\text{P}) + \text{O}(^3\text{P})$, $\text{C}(^1\text{D}) + \text{O}(^3\text{P})$, and $\text{C}(^3\text{P}) + \text{O}(^1\text{D})$. The branching ratios into the three dissociation channels are deduced by integrating the corresponding peaks in the TKER spectra after normalization with respect to the photoionization cross sections of $\text{C}(^3\text{P})$ and $\text{C}(^1\text{D})$, respectively.

Fig. 1. C^+ ion photofragment spectra of $^{13}C^{16}O$ (top) and $^{12}C^{18}O$ (bottom) in the VUV photon energy region from 109 100 cm^{-1} to 109 700 cm^{-1} , which include the following vibronic states: $(6p\sigma) ^1\Sigma^+(v'=0)$, $(6p\pi) ^1\Pi(v'=0)$, $(4p\sigma) ^1\Sigma^+(v'=3)$, $(4s\sigma) ^1\Sigma^+(v'=4)$, $(5p\pi) ^1\Pi(v'=1)$, and $(4p\pi) ^1\Pi(v'=3)$. The relative intensities of the spectra are not normalized according to the corresponding VUV intensities. Red arrows: $(6p\pi) ^1\Pi(v'=0)$; blue arrows: $(4p\sigma) ^1\Sigma^+(v'=3)$ and $(4s\sigma) ^1\Sigma^+(v'=4)$.

Fig. 3. C^+ ion photofragment spectra of $^{13}C^{16}O$ (top) and $^{12}C^{18}O$ (bottom) in the VUV photon energy region from 108 270 cm^{-1} to 108 510 cm^{-1} , which include vibronic states: $(5d\sigma) ^1\Sigma^+(v'=0)$, $C' ^1\Sigma^+(v'=9)$, a newly observed $^1\Pi$ state of $^{13}C^{16}O$ and $^{12}C^{18}O$, and the $(5d\sigma) ^1\Sigma^+(v'=0)$ state of $^{13}C^{18}O$ (see Sect. 3.7 for detail). The relative intensities of the spectra are not normalized according to the corresponding VUV intensities. Black: Experimental spectra. Red: simulated spectra by the PGOPHER program (Western 2017).

Fig. 2. C^+ ion photofragment spectra of $^{13}C^{16}O$ (top) and $^{12}C^{18}O$ (bottom) in the VUV photon energy region from 108 750 cm^{-1} to 108 942 cm^{-1} , which include vibronic states: $(6s\sigma) ^1\Sigma^+(v'=0)$, $^1\Pi(v'=2)$ and an unknown underlying continuum as described in Sect. 3.3. The relative intensities of the spectra are not normalized according to the corresponding VUV intensities. Black: experimental spectra; red: simulated spectra by the PGOPHER program (Western 2017); blue arrows: broad underlying continuum.

Fig. 4. C^+ ion photofragment spectra of the $W(3s\sigma) ^1\Pi(v'=3)$ state for $^{13}C^{16}O$ (top) and $^{12}C^{18}O$ (bottom). The relative intensities of the spectra are not normalized according to the corresponding VUV intensities.

The photoionization cross section of $C(^3P)$ was measured to be ~ 16 Mb with an uncertainty of $\sim 30\%$ in the above-mentioned energy region (Cantu et al. 1981). The photoionization cross section of $C(^1D)$ was calculated by Burke & Taylor (1979). Its value increases abruptly from ~ 25 Mb at ~ 95 nm to ~ 65 Mb at ~ 90 nm under the dipole length CI approximation; while under a different approximation, it increases from ~ 24 Mb at ~ 95 nm

to ~ 50 Mb at ~ 90 nm (see Fig. 4 in Burke & Taylor 1979). This implies a relatively large uncertainty on the photoionization cross section of $C(^1D)$. Furthermore, the previously reported data were presented in the form of figures in large energy scales, which made it hard to obtain accurate cross section values in a wavenumber-resolved level as is needed in the current study. Thus, the photoionization cross sections used in the current study have large uncertainties. Tables 1 and 2 list the photoionization cross section values that we use for all the absorption bands here; these can be used to correct the branching ratio values

easily in case higher accuracy photoionization cross sections of $C(^1D)$ and $C(^3P)$ become available in the future. Fortunately, the large uncertainty of the photoionization cross section does not dramatically affect the comparisons among different absorption bands and different CO isotopologs as presented in the following sections.

Using the method described above, we measured the branching ratio at each of the VUV photon energy positions at least three times on different days. The averaged branching ratio values of $^{13}C^{16}O$ and $^{12}C^{18}O$ are listed in Tables 1 and 2, respectively. The error bars presented in Tables 1 and 2 are simply the standard deviations (1σ) of the three independent measurements, which do not take any possible systematic uncertainties into account. The systematic uncertainty from the present experimental setup was estimated to be $\sim 5\%$ (Chi et al. 2020b), which is probably due to the presence of tripling VUV ($3\omega_1$) in the interaction region, slightly different slicing durations on the MCP, nonuniform efficiency across the whole active area of the MCP detector, and so on. Typical TSVM images of $^{12}C^{16}O$, $^{13}C^{16}O$, and $^{12}C^{18}O$, and the corresponding TKER spectra are presented for absorption bands of $C(^1\Sigma^+(v'=9))$ and $^1\Pi(v'=2)$ in Fig. 5 for direct comparisons. Figure 5 shows immediately that the substitution of ^{12}C for ^{13}C or ^{16}O for ^{18}O can greatly alter the photodissociation branching ratios of CO; while those for $^{13}C^{16}O$ and $^{12}C^{18}O$ are close to each other, which is to be expected due to their similar reduced masses. In the following, we present the detailed analysis of the C^+ ion photofragment spectra and the branching ratio values on a state-by-state basis for $^{13}C^{16}O$ and $^{12}C^{18}O$, with special attention given to their comparisons with $^{12}C^{16}O$. This provides valuable information for understanding the complicated predissociation dynamics of CO and expanding its applications in astronomy. For comparison, the relevant photodissociation branching ratios of $^{12}C^{16}O$ reproduced from previous studies are provided in Appendix A.

3.1. 109 220–109 700 cm^{-1} (Fig. 1)

The photoabsorption and photoionization spectra of the main isotopolog $^{12}C^{16}O$ in the energy region from 109 200 cm^{-1} to 109 650 cm^{-1} have previously been presented and analyzed by Rostas et al. (1994), Huber (1997), and Eidelsberg et al. (2004). According to these spectroscopic studies, five mutually interacting vibronic states of CO, namely $(5p\sigma)^1\Sigma^+(v'=1)$, $(4s\sigma)^1\Sigma^+(v'=4)$, $(4p\sigma)^1\Sigma^+(v'=3)$, $(5p\pi)^1\Pi(v'=1)$, and $(4p\pi)^1\Pi(v'=3)$ are located in this small energy region. These states were believed to predissociate through strong interactions with the well-known $D'^1\Sigma^+$ state, which correlates to the lowest dissociation channel $C(^3P) + O(^3P)$. The recent photodissociation branching ratio measurements of $^{12}C^{16}O$ in this energy region (Gao et al. 2011, 2012) showed that all the states mentioned above (except for $(5p\sigma)^1\Sigma^+(v'=1)$, which was not observed) dissociate not only into the lowest channel $C(^3P) + O(^3P)$ but also into the two spin-forbidden channels $C(^1D) + O(^3P)$ and $C(^3P) + O(^1D)$ in substantial amounts. In this study, we measure the C^+ ion photofragment spectra and the corresponding branching ratios in this region for $^{13}C^{16}O$ and $^{12}C^{18}O$, which are found to be dramatically different from those of $^{12}C^{16}O$, showing strong isotope effect. As shown in Fig. 1, the shapes of the C^+ ion photofragment spectra are almost the same as those of the absorption spectra as previously presented by Huber (1997) except for the cluster of peaks at $\sim 109\,380\,cm^{-1}$. These latter peaks are due to transitions from the ground vibronic state to the $A^1\Pi(v'=4)$ state of $^{13}C^{16}O$ or $^{12}C^{18}O$ by absorbing the difference-frequency VUV at $\sim 70\,340\,cm^{-1}$ (Gavilan et al.

2013), which is also present in the PD/PI region as described in Sect. 2.

3.1.1. $(4s\sigma)^1\Sigma^+(v'=4)$ & $(4p\sigma)^1\Sigma^+(v'=3)$ (Figs. 1, 6)

We remeasured the branching ratios of the $(4s\sigma)^1\Sigma^+(v'=4)$ state for $^{12}C^{16}O$ up to much higher rotational levels and the dependence on the rotational quantum number J' is presented in Fig. 6. At low J' levels, the branching ratio values are consistent with the previous measurements within the experimental uncertainties (Gao et al. 2011). The discrepancy between the R - and P -branches at several J' levels can be explained by overlap with the nearby $(4p\sigma)^1\Sigma^+(v'=3)$ state. As shown in Fig. 6, the percentages into the channel $C(^3P) + O(^3P)$ increase linearly as a function of $J'(J'+1)$, and those into the spin-forbidden channels $C(^1D) + O(^3P)$ and $C(^3P) + O(^1D)$ decrease accordingly. Similar rotational dependence of the branching ratio in this region was also observed in the recent study by the two-color VUV-VUV laser pump-probe time-slice velocity-map ion imaging method (Gao et al. 2020). This observation cannot be explained solely through interactions with the valence $D'^1\Sigma^+$ state. It seems to be consistent with the spectroscopic analyses by Huber (1997) and Eidelsberg et al. (2004) that a dark $^1\Pi$ perturber state must be present in this region, which might be responsible for the strong dissociation into the spin-forbidden channels and its dependence on the rotational quantum number as described above.

As compared with $^{12}C^{16}O$, the photoabsorption peak positions of the $(4s\sigma)^1\Sigma^+(v'=4)$ and $(4p\sigma)^1\Sigma^+(v'=3)$ states for $^{13}C^{16}O$ and $^{12}C^{18}O$ are red shifted by $\sim 150\,cm^{-1}$, and the shape of the spectra transforms from highly rotationally resolved structure in the case of $^{12}C^{16}O$ into totally diffuse structure as indicated by the three broad peaks at $\sim 109\,300\,cm^{-1}$ as shown in Fig. 1. The photodissociation branching ratios at the three diffuse peaks are measured for $^{13}C^{16}O$ and $^{12}C^{18}O$, as listed in Tables 1 and 2, respectively. The $(4s\sigma)^1\Sigma^+(v'=4)$ and $(4p\sigma)^1\Sigma^+(v'=3)$ states of $^{13}C^{16}O$ and $^{12}C^{18}O$ almost completely dissociate into the ground channel $C(^3P) + O(^3P)$; while in the case of $^{12}C^{16}O$, substantial percentages of the dissociation products are formed through the spin-forbidden channels $C(^1D) + O(^3P)$ and $C(^3P) + O(^1D)$ (Gao et al. 2011, 2012). This implies that the valence $D'^1\Sigma^+$ state has become the dominant perturber state in this region for $^{13}C^{16}O$ and $^{12}C^{18}O$, and the interaction with the dark $^1\Pi$ state as identified by Huber (1997) and Eidelsberg et al. (2004) for $^{12}C^{16}O$ becomes negligibly weak. This is also consistent with the observations for the $(5p\pi)^1\Pi(v'=1)$ and $(4p\pi)^1\Pi(v'=3)$ states as described below.

3.1.2. $(5p\pi)^1\Pi(v'=1)$ (Fig. 1)

The $(5p\pi)^1\Pi(v'=1)$ state is buried in the two strong absorption bands of $(4s\sigma)^1\Sigma^+(v'=4)$ and $(4p\sigma)^1\Sigma^+(v'=3)$ for $^{12}C^{16}O$, and was not observed in either our previous studies (Gao et al. 2011, 2012) or the current study. In the cases of $^{13}C^{16}O$ and $^{12}C^{18}O$, the above two strong absorption bands shift away, and a highly rotationally resolved $^1\Pi$ band shows up at $\sim 109\,440\,cm^{-1}$ as shown in Fig. 1, whose upper state is tentatively assigned as $(5p\pi)^1\Pi(v'=1)$. Its C^+ ion photofragment spectra can be well reproduced using the spectrum simulation program PGO-PHER (Western 2017) (not shown in Fig. 1); the band origin and rotational constant determined in this way are listed and compared to those of Eidelsberg et al. (1991) in Table 3. The $(5p\pi)^1\Pi(v'=1)$ state has very narrow rotational transitions implying rather long predissociation lifetimes, which is in marked contrast to the $(4s\sigma)^1\Sigma^+(v'=4)$ and $(4p\sigma)^1\Sigma^+(v'=3)$ states. This

Table 1. Photodissociation branching ratios of the channels $C(^3P) + O(^1D)$, $C(^1D) + O(^3P)$, and $C(^3P) + O(^3P)$ for $^{13}C^{16}O$ in the region from 107 800 to 109 700 cm^{-1} (91.16–92.76 nm).

Upper state	VUV (cm^{-1})	Rotational transition	$C(^3P) + O(^1D)$ (%)	$C(^1D) + O(^3P)$ (%)	$C(^3P) + O(^3P)$ (%)
(4p π) $^1\Pi(v' = 3)$ 50 Mb ^(a)	109 609.6	Q	4.1 ± 0.2 ^(b)	2.1 ± 0.1	93.7 ± 0.3
(5p π) $^1\Pi(v' = 1)$ 50 Mb	109 434.8 109 438.7 109 442.5 109 447.1 109 451.7 109 431 109 427.9	R(0) R(1) R(2) R(3) R(4) Q P(1)	12.4 ± 0.2 11.5 ± 0.3 8.9 ± 0.1 9.4 ± 0.5 16.2 ± 0.2 10.2 ± 0.2 10.1 ± 0.2	0.6 ± 0.1 0.6 ± 0.1 0.6 ± 0.1 0.5 ± 0.1 0.8 ± 0.1 0.6 ± 0.1 1.5 ± 0.2	87.0 ± 0.3 87.9 ± 0.3 90.5 ± 0.1 90.1 ± 0.5 82.9 ± 0.3 89.2 ± 0.1 88.4 ± 0.4
(4p σ) $^1\Sigma^+(v' = 3)$ (4s σ) $^1\Sigma^+(v' = 4)$ 50 Mb	109 351.6 109 328.9 109 295.6		0.1 ± 0.2 0.1 ± 0.1 0.2 ± 0.1	0.1 ± 0.1 0.1 ± 0.1 0.2 ± 0.1	99.7 ± 0.2 99.8 ± 0.1 99.6 ± 0.1
(6p π) $^1\Pi(v' = 0)$ 50 Mb	109 203.0		4.7 ± 0.9	1.5 ± 0.3	93.8 ± 0.6
(6p σ) $^1\Sigma^+(v' = 0)$ 50 Mb	109 171.7 109 166.4 109 155.3		3.2 ± 0.1 1.4 ± 0.1 2.9 ± 0.3	1.8 ± 0.1 0.7 ± 0.1 1.6 ± 0.1	95.0 ± 0.1 97.9 ± 0.1 95.6 ± 0.4
$^1\Pi(v' = 2)$ 50 Mb	108 906.9 108 910.5 108 902.5 108 901.1 108 899.6 108 896.7 108 893.1 108 890.9 108 885.1 108 879.3 108 871.4	R(0) R(1)/R(2) Q(1) Q(2) Q(3) P(2)/Q(4) Q(5) P(3) P(4) P(5) P(6)	11.4 ± 0.5 10.4 ± 0.6 11.1 ± 0.3 11.3 ± 0.2 12.0 ± 0.2 12.3 ± 0.4 11.3 ± 0.5 11.3 ± 0.3 11.7 ± 0.3 10.5 ± 0.5 10.7 ± 0.9	39.5 ± 0.4 39.4 ± 0.8 39.3 ± 0.6 40.2 ± 0.3 40.0 ± 0.2 40.0 ± 0.3 40.4 ± 1.0 39.4 ± 0.9 40.2 ± 1.7 37.9 ± 1.4 36.2 ± 1.9	49.0 ± 0.4 50.2 ± 0.7 49.6 ± 0.4 48.4 ± 0.2 48.0 ± 0.1 47.8 ± 0.2 48.3 ± 1.2 49.3 ± 1.1 48.1 ± 1.7 51.6 ± 1.9 53.1 ± 2.4
(6s σ) $^1\Sigma^+(v' = 0)$ 50 Mb	108 799.3 108 803.6 108 808.7 108 813.7 108 818.7 108 791.4 108 788.6 108 785.7 108 783.6	R(0) R(1) R(2) R(3) R(4) P(1) P(2) P(3) P(4)	1.9 ± 0.1 0.8 ± 0.1 1.0 ± 0.2 1.5 ± 0.3 3.1 ± 0.7 1.1 ± 0.1 0.6 ± 0.1 0.7 ± 0.1 0.7 ± 0.2	4.9 ± 0.4 2.6 ± 0.2 2.4 ± 0.2 1.9 ± 0.1 2.8 ± 0.5 2.5 ± 0.4 1.3 ± 0.2 1.2 ± 0.2 1.5 ± 0.2	93.2 ± 0.3 96.7 ± 0.3 96.6 ± 0.5 96.6 ± 0.4 94.0 ± 0.9 96.3 ± 0.5 98.1 ± 0.2 98.0 ± 0.1 97.7 ± 0.3
New $^1\Pi$ 50 Mb	108 465.1 108 469.3 108 472.8 108 475.1	Q R(0) R(1) R(2)	23.4 ± 0.5 26.5 ± 0.2 20.5 ± 0.6 18.1 ± 0.5	11.3 ± 0.1 11.0 ± 0.3 9.4 ± 0.3 9.0 ± 0.1	65.3 ± 0.5 62.4 ± 0.2 70.1 ± 0.9 72.9 ± 0.6
$C'^1\Sigma^+(v' = 9)$ 50 Mb	108 420.2 108 416.1 108 413.4 108 408.5 108 402.3 108 392.7	R(0)/R(1)/R(2) R(3) P(1) P(2) P(3) P(4)	51.2 ± 0.3 49.4 ± 0.8 48.5 ± 0.9 45.0 ± 0.7 41.2 ± 1.0 34.0 ± 0.9	14.0 ± 0.2 13.4 ± 0.5 12.7 ± 0.3 11.8 ± 0.5 12.0 ± 0.3 10.3 ± 0.4	34.8 ± 0.2 37.2 ± 1.3 38.8 ± 1.2 43.2 ± 0.5 46.9 ± 1.3 55.7 ± 1.3
(5d σ) $^1\Sigma^+(v' = 0)$ $^{13}C^{16}O$ 30 Mb	108 361.2 108 359.1 108 357.0 108 355.0 108 346.8 108 342.7 108 340.0	R R R R P P P	0.3 ± 0.1 0.2 ± 0.1 0.2 ± 0.1 0.2 ± 0.1 0.2 ± 0.1 0.2 ± 0.2 0.3 ± 0.1	0.3 ± 0.1 0.3 ± 0.2 0.3 ± 0.2 0.4 ± 0.1 0.2 ± 0.1 0.2 ± 0.1 0.3 ± 0.1	99.4 ± 0.1 99.5 ± 0.2 99.5 ± 0.1 99.4 ± 0.1 99.4 ± 0.1 99.6 ± 0.2 99.4 ± 0.1
(5d σ) $^1\Sigma^+(v' = 0)$ $^{13}C^{18}O$ 30 Mb	108 309.9 108 313.3 108 316.7 108 319.5 108 322.9 108 303.1 108 299.7 108 296.3 108 292.2	R(0) R(1) R(2) R(3) R(4) P(1) P(2) P(3) P(4)	0.2 ± 0.1 0.5 ± 0.2 0.3 ± 0.1 0.4 ± 0.2 0.6 ± 0.2 0.2 ± 0.1 0.3 ± 0.1 0.8 ± 0.1 1.0 ± 0.2	0.3 ± 0.1 0.4 ± 0.1 0.3 ± 0.1 0.5 ± 0.1 0.5 ± 0.1 0.2 ± 0.1 0.4 ± 0.1 0.7 ± 0.3 0.4 ± 0.2	99.5 ± 0.1 99.1 ± 0.2 99.4 ± 0.1 99.1 ± 0.2 99.0 ± 0.1 99.6 ± 0.1 99.4 ± 0.1 98.5 ± 0.1 98.6 ± 0.1
W(3s σ) $^1\Pi(v' = 3)$ 30 Mb	107 847.2 107 849.9 107 852.0 107 843.7 107 843.1 107 841.6 107 840.1 107 837.7 107 835.0 107 832.6 107 828.5	R(0) R(1) R(2) Q(1) Q(2) Q(3) Q(4) P(2)/Q(5) Q(6) P(3)/Q(7) P(4)/Q(8)	2.6 ± 0.2 1.8 ± 0.1 1.6 ± 0.1 2.7 ± 0.1 3.0 ± 0.2 3.2 ± 0.2 3.0 ± 0.1 2.9 ± 0.3 2.8 ± 0.1 2.2 ± 0.1 1.6 ± 0.3	2.4 ± 0.1 1.9 ± 0.3 1.4 ± 0.1 2.6 ± 0.1 2.6 ± 0.1 2.5 ± 0.1 2.5 ± 0.2 2.3 ± 0.1 2.4 ± 0.1 2.0 ± 0.1 1.7 ± 0.2	94.9 ± 0.2 96.3 ± 0.3 96.9 ± 0.1 94.7 ± 0.1 94.4 ± 0.2 94.3 ± 0.2 94.5 ± 0.3 94.8 ± 0.2 94.8 ± 0.2 95.9 ± 0.1 96.6 ± 0.5

Notes. ^(a)Photoionization cross section values of $C(^1D)$ used for calibrating the measured photodissociation branching ratios; see the first paragraph in Sect. 3 for detail. ^(b)The error bars are the standard deviations (1σ) of three independent measurements, which do not include any possible systematic experimental uncertainties; see the second paragraph in Sect. 3 for details.

Table 2. Photodissociation branching ratios of the channels $C(^3P) + O(^1D)$, $C(^1D) + O(^3P)$, and $C(^3P) + O(^3P)$ for $^{12}C^{18}O$ in the region from 107 800–109 700 cm^{-1} (91.16–92.76 nm).

Upper state	VUV (cm^{-1})	Rotational transition	$C(^3P) + O(^1D)$ (%)	$C(^1D) + O(^3P)$ (%)	$C(^3P) + O(^3P)$ (%)
(4p π) $^1\Pi(v' = 3)$ 50 Mb ^(a)	109 592.5	Q	2.9 ± 0.5 ^(b)	1.7 ± 0.2	95.3 ± 0.6
(5p π) $^1\Pi(v' = 1)$ 50 Mb	109 425.6 109 429.5 109 433.3 109 437.9 109 442.5	Q R(0) R(1) R(2) R(3)	7.1 ± 0.2 4.1 ± 0.3 2.9 ± 0.9 2.0 ± 0.4 1.9 ± 0.4	3.2 ± 0.1 2.3 ± 0.2 2.1 ± 0.1 2.0 ± 0.1 1.4 ± 0.5	89.7 ± 0.3 93.6 ± 0.3 95.0 ± 0.9 96.0 ± 0.3 96.6 ± 0.6
(4p σ) $^1\Sigma^+(v' = 3)$ (4s σ) $^1\Sigma^+(v' = 4)$ 50 Mb	109 342.5 109 313.7 109 295.6		0 0 0.3 ± 0.1	0.1 ± 0.1 0.1 ± 0.1 0.1 ± 0.1	99.9 ± 0.1 99.9 ± 0.1 99.6 ± 0.1
(6p σ) $^1\Sigma^+(v' = 0)$ 50 Mb	109 169.4 109 165.7		3.9 ± 0.1 2.2 ± 0.2	1.8 ± 0.1 1.2 ± 0.1	94.3 ± 0.2 96.6 ± 0.3
$^1\Pi(v' = 2)$ 50 Mb	108 903.1 108 905.3 108 907.5 108 898 108 895.1 108 893 108 889.3 108 887.2 108 881.4 108 874.9 108 867.6	R(0) R(1) R(2) Q(1)/Q(2) Q(3) P(2)/Q(4) Q(5) P(3) P(4) P(5) P(6)	12.3 ± 0.2 11.8 ± 0.4 12.8 ± 0.3 12.2 ± 0.8 12.9 ± 0.6 12.9 ± 0.8 12.5 ± 0.4 12.7 ± 0.8 11.8 ± 1.1 11.0 ± 0.9 10.3 ± 0.8	37.7 ± 0.3 37.9 ± 0.7 38.9 ± 0.6 37.9 ± 0.2 37.9 ± 0.6 37.9 ± 0.7 36.8 ± 0.6 36.1 ± 0.1 35.5 ± 0.8 34.5 ± 1.4 29.0 ± 4.0	49.9 ± 0.4 50.3 ± 1.0 48.4 ± 0.8 49.9 ± 0.7 49.1 ± 0.3 49.2 ± 1.1 50.7 ± 0.9 51.3 ± 0.9 52.9 ± 1.8 54.4 ± 2.3 60.7 ± 4.7
(6s σ) $^1\Sigma^+(v' = 0)$ 50 Mb	108 802.8 108 807.9 108 812.2 108 817.2 108 794.9 108 792.1 108 789.2 108 786.3	R(0) R(1) R(2) R(3) P(1) P(2) P(3) P(4)	0.3 ± 0.1 0.8 ± 0.2 1.3 ± 0.2 2.7 ± 0.2 0.2 ± 0.1 0.2 ± 0.1 0.6 ± 0.1 1.2 ± 0.1	0.6 ± 0.1 1.0 ± 0.2 1.5 ± 0.1 2.5 ± 0.3 0.4 ± 0.1 0.5 ± 0.1 0.8 ± 0.1 1.2 ± 0.1	99.1 ± 0.1 98.3 ± 0.4 97.2 ± 0.2 94.9 ± 0.1 99.4 ± 0.2 99.2 ± 0.1 98.6 ± 0.1 97.6 ± 0.2
New $^1\Pi$ 50 Mb	108 459.6 108 463.1 108 466.5 108 470	Q R(0) R(1) R(2)	30.8 ± 0.6 34.3 ± 0.8 30.2 ± 0.9 26.2 ± 1.3	11.5 ± 0.3 11.4 ± 0.4 10.4 ± 0.2 10.2 ± 0.7	57.7 ± 0.9 54.2 ± 1.2 59.4 ± 1.1 63.7 ± 1.8
$C'^1\Sigma^+(v' = 9)$ 50 Mb	108 407.8 108 403.7 108 401.6 108 395.5 108 390 108 380.3	R(0)/R(1)/R(2) R(3) P(1) P(2) P(3) P(4)	59.6 ± 0.8 57.8 ± 0.1 59.4 ± 0.4 63.1 ± 2.0 51.0 ± 1.5 32.4 ± 2.5	13.5 ± 0.1 12.9 ± 0.5 12.2 ± 0.4 11.7 ± 0.4 11.2 ± 0.4 7.4 ± 0.6	26.9 ± 0.9 29.3 ± 0.5 28.5 ± 0.8 35.2 ± 2.4 37.9 ± 1.7 60.2 ± 3.1
(5d σ) $^1\Sigma^+(v' = 0)$ 30 Mb	108 350.9 108 354.3 108 357.7 108 359.8 108 363.2 108 342.7 108 338.6 108 335.2 108 332.4	R R R R R P P P P	0.4 ± 0.2 0.9 ± 0.1 0.7 ± 0.1 0.6 ± 0.1 0.9 ± 0.1 0.6 ± 0.2 0.7 ± 0.2 0.6 ± 0.1 0.6 ± 0.1	0.4 ± 0.2 0.7 ± 0.1 0.6 ± 0.1 0.7 ± 0.1 0.7 ± 0.1 0.6 ± 0.1 0.6 ± 0.1 0.5 ± 0.1 0.5 ± 0.1	99.2 ± 0.1 98.5 ± 0.2 98.6 ± 0.2 98.7 ± 0.1 98.3 ± 0.1 98.9 ± 0.1 98.7 ± 0.2 98.9 ± 0.1 98.9 ± 0.1
W(3s σ) $^1\Pi(v' = 3)$ 30 Mb	107 837.1 107 839.6 107 841.7 107 843.7 108 338.6 108 335.2 108 332.4 108 342.7 107 832.7 107 831.2 107 829.8 107 827.2 107 824.9 107 822.8 107 818.5	R(0) R(1) R(2) R(3) P P P P Q(1)/Q(2) Q(3) Q(4) P(2)/Q(5) Q(6) P(3)/Q(7) P(4)/Q(8)	3.8 ± 0.2 3.1 ± 0.1 2.6 ± 0.1 2.3 ± 0.1 0.7 ± 0.2 0.6 ± 0.1 0.6 ± 0.1 0.6 ± 0.1 4.2 ± 0.2 4.3 ± 0.1 4.2 ± 0.2 4.0 ± 0.1 3.3 ± 0.3 3.2 ± 0.2 2.7 ± 0.4	2.8 ± 0.1 2.2 ± 0.1 1.9 ± 0.1 1.6 ± 0.1 0.6 ± 0.1 0.5 ± 0.1 0.5 ± 0.1 0.5 ± 0.1 2.8 ± 0.1 2.9 ± 0.1 2.8 ± 0.2 2.5 ± 0.1 2.7 ± 0.4 2.4 ± 0.3 1.9 ± 0.2	93.4 ± 0.2 94.7 ± 0.1 95.5 ± 0.1 96.1 ± 0.2 98.7 ± 0.2 98.9 ± 0.1 98.9 ± 0.1 98.9 ± 0.1 93.0 ± 0.2 92.8 ± 0.1 92.9 ± 0.3 93.4 ± 0.1 93.9 ± 0.1 94.3 ± 0.4 95.4 ± 0.2

Notes. ^(a)Photoionization cross section values of $C(^1D)$ used for calibrating the measured photodissociation branching ratios; see the first paragraph in Sect. 3 for detail. ^(b)The error bars are the standard deviations (1σ) of three independent measurements, which do not include any possible systematic experimental uncertainties; see the second paragraph in Sect. 3 for detail.

is consistent with the above observation that interaction with the $D'^1\Sigma^+$ state is the dominant predissociation pathway for $^{13}C^{16}O$ and $^{12}C^{18}O$ in this region, and direct $^1\Sigma^+ - ^1\Sigma^+$ interaction is usually much stronger than the $^1\Pi - ^1\Sigma^+$ interaction. The photodissociation branching ratios of this state are measured and listed in

Tables 1 and 2 for $^{13}C^{16}O$ and $^{12}C^{18}O$, respectively. For $^{13}C^{16}O$, the percentages into channels of producing $C(^1D)$ and $O(^1D)$ atoms are $<1\%$ and $\sim 10\%$, respectively; while for $^{12}C^{18}O$, the percentages into both of the two spin-forbidden channels are $<5\%$. A weak dependence on the rotation and parity seems to

Fig. 5. Comparison of TSVMI images and the corresponding TKER spectra among $^{12}\text{C}^{16}\text{O}$, $^{13}\text{C}^{16}\text{O}$ and $^{12}\text{C}^{18}\text{O}$ for two absorption bands: R(0) line of the $\text{C}^1\Sigma^+(\nu'=9)$ state ((a), (b), (e), (f), (i), (j)) and R(0) line of the $^1\Pi(\nu'=2)$ state ((c), (d), (g), (h), (k), (l)). The heights of the three peaks in the TKER spectra are rescaled by setting the highest peak in each spectrum to 1.

Fig. 6. Dependence of the photodissociation branching ratio into the three lowest dissociation channels $\text{C}(^3\text{P}) + \text{O}(^3\text{P})$, $\text{C}(^1\text{D}) + \text{O}(^3\text{P})$, and $\text{C}(^3\text{P}) + \text{O}(^1\text{D})$ on $J'(J'+1)$ for the $(4s\sigma) ^1\Sigma^+(\nu'=4)$ state of $^{12}\text{C}^{16}\text{O}$, where J' is the rotational quantum number of the upper level. The error bars represent the standard deviations (1σ) of three independent measurements. Square: $\text{C}(^3\text{P}) + \text{O}(^3\text{P})$; dot: $\text{C}(^1\text{D}) + \text{O}(^3\text{P})$; triangle: $\text{C}(^3\text{P}) + \text{O}(^1\text{D})$. Blue: R-branch. Red: P-branch.

be observable, but cannot be confirmed in the current condition due to the weak signal level.

3.1.3. $(4p\pi) ^1\Pi(\nu'=3)$ (Fig. 1)

The C^+ ion photofragment spectra of the $(4p\pi) ^1\Pi(\nu'=3)$ state for $^{13}\text{C}^{16}\text{O}$ and $^{12}\text{C}^{18}\text{O}$ are observed at $\sim 109\,600\text{ cm}^{-1}$ with partially resolved rotational structures as shown in Fig. 1. The spectra can be well reproduced using the spectrum simulation program PGOPHER (Western 2017) (not shown in Fig. 1);

the band origin and rotational constant determined in this way are listed and compared to those of Eidelsberg et al. (1991) in Table 3. Here, the branching ratios of $^{13}\text{C}^{16}\text{O}$ and $^{12}\text{C}^{18}\text{O}$ are measured only at the strong Q-branches, and the percentages into the two spin-forbidden channels $\text{C}(^1\text{D}) + \text{O}(^3\text{P})$ and $\text{C}(^3\text{P}) + \text{O}(^1\text{D})$ are both $< 5\%$ as listed in Tables 1 and 2. These are much smaller compared with those of $^{12}\text{C}^{16}\text{O}$, for which $\sim 22\%$ and $\sim 30\%$ dissociates into the channels $\text{C}(^1\text{D}) + \text{O}(^3\text{P})$ and $\text{C}(^3\text{P}) + \text{O}(^1\text{D})$, respectively at this state as observed by Gao et al. (2012).

As compared with $^{12}\text{C}^{16}\text{O}$, two facts can be summarized for $^{13}\text{C}^{16}\text{O}$ and $^{12}\text{C}^{18}\text{O}$ in the energy region from $109\,220\text{ cm}^{-1}$ to $109\,700\text{ cm}^{-1}$: the two $^1\Sigma^+$ states ($(4s\sigma) ^1\Sigma^+(\nu'=4)$ and $(4p\sigma) ^1\Sigma^+(\nu'=3)$) are totally diffuse and the two $^1\Pi$ states ($(5p\pi) ^1\Pi(\nu'=1)$ and $(4p\pi) ^1\Pi(\nu'=3)$) show rotational resolved structures; all the four observed states in this region predominantly dissociate into the ground channel $\text{C}(^3\text{P}) + \text{O}(^3\text{P})$. These two facts imply that interactions with the $\text{D}^1\Sigma^+$ state might dominate the predissociation processes of $^{13}\text{C}^{16}\text{O}$ and $^{12}\text{C}^{18}\text{O}$ in this energy region, and the interaction with the dark $^1\Pi$ perturber state as identified in the case of $^{12}\text{C}^{16}\text{O}$ should have become much weaker for the two rare isotopologs.

3.2. $(6p\sigma) ^1\Sigma^+(\nu'=0)$ & $(6p\pi) ^1\Pi(\nu'=0)$ (Fig. 1)

The $(6p\sigma) ^1\Sigma^+(\nu'=0)$ and $(6p\pi) ^1\Pi(\nu'=0)$ states of $^{12}\text{C}^{16}\text{O}$ were presented in the jet absorption spectra (Huber 1997), while only the $(6p\sigma) ^1\Sigma^+(\nu'=0)$ state was observed in photoionization measurements (Eikema et al. 1994; Ubachs et al. 1994). The C^+ ion photofragment spectra of these two states for $^{12}\text{C}^{16}\text{O}$ were obtained recently in our lab (Gao et al. 2012; Chi et al. 2020a) and are similar in shape to the jet absorption spectra as obtained by (Huber 1997). In this study, we collect the C^+ ion photofragment spectra of these two states for $^{13}\text{C}^{16}\text{O}$ and $^{12}\text{C}^{18}\text{O}$, which are shown in Fig. 1. It can be seen that the substitution of ^{12}C by ^{13}C transforms the highly rotationally resolved structure of

Table 3. Band origins and rotational constants for several vibronic states as determined in the present study by the PGOPHER program (Western 2017).

Upper state	Isotopologs	Parameter (cm ⁻¹)	Literature ^(a) (cm ⁻¹)	This study ^(b) (cm ⁻¹)
(4p π) ¹ Π (v' = 3)	¹³ C ¹⁶ O	ν_0	109 610.2	109 610.7
		B'_v	1.83	1.839
	¹² C ¹⁸ O	ν_0	–	109 592.5
		B'_v	–	1.872
(5p π) ¹ Π (v' = 1)	¹³ C ¹⁶ O	ν_0	109 430	109 431.5
		B'_v	1.924	1.95
	¹² C ¹⁸ O	ν_0	109 427.5	109 425.6
		B'_v	1.9237	1.923
¹ Π (v' = 2)	¹² C ¹⁶ O	ν_0	109 017.9	109 019.4
		B'_v	1.671	1.673
	¹³ C ¹⁶ O	ν_0	108 904	108 904
		B'_v	1.597	1.58
	¹² C ¹⁸ O	ν_0	108 900	108 900.3
		B'_v	1.591	1.581
New ¹ Π	¹³ C ¹⁶ O	ν_0	–	108 465.7
		B'_v	–	1.835
	¹² C ¹⁸ O	ν_0	–	108 459.5
		B'_v	–	1.906
C' ¹ Σ^+ (v' = 9)	¹³ C ¹⁶ O	ν_0	–	108 418.9
		B'_v	–	1.032
	¹² C ¹⁸ O	ν_0	–	108 405.2
		B'_v	–	1.147
(5d σ) ¹ Σ^+ (v' = 0)	¹³ C ¹⁸ O	ν_0	108 370	108 307.2
		B'_v	1.7	1.812

Notes. ^(a)The band origins and rotational constants are adopted from the literature (Eidelsberg et al. 1991). ^(b)These values are determined through comparisons between the experimental C⁺ ion photofragment spectra obtained in this study and the simulated spectra by the PGOPHER program (Western 2017).

the (6p σ) ¹ Σ^+ (v' = 0) state for ¹²C¹⁶O into totally diffuse structure for ¹³C¹⁶O. This is consistent with the jet absorption study by Huber (1997). The C⁺ ion photofragment spectra of ¹²C¹⁸O are similar to that of ¹³C¹⁶O, while the (6p π) ¹ Π (v' = 0) state can barely be seen in the spectra of ¹²C¹⁸O. The branching ratios measured for these two states are listed in Tables 1 and 2, with the (6p π) ¹ Π (v' = 0) state of ¹²C¹⁸O not measured due to its rather weak signal level. Dissociation into the ground channel C(³P) + O(³P) dominates the predissociation processes of these two states for both ¹³C¹⁶O and ¹²C¹⁸O, and the percentages into the two spin-forbidden channels are all <5%. It is also the case for ¹²C¹⁶O that the channels producing C and O atoms in the excited states are ~2% and ~3% respectively as observed before (Gao et al. 2012; Chi et al. 2020a). Thus, the predissociation of these two Rydberg states should mainly be caused by the D'¹ Σ^+ state.

3.3. ¹ Π (v' = 2) (Figs. 2, 7)

The C⁺ ion photofragment spectra of this state for ¹³C¹⁶O and ¹²C¹⁸O are obtained as shown in Fig. 2. We employ the spectrum simulation program PGOPHER (Western 2017) to simulate the spectra, which are shown as red in Fig. 2. The band origins and rotational constants determined by the simulation are listed in Table 3, which agree well with the previous spectroscopic study by Eidelsberg et al. (1991). As shown in Fig. 2, the simulated spectra accurately reproduce the peak positions and also reproduce the relative intensities reasonably well at low J' levels. At the VUV photon energy corresponding to high J' lev-

els in Q- and P-branches, which is close to the (6s σ) ¹ Σ^+ (v' = 0) state, a broad underlying continuum can be clearly seen in the spectra of both ¹³C¹⁶O and ¹²C¹⁸O taking into account the fact that the VUV intensity here does not show peak structures. In order to perform a more detailed analysis, we reinvestigated the ¹ Π (v' = 2) state of ¹²C¹⁶O in this study and its C⁺ ion photofragment spectrum is shown in Fig. 7. This latter is dramatically different from the spectrum obtained in the previous study by Gao et al. (2011), where only the Q branch was observed, as shown by the blue spectrum in Fig. 7. This might be due to the different molecular beam temperatures generated by the Even-Lavie valve and the general valve (Jiang et al. 2019a). The simulated spectrum generated using PGOPHER is presented in red in Fig. 7 for comparison with the experimental one. The band origin and rotational constant used in the simulation are listed in Table 3, which are close to that obtained in the previous spectroscopic study by Eidelsberg et al. (1991). As seen in Fig. 7, the R-branch and the low J' levels in Q-branch are reproduced reasonably well by the simulation, while the P-branch and the high J' levels in Q-branch dramatically deviate from the simulation; in particular, the broad peak structure at ~109 002 cm⁻¹ cannot be seen from the simulation. This implies the existence of a new broad absorption band overlapping with the ¹ Π (v' = 2) state, which corresponds to the broad underlying continua as observed in ¹³C¹⁶O and ¹²C¹⁸O described above.

The existence of the new state is also evident from the branching ratio measurements. The branching ratios of the ¹ Π (v' = 2) state for ¹²C¹⁶O measured in the current study are listed in Table 4. The values for the low J' levels in Q-branch are consistent with

Fig. 7. C^+ ion photofragment spectra of the $^1\Pi(v'=2)$ state for $^{12}C^{16}O$. The relative intensities of the spectra are not normalized according to the corresponding VUV intensities. Black: experimental spectrum obtained in the current study. Red: simulated spectrum by the PGOPHER program (Western 2017). Blue: experimental spectrum obtained by Gao et al. (2011).

the previous study within the experimental uncertainty (Gao et al. 2011), and are equal to those of R -branch, which are observed to be independent of the rotational quantum number as shown in Table 4. The branching ratios for $^{13}C^{16}O$ and $^{12}C^{18}O$ are also observed to be independent of both the parity and rotation as listed in Tables 1 and 2, respectively. However, the branching ratios of $^{12}C^{16}O$ measured at the broad peak structure at $\sim 109\,002\text{ cm}^{-1}$ in Fig. 7 are dramatically different from those for R -branch and the low J' levels in Q -branch as listed in Table 4. This again implies that the broad peak structure at $\sim 109\,002\text{ cm}^{-1}$ should originate from a different vibronic state of CO. This new state dissociates with much smaller relative percentages into the $C(^3P) + O(^1D)$ channel compared with the $^1\Pi(v'=2)$ state in the case of $^{12}C^{16}O$; it shifts away from the $^1\Pi(v'=2)$ state in $^{13}C^{16}O$ and $^{12}C^{18}O$ as shown in Fig. 2. Accurate photoabsorption studies are needed to fully characterize this new state.

Despite the fact that the branching ratios for the three CO isotopologs studied here are all independent of the parity and rotation, a strong isotope effect can be seen in the absolute values. The branching ratios of $^{13}C^{16}O$ and $^{12}C^{18}O$ are only slightly different from each other as expected, while they are both dramatically different from that of $^{12}C^{16}O$. For $^{13}C^{16}O$ and $^{12}C^{18}O$, the percentages into the channels $C(^1D) + O(^3P)$ and $C(^3P) + O(^1D)$ are $\sim 40\%$ and $\sim 10\%$, respectively; while for $^{12}C^{16}O$, the percentages are $\sim 20\%$ and $\sim 50\%$, respectively. This strong isotope effect implies complicated predissociation dynamics of CO in this highly excited region.

3.4. $(6s\sigma)^1\Sigma^+(v'=0)$ (Fig. 2)

The $(6s\sigma)^1\Sigma^+(v'=0)$ state of $^{12}C^{16}O$ was observed in the absorption spectra (Eidelsberg & Rostas 1990) and in the triple resonant ion-dip spectra (Komatsu et al. 1995), but it was not observed in any photoionization studies before due to its fast predissociation process (Eikema et al. 1994; Ubachs et al. 1994). Its C^+ ion photofragment spectrum and branching ratios were reported for the first time in our recent study, and no excited atomic products could be detected (Chi et al. 2020a). In the cur-

rent study, the C^+ ion photofragment spectra of $^{13}C^{16}O$ and $^{12}C^{18}O$ are collected and shown in Fig. 2. Weak but detectable signal into the two spin-forbidden channels $C(^1D) + O(^3P)$ and $C(^3P) + O(^1D)$ can be observed for both $^{13}C^{16}O$ and $^{12}C^{18}O$. The measured values are listed in Tables 1 and 2, respectively. A weak dependence of the branching ratios on rotation seems to be observable, but cannot be confirmed with the detection sensitivity of the current setup.

3.5. New $^1\Pi$ state (Fig. 3)

In our recent studies of $^{12}C^{16}O$, a weak absorption band of $^1\Pi$ characters at $\sim 108\,500\text{ cm}^{-1}$ was identified, and substantial percentages of dissociation into the spin-forbidden channels were observed (Gao et al. 2020; Chi et al. 2020a). Here, this new $^1\Pi$ band is also observed for $^{13}C^{16}O$ and $^{12}C^{18}O$ in the C^+ ion photofragment spectra as shown in Fig. 3, which is shifted to $\sim 108\,460\text{ cm}^{-1}$. The spectra can be accurately simulated by PGOPHER using the band origins and rotational constants listed in Table 3. The simulated spectra are presented as red in Fig. 3. The branching ratios of Q - and R -branches for $^{13}C^{16}O$ and $^{12}C^{18}O$ are measured and listed in Tables 1 and 2, respectively. The photodissociation branching ratios of $^{13}C^{16}O$ and $^{12}C^{18}O$ are close to each other at this state and are slightly different from that of $^{12}C^{16}O$ (Chi et al. 2020a). Despite the different branching ratios, the three CO isotopologs show very similar dissociation properties at this state, that is, the branching ratios are parity dependent, and the percentages into the spin-forbidden channels measured in R -branch decrease linearly as a function of $J'(J'+1)$. This indicates that a heterogeneous interaction with a repulsive $^1\Sigma^+$ state correlating to the ground channel $C(^3P) + O(^3P)$ must play a role in the predissociation process. Besides the rotation-dependent photodissociation, we also see photodissociation that is independent of both rotation and parity, which implies that homogeneous interaction with a $^1\Pi$ state is also involved in the predissociation process of this state. Similar phenomena have been observed previously for many $^1\Pi$ states of CO (Gao et al. 2013; Jiang et al. 2019a, 2020; Chi et al. 2020b).

3.6. $C'^1\Sigma^+(v'=9)$ (Fig. 3)

The C^+ ion photofragment spectra of the $C'^1\Sigma^+(v'=9)$ state show partially resolved rotational structures as shown in Fig. 3 for $^{13}C^{16}O$ and $^{12}C^{18}O$, which are in contrast to the totally diffuse structure for $^{12}C^{16}O$ at this state as observed recently by Chi et al. (2020a). The C^+ ion photofragment spectra are well simulated by PGOPHER using the band origins and rotational constants listed in Table 3. The R -bandhead positions agree well with the previous observations by Eidelsberg et al. (2004). As recently measured by Chi et al. (2020a), the percentages into the two spin-forbidden channels $C(^1D) + O(^3P)$ and $C(^3P) + O(^1D)$ are $\sim 6\%$ and $\sim 9\%$, respectively for $^{12}C^{16}O$. While for $^{13}C^{16}O$ and $^{12}C^{18}O$, the percentages into the spin-forbidden channels are much larger as listed in Tables 1 and 2. For $^{13}C^{16}O$, the relative ratios into the two spin-forbidden channels $C(^1D) + O(^3P)$ and $C(^3P) + O(^1D)$ are $\sim 12\%$ and $\sim 50\%$, respectively; for $^{12}C^{18}O$, the percentages are $\sim 12\%$ and $\sim 60\%$ respectively. A similar strong isotope effect was also observed for the $C'^1\Sigma^+(v'=7)$ state recently (Jiang et al. 2019b). The percentages slightly decrease with increasing J' levels, which might be caused by partial overlapping with the nearby $(5d\sigma)^1\Sigma^+(v'=0)$ state. As proposed before (Eidelsberg et al. 2004; Chi et al. 2020a), the highly vibrational excited levels of the valence $C'^1\Sigma^+$ state, for example $C'^1\Sigma^+(v'=9)$, reach into the Franck-Condon-permitted region

Table 4. Photodissociation branching ratios into the channels $C(^3P) + O(^1D)$, $C(^1D) + O(^3P)$, and $C(^3P) + O(^3P)$ for the $^1\Pi(v' = 2)$ state of $^{12}C^{16}O$ at $109\,019.4\text{ cm}^{-1}$.

Upper state	VUV (cm^{-1})	Rotational transition	$C(^3P) + O(^1D)$ (%)	$C(^1D) + O(^3P)$ (%)	$C(^3P) + O(^3P)$ (%)
$^1\Pi(v' = 2)$ 50 Mb ^(a)	109 022.2	R(0)	49.7 ± 0.7 ^(b)	18.3 ± 0.2	31.9 ± 0.7
	109 024.9	R(1)	47.4 ± 1.1	19.2 ± 0.3	33.4 ± 1.0
	109 027.9	R(2)/R(3)	50.9 ± 0.5	18.7 ± 0.3	30.4 ± 0.8
	109 018.4	Q(1)/Q(2)	49.9 ± 0.2	18.8 ± 0.3	31.3 ± 0.1
	109 013.5	Q(4)	44.9 ± 1.6	20.1 ± 0.7	34.9 ± 2.3
	109 011.9	P(2)/Q(5)	33.8 ± 0.7	20.4 ± 0.3	45.7 ± 0.6
	109 004.0	Unknown ^(c)	20.1 ± 0.5	22.0 ± 0.5	57.9 ± 0.4
	109 002.8	Unknown	17.6 ± 0.9	23.7 ± 0.6	58.8 ± 1.5
	108 999.4	Unknown	13.8 ± 0.8	23.3 ± 0.9	62.9 ± 0.2
	108 997.1	Q(9)	18.7 ± 0.8	24.0 ± 0.2	57.3 ± 1.0

Notes. ^(a)Photoionization cross section values of $C(^1D)$ used for calibrating the measured photodissociation branching ratios; see the first paragraph in Sect. 3 for detail. ^(b)The error bars are the standard deviations (1σ) of three independent measurements, which do not include any possible systematic experimental uncertainties; see the second paragraph in Sect. 3 for detail. ^(c)These absorption structures are tentatively assigned to be the unknown underlying absorption band as described in Sect. 3.3.

through interaction with the high vibrational levels of mixed $B(3s\sigma)^1\Sigma^+-D'^1\Sigma^+$ character which dissociates into the ground channel (Eidelsberg et al. 2004), and also through the interaction with nearby Rydberg states of $^1\Pi$ character, which dissociate into the spin-forbidden channels through spin-orbit $^1\Pi-^3\Pi$ couplings (Chi et al. 2020a). The relative branching ratios into the ground channel and the two spin-forbidden channels are determined by the competition between the two interactions mentioned above. If the interacting Rydberg $^1\Pi$ state is assumed to be the newly observed $^1\Pi$ state as described in Sect. 3.5, the mutual interactions between the $C'^1\Sigma^+(v' = 9)$ state and the new $^1\Pi$ state might be closely equal to each other for $^{12}C^{16}O$, $^{13}C^{16}O$, and $^{12}C^{18}O$ by considering the fact that these two states are almost equally separated from each other in the potential energy surfaces of the three CO isotopologs as shown in the C^+ ion photofragment spectra. This indicates that the smaller percentages into the two spin-forbidden channels observed for $^{12}C^{16}O$ (Chi et al. 2020a) are probably due to a stronger interaction between the $C'^1\Sigma^+(v' = 9)$ state and the high vibrational states of mixed $B(3s\sigma)^1\Sigma^+-D'^1\Sigma^+$ character. This is also consistent with the observation that the $C'^1\Sigma^+(v' = 9)$ state of $^{12}C^{16}O$ has a faster predissociation rate than those of $^{13}C^{16}O$ and $^{12}C^{18}O$, which causes its spectrum to appear totally diffuse (Chi et al. 2020a), while the $C'^1\Sigma^+(v' = 9)$ state of $^{13}C^{16}O$ and $^{12}C^{18}O$ show partially resolved rotational structures, as shown in Fig. 3. The tentative picture described here could be oversimplified; accurate ab initio calculation of the potential energy curves and their mutual interactions is needed to fully understand the complicated predissociation dynamics in this highly excited region.

3.7. $(5d\sigma)^1\Sigma^+(v' = 0)$ (Fig. 3)

The $(5d\sigma)^1\Sigma^+(v' = 0)$ state of $^{12}C^{16}O$ was reported to be a diffuse band in the photoabsorption study by Eidelsberg & Rostas (1990) and the $C(^3P)$ ion yield spectra by Okazaki et al. (2001). In the current study, the C^+ ion photofragment spectra of the $(5d\sigma)^1\Sigma^+(v' = 0)$ state for $^{13}C^{16}O$ and $^{12}C^{18}O$ are collected and shown in Fig. 3. Two broad diffuse peaks designated *P* branch and *R* branch can be observed for both $^{13}C^{16}O$ and $^{12}C^{18}O$. The photodissociation branching ratios at these two diffuse peak positions are measured and listed in Tables 1 and 2 for $^{13}C^{16}O$ and $^{12}C^{18}O$, respectively. Similar to the previous branching ratio

measurements of $^{12}C^{16}O$ (Gao et al. 2012), only trace amounts of atomic photodissociation products are formed in the excited states for both $^{13}C^{16}O$ and $^{12}C^{18}O$. This indicates that coupling with the $D'^1\Sigma^+$ state should play a major role in the predissociation process of the $(5d\sigma)^1\Sigma^+(v' = 0)$ state. Slightly to the red side of the $(5d\sigma)^1\Sigma^+(v' = 0)$ state of $^{13}C^{16}O$, a highly rotationally resolved $^1\Sigma^+$ band can be observed in Fig. 3, which does not appear in the C^+ ion photofragment spectrum of $^{12}C^{18}O$. This makes it hard to assign this band to $^{13}C^{16}O$ by considering the great spectral similarities between $^{13}C^{16}O$ and $^{12}C^{18}O$. Further evidence comes from the fact that its relative intensity compared with that of the nearby $(5d\sigma)^1\Sigma^+(v' = 0)$ state dramatically changes if $^{13}C^{16}O$ samples from different gas suppliers are used. This implies that the new band might be due to certain impurities contained in the samples. We collect TSVMI images of this band which appear almost the same as that of the $(5d\sigma)^1\Sigma^+(v' = 0)$ state of $^{13}C^{16}O$ and $^{12}C^{18}O$, while the TKERs only match with the photodissociation of CO if the photofragment combination of ^{13}C and ^{18}O is used. This leads us to tentatively assign this band to the $(5d\sigma)^1\Sigma^+(v' = 0)$ state of $^{13}C^{18}O$, which to the best of our knowledge has not been observed before. In the photoabsorption studies by Eidelsberg & Rostas (1990), Eidelsberg et al. (1991, 1992), the properties of the $(5d\sigma)^1\Sigma^+(v' = 0)$ state of $^{13}C^{18}O$ were predicted through isotopic extrapolation based on the observations for $^{12}C^{16}O$, $^{13}C^{16}O$, and $^{12}C^{18}O$. The band origin and rotational constant are determined to be $108\,307.2\text{ cm}^{-1}$ and 1.812 cm^{-1} , respectively, using PGOPHER simulation as listed in Table 3. The branching ratios into the two spin-forbidden channels $C(^1D) + O(^3P)$ and $C(^3P) + O(^1D)$ are both $<1\%$, similar to $^{12}C^{16}O$, $^{13}C^{16}O$, and $^{12}C^{18}O$; and no rotational dependence can be seen. This is consistent with the judgment that the $(5d\sigma)^1\Sigma^+(v' = 0)$ state predissociates mainly through interaction with the valence $D'^1\Sigma^+$ state.

3.8. $W(3s\sigma)^1\Pi(v' = 3)$ (Figs. 4, 8)

Recent high-resolution spectroscopic studies of the $W(3s\sigma)^1\Pi(v' = 3)$ state for $^{12}C^{16}O$, $^{13}C^{16}O$, and $^{12}C^{18}O$ by Eidelsberg et al. (2012, 2014) show that the predissociation rates are dependent on both rotation and parity. In the recent study of $^{12}C^{16}O$ by Gao et al. (2011), no obvious dependence of the photodissociation branching ratio on either rotation or the

Fig. 8. Dependence of the photodissociation branching ratio on $J'(J'+1)$ for the $W(3s\sigma) \ ^1\Pi(v'=3)$ state of (a) $^{13}\text{C}^{16}\text{O}$ and (b) $^{12}\text{C}^{18}\text{O}$, respectively, where J' is the rotational quantum number of the upper level. The error bars represent the standard deviations (1σ) of three independent measurements. Square: $\text{C}(^3\text{P}) + \text{O}(^3\text{P})$. Dot: $\text{C}(^1\text{D}) + \text{O}(^3\text{P})$. Triangle: $\text{C}(^3\text{P}) + \text{O}(^1\text{D})$. Blue: R -branch. Red: P -branch. Green: Q -branch.

Fig. 9. Comparison of the percent-ages into the dissociation channel $\text{C}(^1\text{D}) + \text{O}(^3\text{P})$ for 27 absorption bands in the VUV region from $102\,807\text{ cm}^{-1}$ (97.27 nm) to $109\,700\text{ cm}^{-1}$ (91.16 nm) between $^{12}\text{C}^{16}\text{O}$ and $^{13}\text{C}^{16}\text{O}$. The branching ratios of $^{12}\text{C}^{18}\text{O}$ are not presented because they are similar to those of $^{13}\text{C}^{16}\text{O}$. The error bars represent the standard deviations (1σ) of three independent measurements. Red: $^{13}\text{C}^{16}\text{O}$. Blue: $^{12}\text{C}^{16}\text{O}$. The dotted box indicates the energy range investigated in the current study. The X-axis shows –1– branching ratios from Gao et al. (2013), Chi et al. (2020b); –2– branching ratios from Shi et al. (2018), Jiang et al. (2019a,b, 2020); and –3– branching ratios from Gao et al. (2011, 2012), Chi et al. (2020a) current study.

e/f parity was noted, probably because only branching ratios of $J' < 4$ levels were measured. In the current study, the C^+ ion photofragment spectra of the $W(3s\sigma) \ ^1\Pi(v'=3)$ state for $^{13}\text{C}^{16}\text{O}$ and $^{12}\text{C}^{18}\text{O}$ are collected and shown in Fig. 4. The photodissociation branching ratios measured in this study are listed in Tables 1 and 2, and plotted versus $J'(J'+1)$ in Figs. 8a and b for $^{13}\text{C}^{16}\text{O}$ and $^{12}\text{C}^{18}\text{O}$, respectively. The dissociation properties of $^{13}\text{C}^{16}\text{O}$ and $^{12}\text{C}^{18}\text{O}$ are very similar to each other, even though the relative values of branching ratios are slightly different. For e -parity levels (R - and P -branch), the percentages into the two spin forbidden channels decrease as J' increases; while for f -parity levels (Q -branch), the percentages into the two spin forbidden channels are almost constant at low J' levels. This observation is similar to that of $W(3s\sigma) \ ^1\Pi(v'=0)$ state as studied previously for $^{12}\text{C}^{16}\text{O}$ (Gao et al. 2013) and

$^{13}\text{C}^{16}\text{O}$ (Chi et al. 2020b). Thus, interactions with repulsive states of both $^1\Pi$ and $^1\Sigma^+$ symmetries must have been involved in the predissociation process of the $W(3s\sigma) \ ^1\Pi(v'=3)$ state, where the $^1\Pi$ state is responsible for the rotation and parity independent part, and the $^1\Sigma^+$ state is responsible for the linear dependence of the branching ratio on $J'(J'+1)$ for the e -parity levels. This is also consistent with recent high-resolution spectroscopic studies (Eidelsberg et al. 2012, 2014) showing that the predissociation rates of the e -parity levels increase linearly as a function of $J'(J'+1)$, while those of the f -parity levels are almost independent of $J'(J'+1)$. Despite the relatively large spectral shift ($\sim 170\text{ cm}^{-1}$) due to the substitutions of ^{12}C by ^{13}C and ^{16}O by ^{18}O , the photodissociation branching ratios of $^{12}\text{C}^{16}\text{O}$, $^{13}\text{C}^{16}\text{O}$, and $^{12}\text{C}^{18}\text{O}$ for this state are all close to each other within the experimental uncertainties.

So far, the photodissociation branching ratios of the vast majority of strong absorption bands of $^{12}\text{C}^{16}\text{O}$ and $^{13}\text{C}^{16}\text{O}$ in the VUV region from $102\,807\text{ cm}^{-1}$ (97.27 nm) to $109\,700\text{ cm}^{-1}$ (91.16 nm) that are of astrophysical interest, as listed in Table 1 by Visser et al. (2009), have been measured and documented (Gao et al. 2011, 2012, 2013; Shi et al. 2018; Jiang et al. 2019a,b, 2020; Chi et al. 2020b,a). Extension of the measurements for $^{12}\text{C}^{18}\text{O}$ in the lower energy region from $102\,807\text{ cm}^{-1}$ (97.27 nm) to $107\,816\text{ cm}^{-1}$ (92.75 nm) is in progress. Due to the potential applications in modeling the C isotope distributions in the Solar System, we present an overall comparison in Fig. 9, where the percentages of dissociation into the channel $\text{C}(\text{D}) + \text{O}(\text{P})$ for all the measured absorption bands of $^{12}\text{C}^{16}\text{O}$ and $^{13}\text{C}^{16}\text{O}$ so far are put together as histograms. It is worth noting that the branching ratios of $^{13}\text{C}^{16}\text{O}$ and $^{12}\text{C}^{18}\text{O}$ are close to each other due to their similar reduced masses, and so the branching ratios of $^{12}\text{C}^{18}\text{O}$ are not presented in the histograms. For absorption bands whose branching ratios are rotation and parity dependent, the highest values measured within those bands are adopted in Fig. 9; and those bands for which both $^{12}\text{C}^{16}\text{O}$ and $^{13}\text{C}^{16}\text{O}$ predominantly dissociate into the ground channel $\text{C}(\text{P}) + \text{O}(\text{P})$ are not included in Fig. 9, such as for example $(4s\sigma)^{-1}\Sigma^{+}(\nu' = 1)$, $(4p\sigma)^{-1}\Sigma^{+}(\nu' = 1)$, and $(5d\sigma)^{-1}\Sigma^{+}(\nu' = 0)$. As shown in Fig. 9, for most of the absorption bands from $102\,807\text{ cm}^{-1}$ to $109\,200\text{ cm}^{-1}$, percentages into the channel of generating the excited $\text{C}(\text{D})$ atoms for $^{13}\text{C}^{16}\text{O}$ are higher than or comparable to those for $^{12}\text{C}^{16}\text{O}$, with the $\text{W}(3s\sigma)^{-1}\Pi(\nu' = 1, 3)$, $(4d\sigma)^{-1}\Sigma^{+}(\nu' = 0)$, $(6p\sigma)^{-1}\Sigma^{+}(\nu' = 0)$, and $\text{I}^1\Pi$ bands being the few exceptions. In the narrow energy window of $109\,200\text{--}109\,650\text{ cm}^{-1}$, a completely reversed scenario is observed, where $^{12}\text{C}^{16}\text{O}$ produces a comparable amount of ground and excited C atoms, while $^{13}\text{C}^{16}\text{O}$ almost completely dissociates into the ground channel. This indicates very different predissociation dynamics between $^{12}\text{C}^{16}\text{O}$ and $^{13}\text{C}^{16}\text{O}$ in this narrow energy region as tentatively described in the above section. This global comparison of the branching ratios into the spin-forbidden channel between different CO isotopologs should be extremely useful in mapping out the detailed Rydberg–Rydberg, Rydberg–valence interactions, which are important for understanding the predissociation dynamics of CO, and should benchmark any future theoretical calculations. Whether or not the strong isotope effect of the photodissociation branching ratio as observed here can affect the C isotope fractionation process that happened in the Solar System is still awaiting quantitative photochemical modeling, which should include the CO self-shielding effect and also the shielding effect from the H/H_2 absorption (Shi et al. 2017; Lyons et al. 2018).

4. Summary

In this study, we collect the C^{+} ion photofragment spectra and measure the photodissociation branching ratios of $^{13}\text{C}^{16}\text{O}$ and $^{12}\text{C}^{18}\text{O}$ in the VUV photon energy region from $107\,800\text{ cm}^{-1}$ (92.76 nm) to $109\,700\text{ cm}^{-1}$ (91.16 nm). Several absorption bands of $^{12}\text{C}^{16}\text{O}$ in this energy region are reinvestigated up to higher J' levels for comparisons with $^{13}\text{C}^{16}\text{O}$ and $^{12}\text{C}^{18}\text{O}$. Strong isotope effects of the photodissociation branching ratios are observed for most of the absorption bands in the above-mentioned energy region due to the substitutions of ^{12}C by ^{13}C and ^{16}O by ^{18}O . On the other hand, the branching ratios of $^{13}\text{C}^{16}\text{O}$ and $^{12}\text{C}^{18}\text{O}$ are close to each other, which is to be expected due to their similar reduced masses. Even though a substantial number of spectroscopic studies have investigated the various CO isotopologs in this

high-energy region (Casey 1978; Eidelsberg & Rostas 1990; Eidelsberg et al. 1991; Eikema et al. 1994; Huber 1997), analyses of the detailed predissociation dynamics in this region are still scarce; in particular, accurate potential energy curves are not available (Lefebvre-Brion & Kalesmos 2016). The photodissociation branching ratio measurements for different CO isotopologs as presented in the current study can provide important information for unraveling the complicated predissociation dynamics of CO in this highly excited region.

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Appendix A: Additional table

Table A.1. Photodissociation branching ratios of the channels $C(^3P) + O(^1D)$, $C(^1D) + O(^3P)$, and $C(^3P) + O(^3P)$ for $^{12}C^{16}O$ in the region from 107 800 to 109 700 cm^{-1} (91.16–92.76 nm).

Upper state	VUV(cm^{-1})	Rotational transition	$C(^3P) + O(^1D)$ (%)	$C(^1D) + O(^3P)$ (%)	$C(^3P) + O(^3P)$ (%)
(4p π) $^1\Pi(v' = 3)$ ^(d) 50 Mb ^(a)	109 564.5	Q(1)	30 ± 4 ^(b)	22 ± 2	48 ± 3
	109 568.6	R(0)	30 ± 3	22 ± 1	48 ± 2
	109 572.3	R(1)	31 ± 6	21 ± 3	49 ± 4
	109 576.3	R(2)	26 ± 3	19 ± 2	55 ± 2
(4p σ) $^1\Sigma^+(v' = 3)$ ^(c) 50 Mb	109 484.7	R(0)	16.0 ± 1.5	11.3 ± 0.2	72.7 ± 1.6
	109 488.2	R(1)	15.0 ± 1.5	10.2 ± 0.3	74.9 ± 2.0
	109 491.4	R(2)	15.3 ± 1.5	8.4 ± 2.3	76.3 ± 1.7
	109 477.4	P(1)	17.6 ± 0.7	12.0 ± 1.4	70.4 ± 2.1
	109 473.2	P(2)	18.9 ± 2.1	11.2 ± 0.7	69.9 ± 2.4
(4s σ) $^1\Sigma^+(v' = 4)$ ^(c) 50 Mb	109 452.5	R(0)	20.8 ± 1.0	32.9 ± 1.0	46.3 ± 1.5
	109 455.7	R(1)	18.8 ± 1.1	27.4 ± 1.6	53.8 ± 1.0
	109 458.9	R(2)	21.6 ± 3.2	32.6 ± 3.0	45.9 ± 2.0
	109 461.5	R(3)	25.6 ± 2.2	30.4 ± 0.9	44.1 ± 1.5
	109 445.1	P(1)	21.3 ± 1.9	32.4 ± 0.9	46.3 ± 1.6
	109 440.9	P(2)	22.0 ± 3.7	32.1 ± 2.8	45.9 ± 2.0
(6p π) $^1\Pi(v' = 0)$ ^(e) 50 Mb	109 202.6		3.1 ± 0.1	2.1 ± 0.1	94.9 ± 0.3
(6p σ) $^1\Sigma^+(v' = 0)$ ^(e) 50 Mb	109 175.7	R(0)	1.6 ± 0.3	0.8 ± 0.1	97.6 ± 0.3
	109 178.7	R(1)	2.9 ± 0.2	1.3 ± 0.1	95.8 ± 0.2
	109 180.9	R(2)	3.1 ± 0.1	1.6 ± 0.1	95.3 ± 0.1
	109 182.7	R(3)	3.2 ± 0.2	1.7 ± 0.1	95.1 ± 0.3
	109 184.5	R(4)	2.9 ± 0.2	1.8 ± 0.2	95.3 ± 0.4
	109 168.7	P(1)	0.2 ± 0.1	0.2 ± 0.1	99.6 ± 0.1
	109 164.2	P(2)	1.6 ± 0.1	0.8 ± 0.1	97.6 ± 0.1
	109 159.3	P(3)	2.9 ± 0.1	1.4 ± 0.1	95.7 ± 0.1
	109 153.8	P(4)	3.3 ± 0.2	2.0 ± 0.1	94.7 ± 0.2
	109 148.4	P(5)	4.2 ± 0.4	3.3 ± 0.3	92.6 ± 0.2
	109 142.6	P(6)	4.9 ± 0.1	3.7 ± 0.1	91.4 ± 0.2
	109 136.3	P(7)	6.3 ± 0.9	5.7 ± 0.2	88.0 ± 1.0
	109 130.0	P(8)	5.9 ± 0.2	6.8 ± 1.7	87.3 ± 1.9
(6s σ) $^1\Sigma^+(v' = 0)$ ^(e) 50 Mb	108 791.7	R(0)	0	0	100
	108 796.6	R(1)	0	0	100
	108 801.5	R(2)	0	0	100
	108 807.1	R(3)	0	0	100
	108 814.1	R(4)	0	0	100
	108 783.3	P(1)	0	0	100
	108 780.5	P(2)	0	0	100
	108 777.7	P(3)	0	0	100
	108 774.9	P(4)	0	0	100
I'(5s σ) $^1\Sigma^+(v' = 1)$ ^(e) 50 Mb	108 682.1	R(0)	0	0.5 ± 0.2	99.5 ± 0.2
	108 685.6	R(1)	0	0.5 ± 0.1	99.5 ± 0.1
	108 690.5	R(2)	0	0.5 ± 0.1	99.5 ± 0.1
	108 695.4	R(3)	0	0.4 ± 0.1	99.6 ± 0.1
	108 674.3	P(1)	0	0.7 ± 0.2	99.3 ± 0.2
	108 670.8	P(2)	0	0.4 ± 0.1	99.6 ± 0.1
	108 666.6	P(3)	0	0.5 ± 0.3	99.5 ± 0.3
	108 662.4	P(4)	0	0.9 ± 0.1	99.1 ± 0.1
Unknown state ^(e) 50 Mb	108 723.6		1.6 ± 0.3	1.6 ± 0.1	96.8 ± 0.2
	108 642.1		2.7 ± 0.6	3.4 ± 0.2	93.9 ± 0.4
	108 625.3		4.5 ± 0.7	4.9 ± 0.4	90.6 ± 1.2
	108 615.5		1.2 ± 0.5	2.2 ± 0.5	96.6 ± 0.5
	108 606.5		2.3 ± 0.2	2.7 ± 0.2	95.0 ± 0.2
	108 598.1		3.7 ± 0.5	4.1 ± 0.2	92.2 ± 0.7
C' $^1\Sigma^+(v' = 9)$ ^(e) 50 Mb	108 575.2		8.9 ± 0.3	6.5 ± 0.2	84.6 ± 0.5
New $^1\Pi$ ^(e) 50 Mb	108 501.9	Q	33.6 ± 1.9	12.8 ± 0.4	53.6 ± 2.3
	108 505.4	R(0)	32.6 ± 1.2	10.2 ± 0.6	57.3 ± 1.7
	108 509.6	R(1)	21.8 ± 0.4	7.5 ± 0.4	70.8 ± 0.1
(5d σ) $^1\Sigma^+(v' = 0)$ ^(d) 30 Mb	108 370.0		<1	<1	100
	108 373.5		<1	<1	100
	108 378.8		<1	<1	100
W(3s σ) $^1\Pi(v' = 3)$ ^(e) 30 Mb	108 012.4	Q(1)	4.0 ± 0.6	6.4 ± 0.3	89.6 ± 0.5
	108 016.4	R(0)	4.2 ± 0.3	6.3 ± 0.4	89.5 ± 0.5
	108 019.3	R(1)	3.8 ± 0.3	6.2 ± 0.3	90.0 ± 0.3
	108 021.9	R(2)	3.6 ± 0.3	6.0 ± 0.2	90.4 ± 0.6

Notes. ^(a)Photoionization cross section values of $C(^1D)$ that are used for calibrating the measured photodissociation branching ratios, see the first paragraph in Sect. 3 for detail. ^(b)The error bars are the standard deviations (1σ) of three independent measurements, which do not include any possible systematic experimental uncertainties, see the second paragraph in Sect. 3 for detail. ^(c)The branching ratios are from Gao et al. (2011). ^(d)The branching ratios are from Gao et al. (2012). ^(e)The branching ratios are from Chi et al. (2020a).