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Communication: Branching ratio measurements in the predissociation of $^{12}C^{16}O$ by time-slice velocity-map ion imaging in the vacuum ultraviolet region

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The first direct branching ratio measurement of the three lowest energy dissociation channels of CO that produce $C(^3P) + O(^3P)$, $C(^1D) + O(^3P)$, and $C(^3P) + O(^1D)$ is reported. Rotational resolved carbon ion yield spectra for two Π bands ($W(3s\sigma)^1\Pi$ ($v' = 3$) at 108 012.6 cm^{-1} and $^1\Pi(v' = 2)$ at 109 017 cm^{-1}) and two Σ bands ($(4s\sigma)^1\Sigma^+(v' = 4)$ at 109 452 cm^{-1} and $(4p\sigma)^1\Sigma^+(v' = 3)$ at 109 485 cm^{-1}) of CO were obtained. Our measurements show that the branching ratio in this energy region is strongly dependent on the electronic and vibrational energy but it is independent or just weakly dependent on the parity and rotational energy levels. To our knowledge, this is the first time that the triplet channel producing $O(^1D)$ has been experimentally observed and this is also the first time that a direct measurement of the branching ratio for the different channels in the predissociation of CO in this energy region has been made. © *2011 American Institute of Physics*. [doi:10.1063/1.3669426]

I. INTRODUCTION

Carbon monoxide is the second most abundant molecule in the interstellar medium. The predissociation of CO and its less abundant isotopologues are important sources of carbon and oxygen atoms in interstellar space. As a result, CO is one of the most studied molecules in astronomy and astrophysics. The first high resolution photoabsorption cross section measurement of CO in the vacuum ultraviolet region showed that predissociation is occurring in the rotationally resolved bands.[1] Further studies showed that the absorption band positions and their predissociation rates are strongly dependent on the isotopic composition of the molecule.[2–4] The isotope dependent predissociation of CO is important for understanding the oxygen isotope abundance in the solar system.[5–9] Observations have shown that the rare heavy isotopes for both O and N are enriched on the Earth compared with the sun and solar nebula.[10,11] A similar behavior is expected in the interstellar medium as well as around young stars. The ^{15}N isotope is more enriched (about 40%) on the Earth than ^{17}O (about 6%) but the reason why it is so is not yet understood. It is possible that this is due to photochemistry producing oxygen atoms that are less reactive than the N atoms produced in the same energy region.[12] Because of this it is important to know the branching ratio for the production of O atoms in the ^1D and ^3P states so that the rate coefficients with H_2 and other gases can be compared to those for N atoms in ^4S and ^2D states.

The branching ratio measurements for the N_2 predissociation were first made by Helm and Cosby[13,14] in their fast molecular beam setup. The N_2 molecules were prepared in a metastable state, which is very similar to the ground state but 12.3 eV higher. Then a tunable dye laser was used to excite the metastable N_2 molecules into each of the predissociative rovibronic states. A direct vacuum ultraviolet (VUV) excitation photodissociation study of N_2 has recently been reported by us.[15] However, similar measurements have not been done for CO predissociation. Photoabsorption and photoionization studies have been used to study the predissociation of CO using both multiphoton[16,17] and single VUV photon[3,18,19] methods. Direct photofragment measurements of the predissociation of CO have also been done by several groups.[20–23] Parker[20] used a tunable 193 nm excimer laser and velocity-map ion imaging to study the multiphoton predissociation of CO, but only the $C(^1D)$ channel was probed, the channel $O(^3P) + C(^1D)$ was identified in the total kinetic energy release (TKER) spectrum, the beta parameter and the predissociation life-time based on the beta parameter were deduced. Ebata and co-workers[21–23] have obtained the photofragment ion yield spectra by probing $C(^3P)$, $C(^1D)$, and $O(^3P)$ separately and observed the triplet channel for the first time. Useful information about the relative branching ratio between the $C(^3P)$ and $C(^1D)$ channels can be deduced by comparing the three ion yield spectra that probe $C(^3P)$, $C(^1D)$, and $O(^3P)$ respectively to the simulated absorption spectra. However, they cannot directly distinguish between the $C(^3P) + O(^3P)$ channel from the $C(^3P) + O(^1D)$ channel.

We have recently combined a tunable VUV system with our time-slice velocity-map ion imaging setup to study the photodissociation of small molecules.[15,24] In this article, we demonstrate that this technique can be used to measure the branching ratio for the different C atom channels in the predissociation of CO in the VUV region. The transitions $W(3s\sigma)^1\Pi(v' = 3)$ at 108 012.6 cm^{-1}, $^1\Pi(v' = 2)$ at 109 017 cm^{-1}, $(4s\sigma)^1\Sigma^+(v' = 4)$ at 109 452 cm^{-1} and

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$(4p\sigma)^1\Sigma^+(v' = 3)$ at 109 485 cm^{-1} are used as examples. The carbon ion yield spectra of these states were obtained. The TKER spectra are used to distinguish the three dissociation channels into $C(^3P) + O(^3P)$, $C(^1D) + O(^3P)$, and $C(^3P) + O(^1D)$ and their branching ratios are measured by integrating the corresponding peaks in the TKER spectrum. Refer to Ref. 15 for experimental details. Here pure CO without isotope purification was used to produce the supersonic molecular beam. The CO molecule will first absorb a sum-frequency VUV photon $(2\omega_1 + \omega_2)$ and is excited to one of the rovibronic states that then undergoes predissociation to produce carbon atoms in the ^3P and ^1D states. A second VUV photon ionizes the carbon atoms in the ground and the first excited electronic state through direct photoionization. Finally the carbon ions are detected by our time-slice velocity-map ion imaging setup.

II. RESULTS AND DISCUSSION

The areas of the peaks in the TKER spectra corresponding to the $C(^3P) + O(^1D)$ and $C(^3P) + O(^3P)$ channels are direct measurements of their relative concentrations because they share the same nascent $C(^3P)$ product. On the other hand, for the channel $C(^1D) + O(^3P)$ we have to consider the different photoionization cross sections between $C(^3P)$ and $C(^1D)$. The VUV photons that ionize these carbon atoms are the resonant sum-frequency photons $(2\omega_1 + \omega_2)$, rather than the tripling $(3\omega_1)$ photons because the former is more intense. This is confirmed by determining the H_2O photoionization peak in the TOF spectrum. The photoionization cross sections of H_2O at these two frequencies are nearly the same[25] and when the visible light (ω_2) is blocked the peak corresponding to H_2O disappears.

A. Π bands

Gating the C^+ ion signal in the TOF spectrum and scanning the VUV photon energy yields the C^+ photofragment spectrum, PHOFEX (C^+), from the predissociation of CO. Fig. 1 shows the PHOFEX (C^+) spectrum for the transitions to $W(3s\sigma)^1\Pi(v' = 3)$ and $^1\Pi(v' = 2)$. Both of the two bands have been observed by Eidelsberg *et al.*[2,18] with a 10 m VUV spectrograph. The $CO(^1\Pi, v' = 2) \leftarrow CO\ (X^1\Sigma^+, v' = 0)$ transition has also been observed as a very weak signal by Ubachs *et al.*[4] by using a tunable VUV laser $(3\omega_1)$ to excite the CO and another ω_1 photon to ionize it. The rotational assignments shown by the lines in Fig. 1 were calculated using the rotational constants obtained by Eidelsberg.[2] Both of the two bands are strongly broadened due to the fast predissociation process.

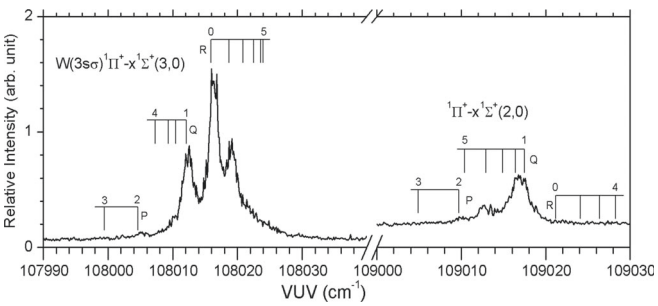

FIG. 1. C^+ ion yield spectra produced from the predissociation of CO following the absorption of a single sum-frequency VUV photon for the bands $W(3s\sigma)^1\Pi(v' = 3)$ (left) and $^1\Pi(v' = 2)$ (right). The drop line positions were calculated according to the rotational constants in Ref. 2. The relative intensity of the spectrum is not normalized according to the VUV intensity.

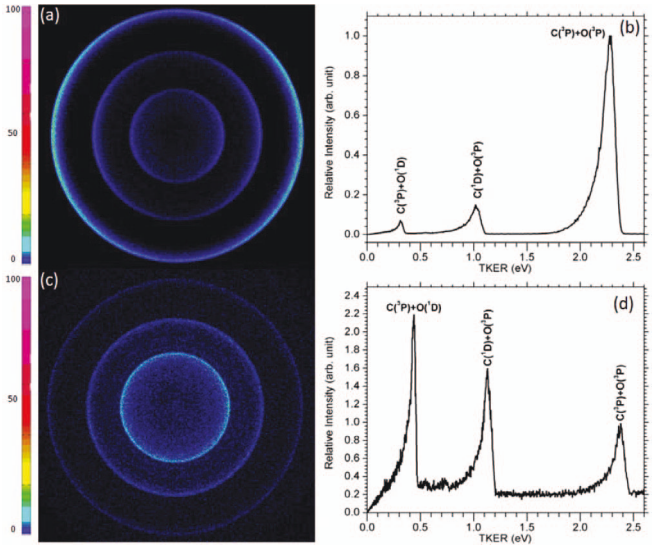

FIG. 2. Raw time-slice velocity-map ion images and their TKER spectra produced from the predissociation of CO following the absorption of a single sum-frequency VUV photon for the R(0) line of the band $W(3s\sigma)^1\Pi(v' = 3)$ ((a) and (b)) at 108 016.4 cm^{-1} and the Q(1) line of the band $^1\Pi(v' = 2)$ ((c) and (d)) at 109 016.9 cm^{-1}. The TKER spectra were normalized by treating the height of the $C(^3P) + O(^3P)$ peak as 1. The assignments for each of the peaks are shown in (b) and (d).

We have obtained time-slice velocity-map ion images at several of the strong rotational lines. The raw images and the corresponding TKER spectra of the $CO(W(3s\sigma)^1\Pi, v' = 3, J' = 1) \leftarrow CO\ (X^1\Sigma^+, v = 0, J = 0)$ transition at 108 016.4 cm^{-1} and the $CO(^1\Pi, v' = 2, J' = 1) \leftarrow CO\ (X^1\Sigma^+, v = 0, J = 1)$ transition at 109 016.9 cm^{-1} are shown in Fig. 2. Three peaks near 0.4 eV, 1.1 eV, and 2.3 eV can be observed in Figs. 2(b) and 2(d), which corresponds to the three energetically available dissociation channels $C(^3P) + O(^1D)$, $C(^1D) + O(^3P)$, and $C(^3P) + O(^3P)$, respectively. Each of the corresponding peaks in Fig. 2(d) is shifted to higher energy compared with those in Fig. 2(b), which confirms the fact that those three peaks are from the predissociation of CO following the absorption of a single sum-frequency VUV photon. By comparing Figs. 2(b) and 2(d), we see that the channel $C(^3P) + O(^3P)$ dominates the predissociation of the R(0) line of $W(3s\sigma)^1\Pi(v' = 3)$ band, while for $^1\Pi(v' = 2)$ band, the channel $C(^3P) + O(^1D)$ dominates. By integrating the areas under each of the peaks, we can obtain the branching ratios for the different channels. Both the cross sections for ionization of $C(^3P)$ and $C(^1D)$ have been calculated before.[26,27] The theoretical photoionization cross sections between 108 020 cm^{-1} and 109 020 cm^{-1} for $C(^3P)$ are 16 Mb and for $C(^1D)$ they are 30 Mb at 108 020 cm^{-1} and 50 Mb at 109 020 cm^{-1}. We used these cross sections to correct the $C(^1D)$ channel for the ionization efficiency. The branching ratios corrected for the photoionization cross section are shown in Table I. Within

TABLE I. Branching ratios of the two Π bands.

Band system	VUV (cm^{-1})	Rotation line[a]	$C(^1D) + O(^3P)$[b] %	$C(^3P) + O(^1D)$ %	$C(^3P) + O(^3P)$ %
$W(3s\sigma)^1\Pi^+(v'=3)$	108 012.4	Q(1)	6.4 ± 0.3[c]	4.0 ± 0.6	89.6 ± 0.5
	108 016.4	R(0)	6.3 ± 0.4	4.2 ± 0.3	89.5 ± 0.5
	108 019.3	R(1)	6.2 ± 0.3	3.8 ± 0.3	90.0 ± 0.3
	108 021.9	R(2)	6.0 ± 0.2	3.6 ± 0.3	90.4 ± 0.6
$^1\Pi^+(v'=2)$	109 013.1	Q(4)	14.2 ± 1.1	57.8 ± 4.2	28.0 ± 2.0
	109 016.9	Q(1)	15.0 ± 0.6	57.1 ± 3.9	27.9 ± 1.8

[a]The rotational lines were calculated by using the constants in Ref. 2.
[b]The ratios to the channel of $C(^1D) + O(^3P)$ have been corrected for the photoionization cross sections of $C(^3P)$ and $C(^1D)$.
[c]The standard errors are generated from three independent measurements.

the experimental error, we did not see obvious dependence of the branching ratio on the parity and the rotational quantum levels in this energy region.

B. Σ bands

The PHOFEX (C^+) spectrum from 109 360 cm^{-1} to 109 520 cm^{-1} produced from the predissociation of CO is shown in Fig. 3. The spectrum is due to two strong Σ bands both of which show sharp rotational structures. There are several previous photoabsorption and photoionization spectroscopy studies in this region.[4,16,19,28] Eidelsberg *et al.* identified two strong Σ bands as $(4s\sigma)^1\Sigma^+(v' = 4)$ and $(4p\sigma)^1\Sigma^+(v' = 3)$ together with a relative weak Π band that we did not observe in our spectrum.[19] The line positions in the C^+ ion yield spectrum are consistent, within the instrumental resolution, to those obtained in Ref. 19 and indicated by drop lines in Fig. 3. We have obtained time-slice velocity-map ion images at several of the strong rotational lines. The raw images and the corresponding TKER spectra of the R(0) line of the band $(4p\sigma)^1\Sigma^+(v' = 3)$ at 109 484.7 cm^{-1} ((a) and (b)) and the R(0) line of the band $(4s\sigma)^1\Sigma^+(v' = 4)$ at 109 452.5 cm^{-1} ((c) and (d)) are shown in Fig. 4. Here again we see very different TKER spectra for the two bands even though they are very close in energy. By integrating the areas for each of the peaks in TKER spectra, we can obtain the branching ratio into each of the channels, after they are corrected for the photoionization cross sections of $C(^3P)$ and $C(^1D)$ of 16 Mb and 50 Mb. The branching ratios for strong lines are reported in Table II.

For the $(4s\sigma)^1\Sigma^+(v' = 4)$ band, the branching ratio is independent of the rotational quantum number within our experimental error, with the exception for the R(1) line. This has a smaller ratio for the two triplet channels compared to the R(0) and R(3). This may be due to an unknown local perturbation. On the other hand, the $(4p\sigma)^1\Sigma^+(v' = 3)$ band shows a weak dependence on the rotation for the $C(^1D)$ channel. This may be caused by the perturbation from the $(5p\pi)^1\Pi(v' = 1)$ band whose R(0) and R(1) lines overlap the R(1) and R(2) of the $(4p\sigma)^1\Sigma^+(v' = 3)$ band.[19]

More detailed measurements about the branching ratios and the angular distributions in several other bands in the frequency region from 108 000 cm^{-1} to 110 400 cm^{-1} are currently being investigated.

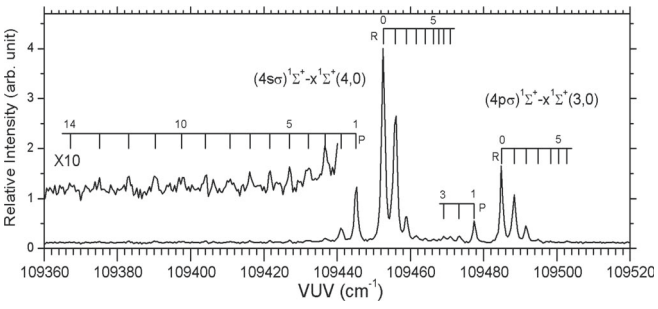

FIG. 3. C^+ ion yield spectra produced from the predissociation of CO following the absorption of a single sum-frequency VUV photon for the bands $(4s\sigma)^1\Sigma^+(v' = 4)$ (left) and $(4p\sigma)^1\Sigma^+(v' = 3)$ (right). The drop line positions were obtained from Ref. 19. The relative intensity of the spectrum is not normalized according to the VUV intensity. The spectrum below 109 440 cm^{-1} was multiplied by a factor of 10 to show in the figure.

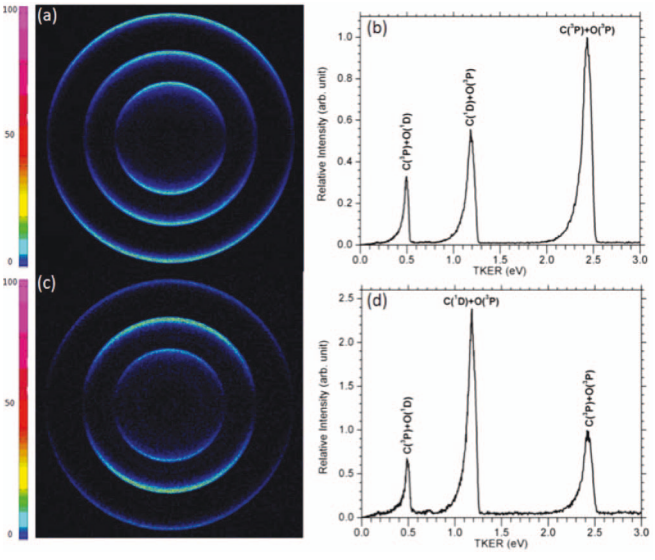

FIG. 4. Raw time-slice velocity-map ion images and their TKER spectra produced from the predissociation of CO following the absorption of a single sum-frequency VUV photon for the R(0) line of the band $(4p\sigma)^1\Sigma^+(v' = 3)$ ((a) and (b)) at 109 484.7 cm^{-1} and the R(0) line of the band $(4s\sigma)^1\Sigma^+(v' = 4)$ ((c) and (d)) at 109 452.5 cm^{-1}. The TKER spectra were normalized by treating the height of the $C(^3P) + O(^3P)$ peak as 1. The assignments for each of the peaks are shown in (b) and (d).

TABLE II. Branching ratios of the two Σ bands.

Band system	VUV (cm^{-1})	Rotation line[a]	$C(^1D) + O(^3P)$[b] %	$C(^3P) + O(^1D)$ %	$C(^3P) + O(^3P)$ %
$(4s\sigma)^1\Sigma^+(v'=4)$	109 452.5	R(0)	32.9 ± 1.0[c]	20.8 ± 1.0	46.3 ± 1.5
	109 455.7	R(1)	27.4 ± 1.6	18.8 ± 1.1	53.8 ± 1.0
	109 458.9	R(2)	32.6 ± 3.0	21.6 ± 3.2	45.9 ± 2.0
	109 461.5	R(3)	30.4 ± 0.9	25.6 ± 2.2	44.1 ± 1.5
	109 445.1	P(1)	32.4 ± 0.9	21.3 ± 1.9	46.3 ± 1.6
	109 440.9	P(2)	32.1 ± 2.8	22.0 ± 3.7	45.9 ± 2.0
$(4p\sigma)^1\Sigma^+(v'=3)$	109 484.7	R(0)	11.3 ± 0.2	16.0 ± 1.5	72.7 ± 1.6
	109 488.2	R(1)	10.2 ± 0.3	15.0 ± 1.5	74.9 ± 2.0
	109 491.4	R(2)	8.4 ± 2.3	15.3 ± 1.5	76.3 ± 1.7
	109 477.4	P(1)	12.0 ± 1.4	17.6 ± 0.7	70.4 ± 2.1
	109 473.2	P(2)	11.2 ± 0.7	18.9 ± 2.1	69.9 ± 2.4

[a]The rotational line assignments are from Ref. 19.
[b]The ratios to the channel of $C(^1D) + O(^3P)$ have been corrected for the photoionization cross sections of $C(^3P)$ and $C(^1D)$.
[c]The standard errors are generated from three independent measurements.

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