Title
Communication: Direct measurements of nascent O($^3\text{P}\,0,1,2$) fine-structure distributions and branching ratios of correlated spin-orbit resolved product channels CO($^1\text{Π}; V$) + O($^3\text{P}\,0,1,2$) and CO($^1\Sigma^+; V$)

Permalink
https://escholarship.org/uc/item/7v04106q

Journal
Journal of Chemical Physics, 140(23)

ISSN
0021-9606

Authors
Lu, Z
Chang, YC
Gao, H
et al.

Publication Date
2014-06-21

DOI
10.1063/1.4883515

Peer reviewed
Communication: Direct measurements of nascent O(3P0,1,2) fine-structure distributions and branching ratios of correlated spin-orbit resolved product channels CO(ä 3Π; ν) + O(3P0,1,2) and CO( X̃ Σ + 1 ; ν) + O(3P0,1,2) in VUV photodissociation of CO2

Zhou Lu, Yih Chung Chang, Hong Gao, Yanice Benitez, Yu Song, C. Y. Ng, and W. M. Jackson

Citation: The Journal of Chemical Physics 140, 231101 (2014); doi: 10.1063/1.4883515
View online: http://dx.doi.org/10.1063/1.4883515
View Table of Contents: http://scitation.aip.org/content/aip/journal/jcp/140/23?ver=pdfcov
Published by the AIP Publishing

Articles you may be interested in
Communication: State-to-state photodissociation study by the two-color VUV-VUV laser pump-probe time-slice velocity-map-imaging-photoion method

Proton formation dynamics in the REMPI [ 2 + n ] process via the F Δ 1 2 and f Δ 3 2 Rydberg states of HCl investigated by three-dimensional velocity mapping

A vacuum ultraviolet laser photoionization and pulsed field ionization study of nascent S ( P 2 , 1 , 0 3 ) and S ( D 2 1 ) formed in the 193.3 nm photodissociation of C S 2

Penning ionization of N 2 O molecules by He * ( 2 S 3 , 1 ) and Ne * ( P 2 , 0 3 ) metastable atoms: A crossed beam study

New results for the OH (ν=0,j=0)+ CO (ν=0,j=0)-- H + CO 2 reaction: Five- and full-dimensional quantum dynamical study on several potential energy surfaces
J. Chem. Phys. 120, 4263 (2004); 10.1063/1.1644101
Communication: Direct measurements of nascent $O(^3P_{0,1,2})$ fine-structure distributions and branching ratios of correlated spin-orbit resolved product channels $CO(\tilde{a}^3\Pi; \nu) + O(^3P_{0,1,2})$ and $CO(\tilde{X}^1\Sigma^+; \nu) + O(^3P_{0,1,2})$ in UV photodissociation of $CO_2$

Zhou Lu, Yih Chung Chang, Hong Gao, Yanice Benitez, Yu Song, C. Y. Ng, and W. M. Jackson

Department of Chemistry, University of California, Davis, Davis, California 95616, USA

(Received 16 April 2014; accepted 3 June 2014; published online 17 June 2014)

We present a generally applicable experimental method for the direct measurement of nascent spin-orbit state distributions of atomic photofragments based on the detection of vacuum ultraviolet (VUV)-excited autoionizing-Rydberg (VUV-EAR) states. The incorporation of this VUV-EAR method in the application of the newly established VUV-VUV laser velocity-map-imaging-photoion (VMI-PI) apparatus has made possible the branching ratio measurement for correlated spin-orbit state resolved product channels, $CO(\tilde{a}^3\Pi; \nu) + O(^3P_{0,1,2})$ and $CO(\tilde{X}^1\Sigma^+; \nu) + O(^3P_{0,1,2})$, formed by VUV photoexcitation of $CO_2$ to the $4s(101)$ Rydberg state at $97,955.7$ cm$^{-1}$. The total kinetic energy release (TKER) spectra obtained from the $O^+$ VMI-PI images of $O(^3P_{0,1,2})$ reveal the formation of correlated $CO(\tilde{a}^3\Pi; \nu = 0–2)$ with well-resolved $\nu = 0–2$ vibrational bands. This observation shows that the dissociation of $CO_2$ to form the spin-allowed $CO(\tilde{a}^3\Pi; \nu = 0–2) + O(^3P_{0,1,2})$ channel has no potential energy barrier. The TKER spectra for the spin-forbidden $CO(\tilde{X}^1\Sigma^+; \nu) + O(^3P_{0,1,2})$ channel were found to exhibit broad profiles, indicative of the formation of a broad range of rovibrational states of $CO(\tilde{X}^1\Sigma^+)$ with significant vibrational populations for $\nu = 18–26$. While the VMI-PI images for the $CO(\tilde{a}^3\Pi; \nu = 0–2) + O(^3P_{0,1,2})$ channel are anisotropic, indicating that the predissociation of $CO_2$ at $157$ nm occurs via a near linear configuration in a time scale shorter than the rotational period, the angular distributions for the $CO(\tilde{X}^1\Sigma^+; \nu) + O(^3P_{0,1,2})$ channel are close to isotropic, revealing a slower predissociation process, which possibly occurs on a triplet surface via an intersystem crossing mechanism. © 2014 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4883515]
channel from its thermochemical threshold at 11.46 eV to a maximum value of 50%–60% near 13.78 eV. Very recently, Song et al. performed a detailed study of the VUV photophysics of CO$_2$ in the VUV energy of 13.540–13.678 eV using the VUV laser time-slice VMI-PI method together with a (2+1) REMPI scheme for O($^3$P$_{0,1,2}$) detection. They were able to identify nearly all energetically accessible photoproduct channels but did not determine the O($^3$P$_{0,1,2}$) fine structure distributions. For the state-resolved photodissociation results to be useful for atmospheric modeling and for rigorous comparisons with first-principle theoretical calculations, it is most important to determine accurate branching ratios for the accessible photoproduct channels.

In this Communication, we present a sensitive and generally applicable experimental scheme for the direct determination of O($^3$P$_{0,1,2}$) spin-orbit state distributions produced by VUV photodissociation of CO$_2$ based on the detection of VUV-excited autoionizing Rydberg (VUV-EAR) states. By using this VUV-EAR method along with time-slice VMI-PI measurements, we have determined the branching ratios for the correlated spin-orbit resolved product channels, CO($^X$Σ$^+$) + O($^3$P$_{0,1,2}$) and CO($^2$Π) + O($^3$P$_{0,1,2}$), formed by VUV photodissociation of CO$_2$ to the 4s($^1$D) Rydberg state at 97 955.7 cm$^{-1}$. This VUV-EAR method is found to exhibit superior detection sensitivity compared to the UV 2+1 REMPI scheme due to the larger photoionization volume used and the higher one photon VUV excitation cross section.

A detailed description of the VUV-VUV laser time-slice VMI-PI apparatus used in the present experiment has been reported previously. The CO$_2$ sample (10% CO$_2$ in He) is introduced into the photoionization/photoexcitation (PI/PEX) region in the form of a pulsed (30 Hz) supersonicbeam. Two independently tunable VUV lasers, designated as VUV-I for photodissociation pump and VUV-II for photoionization probe, are used. Both VUV-I and VUV-II have the same design and are generated by four-wave sum-frequency mixing schemes, providing a tunable VUV output of interest equals to ($\omega_1 + \omega_2$) by using Xe or Kr as the nonlinear medium. Here, $\omega_1$ and $\omega_2$ represent the respective ultraviolet (UV) and visible (VIS) fundamental outputs of the tunable dye lasers. Since no dispersive devise was used to separate the sum-frequency ($\omega_1 + \omega_2$) from the difference-frequency ($2\omega_1 - \omega_2$), the triple frequency $3\omega_1$, and the fundamental frequencies $\omega_1$ and $\omega_2$, all these frequencies entered the PI/PEX center as the VUV-I and VUV-II beams to intersect the CO$_2$ molecular beam. A retractable LiF (or MgF$_2$) window can be inserted in the path of the VUV-I or VUV-II beam to block the VUV sum-frequency. By comparing the O$^+$ ion signals observed with and without the ($2\omega_1 + \omega_2$) frequencies, we conclude that photodissociation of CO$_2$ and photoionization of O($^3$P$_{0,1,2}$) observed here are induced by absorption of the VUV sum-frequencies with little contamination from other VUV and fundamental outputs. The relative intensities for the VUV sum-frequencies of interest were measured by using the photoionization efficiency spectrum of C$_2$H$_2$, which is recorded in situ during the experiment. The photodissociation and photoionization yields presented here have all been normalized by the corresponding VUV intensities.

In a previous experiment, we have reported on the successful determination of C($^3$P$_{0,1,2}$) fine-structure distributions based on the two-color VUV-VIS (1 + 1) photoionization method. The success of this experiment on C($^3$P$_{0,1,2}$) prompted us to seek a similar experimental scheme for measuring the O($^3$P$_{0,1,2}$) fine-structure distribution. A survey of the available O atom Rydberg states lying below the IE(O) at 13.618 eV suggests that O($^3$P$_{0,1,2}$) photofragments can be efficiently detected by the VUV-VIS (1 + 1) REMPI scheme via the intermediate Rydberg states O*$^1[2s^22p^3(S)3d(3D^{2}_{1,2,3})]$. As shown in the left panel of Fig. 1, the first step (shown by blue arrows) of this scheme involved the excitation of O($^3$P$_0$), O($^3$P$_1$), and O($^3$P$_2$) to the common intermediate state O*$^1[2s^22p^3(S)3d(3D^{2}_{1,2,3})]$ by setting VUV-II at 97 261.40, 97 330.11, and 97 488.38 cm$^{-1}$, respectively. Since the second photoionization steps (shown by red arrows in Fig. 1), which involves photoexcitation from this intermediate Rydberg state to the ionization continuum by the absorption of a visible photon at 2.13 eV in this study, have the same cross section, the nascent populations for O($^3$P$_{0,1,2}$) can be determined based on the measured O$^+$ ion intensities from O($^3$P$_{0,1,2}$) and the known cross sections of the first VUV excitation steps. However, due to the small energy separations of the O*$^1[2s^22p^3(S)3d(3D^{2}_{1,2,3})]$ spin-orbit states, the transition energies from O($^3$P$_2$) to these states differ only by $\leq$0.16 cm$^{-1}$ and those from O($^3$P$_1$) to O*$^1[2s^22p^3(S)3d(3D^{2}_{1,2,3})]$ by $\leq$0.07 cm$^{-1}$. These small energy separations do not allow individual transitions to be resolved by using the VUV-II laser. The actual observed transition energies for O($^3$P$_0$) → O*$^1[2s^22p^3(S)3d(3D^{2}_{1,2,3})]$, O($^3$P$_1$) → O*$^1[2s^22p^3(S)3d(3D^{2}_{1,2,3})]$, and O($^3$P$_2$) → O*$^1[2s^22p^3(S)3d(3D^{2}_{1,2,3})]$ are found to be at 97 489.9, 97 331.7, and 97 262.6 cm$^{-1}$, respectively. Although these Rydberg states O*$^1[2s^22p^3(S)3d(3D^{2}_{1,2,3})]$ cannot be used for the direct determination of the O($^3$P$_{0,1,2}$) fine structure distribution due to the unresolved excitations, it can serve to
FIG. 2. Comparison of (a) the absorption spectrum of CO₂ and the O⁺ PHOFEX spectra of (b) O(3P₀), (c) O(3P₁), and (d) O(3P₂) formed by the photodissociation of CO₂ in the range of 97 000–98 400 cm⁻¹. The PHOFEX spectra of O(3P₀), O(3P₁), and O(3P₂) were obtained by setting VUV-II at 97 262.6, 97 331.7, and 97 489.9 cm⁻¹, and scan VUV-I in the range of 97 000–98 400 cm⁻¹.

provide an efficient detection scheme for the O(3P₀,1,2) spin-orbit states. By setting VUV-II at 97 262.6, 97 331.7, and 97 489.9 cm⁻¹, and scan VUV-I in the range of 97 000–98 400 cm⁻¹ (12.03–12.20 eV), we have obtained the O⁺ photofragment excitation (PHOFEX) spectra of O(3P₀), O(3P₁), and O(3P₂) as shown in Figs. 2(b)–2(d), respectively. The structures of these PHOFEX spectra are in excellent agreement with the high-resolution absorption spectrum of CO₂ [shown in Fig. 2(a)] that was previously reported by Cossart-Magos et al. and Archer et al. The strongest absorption peak centered at 97 955.7 cm⁻¹ is assigned to the CO₂[4s(l₀¹)] Rydberg band. Three sharp O⁺ ion peaks at 97 262.6, 97 331.7, and 97 489.9 cm⁻¹ are evident in the PHOFEX spectra that result from the increase of O⁺ ion yields by VUV-VIS (1 + 1') REMPI of O(3P₀,1,2) induced by VUV-I excitation. This observation illustrates the high sensitivity of the VUV-VIS (1 + 1') REMPI scheme for O(3P₀,1,2) detection.

The VUV-EAR scheme used for the direct determination of the O(3P₀,1,2) fine structure distribution in the present study is shown in the right panel of Fig. 1, which requires only a single excitation step (shown by blue arrows), i.e., the direct VUV-II excitation of O(3P₀,1,2) to a common Rydberg state O*(2s²2p³(3P)4s[1P₁]) located at 113 921.39 cm⁻¹ (14.124 eV) lying above the IE(O) = 13.618 eV. The O⁺ ion intensity produced by autoionizing of this common Rydberg state is thus only dependent upon the nascent populations of the O(3P₀,1,2) spin-orbit states and the cross sections for the VUV-II excitation transitions, which are known by close coupling calculations. Figure 3 depicts the observed O⁺ ion intensities induced by the VUV-II excitations O*(3P₀,1,2) → O*[2s²2p³(3P)4s[1P₁]] in the energy range of 113 675–113 950 cm⁻¹. The observed O⁺ ion peaks are assigned to dipole allowed transitions as marked in Fig. 3. The three excitation transitions to the intermediate Rydberg state O*(2s²2p³(3P)3s[1P₁]) from O(3P₀), O(3P₁), and O(3P₂) are highlighted by red asterisks. The integrated areas of the O(3P₀), O(3P₁), and O(3P₂) are used to determine the intensity associated with formation of each of these spin-orbit states from the photodissociation of CO₂ in the 4s(l₀¹) state. After correcting for the calculated transition probabilities of 2.26 × 10⁸, 1.7 × 10⁸, and 2.85 × 10⁸ for the transitions from O(3P₀), O(3P₁), and O(3P₂) to O*(2s²2p³(3P)3s[1P₁]), respectively, we obtained the nascent distribution O(3P₀): O(3P₁): O(3P₂) = 0.12(2): 0.25(3): 0.63(2). The uncertainty assigned to this distribution reflects the maximum deviation observed in more than three independent measurements. Comparing this distribution to the statistical distribution of 0.11: 0.33: 0.56 obtained using the 2J Degeneracy of the M J levels, we find that the distribution obtained here is colder with a slightly higher populations for the ground O(3P₂) state. We note that CO(X¹Σ⁺; v₁ = 0) is also an open product channel from CO₂[4s(l₀¹)] predissociation. The O⁺ ion peaks originated from excitations of O(3P₂) to the autoionizing Rydberg state O*(2s²2p³(3D)4d[1D₂⁺]) and O*(2s²2p³(3D)4d[1P₂⁺]) are also identified in this VUV-II energy range as marked in Fig. 3.

Figures 4(a)–4(c) depict the time-slice O⁺ VMI-PI images of O(3P₀), O(3P₁), and O(3P₂) produced by photodissociation of CO₂ with VUV-I set at exciting the CO₂[4s(l₀¹)] Rydberg state. The corresponding TKER spectra obtained from these images are shown in Figs. 4(d)–4(f). On the basis of the known energetics and vibrational constants of CO(2a¹Π) and CO(X¹Σ⁺), the TKER spectra for the CO(2a¹Π) + O(3P₀,1,2) and the CO(X¹Σ⁺) + O(3P₀,1,2) channels are simulated as shown by the red and the blue curves, respectively. The simulation is guided by the trend of the measured...
TKER spectra. Since the red and blue curves overlap, it is necessary to separate the contribution by the spin-allowed and spin-forbidden channels in the overlap region by simulation in order to determine the branching ratios for these product channels. The uncertainties introduced by the simulation were included in the error limit assigned for the branching ratios reported here. The three sharp, anisotropic inner rings of the VMI-PI images correspond to the formation of the spin-allowed CO( 3P0) and the CO(X1Σ+) + O(2P2,1,0) channels simulated as shown by the red and the blue curves, respectively.

![FIG. 4. Time-slice O+ VMI-PI images for (a) O(3P0), (b) O(3P1), and (c) O(3P2) produced by photodissociation of CO2 with VUV-I set at the CO2[4s(101)] Rydberg state. The corresponding TKER spectra obtained from these images are shown in (d), (e) and (f). The TKER spectra for the CO(3Π1) + O(2P1,0) and the CO(X1Σ+) + O(2P2,1,0) channels are simulated as shown by the red and the blue curves, respectively.](image-url)

We have determined the anisotropy β parameters based on the analysis of the time-slice VMI-PI images for the CO(3Π1; v = 0–2) + O(2P1,2) and CO(X1Σ+; v = 0–30) product channels from the predissociation of CO2[4s(101)]). The β parameter was found to decrease with increasing vibrational excitation of CO(3Π1) and spin-orbit excitation of O(3P2) and fall in the range of 1.0–1.8. For the CO(3Π1; v = 0) + O(3P1) (J = 0, 1, and 2) channels, the β parameters have the respective values of 1.0(2), 1.6(2), and 1.8(1). The change in the β parameter with J implies that the O(3P1,2) spin-orbit states form at different rates. The fastest dissociation occurs for the ground O(3P0) state, while the slowest dissociation takes place for the excited O(3P1) state that is 227.98 cm−1 above the ground O(3P0) state. The β = 1.8 obtained for the CO(3Π1) + O(3P1) product channel indicates a near parallel transition of this channel, and a Σ symmetry for the CO2 4s(101) Rydberg state. The anisotropy β parameters obtained from the outer broad ring structures are 0.52(5), 0.27(3), and 0.37(7) for the respective O(3P0), (3P1), and (3P2) VMI-PI images. These β values correspond to near isotropic angular distributions for the spin-forbidden product channel. This observation is consistent with a slower photodissociation mechanism for the spin-forbidden channel via the triplet potential energy surface with a dissociation lifetime comparable to the rotational period of excited CO2. The smaller β parameters observed for vibrational and spin-orbit excitations may be ascribed to a more efficient singlet-triplet coupling. The ab initio calculation of Hwang and Mebel on CO2 dissociation predicts that the spin-forbidden CO(X1Σ+; v = 0) channel is produced via the triplet potential energy structure of 3A′ electronic symmetry, which has one extended C-O bond, while the other C-O bond is compressed in a bent OCO geometry, leading to the formation of rovibrationally excited CO(X1Σ+) photoproduc
ts.22

By integrating the areas under the red and blue TKER curves of Figs. 4(d)–4(f), we have determined the branching ratios, CO(3Π1; v = 0–2) + O(2P0): CO(3Π1; v ≤ 30) + O(3P1) for J = 0, 1, and 2, to be 0.16(2): 0.84(2), 0.25(2): 0.75(2), and 0.34(3): 0.66(3), respectively. These ratios show that the branching fraction for the spin-allowed channel increases as J is increased. The CO(3Π1; v = 0–2) + O(3P1) channel is observed to have a smaller branching ratio compared to the CO(X1Σ+; v = 0) channel from CO2[4s(101)] dissociation. The normalization of these branching ratios for CO(3Π1; v = 0–2) + O(3P1): CO(X1Σ+; v = 2 + O(3P1) + O(3P2) (J = 0, 1, and 2) by the fine structure distribution O(3P0): O(3P1): O(3P2) = 0.12(2): 0.25(3): 0.63(2) measured in the present study have enabled the determination of the branching ratios for the correlated spin-orbit state resolved product channels, CO(3Π1; v = 0–2) + O(2P0): CO(3Π1; v = 0–2) + O(3P1): CO(3Π1; v = 0–2) + O(3P2): CO(X1Σ+; v ≤ 30) + O(3P0): CO(X1Σ+; v ≤ 30) + O(3P1): CO(X1Σ+; v ≤ 30) + O(3P2) = 0.019(4): 0.063(9): 0.21(2): 0.10(2): 0.19(2): 0.42(2). These quantitative experimental measurements are expected to be useful for modeling the photochemistry occurring in planetary atmospheres as well as providing a benchmark for comparison with rigorous first-principle theoretical predictions on the photodissociation dynamics of CO2.

C.Y.N was supported by the U.S. Department of Energy (DOE) Contract No. DE-FG02-02ER15306. W.M.J was supported by the NSF Grant No. CHE-1301501. We also thank Dr. Glenn Stark for providing the digitized CO2 photoabsorption spectrum.