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the experiments and designed the study. N.R.F. and P.L. conducted the phylogenetic analyses. D.P. performed the recombination analysis and G.B. the model selection analysis. M.A.S. and T.B. contributed methodology. T.B., M.J.W., and N.A. assisted the sequence analysis. J.P., A.J.T., and J.D.S. contributed historical and spatial data. M.P. provided sequence data. N.R.F., P.L., O.G.P., and A.R. wrote the paper. All authors discussed the results and approved the final manuscript. We declare no competing financial interests.

## SUPPLEMENTARY MATERIALS

[www.sciencemag.org/content/346/6205/56/suppl/DC1](http://www.sciencemag.org/content/346/6205/56/suppl/DC1)  
Materials and Methods  
Figs. S1 to S9  
Tables S1 to S9  
References (65–98)

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## REPORTS

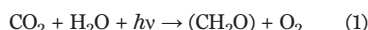
### PHOTOCHEMISTRY

# Evidence for direct molecular oxygen production in CO<sub>2</sub> photodissociation

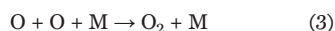
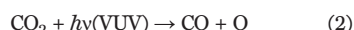
Zhou Lu,<sup>1</sup> Yih Chung Chang,<sup>1</sup> Qing-Zhu Yin,<sup>2</sup> C. Y. Ng,<sup>1\*</sup> William M. Jackson<sup>1\*</sup>

Photodissociation of carbon dioxide (CO<sub>2</sub>) has long been assumed to proceed exclusively to carbon monoxide (CO) and oxygen atom (O) primary products. However, recent theoretical calculations suggested that an exit channel to produce C + O<sub>2</sub> should also be energetically accessible. Here we report the direct experimental evidence for the C + O<sub>2</sub> channel in CO<sub>2</sub> photodissociation near the energetic threshold of the C(<sup>3</sup>P) + O<sub>2</sub>(X<sup>3</sup>Σ<sub>g</sub><sup>−</sup>) channel with a yield of 5 ± 2% using vacuum ultraviolet laser pump-probe spectroscopy and velocity-map imaging detection of the C(<sup>3</sup>P<sub>j</sub>) product between 101.5 and 107.2 nanometers. Our results may have implications for nonbiological oxygen production in CO<sub>2</sub>-heavy atmospheres.

It is widely accepted that the rise of the oxygen-rich atmosphere on Earth, known as the “Great Oxidation Event,” occurred at ~2.4 billion years ago via multistep photosynthetic processes (Eq. 1) (1, 2)



Here,  $h$  is Planck's constant and  $\nu$  is the frequency. Over the past 40 years, biologists and paleontologists have proposed that free oxygen molecules must have been available in small quantities before the rise of oxygenic photosynthesis in Earth's prebiotic primitive atmosphere (3). The only known abiotic production mechanism was through solar vacuum ultraviolet (VUV) photodissociation of CO<sub>2</sub> to form CO + O in the early Earth stratosphere, followed by the three-body recombination reactions shown in Eqs. 2 and 3



Here, M is a third body for carrying off the excess energy involved in the formation of the O<sub>2</sub> chemical bond (4–6). Decades of experimental and theoretical photochemical studies of CO<sub>2</sub>

have been focused on the detection and understanding of the CO + O photoproduct channels.

Recent theoretical calculations (7, 8) suggest that an exit channel to produce C + O<sub>2</sub> upon VUV photoexcitation of the CO<sub>2</sub> molecule is possible. The ab initio calculation (7) has provided the dissociation pathway on the ground-state singlet potential energy surface of CO<sub>2</sub>, leading to the formation of the C(<sup>3</sup>P) + O<sub>2</sub>(X<sup>3</sup>Σ<sub>g</sub><sup>−</sup>) products (where X is indicative of the ground state) (pathway 1 of Fig. 1). If the electronically excited singlet CO<sub>2</sub> molecule initially produced by photoexcitation undergoes internal conversion to the ground-state singlet potential surface, the O atom could migrate through a cyclic CO<sub>2</sub> complex [c-CO<sub>2</sub>(<sup>1</sup>A<sub>1</sub>)] and form a colinear COO(<sup>1</sup>Σ<sup>+</sup>) intermediate before dissociation to C(<sup>3</sup>P) + O<sub>2</sub>(X<sup>3</sup>Σ<sub>g</sub><sup>−</sup>), as shown in pathway 1. The theoretical calculation (7) predicts no potential energy barrier for this dissociation pathway. Grebenshchikov (8) calculated the singlet ground and excited potential energy surfaces of COO, with the O-O bond distance fixed at 2.3 bohr. His calculations indicate that the singlet ground and excited surfaces are connected by conical intersections, and his results support Hwang and Mebel's conclusion (7) that there is no potential energy barrier via the COO colinear state to yield C(<sup>3</sup>P) + O<sub>2</sub>(X<sup>3</sup>Σ<sub>g</sub><sup>−</sup>) on the ground-state singlet surface. Despite these theoretical results, to our knowledge there has been no experimental verification of the C + O<sub>2</sub> channel in CO<sub>2</sub> photodissociation. Here we present the experimental evidence of C(<sup>3</sup>P) + O<sub>2</sub>(X<sup>3</sup>Σ<sub>g</sub><sup>−</sup>)

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products based on VUV-pump and VUV-probe velocity-map imaging (VMI) measurements of  $C(^3P_2)$  atoms. Direct detection of  $O_2(X^3\Sigma_g^-)$  photoproducts is not feasible, in part due to the substantial number of  $O_2^+$  background ions produced by photoionization of ambient  $O_2$  molecules in the experimental chamber. Furthermore, state-selected VUV photoionization of  $O_2(X^3\Sigma_g^-)$  photofragments would result in a much lower signal intensity compared with that of  $C(^3P_J)$  atoms because a small fraction of  $O_2(X^3\Sigma_g^-)$  products at a single rovibrational state is detected among the nascent  $O_2(X^3\Sigma_g^-)$  produced in a wide range of rovibrational states, whereas the  $C(^3P_J)$  atoms are only formed in three spin-orbit states.

In this  $CO_2$  photodissociation experiment, the VUV photoexcitation energy  $h\nu(VUV)$  is distributed between the  $C(^3P_J)$  and  $O_2(X^3\Sigma_g^-)$  product translational energy ( $E_{trans}$ ) and internal energy ( $E_{int}$ ), where  $E_{int}[C(^3P_J)]$  is due to excitation of the spin-orbit state; and the correlated  $O_2(X^3\Sigma_g^-)$  photoproducts can be both rotationally and vibrationally excited. The VMI technique can be used to determine the recoil velocity distribution of the  $C(^3P_J)$  photofragments from the radii of the resolved ring structures in the velocity-map image. The velocities are converted to a total kinetic energy release (TKER) spectrum of the  $C(^3P_J) + O_2(X^3\Sigma_g^-)$  channel by using Eq. 4 based on the conservation of linear momentum and energy

$$h\nu(VUV) = D_0 + E_{int}[C(^3P_J)] + E_{int}[O_2(X^3\Sigma_g^-)] + E_{trans}[C(^3P_J) + O_2(X^3\Sigma_g^-)] \quad (4)$$

Here,  $D_0 = 11.44$  eV is the thermochemical threshold for the formation of the  $C(^3P_J) + O_2(X^3\Sigma_g^-)$  products from  $CO_2$  dissociation (7). Equation 4 can also be used to determine the internal rotational and vibrational energy populations of  $O_2(X^3\Sigma_g^-)$  photofragments from the TKER spectrum.

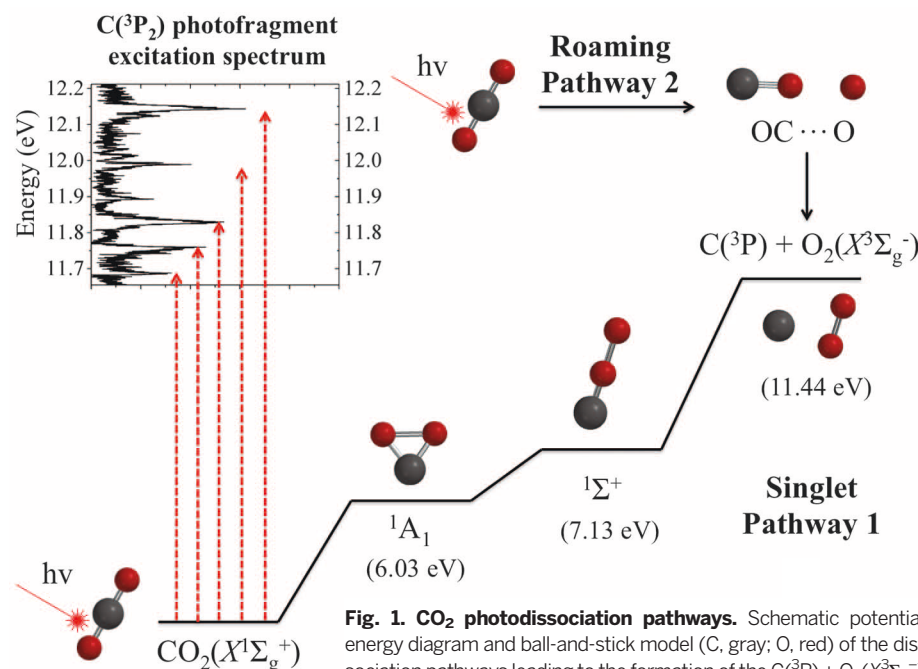
In the present experiment, a skimmed and pulsed supersonic molecular beam generated from ~10%  $CO_2$  seeded in He was irradiated by two counter-propagating unfocused VUV laser beams, hereafter designated as “VUV<sub>1</sub>” and “VUV<sub>2</sub>” (9, 10). The VUV<sub>1</sub> laser output was used to directly excite  $CO_2$  to a dissociative rovibronic state.  $C(^3P_J)$  photofragments were then selectively ionized via a VUV<sub>2</sub>-visible (1+1') resonance-enhanced photoionization scheme, which has been shown to achieve substantially higher detection sensitivities for  $C(^3P_J)$  detection compared with those observed using a direct VUV photoionization method (9).

The ion species formed by photoionization in the interaction region were accelerated by the ion imaging optics into a time-of-flight (TOF) spectrometer for mass analyses and detected by a dual microchannel plates detector. Figure 2 depicts three TOF spectra in the mass range of 10 to 20 atomic mass units (amu) observed in  $CO_2$  photodissociation at  $h\nu(VUV) = 11.832$  eV (95,430.0  $cm^{-1}$ ) under different photoexcitation conditions. The top red trace shows the  $C^+$  ion peak from  $C(^3P_2)$  observed at 12 amu when both VUV<sub>1</sub> and VUV<sub>2</sub> were turned on in the interaction region. No  $C^+$  ion was observed upon tuning of the VUV<sub>2</sub> laser

off-resonance (black trace) or blocking of the VUV<sub>1</sub> beam in the interaction region (blue trace). The data thus clearly demonstrate that the observed  $C^+$  ion intensity depends on both the VUV<sub>1</sub> photoexcitation of  $CO_2$  and the VUV<sub>2</sub> photoionization of  $C(^3P_2)$  photofragments. The ion peak at 18 amu, which was observed in all three mass spectra, is attributed to background  $H_2O^+$  ions produced by VUV photoionization of ambient  $H_2O$  vapor in the photoionization chamber.

In Fig. 3, panels A to C compare the  $CO_2$  photoabsorption spectrum reported by Archer *et al.* (11) to the photofragment excitation spectra obtained by detecting the  $C(^3P_2)$  or the  $O(^1S)$  fragments while tuning the VUV<sub>1</sub> over the energy range 11.562 to 12.212 eV (93,250 to 98,500  $cm^{-1}$ ). The photoabsorption spectrum of Fig. 3A shows the vibrational progressions of the  $3p^1\Pi_u$  and  $4s$  Rydberg states, which were identified previously by Cossart-Magos *et al.* (12) and Kuo *et al.* (13). The  $C(^3P_2)$  and  $O(^1S)$  photofragments were detected by VUV<sub>2</sub>-visible (1+1') photoionization and VUV<sub>2</sub> excited autoionizing Rydberg state schemes with the excited  $C^*[2s^22p3d(^3D^o_3)]$  and  $O^*[2s^22p^3(^4P^o_3)3s(^1P^o_1)]$  Rydberg states, respectively, as VUV<sub>2</sub> resonant intermediate states. As shown in Fig. 3, A to C, the photofragment excitation spectra of  $C(^3P_2)$  and  $O(^1S)$  are in excellent agreement with the  $CO_2$  photoabsorption spectrum, except that the  $4s$  Rydberg peak of  $CO_2$  at 11.967 eV (96,522  $cm^{-1}$ ) resolved in the spectrum of Fig. 3A is strongly perturbed or distorted in the  $C(^3P_2)$  and  $O(^1S)$  photofragment excitation spectra due to a strong dip in the VUV<sub>1</sub> tuning curve in this energy region. Because the  $O(^1S) + CO(X^1\Sigma^+)$  channel is

known to be a major nascent photoproduct channel in  $CO_2$  photodissociation in this VUV energy range, the excellent agreement between the photofragment excitation spectra of  $C(^3P_2)$  and  $O(^1S)$  and the photoabsorption spectrum of  $CO_2$  indicates that the  $C(^3P_2)$  fragments are also nascent photoproducts in  $CO_2$  photodissociation. The identification of  $C(^3P_2)$  as a nascent photofragment clearly shows that the correlated  $O_2$  photoproduct is formed in the VUV photodissociation of  $CO_2$ . The current photodissociation measurements on  $CO_2$  were performed under molecular beam conditions to ensure that secondary collisions were unimportant. As pointed out above, the direct detection of  $C(^3P_2)$  photofragments allows the measurement of the  $E_{int}$  distribution of the  $O_2$  coincident photofragments using the VMI method. Because the photofragment excitation spectra of Fig. 3, B and C, have been normalized by the photodissociation VUV<sub>1</sub> laser intensity, which was monitored by measuring the photoionization efficiency spectrum of acetylene ( $C_2H_2$ ) (14), the relative intensities of the  $C(^3P_2)$  and  $O(^1S)$  photofragment excitation spectra can be used to determine the relative yields of the  $C(^3P_2) + O_2(X^3\Sigma_g^-)$  and  $O(^1S) + CO(X^1\Sigma^+)$  photodissociation channels, respectively, in the  $CO_2$  photodissociation energy range of  $h\nu(VUV) = 11.562$  to 12.212 eV. Previous experimental studies suggest that the yield of the  $O(^1S) + CO(X^1\Sigma^+)$  channel increases as the VUV photodissociation energy decreases (15), which is in good agreement with the  $CO_2$  absorption spectrum and the observed  $O(^1S)$  photofragment excitation spectrum of Fig. 3C. In comparison with the  $CO_2$  absorption spectrum,



**Fig. 1.  $CO_2$  photodissociation pathways.** Schematic potential energy diagram and ball-and-stick model (C, gray; O, red) of the dissociation pathways leading to the formation of the  $C(^3P) + O_2(X^3\Sigma_g^-)$  products. The singlet potential energy pathway (pathway 1) is predicted to involve the formation of the  $c\text{-}CO_2(^1A_1)$  and  $COO(^1\Sigma^+)$  intermediates situated at 6.03 and 7.13 eV above the  $CO_2(X^1\Sigma_g^+)$  ground state. Pathway 2 illustrates the roaming mechanism. The photoexcitation of a  $CO_2$  molecule is indicated by the upward arrows to  $CO_2$  absorption bands manifested by the  $C(^3P_2)$  photofragment excitation spectrum in the energy range of 11.655 to 12.212 eV.

the observed  $C(^3P_2)$  photofragment excitation spectrum of Fig. 3B shows that the yield of the  $C(^3P_2) + O_2(X^3\Sigma_g^-)$  channel decreases as the VUV photodissociation energy decreases toward the thermochemical threshold for the formation of  $C(^3P_2) + O_2(X^3\Sigma_g^-)$  at 11.44 eV. These observed dependences of the  $C(^3P_2)$  and  $O(^1S)$  intensities on the VUV photodissociation energy suggest that the branching ratio of the  $C(^3P) + O_2(X^3\Sigma_g^-)$  channel relative to the  $O(^1S) + CO(X^1\Sigma^+)$  channel is expected to increase as the VUV photodissociation energy increases. Based on the detection efficiencies for  $C(^3P_2)$  and  $O(^1S)$  in the present experiment and the measured  $C(^3P_{2,1,0})$  fine structure distribution produced from  $CO_2$  photodissociation, we have obtained an estimate of  $5 \pm 2\%$  for the intensity of the  $C(^3P) + O_2(X^3\Sigma_g^-)$  channel compared with that of the  $O(^1S) + CO(X^1\Sigma^+)$  channel formed in  $CO_2$  photodissociation in the current VUV photodissociation energy range near the energetic threshold of the  $C(^3P) + O_2(X^3\Sigma_g^-)$  channel (10).

We have measured the  $C(^3P_2)$  velocity-map ion images (Fig. 4) at five selected  $CO_2$  predissociative states, as marked by the red downward pointing arrows in Fig. 3B. As shown below, the analysis of these  $C(^3P_2)$  ion images provides further support for the direct formation of  $O_2$  molecules in  $CO_2$  photodissociation. The radial distribution of the  $C(^3P_2)$  ion image (Fig. 4) provides a measure of the recoil velocity distribution of  $C(^3P_2)$  photofragments produced at a specific VUV frequency for  $CO_2$  excitation. The central donut-shaped ring structures of the  $C(^3P_2)$  ion images originate from the formation of  $C(^3P_2) + O_2(X^3\Sigma_g^-)$  in the photodissociation of  $CO_2$ . As the  $VUV_1$  photon energy increases, the figures show that the radii of the ring structures observed for the  $C(^3P_2)$  photofragments increase as expected. Based on the conservation of energy (Eq. 4) and linear momentum, the measurement of the  $C(^3P_2)$  photofragments' recoil velocities can be used to determine the  $E_{trans}$  distribution of the  $O_2$  counter-fragments and, thus, the TKER of the  $C(^3P_2) + O_2(X^3\Sigma_g^-)$  product channel. The TKER spectra (Fig. 4, A to E) exhibit vibrational structures, from which we simulated the vibrational excitations of  $O_2(X^3\Sigma_g^-)$  in the range of  $v = 0$  to 3, as marked in the figures (10). The best fit to the observed vibrational profiles indicates that  $O_2(X^3\Sigma_g^-)$  photofragments are also rotationally excited, with a rotational temperature well above 500 K. The onset energies of the TKER spectra are in excellent agreement with the thermochemical threshold (i.e.,  $D_0 = 11.44$  eV) for the formation of the  $C(^3P_2) + O_2(X^3\Sigma_g^-)$  products from  $CO_2$  photodissociation. The agreement of the  $C(^3P_2) + O_2(X^3\Sigma_g^-)$  onset energies and the observation of the  $O_2(X^3\Sigma_g^-)$  vibrational distributions are the most unambiguous evidence for the formation of the molecular oxygen channel in the VUV photodissociation of  $CO_2$ . Taking into account the theoretical results, we may rationalize that the production of molecular oxygen at photon energies near the energetic threshold proceeds mostly via the  $c-CO_2(^1A_1)$  and  $COO(^1\Sigma^+)$  intermediates on the singlet ground-state potential energy surface (pathway 1 in Fig. 1), which is predicted

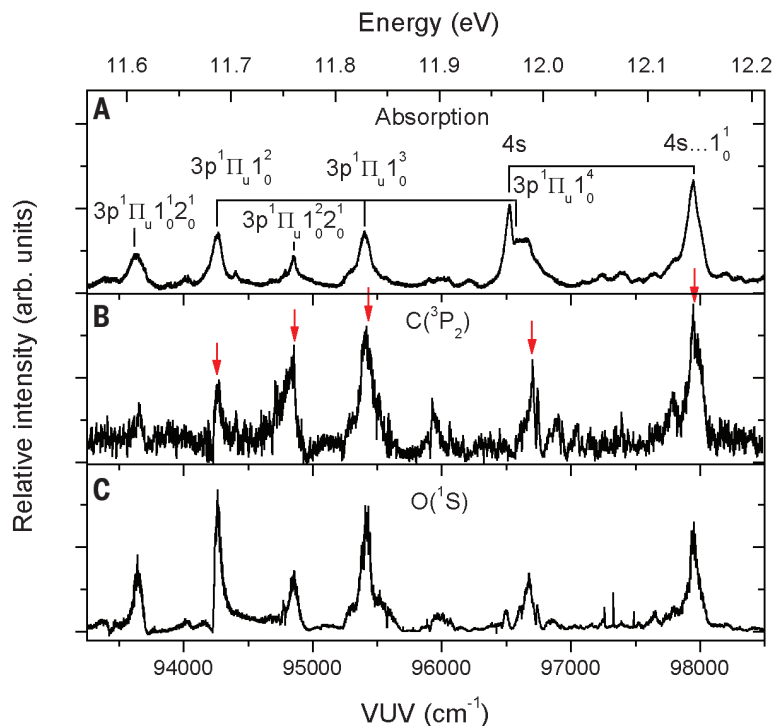
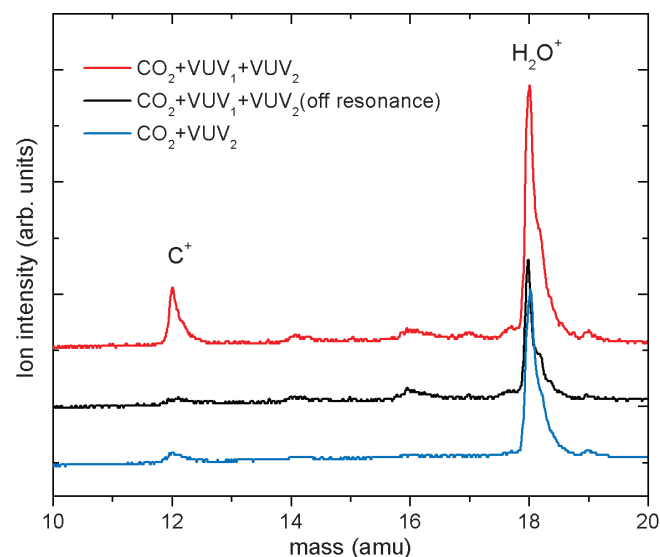
to have no potential energy barrier by the theoretical calculations (7, 8).

The  $C(^3P_2)$  ion image measurements reveal not only the  $E_{trans}$  distribution of the photoproduct channels, but also the angular distribution of the photofragments, which is characterized

by the anisotropy  $\beta$  parameter (16). The angular distribution measurements provide information about the photodissociation rates for the formation of specific photofragments, as well as the geometry of the excited molecule at the time of its dissociation. The upper electronic states for the

**Fig. 2. Time-of-flight mass spectra from  $CO_2$  photolysis at a  $VUV_1$  energy of 11.832 eV ( $95,430.0\text{ cm}^{-1}$ ).**

The top red trace indicates the detection of a  $C^+$  ion from  $C(^3P_2)$  with both  $VUV_1$  and  $VUV_2$  turned on. The black and blue traces below represent the background spectra observed by tuning the  $VUV_2$  frequency off resonance and turning off the  $VUV_1$  laser beam, respectively.



**Fig. 3. Photofragment excitation spectra.** Comparison of (A) the  $CO_2$  absorption spectrum, (B) the photofragment excitation spectrum for  $C(^3P_2)$ , and (C) the photofragment excitation spectrum for  $O(^1S)$  in the  $VUV_1$  energy region 11.562 to 12.212 eV ( $93,250$  to  $98,500\text{ cm}^{-1}$ ) illustrates that the  $C(^3P_2)$  and  $O(^1S)$  photofragments are observed only when  $CO_2$  is photoexcited to an absorption band. The absorption spectrum was recorded by Archer *et al.* at an optical resolution of  $1.15\text{ cm}^{-1}$  (full width at half maximum) (11). The red downward arrows mark the  $VUV_1$  photodissociation energies at which  $C(^3P_2)$  ion images were collected. The photofragment excitation spectra shown in (B) and (C) have been normalized by the corresponding  $VUV_1$  laser intensity (14).

images in Fig. 4, A to C, are assigned as  $3p^1\Pi_u$  (*12, 13*). Thus, perpendicular distribution of the  $C(^3P_2)$  atoms with respect to the  $CO_2$  photolysis laser polarization is expected if  $CO_2$  dissociates in a linear geometry. However, the  $C(^3P_2)$  ion images reveal modest parallel distributions with respect to the transition dipole moment in Fig. 4, A to C. This result suggests that the electronically excited  $CO_2$  molecules dissociate in a bent geometry for the formation of  $C(^3P_2) + O_2(X^3\Sigma_g^-)$  products due to vibronic interaction. The parallel distribution of the photofragments has been observed in other triatomic molecules in perpendicular transitions due to vibronic interactions (*17–19*). The  $3p^1\Pi_u$  Rydberg state of  $CO_2$  is known to involve bending vibrational coupling (*20*), which is caused by the Fermi resonance between the excitation of one quantum of symmetric stretching ( $\nu_1$ ) and two quanta of bending ( $2\nu_2$ ) vibrational modes (*21*). Thus, the inclusion of vibronic interactions would account for the experimental observation of  $CO_2$  dissociation in a bending geometry. The increase of the  $\beta$  value of  $0.72 \pm 0.07$  in Fig. 4C to  $0.97 \pm 0.09$  in Fig. 4D can be attributed to the symmetry change of the upper electronic states from  $3p^1\Pi_u$  to  $4s$ .

The recent experimental and theoretical evidence of a “roaming” dissociation pathway (*22–24*) has prompted us to speculate the involvement of O atom roaming for the formation of  $C(^3P_2) +$

$O_2(X^3\Sigma_g^-)$  products in  $CO_2$  photodissociation (pathway 2 in Fig. 1). The roaming mechanism can be initiated via an incomplete OC-O bond cleavage. The resulting molecular CO and atomic O moieties interact via long-range forces on a flat region of the potential energy surface until they encounter a reactive site, leading to the formation of  $C + O_2$  products by intramolecular O atom abstraction. Based on the theoretical calculation from Grebenshchikov (*8*), the  $CO_2$  potential energy surfaces are relatively flat for the spin-allowed  $CO(a^3\Pi) + O(^3P)$  and  $CO(X^3\Sigma^+) + O(^1S)$  dissociation channels. The formation of  $C(^3P_2) + O_2(X^3\Sigma_g^-)$  products can result from the O atom roaming with CO on these excited singlet surfaces in  $CO_2$  photodissociation, similar to the roaming dissociation mechanism observed in  $NO_3$  photodissociation (*24*).

Recently, Huestis *et al.* (*25*) suggested that the source of  $O(^1S)$  day-glow emission observed from the Mariner 4 and Mars Express missions originates from the dissociative electron-ion recombination reaction (Eq. 5)



even though  $O(^1S)$  atoms are known primary photofragments of VUV  $CO_2$  photodissociation in the  $CO_2$ -dominated atmosphere of Mars. More recent measurements by Herschel spacecraft and

Mars Science Laboratory’s Sample Analyses at Mars provide  $O_2$  abundance measurements of  $1400 \pm 120$  parts per million (ppm) (*26*) and  $1450 \pm 90$  ppm (*27*), respectively. The  $O(^1S)$  optical emission poses an intriguing question about the source of  $O_2^+$ , which can be produced by VUV photoionization of  $O_2$  and/or charge transfer from  $CO_2^+$  to  $O_2$  in the  $CO_2$ -dominated atmosphere of Mars. Our study has provided unambiguous experimental evidence for the formation of  $C + O_2$  photoproducts in  $CO_2$  photodissociation. We suggest that this pathway for generating  $O_2$  be incorporated into future photochemical reaction networks and general circulation models of planetary atmospheres dominated by  $CO_2$ .

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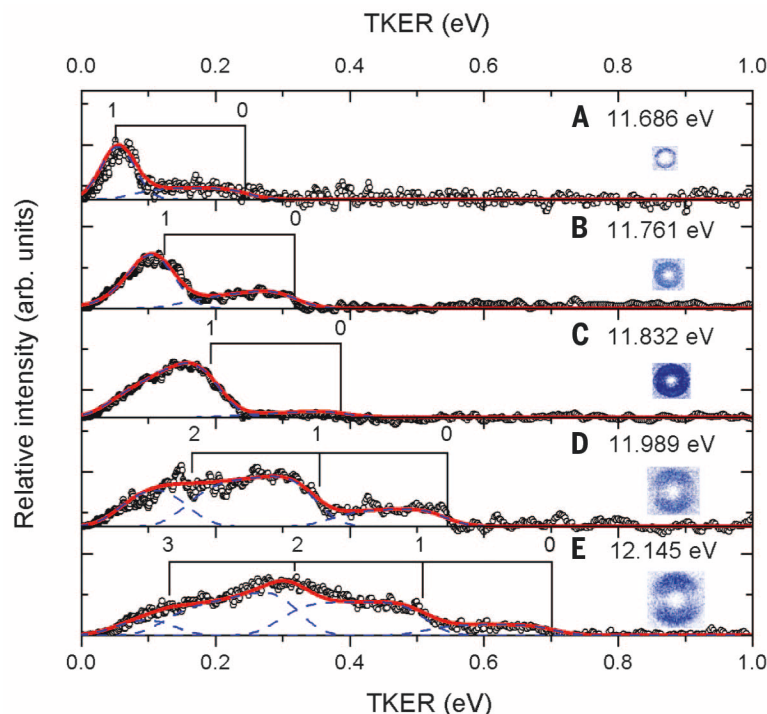
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## SUPPLEMENTARY MATERIALS

www.sciencemag.org/content/346/6205/61/suppl/DC1  
Materials and Methods  
Figs. S1 to S4  
References (28–37)

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**Fig. 4.  $C(^3P_2)$  velocity-map ion images and corresponding TKER spectra.** VUV<sub>1</sub> photoexcitation of  $CO_2$  was tuned to the absorption bands peaked at the energies indicated above the ion image inserts. TKER spectra are plotted as open circles. Angular anisotropy  $\beta$  parameters derived from these  $C(^3P_2)$  ion images are (A)  $\beta = 0.45 \pm 0.09$ , (B)  $\beta = 0.45 \pm 0.08$ , (C)  $\beta = 0.72 \pm 0.07$ , (D)  $\beta = 0.97 \pm 0.09$ , and (E)  $\beta = 1.02 \pm 0.08$ . The simulation (red lines) shows that the threshold energies observed are consistent with the known thermochemical threshold of 11.44 eV for the  $C(^3P) + O_2(X^3\Sigma_g^-)$  channel, and  $O_2(X^3\Sigma_g^-)$  photofragments are formed in  $v = 0$  to 3 vibrational levels, as marked on top of the TKER spectra of (A) to (E). The dashed lines show the simulated rotational profiles of individual vibrational bands of  $O_2(X^3\Sigma_g^-)$ .



## Evidence for direct molecular oxygen production in CO<sub>2</sub> photodissociation

Zhou Lu, Yih Chung Chang, Qing-Zhu Yin, C. Y. Ng and William M. Jackson (October 2, 2014)  
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### Editor's Summary

#### Illuminating oxygen out of carbon dioxide

It has long been known that high-energy ultraviolet light can split carbon dioxide into CO and O fragments. Lu *et al.* have now uncovered a parallel pathway that appears to yield C and O<sub>2</sub> instead (see the Perspective by Suits and Parker). By precisely measuring the energy and trajectory of the carbon fragment after CO<sub>2</sub> irradiation, O<sub>2</sub> formation could be inferred. The results introduce a potential mechanism for abiotic oxygen production in CO<sub>2</sub>-heavy atmospheres of other planets.

*Science*, this issue p. 61; see also p.30

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