# Photodissociation of Ozone from 321 to 329 nm: The Relative Yields of O(<sup>3</sup>P<sub>2</sub>) with O<sub>2</sub>( $X^{3}\Sigma_{q}^{-}$ ), O<sub>2</sub>( $a^{1}\Delta_{q}$ ) and O<sub>2</sub>( $b^{1}\Sigma_{q}^{+}$ )

C. K. Ulrich,<sup>†</sup> J. Chen, O. Tokel,<sup>‡</sup> and P. L. Houston\*

School of Chemistry and Biochemistry, Georgia Institute of Technology, Atlanta, Georgia 30332, United States

# S. Yu. Grebenshchikov

Theoretische Chemie, Technische Universität München, Lichtenbergstraße 4, D-85747 Garching, Germany

Supporting Information

**ABSTRACT:** Product imaging of  $O({}^{3}P_{2})$  following dissociation of ozone has been used to determine the relative yields of the product channels  $O({}^{3}P_{2}) + O_{2}(X {}^{3}\Sigma_{g}^{-})$  of ozone. All three channels are prominent at all wavelengths investigated. O<sub>2</sub> vibrational distributions for each channel and each wavelength are also estimated assuming Boltzmann rotational distributions. Averaged over wavelength in the measured range, the yields of the  $O({}^{3}P_{2}) + O_{2}(X {}^{3}\Sigma_{g}^{-}), O({}^{3}P_{2}) + O_{2}(a {}^{1}\Delta_{g}), \text{ and } O({}^{3}P_{2}) + O_{2}(a {}^{1}\Delta_{g}), O({}^{3}P_{2}) + O_{2}(a {}^{1}\Delta_{g}) + O_{2}(a {}^{1}\Delta_{g}), O({}^{3}P_{2}) + O_{2}(a {}^{1}\Delta_{g}), O({}^{3}P_{2}) + O_{2}(a {}^{1}\Delta_{g}), O({}^{3}P_{2}) + O_{2}(a {}^{1}\Delta_{g}), O({}^{3}P_{2}) + O_{2}(a {}^{1}\Delta_{g}) + O_{2}(a {}^{1}\Delta_{g}) + O_{2}(a {}^{1}\Delta_{g}) + O_{2}(a$  $O_2(b^{-1}\Sigma_{\sigma}^{+})$  channels are 0.36, 0.31, and 0.34, respectively. Photofragment distributions in the spin-allowed channel O(<sup>3</sup>P) +  $O_2(X^{3}\Sigma_{g}^{-})$  are compared with the results of quantum mechanical calculations on the vibronically coupled PESs of the



singlet states B (optically bright) and R (repulsive). The experiments suggest that considerably more vibrational excitation and less rotational excitation occur than predicted by the quantum calculations. The rotational distributions, adjusted to fit the experimental images, suggest that the dissociation takes place from a more linear configuration than the Franck-Condon bending angle of 117°. The dissociation at most wavelengths results in a positive value of the anisotropy parameter,  $\beta$ , both in the experiment and in the calculations. Calculations indicate that both nonadiabatic transitions and intersystem crossings substantially reduce  $\beta$  below the nominal value of 2.

# INTRODUCTION

The dissociation of ozone above the 310-nm wavelength at which the O(<sup>1</sup>D) + O<sub>2</sub>( $a^{1}\Delta_{g}$ ) channel is just accessible has been shown to be interesting, complex, and important to our understanding of atmospheric processes. Vibrationally excited ozone has been implicated as the source of a long, temperature-dependent tail in the yield of  $O(^{1}D) + O_{2}(a^{1}\Delta_{g})$  with increasing wavelength above 310 nm.<sup>1-4</sup> Because  $O(^{1}D)$  plays such an important role in the ozone production, the yield of  $O(^{1}D)$  as a function of wavelength is important input for models of stratospheric chemistry.<sup>5–9</sup> In addition, spin-forbidden products, such as  $O({}^{3}P) + O_{2}(a {}^{1}\Delta_{\sigma})$ , are also produced. Such observations are important to understand because  $O_2(a \ ^1\Delta_{\alpha})$  is the source for the "airglow" in the atmospheres of Earth, Venus, and Mars.<sup>10</sup> Other spin-forbidden channels, such as  $O({}^{3}P) + O_{2}(b {}^{1}\Sigma_{g}{}^{+})$ , and spin-allowed channels, such as  $O({}^{3}P) + O_{2}(X {}^{3}\Sigma_{g}{}^{-})$ , have also been observed in this wavelength range.<sup>11–14</sup> However, a systematic study of the relative yield of these channels as a function of wavelength has yet to be reported.

Ball et al.<sup>1-4</sup> measured the temperature dependence of the yield of  $O_2(a \ ^1\Delta_g)$  by 2 + 1 resonant enhanced multiphoton ionization (REMPI) as a function of wavelength above 310 nm. Below this wavelength, the yield  $O_2(a \ ^1\Delta_g)$  matched accurately

the previously determined  $O(^{1}D)$  yield. However, between 309 and 319 nm, the temperature variation provided convincing evidence that vibrationally excited ozone is responsible for  $O(^{1}D) + O_{2}(a^{1}\Delta_{\sigma})$  production. Above about 320 nm, the yield of  $O_2(a^{-1}\Delta_{\alpha})$  as a function of temperature was nearly invariant, and the authors proposed that the principal mechanism for its production was spin-forbidden formation of  $O(^{3}P) + O_{2}(a^{1}\Delta_{\alpha})$ . Direct measurement of the kinetic energy release of the  $O_2(a)$  $^1\Delta_g)$  and O(<sup>1</sup>D) confirmed these proposals.<sup>4,15</sup> The translational anisotropy and angular momentum polarization of  $O_2(a^{-1}\Delta_{\sigma})$ production as well as the vector properties of the  $O(^{1}D)$  were also subsequently reported.<sup>5,16,17</sup>

While many investigators have studied the fall-off of the quantum yield for O(<sup>1</sup>D)+ O<sub>2</sub>( $a^{1}\Delta_{g}$ ) starting at 310 nm,<sup>5-8,15</sup> O'Keeffe et al.<sup>11-14</sup> were the first to show the complexity of other product channels in the ozone dissociation wavelength range above 320 nm. These include:

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Figure 1. Top view of the interaction chamber and laser setup. The chamber is enlarged with respect to the rest of the diagram for ease of viewing. The molecular beam path and the electrodes are centered within the chamber and with respect to the detector.

$$O_3 \to O_2(X^3 \Sigma_g^-) + O(^3 P) \tag{1}$$

$$\rightarrow O_2(a^1 \Delta_g) + O(^3 P)$$
 (2)

$$\rightarrow O_2(b^1 \Sigma_g^+) + O(^{3}P)$$
(3)

O'Keeffe et al.<sup>11–14</sup> were the first to observe the last channel. By monitoring the arrival time distribution of the O(<sup>3</sup>P) in a time-of-flight mass spectrometer, the authors also obtained some information on the vibrational distributions of the O<sub>2</sub> products in each channel. However, the information was of somewhat low resolution and was provided at a single wavelength. More detailed information was provided for the rotational distribution of O<sub>2</sub> in the O<sub>2</sub> ( $b \ \Sigma^+_g$ ) + O(<sup>3</sup>P) channel.<sup>14</sup>

A second aspect of the studies by O'Keeffe et al. concerns the yield spectrum of  $O_2^+$  as a function of wavelength following dissociation of  $O_3$  and ionization of  $O_2$  at the same wavelength. This yield spectrum is a complicated convolution of the ozone absorption, its dissociation to give various electronic states of  $O_2$ , and the multiphoton ionization probability for the states of  $O_2$  so produced. A simpler yield spectrum, that of  $O(^3P)$  as a function of ozone dissociation wavelength, was also reported.

Schinke and co-workers<sup>18 $\simeq 22^{\circ}$ </sup> examined earlier work,<sup>23–28</sup> performed new ab initio calculations, and found that the explanation for the complicated absorption spectrum of ozone in the region from 200 to 370 nm is due to a transition from the ground state to the bound region of the B 3 <sup>1</sup>A' (<sup>1</sup>B<sub>2</sub>) state. The Hartley band of ozone is due to absorption to the repulsive part of this same state. The optically bright B state has two  $C_s$  symmetric minima, with the O–O bond lengths 2.28 bohr (a<sub>0</sub>) and 3.2 bohr, and the bond angle of 108°. The  $C_{2\nu}$  symmetric Franck–Condon point is a saddle in the B state potential. This state, which correlates to O(<sup>1</sup>D) + O<sub>2</sub>( $a^{1}\Delta_{g}$ ), is bound but forms a crossing with another singlet state, commonly called R, leading to  $O_2(X^{-3}\Sigma_{g}^{-}) + O(^{3}P)$ , channel 1. A recent study by Grebenshchikov and Rosenwaks<sup>29</sup>

Production of the spin-forbidden channels 2 and 3 must take place by more complicated interactions with triplet excited states.

In this paper, we extend and improve on the measurements first made by O'Keeffe et al.<sup>11–14</sup> Improved resolution has been obtained by the use of velocity mapped product imaging.<sup>33,34</sup> Relative  $O(^{3}P)$  yields were measured as a function of wavelength from 321 to 329 nm, and images were analyzed to provide  $O_{2}$ vibrational information and relative yield data for channels 1, 2, and 3 at 17 discrete wavelengths in this region. Photofragment distributions in the spin-allowed channel are further compared to the quantum mechanical calculations in the vibronically coupled B and R singlet states. Preliminary conclusions on the dynamics of intersystem crossing from the singlet to the triplet states are given.

# EXPERIMENTAL SECTION

Briefly, ozone seeded at ~1% in helium was expanded in a skimmed molecular beam and dissociated at wavelengths between 321 and 329 nm. The  $O({}^{3}P_{2})$  and  $O_{2}$  products from this dissociation were then detected by 2 + 1 resonance-enhanced multiphoton ionization (REMPI), providing yield spectra and velocity mapped images at several wavelengths for each product.

**Apparatus.** Ozone was produced in a commercial ozone generator (LG–7, CD Laboratory) and stored in a trap on silica gel at -78 C. It was carried to the pulsed nozzle by ultrahigh purity helium (99.999%, Airgas) at a backing pressure of 2 psig. The mixture was supersonically expanded through the nozzle and collimated by a 0.5-mm diameter conical skimmer before entering the interaction region, defined as the region between a high-voltage repeller and an extractor electrode. One molecular beam of the dual-beam time-of-flight mass spectrometer apparatus<sup>35,36</sup> shown in Figure 1 was used for the experiment. In the interaction region, the ozone was crossed perpendicularly by two lasers, one used for dissociation of ozone, and another for detection of  $O({}^{3}P_{2})$ . The voltages of the repeller and extractor were set to allow the resulting ions to fly through the center holes

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of two grounded electrodes and then through a field-free flight tube to a position-sensitive dual plate MCP/Phosphor detector. The signal was detected by a photomultiplier tube (PMT) for the spectra, or by a CCD camera for velocity mapped images. The detector was gated to allow for the detection of either O or  $O_2$  ions based on their time-of-flight.

**Ozone Dissociation.** The ozone was dissociated by the doubled light of an optical parametric oscillator (Scanmate OPPO) pumped by a Nd:Yag laser (Spectra Physics GCR 230). Approximately 2–3 mJ/pulse of 321–329 nm light was focused by a 25-cm focal length lens to the center of the ozone beam.

 $O({}^{3}P_{2})$  REMPI Detection.  $O({}^{3}P_{2})$  was detected by 2 + 1 REMPI, via the O(3p  ${}^{3}P_{2} \leftarrow 2p {}^{3}P_{2}$ ) transition,  ${}^{37}$  with 1 mJ/ pulse of 225.65 nm light. For the probe laser, 25 mJ/pulse of 355 nm from the third harmonic of a Nd:Yag (Spectra Physics GCR 270), was mixed in a  $\beta$ -BaB<sub>2</sub>O<sub>4</sub> (BBO) crystal with 15 mJ of approximately 619 nm from a tunable dye (Rhodamine 620) laser (Scanmate 2E) pumped by the 532 from the same Nd:Yag. The 225.65 nm light was focused with a 10-cm focal length lens and intersected the molecular beam parallel to but counterpropagating with the dissociation laser, arriving approximately 5 ns later. For the  $O({}^{3}P_{2})$  yield spectrum, the dissociation laser was scanned, and the probe laser was held at the maximum of the  $O({}^{3}P_{2})$  REMPI peak. For the  $O({}^{3}P_{2})$  images, the dissociation laser was held at the wavelength of interest, while the overlapping probe laser was scanned to cover the Doppler width of the  $O(^{3}P_{2})$  detection peak.

**O**<sub>2</sub> **REMPI Detection.** In a single laser experiment, scanning the laser in the 321–329 nm region and detection of the mass corresponding to  $O_2^+$  produced a yield spectrum caused by dissociation of ozone followed by two-photon ionization of  $O_2$ . The yield in this case depends on the absorption of ozone, the production of  $O_2$  in the vibrational and electronic state being ionized, and the ionization probability for that state at the given wavelength. By using product imaging of the resulting  $O_2^+$  at several wavelengths, we were able in many cases to assign the  $O_2$  state that was being ionized as well as the intermediate state in the ionization. The results have been reported elsewhere.<sup>38</sup>

**Experimental Background Signal.** The  $O({}^{3}P_{2})$  images can have a background signal from ozone dissociation by the probe laser alone. This background was only significant when the dissociation laser (321–329 nm) did not have enough power to dissociate all of the ozone in the interaction region of the molecular and laser beams, such as dissociation on very small peaks in the action spectrum. This background only minimally affects the images since the most prominent peak from the 226nm dissociation of O<sub>3</sub> is slower than the peaks from the 321–329 nm dissociation.

**Calibration.** The spectrum and image wavelengths from our dissociation laser were shifted to vacuum wavelength based on calibration with two known Xe lines. Xenon (research-grade purity 99.995%, Airproducts) was introduced into the molecular beam and ionized by 3 + 1 REMPI at 320.450 and 323.575 nm.<sup>37,39</sup>

The magnification factor for the experimental set up was determined for conversion of pixels to millimeters in the images. O<sub>2</sub> (99.997% purity, Matheson Trigas) was introduced into the molecular beam. The 225.65 nm light was used to dissociate it and ionize  $O({}^{3}P_{2})$  by 2 + 1 REMPI. The total kinetic energy distribution was then compared to literature values<sup>40</sup> to determine the correct magnification factor for the apparatus at the voltages employed.

**Image Analysis.** The images were first analyzed in BASEX<sup>41</sup> to obtain the speed distribution of the reconstructed threedimensional (3D) image from its two-dimensional (2D) projection. They were then converted to velocity using the measured flight time and the magnification factor of the apparatus. Finally using conservation of energy and momentum, the velocity distribution was converted to total kinetic energy for the dissociation.

The anisotropy parameter,  $\beta$ , was calculated for the peaks in the images, which are associated with O<sub>2</sub> states, based on the equation  $I(\theta) = C[1 + \beta P_2(\cos \theta)]$ . BASEX was used to calculate  $\beta$  for each pixel of the image. This data was then used to determine the average  $\beta$  for each peak in the images, often associated with a specific O<sub>2</sub> state.

### CALCULATIONS

The calculations reported in this work were performed using two electronic states, appropriate for the description of photodissociation in the Hartley and Huggins bands: (1) The optically dark electronic state R correlating with the "triplet" dissociation channel 1, and (2) the optically bright electronic state B ( $3^{1}A'$ ), correlating with the "singlet" dissociation channel  $O(^{1}D)/O_{2}(a)$  $^{1}\Delta_{\sigma}$ ) lying ~3 eV above the triplet channel. This set will hereafter be termed the "B/R model." The potential energy surfaces (PESs) of the diabatic B and R states, used in this study, have been described;<sup>29</sup> the diabatic coupling matrix element between them is constructed by Schinke and McBane,<sup>30</sup> and the transition dipole moment surface between the states B and X is constructed using the ab initio data of Baloïtcha and Balint-Kurti<sup>31</sup> The potential energy, vibronic coupling, and transition dipole moment surfaces accurately reproduce the UV absorption of ozone in the Huggins and Hartley bands.<sup>29</sup> The diabatic R state is purely repulsive and rather anisotropic. The states B and R cross near equilibrium of the B state. Cuts through the PESs of the these two states are shown in Figure 2b.



**Figure 2.** Shown in panel (a) is the contour map, in the plane of the two O–O bond distances  $R_{1,2}$ , of the optically bright singlet state B, as well as the crossing seams with the repulsive singlet state R (red line), and the triplet states of A' (brown) and A" (black) symmetries; the bending angle is fixed at 117°. Panel (b) shows cuts through the singlet states (red) and the triplet states (brown and black for <sup>3</sup>A' and <sup>3</sup>A", respectively) along one O–O bond. The second O–O bond and the bending angle are fixed at 2.4a<sub>0</sub> and 117°, respectively.

The B-state PES and its topography are discussed in detail elsewhere;<sup>29</sup> a two-dimensional contour map for the angle fixed at the Franck–Condon value is shown in Figure 2a. For a fixed permutation of oxygen atoms, the PES has two equivalent  $C_s$  wells, 4400 cm<sup>-1</sup> deep and separated by a  $C_{2\nu}$  barrier lying slightly above the dissociation threshold. Equilibrium bond lengths in

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each well are 2.28  $a_0$  (short O–O bond) and 3.20  $a_0$  (long O–O bond); the equilibrium bond angle is 108°. Both O–O bonds in the B state deviate noticeably from the  $C_{2v}$  equilibrium of 2.41  $a_0$  in the ground electronic state X, while the bending angle is close to  $117^\circ$  in X. One therefore expects stretching motion to be excited in the optical transition to the B state; bending excitation is less probable.

Quantum mechanical calculations of the angular, rotational, vibrational, and kinetic energy distributions of the photofragments for the photodissociation of ozone excited in a parallel excitation from the state with total angular momentum J = 0 in X to the state J = 1 in B have been performed using the program package "PolyWave" developed by one of the authors.<sup>32</sup>

# RESULTS

Two types of experiments were performed. In the first, the dissociation wavelength was scanned between 321 and 329 nm while monitoring the yield of  $O({}^{3}P_{2})$  by REMPI. The resulting action spectrum is shown in the top panel of Figure 3.



**Figure 3.** Top panel:  $O({}^{3}P_{2})$  yield spectrum from the dissociation of ozone with assignments for the ozone absorption band. The absorption is labeled by the upper vibrational levels as  $(v_{1},v_{2})$ , with  $v_{3} = 0$  for all assignments shown.<sup>13</sup> Bottom panels: Yields for the three electronic channels as a function of dissociation wavelength. The dashed lines give the values averaged over wavelength.

Assignments in the figure are based on the work of O'Keeffe et al.,<sup>13</sup> where the label for the ozone absorption identifies the upper level as  $(v_1, v_2)$  and has  $v_3 = 0$  for all assignments. O'Keeffe et al. assumed the quantum numbers  $v_1$  and  $v_2$  to denote symmetric and antisymmetric stretch excitations in the bright B state. Schinke and co-workers demonstrated that the  $C_s$  wells of this state support local mode vibrations that are best characterized as "long-bond" and "short-bond" stretches. The quantum number  $v_3 = 0$  indicates that the bending mode in the bands is unexcited. In the second type of experiment, product imaging<sup>33,34</sup> of the O(<sup>3</sup>P<sub>2</sub>) was performed at each of 17 wavelengths in the scanned range. A typical image and the total kinetic energy (TKE)

range. A typical image and the total kinetic energy (TKE) spectrum derived from it are shown in Figures 4 and 5. The TKE spectrum is analyzed based on the conservation of energy equation,

$$KE = E_{h\nu} - D(O_2(f) - O) - T_{O_2}(\nu) - F_{\nu,O_2}(J)$$
(4)



**Figure 4.** Image of  $O({}^{3}P_{2})$  velocity for dissociation of  $O_{3}$  at 322.016 nm.

Here, KE is the kinetic energy of dissociation measured from the image,  $E_{h\nu}$  is the energy of the dissociation photon,  $D(O_2(f) - O)$  is the energy for the dissociation of  $O_3 \rightarrow O({}^3P_2) + O_2(f)$ , where  $f = X^3 \Sigma_g^-$ ,  $a^1 \Delta_{g'}$  or  $b^1 \Sigma_b^+$ , and  $T_{O_2}(\nu)$  and  $F_{\nu,O_2}(J)$  are the internal vibrational and rotational energies of the  $O_2$  molecule in the designated final electronic state.<sup>42-45</sup>

Fits to the images were made by assuming a Boltzmann distribution of rotational energy convoluted with experimental parameters for each vibrational level and each electronic state. The populations and the rotational temperature were allowed to vary, while a program minimized the sum of the squares of deviations between the model and the data. A single rotational temperature was used for all vibrational and electronic states. Two variations were run, one, called "full," in which population was allowed in up to 11 vibrational levels for each electronic channel and one, called "restricted," in which only v = 0-5 were allowed for  $O_2(X \, {}^{3}\Sigma_{g}^{-})$ , v = 0-3 for  $O_2(a \, {}^{1}\Delta_{g})$ , and v = 0-6 for  $O_2(b \, {}^{1}\Sigma_{g}^{+})$ .

The dashed lines in Figure 5a,b show the results of these analyses. The red, green, and yellow lines show the contributions from the electronic channels producing  $O_2(X^{3}\Sigma_g^{-})$ ,  $O_2(a^{1}\Delta_g)$ , and  $O_2(b \ ^1\Sigma_g \ ^+)$ , respectively. The dashed blue line gives the sum of all three channels. The vibrational distributions for each channel are also determined, as reported in Table 1. In the full model, higher vibrational levels of  $O_2(X \, {}^3\Sigma_g^{-})$  and  $O_2(a \, {}^1\Delta_g)$  are "recruited" to fit the data where the  $O_2(b \, {}^1\Sigma_g^{+})$  levels are not sufficient. This results in unrealistic, multimodal vibrational distributions for the lower electronic states and probably overestimates their electronic yields, while underestimating the yield of  $O_2(b \ ^1\Sigma_g^{+})$ . The restricted model prevents this effect by cutting off the vibrational distributions when the levels of one electronic state start to overlap with the next higher energy state. It results in more reasonable vibrational distributions but probably underestimates the yield of O<sub>2</sub>  $(X \ ^{3}\Sigma_{g}^{-})$  while overestimating that of O<sub>2</sub> $(b \ ^{1}\Sigma_{g}^{+})$ . The comparison of the two methods provides reasonable error limits on the electronic yield analysis. The fits with the full model have sums of squared di



**Figure 5.** (a) Fit with "full" model; (b) fit with "restricted" model. In each case, the thick black line gives the total kinetic energy distribution for the dissociation of O<sub>3</sub> at 322.016 nm. The red, green, and magenta lines are overlay of the partial distributions for O<sub>2</sub>( $X^{3}\Sigma_{g}^{-}$ ), O<sub>2</sub>( $a^{1}\Delta_{g}$ ), and O<sub>2</sub>( $b^{1}\Sigma_{g}^{+}$ ), respectively. The blue dashed line is the sum of the three partial distributions. The hot band absorption at this wavelength is (5,3) (see Figure 3).

Table 1. The $\beta$	Calculated	for Each	Major Peak	of Each O	$^{3}P_{2}$	) Image <sup>a</sup>
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ssociation wavelength (nm)	$\beta$ a	βb	βc	$\beta$ d
321.199	1.93	1.59	$0.61 ({}^{1}\Delta_{g} + {}^{1}\Sigma_{g}^{+})$	1.29
321.538	1.70	0.89	0.78	
322.016	1.57	0.82 $({}^{3}\Sigma_{g}^{-} \text{ or } {}^{1}\Delta_{g})$	$1.34 \left( {}^{1}\Delta_{g} + {}^{1}\Sigma_{g}^{+} \right)$	
322.628	1.96	1.91	1.96	
322.628	2.00	1.98	1.98	
322.73	1.68	$0.69 ({}^{3}\Sigma_{g}^{-} + {}^{1}\Delta_{g})$	0.80	
322.73	1.68	$0.69 \left( {}^{3}\Sigma_{g}^{-} + {}^{1}\Delta_{g} \right)$	1.06	0.66
323.70	1.57	1.21	$0.56 ({}^{1}\Delta_{g})$	
324.192	1.99	$1.73 ({}^{1}\Delta_{g} + {}^{3}\Sigma_{g}^{-})$	1.78	
324.192	1.99	2.00 $({}^{3}\Sigma_{g}^{-} + \text{little}^{-1}\Delta_{g})$	1.59 $({}^{1}\Delta_{g})$	1.78
324.589	2.00	1.99	1.97	
324.835	1.79	1.64 $({}^{3}\Sigma_{g}^{-} \text{ or } {}^{1}\Delta_{g})$	1.52 $({}^{1}\Sigma_{g}^{+} \text{ or } ({}^{1}\Delta_{g}^{+}+{}^{1}\Sigma_{g}^{+})$	
324.906	1.79	$0.81({}^{1}\Delta_{g} \text{ or } {}^{3}\Sigma_{g}^{-} + {}^{1}\Delta_{g})$	0.99 $({}^{1}\Sigma_{g}^{+} \text{ or } {}^{1}\Delta_{g} + {}^{1}\Sigma_{g}^{+})$	
324.906	1.77	0.79 $({}^{1}\Delta_{g} \text{ or } {}^{3}\Sigma_{g}^{-} + {}^{1}\Delta_{g})$	0.82 $({}^{1}\Sigma_{g}^{+} \text{ or } {}^{1}\Delta_{g}^{+}+{}^{1}\Sigma_{g}^{+})$	
324.954	1.86	1.75	1.57	
325.051	1.57	0.61	0.55	
325.567	1.46	$1.04 (^{3}\Sigma_{g}^{-})$	$0.25 ({}^{1}\Delta_{g} + {}^{1}\Sigma_{g}^{+})$	
325.567	1.34	$0.07 (^{3}\Sigma_{g}^{-} + ^{1}\Delta_{g})$	0.42 $({}^{1}\Delta_{g} + {}^{1}\Sigma_{g}^{+})$	
325.776	1.17	0.64	-0.59	
326.494	1.68	1.22	0.64	
327.157	1.32	$-0.12~(^{1}\Delta_{g} \text{ or } ^{3}\Sigma_{g}^{-})$	0.80 $({}^{1}\Sigma_{g}^{+} \text{ or } {}^{1}\Delta_{g} + {}^{1}\Sigma_{g}^{+})$	$0.21({}^{1}\Sigma_{g}^{+}\text{or}^{-1}\Delta_{g}+{}^{1}\Sigma_{g}^{+})$
328.022	1.84	1.32	1.81	

<sup>*a*</sup>The first column is the dissociation wavelength. The next four columns are  $\beta a - \beta d$ , where the a, b, c, and d represent the order of the  $\beta s$ , a being associated with the fastest peak (or section) and d with the slowest. In general, each can be associated with the sibling O<sub>2</sub> product although some are mixed. Unless otherwise noted,  $\beta a$  goes with O<sub>2</sub> ( $X^3 \Sigma_g^{-}$ ),  $\beta b$  with ( $a^1 \Delta_g$ ), and  $\beta c$  and  $\beta d$  with ( $b^1 \Sigma_g^{+}$ ).

deviations about 30% lower on average than those with the restricted model and result in higher average rotational temperatures, 3580 K versus 1880 K. These higher temperatures minimize the deviations but provide unrealistic fits, particularly at low total kinetic energy (see Supporting Information).

In a similar way, electronic and vibrational distributions were determined at 16 other wavelengths in the scanned range. The electronic distributions with error limits are summarized in Table S1 and shown in the bottom three panels of Figure 3. The vibrational distributions for each wavelength and each analysis method are listed in Table S2–S7 of the Supporting Information. Figures S1–S17 of the Supporting Information show fits to the data similar to those in Figure 5. Angular distributions were also obtained, as summarized in Table 1.

## DISCUSSION

At all wavelengths examined, we found evidence for all three electronic channels 1–3. O'Keeffe et al.<sup>12</sup> detected O(<sup>3</sup>P<sub>0</sub>) at a single wavelength near 322.64 nm and also found evidence in the time-of-flight spectrum for all three channels. They report a 31% yield for O<sub>2</sub>( $X^{3}\Sigma_{g}^{-}$ ), 35% for O<sub>2</sub>( $a^{1}\Delta_{g}$ ), and 34% for O<sub>2</sub>( $b^{1}\Sigma_{g}^{+}$ ). Our results at 322.628 nm give 35%, 25%, and 40%, with error bars that would encompass the O'Keeffe et al. results.

A few correlations can be noted from the data. First, the electronic distribution does show a slight dependence on whether the dissociation takes place on resonant absorptions (assigned in Figure 3) or on nonresonant ones. In general, the fraction of  $O_2(X \ ^3\Sigma_g^{-})$  is somewhat lower than its average, and

the fraction of  $O_2(b\ ^1\Sigma_g\ ^+)$  is somewhat higher for resonant dissociation. The yield of  $O_2(a \, {}^1\Delta_{\sigma})$  is nearly equal to its average throughout the spectral region. Second, while there is substantial variation in the vibrational distributions with analysis method, a few observations can be made. The vibrational distribution for  $O_2(X^{3}\Sigma_g^{-})$  does not peak at  $\nu = 0$  and may be multimodal. The vibrational distributions for  $O_2(a \ ^1\Delta_g)$  and  $O_2(b \ ^1\Sigma_g^+)$  probably peak at v = 0 or v = 1. Third, the temperature characterizing the rotational distributions is high. Its average over the results of all wavelengths is 1880 K for the full analysis and 3660 K for the restricted analysis. The latter is artificially high, since the restriction on vibrational levels is partially overcome by increasing the breadth of the rotational distribution. A value near 2500 K is probably a good average. Although it is expected that the rotational temperature should decrease with increasing electronic and possibly vibrational energy, the fits used a single temperature in order to decrease the number of variables. Thus, rotational temperatures should be regarded as an average over electronic and vibrational distributions. Finally, the angular distributions are characterized by positive values of  $\beta$ , signifying a parallel transition. The  $\beta$  values for the spin-allowed channel,  $O_2(X^{3}\Sigma_g^{-})$ , are generally more positive than those with the spinforbidden channels.

Measured distributions in the spin-allowed channel 1 can be compared with the calculations using the B/R model. Figure 6a



**Figure 6.** Comparison between experimental and theoretical results calculated using the B/R model. In all cases, the red curves are the results calculated for  $\lambda = 320$  nm, the blue curves are the results calculated for  $\lambda = 330$  nm, and the black curves are the experimental results for the restricted fit to  $\lambda = 322.016$  nm. (a) Relative kinetic energy distributions for O(<sup>3</sup>P) and O<sub>2</sub>( $X^{3}\Sigma_{g}^{-}$ ); (b) vibrational distributions for O<sub>2</sub>( $X^{3}\Sigma_{g}^{-}$ ).

shows distributions of relative kinetic energies of  $O({}^{3}P)$  and  $O_{2}(X {}^{3}\Sigma^{-}{}_{g})$  evaluated for the photolysis wavelengths of 320 nm (red) and 330 nm (blue). The most probable kinetic energies lie between 15 000 cm<sup>-1</sup> and 20 000 cm<sup>-1</sup>, implying that on average 75% to 80% of the available energy is converted into translation. At the same time, the distribution tails extend to considerably

smaller energies and become increasingly pronounced with growing wavelength. The calculated distributions are structured, but the peaks only qualitatively follow excitations of O<sub>2</sub> vibrations with the frequency of  $\sim 1550$  cm<sup>-1</sup>. As discussed below, the rotational excitation is strong at all calculated wavelengths. Experimental distributions, shown in red lines in Figure 5 for  $\lambda$  = 322.016 nm, differ considerably for the two fitting models used to analyze the raw images. The calculations demonstrate a considerable degree of similarity to the distributions obtained in the restricted model in Figure 5b, both on terms of the average energy and the distribution width. The black line in Figure 6a shows the restricted model experimental result for  $\lambda = 322.016$  nm. By contrast, the full model results in a much broader distribution with several pronounced low energy peaks that have no counterparts in the calculations for  $\lambda > 300$  nm.

Angular photofragment distributions in the two state calculations are consistent with experiment, too. The anisotropy parameter  $\beta$  can range between 2.0, which indicates a parallel electronic transition, to -1.0, which indicates a perpendicular transition. Shown in Figure 7 are the experimental values of the



**Figure 7.** Calculated and experimental (green dots) values of the anisotropy parameter  $\beta$ a as a function of wavelength. The calculations are for the spin-allowed channels O(<sup>3</sup>P) + O<sub>2</sub>(X <sup>3</sup> $\Sigma_g^-$ ) (lower, red average) and O(<sup>1</sup>D)+O<sub>2</sub>(a <sup>1</sup> $\Delta_g$ ) (upper, black average) channels.

anisotropy parameter  $\beta$  from Table 1, corresponding to  $O_2(X)$  ${}^{3}\Sigma_{\rm g}^{-}$ ), and the quantum mechanical  $\beta_{\rm O1D}$  and  $\beta_{\rm O3P}$  parameters calculated in the spin-allowed channels  $O(^{1}D)/O_{2}(a^{-1}\Delta_{g})$  and  $O({}^{3}P)/O_{2}(X {}^{3}\Sigma_{g})$ , respectively. Both measured and calculated  $\beta$ values are positive with  $\beta > 1$ , indicating a parallel transition, although experimental values tend to exceed theoretical ones for  $\lambda$  > 320 nm. Substantial fluctuations are seen in  $\beta$  values. In the calculations, these fluctuations reflect the diffuse structure of the upper portion of the Huggins absorption band. The wavelength range in Figure 7 extends across the threshold of the  $O(^{1}D)/$  $O_2(a^{-1}\Delta_{\sigma})$  dissociation channel of the optically bright B state and thus includes the red wing of the Hartley band. Photofragments in the singlet channel have consistently larger  $\beta$  values,  $\beta_{\rm O1D} \approx$ 1.8, than those following the adiabatic path into channel 1. The transition probability into channel 1,  $P \sim 1 - \exp(-\Delta E_{ad} \tau_{diss})$ , controlled by the adiabatic Massey parameter  $\Delta E_{\rm ad} \tau_{\rm diss}$ , grows with the ozone lifetime  $\tau_{\rm diss}$ .<sup>22</sup> It is the molecules with large lifetimes that dissociate through channel 1, and this is reflected in the smaller  $\beta_{O3P}$  values. The distinction between  $\beta_{O3P}$  and  $\beta_{O1D}$  is clear even in the immediate vicinity of the threshold of the singlet channel (near 310 nm).

The most substantial differences between two state quantum calculations and the experiment are found in the vibrational and rotational distributions of  $O_2(X^{3}\Sigma_g^{-})$ , shown in Figure 6b,c. The calculated rotational distributions in panel c are approximately bell shaped and "hot", with the maximum reached for  $J_{02} \approx 55$ , nearly independently of the wavelength  $\lambda > 320$  nm. Strong rotational excitation is the result of the strong torque produced on the  $O_2$  rotor at the initial stages of the photodissociation, with about 18% of the available energy going into final rotation.<sup>45</sup> This result is consistent with the impulsive model<sup>46</sup> if the fraction  $E_{rot}$ /  $E_{\rm avl} \approx \sin(\alpha)/4$  is evaluated at the Franck–Condon bending angle  $\alpha = 117^{\circ}$ , implying that the molecule dissociates mainly with this valence angle and the bending excitation in the optical transition is minor. This is expected because the equilibrium angles in the states X and B are similar and also because most assignments of the Huggins band agree<sup>13</sup> that the bending quantum number  $v_3 = 0$  is appropriate for most of the observed bands, including those addressed in the present work. By contrast, the distribution most consistent with the experimental results is a Boltzmann one with  $T \approx 2500$  K, shown as the black line in Figure 6c. It should be kept in mind, however, that the experimental rotational distribution represents a weighted average of many actual distributions in different vibrational and electronic states.

The differences between experiment and theory in the rotational state distributions are paralleled by the differences in the vibrational state distributions. The calculated distributions in Figure 6b all peak at  $v_{O_2} = 0$  and fall off with increasing vibrational quantum number. This is in disagreement with the fit to experimental data which suggests more excited vibrational distributions. The distribution from the restricted fit at  $\lambda$  = 322.016 nm is shown as the black line in Figure 6b. One of the reasons for this discrepancy can be the artificial restriction of the quantum mechanical model to only two states B and R. Indeed, at shorter wavelengths, for example  $\lambda = 234$  nm, this model produces strongly inverted vibrational distributions peaking at  $v_{O_2} > 15$ . At these wavelengths, both the O(<sup>1</sup>D)/O<sub>2</sub>( $a^{-1}\Delta_g$ ) and the O(<sup>3</sup>P)/O<sub>2</sub>(X  ${}^{3}\Sigma_{g}^{-}$ ) dissociation channels are open. The highly vibrationally excited O2 fragments stem from molecules with the longest lifetimes  $au_{ ext{diss}}$ , and, according to the above adiabatic Massey parameter, the longer lifetimes increase the probability of switching from the B state to the R state and ending up in channel 1. At long wavelengths  $\lambda > 310$  nm, the O(<sup>1</sup>D)/  $O_2(a^{-1}\Delta_{\alpha})$  channel is closed, and all molecules are forced to dissociate via the R state. As a result, the selectivity with respect to vibrational excitation in channel 1 is lost, and the calculated distributions are cold. One might expect that some of the selectivity might be recovered by extending the B/R model and adding triplet states and the spin-forbidden triplet channels to the calculation. The other reason for the observed discrepancy could be the functional form of the distributions chosen to fit the experimental images. For example, a fit based on a Boltzmann distribution with one effective rotational temperature for all electronic channels might underestimate the rotational excitation of the lowest channel 1 and compensate the difference by inverting the vibrational populations.

A surprising result of this study is that, over a range of dissociation wavelengths, the yields for the three channels 1–3 are nearly equal to one another. Averaged over wavelength, the quantum yield for  $O_2(X \, {}^3\Sigma_g^{-})$  is 0.36, while those for  $O_2(a \, {}^1\Delta_g)$ 

and  $O_2(b \ {}^{1}\Sigma_g^{+})$  are 0.31 and 0.34, respectively. Of the states crossing the optically bright B state, there is only one surface (the singlet R state) leading to  $O(^{3}P) + O_2(X \ {}^{3}\Sigma_g^{-})$ , while there are five triplet surfaces leading to  $O(^{3}P) + O_2(a \ {}^{1}\Delta_g)$  and three leading to  $O(^{3}P) + O_2(b \ {}^{1}\Sigma_g^{+})$ . Thus, a statistical distribution would give a ratio of 1:15:9, or quantum yields of 0.04, 0.6, 0.36. The spin-allowed channel is consequently about 9.0 times higher than one would expect on statistical grounds.

Direct excitation of the triplet states is expected to be extremely inefficient. Grebenshchikov and Rosenwaks<sup>29</sup> calculated the singlet/triplet transition dipole moments from X to be about 400 times smaller than that from X to B. Thus, the difference between the statistical and the observed populations most probably reflects the difference in strengths of couplings which mediate population of the spin-allowed channel 1 (vibronic coupling at the conical intersection between B and R states) and the spin-forbidden channels 2 and 3 (spin-orbit coupling between singlet and triplet states). In order to clarify the dynamics of the intersystem crossing leading to the spinforbidden channels, 17 triplet PESs of states  $1^{3}A' - 8^{3}A'$  and  $1^{3}A'' - 9^{3}A''$ , relevant for the dissociation into the three lowest spin-forbidden channels, are being currently calculated at the MRD-CI level of theory. Examples of cuts through their surfaces are shown in Figure 2b. The calculated triplet states form multiple conical intersections with each other, which induce strong vibronic couplings inside the triplet manifold. Twelve uppermost calculated states intersect the singlet B (Figure 2a) and R states. At these intersections, the triplet and the singlet states are efficiently coupled via the first order spin-orbit interaction (the matrix elements, ranging from  $20 \text{ cm}^{-1}$  to 80 cm<sup>-1</sup>, are typical for the second row atoms).

Multiple state intersections render ab initio calculations severely unstable. For this reason, construction of the full coupled PESs is not complete yet, and the combined ab initio and quantum dynamical analysis of the experimental data on the spinforbidden photodissociation will be published at a later date. Preliminary results at 320 nm indicate that, if the singlet B/R potentials are coupled to the triplet states, the populations of the spin-allowed channel 1 and the spin-forbidden channels 2 and 3 become approximately equal, at  $\sim 0.5$  (no further discrimination into separate channels is presently possible). Additionally, the calculated anisotropy parameter  $\beta$  for the molecules diverted into the spin-forbidden channels is evaluated to lie below 0.5, substantially smaller than the  $\beta$  parameter in the spin-allowed channel 1. A certain reduction in the  $\beta$  values for the spinforbidden channels can be surmised in the experimental data in Table 1, too. It is interesting to speculate on what might be the cause of the high spin-forbidden yields in the experiment and the calculation. Reduced  $\beta$  parameters indicate that the lifetimes of molecules excited with  $\lambda > 310$  nm become longer. Indeed, the optically bright B state becomes bound at these wavelengths, the spin-allowed channel O(<sup>1</sup>D)/O<sub>2</sub>( $a^{1}\Delta_{g}$ ) becomes accessible only through excitation of the hot bands,<sup>29</sup> resonances in the Huggins band narrow down, and the molecules trapped in the  $C_s$  wells of the B PES are allowed to recross the intersection seams between B and R and the triplet states many times. The weakness of the spin-orbit coupling, driving the intersystem crossing dynamics, might be compensated by the multiple recrossings of the singlet/ triplet intersections. The emerging scheme is reminiscent of the mechanism suggested to explain the nearly gas kinetic efficiency of the spin-forbidden quenching of  $O(^{1}D) \rightarrow O(^{3}P)$  in collisions with  $CO(X \Sigma^+)$ .<sup>47,48</sup> Exact dynamical calculations that prove this

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mechanism in the spin-forbidden dissociation of ozone are still pending.

The experimental results indicate less energy in translation and rotation and substantially more energy in vibration. The difference in the rotational distributions between experiment and theory might indicate that the dissociation takes place from a geometry characterized by a somewhat more linear angle. A 117° angle predicts a peak in the spin-allowed channel 1 at about I =56, whereas the experimental data, assuming a Boltzmann distribution, are consistent with a rotational temperature of about 2500 K, or a value of J = 35 at the peak of the distribution. One has to remember, however, that the experimental distribution refers to a weighted average over all electronic channels. The anisotropy parameters, which are nearly all positive, some near the parallel limit, also indicate that the dissociation takes place from a more linear configuration than 117°. These results might also indicate that either the spin-allowed or the spin-forbidden transition probabilities depend on the vibrational quantum number  $v_{O_2}$ .

# CONCLUSIONS

The relative yields of O(<sup>3</sup>P) with O<sub>2</sub> ( $X^{3}\Sigma_{g}^{-}$ ), O<sub>2</sub>( $a^{-1}\Delta_{g}$ ) and  $O_2(b \ ^1\Sigma_g^+)$  have been measured in the photodissociation of ozone at 17 wavelengths between 321 and 329 nm. The yields are comparable at all wavelengths and close to their wavelengthaveraged values of 0.36, 0.31, and 0.34, respectively. At wavelengths where there is resonant absorption of ozone, the yield of  $O({}^{3}P)$  with  $O_2(X {}^{3}\Sigma_g^{-})$  is slightly diminished, while that with  $O_2(b^{-1}\Sigma_g^+)$  is slightly increased. The vibrational and rotational distributions of the O2 fragment in each electronic channel are determined by fitting the peaks in the observed kinetic energy distributions to a model. The fits predict highly rotationally excited fragments in all channels ( $T_{\rm rot} \approx 2500$  K), accompanied by inverted vibrational excitations. The experimental distributions in the spin-allowed channel  $O(^{3}P)/O_{2}(X)$  ${}^{3}\Sigma_{g}^{-}$ ) are compared to the results of two-state quantum mechanical calculations including the singlet B and R states. Calculations predict highly excited Gaussian-like rotational distributions peaking near  $J_{\rm O_2} \approx 50$  and cold vibrational distributions always peaking at  $v_{O_2} = 0$ . The origin of the discrepancy with experiment might indicate a substantial impact of the triplet states on the photofragment distributions in the spin-allowed channel. Finally, the anisotropy of fragment recoil indicates absorption by a parallel transition with fairly rapid dissociation on the time scale of rotation.

# ASSOCIATED CONTENT

#### Supporting Information

Supporting Information includes graphical results of the analysis of the data at all wavelengths along with tables of electronic and vibrational yields. This information is available free of charge via the Internet at http://pubs.acs.org

## AUTHOR INFORMATION

#### **Corresponding Author**

\*Mailing address: School of Chemistry and Biochemistry, Georgia Institute of Technology, Atlanta, GA 30332, U.S.A.; Phone: 404-385-3410; E-mail: phouston7@gatech.edu.

### **Present Addresses**

<sup>†</sup>Chemistry Department, ISC 331, SUNY Geneseo, 1 College Circle, Geneseo, NY 14454. <sup>‡</sup>Harvard Medical School, Division of Biomedical Engineering at Brigham and Women's Hospital, Bio-Acoustic-MEMS in Medicine (BAMM) Laboratory, Harvard-MIT Health Sciences & Technology, 65 Landsdowne St. PRB 252, Cambridge, MA 02139, USA.

#### Notes

The authors declare no competing financial interest.

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