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Dissociation dynamics of C_3O_2 excited at 157.6 nm

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The dissociation of carbon suboxide by single photon absorption at 157.6 nm has been studied under the collisionless environment of a molecular beam. The primary products are 2CO + C $[{}^{3}P(97\%) \text{ or } {}^{1}D(3\%)]$. The spin-orbit levels of the ${}^{3}P$ carbon are statistically distributed. The CO rotational populations in the first four vibrational levels are found to be well described by Boltzmann distributions with temperatures 3430, 4120, 4670, and 2340 K for v = 0,1,2,3, respectively. A second low temperature component in the v = 0 rotational distribution is attributed to CO produced in coincidence with $C(^{1}D)$. Significant population is found in the first four vibrational levels with less than 3% estimated in the higher levels; a vibrational temperature of 3700 K fits the distribution. Analysis of the Doppler profiles of the CO and carbon suggest that the dissociation is stepwise; the first dissociation appears to be described by an anisotropy parameter near $\beta = 2$, while the second appears to be isotropic. The mean CO fragment speeds were nearly constant for all rotational levels, though slightly faster for v = 1than v = 0. From the translational energetics of the CO at least a small amount of stable C₂O is inferred to exist. The overall energetics place the stable C_2O quantum yield under 2% assuming that excited C_2O is not radiatively stabilized. We were unable to detect C_2O directly in any electronic state. The dissociation of C_3O_2 into $C(^{3}P) + 2CO$ appears to be best described as a stepwise reaction that produces a nearly statistical partitioning into all fragment degrees of freedom. The best agreement is obtained for an intermediate $C_2 O$ electronic state in the vicinity of the \tilde{b} state (e.g., \tilde{b}, \tilde{a} or \tilde{A}); a ground state C_2O intermediate is unlikely. The singlet to triplet crossing most likely occurs in the C_2O system on a time scale longer than a rotation (a few picoseconds).

I. INTRODUCTION ...

The dynamics of molecular dissociations in which two or more bonds are broken and three fragments are produced has drawn increasing attention.¹⁻⁵ Many of the general characteristics of such dissociations are not yet established, and a key question which needs to be answered is whether or not the bonds break in a concerted fashion. The problem is made more complicated by the fact that independently measured states of the three fragments are not uniquely correlated by the conservation laws of energy, linear momentum, and angular momentum. Relatively few detailed product state distributions for triple fragmentations have been reported to date. The photodissociation of carbon suboxide through its 158 nm absorption band is a system which yields three fragments.6 We show below that analysis of the energy distribution in these fragments can yield insight into the mechanism of the dissociation.

Interest in the C_3O_2 molecule has been wide ranging. The photolysis of C_3O_2 has been a subject of study for more than three decades.⁷ C_3O_2 has been proposed as a possible constituent of the Venusian atmosphere,⁸ as the red color of the Martian surface,⁹ and as a primordial biomolecule.¹⁰ It has been used as a convenient source of both electronically excited ¹D and ground state ³P carbon atoms for reaction with H₂, N₂, CO, NO, O₂, N₂O, and CH₄.¹¹⁻¹⁹ Reactions of its C₂O products have also been studied.¹⁷⁻²² Because the CO by-product in carbon production is volatile, C₃O₂ is a potential carbon source for epitaxial diamond film growth. Its unusually low ν_7 bending vibration has been investigated by microwave techniques.²³ It has drawn theoretical interest²⁴ because it is one of the molecules whose ground state is poorly predicted by Hartree–Fock theory,²⁵ and its infrared spectrum has been the subject of controversial interpretations.²⁶⁻²⁸

Bayes has shown that the primary photochemical processes for wavelengths longer than 207 nm are^{7,17}

$$C_{3}O_{2} + h\nu \rightarrow CO(X^{1}\Sigma^{+}) + C_{2}O(\tilde{X}^{3}\Sigma^{-}), \quad \lambda < 290 \text{ nm},$$
(1)

$$C_{3}O_{2} + h\nu \rightarrow CO(X^{1}\Sigma^{+}) + C_{2}O(\tilde{a}^{1}\Delta \text{ or } \tilde{b}^{1}\Sigma^{+})$$

$$\lambda < 240 \text{ nm.}$$
(2)

For wavelengths shorter than 207 nm, single photon carbon atom production becomes energetically possible,^{11,14} schematically indicated as follows, either with a C_2O intermediate,

$$C_{3}O_{2} + h\nu \rightarrow CO(X^{1}\Sigma^{+}) + C_{2}O^{*},$$
 (3)

 $C_2 O^* \to CO(X^1\Sigma^+) + C(^3P), \quad \lambda < 207 \text{ nm},$ (4)

$$C_2 O^* \to CO(X^1 \Sigma^+) + C(^1 D), \quad \lambda < 172 \text{ nm}, \qquad (5)$$

or without an intermediate,

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$$C_{3}O_{2} + h\nu \rightarrow 2CO(X^{1}\Sigma^{+}) + C(^{3}P \text{ or } {}^{1}D),$$

 $\lambda < 207,172 \text{ nm.}$ (6)

Braun *et al.*¹¹ flash photolyzed $C_3 O_2$ in a bulb over the range 140–170 nm and reported production of carbon in its first three electronic states (${}^{3}P, {}^{1}D, {}^{1}S$) in the ratios 4:1: < 0.1 (with ~20% uncertainty). The ${}^{1}S$ production showed a nonlinear power dependence, indicating that a higher order process was contributing. The authors placed a lower limit on the carbon atom quantum yield at 75%. Husain and Kirsch²⁹ provide circumstantial evidence of at least some primary $C_2 O$ production in the same wavelength range. Recently, carbon atom production has been observed directly from excimer photolysis at 193 nm to account for 6% of the dissociating $C_3 O_2$.³⁰

The VUV absorption spectrum of C_3O_2 , observed by Roebber, is highly overlapped but can be broken into three distinct regions: (a) a small peak at 178 nm which overlaps (b) the largest peak centered at 158 nm (extending from 140 to above 170 nm), followed by (c) a congested sequence of Rydberg lines to the ionization limit (~10.60 eV).^{31,32} Roebber persuasively assigns the band at 178 nm as a vibronically allowed electronic transition from a linear ground state (${}^{1}\Sigma_{g}^{+}$) to a mixture of the linear ${}^{1}\Sigma_{g}^{-}$ and ${}^{1}\Delta$ states (7.0 eV). He assigns the major VUV absorption near 158 nm (7.9 eV) to an allowed transition to the first member of a $ns \leftarrow \pi$ Rydberg series with strong contributions from $(2p){}^{1}\Sigma_{u}^{+}$ and $(4\sigma^{+}){}^{1}\Pi_{u}$. He determines this excited state to be linear. It is this absorption that is of principal interest in the current study.

Several questions remain unanswered. Singlet $C_2 O$ is a candidate intermediate in dissociation through both the 178 and 158 nm bands, but detection has proven difficult. Morrow and McGrath³³ reported diffuse bands in the near-UV which they attributed to possible $C_2 O$ singlet transitions, but subsequent attempts to detect the singlet spectroscopically have failed.³⁴ Although the preponderance of kinetic evidence seems to establish singlet production,³⁵ McFarlane *et al.*³⁰ were unable to reconcile the detailed CO rotational and vibrational excitation populations with production of a singlet $C_2 O$. Finally, Bauer *et al.* have reported emission from the $C_2 O$ triplet \tilde{A} state following 178 nm excitation of $C_3 O_2$.³⁶

The identity of the carbon products is not well established either. For the 158 nm absorption band there have been no measurements of the $C({}^{3}P)$ to $C({}^{1}D)$ branching ratios or quantum yields since Braun et al., and Husain and Kirsch flash photolyzed C_3O_2 through a mixture of several excited states. Chemical scavenging studies of the photoproducts are equivocal due to the multiplicity of the chemical pathways for carbon addition reactions.^{12,19} Below the threshold for carbon production, photolysis in the presence of methane produces ethylene, while above this threshold acetylene is also produced.¹⁸ Even though it is attractive to suppose acetylene is produced in a carbon insertion reaction, kinetic evidence has not been able to rule out reaction with an excited C₂O.¹² Okabe has suggested that only the direct three-body fragmentation channel may exist in the VUV, arguing that the two-step process would surely have left detectable quantities of unreacted $C_2 O.^{35}$

In this investigation we have sought to overcome the kinetic obstacles by conducting the experiment in the collisionless environment of a molecular beam. We obtain the nascent product internal state distributions, kinetic energies, and branching ratios for the channels producing CO and carbon atoms. The broadband flash photolysis light sources used in previous investigations are replaced here with an F_2 excimer laser nearly coinciding with the 158 nm absorption peak. We know of no other molecular beam study, and of only one previous application of 157.6 nm laser photolysis to C_3O_2 (in which the authors pointedly called for a better carbon state branching ratio estimate).¹⁵

The aim of this work is not only to establish the primary products of the $C_3 O_2$ dissociation but also to illuminate the dynamics of the dissociation process itself. Does the process occur through an intermediate $C_2 O^*$ which subsequently decomposes, or does it proceed in a concerted three body decomposition?

II. EXPERIMENTAL

A. VUV-LIF apparatus

Molecular (CO) and atomic (carbon) fragments are detected in our experiment by vacuum-ultraviolet laser induced fluorescence (VUV-LIF) following the 157.6 nm photolysis of C_3O_2 . The apparatus is similar to that described previously,³⁷ so only a brief outline is presented here in order to highlight the features particular to this work.

A sample of 0.5% C₃O₂ in 2 atm He was expanded into a vacuum chamber through a pulsed molecular beam valve with a 0.5 mm orifice. A 157.6 nm photolysis beam from a plane polarized F2 excimer laser (Lambda Physik EMG-101) intersected the free jet expansion about 12 mm downstream, where the local rotational and translational temperatures of the C₃O₂ were approximately 2-5 K. A tunable VUV laser source (generated by four-wave sum mixing of two dye laser frequencies in Mg vapor) propagated in a direction mutually orthogonal to the molecular and photolysis beams and probed the nascent CO or carbon photofragments following a 200 ns delay from the photolysis pulse. The resulting VUV fluorescence was imaged onto a solarblind photomultiplier tube (PMT) in the plane of and 45° to the two lasers. Because the photolysis light, probe light, and fluorescence emission are all in the vacuum ultraviolet, the path between every optical element was either evacuated to a pressure below 50 mTorr (0.07 Pa) or purged of air by flowing argon. The fluorescence signal was processed by an SRS boxcar averager and a PDP-11 computer which also controlled the scanning of the VUV dye lasers. The power of each laser was monitored by solar-blind photomultipliers (EMR and EMI) and used for shot-to-shot normalization of the fluorescence intensity. All CO and carbon signals were found to be linear with both pump and probe laser powers over the ranges used for the measurements.

Sub-Doppler measurements were made of several C and CO rovibronic lines by installing etalons in each of the dye lasers used for VUV generation so as to reduce the VUV linewidth from 0.6 to 0.21 cm⁻¹.

B. Visible/IR LIF apparatus

The previously described apparatus was modified in order to search for excited or ground electronic state C₂ O fragments. First, spontaneous fluorescence from electronically excited C₂ O produced by the dissociation event was probed in the 300–900 nm region. The solar-blind PMT was replaced by a 0.4 m Jarrel–Ash monochromator, collection optics to match its *f* number, and an RCA 1500 PMT sensitive from 300 to 900 nm. Emission from the \tilde{A} state of C₂ O is known to lie in the region 680 to 900 nm.²⁰ This region received most of our attention, although the whole 300–900 nm region was examined. The well-known ~750 nm emission from the F₂ laser produced a "blind spot" in our detection at 750 \pm 10 nm.

Secondly, we attempted to observe the presence of ground state C_2O by single photon LIF via the \tilde{A} ${}^{3}\Pi_{i} \leftarrow \tilde{X}$ ${}^{3}\Sigma^{-}$ transition. 34 The experimental arrangement was similar to the VUV-LIF arrangement. The probe laser was a Nd:YAG pumped dye laser (Quanta-Ray) producing light in the 650–700 nm range. The probe laser was slightly focused in the detection zone to a 4 mm² spot with a pulse energy of 30 mJ. The scattered probe light and the red emission from the F₂ laser were removed either partially by glass filters (Corning RG780, RG716) or more completely by the monochromater. The glass filters provided wider band detection at the expense of increased background noise.

C. C₃O₂ synthesis and sample handling

Carbon suboxide was synthesized by the method of Batchelor et al. in which malonic acid is dehydrated and the product distilled.³⁸ For molecular beam expansion, $C_1 O_2$ was seeded in helium at 2 atm by drawing the helium through a stainless steel cold trap containing 1 ml of the sample; concentrations of 0.5% or 5% were maintained by immersing the trap in a -78 °C dry ice/acetone bath or a - 46 °C chlorobenzene slush, respectively.³⁸ Between experiments the sample was stored frozen in glass under liquid nitrogen. Degradation of sample on a scale of weeks³⁹ or surface catalytic degradation³⁸ reported by others was not observed. The mass spectrum of a sample aged two months showed ethylene and methanol impurities; the ethylene impurity is a common synthesis by-product. However, under normal photolysis neither of these are expected to dissociate to CO or C fragments nor interfere with the nozzle delivery. We employed a small procedural modification to the synthesis described by Batchelor. Instead of a U-tube containing Ca + CaO to remove acetic acid product, a further distillation step (acetone/dry ice, -78 °C) was used. In addition to the simplicity afforded by this modification, a 50% improvement in yield was found (1.5 ml of C₃O₂ produced from 20 g of malonic acid).

D. Impurities, nonlinear processes, and secondary processes

Under collisionless molecular beam conditions bimolecular chemistry can usually be ignored; only multiple photon or nonmonomer reactants can confuse the primary process. The C_3O_2 oscillator strength³¹ of 1.5 is very large and further assures that the production of CO from impurities incorporated at the time of synthesis is negligible. The major impurities detected by mass spectral analysis (methanol and ethylene) are unlikely to produce CO, and the undetected trace impurities would be unlikely to have an oscillator strength sufficient to dominate the absorption. Moreover, we observed no batch-to-batch signal variations in spite of variations in impurity concentrations.

Although a direct temperature measurement of the parent C_3O_2 molecules following expansion in the molecular beam was not available, similar expansions of CO were cooled to ~ 3 K. The possible contamination of the monomer parent by clusters must always be addressed in any jet cooled experiment. Consequently, the experiment was repeated using a flowing, room temperature C₃O₂ source, which should be free of any clusters. This flowing source was constructed simply by attaching a convoluted tube to the nozzle, so that wall collisions rethermalize the C₃O₂ and He, which then effuse into the vacuum chamber. The ground state v = 0 bandhead of CO from photolyzed C₃O₂, which we expect to display the highest sensitivity to clustering, was similar at both 3 and 300 K. While this does not eliminate the possibility of C_3O_2 clusters in the jet, it shows that the data can be considered uncontaminated by CO fragments produced from clusters. Further evidence for negligible cluster influence has been seen in a multiphoton ionization apparatus in our laboratory.⁴⁰ Even though the concentration of C₃O₂ was ten times larger in the MPI apparatus than in the LIF apparatus, the measured v = 0 and 1 rotational distributions agreed quantitatively with the LIF measurements.

Although other workers^{11,13,29,35} have demonstrated or suspected multiphoton processes in the VUV absorption, our signals became nonlinear only when the focal point (1 m lens) of the several mJ photolysis laser beam was within \sim 10 cm of the molecular beam. All measurements reported here were carried out under unfocused or loosely focused conditions. These conditions would seem to eliminate the subsequent photolysis of primary photolysis products.

III. RESULTS

A. CO internal energy

The CO rotational and vibrational populations were obtained from spectroscopic measurements of the 0–0, 2–0, 1– 1, 0–1, 0–2, 3–2, 2–3, 4–3, 3–4, and 7–5 vibrational bands of the CO $A \leftarrow X$ transition. The breadth of the spectral region covered by these bands (145–170 nm) was spanned with several laser dyes and two magnesium electronic transitions. A region of the CO LIF spectrum containing the 1–1 and 4–3 bandheads as well as high-J lines of the 0–0 band is shown in Fig. 1. Overlapping this region are some very strong atomic carbon lines.

The population of each rotational level within a vibrational band was determined by weighting each P, Q, and Rline amplitude by its Hönl–London factor and correcting for the known dark state electronic perturbations.⁴¹ The rotational distributions for each vibrational level are shown in Fig. 2. Within each vibrational band the rotational distribution can be fit well by a single temperature, with the excep-



FIG. 1. A region of the CO and C(${}^{3}P$) LIF spectrum containing several carbon lines as well as the CO 1–1 and 4–3 bandheads and high-J lines of the 0–0 band.

tion of v = 0 which shows a 4% contribution at a second, lower temperature. This cold feature, while relatively small in overall population, is concentrated into fewer rotational lines than the hotter feature and so can be easily discerned in the figure. The v = 1 data is the most extensive and is described accurately by a temperature of 4670 K even out to J = 75. Data for v = 2 were difficult to obtain at high J because of overlaps with other strong bands, however the fit to a single temperature is very accurate up to the highest rotational level resolved.

The rotational temperatures for each vibrational level are summarized in Table I. It is interesting to note that the rotational temperature does not decline monotonically with increasing vibration but instead increases from v = 0 to a peak in v = 2. This is contrary to the normal expectation that rotational excitation decreases with increasing vibrational excitation.

The total population of each vibrational level was determined by using its rotational temperature to extrapolate to



FIG. 2. The CO rotational distributions for each vibrational level. The four vibrational levels are shown with the proper relative scaling and the best Boltzmann fit. The v = 0 level is fit to two Boltzmann distributions.

TABLE I. Rotational energy of the CO fragment for each vibrational state.

v	T _{rot}	P _{vib}
0	3430 ± 80 K	0.54
	334 + 20 K	0.04ª
1	4120 + 80 K	0.27
2	4670 + 300 K	0.10
3	2340 + 200 K	0.05
(4)	_	(<0.01) ^c
• •	$(T_{\rm rot} = 3700 {\rm K})^{\rm b}$	$(T_{\rm vib} = 3700 {\rm K})^{\rm b}$

"This cold feature is ascribed to the $C(^{1}D)$ channel.

^b The cold feature is not included in the weighted average temperature.

"Estimated from signal-to-noise ratio.

regions where measurements could not be made. Although this procedure probably results in a slight overestimate of the highest J level populations, it is preferable to ignoring unmeasured lines. The summed rotational amplitude in each band was weighted by a calculated⁴² CO $A \leftarrow X$ Franck– Condon factor to give the relative vibrational level population.

We observe significant population in the first four vibrational levels in the ratios 58:27:10:5 (v = 0,1,2,3, respectively). While v = 4 and v = 5 levels were detected, their intensities were insufficient to determine the rotational distribution; we place an upper bound of < 1% in each. The relative vibrational level populations are described well by a single temperature of 3700 K. Coincidentally, the population-weighted average rotational temperature is also 3700 K. While there is no justification for expecting a Boltzmann distribution to describe the rotational (or vibrational) distributions—especially in the case of fixed available energy—it seems that the large surplus of available energy over the amount in any particular degree of freedom makes the Boltzmann distribution a reasonable characterization of the data.

B. CO sub-Doppler profiles

Doppler line shapes of selected P, Q, and R rotational lines spanning J = 7-60 in v = 0 and J = 15-59 in v = 1were recorded. Some of these for v = 1 are reproduced in Fig. 3; those for v = 0 are similar. The VUV probe laser linewidth (FWHM ≈ 0.21 cm⁻¹) is shown in the lower right panel. There are three factors which influence the Doppler line shape of a fragment: (i) its kinetic energy distribution, (ii) its recoil anisotropy, and (iii) the vector correlation between its rotational angular momentum and its recoil direction.⁴³

Several features, typical of all the CO Doppler profiles, are apparent in top two panels of Fig. 3. (a) The P/R and Qlines for the same (v,J) level are almost identical; (b) the profiles all appear fairly Gaussian in shape (a second Gaussian fitted just to the wings of the profile is for purposes of later discussion); and (c) the width of each line remains fairly constant from v = 0; J = 7 to v = 1 J = 59 even though the internal energy of the CO is increases by 9000 cm⁻¹. Deviations from Gaussian behavior increased with fragment internal energy, but became conspicuous only for the highest J levels measured, as is shown in the lower left panel of Fig. 3. Similarly, the P/R lines became very slightly



FIG. 3. Doppler line shapes for selected lines of CO v = 1. The laser line shape for the Doppler measurements is indicated in the lower right corner. The top two panels are typical of all the low- and mid-J line shapes for v = 0 and 1. Two Gaussian lines are fit to each top panel: (1) a fit over the whole curve, (2) a fit to only the wings, which overshoots the data. The lower right panel was typical of the high-J lines (J>40): the flattening of the peak is pronounced. A Gaussian fit to the wings is also drawn in the figure. The dashed lines indicate the maximum allowed translational energy for a dissociation producing C + 2CO. The dotted lines are explained in Appendix B.

(<5%) narrower than the corresponding Q lines as J increased.

These observations lend insight into the dissociation dynamics of C_3O_2 . The fact that there is at most a small difference between *P*-/*R*- and *Q*-branch line shapes suggests that **v**-**J** vector correlations⁴³ are not sharply defined by the dynamics. In the absence of other information, the small deviations from a Gaussian profile observed here cannot be interpreted exclusively as deviation either from an isotropic recoil distribution or from a Maxwellian speed distribution, the combination of which would produce a Gaussian Doppler profile. The Boltzmann behavior of the rotational and vibrational distributions biases us initially to believe that the deviation may result from the recoil anisotropy and that the speed distribution is fairly Maxwellian. This important distinction is elaborated in the discussion section.

For purposes of preliminary discussion, we calculate the average CO translational energy assuming the case of isotropic recoil. This estimate yields a translational temperature of 2600 K and an average CO kinetic energy of ~ 2700 cm⁻¹ for v = 1 and a temperature and energy of 2000 K and 2100 cm⁻¹ for v = 0; the weighted mean of these energies is 2300 cm⁻¹, equivalent to an rms recoil speed of 1400 m/s. Again, the trend with v is unusual; the normal expectation is that the translational energy will decrease as the internal energy increases. A worst case calculation for possible anisotropy in the Doppler profiles does not alter appreciably these average energies and speeds.

Nearly all of the fragments measured possess speed distributions consistent with the maximum allowed for momentum and energy conservation amongst three bodies (see Fig. 3). The v = 1, J = 59 level is an exception exceeding this limit and is shown in the figure. For an available energy E_{avail} , the maximum speed for a CO fragment with internal energy E_{int} is given by the ratio of the fragment masses:

$$v_{\rm max} = \sqrt{\frac{2(E_{\rm avail} - E_{\rm int})}{m_{\rm CO}}} \frac{(m_{\rm CO} + m_{\rm C})}{(m_{\rm C} + m_{\rm CO} + m_{\rm CO})}.$$
 (7)

For a fragmentation producing carbon $({}^{3}P)$ the available energy is 15 060 cm⁻¹. CO fragments exceeding this v_{max} must come from a process with a greater available energy than 15 060 cm⁻¹. The width corresponding to the v_{max} limit is indicated by dashed vertical lines in the figure.

C. Carbon products

For dissociation of C_3O_2 at 157.6 nm, the formation of atomic carbon in the ${}^{3}P_{0,1,2}$ and ${}^{1}D_2$ states is energetically possible. The energy levels of these states are specified in Table II, which also shows the various electronic transitions used for monitoring these carbon states. The wavelengths for these transitions fortuitously fall within CO vibronic bands as shown in Figs. 1 and 4.

1. Triplet branching ratios

The relative line strengths for the ${}^{3}P$ transitions were obtained from Ref. 44. Although the absolute magnitudes of these transition strengths are quoted as accurate only to 50%, the relative values within the ${}^{3}P$ manifold can be calculated using sum rules and are quite accurate. Using these data and the experimental intensities one obtains the branching ratio of ${}^{3}P_{2}$: ${}^{3}P_{1}$: ${}^{3}P_{0}$ as 5.07:2.78:1.15(\pm 20%). These ratios should be compared with the values 5:3:1 characterizing the statistical spin-orbit distribution.

2. Carbon/CO branching ratio

Measurement of the $C({}^{3}P)$ -CO population ratio can be made by comparing the intensities of the $C({}^{3}P)$ atomic lines to the spectrally neighboring CO rovibronic transitions displayed in Fig. 1. The population ratio is obtained by

$$\frac{N_{\rm CO}}{N_{\rm C}} = \frac{XI_{vJ}g_{\rm C}}{I_{ik}g_{\rm CO}f_{vJ}F_vH_J} \frac{\tau_{\rm CO}}{\tau_{\rm C}},\tag{8}$$

where $I_{v,J}$ is the intensity of a particular CO v'', J'' line,⁴⁵ I_{ik} is the intensity of one carbon line with angular momentum components *i* and *k* in the lower and upper states, $f_{v,J}$ is the normalized fraction of the v,J state in the CO manifold, F_v is the Franck–Condon factor for the CO transition, H_J is the Hönl–London factor for the CO transition, g_C and g_{CO} are

TABLE II. Carbon electronic state branching ratios, energy levels, and probe transitions.

Level	$E_J ({\rm cm}^{-1})^a$	Transition	λ(nm) ^a	Branching ratio
${}^{3}P_{0}$	44	$^{3}D_{1} \leftarrow ^{3}P_{0}$	156.031	55%
³ P ₁	16	$\begin{cases} {}^{3}D_{1} \leftarrow {}^{3}P_{1} \\ {}^{3}D_{2} \leftarrow {}^{3}P_{1} \end{cases}$	156.070 ^b	30%
$^{3}P_{2}$	0	${}^{3}D_{2} \leftarrow {}^{3}P_{2}$	156.129	12%
'D	10194	$^{1}D \leftarrow ^{1}D$	148.77	3%

^a Energies and wavelengths from Ref. 44.

^bOverlapping transitions, see Fig. 1.



FIG. 4. Doppler line shapes for carbon. (a) $C({}^{3}P)$ (all J levels were identical); (b) $C({}^{1}D)$ with CO (J = 27) companion. A best Gaussian fit is overlaid in each panel. The widths indicated are prior to deconvolution of the laser width.

the degeneracies of the upper states ($g_{\rm CO} = 2$), and $\tau_{\rm C}$ and $\tau_{\rm CO}$ are the radiative lifetimes of the upper states. A lifetime of 9.9 ns was used for CO⁴⁶ and lifetimes for the atomic transitions were taken from Ref. 44. The factor X includes any experimental factors that may differ between carbon and CO detection. Special care was taken in this analysis to factor in the response of the solar blind PMT, since the CO(v', J') state may fluoresce in wavelength regions where the PMT is less sensitive. Additionally, the nonlinearity of the PMT to strong signal levels was avoided by significantly reducing the VUV laser power for all data involving C(³P) lines.

The value we obtain for branching ratio of CO to C(${}^{3}P$) is 3.2 \pm 1.5. Since we will show below that the yield of C(${}^{1}D$) is very small, this branching ratio is nearly the same as the branching ratio of CO to total carbon, Φ_{CO}/Φ_{C} . Each dissociation event produces at least one CO fragment, but may produce more if some of the C₂O dissociates to C + CO. Thus, $\Phi_{C} = \Phi_{CO} - 1$, and we can calculate the quantum yields as

$$\Phi_{\rm co} \approx 1.5$$
 (1.3–2.0),
 $\Phi_{\rm co} \approx 0.5$ (0.3–1.0)

The ranges expressed in parentheses above reflect the 50% uncertainty in the relative line strengths for CO and C. While these numbers contain a large uncertainty, it still remains clear that $C({}^{3}P)$ production is a major channel in the photolysis of $C_{3}O_{2}$ at 157.6 nm.

3. The C(3P):C(1D) branching ratio

The atomic C(¹D) line is shown with sub-Doppler resolution in Fig. 4(b), neighbored by a fairly strong CO line. A similar calculation to the one above for C(³P) was performed for the ratio of CO:C(¹D) production. The ratio of C(³P):C(¹D) is then obtained from the two branching ratios with CO as $N(C^{3}P)/N(C^{1}D) = 97/3$, normalized to 100. The uncertainty in this number is somewhat difficult to pinpoint. Although each carbon transition strength in the NBS compendium⁴⁴ is quoted to only 50% accuracy, the relative value may be somewhat better. The result in any case demonstrates that C(¹D) is only a minor channel in the C₃O₂ dynamics. Ironically, the only previous reported use of the 157.6 nm laser photolysis of C₃O₂ was as a singlet D carbon source.¹⁵

D. Carbon sub-Doppler profiles

Sub-Doppler line shapes of carbon ${}^{3}P$ and ${}^{1}D$ fragments are shown in Fig. 4. Each is the sum of several scans. Both line shapes appear to be quite Gaussian, although the fact that the C(${}^{3}P$) profile is 50% wider indicates that it has a much faster recoil velocity than does the C(${}^{1}D$).

The best-Gaussian fit to the $C({}^{3}P)$ data, shown in Fig. 4(a), is almost indistinguishable from the data over the whole curve. Unlike the CO Doppler profiles, this Gaussian fit remains unchanged whether we bias the fit towards the faster C atoms in the wings or the slower ones in the center of the profile. We conclude that the $C({}^{3}P)$ fragments recoil both isotropically *and* with a Maxwellian velocity distribution. Only if some rare conspiracy between the recoil anisotropy and the recoil speed distribution existed could we otherwise observe such a perfect Gaussian Doppler profile.

It is straightforward to ascertain the $C({}^{3}P)$ velocity given the previous conclusion. After deconvolving the 0.21 cm⁻¹ laser line, the width (FWHM) of the carbon line in Fig. 4(a) is 0.73 cm⁻¹, which corresponds to a temperature of 3040 K and corresponds to an average energy of 3170 cm⁻¹ (37.9 kJ/mol) and an rms speed of 2510 m/s. A similar analysis shows the $C({}^{1}D)$ fragment to be highly isotropic with a temperature of 1110 K, an average energy of 1160 cm⁻¹ (13.8 kJ/mol), and an rms speed of 1520 m/s.

E. Attempts at C₂O detection

Little is known spectroscopically about C₂O; only the $\widetilde{A} \leftrightarrow \widetilde{X}$ transition has been positively identified.²⁰ Other states have been assigned energy levels by theoretical calculation.⁴⁷ We looked for evidence of C₂O production, particularly in the triplet states, $\widetilde{X}^{3}\Sigma^{-}$ and $\widetilde{A}^{3}\Pi$, but also in the predicted $\tilde{a}^{1}\Delta$, $\tilde{b}^{1}\Sigma^{+}$, and $\tilde{c}^{1}\Pi$ states shown diagrammatically in Fig. 5. Higher unassigned energy levels were not considered, but seemed unlikely to play a role.

We endeavored to cover this range of possible states by the following schemes. (i) Population of the $\tilde{A}^{3}\Pi$ state can be detected by spontaneous 650–900 nm fluorescence to the triplet ground state.²⁰ (ii) Conversely, the ground state can be detected by LIF through the $\tilde{A}^{3}\Pi$ state at 650 to 700 nm.³⁴ (iii) For the as yet unobserved singlets, the $\tilde{c}^{1}\Pi$ might



FIG. 5. C, symmetry correlation diagram. The triplet correlations are shown in dotted lines, while the singlet correlations are in solid lines. The energy spacings were taken from Roebber (C_3O_2) (Ref. 31); Walch (C_2O) (Ref. 47); and Wiese *et al.* (C) (Ref. 44). The absolute position of the C₂O stack is indicated only figuratively since it is not accurately known.

fluoresce directly to the $\tilde{a} \, {}^{1}\Delta$ (or $\tilde{b} \, {}^{1}\Sigma^{+}$) state or phosphoresce to the \tilde{A} or \tilde{X} states within our detection bandwidth. (iv) The $\tilde{a} \, {}^{1}\Delta$ or $\tilde{b} \, {}^{1}\Sigma^{+}$ states might be detectable by LIF through the $\tilde{c} \, {}^{1}\Pi$ state in the 650–700 nm wavelength range.

 $C_3 O_2$ was photolyzed at both 193 and 157.6 nm. For 193 nm photolysis, a previous study found that $C_2 O$ is formed with 94% quantum yield, although there is disagreement whether the electronic state produced is the \tilde{a} ¹ Π , \tilde{X} ³ Σ^- , or \tilde{A} ³ Π state.^{7,14,30} No spontaneous emission that could be attributed to $C_2 O$ was detected in our experiments at either photolysis wavelength. We also attempted LIF in the 650–700 nm region where the $\tilde{A} \leftarrow \tilde{X}$ (and maybe $\tilde{c} \leftarrow \tilde{a}, \tilde{c} \leftarrow \tilde{b}$) transition lies.^{34,47} Again no signal was observed at either photolysis wavelength. A possible explanation for the lack of signal following 193 nm photolysis is that the C_2O could be formed in the spin-conserving \tilde{a} ¹ Δ state. In the case of 157.6 nm photolysis, it seems likely that the quantum yield of stable C_2O is very small.

An upper bound for $C_2 O$ production from this null result was found by comparison to the sensitivity of the same apparatus (same geometry, same wavelength) for detection of HCO radicals.⁴⁸ With a fluorescence quantum yield of only $\sim 10^{-5}$, we were successful in detecting an HCO concentration of $\sim 10^{12}$ molecules/cc/quantum state. The $C_2 O$ radical, unlike HCO, is not predissociative (in its triplet states) and should have a fluorescence quantum yield many orders of magnitude larger than HCO given a transition mo-

ment of similar magnitude. By this appraisal we should have been able to observe either $\tilde{X} {}^{3}\Sigma^{-}$ or $\tilde{A} {}^{3}\Pi C_{2}O$ at a concentration of 10⁸ molecules/cc/quantum state; this yields an upper bound on the quantum yield for C₂O formation in either the ${}^{3}A$ or ${}^{3}X$ state of 5%. We conclude that if C₂O is formed in the C₃O₂ photodissociation at 157.6 nm then either (a) its quantum yield is smaller than 5%, (b) it is formed in one of the (metastable) singlet states, or (c) that it is formed in an unstable state that decomposes into CO + C with a lifetime that is competitive with emission. Although the negative result for detection of C₂O cannot be viewed as absolutely conclusive, it is consistent with the prediction in the discussion (Sec. IV A) that stable C₂O is not a product of the dissociation.

IV. DISCUSSION: PATHWAYS FOR C3O2 DISSOCIATION

The dissociation of C_3O_2 at wavelengths $\lambda > 207$ nm is known to lead to the production of CO and C_2O via¹⁷

$$C_3O_2 + h\nu \rightarrow CO(X^{\dagger}\Sigma^{+}) + C_2O^*,$$

 $\Delta H = 300 + 50 \text{ kJ/mol.}$ (9)

The electronic state of the C₂O produced has been the subject of some debate with proponents for each of the ground $\tilde{X}^{3}\Sigma^{-}$, $\tilde{A}^{3}\Pi_{i}$ or any of the low-lying singlet states \tilde{a} , \tilde{b} , or \tilde{c} shown in Fig. 5.

For $\lambda < 207$ nm, the chemical reaction producing 2CO molecules and a carbon atom is energetically feasible (see Fig. 5) via reactions (10a) and/or (10b):

$$C_{3}O_{2} + h\nu \rightarrow CO(X^{1}\Sigma^{+}) + C_{2}O^{*}$$

$$\rightarrow 2CO(X^{1}\Sigma^{+}) + C(^{3}P),$$

$$\Delta H = 577 \text{ kJ/mol}, \qquad (10a)$$

$$C_{3}O_{2} + h\nu \rightarrow 2CO(X^{1}\Sigma^{+}) + C(^{3}P),$$

$$\Delta H = 577 \text{ kJ/mol}. \qquad (10b)$$

Reactions (10a) and (10b) differ only in the dynamics and kinetics of formation of the final products. We will call these two pathways "stepwise" (10a) and "concerted" (10b), where what we mean by these two terms is as follows. In a stepwise reaction the C₂O decouples from (and may freely rotate with respect to) the CO before it subsequently dissociates, whereas in a concerted reaction no C₂O is formed as an identifiable intermediate. For dissociation at $\lambda = 193$ nm, McFarlane *et al.*³⁰ have measured the production of CO from C₃O₂ and established that both reactions (9) and (10) proceed, although reaction (10) was a minor pathway ($\approx 6\%$).

At the 157.6 nm dissociation wavelength used here a further channel opens:

$$C_{3}O_{2} + h\nu \rightarrow CO(X^{1}\Sigma^{+}) + C_{2}O^{*}$$

$$\rightarrow 2CO(X^{1}\Sigma^{+}) + C(^{1}D),$$

$$\Delta H = 698 \text{ kJ/mol}, \qquad (11a)$$

$$C_{3}O_{2} + h\nu \rightarrow 2CO(X^{1}\Sigma^{+}) + C(^{1}D),$$

$$\Delta H = 698 \text{ kJ/mol}. \qquad (11b)$$

Figure 5 includes not only the energy levels of C_3O_2 , C_2O , and C but the correlation between the states, based on

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symmetry considerations. These correlations assume a bent dissociation configuration (a bent mechanism has been demonstrated for the 193 nm process).²⁴ If a linear mechanism were assumed, the correlation between the $C_2 O$ and C would remain unchanged but $C_3 O_2$ states would be paired with $C_2 O$ states of the same term symbol. Singlet and triplet (dotted lines) manifolds would remain unmixed. $C_3 O_2$ states whose correlations are not indicated correlate with higher lying $C_2 O$ states that are not shown nor known.

The average energy contained in each fragment degree of freedom, as determined from our experimental data is summarized in Table III. We argue below that (1) stable C_2 O is not a major product of the dissociation at 157.6 nm, and that (2) nonetheless, it is likely that C_2O is an intermediate in the dissociation, i.e., that the dissociation is a stepwise process. We consider in detail only the channel producing $C({}^{3}P)$, which has been shown in the results section to comprise $\geq 97\%$ of the dissociation yield. Little can be said about the $C(^{1}D)$ channel. We have assigned the internal energy distribution of the CO fragments from this channel to the rotationally cold v = 0 feature (see Fig. 2), and we have established the translational energy distribution of the $C(^{1}D)$ (see Fig. 4). The available energy for CO translation can be calculated to be approximately 3500 cm^{-1} , or 42.5kJ/mol, split between the two CO fragments. The fraction of rotationally cold CO, 4%, agrees very well with our determination of the $C(^{1}D)$ quantum yield, 3%. We now turn to the $C({}^{3}P)$ channel.

A. Stable C₂O is not a major product of the dissociation

The available energy for the reaction producing $C({}^{3}P)$ is known accurately to be 15060 ± 350 cm⁻¹ (see Fig. 5).^{49,50} The observed average energy in each fragment degree of freedom for this channel (Table III) sums to 16500 ± 1500 cm⁻¹. The near concordance of these values implies that we have been successful in measuring (or estimating) the entire distribution of energy in each fragment,

TABLE III. Average energy of the fragments from 157 nm dissociation of C_3O_2 .

	Motion	Energy (kJ/mol)				
Species		Exptl.	Impulsive		Statistical	
			Stepwise	Concerted	Stepwise	Concerted
CO ⁽¹⁾	rot	30.1	\$ 51	26	35	29
	vib	17.9	1	1	23	18
	trans	31.6	39	19`	30	25
$C(^{3}P)$	trans	37.9	40	70	33	36
CO ⁽²⁾	rot	30.1	18	35	26	29
	vib	17.9)	1	14	18
	trans	31.6	32	30	26	25
Total		197.1	180ª	180°	(188) ^b	180ª

"Available energy for dissociation into C + 2 CO.

^bDissociation via $C_2O(\tilde{b}, \tilde{a}, \text{ or } \tilde{A})$: Fig. 6 shows that 6% of the C_2O is stable, which raises the apparent total energy.

and that there are no "missing" fragments or channels which have eluded detection.

It is unlikely that stable C_2O is a major product of the dissociation. Stable C_2O can be produced either by direct production with an internal energy lower than the C + CO dissociation threshold or by radiative stabilization of states above the threshold.

The C₂ O is not likely to be radiatively stabilized. This is evident from the absence of visible fluorescence as well as from the radiative lifetime of \tilde{A} state C₂O, which has been measured to be 50–200 μ s.³⁴ It seems reasonable that the radiative lifetime of the singlet states should be at least this long and perhaps many orders of magnitude longer if singlet-triplet phosphorescence is the only radiative channel. From our experiments we know that carbon is produced with a rate that corresponds to a complete yield within 100 ns. We therefore expect that radiative stabilization of a metastable C₂O should not compete with dissociative decay.

In absence of radiative stabilization, the production of a chemically stable C_2 O requires the concomitant production of CO fragment with internal energy а $E_{\rm int} > 15\,060 - E_{\rm trans}$, where $E_{\rm trans}$ is the total CO and C₂O translational energy. Consider specifically the case of the v = 1, J = 59 mentioned previously. CO fragments that absorb beyond the dashed lines in Fig. 3(c) are traveling too fast to have come from a process producing a carbon atom and consequently must be paired with a stable C_2 O. We can calculate the fraction of CO molecules that satisfy the energy inequality integrated over all rovibrational states of the CO. We make use of the observation that the Doppler profiles of CO that have been measured show an average translational energy almost independent of the v, J state examined and assume that this trend is maintained over all v,J. The total fraction of CO molecules produced corresponding to production of a stable $C_2 O$ molecule [reaction (9)] estimated in this manner is less than $\sim 2\%$. Nonetheless, there is some evidence that stable $C_2 O$ is produced in small quantities.

From these observations we establish that reaction (9) above is only a minor channel of the reaction $C_3 O_2 + 157.6$ nm \rightarrow products, and that $\sim 98\%$ of the excited $C_3 O_2$ must eventually dissociate into 2CO + C. These findings are consistent with our previous measurements of the relative CO and C branching ratios ($\Phi_{CO} \approx 1.3-2.0, \Phi_C \approx 0.3-1.0$) and the lack of spontaneous or laser-induced fluorescence from \widetilde{X} or \widetilde{A} state $C_2 O$.

B. The dissociation proceeds by a stepwise mechanism

Having established that stable $C_2 O$ is not a major photoproduct, we now wish to determine if it might still be an intermediate; i.e., whether the dissociation proceeds by reaction (10a) or (10b). In a stepwise reaction mechanism with a $C_2 O$ intermediate, production of two CO species having, on average, different energies is possible, perhaps even likely. Since most CO rovibronic transitions have Doppler profiles consistent with a single speed distribution, one could mistakenly lean toward the concerted mechanism. However, conservation of momentum shows that, even for a stepwise dissociation, assuming an isotropic distribution of fragments from the $C_2 O$ dissociation, the average velocities of the two CO fragments would be indistinguishable under our resolution (1550 vs 1460 m/s).⁵¹ We thus conclude that the lack of bimodality in the CO translational energy distribution does not preclude the stepwise process.

An argument against the concerted mechanism can be based on the measured average velocity of the $C({}^{3}P)$ atom. Conservation of momentum would require that the angle between the recoil directions of the two CO fragments be on average 140° in a concerted mechanism. Although it is known that the $C_{3}O_{2}$ molecule has low bending frequencies, it seems unlikely that an average concerted geometry could be so bent.

Support for the stepwise channel comes from consideration of the rotational line shapes. In Sec. III, we noted that the Doppler profiles of the CO fragments were slightly but noticeably and systematically different from Gaussian line shapes. This deviation is portrayed in Fig. 3; each panel displays a Gaussian fit only to the wings, to the points on the profile beyond the FWHM. For these points, the Gaussian fit to the wings had a deviation about 2.5 times less than did the Gaussian fit to the whole curve. In every case, for both P/R and Q lines, the center of the Doppler profile lies lower than the wing-fit Gaussian. The triplet carbon line shape, on the other hand, is an almost perfect Gaussian shape, from which fact we inferred in the results section that the dissociation produces an isotropically recoiling carbon fragment with a Maxwellian distribution of speeds. For a concerted triple fragmentation, conservation of momentum would ensure that the two associated CO fragments must also have isotropic, Maxwellian distributions. For a stepwise mechanism, on the other hand, the carbon fragment (a product of the secondary dissociation) can be observed to have an isotropic, Maxwellian distribution if either (a) both steps are isotropic and Maxwellian, or (b) the first step is anisotropic while the secondary dissociation is isotropic and produces carbon with a large velocity. In this latter case, if $v_{\rm C} > v_{\rm CCO}$ then the anisotropy produced by the first step will be much diminished by the isotropic recoil of the second. Condition (a) above also produces two CO fragments with isotropic, Maxwellian distributions. Hence, only under condition (b) will carbon and CO Doppler profiles be similar to those shown in Figs. 3 and 4. Since the experimental Doppler profiles indicate that there are two distributions of CO velocities, we conclude that reaction (10a) (stepwise) contributes to the distribution of fragments in this experiment.⁵²

The fact that all measured internal distributions are Boltzmann suggests that the first CO velocity distribution is anisotropic rather than non-Maxwellian. Appendix A demonstrates that the CO(v = 1, J = 59) Doppler profile shown in Fig. 3(a) is comprised >80% from contributions of the primary CO. Using a reasonable Maxwell-Boltzmann distribution of speeds (T = 2300 K), the Doppler profile is consistent with a primary dissociation step characterized by an anisotropy parameter of $\beta = 2$. Appendix B describes a fitting procedure for the Doppler profiles of other CO(v,J) states. The results are consistent with our hypothesis that dissociations producing other CO products are characterized by a primary step with an anisotropy parameter of $\beta = 2$ and a CCO speed distribution corresponding to a temperature of ~1900 K, and a secondary dissociation with a value $\beta = 0$ and a C temperature (in the CCO center of mass) of ~2500 K.

Further support for a C_2O intermediate comes from consideration of various models for the dissociation. Recently, the detailed internal energy distributions of the CO fragment from the (primarily) single bond photolysis of C_3O_2 at 193, 248, and 266 nm wavelengths were compared to both Kent Wilson's impulsive harmonic oscillator model and Wittig's separate statistical ensembles (SSE) model.^{30,53,54} Unfortunately, the added complication of the triple fragmentation makes these models less satisfying. Instead, we have considered four extremes of dissociation dynamics: concerted or stepwise processes occurring either impulsively or statistically. The details of these models have been discussed elsewhere;^{1,55} so only the results are presented here.

The impulsive models fail completely to predict the proper energy distributions. A stepwise, impulsive model fails when considering any of the four lowest C₂O electronic states as intermediates. The \tilde{A} , \tilde{a} and \tilde{b} C₂O intermediate states predict less than 5 kJ/mol for the energy of the carbon and the second CO, whereas the observed average energy of these fragments is $\approx 109 \text{ kJ/mol}$. Similarly, the \tilde{X} state intermediate C₂ O has less energy than the dissociation threshold. Finally, for a *c*-state intermediate the stepwise, impulsive model predicts only 18 kJ/mol for the internal energy of the second CO, a value far to low to be consistent with the 38 kJ/mol average we measure. We also considered an (asymmetric) impulsive and concerted model,¹ but this likewise produced major discrepancies with the data. The carbon translational energy is overestimated by a factor of 2, and the CO internal energies are underestimated by an average of 40%. These results are shown in Table III.

Statistical models reproduce the product energy distributions reasonably well for both the concerted and stepwise limits, as also shown in Table III. The concerted model is in reasonable agreement with the data for both average and overall internal energy distribution, however, the predicted CO translational energies are less than observed. Of course, the statistical model does not predict the increasing rotational temperature with vibrational level nor the increasing translational temperature with vibrational level. The stepwise limit of the statistical model assumes that the bonds are broken in two steps. The first step produces a distribution of CO and C₂O fragment states. In the second step the C₂O fragments into C and CO. The calculation is complicated by the second step, since the C_2 O starts not with a single energy but rather with the energy distribution imparted by the first step. In addition, an intermediate electronic energy level must be assumed for the C_2O . The first five C_2O electronic energy levels have been theoretically calculated, but estimates of the heat of formation are crude, varying by 100 kJ/mol.^{47,49} Essentially, the energy levels lie in three clumps (see Fig. 5) so three representative levels were arbitrarily chosen: the \tilde{X} , \tilde{A} , and \tilde{c} states. The \tilde{c} state was placed near its lowest energy estimate (just above the threshold for ${}^{3}P$ production), while the X state was placed near its highest energy estimate (18 940 cm⁻¹ below the ³P threshold). The molecular constants for the \tilde{X} state were taken from Ref. 20, for the

 \overline{A} state from Ref. 34, and for the \overline{c} state the same constants as for the \overline{A} state were used. The results did not depend strongly on energy or molecular constants so these regimes qualitatively span the behavior of the singlet intermediate states as well as the triplets. In particular, results for the \overline{A} state will apply equally well to the \overline{b} and \overline{a} states.

The \tilde{X} state intermediate produced very poor agreement with the CO rotational distribution, primarily because the first CO received too much energy. The \tilde{A} and \tilde{c} state intermediate calculations produced equally good qualitative agreement for the rotation and vibrational distributions. However, since the position assumed for the \tilde{c} state energy level was a lower bound on its actual position the model's agreement will deteriorate if the state's true position lies, as it most likely does, at higher energies (perhaps by as much as 100 kJ/mol). Moreover, the \tilde{A} state intermediate better matched the translational energy distribution. This result is included in Table III.

A dramatic feature of the distribution was that even if the \tilde{A} state lies 6500 cm⁻¹ below the dissociation threshold, as drawn in Fig. 5, over 94% of the C₂ O \tilde{A} molecules have an energy greater than the dissociation threshold, as shown in Fig. 6. Such a percentage would be undifferentiable in our experiments from the 98% obtained from our 2% quantum yield determination for stable C₂ O. This feature of the energy distribution of the C₂ O intermediate permits C₂ O to be a viable intermediate even in the absence of detectable quantities of stable C₂ O product.³⁵

Four conclusions from the model calculations are immediate. (a) Both sequential models fail when the intermediate C_2O is in its ground electronic state $\tilde{X}^{3}\Sigma$. (b) Neither impulsive model can reproduce the average energies observed. (c) The statistical models do not definitively separate the concerted and stepwise statistical processes. (d) The best overall agreement is obtained by a stepwise model with an intermediate C_2O in the \tilde{A} , \tilde{b} , or \tilde{a} electronic state. In general, the models indicate that a requirement for any plausible sequential mechanism is that the C_2O intermediate



FIG. 6. Statistical distribution of C₂O internal energy using a prior model and assuming the C₂O to be formed in any of the \tilde{a} , \tilde{b} , or \tilde{A} states. Zero on the abscissa represents the dissociation energy of C₂O into CO + C(³P₀). The other dashed line (at 122 kJ/mol) represents the energy required to form C(¹D).

must posses an internal plus electronic energy well above the threshold for dissociation.

The sequential statistical mechanism offers a simple explanation for the carbon electronic state branching ratio, particularly if the intermediate is a singlet state. For the sequential statistical process, Fig. 6 reveals that most of the C₂O intermediates would posses insufficient energy to produce the singlet carbon. On the other hand, most of the statistically populated C_2 O molecules are above the dissociation threshold to ${}^{3}P$ carbon, awaiting a singlet to triplet crossing. The observed fractions of $C({}^{1}D)$ and $C({}^{3}P)$ as well as the limits on stable $C_2 O$ products agree qualitatively with the statistically predicted fractions of C₂O above the corresponding energy thresholds. While the actual branching ratio will depend upon the rates of dissociation into ${}^{1}D$ and ${}^{3}P$ carbon, it is not unreasonable to suppose that, for a singlet intermediate, the spin-allowed ^{1}D path would dominate and proceed towards the limit imposed by the C₂ O energy distribution. This also concurs with Braun's larger measurement of 25% (\pm 20%) for ¹D production;¹¹ he excited several absorption bands including higher energy regions where the statistical fraction of C_2O above the $C(^1D)$ threshold rises steeply.

V. CONCLUSIONS: PROPOSED C_3O_2 DISSOCIATION MECHANISM

We can now sketch a scenario for the dissociation of C_3O_2 at 157.6 nm that includes all of the findings and inferences of our data, modeling, and spectroscopic information. However, the data do not preclude the possibility of a more complex process, including a mixture of dissociation pathways. We consider what follows to be the simplest interpretation of our findings.

The initial excitation of $C_3 O_2$ by a 157.6 nm photon occurs via a very strong transition (k > 6000atm⁻¹ cm⁻¹ base e)³⁵ and probably arises from a singletsinglet transition from the ground state $(\tilde{X} \ ^1\Sigma_g^+)$ to a mixture of the $^1\Sigma$ and $^1\Pi$ states, as assigned by Roebber.³¹ The anisotropy parameter (β) appears positive indicating a $\Sigma - \Sigma$ (parallel) transition. The $^1\Sigma^+$ state (Fig. 5) correlates with higher lying states of $C_2 O + CO$ and is therefore bound. In order for $C_3 O_2$ in the $^1\Sigma^+$ state to dissociate, a crossing to another state must occur.

The existence of a C_2O intermediate in an electronic state below the \tilde{c} state is inferred from the CO fragment Doppler profiles and from the modeling calculations. The, at first, surprising favoritism of the spin-forbidden ³*P* channel over the symmetry- and spin-allowed ¹*D* process also seems reconciled with the stepwise production of singlet C_2O . Statistical calculations suggest that if \tilde{a} - or \tilde{b} -state C_2O were the product of C_3O_2 dissociation then $\geq 94\%$ would have enough energy to dissociate into C + CO and only $\leq 6\%$ would result in a stable C_2O molecule (see Fig. 6).

The existence of an anisotropy in the CO fragment recoil distribution indicates the dissociation from the $C_3 O_2$ is rapid on a rotational time scale (picoseconds). The anisotropy in the ³P carbon is presumably washed out by the slower dissociation of the $C_2 O$. The highly excited \tilde{a} or \tilde{b} state $C_2 O$

molecules survive long enough to undergo several rotational periods before they undergo intersystem crossing to the triplet manifold where they produce CO and $C({}^{3}P)$ with a statistical distribution of spin-orbit states. Experimentally we place the C_2O intermediate dissociation rate between a few picoseconds (the rotational period) and < 100 ns (our reso-

lution on the appearance time). This rapid-then-slow stepwise dissociation order is also consistent with the hypothesis that the singlet-to-triplet curve crossing occurs *after* the first dissociation.

We summarize our description of the primary C_3O_2 dissociation reaction following 157.6 nm excitation as follows:

 $C_3O_2 + 157.6 \text{ nm} \rightarrow C_3O_2^*(^{1}\Pi_u, ^{1}\Sigma_u^+)$

 $C_3O_2^* \rightarrow CO(^1\Sigma^+) + C_2O^*$ (high lying metastable singlet, perhaps $\tilde{a}^{-1}\Delta$ or $\tilde{b}^{-1}\Sigma^+$;

CO anisotropy described by $\beta > 0$).

The product quantum yields are as follows: Of the $C_2 O^*$, less than 2% has an energy below the dissociation threshold and is eventually quenched:

$$\leq 2\%C_2O^* \rightarrow C_2O$$

About 3% of the C₂O* has an energy high enough to dissociation to $C(^{1}D)$,

 $\approx 3\%C_2O^* \rightarrow CO(^{1}\Sigma^+) + C(^{1}D)$ (probably very quickly).

The remainder of the $C_2 O^*$ dissociates to $C({}^{3}P)$;

 $\approx 95\%C_2O^* \rightarrow CO({}^{1}\Sigma^+) + C({}^{3}P)$ (following intersystem crossing to a triplet manifold, perhaps

the $C_2 O \tilde{X}$ or \tilde{A} state).

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APPENDIX A: A DETAILED ANALYSIS OF THE VELOCITY DISTRIBUTION FOR CO(v=1, J=59)

This appendix demonstrates that over 80% of CO molecules produced in v = 1, J = 59 are the result of the primary dissociation process and that this process is characterized by an anisotropy parameter of $\beta = 2$. We begin by calculating for a three-body process, the maximum translational energy that the CO from secondary dissociation may possess, which occurs, of course, when the internal energy of the primary CO is zero. The translational energy of the secondary CO can be decomposed into two parts. First, in the center-ofmass (COM) of C_3O_2 , the C_2O product will carry some translational energy as a result of the primary dissociation. Second, in the COM of the C_2O , the secondary CO will carry translational energy from the secondary dissociation. For an isotropic secondary dissociation, the final velocity of the secondary CO will be the square root of the sum of its squared velocities in these two frames. Conservation of energy and momentum can be used to show that

$$v_{\rm CO^{(2)}} = \sqrt{\frac{2m_{\rm CO}}{m_{\rm C_3O}m_{\rm C_3O_2}}} E_{\rm trans} + \frac{2m_{\rm C}}{m_{\rm CO}m_{\rm C_2O_1}} (E_{\rm avail} - E_{\rm int} - E_{\rm trans}), \tag{A1}$$

where $E_{\text{avail}} = 15060 \text{ cm}^{-1}$ is the total available energy, E_{int} is the internal energy of the CO being probed, and E_{trans} is the total translational energy from the primary dissociation. The maximum velocity of the secondary CO is found by taking the derivative of Eq. (A1) as a function of E_{trans} between the limits of $E_{\text{trans}} = 0$ and $E_{\text{trans}} = E_{\text{avail}}$.

The dotted lines in Fig. 3(c) display the maximum velocity of the secondary CO fragment assuming that the internal energy of the primary CO fragment is zero. Recall from Eq. (7) that for a triple fragmentation the maximum velocity of *either* CO is given by the dashed line. Thus, CO fragments with velocity components larger than indicated by the dotted line are primary fragments, and, of these primary fragments, those with velocity components larger than indicated by the dashed line leave the C₂O fragment with less energy than required for its subsequent dissociation. At least 80% of the integrated intensity of the Doppler profile is due to the primary fragment. When the primary fragment is in v = 1, J = 59, the secondary fragment is presumably in a less energetic state.

If we assume that in fact all of the Doppler profile for CO(v = 1, J = 59) is due to primary fragmentation and

further that the dissociation process produces a Maxwell– Boltzmann speed distribution, we can fit the Doppler profile to an anisotropy paramater β and a translational temperature, where the shape of the profile is given by $(4\pi)^{-1}[1+\beta_{\text{eff}}P_2(\cos\theta)]$. The profile is in excellent agreement with a translational temperature of $T_{\text{CO}} = 2300$ K and a $\beta_{\text{eff}} = 0.5$. Because a plane polarized F₂ laser was employed for these experiments, the effective anisotropy paramater β_{eff} is reduced by a factor of 4 from that which would have been observed with linearly polarized light. It thus appears that $\beta = 2$ for the primary fragment.

APPENDIX B: RECOIL ANISOTROPIES OF FRAGMENTS FOR A STEPWISE DISSOCIATION

The degree of anisotropy for dissociation following single photon absorption is often characterized by an anisotropy parameter β , the coefficient on the second order term in a multipole expansion.⁴³ The universal undershoot of the CO Doppler profiles in Fig. 3 is consistent with $\beta > 0$, although it should be noted that because a plane polarized F_2 laser was employed for these experiments the effective anisotropy parameter β_{eff} is reduced by a factor of 4. In this section we consider the anisotropy produced in a stepwise dissociation and show that the data of Figs. 3 and 4 are consistent with $\beta = 2$ for the primary step, $\beta = 0$ for the secondary one, and reasonable (Maxwell-Boltzmann) speed distributions.

Consider the stepwise dissociation of a molecule ABC into A + BC, the latter of which fragments subsequently dissociates further to B + C. (For the specific case of $C_3 O_2$ we identify A and B with CO fragments and C with the carbon fragment.) We choose to describe the fragment velocities in polar coordinates, with the z axis being taken as the direction of the LIF probe light. The Doppler profile of any fragment will be determined by the distribution of the projection of its velocity onto the z axis. In what follows, we make the simplifying assumption that the speed distribution for each fragment is separable from the angular distribution; i.e., $f(\nu, \theta, \phi) = f(\nu)I(\theta, \phi)$.

Consider the Doppler profile of fragment C. Its velocity projection on the z axis can be decomposed into the sum of two parts, the projection onto z of the velocity of the BC primary fragment in the three-body center-of-mass (COM) frame, and the projection onto z of the C velocity in the BC COM frame. Thus, if w is the total projection of the C velocity onto z, then $w_{\rm C} = v_{\rm BC} \cos \theta_{\rm BC} + u_{\rm C} \cos \theta_{\rm C}$, where $v_{\rm BC}$ and $\theta_{\rm BC}$ are measured in the COM of the three-body system and $u_{\rm C}$ and $\theta_{\rm C}$ are measured in the COM of BC. For a given choice of $v_{\rm BC}$ and $u_{\rm C}$, the shape of the Doppler profile $D(w_{\rm C}, v_{\rm BC}, u_{\rm C})$ will be given by the integral

$$D(w_{\rm C}, v_{\rm BC}, u_{\rm C}) = \int I_{\rm BC}(\theta_{\rm BC}, \phi_{\rm BC}) I_{\rm C}(\theta_{\rm C}, \phi_{\rm C})$$
$$\times d\cos\theta_{\rm BC}d\cos\theta_{\rm C}d\phi_{\rm BC}d\phi_{\rm C}, \quad (B1)$$

where the limits of the integration are determined by the requirement that $w_{\rm C} = v_{\rm BC} \cos \theta_{\rm BC} + u_{\rm C} \cos \theta_{\rm C}$. For a distribution of speeds $v_{\rm BC}$ and $u_{\rm C}$, the Doppler profile will be a convolution:

$$D(w_{\rm C}) = \int f(v_{\rm BC}) f(u_{\rm C}) D(w_{\rm C}, v_{\rm BC}, u_{\rm C}) v_{\rm BC}^2 u_{\rm C}^2 \, dv_{\rm BC} \, du_{\rm C}.$$
(B2)

Doppler profiles for fragments A and B can be determined from the velocity distributions for BC and C, respectively, using conservation of momentum. Equations (B1) and (B2) with $I_{\rm BC} = (4\pi)^{-1} [1 + \beta_{\rm eff-BC} P_2(\cos \theta)], I_{\rm C}$ = $(4\pi)^{-1} [1 + \beta_{\text{eff-C}} P_2(\cos \theta_{\text{C}})]$, and Maxwell-Boltzmann distributions for $f(v_{BC})$ and $f(u_C)$, were integrated numerically using a Monte Carlo technique. We were able to obtain excellent fits simultaneously to the CO J = 20Doppler profiles of Fig. 3 and the $C({}^{3}P)$ Doppler profile of Fig. 4. The former profile, of course, is the sum of the profiles for fragments A and B. The best parameters for the fit appeared to be $\beta_{\text{eff-CCO}} = 0.5$, $\beta_{\text{eff-C}} = 0$, and temperatures for $v_{\rm CCO}$ of 1900 K and for $u_{\rm C}$ of 2500 K. Since the photolysis light was plane polarized, $\beta_{\text{eff-CCO}} = 0.5$ corresponds to maximum parallel anisotropy, $\beta = 2$. It is particularly noteworthy that, while the simulated profile for CO deviated from a Gaussian in that the center of the profile was reduced, the profile for the $C({}^{3}P)$ remained guite close to Gaussian. This situation is possible when $\beta_{eff-C} < \beta_{eff-CCO}$ and $\dot{u}_{\rm C} > v_{\rm CCO}$

The CO Doppler profile may also reflect a v-J vector correlation, which would be manifest for this case in a difference in profile depending on whether the rotational state transition is probed on a P/R or Q line.⁴³ For J larger than about 30, the Q lines appear to be (very slightly) more dipped in the center than the corresponding P and R lines. This observation is consistent with a slight preference for the primary CO fragments to recoil with a velocity vector that is perpendicular to the angular momentum direction.

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