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# Investigation of the two- and three-fragment photodissociation of the *tert*-butyl peroxy radical at 248 nm

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The photodissociation dynamics of the tert-butyl peroxy (t-BuOO) radical are studied by fast-radicalbeam coincidence translational spectroscopy. The neutral *t*-BuOO radical is formed by photodetachment of the corresponding t-BuOO<sup>-</sup> anion at 700 nm (1.77 eV), followed by dissociation at 248 nm (5.00 eV). Photofragment mass and translational energy distributions are obtained. The major channel is found to be three-body fragmentation to form O, CH<sub>3</sub>, and acetone (83%), with minor two-body fragmentation channels leading to the formation of  $O_2 + tert$ -butyl radical (10%) and  $HO_2$ + isobutene (7%). Experimental results show that the translational energy distribution for two-body dissociation peaks is close to zero translational energy, with an isotropic angular distribution of fragments. These results indicate that two-body fragmentation proceeds via internal conversion to the ground electronic state followed by statistical dissociation. For three-body dissociation, the translational energy distribution peaks closer to the maximal allowed translational energy and shows an anisotropic distribution of the plane of the dissociating fragments, implying rapid dissociation on an excited-state surface. A small shoulder in the three-body translational energy distribution suggests that some three-fragment dissociation events proceed by a different mechanism, involving internal conversion to the ground electronic state followed by sequential dissociation. Published by AIP Publishing. https://doi.org/10.1063/1.4994713

# I. INTRODUCTION

Alkyl peroxy (RO<sub>2</sub>) radicals have long been understood to be important species in both atmospheric and combustion chemistry. In atmospheric chemistry, these species are crucial intermediates in the formation of tropospheric ozone from hydrocarbons and oxygen.<sup>1–3</sup> Alkyl peroxy radicals, formed by the reaction of alkyl radicals with O<sub>2</sub>, react with NO in the troposphere to form NO<sub>2</sub> and an alkoxy radical (RO).  $NO_2$  is then photolyzed to produce NO and  $O(^{3}P)$ , and the atomic fragment goes on to react with O<sub>2</sub> to produce ozone. The RO radical further reacts to form an aldehyde or ketone and HO<sub>2</sub>, which can convert a second NO molecule to NO<sub>2</sub> and lead to further ozone production. In low-temperature combustion processes, RO2 radicals are of particular interest, as they can rearrange to form the corresponding hydroperoxy alkyl radical (QOOH).<sup>4-6</sup> These QOOH radicals play a key role in autoignition processes, as they are very unstable and readily decompose or can undergo secondary O2 addition to form OOQOOH radicals. Information on the energetics, spectroscopy, and dynamics of RO2 radicals is therefore crucial for accurate modeling of the atmospheric and combustion chemistry in which these species participate. In this article, we investigate the photodissociation of the *tert*-butyl peroxy radical (t-BuOO) at 248 nm (5.00 eV), focusing on its

primary photochemistry and dissociation mechanism through measurements of product mass and translational energy distributions.

The spectroscopy of t-BuOO has been the focus of a number of experimental and theoretical investigations. The UV absorption spectrum of t-BuOO shows a strong, featureless absorption around 240 nm, in common with many other alkyl peroxy radicals.<sup>7</sup> This UV absorption corresponds to the  $\tilde{B}^{2}A'' \leftarrow \tilde{X}^{2}A''$  transition, which for other RO<sub>2</sub> radicals is known to be dissociative along the O-O bond.<sup>8</sup> The  $\tilde{A}^{2}A' \leftarrow \tilde{X}^{2}A''$  transition has been characterized using cavity ringdown spectroscopy in the near IR, yielding the term energy and several vibrational frequencies in the  $\tilde{A}^2 A'$  state.<sup>9</sup> The  $\tilde{X}$  and  $\tilde{A}$  electronic states of the *t*-BuOO radical have also been probed via anion photoelectron spectroscopy, in which an electron is photodetached from the *t*-BuOO<sup>-</sup> anion, yielding an electron affinity for t-BuOO of 1.196 eV, a term energy of the  $\tilde{A}$ -state of 0.967 eV, and vibrational frequencies for a number of modes in both those states.<sup>10</sup> Most recently, DeVine et al.<sup>11</sup> employed slow-electron velocitymap imaging (SEVI) to obtain a high-resolution photoelectron spectrum of t-BuOO, yielding a refined electron affinity and resolving additional low-frequency vibrational modes of the radical.

Photodissociation experiments on peroxy radicals have predominantly focused on  $HO_2^{12}$  and the methyl peroxy radical<sup>13</sup> (CH<sub>3</sub>OO). Initial theoretical investigations into the electronic states of CH<sub>3</sub>OO found that the potential of the  $\tilde{B}$  state has only a weak minimum along the O–O coordinate, and

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therefore excitation to the  $\hat{B}$  state would result in O–O bond cleavage, producing O and CH<sub>3</sub>O fragments.<sup>8</sup> It was also suggested that three-body fragmentation to  $CH_3 + O + O$  may be open. In experimental studies of the 248 nm (5.00 eV) dissociation of this system, CH<sub>3</sub>O and OH products were detected.<sup>13</sup> These products were attributed to O-O bond cleavage from either direct dissociation from the CH<sub>3</sub>OO radical to form CH<sub>3</sub>O or breaking of the bond following isomerization to the CH<sub>2</sub>OOH radical to produce OH. However, the quantum yields for these processes were low, and it was concluded that the dominant channel was O2 loss to form a methyl radical + O<sub>2</sub>.<sup>13</sup> Recent studies on the photodissociation of a substituted phenyl peroxy cation at 403 nm (3.08 eV) found that 60% of the photofragments corresponded to O2 loss, with 40% due to loss of atomic oxygen.<sup>14</sup> A theoretical study on the dissociation of the phenyl peroxy radical suggested that following photoexcitation to the  $\tilde{B}$  state, O<sub>2</sub> loss would occur on the first excited state of phenyl peroxy and result in  $C_6H_5(X^2A)$ +  $O_2(^1\Delta_g)$  products, whilst O loss would proceed directly along the  $\tilde{B}$  state to form C<sub>6</sub>H<sub>5</sub>O(X<sup>2</sup>A) + O(<sup>3</sup>P).<sup>14,15</sup>

The photodissociation of *t*-BuOO has been limited to *in* situ matrix photolysis studies.<sup>16</sup> In these experiments, *t*-BuOO radicals were formed in an Ar/O<sub>2</sub> matrix and photolyzed at 254 nm (4.88 eV). The IR absorption spectrum was monitored to observe the depletion of the radical and formation of water, carbon monoxide, and carbonyl compounds. The observed carbonyl stretch was attributed to both formaldehyde and acetone and was interpreted as being due to O–O bond cleavage on photolysis, followed by oxidation of the products.<sup>16</sup>



FIG. 1. Energy diagram for *t*-BuOO dissociation. Energies, given in eV, relative to the ground state of *t*-BuOO, are calculated at the RCCSD(T)/CBS level of theory with harmonic vibrational zero point energy and are taken from Ref. 24. The product energies differ slightly from those calculated from experimental heats of formation [given in Eqs. (1)-(4)].

In the present study, we report results on the photodissociation of the gas-phase *t*-BuOO radical at 248 nm (5.00 eV), using the technique of fast-radical-beam photodissociation, in which *t*-BuOO is generated by photodetachment of the corresponding anion. At 248 nm, there are a number of energetically accessible product channels, including dissociation to both two and three fragments. The possible two body-dissociation channels are

$C_4H_9O_2 \rightarrow O_2 + C_4H_9 \ (t\text{-butyl}),$	$D_0 = 1.63 \mathrm{eV},^{10,17,18}$	(1)
$C_4H_9O_2 \rightarrow HO_2 + C_4H_8$ (isobutene),	$D_0 = 1.07 \mathrm{eV},^{19,20}$	(2)
$C_4H_9O_2 \rightarrow O + C_4H_9O (t-butoxy),$	$D_0 = 2.76 \mathrm{eV},^{21,22}$	(3)
$C_4H_9O_2 \rightarrow OH + C_4H_8O$ (2,2-dimethyloxirane),	$D_0 = 0.01 \mathrm{eV}.^{22,23}$	(4)

Figure 1 shows a potential energy diagram for the competing two-body dissociation channels on the ground-state electronic surface. The energies and structures are taken from Ref. 24 and are calculated at the RCCSD(T)/CBS level of theory with harmonic vibrational zero point energy. As can be seen in Fig. 1, the *t*-BuOO molecule can dissociate directly into *t*-butyl and  $O_2$ , for example, or can first isomerize to form the QOOH radical, which subsequently dissociates.

In addition to two-fragment dissociation, there are two possible three-fragment dissociation pathways

$C_4H_9O_2 \rightarrow O + CH_3 + C_3H_6O$ (acetone),	$D_0 = 2.96 \mathrm{eV},^{22,25}$	(5)
$C_4H_0O_2 \rightarrow H + CH_2O$ (formaldehyde) + $C_2H_4O$ (acetone)	$D_0 = -0.08  \mathrm{eV}^{22,25}$	(6)

We find that the dominant pathway for dissociation of *t*-BuOO at 248 nm (5.00 eV) is three-body fragmentation to  $O + CH_3$  + acetone (channel 5). The lower-energy three-fragment dissociation (channel 6) is not observed in this work. The experimental translational energy distribution and Dalitz plots for channel 5 are consistent with the fragmentation predominantly occurring on the initially excited  $\tilde{B}$ -state surface. We also observe two-body dissociation to  $O_2 + t$ -butyl and  $HO_2$  + isobutene (channels 1 and 2), with little evidence of dissociation via channel 3 or 4. Translational energy distributions and

branching ratios for these two-body dissociation channels are found to be consistent with fragmentation occurring on the ground state surface following internal conversion from the  $\tilde{B}$ to the  $\tilde{X}$  state, with no evidence of isomerization to QOOH prior to dissociation.

## **II. METHODS**

The fast-beam coincidence translational spectrometer employed in this study has been described in detail previously,<sup>26,27</sup> so only the details specific to this work will be discussed here. While this instrument was originally designed to measure two-body photodissociation events, more recent detector configurations have enabled coincidence-based detection of three-body dissociation.<sup>28–30</sup>

A fast beam of *tert*-butyl peroxide anions (*t*-BuOO<sup>-</sup>) was generated by flowing 15 psi (1 bar) Ar through a *tert*-butyl hydroperoxide solution (70% *t*-BuOOH in water). The gas mixture was supersonically expanded into the vacuum through an Amsterdam Piezovalve<sup>31</sup> operating at 100 Hz, coupled with a DC grid discharge source<sup>32</sup> to produce *t*-BuOO<sup>-</sup> ions. The ions were accelerated to a beam energy of 6–8 keV and massselected using a collinear beam modulation time-of-flight mass spectrometer as described by Bakker.<sup>33,34</sup> Mass-selected *t*-BuOO<sup>-</sup> ions were subsequently photodetached at 700 nm (1.77 eV) with an Nd:YAG-pumped dye laser (Litron LPY742-100 and Radiant Dyes NarrowScan) to produce a fast beam of neutral *t*-BuOO.

The neutral *t*-BuOO radicals formed in the detachment step were characterized by a photoelectron spectrometer installed in the photodetachment region.<sup>35</sup> The photodetached electrons were extracted perpendicular to the beam of the neutral radicals and velocity-mapped onto a position-sensitive detector consisting of a chevron stack of two multichannel plates (MCPs) and a phosphor screen. Events on the phosphor screen were captured by a camera and transferred to a computer for analysis of the resulting image. Use of the Abel inversion (BASEX)<sup>36</sup> allows the photoelectron kinetic energy (eKE) distributions to be obtained from the recorded images, yielding information on the structure of the radical formed, in addition to the internal energy of both the ions and neutrals.

After photodetachment of t-BuOO<sup>-</sup>, remaining anions in the fast beam were deflected from the beam path using an electric field. The resulting beam of fast neutral t-BuOO was then intersected by a 248 nm (5.00 eV) laser beam generated by an excimer laser (GAM EX-50F). Photodissociation products that scatter from the beam path were then detected in coincidence on a time-and-position-sensitive Roentdek Hex80 delay-line-anode detector,  $2^{\overline{7},30}$  with any undissociated t-BuOO blocked by a 2.5 mm radius beam block in front of the detector face. For each coincident event, which could be a two-body or three-body dissociation, the arrival times and positions of the photofragments were determined and then analyzed to yield the photofragment masses, translational energy release, and scattering angles. The two-body dissociation photofragment translational energy and angular distributions are given by the relation

$$P(E_T, \theta) = P(E_T) \cdot \left[1 + \beta(E_T) P_2(\cos \theta)\right], \quad (7)$$

where  $\beta(E_T)$  is the energy-dependent anisotropy parameter and  $P_2$  is the 2nd-order Legendre polynomial. The  $\beta$  parameter for three-body dissociation is calculated directly from the angular distributions of the scattered products. In the current experiments, the unpolarized output of the excimer laser is used for dissociation, so  $\theta$  is defined as the angle between the dissociation recoil axis (or in the case of the three-body dissociation, the normal to the dissociation plane) and the direction of propagation of the laser. In this case,  $\beta$  takes on values between -1 for parallel and  $+\frac{1}{2}$  for perpendicular transitions, corresponding to the  $\beta$  parameters for linearly polarized light ( $\beta_{lin}$ ) multiplied by  $-\frac{1}{2}$ .<sup>35</sup>

For events with very low or high translational energy release, one or both fragments can either hit the beam block or miss the detector entirely and therefore go undetected. In order to account for this variation of the detection efficiency as a function of scattering angle and translational energy release, the experimental translational energy distributions for two- and three-body dissociation events and corresponding Dalitz plots presented in this work have been corrected using a detector acceptance function (DAF).<sup>30,37</sup>

# **III. RESULTS AND ANALYSIS**

### A. Photoelectron spectrum

Figure 2 displays the photoelectron spectrum of *t*-BuOO<sup>-</sup> at a photodetachment wavelength of  $\lambda = 700$  nm (hv = 1.771 eV). Ideally, a detachment photon energy just above the electron affinity of *t*-BuOO (1.196 eV) would be used so as to produce radicals in their ground vibrational state. However, the vibrational origin, peak A, is quite weak owing to Franck– Condon effects. Hence, a slightly higher photon energy was chosen to achieve reasonable production of neutral *t*-BuOO. As a result, neutral *t*-BuOO radicals are formed with up to 0.5 eV of internal energy.

To aid in assignment of the photoelectron spectrum, Franck–Condon simulations were performed using EZSpectrum.<sup>38</sup> Geometries and vibrational frequencies of the groundstate anion and neutral were calculated via density-functional theory using the B3LYP functional with the 6-311+G(d,p) basis set in the Gaussian 09 package.<sup>39</sup> Frequencies were scaled by 0.9679 as is appropriate for this basis set.<sup>40</sup> The simulation is performed at 300 K to account for the presence of a hot band observed at slightly higher eKE (0.62 eV) than the vibrational origin in the experimental spectrum in Fig. 2. Clifford *et al.*<sup>10</sup> have previously acquired and assigned the



FIG. 2. Anion photoelectron spectrum of *tert*-butyl peroxide at  $\lambda = 700$  nm ( $h\nu = 1.771$  eV) with Franck–Condon simulations (red) overlaying the experimental spectrum (black).

experimental spectrum, identifying the major active modes in their experimental spectrum to be the O–O stretch (1130 cm<sup>-1</sup>) and the C–O–O bend (245 cm<sup>-1</sup>) and reporting an electron affinity of 1.196 eV.

Our spectrum (Fig. 2) looks slightly different from that previously published by Clifford et al.<sup>10</sup> due to a difference in the temperature of the ions produced, but as in the previously reported work, the two most active modes correspond to the O-O stretch and a low-frequency mode involving the C-O-O bend and torsion of the methyl groups. As can be seen by comparing our experimental spectrum to the simulation, there is considerable unresolved structure, and the simulation indicates contributions from numerous different modes. These contributions are more concretely identified in a recently published high-resolution photoelectron spectrum.<sup>11</sup> For the purposes of this work, the consistency between the experimental spectrum and simulation confirms the formation of the t-BuOO radical by photodetachment. The most intense feature around 0.31 eV corresponds to two quanta of excitation in the O-O stretch, indicating an excess 0.28 eV of energy imparted in the radicals prior to dissociation.

#### B. Photofragment mass distributions

Figure 3 shows the mass distributions of coincident events for two- and three-fragment dissociation of the *t*-BuOO radical at 248 nm (5.00 eV). The three-fragment mass distribution [Fig. 3(a)] shows two peaks (see below) around 15.5 and 58 Da. For two-fragment dissociation, shown in Fig. 3(b), two pairs of peaks can be seen in the photofragment mass distributions: the dominant channel peaking around 32 and 57 Da and less intense mass peaks around 18 and 71 Da. The moderate photofragment mass resolution  $m/\Delta m = 10$  of the instrument<sup>27,41</sup> is not sufficient to distinguish mass peaks that are only 1 Da apart.

The three-fragment mass distribution is consistent with three-fragment dissociation via channel 5 to form O (16 Da), CH<sub>3</sub> (15 Da), and acetone (58 Da). The peak at 15.5 Da is twice as intense as that at 58 Da, as the two individual mass peaks corresponding to O and CH<sub>3</sub> are not resolved. No evidence is seen in the three-body mass distribution for dissociation via channel 6 to form H, CH<sub>2</sub>O (formaldehyde, 30 Da), and  $C_3H_6O$  (acetone). It should be noted that due to the geometry of the detector, light fragments such as H atoms are not easily detectable, as they are likely to recoil beyond the edge of the detector. Additionally, H atoms have a low laboratoryframe kinetic energy and therefore a low detection efficiency for those atoms that do impinge on the active area of the detector. However, the remaining two fragments, CH<sub>2</sub>O and  $C_3H_6O$ , would likely be observed in the two-fragment mass distributions as peaks around 30 and 58 Da. Since the peaks in the two-fragment mass distribution appear at slightly different masses (around 32-33 and 57-56 Da), we conclude that dissociation via channel 6 is not observed.

The major two-fragment channel, with peaks at 32 and 57 Da, could correspond to dissociation to either  $O_2 + t$ -butyl (channel 1),  $HO_2$  + isobutene (channel 2), or a mixture of the two. The mass resolution of the photofragment spectrometer is insufficient to distinguish between these channels



FIG. 3. Photofragment coincident mass distributions for three- (a) and twobody (b) dissociation of *t*-BuOO at 248 nm (5.00 eV).

based on the mass distributions alone. Performing this experiment with deuterated tert-butyl peroxy (C<sub>4</sub>D<sub>9</sub>O<sub>2</sub>) could aid with a more definitive assignment for this channel, but our attempts to synthesize the deuterated tert-butyl hydroperoxide precursor were unsuccessful. Some insight into the possible contributions from channels 1 and 2 can be gained by performing simulations of the mass distribution using the experimental conditions and translational energy distributions and varying the contributions of the two channels.<sup>27</sup> A sample simulation for these channels is shown in the supplementary material. Simulating the mass distribution assuming dissociation occurs only via channel 1 or channel 2 gives poor agreement with the experimental distribution, and the best agreement is obtained using a branching ratio between channel 1 and channel 2 of  $1:0.66 \pm 0.13$ . This ratio is consistent with Rice-Ramsperger-Kassel-Marcus (RRKM) calculations as described in Sec. IV A.

The smaller features in Fig. 3(b) peak around 18 and 71 Da, but these peaks are very broad and are asymmetric in appearance. Simulations (shown in the supplementary material) suggest that they result from detecting two fragments

from a three-body dissociation occurring via channel 5. The undetected fragment either hits the beam block, falls outside the detector face, or is simply not detected. The detector has a finite one-particle detection efficiency, which has previously been determined to be p = 0.6, thus the probability of detecting all three fragments for a three-body dissociation is  $p_3 = 0.22.^{30}$  Therefore, there is a significant probability that only 2 of the 3 fragments are detected  $[p_{2/3} = 3p^2(1-p)]$ = 0.43]. The majority of these events should be rejected during the analysis process, as the center of mass of the two observed fragments will be shifted from the center of the beam. However, it is possible that some events in which two fragments from a three-body dissociation event are detected contribute to the two-body mass distribution. In order to assess the effect that these incorrectly classified events have on the two-body mass distribution, we performed simulations in which one of the three fragments is not detected. We found that these "false" two-body events manifest as broad peaks around 18 and 71 Da, i.e., where the smaller features in Fig. 3(b) are seen. We therefore attribute these peaks to three-fragment events in which one fragment remains undetected. Although it is possible that there is some contribution to these peaks from dissociation via channels 3 or 4, either would be a very minor channel, as these peaks correspond to less than 1% of all coincident events.

Using the estimate for the one-particle detection probability, it is also possible to calculate the branching ratio between the two- and three-fragment dissociation channels. It was found to be  $1:5 \pm 1$ , so the majority of dissociation events result in fragmentation to O, CH<sub>3</sub>, and acetone.

## C. Photofragment translational energy and angular distributions

The translational energy available to the dissociation products can be calculated according to

$$E_T = h\nu + E_{\rm int} - E'_{\rm int} - D_0,$$
 (8)

where hv is the photon energy,  $E_{int}$  is the internal energy of the *t*-BuOO radical prior to dissociation,  $E'_{int}$  is the internal energy of the fragments, and  $D_0$  is the dissociation energy. From the photoelectron spectrum presented in Sec. III A, it is clear that the majority of the *t*-BuOO radicals are not produced in the ground vibrational state but have an internal energy between 0 and 0.5 eV. The largest peak in the photoelectron spectrum corresponds to an internal energy of around 0.28 eV; therefore  $E_{int} = 0.28$  eV will be used when calculating the most probable maximal available translational energy for each channel. For two-fragment dissociation via channels 1 and 2, Eq. (1) implies that these energies are 3.65 eV and 4.21 eV, respectively.

Since  $O_2$  and  $HO_2$  loss cannot be resolved in the mass distribution, the translational energy distribution displayed in Fig. 4 contains events from both channels. The major two-body mass channel was treated as having fragment mass of 32 and 57 for the analysis, although it is likely that there is some contribution from  $HO_2$  loss. It is clear from Fig. 4 that the experimental translational energy distribution peaks at around 0.2 eV, well below the maximal available translational energy for either



FIG. 4. Photofragment translational energy distribution for the major twofragment dissociation of *t*-BuOO at 248 nm (5.00 eV). The arrows indicate the most probable maximal available translational energy for channels 1 (blue) and 2 (green), with the horizontal line indicating the range of internal energies of the neutral radicals prior to dissociation. The experimental distribution (black line) is compared with prior distribution calculations for channel 1 (red line).

channel. Furthermore, there is only a single peak in the translational energy distribution, suggesting either that channel 1 and 2 have similar translational energy releases or dissociation products are observed from only one of the two possible channels. The angular distribution of the photofragments is isotropic.

The translational energy distribution for channel 5, threefragment dissociation of *t*-BuOO to  $O({}^{3}P)$ , CH<sub>3</sub>, and acetone, is shown in Fig. 5. The most probable maximal available translational energy for the three-fragment dissociation is 2.32 eV and is indicated by an arrow in Fig. 5. In contrast to the two-fragment dissociation, the translational energy



FIG. 5. Photofragment translational energy distribution for the threefragment dissociation channel of *t*-BuOO to form  $O({}^{3}P)$ , CH<sub>3</sub>, and acetone at 248 nm (5.00 eV). The arrow indicates the most probable maximal available translational energy, with the horizontal line indicating the range of internal energies of the neutral radicals prior to dissociation.

distribution is very broad, extending from zero to close to the maximal available translational energy, with a peak at around 1.35 eV (around 60% of the available energy). Below 0.8 eV (30% of the available energy), there is a slight shoulder to the main peak, which could indicate a different dissociation mechanism for events with low translational energy release. The anisotropy for the distribution of the normal to the plane of the dissociating fragments is also different above and below 0.8 eV. Between 0.3 and 0.8 eV, the distribution of the normal to the plane of the dissociating fragments is nearly isotropic, with  $\beta_{obs} = 0.02 \pm 0.07$ ; however, above 0.8 eV, the distribution becomes anisotropic with  $\beta_{obs} = 0.35 \pm 0.03$ , which would correspond to  $\beta_{\text{lin}} = -0.70 \pm 0.06$  for linearly polarized light. This anisotropy indicates a propensity for the dissociation plane to lie perpendicular to the plane of the laser polarization.

Insight into the three-body dissociation mechanism can be gained from the Dalitz plots 30,42-44 shown in Fig. 6. These plots show the translational energy partitioning between the three fragments, with each fragment i having a fractional translational energy  $\varepsilon_i = E_i/E$ , where *E* is the translational energy release for the event. Each point on the Dalitz plot represents a three-body dissociation event and is constrained to lie within the triangle by conservation of energy, whilst momentum conservation restricts events to within the inscribed ellipse. Points around the edge of the ellipse correspond to dissociation events in which the outgoing momenta of the fragments are collinear, whereas points closer to the middle correspond to more noncollinear arrangements of the fragment momenta. Dalitz plots are shown in Fig. 6 for all dissociation events (left panel), for events with translational energies between 0.3 and 0.8 eV (middle panel), and for events with translational energies between 0.8 and 3.0 eV (right panel). The Dalitz plot for translational energies from 0.3 to 0.8 eV (lowenergy shoulder) has considerable shot noise owing to the relatively small number of events in this energy range. It is also worth noting that owing to the similar masses of O and CH<sub>3</sub>, the analysis program may identify O fragments as CH<sub>3</sub> or vice versa. Therefore the apparent symmetry in the Dalitz plot may be a consequence of incorrectly identified fragments.

It is clear from the middle and right panels of Fig. 6 that the partitioning of translational energy amongst the fragments is quite different for low translational energy events (0.3-0.8 eV) than for higher translational energy events

(0.8–3.0 eV). For low translational energies, the intensity in the Dalitz plot is predominantly in the upper left and lowerright portions of the ellipse. This corresponds to dissociation events with very uneven partitioning of momenta between the O and CH<sub>3</sub> fragments (but we cannot tell which fragment has the high momentum and which has the low momentum). In contrast, in Fig. 6(c), the Dalitz plot for events with higher translational energies shows intensity that is greatest along the blue axis, where the translational energy fractions in the O and CH<sub>3</sub> fragments are equal, and so there is a tendency for equal partitioning of momenta between O and CH<sub>3</sub> fragments. The fractional energy releases  $\langle f_i \rangle$ , averaged over the higher translational energy peak, for the O, CH<sub>3</sub>, and acetone fragments are calculated to be  $\langle f_O \rangle = \langle f_{CH_3} \rangle = 0.4$  and  $\langle f_{acetone} \rangle = 0.2$ .

# **IV. DISCUSSION**

# A. Two-body dissociation

The experimental mass distribution for two-body dissociation peaks around 32–33 Da and 56–57 Da, which, as discussed in Sec. III B, could correspond to  $O_2$  (channel 1) and HO<sub>2</sub> loss (channel 2) or a combination thereof. Since these channels cannot be definitively distinguished in the mass distribution, in this section, we will examine experimental translational energy distributions and product branching ratios to gain insight into the identity and mechanism of formation of the two-body dissociation products.

One aim of the current investigation is to establish whether the dissociation of *t*-BuOO occurs on the initially excited electronic state or if instead the radical first decays to the ground electronic state via non-adiabatic interactions, followed by statistical dissociation. As discussed in Sec. III B, the experimental translational energy distribution for twobody dissociation peaks close to zero translational energy, much lower than the maximal allowed translational energy for either  $O_2$  or  $HO_2$  loss. Such a distribution is characteristic of statistical dissociation on the ground electronic state, as opposed to dissociation along a repulsive excited-state surface, which tends to result in high translational energy release.<sup>26</sup>

For the barrierless loss of  $O_2$  (channel 1), the translational energy release can be modeled using a prior distribution<sup>45,46</sup>

$$p(E_T|E_{\rm av}) \propto (E_T)^{1/2} \rho(E_{\rm av} - E_T),$$
 (9)



FIG. 6. Dalitz plots of translational energy partitioning amongst the O (green axis), CH<sub>3</sub> (red axis), and acetone (blue axis) fragments formed from the three-body dissociation of *t*-BuOO. The Dalitz plots are integrated either over the whole translational energy range (a), from 0.3 to 0.8 eV (b), or from 0.8 to 3.0 eV (c). The three grey lines indicate equal momenta partitioning amongst two of the fragments. The orange cross in (c) indicates the energy partitioning for concerted synchronous dissociation. Relative intensities are shown by shades of gray ranging from white (no intensity) to black (maximal intensity). where  $E_{av}$  is the available energy above the dissociation energy, and  $\rho(E_{av} - E_T)$  is the density of states of the O<sub>2</sub> and *tert*-butyl radical fragments. The rotational density of states was assumed to be constant, and the vibrational density of states was calculated using the Beyer–Swinehart algorithm,<sup>47</sup> treating all modes as harmonic oscillators, with vibrational frequencies obtained from Ref. 48. The calculated distribution, shown in Fig. 4, is in reasonable agreement with the experimental translational energy distribution.

As shown in Fig. 1, there are two possible routes to formation of  $HO_2$  + isobutene (channel 2): direct elimination of HO<sub>2</sub> via TS2 and isomerization to the hydroperoxy alkyl radical (QOOH) over TS3, followed by loss of HO2 through passage over TS5. In the case of ground-state dissociation over a barrier, the energy is initially statistically distributed among internal degrees of freedom prior to dissociation, but passage over the barrier results in a rapid release of energy that is not statistically distributed, and much of this energy is converted into translational energy. However, since the barriers with respect to the products for both indirect and direct HO<sub>2</sub>loss pathways are small (0.29 eV and 0.35 eV, respectively), the translational energy distributions for these pathways would also be expected to peak close to zero. The experimental translational energy distribution is therefore consistent with both O2 loss and HO<sub>2</sub> loss.

Based on the experimental mass distributions and translational energy distributions alone, it is not possible to definitively assign which two-body dissociation channels are observed. However, since the translational energy distributions suggest statistical dissociation on the ground state, it is appropriate to use the RRKM theory to model the rate constants and predict branching ratios for competing dissociation channels.<sup>49</sup> The RRKM rate constant, k(E), can be evaluated according to

$$k(E) = \frac{W(E - E_0)}{h\rho(E)},$$
(10)

where  $W(E - E_0)$  is the sum of states at the transition state,  $E_0$  is the energy of the transition state relative to the ground state, h is Planck's constant, and  $\rho(E)$  is the density of states of the ground electronic state. The sums and densities of states are calculated using the Beyer–Swinehart algorithm. Vibrational modes for the reactant and transition states were treated as harmonic oscillators, with vibrational frequencies from electronic structure calculations at the CCSD(T)/ANO0 level of theory, taken from Ref. 24.

Since channel 1 (O<sub>2</sub> loss) is a barrierless process, the rate constant for this channel was calculated using variational RRKM. Optimized geometries and vibrational frequencies were obtained for C–O bond lengths up to 3 Å, and the dissociation rate for each structure was calculated. The minimal rate, listed in Table I, was found at a C–O bond distance of 2.7 Å. For the direct path to OH + isobutene products, the rate of passage over TS2 was calculated directly.

For indirect  $HO_2$  loss, the *t*-BuOO radical first isomerizes to form the QOOH species, which then dissociates,

$$t$$
-BuOO  $\xleftarrow{k_3}{k_{-3}}$  QOOH  $\xrightarrow{k_5}$  HO<sub>2</sub> + isobutene. (11)

TABLE I. RRKM rates and branching ratios for  $O_2$ , OH, and  $HO_2$  loss pathways.

Rate $(s^{-1})$	Relative rate
$8.46 \times 10^{10}$	1
$3.13 \times 10^{10}$	0.37
$4.81 \times 10^{8}$	0.01
$1.66 \times 10^{9}$	0.02
	Rate $(s^{-1})$ $8.46 \times 10^{10}$ $3.13 \times 10^{10}$ $4.81 \times 10^{8}$ $1.66 \times 10^{9}$

Applying the steady-state approximation to the QOOH radical results in the following expression for the rate constant for indirect HO<sub>2</sub> loss:

$$k_{\text{HO}_2 \text{ loss, indirect}} = \frac{k_5 k_3}{k_{-3} + k_4 + k_5}.$$
 (12)

Similarly, the steady-state approximation was applied to the reaction mechanism for OH loss,

$$t$$
-BuOO  $\xleftarrow{k_3}{k_{-3}}$  QOOH  $\xrightarrow{k_4}$  OH + DMO, (13)

to yield the rate constant

$$k_{\rm OH \ loss} = \frac{k_4 k_3}{k_{-3} + k_4 + k_5}.$$
 (14)

The resulting rates are given in Table I, along with product branching ratios.

The RRKM rates and branching ratios for the competing dissociation channels shown in Table I provide insight into the two-body dissociation products and mechanism. The calculations predict that the dominant two-body dissociation channel will be  $O_2$  loss, with a significant contribution from direct HO<sub>2</sub> elimination. For  $O_2$  loss, the C–O bond lengthens, resulting in a "loose" transition state, whereas for direct HO<sub>2</sub> elimination, the reaction proceeds via a "tight" transition state (TS2). Therefore, although the barrier to  $O_2$  loss is higher in energy than the barrier to HO<sub>2</sub> elimination, the loose transition state for  $O_2$  loss leads to a higher rate for channel 1. According to the RRKM calculations, isomerization to the QOOH radical followed by HO<sub>2</sub> or OH loss is a very minor decay pathway.

The calculated  $O_2$ :HO<sub>2</sub> branching ratio in Table I agrees reasonably well with the experimental branching ratio between channel 1 and channel 2 of  $1:0.66 \pm 0.13$  reported in Sec. III B. Hence, the RRKM analysis gives us confidence in our decomposition of the experimental mass spectrum into the two channels. The barrier height of TS2 has been calculated in a number of previous studies. Zádor et al.<sup>6</sup> and DeSain et al.<sup>50</sup> calculated the height of the TS2 barrier to be 1.32 eV and 1.31 eV, respectively, in agreement with the more recent calculations in Ref. 24. Earlier calculations by Chen and Bozzelli<sup>51</sup> at the CBS-q//MP2(full)/6-31g\* level of theory found TS2 to be slightly lower in energy (1.19 eV), yielding a O<sub>2</sub>:HO<sub>2</sub> branching ratio of 1:0.91 at a dissociation energy of 248 nm. Our experimental branching ratio lies between these two values, although it should be noted that there is a large uncertainty in the experimental branching ratio.

#### B. Three-body dissociation

In contrast to the two-body dissociation pathways discussed in Sec. IV A, the translational energy distribution for three-body dissociation to O, CH<sub>3</sub>, and acetone is broad and peaks well away from zero, with intensity up to the maximal available translational energy. As discussed in Sec. III B, the main distribution peaks at around 1.35 eV, but there is a small shoulder in the distribution at a lower translational energy, around 0.75 eV, which could indicate different dissociation mechanisms in these two translational energy ranges. Above 0.8 eV, the translational energy distribution and anisotropy of the normal to the plane of the dissociating fragments are consistent with rapid dissociation along an excited-state surface, resulting in production of the ground-state products.

Three-body dissociation mechanisms are often classified according to the time interval between which the bonds break. A dissociation event can be classified as either concerted or sequential, depending on whether the bond-breaking process takes place as one single or two distinct kinetic events, respectively.<sup>52</sup> Concerted processes can be further classified

into (a) synchronous, in which the bonds break simultaneously, on a time period much less than the rotational period, and (b) asynchronous, in which the time interval is nonzero but less than or comparable to the rotational period. In a sequential dissociation event, one bond is cleaved first, and one of the resulting fragments subsequently undergoes further dissociation on a time scale exceeding the rotational period.

The Dalitz plots presented in Fig. 6 can be used to help elucidate the mechanism for the three-body dissociation of t-BuOO. A concerted mechanism, in which the C–C and O–O bonds break simultaneously, would result in nearly equal momenta in the O and CH<sub>3</sub> fragments because their masses are so similar.<sup>52</sup> This type of concerted mechanism is therefore consistent with the intense "stripe" along the blue axis that is observed in the Dalitz plot for high translational energies in Fig. 6(c). Along the blue axis, which represents the energy fraction in the acetone fragment, the translational energy fractions in the O and CH<sub>3</sub> fragments are equal. For a synchronous concerted dissociation with sudden recoil along the bonds, the energy fractions in each fragment would be given by<sup>52</sup>

$$\epsilon_{\text{acetone}} = \frac{1}{1 + (m_{\text{acetone}}/4\mu_{\text{CH}_3, 0}) \left[1 + \tan^2(\theta/2)\right]} = 0.29,$$
(15)

$$\epsilon_{\rm CH_3} = \frac{1}{4 \left( m_{\rm CH_3} / m_{\rm acetone} \right) \cos^2 \left( \theta / 2 \right) + \left[ \left( m_{\rm CH_3} + m_{\rm O} \right) / m_{\rm CH_3} \right]} = 0.35, \tag{16}$$

$$f_{\rm O} = \frac{1}{4 \left( m_{\rm O}/m_{\rm acetone} \right) \cos^2\left(\theta/2\right) + \left[ \left( m_{\rm CH_3} + m_{\rm O} \right)/m_{\rm O} \right]} = 0.36, \tag{17}$$

where  $\theta$  is the angle between the O–O and C–C bonds that are breaking. Although the intensity in the Dalitz plot is centered around the point given by these energy fractions, shown by an orange cross in Fig. 6(c), and these values are similar to the experimental average fractional energy release, presented in Sec. III B, the very broad distribution around this point and the geometry of the radical are also consistent with asynchronous concerted dissociation. Either concerted dissociation mechanism could lead to the observed intensity pattern in the Dalitz plot in Fig. 6(c), but we propose that an asynchronous mechanism is more likely than C–O and C–C bond cleavage occurring instantaneously, as discussed below.

6

No calculated potential energy surfaces for electronically excited *t*-BuOO exist to our knowledge, but previous work on the methyl peroxy<sup>8</sup> and phenyl peroxy<sup>15</sup> radicals suggests that the  $\tilde{B}$  state is repulsive along the O–O bond, with a shallow minimum at large O–O distances. It has previously been predicted that after excitation to the  $\tilde{B}$  state, the major dissociation channel for the methylperoxy radical (CH<sub>3</sub>OO) would be O + CH<sub>3</sub>O due to the repulsive nature of the  $\tilde{B}$  state.<sup>8</sup> A possible mechanism for the formation of the three-body dissociation could therefore be direct O–O bond cleavage on the  $\tilde{B}$  state, followed by fragmentation of the *t*-BuO radical. Although at first glance this may appear to be a sequential mechanism, RRKM calculations for the dissociation of the *t*-BuO radical predict a rate of  $2.4 \times 10^{12}$  s<sup>-1</sup>, faster than the rotational period of the *t*-BuO radical. Hence, the overall mechanism would be classified as an asynchronous concerted dissociation, consistent with the experimental Dalitz plots. A similar mechanism has previously been observed for the 248 nm dissociation of *tert*-butyl hypochlorite to form Cl, O, and acetone.<sup>53</sup> In that experiment, the O–Cl bond directly dissociated on an excitedstate surface to form *t*-BuO and Cl fragments, with an average translational energy around 60% of the available energy. It was found that the majority (90%) of the *t*-BuO fragments decomposed to form CH<sub>3</sub> + acetone.

As discussed in Sec. III A, the *t*-BuOO radical has an average internal energy of 0.28 eV prior to the dissociation, localized in the O–O bond stretching mode. It should be noted that as the three body-dissociation mechanism for high translational energy release involves repulsive dissociation along the O–O bond, this additional energy in the O–O stretching mode will likely result in a translational energy distribution that peaks slightly higher than if all *t*-BuOO radicals were in the vibrational ground state. This would not be expected to affect the ground state dynamics that are observed for two-body dissociation of *t*-BuOO, as the internal energy in the O–O stretch prior to the dissociation is much less than 5 eV available to the radical after internal conversion to the ground state.

For dissociation events with translational energies below 0.8 eV, the distribution of the normal to the dissociation plane is isotropic, consistent with dissociation occurring on a time scale that is much longer compared with molecular rotation. Internal conversion to the ground electronic state followed by dissociation generally yields more isotropic distributions of the fragments and lower translational energy release than dissociation along an excited state, and so this could explain the shoulder in the translational energy distribution shown in Fig. 5.

For these low translational energy release events, the Dalitz plot shows unequal momenta partitioning between the O and CH3 fragments. Therefore low translational energy release events are not consistent with the repulsive, concerted dissociation mechanism discussed above. Unequal partitioning of momenta between the O and CH<sub>3</sub> fragments could result from a sequential dissociation, in which the energy fraction of one of the fragments is determined in the first dissociation event.<sup>28,30,54,55</sup> The Dalitz plot in Fig. 6(b) shows two areas of intensity, one in the top left of the inscribed ellipse corresponding to a large  $\epsilon_{\rm O}$  and  $\epsilon_{\rm acteone}$  and small  $\epsilon_{\rm CH_3}$ , and the other in the bottom right of the ellipse with a large  $\epsilon_{CH_3}$  and  $\epsilon_{\text{acteone}}$  and small  $\epsilon_0$ . As mentioned previously, the similar masses of CH3 and O will result in some mislabeling of the fragments in the analysis process, and so it is likely that the symmetry in this plot is an artifact and there should be only a single area of intensity, with either small  $\epsilon_0$  and large  $\epsilon_{CH_3}$ or vice versa. The sequential dissociation of t-BuOO on the ground electronic state will result in little translational energy imparted in the O fragment in a barrierless first dissociation step.<sup>51</sup> The secondary dissociation of t-BuO over a barrier, which has been calculated to be 0.47 eV above the products, will result in a larger translational energy release and therefore a large value of  $\epsilon_{acteone}$  and  $\epsilon_{CH_3}$ , which is consistent with the intensity pattern in the Dalitz plot.

#### V. CONCLUSIONS

The current work has studied the photodissociation of t-BuOO at 248 nm (5.00 eV) by means of fast-beam coincidence translational spectroscopy. Photodissociation via both two- and three-body fragmentation channels is observed, and the mass and translational energy distributions were reported. The dominant channel (83%) is found to be 3-body dissociation into  $O + CH_3$  + acetone products. Above a translational energy release of 0.8 eV, the experimental translational energy distribution and anisotropy for this channel are found to be consistent with dissociation on an electronically excited surface, whilst the momentum partitioning amongst the three fragments suggests an asynchronous concerted fragmentation process. For translational energy release below 0.8 eV, the isotropic distribution of the normal to the dissociation plane and very uneven partitioning of momenta between the O and CH3 fragments are consistent with internal conversion to the ground electronic state, followed by sequential dissociation. The twobody channels,  $O_2 + t$ -butyl (10%) and HO<sub>2</sub> + isobutene (7%), were attributed to internal conversion from the initially excited  $\tilde{B}$  state to the ground electronic state, followed by dissociation. Experimental product branching ratios for the two-body

channels are found to be in good agreement with RRKM calculations and suggest that the  $HO_2$  loss proceeds directly from the *t*-BuOO radical, as opposed to following isomerization to the QOOH radical.

#### SUPPLEMENTARY MATERIAL

See supplementary material for simulations of the twobody mass distribution.

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