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## Competing pathways in the near-UV photochemistry of acetaldehyde

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Time-resolved ion imaging measurements have been performed to explore the photochemistry of acetaldehyde at photolysis wavelengths spanning the range 265–328 nm. Ion images recorded probing CH<sub>3</sub> radicals with single-photon VUV ionization show different dissociation dynamics in three distinct wavelength regions. At the longest photolysis wavelengths,  $\lambda > 318$  nm, CH<sub>3</sub> radicals are formed over tens of nanoseconds with a speed distribution that is consistent with statistical unimolecular dissociation on the S<sub>0</sub> surface following internal conversion. In the range 292 nm  $\leq \lambda \leq$  318 nm, dissociation occurs almost exclusively on the T<sub>1</sub> surface following intersystem crossing and passage over a barrier, leading to the available energy being partitioned primarily into photofragment recoil. The CH<sub>3</sub> speed distributions become bimodal at  $\lambda < 292$  nm. In addition to the translationally fast T<sub>1</sub> products, a new translationally slow, but non-statistical, component appears and grows in importance as the photolysis wavelength is decreased. Photofragment excitation (PHOFEX) spectra of CH<sub>3</sub>CHO obtained probing CH<sub>3</sub> and HCO products are identical across the absorption band, indicating that three-body fragmentation is not responsible for the non-statistical slow component. Rather, translationally slow products are attributed to dissociation on S<sub>0</sub>, accessed via a conical intersection between the S<sub>1</sub> and S<sub>0</sub> surfaces at extended C–C distances. Time-resolved ion images of CH<sub>3</sub> radicals measured using a picosecond laser operating at a photolysis wavelength of 266 nm show that product formation on T<sub>1</sub> and S<sub>0</sub> via the conical intersection occurs with time constants of 240 ps and 560 ps, respectively.

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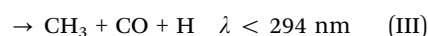
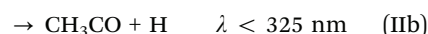
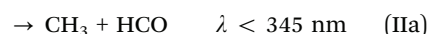
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## Introduction

Interest in the photochemistry of acetaldehyde is driven by its importance in atmospheric chemistry, where absorption of sunlight induces decomposition to form reactive radical species. From a fundamental perspective, as a small molecule amenable to rigorous experimental and theoretical investigation, acetaldehyde presents particularly rich photochemistry and photophysics. The near-UV absorption spectrum of acetaldehyde is a broad continuum spanning 240–336 nm, with diffuse vibrational structure superimposed.<sup>1</sup> The first absorption band arises from excitation of an electron from the oxygen lone pair to the lowest  $\pi^*$  orbital localized on the C–O bond. The 0<sub>0</sub> origin band of the S<sub>1</sub>  $\leftarrow$  S<sub>0</sub> electronic transition has been identified at 335.9 nm (29771 cm<sup>−1</sup>) by laser-induced fluorescence measurements.<sup>2</sup> The spectra show that the hydrogen-wagging and methyl-torsion modes are active, consistent with a large geometric rearrangement at the S<sub>1</sub> minimum.<sup>2–6</sup> The spectroscopy of the triplet state has been explored using laser-induced phosphorescence, with the 0<sub>0</sub> origin band of the T<sub>1</sub>  $\leftarrow$  S<sub>0</sub> electronic transition identified at

367.1 nm (27241 cm<sup>−1</sup>).<sup>7</sup> At all wavelengths, there is competition between radiative and non-radiative decay processes. Both fluorescence and phosphorescence quantum yields decline steeply at  $\lambda < 319$  nm due to the onset of Norrish Type I dissociation over a barrier on the T<sub>1</sub> surface to form CH<sub>3</sub> + HCO.<sup>6,8,9</sup> Quantum beats have been observed in the fluorescence at longer wavelengths, indicating reversible population transfer between the S<sub>1</sub> and T<sub>1</sub> states.<sup>8–10</sup>

At least four chemically distinct product channels are energetically accessible following excitation in the near UV, and each can be reached by multiple photodissociation pathways, giving acetaldehyde a particularly rich photochemistry. The major dissociation products and their threshold wavelengths are



Threshold wavelengths are calculated from 0 K thermodynamic data obtained from the Argonne National Lab Active Thermochemical Tables (ATcT).<sup>11</sup> The threshold wavelength for

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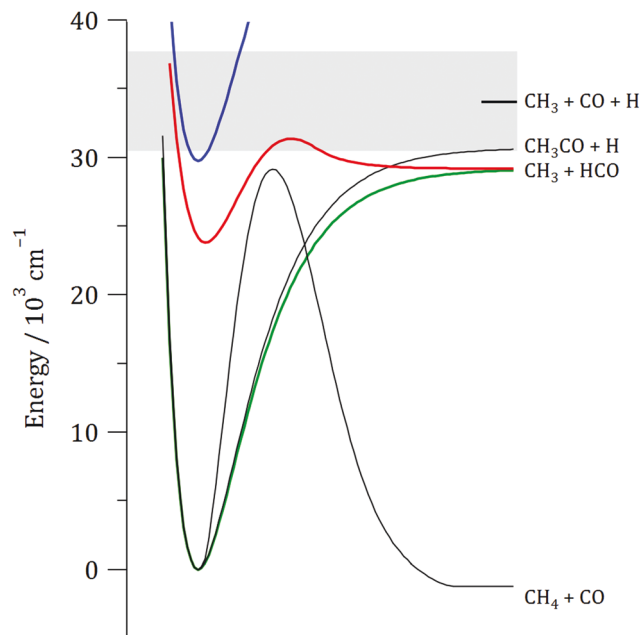


Fig. 1 Schematic potential energy surfaces and dissociation channels for acetaldehyde. The shaded gray area represents the range of photolysis wavelengths used.

channel (I) product formation reflects the barrier to dissociation on the  $S_0$  surface. Fig. 1 illustrates the key features of the  $S_0$ ,  $S_1$  and  $T_1$  potential energy surfaces of acetaldehyde.

The molecular products  $CH_4 + CO$  (channel (I)) are formed with significant quantum yield at shorter excitation wavelengths ( $\lambda < 292$  nm).<sup>1</sup> Molecular products can be formed by dissociation on the  $S_0$  surface *via* a conventional tight transition state following internal conversion (IC), or alternatively by roaming. Gherman *et al.* identified CO products exclusively in  $v = 0$  following photolysis at 248 nm, observing a near-Boltzmann  $1300 \pm 90$  K rotational distribution that was interpreted as being due to dissociation over a barrier on the  $S_0$  surface following internal conversion.<sup>12</sup> Trajectory calculations initiated at the  $S_0$  TS lead to rotationally excited CO products and partitioning of a large fraction of the available energy into translational recoil, in qualitative agreement with the experimental observations.<sup>13,14</sup> Acetaldehyde was the second molecule to show evidence of photochemical roaming, with the observation of low- $J$  CO formed in conjunction with highly internally excited  $CH_4$ ,<sup>15–18</sup> consistent with the dynamical signatures established for roaming in formaldehyde.<sup>19–21</sup> Quasi-classical trajectory calculations on *ab initio* potential surfaces supported this interpretation and indicated that roaming involved frustrated dissociation and subsequent intramolecular reaction between the  $CH_3 + HCO$  radical products.<sup>17,22,23</sup> More recent ion imaging experiments, however, have identified translationally slow low- $J$  CO products, with an onset wavelength consistent with the threshold for channel (IIb), leading to the suggestion that the radical products  $CH_3CO + H$  substantially contribute to roaming.<sup>24</sup>

Of the two radical product channels, (IIa) is most important and dominates the long wavelength ( $\lambda > 266$  nm) photochemistry.<sup>1</sup>

The radical products  $CH_3 + HCO$  can be formed *via* unimolecular dissociation on  $S_0$  following internal conversion or, if sufficient energy is available, dissociation over a barrier on the  $T_1$  surface following intersystem crossing. Involvement of the  $T_1$  surface was initially proposed and first confirmed experimentally by Horowitz and Calvert.<sup>25,26</sup> Threshold wavelengths for dissociation on  $T_1$  between 318.3–323.0 nm have been estimated using a variety of experimental techniques, including fluorescence lifetime collapse and the onset of product formation.<sup>27–32</sup> Laser-induced fluorescence detection of HCO products following photolysis above the  $T_1$  barrier has been used to identify modest rotational excitation and a tendency for vibrational excitation at shorter wavelengths.<sup>27,28,33,34</sup> The energy disposal has been justified based on *ab initio* calculations of the  $T_1$  transition state geometry and trajectory calculations that explore the dissociation dynamics.<sup>35–38</sup> Time-resolved experiments have characterized the appearance times of HCO products as many tens of nanoseconds following photolysis at wavelengths that excite just above the  $T_1$  barrier and sub-nanosecond at 266 nm.<sup>39–41</sup> Ion imaging experiments probing  $CH_3$  and HCO photoproducts confirm that the available energy is partitioned primarily into translation following excitation above the  $T_1$  barrier, although the degree of internal excitation in the products increases at shorter wavelengths.<sup>29,31,32,42</sup> Dissociation on the  $S_0$  surface at longer wavelengths was confirmed by Heazlewood *et al.* who observed distinct HCO product state distributions following photolysis above and below the  $T_1$  barrier.<sup>30</sup> HCO products are formed on  $S_0$  with an effectively statistical product state distribution, while those formed on  $T_1$  retain dynamical signatures of the barrier. Trajectory calculations incorporating surface hopping involving the  $S_1$ ,  $T_1$  and  $S_0$  states have explored the branching between  $CH_3 + HCO$  products over a broad range of photolysis wavelengths.<sup>38</sup> Experiments performed with partially deuterated  $CD_3HCO$  isotopomer identified both HCO and DCO products following excitation to  $S_1$  below the  $T_1$  barrier indicating significant isotope scrambling prior to dissociation on the  $S_0$  surface.<sup>43</sup> Collisions can stabilize the enol form, vinyl alcohol, and photo-tautomerization may be an efficient route to formation of organic acids in the troposphere.<sup>44,45</sup>

At wavelengths shorter than 294 nm, the triple fragmentation channel (III) becomes energetically accessible. Triple fragmentation in acetaldehyde was first postulated by de Wit *et al.* and modelled using a two-step phase space theory calculation that predicts product translational energy distributions similar to those obtained by roaming.<sup>46</sup> Experimental evidence for triple fragmentation at 248 nm comes from time-resolved FTIR emission spectroscopy and also cavity ring-down spectroscopy measurements that indirectly determined radical product yields following conversion to  $HO_2$ .<sup>47,48</sup> Curiously, both studies conclude that the radical channel (IIb) is inactive at 248 nm. This observation is in contrast to earlier estimates,<sup>49</sup> which suggest a quantum yield  $> 10\%$  at this wavelength. Ion imaging measurements have also detected H atoms directly.<sup>16</sup>

In this paper, we report a study of acetaldehyde photochemistry following excitation at wavelengths between 265–328 nm. Ion imaging experiments using single-photon VUV ionization of

CH<sub>3</sub> radicals show three distinct competitive photochemical mechanisms. At the longest wavelengths products are formed *via* statistical unimolecular dissociation on the S<sub>0</sub> surface. Dissociation on the T<sub>1</sub> surface dominates once energetically accessible, leading to translationally fast products. A translationally slow, but non-statistical, channel that opens at shorter wavelengths is assigned to dissociation on S<sub>0</sub>, accessed *via* a conical intersection. The relative yields of CH<sub>3</sub> and HCO products are determined from photofragment excitation action spectra, and suggest that triple fragmentation is not a significant dissociation mechanism over the wavelength range studied. Picosecond time-resolved ion imaging measurements at 266 nm show that two competitive mechanisms for product formation are active. Product formation on T<sub>1</sub> is likely limited by the rate of S<sub>1</sub> → T<sub>1</sub> intersystem crossing, while internal conversion *via* a long range S<sub>1</sub>/S<sub>0</sub> conical intersection leads to S<sub>0</sub> products that form a factor of two more slowly.

## Experimental methods

Experiments were performed in a velocity-map ion imaging mass spectrometer that has been described in detail previously.<sup>50</sup> Ion images were recorded using direct-current (DC) slice velocity map imaging.<sup>51</sup> PHOFEX spectra were recorded with the mass spectrometer operating in a conventional Wiley–McLaren time-of-flight arrangement. Ar carrier gas was flowed over a sample of acetaldehyde (Sigma-Aldrich > 99.5% purity) in a stainless steel finger that was cooled in an ice bath and expanded into high vacuum from a stagnation pressure of 1 atm using a pulsed valve (General Valve, Series 9). The expansion of the 30% CH<sub>3</sub>HCO/Ar was skimmed (Beam Dynamics) to form a molecular beam before being intersected by counter-propagating photolysis and ionization laser beams. A stack of custom DC slice imaging electrodes accelerated the resultant ions towards a microchannel plate and phosphor screen assembly (Photonis) fitted with a fast, high voltage gate module (Photek GM-MCP-2). The phosphorescence from the screen was monitored by a silicon photomultiplier (SenSL) to obtain conventional time-of-flight mass spectra. For DC slice imaging experiments, a CCD camera (Basler a312f) captured the spatial distribution of mass-selected and sliced ions on the detector. Ion images were acquired while gating the detector to obtain the central ~20 ns of the ion packet. Photolysis and probe laser pulse energies were monitored with a photodiode (Thorlabs DET10a) that had been previously calibrated against an energy meter (Gentec Maestro). SPM and photodiode signals were digitized by an oscilloscope (LeCroy HDO4054) interfaced to a data acquisition PC running custom written software (National Instruments LabVIEW).

Experiments were performed using lasers with both nanosecond and picosecond pulse durations. In both cases, products were detected using single photon VUV ionization. For the nanosecond experiments, a mid-band Nd:YAG-pumped optical parametric oscillator (OPO) (Continuum Surelite EX and Horizon II) was used to generate photolysis pulses spanning the wavelength range 260–328 nm with a linewidth of 5–7 cm<sup>-1</sup>. The photolysis beam was loosely focused into the ionization region of

the mass spectrometer with an uncoated fused silica lens of focal length  $f = 1000$  mm. The pulse energy varied from 1.1 to 2 mJ across the wavelength range. VUV radiation at 118.2 nm (10.49 eV) was produced by 3rd harmonic generation in Xe/Ar of the frequency-tripled output of a Nd:YAG laser (Continuum Surelite II-10). A static gas cell containing a Xe/Ar mixture (10:1) at a total pressure of ~80 Torr was separated from the ionization chamber by a MgF<sub>2</sub> lens that focused the 118.2 nm into the molecular beam while re-collimating the residual 355 nm.<sup>52</sup> A digital delay generator (Quantum Composers, 9528) was used to control the time delay between the photolysis and ionization pulses.

The picosecond experiments used the 266 nm and 355 nm output from a Nd:YAG laser (Ekspla PL2143), which generated pulses of 28 ps duration at a repetition rate of 10 Hz. The typical pulse energy at 266 nm was 0.5 mJ, while 2.1 mJ of 355 nm was used to generate picosecond duration VUV pulses in the Xe/Ar gas cell as described above. The time delay between the photolysis and ionization pulses was varied over a 2 ns range using a computer-controlled delay line. All other aspects of the experimental apparatus were identical to those used in the experiments performed with the nanosecond laser systems.

## Results

The 118.2 nm probe radiation can ionize all polyatomic radical photodissociation products as well as the parent CH<sub>3</sub>CHO. The molecular products CH<sub>4</sub> and CO both have ionization energies greater than the 10.49 eV photon energy and were not observed. Two-color signals attributable to ionized CH<sub>3</sub> and HCO photofragments were evident in the time-of-flight mass spectrum, but no signal due to CH<sub>3</sub>CO was observed at any photolysis wavelength within the signal to noise. The ionization cross-sections of CH<sub>3</sub> and HCO are similar in magnitude near 118 nm and relatively small ( $\sim 5 \times 10^{-18}$  cm<sup>2</sup>).<sup>42,53,54</sup> However, ionization is universal. That is, the ionization efficiency is independent of the rovibrational state of the products, which readily compensates for the apparent limitation on the detection sensitivity.<sup>55</sup>

A significant problem for measurements of CH<sub>3</sub>CHO photolysis is formation of clusters in the supersonic expansion, as previously noted by Lee *et al.*<sup>24</sup> Peaks corresponding to (CH<sub>3</sub>CHO)<sub>*n*</sub> clusters up to *n* = 5 were readily observed in the mass spectrum following VUV ionization. Dissociation of CH<sub>3</sub>CHO molecules in clusters produces a translationally slow component that dominates the center of the CH<sub>3</sub> ion images. The cluster contribution could be removed almost completely by careful adjustment of the expansion conditions and operating in the earliest part of the gas pulse. Cluster signals were minimized while monitoring the ion images obtained at a photolysis wavelength of 308 nm. Under cluster-free conditions, the CH<sub>3</sub> ion image is a clean, isotropic ring with a narrow speed distribution centered at 1700 m s<sup>-1</sup>. Fig. 2 shows DC slice ion images of CH<sub>3</sub> products at 308 nm, measured under cluster-forming and cluster-free conditions. The expansion conditions were optimized to remove the cluster contribution prior to all measurements.

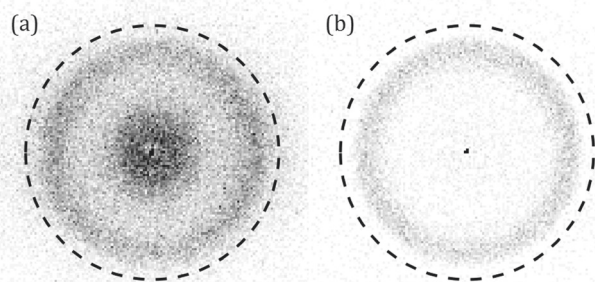


Fig. 2 DC slice ion images of  $\text{CH}_3$  products from the photolysis of  $\text{CH}_3\text{CHO}$  at 308 nm. Image (a) was recorded with clusters were present in the expansion, while image (b) was recorded under cluster-free conditions. The dashed circle indicates the maximum  $\text{CH}_3$  speed, determined by energy conservation.

### 1. Nanosecond ion imaging

DC sliced velocity-map ion images of  $\text{CH}_3$  photoproducts were recorded following excitation of  $\text{CH}_3\text{CHO}$  from 265 nm to 328 nm in 1 nm intervals, spanning available energies  $E_{\text{AVL}} = 1540\text{--}8930\text{ cm}^{-1}$  above the dissociation energy for channel (IIa) ( $D_{0,\text{IIa}} = 28\,950\text{ cm}^{-1}$ ). Speed and angular distributions were obtained by direct integration of the sliced images over angular and radial coordinates. The angular distributions were universally isotropic, indicating dissociation on a time scale that is long relative to the rotational period of the electronically excited acetaldehyde. The complete set of normalized  $\text{CH}_3$  speed distributions is shown as an intensity plot in Fig. 3. The observed  $\text{CH}_3$  speed distributions are wavelength-dependent, but can be broadly categorized into the three regions labeled A, B and C.

Region A ( $\lambda > 318\text{ nm}$ ) corresponds to excitation energies below the  $T_1$  barrier of  $31\,400 \pm 50\text{ cm}^{-1}$  and consequently products can only be formed on the  $S_0$  surface.<sup>31</sup> Few ion counts were recorded at the short photolysis-probe delays (40 ns) used to obtain the data in Fig. 3, although translationally slow methyl products are detected at longer delays as described below. A sharp increase in the total ion count is observed at  $\lambda \leq 318\text{ nm}$  (region B). Throughout region B, sufficient energy is available to overcome the  $T_1$  barrier, leading to  $\text{CH}_3$  radicals with recoil speeds that peak near, and extend to, the maximum allowed by energy conservation. As the photolysis wavelength is decreased, the speed distributions broaden and the most probable speeds deviate increasingly from  $v_{\text{max}}$ . This trend continues through region C ( $\lambda \leq 292\text{ nm}$ ), whereupon the speed distributions also become bimodal. A new translationally slow component first appears weakly at 292 nm and increases in magnitude as the wavelength is further decreased. We assert here, and justify later, that the slow component at short wavelengths results from channel (IIa) products formed on the  $S_0$  surface.

The methyl radical speed distributions were converted into total translational energy distributions using

$$P(E_T) \propto P(v)/v$$

where

$$E_T = \frac{1}{2}m_{\text{CH}_3} \left( 1 + \frac{m_{\text{CH}_3}}{m_{\text{HCO}}} \right) v_{\text{CH}_3}^2$$

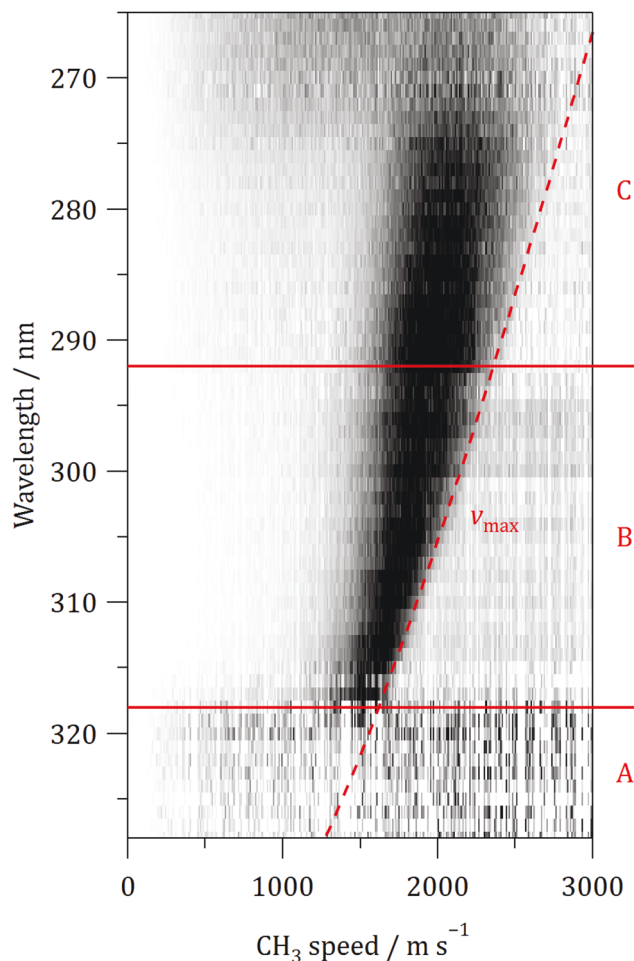


Fig. 3 Intensity plot showing normalized  $\text{CH}_3$  speed distributions from photolysis of  $\text{CH}_3\text{CHO}$  over the wavelength range 265–328 nm. The curved dashed line indicates the maximum  $\text{CH}_3$  speed,  $v_{\text{max}}$ , determined by energy conservation. Region A corresponds to excitation to  $S_1$  at energies below the  $T_1$  barrier and results in no significant  $\text{CH}_3$  production at the photolysis-probe delay of 40 ns; region B is dominated by fast-moving  $\text{CH}_3$  formed by dissociation on the  $T_1$  surface; and region C sees the appearance of a new translationally slow component that is attributed to non-statistical dissociation on  $S_0$  as described in the text.

and it is implicitly assumed that formyl is the momentum-matched co-fragment. The available energy following dissociation,  $E_{\text{AVL}}$ , is partitioned between internal (rotational and vibrational) energy of the fragments,  $E_{\text{INT}}$ , and relative translation,  $E_T$ , according to

$$E_{\text{AVL}} = h\nu - D_0 = E_{\text{INT}} + E_T$$

where  $h\nu$  is the photolysis photon energy and  $D_0$  is the channel (IIa) dissociation energy. Since single-photon VUV ionization of  $\text{CH}_3$  is non-state-selective, the values of  $E_{\text{INT}}$  determined in these measurements are the sums of the internal energies of the  $\text{CH}_3$  and  $\text{HCO}$  fragments. Normalized  $E_T$  distributions obtained at seven selected photolysis wavelengths spanning regions A (320 nm), B (316 nm, 306 nm, and 296 nm), and C (286 nm, 276 nm, and 266 nm) are shown in Fig. 4. These wavelengths correspond to excitation energies ranging from



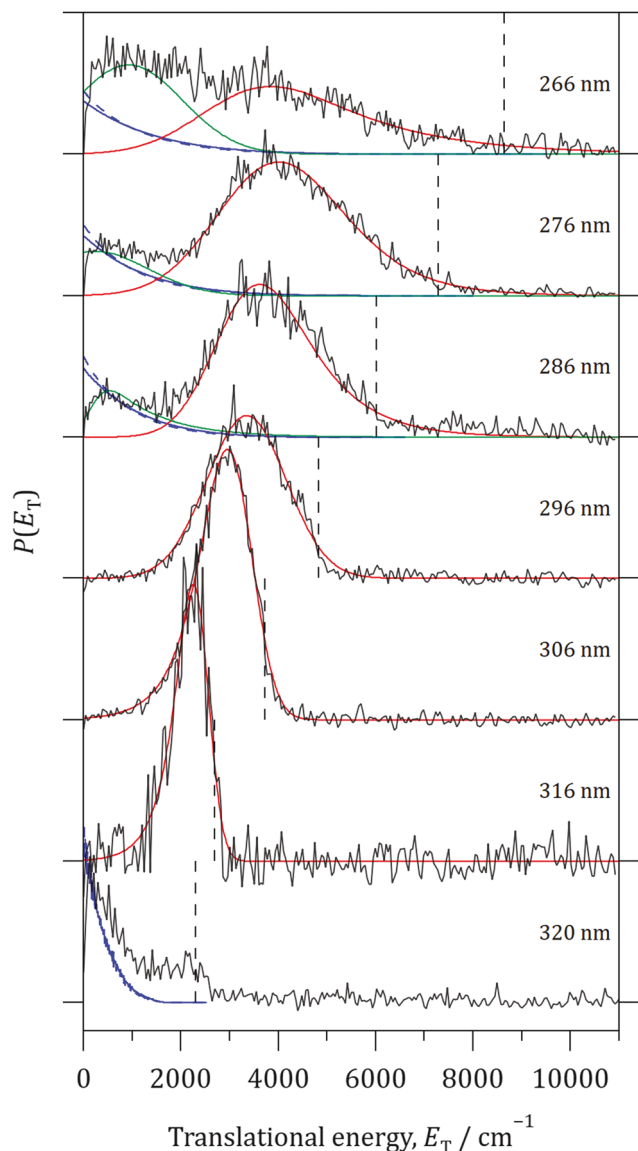


Fig. 4 Normalized product translational energy distributions following photolysis of  $\text{CH}_3\text{CHO}$  at the indicated wavelengths spanning 266–320 nm. The 320 nm data were recorded with a photolysis-probe delay of 210 ns, while all other wavelengths used a delay of 40 ns. Dashed vertical lines indicate the energetic limits at each photolysis wavelength. The green and red curves are fits to the  $E_T$  distributions attributed to products formed on the  $S_0$  and  $T_1$  surfaces, respectively. Blue curves are the predictions for unimolecular dissociation from phase space theory (solid) and separate statistical ensembles (dashed) calculations.

$150\text{ cm}^{-1}$  below to  $250\text{--}6200\text{ cm}^{-1}$  above the  $T_1$  barrier. Excitation just above the  $T_1$  barrier results in a narrow  $E_T$  distribution that cuts off sharply on the high- $E_T$  side near the energetic limit. As the photolysis wavelength is decreased through region B, the  $E_T$  distributions broaden and increasingly shift away from the energetic limit, indicating that a greater fraction of the available energy is partitioned into  $E_{\text{INT}}$ . The onset and subsequent growth of the slow  $S_0$  component through region C is evident in Fig. 4, while the wavelength-dependent evolution of the  $T_1$  component continues with the same trend established in region B.

The bimodal  $E_T$  distributions in region C were decomposed into relative contributions of the fast  $T_1$  and slow  $S_0$  components by fitting to sums of exponentially-modified Gaussian functions (also shown in Fig. 4). The branching between the  $T_1$  and short-wavelength  $S_0$  components is shown in Fig. 5. Products formed on  $S_0$  account for  $\sim 10\text{--}15\%$  of the total near 292 nm and increases to around 40% at the shortest wavelengths used in the measurements. The average translational energy and, by conservation of energy, average radical internal energy are shown as a function of  $E_{\text{AVL}}$  in Fig. 6. For products formed on the  $T_1$  surface, both  $\langle E_T \rangle$  and  $\langle E_{\text{INT}} \rangle$  increase approximately linearly with  $E_{\text{AVL}}$ .  $\langle E_T \rangle$  ranges from  $\sim 2000\text{ cm}^{-1}$  following excitation at 318 nm, just above the  $T_1$  threshold, to  $\sim 5000\text{ cm}^{-1}$  at 265 nm while  $\langle E_{\text{INT}} \rangle$  correspondingly increases by an order of magnitude from  $\sim 400\text{ cm}^{-1}$  to  $\sim 4000\text{ cm}^{-1}$ . The fraction of  $E_{\text{AVL}}$  partitioned into relative translation decreases from 0.85 to 0.56 over the same range. In contrast, products formed on  $S_0$  in region C have significantly smaller  $\langle E_T \rangle$  values that increase only slightly as the available energy increases, ranging from  $\sim 700\text{--}1240\text{ cm}^{-1}$ . The fraction of available energy partitioned into translation is remarkably consistent across this range at  $\sim 0.15$ .  $\langle E_{\text{INT}} \rangle$  for products formed on  $S_0$  following excitation almost doubles from  $\sim 4000\text{ cm}^{-1}$  near the onset wavelength of 292 nm to  $7500\text{ cm}^{-1}$  at 265 nm.

Time-resolved ion images of  $\text{CH}_3$  products were recorded at photolysis wavelengths of 317 nm and 320 nm while stepping the photolysis-probe time delay between 30–210 ns to explore the photochemistry following excitation near the  $T_1$  barrier. Excitation at 320 nm prepares acetaldehyde in the  $S_1$  state with an energy  $150\text{ cm}^{-1}$  below the  $T_1$  barrier, restricting channel (IIa) product formation to the  $S_0$  surface. At 317 nm, the excitation energy is  $150\text{ cm}^{-1}$  above the barrier and products can form on both the  $T_1$  and  $S_0$  surfaces. The maximum  $\text{CH}_3$  speeds allowed by energy conservation following one-photon dissociation at 320 nm and 317 nm are  $1550\text{ m s}^{-1}$  and  $1650\text{ m s}^{-1}$ , respectively. Fig. 7 shows the  $\text{CH}_3$  speed distributions measured

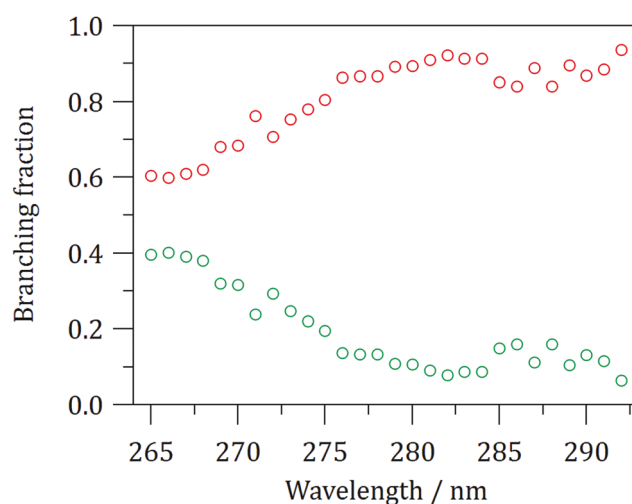


Fig. 5 Branching between  $T_1$  (red) and  $S_0$  via the  $S_1/S_0$  conical intersection (green) pathways derived from  $P(E_T)$  distributions in region C.

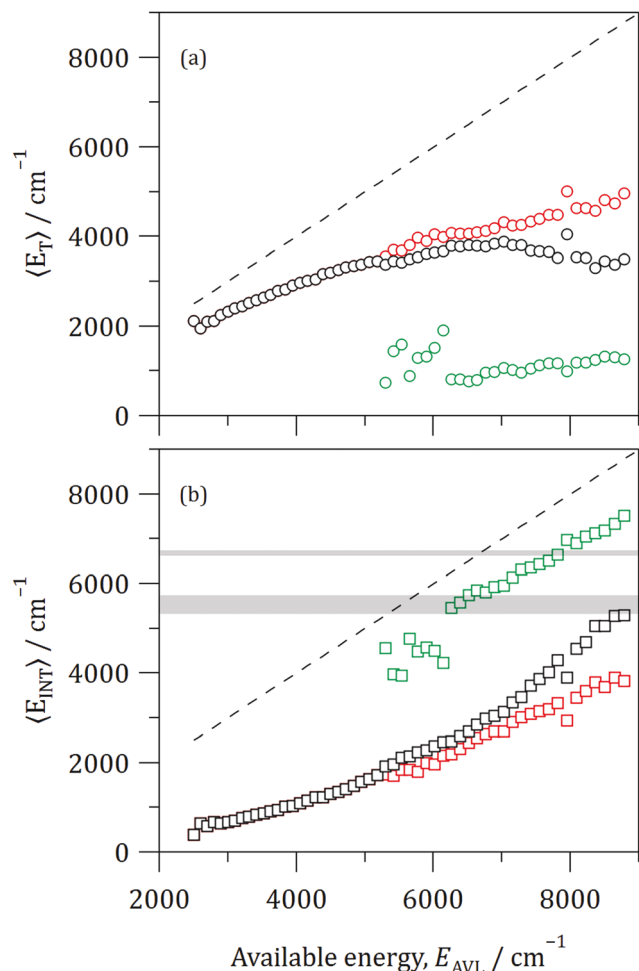


Fig. 6 (a) Average translational energy as a function of available energy for products formed on  $T_1$  (red),  $S_0$  (green), and overall (black). (b) Average radical internal energy as a function of available energy. Shaded areas indicate experimental or theoretical barriers for dissociation of HCO as discussed in the text.

at delays of 30 ns, 90 ns and 210 ns. The  $\text{CH}_3$  speed distributions at both wavelengths can be decomposed into three components; (a) a translationally slow feature, that increases in magnitude with increasing delay, (b) the narrow fast component due to dissociation on  $T_1$  that peaks near  $v_{\text{max}}$ , and (c) a broad feature extending significantly beyond  $v_{\text{max}}$ , that decreases in magnitude with increasing delay. While the relative magnitudes of each component are different at each pump wavelength, they each display similar dependences on the photolysis-probe time delay. The time-dependent magnitudes of each component of the  $\text{CH}_3$  speed distribution are fit to single exponential loss or growth functions, which are also shown in Fig. 7. The time constants are summarized in Table 1.

At 320 nm, the speed distribution is dominated by translationally slow products at long delays. This component grows in with a time constant of  $66 \pm 9$  ns and is assigned to product formation on  $S_0$ . The  $S_0$  pathway appears to remain active at 317 nm, where a weak, but otherwise equivalent, feature grows in with a similar time constant of  $58 \pm 23$  ns. At 317 nm, the speed distribution is dominated at all time delays by fast moving  $\text{CH}_3$  products

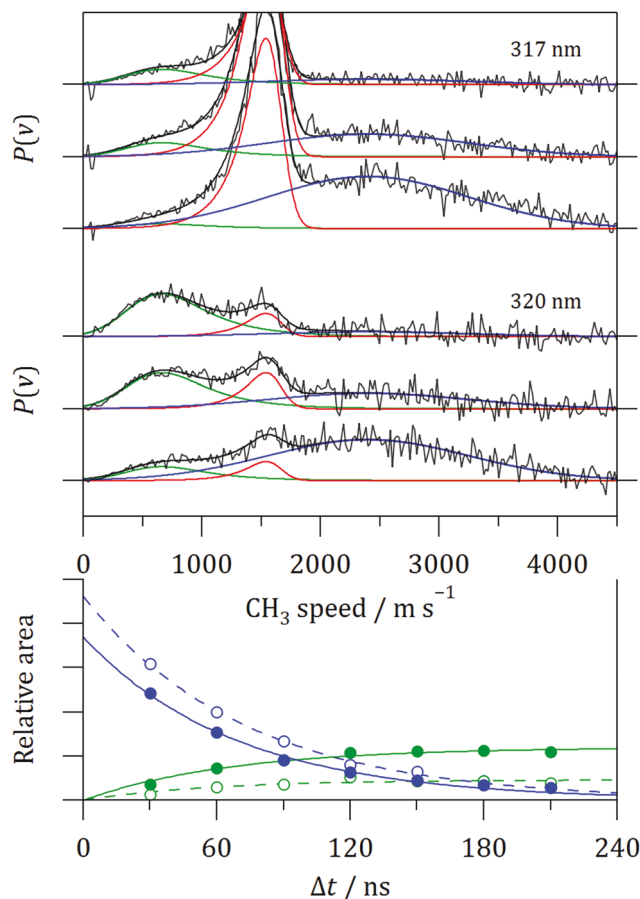


Fig. 7 Time-resolved  $\text{CH}_3$  speed distributions from the photolysis of acetaldehyde at 317 nm and 320 nm. Data shown are for photolysis probe delays of 210 ns, 90 ns and 30 ns (top to bottom). The speed distributions are decomposed into components corresponding to product formation on  $S_0$  via internal conversion (green),  $T_1$  (red) and transient dissociative ionization of  $S_1$  (blue). The lower panel shows the time dependence of the  $S_1$  and  $S_0$  components at 317 nm (open circles) and 320 nm (filled circles).

Table 1 Product formation and transient dissociative ionization time constants

$\lambda/\text{nm}$	$\tau/\text{ns}$		
	320	317	266
$S_0$ formation	$66 \pm 9$	$58 \pm 23$	$0.56 \pm 0.09$
$T_1$ formation	$54 \pm 5$	$18 \pm 2$	$0.24 \pm 0.05$
$S_1$ decay	$69 \pm 3$	$73 \pm 2$	—

formed on the  $T_1$  surface, with most probable speeds around  $1500 \text{ m s}^{-1}$ . A similar, but far weaker feature at 320 nm extends slightly beyond  $v_{\text{max}}$  and likely arises from photolysis of residual vibrationally excited acetaldehyde due to incomplete cooling in the supersonic expansion. Products formed on  $T_1$  do not appear promptly, but rather reach a maximum after tens of nanoseconds. At longer photolysis-probe delays, the magnitude of the  $T_1$  component decays, although this is likely due to flyout of fast-moving photofragments from the small VUV probe laser focal volume. Products formed with velocities perpendicular to the probe propagation direction are particularly affected, leading to the ion images developing an artefactual anisotropy at longer

delays. Finally, the broad, translationally fast components that decay with increasing delay are centered around  $2400 \text{ m s}^{-1}$  and extend far beyond  $\nu_{\text{max}}$ , indicating that a multi-photon process must be responsible. In contrast to the fast-moving products formed on  $T_1$ , however, the angular distributions remain isotropic, indicating that no flyout is occurring, despite the speeds being significantly greater. We will return to the origin of the multi-photon component in the discussion. Fitting to single-exponential decays yields time constants of  $69 \pm 3 \text{ ns}$  at  $320 \text{ nm}$  and  $73 \pm 2 \text{ ns}$  at  $317 \text{ nm}$ .

## 2. PHOFEX spectroscopy

PHOFEX action spectra of  $\text{CH}_3\text{CHO}$  were recorded by scanning the photolysis wavelength between  $260\text{--}328 \text{ nm}$  while monitoring the total two-color ion signals corresponding to  $\text{CH}_3$  and  $\text{HCO}$  photolysis products. The spectra shown in Fig. 8 were recorded using a photolysis-probe time delay of  $40 \text{ ns}$ , and have been corrected for a reproducible wavelength-dependent variation in the photolysis laser fluence. The PHOFEX spectra obtained probing  $\text{CH}_3$  and  $\text{HCO}$  are identical across the wavelength range and qualitatively reproduce the absorption band, including the diffuse structure present near the band maximum. A slight blue-shift of  $\sim 0.5 \text{ nm}$  in the action spectrum is consistent with the low temperature of the molecular beam. Finer structure in the long wavelength region ( $\lambda > 305 \text{ nm}$ ) reproduces that observed in analogous PHOFEX measurements reported by Cruse and Softley, who used  $2 + 1$  resonance-enhanced multiphoton ionization to state-selectively detect ground state  $\text{CH}_3$  and  $\text{HCO}$  fragments.<sup>29</sup> The structure has been attributed to progressions in Franck-Condon active vibrational modes of the  $S_1 \leftarrow S_0$  excitation, most probably combination bands of the CO stretch  $\nu_4$ ,  $\text{CH}_3$  rock  $\nu_{14}$ , and  $\text{CH}_3$  torsion  $\nu_{15}$  modes.<sup>56,57</sup> The expected yield of  $\text{CH}_3$  and  $\text{HCO}$ ,  $Y_{\text{IIa}}(\lambda)$ , can be calculated as the product of the absorption cross section and the photolysis quantum yield for channel (IIa), both functions of the excitation wavelength:

$$Y_{\text{IIa}}(\lambda) = \sigma(\lambda)\Phi_{\text{IIa}}(\lambda)$$

$Y_{\text{IIa}}(\lambda)$  was calculated using the  $295 \text{ K}$  absorption cross section from the UV/VIS Spectral Atlas<sup>58</sup> and atmospheric pressure photolysis quantum yield data from Moortgat *et al.*<sup>49</sup> The predicted yield of channel (IIa) products, shown in Fig. 8, is in excellent agreement with the PHOFEX spectra.

## 3. Picosecond time-resolved ion imaging

Time-resolved DC sliced velocity-map ion images of  $\text{CH}_3$  products of the  $266 \text{ nm}$  photolysis of  $\text{CH}_3\text{CHO}$  were recorded using picosecond duration pulses and the same single-photon VUV ionization detection scheme. The time delay between the  $266 \text{ nm}$  and  $118 \text{ nm}$  pulses is defined as  $\Delta t = t_{118} - t_{266}$ . Consequently,  $\Delta t > 0$  corresponds to the  $266 \text{ nm}$  pulse preceding the  $118 \text{ nm}$  ionization and two-color signals arise from  $266 \text{ nm}$  dissociation of neutral  $\text{CH}_3\text{CHO}$ , followed by subsequent VUV ionization of photoproducts. The measurements are complicated, however, by efficient ionization of the parent  $\text{CH}_3\text{CHO}$  at  $118 \text{ nm}$ . Reversing the time ordering of the pulses ( $\Delta t < 0$ ), leads to significantly larger  $\text{CH}_3^+$  signals due to photolysis of acetaldehyde cations by the  $266 \text{ nm}$  pulse. The rapid onset of  $\text{CH}_3^+$  at negative delay times

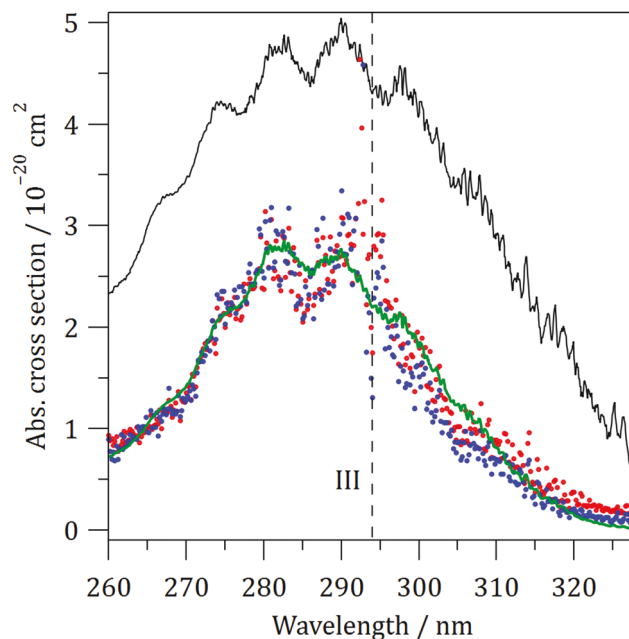


Fig. 8 Acetaldehyde PHOFEX action spectra recorded probing  $\text{CH}_3$  (blue) and  $\text{HCO}$  (red) products by single-photon VUV ionization alongside the conventional absorption spectrum (black) at  $294 \text{ K}$ . The PHOFEX spectra have been scaled to match the predicted product yield (green) calculated as the product of the wavelength-dependent absorption cross section and photolysis quantum yield for the  $\text{CH}_3 + \text{HCO}$  channel.

was used to characterize the  $28 \text{ ps}$  pulse duration, which defines the measurement time resolution and serves as a convenient means to identify when photolysis and probe pulses were coincident.

Ion images of  $\text{CH}_3$  products were recorded over a range of positive time delays spanning  $0\text{--}1420 \text{ ps}$ . The speed distributions shown in Fig. 9 represent the increase in the signal at longer delays after subtraction of the earliest time delay data, which is dominated by a time-independent background signal caused by the high peak power of the picosecond pulses. The speed distributions are bimodal, comprising fast and slow components, and at the longest delay of  $1420 \text{ ps}$  is identical to that observed in the nanosecond experiments. The speed distributions were decomposed by fitting to Gaussian functions; centers and widths were determined from fitting the long-delay data and constrained in subsequent fits of data at shorter delays, allowing only the amplitudes to float. The change in the amplitudes of each component relative to the signal at the shortest delay is shown in Fig. 10 alongside fits to a single exponential rise. The translationally fast component resulting from product formation on the  $T_1$  surface is formed rapidly with a time constant of  $240 \pm 50 \text{ ps}$  while the translationally slow component, attributed to product formation on  $S_0$ , is also formed more slowly, with a time constant of  $560 \pm 90 \text{ ps}$ .

## Discussion

### 1. Photolysis near the $T_1$ barrier: dissociation on $S_0$ and $T_1$

The height of the  $T_1$  barrier leading to channel (IIa) products has been investigated by various groups using spectroscopic approaches<sup>6,8,9</sup> and from wavelength thresholds for product

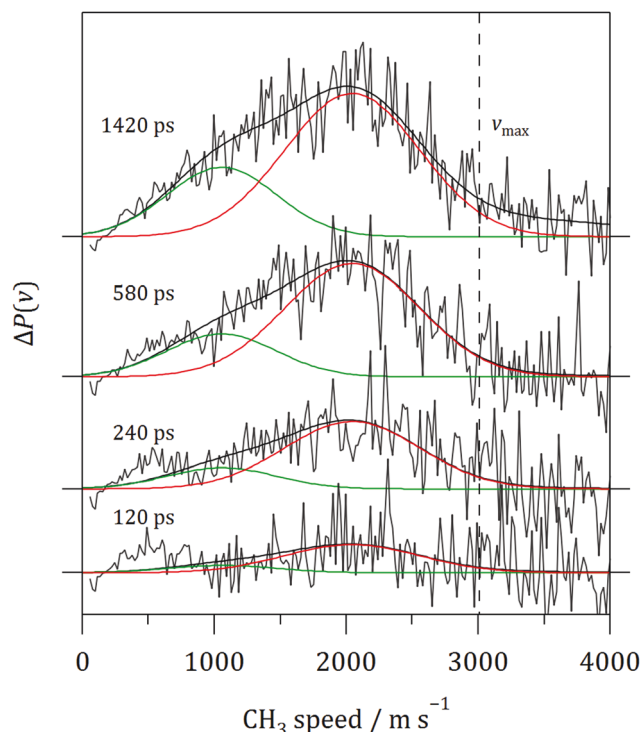


Fig. 9 Time evolution of the  $\text{CH}_3$  speed distributions following photolysis of  $\text{CH}_3\text{CHO}$  at 266 nm using 28 ps pulses. The green and red curves are fits to the speed distributions attributed to products formed on the  $S_0$  and  $T_1$  surfaces, respectively.

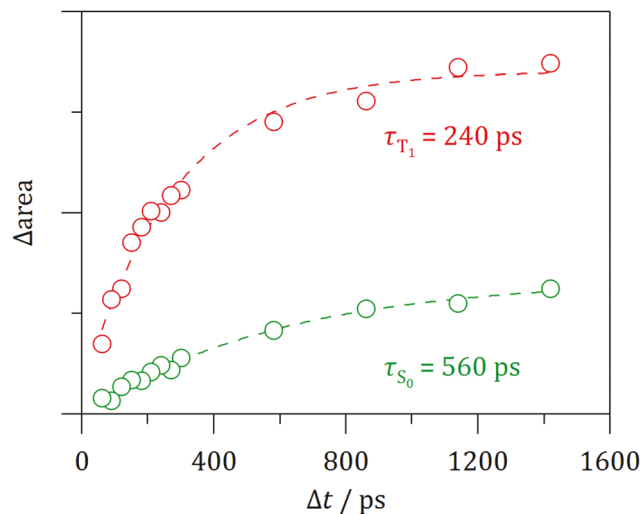


Fig. 10 Time dependence of slow (green) and fast (red) components of the  $\text{CH}_3$  speed distributions obtained at 266 nm. The data have been fit to a single exponential rise to obtain time constants for product formation.

appearance.<sup>27,29–32</sup> Here, we use the barrier height of  $31\,400 \pm 50\text{ cm}^{-1}$  determined in the ion imaging study of Amaral *et al.*, indicating a threshold wavelength of 318.5 nm for dissociation on the triplet surface.<sup>31</sup> This value is consistent with the  $30\,953\text{--}31\,412\text{ cm}^{-1}$  range defined by Heazlewood *et al.*, who used laser-induced fluorescence to measure HCO radical product state distributions, conclusively demonstrating product

formation on  $S_0$  at photolysis wavelengths  $\lambda > 318.35\text{ nm}$ .<sup>30</sup> Excitation at 317 nm and 320 nm initially prepare acetaldehyde in  $S_1$  with energies slightly above and below the apparent  $T_1$  barrier.

The broad features with  $v > v_{\text{max}}$  shown in Fig. 7 that are common to speed distributions at both 317 nm and 320 nm appear promptly and decay exponentially with time constants of  $\sim 70\text{ ns}$ . The time constants are broadly consistent with reported fluorescence lifetimes for the  $S_1$  state in this wavelength range, suggesting that the time dependence of this component reflects the  $S_1$  lifetime.<sup>8,9,40,41</sup> The spectrum of jet-cooled acetaldehyde shows rovibrational structure in this wavelength region and fluorescence lifetimes are strongly dependent on the excitation wavelength and often non-exponential.<sup>9</sup> The comparatively broad bandwidth ( $5\text{--}7\text{ cm}^{-1}$ ) of the OPO inevitably spans multiple lines in the spectrum, which accounts for discrepancies between fluorescence lifetimes and the  $S_1$  lifetime inferred from the time dependence of the transient dissociative ionization signal.

One plausible mechanism for formation of fast  $\text{CH}_3^+$  is dissociative ionization of  $\text{CH}_3\text{CHO}$  in the  $S_1$  state following absorption of a VUV photon. This process would be consistent with the absence of any fly-out anisotropy in the images, as the parent ions will have no significant velocity perpendicular to the molecular beam propagation direction. Sequential absorption of a UV and VUV photon provides a total energy of  $\sim 14.4\text{ eV}$  relative to the ground state, which is above the  $\text{CH}_3^+ + \text{HCO}$  appearance energy of 14.08 eV but insufficient to account for the observed  $\text{CH}_3^+$  speeds.<sup>59–61</sup> The  $\text{CH}_3^+ + \text{HCO}$  appearance energy coincides with excitation to the  $\tilde{B}^2A'$  state of  $\text{CH}_3\text{CHO}^+$ , which is presumably dissociative, but inaccessible in a one-photon transition from the  $S_1$  state of neutral  $\text{CH}_3\text{CHO}$ . Absorption of an additional photon of the relatively intense residual 355 nm (3.49 eV) radiation could drive the  $\tilde{B}^2A' \rightarrow \tilde{X}^2A'$  transition of the acetaldehyde cation, leading to dissociation and formation of fast  $\text{CH}_3^+$ .

Kable and co-workers have shown that the product state distribution for HCO formed on the  $S_0$  surface is approximately statistical, while products formed on  $T_1$  show evidence of impulsive dynamics.<sup>30</sup> In the vicinity of the  $T_1$  barrier, both pathways were shown to be competitive, with dissociation on  $T_1$  becoming increasingly dominant at shorter wavelengths. Ion imaging work by Amaral *et al.* shows  $\text{CH}_3$  and HCO with  $E_T$  distributions that peak close to zero following photolysis at wavelengths that are too long to overcome the  $T_1$  barrier, and are similar to those obtained at long delays following photolysis at 317 nm and 320 nm.<sup>31</sup> Phase Space Theory (PST)<sup>62,63</sup> and Separate Statistical Ensembles (SSE)<sup>64</sup> calculations have been performed using  $E_{\text{AVL}} = 2300\text{ cm}^{-1}$  and  $2600\text{ cm}^{-1}$ , equivalent to excitation at 320 nm and 317 nm. The calculations model  $\text{CH}_3$  and HCO as oblate and prolate symmetric tops, respectively, and used the rotational and vibrational constants reported by de Wit *et al.*<sup>46</sup> PST and SSE weight the product vibrational state distributions differently, based on the number of disappearing vibrational modes, although the distributions in this case are almost indistinguishable.<sup>64,65</sup> The  $E_T$  distributions calculated using PST and SSE are shown in Fig. 4 alongside the experimental data. The  $E_T$  distributions predicted by PST and SSE peak near zero and reproduce the observed slow component at both 317



and 320 nm reasonably well, consistent with unimolecular dissociation on the  $S_0$  surface.

The appearance times for  $\text{CH}_3$  formed on  $S_0$  after photolysis at 317 nm and 320 nm are similar and in good agreement with variational transition state theory (VTST) calculations for various partially deuterated acetaldehyde isotopologues.<sup>43,44</sup> At energies corresponding to excitation at 323 nm and 330 nm, dissociation rates for the partially deuterated species were calculated to range between  $k_D^{S_0} = 1 - 2 \times 10^{-7} \text{ s}^{-1}$ , indicating  $S_0$  lifetimes of 50–100 ns. At 317 nm, the excitation energy is sufficient to overcome the  $T_1$  barrier and dissociation on this surface is the dominant pathway to products. The  $S_0$  pathway remains open, however, and accounts for around 15% of the products. Product formation on  $T_1$  is significantly faster, with an appearance time constant of  $\sim 18$  ns. The dissociation rate on the  $T_1$  surface has been estimated using the standard RRKM expression

$$k(E) = \frac{N(E - E_0)}{h\rho(E)}$$

where  $N(E - E_0)$  is the sum of states at the barrier and  $\rho(E)$  is the  $T_1$  density of states at the total energy  $E$ . Both  $E$  and  $E_0$  are measured relative to the  $T_1$  origin at  $27240 \text{ cm}^{-1}$ , giving a barrier height of  $4160 \text{ cm}^{-1}$ .<sup>7,31</sup> Harmonic vibrational frequencies (collected in Table 2) for the  $T_1$  minimum and transition state were calculated at the CASSCF/def2-svp (18 electrons, 16 orbitals) level of theory using the MOLPRO 2012.1 quantum chemistry package.<sup>66</sup> Sums and densities of states were evaluated using the Stein–Rabinovitch algorithm as incorporated in the multiwell package.<sup>67</sup> At 317 nm ( $E = 4310 \text{ cm}^{-1}$ ), the total energy is only  $150 \text{ cm}^{-1}$  above the barrier and the  $T_1$  density of states is only around 6 per  $\text{cm}^{-1}$ . The RRKM dissociation rate is  $1.6 \times 10^{10} \text{ s}^{-1}$ , which results in an exceptionally short  $T_1$  lifetime of only 63 ps. Previous estimates of the  $T_1$  density of states in this energy region have been significantly larger. Lee and Chen calculated 152 states per  $\text{cm}^{-1}$ , while inferring 518 states per  $\text{cm}^{-1}$  from fitting experimental fluorescence data.<sup>9</sup> These larger values of  $\rho(E)$  extend the  $T_1$  lifetime to a few nanoseconds, but are in general shorter than the observed  $\text{CH}_3$  appearance time of  $\sim 18$  ns, suggesting that dissociation on  $T_1$  is fast and  $S_1 \rightarrow T_1$  intersystem crossing is rate-limiting. Direct  $S_1 \rightarrow S_0$  internal conversion,  $k_{\text{IC}}^{S_1 \rightarrow S_0}$ , is likely to be slow relative to intersystem crossing, therefore the  $S_0$  state is accessed by sequential intersystem crossing events  $S_1 \rightarrow T_1 \rightarrow S_0$ .<sup>38</sup> At 320 nm, the  $T_1$  state is non-dissociative and can act as a temporary population reservoir. As phosphorescence is slow, the dominant loss processes are likely non-radiative, specifically intersystem crossing back to  $S_1$  or to  $S_0$ . The small yield of products formed on  $S_0$  following excitation in excess of the barrier indicates that the rate of  $T_1 \rightarrow S_0$  intersystem crossing must be at least somewhat competitive with dissociation on the  $T_1$  surface. Once the  $S_0$  surface is reached, dissociation occurs statistically.

## 2. Photolysis at $\lambda \leq 318$ nm: dissociation on the $T_1$ surface

Dissociation on the  $T_1$  surface dominates beyond the threshold wavelength of 318.5 nm, and the available energy is partitioned primarily into translation. The  $E_T$  distributions evolve from

**Table 2** Harmonic frequencies for acetaldehyde calculated at the CASSCF/def2-svp level of theory

	$T_1$ (min)	$S_1$ (min)	$T_1$ (TS)	$S_1$ (TS)
$\nu_1$	3259	3293	3394	3397
$\nu_2$	3028	3229	3304	3387
$\nu_3$	2985	2989	3176	3299
$\nu_4$	2923	2923	3073	3038
$\nu_5$	1544	1570	1555	1539
$\nu_6$	1510	1536	1519	1529
$\nu_7$	1443	1481	1483	1474
$\nu_8$	1391	1368	1128	1206
$\nu_9$	1195	1182	1068	1050
$\nu_{10}$	1125	1132	825	724
$\nu_{11}$	1072	1074	714	668
$\nu_{12}$	968	964	650	654
$\nu_{13}$	666	654	314	323
$\nu_{14}$	414	399	129	47
$\nu_{15}$	208	206	679i	837i

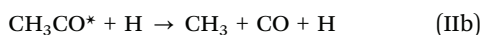
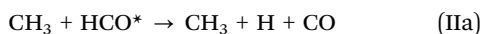
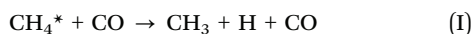
being asymmetric with a sharp cut-off on the high-energy side near threshold, through symmetric near 292 nm, and becoming asymmetric again with a sharper drop on the low-energy edge at the shortest photolysis wavelengths. Fig. 6 shows that both  $\langle E_T \rangle$  and  $\langle E_{\text{INT}} \rangle$  increase as the pump wavelength is decreased for products formed on  $T_1$ . This behavior is qualitatively consistent with the statistical adiabatic impulsive (SAI) model developed by Mordaunt *et al.*<sup>68</sup> in which energy is apportioned impulsively below the barrier and statistically above the barrier. The dynamics are predominantly impulsive near threshold and become increasingly statistical as the available energy is increased, which results in  $E_T$  distributions that shift to higher average values and broaden. Quasi-classical trajectories propagated on an *ab initio*  $T_1$  surface by Thompson *et al.* qualitatively reproduce the evolution of the experimental  $E_T$  distributions as the available energy is increased.<sup>37</sup> HCO is predicted to remain vibrationally cold with additional excitation energy, while the low frequency  $\nu_2$   $\text{CH}_3$  umbrella mode becomes increasingly populated. Fu *et al.* have performed trajectory surface hopping calculations to determine branching between the  $S_0$  and  $T_1$  pathways, finding that majority of surface hops are due to intersystem crossing between  $S_1 \rightarrow T_1$  and subsequently  $T_1 \rightarrow S_0$ .<sup>38</sup> The calculated  $E_T$  distributions for products formed on  $T_1$  at 286 nm agree qualitatively with the experimental results, although the preferred method of dealing with violation of zero-point energy predicts a distribution that is narrower and peaks at lower  $E_T$ . A more significant discrepancy between the calculations and the experiments is the branching between product formation on  $S_0$  and  $T_1$ . The calculations predict significant but monotonically decreasing yields of  $S_0$  products at wavelengths that excite substantially above the  $T_1$  barrier. At 286 nm, the  $S_0$  branching is around 0.5. In contrast, the experiments show that the  $S_0$  pathway quickly diminishes in importance with increasing excitation energy. At 317 nm only  $\sim 15\%$  of channel (IIa) products are formed on  $S_0$ , and contribute negligibly until  $S_0$  photochemical pathways re-open at  $\lambda < 292$  nm.

## 3. Photolysis at $\lambda \leq 292$ nm: dissociation via $S_1/S_0$ conical intersection

The  $\text{CH}_3$  product speed and total  $E_T$  distributions become bimodal at wavelengths shorter than 292 nm. Fig. 5 shows that the new slow

component appears weakly between 277–292 nm but grows more sharply relative to the  $T_1$  component at  $\lambda < 277$  nm, reaching around 40% at 265 nm. The total yield of channel (IIa) products, however, decreases steadily across this in this wavelength range as shown by the PHOFEX spectra in Fig. 8. The bimodal  $E_T$  distribution at 266 nm is effectively identical to that measured previously by Shubert and Pratt, who also used VUV ionization at 119.46 nm (10.379 eV) to detect  $CH_3$  and  $HCO$ .<sup>42</sup> The translational energy distributions extracted from  $CH_3$  and  $HCO$  images were indistinguishable, indicating that internally excited  $HCO$  does not dissociate on the timescale of the measurement. At longer wavelengths in region C, we also find good agreement with the  $E_T$  distributions obtained by Zhang *et al.* when state-selectively probing vibrational ground state products by 1 + 1 REMPI *via* the  $0_0^0$  band of the  $4p\text{-}\tilde{X}$  transition.<sup>32</sup> The slow component makes a much greater contribution when probing out-of-plane bend excited  $CH_3$  products probed *via* the  $2_1^1$  band. Assuming that the VUV ionization is universal, this suggests that (a) overall,  $CH_3$  radicals are predominantly formed in their vibrational ground state, and (b) the mechanism that leads to the slow component is more likely to result in out-of-plane bend excited  $CH_3$  than the  $T_1$  pathway. At 320 nm, products are formed on  $S_0$  with a translational energy distribution that is well-described by SSE and PST statistical models. Fig. 4 shows the predicted  $E_T$  distributions resulting from SSE and PST calculations for channel (IIa) with  $E_{AVL} = 6020\text{ cm}^{-1}$ ,  $7284\text{ cm}^{-1}$ , and  $8645\text{ cm}^{-1}$ , corresponding to photolysis at 286 nm, 276 nm, and 266 nm. Overall, the agreement is poorer than at the longer wavelength as the experimental  $E_T$  distributions tend to peak further from zero than those predicted by the statistical theories. The short-wavelength slow component observed after photolysis in region C cannot solely be described by a statistical distribution.

The appearance wavelength of the slow component is close to the threshold for the triple fragmentation channel (III), which becomes energetically accessible at  $\lambda < 294$  nm. Hobday *et al.* have suggested that the equivalent channel in formaldehyde (forming  $H + H + CO$ ) accounts for up to 25% of products once the threshold wavelength is surpassed.<sup>69</sup> Stepwise fragmentation has been observed in studies of the photochemistry of acetone, wherein vibrationally hot  $CH_3CO$  radicals formed in a primary photolysis step undergo unimolecular decomposition to form  $CH_3 + CO$ .<sup>70</sup> Two-step PST calculations modeling triple fragmentation of acetaldehyde predict translationally slow products.<sup>46</sup> Triple fragmentation has been inferred at 248 nm, and could occur by secondary dissociation of internally excited methane, formyl, or acetyl initially formed *via* channels (I), (IIa) and (IIb):



Highly internally excited  $CH_4$  is associated with roaming, with FTIR measurements showing  $CH_4$  products with an internal energy distribution that extended to the dissociation limit after excitation at 308 nm.<sup>15</sup> Barrierless decomposition of hot methane to form  $CH_3 + H$  would be anticipated to lead to a

statistical disposal of the available energy beyond the threshold wavelength.<sup>71,72</sup> In contrast to channel (I), barriers exist for secondary dissociation of formyl or acetyl radical products formed *via* channels (IIa) or (IIb), which pushes the threshold to shorter wavelengths. The formyl and acetyl dissociation barriers are the subject of some uncertainty. For formyl, the barrier to dissociation has been determined primarily by measurements of the kinetics of the  $H + CO \rightarrow HCO$  recombination reaction, with a value of  $5780 \pm 140\text{ cm}^{-1}$ .<sup>73</sup> High-level *ab initio* calculations have suggested that the experimental value is in error, and that a higher barrier of  $6670\text{ cm}^{-1}$  is more appropriate.<sup>74</sup> Taken in combination with  $D_0$  of  $28\,950\text{ cm}^{-1}$  for channel (IIa), this suggests a threshold wavelength in the range 281–292 nm. Experimental estimates of the barrier to acetyl decomposition have been determined from photodissociation studies of acetone and acetyl chloride. North *et al.* observed that 30% of  $CH_3CO$  radicals formed from acetone dissociation at 248 nm decomposed and determined the barrier to be  $6230 \pm 1100\text{ cm}^{-1}$ .<sup>70</sup> Tang *et al.* estimated a smaller value of  $4970 \pm 170\text{ cm}^{-1}$  from similar experiments exploring acetyl chloride photodissociation.<sup>75</sup> Using  $D_0 = 30\,750\text{ cm}^{-1}$  for channel (IIb), the threshold wavelength for secondary decomposition of acetyl likely falls in the range 271–281 nm.

While the thresholds for the triple fragmentation are broadly consistent with the onset of the slow component at shorter photolysis wavelengths, we think it unlikely to contribute significantly. Roaming is a relatively minor pathway to channel (I) products in region C and the fraction of  $CH_4^*$  with sufficient energy to dissociate will be smaller still.<sup>18</sup> Furthermore, two-step PST calculations modeling triple fragmentation predict  $E_T$  distributions that peak closer to zero than those for primary dissociation,<sup>46</sup> which appears to conflict with the single-step PST and SSE calculations. The application of PST to describe secondary dissociation of  $HCO^*$  or  $CH_3CO^*$  formed *via* channels (IIa) or (IIb) is questionable due to the presence of a barrier. A key assumption in PST is that the reaction coordinate along the potential energy surface does not influence the rate of combination, that is, dissociation is barrierless. The SAI model, which partitions the available energy into statistical and impulsive reservoirs has been used to model unimolecular dissociation of hot acetyl radicals and predicts a greater translational energy release.<sup>68</sup> Once again, only the fraction of acetyl radicals formed with energy greater than the dissociation barrier would dissociate and we see no evidence of any  $CH_3CO$  products. For  $HCO^*$  products formed on  $T_1$ ,  $\langle E_{INT} \rangle$  is always significantly less than the height of the formyl barrier, as shown in Fig. 6, suggesting only a small fraction would have sufficient energy to dissociate. More importantly, a stepwise process involving formation of channel (IIa) products, followed by unimolecular dissociation of  $HCO$ , would not affect the measured  $CH_3$  speeds. Finally, we note that all secondary dissociation pathways should enhance the yield of methyl relative to that of formyl. Decomposition of hot  $CH_4$  or  $CH_3CO$  *via* channels (I) and (IIb) would increase the relative yield of  $CH_3$ , while decomposition of hot  $HCO$  yield would reduce its yield relative to  $CH_3$ . The PHOFEX spectra presented in Fig. 8, however, show identical  $CH_3$  and  $HCO$  yields at all excitation wavelengths, strongly suggesting that triple

fragmentation is not occurring to any significant extent. Shubert and Pratt, also using single photon VUV ionization, have shown that the  $E_T$  distributions obtained from ion images of  $\text{CH}_3$  and  $\text{HCO}$  products at 266 nm are consistent with there being no significant secondary dissociation of hot  $\text{HCO}$ , at least on the time scale of their measurements.<sup>42</sup>

Ohta and Baba originally suggested that a new non-radiative loss process may become available for higher levels of  $S_1$  due to a second sharp decline in the fluorescence quantum yield at  $\lambda < 280$  nm, in line with the onset of the translationally slow component in the  $\text{CH}_3$  speed distributions observed in this work.<sup>6</sup> *Ab initio* calculations by Chen and Fang characterizing stationary points on the  $S_0$ ,  $S_1$  and  $T_1$  surfaces suggest an explanation.<sup>76</sup> They identified a conical intersection between the  $S_1$  and  $S_0$  surfaces at extended C–C bond lengths that could serve as an efficient means of internal conversion prior to dissociation on the  $S_0$  surface. Accessing the conical intersection, however, requires acetaldehyde to overcome a barrier on the  $S_1$  surface of  $5100\text{ cm}^{-1}$  relative to the origin. The  $S_1$  barrier would imply a threshold wavelength of 287 nm, which is close to the onset observed experimentally. More recent calculations have predicted a range of barrier heights spanning energies of  $6000\text{--}8000\text{ cm}^{-1}$  relative to the  $S_1$  origin and correspond to threshold wavelengths between 265–279 nm.<sup>19,38,76</sup>

We propose that the translationally slow component of the  $\text{CH}_3$  speed distribution in region C results from accessing the  $S_1/S_0$  conical intersection with subsequent dissociation on the  $S_0$  surface. Indeed, it is unlikely to be coincidental that the total yield of molecular products (channel (I)) has the same wavelength dependence as  $\text{CH}_3 + \text{HCO}$  formed on  $S_0$  shown in Fig. 5. The dominance of the  $\text{CH}_4 + \text{CO}$  molecular channel at short wavelengths arises as a result of dissociation *via* the  $S_1/S_0$  conical intersection becoming competitive with intersystem crossing. This new pathway results in a non-statistical distribution of the available energy, as evidenced by the marked deviation from SSE and PST predictions shown in Fig. 4. The calculated conical intersection geometry has a C–C distance of  $2.42\text{ \AA}$ , which is significantly extended with respect to the equilibrium bond length of  $1.51\text{ \AA}$  for the  $S_0$  state.<sup>76</sup> Consequently, the ensuing dynamics are likely dictated largely by long-range interactions between the nascent methyl and formyl radicals on the  $S_0$  surface. A further bifurcation of the product flux between trajectories that sample the  $S_0$  minimum and result in a statistical product state distribution and those which effectively skirt around the edge of the  $S_0$  well, resulting in partitioning of a greater fraction of the  $E_{\text{AVL}}$  into relative translation, is also a possibility. From an experimental perspective, state-resolved detection of the  $\text{CH}_3$  and  $\text{HCO}$  and complementary trajectory calculations on accurate potential energy surfaces would shed further light on the details of the mechanism.

The bimodal  $\text{CH}_3$  speed distribution observed using the nano-second laser systems at 266 nm is also observed at picosecond delays, as shown in Fig. 9. The fast and slow components, attributed to dissociation on  $T_1$  and  $S_0$  *via* the  $S_1/S_0$  conical intersection, respectively, are formed with different single-exponential rise time constants. The major  $T_1$  component is formed quickly with a rate  $(4.2 \pm 0.8) \times 10^9\text{ s}^{-1}$ , while the smaller

translationally slow component is also formed more slowly with a rate of  $(1.8 \pm 0.3) \times 10^9\text{ s}^{-1}$ . For products formed on  $T_1$ , the observed rate could be due to either the rate of  $S_1 \rightarrow T_1$  intersystem crossing,  $k_{\text{ISC}}^{S_1 \rightarrow T_1}$ , or the rate of dissociation to products once on the  $T_1$  surface,  $k_{\text{D}}^{T_1}$ . The latter can again be estimated using RRKM theory. Excitation at 266 nm prepares acetaldehyde in  $S_1$  with an energy  $6195\text{ cm}^{-1}$  above the  $T_1$  barrier. The RRKM calculations predict  $k_{\text{D}}^{T_1} = 7.6 \times 10^{11}\text{ s}^{-1}$  and a lifetime on the  $T_1$  surface of only 1.3 ps. This is two orders of magnitude faster than the observed  $\text{CH}_3$  formation rate, suggesting that dissociation on  $T_1$  is comparatively prompt and not rate limiting. Consequently, we attribute the observed formation rate of the translationally fast component to the rate of  $S_1 \rightarrow T_1$  intersystem crossing.

Previously, Abou-Zied and McDonald used picosecond time-resolved REMPI detection to measure single-exponential rise-times of  $667 \pm 43\text{ ps}$  and  $662 \pm 34\text{ ps}$  for  $\text{CH}_3\text{CO}$  and  $\text{HCO}$  products, respectively, following photolysis of acetaldehyde at 266 nm. The time-dependent yield of  $\text{HCO}$  was measured using  $2 + 1$  REMPI *via* the  $3p\text{ }^2\Pi$  state near 400 nm. The appearance times are significantly longer than that determined in this work for the predominant  $T_1$  pathway but in reasonable agreement with the rise time of  $560 \pm 90\text{ ps}$  measured for the smaller  $S_0$  component. The REMPI measurements may not probe  $\text{HCO}$  product quantum states that are preferentially populated by dissociation on the  $T_1$  surface, biasing the detection in favor of products formed on  $S_0$ . Abou-Zied and McDonald noted that they were unable to detect any time-dependent signal at photolysis wavelengths in the range 280–315 nm, which is consistent with this hypothesis; the  $S_0$  pathway is a minor ( $<15\%$ ) contributor in the 280–292 nm range, and is not observed at all at  $\lambda > 292\text{ nm}$ . The observation of acetyl products at all is also somewhat at odds with our measurements, although the detection sensitivity of single photon VUV ionization could be significantly poorer than the unspecified REMPI scheme used to detect  $\text{CH}_3\text{CO}$  in the earlier work. We note that other groups have argued that acetyl products are not formed at the nearby photolysis wavelength of 248 nm.<sup>47,48</sup> The barrier on the  $T_1$  surface for formation of channel (IIb) products is  $\sim 4000\text{ cm}^{-1}$  higher than for channel (IIa),<sup>76</sup> while unimolecular decomposition rates on  $S_0$  also strongly favor channel (IIa).<sup>44</sup>

For the short-wavelength  $S_0$  pathway, there are two steps that are likely rate limiting for product formation: the rate of passage over the  $S_1$  barrier,  $k_{\text{TS}}^{S_1}$ , leading to the conical intersection or the rate of dissociation to products once on the  $S_0$  surface,  $k_{\text{D}}^{S_0}$ . We consider first the possibility that  $k_{\text{TS}}^{S_1}$  is rate limiting by comparison with RRKM calculations using harmonic frequencies calculated at the CASSCF/def2-svp level as before. The RRKM rate is highly sensitive to the barrier height. Using the observed onset  $\lambda = 292\text{ nm}$  results in a rate of,  $k_{\text{TS}}^{S_1} = 6.6 \times 10^{11}\text{ s}^{-1}$  and a lifetime of only 1.5 ps. A barrier of  $6520\text{ cm}^{-1}$ , in the middle of the range predicted by theory, however, results in  $k_{\text{TS}}^{S_1} = 1.7 \times 10^7\text{ s}^{-1}$ , corresponding to a lifetime of 150 ps which is again faster than the observed rise time. However, if passage over the  $S_1$  transition state is fast and the observed formation rate instead reflects  $k_{\text{D}}^{S_0}$ ,

one would expect a ratio of  $T_1$  to  $S_0$  products that was strongly in favor of the latter. That the ratio of the formation rates is close to the observed branching ratios, suggests that they share  $S_1$  as a common precursor state. Assuming passage over the  $S_1$  TS to be rate limiting, the lifetime of the  $S_1$  state is estimated to be  $\sim 170$  ps after excitation at 266 nm, consistent with the sub-ns fluorescence lifetime observed at wavelengths shorter than 280 nm.<sup>6</sup> The branching could be modified to some extent by other dissociation channels once on  $S_0$ , such as the formation of molecular products. Dissociation over the conventional  $S_0$  transition state to form  $CH_4 + CO$  is calculated to have an RRKM rate  $2.5 \times 10^8 \text{ s}^{-1}$  (4 ns), approximately an order of magnitude slower than the  $CH_3$  appearance rate.<sup>12</sup> The time scale for dissociation *via* roaming has not been determined experimentally, but state-resolved measurements probing CO products with picosecond time resolution are likely to be insightful.

## Conclusions

Ion imaging and PHOFEX action spectroscopy with single-photon VUV detection of products have been used to explore the photochemistry of acetaldehyde across a broad wavelength range (265–328 nm) spanning the first absorption band. The radical channel (IIa), leading to  $CH_3$  and HCO products, can be categorized into three distinct photolysis wavelength regions. Region A ( $\lambda > 318$  nm) corresponds to excitation energies below the  $T_1$  barrier and  $CH_3$  products are formed with translational energy distributions that are consistent with statistical model predictions for unimolecular dissociation on the  $S_0$  surface. Dissociation is slow; at 320 nm, products are formed with a single-exponential rise time of  $66 \pm 9$  ns, consistent with predictions of VTST. In region B ( $\lambda \leq 318$  nm) dissociation over the barrier on the  $T_1$  surface becomes energetically accessible and product formation on  $S_0$  effectively ceases. Near the  $T_1$  threshold, radical products are formed with a narrow distribution of recoil speeds that peaks close to the maximum allowed by energy conservation,  $v_{\text{max}}$ . The distributions broaden and deviate increasingly from  $v_{\text{max}}$  as the photolysis wavelength is decreased, consistent with increased partitioning of the available energy into internal degrees of freedom of the radicals as predicted by mixed statistical/impulsive models. In region C ( $\lambda < 292$  nm) a new pathway opens that produces translationally slow, but non-statistical,  $CH_3$  radicals. This new pathway becomes increasingly competitive with dissociation on  $T_1$  at shorter wavelengths. PHOFEX spectra of acetaldehyde probing  $CH_3$  and HCO products between 260–328 nm are identical, an observation incompatible with the three-body fragmentation channel (III), which has a threshold wavelength near the onset of the new translationally slow component. It is proposed that the new component results from dissociation on  $S_0$  after internal conversion *via* a conical intersection between the  $S_1$  and  $S_0$  surfaces that can be accessed over a barrier on the  $S_1$  surface at extended C–C bond lengths. Time-resolved ion imaging measurements using picosecond duration pulses at a photolysis wavelength of 266 nm show that products are formed *via* the  $T_1$  and  $S_0$  pathways with different, but competitive,

rates of  $4.2 \times 10^9 \text{ s}^{-1}$  and  $1.8 \times 10^9 \text{ s}^{-1}$ , respectively. The former is attributed to the rate for  $S_1 \rightarrow T_1$  intersystem crossing and the latter primarily to the rate of passage over the  $S_1$  barrier, prior to accessing the  $S_1/S_0$  conical intersection.

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