H-atom high-*n* Rydberg time-of-flight spectroscopy of C–H bond fission in acrolein dissociated at 193 nm

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The experiments presented in this work use H-atom high-*n* Rydberg time-of-flight spectroscopy to measure the H-atom velocity distribution from one- and multiple-photon dissociation processes in acrolein following excitation at 193 nm. The one-photon H-atom signal is dominated by primary C–H bond fission in acrolein. We compare some of the qualitative features of the recoil translational energy distribution for the observed H atoms with what would be expected based on theoretical results for aldehydic C–H bond fission on the ground and lowest singlet and triplet excited states and conclude that the dissociation cannot proceed through either of these paths. A possible dissociation mechanism is proposed to account for the observed $P(E_T)$ that is consistent with the observation of an isotropic dissociation. Finally, we report results on methyl vinyl ketone photodissociation which provide evidence that the primary C–H bond fission process in acrolein is fission of the aldehydic bond. © *2002 American Institute of Physics.* [DOI: 10.1063/1.1510442]

I. INTRODUCTION

The ultraviolet photolysis of systems containing either the C=C chromophore[1] or the C=O chromophore[2] have been the subject of many studies. On the other hand, acrolein (H_2C=CHCHO), the simplest molecule containing both chromophores, has received only limited attention.[3–9] Furthermore, two closely related molecules, methyl vinyl ketone ($CH_3COCHCH_2$) and methacrolein [$CH_2C(CH_3)HCO$], may play a role in the chemistry of the troposphere.[10] Therefore, we have undertaken the current study of acrolein to investigate the channel leading to production of an H atom through C–H bond fission.

The absorption spectrum of acrolein shows several strong bands in the wavelength region between 400 nm and about 190 nm.[11] Walsh assigned the absorption band near 386 nm as $^1n\pi^*$ (S_1) and the absorption peaking at 193 nm as $^1\pi\pi^*$ (S_2) electronic character,[11] consistent with later electronic structure calculations.[12] Nagakura considered the influence of a charge transfer contribution to the excited state accessed at 193 nm.[13] Photochemical studies using both the 193-nm transition[3–6,8,9] and the 386-nm transition[14] have appeared in the literature. We review here only the work on the 200-nm absorption band which is relevant to the experiments described in this paper.

Before discussing the studies performed on resonance with the excited state accessed at 193 nm, it must be mentioned that two conformers of acrolein are present at room temperature: s-*cis* and s-*trans*. The s-*trans* conformer (shown in Fig. 1) is dominant while s-*cis* conformer accounts for only 4%–5% of room-temperature acrolein.[15] The barrier to internal rotation was measured using microwave techniques, and a lower limit for the barrier was determined as 2.3 kcal/mol.[16]

Following several studies[3–5,8] of the photolysis of acrolein near 193 nm, including studies that measured the na-

scent CO vibrational population and one which measured the $HCO+C_2H_3$ channel directly, Haas *et al.*[6] presented the most comprehensive study prior to 2002 (Ref. 9) on the photofragmentation of acrolein excited to the S_2 ($^1\pi\pi^*$) state. Using 193 nm excitation coupled with photofragment translational energy spectroscopy, they studied three primary channels in the acrolein dissociation:

$$H_2C=CHCHO \rightarrow C_2H_4 + CO, \tag{1}$$

$$H_2C=CHCHO \rightarrow C_2H_3 + HCO, \tag{2}$$

$$H_2C=CHCHO \rightarrow H_2C=CHCO + H. \tag{3}$$

These experiments were performed using high (500 mJ/cm^2) and low (25 mJ/cm^2) photolysis fluences. The first two reactions were observed and the recoiling fragments were momentum matched to determine a $P(E_T)$ for each channel. During the writing of this paper, new results were obtained by Regan *et al.*[9] employing PTS in conjunction with tunable vacuum ultraviolet (VUV) photoionization to analyze the dissociation products; this study found two new reaction channels:

$$H_2C=CHCHO \rightarrow C_2H_2 + H_2CO, \tag{4}$$

$$H_2C=CHCHO \rightarrow HCCO + CH_3. \tag{5}$$

In both the work of Haas *et al.* and the more recent work of Regan *et al.* characterization of the C–H bond fission channel revealed problems. The experiment of Haas *et al.* attempted to characterize the dissociation by detecting H atoms using electron impact ionization. In order to obtain good signal to noise with the high background at $m/e=1$, Haas *et al.* made several important modifications to their apparatus. The skimmer between their pulsed source and their interaction region was removed, and the nozzle was moved closer to the interaction region to increase the overall signal. Furthermore, the free jet was rotated by 90° with respect to
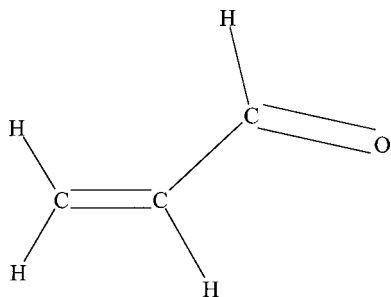
FIG. 1. Structure of the s-*trans* conformer of acrolein which accounts for 95%–96% of room-temperature acrolein.

the detector axis and acrolein was dissociated using both low and high power from the photolysis laser [Haas *et al.* do not state the pulse energy used in the collection of their published $m/e = 1$ time-of-flight (TOF) spectrum]. They assign the dominant feature in the $m/e = 1$ spectrum to reaction (3) and the fast edge appearing in their spectrum to H atoms from the dissociation of C_2H_3 to give $HCCH + H$ after absorption of a second 193-nm photon.[6] The tail at very long flight times (>100 μs) is assigned to H atoms from the dissociation of slowly recoiling hydrocarbons and the formyl radical in reactions (1) and (2) (due to cracking in their electron impact ionizer). The contributions from these channels overlap, and there is no other m/e ratio where they independently detected the shape of the contribution from these channels. Finally, based on their observed $P(E_T)$, the primary H-atom loss channel is assigned as resulting from the aldehydic hydrogen, because the $P(E_T)$ extends to near the available energy $[E_{photon} - D_0(C-H) = 61$ kcal/mol].[6] However, their $P(E_T)$ drops to near zero by ~ 40 kcal/mol, and considering the uncertainty in the fastest observed H atoms resulting from multiphoton absorption, this argument alone does not support the assignment. Finally, the anisotropy of the primary H-atom channel was investigated and they found $\beta = -0.1 \pm 0.05$ consistent with a long-lived complex. More recently, the detailed study by Regan *et al.*[9] characterized the other dissociation channels of acrolein at 193 nm using PTS with VUV photoionization detection of the photofragments, but reported being unable to characterize the recoil kinetic energy distribution for the C–H bond fission channel. Their paper shows a TOF spectrum for the C_3H_3O cofragment, but they stated they were unable to derive a consistent $P(E_T)$ for C–H bond fission presumably because the laboratory velocity of the heavy fragment, with very low recoil velocity in the center-of-mass reference frame, is overly sensitive to the velocity spread of the molecular beam. They also report a photoionization efficiency curve for the cofragment and propose that it is suggestive of aldehydic C–H bond fission in the contributing channel.

One final experimental study of acrolein excited in the 193-nm band must be considered. Arendt *et al.*[7] studied the emission spectroscopy of acrolein excited at 199 nm. Their emission experiment was sensitive to the forces in the Franck-Condon region of the excited state as determined by the electronic character of the excited electronic state. Based on the observed vibrational progressions in the emission

spectra, they concluded that the S_2 excited state has mixed $\pi^*(C=C)/\pi^*(C=O)$.[7]

Finally, Fang performed CASSCF calculations to study the dynamics of acrolein dissociation after excitation to the bright state at 193 nm.[17] Fang concluded that the ground-state products $H_2C=CHCO(^2A') + H(^2S)$ correlate adiabatically with ground-state acrolein and the $^3\pi\pi^*(T_2)$ state of acrolein. On the ground electronic state, there is no barrier to C–H bond fission above the endothermicity[17] [83.2 kcal/mol at the CAS(8,7)/cc-pVDZ level of theory with zero-point correction]. A second set of products 14.9 kcal/mol above the ground-state products, $H_2C=CHCO(^2A'')$ $+ H(^2S)$, correlates adiabatically with the S_1 ($^1n\pi^*$) state and with the T_1 ($^3n\pi^*$) state. Both states have a small barrier to the reverse reaction[17] (2.1 kcal/mol for the $^1n\pi^*$ state and 0.7 kcal/mol for the $^3n\pi^*$ state). Fang states that the barrier to reaction on the $^3\pi\pi^*$ state is expected to be large (implying a large reverse barrier) and therefore concludes that the dissociation takes place after internal conversion to the ground state.[17]

We present the first experiment in our laboratory using a newly constructed H-atom high-n Rydberg TOF (HRTOF) spectrometer. We have determined the velocity distribution of H atoms from the one-photon C–H bond fission channel in the dissociation of acrolein at 193 nm. The TOF spectrum is fit using the standard forward convolution technique. The resulting $P(E_T)$ for the primary H atoms agrees qualitatively with that observed by Haas *et al.*,[6] but with significant differences in both the fast and slow portions of the kinetic energy distribution. The current data are not contaminated by the slow H-atom tail in the work of Haas *et al.* resulting from the cracking of hydrocarbon photoproducts due to electron impact ionization. Furthermore, a systematic power study allows for the multiphoton contributions to the HRTOF spectrum to be removed, significantly improving the fit for the fastest recoiling H-atom signal. Thus, we can unambiguously locate the peak in the $P(E_T)$ for the C–H bond fission channel of acrolein. In the next section we give the experimental details relevant to the current work. In Sec. III, the HRTOF spectra of acrolein taken using three photolysis laser powers are considered and the translational energy distribution used to fit the observed spectra are presented. The results of methyl vinyl ketone are presented as well. In Sec. IV the observed $P(E_T)$ is compared with that observed previously by Haas *et al.* We consider if the observed $P(E_T)$ is consistent with the suggestion that aldehydic C–H bond fission occurs on the ground electronic state as proposed by Fang and a possible mechanism is proposed to account for the observed translational energy distribution. In the final section, we summarize the results of these experiments on the photolysis of acrolein at 193 nm.

II. EXPERIMENT

The experimental aspects of H-atom Rydberg time of flight have been reported by others.[18] We give here the relevant details for the experiments performed in our laboratory. Ground-state H atoms from photolyzed acrolein were promoted to the $2p$ electronic state using 121.6 nm light (Lyman-α). Lyman-α is generated via nonresonant tripling of
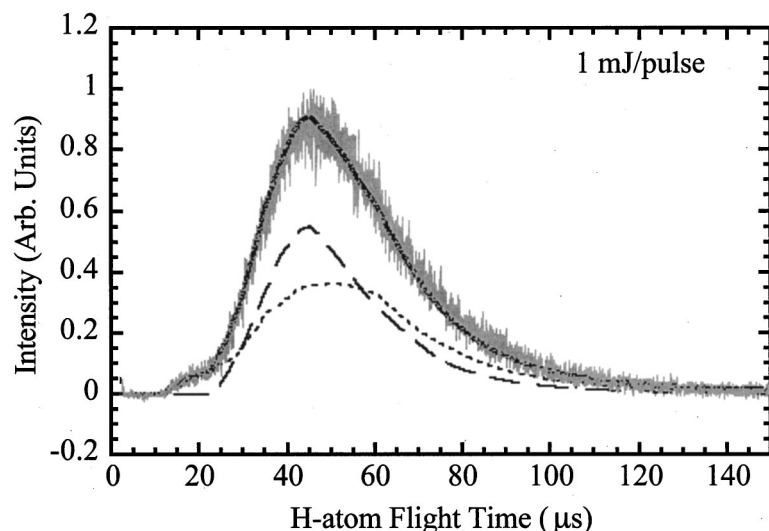
FIG. 2. HRTOF spectrum of acrolein taken at a photolysis energy of 1 mJ/pulse. The dashed line is attributed to a one-photon signal, while the dotted line is attributed to a multiphoton process.

364.8 nm light in a low-pressure Kr cell. The Kr cell mounts onto the side of the vacuum chamber with a MgF_2 lens ($f = 50$ cm) serving as the barrier between the cell and the vacuum chamber. For these experiments, about 40 mbar of Kr was used for the tripling process. The output of a single injection seeded Nd:YAG (Continuum PowerLite 9020) was used to pump both the Lyman-α dye laser and a second dye laser providing the light to promote H atoms from the $2p$ state to a high-n Rydberg state ($n \sim 40$). Light at 364.8 nm is generated by frequency doubling the dye laser (Lambda Physik FL3002) output in a KDP crystal (Lambda Physik FL30). The dye laser provided approximately 55 mJ/pulse near 729 nm using LDS 722 laser dye (Exciton). Under these conditions, about 12–15 mJ/pulse of the frequency-doubled light at 364.8 nm was obtained for the generation of 121.6 nm light. The absolute wavelength of light given by the Lyman-α dye laser was scanned to optimize the H^+ signal given from the dissociation of H_2S at 121 nm. The second dye laser (Lambda Physik FL3002) used for the promotion of $2p$ H atoms to a high-n Rydberg state provided about 35 mJ/pulse near 731 nm using LDS 722 (Exciton). The output of this laser was frequency doubled in a KDP crystal (Inrad M/N 531-120) providing 5–8 mJ/pulse at 365.5 nm. Both dye lasers are synchronized to within 2 ns using optical delay lines.

A Lambda Physik EMG-103-MSC excimer laser operating with an ArF (193 nm) gas fill served as the photolysis laser for these experiments. The photolysis laser energy was maintained by varying the high-voltage power supply during the experiment. The temporal jitter in this laser is on the order of 5 ns. However, a very slow drift was observed for this laser over the course of several hours. Hence the timing between the photolysis laser the Lyman-α laser was checked periodically. The photolysis laser typically intersected the molecular beam about 5 ns preceding the 121.6- and 365.5-nm lasers. The pulse energies reported here are measurements taken before the laser is focused on the molecular beam to an area of ~ 0.01 cm^2.

The detector used in these experiments (Burle TOF-4000) was held at -1.9 kV using a high-voltage power sup-

ply (Bertran model 303). A grid immediately before the detector was held at $+20.0$ V using a constant-voltage power supply (HP E 3611A) and served to simultaneously field ionize H atoms and repel positive ions from the detector. A circular stainless steel ring, about 1 cm below the interaction region, was held at -20.0 V during the experiment using a second constant-voltage power supply (HP E 3611A). This disk served to deflect positive ions from the detector.

The experiments were performed in a vacuum chamber consisting of three differentially pumped regions. A pulsed valve (General Valve Iota-One, 500 μm orifice) introduced the sample gas into the source region. A Balzers-Pfeiffer TMU-520-C turbomolecular pump maintained the pressure around 7×10^{-5} torr during experiments. A skimmer (Precision Instruments, 600 μm orifice) separated the source region from the main chamber/interaction region. The main chamber was pumped with Balzers-Pfeiffer TMH-260 turbomolecular pump. The detector region, oriented at a right angle to the plane formed by the molecular beam and lasers, was pumped with a Balzers-Pfeiffer TMU-065 turbomolecular pump.

Each HRTOF spectrum of acrolein, taken at three photolysis laser energies, is the sum of 100 000 laser shots with background subtraction. Background subtraction was performed by blocking the photolysis laser while allowing both the Lyman-α and Rydberg lasers to pass into the chamber. The photolysis laser power was checked before every 10 000 shot scan.

Acrolein was purchased from Aldrich (90%) and was used without further purification. The sample was placed in a glass bubbler held at 20 °C, giving a vapor pressure of 150 torr acrolein. He buffer gas was slowly bubbled through the liquid, giving a total stagnation pressure of about 450 torr behind the pulsed nozzle during these experiments. The signal taken at a 50% seed ratio and a total backing pressure of 300 torr showed no discernable difference from the spectra presented in this paper, indicating that the data are not altered by potential cluster contributions. Methyl vinyl ketone (Avocado Research Chemicals, 95%) was placed in a bubbler at room temperature and backed with He to a total pressure of
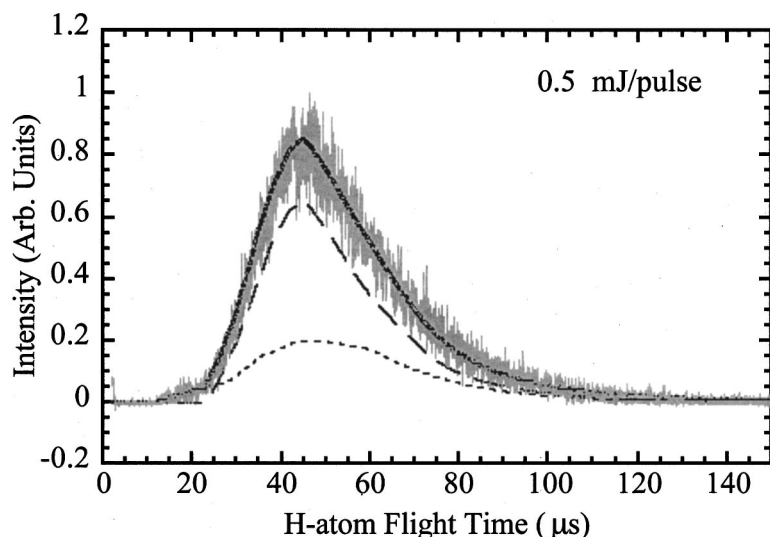
FIG. 3. HRTOF spectrum of acrolein taken at a photolysis energy of 0.5 mJ/pulse. The dashed and dotted lines are the one-photon and multiphoton contributions, respectively.

500 torr. To determine that the observed H-atom signal from methyl vinyl ketone photolyzed at 193 nm was due to a multiphoton process, we took data at photolysis energies of 0.5, 1, and 2 mJ/pulse.

III. RESULTS AND ANALYSIS

The HRTOF spectrum of acrolein taken using 1 mJ/pulse laser energy is shown in Fig. 2. The arrival time of the fastest observed H atoms extends to almost 10 μs. Simple conservation of energy allows us to determine that the fastest observed H atoms must be due to a multiphoton dissociation process. The energy that is partitioned into product translation, E_T, is given as $E_T = E_{photon} - D_0(C-H) - E_{int} + E_{parent}$, where E_{photon} is the energy of a 193-nm photon (147.9 kcal/mol), $D_0(C-H)$ is the C–H bond dissociation energy for the aldehydic C–H bond in acrolein [87.1 $\pm$ 1.0 kcal/mol (Ref. 19)], and E_{int} is the internal energy of the fragments. The maximum energy that may be partitioned into product translation is $E_{avail} = E_{photon} - D_0(C-H) + E_{parent}$. To properly calculate this number, one must consider the contribution of the small amount of internal energy

in the parent molecules. As molecular vibrations are known to relax more slowly than rotational and translational modes in a supersonic expansion,[20] we assume no vibrational relaxation and calculate the vibrational contribution at our nozzle temperature (298 K) to be 1 kcal/mol. Assuming the rotational temperature cools to about 200 K allows us to estimate the average rotational energy of the parent molecules as 1.2 kcal/mol. With this value, the maximum energy (E_{avail}) that can be partitioned into product translation is approximately 63 kcal/mol (e.g., $\langle E_{rot} \rangle = 1.2$ kcal/mol, $\langle E_{vib} \rangle = 1.0$ kcal/mol). A small portion of this is partitioned into the heavy cofragment in C–H bond fission, so the maximum possible kinetic energy of the H atoms can be found as

$$E_{T,max,H} = E_{T,max,total} \left/ \left(1 + \frac{m_H}{m_{H_2C=CHCO}} \right) \right.$$

$$= \frac{63 \text{ kcal/mol}}{1 + \frac{1}{55}} = 62 \text{ kcal/mol}, \tag{6}$$

where $E_{T,max,H}$ is the maximum possible kinetic energy imparted to hydrogen, $E_{T,max,total}$ is the maximum total recoil
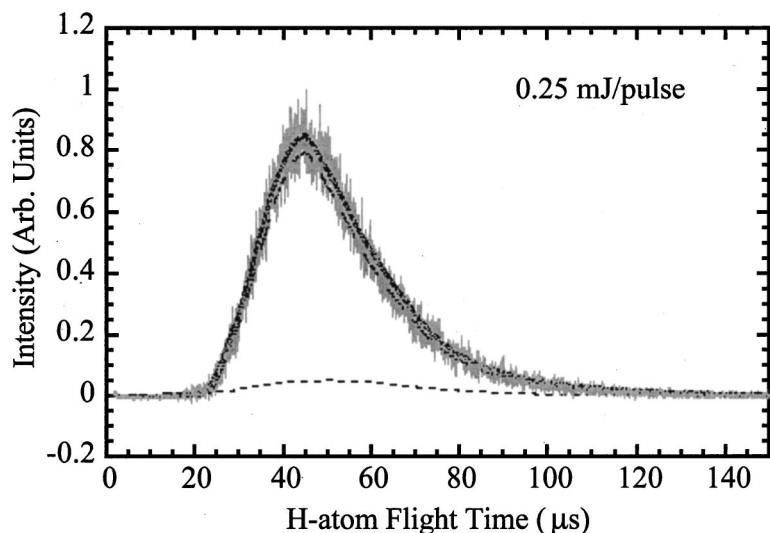

FIG. 4. HRTOF spectrum of acrolein taken at a photolysis energy of 0.25 mJ/pulse. The dashed and dotted lines are the one-photon and multiphoton contributions, respectively.
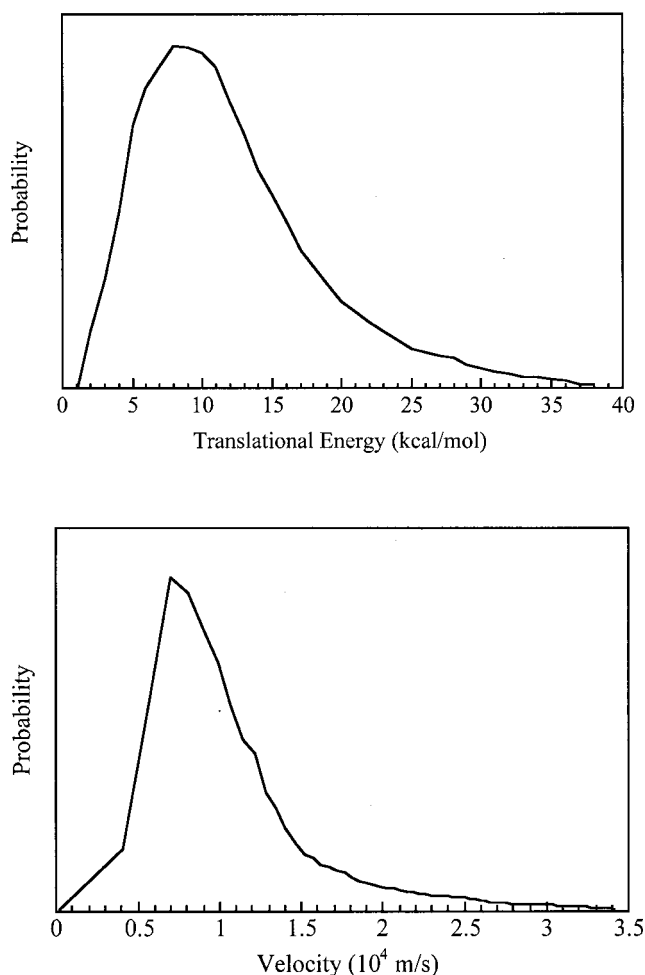
FIG. 5. Translational energy distribution $P(E_T)$ (top panel) and recoil velocity distribution $P(v)$ (bottom panel) derived from the forward convolution fit of the acrolein spectra taken at a photolysis energy of 1, 0.5, and 0.25 mJ/pulse. The $P(E_T)$ is attributed to a one-photon C–H fission process, while the $P(v)$ is attributed to the H-atom signal from a multiphoton process.

technique, allowing us to separate the multiphoton signal from the one-photon signal. The data show that the multiphoton signal begins on the fast side of the one-photon signal, but significantly underlies a portion of the one-photon signal. An acceptable fit was obtained using a $P(E_T)$ for reaction (3), resulting in the formation of $H + H_2C=CHCO$ and a single velocity distribution for the H atoms resulting from a multiphoton process. These two distributions are shown in Fig. 5. The H-atom signal resulting from multiphoton absorption (Fig. 5, bottom) is presented as a recoil velocity distribution. If the signal had resulted from a single-step dissociation, the relationship between $P(u_1)$ and $P(E_T)$ would be $P(u_1) = m_1 u_1 P(E_T)$.[21] The signal from one-photon dissociation resulting in C–H bond fission is fit by a $P(E_T)$ (Fig. 5, top) which scales linearly with the photolysis laser energy in all three HRTOF spectra and therefore results from single-photon dissociation of acrolein. This single-photon $P(E_T)$ agrees roughly with that obtained by Haas et al. (with differences in the high-energy tail and the position of the peak in the translational energy distribution).[6] The contribution of the second velocity distribution (Fig. 5, bottom) scales approximately as the square of the photolysis laser energy, but a reasonably good fit could also be obtained by scaling the multiphoton velocity distribution with the cube of the photolysis laser power. However, neither scaling of the multiphoton velocity distribution requires any modification to the single-photon $P(E_T)$. Thus the actual process described by the multiphoton velocity distribution may require either two or three 193-nm photons. However, the contribution of the multiphoton velocity distribution to the 0.25 mJ/pulse spectrum (Fig. 4) is almost negligible, as the relative weightings, accounting for all Jacobians, used in the fit are 10:1 in favor of the single-photon process.

The dependence of the observed HRTOF spectrum on laser polarization was also investigated. For this study, the photolysis laser was passed through a birefringent Pellin-Broca prism to separate the unpolarized output into two linearly polarized components. The linearly polarized light was then directed through a half-wave plate (optimized for 193 nm light) to rotate the polarization vector of the photolysis laser. The HRTOF spectrum of acrolein was then collected using approximately 1 mJ/pulse photolysis energy. No significant difference between the HRTOF spectrum using light polarized either parallel or perpendicular to the plane defined by the molecular beam and the photolysis laser was observed, indicating an isotropic distribution. Based on the integrated area of the two HRTOF spectra from 32 to 120 μs (where the single-photon distribution dominates over the multiphoton velocity distribution), the anisotropy parameter is $\beta = 0.01 \pm 0.42$. The absolute error on this measurement is larger than that of Haas et al. who found $\beta = -0.1 \pm 0.05$; however, both results are consistent with an isotropic distribution.

Secondary dissociation processes were also considered. Regan et al.[9] found a secondary H loss channel due to the dissociation of the vinyl radical ($H_2C=CH$) formed in the $HCO + C_2H_3$ product channel. A simple calculation reveals if we are sensitive to these secondary H atoms in our TOF spectra. Assuming that no energy is partitioned to translation

kinetic energy ($\frac{1}{2}\mu v_{rel}^2$) from the dissociation (63 kcal/mol; calculated above), m_H is the mass of hydrogen, and $m_{H_2C=CHCO}$ refers to the mass of the other recoiling fragment. Given that conservation of energy allows no more than 63 kcal/mol of energy to be partitioned into product translation, the maximum kinetic energy of the H-atom fragment is ~62 kcal/mol, corresponding to a flight time of about 18 μs in our apparatus. Thus the signal in the fast shoulder in Fig. 2, appearing at flight times as short as 10 μs, must result from a multiphoton dissociation process. To characterize the multiphoton contribution to the H-atom signal, we collected the HRTOF spectrum of acrolein at two lower photolysis laser powers, 0.5 mJ/pulse (Fig. 3) and 0.25 mJ/pulse (Fig. 4). The fast shoulder decreases considerably when the photolysis energy is dropped to 0.5 mJ/pulse and shows almost no contribution at 0.25 mJ/pulse. The HRTOF spectrum of acrolein at 0.125 mJ/pulse was attempted, but no signal was observed above the background.

The HRTOF spectra of acrolein at these three photolysis laser energies are fit using the standard forward convolution

in the secondary dissociation, and using the $P(E_T)$ of Regan *et al.* for the portion of the primary process that produces unstable C_2H_3, one concludes that the secondary-H-atom velocity (in the center-of-mass reference frame) from dissociation of C_2H_3 at the peak of the $P(E_T)$ for the primary process is approximately 6.93×10^4 cm/s. This is well outside the range necessary for signal to be visible in our spectra. In order for the signal to appear in the 140-μs window observed here, the H-atom fragment would need a net recoil velocity in the center-of-mass reference frame of 31.2×10^4 cm/s, so one would not expect the H-atom secondary fragments from the dissociation of the unstable C_2H_3 to be observable in this experiment. However, signal appearing at 140 μs corresponds to an E_T of $\sim$16.3 kcal/mol (again assuming the velocity of the secondary H atoms is determined by the recoil velocity of C_2H_3 in the primary dissociation), which lies within the high-energy tail of the $P(E_T)$ of Regan *et al.* It should therefore be possible to observe the tail of the H-atom signal at the longest arrival times in our TOF spectra, although no significant signal is apparent. It must also be noted that although we refer to the H-atom channel as a primary dissociation process following the assignment of Haas *et al.*,[6] there is no evidence to rule out the possibility that the observed signal is in fact due to a secondary C–H fission process.

Finally, to explicitly consider the possibility of aldehydic C–H bond fission, we examined the dissociation of methyl vinyl ketone following excitation at 193 nm. Methyl vinyl ketone is the simplest ketone derivative of acrolein (replacing the aldehydic hydrogen with a methyl group) and therefore provides a model system for investigation of aldehydic C–H bond fission in acrolein. Our HRTOF experiments revealed significant two-photon H-atom signal, but no H-atom contribution that could be attributed to a single-photon process. It is possible that a small underlying one-photon primary or secondary contribution is present, but such a signal is not discernable in the data collected.

IV. DISCUSSION

The measured H-atom TOF spectra presented here definitively determine the high-energy portion of the $P(E_T)$ for the primary H-atom channel which was crucial to prior arguments on whether the C–H bond fission is the cleavage of the aldehydic bond or not. The single-photon translational energy distribution peaks at 8 kcal/mol and extends to 38 kcal/mol. When the single-photon $P(E_T)$ was truncated to 37 kcal/mol and the relative scaling from the multiphoton velocity distribution was increased, the fast edge of the 0.25 mJ/pulse spectrum (Fig. 4) was underfit while the slowest H-atom signal was overfit, indicating that the truncation was not reasonable. Thus the higher-kinetic-energy limit in the primary C–H bond fission is 38 ± 1 kcal/mol. In contrast, the $P(E_T)$ for the $H + H_2CCHCO$ channel, observed by Haas *et al.*,[6] peaks around 4 kcal/mol and extends out to near the energetic limit of about 60 kcal/mol. Haas *et al.* could not determine conclusively which part of the fastest H-atom signal was due to multiphoton processes and therefore could not separate this unambiguously from the one-photon H-atom signal. This likely introduces an error in their published

$P(E_T)$ at high recoil kinetic energies. As they used their erroneous high-energy tail to argue in favor of aldehydic C–H bond fission, it became important in this work to find an independent way to determine whether it is aldehydic C–H bond fission. For this reason, we used HRTOF spectroscopy to detect H atoms from methyl vinyl ketone photolysis; this molecule has no aldehydic hydrogen. The lack of a discernible one-photon signal in the methyl vinyl ketone spectrum gives evidence that the acrolein H loss channel involves the loss of an aldehydic hydrogen.

The data here also better determine the low-recoil-energy portion of the C–H bond fission $P(E_T)$. The slowest H atoms in the $m/e = 1$ TOF spectrum of Haas *et al.* show considerable signal resulting from hydrocarbons (C_2H_4, C_2H_3, and HCO) cracking in the ionizer (the HRTOF experiment, of course, does not suffer from this problem). This high background makes the fit for the low kinetic energies of the slowest recoiling H atoms uncertain. Therefore, the peak at 4 kcal/mol is probably not accurately determined in that data, so we adopt our value of 8 kcal/mol. Finally, our experiment agrees with the conclusions of Haas *et al.* that the dissociation is isotropic.

One may consider whether the current data are consistent with the dissociation of acrolein to give $H_2C=CHCO + H$ occurring on the ground electronic state, as previously proposed,[17] or occurring on some excited state. The $P(E_T)$ peaks at 8 kcal/mol translational energies, indicating a small, but significant barrier to the reverse reaction. However, the CASSCF calculations of Fang indicate that there is no barrier to dissociation on the ground electronic state above the reaction endothermicity, so dissociation following internal conversion to the ground state should yield a statistical recoil kinetic energy distribution peaked near 0 kcal/mol.[17] Fang also considers two transition states leading to aldehydic C–H bond fission, both leading to CH_2CHCO ($^2A''$) + H (^2S). A transition state on the triplet manifold connects CH_2CHCHO ($^3n\pi^*$) with the CH_2CHCO ($^2A''$) product, but has a reverse barrier of about 0.7 kcal/mol at the CAS(8,7)/cc-pVDZ level. A second transition state connects CH_2CHCHO ($^1n\pi^*$) with the CH_2CCHO ($^2A''$) product and has a reverse barrier of about 2.1 kcal/mol at the CAS(8,7)/cc-pVDZ level. The ground-state products also correlate with CH_2CHHCO ($^3\pi\pi^*$) which should present a relatively large barrier to the dissociation because the electronic structures of the products and reactants differ significantly.[17] Fang discounted dissociation on the $^3\pi\pi^*$ state because of this barrier.

One possible mechanism that could lead to the production of excited-state products and account for the observed $P(E_T)$ is intersystem crossing from the bright state (S_2, $^1\pi\pi^*$) to the lowest triplet state (T_1, $^3n\pi^*$). After excitation to the second singlet state, simple aldehydes[22] and ketones[23] are known to dissociate through internal conversion to T_1. Furthermore, the *ab initio* calculations of Fang[17] show that the products of the dissociation on T_1 lie 14.9 kcal/mol above ground-state products. Thus the available energy for dissociation on T_1 is $E_{avail} = 147.9 + 2.2 - 87.1 - 14.9 = 48.1$ kcal/mol [roughly 10 kcal/mol higher than observed in our $P(E_T)$, Fig. 5, top]. $CH_2CHCO(^2A'')$ may then internally convert or fluoresce to form ground state products.

Regan *et al.*[9] concluded that the dissociation forms ground-state products based on the onset for the photoionization efficiency curve and the G3 calculated ionization potential. Ground-state products result from dissociation on either S_0 or T_2 ($^3\pi\pi^*$). Since dissociation on the ground state would give a statistical $P(E_T)$, only dissociation on T_2 would be consistent with a large barrier in the exit channel. Furthermore, T_2 could be accessed through an avoided crossing with T_1 in nonplanar geometries.

V. CONCLUSIONS

We have detailed here the first experiment performed on a newly constructed H-atom Rydberg time-of-flight spectrometer. The HRTOF spectrum of acrolein photolyzed at 193 nm shows considerable multiphoton signal at all but the lowest photolysis laser energy used (0.25 mJ/pulse). Both the single-photon and multiphoton contributions to the observed translational energy spectrum were fit using the forward convolution method. The single-photon translational energy distribution almost completely describes the observed H-atom translational spectrum in the lowest-energy spectrum taken with 0.25 mJ/pulse photolysis energy and qualitatively resembles that previously given in the literature.[6] The differences between our $P(E_T)$ and that given previously may be accounted for by the experimental difficulties involved in detecting the $m/e = 1$ spectrum by traditional methods. The dissociation is isotropic, in accordance with previous studies.[6] The observation of a translational energy distribution peaked away from zero is consistent with a significant barrier to the reverse reaction. Thus the observed $P(E_T)$ for the C–H fission channel of acrolein excited at 193 nm is not consistent with dissociation on the ground electronic state, but may result following intersystem crossing to the lowest triplet state. Dissociation could then lead to electronically excited products via T_1 or ground-state products via an avoided crossing at nonplanar geometries with the second triplet state.

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