### Photodissociating methyl vinyl ether to calibrate O+ethylene product branching and to test propensity rules for product channel electronic accessibility

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These experiments investigate the photodissociation of methyl vinyl ether at 193 nm in a crossed laser-molecular beam apparatus. We observe two C-O bond fission channels, a minor channel producing CH<sub>3</sub>+CH<sub>2</sub>CHO ( $\tilde{X}^2 A''$ ) and the major channel yielding CH<sub>3</sub>+CH<sub>2</sub>CHO ( $\tilde{A}^2 A'$ ). Some of the neutral  $\tilde{A}$  state vinoxy product undergoes secondary dissociation to produce ketene+H. These experiments on the photodissociation of methyl vinyl ether, which produce nascent vinoxy and methyl radicals cleanly in a one-to-one ratio, serve two purposes. First, using the measured photofragment velocities and product branching we calibrate the relative sensitivity of mass spectrometric detection to the methyl and vinoxy polyatomic radical products at the m/e = 15daughter ion, taking into account the loss of neutral vinoxy to ketene+H formation. This relative mass spectrometric sensitivity calibration factor is determined to be  $0.116\pm0.022$ . Knowledge of this factor allows us to extract the product branching ratio between the two major competing primary product channels from the  $O({}^{3}P)$  + ethylene reaction, a branching ratio that has been much disputed in the literature. Our results give a CH3+HCO/H+CH2CHO product branching ratio of  $R = 0.61 \pm .11$ , corresponding to 38% ( $\pm 5\%$ ) branching to the CH<sub>3</sub>+HCO channel. Second, we use the result that the channel producing  $\overline{A}$ -state vinoxy dominates over the formation of ground-state vinoxy to test propensity rules being developed to help predict what product channels may be suppressed by electronically nonadiabatic effects in chemical reactions. These propensity rules discriminate between channels that are "electronically facile" and "electronically difficult/ prohibitive." We find that a qualitative analysis of the changes in electronic configuration along the reaction coordinates for the photodissociation of methyl vinyl ether correctly predicts the dominant channel to be the production of excited state  $(\tilde{A})$  vinoxy, the electronically facile channel. © 2001 American Institute of Physics. [DOI: 10.1063/1.1369662]

### I. INTRODUCTION

This paper reports a crossed laser-molecular beam photofragment scattering experiment on methyl vinyl ether at 193.3 nm, a study motivated in part by the need to calibrate product branching in the thermal O+ethylene reaction. This bimolecular reaction is of importance not only in the combustion of ethylene, but also in the combustion of methane and of larger aliphatic hydrocarbons and aromatics where ethylene is a key intermediate. Prior molecular beam reactive scattering experiments<sup>1</sup> by Lee and co-workers on the  $O({}^{3}P)$  + ethylene reaction detected two major product channels consistent with most prior work,<sup>2-11</sup> CH<sub>3</sub>+CHO and CH<sub>2</sub>CHO(vinoxy)+H, but met with considerable obstacles in determining the branching between those two channels. The reported branching ratio, derived from the relative signals from daughter ions at m/e = 30 from HC<sup>18</sup>O and m/e=42 from CH<sub>2</sub>CHO and using semiempirical estimates of the products' ionization cross sections, did not agree with that determined using the signal attributed to the methyl and vinoxy products at m/e = 15. The experiments reported in this paper overcome these obstacles, using the photodissociation of  $CH_2$ =CHOCH<sub>3</sub> to give  $CH_3$ +CH<sub>2</sub>CHO to calibrate

the relative sensitivity of mass spectrometric detection of the methyl and vinoxy polyatomic radical products at the m/e=15 daughter ion. Determination of this calibration factor allows us to extract the branching ratio between the two major competing primary product channels in the prior work on the  $O({}^{3}P)$  + ethylene reaction from the relative signals from these two channels at m/e = 15 with a method that in principle circumvents the need to estimate ionization cross sections and determine daughter ion cracking patterns. This is the first time this methodology has been applied to determining product branching in a thermal bimolecular reaction, although its analog<sup>12,13</sup> has proven useful in a variety of photodissociation reactions. In general we expect that this method, which generates polyatomic radicals in a 1:1 ratio in a photodissociation experiment to calibrate the mass spectrometric sensitivity to polyatomic radical products, will be useful in determining product branching in a wide range of mass spectrometric and photoionization experiments without resorting to unreliable estimates of total ionization cross sections.

We also became interested in studying the photodissociation of methyl vinyl ether because it provides an opportu-

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nity to further develop our predictive ability in reactions where branching to primary product channels is altered by electronically nonadiabatic dynamics.14 If electronic nonadiabaticity does not influence the dynamics, then the usual way to predict the branching between product channels is to identify what adiabatic product channels are energetically allowed, and then consider the relative barrier heights and calculated Arrhenius A factors for each possible chemical reaction pathway to estimate which chemical reaction will dominate. However, when the change in electronic wave function along one or more reaction coordinates is too large for the electrons to adjust adiabatically from the reactant electronic wave function to the adiabatic product electronic wave function, those reaction channels become "electronically inaccessible" to some extent, slowing their rate relative to other channels or allowing access to electronically nonadiabatic reaction channels. Understanding how branching to a product channel can be hindered by its electronic inaccessibility is a key advance in developing our intuition about chemical reactivity. The competition between the two O-CH<sub>3</sub> bond fission channels in methyl vinyl ether photodissociation, one forming ground-state vinoxy product +methyl and the other forming  $\widetilde{A}$ -state vinoxy product+methyl, affords the opportunity to test electronic propensity rules being developed to help predict what product channels may be suppressed by the inability of the electronic wave function to change along the reaction coordinate.<sup>15,16</sup> In the discussion we classify the two O-CH<sub>3</sub> bond fission reactions in terms of those electronic propensity rules<sup>15</sup> such that the channel forming excited-state vinoxy radicals is electronically facile, while the one forming ground-state radicals is electronically prohibitive because it requires a two-electron change in electronic configuration as the molecule evolves from reactant to ground-state products.

Despite the fact that methyl vinyl ether has been used as a photolytic precursor of the vinoxy radical<sup>17–19</sup> for use in dynamics and spectroscopic studies, information on the branching to primary product channels or the electronic states of the photoproducts are unavailable. Work in progress by Su and Bersohn<sup>20</sup> has also recently sought to determine the vibrational distribution of ground-state vinoxy product from methyl vinyl ether photodissociation at 193 nm. The vinoxy radical is of considerable interest not only as an important intermediate in combustion, but also because of its role in photochemical smog cycles, as it can undergo fast reaction with NO<sub>2</sub> in the atmosphere.<sup>21</sup>

While methyl vinyl ether in its ground state has been of considerable interest due to its gearing-type torsional interaction of the methyl internal rotation with the skeletal torsion,<sup>22</sup> information on electronic states of this molecule is relatively scarce. The UV absorption spectrum was published by Planckaert *et al.*<sup>23</sup> and two overlapping transitions near 200 nm were assigned. Methyl vinyl ether has a broad strong  $\pi^* \leftarrow \pi$  absorption with a maximum at 188 nm ( $\sigma_{193 \text{ nm}} = 8 \times 10^{-18} \text{ cm}^2 \text{ molecule}^{-1}$ ) with an overlapping lower energy vibrational progression that has been assigned to a Rydberg transition. No theoretical studies to date have examined the excited-state potential energy surfaces of methyl vinyl ether, but within this paper we present a simple

configuration interaction with single electron excitations calculation (CIS)<sup>24</sup> that yields an oscillator strength of f>0.5for excitation to the second excited state, the experimentally accessed  $\pi\pi^*$  transition.

The most probable reactions of methyl vinyl ether photoexcited at 193 nm are the following:

$$CH_2 = CH - O - CH_3 \rightarrow CH_2 CHO + CH_3, \tag{1}$$

$$\rightarrow$$
 CH<sub>2</sub>=CH+OCH<sub>3</sub>, (2)

$$\rightarrow C_2 H_4 + H_2 CO. \tag{3}$$

If enough energy is available, the product of reaction (1) above, the vinoxy radical,  $CH_2CHO$ , can undergo loss of hydrogen to form ketene

$$CH_2CHO \rightarrow CH_2 = C = O + H.$$
(4)

In the experiments undertaken here, enough energy was available for this reaction (4) to occur. Thus, we needed to account for the loss of vinoxy to secondary dissociation to form ketene+H in the calibration of the mass spectrometric sensitivity to the vinoxy and methyl fragments produced in the photodissociation of methyl vinyl ether.

After outlining the experimental method, we present our results and analysis in four subsections. The first, Sec. III A, investigates the primary photofragmentation channels of methyl vinyl ether at 193 nm excitation and gives the results of the angular distribution measurements. Section III B describes how we used the relative signal levels at m/e = 14, 15, and 42 along with literature daughter ion fragmentation patterns to determine, and provide an internal consistency check on, what fraction of the nascent vinoxy product from the primary dissociation underwent secondary dissociation to ketene+H. Section IIIC describes how we calibrated our detection sensitivity at the m/e = 15 daughter ion for the vinoxy and methyl photoproducts, and Sec. III D uses this calibrated sensitivity ratio to derive, from data taken by Schmoltner et al., the branching between the CH<sub>3</sub>+CHO and the vinoxy+H product channels in the O+ethylene thermal reaction. In the discussion we focus on both the new O+ethylene product branching calibration and on understanding the key experimental result that the formation of methyl+excited state vinoxy dominates over the formation of electronic ground-state products. We analyze that result to test propensity rules being developed to help predict what product channels may be suppressed by electronically nonadiabatic effects in chemical reactions.

### **II. EXPERIMENT**

In these experiments, the velocity and angular distributions of the products of the photodissociation of methyl vinyl ether at 193.3 nm are measured using a crossed lasermolecular beam apparatus. After photodissociation with a pulsed excimer laser, the neutral photofragments produced scatter from the crossing point of the laser and molecular beam with velocities determined by the vector sum of the molecular beam velocity and the recoil velocity imparted by the photodissociation event. The fragments that scatter into the  $1.5^{\circ}$  acceptance angle of the detector travel 44.4 cm to an electron bombardment ionizer, where they are ionized by 200 eV electrons. After mass selection by a quadrupole mass filter, the ions are counted with a Daly detector and recorded with a multichannel scalar with respect to their time-of-flight (TOF) from the interaction region after the dissociating laser pulse. The ion flight time constant of  $\alpha = 4.5 \,\mu$ s/amu<sup>1/2</sup> was used to correct for the flight time of the ion through the mass spectrometer; figures within show total (ion+neutral) flight times. Forward convolution fitting of the TOF spectrum determines the distribution of energies released to relative product translation. The plane defined by the molecular beam and the detector axis is perpendicular to the direction of laser propagation, and molecular beam source angles are given with respect to the detector axis.

To form the molecular beam, a 9% mixture of methyl vinyl ether in helium was expanded through a 0.10 mm diameter nozzle heated to approximately 200 °C at a stagnation pressure of 500 Torr. The methyl vinyl ether was obtained from Aldrich (98% purity) and used without further purification. The high nozzle temperature reduced cluster formation in the methyl vinyl ether beam, which we found to be a significant problem with a room temperature nozzle. The temperature was measured using a chromel alumel thermometer that was calibrated using a helium beam TOF. The velocity of the parent beam was measured by rotating the molecular beam source to point into the detector and raising a chopper wheel into the beam. A typical peak molecular beam velocity in the number density distribution, N(v), was 1360 m/s with a velocity spread  $(\Delta v / v_{\text{peak}})$  of 19% with  $\Delta v$  calculated from the full width at half maximum (FWHM) of N(v).

Pulsed light at 193 nm from a Lumonics PM-848 excimer laser with an ArF fill photodissociated the methyl vinyl ether. For the time-of-flight measurements, the unpolarized, attenuated laser energy in the interaction region was focused to a 5 mm<sup>2</sup> spot size in the interaction region at pulse energies typically 5 mJ/pulse. The intensity of the signal observed from the photodissociation of methyl vinyl ether was found to be linear with increased power, indicating that only one-photon processes contributed significantly. For the anisotropy measurements, we dispersed the unpolarized laser light into two linearly polarized components with a single quartz Pellin-Broca. The horizontal component is utilized, and the polarization is rotated into the desired direction with a half-wave retarder. The angular distributions are obtained by measuring the change in signal intensity with laser polarization angle by finding the area under the peak in the m/e=42 spectrum with the laser set to the specified polarization angles. The polarization-dependent signal, integrated in many repeated short scans and alternating between each laser polarization direction (50 000 shots to a total of 750 000 at each angle), required no additional normalization to laser power or detector efficiency. Laser polarization angles are defined with respect to the detector axis, but counter-rotated from the source angle.

Signal was observed at various angles for several parent and daughter ions of the primary neutral photofragments: at m/e=58 (parent, at a source angle of 6°, for clusters only), 42 (C<sub>2</sub>H<sub>2</sub>O<sup>+</sup>, 10° and 15°), 15 (CH<sub>3</sub><sup>+</sup>,10°), and 14 (CH<sub>2</sub><sup>+</sup>,



FIG. 1. Experimental TOF spectrum for the photodissociation of methyl vinyl ether, collected at m/e = 42, at a 10° source angle and over 3 million laser shots. Open circles represent data points; the total fit (shown in a bold line) is a sum of contributions from channels shown in dashed lines. This signal is attributed to  $C_2H_2O^+$  from the heavy photofragments produced in O-CH3 fission of CH2=CHOCH3 with a very small contribution from cluster photodissociation (the long-short-long dashed peak buried inside the largest peak). The large slow peak is fit with the lower energy  $P(E_T)$  shown in Fig. 2; this signal contains contributions from both CH<sub>2</sub>CHO radicals cracking in the ionizer to give signal at m/e = 42 and from the secondary dissociation ketene products cracking at parent ion. As expected, the secondary dissociation does not significantly alter the velocity of ketene from the vinoxy radical precursor, so one sees the required momentum match between all m/e = 42 signal and that at methyl (m/e = 15, Fig. 3). The small fast peak is fit with the higher translational energy  $P(E_T)$  shown in Fig. 2 and is assigned to daughter ions of ground-state vinoxy radicals produced in the initial dissociation event.

10° and 15°). A small amount of signal was observed at  $m/e = 41 (10^{\circ} \text{ and } 15^{\circ}), 29 (10^{\circ}), 26 (10^{\circ}), \text{ and } 25 (10^{\circ}), \text{ and } 15^{\circ})$ was adequately fit within the limits of the poor signal-tonoise ratio using the mass 42 and cluster distributions. No discernible signal other than cluster contribution was observed at  $m/e = 43 (10^{\circ})$ , 31 (10°), 30 (10°), 27 (10°), or 16 (10°). The high natural background at m/e = 28 (caused by CO<sup>+</sup>) prevented collection of data at this mass. For the measurements in Sec. III B, when we needed to determine the ratios between signal levels at m/e = 14, 15, and 42, we proceeded as follows. Systematic errors (including fluctuations in the parent molecular beam) were averaged out by alternating data collection between  $m/e = 15(CH_3)$  and m/e $=42(C_2H_2O)$ . 500 K shots were taken in each scan and the scans repeated until 2 M shots were collected at each mass. We collected data with the same method of alternating scans of 500 K shots at  $m/e = 14(CH_2)$  and  $m/e = 42(C_2H_2O)$ , with scans taken until 2 M shots total at each mass were collected. Quadrupole resolution for all measurements in this paper was adjusted to roughly 1.0 amu FWHM at each mass.

To characterize the excited state accessed at 193 nm, we ran a configuration interaction with single excitations (CIS) calculation<sup>24</sup> with GAUSSIAN 94 using a 6-311G\* basis set of atomic orbitals. The ground-state geometry (in  $C_s$  symmetry) used for these calculations was taken from a theoretical paper by Leibovitch *et al.*<sup>25</sup>

### **III. RESULTS AND ANALYSIS**

## A. Identification of primary product channels in methyl vinyl ether photodissociation

The data for methyl vinyl ether excited at 193 nm show evidence for two competing product channels, both of which are C-O bond fission pathways leading to vinoxy plus methyl  $(C_2H_3O+CH_3)$  formation, reaction (1). No evidence for vinyl plus methoxy formation, reaction (2), nor ethene plus formaldehyde formation, reaction (3), was seen in our data. Figure 1 shows the TOF spectrum taken at m/e = 42 at a source angle of  $10^{\circ}$ . We attributed this signal to the heavy photofragment from  $O-CH_3$  fission, reaction (1), to form the vinoxy radical  $CH_2CHO$  (mass 43)+ $CH_3$ , since the TOF spectrum at m/e = 15 has a fast component with arrival times that closely correspond to that predicted for the methyl co-fragment using the usual requirement of conservation of linear momentum in the primary dissociation and the  $P(E_T)$ derived from forward convolution fitting of the m/e = 42TOF shown in Fig. 2. However, not all the signal at m/e=42 results from simple cracking of the mass 43 vinoxy radical product to m/e = 42 in the electron bombardment mass spectrometer. Some of the vinoxy radical product is formed with enough internal energy to undergo C-H fission as a neutral and produce the neutral molecule ketene (CH<sub>2</sub>=C=O), which gives some signal at parent mass 42 upon electron bombardment ionization. As has been seen before by Schmoltner *et al.*,<sup>1</sup> very little (or none at all) of the vinoxy radical produced in the interaction region survives intact through electron bombardment ionization to give m/e=43; we saw no signal other than clusters at the massto-charge ratio corresponding to the parent vinoxy radical



FIG. 2. Translational energy distributions,  $P(E_T)$ 's, used to fit the O-CH<sub>3</sub> bond dissociation pathways of methyl vinyl ether. The two distributions are derived from forward convolution fitting the m/e = 42 TOF spectra. The faster  $P(E_T)$  is assigned to formation of ground-state vinoxy ( $\tilde{X}^2A''$ ) and ground-state methyl ( $\tilde{X}^2A_1$ ) radicals. The slower distribution, which peaks at ~8 kcal/mol, corresponds to a channel producing methyl+excited state vinoxy radicals, which we assign as CH<sub>2</sub>CHO ( $\tilde{A}^2A'$ ). These nascent  $\tilde{A}$  state CH<sub>2</sub>CHO radicals have enough internal energy that they may dissociate to form to ketene+H, fluoresce, or undergo internal conversion and dissociate on the ground state. See the Results and Analysis section for further details. The normalized  $P(E_T)$ 's are scaled according to the following:

$$\frac{\phi_{\text{fast}}}{\phi_{\text{slow}}} = \left(\frac{\text{rprob}_{\text{fast}}^{42}}{\text{rprob}_{\text{slow}}^{42}}\right) \left(\frac{0.35Q_{\text{vinoxy}} + 0.65Q_{\text{ketene}}}{Q_{\text{vinoxy}}}\right) \left(\frac{0.35f_{\text{vinoxy}}^{42} + 0.65f_{\text{ketene}}^{42}}{0.35f_{\text{vinoxy}}^{42}}\right)$$

ion.] As expected, this secondary dissociation does not significantly alter the velocity of the ketene from the vinoxy product from which it was born, so one sees the required momentum match between the methyl signal and all the signal at mass 42, even though some of that signal is not from vinoxy daughter ions. Interestingly, it appears that not all the nascent vinoxy product with enough internal energy to dissociate to ketene+H does (see Sec. III B). This may be understood if some of the vinoxy product is formed electronically excited and loses energy via fluorescence before undergoing C-H fission. Inspection of the center-of-mass translational energy distributions  $[P(E_T)'s]$  for O-CH<sub>3</sub> fission yielding C<sub>2</sub>H<sub>3</sub>O+CH<sub>3</sub> derived by forward convolution fitting of the m/e = 42 TOF spectrum evidences two different O-CH<sub>3</sub> fission pathways occurring at 193 nm. One channel yields fragments with high translational energies; the faster  $P(E_T)$  (see Fig. 2) extends from 45 kcal/mol to almost 70 kcal/mol. Because this distribution extends to close to the available energetic limit ( $E_{avail} \sim 86 \text{ kcal/mol}$ ), this pathway is assigned to formation of ground-state vinoxy ( $\tilde{X}^2 A''$ ) and ground-state methyl  $(\tilde{X}^2A_1)$  radicals. This will be called the "fast" channel. The second pathway, fit by the slower  $P(E_T)$  in Fig. 2, produces photofragments with low translational energy and from now on will be termed the "slow" channel. This translational energy distribution extends to only 45 kcal/mol and peaks at a much lower energy of  $\sim 8$ kcal/mol, and so the photoproducts are initially formed with considerable internal energy. It is likely that the initial electronic state of the nascent vinoxy radical products formed in this slow channel is the  $\tilde{A}(^{2}A')$  state of vinoxy, as the zero point level of the  $\tilde{B}$  state lies about 82 kcal/mol above the ground state and thus is not energetically accessible except for the smallest recoil kinetic energies in the slow distribution in Fig. 2. The zero point level of the  $\tilde{A}(^{2}A')$  state of vinoxy lies only  $\sim$ 23 kcal/mol above the ground state and so is easily accessible with the available energy. The nascent vinoxy radical product may dissociate to ketene+H, fluoresce, or undergo internal conversion and dissociate on the ground state. The secondary dissociation is considered further in the next section.

The fits to the m/e = 42 TOF spectrum are supported by fitting the TOF spectra taken at m/e = 15 and 14, seen in Fig. 3 and Fig. 4, respectively. In Fig. 3, the momentum-matched methyl fragments to the two O-CH<sub>3</sub> fission channels observed at m/e = 42 are the small peak observed at the fastest arrival time and the bulk of the largest peak which arrives between  $\sim 100$  and 200  $\mu$ s, although the contribution from daughter ions produced by cracking of the fast vinoxy radicals in the ionizer can be clearly seen in this largest peak as well. Finally, the slower shoulder is signal from cracking of the vinoxy radicals formed via the slow O-CH<sub>3</sub> fission channel which forms nascent radicals with higher internal energy. (Although some of the slow vinoxy product undergoes secondary dissociation to ketene+H, ketene does not have an m/e = 15 daughter ion so those products do not contribute to the slow shoulder in the m/e = 15 TOF spectrum. They do at m/e = 14.) A miniscule contribution from clusters is also included, which is fit in the following manner: Fig. 5 shows the

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FIG. 3. Experimental TOF spectrum for the photodissociation of methyl vinyl ether, collected at m/e = 15, at a 10° source angle and over 5.5 million laser shots. Open circles represent data points; the total fit (shown in a bold line) is a sum of contributions from channels shown in dashed lines. The momentum-matched methyl fragments to the two O–CH<sub>3</sub> fission channels observed at m/e = 42 (Fig. 1) are the small peak observed at the fastest arrival time and the bulk of the largest peak. Clearly also seen in the largest peak is signal assigned to daughter ions of the ground-state vinoxy ( $\tilde{X}^2A''$ ) product. The slow shoulder is assigned to signal produced from daughter ions of the excited state vinoxy ( $\tilde{A}^2A'$ ) formed via the slow O–CH<sub>3</sub> fission channel. Note that this peak is much smaller than the corresponding one in the m/e = 14 spectrum (Fig. 4), as ketene does not crack to give m/e = 15. This fact was used in the calibration for the loss of nascent vinoxy radicals to ketene formation, as explained in the text.

TOF signal observed at m/e = 58 (CH<sub>2</sub>==CHOCH<sub>3</sub><sup>+</sup>) at a 6° source angle. Because this signal was observed at the mass/ charge ratio of the parent methyl vinyl ether molecule, it must arise from photodissociation of clusters present in the expansion. While such clusters were minimized by heating the nozzle, they still represent a small percentage of the species in the expansion. The TOF spectrum shown in Fig. 5 is fit to determine the center-of-mass recoil speed distribution P(v), and as the signal attributable to cracking of the photoproduced monomer appears at late arrival times for most mass/charge ratios, the contribution from clusters in the expansion can be accounted for by fitting the P(v) to the slow signal at the mass/charge ratios of interest.

In the TOF spectrum at m/e = 14, Fig. 4, what was the slower shoulder at m/e = 15 has grown to the largest peak in the m/e = 14 spectrum. This is because at the energies used in this experiment, more than half of the vinoxy formed via the slow channel undergoes unimolecular dissociation to form ketene+H as a neutral. Ketene does not crack to m/e = 15, but has a strong daughter ion at m/e = 14. In the next section (III B) we detail how we estimated what fraction of the nascent vinoxy radical product in the slow channel underwent secondary dissociation. This was found by using the relative signal levels at m/e = 42 vs that in the slow shoulder at m/e = 15 versus that at m/e = 14. The internal consistency of the estimate was checked with the m/e = 14 data.

Angular distribution measurements of the photofragments from methyl vinyl ether photodissociation were taken



FIG. 4. Experimental TOF spectrum for the photodissociation of methyl vinyl ether, collected at m/e = 14, at a 10° source angle and over 3 million laser shots. Open circles represent data points; the total fit (shown in a bold line) is a sum of contributions from channels shown in dashed lines, which are scaled assuming a 35% survival probability for vinoxy radicals from the slow channel and 100% survival probability for vinoxy radicals from the fast channel. The CH<sub>2</sub><sup>+</sup> daughter ions of the momentum-matched methyl fragments to the two O-CH<sub>3</sub> fission channels observed at m/e = 42 (Fig. 1) are the small peak observed at the fastest arrival time and the bulk of the second largest peak (from about 100 to 200  $\mu$ s). The tiny peak buried in this larger one is signal assigned to daughter ions of the ground-state vinoxy  $(\tilde{X}^2 A'')$  produced by cracking in the ionizer. The largest peak, beginning from about 200  $\mu$ s with a long slow tail, is the m/e = 14 signal corresponding to that seen in the slow shoulder in the m/e = 15 spectrum; this signal has arrival times corresponding to the daughter ions of the excited state vinoxy ( $\tilde{A}^{2}A'$ ) formed via the slow O-CH<sub>3</sub> fission channel and includes the daughter ions of the secondary dissociation product ketene, which will not have significantly altered arrival times from those from the vinoxy radical precursor. Note that this peak is much larger than the corresponding one in the m/e = 15 spectrum (Fig. 3), as ketene does not crack to give m/e= 15. This fact was used in the calibration for the loss of nascent vinoxy radicals to ketene formation, as explained in the text.



FIG. 5. Experimental TOF spectrum for the photofragments of detected at m/e = 58, at a 6° source angle and over 2 million laser shots. Since the signal occurs at the parent mass, it must result from photodissociation of clusters present in the supersonic expansion. The fit (shown in a bold line) is the center-of-mass recoil speed distribution P(v) assigned to cluster dissociation. The slow arrival time and small amount of signal attributable to clusters ensures that that contribution to signal at most mass/charge ratios can be accounted for by fitting the P(v) to the slow signal at the mass/ charge ratios of interest.



FIG. 6. Experimental angular distributions of the slow vinoxy+methyl channel, measured at m/e=42 (C<sub>2</sub>H<sub>2</sub>O<sup>+</sup>), with a linearly polarized laser and a source angle of 10°.  $\Theta_{\rm lab}$  is the angle of the laser electric vector with respect to the detector axis. The data points represent the integrated experimental TOF signal between 204  $\mu$ s and 286  $\mu$ s measured at six different laser polarization angles. Line fits show the predicted change in integrated signal with polarization angle obtained, after transformation from the center-of-mass to the laboratory frame, with five trial anisotropy parameters;  $\beta = -0.2, -0.1, 0.0, 0.1,$  and 0.2. The angular distribution is best fit with a  $\beta$ =0, corresponding to a nearly isotropic distribution.

at m/e = 42 using the procedure outlined in the experiment section. It is well known that the angular distribution of products from dissociation can be described in the center-of-mass frame by the classical electric dipole expression,

$$I(\Theta_{\rm cm}) = 1/(4\pi) [1 + \beta P_2(\cos\Theta_{\rm cm})],$$
 (5)

where  $\Theta_{cm}$  is the angle between the photofragment recoil direction in the center-of-mass reference frame and the electric vector of the linearly polarized light. In the limit of prompt axial photofragment recoil, the anisotropy parameter,  $\beta$ , is given by

$$\beta = 2P_2(\cos\alpha),\tag{6}$$

where  $\alpha$  is the angle between the transition dipole moment for the absorption and the breaking bond. Figure 6 shows the experimentally measured angular distribution of vinoxy fragments along with curves simulated using different values of  $\beta$  in the procedure above. By comparing the experimental points with the simulated curves, we see that  $\beta \approx 0$ , which means that the photodissociation of CH<sub>2</sub>==CHOCH<sub>3</sub> to give CH<sub>3</sub>+CH<sub>2</sub>CHO gives a largely isotropic distribution. According to the CIS calculations performed,  $\alpha$  is about 25°, suggesting that the isotropy results because the time scale of dissociation is long with respect to molecular rotation.

Breaking the vinyl-methoxy bond, reaction (2), is also possible at the energies available in this experiment. To check for this reaction, we took data at the masses of the different daughter ions that would be produced from the photofragments of reaction (2): m/e = 31 (OCH<sub>3</sub><sup>+</sup>), 30 (OCH<sub>2</sub><sup>+</sup>), 29 (OCH<sup>+</sup>, also see cracking from C<sub>2</sub>H<sub>3</sub>O), 27 (C<sub>2</sub>H<sub>3</sub><sup>+</sup>, also might see a small amount from cracking of C<sub>2</sub>H<sub>3</sub>O), 26 (C<sub>2</sub>H<sup>+</sup>, also see cracking from C<sub>2</sub>H<sub>3</sub>O), 25 (C<sub>2</sub><sup>+</sup>, also see cracking from C<sub>2</sub>H<sub>3</sub>O), and 16 (CH<sub>4</sub><sup>+</sup>). We saw no evidence for the production of vinyl and methoxy radicals as a primary dissociation channel of methyl vinyl ether at 193 nm: if any signal at all was visible at m/e = 31, 30, 27, or 16 it was easily assigned to the cluster contribution; for m/e = 29, 26, and 25, the signal seen was adequately fit by assuming it arose from vinoxy radicals and using the  $P(E_T)$  in Fig. 2. The lack of signal at m/e = 31, 30, and 27 also eliminated the reaction (R3) producing formaldehyde and ethene as a significant primary product channel for the photodissocation of methyl vinyl ether at 193 nm.

## B. Secondary dissociation of vinoxy radical to form ketene+H

This section first assesses which nascent vinoxy products have enough internal energy to undergo secondary dissociation to ketene+H and speculates on the mechanism. Then, we estimate from the pertinent signal intensities at m/e=42, 15, and 14 what fraction of the vinoxy radicals potentially subject to secondary dissociation actually does so rather than losing the energy via fluorescence. The energy available for translational and internal energies of the photoproducts formed from O–CH<sub>3</sub> cleavage was estimated using bond dissociation energies provided by Ruscic,<sup>26</sup> which were calculated at the G3 level for methyl vinyl ether at 0 K:

$$E_{avl} = h \nu - D_o (O - CH_3 \text{ bond})$$
  

$$\approx 148.0 \text{ kcal/mol} - 61.6 \text{ kcal/mol}$$
  

$$\approx 86.4 \text{ kcal/mol}.$$
(7)

Thus, the internal energy of the methyl+vinoxy (electronic+vibrational+rotational) is  $E_{avl}-E_T=86.4$  kcal/mol- $E_T$  (where  $E_T$  is the kinetic energy partitioned to product recoil in the primary dissociation, Fig. 2) and we expect most of this internal energy to be partitioned to the vinoxy product, not the methyl. The photodissociation spectroscopy and dynamics of the vinoxy radical have been studied in detail by Osborn *et al.*<sup>27</sup> at selected excitation energies up to almost 4000 cm<sup>-1</sup> above the  $\tilde{B}$  state zero point level. They found that upon excitation to the  $\tilde{B}$  state at energies 1400 cm<sup>-1</sup> over the zero point level, the vinoxy radical undergoes fast internal conversion ( $\tilde{B} \rightarrow \tilde{A} \rightarrow \tilde{X}$ ) to the ground state followed by dissociation dynamics that branches to two product channels

$$CH_{2}CHO \xrightarrow{h\nu} CH_{3} + CO$$

$$\Delta H = 0.08 \pm 0.09 \text{ eV} (1.8 \pm 2.1 \text{ kcal/mol}), \quad (8)$$

$$\stackrel{h\nu}{\rightarrow} H + CH_{2}CO$$

$$\Delta H = 1.49 \pm 0.09 \text{ eV} (34.4 \pm 2.1 \text{ kcal/mol}). \quad (9)$$

On the ground-state potential energy surface, one expects a large exit barrier to product channel (8) to form methyl+CO and a small exit barrier (beyond the endothermicity) to product channel (9). The calculated<sup>27</sup> barriers (with zero-point corrections) to (8) and (9) are 1.78 and 1.63 eV, respectively, with channel (9) having a looser transition state. Thus, since the internal energy of the nascent vinoxy radical product in our experiments is the bulk of 86.4 kcal/mol- $E_T$ , there is more than enough energy for either (8) or (9) to occur for all of the nascent vinoxy products in the slow channel if the dissociation proceeds via internal

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conversion to the ground state. Most of the vinoxy radical products formed in the fast channel have low enough internal energies to be stable to secondary dissociation. If the secondary dissociation occurs from the  $\tilde{A}$  state of vinoxy rather than via internal conversion to the ground state, Ref. 27 gives a barrier 2.09 eV above the ground-state zero-point level for reaction (9) to form ketene, but does not calculate the barrier to reaction (8).] We should note that Osborn *et al.* found that upon exciting vinoxy radical to the  $\tilde{B}$  state that the product channel branching was  $4(\pm 2)$ :1 for channel (8): channel (9), in good agreement with their RRKM calculations that presumed that dissociation occurred upon internal conversion to the ground state, but in our experiments a negligible fraction of the nascent vinoxy product undergoes dissociation via reaction (8). The entire signal at m/e = 15 and 14 is accounted for in the fits shown in Figs. 3 and 4 by three sources: primary methyl product from O-CH<sub>3</sub> fission, daughter ions of vinoxy radicals, and daughter ions of the secondary ketene product. (We can predict the arrival times of the ketene daughter ions at m/e = 14 as they are essentially the same as for the vinoxy reactant from which they were born, so are determined by momentum matching with the primary methyl product.) A possible explanation for the difference in product branching is that the internal energy of the nascent vinoxy radical product in our experiments, 86.4 kcal/mol- $E_T - E_{int,CH_3}$ , is not enough energy to form vinoxy in the  $\tilde{B}$  state for primary dissociation events releasing more than a few kcal/mol to product translation, since the  $\tilde{B}$  state origin lies 82 kcal/mol above ground-state vinoxy radical. Thus, most of the nascent vinoxy products in the slow kinetic energy channel in our experiments are likely formed in the  $\tilde{A}$  state.

Because the goal in the next section is to use our data at m/e = 15 to calibrate the relative mass-spectrometric detection sensitivity for methyl vs vinoxy radicals, we must account for the fact that some of the nascent vinoxy product is lost to secondary dissociation to ketene and so does not contribute to the m/e = 15 signal. The relative signal levels at m/e = 15 in these data from the slow channel would normally, if the vinoxy did not undergo secondary dissociation, represent production in the interaction region of one vinoxy radical for each momentum-matched methyl radical. Then, application of the method used in Sec. III D to determine mass-spectrometric sensitivity to radical products and help determine product branching in the O+ethylene experiments detecting methyl and vinoxy products at m/e = 15 would not involve any assumptions about the daughter ion cracking fractions or require error-prone semiempirical estimates of ionization cross sections. However, since some of the vinoxy radicals in our calibration in Sec. III C are lost to secondary dissociation to ketene, which does not crack to m/e = 15, we need to determine what fraction of the nascent vinoxy products does not undergo secondary dissociation. We derive the result in the next paragraph that about 35% of the nascent vinoxy product does not undergo secondary dissociation  $(\phi_{\text{vinoxy}}=35\%)$ , so the relative signal levels at m/e=15 in these data from the slow channel represent production in the interaction region of 0.35 vinoxy radicals for each momentum-matched methyl radical. Unfortunately, determining this 35% survival fraction does require us to use ratios between selected daughter ion cracking probabilities and semiempirical estimates of the ionization cross sections for vinoxy vs ketene, but fortunately the ionization crosssection ratios ( $Q_{\text{ketene}}/Q_{\text{vinoxy}}$ ) are relatively robust to the semiempirical method used to estimate them. Thus, this does not introduce significant errors in the sensitivity calibration. We also provide a double-check below, showing that the ratio between the m/e = 42 and m/e = 14 signals is predicted to be within 10% of our observed signal intensity ratio when we use the literature daughter ion cracking probabilities from vinoxy and ketene and the derived survival fraction of the vinoxy to secondary dissociation.

To determine from our data what fraction of the nascent vinoxy products does not undergo secondary dissociation, we begin by noting that both the m/e = 42 and the m/e= 14 signal have contributions from daughter ions of both stable vinoxy radicals and secondary ketene, while the m/e=15 signal in the same range of arrival times has no contribution from ketene since ketene does not have m/e = 15daughter ion. In general, the observed integrated signal (IS) at a particular daughter ion from a reaction product in a scattering experiment with electron bombardment detection depends on several factors (3D velocity and angular distributions of products, reactant beam intensities, ionizer transit times, ionization cross sections, daughter ion cracking patterns, etc). Fortunately, we only require ratios between signal intensities, so the signal intensity factors relevant to this experiment that differ between vinoxy and the secondary ketene product are simply: (1) the electron bombardment ionization cross sections,  $Q_{\mathrm{vinoxy}}$  and  $Q_{\mathrm{ketene}}$ , of vinoxy and ketene at 200 eV; (2) the probability of the ionized product appearing at a particular daughter ion (calculated from normalizing literature daughter ion cracking patterns for vinoxy<sup>1</sup> and ketene<sup>28</sup> measured at a similar high energy electron bombardment), e.g.,  $f_{\text{vinoxy}}^{42}$ ; and (3) the ratio of quadrupole transmission factors  $T_{mion}$ , if signal intensities at two different mass to charge ratios are being compared. (Our experiments use a Daly detector, which is insensitive to the chemical identity of the ion.) Thus, the integrated signal over a selected range of arrival times at m/e = 42 for the slow channel can be expressed as the sum of the signals from daughter ions of the surviving vinoxy, IS42,vinoxy, and from the parent ion of the secondary ketene, IS42,ketene, and each of those can be individually expressed as follows:

$$IS_{42} = IS_{42,\text{vinoxy}} + IS_{42,\text{ketene}}$$
$$= C \phi_{\text{vinoxy}} Q_{\text{vinoxy}} f_{\text{vinoxy}}^{42} + C' \phi_{\text{ketene}} f_{\text{ketene}}^{42}$$
where  $C \approx C'$ . (10)

In Eq. (10) above the multiplicative constants *C* and *C'* collect together all the factors above that affect the signal intensity that do not differ between vinoxy and ketene. Letting C = C' requires only one assumption, that the survival probability of nascent vinoxy does not vary significantly for the range of recoil velocities sampled in the slow dissociation channel (e.g., that the branching  $\phi_{\text{vinoxy}}/\phi_{\text{ketene}}$  between stable vinoxy and vinoxy that dissociates to ketene does not

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depend strongly on internal energy in the range of internal energies relevant to the slow channel). The reliability of this assumption is supported by the fact that the slow daughter ion signal at m/e = 15 has only contribution from stable vinoxy, while the signal at m/e = 42 has contribution from both stable vinoxy and secondary ketene, yet the shape of the TOF spectra in the vicinity of the slow vinoxy product at m/e = 15 is fit well by the  $P(E_T)$  derived from the m/e=42 data. If the survival probability of nascent vinoxy  $\phi_{
m vinoxy}$  varied significantly across the internal energies represented by that range of arrival times (e.g., if the nascent vinoxy from the slow channel arriving at earlier times and thus having lower internal energies was less likely to undergo secondary dissociation that the vinoxy at longer arrival times), then the shape of the TOF spectra in the vicinity of the slow vinoxy product at m/e = 15 would not be fit well by the P(E) derived from the m/e = 42 data. Now, deriving the branching  $\phi_{\rm vinoxy}/\phi_{\rm ketene}$  between stable vinoxy and vinoxy that dissociates to ketene is trivial using Eq. (10) and the relevant integrated signal intensities (signal from only the slow channel attributed to the nascent vinoxy product, some of which survives as vinoxy and some of which gives ketene) at m/e = 15 and m/e = 42:

$$\frac{IS_{42}}{IS_{15}} = \frac{IS_{\text{vinoxy},42} + IS_{\text{ketene},42}}{IS_{\text{vinoxy},15} + 0} \\
= \left(\frac{IS_{\text{vinoxy},42}}{IS_{\text{vinoxy},15}} + \frac{IS_{\text{ketene},42}}{IS_{\text{vinoxy},15}}\right) \\
= \left(\frac{f_{\text{vinoxy}}^{42}}{f_{\text{vinoxy}}^{15}} + \frac{\phi_{\text{ketene}}}{\phi_{\text{vinoxy}}} \frac{Q_{\text{ketene}}f_{\text{ketene}}^{42}}{Q_{\text{vinoxy}}f_{\text{vinoxy}}^{15}}\right) \\
\times \frac{T_{42}}{T_{15}} \frac{881\,068 \text{ counts}}{214\,080 \text{ counts}} \\
= \left(\frac{0.2435}{0.1834} + \frac{\phi_{\text{ketene}}}{\phi_{\text{vinoxy}}} \frac{Q_{\text{ketene}}(0.3316)}{Q_{\text{vinoxy}}(0.1834)}\right) \cdot 1, \quad (11)$$

where we have assumed the quadrupole transmission is the same at m/e = 42 and m/e = 15 since we have adjusted it to the same resolution at these two masses and have used the same hi-O head. (In actuality, the literature daughter ion cracking pattern we are using for vinoxy did not include correction for quadrupole transmission, so the T factors above are buried in the daughter ion cracking probability ratios.) Solving Eq. (11) for  $\phi_{\text{ketene}}/\phi_{\text{vinoxy}}$  and using the semiempirical method of Fitch and Sauter<sup>29</sup> to estimate the electron bombardment ionization cross sections for vinoxy and ketene (FS:  $Q_{\text{vinoxy}} = 6.743 \text{ Å}^2$  and  $Q_{\text{ketene}} = 5.723 \text{ Å}^2$ ), we get  $\phi_{\text{ketene}}/\phi_{\text{vinoxy}} = 1.82$ . Thus, the survival probability of the nascent vinoxy product is determined to be  $\phi_{\text{vinoxy}}$ =0.36 (36% of the nascent vinoxy radicals do not undergo secondary dissociation to ketene+H). Fortunately, the derivation is only sensitive to the ratio of the ionization cross sections, because an estimate of the individual cross sections using the other commonly used semiempirical method of Center and Mandl<sup>30</sup> (CM) using sums of atomic polarizabilities<sup>31</sup> gives ionization cross sections almost ten times larger for each (CM:  $Q_{\text{vinoxy}} = 72.52 \text{ Å}^2$  and  $Q_{\text{ketene}}$  = 67.61 Å<sup>2</sup>), but the ratio  $Q_{\text{ketene}}/Q_{\text{vinoxy}}$  is similar to that from the Fitch and Sauter method. Carrying the calculation through using the Center and Mandl estimate for the ionization cross sections gives  $\phi_{\text{ketene}}/\phi_{\text{vinoxy}}=1.65$ , corresponding to a survival probability of the nascent vinoxy product of  $\phi_{\text{vinoxy}}=0.38$ . Thus, using either method for estimating the electron bombardment ionization cross sections, we determine that about 36% of the nascent vinoxy product is stable to secondary dissociation and contributes to the m/e = 15 signal at slow arrival times and 64% of the nascent vinoxy product in the slow channel undergoes secondary dissociation to ketene+H.

Since the determination above of the fraction of nascent vinoxy product that survives secondary dissociation is dependent on estimated ionization cross sections and literature daughter ion fragmentation patterns, we did try to assess the reliability of the estimate. In particular, we were concerned that the literature daughter ion cracking patterns, since they are determined for relatively cold vinoxy radicals, may not be a good approximation to that for the highly internally excited vinoxy product from this photodissociation experiment, even though the electron bombardment energy is quite high (200 eV). (The high electron energy helps ensure that the daughter ion fragmentation pattern is not strongly dependent on internal energy.) To assess the reliability of the 40% estimate, we did two analyses. First, we followed the procedure above but used the ratio of the integrated signal in the m/e = 14 data (instead of m/e = 42) to the m/e = 15 data to determine the fraction of nascent vinoxy that survived secondary dissociation. Using the Fitch and Sauter ionization cross sections, this gave a value of 35% (as compared to 36%) using the m/e = 42 over m/e = 15 integrated signals). We then used that 35% determination to try to predict the ratio between signal level at m/e = 42 and the signal level at m/e = 14. While the predicted integrated signal ratio obtained with literature daughter ion fragmentation patterns was 1.06, the experimentally determined signal ratio was 0.98. Thus, the error introduced by these estimates appears to be roughly 10% in the determination of signal intensity ratios, or corresponding apparent cross-section ratios. This is somewhat larger than the error introduced in the integrated signals by Poisson counting error alone. A correct prediction requires a considerably lower survival probability for the nascent vinoxy, but the calculation involves subtracting two similar numbers in the denominator, so is subject to considerable error. Thus, we adopt the survival probability of 35% ±5% ( $\phi_{\text{ketene}}/\phi_{\text{vinoxy}}$ =1.86) for the best determination of the fraction of the nascent vinoxy product that is stable to secondary dissociation and contributes to the m/e=15signal.

We should clarify the integration ranges for the relevant integrated signals at m/e = 42, 14, and 15 used in this section. In all cases we wanted to integrate daughter ions from the same set of neutrals, and the ion flight time is different at m/e = 42 than at 14 or 15, so we needed to shift the integration range depending on the spectrum we were integrating. We chose an integration range for the m/e = 42 TOF spectrum of channel 88 through channel 150 (at 2  $\mu$ s/channel), corresponding to total flight times between 174 and 300  $\mu$ s, while for m/e = 14 and 15 the corresponding integration range needed to be shifted to shorter times by 6 channels or 12  $\mu$ s. In addition, since we only wanted to include integrated signal from the vinoxy/ketene products from the slow distribution and not from the fast distribution or from methyl products, we subtracted from the total integrated signal in these ranges the contribution from those other sources as determined by the fits shown in Figs. 1, 3, and 4. At m/e=42, the signal from slow vinoxy/ketene corresponds to 95.73% of the total integrated signal, while at m/e = 15 and 14 it is 24.47% and 79.51%, respectively. (The m/e = 15 data have a large overlap from the slow methyl product.) We repeated the determination (using the m/e = 42 over m/e=15 integrated signals) for a different integration range, channel 98 to 160 for m/e = 42 and the 6 channel shifted range at m/e = 14 and 15) to assess any errors. We found that using the new integration ranges and the Fitch and Sauter estimates for the ionization cross sections gave (rather  $\phi_{\text{ketene}}/\phi_{\text{vinoxy}} = 1.79$ than 1.82) and gave  $\phi_{\text{ketene}}/\phi_{\text{vinoxy}} = 1.63$  (rather than 1.65 when using Center and Mandl ionization cross sections). Thus, the derived survival probability for the nascent vinoxy radicals of about  $35\% \pm 5\%$  is, as expected, robust with respect to the integration range chosen to make the determination.

# C. Calibrating the relative mass spectrometric detection sensitivity to vinoxy and methyl radicals at the m/e=15 daughter ion for use in product branching determinations

Determining a branching ratio between different reaction channels can be a difficult task, especially when one or more of the products are polyatomic radical species which can crack into many different daughter ions in the electron bombardment ionizer. One method of determining the total amount of neutral parent fragment depends on collecting data at and summing up the contribution from each of the many possible daughter ion masses. This signal is then corrected for quadrupole transmission (if possible) and divided by an estimated ionization cross section. There are often large sources of error in this method, arising from high background or limited signal that might obscure or reduce signal from the daughter ions at some masses such as m/e= 28 (CO+) and m/e = 16 (O<sup>+</sup>). There is also error from the value used for the total ionization cross section, which is rarely experimentally determined and instead is estimated with one of two semiempirical methods,<sup>29,30</sup> neither of which is tested for polyatomic radicals.

The data here on methyl vinyl ether photodissociation provide the essential calibration factor to circumvent the above problems when one wishes to derive a branching ratio in a mass-spectrometric experiment that produces vinoxy radicals in one channel and methyl radicals in another, such as in the bimolecular reactive scattering data of Schmoltner *et al.* on  $O({}^{3}P)$  + ethylene discussed in the next section. We can use the methyl vinyl ether photodissociation data to calibrate<sup>13</sup> the relative mass-spectrometric detection sensitivity to methyl vs vinoxy radical products at the m/e = 15daughter ion, since both the methyl and vinoxy products from the slow O–CH<sub>3</sub> fission channel in the 193 nm dissociation of methyl vinyl ether give a signal at m/e = 15 and that relative signal arises from a 1:0.35 ratio of methyl:vinoxy neutral products. (This is normally a 1:1 ratio, since photodissociation produces one methyl fragment for each vinoxy fragment, but in the previous section we showed that only 35% of the vinoxy products from the slow O-CH<sub>3</sub> fission channel survive secondary dissociation and contribute to the m/e = 15 signal.) The signal intensities at m/e = 15 are fit by varying the "relative probability weightings" for the daughter ion signal from primary methyl products and from the 35% of the momentum-matched vinoxy partners in the slow dissociation channel that survive secondary dissociation. These relative probability weightings, rprobs (also termed the "apparent cross sections  $\sigma^{o}$ " in Ref. 1), include the usual correction for kinematic factors in the 3D velocity and angular distributions of the products and transit time through the electron bombardment ionizer, but do not correct for the effect on the signal intensities from the relative cracking efficiencies of  $CH_3$  and  $CH_2CHO$  to  $CH_3^+$  or the total ionization cross section of each species. (e.g., an rprob for a given channel may be quite low if it is derived from fitting data at a minor daughter of the neutral product.) We will designate each rprob (or apparent cross section) used to fit the relative signal levels in our photodissociation experiment in the m/e = 15 data as  $\sigma_{15}^o$ . Then, the true ratio between the methyl fragments from the slow dissociation channel and the surviving momentum-matched vinoxy product, 1.0/0.35, is related to the ratio of rprob's ( $\sigma_{15}^{o}$ 's) determined from fitting the relative signal intensities (long-dashed and short-dashed contributions, respectively) in the m/e = 15 TOF spectrum in Fig. 3 by the following equation:

1.0 (slow methyl products)

0.35 (slow stable vinoxy products)

$$= \frac{\sigma_{15 \text{ slow methyl}}^o}{\sigma_{15 \text{ slow stable vinoxy}}^o} \frac{Q_{\text{vinoxy}} f_{\text{vinoxy}}^{15}}{Q_{\text{methyl}} f_{\text{methyl}}^{15}}.$$
 (12)

(Note that the apparent cross section derived from fitting the data for the slow methyl products  $\sigma_{15 \text{ slow methyl}}^{o}$  is divided by  $Q_{\text{methyl}}$  because if the ionization cross section for methyl is large it will give an anomalously high apparent cross section.) We can thus use Eq. (12) above to determine  $(Q_{\text{vinoxy}}f_{\text{vinoxy}}^{15})/(Q_{\text{methyl}}f_{\text{methyl}}^{15})$  from our photodissociation experiment from the ratio  $\sigma_{15 \text{ slow methyl}}^o/\sigma_{15 \text{ slow stable vinoxy}}^o$  determined from fitting the corresponding relative signal intensities in our m/e = 15 data. The ratio of rprobs or  $\sigma_{15}^o$ 's determined by fitting the signal assigned to "slow" CH<sub>3</sub> products and their momentum-matched vinoxy was 22:0.9 = slow CH<sub>3</sub>: their momentum-matched vinoxy in the m/e= 15 TOF spectrum (Fig. 3). Inserting  $\sigma_{15 \text{ slow methyl}}^{o}$  $\sigma_{15 \text{ slow stable vinoxy}}^{o} = 22/0.9 \text{ in Eq. (12) gives a value for}$  $(Q_{\text{vinoxy}}f_{\text{vinoxy}}^{15})/(Q_{\text{methyl}}f_{\text{methyl}}^{15})$  from our photodissociation obtaining  $(Q_{\text{vinoxy}} f_{\text{vinoxy}}^{15})/(Q_{\text{methyl}} f_{\text{methyl}}^{15})$ experiment,  $=0.116\pm0.022$ . This sensitivity calibration factor can now be used to convert apparent cross sections to real branching ratios for any experiment which produces methyl radicals in one channel and vinoxy radicals in another, such as in the bimolecular reactive scattering data of Schmoltner et al. on  $O({}^{3}P)$  + ethylene discussed in the next section. We use only their m/e = 15 data, from which one obtains the apparent cross sections of the CH<sub>3</sub>+HCO vs the vinoxy+H product channels from fitting the relative signal intensities of the CH<sub>3</sub> signal at m/e = 15 and the vinoxy signal at m/e = 15 with the usual cm→lab forward convolution fitting procedure. One does not need to sum up signal at any other daughter ion nor rely on semiempirical estimates of the ratio of total ionization cross sections of methyl to vinoxy radicals, as that information is provided by the calibration factor at m/e = 15 from our photodissociation experiment. (Normally this method does not rely on any estimates of ionization cross section or daughter ion fragmentation patterns; we only had to do so in the methyl vinyl ether calibration because some of the vinoxy was lost to secondary dissociation to ketene. See Sec. III B.)

### D. Determining the CH<sub>3</sub>+HCO/H+CH<sub>2</sub>CHO product branching ratio in prior O+ethylene reactive scattering experiments by using our calibrated detection sensitivity to vinoxy and methyl radicals at the m/e=15 daughter ion

Schmoltner *et al.*'s crossed molecular beams scattering experiment<sup>1</sup> on the  $O({}^{3}P)$  + ethylene reaction at a 6 kcal/mol collision energy detected, in qualitative agreement with prior work, two significant primary product channels,

$$O(^{3}P) + C_{2}H_{4} \rightarrow CH_{3} + HCO, \qquad (13)$$

$$\rightarrow$$
H+CH<sub>2</sub>CHO. (14)

Experimental determinations of the branching ratio for the O+ethylene reaction (see the Discussion section) have varied widely. While the work of Schmoltner et al. is likely the benchmark for further work on this system, their method of calculating branching ratios gave a larger branching, 71% (62%-77%), to the CH<sub>3</sub>+HCO channel (13) than any of the other determinations published at that time. Their method of extracting branching ratios from their data relied on commonly used but unreliable (by virtue of being untested for polyatomic radicals) estimates of the ratio of the ionization cross sections of the polyatomic radical products. They also needed to sum up all the signal from all the possible daughter ions, which was done by estimating by comparison with "related compounds" to estimate the cracking to missing masses in their daughter ion fragmentation pattern and compare signal from two different reactive scattering experiments. From one experiment they used their data at m/e=42 for vinoxy and from the second experiment, done with isotopically labeled reactants, they used their data at m/e= 30 ( $C^{18}O^+$ ) for CH<sup>18</sup>O, obtaining their branching ratio R with

$$R = \frac{\sigma_a}{\sigma_b} = \frac{\sigma_a^o}{\sigma_b^o} \times \frac{Q_{\text{vinoxy}}}{Q_{\text{CHO}}} \times \frac{f_{\text{vinoxy}}^{42}}{f_{\text{CHO}}^{30}}.$$
 (15)

In their equation above  $\sigma_o^a$  is the apparent cross section for the CH<sub>3</sub>+HCO channel from the m/e = 30 data and  $\sigma_b^o$  is the apparent cross section for the vinoxy+H product channel from their m/e = 42 data, and they derived each from fitting the relative signal intensities in the two experiments, obtaining  $R = 2.5 \pm 0.9$ . The calculations used the Fitch and Sauter method for estimating ionization cross sections and estimates of the relevant daughter ion cracking patterns.

We can circumvent virtually all the sources of errors in Schmoltner *et al.*'s branching ratio determination by simply using only their data at m/e = 15, which have contributions from both methyl from the CH<sub>3</sub>+HCO product channel (a) [channel (13) above] and vinoxy from the vinoxy+H product channel (b) [channel (14) above]. We correct the apparent cross sections from fitting the methyl and vinoxy signal in their m/e = 15 data to real product branching ratios using the mass-spectrometric sensitivity calibration factor for methyl and vinoxy products that we derived in Sec. III C from the photodissociation of methyl vinyl ether to methyl+vinoxy. We proceed as follows: As Schmoltner et al. did not report the apparent cross sections they used to fit their m/e = 15 data, we refit the m/e = 15 O+ethylene data using their published product translational energies and angular distributions and varied the ratio between the two apparent cross sections until we obtained a good fit to their data. (We used the standard forward convolution bimolecular scattering program of Lee and co-workers, GMT, provided generously by A. Suits. Most of the needed input parameters, such as beam velocities, were given in the paper by Schmoltner et al., with the exception of the interaction region to chopper flight path, which needed to be set at 17.6 cm for the published translational energy distribution to fit the data.) The apparent cross sections that fit the contributions from methyl and from vinoxy products in the m/e = 15 data of Schmoltner *et al.* were 0.84:0.16 (CH<sub>3</sub>+HCO:vinoxy+H). The branching ratio between the two channels is then trivially calculated using that ratio and the mass-spectrometric sensitivity calibration factor 0.116 for methyl and vinoxy products at m/e = 15 that we derived in Sec. III C from the photodissociation of methyl vinyl ether:

$$R = \frac{\sigma_{\rm CH_3+HCO}}{\sigma_{\rm H+CH_2CHO}}$$
$$= \frac{\sigma_{15 \text{ methyl from CH_3+HCO}}^o}{\sigma_{15 \text{ vinoxy from H+CH_2CHO}}^0} \times \frac{Q_{\rm vinoxy} f_{\rm vinoxy}^{15}}{Q_{\rm methyl} f_{\rm methyl}^{15}}$$
$$= \frac{0.84}{0.16} \times 0.116 = 0.61(\pm 0.11). \tag{16}$$

If only these two product channels contribute significantly, this corresponds to a 38% (with estimated error bars of about  $\pm$  5%) branching to the CH<sub>3</sub>+HCO product channel (a) [channel (13) above] and 62% branching to vinoxy+H product channel (b) [channel (14) above]. This is considerably different than the 71% branching (R=2.5±0.9) to the CH<sub>3</sub>+HCO product channel that Schmoltner *et al.* derived from comparing the isotopically labeled experiment for the HC<sup>18</sup>O daughter signal at m/e=30 with the vinoxy signal at m/e=42. The 38% branching to the CH<sub>3</sub>+HCO product channel we derive using our 0.116 calibration factor from the methyl vinyl ether photodissociation is in reasonable agreement with the 44±15% contribution reported by Bley *et al.*,<sup>3</sup>

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TABLE I. Prior determinations of the product branching to the two primary channels formed in the bimolecular  $O(^{3}P)$ +ethylene reaction.

Reference	% (CH <sub>3</sub> +CHO)	% (H+CH <sub>2</sub> CHO)	% (CH <sub>2</sub> +CH <sub>2</sub> O) (minor channel)	Method
1	$71 \ (62-77)^a$	$29\pm5^{a}$	•••	Crossed
Our work	$38\pm5^{a}$	$62\pm5^{a}$		molecular beam Recalibrated crossed molecular beam
2	52-58	36±4		Photochemical modulation
				spectroscopy
4	•••	$27 \pm 5$	•••	Resonance fluorescence
5		$79 \pm 14$		Resonance fluorescence
6	$50 \pm 10$	$40 \pm 10$		Microwave spectroscopy
3	44±15	50±10	6±3	LMR, ESR

<sup>a</sup>Assumes these channels are the only significant ones, as the experiment only determines ratio between these two.

whereas the 71% determination Schmoltner *et al.*<sup>1</sup> reported is well outside the error bar range of this and most other measurements of this branching.

### **IV. DISCUSSION**

## A. Product branching in the O+ethylene bimolecular reaction

In this paper we used methyl vinyl ether photodissociation to derive the relative mass-spectrometric sensitivity calibration factor of 0.116 for methyl to vinoxy products at m/e = 15 and then used that calibration factor to derive the product channel branching in prior O+ethylene reactive scattering experiments using only their m/e = 15 signal intensities. Our determination gave a CH<sub>3</sub>+HCO/H+CH<sub>2</sub>CHO product branching ratio of R = 0.61, corresponding to 38%  $(\pm 5\%)$  branching to the CH<sub>3</sub>+HCO channel, while the more error-prone method used in the prior work gave a value reported as  $R = 2.5 \pm 0.9$ , corresponding to 71% branching to the CH<sub>3</sub>+HCO channel. Table I shows a summary of the widely varying determinations of the product branching for the O+ethylene reaction that were published near the time of the prior work. Clearly the 71% (62%–77%) value for the CH<sub>3</sub>+HCO channel that Schmoltner et al. derived in 1989 from their data was at the upper limit of prior determinations. Furthermore, that value as well as many others were outside the error bars of many of the other reported branching percentages.

We can try to assess whether the 71% branching to the  $CH_3+HCO$  product channel determined by Schmoltner *et al.* was high due to the difficulty of comparing signal in an isotopically labeled experiment for the  $HC^{18}O$  daughter signal at m/e = 30 with the vinoxy signal at m/e = 42. Interestingly, Schmoltner *et al.* did try to use the m/e = 15 data alone to determine a branching ratio. That should have given a more reliable determination, as it does not rely on comparing an isotopically labeled with an unlabeled experiment. However, their paper states that "the intensity derived from the fast feature in the m/e = 15 data would correspond to a much larger branching ratio (favoring channels 1a)" (the  $CH_3+HCO$  product channel), so they conclude that the fast feature is probably "only partly due to [the methyl product]

and partly due to other unidentified sources." To us, this seems like an odd conclusion since the product translational energy distribution they report for the CH<sub>3</sub>+HCO channel gave a good fit to the fast m/e = 15 signal, so it is hard to imagine an unidentified source having the same TOF distribution. Indeed, when we use the same m/e = 15 data, but with our 0.116 calibration factor from the methyl vinyl ether photodissociation, we get the reasonable branching ratio given above (smaller, not larger, than Schmoltner et al. report and well within the range of other measurements on this branching). Clearly, it is their estimates of the daughter ion cracking patterns and/or total ionization cross sections of methyl and vinoxy that are causing their difficulty in deriving a branching ratio from their m/e = 15 data. They did not report the daughter ion cracking patterns they used for methyl radicals.<sup>32</sup> This daughter ion cracking pattern of methyl radicals, however, is dependent on both internal energy and ionization energy used. Thus, to attempt to determine the source of the possible error in the calculations of Schmoltner et al., we repeated their calculations using a value for  $f_{\text{methyl}}^{15}$ obtained from a study of methyl radical daughter ion cracking collected as a function of internal energy of the methyl, taken at a 70 eV electron bombardment energy.<sup>33</sup> Schmoltner et al. collected their data using 200 eV ionization energy, but the absolute cross sections for the formation of the  $CD_3^+$  and  $CD_2^+$  ions from  $CD_3$  radicals were studied as a function of electron impact ionization energy by Tarnovsky et al., who show that between 70 and 200 eV the measured cross sections flatten out.<sup>34</sup> We would therefore expect the methyl cracking pattern not to change dramatically at 200 eV vs at 70 eV. Since Schmoltner et al. used an average collision energy of only 6 kcal/mol in their experiments, we used the lower internal energy methyl daughter ion cracking patterns provided by Lin *et al.*, and found that the value for R that this gives, 3.0, is indeed also larger rather than smaller than the value of 2.5 adopted by Schmoltner et al. Thus, using estimated ionization cross sections and literature daughter ion cracking patterns does not give a reliable branching ratio determination, whereas our calibration of the m/e = 15 signal intensities using methyl vinyl ether does. As  $f_{vinoxy}^{42}$  was measured by Schmoltner et al., we believe that the error must reside in the value obtained for  $Q_{\rm vinoxy}/Q_{\rm methyl}$ . As can be

seen from the order-of-magnitude difference obtained for  $Q_{\text{vinoxy}}$  and  $Q_{\text{ketene}}$  using the Fitz and Sauter vs the Center and Mandl semiempirical methods for calculating total ionization cross sections, such estimations are extremely unreliable. We did rely on the same methods to calculate  $Q_{\text{vinoxy}}/Q_{\text{ketene}}$ , but apparently that ratio is more reliable as vinoxy and ketene should have more similar ionization cross sections, and the value for the ratio calculated by the two methods was consistent.

The largest potential source of error in our determination of the O+ethylene product branching from the Schmoltner data is any error in our calibration of  $(Q_{\text{vinoxy}}f_{\text{vinoxy}}^{15})/$  $(Q_{\text{methyl}}f_{\text{methyl}}^{15}) = 0.116$  introduced by a poor estimate of the fraction of the slow nascent vinoxy radicals that survives secondary dissociation. An independent determination of this fraction would be most valuable. Since the slow nascent vinoxy radicals are most likely formed in the  $\tilde{A}$  state, one might envision a fluorescence quantum yield measurement (since the vinoxy that survives probably does so by losing energy via emission of a photon). Such a measurement is outside of the scope of the present work; indeed, there is only one very recent study, by Su and Bersohn,<sup>20</sup> of vinoxy radicals from methyl vinyl ether photodissociation at 193 nm, and it focuses on the vibrational distribution of the ground-state vinoxy product. That work, which measures the nascent (and relaxed) vibrational distribution of vinoxy produced by photodissociation and by the reaction of O atoms with various alkenes, finds the nascent distributions become colder as the alkene size increases. As that work probes ground-state vinoxy product, however, it is sensitive to the vinoxy product formed in what we detect as a minor O-CH<sub>3</sub> photofragmentation channel, with the kinetic energy distribution peaking near 54 kcal/mol. (Comparing the rprob that fit the fast methyl signal to the rprob that fit the slow methyl signal in Fig. 3 suggests the branching to this minor  $O-CH_3$ fission channel is roughly 5%, while the  $P(E_T)$ 's used to fit the m/e = 42 data suggest that it is ~10%, but the relative vinoxy signals at m/e = 15 do not give a consistent branching.) Near the peak of the kinetic energy distribution there remains about  $10^4 \text{ cm}^{-1}$  of energy to be partitioned to methyl and vinoxy vibrational and rotational energy; Bersohn's work indicates that typically less than half of this is partitioned to vinoxy vibration.

## B. Analyzing the dominance of the $CH_3+CH_2CHO \tilde{A}(^2A')$ product channel to test propensity rules for product electronic accessibility

A marked result in this experiment was that the  $\pi\pi^*$  excitation of methyl vinyl ether at 193 nm resulted in primarily the CH<sub>3</sub>+CH<sub>2</sub>CHO ( $\tilde{A}^2A'$ ) product channel, with a very minor branching to the CH<sub>3</sub>+CH<sub>2</sub>CHO ( $\tilde{X}^2A''$ ) products. This observation afforded the opportunity to test our qualitative propensity rules for how electronically accessible possible product channels are and how this influences the branching between energetically allowed product channels. These propensity rules, developed in prior work by this group, <sup>15,16,35</sup> make the distinction between two types of reaction channels, "electronically facile" and "electronically difficult/prohibitive." Previous work has demonstrated that, at least for bond fission reactions, a reaction channel which requires only a one-electron (or a no-electron) change in the electronic configuration of the system as the reactant evolves to products should be characterized as electronically facile. Such reactions can be adequately predicted by the usual electronically adiabatic formulation of transition state theory or exact quantum reactive scattering. The second category of reaction channels are those that are electronically difficult/ prohibitive. Such reaction pathways require a two-electron change in electronic configuration to evolve to a particular product channel. If the two-electron change in configuration further involves orbitals on two spatially separated functional groups, we classify it as electronically prohibitive and then expect the reaction rate to be markedly suppressed, as was observed for the C-Br fission channel in the experiment on the  $n\pi^*$  photodissociation of bromopropionyl chloride.<sup>36</sup>

In order to test these electronic propensity rules for the O-CH<sub>3</sub> bond fission channel of methyl vinyl ether, we now qualitatively examine the changes in electronic configuration from the  $\pi\pi^*$  excitation required to access the  $CH_3+CH_2CHO(\tilde{X}^2A'')$  and the  $CH_3+CH_2CHO(\tilde{A}^2A')$ product channels. (Note that neither of these channels corresponds to the adiabatic product channel.) The analysis below shows that the reaction does indeed primarily give the product channel that is electronically facile, while the electronically prohibitive channel (involving a two-electron change on spatially distinct functional groups) is a minor contributor to the energetically allowed products of this reaction. In agreement with the assignment of the absorption spectrum by Planckaert et al.,<sup>23</sup> our CIS calculations show that the excitation of methyl vinyl ether at 193 nm involves a  $\pi^*$  $\leftarrow \pi$  excitation that is localized primarily on the C=C bond with some contribution of the out-of-plane nonbonding oxygen orbital. (The calculations also show a lower energy A''excited state with small oscillator strength.) Therefore, in  $C_s$ symmetry an electron photoexcited at 193 nm is promoted from an a'' orbital to another a'' orbital, giving a state symmetry of A'. (The expected torsion about the C=C bond upon  $\pi\pi^*$  excitation will allow the reaction to access both A' -and A'' product asymptotes.) To describe the energetically allowed vinoxy products, we use the results of Yamaguchi<sup>37</sup> and give the electronic configuration described by the active orbitals he chose for his calculations. The main electronic configuration of the ground-state vinoxy radical  $(\tilde{X}^2 A'')$  in  $C_s$  symmetry can be described as  $(1a'')^2(10a')^2(2a'')^1(3a'')^0$ , so the radical can be regarded as the formyloxy radical ( $\cdot$ CH<sub>2</sub>–CH=O). This theoretical assignment of the main electronic configuration for groundstate vinoxy which places the unpaired spin density primarily on the methylene carbon is supported by the experimental work of Endo et al.38 In planar geometry in the Franck-Condon region, the first excited state  $(\tilde{A}^2 A')$  of vinoxy has the dominant configuration  $(1a'')^2(10a')^1(2a'')^2(3a'')^0$ , and thus can be regarded as the vinyloxy radical  $(CH_2 = CHO \cdot)$ , where the unpaired electron is primarily localized in the in-plane oxygen orbital. The methyl radical orbital participating in the reaction is also a', since only ground-state methyl ( $\tilde{X}^2 A'$  with respect to the  $C_s$  symmetry plane) is energetically allowed in these experiments. The doubly occupied O-CH<sub>3</sub> sigma bonding orbital in groundstate methyl vinyl ether is the bonding linear combination of the 10a' vinoxy orbital and the a' methyl radical orbital. Thus, from the  $\pi\pi^*$  excited state of methyl vinyl ether, the reaction only requires a one-electron change  $(\pi \leftarrow \pi^*)$  to access the  $CH_3+CH_2CHO(\widetilde{A}^2A')$  products. The bond that is broken leaves one electron in the vinoxy in-plane (10a')oxygen orbital and one electron in the methyl a' orbital giving  $\tilde{A}$ -state vinoxy and ground-state methyl. Thus, in the application of the electronic propensity rules we would classify this channel as electronically facile. Formation of ground-state vinoxy, however, requires a two-electron change among spatially distinct functional groups along the reaction coordinate, so this channel is electronically prohibitive, and indeed we see that this channel is suppressed experimentally.

Analysis of the changes of electronic configuration required to access the CH<sub>3</sub>+CH<sub>2</sub>CHO( $\tilde{X}^2A''$ ) vs the CH<sub>3</sub>+CH<sub>2</sub>CHO( $\tilde{A}^2A'$ ) product channels correctly predicts that the dominant channel observed experimentally is the electronically facile one. Although this gives qualitative predictive ability, it remains to gain a detailed picture of the  $\pi\pi^*$  photodissociation dynamics. To this end, we plan to pursue calculations examining the potential energy surfaces as the C–O bond is stretched using the Hv method.<sup>39</sup>

*Note added in proof.* Recent experiments, in preparation for publication, by A. Miyoshi, J. Yashida, M. Koshi, and H. Matsui have measured the product branching in the  $O({}^{3}P) + C_{2}H_{4}$  reaction, obtaining a yeild of  $64\pm12\%$  of methyl radicals.

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