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Photodissociation dynamics of 1,1-difluoroethylene at 157 nm excitation

J. J. Lin, S. M. Wu, and D. W. Hwang

Department of Chemistry, National Taiwan University, Taipei, Taiwan, Republic of China

Y. T. Lee

Department of Chemistry, National Taiwan University and Institute of Atomic and Molecular Sciences, Academia Sinica, Taipei, Taiwan, Republic of China

X. Yang^{a)}

Institute of Atomic and Molecular Sciences, Academia Sinica, Taipei, Taiwan, Republic of China

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Photodissociation of 1,1-difluoroethylene (F_2CCH_2) at 157 nm has been investigated using photofragment translational spectroscopy. Five dissociation channels have been experimentally observed; molecular HF elimination, H atom elimination, molecular hydrogen (H₂) elimination, F atom elimination, and double bond breaking. Molecular HF elimination and H atom elimination channels are found to be the two major dissociation pathways in photodissociation of F_2CCH_2 at 157 nm excitation. Molecular hydrogen (H₂) elimination and double bond cleavage are also significant, while F atom elimination is a minor process. Product translational energy distributions for all dissociation channels have also been measured. All translational energy releases are peaked at energies away from zero, indicating that the dissociation of F_2CCH_2 at 157 nm excitation most likely occurs with exit barriers on the ground electronic potential surface through internal conversion from the initially excited electronic state. Branching ratios and averaged energy partitions for different channels have also been estimated. © *1998 American Institute of Physics*. [S0021-9606(98)00948-9]

I. INTRODUCTION

Photodissociation at very high energy excitation is interesting and also of fundamental importance in chemistry. Most molecules have extensive absorption at high energy excitation (8 eV), and yet photochemistry in this energy regime has been very rarely studied. This is largely due to the lack of strong photolysis light sources in the vacuum ultraviolet (VUV) region. Only until recently are strong VUV light sources becoming available.¹ Bond selectivity in photochemical processes at such high energy excitation is also an interesting topic in general. Bond selectivity in dissociation processes generally can result from two main sources: selectivity due to energetics or selectivity due to purely dynamics. Selectivity due to energetics means that the weaker the chemical bond, the easier it is to break. However, if it is purely due to dynamics,² the resulting selectivity will not be decided by thermodynamics. It is not immediately clear whether the photochemistry at extremely high energy electronic excitation, where every bond is breakable, is purely determined by energetics or by pure dynamics, especially in relatively large molecules. At about 8 eV excitation, where strong photolysis lasers (157 nm) are already available, almost every chemical bond existed in nature is already breakable. Many interesting questions can then be posed: At this excitation of energy, how are these chemical bonds broken? Are the bonds broken in a selective way, or are the dissociation pathways purely determined by energetics? Fluoroethylene molecules are good candidates for experimental studies of this topic. At about 8 eV excitation, most of the fluoroethylenes have significant absorption cross sections.^{3,4} This will allow us to look at photodissociation processes at high energy excitation in greater detail using the commercially available F_2 laser as the photolysis laser. Different fluorinated ethylenes actually have very interesting chemical properties. As the number of fluorine substitutions increases in ethylene, the double bond (C=C) actually becomes weaker. Figure 1 shows the double bond energies of the different fluorinated ethylene molecules.⁵ It is therefore noteworthy to look at the trends of the branching ratio of double bond breaking relative to the other dissociation channels at the VUV excitation in different fluorinated ethylenes.

Fluoroethylene molecules also serve as a good example in studying molecular elimination processes, especially in HF elimination processes. During the last decades, many experimental studies on the photodissociation of fluorinated ethylenes have been conducted. Various methods were employed to excite the precursor molecules to energies at which molecular fragmentation can take place. Photodissociation by excitation to a higher electronic state, through absorption of pulsed ultraviolet (UV) light from a flash lamp or laser, were frequently used. Photofragmentation following UV excitation is now believed to proceed largely from a highly excited ground electronic state, formed by internal conversion or intersystem crossing from the initially excited electronic state. The infrared multiphoton dissociation technique was also applied to study the molecular dissociation of fluoroethylenes. In many of these experiments, the molecular

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^{a)}Author to whom correspondence should be addressed; electronic mail: xmyang@po.iams.sinica.edu.tw



FIG. 1. Graph shows the C=C double bond energies of the fluorinated ethylenes. The double bond energy decreases as the number of the substituted fluorine atoms increases.

hydrogen halide elimination channel was carefully studied by observing infrared emission from specific rovibrational levels. The results of these investigations carried out before 1980 can be found in several review articles,⁶⁻⁸ and references therein. More recently, Setser, Arunan, and Wategaonkar⁹ studied several three-center and four-center HF and HCl eliminations from molecules formed by the reaction of H atoms with radicals by detecting the steady-state infrared (IR) emission from HF or HCl, respectively. Similar experiments on vinyl fluoride were performed by Donaldson *et al.*^{10,11} Leone and co-workers^{12,13} have used novel timeresolved Fourier transform infrared (FTIR) spectroscopy to investigate the dissociation of vinylfluoride, trans-1,2dichloroethylene and 1,1-chlorofluoroethylene. Gordon and co-workers^{14–16} also investigated dichloroethylene isomers and vinyl chloride using time-of-flight resonance-enhanced multiphoton ionization, to detect the photofragment products. Recently, Hall and co-workers studied the photodissociation dynamics of 1,1-difluoroethylene at 193 nm excitation using time-resolved FTIR emission.¹⁷ Photofragment translational spectroscopy was employed to study vinyl chloride, trans- and cis-dichoroethylene, and 1,1-dichloroethylene at 193 nm excitation.¹⁸ The photodissociation dynamics of vinyl fluoride at 157 nm was studied recently using photofragment translational spectroscopy.¹⁹ Only the HF elimination channel was clearly identified. Photodissociation of 1,1- and 1,2-difluoroethylene at 193 nm was also studied very recently.²⁰ Experimental results show that the translational energy distributions of the HF elimination channel for the 1,1- and 1,2-difluoroethylene are significantly different, indicating very different dynamics for the two molecules. H₂ and H elimination channels were also observed for both molecules. The translational energy distribution of H₂ elimination displays a significant exit barrier in the dissociation process, similar to that of ethylene photodissociation.

The experiments described in this article aim to understand the photodissociation dynamics of 1,1-difluoroethylene at 157 nm. At 157 nm excitation, 1,1-difluoroethylene involves mostly Rydberg excitation. Figure 2 shows the energy diagram of possible dissociation channels of 1,1-difluoro-



FIG. 2. Energy diagram of possible photodissociation pathways from 1,1diffuoroethylene at 157 nm excitation.

ethylene.⁴ Five possible binary dissociation channels are listed in the energy diagram—three simple bond rupture channels and two molecular elimination channels:

$$F_{2}C = CH_{2} + h\nu(157 \text{ nm}) \rightarrow F_{2}C: +:CH_{2}$$
$$\rightarrow FC = CH_{2} + F$$
$$\rightarrow F_{2}C = CH + H$$
$$\rightarrow F_{2}C = C: +H_{2}$$
$$\rightarrow FC = CH + HF.$$

Triple dissociations are only energetically possible after HF elimination from 1,1-difluoroethylene at 157 nm excitation. From the energy diagram, the available energies for the triple dissociation channels are very small. Therefore it would be difficult to detect them experimentally. In this work, photodissociation products are measured by photofragment translational spectroscopy. Product translational energy distributions are mapped out from time-of-flight spectra of photodissociation products. Relative contributions of different channels are also estimated, giving us a valuable set of data for comparisons with other fluoroethylene molecules.

II. EXPERIMENT

The instrument used in the experimental investigation of 1.1-difluoroethylene photodissociation at 157 nm is a newly built crossed molecular beam apparatus. A detailed description of the new machine can be found in Ref. 21. Briefly, the new apparatus consists of three parts: a main chamber, a source chamber, and a rotatable detector. The source chamber generates molecular beams for studies of crossed molecular beam reactions or molecular photodissociations. The apparatus can be set up in two different running modes for photodissociation studies: heavy fragment detection and light fragment detection (mainly H and H₂). For heavy fragment detection, the main chamber is where the laser beam and the molecular beam interact with each other for photodissociation experiments. While for light atom detection (H and H_2), laser and molecular beams interact with each other in the source chamber with the molecular beam perpendicular to the detection axis. The interaction region is about 8 mm away from the nozzle. Such close distance is used is to compensate for low detection efficiency in the detector of the lighter fragments (H and H_2) because of the shorter residence time in the ionizer. The photodissociation products are detected using a differentially pumped universal detector. A neat sample is used in this detection scheme. For heavy fragment detection, the laser, the molecular beam, and the detection axes are in the same plane. Normally, a molecular beam seeded in Ar is used. The F_2CCH_2 sample in the molecular beam are then intercepted by an unpolarized 157 nm laser beam, which is generated by a Lambda Physik LPX210I laser with a NOVA tube laser cavity. About 1-3 mJ of 157 nm laser light was normally used during the experiment to avoid multiphoton effects. The laser pulse duration is about 15 ns. The laser beam is focused to a 5 mm (width) \times 2 mm (height) spot size in the interaction region using a MgF₂ lens with a focal length of 100 cm. Since black deposits on the focus lens, which reduce laser power to the interaction region, can be easily formed by the 157 nm high power laser beam, a differentially pumped laser beam path is used so that this problem can be avoided. The whole laser beam path is in a vacuum tube with a vacuum of about 1×10^{-7} Torr or better. The focusing lens can then be easily cleaned without changing the laser beam path and without venting the main chamber of the apparatus. Photodissociation products recoiled from the interaction region are detected by an electron impact ionization detector. The electron impact ionizer is located in the detection region where ultrahigh vacuum (10^{-12} Torr) is maintained. The ions are then extracted from the ionizer and guided into a quadrupole mass filter (Extrel) and counted by a Daly-type detector. A multichannel scaler (Turbo MCS by EG&G) is then used to record the product time of flight spectra at different angles between the molecular beam and the detector axis.

The F_2CCH_2 sample was purchased from PCR, Co. The sample is used without further purification. For heavy fragment detection, the F_2CCH_2 molecular beam is generated by expanding a 5% premixture of F_2CCH_2 in Ar through a commercially available pulsed nozzle (General Valve Co.). The nozzle is maintained at 120 °C during the experiment in order to avoid possible clustering in the molecular beam.

Since the product time-of-flight (TOF) spectra from photodissociation of F₂CCH₂ are measured in laboratory frame, in order to obtain the center-of-mass (CM) translational energy distribution P(E), a laboratory-to-center of mass conversion is required. This conversion is done using an already available program CMLAB2 running on a Pentium PC. The analysis program uses an iterative forward convolution method which is described elsewhere.²² In this program, a trial P(E) and CM angular distribution (β parameter) is used to calculate the TOF spectrum for a photofragment mass at a given molecular beam-detector angle using the known apparatus parameters and the measured beam velocity distribution. The calculated TOF is compared with the experimental TOF spectrum and the P(E) was then improved by adjusting the distribution point by point on the computer screen until satisfactory fits are achieved for TOF spectra measured at different angles. In the experimental set up for heavy fragment detection, the laser beam, the molecular beam, and the detection direction are in the same plane, as pointed out above. In this configuration, the photofragment anisotropy (β



FIG. 3. TOF spectrum at m/e=1, $\Theta=90^{\circ}$ from photodissociation of 1,1difluoroethylene. This spectrum was taken by accumulating signals over 100 k laser shots using the light mass detection scheme. The open circles are the experimental data points, while the solid line is the fit to this spectrum using the translational energy distribution shown in Fig. 5 (curve 1).

parameter) will couple to the angular distribution of products even if an *unpolarized* laser beam is used as the photolysis source. In this experiment, however, the anisotropy is not considered.

III. RESULTS

TOF spectra of photofragments from the F_2CCH_2 photodissociation at 157 nm were measured using the mass filtered photofragment translational spectrometric detector, as described above. Signals at m/e = 63, 62, 50, 45, 44, 43, 31, 25, 24, 20, 19, 14, 13, 12, 2, 1 were detected from photodissociation of F_2CCH_2 . After detailed analyses of the experimental data, all five dissociation channels listed in the energy diagram (Fig. 2) were observed. No experimental evidence for triple dissociations is found for 1,1-difluoroethylene at 157 nm excitation. Multiphoton effects have been checked carefully during the experiment. All results shown here should have little multiphoton effect. In the next few paragraphs, the experimental data and detailed analyses will be described.

A. Atomic hydrogen elimination: $F_2CCH_2 + h\nu \rightarrow F_2CCH + H$

H atom elimination from the 1,1-difluoroethylene at 157 nm excitation has been experimentally observed. The TOF spectrum of the H atom (m/e=1) product was measured at the perpendicular direction of the molecular beam using the light mass detection scheme described above. Figure 3 shows the TOF spectrum of the H atom product from the photolysis of F₂CCH at 157 nm. The heavy fragmentation partner of the H atom elimination channel is the F_2CCH radical (*m/e*) =63), which would also go through dissociative ionization to form daughter ions in the electron bombardment ionizer, for example, F_2CC^+ , CF_2^+ , CF^+ , etc. Figure 4 shows the TOF spectra at mass 63 (F₂CCH⁺) at two different laboratory angles. Since TOF spectra of H and F₂CCH fragments are from the same dissociation channel, total linear momentum should be conserved in this process. Figure 5 shows the translational energy distributions used to model the TOF spectra at m/e = 1 (H, curve 1) and m/e = 63 (F₂CCH, curve



FIG. 4. TOF spectra at m/e=63, $\Theta=7.5^{\circ}$ (upper trace) and 20° (lower trace). The spectrum at 7.5° was taken by accumulating signals over 100 k laser shots and the spectrum at 20° over 25 k laser shots. The open circles are the experimental data points, while the solid lines are the fits to the spectra using the translational energy distribution shown in Fig. 5 (curve 2).

2) using the CMLAB2 program. The two translational energy distributions actually show a significant difference in the lower energy part of the distribution, which should be exactly the same due to total linear momentum conservation. It seems that some of the lower energy part of the translational energy distribution derived from the m/e = 63 data is missing. The lower translational energy part of the m/e = 63 data represents the F₂CCH product radicals with lower translational



FIG. 5. Translational energy distributions used to fit the TOF spectra of the dissociation products from the H atom elimination channel. The distribution shown in curve 1 here is used to fit the H atom product TOF spectrum, which should be the complete translational distribution of the H atom elimination process. The distribution of curve 2 is used to fit the m/e=63 (F₂CCH radical) TOF spectrum, representing the *cold* F₂CCH radical fragments which survive in the electron impact ionizer. The distribution of curve 3 is the subtraction of curve 2 from curve 1, representing the *hot* F₂CCH radical fragments that do not survive in the electron impact ionizer.



FIG. 6. TOF spectrum at m/e=2, $\Theta=90^{\circ}$ from photodissociation of 1,1difluoroethylene. This spectrum was taken by accumulating signals over 100 k laser shots using the light mass detection scheme. The open circles are the experimental data points, while the solid line is the fit to this spectrum using the translational energy distribution shown in Fig. 7.

tional energy, and subsequently higher internal excitation (internally hot). The internally hot F₂CCH radicals might go through complete dissociative ionization much more easily than the internally cold ones, which could make the dissociative ionization patterns of the hot and cold radicals significantly different. In the H atom elimination channel, the internally hot F_2CCH (m/e = 63) might not survive at all in the electron bombardment ionizer. Therefore, the slower part of the TOF spectrum at m/e = 63 is missing. Curve 3 in Fig. 5 represents the translational energy distribution of the F₂CCH radical products which are internally hot and go through dissociation ionization in the ionizer. Hence in the fitting of the daughter ion masses from the dissociation ionization of the F₂CCH product radicals, the translational energy distributions for both the *cold* and *hot* radicals were used. This approach works well in fitting the TOF spectra of all daughter ion masses cracked from the F2CCH radical product due to the H atom elimination channel. This indirectly supports the *cold* and *hot* radical assumption.

In Fig. 5, the translational energy distribution of the H atom elimination channel (curve 1) is peaked at \sim 5 kcal/mol, indicating that a small barrier exists in the dissociation process. This result implies that H atom elimination most likely occurs through the ground potential energy surface.

B. Molecular hydrogen elimination: $F_2CCH_2 + h\nu \rightarrow F_2CC:+H_2$

The molecular hydrogen elimination channel from the F_2CCH_2 molecule at 157 nm excitation was also observed experimentally. TOF spectra at m/e=2 and 62 show the existence of the molecular hydrogen elimination channel. Figure 6 shows the TOF spectrum of the H₂ product from the photolysis of the F_2CCH_2 molecule using the light mass detection configuration. The translational energy distribution used to model the TOF spectrum of H₂ is shown in Fig. 7. The heavy fragment of the H₂ elimination channel should be the difluorovinylidene radical ($F_2CC:$, m/e=62). The TOF spectrum at m/e=62 ($F_2C_2^+$) (Fig. 8) shows the contribution

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FIG. 7. Translational energy distribution for the H_2 elimination channel from photodissociation of 1,1-difluoroethylene at 157 nm.

of the H₂ elimination channel calculated using the translational energy distribution in Fig. 7. In addition, the contribution to the TOF at m/e = 62 from the dissociative ionization of the F₂CCH radical in the ionizer is also clear. The two curves to fit the H atom elimination channels representing the *hot* F₂CCH fragment and the *cold* F₂CCH fragment are shown in Fig. 8. The translational energy shown in Fig. 7 is a peaked distribution with its peak at about 15 kcal/mol, indicating that the H₂ elimination channel has an exit barrier in the dissociation process. This result implies that the H₂ elimination process likely occurs on the ground electronic



FIG. 8. TOF spectra at m/e = 62, $\Theta = 7.5^{\circ}$ (upper trace) and $\Theta = 15^{\circ}$ (lower trace). The spectrum at 7.5° was taken by accumulating signals over 500 k laser shots and the spectrum at 15° over 500 k laser shots. The open circles are the experimental data points, while the solid lines are the fits to the spectra using the translational energy distribution shown in Fig. 7. Curve 1 is the contribution of the H₂ elimination channel, while curves 2 and 3 are the contributions from the so-called *cold* and *hot* F₂CCH fragments from the H elimination channel. Curve 4 is the overall fit to the spectrum.



FIG. 9. TOF spectrum at m/e=50, $\Theta=15^{\circ}$ from photodissociation of F₂CCH₂ at 157 nm. The spectrum was taken by accumulating signals over 100 k laser shots. The open circles are the experimental data points, while the solid lines are the fits to the spectra using the CMLAB2 program. Curve 1 is the contribution attributed to the double bond cleavage process using the translational energy distribution shown in Fig. 11, while curve 2 is the contribution from the H atom elimination channel in which the cold F₂CCH fragments dissociatively ionizes to F₂C⁺ in the electron impact ionizer. Curve 3 is the overall fit the spectrum combining the above two contributions.

state through internal conversion from the initially excited electronic state, similar to the H atom elimination process.

The H₂ elimination from the F₂CCH₂ molecule is a three-center elimination process. The reverse barrier height for a three-center H₂ elimination from ethylene on the ground electronic surface is calculated to be about 12 kcal/mol.²³ The result here is somewhat consistent with the three-center elimination process, which implies that when H₂ leaves the F₂CCH₂ molecule the C₂F₂ radical should be still in the vinylidene structure.

C. C=C double bond cleavage: $F_2CCH_2 + h\nu \rightarrow F_2C:+CH_2$

The C=C double bond fission from the excited F_2CCH_2 molecule at 157 nm excitation was also observed. The TOF spectra of the two fragments: mass 50 and mass 14 are



FIG. 10. TOF at m/e = 14 (CH₂), $\Theta = 20^{\circ}$ from the photodissociation of F₂CCH₂ at 157 nm. The spectrum was taken by accumulating signals over 750 k laser shots. The open circles are the experimental data points, while the solid line is the fit to the TOF spectrum from the translational energy distribution shown in Fig. 11 using the CMLAB2 program.



FIG. 11. Translational energy distribution for the double bond cleavage channel of 1,1-difluoroethylene at 157 nm.

shown in Figs. 9 and 10. The feature in the TOF spectrum of mass 14 (:CH₂) is assigned to the double bond cleavage channel, the translational energy distribution (Fig. 11) derived from the TOF spectrum of mass 14 should be the kinetic energy distribution for the C=C bond breaking process. Using this translational energy distribution, the fast peak shown in the TOF spectrum of mass 50 (F₂C:⁺) can be momentum matched as the fragment partner of the CH₂ fragment using the CMLAB2 program, indicating that the fast peak in the TOF spectrum at mass 50 is indeed from the F₂C: fragment of the double bond cleavage process. The slower peak in the TOF spectrum of m/e = 50 is due to the disso-



FIG. 12. TOF spectra at m/e=45 (FCCH₂⁺), $\Theta=20^{\circ}$ (upper trace) and $\Theta=30^{\circ}$ (lower trace). The spectrum was taken by accumulating signals over 100 k laser shots. The open circles are the experimental data points, while the solid lines are the fits to the spectra using the translational energy distribution, shown in Fig. 13, for the F atom elimination channel.





FIG. 13. Translational energy distribution used to fit the TOF spectra at m/e = 45 for F atom elimination from 1,1-difluoroethylene at 157 nm.

ciative ionization of the F_2CCH fragment in the ionizer from the hydrogen elimination channel. The translational energy distribution (Fig. 11) obtained for the double bond cleavage also peaks at about 10 kcal/mol. This result indicates that the double bond cleavage processes in the F_2CCH_2 photodissociation of 157 nm has an exit barrier, implying that the dissociation of the C=C bond breaking may not be an event occurring on the initially excited electronic state. It likely occurs on the ground electronic potential energy surface.

D. F atom elimination: $F_2CCH_2 + h\nu \rightarrow FCCH_2 + F$

The C—F bond rupture channel was also observed from the photolysis of F_2CCH_2 at 157 nm. The TOF spectra at m/e=45, $\Theta=20^\circ$, 30° (FCCH₂ radical) are shown in Fig. 12. The feature shown in these spectra is assigned to the F atom elimination process. The translational energy distribution derived from the TOF spectra at m/e=45 is shown in Fig. 13. Because of the dissociative ionization in the ionizer, the TOF spectrum at m/e=19 (F⁺) is very complicated



FIG. 14. TOF spectrum at m/e = 19 (F⁺), $\Theta = 20^{\circ}$. The spectrum was taken by accumulating signals over 50 k laser shots. The open circles are the experimental data points, while the solid lines are the modeled fits to the spectrum using CMLAB2 program. Curve 1 is the contribution from the primary HF product (HF elimination) cracking to F⁺ in the ionizer, curve 2 is from the primary F product F atom elimination), curve 3 is from the primary FCCH product (HF elimination) cracking to F⁺, curve 4 is resulted from the primary CF₂ product cracking to F⁺, curve 5 is due to the primary F₂CC: product cracking to F⁺, and curve 6 is the overall fit.



FIG. 15. TOF spectrum at m/e = 20 (HF⁺), $\Theta = 20^{\circ}$. The open circles represent the experimental data points, while the solid line is the fit to the spectrum using the translational energy distribution shown in Fig. 16.

since other primary photodissociation products which contain F atom would also eventually contribute to the TOF spectrum at m/e = 19 (F⁺) (see Fig. 14). The fitting to the TOF spectrum in Fig. 14 shows that there is some contribution from the F atom elimination channel, or at least some feature in the spectrum is consistent with the F atom elimination channel. The contribution from the F atom elimination channel is calculated using the translational distribution derived from the TOF spectrum at m/e = 45 (FCCH₂ fragment). Other channels also exist in the TOF spectrum at m/e = 19. The TOF spectrum in Fig. 14 is modeled using a total of five different contributions (see Fig. 14 caption) including F atom elimination. The fitting to the TOF spectrum of mass 19 only serves the purpose to show that it is possible to model this complicated TOF spectrum using the known existing channels, including the HF elimination channel which will be described in the next paragraph. The translational energy distribution for the F atom elimination derived from the TOF spectra at mass 45, shown in Fig. 13, is also very similar to those of other dissociation channels. The distribution is peaked at approximately 13 kcal/mol, indicating a possible dissociation mechanism from the ground potential energy surface.



FIG. 16. Translational energy distribution for the HF atom elimination channel from photodissociation of 1,1-difluoroethylene at 157 nm excitation.



FIG. 17. TOF spectrum at m/e = 44 (HCCF⁺), $\Theta = 15^{\circ}$. The spectrum was taken by accumulating signals over 500 k laser shorts. The open circles represent the experimental data points, while the solid lines are the modeled fits to the spectrum. Curve 1 is the contribution from the FCCH product (HF elimination) calculated using the translational energy distribution shown in Fig. 16. Curve 2 is from the F₂CCH product (H atom elimination) cracking to the FCCH⁺ ion in the ionizer. Curve 3 is the overall fit to the spectrum.

E. Molecular HF elimination: $F_2CCH_2 + h\nu \rightarrow FCCH + HF$

Molecular HF elimination was also detected from the photolysis of 1,1-difluoroethylene at 157 nm. Most of the previous studies on photodissociation of fluorinated ethylenes involve detection of HF products using the IR emission technique. Nascent vibration state distributions of HF have been mapped out using this method. In this study, the TOF spectra of the photodissociation products (FCCH and HF) were measured. Figure 15 shows the TOF spectrum at m/e=20 (HF⁺), Θ =30°. The feature shown in this spectrum is attributed to the HF elimination channel. The translational energy distribution (see Fig. 16) for the HF elimination can then be derived from the TOF spectrum in Fig. 15. Figure 17 shows the TOF spectrum at m/e = 44, $\Theta = 15^{\circ}$. The fast peak shown in the spectrum can clearly be modeled as the momentum-matched partner to the HF fragment, indicating that the fast peak in Fig. 17 is from the FCCH photofragment, while the slower peak is mainly due to the dissociative



FIG. 18. TOF spectrum at m/e = 43 (CCF⁺), $\Theta = 15^{\circ}$. The spectrum was taken by accumulating signals over 250 k laser shorts. The open circles are the experimental data points, while the solid lines are the fits to the spectrum. Curve 1 is the contribution from the primary FCCH (mass 44) product (HF elimination) cracking to FCC⁺ in the ionizer, curve 2 is resulted from the F₂CC product (H₂ elimination) cracking to FCC⁺, curve 3 is from the F₂CCH product H atom elimination), and curve 4 is the overall fit.



FIG. 19. TOF spectrum at m/e=31 (CF⁺), $\Theta=25^{\circ}$. The spectrum was taken by accumulating signals over 100 k laser shorts. The open circles represent the experimental data points, while the solid lines are the fits to the spectrum. Curve 1 is the contribution from the primary FCCH product (HF elimination) cracking to CF⁺ in the ionizer, curve 2 is resulted from the CF₂ product (double bond rupture) dissociatively ionizing to CF⁺, curve 3 is from the F₂CCH product (H atom elimination), and curve 4 is the overall fit.

ionization of the F_2CCH product from the H atom elimination channel. TOF spectra at mass 43 (Fig. 18) and mass 31 (Fig. 19) were also measured. The different features in these spectra can all be attributed to dissociative ionization in the electron impact ionizer from different primary dissociation channels (see figure captions in Figs. 18 and 19). The translational energy release for the HF elimination channel also has a peaked distribution, similar to those of other dissociative channels. The peak of the translational energy distribution is at about 20 kcal/mol. Therefore it is clear that all dissociation processes of 1,1-difluoroethylene at 157 nm excitation likely occur through the ground state potential, not through direct dissociation on the initially excited electronic state potential.

IV. DISCUSSION

A. Branching ratio

Branching ratios for photodissociation processes can give us very important information on the dynamics of photodissociation in general. In this work, TOF spectra for all primary product masses and cracking masses from the photodissociation of 1,1-difluoroethylene were carefully measured. Laser power for each TOF spectrum was also rather well controlled and measured. By accumulating the contributions of the different fragment ions to each channel, the branching ratios of each individual channel were estimated. The estimated branching ratios are listed in Table I. During

TABLE I. Branching ratios for different dissociation channels of 1,1-diffuoroethylene at 157 nm excitation.

| Dissociation channel | Branching ratio(%) | | |
|--|--------------------|--|--|
| $F_2C = CH_2 + h\nu \rightarrow F_2C: +:CH_2$ | 10 | | |
| $F_2C = CH_2 + h\nu \rightarrow FC = CH_2 + F$ | 2 | | |
| $F_2C = CH_2 + h\nu \rightarrow F_2C = CH + H$ | 25 | | |
| $F_2C = CH_2 + h\nu \rightarrow F_2C = C:+H_2$ | 11 | | |
| $F_2C = CH_2 + h\nu \rightarrow FC = CH + HF$ | 52 | | |

TABLE II. Energy partition of different dissociation channels of 1,1difluoroethylene at 157 nm excitation^a

| Dissociation channel (157 nm excitation) | Total available energy E_{tot} | Averaged E_{trans} | Averaged E_{int} | $E_{\rm tran}$ / $E_{\rm int}$ ratio |
|--|----------------------------------|-----------------------------|--------------------|--|
| $\begin{array}{l} F_2C=\!$ | 44.1 | 11.0 | 33.1 | 25/75 |
| | 55.9 | 19.6 | 36.3 | 35/65 |
| | 65.1 | 16.7 | 48.4 | 26/74 |
| | 66.0 | 18.5 | 47.5 | 28/72 |
| | 136.3 | 25.4 | 110.9 | 19/81 |

^aThe averaged translational energies (E_{trans}) are experimentally measured values, while the averaged internal energy is calculated by subtracting the E_{trans} from the total available energy ($E_{\text{int}} = E_{\text{tot}} - E_{\text{trans}}$). All energies are in kcal/mol.

the estimation, the detection efficiencies of different observed ions are assumed to be the same. There are also other sources of errors in the fittings of some TOF spectra since the correlations between the contributions from different channels are rather significant. The anisotropy of the dissociation processes will also likely increase the errors in calculating the branching ratios. In this experiment, however, this effect is considered to be small since all dissociation processes most likely occur from the ground potential energy surface through internal conversion, which will wash out most of the anisotropy in the dissociation processes. Due to the above sources of error in estimation, the branching ratios obtained here should be regarded as estimated values rather than accurate measurement results. Nevertheless, these estimated branching ratios should provide a good base for a rough picture of the important dissociation channels. From Table I, it is clear that the major dissociation channels are the H atom elimination and the HF elimination channels. The H_2 elimination and the double bond breaking channels are also rather significant. The contribution from the F atom elimination channels is, however, minor.

B. Energy partition

From the translational energy distributions of all different channels, all averaged translational energy releases can be determined. Assuming p(E) is the translational energy distribution of a dissociation process, the averaged energy E_{ave} can be calculated using the following formula:

$$E_{\text{ave}} = \frac{\int Ep(E)dE}{\int p(E)dE}$$

Table II shows the averaged kinetic and internal energy release, and their ratios. From Table II, it is clear that the product internal energy partition in photodissociation of 1,1difluoroethylene at 157 nm excitation are always significantly larger than the translational energy release, with the internal energy release ranging from 19% to 35% of the total available energy.

V. CONCLUSION

Photodissociation dynamics of 1,1-difluoroethylene at 157 nm excitation have been studied using photofragment translational spectroscopy. Five dissociation channels have

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been experimentally observed. The main photodissociation pathways are the HF elimination process and the H atom elimination process. The H₂ elimination and the double bond breaking channels are also significant, while F atom elimination is a minor process in the photodissociation. The kinetic energy releases for the five dissociation channels observed in this work all show distributions peaked at energies higher than zero, indicating that the photodissociation processes for the difluoroethylene are not direct dissociation processes from the initially excited electronic state. The excited 1,1difluoroethylene molecules most likely go through some type of internal conversion from the initially excited electronic state to the ground electronic potential energy surface, then dissociate into different dissociation products. Experimental results show that all dissociation channels experience some exit barriers. Looking at the averaged kinetic energy releases for different dissociation channels, it is clear that the internal energy partitions are all significantly larger than the translational energy partitions.

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