JOURNAL OF CHEMICAL PHYSICS VOLUME 114, NUMBER 8 22 FEBRUARY 2001

Chemical dynamics of d1-methyldiacetylene (CH_3CCCCD; $X\ ^1A_1$) and d1-ethynylallene ($H_2CCCH(C_2D)$; $X\ ^1A'$) formation from reaction of $C_2D(X\ ^2\Sigma^+)$ with methylacetylene, $CH_3CCH(X\ ^1A_1)$

R. I. Kaiser,[a] C. C. Chiong, O. Asvany, and Y. T. Lee
Institute of Atomic and Molecular Sciences, 1, Section 4, Roosevelt Road, 107 Taipei, Taiwan, Republic of China

F. Stahl[b] and P. von R. Schleyer[b),c)]
Institut für Organische Chemie der Universität Erlangen-Nürnberg, Henkestrasse 42, 91054 Erlangen, Germany

H. F. Schaefer III
Center for Computational Quantum Chemistry, The University of Georgia, Athens, Georgia 30602

(Received 28 July 2000; accepted 13 October 2000)

The crossed beam reaction of the d1-ethynyl radical $C_2D(X\ ^2\Sigma^+)$, with methylacetylene, $CH_3CCH(X\ ^1A_1)$, was investigated at an average collision energy of 39.8 $kJ\,mol^{-1}$. Our experimental results were combined with electronic structure calculations. The chemical reaction dynamics are indirect, involve three distinct channels, and are initiated via a barrierless addition of C_2D to the acetylenic bond through long lived *cis* and *trans* $CH_3CCH(C_2D)$, 1-ethynylpropen-2-yl, intermediates. The reduced cone of acceptance of the carbon atom holding the methyl group favors a carbon–carbon σ bond formation at the carbon atom adjacent to the acetylenic hydrogen atom. A crossed beam experiment of C_2D with partially deuterated methylacetylene, CD_3CCH, shows explicitly that the reactive intermediates decompose to form both methyldiacetylene, CD_3CCCCD (channel 1, 70%–90%), and to a minor amount ethynylallene, $D_2CCCH(C_2D)$ (channel 2; 10%–30%), isomers through exit transition states located 7–15 $kJ\,mol^{-1}$ above the products. The computed reaction energies to form both isomers are -135 and -107 $kJ\,mol^{-1}$, respectively, with respect to the separated reactants. A minor reaction pathway involves a H shift in $CH_3CCH(C_2D)$ to an 1-ethynylpropen-1-yl radical which fragments to methyldiacetylene via a barrier of 8.8 $kJ\,mol^{-1}$ (channel 3). Neither methyl group elimination nor the formation of the $CC(CH_3)(C_2D)$ carbene was observed in our experiments. The experimentally observed ''sideways scattering'' and *ab initio* investigation verify our conclusions of a predominate formation of the methyldiacetylene isomer. These electronic structure calculations depict a hydrogen atom loss in the exit transition state to methyldiacetylene almost parallel to the total angular momentum vector **J** as found in our center-of-mass angular distribution. Since the title reaction and the corresponding reaction of the C_2H radical with CH_3CCH both have no entrance barriers, are exothermic, and all the involved transition states are located well below the energy of the separated reactants, the assignment of the ethynyl versus H atom exchange suggests the formation of both isomers under single collision conditions in extraterrestrial environments such as cold, molecular clouds as well as the atmosphere of Saturn's moon Titan. [DOI: 10.1063/1.1330233]

I. INTRODUCTION

The intimate chemical reaction dynamics of ground state ethynyl radicals, $C_2H\,(X\ ^2\Sigma^+)$, are of paramount significance in numerous extraterrestrial environments and combustion flames. After its first detection in 1974,[1] it became clear that C_2H is ubiquitous in the interstellar medium and might be the key radical involved in the formation of the polyynes $CH_3C\equiv C-C\equiv C-H$ and $H(C\equiv C)_n$ $(n=2-4)$ as detected in cold molecular clouds TMC-1 and OMC-1 and circumstellar envelopes around carbon-rich asymptotic giant branch (AGB) stars such as the red giant star IRC+10216. Further, diacetylene, $HC\equiv C-C\equiv CH$, has been observed in the atmosphere of Saturn's moon Titan.[2] Whereas the main source of the interstellar and planetary ethynyl radicals has been unambiguously identified as a photolyses of acetylene, C_2H_2,[2] and to a minor amount of diacetylene, HCCCCH, the mechanisms to synthesize the observed polyacetylenes are far less clear. Based on chemical intuition astrochemists speculate that ethynyl radicals react with (substituted) alkynes via a hydrogen replacement forming the dialkyne product

$$C_2H+H(C\equiv C)_nH\rightarrow H(C\equiv C)_{n+1}H+H, \quad (1)$$

---

[a] Also at: Department of Physics, National Taiwan University, 1, Section 4, Roosevelt Rd., 107 Taipei, Taiwan, ROC, and Department of Physics, TU Chemnitz, Chemnitz, Germany. Present address: Department of Chemistry, University of York, UK; electronic mail: rik1@york.ac.uk

[b] Also at: Center for Computational Quantum Chemistry, The University of Georgia, Athens, GA 30602.

[c] Electronic mail: schleyer@uga.edu

$$C_2H+CH_3(C{\equiv}C)_nH \rightarrow CH_3(C{\equiv}C)_{n+1}H+H. \qquad (2)$$

Recent low temperature laboratory experiments at temperatures as low as 15 K show indeed that $C_2H\,(X\,^2\Sigma^+)$ can react with unsaturated hydrocarbons. Chasting *et al.* measured reaction rate constants of ethynyl radicals with acetylene and ethylene which increase as the temperature decreases reaching about $2.2-2.3\times10^{-10}\,cm^3\,s^{-1}$ at 15 K.[3] These experiments indicate a high reactivity of these systems even in very cold molecular clouds within the order of gas kinetics at ultralow temperatures. At elevated temperatures as high as 854 K, the rate constants are slightly smaller between 0.78 and $1.6\times10^{-10}\,cm^3\,s^{-1}$.[4] Recently, Leone *et al.* published experimental rate constants on C_2H reactions with C_3H_4 isomers methylacetylene and allene in the temperature range of 155–298 K to $1.6\times10^{-10}\exp(71/T)\,cm^3\,s^{-1}$ and $1.3\times10^{-10}\exp(103/T)\,cm^3\,s^{-1}$;[5] their data confirm the slight negative temperature dependence as reported in the low temperature measurements.

However, these kinetic experiments can monitor only the decay kinetics of the photolytically generated C_2H radical, and hence reaction products could not be investigated. These products and especially the assignment of the isomers are of paramount importance to a detailed understanding of the formation of polyynes in extraterrestrial environments. This limitation clearly reveals that systematic experiments are necessary to probe the detailed chemical dynamics and reaction product(s) of the title reaction under single collision conditions as employed in crossed molecular beam experiments. Whereas to our best knowledge, no crossed beam reaction has been performed employing supersonic beams of ethynyl radicals, isoelectronic cyano radicals, $CN(X\,^2\Sigma^+)$, were crossed very recently with beams of unsaturated hydrocarbons acetylene,[6] ethylene, methylacetylene, allene, dimethylacetylene, and benzene. All these experiments documented the existence of a CN vs H atom exchange channel via addition of the cyano radical to the π system to form unsaturated nitriles.

The present paper is the first in a series of systematic and detailed investigations on the chemical reaction dynamics of deuterated ethynyl radical, $C_2D(X\,^2\Sigma^+)$, reactions with unsaturated hydrocarbons, here methylacetylene, CH_3CCH. Our studies are supplemented by electronic structure calculations. The paper is structured as follows: Sections II and III describe the experimental setup, data processing, and the electronic structure calculations. The results (Sec. IV) focus on the laboratory angular distributions, time-of-flight data, and the derived center-of-mass functions together with the flux contour map. Section V discusses the involved potential energy surface (PES) as obtained from our theoretical investigations and compares the experimental findings with the theoretical results. Crossed beam experiments of the related $CN+CH_3CCH$ system are discussed as well.

II. EXPERIMENT AND DATA PROCESSING

All experiments are performed under single collision conditions employing the 35″ crossed molecular beam machine.[7] Briefly, a pulsed supersonic ethynyl radical beam, $C_2D(X\,^2\Sigma^+)$, is generated in the primary source *in situ* via laser ablation of graphite at 266 nm.[8,9] Neat deuterium is used as a carrier and reactant gas and released by a Proch–Trickl pulsed valve which is driven at −600 V with 60 Hz, 80 μs pulses, and 5 atm backing pressure.[10] The Spectra Physics GCR 270-30 Nd-YAG laser operates at 30 Hz; 30–35 mJ per pulse are focused onto a rotating graphite rod to a spot of 0.3 mm diameter. After the pulsed C_2D beam passes the skimmer of 1.0 mm diameter, a four-slot chopper wheel mounted 40 mm after the ablation zone selects a 9.0 μs segment of the pulse. The primary beam was characterized on axis employing a triply differentially pumped detector consisting of an electron impact ionizer followed by a quadrupole mass spectrometer and a Daly-type scintillation particle detector. Under the above-described operation conditions, the number density of the ethynyl radicals in the interaction region in the scattering chamber is estimated to be about 0.5×10^{11} C_2D radicals cm^{-3}.[11] For our experiments, we chose a peak velocity of $2080\pm15\ m\,s^{-1}$ and speed ratio S of 7.7 ± 0.2. This C_2D beam crosses a methylacetylene beam (MG Industries) in the interaction region of the main chamber at a collision energy of 39.8 $kJ\,mol^{-1}$ ($v_p=850\pm10\,m\,s^{-1}$, $S=9.0$). Reactively scattered species are detected using a triply differentially pumped detector consisting of a Brink-type electron impact ionizer, quadrupole mass-filter, and a Daly ion detector[12] recording time-of-flight spectra (TOF). This detector is rotatable in the scattering plane defined by both beams, and we record TOF spectra at different laboratory angles. Integrating these TOFs at each laboratory angle and correcting for different data accumulation times gives the laboratory angular distribution (LAB). Total data accumulation times are up to 20 h per angle. To identify the site of the H atom loss in the methylacetylene molecule, we performed experiments with partially deuterated methylacetylene CD_3CCH at the center-of-mass angle as well.

We would like to point out that we have no definite conclusion on the formation mechanism of the C_2D radicals. However, a simple look at the thermochemistry suggests that $C_2(X\,^1\Sigma_g^+)$ likely reacts with $D_2(X\,^1\Sigma_g^+)$:

$$C(^3P_j)+D_2(X\,^1\Sigma_g^+)\rightarrow CD(X\,^2\Pi_j)+D(^2S_{1/2}), \qquad (3)$$

$$C_2(X\,^1\Sigma_g^+)+D_2(X\,^1\Sigma_g^+)\rightarrow C_2D(X\,^2\Sigma^+)+D(^2S_{1/2}), \qquad (4)$$

$$C_3(X\,^1\Sigma_g^+)+D_2(X\,^1\Sigma_g^+)\rightarrow 1-C_3D(X\,^2\Pi_j)+D(^2S_{1/2}). \qquad (5)$$

Here, reactions (3) and (5) are endothermic by 97 and 124 $kJ\,mol^{-1}$, respectively.[13] However, the reaction of dicarbon with deuterium (4) is exothermic by 48 $kJ\,mol^{-1}$. This pathway could be the dominant process to C_2D radicals.

Information on the chemical dynamics of the reaction was gained by fitting the TOF spectra and the product angular distribution in the laboratory frame (LAB) using a forward-convolution routine.[14] This procedure initially assumes an angular distribution $T(\theta)$ and a translational energy distribution $P(E_T)$ in the center-of-mass reference frame (c.m.). Laboratory TOF spectra and the laboratory angular distribution were then calculated from $T(\theta)$ and $P(E_T)$ accounting for the transformation Jacobian and averaging over the apparatus and beam functions. Best TOF and the laboratory angular distribution were achieved by refining

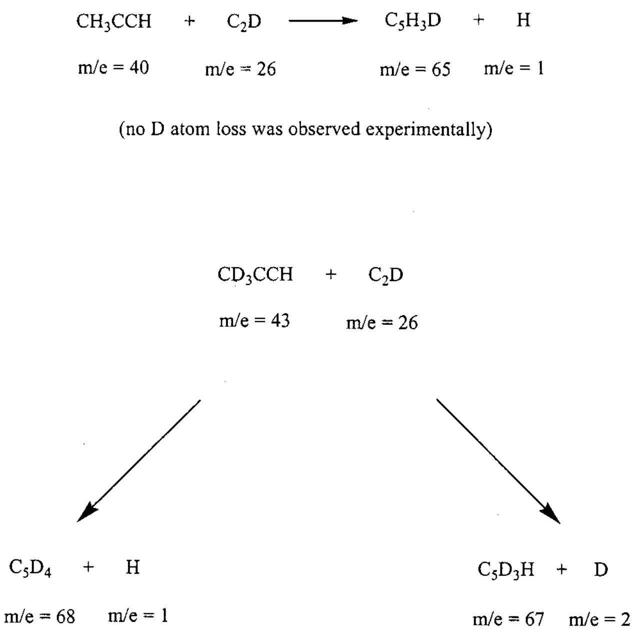

FIG. 1. Schematic representation of the mass to charge ratios of the H and D atom exchange pathway in the reaction of the $C_2D(X\,^2\Sigma^+)$ with $CH_3CCH(X\,^1A_1)$ at a collision energy of 39.8 kJ mol^{-1}.

adjustable $T(\theta)$ and $P(E_T)$ parameters. The ultimate outcome is the generation of a product flux contour map which reports the differential cross section, $I(\theta,u) \sim P(u)*T(\theta)$, as the intensity as a function of angle θ and product center-of-mass velocity u. This map serves as an image of the reaction and contains all the information of the scattering process.

III. ELECTRONIC STRUCTURE CALCULATIONS

Geometries of stationary points were optimized with the 6-311+G** basis set[15] and Becke's[16] three parameter hybrid functional in conjunction with the correlation functional of Lee, Yang, and Parr[17] (B3LYP) as implemented in the GAUSSIAN 98[18] program package. The spin-unrestricted formalism was employed for all species, spin contamination turned out to be negligible. Harmonic vibrational frequencies and zero-point vibrational energy (ZPVE) correction were computed at UB3LYP/6-311+G**. For a more accurate assessment of the reaction enthalpies we calculated single point energies at the coupled cluster single double and perturbative triples/cc-pVTZ level of theory using the UB3LYP/6-311+G** geometries and unscaled ZPVEs. The ACES II program suite[19] was used to perform the coupled cluster computations. All energies referred to in the text are computed at UB3LYP/6-311+G** including unscaled ZPVE unless noted otherwise.

IV. RESULTS

A. Reactive scattering signal

In our C_2D/CH_3CCH experiment, the d1-ethynyl vs hydrogen exchange pathway was detected; reactive scattering signal was observed at mass-to-charge ratios 65 $(C_5H_3D^+)$, 64 $(C_5H_2D^+/C_5H_4^+)$, 63 $(C_5H_3^+/C_5HD^+)$, 62 $(C_5H_2^+/C_5D^+)$, 61 (C_5H^+), and 60 (C_5^+). All TOF spectra observed at lower m/e ratios down to $m/e = 60\,(C_5^+)$ were fit with the same center-of-mass functions as the parent ion. Hence these ions originate from cracking of the parent in the electron impact ionizer, and only the C_2D vs H exchange channel but not the C_2D vs D exchange pathway is present. We like to stress that no radiative association to C_5H_4D was observed experimentally.

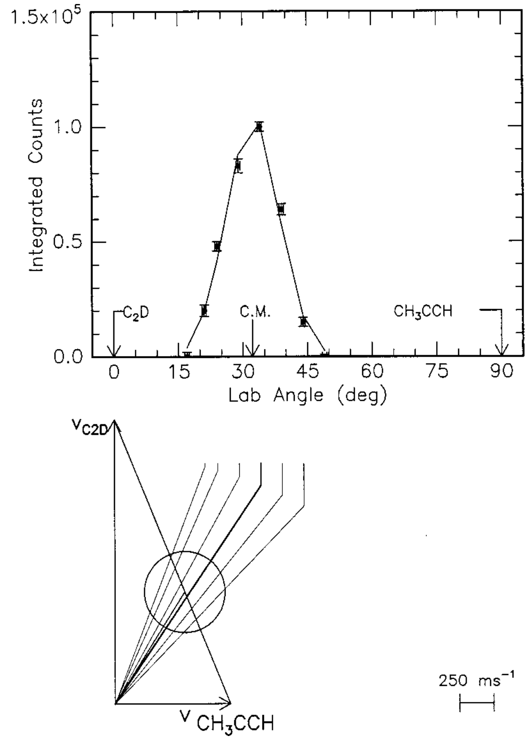

FIG. 2. Laboratory angular distribution together with the most probable Newton diagram for the $C_2D(X\,^2\Sigma^+) + CH_3CCH(X\,^1A_1)$ reaction at a collision energy of 39.8 kJ mol^{-1}. The circle centrosymmetric around the center of mass stands for the maximum center-of-mass recoil velocity of the methyldiacetylene, CH_3CCCCD, product.

Since the H atom loss can occur either from the methyl group or from the H atom adjacent to the acetylenic carbon, we performed a crossed beam experiment with partially deuterated methylacetylene, CD_3CCH, and recorded TOF spectra at the center-of-mass angle. If a H atom loss occurred at the acetylenic group, we should have monitored reactive scattering signal at $m/e = 68\,(C_5D_4^+)$, cf. Fig. 1. If the D atom emission takes place at the methyl group, $m/e = 67\,(C_5D_3H^+)$ should be present. Since we found both $m/e = 67$ and 68, two channels to C_5D_4 and C_5D_3H must exist. However, the integrated TOFs at the c.m. angle show a higher intensity of $m/e = 68$ compared to $m/e = 67$. No methyl loss channel could be observed.

B. Laboratory angular distribution (LAB) and TOF spectra

The most probable Newton diagram of the $C_2D(X\,^2\Sigma^+) + CH_3CCH(X\,^1A_1)$ reaction is shown in Fig. 2 together with the laboratory product angular distribution (LAB) and the calculated curves using the center-of-mass best fit functions at a collision energy of 39.8 kJ mol^{-1}. The

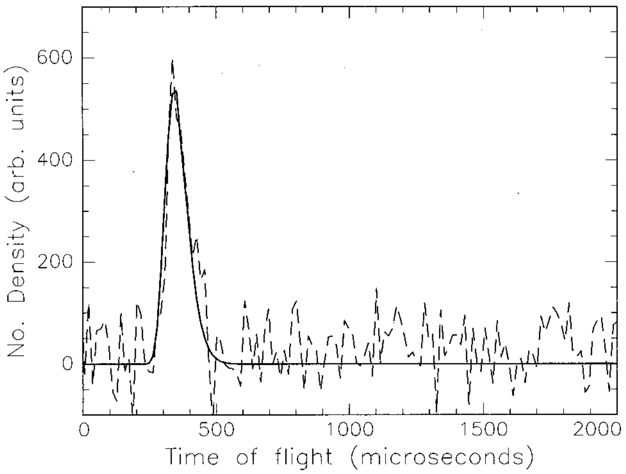

FIG. 3. Time-of-flight data at 32.5° for the $C_2D(X\ ^2\Sigma^+) + CH_3CCH(X\ ^1A_1)$ reaction at a collision energy of 39.8 $kJ\ mol^{-1}$. The dashed line indicates the experimental data, the solid line the calculated fit.

LAB distribution peaks at 34.0° close to the center-of-mass angle of 32.9° and the reactive scattering products are spread within 30° in the plane defined by both beams. If we compare this range with the limiting Newton circles of the C_5H_3D product isomers, it is apparent that at least the thermodynamically more stable methyldiacetylene, CH_3CCCCD, is formed. Figure 3 depicts the TOF spectrum recorded at 32.5° and the best fit.

C. Center-of-mass translational energy distribution, $P(E_T)$

Our data were fitted assuming a single center-of-mass translational energy and angular distribution, cf. Figs. 4 and 5 for the best fit functions. Within the experimental error limits, the best-fit high-energy tails $E_{\max}$ extend between 140 and 170 $kJ\ mol^{-1}$. If we take into account the relative collision energy of 39.8 $kJ\ mol^{-1}$, the exothermicity of the reaction is calculated to be about 100–130 $kJ\ mol^{-1}$. Further, the $P(E_T)$ peaks between 15 and 28 $kJ\ mol^{-1}$ within our error limits. This suggests that the exit transition state from the intermediate(s) to the reaction products is likely to be rather tight. Finally, about 50–60 $kJ\ mol^{-1}$ of the total available energy is channeling into the translational degrees of freedom of the reaction products.

D. Center-of-mass angular distribution, $T(\theta)$, and flux contour map, $I(\theta,u)$

At our collision energy of 39.8 $kJ\ mol^{-1}$, the $T(\theta)$ and $I(\theta,u)$ are forward–backward symmetric. This suggests that the reaction involves indirect scattering dynamics through a C_5H_5 complex. The 0°–180° symmetry documents either a lifetime of the decomposing complex longer than its rotational period or a ''symmetric exit transition state.'' In the latter case, the rotation interconverts leaving hydrogen atoms in the decomposing complex via a proper rotation axis, and the complex fragment with equal probability in θ and $\pi-\theta$. This behavior would result in a symmetric flux distribution although the lifetime of the complex might be less than a rotational period,[20] cf. the involved potential energy surface Fig. 6. Most important, the $T(\theta)$ and $I(\theta,u)$ distributions peak at $\pi/2$; within our error limits, the intensity at the poles to 90° relates to $I(90°)/I(0°) = 1.2–1.4$. This ''sideway''

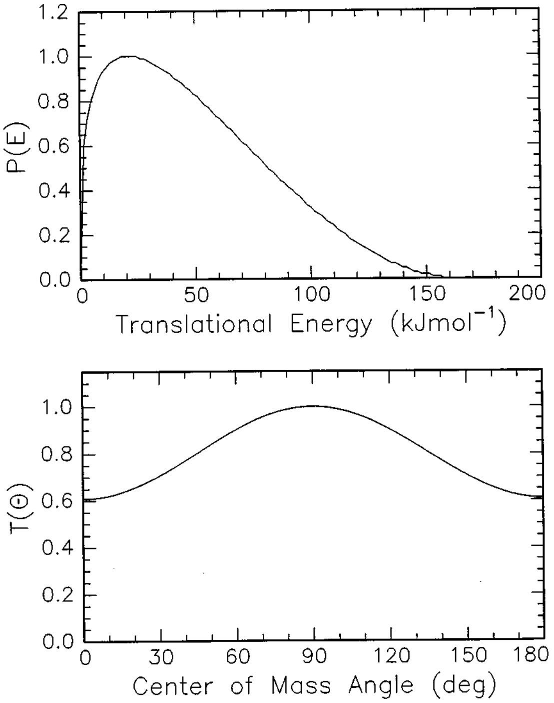

FIG. 4. Center-of-mass angular flux distribution (lower) and translational energy flux distribution (upper) for the $C_2D(X\ ^2\Sigma^+) + CH_3CCH(X\ ^1A_1)$ reaction at a collision energy of 39.8 $kJ\ mol^{-1}$.

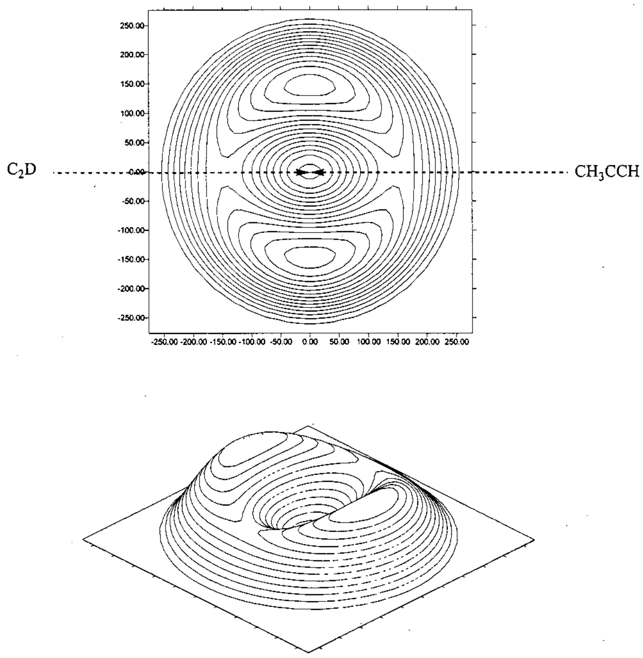

FIG. 5. Center-of-mass velocity contour flux map distribution for the $C_2D(X\ ^2\Sigma^+) + CH_3CCH(X\ ^1A_1)$ reaction at a collision energy of 39.8 $kJ\ mol^{-1}$; top: two-dimensional view, bottom: three-dimensional view. The contour lines connect data points with an identical flux. Units of the x and y axes are given in ms^{-1}.

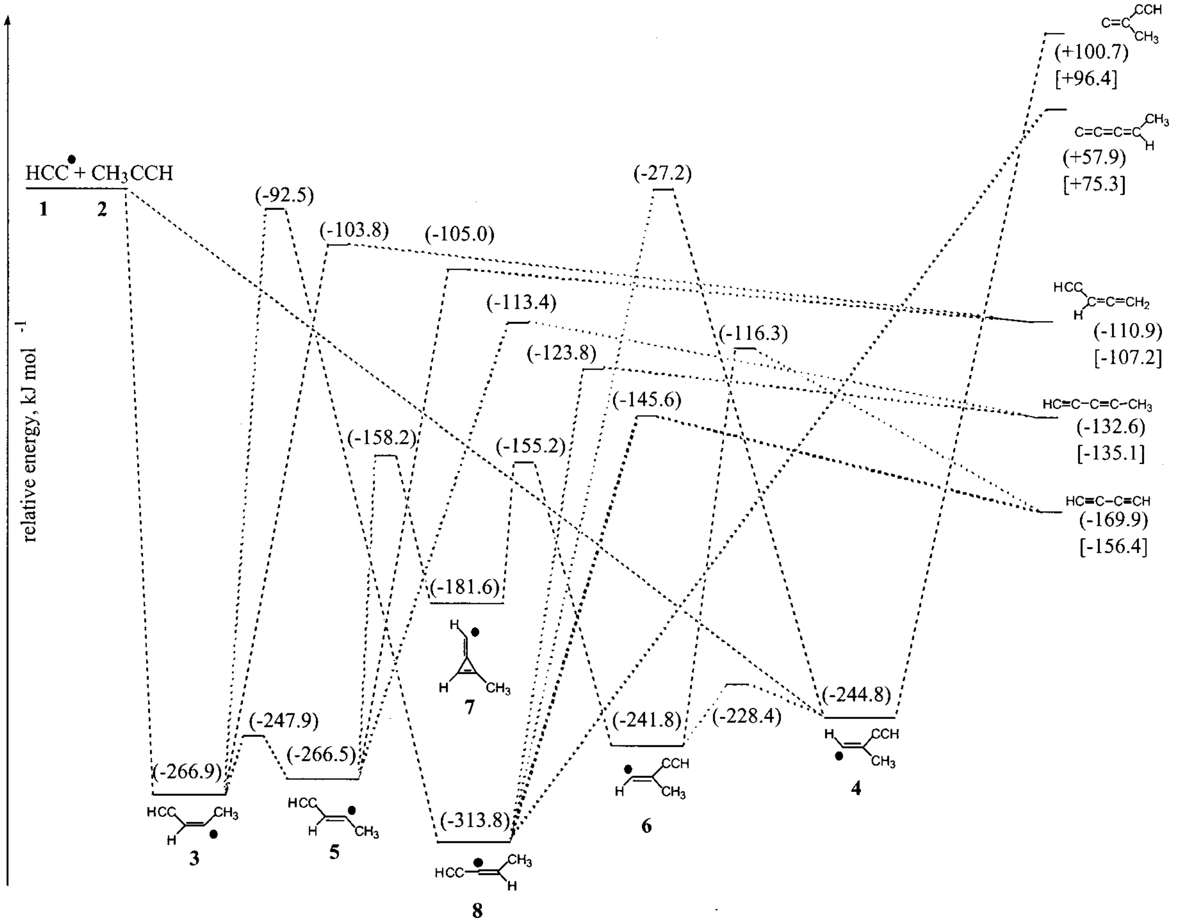

FIG. 6. Schematic representation of the C_5H_5 potential energy surface. Relative energies in kJ mol^{-1} for intermediates and products computed at UB3LYP/6-311+G** are given in parentheses. For the products the CCSD(T)/cc-pVTZ//UB3LYP/6-311+G** results are also indicated in brackets.

peaking of the center-of-mass angular distribution is the result of geometrical constraints of the direction of the H atom emission in the fragmenting C_5H_4D intermediate, cf. Sec. V for a detailed discussion.

V. DISCUSSION

A. *Ab initio* doublet C_5H_5 potential energy surface (PES)

In Sec. V B we present the computational investigation of the interaction of the ethynyl radical, $C_2H\,(X\,^2\Sigma^+)$, **1**, with the methylacetylene molecule, $CH_3CCH\,(X\,^1A_1)$, **2**. Here, we discuss only those structures relevant to our crossed beam study. Although our experiments were performed with C_2D and not with C_2H, the energetics of the intermediates and products change only slightly by 1–2 kJ mol^{-1} due to the difference in zero point vibrational energy. A complete treatment of the C_5H_5 PES including the tri-, tetra-, and pentacyclic structures is given in Ref. 21. In the following discussion, we will refer to the terminal, acetylenic carbon atom of methylacetylene as C1 and subsequently number the other ones as C2 and C3. The ethynyl radical can attack the methylacetylene molecule either at C1 to form *trans*-1-ethynylpropen-2-yl, **3**, or at the C2 to give *trans*-2-ethynylpropen-1-yl, **4**, in strongly exothermic reactions of 266.9 and 244.8 kJ mol^{-1}, cf. Figs. 6 and 7.[22] Both *trans* forms can isomerize via barriers located well below the energy of the separated reactants (−247.9 and −228.5 kJ mol^{-1}, respectively) to the corresponding *cis* isomers **5** and **6**. All ethynylpropenyl isomers **3–6** belong to the C_s point group and have a $^2A'$ electronic wave function. The *cis* structures **5** and **6** can transform into each other via a tricyclic intermediate **7** which is stabilized by 181.6 kJ mol^{-1} with respect to the reactants. Further, 1-ethynylpropen-1-yl **8** can be formed by 1,2 hydrogen shift from **3**. The intermediates **3–6** and **8** can fragment via homolytic C–H bond ruptures. Here, *cis* and *trans* 1-ethynylpropen-2-yl, **3/5**, can emit a H atom of the CH_3 group to form the ethynylallene isomer via exit transition states located only 7 and 15 kJ mol^{-1} above the products; alternatively, **5** can decompose via C1–H fission to form methyldiacetylene through a tight transition state of 19 kJ mol^{-1}. In addition, intermediate **8** can show two decomposition pathways either to methyldiacetylene through H atom loss or to butadiyne (diacetylene) via methyl group emission. Finally, a diacetylene molecule can be formed from intermediate **6** via CH_3 elimination as well. With respect to the separated reactants, all reactions to diacetylene plus methyl, methyldiacetylene plus atomic hydrogen, and ethynylallene plus hydrogen atom are exothermic by 156.4, 135.1, and 107.2 kJ mol^{-1} as based on our compu-

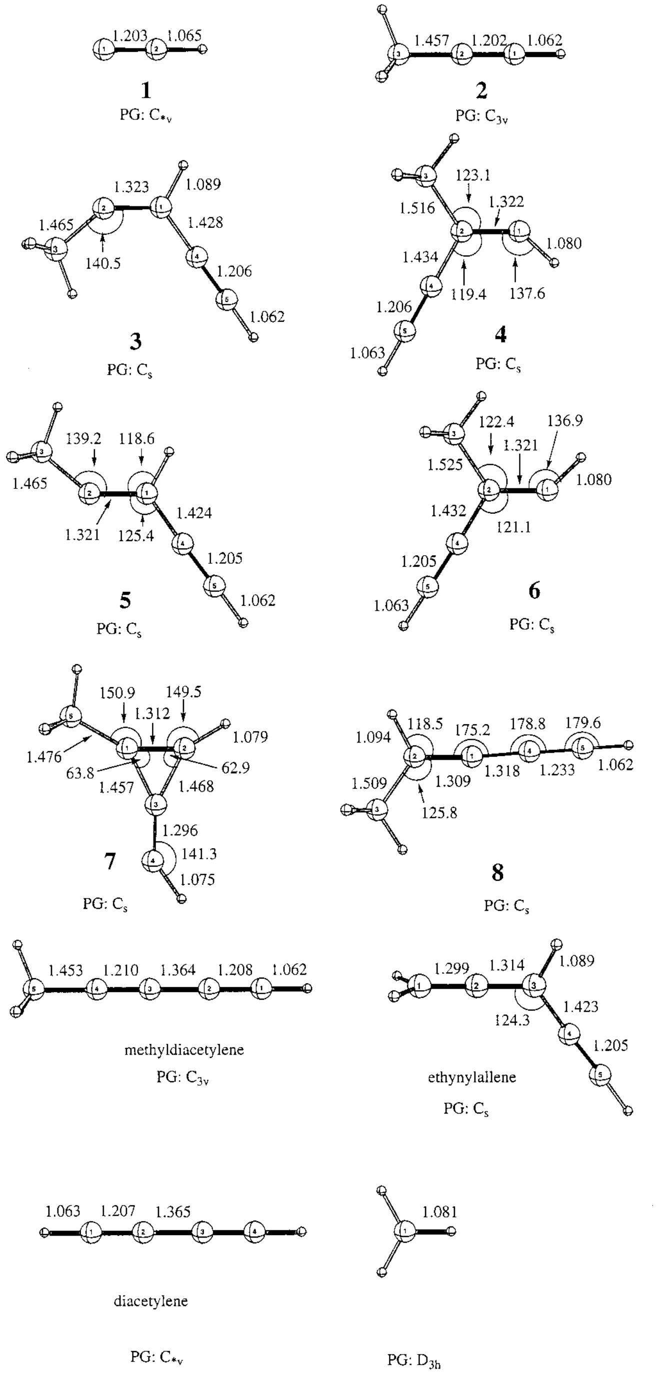

FIG. 7. Optimized geometries of reactants, intermediates, and potential products of the C_5H_5 potential energy surface at UB3LYP/6-311+G**. Bond distances are in Å and bond angles in deg (PG: point group).

tations at the CCSD(T)/cc-pVTZ level of theory. The formation of carbene isomers is highly endothermic by about 100 $\mathrm{kJ\,mol^{-1}}$ [singlet $CC(CH_3)(C_2H)$]. Since the collision energy in our experiment is 39.8 $\mathrm{kJ\,mol^{-1}}$, this isomer cannot be formed, and they are discussed in detail Ref. 21. The energy difference between methyldiacetylene and the corresponding singlet carbene of 190.6 $\mathrm{kJ\,mol^{-1}}$ is close to a data of 180.2 $\mathrm{kJ\,mol^{-1}}$ as computed previously in the $HCCCCH/CCCCH_2$ system.[23]

B. Reaction pathway

1. Energetical considerations and isotopic substitutions

The experimentally determined reaction exothermicity of 100–130 $\mathrm{kJ\,mol^{-1}}$ together with the assignment of the C_2D vs H exchange channel can account for the formation of both the methyldiacetylene and ethynylallene isomers. As shown by our electronic structure computations, the formation of the isomers is exothermic by 132.6 and 110.9 $\mathrm{kJ\,mol^{-1}}$, respectively, and is well within our experimental error limits. To distinguish between both isomers, we conducted the reaction of C_2D with partially d3-methylacetylene, CD_3CCH, cf. Sec. IV. First, our crossed beam study showed a dominating H atom loss channel from C_5D_4H intermediate(s). This atomic hydrogen emission could result in either the formation of CD_3CCCD or the singlet $CCCCD(CD_3)$ isomer. As pointed our in the previous paragraph, the carbene structure is energetically not accessible under our experimental collision energy; therefore, the methyldiacetylene isomer must be formed in our crossed beam experiment. Second, the CD_3CCH/C_2D system showed the emission of a D atom as a second reaction channel. This pathway can form either the ethynylallene isomer via emission of a D atom from the d3-methyl group or the $CCCCH(CD_3)$ isomer through ejection of the acetylenic D atom. However, formation of the latter isomer is endothermic by 96.4 $\mathrm{kJ\,mol^{-1}}$, and therefore we conclude that ethynylallene is formed in our crossed beam experiment as well. Summarized, our high-energy cutoff and isotopic experiments establish the synthesis of two C_5H_4 isomers, methyldiacetylene and ethynylallene, under single collision conditions.

2. Center-of-mass angular distribution considerations and exit transition states

The formation of a long-lived complex during a crossed beam reaction is reflected in a forward–backward–symmetric $T(\theta)$.[24] The detailed shape of the center-of-mass angular distribution is governed by the disposal of the total angular momentum **J**. Since in our experiments, the reactant molecules undergo a supersonic expansion, a significant rotational cooling occurs, and hence the total angular momentum is predominantly identical to the initial orbital angular momentum **L**. The C_5H_3D products can be rotationally excited, so that angular momentum dictates Eq. (6) with the rotational angular momenta of the products $\mathbf{j}'$, and the initial and final orbital angular momenta **L** and $\mathbf{L}'$:

$$\mathbf{J}\approx\mathbf{L}\approx\mathbf{L}'+\mathbf{j}'. \tag{6}$$

The shape of $T(\theta)$ depends strongly on the values of M and M', where M and M' are the projections of **J** on the initial and final relative velocity, respectively.[24] In our case, the $T(\theta)$ peaks at $\theta=90°$; as documented by this sideways scattering, the H atom in our crossed beam experiment is scattered almost parallel to **J** as found previously in the reactions $F+C_6D_6\rightarrow C_6D_5F+D$[25] and the similar system $CN+C_6D_6\rightarrow C_6D_5CN+D$.[26] Therefore, the theoretically investigated

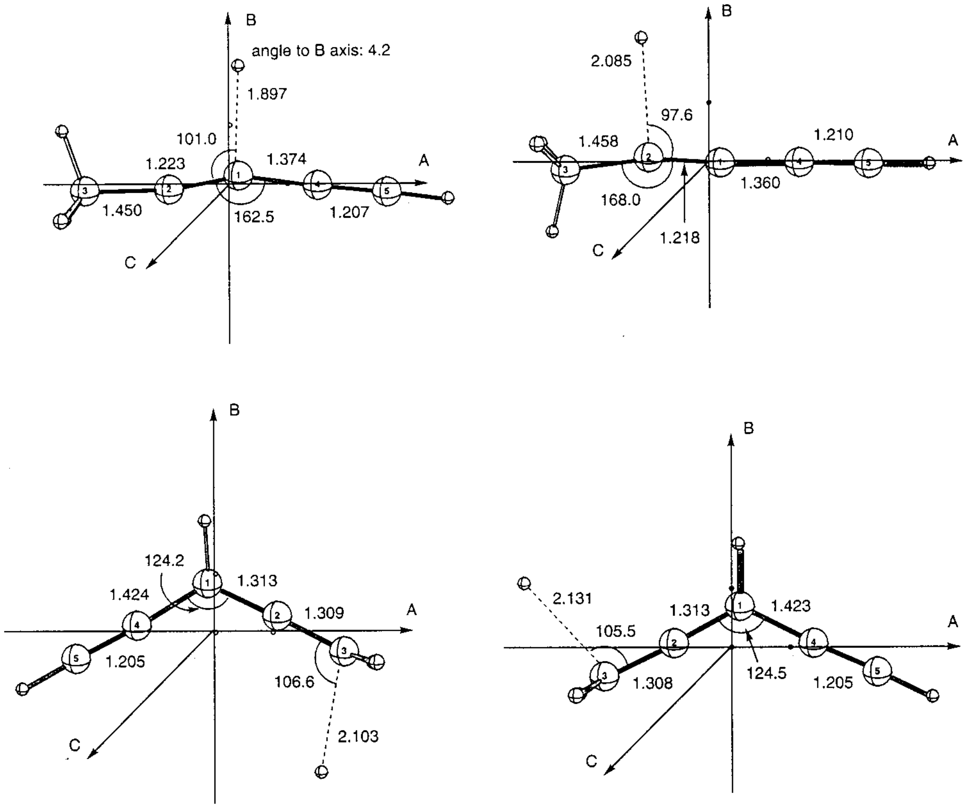

FIG. 8. Structure of four exit transition states from **5** to CH_3CCCCH (top left), **8** to CH_3CCCCH (top right), **3** to $H_2CCCH(C_2H)$ (bottom left), and **5** to $H_2CCCH(C_2H)$ (bottom right). Bond distances are given in Å and bond angles in deg.

exit transition state(s) from the decomposing complex(es) to the products must account for this experimental finding.

Figure 8 displays the computed structures of four exit transition states together with the principal rotation axes *A*, *B*, and *C*. Based on these calculations, both exit transition states from intermediates **5** and **8** to the methyldiacetylene isomer can account for the experimentally found sideways peaking of the center-of-mass angular distribution; the H atom can be emitted parallel to **J**, which is in turn parallel to the *B* rotation axis of the decomposing complex. The exit transition states to the ethynylallene isomer cannot account for the sideways scattering, as the angles between the direction of the departing H atom and **J** are about 74° and 43° from intermediate **3** and **5**, respectively. This result supports our previous conclusion that the CH_3CCCCH isomer is the predominant reaction product, and formation of the ethynylallene isomer represents a less dominant reaction pathway. If we account for the intensity of the TOFs and the chemical reaction dynamics, about 70%–90% of the complexes fragment to methyldiacetylene whereas 10%–30% decompose to ethynylallene. Finally, we have to unravel if **5** or **8** is the prevailing fragmenting complex. We recall that **8** is formed via a hydrogen shift in **3** (pathway 1) and **5** through *cis–trans* isomerization of the initial collision complex **3** (pathway 2). Since both isomerization processes involve **3** and the barrier of pathway 2 is about 150 $kJ\,mol^{-1}$ less than the H shift barrier of pathway 1, we conclude that intermediate **8** plays only a minor role in the chemical reaction dynamics leading to the methyldiacetylene isomer. This conclusion is in line with the order of magnitude of the experimentally determined exit transition state (15–28 $kJ\,mol^{-1}$) and the theoretical data of about 19 $kJ\,mol^{-1}$ from a decomposing complex **5**; a fragmenting intermediate **8** should have depicted a distribution maximum in the center-of-mass translational energy distribution closer to zero translational energy, thus accounting for the loose exit transition state located only 9 $kJ\,mol^{-1}$ above the products.

3. The actual reaction pathway

The distinct identification of the C_2D vs hydrogen replacement channel, the assignment of two product isomers, methyldiacetylene and ethynylallene, and the shape of the center-of-mass angular distribution help us to unravel the underlying chemical reaction dynamics. The $C_2D(X\,^2\Sigma^+)$ radical attacks the π electron density of the carbon–carbon triple bond of the methylacetylene molecule at the C1 atom without an entrance barrier to form *trans* 1-ethynylpropen-2-yl, **3**. An alternative carbon–carbon σ bond formation with the C2 of the methylacetylene molecule is unlikely. First, the steric effect of the methyl group at C2 reduces the cone of acceptance at C2 compared to C1. Second, the CH_3 substituent enhances the spin density at C1 at the expense of C2. This directing and screening power of the methyl group together with the site-specific radical attack has already been observed in the crossed beam reactions of CH_3CCH with $C(^3P_j)$,[27] $CN(X\,^2\Sigma^+)$, and $C_6H_5(X\,^2A')$[28] as studied previously. The *trans* 1-ethynylpropen-2-yl radical resembles a prolate asymmetric top, and the heavy atoms are expected to rotate nearly in a molecular plane perpendicular to the total angular momentum vector **J**. Since the *trans–cis* isomerization barrier from **3** to **5** is only 19 kJ mol^{-1} and ranges well below the energy of the reactant molecules, an ultrafast isomerization process as well as an equal concentration of **3** vs **5** is expected.

What is the fate of both 1-ethynylpropen-2-yl radicals? The *trans* isomer can decompose via a hydrogen atom emission from the methyl group via a rather loose exit transition state located about 7 kJ mol^{-1} above the separated products to yield the experimentally observed ethynylallene isomer to a minor amount. An alternative H atom migration in **3–8** involves a barrier of 174.4 kJ mol^{-1}; since this isomerization barrier is located 92.5 kJ mol^{-1} below the reactants, but the barrier to H atom loss ranges 103.8 kJ mol^{-1} below the separated reactants, the latter fragmentation pathway is likely to dominate, and **3** fragments to the ethynylallene isomer. The *cis* isomer **5** shows an atomic hydrogen release either from the methyl group to give the ethynylallene isomer or from the C1 atom to form the methyldiacetylene molecule via transition states of 6 and 19 kJ mol^{-1} located 105.1 and 113.5 kJ mol^{-1} below the reaction products. Based on these considerations, the formation of the CH_3CCCCH isomer is expected to be the dominant decay route of **5**; due to conservation of angular momentum, **5** is excited to rotations around its B/C axis. This finding correlates very nicely with our experimental data. Here, the integrated data of the CD_3CCH/C_2D experiment show an enhanced signal of the H emission compared to the D atom release. Therefore, we can conclude that the methyldiacetylene isomer is the dominant isomer as formed under single collision conditions in our crossed beam experiments. Besides the decomposition of **5**, a minor pathway to methyldiacetylene is a fragmenting intermediate **8** as formed via H atom shift from **3**. All complexes **3**, **5**, and **8** leading to the reaction products reside in a deep potential energy well located between −244.8 and −313.8 kJ mol^{-1} with respect to the products. This can account for the experimentally observed forward–backward symmetric center-of-mass angular distribution demonstrating that the lifetime of the decomposing complex(es) is longer than the rotation period, which is often on the order of 1 ps. Further, the energetics of the exit transition states from **3**/**5** to ethynylallene and methyldiacetylene as investigated computationally (7–19 kJ mol^{-1}) are in line with a barrier of a reversed addition of atomic hydrogen to a carbon–carbon triple/double bond. In addition, the $P(E_T)$ peaks around 15–25 kJ mol^{-1}, hence clearly verifying an existing exit barrier.

We would like to underline that the addition of the C_2D radical to C2 of methylacetylene is energetically feasible as well. As stated previously the methyl substituent screens the C2 position, and this reaction pathway is likely to be of minor importance. As a matter of fact, the intermediates **4/6** cannot account for the reactive scattering signal since an H atom loss would lead to a carbene isomer singlet $CC(CH_3)(C_2H)$; this reaction endothermicity cannot be compensated by our collision energy of 39.8 kJ mol^{-1}. However, a methyl loss in **6** can lead to the diacetylene molecule. Nevertheless, we were unable to observe the CH_3 loss pathway experimentally. Therefore, the C_2D radical does not add to C2 to give intermediate **4** followed by isomerization to **6**, or due to the different kinematics, the reactive scattering signal is too low to be observable.

C. Comparison with the reaction $CN(^2\Sigma^+)+CH_3CCH$

Both C_2D and the CN radicals have a $^2\Sigma^+$ electronic ground state; the unpaired electron is localized in a centrosymmetrical orbital on the radical carbon atom of the reactants. Directed by a screening effect of the CH_3 group together with an increased spin density at the C1 carbon atom of the methylacetylene molecule, the radical adds to the π electron density to form a new carbon–carbon σ bond to give a CH_3CCHX ($X=CN$, C_2D) complex. The initial addition complexes reside in a deep potential energy well of about 253 kJ mol^{-1} ($X=CN$) and 267 kJ mol^{-1} ($X=C_2D$). Both reactions proceed via indirect scattering dynamics through a complex formation. But whereas the CN reaction goes through an osculating complex at a collision energy of 24.7 kJ mol^{-1}, the C_2D/CH_3CCH system shows a long-lived CH_3CCHC_2D intermediate, though the collision energy of 39.8 kJ mol^{-1} is higher than in the CN plus CH_3CCH reaction. This is likely the effect of an additional atom of the C_2D vs CN reactants (increasing the number of vibration modes by three) and low frequency modes of the C–D wagging/bending vibrations in the range of 100–260 cm^{-1}. Further, the lifetime of the decomposing intermediates in both systems are long enough for the energy to flow from the activated C–X bond at the C1 to the breaking C–H bond of the methyl group to give a substituted allene product. Therefore, the energy randomization in the CH_3CCHX intermediates is likely to be complete. Despite these similarities, one significant difference exists. The branching ratio of the formation of the $CH_3-C\equiv C-X$ vs H_2CCCHX is unity for $X=CN$ but increases from three to nine for $X=C_2H$ as based on our experiment. This can be rationalized in terms of a larger difference in the energetics of the exit transition states to both isomers in the title reaction (22.3 kJ mol^{-1}) compared to the CN/CH_3CCH reaction (2 kJ mol^{-1}) and hence inherent larger unimolecular rate constants in the decomposition of the involved intermediates to the products.

VI. CONCLUSIONS

The crossed beam reaction of the d1-ethynyl radical $C_2D(X\,^2\Sigma^+)$, with methylacetylene, CH_3CCH ($X\,^1A_1'$), was investigated at an average collision energy of 39.8 kJ mol^{-1} in a crossed molecular beams experiment and electronic structure calculations. The chemical reaction dynamics are indirect and advance via long-lived *cis* and *trans* $CH_3CCH(C_2D)$ intermediates. The initial addition of the ethynyl radical to the π orbital of the methylacetylene unit has no entrance barrier. As verified in our experiments, the reduced cone of acceptance of the carbon atom adjacent to the methyl group favors a carbon–carbon σ bond formation at the C1 atom—the carbon atom adjacent to the acetylenic hydrogen atom—in the methylacetylene molecule. A crossed beam experiment of C_2D with partially deuterated methylacetylene, CD_3CCH, shows explicitly that the reactive intermediates decompose via two distinct channels to form both methylacetylene and ethynylallene isomers through transition states located 7–15 $\mathrm{kJ\,mol^{-1}}$ above the products. We would like to point out that substituting the C_2D reactant by C_2H changes the calculated reaction energies and the energetics of the intermediates only slightly—by 1–2 $\mathrm{kJ\,mol^{-1}}$. Therefore, the definite assignment of the ethynyl vs H atom exchange is the first ever experimental proof that upon reaction with methylacetylene, two distinct isomers, methyldiacetylene and ethynylallene, can be formed under single collision conditions as well as in cold molecular clouds and the atmosphere of Saturn's moon Titan.[29–31] We would like to stress that our results underline unambiguously that a detailed investigation of the involved chemical reaction dynamics of astrophysically relevant reactions is of crucial importance rather than ''postulating'' reaction products based on simple thermochemistry. Our investigation unravels the formation of two isomers, the thermodynamically most stable methyldiacetylene structure, CH_3CCCCH ($\Delta_R H^0 = 135.1\,\mathrm{kJ\,mol^{-1}}$), and the less stable ethynylallene isomer, C_2HHCCH_2 ($\Delta_R H^0 = 107.2\,\mathrm{kJ\,mol^{-1}}$). The pentatetraene isomer, $H_2CCCCCH_2$ ($\Delta_R H^0 = 122.7\,\mathrm{kJ\,mol^{-1}}$), is not formed. This is a direct consequence of the involved potential energy surface, which is presented in detail in Ref. 21.

ACKNOWLEDGMENTS

R.I.K. is indebted to the Deutsche Forschungsgemeinschaft (DFG) for a *Habilitation* fellowship (IIC1-Ka1081/3-2). This work was supported by Academia Sinica, Taiwan. Partial support from the Petroleum Research Fund of R.O.C. is also appreciated. F.S. greatly acknowledges a HSP III-*Doktoranden* fellowship (D/99/22963) from DAAD. The work in Erlangen was also supported by the DFG, the computations in Georgia by the US Department of Energy. We thank Dr. H. Bettinger (Rice University, Houston, TX) for his comments. This work was performed within the international astrophysics network http://po.iams.sinica.edu.tw/~kaiser/network.htm.

[1] K. D. Tucker, M. L. Kunter, and P. Thaddeus, Astrophys. J. Lett. **L115**, 193 (1994).

[2] R. E. Bandy, C. Lakshiminaragan, R. K. Frost, and T. S. Zwier, Science **258**, 1630 (1992).

[3] D. Chastaing, P. L. James, I. R. Sims, and W. M. Smith, Faraday Discuss. **109**, 165 (1998).

[4] B. J. Opansky and S. R. Leone, J. Phys. Chem. **100**, 19904 (1996); H. Look and J. Peeters, *ibid.* **99**, 16284 (1995); S. K. Farhat, C. L. Morter, and G. P. Glass, *ibid.* **97**, 12789 (1993); M. Koshi, N. Nishida, and H. Matsui, J. Phys. Chem. **96**, 5875 (1992).

[5] R. J. Hoobler and S. R. Leone, J. Phys. Chem. **103**, 1342 (1991).

[6] L. C. L. Huang, Y. T. Lee, and R. I. Kaiser, J. Chem. Phys. **110**, 7119 (1999).

[7] Y. T. Lee, J. D. McDonald, P. R. LeBreton, and D. R. Herschbach, Rev. Sci. Instrum. **40**, 1402 (1969).

[8] R. I. Kaiser and A. G. Suits, Rev. Sci. Instrum. **66**, 5405 (1995).

[9] R. I. Kaiser *et al.*, Rev. Sci. Instrum. **70**, 4185 (1999).

[10] D. Proch and T. Trickl, Rev. Sci. Instrum. **60**, 713 (1989).

[11] First we tried to obtain a beam of C_2H seeding the ablated species in neat molecular hydrogen. However, the signal at $m/e = 25$ was very weak within 3%–4% of the intensity of the $^{12}C_2$ beam, and we could not be sure if it originated from $^{13}C^{12}C$ or $^{12}C_2H$. Hence we decided to seed the ablated species in deuterium since the contribution of $^{13}C_2$ to $m/e = 26$ is marginal.

[12] G. O. Brink, Rev. Sci. Instrum. **37**, 857 (1966); N. R. Daly, *ibid.* **31**, 264 (1960).

[13] Data were taken from http://webbook.nist.gov/.

[14] M. S. Weis, Ph.D. thesis, University of California, Berkeley, 1986; M. Vernon, Thesis, University of California, Berkeley, 1981.

[15] W. J. Hehre, L. Radom, P. V. R. Schleyer, and J. A. Pople, *Ab initio Molecular Orbital Theory* (Wiley Interscience, New York, 1986).

[16] A. D. Becke, J. Chem. Phys. **98**, 5648 (1993).

[17] C. Lee, W. Yang, and R. G. Parr, Phys. Rev. B **37**, 785 (1987).

[18] M. J. Frisch *et al.*, GAUSSIAN 98; Revision A.7 ed.; Gaussian Inc.: Pittsburgh (1998).

[19] J. F. Stanton, J. Gauss, J. D. Watts, M. Nooijen, N. Oliphant, S. A. Perera, P. G. Szaley, and R. J. Bartlett, ACES II, Release 2.0 ed., University of Florida, Gainesville, FL, 1995.

[20] R. I. Kaiser, C. Ochsenfeld, M. Head-Gordon, and Y. T. Lee, Science **274**, 1508 (1996).

[21] F. Stahl *et al.*, J. Chem. Phys. **114**, 3476 (2001).

[22] The *cis* and *trans* notation refers to the position of the H atom and CH_3 group of the former methylacetylene.

[23] N. Goldberg, D. Suelzle, and H. Schwarz, Chem. Phys. Lett. **213**, 593 (1993).

[24] In theory, a deviation from this forward–backward symmetry can happen if energy conservation excludes higher M states. W. B. Miller, S. A. Safron, and D. R. Herschbach, Discuss. Faraday Soc. **44**, 108 (1967).

[25] K. Shobatake, J. M. Parson, Y. T. Lee, and S. A. Rice, J. Chem. Phys. **59**, 1427 (1973).

[26] N. Balucani *et al.*, J. Chem. Phys. **111**, 7457 (1999).

[27] R. I. Kaiser, D. Stranges, Y. T. Lee, and A. G. Suits, J. Chem. Phys. **105**, 8721 (1996).

[28] R. I. Kaiser, O. Asvany, Y. T. Lee, H. F. Bettinger, P. v. R. Schleyer, and H. F. Schaefer III, J. Chem. Phys. **112**, 4994 (2000).

[29] B. Letourneur and A. Coustenis, Planet. Space Sci. **41**, 393 (1993).

[30] F. Raulin *et al.*, Adv. Space Res. **22**, 353 (1998).

[31] D. W. Clarke and J. P. Ferris, Icarus **115**, 119 (1995).