

# A crossed beams and *ab initio* investigation on the formation of cyanodiacetylene in the reaction of cyano radicals with diacetylene

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The crossed molecular beams reaction of ground state cyano radicals (CN) with diacetylene (HCCCCH) was studied in the laboratory under single collision conditions. Combining the derived center-of-mass translational energy and angular distributions with novel electronic structure calculations, we show that the linear cyanodiacetylene molecule (HCCCCCN) is the sole reaction product. Our study provided no substantiation of two alternative products which have been suggested previously: cyanoacetylene (HCCCN), speculated to be synthesized via the exchange of the ethynyl by the cyano group, and the 1,3-butadiynyl radical (HCCCC), thought to be formed via hydrogen abstraction. The unambiguous identification of cyanodiacetylene formed in an exoergic, barrierless bimolecular reaction of the cyano radical with diacetylene strongly suggests that cyanodiacetylene can be also synthesized via this process in the interstellar medium (cold molecular clouds) and in hydrocarbon-rich atmospheres of planets and their moons such as Titan. © 2009 American Institute of Physics. [DOI: 10.1063/1.3152714]

## I. INTRODUCTION

Closed shell polyynes and cyanopolyynes belong to a group of organic molecules with alternating single and triple bonds holding the generic chemical formulas  $H-(C\equiv C)_m-H$  and  $H-(C\equiv C)_n-CN$ .<sup>1</sup> They are linear in structure and belong to the  $D_{\infty h}$  (polyynes) and  $C_{\infty v}$  (cyanopolyynes) point groups with  $^1\Sigma_g^+$  and  $^1\Sigma^+$  electronic ground states, respectively. Due to their distinctive molecular and electronic structures, polyynes and cyanopolyynes together with their corresponding cations have promising technological applications such as building blocks in molecular nanotechnology,<sup>2</sup> intermediates in combustion flames,<sup>3</sup> and in chemical vapor deposition processes<sup>4</sup> leading to polycyclic aromatic hydrocarbons and ultimately to soot particles. Note that naturally occurring polyynes are associated with medicinal properties and often utilized in, for instance, cancer research and inhibition of skin infections.<sup>5</sup> These are acetylenic fatty acids extracted from the root bark of the legume *Paramacrolobium caeruleum*<sup>6</sup> and the pigment thiarubrine B (Ref. 7) isolated from the ragweed plant. Likewise, the polyynes oplopandiolacetate,<sup>8</sup> dihydromatricaria acid,<sup>9</sup> oenanthotoxin,<sup>10</sup> cicutoxin,<sup>11</sup> and falcarinol<sup>12</sup> have been exploited by native Americans to treat various health disorders. The synthetic pathways of these naturally occurring polyynes have been studied in depth often utilizing coupling reactions (Cadiot–Chodkiewicz,<sup>13</sup> Glaser,<sup>14</sup> and Hay<sup>15</sup>) and the Eglinton reaction.<sup>16</sup> Finally, polyynes and cyanopolyynes have been implicated in the astrochemical evolution of the interstellar medium<sup>17</sup> such as of cold molecular clouds such as TMC-1, the planetary nebula CRL 618, and the circumstellar envelope of the carbon star IRC+10216.<sup>18</sup> In cold molecular clouds, all cyanopolyynes up to

$H-(C\equiv C)_5-CN$  were detected;<sup>19</sup> diacetylene  $H-(C\equiv C)_2-H$  (Ref. 20) and triacetylene  $H-(C\equiv C)_3-H$  (Ref. 20) have been monitored toward CRL 618.

In extraterrestrial environments, photochemical models predict that these highly unsaturated molecules are also key building blocks to understand the origin and chemical evolution of hydrocarbon-rich atmospheres of planets and their satellites such as of Titan.<sup>21</sup> Here, Titan presents a natural laboratory on the planetary scale. Molecular nitrogen and methane are the main constituents of Titan's atmosphere followed by hydrogen, nitrogen bearing molecules, and hydrocarbons.<sup>22</sup> Even though the unsaturated hydrocarbon molecules such as acetylene ( $C_2H_2$ ), ethylene ( $C_2H_4$ ), diacetylene ( $C_4H_2$ ), and benzene ( $C_6H_6$ ) occur only in trace amounts,<sup>23</sup> they are of particular importance because they are thought to be key intermediates to form Titan's organic, aerosol-particle based haze layers. The latter are of basic significance to Titan's chemistry and to hydrocarbon-rich atmospheres of planets in the outer Solar System in general. They absorb the destructive ultraviolet (UV) radiation to protect astrobiologically important molecules from being destroyed in the lower parts of the atmosphere (thus acting as prebiotic ozone),<sup>24</sup> prevent Titan's atmosphere from heating up (temperature inversion at the tropopause),<sup>25</sup> and play a crucial role in Titan's radiation and temperature balance including Titan's seasonal weather pattern.<sup>26</sup> However, on Titan, only the simplest members of the polyacetylene and cyanopolyne families have been observed in the gas phase: diacetylene (HCCCCH) and cyanoacetylene (HCCCN);<sup>27</sup> di-cyanodiacetylene (NCCCCN) is suggested to exist as a solid on Titan. Among them, cyanopolyynes, which may act as precursors to amino acids, received particular attention.<sup>28</sup> Specifically the cyanoacetylene molecule is known to be

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formed in the Miller–Urey experiment—an experiment which presumably mimics the chemical processing of the atmosphere of early Earth.<sup>29</sup>

However, to evaluate the validity of these models which predict the existence of even higher cyanopolyynes such as cyanodiacetylene on Titan, it is crucial to understand the formation mechanisms of these molecules in depth. Here, we report on the gas phase crossed molecular beams reaction of the cyano radical [ $\text{CN}(X^2\Sigma^+)$ ] with diacetylene ( $\text{HCCCCH}$ ) in the hope of synthesizing the next member of the cyanopolyne family: cyanodiacetylene. In the laboratory, its microwave<sup>30</sup> and infrared (IR) spectra<sup>31</sup> were recorded accompanied by electronic structure calculations to predict its geometry and rotational and vibrational parameters.<sup>32</sup> However, these efforts were hindered by the lack of pure and isolated cyanodiacetylene samples. This was finally resolved by Trolez and Guillemin in 2005 (Ref. 33) and paved the way for high quality spectroscopic and photochemistry studies. Since then, Benilan *et al.* measured the gas phase far UV (Ref. 34) and mid- IR spectra;<sup>17</sup> Coupeaud *et al.* recorded the UV and IR spectra of cyanodiacetylene isolated in low temperature argon matrices.<sup>35</sup> Meanwhile Coupeaud *et al.* carried out the first photochemical study on this compound; after irradiating this compound isolated in an argon matrix with 267 nm light, they found evidence for the formation of isocyanodiacetylene.<sup>35</sup> In a more recent paper they also reported the identification of the anion  $\text{C}_5\text{N}^-$  and a branched carbene structure via IR spectroscopy.<sup>36</sup> In a related study, they investigated spectroscopically a mixture of cyanodiacetylene with water and combined their findings with theoretical calculations. The analysis of their results shows that cyanodiacetylene is both electrophilic (by its acetylenic hydrogen atom) and nucleophilic (by the nitrogen atom of the cyano group).<sup>37</sup> Further, kinetics studies of the reaction of cyano radicals with diacetylene at room temperature suggested large rate constants of  $(4.2 \pm 0.2) \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$ .<sup>38</sup> However, these kinetics studies were not able to identify the reaction products. The following reaction pathways were only suggested [reactions (1)–(3)] and branching ratios could not be provided:



The failed detection of any reaction products and the ambiguity of the kinetics results for the primary reaction processes involved make it clear that the formation pathways of the cyanodiacetylene molecule are clearly elusive. Since the macroscopic alteration of Titan’s atmosphere consists of multiple elementary reactions that are a series of *bimolecular* encounters between radicals and molecules, this detailed understanding of this mechanism involved at the *microscopic level* is crucial to unravel the chemical evolution and processing of low temperature environments in general. These are experiments under *single collision conditions* in which particles of one supersonic beam (the cyano radical beam) are made to “collide” only with particles of a second beam

(the diacetylene beam). This experimental setup is well suited to study the primary processes involved in the reactivity of radicals and also the unimolecular decomposition of chemically activated radical intermediates under collision-free conditions and absence of any wall effects.<sup>1,33</sup> Therefore, experiments under single collision conditions are imperative to unravel the mechanism(s) involved in the synthesis of cyanodiacetylene and possibly other reaction products via the bimolecular gas phase reaction of the cyano radical [ $\text{CN}(X^2\Sigma^+)$ ] with diacetylene ( $\text{HCCCCH}$ ) utilizing the crossed molecular beams approach as reported here.

## II. EXPERIMENTAL SECTION

The reactive scattering experiments were conducted in a crossed molecular beams machine under single collision conditions at The University of Hawai’i.<sup>39</sup> A pulsed supersonic beam of cyano radicals in their electronic ground state,  $\text{CN}(X^2\Sigma^+)$ , was generated *in situ* in the primary source chamber via laser ablation of graphite at 266 nm and consecutive reaction of the ablated species with neat nitrogen gas (99.9999%; Gaspro). Nitrogen also acts as a seeding gas of the cyano radicals.<sup>40</sup> The pressure in the source chamber was maintained at about  $10^{-4}$  torr. The velocity and speed ratio of the cyano radical beam were determined after the beam passed a skimmer and a four slot chopper wheel to be  $1690 \pm 20 \text{ ms}^{-1}$  and  $3.0 \pm 0.3$ , respectively. This part of the radical beam crossed a pulsed diacetylene beam (99.5%+) seeded in argon (99.9999%) at fractions of 5%. Diacetylene was synthesized according to literature.<sup>41</sup> The segment of the diacetylene beam which crossed the cyano radical beam had a peak velocity and speed ratio of  $580 \pm 20 \text{ ms}^{-1}$  and  $8.0 \pm 0.5$ , respectively. This resulted in a collision energy of  $27.3 \pm 0.6 \text{ kJ mol}^{-1}$  and a center-of-mass (CM) angle of  $33.4 \pm 0.5$ . It is important to outline that the primary reactant beam also contains carbon atoms as well as dicarbon and tricarbon molecules. Test experiments showed that tricarbon molecules have a significant entrance barrier upon reacting with diacetylene of about  $80 \text{ kJ mol}^{-1}$ ; therefore, under our experimental conditions, tricarbon does not react with diacetylene. The lighter carbon (12 amu) and dicarbon reactants (24 amu) react with diacetylene;<sup>41,42</sup> due to the heavier cyano radical (26 amu), carbon and dicarbon reactions lead only to products which are lower in mass by 2 and 14 amu compared to those formed in the reaction of cyano radicals with diacetylene. Consequently, neither dicarbon nor carbon atoms interfered in the present study.

We monitored the reactively scattered products via a quadrupole mass spectrometric detector operated in the time-of-flight (TOF) mode at a constant mass-to-charge ratio ( $m/z$ ) after electron-impact ionization of the molecules at 80 eV at an emission current of 2 mA. Up to  $2.6 \times 10^6$  TOF spectra were recorded at each angle. The detector is rotatable within the plane defined by the cyano radical and diacetylene beams; this allows angularly resolved TOF spectra to be resolved and—by integrating the TOF spectra at the laboratory angles—the laboratory angular distribution to be extracted. The latter reports the integrated intensity of an ion of distinct  $m/z$  versus the laboratory angle. To gain additional informa-

tion on the chemical dynamics and underlying reaction mechanism, the TOF spectra and laboratory angular distribution were fitted and transformed into the CM reference frame using a forward-convolution routine.<sup>43</sup> This approach initially presumes the angular flux distribution,  $T(\theta)$ , and the translational energy flux distribution,  $P(E_T)$ , in the CM system assuming mutual independence. The laboratory data (TOF spectra and the laboratory angular distribution) are then calculated from these  $T(\theta)$  and  $P(E_T)$  and convoluted over the apparatus functions to obtain a simulation of the experimental data. The crucial output of this fitting routine is the product flux contour map,  $I(\theta, u) = P(u) \times T(\theta)$ , which plots the intensity of the reactively scattered products ( $I$ ) as a function of the CM scattering angle ( $\theta$ ) and product velocity ( $u$ ). This plot is called the reactive *differential cross section* and can be seen as the *image* of the chemical reaction.

### III. THEORETICAL METHODS

The  $C_5NH_2$  and  $C_5NH$  potential energy surfaces (PESs) were optimized via the hybrid density functional B3LYP method with the 6-311G\*\* basis set.<sup>44</sup> The same method was utilized to gain vibrational frequencies, molecular structural parameters, and zero-point energy (ZPE) corrections and to characterize the stationary points as minima or first-order saddle points. To obtain more accurate energies, we utilized the coupled cluster CCSD(T) method<sup>45</sup> with Dunning's correlation-consistent cc-pVTZ basis set.<sup>46</sup> For the reactants and various products, we performed additional CCSD(T)/cc-pVDZ, CCSD(T)/cc-pVQZ, and CCSD(T)/cc-pV5Z calculations to extrapolate their CCSD(T) total energies to the complete basis set (CBS) limit by fitting the following equation:<sup>47</sup>  $E_{\text{tot}}(x) = E_{\text{tot}}(\infty) + Be^{-Cx}$ , where  $x$  is the cardinal number of the basis set (2, 3, 4, and 5) and  $E_{\text{tot}}(\infty)$  is the CCSD(T)/CBS total energy. It should be noted that the relative energies obtained at the CCSD(T)/cc-pVTZ and CCSD(T)/CBS levels agree with each other within 0.5 kJ mol<sup>-1</sup>. We expect that our CCSD(T)/CBS + ZPE(B3LYP/6-311G\*\*) relative energies should be accurate within 5 kJ mol<sup>-1</sup>. We applied the GAUSSIAN98 program package<sup>48</sup> to carry out B3LYP and MP2 calculations and the MOLPRO 2006 program package<sup>49</sup> to conduct calculations of spin-restricted coupled cluster RCCSD(T) energies. B3LYP and CCSD(T) calculated total energies at 0 K, ZPE corrections, B3LYP/6-311G\*\* optimized Cartesian coordinates, unscaled vibrational frequencies ( $\nu_i$ ), moments of inertia ( $I_i$ ), and rotational constants ( $B_i$ ) of all species involved in the reaction are given in the supporting information for this paper. Further, relative yields of the products under single collision conditions were evaluated by Rice–Ramsperger–Kassel–Marcus calculations<sup>50</sup> of energy-dependent rate constants for individual unimolecular steps and of branching ratios of different channels.<sup>51</sup>

### IV. RESULTS AND DISCUSSION

#### A. Laboratory data

Signal was monitored for  $m/z=75$ , 74, and 51 corresponding to ions with the molecular formulas  $HC_5N^+$ ,  $C_5N^+$ ,

and  $HC_3N^+$ . After scaling, the TOF spectra recorded at lower  $m/z$  ratios of 74 and 51 show an identical shape to those recorded at  $m/z=75$ . Therefore, we can conclude that a molecule of the formula  $HC_5N$  presents the reaction product and that ions at 74 and 51 are formed via dissociative ionization of the parent molecule in the electron-impact ionizer. Consequently, the hydrogen exchange pathway is open [reaction (1)], but the cyano versus ethynyl substitution [reaction (2)] is closed under our experimental conditions. The TOF data and the corresponding laboratory angular distribution are shown in Fig. 1. Note that the laboratory angular distribution is relatively narrow and spreads only over 40° within the scattering plane. Further, the laboratory angular distribution peaks close to the CM angle of the system.

#### B. Center-of-mass translational energy, $P(E_T)$ , and angular distribution, $T(\theta)$

As depicted in Fig. 1, a rational fit of the laboratory data at  $m/z=75$  ( $HC_5N^+$ ) could be achieved with one reaction channel leading to the reaction product(s) of the molecular formula  $HC_5N$  and atomic hydrogen. The CM translational energy distribution,  $P(E_T)$ , extends up to a maximum translational energy of 110 kJ mol<sup>-1</sup> (Fig. 2). Adding or subtracting 15 kJ mol<sup>-1</sup> does not change the fits significantly. Since the high energy cutoff corresponds to the sum of the reaction energy and the collision energy, we can subtract the collision energy to compute the reaction energy to be  $-87 \pm 15$  kJ mol<sup>-1</sup>. Second, the  $P(E_T)$  is relatively broad and depicts a distribution maximum away from zero translational energy at about 20 kJ mol<sup>-1</sup>. This finding indicates that the exit barrier is likely to be tight and that a significant reorganization of the electron density occurs when the reaction intermediate decomposes.<sup>52</sup> Finally, by integrating the CM translational energy distribution and accounting for the available energy, the average fraction of available energy channeling into the translational degrees of freedom is computed to be 30(±5%). This order of magnitude likely indicates indirect scattering dynamics via complex formation. Let us turn our attention now to a detailed analysis of the CM angular distribution,  $T(\theta)$ , to gather additional data on the reaction dynamic. Most important, the angular flux distribution depicts intensity over the complete angular range from 0° to 180°. This is evident of indirect scattering dynamics and the involvement of  $H_2C_5N$  collision complex(es). Within the error limits, which are depicted as hatched areas, best fits could be achieved with distributions ranging from isotropic (flat) up to slightly forward scattered with respect to the cyano radical beam. A flat distribution indicates that the lifetime of the decomposing complex is longer than its rotational period; the intensity of the poles of the slightly forward scattered distribution proposes that the lifetime of the fragmenting intermediate is at least 1.0–1.4 ps, i.e., a time comparable to the rotational period of the decomposing complex.<sup>53</sup> These findings are compiled in the flux contour plot (Fig. 3).

#### C. Potential energy surface

To guide the subsequent discussion of the underlying reaction mechanism and the chemical dynamics, it is useful

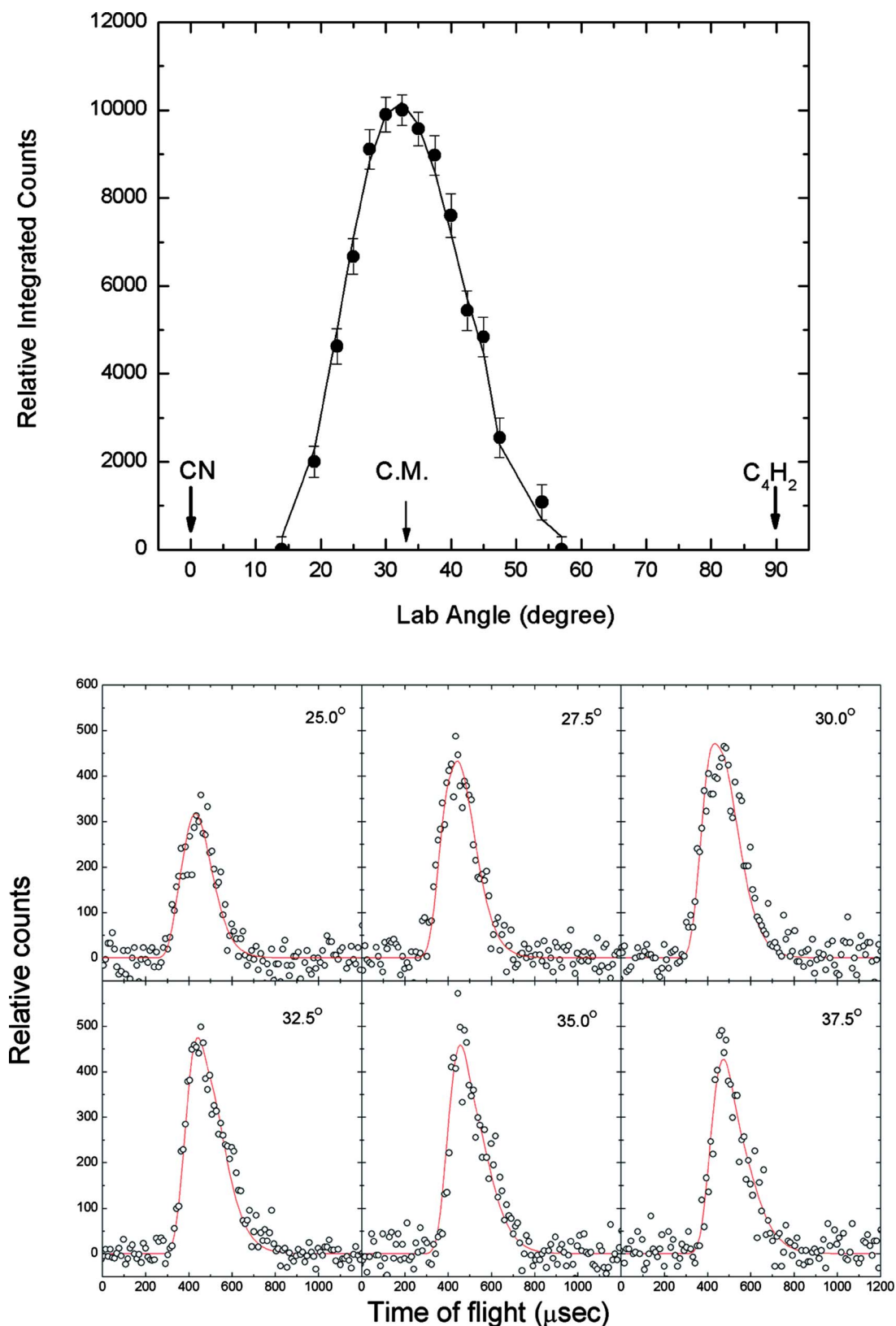


FIG. 1. (Color online) Top: Selected TOF data recorded at mass to charge ( $m/z$ ) of 75 ( $C_4HN^+$ ) in the reaction of cyano radicals with diacetylene. Bottom: Corresponding laboratory angular distribution of ion counts recorded at mass to charge ( $m/z$ ) of 75 ( $C_4HN^+$ ). In both figures, the circles are the experimental data and the solid lines the fits. CM defines the CM angle.

to discuss the computed  $H_2C_5N$  surface (Fig. 4). This enables us to combine the experimental with the theoretical data so that a comprehensive picture of the reaction mechanism emerges. The computations reveal the existence of two

low lying closed shell  $HC_5N$  isomers: the linear,  $C_{\infty v}$  symmetric cyanodiacetylene (HCCCCCN; [p1]) and isocyanodiacetylene molecules (HCCCCNC; [p2]). The cyanodiacetylene structure [p1] is lower in energy by  $112 \pm 5$   $\text{kJ mol}^{-1}$

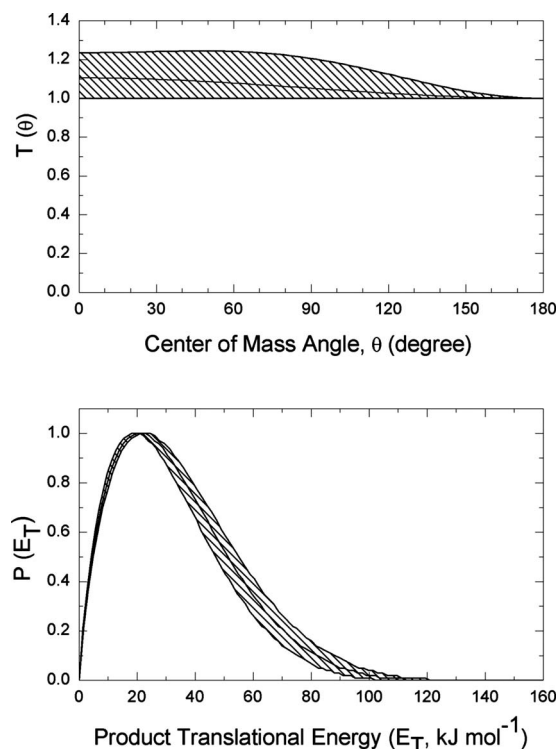


FIG. 2. CM translational (lower) and angular distributions (upper) of the cyanodiacetylene (HCCCCCN) product formed in the reaction of cyano radicals with diacetylene. The hatched areas account for the experimental error limits of the laboratory angular distribution as well as the peak velocity and speed ratio. The solid line presents the “best fit.”

compared to [p2]; this energy difference agrees nicely with a previous study computing  $100 \text{ kJ mol}^{-1}$ .<sup>54</sup> Therefore, the reaction pathway to [p2] is endoergic by  $32 \text{ kJ mol}^{-1}$ . Considering our collision energy of  $27.3 \text{ kJ mol}^{-1}$ , we conclude that isomer [p2] can neither be formed in our experiments nor in low temperature extraterrestrial environments such as in planetary atmospheres and cold molecular clouds. For completeness, it should be mentioned that three more isomers exist which are energetically even less favorable: HNC-CCCC [p3], CC(H)CCCN [p4], and CCCC(H)CN [p5] by  $255$ ,  $209$ , and  $206 \text{ kJ mol}^{-1}$  compared to cyanodiacetylene,

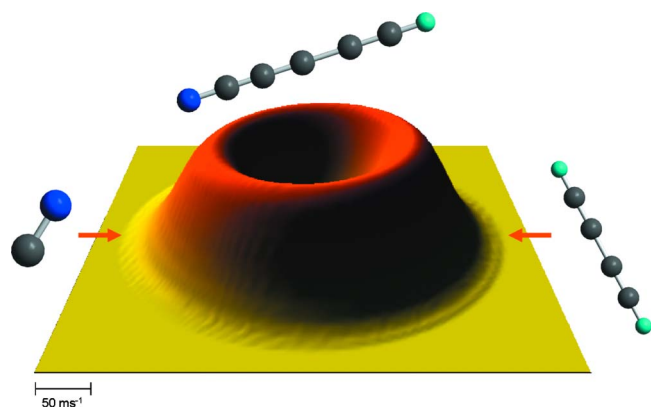


FIG. 3. (Color online) CM velocity contour flux map for the reaction of ground state cyano radicals (left;  $0^\circ$ ) with diacetylene (right;  $180^\circ$ ) forming atomic hydrogen plus the cyanodiacetylene molecule. The colors connect data points with an identical flux and range from highest flux (red) to lowest flux (yellow). The units of axis are given in  $\text{ms}^{-1}$  (see legend).

respectively. Hence, the following discussion focuses on the formation of the cyanodiacetylene molecule via the bimolecular reaction of cyano radicals with diacetylene. Three entrance channels were identified. The electron-deficient cyano radical can add without entrance barrier to the terminal carbon atom (C1), to the center carbon atom (C2), or to both C1 and C2 simultaneously. The electrophilic radical addition to the  $\pi$  system leads to doublet radical intermediates [1], [2], and [3], respectively. Here, isomer [1] is the lowest in energy and stabilized by  $251 \text{ kJ mol}^{-1}$  with respect to the separated reactants. The cyclic structure [2] is formally an intermediate which also can be accessed via the cyano group migration from C1 (in [1]) via [3] to the C2 atom (in [2]). All barriers involved are lower in energy than the cyano and diacetylene reactants. A C1–C2 hydrogen shift in [1] leads to a fourth  $\text{H}_2\text{C}_5\text{N}$  isomer: structure [4]. Both intermediates [1] and [4] can emit a hydrogen atom via tight exit transition states located  $20$  and  $25 \text{ kJ mol}^{-1}$  above the separated products, respectively. Other isomerization channels shown in Fig. 4 do not compete with the hydrogen loss from [1] and [4] owing to much higher barriers. For instance, consecutive 1,2-H shifts in [4] in the direction of the terminal CH group can lead to intermediates [5] and [6], whereas 1,2-hydrogen migrations in [1] toward the nitrogen atom can produce [7] and then [8]. All isomers [5]–[8] can serve as precursors for the formation of the main reaction product, cyanodiacetylene, by hydrogen elimination; however, none of them are likely to be accessed in this reaction because, at each step, the hydrogen loss barrier is significantly lower than the barrier for the hydrogen shift. Isomer [3] could rearrange to [5] via a four-member ring intermediate [9] by ring closure–ring opening processes, but the corresponding transition states reside  $21 \text{ kJ mol}^{-1}$  above the initial reactants, rendering such rearrangement uncompetitive. Note finally that the cyano versus ethynyl exchange [reaction (2)] and the hydrogen abstraction channel [reaction (3)] were found to be endoergic by  $40$  and  $33 \text{ kJ mol}^{-1}$ .

## D. Combination of experimental and theoretical data

The combination of the crossed molecular beams data and the electronic structure calculations provides a comprehensive picture of the underlying reaction mechanism. First of all, let us consider the energetics of the reaction. The experimentally derived reaction energy of  $-87 \pm 15 \text{ kJ mol}^{-1}$  agrees very well with the computed data to form the cyanodiacetylene isomer [p1] plus a hydrogen atom ( $-79 \pm 5 \text{ kJ mol}^{-1}$ ). Based on these energetical constraints, the isocyanodiacetylene isomer [p2] cannot be formed since this reaction would be too endoergic. Consequently, the cyanodiacetylene molecule is the sole molecular product of the bimolecular gas phase reaction of cyano radicals with diacetylene in our experiment, in hydrocarbon-rich atmospheres of planets and their satellites, and in the interstellar medium. We would like to propose the following reaction mechanism to form this important molecule. Dictated by a barrierless addition with its unpaired electron at the carbon atom, the cyano radical adds to the carbon-carbon triple bond of the diacetylene molecule leading to the  $\text{H}_2\text{C}_5\text{N}$

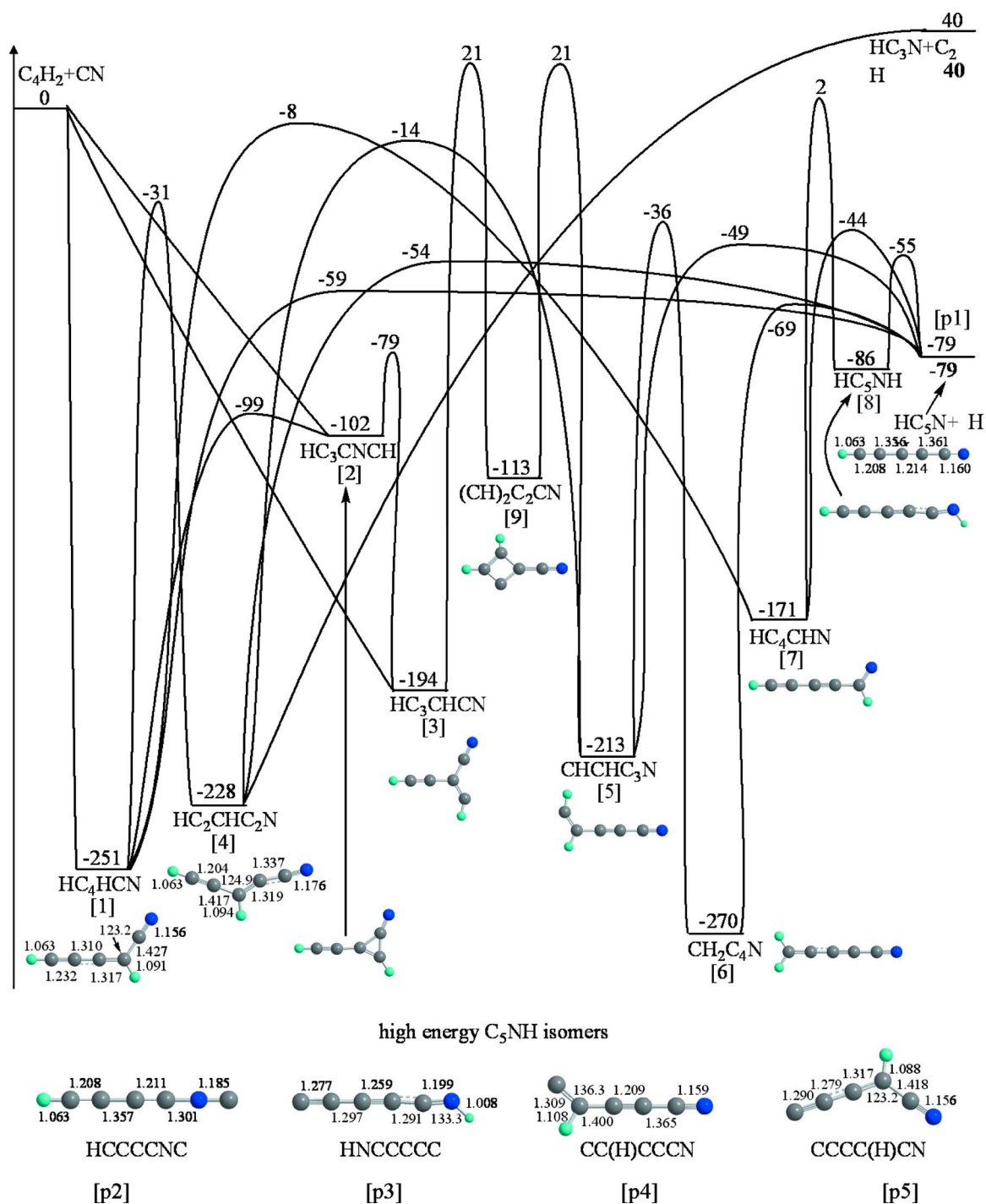


FIG. 4. (Color online) PES of the reaction of cyano radicals with diacetylene molecules under single collision conditions to form cyanodiacetylene in low temperature environments computed at the CCSD(T)/cc-pVTZ//B3LYP/6-311G\*\* level of theory. Relative energies are given with respect to the separated reactants in  $\text{kJ mol}^{-1}$ . Bold numbers show relative energies of the products calculated at the CCSD(T)/CBS/B3LYP/6-311G\*\* level. The accuracy of all energies is expected to be  $\pm 5 \text{ kJ mol}^{-1}$ . Also shown are the structures of higher energy isomers of cyanodiacetylene. Bond angles and lengths are given in degrees and angstrom, respectively, for selected species (Ref. 57).

intermediates [1], [2], and/or [3]. The barrierless addition suggests that large impact parameters dominate the formation of the reaction intermediate.<sup>52</sup> This likely results in a preferential formation of [1] via addition to the terminal (C1) carbon atom of the diacetylene molecule. The indirect nature of this process was verified by the CM angular distribution and flux contour map (Figs. 2 and 3, respectively) which depict flux over the complete angular range. Also, the fraction of available energy channeling into the translational de-

grees of freedom of the reaction products of  $30(\pm 5\%)$  suggested indirect scattering dynamics via reaction intermediate(s). What is the fate of these reaction intermediates? The structure of the cyclic intermediate [2] cannot lead within one step to the cyanodiacetylene reaction product. The calculations suggest that [2] isomerizes via ring opening to [1] and/or [3]. Considering the inherent barriers to rearrangement of 23 and 3  $\text{kJ mol}^{-1}$ , it is likely that [2] rearranges preferentially to intermediate [1]. Intermediate [3] it-

self can either fragment back to the initial reactants or isomerize to [2] which in turn yields [1]. Since the barrierless entry channel is far above the barriers to rearrangement from the intermediates, the hydrogen atom might migrate fairly freely in the intermediates involved. Nevertheless, all initial reaction intermediates yield eventually isomer [1]. The latter can either undergo a hydrogen migration to form [4] or decomposes via hydrogen elimination. This process involves a tight exit barrier and a transition state located 20 kJ mol<sup>-1</sup> above the final products. The tight nature of an exit transition state is also supported by the distribution maximum of the CM translational energy distribution peaking at about 20 kJ mol<sup>-1</sup>. Therefore, both the electronic structure calculations and the experiments support the existence of a tight exit transition state. In other words, the reversed reaction of an addition of a hydrogen atom to a carbon-carbon triple bond of a closed shell molecule involves an entrance barrier. The magnitude of this barrier is close to the one of 18 kJ mol<sup>-1</sup> documented in the addition of a hydrogen atom to acetylene forming the vinyl radical.<sup>55</sup> For completeness, it should be mentioned that [4] could also decompose to the cyanodiacetylene product. However, [4] can only be formed via hydrogen shift from [1]. Considering the barriers involved in the hydrogen migration from [1] versus the unimolecular decomposition of [1] to cyanodiacetylene plus a hydrogen atom, we expect that [1] fragments preferentially to cyanodiacetylene. Our statistical calculations confirm this deduction. 96.7% of cyanodiacetylene was found to be formed via unimolecular decomposition of intermediate [1].

## V. CONCLUSIONS

We have presented a combined crossed molecular beams and *ab initio* study on the bimolecular gas phase reaction of cyano radicals with diacetylene. A key aspect of this study is the determination of the reaction mechanism of an open shell radical reactant and the elucidation of the primary reaction products under single collision conditions *excluding* secondary wall effects. The reaction was found to be barrierless and is initiated by an addition of the cyano radical to the carbon-carbon triple bond of the diacetylene reactant. Some reaction intermediates isomerize to yield ultimately a C<sub>s</sub> symmetric doublet HCCCCHCN structure. The latter underwent unimolecular decomposition on the ground state surface to form the linear cyanodiacetylene molecule (HCCCCCN) via a tight exit transition state. Cyanodiacetylene presented the *sole* reaction product. Since the reaction is barrierless and exoergic (by about 80–90 kJ mol<sup>-1</sup>) and all involved transition states are lower in energy than the separated reactants, bimolecular reactions of cyano radicals with diacetylene can form cyanodiacetylene in the interstellar medium and in the atmosphere of Saturn's moon Titan, thus providing a vital ingredient in the chemical evolution of Titan's organic haze layers. The cyanodiacetylene molecule may react with yet another cyano radical through a hydrogen replacement mechanism to synthesize dicyanodiacetylene (NCCCCCN)—a crucial condensable species supposed to exist on Titan.<sup>56</sup> Supporting information contains B3LYP and CCSD(T) calculated total energies at 0 K, ZPE corrections,

B3LYP/6-311G\*\* optimized Cartesian coordinates, unscaled vibrational frequencies ( $\nu_i$ ), moments of inertia ( $I_i$ ), and rotational constants ( $B_i$ ) of all species involved in the reaction (Table S1).

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