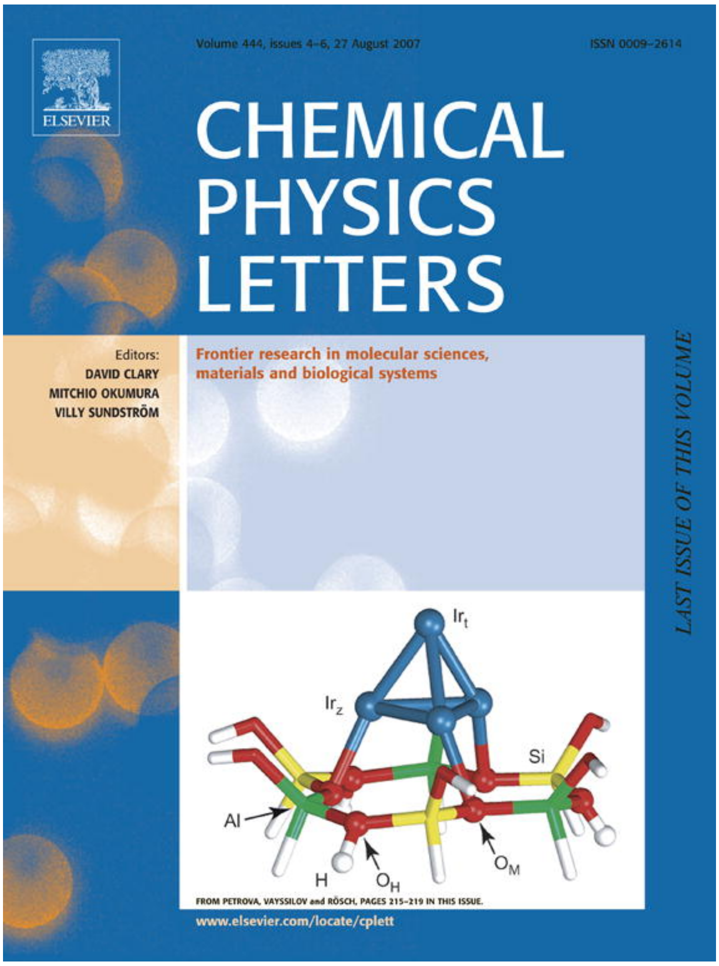
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Unimolecular decomposition of chemically activated singlet and triplet D3-methyldiacetylene molecules

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Abstract

The reaction dynamics of the dicarbon molecule with D3-methylacetylene, $CD_3CCH(X^1A_1)$, were investigated utilizing the crossed molecular beams approach. By combining the experimental results on the atomic hydrogen versus deuterium loss channels with electronic structure calculations, we could substantiate that the $D_3CCCCC(X^2A)$ radical is neither formed on the singlet nor on the triplet surface. Secondly, the isotopic studies showed explicitly that on the triplet surface, only the 2,4-pentadiynyl-1 radical – detected via its isotopomer [$C_5HD_2(X^2B_1)$; $HCCCCCD_2$] – was synthesized. On the singlet surface, both the 2,4-pentadiynyl-1 [$C_5HD_2(X^2B_1)$, $HCCCCCD_2$] and 1,4-pentadiynyl-3 radical [$C_5HD_2(X^2B_1)$ HCCCDCCD] can account for the experimental data.
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1. Introduction

During the last years, the chemistry of methyldiacetylene, $CH_3CCCCH(X^1A_1)$, has received particular attention due to the importance of this molecule in combustion processes [1], astrochemistry [2], and the chemical evolution of the atmosphere of Saturn's moon Titan [3]. Methyldiacetylene is considered as a precursor to the formation of complex polycyclic aromatic hydrocarbons (PAHs) and their methyl-substituted counterparts and was first observed in the Taurus Molecular Cloud-1 via microwave spectroscopy [4] followed by an infrared spectroscopic detection towards the planetary nebula CRL 618 [5]. The presence of this molecule shows that long carbon chain species in the interstellar medium can be built with a terminal methyl group. Compared to the related methylacetylene molecule, the abundance of methyldiacetylene decreases with increasing complexity; in TMC-1, methylacetylene to methyldiacetylene ratios were determined to be about four suggesting that the CH_3CCH (X^1A_1) species might be actually a precursor to the interstellar CH_3CCCCH (X^1A_1) molecule [6].

Although the synthetic routes to methyldiacetylene in these extreme environments have been resolved and are expected to proceed via the of reaction of ethynyl radicals (C_2H; $X^2\Sigma^+$) with methylacetylene $CH_3CCH(X^1A_1)$ [7,8], the unimolecular decomposition and hence the inherent stability of the methyldiacetylene molecule has not been fully understood. The unimolecular decomposition of singlet and triplet methyldiacetylene were probed by accessing the triplet and singlet C_5H_4 surfaces via the reaction of $C_2(X^1\Sigma_g^+/a^3\Pi_u)$ with methylacetylene (CH_3CCH (X^1A_1)) [9,10]. These studies suggested the formation of two radicals: 2,4-pentadiynyl-1 [$C_5H_3(X^2B_1)$; $HCCCCCH_2$] and 1, 4-pentadiynyl-3[$C_5H_3(X^2B_1)$; HCCCHCCH] (Fig. 1). However, a couple of questions have remained unanswered. First, it was not feasible to elucidate to what extent a third isomer, $H_3CCCCC(X^2A)$, was formed. Secondly, the authors could not unravel explicitly if the $C_5H_3(X^2B_1)$ radicals were synthesized on the singlet and/or triplet surfaces. In an attempt to solve these open questions, we conducted a crossed beams study of the reaction of singlet and triplet dicarbon with partially deuterated D3-methylacetylene

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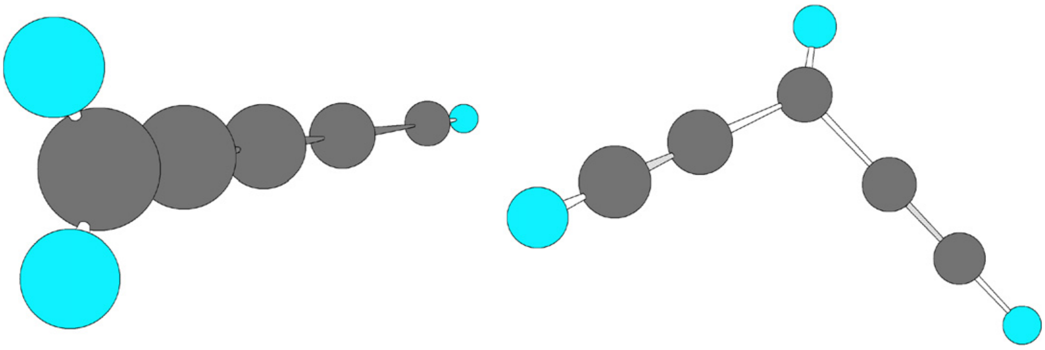

Fig. 1. Structures of the 2,4-pentadiynyl-1 [$C_5H_3(X^2B_1)$; $HCCCCCH_2$] and 1,4-pentadiynyl-3 [$C_5H_3(X^2B_1)$; HCCCHCCH] radicals.

(CD_3CCH). Replacing the hydrogen at the methyl group by deuterium and combining the experimental results with electronic structure calculations [11], allows us to verify and/or eliminate distinct reaction pathways and the contribution of various C_5HD_2 and/or C_5D_3 isomers. A similar approach employing partially deuterated reactants has been utilized previously to successfully identify the position of the atomic hydrogen versus deuterium loss in the reactions of D3-methylacetylene with, for instance, the cyano radical [12] and ground state carbon atoms [13].

2. Experimental setup and data analysis

The crossed beams experiments were carried out under single collision conditions in a crossed molecular beams machine at The University of Hawai'i [14]. Briefly, pulsed dicarbon beams were obtained in the primary source via laser ablation of graphite at 266 nm [15] (30 Hz). The ablated species were seeded in neat carrier gas at 4 atm backing pressure (neon and helium; 99.9999%) which are released by a Proch–Trickl pulsed valve [16]. After passing a skimmer, a four-slot chopper wheel picked a part of the dicarbon beam holding peak velocities v_p of 2076 ± 31 and a speed ratio of 3.8 ± 0.3. Note that at this velocity, the beam contains dicarbon in its $X^1\Sigma_g^+$ electronic ground and in its first excited $a^3\Pi_u$ state; the energy separation between both states is only 8.6 kJ mol^{-1}; we acknowledge that the ratio between the singlet and triplet states is currently unknown. The dicarbon beam intersects a pulsed D3-methylacetylene beam (CD_3CCH; 99% deuterium enrichment; 300 torr; $v_p = 830\ ms^{-1}$) released by a second pulsed valve perpendicularly under a well-defined collision energy at 38.5 ± 1.1 kJ mol^{-1} in the interaction region. The ablation beam contains also carbon atoms and tricarbon molecules. However, the latter do not interfere with the scattering signal of the dicarbon – D3-methylacetylene reaction since tricarbon reacts with methylacetylene only at collision energies larger than 45 ± 5 kJ mol^{-1} [17]. Signal from the reaction of carbon atoms with methylacetylene is only present at m/z values of 53 $C_4HD_2^+$ and lower [18]. The reactively scattered species are monitored using a triply differentially pumped quadrupole mass spectrometric detector in the time-of-flight (TOF) mode at distinct laboratory angles after electron-impact ionization of the molecules [14]. Information on the chemical dynamics was extracted by fitting the laboratory data using a forward-convolution routine described in Ref. [19] in detail. This method initially presumes an angular distribution $T(\theta)$ and a translational energy distribution $P(E_T)$ in the center-of-mass reference frame (CM). TOF spectra and the laboratory angular distribution are then calculated from these center-of-mass functions. The ultimate result is the generation of a product flux contour map which states the differential cross section, $I(\theta, u) \sim T(\theta) \times P(u)$, of the product as the intensity as a function of angle θ and product center-of-mass velocity u. This map serves as an image of the scattering process.

3. Results

3.1. Laboratory data: reactive scattering signal, TOF spectra, angular distribution

To determine whether the hydrogen atom is released from the methyl group or from the acetylenic carbon atom, we conducted experiments utilizing D3-methylacetylene (CD_3CCH). Here, we expected to observe signal at $m/z = 65$ ($C_5D_2H^+$) and/or at $m/z = 66$ ($C_5D_3^+$) in case of a deuterium and hydrogen atom losses, respectively. Most important, $m/z = 66$ cannot fragment to $m/z = 65$, but only to $m/z = 64$ ($C_5D_2^+$). Therefore, this approach should enable us to resolve the position of the hydrogen versus deuterium loss. In our experiments, we detected signal only at $m/z = 65$ ($C_5D_2H^+$), but not at $m/z = 66$ ($C_5D_3^+$) confirming experimentally that – in case of the dicarbon – methylacetylene reaction – the emitted hydrogen atom originates from the methyl group (Fig. 2). We can integrate the collected TOF spectra and extract the laboratory angular distribution (LAB) which reports the integrated intensity (total ion counts) of an ion at a distinct m/z value (here: $m/z = 65$) versus the laboratory angle (Fig. 2). The LAB distribution has a rather small angular spread of only 45° in the scattering plane. This finding indicates that only a relatively small fraction of the available energy is released as translational motion of the C_5HD_2 molecule(s) plus the deuterium atom.

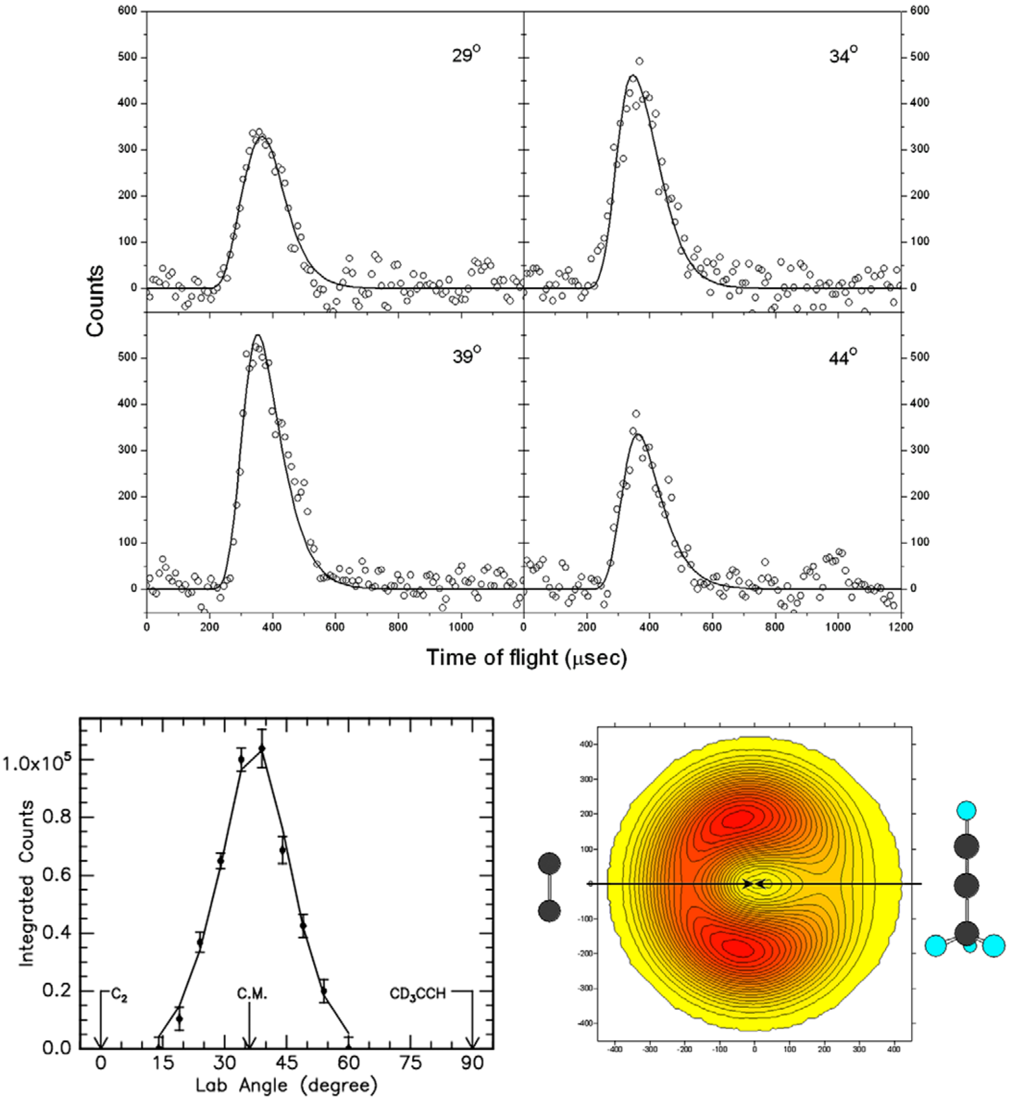

Fig. 2. Selected time-of-flight spectra for $m/z = 65$ ($C_5D_2H^+$) recorded at a collision energy of 37.6 kJ mol^{-1}. Circles and error bars indicate experimental data, the solid line the calculated distribution with the best-fit center-of-mass functions. The corresponding laboratory angular distribution of the C_5D_2H radical(s) recorded at $m/z = 65$ is also shown. The circles and error bars indicate experimental data, the solid line the calculated distribution with the best-fit center-of-mass functions. The flux contour plot of the C_5D_3H radical is also shown.

3.2. Center-of-mass translational energy, $P(E_T)$s, and angular distributions, $T(\theta)$s

Best fits of the TOF spectra and of the LAB distributions of the C_5D_2H product were achieved with corresponding translational energies extending to a maximum, E_{max}, of about 210 kJ mol^{-1}. It is worth mentioning that due to the emission of a light deuterium atom, the fits are relatively insensitive to the high energy cut-off; extending or cutting the tail by ±15 kJ mol^{-1} did not influence the quality of the fit. Recall that the maximum translational energy determined by represents the sum of the collision energy plus the reaction energy. Therefore, E_{max} allows us to determine reaction exoergicity. Therefore, we determine that the formation of the C_5HD_2 radical(s) and atomic hydrogen is exoergic by 172 ± 15 kJ mol^{-1}. We should mention that in the most favorable situation, the most probable translational energy represents the order-of-magnitude of the barrier height in the exit channel [17]. Here, the flux contour map shows a plateau between 15 and 40 kJ mol^{-1}. This might suggest the existence of at least one microchannel which involves an exit barrier and hence a relatively tight exit transition state. Compared to the reaction of dicarbon with methylacetylene at a similar collision energy [10], the angular parts of the flux contour maps are similar. The distribution depicts intensity over the entire angular range from 0° to 180° implying indirect reaction dynamics and the involvement of C_5HD_3 complex(es). Also, the weak polarization is associated with an insignificant correlation between the initial and final angular momentum and the inability of the light hydrogen to carry away a significant fraction of the orbital angular momentum. Therefore, the total angular momentum is released preferentially as rotational excitation of the C_5HD_2 product(s). Note that the sideways-peaking of the contour map indicates geometrical constraints in the exit channel, i.e. the emission of a deuterium atom.

4. Discussion

Recall that the main goals of this study are twofold. First, we are eager to elucidate to what extent a third isomer, $H_3CCCCC(X^2A)$, in addition to the previously observed isomers was formed. Secondly, our experiments aimed to expose if the 2,4-pentadiynyl-1 [$C_5H_3(X^2B_1)$; $HCCCCCH_2$] and 1,4-pentadiynyl-3 [$C_5H_3(X^2B_1)$; HCCCHCCH] radicals are formed on the singlet and/or triplet C_5H_3 surfaces. Considering the existence of a third C_5H_3 isomer, the results of the crossed beams experiments utilizing D3-methylacetylene allow us to dismiss the formation of the $D_3CCCCC(X^2A)$ isomer; recall that no signal was observed at $m/z = 66$ ($C_5D_3^+$). Based on the involved potential energy surfaces (Fig. 3), $D_3CCCCC(X^2A)$ can only be formed via a hydrogen atom loss from a singlet methyldiacetylene intermediate **s3** or on the triplet surface via a hydrogen atom ejection from **t2**, **t6**, or **t7**. However, in case of the CD_3CCH reactant, the fragmentation of each of the C_5D_3H intermediates would form solely D_3CCCCC (X^2A) through a hydrogen atom emission to form a C_5D_3 isotopomer ($m/z = 66$). However, experimentally, we only detected signal at $m/z = 65$ (C_5D_2H), but not at $m/z = 66$. This verifies explicitly that the released atom is a deuterium atom. On the singlet surface, the formation of the $D_3CCCCC(X^2A)$ isomer requires the existence of a methyldiacetylene intermediate **s3**. Considering partially deuterated methylacetylene (D3-methylacetylene), this translates into a CD_3CCCCH structure which loses a hydrogen atom to form $D_3CCCCC(X^2A)$. Since only a deuterium loss was observed experimentally, we can exclude the formation of D_3CCCCC (X^2A) on the singlet surface. As outlined previously, on the triplet surface, the synthesis of the $D_3CCCCC(X^2A)$ isomer must involve the presence of intermediates **t2**, **t6**, or **t7**. Again, in case of a D3-methylacetylene reactant (CD_3CCH), this process would lead to the emission of a hydrogen atom from the acetylenic group giving signal solely at $D_3CCCCC(X^2A)$. Similar to the singlet surface, no hydrogen emission was observed, and the formation of $D_3CCCCC(X^2A)$ can be ruled out.

The exclusion of the hydrogen loss pathway has further implications for the triplet surface (Fig. 3) and helps us to determine which of the isomers 2,4-pentadiynyl-1 [$C_5H_3(X^2B_1)$; $HCCCCCH_2$] and 1,4-pentadiynyl-3 [$C_5H_3(X^2B_1)$; HCCCHCCH] (or both) are formed. The electronic structure calculations suggest that intermediate **t8** can be only formed via hydrogen shift from **t3**. Due to similar energetics and exit barriers which differ by only 1–4 kJ mol^{-1}, **t8** should decompose to the 2,4-pentadiynyl-1 [$C_5H_3(X^2B_1)$, $HCCCCCH_2$] and to the 1,4-pentadiynyl-3 [$C_5H_3(X^2B_1)$, HCCCHCCH] radical. In case of the D3-methylacetylene (CD_3CCH) reactant this would translate to the formation of a $D_2CCCHCCD$ **t8** transient species synthesized via a deuterium atom migration from a D3-substituted **t3** isomer to **t8**. A fragmentation of $D_2CCCHCCD$ (**t8**) should yield the d3-2,4-pentadiynyl-1 [C_5D_3, $DCCCCCD_2$] and d2-1,4-pentadiynyl-3 [C_5HD_2, DCCCHCCD] via atomic hydrogen or deuterium emission, respectively. However, since no hydrogen elimination was observed, we can conclude that the reaction does not proceed via **t8**. This could be rationalized considering the pertinent part of the underlying triplet potential energy surface. The formation of **t8** requires the rearrangement of **t3** via a barrier located about 137 kJ mol^{-1} above **t3**. On the other hand, a second pathway to form the partially deuterated isotopomer of the 2,4-pentadiynyl-1 radical [$C_5H_3(X^2B_1)$, $HCCCCCH_2$], i.e. D2-2,4-pentadiynyl-1 [C_5D_2H, $HCCCCCD_2$], can proceed via the reaction (**t3 → t2 → t1 → t4 → t5 → t6 → t7**). Here, the critical, rate-determining transition state for the **t4 → t5** isomerization has a similar energy, −58.2 kJ mol^{-1} relative to the initial reactants, as the transition state for the **t3 → t8** rearrangement, −56.7 kJ mol^{-1}. In order to evaluate relative importance of the two reaction channels, we calculated RRKM rate constants for the processes starting from the common intermediate **t3** and passing through the critical transition states. The results show that the reaction leading to $HCCCCCH_2 + H$ via the **t4 → t5** TS is 6.2 times faster than that leading to $HCCCCCH_2$/$HCCCHCCH + H$ via TS **t3 → t8** at collision energies of 0–50 kJ mol^{-1}. Although the two critical transition states have similar energies, the **t4 → t5** TS involving a ring opening process is much looser than the **t3 → t8** TS for H migration. Indeed, the four lowest calculated real vibrational frequencies for the former are 152, 228, 264, and 356 cm^{-1} as compared to 316, 388, 408, and 483 cm^{-1} for the latter. This makes the number of vibrational states for the **t4 → t5** TS significantly higher than that for the **t3 → t8** TS and thus leads to higher rate constants for the former process. As a result, the pathway via **t4 → t5** to **t7** is significantly more favorable than that via **t3 → t8**, 86% vs. 14%, and we expect that $HCCCCCD_2$ formed by D elimination from **t7** should be the dominant reaction product. The decomposition of **t7** to the D2-2,4-pentadiynyl-1 radical [$C_4D_2H(X^2B_1)$ $D_2CCCCCH$] can account for the deuterium loss pathway. Although a minor amount of C_5H_3 products could be formed by the H loss from **t8** (a fraction of 14%), they were not detected in the experiments. Summarized, on the triplet potential energy surface of the dicarbon with D3-methylacetylene reaction, the thermodynamically more stable 2,4-pentadiynyl-1 radical [$C_5HD_2(X^2B_1)$ $D_2CCCCCH$] presents the only observable C_5HD_2 isomer. It should be noted that the flux contour map shows a pronounced sideways-peaking. This means that the deuterium atom is emitted preferentially almost parallel to the total angular momentum vector. The experimentally found geometrical constraints are verified by electronic structure calculations depicting a $H_2CC–H$ angle

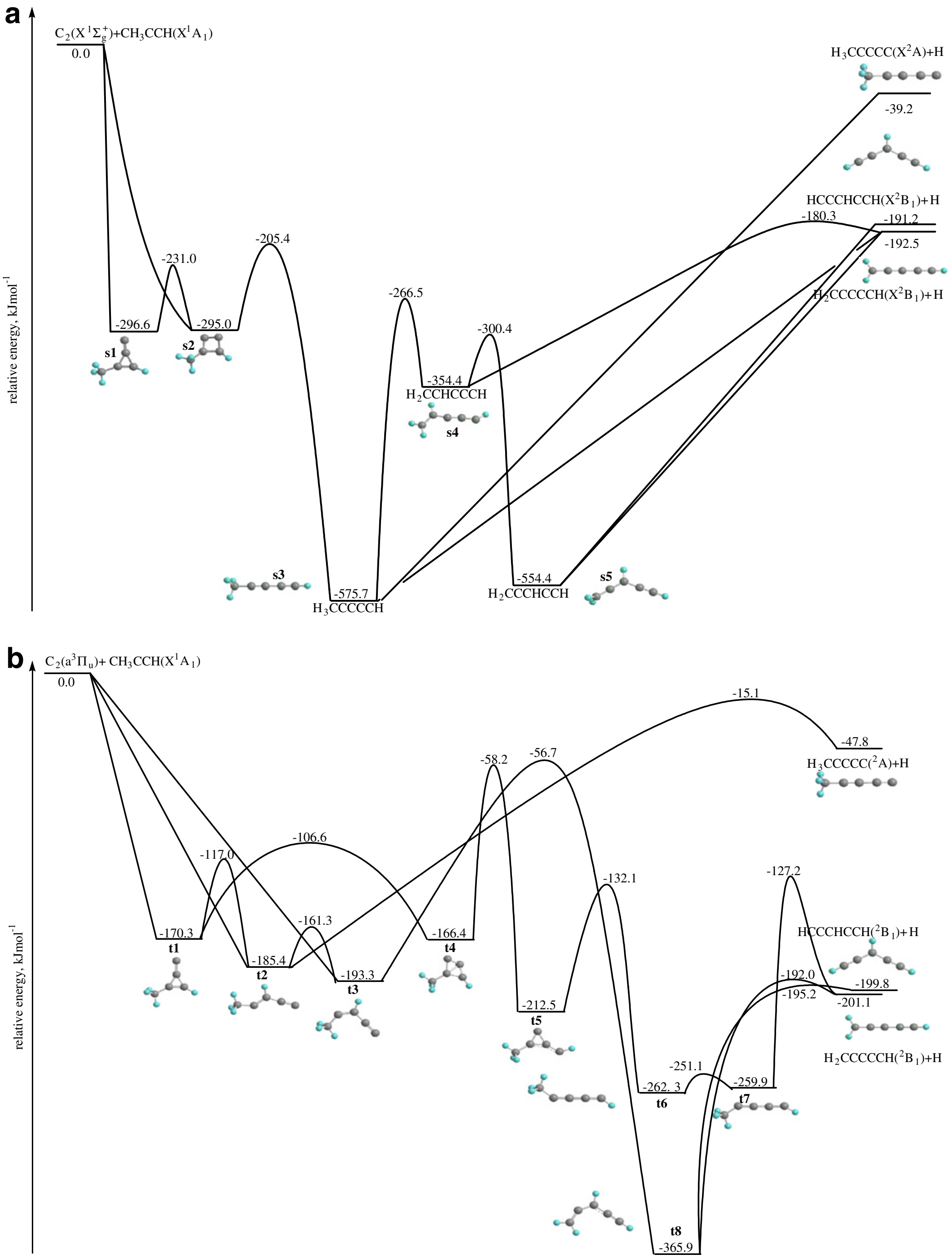

Fig. 3. Simplified singlet (top) and triplet (bottom) C_5H_4 potential energy surfaces involving atomic hydrogen loss pathways in the reaction of dicarbon, $C_2(X^1\Sigma_g^+/a^3\Pi_u)$, with methylacetylene to form C_5H_3 extracted from Refs. [12,13].

of about 79° [11]. Similar geometrical constraints were found in the CN/C_6H_6 [20], CN/C_2H_4 [21], F/C_6D_6 [22], and F/C_2D_4 [23] systems.

Can our studies also shed light on which isomer is formed on the singlet surface? We combine the information from the contour map with the computed potential energy surfaces to resolve this question. Recall that the center-of-mass angular distributions suggest indirect scattering dynamics and hence the existence of C_5HD_3 intermediate(s). On the singlet surface, the calculations indicate that the addition of dicarbon to the carbon–carbon triple bond of the methylacetylene is barrier-less and forms cyclic intermediates **s1** and/or **s2**; both structures can be interconverted via a low barrier located only 66 kJ mol^{-1} above **s1**. Intermediate **s2** can undergo ring opening to the D3-methyldiacetylene molecule **s3**. The latter either isomerizes via **s4** to **s5** or loses a hydrogen atom to form the 2,4-pentadiynyl-1 radical [$C_5HD_2(X^2B_1)$, $HCCCCCD_2$] via a loose transition state. Note that **s4** also correlates with the 2,4-pentadiynyl-1 radical plus atomic hydrogen; however, this hydrogen emission would involve a tighter transition state located 12 kJ mol^{-1} above the separated products so that this pathways becomes unfavorable. The two lowest calculated vibrational frequencies for this transition state are in the range of 150 cm^{-1}, while those for loose variational transition state for an atomic hydrogen loss from **s3** and **s5** are typically below 100 cm^{-1}. This fact, in conjunction with the higher energy of the transition state for an atomic hydrogen elimination from **s4**, makes the rate constant for an atomic hydrogen loss via this intermediate much lower than those for direct processes from **s3** and **s5**. Note that the reversed reaction would involve an addition of a hydrogen atom to a carbon–carbon triple bond of the 2,4-pentadiynyl-1 radical, but not a reaction with the radical center; this can account for the exit barrier. On the other hand, the exit transition states to form the 2,4-pentadiynyl-1 radical and the 1,4-pentadiynyl-3 radicals from **s5** are both loose; therefore, a decomposing intermediate **s5** is expected to form both $C_5HD_2(X^2B_1)$ radicals. The RRKM calculations confirm these conclusions and predict a ratio of the 2,4-pentadiynyl-1 versus 1,4-pentadiynyl-3 radical of about 2:1.

5. Conclusions

The reaction dynamics of the dicarbon molecule C_2 in the $^1\Sigma_g^+$ singlet ground state and $^3\Pi_u$ first excited triplet state with D3-methylacetylene were investigated under single collision conditions utilizing the crossed molecular beams approach. By combining the experiments results on the atomic hydrogen versus deuterium loss with previous electronic structure calculations, we could verify that the $D_3CCCCC(X^2A)$ radical is formed neither on the singlet nor triplet surfaces. Secondly, the isotopic studies showed explicitly that on the triplet surface, only the 2,4-pentadiynyl-1 radical – detected via its isotopomer – [$C_5HD_2(X^2B_1)$; $HCCCCCD_2$] was synthesized. On the singlet surface, both the 2,4-pentadiynyl-1 [$C_5HD_2(X^2B_1)$, $HCCCCCD_2$] and 1,4-pentadiynyl-3 radical [$C_5HD_2(X^2B_1)$ HCCCDCCD] can account for the experimental data.

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