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# A combined crossed molecular beams and computational study on the formation of distinct resonantly stabilized $C_5H_3$ radicals *via* chemically activated $C_5H_4$ and $C_6H_6$ intermediates†

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The crossed molecular beams technique was utilized to explore the formation of three isomers of resonantly stabilized ( $C_5H_3$ ) radicals along with their  $d_2$ -substituted counterparts *via* the bimolecular reactions of singlet/triplet dicarbon [ $C_2(X^1\Sigma_g^+/a^3\Pi_u)$ ] with methylacetylene [ $CH_3CCH(X^1A_1)$ ],  $d_3$ -methylacetylene [ $CD_3CCH(X^1A_1)$ ], and 1-butyne [ $C_2H_5CCH(X^1A')$ ] at collision energies up to 26 kJ mol<sup>-1</sup> *via* chemically activated singlet/triplet  $C_5H_4/C_5D_3H$  and  $C_6H_6$  intermediates. These studies exploit a newly developed supersonic dicarbon [ $C_2(X^1\Sigma_g^+/a^3\Pi_u)$ ] beam generated *via* photolysis of tetrachloroethylene [ $C_2Cl_4(X^1A_g)$ ] by excluding interference from carbon atoms, which represent the dominating (interfering) species in ablation-based dicarbon sources. We evaluated the performance of the dicarbon [ $C_2(X^1\Sigma_g^+/a^3\Pi_u)$ ] beam in reactions with methylacetylene [ $CH_3CCH(X^1A_1)$ ] and  $d_3$ -methylacetylene [ $CD_3CCH(X^1A_1)$ ]; the investigations demonstrate that the reaction dynamics match previous studies in our laboratory utilizing ablation-based dicarbon sources involving the synthesis of 1,4-pentadiynyl-3 [ $HCCCHCCH(X^2B_1)$ ] and 2,4-pentadiynyl-1 [ $H_2CCCCCH(X^2B_1)$ ] radicals *via* hydrogen (deuterium) atom elimination. Considering the  $C_2(X^1\Sigma_g^+/a^3\Pi_u)$ -1-butyne [ $C_2H_5CCH(X^1A')$ ] reaction, the hitherto elusive methyl-loss pathway was detected. This channel forms the previously unknown resonantly stabilized penta-1-yn-3,4-dienyl-1 [ $H_2CCCHCC(X^2A)$ ] radical along with the methyl radical [ $CH_3(X^2A_2'')$ ] and is open exclusively on the triplet surface with an overall reaction energy of  $-86 \pm 10$  kJ mol<sup>-1</sup>. The preferred reaction pathways proceed first by barrierless addition of triplet dicarbon to the  $\pi$ -electronic system of 1-butyne, either to both acetylenic carbon atoms or to the sterically more accessible carbon atom, to form the methyl-bearing triplet  $C_6H_6$  intermediates [**i4<sub>1b</sub>**] and [**i8<sub>1b</sub>**], respectively, with the latter decomposing *via* a tight exit transition state to penta-1-yn-3,4-dienyl-1 [ $H_2CCCHCC(X^2A)$ ] plus the methyl radical [ $CH_3(X^2A_2'')$ ]. The successful unraveling of this methyl-loss channel – through collaborative experimental and computational efforts – underscores the viability of the photolytically generated dicarbon beam as an unprecedented tool to access reaction dynamics underlying the formation of resonantly stabilized free radicals (RSFR) that are vital to molecular mass growth processes that ultimately lead to polycyclic aromatic hydrocarbons (PAHs).

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## 1. Introduction

During the last decades, reactions of the dicarbon molecule ( $C_2$ ), which has been detected in combustion flames,<sup>1–3</sup> cometary comae,<sup>4,5</sup> and in the interstellar medium (ISM),<sup>6,7</sup> with unsaturated

hydrocarbons have received considerable attention due to its role as a key reactant in gas phase molecular growth processes. These can lead to polyynes ( $C_{2n}H_2$ ) along with their radicals ( $C_{2n}H$ ), resonantly stabilized free radicals (RSFRs), and ultimately to polycyclic aromatic hydrocarbons (PAHs) through the production of open shell reaction intermediates formed *via* bimolecular collisions characterized by barrierless entrance channels and overall exoergic pathways. Strong transitions from its electronic ground  $X^1\Sigma_g^+$  and first excited  $a^3\Pi_u$  states have made dicarbon a tracer for determining chemical rate constants,<sup>8</sup> measuring stellar temperatures and composition,<sup>9–11</sup> and unraveling the molecular complexity of macrostructures like cold clouds<sup>12</sup> and

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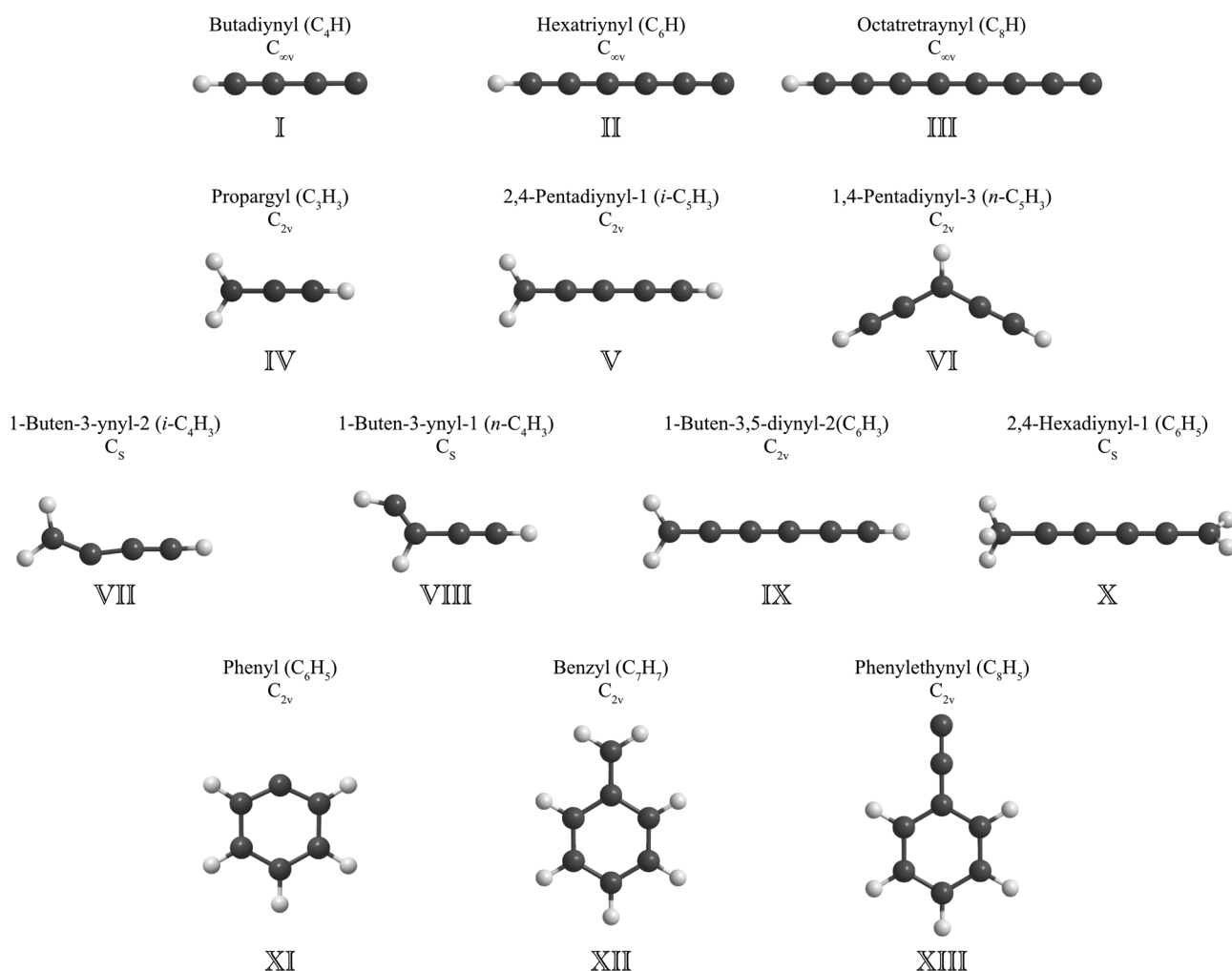
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protoplanetary nebulae.<sup>13,14</sup> Consequently, the formation,<sup>15–17</sup> structure,<sup>18–20</sup> and reactivity<sup>21–23</sup> of dicarbon remains of broad interest as evidenced by the continued expansion of the kinetics and chemical dynamics underscoring dicarbon reactivity.

More specifically, dicarbon is instrumental in the growth of polyynes ( $C_{2n}H_2$ ) and their radicals through addition mechanisms *via* the  $C_2 + C_{2n}H_2 \rightarrow C_{2n+2}H + H$  reaction sequence.<sup>24–30</sup> These reactions are barrier-less and proceed *via* addition of dicarbon to the acetylenic  $\pi$  electrons. Singlet dicarbon adds to the carbon–carbon triple bond of  $C_{2n}H_2$  forming first a tricyclic reaction intermediate  $[C_{2n+2}H_2]^*$  that then isomerizes to a linear  $HC_{2n+2}H$  global minimum before dissociation *via* elimination of a hydrogen atom to form the  $C_{2n+2}H$  radical. On the other hand, the addition of triplet dicarbon to  $C_{2n}H_2$  is more complex as it can occur at a single carbon atom or to both carbon atoms of the acetylenic moiety ( $C \equiv C$ ) simultaneously – as in the singlet case – followed by isomerization and cleavage of the carbon–carbon bond in dicarbon. The experimental chemistry of dicarbon reactions with (poly)acetylenes has culminated in the synthesis of key polyethynyls: butadiynyl ( $C_4H$ ),<sup>24–28</sup> hexatriynyl ( $C_6H$ ),<sup>29</sup> and octatetraynyl ( $C_8H$ ) (Scheme 1).<sup>30</sup> These radicals

undergo exoergic reactions with acetylene to form  $C_{2n+2}H_2$  alongside atomic hydrogen;<sup>31</sup> this furthers the chain elongation initiated by dicarbon. Notably, the spectroscopic signatures for dicarbon along with the aforementioned polyethynyls and their relevant (poly)acetylene precursors [acetylene ( $HCCH$ ), diacetylene ( $HCCCCH$ ), triacetylene ( $HCCCCCCH$ )] have been identified in circumstellar envelopes of the dying carbon star IRC + 10216 and also in cold molecular clouds.<sup>32–39</sup>

Further, resonantly stabilized free radicals (RSFRs) – relatively long lived open shell transient molecules with added stability due to electron delocalization – can be formed in hydrogen exchange reactions with carbon<sup>40–43</sup> and dicarbon,<sup>44–48</sup> or as reactive intermediates from their radical hydrides methylidyne ( $CH$ )<sup>49–51</sup> and ethynyl ( $C_2H$ ).<sup>52–55</sup> The propargyl ( $H_2CCCH$ , IV) abundance is suggested to be strongly correlated with the formation of the simplest aromatic systems benzene ( $C_6H_6$ ) and phenyl ( $C_6H_5$ , XI) (Scheme 1).<sup>56</sup> Oxidation of phenyl radicals yields cyclopentadienyl ( $c-C_5H_5$ ),<sup>57</sup> which may initiate naphthalene ( $C_{10}H_8$ ) formation *via* the self-reaction  $C_5H_5 + C_5H_5 \rightarrow C_{10}H_8 + 2H$ .<sup>58,59</sup> The conversion of naphthyl ( $C_{10}H_7$ ) to indenyl ( $C_9H_7$ ) through oxidation is analogous to the aforementioned



**Scheme 1** Structures and point groups of selected radicals synthesized *via* bimolecular reactions of dicarbon with unsaturated hydrocarbons.

$\text{C}_6\text{H}_5\text{O}_2 \rightarrow \text{C}_5\text{H}_5 + \text{O} + \text{CO}$  pathway with the resulting  $\text{C}_9\text{H}_7$  radicals suggested to react with propargyl ( $\text{C}_3\text{H}_3$ ) and cyclopentadienyl ( $\text{c-C}_5\text{H}_5$ ) to ultimately form PAHs acenaphthylene<sup>56</sup> ( $\text{C}_{12}\text{H}_8$ ) and phenanthrene ( $\text{C}_{14}\text{H}_{10}$ ),<sup>60</sup> respectively. Hence resonantly stabilized free radicals are critical for mass-growth processes leading to PAHs. In this context, the  $\text{C}_5\text{H}_3$  isomers have garnered considerable interest due to their presence in benzene flames.<sup>61–63</sup> The global minimum is a resonantly stabilized propargyl derivative,  $\text{i-C}_5\text{H}_3$  ( $\text{H}_2\text{CCCCCH}$ ), that has also been observed in allene, methylacetylene, and cyclopentene ( $\text{c-C}_5\text{H}_8$ ) flames.<sup>63</sup>  $\text{C}_5\text{H}_3$  radicals therefore have been explored in PAH formation networks.<sup>64,65</sup>

The  $\text{H}_2\text{CCCCCH}$  radical (Scheme 1, V) has been synthesized under single collision conditions in bimolecular reactions of dicarbon with methylacetylene ( $\text{CH}_3\text{CCH}$ )<sup>66</sup> and allene ( $\text{H}_2\text{CCCH}_2$ )<sup>67</sup> and is predicted to be a methyl-loss product of dicarbon reactions with three  $\text{C}_4\text{H}_6$  isomers: 1,2-butadiene ( $\text{H}_2\text{CCCHCH}_3$ ), 1-butyne ( $\text{C}_2\text{H}_5\text{CCH}$ ), and dimethylacetylene ( $\text{CH}_3\text{CCCH}_3$ ).<sup>68</sup> Under single-collision conditions afforded by crossed molecular beams (CMB) experiments, several radicals,<sup>24–30,69,70</sup> including resonantly stabilized<sup>44–48,71</sup> and aromatic<sup>48,72–75</sup> varieties, have been produced in dicarbon reactions with closed shell reaction partners. Despite these successes, hydrocarbons produced *via* methyl-loss channels have remained elusive. In a recent CMB study of dicarbon with 1-butyne ( $\text{C}_2\text{H}_5\text{CCH}$ ),<sup>68</sup> in which dicarbon was

produced alongside atomic carbon and tricarbon ( $\text{C}_3$ ) using a versatile ablation source,<sup>76–81</sup> only those reactions leading to  $\text{C}_6\text{H}_5$  isomers could be observed. Any  $[\text{C}_6\text{H}_6]^*$  dissociations leading to methyl-loss channels were obscured by products of the simultaneous reaction of carbon<sup>82</sup> with any  $\text{C}_4\text{H}_6$  isomer leading to  $\text{C}_5\text{H}_5$  plus atomic hydrogen.<sup>83–85</sup> Here, upon ionization and fragmentation by electron impact (80 eV), the  $\text{C}_5\text{H}_5^+$  molecular ion fragments to  $\text{C}_5\text{H}_4^+$ ,  $\text{C}_5\text{H}_3^+$ , and smaller species thus masking the  $\text{C}_5\text{H}_3$  product in the unimolecular decomposition of any  $[\text{C}_6\text{H}_6]^*$  intermediate *via* the methyl-loss pathway. Furthermore, the number density of products  $N$  reaching the detector is defined as  $N(\theta, \nu) = I_{\text{CM}}(\theta, u)\nu u^{-2}$  with the velocities  $u$  and  $\nu$  and scattering angles  $\theta$  and  $\Theta$  of the product in the laboratory and center-of-mass (CM) reference frames, respectively, and  $I_{\text{CM}}(\theta, u)$  is the CM reactive differential cross-section.<sup>86</sup> For a unimolecular decomposition, the velocity of the heavy product is proportional to the mass of the light product, *i.e.*  $\text{C}_5\text{H}_5$  formed in the atomic carbon reaction ( $[\text{C}_5\text{H}_6]^* \rightarrow \text{C}_5\text{H}_5 + \text{H}$ ) will carry a smaller velocity than the  $\text{C}_5\text{H}_3$  formed in the dicarbon system ( $[\text{C}_6\text{H}_6]^* \rightarrow \text{C}_5\text{H}_3 + \text{CH}_3$ ). Considering the effects of dissociative ionization, methyl-loss channels of dicarbon reactions are not likely observable using electron impact ionization, if a simultaneous atomic carbon reaction is ongoing (Fig. 1) in particular since the concentration of carbon is typically one order of magnitude higher than the dicarbon concentration.

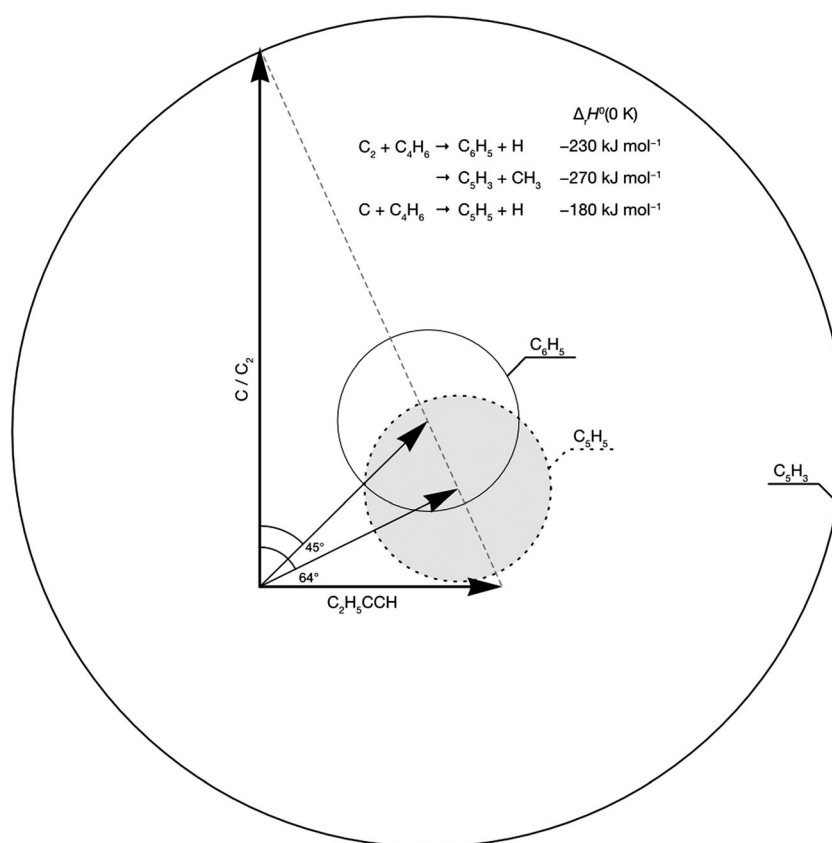


Fig. 1 Newton diagram for the atomic hydrogen and methyl loss channels in the reaction of dicarbon ( $\text{C}_2(X^1\Sigma_g^+)$ ) with 1-butyne ( $\text{C}_2\text{H}_5\text{CCH}$ ) (solid circles); the atomic hydrogen loss channel for the atomic carbon–1-butyne reaction is also shown (dashed circle).

Considering the complication of currently operating dicarbon ablation and discharge sources in molecular beams machines, a new source design is clearly needed to access potential methyl-loss channels. Here, we present a novel supersonic source of dicarbon produced *via* photodissociation of tetrachloroethylene ( $\text{C}_2\text{Cl}_4$ ). While tetrachloroethylene ( $\text{C}_2\text{Cl}_4$ ) has long been exploited as a dicarbon precursor in kinetic assessments,<sup>87–94</sup> it has not been introduced as a dicarbon source in CMB experiments which have thus far relied on graphite ablation,<sup>76,95</sup> electrical (DC)<sup>96</sup> or radio-frequency (RF)<sup>97</sup> discharge into gaseous carbon-bearing precursors for dicarbon production. Photolysis (248 nm) of a tetrachloroethylene–helium mixture yields ground and electronically excited dicarbon with no interference from atomic carbon or tricarbon making it a valuable tool for fully exploring dicarbon reaction pathways that would otherwise be obscured by reactive scattering originating from reactive carbon atoms. The performance of this source is tested for the well-characterized methylacetylene–dicarbon<sup>66,98–100</sup> and  $\text{d}_3$ -methylacetylene–dicarbon systems<sup>101</sup> before demonstrating its potential for the detection of the hitherto elusive methyl-loss channel in the dicarbon–1-butyne ( $\text{C}_2\text{H}_5\text{CCH}$ ) system.

## 2. Experimental and calculation methods

### 2.1. Experiment

The dicarbon ( $\text{C}_2$ ;  $X^1\Sigma_g^+/a^3\Pi_u$ ) reactions with methylacetylene ( $\text{CH}_3\text{CCH}$ ;  $X^1A_1$ ),  $\text{d}_3$ -methylacetylene ( $\text{CD}_3\text{CCH}$ ;  $X^1A_1$ ), and 1-butyne ( $\text{C}_2\text{H}_5\text{CCH}$ ;  $X^1A'$ ) were conducted under single-collision conditions using a crossed molecular beams (CMB) machine at the University of Hawaii.<sup>49</sup> The machine employs two orthogonal fixed molecular beam sources and a detector that is rotatable in the plane defined by both reactant beams. The detector comprises a Brink-type ionizer,<sup>102</sup> quadrupole mass spectrometer (QMS), and a Daly-type ion counter.<sup>103</sup> Subdivided into three regions, differential pumping of the detector reduces operating pressures to less than  $10^{-11}$  Torr in the inner most section that houses the ionizer. Products of the reactive scattering process in the dicarbon reactions with methylacetylene (Organic Technologies, 99%+),  $\text{d}_3$ -methylacetylene (CDN Isotopes, 99%+), and 1-butyne (Aldrich Chemistry,  $\geq 98\%$ ) were ionized by electron impact (40 eV; 1.4 mA) and filtered according to mass-to-charge ( $m/z$ ) ratios using the QMS (Extrel; QC 150) equipped with a 2.1 MHz oscillator. The resulting ions were accelerated by a negative 22.5 kV potential onto an aluminum coated stainless-steel target, generating a cascade of secondary electrons directed toward an aluminum coated scintillator. The photoemission was collected by a photomultiplier tube (PMT, Burle, Model 8850) operated at a negative potential of 1.35 kV, whose output was discriminated at 1.6 mV (Advanced Research Instruments, Model F-100TD).

The data collection was coordinated by a four-slot (0.76 mm) chopper wheel rotating at 120 Hz equipped with an infrared photodiode that permits system-wide synchronization by acting as a time zero and trigger ( $T_0 = 0 \mu\text{s}$ ) for the equipment

discussed herein. The resulting 480 Hz signal was processed by an f/8 frequency divider and ultimately distributed amongst four Stanford Research Systems (SRS) DG535 delay/pulse generators (PDG I–IV). The +4 V, 50  $\Omega$  outputs AB ( $A_I = T_0 + 1888 \mu\text{s}$ ,  $B_I = A_I + 80 \mu\text{s}$ ) & CD ( $C_I = A_I - 50 \mu\text{s}$ ,  $D_I = C_I + 80 \mu\text{s}$ ) of PDG I were fed into a homemade pulse shaper and then amplified by a power amplifier (Physik Instrumente, E-421). These 60 Hz signals were sent to the primary and secondary pulsed valves (Proch-Trickl),<sup>104</sup> each containing a piezoelectric disc translator (Physik Instrumente, P-286.23), resulting in 80  $\mu\text{s}$  opening times using amplitudes of  $-360 \text{ V}$  to  $-400 \text{ V}$  for this set of experiments. PDG I A (TTL, high impedance) was halved to 30 Hz and delivered to PDGs II and III for further distribution. PDG II AB ( $A_{II} = T_0 + 1888 \mu\text{s}$ ;  $B_{II} = A_{II} + 5 \mu\text{s}$ ) was used to trigger a SRS 430 multichannel scaler (MCS). PDG III output CD ( $C_{III} = T_0 + 2048 \mu\text{s}$ ;  $D_{III} = C_{III} + 15 \mu\text{s}$ ; TTL; 50  $\Omega$ ) was sent to an excimer laser (Coherent: Compex110, 120 mJ pulse<sup>-1</sup>), while PDG III A (TTL high impedance) was divided by 3 and delivered to PDG IV, which provided 10 Hz TTL (50  $\Omega$ ) signals to the flash lamp and Q-switch of a Quantel Brilliant Nd:YAG laser *via* outputs AB ( $A_{IV} = T_0 + 1889 \mu\text{s}$ ,  $B_{IV} = A_{IV} + 5 \mu\text{s}$ ) and CD ( $C_{IV} = T_0 + 2075 \mu\text{s}$ ,  $D_{IV} = C_{IV} + 5 \mu\text{s}$ ), respectively, used to pump a tunable dye laser (Lambda Physik Scanmate Pro). This synchronization scheme is compiled in Fig. 2.

Dicarbon was produced by photodissociation of tetrachloroethylene ( $\text{C}_2\text{Cl}_4$ , Sigma Aldrich,  $\geq 99.9\%$ ), purified by multiple freeze–pump–thaw cycles and seeded in helium (99.9999%; AirGas) at 2.2 atm in a room temperature (300 K) stainless steel bubbler. Photodissociation of the tetrachloroethylene in this gas mixture (1.4%  $\text{C}_2\text{Cl}_4$ ) was accomplished using 248 nm focused to  $1.2 \times 4.0 \text{ mm}^2$  approximately 1 mm downstream of the pulsed valve; the distance between the nozzle and the skimmer was optimized to  $19 \pm 1 \text{ mm}$ . The resulting dicarbon molecules passed through a 1 mm skimmer before velocity-selection by the chopper wheel. On-axis ( $\theta = 0^\circ$ ) characterization of dicarbon at 34 eV electron energy reveals a high intensity beam (2.5 that achieved by graphite ablation) with a narrow velocity distribution, with peak velocities  $v_p$  ranging from 1567 to 1596  $\text{m s}^{-1}$  and speed ratios  $S$  ranging from 9.6 to 12.0. The hydrocarbon reactants were expanded neat from a pulsed valve in the secondary source chamber and then skimmed before perpendicularly intersecting the dicarbon beam. Unlike the dicarbon beam, whose velocity was selected *in situ*, the velocity distributions of the hydrocarbon beams were characterized on axis ( $\theta = 90^\circ$ ) prior to reactive scattering experiments using a detector-mounted chopper wheel. For the dicarbon–methylacetylene [ $\text{CH}_3\text{CCH}$  ( $\text{CD}_3\text{CCH}$ )] reaction, the secondary pulsed valve was backed by 600 (500) Torr with  $v_p = 800 \pm 10$  ( $790 \pm 10$ )  $\text{m s}^{-1}$  and  $S = 12.0 \pm 0.4$  ( $12.0 \pm 0.4$ ), resulting in a collision energy  $E_C$  of  $23.2 \pm 0.3$  ( $24.0 \pm 0.2$ )  $\text{kJ mol}^{-1}$  and a center-of-mass angle  $\theta_{\text{CM}}$  of  $40.4 \pm 0.4^\circ$  ( $41.9 \pm 0.4^\circ$ ). The heavier 1-butyne ( $\text{C}_2\text{H}_5\text{CCH}$ ) (550 Torr) reactant intersects the dicarbon beam in the reaction center with  $v_p = 782 \pm 14 \text{ m s}^{-1}$  and  $S = 8.6 \pm 0.5$ , and therefore  $E_C = 26.2 \pm 0.8 \text{ kJ mol}^{-1}$  and  $\theta_{\text{CM}} = 47.8 \pm 0.7^\circ$  for reactive collisions with dicarbon. The peak velocities  $v_p$  and speed ratios  $S$ , along with relevant collision energies  $E_C$  and center-of-mass angles  $\theta_{\text{CM}}$  for  $\text{C}_2$ ,  $\text{CH}_3\text{CCH}$ ,  $\text{CD}_3\text{CCH}$ , and  $\text{C}_2\text{H}_5\text{CCH}$  are tabulated in Table 1.

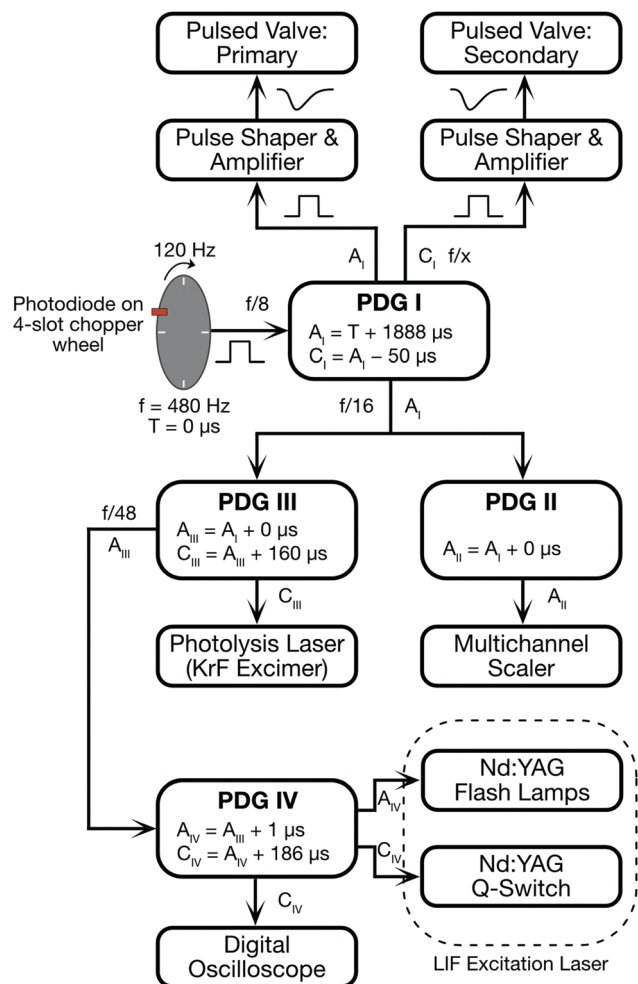


Fig. 2 Pulse sequence applied for the crossed molecular beam reactions of dicarbon ( $C_2$ ;  $X^1\Sigma_g^+/a^3\Pi_u$ ) with methylacetylene ( $CH_3CCH$ ;  $X^1A_1$ ),  $d_3$ -methylacetylene ( $CD_3CCH$ ;  $X^1A_1$ ), and 1-butyne ( $C_2H_5CCH$ ;  $X^1A'$ ). The timing scheme used for the laser-induced fluorescence (LIF) for singlet and triplet dicarbon is also included. PDG: pulse/delay generator.  $x = 8$  for methylacetylene and 1-butyne;  $x = 16$  for  $d_3$ -methylacetylene.

Angularly resolved time-of-flight (TOF) spectra were obtained in the plane of the reactant beams at laboratory angles  $0^\circ \leq \theta \leq 69^\circ$  with respect to the dicarbon beam ( $\theta = 0^\circ$ ) and analyzed using a forward-convolution routine<sup>105,106</sup> that relies on user-defined center-of-mass (CM) frame translational energy  $P(E_T)$  and angular  $T(\theta)$  flux distributions. Accounting for the reactant beam divergences, velocity spreads, and machine parameters, laboratory-frame TOF spectra and angular distributions (LAD) are calculated and compared with the experimental data. The  $P(E_T)$  and  $T(\theta)$  functions are varied iteratively until a best fit of the experimental dataset are obtained. These functions comprise the reactive differential cross section  $I(\theta, u)$ , which is taken to be separable into its CM scattering angle  $\theta$  and CM velocity  $u$  components,  $I(u, \theta) \sim P(u) \times T(\theta)$ . The differential cross section is plotted as a flux contour map that serves as an image of the reaction. Errors of the  $P(E_T)$  and  $T(\theta)$  functions are determined within the  $1\sigma$  error limits of the accompanying LAD while maintaining a good fit of the laboratory TOF spectra.

Table 1 Peak velocities ( $v_p$ ) and speed ratios ( $S$ ) of the dicarbon ( $C_2$ ), 1-butyne ( $C_2H_5CCH$ ), methylacetylene ( $CH_3CCH$ ), and  $d_3$ -methylacetylene ( $CD_3CCH$ ) beams along with the corresponding collision energies ( $E_C$ ) and center-of-mass angles ( $\theta_{CM}$ )

Beam	$v_p$ (m s <sup>-1</sup> )	$S$	$E_C$ (kJ mol <sup>-1</sup> )	$\theta_{CM}$ (degree)
$C_2(X^1\Sigma_g^+/a^3\Pi_u)$	$1567 \pm 12$	$11.9 \pm 0.6$	$23.2 \pm 0.3$	$40.4 \pm 0.4$
$CH_3CCH(X^1A_1)$	$800 \pm 10$	$12.0 \pm 0.4$		
$C_2(X^1\Sigma_g^+/a^3\Pi_u)$	$1579 \pm 8$	$12.1 \pm 0.6$	$24.0 \pm 0.2$	$41.9 \pm 0.4$
$CD_3CCH(X^1A_1)$	$790 \pm 10$	$12.0 \pm 0.4$		
$C_2(X^1\Sigma_g^+/a^3\Pi_u)$	$1596 \pm 29$	$9.6 \pm 0.9$	$26.2 \pm 0.8$	$47.8 \pm 0.7$
$C_2H_5CCH(X^1A')$	$782 \pm 14$	$8.6 \pm 0.5$		

Molecular beams of dicarbon are known to contain both the singlet ground ( $X^1\Sigma_g^+$ ) state and the lowest lying triplet state ( $a^3\Pi_u$ ),<sup>49,107</sup> which are separated by only 7.3 kJ mol<sup>-1</sup>.<sup>108</sup> While higher energy states may be products of the initial tetrachloroethylene photodissociation, the  $b^3\Sigma_g^-(v=0)$  and  $A^1\Pi_u(v=0)$  lifetimes are only 16.6  $\mu$ s and 13.0  $\mu$ s, respectively,<sup>109</sup> and less than the  $29.2 \pm 0.6$   $\mu$ s flight time of dicarbon to the reaction center. The rovibrational energy distributions of the ground and first excited states of dicarbon were characterized by laser induced fluorescence (LIF) using a tunable dye laser pumped by the third harmonic of an integrated Nd:YAG laser. Emissions from dicarbon were focused before passing an interference filter (Andover Corporation) centered at 230.40 nm (FWHM of 10.09 nm) or 561.20 nm (FWHM of 9.25 nm) mounted at the entrance window of a Hamamatsu R955 PMT. The ground state was probed using the Mulliken  $D^1\Sigma_u^+-X^1\Sigma_g^+(0,0)$  and (1,1) transitions. Tunable radiation near 231 nm (6 nJ pulse<sup>-1</sup>) was obtained by frequency-doubling the fundamental output of the dye laser circulating Coumarin 460 (Exciton). The triplet state was accessed using the Swan  $d^3\Pi_g \leftarrow a^3\Pi_u$  excitations near 512.5 nm (1,1) and 517.5 nm (0,0) using light obtained by circulating Coumarin 503 (Exciton) attenuated to 16 nJ pulse<sup>-1</sup>. Fluorescence was captured on the  $\Delta v = -1$  sequence near 563.5 (0,1) and 558.5 (1,2) nm. The LIF spectra were analyzed by comparison with spectral simulations obtained from PGOPHER<sup>110</sup> using spectroscopic constants for the  $D^1\Sigma_u^+-X^1\Sigma_g^+$  system from Schmidt and Baskay,<sup>109</sup> and from Brooke *et al.*<sup>111</sup> for the  $d^3\Pi_g-a^3\Pi_u$  system. The LIF spectra of the Mulliken ( $D^1\Sigma_u^+-X^1\Sigma_g^+$ ) and Swan ( $d^3\Pi_g-a^3\Pi_u$ ) bands are provided in Fig. 3. A comparison with spectral simulations suggest the  $X^1\Sigma_g^+(v=0)$  and  $a^3\Pi_u(v=0)$  states are the most populated, each with a bimodal temperature representation as typified in radical beams.<sup>49,112</sup> The  $X^1\Sigma_g^+(v=1)$  state lies 22 kJ mol<sup>-1</sup> above  $X^1\Sigma_g^+(v=0; j=0)$ , with rotational temperatures of 1000 K contributing an additional 4 kJ mol<sup>-1</sup>. Rotational temperatures of 300 K in the  $a^3\Pi_u(v=1)$  state bring the energy to 26 kJ mol<sup>-1</sup> above dicarbon's ground singlet state.<sup>108</sup> The relative vibrational populations and rotational temperatures for  $X^1\Sigma_g^+$  and  $a^3\Pi_u$  are compiled in Table 2.

## 2.2. Calculations

Stationary points on the triplet  $C_6H_6$  potential energy surfaces (PES) accessed by the  $C_2(a^3\Pi_u) + 1$ -butyne reaction, which were not considered in the previous work, were calculated at the



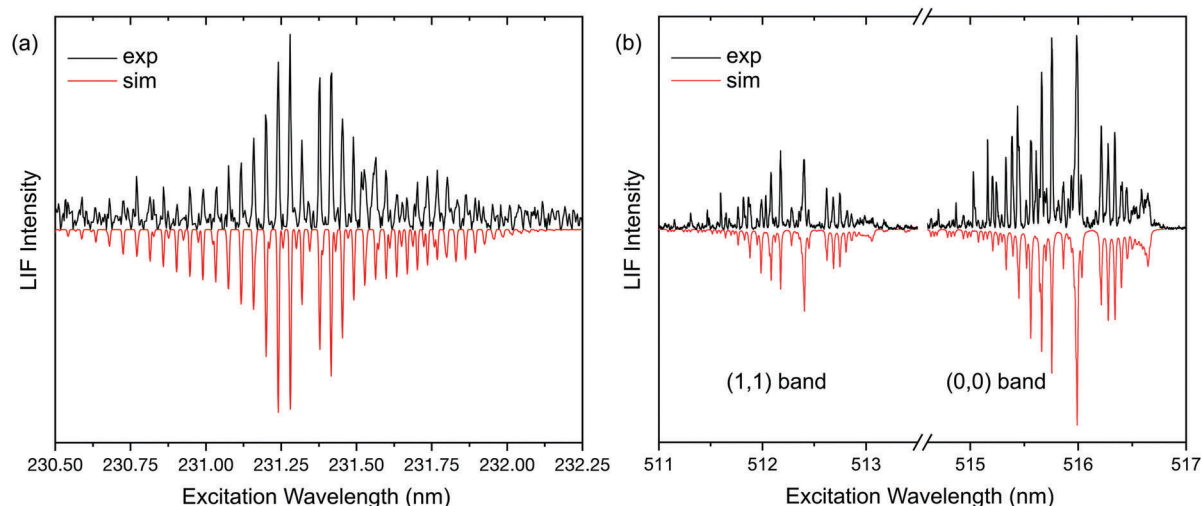


Fig. 3 (a) Laser induced fluorescence (LIF) excitation spectrum of the Mulliken band ( $D^1\Sigma_u^+ - X^1\Sigma_u^+$ ) in singlet dicarbon. (b) LIF excitation spectrum of the Swan band ( $d^3\Pi_g - a^3\Pi_u$ ) in triplet dicarbon. Both the experimental spectrum (black) and best-fit simulation (red) are shown.

Table 2 Rotational temperatures and vibrational energy distribution in the two lowest electronic states of dicarbon

Electronic state	Temperature (K)	$v = 0$ (%)	$v = 1$ (%)
Singlet ( $X^1\Sigma_g^+$ )	Total	81	19
	65	35	3
	1000	46	16
Triplet ( $a^3\Pi_u$ )	Total	74	26
	30	53	20
	300	21	6

same level of theory as earlier.<sup>68</sup> In particular, geometries of all structures were optimized and vibrational frequencies were computed at the hybrid density functional B3LYP/6-311G\*\* level of theory.<sup>113,114</sup> Energies of various species were refined using the coupled cluster CCSD(T) method<sup>115</sup> with Dunning's correlation-consistent cc-pVDZ, cc-pVTZ, and cc-pVQZ basis sets<sup>116</sup> and then the total energies were extended to the complete basis set (CBS) limit using either two-point (CBS(dt)) or three-point (CBS(dtq)) extrapolation.<sup>68,117</sup> For the  $C_2(a^3\Pi_u) + \text{methylacetylene}$  system, extrapolation to the CBS limit was achieved *via* explicitly correlated CCSD(T)-F12 calculations<sup>118,119</sup> with the cc-pVTZ-f12 basis set. The B3LYP and CCSD(T) quantum chemical calculations were performed using the GAUSSIAN 09<sup>120</sup> and MOLPRO 2010<sup>121</sup> program packages. Rate constants of all unimolecular reaction steps on the triplet  $C_6H_6$  PES following initial association of  $C_2(a^3\Pi_u)$  with 1-butyne were computed using Rice–Ramsperger–Kassel–Marcus (RRKM) theory,<sup>122–124</sup> as functions of available internal energy of each intermediate or transition state, where numbers and densities of states were obtained within the harmonic approximation using B3LYP/6-311G\*\* computed frequencies. The internal energy was taken as a sum of the collision energy and a negative of the relative energy of a species with respect to the reactants (the chemical activation energy). One energy level was considered throughout as at a zero pressure limit. Then, RRKM rate constants were

utilized to compute product branching ratios by solving first-order kinetic equations within steady-state approximation. More detail on the *ab initio*/RRKM calculations can be found in the previous publication.<sup>68</sup>

## 3. Results

### 3.1. Laboratory data

**3.1.1. Dicarbon–methylacetylene.** Dicarbon ( $C_2$ ; 24 amu) reacted with methylacetylene ( $CH_3CCH$ ; 40 amu) with an average collision energy  $E_C$  of  $23.2 \pm 0.3$  kJ mol<sup>−1</sup>. We monitored potential reaction products at mass-to-charge ratios ( $m/z$ ) 64 ( $C_5H_4^+$ ), 63 ( $C_5H_3^+$ ), 62 ( $C_5H_2^+$ ), and 49 ( $C_4H^+$ ) and were able to collect a TOF at each mass except for  $m/z$  49, at which no signal was detected. The TOF signal at  $m/z$  64 ( $C_5H_4^+$ ) and 62 ( $C_5H_2^+$ ) are superimposable with  $m/z$  63 ( $C_5H_3^+$ ) after scaling, and hence  $C_5H_2^+$  derives from fragmentation of  $C_5H_3^+$  in the ionizer, whereas the signal at  $m/z$  64 is attributable to  $^{13}CC_4H_3^+$ . Accordingly, TOFs were recorded at  $m/z$  63 in  $2.5^\circ$  steps from  $8.5^\circ$  to  $67.5^\circ$  (Fig. 4). The laboratory angular distribution (LAD) of  $C_5H_3^+$ , which contains information from  $2.1 \times 10^6$  TOF spectra, is plotted as a function of the laboratory angle ( $\theta$ ) in Fig. 5 as black dots with  $1\sigma$  error bars. It is clear that the distribution has two distinct contributions from the two maxima in the total distribution occurring at  $20^\circ$  and  $40^\circ$ . The LAD maximum at  $40.0^\circ$  falls within  $1\sigma$  of the  $\theta_{CM}$  for dicarbon–methylacetylene reactive scattering. The second channel peaking at  $\theta = 20^\circ$  can only be fit with the mass combination of the chloroethynyl radical ( $C_2Cl$ ,  $X^2\Pi$ ) – a byproduct of the tetrachloroethylene photodissociation leading to  $C_2^{35}Cl$  (59 amu) and  $C_2^{37}Cl$  (61 amu)<sup>125</sup> – with methylacetylene ( $C_3H_4$ ; 40 amu). The center-of-mass angle  $\theta_{CM}$  of this system is  $19.6 \pm 0.3^\circ$ , close to the distribution maximum of this channel. The LAD taken at  $m/z$  63 is thus split into two components owing to scattering of dicarbon ( $C_2$ ) and chloroethynyl ( $C_2Cl$ ) with the hydrocarbon as shown as red and blue curves, respectively (Fig. 5). For  $\theta < 25^\circ$  the data are best fit with the reaction

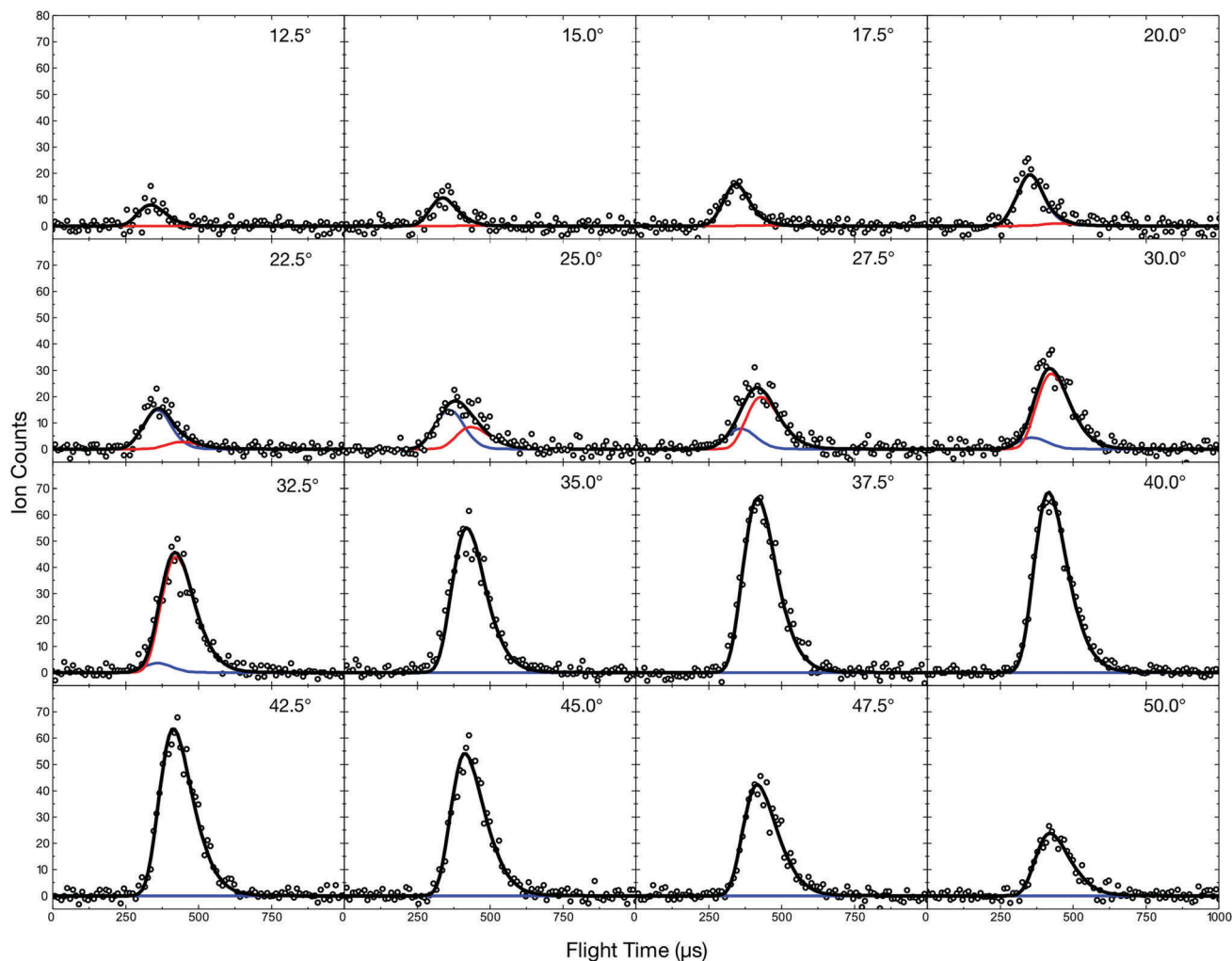


Fig. 4 Time of flight (TOF) spectra (open circles) recorded at mass-to-charge ratio ( $m/z$ ) 63 ( $C_5H_3^+$ ) produced from the reaction of dicarbon ( $C_2$ ) and chloroethynyl ( $C_2Cl$ ) with methylacetylene ( $CH_3CCH$ ) at various laboratory angles. Contributions to each TOF spectrum from dicarbon ( $C_2$ ) and chloroethynyl ( $C_2Cl$ ) channels are indicated by red and blue curves, respectively. The black line represents the sum of both channels.

$C_2^{35}Cl + CH_3CCH$  leading to atomic chlorine and/or hydrogen chloride products. The imposing product signal from reactive scattering of  $C_2 + CH_3CCH$  limits our ability to reasonably constrain this channel, and we find that acceptable fits of the total signal obtained at  $m/z$  63 can be obtained with either a Cl or HCl loss. The center-of-mass functions for the HCl loss channel, used to fit the  $C_2Cl$  contribution to the reactive scattering signal recorded at  $m/z$  63, depict a slightly backward distribution and suggest a reaction energy of about  $13 \pm 3 \text{ kJ mol}^{-1}$  (Fig. S1, ESI<sup>†</sup>). A full investigation of the  $C_5H_4Cl$  potential energy surface is beyond the scope of this paper and therefore the remainder of our discussion will focus on the reactivity of dicarbon. For  $\theta > 25^\circ$ , ion counts from the  $C_2 + CH_3CCH \rightarrow C_5H_3 + H$  reaction dominate the LAD, with  $C_5H_3$  products being spread from  $17.5^\circ$  to  $62.5^\circ$  in the laboratory frame. In this regime the TOFs and LAD could be fit with a single channel, namely  $C_2$  (24 amu) +  $CH_3CCH$  (40 amu)  $\rightarrow$   $C_5H_3$  (63 amu) + H (1 amu), resulting in a nearly symmetric distribution about the maximum at  $40^\circ$ .

**3.1.2. Dicarbon- $d_3$ -methylacetylene.** The dicarbon ( $C_2$ ; 24 amu) reaction with  $d_3$ -methylacetylene ( $CD_3CCH$ ; 43 amu) was carried out at a collision energy  $E_C = 24.0 \pm 0.2 \text{ kJ mol}^{-1}$ . Reactive scattering products were monitored at  $m/z$  66 ( $C_5D_3^+$ ) and 65 ( $C_5HD_2^+$ ) along  $\theta_{CM} = 41.9 \pm 0.4^\circ$  to discriminate if the aforementioned atomic hydrogen loss originated from the methyl group (here:  $CD_3$ ) or from the acetylenic moiety. Ion signal was observed at both  $m/z$  66 and  $m/z$  65. The signal at  $m/z$  66 is much weaker than  $m/z$  65 and is superimposable with  $m/z$  65 after scaling. Signal at  $m/z$  65 cannot derive from fragmentation of  $C_5D_3^+$  ( $m/z$  66) since the latter can only fragment *via* deuterium loss to  $C_5D_2^+$  ( $m/z$  64). Since no adduct was detected, the signal recorded at  $m/z$  65 is attributed to  $C_5HD_2^+$ , whereas that observed at  $m/z$  66 must originate from  $^{13}CC_4HD_2^+$ . Therefore, TOF spectra were collected at  $m/z$  65 from  $11^\circ$  to  $66^\circ$  in  $5^\circ$  steps (Fig. 6). The broadening of the LAD at  $\theta < 30^\circ$  is due to scattering of the  $d_3$ -methylacetylene reactant with chloroethynyl ( $C_2Cl$ ) as seen in the analogous dicarbon-methylacetylene system discussed above. Considering the decreased signal-to-noise

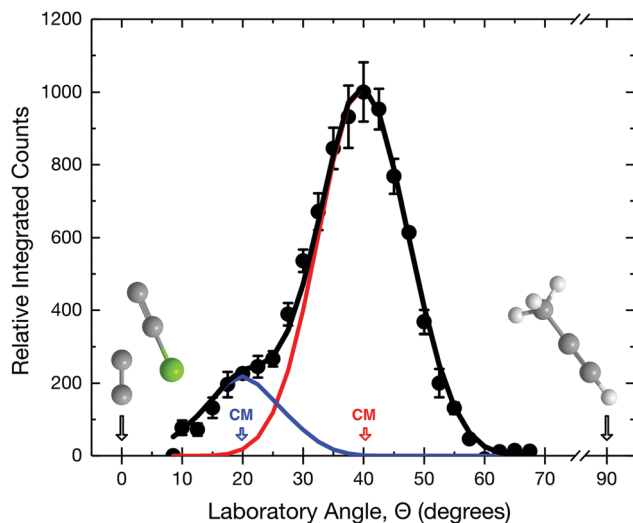


Fig. 5 Laboratory angular distribution (LAD) recorded at mass-to-charge ratio ( $m/z$ ) 63 ( $C_5H_3^+$ ) produced from the reaction of dicarbon ( $C_2$ ) and chloroethynyl ( $C_2Cl$ ) with methylacetylene ( $CH_3CCH$ ). Experimental data are indicated by black dots and the simulation represented by a black curve. Simulated contributions originating from dicarbon ( $C_2$ ) and chloroethynyl ( $C_2Cl$ ) channels are indicated by red and blue curves, respectively. CM defines the center of mass.

( $C_5HD_2$  analysis derives from about  $5.3 \times 10^5$  TOF spectra), contributions from chloroethynyl are more difficult to resolve in the TOF spectra. Accounting for the chloroethynyl contributions to the  $m/z$  65 signal, the dicarbon component could be fit with a single channel,  $C_2 + CD_3CCH \rightarrow C_5HD_2$  (65 amu) + D (2 amu).

The  $C_5HD_2$  signal is confined to a spread of about  $55^\circ$  in the laboratory frame and is nearly symmetric about  $\theta_{CM}$  (red curve, Fig. 7).

**3.1.3. Dicarbon-1-butyne.** Finally, the products of the dicarbon ( $C_2$ ; 24 amu) plus 1-butyne ( $C_2H_5CCH$ ; 54 amu) reaction were monitored at  $m/z$  78 ( $C_6H_6^+$ ), 77 ( $C_6H_5^+$ ), 76 ( $C_6H_4^+$ ), and 63 ( $C_5H_3^+$ ). Scattering signals were observed along  $\theta_{CM} = 47.8 \pm 0.7^\circ$  at  $m/z$  77, 76 and 63. The superimposability of the  $m/z$  76 and  $m/z$  77 TOF spectra indicate that each arise from  $C_6H_5^+$ , with  $C_6H_5^+$  fragmenting upon ionization of the neutral product to  $C_6H_4^+$ . The  $C_2 + C_2H_5CCH \rightarrow C_6H_5 + H$  reaction was previously interrogated in a combined experimental and computational study;<sup>68</sup> an examination of this channel is not repeated here. Regarding the signal at  $m/z$  63, we collected  $1.4 \times 10^7$  TOF spectra (Fig. 8) in  $10^\circ$  steps from  $18^\circ$  to  $68^\circ$  (Fig. 9). A fast feature is apparent in TOF spectra at  $\theta \leq 28^\circ$ . Unlike the  $C_2 + CH_3CCH/CD_3CCH$  reactions that were accompanied by a reactive chloroethynyl partner, the magnitude of this signal increases monotonically toward the dicarbon beam and is thus attributed to nonreactive scattering of the  $C_2Cl_4$  precursor – a phenomenon in radical beam sources at angles close to the primary beam.<sup>126</sup> Considering the methyl co-fragment, the heavy  $C_5H_3$  product scatters broadly in our CMB and extends well beyond the angular limitations of our apparatus.

### 3.2. Center-of-mass functions

The center-of-mass functions hold important information and assist in the elucidation of the underlying reaction dynamics (Fig. 10–12). For the  $C_2$ – $CH_3CCH$  system, the  $T(\theta)$  of the atomic

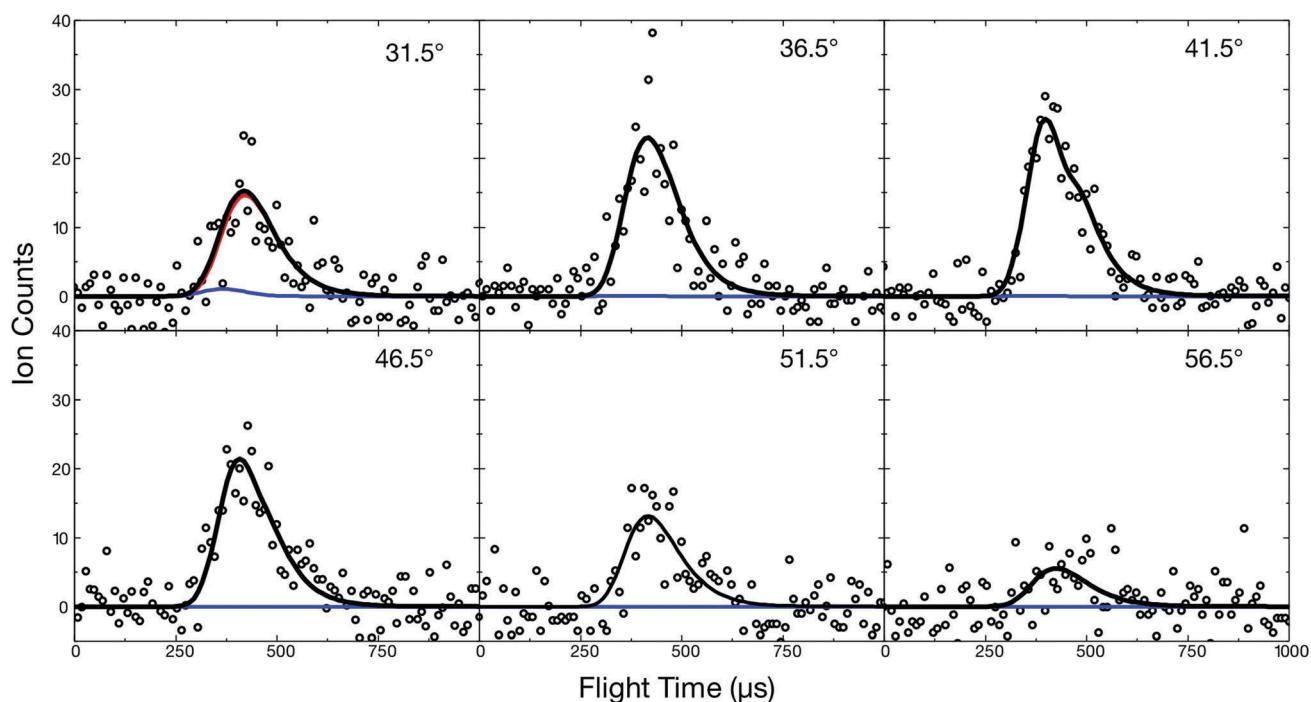


Fig. 6 Time of flight (TOF) spectra (open circles) recorded at mass-to-charge ratio ( $m/z$ ) 65 ( $C_5HD_2^+$ ) produced from the reaction of dicarbon ( $C_2$ ) and chloroethynyl ( $C_2Cl$ ) with  $d_3$ -methylacetylene ( $CD_3CCH$ ). Contributions to each TOF spectrum from dicarbon ( $C_2$ ) and chloroethynyl ( $C_2Cl$ ) channels are indicated by red and blue curves, respectively. The black line represents the sum of both channels.



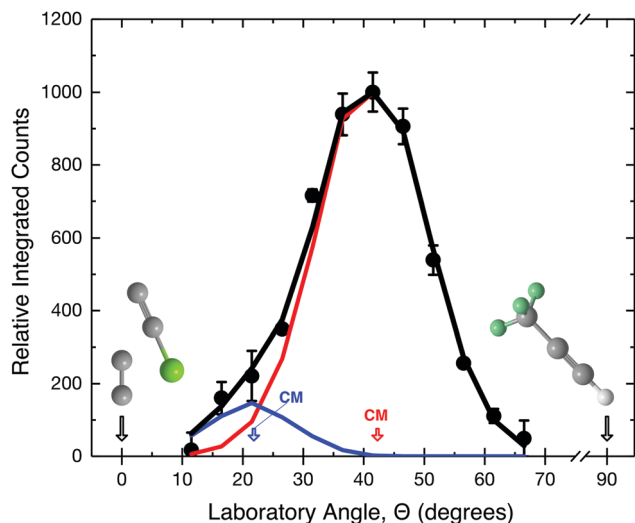


Fig. 7 Laboratory angular distribution (LAD) recorded at mass-to-charge ratio ( $m/z$ ) 65 ( $C_5HD_2^+$ ) produced from the scattering of dicarbon ( $C_2$ ) and chloroethynyl ( $C_2Cl$ ) with d3-methylacetylene ( $CD_3CCH$ ). Experimental data are indicated by black dots and the simulation represented by a black curve. Simulated contributions originating from dicarbon ( $C_2$ ) and chloroethynyl ( $C_2Cl$ ) channels are indicated by red and blue curves, respectively. CM defines the center of mass.

hydrogen loss channel forming  $C_5H_3$  isomers exhibits intensity at all angles, but slightly favors intensity in the forward hemisphere with respect to the dicarbon beam ( $\theta = 0^\circ$ ) with a forward-backward ratio at the poles of  $T(0^\circ)/T(180^\circ) = 1.5 \pm 0.4$  (Fig. 10,  $T(\theta)$ ). This distribution suggests indirect scattering dynamics<sup>127</sup>

and the existence of a  $[C_5H_4]^*$  intermediate(s) possessing a mean lifetime  $\tau$  approximately twice of its rotational period  $\tau_r$ , where  $\tau$  is given by  $\log_e(T(0^\circ)/T(180^\circ))^2 \tau_r$ .<sup>128</sup> The corresponding translational energy flux distribution  $P(E_T)$  extends out to a maximum translational energy  $E_{max}$  of  $204 \pm 24$  kJ mol<sup>-1</sup>. Considering that the maximum available energy for translation ( $E_{max}$ ) represents the sum of the absolute of the reaction energy ( $\Delta_r G$ ) plus the collision energy ( $E_C$ ), the best fitting indicated a reaction energy of  $-181 \pm 25$  kJ mol<sup>-1</sup>. The derived reaction energy can be reduced by up to 26 kJ mol<sup>-1</sup> for reactions with singlet dicarbon, or by up to 28 kJ mol<sup>-1</sup> for those involving triplet dicarbon ( $a^3\Pi_u$ ) when accounting for the rovibrational distribution of our beam (LIF section of Experimental methods). The best fitting  $P(E_T)$  peaks near 19 kJ mol<sup>-1</sup>, although the experimental data could be fit reasonably well with a plateau-like maximum that ranges from 3 to 23 kJ mol<sup>-1</sup> (Fig. 10,  $P(E_T)$ ). This broad feature suggests that  $C_5H_3$  formation occurs through multiple exit transition states.<sup>98</sup> This peaking of the  $P(E_T)$  at low translational energies suggests that  $C_5H_3$  formation occurs through relatively loose exit transition state(s). Moreover, the average translational energy ( $E_T$ ) of  $50 \pm 6$  kJ mol<sup>-1</sup> reveals that only  $25 \pm 4\%$  of the available energy is deposited into translational degrees of freedom. The latter suggests the reaction pathway is indirect.

For the  $C_2$ - $CD_3CCH$  reaction, the  $T(\theta)$  of  $C_5HD_2$  formed by atomic deuterium loss is also weakly polarized peaking in the forward direction ( $T(0^\circ)/T(180^\circ) = 1.1 \pm 0.1$ ) with intensity at all angles (Fig. 11,  $T(\theta)$ ). This CM angular flux distribution suggests indirect reaction dynamics as well involving one or more

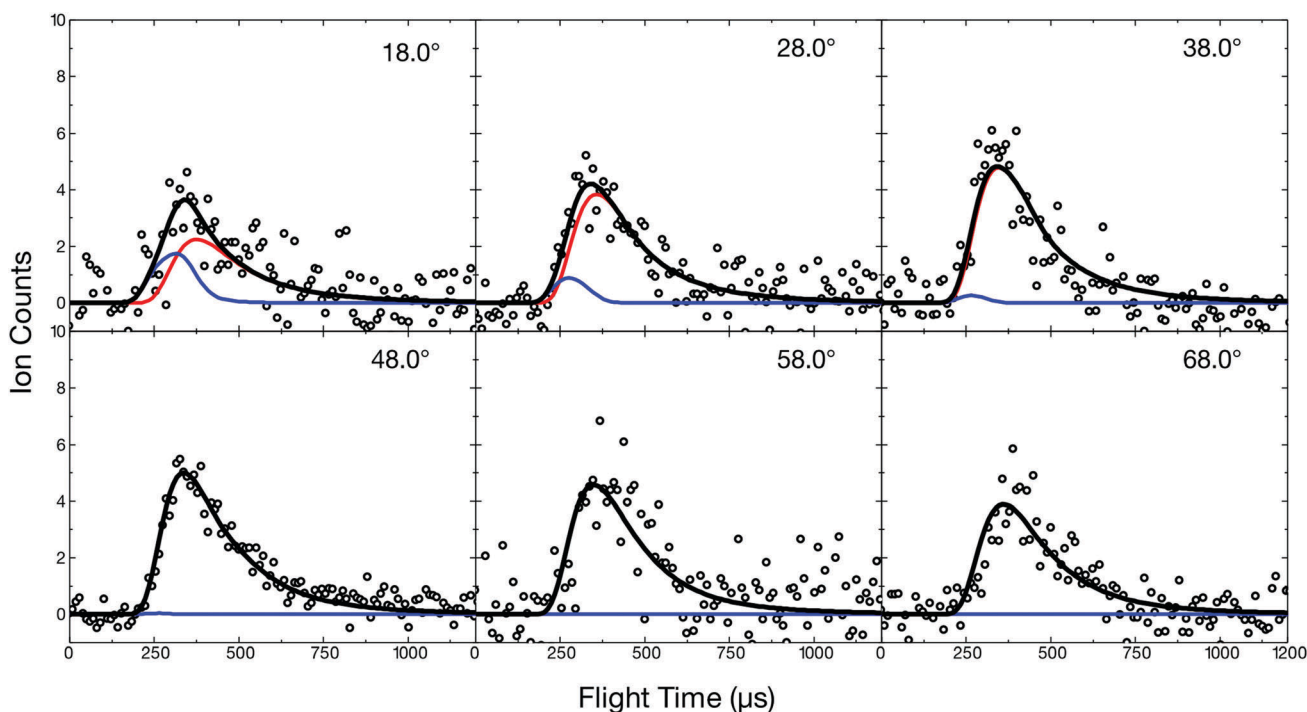


Fig. 8 Time of flight (TOF) spectra (open circles) recorded at mass-to-charge ratio ( $m/z$ ) 63 ( $C_5H_3^+$ ) produced from the reactive scattering of dicarbon ( $C_2$ ) with 1-butyne ( $C_2H_5CCH$ ) at selected laboratory angles. Contributions to each TOF spectrum (black) from dicarbon ( $C_2$ ) and non-reactive scattering are indicated by red and blue curves, respectively.

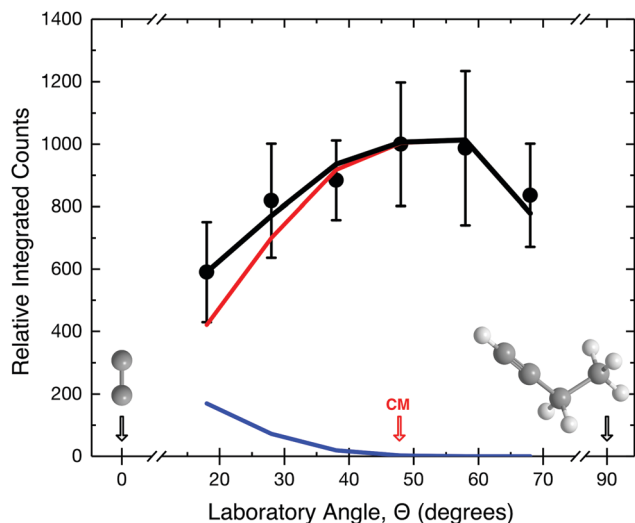


Fig. 9 Laboratory angular distribution (LAD) recorded at mass-to-charge ratio ( $m/z$ ) 63 ( $C_5H_3^+$ ) produced from the scattering of dicarbon ( $C_2$ ) with 1-butyne ( $C_2H_5CCH$ ). Experimental data are indicated by black dots and the simulation represented by a black curve. The reactive and non-reactive scattering channels are indicated in red and blue, respectively. CM defines the center of mass.

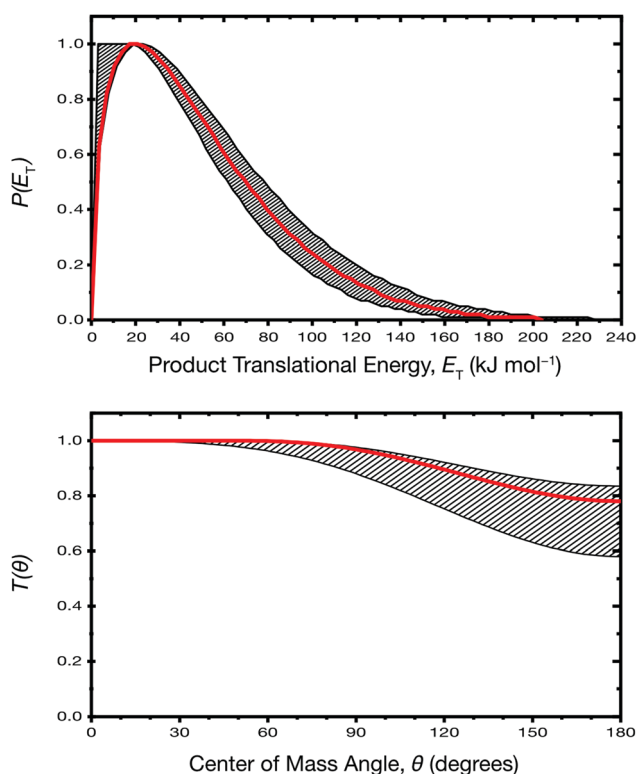


Fig. 10 Center-of-mass translational energy  $P(E_T)$  (upper) and angular  $T(\theta)$  flux distributions (lower) for the reaction of dicarbon with methylacetylene forming  $C_5H_3$  isomers via an atomic hydrogen (H) emission. The best-fit functions are represented by red lines with error fitting indicated by hatching.

$C_5HD_3$  isomers with an average lifetime of about  $2.7\tau_r$ . The translational energy flux distribution  $P(E_T)$  could be fit with a

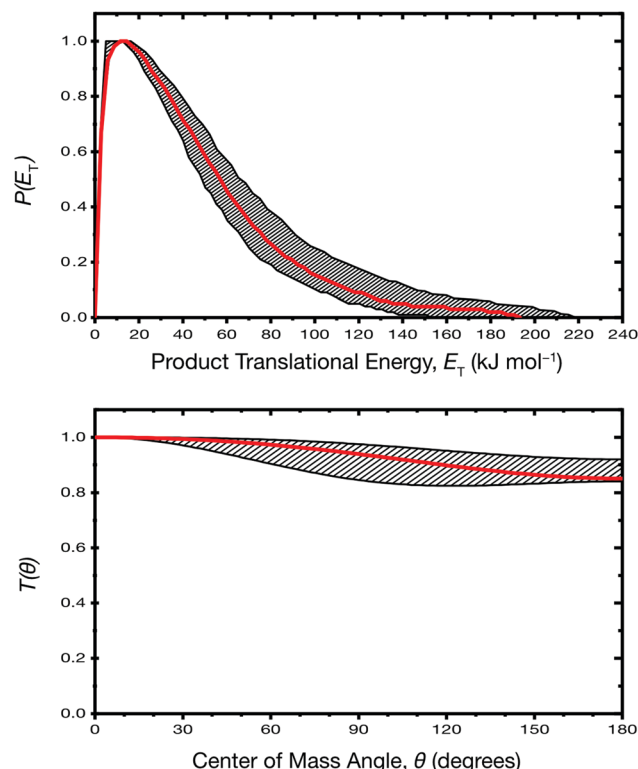


Fig. 11 Center-of-mass translational energy  $P(E_T)$  (upper) and angular  $T(\theta)$  flux distributions (lower) for the reaction of dicarbon with  $d_3$ -methylacetylene forming  $C_5HD_2$  isomers via an atomic deuterium (D) emission. The best-fit functions are represented by red lines with error fitting indicated by hatching.

high energy cutoff in the region  $153 \leq E_{\max} \leq 219 \text{ kJ mol}^{-1}$  (Fig. 11,  $P(E_T)$ ). The best fit corresponds to  $E_{\max} = 193 \text{ kJ mol}^{-1}$  which gives a derived reaction energy of  $-169 \pm 25 \text{ kJ mol}^{-1}$  for the deuterium atom loss channel. The best fitting  $P(E_T)$  peaks near  $13 \text{ kJ mol}^{-1}$ , but the data could also be fit with a broad distribution maximum ranging from  $5$  to  $16 \text{ kJ mol}^{-1}$ . Once more, the latter suggests that  $C_5HD_2$  formation involves at least two dissociation channels. This  $P(E_T)$  also indicates that on average  $24 \pm 6\%$  of the available energy is disposed into translation, further suggesting contributions from an indirect reaction mechanism as noted in  $T(\theta)$ .

In the  $C_2$ - $C_2H_5CCH$  system the CM angular flux distribution of the methyl ( $CH_3$ ) elimination channel exhibits intensity across all angles (Fig. 12,  $T(\theta)$ ). This  $T(\theta)$  is slightly backward scattered with respect to dicarbon, with  $T(0^\circ)/T(180^\circ) = 0.9 \pm 0.1$ . Furthermore, the  $T(\theta)$  dips near  $\theta = 63^\circ$ . This suggests that at least one exit channel involves the methyl-loss within the rotational plane of the dissociating  $[C_6H_6]^*$  complex due to efficient coupling of orbital angular momentum between the reactants and products. The translational energy flux distribution (Fig. 12,  $P(E_T)$ ) for  $C_5H_3$  formation extends out to  $E_{\max} = 118 \pm 16 \text{ kJ mol}^{-1}$ , from which we obtain a reaction energy of  $-92 \pm 16 \text{ kJ mol}^{-1}$ . The most probable  $E_T$  is  $15 \pm 2 \text{ kJ mol}^{-1}$  indicating a loose, product like transition state(s) leading to  $C_5H_3$  plus  $CH_3$ . The average translational energy  $\langle E_T \rangle$  of  $32 \pm 4 \text{ kJ mol}^{-1}$  derived from  $P(E_T)$  reveals that only  $27 \pm 5\%$

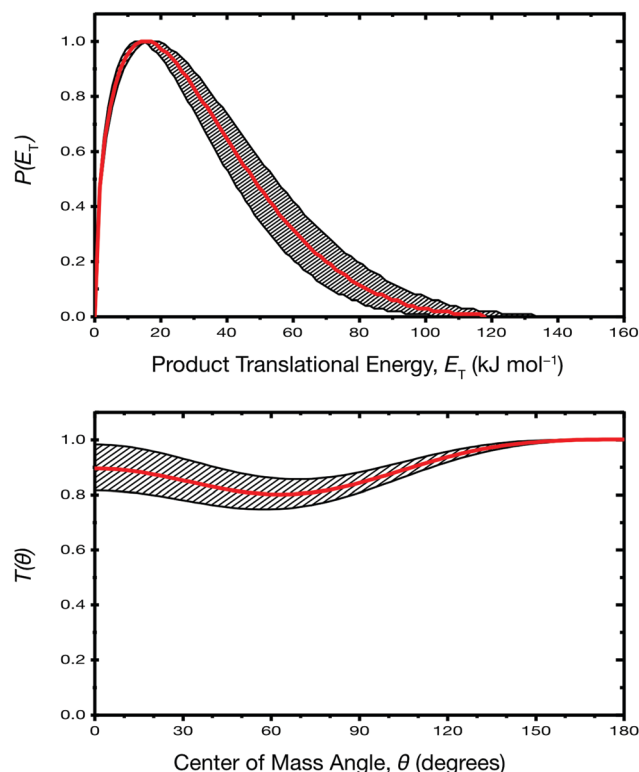


Fig. 12 Center-of-mass translational energy  $P(E_T)$  (upper) and angular  $T(\theta)$  flux distributions (lower) for the reaction of dicarbon with 1-butyne forming  $C_5H_3$  isomers via methyl ( $CH_3$ ) emission. The best-fit functions are represented by red lines with error fitting indicated by hatching.

channels into translational energy. Accordingly, at least one reaction channel leading to the  $C_5H_3$  product isomers is indirect. Velocity vector (Newton) diagrams relating the laboratory and CM observations of  $C_5H_3$  along with flux contour maps of the

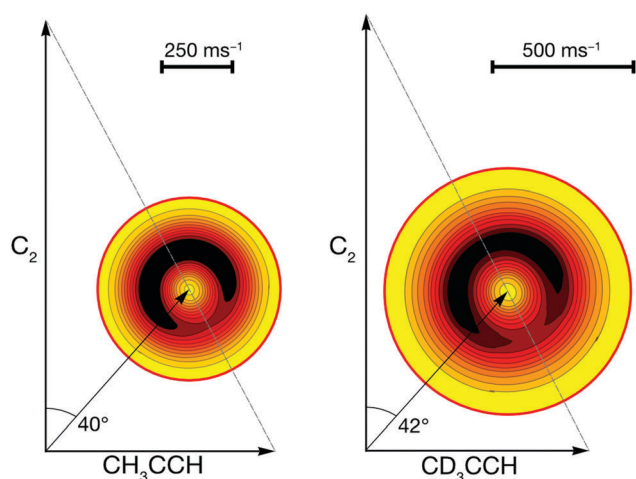


Fig. 13 Newton diagrams of the distribution of  $C_5H_3$  isomers formed via reactive scattering of dicarbon ( $C_2$ ) with methylacetylene ( $CH_3CCH$ ) (left) and  $d_3$ -methylacetylene ( $CD_3CCH$ ) (right). The Newton circle (red) has a radius corresponding to the maximum velocity of  $C_5H_3$  (or  $C_5HD_2$ ) in the CM frame for each respective reaction and visualizes the flux distribution of heavy products as determined by the CM functions.

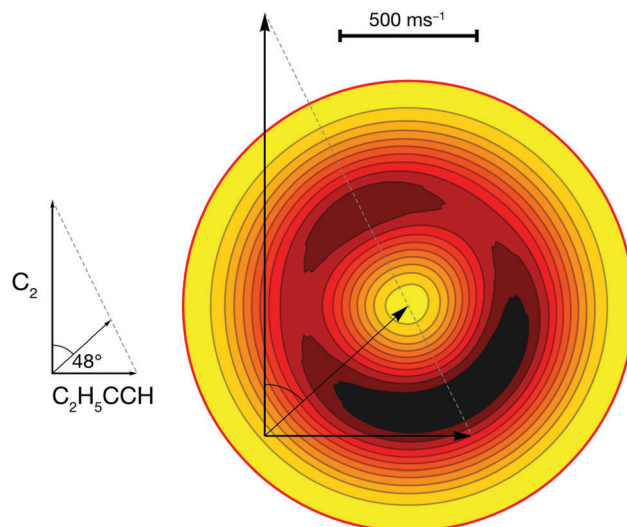


Fig. 14 Newton diagram of the distribution of  $C_5H_3$  isomers formed via reactive scattering of dicarbon ( $C_2$ ) with 1-butyne ( $C_2H_5CCH$ ). The Newton circle (red) has a radius corresponding to the maximum velocity of  $C_5H_3$  in the CM frame and visualizes the flux distribution of  $C_5H_3$  as determined by the CM functions.

derived reactive differential cross section for each of the dicarbon reactions are compiled in Fig. 13 and 14.

## 4. Discussion

In each of the three dicarbon reactions –  $C_2 + CH_3CCH$ ,  $C_2 + CD_3CCH$ , and  $C_2 + C_2H_5CCH$  – we observed ions at  $m/z$  63 (65) with time-of-flight (TOF) profiles indicative of  $C_5H_3$  ( $C_5HD_2$ ) formation in overall exoergic reactions. Recall that our dicarbon beam contains both  $C_2(X^1\Sigma_g^+)$  and  $C_2(a^3\Pi_u)$  reactants with  $v = 0$  states that differ by  $7.3 \text{ kJ mol}^{-1}$ . In discussing the results of our experiment, we leverage electronic structure calculations to determine which isomers represent the products formed in our experiments and to expose the underlying reaction mechanism governing their formation. This section is presented in two parts. The first part deals with the dicarbon–methylacetylene/ $d_3$ -methylacetylene system demonstrating that – in comparison with previous studies on this system<sup>66,67,98</sup> – our new dicarbon source can be exploited for reactive scattering experiments. The second part elucidates a newly observed methyl-loss channel from a  $C_6H_6$  reaction intermediate formed in the dicarbon plus 1-butyne system that was previously obscured due to complications arising from the ablation-sourced dicarbon beam and interference from reactions of carbon atoms.<sup>68</sup>

### 4.1. Dicarbon-( $d_3$ )-methylacetylene

To facilitate discussion of the dicarbon plus methylacetylene reaction we first consider the relevant  $C_5H_4$  potential energy surface relating those bimolecular reactions of triplet ( $a^3\Pi_u$ ) and singlet ( $X^1\Sigma_g^+$ ) dicarbon with methylacetylene ( $X^1A_1$ ) via  $C_5H_4$  intermediates to dissociation product channels via atomic and/or molecular elimination. The singlet and triplet potential energy surfaces have been established by Mebel *et al.*<sup>99</sup> and

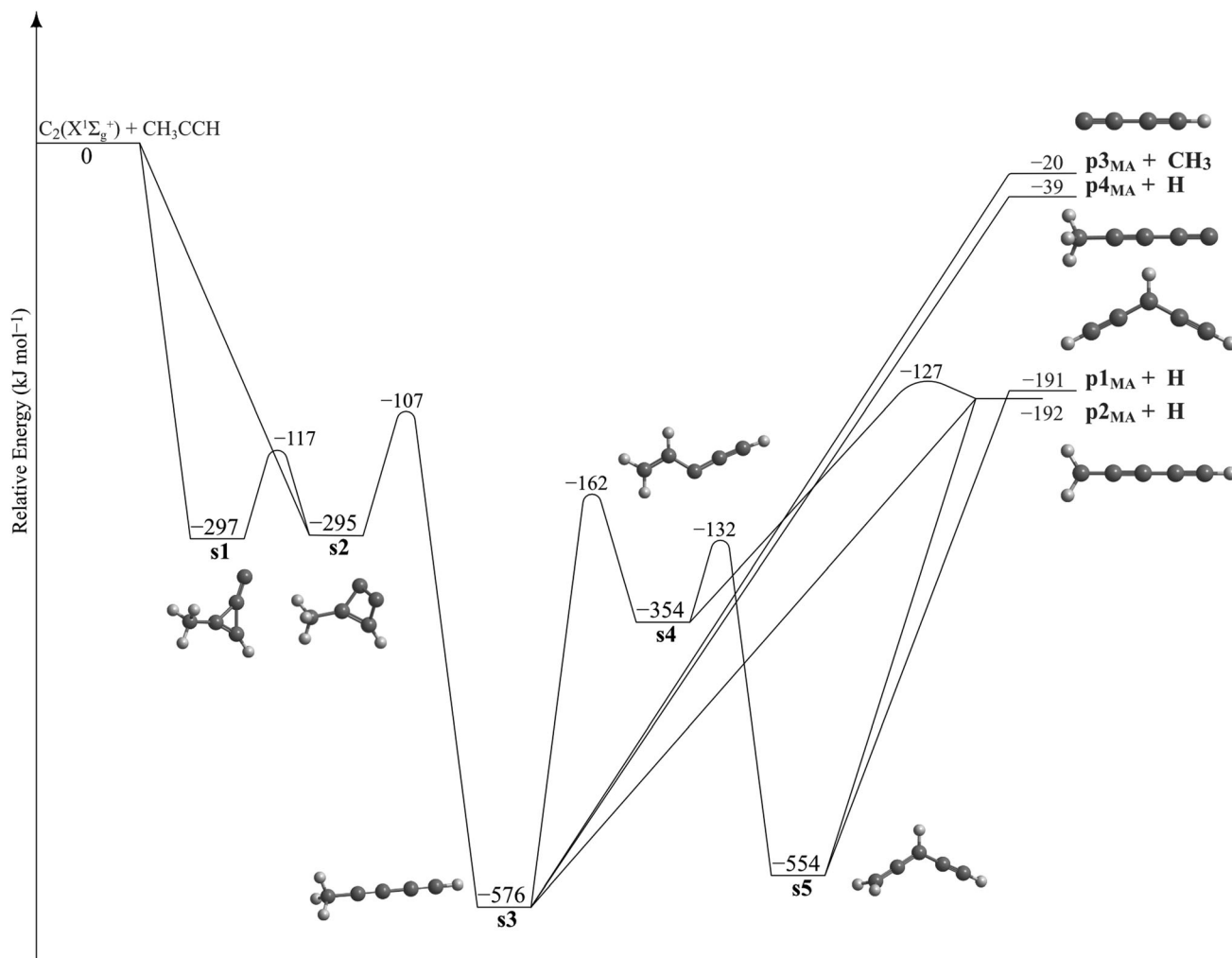


Fig. 15 Schematic representation of the potential energy surface (PES) accessed by the reaction of dicarbon ( $C_2(X^1\Sigma_g^+)$ ) plus methylacetylene ( $CH_3CCH(X^1A_1)$ ) adopted from Mebel *et al.*<sup>99</sup> Energies are determined at the G2M(RCC,MP2) level of theory and given relative to the separated reactants in  $\text{kJ mol}^{-1}$ .

by Gu *et al.*,<sup>101</sup> respectively, and have been reproduced in Fig. 15 and 16. The triplet surface has been extended to include methyl-loss pathways that were not previously considered (Fig. 16, red). Let us begin with events as they unfold on the singlet surface. Dicarbon in its singlet ground state can add without an entrance barrier either with its terminal end to the methylacetylene triple bond forming intermediate [s1] ( $CH_3CC_2CH$ ), or across the triple bond to form a disubstituted tetracarbon ring [s2] ( $CH_3C_4H$ ). All routes to dissociation products include the methylidyne ( $CH_3CCCCH$ ) global minimum, intermediate [s3], that lies  $576 \text{ kJ mol}^{-1}$  below the bimolecular entrance channel, and from which four new pathways emerge. Cleavage of the C–CH<sub>3</sub> bond leads to the butadiynyl [ $C_4H(^2\Sigma^+)$ ] (**p3<sub>MA</sub>**) plus methyl ( $CH_3$ ) product pair lying  $20 \text{ kJ mol}^{-1}$  below the separated reactants. Hydrogen loss can occur either from the acetylene end of [s3] ( $\equiv C-H$ ) to form the methylbutadiynyl radical ( $CH_3CCCC$ ; **p4<sub>MA</sub>**), or from the [s3] methyl group ( $CH_2-H$ ) to form the resonantly stabilized 2,4-pentadiynyl-1 (**p2<sub>MA</sub>**) [ $H_2CCCCCH(X^2B_1)$ ] radical in overall exoergic reactions.

The **p4<sub>MA</sub>** + H and **p2<sub>MA</sub>** + H products lie  $39 \text{ kJ mol}^{-1}$  and  $192 \text{ kJ mol}^{-1}$ , respectively, below  $C_2(X^1\Sigma_g^+) + CH_3CCH(X^1A_1)$ . Lastly, successive hydrogen migration from the [s3] methyl group *via* [s4] ultimately accesses the 1,4-pentadiynyl-3 product isomer *via* hydrogen atom emission from [s5]. Intermediate [s3] isomerizes to the planar [s4] ( $CH_2CHCCCCH$ ) by hydrogen migration from the methyl group. Hydrogen atom loss from [s4] yields **p2<sub>MA</sub>**, while isomerization from [s4] to [s5] ( $CH_2CCHCCH$ ) *via* hydrogen shift eventually results in elimination of atomic hydrogen from the [s5] central carbon to form **p2<sub>MA</sub>**, or from the [s5] methylene group to form 1,4-pentadiynyl-3 (**p1<sub>MA</sub>**) [ $HCCCCHCCH(X^2B_1)$ ] with an overall reaction energy of  $-191 \text{ kJ mol}^{-1}$ .

On the triplet surface three pathways are possible from the initial attack of dicarbon at the methylacetylene triple bond (Fig. 16). Addition across the triple bond is barrierless and forms a tricarbon ring [t1] ( $CH_3CC_2CH$ ) at the attack site that lies  $170 \text{ kJ mol}^{-1}$  below the separated reactants. Acyclic isomers of  $C_5H_4$  are also possible *via* the barrierless addition of dicarbon to the terminal acetylenic carbon atom forming *trans* [t2] or



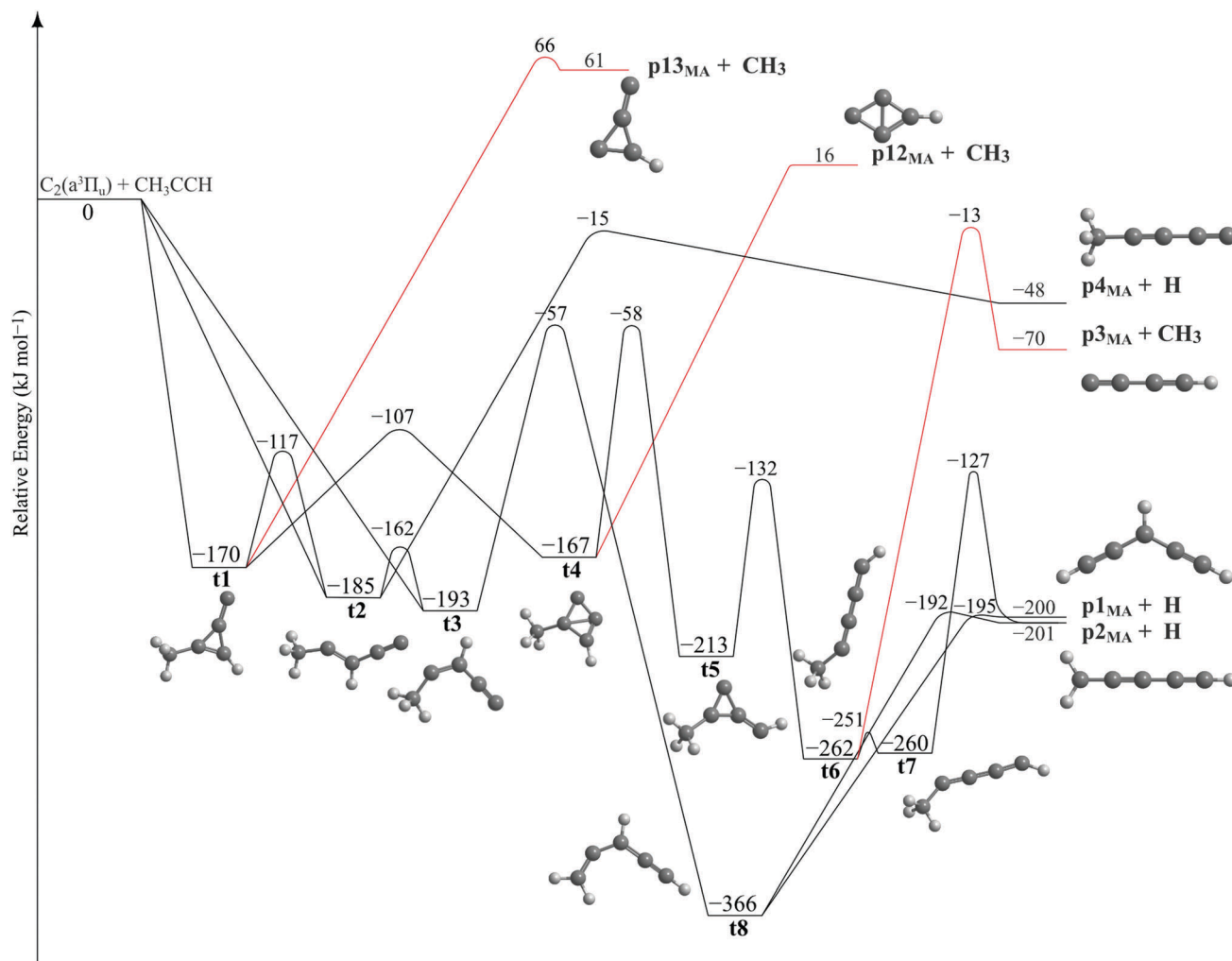


Fig. 16 Schematic representation of the potential energy surface (PES) accessed by the reaction of dicarbon ( $C_2(a^3\Pi_u)$ ) plus methylacetylene ( $CH_3CCH(X^1A_1)$ ) adopted from Gu *et al.*<sup>101</sup> All energies are relative to the separated reactants and given in  $\text{kJ mol}^{-1}$ . New  $C_4H + CH_3$  pathways developed in this study are shown in red.

*cis* [t3] pent-1-yn-3-en-diyl-1,4 ( $CH_3CCHC_2$ ) radical intermediates. The cyclic [t1] can dissociate by methyl emission in an overall endoergic reaction ( $61 \text{ kJ mol}^{-1}$ ) *via* a loose transition state forming  $p13_{MA}$  ( $C_4H$ ). [t1] can isomerize to [t2] by cleaving the C–C bond over a  $53 \text{ kJ mol}^{-1}$  barrier, or to an exotic rhomboid [t4] ( $CH_3C_4H$ ) bicycle by ring closure to the methyl-bearing carbon atom in [t1], from which loss of the methyl group forms the bicyclic  $c\text{-}C_4H$  ( $p12_{MA}$ ) product in an overall endoergic reaction ( $16 \text{ kJ mol}^{-1}$ ). Intermediate [t4] could also proceed to the disubstituted tricarbon ring [t5] ( $CH_3C_3CH$ ) by ring opening *via* a  $109 \text{ kJ mol}^{-1}$  barrier. [t5] can undergo further ring opening by cleavage of the C–C bond joining the substituted carbon atoms producing a 5-carbon backbone [t6] (*trans*- $CH_3CCCCH$ ) with methyl and hydrogen termini. The exoergic butadiynyl ( $C_4H$ ) plus methyl ( $CH_3$ ) product channel is accessible from [t6] through loss of its methyl group and has an overall reaction energy of  $-70 \text{ kJ mol}^{-1}$ . [t6] can also isomerize to [t7] (*cis*- $CH_3CCCCH$ ) *via* a low-lying barrier of  $11 \text{ kJ mol}^{-1}$ , from which follows atomic hydrogen loss from the methyl substituent to yield the

2,4-pentadiynyl-1 ( $H_2CCCCCH$ ) radical ( $p2_{MA}$ ) in an overall exoergic reaction ( $-201 \text{ kJ mol}^{-1}$ ). Hydrogen loss from [t2] at the central carbon might form the methylbutadiynyl radical [ $CH_3CCCC(X^2A_1)$ ],  $p4_{MA}$ , with an overall reaction exoergicity of  $-48 \text{ kJ mol}^{-1}$ . Alternatively, [t2] can isomerize to the slightly more stable [t3] structure by traversing a relatively small barrier of  $23 \text{ kJ mol}^{-1}$ . From [t3] the system can pass through a  $136 \text{ kJ mol}^{-1}$  barrier *via* long range hydrogen migration, *i.e.* from the terminal methyl group to the terminal carbon atom of the dicarbon moiety resulting in an ethynyl-substituted propargyl-like system [t8] ( $CH_2CCHC_2H$ ) that is stabilized by  $366 \text{ kJ mol}^{-1}$  relative to the separated reactants. Loose exit transition states from intermediate [t8] yield the  $C_5H_3$  radicals 1,4-pentadiynyl-3 ( $p1_{MA}$ ) and 2,4-pentadiynyl-1 and ( $p2_{MA}$ ) *via* atomic hydrogen loss. The  $p1_{MA} + H$  and  $p2_{MA} + H$  product channels are overall exoergic by 200 and  $201 \text{ kJ mol}^{-1}$ , respectively.

Through consideration of our experimental results with the preceding discussion of the dicarbon–methylacetylene potential energy surface we can postulate the reaction mechanism(s)

underlying the formation of  $C_5H_3$  in our crossed molecular beams experiment. Recall that our derived reaction energy forming the  $C_5H_3$  product isomer(s) plus atomic hydrogen is  $-181 \pm 25 \text{ kJ mol}^{-1}$  and agrees well with predicted reaction energies of the atomic hydrogen loss product channels leading to the 2,4-pentadiynyl-1 ( $H_2CCCCCH$ ) and 1,4-pentadiynyl-3 ( $HCCCHCCH$ ) radicals on the singlet and triplet potential energy surfaces,<sup>101</sup> and that the CM flux distributions reveal that the reaction proceeds through at least one  $[C_5H_4]^*$  intermediate as indicated by the relatively low release of available energy into the  $C_5H_3$  translational degrees of freedom along with its distribution at all angles in the center-of-mass frame.

The paths connecting  $C_2(X^1\Sigma_g^+/a^3\Pi_u)$  plus  $CH_3CCH(X^1A_1)$  to the 2,4-pentadiynyl-1 ( $H_2CCCCCH$ ) and 1,4-pentadiynyl-3 ( $HCCCHCCH$ ) radicals *via* atomic hydrogen loss on the  $C_5H_4$  potential energy surface involve multiple  $C_5H_4$  intermediates. On the singlet surface  $H_2CCCCCH$  (**p2<sub>MA</sub>**) is formed alongside the slightly less stable  $HCCCHCCH$  isomer (**p1<sub>MA</sub>**) with respective yields of 65% and 32% at  $20 \text{ kJ mol}^{-1}$  as determined by RRKM.<sup>99</sup>  $C_5H_3$  formation on the singlet surface requires as few as two intermediates by  $C_2(X^1\Sigma_g^+)$  addition across the acetylene group, while on the triplet surface a minimum of four intermediates is required if addition similarly occurs across the  $CH_3CCH$  triple bond and only two intermediates if  $C_2(a^3\Pi_u)$  adds to the terminal ( $\equiv C-H$ ) carbon atom.<sup>101</sup> On the triplet surface production of the  $H_2CCCCCH$  isomer (**p2<sub>MA</sub>**) is strongly preferred to  $HCCCHCCH$  (**p1<sub>MA</sub>**) due to the rate determining  $[t4] \rightarrow [t5]$  and  $[t3] \rightarrow [t8]$  transition states, with the former being about 6 times faster than the latter.<sup>101</sup> The methyl-bearing *cis*-2,3,4-pentatrien-2,5-diyl  $[t7]$  intermediate, accessed *via* the relatively loose  $[t4] \rightarrow [t5]$  ring-opening transition state, is thus favored for dissociation to 2,4-pentadiynyl-1 + H. Note that while hydrogen atom loss from the central carbon of  $[t8]$  is also possible, we did not observe a hydrogen loss channel using the d3-methylacetylene ( $CD_3CCH$ ) isotopologue and thus exclude the formation  $H_2CCCCCH$  *via* this path. Therefore, those dissociation products formed *via*  $[t8]$  do not contribute to our reactive scattering signal. Furthermore, the absence of an atomic hydrogen loss also removes the  $CH_3CCCC$  (**p4<sub>MA</sub>**) isomer from consideration and thus  $C_5H_3$  formation on the triplet surface is limited to  $H_2CCCCCH$  (**p2<sub>MA</sub>**). Considering the CM translational flux distribution  $P(E_T)$ , the plateau spanning  $3 \leq E_T \leq 23 \text{ kJ mol}^{-1}$  (Fig. 10) suggests at least two reaction pathways are responsible for  $C_5H_3$  formation, where the distribution maximum contains information about the unimolecular dissociation of  $[C_5H_4]^*$ . As discussed,  $H_2CCCCCH$  (**p2<sub>MA</sub>**) is formed on the triplet surface *via* the  $[t7]$  intermediate only. On the singlet surface, both  $H_2CCCCCH$  (**p2<sub>MA</sub>**) and  $HCCCHCCH$  (**p1<sub>MA</sub>**) are predicted to form with a relative yield of 2:1. The absence of a strong sideways peaking of the CM angular flux distribution might hint to a lack of significant reactive scattering signal arising from the singlet surface – *i.e.* a triplet rich dicarbon beam – where geometrical constraints on the decomposition of the highly symmetric methyldiacetylene  $[s3]$  intermediate would otherwise manifest in  $T(\theta)$  by a maximum near  $\theta = 90^\circ$  for the  $C_5H_3$  product.

Notably, the energetics forming  $C_5H_3$  product isomers plus atomic hydrogen of  $-181 \pm 25 \text{ kJ mol}^{-1}$  are identical within the error limits to those derived by Guo *et al.* of  $-182 \pm 10 \text{ kJ mol}^{-1}$ ,<sup>66</sup> who sourced their dicarbon beam from graphite ablation. In the experiment conducted by Guo *et al.*, the resulting data were best fit with a backward peaking  $T(\theta)$  that featured a maximum near  $\theta = 100^\circ$ .<sup>66</sup> The sideways character of this distribution was attributed to a decomposing methyldiacetylene intermediate where the departing hydrogen atom held a perpendicular trajectory with respect to the rotational plane of the  $[C_5H_4]^*$  to form  $H_2CCCCCH$  (**p2<sub>MA</sub>**) and was later corroborated by the singlet potential energy surface of Mebel *et al.* that indicates a  $C_{3v}$  symmetric methyldiacetylene intermediate that precedes dissociation *via* hydrogen atom emission from the methyl group.<sup>99</sup> In contrast with the ablation-sourced dicarbon experiment performed by Guo *et al.*,<sup>66</sup> our center-of-mass angular distribution is slightly forward and does not depict a maximum near  $\theta = 90^\circ$  (Fig. 10). The change in  $T(\theta)$  polarization, *i.e.* forward *vs.* backward scattering of  $C_5H_3$  products, is likely due to the difference in collision energies  $E_C$  employed in the two sets of experiments with  $E_C = 37.6 \pm 0.8 \text{ kJ mol}^{-1}$  in the ablation study (compare to the much lower  $E_C = 23.2 \pm 0.3 \text{ kJ mol}^{-1}$  used in the present study). Furthermore, the distribution maximum at  $T(100^\circ)$  by Guo *et al.* attributed to the formation of 2,4-pentadiynyl-1 on the singlet surface *via*  $[s3] \rightarrow \text{p2<sub>MA</sub>} + H$  (Fig. 15) is noticeably absent from the  $T(\theta)$  derived in the present study (Fig. 10). The dissimilarity of CM angular flux distributions in polarization and behavior near  $\theta = 90^\circ$  highlight a change in the reaction mechanism most representative of  $C_5H_3 + H$  formation in the two studies which could owe to differing  $C_2(a^3\Pi_u)/C_2(X^1\Sigma_g^+)$  ratios derived from the ablation and photolytic dicarbon sources.

In the dicarbon plus methylacetylene ( $CH_3CCH$ ) reaction we also probed for methyl-loss products at  $m/z$  49 ( $C_4H^+$ ) but detected no signal indicative of product formation. On the singlet surface (Fig. 15), the  $C_4H + CH_3$  product channel is exoergic by  $20 \text{ kJ mol}^{-1}$  but statistically accounts for about 5 of every million dissociation products at  $E_C = 20 \text{ kJ mol}^{-1}$ . Through extension of the triplet surface formulated by Gu *et al.*<sup>101</sup> we identified three distinct  $C_4H + CH_3$  dissociation channels on the triplet surface: two endoergic pathways leading to cyclic moieties and an exoergic route that produces the butadiynyl radical plus atomic hydrogen through the liberation of  $70 \text{ kJ mol}^{-1}$  (Fig. 16, red paths); the noticeable difference in the energy of the  $C_4H + CH_3$  product in the present calculations is attributed to the use of the higher CCSD(T)-F12/cc-pVTZ-f12 level of theory as compared to the G2M(RCC,MP2) level employed in the previous work.<sup>99</sup> The combined branching ratio for these channels is negligibly low and thus the absence of a product signal corresponding to  $C_4H + CH_3$  in our  $C_2(X^1\Sigma_g^+/a^3\Pi_u) + CH_3CCH$  reaction system is consistent with the existing theoretical framework.

Finally, in our dicarbon plus d3-methylacetylene ( $CD_3CCH$ ) system we observed only the atomic deuterium channel leading to  $C_5HD_2 + D$  from which we derived a reaction energy of  $-169 \pm 25 \text{ kJ mol}^{-1}$ . This closely agrees with the formation of the  $D_2CCCCCH$  and/or  $DCCCHCCD$  isomer(s) from the  $C_2(X^1\Sigma_g^+/a^3\Pi_u) + CH_3CCH$  potential energy surface (Fig. 15 and 16).

On the singlet surface, both the  $D_2CCCCCH$  and  $DCCCHCCD$  products can be formed by deuterium atom emission from intermediate [s3], [s4], or [s5] (Fig. 15). On the triplet surface, the path through [t8], here considered as  $D_2CCCHCCD$ , can undergo atomic hydrogen emission from the central carbon to form  $D_2CCCCCH + H$ , or atomic deuterium loss from the [t8] methylene group to form  $DCCCHCCD + D$ ; however, the absence of the hydrogen loss channel suggests that the unimolecular dissociation of [t8] does not contribute to product formation as measured by the signal recorded at  $m/z$  65 ( $C_5HD_2^+$ ). Product formation on the triplet surface thus lies with the statistically favored path to dissociation *via* intermediate [t7], here  $D_3CCCCCH$ , by deuterium atom emission from the d3-methyl ( $CD_3$ ) group to form  $D_2CCCCCH + D$ . Note that absence of a hydrogen loss channel in the dicarbon plus d3-methylacetylene reaction system parallels the experimental outcome of Gu *et al.*<sup>101</sup>

#### 4.2. Dicarbon-1-butyne

In our reactive scattering of dicarbon with 1-butyne we found that the reaction forms  $C_5H_3$  in an overall exoergic reaction ( $-92 \pm 16$  kJ mol<sup>-1</sup>). To assign a structure to the product formed in our experiment we turned to the  $C_2(X^1\Sigma_g^+/a^3\Pi_u)$  plus  $C_2H_5CCH(X^1A')$  potential energy surfaces formulated by Parker *et al.* (Fig. 5 in ref. 68) which contained a single methyl-loss forming the  $H_2CCCCCH$  (**p2<sub>1b</sub>**) propargyl analog. We extended the existing triplet  $C_6H_6$  potential energy surface at the CCSD(T)/CBS(dt) level of theory to include pathways leading to three additional methyl-loss product channels: **p11<sub>1b</sub>** +  $CH_3$  ( $-91$  kJ mol<sup>-1</sup>), **p12<sub>1b</sub>** +  $CH_3$  ( $-29$  kJ mol<sup>-1</sup>), and **p13<sub>1b</sub>** +  $CH_3$  ( $-25$  kJ mol<sup>-1</sup>). The  $C_5H_3$  products **p2<sub>1b</sub>**, **p11<sub>1b</sub>**, **p12<sub>1b</sub>**, & **p13<sub>1b</sub>** were further explored at CCSD(T) using the CBS(dtq) basis set

resulting in reaction energies of  $-281$ ,  $-86$ ,  $-30$ , &  $-21$  kJ mol<sup>-1</sup> for each respective methyl-loss channel. The energies derived from the CCSD(T)/CBS(dt) and CCSD(T)/CBS(dtq) methods are accurate to within  $\pm 15$  kJ mol<sup>-1</sup> and  $\pm 10$  kJ mol<sup>-1</sup>, respectively. Importantly, viable pathways forming **p11<sub>1b</sub>**, **p12<sub>1b</sub>**, or **p13<sub>1b</sub>** do not exist on the singlet surface. The relevant intermediates and transition states connecting  $C_2(a^3\Pi_u) + C_2H_5CCH(X^1A')$  to the aforementioned  $C_5H_3 + CH_3$  product channels are compiled in Fig. 18 and discussed below.

On the  $C_2 + C_2H_5CCH$  singlet surface (Fig. 17), dicarbon adds to the triple bond ( $-C\equiv C-$ ) of 1-butyne forming either a three-membered [**i1<sub>1b</sub>**] or four-membered [**i2<sub>1b</sub>**] ring intermediate. Intermediate [**i1<sub>1b</sub>**] is connected to [**i2<sub>1b</sub>**], and both ultimately to [**i3<sub>1b</sub>**] which lies 602 kJ mol<sup>-1</sup> below  $C_2(X^1\Sigma_g^+) + C_2H_5CCH(X^1A')$ . From [**i3<sub>1b</sub>**], three dissociation channels are accessible but only one involves methyl-loss: **p2<sub>1b</sub>** +  $CH_3$ . The surface involving triplet  $C_2$  is decisively more complex with an increased number of initial addition complexes that are both cyclic and acyclic (Fig. 18). Specifically, the triplet reaction can proceed by barrierless addition of  $C_2(a^3\Pi_u)$  to one or both carbon atoms in the  $C_2H_5-C\equiv C-H$  acetylene group. Addition to the terminal ( $\equiv C-H$ ) or ethyl-substituted ( $\equiv C-C_2H_5$ ) carbon yields the dicarbon-substituted intermediates [**i8<sub>1b</sub>**] and [**i5<sub>1b</sub>**], respectively. Dicarbon can also add barrierlessly to both acetylenic carbon atoms simultaneously ( $-C\equiv C-$ ) forming a disubstituted tricarbon ring [**i4<sub>1b</sub>**] that can isomerize to [**i5<sub>1b</sub>**] or directly to [**i8<sub>1b</sub>**] by ring opening *via* 60 kJ mol<sup>-1</sup> and 62 kJ mol<sup>-1</sup> barriers, respectively. Intermediate [**i5<sub>1b</sub>**] is also connected to [**i8<sub>1b</sub>**] by intermediate [**i6<sub>1b</sub>**] which bears a tetracarbon ring and is the least stable  $C_6H_6$  isomer on our triplet PES at 138 kJ mol<sup>-1</sup> below the separated reactants. The four-membered ring of [**i6<sub>1b</sub>**]

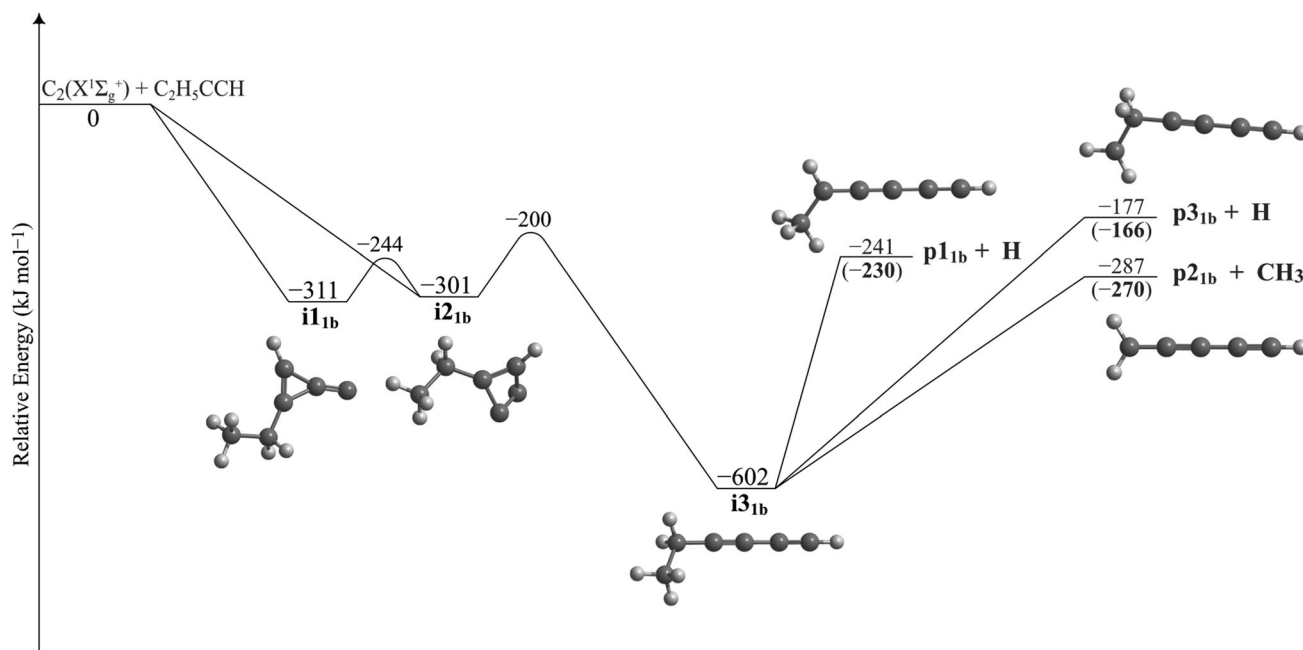


Fig. 17 Schematic representation of the potential energy surface (PES) accessed by the reaction of dicarbon ( $C_2(X^1\Sigma_g^+)$ ) plus 1-butyne ( $C_2H_5CCH(X^1A')$ ) adopted from Parker *et al.*<sup>68</sup> All energies are relative to the separated reactants and given in kJ mol<sup>-1</sup>. Plain and bold numbers show relative energies computed at the CCSD(T)/CBS(dt) and CCSD(T)/CBS(dtq) levels of theory respectively.

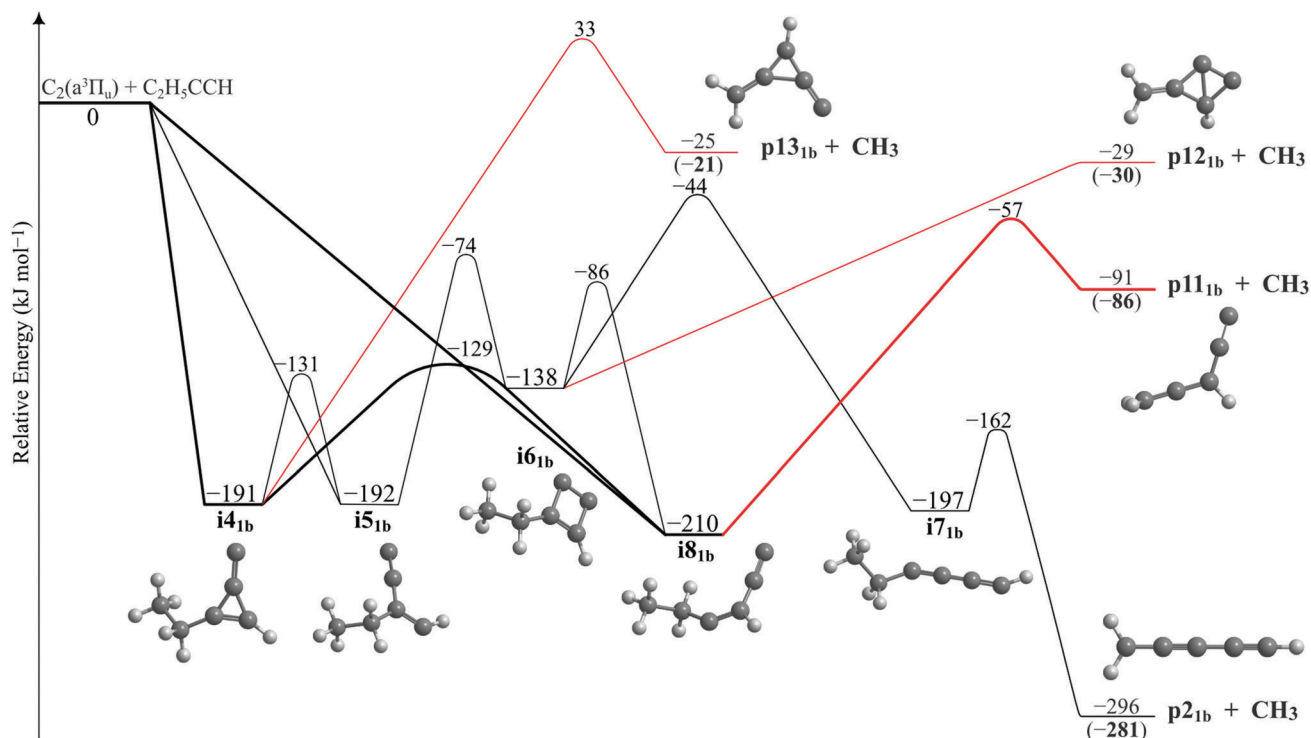


Fig. 18 Schematic representation of the potential energy surface (PES) accessed by the reaction of dicarbon ( $C_2(a^3\Pi_u)$ ) plus 1-butyne ( $C_2H_5CCH(X^1A')$ ) adopted from Parker *et al.*<sup>68</sup> All energies are relative to the separated reactants and given in  $\text{kJ mol}^{-1}$ . Plain and bold numbers show relative energies computed at the CCSD(T)/CBS(dt) and CCSD(T)/CBS(dtq) levels of theory respectively. New pathways to  $C_5H_3 + CH_3$  dissociation are shown in red and the dominant reaction channels are highlighted in bold.

can open to give the five-carbon chain structures [ $i7_{ib}$ ] or [ $i8_{ib}$ ] through respective barriers of 94 or 52  $\text{kJ mol}^{-1}$ . From [ $i7_{ib}$ ] and [ $i8_{ib}$ ], several paths leading to numerous  $C_6H_6$  intermediates and  $C_6H_5$  product channels along with the resonantly stabilized  $c\text{-C}_5\text{H}_5$  radical were developed, but are beyond this scope of this discussion. An extensive summary of these pathways is given by Parker *et al.* (2014).<sup>68</sup>

The products  $p2_{ib}$ ,  $p11_{ib}$ ,  $p12_{ib}$ , &  $p13_{ib}$  are attainable through C- $CH_3$  bond cleaving transition states from the methylated intermediates [ $i4_{ib}$ ], [ $i6_{ib}$ ], [ $i7_{ib}$ ], and [ $i8_{ib}$ ]. Intermediate [ $i4_{ib}$ ], which is stabilized by 191  $\text{kJ mol}^{-1}$  relative to the separated reactants, can form  $p13_{ib} + CH_3$  through an exit barrier that lies 33  $\text{kJ mol}^{-1}$  above the bimolecular entrance channel. [ $i6_{ib}$ ] is bound by 138  $\text{kJ mol}^{-1}$  and can yield  $p12_{ib} + CH_3$  by barrierless dissociation. Intermediate [ $i7_{ib}$ ] is stabilized by 197  $\text{kJ mol}^{-1}$  and leads to the energetically most favorable methyl-loss channel,  $p2_{ib} + CH_3$ , via a barrier located 35  $\text{kJ mol}^{-1}$  above the separated products. Intermediate [ $i8_{ib}$ ] lies 210  $\text{kJ mol}^{-1}$  below the separated reactants and can form  $p11_{ib} + CH_3$  via a transition state 34  $\text{kJ mol}^{-1}$  above this product channel.

Considering the collision energy of our  $C_2 + C_2H_5CCH$  reaction system, along with the rovibrational excitation in dicarbon's  $X^1\Sigma_g^+$  and  $a^3\Pi_u$  states, all  $C_5H_3 + CH_3$  product channels are open under our experimental conditions. A comparison of the experimentally derived reaction energy ( $-92 \pm 16 \text{ kJ mol}^{-1}$ ) with the  $C_5H_3$  isomers  $p2_{ib}$ ,  $p11_{ib}$ ,  $p12_{ib}$ , &  $p13_{ib}$  formed in tandem with

the methyl radical indicates that  $p11_{ib} + CH_3$  ( $-86 \pm 10 \text{ kJ mol}^{-1}$ ) most readily agrees with the experiment. The  $p11_{ib}$  ( $H_2CCCHCC$ ) product is only formed on the triplet surface via  $C_2(a^3\Pi_u) + C_2H_5CCH(X^1A')$ , and only by methyl emission from [ $i8_{ib}$ ]. Hence the following mechanisms are feasible:  $C_2 + C_4H_6 \rightarrow [i4_{ib}] \rightarrow [i5_{ib}] \rightarrow [i6_{ib}] \rightarrow [i8_{ib}]/[i4_{ib}] \rightarrow [i8_{ib}]/[i5_{ib}] \rightarrow [i6_{ib}] \rightarrow [i8_{ib}]/[i8_{ib}] \rightarrow p11_{ib} + CH_3$ . RRKM analysis indicates that the path through [ $i4_{ib}$ ]  $\rightarrow$  [ $i8_{ib}$ ] is favored in the formation of  $p11_{ib} + CH_3$ . Our CM flux distributions cannot completely exclude the formation of the less stable  $C_5H_3$  isomers  $p12_{ib}$  and  $p13_{ib}$ , whose minor contributions would be obscured by the imposing  $p11_{ib} + CH_3$  channel. On the other hand, evidence for the rather exoergic  $p2_{ib}$  ( $H_2CCCCCH$ ) +  $CH_3$  channel is absent from the experimental data; this is consistent with the inherent higher barriers involved in the [ $i5_{ib}$ ]  $\rightarrow$  [ $i6_{ib}$ ]  $\rightarrow$  [ $i7_{ib}$ ] reaction sequence. While we can positively attribute  $p11_{ib}$  formation to the  $C_2(a^3\Pi_u) + C_2H_5CCH(X^1A')$  reaction, we have not accounted for the most exoergic methyl-loss channel. On the triplet surface, RRKM calculations predict that  $H_2CCCHCC$  ( $p11_{ib}$ ) is produced alongside  $H_2CCCCCH$  ( $p2_{ib}$ ) with a relative yield of 7 : 1. On the singlet surface, however,  $H_2CCCCCH$  ( $p2_{ib}$ ) is expected to be the dominant product representing 92% of the total yield via intermediates [ $i2$ ] and [ $i3$ ].<sup>68</sup> The  $a^3\Pi_u/X^1\Sigma_g^+$  ratio in our dicarbon beam could be much greater than unity. Spectroscopic signatures for the singlet ground state with vibrational excitation up to  $v = 1$  were recorded, but we are unable to quantify the concentration of singlet species in the beam.



One indicator may be in the CM functions for the  $C_2 + CH_3CCH$  reactions conducted in this study, specifically the polarization of the  $T(\theta)$  flux distribution where characteristics of a singlet reaction coordinate are absent. Therefore, the highly favored  $H_2CCCCCH$  (**p2<sub>1b</sub>**) formation on the singlet surface may be negated by a reduced fraction of singlet dicarbon in the beam.

## 5. Conclusion

The crossed molecular beam technique was exploited to explore the formation of three isomers of resonantly stabilized ( $C_5H_3$ ) radicals along with their  $d_2$ -substituted counterparts *via* the bimolecular reactions of singlet/triplet dicarbon [ $C_2(X^1\Sigma_g^+/a^3\Pi_u)$ ] with methylacetylene [ $CH_3CCH(X^1A_1)$ ],  $d_3$ -methylacetylene [ $CD_3CCH(X^1A_1)$ ], and 1-butyne [ $C_2H_5CCH(X^1A')$ ] at collision energies of  $23.2 \pm 0.3$ ,  $24.0 \pm 0.2$ , and  $26.2 \pm 0.8$  kJ mol<sup>-1</sup>, respectively, through chemically activated singlet/triplet  $C_5H_4/C_5D_3H$  and  $C_6H_6$  intermediates. Considering the experimental challenges of graphite ablation sources as a dicarbon precursor, our present study utilizes a newly developed supersonic dicarbon [ $C_2(X^1\Sigma_g^+/a^3\Pi_u)$ ] beam generated *via* photolysis of helium-seeded tetrachloroethylene [ $C_2Cl_4(X^1A_g)$ ]. The number densities of dicarbon of this photolysis source are higher by a factor of 2.5 compared to ablation sources with significantly enhanced speed ratios of up to about 12. Most importantly, the photolytic source eliminates the generation of carbon atoms, which are dominating co-reactants in ablation-based dicarbon sources thus hindering the detection of potential methyl loss channels. We first demonstrated the performance of our dicarbon [ $C_2(X^1\Sigma_g^+/a^3\Pi_u)$ ] beam in reactions with methylacetylene [ $CH_3CCH(X^1A_1)$ ] and  $d_3$ -methylacetylene [ $CD_3CCH(X^1A_1)$ ] and demonstrated that the reaction dynamics match previous studies of these systems in our laboratory utilizing ablation-based dicarbon sources. These involve the formation of 1,4-pentadiynyl-3 [ $HCCCCCH(X^2B_1)$ ] and 2,4-pentadiynyl-1 [ $H_2CCCCCH(X^2B_1)$ ] *via* atomic hydrogen (deuterium) atom elimination *via* overall barrierless and exoergic reactions on the singlet and triplet surfaces; no methyl-loss channel was detected, which correlated with predictions from RRKM calculations.

We also examined the  $C_2(X^1\Sigma_g^+/a^3\Pi_u)$ -1-butyne [ $C_2H_5CCH(X^1A')$ ] reaction for the hitherto elusive methyl-loss pathway and detected reactive scattering signal at  $m/z$  63 ( $C_5H_3^+$ ) with a laboratory angular distribution characteristic of indirect scattering dynamics. The experimentally derived reaction energy of  $-92 \pm 16$  kJ mol<sup>-1</sup> matches the computationally predicted product channel forming the resonantly stabilized penta-1-yn-3,4-dienyl-1 ( $H_2CCCHCC$ ;  $X^2A$ ) radical along with the methyl radical  $CH_3(X^2A_2'')$ . This channel is exclusively open on the triplet surface with an overall reaction energy of  $-86 \pm 10$  kJ mol<sup>-1</sup>. The preferred reaction pathways proceed *via* barrier-less addition of triplet dicarbon to the  $\pi$ -electronic system of 1-butyne to both or to the sterically more accessible carbon atom *via* methyl-bearing triplet  $C_6H_6$  intermediates [**i4<sub>1b</sub>**] and [**i8<sub>1b</sub>**], respectively, with the latter decomposing *via* a tight exit transition state to penta-1-yn-3,4-dienyl-1 ( $H_2CCCHCC$ ;  $X^2A$ ) plus the methyl radical  $CH_3(X^2A_2'')$ . It should

be recalled that based on its reactivity and open shell character, triplet dicarbon has been dubbed a 'pseudo-halogen'. The addition of triplet dicarbon to the  $\alpha$ -carbon atom of 1-butyne leading to [**i8<sub>1b</sub>**] followed by methyl group loss mirrors the addition – hydrogen/methyl group loss sequence in alkyne-halogen systems and also resembles the dicarbon addition – hydrogen atom loss sequence in the reaction of dicarbon with benzene forming the phenylethynyl radical ( $C_6H_5CC$ ;  $X^2A'$ ).<sup>74</sup> The successful unraveling of this methyl-loss channel demonstrates the viability of the photolytically generated dicarbon beam as an unprecedented tool to probe the underlying reaction dynamics involved in the formation of resonantly stabilized free radicals (RSFR) – and in particular of exotic radicals formed *via* one-step triplet dicarbon addition – hydrogen/methyl loss elimination sequences highlighting the role of dicarbon as a pseudo halogen – of vital importance in molecular mass growth processed leading ultimately to polycyclic aromatic hydrocarbons (PAHs) previously beyond the reach of the crossed molecular beams community.

## Conflicts of interest

There are no conflicts to declare.

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