

Photodissociation Pathways of Vinylacetylene (C₄H₄) and Implications for the Interstellar Hydrocarbon Chemistry

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Abstract

Vinylacetylene represents a key molecular building block in the hydrogen-abstraction–vinylacetylene-addition pathway leading barrierlessly to polycyclic aromatic hydrocarbons (PAHs) via benzene ring annulation. Although the formation of vinylacetylene in cold molecular clouds is well understood and proceeds via the barrierless and exoergic neutral – neutral reaction of ethynyl radicals (C_2H) with ethylene (C_2H_4), its photodissociation channels have been poorly constrained. Here, we investigate the photodissociation dynamics of vinylacetylene at 193 nm under collision-free conditions using a supersonic molecular beam coupled with a rotatable mass-spectrometric detector. Time-of-flight spectra were recorded for $m/z = 51$, 50, 26, and 25 and analyzed through forward-convolution fitting. Three primary dissociation pathways are identified: H-loss yielding C_4H_3 radicals, H_2 -loss forming C_4H_2 isomers, and C–C bond cleavage producing C_2H_2/CCH_2 fragments with experimental branching ratios of $C_4H_3 : C_4H_2 : C_2H_2/CCH_2 = (75 \pm 2) : (10 \pm 2) : (15 \pm 2)$. For the dominant H-loss channel, the high-energy cutoff of the translational energy distribution is consistent with formation of trans-/cis-1-buten-3-yne-1-yl ($\cdot CH=CH-C\equiv CH$), whereas RRKM calculations predict that the resonance-stabilized 1-buten-3-yne-2-yl radical ($H_2C=C=C=CH\cdot$) is the dominant statistical product. These findings can be reconciled if the latter is formed with substantial rovibrational excitation, reducing the energy released into translation. The molecular hydrogen elimination channel is assigned mainly to the formation of butatrienylidene ($H_2C=C=C=C:$), while C–C bond-cleavage is consistent with the formation of acetylene plus vinylidene. These findings provide isomer-specific laboratory constraints on the photodissociation of vinylacetylene and help refine astrochemical models of the hydrocarbon evolution and PAH growth in low-temperature cold molecular clouds like TMC-1.

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) constitute a major reservoir of cosmic carbon with up to 30 % and are widely regarded as the carriers of the unidentified infrared (UIR) emission bands observed throughout the interstellar medium (ISM), in the 3–14 μm region (Allamandola, Tielens, & Barker 1989; Ricks, Douberly, & Duncan 2009; Tielens 2008) as well as potential contributors to the diffuse interstellar bands (DIBs) detected in the 200–400 nm wavelength range (Duley 2006). Beyond unsubstituted PAHs, functionalized PAHs, including cyano-, ethynyl-, and vinyl-substituted derivatives, are of particular astrochemical interest since substitution alters permanent dipole moments, enhances rotational detectability, and modifies chemical reactivity under low-temperature interstellar conditions (Hudgins, Bauschlicher, & Allamandola 2005; Kaiser & Hansen 2021; Kaiser, Parker, & Mebel 2015; Kaiser et al. 2022b; McGuire et al. 2018; Parker & Kaiser 2017; Ricca et al. 2012; Wang, Zhao, & Kaiser 2024; Zhao et al. 2019a). Elucidating the formation pathways of both PAHs and substituted PAHs in cold molecular clouds is therefore essential for tracing bottom-up molecular mass growth, linking small hydrocarbon radicals to increasingly complex aromatic frameworks that contribute to the organic inventory of the interstellar medium (ISM) (Goettl et al. 2025; Herbst & Van Dishoeck 2009; Kaiser & Hansen 2021; Parker et al. 2012a).

In high-temperature environments such as combustion systems and carbon-rich circumstellar envelopes, the formation of polycyclic aromatic hydrocarbons (PAHs) is predominantly inferred by the hydrogen- abstraction–acetylene-addition (HACA) mechanism (Frenklach 2002; Frenklach & Warnatz 1987; Wenzel et al. 2025). However, HACA involves substantial entrance barriers of up to 20 kJ mol^{-1} , rendering it inefficient at the 10 K temperatures characteristic for cold dark clouds such as the Taurus Molecular Cloud-1 (TMC-1). The detection of unsaturated hydrocarbons and long carbon-chain polyynes in TMC-1 has therefore motivated the search for alternative low-temperature growth pathways capable of proceeding through barrierless or submerged-barrier reaction channels (Cernicharo et al. 2021b; Jones et al. 2011; Kaiser & Mebel 2002; Kaiser, et al. 2015; Kaiser, et al. 2022b; McGuire, et al. 2018; Parker, et al. 2012a). Laboratory reaction-dynamics studies have demonstrated that neutral–neutral reactions involving unsaturated hydrocarbons can indeed proceed without entrance barriers under single-collision conditions, providing viable low-temperature routes to aromatic ring formation (Goettl et al. 2023; Kaiser, et

al. 2015; Medvedkov et al. 2026; Parker et al. 2015; Parker, et al. 2012a; Yang et al. 2025a; Yang et al. 2025b; Yang et al. 2024a; Zhao et al. 2018) These findings support a bottom-up picture in which PAH precursors can assemble efficiently even in the coldest regions of the ISM forming aromatics as complex as [4], [5], and [6]helicenes ($C_{18}H_{12}$, $C_{22}H_{14}$, $C_{26}H_{16}$) (Kaiser et al. 2022a; Zhao et al. 2020; Zhao et al. 2019) (Scheme 1).

A particularly promising low-temperature pathway for PAH growth is the hydrogen-abstraction–vinylacetylene-addition (HAVA) mechanism, in which radical sites on aromatic precursors such as phenyl ($C_6H_5^\cdot$) and naphthyl radicals ($C_{10}H_7^\cdot$) react with vinylacetylene (C_4H_4 ; $CH_2=CH-C\equiv CH$, X^1A') to larger aromatic frameworks via benzene ring annulation, e.g., naphthalene (He et al. 2022; Kaiser, et al. 2015; Parker, et al. 2012a; Yang et al. 2015; Zhao, et al. 2018; Zhao, et al. 2019). Crossed molecular-beam experiments combined with high-level electronic-structure calculations have demonstrated that reactions such as phenyl ($C_6H_5^\cdot$, X^2A_1) plus vinylacetylene (C_4H_4 , X^1A') proceed via a weakly bound van der Waals complex and a submerged transition state, ultimately yielding naphthalene ($C_{10}H_8$) and atomic hydrogen as a dominant product channel under single-collision conditions (Parker et al. 2012b). This chemistry stands in sharp contrast to high-temperature soot-formation analogs, revealing that stepwise PAH growth through successive C_4 -unit addition is feasible even under cold interstellar conditions. Such barrierless or near-barrierless growth mechanisms provide a compelling bottom-up framework for PAH formation in dense molecular clouds, complementing and extending traditional high-temperature routes (Scheme 1). The astronomical relevance of this chemistry is underscored by the recent detection of vinylacetylene toward TMC-1 in highly sensitive radio surveys led by Cernicharo and coworkers (Cernicharo, et al. 2021b). Vinylacetylene was identified as one of the more abundant closed-shell hydrocarbons in the source, with column densities on the order of 10^{13} cm^{-2} , confirming that this highly unsaturated C_4 species is readily available in the cold gas phase (Cernicharo, et al. 2021b). The presence of vinylacetylene—together with the rich inventory of carbon-chain radicals and substituted hydrocarbons detected in TMC-1—supports the view that carbon growth proceeds efficiently through neutral–neutral chemistry even at temperatures near 10 K, as suggested previously (Kaiser 2002).

The formation of vinylacetylene itself has been examined extensively through laboratory kinetics and crossed molecular beam reaction-dynamics studies. In particular, the reaction of the

ethynyl radical (C_2H , $\text{X}^2\Sigma^+$) with ethylene (C_2H_4 , X^1A_g) has been shown to produce vinylacetylene as the dominant product via hydrogen atom elimination from a the C_4H_5 intermediate (Kaiser ; Zhang et al. 2009c). Low-temperature kinetic measurements further indicate that the rate coefficient approaches the collision limit, with values of order $10^{-10} \text{ cm}^3 \text{ s}^{-1}$, fully consistent with rapid vinylacetylene production in cold molecular clouds (Bouwman et al. 2012; Opansky & Leone 1996). This near-gas-kinetic efficiency makes the reaction between ethynyl radical (C_2H , $\text{X}^2\Sigma^+$) and ethylene (C_2H_4 , X^1A_g) the primary source of vinylacetylene in contemporary astrochemical models of TMC-1.

While formation pathways for vinylacetylene are highly efficient, astrochemical models invoking HAVA-type PAH growth must also account for its destruction processes. In dense clouds such as TMC-1, the external interstellar ultraviolet (UV) radiation field is strongly attenuated; however, secondary UV photons generated by cosmic-ray excitation of molecular hydrogen sustain a low but chemically significant photochemical flux of about $10^3\text{--}10^4 \text{ photons cm}^{-2}\text{s}^{-1}$ (Prasad & Tarafdar 1983). Laboratory photodissociation studies of vinylacetylene, conducted primarily in the vacuum ultraviolet (VUV) (193nm) at room temperature, show that excitation leads predominantly to C–H bond cleavage and fragmentation into smaller C_2 and C_3 hydrocarbons, mediated by $\pi\pi^*$ excited states and rapid internal conversion (reactions (1) – (4)). However, branching ratios among distinct hydrogen atom loss channels, molecular hydrogen elimination pathways, and C–C bond-fission channels under collisionless conditions remain poorly constrained. These uncertainties propagate directly into modeled photodestruction processes and steady-state abundances of vinylacetylene, thereby affecting predicted PAH growth efficiencies in cold clouds.



Thus, although laboratory reaction-dynamics experiments (Yang et al. 2024b) and astronomical observations (Cernicharo et al. 2021a) support vinylacetylene as a key intermediate in low-temperature PAH formation, significant uncertainties remain regarding the photochemical stability of vinylacetylene under dense cloud conditions. Constraining the balance between its efficient

formation and photon-driven destruction is essential for reliable astrochemical modeling of aromatic mass growth in TMC-1. These considerations motivate the present experimental study, which probes the photodissociation dynamics of vinylacetylene in a supersonic molecular beam.

2. Methods

2.1. Experimental Methods

The photodissociation dynamics of vinylacetylene (C_4H_4 , X^1A') were investigated using a rotating-detector, fixed-source molecular beam apparatus (Goettl et al. 2021; Gu & Kaiser 2009; Kaiser 2002; Kaiser et al. 1999; Kaiser et al. 2010; Lee 1987). The setup consists of a source chamber and a triply differentially pumped ultrahigh-vacuum detector chamber operated at 5×10^{-12} Torr, both housed within a large stainless-steel main chamber maintained at 1×10^{-7} Torr. A pulsed molecular beam of vinylacetylene (99.5%; synthesized in-house (Zhang et al. 2011)) seeded in argon (99.9999 %; BOC Gases) at a level of 5% was generated using a 120 Hz Proch–Trickl (Proch & Trickl 1989) pulsed valve operated at -400 V under a backing pressure of 1 atm. The beam was skimmed and subsequently velocity-selected using a four-slot chopper wheel operating at 120 Hz. The peak velocity (v_p) of the beam was determined to be 660 ± 21 m s $^{-1}$ with a speed ratio of 23 ± 1 . The pulsed molecular beam of vinylacetylene was intersected at 90° by the output of an excimer laser (COMPex 110, Coherent) operating on the ArF transition at 193 nm, with a laser delay of 195 μ s relative to the opening of the pulsed valve. The laser pulse energy of 1 mJ was less tightly focused to a spot size of 5 mm $\times$ 1 mm to reduce the multiphoton process during the photodissociation. Photo fragmented products are detected by the rotatable detector at different angles from 9.25° to 49.25° . The neutral photo dissociation products traveled 33.75 cm and were then ionized first by electron impact after the entrance of the detector using 80 eV electrons with an emission current of 2 mA in a Brink-type electron ionizer. The resulting ions were then mass-selected according to their m/z using a quadrupole mass spectrometer (QMS; Extrel QPS, 1.2 MHz) and subsequently detected with a Daly-type particle ion counter (Daly 1960). Real-time background subtraction was achieved by synchronizing the laser to operate at half of the repetition rate of the pulsed valve via ‘laser on’ minus ‘laser off’ subtraction, thereby improving the precision of the TOF measurements. A forward-convolution approach was utilized to analyze the data (Zhao 1988). In this method, a trial center-of-mass translational energy distribution, $P(E_T)$, is combined

with the instrumental response functions and beam parameters to simulate a TOF spectrum in the laboratory frame. The simulated spectrum is then compared with the experimental measurements, and the energy distribution is systematically adjusted through successive iterations until optimal agreement is obtained.

2.2. Computational methods

Computations of stationary point structures, vibrational frequencies, and zero-point energies (ZPEs) across the C_4H_4 PES were carried out using density functional theory (DFT) utilizing the long-range corrected hybrid density functional ω B97X-D (Chai & Head-Gordon 2008) alongside the 6-311G(d,p) (Krishnan et al. 1980) basis set. Optimized local minima exhibited no imaginary frequencies, whereas all transition states (TSs) have exactly one imaginary frequency. To verify the reaction pathways, we conducted intrinsic reaction coordinate (IRC) calculations (Hratchian & Schlegel 2004) at the same ω B97X-D/6-311G(d,p) level of theory. Energies of the DFT-optimized structures were subsequently refined via explicitly correlated coupled clusters calculations at the CCSD(T)-F12 (Adler, Knizia, & Werner 2007; Knizia, Adler, & Werner 2009)/cc-pVQZ-F12 (Peterson, Adler, & Werner 2008) level of theory. Whenever the T1 diagnostic in these coupled cluster calculations exceeded 0.02, indicating the wave function had a significant multireference character, the energies were further refined using the multireference perturbation theory with internally contracted configurations (RS2C)(Celani & Werner 2000; Shiozaki et al. 2011). This calculation was performed at the RS2C(8e,8o)/cc-pVQZ (Dunning 1989) level, and the relative energy was evaluated with respect to an adjacent local minimum with $T1 < 0.02$. The (8e,8o) active space comprised the (6e,6o) π system of the C_4H_4 species, supplemented by the (2e,2o) σ electrons and orbitals participating in the bond cleavage/formation process. The electronic structure calculations employed the Gaussian 16 (Frisch et al. 2019) and MOLPRO 2021 software packages (Werner et al. 2021). It should be noted that no significant changes in relative energies were found here as compared to the previous theoretical exploration of the C_4H_4 PES (Mebel, Kislov, & Kaiser 2006).

To characterize the transition state associated with frustrated dissociation—a roaming pathway wherein a hydrogen atom orbits the C_4H_3 fragment, abstracting a hydrogen from the CH tail to yield $C_4H_2 + H_2$ —we performed a two-dimensional coordinate scan. This procedure mapped the C–H bond length of the C_4H_3 tail against the distance between this specific tail hydrogen and the

roaming hydrogen. The transition state geometry identified by this scan was further refined using TS optimization. Both the initial coordinate scan and the TS optimization employed the RS2C(10e,10o)/cc-pVDZ (Dunning 1989) level of theory. Building upon the previously described (8e,8o) active space, this expanded (10e,10o) active space incorporates the additional orbitals and electrons involved in the C-H bond cleavage and formation of molecular hydrogen. Finally, a single-point energy refinement of this optimized structure was conducted at the RS2C(10e,10o)/cc-pVQZ level, with the resulting energy evaluated relative to the H₂C₄H₂ isomer **i4**.

Microcanonical rate coefficients for individual unimolecular reactions were evaluated using Rice-Ramsperger-Kassel-Marcus (RRKM) theory (Marcus 1952). The rigid-rotor, harmonic-oscillator (RRHO) model was employed to compute partition functions, densities of states, and total numbers of states. Eckart's tunneling correction was applied to estimate tunneling effects (Miller 1979). For reactions with explicit barriers, the molecular properties of the optimized TSs were used in the RRKM calculations. For H-elimination channels, the bottleneck of the RRKM reaction flux was determined by utilizing the microcanonical variational transition state theory (VTST) (Bao & Truhlar 2017). Steady-state approximation was employed in solving the system of master equations (ME) to compute product branching ratios. Pressure-dependent branching ratios were evaluated using the ME framework (Georgievskii et al. 2013) using the MESS software package (Georgievskii & Klippenstein 2015). The Lennard-Jones parameters and the parameters for the “exponential down” model (Troe 1977) of the collisional energy transfer were adopted from Stearns et al (Stearns et al. 2006).

3. Results

3.1. Newton diagrams

Multiple photodissociation channels of vinylacetylene were investigated using 193 nm laser excitation. The possible photoproducts and their corresponding reaction energies are summarized in Table 1. In this experiment, the energy balance for each channel can be expressed as

$$E_{\text{avail}} = h\nu + E_0 - D_0 = E_{\text{int}} + E_{\text{T}}$$

The available energy (E_{avail}) for a given photodissociation channel equals the photon energy ($h\nu$) plus any initial internal energy (E_0), minus the channel-specific dissociation energy (D_0). This energy is subsequently partitioned between internal excitation of the fragments (E_{int}) and their

relative translational energy (E_T). The initial internal energy of vinylacetylene in the supersonic beam is negligible. Consequently, the available energy can be taken as the difference between the photon energy and the channel-specific dissociation energy. If all of this energy is converted into translational energy, the maximum laboratory recoil angle can be determined from the known velocity of the vinylacetylene beam and the thermodynamics of the dissociation process. These recoil angles for the photofragments are depicted in the Newton diagram (Figure 1). These involve atomic hydrogen loss accompanied by the formation of C_4H_3 isomers (51 amu), molecular hydrogen loss plus distinct C_4H_2 isomers (50 amu), generation of two C_2H_2 species (26 amu), and the vinyl (C_2H_3 , 27 amu) plus ethynyl (C_2H , 25 amu) pathway.

Therefore, time-of-flight mass spectra were recorded for $m/z = 51$ ($C_4H_3^+$), $m/z = 50$ ($C_4H_2^+$), $m/z = 26$ ($C_2H_2^+/CCH_2^+$), and $m/z = 25$ (C_2H^+). No measurable signal was detected at $m/z = 27$ ($C_2H_3^+$). The photodissociation experiment is conducted with an unpolarized laser beam, which results in an isotropic laboratory photofragment distribution in the plane defined by the molecular beam and detector axis. Possible contributions from multi-photon processes were evaluated through a laser power-dependence study. TOF spectra recorded over the energy range of 100 μJ pulse⁻¹ to 2 mJ pulse⁻¹ exhibit a linear dependence of signal intensity on laser power, with no observable changes in the shape of the corresponding TOFs.

Table 1. Predicted reaction channels for the photodissociation of the vinylacetylene (C_4H_4) at 193 nm. The expected m/z values for all species are given in parentheses. Reaction energies for the dissociation channels are given in $kJ\ mol^{-1}$.

Fragment I	Fragment II	Reaction Energy* ($kJ\ mol^{-1}$)	Maximum translational energy ($kJ\ mol^{-1}$)
$H_2C=C=C=CH\cdot$ ($m/z = 51$)	$H\cdot$ ($m/z = 1$)	416	204
<i>trans</i> - $\cdot CH=CH-C\equiv CH$ ($m/z = 51$)	$H\cdot$ ($m/z = 1$)	466	154
<i>cis</i> - $\cdot CH=CH-C\equiv CH$ ($m/z = 51$)	$H\cdot$ ($m/z = 1$)	465	155
$H_2C=CH-C\equiv C\cdot$ ($m/z = 51$)	$H\cdot$ ($m/z = 1$)	568	52
$CH\equiv CH-C\equiv CH$ ($m/z = 50$)	H_2 ($m/z = 2$)	162	458

$\text{H}_2\text{C}=\text{C}=\text{C}=\text{C}\cdot$ (m/z = 50)	H_2 (m/z = 2)	352	268
$\text{HC}\equiv\text{CH}$ (m/z = 26)	$\text{HC}\equiv\text{CH}$ (m/z = 26)	164	456
$\text{HC}\equiv\text{CH}$ (m/z = 26)	$\cdot\text{C}=\text{CH}_2$ (m/z = 26)	341	279
$\cdot\text{C}=\text{CH}_2$ (m/z = 26)	$\cdot\text{C}=\text{CH}_2$ (m/z = 26)	519	101
$\text{HC}\equiv\text{C}\cdot$ (m/z = 25)	$\text{HC}\cdot=\text{CH}_2$ (m/z = 27)	580	40

* Calculated at the CCSD(T)-F12/cc-pVQZ-F12 level in the present work.

3.2. Atomic Hydrogen Elimination

TOF spectra at $m/z = 51$ (C_4H_3^+) at angles of 9.25° , 14.25° , and 19.25° are shown in Figure 2a; the translational energy distribution, $P(E_T)$, corresponding to the best fit of the TOF data, is shown in Figure 2b. No signal was observed at laboratory angles beyond 19.25° . For the hydrogen atom loss channel, the translational-energy distribution $P(E_T)$ could be fit with a single channel and peaks near 0 kJ mol^{-1} ; this distribution has an average translational energy $\langle E_T \rangle$ of $35 \pm 2 \text{ kJ mol}^{-1}$. The high-energy cutoff of the distribution occurs at $E_{T(max)} = 154 \pm 9 \text{ kJ mol}^{-1}$.

3.3. Molecular Hydrogen elimination

Figure 3a presents the TOF data at $m/z=50$ (C_4H_2^+) recorded at laboratory angles ranging from 9.25° to 39.25° at 5° intervals; no signal was observed beyond this angular range. The slower component of the TOF signal at laboratory angles 9.25° , 14.25° , and 19.25° overlaps with the TOF of $m/z = 51$, indicating that the TOFs at $m/z = 50$ comprises of two contributions: a molecular hydrogen (H_2) elimination plus the heavy C_4H_2 (50 amu) counter fragment and an additional component arising from dissociative electron impact ionization of C_4H_3 (51 amu) contributing to C_4H_2^+ ions at $m/z = 50$. Notably, the signal at $m/z = 50$ persists beyond the angular range of the ion signal of $m/z = 51$ (9.25° - 19.25°), confirming that the ion counts at $m/z = 50$ originate not only from dissociative ionization of C_4H_3 (51 amu) but also from the molecular hydrogen dissociation. The simulated TOF spectrum is accurately reproduced with a two-channel fit that incorporates both molecular-hydrogen loss (fast component) and atomic-hydrogen loss (slow component). The corresponding translational-energy distributions for these primary dissociation pathways are shown in Figure 3b. The $P(E_T)$ distribution for the molecular hydrogen elimination channel exhibits a nearly Gaussian profile with $\langle E_T \rangle = 108 \pm 2 \text{ kJ mol}^{-1}$ and a full width half maximum

(FWHM) of 120 kJ mol^{-1} . Also, the $P(E_T)$ for this channel peaks at 84 kJ mol^{-1} and extends to $E_{T(max)} = 268 \pm 12 \text{ kJ mol}^{-1}$.

3.4. C-C bond breaking ($\text{C}_2\text{H}_2/\text{CCH}_2$ elimination)

Figure 4a displays the TOF data for $m/z = 26$ ($\text{C}_2\text{H}_2^+/\text{CCH}_2^+$) recorded at angles from 9.25° to 49.25° in 5° increments. At the lower angles (9.25° – 24.25°), an additional slow feature appears that overlaps with the signal at $m/z = 51$ and $m/z = 50$. This indicates that signal at $m/z = 26$ carries contributions from dissociative electron impact ionization of C_4H_3 and C_4H_2 . This finding is fully consistent with the translational energy distributions obtained for the atomic- and molecular-hydrogen loss channels in the forward-convolution analysis. The faster part of the TOF signal is fitted with $\text{C}_2\text{H}_2/\text{CCH}_2$ elimination channel; the corresponding translation energy distribution is displayed in Figure 4b. The $P(E_T)$ for the $\text{C}_2\text{H}_2/\text{CCH}_2$ elimination channel also exhibits a nearly Gaussian profile, with an average translational energy of $\langle E_T \rangle = 85 \pm 5 \text{ kJ mol}^{-1}$ and a FWHM of about 81 kJ mol^{-1} . The distribution peaks at 54 kJ mol^{-1} and extends to a maximum translational energy of $E_{T(max)} = 276 \pm 17 \text{ kJ mol}^{-1}$.

3.5. C-C bond breaking ($\text{C}_2\text{H}_3/\text{C}_2\text{H}$ elimination)

TOF spectra for $m/z = 25$ (C_2H^+) were recorded at the angle starting from 9.25° to 49.25° in 5° intervals (Figure 5a). TOF spectra are identical with TOF recorded for $m/z = 26$ when recorded at the same laboratory angle. This suggests $m/z = 25$ originates from dissociative electron impact ionization of $\text{C}_2\text{H}_2/\text{CCH}_2$. Also, the absence of the counter fragment at $m/z = 27$ suggests that C-C bond breaking to $\text{C}_2\text{H} + \text{C}_2\text{H}_3$ is likely absent. The TOF spectra of $m/z = 25$ were also fit with the translational energy distribution $P(E_T)$ for the atomic and molecular hydrogen loss and $\text{C}_2\text{H}_2/\text{CCH}_2$ loss channels (Figure 5b).

3.6. Branching ratios

The branching ratios of the dissociation channels were derived from the experimental data using

$$\text{BR}_i = \frac{w_i / \sigma_i \times f_i}{\sum (w_i / \sigma_i \times f_i)}$$

where W_i represents the weighting factor associated with the translational energy distribution $P(E_T)$ for channel 'i' (Shapero 2017). The weighting factors were obtained by fitting the simulated time-of-flight (TOF) spectra to the experimental data using a consistent set of parameters across all laboratory angles. These weights were subsequently corrected by the ionization cross section (σ_i) of the parent fragment and by f_i , the probability that each fragment undergoes dissociative ionization in the electron-impact ionizer. The ionization cross sections were determined using the empirical relation $\sigma = 36\sqrt{\alpha} - 18$ (Krajnovich 1995), where α is the molecular polarizability as the sum of the atomic polarizabilities. The atomic polarizabilities were taken as $0.667 \text{ \AA}^3$ for hydrogen and $1.76 \text{ \AA}^3$ for carbon (Miller & Bederson 1978). The dissociative ionization probabilities (f_i) were evaluated at a laboratory angle of 9.25° for all mass channels with measurable signal intensities. Taking these corrections into account, the experimentally derived branching ratios are determined to be $\text{C}_4\text{H}_3 : \text{C}_4\text{H}_2 : \text{C}_2\text{H}_2/\text{CCH}_2 = (75 \pm 2) : (10 \pm 2) : (15 \pm 2)$.

4. Discussion

4.1 Potential Energy Surface (PES)

The aim of this study is to determine the photodissociation channels of vinylacetylene at 193 nm under collision-free conditions, with a focus on identifying the resulting photofragments and elucidating the underlying dissociation pathways. The results indicate the presence of three competing channels: atomic hydrogen loss plus C_4H_3 isomers, molecular hydrogen loss plus C_4H_2 isomers, and $\text{C}_2\text{H}_2/\text{CCH}_2$ elimination. To illustrate the mechanisms, these experimental results are compared with the *ab initio* calculations at the CCSD(T)-F12/cc-pVQZ-F12 level of theory (Peterson, et al. 2008; Raghavachari et al. 1989) (Figure 6). Following photoexcitation and internal conversion to the singlet ground state, vinylacetylene can evolve along several competing pathways on the singlet C_4H_4 potential energy surface. These include isomerization to multiple C_4H_4 isomers, atomic and molecular hydrogen elimination, and C-C bond cleavages.

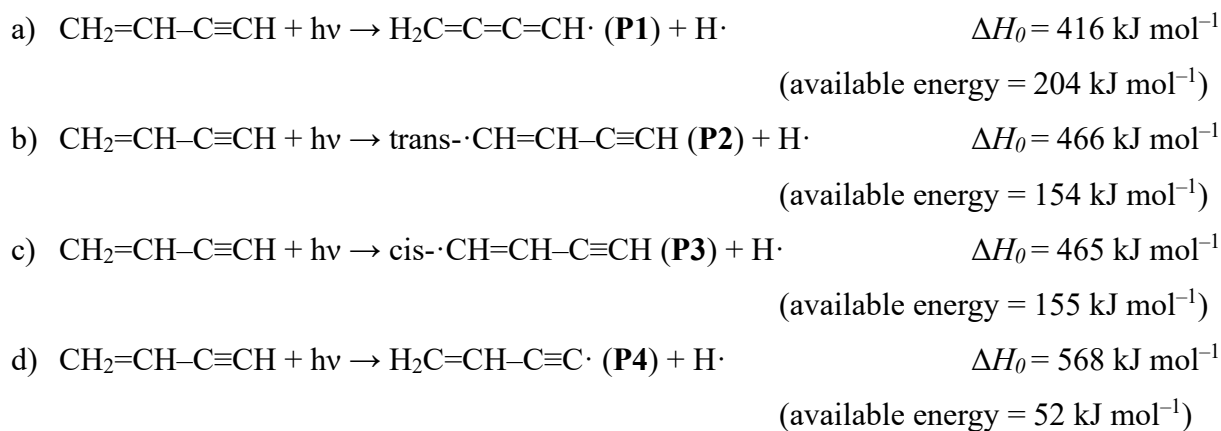
The hydrogen atom loss occurs through cleavage of the C-H bond and leads to the formation of several C_4H_3 radical products, including 1-buten-3-yne-2-yl (**P1**, C_4H_3 , X^2A' , C_s), trans-/cis-1-buten-3-yne-1-yl (**P2/P3**, C_4H_3 , X^2A' , C_s) and vinyl ethynyl (**P4**, C_4H_3 , X^2A' , C_s). Alternatively, vinylacetylene may undergo isomerization prior to dissociation. Cyclization through C-C bond formation yields the three-membered-ring intermediate methylenecyclopropene **i1** (C_{2v} , X^1A_1) located 98 kJ mol^{-1} above vinylacetylene. Additional rearrangement channels provide access to

higher-energy C_4H_4 isomers. These include formation of a carbene **i2** (C_s , X^1A') at 287 kJ mol^{-1} through a 1,2-hydrogen migration with a barrier of 350 kJ mol^{-1} ; **i5** (C_s , X^1A') at 225 kJ mol^{-1} through isomerization via a 414 kJ mol^{-1} barrier; the four-membered-ring intermediate cyclobutadiene **i6** (D_{2h} , X^1A_g) at 140 kJ mol^{-1} over a 367 kJ mol^{-1} barrier; and **i9** (C_1 , X^1A) at 251 kJ mol^{-1} through isomerization over a 294 kJ mol^{-1} barrier. Intermediate **i1** can subsequently undergo ring opening to form **i2** over a barrier of 192 kJ mol^{-1} with respect to **i1**. In addition, **i1** may isomerize through hydrogen migration pathways to **i3** (C_s , X^1A') and **i8** (C_s , X^1A'), located 295 and 370 kJ mol^{-1} above the energy of vinylacetylene, respectively. Alternatively, intermediate **i1** can undergo C–C bond dissociation through two distinct pathways: one leading to the formation of two acetylene molecules ($C_2H_2 + C_2H_2$) (**P7**) over a transition state located 465 kJ mol^{-1} above vinylacetylene, and the other producing acetylene plus vinylidene ($C_2H_2 + C=CH_2$) (**P8**) through a lower barrier with the transition state 358 kJ mol^{-1} above vinylacetylene. However, the former dissociation channel can also be accessed from intermediate **i8**, proceeding over the highest in energy transition state for the **i1-i8** step positioned 423 kJ mol^{-1} relative to vinylacetylene. Interestingly, intermediates **i2**, **i3**, and **i5** can each rearrange to intermediate **i4** (butatriene) through either hydrogen migration or ring opening. Intermediate **i4** can subsequently undergo molecular hydrogen elimination to form butatrienylidene (**P6**, $H_2C=C-C=C\cdot$, X^1A_1 , C_{2v}) or, alternatively, dissociate through C–C bond cleavage to produce two vinylidene molecules ($CCH_2 + CCH_2$) (**P9**). Intermediate **i4** can also undergo unimolecular decomposition via C–H bond cleavage to **P1** plus atomic hydrogen. On the other hand, intermediate **i6** can rearrange to intermediate **i7** (C_{2v} , X^1A_1), located 218 kJ mol^{-1} above vinylacetylene, by forming a bicyclic structure through C–C bond formation over a barrier of 89 kJ mol^{-1} . Intermediate **i7** can then isomerize to **i8** through the opening of one ring of the bicyclic structure, overcoming only a 2 kJ mol^{-1} barrier. The PES also shows that vinylacetylene can isomerize to **i9** through hydrogen migration. From **i9**, two competing pathways are open: atomic hydrogen loss to product **P1** and molecular hydrogen elimination to diacetylene (**P5**, $D_{\infty h}$, $X^1\Sigma_g^+$) over barriers located at 419 and 415 kJ mol^{-1} with respect to vinylacetylene.

4.2. Atomic Hydrogen Loss Channel

The translational energy distribution, $P(E_T)$, for the atomic hydrogen elimination channel shows a high-energy cutoff at $154 \pm 9\text{ kJ mol}^{-1}$. For those products formed with zero internal excitation,

the experimental reaction energy was obtained from the energy-balance relation ($E_{hv} - E_{T(max)}$). Using the 193 nm photon energy, (E_{hv}) = 620 kJ mol⁻¹, and $E_{T(max)}$ = 154 ± 9 kJ mol⁻¹, the photodissociation process is endoergic by 466 ± 9 kJ mol⁻¹. The calculated potential energy surface identifies four competing atomic hydrogen loss pathways energetically accessible upon 193 nm photoexcitation. These are:

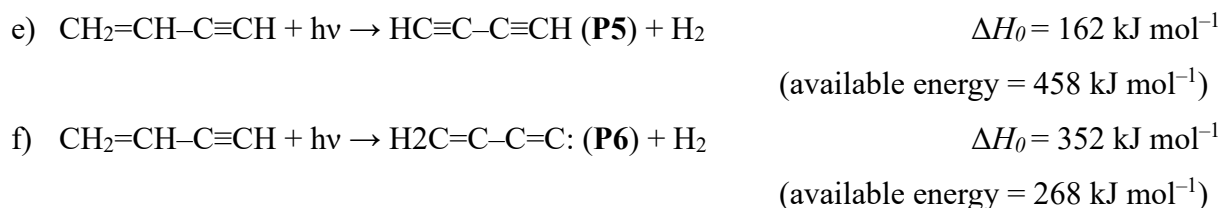


Among the four reaction channels, the hydrogen atom loss channel matches nicely the formation of **P2/P3** (trans/cis- $\cdot\text{CH}=\text{CH}-\text{C}\equiv\text{CH}$). The calculated PES indicates that the pathways for channels (b–c) proceed through C–H bond cleavage from the terminal vinylic carbon of vinylacetylene (C₄H₄). This C–H bond dissociation involves a barrierless exit channel, consistent with the experimental translational energy distribution, $P(E_T)$, which peaks near 0 kJ mol⁻¹. The stability difference between the cis- and trans-1-buten-3-yne-1-yl radicals (**P2/P3**) is very small (1 kJ mol⁻¹) and cannot be resolved within the experimental uncertainty. In case of the formation of **P4** (channel d), the available energy is much lower, which means if this channel is present, it should contribute to fluxes at lower E_T . Product **P1** is predicted to be the resonance-stabilized, lowest energy isomer of C₄H₃. The calculated PES reveals multiple pathways, in addition to a one-step dissociation, for the formation of C₄H₃ and a hydrogen atom from vinylacetylene (C₄H₄). Vinylacetylene can isomerize to intermediate **i4** through the lowest-energy pathways, **VA** → **i1** → **i2** → **i4**, followed by barrierless dissociation to C₄H₃ and a hydrogen atom. Alternatively, it can rearrange to intermediate **i9**, which subsequently dissociates to C₄H₃ plus atomic hydrogen. Although formation of the resonance-stabilized **P1** radical is energetically accessible, it cannot be uniquely identified from the present translational energy distribution. Internally cold **P1** products would permit translational energies up to approximately 204 kJ mol⁻¹, significantly higher than

the experimentally observed cutoff of 154 ± 9 kJ mol⁻¹. One possible explanation supporting the formation of the resonance-stabilized C₄H₃ isomer (1-buten-3-yne-2-yl) is that radicals are produced with substantial internal (rovibrational) excitation. Consequently, a smaller fraction of the available energy is released as translational energy, making its formation compatible with the experimentally observed $P(E_T)$ distribution.

4.3. Molecular hydrogen loss channel

For the molecular hydrogen-loss channel, the translational energy distribution, $P(E_T)$, shows a maximum translational energy release, $E_{T(max)}$, of 268 ± 12 kJ mol⁻¹. Considering the 620 kJ mol⁻¹ of the 193 nm photon, the molecular hydrogen-loss channel is endoergic by 352 ± 12 kJ mol⁻¹. The computed PES shows two molecular hydrogen elimination channels:



Energetically, reaction (f) reproduces the experimentally derived reaction energy with good fidelity. This agreement indicates that, under the experimental conditions, photodissociation predominantly forms butatrienyldiene (**P6**, H₂C=C=C=C:) via the molecular-hydrogen loss channel. The potential energy surface further reveals four competitive pathways capable of producing the **P6** product; these are: (i) **VA** → **i1** → **i2** → **i4** → **P6**; (ii) **VA** → **i1** → **i3** → **i4** → **P6**; (iii) **VA** → **i2** → **i4** → **P6**; (iv) **VA** → **i5** → **i4** → **P6**. The energy barrier for the **VA** → **i1** isomerization is much lower than that for **VA** → **i2** or **VA** → **i5**, favoring the dominant formation of **i1**. Furthermore, the subsequent isomerization from **i1** to **i3** involves a substantially higher barrier than the **i1** → **i2** pathway. Overall, pathway (i) is the energetically most feasible route leading to **P6**. The exit barrier forming to **P6** formation is 56 kJ mol⁻¹; this tight exit channel is consistent with the experimental result revealed through the peak in the translational-energy distribution of 84 kJ mol⁻¹.

4.4. C₂H₂/CCH₂ loss channel

The translational energy distribution, $P(E_T)$, for the C₂H₂/CCH₂-loss channel, monitored at $m/z = 26$, extends to a maximum translational energy release ($E_{T(max)}$) of 276 ± 17 kJ mol⁻¹. Accounting

1 The experimentally determined branching ratios indicate that the hydrogen atom loss channel
2 accounts for $75 \pm 2\%$, whereas the molecular hydrogen loss channel leading to **P6** contributes 10
3 $\pm 2\%$. The remaining $15 \pm 1\%$ is assigned to the $\text{C}_2\text{H}_2/\text{CCH}_2$ -loss channel. Overall, the close
4 agreement between the RRKM-predicted and experimentally derived total yield of the hydrogen
5 atom loss channel suggests that statistical ground-state dissociation following internal conversion
6 is an important component of the 193 nm photodissociation dynamics of vinylacetylene. Within
7 this statistical picture, the dominant formation of rovibrationally excited **P1** provides a plausible
8 interpretation of the hydrogen loss data.

9 The present results on the ultraviolet photodissociation of vinylacetylene (C_4H_4) show that the
10 hydrogen atom loss channel dominates, with smaller contributions from molecular hydrogen
11 elimination and C–C bond cleavage. This behavior differs from the study by Stearns (Stearns, et
12 al. 2006), where the primary detected products were 1-buten-3-yne-2-yl (C_4H_3 , $\text{H}_2\text{C}=\text{C}=\text{C}=\text{CH}\cdot$)
13 and diacetylene (C_4H_2 , $\text{HC}\equiv\text{C}-\text{C}\equiv\text{CH}$); simulations suggested that acetylene (C_2H_2) is in fact the
14 dominant product, with an overall branching of $\text{C}_4\text{H}_3 : \text{C}_4\text{H}_2 : \text{C}_2\text{H}_2 \approx 27 : 8 : 65$. This difference
15 can be attributed mainly to the experimental conditions. In the reaction-tube experiments of
16 Stearns et al., multiple collisions during the residence time allow for energy relaxation and
17 secondary reactions, whereas the present collision-free conditions isolate the primary dissociation
18 dynamics (Stearns, et al. 2006). As a result, the current branching ratios reflect more accurately
19 the intrinsic unimolecular pathways, such as in cold molecular clouds, while the previous work
20 captures a collision-influenced environment relevant to Titan's atmosphere (Stearns, et al. 2006;
21 Wilson & Atreya 2004; Yung, Allen, & Pinto 1984). Moreover, in the previous experimental work,
22 the branching ratios were measured at a different photodissociation wavelength of 220 nm,
23 corresponding to a lower energy intake, 544 kJ mol^{-1} , vs. 620 kJ mol^{-1} for 193 nm. The
24 microcanonical statistical, RRKM product branching ratio computed for the internal energy of 544
25 kJ mol^{-1} is $\text{C}_4\text{H}_3 : \text{C}_4\text{H}_2 : \text{C}_2\text{H}_2 \approx 56 : 2 : 42$, reproducing the trend of the decreasing yield of C_4H_3
26 and the increasing yield of C_2H_2 as the available internal energy falls. In fact, the RRKM
27 calculations show that the $\text{C}_4\text{H}_3 : \text{C}_2\text{H}_2$ ratio is very sensitive to the available energy, with the lower
28 energies favoring the production of **P8** and higher energies favoring **P1** (Figure 7). When the
29 pressure effect is included in RRKM – Master Equation calculations at 1 and 3 mbar, the agreement
30 of the computed branching ratios, e. g., $\text{C}_4\text{H}_3 : \text{C}_4\text{H}_2 : \text{C}_2\text{H}_2 \approx 46 : 2 : 52$ at 1 mbar, with experiment
31 further improves. This is in line with the fact that collisions deactivate highly energized

vinylacetylene molecules reducing the available internal energy and hence, favoring the $\text{H}_2\text{CC} + \text{C}_2\text{H}_2$ products **P8**. Overall, the comparison highlights that vinylacetylene photochemistry is strongly dependent on the excitation energy and, to a less extent, on the collisional environment. While both studies confirm the importance of C_4H_3 radicals, the present results indicate that the hydrogen atom loss products may include a substantial contribution from rovibrationally excited resonance-stabilized 1-buten-3-yne-2-yl (**P1**), as predicted by RRKM theory, together with smaller contributions from trans-/cis-1-buten-3-yne-1-yl (**P2/P3**).

The underestimation of the H_2 loss channel by RRKM calculations may be attributed to a roaming (frustrated dissociation) mechanism where a hydrogen atom tries to leave the C_4H_3 fragment and roams around it, eventually abstracting another H and forming the $\text{C}_4\text{H}_2 + \text{H}_2$ products rather than $\text{C}_4\text{H}_3 + \text{H}$. We were able to locate a second-order saddle point for the roaming process linked to **P6** on the product side and, possibly, to **VA**, **i4**, or **i9** as the reactants (Figure 8). The computed energy of this structure is 414 kJ mol^{-1} above **VA**, just 2 kJ mol^{-1} under the energy of **P1**. While a statistical treatment of the roaming mechanism based on a distinct transition state is usually imprecise (Klippenstein, Georgievskii, & Harding 2011), the inclusion of the $\text{VA} + h\nu \rightarrow \text{P6}$ roaming pathway in the RRKM calculations with the second, non-reactive imaginary frequency changed to its absolute value close to 100 cm^{-1} (Zhao & Truhlar 2008) raises the branching ratio of **P6** to 34% and 16% at 193 and 220 nm, respectively. Thus, the inclusion of the roaming mechanism clearly boosts the $\text{C}_4\text{H}_2 + \text{H}_2$ product yield, but the RRKM calculations overestimate their branching ratio as compared to experiments. Therefore, both statistical and channel-specific non-statistical effects should be considered when modeling the ultraviolet photochemistry of vinylacetylene in astrophysical environments.

5. Astrophysical Implications

The present photodissociation study of vinylacetylene (C_4H_4) provides constraints on the primary product channels that may operate in cold molecular clouds and also in hydrocarbon-rich atmospheres of planets and their moons such as Titan.

The dominant channel for the photodissociation of vinylacetylene at 193 nm is the hydrogen atom loss channel, which forms C_4H_3 radicals 1-buten-3-yne-2-yl (**P1**) and potentially trans-/cis-1-buten-3-yne-1-yl (**P2/P3**). These C_4H_3 photoproducts are resonance-stabilized free radicals (RSFR) and are therefore not expected to react efficiently with closed-shell hydrocarbons under

low-temperature astrophysical conditions, considering their high entrance barriers ranging from 24 to 48 kJmol⁻¹ (Landera et al. 2008; Stearns, et al. 2006). Their subsequent chemistry is more plausibly associated with reactions involving atoms and open-shell radical partners such as ethynyl (C₂H), vinyl (C₂H₃), and propargyl (C₃H₃), which are barrierless. Although isomer-resolved crossed molecular beam studies remain limited, theoretical work indicates that dicarbon (C₂) reacts with C₄H₃ isomers to access C₆H₃ intermediates (Landera, et al. 2008), while recent calculations demonstrate barrierless low-temperature reactions of 1-buten-3-yne-2-yl (C₄H₃) with the methylene amidogen (H₂CN·) and cis-iminomethyl (HCNH·) radical toward pyridine and the pyridinyl radical (Yang et al. 2024a).

The molecular hydrogen loss channel yields C₄H₂ products detected at m/z=50. Our analysis supports the formation of the cumulene carbene butatrienylidene, H₂C=C=C=C: (**P6**), rather than the thermodynamically more stable diacetylene isomer, H-C≡C-C≡C-H (**P5**). This distinction is astrochemically important since both C₄H₂ isomers are expected to exhibit markedly different chemical reactivities. For diacetylene, the best-established low-temperature neutral-neutral growth chemistry involves barrierless and exoergic reactions with open-shell species, including carbon atoms (C), dicarbon (C₂), cyano (CN), and ethynyl (C₂H) radical, leading to molecular mass growth processes and the formation of the 2,4-pentadiynylidyne radical (C₅H), the 1,3,5-hexatriynyl radical (C₆H), cyanodiacetylene (HC₅N), and triacetylene (HCCCCCCH) (Gu et al. 2009; Zhang et al. 2009a; Zhang et al. 2009b; Zhang et al. 2008). By contrast, **P6** possesses a carbene functionality, and its divalent carbon center enables a distinct chemistry, potentially including reactions with closed-shell unsaturated species, as in the case of electronically excited singlet carbene (CH₂) – the simplest representative of a carbene (Gannon et al. 2010a; Gannon et al. 2010b; Polino et al. 2013). Similar to vinylidene (CCH₂, X¹A₁), singlet carbene undergoes facile addition to C=C and C≡C bonds; however, the specific low-temperature bimolecular reactivity of butatrienylidene remains to be established. Therefore, astrochemical models should strongly discriminate between the reactivities of distinct C₄H₂ isomers rather than treating photoproducts generically as diacetylene, since isomer-specific reactivity may redirect subsequent carbon-chain growth chemistry.

Finally, the carbon-carbon bond cleavage channel yields acetylene (HC≡CH, C₂H₂) together with vinylidene (H₂C=C:, CCH₂). The failure of any astronomical detection of vinylidene (CCH₂) is

understandable from both chemical and spectroscopic considerations. First, CCH_2 is a carbene/vinylidene-type species and is less stable by 182 kJ mol^{-1} than acetylene (Lee et al. 2013). Previous calculations discussed in the vinylacetylene photochemistry literature indicate that the vinylidene-to-acetylene isomerization is rapid, as it requires only a small barrier, about 10 kJ mol^{-1} (Zou & Bowman 2003). Therefore, if vinylidene (CCH_2) is produced with significant internal excitation, it can rapidly rearrange to the more stable acetylene (C_2H_2); this would lead to an equilibrium population of vibrationally excited vinylidene (CCH_2) versus acetylene (C_2H_2) in cold molecular clouds. From a spectroscopic perspective, vinylidene (CCH_2) is not excluded from radioastronomical detection by symmetry, since it represents a polar asymmetric-top molecule with a permanent dipole moment of $\mu=2.5 \text{ D}$ (Sharma et al. 2014). Thus, its non-detection is unlikely to arise from an intrinsically weak rotational dipole moment, but more plausibly from its low steady-state abundances.

Altogether, our results reveal that photodissociation of vinylacetylene (C_4H_4) should be treated in an isomer-specific manner in astrochemical models. The hydrogen atom loss channel generates resonance-stabilized C_4H_3 radicals, the molecular hydrogen loss channel preferentially forms the carbene structure butatrienylidene rather than diacetylene, and the C–C bond cleavage channel produces stable acetylene (C_2H_2) together with transient vinylidene (CCH_2). Thus, the individual photoproduct isomers, rather than only their molecular formulas, are expected to control the subsequent chemical evolution of vinylacetylene in photon-processed astrophysical environments.

1 **Acknowledgements**

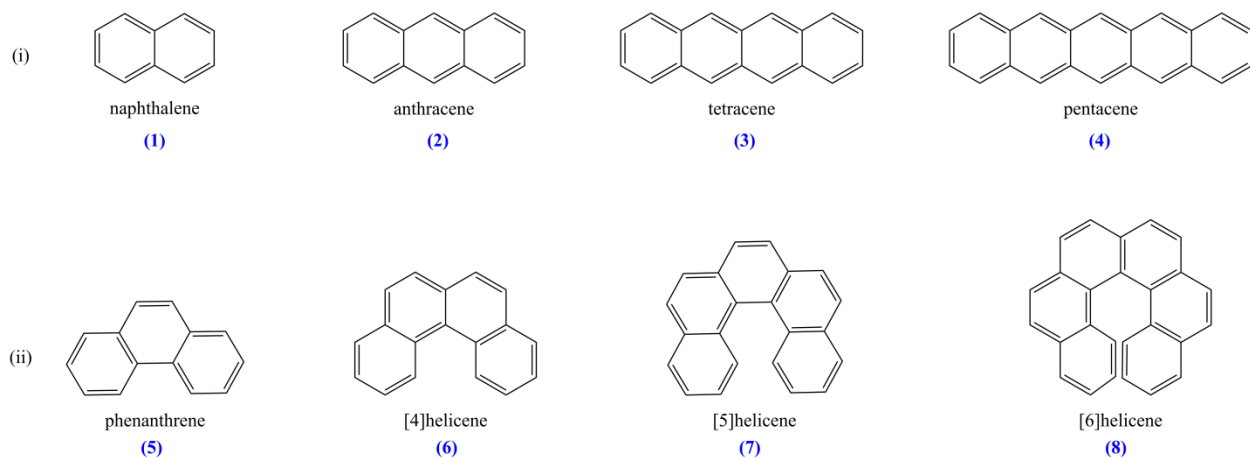
2 The experimental studies at the University of Hawaii were supported by the US Department of
3 Energy, Basic Energy Sciences DE-FG02-03ER15411.

4

5 **Conflict of interest**

6 The authors declare no conflict of interest.

7



Scheme 1. Representative PAHs formed through vinylacetylene-mediated molecular growth: (i) linearly fused acenes and (ii) ortho-condensed PAHs, including phenanthrene and helicenes.

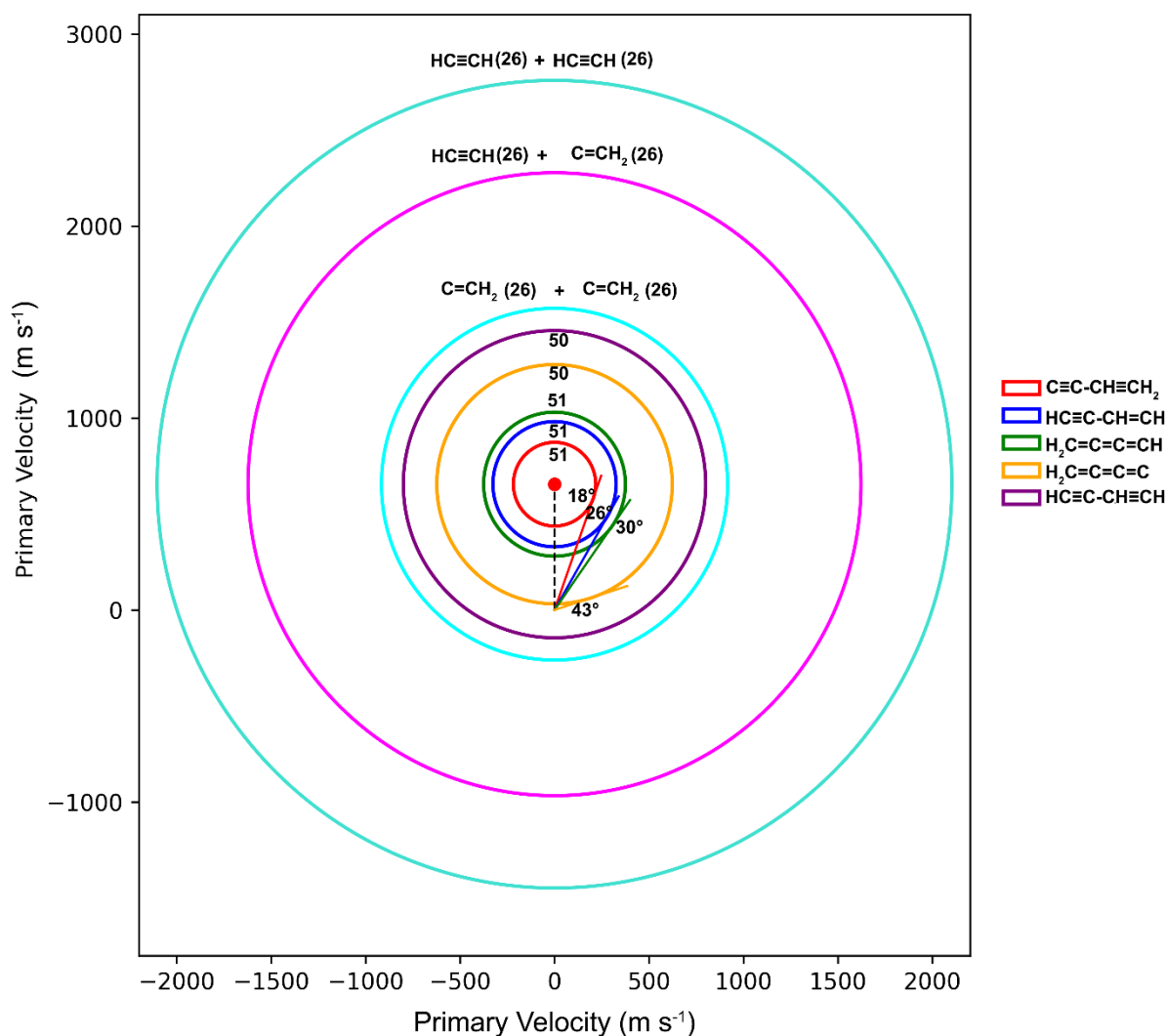


Figure 1. Newton diagram illustrating the kinematic constraints for the photodissociation channels of vinylacetylene (C_4H_4) at 193 nm. The primary beam velocity vector is shown along the vertical axis, while the concentric circles represent the maximum scattering angle of product fragments for different dissociation channels. The inner three circles correspond to H-loss channels ($m/z = 51$), whereas the intermediate two circles represent H_2 -loss channels ($m/z = 50$). The outer circles correspond to C_2H_2/CCH_2 -loss channels ($m/z = 26$), including symmetric and asymmetric fragmentations such as $HC\equiv CH + HC\equiv CH$, $HC\equiv CH + C=CH_2$, and $C=CH_2 + C=CH_2$.

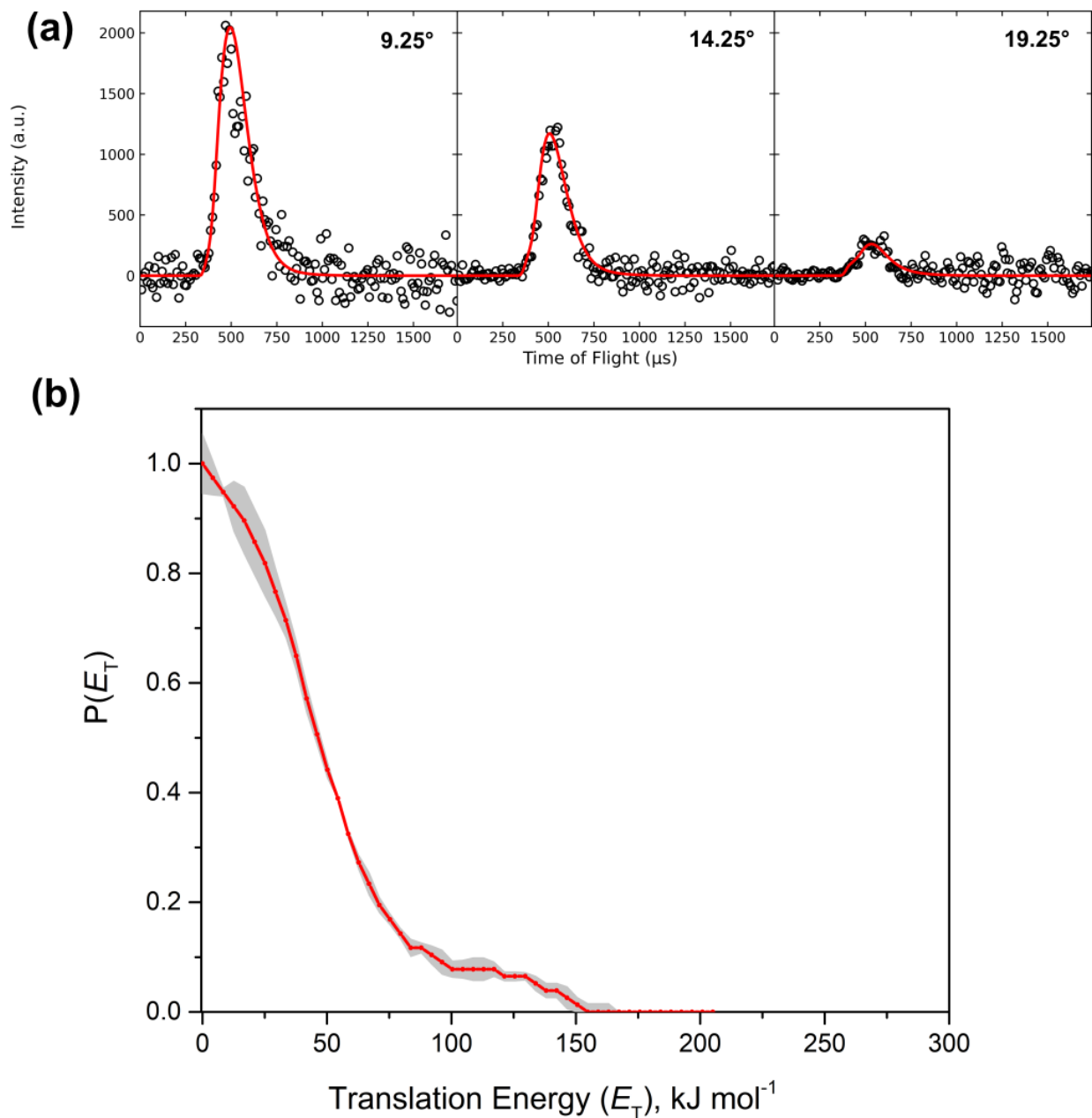


Figure 2. (a) Time-of-flight (TOF) spectra recorded at selected laboratory angles (9.25°, 14.25°, and 19.25°) for the H-loss channel ($m/z = 51$) in the 193 nm photodissociation of vinylacetylene (C_4H_4). Open circles represent the experimental data, while the red lines correspond to the best-fit forward convolution simulations using a single-channel model. (b) Center-of-mass translational energy distribution, $P(E_T)$, derived from the best-fit simulation. The shaded region indicates the uncertainty range in the fit.

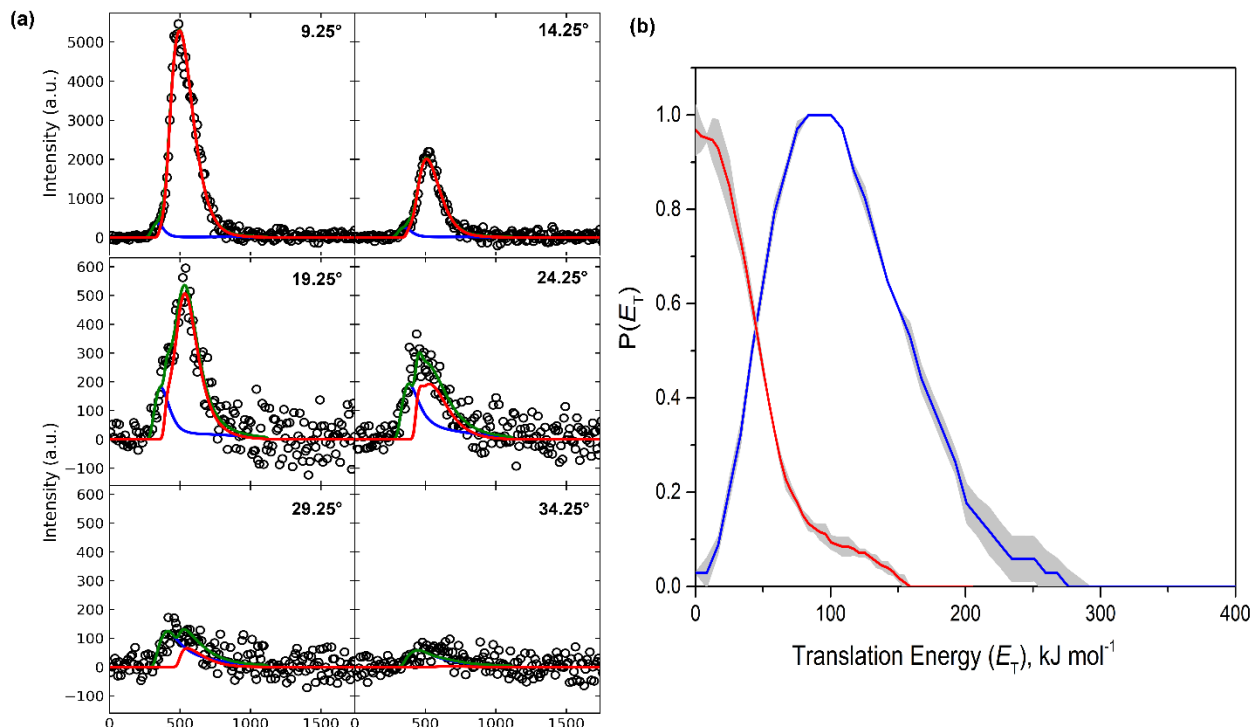


Figure 3. (a) Time-of-flight (TOF) spectra recorded at selected laboratory angles (9.25° – 34.25°) for the H_2 -loss channel ($m/z = 50$) in the 193 nm photodissociation of vinylacetylene (C_4H_4). Open circles represent the experimental data. The green lines correspond to the best-fit forward convolution simulations, while the blue and red lines indicate the individual contributions from true H_2 -loss and dissociative ionization of the H-loss channel ($m/z = 51$), respectively. (b) Center-of-mass translational energy distributions, $P(E_T)$, for the H_2 -loss channel (blue) and the H-loss contribution (red) derived from the best-fit simulations. The shaded regions represent the uncertainties in the fits.

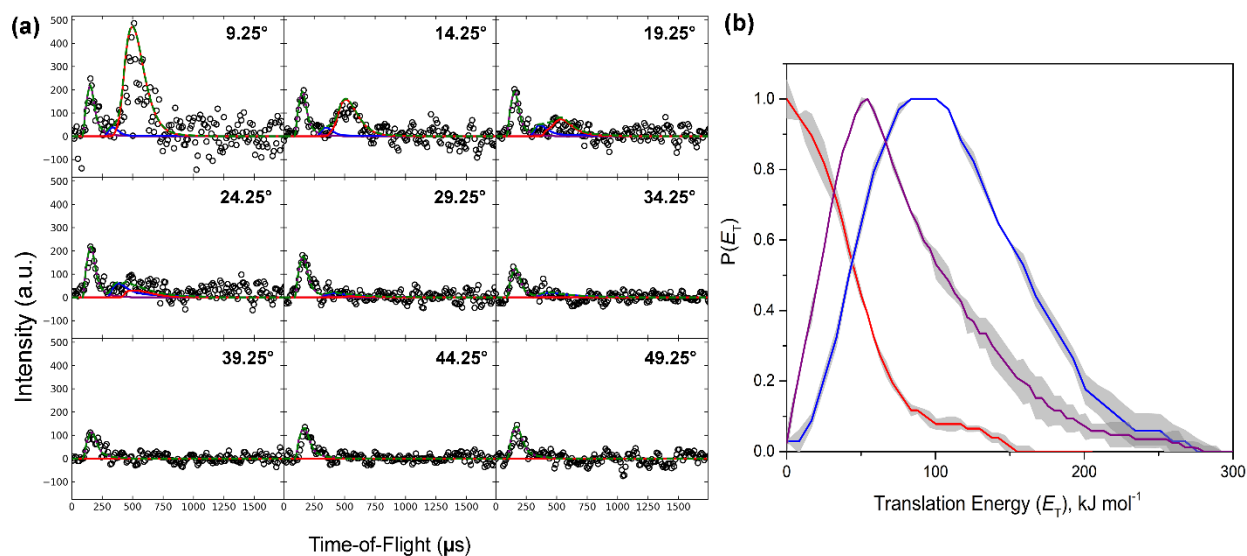


Figure 4. (a) Time-of-flight (TOF) spectra recorded at laboratory angles from 9.25° to 49.25° for the C₂H₂/CCH₂-loss channel ($m/z = 26$) in the 193 nm photodissociation of vinylacetylene (C₄H₄). Open circles represent the experimental data. The green dotted line corresponds to the best-fit forward convolution simulation, while the red, blue, and purple curves (solid line) denote the individual contributions from dissociative ionization of the H-loss channel ($m/z = 51$), H₂-loss channel ($m/z = 50$), and the true C₂H₂/CCH₂-loss channel, respectively. (b) Center-of-mass translational energy distributions, P(E_T), for the H-loss (red), H₂-loss (blue), and C₂H₂/CCH₂-loss (purple) channels derived from the best-fit simulations. The shaded regions indicate the uncertainties in the fits.

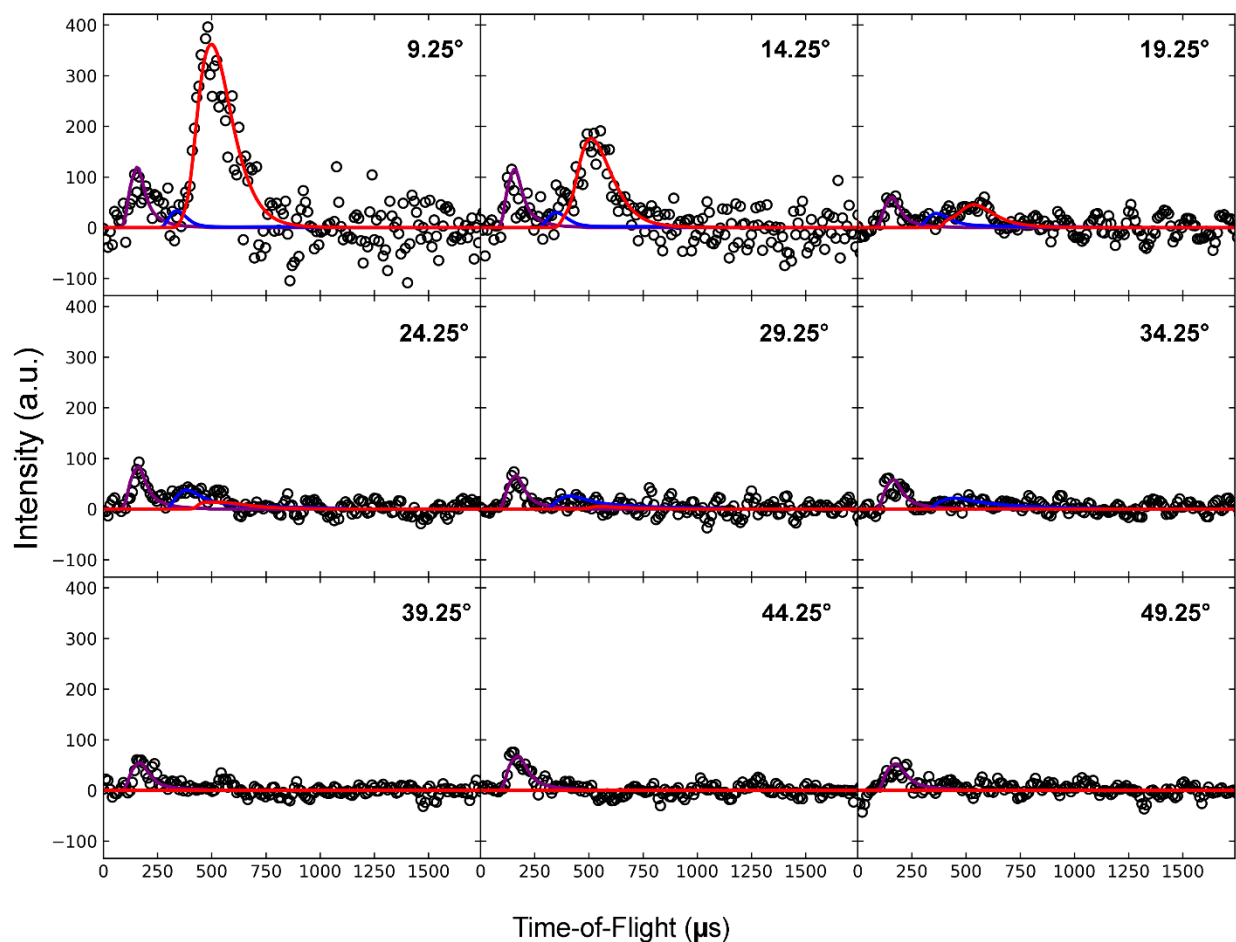


Figure 5. Time-of-flight (TOF) spectra recorded at laboratory angles from 9.25° to 49.25° for $m/z = 25$ in the 193 nm photodissociation of vinylacetylene (C_4H_4). Open circles represent the experimental data. The spectra are reproduced by forward convolution simulations incorporating contributions from atomic hydrogen loss, molecular hydrogen loss, and the C_2H_2/CCH_2 -loss channel. The red, blue, and purple curves denote the individual contributions arising from dissociative ionization of the H-loss channel ($m/z = 51$), the H_2 -loss channel ($m/z = 50$), and the true C_2H_2/CCH_2 -loss channel, respectively.

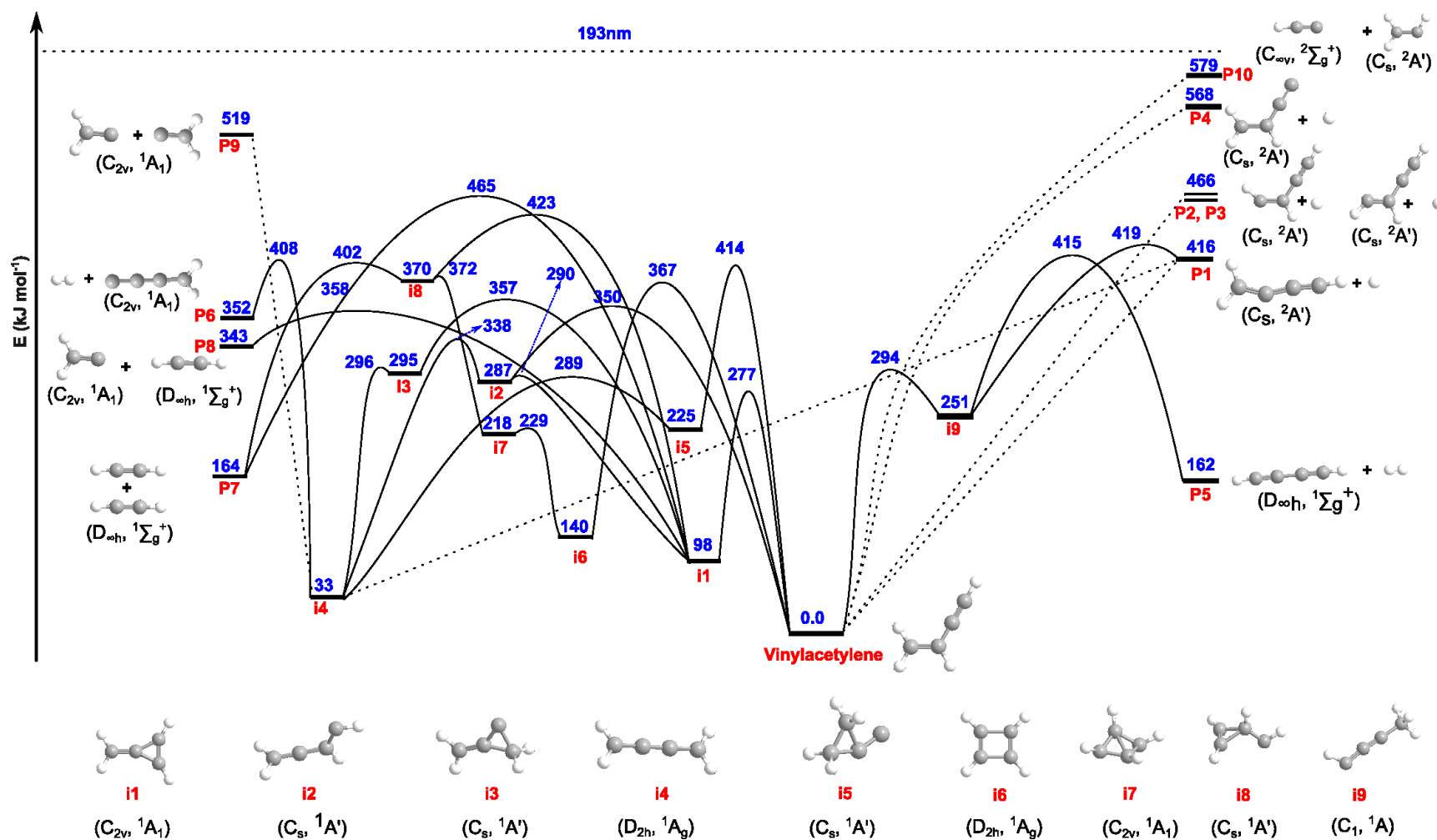


Figure 6. Potential energy surface (PES) for the photodissociation of vinylacetylene (C_4H_4) on the ground electronic state. Energies (in kJ mol^{-1}), computed at the CCSD(T)-F12/cc-pVQZ-F12 level of theory, are given relative to the separated reactants. Key intermediates and transition states connecting the H-loss, H_2 -loss, and C_2H_2/CCH_2 -loss channels are shown. Note that the $C_3H_3 + CH$ channel (650 kJ mol^{-1}) is not energetically accessible in photodissociation at 193 nm.

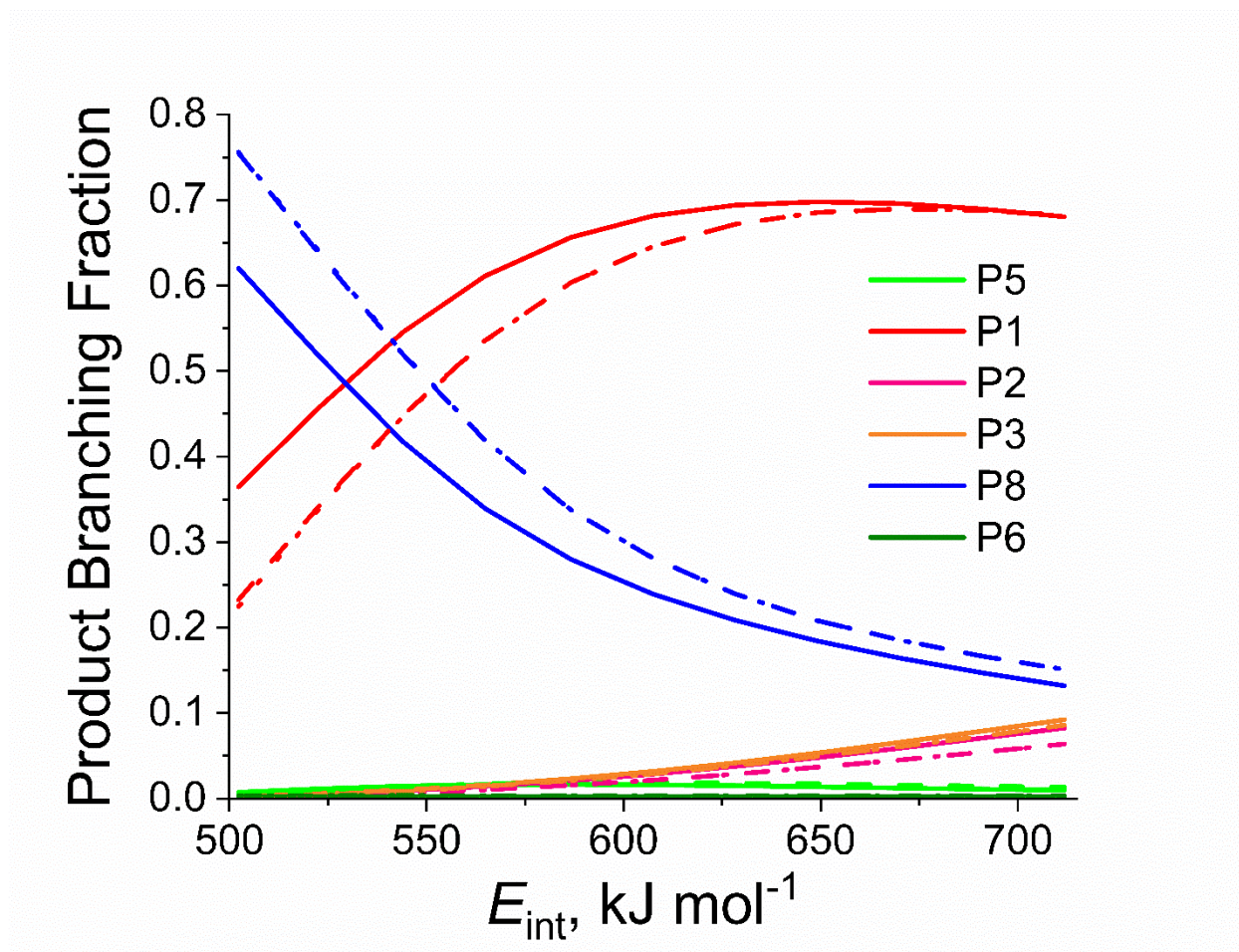
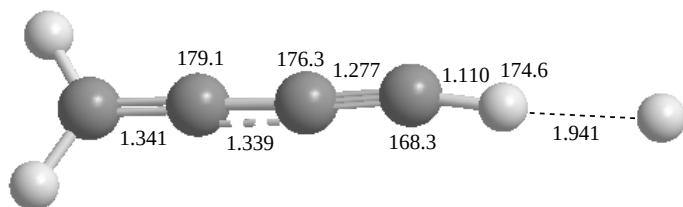


Figure 7. Statistical branching ratios as functions of the available internal energy E_{int} in the zero-pressure limit (solid lines) and at pressures of 1 mbar (dashed lines) and 3 mbar (dotted lines).

1



2

3 **Figure 8.** Optimized structure of a second-order saddle point for the H atom roaming pathway
4 leading to **P6**. The distances are shown in angstroms and bond angles in degrees

5

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