



Photodissociation Pathways of Vinylacetylene (C_4H_4) and Implications for the Interstellar Hydrocarbon Chemistry

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Abstract

Vinylacetylene (C_4H_4 ; $CH_2=CH-C\equiv CH$) 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 $C_4H_3:C_4H_2:C_2H_2/CCH_2 = (74 \pm 2):(12 \pm 2):(14 \pm 1)$. 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 ($CH=CH-C\equiv CH$), whereas RRKM calculations predict that the resonance-stabilized 1-buten-3-yne-2-yl radical ($H_2C=C=C=CH$) 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 butatrienyldiene ($H_2C=C=C:$), 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.

Unified Astronomy Thesaurus concepts: Photodissociation reactions (2266); Astrochemistry (75); Laboratory astrophysics (2004); Potential energy surfaces (2234); Quantum-chemical calculations (2232); Molecular physics (2058)

1. Introduction

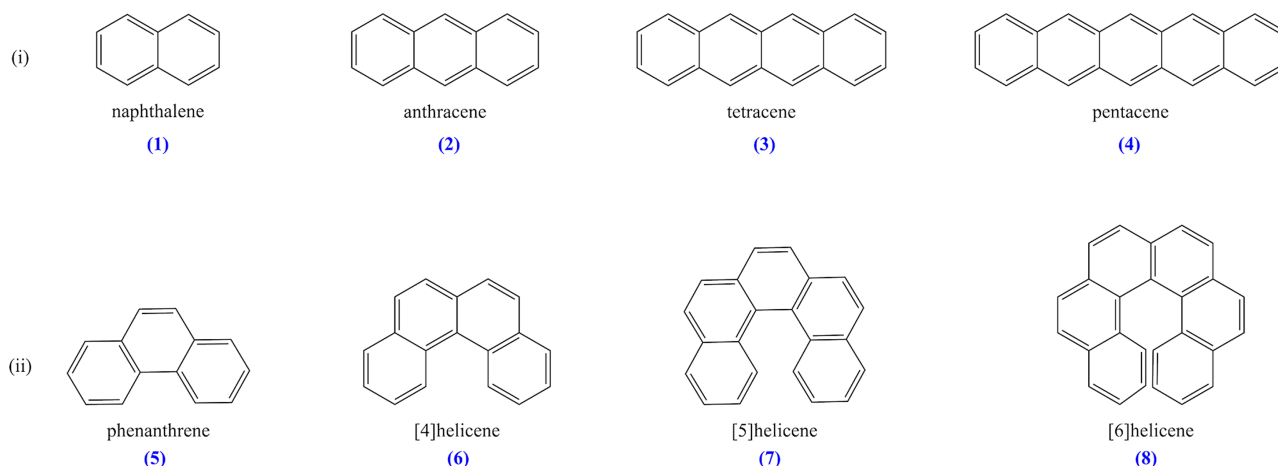
Polycyclic aromatic hydrocarbons (PAHs) constitute a major reservoir of cosmic carbon with up to 30% of the total carbon content and are widely regarded as the carriers of the unidentified infrared (UIR) emission bands observed throughout the interstellar medium (ISM), in the 3–14 μm region (L. J. Allamandola et al. 1989; A. G. Tielens 2008; A. M. Ricks et al. 2009) as well as potential contributors to the diffuse interstellar bands (DIBs) detected in the 200–400 nm wavelength range (W. W. 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 (D. M. Hudgins et al. 2005; A. Ricca et al. 2012; R. I. Kaiser et al. 2015; D. S. N. Parker & R. I. Kaiser 2017; B. A. McGuire et al. 2018; L. Zhao et al. 2019; R. I. Kaiser & N. Hansen 2021; R. I. Kaiser et al. 2022b; C. Y. Wang et al. 2024). 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 ISM (E. Herbst & E. F. Van Dishoeck 2009; D. S. N. Parker et al. 2012a; R. I. Kaiser & N. Hansen 2021; S. J. Goettl et al. 2025).

In high-temperature environments such as combustion systems and carbon-rich circumstellar envelopes, the formation of PAHs is predominantly inferred by the hydrogen abstraction–acetylene addition (HACA) mechanism (M. Frenklach & J. Warnatz 1987; M. Frenklach 2002; G. 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 of 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 sub-merged-barrier reaction channels (R. I. Kaiser & A. M. Mebel 2002; B. M. Jones et al. 2011; D. S. N. Parker et al. 2012a; R. I. Kaiser et al. 2015; B. A. McGuire et al. 2018; J. Cernicharo et al. 2021a; R. I. Kaiser et al. 2022b). Laboratory reaction-dynamics studies have demonstrated that neutral–neutral reactions involving unsaturated hydrocarbons can indeed



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

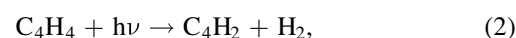
proceed without entrance barriers under single-collision conditions, providing viable low-temperature routes to aromatic ring formation (D. S. N. Parker et al. 2012a; R. I. Kaiser et al. 2015; D. S. N. Parker et al. 2015; L. Zhao et al. 2018; S. J. Goettl et al. 2023; Z. Yang et al. 2024a; Z. Yang et al. 2025a, 2025b; I. A. Medvedkov et al. 2026). 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 ($C_{18}H_{12}$, $C_{22}H_{14}$, $C_{26}H_{16}$) (L. Zhao et al. 2020; R. I. Kaiser et al. 2022a) (Scheme 1).

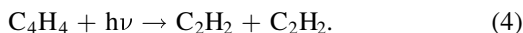
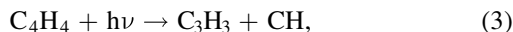
A particularly promising low-temperature pathway for PAH growth is the hydrogen abstraction–vinylacetylene addition (HAVA) mechanism, in which radical sites on aromatic precursors such as phenyl (C_6H_5) and naphthyl radicals ($C_{10}H_7$) react with vinylacetylene (C_4H_4 ; $CH_2=CH-C\equiv CH$, X^1A') to larger aromatic frameworks via benzene ring annulation, e.g., naphthalene (D. S. N. Parker et al. 2012a; R. I. Kaiser et al. 2015; T. Yang et al. 2015; L. Zhao et al. 2018; C. He et al. 2022). Crossed molecular-beam experiments combined with high-level electronic-structure calculations have demonstrated that reactions such as phenyl (C_6H_5 , X^2A_1) plus vinylacetylene (C_4H_4 , X^1A') proceed via a weakly bound van der Waals complex and a submerged transition state (TS), ultimately yielding naphthalene ($C_{10}H_8$) and atomic hydrogen as a dominant product channel under single-collision conditions (D. S. N. 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 (J. 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 (J. 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 (R. I. 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 , $X^2\Sigma^+$) with ethylene (C_2H_4 , X^1A_g) has been shown to produce vinylacetylene as the dominant product via hydrogen atom elimination from the C_4H_5 intermediate (F. 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 (B. J. Opansky & S. R. Leone 1996; J. Bouwman et al. 2012). This near-gas-kinetic efficiency makes the reaction between ethynyl radical (C_2H , $X^2\Sigma^+$) 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 – 10^4 photons $\text{cm}^{-2} \text{ s}^{-1}$ (S. S. Prasad & S. P. Tarafdar 1983). Laboratory photodissociation studies of vinylacetylene, conducted primarily in the vacuum UV (VUV) (193 nm) 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 (Z. Yang et al. 2024b) and astronomical observations (J. 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 (Y. T. Lee 1987; R. I. Kaiser et al. 1999; R. I. Kaiser 2002; X. Gu & R. I. Kaiser 2009; R. I. Kaiser et al. 2010; S. J. Goettl et al. 2021). 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; F. Zhang et al. 2011) seeded in argon (99.9999%; BOC Gases) at a level of 5% was generated using a 120 Hz Proch-Trickl (D. Proch & T. Trickl 1989) pulsed valve operated at -400 V under a backing pressure of 1 atm. The chopper wheel had a diameter of 17.0 ± 0.1 cm and a slit width of 0.76 ± 0.01 mm, corresponding to a temporal gate of approximately $11.9 \mu\text{s}$. 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 $660 \pm 21 \text{ m s}^{-1}$ 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 (620 kJ mol^{-1}), with a laser delay of $195 \mu\text{s}$ relative to the opening of the pulsed valve. The laser pulse energy of 1 mJ was less tightly focused to a spot size of $5 \text{ mm} \times 1 \text{ mm}$ to reduce the multiphoton process during the photodissociation. Photofragmented products are detected by the rotatable detector at different angles from 9.25 to 49.25 . The laboratory angular range was selected from the kinematic limits predicted by the Newton diagrams and extended until no significant product signal was observed. Time-of-flight (TOF) spectra were recorded at 5° increments and fitted simultaneously using a common $P(E_T)$. Therefore, the 5° sampling is not expected to introduce systematic bias, although it defines the angular sampling resolution. The neutral photodissociation products traveled 33.75 ± 0.20 cm before entering the detector, where they were ionized in a 1.00 ± 0.05 cm long Brink-type electron-impact ionizer using 80 eV electrons at an emission current of 2 mA. Electron-impact ionization at 80 eV can cause fragmentation of the neutral photoproducts through dissociative ionization. These contributions were identified from matching TOF profiles at different m/z values and explicitly included in the multichannel forward-convolution

analysis. 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 (N. R. 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 (X. Zhao 1988). In this method, a trial center-of-mass translational energy distribution, $P(E_T)$, was combined with the apparatus and beam parameters, including source and detector angular half-spreads of $0.^\circ79 \pm 0.^\circ02$ and $1.^\circ70 \pm 0.^\circ02$, respectively, together with the experimentally measured beam velocity distribution, to simulate the TOF spectra 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 potential energy surface (PES) were carried out using density functional theory (DFT) utilizing the long-range corrected hybrid density functional $\omega\text{B97X-D}$ (J.-D. Chai & M. Head-Gordon 2008) alongside the 6-311G(d,p) (R. Krishnan et al. 1980) basis set. Optimized local minima exhibited no imaginary frequencies, whereas all TSs have exactly one imaginary frequency. To verify the reaction pathways, we conducted intrinsic reaction coordinate (IRC) calculations (H. P. Hratchian & H. B. Schlegel 2004) at the same $\omega\text{B97X-D}/6\text{-}311\text{G(d,p)}$ level of theory. Energies of the DFT-optimized structures were subsequently refined via explicitly correlated coupled-cluster calculations at the CCSD(T)-F12 (T. B. Adler et al. 2007; G. Knizia et al. 2009)/cc-pVQZ-F12 (K. A. Peterson et al. 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 multireference perturbation theory with internally contracted configurations (CASPT2) (P. Celani & H.-J. Werner 2000; T. Shiozaki et al. 2011). This calculation was performed at the CASPT2(8e, 8o)/cc-pVQZ (T. H. 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 CASPT2 calculations were carried out for a single-state wave function of the ground electronic state. The electronic-structure calculations employed the Gaussian 16 (M. J. Frisch et al. 2019) and MOLPRO 2021 software packages (H. J. 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 (A. M. Mebel et al. 2006).

To characterize the TS 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 $\text{C}_4\text{H}_2 + \text{H}_2$ —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 TS geometry

Table 1
Predicted Reaction Channels for the Photodissociation of Vinylacetylene (C_4H_4) at 193 nm

Fragment I	Fragment II	Reaction Energy ^a (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
$HC\equiv C-C\equiv CH (m/z = 50)$	$H_2 (m/z = 2)$	162	458
$H_2C=C=C=C\cdot (m/z = 50)$	$H_2 (m/z = 2)$	352	268
$HC\equiv CH (m/z = 26)$	$HC\equiv CH (m/z = 26)$	164	456
$HC\equiv CH (m/z = 26)$	$\cdot C=CH_2 (m/z = 26)$	341	279
$\cdot C=CH_2 (m/z = 26)$	$\cdot C=CH_2 (m/z = 26)$	519	101
$HC\equiv C\cdot (m/z = 25)$	$HC\equiv CH_2 (m/z = 27)$	580	40

Note. The expected m/z values for all species are given in parentheses. Reaction energies for the dissociation channels are given in kJ mol⁻¹.

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

identified by this scan was further refined using TS optimization. Both the initial coordinate scan and the TS optimization employed the CASPT2(10e, 10o)/cc-pVDZ (T. H. 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 CASPT2(10e, 10o)/cc-pVQZ level, with the resulting energy evaluated relative to the $H_2C_4H_2$ isomer i4.

At the zero-pressure limit, microcanonical energy-dependent rate coefficients for individual unimolecular reactions involved in isomerization and decomposition of a “hot” C_4H_4 molecule with internal energy equal to that of an absorbed photon were evaluated using Rice–Ramsperger–Kassel–Marcus (RRKM) theory (R. A. 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 (W. H. 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 TS theory (VTST; J. L. Bao & D. G. Truhlar 2017). VTST calculations did not include tunneling correction. For all other unimolecular reaction steps involved, based on the comparison between results computed with and without tunneling, its effects appeared to be insignificant due to the large excess of internal energy. The steady-state approximation was employed in solving the system of master equations (MEs) to compute product branching ratios. We used our internal UNIMOL code (C. He et al. 2019) for the calculations of RRKM rate constants and product branching ratios at the zero-pressure limit. Pressure-dependent rate constants and branching ratios were evaluated using the ME framework (Y. Georgievskii et al. 2013) and the MESS software package (Y. Georgievskii & S. J. Klippenstein 2015). The Lennard-Jones parameters and the parameters for the “exponential down” model (J. Troe 1977) of the collisional energy transfer were adopted from J. A. Stearns et al. (2006).

3. Results

3.1. Newton Diagrams

Multiple photodissociation channels of vinylacetylene were investigated using 193 nm laser excitation (620 kJ mol⁻¹). 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

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

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, TOF 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 multiphoton processes were evaluated through a laser power-dependence study. TOF spectra recorded over the energy range of 100 $\mu\text{J pulse}^{-1}$ 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.

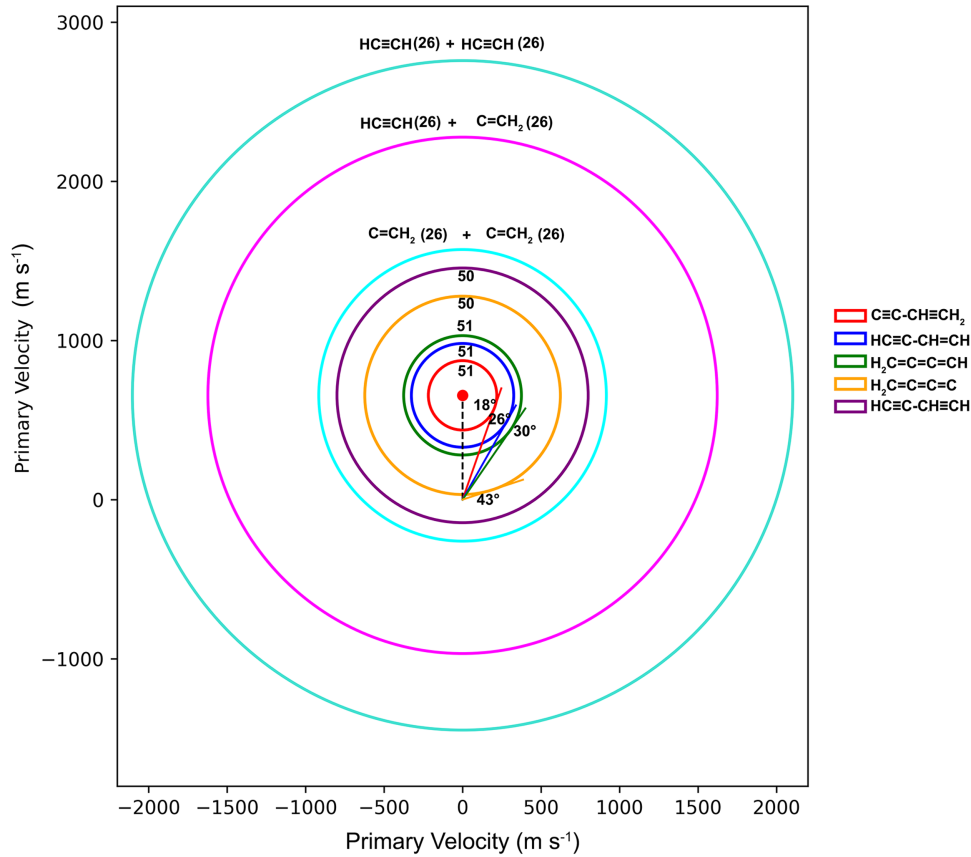


Figure 1. Newton diagram illustrating the kinematic constraints for the photodissociation channels of vinylacetylene (C_4H_4) at 193 nm. The primary beam velocity vector is shown along the vertical axis, while the concentric circles represent the maximum scattering angle of product fragments for different 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 $C=CH_2 + C=CH_2$.

3.2. Atomic Hydrogen Elimination

TOF spectra at $m/z = 51$ ($C_4H_3^+$) at angles of $9.^\circ25$, $14.^\circ25$, and $19.^\circ25$ are shown in Figure 2(a); the translational energy distribution, $P(E_T)$, corresponding to the best fit of the TOF data, is shown in Figure 2(b). No signal was observed at laboratory angles beyond $19.^\circ25$. 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 $E_{T(\text{max})} = 154 \pm 9 \text{ kJ mol}^{-1}$.

3.3. Molecular Hydrogen Elimination

Figure 3(a) presents the TOF data at $m/z = 50$ ($C_4H_2^+$) recorded at laboratory angles ranging from $9.^\circ25$ to $39.^\circ25$ at 5° intervals; no signal was observed beyond this angular range. The slower component of the TOF signal at laboratory angles $9.^\circ25$, $14.^\circ25$, and $19.^\circ25$ 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 $m/z = 51$ ($9.^\circ25$ – $19.^\circ25$), 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 3(b). 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 an FWHM of 120 kJ mol^{-1} . Also, the $P(E_T)$ for this channel peaks at 84 kJ mol^{-1} and extends to $E_{T(\text{max})} = 268 \pm 12 \text{ kJ mol}^{-1}$.

3.4. C–C Bond Breaking (C_2H_2/CCH_2 Elimination)

Figure 4(a) displays the TOF data for $m/z = 26$ ($C_2H_2^+/CCH_2^+$) recorded at angles from $9.^\circ25$ to $49.^\circ25$ in 5° increments. At the lower angles ($9.^\circ25$ – $24.^\circ25$), an additional slow feature appears that overlaps with the signal at $m/z = 51$ and $m/z = 50$. This indicates that the 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 the C_2H_2/CCH_2 elimination channel; the corresponding translational energy distribution is displayed in Figure 4(b). The $P(E_T)$ for the C_2H_2/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 $E_{T(\text{max})} = 276 \pm 17 \text{ kJ mol}^{-1}$.

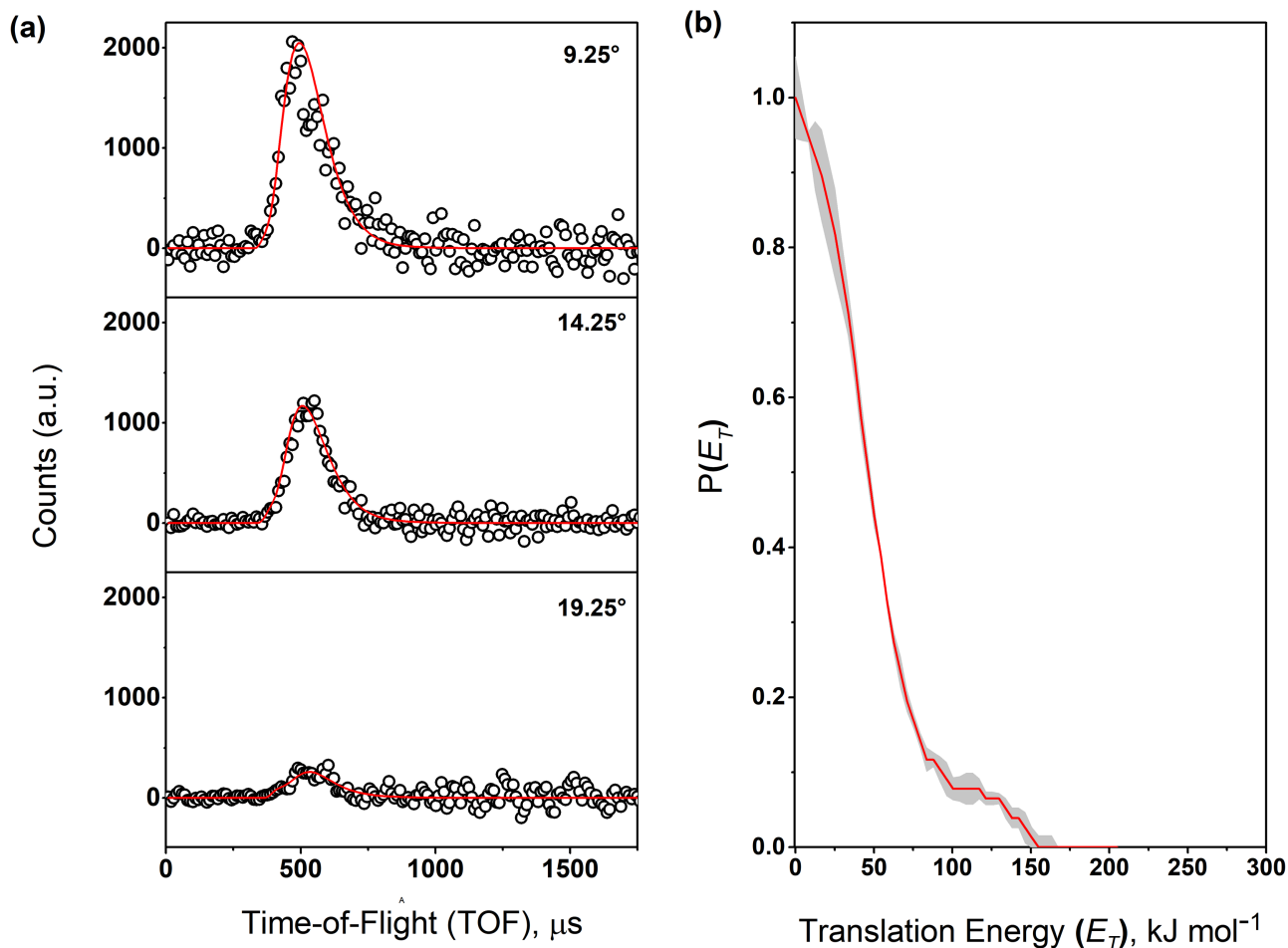


Figure 2. (a) TOF spectra recorded at selected laboratory angles (9.25° , 14.25° , and 19.25°) for the H loss channel ($m/z = 51$) in the 193 nm photodissociation of vinylacetylene (C_4H_4). Open circles represent the experimental data, while the red lines correspond to the best-fit forward-convolution 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.

3.5. C–C bond Breaking (C_2H_3/C_2H Elimination)

TOF spectra for $m/z = 25$ (C_2H^+) were recorded at angles starting from 9.25° to 49.25° in 5° intervals (Figure 5). TOF spectra are identical to the 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 C_2H_2/CCH_2 . Also, the absence of the counter fragment at $m/z = 27$ suggests that C–C bond breaking to $C_2H + C_2H_3$ 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 C_2H_2/CCH_2 loss channels (Figure 4(b)).

3.6. Branching Ratios

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

$$BR_i = \frac{W_i / \sigma_i \times f_i}{\sum (W_i / \sigma_i \times f_i)},$$

where W_i represents the weighting factor associated with the translational energy distribution $P(E_T)$ for channel “ i ” (M. J. Shapero 2017). The weighting factors were obtained by fitting the simulated 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 binary-encounter-Bethe (BEB) model. The BEB ionization cross sections for C_4H_2 and C_2H_2 are (8.88×10^{-16}) and (4.36×10^{-16}) cm^2 , respectively. For C_4H_3 , the required BEB parameters were calculated at the Hartree–Fock level using the optimized geometry, yielding an ionization cross section of (13.7×10^{-16}) cm^2 . The dissociative ionization probabilities (f_i) were evaluated for all mass channels with measurable signal intensities. Taking these corrections into account, the experimentally derived branching ratios are determined to be $C_4H_3:C_4H_2:C_2H_2/CCH_2 = (74 \pm 2):(12 \pm 2):(14 \pm 1)$.

4. Discussion

4.1. PES

The aim of this study is to determine the photodissociation channels of vinylacetylene at 193 nm (620 $kJ\ mol^{-1}$) under collision-free conditions, with a focus on identifying the resulting photofragments and elucidating the underlying dissociation pathways. The first two excited electronic states of vinylacetylene are $^1A''$ and $^2^1A'$ with vertical excitation energies of 555 and 584 $kJ\ mol^{-1}$, respectively, calculated at the CASPT2/cc-pVTZ level of theory, and both excited states are likely responsible for the

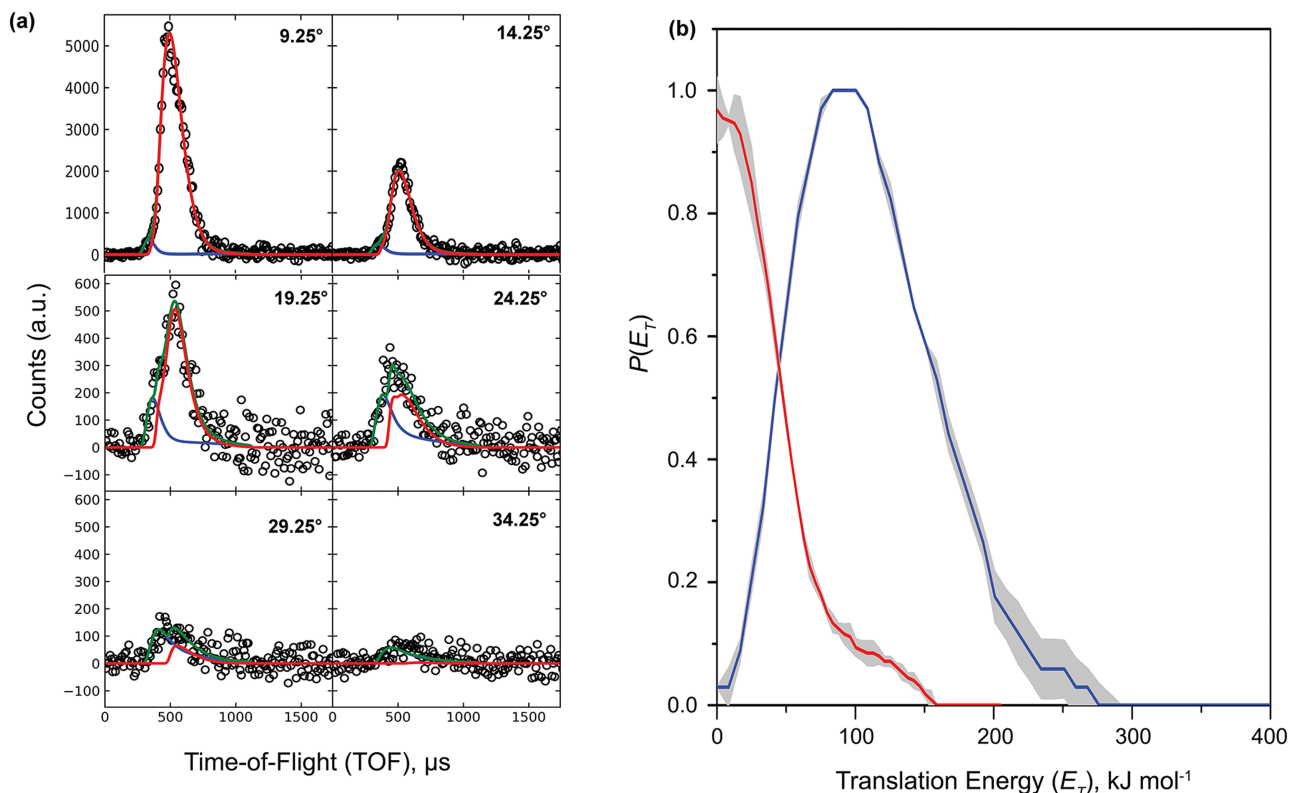


Figure 3. (a) TOF spectra recorded at selected laboratory angles (9.25° – 34.25°) for the H_2 loss channel ($m/z = 50$) in the 193 nm photodissociation of vinylacetylene (C_4H_4). Open circles represent the experimental data. The green lines correspond to the best-fit forward-convolution simulations, 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.

broad absorption band observed between 240 and 180 nm (A. Fahr & A. Nayak 1996). Geometry optimization of the first excited $^1A''$ state leads to a large structural change. While the molecule remains planar, the CCCH group on the acetylenic side of vinylacetylene loses its linearity, and the optimized geometry is akin to the structure of electronically excited *trans*-acetylene. The calculated adiabatic excitation energy of $^1A''$ including ZPE is 421 kJ mol^{-1} , significantly lower than the vertical excitation energy. The large geometry change and the difference between the adiabatic and vertical excitation energies account for the broadness of the corresponding absorption band. We assume that, following photoexcitation, vinylacetylene undergoes rapid internal conversion to the electronic ground state before dissociation. This interpretation is supported by the broad, unstructured UV absorption spectrum of vinylacetylene, which closely resembles that of 1,3-butadiene and has previously been attributed to similar nonradiative relaxation dynamics (J. C. Robinson et al. 2002; J. A. Stearns et al. 2006; M. Steinbauer et al. 2012; D. V. Chicharro et al. 2019). In the meantime, dissociative photoexcitation is unlikely to significantly contribute to the observed products. None of the ground-state molecular fragments have degenerate electronic states, and hence, the excited electronic state of C_4H_4 correlates with excited electronic states of at least one fragment in each product pair, which would largely decrease the energy available to the other degrees of freedom, rotational, vibrational, and translational. Moreover, electronically excited products may not even be accessible within the available energy of 620 kJ mol^{-1} .

Therefore, let us focus on the ground electronic PES. 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 (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 PES. 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

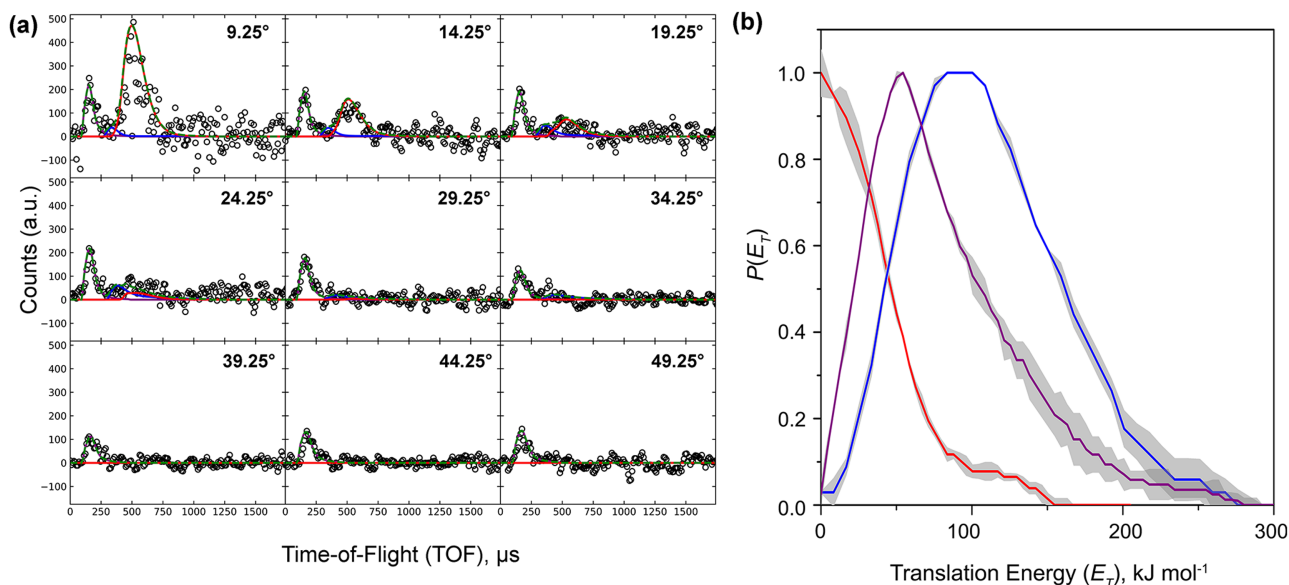


Figure 4. (a) TOF spectra recorded at laboratory angles from 9.25° to 49.25° for the C_2H_2/CCH_2 loss channel ($m/z = 26$) in the 193 nm photodissociation of vinylacetylene (C_4H_4). Open circles represent the experimental data. The green dotted line corresponds to the best-fit forward-convolution simulation, while the red, blue, and purple curves (solid lines) denote the individual contributions from dissociative ionization of the H loss channel ($m/z = 51$), H_2 loss channel ($m/z = 50$), and the true C_2H_2/CCH_2 loss channel, respectively. (b) Center-of-mass translational energy distributions, $P(E_T)$, for the H loss (red), H_2 loss (blue), and C_2H_2/CCH_2 loss (purple) channels derived from the best-fit simulations. The shaded regions indicate the uncertainties in the fits.

(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 TS 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 TS 358 kJ mol^{-1} above vinylacetylene. However, the former dissociation channel can also be accessed from intermediate i8, proceeding over the highest-energy TS 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 ($E_{h\nu} - E_{T(\text{max})}$). Using the 193 nm photon energy, ($E_{h\nu}$) = 620 kJ mol^{-1} , and $E_{T(\text{max})} = 154 \pm 9 \text{ kJ mol}^{-1}$, the photodissociation process is endoergic by $466 \pm 9 \text{ kJ mol}^{-1}$. The calculated PES identifies four competing atomic hydrogen loss pathways energetically accessible upon 193 nm photoexcitation. These are:

(a) $CH_2=CH-C\equiv CH + h\nu \rightarrow$ $H_2C=C=C=CH(P1) + H\cdot$	$\Delta H_0 = 416 \text{ kJ mol}^{-1}$ (available energy = 204 kJ mol^{-1})
(b) $CH_2=CH-C\equiv CH + h\nu \rightarrow$ $trans\text{-}CH=CH-C\equiv CH(P2) + H\cdot$	$\Delta H_0 = 466 \text{ kJ mol}^{-1}$ (available energy = 154 kJ mol^{-1})
(c) $CH_2=CH-C\equiv CH + h\nu \rightarrow$ $cis\text{-}CH=CH-C\equiv CH(P3) + H\cdot$	$\Delta H_0 = 465 \text{ kJ mol}^{-1}$ (available energy = 155 kJ mol^{-1})
(d) $CH_2=CH-C\equiv CH + h\nu \rightarrow$ $H_2C=CH-C\equiv C\cdot(P4) + H\cdot$	$\Delta H_0 = 568 \text{ kJ mol}^{-1}$ (available energy = 52 kJ mol^{-1})

Among the four reaction channels, the hydrogen atom loss channel matches nicely the formation of P2/P3 ($trans/cis\text{-}CH=CH-C\equiv CH$). The calculated PES indicates that the pathways for channels (b–c) proceed through C–H bond cleavage from the terminal vinylic carbon of vinylacetylene (C_4H_4). 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 the case of the formation of P4 (channel d), the available energy is much lower, which means that 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 C_4H_3 . The calculated PES reveals multiple pathways, in addition to a one-step dissociation, for the

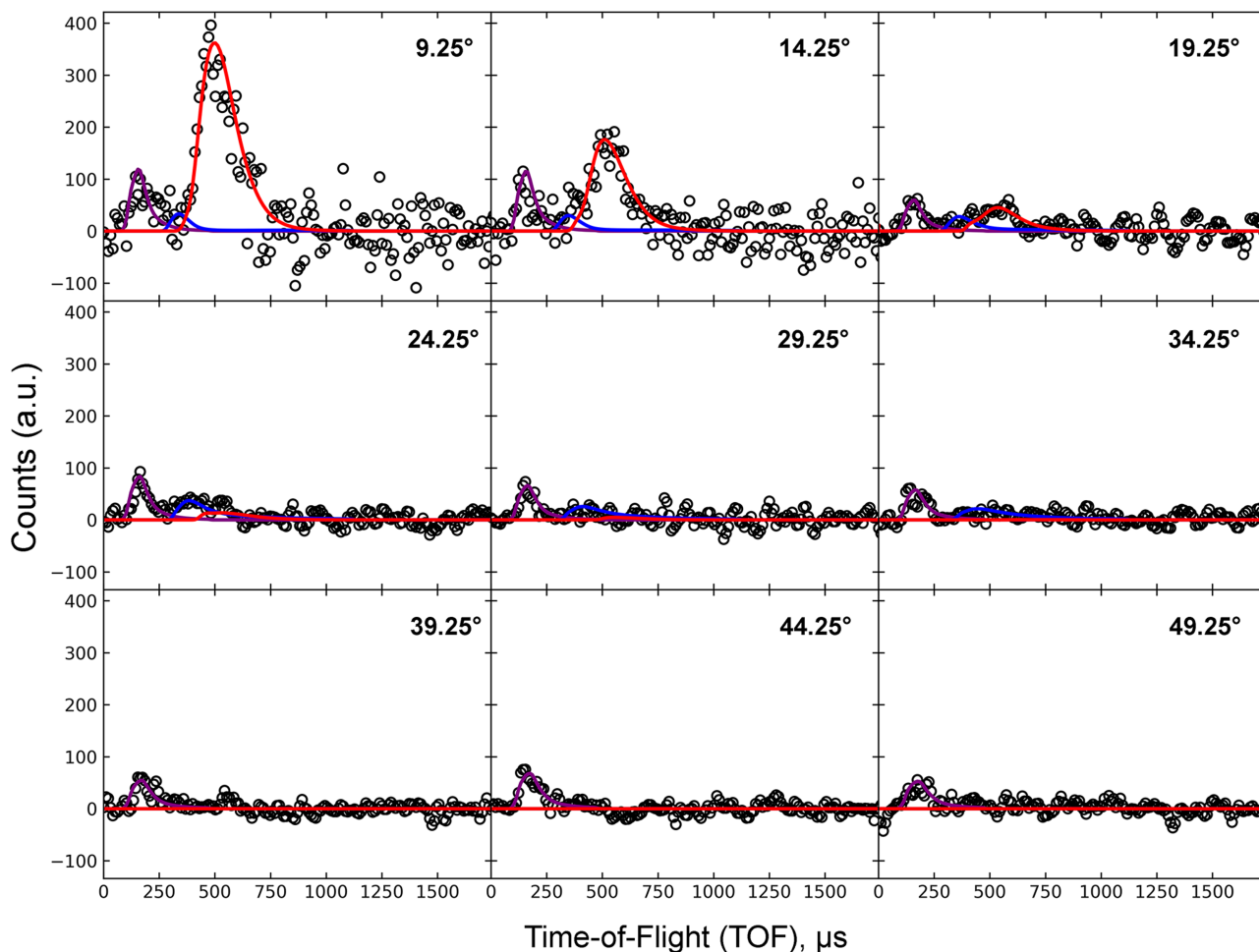


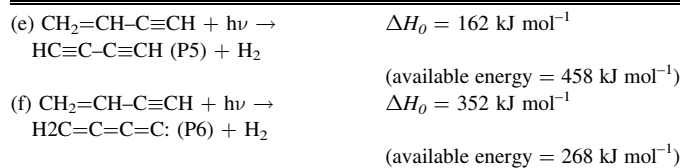
Figure 5. TOF spectra recorded at laboratory angles from 9.°25 to 49.°25 for $m/z = 25$ in the 193 nm photodissociation of vinylacetylene (C_4H_4). Open circles represent the experimental data. The spectra are reproduced by forward-convolution simulations incorporating contributions from atomic hydrogen 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.

formation of C_4H_3 and a hydrogen atom from vinylacetylene (C_4H_4). Vinylacetylene (VA) can isomerize to intermediate i4 through the lowest-energy pathways, $VA \rightarrow i1 \rightarrow i2 \rightarrow i4$, followed by barrierless dissociation to C_4H_3 and a hydrogen atom. Alternatively, it can rearrange to intermediate i9, which subsequently dissociates to C_4H_3 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 $154 \pm 9 \text{ kJ mol}^{-1}$. One possible explanation supporting the formation of the resonance-stabilized C_4H_3 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. Atomic hydrogen possesses no rovibrational degrees of freedom, whereas C_4H_3 contains a dense manifold of rotational and vibrational states into which the available energy can be partitioned. Similar behavior has been observed in H-atom velocity-map-imaging (VMI) studies of hydrocarbon radicals, where low translational-energy H-atom components were associated with highly

rovibrationally excited polyatomic coproducts and statistical ground-state dissociation (M. Steinbauer et al. 2012; D. V. Chicharro et al. 2019). These observations support the assignment of the C_4H_3 products in the present experiment as substantially rovibrationally excited.

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, $E_{T(\text{max})}$, of $268 \pm 12 \text{ kJ mol}^{-1}$. Considering the 620 kJ mol^{-1} of the 193 nm photon, the molecular hydrogen loss channel is endoergic by $352 \pm 12 \text{ kJ mol}^{-1}$. 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

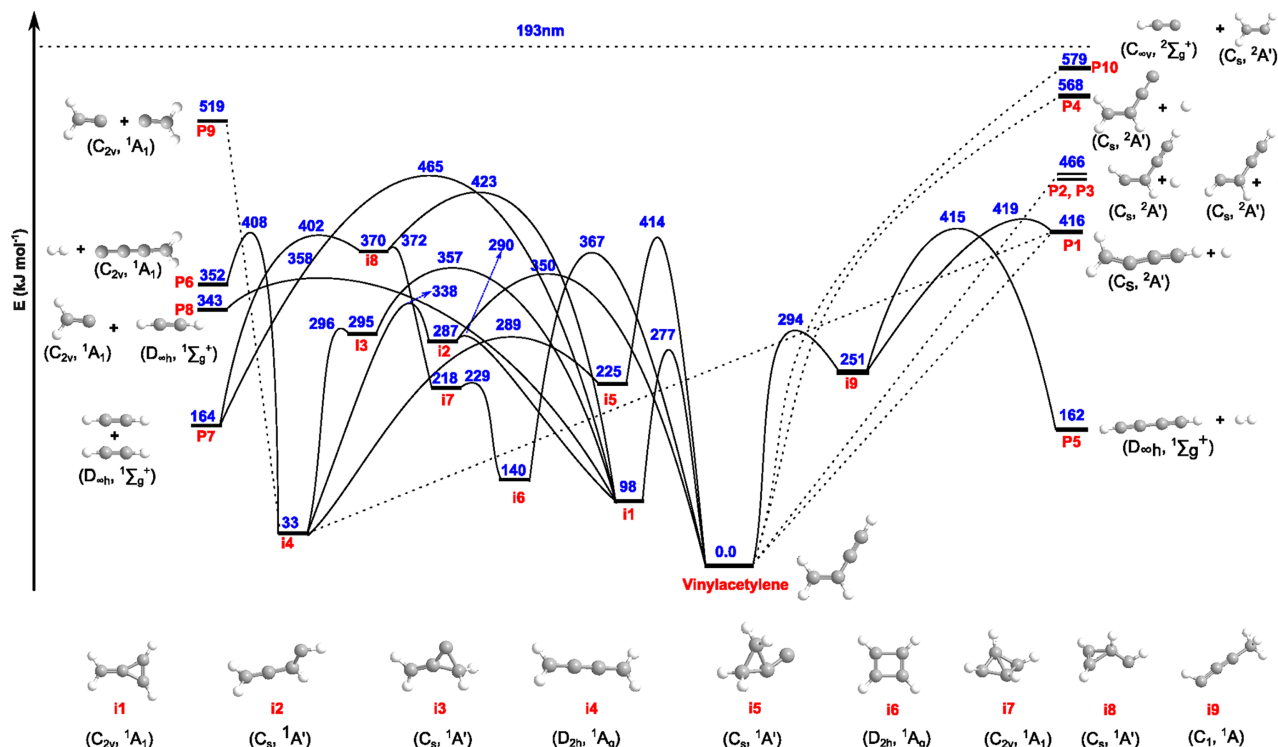


Figure 6. PES for the photodissociation of vinylacetylene (C_4H_4) on the ground electronic state. Energies (in kJ mol^{-1}), computed at the CCSD(T)-F12/cc-pVQZ-F12 level of theory, are given relative to ground-state vinylacetylene. Key intermediates and TSs connecting the H loss, H_2 loss, and C_2H_2/CCH_2 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.

predominantly forms butatrienylidene (P6, $H_2C=C=C=C:$) via the molecular hydrogen loss channel. The PES further reveals four competitive pathways capable of producing the P6 product; these are: (1) $VA \rightarrow i1 \rightarrow i2 \rightarrow i4 \rightarrow P6$; (2) $VA \rightarrow i1 \rightarrow i3 \rightarrow i4 \rightarrow P6$; (3) $VA \rightarrow i2 \rightarrow i4 \rightarrow P6$; (4) $VA \rightarrow i5 \rightarrow i4 \rightarrow P6$. The energy barrier for the $VA \rightarrow i1$ isomerization is much lower than that for $VA \rightarrow i2$ or $VA \rightarrow i5$, favoring the dominant formation of $i1$. Furthermore, the subsequent isomerization from $i1$ to $i3$ involves a substantially higher barrier than the $i1 \rightarrow i2$ pathway. Overall, pathway (1) is the energetically most feasible route leading to P6. The exit barrier for 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. C_2H_2/CCH_2 Loss Channel

The translational energy distribution, $P(E_T)$, for the C_2H_2/CCH_2 loss channel, monitored at $m/z = 26$, extends to a maximum translational energy release ($E_{T(\text{max})}$) of $276 \pm 17 \text{ kJ mol}^{-1}$. Accounting for the 620 kJ mol^{-1} of the 193 nm photon, the experimental reaction energy is determined to be $344 \pm 17 \text{ kJ mol}^{-1}$. Calculated PES shows three C_2H_2/CCH_2 elimination channels, which are:

(g) $CH_2=CH-C\equiv CH + h\nu \rightarrow$ $HC\equiv CH + HC\equiv CH$	$\Delta H_0 = 164 \text{ kJ mol}^{-1}$ (available energy = 456 kJ mol^{-1})
(h) $CH_2=CH-C\equiv CH + h\nu \rightarrow$ $HC\equiv CH + C=CH_2$	$\Delta H_0 = 343 \text{ kJ mol}^{-1}$ (available energy = 277 kJ mol^{-1})
(i) $CH_2=CH-C\equiv CH + h\nu \rightarrow$ $C=CH_2 + C=CH_2$	$\Delta H_0 = 519 \text{ kJ mol}^{-1}$ (available energy = 101 kJ mol^{-1})

The experimental value of reaction energy is in excellent agreement with the energetics of the pathway leading to the formation of acetylene plus vinylidene ($HC\equiv CH + C=CH_2$) (P8) on the computed PES. Multiple pathways can lead to P8 (Figure 6). However, the energetically preferred route proceeds through $VA \rightarrow i1 \rightarrow P8$ since it involves the lowest overall barrier among the accessible pathways. The calculated PES also predicts a 15 kJ mol^{-1} exit barrier for this channel, consistent with the experimental translational energy distribution, which peaks at 54 kJ mol^{-1} in the corresponding translational energy distribution, $P(E_T)$.

4.5. RRKM Calculation

If internal conversion to the electronic ground state is followed by rapid intramolecular vibrational energy redistribution (IVR), then RRKM theory provides an appropriate statistical framework for comparison with the experimental results. Considering all energetically accessible pathways on the computed PES surface (Figure 6), the RRKM calculations predict branching ratios of H loss: H_2 loss: C_2H_2/CCH_2 loss = 76:2:22. For the H loss channel, the calculations indicate that product P1 dominates, contributing 69%, whereas products P2 and P3 each contribute only about 3.5%; the contribution from P4 is negligible. The H_2 loss channel is also predicted to be minor, with contributions of 1.6% and 0.2% through P5 and P6, respectively. RRKM results estimate the formation of vibrationally excited 1-buten-3-yne-2-yl (P1) along with a small contribution of products P2/P3. In the case of molecular hydrogen loss, the RRKM calculations indicate that this pathway is only a minor contributor to the overall photodissociation, proceeding predominantly to P5 with a

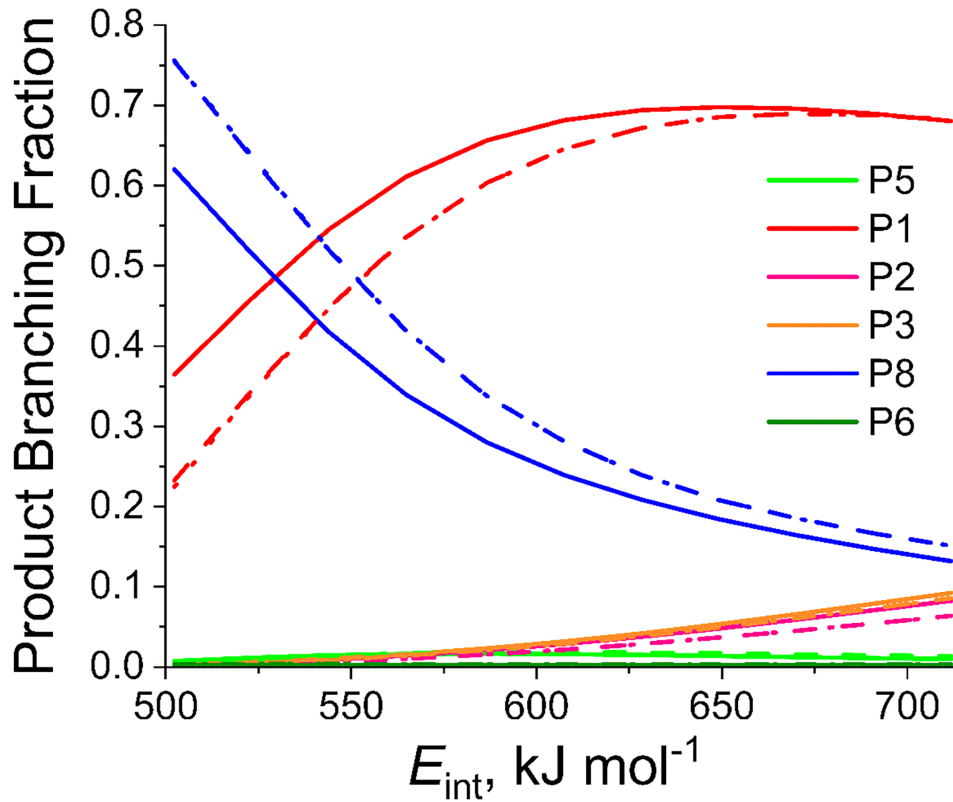


Figure 7. Statistical branching ratios as functions of the available internal energy E_{int} in the zero-pressure limit (solid lines) and at pressures of 1 mbar (dashed lines) and 3 mbar (dotted lines). Note that the dashed and dotted lines nearly coincide because the difference between the 1 and 3 mbar results is insignificant.

much smaller contribution from P6. The $\text{C}_2\text{H}_2/\text{CCH}_2$ loss channel, assigned exclusively to P8, is predicted by RRKM to contribute 22%.

The experimentally determined branching ratios indicate that the hydrogen atom loss channel accounts for $74\% \pm 2\%$, whereas the molecular hydrogen loss channel leading to P6 contributes $12\% \pm 2\%$. The remaining $14\% \pm 1\%$ is assigned to the $\text{C}_2\text{H}_2/\text{CCH}_2$ loss channel. Overall, the close agreement between the RRKM-predicted and experimentally derived total yield of the hydrogen atom loss channel suggests that statistical ground-state dissociation following internal conversion is an important component of the 193 nm photodissociation dynamics of vinylacetylene. Within this statistical picture, the dominant formation of rovibrationally excited P1 provides a plausible interpretation of the hydrogen loss data.

The present results on the UV photodissociation of vinylacetylene (C_4H_4) show that the hydrogen atom loss channel dominates, with smaller contributions from molecular hydrogen elimination and C–C bond cleavage. This behavior differs from the study by J. A. Stearns et al. (2006), where the primary detected products were 1-buten-3-yne-2-yl (C_4H_3 , $\text{H}_2\text{C}=\text{C}=\text{C}=\text{CH}\cdot$) 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 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 can be attributed mainly to the experimental conditions. In the reaction-tube experiments of J. A. Stearns et al. (2006), multiple collisions during the residence time allow for energy relaxation and secondary reactions, whereas the present collision-free conditions isolate the primary dissociation dynamics. As a result, the current branching ratios reflect more accurately the intrinsic unimolecular pathways, such as in cold molecular clouds, while the previous work captures a collision-influenced environment relevant to

Titan’s atmosphere (Y. L. Yung et al. 1984; E. H. Wilson & S. K. Atreya 2004; J. A. Stearns et al. 2006). Moreover, in the previous experimental work, the branching ratios were measured at a different photodissociation wavelength of 220 nm, corresponding to a lower energy intake, 544 kJ mol^{-1} , versus 620 kJ mol^{-1} for 193 nm. The microcanonical statistical RRKM product branching ratio computed for the internal energy of 544 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 and the increasing yield of C_2H_2 as the available internal energy falls. In fact, the RRKM 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 energies favoring the production of P8 and higher energies favoring P1 (Figure 7). Here, we considered the energy range corresponding to the lowest broad absorption band of vinylacetylene between 240 and 180 nm (A. Fahr & A. Nayak 1996). At the lowest energy, the main product is P8, $\text{H}_2\text{CC} + \text{C}_2\text{H}_2$, with the yield of 62%, followed by P1, $\text{H}_2\text{C}=\text{C}=\text{C}=\text{CH}\cdot + \text{H}$, 36%. Combined branching ratios of all other products are under 2%. When the available internal energy grows, the branching ratio of P8 steadily decreases to $\sim 14\%$ at the highest energy considered. The branching ratio of P1 increases with internal energy, reaching a maximum of $\sim 70\%$ at 649 kJ mol^{-1} (184 nm) and then slightly decreasing to $\sim 68\%$. The relative yield of P1 begins to exceed that of P8 at internal energies above 530 kJ mol^{-1} . Among other products, P2 and P3, *trans/cis*- $\text{CH}=\text{CH}-\text{C}\equiv\text{CH} + \text{H}$, provide increasing contributions at higher internal energies, reaching 7%–8% each at the highest energy considered. The calculated yield of the H_2 loss products P5 and P6 remains under 2% in the entire energy range. When the pressure effect is included in RRKM–ME calculations at 1 and 3 mbar, the agreement 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,

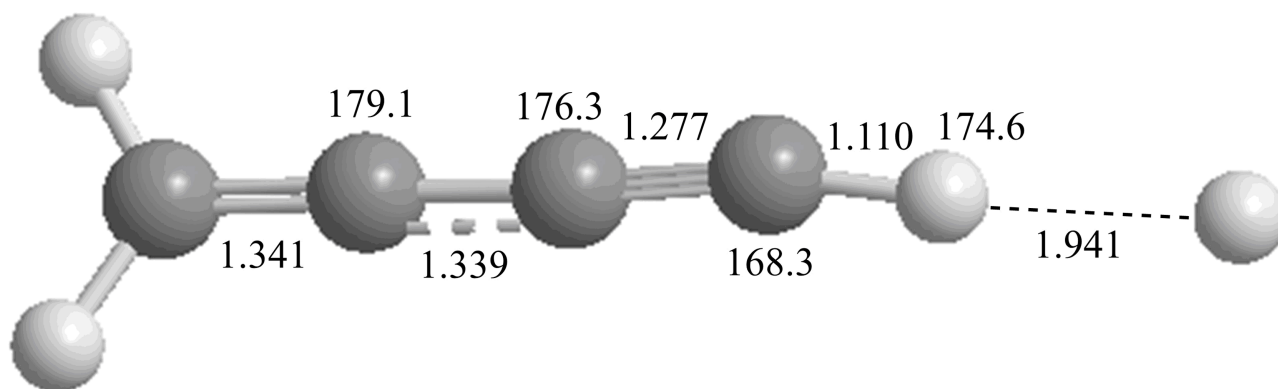


Figure 8. Optimized structure of a second-order saddle point for the H atom roaming pathway leading to P6. The distances are shown in angstroms and bond angles in degrees.

with the J. A. Stearns et al. (2006) experiment 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. At 1–3 mbar pressures, the branching ratio of P8 is higher than that of P1 at internal energies below 560 kJ mol^{-1} , and the situation is reversed at higher available energies. Overall, the comparison highlights that vinylacetylene photochemistry is strongly dependent on the excitation energy and, to a lesser 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} below the energy of P1. While a statistical treatment of the roaming mechanism based on a distinct TS is usually imprecise (S. J. Klippenstein et al. 2011), the inclusion of the $\text{VA} + h\nu \rightarrow \text{P6}$ roaming pathway in the RRKM calculations with the second, nonreactive imaginary frequency changed to its absolute value close to 100 cm^{-1} (Y. Zhao & D. G. 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 nonstatistical effects should be considered when modeling the UV photochemistry of vinylacetylene in astrophysical environments.

5. Astrophysical Implications

The present photodissociation study of vinylacetylene (C_4H_4) provides laboratory constraints on the energetically accessible primary photodissociation channels of vinylacetylene; however, the corresponding branching ratios under interstellar conditions may differ because the present 193 nm

excitation does not directly reproduce the cosmic-ray-induced UV radiation field of dense molecular clouds.

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 kJ mol^{-1} (J. A. Stearns et al. 2006; A. Landera et al. 2008). Their subsequent chemistry is more plausibly associated with reactions involving atoms and open-shell radical partners such as ethynyl (C_2H), vinyl (C_2H_3), and propargyl (C_3H_3), which are barrierless. Although isomer-resolved crossed molecular-beam studies remain limited, theoretical work indicates that dicarbon (C_2) reacts with C_4H_3 isomers to access C_6H_3 intermediates (A. Landera et al. 2008), while recent calculations demonstrate barrierless low-temperature reactions of 1-buten-3-yne-2-yl (C_4H_3) with the methylene amidogen ($\text{H}_2\text{CN}\cdot$) and *cis*-iminomethyl ($\text{HCNH}\cdot$) radical toward pyridine and the pyridinyl radical (Z. Yang et al. 2024a).

The molecular hydrogen loss channel yields C_4H_2 products detected at $m/z=50$. Our analysis supports the formation of the cumulene carbene butatrienylidene, $\text{H}_2\text{C}=\text{C}=\text{C}=\text{C}:$ (P6), rather than the thermodynamically more stable diacetylene isomer, $\text{H}-\text{C}\equiv\text{C}-\text{C}\equiv\text{C}-\text{H}$ (P5). This distinction is astrochemically important since both C_4H_2 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 (C_2), cyano (CN), and ethynyl (C_2H) radical, leading to molecular mass growth processes and the formation of the 2,4-pentadiynylidene radical (C_5H), the 1,3,5-hexatriynyl radical (C_6H), cyanodiacetylene (HC_5N), and triacetylene (HCCCCCCH) (F. Zhang et al. 2008; X. Gu et al. 2009; F. Zhang et al. 2009a, 2009b). 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 (CH_2)—the simplest representative of a carbene (K. L. Gannon et al. 2010a; K. L. Gannon et al. 2010b; D. Polino et al. 2013). Similar to vinylidene (CCH_2 , $X^1\text{A}_1$), singlet carbene undergoes facile addition to $\text{C}=\text{C}$ and $\text{C}\equiv\text{C}$ 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 C_4H_2 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 ($HC\equiv CH$, C_2H_2) together with vinylidene ($H_2C=C:$, CCH_2). The failure of any astronomical detection of vinylidene (CCH_2) 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 (H. 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} (S. Zou & J. M. 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 $\mu = 2.5D$ (M. K. Sharma et al. 2014). Thus, its nondetection 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. The present branching ratios therefore provide a benchmark at 193 nm, while wavelength-dependent measurements in the 90–165 nm region will be necessary to establish quantitative photodissociation branching fractions for dense-cloud astrochemical models.

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Conflict of interest

The authors declare no conflict of interest.

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