

Bottom-Up Formation of Antiaromatic Cyclobutadiene ($c\text{-C}_4\text{H}_4$) in Interstellar Ice Analogs

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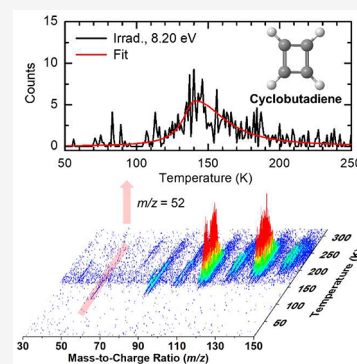


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ABSTRACT: Antiaromatic cyclobutadiene ($c\text{-C}_4\text{H}_4$) is the simplest prototype of $[n]$ -annulenes and a key reactive intermediate with significant ring strain, serving as the model compound for antiaromatic systems in organic chemistry. Here, we report the first bottom-up formation of cyclobutadiene in low-temperature acetylene (C_2H_2) ices exposed to energetic electrons. Cyclobutadiene was isolated and detected in the gas phase upon sublimation utilizing vacuum ultraviolet photoionization reflectron time-of-flight mass spectrometry along with ultraviolet photolysis studies. These findings advance our fundamental understanding of the exotic chemistry and preparation of highly strained antiaromatic cycles through non-equilibrium chemistry in interstellar environments, thus affording a possible route for the formation of highly strained molecules such as the hitherto elusive tetrahedrane (C_4H_4). Because acetylene is a major product of the photolysis and radiolysis of methane (CH_4) ice, an abundant component of interstellar ices, our results suggest that cyclobutadiene can likely be formed in methane-rich ices of cold molecular clouds.



Since the very first attempt to prepare antiaromatic cyclobutadiene [[4]annulene, $c\text{-C}_4\text{H}_4$ (**1**)], the simplest cyclic hydrocarbon bearing conjugated double bonds, by Kekulé more than 150 years ago (1872),¹ **1** has attracted considerable attention as a key reactive intermediate from the synthetic,^{2–7} physical,^{8–10} astrochemistry,¹¹ and theoretical chemistry communities.^{12–21} Historically, **1** was predicted to have a D_{4h} symmetric structure with 4π Hückel antiaromaticity in a square triplet ground state (3A_g).^{22,23} However, the Jahn–Teller distortion lowers the symmetry to a rectangular, D_{2h} symmetric molecule with a closed-shell singlet ground state (1A_g).^{8,16,21} Considering the significant ring strain and repulsion between the localized π electrons,²⁴ cyclobutadiene is an exceptionally reactive compound^{14,19} with a ring strain energy of 149 ± 12 kJ mol^{−1} and a high heat of formation of 428 ± 16 kJ mol^{−1}.⁶ In the early 1970s, Krantz et al.^{22,25} and Chapman et al.²⁶ provided spectral evidence for the formation of **1** in argon and nitrogen matrices at temperatures of 8–20 K through photoexcitation of 2-pyrone ($\text{C}_5\text{H}_4\text{O}_2$), which decomposes to **1** and carbon dioxide (CO_2). Subsequent work by Arnold et al. presented its ultraviolet–visible (UV–vis), Fourier transform infrared (FTIR), and Raman spectra in an argon matrix.⁴ As **1** can undergo photodecomposition to acetylene (C_2H_2)^{2,25} or dimerization to tricyclooctadiene (C_8H_8) upon warming of the matrices at temperatures of >35 K,²⁶ synthetic methods that prevent photodecomposition and dimerization such as kinetic trapping are critical factors in isolating **1**.²⁰ Upon the photolysis of trapped 2-pyrone, Cram et al. isolated **1** in the inner phase of a hemicarceplex and obtained its nuclear magnetic resonance (NMR) spectra at ordinary temperatures.³ Substituted cyclobutadienes such as

tetra-*tert*-butylcyclobutadiene [$\text{C}_{20}\text{H}_{36}$ (**3**)] were prepared with bulky substituents that prevent dimerization.^{27–30} Maier et al. synthesized a more stable cyclobutadiene bearing bulky trimethylsilyl [$-\text{Si}(\text{CH}_3)_3$ (TMS)] groups, tetrakis-(trimethylsilyl)cyclobutadiene [$\text{C}_{16}\text{H}_{36}\text{Si}_4$ (**5**)], which converts to tetrakis(trimethylsilyl)tetrahedrane [$\text{C}_{16}\text{H}_{36}\text{Si}_4$ (**6**)] after prolonged irradiation (Scheme 1).³¹ However, despite the top-down formation of **1** in matrix isolation, this molecule has not yet been isolated in its pure form through bottom-up formation.

Here, we report the first bottom-up formation of cyclobutadiene (**1**) in low-temperature (5 K) interstellar ice analogs, which is composed of acetylene (C_2H_2) ices exposed to energetic electrons, simulating secondary ionizations produced by the passage of galactic cosmic rays (GCRs). The simulated radiation doses used in the experiments are equivalent to exposure to GCRs for $(4 \pm 1) \times 10^7$ years inside a cold molecular cloud, the density of which blocks ultraviolet (UV) light from penetrating to its icy interior.³³ Utilizing vacuum ultraviolet (VUV) photoionization reflectron time-of-flight mass spectrometry (PI-ReTOF-MS) along with ultraviolet photolysis studies, **1** was isomer-selectively photoionized in the gas phase during temperature-programmed desorption (TPD)

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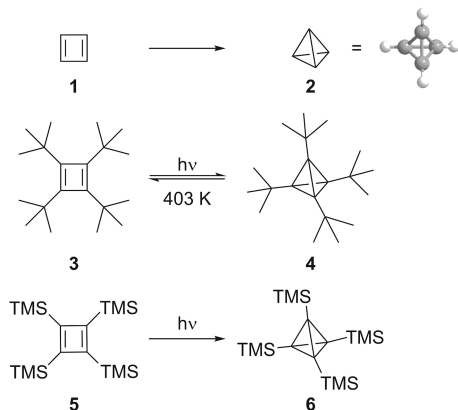
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Scheme 1. Possible Routes Leading to Tetrahedrane (2)³² and Substituted Tetrahedranes Bearing Bulky *tert*-Butyl [$-C(CH_3)_3$] Groups (4)²⁸ and Trimethylsilyl [$-Si(CH_3)_3$] Groups (6)³¹



of the processed ices based on computed adiabatic ionization energies (IEs) of distinct C_4H_4 isomers (Figure 1). Our findings advance our fundamental understanding of the exotic chemistry and preparation of highly strained rings and antiaromatic systems through non-equilibrium chemistry in low-temperature environments, thus affording a possible route for the formation of elusive molecules such as tetrahedrane **2** (Scheme 1).^{34,35} Acetylene is a major product of the photolysis and radiolysis of interstellar methane (CH_4) ices,³⁶ which has

been detected toward low-mass young stellar objects with an abundance up to 11% relative to water (H_2O).³⁷ Therefore, **1** can likely be formed in methane-rich ices in cold molecular clouds.

The infrared absorptions are dominated by the fundamentals and combination modes of acetylene (Figure S1 and Table S1). After irradiation, several new absorption features were observed.

Most prominently, the products include diacetylene (C_4H_2) at 3325 cm^{-1} (ν_4),³⁸ vinylacetylene (CH_2CHCCH , **7**) at 3284 cm^{-1} (ν_1), 2974 cm^{-1} ($\nu_6 + \nu_7$), 1599 cm^{-1} (ν_6), and 978 cm^{-1} (ν_{14}),^{38,39} ethylene (C_2H_4) at 3090 cm^{-1} (ν_9), 2974 cm^{-1} (ν_{11}), and 1435 cm^{-1} (ν_{12}),^{38,40,41} ethane (C_2H_6) at 2880 cm^{-1} (ν_5),³⁸ and cyclopropane ($c\text{-}C_3H_6$) at 1005 cm^{-1} (ν_{10}).⁴² In addition, absorption at 3033 cm^{-1} is assigned to benzene [C_6H_6 (ν_{18})] and absorption at 959 cm^{-1} can be linked to the out-of-plane aromatic CH deformations of (substituted) benzene.^{38,43,44} Absorptions at 3157 , 3090 , and 1005 cm^{-1} might be assigned to cyclobutadiene (**1**); these positions are close to previously measured absorptions of **1** in an argon matrix at 3140 , 3093 , and 989 cm^{-1} ,⁴ respectively, and also correlate well with scaled frequencies of **1** at 3146 cm^{-1} (ν_1), 3083 cm^{-1} (ν_{15}), and 1011 cm^{-1} (ν_{10}), respectively, calculated at the CCSD(T)=FULL/aug-cc-pVTZ level of theory.⁴⁵ However, vibrations of C_4H_4 isomers such as **1** may overlap with those of the many hydrocarbons evidently formed; hence, only a tentative assignment can be obtained utilizing FTIR

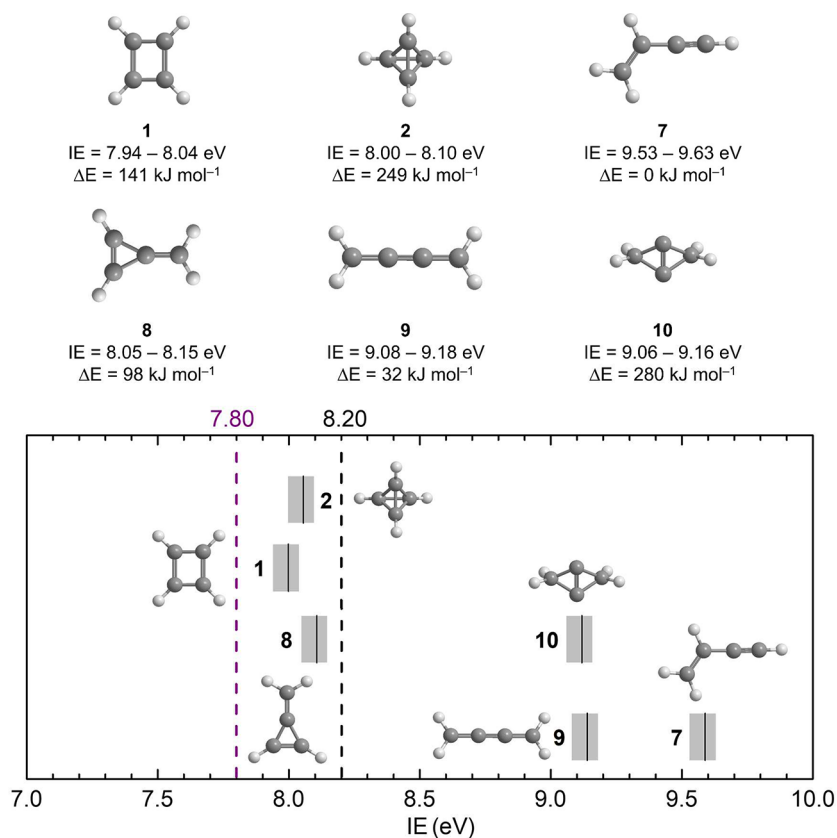


Figure 1. Structures and adiabatic ionization energies (IEs) of closed-shell C_4H_4 isomers. IEs corrected for the Stark effect and relative energies (ΔE) are calculated at the CCSD(T)/CBS//B3LYP/cc-pVTZ level of theory (Table S2). The bottom figure compiles the computed IEs (black solid lines) and their error ranges (gray area). VUV photons (dashed lines) at 8.20 and 7.80 eV were used to ionize subliming molecules in the gas phase.

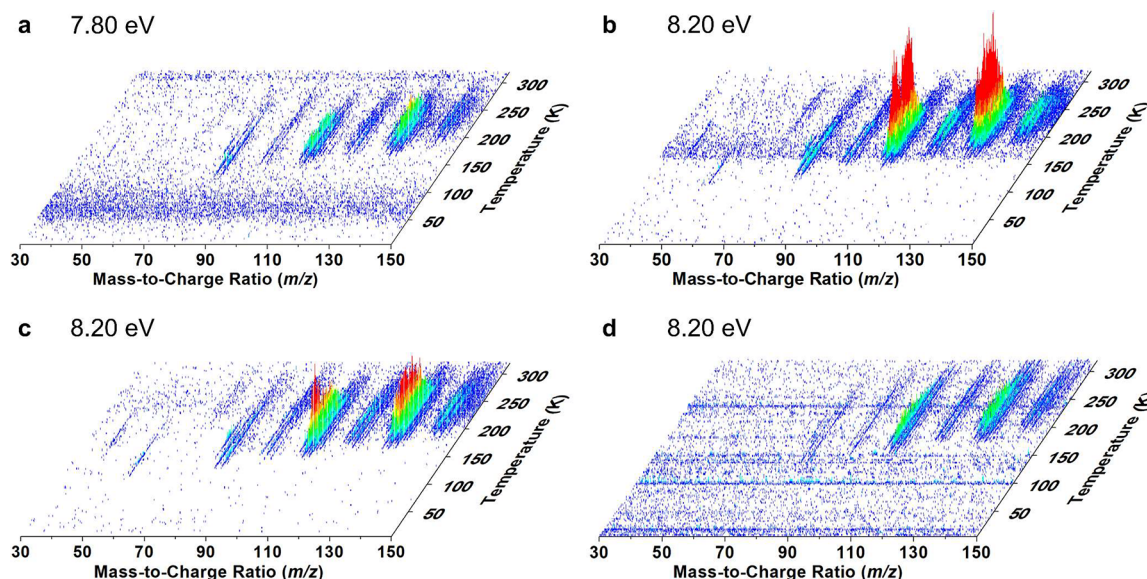


Figure 2. PI-ReTOF-MS data as a function of temperature and mass-to-charge ratios (m/z) during TPD of irradiated acetylene (C_2H_2) ices. Data were recorded at both (a) 7.80 eV and (b) 8.20 eV for irradiated C_2H_2 ices and at 8.20 eV for the C_2H_2 ices photolyzed with photon wavelengths of (c) 299 nm and (d) 221 nm after irradiation.

alone, highlighting the need for a more selective detection method for identifying C_4H_4 isomers.^{46,47}

This requirement is accomplished by PI-ReTOF-MS studies in identifying specific C_4H_4 isomers in the gas phase upon sublimation, in conjunction with UV photolysis in the icy matrix. By tuning the photon energies above or below the IE of a particular isomer, PI-ReTOF-MS allows the *isomer-specific* identification of gas-phase molecules via soft photoionization based on their ionization energies and temperature-dependent sublimation profiles.⁴⁶ Considering the computed IEs of the C_4H_4 isomers (Figure 1), photons at 8.20 eV can ionize only isomers 1 (IE = 7.94–8.04 eV), 2 (IE = 8.00–8.10 eV), and 8 (IE = 8.05–8.15 eV). Figure 2 compiles the PI-ReTOF mass spectra of the desorbed molecules from the irradiated acetylene ices. The TPD profiles of the target ions at $m/z = 52$ ($C_4H_4^+$) are of particular interest. The ion signal at $m/z = 52$ contains hydrogen and carbon atoms, so it can only be assigned to the molecular formula C_4H_4 . At 8.20 eV, the averaged signal from three independent experiments at $m/z = 52$ ($C_4H_4^+$) exhibits a sublimation peak at 141 K in irradiated acetylene ices (Figure 3a). Decreasing the photon energy to 7.80 eV eliminates all signals for the ion at $m/z = 52$. Therefore, the assignment of this ion signal is limited to isomers 1, 2, and/or 8. In addition, a blank experiment was carried out under identical conditions but without electron irradiation of the ices; no ion signal at $m/z = 52$ was observed (Figure 3a), verifying that this sublimation event is the result of chemical processing of the acetylene ice by radiolysis.

Because the IEs of 1, 2, and 8 partially overlap, we performed additional isomer-selective ultraviolet photolysis experiments. The ultraviolet spectra of these isomers were calculated at the TD-B3LYP/cc-pVTZ level of theory (Figure S2). Previously measured UV spectra of top-down matrix-isolated 1 revealed that no UV–vis band maximum above 230 nm was observed;⁴ this result agrees well with our simulated spectra. For the UV photolysis experiments, we first irradiated acetylene ices with energetic electrons to prepare C_4H_4 isomers, then subjected them to UV photolysis at either 221 or 299 nm to selectively excite and thereby destroy 1 or 8,

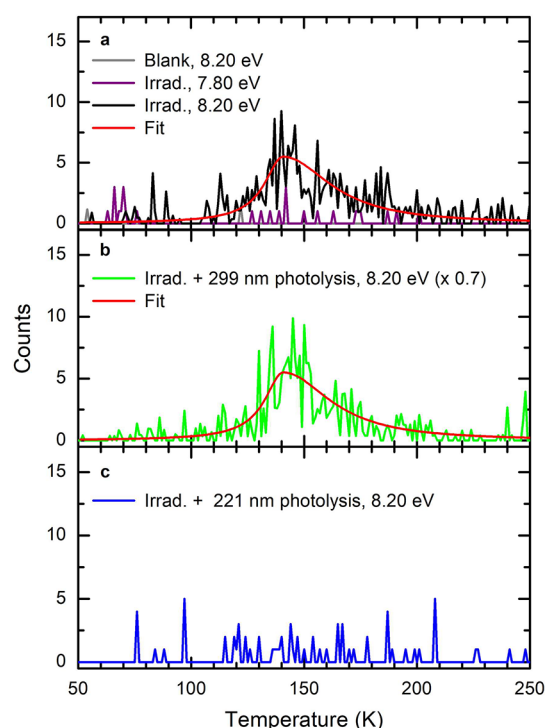


Figure 3. Ion signals at $m/z = 52$ during TPD of irradiated acetylene (C_2H_2) ices shown as a function of temperature. (a) TPD profiles recorded at 8.20 eV for both unirradiated (blank) and irradiated ices as well as at 7.80 eV for irradiated ice. For the photolysis experiments, TPD profiles were recorded at 8.20 eV for C_2H_2 ices photolyzed at (b) 299 nm or (c) 221 nm after irradiation. The red lines in panels a and b indicate the same peak fits using a split Pearson VII function.

respectively. In the case of the “electron plus 299 nm photolysis” experiment at 8.20 eV, the averaged signal from three independent measurements at $m/z = 52$ ($C_4H_4^+$) shows that the sublimation event peaking at 141 K remains (Figure 3b). This TPD profile matches well with the result of the earlier “electron only” experiment, ruling out the presence of

isomer **8**. However, the “electron plus 221 nm photolysis” experiment at 8.20 eV, which only photolyzes and/or isomerizes **1**, eliminates the peak at 141 K; no other sublimation events were observed (Figure 3c), indicating that the ion signal at $m/z = 52$ ($C_4H_4^+$) must be assigned to isomer **1**. Overall, the aforementioned studies utilizing PI-ReTOF-MS along with UV photolysis reveal the formation of **1**; no evidence of isomers **2** and **8** could be provided.

Having provided compelling evidence of the preparation of cyclobutadiene (**1**) in low-temperature acetylene ices, we turned our attention to its possible formation mechanisms. The first feasible pathway involves two acetylene molecules. Previously, theory work by Mebel et al. revealed that two ground state acetylene molecules can react to form an *anti*-oriented intermediate ($H\dot{C}CHCH\dot{C}H$) through a barrier of 140 kJ mol^{-1} ; subsequent ring closure forms **1** by rotation around the central C–C bond via a barrier of 39 kJ mol^{-1} .³² Overall, the reaction to **1** from two acetylene molecules is predicted to be exoergic by 24 kJ mol^{-1} at the G2M-(RCC,MP2)//B3LYP/6-311G(d,p) level of theory.³² It is worth noting that the formation of **1** may involve the excited state photochemistry of low-lying electronic states of acetylene, which can be accessed by the kinetic energy of the impinging electrons during the irradiation. Recent studies have shown that excited states of acetylene play key roles in the formation of cyclopropenone ($c\text{-}C_3H_2O$) and benzene (C_6H_6) in interstellar acetylene-containing analog ices.^{44,48,49} The excited acetylene molecule may react with the nearby acetylene molecule to form **1** via a concerted mechanism in low-temperature ices. The second pathway for the formation of **1** may involve vinylacetylene (**7**), which undergoes isomerization to form **1** via a barrier of 203 kJ mol^{-1} and a reaction energy of 140 kJ mol^{-1} .³² Previous experiments on the exposure of low-temperature acetylene ices to energetic electrons³⁸ and UV photons⁴⁴ revealed the formation of **7**. This is consistent with our FTIR results in which absorptions of **7** at 3284 cm^{-1} (ν_1), 1599 cm^{-1} (ν_6), and 978 cm^{-1} (ν_{14}) were observed. The high reaction barriers in these pathways require non-equilibrium reactions by imparting excess energy from the energetic electrons into the system.

To conclude, we present the first bottom-up formation of cyclobutadiene (**1**) in low-temperature acetylene (C_2H_2) ices exposed to energetic electrons, which simulates secondary electrons produced by the passage of GCRs. Utilizing PI-ReTOF-MS along with UV photolysis studies, **1** was isolated and detected in the gas phase during TPD. Considering the average velocity of 239 m s^{-1} of **1** subliming at 141 K and the distance of $2.0 \pm 0.5\text{ mm}$ between the ice surface and photoionization laser region, the lifetime of neutral molecule **1** in the gas phase exceeds $8 \pm 2\text{ }\mu\text{s}$ to survive the flight time from the sublimation to the photoionization region. These findings not only advance our fundamental understanding of the exotic chemistry and preparation of highly strained cyclobutadienes through non-equilibrium chemistry but also provide a potentially viable pathway for producing tetrahydrocarbons such as the hitherto elusive tetrahydrodrane **2**, which represents one of the most attractive challenges in organic chemistry that has not yet been accomplished.^{34,35,50,51} As acetylene has been detected in the gas phase in circumstellar envelope and molecular clouds^{52,53} and represents a major product of the photolysis and radiolysis of interstellar methane (CH_4) ices,³⁶ our results indicate that **1** can likely be formed within interstellar ices from methane-rich regions in deep

space. Future laboratory experiments to identify **1** in processed methane ices can be carried out. Once formed, **1** can be released into the gas phase in the hot-core stage, serving as a promising candidate for astronomical searches via telescopes, such as the James Webb Space Telescope (JWST).

METHODS

Experimental Section. All experiments were performed in a stainless steel chamber at pressures of a few 10^{-11} Torr utilizing hydrocarbon-free turbomolecular pumps backed by a dry scroll pump.^{36,54} A closed-cycle helium cryostat (Sumitomo Heavy Industries, RDK415E) interfaced with a polished silver substrate that was cooled to low temperatures of $5.3 \pm 0.2\text{ K}$. During the experiments, the substrate can be moved horizontally and vertically via a rotatable flange (Thermionics Vacuum Products, RNN-600/FA/MCO) and an adjustable bellows (McAllister, BLT106). Traces of acetone in acetylene (C_2H_2 , 99.9%, Airgas) were removed using a dry ice/ethanol slush bath.⁵⁵ During the deposition, acetylene gas was introduced into the main chamber through a glass capillary array at a pressure of 4.0×10^{-8} Torr and deposited onto the cold substrate at 5 K. The thickness of acetylene ice was monitored *in situ* via laser interferometry utilizing a He–Ne laser (632.8 nm).⁵⁶ By accounting for the refractive index of 1.34 ± 0.02 ⁵⁷ and the density of $0.76 \pm 0.08\text{ g cm}^{-3}$ for acetylene ice,^{38,57} we calculated the ice thickness to be $830 \pm 50\text{ nm}$ (Table S3). After deposition, ices were irradiated with 5 keV electrons (Specs EQ 22-35) at a current of $106 \pm 2\text{ nA}$ for 60 min, corresponding to a dose of $9.1 \pm 1.4\text{ eV molecule}^{-1}$ and replicating lifetimes of molecular clouds of $(4 \pm 1) \times 10^7$ years.³³ The ice thickness ($830 \pm 50\text{ nm}$) is much larger than the average penetration depth of $370 \pm 40\text{ nm}$ for the electrons based on the Monte Carlo simulations performed in CASINO;⁵⁸ 99% of the electron energy was absorbed in the upper 600 nm layers of acetylene ice, thus excluding the interactions between the substrate and electrons. The infrared spectra of acetylene ices were monitored before, during, and after the irradiation utilizing an FTIR spectrometer (Nicolet 6700, 4 cm^{-1} spectral resolution).

After the irradiation, the ices were heated to 320 K at a rate of 0.5 K min^{-1} . For successive photolysis experiments, the irradiated ices were photolyzed by 299 nm photons at $20 \pm 2\text{ mW}$ for 2 h or by 221 nm photons at $8 \pm 3\text{ mW}$ for 10 h and then heated to 320 K. The 299 nm laser light was produced via the frequency doubling of 598 nm light that was generated by a dye laser (Sirah, Cobra-Stretch) using the dye rhodamine 610. This dye laser was pumped by the second harmonic of a pulsed (30 Hz) Nd:YAG laser (Spectra-Physics, PRO-270-30). The 221 nm laser light was produced via the frequency doubling of 442 nm light that was generated by a dye laser using the dye coumarin 440. During TPD, the subliming molecules were analyzed utilizing PI-ReTOF-MS. The 8.20 and 7.80 eV photons were generated by resonant four-wave mixing processes using xenon gas as a nonlinear medium (Table S4). In particular, the third harmonic of a pulsed Nd:YAG laser pumped a dye laser (Sirah, Cobra-Stretch) using coumarin 503 to produce light at a wavelength of 249.628 nm (ω_1) via a double frequency of 499.256 nm light. To generate 8.20 or 7.80 eV light, a second harmonic (532 nm) from another Nd:YAG laser (Spectra-Physics, Pro 250-30) pumped a dye laser using LDS 722 dye or pyromethene 597 dye to obtain 715.207 nm (ω_2) or 581.119 nm (ω_2) light, respectively. After being separated from other wavelengths through a lithium

fluoride (LiF) lens in off-axis geometry, the VUV light passed 2.0 ± 0.5 mm above the substrate and ionized the subliming molecules in the gas phase. The ions were mass analyzed with a reflectron time-of-flight mass spectrometer (Jordan TOF Products, Inc.). The ion signals were amplified by a preamplifier (Ortec 9305) and analyzed according to their arrival by a multichannel scaler (FAST ComTec, MCS6A). The accumulation time is 2 min (3600 sweeps) for each recorded mass spectra.

Computational Section. All computations of the C_4H_4 isomers were performed with Gaussian 16, revision C.01.⁵⁹ The density functional theory (DFT) B3LYP functional^{60–62} using the Dunning correlation consistent split valence basis set cc-pVTZ⁶³ was utilized for geometry optimizations and frequency computations. We calculated the frequencies of all stationary geometries, and no imaginary frequencies for minima were found. On the basis of these geometries, the corresponding frozen-core coupled cluster^{64–67} CCSD(T)/cc-pVTZ, and CCSD(T)/cc-pVQZ single-point energies were computed using the built-in extrapolation routine with ORCA 5.0.3.⁶⁸ With B3LYP/cc-pVTZ zero-point vibrational energy (ZPVE) corrections, these energies were extrapolated to complete basis set limit⁶⁹ CCSD(T)/CBS. To determine the IEs, the ZPVE-corrected energy difference between the ionic and neutral species with similar conformations was used. All ultraviolet spectra were computed at the TD-B3LYP/cc-pVTZ level. The IE error analysis includes corrections for the thermal and Stark effect by -0.03 eV (Table S2).⁷⁰ The computed Cartesian coordinates and vibrational frequencies for the structures of the C_4H_4 isomers are listed in Table S5.

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.jpcllett.3c03524>.

FTIR spectra and assignments, simulated ultraviolet (UV) spectra of C_4H_4 isomers **1**, **2**, and **8**, error analysis of IEs, experimental conditions, VUV parameters, and Cartesian coordinates and harmonic frequencies for C_4H_4 structures (PDF)

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Notes

The authors declare no competing financial interest.

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