

A Combined Experimental and Computational Study on the Ionization Energies of the Cyclic and Linear C₃H Isomers

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For the first time, two hydrogen-deficient hydrocarbon radicals are generated *in situ* via laser ablation of graphite and seeding the ablated species in acetylene gas, which acts as a carrier and reactant simultaneously. By recording photoionization efficiency curves (PIE) and simulating the experimental spectrum with computed Franck–Condon (FC) factors, we can reproduce the general pattern of the PIE curve of $m/z = 37$. We recover ionization ener-

gies of 9.15 eV and 9.76 eV for the linear and cyclic isomers, respectively. Our combined experimental and theoretical studies provide an unprecedented, versatile pathway to investigate the ionization energies of even more complex hydrocarbon radicals *in situ*, which are difficult to prepare by classical synthesis, in future experiments.

1. Introduction

During the last decade, both the linear and cyclic tricarbon hydride isomers, *l*-C₃H ($X^2\Pi_{g^-}$) and *c*-C₃H (X^2B_2 ; Figure 1), have received considerable attention due to their role as a benchmark

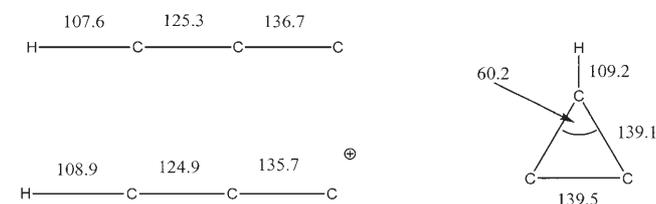


Figure 1. Linear (C_{3v}) and cyclic (C_{2v}) C₃H isomers together with the cation of the singly ionized, linear C₃H structure. Bond lengths are given in picometers and bond angles in degrees.

system in understanding the chemical evolution of the interstellar medium.^[1,2] General interest in these radicals also comes from combustion^[3] and plasma^[4] chemical processes, where these ubiquitous carbon-rich radicals have been implicated in a number of processes. Both isomers are typical representatives of hydrogen-deficient hydrocarbon radicals, which serve as precursor molecules to form polycyclic aromatic hydrocarbons (PAHs) in cold molecular clouds and circumstellar envelopes of dying carbon stars.^[5] The electronic spectrum of the C₃H radical has been measured recently.^[6] Although a formation route to tricarbon hydride radicals has been well-established to proceed via the reaction of ground-state carbon atoms with acetylene, C₂H₂,^[1] the ionization energies (IEs) of the radicals are still elusive. For such systems, the adiabatic ionization energy—a measure of the energy required to remove an electron from a molecule in its rotational, vibrational, and electron-

ic ground state, thus forming a cation in its lowest electronic, vibrational, and rotational level—is one of the most relevant thermochemical measurements. It dictates electron-transfer processes in biological systems and the direction of ion–molecule reactions in planetary atmospheres as well as in interstellar space.^[7] Ionization energies combined with thermochemical cycles can also be utilized to extract enthalpies of formation of hydrocarbon radicals—crucial data which in turn yield information on the outcome of a chemical reaction.^[8] But is it possible to produce significant concentrations of the cyclic and linear C₃H isomers in the laboratory to extract their ionization energies?

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Herein, we present a combined experimental and theoretical study on the adiabatic ionization energies of the cyclic and linear C₃H isomers. By synthesizing both radicals in situ by laser ablation of a graphite rod plus reaction of the ablated carbon atoms with acetylene, we produce an intense, supersonic beam containing *l*-C₃H ($X^2\Pi_\Omega$) and *c*-C₃H (X^2B_2). Subjecting the neutral molecules of this beam to vacuum ultraviolet (VUV) photoionization, we record the mass spectra of the ionized molecules at various photon energies. This method presents a versatile and elegant route to form unstable radicals, which are difficult to synthesize by classical organic chemistry, allowing us to determine their ionization energies efficiently.

Experimental Section

The experiments were carried out at the Chemical Dynamics Beamline of the Advanced Light Source at Lawrence Berkeley National Laboratory by generating both C₃H isomers in situ with a laser ablation source.^[9] Briefly, 50 mJ of the second harmonic (532 nm) of a Neodymium-Yttrium-Aluminum-Garnet (Nd:YAG) laser were focused to a 1 mm spot onto a rotating graphite rod (99.995%, Aldrich). The ablated species, predominantly atomic carbon together with dicarbon (C₂) and tricarbon molecules (C₃), were seeded in acetylene gas released by a Proch-Trickl pulsed valve at a stagnation pressure of about 560 torr. The acetylene carrier gas also acted as a reactant to synthesize the C₃H radicals in situ. Ions produced in the ablation process were deflected out of the molecular beam prior to the skimmer by a pair of deflection plates. Tunable VUV light from the Advanced Light Source crossed the neutral molecular beam downstream of the ablation center in the extraction region of a Wiley–McLaren time-of-flight (TOF) mass spectrometer. By measuring the arrival time of the ions, we obtained their mass-to-charge (m/z) ratios. The ionized neutral molecules (photo ions) were extracted with a high voltage pulse, collected by a micro-channel plate detector, and recorded in the TOF mode utilizing a multi channel scaler. Finally, photoionization efficiency (PIE) curves reporting the ion counts versus the VUV energy were measured by integrating the C₃H⁺ signal at $m/z=37$ and normalizing it to the photon flux.^[10] TOF spectra were recorded for the photoionization energy between 8.8 eV and 10.2 eV in steps of 0.1 eV. These PIE curves can be utilized to extract the adiabatic ionization energies of radicals.^[11]

2. Results and Discussion

Figure 2 depicts the mass spectrum of those hydrocarbon species detected in the supersonic beam with a photon energy of 11.0 eV. The mass spectrum is relatively simple. The species can be attributed to C₃H⁺ ($m/z=37$), C₄H⁺ ($m/z=49$), C₄H₂⁺ ($m/z=50$), C₆H⁺ ($m/z=73$), and C₆H₂⁺ ($m/z=74$). Here, neutral C₃H is likely formed via the reaction of atomic carbon with acetylene, as demonstrated in earlier crossed molecular beams experiments.^[1] C₆H₂ could be a radical–radical recombination product of two C₃H species stabilized by a third-body collision; the corresponding C₆H radical may be formed via unimolecular decomposition of those internally excited C₆H₂ molecules that cannot eliminate their excess energy before decomposition. Note that the ablation beam also contains dicarbon molecules. These species were found to react with acetylene molecules to produce C₄H₂ intermediates, which can be stabilized in the

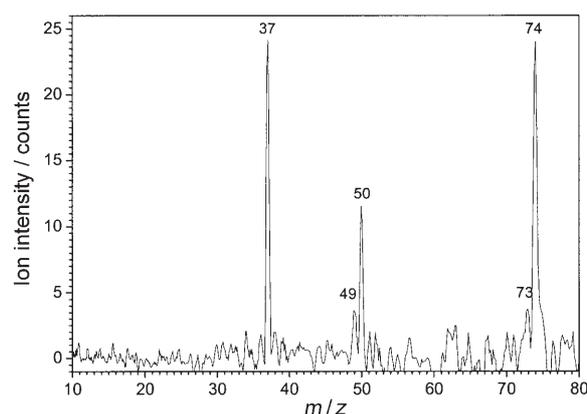


Figure 2. Corrected mass spectrum of the ionized C₃H ($m/z=37$), C₄H ($m/z=49$), C₄H₂ ($m/z=50$), C₆H ($m/z=73$), and C₆H₂ ($m/z=74$) species generated during the laser ablation of graphite (Nd:YAG laser; 532 nm; 100 Hz; 50 mJ mm⁻²) with acetylene as a seeding and reactant gas. The spectrum was obtained by ionizing the neutral molecules at a photon energy of 11.0 eV.

ablation source by forming C₄H radicals.^[12] These suggestions can explain the mass spectrum qualitatively.

In the following discussion, we focus on the C₃H⁺ ions to extract the adiabatic ionization energies of the cyclic and linear C₃H isomers. Figure 3 shows the photoionization efficiency (PIE) curve of the tricarbon hydride cation. In the absence of complications caused by autoionization, for instance, the basic PIE curve (the photoionization spectrum) arises from direct ionization appearing as a series of step-like features,^[8] which are proportional to the Franck–Condon factor.^[13,14] A similar geometry of the neutral molecule and the cation is expected to

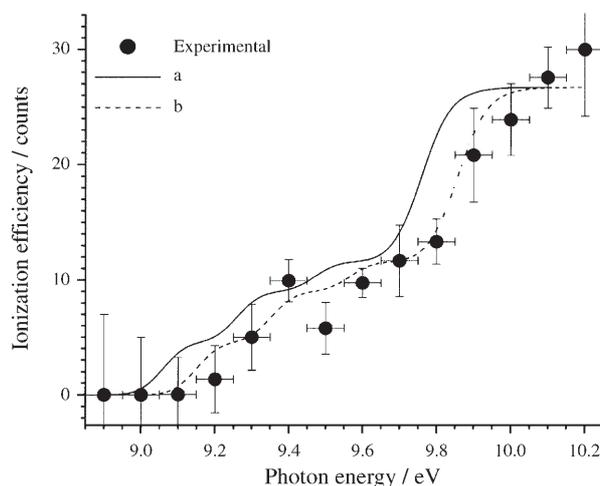


Figure 3. Efficiency curve of $m/z=37$ (C₃H⁺) depicting the photon energy of the ionizing light versus the ionization efficiency (PIE). The ordinate error bars are an average of seven scans; abscissa error bars correspond to the photon flux accuracy of the vacuum ultraviolet light. Overlaid are the theoretically predicted PIE curves based on calculated Franck–Condon (FC) factors, the temperature of the molecular beam (580 K), and the probable neutral populations of the linear and cyclic isomers. a) Unconstrained fit using data directly from the calculations with 1:1 *l*-C₃H/*c*-C₃H population. b) Constrained fit using a scaling factor of 1.01 for the calculated vibrational frequencies of the linear and cyclic isomer with a 1:1 *l*-C₃H/*c*-C₃H population.

result in a narrow spectrum, whereas a substantial change in geometry will be reflected in a broader, less abrupt slope.^[15] In reaction dynamics, it is often powerful to combine the experimental data with theoretical calculations. Here, we performed a Franck–Condon (FC) analysis in reduced dimensionality of the ionization thresholds of linear $I\text{-C}_3\text{H}$ and cyclic $c\text{-C}_3\text{H}$ using MP2-based potential energy surfaces and CCSD(T)/aug-cc-pVTZ calculations of electronic energies at selected geometries. Details of the methods employed are available in ref. [16]. The potential energy surfaces are fits to tens of thousands of MP2/aug-cc-pVTZ energies for the neutral and cationic systems. These fits properly describe the invariance of the potential with respect to all permutations of the three carbon atoms. Several key vibrational modes in this ionization process are located at saddle points, and so a numerical approach to obtain the FC factors for those modes was done. Based on these calculations, we obtain a threshold ionization energy for $I\text{-C}_3\text{H}$ of 9.06 eV, thus making it the strongest FC factor for the 0–0 transition. For the ionization of $c\text{-C}_3\text{H}$, the analysis is more involved, because $c\text{-C}_3\text{H}^+$ is a saddle point roughly 6000 cm^{-1} above the $I\text{-C}_3\text{H}^+$ minimum. Due to the significant change in the ground-state geometry of neutral $c\text{-C}_3\text{H}$ and its cationic form, the 0–0 transition is not longer the dominant one, and the largest FC factor is computed for an excited vibrational state of C_3H^+ . However, there are significant FC factors for lower-energy vibrational states of the cyclic form, which can be characterized by excitation to highly excited $I\text{-C}_3\text{H}^+$ states. From this analysis we conclude that the threshold ionization of $c\text{-C}_3\text{H}$ is at 9.61 eV, albeit very weak. Based on the accuracy of the electronic structure methods used and the reduced-dimensionality treatment of the FC calculations, we estimate these calculated values to be accurate to within $\pm 0.05\text{ eV}$. All values are corrected for the zero-point vibrational energy.

Based on these results, we can first interpret the PIE curve qualitatively. The first step onset can be seen between 9.1 eV and 9.2 eV. By intersection of the photon energy axis with a linear fit, we obtain an onset of $9.15 \pm 0.05\text{ eV}$ corresponding (within error limits) to the calculated threshold ionization energy for the linear isomer. Up to 9.4 eV, the PIE graph has a relatively steep slope, suggesting that the inherent geometry change from the neutral molecule to the C_3H^+ cation is minor, which agrees with the calculations. Both $I\text{-C}_3\text{H}$ and $I\text{-C}_3\text{H}^+$ are linear and belong to the $C_{\infty v}$ point group; the C–C bond distances change only slightly by 0.4–1.3 pm. However, as the photon energy rises to 10.2 eV, the curve becomes less steep, indicating a significant change in geometry from the neutral molecule to the ion. In addition, there is a dip in the signal at 9.5 eV, which could arise from electronically excited states of the cation being populated, as has been seen clearly in the case of C_3 .^[9] The theoretical calculations suggest significant geometry changes from the neutral $c\text{-C}_3\text{H}$ to the $I\text{-C}_3\text{H}^+$ cation, that is, a switch from a cyclic to a linear structure. This could be rationalized with a less steep slope of the PIE curve at higher photon energies. While the correspondence of the calculated and measured ionization energy for $I\text{-C}_3\text{H}$ is excellent, it is not trivial to reach the same agreement for $c\text{-C}_3\text{H}$. However, a judicious combination of the calculated FC factors and

measured PIE curve might shed some light on the determination of ionization energy for $c\text{-C}_3\text{H}$.

The PIE curve of the C_3H^+ channel can be simulated by using a calculated FC factor as a fitting function to determine the adiabatic IEs of the C_3H isomers.^[17,18] Gaussian distributions were utilized to account for the homogeneous line broadening. To fit the experimental PIE spectrum with calculated FC factors of the cyclic and the linear isomers, the cumulative (inverse) Gaussian distributions are utilized. In this simulation, the relative abundances of the two isomers have been varied in addition to the internal temperature of the molecules in the beam (50 K–1500 K). In Figure 3, curve a, an unconstrained fit at 580 K with a 1:1 population of the two isomers shows that while the shape of the experimental PIE is reproduced, a quantitative match between the calculation and experiment is poor. By constraining the fits in energy space by scaling the calculated vibrational frequencies by a factor of 1.01 for both isomers, a standard scaling factor utilized at this level,^[16] a much better correspondence is reached between the experiment and simulated PIEs (Figure 3, curve b). Using the values from Figure 3, curve b, provides adiabatic ionization energies of 9.15 eV for $I\text{-C}_3\text{H}$ and 9.76 eV for $c\text{-C}_3\text{H}$. Two sources of error in this determination could arise from inaccurate FC factors or nonequilibrium distributions of the relative populations of the internal energy of the two isomers. Future experiments with energy selection, as done in coincidence experiments, should allow for an unambiguous determination for the ionization energy for the cyclic isomer. Note that by probing argon–acetylene plasmas using threshold ionization mass spectrometry, Benedikt et al. estimated the ionization energy of a C_3H isomer to be $9.7 \pm 0.2\text{ eV}$.^[4] However, this early study did not assign the structure of the tricarbon hydride isomer formed. Based on the present investigations, we can conclude that Benedikt et al. observed the cyclic C_3H isomer.

3. Conclusions

In summary, this study suggests the formation of both the cyclic and the linear C_3H radicals in the supersonic beam. For the first time, two hydrogen-deficient hydrocarbon radicals are generated in situ via laser ablation of graphite and seeding the ablated species in acetylene gas, which acts as a carrier and reactant simultaneously. By recording photoionization efficiency curves and simulating the experimental spectrum with computed FC factors, we can reproduce the general pattern of the PIE curve of $m/z=37$, with the exception of the dip at 9.5 eV. The experimental and computational evidence supports the assignment of ionization energies of 9.15 eV and 9.76 eV for the linear and cyclic isomers, respectively. Our combined experimental and theoretical studies provide an unprecedented, versatile pathway for future investigation of the ionization energies of even more complex hydrocarbon radicals in situ, which are difficult to prepare by classical synthesis.

Note Added in Proof: Casavecchia^[19] estimated the ionization potential of the linear and cyclic isomers to be 9.7 eV and 11.2 eV, respectively. These results agree qualitatively with the present ones for the order of the ionizations potentials, how-

ever, they disagree significantly with the values we report herein.

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