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Direct IR Absorption Spectra of Propargyl Cation Isolated in Solid Argon

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The direct infrared (IR) absorption spectra of propargyl cations were recorded. These cations were generated via the electron bombardment of a propyne/Ar matrix sample during matrix deposition. Secondary photolysis with selected ultraviolet (UV) light was used for grouping the observed bands of various products. The band assignment of the propargyl cation in solid Ar was performed according by referring to the previous infrared photodissociation (IRPD) and velocity-map imaging photoelectron (VMI-PE) data, and via theoretical predictions of the anharmonic vibrational wavenumbers, band intensities, and deuterium-substituted isotopic ratios. Almost all the IR active bands with an observable intensity were recorded and the ν_{11} mode was reported for the first time.

$C_3H_3^+$ ions are important in many diverse applications and fields, such as flame and combustion processes, and planetary and interstellar chemistry^{1–5}. The two most stable isomers of $C_3H_3^+$, cyclopropenyl cations ($c-C_3H_3^+$) and propargyl cations ($H_2C_3H^+$), have received much attention in the past decades. Both are commonly observed fragments in the combustion of hydrocarbons and are proposed as reactants in the synthesis of cumulenyl and cyclic C_3H_2 in the interstellar medium through ion–molecule reactions^{6,7}. They have also been detected in the tail of Halley's comet⁸. In addition, because these cations and their neutral counterparts are the smallest π -conjugated hydrocarbon systems, their molecular structures, reactivities, and spectroscopic parameters have been extensively investigated both theoretically and experimentally^{9–15}.

Theoretical works have indicated that the energy of planar $H_2C_3H^+$ (C_{2v}) is ~ 28 kcal mol⁻¹ greater than that of cyclic planar $c-C_3H_3^+$ (D_{3h})^{16,17}. The vibrational fundamentals of both cations complexed with several ligands recorded via infrared photodissociation (IRPD) have been reported, and with the complexation with Ar, there are obvious shifts of the C–H stretching bands, but the C–C stretches are unaffected^{11,18,19}. The infrared (IR) spectra of both cations were also recorded in neon matrices at 5 K, but only the $C\equiv C$ stretching mode (ν_3) of $H_2C_3H^+$ and the C–H asymmetric stretching mode (ν_4) of $c-C_3H_3^+$ were observed²⁰. Recently, Gao *et al.* combined the vacuum ultraviolet (VUV) lasers and velocity-map imaging (VMI) techniques to obtain the vibrationally resolved photoelectron spectrum (PE) of gaseous H_2C_3H radicals and determined the $C\equiv C$ stretching (ν_3), C–C stretching (ν_5), and out-of-plane bending (ν_7) modes of the ground-state $H_2C_3H^+$ ²¹. A discrepancy was observed in the band position of the C–C stretching mode by 102 cm⁻¹ when the IRPD and VUV-VMI-PE results were compared. Later, Botschwina *et al.*¹⁷, performed explicitly correlated coupled cluster calculations for $C_3H_3^+$ species and confirmed the assignment of the C–C stretching mode of H_2CCCH^+ determined by Gao *et al.* They also suggested that the assignment of the asymmetric CH stretching mode (ν_4) of $c-C_3H_3^+$ -Ar at 3182 cm⁻¹ reported by Ricks *et al.*¹⁸ should be the combination band ($\nu_3 + \nu_5$) of $H_2C_3H^+$ -Ar. In addition, the $A^1A_1 \leftarrow X^1A_1$ electronic transition of H_2CCCH^+ in the neon matrix, and that tagged with Ne and N₂ were measured in the spectral region of 230–270 nm²². In contrast, the electronic transitions of $c-C_3H_3^+$ are expected to appear at less than 200 nm, but no experimental values for the same have been reported in any conditions²⁰.

Although the spectroscopic information of $H_2C_3H^+$ has been obtained by various experimental techniques, there is lack of clarity with regard to its vibrational structures. The IRPD method could not provide the true (relative) IR intensities of species, and laser frequencies are typically useful above 1000 cm⁻¹ which limit the probing spectral region¹⁸. The VUV-VMI-PE method can be used to obtain information about the low-frequency vibrational modes, but the selection rule of photoelectron spectroscopy differs from that of IR absorption spectroscopy²¹. We employed a “clean” method of matrix isolation for investigating the IR spectra of cations of interest using electron bombardment of an Ar matrix containing a small proportion of neutral counterparts during

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Species	Observed band positions/cm ⁻¹	Ref.	385 nm	160 nm
HC ₃ H ^a	547.6, 3266.2 (3262.9) ^b	25	↑ ^c	— ^c
H ₃ C ₃ H ⁺	583.2 (581.1), 1243.0	24	↑	↓
CH ₃	619.9	33	↑	↓
H ₂ C ₃ H ^a	686.5, 1061.8, 1935.4, 3028.3, 3310.0	25	↑	↓
HCCCH ^a	737.2, 3285.7 (3287.9), 3293.3	34	↑	—
C ₆ H ₄	740.7 (743.7), 1008.7, 1040.9,	35	↑	↓
H ₂ C ₃ H ₂ ^{+a}	791.4, 874.4, 1307.3, 2929.0, 3020.8	25	↓	↓
H ₂ CC(H)CH ₂	800.9, 1179.4, 3018.9	36	↓	↑
H ₂ C ₃ H ₂ ^a	837.7, 996.2, 1390.6, 1955.3, 1998.4, 3000.1	24	↑	↓
Ar ₂ H ^{+a}	903.4	24	↓	↓
C ₄ H ₆ ^a	910.8, 1016.8, 1382.9	37	—	↓
H ₂ C ₃	999.2 (1003.0), 1446.8 (1448.6)	38	↓	—
HC ₃ ^a	1824.8 (1832.6), 3238.3	38	↓	↑
H ₂ C ₃ H ^{-a}	1856.4	25	↓	—
C _n	1913.8, 1941.8, 1945.8		↑	—
C ₃	2039.2 (2034.8)	25	↓	↑
H ₂ C ₃ H ⁺	606.8, 1105.2, 1140.6, 1433.2, 2075.2 (multiplet), 3000.6, 3063.4, 3195.3	TW	↓	↓

Table 1. Observed species generated from bombardment of H₃C₃H/Ar matrix sample with 200-eV and 2000-eV electrons and their photolytic behaviors. ^aSpecies also observed in experiments on electron bombardment with 200-eV electrons. ^bBands in minor matrix sites. ^cSymbols indicate band intensity increase (↑), decrease (↓), and no change (—) upon photolysis.

matrix deposition. We demonstrated the advantages of this method with ethylene and allene cations^{23,24}. Our method can be used to obtain IR spectra with a high resolution, the true IR intensities, and a wider spectral coverage of cations of interest.

In our previous works, we produced allene cations (H₂C₃H₂⁺) in solid Ar via electron bombardment (200 eV) of an allene/Ar matrix sample during matrix deposition²⁴. Subsequently, we irradiated the matrix sample with 365-nm light, which resulted in isomerization from allene cations to propyne cations (H₃C₃H⁺) in the solid Ar. We further characterized the IR signatures of the allene and propyne cations, and the IR absorption spectrum of the propyne cations was reported for the first time. Forney *et al.* used excess excited Ne atoms to enable collisions with allene or propyne, followed by co-deposition at 5 K; they observed similar products including H₂C₃H₂⁺, H₂C₃H⁻, HC₃H, and C₃, in both cases²⁵. They concluded that propyne cations might predominantly isomerize to the more stable allene cations in the experiments²⁵. In this work, we subjected propyne/Ar matrix samples to electron bombardment at 200 or 2000 eV, followed by deposition at 8 K. H₂C₃H₂⁺ cations were found to be dominant for low-energy bombardment, similar to the case in previous allene experiments. This suggests that the loss of H atoms from the two precursors might be inhibited due to the rapid excess energy quenching after bombardment, while several H-degradation species including H₂C₃H⁺ were formed in the high-energy bombardment experiment.

Results and Discussion

IR absorption spectra of matrix samples in natural isotopic abundance. We subjected the propyne/Ar matrix sample to bombardment with 200-eV electrons and recorded the corresponding IR spectra, as shown in Fig. S1 in supplementary information (SI). The products and observed absorptions are summarized in Table 1. Compared to the previous studies on the electron bombardment of allene²⁴, the observed products are similar and no propyne cations were observed. The allene neutrals and cations were the main products, indicating that the fragmentations of the precursor were less prominent upon low-energy bombardment. The IR spectra of both the neutral and cationic allene and propyne species have been well studied, and therefore we increased the electron energy to 2000 eV to increase the efficiency of the production of fragments from the precursor. Partial IR spectra of the electron-bombarded propyne/Ar matrix sample are shown in Fig. 1(A) and the observed bands and assignments are summarized in Table 1.

Besides the species observed in the 200-eV experiments, more types of C₃H_n species were formed in observable concentrations. For example, another C₃H₂ form, H₂C₃, was observed with IR bands at 999.2 and 1446.8 cm⁻¹ corresponding to the H₂CC OPLA and CH₂ scissoring modes, respectively. The absorptions of HC₃ and C₃ were also observed to be moderately intense. This indicates that increasing the bombardment energy of electrons is useful for promoting the removal of H atoms from the precursors. In addition, we observed larger species, such as C₆H₄ (benzyne) and C₄H₆ (1,3-butadiene), which may be a result of the recombination reactions of the small fragments. We also confirmed the formation of allyl radicals (H₂CCHCH₂) based on the IR bands at 800.9, 1179.4, and 3018.9 cm⁻¹. The formation of the allyl radicals may be due to the H-addition reaction of the allene neutrals.

Despite the reported information of the IR spectra of the above-mentioned species in solid matrices, which are easily assigned in our study, there are several unknown bands. Therefore, we performed further experiments on the photolysis of the matrix sample with 385- and 160-nm light to classify the unknown bands. The photolytic behaviors of the observed products are summarized in Table 1. Figure 1(B) shows the IR difference spectrum of

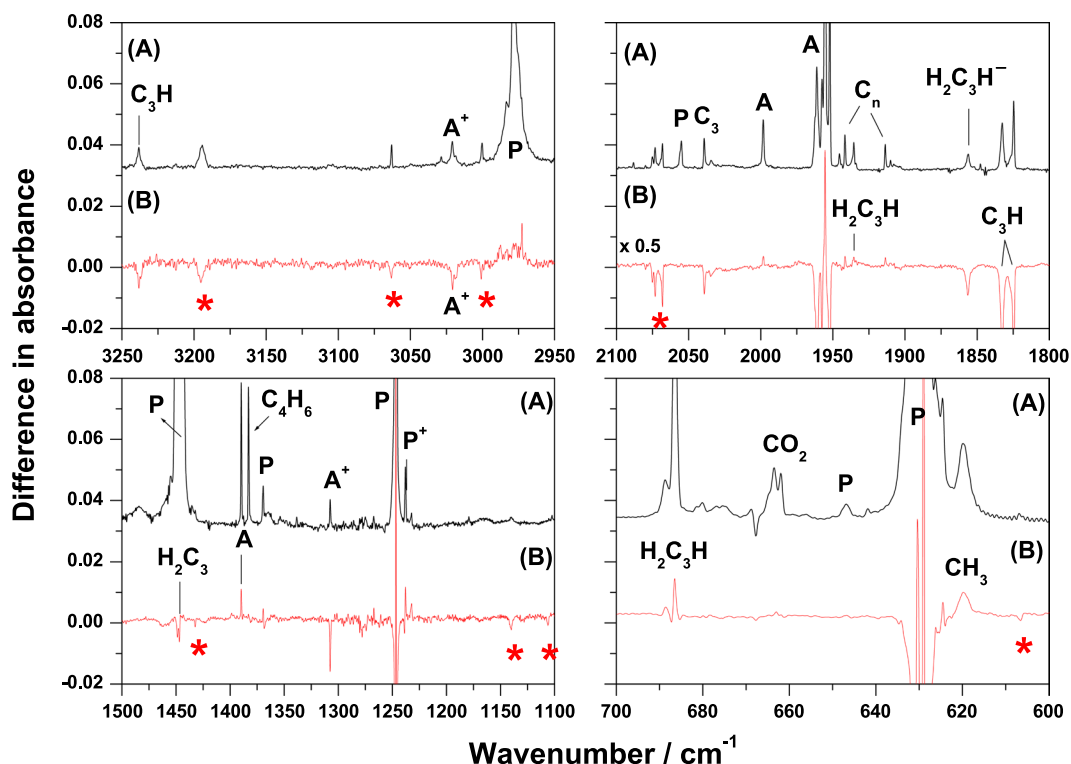


Figure 1. (A) Partial IR spectrum of a propyne/Ar (1/500) matrix sample bombarded with 2000-eV electrons at 8 K (absorption multiplies 0.2) and (B) IR difference spectrum of sample in (A) upon photolysis with 385-nm light for 1 h. A: $\text{H}_2\text{C}_3\text{H}_2$, P: $\text{H}_3\text{C}_3\text{H}$, A^+ : $\text{H}_2\text{C}_3\text{H}_2^+$, P^+ : $\text{H}_3\text{C}_3\text{H}^+$, *: $\text{H}_2\text{C}_3\text{H}^+$, C_n : carbon clusters.

the electron-bombarded matrix sample irradiated with 385-nm light, in which a positive value indicates a species produced after irradiation, whereas a negative value indicates the destruction of a species. The IR difference spectrum of the matrix sample further irradiated with 160-nm light is shown in Fig. S2 in SI. A set of unknown bands at 606.8, 1105.2, 1140.6, 1433.2, 2075.2 (multiplet), 3000.6, 3063.4, and 3195.3 cm^{-1} , indicated by asterisks (*) in Fig. 1(B), showed a decrease in intensity upon photolysis at both wavelengths. The positions of this set of bands correlate well with those of most bands of gaseous $\text{H}_2\text{C}_3\text{H}^+$ determined via IRPD measurements¹⁸ and with the only reported IR band at 2080 cm^{-1} for $\text{H}_2\text{C}_3\text{H}^+$ in solid neon²⁰, as shown in Table 2. Furthermore, the observed photolytic behavior of the * bands is similar to that of $\text{H}_2\text{C}_3\text{H}_2^+$ and Ar_2H^+ cations suggesting it might be a charged species. The decrease in the cationic species upon irradiation with 385-nm light has been demonstrated in many previous studies^{23,24,26} and this may be because the UV light caused the slowly diffusing trapped electrons to recombine with the cations. The increase in the $\text{H}_3\text{C}_3\text{H}^+$ cations upon irradiation with 385-nm light in this study is due to the isomerization of $\text{H}_2\text{C}_3\text{H}_2^+$.²⁴ In contrast, the intensities of the other unknown bands at 1913.8, 1941.8, and 1945.8 cm^{-1} increased upon irradiation with 385-nm light, but showed no change with further irradiation of 160-nm light. In addition, there was no correlation to each other at the photolysis stage. These bands are the result of the absorption of typical multiple CC stretches and may correspond to carbon-chain species. Deuterium-isotopic experiments and quantum-chemical calculations were also performed to obtain information for assigning these bands.

IR absorption spectra of deuterium-substituted samples. To confirm the preliminary assignments of the unknown bands, the fully deuterium-substituted propyne ($\text{D}_3\text{C}_3\text{D}$) was used to determine the isotopic shifts of the corresponding bands. Experiments on the electron bombardment of $\text{D}_3\text{C}_3\text{D}/\text{Ar}$ (1/500) were performed. The representative IR difference spectrum in the range of 850–1300 and 1900–2500 cm^{-1} for irradiation at 385 nm is shown in Fig. 2. The lines observed for $\text{D}_2\text{C}_3\text{D}^+$ and $\text{H}_2\text{C}_3\text{H}^+$ are listed in Table 3 with the vibrational wavenumbers and isotopic ratios. Based on the observed photolytic behavior, relative band intensity, and expected D-isotopic shift ratios of the vibrational modes, the set of unknown bands at 1105.2, 1140.6, 1433.2, 2075.2 (multiplet), 3000.6, 3063.4, and 3195.3 cm^{-1} were found to shift to 891.3, 938.7, 1191.7, 1942.1 (multiplet), 2201.0, 2301.9, and 2487.3 cm^{-1} , respectively, as indicated by the asterisk (*) in Fig. 2. The band corresponding to that at 606.8 cm^{-1} observed in natural abundance was not observed in the D-isotopic experiment. It may have shifted to the spectral region beyond detection.

In contrast, there was no shift in the unassigned bands at 1913.8, 1941.8, and 1945.8 cm^{-1} in the natural isotopic abundance sample during the D-isotopic substitution, suggesting that the carriers of these bands contain no H atoms; rather, they may be neutral and/or ionic carbon clusters (C_n).

Mode	Sym	B3LYP/aug-cc-pVTZ	CCSD(T*)-F12a/VTZ-F12	IRPD	PE	Matrix
ν_1	A ₁	3226.4 (115) ^a	3236 (112) ^a	3238		3195.3 (28) ^b
ν_2	A ₁	3007.1 (30)	2990 (29)	3004		3000.6 (10)
ν_3	A ₁	2088.1 (370)	2080 (371)	2077	2086	2075.2 ^c (100)
ν_4	A ₁	1458.3 (9)	1446 (12)	1445		1433.2 (6)
ν_5	A ₁	1137.2 (25)	1123 (19)	1222	1120	1140.6 (13)
ν_6	B ₁	1112.4 (10)	1099	1111		1105.2 (6)
ν_7	B ₁	904.4 (5)	872		858	
ν_8	B ₁	279.3 (25)	264			
ν_9	B ₂	3043.0 (45)	3080	3093		3063.4 (22)
ν_{10}	B ₂	1012.4 (1)	1017			
ν_{11}	B ₂	625.7 (58)	615			606.8 (15)
ν_{12}	B ₃	331.2 (15)	298			
Ref		This work	¹⁷	¹⁸	²¹	This work

Table 2. Comparison of experimental and predicted anharmonic vibrational wavenumbers of propargyl cations. Predicted IR intensities are listed in parentheses. ^aThe unit of the calculated IR band intensity shown in the parentheses is km mol⁻¹. ^bThe relative band intensities of the observed IR bands of H₂CCCH⁺ are shown in the parentheses. ^cThis band was reported at 2080 cm⁻¹ for solid Ne²⁰.

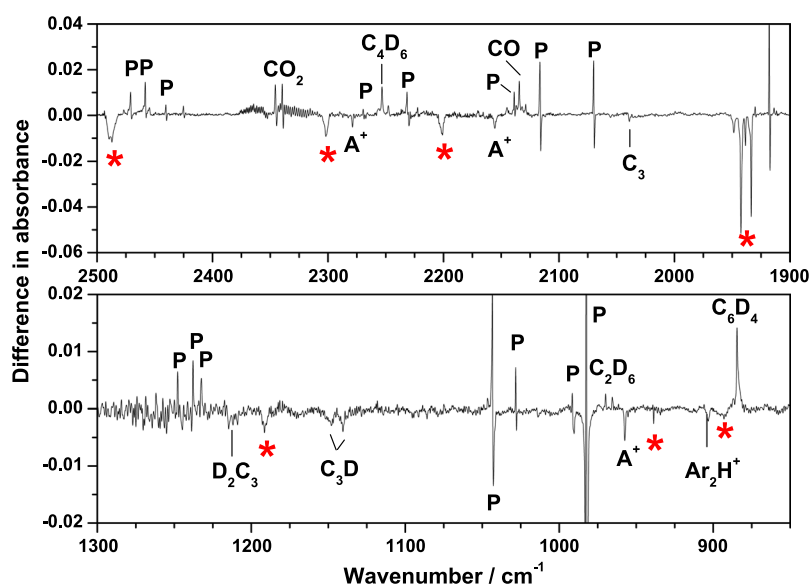


Figure 2. Partial IR spectrum of electron-bombarded deuterium-substituted D₃C₃D/Ar (1/500) matrix sample upon photolysis with 385-nm light at 8 K. P: D₃C₃D, A⁺: D₂C₃D₂⁺, and *: D₂C₃D⁺.

Quantum chemical calculations and band assignments. We performed quantum-chemical calculations with the B3LYP/aug-cc-pVTZ basis set to determine the stable structure of H₂C₃H⁺ (C_{2v}). The structural parameters for the propargyl cation are shown in Fig. S3. Information about the mode symmetry, vibrational motion, anharmonic vibrational frequencies, and IR intensities of the propargyl cation is summarized in Table 2 and Fig. S4, along with the values in the literature for comparison. Compared to the anharmonic vibrational wavenumbers of H₂C₃H⁺ predicted using CCSD(T*)-F12a¹⁷, the deviation is less than 3.5% for all vibrational modes, except for the low vibrational frequency mode for the CCC bending (ν_{12}). Our calculated band intensities are also consistent with the high-level theoretical work¹⁷.

Compared to our experimental observations, almost all the features predicted with an observable IR intensity in the probed spectral region were observed. For example, the C-H stretching modes predicted at 3226.4, 3007.1, and 3043.0 cm⁻¹ with a moderate intensity were observed at 3195.3, 3000.6, and 3063.4 cm⁻¹, respectively. The most intense mode of the C≡C stretch predicted at 2088.1 cm⁻¹ fitted well with the strong absorption observed at 2075.2 cm⁻¹ (multiplet). The other weak absorption bands observed at 1433.2, 1140.6, 1105.2, and 606.8 cm⁻¹ were also consistent with the predictions in terms of both the band positions and band intensities. Table 3 lists the vibrational wavenumbers and isotopic ratios predicted using the B3LYP/aug-cc-pVTZ level of theory along with the experimental observations. The observed deuterium isotopic ratios for D₂C₃D⁺ agreed with the theoretically predicted values with the largest deviation of only ~0.53% for the ν_6 mode. The findings of the deuterium isotopic experiments clearly support the previous assignments of the * bands to the propargyl cation.

Mode	Line position/cm ⁻¹		Isotopic ratio ^a		
	H ₂ C ₃ H ⁺	D ₂ C ₃ D ⁺	Prediction ^b	Ne matrix	Ar matrix
ν_1	3195.3	2487.3	0.7768		0.7784
ν_2	3000.6	2201.0	0.7304		0.7335
ν_3	2075.2	1942.1	0.9352	0.9399	0.9368
ν_4	1433.2	1191.7	0.8327		0.8315
ν_5	1140.6	938.7	0.8315		0.8330
ν_6	1105.2	891.3	0.8012		0.8065
ν_9	3063.4	2301.9	0.7458		0.7514
ν_{11}	606.8	—	0.7765		—
Ref	This work	This work	This work	²⁰	This work

Table 3. Comparison of D-isotopic ratios of experimental and theoretical vibrational wavenumbers of propargyl cations. ^aThe ratio of the wavenumber of the deuterium isotopic species to that of H₂C₃H⁺. ^bTheoretical values predicted using B3LYP/aug-cc-pVTZ.

There was a discrepancy between the IRPD and VMI-PE results of the vibrational wavenumbers of the ν_5 mode of the propargyl cation by 102 cm⁻¹^{18,21}. In our study, the absorption was determined to be at 1140.6 cm⁻¹ for the ν_5 mode, close to the VMI-PE result²¹. Furthermore, the CCH bending (ν_{11}) mode of the propargyl cation was determined for the first time. Although the cyclopropenyl cation is more stable than the propargyl cation, we did not observe any bands correlated to the absorption of the cyclopropenyl cation. This may be due to the following reasons: (i) the linear precursor, H₃C₃H, was used to generate the C₃H₃⁺ species, and (ii) H₂C₃H⁺ was formed and subsequently trapped in the solid Ar, which may have inhibited further isomerization.

Conclusion

Propargyl cations were generated from bombardment of a mixture of propyne and Ar with 2000-eV electrons during deposition at 8 K. The lines of the propargyl cation were diminished via irradiation of the matrix with UV light at 385 and 160 nm. The assignment of vibrational bands was based on a comparison with results from previous reports and anharmonic vibrational wavenumbers, IR intensities, and deuterium-substituted isotopic ratios predicted for the propargyl cation. This study confirmed the assignment of the ν_5 mode at 1140.6 cm⁻¹ and recorded the IR absorption of the ν_{11} mode for the first time. The “true” experimental relative IR intensities of the observed vibrational modes of the cation were also determined.

Experimental and Theoretical Methods

The experimental setup has been described previously^{27,28}. The IR absorption spectra covering the spectral range of 500–4000 cm⁻¹ were recorded with an interferometric spectrometer (Bruker v80) equipped with a KBr beam splitter and a Hg–Cd–Te detector cooled to 77 K. Typically, 400 scans at a resolution of 0.5 cm⁻¹ were recorded at each stage of the experiment.

The cations were produced via the electron bombardment of a gaseous Ar sample containing a small proportion of propyne during the deposition stage. A 200- or 2000-eV electron beam at a current of 0.3 mA was generated with an electron gun (Kimball Physics, Model EFG-7). A gaseous mixture of H₃CCCH/Ar (1/500) was deposited over a period of 4 h at a flow rate of 5–8 mmol h⁻¹. Experiments with a deuterium-substituted sample, D₃CCCD/Ar (1/500), were conducted under the same conditions. Photolysis experiments were performed with synchrotron radiation at BL03 of NSRRC (~5 mW at 160 nm), and with a light-emitting diode (bandwidth ~10 nm, 350 mW at 385 nm). Ar (99.9999%, Scott Specialty Gases), H₃CCCH (99.5%, Aldrich), and D₃CCCD (deuterium ~99%, Aldrich) were used without further purification, except for a freeze–pump–thaw procedure at 77 K.

The energy, equilibrium structure, anharmonic vibrational wavenumbers, and IR intensities of the propargyl cation were calculated using the Gaussian 09 program²⁹ at the B3LYP/aug-cc-pVTZ level of theory^{30–32}.

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Author Contributions

H.C.C., M.Y.L., P.Z.W. and T.P.H. performed the experiments and all members discussed the results. Y.J.W. designed the project, performed the data analysis and wrote the manuscript.

Additional Information

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