Infrared Spectroscopy of Isomers of $C_3H_4^+$ in Superfluid Helium Droplets

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Abstract

Superfluid helium nanodroplets are unique nano-matrices for the isolation and study of transient molecular species, such as radicals, carbenes, and ions. In this work, isomers of $C_3H_4^+$ were produced upon electron ionization of propyne and allene molecules and interrogated via infrared spectroscopy inside He nanodroplet matrices. It was found that the spectrum of $C_3H_4^+$ has at least three distinct groups of bands. The relative intensities of the bands depend on the precursor employed and its pickup pressure, which indicates the presence of at least three different isomers. Two isomers were identified as allene and propyne radical cations. The third isomer, which has several new bands in the range of 3100-3200 cm^{-1}, may be the elusive vinylmethylene $H_2C=CH-CH^+$ radical cation. The observed bands for the allene and propyne cations are in good agreement with the results of density functional theory calculations. However, there is only moderate agreement between the new bands and the theoretically calculated vinylmethylene spectrum, which indicates more work is necessary to unambiguously assign it.

Introduction

C_3H_4 is the smallest alkyne to show structural isomers. The isomers of C_3H_4 are allene, propyne, and cyclopropene. Allene and propyne are considered to be precursors for the formation of polyaromatic hydrocarbons (PAHs) in the interstellar medium.[1] The Infrared Space Observatory (ISO) reported the infrared bands of allene in the 7-30 μm range in Titan's atmosphere.[2] Photoionization efficiency spectra of combustion products show isomerization of allene and propyne in flames.[3] Similar to its neutral parent molecules, the $C_3H_4^+$ radical cation has several isomers which are comparatively less explored.[4-6] The experimental observation of $C_3H_4^+$ cations goes back to ion-molecule reaction studies performed by Harrison and Myher via mass spectrometery.[7] Upon ionization, allene changes its symmetry from D_{2d} to D_2.[4] Similarly, propyne, which is in the C_{3V} point group, attains C_S symmetry when an electron is removed from its highest occupied molecular orbital (HOMO).[5] Quantum chemical calculations show that the allene cation, $H_2CCCH_2^+$, is the most stable isomer of $C_3H_4^+$ and is followed by the propyne cation, $HCCCH_3^+$ which lies higher in energy by ~15 kcal/mol.[4-6] In addition, calculations predict two other structures; the vinylmethylene cation $H_2C{=}CH{-}CH^+$ and the cyclic c-$C_3H_4^+$ cation which have energies of 22.4 and 21.6 kcal/mol, respectively.[6] The isomerization and decomposition pathways for $C_3H_4^+$ were studied in detail by *ab initio* calculations.[6] The $C_3H_4^+$ cations were also studied via photoelectron spectroscopy of allene and propyne molecules.[8-12] Additionally, the rovibrational spectrum of H_3CCCH^+ cation was obtained in pulse field ionization photoelectron spectroscopic experiments by Xing et al..[13]

The products of dissociative ionization of allene and propyne molecules were studied in Refs.[11, 14, 15] The threshold photoelectron–photoion coincidence (TPEPICO) studies on propyne and allene yielded the threshold energies for the formation of different fragments, such as $C_3H_3^+$,

$C_3H_2^+$, and C_3H^+.[14, 15] The similarity of the appearance potentials of the fragments[14, 15] led to the conclusion that the formation of propyne and allene ions proceeds through a common potential energy surface before ion fragmentation, which may include the vinylmethylene cation H_2C=CH-CH^+ and cyclic c-$C_3H_4^+$ cations.[5, 6] The infrared spectra of $H_2CCCH_2^+$, as well as for its anionic counterpart $H_2CCCH_2^-$, were first obtained in a solid neon matrix by Forney et al..[16] More recently, the infrared spectra of propyne and allene cations were reported in solid argon matrices.[17] However, the other higher energy isomers that may play an important role in the isomerization, the vinylmethylene and cyclic c-$C_3H_4^+$ cations, were not observed experimentally.[6]

In this work, we report an infrared spectroscopic study of $C_3H_4^+$ cations which were produced and isolated within helium droplets. Helium remains liquid down to absolute zero temperature and becomes superfluid below 2 K. Helium atoms interact weakly with encapsulated species. Additionally, helium atoms have a high ionization potential which makes them an exceptionally soft medium for the matrix-assisted isolation spectroscopy of ions.[18-24] The low temperature of the droplets in vacuum, 0.4 K, and their high thermal conductivity could enable the stabilization of the embedded ions into some unusual structures corresponding to local minima on the potential energy surface.[25] In this work, the helium nanodroplets were doped with allene and propyne molecules. The droplets containing a single precursor molecule or small clusters are ionized by electron impact, leading to the formation of a variety of $C_3H_y^+$ cations (y = 1-5).

To assign the bands, we performed geometry optimization and harmonic frequency calculations for the propyne, allene, vinylmethylene and the cyclic $C_3H_4^+$ cations at the B3PW91/aug-cc-pVTZ level of theory using Gaussian 16.[26-28] The observed spectra for allene cations and propyne cations are in good agreement with the calculations in this work as well as with previous experimental and computational studies.[13, 17] In addition, we identified a set of new bands in the infrared spectrum, which could not be unambiguously assigned to any of the calculated isomers of $C_3H_4^+$.

Experimental

The experimental setup for the mass-selected infrared spectroscopy of ions in helium droplets is described elsewhere.[29] Helium droplets are produced by the expansion of helium gas at a stagnation pressure of 22 bar and a temperature of 23 K (maintained by an RDK cryocooler) into a UHV source chamber through a pulsed nozzle (General valve series 99) of 1 mm in diameter. The droplets pass through a 2 mm diameter skimmer to enter a 44 cm long pickup chamber filled with allene or propyne precursors. Further downstream the droplets are ionized by electron impact and traverse through an RF octupole ion guide - collision cell filled with helium gas at $\sim 10^{-5}$ mbar. The collisions with helium atoms in the cell reduce the droplets' size, which increases the sensitivity of the laser experiment. The droplets interact with a pulsed laser beam while they pass through an ion region of the quadrupole mass spectrometer (QMS). When the laser frequency is in resonance with the vibrational transitions of the ions, the absorption leads to the evaporation of the entire droplet and release of the bare molecular ions. The liberated ions pass through the benders and are mass-selected by the QMS and detected by a Channeltron electron multiplier. The signal is amplified by the SR270 amplifier and recorded by a SR250 boxcar integrator with a gate width of ~5 µs. In this work, we used a mid-infrared OPO/OPA system from LaserVision with a nominal spectral linewidth of 1 cm^{-1}, pulse width of ~7 ns, and a 20 Hz repetition rate. The system is equipped with KTP and KTA nonlinear crystals which limit the lowest frequency practical to this work to about 2500 cm^{-1}. The system delivered 5-8 mJ pulses as measured at the laser cabinet.

The laser system is calibrated by recording the ν_3 rovibrational band of methane in an optoacoustic cell.

Computational Details

We employed Gaussian 16 [26] software to facilitate computations that complemented our experimental results. Density functional theory calculations were carried out using the B3PW91 method (Becke's three-parameter hybrid exchange functional and an exchange functional of Perdew and Wang as the correlation functional), [27, 28, 30] for optimizing geometries and predicting harmonic vibrational frequencies. Dunning's diffused correlation-consistent polarized valence triplet-zeta basis set, enhanced with s, p, d, and f functions (aug-cc-pVTZ) served as the basis set for all the atoms.[27] The optimized geometries were verified to be either minima or saddle points by confirming the number of imaginary frequencies (zero for minima and one for first order saddle point). In order to account for the harmonic approximation, a scaling factor (0.965) was applied to the computed vibrational frequencies at the B3PW91/aug-cc-pVTZ level of theory.[31]

Results

1. Allene precursor:

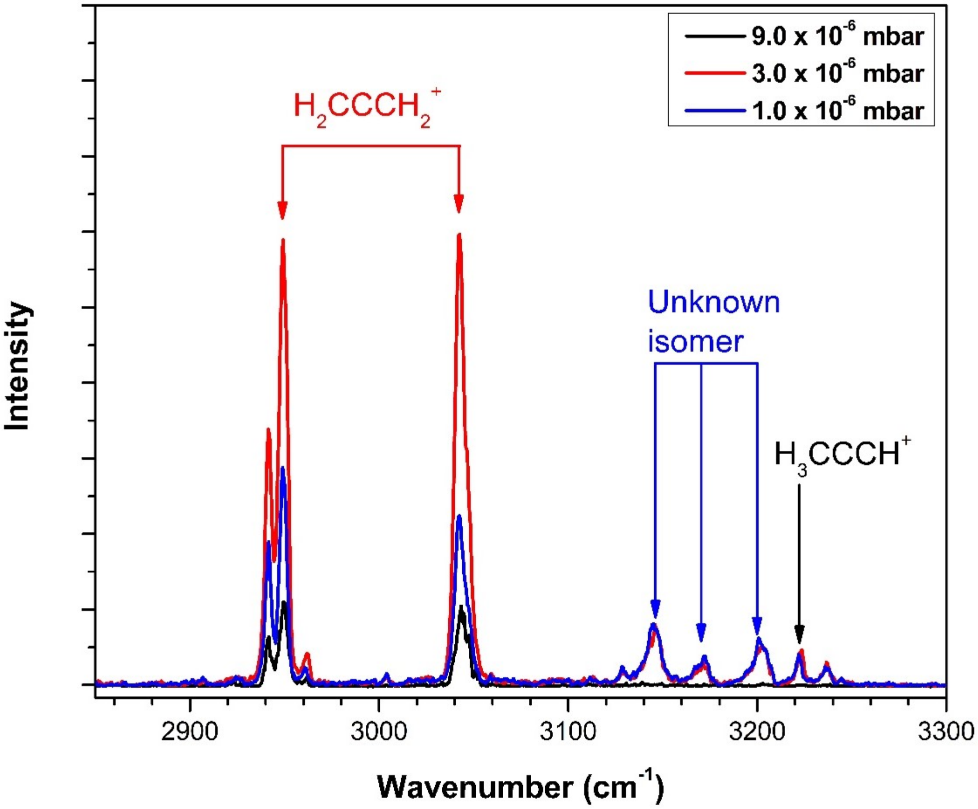

Figure 1: The infrared spectra of $C_3H_4^+$ cations (m/z = 40 channel) obtained from the ionization of helium droplets doped with allene at pickup pressure 1.0×10^{-6} mbar (blue), 3.0×10^{-6} mbar (red), and 9.0×10^{-6} mbar (black)

Before measuring the infrared spectra, mass spectra were recorded in the standard operation mode of the QMS for allene and propyne doped droplets, which were ionized by electron impact. The spectra in Figure SM 1 in Supplementary Materials (SM) show several intense peaks due to $C_3H_{y=2\text{-}5}^+$. Figure 1 shows the infrared spectra of the $C_3H_4^+$ cations obtained at mass channel m/z = 40 upon ionization of droplets doped with the allene precursor. The spectra are obtained at three different pickup pressures of allene: 1.0×10^{-6} mbar (blue), 3.0×10^{-6} mbar (red), and $9.0 \times$

10^{-6} mbar (black). Here, and later, the pressure corresponds to the nominal ion gauge reading. The absolute pressure could be obtained by dividing the nominal pressure reading by the molecule specific sensitivity coefficient. While the sensitivity coefficient is not known for allene and propyne, it is expected to be in the range of 3 to 4 based on the known coefficients for propene and propane. The spectrum in Figure 1 has three strong bands at 2941.6 cm^{-1}, 2949.6 cm^{-1}, and 3042.9 cm^{-1} which were assigned to allene cations as it will be discussed in the following. The intensity of these bands increases within the pickup pressure range of 1.0×10^{-6} mbar to 3.0×10^{-6} mbar but drops at higher pressures of allene. The spectrum in Figure 1 has several low intensity new bands above 3100 cm^{-1} which are marked as "unknown isomer". The bands have the same intensity at 1.0×10^{-6} mbar and 3.0×10^{-6} mbar but completely diminish at the higher pickup pressure of allene of 9.0×10^{-6} mbar. Figure SM 2 in SM shows the pickup pressure dependency of the intensities of the bands in Figure 1. The difference in pressure dependence of the intensity signifies the presence of at least two different groups of bands corresponding to different isomers of $C_3H_4^+$. Figure SM 2 (a-c) shows that the intensities of the allene cation bands reach their maxima at the allene pickup pressure of $\sim 2.5 \times 10^{-6}$ mbar, whereas the new bands reach their maximum intensities at $\sim 1.5 \times 10^{-6}$ mbar.

2. Propyne precursor:

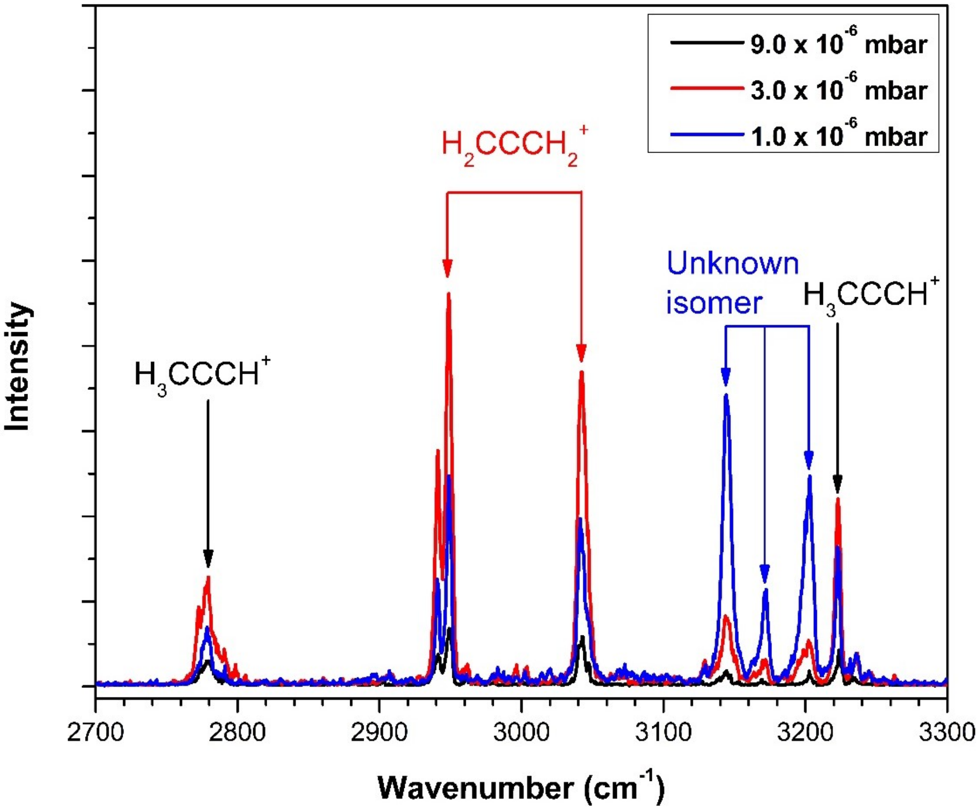

Figure 2: The infrared spectra of $C_3H_4^+$ cations (m/z = 40 channel) obtained from the ionization of helium droplets doped with propyne at pickup pressure 1.0 × 10^{-6} mbar (blue), 3.0 × 10^{-6} mbar (red), and 9.0 × 10^{-6} mbar (black)

Similar measurements were done using the droplets doped with propyne as a precursor. The spectra obtained with the propyne precursor in Figure 2 show bands at the same frequencies as obtained with the allene precursor but with different relative intensities. The spectra in Figure 2 were recorded in a broader range and show a new band at 2777.0 cm^{-1}. Figure SM 3 in the SM shows that the intensities of the bands at 2777.0 cm^{-1}, 2941.6 cm^{-1}, 2949.0 cm^{-1}, 3042.9 cm^{-1} and 3223.0 cm^{-1} reach their maxima at the propyne pickup pressure of ~2.5 × 10^{-6} mbar. The groups of the bands i) at 2777.0 cm^{-1} and 3223.0 cm^{-1} and ii) at 2941.6 cm^{-1}, 2949.0 cm^{-1}, and 3042.9 cm^{-1} belong to different isomers because the relative intensities of the groups i) and ii) change when the droplets were doped with propyne instead of allene. The bands at 2777.0 cm^{-1} and 3223.0 cm^{-1} were assigned to propyne cations.

The pickup pressure dependence of the intensities for the infrared bands of allene cations is similar to that of propyne cations, with both reaching a maximum at the pickup pressure of about 2.5×10^{-6} mbar. On the other hand, the intensity of the new bands is maximized at a lower pressure of about 1.5×10^{-6} mbar, indicating they originate from different isomers of $C_3H_4^+$. The intensities of the new bands are well fitted using the Poisson eq. (S1), given in SM, showing the corresponding cations are produced upon ionization of single precursor molecules, see Figures SM 2 and SM 3 in SM. However, the pressure dependencies of the intensities of the bands of the allene and propyne cations can be reasonably well fitted with the Poisson equation for the pickup of one or two molecules and show maxima at about twice the pickup pressure of the new bands. This indicates that the allene cations and propyne cations are produced from droplets containing single molecules as well as dimers.

The determination of three groups of bands in Figures 1 and 2 with distinctly different relative intensities for different experimental conditions indicates the presence of at least three unique isomers of $C_3H_4^+$.

Discussion

Quantum chemical calculations in this work and by others[4-6] show that the allene cation is the most stable form of $C_3H_4^+$. Our calculations at B3PW91/aug-cc-pVTZ level of theory show that the next higher energy isomers relative to the allene cation are the propyne (15.2 kcal/mol), cyclopropene (21.1 kcal/mol), *cis*-vinylmethylene(25.5 kcal/mol), and *trans*-vinylmethylene cations (26.7 kcal/mol). These results are in good agreement with previous calculations.[6] The strong bands at 2949.5 cm^{-1} and 3042.0 cm^{-1} are assigned to allene cations and correspond to the anti-symmetric C-H stretching mode (B_1) with the transition dipole moment parallel to the molecular axis and to the B_2 type C-H stretching mode which has the transition dipole moment axis perpendicular to the molecular axis, respectively. The pictorial representations of the vibrational modes are shown in Table SM 4 of the SM. The assignments of these bands are in good agreement with the previous measurements done in solid argon and neon matrices.[16, 17] We tentatively assigned the split band at 2941.6 cm^{-1} to the combination band of a C-C stretching (B_1 symmetry) and CH_2 deformation (B_1 symmetry) modes.

The band at 3223.0 cm^{-1} in Figure 2 is assigned to the acetylenic C-H stretching vibration (A') of the propyne cation, whereas the band at 2777.0 cm^{-1} is assigned to the asymmetric C-H stretch of the methyl group of the propyne cation. The frequencies of the propyne bands are in good agreement with measurements done in solid argon matrices at 3214.5 cm^{-1} and 2780.2 cm^{-1}, respectively.[13, 17] The bands were also observed in the gas phase using photoionization rovibrational spectroscopy at 3217.1 cm^{-1} and 2767 cm^{-1}.[11] The frequencies of the allene and propyne cations' bands, their assignments, and the results of previous measurements are summarized in Table 1 and compared to quantum chemical calculations done in this work. The computed frequencies and infrared intensities for the $C_3H_4^+$ isomers are reported in Tables SM 4-

SM 8 in SM. Tables SM 9-SM 10 list the calculated electronic and thermodynamic parameters of the isomers and the cartesian coordinates of the atoms.

Figure 3 (b-f) shows the infrared spectra of the five isomers of the $C_3H_4^+$ cation and their corresponding relative energies (kcal/mol) in parentheses at the B3PW91/aug-cc-pVTZ level of theory as calculated in this work.[26-28] The calculated frequencies are further scaled by a factor of 0.965. The panel (a) of Figure 3 shows the experimental spectrum recorded in this work upon the ionization of propyne doped droplets. Figure 3 shows that the measured spectra for allene and propyne cations are in good agreement with the calculated spectra. We did not find any indication of the formation of cyclopropene cations. According to calculations, cyclopropene cations should have a band around 3100 cm^{-1} and two bands around 2800 cm^{-1} which were not observed in the measured spectra in Figures 1 and 2.

Table 1: The C-H stretching modes of the allene and propyne cations, symmetry of the mode, and the frequencies observed in superfluid helium nanodroplets, in solid argon matrices, and in solid neon matrices. The theoretical calculations are performed at B3PW91/aug-cc-pVTZ theory level which were scaled by a factor of 0.965. All frequencies are in wavenumbers.

Cation	Vibration Symmetry	helium droplet	Argon matrix[17]	Neon matrix[16]	Photoionization spectroscopy[11]	Computed Harmonic Frequencies
$H_2CCCH_2^+$	B_1	2949.5	2929	2956		2957.2
$H_2CCCH_2^+$	B_2	3042.0	3020.8	3047		3050.9
$H_2CCCH_2^+$	Combination band	2949.3				2859.5
H_3CCCH^+	A'	3223.0	3214.5		3217.1	3236
H_3CCCH^+	A'	2777.0	2780.2		2767	2770.9

The new bands at 3145.7, 3172.0, and 3202.7 cm^{-1} remain unassigned. Figure 3 shows that only the $H_2C=CH-CH^+$ isomers (*cis*-vinylmethylene cation and *trans*-vinylmethylene) have all of their C-H stretching bands in the high frequency region. Starting from the highest frequency calculated bands of vinylmethylene, the bands correspond to the antisymmetric C-H stretch on the CH_2 end of vinylmethylene cation, the C-H stretch on the other terminal of the cation, and the C-H stretching mode of the middle C-H bond (see Table SM 6 in SM). The symmetric stretching mode of the CH_2 unit has the lowest frequency. However, the calculated intensity pattern and frequencies of the bands of vinylmethylene cations deviate considerably from the experimental spectrum. The bands in the CH stretching region for the carbocations may be affected by Fermi-resonances with overtones of the CH bending vibrations whose frequencies are near 1500 cm^{-1}, see Tables SM 4-SM 8 in SM. The new bands could not be assigned to Fermi-resonances of the allene and propyne cations, because of their different pickup pressure dependences of the intensity. We searched for other possible explanations for the unassigned bands as detailed in section SM 11 of the SM, however neither of which appear satisfactory.

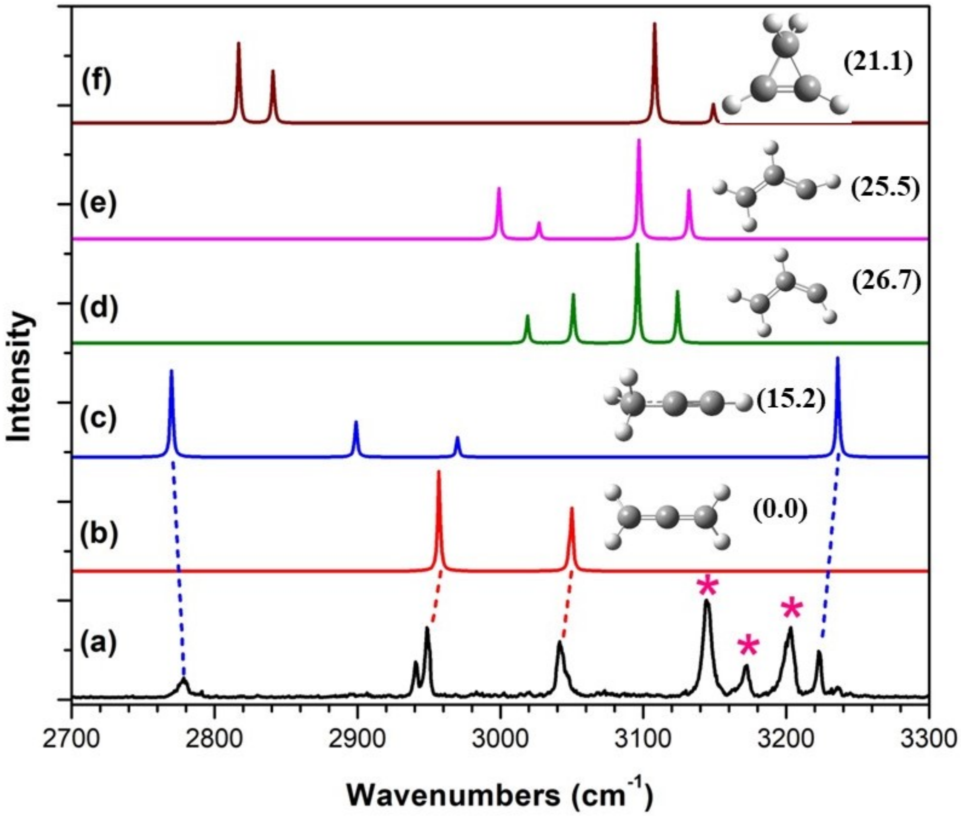

Figure 3: The comparison of the experimental spectrum obtained by ionizing the propyne doped droplets at m/z = 40 channel (a), with the computed spectra of allene cation (b), propyne cation (c), trans-vinylmethylene cation (d), cis-vinylmethylene cation (e), and cyclopropene cation (f) at B3PW91/aug-cc-pVTZ level of theory. The computed spectra are scaled by a factor of 0.965. The bands marked with an asterisk are unassigned. The numbers in parenthesis are relative energies of the isomers with zero-point energy correction in units of kcal/mol calculated in this work.

The spectra in Figure 1 show that the ionization of allene molecules mainly leads to the formation of allene ions with a small yield of propyne ions as indicated by the very weak intensities of the acetylenic CH stretching band at 3223 cm^{-1} as well as for the new bands. In comparison, the spectrum in Figure 2, measured upon the ionization of propyne molecules, shows significantly larger intensities of the propyne bands, although the allene cation bands still dominate the spectrum. The spectrum in Figure 2 also exhibits much larger intensities of the new bands. These findings show the propensity of the system to relax towards the formation of the lowest energy allene cation isomer. Nevertheless, some higher energy propyne cations are formed even upon the ionization of allene precursors, a process which requires proton migration.

Previously Mebel et al., [6] predicted that a rich landscape of isomers of $C_3H_4^+$, $C_3H_3^+$ and $C_3H_2^+$ ions are connected by transition states up to an energy of about 65 kcal/mol relative to the allene ions. The ionization potential of helium atoms is 24.6 eV, much larger than that for allene (9.7 eV) [32] and propyne (10.36 eV).[33] It follows that ionization of the precursor molecules by charge transfer from He^+ ions will be associated with the release of up to 14 eV (320 kcal/mol) energy, much larger than the activation barriers between any isomers. Therefore, the formation of different isomers of $C_3H_4^+$ upon ionization of the neutral precursors is energetically feasible. The incipient allene and propyne cations are likely formed from some excited electronic states whose decay may involve fragmentation. The products of the charge transfer reactions from He^+ ions to allene and propyne molecules in the gas phase remain poorly studied.[34, 35] Charge transfer in He droplets may be influenced by the presence of He atoms in the environment as well as by the possible formation of He_2^+ ion intermediates, which have binding energies of about 55 kcal/mol (2.4 eV).[31] Some insights could be gained from studies of the photoionization of allene and propyne molecules.[11, 14, 15] The dissociative photoionization of propyne and allene molecules has been studied for photon energies up to 21 eV.[8, 9, 11] The appearance potentials for $C_3H_4^+$, $C_3H_3^+$, $C_3H_2^+$ and C_3H^+ ions were reported to be 10.4, 11.6, 13.3 and 17.1 eV, respectively.[11] At the photon energy of 18 eV the yield of ions was found to be 26.4:56.6:15.8:1.1, respectively. The same ions are produced in the He droplets with the relative abundances of the ions in Figure SM 1 being in qualitative agreement with the dissociative photoionization results. [11]

Interactions with the He environment may affect the final composition of cold products studied in this work by IR spectroscopy. Energetic $C_3H_4^+$ ions may explore different isomeric forms and, upon relaxation in the liquid helium bath, may fall into several local minima corresponding to the isomers. If the incipient ion dissociates, the produced hydrogen atoms or molecules may leave the droplet yielding isolated fragments, such as $C_3H_3^+$ and $C_3H_2^+$ whose spectra were indeed observed. However, the hydrogen may remain trapped in the droplets and recombine with the ionic fragments, a process which may give rise to unusual isomers of $C_3H_4^+$.

Conclusions

This work expands our study of carbo-ions in helium droplets to precursors having three carbon atoms, such as allene and propyne. Electron impact ionization of the droplets doped with single precursor molecules or small clusters yield embedded $C_3H_4^+$, $C_3H_3^+$ and $C_3H_2^+$ cations. Infrared spectra of the $C_3H_4^+$ cations show three distinct groups of bands, whose relative intensities depend on the precursors and their pickup pressures, indicating the presence of at least three different isomers. The two isomers were identified as allene and propyne radical cations. The third isomer has several bands in the range of 3100-3200 cm^{-1} which may be due to an elusive vinylmethylene $H_2C{=}CH{-}CH^+$ radical cation. The observed bands for allene and propyne cations are in good agreement with the results of density functional theory calculations. However, the agreement of the new bands with the calculated vinylmethylene spectrum is poor. More work is required for the assignment of this new isomer. Future experiments may be extended towards examining deuterated ions which may facilitate the assignments. The experiments should also look further at the low frequency fingerprint spectral region. High level anharmonic frequency calculations may also be needed to corroborate the assignments. The infrared spectra show no evidence of the cyclic $C_3H_4^+$ ions. It is possible that the formation of cyclic ions from linear precursor molecules is inefficient in He droplets. It would be interesting to study the formation of the cyclic cations in helium nanodroplets, which may be produced from cyclic precursors, such as cyclopropane, cyclopropene, methylcyclopropane, etc.

Supplementary Material

The Supplementary Material contains three additional figures and five tables.

Figure SM 1 shows the mass spectra obtained upon ionization of the doped droplets by electron impact.

Figures SM 2 and SM 3 show the pickup pressure dependences of the intensity of the infrared bands,

Tables SM 4-SM 8 list calculated frequencies, infrared intensities, and mode assignments for allene, propyne, *cis*-vinylmethylene, *trans*-vinylmethylene and cyclopropene cations, respectively.

Tables SM 9-SM 10 list the calculated electronic and thermodynamic parameters of the isomers and the cartesian coordinates of the atoms.

Section SM 11 contains the discussion of the alternative assignment of the new bands.

SM contains references [6, 19, 36-40].

Acknowledgements

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Author Declarations

Conflict of Interest

The authors have no conflicts to disclose.

Data Availability

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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