Formation of the $C_4H_n^+$ (n=2–5) ions upon ionization of acetylene clusters in helium droplets

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Abstract

Infrared (IR) spectroscopy using ultracold helium nanodroplet matrices has proven to be a powerful method to interrogate encapsulated ions, molecules, and clusters. Due to the droplets' high ionization potential, optical transparency, and ability to pick-up dopant molecules, the droplets offer a unique modality to probe transient chemical species produced via photo- or electron impact ionization. In this work, helium droplets were doped with acetylene molecules and ionized via electron impact. Ion-molecule reactions within the droplet volume yield larger carbo-cations which were studied via IR laser spectroscopy. This work is focused on cations containing four carbon atoms. The spectra of $C_4H_2^+$, $C_4H_3^+$, and $C_4H_5^+$ are dominated by diacetylene, vinylacetylene and methylcyclopropene cations, respectively, which are the lowest energy isomers. On the other hand, the spectrum of $C_4H_4^+$ ions hint at the presence of several co-existing isomers, the identity of which remains to be elucidated.

1. Introduction

The first quantitative investigations of unimolecular decomposition reactions began with the study of benzene ions, which were produced at different excess energies by charge transfer.[1, 2] It was shown that the primary reaction pathway involved the formation of a variety of products ($C_6H_5^+$ + H, $C_6H_4^+$ + H_2, $C_4H_4^+$ + C_2H_2, and $C_3H_3^+$ + C_3H_3) that proceeded via some common intermediate state of $C_6H_6^+$ ions. Later, related studies on the photoionization of acetylene trimers were found to yield the same primary ions, supporting the hypothesis of prior rearrangement of the system to a common intermediate state.[3-5] More recently, the interest in this system was renewed by the need to explain the formation of aromatic molecules in outer space.[6] Experiments on photo- or electron impact (EI) ionization of acetylene dimers and larger clusters demonstrated the formation of covalently bound $C_4H_4^+$ ions, as well as fragment ions such as $C_4H_2^+$ and $C_4H_3^+$ [4, 5, 7-12]. Quantum chemical calculations show that the ionization of acetylene dimers leads to the initial formation of a bridged CH-CH-CH-CH^+ species which can evolve into stable cyclobutadiene, methylenecyclopropene or 1,2,3-butatriene ions.[5, 10, 11, 13] It was predicted that larger cations such as allylcyclopropenyl, vinylcyclobutadienyl and benzene ions could be formed from larger acetylene clusters, a process which is facilitated by energy transfer to the spectator acetylene molecules in the cluster.[10, 14, 15] Although the calculations yield the formation mechanisms of the different isomers of $C_4H_4^+$ and $C_6H_6^+$, there are few experimental studies from which the information on the isomeric composition of the ions could be deduced. Noticeably, the mobility measurement for $C_4H_4^+$ ions produced upon ionization of acetylene clusters indicated the formation of more than one isomer, which was assigned to cyclobutadiene and vinylacetylene ions.[7, 8] Cationic acetylene clusters $(C_2H_2)_n^+$ tagged with argon atoms were produced by charge transfer from Ar+ clusters to acetylene molecules.[16] The $(C_2H_2)_2^+ \cdot Ar$ spectrum indicated that these species are predominantly present as the cyclobutadiene cation.

Using helium droplets as ultracold (0.4 K) matrices for isolation spectroscopy is a promising technique that has recently been developed by several groups.[17-22] This work is aimed at the IR spectroscopic investigation of carbocations produced upon ionization of acetylene dimers and trimers in helium droplets. Our investigation builds on our group's related studies involving the ionization of the ethane and ethylene molecules in helium droplets.[22, 23] Our experiment starts with neutral helium droplets capturing a few acetylene molecules in accordance with Poissonian

statistics.[24-29] The droplets subsequently undergo EI ionization. This process yields diverse ionic species, with a sizable fraction remaining inside the droplets.[24-29] IR laser excitation of the cations in the range of C-H stretching bands (2600-3500 cm^{-1}) leads to the release of bare cations which are detected by mass spectrometry.

In this work, we have recorded IR spectra for the four carbon-containing ions that were produced upon EI ionization of acetylene in helium droplets. To assign the isomers, we have calculated the structure, relative energies and infrared spectra of the isomers at MP2/aug-cc-pVDZ level of theory. The spectra of the $C_4H_2^+$, $C_4H_3^+$, and $C_4H_5^+$ are dominated by diacetylene, vinylacetylene and methylcyclopropene cations, respectively. On the other hand, the spectrum of the $C_4H_4^+$ ions hints on the presence of several isomers, the identity of which remains to be elucidated. The mechanism behind the ion formation is discussed in accordance with theoretical calculations.

2. Experiments and Calculations

The experimental apparatus used for production and spectroscopy of molecular cations in helium droplets has been previously described in other publications.[19, 23] Briefly, helium droplets are produced upon expansion of helium gas through a 0.5 mm diameter pulsed nozzle (General Valve series 99) attached to a cryo-cooler (Sumitomo RDK 408).[30] In our experiment, the nozzle operated at a stagnation pressure of P_0 = 20 bar and temperature of T_0 = 23 K, and employed pulses of ~ 180 μs width. At these conditions, the produced droplets contained on average about 5000 helium atoms, as estimated from the pickup pressure dependencies of the signal.[19] Upon collimation by a 2 mm diameter skimmer, droplets enter the pickup chamber (44 cm long) where they capture acetylene molecules. The acetylene pressure in the chamber is regulated by a leak valve and measured by an ionization pressure gauge; throughout this paper, the given pressure corresponds to the nominal ion gauge reading. The absolute pressure can be obtained by dividing the reading by the sensitivity coefficient for acetylene of 2.0. Acetylene was taken from a cylinder containing acetone stabilizer without further purification. Based on the total cylinder pressure and acetone vapor pressure, the gas may contain about 2% acetone by volume. Further downstream,

doped droplets pass through a differential pumping stage and enter the detection chamber that hosts a quadrupole mass spectrometer (QMS) (Extrel MAX 500) with an additional axial external ionizer placed ~ 20 cm upstream from the ion region of the QMS. During the spectroscopic experiments reported in this work, the droplets are ionized with the external ionizer set to 100 eV and 10 mA. Upon ionization, heavy droplet-ion moieties continue traversing toward the ion range of the QMS, whereas light moieties are rejected by the einzel lenses which act as a high-pass filter.

Doped ionic droplets are irradiated by a focused infrared laser beam when they pass through the ion range of the QMS. Absorption of several infrared quanta leads to the production of free ions, which are then extracted, mass selected by the QMS, and detected by an electron multiplier.[19] The signal from the electron multiplier is amplified and measured by an SR250 boxcar integrator. For measurements of the IR spectra, the QMS was tuned to a particular mass, and the gate was set to ~ 10 μs. This work employed an unseeded pulsed optical parametric oscillator-amplifier (Laser Vision, spectral resolution: ~ 1 cm^{-1}, pulse duration ~ 7 ns, pulse energy ~ 3 - 4 mJ at the entrance window of the vacuum apparatus, repetition rate 20 Hz). The absolute frequency of the laser spectrometer is calibrated using the photo-acoustic spectrum of methane and water molecules.

The structure, energies, and spectra of $C_4H_n^+$ isomers calculated via various levels of theory have been reported in number works. However, each work employed a different level of theory (see the references in the following). For the sake of uniformity, in this work, we have performed new quantum chemical calculations using a consistent level of theory (MP2/aug-cc-pVDZ) for all isomers. Our calculations were performed using the Gaussian 16 computer application.[31]

3. Results and Discussion

3.1 Mass spectra upon ionization of doped droplets

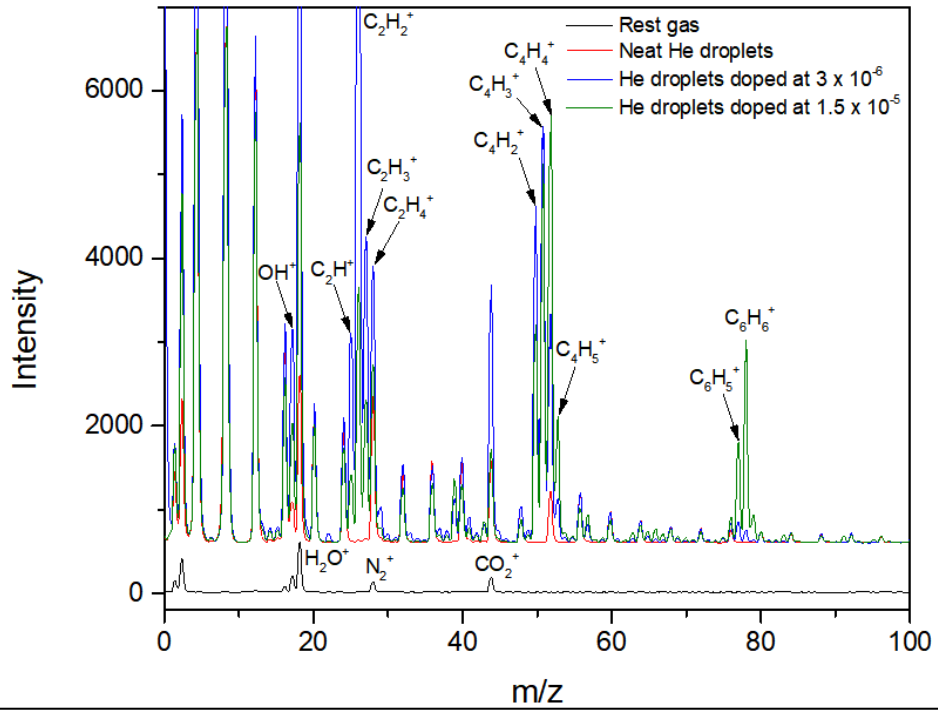

Figure 1. Mass spectra obtained upon standard ionization by the QMS ionizer. Black trace - baseline due to residual gas in the detection chamber. Red trace - neat helium droplets. Blue and green traces - helium droplets dopped at 3×10^{-6} and 1.5×10^{-5} mbar of acetylene, respectively. The traces are plotted to the same scale.

Figure 1 shows the mass spectra of helium droplets as recorded with the boxcar integrator upon standard ionization by the QMS ionizer. The black trace shows the mass spectrum of the residual gas in the detection chamber at the nominal rest gas pressure of ~ 5×10^{-9} mbar. The peaks correspond to the H^+, H_2^+, OH^+, H_2O^+, N_2^+, and CO_2^+ ions. The red trace shows the mass spectrum upon ionization of the neat (not doped) helium droplet beam. It contains a sequence of He_N^+ peaks which intensity decreases with N. It is seen that with the helium droplet beam on, the intensity of

the residual gas peaks of H_2O^+ and OH^+ increases. We assign this effect to ionization of water molecules in the residual gas by He* and He^+, which are produced upon electron impact. Some intensity may also stem from some minor content of water molecules in the droplets that were captured from the rest gas, whose pressure along the helium droplet beam path was ~10^{-8} mbar. Peaks due to N_2^+ and CO_2^+ overlap with He_7^+ and He_{11}^+, respectively. Blue and green traces show the mass spectrum with 3.0 $\times 10^{-6}$ and 1.5 $\times 10^{-5}$ mbar of acetylene in the pickup chamber, respectively, which corresponds to the pickup of an average of 1.5 and 7.5 acetylene molecules per droplet. New intense peaks in the blue trace at 3.0 $\times 10^{-6}$ mbar correspond to C_2H^+, $C_2H_2^+$, $C_2H_3^+$, $C_4H_2^+$, $C_4H_3^+$, and $C_4H_4^+$. The spectrum at higher pickup pressure of 1.5 $\times 10^{-5}$ mbar shows additional peaks assigned to $C_4H_5^+$, $C_6H_5^+$, and $C_6H_6^+$, as well as some other minor peaks. Similar ions albeit with different relative intensities were previously observed upon ionization of free acetylene clusters.[3, 5, 7, 9-12] The mass spectra for the doped droplets allows one to determine the possible contribution of acetone traces in the acetylene gas. EI ionization of acetone is known to yield prominent peaks at masses of M=43 and 58. The mass spectra in Fig. 1 shows that the intensity at these masses is about a factor of 50 smaller than the main peaks due to acetylene. We therefore render any possible effect of the residual acetone impurity as negligible.

Due to the large number of He atoms in the droplets, the ionization event is considered to produce He^+ ions initially, which in turn rapidly migrate to ionize any embedded acetylene molecules by charge transfer. Charge transfer reactions between He^+ ions and acetylene molecules in the gas phase is known to produce $C_2H_2^+$, as well as C_2H^+, C_2^+, and CH^+ fragment ions whose intensity ratio were found to be 7:25:46:22.[32] Figure 1 shows that $C_2H_2^+$ and C_2H^+ are the primary products of ionization of single acetylene molecules in helium droplets. The mass spectra in Fig. 1 shows only a trace amount of C_2^+ and CH^+, which accounts for 75% of the ionization events in the gas phase. It is interesting to note that the relative intensities of the ion fragments are in much better agreement with that obtained for the EI ionization of free acetylene molecules, showing $C_2H_2^+$, CH_2^+, and C_2^+ yield in the ratio of about 100:20:5.[33] This is puzzling, because the direct ionization of acetylene molecules by electrons should not be important due to the overwhelming number of He atoms in the droplets. Most likely, this observation indicates that the branching ratio for charge transfer mediated ionization in the droplets differs significantly from in the gas phase. Upon ionization, He ions form tightly bound He_2^+ and He_3^+. The reaction of acetylene with these ions may cause less fragmentation due to the presence of several He atoms. Additionally, the

reaction proceeds inside the droplet, whose atoms may lead to some moderation of the fragmentation.

The mass spectra in Fig. 1 show that the intensities of the residual gas peaks such as OH^+, H_2O^+, N_2^+, and CO_2^+ ions rise by about a factor of about three to four in the mass spectra of the doped droplets. The origin of this effect requires more investigation. Because of base pressure of about 10^{-8} mbar throughout the beam path, any content of the H_2O, N_2, and CO_2 molecules in the droplets should be about twenty times less than that of the acetylene molecules.

3.2 Total ion yield spectra.

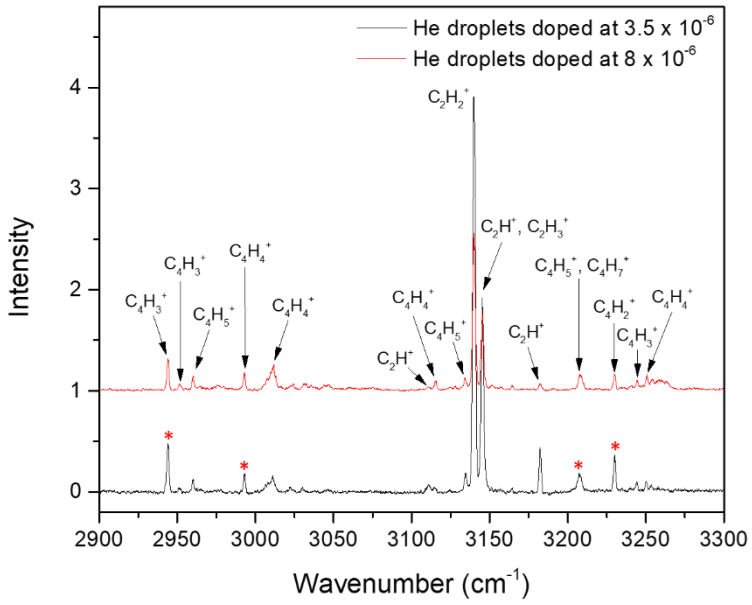

Figure 2. The total yield of ions upon laser irradiation of the acetylene doped ionized droplets. Black and red traces were obtained with acetylene pickup pressure of 3.5×10^{-6} and 8×10^{-6} mbar, respectively. The assignment of the prominent spectral peaks is indicated. Marked with asterisks the spectral peaks for which the mass spectra and the pickup pressure dependence were studied as described in SM sections S1 and S2, respectively.

Based on our previous study of ethylene ionization in He droplets[23], we expect that the same carbo-cations that leave the droplet upon ionization produce the prominent peaks in Fig. 1. They may also remain trapped inside the droplets and can be studied via IR laser spectroscopy. In

the following, the results were obtained upon the ionization of the droplets in the external ionizer. Figure 2 shows the spectra of the total ion yield in the range of 2900 to 3300 cm^{-1} upon laser irradiation of droplets doped with acetylene at 3.5×10^{-6} and 8×10^{-6} mbar, which correspond to an average pickup of about two and four acetylene molecules per droplet. No additional spectral features were detected in broader scans from 2600 to 3500 cm^{-1}. During the measurements, the DC of the QMS was switched off so that all ions produced upon laser irradiation were guided to the detector independent of their masses. The boxcar gate was set to 150 μs to accept different ions which have different times of flight through the QMS. Figure 2 shows that the total ion yield spectrum has several peaks that could be assigned to different ions as indicated. The spectra of some of the ions, such as $C_2H_2^+$, and $C_2H_3^+$ have already been identified in our previous work with ethylene precursor.[23] The spectra of the C_2H^+ ions will be discussed elsewhere. The other prominent new peaks were assigned to $C_4H_2^+$, $C_4H_3^+$, $C_4H_4^+$, and $C_4H_5^+$ by the mass spectrometric measurements as described in supplemental materials (SM), section S1. Pickup pressure dependences marked by asterisks are described in Section S2 of the SM. The pickup pressure dependencies indicate that the $C_4H_2^+$, $C_4H_3^+$, and $C_4H_4^+$ that remain in helium droplets predominantly form from dimers and $C_4H_5^+$ from trimers of acetylene. It is interesting that the IR spectra in Fig. 2 as well as the mass spectra in Fig. 1 do not show any significant features that could be assigned to the formation of the ions with three carbon atoms, which were prominent in our study of ethylene ionization in He droplets.[23]

3.3 $C_4H_2^+$ ions.

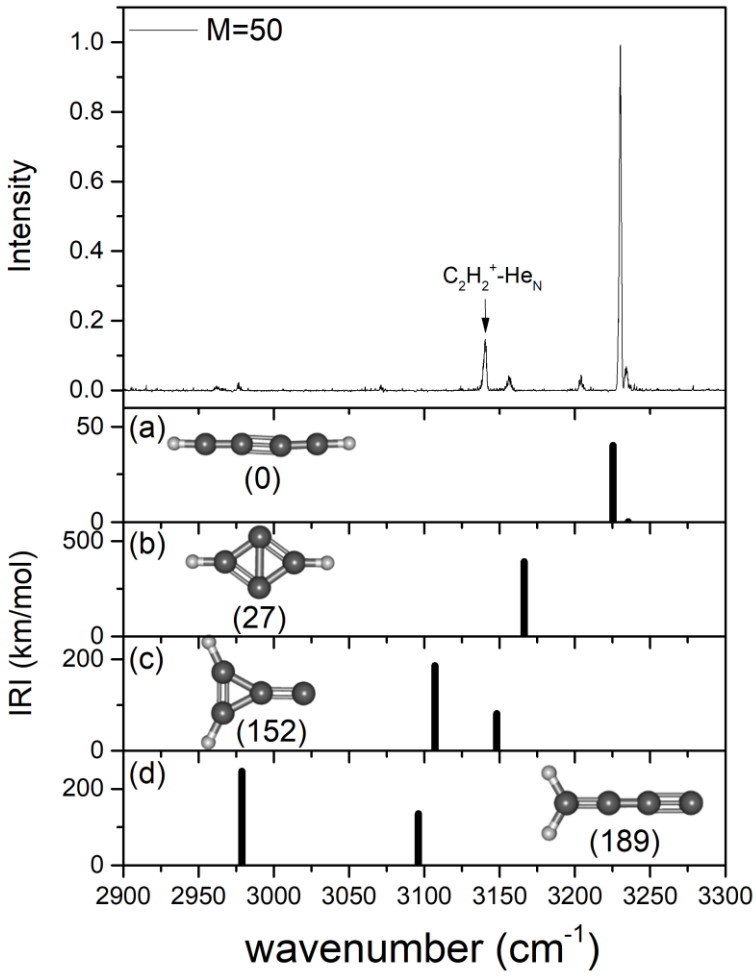

Figure 3. Spectrum of $C_4H_2^+$ ions recorded at M=50. The lower panels show the spectra calculated for different isomers of $C_4H_2^+$ at MP2/aug-cc-pVDZ level of theory. The frequencies were scaled by a factor of 0.95. The inserts show the structure of the isomers and their relative energies in kJ/mol units.

Figure 3 shows the spectrum recorded at M=50. The spectrum has a strong peak at 3230.2 cm^{-1}, a medium intensity peak at 3140.3 cm^{-1} and several weaker features at 3156.7, 3203.8, 3234.0 cm^{-1} and very weak peaks at 2962.2, 2976.5, 3071.6 cm^{-1}. The peak at 3140.3 cm^{-1} coincides with the very strong peak from $C_2H_2^+$ identified in our previous work with ethylene.[23] The mass spectrum of the laser ejected ions contains a long progression due to $C_2H_2^+$-He_N clusters with the well discernable peak at M=50.[23] Therefore, the peak at 3140.3 cm^{-1} is ascribed to $C_2H_2^+$-He_6

clusters. The other peaks are free from any overlap with the spectra of the smaller ions and are identified with $C_4H_2^+$ cations.

The lower panels in Fig. 3 show the spectra calculated in this work for different isomers of $C_4H_2^+$ at MP2/aug-cc-pVDZ level of theory. The inserts show the structure of the isomers and their relative energies in kJ/mol units. Similar isomers were identified in previous calculations, see refs.[34-36] and refs. therein. Although the relative energies of the isomers vary in different calculations, they agree that the lowest energy $C_4H_2^+$ isomer is linear diacetylene cation (a), see refs.[34-36] and refs. therein. The higher energy isomers include bicyclo[1.1.0]buta-1(4),2-diene (4-carbon ring structure, (D_{2h}) (b), Y-shaped vinylidene-like structure (C_{2v}) (c) and 3-carbon ring structure (C_{2v}) (d) as found in this work and in refs.[1337]. We could not find any previous gas phase study of the infrared spectra of the $C_4H_2^+$ cations. Previous experimental studies involved photoelectron spectroscopy or the study of the optical transitions between the $X^+\ ^2\Pi_g$ and $A\ ^2\Pi_u$ first electronically excited state. [35, 36] Such experiments yield information on the frequencies of the symmetric fundamentals, overtones, or combination bands. On the other hand, IR spectra give access to the non-totally symmetric vibrations bearing infrared intensity.

Both linear and D_{2h} structures in panels (a) and (b) should have a single intense band due to antisymmetric C-H vibrations. The corresponding harmonic vibration frequencies (infrared intensities) were calculated in this work to be 3395 cm^{-1} (40 km/mol) and 3333 cm^{-1} (394 km/mol). Previous calculations gave 3376 cm^{-1} (252 km/mol) and 3325 cm^{-1} (278 km/mol), respectively.[37] On the other hand, IR spectra of the other two C_{2v} isomers have two infrared C-H stretching bands at lower frequency. We assigned the intense band at 3230.2 cm^{-1} to the ν_4 antisymmetric C-H band of the linear, most energetically favorable diacetylene cation. Accordingly, the calculated frequencies were scaled by a factor 0.95 to match the experimental value. Same scaling factor was applied to all calculated frequencies in this work. Acetylenic bands close to this frequency (±10 cm^{-1}) were observed in our studies of several cations containing three carbon atoms, as well as in publications from other groups.[38] The weak bands may hint at some contributions from the isomers. For example, the bands at 3156.7 and 3203.8 cm^{-1} fall into the range expected for the Y-shaped isomer, panel (d). Some weak features may also arise due to the combination bands, such as of intense ν_5 antisymmetric C-C stretch with C-C symmetric stretch or with overtones of bending vibrations.

3.4 $C_4H_3^+$ ions.

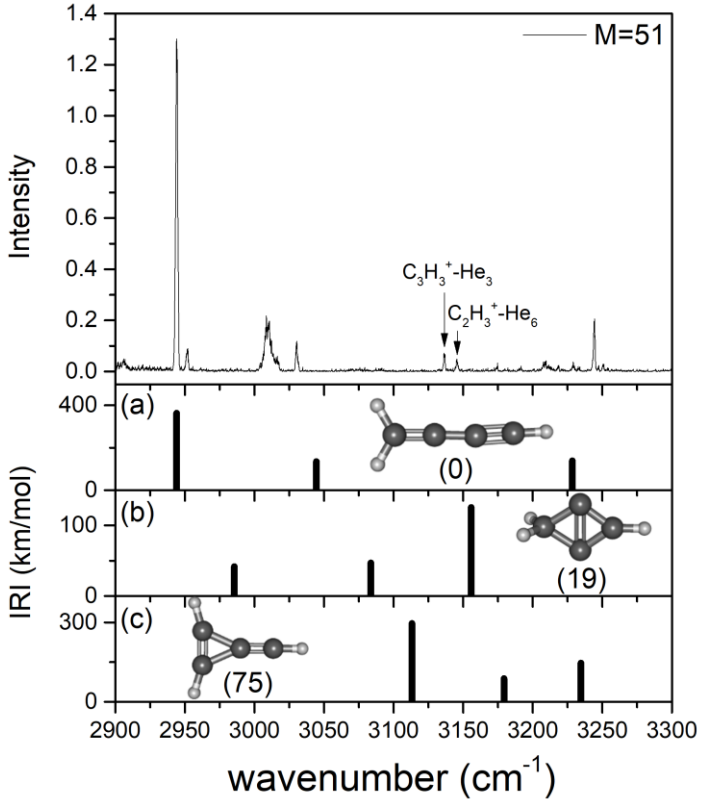

Figure 4. Spectrum of $C_4H_3^+$ ions recorded at M=51. The lower panels show the spectra calculated for different isomers of $C_4H_3^+$ at MP2/aug-cc-pVDZ level of theory. The frequencies were scaled by a factor of 0.95. The inserts show the structure of the isomers and their relative energies in kJ/mol units.

Figure 4 shows the spectrum of $C_4H_3^+$ ions recorded at M=51. The spectrum has a strong peak at 2944.0 cm^{-1}, medium intensity peaks at 3009, 3030.3, and 3244.4 cm^{-1} and several weaker features at 2905, 2952, 3136, and 3145.3 cm^{-1}. The peaks at 3136 and 3145.3 cm^{-1} were assigned to $C_3H_3^+$-He_3 and $C_2H_3^+$-He_6 clusters, respectively. We could not find any previous gas phase study of the infrared spectra of the $C_4H_3^+$ cations. Calculations yielded the aliphatic open chain vinylacetylene ion ($H_2C_4H^+$) (a) to be the most stable isomer, followed by bicyclo[1.1.0]but-2-en-1-ylium (4 carbon ring) (b), and 3-methylidenecyclopropene (3 carbon ring) (c). Same low laying isomers along with some other higher energy isomers were found in previous calculations.[39] The spectrum in Fig. 4 is consistent with the open chain structure in panel (a) which should have three bands in the C-H stretching range.[3940] Accordingly, the bands 2944.0, 3009, and 3244.4 cm^{-1} could

be assigned to the symmetric stretch of CH_2, the antisymmetric stretch of CH_2, and the stretch of the acetylenic C-H group. The corresponding scaled values from the harmonic calculations in Fig. 4 are: 2943, 3044, and 3228 cm^{-1}, respectively.

3.5 $C_4H_4^+$ ions.

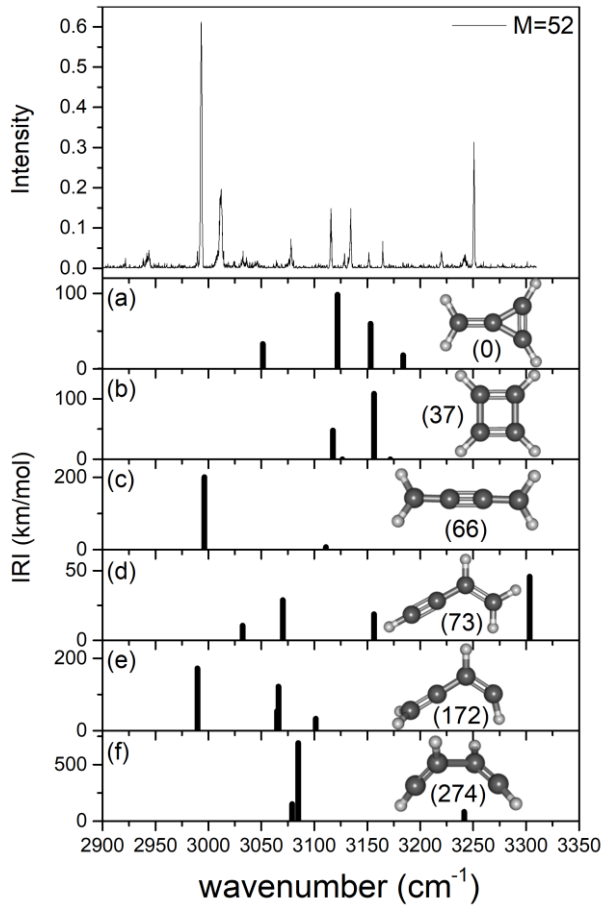

Figure 5. Spectrum of $C_4H_4^+$ ions recorded at M=52. The lower panels show the spectra calculated for different isomers of $C_4H_4^+$ at MP2/aug-cc-pVDZ level of theory. The frequencies were scaled by a factor of 0.95. The inserts show the structure of the isomers and their relative energies in kJ/mol units.

Figure 5 shows the spectrum of $C_4H_4^+$ ions recorded at M=52. The spectrum has strong bands at 2993.2, 3012.1, 3115.7, 3134.5 and 3250.8 cm^{-1} and several weaker bands. The high frequency peak must be due to acetylenic stretch, whereas peaks around 3000 cm^{-1} may stem from a methyl group. The peaks in the range of 3050–3150 cm^{-1} may come from methylene or methine

groups. There is no overlap with the spectra of the previously studied smaller ions such as $C_2H_4^+$ which clusters with 6 He atoms may contribute to the signal at M=52.

Quantum chemical calculations yielded the structure of the six low laying isomers of $C_4H_4^+$ to be methylene 14 cylopropane cation (a), cyclobutadiene cations (b). 1,2,3-butatrilene ($H_2CCCCH_2^+$) (c), 1-buten-3-yne cation ($HCCCHCH_2^+$) (d), buta-1,3-diene-1,3-diylium ($H_2CCCHCH^+$) (e) and buta-1,3-diene-1,4-diylium (HCCHCHCH) (f). Similar isomers with somewhat different relative energies were found in previous calculations.[7, 10-12, 41] $C_4H_4^+$ ions tagged with Ar atoms were obtained from discharged mixture of acetylene and argon and studied by vibrational photodissociation technique.[16] The spectrum of the Ar-tagged ions shows an intense doublet ($\Delta\nu$ =14 cm^{-1}) centered at 3117 cm^{-1} with a set of weaker transitions in the C–H stretching region of 2900–3300 cm^{-1}. The lower frequency range featured two strong bands at 1284 and 1450 cm^{-1}. The two strong bands were assigned to cyclobutadiene cations based on the good agreement of the observed frequencies with the results of the quantum chemical calculations.[16] The spectrum measured in He droplets in Fig. 5 shows medium intensity bands at 3115.7 and 3134.5 cm^{-1} in close proximity with the C-H stretching band of cyclobutadiene ion identified in ref.[16]. The calculated spectrum of cyclobutadiene cations in Fig. 5 (b) have two bands at 3117 and 3156 cm^{-1}. However the frequency difference is larger than observed in ref. [16] and the relative intensities differ from the calculations. Therefore, the bands cannot be unambiguously assigned to cyclobutadiene cations and may belong to some different isomers. The spectrum in Fig. 5 contains large number of bands which hint on the presence of multiple isomers. Some of those bands are in the vicinity of the weak bands previously observed in ref.[16]. The three intense bands at 2993.2, 3012.1, and 3250.8 cm^{-1} do not match the spectra of any $C_4H_4^+$ isomer calculated in ref.[16] or in this work. An intense high-frequency band at 3250.8 cm^{-1} indicates the presence of some open chain isomer of $C_4H_4^+$ with an acetylenic group such as in the $HCCCHCH_2^+$ isomer in panel (d). However, the spectra of this isomer calculated in ref.[16] and in this work show only very weak bands around 3000 cm^{-1}. On the other hand, calculations predict intense bands around 3000 cm^{-1} for the $H_2CCCCH_2^+$ (c) and $HCCHCCH_2^+$ (e) isomers. Therefore, we concluded that the spectrum in Fig. 5 is consistent with the presence of cyclobutadiene ions (b) and several open chain isomers of $C_4H_4^+$, such as $HCCCHCH_2^+$ (d), $H_2CCCCH_2^+$ (c), or $HCCHCCH_2^+$ (e). The identification of the open chain isomers will require more work in the future. The presence of open chain $C_4H_4^+$

among the products is interesting because they may serve as intermediates for the further condensation reaction with acetylene molecules leading to some larger products.

3.6 $C_4H_5^+$ ions.

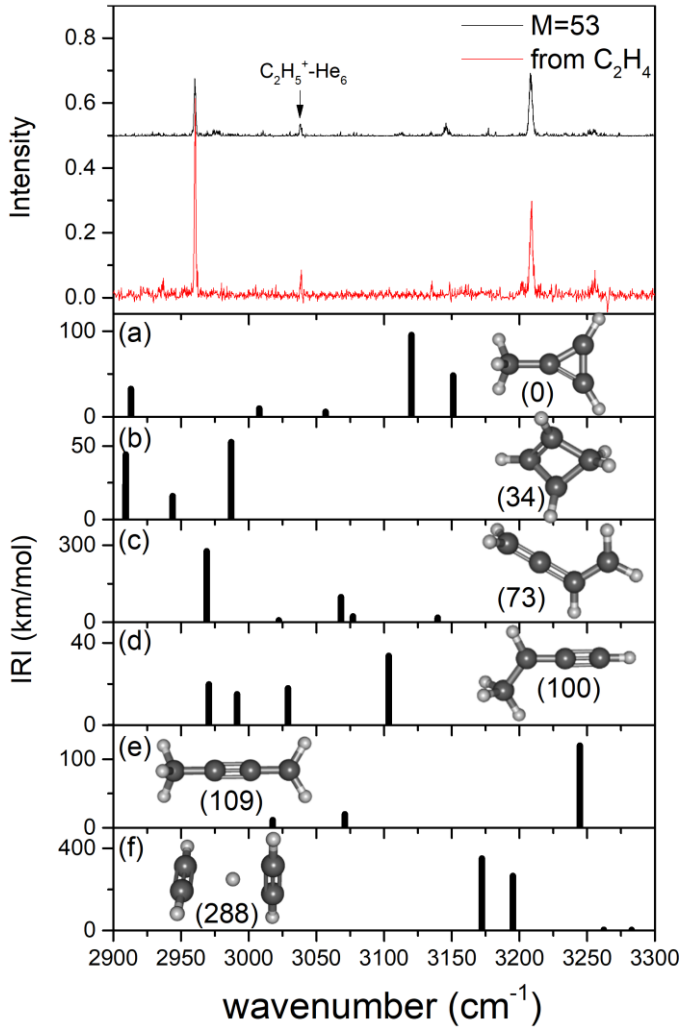

Figure 6. Comparison of the measured spectra of $C_4H_5^+$ (upper panel) and calculated (lower panel) spectra of $C_4H_5^+$. The spectra in the upper panel were recorded at M=53. Black trace from acetylene precursor measured in this work. Red trace from ethylene precursor, unpublished results from Ref. 23 . The lower panels show the spectra calculated for different isomers of $C_4H_5^+$ at MP2/aug-cc-pVDZ level of theory. The frequencies were scaled by a factor of 0.95. The inserts show the structure of the isomers and their relative energies in kJ/mol units.

Upper panel in Fig. 6 shows the spectrum of $C_4H_5^+$ ions recorded at M=53. The black trace was recorded in this work. Red trace was obtained during our previous measurements using ethylene precursors.[23] Both spectra show two prominent bands at 2960.2 and 3208.2 cm^{-1}, as well as some weaker features at 3038, 3146, and 3256 cm^{-1}. The similarity between the spectra indicates that the same isomers of $C_4H_5^+$ are produced in ion-molecule reactions involving ethylene and acetylene clusters. The difference of relative intensity of the strong bands is likely an effect of the inconsistent laser energy output in different spectral ranges. The measurements were done about two months apart from each other. Due to the nonlinear dependence of the intensity vs laser pulse energy[23], the intensity becomes very sensitive to variations of the laser pulse energy. The band at 3038 cm^{-1} was previously observed in the spectra of the $C_2H_5^+$ ions.[22] Therefore the weak band at the same frequency in Fig. 6 may stem from $C_2H_5^+$-He_6 clusters.

The low energy isomers of $C_4H_5^+$ were calculated to be the methylcyclopropene cation (a), protonated cyclobutadiene (b), allyl chains: $CH_2CHCCH_2^+$ (c) , $H_3CCCCH_2^+$ (d) and $H_3CCHCCH^+$ (e) and the proton-bound acetylene dimer (f). Similar isomers with somewhat different relative energies were found in previous calculations. [4243] The calculated spectra for the methylcyclopropene cation, protonated cyclobutadiene, allyl chain and proton-bound acetylene dimer in this work are in good agreement with previous calculations at the same level of theory.[42]

The C-H spectrum of the Ar tagged $C_4H_5^+$ ions produced upon co-expansion of acetylene with Ar passing through a discharge revealed two strong bands at 3129 and 3158 cm^{-1} with similar intensity, and some very weak features in the range of 2800–3100 cm^{-1}.[42] The spectrum was assigned to proton bound acetylene dimers.[42] On the other hand, the study of the electronic excitation spectrum ($\tilde{B}^1A' \leftarrow \tilde{X}^1A'$) of the Ne-tagged $C_4H_5^+$ produced upon co-expansion and discharge of 3-bromo-1-butyne was assigned to 1-butyn-3-yl ($H_3CCHCCH^+$) (panel d) cations based on the progression of vibronic bands.[43] The measured spectra in Fig. 6 show two strong bands at 3208 and 2960 cm^{-1} that cannot be assigned to the proton bound acetylene dimer (panel (f)). [42] The band at 2960.2 cm^{-1} is in the frequency range of the methyl group.

We found that the spectra of the calculated $H_3CCHCCH^+$ (d) and $H_3CCCCH_2^+$ (e) cations disagree with the measurements as they have different band patterns. The calculated spectrum of the methylcyclopropene cation exhibits the closest resemblance to the experimental spectrum. Accordingly, the low frequency band is due to the CH_3 group, and the two high frequency bands at 3208.2 and 3256 cm^{-1} are due to symmetric and antisymmetric bands of the H- atoms of the

cyclopropene group. It occurs that the ionization of the acetylene trimers in He droplets yields the lowest energy methylcyclopropene cation isomers (a).

3.7. The formation of cations from acetylene clusters.

The pickup pressure dependence of the signals discussed in SM2 show that $C_4H_2^+$ and $C_4H_3^+$ are predominantly formed upon the EI ionization of He droplets containing acetylene dimers. $C_4H_4^+$ ions are formed from acetylene dimers, with some contribution from trimers. $C_4H_5^+$ ions are formed from acetylene trimers. Quantum chemical calculations show that neutral acetylene dimers have T-shaped configuration.[5, 12] The T-shape configuration was also confirmed by the recent IR spectroscopic study of the dimers in helium droplets.[44] Quantum chemical dynamics calculations show that the near threshold ionization of the acetylene dimers leads to the initial formation of open chain aliphatic (C_2) or open chain bridged $C_4H_4^+$ ions.[5, 10, 11, 13] These isomers are separated by a very small barrier and evolve over small barriers into stable isomers. Molecular dynamics calculations show that the incipient isomers evolve into cyclobutadiene, methylenecyclopropene and 1,2,3-butatriene ions on a sub-picosecond timescale. For vertical ionization of the dimers at 10.75 eV, the trajectories yield the above isomers with the probability of about 35, 57, and 8%, respectively.[11] The formation of the $C_4H_2^+$ and $C_4H_3^+$ ions from the dimers require higher ionization energy of about 12 eV.[12]

In this work, the droplets are ionized by electrons having energies of 100 eV. The electron ionization cross section of acetylene molecules is an order of a magnitude larger than that for He atoms. However, because the droplet contains about 5000 He atoms, the primary products of the electron impact are He^+ ions and He* excited atoms which are produced in a ratio of about 1:3.[45] The mean free path of 100 eV electrons was estimated from the total inelastic collision cross section to be about 10 nm,[45] whereas the average diameter of the droplets in this work is about 4 nm. Therefore, the EI leads to the creation of a single ion or excited atom in the droplet. He^+ ions form He_2^+ and He_3^+ units with dissociation energy of about 2.6 eV and a solvation energy in He droplet of about 1 eV.[46] Excited He* atoms evolve into He_2^* excimers. Helium ions have energy in excess of 21 eV and excimers in different electronic states have energy in excess of about 18 eV.[47] This is larger than required for the ionization of the acetylene dimers of about 11 eV and for creation of the $C_4H_2^+$ and $C_4H_3^+$ ions. He_2^* excimers only have a weakly bound state on the surface of the droplets and move towards the surface. Therefore, it is plausible that the acetylene dimers

which reside in the interior of the droplet are primarily ionized by charge transfer from helium ions.

Ionization of acetylene molecules and small clusters by 90 eV electrons in a molecular beam were found to produce C_2^+, C_2H^+, $C_2H_2^+$, $C_2H_3^+$, $C_4H_3^+$, $C_4H_4^+$, and $C_4H_5^+$ [11] in agreement with our results in Fig. 1. The ionization of the dimers involves removal of an electron from the HOMO $1\pi_u$ or inner $3\sigma_g$, $2\sigma_u$, and $2\sigma_g$ orbitals of the acetylene molecule in the dimer. Only the ionization from the $1\pi_u$ orbital yields $C_4H_4^+$ ions. Calculations show that upon the vertical ionization of acetylene dimers, different isomers of $C_4H_4^+$ are formed within less than about 400 femtoseconds and with excess vibrational energy of about 3-4 eV.[11] The experimental observations of the $C_4H_4^+$ ions indicates that those highly vibrationally excited ions avoid fragmentation during the time of flight.[11] In comparison, $C_4H_3^+$ ions are formed upon ionization from the HOMO $1\pi_u$ as well as the inner orbitals of acetylene. Calculations show that the formation of the $C_4H_3^+$ (and $C_4H_2^+$) ions requires about 1.5 eV higher energy than the vertical ionization energy of the dimers.[12]

The ionization of acetylene molecules and clusters via charge transfer from He_2^+ or He_3^+ ions have an excess energy of about 10 eV as compared with the vertical ionization energy of the acetylene dimers. Moreover, the ion-molecule reactions in this work occur within the liquid helium surrounding of the droplets. The product ions captured by the droplet cool to the droplet's temperature of 0.4 K before they experience laser excitation. If the formation of the isomers upon ionization proceeds faster than the energy exchange with the helium environment, the isomers probed in this work may reflect the nascent distribution. However, the rate of the relaxation of the highly vibrationally excited ions in liquid helium is currently unknown. IR spectroscopic studies usually address the fundamental vibrations which linewidth was found to be in the range of 1 to 10 cm^{-1} giving an estimate for the relaxation time between 5 ps and 500 fs.[24] The relaxation rate may be faster for ions taking into account the stronger interaction of the ions with He atoms.

Calculations also show that larger $C_6H_6^+$ cations such as allyl–cyclopropenyl, vinyl–cyclobutadiene and benzene ions are formed upon ionization of larger acetylene clusters. The formation of the larger carbo-cations is facilitated by the transfer of the reaction energy to the spectator acetylene molecules in the cluster.[10, 14, 15] Quantum molecular dynamics calculations show that among the trajectories leading to covalently bound $C_6H_6^+$ starting upon ionization of the acetylene tetramers about 20% of the trajectories yield benzene ions.[10] The calculated yield of benzene ions increases upon ionization of the larger acetylene clusters. On the other hand, it was

found that even in the larger acetylene clusters the formation of the different ions is strongly tilted towards $C_4H_4^+$ with the yield of covalent $C_4H_4^+$, $C_6H_6^+$, and $C_8H_8^+$ products to be in the ratio of about 58, 40, and 2 % obtained upon ionization of acetylene clusters containing 20 molecules.

The mass spectrum obtained upon ionization of larger clusters in helium droplets in Fig. 1 shows some pronounced peaks due to $C_6H_5^+$ and $C_6H_6^+$, which could not be identified among the major infrared peaks in Fig. 2. Some broad feature around 3240–3270 cm^{-1} appears at higher pickup pressure. This frequency range is close to the 3236 cm^{-1} where the band of the large neutral acetylene clusters was observed.[48] Therefore, the broader features are tentatively assigned to the absorption of acetylene molecules in clusters containing an ionic core with some loosely attached acetylene molecules, similar to our recent work on ethane.[22] The total ion yield spectrum does not indicate any prominent peak around 3097 cm^{-1} which could be identified with benzene ions.[49] This may indicate that the formation yield of the benzene ions in our experiments is small. In the future, we plan some more studies into the origin of the ions containing six and more carbon atoms.

4. Conclusions

In this work, we employed IR spectroscopy to study the products of ion-molecule reactions upon ionization of acetylene dimers and trimers in He droplet matrices. Acetylene clusters are formed within helium droplets after their pickup in vacuum. The doped droplets are ionized by EI, leading to the formation of $C_4H_2^+$, $C_4H_3^+$, $C_4H_4^+$, and $C_4H_5^+$ cations. The formed cations may be ejected, or stay trapped inside the He droplets where they thermalize to the host's temperature of 0.4 K. The vibrational excitation of ions by a pulsed IR laser leads to droplet evaporation and the release of free ions that are detected via mass spectrometry. IR spectra are recorded by monitoring the signal of bare ions as the laser frequency is scanned.

We found that the ionization of the acetylene dimers and trimers yields diacetylene - $C_4H_2^+$, vinylacetylene - $C_4H_3^+$ and methylcyclopropene - $C_4H_5^+$ cations, which are the lowest energy isomers for the corresponding ions. In comparison, the spectrum of $C_4H_4^+$ shows the presence of several isomers which could not be unambiguously identified. The isomers may include cyclobutadiene, based on the close proximity of the band frequencies to those found in previous molecular beam studies.[16] The other prominent bands hint at the presence of some open chain aliphatic isomers, such as $HCCCHCH_2^+$, $H_2CCCCH_2^+$, or $HCCHCCH_2^+$. The presence of $C_4H_4^+$ among the products is interesting because it may serve as an intermediate for the further

condensation reactions, leading to some larger products. Quantum chemical calculations show that the ionization of the acetylene dimers yields cyclobutadiene, methylenecyclopropene and 1,2,3-butatriene ions. [5, 10, 11, 13] The identification of the linear isomers will require more work, which may involve using different tetracarbon precursor molecules, such as methylcyclopropene, cyclobutene or different chain hydrocarbon molecules. Calculations predicted that the cations containing six carbon atoms such as allyl–cyclopropenyl, vinyl–cyclobutadienyl and benzene ions could be formed upon ionization of acetylene clusters.[10, 14, 15] Future IR spectroscopic studies should test this prediction and determine if $C_6H_N^+$ cations, which were observed in the mass spectrum, are covalently bound or merely the complexes of $C_4H_N^+$ cations with acetylene molecules. In relation to the mechanism for the formation of the larger cyclic ions, it would also be desirable to expend the studies to ionization of the dimers of larger unsaturated molecules, such as allene and propyne. Due to its mass and isomer specificity, ionization in He droplets is a fruitful technique to study the diverse products of ion-molecule reactions at ultra-low temperatures.

Supplementary Materials (SM)

The supplementary materials contain two additional figures. Fig. S1 shows the mass spectra measured with laser parked at the spectral peaks due to $C_4H_2^+$, $C_4H_3^+$, $C_4H_4^+$, and $C_4H_5^+$ cations. Fig. S2 shows the acetylene pickup pressure dependence of the signal for $C_4H_2^+$, $C_4H_3^+$, $C_4H_4^+$, and $C_4H_5^+$ ions upon electron impact ionization of doped droplets.

Acknowledgements

This work was supported by the NSF under Grant Nos. CHE-1664990 and CHE-2102318 (A.F.V.) and by the Korea Institute for Advancement of Technology (KIAT) grant funded by the Korea Government (MOTIE) (P0017310, Human Resource Development Program for Industrial Innovation (global)) and by Korea Basic Science Institute (KBSI) National Research Facilities & Equipment Center (NFEC) (No. 2019R1A6C1010042) from the Ministry of Education of Korea. (M.Y.C).

Author Declarations

Conflict of Interest

The authors have no conflicts to disclose.

Author Contributions

Cheol Joo Moon: Conceptualization (supporting); Data curation (equal); Formal analysis (lead); Investigation (equal); Visualization (lead); Writing – original draft (supporting).

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Data Availability Statement

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

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