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Hydrocarbon growth via ion-molecule reactions: Computational studies of the isomers of $C_4H_2^+$, $C_6H_2^+$ and $C_6H_4^+$ and their formation paths from acetylene and its fragments

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Abstract

We seek insight into the origin of observations made in plasma experiments mimicking interstellar and circumstellar conditions. To this end theory is applied to the low-energy isomers of $C_4H_2^+$, $C_6H_2^+$ and $C_6H_4^+$ and their formation paths from acetylene and its fragments. *Ab initio* molecular dynamics trajectories are performed to explore which isomers are readily accessible from acetylene and its ion fragments. Structural information at a high level of electronic structure theory [CCSD(T)/cc-pVTZ], as well as information on the vibrational [UMP2] and electronic spectra [wB97X] of the low-energy isomers is reported.

I. Introduction

Complex organic molecules and ions have been discovered in the interstellar gas clouds, including some large acyclic hydrocarbons, polycyclic aromatic hydrocarbons (PAH), fullerenes, nitrogen and oxygen containing hydrocarbon, and even some inorganic molecules.[1] Laboratory and computational investigations have helped in identifying these molecules from astronomical data. Organic molecules with biological significance have also been found embedded on meteorites and comets. How these complex organic species arise is as yet unknown.[2]

Small carbon molecules can form and grow in the circumstellar envelopes surrounding carbon rich stars, and in asymptotic giant branch stars that produce carbon in their cores. Larger polycyclic aromatic hydrocarbons are synthesized in the outflow of carbon rich stars, and are known to exist in many environments in space.[3] In the diffuse and dense interstellar medium (ISM) small molecule formation, PAH cluster formation, evolution, and destruction of molecular species are known to occur. Complex and as yet incompletely understood chemistry occurs in these exotic environments driven by extreme temperature, shock, radiation field, and density. Some theories of how these large organic molecules such as PAHs are formed in the ISM have been proposed.[4] These include the well-known hydrogen abstraction acetylene addition (HACA) mechanism,[5]– a repetitive abstraction of hydrogen atom followed by acetylene addition, as well as some possible ionic mechanisms[6] for their formation. Recently the HACA mechanism has been shown to be operative through formation of naphthalene.[7]

Acetylene is likely to play an important role in the formation of unsaturated hydrocarbons, as has been pointed out by various experimental,[8,9] and theoretical studies.[10-12] Clustering of acetylene molecules under ionizing radiation has been shown to produce benzene and polycyclic aromatic hydrocarbons under a variety of conditions.[8,9,13-16] Growth of carbonaceous molecules has been shown to proceed starting from acetylene in low-density selected ion flow tube experiments,[13] as well as in plasma conditions.[14-16] These processes have been probed using mass spectrometry and various spectroscopic techniques. The product distributions in these experiments are influenced by the conditions of these experiments, which may indicate the feasibility of such molecules forming in specific space environments. Flow-tube experiments[13] show that ion-molecule reactions of acetylene with acetylene fragments, may produce complex molecules including cyclic molecules after successive additions. In low-pressure plasmas also, acetylene produces larger mass molecules made of carbon and hydrogen via hydrocarbon plasma chemical reactions,[14] such as through ion-molecule mechanisms. Heteroatoms, such as nitrogen and oxygen, can be incorporated into the carbon framework, and even into the cyclic framework, in the process of simple associative growth.[10, 17] However, formation mechanisms of larger hydrocarbon molecules via the plasma chemical reactions are not yet understood in any detail. Both experimental and computational investigations into the process of hydrocarbon growth in low-temperature gases or in the plasma can potentially reveal key information about the likelihood of formation of large hydrocarbon species in specific astronomical environments, and their detectability.

Towards this goal, Contreras and Salama created an instrument called the COSmIC in which they produce reactive plasmas of carbon bearing molecules mimicking interstellar and circumstellar conditions.[8] For analysis of the resulting species COSmIC includes an orthogonal reflectron Time-of-Flight Mass Spectrometer (TOFMS) and a cavity ring-down spectrometer (CRDS) to probe electronic spectra. Employing a range of simple hydrocarbon molecules including acetylene as feedstock gas, the COSmIC chamber can create a range of reactive plasmas to be probed by these spectroscopic and spectrometric techniques. When using acetylene as feedstock gas, Contreras and Salama observed a number of mass fragments in the TOFMS that indicated growth of the carbon framework.[8] Some of these peaks stood out with very large intensities compared to others, and indicated plausible routes for carbon framework growth. Some of the acetylene mass fragments are C_2^+, C_2H^+ and $HCCH^+$. The most intense mass fragment beyond C2 species appeared at 51 amu ($C_4H_3^+$) and followed by one that appeared at 50 amu ($C_4H_2^+$). Some other peaks that suggest association of three two-carbon units appeared at m/z values of 74, 75 and 76 (possibly reflecting $C_6H_2^+$, $C_6H_3^+$ and $C_6H_4^+$ respectively).

We have been investigating the growth of the carbon framework in the acetylene plasma via two-carbon unit additions. In this manuscript we report the growth process by concentrating on three radical cation species: $C_4H_2^+$, $C_6H_2^+$, and $C_6H_4^+$. Nominally, these species can be synthesized in the COSmIC experiment, or in other plasma experiments, by the association of C_2 with $HCCH^+$ (or vice versa), and successive addition of either C_2 or HCCH. Most astrochemical reactions of this size, however, are dissociative attachment i.e. of the type: A + B = C + D. Therefore, other asymptotes for their formation involving different precursors are not ruled out, and we consider them in our discussion in the results section. In a separate forthcoming manuscript[18] we explore the potential energy surface of the three additional closed shell cation fragments that are also created in the COSmIC experiment: $C_4H_3^+$, $C_6H_3^+$, and $C_6H_5^+$.

Investigation of these species is interesting from another perspective. Small hydrocarbon ions have been recently investigated as some of their electronic transitions fall in the vicinity of known diffuse interstellar bands (DIBs), which are hundreds of enigmatic large intensity transition lines whose origin are not yet established. Recent identification of C_3 in the diffuse interstellar clouds raised the possibility that small hydrocarbon chains and rings could be amongst the carriers of DIBs.[19] For instance, the homologous series of polyacetylene cations (such as $C_6H_2^+$) have electronic excitation bands of $\tilde{A}^2\pi \leftarrow X^2\pi$ type that fall in the range of DIB observations.[19] Small carbon chains up to twenty carbon atoms, and rings with up to a hundred carbon atoms, their radicals, and ions remain as attractive candidates of DIB carriers. In this manuscript we report the electronic absorption excitation energies of not only the global minima, but also of all the low-lying isomers of $C_4H_2^+$, $C_6H_2^+$ and $C_6H_4^+$.

Here we restrict ourselves to the $C_xH_y^+$ type of complexes where both x (4,6) and y (2,4) are even integers, and the resulting products are all open-shell radical cations. In a separate paper[18] we examine closed-shell hydrocarbon cations having the general formula, $C_xH_{y+1}^+$. Our goals in this paper are many fold. Firstly, we explore the doublet potential energy surface of three molecules $C_4H_2^+$, $C_6H_2^+$, and $C_6H_4^+$, and characterize the low-lying isomers using accurate *ab initio* quantum chemistry methods. Secondly, we explore the formation pathway of the first carbocyclic rings starting from acetylene and its fragments in a plasma environment. Thirdly, we compute the vibrational harmonic frequencies and intensities of the isomers, and the electronic excitation spectra and oscillator strengths of the isomers to aid with their laboratory and astronomical observation. We want to investigate how the electronic spectra of the hydrocarbons are different from those of the pure carbon species, and what effect varying degrees of hydrogenation has on them. Finally, we have computed the structures and relative energies of the isomers using multiple theoretical methods, and compared them with results from highly reliable coupled cluster methods in order to benchmark their suitability to predict the structural, energetic and spectroscopic parameters.

II. Theoretical Methods

We obtained accurate geometrical parameters using coupled cluster singles and doubles with perturbative triples CCSD(T)[20] along with Dunning's correlation consistent valence triple zeta basis set (cc-pVTZ).[21] Coupled cluster calculations were performed using the MOLPRO 2008 quantum chemistry package.[22]

In addition to investigating the growth of larger oxygen containing molecules using accurate benchmark quantum chemical coupled cluster methods, we compared the performance of the more computationally affordable methods for future studies. We used the unrestricted second order Møller-Plesset perturbation theory (UMP2) to optimize the geometries. In some cases the underlying unrestricted Hartree-Fock (UHF) reference showed significant spin contamination, which can lead to poor UMP2 results. Therefore, we also optimized geometries using second-order Z-averaged perturbation theory (ZAPT2) based on a symmetric spin orbital basis.[23, 24] ZAPT2 also reduces the computational cost compared to unrestricted perturbation theories.[25, 26]

Finally, we optimized geometries with the hybrid B3LYP density functional method.[27, 28] We computed the harmonic vibrational frequencies and intensities using the double harmonic approximation with the B3LYP/cc-pVTZ method. In addition, we computed the energies of the isomers using the meta-GGA functionals M06-2X and M11 due to Truhlar and co-workers,[29, 30] and with ωB97X, a range-separated density functional due to Chai and Head-Gordon.[31] We used ωB97X to compute the electronic spectra employing time dependent density functional theory (TDDFT). In order to gain better insight into the potential energy surfaces, we performed *ab initio* molecular dynamics (AIMD) calculations using the M06-2X functional, with time steps of 1.21 fs

(50 a.u.) and for simulation times of 1.2 ps (1000 time steps). We used an initial random orientation of the reacting fragments and provided a minimal amount of thermal energy (50K) to initiate the motion of the nuclei. We employed the Q-Chem 4.1 quantum chemistry package[32] for all the perturbation theory, DFT, and AIMD computations. In order to identify all low-lying isomers, we performed an automated unbiased stochastic search, called Kick,[33] to locate minima on the doublet potential energy surfaces of $C_4H_2^+$, $C_6H_2^+$, and $C_6H_4^+$.

III. Results and Discussion

We have studied the structures of the lowest energy isomers of $C_4H_2^+$, $C_6H_2^+$ and $C_6H_4^+$. Our investigation of the potential energy surfaces of these three ions have been motivated by the observation of their respective masses in a previous experiment conducted by Contreras et al.[8] C_2^+, among others, is a significant component of the fragments produced in the experiment, when acetylene was used as a feedstock gas.[6] Associative addition of HCCH with C_2^+ can lead directly to $C_4H_2^+$. Further association of either C_2 or HCCH may lead to the formation of $C_6H_2^+$ or $C_6H_4^+$. Therefore, this series of hydrocarbon cations can be synthesized in an ionizing discharge environment via addition of even-carbon units, and their respective ions, via ion-molecule reactions.

$C_4H_2^+$

In the acetylene plasma experiment coupled with the time-of-flight mass spectrometer, the mass fragment 50 amu (presumably $C_4H_2^+$) was the second largest peak recorded, apart from C2 fragments[8] The largest peak was of mass 51 amu ($C_4H_3^+$). Based on other fragment ions recorded by the experiment it is likely that $C_4H_2^+$ was synthesized by an association of $HCCH^+$ and HCCH, followed by the elimination of H_2. In an earlier study Knight et al.[13] showed that the two dominant channels that follow the reaction of HCCH with $HCCH^+$ lead to the formation of $C_4H_2^+$ and $C_4H_3^+$, with branching ratios of 0.43 and 0.49 respectively. C_2H^+ constitutes the second largest concentration of two-carbon ions that can directly originate from acetylene and therefore can serve as a reactant for growth.

The largest concentrations of product neutrals and ions in this plasma are those of C_4H_2 (and its ion $C_4H_2^+$), and C_6H_2 (and its ion $C_6H_2^+$).[16] The rate constants of such reactions are very fast, and in the range of 10^{-9} cm^3/s.[13, 16] In low-pressure plasma conditions, reaction of HCCH with C_2H^+ serves as one of the main routes to formation of $C_4H_2^+$, after a loss of H atom.[14] An association reaction of C_2^+ with HCCH can also form some isomers as discussed in the next section. But as Knight et al. pointed out that there could be multiple isomers, and the actual predominant route to formation of those isomers are dependent upon the environmental conditions; most importantly, pressure. Reaction of HCCH with $HCCH^+$ can also form $C_4H_4^+$ under some conditions,[34], but is a less significant process[13] due to the large internal energy of the products[17].

The preponderance of fragments with even numbers of carbon atoms found by Contreras et al. shows that the C-C triple bond largely stays intact in the plasma experiment involving acetylene.. Major growth of the carbon framework, therefore, occurs via the increment of two-carbon units, with the addition or subtraction of hydrogen afterwards. In a separate study Angelova et al.[35] showed that the neutral four carbon units (C_4H_p) are the predominant reaction product when ionic $C_4H_{p+q}^+$ undergoes dissociative recombination with electrons, which indicates that the four-carbon hydrocarbon ions occur in stable isomeric form. These studies, however, do not give any information about the structures of the isomers of $C_4H_2^+$, their spectroscopic properties, and the growth process.

We explored the doublet potential energy surface of $C_4H_2^+$ ion, and found eight low-lying isomers within about 50 kcal/mol of the global minimum. The relative energies of the isomers are presented in Table 1 using the B3LYP, M06-2X, M11, ωB97X, UMP2, ZAPT2 and CCSD(T) levels of theory with the cc-pVTZ basis set. The structures of the isomers of $C_4H_2^+$ are presented in Figure 1 at the CCSD(T)/cc-pVTZ level of theory. 1,3-butadiyne ion (i.e. diacetylene ion) is the global minimum. It is followed by a four-membered cyclic isomer (beta-cyclobutadienediide ion) 33.68 kcal/mol above at the CCSD(T)/cc-pVTZ level. The third lowest energy isomer is H_2CCCC^+, and is 38.98 kcal/mol above. Isomers A4, A5, A6, A7, and A9 are cyclic in nature, and are located 40.90, 42.46, 44.26, 46.59 and 51.85 kcal/mol above the global minimum.

The relative energies of the isomers predicted by different methods vary significantly as seen from Table 1. B3LYP density functional predicts the relative order of the isomers correctly, except for one pair, isomers A5 and A6, with respect to the CCSD(T) predicted order. Both ωB97X and M11 density functionals predict the same relative order of the isomers. However, when compared with CCSD(T), the relative ordering of the isomers differ for four pairs of isomers. Relative energy ordering differs from the CCSD(T) significantly. Moreover, the energies predicted by UMP2 also vary significantly for most isomers, in the case of isomer A2 by as much as 15.88 kcal/mol as compared to CCSD(T). The largest difference between the ZAPT2 predicted relative energies, compared to CCSD(T), is 13.95 kcal/mol. In an earlier study Zhao et al.[36] predicted the structures and relative energies of the isomers of $C_4H_2^+$ using CCSD(T)/6-311+G(2df,2pd)//B3LYP/6-311+G(d,p) level of theory. Their relative ordering of the isomers match with the relative ordering we predict using higher levels of theory.

The potential energy surface of $C_4H_2^+$ is quite complicated. The global minimum is separated by at least 33.7 kcal/mol or more from the other isomers, which are rather close to each other in terms of energy. However, these isomers may have large barriers to cross to interconvert to one another. Direct association of C_2^+ with HCCH may lead to A4, which has a triangular structure. We have computed the transition state that interconverts A4 to A5 with a barrier height of 60.1 kcal/mol at the B3LYP/cc-pVTZ level of theory, and the transition state that connect A5 with A1 (diacetylene cation), with a barrier height of 5.3 kcal/mol. This is the simplest way for the formation of diacetylene ion starting from HCCH and C_2^+, both observed in the plasma experiment of Contreras et al.

To further explore the formation mechanism of $C_4H_2^+$ ions, we performed a total of 50 AIMD calculations on the doublet surface starting from a random orientation of C_2^+ and HCCH. Interestingly, within the 1.2 ps timescale of our simulation, all reactive trajectories (84% of the calculations) reached the global minimum. Analysis of the trajectories revealed that 70% of the calculations went through a first encounter complex (FEC) with a geometry similar to A4, while the remaining calculations went through a FEC with geometries closer to A6. Despite a barrier of 60.1 kcal/mol, the dynamics from the reacting fragments C_2^+ and HCCH easily reach the global minimum because A1 is more than 200 kcal/mol more stable than the reactants.. For this formation path, trapping in other local minima therefore appears unlikely, as a result of the very large initial kinetic energy release.

The harmonic vibrational frequencies of the isomers of $C_4H_2^+$ are presented in Table 2. The lowest five electronic excitation energies, computed using a range-separated density functional ωB97X, for the isomers of $C_4H_2^+$, along with their oscillator strengths, are presented in Table 3. The most intense electronic transition is from the ground state to the third excited state of the global minimum diacetylene ion and occurs at 3.38 eV (~366 nm). There has been considerable attention paid to the $^2\pi \leftarrow X^2\pi$ transition of $HC_{2n}H^+$ type radical cations for their possible role in the diffuse interstellar bands,[37] including HC_4H^+.[38] In Table 3 we list the electronic excitation energies of the linear diacetylene cation, but also those of the other nine isomers. These TDDFT estimates of electronic excitation energies for all isomers indicate that, like the global minimum diacetylene (A1), the other isomers also have excitation energies that fall in the near infrared to the UV/Vis region. Isomers A4, A5, A7 and A8 have at least one excitation that is as strong as that of the global minimum.

Although neutral diacetylene has been observed in the interstellar medium,[39] neither diacetylene cation nor any of its isomers have been identified. Due to the nature of the potential energy surface and the structure of the isomers it is possible for one of the cyclic isomers to be long lived even though it is not the lowest energy form. For example, both the “linear” and cyclic isomers of $C_3H_3^+$ are routinely found in laboratory experiments even though there is a large energy difference between them,[40, 41] which is attributed to different formation mechanisms. Relatively high-energy structural isomers of triacetylene have been observed in the circumstellar envelops of evolved stars.[42]

$C_6H_2^+$

In the COSmIC plasma experiment of Contreras et al. mass fragment 72 amu ($C_6H_2^+$) was recorded. Herrebout et al. and Bleeker et al. showed that $C_6H_2^+$ is the most abundant ion, after $C_4H_2^+$, produced in other acetylene discharge plasma experiments.[15, 16] $C_6H_2^+$ can be synthesized by the direct association of C_2 with $C_4H_2^+$, both of which are produced in large quantities in the plasma experiments. Dissociative attachment type reactions involving other precursors is a major pathway of producing ions without excess internal energy, although the most favored asymptote of its formation will be dependent on the conditions. As a known example, in a flow-tube study involving reaction between HCCH and C_4H^+, $C_6H_2^+$ is produced almost exclusively.[13] In low-pressure acetylene plasma experiments the dissociative attachment of C_4H_2 and C_2H^+ can produce C_6H_2 and H^+.[14]

We explored the doublet potential energy surface of the $C_6H_2^+$ mass fragment seen in the experiment and located nine low-lying isomers within 50 kcal/mol of the global minimum. In Table 4 the relative energies of all the isomers are presented at various levels of theory for comparison. The first few isomers are well separated by energy, and in terms of their spatial connectivity. The global minimum is the linear hexatriene cation. The nearest two lowest energy isomers are 20.93 and 29.94 kcal/mol above the global minimum at the CCSD(T)/cc-pVTZ level. Other low-lying isomers are 32.84, 38.70, 40.32, 41.38, 43.29, 48.70 kcal/mol above the global minima respectively. The structures of all nine isomers are presented in Figure 2 at the CCSD(T)/cc-pVTZ level of theory. The lowest energy cyclic isomer, B2, is 20.93 kcal/mol above the global minimum, and is the second lowest energy isomer overall.

From the results presented in Table 4 we can see that the M06-2X, M11 and ωB97X functionals predict the relative energies very well when compared with the relative energies computed using CCSD(T). These functionals predict the relative order of the isomers mostly correctly as well (correct up to B6 for M06-2X and M11, and correct all the way up to B8 for ωB97X). The B3LYP, UMP2 and ZAPT2 theories, however, do not compare as well with the CCSD(T) benchmark values. B3LYP makes significantly larger errors in the relative energies of the low-lying isomers (e.g. 13, 12, 14 and 14 kcal/mol for isomers B2-B5 vs isomer B1), presumably because of significant self-interaction error in B1). By contrast, the largest error in the relative energies of isomers B2-B5 relative to B1 using the M06-2X, M11, and ωB97 functionals are 3.6, 2.2 and 1.4 kcal/mol, respectively. UMP2 and ZAPT2 show largest relative errors of 10.6 and 0.98 [Roberto told me that earlier it had converged in a wrong electronic state; fixed now] kcal/mol respectively.

Triacetylene cation ($HCCCCCCH^+$) is the lowest energy isomer. But it may not be that easily accessed from the separated precursors. Hexapentaenylidine ($H_2CCCCCC$), a high-energy isomer, has been identified in the ISM,[42] although triacetylene (HCCCCCCH), the global minimum of the neutral, has not been observed thus far. The ion of hexapentaenylidine is the seventh lowest-energy isomer on the doublet potential energy surface of the cation, 41.38 kcal/mol above the global minimum, triacetylene ion. The results of the AIMD calculations on the association of $C_4H_2^+$ with C_2 found that all calculations reached linear isomers with structures similar to either B8, or other high-energy isomers. In this case, the initial precursors, their orientation, internal energies, and barrier heights will be important for the formation of specific isomers presented above.

The harmonic vibrational frequencies of all nine isomers of C_6H_2 are presented in Table 5. These were computed using the B3LYP functional along with the cc-pVTZ basis set. All the isomers presented in Figure 2 represent true minima on the doublet potential energy surface. The most important of these harmonic frequencies are those of the global minimum – appearing in the left-most column. However, the vibrational frequencies of the other isomers can also be important for the identification of higher lying isomers, especially as some of these isomers may represent minimum that are not easily converted to other isomers, but rather has a large barrier to cross. In Table 6 the first five electronic excitation energies are presented along with the associated oscillator strengths. Some of the electronic excitation energies are very small and appear in the visible, if not infrared region of the electromagnetic spectrum. The lowest excitation energy for the ground to the first excited state is 0.27 eV (4592 nm). An electronic excitation appearing in the infrared region where generally fundamental molecular vibrations appear is uncommon, but they do exist.[43] Fulara et al.[37, 44] observed three electronic transition lines of linear $C_6H_2^+$ at 417.2, 406.0 and 381.0 nm. Zhang et al. predicted the first four excitation energies to be 2.62, 3.93, 4.53, and 5.21 eV at the CASPT2 level of theory. The electronic excitations energies of the other isomers are have not been previously reported earlier to our knowledge.

$C_6H_4^+$

In the plasma experiment performed in the COSmIC chamber by Contreras et al.[8] the mass fragment 76 amu was found, and can be associated with $C_6H_4^+$. The signal strength of $C_6H_4^+$ is largest among all the C6 hydrocarbon ions detected. The concentrations of C6 species were smaller than those of the C4 species in the plasma chamber, due mainly to the lower concentration of C4 precursors relative to C2 ones. Knight et al.[13] showed that in a flow tube environment $C_4H_2^+$ combines with HCCH to produce $C_6H_4^+$. The branching ratio for the reaction between $C_4H_2^+$ and HCCH is almost 1 for the production of $C_6H_4^+$, and the rate constant for such process is of the order of 10^{-9} cm^3/s. An electron recombination with $C_6H_4^+$ will produce the neutral closed shell C_6H_4 molecule. Other asymptotes of its formation may involve reaction of $C_4H_4^+$ with C2, or the reaction of C_2^+ with C_4H_4.

In Table 7 we present the relative energies of the lowest sixteen isomers on the doublet potential energy surface of the $C_6H_4^+$ ion. These isomers span from 0 to 44 kcal/mol above the global minimum. The density of low-energy isomers on the PES is higher than that seen for either the $C_4H_2^+$ or $C_6H_2^+$ ions. The global minimum is a planar cyclic double dehydrogenated benzene ring, the meta-benzyne cation. Unlike in the case of diacetylene and triacetylene cations, which are linear, the $C_6H_4^+$ cation global minimum is cyclic. The geometric structures of the $C_6H_4^+$ isomers are presented in Figure 3. The second lowest energy isomer is only 8.42 kcal/mol above the global minimum, and is partially cyclic. The nearest fully cyclic isomer with a six-membered carbocyclic ring is 15.26 kcal/mol above the global minimum. Many low-energy isomers are branched carbon chains. Interestingly, the M06-2X, M11, and ωB97X density functionals that performed well for the lower energy isomers of $C_6H_2^+$ exhibit larger errors for the $C_6H_4^+$ ion (e.g. see the relative energies of C2 and C3 vs C1).

Fulara et al (2014)[45] reported using the geometrical structures and electronic excitation spectra of isomers of $C_6H_4^+$ the CCSD(T)/cc-pVDZ method. They reported twelve isomers on the doublet potential energy surface of $C_6H_4^+$. We report here 17 isomers on the doublet potential energy surface spanning a range of 43.89 kcal/mol using a significantly better basis set. Fulara et al. did not locate some relatively low-energy isomers including C3, C10, C12, C15 and C17. For isomers in common, the relative energy ordering presented in Table 7 matches the ordering calculated by Fulara et al.[45]

The harmonic vibrational frequencies are presented in Table 8 at the B3LYP/cc-pVTZ level of theory. All isomers presented in this study are found to represent true minima on the doublet PES, as evidenced by no imaginary vibrational frequencies, except one – isomer 8. The isomer C8, reported to be a minimum by Fulara et al. using the UHFfc-MP2/cc-pVDZ level, has an imaginary frequency of 273 cm^{-1}, when we used the UMP2/cc-pVTZ level of theory. These vibrational frequencies are presented here for comparison with those reported earlier. The lowest five electronic excitation energies and the oscillator strengths of $C_6H_4^+$ computed using ωB97X functional is presented in Table 9. Some of the isomers of $C_6H_4^+$ have very low excitation energies. The global minimum, meta-benzyne cation (isomer C1), has a number of low-energy electronic excitations in the IR and in the UV region, but most of them are devoid of any significant oscillator strength, except one. The ground state doublet to fourth excited doublet state excitation energy is 3.39 eV and has an oscillator strength of 0.0381. Fulara et al.[45] identified five isomers by comparing *ab initio* results with the excitation energies measured by Ne-matrix trapped cations. Three open chain acyclic (Isomers C4, C6, and C11), and two cyclic isomers (isomers C2, and C7) were identified by the joint experimental and theoretical exercise. Interestingly, the global minimum, meta-benzyne, was not identified in this laboratory study.

If we consider the major pathway for the formation of $C_6H_4^+$ to be an association of $C_4H_2^+$ with C_2H_2 as pointed out by Knight et al.,[13] then there is only one isomer that is suitable to be asymptotically connected with the global minima of these two precursors. The linear diacetylene cation can associate with acetylene via a Diels-Alder type [4+2] cyclization reaction to make the benzyne cation (C7), which is the seventh isomer on the doublet potential energy surface. The AIMD calculations of reaction between the lowest energy isomer of $C_4H_2^+$ and C_2H_2 were somewhat problematic, with many calculations failing to reach convergence on the doublet surface and only four calculations out of 50 reaching C7. In a more detailed analysis of the AIMD trajectories, we found no other association paths, however, we noticed a few calculations with linear FECs that failed to reach convergence after a few steps after their formation. Despite the fact that not enough AIMD calculations were run to be statistically significant, they still provide some confirmation for the results of Knight et al.[13] that the association between diacetylene cation with accetylene is likely the most probable pathway to the formation of cyclic $C_6H_4^+$ isomers. Other isomers are not readily accessible by direct association, but may become accessible if the barriers for their internal rearrangement are low. Sometimes the barriers to their inter-conversion are rather high.[46] A number of other isomers can be synthesized by the direct association of HCCH with some of the higher-lying isomers of $C_4H_2^+$ presented in figure 1, but we did not conduct any further calculations to identify these isomers or pathways.

IV. Concluding Remarks

In this work we have explored the low-lying isomers on the doublet potential energy surface of diacetylene cation ($C_4H_2^+$), triacetylene cation ($C_6H_2^+$), and $C_6H_4^+$. We found a number of isomers that can be stable and can potentially be identified by laboratory experiments. The linear diacetylene and triacetylene cations are global minima like their neutral counterparts. But second lowest energy isomers of both the molecules are cyclic isomers. The gap between the global minimum and the cyclic isomer (isomer above the global minimum) becomes smaller on going from $C_4H_2^+$ to $C_6H_2^+$. In the case of $C_6H_4^+$ the cyclic isomer, meta-benzyne, is the global minimum.

We have benchmarked the performance of a number of density functional theory methods in predicting the relative energies of the isomers these hydrocarbon cations as compared to those predicted by the CCSD(T) method. The widely used B3LYP density functional performs noticeably more poorly than some of the newer density functionals such as M06-2X, M11 or ωB97X. All exhibited limitations relative to CCSD(T) for low-lying isomers of $C_6H_4^+$. Perturbation theory methods using unrestricted reference wave function and the Z-averaged perturbation theory (ZAPT2) show quite large errors in predicting the relative energies of these isomers.

These results show that acetylene and its fragments in plasma can synthesize larger linear, branched, or cyclic, even benzene-like, molecules. The computed electronic spectra can be compared with the laboratory spectra in order to identify them.

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VI. Tables

Table 1: Relative energies of the isomers of $C_4H_2^+$ ion calculated using the cc-pVTZ basis set and various quantum chemical methods. Energies computed using B3LYP, UMP2, ZAPT2 and CCSD(T) methods represent minimum of the potential well of the respective isomers. The energies of the M06-2X, M11 and ωB97X functionals were computed at the CCSD(T)/cc-pVTZ optimized geometries.

Isomers	B3LYP	M06-2X	M11	ωB97X	UMP2	ZAPT2	CCSD(T)
A1	0	0.00	0.00	0.00	0.00	0.00	0.00
A2	29.22	40.52	40.57	39.38	49.56	33.15	33.68
A3	39.62	40.32	41.05	39.53	53.34	52.93	38.98
A4	46.56	37.38	35.75	35.43	47.21	48.19	40.90
A5	53.71	47.76	47.91	46.61	59.15	56.83	42.46
A6	50.04	44.60	45.13	45.72	56.97	63.54	44.26
A7	57.39	44.63	45.68	45.32	41.08	47.37	46.59
A8	60.87	51.71	51.42	49.81	61.45	59.35	51.84
A9	104.99	113.86	105.82	99.28	104.27	117.82	123.98
A10	106.90	123.61	116.80	101.08	115.09	127.45	132.51

Table 2. The harmonic vibrational frequencies of the $C_4H_2^+$ ion computed using the UMP2/cc-pVTZ method.

A1	A2	A3	A4	A5	A6	A7	A8	A9	A10
210	500	79	201	429	286	439	130	144	150
217	537	137	326	692	397	584	559	188	230
483	555	381	797	765	536	823	777	217	252
508	745	402	844	901	584	1022	838	717	533
662	759	900	906	958	707	1026	941	839	854
665	861	934	998	990	792	1133	1059	1012	980
775	1037	955	1000	1069	839	1173	1081	1076	1029
776	1054	1367	1033	1152	964	1248	1288	1162	1042
958	1368	1515	1335	1337	1502	1463	1321	1368	1497
1919	1408	2071	1724	1356	1690	1743	1427	1578	1590
2249	3289	3074	3226	3213	3244	3111	3199	3077	3012
3364	3307	3167	3274	3216	3324	3202	3219	3078	3027

Table 3. Table of first five electronic excitation energies (EE) in eV and oscillator strengths (OS) of $C_4H_2^+$ ion computed using TDDFT ωB97X functional with cc-pVTZ basis set.

	E1		E2		E3		E4		E5	
	EE	OS	EE	OS	EE	OS	EE	OS	EE	OS
A1	0.25	0.00	3.05	0.00	3.38	0.06	3.94	0.00	4.31	0.00
A2	2.58	0.00	2.71	0.00	2.93	0.00	3.02	0.00	3.79	0.00
A3	1.30	0.002	1.71	0.00	2.33	0.00	2.49	0.00	2.80	0.00
A4	1.21	0.00	1.79	0.00	1.94	0.00	3.83	0.02	4.85	0.00
A5	1.76	0.03	2.80	0.00	3.02	0.00	3.05	0.00	3.32	0.00
A6	1.25	0.00	1.99	0.01	2.95	0.00	4.01	0.01	4.61	0.00
A7	3.05	0.01	3.43	0.00	3.49	0.00	4.45	0.004	4.84	0.00
A8	1.85	0.01	2.03	0.00	4.06	0.04	4.47	0.00	4.57	0.003
A9	1.06	0.00	1.19	0.00	1.20	0.00	1.74	0.000	3.00	0.00
A10	1.08	0.00	1.17	0.00	2.93	0.003	2.95	0.00	3.04	0.09

Table 4. Relative energies of the isomers (B) of $C_6H_2^+$ ion calculated using the cc-pVTZ basis set and various quantum chemical methods. Energies computed using B3LYP, UMP2, ZAPT2 and CCSD(T) methods represent minimum of the potential wells of the respective isomers. The energies for M06-2X, M11 and ωB97X functionals were computed at the CCSD(T)/cc-pVTZ optimized geometries.

	B3LYP	M06-2X	M11	ωB97X	UMP2	ZAPT2	CCSD(T)
B1	0.00	0.00	0.00	0.00	0.00	0.00	0.00
B2	34.07	22.63	21.48	21.40	12.97	29.98	20.93
B3	41.96	30.62	28.98	28.62	24.58	28.96	29.94
B4	47.02	34.51	33.42	33.33	29.90	39.95	32.84
B5	53.16	42.31	40.92	40.10	28.10	43.65	38.70
B6	44.47	39.49	39.48	40.61	42.49	45.10	40.32
B7	39.48	41.53	42.48	40.92	62.77	64.09	41.38
B8	47.44	38.96	36.42	35.98	39.55	58.75	43.29
B9	51.93	42.31	40.92	48.02	28.10	43.65	48.70

Table 5. The harmonic vibrational frequencies of the $C_6H_2^+$ ion computed using the UMP2/cc-pVTZ method.

B1	B2	B3	B4	B5	B6	B7	B8	B9
107	442	137	338	304	92	39	113	55
111	508	178	466	321	118	47	125	133
253	516	395	469	468	300	167	242	156
255	534	506	509	514	383	169	326	313
437	623	538	638	541	487	365	444	356
467	640	654	757	615	523	392	565	419
514	778	654	761	827	619	517	640	588
567	783	681	930	850	648	548	789	739
656	971	691	1051	884	729	656	922	786
662	1071	764	1096	1107	756	904	957	812
663	1138	905	1116	1147	829	948	1011	885
766	1215	956	1246	1213	983	1181	1099	1107
766	1227	1065	1336	1302	1147	1391	1195	1314
1264	1371	1513	1395	1339	1568	1655	1493	1572
1983	1729	1597	1699	1551	1835	1993	1784	2147
2105	1798	2083	1822	1798	2014	2121	2111	2164
2258	3241	3259	3176	3264	3231	3156	3257	3064
3393	3244	3385	3237	3273	3373	3252	3318	3360

Table 6. TDDFT estimates of the first five electronic excitation energies (eV) of $C_6H_2^+$ computed using ωB97X functional along with cc-pVTZ basis set.

	E1		E2		E3		E4		E5	
	EE	OS	EE	OS	EE	OS	EE	OS	EE	OS
B1	0.27	0.0000	2.51	0.0000	2.74	0.1115	2.99	0.0001	3.32	0.0000
B2	2.23	0.0014	2.82	0.0000	3.21	0.0001	3.76	0.0000	4.01	0.0000
B3	2.51	0.0000	2.83	0.0000	2.98	0.0000	2.99	0.0000	3.39	0.0507
B4	1.79	0.0013	2.38	0.0001	2.58	0.0010	2.77	0.0000	2.99	0.0000
B5	2.09	0.0018	2.47	0.0000	3.33	0.0007	3.49	0.0000	3.61	0.0004
B6	1.22	0.0003	1.62	0.0053	2.00	0.0001	3.18	0.097	3.50	0.0002
B7	1.62	0.0019	1.76	0.0000	1.81	0.0000	1.85	0.0019	1.89	0.0000
B8	1.06	0.0000	1.44	0.0001	2.18	0.0036	2.59	0.0006	3.07	0.0000
B9	1.48	0.0001	1.87	0.0000	1.94	0.0014	2.03	0.0009	2.51	0.0375

Table 7: Relative energies of the isomers (C)of $C_6H_4^+$ at using B3LYP, M06-2X, UMP2, ZAPT2, and CCSD(T) along with cc-pVTZ.

	B3LYP	M06-2X	M11	ωB97X	UMP2	ZAPT2	CCSD(T)
C1	0.0	0.00	0.00	0	0.0	0.0	0.0
C2	0.96	4.10	2.80	3.22	7.54	7.11	8.42
C3	7.98	6.17	6.32	6.24	15.44	15.39	11.60
C4	4.87	11.44	13.29	12.13	16.48	16.27	12.05
C5	13.48	14.13	14.73	14.76	21.72	30.56	14.55
C6	6.24	14.65	16.39	15.21	17.15	16.87	14.64
C7	9.49	14.88	15.25	15.18	10.53	11.72	15.26
C8	4.61	15.01	17.26	17.09	24.51	21.46	17.70
C9	15.29	22.94	26.24	24.83	16.48	27.01	20.78
C10	25.35	19.08	19.12	17.42	26.54	27.01	21.05
C11	19.88	10.46	12.79	11.76	14.80	15.10	22.44
C12	11.80	15.96	12.30	14.9	17.66	17.21	24.54
C13	26.76	27.82	28.04	24.87	37.32	36.75	24.65
C14	18.98	24.78	26.61	25.46	21.49	21.63	25.47
C15	25.35	36.65	37.02	36.66	42.98	43.21	37.13
C16	44.91	49.79	49.55	48.89	55.17	58.64	43.89

Table 8. The harmonic vibrational frequencies of the $C_6H_4^+$ ion computed using the UMP2/cc-pVTZ method.

C1	C2	C3	C4	C5	C6	C7	C8	C9	C10	C11	C12
374	129	141	96	257	109	283	273i	135	292	106	175
449	131	187	126	375	175	364	91	197	348	132	188
523	343	295	230	417	239	414	107	229	572	239	234
530	394	327	315	441	322	526	267	290	584	309	407
537	427	373	440	453	438	617	280	476	735	476	509
595	547	551	505	489	468	734	427	480	757	489	606
753	685	597	531	747	689	767	480	584	820	534	752
821	699	707	670	752	692	885	558	627	856	624	763
830	770	711	671	872	733	906	604	717	899	672	940
928	847	812	750	913	764	969	650	718	945	715	941
975	849	855	751	925	772	1006	895	771	972	769	947
1044	981	881	893	996	787	1036	912	781	999	914	973
1079	984	893	927	1052	925	1074	954	782	1130	1053	996
1087	1031	1033	1075	1058	983	1174	960	978	1157	1053	1021
1119	1128	1065	1121	1118	1087	1215	1189	1012	1253	1262	1128
1279	1229	1259	1284	1224	1238	1258	1359	1331	1333	1293	1149
1297	1389	1457	1313	1319	1446	1285	1415	1354	1367	1457	1284
1389	1456	1495	1556	1395	1494	1405	1871	1509	1437	1554	1533
1533	1763	1767	2108	1494	2107	1494	1930	2118	1539	2051	1636
1744	2081	2203	2139	1760	2143	1779	2192	2195	1754	2254	1907
3173	3166	3158	3166	3182	3154	3176	3143	3150	3028	3155	3249
3195	3248	3254	3174	3183	3166	3179	3150	3266	3053	3160	3249
3208	3283	3272	3432	3216	3405	3195	3227	3409	3201	3262	3288
3212	3413	3419	3434	3220	3407	3206	3228	3412	3246	3398	3290

C13	C14	C15	C16
157	57	165	208
186	97	171	342
453	202	369	422
495	253	489	510
666	335	588	568
781	358	604	590
802	501	744	815
840	555	756	819
937	689	792	858
941	763	801	966
1000	861	940	989
1039	877	987	1115
1080	996	1051	1131

1099	1033	1073	1225
1120	1095	1089	1253
1302	1305	1201	1262
1385	1442	1219	1366
1399	1521	1485	1378
1471	2118	1632	1527
1680	2196	2223	1566
3223	3123	3106	2944
3233	3124	3129	2947
3240	3219	3188	3181
3246	3407	3420	3182

Table 9. Table of first five electronic excitation energies of $C_6H_4^+$ computed using TDDFT ωB97X functional with cc-pVTZ basis set.

	E1		E2		E3		E4		E5	
	EE	OS	EE	OS	EE	OS	EE	OS	EE	OS
C1	1.58	0.0000	2.19	0.0002	3.23	0.0004	3.39	0.0381	3.71	0.0000
C2	1.85	0.0000	3.26	0.1010	4.57	0.0000	4.63	0.0621	4.86	0.0171
C3	3.12	0.0000	3.26	0.0040	4.02	0.0000	4.32	0.1222	4.46	0.0000
C4	1.74	0.0000	1.97	0.0000	2.53	0.1275	3.81	0.4662	3.95	0.0000
C5	1.93	0.0003	2.06	0.0000	2.41	0.000	2.50	0.0009	2.69	0.0097
C6	1.62	0.0000	1.70	0.0000	2.28	0.0856	3.83	0.0366	3.92	0.2979
C7	0.50	0.0003	0.75	0.0000	2.35	0.0000	2.40	0.0004	3.17	0.0171
C8	0.36	0.0000	1.55	0.0013	2.67	0.0000	3.05	0.0000	3.17	0.0011
C9	1.65	0.0000	1.71	0.0920	2.05	0.0000	3.68	0.0248	4.37	0.0000
C10	3.27	0.0000	3.43	0.0001	3.56	0.0001	4.41	0.0051	4.55	0.0463
C11	0.64	0.0000	2.53	0.1416	3.11	0.1204	3.45	0.0001	3.69	0.0000
C12	3.26	0.0156	3.42	0.0000	4.25	0.0000	5.14	0.0632	5.88	0.5118
C13	0.89	0.0000	1.18	0.0074	2.76	0.0000	2.89	0.0000	3.44	0.0000
C14	0.81	0.0000	1.63	0.0000	2.25	0.1031	3.22	0.0000	3.67	0.8217
C15	2.58	0.0050	3.49	0.0005	3.59	0.0045	3.97	0.0004	4.15	0.0047
C16	1.96	0.0013	2.59	0.0000	3.16	0.0012	3.22	0.0000	3.34	0.0006

VII. Figures

Figure 1. Geometrical structures of the isomers (A) of diacetylene ($C_4H_2^+$) cation computed using the CCSD(T)/cc-pVTZ method.

Figure 2. Geometrical structures of the isomers (B) of triacetylene ($C_6H_2^+$) cation computed using the CCSD(T)/cc-pVTZ method.

Figure 3. Geometrical structures of the isomers (C) of $C_6H_4^+$ cation computed using the CCSD(T)/cc-pVTZ method

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