Association Mechanisms of Unsaturated C2 Hydrocarbons with their Cations: Acetylene and Ethylene

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Abstract

The ion-molecule association mechanism of acetylene and ethylene with their cations is investigated by *ab initio* quantum chemical methods to understand the structures, association energies, and the vibrational and electronic spectra of the products. Stable puckered cyclic isomers are found as the result of first forming less stable linear and bridge isomers. The puckered cyclic complexes are calculated to be strongly bound, by 87, 35 and 56 kcal/mol for acetylene-acetylene cation, ethylene-ethylene cation and acetylene-ethylene cation, respectively. These stable complexes may be intermediates that participate in further association reactions. There are no association barriers, and no significant inter-conversion barriers, so the initial linear and bridge encounter complexes are unlikely to be observable. However, the energy gap between the bridged and cyclic puckered isomers greatly differs from complex to complex: it is 44 kcal/mol in $C_4H_4^+$, but only 6 kcal/mol in $C_4H_8^+$. The accurate CCSD(T) calculations summarized above are also compared against less computationally expensive MP2 and density functional theory (DFT) calculations for structures, relative energies, and vibrational spectra. Calculated vibrational spectra are compared against available experiments for cyclobutadiene cation. Electronic spectra are also calculated using time-dependent DFT.

I.   Introduction

Large carbonaceous molecules are synthesized in the outflow of carbon stars where, small, unsaturated hydrocarbons nucleate into large molecules via cold condensation. Ionic association pathways leading to growth of large conjugated molecules are of immense importance in these low temperature interstellar conditions.[1-4] Ions are abundant in the interstellar medium due to the often intense radiation fields in which astrochemical molecules exist, and therefore barrierless ion-molecule reactions are a very effective growth mode for clusters. Under very different conditions, investigation of dissociation pathways of organic molecules by ionization (i.e. the reverse process) is important to understand processes such as flash pyrolysis, plasma discharge, and combustion.[5-7] The specific example that this work addresses is the formation of conjugated hydrocarbons by the combination of small, unsaturated units, such as acetylene and ethylene, with their cationic counterparts.

Conjugation of acetylene units is reported to occur spontaneously in electron impact ionization of neutral acetylene clusters in a supersonic beam expansion.[6] $(C_2H_2)_N^+$ species with magic numbers 2, 3 and 14 dominate (2 and 3 being most important) the mass spectra reported by Momoh et al. in their 2006 and 2007 papers: "the distribution of cluster ions formed reveals striking features corresponding to the enhanced intensities (magic numbers) for the $(C_2H_2)_n^+$ with n = 3,14,29,35 and 46".[6, 8] The $(C_2H_2)_3^+$ species demonstrates extraordinary stability. Plasma discharge experiments conducted to simulate the ionic association of acetylene and ethylene units produced larger hydrocarbons, indicating growth under these conditions.[5] In the reverse process,

degradation of larger conjugated hydrocarbons, such as polycyclic aromatic hydrocarbons in a plasma discharge also produced acetylene and ethylene fragments.[5]

The key species obtained in the first step of the association for acetylene is $C_4H_4^+$. While the pioneering experiments discussed above provide evidence of associative growth, they do not provide much information on the nature of the ensuing species. Some intermediate species, e.g. cyclobutadiene cation (CBC), have been characterized by theoretical[9-14] and experimental methods.[6, 15-18] In a recent extensive study of vibrational predissociation spectra of argon tagged acetylene cluster ions Relph et al.[15] found that the $(C_2H_2)_2^+$ ion predominantly occurs as CBC, although other isomers also form - a finding also supported by the predictions of Momoh et al.[16] Further association of acetylene, Relph et al. concludes, is based on a covalently bound core $C_4H_4^+$ ion. The most extensive computational exploration of the $C_4H_4^+$ potential energy surface is probably due to Hrouda and co-workers,[11, 12] who identified at least 8 local minima, and transition states interconnecting many of them.

The most stable encounter isomer is probably the CBC. Relph et al.[15] predict a planar D_{2h} symmetry cyclobutadiene cation geometry based on density functional theory (DFT) calculations (at the B3LYP/6-31++G** level) and experimental considerations. Earlier theoretical studies by Reselova et al. and [9] Hrouda et al. [11, 12] elaborately explored the nature of Jahn-Teller distortion of CBC. Furthermore, a recent experimental and theoretical study by Momoh et al. suggested the presence of more than one isomer of $C_4H_4^+$ in their clusters.[16] Their experimentally observed ion-mobility profile and measured collision cross section matched with the cyclobutadiene and vinylacetylene cations. $C_4H_4^+$ also appears as the primary degradation product in the mass spectra of

ionized acetylene trimer,[6, 16] indicating a loss of acetylene. An intriguing possibility, then, would be the formation of benzene cation by association of acetylene with acetylene dimer cation. This topic is not studied in the present study, but will be in due course.

Reaction of ethylene with ethylene cation may also lead to the growth of hydrocarbon molecules. There have been numerous computational studies on the cyclobutane cation isomer,[13,14,10,19, 20] examining the effect of Jahn Teller distortion from a D_{2h} starting structure. Jungwirth[19, 20] predicted that a puckered rhombus cyclobutane cation structure is the global minimum on the doublet potential energy surface of $C_4H_8^+$. Wiest,[10] using DFT calculations (with B3LYP), predicted that the cyclo-reversion reaction of cyclobutane radical cation into a complex of ethylene and ethylene cation occurs via a concerted mechanism with a transition barrier of 14.8 kcal/mol. Ohta et al.[13] predicted that the doublet radical cation of cyclobutane produces the two lowest electronic states due to two Jahn-Teller distortions. A $^2B_3$ state is generated due to a D_{2h} to D_2 distortion while a $^2B_2$ state is produced by a D_{2h} to C_{2v} distortion. The D_2 symmetry $^2B_3$ state is 1.1 kcal/mol lower in energy than the C_{2v} symmetry $^2B_2$ state.

In this research we take a closer look at the association products of acetylene with acetylene cation, ethylene with ethylene cation and acetylene with ethylene cation, and vice versa, using state-of-the-art *ab initio* quantum chemical methods. To our knowledge the cross-dimers have not been previously investigated. Since the purpose of this study is to investigate the ionic growth mechanisms of acetylene and ethylene into larger conjugated hydrocarbons, we have not investigated $C_4H_4^+$, $C_4H_6^+$, and $C_4H_8^+$ isomers in which hydrogen rearrangements have taken place. In other words, this is not an exhaustive search of the potential energy surface for all possible isomers. Instead we

explore barrierless association mechanisms that are relevant to hydrocarbon growth. We will clarify some structural features of the $(C_2H_2)_2^+$ association products in light of recent experimental results.[15] Additionally we report data on the association mechanism, product structures, energies, vibrational, and electronic spectroscopic properties of these complexes to advance our understanding about small ionic hydrocarbon growth with relevance to laboratory experiments and identification in astrophysical environments. This work complements recent studies of the association mechanism of small unsaturated nitrogenous hydrocarbons with their cations.[21, 22]

II.   Theoretical Methods

Since the association complexes of acetylene and ethylene are small systems, high quality benchmark-level calculations are possible. For this purpose, very accurate geometrical parameters and harmonic vibrational frequencies were obtained using coupled cluster singles and doubles plus perturbative triples [RHF/UCCSD(T)][23] with Dunning's correlation consistent valence triple zeta basis set (cc-pVTZ).[24] The coupled cluster calculations were performed using the MOLPRO 2006 quantum chemistry code.

We also intend to build upon the foundation of these small complexes and investigate the growth of larger molecules in the future. Therefore, in addition to using high accuracy benchmark quantum chemical methods, we will also compare against more affordable lower level methods. Thus we used unrestricted Møller-Plesset perturbation theory (UMP2) to optimize the geometries of the monomer and dimer complexes. In some cases the underlying unrestricted Hartree-Fock (UHF) reference showed significant spin contamination, which can lead to poor UMP2 results.[25] Therefore we also optimized

geometries using second order Z-averaged perturbation theory (ZAPT2) based on a symmetric spin orbital basis.[26-28] ZAPT2 also reduces the computational cost compared to unrestricted perturbation theories.

Finally, geometries were also optimized using unrestricted DFT with the B3LYP[29, 30] density functional using a very fine grid of 75 radial points and 590 angular points. Electronic spectra of the complexes were computed using time dependent density functional theory (TDDFT) using B3LYP and range separated ωB97x[31] density functionals. All the perturbation theory and DFT computations were performed using the Q-Chem 3.2 quantum chemistry package.[32]

III.   Results

Three energy minima were identified as products of the association reaction of acetylene with acetylene cation. Similarly, three association complexes were identified on the potential energy surface of ethylene and ethylene cation reaction. A cross dimer of the ethylene cation and acetylene (and vice versa), was also explored. In all cases the products included a structure with linear connectivity, a bridged structure and a puckered cyclic structure as minima. In all cases, the puckered cyclic isomer is the lowest in energy.

When our computational results are discussed below, all numerical values mentioned (for energies, geometrical parameters, etc), refer to the highest level of theory we have performed, namely CCSD(T)/cc-pVTZ results, unless otherwise specified.

A. Acetylene dimer cation

We shall first discuss the relative energies of the local minima (summarized in Table 1), then turn to structural aspects and associated vibrational frequencies, and finally consider the mechanistic implications of our results for association reactions.

The lowest energy product of the acetylene and acetylene cation association is the four-membered cyclic cyclobutadiene cation, which is shown in Figure 1 (the full Cartesian coordinates for all of the compounds/complexes in the present study are included in the Supplementary Information). While neutral cyclobutadiene is planar, the doublet cation is slightly puckered. The association energy is 86.8 kcal mol^{-1}, (non-ZPVE corrected) as reported in Table 1. The lower levels of theory shown in Table 1 are in mostly very good agreement with this result, with deviations of 0.4 (MP2), 7.0 (ZAPT2), and −1.0 (B3LYP) kcal, mol^{-1}, using the same basis set. The association energy computed using ωB97x/cc-pVTZ is slightly higher, 94.74 kcal/mol.

The second lowest energy isomer, a bridge structure, is 44.1 kcal mol^{-1} above the puckered cyclobutadiene cation, with an association energy of the 42.7 kcal mol^{-1}. Relatively small deviations of 0.0 (B3LYP), 4.9 (ωB97x), 2.0 (UMP2), and 2.6 (ZAPT2) kcal mol^{-1} are seen with the lower level theories. A third isomer with linear connectivity and C_2 symmetry, presented in Figure 1, has an association energy of 39.3 kcal mol^{-1}. The deviations of lower level methods are 4.2 (B3LYP), 1.1 (ωB97x) and −8.1 (UMP2) kcal mol^{-1}. In this case, UMP2 suffers from spin contamination in the UHF reference ($<S^2>$ 1.02), but the ZAPT2 method consistently converges to the bridge structure, not the C_2 symmetry structure. Hence no ZAPT2 results appear for the C_2 symmetry structure.

Structural features of the cyclobutadiene cation have already been much discussed. Bally et al. performed B3LYP and QCISD calculations (with CCSD(T) energies), and predicted a puckered cyclobutadiene structure due to Jahn-Teller distortion.[11, 12, 14] A recent DFT and experimental study[15], however, predicted a planar cyclobutadiene cation structure. We find that the cyclobutadiene cation optimizes to a puckered cyclic structure at the benchmark CCSD(T)/cc-pVTZ level of theory (Figure 1). By contrast, the structure is planar at the B3LYP/cc-pVTZ level of theory, which is incorrect (despite its good association energy). This incorrect B3LYP structure probably reflects self-interaction error, which should favor geometries at which greater delocalization of the single positive charge is possible. CCSD(T) (as well as the MP2 methods) predict that the planar structure is a transition state between the two identical puckered structures. The four carbon-carbon distances are equal with a value of 1.43 Å, roughly consistent with a formal bond order of 1.4.

The harmonic vibrational frequencies obtained using CCSD(T)/cc-pVTZ are presented in Table 2, and together with the structures are the most advanced reported to date. Relph et al. observed two closely spaced bands at 1284 and 1450 cm^{-1} in their vibrational predissociation spectra of $(C_2H_2)_2^+$, and attributed at least one of them to a CC stretch. From Table 2, the puckered cyclobutadiene structure, at the CCSD(T)/cc-pVTZ level, exhibits a CC stretching harmonic frequency at 1526 cm^{-1}, which could be consistent with the 1450 cm^{-1} band. Further, there are two CCH bends located at 1327 and 1330 cm^{-1}, which would be consistent with the 1284 cm^{-1} band. Two closely-spaced CH stretching peaks were observed by Relph et al. in the vicinity of 3100 cm^{-1}. We obtain large and medium intensity (intensity from the UMP2 frequency calculation – see

table 2) CH stretching frequencies at 3192 and 3290 cm^{-1} [CCSD(T) level of theory], though the large intensity mode is the higher frequency value, which is not consistent. However, unlike the B3LYP spectra reported by Relph et al., the relative intensity values we calculate between the CH stretches and the frequencies in the 1200 to 1500 cm^{-1} region are consistent with the observed spectra reported by Relph et al. This suggests that further theoretical work is needed to adequately reproduce the IR intensities.

The bridge isomer, presented in Figure 2, has interesting structural features. The acetylene cation attaches to the triple bond via a bridging carbon, making a three-membered ring. The C-C triple bond elongates to a bond distance of 1.25 Å. The distances of the two identical C-C bonds of the isosceles triangle are 1.68 Å, which is noticeably longer than a single C-C bond – the C-C single bond distance in ethane is 1.54 Å – yet much shorter than a van der Waal's distance. It is fair to describe it as an elongated covalent bond. The C–C bond external to the ring is also elongated to a more classical double bond distance (1.33 Å), and the two hydrogen atoms are present in an sp^2 arrangement with respect to the carbon atoms.

It is striking that the central carbon atom involved in the cyclic bridge structure is pentavalent. The bridging carbon makes a double bond (1.33 Å) with the external carbon atom, two elongated C-C single bonds with the two acetylene carbon atoms (the two sides of an isosceles triangle, 1.68 Å each), and a C-H single bond (1.08 Å) with a H-atom. Wiberg bond indices (WBI),[33, 34] computed using B3LYP/cc-pVTZ at the CCSD(T) geometry, for all the bonds to the bridging carbon atom support this assertion. The computed WBI index for the C-C external bond is 1.69, which is suggestive of a C-C double bond, while the WBI for the C-H bond is 0.87. The WBI for the two equal

bridging bonds is 0.63 each, suggestive of two C-C partial single bonds. Note that the 0.63 and 1.69 WBI bond orders reported here are in the vicinity of the 0.54 and 1.73 WBI bond orders reported earlier for single and double bonds, respectively.[35-37] Both the structure based analysis and the Wiberg bond indices indicate the pentavalent nature of the bridging carbon atom. However, we note a point of caution since this is an open-shell radical system, and clearly there is an electron-hole within the carbon framework.

The third isomer identified on the potential energy surface has a C_2 symmetry and linear carbon chain connectivity. The C_2 isomer is a minimum at the CCSD(T)/cc-pVTZ level and other levels of theory. The central bond between the two acetylenes in this complex is an elongated single bond (1.68 Å), strikingly similar to the ones already discussed in the bridge complex above. The acetylene double bond elongates to 1.27 Å; roughly half-way towards the geometry of the bridge compound. The structural similarity between linear and bridge is consistent with their small energy separation, and suggests ready interconversion between them, a point to which we shall return shortly.

Let us next consider a comparison of structural predictions using the reference CCSD(T) method against the more economical lower level theories, focusing primarily on the MP2 methods, since B3LYP yields incorrect topology at the puckered cyclic minimum. For the puckered cyclic and bridge structures, it is evident from inspection of Fig. 1 that critical ZAPT2 C-C geometrical parameters are closer than UMP2 values to the CCSD(T) benchmarks. However, UMP2 yields a potential energy surface that has qualitatively correct potential energy surface topology, whereas ZAPT2 does not exhibit the linear C_2 isomer.

Finally, let us discuss the mechanistic implications of our results. The puckered cyclic isomer, although lowest in energy, does not form directly upon optimization of the acetylene and acetylene cations. Instead, initial encounter leads to either the linear C_2 or the bridge isomers (depending upon the impact parameter). However, the potential energy surface is very flat in the vicinity of the linear and bridge isomers. The linear isomer is separated by a very small barrier from the bridge, which is a slightly more stable isomer. Given the kinetic energy release upon association, crossing will be prompt. The bridge itself is a very shallow minimum, whose transition state to the much lower-lying puckered cyclic isomer is only 0.20 kcal mol^{-1} above the bridge isomer and looks much like it.

One can thus think of the linear-bridge part of the PES as essentially a nearly flat ledge that lies about half-way down a deep narrow well. The top of the well is the flat, weakly attractive surface of separated reactants. The bottom of the well corresponds to the puckered cyclic isomer (of course there are numerous other details corresponding to further intramolecular rearrangements, and different dissociation channels but we do not consider them here). Our results indicate that formation of the cyclobutadiene cation due to the ion-molecule reaction between acetylene and its cation is easily achieved via the two higher lying isomers, which are essentially precursors to forming the stable cyclobutadiene cation. This pathway to the puckered cyclic framework represents the inception of the cyclization process in the acetylene ion – acetylene molecule reaction.

B.   Ethylene dimer cation

Association of ethylene with ethylene cation leads to three energetically bound isomers that are analogous to the puckered cyclic, bridge and chain isomers discussed above for the acetylene dimer cation. However, as presented in Table 1, the relative values of these association energies are quantitatively very different for the ethylene dimer cation. The four membered puckered cyclic isomer is most stable, with an association energy of 35.4 kcal mol^{-1}. This value is less than half the association energy of the cyclobutadiene cation. Above the cyclobutane cation is a bridge structure that is just 5.8 kcal mol^{-1} higher, and a C_2 symmetry chain structure that is 3.3 kcal mol^{-1} higher again. Comparison of the association energies using different levels of theory (Table 1), reveals that B3LYP association energies are very close to the reference values for the puckered cyclic and bridge structures. By contrast, UMP2 and ZAPT2, bind these association complexes too tightly, by up to 20-25%. As was also the case for acetylene, B3LYP does not exhibit a minimum on the PES for the chain isomer, while the MP2 methods correctly do. The ωB97x functional, however, predicts the linear connectivity isomer to be a minimum, with an association energy of 30.3 kcal/mol.

The lowest energy isomer for the ethylene dimer cation is the puckered cyclic geometry of the cyclobutane cation, Figure 2. The carbon framework in cyclobutane cation slightly puckers from planarity and assumes C_{2V} symmetry, unlike the neutral, which is planar and has C_{2h} symmetry. The nearest distance between the two carbons is 1.53 Å, which is very close to a standard C–C single bond (1.54 Å). The nearest distance between the two diagonal carbons is 1.92 Å.

The open shell ethylene dimer cation is qualitatively different than the closed shell neutral dimer. Neutral parallel and parallel slipped dimers have been studied computationally for closed shell cumulenes, and larger olefins. Tschumper found that neutral closed shell olefins bind with each other by stacking with very little energy, 3-5 kcal mol^{-1},[38] corresponding to the Van der Waal's interaction of the two monomers. A parallel stacked ethylene dimer cation has been investigated by Pieniazek et al.[39] A parallel slipped geometry was optimized and found to represent a transition state towards the open shell cation of ethylene dimer with MP2 theory. Following the imaginary mode led to a slightly puckered cyclobutane cation structure similar to that presented in Figure 2. A computational study of $C_4H_8^+$ by Wiest et al.[10] using the QCISD method found that a parallelogram represents a minimum, and a rhombus and a rectangular structure represent transition state and a second order saddle points, respectively. Jungwirth, et al., after exploration of the PES of the cyclobutane cation at the UMP2/6-31G* level (with QCISD(T)/6-31G* single point energy calculations), concluded that the rhomboid structure is the global minimum.

We found a puckered rhomboidal structure with C_{2V} symmetry structure similar to Wiest et al. and Jungwirth et al., but employing a significantly higher CCSD(T)/cc-pVTZ level of theory. The best structural parameters presented in Fig. 2, therefore, are a significant improvement relative to the previously available data. Additionally, the harmonic vibrational frequencies reported in Table 3 (computed at the UMP2/cc-pVTZ level of theory), should aid in the analysis of future experimental vibrational spectra of ethylene dimer cation.

The second-lowest energy encounter-complex of ethylene with ethylene cation that we have identified is the bridge structure presented in Figure 2. Its structure is quite fascinating. The distance between the carbon atoms of the two monomers, two equal bonds of the isosceles triangle, is intermediate between conventional covalent and non-bonded distances at 1.97 Å. This distance is notably longer than 1.68 Å in the bridge structure of $C_4H_4^+$, and is therefore a weaker interaction. This weak bond has implications for the C–C bond in ethylene involved in the cyclic bond formation, which only elongates to 1.38 Å, still well short of a single bond. Meanwhile the C-C bond external to the cyclic framework is longer at 1.45 Å. This reflects its origin in the ethylene cation. The bridgehead C atom is pentavalent, as it was for the bridge structure of $C_4H_4^+$.

There is also another isomer whose C4 backbone has linear connectivity. While this C_{2h} symmetry quasi-linear isomer is a local minimum on the B3LYP/cc-pVTZ potential energy surface, it exhibits an imaginary frequency (see Table 3) at the UMP2/cc-pVTZ level of theory. Additionally, the CCSD(T)/cc-pVTZ equilibrium structure is quite a bit different relative to the UMP2/cc-pVTZ structure. The T_1 diagnostics[40, 41] for all of the structures contained in this study are 0.021 or lower, indicating that the CCSD(T) method should perform well, though it is possible that perturbation theory methods are more challenged, and that would seem to be the case for this C_{2h} isomer. The D_1 diagnostics[42, 43] tell a similar story, with all values being 0.068 or smaller. Similar to $C_4H_4^+$, direct association of ethylene and ethylene cation can occur via either the linear or bridge structures, which are separated from the deeper cyclobutane cation minimum by small barriers.

C.   Acetylene-Ethylene cation association

The association process between ethylene cation and acetylene (or vice versa) was also investigated in this research. As far as we aware, these cross dimers have not been previously studied. We find similar bonding motifs to those observed for acetylene and ethylene association. A four membered cyclic structure, the cyclobutene cation, is the most stable isomer that does not involve H migration, followed by a bridge and a π-complex. We predict that the cyclobutene cation is bound by 55.8 kcal mol^{-1} relative to the ethylene cation and acetylene dissociation channel, as presented in Table 1. The bridge isomer has a significantly lower association energy of 37.4 kcal mol^{-1}. The transition state between the bridge and cyclobutene cation lies only 1.1 kcal mol^{-1} above the bridge isomer, meaning that the bridge will not be seen as a distinct isomer. A third minimum on the potential energy surface is a novel π-complex, which is bound by 22.1 kcal mol^{-1}. The cross complexes between the ethylene cation and acetylene are more strongly bound than the corresponding ethylene dimers, but less strongly bound than the acetylene dimer cations. Like the acetylene and ethylene complexes, inspection of Table 1 shows that the perturbation theory methods slightly overestimate the binding energies compared to CCSD(T).

The cyclobutene cation has three different types of C-C linkages as seen in Figure 3. The C–C distance of acetylene elongates to 1.43 Å and the C–C distance in ethylene elongates to 1.57 Å. The carbon-carbon distance between the acetylene and ethylene is 1.49 Å.

Turning to bridge isomers, unlike the pure dimer open shell complexes, the cross association complex has two isomers of interest. The first is a regular bridge structure and

the second is an electrostatically bound π-complex. The first bridge isomer, seen in Figure 3, has a geometry that somewhat resembles the bridged structure of $C_4H_4^+$ shown in Fig. 1. The ethylene carbon-carbon distance also elongates to almost a single bond distance of 1.42 Å. The acetylene moiety bends and the distance between the two carbon atoms becomes almost a standard C=C double bond distance. At the same time, the C–C distance between the bridging carbon and the ethylene carbons is 1.67 Å. The central carbon atom is again formally pentavalent like the bridge analogs of the acetylene and ethylene dimer cations.

The third isomer is also a bridged complex, but with slightly elongated bonds as seen in Figure 3. One of the carbons of ethylene binds with the π-electron cloud of acetylene. The C-C distance corresponding to the equal sides of an isosceles triangle, is 2.30 Å. This is a longer distance than the bridged isomers of $C_4H_4^+$ (1.68 Å) or $C_4H_8^+$ (1.97 Å), suggesting a key role for steric repulsion between two sets of hydrogen atoms as evident from Figure 3. The ethylene CC bond elongates slightly, while the acetylene CC bond does not change much, suggesting that the positive charge is localized on the ethylene unit, which is consistent with ethylene possessing a smaller ionization potential relative to acetylene. The association energy predicted by the ωB97x functional (22.8 kcal/mol) matches very well with that predicted by the CCSD(T) method (22.1 kcal/mol).

Harmonic vibrational frequencies for all the acetylene-ethylene cation association complexes calculated at the UMP2/cc-pVTZ level of theory, with IR intensities, are presented in Table 3. It is hoped that these will be of use in the assignment of future experiments.

D.   Excitation energies

The excitation energies are calculated using time-dependent density functional theory (TDDFT) using the B3LYP density functional. The major doublet-doublet excitations (based on relative intensities for 1-photon transitions) are plotted in Figures 4 a-h. Note that the scales in the various parts of Fig. 4 are not the same, depending on the oscillator strength of excitations in that particular complex. In our earlier study[21] of excitation energies of closed and open shell association complexes of conjugated hydrocarbons and ionic nitrogen containing organic molecules, we found that B3LYP predicts the excitation energies well when compared with the excitation energies calculated using a range separated density functional (ωB97x) and equation-of-motion coupled cluster (EOM-CC) theories for states that do not show significant charge transfer character. All the molecular complexes described here, except for the π-complex (see Fig 3), are covalently bound for which the charge transfer type excitation between two parts of the molecule is not very significant. Not surprisingly, then, excitation energies calculated using the B3LYP and ωB97x density functionals agree reasonably well.

Since the puckered cyclic isomer is the global minima for all three association complexes investigated here, and hence the most important in the current context, we focus on the excitation spectra obtained for those. Electronic absorption lines for the $C_4H_4^+$ puckered cyclic isomer are shown in Figure 4a, and similarly for the $C_4H_8^+$ puckered cyclic isomer in 4d, and the $C_4H_6^+$ puckered cyclic isomer in Figure 4f. All three puckered cyclic global minima exhibit relatively weak absorption lines in the near ultraviolet. The spectra for the pure dimer cations are more similar, with the largest oscillator strength excitation occurring below 200 nm, and then the second largest

oscillator strength excitation occurring near 300 nm. All other excitations have very small oscillator strengths. The electronic spectra for the mixed dimer cation, Fig. 4f, exhibits its largest oscillator strength for an excitation near 235 nm, while the next most intense peaks are centered around 170 nm and 210 nm in descending order.

Electronic spectra for the other complexes found in the present study are included in Fig. 4 for completeness. For the ethylene-acetylene cation π-complex, see Fig. 4h, it was thought that the most intense peak may exhibit significant charge-transfer character and thus we computed excitation energies at the EOM-CCSD/cc-pVTZ level of theory (see the Supplementary Information). The differences between the B3LYP and EOM-CCSD excitation energies are consistent with previous studies, and while the difference for the most intense peak, 5.11 eV (B3LYP) vs. 5.70 eV (EOM-CCSD), is one of the larger discrepancies, it is not nearly large enough to possess significant charge-transfer character. In fact, none of the lowest 10 electronic excitations exhibit a large degree of charge transfer character as evidenced by the reasonable agreement between B3LYP and EOM-CCSD. As indicated above, none of the other complexes should exhibit charge-transfer type behavior, so it is hoped their electronic spectra in Fig. 4 will be useful in the assignment of future experiments.

As an example of the nature of the electronic excitations, we have computed attachment/detachment[44] densities for the $C_4H_4^+$ puckered ring structure, see Fig. 5. Focusing on the two most intense excitations, the peak at 296 nm has an oscillator strength of 0.022 while the peak at 183 nm has an oscillator strength of 0.083. Examination of the densities (α and β attachment/detachment densities are shown) suggest that the peak at 296 nm is mainly from the singly occupied orbital (which has π

character on two carbon atoms that are not bonded) and into an unoccupied orbital that is dominated by p-orbital character involving all of the carbon atoms, while the peak at 183 nm is from a doubly occupied orbital that is dominated by σ-character among the carbon atoms and into an unoccupied orbital that again appears to be dominated by p-orbital character on the carbon atoms. Additionally, the 183 nm excitation shows slightly more amplitude in the α density relative to β density, suggesting a small amount of spin contamination.

E. Comparison of three association processes: $C_4H_4^+$, $C_4H_6^+$ and $C_4H_8^+$

In this section we compare the three association processes, acetylene-acetylene cation, ethylene-ethylene cation and acetylene-ethylene cation, via an ion-neutral pathway. Firstly, all of the products we have identified form from barrierless mechanisms, which are common in ion-neutral reactions. Another unifying feature of the three association processes is the formation of a robust four-membered cyclic ring that is the most stable product. The association energies vary according to the hybridization state of the associated carbon atoms involved, although they are all very strong. Association of two sets of sp-hybrid carbons results in the strongest bonding for the cyclobutadiene ion, followed by bonding between one set of sp and one set of sp^2 hybridized carbon atoms in cyclobutene ion, followed by bonding between two sets of sp^2 hybridized carbon atoms in cyclobutane ion.

Although they are shallow minima on their respective potential energy surfaces, the bridge isomers are also a common feature of the three association processes as they are the second most stable isomer in all three cases studied here, and they all exhibit a

three-membered cyclic structure with one carbon atom external to the ring. One difference concerning the bridge isomer is that the difference in energy between the puckered cyclic and bridge isomer is much larger for the acetylene dimer cation relative to the ethylene dimer cation. This suggests that there might be situations (e.g., with substitution of certain H atoms with larger groups) where the bridge isomer is lower in energy than the puckered cyclic isomer.

IV.   Conclusions

Association mechanisms of acetylene and ethylene with their cationic counterparts, and the mixed dimer cation, were investigated using high accuracy *ab initio* quantum chemical methods. Association of acetylene with acetylene cation leads to the formation of cyclobutadiene cation, as was previously found by Momoh et al.[6, 16] and Relph et al.[15] Our CCSD(T)/cc-pVTZ optimization of the structure and subsequent harmonic frequency calculation indicates that the cyclobutadiene has an out-of-plane puckered cyclic structure, unlike the planar structure predicted by the two previous studies in which DFT was used. In fact, we found that B3LYP indeed predicts the cyclobutadiene cation to be planar, but UMP2, ZAPT2 and CCSD(T) all predict its geometry to be puckered.

It is found, for all three association processes studied here, that the formation of a four-membered cyclic puckered structure is favored for these fundamental ion-molecule reactions. All three systems studied here, acetylene-acetylene cation, ethylene-ethylene cation, and acetylene-ethylene cation exhibit weakly bound linear (in connectivity) intermediates, somewhat more strongly bound bridge isomers, and a low transition state

connecting the bridge isomer to the respective puckered cyclic isomer. The bridge structures identified in the association processes have a three membered cyclic carbon framework with a pentavalent bridging carbon. While the energy difference between the bridge and puckered cyclic structures is very large for the acetylene dimer cation and the acetylene-ethylene cation, it is significantly smaller (≈ 6 kcal/mol) for the ethylene dimer cation, suggesting that with the right substituents replacing some of the hydrogen atoms, the bridge isomer may become more stable than the puckered cyclic isomer.

It is also interesting to contrast the relative binding energies across the different dimer cations. The acetylene-acetylene cation exhibits the strongest association complexes followed by the acetylene-ethylene cationic complexes, and lastly the ethylene-ethylene cationic complexes in terms of binding energy.

Another purpose of the present study was to assess the performance of the B3LYP and perturbation theory methods, UMP2 and ZAPT2, relative to the more accurate CCSD(T) approach, all using the cc-pVTZ basis set. Such an assessment is necessary, as we plan to study association processes that ultimately lead to polycyclic aromatic hydrocarbons. In the present study, B3LYP performed well in predicting association energies compared to CCSD(T), although it incorrectly predicts a planar structure for cyclobutadiene cation. Generally, geometrical structures predicted by UMP2 and ZAPT2 are in very good agreement with those of CCSD(T), but the perturbation theory approaches slightly overestimate the association energies.

Structural parameters presented in this work at the CCSD(T)/cc-pVTZ level of theory are the most advanced to date and exhibit significant differences over previously available results. It is hoped that the harmonic vibrational frequencies (with IR

intensities) presented here [CCSD(T)/cc-pVTZ for acetylene dimer cation and UMP2/cc-pVTZ for the other two dimer cations] should aid in the identification of these species in laboratory experiments.   Similarly, the electronic spectra presented in Figure 4 should also aid in the identification of these species.

V.   Acknowledgements

VI. Tables

Table 1. Association energies of the neutral and ionic acetylene, ethylene species at various levels of theories.

	Formula	Binding Energies, kcal mol^{-1}				
		B3LYP/ cc-pVTZ	ωB97x/cc -pVTZ	UMP2/cc- pVTZ	ZAPT2/cc- pVTZ	CCSD(T)/ cc-pVTZ
	HCCH + HCCH$^+$ = [HCCH]$_2^+$					
Puckered	[HCCH]$_2^+$	85.8	94.7	87.2	93.8	86.8
Bridge	[HCCH]$_2^+$	42.7	46.9	44.7	45.3	42.7
TS	Puckered–Bridge	+0.3	---	+1.3	+0.6	+0.2
C2	[HCCH]$_2^+$	43.5	40.4	31.3^a	29.5^a	39.3
	H$_2$CCH$_2$ + H$_2$CCH$_2^+$ = [H$_2$CCH$_2$]$_2^+$					
Puckered	[H$_2$CCH$_2$]$_2^+$	33.1	40.8	43.8	46.2	35.4
Bridge	[H$_2$CCH$_2$]$_2^+$	30.8	---	33.9	34.3	29.6
TS	Puckered-Bridge	+0.5	---	+3.8	+2.3	+0.5
C2	[H$_2$CCH$_2$]$_2^+$	---	30.3	29.9	32.3^a	26.2
	HCCH + H$_2$CCH$_2^+$ = [H$_2$CCH$_2$-HCCH]$^{+\ b}$					
Puckered	[H$_2$CCH$_2$-HCCH]$^+$	55.1	63.8	56.8	57.2	55.8
Bridge	[H$_2$CCH$_2$-HCCH]$^+$	34.0	39.8	38.5	39.1	37.4
TS	Puckered-Bridge	+0.4^c	---	+0.1	+0.0	+1.1
π-complex	[HCCH-H$_2$CCH$_2$]$^+$	---	22.8	22.9	23.1	22.1

a: Energy calculation at the CCSD(T)/cc-pVTZ optimized geometry.
b: These association energies are with respect to the HCCH + H$_2$CCH$_2^+$ asymptote. The association energies for the HCCH$^+$ + H$_2$CCH$_2$ asymptote are 75.1, 56.7 and 41.4 kcal mol^{-1} for the cyclobutane puckered cyclic cation, bridge, and the C$_2$ isomers, respectively, at the CCSD(T)/cc-pVTZ level of theory.
c: TS is 0.4 kcal/mol above the bridge isomer; all the TS energies are with respect to the corresponding bridge isomers.

Table 2. Harmonic vibrational frequencies of acetylene-acetylene cation using UMP2/cc-pVTZ, ZAPT2/cc-pVTZ and CCSD(T)/cc-pVTZ theory. Intensities are in km/mol

| Puckered Cyclic | | | | Bridge | | | | C_2 | | |
| UMP2 | | ZAPT2 | CCSD(T) | UMP2 | | ZAPT2 | CCSD(T) | UMP2 | | CCSD(T) |
Freq	*Int*	Freq	Freq	Freq	*Int*	Freq	Freq	Freq	*Int*	Freq
391	*12.8*	434	378	247	*6.3*	76	32	189	*1.0*	156
657	*42.8*	657	646	388	*17.3*	368	353	247	*0.4*	215
675	*37.7*	715	676	523	*19.4*	442	359	302	*4.2*	221
897	*0.0*	901	869	714	*2.2*	693	647	663	*0.1*	516
924	*25.7*	910	894	722	*89.9*	702	665	778	*177.1*	590
972	*3.3*	953	944	785	*82.1*	731	690	833	*9.8*	616
979	*61.3*	1044	1032	803	*3.5*	753	726	860	*17.5*	685
1062	*16.9*	1047	1052	874	*7.7*	842	831	920	*91.2*	713
1068	*0.0*	1073	1052	931	*2.2*	909	890	953	*0.3*	763
1096	*2.5*	1201	1094	968	*31.1*	944	918	1067	*100.0*	771
1217	*0.0*	1207	1194	1051	*37.0*	1032	996	1095	*1.6*	1017
1376	*71.8*	1343	1327	1291	*2.8*	1283	1262	1269	*42.1*	1087
1383	*5.0*	1347	1330	1539	*210.3*	1552	1497	1555	*6.2*	1708
1385	*5.9*	1525	1526	1833	*19.6*	1841	1827	1824	*32.0*	1738
3239	*13.4*	3196	3191	3261	*31.1*	3259	3212	3070	*93.8*	3234
3241	*39.2*	3234	3192	3291	*22.7*	3302	3239	3224	*109.7*	3234
3337	*161.7*	3235	3290	3315	*212.2*	3314	3286	3230	*392.1*	3340
3351	*1.0*	3339	3293	3400	*30.3*	3400	3364	3396	*77.9*	3350

Table 3. Harmonic Vibrational Frequencies and infrared intensities (in italics) of ethylene-ethylene cation and ethylene-acetylene cation association molecules using UMP2/cc-pVTZ

[Ethylene]$_2^+$						[Acetylene-Ethylene]$^+$					
Puckered		Bridge		C2		Puckered		Bridge		π-complex	
34	0.2	124	7.3	92i	81.9	108	0.0	139	8.0	95	0.2
210	0.0	211	1.0	86	0.1	589	0.0	366	14.6	172	47.3
659	0.1	336	3.4	185	0.1	592	26.2	614	13.3	231	9.1
776	0.2	397	12.6	250	0.4	665	7.4	736	0.0	257	2.0
786	4.5	402	11.1	482	0.0	873	23.4	746	59.4	371	0.0
808	0.8	634	22.8	568	2.0	889	34.0	795	14.1	609	0.0
914	0.1	659	50.4	843	2.3	926	0.0	853	3.8	731	2.5
936	0.1	798	0.6	847	0.1	1014	15.8	979	21.4	770	84.7
946	0.0	875	0.3	988	129.8	1043	1.8	986	32.7	812	0.9
988	0.0	972	6.7	1002	0.0	1045	0.0	1098	15.0	856	86.1
1048	5.6	1108	3.9	1040	1.0	1161	0.5	1127	8.6	966	0.0
1095	1.2	1114	14.4	1090	59.3	1201	0.0	1132	7.1	993	30.4
1101	0.0	1159	0.1	1124	3.5	1240	2.5	1230	0.8	1120	3.1
1162	0.0	1165	7.5	1163	0.1	1244	34.4	1264	1.4	1243	0.5
1211	0.0	1221	14.9	1247	22.0	1347	2.9	1272	7.5	1278	15.5
1221	27.1	1245	0.0	1266	1.1	1400	42.3	1497	15.9	1501	23.2
1255	48.7	1278	0.9	1274	0.1	1406	44.8	1545	14.4	1585	3.1
1273	23.6	1349	2.7	1307	0.1	1461	7.9	1619	380.3	1944	21.3
1379	3.1	1452	30.7	1498	63.2	3073	34.3	3207	14.6	3198	7.1
1458	0.0	1502	18.5	1501	0.9	3088	51.4	3211	6.9	3226	18.6
1531	7.7	1518	3.4	1561	10.0	3115	0.0	3263	33.8	3276	5.2
1552	0.0	1600	2.7	1595	0.0	3127	32.9	3292	21.4	3329	10.5
3085	65.4	3111	30.7	3190	6.4	3248	25.1	3296	0.2	3360	297.1
3096	1.1	3129	27.7	3193	0.2	3273	6.8	3312	37.7	3480	9.6
3204	9.2	3200	17.0	3207	103.3						
3206	3.6	3209	3.2	3216	0.3						
3206	43.6	3248	5.2	3274	0.7						
3209	0.0	3293	0.2	3276	6.8						
3284	0.1	3315	32.8	3318	0.8						
3289	21.8	3355	6.4	3319	27.0						

VII. Figures

Figure 1. Structural parameters of the acetylene-acetylene cation association products (cyclobutadienyl cation, bridge and C2) are presented here at the UMP2/cc-pVTZ, ZAPT2/cc-pVTZ and CCSD(T)/cc-pVTZ levels of theory.
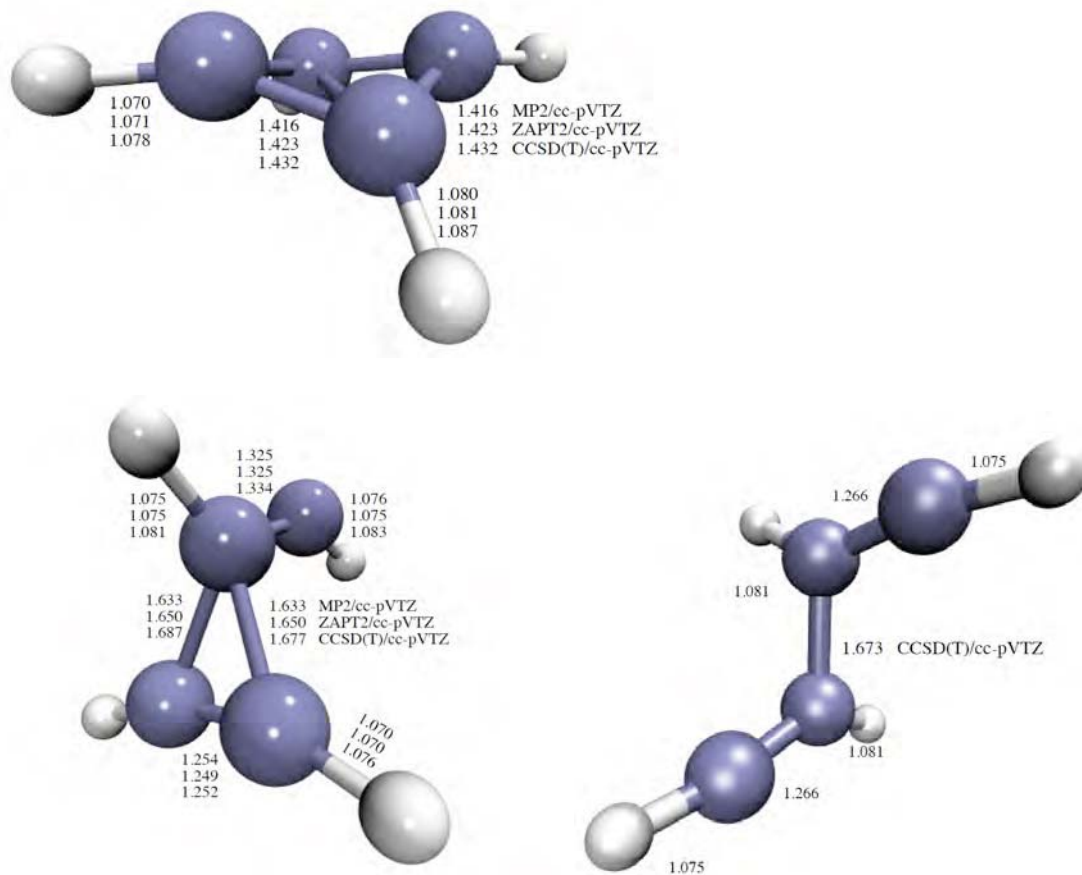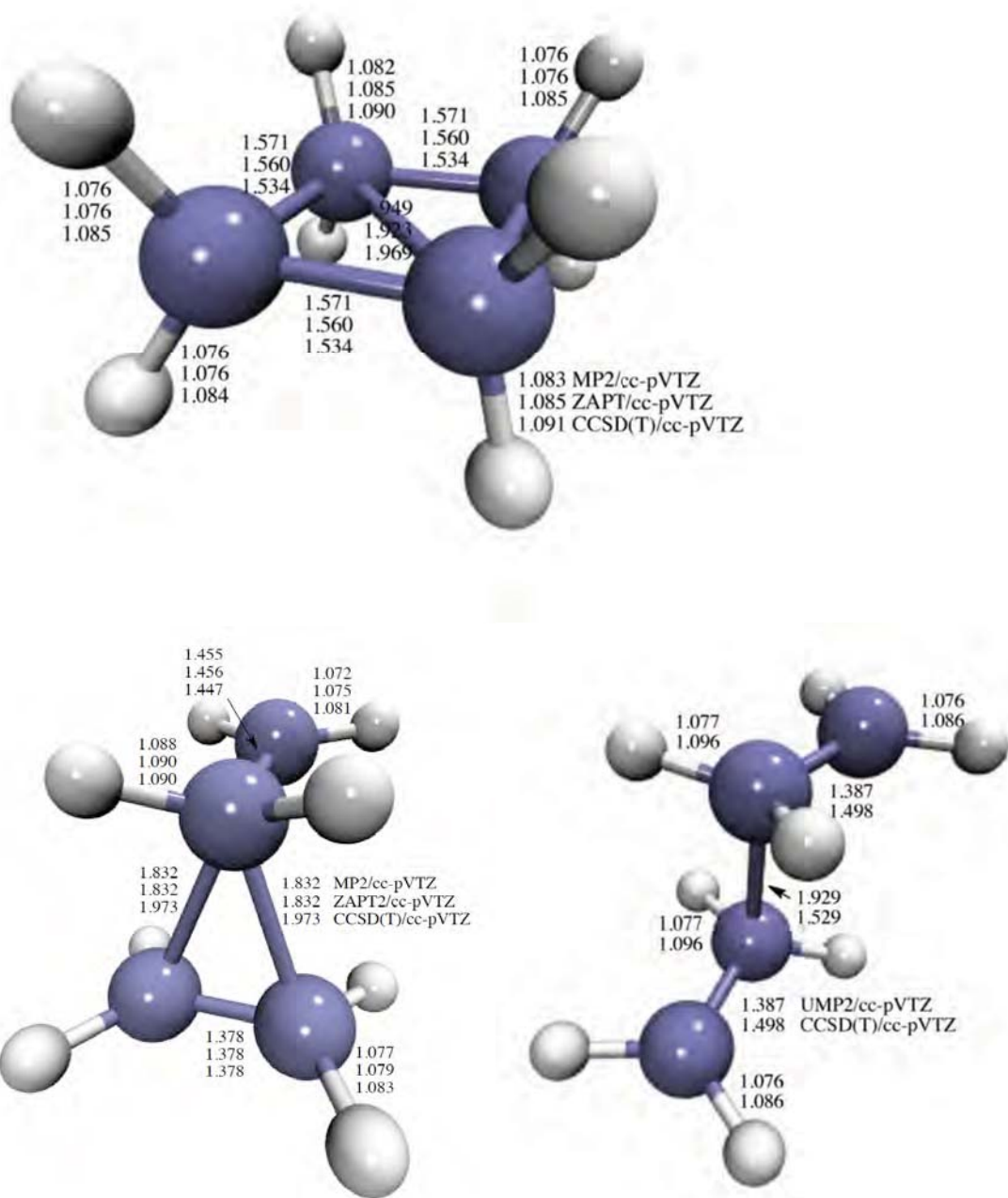
Figure 2. Structural parameters of the ethylene-ethylene cation association products (cyclobutane cation, bridge and C$_2$) is presented here at the MP2/cc-pVTZ, ZAPT2/cc-pVTZ and CCSD(T)/cc-pVTZ levels of theory.

Figure 3. Structural parameters of the acetylene-ethylene cation association products (cyclobutenyl cation, bridge and π-complex) are presented here at the MP2/cc-pVTZ, ZAPT2/cc-pVTZ and CCSD(T)/cc-pVTZ levels of theory.
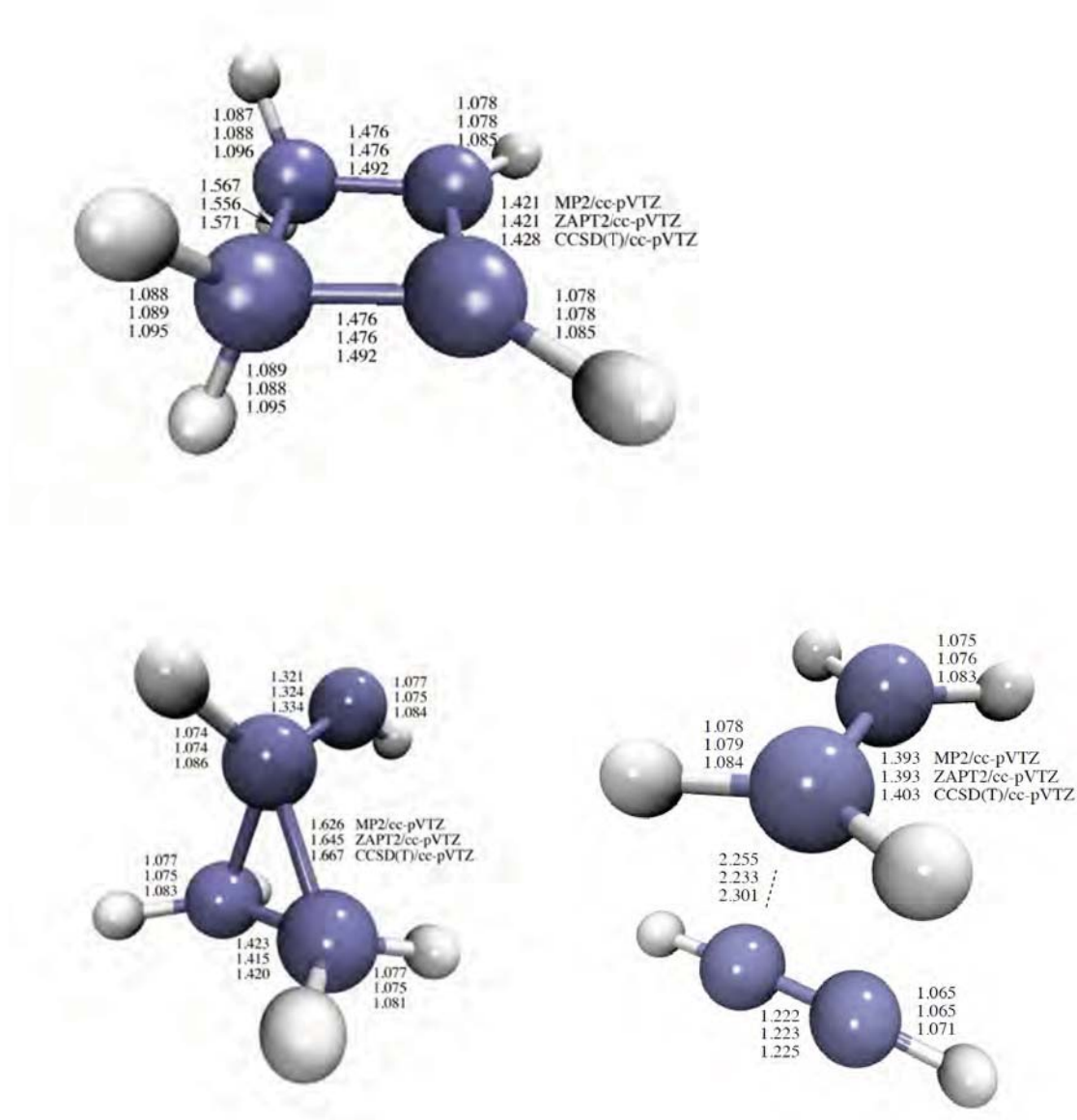
Figure 4. Electronic excitation spectra using time dependent density functional theory at the B3LYP/cc-pVTZ level. Acetylene dimer cation: (a) cyclobutadiene puckered cyclic, (b) bridge, (c) C2. Ethylene dimer cation: (d) cyclobutane puckered cyclic cation, (e) bridge. Acetylene-ethylene cation: (f) cyclobutene cation (g) bridge isomer (h) π complex.
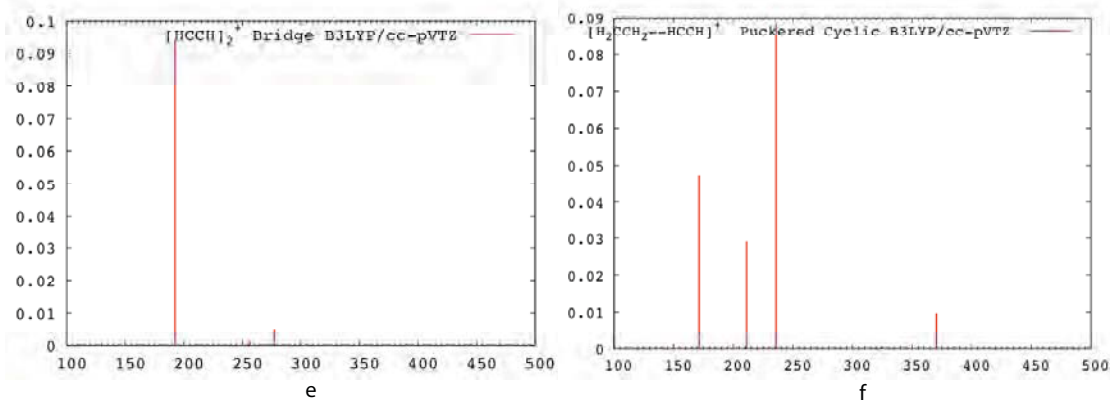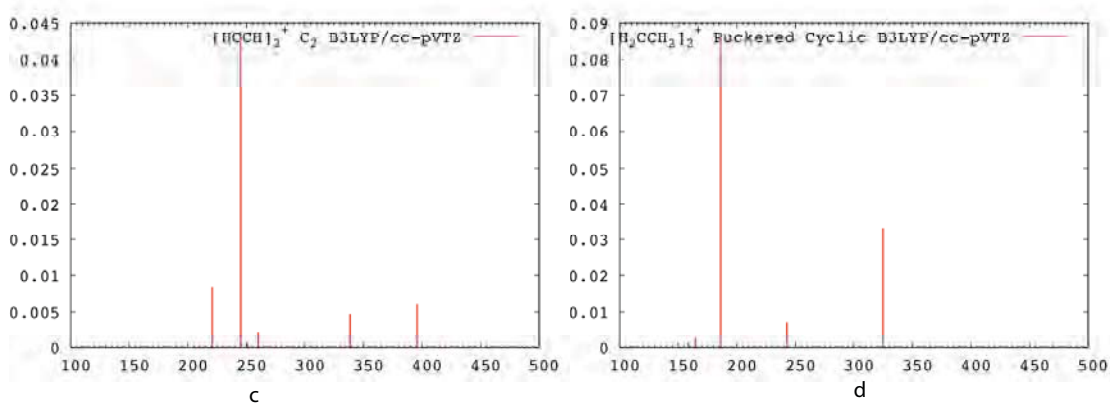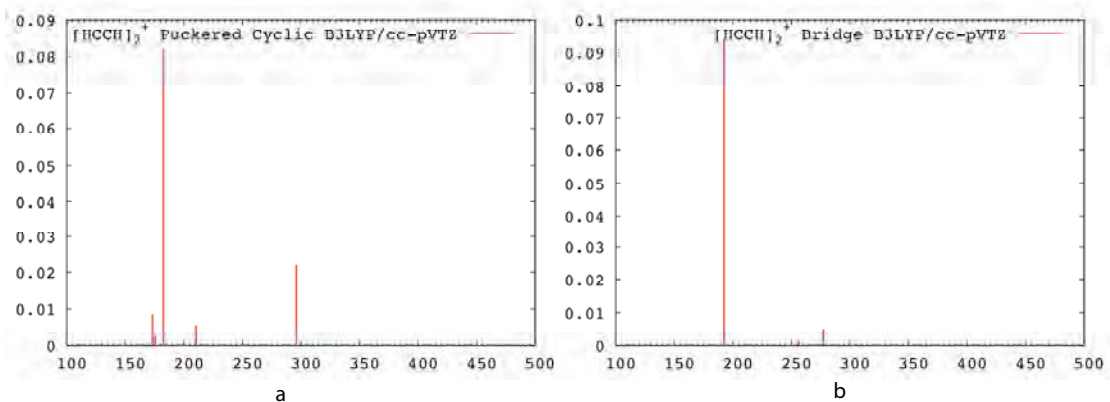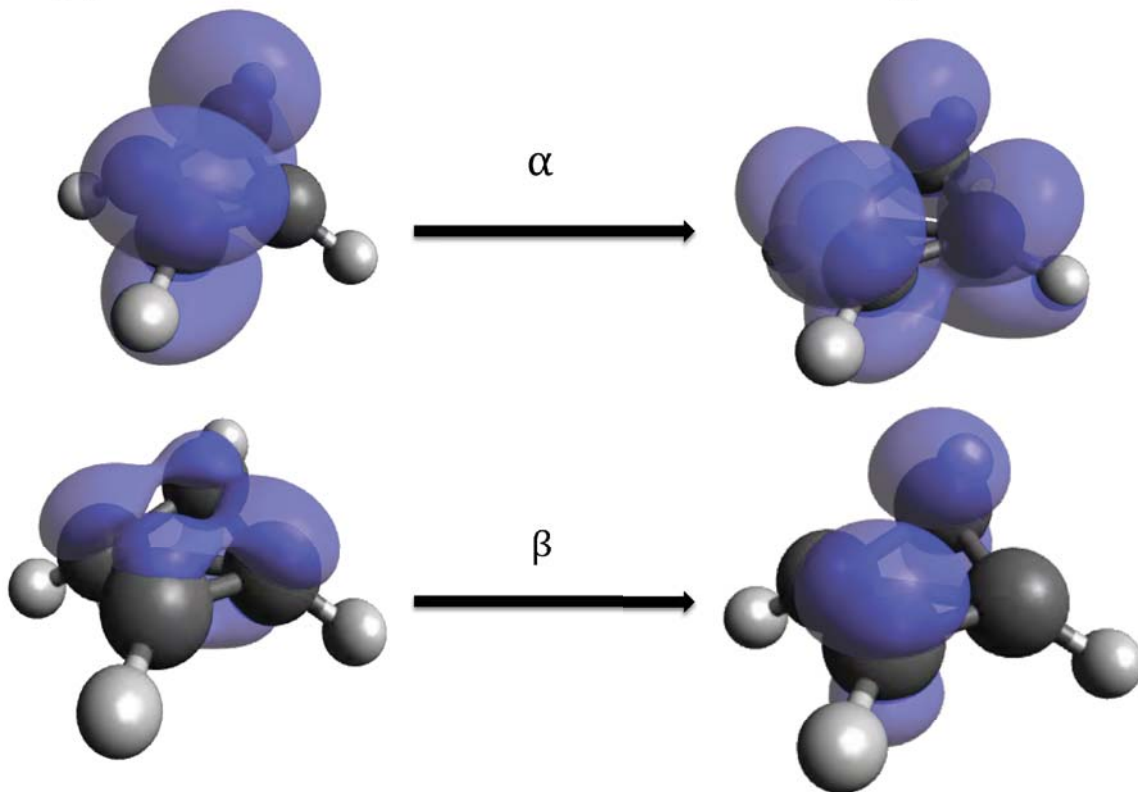
a

b

c

d

e

f

g

h
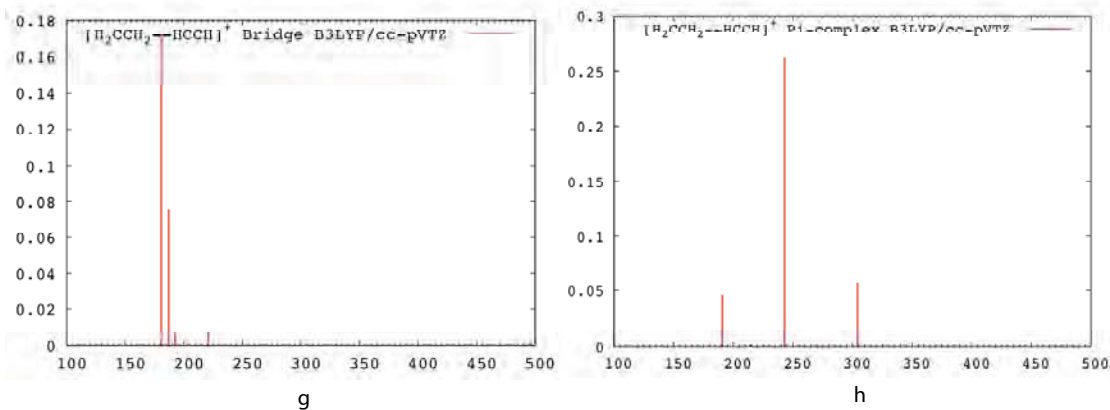
Figure 5. Detachment/attachment densities for the two most intense peaks in the computed electronic spectrum of the puckered ring structure of acetylene dimer cation (spectrum shown in Fig. 4a). See text for discussion of the attachment/detachment densities.

(a) The transition at 296 nm with oscillator strength 0.022

(b) The transition at 183 nm with oscillator strength 0.082
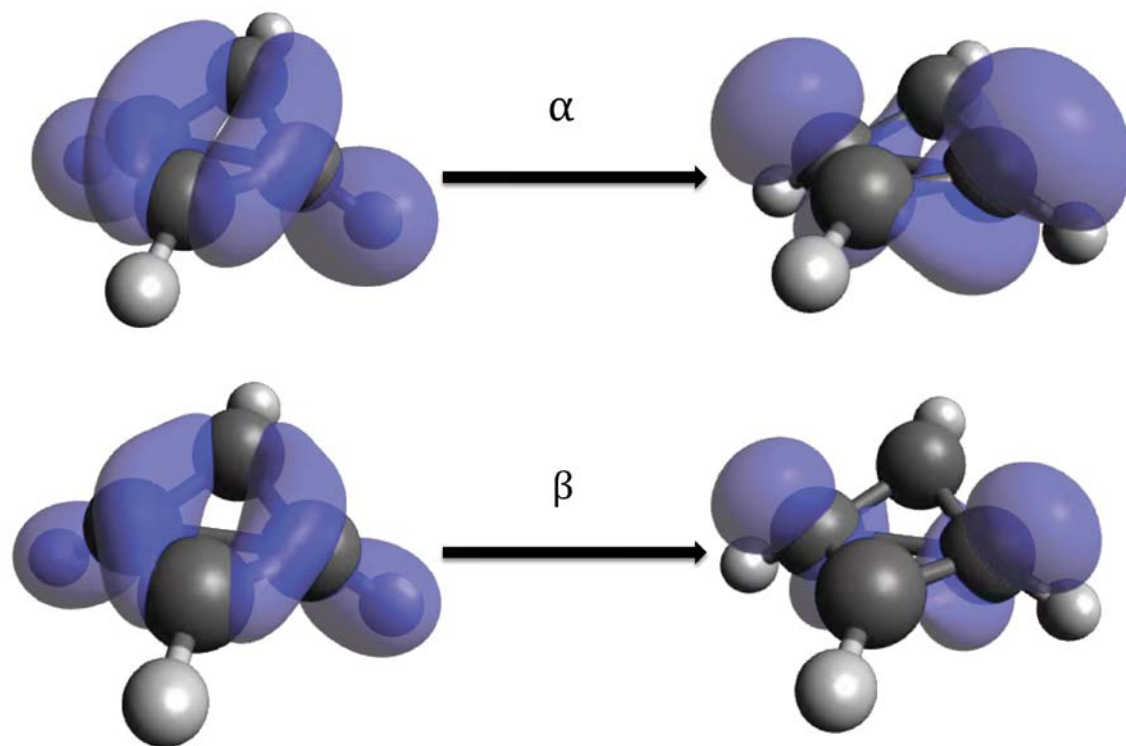
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