

Acetylene aggregates via cluster-building algorithm and molecular tailoring approach

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Abstract Acetylene clusters are prototypical of simple non-aromatic systems bonded through C–H... π interactions. The present work explores structures and properties of acetylene clusters (C₂H₂)_n, $n = 8$ and 10, employing cluster-building algorithm and molecular tailoring approach (MTA). The former uses electrostatics guidelines for building (C₂H₂)₈ and (C₂H₂)₁₀ structures. These clusters are treated at MP2 level of theory with correlation-consistent basis sets using MTA. The Hessian matrix and vibrational spectra for the best five structures of (C₂H₂)₈ and (C₂H₂)₁₀ are computed employing MTA. Actual calculations on these clusters using conventional methods employing large basis sets are prohibitively difficult to perform. All the frequencies for these structures extracted using MTA-based Hessian matrix are found to be real, confirming their local minimum nature. This study points to the possibility of using the present approach for exploring structures, energetics and vibrational spectra of even larger clusters at higher levels of theory.

Keywords Acetylene · Møller–Plesset second-order perturbation theory (MP2) · Molecular clusters · Hessian matrix · Vibrational spectra · Molecular tailoring approach (MTA)

Dedicated to Professor Eluvathingal Jemmis and published as part of the special collection of articles celebrating his 60th birthday.

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1 Introduction

Exploring structures and energetic of molecular clusters is a problem of considerable interest because they lie between isolated gas-phase molecules and the bulk condensed matter. Acetylene (C₂H₂) clusters have been subjected to detailed studies [1–14] because they are representative of non-aromatic ones exhibiting C–H... π contacts just like their aromatic counterparts, viz. benzene clusters [15–18]. These weak interactions are found to play a significant role in various chemical systems and dynamic processes. The other reason for interest in the weak interactions of acetylene is that although acetylene molecule has no net dipole moment, upon its aggregation, the hydrogen atoms may participate in weak bonding with the π -cloud of another acetylene molecule. Although these interactions are small, when compared with those of molecules having permanent dipole moment (e.g., water clusters), they are presumably quite strong when dissolved in acetone. It is well-known that acetone is used for storing and transporting acetylene as 1 liter of acetone dissolves about 250 liters of acetylene [19].¹

For the past few years, some experimental studies have been reported on acetylene clusters. Ohshima et al. [1] determined the rotational constants of dimer by free-jet infrared absorption spectroscopy and concluded that the dimer has a T-shaped geometry. Prichard et al. [2] proposed a planar cyclic structure for (C₂H₂)₃, on the basis of measured infrared spectrum, while Bryant et al. [3] suggested that (C₂H₂)₄ has a puckered ring structure. Hirabayashi et al. [4] have used step-scan Fourier-transform infrared absorption spectroscopy to study large clusters of

¹ History-Acetylene dissolved in acetone: http://www.aga.com/web/web2000/com/wppcom.nsf/pages/History_Acetylene_1.

C_2H_2 and C_2D_2 formed in pulsed supersonic jets. They reported the mean size of the clusters as ~ 10 nm.

On the theoretical front, in early nineties, Muentert [5] investigated the structure of acetylene dimer, and Karpfen [6] further investigated the intermolecular energy of the dimer at the MP2 level of theory. These studies confirmed the T-shaped structure for dimer in agreement with the experiments. Different structures of trimer were studied at Hartree–Fock (HF) and Møller–Plesset second-order perturbation theory (MP2) levels [7, 8], and cyclic form was suggested to be the global minimum. Shuler and Dykstra [9] investigated structures of acetylene clusters with $2 \leq n \leq 19$ by using molecular mechanics. Structures of four different acetylene clusters, from dimer to pentamer, were studied by Yu et al. [10]. They predicted a non-planar structure to be most stable for pentamer, and the study also revealed that for clusters larger than dimer show a preference for multiple T-type hydrogen bonding. More recently, Kim and co-workers [11] reported a detailed theoretical investigation on $(C_2H_2)_n$, $n = 2-5$ at higher level of theories such as MP2 and Coupled Cluster with Singles, Doubles and Perturbative Triple excitations (CCSD(T)) at the complete basis set (CBS) limit. Takeuchi [12] reported the geometries of acetylene clusters containing up to 55 monomers using intermolecular potential developed by Garrison and Sandler [13]. In a recent work, Gadre and co-workers [14] reported investigation of structure and energetics of $(C_2H_2)_5$ and $(C_2H_2)_6$ at MP2 and CCSD(T) levels employing correlation-consistent basis sets and the corresponding stabilization energies at the CBS limit. This work has reported some new structures for $(C_2H_2)_5$ and $(C_2H_2)_6$, which are not considered in studies by Dykstra et al. [9] and Kim et al. [11]. In order to reduce the complexity of these calculations, especially those at CCSD(T) level, a linear scaling technique, viz. molecular tailoring approach (MTA), is employed.

It is a well-known fact that with an increase in size of the cluster, the number of minima in the corresponding potential energy surface (PES) also increases. This, in turn, necessitates larger number of structures to be scanned. This is one of the main reasons why studies on large clusters are rare, since generally there is no systematic building-up strategy. Hence, in order to reduce the effort of scanning large number structures, our group has recently proposed an algorithm for building molecular clusters [20] based on the electrostatic guidelines. The algorithm has been tested on a variety of molecular clusters, such as ZnS, benzene and water clusters. The present work exploits the use of this cluster-building algorithm for generating good starting geometries for structures of $(C_2H_2)_n$ with $n = 8$ and 10, for a subsequent ab initio treatment.

For studying the C–H... π interactions involved in acetylene clusters, ab initio treatment at higher levels of

theory such as second-/third-/fourth-order MP theories or CCSD(T), etc. is recommended. But these methods are very demanding in terms of computing hardware and CPU time. This is one of the main reasons why studies of acetylene clusters beyond pentamers generally are restricted to only molecular mechanics and molecular dynamics. This hurdle can be overcome by using the state-of-art software MTA [21–25]. The basic idea of MTA involves fragmenting a large parent system into a set of smaller, overlapping subsystems and performing the calculations on these manageable subsystems. The energy, gradient and other required properties of the parent system are estimated by using those of the subsystems (fragments) employing the set inclusion–exclusion principle. The MTA method has been successfully applied for geometry optimization [15, 21–23], Hessian matrix calculation [24], etc. of a variety of large molecules and molecular clusters. There are other fragmentation methods available in the literature such as DC method of Li et al. [26], fragment molecular orbital (FMO) proposed by Kitaura et al. [27] and others by Nakai et al. [28], Bettens et al. [29] and Collins [30], which are aimed to reduce the computational requirements of the ab initio calculations.² FMO has been reported to be highly successful for accurate treatment of large biomolecules. However, MTA is applicable for large molecules as well as molecular clusters.

In the present work, MTA is employed for optimizing the geometries of $(C_2H_2)_n$, $n = 8$ and 10, generated by cluster-building algorithm at MP2/aug-cc-pVDZ level of theory employing contemporary off-the shelf hardware. Further, various properties of these optimized clusters such as the Hessian matrix, vibrational frequencies, etc. are investigated.

2 Computational details

In the present work, an attempt to scan local minima of $(C_2H_2)_8$ and $(C_2H_2)_{10}$ at MP2 level of theory is made. For building the acetylene clusters, use of cluster-building algorithm [20] is made. The cluster-building algorithm exploits the “lock-and-key” type features captured by the electrostatics of interacting moieties for growing a molecular cluster. The local negative minimum in the molecular electrostatic potential (MESP) of a cluster acts as a site of attack for positioning the positively charged atom of the incoming monomer. In the cluster builder code, basic ideas in electrostatics, viz. point charge energy as well as the previously proposed electrostatic potential for intermolecular complexation (EPIC) [31, 32] model, are

² See, for some representative works on fragmentation-based methods [21–30].

applied for computing the interaction energy of the added monomer, which is subsequently minimized. Through the cluster-building algorithm, one can add monomer, dimer as well as trimer to the parent cluster system.

To begin with, various $(\text{C}_2\text{H}_2)_8$ structures are built from the three energetically favorable $(\text{C}_2\text{H}_2)_6$ structures reported in Ref. [14] by adding either 2 acetylene monomers or a T-shaped acetylene dimer. MESP calculated at MP2/3-21G level of theory is employed for building these $(\text{C}_2\text{H}_2)_8$ structures. It has been known [33] that at a fixed geometry, change in basis set does not affect the essential topographical features of MESP, which is why a small basis set, viz. 3-21G, is chosen for MESP calculations. This exercise resulted into 40 different structures of octamers, which are subjected to geometry optimization MP2/3-21G level of theory. This small basis set is chosen in order to scan the best candidates for energetically most favorable assemblies. Out of these 40 structures, best 15 are further optimized at MP2/aug-cc-pVDZ (aug-cc-pVDZ named as DZ henceforth in this article) employing the tool of MTA. Although geometry optimization of $(\text{C}_2\text{H}_2)_8$ is possible with conventional methods at MP2/DZ level of theory, MTA is used to accelerate this process, resulting into a substantial reduction in computational resources.

MTA is a divide-and-conquer (DC) type algorithm, in which the parent large molecule/molecular cluster is broken into overlapping fragments. The details of fragmentation procedure can be found elsewhere [21–23]. In the case of molecular clusters such as $(\text{C}_2\text{H}_2)_n$, the covalent bonds are kept intact and only weak bonds are scissored. Due to the simplicity of these structures, manual fragmentation via MeTASudio³ [34] is preferred over the automatic fragmentation [21–23]. The calculations at the desired level of theory are performed on the fragments, results of which are then patched back as per the cardinality-guided expression. For example, the energy for the parent system can be estimated as,

$$E = \sum E^{f_i} - \sum E^{f_i \cap f_j} + \dots + (-1)^{k-1} \sum E^{f_i \cap f_j \cap \dots \cap f_k} \quad (1)$$

where, E^{f_i} stands for the energy of fragment f_i , $E^{f_i \cap f_j}$ stands for the energy of binary overlapping fragment $f_i \cap f_j$ and $E^{f_i \cap f_j \cap \dots \cap f_k}$ is the energy of k th order overlapping fragment $f_i \cap f_j \cap \dots \cap f_k$.

On similar lines, the Hessian matrix and any other properties can be estimated as per following generalized cardinality-based prescription,

$$\mathbf{H}_{ab} = \sum \mathbf{H}_{ab}^{f_i} - \sum \mathbf{H}_{ab}^{f_i \cap f_j} + \dots + (-1)^{k-1} \sum \mathbf{H}_{ab}^{f_i \cap f_j \cap \dots \cap f_k} \quad (2)$$

$$\mathbf{P}_{ab} = \sum \mathbf{P}_{ab}^{f_i} - \sum \mathbf{P}_{ab}^{f_i \cap f_j} + \dots + (-1)^{k-1} \sum \mathbf{P}_{ab}^{f_i \cap f_j \cap \dots \cap f_k} \quad (3)$$

where, \mathbf{H}_{ab} denotes element of Hessian matrix for nuclear coordinates 'a' and 'b', while $\mathbf{H}_{ab}^{f_i}$ depicts the corresponding value in fragment f_i . In Eq. 3, \mathbf{P}_{ab} represents any other property such as dipole derivative tensor for nuclear coordinate 'a' and tensorial index 'b', which goes from 1 to 3 in case of dipole derivatives and so on.

Further, this MTA-based Hessian matrix (\mathbf{H}) is subjected to standard procedure for extracting the vibrational frequencies, that is, by diagonalizing the mass-weighted Hessian matrix (\mathbf{H}_m) as,

$$\mathbf{H}_m = \mathbf{M}^{-1/2} \mathbf{H} \mathbf{M}^{1/2} \quad (4)$$

$$\mathbf{H}_m \mathbf{L}_k = \lambda_k \mathbf{L}_k \quad (5)$$

Here, \mathbf{M} is the array of atomic masses while \mathbf{L}_k and λ_k are the displacements and frequencies, respectively.

The vibrational intensities (\mathbf{I}) are determined by,

$$\mathbf{I} = \mathbf{L}_k \cdot \mathbf{P} \cdot \mathbf{M}^{-1/2} \quad (6)$$

where \mathbf{P} denotes dipole derivative tensor with \mathbf{L}_k and \mathbf{M} being the displacement vectors and array of atomic masses, respectively.

The five most stable $(\text{C}_2\text{H}_2)_8$ are subjected to MTA-based Hessian calculation MP2/DZ level to confirm their local minimum nature. The stabilization energies ($\Delta E_{(ac)n}$ in kcal/mol) for these clusters is calculated as,

$$\Delta E_{(ac)n} = (E_{(ac)n} - n \times E_{\text{mono}}) \times 627.51 \quad (7)$$

where $E_{(ac)n}$ and E_{mono} are the MTA-based total energy (in a.u.) of $(\text{C}_2\text{H}_2)_n$ and energy of the acetylene monomer at the same level of theory, respectively. In order to eliminate the basis set superposition error (BSSE), the stabilization energy of a cluster is extrapolated to the complete basis set limit (CBS) using Helgaker's two-point formula [35],

$$\text{CBS}(DT) = [27 \times \Delta E(TZ) - 8 \times \Delta E(DZ)]/19 \quad (8)$$

where $\Delta E(XZ)$, $X = D, T$ stands for binding energy of a cluster with aug-cc-pVXZ basis set (XZ).

For building up decamers, use is made of the octameric structures that have been described above. For this purpose, along with the best octamer, the second and third best structures are also used, for generating and scanning decameric structures. MESP of these best three $(\text{C}_2\text{H}_2)_8$ is calculated at MP2/3-21G level of theory and fed to cluster-building algorithm to generate good guess geometries for $(\text{C}_2\text{H}_2)_{10}$. Following this, these decamer geometries are

³ The MeTASudio package, an open-source programmable IDE for computational chemists, <http://code.google.com/p/metastudio/>, See [34].

scanned at MP2/3-21G level, out of which the best 10 lowest energy decamers are chosen for MTA-based optimization at MP2/DZ level of theory. Here also, the MTA-based Hessian calculations are performed on the 5 most stable $(\text{C}_2\text{H}_2)_{10}$ structures at MP2/DZ level. The stabilization energies at MP2/CBS limit are evaluated following Eqs. 7 and 8. All the above-mentioned calculations are performed by using Gaussian 09 package [36] at the back-end of MTA.

3 Results and discussion

As described in the previous section, different structures for acetylene octamers are generated by running the cluster-building algorithm and scanned at MP2/3-21G level of theory. Only lowest lying 15 structures from these are subjected to further geometry optimization at MP2/DZ level of theory, followed by a single-point calculation at MP2/TZ level. The MTA-optimized energies of acetylene octamers at MP2/DZ along with their stabilization energies are reported in Table 1, along with the corresponding MP2/TZ MTA single-point energies. Structures of the best three octamers among these five are displayed⁴ [37] in Fig. 1. The CBS limit energies for all the octamers at MP2 level of theory are obtained by applying Helgaker's two-point formula given in Eq. 8. These stabilization energies are very close, with all energies lying within 0.6 kcal/mol (cf. Table 1), of each other. It should be noted that all best five structures listed in Table 1 are non-planar. In the lowest energy octamer, that is, $(\text{C}_2\text{H}_2)_8\text{-I}$ (cf. Fig. 1), all the interactions are T-shaped ones and maximum in number among all the octameric structures. The second best structure $(\text{C}_2\text{H}_2)_8\text{-II}$ exhibits lesser number of T-shaped interactions than in $(\text{C}_2\text{H}_2)_8\text{-I}$. It also exhibits some $\text{CH}\cdots\pi$ stacking interactions. This shows that the T-shaped interactions play an important role in stabilization of geometry of an acetylene cluster.

Similarly, for acetylene decamers, the structures generated from octamers by cluster-building algorithm are also scanned at MP2/3-21G level of theory. Out of these, ten lowest energy structures are subjected to MTA optimization at MP2/DZ level of theory. From these structures, the MP/DZ optimized energies and MP2/TZ single-point energies for the best five geometries are reported in Table 2, along with the respective stabilization energies. The stabilization energies at MP2 level CBS limit for these structures are also reported in Table 2. The three best decamers are displayed in Fig. 2. Here also, all

Table 1 MTA-optimized energies (in a.u.) of acetylene octamers at MP2/DZ and MTA single-point energies at MP2/TZ level of theory

Acetylene- 8mer	MP2/DZ	MP2/TZ	CBS limit
$(\text{C}_2\text{H}_2)_8\text{-I}$	−616.795503 (−32.3)	−617.348612 (−27.1)	−24.9
$(\text{C}_2\text{H}_2)_8\text{-II}$	−616.795479 (−32.3)	−617.348156 (−26.9)	−24.6
$(\text{C}_2\text{H}_2)_8\text{-III}$	−616.794998 (−32.0)	−617.347732 (−26.6)	−24.3
$(\text{C}_2\text{H}_2)_8\text{-IV}$	−616.794416 (−31.7)	−617.347317 (−26.4)	−24.2
$(\text{C}_2\text{H}_2)_8\text{-V}$	−616.794415 (−31.7)	−617.347555 (−26.5)	−24.3

The numbers in parentheses are the corresponding stabilization energies (in kcal/mol) with respect to acetylene molecule (the MP2 energies of acetylene molecule optimized at DZ and single-point at TZ basis are: −77.092997 and −77.163163 a.u., respectively) at the corresponding level of theory

the decameric structures are seen to possess non-planar geometries. The most stable decamer $(\text{C}_2\text{H}_2)_{10}\text{-I}$ has maximum number of T-shaped interactions, although there are some stacking interactions present as well. All the decameric structures in Fig. 3 show a kind of zig-zag arrangement of monomers. In the most stable decamer, the monomers are arranged in highly ordered manner while the disorder goes on increasing as the energy of the cluster increases.

The efficacy of MTA in calculating highly accurate Hessian and frequencies, with large computational time advantage, has been already demonstrated [24] for structurally diverse, spatially extended molecules. However, to assure a similar accuracy for the present study, a benchmark for Hessian matrix and vibrational spectra is performed for $(\text{C}_2\text{H}_2)_8\text{-I}$ employing 3-21G basis set, for which conventional calculation is readily possible. The earlier studies [25] on MTA have revealed that the accuracy of MTA is independent of the basis set and level of theory used. Therefore, the accuracy of MTA at 3-21G and DZ basis sets is expected to be similar. The MTA-based Hessian is computed employing Eq. 2, based on only tetrameric main fragments. On comparing MTA-based Hessian matrix with the corresponding actual one, the maximum error in the Hessian element turns out to be 4.4×10^{-4} a.u. for the actual value of 0.0423 a.u., with 2.4×10^{-5} a.u. as the RMS error. On similar lines, when MTA-based dipole derivative tensors (as per Eq. 3) are compared, the maximum error is 0.0075 (corresponding actual value being 0.2365 a.u.) while the RMS error is 0.0020 a.u. A comparison of MTA-based vibrational spectrum for $(\text{C}_2\text{H}_2)_8\text{-I}$ with that obtained by conventional (actual) calculation on the entire cluster is shown in Fig. 3. As seen from Fig. 3, MTA-based vibrational frequencies match well with their counterparts in actual calculation, while intensities show a reasonably good agreement. In both of these spectra, the vibrational frequencies appear in

⁴ UNIVIS-2000: A comprehensive visualization package, See [37].

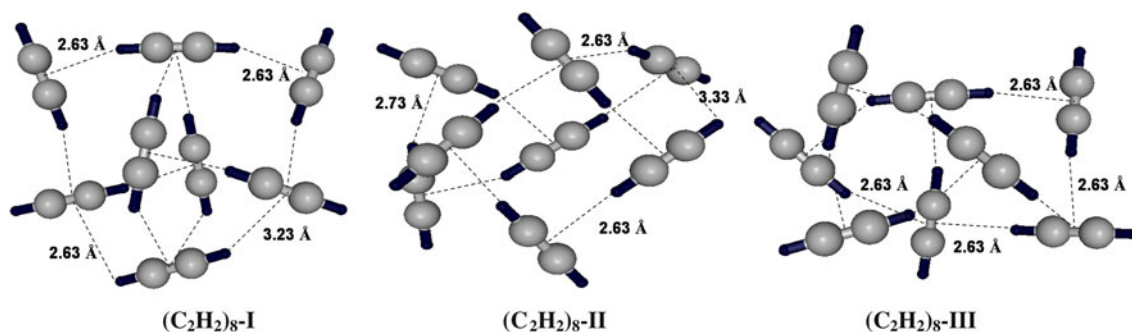


Fig. 1 Three best acetylene octamers MTA-optimized at MP2/DZ level of theory. See text and Table 1 for details

Table 2 MTA-optimized energies (in a.u.) of acetylene decamers at MP2/DZ and MTA single-point energies at MP2/TZ level of theory

Acetylene-10mer	MP2/DZ	MP2/TZ	CBS Limit
(C ₂ H ₂) ₁₀ -I	-770.001236 (-44.7)	-771.691170 (-37.3)	-34.2
(C ₂ H ₂) ₁₀ -II	-770.999224 (-43.5)	-771.689241 (-36.2)	-33.1
(C ₂ H ₂) ₁₀ -III	-770.998279 (-42.8)	-771.688450 (-35.7)	-32.7
(C ₂ H ₂) ₁₀ -IV	-770.997576 (-42.4)	-771.687789 (-35.2)	-32.2
(C ₂ H ₂) ₁₀ -V	-770.997387 (-42.3)	-771.687609 (-35.1)	-32.1

The numbers in parentheses are the respective stabilization energies (in kcal/mol) with respect to acetylene molecule (the MP2 energies of acetylene molecule optimized at DZ and single-point at TZ basis are: -77.092997 and -77.163163 a.u., respectively) at the corresponding level of theory

ranges of 700–850 cm⁻¹ and 3,400–3,500 cm⁻¹. The most intense peaks of C C stretching are around 780–800 cm⁻¹ in both MTA-based as well as actual spectra. However, intensity of one of these peaks is slightly overestimated by MTA. The intensities of C–H stretch modes in 3,400 to 3,500 cm⁻¹ region are quite accurately mimicked by MTA as in actual spectra.

With this assurance of accuracy, MTA-based Hessians for best five acetylene octamers are evaluated at final

MP2/DZ level of theory. All the frequencies for these five octamers are found to be real confirming the local minimum nature of these structures. This again proves the effectiveness of the cluster-building algorithm, capturing different kinds of local minimum structures on PES of the cluster. The vibrational spectra for (C₂H₂)₈-I and (C₂H₂)₈-II calculated by employing MTA are shown in Fig. 4. The overall nature of the spectrum and the regions of vibrational frequencies (viz. 700–800 cm⁻¹ and 3,350–3,450 cm⁻¹) are similar for both the octamers. However, in case of (C₂H₂)₈-II, some of the C–H stretches are slightly downshifted and hence more widespread in the region of 3,350–3,450 cm⁻¹.

As in the case of octamers, the MTA-based Hessian calculations are carried out on five best decamers at MP2/DZ level of theory. All the frequencies for each decamer are found to be real, again confirming the nature of the structures as stationary points on the PES. Again, the main features of (C₂H₂)₁₀-I and (C₂H₂)₁₀-II are similar, and the bands in (C₂H₂)₁₀-II are more widespread (cf. Fig. 4). Also, C≡C stretches in spectra of (C₂H₂)₁₀-I appear more intense and close to each other, while those for (C₂H₂)₁₀-II are farther and less intense as compared to those of (C₂H₂)₁₀-I.

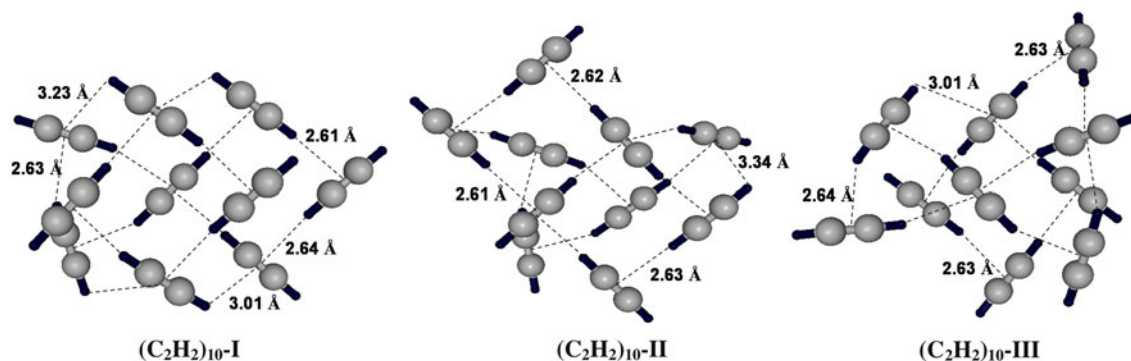


Fig. 2 Three best acetylene decamers MTA-optimized at MP2/DZ level of theory. See text and Table 2 for details

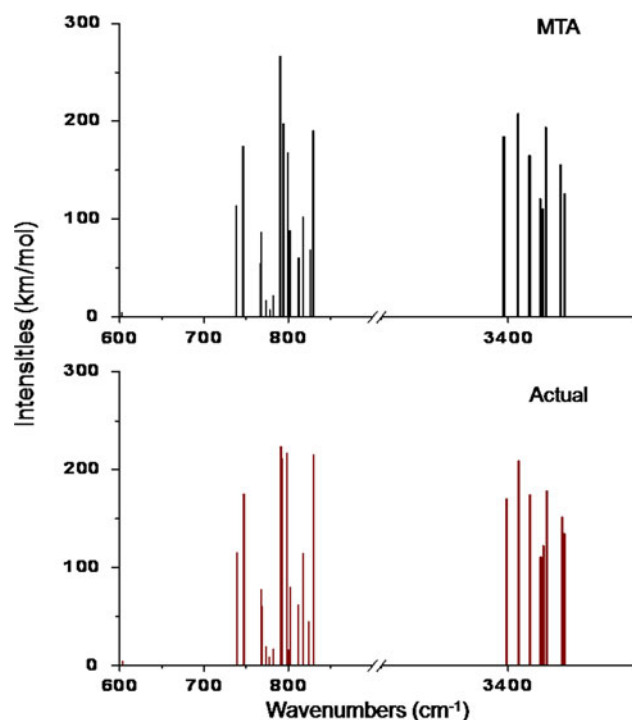


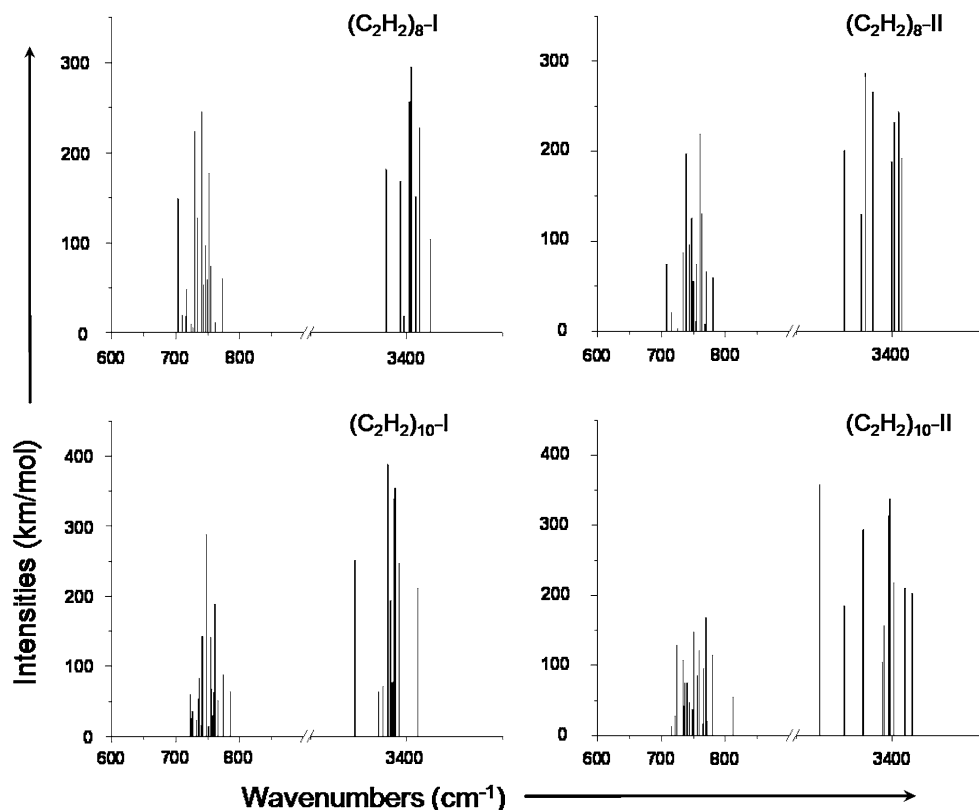
Fig. 3 A comparison of the vibrational spectrum of $(\text{C}_2\text{H}_2)_8\text{-I}$ obtained by MTA with that obtained by actual calculation at MP2/3-21G level of theory. See text for details

4 Concluding remarks

Studies of oligomers of acetylene are interesting since they represent a class of weakly bound molecular clusters involving C–H... π interactions. A systematic way of growing a cluster, viz. a combination of cluster-building algorithm and molecular tailoring approach, is effectively employed for this investigation. Search for minimum structures on the PES of a cluster becomes increasingly more difficult with growing cluster size, as the number of possible orientations enhances non-linearly. However, by using MESP guidelines to capture the directionality of the interaction, the cluster-building algorithm [20] offers a promising method that attempts to consider all energetically favorable arrangements. Moreover, it is certainly a better method than growing the cluster at random locations, since it substantially reduces the number of initial geometries to be scanned.

Another hurdle in exploring structures and energetics of large clusters is the high scaling order of ab initio methods. For post-HF methods such as MP2 or coupled cluster methods, which capture electron correlation effects from a reasonable to good extent, the scaling order is $O(N^5)$ or even higher. Thus, in such cases, DC-based methods are expected to play a significant role in reducing the

Fig. 4 MTA-based vibrational spectra for two best acetylene octamers and decamers at MP2/DZ level of theory. See text for details



computational requirements of the calculation. MTA is a well-established method for ab initio treatment of large molecules and molecular clusters. Though the geometry optimization of $(C_2H_2)_8$ and $(C_2H_2)_{10}$ can be performed by conventional methods at MP2/DZ level of theory, MTA indeed accelerates the calculation. Further, the present work demonstrates how MTA can handle the expensive calculations of Hessian matrix of large clusters at MP2 level of theory efficiently, while retaining the accuracy. It may be pointed out that the present MTA has been parallelized and can use a large number of nodes in a computer cluster as per the requirement of the calculation. This is in continuation with the earlier efforts of parallelization of quantum chemistry codes from our laboratory [38, 39].

The present study clearly shows that the local minima of the acetylene aggregates, though structurally very different, are energetically close. Extrapolation of the stabilization energies to complete basis set limit further narrows down this energy range. On the other hand, the vibrational spectra of these clusters are quite different from each other, which may be useful in differentiating these clusters if they could be experimentally generated.

In summary, the present work is a clear demonstration of the efficacy of cluster-building algorithm for generating good candidates for energetically favorable molecular assemblies. This algorithm when coupled with MTA indeed offers a powerful tool for studying structures, energetics and other properties such as vibrational spectra of large clusters.

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