Ab Initio Study on $(\text{CO}_2)_n$ Clusters via Electrostatics- and Molecular Tailoring-Based Algorithm

K. V. JOVAN JOSE, SHRIDHAR R. GADRE
Department of Chemistry, University of Pune, Ganeshkhind-411007, India

Received 2 November 2008; accepted 12 January 2009
Published online 30 March 2009 in Wiley InterScience (www.interscience.wiley.com).
DOI 10.1002/qua.22110

ABSTRACT: An algorithm based on molecular electrostatic potential (MESP) and molecular tailoring approach (MTA) for building energetically favorable molecular clusters is presented. This algorithm is tested on prototype $(\text{CO}_2)_n$ clusters with $n = 13, 20,$ and 25 to explore their structure, energetics, and properties. The most stable clusters in this series are seen to show more number of triangular motifs. Many-body energy decomposition analysis performed on the most stable clusters reveals that the 2-body is the major contributor ($> 96\%$) to the total interaction energy. Vibrational frequencies and molecular electrostatic potentials are also evaluated for these large clusters through MTA. The MTA-based MESPs of these clusters show a remarkably good agreement with the corresponding actual ones. The most intense MTA-based normal mode frequencies are in fair agreement with the actual ones for smaller clusters. These calculated asymmetric stretching frequencies are blue-shifted with reference to the CO$_2$ monomer. © 2009 Wiley Periodicals, Inc. Int J Quantum Chem 109: 2238–2247, 2009

Key words: molecular tailoring approach; linear scaling methods; Hessian; IR frequencies; molecular electrostatic potential; EPIC; density functional theory

Introduction

Clusters exhibit properties which are quite distinct from those of constituent molecules and those of the condensed matter. One of the fascinating questions raised by Jortner [1] is when and how the bulk-like properties emerge from the small cluster regime? This turning point from cluster to bulk region is called the “critical size” of the cluster. Even though the critical size is dependent on the type of the chemical system, the predominant contributing factor will be the nature of interactions. From the many attempts to understand the physics and chemistry of this transition region, it is observed that the ionic system requires few tens of atoms, while atomic clusters a few thousands of atoms to reach the bulk state. It is well-known that with the cluster size, the number of local minima in
the potential energy surface (PES) will grow exponentially [2]. At this juncture, locating energetically favorable structures is a great challenge and thus a very efficient cluster building algorithm is warranted for studying large clusters.

Experimentally and theoretically well-studied prototype systems are \((\text{CO}_2)_n\) clusters. Torchet et al. [3] have explored the structural transformations with cluster size using molecular beam electron diffraction and found a crossover regime from icosahedral to cubic-cluster morphology at \(n = 30\). This observation is further justified through molecular dynamics (MD) simulation studies of Mailet et al. [4]. It is observed that, with the increasing cluster size, the strain energy increases in magnitude and brings forth the above geometrical morphological transformation. The larger \((\text{CO}_2)_n\) clusters have been studied through slow electron attachment time of flight mass spectrometry with geometrical shell closing analysis of Negishi et al. [5] and led to a cuboctahedral motif for clusters with \(n > 80\). On the other hand, a distorted face centered-cubic packing is assumed by Ingolfsson and Wodke [6] for the same cluster regime.

Earlier theoretical investigations on \((\text{CO}_2)_n\) have employed empirical force fields [7]. The individual noncovalent interactions between molecules may be weak, but they may contribute substantially collectively. The strength of these interactions depends on the type of the system and the relative orientation of the interacting species. Liu and Jordan [8] have employed Monte Carlo simulation technique for investigating \((\text{CO}_2)_n\) clusters with \(n = 6\) to 19. Empirical potential was employed to locate geometries of \((\text{CO}_2)_n\) clusters with \(13, 19, 55, 147, 309,\) and 561 by van de Waal [9]. A cluster builder algorithm based on Lennard-Jones potential (LJ) has recently been developed by Takeuchi [10] and tested on \((\text{CO}_2)_n\) clusters with \(4 \leq n \leq 40\). The larger clusters showed geometries which are very close to that of crystal structures.

From the previous works from our group on clusters, it is noted that the molecular electrostatic potential (MESP) is a useful tool for building initial cluster geometries. Tomasi et al. [11] have pioneered the applications of MESP for understanding intermolecular interactions. Some of the earlier models, which make use of the MESP as a basic parameter for studying clusters, include Buckingham–Fowler model [12], molecular mechanics for clusters [13], and Alhambra, Luque, and Orozco model [14]. An MESP-based model [15] developed earlier in our laboratory for studying weak interaction is electrostatic potential for intermolecular complexation (EPIC). This model has been employed for studying several homo- and hetero-molecular complexes [16]. It is apparent in the literature that the genetic algorithm (GA) has great strength in efficiently searching the multidimensional potential energy surface [17]. GA is generally a common name given to the set of algorithm based on Darwinian evolution. Hence, a genetic algorithm employed in conjunction with EPIC model is expected to be helpful in locating energetically favorable initial clusters.

Some of the cluster properties of interest are vibrational frequencies in the asymmetric stretching region and the scalar field of MESP [18]. IR spectroscopic experiments have been employed to characterize the influence of particle shape, size and composition [2, 4, 19]. An ab initio investigation of frequency shifts of smaller \((n \leq 8)\) \((\text{CO}_2)_n\) clusters has been reported in our earlier work [20]. Although some larger clusters have also been dealt with in that work, the EPIC model has not been employed for systematically scanning the PES. Further, the number of structures explored was also rather limited. It is observed that with increasing cluster size, there is a blue-shift in the asymmetric stretching frequencies. Bonnamy et al. [21] have studied the shape and structural effects through direct IR supersonic jet expansion spectroscopy in this asymmetric stretching region. It is experimentally noticed that the band peak shifts toward blue region with increasing cluster size.

The present work explores the structures, energetics, and properties of \((\text{CO}_2)_n\) clusters at the cluster to bulk crossover regime, so as to shed further light on the physics and chemistry behind these transformations. The various initial structures of \((\text{CO}_2)_n\) were generated employing EPIC-model employing the algorithm discussed in the Methodology Section. The relative changes in geometries and the energetics of a number of local minima by this simple model help in generating initial geometries for a follow-up at higher levels of theory to explore structural changes on increasing the cluster size. An attempt has been made in the current work to extend the ab initio level \((\text{CO}_2)_n\) cluster calculations using molecular tailoring approach (MTA) to the cluster to bulk crossover regime as stipulated in the literature.

**Methodology**

In this section, the electrostatics- and molecular tailoring approach-based algorithm for cluster building is discussed first. This is followed by a
brief presentation of the methodology for evaluation of two molecular properties, viz., MESP and vibrational frequencies through MTA.

The EPIC and MTA-based algorithm is aimed for building energetically favorable clusters with M-monomers, from the monomer coordinates and its MESP. This algorithm is schematically depicted in Figure 1. In the present work, calculations have been performed at MPWB1K/6-31 + +G (2d, 2p) level of theory. Further, genetic algorithm (GA) is implemented within the EPIC regime for locating the most favorable cluster geometry in its multidimensional potential energy surface (PES). Foremost aspect for implementing GA is to define the genome of the cluster. Each individual (cluster) in a population (N-clusters) is defined through a set of genes \( \{R_x, R_y, R_z, T_x, T_y, T_z\} \). Here, \( R_x, R_y, \) and \( R_z \) are the orthogonal components of a vector (\( \mathbf{R} \)), connecting the center of mass of the individual monomer units (e.g., molecules in a cluster) and the origin, and \( T_x, T_y, \) and \( T_z \) are the angles between the \( \mathbf{R} \) vector and \( x, y, z \) directions, respectively. Once the N clusters, each containing M monomers, are generated through genome generated at random, the EPIC [16] energy of these clusters is evaluated using the expression

\[
E_{\text{EPIC}} = \frac{1}{2} \left( \sum_i V_A q_{Ai} + \sum_j V_B q_{Bj} \right) 
\]

Here, \( V_A, V_B, q_A, \) and \( q_B \) are the MESP [22] and the MESP fitted charges on the molecules A and B, respectively. The MESP at a point \( \mathbf{r} \) is defined as

\[
V(\mathbf{r}) = \sum_A Z_A \left( \frac{\rho(\mathbf{r})}{|\mathbf{r} - \mathbf{r}_A|} \right) d^3 \mathbf{r} 
\]

The first and second terms on the r. h. s. represent the bare nuclear and electronic contributions, respectively. The sign of the \( V(\mathbf{r}) \) in any particular region depends on whether the nuclear or electronic effects are dominant there. Once the energies of all the first generation clusters are calculated, new daughter clusters is generated through mutation and crossover of the parent clusters in the mating pool, employing Roulette wheel method. It is observed that only multimutations and multicrossover can give rise to energetically favorable daughter cluster geometries. This multidimensional genetic algorithm search is performed for prescribed number of cycles and a local optimization of each of these clusters carried out employing a function minimization Subroutine, STEPTIT [23]. This Subroutine works by minimizing the function, \( E_{\text{EPIC}} \) [Eq. (1)] by varying the function-dependant parameters \( \{R_x, R_y, R_z, T_x, T_y, T_z\} \) cyclically, one at a time. The best clusters thus engendered are subjected to ab initio geometry optimization within MTA framework. The details of this method can be found in Ref. [24], but are summarized briefly below. In MTA, the whole cluster is divided into a set of \( k \) main fragments \( \{f_1, f_2, \ldots, f_k\} \), with secondary overlapping fragments \( \{f_i \cap f_j\} \), and tertiary ones, viz. \( \{f_i \cap f_j \cap f_k\} \) etc. For this purpose, the best fragmentation scheme for each cluster is carried out based on R-goodness parameter. The energy for the whole cluster is calculated from the fragment energies \( E^1, E^2, \ldots, E^{(n)}, \ldots, E^{(n)} \) using the general energy expression.

\[
E = \sum E^1 - \sum E^{(n)} + \ldots + (-1)^{k-1} \sum E^{(n) \cap \ldots \cap (n)}
\]

Once the energy of the cluster is evaluated, the atomic gradients of the whole cluster are obtained [24] through the general expression...
A local gradient-based optimization is performed employing these gradients. A search over several starting geometries is carried out leading to energetically favored cluster. These ab initio fragment energy and gradient calculations were performed using Gaussian 03 package [25].

The EPIC-MTA program is coded in FORTRAN-90 and compiled using Intel FORTRAN compiler (IFC) on a GNU Linux operating system. The cluster search is carried out for a population size of 1000 and 50 generations with 300 new-offspring replacing the parents after each generation. The MTA optimization time scales [24] as \( n^2 \) here, \( m \) is the number of fragments and \( N_f \) is the average number of contractions in fragments. Thus generated clusters were visualized in indigenously developed visualization package [26], UNIVIS-2000. The strength of this novel algorithm is judged by comparing the already existing cluster geometries with the literature ones in the Results and Discussion part.

The many body analysis of clusters (MBAC) scheme of Xantheas as implemented by Kulkarni et al. [27] is employed for estimating the strength of two-, three-, and higher-body contribution to the total interaction. These MBAC calculations were performed via a code developed in our laboratory based on above energy partitioning scheme [27].

The MESP of the molecules is evaluated using INDPROP code [28] [INDPROP, the molecular property calculation package developed at Theoretical Chemistry Group, Department of Chemistry, University of Pune, Pune, India] developed in our laboratory. The MESP of the larger clusters was calculated via MTA [via Eq. (3)]. This method of evaluation of MESP of larger clusters is justified by the remarkably good agreement between the MTA-based and actual MESP minimum and function distributions [29]. The IR frequencies of larger (CO\(_2\))\(_n\) clusters are evaluated through MTA-based Hessian [30] calculations [Eq. (3)]. Here, the Hessian is a \( 3n \times 3n \) matrix of second partial derivative of energy with respect to each atomic orthogonal atomic displacement with \( n \) being the number of atoms in the cluster.

\[
\frac{\partial E}{\partial X_{\mu}} = \sum \frac{\partial E^{f}}{\partial X_{\mu}} - \sum \frac{\partial E^{f(\gamma)}_{\mu\gamma}}{\partial X_{\mu}} + \cdots + (-1)^{k-1} \sum \frac{\partial E^{f(\gamma\cdots\gamma)}}{\partial X_{\mu}}_k, \tag{4}
\]

\[
\frac{\partial^2 E}{\partial X_{\mu} \partial X_{\nu}} = \sum \frac{\partial^2 E^{f}}{\partial X_{\mu} \partial X_{\nu}} - \sum \frac{\partial^2 E^{f(\gamma)}_{\mu\gamma}}{\partial X_{\mu} \partial X_{\nu}} + \cdots + (-1)^{k-1} \sum \frac{\partial^2 E^{f(\gamma\cdots\gamma)}}{\partial X_{\mu} \partial X_{\nu}}_k. \tag{5}
\]

This Hessian is multiplied with square root of \( 1/m_\mu \) and the resulting matrix is diagonalized through Jacobi method to obtain the eigenvalues via GAMESS package [31]. These eigenvalues are employed for further evaluation of the vibrational frequencies.

Results and Discussion

In the first subsection, a comparison and analysis of the energetically most favorable clusters of (CO\(_2\))\(_n\) with \( n = 13, 20, \) and 25 is carried out with the ones reported in the literature. The next subsection discusses the energy decomposition analysis of these clusters and the third one discusses the cluster properties, viz., MESP and vibrational frequencies, obtained through MTA.

GEOMETRY ANALYSIS

For appraising the MTA algorithm, a comparison of the geometries located using this algorithm is done with the ones reported in the literature for (CO\(_2\))\(_n\) clusters with \( n = 13, 20, \) and 25. Table I gives, in a nutshell, the series of energetically favored clusters located for \( n = 13 \). Figure 2 [13-I, 13-II, 13-III, and 13-IV], shows four energetically most favorable (CO\(_2\))\(_{13}\) clusters. The first (13-I) and third (13-III) clusters are endowed with maximum number of C \( \cdots \) O interactions with triangular motifs, while the second (13-II) geometry contains maximum number of tetragonal bipyramid motifs.

The fourth cluster exhibits icosahedral geometry. The earlier works in the literature report the energetically most favorable \( n = 13 \) geometry to be icosahedral one [2]. Our study has also found four other clusters which are energetically close (within \( \sim 0.6 \) kcal/mol) to the icosahedral one. The higher clusters are built by employing the MESP characteristics of the lower ones. Figure 3 shows schematically the MESP-guided method for building clusters based on the MESP distribution of the starting clusters. The relatively deep seven MESP minima are indicated as X’s and the site of approach of the added CO\(_2\) is shown with an arrow. Seven more
CO₂ molecules are added, each around an MESP minimum, so as to yield a good starting geometry for (CO₂)ₙ clusters. These clusters were optimized using the subroutine STEPIT [23] with EPIC energy as the minimization function. A large number of (CO₂)₂₀ and (CO₂)₂₅ clusters are searched using this GA-EPIC code. Further, these clusters are then subjected to MTA-based ab initio optimization.

Table I reports the energies of (CO₂)₂₀ such clusters and Figure 4 [20-I, 20-II, 20-III, and 20-IV] depicts the respective geometries. The most stable (CO₂)₂₀ clusters are seen to bear a large number of triangular motifs and evolved from 13-I cluster as shown in Figure 3. The second most stable cluster [20-II] belongs to double icosahedral geometry and this is equivalent to the best (CO₂)₂₀ cluster reported in the literature [4]. Again, for n = 20 clusters, some other local minima [20-III and 20-IV] which are energetically quite close to the double icosahedral [20-II] geometry are also located. The MESP distribution of (CO₂)₂₀ is utilized for building (CO₂)₂₅ clusters, as shown in Figure 3. The deepest MESP minima are indicated as Y’s. The addition of five more CO₂ molecules is done based on MESP and followed up by EPIC- and MTA-based calculations. This method is also seen to endow the resulting clusters with maximum number of triangular motifs so as to have higher number of C = O . . . C interactions. Four most stable clusters are shown in Figure 5 [25-I through 25-IV] with the respective energies reported in Table I. It is noted that the one with regular arrangement is more stable than the other clusters with same number of molecules. The second and the third most stable clusters [25-II and 25-III] are seen to incorporate more number of pentagonal pyramidal and triangular motifs, respectively.

Further, a critical comparison of the geometries is performed through distance and angular distribution analysis. These analyses are performed on the three most stable clusters with n = 13, 20, and 25. An analysis of the number of C = O . . . C neighboring interactions within 7.5 Å (thrice the sum of van der Waals radii of oxygen and carbon atoms) is depicted in Figure 6. The clusters with more number of short C = O . . . C interactions are seen to possess higher stabilization energies compared to the other ones, as from Figures 2, 4, and 5 and Table I. The solid CO₂ exist in two polymorphic forms, one in P42/mnm and second one in Pnma space groups [32]. Both these space groups exhibit larger number of T-type contacts than the shifted parallel ones. The distance and angular distribution in (CO₂)₂₅ clusters are found to be similar to those found in these polymorphs. Also, a reduction in the C = O . . . C bond length indicates that the cluster is approaching the bulk region. Figure 6 shows three major peaks because of the primary (2.7–3.5 Å), secondary (3.5–4.3 Å) and tertiary (4.3–5.3 Å) interaction spheres. The clusters with same number molecules show similar trend in distance distribution. The angular distribution depicted in Figure 7 shows a major peak at 90°, indicating a predominant T-type C = O . . . C of interactions. This predominance of the number of T-type interactions with cluster size is akin to that shown by the bulk.

**ENERGY DECOMPOSITION ANALYSIS**

MBAC energy partitioning scheme of Xantheas and Kulkarni et al. [27] is performed on the most stable (CO₂)ₙ clusters with n = 13, 20, and 25, with a view to partition the total interaction energy into

<table>
<thead>
<tr>
<th>Cluster</th>
<th>E (a. u.)</th>
<th>ΔE (kcal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>13-I</td>
<td>−2450.83968</td>
<td>−25.61</td>
</tr>
<tr>
<td>13-II</td>
<td>−2450.83931</td>
<td>−25.38</td>
</tr>
<tr>
<td>13-III</td>
<td>−2450.83873</td>
<td>−25.01</td>
</tr>
<tr>
<td>13-IV</td>
<td>−2450.83871</td>
<td>−25.00</td>
</tr>
<tr>
<td>13-V</td>
<td>−2450.83826</td>
<td>−24.72</td>
</tr>
<tr>
<td>13-VI</td>
<td>−2450.83790</td>
<td>−24.49</td>
</tr>
<tr>
<td>13-VII</td>
<td>−2450.83774</td>
<td>−24.39</td>
</tr>
<tr>
<td>13-VIII</td>
<td>−2450.83771</td>
<td>−24.37</td>
</tr>
<tr>
<td>13-IX</td>
<td>−2450.83766</td>
<td>−24.34</td>
</tr>
<tr>
<td>13-X</td>
<td>−2450.83601</td>
<td>−23.31</td>
</tr>
<tr>
<td>20-I</td>
<td>−3770.52206</td>
<td>−39.07</td>
</tr>
<tr>
<td>20-II</td>
<td>−3770.52124</td>
<td>−38.55</td>
</tr>
<tr>
<td>20-III</td>
<td>−3770.52105</td>
<td>−38.45</td>
</tr>
<tr>
<td>20-IV</td>
<td>−3770.52022</td>
<td>−37.91</td>
</tr>
<tr>
<td>20-V</td>
<td>−3770.51865</td>
<td>−36.93</td>
</tr>
<tr>
<td>25-I</td>
<td>−4713.14968</td>
<td>−47.02</td>
</tr>
<tr>
<td>25-II</td>
<td>−4713.14902</td>
<td>−46.61</td>
</tr>
<tr>
<td>25-III</td>
<td>−4713.14889</td>
<td>−46.49</td>
</tr>
<tr>
<td>25-IV</td>
<td>−4713.14880</td>
<td>−46.47</td>
</tr>
<tr>
<td>25-V</td>
<td>−4713.14799</td>
<td>−45.96</td>
</tr>
<tr>
<td>25-VI</td>
<td>−4713.14740</td>
<td>−45.59</td>
</tr>
<tr>
<td>25-VII</td>
<td>−4713.14700</td>
<td>−45.34</td>
</tr>
<tr>
<td>25-VIII</td>
<td>−4713.14683</td>
<td>−45.23</td>
</tr>
</tbody>
</table>

See Figures 2, 4, 5 and text for details.

*Energy of CO₂ at this level of theory is −188.52299 a.u.*
2-body, 3-body contributions in order to get a better molecular level understanding. Table II gives in brief the summary the MBAC results. With increasing cluster size, the maximum 2- and 3-body are almost constant. However, the fraction of 2-body energy to $\Delta E$ is seen to slowly decrease with $n$ going from 13 to 25 (cf. Table II). In all these clusters, the 2-body contribution constitutes more than 96% of the total interaction energy. From these energy patterns, it is clear that the clusters grows in size so as to have maximum number of C..C interactions. This results into enhancement of the total 2-body and 3-body contributions as is evident from the distance and angular distribution analysis. This energy partitioning scheme brings out the fact that the EPIC and MTA-based way of building is a valid method of generating large molecular clusters because this way of building increases the energy contribution from 2- and 3-bodies.

**CLUSTER PROPERTIES: MESP, HESSIAN, AND IR FREQUENCIES**

It is instructive to look at some of the physical observables such as MESP of the most stable clusters for understanding the direction of cluster growth. The MESPs of the most stable clusters with $n = 13, 20, and 25$ are depicted in Figures 3 and 8. Evaluation MESP on a large three-dimensional grid of points is time-consuming for large clusters and hence is performed through cluster fragmentation employing MTA. For a test case, the (CO$_2$)$_{13}$ clus-


FIGURE 4. The geometries of the most stable MTA-optimized (CO$_2$)$_{20}$ clusters at MPWB1K/6-31+ +G(2d,2p) level of theory. Distances are in Å and the corresponding energies are given in Table I. See text for details.

FIGURE 5. The geometries of most stable MTA-optimized (CO$_2$)$_{25}$ clusters at MPWB1K/6-31+ +G(2d,2p) level of theory and the corresponding energies are given in Table I. Distances are in Å. See text for details.

FIGURE 6. The number of C—O...C interactions in the specific distance range for energetically most favorable $n = 13$, 20, and 25 clusters. The geometry numbers are as in Table I. See text for details.

FIGURE 7. The number of $\angle$ O—C...O angular distributions within 4 Å vs. number of interactions in the specific angular range for energetically most favorable (CO$_2$)$_n$ with $n = 13$, 20, and 25. The geometry numbers are as given in Table I. See text for details.
MESP minima for 13-I and 20-I through MTA [and direct] methods are $-0.027$ $[-0.026]$ and $-0.029$ $[-0.028]$, respectively, showing good quantitative agreement between the two sets. It is observed that the MESP minimum becomes more negative viz. from $-0.026$ to $-0.029$ (through $-0.028$) a.u. on increasing the cluster size from 13 to 25 through 20.

The vibrational spectrum is yet another experimentally measurable property of molecular clusters. In the previous work [20] on small clusters, a comparison of asymmetric stretching frequencies at MPWB1K/6-31++G(2d,2p) level of theory has been done with experiment and an increasing blue-shift with increasing cluster size noted. In the present work, the larger cluster frequencies are evaluated through MTA [30]. For instance, the $(\text{CO}_2)_{13}$ clusters is fragmented into two main fragments of nine molecules with one secondary overlap fragment of six $\text{CO}_2$ molecules. Similarly, the $(\text{CO}_2)_{20}$ clusters is divided into three main fragments with two secondary overlaps. The fragment Hessians are evaluated separately and the total Hessian matrix elements are obtained through cardinality guidance [Eq. (5)]. Table III reports the asymmetric stretching frequencies of the most stable $\text{CO}_2$ clusters with $n = 13$ and 20. The MTA-based Hessian matrix elements of numerical value $>0.01$ were seen to be in agreement up to at least

<table>
<thead>
<tr>
<th>Geometry</th>
<th>$E$ (a. u.)</th>
<th>$\Delta E$</th>
<th>Max 2-body</th>
<th>Total 2-body</th>
<th>Max 3-body</th>
<th>Total 3-body</th>
</tr>
</thead>
<tbody>
<tr>
<td>13-I</td>
<td>-2450.83968</td>
<td>-25.6</td>
<td>-0.93</td>
<td>-24.78</td>
<td>-0.16</td>
<td>-1.49</td>
</tr>
<tr>
<td>20-I</td>
<td>-3770.52206</td>
<td>-39.0</td>
<td>-0.94</td>
<td>-37.78</td>
<td>-0.11</td>
<td>0.81</td>
</tr>
<tr>
<td>25-I</td>
<td>-4713.14968</td>
<td>-47.0</td>
<td>-0.96</td>
<td>-45.88</td>
<td>-0.11</td>
<td>0.53</td>
</tr>
</tbody>
</table>

See text for details.

$^a$ $E(\text{CO}_2)$ at MPWB1K/6-31++G(2d,2p) level of theory is $-188.52298$ a.u.

**FIGURE 8.** A comparison of MESP isosurfaces at $-0.014$ a.u. evaluated through [A] MTA and [B] actual whole cluster calculation of $(\text{CO}_2)_{13}$ and $(\text{CO}_2)_{20}$ clusters. See Table III and text for details.
three significant digits with their directly calculated counterparts. All the reported MTA-frequencies are found to be real. The actual and MTA frequencies for (CO$_2$)$_{13}$ reported in Table III bring out very good agreement, typically to within 1.0 cm$^{-1}$ of each other. The actual most intense peak of (CO$_2$)$_{13}$ is at 2501.4 cm$^{-1}$, which is blue-shifted by 5.4 cm$^{-1}$ relative to CO$_2$ molecule asymmetric stretching mode. The corresponding MTA-frequency is at 2502.4 cm$^{-1}$.

The asymmetric frequencies of the larger clusters show saturation in blue-shift, in agreement with the experiment. It may thus be hoped that in this era of nanoscience, a combination of electrostatics- and MTA-based algorithm will offer an attractive alternative for exploring the geometries, electronic, and spectral properties of large molecular clusters.

### Conclusions

A novel algorithm for building molecular clusters is presented in the present work. The algorithm is tested on prototype (CO$_2$)$_n$ clusters. A comparative study of energetics and structures generated through EPIC- and MTA-based algorithm is also carried out with the smaller ones reported in the literature. Further, the algorithm enables generation of energetically favorable clusters which were not reported in the literature. A critical comparison of geometries is performed through the distance and angle statistical distribution analysis. This analysis reveals that the number of T-type C = O...C interactions increases with the cluster size. The MESP of the (CO$_2$)$_n$ clusters was evaluated for $n = 13, 20$, and 25 through MTA. It was found to agree excellently with the corresponding actual ones. Further, MTA frequencies evaluated for $n = 13$ shows an agreement typically within 1.0 cm$^{-1}$ with the actual ones, bringing out the reliability of MTA-based Hessian for large molecular clusters. The asymmetric frequencies of the larger clusters show saturation in blue-shift, in agreement with the experiment.

### ACKNOWLEDGMENTS

JJKV is thankful to the Council of Scientific and Industrial Research (CSIR), New Delhi, and CDAC, Pune, for the award of a Fellowship. SRG thanks the Department of Science and Technology for the

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**TABLE III**

The MTA- and actual asymmetric unscaled stretching frequencies (v) (in cm$^{-1}$) of the most stable (CO$_2$)$_{13}$ cluster at MPWB1K/6-31++G(2d,2p) level of theory. The MTA-based frequencies of (CO$_2$)$_{20}$ are also reported.

<table>
<thead>
<tr>
<th>Geometry</th>
<th>$v_{MTA}$</th>
<th>$v_{Actual}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>13-I</td>
<td>2487.5 (2483.7)</td>
<td>2491.2 (2490.5)</td>
</tr>
<tr>
<td></td>
<td>2496.2 (2496.0)</td>
<td>2497.4 (2496.8)</td>
</tr>
<tr>
<td></td>
<td>2498.3 (2497.7)</td>
<td>2498.9 (2498.5)</td>
</tr>
<tr>
<td></td>
<td>2502.4 (2501.4)</td>
<td>2502.7 (2503.1)</td>
</tr>
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<td>2507.1 (2508.1)</td>
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The asymmetric stretching frequency of CO$_2$ at MPWB1K/6-31++G(2d,2p) level of theory 2496.04 cm$^{-1}$.

See text for details.
award of J. C. Bose Fellowship. The authors are grateful to UGC for computational facilities under the CAS program of the UGC.

References