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Theoretical investigation on structural properties of ethylene clusters $(\text{C}_2\text{H}_4)_n$ ($n \leq 25$)

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ABSTRACT

Geometries of ethylene clusters $(C_2H_4)_n$ in the range of $n \leq 25$ are optimized with the intermolecular potential based on the ab initio calculations of the dimer. The heuristic method combined with geometrical perturbations is used for geometry optimization. Ethylene clusters do not take the icosahedral motif characteristic of some van der Waals molecular clusters. The structural evolution of ethylene clusters is complicated in contrast with that of acetylene clusters. The anisotropy of intermolecular potential is considered to be an important factor determining the structures of ethylene clusters.

Key words: ethylene cluster; optimal geometry; Morse potential; structural evolution

1. Introduction

Molecular clusters correspond to intermediates between isolated and condensed states. In the case of a cluster with less than 30 molecules, most of molecules exist on the surface and this situation never occurs in a bulk crystal or liquid. Because of the surface effect, the clusters must exhibit some structural features. To theoretically examine structural features of molecular clusters, geometry optimization of them is carried out. However, the geometry optimization is a difficult issue and the difficulty arises from the evidence that the optimal geometry of a cluster must be searched from enormous number of stable geometries. Hence a strategy to efficiently move from a local minimum to the global minimum on the potential energy surface of a cluster is indispensable.

Previously the present author proposed a geometry optimization method for molecular clusters (the Heuristic Method combined with Geometrical Perturbations, HMGP) [1, 2]. The method was applied to carbon dioxide clusters $(\text{CO}_2)_n$ ($n \leq 40$) [3] and acetylene clusters $(\text{C}_2\text{H}_2)_n$ ($n \leq 55$) [4]. These clusters have three common features: (1) Transformation from cluster-specific geometries to the crystal-like ones is observed. The calculations suggest that it occurs for $(\text{CO}_2)_n$ with $n = 35$ and for $(\text{C}_2\text{H}_2)_n$ with $n = 25$; (2) Icosahedral geometries are found in the clusters. The smallest size of the cluster which constructs an icosahedron is thirteen as shown in Fig. 1. Because of the surface effect, the clusters tend to take nearly spherical geometries like icosahedrons. The geometries of $(\text{X})_n$ (X denotes CO_2 or C_2H_2) with $7 \leq n \leq 12$ correspond to icosahedrons with missing vertexes; (3) Except for the structural transformation, the structure of $(\text{X})_n$ is similar to that of $(\text{X})_{n-1}$. The main differences between them are found for a few molecules.

The structure of $(\text{C}_2\text{H}_6)_{13}$ takes a significantly distorted icosahedron and no

icosahedral motif is observed for the ethane clusters with $n > 13$ [2]. The structural feature (3) is rarely found in structural evolution of the ethane clusters. Hence the structural properties of $(C_2H_6)_n$ are different from those of $(C_2H_2)_n$. The present study is aimed at examining structural properties of ethylene clusters $(C_2H_4)_n$ compared with the structures of $(C_2H_2)_n$ and $(C_2H_6)_n$.

Some investigations on ethylene clusters were carried out [5-13]. Chan et al. [5] examined the structure of the dimer with rotationally resolved infrared spectroscopy; from the experimental rotational constants the dimer was estimated to take the D_{2d} cross form shown in Fig. 2. Infrared spectra of the dimer in argon matrices were reported by Rytter and Gruen [6], who proposed that the dimer has D_{2d} symmetry.

Structures of the ethylene dimer, trimer, and tetramer were examined by Ahlrichs et al. [7] with a pairwise additive potential which is different from the potential [8] used in the present study. The dimer takes the cross geometry with D_{2d} symmetry. Alberts et al. [9] carried out ab initio calculations at the MP2 level, in which the D_{2d} cross form was not taken into account. Tsuzuki and Tanabe [11] calculated energies of a variety of dimer structures at the MP2/6-311G(2d, 2p) level and concluded that the D_{2d} structure is the most stable, in agreement with the results obtained by Ritter and Gruen [6], Chan et al. [5], and Ahlrichs et al. [7].

Ab initio calculations are carried out for only the dimer [8, 11]. The model based on the pairwise potential [7] predicts the structures of the clusters for $n = 2 - 4$. Hence no structural information is given for the $n \geq 5$ clusters. The present study reports putative global minima of the ethylene clusters $(C_2H_4)_n$ ($n \leq 25$).

2. Calculation

Jalkanen et al. [8] developed Morse potentials from the potential energy surfaces calculated for ethylene and propene dimers at the MP2/6-311+G(2df, 2pd) level. In the study by Ahlrichs et al. [7], the intermolecular potential is constructed with the aid of ab initio calculations with no electron correlation effect. Tsuzuki and Tanabe [11] indicate that potentials of the ethylene dimer without the electron correlation effect are very shallow. Accordingly the intermolecular potential in Ref. [8] is considered to be more reliable than the potential of Ahlrichs et al. [7]. Hence the former potential was adopted in the present study. The details of the potential are described below.

In the evaluation of the model potential [8], rigid structure with D_{2h} symmetry is assumed for the ethylene molecule and four dummy sites (Du) are placed symmetrically above and below two carbon atoms in a molecule. The structural parameter values [8] are as follows: $r(\text{C}=\text{C}) = 1.3316 \text{ \AA}$, $r(\text{C}-\text{H}) = 1.0804 \text{ \AA}$, $r(\text{C}-\text{Du}) = 0.7856 \text{ \AA}$, $\angle\text{CCH} = 121.3597^\circ$, $\angle\text{CCDu} = \angle\text{HCDu} = 90^\circ$.

The potential energy of $(\text{C}_2\text{H}_4)_n$ takes the pairwise-additive form:

$$V_n = \sum_{i=1}^{n-1} \sum_{j=i+1}^n V(i, j) \quad (1)$$

Here $V(i, j)$, the potential energy between molecules i and j , is given by the Morse function:

$$V(i, j) = - \sum_k \sum_l \varepsilon_{kl} \left[1 - \left\{ 1 - e^{-A_{kl}(r_{kl} - r_{kl}^*)} \right\}^2 \right] \quad (2)$$

In eq 2, k and l represent numbering of atoms/sites in the two molecules i and j , respectively, and r_{kl} means a distance between the atoms/sites. The values [8] of the Morse parameters, ε , A , and r^* , are listed in Table 1.

Optimal geometries of ethylene clusters were calculated with HMGP. The number of initial geometries is 200 for $n = 2 - 7$, 2000 for $n = 8 - 10$, 10000 for $n = 11$, and 50000 for $n = 12 - 25$; these values are taken from the literature on the ethane clusters

[2]. The initial geometries were locally optimized with a quasi-Newton method (the L-BFGS method [14]) and further improved with HMGP. The detail of the method is described in Ref. [2]. Calculation was executed in a serial mode with dual core 3 GHz Intel Xeon 5160 processors. The potential energies of the global minima of the ethylene clusters are listed in Table 2. The optimal geometry of the dimer is shown in Fig. 2. The lowest-energy structures of the clusters for $n \geq 3$ are shown in Figs. 3 and 4. The Cartesian coordinates of the ethylene clusters are obtained from the supplementary material.

3. Discussion

The relative stability of the clusters is calculated by

$$S_n = V_{n-1} + V_{n+1} - 2V_n \quad (3)$$

The values of S_n were evaluated from the potential energies listed in Table 2. The results are shown in Fig. 5. The clusters with $n = 6, 10, 12, 17, 21$ are relatively stable. These numbers are different from those obtained for acetylene clusters [4] ($n = 13, 16, 19, 25$) and ethane clusters [2] ($n = 6, 16, 19, 22$), suggesting that the structures of the ethylene clusters are different from those of the acetylene and ethane clusters.

The optimal configuration of the dimer (Fig. 2) is different from the cross structure with D_{2d} symmetry [5-7, 11]. The D_{2d} form does not correspond to the minimum on the potential energy surface calculated from the present Morse functions. Its energy is higher than that of the global minimum by 0.1 kJ mol^{-1} . The small energy difference indicates the possibility of the large-amplitude motion including interconversion of the two forms. The structure averaged over the large-amplitude motion must take D_{2h} symmetry. The possibility of large amplitude motion is pointed out in the IR spectroscopic investigation [5].

Fig. 3 shows that the ethylene trimer and the tetramer take C_2 and C_1 symmetry, respectively. The centers of mass of molecules in the tetramer construct a considerably distorted tetrahedron. The structure of the Lennard-Jones cluster with three atoms takes D_{3h} symmetry and the 4-atom Lennard-Jones cluster displays a regular tetrahedron [15]. Hence the anisotropy of interactions between ethylene molecules results in the deviation of the geometries of the ethylene clusters from the regularity.

Since structural features cannot be easily found in Figs. 3 and 4, the structures are discussed by using relative positions of the centers of mass of molecules. To analyze the local structure around a molecule, distances between the center of mass of it and the centers of mass of the molecules surrounding it were calculated. Then the number of the distances smaller than a tentative cutoff distance 4.7 \AA (a value slightly larger than the equilibrium distance of the dimer) was obtained for each molecule. From the numbers for all molecules in a cluster, the maximum number N_{\max} was determined. The results are plotted in Fig. 6. For comparison the data obtained for the acetylene clusters and ethane clusters are plotted in the same figure. The acetylene clusters with $n \geq 13$ take a number of twelve and this is consistent with the evidence that these clusters have the icosahedral motif [4]. The maximum number of N_{\max} is nine for the ethylene clusters. This indicates that the ethylene clusters do not take icosahedral structures. The results obtained for the ethane clusters are different from those for the ethylene clusters. Hence the three clusters exhibit different local structures.

The molecule closest to the center of mass of the cluster is selected as an origin. The distances between the centers of mass of the origin molecule and the other molecules are plotted for the three clusters in Fig. 7. If structures take any structural regularity, distribution of the distances would show some features. This is the case of the acetylene clusters. On the other hand, the ethylene clusters show broad distribution

of the intermolecular distances. Moreover, the pattern of the n -molecule cluster is considerably different from that of the $(n + 1)$ -molecule cluster. These features are commonly found for the ethane clusters which take no gradual and regular evolution of the structures [2]. Hence the structures of the ethylene clusters are not ordered and the evolution of the clusters is complicated.

Another way to obtain information on the structures of the ethylene clusters is to calculate rotational constants A , B , and C of clusters. The results calculated from the optimal structures are shown in Fig. 8. The dimer structure is prolate ($A > B \approx C$) and the structures of the other clusters are roughly spherical since the three rotational constants are similar to each other. No oblate structure is found for the ethylene clusters.

The above discussion is made for the lowest-energy configurations. It is also important to investigate energies and geometries of other stable configurations. The energies of stable configurations were compared with the lowest energy. Except the dimer, several configurations with the relative energies less than 0.5 kJ mol^{-1} are found as shown in Fig. 9. For the low-lying configurations, their geometrical similarities to the corresponding global-minimum configuration (σ_{rot}) were evaluated by the following equation:

$$\sigma_{\text{rot}} = \left[\left(\frac{A_i - A_{\text{gm}}}{A_{\text{gm}}} \right)^2 + \left(\frac{B_i - B_{\text{gm}}}{B_{\text{gm}}} \right)^2 + \left(\frac{C_i - C_{\text{gm}}}{C_{\text{gm}}} \right)^2 \right]^{1/2} \quad (4)$$

Here A_{gm} , B_{gm} , and C_{gm} denote the rotational constants of the global-minimum configuration and A_i , B_i , and C_i correspond to those of the i th low-lying configuration.

Fig. 10 shows the result obtained for the cluster with $n = 25$. Some low-lying configurations are similar to the global-minimum configuration; main differences between the low-lying and global-minimum geometries are related to orientations of a

few molecules. The geometries of other configurations are considerably different from the global-minimum geometry. The results obtained for other clusters (not shown here) are qualitatively in agreement with the above result. The analysis of local structures of the low-lying configurations of the $n = 25$ clusters indicates that $N_{\max} = 7, 8, \text{ and } 9$. Hence there is no icosahedral geometry in the configurations. For other clusters, no icosahedron is included in the low-lying configurations with the relative energies less than 0.5 kJ mol^{-1} .

An interesting structure is observed for the 13-molecule cluster; the geometry of $(\text{C}_2\text{H}_4)_{13}$ does not have an icosahedral motif (Fig. 3). The non-icosahedral geometry is first observed for van der Waals homoclusters consisting of thirteen molecules; the clusters previously investigated (benzene [1], carbon dioxide [3], acetylene [4], ethane [2], and molecular nitrogen [16] clusters) take icosahedrons. This can be explained using the deviation of the tetramer geometry from a regular tetrahedron.

Twenty tetrahedra overlap with each other to form a regular icosahedron [17]. In this case, each of the tetrahedra must be slightly distorted from a regular tetrahedron. On the other hand, the ethylene tetramer takes the significantly distorted tetrahedron as mentioned before. This distortion makes it impossible for the $n = 13$ ethylene cluster to form an icosahedron. This suggests that anisotropy of intermolecular potential plays an important role for determining structures of ethylene clusters.

4. Conclusion

Geometry optimization of ethylene clusters $(\text{C}_2\text{H}_4)_n$ with $n \leq 25$ was performed with the Morse potential developed by Jalkanen *et al.* [8]. The equilibrium structure of the dimer is not the cross D_{2d} form reported in Refs. [5-7, 11]. The energy difference between the global-minimum and cross forms is small (0.1 kJ mol^{-1}) and thereby it is

important to take into account large-amplitude motion involving deformations from the equilibrium structure.

The structure evolution of the ethylene clusters is complicated in contrast with that of the acetylene clusters. According to previous investigations on molecular clusters, a key point to know structural features of clusters is to examine if the 13-molecule cluster takes an icosahedral geometry. At present, information on structures of molecular clusters is rather limited. It would be necessary to enhance structural data of molecular clusters.

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:xxxxx/yyyyyy.

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Table 1

The potential parameters used in the geometry optimization of ethylene clusters.

pair	$\varepsilon/\text{kJ mol}^{-1}$	$A/\text{\AA}^{-1}$	$r^*/\text{\AA}$
C...C	5.501165	1.60410	3.22522
C...H	-0.108951	3.07464	2.63311
H...H	0.043848	1.26072	3.97536
C...Du	-0.060291	2.29966	3.11143
H...Du	0.000167	1.50785	5.04053
Du...Du	0.003389	0.75152	6.89864

Table 2

The potential energies V_n (in kJ mol^{-1}) of ethylene clusters $(\text{C}_2\text{H}_4)_n$.

n	V_n	n	V_n	n	V_n	n	V_n
2	-4.927	8	-59.231	14	-127.268	20	-202.970
3	-11.436	9	-69.350	15	-139.405	21	-216.378
4	-19.206	10	-80.749	16	-151.674	22	-228.772
5	-29.013	11	-91.692	17	-164.780	23	-240.795
6	-39.317	12	-103.572	18	-177.580	24	-253.634
7	-49.265	13	-114.979	19	-190.262	25	-266.710

Figure captions

Fig. 1. Stereographic views of $(\text{CO}_2)_{13}$. To easily identify the icosahedron, lines are drawn between carbon atoms.

Fig. 2. Stereographic views of the global-minimum and cross forms of $(\text{C}_2\text{H}_4)_2$. The cross D_{2h} form corresponds to a stationary point and it is higher than the global minimum by $0.125 \text{ kJ mol}^{-1}$ in energy.

Fig. 3. Stereographic views of the global-minimum geometries for $n = 3 - 15$.

Fig. 4. Stereographic views of the global-minimum geometries for $n = 16 - 25$.

Fig. 5. The relative stability S_n of $(\text{C}_2\text{H}_4)_n$ evaluated by eq 3.

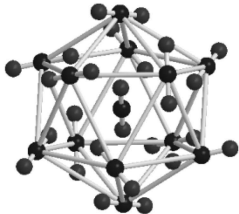
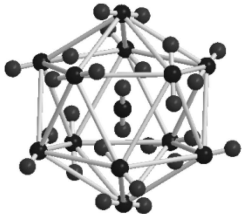
Fig. 6. The results obtained by analyzing relative positions of a molecule and the molecules around it. The maximum number of the intermolecular distances smaller than the cutoff distance is plotted against cluster size (see text): closed circles, acetylene clusters; open circles, ethylene clusters; closed squares, ethane clusters.

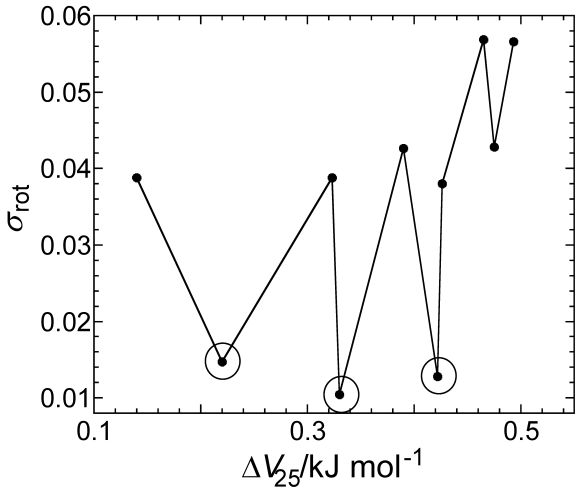
Fig. 7. Distribution of distances between the centers of mass of the origin molecule and the other molecules: A; acetylene clusters, B; ethylene clusters, C; ethane clusters.

Fig. 8. The rotational constants A (circles), B (squares), and C (triangles) calculated from the optimal structures of the ethylene clusters.

Fig. 9. Energy differences between low-lying configurations and the corresponding global-minimum configurations. Relative energies less than 0.5 kJ mol^{-1} are shown as horizontal bars.

Fig. 10. Geometrical similarities of the low-lying configurations of $(\text{C}_2\text{H}_4)_{25}$ to the global-minimum configuration. The closed circles accompanied with open circles indicate that the configurations can be converted to the global-minimum configuration by modifying orientations of a few molecules.



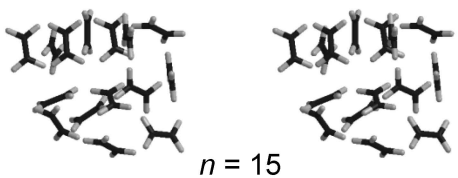
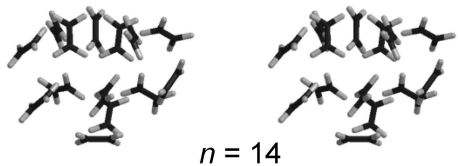
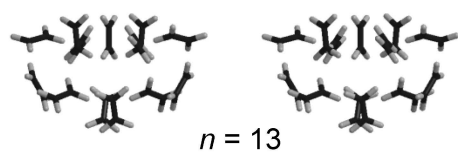
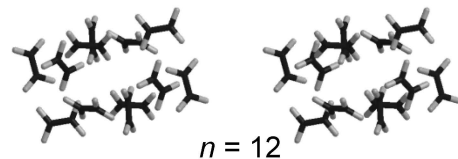
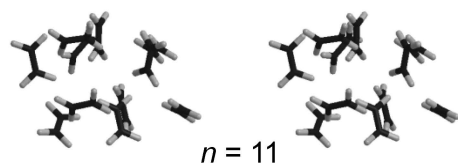
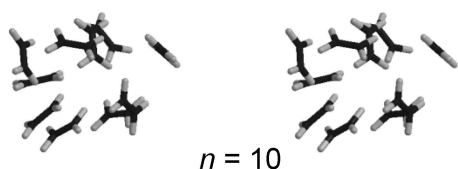
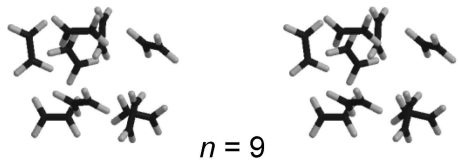
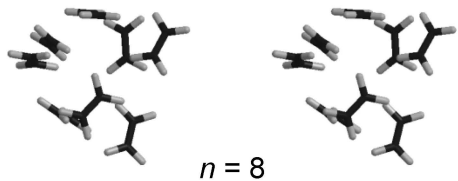
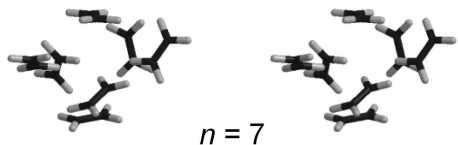
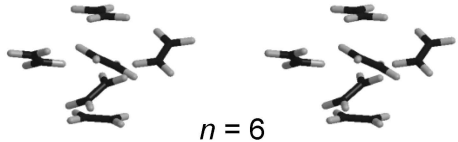
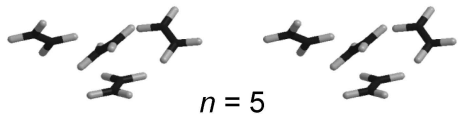
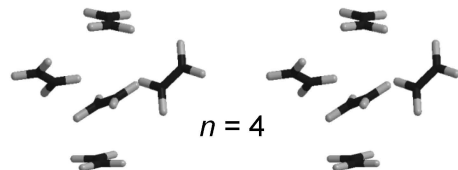
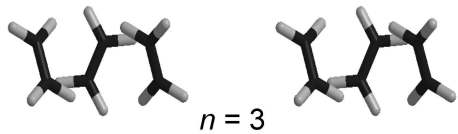


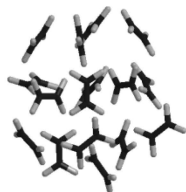


Global-minimum form

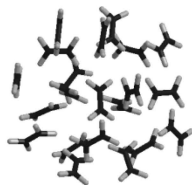
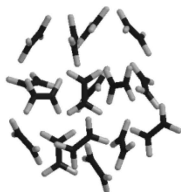


Cross form

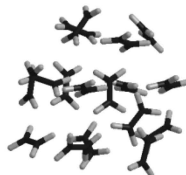
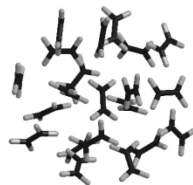




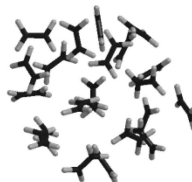
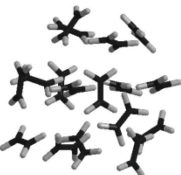
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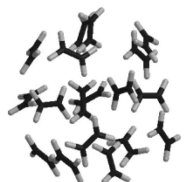
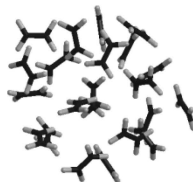
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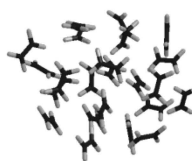
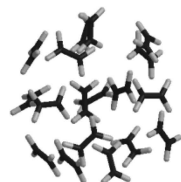
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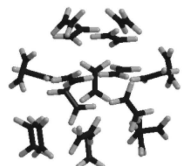
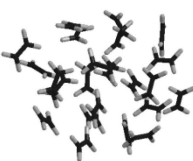
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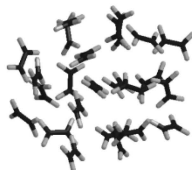
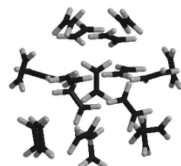
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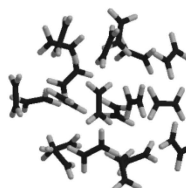
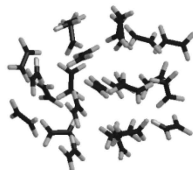
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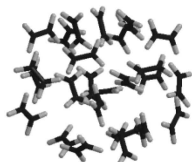
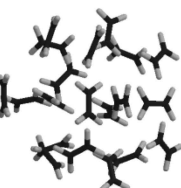
$n = 19$



$n = 24$



$n = 20$



$n = 25$

