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Author(s)	Takeuchi, Hiroshi
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The Structural Investigation on Small Methane Clusters Described by Two Different Potentials

Hiroshi Takeuchi *

Division of Chemistry, Graduate School of Science, Hokkaido University, 060-0810, Sapporo, Japan

*Corresponding author

E-mail address: takehi@sci.hokudai.ac.jp (H. Takeuchi)

ABSTRACT

Structures of molecular clusters have not been well elucidated. In the present study, a fundamental cluster $(\text{CH}_4)_n$ ($n \leq 40$) was theoretically investigated with two potentials; one is a well-known potential called OPLS and the other is a Morse potential obtained from ab initio calculations of the methane dimer. The global minima of methane clusters were searched with the heuristic method combined with geometrical perturbations. The local structure analysis of the global-minimum geometries of the clusters shows that they contain spherical geometries where twelve to sixteen molecules surround a molecule. The structural growth sequences of the OPLS and Morse-potential-based clusters were examined with rotational constants of them and core structures formed by interior molecules. The global-minimum geometries of most of the OPLS clusters with $n \leq 30$ are similar to those of the corresponding Morse-potential-based clusters.

Keywords: global minimum; local structure; OPLS potential; Morse potential; growth sequence; potential energy surface

1. Introduction

Molecular clusters are intermediates between isolated and condensed states. In the case of a cluster with several molecules, most of molecules exist on the surface and thereby the cluster exhibits structural features due to the surface effect. This is also correct for atomic clusters. A feature observed for small Lennard-Jones clusters is that they prefer a spherical geometry, icosahedron [1]. Geometrical features of molecular clusters have not been well elucidated. Many researchers have investigated structural features of two fundamental molecular clusters, CO₂ clusters [2-7] and water clusters [8-18]; small CO₂ clusters take structures based on the icosahedron and water clusters exhibit structures specific to hydrogen-bond networks. Methane clusters are also essential since methane is one of the simplest hydrocarbon molecules. However, structural data of methane clusters have been limited as described below [19-26]. Hence the present study is aimed at theoretically investigating structures of methane clusters (CH₄)_n with $n \leq 40$.

Ab initio calculations on the methane dimer have been carried out [19-23, 26]. Chao et al. [23] reported ab initio potential energy curves for a variety of conformers of the dimer. They adopted only a hydrogen-hydrogen Lennard-Jones potential function to produce the ab initio potential energy surface. With the potential function, molecular dynamics simulations of fluid methane properties were carried out. Rowley and Pakkanen [26] calculated the MP2/6-311+G(2df, 2pd) potential energy surface corrected for basis set superposition error. From the ab initio potential energy surface, the C...C, C...H, and H...H interatomic potentials were developed.

Govender and Ford [19] suggested the existence of the dimer in the nitrogen matrix. According to their calculations at the MP2/6-31G(d,p) level, the global-minimum configuration has a C-H bond of one molecule which is perpendicular to a triangular H₃ plan of the other molecule. This configuration is different from the most stable configuration predicted in Refs. 20 – 23 and 26 where a H₃ plane of one molecule faces a corresponding plane of the other. Experimental structures of the clusters with $n \geq 3$ have never been reported.

Molecular dynamic simulations of methane clusters were carried out with the all-atom [24] and

united-atom [24, 25] models. In these studies, the number of methane molecules is restricted to 3 [24], 13 [24], 64 [25], 128 [25], and 256 [25]. For the first two clusters, Calvo [24] searched their global-minimum geometries using the Monte Carlo basin-hopping method [1]. In the global-minimum geometries of $(\text{CH}_4)_3$ and $(\text{CH}_4)_{13}$, the carbon atoms formed an equilateral triangle and an icosahedron, respectively.

The present author proposed an efficient geometry optimization method for atomic/molecular clusters (the Heuristic Method combined with Geometrical Perturbations, HMGP) [27, 28]. In this work, the geometries of the methane clusters $(\text{CH}_4)_n$ with $n \leq 40$ expressed by two different interatomic potentials are optimized with HMGP and geometrical features of the clusters are reported.

2. Intermolecular Potential

The potentials proposed by Jorgensen et al. [29] and by Rowley and Pakkanen [26] were used in the present study. The former is called the OPLS all-atom potential and is used in molecular dynamics simulations of methane clusters in Ref. 24. The latter is called the RP potential hereafter. The OPLS potential is empirically determined while the RP model is obtained by fitting it to the ab initio results. Consequently the former potential is expected to be considerably different from the latter one.

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

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

Here $V(i, j)$ denotes the potential energy between molecules i and j . In the OPLS model [29], intermolecular potential consists of Coulomb and Lennard-Jones terms:

$$V(i, j) = \sum_k \sum_l \left[\frac{B_{kl}}{r_{kl}^{12}} - \frac{C_{kl}}{r_{kl}^6} + \frac{Q_{kl}}{r_{kl}} \right] \quad (2)$$

In eq 2, k and l represent atoms in the two molecules i and j , respectively, and r_{kl} means a distance between the atoms. On the other hand, the RP intermolecular potential is expressed by the modified

Morse function:

$$V(i, j) = -\sum_k \sum_l \varepsilon_{kl} \left[1 - \left\{ 1 - e^{-A_{kl}(r_{kl} - r_{kl}^*)} \right\}^2 \right] \quad (3)$$

The values of the potential coefficients are listed in Table 1. The rigid structure with T_d symmetry was assumed for the methane molecule. The C-H bond length is 1.09 and 1.089678 Å for the OPLS [29] and RP [26] models, respectively.

In Ref 26, several functions are used to describe the ab initio potential surface. Only the Morse function (3) adequately reproduced the ab initio values and other functions were improper for expressing them.

Rowley and Pakkanen [26] evaluated multibody effects using ab initio calculations for six configurations of methane trimer, tetramer and pentamer. The differences between the results of the ab initio calculations and those obtained with the pairwise Morse potentials were smaller than uncertainties of the interatomic potentials, indicating that the pairwise additivity is a good approximation.

In the ab initio calculations performed in Refs. 23 and 26, the value of $r(\text{C-H})$ was fixed. Chao and coworkers [22, 23] showed that the optimization of the C-H bond length gives very small effect on the ab initio potentials. Hence the assumption that the structure of the methane molecule is rigid is reasonable in simulations of methane clusters.

The intermolecular potential curves of the methane dimer were calculated keeping the molecular orientations in the global-minimum geometry [26] and varying the C...C distance. The obtained intermolecular potentials are shown in Fig. 1. This figure also shows the potential curves of the configuration where two hydrogen atoms are head-on.

The potential curves of the global-minimum configurations of the two models give large differences in the minimum energies and the equilibrium distances (r_e). The difference between the potential curves of the global-minimum and head-on configurations shows that the OPLS and RP potentials are anisotropic.

It is known that potential widths have a considerable influence on optimal geometries of the

Morse clusters [30, 31]. The RP and OPLS potential curves of the global-minimum configuration were well fitted by using a single Morse function and resulting values of A were 1.4 and 1.7 Å⁻¹ for the potentials, respectively (the definition of A is identical to that in eq 2). The corresponding values are 1.2 and 3.5 Å⁻¹ for the potentials of the head-on configuration. Accordingly the width of the RP potential is wider than that of the OPLS potential. This must affect geometries of the methane clusters.

3. Geometry Optimization

Optimal geometries of methane clusters were searched with HMGP [28]. Starting geometries were generated by randomly placing molecules in a sphere with a radius of $(3n/4\pi)^{1/3}r_e$ (a value of 3.8 Å is used for r_e). The number of starting geometries is 100 for $n = 2 - 12$, 500 for $n = 13 - 20$, 1000 for $n = 21 - 25$, 3000 for $n = 26 - 28$, 5000 for $n = 29 - 37$, 39, 40, and 10000 for $n = 38$, respectively. These geometries were locally optimized with a quasi-Newton method (the L-BFGS method [32]). Since global optimization of the Lennard-Jones cluster with 38 particles was known to be difficult [1], a large number of starting geometries were used for (CH₄)₃₈.

For each of the clusters with $n = 2 - 5$, the global minimum was easily located after local optimizations of starting geometries since several optimizations yielded the same lowest energy. However, it was difficult to obtain the same lowest energy for a larger cluster after local optimizations of starting geometries. Hence geometrical-perturbation operators [28] with subsequent local optimizations were used for searching lower-energy configurations.

The geometry is modified with interior, surface, and orientation operators. The interior operator perturbs a cluster configuration by moving some molecules to the neighborhood of the center of mass of a cluster. The surface operator partially modifies a cluster configuration by moving them to the most stable positions on the surface of a cluster. The orientation operator randomizes orientations of molecules in a cluster. The modified geometry is always optimized with the L-BFGS method [32].

The number of molecules moved by the interior operator is randomly selected from 1 to 5. As a molecule or molecules moved by the operator, the highest-energy molecule or the highest-energy group of molecules is selected (the selected molecules are usually on the surface of the cluster). The number of molecules surrounding a moved molecule generally increases after the operator moves it. Hence its potential energy obtained after local optimization is expected to be lower than that at the original position. This leads to a probability that the potential energy of the cluster is improved with the operator.

The surface operator also moves the highest-energy molecule or group. The most stable set of positions on the surface is selected as positions of the moved molecules. The number of moved molecules m is initially set at 1. It increases to 4 at an interval of 1 when the energy of the cluster is not lowered with this operator. In the operator with $m = 1$, the second highest-energy molecule and the third highest-energy molecule are also selected as a moved molecule.

According to the studies on the ethane clusters [28], the orientation operator randomly modifies orientations of one and two molecules three and nine times, respectively. The methane molecule takes higher symmetry than the ethane molecule. This reduces the number of stable configurations generated by perturbing molecular orientations. Accordingly the orientational perturbations of one and two methane molecules were carried out twice and four times, respectively. All the molecular combinations were taken into account in the operator. Hence $2n^2$ orientational perturbations were performed for a cluster configuration.

In the first stage of HMGP, geometries are optimized with the interior operator and then with surface operator. A hundred low-lying configurations are selected for further optimizations with the orientation operator. The details of HMGP are described in Refs. 27 and 28.

In geometries obtained with the interior operator, two molecules are often very close to each other. Hence the Cartesian displacements, Δx , Δy , and Δz , of the molecules caused by local optimization are very large, leading to the possibility of evaporation of them. Hence if $|\Delta x|$, $|\Delta y|$, and $|\Delta z|$ are larger than r_e , the magnitudes are reduced to $r_e/10$.

Calculation was executed in a serial mode with dual core 3 GHz Intel Xeon 5160 processors. The lowest energies of the clusters are listed in Table 2. The global-minimum configurations described by the RP [26] and OPLS [29] potentials are shown in Figs. 2, 3, and 4. The Cartesian coordinates of them and the figure of the skeletal geometries formed by carbon atoms are obtained from supplementary material. Computational times required for typical clusters, the OPLS clusters with $n = 10, 20, 30, 40$, were approximately 5 minutes, 7 hours, 80 hours, and 15 days, respectively.

4. Discussion

The relative stability of the methane clusters is first discussed. Then structural features of the OPLS and RP clusters are presented.

4.1 Relative Stability

To calculate the relative stability of the methane clusters, the potential energies listed in Table 2 were substituted into the equation

$$S_n = V_{n-1} + V_{n+1} - 2V_n \quad (4)$$

The results are shown in Fig. 5. Since the S_n value is the curvature of V_n , a positive value of S_n shows that the n -molecule cluster is more stable than the clusters with the sizes of $n - 1$ and $n + 1$. For the OPLS and RP models, the clusters with $n = 10, 15, 19, 22, 24$ are relatively stable.

Discrepancies are found for some cluster sizes; the OPLS clusters with $n = 8, 17$ are stable whereas the RP clusters with $n = 13, 31$ are stable. Consequently the relative stability predicted with the OPLS [29] potential is in poor agreement with that with the RP [26] potential. This discrepancy may be unraveled by using more reliable theoretical methods (dispersion corrected density functional theory methods or ab initio methods including electron correlation effects).

4.2 Geometries of the Optimized OPLS Clusters

The OPLS model shows that the dimer evolves to triangular trimer, tetrahedral tetramer, trigonal bipyramidal pentamer, tetragonal bipyramidal hexamer, and pentagonal bipyramidal heptamer (see Fig. 2). The heptamer changes to an icosahedral cluster at the size of thirteen; the icosahedron

formed by the carbon atoms in $(\text{CH}_4)_{13}$ is shown in Fig. 6. The clusters with $n = 9 - 12$ geometrically resemble icosahedra with missing vertexes.

Since structural features of a larger cluster could not be easily found in the stereographic views, local structures were analyzed using relative positions of the carbon atoms in a cluster. For each carbon atom in a cluster, distances of other carbon atoms from it were calculated and the number of the distances smaller than a cutoff distance was obtained; the cutoff distance was set at a value larger than the equilibrium distance of the dimer (4.3 Å and 4.6 Å for the OPLS and RP clusters). From the numbers for all C atoms in a cluster, the maximum number N_{max} was determined. The results are plotted in Fig. 7.

The relation of $N_{\text{max}} \geq 12$ holds for many clusters with $n \geq 13$. The cluster with $n = 15$ ($N_{\text{max}} = 14$) adopts an icositetrahedron (see Fig. 6). Two icositetrahedra are overlapped in the $n = 22$ cluster. Moreover, the $n = 17$ cluster ($N_{\text{max}} = 16$) takes a polyhedron with twenty-eight triangles on the surface. These polyhedra are first found for molecular clusters although the icositetrahedron is previously observed for metallic clusters, technetium clusters [33] and cationic vanadium clusters [34].

Geometrical information is obtained from rotational constants, A_n^{gm} , B_n^{gm} , and C_n^{gm} , of the global-minimum geometry of $(\text{CH}_4)_n$. These values are shown in Fig. 8 and the results are as follows: (1) the structures of the clusters with $n = 2, 8, 21 - 26, 31 - 33, 35, 37 - 40$ are prolate or nearly prolate ($A > B \approx C$); (2) oblate or nearly oblate structures ($A \approx B > C$) are found for $n = 3, 7, 10, 14, 27 - 30, 36$; (3) the clusters with $n = 4, 13, 15 - 20, 34$ take spherical or nearly spherical shapes ($A \approx B \approx C$). A series of the structural variations obtained from the rotational constants is discussed below.

The $n = 13$ cluster takes a spherical shape, an icosahedron with an interior molecule. The spherical geometry changes to a pan-cake-like shape (the $n = 14$ cluster). This cluster takes no interior molecule (see Fig. 3) and thereby the N_{max} value is much smaller than 12 (Fig. 7). When a molecule is added to the 14-molecule cluster, the oblate geometry develops to a spherical one, an

icositetrahedron.

Spherical geometries are observed up to $(\text{CH}_4)_{20}$ and the change from a spherical structure to a cigar-like one occurs at $n = 21$. The geometrical difference between $(\text{CH}_4)_{20}$ and $(\text{CH}_4)_{21}$ is associated with the number of interior molecules in the clusters. As shown in Fig. 3, the $n = 21$ cluster has two interior molecules and thereby surface molecules surrounding the interior molecules form a cigar-like shape. On the other hand, the $n = 20$ cluster takes a spherical shape since many molecules enclose an interior molecule. The shapes of the $n = 21 - 26$ clusters are prolate because of two interior molecules.

The $n = 27$ cluster takes three interior molecules and they construct a triangle. Hence the shape of the cluster is oblate. The number of interior molecules changes from three ($n = 27 - 30$) to four ($n = 31 - 34$). This leads to the difference between shapes of the clusters with $n = 30, 31$. The $n = 33, 34$ clusters have different (prolate and spherical) shapes. The geometrical difference is ascribed to shapes constructed by four interior molecules (a nearly planar core and a tetrahedral core are shown in Fig. 4). The structure growth sequence of the OPLS clusters and the shapes of interior molecules are summarized in Fig. 9.

4.3 Comparison of the Optimized RP Clusters with the Corresponding OPLS Clusters

The geometries of the RP clusters with $n \leq 13$ are similar to those of the corresponding OPLS clusters except for $(\text{CH}_4)_9$ and $(\text{CH}_4)_{12}$. The calculated rotational constants shown in Fig. 8 indicate that the structures of the clusters with $n = 2, 5, 8, 20 - 25, 33 - 35, 39, 40$ are prolate. The $n = 3, 6, 7, 9, 10, 26 - 29, 36$ clusters take oblate structures and the clusters with $n = 4, 13 - 19, 31, 32, 37, 38$ take spherical shapes. The above structural data are analyzed in a manner used for the OPLS clusters and the results are shown in Fig. 9.

The differences and similarities between the OPLS and RP geometries can be easily detected from Figs. 2 ($n \leq 13$) and 9 ($n \geq 13$). The differences are found for $n = 9, 12, 14, 20, 26, 30, 31, 32, 34, 35, 36, 37, 38$. Accordingly the global-minimum geometries of the RP clusters are similar to those of the OPLS clusters for approximately two thirds of the cluster sizes under investigation.

The global-minimum configurations of most of the clusters with $n \leq 30$ are independent of the potentials used in the calculation. For the clusters with $n \geq 30$, variations are found for core shapes constructed by more than three interior molecules. A series of the core variations depends on the potentials used.

Fig. 7 shows that most of the RP clusters with $n \geq 13$ include spherical geometries where at least twelve surface molecules surround a molecule. The icositetrahedron with $N_{\max} = 14$ is also found in the RP clusters. The geometry of the RP cluster with $n = 17$ is similar to that of the corresponding OPLS cluster (see Fig. 2). The observation of icosahedron, icositetrahedron, and polyhedron with twenty-eight triangles is peculiar to the methane clusters.

4.4 Comparison to the Lennard-Jones Clusters

In molecular simulations performed in Refs. 24 and 25, all-atom and united-atom models were used. In the latter model, the CH_4 molecules are represented as pseudo-atoms and the interaction between them is expressed by the Lennard-Jones (LJ) potential. In this case, methane clusters are equivalent to LJ atomic clusters; the geometries and energies of global minima of the LJ clusters are tabulated in Ref 35. The potential energies of the LJ clusters show that the clusters with $n = 13, 19, 23, 26, 29$ are relatively stable. This indicates that the united-atom model reproduces neither the OPLS model nor RP model (Fig. 5). Hence the united-atom model contradicts the methane clusters described by the OPLS and RP models.

The structural evolution of the small LJ clusters is explained by taking into account an icosahedron as a building unit. The methane clusters also include the icosahedron. In addition, other spherical geometries, icositetrahedra and polyhedra with twenty-eight triangles, are observed in the methane clusters. An icositetrahedron of the LJ cluster with 15 particles corresponded to a local minimum. The polyhedron with twenty-eight triangles was found not to correspond to a minimum of the LJ clusters. The stability of the icositetrahedron and polyhedron with twenty-eight triangles observed for the methane clusters results in the difference between the relative stability of the LJ clusters and that of the methane clusters.

4.5 Low-Lying Geometries of the RP and OPLS Clusters

Low-lying configurations of the RP clusters are compared with ones of the OPLS clusters with rotational constants of them. The RP and OPLS clusters with the same size take different equilibrium C...C distances because of the difference shown in Fig. 1. Hence positions of the carbon atoms in the RP cluster were corrected for the geometrical differences by using the equation:

$$\vec{r}_C^{\text{RP,corrected}} = \left(r_{\text{C...C,ave}}^{\text{OPLS}} / r_{\text{C...C,ave}}^{\text{RP}} \right) \cdot \vec{r}_C^{\text{RP}} \quad (5)$$

Here $\vec{r}_C^{\text{RP}}$ and $\vec{r}_C^{\text{RP,corrected}}$ denote the vectors directed to the uncorrected and corrected C positions in the RP cluster, and $r_{\text{C...C,ave}}^{\text{OPLS}}$ and $r_{\text{C...C,ave}}^{\text{RP}}$ are the average values of the C...C distances in the OPLS and RP clusters with the same size, respectively. This equation indicates that the rotational constants of the RP clusters depend on the two geometries under comparison. In the present study, the lowest 100 RP geometries were compared with the corresponding OPLS geometries in order of relative stability; the m -th ($m = 1$ to 100) lowest-energy configurations of the RP and OPLS clusters were used in eq 5. Typical results are shown in Fig. 10.

At nearly half of the cluster sizes, the values of the rotational constants of the RP clusters were similar to those of the OPLS clusters (see the result obtained for $n = 28$). For $n = 26$ and 30, similarity was rarely observed for the rotational constants of the two models. For the remaining clusters, the rotational constants were scattered and thereby both similarities and differences between the two models were observed ($n = 32$). In the cases, the global-minimum configuration of one model was often similar to a low-lying configuration of the other model. This means that the relative stabilities of the low-lying configurations of the RP clusters are different from those of the OPLS clusters. Consequently the global-minimum configurations of most of the clusters with $n > 30$ depend on the potentials used in the calculation.

Fig. 10C shows that the rotational constants A are divided into two groups with values of 68 and 58 MHz. This is commonly found for the two models, indicating the existence of at least two types of stable configurations which correspond to different funnels on the potential energy surfaces.

Similar situations occur for other clusters. The surfaces with one funnel are also observed for many

clusters and an example is the $n = 28$ cluster shown in Fig. 10B. These results suggest that the low-lying region of the RP potential energy surfaces are similar to that of the OPLS ones except for the $n = 26$ and 30 clusters.

5. Conclusion

Geometry optimization of methane clusters $(\text{CH}_4)_n$ with $n \leq 40$ was performed with the OPLS potential [29] and the Morse potential developed by Rowley and Pakkanen [26]. The intermolecular potential of the methane dimer was calculated with these potentials. The results show the significant difference between the two intermolecular potentials. The structural features of the optimized OPLS and RP clusters were examined with the local structure analysis and the rotational constants. The stability of the icositetrahedron and polyhedron with twenty-eight triangles is a feature of the methane clusters. Most of the OPLS clusters with $n \leq 30$ take the global-minimum structures similar to those of the RP clusters. Hence the calculated structures of the clusters with $n \leq 30$ are considered to be reliable. For larger clusters, structural variations are found for the cores constructed by at least four interior molecules. The core variations depend on the potentials and thereby the global-minimum geometries of the OPLS clusters with $n > 30$ are different from those of the RP clusters. This difference mainly originates from the difference between the relative stabilities of the RP and OPLS low-lying configurations.

Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version, at [doi:xx.xxxx/jcompt.xxxxxx](https://doi.org/10.1016/j.compt.2019.00000).

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Table 1

The coefficients in the OPLS and Rowley-Pakkanen (RP) potentials

Atom pair	OPLS			RP		
	$B/\text{kJ mol}^{-1} \text{ \AA}^{12}$	$C/\text{kJ mol}^{-1} \text{ \AA}^6$	$Q/\text{kJ mol}^{-1} \text{ \AA}$	$\epsilon/\text{kJ mol}^{-1}$	$A/\text{\AA}^{-1}$	$r^*/\text{\AA}$
C...C	3.73261×10^6	2.03050×10^3	80.02684	0.15539	1.25450	4.63470
C...H	3.34220×10^5	4.98895×10^2	-20.00671	0.53162	1.45976	2.95597
H...H	2.99263×10^4	1.22578×10^2	5.00168	-24.82798	3.39527	1.27724

Table 2

The lowest potential energies (in kJ mol⁻¹) of methane clusters (CH₄)_n obtained with the OPLS and Rowley-Pakkanen (RP) models

<i>N</i>	OPLS	RP	<i>n</i>	OPLS	RP	<i>n</i>	OPLS	RP
2	-2.189	-1.431	15	-89.378	-56.145	28	-198.680	-122.617
3	-6.176	-3.951	16	-97.990	-61.343	29	-207.637	-127.620
4	-11.087	-7.043	17	-106.946	-66.380	30	-216.261	-132.698
5	-16.526	-10.525	18	-115.013	-71.278	31	-224.902	-138.434
6	-22.680	-14.364	19	-122.934	-76.159	32	-234.015	-143.610
7	-28.865	-18.305	20	-130.156	-80.453	33	-243.316	-149.182
8	-35.777	-22.580	21	-137.526	-85.584	34	-252.103	-154.485
9	-42.271	-26.754	22	-146.651	-91.536	35	-261.365	-160.229
10	-49.912	-31.563	23	-155.286	-96.371	36	-270.474	-165.505
11	-56.869	-35.774	24	-164.291	-101.690	37	-279.452	-170.996
12	-63.992	-40.205	25	-172.405	-106.164	38	-288.934	-176.593
13	-71.765	-45.479	26	-181.045	-111.503	39	-298.314	-182.143
14	-80.312	-50.415	27	-189.590	-117.118	40	-307.882	-187.754

Figure Captions

Fig. 1. Intermolecular potentials of the dimer obtained from the Rowley-Pakkanen model (solid line) and OPLS model (dashed line). The potentials for the global-minimum (upper) and head-on (lower) configurations are shown.

Fig. 2. Stereographic views of the global-minimum geometries for $n = 2 - 17$; upper view, OPLS clusters; lower view, Rowley-Pakkanen clusters.

Fig. 3. Stereographic views of the global-minimum geometries for $n = 18 - 30$; upper view, OPLS clusters; lower view, Rowley-Pakkanen clusters.

Fig. 4. Stereographic views of the global-minimum geometries for $n = 31 - 40$; upper view, OPLS clusters; lower view, Rowley-Pakkanen clusters.

Fig. 5. The relative stability S_n of the global-minimum configurations; closed circles, Rowley-Pakkanen (RP) clusters; open circles, OPLS clusters.

Fig. 6. Geometries constructed by carbon atoms in the OPLS clusters with $n = 13, 15, 17$. Lines are drawn to easily find triangles on the cluster surfaces.

Fig. 7. The results of the local structure analysis (see text); closed circles, the Rowley-Pakkanen (RP) clusters; open circles, OPLS clusters.

Fig. 8. The rotational constants of the global-minimum geometries; A , circles; B , squares; C , triangles. The rotational constants (closed symbols) of the Rowley-Pakkanen (RP) clusters are multiplied by ten to avoid overlap with the results (open symbols) of the OPLS clusters.

Fig. 9. Structure growth sequences of the OPLS and Rowley-Pakkanen (RP) clusters. Black balls represent interior molecules.

Fig. 10. The rotational constants of the lowest 100 configurations of the Rowley-Pakkanen (closed symbols) and OPLS (open symbols) clusters with $n = 26$ (A), 28 (B), and, 32 (C); A , circles; B , squares; C , triangles. The global-minimum configuration corresponds to Configuration 1.

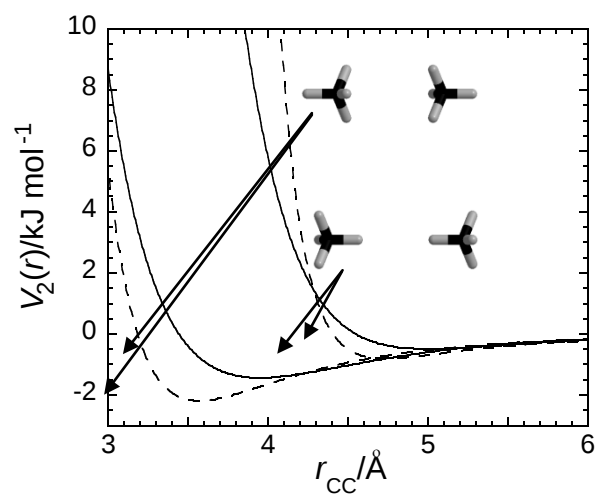


Fig. 1

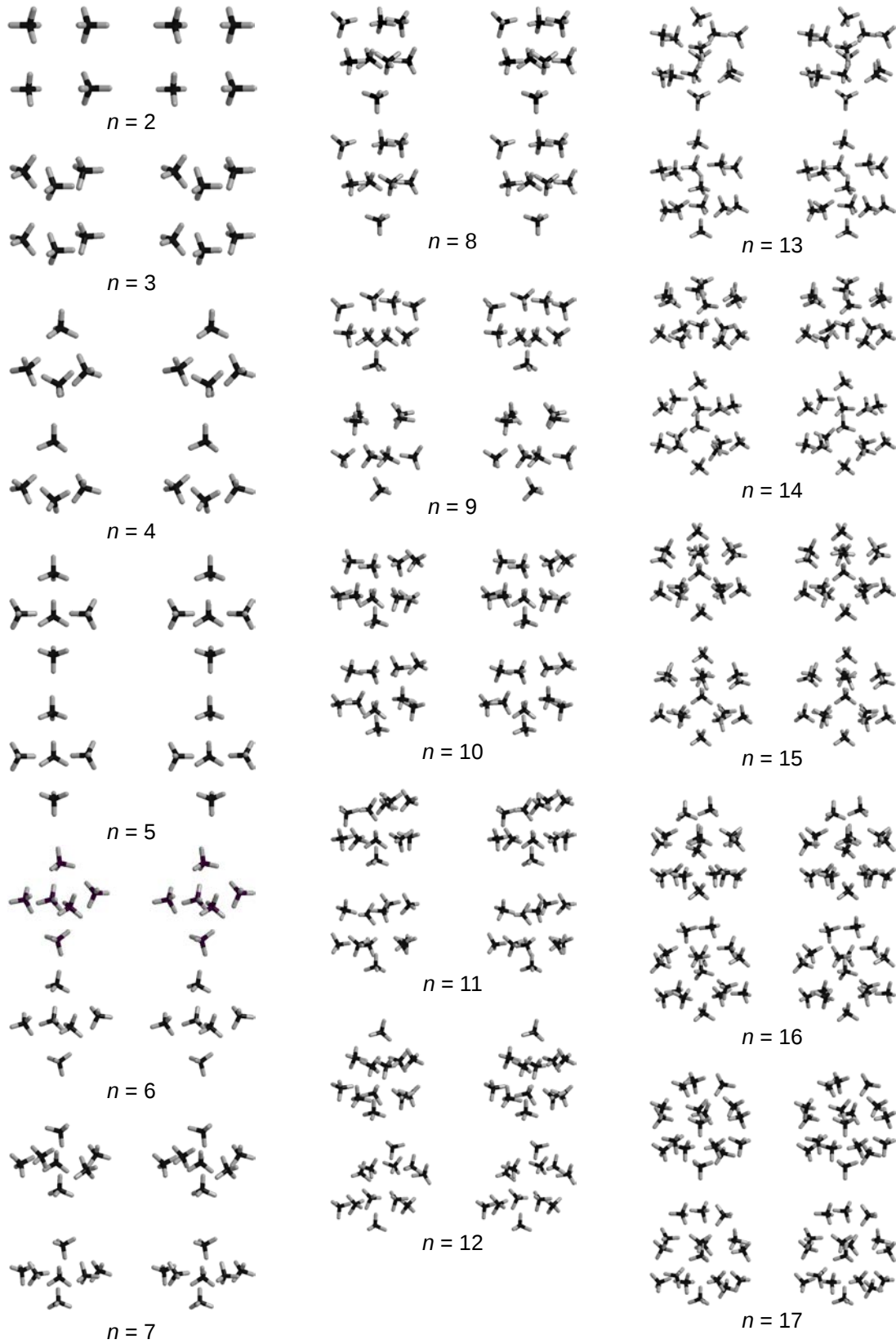


Fig. 2

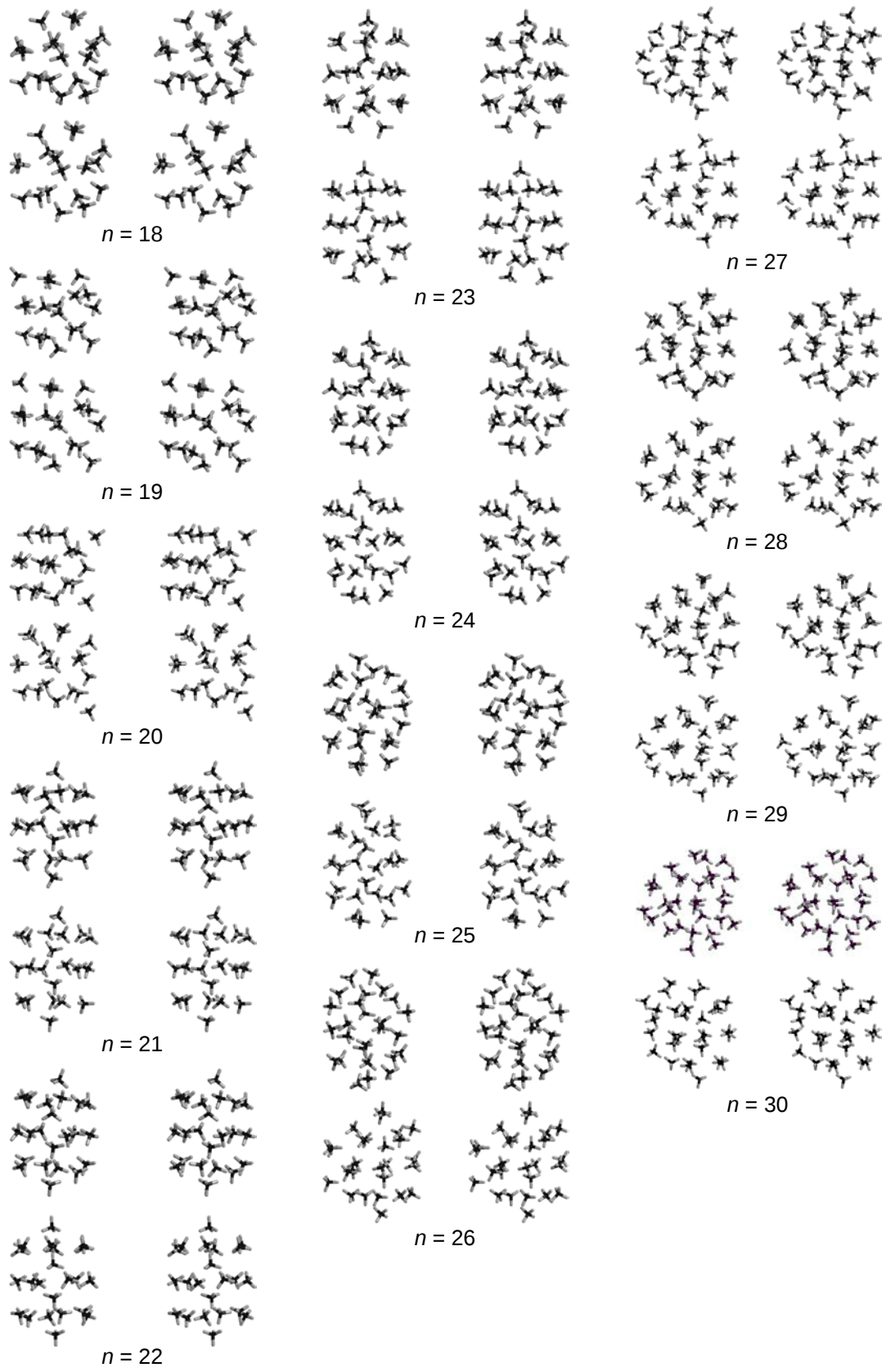


Fig. 3

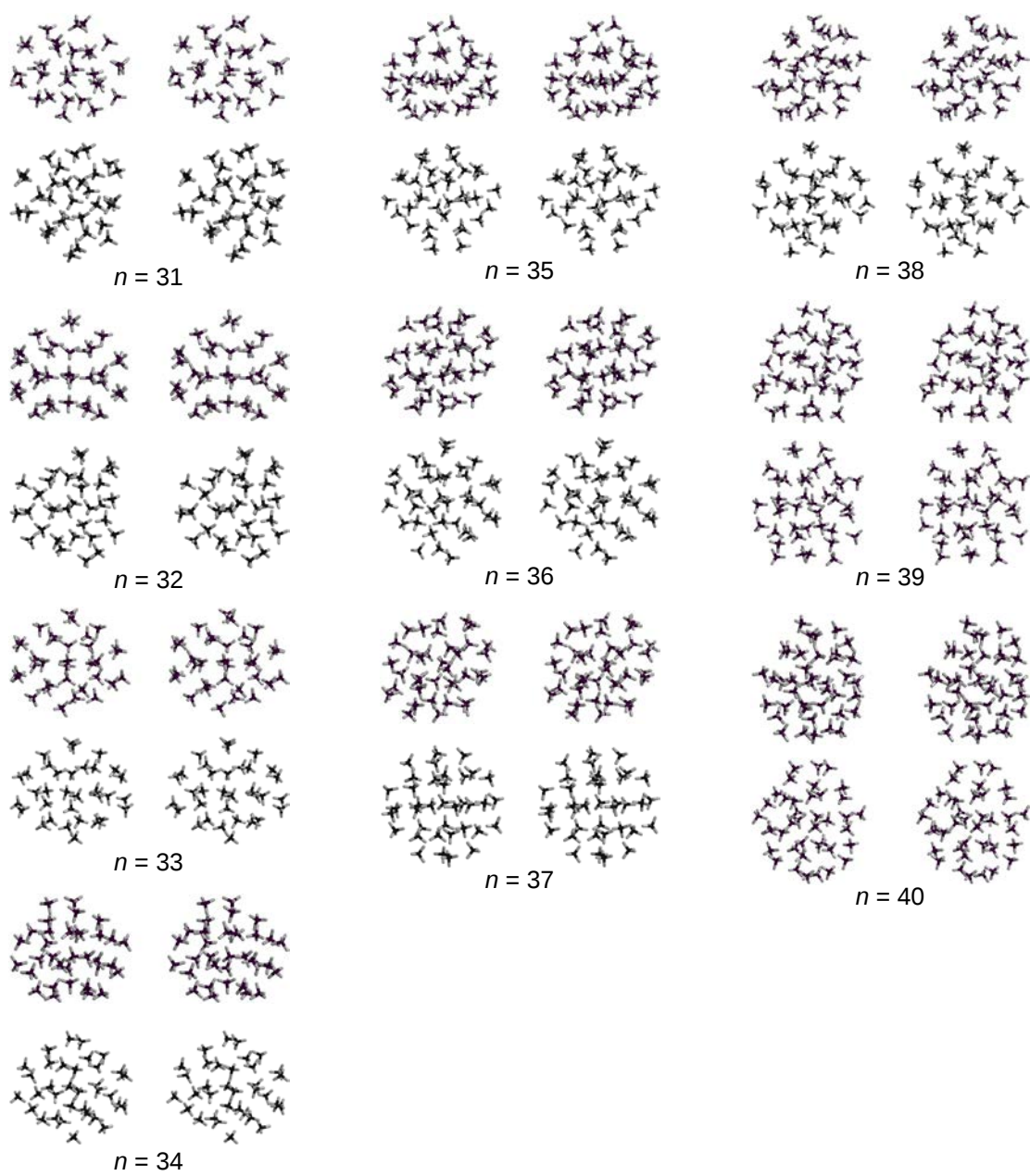


Fig. 4

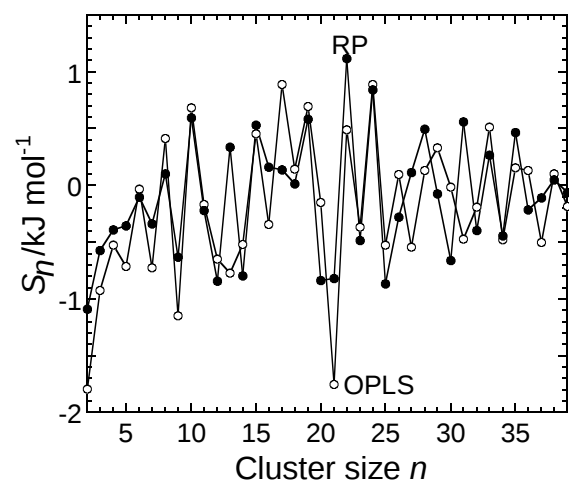


Fig. 5

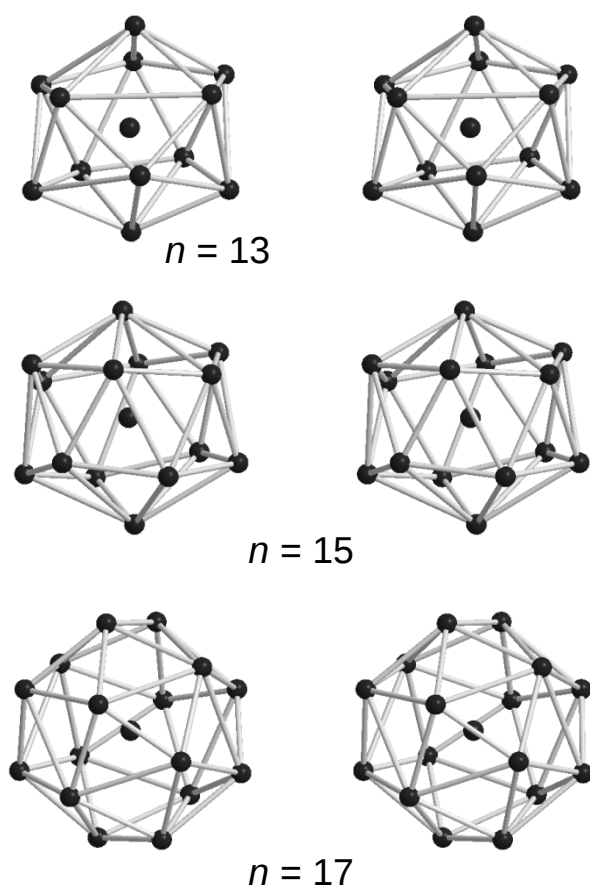


Fig. 6

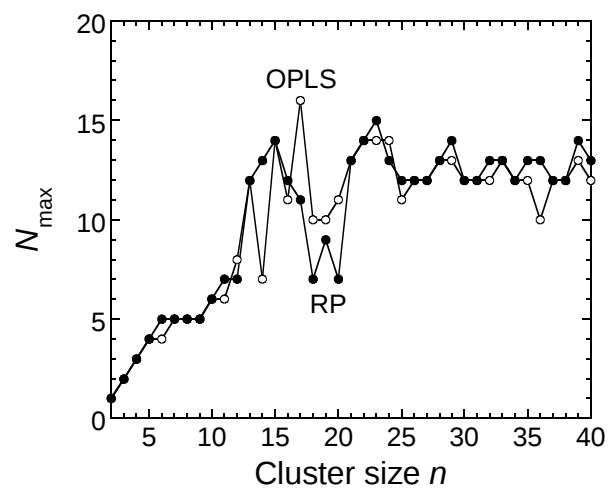


Fig. 7

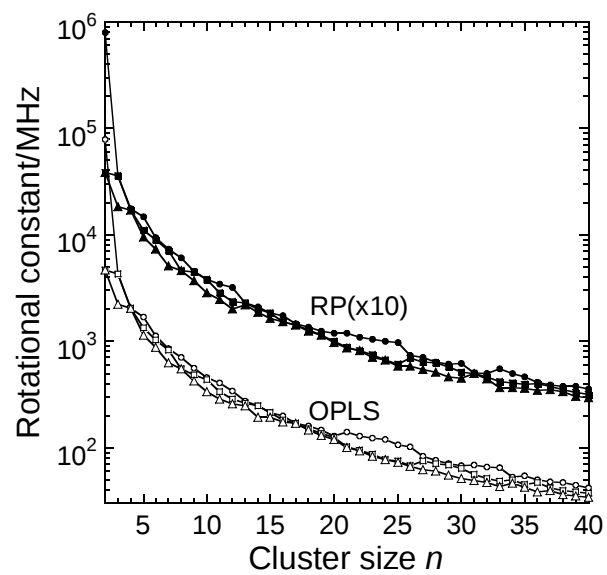


Fig. 8

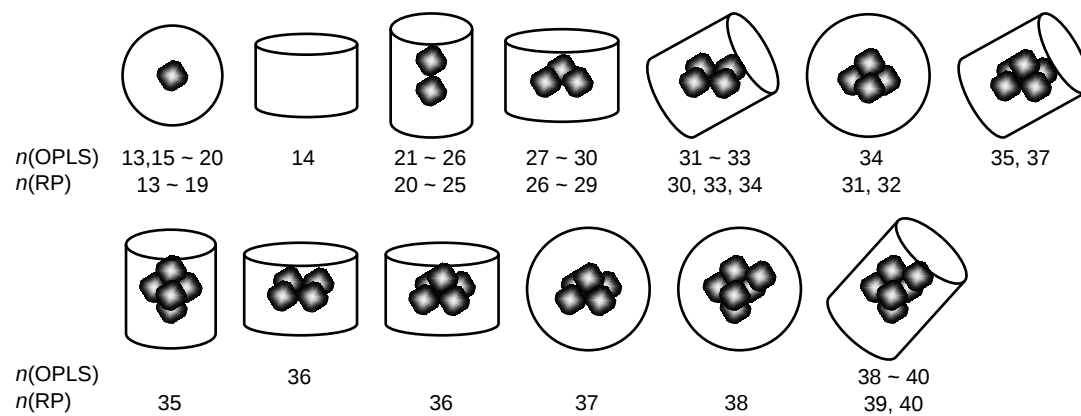


Fig. 9

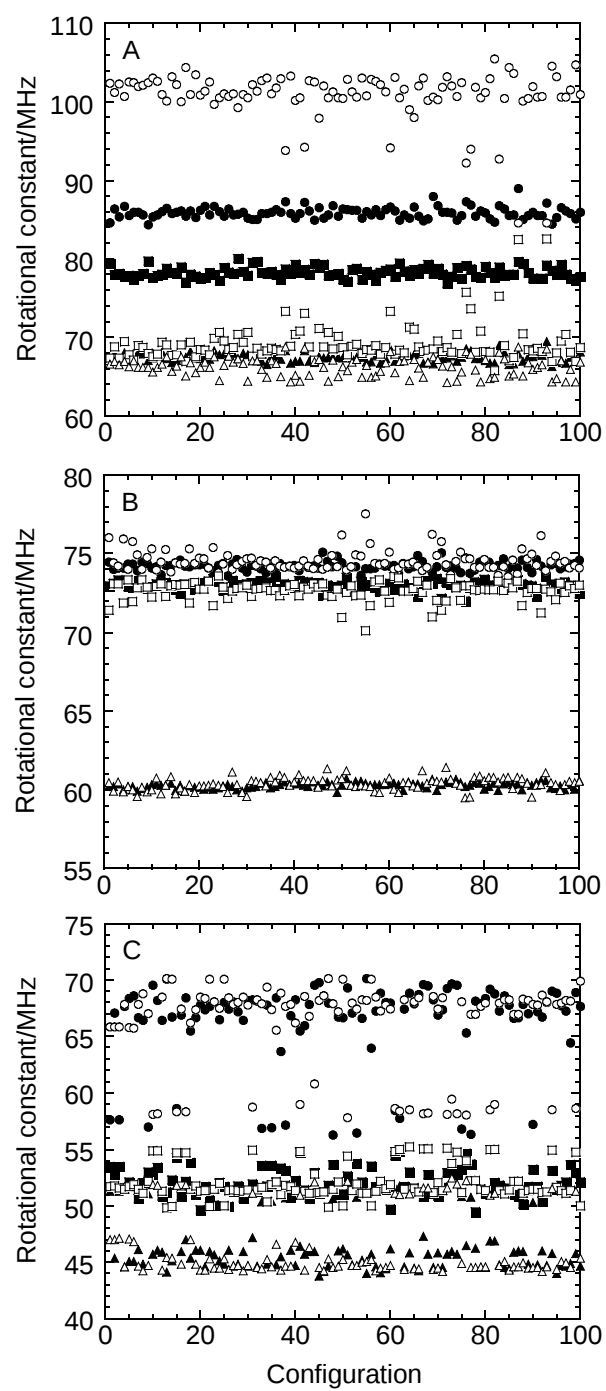


Fig. 10