

Structure of nitrogen molecular clusters $(\text{N}_2)_n$ with $13 \leq n \leq 55$

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Abstract. We investigate the structural properties of nitrogen molecular clusters $(\text{N}_2)_n$ using classical Monte Carlo simulations and optimization methods. As is the case for argon clusters, we find polyicosahedral (anti-Mackay) geometries above 13 molecules, and multilayer icosahedra with uncomplete outer shell (Mackay) geometries below 55 molecules. The crossover point between these two kinds of structures is located near 42 molecules, whereas it is at only 31 for argon. With a simple three-body (Axilrod–Teller) potential added to the standard Lennard–Jones model, we interpret this difference as the result of the strong anisotropy of the molecular potential.

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1 Introduction

Over the past decade, simple atomic clusters bound by the common Lennard–Jones (LJ) or Morse potentials have been extensively studied for their static and dynamical properties. They have also provided prototype models for testing methodology in areas such as global optimization [1, 2] or for carrying out numerical calculations of thermodynamical quantities [3, 4]. More complex species, especially metallic clusters [5], could then be efficiently investigated by the use of the techniques developed on these simple systems.

By comparison, molecular systems have been given much less attention, perhaps with the exception of water [6]. Van der Waals molecular clusters are probably the most simple to model and describe. With the increasing computational power available, it has become possible to undertake studies for molecular clusters that are similar to those done on atomic clusters and in which the clusters are in the same size range (up to about a few hundred molecules).

For instance, the crystalline crossover size could be properly determined for both sulfur hexafluoride [7] and carbon dioxide [8] through the use of computer simulations as well as experiments. Below this size, van der Waals clusters usually exhibit size-dependent shapes, often with pentagonal symmetry and icosahedral units. Larger clusters tend to adopt a more pronounced face-centered cubic (FCC) character, which leads to bulk matter. While the

crystalline crossover point is estimated in the range 1000–2000 for argon [9], it is only ~ 15 for SF_6 [7] and ~ 30 for CO_2 [8]. These differences between atomic and molecular van der Waals clusters were attributed to the strong anisotropy of the intermolecular potentials [10].

A recent theoretical estimation [11] based upon a model by Doye *et al.* [12] and the experimental results of Torchet and De Feraudy [13] have both predicted the crystalline crossover size to be located near 100–200 molecules for nitrogen molecular clusters. At the present time, no direct comparison with simulation has been made to check and specify this value, and the relatively large critical size makes extensive numerical studies harder to undertake than they have been for carbon dioxide. However, smaller nitrogen clusters remain interesting in many aspects. Up to the size $n = 13$, the structures formed by the molecular centers of mass in $(\text{N}_2)_n$ free clusters are the same as the atoms' locations in simpler LJ_n clusters [14, 15], whereas some differences seem to appear in the vapor phase [16]. In other terms, there is a general isomorphism between the preferred geometries of LJ_n and the centers of mass in $(\text{N}_2)_n$. In this paper, we investigate the structure of $(\text{N}_2)_n$ clusters in the size range $13 \leq n \leq 55$, by means of simulations and numerical methods. In this size range, a crossover between polyicosahedral and multilayer icosahedral structures occurs. We seek to answer the question: How is such a crossover displaced by the molecular character of the clusters?

This paper is organized as follows. In Sect. 2 we briefly describe the potential chosen to model the interaction between N_2 molecules, and the methodology used through-

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out. The structures found are presented in Sect. 3, and the results are interpreted with a simple anisotropic atomic model. We finally summarize and conclude in Sect. 4.

2 Methods

The potential used to model the interaction between N_2 molecules has been widely employed in previous studies on bulk [17] and clusters [11, 18, 19]. The molecules are considered to be rigid, and the interaction between them is modeled by four partial Coulombic charges located on the N–N bond, plus a repulsion-dispersion term of the Buckingham form on the nitrogen atoms. Four global optimization methods were used to find the lowest structures of $(N_2)_n$ clusters, $13 \leq n \leq 55$. First, a standard Monte Carlo simulated annealing (MCSA) was performed from randomly placed and oriented molecules inside a cubic box. A steepest descent quenching procedure with adaptive stepsize ended the MCSA searches. Regular quenching along a high-temperature MC trajectory also provided bunches of structures lying low in energy. A Monte Carlo growth algorithm was used, in a similar way as in [14]. Finally, we also used a slightly modified version of the basin-hopping method of Wales and Doye [1].

Up to now, this “basin-hopping” method has been the most successful in finding the absolute minima of LJ_n clusters up to size 110, including pathological structures such as LJ_{38} (truncated octahedral) or LJ_{75} (decahedral). More recently, it has also been applied to Sutton–Chen clusters [20]. Its basic principle is that a Monte Carlo simulation is performed on the deformed and discontinuous potential-energy surface (PES) $\tilde{V}(\mathbf{R})$ obtained by quenching from configuration \mathbf{R} . In the original method [1], all atoms are initially randomly placed inside a cubic box. After each quench, collective random displacements of all atoms are followed by another quench leading to the next possible configuration, accepted with the Metropolis probability. In order to more easily find several structures close in geometry and/or in energy, we chose to displace only a subset of the whole cluster. Every 500 quenches, we regularly decreased the number n^* of molecules to be moved (n^* becoming $n^* - 2$). A total of 5000 quenches were performed for each simulation at a given size, starting with $n^* = n$.

After a good candidate for the global minimum was found by one of the methods described above, we carried out a series of regular quenches along an MC trajectory at $T = 25$ K to further optimize the molecular orientations, since orientational disorder prevails at this temperature [18].

3 Structures of $(N_2)_n$ clusters, $13 \leq n \leq 55$

The lowest energies of the structures found by the various algorithms described above for the $(N_2)_n$ clusters are plotted in Fig. 1 versus the molecular size n . The main result is

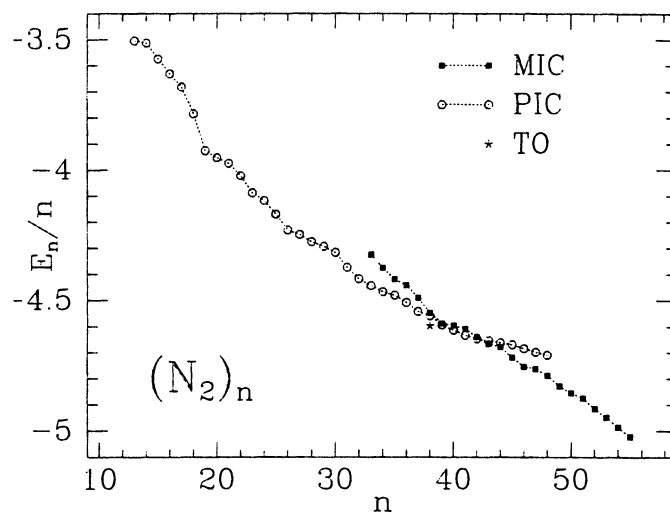


Fig. 1. Energies of the lowest structures of $(N_2)_n$ clusters. The three different kinds of arrangements found for the molecular centers of mass are polyicosahedral (PIC, open circles), multi-layer icosahedral (MIC, full squares), and truncated octahedral (TO, star). E_n/n is in $\text{kJ mol}^{-1} \text{molecule}^{-1}$.

the classification of most structures between the two categories already known for argon clusters [21], namely polyicosahedral (PIC, or anti-Mackay) and multilayer icosahedral with uncomplete external layer (MIC, or Mackay). In both categories, one considers the growth of clusters either over the center of triangular facets (anti-Mackay construction), or on the edges of these facets. This latter construction leads to the perfect Mackay icosahedron at $n = 55$. Just above the simple icosahedron made of 13 molecules, the clusters tend to maximize the number of nearest-neighbor bonds between molecules. The resulting anti-Mackay construction is illustrated in Fig. 2(a) on the example of $(N_2)_{34}$. As the number of external molecules increases, the stress exerted by these molecules on the inner part of the cluster also increases. On the other hand, the Mackay construction is less local, and favors the building of larger sizes by entire planes. The inner molecules are much less constrained, and the number of nearest neighbors is smaller than in the polyicosahedra. $(N_2)_{49}$, in its lowest-energy configuration, has a Mackay-type geometry represented in Fig. 2(b).

The perfect Mackay icosahedra are well-known magic numbers in argon clusters. By adding capped pentagonal rings over the primitive icosahedron, one creates clusters made of intertwined double icosahedron units [22]. The extra stability of these geometries is reflected in the secondary magic numbers 19, 23, 26, 29, 32, and 34 seen by Harris and his coworkers in mass spectra experiments on argon microclusters [23]. Similarly, missing facets on the external layer of the $n = 55$ icosahedron lead to another series of secondary magic numbers, 49, 46, 43, and 39, also seen by Harris *et al.* [23]. In Fig. 3, we have calculated the relative energetic stability $\Delta_2 E(n) = E_{n+1} + E_{n-1} - 2E_n$ as a function of the size n . Indeed, both series can be seen in Fig. 3. However, the numbers 32 and 34