J. At. Mol. Sci.
doi: 10.4208/jams.072512.092112a

Vol. **4** , No. 4 , pp. 357-366
November 2013

A new global search for the ground state structure of small cluster: application to S_6

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Received 25 July 2012; Accepted (in revised version) 21 September 2012
Published Online 30 August 2013

Abstract. Initial configuration plays an important role in molecular dynamics (MD) simulation. Based on *ab initio* MD simulation used widely, we here first introduce a global search method for the ground state structure of clusters. We think that during a simulation, each type of atoms in cluster should be in equivalent sites when we choose the initial configuration. Thus, our proposal is an improvement in eliminating the "unequal" in traditional annealing technology, and the results should be more convinced. Moreover, our method can make us obtain all possible structures of clusters, and also get some new structures, which are left out by previous studies. As an illustrative application, we here examine the S_6 cluster and found many structures (e.g. D_{3d}, C_{2v}, D_{3h}, C_s and C_1). The geometrical parameters and vibrational frequencies are in agreement with experimental values.

PACS: 31.15.Ew, 31.15Qg, 36.40.-c

Key words: sulfur cluster, Langevin molecular dynamics, density functional theory

1 Introduction

Clusters exhibit distinct properties from atoms, molecules and solid states. It provides the possibility of understanding the transitions from atoms, molecules to crystalline solids. Among all the properties of clusters, the ground state structure is one of the most important properties. For very small clusters, one can create all conceivable structures and examine the total energy of each structure. However, once cluster size exceeds half a dozen atoms or so, it becomes nearly impossible to build all topologically distinct structures. Fortunately, computer simulations can help people to overcome this obstacle [1].

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As is known that, Monte Carlo (MC) and molecular dynamics (MD) simulations are the two useful numerical technologies. Compared with the MC simulation, the traditional Newtonian MD simulation is much more efficient when energy surface is smooth, however, it is likely to be affected by the existence of local minima in complex energy surface. In 1986, Biswas and Hammann [2] proposed a procedure which combined some advantages of the MC technology with MD technology. They implemented a Langevin MD simulation for simulated annealing. Up to now, the Langevin MD simulations are widely applied to investigate the ground state structures of clusters [3-7].

Recently, we have investigated the ground state structure and optical properties of S_n and $C_n(1 < n < 10)$ [6,7] by using a finite-difference pseudopotential density-functional theory method in real space and Langevin MD annealing technique through PARASEC code [8-10]. In general one can easily obtain the so-called ground state structures of clusters during a Langevin MD simulation. In fact, the so-called ground state of clusters is not a real ground state structure, but a metastable structure, because it depends on the chose of initial configuration of clusters.

Thus, we here place special emphasis on the initial configuration of cluster when an MD simulation is made. The initial configuration is related to the sample regions of phase space. In a traditional computer simulation, it is usually randomly constructed, which leads to the "unequal" atomic coordinates and then different force and potential energy. In other words, random coordinates let all atoms be in different surroundings. Moreover, many clusters, especially in large size, have complex energy surfaces with a number of candidate local energy minima and high-energy barriers, which trap the simulation in one of the numerous metastable configurations. Thus, the probability that a random initial structure leads to a global minima is very low. Due to these reasons, we here introduce a new global search for the ground state structure of clusters. We propose that each type of atoms in cluster should be in equivalent site. For instance, each type of atoms can be evenly distributed on a circle or on a round ball. To get the next initial configuration, we can only change the bond length r between two nearest atoms to $r+\Delta r$, where Δr is defined as configuration step.

As an illustrative application, we make an investigation on the ground structure of S_6 cluster. Our choice is motivated by several factors. Sulfur has the largest number of allotropic forms of any other elements in the period table [11,12], and it is unique in the propensity to catenation. The most interesting aspect is that many of the larger clusters S_n ($n > 5$) [12,13] occur as monocyclic rings. Moreover, we are familiar with sulfur clusters, especially for S_6 [6]. Extensive studies of sulfur clusters have been performed [14-21], e.g. S_5-S_8 rings by Cioslowski *et al.* [14], S_2-S_{11} by Chen *et al.* [15], S_2-S_{12} by Millefiori and Alparone [16], S_6-S_{16} by Peter [17], S_2-S_{20} by Ludwig *et al.* [18], S_2-S_{18} by Jones and Ballone [19], S_2-S_{10} by Steudel *et al.* [20], and S_6 by Wong *et al.* [21].

The rest of the paper is organized as follows. The theoretical method and the calculation details are given in Section 2. Some results and discussion are presented in Section 3. Finally, the summary of our main results are given in Section 4.