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Ab Initio Molecular Dynamics Study Of Isomers Of Tin Clusters

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ABSTRACT: Recent experiments on tin clusters show higher melting temperatures of clusters as compared to bulk. It is speculated that the different (from bulk) structures of clusters as well as a change in the bonding nature could be possible reasons for this unusual behavior. In bulk, tin has two allotropes and therefore, there could even be isomers with different bonding natures. In order to understand this we report results of *ab initio* molecular dynamics simulations on isomers of tin clusters with upto 20 atoms using the ultrasoft pseudopotentials and generalized gradient approximation for the exchange and correlation energy. Our results show 7, 10 and 18 atom clusters to be magic in agreement with experiments. The lowest energy isomers upto 8 atoms have the same structures as Si clusters but larger clusters seem to favor a different growth. The calculated binding energies and highest occupied – lowest unoccupied molecular orbital (HOMO-LUMO) gaps show in some cases significant deviation from the results reported on small clusters using local density approximation. Our results also show that small clusters upto n = 8 favor monomer dissociation, but larger clusters fragment into two small clusters. We discuss the bonding nature and its consequences for melting of these clusters.

Key Words: Tin clusters, *ab initio* molecular dynamics, atomic and electronic structure, melting, fragmentation.

INTRODUCTION

Structural elucidation of free atomic clusters has been an intense area of research for the past two decades. Depending on the size of the clusters and the elemental electronic configuration, these adopt different geometries for the lowest energy configuration. Clusters of free electron-like metals with weakly directional bonding prefer an electronic shell structure [1]. This is characteristic of alkali metals, coinage metals and group 13 elements like Al, Ga, In, etc. Clusters of noble gas elements, alkaline earths and transition metals, however, adopt an atomically closed shell growth mode and most often it is icosahedral [1,2,3]. Clusters composed of tetravalent elements provide interesting results for the understanding of chemical bonding. It has been found that group 14 elements adopt non-compact geometries and undergo rearrangements in the progression of their growth. For example, carbon clusters undergo structural transitions from linear chain to monocyclic rings to fullerene like growth [4].

Clusters of Si and Ge are reported to undergo a structural reconstruction as the size increases. Jarrold and co-workers have measured the ion-mobilities of Si^+_n and Ge^+_n by using injected-ion drift-tube technique [5-7]. They have elucidated the existence of different isomers and proposed that a structural transition from prolate to spherical geometry occurs at ~27 atoms for Si^+_n and ~70 atoms for Ge^+_n clusters. Tin is just below Ge in the periodic table. Bulk tin is known to be at the border between semiconductor and metal with a nearly zero band gap. It is unknown whether small tin clusters will prefer a covalent bonding or metallic. It has two allotropes, white or β tin with body centered tetragonal lattice and grey or α tin with tetrahedral diamond lattice as Si or Ge. In the ambient condition, white tin shows the behavior of metal while α tin is semiconducting below 286K. So far, very little is known about tin clusters both theoretically and experimentally. Recent experiments by Jarrold and his co-workers predict that tin clusters between 15 and 30 atoms have melting points at least 50 K higher than the bulk tin [8]. They used ionic mobilities of the charged cation clusters as a parameter for the prediction of melting point. It is interesting to note that although large clusters with thousands of atoms have lower melting points than bulk crystals, very small tin clusters melt at temperatures higher than the bulk melting point. It has been suggested that the higher melting temperature of small tin clusters could be due to the elongated structures of these clusters [9]. In fact they did not see a transition of tin clusters from prolate to spherical structures up to 555 K. It is speculated that the different (from bulk) structures of clusters as well as a change in the bonding nature could be possible reasons for this unusual behavior. Also there could be isomers with different bonding natures due to two bulk allotropes.

The mass spectrum of tin clusters produced by elemental vapor condensation resembles the one of lead clusters and not Ge clusters [10]. On the other hand the mass spectrum of tin clusters produced in the liquid ion source is almost identical to those of Si_n and Ge_n clusters obtained under similar conditions but different from the one of lead clusters. For example, while all Si, Ge and Sn clusters show maximum abundance for n = 4, 6 and 10, the mass spectrum of lead cluster does not show any signature of magic clusters [11,12]. It is well know that the stability pattern in the mass spectrum can strongly depend on the source conditions and the energy of the ionizing photons. Duncan and coworkers have surveyed the abundance spectrum of tin clusters by using different source conditions. They concluded that the properties of tin clusters are intermediate between Ge and Pb clusters [13]. In contrast to this, Gantefor et.al. showed that the photoelectron spectra of Sn anion clusters for n <22 resemble with those of Ge anion clusters and not with Pb anion clusters [14]. This intermediate behavior of tin clusters along with the unusual high melting temperature led to our motivation for this present work to study the electronic and geometrical structures of small tin clusters in the range of n = 1-20. To the best of our knowledge no reports are available in the literature for tin clusters above n = 13 atoms. In the present paper we present the ground state geometries and electronic structure of tin clusters upto 20 atoms. We also compare these results with those reported by using LDA [15] upto n = 13 atoms.

The calculations have been performed using the Vienna *ab initio* molecular dynamics method [16-18]. We used GGA exchange-correlation as compared to the LDA calculations reported in an earlier study [15]. Ultrasoft Vanderbilt pseudopotentials [19] and a plane wave basis set with a cut-off energy of19.1 Ry are used. The geometries are optimized using conjugate-gradient technique. A large simple cubic cell (20A^0) is used through out these calculations.

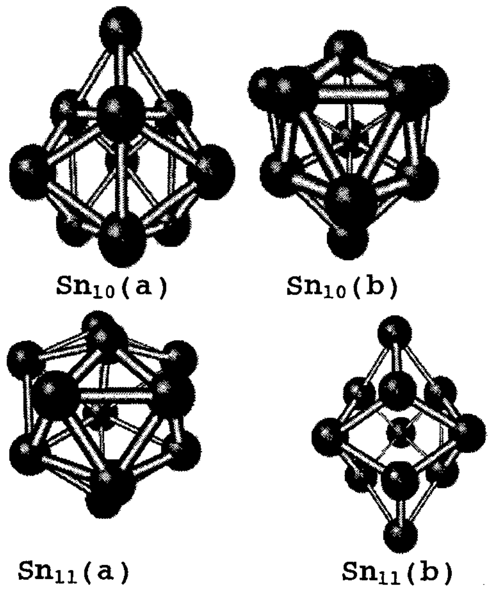
RESULTS:

Structures of Sn_n (n = 2-8) clusters:

The present calculations predict ground state geometries of tin clusters (Sn_2 to Sn_8) to be similar to those found previously for Sn clusters using LDA calculations [15]. The dimer of tin cluster shows an interatomic separation of 2.81 A with binding energy of 1.161 eV. The corresponding cohesive energy of tin in the bulk is 3.14 eV/atom. To check the effect of *d* electrons, we have also calculated Sn_2 cluster including *d* electrons as valence orbital but no significant effect was observed in the bond length as well as in the binding energy. Spin-polarized calculation for tin dimer shows a higher binding energy of 1.370 eV and a bond length of 2.79 A. Other clusters have no spin-polarisation. The trimer shows an isosceles triangle as the lowest energy structure. For n = 4, 5 and 6 tin clusters show a rhombus, elongated trigonal bipyramid and intersecting rhombus structures respectively as the lowest energy structures which are similar to Si and Ge clusters [15]. For Sn_7, we have calculated three different geometries starting with (a) Capped octahedron, (b) pentagonal bypiramid (PBP) and (c) capped prism. The PBP structure is found to be of the lowest energy as it has also been observed by Ho and coworkers [15]. For Sn_8, five different geometries are taken as the initial configuration: (a) bicapped octahedron, (b) capped PBP, (c) D_{2d} structure, (d) simple cube, and (e) bicapped prism. The capped PBP structure is found to have the lowest energy. The second lowest minimum structure is found to be bicapped octahedron. It is 0.03 eV higher in energy than the PBP structure.

Structures of Sn_n (n = 9-13) clusters:

For Sn_9 we used many different geometries as the starting configuration and a tetra capped trigonal bipyramid and bicapped PBP structure are found to have similar energies. The tricapped octahedron isomer is found to be 0.75 eV higher in energy. For Sn_{10} a capped prism (Fig. 1), which has been obtained for Si_{10} and Ge_{10} clusters, also has the lowest energy. A tetracapped octahedron structure is 0.23 eV higher in energy as compared to the capped prism structure. Another structure of Sn_{10} (Fig. 1) has been found to be very close in energy to the Sn_{10} (a) structure with only 0.09 eV difference in enegy. Further to confirm this growth motif, we capped this isomer with one more atom to obtain the initial configuration for Sn_{11} which turned out to be lower in energy (Fig. 1) than the previously believed penta-capped trigonal prism structure of Sn_{11} cluster. The pentacapped trigonal prism (Sn_{11}(b)) is 0.4 eV higher in energy than the presently obtained lowest energy structure of Sn_{11}(a) cluster. For Sn_{12} cluster three closely competing structures have been found which are within 0.03 eV difference of energy. The lowest energy structure is 0.03 eV lower in energy from the one reported by Ho-and his coworkers [15]. For Sn_{13} cluster the lowest energy structure is similar to what has been obtained previously by Ho and coworkers. The icosahedral structure for Sn_{13} is 0.59 eV higher in energy as compared to the C_{2v} isomer of Sn_{13} cluster.



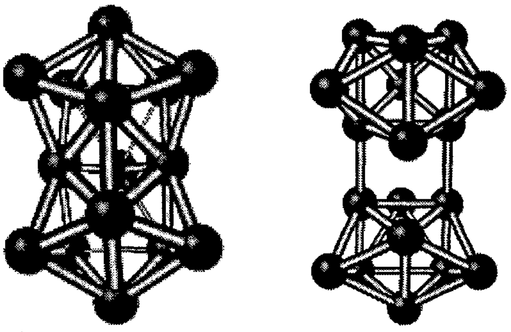
Sn_{10}(a) Sn_{10}(b)

Sn_{11}(a) Sn_{11}(b)

Fig.1 Structures of Sn_{10} and Sn_{11} clusters (a represents the lowest energy structure).

Lowest energy isomers of Sn_n (n = 14-20) clusters:

In the following section we describe few lowest energy isomers of tin clusters in the size range of n = 14-20. So far no reports are available for tin clusters in this size range. However, as calculations are available for Si and Ge clusters in this size range, we compare the geometries of Sn clusters with them. In general all these structures consist of capped prism units and prolate structures are more favorable as compared to the corresponding spherical structures. We show (Fig. 2) two typical examples of compact and prolate structures for Sn_{15} (compact) and Sn_{18} (elongated) clusters. For Sn_{14} cluster the lowest energy structure is similar to that obtained for Si_{14} cluster with little distortion. The other structure where tricapped prisms are fused with one capping atom removed shows 0.53 eV higher in energy. For Sn_{15} cluster, fused tricapped prism structure is found to be of the lowest energy, which is different from Si_{15} and Ge_{15} structures. For Sn_{16} cluster the lowest energy structure is similar to that of Ge_{16} cluster. For Sn_{17}, Sn_{18}, Sn_{19} and Sn_{20} a prolate structure consisting with the tetracapped prism as the basic unit forms the lowest energy structure.



Sn_{15} Sn_{18}

Fig. 2 Structures of Sn_{15} and Sn_{18} clusters.

Energetics

Table shows the binding energies of the lowest energy structures for Sn_n (n = 2-20) clusters. It is seen that these energies calculated by GGA are significantly lower than the corresponding LDA values and are important to understand the melting behavior. It is found that the binding energy of clusters with about 10 atoms is already within about 5% of the bulk value. This is very unusual as compared to the behavior known for metal clusters in this size range where all atoms lie at the surface. For comparison, the binding energy of Al_{13} is about 35% lower than the bulk value [20]. This shows that the binding in small clusters is unusually strong in the case of tin clusters which could be a possible reason for higher melting temperatures. The corresponding difference of binding energies for Si_{10} and Ge_{10} from bulk is higher. Therefore, our results suggests that these clusters tend to have prolate structures because compact 3-d structures have lower binding energies. As the size of the cluster increases, the compact structures would become favorable to reduce the overall surface energy though the binding energy of inner core may not be as large as prolate structures. Our binding energy values also shows 7, 10, and 18 atoms clusters to be magic. These results are in excellent agreement with the available experimental data [13]. Also we obtain monomer dissociation as the preferred fragmentation channel. However for Sn_{13}, (6,7) and for Sn_{17}, (7,10) become the more preferred channels. These are again in excellent agreement with experiments. A detailed report of this work will be published elsewhere.

Table: Binding energies of tin clusters. The LDA results are from Ref. [15].

Cluster	B.E. (eV/atom) (GGA)	B.E. (eV/atom) (LDA)
Sn_2	1.370	-
Sn_3	1.939	2.227
Sn_4	2.382	2.736
Sn_5	2.560	2.965
Sn_6	2.737	3.167
Sn_7	2.854	3.308
Sn_8	2.790	3.236
Sn_9	2.870	3.334
Sn_{10} (a)	2.936	3.432
Sn_{10} (b)	2.927	
Sn_{11} (a)	2.869	
Sn_{11} (b)	2.838	3.382
Sn_{12}	2.871	
Sn_{13}	2.882	3.407
Sn_{14}	2.939	
Sn_{15}	2.946	
Sn_{16}	2.956	
Sn_{17}	2.915	
Sn_{18}	2.947	
Sn_{19}	2.936	
Sn_{20}	2.959	

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