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Ionization potentials of small tin clusters: first principles calculations

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Abstract

Vertical and adiabatic ionization potentials of small tin clusters having upto 20 atoms are numerically estimated using ab initio quantum mechanical methods. The ground state geometries and energetics of neutral and singly positively charged clusters are obtained using ultrasoft pseudopotential plane wave method with generalized gradient approximations. The calculated ionization potentials (IPs) show good agreement with the experimental results. The IPs of Sn₇ and Sn₁₀ show local maxima that corroborate the magic behavior of these clusters as found in the mass abundance spectra and photoionization experiments. A comparative study is also made to understand the effect of different exchange correlation functionals on the IPs using Gaussian molecular orbital methods. © 2002 Published by Elsevier Science B.V.

1. Introduction

Studies on atomic clusters provide fundamental understanding of materials at the nanoscale and could lead to species for novel cluster assembled materials [1]. During the past decade a large number of experimental and theoretical works have been performed for neutral and charged metal clusters to understand their physico-chemical properties like ionization potentials (IP), electron affinity (EA), reactivity, magnetic behavior,

etc. Magic clusters show relatively high IPs as compared to other clusters. Also such clusters have large highest occupied–lowest unoccupied molecular orbital (HOMO–LUMO) gaps. Clusters of tetravalent elements C, Si, Ge and Sn are among the most actively researched and are interesting to understand the growth behavior and chemical bonding in this group as carbon clusters adopt non-compact geometries that progressively undergo rearrangements with an increase in size from linear chain to monocyclic rings to fullerene like growth [2]. Small clusters of Si and Ge undergo structural changes as the size increases [3–5] but the growth behavior for clusters with more than 20 atoms is still not well understood.

Tin is unique in the way that it exists both in covalent (α) and metallic (β) bulk phases. In the periodic table tin is below germanium and above

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lead. It is observed that the mass spectrum of tin clusters shows similarities with those obtained for both germanium and lead clusters [6]. Although some theoretical and experimental reports are available on these systems, very little is known about tin clusters in the range of 10–20 atoms. Recently tin clusters have been reported to have abnormal melting temperatures that are higher than the bulk value [7]. A detailed theoretical study on tin clusters with up to 20 atoms has recently been carried out that showed unusually high binding energies (BEs) of these clusters, which could be responsible for higher melting temperatures [8].

The IP of a cluster is an important physical property governed by its electronic structure. The changes in the structural motif and the associated electronic structures are reflected in sharp changes of the IPs. Particularly it is useful to study the variation in IP as a function of the cluster size to understand the growth pattern, stability, and abundances of clusters. The IP of a cluster can be predicted from calculation of the difference in total energies of neutral and singly positively charged states. Therefore, a detailed knowledge of the atomic and electronic structures is necessary for this purpose. Photoionization experiments on small tin clusters have been carried out by Duncan and coworkers [6] using ArF (6.43 eV) and F2 (7.87 eV) lasers. The IPs of tin clusters have been bracketed into three size ranges. For example, IPs of tin clusters with $n \geq 11$, have been found to be less than 6.43 eV. For $n = 7$ –10, the IPs are about 6.43 eV and for $n = 1$ –6, the values lie in the range of 6.43–7.87 eV. Recently, Yoshida et al. [9] have studied the IPs of tin clusters using photoionization spectroscopy method and reconfirmed the results of [6]. In both the cases tunable ionizing energy was not used and therefore, precise determination of IPs was not possible.

Results of several experiments suggest that quite often Sn clusters show resemblance with Si and Ge clusters in the small size range. However, for medium size range tin clusters exhibit a quite different trend. For example, both Si_n and Ge_n clusters show rapid decrease in the IP values at around 20 atoms [9]. This phenomenon has been suggested to be due to a change in the structural

motif of these clusters in this size range leading to a significant change in their electronic structure. It is noted that for tin clusters with $n = 14$ –40, the IPs decrease gradually without a sharp change. Theoretically, not many reports are available for the calculation of IPs of tin clusters. Jo and Lee [10] have reported the IPs of small tin clusters using semi-empirical tight binding calculation. However, in these calculations the IPs were calculated using a constant downward shift of 3.0 eV. Still a large difference between theoretical and experimental results prevailed that has been explained to be due to the assumption of an icosahedral structure of these clusters. However, we find that these do not have the lowest energies. Balsubramanian and coworkers [11,12] have carried out ab initio quantum chemical calculations for very small neutral and charged tin clusters. These calculations are limited to only Sn_4 and Sn_5 clusters. To our knowledge no systematic calculations are available on IPs of tin clusters from first principles. In the present work we present results of IPs of tin clusters upto $n = 20$ using first principles total energy calculations.

2. Computational details

The calculations have been performed using ab initio ultrasoft pseudopotential plane wave method [13] with generalized gradient approximation (GGA) for the exchange–correlation energy. Spin-polarized calculations have been done for charged clusters. The cut-off energy for the plane wave expansion is taken to be 19.1 Ry. The structures are optimized using the conjugate gradient method. The clusters are placed in a large simple cubic cell (20 Å) for the neutral clusters. For positively charged clusters the geometries are optimized starting with the ground state structures of neutral clusters. A unit cell of 25 Å side is used with neutralizing uniform background. The corresponding dipole correction energy is included in the total energy calculations for charged clusters.

In order to further understand the effects of correlation, a set of hybrid exchange–correlation energy functionals, BLYP, B3LYP, and B3PW91, have been used to calculate the IPs. For this,

calculations are done using the GAUSSIAN-98 software [14]. The notation BLYP represents the combination of Becke exchange and Lee, Yang, and Parr (LYP) correlation functional [15,16], while B3LYP and B3PW91 are hybrid functionals where the exchange functional is a linear combination of Hartree–Fock, local and gradient-corrected exchange terms that are combined with a gradient-corrected correlation functional. The best known of these hybrid functionals is Becke's three-parameter formulation noted as B3LYP where LYP correlation functional is used and B3PW91 where PW91 correlation functional [17] is used.

3. Results and discussion

3.1. Ground state geometries

The ground state structures of neutral clusters have been studied recently. For positively charged clusters, these are obtained by optimization of the geometries of neutral clusters that are taken to be the starting configurations. It is found that the equilibrium geometries of charged clusters are not significantly different from those of the corresponding neutral ones. As expected the changes in the inter-atomic distances are more in the smaller size region. Due to odd number of electrons the equilibrium structures of charged clusters are distorted as compared to the neutral ones. In the following we briefly discuss the ground state structures of charged clusters. A detailed discussion on the structures can be found elsewhere [18]. For $n = 3, 4, 5$, and 6 these are triangle, rhombus, trigonal bipyramid, and intersecting rhombus structures, respectively. Starting from $n = 9$, the ground state structures diverge as compared to those of Si and Ge clusters except for $n = 10$. We have found a new close packed isomer for $n = 11$ [8]. This is 0.42 eV lower in energy than the pentacapped trigonal prism structure reported from LDA calculations [19]. Sn_{12} follows a similar trend of close packed structure but Sn_{13} prefers an elongated structure as compared to the close packed icosahedron, frequently found for metal clusters. In the size range of $n = 14$ – 20 atoms, the growth behavior flip-flops between partial metal-

like and silicon type structures. Some clusters like $n = 15$ and 16 prefer close packed structures whereas $n = 14, 17, 18, 19$ and 20 prefer prolate structures.

3.2. Ionization potentials

Table 1 summarizes the results of the binding energies (BEs), adiabatic ionization potentials (AIPs), vertical ionization potentials (VIPs), HOMO–LUMO gaps, and the experimental IPs of tin clusters. The values of VIPs are higher than those of the AIPs as these are obtained from unrelaxed geometries of neutral clusters. Fig. 1 shows a comparison of the calculated VIPs with those of experimentally reported values [9] as a function of the cluster size. The IPs are determined using ultrasoft pseudopotentials and gradient corrected exchange–correlation functionals. In general it has been observed that the nature of the variation in the IP values of Sn clusters is similar to that of Si and Ge clusters. In the following section we discuss the IP behavior of Sn clusters for $n = 2$ – 20 and compare these results with those of the Si and Ge clusters wherever necessary. Further correlation between the HOMO–LUMO gaps and IP values has been drawn to understand the stability of magic clusters.

The calculated trend of the IPs as a function of n is similar to the one obtained from experiments. Exceptions are found only for $n = 4$ and 15 that show minima in the calculated IP while a local maxima in experiments. The IP of Sn_4 cluster has been calculated to be 6.86 eV, significantly lower than the experimental value of 7.58 – 7.76 eV obtained by Yoshida and Fuke [9]. In another theoretical calculation [10] using CASSCF and MRDSCI methods, the IP of Sn_4 cluster was reported to be 6.86 eV for rhombus geometry, showing a close agreement with our calculations. For Sn_5 the calculated IP is 7.07 eV. It is noted that this is an improvement over the previous calculation of Balasubramanian and coworkers [11] where the IP value of Sn_5 was predicted to be 6.76 eV, substantially lower than the observed value. From Fig. 1 it is clear that IPs of Sn_6 and Sn_7 are relatively high and then there is a sharp decrease for Sn_8 . Similar trend has been found in the ex-

Table 1

Binding energy (BE), ionization potential (IPs) and HOMO–LUMO energy gap of Sn_n clusters for $n = 2$ –20 atoms calculated by using ultrasoft pseudo-potentials and gradient corrected exchange–correlation functionals

Cluster	BE (eV/atom)	AIP (eV)	VIP (eV)	GAP (eV)	IP (Exp) (eV)
Sn_2	1.370	6.91	6.95	0.32	7.06–7.24
Sn_3	1.939	7.07	7.17	0.84	7.58–7.76
Sn_4	2.382	6.86	7.06	1.05	7.58–7.76
Sn_5	2.560	7.08	7.18	1.58	7.46–7.58
Sn_6	2.737	6.70	6.94	1.61	7.06–7.24
Sn_7	2.854	6.77	7.00	1.50	7.06–7.24
Sn_8	2.790	6.08	6.25	1.01	6.29–6.36
Sn_9	2.870	6.21	6.33	1.45	6.55–6.72
Sn_{10}	2.936	6.43	6.51	1.54	6.72–6.94
Sn_{11}	2.869	5.71	5.91	0.92	6.05–6.15
Sn_{12}	2.871	5.81	5.95	0.98	5.99–6.05
Sn_{13}	2.882	5.83	5.94	0.91	6.17–6.23
Sn_{14}	2.939	5.96	6.08	1.34	6.29–6.43
Sn_{15}	2.946	5.65	5.85	0.77	6.29–6.43
Sn_{16}	2.956	5.87	6.03	1.37	6.29–6.43
Sn_{17}	2.915	5.55	5.71	0.63	–
Sn_{18}	2.947	5.53	5.73	0.88	6.29–6.36
Sn_{19}	2.936	5.38	5.68	0.60	6.05–6.11
Sn_{20}	2.959	5.52	5.77	0.84	6.29–6.43

periments also. This feature is further corroborated from the variation in HOMO–LUMO gaps for these clusters as shown in Fig. 2. The reason

for this sharp drop in IP value for Sn_8 is attributed to the loss of symmetry from Sn_7 to Sn_8 cluster. For Si and Ge clusters also similar features have

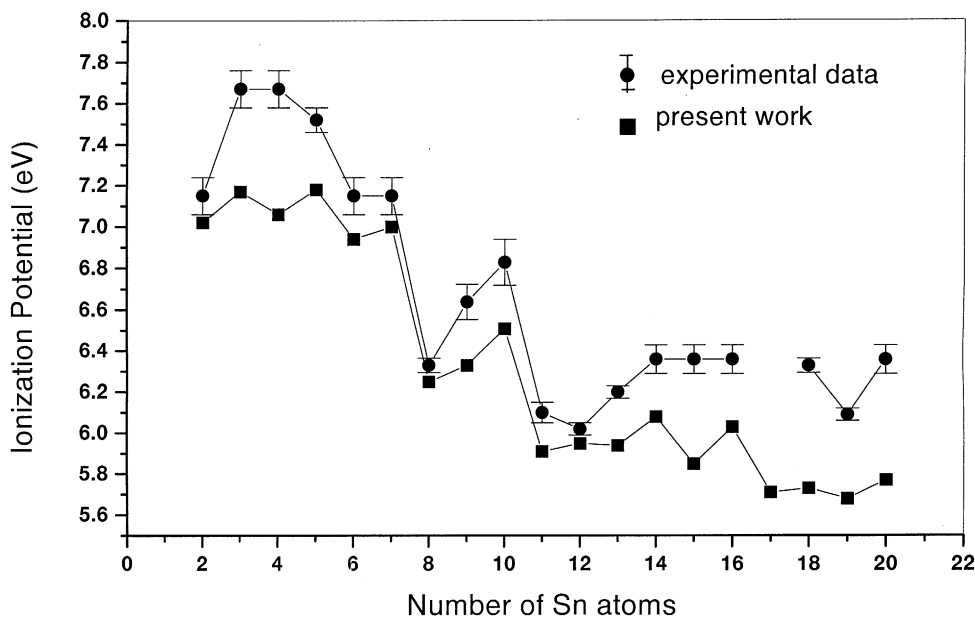


Fig. 1. Calculated VIPs of tin clusters compared with experimental data as a function of cluster size.

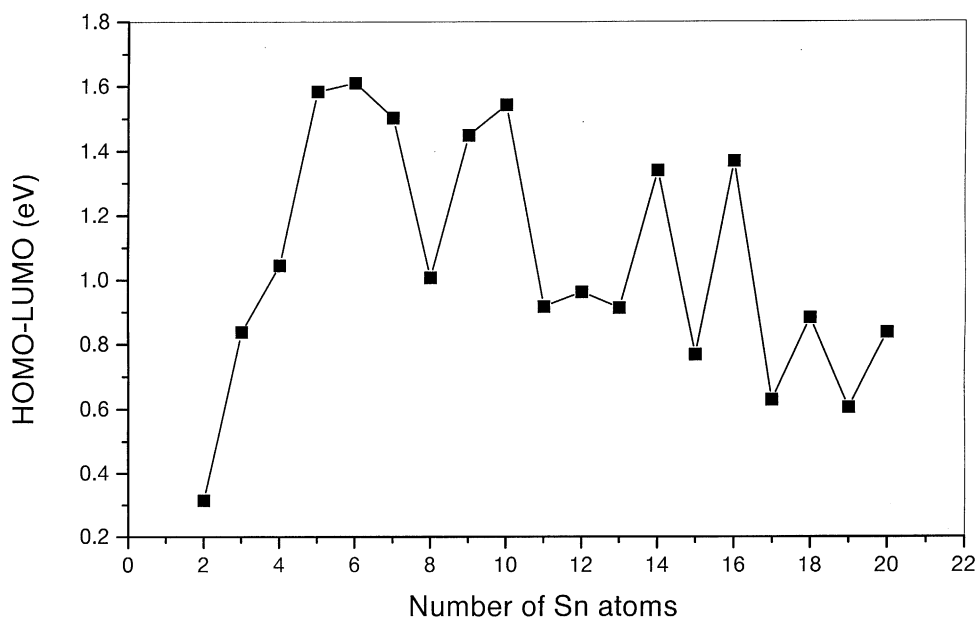


Fig. 2. Plot of the HOMO–LUMO gap for tin clusters as a function of the cluster size.

been observed. For Si_7 , Ge_7 and Sn_7 clusters, a pentagonal bipyramid structure is found to have the lowest energy with D_{5h} symmetry. After addition of one more atom the equilibrium structure is capped PBP leading to a reduction in symmetry. Another sharp drop in IP of Sn_n cluster is found from Sn_{10} to Sn_{11} . In this context it can be mentioned that in the mass abundance spectra Sn_{10} and Sn_7 show magic behavior. The present calculations also predict higher IPs for Sn_7 and Sn_{10} clusters confirming their higher stability. The corresponding HOMO–LUMO gaps are found to be 1.50 and 1.54 eV, respectively.

Although IPs of small Sn_n clusters ($n < 14$) show similarities with those of Si_n and Ge_n , for larger size these exhibit quite different trends. In the following section we discuss the differences in the size dependence of Si_n , Ge_n and Sn_n clusters in the range of 14–20 atoms. For Ge clusters, IPs decrease gradually from Ge_3 to Ge_{15} and then rapidly between $n = 15$ and 26. Again for large Ge clusters ($N > 27$), the IPs decrease gradually to the value of the bulk work function with increasing cluster size. This feature of a gradual decrease in IP for small Si clusters is the same up to $n = 17$. The sharp changes in the IP values could be cor-

related with a structural transition. The experimental IPs of Sn_n clusters show a flat nature in the range of $n = 14$ –20. However, theoretically an oscillatory behavior in the IPs has been found in our calculations. The IPs obtained from experiments are bracketed within an error bar that varies from 0.06 to 0.16 eV. Therefore it is possible that small oscillations in the IPs are not reflected in the experimental values. Moreover, bulk tin has two allotropes with metallic and covalent bonding. This could also lead to a change in the bonding nature as a function of the cluster size. Also there could be isomers present under the experimental conditions. The different nature of bonding is corroborated from our calculations where a flip-flop behavior is observed between metallic and silicon type in the geometries of tin clusters in this size range as mentioned in the first section.

Table 2 shows the IPs of Sn_n clusters obtained by using different hybrid exchange and correlation functionals. The geometries for these calculations were taken to be the same as obtained from the ultrasoft pseudopotential calculations. Comparing these values it is clearly seen that there is a significant effect on the IP values if different ex-

Table 2

The AIP values of Sn_n clusters for $n = 2$ –20 atoms obtained by using different exchange–correlation functionals

SIZE	BLYP	B3LYP	B3PW91	VASP	EXPT.
2	8.40	7.12	7.28	6.91	7.06–7.24
3	6.82	7.29	7.45	7.07	7.58–7.76
4	6.61	6.87	6.93	6.86	7.58–7.76
5	6.88	7.12	7.25	7.08	7.46–7.58
6	6.70	6.94	7.06	6.99	7.06–7.24
7	6.69	6.96	7.15	6.08	6.29–6.36
9	6.23	6.46	6.59	6.21	6.55–6.72
10	6.49	6.77	6.97	6.43	6.72–6.94
11	5.86	6.09	6.22	5.71	6.05–6.17
12	5.94	6.18	6.33	5.81	5.99–6.05
13	5.93	6.21	6.34	5.83	6.17–6.23
14	6.08	6.37	6.53	5.96	6.29–6.43
15	5.79	6.01	6.11	5.65	6.29–6.43
16	6.01	6.33	6.51	5.87	6.29–6.43
17	5.77	6.05	6.22	5.55	–
18	5.76	6.03	6.18	5.53	6.29–6.36
19	6.02	6.23	6.22	5.38	6.05–6.11
20	5.86	6.14	6.26	5.52	6.29–6.36

Experimental values are taken from [9].

change–correlation energies are used in the small size range. It is found that in general B3LYP and B3PW91 results are in very good agreement with the experimental results. Moreover, it can be mentioned that the trend observed in all the cases are also in good agreement with those of experiments. This fact illustrates that the theoretically obtained geometries for the neutral and positively charged clusters are very close to the global minimum. The small discrepancies observed between theoretical and experimental results could arise due to the following reasons: (1) While doing experiments, tunable laser was not used and therefore, obtaining the exact values of the IPs is not possible. (2) It is possible that in experiments other isomers are also abundant which could lead to a disagreement with the theoretical predictions. Small differences could also arise if the structures were fully relaxed for different exchange–correlation functionals as well as due to finite temperatures in experiments.

4. Summary

In summary, we have performed ab initio electronic structure calculations for neutral and singly

positively charged tin clusters in the size range of $n = 2$ –20 atoms. The IPs are determined from the difference in the total energies of the neutral and charged clusters. From these results the following features have been observed.

1. The IPs of 3, 5 and 6 atom clusters are higher than a dimer.
2. Sn_7 and Sn_{10} show higher IP values in this series of clusters indicating magic nature.
3. A sharp drop in IP from Sn_7 to Sn_8 cluster is in good agreement with experiments. This is likely to be due to the lowering of the symmetry for $n = 8$.
4. Sharp drop from Sn_{10} to Sn_{11} clusters reconfirms the change in the structural growth motif.
5. Unlike Si_n and Ge_n clusters the IPs of Sn_n clusters show oscillations in the size range of 14–20 atoms.
6. Correlation of IPs with HOMO–LUMO energy gap shows good agreement.

Results of the IPs have been further improved by using hybrid exchange–correlation functionals in total energy calculations. In particular, B3PW91 exchange correlation functional shows significant improvement over the results obtained from pseudopotential GGA calculations.

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