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Computational Insight into the Static and Dynamic Polarizabilities of Aluminum Nanoclusters

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The static and dynamic polarizabilities for the lowest-energy structures of pure aluminum clusters up to 31 atoms have been investigated systematically within the framework of density functional theory. The size evolution of several electronic properties such as ionization potential, electron affinity, the energy gap between the highest occupied molecular orbital and lowest unoccupied molecular orbital, and chemical hardness have also been discussed for aluminum clusters. Our primary focus in this article, however, has been upon the study of polarizability of aluminum clusters, although we also looked at the role of other electronic properties. From the energetics point of view, the relative stability of aluminum clusters at different sizes is studied in terms of the calculated second-order difference in the total energy of cluster and fragmentation energy, exhibiting that the magic numbers of stabilities are $n = 7, 13$, and 20 . Moreover, the minimum polarizability principle is used to characterize the stability of aluminum clusters. The results show that polarizabilities and electronic properties can reflect obviously the stability of clusters. Electronically, the size dependence of ionization potential and electron affinity of clusters is determined. On the basis of the Wood and Perdew model these quantities converge asymptotically to the value of the bulk aluminum work function.

Introduction

Clusters are currently the central interest of research because of the considerable position to occupy between molecules and condensed matters. These materials enable the study of the development of bulk properties with increasing cluster size.^{1–3} Cluster science is a fascinating field, which not only enriches the fields around it but also offers tantalizing possibilities for new materials and processes. In this respect, cluster physics has been a subject of intense research activities in recent years due to the potential technological applications like fabrication of materials with desired properties. As cluster species, metallic clusters have been studied to a reasonable extent,⁴ and they are highly reactive species which are typically prepared by molecular beam techniques or by matrix isolation. Among different metallic clusters that have been previously studied, aluminum clusters have been the subject of a large amount of experimental and theoretical investigations due to the applications in diverse fields such as nanocatalysis,⁵ microelectronics,⁶ and so on. Aluminum nanoclusters play important roles in chemical reactions and nanosized devices with many chemical and physical properties such as conductivity, superconductivity, and also magnetic properties. Therefore, there is a significant technological and fundamental motivation to understand the electronic properties of aluminum clusters which is also our main focus in the present study.

Before turning to our work, we provide here a summary of the previous investigations on the aluminum clusters. In the context of experimental studies, we only mention that there are many works on clusters of aluminum and their ions.^{7–16} Theoretically, since the structure is the most basic property it is not surprising that intensive efforts have been devoted to elucidate this property for clusters. Studies on the structures of aluminum clusters and some of their properties have been carried

out during past decade^{17–42} and followed up by other groups more recently.^{43–45} A lucid account of different experimental and theoretical works on clusters of aluminum and their ions has been given by Aguado and López.⁴³

From the studies that mentioned above, it can be seen that the recent theoretical researches on aluminum clusters have mainly focused on the structural growth as the size increases and have less attention to the various properties of these clusters. However, the study of chemical and physical properties of metallic and semiconductor clusters is a long-standing area of academic and technological scientific interest. On the other hand, linear optical properties of clusters have attracted meticulous attention in the recent years due to their exotic properties which are different from the bulk, and could be proven valuable to the future nanostructure technologies. Deshpande and Kanhere⁴⁶ have investigated the optical absorption spectra of aluminum clusters using the time-dependent spin polarized local-density approximation. Phung et al.^{47,48} studied the properties such as ionization potential and magnetic properties for aluminum clusters using calculations based on the plane-wave basis set and the projector-augmented wave method. A theoretical study on the neutral, cationic, and anionic clusters of aluminum up to ten atoms and also on the interaction of oxygen with these clusters has been done by Sun et al.⁴⁹ More recently, the reactivity of aluminum cluster anions with respect to water molecule have been studied by Reber et al.⁵⁰

Lastly, we close this introductory section by emphasizing the features of the present contribution. On one hand, one of the fundamental goals of cluster science is to understand how the properties of clusters evolve with cluster size. Progress toward this goal has been slow, however, due in part to a lack of reliable information about the arrangement. On the other hand, no systematic density functional theory (DFT) investigation on the correlations of the stability with the static and dynamic polarizabilities of aluminum clusters has been conducted thus far. Therefore, in this research we extend our previous study

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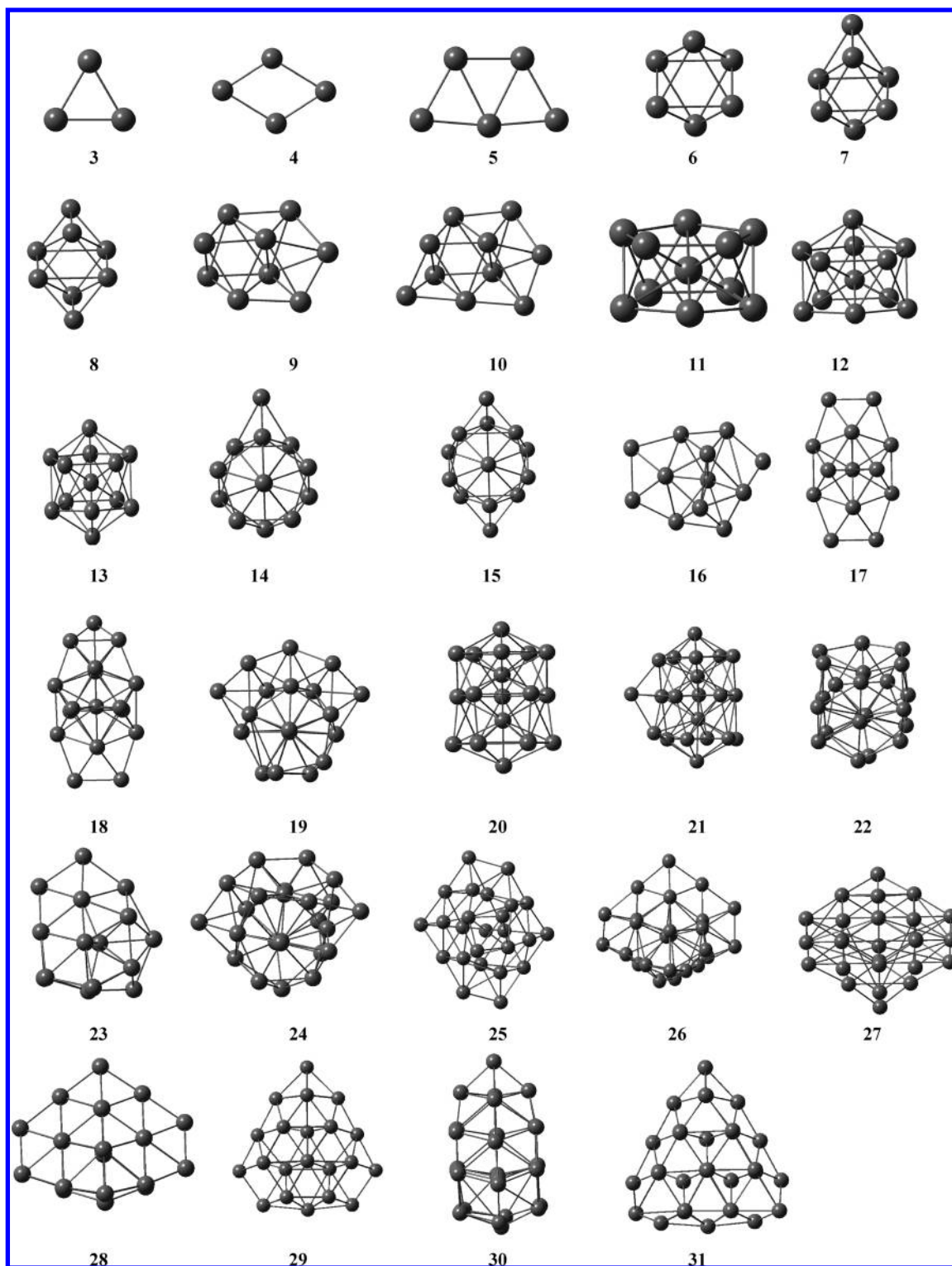


Figure 1. The lowest energy structures of Al_n clusters with $n = 3\text{--}31$. The numbers below the structures give the total number of atoms in each cluster.

on the polarizability and electronic properties of molecular zinc sulfide clusters⁵¹ to pure aluminum clusters. The size dependence of several reactivity descriptors, such as the ionization potential, electron affinity, highest occupied molecular orbital–lowest unoccupied molecular orbital (HOMO–LUMO) energy gap, and hardness is explored. Moreover, the relationships of the relative stability, polarizabilities, and electronic properties are discussed in this work.

Computational Details

Although the scope of this paper is far from determining the ground-state structure of aluminum clusters, the geometry is a key property of a cluster in understanding the transition from the microscopic structure to the macroscopic structure of materials. It is important to identify the correct ground state structures for the aluminum cluster because the polarizability is a ground-state property that is close to its geometrical

characteristic. In a more recent paper, Drebov and Ahlrichs⁴⁴ have investigated a comprehensive analysis on the structures of aluminum clusters. They carried out a thorough search for global minimum structures employing genetic algorithm (GA)^{52–54} and basin-hopping (BH)⁵⁵ procedures. The key point of the calculations is that the proper estimation of the starting geometry of cluster leads to faster convergence during the calculation to a local minimum or to the global energy minimum structure. Accordingly, to avoid trapping in the local minima of the potential energy surface, in the present study we have adopted the lowest energy structures of aluminum clusters up to 31 atoms reported by Drebov and Ahlrichs⁴⁴ and reoptimized the geometries with the Perdew–Burke–Ernzerhof (PBE) functional.⁵⁶ The use of PBE for aluminum clusters has been advocated by Aguado et al.⁴³ and accuracy of 0.01 eV has been claimed for relative energies. More recently, Drebov and Ahlrichs⁴⁴ suggested more conservative error of 0.1 eV for accuracy of aluminum clusters. On the other hand, electronic exchange and correlation effects are well-known to play a primary role in determining molecular polarizability.⁵⁷ Moreover, in the calculations of linear and nonlinear optical properties, the DFT methods provide significant improvement compared to the Hartree–Fock (HF) method and less computer time than the ab initio methods.^{58,59} Therefore, we rely on the PBE method for both geometry optimization and property calculation of the studied clusters.

It should be mentioned that the odd number of valence electrons in aluminum makes the clusters with an odd number of atoms in an electronically open-shell system. Therefore, the cluster properties were calculated in their singlet and doublet (triplet) states using the restricted and unrestricted schemes for closed-shell and open-shell systems, respectively. For all clusters we employed the sufficiently flexible triple- ζ valence plus polarization (TZVP) type basis,^{60–62} which gives results close to the basis set limit in DFT calculations.

Initial structures for each cluster were constructed using HyperChem 7.0 program.⁶³ All the geometry optimizations and frequency calculations have been carried out with the GAUSS-IAN03 suite of programs.⁶⁴ GaussView 4.1 software⁶⁵ has been employed to visualize the shape of global minima structures of clusters.

Results and Discussion

Energetics. The optimized structures for the lowest energy state of aluminum clusters are displayed in Figure 1 and their symmetries and electronic states are listed in Table 1. As mentioned before, details of the structural analysis of the clusters have been studied in a more recent paper⁴⁴ and thus will not be discussed in the present article. The obtained structures provide an opportunity to explore the electronic properties of clusters and also the relationship between these properties and cluster size.

We first discuss the relative stability of Al_n clusters ($n \leq 31$) from the energetics point of view. In cluster physics, the second-order difference in the total cluster energy, $\Delta_2 E(n)$, and the fragmentation energy, $D(n, n-1)$, are sensitive quantities that reflect the relative stabilities of the investigated clusters. To predict the relative stability of aluminum clusters, these quantities are calculated as follows

$$\Delta_2 E(n) = E(Al_{n+1}) + E(Al_{n-1}) - 2E(Al_n) \quad (1)$$

TABLE 1: Computed Values of the Second-Order Difference in the Total Cluster Energy, $\Delta_2 E(n)$, Fragmentation Energy, $D(n, n-1)$, HOMO–LUMO Energy Gap, Δ , Vertical Ionization Potential (IP), and Vertical Electron Affinity (EA) for Lowest-Energy Structures of Aluminum Clusters with their Symmetries and Electronic States^a

cluster	symmetry	state	$\Delta_2 E(n)$	$D(n, n-1)$	Δ	IP	EA
Al ₃	D_{3h}	$^2A''_1$	1.093	3.132	0.707	6.806	1.625
Al ₄	D_{2h}	1A_g	−0.848	2.039	0.107	6.499	2.127
Al ₅	C_{2v}	2B_2	−0.130	2.887	0.894	6.657	2.001
Al ₆	D_{3d}	$^1A_{1g}$	−0.502	3.017	0.648	6.823	2.215
Al ₇	C_{3v}	2A_1	1.107	3.519	0.835	6.315	1.806
Al ₈	C_{2h}	1A_g	−0.355	2.412	0.860	6.477	1.964
Al ₉	C_s	$^2A'$	−0.045	2.767	0.696	6.574	2.357
Al ₁₀	C_s	$^1A'$	−0.207	2.812	0.614	6.320	2.291
Al ₁₁	C_{2v}	2A_1	−0.193	3.020	0.819	6.299	2.517
Al ₁₂	C_1	1A	−0.514	3.213	0.943	6.289	2.115
Al ₁₃	D_{3d}	$^2A_{2u}$	0.717	3.727	1.790	6.835	3.099
Al ₁₄	C_{3v}	1A_1	0.435	3.010	0.896	6.305	2.223
Al ₁₅	C_{2h}	2A_g	−0.414	2.575	0.719	6.086	2.529
Al ₁₆	C_s	$^1A'$	0.081	2.990	0.777	6.016	2.206
Al ₁₇	D_{2h}	$^2B_{2u}$	0.099	2.909	0.649	5.859	2.507
Al ₁₈	C_s	$^1A'$	0.127	2.810	0.849	6.066	2.341
Al ₁₉	C_1	2A	−1.010	2.682	0.603	5.783	2.639
Al ₂₀	C_s	$^1A'$	1.163	3.693	0.788	6.105	2.457
Al ₂₁	C_1	2A	−0.786	2.530	0.356	5.790	2.637
Al ₂₂	C_1	1A	0.342	3.316	0.865	6.011	2.404
Al ₂₃	C_{3v}	2A_1	0.030	2.974	0.848	5.879	2.574
Al ₂₄	C_1	1A	0.178	2.943	0.748	5.977	2.536
Al ₂₅	C_2	2B	−0.338	2.765	0.688	5.759	2.775
Al ₂₆	C_1	1A	0.152	3.104	0.758	5.903	2.569
Al ₂₇	C_s	$^2A''$	0.183	2.951	0.594	5.711	2.881
Al ₂₈	C_{2v}	3B_2	−0.311	2.768	0.311	5.293	3.004
Al ₂₉	C_{2v}	2A_1	−0.054	3.079	0.260	5.557	2.798
Al ₃₀	C_1	1A	−0.066	3.132	0.251	5.623	2.876
Al ₃₁	C_2	2B	0.028	3.198	0.704	5.669	2.993

^a Units are in eV.

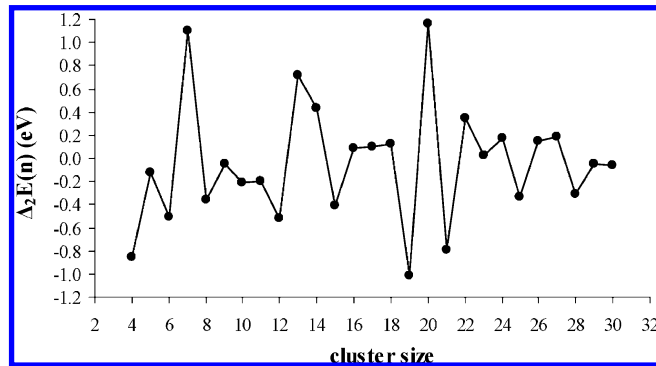


Figure 2. Size dependence of the second-order difference in the total cluster energies for lowest energy Al_n clusters.

$$D(n, n-1) = E(Al_{n-1}) + E(Al) - E(Al_n) \quad (2)$$

where $E(Al)$, $E(Al_n)$, $E(Al_{n-1})$, and $E(Al_{n+1})$ are the total energies of aluminum atom, n -, $(n-1)$ -, and $(n+1)$ -atom clusters, respectively. The values of $\Delta_2 E(n)$ and $D(n, n-1)$ are reported in Table 1. Figures 2 and 3 show the plots of these quantities as a function of the cluster size, n . Peaks in these quantities represent relatively more stable clusters. As seen from these figures, apart from the relatively maxima, the magic numbers of stabilities are found at $n = 7, 13$, and 20 implying that these clusters are obviously more stable than their neighboring clusters. The high stability of clusters, however, may be partially attributed to the high-symmetry geometries and compact atomic

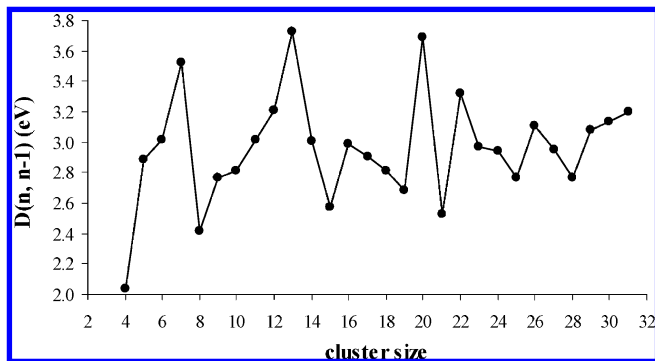


Figure 3. Size dependence of the fragmentation energies for lowest energy Al_n clusters.

arrangements of the clusters.⁶⁶ The results also show that the maximum magic number for the relative stability is $n = 20$ among the Al_n clusters ($n \leq 31$) reflecting that the Al_{20} is the most stable geometry. It has a more compact structure than Al_{19} and Al_{21} , and it can be considered a geometrical shell closing. It is also has been shown that this magic cluster is electronically very stable.⁴³

Apart from $\Delta_2 E(n)$ and $D(n, n-1)$, the energy difference between HOMO and LUMO can be considered as a good indicator of the electronic stability for clusters. For closed-shell systems the calculation of HOMO–LUMO gap is straightforward, while for clusters with odd number of atoms the difference has been calculated within the unrestricted open shell scheme. It is obvious that the HOMO–LUMO gaps are less than 1 eV for all sizes of the clusters (except Al_{13}), and there are some local oscillations in odd–even trend. Overall the greater values of the gap for $n = 7, 13$, and 20 point to an enhanced stability of these clusters.

Now, turning our attention to the main objective of the present paper, we discuss the polarizabilities and other properties of aluminum clusters, their variations with cluster size and relationship between them.

Static and Dynamic Polarizabilities. In the field of chemistry and physics, dipole polarizability is one of the important fundamental properties of any atomic or molecular system.^{67–69} Polarizability is one of the characteristic properties that can be obtained by experiment, and it provides information on the bonding and geometrical features of the clusters. In particular, study of the polarizability of metallic and molecular clusters has been considered one of the challenging and interesting tasks and has emerged as an active research field in recent years. Normally, polarizabilities are computed using static frequencies. However, frequency-dependent polarizabilities and nonlinear optical properties may be computed.^{70–73} In the present work, we investigate the evolution of polarizability at frequency of 0.0 au and Nd:YAG laser frequency, i.e., 0.04283 au. The later choice would be helpful for experimentalist to have a preliminary theoretical estimation of dynamic polarizability of aluminum clusters. The dipole polarizabilities of all considered clusters were calculated analytically using the coupled perturbed HF (CPHF) method^{74–78} at the PBE/TZVP level of theory. The measured data in experiments are usually the mean dipole polarizability, which can be obtained by the trace of the polarizability tensor.⁷⁹ The values of the mean polarizabilities are calculated as follows

$$\langle \alpha \rangle = \frac{\alpha_{xx} + \alpha_{yy} + \alpha_{zz}}{3} \quad (3)$$

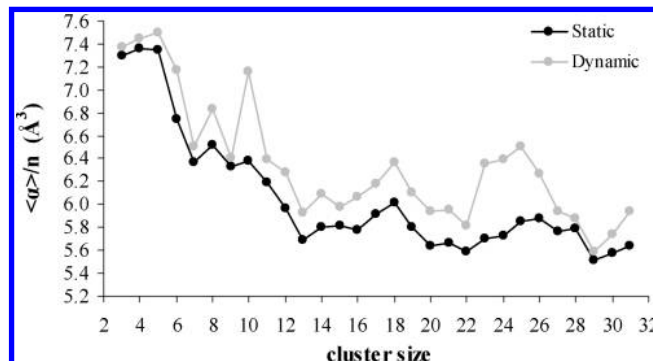


Figure 4. Size dependence of the polarizabilities per atom for lowest energy Al_n clusters.

TABLE 2: Values of Mean Polarizabilities per Atom, $\langle \alpha \rangle/n$, Dipole Moments, μ , and Effective Polarizabilities per Atom, α_{eff}/n , at 0.0 au (Static) and 0.04283 au (Dynamic) Frequencies

cluster	$\langle \alpha \rangle/n$ (\AA^3)		μ (Debye)	α_{eff}/n (\AA^3)	
	static	dynamic		static	dynamic
Al_3	7.300	7.381	0.000	7.300	7.381
Al_4	7.361	7.455	0.000	7.361	7.455
Al_5	7.349	7.500	0.346	7.543	7.695
Al_6	6.740	7.179	0.000	6.740	7.179
Al_7	6.364	6.511	0.611	6.796	6.943
Al_8	6.521	6.829	0.000	6.521	6.829
Al_9	6.329	6.410	0.508	6.561	6.643
Al_{10}	6.375	7.166	0.275	6.436	7.227
Al_{11}	6.194	6.394	0.293	6.257	6.458
Al_{12}	5.965	6.286	0.506	6.138	6.459
Al_{13}	5.684	5.930	0.000	5.684	5.930
Al_{14}	5.809	6.095	0.953	6.335	6.621
Al_{15}	5.816	5.985	0.000	5.816	5.985
Al_{16}	5.777	6.071	1.048	6.333	6.627
Al_{17}	5.912	6.183	0.000	5.912	6.183
Al_{18}	6.022	6.374	1.305	6.789	7.141
Al_{19}	5.799	6.101	0.151	5.809	6.111
Al_{20}	5.645	5.939	0.586	5.785	6.078
Al_{21}	5.663	5.958	0.572	5.790	6.085
Al_{22}	5.588	5.815	0.445	5.661	5.889
Al_{23}	5.701	6.350	0.355	5.745	6.394
Al_{24}	5.722	6.391	0.770	5.923	6.591
Al_{25}	5.858	6.511	0.217	5.873	6.526
Al_{26}	5.877	6.262	0.723	6.040	6.424
Al_{27}	5.761	5.936	0.162	5.769	5.943
Al_{28}	5.785	5.877	0.451	5.844	5.936
Al_{29}	5.512	5.598	0.275	5.533	5.619
Al_{30}	5.571	5.740	0.531	5.647	6.591
Al_{31}	5.635	5.945	0.621	5.736	6.046

A plot of the mean static and dynamic polarizabilities computed for the most stable structures of Al_n clusters vs clusters size is depicted in Figure 4, and the numerical values are reported in Table 2. The polarizability certainly increases if the frequency is increased (starting from 0) and then has a pole at the lowest electronic excitation. Thus, for all clusters the values of dynamic polarizabilities are larger than of the static polarizabilities. On one hand, it is observed that the values of static and dynamic polarizabilities strongly depend on size and symmetry, irrespective of the applied frequency. On the other hand, the minimum polarizability principle (MPP) states that the natural direction of evolution of any system is toward a state of minimum polarizability.⁸⁰ Therefore, by applying the MPP, those clusters with the local minimum polarizability are more stable than the neighboring clusters. Although the variation in the polarizability values observed at Nd:YAG laser frequency is very fluctuating, it can be seen there is a same trend for static and dynamic polarizabilities, particularly for magic number clusters. The observation of minimum at $n = 7, 13$, and 20 is

consistent with our discussion on the stability by energetic analysis for aluminum clusters. Moreover, there exists marked minima at $n = 22$ and 29 , which are not obviously confirmed by using energetic analysis. Nonetheless, in our previous study it has been demonstrated that MPP might be applicable to show the cluster stability.⁵¹ However, this principle cannot be assumed to be definitely hold for aluminum clusters with $n > 20$.

It is essential to keep in mind that the average polarizability can be directly measured in experiments only if the dipole moment, μ , of the cluster is zero. Otherwise, the experimental value typically includes an additional contribution from the electric dipole moment. Table 2 lists the computed values of electric dipole moment for aluminum clusters. As can be seen, most of the clusters have a permanent dipole moment. The value of μ fluctuates considerably from one cluster to another and reflects primarily the cluster symmetry. Components of the electric dipole in directions perpendicular to either reflection planes or rotation axes must vanish by symmetry. Highly symmetric clusters thus have small or vanishing dipole moments. A close agreement between theory and experiment, however, would require that temperature and dipole moment effects be taken into account. This means that the measured effective polarizability should be bigger than the average polarizability and becomes as follows

$$\alpha_{\text{eff}} = \langle \alpha \rangle + \frac{\mu^2}{3kT} \quad (4)$$

where k and T are Boltzmann constant and temperature, respectively. For completeness, the computed values of α_{eff}/n by using the static and dynamic polarizabilities at room temperature are also reported in Table 2. It can be seen that this correction, however, is not large for our studied clusters. It is important to note that the eq 4 assumes the clusters to be in thermal equilibrium in the external field and this condition may not be satisfied in beam experiments in which the clusters spend a very short time in the external field.

Ionization Potential and Electron Affinity. In this subsection we discuss the variations of the ionization potentials (IPs) and electron affinities (EAs) as measures of electronic stability with respect to the size evolution of clusters under study. The ionization potential and electron affinity are the most important quantities that can be used to signal the onset of metallic characteristics in the metal cluster. The ionization potential of a cluster is evaluated by detaching one electron from the neutral cluster in its ground state. On the other hand, the electron affinity of the cluster is energy required to detach an electron from a singly charged negative ion, namely, it is the energy released when an electron is attached to the neutral cluster.

For aluminum clusters, we have calculated the vertical ionization potentials and electron affinities (see Table 1), which are the energies required removing or adding one electron without allowing for structural relaxation. We represent the variations of the vertical IPs and EAs as a function of cluster size in Figures 5 and 6, respectively. As the reference for comparison, in each case, available experimental data from threshold ionization by photoionization spectroscopy¹¹ and ultraviolet photoelectron spectroscopy¹² are also shown. As seen from these figures, our results not only in trend but also in values are in good agreement with the experimental measurements. Our results are also consistent with the previous theoretical works.^{19,43,48} However, there are some discrepancies between the experiment and theory which can be attributed to various

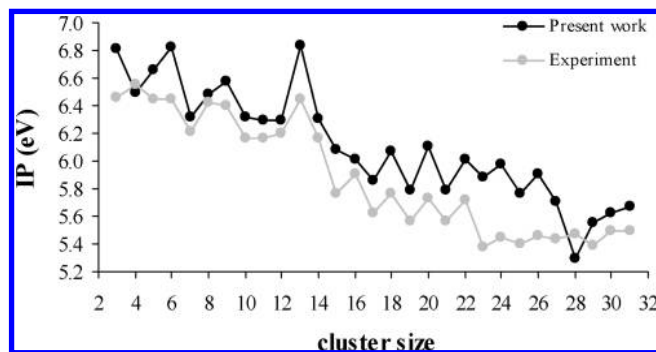


Figure 5. Size dependence of the vertical ionization potentials for lowest energy Al_n clusters.

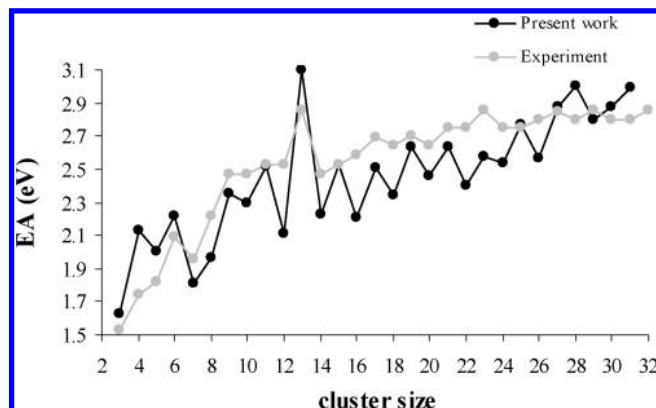


Figure 6. Size dependence of the vertical electron affinities for lowest energy Al_n clusters.

factors such as geometrical structures, experimental measurements, methods of calculation, level of theory and so on.

According to the liquid drop model, it has been demonstrated that many cluster properties lie within lines when plotted vs the inverse cube root of cluster size, i.e., $n^{-1/3}$.⁸¹ The value from such a plot extrapolated to zero, corresponds to the bulk parameter. IP and EA are of these properties. The size dependence of the measured IPs and EAs for simple metal clusters follow an average trend which first is given by Wood⁸² and then has been improved by Perdew et al.^{83,84} as follows

$$\text{IP} = W + \frac{1}{2}e^2\left(\frac{\alpha}{x} + d\right)^{-1} \quad (5)$$

$$\text{EA} = W - \frac{1}{2}e^2\left(\frac{\alpha}{x} + d\right)^{-1} \quad (6)$$

in which W is work function of the bulk metal, $x = n^{-1/3}$, and d is an electronic spill-out factor⁸³ and the finite value of α is related to the number of valence electrons and the Wigner–Seitz radius of the bulk metal which in our discussion we do not need its explicit expression. Equations 5 and 6 show that the values of IPs and EAs converge to W as $n \rightarrow \infty$. As shown in Figure 7, the results of IP and EA show a very good agreement with the well-known predictions of Wood and Perdew. As the cluster size increases, the IP and EA show the tendency toward the experimental bulk aluminum work function value of 4.28 eV. However, there are discrepancies in such correlations because the structures used for extrapolation are not exactly corresponding to crystalline structures of aluminum clusters at small scale.

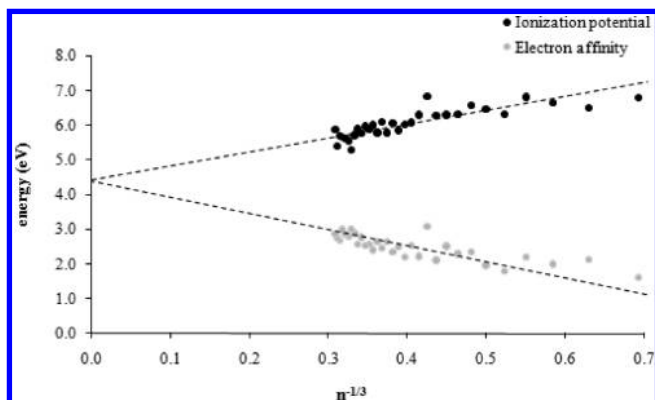


Figure 7. Extrapolation of the ionization potential and electron affinity of aluminum clusters to the bulk limit.

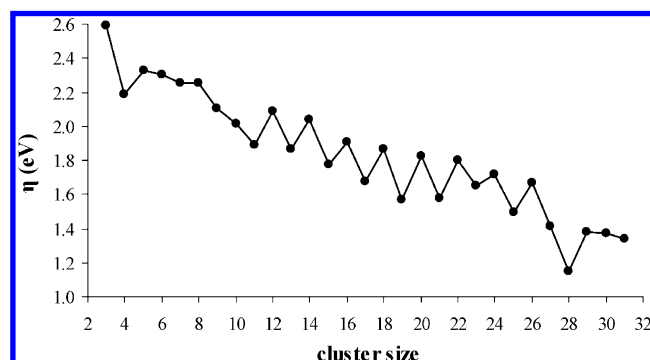


Figure 8. Size dependence of the chemical hardness for lowest energy Al_n clusters.

Chemical Hardness. With the knowledge of IP and EA, it is possible to calculate yet another useful quantity called the global chemical hardness as we discussed below.

In DFT the ground state energy of an atom or a molecule, $E(\rho)$, can be expressed as a functional of its electron density, $\rho(r)$, as follows

$$E(\rho) = F(\rho) + \int \rho(r)v(r) dr \quad (7)$$

where $v(r)$ is the external potential that includes the nuclear potential and $F(\rho)$ is the universal Hohenberg–Kohn functional composed of the electronic kinetic energy and the electron–electron interaction energy.⁸⁵ The second partial derivative of $E(\rho)$ with respect to the number of electrons N at constant external potential defines the global hardness of the system^{86,87}

$$\eta = \frac{1}{2} \left(\frac{\partial^2 E}{\partial N^2} \right)_{v(r)} \quad (8)$$

The global hardness is an indicator of overall stability of the system. By employing the finite difference approximation in DFT framework, η can be estimated as follows⁸⁷

$$\eta \approx \frac{IP - EA}{2} \quad (9)$$

By use of the vertical ionization potentials and electron affinities, the value of hardness for each cluster is calculated via eq 9. In Figure 8, the plot of chemical hardness vs cluster size is shown. Chemical hardness has been established as an

electronic quantity which may be used to characterize the relative stability of molecules which is associated with the concept of principle of maximum hardness (PMH) which states “molecules arrange themselves so as to be as hard as possible.”⁸⁸ According to this principle, the larger chemical hardness indicates the more stable cluster. For example, from Figure 8 it is seen that the maximum magic number, i.e., Al_{20} is harder than neighboring clusters. However, in general, principle of maximum hardness is not obviously observed for aluminum clusters. As shown in Figure 8, for the clusters considered here, the odd–even oscillations pattern was found and PMH cannot easily be applied in this case.

Conclusions

In this work, DFT calculations have been performed on Al_n clusters ($n \leq 31$) to evaluate the variation in polarizability at both static and Nd:YAG laser frequencies and also in other electronic properties with increase in the cluster size. Our results suggest that the PBE/TZVP level of the DFT methods can be applied not only to predict the geometry but also to compute the various properties for aluminum clusters. According to the calculated second-order difference in the total energy and fragmentation energy of the aluminum clusters, the relative stability is discussed. Our theoretical results show that the Al_n clusters with $n = 7, 13$, and 20 are stable than their neighboring clusters. It is found that the relative stability can be related to the static and dynamic polarizabilities. In general, the nature of variations observed in the static and dynamic polarizabilities is almost similar irrespective of the applied frequency. The minimum polarizability principle was used to characterize the stability of aluminum clusters. For chemical hardness, we found the odd–even alternation behavior and thus principle of maximum hardness cannot be used obviously for specifying the relative stability in these clusters. Also, the dipole moments are related to the geometrical and electrical structures. The high symmetry prefers a small dipole moment, while clusters with lower symmetry have higher dipole moment. The effect of temperature and dipole moment on polarizabilities takes into account, and we found that this correction is not significant for clusters under consideration. Moreover, in the framework of the Wood and Perdew model, size dependent on IP and EA were studied, and we found that the IPs and EAs for infinite size would approach to the bulk work function for aluminum clusters.

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