

Understanding the Site Selectivity in Small-Sized Neutral and Charged Al_n ($4 \leq n \leq 7$) Clusters Using Density Functional Theory Based Reactivity Descriptors: A Validation Study on Water Molecule Adsorption

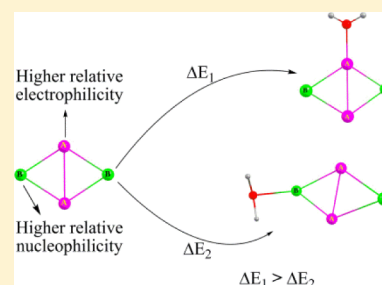
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ABSTRACT: Aluminum clusters are now technologically important due to their high catalytic activity. Our present study on the small-sized aluminum clusters applies density functional theory (DFT)-based reactivity descriptors to identify potential sites for adsorption and eventual chemical reaction. Depending on symmetry, susceptibility of various type of reactive sites within a cluster toward an impending electrophilic and/or nucleophilic attack is predicted using the reactivity descriptors. In addition, the study devises general rules as to how the size, shape, and charge of the cluster influences the number of available sites for an electrophilic and/or nucleophilic attack. The predictions by reactivity descriptors are validated by performing an explicit adsorption of water molecule on Al clusters with four atoms. The adsorption studies demonstrate that the most stable water–cluster complex is obtained when the molecule is adsorbed through an oxygen atom on the site with the highest relative electrophilicity.



1. INTRODUCTION

During the last two decades, aluminum-based clusters have attracted a considerable amount of interest due to their catalytic properties.^{1–5} Their catalytic properties are comparable with those of transition-metal clusters such as Au, Pt, Pd, and so forth.^{6–10} These properties are specifically seen in small-sized Al clusters, namely, between 2 and 50 atoms.^{11–15} In this size range, the catalytic property is seen to be size-specific, and this makes them attractive especially in the area of nanocatalysis.^{16,17} Aluminum nanoclusters^{18–20} and aluminum nitrides²¹ are the most prominent and well-studied systems among the aluminum-based clusters for the catalytic properties. Interestingly, small-sized aluminum nanoclusters are also reported to behave as superatoms,^{22,23} which can potentially lead to a huge impact in the area of nanoscience.^{24–26} Following this understanding, many experimental and theoretical studies have attempted to address or investigate the structure–property (catalytic property) correlation within the aluminum clusters.^{27–32} Khanna et al. have shown that some of the aluminum clusters are reactive toward even less reactive hydrocarbons.^{43,44} Several diatomic molecules such as H_2 ,^{31,34,35} D_2 ,^{36,37} O_2 ,^{14,38} and so forth are seen to adsorb very strongly on aluminum clusters. Oxidation and photochemical reactions^{39–41} on aluminum cluster anions are also being explored experimentally as well as theoretically, and a tendency to form alumina oxides is noted.⁴² One of the significant experimental and theoretical studies is a report by

Johnson et al.³³ that clearly demonstrates that the oxidation behavior of the metal cluster depends upon size, stoichiometry, and ionic charge. However, a more surprising result is that a high-energy bond in the N_2 molecule is cleaved following a chemisorption on aluminum clusters in the size range of 44–100 atoms.⁴⁵ The N_2 adsorption has also been theoretically studied by Romanowski et al.⁴⁶ and Pal and co-workers.⁴⁷ An important conclusion of the above studies is that the reactivity of aluminum clusters critically depends on not only the cluster size but also its shape. The highlight of this finding is that a high-energy conformation can at times be more catalytically active as compared to the ground-state conformation. This increases the complexity in identifying the most catalytically active conformation within a given size. Hence, there is now a necessity to diagnose some leads in identifying the catalytically most promising cluster.

In a recent paper, Khanna et al.⁴⁸ have brought out factors that make a cluster reactive or otherwise. They have in their work analyzed the mechanism behind the dissociative chemisorption of water to produce hydrogen gas in various neutral and charged aluminum clusters.⁴⁸ They examined the

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reactions of $\text{Al}_n^- + \text{H}_2\text{O}$, where $n = 7-18$, and have shown that the complementary active sites⁴⁹ play a predominant role in the chemisorption. In other words, clusters with a pair of adjacent sites, which behave as a Lewis acid and Lewis base, redistribute the charge within a cluster and hence are responsible for the remarkable reactivity exhibited by it. Following their work, Henry et al. also noticed the same on charged and neutral aluminum clusters and determined the comparative reaction barriers and enthalpies for both neutral and singly charged clusters.⁵⁰ A few other groups have also theoretically addressed the $\text{Al}-\text{H}_2\text{O}$ reaction mechanisms.^{51,52}

Thus, if a cluster with complementary active sites is identified, it will help greatly in potential applications of aluminum clusters in nanocatalysis.^{53,54} Hence, in this work, we aim to identify the aluminum clusters with complementary reactive sites. For this purpose, we have chosen clusters with 4–7 atoms in neutral, cationic, and anionic states. One of the approaches to identify complementary active sites is using density functional based reactivity descriptors.⁵⁵ We have discussed in detail the response of various sites in clusters toward an impending electrophilic or nucleophilic attack. For this purpose, the relative nucleophilicity and electrophilicity of the various aluminum clusters are calculated, and an analysis of this is presented in section 4.A. Following the identification of the potential reactive cluster, we carry out an explicit water molecule adsorption on a few of the clusters and validate the results obtained from the reactivity descriptor based studies.

2. THEORETICAL METHODS

The ground-state energy of an atom or a molecule, in DFT, is expressed in terms of electron density $\rho(\vec{r})$.⁵⁶ The response of $\rho(\vec{r})$ to the number of electrons is called the Fukui function $f(\vec{r})$.⁵⁵ Thus, $f(\vec{r})$ is defined as

$$f(\vec{r}) \equiv \left(\frac{\delta\mu}{\delta v(\vec{r})} \right)_N = \left(\frac{\delta\rho(\vec{r})}{\delta N} \right)_{v(\vec{r})} \quad (1)$$

Here, μ and N represent the chemical potential and the total number of electrons of the system respectively. $v(\vec{r})$ is the external potential (i.e., the potential due to the positions of the nuclei plus the applied external field, if any) at position \vec{r} of the chemical species. $f(\vec{r})$ is called the Fukui function (FF). The middle term, that is, $[\delta\mu/\delta v(\vec{r})]_N$ of eq 1 measures the sensitivity of a chemical potential to an external perturbation at a particular point. $[\delta\rho(\vec{r})/\delta N]_{v(\vec{r})}$ shows the change of the electron density for a system with N electrons. The N discontinuity problem of atoms and molecules in eq 1 leads to the introduction of both right- and left-hand side derivatives at a given number of electrons,^{57–59} $N_0 (=N)$. By the finite difference method, using the electron densities of N_0 , $(N_0 + 1)$, and $(N_0 - 1)$ electron systems, FF's for nucleophilic and electrophilic attack can be defined, respectively, as

$$f^+(\vec{r}) \approx \rho_{N_0+1}(\vec{r}) - \rho_{N_0}(\vec{r}) \quad (2)$$

$$f^-(\vec{r}) \approx \rho_{N_0}(\vec{r}) - \rho_{N_0-1}(\vec{r}) \quad (3)$$

and for radical attack is

$$f^0(\vec{r}) \approx \frac{1}{2}(\rho_{N_0+1}(\vec{r}) - \rho_{N_0-1}(\vec{r})) \quad (4)$$

Here, $\rho_{N_0}(\vec{r})$, $\rho_{N_0+1}(\vec{r})$, and $\rho_{N_0-1}(\vec{r})$ are the electron densities of N_0 , $(N_0 + 1)$, and $(N_0 - 1)$ electronic systems at a particular

point \vec{r} . $f^+(\vec{r})$ and $f^-(\vec{r})$ are known as the local electrophilicity and nucleophilicity, respectively.

Parr pointed out, in the frozen core approximation, that $f^+(\vec{r})$ and $f^-(\vec{r})$ can be approximated with the density of the lowest unoccupied molecular orbital (LUMO) and highest occupied molecular orbital (HOMO).

$$f^+(\vec{r}) \approx \rho^{\text{LUMO}}(\vec{r}) \quad (5)$$

measures the reactivity toward a nucleophilic reagent

$$f^-(\vec{r}) \approx \rho^{\text{HOMO}}(\vec{r}) \quad (6)$$

measures the reactivity toward an electrophilic reagent, and

$$f^0(\vec{r}) \approx \frac{1}{2}[\rho^{\text{HOMO}}(\vec{r}) + \rho^{\text{LUMO}}(\vec{r})] \quad (7)$$

measures the reactivity toward a radical reagent. Here, $\rho^{\text{HOMO}}(\vec{r})$ and $\rho^{\text{LUMO}}(\vec{r})$ are the densities of the HOMO and LUMO, respectively.

To describe the site reactivity or site selectivity, Yang and Mortier⁶⁰ proposed the condensed FF's for an atom k . The condensed electrophilicity for an atom k is defined as

$$f_k^+ \approx q_k^{N_0+1} - q_k^{N_0} \quad (8)$$

Similarly, the condensed nucleophilicity for an atom k is defined as

$$f_k^- \approx q_k^{N_0} - q_k^{N_0-1} \quad (9)$$

The condensed reactivity descriptor of the site appropriate for the radical attack is f_k^0 and can be defined as

$$f_k^0 \approx \frac{1}{2}(q_k^{N_0+1} - q_k^{N_0-1}) \quad (10)$$

where $q_k^{N_0}$, $q_k^{N_0+1}$, and $q_k^{N_0-1}$ are the electronic populations on the atom k for the N_0 , $(N_0 + 1)$, and $(N_0 - 1)$ electron systems, respectively.

Roy et al. proposed a new set of relative indices that are more appropriate for intramolecular reactivity.^{61,65} The condensed relative electrophilicity of an atom k can be defined as

$$f_k^{\text{el}} \approx \frac{f_k^+}{f_k^-} \quad (11)$$

Similarly, the relative nucleophilicity is defined as

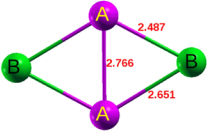
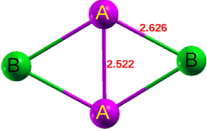
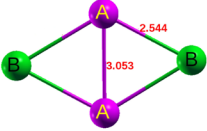
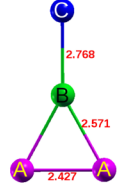
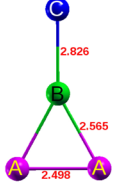
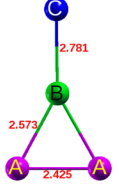
$$f_k^{\text{nu}} \approx \frac{f_k^-}{f_k^+} \quad (12)$$

f_k^{el} and f_k^{nu} are found to be very effective in comparing the site reactivity across the molecule. A site with $f_k^{\text{el}} > f_k^{\text{nu}}$ is favorable for a nucleophilic attack, while a site with $f_k^{\text{nu}} > f_k^{\text{el}}$ is clearly a site favorable toward an electrophilic attack. A site with f_k^{el} is nearly equal to f_k^{nu} and is likely to both give and take electrons with equal ease, making it an amphiphilic site, likely to participate in both oxidation and reduction chemical reactions.

3. COMPUTATIONAL DETAILS

Various conformations of Al_4 , Al_5 , Al_6 , and Al_7 are generated and optimized in mono positive, neutral, and mono negative charge states. All of the structures are optimized at the DFT^{62,63} level of theory using the Gaussian 09 software package⁶⁴ with the aug-cc-PVTZ^{66,67} basis set and B3PW91 functional.^{68–71} This functional has proved to be suitable to describe such kinds

Table 1. Structural, Electronic, and Reactivity Parameters of Al₄ Conformations^a

State	Structure	Total Binding energy (eV)	Sites	Hirshfeld	f_k^{el}	f_k^{nu}
Neutral (I)		5.51	A	0.009	1.300	0.770
			B	-0.009	0.800	1.254
Positive (I)		23.63	A	0.225	1.027	0.9734
			B	0.275	0.966	1.035
Negative (I)		8.09	A	-0.239	2.536	0.394
			B	-0.260	1.416	0.706
Neutral (II)		5.21	A	-0.015	1.272	0.786
			B	-0.100	0.706	1.418
			C	0.131	0.917	1.090
Positive (II)		23.47	A	0.240	1.023	0.977
			B	0.0317	0.945	1.058
			C	0.488	0.998	1.002
Negative (II)		7.27	A	-0.316	0.943	1.061
			B	-0.202	1.774	0.564
			C	-0.165	5.993	0.167

^aThe values in blue, red, and black correspond to electrophilic, nucleophilic, and amphiphilic attack sites, respectively. The values given next to the conformations in column II of the table correspond to the interatomic distances (in Å) between various unique sites.

of systems.^{72–74} Harmonic vibrational frequencies and binding energies are computed for all of the conformations at the end of optimization. Before calculating the relative reactivity descriptor, the total binding energy of each cluster is calculated as

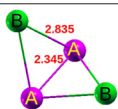
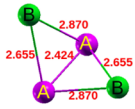

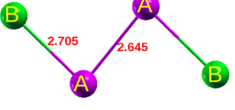
$$E_{B.E.} = nE_{Al} - E_{Al_n} \quad (13)$$

Here, nE_{Al} is the total energy of free atoms, and E_{Al_n} is the energy of the cluster.

Only conformations with all positive frequencies are taken for further study of site selectivity using reactivity descriptors.

To obtain the reactivity descriptor at a given site, single-point energy calculation is done at the DFT/B3PW91/aug-cc-PVTZ level on the charged counterparts by maintaining them at the optimized geometry of the neutral conformation. The finite difference approximation is considered to calculate FF's, as discussed in section 2. The condensed FF's are calculated with Hirshfeld population analysis.⁷⁵ The relative reactivity descriptors are calculated from the FF's to evaluate the electrophilicity and nucleophilicity of various sites. Following the reactivity descriptor calculations, a water molecule is

Table 2. Structural, Electronic, and Reactivity Parameters of Al_4 Conformations^a

State	Structure	Total Binding Energy (eV)	Sites	Hirshfeld	f_k^{el}	f_k^{nu}
Neutral (III)		5.31	A	-0.006	1.396	0.716
			B	0.006	0.763	1.310
Negative (III)		8.09	A	-0.239	2.542	0.393
			B	-0.257	1.415	0.707
Positive (IV)		23.28	A	0.138	0.762	1.312
			B	0.363	1.387	0.721
Neutral (V)		4.17	A	-0.108	1.001	0.999
			B	0.108	1.098	0.911

^aThe values in blue, red, and black correspond to electrophilic, nucleophilic, and amphiphilic attack sites, respectively. The values given next to the conformations in column II of the table correspond to the interatomic distances (in Å) between various unique sites.

adsorbed at various sites of a few Al_4 clusters. The interaction energy of the cluster–water complex is calculated as

$$E_{AB}^{int} = E_A + E_B - E_{AB} \quad (14)$$

where E_A and E_B are the energies of the monomers and E_{AB} is the energy of the complex.

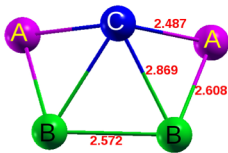
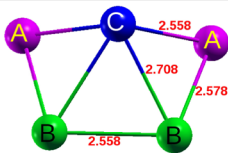
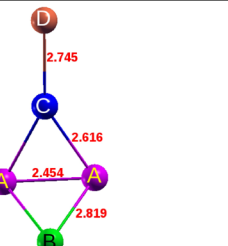
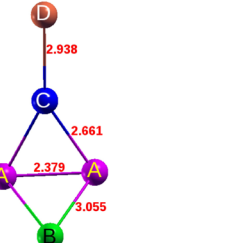
4. RESULTS AND DISCUSSION

A. Site Selectivity of Aluminum Clusters Using Relative Reactivity Descriptors. 1. Al_4 . The structure, electronic properties, and the reactivity parameters for all of the Al_4 clusters are given in Tables 1 and 2. We begin our discussion with conformation I, which is stable in all three states, namely, the neutral, positive, and negative. This conformation has the highest binding energy for an Al_4 cluster in neutral, cationic, and anionic states. All three conformations have two sites, namely, A and B, which have distinct chemical environments and are situated alternatively. Sites A and B are bonded to each other at 2.49 and 2.65 Å in the neutral state. This structure does not show much charge redistribution among both sites. Site A has higher relative electrophilicity (1.30), while site B has higher relative nucleophilicity (1.25) value. Hence, sites A behaves as the site most probable for attack by a nucleophile, whereas sites B is most likely to be attacked by an electrophile. In positive and negative states, interatomic bond distances are uniform, as shown in Table 1. In

both of these conformations, there is a small amount of charge localization on site B with respect to site A. In the positively charged conformation, site A is electrophilic, and site B is nucleophilic. In the negatively charged conformation, both sites act as an electrophilic center, as seen from the reactivity descriptor values, which are 2.54 and 1.41 for sites A and B, respectively.

The next conformation (II) is a pendent, which is also stable in all three charged states. All three conformations have three chemically distinct sites, namely, A, B, and C. Site B is bonded to A and C, and the two equivalent atoms of site A are connected to each other. Compared to the neutral and negative conformations, the B–C and A–A bonds of the positively charged conformation are slightly elongated, while the trend is reversed for A and B interatomic distances. Site C is the most positively charged atom in the neutral and positively charged conformations, whereas in the negatively charged conformation, charge-enriched sites are A atoms (−0.316). Sites A are electrophilic centers, and site B is a nucleophilic center in the neutral and positively charged state. Site C is a nucleophilic center in the neutral cluster, while in the positively charged one, the relative electrophilicity and relative nucleophilicity are nearly equal on this site. Such a site has been referred to as an amphiphilic site in one of the earlier papers.⁷⁶ Sites B and C are highly electrophilic centers in the negatively charge cluster.

Table 3. Structural, Electronic, and Reactivity Parameters of Al_5 Conformations^a

State	Structure	Total Binding Energy (eV)	Sites	Hirshfeld	f_k^{el}	f_k^{nu}
Neutral (I)		8.24	A	0.016	1.043	0.959
			B	0.007	1.070	0.934
			C	-0.045	0.954	1.049
Negative (I)		10.60	A	-0.242	1.543	0.648
			B	-0.161	2.380	0.420
			C	-0.192	0.655	1.526
Neutral (II)		7.13	A	-0.041	0.808	1.238
			B	0.026	1.167	0.859
			C	-0.059	0.936	1.069
			D	0.122	1.424	0.702
Positive (II)		31.88	A	0.147	0.995	1.006
			B	0.260	0.704	1.420
			C	0.078	1.389	0.720
			D	0.368	1.127	0.887

^aThe values in blue, red, and black correspond to electrophilic, nucleophilic, and amphiphilic attack sites, respectively. The values given next to the conformations in column II of the table correspond to the interatomic distances (in Å) between various unique sites.

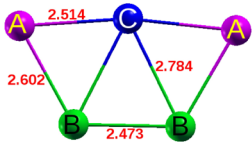
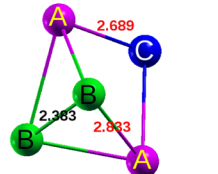
Conformation III is tetrahedral in shape and is stable only in the neutral and negatively charged states. In the case of the positively charged conformation, one of the vibrational modes is imaginary. Negatively charged conformation III is as equally stable as the negatively charged conformation I. The binding energy of this conformation is 8.09 eV. Both of the states of conformation III have two distinct sites, namely, A and B. It is seen from Table 2 that the neutral conformation does not have much charge redistribution among both sites. However, in the case of the negatively charged conformation, there is a small amount of charge localization on site B with respect to site A. Analysis of the relative reactivity descriptors reveals that site A is electrophilic and site B is nucleophilic in the neutral conformation. On the other hand, in the negatively charged conformation, both sites behave as an electrophilic center.

Two other conformations that we have studied here are stable only in one of the states, with the other two states having imaginary vibrational frequencies. Conformation IV is linear and is stable in the positively charged state. It has two distinct reactive sites, namely, A and B. There is a charge redistribution

in conformation IV. Site B has higher charge localization as compared to site A. Site B is an electrophilic center (with a relative electrophilicity of 1.38), while site A is nucleophilic in nature (the relative nucleophilicity is 1.31). Conformation V has a zigzag form and is stable in the neutral state. It also has two chemically distinct reactive sites, namely, A and B. These two sites are situated alternatively. Compared to A–A, the A–B bond distance is higher by 0.06 Å. The Hirshfeld charge shows that A is negatively charged (−0.108) while B is positively charged (0.108). Site A is amphiphilic in nature, and site B is electrophilic, as seen from the values of the relative reactivity descriptors.

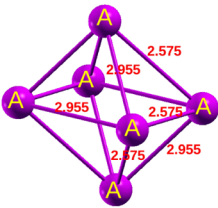
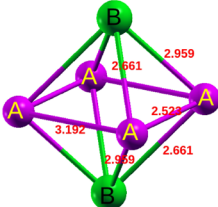
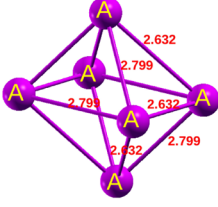
2. Al_5 . The structure, electronic properties, and reactivity parameters for all of the studied Al_5 clusters are given in Tables 3 and 4. We have optimized several conformations for the Al_5 cluster. However, only a few of them had all positive frequencies. We here discuss the reactivity patterns in the clusters with all positive vibrational modes. Conformation I is stable in two state, namely, the neutral and negative. Both conformations have three chemically distinct sites, namely, A,

Table 4. Structural, Electronic, and Reactivity Parameters of Al_3 Conformations^a

State	Structure	Total Binding Energy (eV)	Sites	Hirshfeld	f_k^{el}	f_k^{nu}
Neutral (III)		8.28	A	0.036	1.088	0.919
			B	0.000	0.980	1.020
			C	-0.073	0.850	1.177
Positive (IV)		32.45	A	0.155	1.049	0.954
			B	0.222	1.046	0.956
			C	0.246	0.807	1.243

^aThe values in blue, red, and black correspond to electrophilic, nucleophilic, and amphiphilic attack sites, respectively. The values given next to the conformations in column II of the table correspond to the interatomic distances (in Å) between various unique sites.

Table 5. Structural, Electronic, and Reactivity Parameters of Al_6 Conformations^a

State	Structure	Total Binding Energy (eV)	Sites	Hirshfeld	f_k^{el}	f_k^{nu}
Neutral (I)		11.13	A	0.000	1.019	0.982
Positive (I)		41.24	A	0.179	0.994	1.006
			B	0.141	1.023	0.977
Negative (I)		13.92	A	-0.167	1.300	0.769

^aThe values in blue, red, and black correspond to electrophilic, nucleophilic, and amphiphilic attack sites, respectively. The values given next to the conformations in column II of the table correspond to the interatomic distances (in Å) between various unique sites.

B, and C. In the neutral state, sites A and B are bonded to each other with an interatomic distance of 2.60 Å. Sites B and C are bonded through a distance of 2.87 Å. Sites C and A are 2.49 Å

apart from each other. Two equivalent atoms (B) are connected by a bond distance of 2.57 Å. In the negative state, the distance between sites A and C is larger by 0.07 Å,

Table 6. Structural, Electronic, and Reactivity Parameters of Al_6 Conformations^a

State	Structure	Total Binding Energy (eV)	Sites	Hirshfeld	f_k^{el}	f_k^{nu}
Neutral (II)		10.39	A	-0.008	0.973	1.028
			B	0.005	1.035	0.966
			C	0.002	1.226	0.816
			D	0.008	0.648	1.544
			E	0.0136	1.676	0.597
			F	-0.020	1.181	0.847
Positive (II)		41.02	A	0.189	1.144	0.874
			B	0.122	1.050	0.952
			C	0.190	0.908	1.101
			D	0.188	1.137	0.887
Negative (II)		13.04	A	-0.186	1.634	0.612
			B	-0.125	1.482	0.675
			C	-0.133	1.051	0.951
			D	-0.243	1.838	0.544

^aThe values in blue, red, and black correspond to electrophilic, nucleophilic, and amphiphilic attack sites, respectively. The values given next to the conformations in column II of the table correspond to the interatomic distances (in Å) between various unique sites.

whereas other interatomic distances decrease slightly, as shown in the figure (in the second column of Table 3). The neutral conformation does not show much charge redistribution among all of the sites. However, in the case of the negatively charged conformation, the charge distribution is unequal. There is a small amount of charge localization on site A with respect to the other two. In the neutral conformation, all of the sites have nearly equal relative reactivity descriptors. Thus, all sites are amphiphilic in nature. On the other hand, in the negatively charged conformation, site B has a higher relative electrophilicity (2.38), while site C has a higher relative nucleophilicity (1.52) value. Thus, site B behaves as an electrophilic center and site C as a nucleophilic center. Site A is a weaker electrophilic center as compared to site B.

Conformation II is stable in the neutral and positively charged states. In the negatively charged conformation, one of the vibrational modes is imaginary. This conformation has a higher number of chemically distinct reactive sites. Both states have four distinct reactive sites, namely, A, B, C, and D. Site B is connected to two equivalent atoms, namely, A, which are in turn connected to site C. Site C is connected to site D. Compared to the neutral conformation, the C–D and A–B interatomic distances of the positively charged conformation are larger by 0.19 and 0.23 Å, respectively. The reverse is observed in the other bonds. It has been shown from Table 2 that there is a charge localization in site B in both states. However, greater charge localization is seen for the positively charged conformation. Relative reactivity analysis indicates that sites D and B are electrophilic in the order $D > B$. Sites A and C are nucleophilic in the order of $A > C$. On the other hand, in the positively charge conformation, sites C and D have higher relative electrophilicity (1.38 and 1.12, respectively) values. Site

A is amphiphilic in nature, while site B is nucleophilic, as predicted by the relative reactivity descriptors.

The other two conformations are stable in only one of the charged states. Other states have imaginary vibrational frequencies. Binding energy analysis shows that among all Al_3 conformations, these two clusters are most stable, with binding energy values of 8.28 and 32.45 eV for conformations III and IV, respectively. However, we present their reactivity descriptors for the sake of completeness. Conformation III is stable in the neutral state. It has three unique sites, namely, A, B, and C. A–B, A–C, B–C, and B–B interatomic distances are 2.60, 2.51, 2.78, and 2.47 Å, respectively. There is a very little charge distribution in conformation III. Site A is electrophilic, and site B is amphiphilic in nature according to the relative reactivity descriptor analysis. Site C acts as a nucleophilic site. Conformation IV is stable in the positively charged state. It also has three distinct reactive sites, namely, A, B, and C. The interatomic distance between sites A and B is comparatively higher than that in other bonds. Sites A and B are electrophilic in nature, whereas site C behaves as a nucleophilic site due to its higher relative nucleophilicity value.

3. Al_6 . The structure, electronic properties, and reactivity parameters for all Al_6 clusters are given in the Tables 5 and 6. We have chosen two conformations for this cluster size. Conformation I is octahedral and is stable in three states, namely, neutral, positive, and negative states. All of the states of this conformation have higher binding energies as compared to the other conformations. In neutral and negative states, all of the atoms are equivalent, that is, they have one chemically distinct site, namely, A. In both states, the bond distance is identical. Interestingly, in both of these conformations, charge is uniformly distributed among all six atoms. The reactivity descriptors indicate that in the neutral conformations, all of the

Table 7. Structural, Electronic, and Reactivity Parameters of Al_7 Conformations^a

State	Structure	Total Binding Energy (eV)	Sites	Hirshfeld	f_k^{el}	f_k^{nu}
Neutral (I)		41.51	A	-0.007	0.876	1.142
			B	0.006	1.010	0.990
			C	0.006	1.013	0.987
			D	0.0038	1.258	0.795
			E	-0.007	0.877	1.140
Negative (I)		16.92	A	-0.141	3.250	0.308
			B	-0.115	2.116	0.4727
			C	-0.140	0.996	1.004
			D	-0.231	1.042	0.960
			E	-0.115	1.081	0.925

^aThe values in blue, red, and black correspond to electrophilic, nucleophilic, and amphiphilic attack sites, respectively. The values given next to the conformations in column II of the table correspond to the interatomic distances (in Å) between various unique sites.

sites are amphiphilic in nature. On the other hand, in the negatively charged conformation, all of the sites are electrophilic in nature. In the positively charged conformation, the cluster modifies marginally to result in two chemically distinct sites, namely, A and B. In this conformation, the alternate interatomic distances between sites A are 3.19 and 2.52 Å, respectively, while the alternate bond distances between sites A and B are 2.95 and 2.66 Å, respectively. This leads to a charge redistribution within the cluster, as seen from Table 5. Site A of the positively charged conformation is amphiphilic, and site B is weakly electrophilic.

Conformation II is also stable in all three states. The neutral conformation is unsymmetrical, leading to six chemically distinct sites, namely, A, B, C, D, E, and F. A–B and D–E interatomic distances are equal (2.52 Å). Positive and negatively charged conformations have four distinct sites, namely, A, B, C, and D. The A–A and A–B interatomic distances are larger (0.2 Å) in the positively charged conformation than those in the negative one. On the other hand, other bond distances are lower by 0.18 Å. The neutral and positive conformations do not exhibit much charge redistribution, unlike the negatively charged conformation, which has 0.24 electrons localized (−0.24) on site D. Analysis of relative reactivity descriptors reveals that in the unsymmetrical neutral conformation, electrophilic sites are B, C, E, and F in the order of $E > C > F > B$. Site D behaves as a nucleophilic center (relative nucleophilicity, 1.54). Site A is very weakly nucleophilic. However, in the case of the positively charged conformation, sites A and D are strong electrophilic centers followed by site B. Site C is the only nucleophilic site. In the negatively charged conformation, all sites are electrophilic in nature.

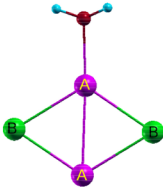
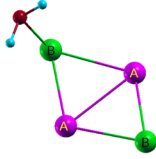
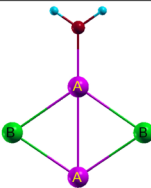
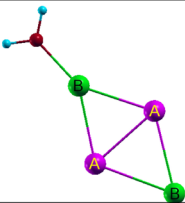
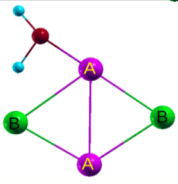
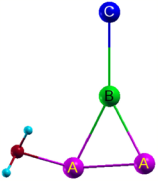
4. Al_7 . Table 7 describes the structure, electronic properties, and reactivity parameters for the studied Al_7 cluster. Conformation I is stable in the neutral and negatively charged states. Both structures have five chemically distinct sites, namely, A, B, C, D, and E. In the negatively charged conformation, most of the interatomic distances are higher as

compared to the those for neutral one, except for A–E and B–C bonds. The charge in the neutral conformation is almost equally distributed on all seven atoms. On the other hand, more charge is localized on site D (−0.23) in the negative conformation. According to the above discussion, sites A and C are nucleophilic, and site D is electrophilic in the neutral state. Sites B and C are amphiphilic centers. In the negative conformation, all sites are electrophilic, with the exception of site C, which is amphiphilic. Binding energies of neutral and negatively charged clusters are 14.51 and 16.92 eV, respectively.

It is important to note here that the reactivity trends within the above-studied atomic clusters (relative electrophilicity or nucleophilicity) are in some cases different from the trend implied by the atomic charges. Relative reactivity descriptors for a given site (f_k^{el} and f_k^{nu}) are a ratio of two individual descriptors, namely, the nucleophilic FF ($f^-(\vec{r})$) and electrophilic FF ($f^+(\vec{r})$) of that particular site. The individual descriptors are, in turn, calculated from the difference of the electronic population between charged states for a particular site. Hence, as compared to the absolute atomic charge, it is a more reliable reactivity descriptor of a chemical environment. In other words, a negatively charged site may be more prone to accept electrons and behave as an electrophilic site, as indicated by the higher relative electrophilicity values. Similarly, despite being positively charged, a particular site can be more prone to electrophilic attack, as indicated by its higher relative nucleophilicity.

B. Understanding the Site Selectivity in Aluminum Clusters Using Explicit Water Molecule Adsorption: Case Study on Al_4 . A case study of water molecule adsorption has been carried out on Al_4 cyclic and pendent conformations. It is expected that a site with a higher value of the relative electrophilicity will form a stronger bond with the oxygen atom of the water molecule (or alternatively, the site with the higher relative nucleophilicity will form a stronger bond with one of the hydrogen atoms of the water molecule). Neutral and positive conformations of cyclic Al_4 have two chemically distinct sites each, namely, A and B. Site A (Table 1) has a higher relative electrophilicity in both cases. As seen from the

Table 8. Interaction Energy of Water Adsorption on Al_4 Conformations

State	Structure	Water adsorption site	Interaction energy (eV)
Neutral		A	0.75
Neutral		B	0.27
Positive		A	1.72
Positive		B	1.56
Negative*		A	1.81
Neutral		A	0.29

*This conformation undergo structural fluxionality. Optimize geometry is a square structure.

Table 8, the neutral cyclic conformation–water molecule complex has an interaction energy of 0.75 eV for site A as compared to the 0.27 eV for site B. A similar observation is seen in the case of the positive cyclic Al_4 conformation–water complexes. Interestingly, in the case of both neutral and positively charged cyclic Al_4 conformations, we have alternating electrophilic and nucleophilic sites. In the case of the negatively charged cyclic Al_4 conformation, the water molecule adsorbs strongly on both sites. However, upon adsorption, the structure modifies itself into a square conformation. The water molecule dissociates into OH^- and H^+ . Thus, while the high electrophilicity on both sites favors the adsorption of H_2O via the O atom, absence of adjacent nucleophilic sites makes the conformation unstable after adsorption. On the other hand, in the case of the neutral Al_4 pendent conformation, electrophilic site A adsorbs a water molecule with an interaction energy of 0.29 eV. This is much less than the corresponding

value for the cyclic Al_4 conformation (site A), a cluster with alternating nucleophilic and electrophilic sites. Similar consistent observations are also noted for other Al clusters, whose results are not reported here.

5. CONCLUSION

In the above work, we have attempted to understand the site-selective reactivity patterns in Al clusters with 4–7 atoms. Our work shows that the reactivity changes as a function of both the size and charge of the clusters. Reactivity descriptors can effectively be used as screening tools to isolate clusters with higher reactivity as well as clusters with alternating Lewis acid–base sites. Among the neutral, positive, and negatively charged clusters, negatively charged Al clusters are seen to have the strongest electrophilic centers. Positively charged and neutral clusters have alternating electrophilic and nucleophilic centers.

The water molecule is expected to adsorb strongly on all of the electrophilic centers via the oxygen atom, and this is validated in our water adsorption case studies. While the water molecule adsorbs strongly on the electrophilic centers of the positive and neutral clusters, the adsorption is followed by water molecule dissociation in the negatively charged clusters. However, due to the absence of adjacent nucleophilic centers in the negatively charged clusters, the cluster is seen to undergo structural fluxionality. This is consistent with observations in earlier reports that negatively charged Al clusters are more catalytically active clusters for the case of water splitting.

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Notes

The authors declare no competing financial interest.

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