Computational screening of carbon monoxide (CO) adsorption over neutral and charged Al7 clusters

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ABSTRACT

A density functional theory study on the structures and chemical bonding of charged (AlF and AlF) and neutral Al7 clusters is presented. A distorted octahedral structure with an aluminum atom decorating one of the aluminum faces of the octahedron is predicted for these clusters. The AdNDP analysis reveals double (σ- and π-) aromatic and antiaromatic characteristics of AlF and AlF clusters, respectively. The UV-Vis spectra of these clusters are also investigated using TD-DFT method. The molecular adsorption of carbon monoxide on the mentioned clusters is also explored. It is found that, the binding of CO through its carbon atom on considered clusters is a physical adsorption and AlF cluster shows the most tendency for the CO adsorption. The NBO analysis and density of states spectra confirm the weak interaction between carbon atom of CO and the aluminum atom of these clusters.

1. Introduction

Clusters are defined as an assembly of molecules or atoms that are weakly bound together and display properties, intermediate between those of isolated gas-phase molecules and bulk solid. Therefore, they allow one to study how physical and chemical properties change in transition from an isolated molecule to a condensed phase. Interest in small metallic clusters has grown dramatically in the past few decades [1, 2, 3, 4, 5, 6, 7, 8] and since aluminum is a common and cheap metal, its clusters are probably the most studied systems among the other metallic clusters [9, 10, 11, 12, 13, 14]. Atomic clusters that exhibit some properties of elemental atoms are called superatoms. Certain aluminum clusters show superatom properties. For example, Al7 is known as superatom and its potential to construct excellent non-linear optical materials has been investigated [14]. Anionic Al clusters (Aln− with n = 1, 2, 3, ...) also have superatomic properties [15, 16]. The properties of atomic clusters depend on cluster size. Different studies show that the binding energies of Al clusters increase monotonically with size, but some of them, such as Al12 and Al13 are more stable than their neighbors [10, 12]. The enhanced stability of these clusters can be accounted for by the electronic shell approach of jellium model [17, 18]; in which, clusters with 2, 8, 20, 40, ... electrons that have close electronic shell show more stability and are known as magic clusters [19]. Therefore, Al7 and Al13 clusters with 20 and 40 valence electrons, respectively, according to jellium model are two examples of magic clusters [10, 12].

During the past few decades, density functional theory (DFT) has been frequently used to study a wide variety of properties of metal clusters [12, 20, 21, 22, 23, 24, 25, 26, 27, 28, 29, 30]. Interaction of clusters with different atoms or molecules is the interesting topic in cluster science, which investigates the stability and catalytic properties of clusters. It is shown that, these interactions are influenced by the size of cluster. For instance, Upton and coworkers [31] showed that smallest aluminum cluster could adsorb H2 molecule is Al6 and for clusters containing more than 6 atoms, the reactivity decrease rapidly with increasing the cluster size. The interaction of hydrogen molecule with neutral and charged AlnX clusters (X = Mg, Al, Si) was investigated and obtained results indicate that this adsorption is dissociative chemisorption [32]. Mohamed Maatallah and coworkers [33] studied bare and hydrogenated Aln (n = 5–7) clusters to evaluate the ability of storing molecular hydrogen. Dissociative adsorption of deuterium molecule (D2) on the neutral and anionic Aln ( n = 1–9) clusters has also been investigated [34].

Since the presence of toxic gases in environment affects human health, production of a sensor or a device able to detect or adsorb pollutant gases and remove them from the air is important. The adsorption of carbon monoxide on metal surfaces is probably one of the most studied systems in surface science [35, 36, 37, 38, 39]. The interaction of the lone pair ligands, such as CO, with one metal atom leads, very often, to a repulsive potential curve [40] which is largely due to the repulsion between the metal valence electron(s) and the ligand lone pair.

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If, however, the cluster contains four or five metal atoms chosen to represent the first two layers of a single crystal surface, the interaction energy is in reasonable agreement with the chemisorption energy of the ligand on a metal surface [41]. The structure and temperature of surface can influence the adsorption nature. Adsorption of CO on some metal clusters such as Na, Ca and Ti leads to dissociation of carbon monoxide to carbon and oxygen atoms and forming the C-Metal and O-Metal bonds. On the other hand, for some d-block metals such as Cu and Ag the carbon monoxide remains in molecular form after adsorption. Since the formed Metal-CO bond is weak, it is possible that Metal-CO bond is broken and CO desorbed from the surface by increasing the temperature of surface.

Although the chemistry of superatom draws a great deal of attention, research on the potential applications of superatom compounds is rare. In this article, the adsorption of CO molecule on $\text{Al}_7$, $\text{Al}_7^+$ and $\text{Al}_7^2$ clusters are investigated. Also, Density of States (DOS), Natural Bond Orbital (NBO) and Adaptive Natural Density Partitioning (AdNDP) analysis as well as UV-Vis spectra of these clusters are investigated. We hope this study could extend the field of superatom chemistry.

### 2. Calculation

All calculations are performed without symmetry constraints using both B3LYP and CAM-B3LYP methods with 6-311G* basis set, as implemented in Gaussian 09 suite of program [42]. These levels of theory have been used to investigate of different properties of nanocages [43, 44, 45] and various aluminum systems [46, 47, 48] in several studies. Therefore, it seems these methods are reliable for study of the considered systems.

The adsorption energy ($E_{\text{ads}}$) due to the interaction of CO molecule with the mentioned clusters ($\text{Al}_7$, $\text{Al}_7^+$ and $\text{Al}_7^2$) is calculated as:

$$E_{\text{ads}} = E_{\text{cluster-CO}} - (E_{\text{cluster}} + E_{\text{CO}})$$  \hspace{1cm} (1)

where $E_{\text{cluster-CO}}$ denotes the total energy of CO-adsorbed system and $E_{\text{cluster}}$ and $E_{\text{CO}}$ are the total energies of free cluster and CO molecule, respectively. The negative adsorption energy indicates an exoergic pro-

### Table 1

| Cluster | Multiplicity | $E$     | $E_H$   | $E_L$   | HL gap |
|---------|--------------|---------|---------|---------|--------|
| $\text{Al}_7$ | 1          | -1697.2218 | -0.0358 | 0.0228  | 0.0586 |
|         | 3          | -1697.2171 | -0.0261 | 0.0212  | 0.0473 |
| $\text{Al}_7^+$ | 1         | -1696.9389 | -0.3443 | 0.2463  | 0.0980 |
|         | 3          | -1692.7222 | -0.3797 | -0.2088 | 0.1799 |
| $\text{Al}_7^2$ | 2         | -1697.1482 | -0.1695 | -0.1077 | 0.0618 |
|         | 4          | -1697.1173 | -0.1701 | -0.1121 | 0.0580 |

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Fig. 1. Optimized structures as well as calculated bond lengths (in Å) of a) $\text{Al}_7$, b) $\text{Al}_7^+$ and c) $\text{Al}_7^2$ clusters at B3LYP/6-311G* and CAM-B3LYP/6-311G* [values in bracket].

Fig. 2. UV-Visible spectra of a) $\text{Al}_7$, b) $\text{Al}_7^+$, c) $\text{Al}_7^2$ clusters.
Ebin to separate these contributions from each other:

\[ E_{\text{bin}} = E_{\text{cluster}} - (E_{\text{co}} + E_{\text{co}}) \]

where \( E_{\text{bin}} \) and \( E_{\text{co}} \) are the total single point energies of cluster and CO in their relaxed complex geometries. All energies are corrected through basis set superposition error (BSSE) using the counterpoise method [49].

The charge transfer is also investigated using both Natural Bond Orbital (NBO) scheme and Electron Density Difference (EDD) maps. EDD is expressed as:

\[ \nabla \rho = \rho_{\text{cluster}} - (\rho_{\text{CO}} + \rho_{\text{cluster}}) \]

where \( \rho_{\text{cluster}} \) is the electron density of the total CO + Al7 complex, and \( \rho_{\text{CO}} \) as well as \( \rho_{\text{cluster}} \) are the unperturbed electron densities of the carbon monoxide and aluminum cluster, respectively.

The changes in electronic structures of aluminum clusters are

| Excitation | \( E_\text{in} \) (eV) | \( \lambda \) (nm) | \( f \) | Maximum Transition |
|------------|-----------------|----------------|-----|------------------|
| S0 \( \rightarrow \) S1 | 2.1163 | 585.85 | 0.029 | H \( \rightarrow \) L(106.9%) |
| S0 \( \rightarrow \) S2 | 2.1163 | 585.85 | 0.029 | H \( \rightarrow \) L(106.9%) |
| S0 \( \rightarrow \) S4 | 2.1768 | 569.58 | 0.013 | H \( \rightarrow \) L(83.6%) |
| S0 \( \rightarrow \) S7 | 2.3112 | 536.45 | 0.026 | H \( \rightarrow \) L(275.6%) |
| S0 \( \rightarrow \) S13 | 2.7669 | 448.09 | 0.010 | H \( \rightarrow \) L(78.3%) |
| S0 \( \rightarrow \) S14 | 2.7669 | 448.09 | 0.010 | H \( \rightarrow \) L(78.3%) |
| S0 \( \rightarrow \) S22 | 3.3143 | 374.09 | 0.020 | H \( \rightarrow \) L(81.8%) |
| S0 \( \rightarrow \) S29 | 3.6990 | 335.18 | 0.022 | H \( \rightarrow \) L(59.6%) |
| S0 \( \rightarrow \) S30 | 3.6990 | 335.18 | 0.022 | H \( \rightarrow \) L(59.6%) |

Fig. 3. Frontier molecular orbitals involved in the crucial excitations for Al7 Cluster.

| Excitation | \( E_\text{in} \) (eV) | \( \lambda \) (nm) | \( f \) | Maximum Transition |
|------------|-----------------|----------------|-----|------------------|
| D0 \( \rightarrow \) D16 | 1.8891 | 656.32 | 0.022 | H(\( \beta \)) \( \rightarrow \) L(2(β) (47.8%) |
| D0 \( \rightarrow \) D17 | 1.9435 | 637.94 | 0.016 | H(\( \beta \)) \( \rightarrow \) L(2(β) (45.3%) |

Table 2

Table 3

Table 4

Fig. 4. Frontier molecular orbitals involved in the crucial excitations for Al7 Cluster.
evaluated through Frontier Molecular Orbitals (FMO); i.e. HOMO-LUMO (H-L) gap. The AdNDP analysis, density of states (DOS) and Partial Density of States (PDOS) are also evaluated using Multiwfn 3.3.9 software [50].
Time-dependent density functional theory (TD-DFT) is used to predict

**Fig. 9.** Optimized structures of Al₇-CO complexes in which oxygen atom of CO approaches to Al₇ from a') top, b') below, c') below-beside and d') top-beside.

**Fig. 10.** Optimized structures of Al₇⁺-CO complexes in which oxygen atom of CO approaches to Al₇⁺ from a') below, b') beside and c') top.

**Fig. 11.** Optimized structures of Al₇-CO complexes in which oxygen atom of CO approaches to Al₇ from a') below-beside, b') below, c') top and d') top-beside.

### Table 5

The obtained basis set superposition errors (δ<sub>BSSE</sub>), deformation (E<sub>def</sub>), corrected binding (E<sub>corr</sub><sup>bin</sup>), and adsorption energies (E<sub>corr</sub><sup>ads</sup>) for the binding of CO through its oxygen atom to Al₇--(all in eV) using B3LYP/6-311G* and Cam-B3LYP/6-311G* [values in bracket] methods.

| Configuration | δ<sub>BSSE</sub> | E<sub>def</sub> | E<sub>corr</sub><sup>bin</sup> | E<sub>corr</sub><sup>ads</sup> |
|---------------|-----------------|----------------|---------------------------|-----------------|
| a'            | 0.0222          | 0.0011         | -0.0167                   | -0.0156         |
|               | (0.0331)        | (0.0004)       | [-0.0062]                 | [-0.0058]       |
| b'            | 0.0249          | 0.0004         | 0.0008                    | 0.0012          |
|               | (0.0287)        | (0.0003)       | [0.0001]                  | [0.0004]        |
| c'            | 0.0248          | 0.0003         | -0.0003                   | 0.0000          |
|               | (0.0331)        | (0.0001)       | [-0.0082]                 | [-0.0081]       |
| d'            | 0.0222          | 0.0008         | -0.0174                   | -0.0166         |
|               | (0.0331)        | (0.0002)       | [-0.0060]                 | [-0.0058]       |

### Table 6

The obtained basis set superposition errors (δ<sub>BSSE</sub>), deformation (E<sub>def</sub>), corrected binding (E<sub>corr</sub><sup>bin</sup>), and adsorption energies (E<sub>corr</sub><sup>ads</sup>) for the binding of CO through its oxygen atom to Al₇⁺--(all in eV) using B3LYP/6-311G* and Cam-B3LYP/6-311G* [values in bracket] methods.

| Configuration | δ<sub>BSSE</sub> | E<sub>def</sub> | E<sub>corr</sub><sup>bin</sup> | E<sub>corr</sub><sup>ads</sup> |
|---------------|-----------------|----------------|---------------------------|-----------------|
| a'            | 0.0537          | 0.0024         | -0.0348                   | -0.0325         |
|               | (0.0613)        | (0.0033)       | [-0.0556]                 | [-0.0522]       |
| b'            | 0.0532          | 0.0029         | -0.0349                   | -0.0320         |
|               | (0.0607)        | (0.0049)       | [-0.0549]                 | [-0.0500]       |
| c'            | 0.0509          | 0.0036         | -0.0434                   | -0.0399         |
|               | (0.0575)        | (0.0052)       | [-0.0708]                 | [-0.0655]       |

Time-dependent density functional theory (TD-DFT) is used to predict
the UV-Vis absorption spectra of the considered clusters using CAM-
B3LYP/6-311+G* level of theory. Note that, diffuse and polarized or-
bitals, which are necessary for a reliable TD calculation, are included in
this basis set. Different numbers of excited states are checked and
other considered clusters. On the other hand, according to the obtained
atom causes a distortion in the Al6 octahedron skeleton. The most devi-
aluminum faces of the octahedron. The presence of the capped aluminum
hedral structures with an aluminum atom decorating one of the
characteristics are minimum on the potential energy surface.
 assert that the obtained structures are minimum on the potential energy surface.

The obtained stable structures for Al7, Al7 + and Al7 clusters optimized at
B3LYP/6-311G* and CAM-B3LYP/6-311G* levels of theory are shown in
Fig. 1. The evaluated bond lengths for these clusters are also given in
this figure. Both computational methods predict the same stable geom-
metries for the considered clusters. The considered Al clusters have octa-
edron structures with an aluminum atom decorating one of the
aluminum faces of the octahedron. The most deviation from Oh symmetry is observed for neutral Al7 (with Cs symmetry point group) and the less distortion is observed for charged clusters (with C3v symmetry point group). These findings are in agreement with the previously report [11]. It is clear that the evaluated bond lengths using CAM-B3LYP method are slightly shorter than those calculated by B3LYP method. The attractive nature of long-range interactions considered in
CAM-B3LYP method is responsible for this observation. The evaluated average bond lengths using B3LYP for Al7, Al7 + and Al7 + are 2.72 Å, 2.70 Å and 2.66 Å, respectively, imply to more stability of Al7 + with respect to the other considered clusters. On the other hand, according to the obtained HOMO-LUMO energy gaps (H-L gaps; a measure of hardness) and based

3. Results and discussion

A) Geometrical structures

The initial structures for geometry optimization of Al7, Al7 + and Al7 clusters are given from Li et al. study [11]. Different spin multiplicities are considered for the mentioned neutral (doublet and quartet) and charged (singlet and triplet) clusters for the geometry optimization. It is found that smaller multiplicity causes more stability in all cases (see Table 1). Therefore, just singlet and doublet multiplicities are selected for the charged and neutral clusters, respectively. The stability of the mentioned clusters is confirmed with the vibrational frequency analysis. The absence of imaginary frequencies indicates that the obtained structures are minimum on the potential energy surface.

The obtained stable structures for Al7, Al7 + and Al7 clusters optimized at B3LYP/6-311G* and CAM-B3LYP/6-311G* levels of theory are shown in Fig. 1. The evaluated bond lengths for these clusters are also given in this figure. Both computational methods predict the same stable geometries for the considered clusters. The considered Al clusters have octahedral structures with an aluminum atom decorating one of the aluminum faces of the octahedron. The presence of the capped aluminum atom causes a distortion in the Al6 octahedron skeleton. The most deviation from Oh symmetry is observed for neutral Al7 (with Cs symmetry point group) and the less distortion is observed for charged clusters (with C3v symmetry point group). These findings are in agreement with the previously report [11]. It is clear that the evaluated bond lengths using CAM-B3LYP method are slightly shorter than those calculated by B3LYP method. The attractive nature of long-range interactions considered in CAM-B3LYP method is responsible for this observation. The evaluated average bond lengths using B3LYP for Al7, Al7 + and Al7 + are 2.72 Å, 2.70 Å and 2.66 Å, respectively, imply to more stability of Al7 + with respect to the other considered clusters. On the other hand, according to the obtained HOMO-LUMO energy gaps (H-L gaps; a measure of hardness) and based on the Maximum Hardness Principle (MHP) [51], the Al7 + species with the most hardness (H-L = 2.6672 eV) should be more stable than Al7 (H-L = 1.6817 eV) and Al7 + (H-L = 1.5946 eV) clusters. All of these findings are

| Configuration | δ(REE) | E(RR) | E(REE corr) | E(REE corr) | H-L gap |
|---------------|--------|-------|-------------|-------------|---------|
| a'            | 0.0364 | 0.0002| 0.0033      | 0.0035      |         |
| b'            | 0.0319 | 0.0000| 0.0063      | 0.0064      |         |
| c'            | 0.0291 | 0.0001| 0.0062      | 0.0063      |         |
| d'            | 0.0360 | 0.0001| 0.0049      | 0.0051      |         |

Fig. 12. Optimized structures of Al7CO complexes in which carbon atom of CO approach to Al7 from a) top-beside, b) below-beside, c) below and d) top.
Table 9
Natural charge population of the Al\textsuperscript{7}CO complex by B3LYP/6-311G* method. The charge values of Al atoms that are bonded to CO are bolded.

|     | Al\textsuperscript{1} | Al\textsuperscript{2} | Al\textsuperscript{3} | Al\textsuperscript{4} | Al\textsuperscript{5} | Al\textsuperscript{6} | Al\textsuperscript{7} | C    | O    |
|-----|-----------------------|-----------------------|-----------------------|-----------------------|-----------------------|-----------------------|-----------------------|------|------|
| Al\textsuperscript{7}/CO| -0.106                | -0.106                | -0.106                | -0.212                | -0.212                | -0.212                | -0.046                |      |      |
| a   | -0.103                | -0.103                | -0.009                | -0.149                | -0.468                | -0.149                | 0.015                 | 0.400| -0.434|
| b   | 0.232                 | 0.000                 | -0.006                | -0.130                | -0.290                | -0.263                | 0.040                 | -0.071| -0.512|
| c   | 0.231                 | -0.263                | -0.290                | 0.040                 | -0.005                | -0.001                | -0.129                | -0.071| -0.512|
| d   | 0.040                 | -0.007                | -0.129                | 0.001                 | -0.261                | -0.291                | 0.232                 | -0.071| -0.512|

Fig. 14. Total DOS (TDOS) of a) Al\textsuperscript{7} cluster, b) Al\textsuperscript{7}CO complex (c configuration) as well as Partial DOS (PDOS) of c) 3s and d) 3p valence orbitals of Al atom and e) 2s and f) 2p valence orbitals of carbon atom, before and after adsorption.

Fig. 15. Optimized structures of Al\textsuperscript{7}CO complexes in which carbon atom of CO approach to Al\textsuperscript{7} from a) below, b) beside, c) top.
Table 10
The obtained basis set superposition errors (Δbasis), deformation (Δdef), corrected binding (Δcorr), and adsorption energies (Eads) as well as H-L gaps for the considered configurations of Al7 (all in eV) using B3LYP/6-311G* and CAM-B3LYP/6-311G* [values in bracket] methods.

| Configuration | Δbasis | Δdef   | Δcorr  | Δads  | H-L gap |
|---------------|--------|--------|--------|-------|---------|
| a             | 0.0697 | 0.0403 | -0.1490| -0.1087| 2.2174  |
|               | [0.0756]| [0.0499]| [-0.2094]| [-0.1595]| [4.2613]|
| b             | 0.0537 | 0.0555 | -0.2009| -0.1495| 2.5191  |
|               | [0.0539]| [0.0524]| [-0.2593]| [-0.2068]| [4.4523]|
| c             | 0.0518 | 0.0549 | -0.2008| -0.1459| 2.5355  |
|               | [0.0540]| [0.0528]| [-0.2594]| [-0.2066]| [4.4521]|}

Fig. 16. Difference of electron density of Al7–CO (e configuration). The blue and green isosurfaces represent the region in which electron density is increased and decreased, respectively after CO binds to Al7 (isovalue = 0.005a.u.).

in accordance with the jellium model, which suggests that the Al7 cluster with electronic configuration of 1s² 1p⁶ 1d¹⁰ 2s² 2p² prefers to lose the 2p electron to satisfy the magic electron number of 20. Then, it is easy to anticipate that Al7 is a suitable excess electron donor. It should be mentioned that, the clusters with smaller multiplicities show lower energy and larger H-L gap (see Table 1); which according to the MHP reveals the stability of these multiplicities. This stability should be also due to the aromaticity of Al7 cluster; which will be discussed later.

B) UV-Vis Spectrum
The obtained UV-Vis spectra of the Al7, Al7 and Al7 clusters using TD-DFT calculations, are shown in Fig. 2. The corresponding UV-V is spectrum of Al7 (see panel a in Fig. 2) consists of two peaks; a nearly sharp peak at about 395 nm and a broad band around 801 nm. Those excited states which have more contributions in these absorption bands are given in Table 2. Transitions from electronic ground state (S0) to S25 and S30 excited states show more contributions (with considerable oscillator strength; f) in the 395 nm absorption band; and the dominating excitations are H→L+1 and H→L+5 transitions, respectively. On the other hand, transitions to S9, S5 and S6 excited states have more contributions in the broad band at 801 nm. The S9→S4 excitation is dominated by H→L+1 transition; whereas H→L’ and H→L+1 transitions have more contributions in excitations from S0 to degenerate S5 and S6 excited states. The molecular orbitals in crucial excitations are depicted in Fig. 3.

The UV-Vis spectrum of Al7 shows two peaks at 345 nm and 558 nm. The excited states with more contributions in these absorption bands are given in Table 3. Excitation from electronic ground state to degenerate S29 and S30 excited states that have the same oscillator strength (f = 0.022) as well as S22 excited state have more contributions in the 345 nm absorption band (f = 0.020). Degenerate first and second excited states (S1 and S2) as well as S7 excited state have more contributions in the bands at about 558 nm. The S0→S1 and S0→S2 transitions are more contributed (866.9) from H to degenerate L+1 and L+1’ molecular orbitals, respectively. Fig. 4 shows the main orbitals (H, L+1 and L+1’) that in which are contributed the vertical electronic transition in Al7 cluster. Note that, L+1 and L+1’ orbitals are centered on the octahedron aluminum atoms but not on the capped Al atom. Therefore, these transitions decrease the electron density of the capped aluminum atom.

The UV-Vis spectrum of Al7 shows a nearly broad peak at about 639 nm. According to the reported results in Table 4, transitions from the electronic ground state (D0) to D14 and D17 excited states have more contributions (more oscillator strength; f) in this peak. These transitions are significantly due to H(β→L+1) and H(α→L+1) electron transfers. The majority of H(β) and L+2(β) electron densities (see Fig. 5) are lying on the octahedron aluminum atoms and the capped Al atom, respectively. Therefore, this transition causes an electron transfer from peripheral binding of Oh atoms to the capped aluminum atom. But in H(α→L+1) transition, the electrons are moved to the Al-Al bonds of the cluster.

C) AdNDP analysis
Atomic clusters, in general, are stabilized through non-classical chemical bonding patterns. Therefore, some concepts such as aromaticity are frequently used to describe the stability and structure of a given metallic cluster [52]. To better understand the chemical bonding in the considered aluminum clusters, electron localization analysis using the Adaptive Natural Density Partitioning (AdNDP) is carried out. In fact, AdNDP is a theoretical tool to characterize the chemical bonding [53], and does not depend significantly on the method or basis set [54]. In this approach, the electronic structure of system represents in terms of nc-2e orbitals, in which n can vary from one to the total number of atoms in the corresponding system. It should be mentioned that, nc-2e orbitals with n > 2 are associated with the concept of delocalization and therefore aromaticity of the system. Hence, the AdNDP approach is used to anticipate the aromaticity of the considered Al7 and Al7 clusters. It should be recalled that, both Al7 and Al7 have closed-shell electronic structures and AdNDP analysis could be performed appropriately; whereas for neutral Al7 cluster with odd number of electrons the AdNDP calculations may lead to unreliable results. Therefore, this approach is not considered for Al7 cluster. The results are depicted in Figs. 6 and 7.
bonds (three 3c-2e σ-bonds as well as one 4c-2e σ-bond). All 2c-2e and 4c-2e orbitals are responsible for bonding between the capped aluminum atom and the aluminums of the corresponding face of octahedron. On the other hand, three 3c-2e σ-bonds correspond to three aluminum faces of octahedron. For the π-bonding, the AdNDP analysis reveals three 6c-2e π-bonds and one 7c-2e π-bond involving all aluminum atoms of the cluster. According to this partitioning, Al7 possesses 8 delocalized σ and 8 delocalized π electrons, which conform to the 4n Hückel rule for antiaromaticity, for n = 2. Thus, AdNDP anticipates that Al7 is both σ- and π-antiaromatic. The double antiaromaticity of Al7 cluster justifies its less stability with respect to the Al7 and Al7⁺.

AdNDP analysis of Al7⁺ reveals ten delocalized bondings consist of three 3c-2e σ-bonds as well as one 4c-2e σ-bond and three 5c-2e σ-bonds as well as two 6c-2e and one 7c-2e σ-bonds (see Fig. 7). It should be mentioned that, the

Table 11
Natural charge population of the Al7CO complex by B3LYP/6-311G* method. The charge values of Al atoms that are bonded to CO are bolded.

|     | Al1 | Al2 | Al3 | Al4 | Al5 | Al6 | Al7 | C   | O   |
|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| Al7 | 0.132 | 0.132 | 0.132 | 0.154 | 0.154 | 0.154 | 0.140 | 0.549 | -0.317 |
| a   | -0.153 | 0.162 | 0.163 | 0.114 | 0.145 | 0.145 | 0.191 | 0.564 | -0.3115 |
| b   | 0.145 | 0.154 | 0.152 | -0.145 | 0.143 | 0.144 | 0.154 | 0.564 | -0.311 |
| c   | 0.143 | 0.143 | 0.145 | 0.154 | 0.153 | 0.154 | -0.145 | 0.564 | -0.311 |

Fig. 17. Total DOS (TDOS) of a) Al7⁺ cluster, b) Al7⁺CO complex (c configuration) as well as partial DOS (PDOS) of c) 3s and d) 3p valence orbitals of Al atom and e) 2s and f) 2p valence orbitals of carbon atom, before and after adsorption.

Fig. 18. Optimized structures of Al7CO complexes in which carbon atom of CO approach to Al7 from a) below-beside, b) below, c) top and d) top-beside.
same AdNDP orbitals were also predicted for the isoelectronic MgAl$_6$ cluster [55]. Based on this partitioning, seven $\sigma$-radial AdNDPs are responsible for $\sigma$-aromaticity and three $\pi$ AdNDP orbitals are responsible for $\pi$-aromaticity. Therefore, the system should be considered as doubly ($\sigma$- and $\pi$-) aromatic. These results are in agreement with the previous findings reported by Sun and coworkers [11], and explain the significant stability of this cluster with respect to Al$_7$ one. Note that, all AdNDP orbitals have occupation number (ON) values close to the ideal value of 2.00(e); which validates these chemical bonding representations.

### D) Adsorption of CO on Al$_7$, Al$_7^+$ and Al$_7$ clusters

In this section, the interaction of carbon monoxide molecule with Al$_7$, Al$_7^+$ and Al$_7$ clusters is investigated using both B3LYP/6-311G* and CAM-B3LYP/6-311G* levels of theory. The possibility of adsorption of CO from both carbon and oxygen atoms and on different sites of each cluster (on top of an aluminum atom, bridge and hallow sites) is examined to determine the most favorable adsorption site for each case. It is found that, those configurations in which the CO molecule is on bridge or hallow sites, rearrange to geometries in which the CO is bonded to an Al atom. Therefore, just the configurations that the carbon monoxide is on top of a given aluminum atom, are considered in the rest of this study (see Fig. 8).

The optimized structures of Al$_7$–CO, Al$_7^+$CO and Al$_7$CO in which CO molecule approaches to Al$_7$, Al$_7^+$ as well as neutral Al$_7$ clusters from oxygen atom are shown in Figs. 9, 10, and 11. The obtained energies (see Tables 5, 6, and 7) reveal that the considered clusters do not show a tendency for adsorption of CO molecule through its oxygen atom. For instance, calculated deformation energies for those configurations in which CO molecule is approached to Al$_7$ cluster through its oxygen atom (Table 5), are nearly zero. Therefore, it seems that Al$_7$ cluster and CO molecule undergo no distortion during this interaction. On the other hand, the corrected adsorption energies for these configurations are positive that indicate to repulsive nature of these interactions. These findings reveal no tendency for adsorption of CO through the oxygen atom on Al$_7$ cluster. The same behavior is also observed for the other clusters (see Tables 6 and 7). Therefore, just those configurations corresponded to the adsorption of CO from C atom are considered in the rest of this study.

The optimized structures for different configurations of the Al$_7$–CO are shown in Fig. 12. The evaluated deformation as well as corrected binding and adsorption energies using B3LYP and CAM-B3LYP methods are also collected in Table 8. The obtained results with B3LYP method show that, the three aluminum atoms of the capped face do not show a tendency for the adsorption of CO molecule (a configuration with $E_{ads} = 0.0382$ eV); whereas the evaluated negative adsorption energies for b, c and d configurations ($E_{ads} = -0.3470$ eV) reveal the considerable ability of the other Al atoms to adsorb the CO molecule. The calculated deformation energies for these configurations are all about 0.590 eV that indicate a moderate distortion for Al$_7$ cluster when CO molecule is approached to it. However, the corrected adsorption energy values of these configurations show that the interaction of CO with this cluster is a physical adsorption, which could be due to a weak van der Walls interaction between the fragments. Therefore, all Al atoms of Al$_7$ cluster have the same tendency for adsorbing CO molecule, except three capped face aluminum atoms. Note that, in d configuration, the carbon atom of CO is bonded to the capped Al atom of Al$_7$ cluster, and this aluminum atom is to some extent pulled out of cluster in the adsorbed structure.

In all b, c and d configurations, the Al–C distance is about 2.03 Å, which is close to the experimental Al–C bond length reported for aluminum carbide (1.955 Å) [56]. This matches our expectation for carbon-metal bonding. The C–O bond length is merely elongated to 1.183 Å from 1.127 Å (evaluated for the isolated CO using the same computational method) during the adsorption process. The structural variation of CO should be related to the electron donation and back-donation between Al atom and CO molecule. It is recalled that, according to the Dewar–Chatt–Duncanson model [57] the CO molecule donates electrons to some extent into the metal.
from carbon atom into the metal d-orbital and simultaneously the metal donates electrons back from a different filled orbital into the empty $\pi^*$ antibonding orbital of CO. Both of these effects tend to reduce the carbon-oxygen bond order, leading to an elongated C–O distance and a lowering of its vibrational frequency as well as bond strength. But it should be mentioned that, this elongation is not dissociative. The obtained results from CAM-B3LYP calculations are also in the same line (see Table 8).

The Electron density difference (EDD) map can be used to accurately treat the local changes in charge density which occur when the adsorbate-substrate chemical bond is formed. In the considered system (Al$_7$–CO), EDD reveals how the bonding of the CO molecule affects the electron distribution relative to the isolated CO molecule and the unperturbed aluminum cluster. The EDD isosurface of the configuration, which is obtained by subtracting the SCF densities of the individual CO and aluminum cluster from the entire Al$_7$–CO complex, is depicted in Fig. 13. The blue and green isosurfaces represent the region in which electron density is increased and decreased after CO binds to cluster. The obtained EDD map reveals an electron density loss near the carbon atom along the Al–C bond, and a considerable electron accumulation in perpendicular antibonding C–O orbital located mainly on C atom; which are in accordance with the Dewar-Chatt-Duncanson model. The EDD also shows that electron back donation from Al to C is more than the reverse charge transfer; which could be due to the negative charge of the aluminum cluster.

The obtained NBO charges for the Al$_7$–CO complex using B3LYP/6-311G* level of theory are gathered in Table 9. For each configuration the charge value of the Al atom which is bonded to CO molecule is bolded. In this table, charges of aluminum atoms in the isolated Al$_7$ cluster are also given for comparison. Although the charge of Al5 atom in the a configuration becomes more negative during the complexation (-0.466 a.u.), the total charge on CO fragment does not change considerably (~0.034 a.u.). This is in accordance with the repulsive nature of this interaction. On the other hand, the charges of Al1 (in b and c configurations) and Al7 (in d configuration) atoms change to positive values; which imply to decrease of electron density around those atoms during the adsorption of CO molecule. The evaluated considerable negative charge for CO fragment in these interactions (~0.584 a.u.) reveals electron transfer from Al cluster to CO molecule; which confirms the results of EDD analysis. Therefore, it seems that the stability of Al$_7$–CO should be due to an electron transfer from aluminum cluster to the CO fragment.

The obtained frontier molecular orbitals (HOMO and LUMO) of the Al$_7$/CO cluster using B3LYP/6-311G* are depicted in Fig. 3. The distribution of electron density of these orbitals around the whole aluminum atoms reveals both the electron donor and electron acceptor character of these atoms. Increasing the H-L gap during the complexation with CO (H-L gap changes from 1.59 eV to 1.73eV) indicates that further interaction of CO molecule with this cluster is not favorable.

The partial density of states (PDOS) of free CO and Al$_7$/CO cluster as well as Al$_7$–CO complex are analyzed to understand the bonding characteristics of CO adsorbed system. The obtained plots are depicted in Fig. 14. There exist new peak around -8.5 eV in the Al$_7$–CO complex in comparison with the free Al$_7$ cluster, stemming from the 3p electron of Al atoms due to the 3s to 3p electron promotion. Additionally, the new peak at -12.5 eV can participate into the orbital overlaps with CO molecule. This results into the physical interaction between CO and Al$_7$ cluster.

In a’, b’ and c’ configurations shown in Fig. 10, CO molecule approaches to Al$_7$ cluster through oxygen atom. Calculated deformation energies of those complexes (with B3LYP method) are 0.0024, 0.0029, 0.0036 (in eV) and the evaluated adsorption energies are just -0.0325, -0.0320, -0.0399 (in eV), respectively. Calculated adsorption energies using CAM-B3LYP/6-311G* are to some extent greater than those
evaluated by B3LYP/6-311G* method (see Table 6); but are in the same line. Note that, the calculated adsorption energies for those configurations in which CO approaches to the Al$_7^+$ cluster from the oxygen atom are negligible.

Fig. 15 shows three different optimized configurations of Al$_7$CO complex in which binding is occurred through C atom. The deformation as well as corrected binding and adsorption energies at B3LYP and CAM-B3LYP are also gathered in Table 10. Note that in B3LYP method, the evaluated deformation (0.0403, 0.0555, 0.0549), adsorption (-0.1087, -0.1455, -0.1459) and binding (-0.1490, -0.2009, -0.2008) energies for the adsorption of CO on Al$_7^+$ cluster are considerably smaller than the corresponding values for Al$_5^+$ cluster. This implies that there is fewer tendency for adsorbing CO molecule; which could be due to more stability of Al$_5^+$ cluster resulted from its aromaticity. The similar conclusion is obtained from the CAM-B3LYP calculations (see Table 10).

The Al–C bond lengths in a, b and c configurations are 2.277 Å, 2.265 Å and 2.266 Å, respectively; which are longer than the corresponding Al–C bond lengths in Al$_7$–CO complex (2.029 Å). In these configurations, the C–O bond lengths vary slightly from 1.127 Å (in isolated CO) to 1.122 Å (a), 1.121 Å (b) and 1.121 Å (c). Therefore, it seems that CO molecule just undergoes a weak physical adsorption through its carbon atom on Al$_5^+$ cluster. All of these results indicate to more stability (fewer tendency for CO adsorption) of Al$_5^+$ cluster with respect to Al$_7^+$; which is revealed by aforementioned AdNDP analysis.

The calculated H-L gaps for all Al$_7$–CO complexes (~2.35 eV) are to some extent less than the H-L gap of the pristine cluster (~2.67 eV). This indicates to decreasing the stability of the system upon the adsorption of CO molecule; which should be due to the loosing of aromaticity. In fact, special stability of Al$_5^+$ cluster is reflected in its aromaticity and large H-L gap. Electron density difference surface of the c configuration for Al$_7$–CO is depicted in Fig. 16. The obtained EDD maps indicates the increasing electron density along the Al–C bond while near the oxygen atom, electron density is decreased. Indeed the NBO atomic charges of Al$_7$–CO complex for a, b and c configurations are gathered in Table 11. The results show that in each configuration the positive charge of Al atom bonded to CO molecule is changed to negative value after adsorption. In these configurations the sum of positive charges of all Al atoms in Al$_7$–CO complex is reduced with respect to the bare Al$_7^+$ cluster; whereas the charge of CO becomes positive after the adsorption. Therefore, NBO results reveal electron transfer from CO molecule to Al$_7^+$ cluster. Although the DOS plot of Al$_7^+$ does not alter during the adsorption of CO (see Fig. 17), the appeared peak at -5 eV of Al$_7$–CO complex could be participate into the orbital overlaps with CO molecule.

The different optimized structures of Al$_7$–CO (by B3LYP) that binding is occurred from C atom are shown in Fig. 18. The obtained distances between two fragments (Al–C bond length) using B3LYP method in a, b and c configurations are 1.960 Å; which is very close to the Al–C bond length in aluminum carbide (1.955 Å). In these configurations the C–O bond lengths are 1.153 Å, which is to some extent larger than the bond length of free CO (1.127 Å). But for d configuration, in which the CO is approached to one of the aluminum atoms of the capped face, the Al–C and C–O bond lengths are 2.180 Å and 1.133 Å, respectively. Therefore, it seems that CO molecule does not prefer these Al atoms for binding.

The evaluated corrected binding, adsorption and deformation energies for Al$_7$–CO using B3LYP and CAM-B3LYP methods are given in Table 12. The obtained results from CAM-B3LYP method show that in a, c and d configurations the neutral Al$_7^+$ has no tendency to adsorb CO molecule; whereas negligible negative adsorption energy is predicted for b configuration. The obtained results from B3LYP calculation are not in agreement with the CAM-B3LYP results. It should be due to long-range interactions which are important in neutral systems such as Al$_7^+$ and CO. Note that for charged systems (like Al$_5^+$ and Al$_7^+$), in which the electrostatic contribution is dominant, these effects are negligible and therefore the obtained results from both B3LYP and CAM-B3LYP methods are in the same line.

The Natural Bond Orbital analysis results for different configurations of Al$_7$–CO complex are gathered in Table 13. It is clear that, in each case the bonded aluminum atom becomes more negative with respect to the bare cluster. On the other hand, the charges of CO fragment in stable a, b and c configurations are negative; whereas for d configuration a positive value is obtained for carbon monoxide fragment. Therefore, a charge transfer from cluster to the CO molecule is expected in this system. This prediction is confirmed by EDD isosurface of this complex shown in Fig. 19. This figure reveals electron accumulation between the carbon and aluminum atoms, which indicates to an interaction between the fragments.

The partial density of states (PDOS) of free CO molecule and Al$_7^+$ cluster as well as Al$_7$–CO complex are shown in Fig. 20. Comparing to the free Al$_7^+$ cluster, there exist new peak around -10.7 eV in the Al$_7$–CO complex. Although the DOS and PDOS of aluminum atom does not change considerably; s and p electrons of carbon atom with -10.5 eV energies are absent after adsorption. This may show the orbital overlaps between CO molecule and cluster.

4. Conclusion

All the considered Al clusters have octahedral structures with an aluminum atom decorating one of the aluminum faces of the octahedron. AdNDP analysis predicts aromatic and antiaromatic characters (double σ- and π-) for Al$_7^+$ and Al$_5^+$ clusters, respectively. Al$_7^+$ has special stability and larger H-L gap as a result of its aromaticity and its electron count (20) matching a shell closing in the Jellium model. Among the considered aluminum clusters, Al$_7^+$ shows the most tendency for the adsorption of CO molecules, whereas the evaluated smaller adsorption energies of CO on Al$_5^+$ and Al$_7^+$ suggest an inadequate physisorption of carbon monoxide by these clusters. The electronic and structural investigations prove that the adsorption is not dissociative.

Declarations

Author contribution statement

Zeinab Abdeveiszadeh: Performed the experiments; Analyzed and interpreted the data.
Ehsan Shakerzadeh: Analyzed and interpreted the data.
Siamak Noorizadeh: Conceived and designed the experiments; Analyzed and interpreted the data; Wrote the paper.

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Competing interest statement

The authors declare no conflict of interest.

Additional information

No additional information is available for this paper.

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