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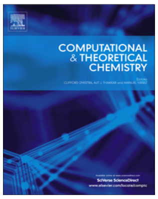

Theoretical studies on the interaction of some endohedral fullerenes $\{[X@C_{60}]^{-}$ ($X = F^{-}, Cl^{-}, Br^{-}$) or $[M@C_{60}]$ (M = Li, Na, K)$\}$ with $[Al(H_2O)_6]^{3+}$ and $[Mg(H_2O)_6]^{2+}$ cations

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ABSTRACT

The effect of various encaged species (F^{-}, Cl^{-}, Br^{-}, Li, Na and K) on the interaction of fullerene molecule with $[Al(H_2O)_6]^{3+}$ and $[Mg(H_2O)_6]^{2+}$ cations was theoretically studied. At first, the possibility of encapsulation of above species into the fullerene cage was studied. Therefore, the formation energies were calculated for all of these compounds. Then the interactions between $[X@C_{60}]^{-}$ ($X = F^{-}, Cl^{-}, Br^{-}$) or $[M@C_{60}]$ (M = Li, Na, K) complexes, with $[Al(H_2O)_6]^{3+}$ and $[Mg(H_2O)_6]^{2+}$ cations were investigated. Density functional theory (DFT), atoms-in-molecules (AIM) and natural bond orbital (NBO) calculation were applied to understand the nature of the interactions. The interaction energies were also calculated for all compounds. Generally, our computations reveal that the encapsulated atom/ion increases the interaction of the fullerene surface with above cations. It was shown that the negative charge of carbon atoms in $[M@C_{60}]$ complexes is larger than in $[X@C_{60}]^{-}$ anions. However, the strength of the reactions/interactions of $[Al(H_2O)_6]^{3+}$ and $[Mg(H_2O)_6]^{2+}$ cations with $[X@C_{60}]^{-}$ endofullerenes is considerably greater than that with $[M@C_{60}]$. Thus the results show that the total negative charge of endofullerene has significantly greater effect on the above interaction than the negative charge of fullerene carbon atoms.

1. Introduction

Since the discovery of buckminsterfullerene in 1985 [1], and especially after the macroscopic preparation of fullerenes in 1990 [2], many theoretical and experimental investigations have been carried out on these molecules. As the radius of the C_{60} is approximately 3.5 Å, small guest species such as atoms, ions and molecules can be placed inside its cavity to generate endohedral (inside the cage) complexes. Endohedral complexes have appeared in different areas of science and technology, ranging from medicine [3,4] and environmental protection [5] to molecular optoelectronics [6] and renewable energetic [7]. Following the first successful enclosure of a La atom inside the C_{60} cage [8], a number of endofullerene have been synthesized from alkali metal ions (especially Li^{+}) [9–11], groups II metals (Ca, Sr, Ba) [12–14], groups III metals (Sc, Y, La) [14,15], all the lanthanides (Ce–Lu) [16,17], nitrogen [18], phosphorus [19], noble gases [20,21], and many other atoms and species [22,23]. Due to the extreme difficulty in producing macroscopic quantities and isolating pure samples, theoretical studies have been playing an important role in investigating the structural and electronic properties of endofullerenes and predicting their striking characteristics. Several theoretical studies have been made on the encapsulation of a variety of atoms and ions inside the fullerene cage of different dimensions [22–32]. Additionally, there are some theoretical reports on interaction between endofullerene surface and external molecules, in which charge transfer between the encaged species and C_{60} influences the strength of these interactions. For example the interaction of $Li@C_{60}$ with amino acids has been investigated by Jalbout [33]. Their results suggested that there is an interaction of the amino acids with the fullerene surfaces that can be attributed to some form of charge transfer effects. Other efforts in this group have demonstrated that the encapsulation of metals inside fullerenes improves external interactions with small polar molecules [34–37].

Recently, we reported a theoretical study on the interaction of hydrated Al(III) and Mg(II) ions with C_{60} molecule and two other Π-systems [38]. The results showed that among the three studied Π-systems, the fullerene molecule has a stronger bonding interaction with both the $[Al(H_2O)_6]^{3+}$ and $[Mg(H_2O)_6]^{2+}$ cations. In the present work, we report a theoretical study on the interaction of $[X@C_{60}]^{-}$ ($X = F^{-}, Cl^{-}, Br^{-}$) or $[M@C_{60}]$ (M = Li, Na, K) endohedral fullerenes with $[Al(H_2O)_6]^{3+}$ and $[Mg(H_2O)_6]^{2+}$ cations.

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We want to know which of the encaged halide anions or neutral alkaline atoms will significantly increase the interaction of fullerene surface with the hydrated metal ions. In our previous work we used only the B3LYP which is a hybrid DFT method. However in present calculations we also used the PBE, which is one of the known pure DFT methods.

2. Computational details

Geometry optimization for all systems under investigation was carried out using the Gaussian 03 [39] set of programs. The geometries of the isolated $[X@C_{60}]^-$ ($X = F^-, Cl^-, Br^-$) and $[M@C_{60}]$ ($M = Li, Na, K$) endofullerenes were fully optimized at B3LYP/6-311++G** levels of theory. Single point energy calculation at MP2/6-311++G** and PBE/6-311++G** level were carried out on the B3LYP/6-311++G** optimized geometries of isolated endofullerenes. The geometries of $\{[X@C_{60}]^-\ldots[Mg(H_2O)_6]^{2+}\}$, $\{[M@C_{60}]\ldots[Mg(H_2O)_6]^{2+}\}$, $\{[X@C_{60}]^-\ldots[Al(H_2O)_6]^{3+}\}$ and $\{[M@C_{60}]\ldots[Al(H_2O)_6]^{3+}\}$ ($X = F^-, Cl^-, Br^-$; $M = Li, Na, K$) complexes were optimized at the B3LYP/6-31G** level of theory. Then the single point calculations were only carried out on above optimized Mg systems and also related $[X@C_{60}]^-$, $[M@C_{60}]$ and $[Mg(H_2O)_6]^{2+}$ fragments at B3LYP/6-311++G** and PBE/6-311++G** levels. The calculated interaction energies between the endofullerenes and $[Mg(H_2O)_6]^{2+}$ cation were corrected for basis set superposition error (BSSE) using the counterpoise method [40]. The AIM 2000 package was used to obtain the bond properties. Wave function files were generated from the Gaussian output files at B3LYP/6-311++G** level of theory to perform AIM calculations [41]. Natural bond orbital analyses (NBO) have also been performed at B3LYP/6-31G** level of theory [42].

3. Results and discussion

The B3LYP/6-31G** optimized geometries of $\{[X@C_{60}]^-\ldots[Mg(H_2O)_6]^{2+}\}$, $\{[M@C_{60}]\ldots[Mg(H_2O)_6]^{2+}\}$, $\{[X@C_{60}]^-\ldots[Al(H_2O)_6]^{3+}\}$ and $\{[M@C_{60}]\ldots[Al(H_2O)_6]^{3+}\}$ ($X = F^-, Cl^-, Br^-$; $M = Li, Na, K$) complexes are given in Figs. 1 and 2. As can be seen in Fig. 1, in all of the Al(III) complexes studied here, when the anion X^- or the atom M is encapsulated in fullerene cavity, the proton transfer occurs from cation to the endohedral fullerene. For example, in $\{[X@C_{60}]^-\ldots[Al(H_2O)_6]^{3+}\}$ complexes one, two and three protons are transferred from the $[Al(H_2O)_6]^{3+}$ cation to $[F@C_{60}]^-$, $[Cl@C_{60}]^-$ and $[Br@C_{60}]^-$ anions, respectively. On the other hand, in the case of $\{[M@C_{60}]\ldots[Al(H_2O)_6]^{3+}\}$ complexes the results show that in all cases only one proton is transferred from the $[Al(H_2O)_6]^{3+}$ cation to the endofullerene molecule. Obviously, the proton transfer is the result of a very strong interaction between the endofullerene and $[Al(H_2O)_6]^{3+}$ cation. In contrast, in the case of both $\{[X@C_{60}]^-\ldots[Mg(H_2O)_6]^{2+}\}$ and $\{[M@C_{60}]\ldots[Mg(H_2O)_6]^{2+}\}$ complexes, there is no proton transfer from the cation to the endofullerene (Fig. 2). As can be seen in Fig. 2, three H_2O molecules of $[Mg(H_2O)_6]^{2+}$ cations, through their hydrogen atoms, interact with the carbon atoms of the six-membered ring in the endofullerene molecule. What is very interesting is that, the F^- ion due to its small size show a large off-center displacement in the C_{60} molecule when the C_{60} molecule interact with hydrated Al^{3+} and Mg^{2+} ions. Therefore, the motion of F^- anion from the center of fullerene cage toward

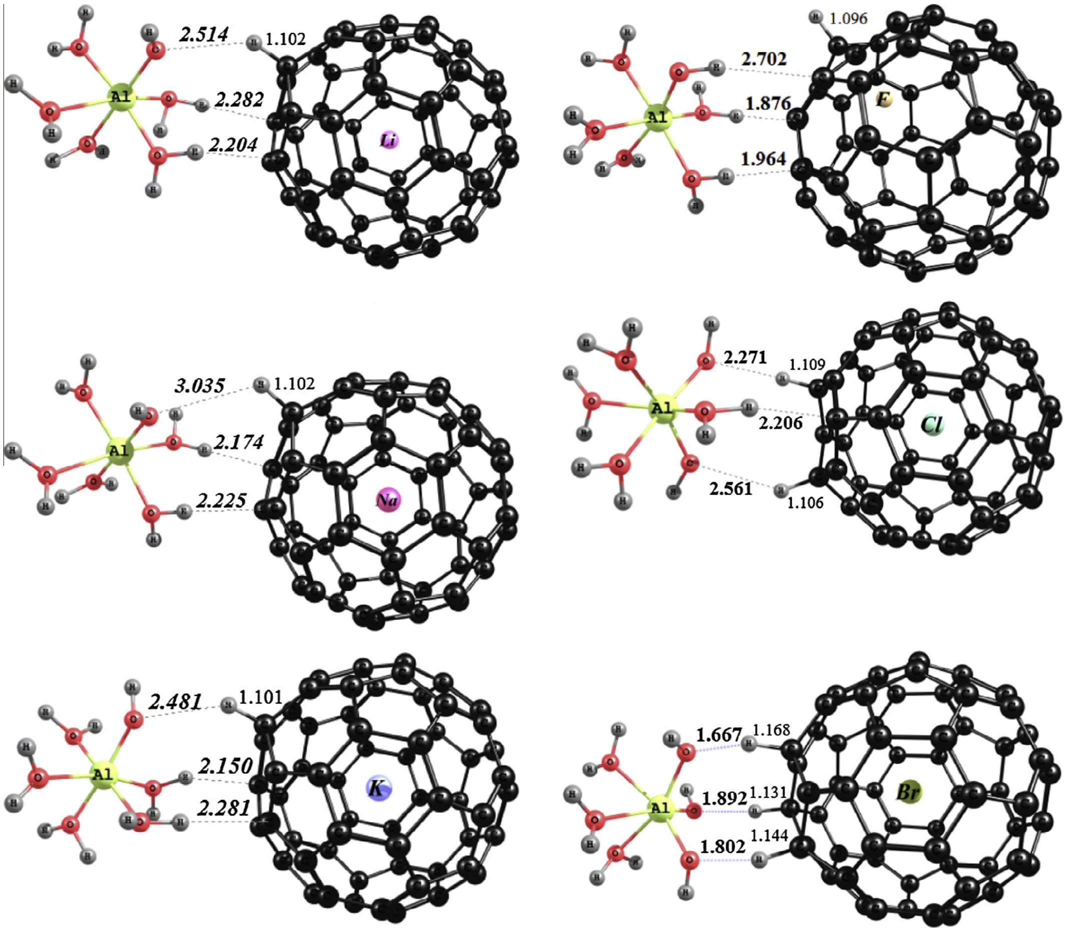

Fig. 1. Optimized geometries along with selected calculated bond lengths (Å) for the $\{[X@C_{60}]^-\ldots[Al(H_2O)_6]^{3+}\}$ and $\{[M@C_{60}]\ldots[Al(H_2O)_6]^{3+}\}$ ($X = F^-, Cl^-, Br^-$; $M = Li, Na, K$) complexes. In all of above complexes the proton transfer occurs from $[Al(H_2O)_6]^{3+}$ to the endofullerene.