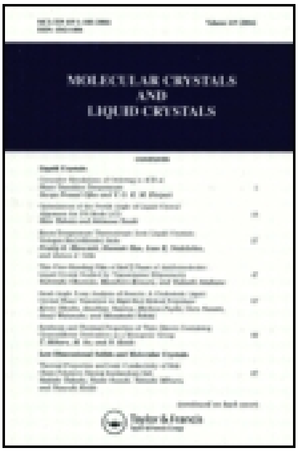

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DFT Study on the Interaction of Carbon Nano-Materials with Sodium Ion and Atom

Takahiro Fukuzumi [a], Hiroto Tachikawa [a] & Kazuhisa Azumi [a]
[a] Division of Materials Chemistry, Graduate School of Engineering, Hokkaido University, Sapporo, Japan

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DFT Study on the Interaction of Carbon Nano-Materials with Sodium Ion and Atom

TAKAHIRO FUKUZUMI, HIROTO TACHIKAWA, AND KAZUHISA AZUMI

Division of Materials Chemistry, Graduate School of Engineering,
Hokkaido University, Sapporo, Japan

The binding structures and electronic states of sodium ion and atom (Na^+ and Na) trapped on the smallest fullerene surface (C_{20}) have been investigated by means of density functional theory (DFT) calculation to elucidate the nature of interaction. It was found that the Na^+ ion can bind two sites of C_{20}: one is on-top site where Na^+ ion binds to the carbon atom of C_{20}, while the other is a pentagonal site where the Na^+ ion binds to five membered ring of C_{20}. In case of sodium atom, the similar binding structures were obtained on C_{20} surface. The nature of the interaction between Na^+(Na) and the C_{20} cluster was discussed on the basis of theoretical results.

Keywords Ab-initio calculation; C_{20}; charge distribution; interaction; sodium ion

1. Introduction

Carbon materials have potential to interact a variety of chemical species on both surface and edge regions of the carbon sheet [1–7]. In particular, the interaction of the carbon with alkali metal ion and atom are much important in the field of secondary rechargeable batteries and hydrogen storage materials. In case of lithium ion (Li^+) and graphite, a theoretical maximum capacity of normal graphite material for lithium ion (LiC_6) is 372 mAh/g. If the carbon material is changed from graphite to amorphous carbon, the maximum capacity increases up to 500–1100 mAh/g. The characteristics are originated from non-layer structure of amorphous carbon where Li atom and ion are stored in the edge region of the carbon sheet.

The interactions of alkali ion with fullerenes and carbon nanotubes (CNTs) are important in development of new molecular devices of nano-carbon materials beyond the amorphous carbon. It is known that the electronic states of the fullerenes are drastic changed by doping of the alkali metals. Also, the doping to the fullerenes increases a capacity of molecular hydrogen as a hydrogen storage.

Prinzbach *et al.* measured a photo-electron spectra of the mass selected C_{20}^- cluster using an electron-impact ionization in a time-of-flight mass spectrometer.

Address correspondence to Dr. Hiroto Tachikawa, Division of Materials Chemistry, Graduate School of Engineering, Hokkaido University, Sapporo 060-8628, Japan. Fax: +81-11-706-7897; E-mail: hiroto@eng.hokudai.ac.jp

They showed that the the C_{20} fullerene is stable and has an electron affinity of 2.25 ± 0.03 eV [8].

In the present paper, we applied density functional theory (DFT) method to the Na atom and Na^+ ion on the simplest fullerene, C_{20}. In particular, we focus our attention on interaction of Na atom with C_{20}. In previous papers [9–15], we investigated preliminary the electronic states of Li^+ and Na^+ ion adsorbed on graphene surface using DFT and direct MO-MD calculations. It was found that the Na^+ ion is preferentially bound to a hexagonal site of graphene surface. The similar technique will be applied to the Na atom (and Na^+)-graphene system in the present work.

2. Method of Calculation

The binding structures of sodium ion and atom (Na^+ and Na) on the small sized fullerene (C_{20}) were fully optimized at the B3LYP/6-311G(d,p) level of theory. Several positions of Na^+ (or Na atom) on C_{20} were examined as initial geometries in the geometry optimization. All density functional theory (DFT) calculation was carried out using Gaussian 03 program package [16].

3. Results

A. *Binding Structures of the Na^+ Ion and Na Atom on C_{20}*

Na^+-C_{20}. The optimized structures of Na^+-C_{20} complexes are illustrated in Figure 1. Several initial positions of Na^+ were generated randomly around C_{20}, and then the

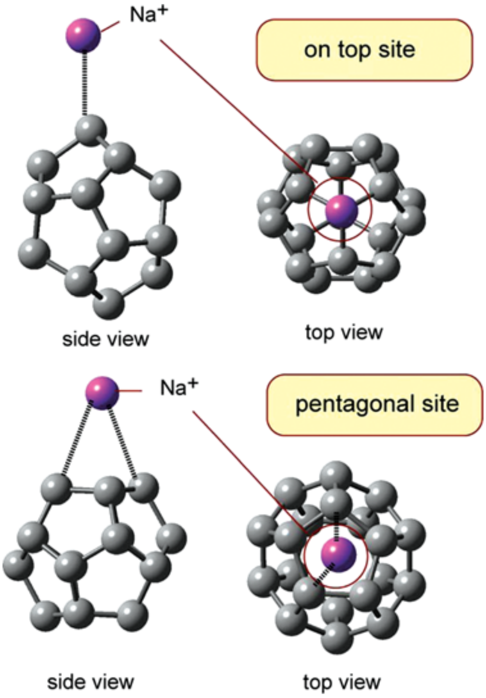

Figure 1. Optimized structures of Na^+ ion adsorbed on C_{20} calculated at the B3LYP/6-311G(d,p) level. Two binding sites (on-top and pentagonal sites) were obtained.

geometries were fully optimized at the B3LYP/6-311G(d,p) level. Two structures were obtained as stable structures of Na^+ on C_{20}: these are on top and pentagonal sites. In the on top site, the Na^+ ion is located over the carbon atom with a distance $R_1 = 2.439$ A. On the other hand, in the pentagonal site, the sodium ion is located as $R_1 = 2.735$ A and $R_2 = 2.912$ A.

Na-C_{20}. For the system of sodium atom Na-C_{20}, the geometries were fully optimized at the B3LYP/6-311G(d,p) level. The optimized structures of Na-C_{20} are illustrated in Figure 2. Two stable structures were obtained: on top and pentagonal sites as well as the Na^+-C_{20} complexes. In the on top site, the Na atom is located as $R_1 = 2.340$ A and $R_2 = 2.590$ A above C_{20}, indicating that one of the carbon atoms of C_{20} is close to the Na atom. The sodium atom is also located above the C–C bond line. In the pentagonal site, the sodium atom is located over the pentagonal site composed of five carbon atoms. The bond distances from carbon atoms are $R_1 = 2.594$ A and $R_2 = 2.616$ A.

The binding energies of Na^+ ion and Na atoms to C_{20} were given in Table 1. The binding energies of Na^+ to C_{20} for on top and pentagonal sites were calculated to be 29.0 and 19.0 kcal/mol, respectively, indicating that the Na^+ ion can bind preferentially to on top site. The sodium atom also binds to C_{20}: the binding energies are 32.0 kcal/mol (on top site) and 27.5 kcal/mol (pentagonal site). The binding energies of both ion and atom are larger in the on-top site than pentagonal site. The

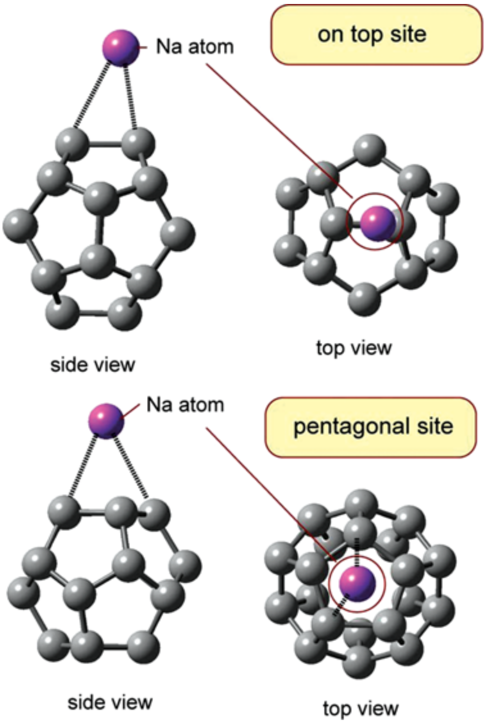

Figure 2. Optimized structures of Na atom adsorbed on C_{20} calculated at the B3LYP/6-311G(d,p) level. Two binding sites (on-top and pentagonal sites) were obtained.

Table 1. Binding energies (ΔE in kcal mol^{-1}) of Na^+ ion and Na atom to the C_{20} cluster calculated at the B3LYP/6-311G(d,p) level

Adatom	Binding site	Binding energy (ΔE)	Charge
Na^+ ion	On top site	29.0	+0.94
	Pentagonal site	19.0	+0.98
Na atom	On top site	32.0	+0.88
	Pentagonal site	27.5	+0.95

excitation energies were calculated by means of time dependent (TD) DFT method at the B3LYP/6-31G(d) level.

B. *Atomic Charges of Na/Na^+ on C_{20}*

The atomic charges of Na^+ ion and atom, obtained by NPA analysis, are given in Table 1. The charges of Na^+ ion are +0.94 for on top site and +0.98 for the pentagonal site, indicating that the electron transfer occurs hardly in Na^+C_{20} system. In case of Na atom, the charges of Na atom have positive values (+0.88 and +0.95). This result strongly indicates that the charge transfer takes place at the ground state such as $Na + C_{20} \rightarrow Na^+ C_{20}^-$, suggests that the electron transfer from the Na tom to C_{20} is important in the interaction.

C. *Band Gaps*

The excitation energies of C_{20}, Na^+C_{20} (on top site), and NaC_{20} (on top site) were calculated by means of time dependent (TD) DFT method. The results are given

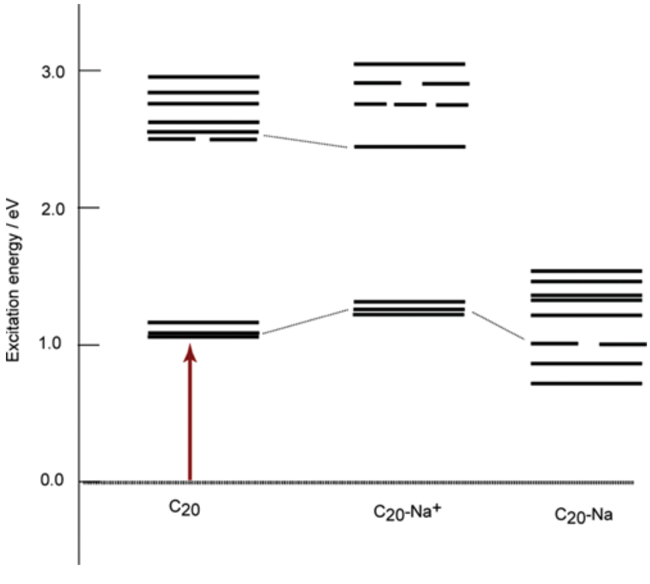

Figure 3. Excitation energies of C_{20}, Na^+C_{20}, and Na-C_{20}, calculated at the B3LYP/6-31G(d) level.

in Figure 3. In free C_{20}, the first excitation band is located in the range 1.03–1.14 eV. The second band is 2.51 eV. The first excitation band of C_{20} is slightly blue-shifted by the interaction with Na^+: 1.21–1.31 eV. This is due to the fact that the energy level of the ground state of C_{20} is stabilized by the binding of Na^+ ion to C_{20}.

In case of C_{20}-Na, on the other hand, the lower energy levels (0.72 and 0.86 eV) were appeared as a charge transfer band from Na to C_{20}: namely, Na-C_{20} + hv → Na^+ C_{20}^-. Thus, the interaction of C_{20} with alkali metal changes drastically the electronic sates of C_{20}.

Conclusion

In the present study, DFT calculation has been carried out for the Na^+/Na-C_{20} system to elucidate the nature of Na^+/Na-C_{20} interaction. Both Na and Na^+ bind preferentially to the on top site of C_{20} surface. After the binding of Na atom to C_{20}, a charge transfer takes place as $Na^+C_{20}^-$. The Na atom has a positive charge on C_{20}. The band gaps of C_{20} is blue-shifted by the interaction with Na^+, whereas that is red-shifted by Na atom.

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