

# THEORETICAL STUDY OF ALKALINE METAL CATIONS IN CARBON NANOTUBES\*

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**Abstract.** Using both ab-initio and Molecular Mechanic calculations we have investigated the interaction between different types of carbon nanotubes with alkali metal cations. Our results show that the alkaline cation is located on top of a phenyl group of the nanotube, resulting a strong cation- $\pi$  interaction. This interaction is not affected by the type or the curvature of the nanotube.

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## 1. INTRODUCTION

Few years after the discovery of carbon nanotubes by Iijima [1], Smalley and his group showed that single-wall nanotubes (SWNT) self assembled during growth into partially ordered two dimensional bundles or ropes [2]. The recent reports that these SWNT ropes can be doped to form metallic conductors [3,4] gives further hope for useful devices and applications. The chemical doping of single-wall carbon nanotubes [5] is a reaction-procedure that would likely be accompanied by charge exchange between host and guest. This charge transfer is the key point that plays the major role in energy storage. Recent findings in hydrogen storage have revealed that alkali doped carbon nanotubes (CNTs) can absorb higher percentages of hydrogen than pure nanotubes [6,7]. Another tremendous application of alkali doped nanotubes is the rechargeable Li batteries [8-10]. All these applica-

tions are based on a special chemical interaction, the cation -  $\pi$  interaction. This cation -  $\pi$  interaction facilitates the storage of electric energy as a consequence of the transport of alkaline cations through the irregularities-defects of the walls of carbon nanotubes [11] and has been extensively studied in the literature. Theoretically first Dougherty and Kumpf using a combination of computational methods had evaluated the interaction between the p face of benzene and the monovalent cations of alkali metals [12]. A complete basis set extrapolation of cation -  $\pi$  bond strengths of Na<sup>+</sup> interacting with ethylene and benzene has been implemented by Feller [13]. Experimental evidence for cation -  $\pi$  interactions and their importance in various areas of sciences have been also reported by Cokel and coworkers [14].

Since CNTs possess delocalized  $\pi$  systems, the detailed analysis of cation -  $\pi$  interaction in CNTs is the aim of the present work. A series of ab initio

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**Table 1.** Characteristics of the cation –  $\pi$  interaction between different alkali metal cations and (4,4) CNT.

Alkaline cation	Binding Energy (Kcal/mole)	Distance from center of phenyl group of the CNT (Å)	Charge of alkaline cation ( $ e $ )
Li <sup>+</sup>	-47,50	1,81	+0,66
Na <sup>+</sup>	-41,51	2,40	+0,72
K <sup>+</sup>	-23,98	2,91	+0,87

and Molecular Mechanics calculations are implemented to various type of nanotubes interacting with alkaline cations.

## 2. RESULTS AND DISCUSSION

### Ab initio results

Our initial purpose was to explore all the possible positions that an alkaline cation can be stabilized on different type of nanotubes, with similar diameters. According to this we had examined the zigzag (7,0) and the armchair (4,4) carbon nanotubes. In order to treat our systems with ab initio methods we cut several rings of CNT and treat them as independent clusters. At the end of these systems we put hydrogen atoms in order to saturate the dangling bonds. In this way (7,0) CNT consists of 56 carbon atoms and 14 hydrogen atoms, while (4,4) CNT consists of 40 carbon atoms and 16 hydrogen atoms.

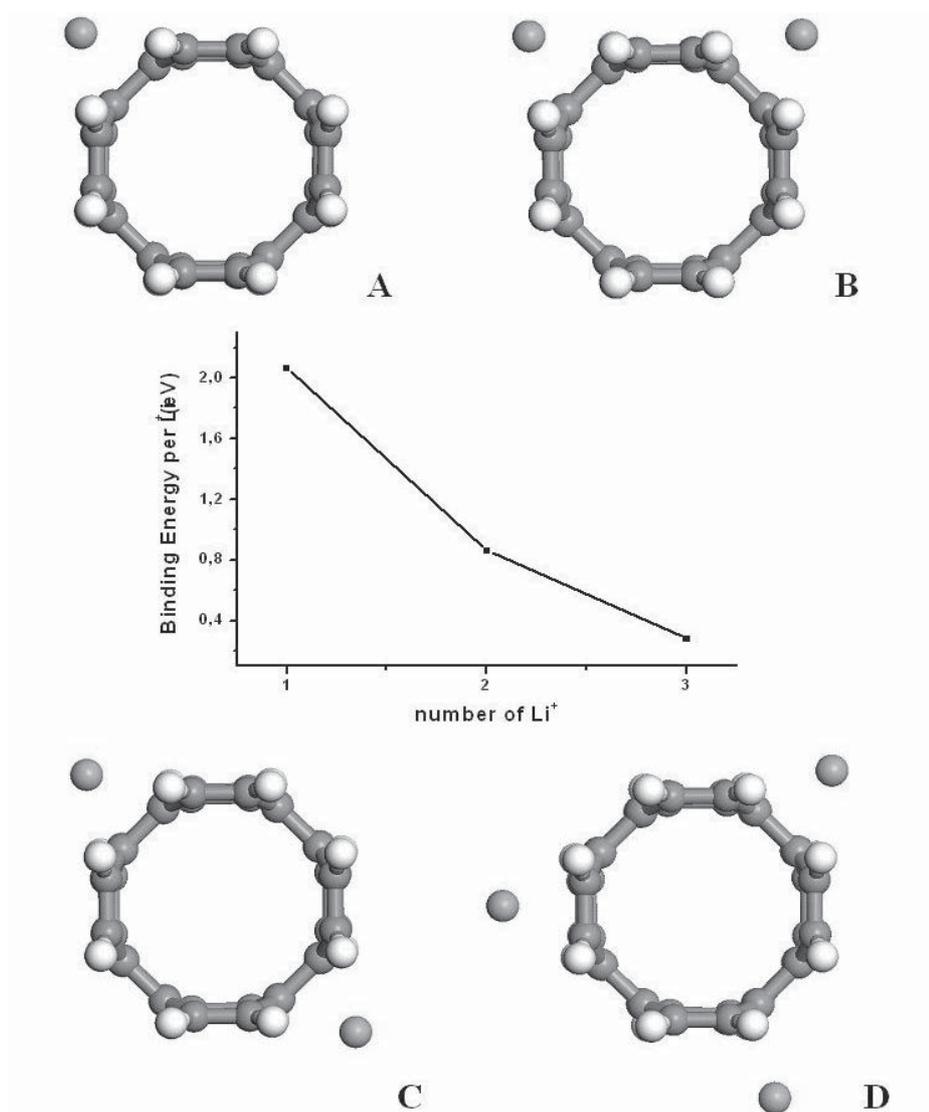
The ab initio electronic structure calculations were performed using the Density Functional Theory within the B3LYP hybridic functional and the sv(p) basis set. These calculations were performed using the Turbomole [15] program package. All possible structural configurations we checked in both nanotubes resulted in only one site that Li<sup>+</sup> can be stabilized. This site is on top of a phenyl group center. Li<sup>+</sup> ion binds on the (7,0) CNT with 44,28 Kcal/mole in 2,03 Å distance from the center of the phenyl while on the (4,4) CNT with 47,50 Kcal/mole in 1,81 Å distance. A charge transfer from the nanotube to the alkali cation is observed in both cases. In (7,0) CNT a charge of -0,31 $|e|$  is transferred from the nanotube to the Li cation. Similarly in (4,4) CNT a charge of -0,34 $|e|$  is transferred from the nanotube to the Li cation.

The next task in our study is to examine the variation of the binding energy as we change the type and the number of the cations. The binding energy, the distance from the center of the phenyl

group of the nanotube, and the charge transfer of different alkali metals interacting with the (4,4) carbon nanotube are demonstrated in Table 1. The binding energy of the alkaline cation on the outer sidewall of the nanotube follows the same trend as in the case of benzene in gas face [12] which is expected from the electrostatic trend ( $BE_{Li^+} > BE_{Na^+} > BE_{K^+}$ ). Another observation is that the larger the binding energy of a cation the smaller the positive charge remains to it.

In Fig. 1 we show a (4,4) carbon nanotube interacting: a) with one Li cation, b,c) with two Li cations, and d) with three Li cations, and, a graph showing the binding energy per alkali atom. It is worth mentioning that for the case of two Li cations interacting with the nanotube, we examined the structural configuration where two Li cations can be placed in neighboring phenyl groups. After relaxation of the structure, one Li atom moved to a neighboring phenyl increasing the distance between the two Li cations. This result indicates that Li<sup>+</sup> ions cannot be placed in neighboring phenyl groups of a nanotube because each alkali atom ‘feels’ the repulsive potential of the other. The former structure we mentioned is shown in Fig. 1b and lies 4,84 Kcal/mole higher in energy than the structure shown in Fig. 1c which is the ground state. This energy difference of 4,84 Kcal/mole can be attributed to the interaction of the positive charges of the two Li cations, which is larger in case of Fig. 1b and minimized in Fig. 1c.

For purposes of completeness, we examined the interaction of Li cation with a series of different nanotubes. We tested if the binding energy of Li cation depends on the type of the nanotube (armchair - zigzag), or the diameter (curvature), or their chirality. Firstly we created armchair carbon nanotubes with different diameters ((5,5), (9,9), (10,10), (11,11), (20,20), (40,40), (80,80)), zigzag carbon nanotubes with different diameters ((9,0), (17,0), (35,0)) and carbon nanotubes with different chiralities ((12,6), (13,10)). Secondly we cut a curved



**Fig. 1.** (4,4) carbon nanotube interacting from its outer sidewalls a) with one Li cation, b,c) with two Li cations, and d) with three Li cations. In the center of the figure, the graph shows the binding energy per alkali atom.

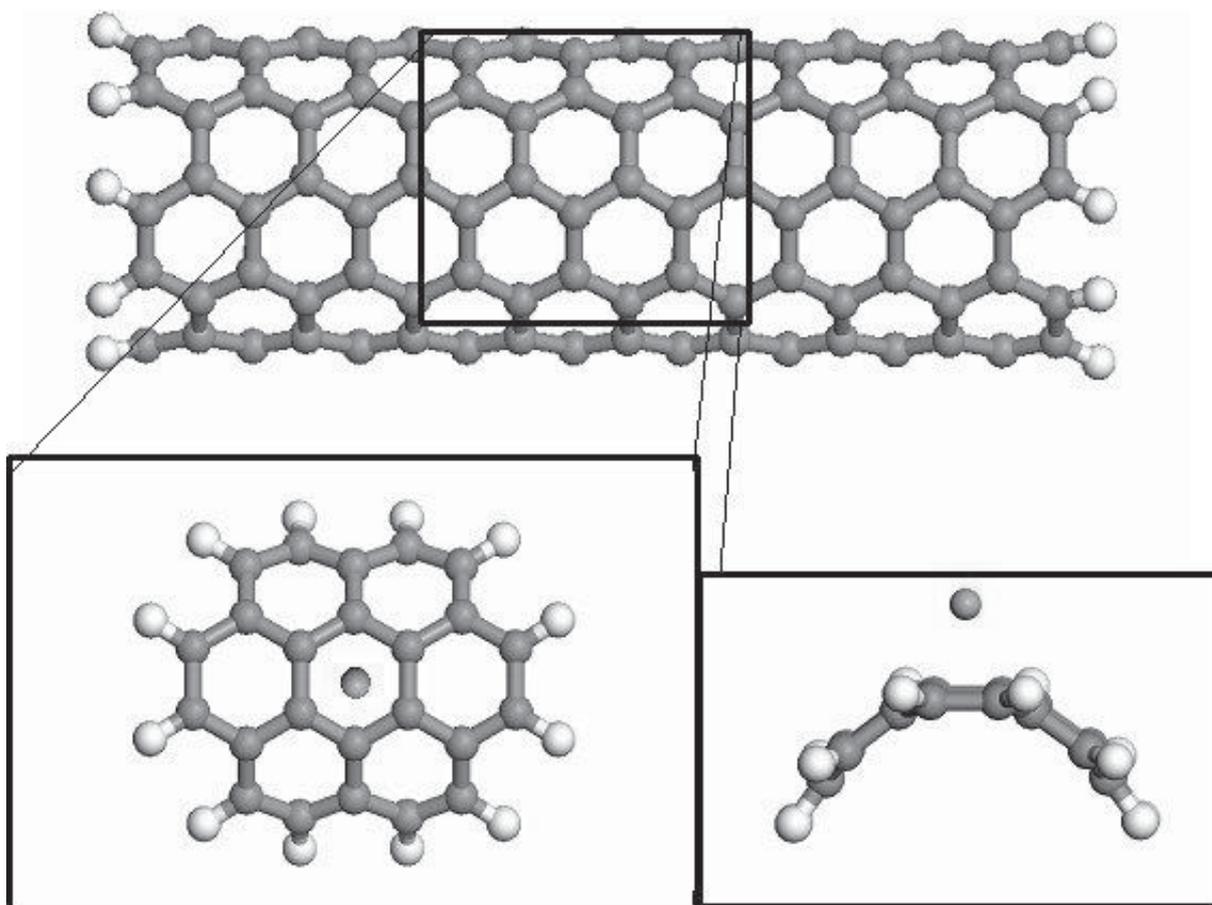
part of the CNT's wall, consisting of 24 carbon atoms and we saturate the dangling bonds with hydrogens. Our model-nanotube system results in  $C_{24}H_{12}$  cluster (Fig. 2). For comparing with graphite we also created the  $C_{24}H_{12}$  system in its planar form.

We implemented the Density Functional Theory on the B3LYP level of approximation using the Gaussian 98 program package [16]. A mixed type of basis is used, describing the central phenyl carbons (6 carbons) and the Li metal with 6-311++G\*\* basis set and the rest of the atoms with the 3-21G basis set. We performed a partial optimization keeping frozen the  $C_{24}H_{12}$  part and relaxing the alkali metal

on the outer sidewall of the nanotube on top of the central phenyl group (Fig. 2). In all the systems studied we obtained the same result: The alkali cation was stabilized on the top of the central phenyl group with almost the same binding energy. The mean value of this interaction is calculated at -48,4 kcal/mole. Our results indicate that there is no dependence on Li<sup>+</sup> binding energy with the type or with diameter of the CNT.

### Molecular Mechanics results

Molecular mechanics calculations were performed in an effort to extend the study of the alkali



**Fig 2.** The procedure of the CNT cut and the resulting model-system of CNT interacting with a  $\text{Li}^+$  ion.

nanotubes interaction to larger systems. The application of *ab initio* calculations in such large systems is prohibitive. We constructed carbon nanotubes of the same length (9.72 Å) resulting in systems containing 120, 240, 480, 960, and 1920 carbon atoms for (5,5), (10,10), (20,20), (40,40), and (80,80) nanotubes, respectively. We implemented the Discover Force Field, and the Compass force-field, of the Materials Studio program package [17].

The calculation of the binding energy of different nanotubes interacting with a single  $\text{Li}^+$  ion, is similar in all cases and follows the same trend as observed in our *ab initio* results. A slightly increasing trend of the binding energy as we go to the tubes of large radius and hence of smaller curvature can be observed. This trend is attributed to the fact that the non-bonding interactions of molecular mechanic calculations were treated with respect to the pair type atoms that interact and to their distances. Hence a Li cation situated above the phenyl center

interacts in the same way with all carbon atoms in the case of planar or quasi-planar phenyl groups i.e. nanotubes with small curvature e.g. (80,80). This result to almost the same  $\text{Li}^+$ -C distance for all carbon atoms of the phenyl group. The value of this distance is very close to the optimum value of  $\text{Li}^+$  - phenyl interaction and to our *ab-initio* results.

The same type of calculations were performed in different type nanotubes for 2, 3, and 4  $\text{Li}^+$  ions in order to see the trend of binding energy as a function of the number of  $\text{Li}^+$  ion placed in the largest possible distance. The binding energy remains constant in almost all cases.  $\text{Li}^+$  ions were far apart so the Coulombic interaction between the ions is negligible, even in the case of four  $\text{Li}^+$  ions peripherally the tube. However, this cannot happen in the narrow 5-5 CNT, where no more than 2  $\text{Li}^+$  ions can be placed far enough. In this case, the Coulombic repulsion increases with the number of ions (Table 2).

**Table 2.** Binding energy (kcal/mole) of different number of alkaline cations and armchair nanotubes of different diameter.

Nanotube type	Number of Li <sup>+</sup> ions				
	1	2	3	4	1(inside)
(5,5)	27.740	27.750	23.260	20.650	58.030
(10,10)	29.090	29.100	29.150	29.110	54.850
(20,20)	30.300	30.260	30.200	30.170	56.280
(40,40)	30.370	30.380	30.450	30.370	31.180
(80,80)	31.150	31.580	31.370	31.260	31.440

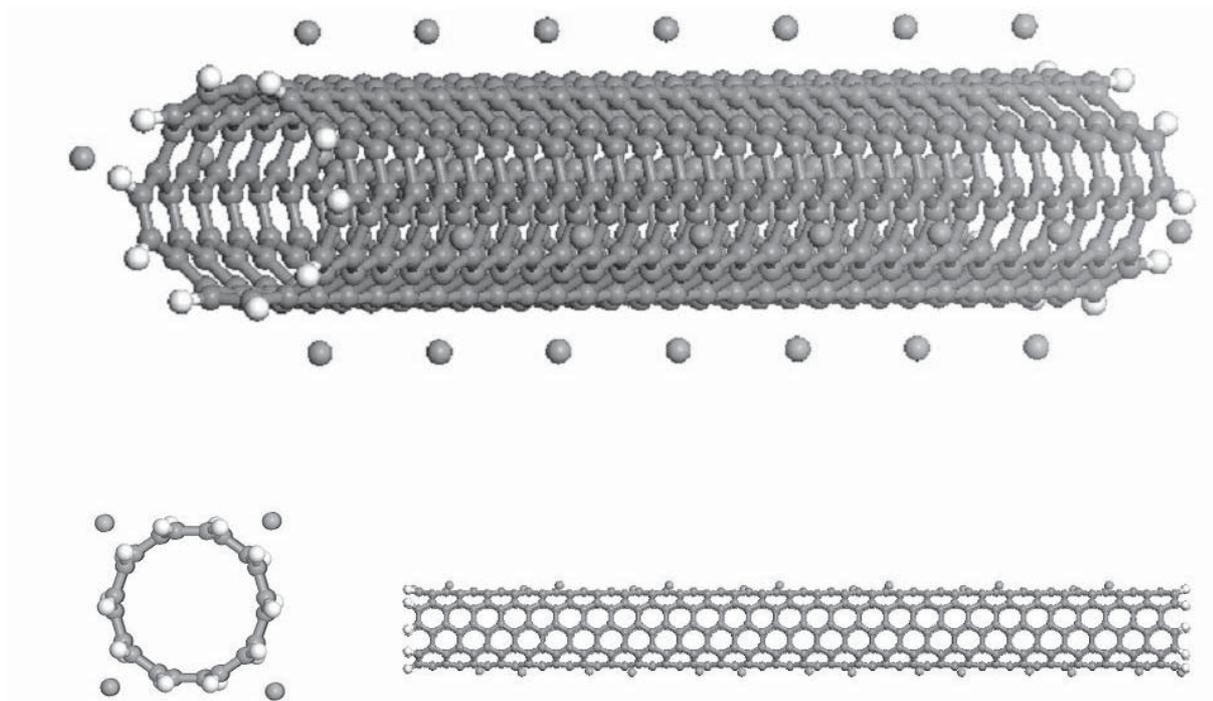
We also tested with molecular mechanic calculations the case of Li<sup>+</sup> ion inside the nanotubes. Binding energies are remarkably larger for tubes (5,5), (10,10), and (20,20). This was expected since the Li<sup>+</sup> inside the nanotube interacts with more carbon atoms than outside. However, this trend vanishes in the case of larger CNTs like (40,40) and (80,80) where Li<sup>+</sup> interacts with the same part of nanotube as in the case of being outside the nanotube. This happens due to the fact that the large CNT radius puts the other peripheral carbon atoms far enough from Li<sup>+</sup> which feel no interaction.

When we increase the number of Li<sup>+</sup> ions inside the tube is the binding energy per Li<sup>+</sup> ion decreases. The larger the tube curvature the more pronounced

decrease is observed. For tubes of small radius, the inner space is too small, so the repulsive interaction between the cations becomes large. Additionally for tubes of larger radius, the inner space is bigger, so the repulsion becomes significant less.

Finally we calculate the highest storage capacity of Li<sup>+</sup> ions interacting with the outer sidewalls of the CNTs. That was found to be C<sub>26</sub>Li (Fig. 3). In a similar study [18] a better ratio was obtained for K, which was C<sub>16</sub>K. However, in that work was also taken into account the interaction of the cation with the inner sidewalls of the nanotubes.

In conclusion, a series of *ab initio* and Molecular Mechanics calculations have been performed to examine the interaction of alkaline cations with car-

**Fig 3.** The structure of higher achieved Li<sup>+</sup> ions to carbon atoms analogy in different views.

bon nanotubes. Our results showed that this interaction is not affected by the type or the diameter of the nanotube when the cation interacts with the outer sidewalls of the CNT. This interaction has a cation –  $\pi$  character and is located between the cation and a phenyl group of the CNT.

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