Adsorption of NH₃ and NO₂ molecules on carbon nanotubes

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Adsorption of NH₃ and NO₂ molecules on semiconducting single-walled carbon nanotubes is investigated using density functional theory. Both NH₃ and NO₂ molecules are found to bind to carbon nanotubes via physisorption. Electron charge transfer is found to be a major mechanism determining the conductivity change in carbon nanotubes upon exposure to NH₃ and NO₂ molecules. The calculated density of states is also considered to elucidate the differences in the NO₂ and NH₃ gas detection mechanism of carbon nanotubes. © 2001 American Institute of Physics.

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Since the discovery of the structure of carbon nanotubes (CNTs),¹ much effort has been devoted to finding uses for these structures in applications ranging from electron field emitters² to nanodevices.³ Recently, Kong et al. proposed the use of CNTs as gas sensors⁴ based on results showing that the electrical conductivity of single-walled CNTs changes dramatically upon exposure to gaseous molecules of NO₂ and NH₃. This observation motivated us to undertake calculations aimed at elucidating the mechanism by which NO₂ and NH₃ molecules are adsorbed on CNTs. Although some studies have investigated the adsorption of other gases such as H₂ and O₂,⁵,⁶ the adsorption of NO₂ and NH₃ on CNTs is not yet clearly understood. In this letter, we report the results of density functional calculations that investigate the change in the electronic structure of CNTs on exposure to NO₂ and NH₃ molecules.

The atomic orbital basis density functional method implanted in DMol³ (Ref. 7) was used. All calculations employed Perdew and Wang’s local density approximation (LDA) functional and double-numerical basis functions (DND).⁷ The adsorption of NH₃ and NO₂ molecules on a (10,0) CNT (Ref. 8) was chosen for study, because the possibility of a NH₃ and NO₂ gas sensor was reported for semiconducting single-walled CNTs.⁴ The (10,0) CNT was calculated by taking a supercell of eight layers along the tube axis (z axis), such that 80 atoms were included in the unit cell.⁹ The CNT was initially constructed maintaining the C–C distance at 1.42 Å, and the structure was then optimized. After optimization, one NH₃ molecule was attached to the tube wall in each unit cell, as shown in Fig. 1(a). Two rotational geometries were considered, as shown in Figs. 1(b) and 1(c), denoted type (I) and type (II). The calculations for the (CNT+NO₂) system were similar to the (CNT+NH₃) calculations. Two geometries of (CNT+NO₂) were considered, type (a) and type (b), as shown in Figs. 2(a) and 2(b), respectively.

The partial density of states (PDOS) of the carbon atoms in the pure (10,0) CNT is plotted in Fig. 3, which was calculated using Loewdin’s population analysis with Gaussian broadening.⁷ In this case, the total DOS (TDOS) per atom is the same as the PDOS of each carbon atom. The TDOS agrees with the experimental observation of zero DOS near the Fermi energy,¹⁰ which is a characteristic of semiconducting CNTs. Here, the Fermi energy was taken to be 0 eV. The energy gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO), Δ, was found to be 0.93 eV, which is close to the experimentally estimated band gap, 0.97 eV.¹¹ These results indicate that the calculation method well describes the local electronic structure of the CNT.

To find the binding configuration, we calculated the binding energy as a function of the distance between the N and C atoms in the CNT. The binding energy, \( E_b(CNT-NH₃) \), was calculated using

\[
E_b(CNT-NH₃) = E_i(CNT+NH₃) - E_i(CNT) - E_i(NH₃),
\]

(1)

FIG. 1. (10,0) CNT with a NH₃ molecule. One NH₃ molecule is attached to each eight-layer unit cell. (a) Two unit cells are shown. (b) Top view of the NH₃ molecule attached to the CNT in type (I) geometry. (c) In type (II) geometry.
where $E_b(CNT+NH_3)$ and $E_b(CNT)$ are the total energies of the CNT with and without a NH$_3$ molecule attached, respectively. $E_b(NH_3)$ is the total energy of an isolated NH$_3$ molecule. First, we located the minimum $E_b$ by varying the C–N distance. The structure of NH$_3$ was then reoptimized, allowing the atoms of the NH$_3$ to relax while the C atoms in the CNT were constrained to their initial positions. The (CNT+NO$_2$) calculations were carried out in a similar way. Optimization did not cause any noticeable change in the molecular geometries of NH$_3$ and NO$_2$. The binding energies and optimized C–N distances calculated for both molecules are listed in Table I. The binding energies are less than 0.5 eV in all cases, which supports the hypothesis that the adsorption of both molecules, (CNT+NH$_3$) and (CNT+NO$_2$), is physisorption.

In contrast to previous studies, a binding configuration for NH$_3$ could be found. Calculations were performed for six different geometries generated by rotating the NH$_3$ molecule between the configurations of type (I) and type (II), as shown in Figs. 1(b) and 1(c). All geometries gave similar optimized distances and binding energies (about −0.18 eV), with differences in energy and distance of less than 0.005 eV and 0.05 Å. These results suggest that the adsorption mechanism in (CNT+NH$_3$) does not depend on the orientation of the NH$_3$ molecule.

Bound configurations were also found for the (CNT+NO$_2$) system, in accord with previous studies. The binding energies for the geometries of type (a) and type (b) in this system were found to be −0.42 eV, which is close to the binding energy of NO$_2$ molecules on graphite (−0.40 eV). For the NO$_2$ molecule, electron charge transfer was found to be from the CNT to the NO$_2$ molecule, whereas for the NH$_3$ molecule electron charge transfer was from the NH$_3$ molecule to the CNT. If the (10,0) semiconducting CNT had hole carriers, NO$_2$ would enhance the carrier concentration by capturing electrons from the CNT, whereas NH$_3$ would reduce the hole concentration by giving up electrons to the CNT. This behavior is in agreement with the experimental observation that the conductivity of CNTs increases on exposure to NO$_2$ gas and decreases on exposure to NH$_3$ gas.

The sensitivity of the response to the gas molecule seems to be related to the amount of electron charge transfer and the binding energy. It was also reported that CNTs respond more quickly and sensitively to NO$_2$ gas than to NH$_3$ gas. Table I shows that the amount of electron charge transfer in the NO$_2$ molecule is twice that in the NH$_3$ molecule. This is also reflected in the stronger binding energy of NO$_2$ than NH$_3$.

The TDOS and PDOS of the (CNT+NH$_3$) system [type (I)] are plotted in Fig. 4. The TDOS of (CNT+NH$_3$) in Fig. 4(a) is not much different from the carbon PDOS near the Fermi energy in Fig. 3. The PDOS of the carbon atom to which the NH$_3$ molecule is attached, shown in Fig. 4(b), is also very similar to the carbon PDOS shown in Fig. 3. This result implies that the electronic structure of the CNT changes only a small amount on addition of the NH$_3$ molecule. The PDOS of the N and H atoms for the system with NH$_3$ attached to the CNT and the isolated NH$_3$ are shown in Figs. 4(c) and 4(d), respectively. The PDOS of N and H lie far below and above the Fermi energy, respectively, and, therefore, hardly change the electronic properties of the CNT near the Fermi energy. Yet, the N atom binds weaker by about 1.5 eV when it is adsorbed on the CNT wall, compared

### Table I. Parameters calculated for adsorption of NH$_3$ and NO$_2$ on the (10,0) CNT wall.

<table>
<thead>
<tr>
<th></th>
<th>CNT+NH$_3$</th>
<th>CNT+NO$_2$</th>
</tr>
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<tbody>
<tr>
<td>$E_b$ (eV)$^a$</td>
<td>−0.18</td>
<td>−0.42</td>
</tr>
<tr>
<td>$R_0$ (Å)$^b$</td>
<td>2.87</td>
<td>2.31</td>
</tr>
<tr>
<td>CT (eV)$^c$</td>
<td>0.04</td>
<td>0.11</td>
</tr>
<tr>
<td>$\Delta$ (eV)$^d$</td>
<td>0.91</td>
<td>0.54</td>
</tr>
</tbody>
</table>

$^a$Binding energy.
$^b$C–N distance.
$^c$Charge transfer from the molecule to the CNT.
$^d$Energy gap between HOMO and LUMO.
to the bare NH$_3$ molecule. In addition, energy gap $\Delta$ hardly changes from the value of the pure CNT, as listed in Table I. The PDOS plots of the type (II) system were very similar to those of type (I). This represents further evidence that the adsorption of NH$_3$ on the CNT does not depend on the orientation of the NH$_3$ molecule.

The TDOS and PDOS for the (CNT+NO$_2$) system in type (a) are plotted in Fig. 5. In contrast to the (CNT+NH$_3$) system, NO$_2$ has a significant effect on the electronic structure of the CNT. The TDOS of (CNT+NO$_2$) shown in Fig. 5(a) differs from the PDOS of the carbon atom in Fig. 3. When NO$_2$ is attached to the CNT, the energy gap ($\Delta$) disappears and a peak appears near the Fermi level, i.e., the tube becomes metallic. This peak originates from the NO$_2$ molecule, as shown by the PDOS plots of N and O in Fig. 5(c). A small peak is observed in the carbon atom PDOS near the Fermi level in Fig. 5(b), which indicates some hybridization of N and O with the C atom. This peak can be assigned as an acceptor level of this system, which enhances the conductivity of the CNT. In the type (b) geometry of the (CNT+NO$_2$) system, a similar acceptor level is found. This acceptor level comes from the electronic properties intrinsic to NO$_2$. The NO$_2$ molecule possesses an unpaired electron, which seems to actively participate in hybridization near the C atom when it is attached to the CNT. On the contrary, NH$_3$ has no unpaired electrons. The paired electrons of the NH$_3$ molecule do not seem to actively interact with the C atom in the CNT wall. Therefore, the electronic structure of the CNT hardly changes in the presence of NH$_3$.

In conclusion, the small binding energies of NO$_2$ and NH$_3$ molecules with the CNT wall indicate that these molecules undergo physical adsorption, and not chemical adsorption. We have found that the electron charge transfer is an important mechanism in changing conductivity in the CNT on adsorption of NO$_2$ or NH$_3$ gas. The charge transfer between the adsorbed molecule and CNT was in opposite directions for the (CNT+NO$_2$) and (CNT+NH$_3$) systems, with electron charge transfer from CNT to NO$_2$ and electron charge transfer from NH$_3$ to CNT. The charge transfer behavior affects the hole concentration of the CNT, giving rise to a change in conductivity. From the PDOS of the calculations, we have found an acceptor level in the (CNT+NO$_2$) system. This strongly suggests that the NO$_2$ molecule accepts electrons from the CNT, in agreement with the electron charge transfer results discussed above. However, we did not find any noticeable change in the PDOS of the (CNT+NH$_3$) system. This may be due to the small amount of charge transfer in the NH$_3$ system compared to the NO$_2$ system. From our calculations, we can explain the difference in adsorption mechanism of NO$_2$ and NH$_3$ molecules on the CNT wall. Our calculations provide theoretical evidence of charge transfer between the molecules and the CNT, as expected from the experimental observations.

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7. Dmol$^3$ is a registered software product of Molecular Simulation Inc.; B. Delley, J. Chem. Phys. 92, 508 (1990), and other references therein.
9. An 80 atom unit cell was chosen after considering the size effects of the unit cell. We calculated the (10, 0) CNT of a 120 atom (12 layer) unit cell. We found that the change of the binding energy was less than 0.05 eV/atom on increasing the size of the unit cell.
11. This value was calculated from the equation in Ref. 10, $F_{pp} = 2\gamma_0\mu_{C,C}/d$, where $\gamma_0$ is 2.7 eV, obtained from the experimental fitting, $\mu_{C,C}$ is the nearest-neighbor C–C distance (1.42 Å), and $d$ is the diameter of the CNT (7.91 Å).