Single molecule capture by a doped monatomic carbon chain

This article has been downloaded from IOPscience. Please scroll down to see the full text article.
2013 J. Phys.: Condens. Matter 25 205302
(http://iopscience.iop.org/0953-8984/25/20/205302)
View the table of contents for this issue, or go to the journal homepage for more

Download details:
IP Address: 123.138.79.27
The article was downloaded on 24/04/2013 at 01:26

Please note that terms and conditions apply.
Single molecule capture by a doped monatomic carbon chain

Zheng-Zhe Lin\textsuperscript{1} and Xi Chen\textsuperscript{2}

\textsuperscript{1}School of Science, Xidian University, Xi’an 710071, People’s Republic of China
\textsuperscript{2}Department of Applied Physics, School of Science, Xi’an Jiaotong University, Xi’an 710049, People’s Republic of China

E-mail: linzhengzhe@hotmail.com

Received 3 January 2013, in final form 7 April 2013
Published 23 April 2013
Online at stacks.iop.org/JPhysCM/25/205302

Abstract

A B-doped monatomic carbon chain has fine molecular capture ability for H\textsubscript{2}O and especially for NO\textsubscript{2}, which is better than that of other doped monatomic carbon chains. At 300 K and 1 atm, the capture probability of a B-doped monatomic carbon chain is appreciable even in a NO\textsubscript{2} concentration of 1 ppm, and the influence of the adsorbate on the quantum transport is notable for the detection. In contrast, a pure monatomic carbon chain shows its invulnerability to N\textsubscript{2}, O\textsubscript{2}, H\textsubscript{2}O, NO\textsubscript{2}, CO and CO\textsubscript{2}, and is incapable of molecule capture due to having too low adsorption ability and weak response to quantum conductance. In the investigation of these issues, a statistic mechanical model (Lin et al 2011 Europhys. Lett. 94 40002; 2012 Chin. Phys. Lett. 29 080504) was extended to predict the adsorption and desorption rates of molecules on nanodevices. The theoretical foundation of this model was further discussed and its accuracy was verified by molecular dynamics simulations.

1. Introduction

The ideal goal of a detection method is to achieve an ultimate sensitivity such that an individual quantum can be resolved. In the case of molecular sensors, the quantum is a single atom or molecule. In order to reach this goal, a great deal of effort has been focused on solid sensors because of their high sensitivity and miniature sizes, leading to their wide use in many applications. As next-generation sensors, detectors made of low-dimensional materials have especially high sensitivity because their whole volume is exposed to adsorbates and the effect is maximized. Such detectors were first prepared using carbon nanotubes and semiconductor nanowires [1, 2], and their high sensitivity to toxic gases in very low concentrations was valuable for industrial and environmental monitoring. Then, a new detection method using single-layer graphene was developed [3]. The signal of even an individual molecule can be detected in the strong magnetic field due to the Hall effect of electrons or holes induced by the adsorbed molecules on the graphene surface acting as electronic donors or acceptors. For one-dimensional monatomic chains, the influence of adsorbates on the electronic properties may be even stronger than that for two-dimensional materials. In recent years, free-standing monatomic carbon chains (MCCs) have been carved out of single-layer graphene by a high-energy electron beam [4], or unraveled from sharp carbon specimens [5, 6] or carbon nanotubes [7], and MCCs have been predicted to be remarkably stable [8]. Recently, a mechanical procedure was proposed to prepare long pure and doped MCCs [9–11] using a nanorectifier [9] or the medium of a tunable infrared laser [12]. It was proposed that the electronic properties of MCCs could be controlled by doping a single atom or a diatomic molecule [9]. As the thinnest natural wires, MCCs should also be greatly influenced by the electronic properties of the molecules adsorbed on them.

In this work, the adsorption and desorption rates of N\textsubscript{2}, O\textsubscript{2}, H\textsubscript{2}O, NO\textsubscript{2}, CO and CO\textsubscript{2} on pure and doped MCCs were studied by an extension of a newly developed statistic mechanical model [8, 13], and the influence of these adsorbates on the current–voltage curves were investigated by quantum transport calculations. The pure MCC was found to be incapable of performing as a molecular capturer due to having too low adsorption ability and the weak response to quantum conductance. In contrast, the B-doped MCC has fine capture ability for H\textsubscript{2}O and remarkably for NO\textsubscript{2}. In the ambient of 300 K and 1 atm, the molecular capture probability is appreciable and the electric signal is notable even in a NO\textsubscript{2} concentration of 1 ppm.
2. Theoretical model and methodology

Generally, elementary processes correspond to some individual events in which one or two ‘key atoms’ cross over a static barrier \(E_0\). For the adsorption of molecules on nanodevices, a basic event takes place when a molecule hits the nanodevice with a translational kinetic energy \(\varepsilon \geq E_0\) and a specific orientation for the key atom in the molecule and the nanodevice to contact with each other. At room temperature or above, the thermal De Broglie wavelength of a molecule is at least 100 times smaller than its size, and then the molecular motion can be understood in a classical picture. By the classical ensemble theory, the distribution of molecular translational kinetic energy is Boltzmann, i.e. \(f(\varepsilon) \sim e^{\varepsilon/k_B T}/\sqrt{\pi (k_B T)^3/2}\). On this basis, a simple model was built for the prediction of bimolecular chemical reaction rates [13]. Here, a similar idea was provided for predicting the molecular adsorption rate on nanodevices. By the Boltzmann distribution, the probability for the molecular translational kinetic energy \(\varepsilon \geq E_0\) reads

\[
P = \frac{1}{Z} \int_{E_0}^{+\infty} e^{\varepsilon/k_B T} \, d\varepsilon, \tag{1}
\]

where \(Z = \int_0^{+\infty} e^{\varepsilon/k_B T} \, d\varepsilon = \sqrt{\pi (k_B T)^{3/2}}\) is the partition function. Therefore, for molecules at a concentration \(c\), the corresponding adsorption rate should be

\[
\Gamma = \frac{c \nu v e}{2Z} \int_{E_0}^{+\infty} e^{\varepsilon/k_B T} \, d\varepsilon, \tag{2}
\]

where \(\sigma\) is the effective cross-section of the nanodevice and \(v = \sqrt{2k_B T/\pi M}\) is the average thermal velocity of a molecule along the cross-section normal. The factor 1/2 is because only half of the molecules move towards the cross-section. It should be noted that \(\sigma\) is not equal to the geometry cross-section \(S\) of the key atom in the nanodevice (figure 1(a)), but instead \(\sigma = \Omega_m/4\pi\), where \(\Omega_m\) is the solid angle opened by the key atom in the molecule. In practical applications, \(\Omega_m\) can be estimated by the atomic distance to the molecular mass center and atomic covalent radius [13].

For the elementary processes within a system, e.g. the molecular desorption from a nanodevice, a basic event takes place when the key atom in a potential valley crosses over the barrier with a kinetic energy \(\varepsilon\) at the valley bottom larger than \(E_0\). The atomic kinetic energy distribution is determined by

\[
f(\varepsilon) = \sum f_i(\varepsilon) e^{-E_i/k_B T}/\sum e^{-E_i/k_B T},
\]

where \(f_i(\varepsilon)\) is the kinetic energy distribution of the quantum state \(E_i\). As an example, \(f(\varepsilon)\) of an atom in a \(\text{Cl}_2\) molecule is shown in figure 1(b). At room temperature or above, the distribution \(f(\varepsilon)\) turns into the classical one. For a classical system including \(N\) atoms, the total energy \(E = \sum_{i=1}^N E_i/2m_i + \sum_{i=1}^N V(x_1, \ldots, x_N)\) and the kinetic energy distribution of the \(i\)th atom reads

\[
f(\varepsilon) = \int \delta(P_i/2m_i - \varepsilon) e^{-E_i/k_B T} \, dP_1 \ldots dP_N \, d\varepsilon_1 \ldots d\varepsilon_N = \frac{\pi^{N/2} e^{\varepsilon_0/k_B T}}{\sqrt{2\pi m_i k_B T}}\, \frac{1}{\Gamma} \int e^{\varepsilon_0/k_B T} \, d\varepsilon_0
\]

\[
= \varepsilon^{N/2} e^{-\varepsilon/k_B T}/Z. \tag{3}
\]

This Boltzmann distribution for the atomic kinetic energy is in very good agreement with MD simulations [8]. In most cases, the atomic kinetic energy \((\sim k_B T)\) at the valley bottom is significantly smaller than \(E_0\), and the atom vibrates many times within the valley before crossing over the barrier. With a vibration frequency \(\Gamma_0\), the rate for the atomic event reads

\[
\Gamma_0 = \frac{\Gamma_0}{Z} \int_{E_0}^{+\infty} e^{\varepsilon/k_B T} \, d\varepsilon. \tag{4}
\]

For a given \(\varepsilon\), the oscillation period \(\tau(\varepsilon) = \sqrt{m} \int \, d\varepsilon / 2[\varepsilon - V(\varepsilon)]\) along the minimum energy path (MEP) can be determined by \(V(\varepsilon) = \int \vec{F}(\varepsilon) \cdot d\vec{x}\), where \(\vec{F}(\varepsilon)\) is the force felt by the key atom at position \(\varepsilon\) [8]. With the corresponding oscillation frequency \(\nu(\varepsilon) = 1/\tau(\varepsilon)\), the averaged frequency reads

\[
\nu(\varepsilon) = \frac{\int_{E_0}^{E_0} \nu(\varepsilon) e^{\varepsilon/k_B T} \, d\varepsilon}{\int_{E_0}^{E_0} e^{\varepsilon/k_B T} \, d\varepsilon}. \tag{5}
\]

For two-key-atom processes, an event takes place when the atomic kinetic energy sum \(\varepsilon_1 + \varepsilon_2 \geq E_0\), and the

![Figure 1](image-url)
corresponding rate should be
\[
\Gamma = \frac{\Gamma_0}{Z^2} \int_{\epsilon_1+\epsilon_2 \geq E_0} \epsilon_1^{1/2} \epsilon_2^{1/2} e^{-((\epsilon_1+\epsilon_2)/k_B T)} d\epsilon_1 d\epsilon_2
\]
\[
= \frac{\Gamma_0}{2(k_B T)^2} \int_{E_0}^{+\infty} \epsilon^2 e^{-\epsilon/k_B T} d\epsilon.
\]

In our previous work [8], equations (4) and (6) were verified by MD simulations and successfully applied to predict the stability of an MCC–graphene junction and bonds in the MCC body, producing results in good agreement with the experimental data.

To investigate the molecular adsorption and desorption rates on MCCs, ab initio calculations were performed for a ten-atom pure or doped MCC bridged between two graphene lattices in the armchair (figure 2(a)) or zigzag (figure 2(b)) orientation with the atoms shown in black fixed. Simulations were carried out for pure, B-doped, N-doped and BN-doped MCCs coupling with N₂, O₂, H₂O, NO₂, CO and CO₂ molecules. The geometry optimizations, reaction barriers \( E \) and MEPs and forces \( F(x) \) felt by the key atom were calculated using the pseudoreaction coordinate method on the level of density functional theory (DFT) via the Gaussian 03 package [14] with the 6-31G(d, p) basis set and the newly developed hybrid X3LYP functional including dispersion interactions [15], which is considered to be more accurate than other functionals in potential surface and MEP calculations. Canonical modes for the geometries of potential minima and transition states were calculated to confirm the optimization results.

For quantum transport, the simulation system was set up by appending semi-infinite graphene electrodes in the armchair (figure 2(a)) or zigzag (figure 2(b)) orientation to the two terminals of the pure or doped MCC, with or without the adsorbed molecule. Calculations were performed by the TRANSIESTA package [16], using a non-equilibrium Green’s function [17] at the level of the Perdew–Burke–Ernzerhof parameterized generalized-gradient approximation [18] with the Troullier–Martins pseudopotential [19] and a localized double-zeta polarized basis set in order to preserve a correct description of \( \pi \)-conjugated bonds. The mesh cutoff energy was 150 Ryd, and a \( k \)-point sampling of \( 1 \times 8 \times 100 \) was used. For a bias voltage \( V_b \) applied on the electrodes, the current is given by the Landauer–Büttiker equation [16]
\[
I = \frac{2e}{h} \int T(E, V_b) \left[ f_L \left( E - E_F - \frac{eV_b}{2} \right) - f_R \left( E - E_F + \frac{eV_b}{2} \right) \right] dE,
\]
where \( T(E, V_b) \) is the scattering coefficient of the band state at energy \( E \), \( E_F \) is the Fermi energy of the electrodes and \( f_L \) and \( f_R \) are the Fermi–Dirac distribution functions of the two electrodes, respectively. As buffer layers, sufficient graphene lattices in the scattering region are essential to screen the induced electric field between the two electrodes. Our calculations showed that the transport properties do not change appreciably when there are at least two buffer layers for the armchair orientation, or three for the zigzag orientation.

3. Results and discussion

3.1. MD simulation
To verify equation (2), molecular dynamics (MD) simulations were performed for molecular adsorption on a monatomic chain. The simulation system was set up by placing a 20-atom MCC with its terminals fixed and 33 helium atoms as the buffer gas (BG) along with a diatomic molecule initialized in a random position in a periodic cubic box with a side length of 30 Å. The BG atoms were controlled by a thermal bath at temperature \( T \). The Brenner potential [20, 21] was applied for C–C interactions, and the interaction between the atoms of the diatomic molecule reads
\[
V_{mm}(r) = C_1 e^{C_2r} - C_3 e^{-C_4r},
\]
with a bond energy of 1.05 eV (\( C_1 = 9.073 \times 10^5 \) eV, \( C_2 = 10.925 \text{ Å}^{-1} \), \( C_3 = 3.514 \text{ eV} \) and \( C_4 = 0.764 \text{ Å}^{-1} \)). A modified Lennard-Jones potential
\[
V_{cm}(r) = D_1/r^{12} - D_2/r^6 + D_3/r^3
\]
was designed for the interaction between C and the atoms of the diatomic molecule (\( D_1 = 3.028 \times 10^3 \text{ eV Å}^{12} \), \( D_2 = 3.177 \times 10^2 \text{ eV Å}^6 \) and \( D_3 = 33.348 \text{ eV Å}^3 \)). These parameters for the artificially constructed potential equations (8) and (9) were
The molecule can go away from the MCC along the radial atoms is larger than $E_\epsilon$ place when the bond between the MCC and the molecule equation (2) becomes $\text{MCC}$ is estimated as follows. For the barrierless adsorptions, for $N_2$ without barriers, while only repulsive interactions were found a pure MCC, the potential drops to a valley of 0.017–0.028 eV by an atom in the molecule gets close to $2\pi(\text{figure 3(a)})$. For a diatomic molecule, the solid angle taken appears, and $L$ verification of the model. For chosen parameters for equations (8) and (9) do not affect the of any diatomic molecule on a monatomic chain, and the it is suitable for the adsorption and desorption progress not depend on the specific form of the interaction potential, the time scale of MD simulations. Because our model does adjusted to let the adsorption and desorption occur within the time scale of MD simulations. Because our model does not depend on the specific form of the interaction potential, it is suitable for the adsorption and desorption progress of any diatomic molecule on a monatomic chain, and the chosen parameters for equations (8) and (9) do not affect the verification of the model. For $T = 700$–$2000$ K, the average time for one event is in the range of several $\mu$s to several hundreds of ps, and simulations were performed repeatedly at every temperature until the average adsorption rate changed by less than 5% (about 10 times for low temperature and $10^3$ times for high temperature). The geometry cross-section $\sigma$ of the 20-atom MCC is estimated as $S = 20 \times 2\pi dL = 1101.07$ Å$^2$, where $d = 6.74$ Å is the distance from the molecular mass center to the MCC axis where the barrier $E_0$ appears, and $L = 1.30$ Å is the C–C bond length in the MCC (figure 3(a)). For a diatomic molecule, the solid angle taken by an atom in the molecule gets close to $2\pi$, and for the two atoms $\sigma = S\Omega_m/4\pi \approx S$. From the results, the adsorption rates predicted by equation (2) are in good agreement with MD (figure 3(b)). It is worth noting that the model is also applicable to triatomic or polyatomic molecules because equation (2) is independent of the molecular geometry.

### 3.2. DFT calculation for a pure MCC

Along the MEPs of NO$_2$, CO and CO$_2$ molecules approaching a pure MCC, the potential drops to a valley of 0.017–0.028 eV without barriers, while only repulsive interactions were found for $N_2$ and H$_2$O (table 1). The molecular coverage of the MCC is estimated as follows. For the barrierless adsorptions, equation (2) becomes $\Gamma_a = \sigma v_c/2$. The desorption event takes place when the bond between the MCC and the molecule breaks, i.e., the kinetic energy sum $\epsilon_1 + \epsilon_2$ of the two bonding atoms is larger than $E_0$, and equation (6) should be applied. The molecule can go away from the MCC along the radial direction and two tangential directions perpendicular to the chain axis, and, indeed, three equivalent paths were found in the MEP calculations. In the NO$_2$ ambient of 300 K and 1 atm, by $\sigma \approx 28.0$ Å$^2$ the molecular adsorption rate on one C atom is about $\Gamma_a = 6.4 \times 10^9$ s$^{-1}$. By $E_{0a} = 0.024$ eV and $\Gamma_0 = 1.0 \times 10^{13}$ s$^{-1}$, the corresponding desorption rate is estimated to be $\Gamma_d = 2.8 \times 10^{12}$ s$^{-1}$, and so in equilibrium the ratio of C atoms covered by NO$_2$ molecules is $R = \Gamma_d/(\Gamma_a + \Gamma_d) \approx 0.02\%$. At 1000 K, the ratio even decreases to $R \approx 0.01\%$. Such weak interaction presents the invulnerability of MCCs to these molecules, and they have little influence on the quantum transport. The $I$–$V_6$ curves are shown in figures 4(a) and (b), for the graphene electrodes in the armchair and zigzag orientations, respectively. Similar situations are also found for CO and CO$_2$. Such small molecular coverage probability and small difference of the $I$–$V_6$ curve between a solo MCC and an MCC with an adsorbed molecule means that a pure MCC could not be used as a capturer or detector for these molecules.

For the O$_2$ molecule, barriers of $E_{0a} = 0.93$ eV for the adsorption and $E_{0d} = 0.38$ eV for the desorption (table 1) were found in the MEP calculation (figure 4(c)), respectively, corresponding to adsorption and desorption rates much slower than those in NO$_2$, CO and CO$_2$ due to these barriers. In the ambient of 1 atm O$_2$ at 300 K, it takes $\tau_a = 1/\Gamma_a = 222$ h and $\tau_d = 1/\Gamma_d = 346$ h for a C atom to capture and release one O$_2$ molecule, respectively (figure 4(d)). Note that although $E_{0a} > E_{0d}$, the adsorption time $\tau_a$ is shorter than the desorption time $\tau_d$ because of the high O$_2$ concentration $c$. In equilibrium the coverage ratio of O$_2$ on the MCC is up to $R = \Gamma_d/(\Gamma_a + \Gamma_d)$ $\approx 60.9\%$. However, such status cannot be achieved in a short time due to too long $\tau_a$ and $\tau_d$. At higher temperature, $\tau_a$ becomes much shorter than $\tau_d$ by orders of magnitude, and so the coverage of O$_2$ sharply increases. For example, at 400 K it takes $\tau_a = 132$ s for a C atom to capture an O$_2$, but $\tau_d = 15$ h for the release process (figure 4(d)). In this case, the MCC will be rapidly oxidized because the coverage of O$_2$ becomes

---

### Table 1. The adsorption and desorption barriers of some molecules against a pure MCC, in which ‘—’ means unable to be adsorbed.

<table>
<thead>
<tr>
<th></th>
<th>NO$_2$</th>
<th>CO</th>
<th>CO$_2$</th>
<th>$N_2$</th>
<th>H$_2$O</th>
<th>O$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Adsorption barrier $E_{0a}$ (eV)</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>—</td>
<td>—</td>
<td>0.93</td>
</tr>
<tr>
<td>Desorption barrier $E_{0d}$ (eV)</td>
<td>0.024</td>
<td>0.017</td>
<td>0.028</td>
<td>—</td>
<td>—</td>
<td>0.38</td>
</tr>
</tbody>
</table>

---

**Figure 3.** The cross-section $\sigma$ for the adsorption of a molecule (a) described by the artificially constructed potential equations (8) and (9), and the corresponding adsorption rate (b) on a 20-atom MCC.
Figure 4. The $I-V_b$ curves for a solo MCC and an MCC with an adsorbed NO$_2$ molecule, with the graphene electrodes in the armchair (a) or zigzag (b) orientation. The potential energy profile along the MEP with the changing distance from the O$_2$ mass center to the MCC axis (c). The average time $\tau = 1/\Gamma$ taken for a C atom in the MCC to capture (solid line) or release (dashed line) a molecule in the ambient of 1 atm O$_2$ (d).

Table 2. The adsorption and desorption barriers of some molecules against a B-doped MCC.

<table>
<thead>
<tr>
<th></th>
<th>NO$_2$</th>
<th>CO</th>
<th>CO$_2$</th>
<th>N$_2$</th>
<th>H$_2$O</th>
</tr>
</thead>
<tbody>
<tr>
<td>Adsorption barrier $E_{0a}$ (eV)</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.75</td>
</tr>
<tr>
<td>Desorption barrier $E_{0d}$ (eV)</td>
<td>1.27</td>
<td>0.001</td>
<td>0.012</td>
<td>0.021</td>
<td>1.12</td>
</tr>
</tbody>
</table>

$R = \Gamma_a/(\Gamma_a + \Gamma_d) \approx 99.8\%$. Therefore, a pure MCC is not suitable for O$_2$ capture either at room temperature or at higher temperature.

3.3. DFT calculation for B- and N-doped MCCs

The molecular adsorption ability could be enhanced by doping one B atom in the MCC because of the bonding by the injecting electrons of the molecule to the empty orbital of the B atom. According to the result, such bonding was found for H$_2$O and NO$_2$ molecules. For H$_2$O, the unshared pair of electrons on the O-atom couples with the B atom, providing an adsorption barrier $E_{0a} = 0.75$ eV and a desorption barrier $E_{0d} = 1.12$ eV (table 2). For a longer MCC, $E_{0a}$ becomes a little lower. At the saturated vapor pressure of H$_2$O at 300 K (3.6 kPa, corresponding to a concentration of $1.4 \times 10^{-3}$ mol l$^{-1}$), it takes $\tau_a = 1/\Gamma_a = 3.7$ h for the B atom to capture an H$_2$O molecule, and the H$_2$O molecule stays on the B atom for $\tau_d = 1/\Gamma_d = 12$ min, which is long enough for detection of the captured molecule (figure 5(a)). Although $E_{0a} < E_{0d}$, $\tau_a$ is longer than $\tau_d$ due to the low H$_2$O concentration $c$. At higher temperature, although the time $\tau_a$ for the capture is much shorter, detection becomes unfeasible because $\tau_d$ decreases by orders of magnitude and the captured molecule cannot stay for an appreciable time. For example, at 400 K it takes $\tau_a = 13$ s for one capture, but the H$_2$O molecule only stays for $\tau_d = 26$ ms on the B atom. When the temperature is below 250 K, $\tau_a$ becomes much larger than that at 300 K by orders of magnitude, indicating that the molecule capture event can hardly occur at low temperature. Therefore, the B-doped MCC could be an H$_2$O capturer only at a temperature near 300 K. For quantum transport, the adsorption of H$_2$O leads to an obvious reduction in the current $I$ for the graphene electrodes, no matter whether they are in the armchair (figure 5(c)) or zigzag (figure 5(d)) orientation, which acts as a notable detectable signal of the B-doped MCC capturing an H$_2$O molecule.

The adsorption of NO$_2$, CO, CO$_2$, and N$_2$ molecules on the B atom of the doped MCC was found to be barrierless (table 2). For CO, CO$_2$, and N$_2$, the adsorbed molecule leaves the MCC quickly with a high rate $\dot{\omega}_d$ because of too small $E_{0d}$. For NO$_2$, the corresponding adsorption rate $\Gamma_a = \sigma v_c/2$ is much faster than that of H$_2$O by orders of magnitude. In the NO$_2$ ambient of 1 atm and the temperature range of $T = 300$–1000 K, the time $\tau_a = 1/\Gamma_a = 2 \times 10^{-3}$–3 $\times 10^{-3}$ $\mu$s means that the adsorption of NO$_2$ on the B atom takes place quickly. The desorption barrier, i.e. the adsorption energy, was found to be $E_{0d} = 1.27$ eV. At 300 K, the time $\tau_d = 1/\Gamma_d = 20$ h for which the captured NO$_2$ molecule stays on the B atom means that the molecule can hardly escape (figure 5(b)).
The average time $\tau = 1/\Gamma$ taken for the B atom in the doped MCC to capture a molecule in an H$_2$O vapor of 3.6 kPa (solid line), or to release an adsorbed H$_2$O molecule (dashed line) (a); $\tau$ for the B atom releasing an adsorbed NO$_2$ molecule (b). The $I$–$V_b$ curves for a solo B-doped MCC or a B-doped MCC with an adsorbed H$_2$O or NO$_2$ molecule on the B atom, with the graphene electrodes in the armchair (c) or zigzag (d) orientation.

$\tau_d$ decreases with increasing temperature (figure 5(b)), and the desorption event, i.e. $\tau_d < \tau_a$, occurs at temperatures above 1000 K. At 300 K and 1 atm, even when the NO$_2$ concentration decreases to 1 ppm (i.e. a partial pressure of 0.1 Pa), the time $\tau_a = 1.9$ ms to capture an NO$_2$ molecule is still short. Therefore, the B-doped MCC should be a very good capturer for NO$_2$ even in very low concentration. However, notable reduction in the quantum transport current $I$ was only found for the graphene electrodes in the zigzag orientation (figure 5(d)), while no obvious change in the $I$–$V_b$ curve was found for the armchair one (figure 5(c)).

An MCC doped by an N atom or a BN diatomic molecule has much lower molecule capture ability than the B-doped MCC. The desorption barrier $E_{0d}$ is in the range of 0.1–0.4 eV for a captured H$_2$O or NO$_2$ molecule to leave an N-doped or BN-doped MCC, while repulsive interactions were found for N$_2$, CO and CO$_2$. Such low $E_{0d}$ corresponds to a very small $\tau_d$ of the order of magnitude of $10^{-7}$–$10^{-3}$ µs at room temperature, indicating that the N-doped and BN-doped MCCs could not be used as molecular capturers.

3.4. Conditions for a good molecular capturer

A good molecular capturer should have a short molecular adsorption time $\tau_a = 1/\Gamma_a$ and a long desorption time $\tau_d = 1/\Gamma_d$. For general molecules, the molecular mass and collision cross-section with one atom in the monatomic chain could be roughly estimated as $M \approx 10$–50 amu and $\sigma \approx 10$–50 Å$^2$, respectively, and by equation (5) $\Gamma_0$ generally has a value in the range of $10^{13}$–$10^{14}$ s$^{-1}$. Therefore, $\tau_a$ and $\tau_d$ can be estimated by equations (2) and (6). At 300 K, in the 1 atm ambient of the molecule $\tau_a$ is less than several hours if $E_{0a} < 0.8$ eV, and $\tau_d$ is longer than dozens of minutes if $E_{0d} > 1.1$ eV. For a B-doped MCC, the H$_2$O molecule against the B atom just fits this condition, and the NO$_2$ molecule could be well captured by the B atom because $E_{0a} = 0$ and the $E_{0d}$ is larger than that of H$_2$O. In contrast, a pure or N-doped MCC could not be a good molecular capturer due to too low $E_{0d}$.

4. Summary

In this work, a statistic mechanical model [8, 13] was extended to the predict the adsorption and desorption rates of small molecules on nanodevices. This model is based on the fact that the kinetic energy distribution of atoms or molecules always obeys $\epsilon^{3/2}e^{-\epsilon/k_B T}$, and its theoretical foundation was further investigated. The accuracy of the corresponding extension was verified by MD simulations. By ab initio calculations, the extended model was applied to prediction of the adsorption and desorption rates of N$_2$, O$_2$, H$_2$O, NO$_2$, CO and CO$_2$ on pure and doped MCCs. From the results, a pure MCC is incapable of being a molecular capturer due to low adsorption probability for N$_2$, H$_2$O, NO$_2$, CO and CO$_2$ molecules at room temperature, and the influence of these molecules on the current–voltage curves is weak due to the poor adsorption. For O$_2$, at room temperature the corresponding adsorption rate is too slow, while at higher temperature the MCC will be rapidly oxidized. In contrast, a B-doped MCC has fine capture ability for H$_2$O and remarkably for NO$_2$, which is better than that of N-doped or BN-doped MCCs, and the
reduction of the quantum transport current by the captured molecule is notable, which could be a detectable electronic signal of the molecule capture. At room temperature and 1 atm, even in a NO$_2$ concentration of 1 ppm, the change in the current–voltage curves of the B-doped MCC is appreciable and the captured NO$_2$ could stay for a long time on the B atom, indicating that the B-doped MCC could be a very good single molecule capturer and detector for NO$_2$.

Acknowledgment

This work was supported by the Fundamental Research Funds for the Central Universities.

References