# BINDING OF A FLUORINE ATOM TO THE SIDEWALL OF SINGLE-WALLED CARBON NANOTUBES

**Margulis Vl.A.*, Muryumin E.E., Tomilin O.B.**
N.P. Ogarev Mordovian State University,
Bolshevistskaya str. 68, Saransk, 430000 Russia
* *E-mail: 612033@inbox.ru*

## Introduction

In the present report we aim to investigate the chemisorption of a fluorine atom on the outer surface of zigzag single-walled carbon nanotubes (SWCNTs). Our treatment of this problem follows the line of the theory originally developed by Newns [1] based on a model proposed by Anderson [2] for the similar problem of a magnetic impurity in the bulk of a metal. Recently, we have employed this model to study atomic hydrogen chemisorption on the SWCNTs [3] and obtained reasonably good results for the chemisorption energy. There is also good reason to believe that the model with an appropriate set of parameters is suitable for the study of atomic chemisorption of fluorine, presented in this report.

## Theoretical background

We adopt the same chemisorption model as in our previous work [3], which within the unrestricted Hartree-Fock approximation involves a self-consistent calculation of the electronic charge on the adatom. The basis elements needed for the calculation are the adsorbate spectral density $\rho_a^\sigma(\varepsilon)$ and the adatom Green's function $G_a^\sigma(\varepsilon)$ which are connected by the relation

$$\rho_a^\sigma(\varepsilon) = -\frac{1}{\pi}\,\mathrm{Im}\,G_a^\sigma(\varepsilon), \tag{1}$$

where

$$G_a^\sigma(\varepsilon) = \left[\varepsilon - E_{a\sigma} - \Lambda_a^{(\nu)}(\varepsilon) + i\Delta_a^{(\nu)}(\varepsilon)\right]^{-1} \tag{2}$$

with $E_{a\sigma}$ being an effective adatom energy level and with the so-called chemisorption functions $\Delta_a^{(\nu)}(\varepsilon)$ and $\Lambda_a^{(\nu)}(\varepsilon)$ defined as

$$\Delta_a^{(\nu)}(\varepsilon) = \frac{\pi}{\sqrt{N}} V_0 \sum_\lambda \delta(\varepsilon - \varepsilon_{\nu\lambda}), \tag{3}$$

$$\Lambda_a^{(\nu)}(\varepsilon) = \frac{1}{\pi} P \int_{-\infty}^{\infty} \frac{\Delta_a^{(\nu)}(\varepsilon')}{\varepsilon - \varepsilon'}\,\mathrm{d}\varepsilon'. \tag{4}$$

Here $\lambda$ labels the electronic states of the SWCNT with the chiral index ($p$,0), which are described by a simple two-band $\mathbf{k}\cdot\mathbf{p}$ model based on an effective mass approximation [4], $p$ being equal to $3M+\nu$ with integer $M$ and $\nu = 0(\pm 1)$ for metallic (semiconducting) SWCNTs. The energy bands in Eq.(3) are given by

$$\varepsilon_{\nu\lambda}(k) = \pm\sqrt{\varepsilon_{\nu m}^2 + \gamma^2 k^2} \tag{5}$$

with

$$\varepsilon_{\nu m} = \frac{\gamma}{R}\left(m - \frac{\nu}{3}\right), \tag{6}$$

where the sign $+(-)$ refers to the conduction (valence) band, $m = 0, \pm1, \pm2, \ldots \pm (p-1)$, $R$ is the tube radius, $\gamma$ is the $\mathbf{k}\cdot\mathbf{p}$ interaction parameter, $k$ is the wave vector along the tube axis. In Eq.(3), $V_0$ denotes the transfer integral between the adatom orbital $|a\rangle$ and the $\pi$-orbital of the nearest-neighbouring C atom of the SWCNT, and $N$ is equal to $4p$.

Within the Anderson-Newns model of chemisorption [1,2], the effective adatom level $E_{a\sigma}$ is shifted to

$$E_{a\sigma} = \varepsilon_a + V_{\mathrm{im}} + (U - 2V_{\mathrm{im}})\langle n_{a-\sigma}\rangle, \tag{7}$$

where $V_{\mathrm{im}}$ is the image potential energy, $U$ is the intra-atomic Coulomb repulsion on the adatom and $\langle n_{a-\sigma}\rangle$ is the expected occupancy of the adatom by an electron of spin $-\sigma$.

Integrating $\rho_a^\sigma(\varepsilon)$ with a cutoff function $g_c(\varepsilon)$ introduced by Ando et al. [5] yields

$$\langle n_{a\sigma}\rangle = \int_{-\infty}^{\mu_\nu} \rho_a^\sigma(\varepsilon) g_c(\varepsilon)\,\mathrm{d}\varepsilon + \delta_{\nu,\pm1}\langle n_{a\sigma}\rangle_{\mathrm{loc}}, \tag{8}$$

where $\mu_\nu = (\gamma/3R)\delta_{\nu,\pm1}$ and

$$\langle n_{a\sigma}\rangle_{\mathrm{loc}} = \left[1 - \partial\Lambda_a^{(\nu=\pm1)}(\varepsilon)/\partial\varepsilon\right]^{-1}_{\varepsilon=\varepsilon_{\mathrm{loc}}}, \tag{9}$$

$\varepsilon_{\mathrm{loc}}$ being the solution of the equation

$$\varepsilon - E_{a\sigma} - \Lambda_\sigma^{(\nu=\pm1)}(\varepsilon) = 0, \tag{10}$$

which determines the localized state energy in the band gap of semiconducting SWCNTs.

The $\langle n_{a\sigma}\rangle$ in Eq.(8) via $E_{a\sigma}$ is a function of $\langle n_{a-\sigma}\rangle$

$$\langle n_{a\sigma}\rangle = f\left(\langle n_{a-\sigma}\rangle\right) \qquad (11)$$

and similarly the $\langle n_{a-\sigma}\rangle$ is a function of $\langle n_{a\sigma}\rangle$

$$\langle n_{a-\sigma}\rangle = f\left(\langle n_{a\sigma}\rangle\right), \qquad (12)$$

so the self-consistent condition is

$$f\left[f\left(\langle n_{a\sigma}\rangle\right)\right] - \langle n_{a\sigma}\rangle = 0, \qquad (13)$$

which always has a non-magnetic solution at $\langle n_{a\sigma}\rangle = \langle n_{a-\sigma}\rangle$.

Lastly, the chemisorption energy $\Delta E$ may be written as

$$\Delta E = \sum_{\sigma} \Delta E^{1\sigma} - U\langle n_{a\sigma}\rangle\langle n_{a-\sigma}\rangle - \varepsilon_a - V_{\mathrm{im}}, \qquad (14)$$

where the change in the one-electron energy produced by chemisorption is

$$\Delta E^{1\sigma} = \varepsilon_{\mathrm{loc}}^{\sigma} + \frac{1}{\pi}\int_{-\infty}^{\mu_v} g_c(\varepsilon)\tan^{-1}\left[\frac{\Delta_a^{(v)}(\varepsilon)}{\varepsilon - E_{a\sigma} - \Lambda_a^{(v)}(\varepsilon)}\right] \mathrm{d}\varepsilon. \qquad (15)$$

## Results and discussion

Using the above formulas we have calculated $\Delta E$ for a single fluorine atom adsorbed on top of a carbon atom. We have considered a number of zigzag SWCNTs ($p$,0) with $p$ changing from 5 to 15 in order to investigate how their electronic structure, which may be either metallic or semiconducting, affects the chemisorption energy. The parameters needed for the calculation are chosen to be as follows: $U$ = 13.9 eV, $V_{\mathrm{im}}$ = 4 eV and $B$ = 0.9. The values of $V_{\mathrm{im}}$ and $B$ are adjusted, ad hoc, so that the calculated adsorption energy $\Delta E$ for a grapheme plane is equal to the experimental value (about 1.8 eV) reported in the literature. The results of our calculations are shown in Fig. 1.

The curves in this figure clearly show significantly different behaviour of $\Delta E$ for metallic and semiconducting SWCNTs. For the latter $|\Delta E|$ decreases with increasing the radius (or increasing $p$) of the tube and eventually saturates (for large enough $R$) at the value corresponding to the adsorption energy of a single fluorine atom on a graphene plane. On the contrary, in the case of metallic SWCNTs $|\Delta E|$ increases with increasing $R$, being always smaller than $|\Delta E|$ for semiconducting nanotubes. Such contrasting behaviour is attributed to the contribution to $\Delta E$ originating from a localized state, occurring in the band gap of semiconducting SWCNTs, which leads to a remarkable decrease of $\Delta E$ and, hence, to a significant strengthening of the chemisorption bond. This finding also suggests that fluorination of semiconducting SWCNTs is energetically more effective than metallic ones, especially for the smallest (in radius) tubes.

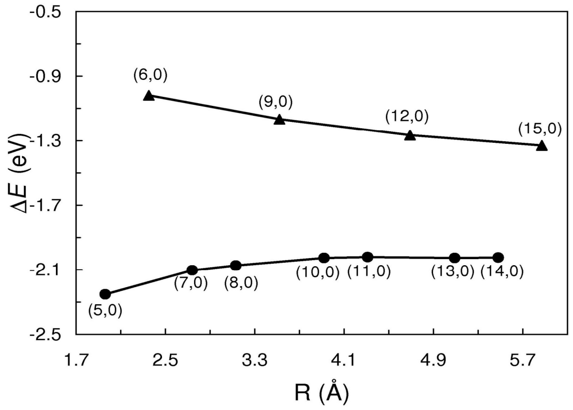

Fig.1. Chemisorption energies $\Delta E$ of a single fluorine atom adsorbed on the outer surface of the zigzag SWCNTs ($p$,0) with $p$ = 5 – 15 versus the radius $R$ of the tubes. The solid circles and triangles refer to semiconducting and metallic tubes, respectively.

This work was supported by the Ministry of Education of Russian Federation though the program “Universities of Russia” (Grant No. 01.01.111).

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