Modeling of DNA Base Interactions with Carbon Nanotubes: 
*ab initio* Calculations and SEIRA Data

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**Abstract.** SEIRA spectroscopy data was compared with *ab initio* calculations for thymine and adenine adsorbed on carbon nanotubes. Numerous changes in spectral features of thymine and adenine adsorbed on carbon nanotubes in comparison with spectra of thymine and adenine adsorbed on neutral substrate (CaF₂) and gold substrate were observed. The changes occur in the region of C=O stretching vibrations for thymine and NH₂ and C=C for adenine, and they are evidence of protonation of nitrogenous bases and redistribution of H-bond net under interaction with carbon nanotubes. We have registered the enhancement of intensity of vibration of thymine and adenine adsorbed on gold and nanotube surface (about 3-5) for some bands as well as a several stable states of the thymine and adenine adsorbed on the nanotubes. These partially coincide with the calculated results. Based on IR data we suppose that thymine forms monolayer and multi-layer films on the nanotube surface with tilted to the surface of nanotube, adenine forms separate molecules and island films on the nanotubes rather than layers. Energy of interaction between bases and nanotubes estimated from spectra was less than energy calculated with ab initio.

**Keywords:** thymine, adenine, single walled carbon nanotube, gold, adsorption, SEIRA spectroscopy, DFT.

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**INTRODUCTION**

DNA adsorption on single wall carbon nanotubes (SWCNTs) is a subject of particular importance due to promising biochemical application in future [1-4]. Biocompatibility, in-vivo application, high sensitivity of SWCNTs is some of their attractive features in this regard. The creation of new devices and new materials on the basis of DNA (RNA)-nanotube hybrids requires fully understanding an interaction mechanism. Despite numerous publications, understanding of the mechanism of how SWCNTs interact with DNA has not been established up to date [5-9]. That is why here we present the results of the interaction of nucleobases, namely, thymine (Thy) and adenine (Ade), DNA nucleic blocks with SWCNT. Thymine was a model of pyrimidine adsorption at the nanotube surface and adenine was a model of purine adsorption.

**METHOD AND MATERIALS**

The adenine is a nitrogenous molecule (N in position N₁, N₃, N₇, and N₉) consisting of one six-member pyrimidine ring and one five-member imidazole ring with an NH₂ functional group in the position of C₆ (Fig. 1) [10]. The thymine is nitrogenous bases consisting of one six-member pyrimidine ring with a CH₃ and CO groups (Fig.2). Thymine has two C=O moieties in the position of 2 and 4, one CH₃ in the 5 position and two NH groups in the ring of the 1 and 3 position [11]. Purines and pyrimidines have the π-orbitals perpendicular to the molecular plane. The functional groups provide their different electron affinities and existence of different tautomeric forms [12] (Fig.1,2). In the experiment we used thymine from Sigma (Germany) and adenine from Fluka (Germany). The concentration of adenine and thymine solutions in SEIRA experiment was 1 mg/ml. In the experimental the first we isolated the nanotubes with aqueous (alcoholic) solution of Thy (Ade) (1:1 weight ratio) by ultra-sound mixing (UZDN-A, Sunny, Ukraine) during 1 hour. Than we have deposited a drop of the solution of Ade (Thy) with carbon nanotubes on gold and CaF₂ substrate.

We apply a new modified and sensitive technique for spectra registering on the basis of enhancement of infrared (IR) absorption by rough metallic surface (SEIRA- surface enhanced infrared absorption) [13]. SEIRA spectroscopy
was used for registration of features of thymine and adenine interaction with carbon nanotubes. Infrared spectra of the samples were observed on a Bruker IFS-66 instrument in the 4000-400 cm\(^{-1}\) region.

![FIGURE 1. The adenine tautomeric forms.](image)

![FIGURE 2. The 2 from 13 tautomeric forms of thymine.](image)

The \textit{ab initio} calculations of thymine and adenine adsorption were using density function theory (DFT) implemented in the Vienna Ab Initio Simulation Package (VASP) [14]. This code uses a plane wave basis and a periodic supercell method with Vanderbilt pseudopotentials or a projector-augmented wave method to account for the electron core. The adsorption on the metallic SWCNT (6,6) with length of 12.25 Å, and the adsorption of thymine on the semiconducting (8,0) SWCNT with length of 17.035 Å, were considered with nonspin-polarized LDA (local density approximation) for the exchange-correlation functional. In general DFT is most successful for short-ranged chemical forces, however DFT-LDA shows good results for graphitic systems [14].

RESULTS AND DISCUSSION

It is well-known from calculation data [14,15] that a process of adsorption of nucleobases on carbon nanotubes occurs by \( \pi-\pi \) stacking between carbon nanotube surface and bases resulted to flat-laying thymine (or adenine). We are going to compare the calculation data with experimental data obtained with vibration spectroscopy for Thy and Ade adsorbed on SWCNT and located on gold in comparison with neutral substrate CaF\(_2\).

Nanotube-Thy interaction resulted to the following spectroscopic features:

1) Widening of H-bonded NH vibrations in the range of 3500-2000 cm\(^{-1}\) (Fig.3) and enhance of the intensity of the low-frequency shoulder.

![FIGURE 3. SEIRA spectra: 1- Thy+SWCNT and 2- Thy on gold.](image)

2) Missing of Thy band at 3509 cm\(^{-1}\) assigned to \( \text{N}_4\text{H} \) under absorption of SWCNT for both Au and CaF\(_2\) substrates (Fig.4). The last point could be connected with protonation of the Thy ring. We suppose that possible point of Thy interaction with SWCNT is \( \text{N}_1\) position.

3) Enhancement of a intensity of the band of NH for the Thy-SWCNT on CaF\(_2\) (Fig.4) substrate and a shift from 3345 (Thy) to 3312 cm\(^{-1}\) (Thy-SWCNT). One more NH vibration (seems \( \text{N}_3\)) shows an increase of the intensity and shift from 3206 (Thy) to 3212 cm\(^{-1}\) (Thy-SWCNT).

4) In Thy-SWCNT at Au and CaF\(_2\) we could registered C=O vibrations such as 1861, 1805 that could be assigned to \( \text{C}_2\text{=O} \) and \( \text{C}_3\text{=O} \) respectively for isolated Thy molecules (Fig.4). We supposed that it connected with adsorption of separated molecules of Thy on carbon nanotubes resulted to island film formations due the \( \pi-\pi \) stacking interaction.

5) Thy-SWCNT on CaF\(_2\) (Fig.4) shows decrease of the intensity of \( \text{C}_3\text{=O} \) vibration and a shift from 1668 to 1679 cm\(^{-1}\), indicating to breaks some of the inter- or intra-molecular H-bonds with participation of \( \text{C}_3\text{=O} \).
7) In Thy-SWCNT (Fig.4) the $\text{C}_2=\text{O}$ vibration shows the enhancement of the intensity and the shift it in the low-frequency region from 1774 to 1761 cm$^{-1}$ (Thy-SWCNT on CaF$_2$) and to 1755 cm$^{-1}$ (Thy-SWCNT on Au) that indicated to formation of new intermolecular H-bonds with C$_2=\text{O}$ participation.

8) The bands at 1023, 831, 557, 475, 428 assigned to $\text{CH}_3$ and $\text{N}_1\text{C}_2$, $\text{C}_2=\text{O}$, $\text{C}_4=\text{O}$, $\text{N}_3\text{H}$, $\text{N}_3\text{C}_4$, $\text{N}_1\text{C}_2=\text{O}$ SWCNT for Thy-SWCNT on gold show an enhancement of their intensity in 3-5 times (Fig.3). It could be connected with enhancement of local electrical fields in the system SWCNT-gold. In general, one more reason of the enhancement of intensity of vibrations of Thy adsorbed at nanotubes in low frequency region is connected with crystalline packing of Thy molecules.

![FIGURE 4. FTIR spectra: 1 - Thy-SWCNT and 2 – Thy on CaF$_2$, 3 - Thy-SWCNT on gold.](image)

For Ade-SWCNT on gold (Fig.5) the enhancement of intensity of the numerous vibration NH$_2$, C=C in the region of stretching and deformation bands in the 3400-1100 cm$^{-1}$ was observed also and decrease of many vibrations lower 1100 cm$^{-1}$ up to 400 cm$^{-1}$ in contrast to Thy adsorption on nanotubes. This fact demonstrates a difference in behavior of the intensity of the bands of Thy in comparison with Ade molecules and, from our point of view, could be connected with different formation of layers by Thy and Ade molecules. Ade, seems, forms the isolated islands and does not cover the nanotube by monolayer or multilayer films as it does Thy preferentially.

![FIGURE 5. FTIR spectra on Au: 1-Ade in H$_2$O, 2- Ade-SWCNT in solution of H$_2$O/C$_2$H$_5$OH (1:1), 3- Ade-SWCNT in H$_2$O.](image)

![FIGURE 6. Possible orientation of a thymine molecule on surface of SWCNT.](image)
Modeling and calculation of the process of the adsorption of thymine on carbon nanotubes have showed the numerous cites of its adsorption on the carbon nanotube surface with weak energy of interaction [14-16]. On the basis of the spectral data and the Badger-Bauer rule ($\Delta H = 0.3(\Delta v - 40)^{1/3}$, where $\Delta H$ – enthalpy of H-bond formation) [17] we have estimated the energy of H-bond formation and break under Thy and Ade interaction with carbon nanotubes. We suppose that break of the H-bonds is due to nanotube interaction with bases, so this energy was accepted by us as array for base-nanotube interaction. Data for Ade and Thy in gas phase was taken from [18,19], correspondingly and in our calculation stretching vibration was taken into account.

**TABLE 1. Energy of interaction of bases with gold, nanotubes and graphene sheet.**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Thy on gold</th>
<th>Ade on gold</th>
<th>Thy on nanotubes</th>
<th>Thy on graph sheet</th>
<th>Ade on nanotubes</th>
<th>Ade on graph sheet</th>
</tr>
</thead>
<tbody>
<tr>
<td>Energy, kcal/mol</td>
<td>11.29</td>
<td>0.07-0.23</td>
<td>11.29</td>
<td>8.16</td>
<td>10.6</td>
<td></td>
</tr>
<tr>
<td>Distance, Å</td>
<td>3.5</td>
<td>-</td>
<td>3.5</td>
<td>3.1-3.31</td>
<td>-</td>
<td>3.05-3.25</td>
</tr>
</tbody>
</table>

Table 1 shows that energy of interaction estimated from SEIRA spectra is less than calculated one. The main reason of non-coinciding of the experimental and calculated data is the fact that more complicated system takes place in the experiment than in calculation. In the calculation we did not take into account an aqueous solution, IR substrate, defects in nanotubes as well we suppose that covering of nanotube by Thy or Ade is a single molecules as not in the experiment.

**CONCLUSION**

In conclusion, Ade adsorbed on carbon nanotubes forms mostly islands and Thy forms monolayer or multilayer films by $\pi$-$\pi$ stacking interaction with tilted bases to plane of carbon nanotube. Non-coincidence of experimental and calculated energy of Thy (Ade)-carbon nanotube interaction is an evidence of complicated system under study, numerous of possible sites of interactions with tautomeric forms of bases and rough estimation of energy of interaction with Badger-Bauer rule.

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