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1,2-Dichlorobenzene Interacting with Carbon Nanotubes

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ABSTRACT

The interaction of 1,2-dichlorobenzene (DCB) with carbon nanotubes is analyzed by experimental and theoretical methods. Using first-principles calculations we studied the structural and electronic behavior of DCB interacting with a semiconductor (8,0) single-wall carbon nanotube (SWNT). We have found that the DCB weakly interacts with a perfect SWNT surface, but this interaction is slightly stronger when the SWNT surface has structural vacancies. Resonant Raman experiments performed on DCB-adsorbed SWNTs confirm the weak DCB–SWNT interaction, as suggested by the *ab initio* simulations.

Since their discovery by Iijima,¹ carbon nanotubes have been intensively studied as a potential material to be used in a variety of applications based on their unusual physical and chemical properties. This material can be used, for example, to build molecular sensors, nanoscale devices, or materials with novel properties that may be synthesized using SWNTs as the starting point.^{2,3}

In particular, SWNT-based sensor devices are capable of detecting molecules, such as NO₂, NH₃, and O₂, because when these chemical species are adsorbed on the tube surface, significant changes in the conductance occur.⁴ An open problem arises when the molecules we are interested in detecting do not really bind to the SWNT surface, such as CO and H₂O.⁵ These limitations are consequences of the van der Waals interactions between the tube surface and the molecules, thus resulting in what is called a physisorption process. Carbon nanotubes were recently proposed as a promising material to be used for removing 1,2-dichlorobenzene (DCB) from water solution.⁶ Chlorobenzenes are used as solvents, heat transfer agents, insect repellents, deodorants, degreasers, and intermediates in dye and pesticide synthesis. They are detected in both surface- and groundwater and in some biological tissues as well. These chemicals are identified as priority pollutants by the U.S. Environmental Protection Agency.⁷ The DCB is chemically stable, slightly soluble,

and it often occurs at low concentrations in water. The removal of toxic compounds, such as DCB, is a hard task, particularly when they are at low concentrations. Adsorption is regarded as a promising method for removing micro-pollutants (such as DCB) as proposed by Peng et al.⁶

In this work we report a study of DCB interacting with SWNTs. By using first-principles calculations based on density functional theory, we have investigated different DCB–SWNT configurations and their interactions. Resonant Raman experiments were used to probe the DCB–SWNT interaction. Good qualitative agreement between experiment and theory was observed.

Theoretical Procedures. The theoretical calculations are based on first-principles density functional theory using numerical atomic orbitals as basis sets. We have used the SIESTA code,⁸ which solves the standard Kohn–Sham (KS) equations. The calculations are done using the local density approximation for the exchange–correlation term, as proposed by Perdew–Zunger.⁹ The standard norm-conserving Troullier–Martins pseudopotentials are used.¹⁰ The KS orbitals are expanded using a linear combination of numerical pseudoatomic orbitals, similar to the ones proposed by Sankey and Niklewski.¹¹ In all procedures we have used a split-valence double- ζ basis set with a polarization function.¹² A cutoff of 150 Ry for the grid integration was utilized to represent the charge density.

Our calculations were performed using a (8,0) semiconductor SWNT. Periodic-boundary conditions and a supercell

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approximation with a lateral separation of 35 Å between tube centers are used to make sure that the nanotubes plus DCB do not interact with their periodic images. The supercell had 64 C atoms, with a total length of 8.52 Å. Along the tube axis, five Monkhorst-Pack **k**-points for the Brillouin zone integration were used.⁵ The relaxed atomic structures of the tubes were obtained by a minimization of the total energy using Hellmann–Feynman forces including Pullay-like corrections. Structural optimizations were performed until the residual forces were smaller than 0.05 eV/Å.

Experimental Procedures. *Materials.* The as-grown SWNTs were obtained from the Carbolex Company. The diameter distribution of the sample was determined by analysis of the radial breathing mode profile as being $d_o = 1.34 \pm 0.20$ nm. DCB of 99% purity purchased from VETEC was used in the experiments.

Experiments. The adsorption of DCB by SWNTs was performed using the same experimental procedure as reported in ref 6. The DCB was dissolved in deionized water through a sonication process. The DCB adsorption was performed in a closed glass bottle. A quantity of 50 mg of SWNTs was added to the DCB/water solution. The batch was submitted to stirring, and after the equilibrium was reached, the solution was centrifugated. The Raman scattering experiments were carried out at room temperature using a Jobin Yvon T64000 spectrometer equipped with an N₂-cooled charged coupled device (CCD). The 514.5 nm (2.41 eV) laser line from an Ar⁺ laser was used as excitation. To avoid heating effects on the samples and further volatilization of the DCB from the SWNTs, extremely weak laser power was used. The power density was 1 μW/μm².

Results and Discussion. We theoretically analyze three possibilities of DCB adsorption on SWNT bundles. The interaction of DCB with a pristine SWNT was done by approaching the DCB molecule to the outer surface of the tube in two ways: the DCB molecule plane perpendicular [parallel] to the tube axis, as shown in Figure 1a [Figure 1b]. The third studied DCB–SWNT configuration was for a defective SWNT (a vacancy generated by removing one C atom from the tube surface), as illustrated in Figure 1c.

The binding energies from the studied systems are calculated by using the following equation:

$$E_B = E(\text{DCB-SWNT}) - E(\text{SWNT}) - E(\text{DCB})$$

where $E(\text{SWNT})$ is the total energy for the isolated tube, perfect or with a vacancy, $E(\text{DCB})$ is the total energy of an isolated DCB molecule, and $E(\text{DCB-SWNT})$ is the total energy of the DCB interacting with the SWNT system under consideration.

In Table 1 are listed the binding energies calculated for the different DCB–SWNT configurations shown in Figure 1. The interaction for the first case shown in Figure 1a, in terms of binding energies, is very small ($E_B = -0.03$ eV). For the second configuration illustrated in Figure 1b, for which the DCB plane is parallel to the tube axis, the interaction is slightly stronger, with a binding energy of -0.31 eV. Thus, this interaction is related to the π -orbital

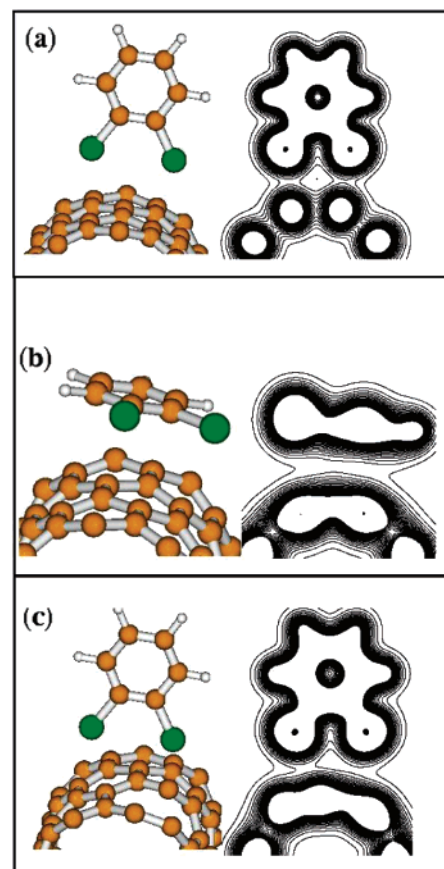


Figure 1. Schematic view (left panels) and contour plot of the total charge densities (right panels) of DCB interacting with a pristine SWNT (a) and (b); and a defective (vacancy) SWNT (c).

Table 1. Binding Energies (E_B) Calculated for the DCB–SWNT Configurations Shown in Figure 1 and Minimum Distance between the DCB Atoms and the Tube Atoms

	E_B (eV)	minimum distance DCB–SWNT (Å)
SWNT–DCB (Figure 1a)	−0.03	3.20 ($C_{\text{DCB}}-C_{\text{tube}}$)
SWNT–DCB (Figure 1b)	−0.31	3.20 ($C_{\text{DCB}}-C_{\text{tube}}$)
SWNT/vc–DCB (Figure 1c)	−1.22	3.02 ($C_{\text{DCB}}-C_{\text{tube}}$)

interaction between the DCB aromatic ring and the C-ring of the SWNT. When the DCB approaches a SWNT with a vacancy, the binding energy is -1.22 eV, thus indicating that the interaction is stronger than for the configurations shown in Figures 1a and 1b. The contour plots for the total charge densities (right panels) shown in Figure 1 indicate a weak interaction between the DCB molecule and the SWNT as we observed in terms of binding energy values.

In Figure 2 we plot the total electronic density of states (DOS) for both the pristine SWNT (black curves) and the DCB–SWNT system (red curves). From Figures 2a and b, we can observe no changes in the DOS, near the Fermi level (0.0 eV), for the case of a pure or a DCB-adsorbed SWNT. These results show a weak interaction between the DCB and the perfect tube surface that was also observed in terms of binding energies. The contribution of the DCB electronic levels to the total DOS for both configurations shown in Figures 1a and b are localized between -2.8 eV and -1.5

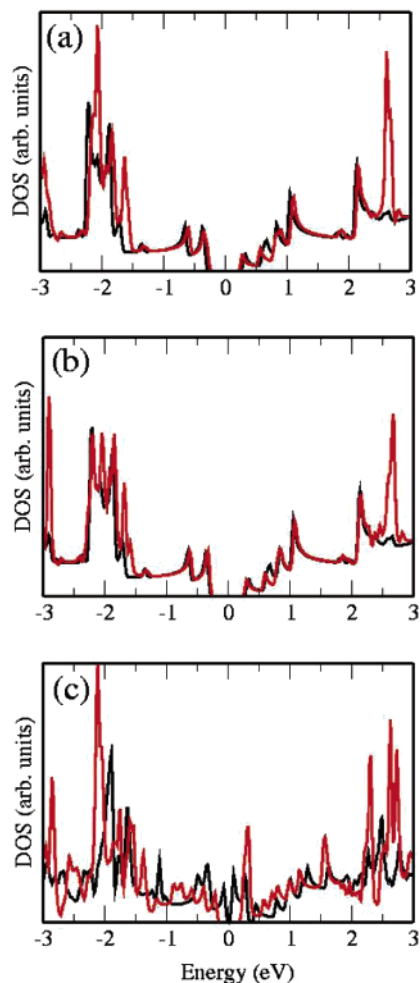


Figure 2. Total electronic densities of states for pristine SWNT (black curves) and DCB-SWNT systems (red curves) calculated for the corresponding configurations shown in Figure 1.

eV in the valence bands and around 2.5 eV in the conduction bands, as can be observed in Figures 2a and 2b. Conversely, when the DCB molecule is adsorbed on the defective SWNT, the vacancy level becomes strongly localized at approximately 0.2 eV above the Fermi level. The small band dispersion of the vacancy level, when compared with the system without DCB, where the vacancy level is delocalized, is associated with the reduction in the interaction between vacancies in adjacent supercells through the DCB vacancy interaction. This result along with the binding energy values show that the interaction of the DCB with the defective tube is stronger when compared with the pristine SWNT. Such an increase in interaction can be directly associated with the rearrangement of the defect structure in the presence of the DCB.

To validate the theoretical predictions about the DCB-SWNT interaction, we have carried out resonant Raman scattering experiments on both pristine and DCB-adsorbed SWNT bundles. Raman spectroscopy is a well-established technique for investigating changes in the electronic properties of SWNTs through the special electron-phonon coupling that occurs under strong resonant conditions.^{14,15} Therefore,

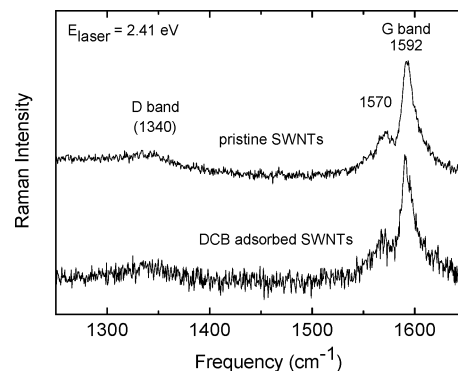


Figure 3. Raman spectra of both pristine and DCB-adsorbed SWNT bundles. The laser energy used for excitation was 2.41 eV.

Raman spectra are very sensitive to modifications of the nanotube surface, such as by the introduction of surface species and the charge-transfer effects resulting from both functionalization and intercalation processes.¹⁶⁻¹⁸

In Figure 3 we show the Raman spectra of both pristine and DCB-adsorbed SWNT bundles in the spectral region of the disorder induced D-band and the tangential mode G-band. The observation of the D-band in the spectrum indicates that the tube surfaces are somewhat defective, but since the intensity ratio of the D-band to G-band intensity is small, the tubes are considered to have a good crystallinity.^{14,15} As one can observe, the Raman spectra shown in Figure 3 are almost the same and exhibit only a slight change in the signal-to-noise ratio for the DCB-adsorbed SWNTs (lower trace). No significant shifts of the bands were observed when the SWNTs were intercalated with DCB molecules. It is well-known that charge-transfer effects appear in the G-band Raman spectra through upshifts (downshifts) of the G-band phonon frequencies when the chemical species interacting with the SWNTs are acceptors (donors).^{16,17} The results shown in Figure 3 tell us that the DCB-SWNT interaction is weak, in qualitative agreement with the calculations whose results indicated that the charge transfer from the DCB to SWNT is 0.004 electron/DCB-molecule. Therefore, the very weakly adsorbed DCB is not detectable in Raman scattering experiments. We have carried out calculations for Ag interacting with SWNTs and we find that the charge transfer is 0.280 electron/Ag-atom, being very much larger than in the case of DCB. This prediction is consistent with the experimental results reported in ref 17, whereby measurable downshifts in the tangential modes were detected in the Raman spectra.

Conclusions. In summary, we observed that the DCB and the perfect tube surface have a very small interaction, and this should be due to the fact that both DCB molecules and perfect carbon nanotubes are very stable systems when they are isolated. Thus, if we are interested to obtain a more effective interaction between this molecule and the SWNT surface, it will be necessary to chemically/physically modify the tube surface. This can be achieved by introducing either vacancies or reactive chemical groups through functionalization that in turn will improve the adsorption of the DCB on the SWNTs.

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