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Dynamics of the exohedral complex composed of Ar atomic film adsorbed on the surface of single-walled carbon nanotube. Computer simulation study

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A molecular dynamics study of the monolayer Ar atomic film adsorbed on the outer surface of single-walled (10,10) carbon nanotube has been undertaken and the vibrational spectra of this system have been determined. It was found that vibrations of the atoms in the argon film considerably influence the low-frequency vibrational dynamics of the nanotube.

Key words: *adsorption; carbon nanotubes; molecular dynamics*

1. Introduction

Carbon nanotubes are of interest as gas adsorbents [1–7] because of their unique structural properties which make them prospective materials for many applications, including sensing, storing, purification and isotope separation of gases [8–11]. Studies of new carbon nanotube-based materials and devices require an understanding of the vibrational properties of nanotubes [12, 13] and the adsorbed atoms or molecules [14, 15].

In this work, a molecular dynamics simulation of the system composed of a monolayer of an Ar atomic film adsorbed on the outer surface of a single-walled (10,10) carbon nanotube has been carried out. This was performed in order to determine the vibrational properties of the system and to study the influence of the dynamics of the adsorbate Ar atoms on the low-frequency vibrational dynamics of the nanotube.

2. Simulation details

The intra-molecular interactions between the carbon atoms of the nanotubes and the fullerene has been modelled using the potential composed of the components rep-

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resenting the energy of the bonded C atoms and the energy of the van der Waals interaction between the non-bonded C atoms [16, 17]

$$V = V_{\mathrm{bond}} + V_{\mathrm{vdW}} \tag{1}$$

The V_{bond} component is composed of terms representing the energies of the stretching (Morse), bending (harmonic cosine) and twisting (2-fold torsion angle) of the C–C bond

$$\begin{aligned} V_{\mathrm{bond}}(r_{ij}, \Theta_{ijk}, \varphi_{ijkl}) = K_r \left(e^{-\gamma(r_{ij}-r_C)} - 1\right)^2 + \frac{1}{2}K_\Theta (\cos\Theta_{ijk} - \cos\Theta_C)^2 \\ + \frac{1}{2}K_\varphi (1 - \cos 2\varphi_{ijkl})^2 \end{aligned} \tag{2}$$

where r_{ij} is the distance between a given pair of bonded atoms, Θ_{ijk} is the bending angle between a given three atoms and φ_{ijkl} is the torsional angle between a given four atoms. The values of K_r, K_Θ, K_φ, γ, r_C, Θ_C and φ_C parameters are given in Table 1.

Table 1. Parameters of the carbon interaction potentials

Parameter	Value	Parameter	Value
K_r	478.9 kJ/mol	Θ_C	120°
K_Θ	562.2 kJ/mol	γ	2.1867 Å^{-1}
K_φ	25.12 kJ/mol	$\varepsilon_{\mathrm{C-C}}$	0.4396 kJ/mol
R_C	1.418 Å	$\sigma_{\mathrm{C-C}}$	3.851 Å

The van der Waals interaction V_{vdW} between the non-bonded atoms is modelled as a pairwise additive Lennard–Jones (L–J) potential of the form

$$V_{\mathrm{vdW}}(r_{ij}) = 4\varepsilon_{CC}\left[\left(\frac{\sigma_{CC}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{CC}}{r_{ij}}\right)^{6}\right] \tag{3}$$

over all pairs of atoms except 1–2 and 1–3 pairs. The values of the ε_{CC} and σ_{CC} parameters are given in Table 1. The simulated nanotube consisted of 1600 C atoms. Initial velocities of the carbon atoms were assigned according to the Maxwell distribution, for the temperature of 15 K. The nanotube system was equilibrated for 200 ps. The overall rotation and translation of the nanotube were continuously stopped. The interactions between rare gas atoms have been modelled using the HFD-B potentials developed by Aziz et al. [18–20]

$$V(r_{ij}) = \varepsilon_a V^*(x_{ij}) \tag{4}$$

where

$$V^*(x_{ij}) = A^* \exp(-\alpha^* x_{ij} + \beta^* x_{ij}^2) - F(x_{ij}) \sum_{j=0}^{2} \frac{c_{2j+6}}{x_{ij}^{2j+6}} \tag{5}$$

$$F(x_{ij}) = \begin{cases} \exp[-(D/x_{ij} - 1)^2], & x_{ij} < D \\ 1, & x_{ij} \geq D \end{cases} \tag{6}$$

$$x_{ij} = \frac{r_{ij}}{r_m} \tag{7}$$

The values of the parameters A^*, α^*, β^*, c_6, c_8, c_{10}, D, r_m, ε_a are presented in Table 2.

Table 2. Parameters of the HFD–B Ar–Ar potential

Parameter	Value
A^*	87393.3927
α^*	9.03228328
β^*	–2.371328328
c_6	1.0948575
c_8	0.5917572
c_{10}	0.3450815
D	1.4
r_m	3.759 Å
ε_a	1.190334664 kJ/mol

The simulated argon system was composed of 240 Ar atoms, forming a monolayer atomic film covering the nanotube. The temperature of the argon system was controlled by scaling the velocities. All calculations were performed for the temperature of 15 K.

The adsorption between the nanotube and rare gas film has been modelled atomically, using the potential developed by Carlos and Cole [21]

$$\begin{aligned} V(r_{ij}, \Theta_{ij-n}) = 4\varepsilon_{Ar-C} \bigg\{ &(\sigma_{Ar-C}/r_{ij})^{12} \left[1 + \gamma_R \left(1 - \frac{6}{5}\cos^2 \Theta_{ij-n}\right)\right] \\ &-(\sigma_{Ar-C}/r_{ij})^6 \left[1 + \gamma_A \left(1 - \frac{3}{2}\cos^2 \Theta_{ij-n}\right)\right] \bigg\} \end{aligned} \tag{8}$$

where r_{ij} is the distance between i-th Ne and j-th C atoms, while Θ_{ij-n} is the angle between r_{ij} and the nanotube surface normal. The values of the parameters ε_{Ar-C}, σ_{Ar-C}, γ_R, and γ_A are given in Table 3.

Table 3. Parameters of the Ar–C adsorption potential

Parameter	Value
$\varepsilon_{\mathrm{Ar–C}}$	0.99768 kJ/mol
$\sigma_{\mathrm{Ar–C}}$	3.4 Å
γ_R	–0.54
γ_A	–0.40

The Newtonian equations of motion were integrated up to 250 ps (after equilibration) with the time step 0.2 fs.

3. Results and discussion

No liquid-like phase was found for the Ar layer adsorbed on the surface of the (10,10) nanotube studied. The argon cluster forming the monolayer atomic film adsorbed on the surface of the nanotube retains its solid-like phase at temperatures below 38 K. Above this temperature, the Ar atoms start evaporating. Figure 1 shows a snapshot of the simulated system. It can be seen that the argon atoms form chains oriented along the nanotube axis.

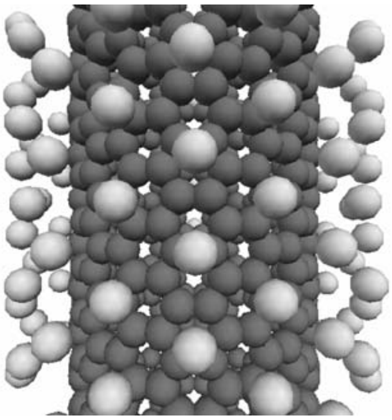

Fig. 1. Ar monolayer atomic film adsorbed on the outer surface of the (10,10) armchair carbon nanotube

One of the standard methods for studying microscopic dynamics is the calculation of spectral densities from microscopic correlation functions. In this work, the dynamics of the system have been studied in terms of the spectral density

$$D(\omega) = \int_0^\infty C_V(t)\cos(2\pi\omega t)\,dt$$

computed as the cosine Fourier transform of the atomic normalized velocity autocorrelation function

$$C_V(t) = \frac{<\mathbf{v}(t)\cdot\mathbf{v}(0)>}{<\mathbf{v}(0)\cdot\mathbf{v}(0)>}$$

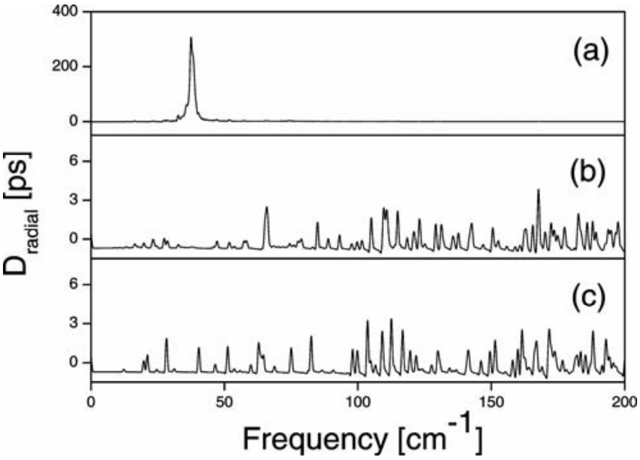

Fig. 2. The radial component of the vibrational spectrum $D_{\text{radial}}(\nu)$ of the Ar atoms (a) and the low-frequency portion of the respective spectrum of the nanotube (b) in the system composed of the Ar monolayer atomic film adsorbed on the surface of the single-walled (10,10) carbon nanotube, compared to the low-frequency portion of the vibrational spectrum of the (10,10) nanotube simulated without the adsorbed Ar layer (c)

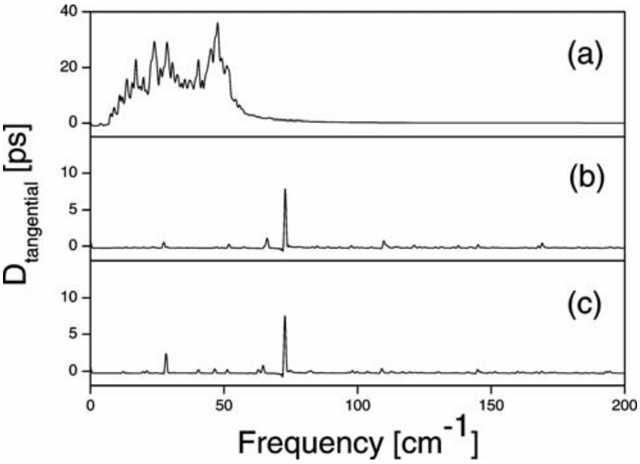

Fig. 3. The tangential component of the vibrational spectrum $D_{\text{tangential}}(\nu)$ of the Ar atoms (a) and the low-frequency portion of the respective spectrum of the nanotube (b) in the system composed of the Ar monolayer atomic film adsorbed on the surface of the single-walled (10,10) carbon nanotube, compared to the low-frequency portion of the vibrational spectrum of the (10,10) nanotube simulated without the adsorbed Ar layer (c)

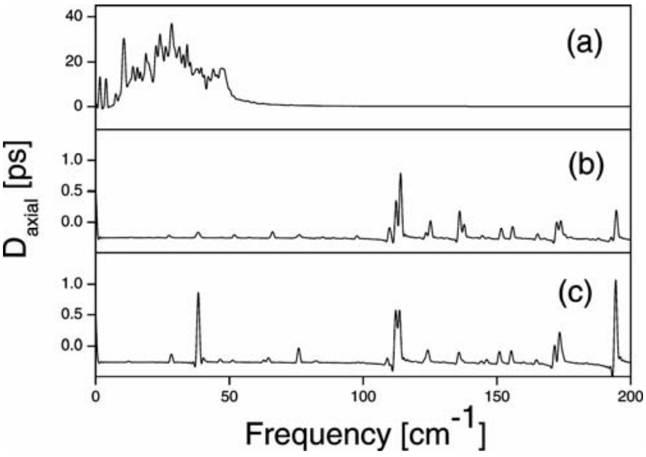

Fig. 4. The axial component of the vibrational spectrum $D_{axial}(\nu)$ of the Ar atoms (a) and the low-frequency portion of the respective spectrum of the nanotube (b) in the system composed of the Ar monolayer atomic film adsorbed on the surface of the single-walled (10,10) carbon nanotube, compared to the low-frequency portion of the vibrational spectrum of the (10,10) nanotube simulated without the adsorbed Ar layer (c).

which is usually employed in molecular dynamics simulations to study molecular or atomic vibrations and hindered translations. The radial $D_{radial}(\nu)$, tangential $D_{tangential}(\nu)$ and axial $D_{axial}(\nu)$ spectral densities are calculated from the respective velocity components: radial, tangential and axial (parallel) to the nanotube. Figures 2–4 show the radial, tangential and axial components of the vibrational spectra of the Ar film covering the nanotube and the low-frequency portion of the respective spectra of the nanotube.

To enable comparison between the dynamics of the nanotube covered with the adsorbed argon film, the spectra are accompanied by the low-frequency spectra calculated for the nanotube not covered with the argon layer (c). The vibrational spectrum of the argon monolayer adsorbed on the surface of the (10,10) nanotube shows the vibrations of the argon atoms at frequencies below 60 cm^{-1} and no vibrational modes at higher frequencies. Although the spectrum of the nanotube reveals the vibrational modes at frequencies up to about 1700 cm^{-1}, only its low-frequency portion, covering the frequency range comparable to that of the adsorbed argon layer, is presented in the figure. It can be observed that the vibrational modes of the nanotube at frequencies lower than 60 cm^{-1} are considerably influenced by the dynamics of the Ar atoms monolayer adsorbate. At higher frequencies, the constrained geometry imposed by the presence of the argon atoms in the vicinity of the nanotube have only a very slight influence on the internal dynamics of the nanotube.

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