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# Interaction-induced depolarized light scattering spectra of exohedral complexes of Ne and Ar with fullerenes and nanotubes

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Recently, Dawid and Gburski (Phys. Rev. A, 68 (2003), 065202) have studied the molecular dynamics of a system consisting of a $C_{60}$ molecule surrounded by a monolayer argon film and determined the interaction induced polarizability correlation function and the depolarized light scattering spectra of this system. In the present work a number of exohedral complexes of Ar and Ne forming an ultrathin monolayer film physisorbed on a fullerene or nanotube surface have been studied.

Key words: *nanotubes; fullerenes; adsorption; depolarized light scattering, molecular dynamics*

## 1. Introduction

Interaction induced depolarized light scattering spectra of monoatomic fluids has been studied both experimentally and by computer simulation for many years, as useful information concerning the dynamics of atoms can be provided [1–6]. Fullerenes and carbon nanotubes are of interest as gas adsorbents [7–13] because of their unique structural properties. Recently, Dawid and Gburski [1] have studied the interaction induced depolarized scattering in a system composed of a fullerene covered with an ultrathin spherical argon film using a rigid body model of the $C_{60}$ molecule. In the present work a number of exohedral complexes composed of rare gas ultra-thin atomic films adsorbed on a fullerene or nanotube surface, were studied using more realistic modelling.

## 2. Simulation details

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

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representing the energy of the bonded C atoms and the energy of the van der Waals interaction between the non-bonded C atoms [14, 15]

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

The $V_{\text{bond}}$ 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

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

where $r_{ij}$ is the distance between a given pair of bonded atoms, $\Theta_{ijk}$ is the bending angle between a given three atoms and $\varphi_{ijkl}$ is the torsional angle between a given four atoms. The values of the $K_r$, $K_\Theta$, $K_\varphi$, $\gamma$, $r_C$, $\Theta_C$ and $\varphi_C$ parameters [3] are given in Table 1. The van der Waals interaction $V_{\text{vdV}}$ between the non-bonded atoms is modelled as a pairwise additive Lennard–Jones (L–J) potential of the form

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

over all pairs of atoms except 1–2 and 1–3 pairs. The values of the $\varepsilon_{CC}$ and $\sigma_{CC}$ parameters are given in Table 1.

Table 1. Parameters of the carbon interactions potentials

| Parameter | Value | Parameter | Value |
|---|---|---|---|
| $K_r$ | 478.9 kJ/mol | $\Theta_C$ | 120° |
| $K_\Theta$ | 562.2 kJ/mol | $\gamma$ | 2.1867 Å$^{-1}$ |
| $K_\varphi$ | 25.12 kJ/mol | $\varepsilon_{C\text{–}C}$ | 0.4396 kJ/mol |
| $R_C$ | 1.418 Å | $\sigma_{C\text{–}C}$ | 3.851 Å |

The interactions between rare gas atoms have been modelled using the HFD–B potentials developed by Aziz and co-workers [16–18]

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

where

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

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

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

The values of the parameters $A^*$, $\alpha^*$, $\beta^*$, $c_6$, $c_8$, $c_{10}$, $D$, $r_m$, $\varepsilon_a$ are given in Table 2.

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

| Parameter | Value | |
|---|---|---|
| | Ne–Ne | Ar–Ar |
| $A^*$ | 895717.95 | 87393.3927 |
| $\alpha^*$ | 13.86434671 | 9.03228328 |
| $\beta^*$ | –0.12993822 | –2.37132823 |
| $c_6$ | 1.21317545 | 1.0948575 |
| $c_8$ | 0.53222749 | 0.5917572 |
| $c_{10}$ | 0.24570703 | 0.3450815 |
| $D$ | 1.36 | 1.4 |
| $r_m$ | 3.091 Å | 3.759 Å |
| $\varepsilon_a$ | 0.35113975 kJ/mol | 1.190334664 kJ/mol |

The adsorption between the nanotube and rare gas film has been modelled atomically, using the potential developed by Carlos and Cole [19]

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

where $r_{ij}$ is the distance between $i$-th Ne and $j$-th C atoms, while $\Theta_{ij-n}$ is the angle between $r_{ij}$ and the nanotube surface normal and $X$ denotes Ne or Ar. In the case of the fullerene systems, the pairwise L–J potential has been employed as the adsorption potential. The values of the parameters $\varepsilon_{X-C}$, $\sigma_{X-C}$, $\gamma_R$, $\gamma_A$ are given in Table 3.

Table 3. Parameters of the Ne–C and Ar–C adsorption potentials

| Parameter | Value | Parameter | Value |
|---|---|---|---|
| $\varepsilon_{\mathrm{Ne-C}}$ | 0.2786 kJ/mol | $\gamma_A$ | 0.40 |
| $\sigma_{\mathrm{Ne-C}}$ | 3.3 Å | $\varepsilon_{\mathrm{Ar-C}}$ | 0.99768 kJ/mol |
| $\gamma_R$ | –0.54 | $\sigma_{\mathrm{Ar-C}}$ | 3.4 Å |

The depolarized light scattered by a monoatomic fluid provides information on the time characteristic of the polarizability anisotropy of colliding pairs of atoms. The major contribution to the anisotropy is described by the dipole-induced dipole (DID) mechanism [6]. The DID interaction results from the fact that the incident light beam induces an oscillating dipole on the $i$-th particle and this dipole generates an oscillating local field on the $j$-th particle. The DID mechanism is a two-body interaction which gives rise to the two-, three- and four-body correlations contributing to the intensity of the scattered light and can be described by the polarizability anisotropy correlation function

$$G(t) = G_2(t) + G_3(t) + G_4(t) \tag{9}$$

For a monoatomic sample of $N$ atoms, pair, triplet and quadruplet contributions to $G(t)$ are calculated as

$$G_2(t) \propto \left\langle \sum_{i,j=1}^{N} \beta_{ij}(t)\beta_{ij}(0) \right\rangle \tag{10}$$

$$G_3(t) \propto \left\langle \sum_{i,j,k=1}^{N} \beta_{ij}(t)\beta_{ik}(0) \right\rangle \tag{11}$$

$$G_4(t) \propto \left\langle \sum_{i,j,k,l=1}^{N} \beta_{ij}(t)\beta_{kl}(0) \right\rangle \tag{12}$$

where $i$, $j$, $k$, $l$ identify different atoms. The pair anisotrophy $\beta_{ij}$ in the DID limit is [6]

$$\beta_{ij}(t) = \sigma^3 \frac{3x_{ij}(t)z_{ij}(t)}{r_{ij}^5(t)} \tag{13}$$

where $x_{ij}$ and $z_{ij}$ are components of the separation vector between the $i$-th and $j$-th atom. The depolarized spectrum $I(\nu)$ is calculated as the cosine Fourier transform of the polarizability anisotropy autocorrelation function.

## 3. Results and discussion

A molecular dynamics study of the monolayer Ar and Ne atomic films adsorbed on the outer surface of the (5,5) single-walled carbon nanotube and the $C_{60}$ fullerene molecule has been undertaken. The snapshots of the simulated systems are presented in Figs. 1–3.

In order to enable direct comparison between the dynamics of the rare gas films in different geometries, we have chosen the (5,5) armchair nanotube as a counterpart to

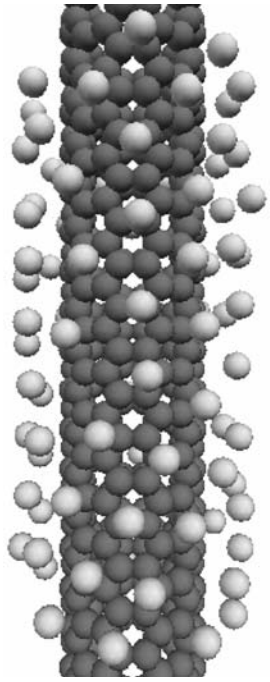

Fig. 1. Monolayer Ne atomic film covering (5,5) single-walled carbon nanotube

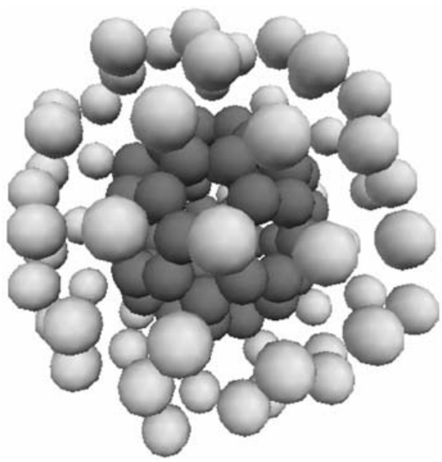

Fig. 2. Monolayer Ne atomic film (68 atoms) covering the fullerene $C_{60}$ molecule

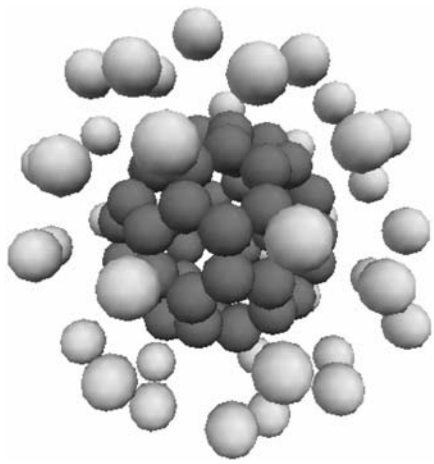

Fig. 3. Monolayer Ar atomic film (44 atoms) covering the fullerene $C_{60}$ molecule

the fullerene systems, as its diameter is very close to the diameter of the fullerene. Liquid phases have been found in the case of the Ar and Ne films covering the $C_{60}$ molecule and in the case of the Ne film covering the (5,5) nanotube. In the case of the Ar film covering the (5,5) nanotube no liquid phase was found and this system was excluded from further analysis. In the case of both fullerene systems, Ne and Ar film formed a complete monolayer covering the fullerene (44 Ar atoms or 68 Ne atoms). In all cases studied, spectra have been determined for the highest temperature at which the film retains its liquid phase (35 K for the Ne–nanotube system, 20 K for the Ne–fullerene system and 50 K for the Ar–fullerene system).

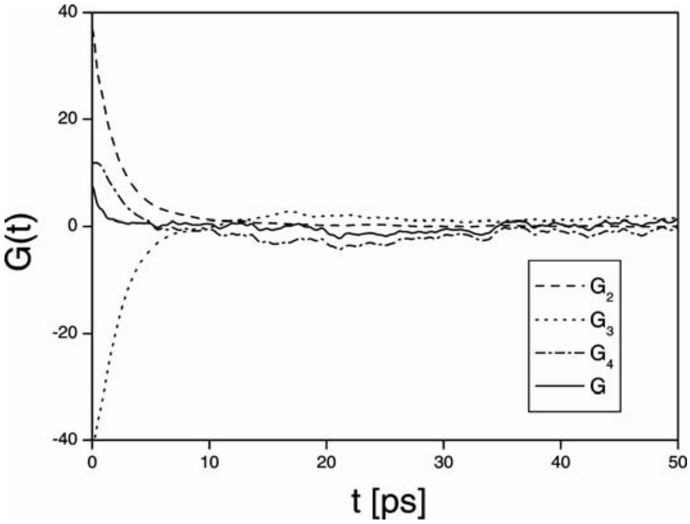


Fig. 4. The polarizability anisotropy correlation function $G(t)$ (solid line) along with its two- (dashed line), three- (dotted line) and four-particle (dash-dot line) components, of Ne film covering the (5,5) armchair nanotube at the temperature $T = 35$ K

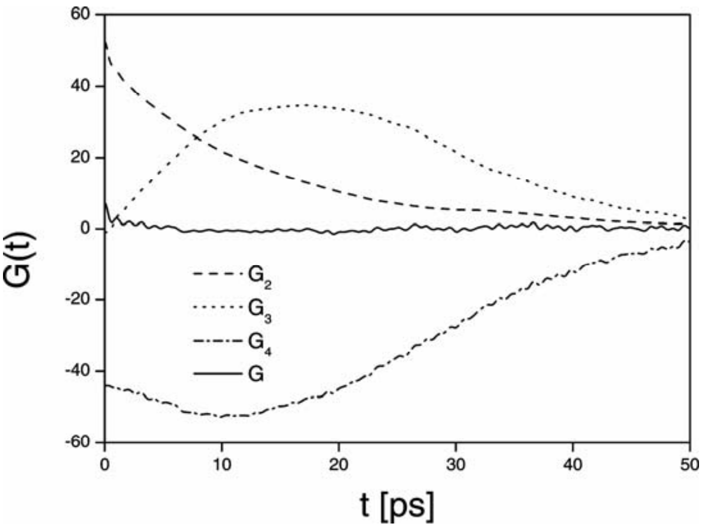


Fig. 5. The polarizability anisotropy correlation function $G(t)$ (solid line) along with its two- (dashed line), three- (dotted line) and four-particle (dash-dot line) components, of Ne film covering the fullerene $C_{60}$ molecule $T = 20$ K

Figure 4 shows the polarizability anisotropy correlation function for the Ne film covering the (5,5) nanotube, along with the pair, triplet and quadruplet components of the correlation function. Analogous results for the case of the $(C_{60})Ne_{68}$ and $(C_{60})Ar_{44}$ systems are shown in Figs. 5 and 6.

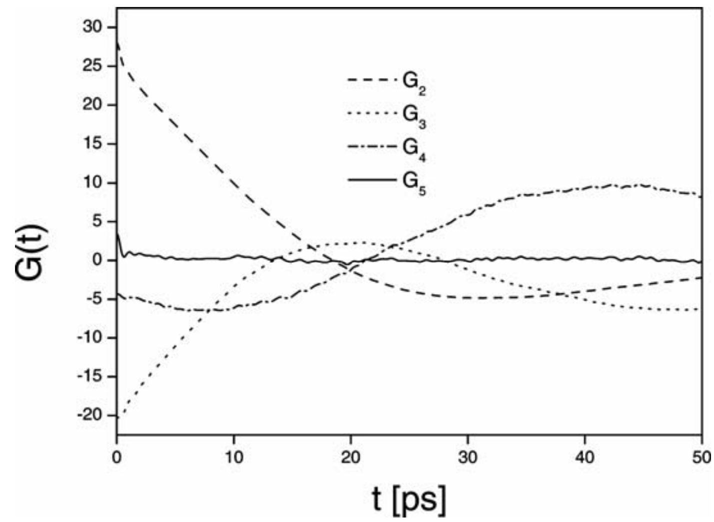


Fig. 6. The polarizability anisotropy correlation function $G(t)$ (solid line) along with its two- (dashed line), three- (dotted line) and four-particle (dash-dot line) components, of Ar film covering the fullerene $C_{60}$ molecule $T$ = 50 K

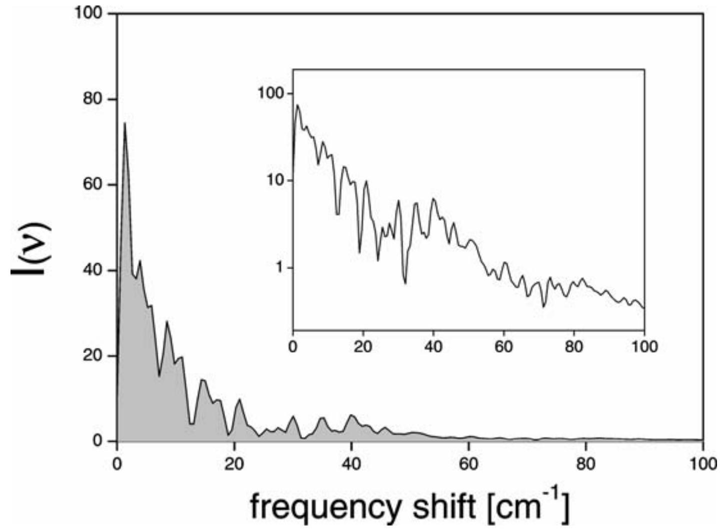


Fig. 7. The interaction induced depolarized scattering spectrum $I(\nu)$ of the Ne film covering the armchair (5,5) nanotube at the temperature $T$ = 35 K. The inset shows the same in logarithmic plot

The interaction induced depolarized scattering spectra of all studied systems are shown in Figs. 7–9.

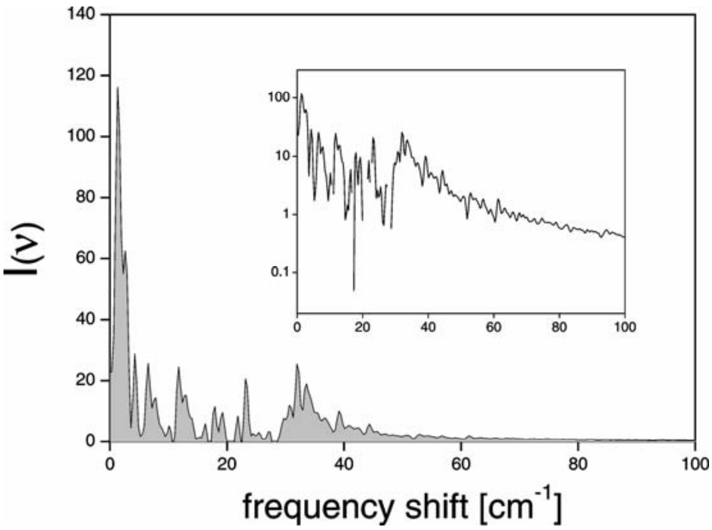


Fig. 8. The interaction induced depolarized scattering spectrum $I(\nu)$ of the Ne film covering the fullerene $C_{60}$ molecule at the temperature $T$ = 20 K. The inset shows the same in logarithmic plot

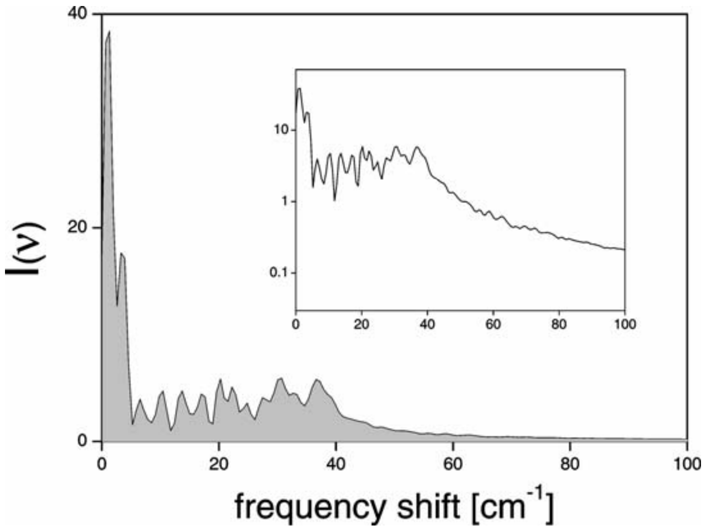


Fig. 9. The interaction induced depolarized scattering spectrum $I(\nu)$of the Ne film covering the fullerene $C_{60}$ molecule at the temperature $T$ = 50 K. The inset shows the same in logarithmic plot

It can be clearly discerned that the spectrum of the Ne film covering the (5,5) nanotube has almost exponential characteristic. The spectra of the Ne and Ar film covering the $C_{60}$ molecule are considerably more complex. This may suggests that the dynamics, in the case of the system covering the (5,5) nanotube, are more liquid-like than in the case of both fullerene systems, and that the adsorption potential between the rare gas atoms and the fullerene has more corrugated characteristic than in the case of the (5,5) nanotube system. Figure 10 shows the mean square displacement of the Ne and Ar atoms in the film covering the (5,5) nanotube and in the $(C_{60})Ne_{68}$ and $(C_{60})Ar_{44}$ systems, which agrees with the above findings and indicates the Ne film covering the (5,5) nanotube exhibit considerably higher diffusion coefficient than in the case of both fullerene based systems.

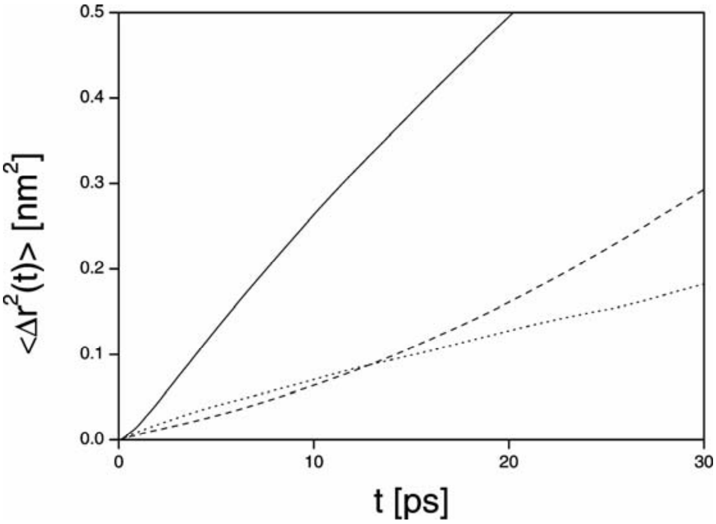


Fig. 10. The mean square displacement of Ne film covering the armchair (5,5) nanotube at the temperature $T = 35$ K (solid line), Ne film covering the fullerene $C_{60}$ at the temperature $T = 20$ K (dashed line) and Ar film covering the fullerene $C_{60}$ at the temperature $T = 35$ K (dashed line)

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