DYNAMICS OF ENDOHEDRAL FULLERENE $K^+@C_{60}$ INSIDE SINGLE WALLED CARBON NANOTUBE: MD SIMULATION

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Abstract: $K^+@C_{60}$ endohedral fullerenes inside *armchair*, *zigzag* and chiral nanotubes were simulated using the MD technique. The structure of the endohedral fullerene sample was estimated by calculating the radial distribution function. The angular and translational velocity autocorrelation functions and their Fourier transforms were also calculated. The frequency dependence of potassium ion vibrations in different nanotubes at room temperature was observed and discussed. A dependency between the angular motion of *endo*-fullerenes and the nanotube chirality was found.

Keywords: *endo*-fullerenes, doped C_{60}, nanotubes, potassium ion, confined geometry

1. Introduction

Fullerenes, new allotropes of carbon, have attracted scientific attention ever since they were discovered [1]. The empty space inside a fullerene cage is a good place to accommodate a wide variety of atoms and small molecules [2]. *Endo*-fullerenes have been synthesized and investigated by several experimental and theoretical methods [3–5].

Among them, such metal atoms as potassium ions are usually taken as fullerene dopants [6]. The external field controlled dynamics of $K^+@C_{60}$ has been also reported [7]. Another interesting carbon structure is the nanotube. Carbon nanotubes reveal many interesting physical properties [8–12]. Composites of *endo*-fullerenes and carbon nanotubes have many interesting electrical and mechanical properties that make them candidates for a nanoelectronic switching devices [13]. The study of nanosystems attracts scientific attention because their properties differ from those of bulk materials [14–20]. The purpose of this work was a computer simulation study of the dynamics of endohedral fullerenes inside a small nanotubes.

2. Computational procedure

The C_{60} molecule and the nanotube were treated as rigid bodies with discrete sites. The interaction between each interacting non-charged site in the C_{60} molecules

and the nanotube or a potassium ion was described by the Lennard-Jones potential $V_{\mathrm{L-J}}(r_{ij}) = 4\varepsilon_{ij}\left[(\sigma_{ij}/r_{ij})^{12} - (\sigma_{ij}/r_{ij})^{6}\right]$, and the interaction between positive charges of potassium ions was described by the Coulomb potential $V_C(r_{ij}) = Z_i Z_j e^2 / 4\pi\varepsilon_0 r_{ij}$, where r_{ij} was the distance between the i-th and j-th atoms of a pair of different molecules, Z_n denoted the charges of each n-th site, e was the electron charge. The σ and ε parameters of the potential used in the simulation are given in Table 1. The parameters of unlike atoms were calculated with the Lorentz-Berthelot rules:

$$\sigma_{ij} = \frac{\sigma_i + \sigma_j}{2}, \quad \varepsilon_{ij} = \sqrt{\varepsilon_i \varepsilon_j}. \tag{1}$$

The classical equations of motion were solved by the Adams-Moulton predictor-corrector algorithm [21]. The integration time step used in simulation was 1 fs. The calculations were carried out for an NVT ensemble. The system was equilibrated to the desired temperature by a Berendsen thermostat [21] for 10^6 MD steps. The Berendsen thermostat was switched on during the collection of MD data. The temperature was defined from the energy equipartition principle:

$$T = \frac{2}{f_d} \frac{\bar{E}_k}{k_{\mathrm{B}}}, \tag{2}$$

where k_{B} was the Boltzmann constant, $\bar{E}_k$ was the average kinetic energy over the ensemble, the coefficient $f_d = 6N - 6$ was a sum of the total number of translational ($3N$) and rotational ($3N$) degrees of freedom minus 3 translational and 3 rotational degrees of whole nanosystem movement, N was the total number of molecules. The total momentum of molecules was conserved to within 0.05%. The autocorrelation functions of linear $\vec{v}$ of K^+ and angular $\vec{\omega}$ velocities of C_{60} and SWCNT molecule were calculated by averaging the translational velocity autocorrelation function $C_v(t) = \langle \vec{v}(0) \cdot \vec{v}(t) \rangle / \langle \vec{v}(0) \cdot \vec{v}(0) \rangle$ and the angular velocity autocorrelation function $C_\omega(t) = \langle \vec{\omega}(0) \cdot \vec{\omega}(t) \rangle / \langle \vec{\omega}(0) \cdot \vec{\omega}(0) \rangle$ over 10^5 time origins. The origins were separated by a time interval equal to 50 integration time steps.

**Table 1.** Lennard-Jones potential parameters taken from [13]

Atom (*site*)	ε [10^{-21} J]	σ [10^{-10} m]	m [10^{-26} kg]
Carbon	0.387	3.4	1.99
Potassium	0.48	3.56	6.49

3. Results and discussion

The *endo*-fullerene model was formed by placing a K^+ ion inside a fullerene cage which was followed by inserting five endohedral fullerenes into a carbon nanotube (Figure 1). The simulation was prepared for three nanotubes, which differed in chirality and diameter (Figure 2). All the nanotubes used in the calculations had the same length of 5 nm. The surface of nanotube was treated as a rigid body. The confined geometry of the system was checked by calculating the radial distribution function $g(r)$ of the C_{60} molecules at $T = 300$ K in a $(10,10)$ armchair nanotube (Figure 3). The plot suggests a solid state structure of *endo*-fullerenes. The nanotube chirality does not change the structure. The nanotube diameter influences the structure of
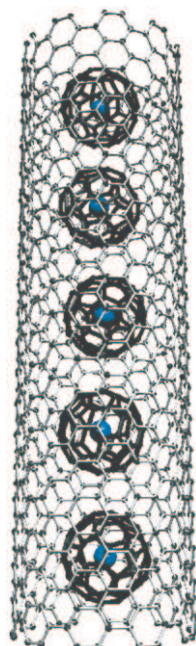
Figure 1. Instantaneous configuration of $K^+@C_{60}$ in the armchair $(10,10)$ nanotube at $T = 300\,\text{K}$
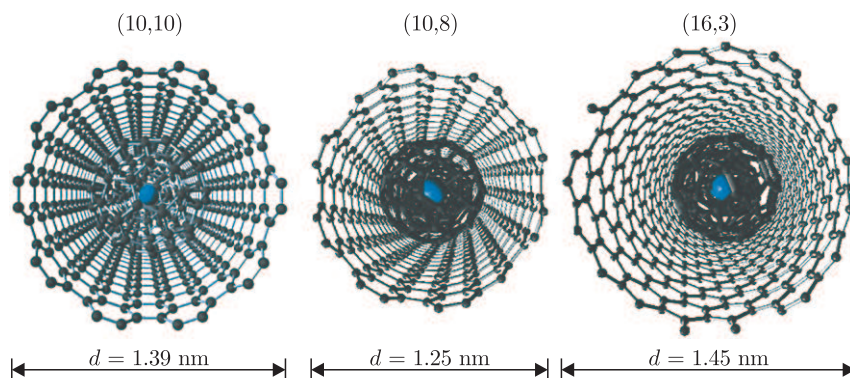

Figure 2. Nanotubes of different chirality cross-sections

endo-fullerenes, see the dashed line in Figure 3. The smaller the nanotube diameter is, the larger the near neighbor distance between the fullerene molecules located inside the nanotube. The fullerene molecules seems to be a bit loosely packed due to an additional interaction with the nanotube surface. The motion of $K^+@C_{60}$ inside the nanotube was investigated by calculating the mean square displacement $\langle \Delta r^2(t) \rangle$ (Figure 4). The slope of the function at higher temperatures shows slow motion of the *endo*-fullerenes inside the nanotube. The bumping in the plot is associated with the vibrations of the C_{60} molecule between the nanotube walls. The dynamics of the fullerenes changes with the diameter of the nanotubes (Figure 5). Less space for movement in the nanotube gives a lower amplitude of vibrations and the molecules move slower along the nanotube long axis. The rotation of the C_{60} molecules is reflected in the $C_\omega(t)$ function at three temperatures for the armchair nanotube $(10,10)$. In
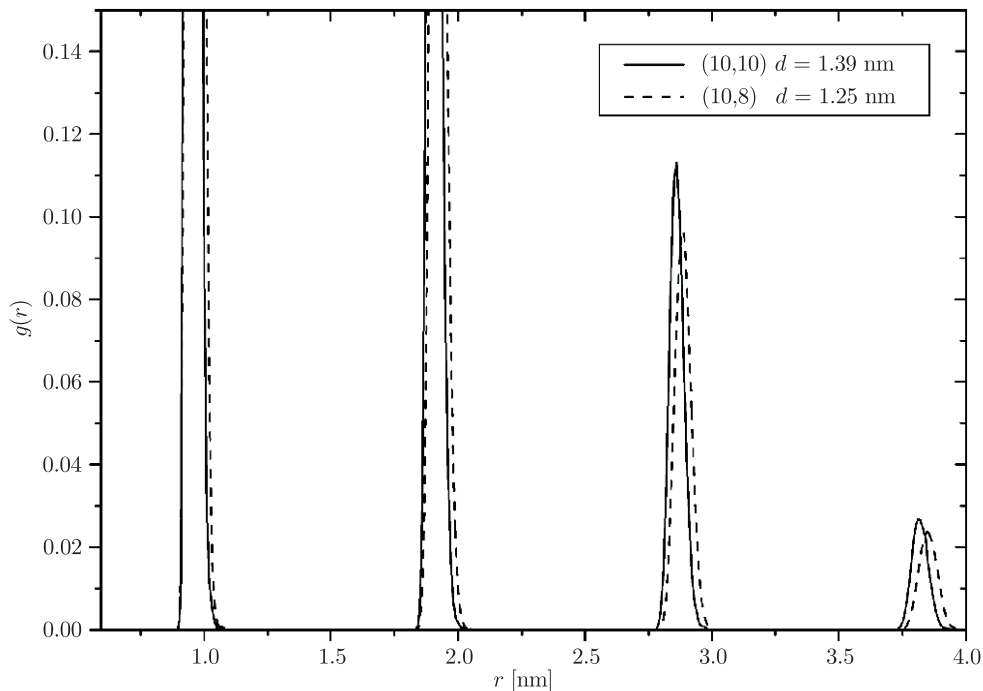
Figure 3. Radial distribution function of C_{60} molecules for two different chirality vectors
at $T = 300\,\mathrm{K}$

the lower temperature ($T = 200\,\mathrm{K}$) the first dip at $t = 4\,\mathrm{ps}$ is visible. The rising of
the temperature causes this firs dip ($T = 350\,\mathrm{K}$) to disappear. The relaxation of the
angular velocity occurs within $60\,\mathrm{ps}$ at $T = 200\,\mathrm{K}$ and $140\,\mathrm{ps}$ at $T = 350\,\mathrm{K}$. Some more
interesting behavior was observed in the plot of the $C_\omega(t)$ function depending on the
chirality and the diameter at the same temperature of $T = 300\,\mathrm{K}$ (Figure 7). The
correlation function $C_\omega(t)$ for the nanotubes with larger diameters decays featureless
and very slowly, up to $180\,\mathrm{ps}$. On the other side in the smaller nanotubes, the function
$C_\omega(t)$ decays also featureless but much faster, approaching almost zero at $t \approx 6\,\mathrm{ps}$. The
last plot for the armchair $(10,10)$ shows a small dip at $2\,\mathrm{ps}$, this can be related to dif-
ferent chirality of nanotubes. The chiral ones $(10,8)$ and $(16,3)$ have some prepared
path that ease the C_{60} molecule rotation. The charged K^+ ions potentially gener-
ate electromagnetic waves of a frequency proportional to their vibrational motion.
To investigate this property, the translational velocity autocorrelation function of
the K^+ ion at $T = 300\,\mathrm{K}$ in a armchair nanotube was calculated (Figure 8). A first
look at this plot reveals at least two characteristic frequencies. A fast vibration of
the ion against the fullerene cage is combined with the motion along the nanotube.
The function $C_v(t)$ decays to zero within $15\,\mathrm{ps}$. The cosine Fourier transform of the
$C_v(t)$ shows two frequency bands (Figure 9). The sharp peak at $\nu = 158\,\mathrm{cm}^{-1}$ is
the oscillation frequency of the K^+ ion in a fullerene cage [22]. Several peaks show
up between 0–$40\,\mathrm{cm}^{-1}$ in the low frequency band. These can be related to the slow
motion of fullerenes. The lower peak at $\nu = 7.56\,\mathrm{cm}^{-1}$ can be related to bouncing
along the nanotube long axis and the higher groups of peaks can be related to an
interaction between the *endo*-fullerenes and the nanotube surface. A modification
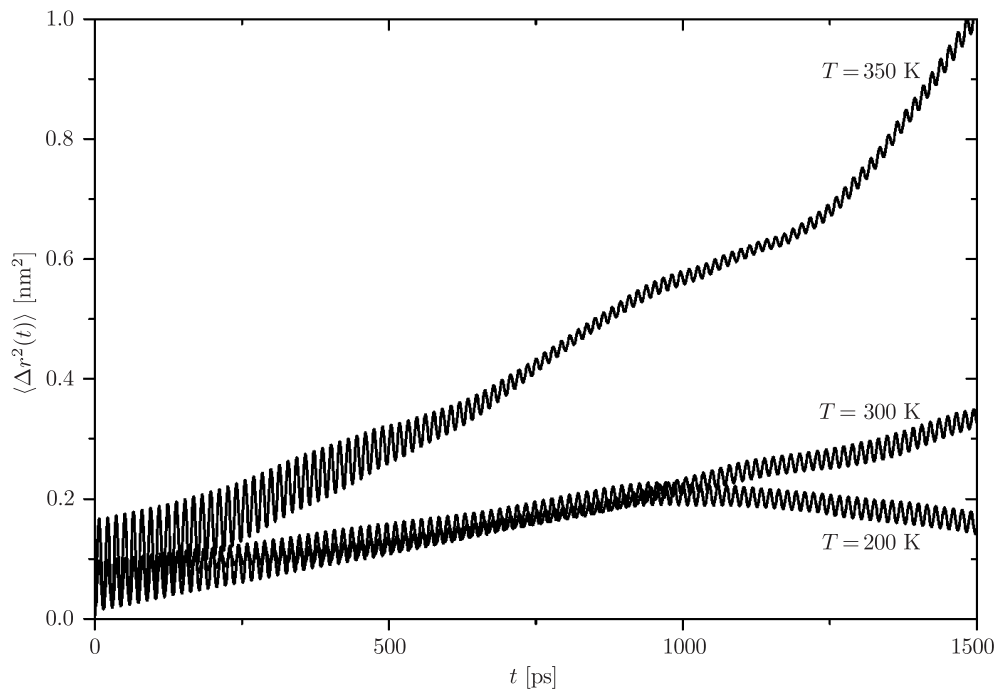
Figure 4. Mean square of the C_{60} molecule center of mass displacement at three temperatures; the molecules are inside the armchair carbon nanotube with chirality (10,10)
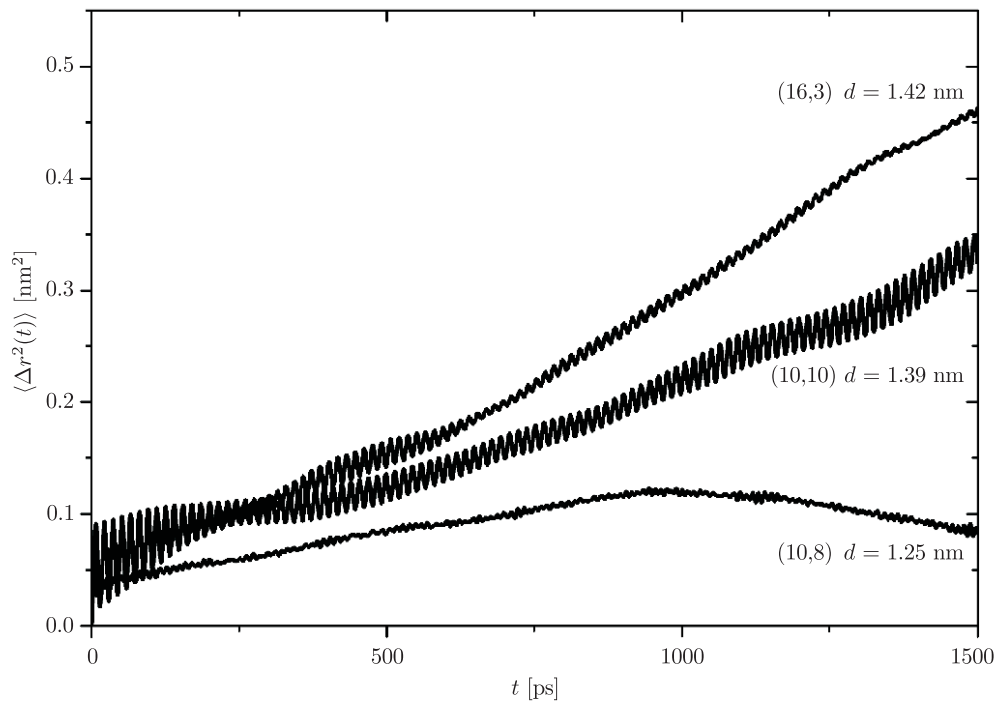
Figure 5. Mean square of the C_{60} molecule center of mass displacement at $T = 300 \, \text{K}$; the molecules are inside three different nanotubes with different chiralities and diameters
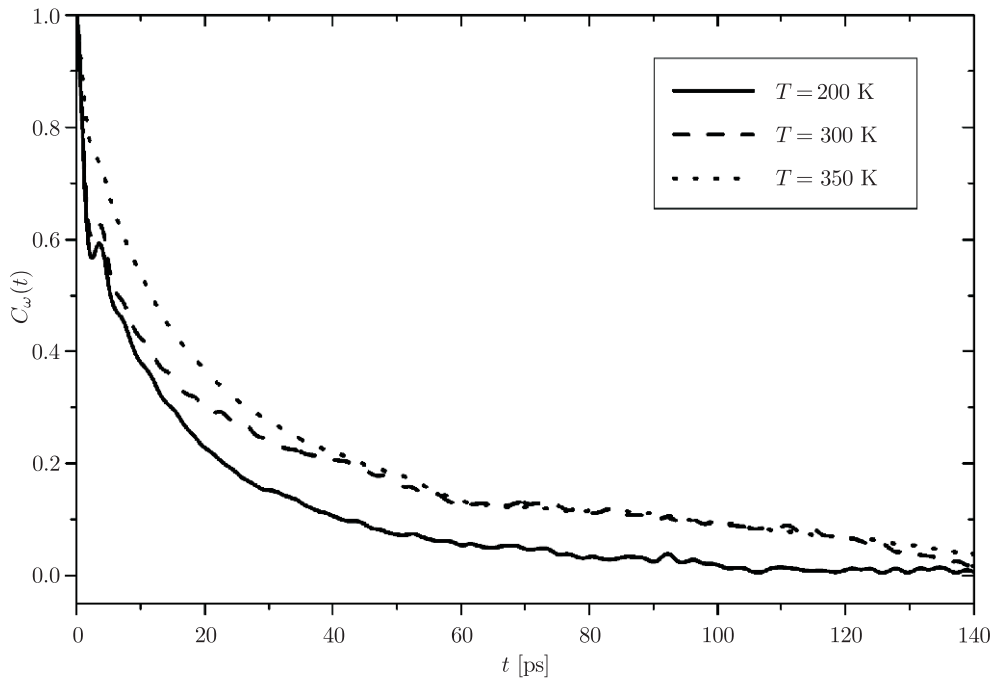
Figure 6. $C_\omega(t)$ function of the C_{60} molecules in the armchair (10,10) carbon nanotube
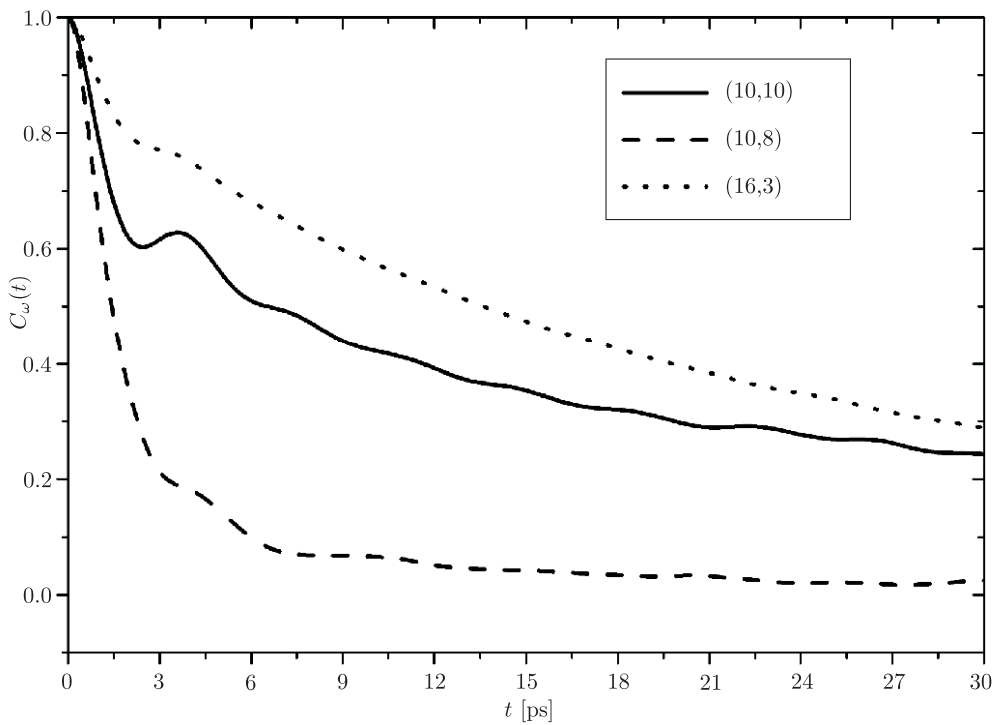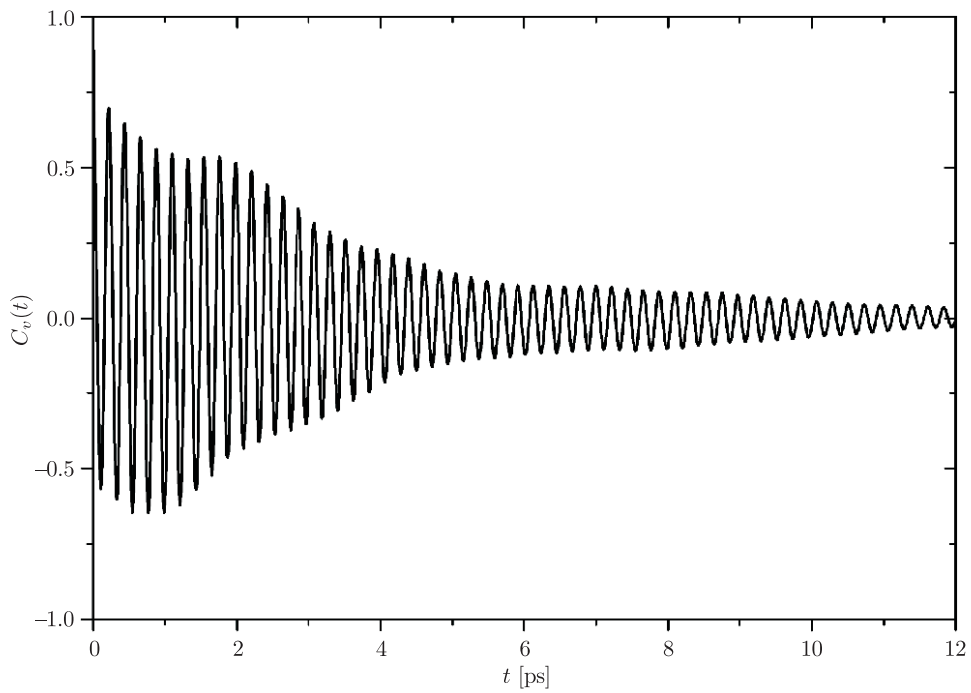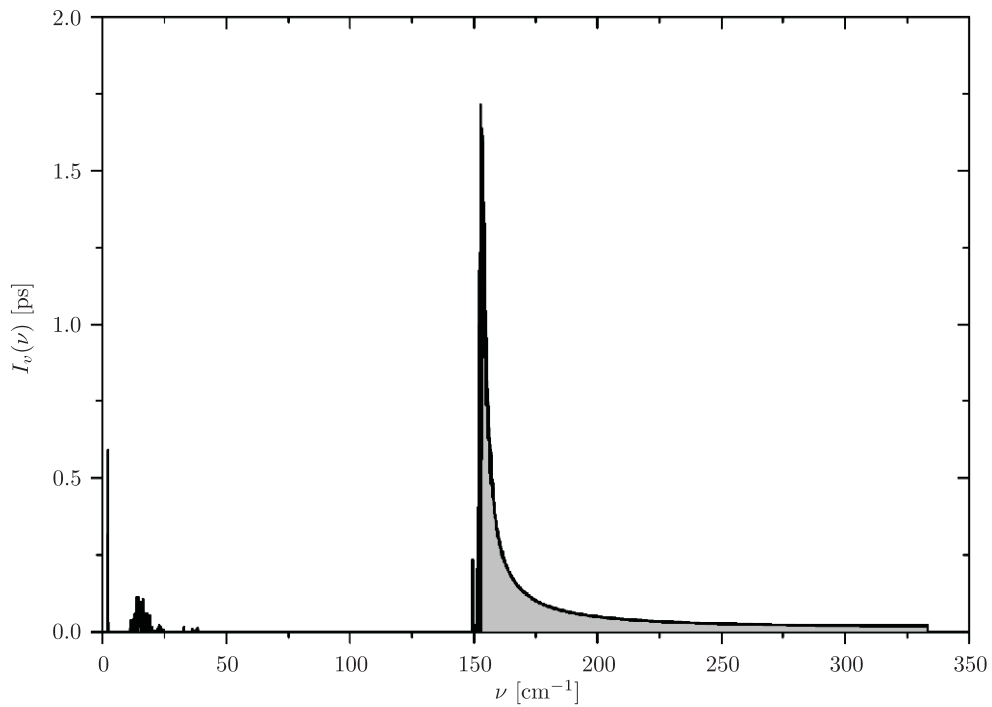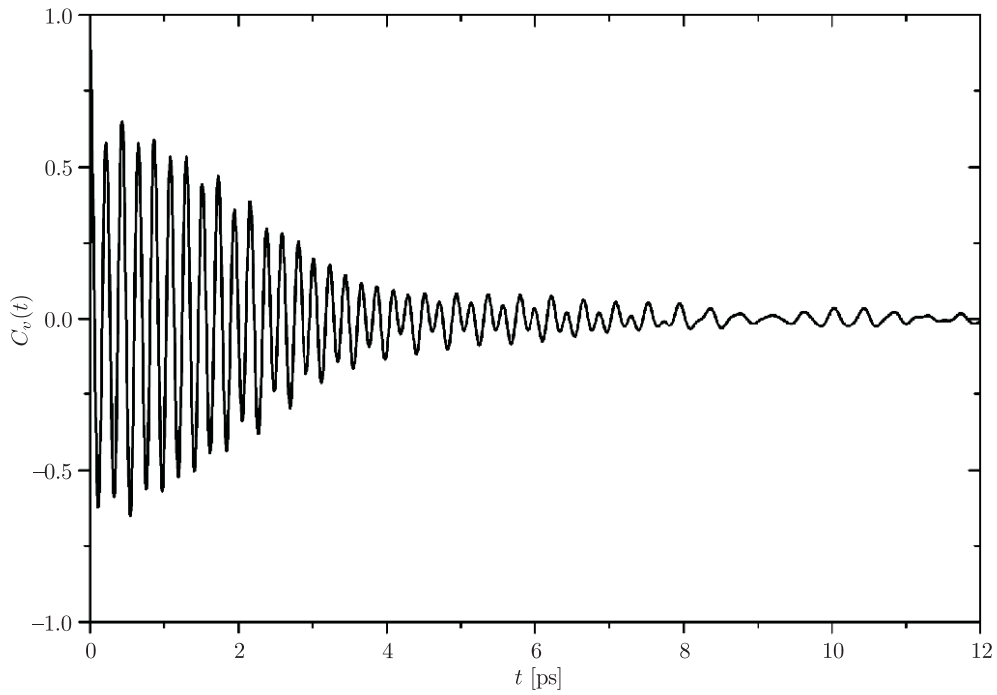at three temperatures

Figure 7. $C_\omega(t)$ function of the C_{60} molecule for three different chiralities of carbon nanotubes
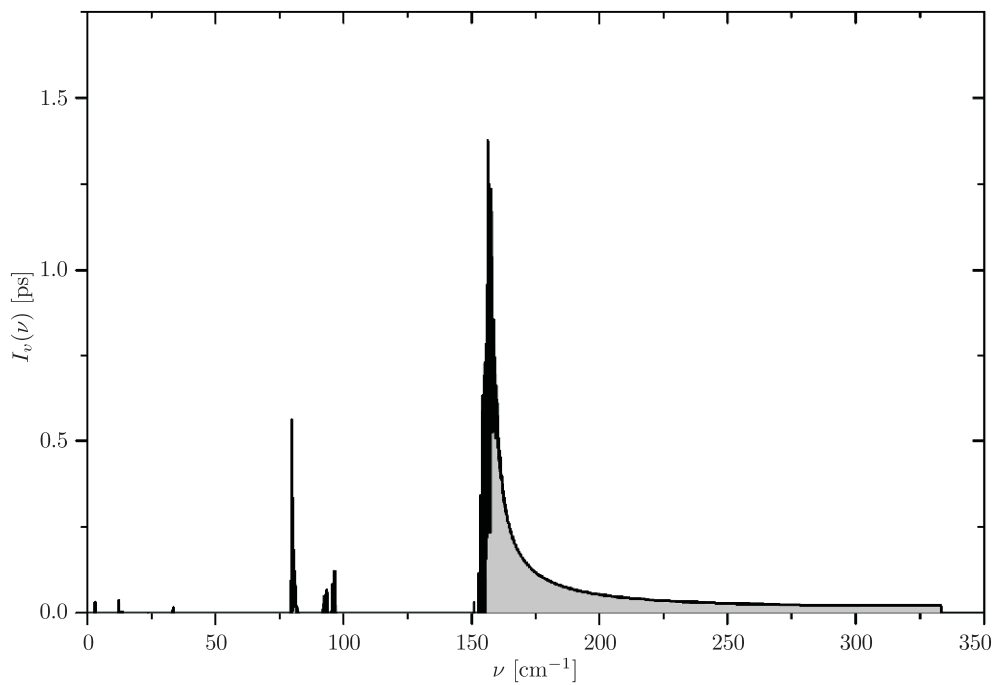at $T = 300\,\text{K}$

Figure 8. $C_v(t)$ function of K^+ ions inside the armchair (10,10) carbon nanotube at $T = 300\,\mathrm{K}$

Figure 9. Cosine Fourier transform of the $C_v(t)$ function of K^+ ions inside fullerenes at $T = 300\,\mathrm{K}$ in the armchair (10,10) nanotube

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Figure 10. $C_v(t)$ function of K^+ ions at $T = 300\,\mathrm{K}$ in the chiral (10,8) carbon nanotube

Figure 11. Cosine Fourier transform of the $C_v(t)$ function of K^+ ions at $T = 300\,\mathrm{K}$ in the chiral (10,8) carbon nanotube

of the nanotube diameter and chirality effects the $C_v(t)$ correlation function. For a nanotube with chirality (10,8) and diameter $d = 1.25\,\text{nm}$ the function $C_v(t)$ decays faster, within 8 ps (Figure 10). The cosine Fourier transform of this function shows a new band in the frequency range from 75 to $100\,\text{cm}^{-1}$ (Figure 11). This band can be related to the bumping motion of fullerenes between tight nanotube walls.

4. Conclusions

A simulation of small cluster of five $K^+@C_{60}$ inside a carbon nanotube shows a few interesting properties. First of all, the potassium atom vibrations inside the cage strongly depend on the carbon nanotubes diameter. The angular motion of *endo*-fullerene in chiral nanotubes is easier than in an armchair nanotube. This property of $K^+@C_{60}$ can be used for probing the nanotube structure. These studies may contribute to future experimental and computational research of endohedral fullerenes in confined geometries.

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