Microscopic polarization in ropes and films of aligned carbon nanotubes

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Abstract. The microscopic electric polarization in terms of the dipole-dipole polarizability and its second hyperpolarizability of aligned films and ropes of carbon nanotubes has been studied theoretically by a point-dipole interaction model. The results show clearly the influence of intertube interactions on the microscopic polarization demonstrating the sensitivity of the electronic structure of carbon nanotubes to the surroundings. Both the polarizability and the second hyperpolarizability are screened due to the intertube interactions and deviate substantially from an additive model. It is noted that both the polarizability and the second hyperpolarizability reach their minimum values around the van der Waals separation. In the rope arrangement the polarizability of a tube is reduced by 10% and the second hyperpolarizability by as much as 50% as compared to an unperturbed tube.

1. Introduction

The physical properties of carbon nanotubes is, due to their low dimensional structures, of great interest with respect to design of potential devices within nanotechnology [1–11]. Carbon nanotubes occur as single- or multi-walled tubes, where single-walled carbon nanotubes tend to bundle up into ropes due to weak van der Waals interactions [12]. Although, it is mainly the electronic and mechanical properties of carbon nanotubes which have been studied [13–15], the optical properties have also achieved considerable interest due to the potential applications of carbon nanotubes in nanophotonics. Due to a high signal-to-noise ratio for its nonlinear optical (NLO) properties [16], carbon nanotubes have been considered for optical limiting materials [17], photonic crystals [18] and as ultrafast all-optical switches [19,20], which are expected to be important components of future optical communication devices [21]. Knowledge of how changes in NLO properties are related to structural configurations of the carbon nanotubes is thus crucial for obtaining nano-optical switches by a suitable assembly of carbon nanotubes.

For all-optical switches the property of interest is the intensity-dependent refractive index. At a microscopic level the refractive index is governed by the polarizability and the intensity dependence by the second hyperpolarizability. Thus design of new NLO materials on an atomistic level requires a detailed understanding of the electronic structure of the molecular units including the polarization...
from the surroundings [22,23]. Unfortunately, high-accuracy electronic structure calculations of fourth-order molecular properties, like the second hyperpolarizability, are presently limited to relatively small molecules. Methods based on classical electrostatics, or additive approaches, are from a computational point of view many orders of magnitude faster than the corresponding quantum chemical methods, and they are of general interest when considering nanosized systems.

One such classical model is the point-dipole interaction (PDI) model which is based on representing the molecule as a set of interacting point (hyper)polarizabilities [24–28]. Previously, the PDI model has been used to study the NLO properties of carbon nanotubes and fullerene aggregates [28–33]. Related work is based on capacitance models [34,35] and electronegativity equalization models [36], which have been used for the calculation of polarizabilities of carbon nanotubes and fullerenes [37–40]. Similar models have been used to describe molecular polarizabilities [25,27,41–48], polarization in molecular clusters [49–51], and polarization in molecular crystals [52]. Furthermore, molecular modelling has been adopted extensively to study mechanical properties of carbon nanotubes and fullerenes by molecular mechanics and molecular dynamics methods [53–60], and electronic properties by semi-empirical, density functional theory and ab initio quantum chemical methods [61–76]. In the present work, the PDI model is used to investigate how the polarizability and second hyperpolarizability of carbon nanotube aggregates change due to intertube interactions when the nanotubes bundle up into ropes and films.

2. Theoretical background

In the PDI model, a system is considered to consist of \( N \) interacting point polarizabilities, \( \alpha_{I,\alpha\beta} \), and second hyperpolarizabilities, \( \gamma_{I,\alpha\beta\gamma\delta} \), for which the atomic induced dipole moment, \( \mu_{I,\alpha}^{\text{ind}} \), of atom \( I \) is given as

\[
\mu_{I,\alpha}^{\text{ind}} = \alpha_{I,\alpha\beta} E_{I,\beta}^{\text{tot}} + \frac{1}{6} \gamma_{I,\alpha\beta\gamma\delta} E_{I,\gamma}^{\text{tot}} E_{I,\delta}^{\text{tot}} E_{I,\beta}^{\text{tot}},
\]

where the total electric field, \( E_{I,\beta}^{\text{tot}} \), at atom \( I \), is the sum of the external field and the electric field from all other induced dipole moments. Greek subscripts denote the Cartesian coordinates, \( x, y, \) or \( z \) and the Einstein summation convention is used for repeated Greek subscripts. This represents a set of \( 3N \) coupled linear equations for which a self-consistent solution can be written as [26,28]

\[
\mu_{I,\alpha}^{\text{ind}} = \sum_{J} B_{IJ,\alpha\beta}^{(2)} E_{I,\beta}^{\text{ext}} + \frac{1}{6} \sum_{J,K,L} B_{IJKL,\alpha\beta\gamma\delta}^{(4)} E_{I,\gamma}^{\text{ext}} E_{I,\delta}^{\text{ext}} E_{I,\beta}^{\text{ext}},
\]

where \( B_{IJ,\alpha\beta}^{(2)} \) is the two-atom relay tensor, \( B_{IJKL,\alpha\beta\gamma\delta}^{(4)} \) is the four-atom relay tensor, and \( E_{I,\beta}^{\text{ext}} \) is the external electric field at atom \( I \). The two-atom relay tensor, \( B_{IJ,\alpha\beta}^{(2)} \), describes the response at atom \( I \) from a perturbation at atom \( J \), and the four-atom relay tensor can be interpreted in a similar way. If the external electric field is regarded as homogeneous, the resulting molecular polarizability, \( \alpha_{\alpha\beta}^{\text{mol}} \), and molecular second hyperpolarizability, \( \gamma_{\alpha\beta\gamma\delta}^{\text{mol}} \), are given in terms of relay tensors as

\[
\alpha_{\alpha\beta}^{\text{mol}} = \sum_{IJ} B_{IJ,\alpha\beta}^{(2)} ,
\]

\[
\gamma_{\alpha\beta\gamma\delta}^{\text{mol}} = \sum_{IJKL} B_{IJKL,\alpha\beta\gamma\delta}^{(4)} .
\]
and
\[
\gamma_{\alpha\beta\gamma\delta}^{\text{mol}} = \sum_{IJKL} N B_{IJKL,\alpha\beta\gamma\delta}^{(4)}.
\]

This kind of relay tensors is thus a viable partition scheme of the molecular (hyper)polarizability into local contributions. The theoretical background is described in more detail in previous work [28].

If the atoms are regarded as spherically symmetric particles, the molecular properties, \(\alpha_{\alpha\beta}^{\text{mol}}\) and \(\gamma_{\alpha\beta\gamma\delta}^{\text{mol}}\), may be parametrized by adopting atomic (hyper)polarizabilities, \(\alpha_P\) and \(\gamma_P\), which are considered as atom-type parameters. An improved parametrization is obtained if charge distributions are included in terms of a damping of the dipole-dipole interactions at short distances instead of using a point-particle model [29,77]. Consequently, by adopting three parameters for each element, a polarizability, \(\alpha_P\), a second hyperpolarizability \(\gamma_P\), and a damping parameter, \(\Phi_P\), good results can be obtained for the molecular polarizability and second hyperpolarizability [28,29,78]. It has also been demonstrated that accurate parameters are obtained if they are parametrized from a training set of molecular polarizabilities obtained from quantum chemical calculations instead of experimental data [78]. One reason is that experimental polarizabilities also include vibrational contributions in addition to the electronic polarization included in Eq. (1). In addition, experimental results are often obtained from condensed phases and thus include also solvent effects and a model for conversion from macroscopic to microscopic polarization.

Due to their unique electronic properties carbon nanotubes may exhibit metallic or semi-conductor character depending on the radius, length and folding of the tube [4]. The folding and diameter of nanotubes are described in terms of a vector \((n,m)\) where the tube is referred to as armchair if \(n = m\), zig-zag if \(n = 0\) or \(m = 0\), and otherwise chiral [4,15]. Tight-binding calculations predict all armchair tubes to be metallic, zig-zag tubes to be metallic if \(n/3\) is an integer, and otherwise semiconducting with the inverse of the band gap proportional to the tube radius [62–64]. However, the finite curvature of the tube has been predicted to produce small gaps in “metallic” zigzag tubes [63,64,79]. In addition, intertube interactions can break the rotational symmetry of armchair nanotubes which should lead to a pseudo-gap [62–64]. These predictions have been confirmed experimentally by scanning tunneling microscopy (STM) showing that “metallic” zigzag nanotubes in fact are small-gap semiconductors [83]. Isolated armchair nanotubes were found to have zero band gap, however, in nanotube bundles a pseudo-gap opened up due to the intertube interactions. For both types of systems, the inverse of the band gaps was found to be proportional to the nanotube radius [83].

All of these results refer to very long nanotubes, i.e. infinitely long tubes were considered in the calculations and the nanotubes investigated in the experiments were typically several microns long. Experimentally, it has been shown using STM spectroscopy that by cutting long isolated metallic nanotubes into smaller segments of about 30 nm, a band gap opened up due to quantum confinement along the tube [84]. Theoretical calculations on small finite-length nanotubes have also shown that there is a band gap which slowly diminishes when the length increases and is expected eventually to converge to zero [71,85,86]. Exactly for which lengths the transition to the metallic state occurs is not known but estimates indicate in the range of 10–20 nm [71].

In the PDI model, a system, e.g. a tube, is regarded to be non-metallic, i.e. the polarizability per length unit, \(\alpha/N\), as a function of the length of the tube approaches a constant value. In contrast, a capacitance or electronegativity equalization model regard the system to be metallic, i.e. \(\alpha/N\) approaches infinity for an infinitely large system [35,38–40]. However, this also means that these latter models predict an infinite polarizability for two particles infinitely separated [35], and these models can therefore not be
used to study the interaction (hyper)polarizabilities as a function of the separation which is the aim of this work.

A recent study of the size-scaling of the polarizability for small tubular fullerenes showed that the PDI model gives results in good agreement with results obtained using time-dependent current-density functional theory (TDCDFT) [87]. The good agreement between DFT and the PDI model is further supported by considering the transverse polarizability of carbon nanotubes. Using the PDI model, we have calculated the transverse polarizability per length unit of a (5,5) and (9,0) nanotube and found values of 8.49 Å² and 8.62 Å², respectively [32]. The results are in good agreement with a recent DFT study where values of 7.66–7.79 Å² were found for the (5,5) tube and values between 8.04–8.19 Å² for a (9,0) tube [76]. Both of these results are in agreement with results for the (5,5) nanotubes of 7.92 Å² obtained using TDCDFT and 9.28 Å² obtained using conventional DFT [87]. These results illustrate the usefulness of the PDI model for studying these large carbon nanostructures.

3. Calculational details

As a model system, we have considered structures of (5,5) carbon nanotubes with a uniform bond length of 1.42 Å and a length of ~ 6.3 nm, corresponding to 500 carbon atoms per tube. The length of the tubes is thus sufficiently short so that the transition to a metallic state for an isolated (5,5) nanotube has not occurred. The PDI model should therefore provide a realistic description of both the isolated tube and the intertube interactions.

The values of the atom-type parameters used in this work are \( \alpha_C = 8.465 \) a.u., \( \Phi_C = 0.124 \) a.u., and \( \gamma_C = 1600.0 \) a.u. These parameters have been taken from our previous work [29,28,30], where it has been shown that they give reliable results for polarizabilities and hyperpolarizabilities of fullerenes and nanotubes.

The deviation from additivity has been calculated, i.e. the relative difference, \( \delta B(R) \), between the property \( B \) of the nanotubes at the distance \( R \), denoted \( B(R) \), and at infinite distance \( \infty \), denoted \( B(\infty) \), given as

\[
\delta B(R) = \frac{B(R) - B(\infty)}{B(\infty)} \times 100\%.
\]  

(5)

We have considered the dependence of the polarizability and second hyperpolarizability on the distance between two nanotubes positioned as indicated in Fig. 1(a). The two nanotubes are placed in the \( yz \)-plane with parallel cylindrical axes along the \( z \)-axis. The distance between the nanotubes (the wall-to-wall intertube distance, \( R \)) is given by the separation in the \( y \)-direction. The films (F-N) and the rope (R-N) of nanotubes, where \( N \) is the number of tubes, have been generated such that the neighbouring carbon nanotubes are separated by a distance corresponding to the van der Waals intertube distance of 3.2 Å [12]. The films of the nanotubes are placed in the \( yz \)-plane with the axis of the carbon nanotubes parallel to the \( z \)-axis. The rope of nanotubes is oriented such that the nanotubes are parallel to the \( z \)-axis. Figures 1b and 1c depict the arrangements of the nanotubes for the configurations of the films and the rope, respectively.

The isotropic polarizability is given by

\[
\alpha = \frac{1}{3} (\alpha_{xx} + \alpha_{yy} + \alpha_{zz})
\]  

(6)
Fig. 1. Orientation of the carbon nanotubes in (a) dimer, (b) film, and (c) rope configuration.

Fig. 2. Deviation from additivity in the polarizability ($\delta \alpha$) as a function of the intertube distance in Å.

and the mean second hyperpolarizability by [88–90]

$$\gamma = \frac{1}{5} (\gamma_{xxxx} + \gamma_{yyyy} + \gamma_{zzzz} + 2\gamma_{xxyy} + 2\gamma_{xxzz} + 2\gamma_{zzyy}).$$  \hspace{1cm} (7)

4. Results

4.1. Polarizability of carbon nanotube dimers

In Figs 2 and 3, it is illustrated how the polarizability and hyperpolarizability tensor components along with $\alpha$ and $\gamma$ depend on the intertube distance, respectively. $\delta \alpha (R)$ is less than 3% at all distances, and it is observed that the isotropic polarizability is rather insensitive to the distance between the nanotubes. On the other hand, its three non-zero components, $\alpha_{xx}$, $\alpha_{yy}$, $\alpha_{zz}$, depend strongly on the intertube distance. For example, the component along the intertube separation axis, $\alpha_{yy}$, increases with decreasing distance between the nanotubes. At an intertube separation distance corresponding to the van der Waals (vdW) distance of $\sim 3.2$ Å [12], $\delta \alpha_{yy}$ is 20%, and even at distances around 10 Å it is as large as 5%. In contrast, $\alpha_{xx}$ and $\alpha_{yy}$ decrease as the two nanotubes approach each other and at the vdW distance, they amount to about 10% and 5%, respectively.
Table 1

<table>
<thead>
<tr>
<th>N</th>
<th>$\alpha_{xx}$</th>
<th>$\alpha_{yy}$</th>
<th>$\alpha_{zz}$</th>
<th>$\tau$</th>
<th>$\tau/N$</th>
</tr>
</thead>
<tbody>
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<td>Films</td>
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<td>3560.9</td>
<td>3560.9</td>
<td>11987.6</td>
<td>6369.8</td>
<td>6369.8</td>
</tr>
<tr>
<td>F-2</td>
<td>6372.2</td>
<td>8493.5</td>
<td>22746.1</td>
<td>12537.3</td>
<td>6268.6</td>
</tr>
<tr>
<td></td>
<td>(−11%)</td>
<td>(+19%)</td>
<td>(−5%)</td>
<td>(−2%)</td>
<td>(−2%)</td>
</tr>
<tr>
<td>F-3</td>
<td>9082.0</td>
<td>14074.1</td>
<td>32837.9</td>
<td>18664.7</td>
<td>6221.6</td>
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<td></td>
<td>(−15%)</td>
<td>(+32%)</td>
<td>(−9%)</td>
<td>(−2%)</td>
<td>(−2%)</td>
</tr>
<tr>
<td>F-5</td>
<td>14417.9</td>
<td>26188.4</td>
<td>52196.4</td>
<td>30934.2</td>
<td>6186.8</td>
</tr>
<tr>
<td></td>
<td>(−19%)</td>
<td>(+47%)</td>
<td>(−13%)</td>
<td>(−3%)</td>
<td>(−3%)</td>
</tr>
<tr>
<td>F-7</td>
<td>19712.1</td>
<td>38916.4</td>
<td>71094.4</td>
<td>43241.0</td>
<td>6177.3</td>
</tr>
<tr>
<td></td>
<td>(−21%)</td>
<td>(+56%)</td>
<td>(−15%)</td>
<td>(−3%)</td>
<td>(−3%)</td>
</tr>
<tr>
<td>Rope</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>R-7</td>
<td>26796.3</td>
<td>26805.9</td>
<td>66174.6</td>
<td>39925.6</td>
<td>5703.7</td>
</tr>
<tr>
<td></td>
<td>(+8%)</td>
<td>(+8%)</td>
<td>(−21%)</td>
<td>(−10%)</td>
<td>(−10%)</td>
</tr>
</tbody>
</table>

Both $\delta \alpha$ and $\delta \alpha_{zz}$, and thus also $\alpha$ and $\alpha_{zz}$, decrease with diminishing separation at large distances but close to the vdW distance between the nanotubes they reach a minimum. This is in agreement with the minimum polarizability principle, which states that a system will tend to the minimum value of the polarizability at the equilibrium geometry [91]. At the minimum energy distance, the energy is a balance between electrostatic, polarization, dispersion and exchange repulsion contributions, and also the intermolecular effect on the polarizability at this distance contains the same contributions. In the PDI model, however, only a polarization term is included for the change in the molecular polarizability. It is also noted that $\delta \alpha_{zz}$ ($R$) is dominated by the contribution from $\alpha_{zz}$, since the value of $\alpha_{zz}$ is about a factor of 2 larger than the sum of the two other components (see Table 1).

For the PDI model, the dependence of the polarizability on the interparticle distances may be interpreted in terms of Silberstein’s equations, i.e. the solutions of the two-particle PDI model [24],

$$
\alpha = \frac{\alpha_1 + \alpha_2 + \frac{4 \alpha_1 \alpha_2}{N_{12}^2}}{1 - \frac{4 \alpha_1 \alpha_2}{N_{12}^4}}
$$

(8)
and

$$\alpha_\perp = \frac{\alpha_1 + \alpha_2 - \frac{2\alpha_1\alpha_2}{R_{12}^6}}{1 - \frac{\alpha_1\alpha_2}{R_{12}^6}},$$  \hspace{1cm} (9)$$

where $\alpha_\parallel$ and $\alpha_\perp$ are the components along and perpendicular to the vector connecting particles 1 and 2, respectively. At very long interparticle distances, $R_{12}^{-6} \approx R_{12}^{-3} \approx 0$, an additive model is obtained, which is expected since two particles placed infinitely far away from each other do not interact. At intermediate distances, $R_{12}^{-6} \approx 0$ and $R_{12}^{-3} \neq 0$, it is found that the isotropic polarizability,

$$\bar{\alpha} = \frac{1}{3} (\alpha_{xx} + \alpha_{yy} + \alpha_{zz}) = \frac{1}{3} (\alpha_\parallel + 2\alpha_\perp) = \alpha_1 + \alpha_2,$$  \hspace{1cm} (10)$$
is additive whereas the individual components have substantial contributions from interparticle interactions. This is consistent with what we find here for two interacting nanotubes. At sufficiently short distances, $R_{12}^{-6} \neq 0$, both components increase with decreasing distance, which eventually leads to a polarization catastrophe if not a short-range damping term is included. As seen in Eqs (8) and (9), $\alpha_\perp$ has a minimum at some distance $R$, whereas $\alpha_\parallel$ is monotonically decreasing with $R$ beyond the distance for the polarization catastrophe. This explains why $\alpha_{zz}(R)$ (and also $\bar{\alpha}(R)$ since it is dominated by $\alpha_{zz}(R)$) has a minimum, but we cannot provide an explanation for why it appears at the vdW distance.

4.2. Second hyperpolarizability of carbon nanotube dimers

Compared to the linear polarizability, $\bar{\gamma}$ has a much stronger dependence on the intertube distance (see Fig. 3), but the overall behaviour of $\alpha$ and $\gamma$ are similar. As for $\bar{\alpha}$, the second hyperpolarizability decreases steadily until it reaches a minimum at the vicinity of the vdW distance. For any given intertube distance, the effects on $\bar{\gamma}$ are about a factor of 4 larger than those observed for $\bar{\alpha}$. Even at intertube distances around 10 Å, the intermolecular effects on $\bar{\gamma}$ amount to more than 10%.

Also the dependence of the non-zero tensor components, $\gamma_{xxxx}$, $\gamma_{yyyy}$, $\gamma_{zzzz}$, $\gamma_{xxyy}$, $\gamma_{xxzz}$ and $\gamma_{yyzz}$ on the intertube distance is presented in Fig. 3. The component along the intertube separation axis, $\gamma_{yyyy}$, increases strongly as the distance between the two nanotubes becomes smaller. The enhancement of $\gamma_{yyyy}$ at the vdW distance is larger than 80% and even at larger distances, around 10 Å, the effect is around 3 % The two other components, $\gamma_{xxxx}$ and $\gamma_{zzzz}$, decrease as the distance between the nanotubes gets smaller. They are diminished by a similar amount until an intertube distance around 10 Å, but for shorter distances the reduction of $\gamma_{xxxx}$ is larger than for $\gamma_{zzzz}$. As for $\alpha_{zz}$, $\gamma_{zzzz}$ reaches a minimum in the vicinity of the vdW distance between the two nanotubes. The overall distance dependence of $\bar{\gamma}$ is determined by $\gamma_{zzzz}$ due to its much larger value compared to the magnitudes of the other components (see Table 2). For completeness, the results for the non-zero off-diagonal components, $\gamma_{xxyy}$, $\gamma_{xxzz}$ and $\gamma_{yyzz}$ are also presented in Fig. 3, but they are not discussed further.

4.3. Polarizabilities and hyperpolarizabilities of films and a rope of carbon nanotubes

In Tables 1 and 2, results are presented for the polarizabilities and hyperpolarizabilities for five different arrangements of carbon nanotubes and the deviations from an additive model are presented by the values in the parentheses. The isotropic polarizabilities of the films deviate with less than 3% from an additive model. On the other hand, the three components, $\alpha_{xx}$, $\alpha_{yy}$, $\alpha_{zz}$, deviate significantly which again
Table 2

Static second hyperpolarizability ($10^4$ atomic units) for carbon nanotube films and rope. Percent deviation from additivity in parentheses. N is the number of tubes.

<table>
<thead>
<tr>
<th>N</th>
<th>$\gamma_{xxx}$</th>
<th>$\gamma_{yyy}$</th>
<th>$\gamma_{zzz}$</th>
<th>$\gamma_{xxy}$</th>
<th>$\gamma_{xxz}$</th>
<th>$\gamma_{yyz}$</th>
<th>$\gamma$</th>
<th>$\gamma$/N</th>
</tr>
</thead>
<tbody>
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<td>Film</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>57.8</td>
<td>57.82</td>
<td>5606.8</td>
<td>19.3</td>
<td>166.4</td>
<td>166.4</td>
<td>1285.3</td>
<td>1285.3</td>
</tr>
<tr>
<td>F–2</td>
<td>74.9 (−35%)</td>
<td>231.2 (+100%)</td>
<td>9421.8 (−16%)</td>
<td>50.7 (+32%)</td>
<td>248.1 (−25%)</td>
<td>449.1 (+35%)</td>
<td>2244.7</td>
<td>1122.4 (−13%)</td>
</tr>
<tr>
<td>F–3</td>
<td>92.9 (−46%)</td>
<td>514.3 (+197%)</td>
<td>12070.7 (−28%)</td>
<td>86.3 (+49%)</td>
<td>314.1 (−37%)</td>
<td>769.2 (+54%)</td>
<td>3003.4</td>
<td>1001.1 (−22%)</td>
</tr>
<tr>
<td>F–5</td>
<td>128.9 (−55%)</td>
<td>1326.1 (+359%)</td>
<td>16542.6 (−41%)</td>
<td>165.5 (+72%)</td>
<td>436.7 (−48%)</td>
<td>1450.6 (+74%)</td>
<td>4420.6</td>
<td>884.1 (−31%)</td>
</tr>
<tr>
<td>F–7</td>
<td>164.5 (−59%)</td>
<td>2346.6 (+480%)</td>
<td>20699.8 (−47%)</td>
<td>250.5 (+86%)</td>
<td>554.6 (−52%)</td>
<td>2150.2 (+85%)</td>
<td>5824.3</td>
<td>832.0 (−35%)</td>
</tr>
<tr>
<td>Rope</td>
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<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>R–7</td>
<td>586.0 (+45%)</td>
<td>587.8 (+45%)</td>
<td>15796.3 (−60%)</td>
<td>195.7 (+45%)</td>
<td>953.2 (−18%)</td>
<td>954.4 (−18%)</td>
<td>4235.3</td>
<td>605.0 (−53%)</td>
</tr>
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</table>
Fig. 4. Isotropic polarizability (atomic units) and mean second hyperpolarizability ($10^4$ atomic units) for the individual tubes in the film (a) and rope (b) arrangement.

illustrates the limitations of the additive model when scrutinizing the components of the polarization tensor. For the $\alpha_{yy}$ component, we observe an increase of the tensor element as the number of nanotubes in the film is increased and for F-7 we obtain an increase of 56% whereas the two other tensor elements, $\alpha_{xx}$ and $\alpha_{zz}$, decrease as compared to the additive model by about 21% and 15%, respectively.

For the rope, R-7, $\alpha_{xx}$ and $\alpha_{yy}$ increase with around 8%, whereas $\alpha_{zz}$ is decreased by 21% as compared to an additive model. This leads to that the isotropic polarizability is lowered by around 10%. Similar effects on the linear polarizability have been found for hexatriene clusters [50].

The deviations from an additive model are substantial for the second hyperpolarizabilities. For the four different films, the effects on $\gamma$ change from $-13\%$ to $-35\%$ as the number of nanotubes is increased from 2 to 7. Also, the tensor components deviate substantially from an additive polarization model. For example, the $\gamma_{yyyy}$ component is enhanced by 480% for the largest film, but the magnitude of $\gamma_{yyyy}$ is still much smaller than $\gamma_{zzzz}$ and $\gamma$ is clearly dominated by $\gamma_{zzzz}$.

For the nanotube rope, R-7, $\gamma$ is diminished substantially compared to the nanotube films and the corresponding result from the additive model. The two tensor elements, $\gamma_{xxxx}$ and $\gamma_{yyyy}$ increase by 45% compared to an additive model, but their magnitudes are about a factor of 30 smaller than $\gamma_{zzzz}$. Therefore, the reduction of $\gamma$ is dominated by the 60% reduction of $\gamma_{zzzz}$. Also for the second hyperpolarizability, similar effects have been found for hexatriene clusters [51].

Finally, we consider the magnitudes of the isotropic polarizability and mean second hyperpolarizability for the seven individual nanotubes that are forming the film denoted F-7 and the rope R-7. The individual contribution have been calculated using a localization scheme [92], which we have used previously to study fullerene aggregates [31]. In Fig. 4, the values of $\alpha$ and $\gamma$ are indicated for each nanotube. For the film F-7, we observe a small fluctuation of $\alpha$ as we proceed from one end of the film to the other end. From the center nanotube to the second outermost nanotube, an increase in $\alpha$ is observed. The outermost nanotube has, however, the smallest $\alpha$ of the individual nanotubes. The second hyperpolarizability increases steadily by more than 10% from the center nanotube to the outermost nanotube. For the rope
arrangement, $\alpha$ has the smallest value for the center nanotube and $\alpha$ is only about 2% larger for the outer nanotubes. On the other hand, $\gamma$ is about 5% larger for the center nanotube than for the outer nanotubes.

5. Conclusions

In conclusion, we have investigated the microscopic polarization in aligned carbon nanotube film and rope arrangements using a PDI model. The calculated polarizability and second hyperpolarizability show a strong dependence on the intertube separations. For the dimer, both the polarizability and the second hyperpolarizability are screened due to the intertube interaction and reaches their minimum values at tube separations around the vdW distance. The largest screening effect was found for the rope arrangement where the polarizability was reduced by 10% and the second hyperpolarizability by 50%. The effects are in general, however, much larger for the individual tensor components.

In the design of molecular photonic components based on carbon nanotubes, the intertube interactions are substantial and have to be considered. The screening effects are in the best cases modest for properties dependent on the isotropic polarizabilities as the refractive index, whereas the may be around 50% for the second hyperpolarizability. Furthermore, if the anisotropies or individual tensor components contribute to the mesoscopic or macroscopic property of interest, the effects on the neighbouring tubes may be dramatic.

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References


