Microscopic and Macroscopic Polarization in C$_{60}$ Fullerene Clusters as Calculated by an Electrostatic Interaction Model

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The dipole—dipole polarizability, $\alpha$, and the second hyperpolarizability, $\gamma$, as well as the corresponding linear and third-order susceptibilities, $\chi^{(1)}$ and $\chi^{(3)}$, have been calculated for C$_{60}$ fullerene clusters by a point—dipole interaction (PDI) model. The size dependences of a linear chain, a monolayer film, and a face-centered cubic crystal cluster have been investigated. It is found that the effects of the surrounding molecules on the molecular $\alpha$ and $\gamma$ are large, in particular for the chain and the film because of the anisotropic surroundings, and that large clusters are required to obtain converged results. A localized PDI model gives the opportunity to divide $\alpha$ and $\gamma$ into fragment contributions, and it is found that $\alpha$ and $\gamma$ of molecules in the middle of the chain converge slower than the properties for the end molecules with respect to the length of the chain. Similar results are found for the monolayer film. Finally, $\chi^{(1)}$ and $\chi^{(3)}$ have been calculated by using a modified local-field theory including the induced dipole moments of the surrounding molecules explicitly. The corresponding refractive index and dielectric constant compare well with experiments. On the other hand, the comparison of $\chi^{(3)}$ with experiments is complicated by dispersion and vibrational contributions. Nonetheless, our value of $\chi^{(3)}$ is in good agreement with a recent quantum chemical calculation adopting a self-consistent reaction-field model.

1. Introduction

The development of new functional materials exhibiting nonlinear optical (NLO) effects holds great potential for future application in electronics and photonics. An important prospect is the utilization of the intensity dependence of the refractive index in all-optical switching devices, an essential element in future information processing technology. Because the refractive index is governed by the linear susceptibility, $\chi^{(1)}$, and the intensity dependence of the refractive index by the third-order susceptibility, $\chi^{(3)}$, an in-depth understanding of these properties is required. These new materials will be designed on a molecular scale. Consequently, a detailed understanding of the electronic structure of the molecular building blocks, the dependence of the microscopic optical response properties on the molecular structure, and the differences between the properties of isolated molecules and molecules embedded in the actual macroscopic devices are of fundamental importance. Therefore, it has been conjectured that applied quantum chemistry will play a central role in the development of such new NLO materials.

Since the discovery of fullerenes and later carbon nanotubes, they have been strong candidates for the next generation of functional materials. Carbon-based materials provide numerous possibilities to design molecular functionality because of the large variety of molecules that can be synthesized in organic chemistry. This is indeed the case in nature where all functionality exists that we can expect that nanotechnology can provide. The particular reason that carbon fullerenes are of interest in NLO applications is their extended $\pi$-system and that no absorption occurs due to C–H bonds. Recently, the scaling behavior of the second hyperpolarizability of carbon nanotubes with increasing system size has been investigated theoretically and it was demonstrated that carbon nanotubes can be considered as a valid alternative to conjugated polymers for constructing new materials for use in NLO devices. Since the C$_{60}$ molecule was the first fullerene to be discovered, numerous theoretical and experimental investigations have been performed of its linear and nonlinear optical properties, see e.g. refs 15 and 17–20 and references therein.

Recently, accurate experimental results have been presented for the dipole-dipole polarizability of the C$_{60}$ molecule in the gas phase. A value of 76.5 ± 8.0 Å$^3$ was reported for the static polarizability, and a value of 79 ± 4 Å$^3$ was measured for the polarizability at the frequency 0.0428 au ($\lambda = 1064$ nm). For both the static and the frequency-dependent polarizability, the results are in good agreement with recent quantum chemical calculations and results from a frequency-dependent point-dipole interaction (PDI) model. In contrast, the DFT results of 80.6 and 82.4 Å$^3$ for the static and frequency-dependent polarizability, respectively, are slightly higher than the ab initio SCF results of 75.1 and 76.4 Å$^3$ and the results from the PDI model of 77.5 and 78.2 Å$^3$. The overestimation of the polarizability of C$_{60}$ with conventional density functionals can, however, be improved by using, e.g., time-dependent current-DFT. Similarly, the overestimation of the polarizability in DFT for linear polymers is considerably larger, in particular...
for longer chains. In addition, comparison between calculated molecular properties and experiments in the gas phase is complicated by vibrational contributions. However, the pure vibrational polarizability for the isolated C₆₀ molecule has been calculated by using first principles methods and is found to be small, ~0.8 Å³, as compared with the electronic polarizability of around 80 Å³.

In the condensed phase, experiments are usually carried out on thin films of C₆₀ molecules and the molecular polarizability is extracted from measurements of the refractive index or the dielectric constant by means of the Clausius–Mossoti equation and gives results in the range between 80.5 and 91.9 Å³. These values are, as expected, slightly higher than the results for the isolated molecule. The contribution to the polarizability from pure vibrational lattice effects has been estimated experimentally to ~2 Å³, and it is therefore too small to account for the difference between the experiments in the gas phase and in the condensed phase. Most theoretical studies have considered the isolated molecule C₆₀ and therefore neglect intermolecular interactions. There is, however, a quantum chemical calculation of the polarizability of C₆₀, C₇₀, and C₈₄ in the condensed phase, using self-consistent reaction-field (SCRF) theory. The polarizability of C₆₀ was calculated to 93.8 Å³ compared with 75.1 Å³ in the gas phase. In addition, the PDI model has been used to calculate the polarizability of fullerene monolayer films which resulted in 83.9 Å³ for a C₆₀ molecule in the film and 77.5 Å³ for the isolated molecule, also in good agreement with experimental results.

For the second hyperpolarizability, the situation is less clear and the differences between theory and experiment are much larger. In contrast to the polarizability, experiments have been carried out only for the condensed phase, usually for thin films or in solution, and the differences between various measurements are substantial. The third-order susceptibility is very sensitive to the experimental conditions such as the experimental measuring techniques, laser power, frequency-dispersion, condensed phase, and even the sample preparation method. Furthermore, most experimental results have been obtained for the resonant third-order susceptibility, which is in the region where the frequency dispersion is the largest. The theoretical results have usually been calculated for the isolated molecule and often for the static case or at nonresonant frequencies. Even if only the theoretical results for the static second hyperpolarizability are compared with each other, the spread of the data is large.

In particular, methods using a semiempirical sum-over-states (SOS) approach seem to give results significantly higher than other theoretical models. Among methods such as DFT and SCF the agreement is much better. There has been a study of the static second hyperpolarizability in the condensed phase calculated with SCRF at the SCF level of theory, where a value of 278 × 10⁻³ au (140 × 10⁻³6 au) was found compared with a value of 109 × 10⁻³ au (55 × 10⁻³6 au) in the gas phase. In ref 35, the third-order susceptibility was also calculated by using a general local field theory obtained from the Onsager–Böttcher relation and good agreement with experiments was claimed. However, the comparison between the experimental and the theoretical susceptibility was carried out without correcting for different conventions adopted.

In this work, we combine the point–dipole interaction (PDI) model with a local-field ansatz with the result that the linear and third-order macroscopic susceptibilities may be obtained. Furthermore, adopting a localized PDI model, the (hyper-)polarizability of a molecule in a cluster may be calculated. Calculations have been carried out for C₆₀ fullerene clusters: linear chains, monolayer films, and face-centered cubic clusters. The presentation is organized as follows. A theoretical background is given in section 2, computational details are given in section 3, our results are presented in section 4, and, finally, the conclusions are given in section 5.

2. Theoretical Background

2.1. The Point–Dipole Interaction Model. An alternative approach to quantum chemical methods is based on representing the molecule as a set of interacting induced point dipoles and a model exploited extensively by Applequist and co-workers. In a system of N point polarizabilities, αₐβγ, the atomic induced dipole moment of atom I, µₐₙᵣ, is given as:

\[ \mu_{I,\alpha}^{\text{ind}} = \alpha_{I,\alpha} \mathbf{E}_I^{\text{tot}} + \frac{1}{6} \sum_{J \neq I} T_{I,J,\alpha \beta} \mathbf{E}_J^{\text{tot}} \mathbf{E}_I^{\text{tot}} \mathbf{E}_J^{\text{tot}} \]

where the total microscopic electric field, \( \mathbf{E}_I^{\text{tot}} \), is given by:

\[ \mathbf{E}_I^{\text{tot}} = \mathbf{E}_I^{\text{vac}} + \mathbf{E}_I^{\text{disp}} = \mathbf{E}_I^{\text{vac}} + \frac{4\pi}{3} \sum_{J \neq I} T_{I,J,\alpha \beta} \mathbf{\mu}_{J,\gamma}^{\text{ind}} \]

Here, \( \mathbf{E}_I^{\text{vac}} \) is the local field experienced due to the external electric field, which is given as the sum of the macroscopic electric field, \( \mathbf{E}_I^{\text{vac}} \), and the macroscopic polarization, \( \mathbf{P}_I^{\text{ext}} \). The term \( T_{I,J,\alpha \beta} \mathbf{\mu}_{J,\gamma}^{\text{ind}} \) denotes the electric field of the induced dipole moment at site J calculated at atom I, and \( T_{I,J,\alpha \beta} \) is given in a standard way as:

\[ T_{I,J,\alpha \beta} = \frac{3R_{I,J,\alpha \beta}R_{I,J,\gamma} - \delta_{\alpha \beta}R_{I,J}^2}{R_{I,J}^5} \]

where \( R_{I,J,\alpha \beta} = R_{I,J} - R_{I,\alpha} \) is the distance vector between atoms I and J, and \( R_{I,J} \) is the length of this vector. \( E_I^{\text{disp}} \) is thus the electric field at site I from all other induced dipole moments. Greek subscripts denote Cartesian coordinates x, y, or z, and the Einstein summation convention is used for repeated subscripts.

The atoms are regarded as spherically symmetric particles, \( \alpha_{\text{p,ab}} = \alpha_{\text{p}} \delta_{\text{ab}} \)

where the isotropic atomic polarizabilities, \( \alpha_{\text{p}} \), are treated as atom-type parameters where one parameter is used for each element. It should be noted that even though isotropic atomic polarizabilities are adopted the full molecular polarizability tensor is obtained as a result of interactions between the induced atomic dipoles.

Modifications may be included to correct for the fact that the interactions between atoms in a molecule are approximated by the classical electrostatic interaction between two point particles. In principle, both the polarizability in eq 4 and the T-tensor in eq 3 should be modified. The atomic polarizability in eq 4 can be modified directly. However, since these modifications are dependent on the interatomic distances, it may be preferred to include this correction as a part of the T-tensor. An improved parametrization is obtained if the contributions from a smeared-out charge distribution are included in terms of a damping of the interaction in eq 1 by modifying the \( T_{I,J,\alpha \beta} \) tensor. The damping of the interactions arises from the overlap of the smeared-out charge distributions and the model used here is obtained by considering the overlap between two Gaussian charge distributions. Consequently, by adopting two
parameters for each element, a polarizability, \( \alpha_P \), and a damping parameter, \( \Phi_P \). Good results have been obtained for example for the polarizability of large molecular clusters.\(^\text{17}\) Because it is parametrized from quantum chemical calculations, \( \Phi_P \) accounts not only for the damping of the electrostatic interaction between two Gaussian charge distributions but also for other short-range contributions such as the atomic polarizability in eq 4 in principle not being spherically symmetric for an atom in a molecule. A parametrization of the molecular \( \gamma \) includes an atomic \( \gamma \) parameter, \( \gamma_P \), in addition to the parameters adopted for the molecular polarizability.\(^\text{58}\) It has 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.\(^\text{40}\)

One reason for that is that experimental polarizabilities often have been converted from macroscopic susceptibilities, which, as demonstrated here, is a nontrivial task.

The solutions of the coupled set of linear equations in eq 1 may be expressed in terms of a two-atom relay tensor, \( B_{IJ}^{(2)} \), and a four-atom relay tensor \( B_{IJKL}^{(4)} \), as\(^\text{50,44}\)

\[
B_{IJ}^{\text{ind}} = \sum_{J} B_{IJ}^{(2)} E_{IJ} + \sum_{JKL} B_{IJKL}^{(4)} E_{IJKL}^{\text{loc}}
\]

where \( B_{IJ}^{(2)} \) gives the induced dipole moment at atom \( I \) from a local electric field on atom \( J \). The two-atom relay tensor is given in the regular way as an inverse of a matrix,\(^\text{12,46}\)

\[
B^{(2)} = (\alpha^{-1} - T)^{-1}
\]

Analogously, \( B_{IJKL}^{(4)} \) gives the induced dipole moment at atom \( I \) from a local electric field on atoms \( J, K, \) and \( L \). The four-atom relay tensor for a system of spherically symmetric particles may be written as\(^\text{48}\)

\[
B_{IJKL}^{(4)} = \sum_{M} \gamma_{M,uvw} B_{ML,\beta}^{(2)} B_{MK,\gamma}^{(2)} B_{MI,\alpha}^{(2)} B_{IJ,\alpha}^{(2)}
\]

where \( B_{IJ}^{(2)} \) is defined as

\[
B_{IJ}^{(2)} = \delta_{I}^{J} \alpha_{I} + \sum_{K=1}^{N} \gamma_{IK,\alpha}^{(2)} B_{JK,\beta}^{(2)} = \alpha_{I}^{(1)} B_{IJ,\beta}^{(2)}
\]

The resulting molecular polarizability, \( \alpha_{ijkl}^{\text{mol}} \), and molecular second hyperpolarizability, \( \gamma_{ijkl}^{\text{mol}} \), are given as

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

and

\[
\gamma^{\text{mol}}_{ijkl} = \sum_{IJKL} B_{IJKL,\alpha}^{(4)}
\]

The theoretical background of the calculation of second hyperpolarizabilities within a PDI model is described in more detail in a previous work.\(^\text{48}\)

\[2.2. \text{The Localized Point–Dipole Interaction Model.} \] A localized point–dipole interaction model (LPDI) is utilized to calculate the (hyper)polarizability of the individual molecules (or subgroups) in a cluster.\(^\text{51}\) The partitioning is carried out by first decomposing the two-atom matrix into a block diagonal form with \( M \) blocks, \( B_{ijQP}^{(2)} \), corresponding to a relay tensor for the \( I \)th molecule or subgroup, where \( M \) is the total number of molecules or subgroups in the cluster. In the decomposition of the relay matrix, the interaction blocks \( B_{ijQP}^{(2)} \), where atom \( P \) belongs to molecule \( I \) and atom \( Q \) to molecule \( J \), is assigned to the diagonal blocks \( B_{ijQP}^{(2)} \) where both atoms \( P \) and \( Q \) belong to molecule \( I \). This assignment is a more or less arbitrary procedure but can be done similarly to the Mulliken population analysis.\(^\text{52}\) Therefore, we have for molecule \( I \),

\[
\vec{B}_{IJQP}^{(2)} = B_{ijQP}^{(2)} + \frac{1}{M} \sum_{J=1}^{M} (B_{ijQP}^{(2)} + B_{ijQP}^{(2)})
\]

The polarization and second hyperpolarizability can subsequently be calculated by eqs 8, 9, and 10, using the diagonal blocks of the decomposed relay matrix, \( \vec{B}_{IJQP}^{(2)} \). They also give the polarizability and hyperpolarizability of each of the \( M \) individual molecules in the molecular cluster.

\[2.3. \text{The Linear and Nonlinear Susceptibility.} \] In a similar way to the induced dipole moment, the macroscopic polarization, \( P \), can be expanded in powers of the macroscopic electric field, \( E_{\text{mac}} \),

\[
P_{j} = \chi_{ij}^{(1)} E_{j}^{\text{mac}} + \chi_{ijkl}^{(3)} E_{j}^{\text{mac}} E_{k}^{\text{mac}} E_{l}^{\text{mac}}
\]

where \( \chi_{ij}^{(1)} \) is the linear susceptibility and \( \chi_{ijkl}^{(3)} \) is the third-order susceptibility. The macroscopic polarization is also given in terms of the microscopic induced molecular dipole moments, \( \mu \), as\(^\text{53,37}\)

\[
P_{j} = N_{d} \mu_{j} = N_{d} \langle \alpha_{ijkl}^{\text{mol}} \rangle_{ij} E_{j}^{\text{loc}} + \frac{1}{6} N_{d} \langle \gamma_{ijkl}^{\text{mol}} \rangle_{ijkl} E_{j}^{\text{loc}} E_{k}^{\text{loc}} E_{l}^{\text{loc}}
\]

where \( N_{d} \) is the number density and \( \langle \cdot \rangle \) denotes orientation averaging, which relates the molecule-fixed axes, \( \alpha, \beta, .... \) to the space-fixed axes, \( I, J, .... \).\(^\text{54}\) Inserting the definition of the local field, eq 2, in eq 13 the polarization in the \( Z \) direction due to a electric field in the \( Z \) direction can be written as

\[
P_{Z} = N_{d} \alpha_{Z}^{\text{mol}} \left[ E_{Z}^{\text{mac}} + \frac{4\pi}{3} P_{Z} \right] + \frac{1}{6} N_{d} \gamma_{Z}^{\text{mol}} E_{Z}^{\text{mac}} + \frac{4\pi}{3} P_{Z}^{3}
\]

where the average molecular polarizability is given by\(^\text{54}\)

\[
\alpha^{\text{mol}} = \langle \alpha_{ijkl}^{\text{mol}} \rangle_{ijkl} = \frac{1}{3} \left( \alpha_{xx} + \alpha_{yy} + \alpha_{zz} \right)
\]

and the average molecular second hyperpolarizability by\(^\text{55,54}\)

\[
\gamma^{\text{mol}} = \langle \gamma_{ijkl}^{\text{mol}} \rangle_{ijkl} = \frac{1}{15} \left( \gamma_{xxxy} + \gamma_{xxyz} + \gamma_{xyxx} \right)
\]

Combining this equation with the power expansion of the polarization in eq 12, the linear electric susceptibility, \( \chi_{ZZ}^{(1)} \), is obtained as

\[
\chi_{ZZ}^{(1)} = \frac{\partial P_{Z}}{\partial E_{Z}^{\text{mac}}}
\]

resulting in

\[
\chi_{ZZ}^{(1)} = \frac{N_{d} \alpha^{\text{mol}} \left[ 1 + \frac{4\pi}{3} \chi_{ZZ}^{(1)} \right]}{1 - \frac{4\pi}{3} N_{d} \alpha^{\text{mol}}}
\]
The related refractive index, \( n^{(1)} \), and dielectric constant, \( \varepsilon^{(1)} \), are given as,

\[
n^{(1)} = \sqrt{\varepsilon^{(1)}} = \sqrt{1 + 4\pi\chi^{(1)}_{ZZZZ}} = \sqrt{1 + \frac{8\pi}{3}N_d\chi^{(1)}_{mol} + \frac{4\pi}{3}N_d\chi^{(1)}_{mol}}
\]

which is the familiar Lorentz-Lorenz equation or Clausius-Mossotti equation. The corresponding third-order susceptibility, \( \chi^{(3)}_{ZZZZ} \), is given as

\[
\chi^{(3)}_{ZZZZ} = \frac{\partial^3 P_Z}{\partial E_Z^{\text{mac}} \partial E_Z^{\text{mac}} \partial E_Z^{\text{mac}}} = \left. \frac{1}{6}N_d\chi^{(1)}_{mol}\left(1 - N_d\chi^{(1)}_{mol}\right)^{-1}\left(1 + \frac{4\pi}{3}N_d\chi^{(1)}_{mol}\right)^3 \right|_{E_{mac}=0}
\]

which may be rewritten as

\[
\chi^{(3)}_{ZZZZ} = \frac{1}{6}N_d\chi^{(1)}_{mol} \left(\frac{\varepsilon^{(1)} + 2}{3}\right)^4
\]

Although the equations for \( \chi^{(1)} \) and \( \chi^{(3)} \) presented here look identical with the standard Lorentz local-field treatment, it should be emphasized that they are different since the electric field from the nearby dipoles, \( E_{mac} \), is included in eq 2. In the standard Lorentz local-field approach, this field is ignored since it is zero in a simple cubic lattice and assumed likewise in a completely random situation.

3. Computational Details

The parameters, \( \alpha_c \) and \( \Phi_c \) have been obtained in a previous work where the molecular \( \alpha \) was parametrized from Hartree-Fock calculations on 184 molecules,\(^{17}\) where it was shown that the model reproduces the ab initio results within 6%. The use of this set of parameters enables us to study large systems, such as carbon nanotubes, boron nitride nanotubes, and clusters of molecules, for which quantum chemical calculations would not be feasible. We have shown that the model using these general parameters gives good results for \( \alpha \) for carbon nanotubes,\(^{24}\) boron nitride tubes,\(^{56}\) and \( C_{60} \) fullerene clusters.\(^{17}\) In a previous work\(^{17}\) we have shown that for the isolated \( C_{60} \) molecule the model was within 3% of both experiments and ab initio calculation for the molecular polarizability. Since a good description of the polarizability of \( C_{60} \) is obtained already with use of these parameters there is no need for a reparametrization. Although quantum chemical results are available for the \( C_{60} \) molecule and we could have chosen to fit the parameters directly to these results, we prefer to use the general parameters. The reason for this, besides an already good description, is that the polarizability of \( C_{60} \) is isotropic and we could therefore only determine one of the parameters needed. Also, the general parameters have been tested on molecular complexes\(^{17}\) and shown to be accurate over a wide range of intermolecular distances.

The remaining parameter \( \gamma_c \) has been chosen to describe the molecular \( \gamma \) of \( C_{60} \) obtained from Hartree-Fock calculations taken from ref 29. The reason for not also using the \( \gamma_c \) parameter obtained for a large set of training molecules is that it was not able to give a good description of both the molecular polarizability and the molecular second hyperpolarizability.\(^{48}\) The values used in this work are \( \alpha_c = 9.312 \text{ au}, \Phi_c = 0.124 \text{ au}, \) and \( \gamma_c = 1600.0 \text{ au}. \) This set of parameters has previously been used to study the saturation of the second hyperpolarizability of carbon nanotubes with increasing tube length.\(^{16}\)

The structure of the \( C_{60} \) molecule was taken from our previous work.\(^{24}\) In the solid phase at room temperature, \( C_{60} \) exhibits a face-centered-cubic (FCC) structure with a lattice vector of \( a_0 = 14.17 \text{ Å}, \) giving a nearest-neighbor distance of \( a = 10.04 \text{ Å}. \)\(^{37,34}\) At room temperature the \( C_{60} \) molecules in the FCC structure exhibit nearly free rotations;\(^{57}\) however, here we will assume an average structure where all molecules are ideally oriented. In this study, we have investigated chains, monolayers, and FCC clusters of \( C_{60} \) molecules and all the structures have been constructed by using this nearest-neighbor distance. The two different monolayers (A and B) used in this work are illustrated in Figure 1, which correspond to the (100) surfaces of the FCC crystal. The chains of \( C_{60} \) molecules correspond to the diagonal of the A-layer, the monolayers studied are A-layers, and the FCC clusters are constructed by combinations of A- and B-layers.
4. Results

The polarizability and the second hyperpolarizability of a C$_{60}$ molecule in a fullerene cluster have been calculated in three different ways. In the following $\xi$ represents either $\alpha$ or $\gamma$. The first method is to calculate the average value per molecule $\frac{\xi(N)}{N}$, the second way is the $\Delta$ approach, i.e., the difference between the value for $N$ molecules and for $N - 1$ molecules $\Delta\xi = \frac{1}{N} \left( \frac{\xi(N)}{N} - \frac{\xi(N-1)}{N-1} \right)$, where $N$ is the step size, and finally the localized PDI model $\alpha_{\text{LPDI}}$ as described in section 2.2. In the average approach, the total $\xi$ of the system is distributed evenly between the molecules and for this reason resembles the experimental results. The average approach requires, however, a very large number of molecules in the cluster before $\frac{\xi}{N}$ converges due to a large number of molecules in the outer part of the cluster. For this reason, the $\Delta$ approach has been introduced to improve the slow convergence by removing the effect of the outlying molecules. As realized from the definition of the $\Delta$ approach it is most efficient when the step size is small compared with the total number of molecules in the cluster, i.e., if $N$ is identical with the average approach in the limit where $X$ becomes identical with $N$. Here, these approaches are compared to the LPDI approach.

4.1. Chains of C$_{60}$ Molecules. The dependence of the (hyper)polarizability of a C$_{60}$ molecule in a linear chain of C$_{60}$ molecules on the length of the chain has been investigated. The fullerene chain is not only a suitable model system for investigating this approach but is also considered as a model of the edges of a fullerene crystal. Furthermore, linear chains of C$_{60}$ molecules have also been found inside carbon nanotubes, so-called peapods, with the same spacing between the C$_{60}$ molecules.

In Figures 2 and 3, respectively, the polarizability and second hyperpolarizability of a C$_{60}$ molecule in a chain of C$_{60}$ molecules are presented as a function of the number of molecules in the chain. The longest chain contains 35 C$_{60}$ molecules corresponding to a chain length of ~35 nm. For this chain, the polarizability was obtained as $\bar{\alpha}/N = 564.76$ au, $\Delta\bar{\alpha} = 567.57$ au, and $\alpha_{\text{LPDI}} = 567.46$ au. In the $\Delta$ approach a step size of 1 was used until $N = 11$, then a step size of 2 until $N = 15$, and for the rest a step size of 5 was used. The second hyperpolarizability was calculated to be $\gamma/N = 213.89 \times 10^{3}$ au, $\Delta\gamma = 221.67 \times 10^{3}$ au, and $\gamma_{\text{LPDI}} = 221.34 \times 10^{3}$ au. A good agreement is found between the $\Delta$ approach and the LPDI model both for the polarizability and for the second hyperpolarizability, whereas the average approach gives values that are slightly smaller. In Figures 2 and 3, it is also noted that the $\Delta$ approach converges faster than the other approaches. The LPDI approach converges slightly slower but still much faster than the average method. If the linear chain of C$_{60}$ molecules is compared with a carbon nanotube with the same diameter, i.e. a [5,5] or [9,0] carbon nanotube, $\bar{\alpha}/N_{\text{atom}}$ is ~9.5 au for the chain whereas it is ~14.2 au for the nanotube, where $N_{\text{atom}}$ is the number of carbon atoms. Analogously, $\gamma/N_{\text{atom}}$ is ~3.7 $\times$ 10$^3$ au for the chain and ~48 $\times$ 10$^3$ au for the nanotube. Thus, $\bar{\alpha}/N_{\text{atom}}$ and in particular $\gamma/N_{\text{atom}}$ are expected much larger for the carbon nanotube than for the chain of C$_{60}$ molecules because of the extended conjugated electronic structure.

In Figures 4 and 5, $\alpha$ and $\gamma$ are presented for a C$_{60}$ molecule in the chain calculated with the LPDI model where the molecule is situated either in the middle of the chain or at the end of the chain. It is found that $\alpha_{zz}$ and $\gamma_{zzzz}$ increase and $\alpha_{xx}$ and $\gamma_{xxxx}$ decrease with increasing chain length for both the middle and the end molecules, and that the perturbation is larger along the $z$-axis and, therefore, the components in this direction converge slower with respect to the length of the chain. Furthermore, the differences are significant between the middle and the end molecules of the chain. For the chain of 35 C$_{60}$ molecules, we obtained $\alpha_{zz} = 803.89$ au and $\gamma_{zzzz} = 646.26 \times$
TABLE 1: Static Polarizability and Second Hyperpolarizability for C_{60} in a Fullerene Monolayer Film

<table>
<thead>
<tr>
<th>N =</th>
<th>1</th>
<th>5</th>
<th>13</th>
<th>25</th>
<th>41</th>
<th>61</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\alpha/N)</td>
<td>522.76</td>
<td>541.05</td>
<td>555.24</td>
<td>566.19</td>
<td>574.58</td>
<td>581.15</td>
</tr>
<tr>
<td>(\Delta\alpha)</td>
<td>522.76</td>
<td>545.62</td>
<td>564.11</td>
<td>578.06</td>
<td>587.69</td>
<td>594.61</td>
</tr>
<tr>
<td>(\alpha^{LPDI})</td>
<td>522.76</td>
<td>568.74</td>
<td>575.07</td>
<td>586.23</td>
<td>595.05</td>
<td>601.73</td>
</tr>
<tr>
<td>(\gamma/N)</td>
<td>115.21</td>
<td>150.91</td>
<td>178.06</td>
<td>200.52</td>
<td>218.70</td>
<td>233.55</td>
</tr>
<tr>
<td>(\Delta\gamma)</td>
<td>115.21</td>
<td>139.83</td>
<td>195.02</td>
<td>224.85</td>
<td>247.12</td>
<td>263.99</td>
</tr>
<tr>
<td>(\gamma^{LPDI})</td>
<td>115.21</td>
<td>196.35</td>
<td>218.63</td>
<td>244.86</td>
<td>265.81</td>
<td>282.22</td>
</tr>
</tbody>
</table>

* \(\alpha\) in au and \(\gamma\) in \(10^3\) au.

10^3 au for the middle molecule and \(\alpha_{\text{C}_{60}} = 655.33\) au and \(\gamma_{\text{C}_{60}} = 299.72 \times 10^3\) au for the end molecules, respectively. For the end molecules, both \(\alpha\) and \(\gamma\) converge much faster with respect to the length of the chain than the molecule in the middle, which illustrates clearly why the \(\Delta\) approach converges much faster than the average method.

4.2. Monolayer Films of C_{60} Molecules. The second type of system is a C_{60} molecule in monolayer films of C_{60} molecules. The monolayer is considered as a model of the (1 0 0) surface of the fullerene crystal.

In Table 1, \(\alpha\) and \(\gamma\) are presented for a C_{60} molecule in a monolayer film of C_{60} molecules calculated using the average, \(\Delta\), and LPDI approaches. We find for the largest film, containing 61 C_{60} molecules, a polarizability of \(\alpha/N = 581.15\) au, \(\Delta\alpha = 594.61\) au, and \(\alpha^{LPDI} = 601.73\) au. For the second hyperpolarizability, we find \(\gamma/N = 233.55 \times 10^3\) au, \(\Delta\gamma = 263.99 \times 10^3\) au, and \(\gamma^{LPDI} = 282.22 \times 10^3\) au. Compared with the results for the longest chain, \(\alpha\) is increased by \sim 3\%, \sim 5\%, and \sim 6\% for the various methods and \(\gamma\) by \sim 9\%, \sim 19\%, and \sim 28\%, respectively. For the films, the LPDI approach gives the largest \(\alpha\) and \(\gamma\) values in good agreement with the expectation that the LPDI model will converge faster than both the \(\Delta\) and the average approach when the dimension of the system increases. For the monolayer films, both \(\alpha\) and \(\gamma\) show similar trends with increasing system size as was found for the chains.

Using the LPDI model, the results of a C_{60} molecule in one of the corners of the monolayer film with 61 C_{60} molecules are \(\bar{\alpha} = 547.79\) \(\text{Å}^3\) and \(\bar{\gamma} = 168.66 \times 10^3\) au. This is as expected much lower than the values of \(\bar{\alpha} = 601.73\) \(\text{Å}^3\) and \(\bar{\gamma} = 282.22 \times 10^3\) au found for the molecule in the middle of the film.

TABLE 2: Static Polarizability and Second Hyperpolarizability for C_{60} in a Fullerene FCC Cluster

<table>
<thead>
<tr>
<th>N =</th>
<th>1</th>
<th>13</th>
<th>37</th>
<th>63</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\alpha/N)</td>
<td>522.76</td>
<td>533.22</td>
<td>545.91</td>
<td>546.05</td>
</tr>
<tr>
<td>(\Delta\alpha)</td>
<td>522.76</td>
<td>539.50</td>
<td>550.09</td>
<td>548.09</td>
</tr>
<tr>
<td>(\alpha^{LPDI})</td>
<td>522.76</td>
<td>582.71</td>
<td>578.16</td>
<td>571.84</td>
</tr>
<tr>
<td>(\gamma/N)</td>
<td>115.21</td>
<td>142.17</td>
<td>157.53</td>
<td>158.75</td>
</tr>
<tr>
<td>(\Delta\gamma)</td>
<td>115.21</td>
<td>144.42</td>
<td>165.85</td>
<td>163.06</td>
</tr>
<tr>
<td>(\gamma^{LPDI})</td>
<td>115.21</td>
<td>182.68</td>
<td>194.66</td>
<td>169.12</td>
</tr>
</tbody>
</table>

* \(\alpha\) in au and \(\gamma\) in \(10^3\) au.

Compared with the isolated molecule, the changes in \(\alpha\) and \(\gamma\) for the corner molecule are only \sim 5\% and \sim 45\%, respectively, whereas the changes are \sim 15\% and \sim 145\%, respectively, for the molecule in the middle, i.e., around three times larger. For the chain with the same number of molecules as on the diagonal of the film (11 C_{60} molecules), the results for an end molecule are \(\bar{\alpha} = 541.96\) \(\text{Å}^3\) and \(\bar{\gamma} = 149.96 \times 10^3\) au. Thus, only small differences are found for the molecule in the corner of the film as compared with the molecule at the end of the chain.

4.3. FCC Cluster of C_{60} Molecules. The final type of system is a C_{60} molecule in a FCC cluster of C_{60} molecules. The smallest FCC structure contains 13 C_{60} molecules and was built as one A-layer with 5 molecules and two B-layers with 4 molecules (see Figure 1), one above and one below the A-layer (\(B_2A_2B_4\) cluster). The spacing between two A-layers is 14.17 \(\text{Å}^2\) and the spacing between the B-layers and the A-layer is half of the \(\text{Å}A\) distance, 7.09 \(\text{Å}\). The second structure contains 37 C_{60} molecules (\(B_2A_2B_12\) cluster), and the last structure contains 63 C_{60} molecules (\(A_1B_2A_1B_3A_3B_3\) cluster).

The results for \(\alpha\) and \(\gamma\) for a C_{60} molecule in a FCC crystal are presented in Table 2. The difference is small between the results obtained with the average and the \(\Delta\) approaches. The reason for this is that the step size, \(X\), is too large relative to the system size in the three-dimensional cluster such that the \(\Delta\) approach will not be significantly different from the average approach. Second, as was the case for the monolayer films the results obtained with the LPDI model are larger than the results obtained with both the average and the \(\Delta\) approach. Furthermore, \(\alpha\) and \(\gamma\) calculated with the LPDI model are larger for the \(N = 13\) and 37 clusters than for the \(N = 63\) cluster. Furthermore, \(\alpha\) decreases whereas \(\gamma\) increases when going from the \(N = 13\) cluster to the \(N = 37\) cluster. On the other hand, both \(\alpha\) and \(\gamma\) decrease when going from the \(N = 37\) cluster to the \(N = 63\) cluster and they also become smaller than the results for the \(N = 13\) cluster. Because of these irregularities, it becomes important to have a large cluster for the three-dimensional cluster.

In Table 3, we present a comparison of \(\alpha\), \(\gamma\), and their tensor components \(\alpha_{xx}, \alpha_{yy}, \gamma_{xxxx}, \gamma_{yyyy}\) for a C_{60} molecule in a chain, a monolayer film, and a FCC cluster calculated with the LPDI approach. The FCC cluster is the cluster with 63 C_{60} molecules, 

TABLE 3: Comparing the Chain, Film, and Crystal of C_{60} Molecules

<table>
<thead>
<tr>
<th>(\alpha_{xx})</th>
<th>(\alpha_{yy})</th>
<th>(\gamma_{xxxx})</th>
<th>(\gamma_{yyyy})</th>
</tr>
</thead>
<tbody>
<tr>
<td>isolated, (N = 1)</td>
<td>522.76</td>
<td>543.18</td>
<td>363.32</td>
</tr>
<tr>
<td>chain, (N = 5)</td>
<td>522.76</td>
<td>767.12</td>
<td>681.38</td>
</tr>
<tr>
<td>monolayer, (N = 13)</td>
<td>522.76</td>
<td>557.83</td>
<td>575.07</td>
</tr>
<tr>
<td>FCC cluster, (N = 63)</td>
<td>522.76</td>
<td>538.22</td>
<td>545.91</td>
</tr>
</tbody>
</table>

* \(\alpha\) in au and \(\gamma\) in \(10^3\) au. The z is the long axis and x the short axis.
the monolayer film corresponds to the middle layer of the FCC cluster and contains 13 molecules, and the chain corresponds to the diagonal of the film and contains 5 molecules. From the table, the differences in the anisotropy of the various types of systems may be compared with the gas phase. For the chain, the component \((z)\) along the chain is enhanced whereas the components \((x, y)\) perpendicular to the chain are screened. In the film, the components \((z, y)\) in the plane are enhanced and the component \((x)\) perpendicular to the plane is screened. All components for the film are smaller than those for the chain but two directions are enhanced and only one direction is accounted for the film are smaller than those for the chain. In the FCC cluster, \(\alpha\) and \(\gamma\) are larger for the film than for the chain. In the FCC cluster, \(\alpha\) and \(\gamma\) are enhanced in all directions and the properties become isotropic as in the gas phase. The enhancements are smaller in the FCC cluster than in the film and chain illustrating the importance of considering a realistic cluster model to account for both the enhancement and the screening of \(\alpha\) and \(\gamma\).

4.4. Susceptibilities. For the largest FCC cluster, we have also calculated the linear refractive index and the third-order nonlinear susceptibility and compared our findings with experimental results. The results for the refractive index are \(n^{(1)} = 2.0\ (e^{(1)} = 4.0)\) as calculated from eq 19 with the number density, \(N_0 = 4a^3\), and a lattice constant of \(a = 14.17\ \text{Å}\).\(^{34}\) Our results are in excellent agreement with the experimental results for the refractive index, \(n^{(1)} \approx 2.29^{31,61}\) and for the dielectric constant, \(e^{(1)} \approx 4.0-4.6^{30,33,34,62}\) This good agreement, especially with the refractive index, illustrates the accuracy of the local-field approach used here and indicates that the dipolar term ignored in standard Lorentz local-field theory is required to get good agreement between theory and experiments. If we use the standard Lorentz–Lorenz equation, i.e. adopting eq 19 with the gas-phase value for the polarizability, a refractive index of \(n^{(1)} = 1.89\) is obtained, and if we use the standard Lorentz local-field theory, i.e. eq 17, with the gas-phase polarizability and the experimental susceptibility, we find a refractive index of \(n^{(1)} = 1.94\). Although the differences in the refractive indexes are small, it becomes important when considering the nonlinear susceptibilities as realized from eq 21.

For the third-order nonlinear susceptibility, a value of \(\chi^{(3)} = 3.2 \times 10^{-13}\) esu is obtained with eq 21 and the dielectric constant calculated here. Only a few experimental studies have been carried out of the nonresonant third-order nonlinear susceptibility for \(C_{60}\) films. A third-harmonic generation (THG) experiment at frequency 0.019 au (\(\lambda = 2380\) nm) results in \(\chi^{(3)} = 4.1 \pm 0.6 \times 10^{-12}\) esu.\(^{61}\) This value was measured relative to fused silica and a reference value of \(\chi^{(3)} = 2.8 \times 10^{-14}\) esu was adopted. However, recently a value for the THG susceptibility for fused silica of \(\chi^{(3)} = 1.1 \times 10^{-14}\) esu was found and believed to be more accurate.\(^{63,64}\) Correcting for this difference in reference values gives a value of \(\chi^{(3)} = 161.1 \pm 2.4 \times 10^{-13}\) esu for the \(C_{60}\) thin film. The second experiment is a degenerate four-wave mixing (DFWM) study where the static limit of the third-order nonlinear susceptibility was found to be \(\chi^{(3)} = 36 \pm 12 \times 10^{-13}\).\(^{65}\) This value was reported in the so-called “Maker-Terhune”\(^{66}\) convention and is therefore multiplied by a factor of 4 to compare with the convention used here. They used a reference value for fused silica of \(\chi^{(3)} = 1.6 \times 10^{-14}\) at \(\lambda = 1064\) nm, which is in good agreement with THG results at the same frequency.\(^{63,64}\) The two experiments agree within a factor of 2 which, considering the fact that DFWM can be higher than the corresponding THG due to vibrational contributions,\(^{63}\) is a good agreement. Theoretically, it has also been found for the isolated \(C_{60}\) molecule that the vibrational contribution to \(\gamma\) obtained in a DFWM experiment is of the same order as the electronic contribution.\(^{28}\)

Comparing our theoretical value for \(\chi^{(3)}\) with the experimental results, it is a factor of 5 lower than the THG experiment and a factor of 10 lower than the DFWM experiment. Since in this study only the pure electronic contribution to \(\chi^{(3)}\) is calculated, we would expect a better agreement with the THG results than with the DFWM results, which is also the case. There has been one previous theoretical study of the third-order susceptibility where the molecular environment was taken explicitly into account by using a general local-field theory obtained from the Onsager–Böttcher relation and the gas-phase \(\alpha\) and \(\gamma\) calculated within the Hartree–Fock approximation.\(^{35}\) They found for the static third-order susceptibility a value of \(\chi^{(3)} = 2.7 \times 10^{-13}\) esu, which here is divided by a factor of 6 to make the comparison in the convention used here. This value is in very good agreement with our value of \(3.2 \times 10^{-13}\) esu considering the different methods used.

5. Conclusion

We have investigated the dependence of \(\alpha\) and \(\gamma\) on the size of \(C_{60}\) fullerene clusters. It is found that both the \(\Delta\) approach\(^{58}\) and the LPDI model\(^{51}\) give a rapid convergence of \(\alpha\) and \(\gamma\) with respect to the chain length and the size of the monolayer. Furthermore, the LPDI model gives the molecular properties of the individual molecules in a cluster. For a \(C_{60}\) chain and monolayer film, it is found that the surrounding molecules perturb the middle \(C_{60}\) molecule much more than the end or corner molecules, which also results in a slower convergence of \(\alpha\) and \(\gamma\) for the middle molecule with respect to the system size. In addition, the linear and third-order susceptibilities have been calculated by combining the PDI model with a local-field ansatz. The calculated refractive index and dielectric constant are in good agreement with experiments. The result for \(\chi^{(3)}\) is less clear, but a good agreement with a quantum chemical SCRF calculation is found.\(^{35}\)

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References and Notes
