Saturation of the Third-Order Polarizability of Carbon Nanotubes Characterized by a Dipole Interaction Model

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ABSTRACT

An atomic dipole interaction model has been used for calculating the second hyperpolarizability of carbon nanotubes on a length scale up to 75 nm. It is demonstrated that an atomistic representation of mesoscale systems such as nanotubes can be used to obtain a cubic response property up to a size of the system where the property scales linearly with increasing size. In particular, it demonstrates that atomistic models are useful also for designing nonlinear molecular materials, where local modifications may give large macroscopic contributions. The saturation length has been calculated for carbon nanotubes. It is found that carbon nanotubes are comparable to conjugated polymers with respect to the magnitude of the second hyperpolarizability and are therefore very promising candidates for future nonlinear optical materials.

Introduction. The prospect of utilizing optical nonlinearities of materials in constructing all-optical devices holds great promise. Particularly promising is the exploitation of the intensity dependence of the refractive index due to the second hyperpolarizabilities for constructing all-optical switching devices, which provides the basis for an all-optical information technology.[1] This requires novel materials exhibiting large nonlinearities characterized at the macroscopic level by the third-order optical susceptibility, $\chi^{(3)}$, and at the microscopic level by the third-order polarizability or second hyperpolarizability, γ. It has been conjectured that computer modeling will play an essential role in the development of new materials.[2] In particular, the modeling of new nonlinear optical materials will require a detailed model of the electronic structure and its response to an external electric field.[3] Since the discovery of fullerenes[4] and later carbon nanotubes,[5] they have been strong candidates for the next generation of functional materials. The reason that these all-carbon molecules are of interest in nonlinear optical applications is their extended π-system and that no absorption occurs due to C−H bonds.[6,7]

An important concept for designing new materials is the scaling behavior of the nonlinear optical properties of the molecule with increasing system size, and in particular the saturation limit, i.e., where the property scales linearly with increasing size. For polyenes it is well known that for small chain lengths, N, the molecular γ obey a power law $\gamma \sim N^a$ with a between 3 and 6.[8−10] At large N, γ/N will saturate and the scaling exponent a will tend toward one. Obviously, the reason is that the most long-range interaction behaves as $1/R$ and thus approaches zero when R goes to infinity.

A cubic response property like the second hyperpolarizability is, however, a challenge to determine accurately both theoretically and experimentally. Considering γ of fullerenes, experimental results show large variations with respect to the choice of structure and experimental conditions.[6,7] The third-order polarizability of carbon nanotubes or tubular fullerenes has been studied both theoretically and experimentally to a much lesser degree than the small fullerenes.[6,7] However, in general it is found theoretically that γ varies strongly with the length, diameter, and symmetry of the nanotubes, see e.g., ref 6. Theoretically, a scaling law for γ for small nanotubes has been found using a semiempirical Su−Schrieffer−Heeger model with the Coulomb interaction included,[11] but the saturation limit was not investigated. Ab initio quantum chemical calculations would, in principle, be

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a valuable tool to study γ of these kinds of systems, but currently they are too computer-demanding to be used systematically to study, for example, the scaling of γ with respect to the length of a carbon nanotube. It is noted, however, that accurate calculations have been carried out for γ of the smallest fullerenes at the Hartree−Fock level.[12]

An alternative approach is based on representing the molecule as a set of interacting point polarizabilities,[13,14] a model which has been exploited extensively by Applequist and co-workers.[15] In a system of N interacting point polarizabilties, $\alpha_{I,\alpha\beta}$, the atomic induced dipole moment of atom I, $\mu_{I,\alpha}^{\text{ind}}$, is given as

$$\mu_{I,\alpha}^{\text{ind}} = \alpha_{I,\alpha\beta}\left(E_{I,\beta}^{\text{ext}} + \sum_{J\neq I}^{N} T_{IJ,\beta\gamma}\mu_{J,\gamma}^{\text{ind}}\right) \quad (1)$$

where $E_{I,\beta}^{\text{ext}}$ is the external electric field at atom I and $T_{IJ,\beta\gamma}\mu_{J,\gamma}^{\text{ind}}$ is the electric field of the induced dipole moment at site J calculated at atom I. Greek subscripts denote the Cartesian coordinates, x, y, or z, and the Einstein summation convention is used for repeated indices.

If the atoms are regarded as spherically symmetric particles, $\alpha_{P,\alpha\beta} = \alpha_P\delta_{\alpha\beta}$, where the isotropic atomic polarizabilities, α_P, are atom-type parameters, 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 from experimental data.[16] One reason is that experimental data are taken from various sources, and inconsistent quality of the data may affect the parametrization. For example, often only the isotropic part of the polarizability is available from experiments. Furthermore, experimental polarizabilities are often taken from refractive indices, which include also local field factors as well as solvent and temperature effects in addition to the electronic polarization in eq 1.

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 $T_{IJ,\alpha\beta}$ tensor.[17] Consequently, by adopting two parameters for each element, a polarizability, α_P, and a damping parameter, Φ_P, good results have been obtained, for example, for the polarizability of large molecular clusters.[18]

The solutions of the coupled set of linear equations in eq 1 may be expressed in terms of a two-atom relay tensor, $B_{IJ,\alpha\beta}^{(2)}$, as[19]

$$\mu_{I,\alpha}^{\text{ind}} = \sum_{J}^{N} B_{IJ,\alpha\beta}^{(2)} E_{J,\beta}^{\text{ext}} \quad (2)$$

where $B_{IJ,\alpha\beta}^{(2)}$ gives the induced dipole moment at atom I from an external field on atom J. The molecular second hyperpolarizability, $\gamma_{\alpha\beta\gamma\delta}^{\text{mol}}$, may be obtained by including higher-order terms in eq 1,

$$\mu_{I,\alpha}^{\text{ind}} = \alpha_{I,\alpha\beta}E_{I,\beta}^{\text{tot}} + \frac{1}{6}\gamma_{I,\alpha\beta\gamma\delta}E_{I,\delta}^{\text{tot}} E_{I,\gamma}^{\text{tot}} E_{I,\beta}^{\text{tot}} \quad (3)$$

where the total electric field, $E_{I,\beta}^{\text{tot}}$, is the sum of the external field and the electric field from all other induced dipole moments (see eq 1). A parametrization of the molecular γ thus includes an atomic γ parameter, γ_P, in addition to the parameters adopted for the molecular polarizability. Equivalently, the solutions of eq 3 may be expressed with an additional four-atom relay tensor, $B_{IJKL,\alpha\beta\gamma\delta}^{(4)}$, as[19]

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

The resulting molecular polarizability, $\alpha_{\alpha\beta}^{\text{mol}}$, and molecular second hyperpolarizability, $\gamma_{\alpha\beta\gamma\delta}^{\text{mol}}$, are given as

$$\alpha_{\alpha\beta}^{\text{mol}} = \sum_{IJ}^{N} B_{IJ,\alpha\beta}^{(2)} \quad (5)$$

and

$$\gamma_{\alpha\beta\gamma\delta}^{\text{mol}} = \sum_{IJKL}^{N} B_{IJKL,\alpha\beta\gamma\delta}^{(4)} \quad (6)$$

The theoretical background is described in more detail in a previous work.[20] For the molecular polarizability, the dipole interaction model has been extended by atomic monopole polarizabilities.[21,22] Calculations on fullerenes indicate that monopole terms are of significance,[23] and it would clearly be of interest to extend a model for hyperpolarizabilities with this kind of terms.

In this work, it is demonstrated that an atomistic model can be used for calculating a cubic response property, the molecular γ, for carbon nanotubes up to a length where γ scales linearly with the length of the tube. In principle, it is thus possible to use atomistic models to calculate electronic response properties at all relevant length scales. As in many other areas, molecular modeling can thus be adopted also in nonlinear optics for asking and answering questions regarding what happens if specific functional groups are added or modified.

Results. The parameters, α_C and Φ_C have been obtained in a previous work where α^{mol} is parametrized from Hartree−Fock calculations on 184 molecules.[18] These parameters have been shown to give good results for α^{mol} for nanotubes[24] and fullerene clusters.[18] The last parameter γ_C has been chosen to describe γ^{mol} of C_{60} obtained from Hartree−Fock calculations taken from ref 12. The values used in this work are $\alpha_C = 9.312$ au, $\Phi_C = 0.124$ au, and $\gamma_C = 1600.0$ au. We have shown that these parameters give good results for α^{mol} for fullerenes and nanotubes[18,24] and for γ^{mol} for small fullerenes,[25] and it is therefore expected that they will give reasonable results also for carbon nanotubes.

It has also been demonstrated that the differences for γ^{mol} between quantum chemical calculations and the interaction model are on average around 10% and below 30%.[20] Although, Hartree−Fock calculations by no means represent the true answer, it is encouraging that a simple model like
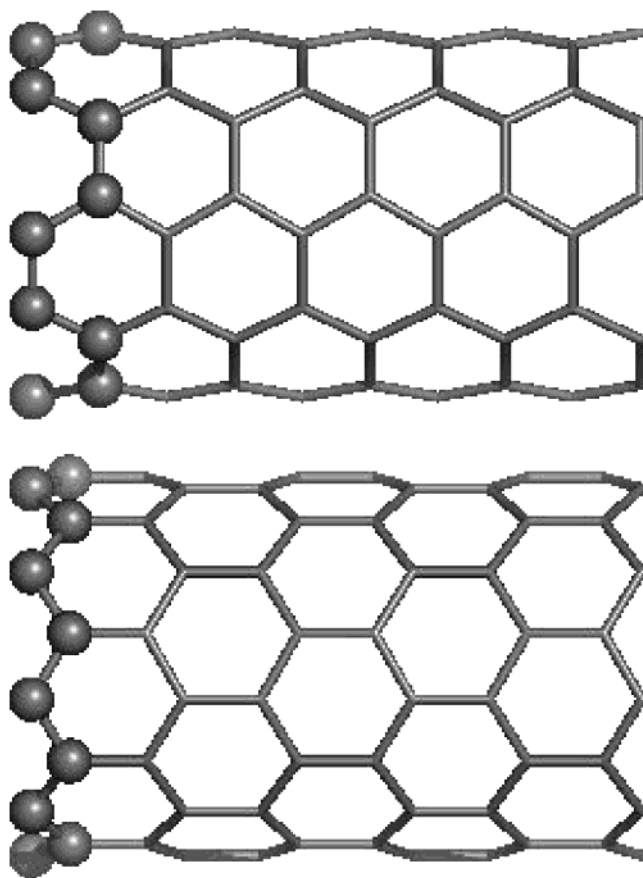
Figure 1. (Top) Structure of a [5,5] carbon nanotube with 100 carbon atoms. (Bottom) Structure of a [9,0] carbon nanotube with 108 carbon atoms. For both carbon nanotubes the bond length of the C−C bond is 1.42 Å. The atoms displayed with ball structure represent the definition of the unit cell used in this work. The unit cell of the [5,5] carbon nanotube contains 20 carbon atoms, whereas the unit cell of the [9,0] nanotube contains 18 carbon atoms.

the interaction model can reproduce quantum chemical calculations consistently. It should therefore be relatively straightforward to reparametrize the model when more sophisticated quantum chemical methods become routine for the calculation of γ for medium-sized molecules. For comparison, most semiempirical calculations give unrealistic values for γ (see examples in ref 20), and density functional theory still presents difficulties for electric response properties, although some recent achievements have been presented.[26]

The molecular γ has been calculated for [5,5] and [9,0] open-ended carbon nanotubes (see Figure 1 for structures) as a function of the tube length. The results are given in Figures 2 and 3 as γ/N, where N is the number of unit cells (see caption of Figure 1 for the definition of unit cells). Results are presented for the average $\bar{\gamma}$, defined as[27]

$$\bar{\gamma} = \frac{1}{15}\sum_{\alpha,\beta}\gamma_{\alpha\alpha\beta\beta} + \gamma_{\alpha\beta\alpha\beta} + \gamma_{\alpha\beta\beta\alpha} \qquad (7)$$

and for the individual components γ_{zzzz}, γ_{xxxx}, and γ_{xxzz}, where the z axis is directed along the tube and the x axis is perpendicular to the tube. The largest tubes of $\sim$300 unit cells correspond to $\sim$6000 atoms and a length of $\sim$75 nm.
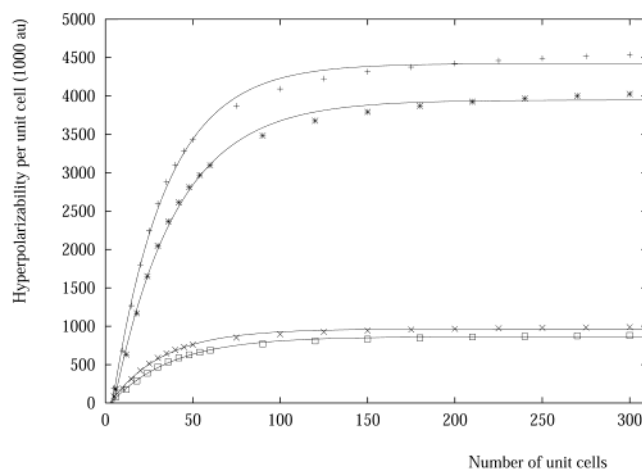
Figure 2. Mean and *zzzz* component of the third-order polarizability per unit cell as a function of the number of unit cells for the [5,5] and [9,0] carbon nanotubes. All results are in 10^3 a.u. Symbols (+) and (×) denote *zzzz* component and mean value, respectively, for the [5,5] nanotube. For the [9,0] nanotube (*) denotes the *zzzz* component and (□) the mean value. Solid lines are the plot of the corresponding fit.
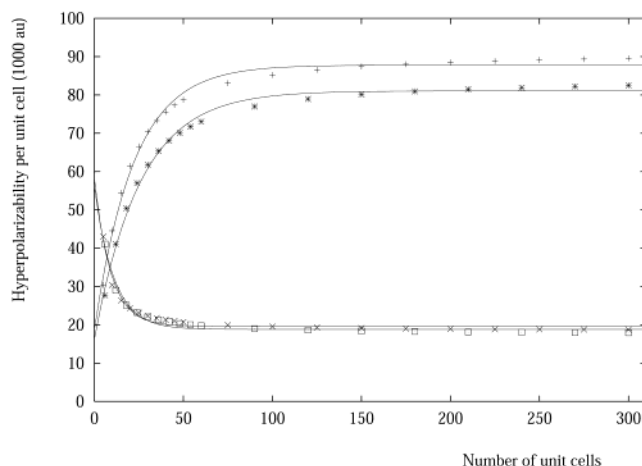

Figure 3. *xxzz* and *xxxx* components of the third-order polarizability per unit cell as a function of the number of unit cells for the [5,5] and [9,0] carbon nanotubes. All results are in 10^3 a.u. Symbols (+) and (×) denote *xxzz* and *xxxx* components, respectively, for the [5,5] nanotube. For the [9,0] nanotube (*) denotes the *xxzz* component and (□) the *xxxx* component. Solid lines are the plots of the corresponding fits.

All of the results for the molecular γ have been characterized by fitting the results to the expression

$$\frac{\gamma(N)}{N} = \gamma^{\infty} - C\exp\left(-\frac{N}{N^{\text{sat}}}\right) \qquad (8)$$

used by Schulz et al.[10] to characterize the saturation of γ^{mol} of organic oligomers. This allows for a description of γ^{mol} in terms of three parameters that are independent of the tube or chain length. The parameter γ^{∞} represents the asymptotic value, and N^{sat} represents the onset of the saturation. The parameters for all the fits are displayed in Table 1 and are plotted with solid lines in Figures 2 and 3. It is found that all the γ components and $\bar{\gamma}$ are well characterized by this model.

Table 1. Fitting Parameters for Characterizing Mean Value and Individual Components of the Third-Order Polarizability for [5,5] and [9,0] Carbon Nanotubes (all parameters in a.u.)

	mean	*zzzz*	*xxzz*	*xxxx*
[5,5]				
N^{sat}	30.47 ± 0.93	30.64 ± 0.94	22.14 ± 0.96	9.13 ± 0.82
γ^{∞}	965.07 ± 5.95	4421.99 ± 28.6	87.79 ± 0.49	19.65 ± 2.96
C	1048.17 ± 18.02	5039.3 ± 86.2	69.10 ± 1.90	-38.50 ± 2.96
[9,0]				
N^{sat}	35.40 ± 1.07	35.58 ± 1.07	25.78 ± 1.13	10.74 ± 0.99
γ^{∞}	864.28 ± 5.45	3947.04 ± 26.15	81.05 ± 0.48	18.81 ± 0.29
C	940.98 ± 15.87	4517.83 ± 75.81	64.80 ± 1.80	-37.21 ± 2.94

By comparing the two types of nanotubes, i.e., [5,5] and [9,0], it is noted that nearly identical results are obtained. The parameters for the [5,5] nanotube obtained from eq 8 are ~10% higher than the corresponding parameters for the [9,0] nanotube, except for N^{sat} which is ~10% lower. The main reason for this is not due to a different behavior of the two types of nanotubes but reflects that the unit cell of [5,5] is ~10% longer than the [9,0] unit cell. The saturation parameter, N^{sat}, for $\bar{\gamma}$ is for the [5,5] nanotube ~30 unit cells and for [9,0] about 35 unit cells, which corresponds to a tube length of 7.3 nm for the [5,5] nanotube and 7.5 nm for the [9,0] nanotube, respectively. As put forward by Schulz et al.,[10] a characterization of γ in terms of a power law, i.e., $\gamma \sim N^a$, is not appropriate since the exponent a varies strongly with N. This can be illustrated by plotting the variation in a defined as $b \equiv (d \ln(\gamma)/d \ln(N))$ as a function of N, which is displayed in Figure 4. From Figure 4, it is seen that b tends slowly toward one for long nanotubes and that the strongest variation in b is found for the small tubes. It is also found that N^{sat} corresponds well with the point where the variation of b starts to decrease.

As expected, it is found that γ_{zzzz} has the longest saturation length and the smallest saturation length is found for γ_{xxxx}. For this reason, the saturation of $\bar{\gamma}$ is determined by the saturation of γ_{zzzz}. However, its asymptotic value, γ^{sat}, as obtained from the fit to $\bar{\gamma}$ is ~10% higher than that obtained from $\gamma_{zzzz}/5$. Therefore, when extrapolating γ to the asymptotic limit by only considering the longitudinal components, which is typically done (see, e.g., ref 28), an error of ~10% is introduced as compared with extrapolating the mean value.

Even if it is difficult to strictly define where the scaling of γ becomes linear with tube length, it can be concluded that for tubes shorter than 100 unit cells $\bar{\gamma}$ and γ_{zzzz} behave in a clearly nonlinear way. For example, γ_{zzzz}/N of the [5,5] tube increases by a factor of 20 if the length of the tube is increased from 5 to 100 unit cells, but only with an additional 10% if the tube is extended to 300 unit cells.

The scaling parameters obtained for the nanotubes can be compared with the characterization of a series of conjugated organic oligomers carried out by Schulz et al.[10] The saturation lengths obtained for the oligomers are between 2 and 8 nm, in comparison to 7.5 nm obtained for the carbon nanotubes in this work. If γ^{∞}_{zzzz} is considered, a value of 1.8×10^6 a.u/Å is found for both types of nanotubes compared with the values for the conjugated oligomers, which vary between
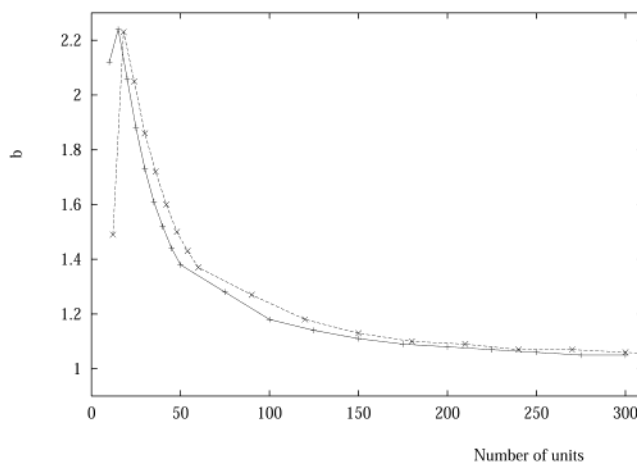

Figure 4. The variation, $b \equiv (d \ln(\gamma)/d \ln(N))$, of a power law representation of the mean third-order polarizability for the [5,5] and [9,0] carbon nanotubes as a function of the number of unit cells. The symbol (+) denotes [5,5] nanotube and (×) [9,0] nanotube.

6×10^4 a.u/Å and 1.2×10^6 a.u/Å. If γ^{∞} for polyacetylene of 0.66×10^6 a.u./Å obtained using the semiemperical INDO/S method[10] is compared with the ab initio Hartree−Fock result of 1.3×10^6 a.u./Å,[28] it is noted that the INDO/S result is about a factor of 2 smaller than the ab initio result. Therefore, even if a possible underestimation of γ using the INDO/S method instead of ab initio methods is considered, it is found that the magnitude of γ with respect to the length of carbon nanotubes is comparable with that of conjugated polymers. For this reason, carbon nanotubes are demonstrated to be a valid alternative to conjugated polymers for constructing new materials for use in nonlinear optical devices, especially considering the possibilities of enhancing the nonlinearities of carbon nanotubes by means of either endohedral, exohedral, or substitutional doping (see, e.g., refs 6 and 7).

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