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Static and Frequency-Dependent Polarizability Tensors for Carbon Nanotubes

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We have calculated the static and frequency-dependent polarizability tensors of a series of (5,5)- and (9,0)-carbon nanotubes. The calculations have been performed by a dipole–dipole interaction model based on classical electrostatics and an Unsöld dispersion formula. The model has previously been shown to predict successfully the frequency-dependent polarizability tensors of both aliphatic and aromatic molecules. In comparison we have carried out ab initio calculations at the Hartree–Fock level of the static polarizability of C_{60}, C_{70}, and the smaller carbon nanotubes using the STO-3G basis set. We find that the interaction model is in good agreement with the self-consistent field calculations and can be used to predict the polarizability tensors of carbon nanotubes. In addition, we find that the symmetry and intramolecular geometry of the tube have great influence on the polarizability.

I. Introduction

As discussed recently, the miniaturization of the traditional silicon-based transistors will reach its intrinsic limit soon.[1] There will, with the increasing demand for faster computers and information distribution, therefore be a need for new approaches. One approach emerges from Feynman's famous talk "There's Plenty of Room at the Bottom".[2] The "bottom-up" approach implies the construction of molecular-level components capable of performing the functions needed.[3] The way that information is distributed is also changing, going from electronic devices toward photonic devices. In the future a major goal will be the use of light as information carrier, to speed up the process of data transmission. This change will rely on the development of new photonic materials.[4] In the development of photonic materials it is of fundamental importance to understand the optical response properties of the materials. Especially, the understanding of not only the static but also the frequency-dependent polarizability and hyperpolarizability at the molecular level is of fundamental importance.[5–12]

Conjugated organic molecules with delocalized electron systems are interesting because of their potentially large optical response properties. The new class of carbon materials, fullerenes and carbon nanotubes, has an extended π-system and is therefore a promising group of candidates for new photonic materials. The linear and nonlinear optical properties of C_{60} and C_{70} have been studied extensively, both theoretically[13–19] and experimentally[20–26] since their discovery. The polarizabilities of the larger fullerenes and the carbon nanotubes have been studied less extensively and only in the static limit. The static polar-

izabilities of the larger fullerenes have been calculated within the atom monopole–dipole interaction (AMDI) theory[27] by Shanker and Applequist.[17] In the case of the carbon nanotubes Benedict et. al used a tight-binding model[28] to study the static polarizability of infinitely long tubes.

The basic research on fullerenes and carbon fibers has provided ways to synthesize, characterize, and understand carbon nanotubes.[29–32] The work by Kroto et. al on laser vaporization of graphite giving C_{60} clusters has led to the large family of fullerenes.[33] The synthesis procedure by Kratschmer et. al giving macroscopic amounts of fullerenes was a giant step forward.[20] Iijima utilized this procedure for making multiple-shell carbon nanotubes.[34] These nanotubes were much smaller than the ones normally obtained when making graphite fibers.[35]

We investigate the frequency-dependent polarizability of single-walled carbon nanotubes by a modified version of Thole's interaction model[36] extended to the frequency-dependent regime.[37] Both zigzag, (9,0), and armchair, (5,5), nanotubes and the effects of closing one or two ends are investigated. This is done in order to investigate purely geometric factors involved in the determination of the polarizability. Here we regard fullerenes as end-capped nanotubes.

II. Theory

The molecular polarizability, $\alpha_{\alpha,\beta}^{\text{mol}}$, is defined as the linear response to an external electric field,

$$\mu_{\alpha}^{\text{ind}} = \alpha_{\alpha,\beta}^{\text{mol}} E_{\beta}^{\text{ext}} \tag{1}$$

where $\mu_{\alpha}^{\text{ind}}$ is the induced molecular dipole moment. Considering a set of N interacting atomic polarizabilities, the atomic

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induced dipole moment has a contribution also from the other atoms,

$$\mu_{p,\alpha}^{\text{ind}} = \alpha_{p,\alpha\beta}\left(E_\beta^{\text{ext}} + \sum_{q \neq p}^{N} T_{pq,\beta\gamma}^{(2)} \mu_{q,\gamma}^{\text{ind}}\right) \tag{2}$$

where $T_{pq,\beta\gamma}^{(2)}$ is the interaction tensor as modified by Thole[36]

$$T_{pq,\alpha\beta}^{(2)} = \frac{3v_{pq}^4 r_{pq,\alpha} r_{pq,\beta}}{r_{pq}^5} - \frac{(4v_{pq}^3 - 3v_{pq}^3)\delta_{\alpha\beta}}{r_{pq}^3} \tag{3}$$

where $v_{pq} = r_{pq}/s_{pq}$ if $r_{pq} < s_{pq}$; otherwise $v_{pq} = 1$. The term s is defined as $(\Phi_p\Phi_q)^{1/4}$ where Φ_p is a fitting parameter proportional to the atomic second-order moment.[37] The molecular polarizability can then be written as[38]

$$\alpha_{\boldsymbol{\alpha},\boldsymbol{\beta}}^{\text{mol}} = \sum_{q,p}^{N} B_{pq,\alpha\beta} \tag{4}$$

where **B** is the relay matrix defined as (in a supermatrix notation)

$$\mathbf{B} = (\alpha^{-1} - T^{(2)})^{-1} \tag{5}$$

The frequency dependence of the molecular polarizability is often modeled with an Unsöld-type of expression.[8] Here we assume that the atomic polarizability has a similar frequency dependence[37]

$$\alpha_p(-\omega;\omega) = \alpha_p(0;0)\left[\frac{\bar{\omega}_p^2}{\bar{\omega}_p^2 - \omega^2}\right] \tag{6}$$

The atomic parameters α_p, Φ_p, and $\bar{\omega}_p$ have previously been fitted to the full polarizability tensors of quantum-mechanical computed molecular polarizabilities of a series of 115 substituted aliphatic and aromatic molecules containing the elements C, H, N, O, F, and Cl.[37] The parameters are therefore not reparametrized in this work but adopted as the values previously reported. Of the molecules included in the original learning set, only benzene is used in this work.

III. Computational Methods

The quantum chemical computations of the polarizability tensors were for the nanotubes restricted to the static regime at the self-consistent field (SCF) level using the Gaussian 94 program package.[39] A minimal basis set, STO-3G, was used in order to get the results of the larger carbon nanotubes. The geometries of the nanotubes were first optimized with a molecular mechanics (MM2) method and afterwards with a semiempirical method (PM3). The optimized bond length is between 1.35 and 1.45 Å for the (9,0) nanotube and between 1.38 and 1.45 Å (1.23 Å in the ends) for the (5,5) nanotube. Two structures of C_{60} were used. One is referred to as C_{60} (MM2), which was optimized only with the MM2 method and has a uniform bond length of 1.46 Å. A second structure, referred to as C_{60} (PM3), was first optimized with MM2 and then PM3, having two distinct bond lengths of 1.46 and 1.38 Å, respectively. The structure of benzene was taken as standard bond lengths and angles adopted from ref 40. The specific geometries are available from the authors on request. Also, frequeny-dependent polarizability tensors were calculated for C_{60} (PM3) using the Dalton program package.[41] The frequencies used were $\omega = 0.0$, 0.023 89, 0.042 82 and 0.0774 au. The frequency-dependent calculation was performed using the STO-

TABLE 1: Static Mean Polarizability, Anisotropy, and Polarizability Tensor Components of Benzene (au)

	$\bar{\alpha}$	κ^2	α_{xx}	α_{zz}	ref
Experimental					
laser Stark spectroscopy	68.7	0.0234	79.2	47.7	46
depolarized Rayleigh scattering	67.47	0.0299	79.15	44.13	44
static Kerr effect	70.04	0.0371	83.53	43.05	45
Theoretical					
SCF Sadlej	69.50	0.0294	80.97	45.21	19
SCF 6-31++G**	66.73	0.0339	79.01	42.17	50
SCF TZ2P	65.08	0.0332	76.94	41.36	51
MCSCF ANO[432/32]	66.16	0.0241	76.43	45.62	52
AMDI	67.59	0.0380	80.77	41.23	27
This Work					
SCF Sadlej/Dalton	68.42	0.0281	79.89	45.49	
IM	63.81	0.0414	76.79	37.84	
SCF STO-3G/Gaussian	32.71	0.1676	46.10	5.93	

3G and 4-31G basis sets. The interaction model (IM) parameters used for carbon are as follows (in atomic units): $\alpha_C = 11.52$, $\Phi_C = 20.99$, and $\bar{\omega}_C = 0.39$. The parameters used were taken from ref 37 assuming a benzene-like dispersion.

IV. Results

The results for the static mean polarizability, anisotropy, and polarizability tensor components of benzene are presented in Table 1 and are compared to a collection of experimental and other theoretical studies. The mean polarizability, $\bar{\alpha}$, is defined as

$$\bar{\alpha} = \frac{1}{3}(\alpha_{xx} + \alpha_{yy} + \alpha_{zz}) \tag{7}$$

and the anisotropy, κ^2, as[42]

$$\kappa^2 = [(\alpha_{xx} - \bar{\alpha})^2 + (\alpha_{yy} - \bar{\alpha})^2 + (\alpha_{zz} - \bar{\alpha})^2]/6\bar{\alpha}^2 \tag{8}$$

The mean polarizability can be obtained by measurements of the dielectric constant or the refractive index. The dielectric constant, ϵ, can be converted to molecular polarizability using the Clausius−Mossotti equation[43]

$$\bar{\alpha} = \frac{3M}{4\pi N_a \rho} \frac{\epsilon - 1}{\epsilon + 2} \tag{9}$$

where M is the molecular weight, N_a is Avogadro's number and ρ is the density. In the case of the refractive index, the Lorenz−Lorentz equation (eq 9 with $n^2 = \epsilon$)[43] can be used. The anisotropy can be related to the depolarization ratio measured in Rayleigh scattering,[44] the static Kerr effect,[45] or the static Stark effect.[46] The mean polarizability and the anisotropy are therefore important quantities when comparing to experiments.

The results in Table 1 show that there is a good agreement between experimental and theoretical polarizability and anisotropy for benzene. Experiments yield a mean polarizability $\bar{\alpha}$ between 68 and 70 au and an anisotropy κ^2 in the range of 0.0234−0.0371. The range of the theoretically calculated polarizability is 64−70 au, apart from the calculation using a STO-3G basis set. The theoretical anisotropy lies between 0.0241 and 0.0414. In both experiments and calculations there is a larger scattering in the anisotropy data than in the mean polarizability data. The values obtained using the IM gives slightly lower mean polarizability and overshoots the anisotropy. This is due to the low value af the polarizability perpendicular to the benzene ring.

TABLE 2: Frequency-Dependent Polarizability of Benzene (au)

ω (au)/λ (nm)	0/∞		0.02389 /1907		0.04282 /1064		0.0720/ 632.8		ref
	$\bar{\alpha}$	κ^2	$\bar{\alpha}$	κ^2	$\bar{\alpha}$	κ^2	$\bar{\alpha}$	κ^2	
MCSCF	66.16	0.0241	66.38	0.0242	66.89	0.0244	68.26	0.0249	52
SCF	68.42	0.0281	68.67	0.0282	69.24	0.0285	70.81	0.0292	this work
IM	63.78	0.0414	64.01	0.0416	64.54	0.0421	66.00	0.0453	this work
expt	67.47	0.0299					70.11	0.0325	44
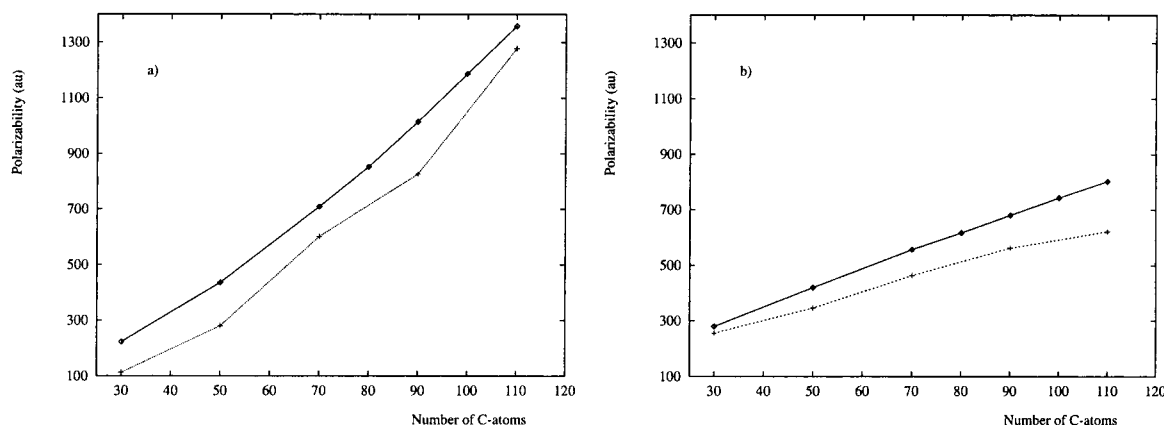
Figure 1. Static polarizability of the (5,5) nanotube as a function of the number of atoms. ($-$, ($\blacklozenge$) IM and (--, $+$) SCF STO-3G: (a) Polarizability along the tube and (b) polarizability perpendicular to the tube.

TABLE 3: Static Isotropic Polarizability of C_{60} and C_{70} (Å^3)

	$\bar{\alpha}$		
technique	C60	C70	ref
Experimental			
refractive index of thin film[a]	86.5		20, 22
dielectric constant of thin film[b]	91.9	107.2	21
dielectric constant of thin film[c]	80.5	96.8	23
dielectric constant of thin film[c]	87.6		25, 24
molecular beam deflection	76.5		26
Theoretical			
SCF 6-31+G	75.1	89.8	19
SCF 6-31+G d	78.8		16
MNDO/PM3	63.9	79.0	14
LDF	79.9		15
INDO-TDCPHF	81.69		13
AMDI	60.8	73.8	17
This Work			
SCF STO-3G/Gaussian	51.1	57.6	MM2[c]
SCF STO-3G/Dalton	45.6		PM3
SCF 4-31G/Dalton	62.2		PM3
IM	65.2	77.2	PM3
IM	66.2		MM2

[a] Calculated using the Lorenz−Lorentz equation and a density of 1.65 g/cm^3.[20] [b]Calculated using the Clausius−Mossotti equation and the same density as in a. [c] Only C_{60} is MM2-optimized.

In Table 2 the frequency-dependent mean polarizability and anisotropy of benzene calculated using the IM are compared to quantum mechanical and experimental data. Again, we find good agreement between experimental and theoretical frequency-dependent mean polarizabilities. The frequency-dependence of the anisotropy for the quantum mechanical result is lower than the experimental data. The anisotropy calculated using IM is larger than both experiment and quantum mechanical results. This is again due to the low value of the out of plane polarizability.

The results for the static mean polarizability of C_{60} and C_{70} are presented in Table 3 and are again compared to a collection of experimental and other theoretical studies. Most of the experiments have been done on films, and they include the determination of the refractive index[20,22] or the dielectric

constant.[21,23−25] The experimental data from films yield polarizabilities between 80.5 and 91.9 Å^3 for C_{60}, 96.8−107.2 Å^3 for C_{70}, and a ratio C_{60}/C_{70} of 1.17−1.20. Recently, a measurement of the polarizability of molecular C_{60} using a molecular beam deflection technique[26] was reported, yielding a polarizability of 76.5 $\pm$ 8 Å^3. This value indicates that the molecular polarizability is only slightly lower than the results measured for films. The theoretical polarizabilities are in good agreement with experiments, yielding polarizabilities of 45.6−81.7 Å^3 for C_{60}, 57.6−89.8 Å^3 for C_{70}, and a ratio C_{70}/C_{60} of 1.13−1.24. Our SCF calculation using a STO-3G basis set gives values that are low compared to the previous results, indicating the need for having polarization functions in the basis set. The IM value of 65.2 Å^3 for C_{60} (PM3) is about 16% lower than the best SCF calculation[16,19] and 7% higher that the value of the similar AMDI model.[27] The difference in the polarizability between the two different structures of C_{60} is for the quantum mechanical result around 10% and for the IM result around 1.5%. This indicates that the interaction model is less sensitive to small changes in bond lengths, in agreement with previous findings.[17]

In Figure 1, we present a comparison of the static polarizability of (5,5) tubes calculated with SCF and the interaction model as a function of the number of carbon atoms. We find an excellent agreement between the two methods. The value of polarizability calculated with IM is higher than the corresponding SCF value, which is in good agreement with the results of Table 1 and Table 3. If we extend the number of carbon atoms beyond the SCF regime, see Figure 2, we observe that the polarizability along the tube increases rapidly compared to the polarizability perpendicular to the tube. Both $\alpha_{\parallel}$ and $\alpha_{\perp}$ increase in a nonlinear way and can therefore not be described using an additivity model.[47,48] The increase of $\alpha_{\perp}$ slows down, whereas for $\alpha_{\parallel}$ it continues. The large difference between the polarizability along the tube and perpendicular to the tube is also found in the case of infinitely long tubes.[28]

The frequency-dependent polarizability of C_{60} is displayed in Figure 3. We have also included the work by Weiss et al.[16] From this we see that if we use a dispersion similar to what we

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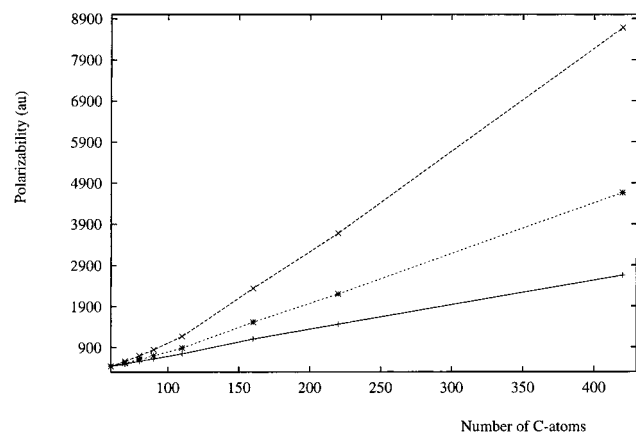*J. Phys. Chem. B, Vol. 104, No. 45, 2000* **10465**

Figure 2. IM static polarizability tensors of the (5,5) carbon nanotube: (--, ×) polarizability along the tube, (···, ∗) mean polarizability, and (—, +) polarizability perpendicular to the tube.
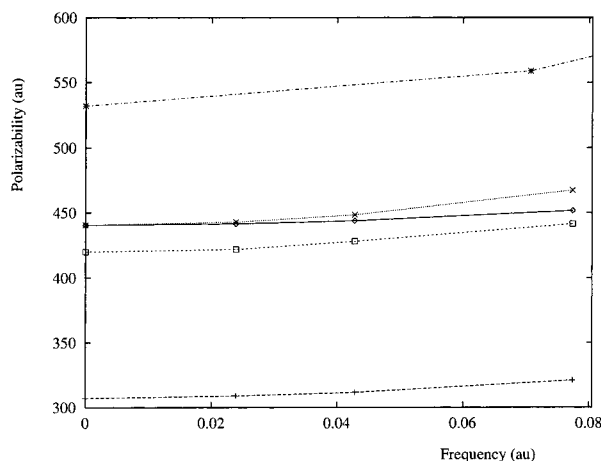

Figure 3. Polarizability of C_{60} (PM3) as a function of frequency (au): (− · −, ∗) SCF 6-31G + sd[16], (···, ×) IM with $\bar{\omega}_C = 0.26$ au, (—, ◇) IM with $\bar{\omega}_C = 0.39$ au, (--, □) SCF 4-31G, and (− −, +) SCF STO-3G.

found for a series of substituted benzenes,[37] we underestimate the frequency-dependence. This can be corrected by choosing another value of the frequency parameter $\bar{\omega}_C$. This has been done by inspection of Figure 3, and a reasonable value was found to be $\bar{\omega}_C = 0.26$ au. Adopting this value for $\bar{\omega}_C$, in the case of the carbon nanotubes, we present in Figure 4 the frequency-dependent polarizability of a (5,5) nanotube with 110 carbon atoms. We find that the frequency-dependence along the tube is larger than that perpendicular to the tube, giving a large anisotropy.

The geometric influence on the polarizability is illustrated in Table 4. Keeping the total number of carbon atoms constant, we find that closing the ends lowers the polarizability, especially along the tube. This means that the polarizability of a fullerene is lower that the polarizability of a nanotube with the same number of atoms. Also, going from an armchair configuration to a zigzag configuration lowers the polarizability along the tube, but the polarizability perpendicular to the tube increases, keeping the mean polarizability almost constant. This trend for the polarizability perpendicular to the tube is also found by Benedict et al.[28] and is similar to that Jiang et al. found for the static mean hyperpolarizability of C_{60}-derived tubes.[49] The anisotropies of the nanotubes are an order of magnitude greater than for benzene. The same trends as for the mean polarizability are also present in the anisotropy. However, the anisotropy is different for a zigzag configuration than that for an armchair; it is lowest
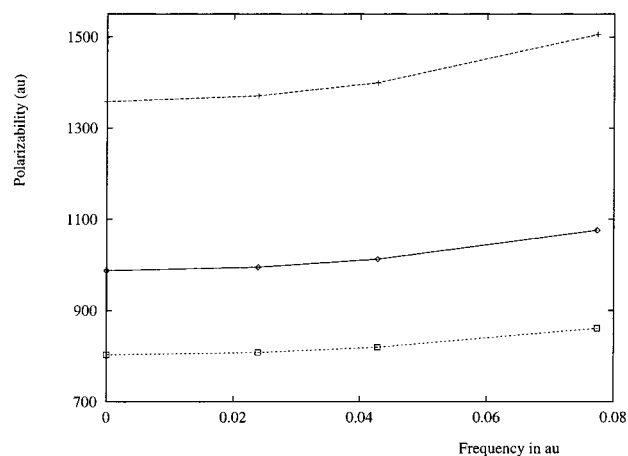

Figure 4. Frequency-dependent polarizability of the (5,5) carbon nanotube with 110 atoms, calculated using IM with $\bar{\omega}_C = 0.26$: (- -, □) polarizability perpendicular to the tube, (—, ◇) mean polarizability, and (--, +) polarizabilty along the tube.

TABLE 4: Static Polarizabilities of Selected Nanotubes (au)

nanotube[a]	$\bar{\alpha}$	κ^2	$\alpha_{\parallel}$	$\alpha_{\perp}$
$(5,5)_0^{110}$	987.7	0.187	1357.8	802.6
$(5,5)_1^{110}$	936.5	0.173	1260.1	774.7
$(5,5)_2^{110}$	886.2	0.159	1168.2	745.2
$(5,5)_0^{90}$	792.3	0.141	1015.4	680.7
$(9,0)_0^{90}$	791.7	0.122	984.4	695.4

[a] Superscript indicates number of atoms and subscript indicates number of closed ends.

for the zigzag nanotube. From this we see that the specific symmetry and intramolecular geometry of the tube have a great influence on the molecular polarizability.

V. Conclusion

We have successfully used a frequency-dependent interaction model to calculate the frequency-dependent polarizability of C_{60}, C_{70}, (5,5) nanotubes and (9,0) nanotubes. The usefulness of the interaction model in dealing with systems out of the normal ab initio regime has been illustrated. The IM provides a straightforward way of dealing with large systems. The inclusion of new types of atom is also straightforward and opens the possibility of dealing with other types of nanosystems. The calculated polarizabilities of C_{60} and C_{70} are around 15% lower that the best SCF calculations. We find excellent agreement between the SCF calculations and our model calculation of the increase in polarizability when the number of carbon atoms is increased. It is also found that the symmetry and intramolecular geometry of the tube and caps have great influence on the polarizability of the tubes.

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