A Charge−Dipole Model for the Static Polarizability of Nanostructures Including Aliphatic, Olephinic, and Aromatic Systems

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We present an electrostatic interaction model for the calculation of the static electronic polarization of hydrocarbons. In previous work, models have often been presented for one single type of hydrocarbons. Here, we discuss the different requirements for a model to describe aliphatic, olephinic, and aromatic systems. The model is based on the representation of the carbon and hydrogen atoms by induced electric charges and dipoles, where the actual values of the charges and dipoles are those that minimize the electrochemical energy of the molecule. The electrostatic interactions are described in terms of normalized propagators, which improves both the consistency and the numerical stability of the technique. For the calibration of our model, we sought at reproducing the molecular polarizabilities obtained by current density functional theory for a set of 48 reference structures. We propose parameters for each type of hydrocarbon, which provide an excellent agreement with the reference data (relative error on the mean molecular polarizabilities of 0.5, 1.4, and 1.9% for alkanes, alkenes, and aromatic molecules, respectively). We also propose parameters based on the local environment of each atom, which are better suited for the description of more complex molecules. We finally study the polarizability of fullerenes and small hydrogen-terminated (5,5) carbon nanotubes.

I. Introduction

In fundamental science as well as for the development of nanotechnology, one encounters the problem of predicting the response of molecular systems to electric fields. In this context, molecular modeling in terms of both quantum chemical and classical electrostatics models plays a prominent role.[1−3] In particular, obtaining the polarization of molecules enables the computation of electric forces acting on molecules as well as the force exerted on other structures. Electronic polarization properties thus contribute to simulate the dynamics of complex systems[4−6] and to obtain properties such as the preferential adsorption sites of macromolecules,[7,8] the field-induced organization of these structures,[9] hypersusceptibilities,[10,11] macroscopic polarization,[12] Raman intensities,[13,14] field-emission properties,[15,16] and so forth.

First-principles techniques provide the most accurate theoretical values for polarizabilities.[17−19] Their memory and time requirements limit however their applicability to systems usually not exceeding a few hundred atoms. In molecular mechanics (or force-field) models, the molecular energy is described with simplified models, where, for example, the electrostatics is described by classical models. Because of the reduced computational requirements, force-field models are widely used in molecular dynamics simulations, where forces have to be computed for every time step,[4,5] or in problems where many configurations have to be considered.[8]

In the point−dipole interaction (PDI) model, a polarizability is associated with each atom, and an atomic induced dipole moment is thus obtained from the interaction with the external electric field and the electric field due to the other atomic induced dipole moments. This technique was introduced by Silberstein[20] and has been improved by others. If the electric fields associated with a given distribution of atomic charges were included, the resulting atomic dipole moments would consist of two contributions, one permanent atomic dipole moment that, together with these atomic charges, should give a good model of the permanent molecular dipole moment and a field-induced atomic dipole moment that is supposed to give a model of the molecular polarizability (by "permanent", we always mean "independent of the external field"). However, the PDI model normally only consists of a model for the molecular polarizability, and any dependence of the atomic charges on the external field is not considered. Different versions of the PDI models exist, each one having a specific approach to deal with short-range effects. One way is to include anisotropic atomic polarizabilities,[21] and models also differ in the way that the electrostatic interactions are normalized. Normalization has the effect to give the dipole−dipole energy a finite value at the limit where the interatomic distance tends to zero. It also has the effect to damp the electrostatic interactions at short distances.[7,22−27] The PDI model has been applied by many authors to the study of fullerenes and carbon nanotubes.[6−8,27−35]

This technique has been extended by associating an atomic charge to each atom in addition to the atomic polarizability.[9,36−41] In contrast with the PDI model, the atomic charges contain a part that is induced by the external field. This consideration of induced atomic charges is modeled either by an atomic capacitance[36] or by an atomic electronegativity and chemical hardness (inverse of capacitance), in line with the electronegativity equalization model.[42] An electronegativity difference between two atoms results in an inherent potential difference, leading to a charge flow between the two atoms. In addition, if an external electric field is added to the model, a charge flow

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contributing to the molecular polarizability is obtained. In general, the partitioning of a charge distribution into subsystems leads to two contributions to the system polarizability, an internal polarization within each subsystem represented by an induced dipole moment and a charge flow between the subsystems represented by induced atomic charges. This picture is consistent with other models for the partitioning of the molecular polarizability into atomic contributions, such as, for example, the model by Stone including atomic monopole polarizabilities.[43] The formulations of a combined charge−dipole model again differ by the normalization of the electrostatic interactions, by the definition of the self-energies, and by the method used to enforce charge neutrality. In recent publications,[44−47] one of us proposed a formulation in which the electrostatic interactions between the charges and the dipoles are normalized in a way that is fully consistent with the definition of their self-energy.

We extend, in this paper, the range of applicability of this technique by considering hydrocarbons. In particular, we seek at reproducing the molecular polarizability of alkanes, alkenes, and aromatic molecules, the reference data being obtained by current density functional theory using the Amsterdam density functional (ADF) software.[48−53] Transferability of atom-type parameters is a central theme in the construction of parametrized molecular mechanics models. For this kind of electrostatic model, different models have usually been constructed for aliphatic, olephinic, or aromatic systems, with the argument that charge-transfer contributions are more important for π-conjugated systems. In a combined charge−dipole model, we will therefore, in this work, focus on the different requirements to get accurate models for the different types of systems. The theoretical framework is developed in section II. In section III, we propose parameters that are specific to alkanes, alkenes, and aromatic molecules and enable the calculation of their molecular polarizability. In section IV, we propose parameters based on the local environment of each atom, which are more appropriate for the description of molecules that combine these three chemical groups. The agreement with the reference data turns out to be excellent, which proves the validity and usefulness of this technique. Section V finally extrapolates these results to fullerenes and small hydrogen-terminated carbon nanotubes.

II. Theory: A Charge−Dipole Model to Compute the Molecular Polarizability of Molecules

A. Molecular Energy. In this paper, we focus on the calculation of the molecular polarizability of hydrocarbons, in particular, that of alkanes, alkenes, and aromatic molecules. Although hydrogen will turn out to be described accurately without charge for these systems, we assume for the moment that every atom is represented by an atomic charge q_i and a dipole moment $\mathbf{p}_i$. According to our previous work,[45,47] the total electrochemical energy E_{tot} associated with a given distribution $\{q_i, \mathbf{p}_i\}$ of charges and dipoles placed at the atomic positions $\mathbf{r}_i$ and subject to an external field $\mathbf{E}_{\text{ext}}$ is given by

$$E_{\text{tot}} = \frac{1}{2}\sum_{i=1}^{N}\sum_{j=1}^{N} q_i T^{i,j}_{\text{q-q}} q_j - \frac{1}{2}\sum_{i=1}^{N}\sum_{j=1}^{N} \mathbf{p}_i \cdot \mathbf{T}^{i,j}_{\text{p-p}} \mathbf{p}_j - \sum_{i=1}^{N}\sum_{j=1}^{N} \mathbf{p}_i \cdot \mathbf{T}^{i,j}_{\text{p-q}} q_j + \sum_{i=1}^{N} q_i(\chi_i + V_i) - \sum_{i=1}^{N} \mathbf{p}_i \cdot \mathbf{E}_{\text{ext}} \quad (1)$$

In this expression, N refers to the number of atoms in the structure considered, χ_i stands for the electronegativity of the atom i, and $V_i = -\mathbf{E}_{\text{ext}} \cdot \mathbf{r}_i$ refers to the external potential at the atomic position $\mathbf{r}_i$. The three first terms account for the charge−charge, the dipole−dipole, and the charge-dipole interactions, respectively. The last two terms account for the interactions between the charges or the dipoles and the external field. The quantities to determine are the atomic charges q_i and the atomic dipoles $\mathbf{p}_i$, which depend on the electronegativities χ_i and on the electric field $\mathbf{E}_{\text{ext}}$ externally applied to the structure. $\mathbf{E}_{\text{ext}}$ is the external field, as obtained by an external device, and we assume for simplicity that it is uniform. The external field $\mathbf{E}_{\text{ext}}$ does not include the fields that are induced by the charges q_i and the dipoles $\mathbf{p}_i$. These local fields are taken into account by the terms that involve $T^{i,j}_{\text{q-q}}$, $\mathbf{T}^{i,j}_{\text{p-p}}$, and $\mathbf{T}^{i,j}_{\text{p-q}}$ in eq 1.

The electronegativities χ_i turn out to be responsible for the permanent (or field-independent) values of the atomic charges and for the permanent atomic electric moments. The external field is included with the purpose to calculate the molecular polarizability, α_{molec}, according to its definition

$$\mathbf{P}^{\text{ind}} = \alpha_{\text{molec}} \mathbf{E}_{\text{ext}} \quad (2)$$

where the molecular induced dipole moment

$$\mathbf{P}^{\text{ind}} = \sum_i q_i^{\text{ind}} \mathbf{r}_i + \sum_i \mathbf{p}_i^{\text{ind}}$$

is simply the sum of the atomic induced dipole moments, $\mathbf{p}_i^{\text{ind}}$, completed by the contribution due to the induced atomic charges, q_i^{ind}. As demonstrated with more details in the next section, the charges, q_i, and the dipole moments, $\mathbf{p}_i$, may be partitioned into a permanent part, q_i^0 and $\mathbf{p}_i^0$, and a part induced by the external electric field, q_i^{ind} and $\mathbf{p}_i^{\text{ind}}$, from which we obtain the molecular polarizability.

We make the assumption that the atomic charges q_i are distributed according to Gaussian charge densities of the form $\rho_i(\mathbf{r}) = (q_i/\pi^{3/2}(R_{\text{q}}^i)^3)\ \exp[-|\mathbf{r} - \mathbf{r}_i|^2/(R_{\text{q}}^i)^2]$. The parameter R_{q}^i that characterizes the width of these distributions is specific to each type of atom. In a similar way, the extension of the elementary charges associated with the atomic dipoles $\mathbf{p}_i$ is characterized by a parameter R_{p}^i, which is actually determined by the atomic polarizabilities α_i (see section II.C).[47] Within these assumptions, the quantities $T^{i,j}_{\text{q-q}}$, $\mathbf{T}^{i,j}_{\text{p-q}}$, and $\mathbf{T}^{i,j}_{\text{p-p}}$ that express the electrostatic interactions between the charges and the dipoles turn out to be given by

$$T^{i,j}_{\text{q-q}}[R^{i,j}_{\text{q-q}}] = \frac{1}{4\pi\epsilon_0} \frac{\text{erf}\left(\frac{r_{i,j}}{R^{i,j}_{\text{q-q}}}\right)}{r_{i,j}} \quad (3)$$

$$\mathbf{T}^{i,j}_{\text{p-q}}[R^{i,j}_{\text{p-q}}] = \frac{1}{4\pi\epsilon_0} \frac{\mathbf{r}_{i,j}}{r_{i,j}^3}\left[\text{erf}\left(\frac{r_{i,j}}{R^{i,j}_{\text{p-q}}}\right) - \frac{2}{\sqrt{\pi}} \frac{r_{i,j}}{R^{i,j}_{\text{p-q}}} \text{e}^{-(r_{i,j}/R^{i,j}_{\text{p-q}})^2}\right] \quad (4)$$

$$\mathbf{T}^{i,j}_{\text{p-p}}[R^{i,j}_{\text{p-p}}] = \frac{1}{4\pi\epsilon_0}\left\{\frac{3\mathbf{r}_{i,j} \otimes \mathbf{r}_{i,j} - r_{i,j}^2 \mathbf{I}}{r_{i,j}^5}\left[\text{erf}\left(\frac{r_{i,j}}{R^{i,j}_{\text{p-p}}}\right) - \frac{2}{\sqrt{\pi}} \frac{r_{i,j}}{R^{i,j}_{\text{p-p}}} \text{e}^{-(r_{i,j}/R^{i,j}_{\text{p-q}})^2}\right] - \frac{4}{\sqrt{\pi} R^{i,j}_{\text{p-p}}{}^3} \frac{\mathbf{r}_{i,j} \otimes \mathbf{r}_{i,j}}{r_{i,j}^2} \text{e}^{-(r_{i,j}/R^{i,j}_{\text{p-p}})^2}\right\} \quad (5)$$

where $R^{i,j}_{\text{q-q}} = \sqrt{(R_{\text{q}}^i)^2 + (R_{\text{q}}^j)^2}$, $R^{i,j}_{\text{p-q}} = \sqrt{(R_{\text{p}}^i)^2 + (R_{\text{q}}^j)^2}$, and $R^{i,j}_{\text{p-p}} = \sqrt{(R_{\text{p}}^i)^2 + (R_{\text{p}}^j)^2}$ are the effective radii relevant to these electrostatic interactions.[27] The tensors $T^{i,j}_{\text{q-q}}$, $\mathbf{T}^{i,j}_{\text{p-q}}$, and $\mathbf{T}^{i,j}_{\text{p-p}}$ describe "normalized" interactions because giving the electric charges a finite extension has the effect to screen these interactions and remove the divergences that occur otherwise

when taking the limit $r_{ij} \rightarrow 0$. Other normalization schemes result from the consideration of different distributions for the electric charges (these distributions are Gaussian in the current paper). The relations in eqs 3, 4, and 5 can finally be related to the self-energies by taking the limit $r_{i,j} \rightarrow 0$ of these expressions. The chemical hardness (or inverse of the capacitance), $\eta_i = T^{i,i}_{\mathrm{q-q}} = (1/4\pi\epsilon_0)\sqrt{(2/\pi)}(1/R^i_{\mathrm{q}})$, and the inverse of the polarizability, $\alpha_i^{-1} = -\mathbf{T}^{i,i}_{\mathrm{p-p}} = (1/4\pi\epsilon_0)\sqrt{(2/\pi)}(1/3(R^i_{\mathrm{p}})^3)$, are thus determined by R^i_{q} and R^i_{p}, respectively (these relations are demonstrated in refs 45 and 47). Consequently, the model consists of three atom-type parameters, χ_i, R^i_{q} (or η_i), and R^i_{p} (or α_i), to be determined.

B. Determination of the Molecular Polarizability. For a molecule that carries a net electric charge Q_{tot}, the actual values of the atomic charges q_i and of the dipoles $\mathbf{p}_i$ are those that minimize

$$f = E_{\mathrm{tot}} + \lambda\left(\sum_{i=1}^{N} q_i - Q_{\mathrm{tot}}\right)$$

The Lagrange multiplier λ is related to the chemical potential of the molecule.[47] Writing $\mathrm{d}f/\mathrm{d}q_i = 0$, $\mathrm{d}f/\mathrm{d}p_{x,i} = 0$, $\mathrm{d}f/\mathrm{d}p_{y,i} = 0$, $\mathrm{d}f/\mathrm{d}p_{z,i} = 0$, and $\mathrm{d}f/\lambda = 0$ explicitly provides a system of $4N + 1$ linear and symmetric equations for determining the q_i, the $\mathbf{p}_i$, and λ. This system of equations can be written in the form

$$\begin{pmatrix} \mathbf{T}_{\mathrm{q-q}} & -\mathbf{T}_{\mathrm{q-p}} & 1 \\ -\mathbf{T}_{\mathrm{p-q}} & -\mathbf{T}_{\mathrm{p-p}} & 0 \\ 1 & 0 & 0 \end{pmatrix}\begin{pmatrix} \mathbf{q} \\ \mathbf{p} \\ \lambda \end{pmatrix} = \begin{pmatrix} -\chi - \mathbf{V} \\ \mathbf{E} \\ Q_{\mathrm{tot}} \end{pmatrix} \quad (6)$$

where $\mathbf{T}_{\mathrm{q-q}}$ is an $N \times N$ matrix that contains the $T^{i,j}_{\mathrm{q-q}}$, $\mathbf{T}_{\mathrm{p-q}}$, is a $3N \times N$ matrix that contains the $\mathbf{T}^{i,j}_{\mathrm{p-q}}$, $\mathbf{T}_{\mathrm{q-p}} = \mathbf{T}^{\mathrm{t}}_{\mathrm{p-q}}$, and $\mathbf{T}_{\mathrm{p-p}}$ is a $3N \times 3N$ matrix that contains the $\mathbf{T}^{ij}_{\mathrm{p-p}}$. The $\mathbf{q}$ and $\mathbf{p}$ are two vectors of length N and $3N$ that contain the q_i and the components of the $\mathbf{p}_i$, respectively; χ and $\mathbf{V}$ are two vectors of length N that contain the χ_i and V_i. $\mathbf{E}$ is here a vector of length $3N$ that contains the components of the external field $\mathbf{E}_{\mathrm{ext}}$ on each atom.

From the solutions q_i and $\mathbf{p}_i$ of this equation, one can compute the first moment of the charges of the molecule by

$$\mathbf{P} = \sum_{i=1}^{N} (q_i\mathbf{r}_i + \mathbf{p}_i)$$

This quantity may be partitioned as

$$\mathbf{P} = \mathbf{P}^0 + \alpha_{\mathrm{molec}}\mathbf{E}_{\mathrm{ext}} \quad (7)$$

where $\mathbf{P}^0$ is independent of $\mathbf{E}_{\mathrm{ext}}$, α_{molec} is the molecular polarizability, and $\mathbf{E}_{\mathrm{ext}}$ is the external field. This decomposition is justified by the fact that the solution of eq 4 can be written as

$$\begin{pmatrix} \mathbf{q} \\ \mathbf{p} \\ \lambda \end{pmatrix} = \begin{pmatrix} \mathbf{T}_{\mathrm{q-q}} & -\mathbf{T}_{\mathrm{q-p}} & 1 \\ -\mathbf{T}_{\mathrm{p-q}} & -\mathbf{T}_{\mathrm{p-p}} & 0 \\ 1 & 0 & 0 \end{pmatrix}^{-1}\begin{pmatrix} -\chi \\ 0 \\ Q_{\mathrm{tot}} \end{pmatrix} + \begin{pmatrix} \mathbf{T}_{\mathrm{q-q}} & -\mathbf{T}_{\mathrm{q-p}} & 1 \\ -\mathbf{T}_{\mathrm{p-q}} & -\mathbf{T}_{\mathrm{p-p}} & 0 \\ 1 & 0 & 0 \end{pmatrix}^{-1}\begin{pmatrix} -\mathbf{V} \\ \mathbf{E} \\ 0 \end{pmatrix} \quad (8)$$

in which the first term of the right-hand side is independent of the external field, while the second term contains the dependence on the external field. The charges q_i^0 and the dipoles $\mathbf{p}_i^0$ that result from the first term define, within this model, the permanent molecular dipole moment, $\mathbf{P}^0$, which is given by

$$\mathbf{P}^0 = \sum_{i=1}^{N} (q_i^0\mathbf{r}_i + \mathbf{p}_i^0)$$

In the case of a neutral molecule ($Q_{\mathrm{tot}} = 0$), $\mathbf{P}^0$ only exists if the molecule is made of different types of atoms (i.e., when the χ_i are not identical). In the case where the molecule is charged ($Q_{\mathrm{tot}} \neq 0$), $\mathbf{P}^0$ also contains the origin dependence of the first moment $\mathbf{P}$. The second part of $\mathbf{P}$, which is associated with α_{molec}, is thus guaranteed to give an origin-independent molecular polarizability.

The second term of the right-hand side of eq 6 provides the charges q_i^{ind} and the dipoles $\mathbf{p}_i^{\mathrm{ind}}$ that are induced by the external field. Their values are directly proportional to the external field. Writing

$$\mathbf{P}^{\mathrm{ind}} = \sum_{i=1}^{N} (q_i^{\mathrm{ind}}\mathbf{r}_i + \mathbf{p}_i^{\mathrm{ind}}) = \alpha_{\mathrm{molec}}\mathbf{E}_{\mathrm{ext}}$$

enables the calculation of the molecular polarizability α_{molec}. One can notice that α_{molec} is independent of the χ_i and of Q_{tot} since these two terms only appear in the first term of the right-hand side of eq 6. Within this model, α_{molec} will only depend on the atomic positions $\mathbf{r}_i$, on the widths R^i_{q} of the atomic charges, and on the atomic polarizabilities α_i (or equivalently R^i_{p}) since these parameters determine entirely the matrices $\mathbf{T}_{\mathrm{q-q}}$, $\mathbf{T}_{\mathrm{p-q}}$, and $\mathbf{T}_{\mathrm{p-p}}$.

C. Isotropic and Anisotropic Atomic Polarizabilities. In the applications presented, we will consider either isotropic or anisotropic atomic polarizabilities. In the case where isotropic atomic polarizabilities α^i_{iso} are considered, the parameter R^i_{p} is given by[47]

$$R^i_{\mathrm{p}} = \left(\sqrt{\frac{2}{\pi}}\frac{\alpha^i_{\mathrm{iso}}/3}{4\pi\epsilon_0}\right)^{1/3} \quad (9)$$

The parameters to be adjusted are hence the width R^i_{q} of the excess charges and the atomic polarizability α^i_{iso} for each type of atom (carbon and hydrogen). The χ^i have no influence on the molecular polarizabilities and will not receive further consideration in this paper. The atomic charges and dipoles calculated in this paper are therefore exclusively those induced by the external field. This first version of our model will be referred to by the acronym "Q+P iso [R,α_{iso}]". The "Q+P" refers to the use of charges and dipoles for the representation of the atoms, "iso" refers to the use of isotropic atomic polarizabilities, and "R,α_{iso}" refers to the parameters to be adjusted for each atom.

In the case where anisotropic atomic polarizabilities $\alpha^i_{\mathrm{aniso}}$ are considered, the parameter R^i_{p} turns out to be given by[47]

$$R^i_{\mathrm{p}} = \left(\sqrt{\frac{2}{\pi}}\frac{(2/\alpha^i_{\mathrm{par}} + 1/\alpha^i_{\mathrm{perp}})^{-1}}{4\pi\epsilon_0}\right)^{1/3} \quad (10)$$

In the derivation of this expression, it is assumed that the principal components of the anisotropic atomic polarizabilities $\alpha^i_{\mathrm{aniso}}$ are given by (α^i_{par},α^i_{par},α^i_{perp}). The components α^i_{par} of these anisotropic atomic polarizabilities are associated with the plane defined by the three neighbors of the atom i. The component α^i_{perp} is associated with the direction perpendicular to that plane. In situations where the atom i does not possess three neighbors, we consider instead an isotropic atomic

polarizability, whose value is related to the parameters α^i_{par} and α^i_{perp} of the anisotropic model by $\alpha^i_{iso} = 3/(2/\alpha^i_{par} + 1/\alpha^i_{perp})$. This second version of our model will be referred to by the acronym "Q+P aniso [R,α_{par},α_{perp}]". The "aniso" refers to the use of anisotropic polarizabilities, and "R,α_{par},α_{perp}" refers to the parameters to be adjusted for each atom. Since R^i_p is completely fixed by the atomic polarizabilities, which are considered as the adjustable parameters, it is understood from this point that the notation R^i refers to the width R^i_q of the atomic charges.

III. Application: Molecular Polarizability of Alkanes, Alkenes, and Aromatic Molecules

The technique discussed in section II has been applied to alkanes, alkenes, and aromatic molecules. The objective is to reproduce the full molecular polarizability tensor of these structures. The reference data were obtained using current density functional theory (c-DFT) in the Amsterdam density functional (ADF) software,[48−50] which provides a better description of the nonlocal exchange and correlation effects that appear in structures subject to external electric fields.[51−53] The geometry optimizations have been carried out with the BLYP functional and a triple-ζ basis set, TZP, whereas the polarizability calculations were done with the c-DFT module using a triple-ζ basis set augmented with diffuse functions, aug-ATZP. Diffuse functions are well-known to be crucial for polarizability calculations.

We present in this section the parameters obtained by considering the different types of hydrocarbons separately. The parameters were obtained by minimizing the deviations between the molecular polarizability tensors calculated using c-DFT and those calculated using our model (deviations in the nine components of these tensors were considered for the full set of molecules considered). This minimization was achieved by applying a Monte Carlo technique for the global optimization, followed by a conjugated gradient method to refine the solution obtained in this first step.[54] In section IV, we will present the adjustments obtained by addressing these three types of molecules simultaneously with parameters based on the local environment of each atom.

A. Molecular Polarizability of Alkanes. The alkanes considered in the parametrization are methane to decane (C_nH_{2n+2}, with $n = 1-10$). When reproducing the molecular polarizability of these structures, it turns out that neither hydrogen nor sp^3 carbon require the consideration of atomic charges. The molecular polarizability of alkanes is indeed well accounted for by representing the carbon and hydrogen atoms by dipoles only. This result is expected from the absence of mobile electrons in alkanes (the four valence electrons of the carbon atoms are involved in σ-bonding). This point was also observed by Applequist.[37] The fact the hydrogen atoms have only one neighbor while the sp^3 carbon atoms have four neighbors implies the use of isotropic atomic polarizabilities. This representation of hydrogen by a dipole (without an atomic charge and using an isotropic atomic polarizability) was adopted in the remaining part of this paper.

In the model presented in section II, electric charges can be removed from the representation by setting $R^i_q = 0$. Since this involves an infinite self-energy for the charges q_i, it enforces q_i to be zero. In a numerical implementation of this model, the charges q_i are simply skipped from the representation. In the case where charges are removed from all of the atoms, eq 6 is reduced to $-\mathbf{T}_{p-p}\mathbf{p} = \mathbf{E}$, which is the dipole interaction model. The difference with the work presented by other authors[7,22,23,26,27] lies in the normalization of the electrostatic interactions, in the relation we established between the atomic polarizabilities α_i and the parameter R^i_p used in the normalization of these interactions, and in the reference data we used for the parametrization.

TABLE 1: Parameters Used to Compute the Molecular Polarizability of Alkanes, Alkenes, and Aromatic Molecules Using the Q+P Model with Either Isotropic or Anisotropic Atomic Polarizabilities; the Values in the Last Two Columns Provide the Isotropic Atomic Polarizabilities When They Are Equal and the Components of the Anisotropic Atomic Polarizabilities Otherwise

	R (Å)	$\alpha_{par}/(4\pi\epsilon_0)$ (Å^3)	$\alpha_{perp}/(4\pi\epsilon_0)$ (Å^3)
		Alkanes	
hydrogen	0	0.4471	0.4471
carbon	0	0.9639	0.9639
		Alkenes	
hydrogen	0	0.3662	0.3662
carbon	0.01048	1.3199	1.3199
hydrogen	0	0.3066	0.3066
carbon	0.01126	1.6573	2.4726
		Aromatic Molecules	
hydrogen	0	0.3384	0.3384
carbon	0.01945	1.2885	1.2885
hydrogen	0	0.3057	0.3057
carbon	0.02279	1.4755	2.2611

When comparing the results of the Q+P iso [R,α_{iso}] model with those provided by c-DFT, the relative error on the mean molecular polarizabilities $\bar{\alpha} = (\alpha_{xx} + \alpha_{yy} + \alpha_{zz})/3$ turns out to be 0.5% on average, with a maximal value of 2.6%, while the relative error on the full molecular polarizability tensors is 2.8% on average, with a maximal value of 5.1%. The average value of these relative errors is defined, respectively, by

$$\bar{\epsilon}_{rel} = \frac{\sum_{k=1}^{N_{alkanes}} \left| \sum_{i=1}^{3} (\alpha^{c-DFT}_{molec[k]})_{i,i}/3 - \sum_{i=1}^{3} (\alpha^{Q+P}_{molec[k]})_{i,i}/3 \right|}{\sum_{k=1}^{N_{alkanes}} \left| \sum_{i=1}^{3} (\alpha^{c-DFT}_{molec[k]})_{i,i}/3 \right|} \quad (11)$$

$$\epsilon_{rel} = \frac{\sum_{k=1}^{N_{alkanes}} \sum_{j=1}^{3} \sum_{i=1}^{3} \left| (\alpha^{c-DFT}_{molec[k]})_{i,j} - (\alpha^{Q+P}_{molec[k]})_{i,j} \right|}{\sum_{k=1}^{N_{alkanes}} \sum_{j=1}^{3} \sum_{i=1}^{3} \left| (\alpha^{c-DFT}_{molec[k]})_{i,j} \right|} \quad (12)$$

where k enumerates the alkanes considered in these simulations. In these expressions, c-DFT refers to the molecular polarizabilities calculated with the c-DFT method and Q+P to the molecular polarizabilities calculated using our model. The maximal value of these relative errors is obtained by looking for which molecule has the highest ratio between the deviations in the molecular polarizability of this molecule and its mean molecular polarizability. The parameters obtained from these calculations are given in Table 1.

These relative errors of 0.5 and 2.8%, which correspond, respectively, to the mean polarizabilities and to the components of the full polarizability tensors, compare very well with previous work.[23,27] For example, Birge obtained a relative error of 3.26% on the mean polarizabilities of a set of molecules that includes alkanes and a relative error of 6.68% on the components of the full polarizability tensors.[23] Since the reference data are

not the same, it is not appropriate to push further the comparison with results provided by other models. The parameters α_{iso}^{H} and α_{iso}^{C} of our model are on the same order as those used by others.[21−23,27,37] A quantitative comparison between the parameters used by different models is again not appropriate because these parameters are specific to each model. In particular, they depend strongly on the scheme used to normalize the electrostatic interactions.[27] It would be interesting to extend the study to different conformations. Polarizable force fields have been constructed successfully for conformational degrees of freedom, such as, for example, for dimethoxyethane,[55] and the model discussed here may be included in such a framework.

B. Molecular Polarizability of Alkenes. The structures considered for the parametrization of alkenes are C_nH_{2n}, with $n = 2$, 4, 6, 8, 10, 14, 18, 22, and 26. We thus consider in this section π-conjugated hydrocarbons in which the carbon atoms form linear structures. As for alkanes, hydrogen was represented without atomic charges. For the representation of sp^2 carbon, it turns out that both an atomic charge q_i and a dipole $\mathbf{p}_i$ are necessary. This necessity to include atomic charges for the representation of sp^2 carbon is in agreement with the existence of π-electrons in the C═C double bonds of these structures. Since every carbon atom has three neighbors in a planar arrangement, we consider both isotropic and anisotropic atomic polarizabilities for their representation.

When comparing the results of the Q+P iso [R,α_{iso}] model with those provided by c-DFT, the relative error on the mean molecular polarizability of the alkenes turns out to be 2.4% on average, with a maximal value of 3.3%. The relative error on the components of the full polarizability tensors is 4.5% on average, with a maximal value of 24%. When using isotropic atomic polarizabilities for the representation of carbon in these alkenes, the out-of-plane component of the molecular polarizabilities turns out to be systematically smaller than the values predicted by c-DFT (by typically 20%). One can improve the modeling of alkenes by using anisotropic atomic polarizabilities for the carbon atoms. The relative error on the mean molecular polarizabilities is then reduced to 1.4% on average, with a maximal value of 7%, while the relative error on the components of the full polarizability tensors is reduced to 2.6% on average, with a maximal value of 14%. The parameters used for these simulations are given in Table 1. In this table, α_{par} and α_{perp} refer to the components of the atomic polarizabilities. These components correspond, respectively, to the plane defined by the three neighbors of each atom and to the direction perpendicular to that plane.

C. Molecular Polarizability of Aromatic Molecules. We also aimed at reproducing the molecular polarizability of aromatic molecules. This section therefore focuses on π-conjugated hydrocarbons in which the carbon atoms appear in aromatic rings. However, we restricted this study to structures that consist of adjacent aromatic rings: benzene, naphthalene, anthracene, phenanthrene, and eighteen other structures, g(1,4), g(2,2), g(2,3), g(3,2), g(3,3), g(4,1), g(4,2), g(4,3), g(5,1), g(6,1), g(6,2), g(6,3), g(7,1), g(8,1), g(8,2), g(8,3), g(10,1), and g(10,2), where the two numbers in these notations refer, respectively, to the number of aromatic rings in the zigzag and armchair directions. The structures whose aromatic rings are connected in the "zigzag direction" are the naphthalene, anthracene, phenanthrene, g(5,1), g(6,1), and so forth. In these structures, each aromatic ring has a C−C bond in common with the next ring, and these aromatic rings are aligned along a common direction. Expanding these structures in the "armchair" direction consists of reproducing these rows of aromatic rings along a direction perpendicular to the zigzag direction. These aromatic rings are placed in the same way as in a honeycomb lattice, and the pending bonds are terminated by hydrogen. The g(3,1) or anthracene hence consists of a single row of three aromatic rings. The g(3,2) consists of two rows of three aromatic rings, and so forth. Figure 1 provides an illustration of the g(3,2).

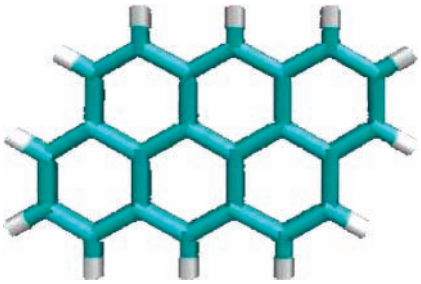

Figure 1. Illustration of a g(3,2) structure. It consists of two rows of three aromatic rings. The pending bonds are terminated by hydrogen. In this illustration, we refer by "zigzag" and "armchair" to the horizontal and vertical directions, respectively.

As for the alkenes, we investigate the use of both isotropic and anisotropic atomic polarizabilities for the representation of carbon. When using isotropic atomic polarizabilities for the representation of hydrogen and carbon, the relative error on the mean molecular polarizabilities turns out to be 2.5% on average, with a maximal value of 10%, while the relative error on the components of the full polarizability tensors is 6.2% on average, with a maximal value of 22%. As for alkenes, the out-of-plane component of the molecular polarizabilities turns out to be systematically smaller than the values provided by c-DFT. One can however improve the modeling of these aromatic molecules by using anisotropic atomic polarizabilities for the representation of carbon. The relative error on the mean polarizabilities is then reduced to 1.9% on average, with a maximal value of 8.7%, while that on the components of the full polarizability tensors is reduced to 3.5% on average, with a maximal value of 23% (unlike results achieved with isotropic atomic polarizabilities, deviations of this order of magnitude are not systematic). Figure 2 provides a better illustration of the agreement we achieved between the data provided by c-DFT and those obtained using our model (this figure contains the results obtained for alkanes, alkenes, and aromatic molecules when anisotropic atomic polarizabilities are used). The parameters used for these simulations are given in Table 1.

For the parametrization of aromatic molecules, we had to exclude structures in which the aromatic rings are separated by C−C bonds (like biphenyl or triphenyl) since these bonds apparently limit the mobility of electrons so that the displacement of free charges essentially occurs within the different aromatic rings rather than within the whole structure. The parameters determined for structures that consist of adjacent aromatic rings and in which the displacement of free charges occurs in the whole structure apply therefore with less success. Structures like biphenyl or triphenyl will however be considered in the next section, where we seek to determine parameters based on the local environment of each atom. These global adjustments are better suited for the description of structures that combine the three chemical groups considered so far. The adjustments presented in this section, which focus on alkanes, alkenes, and aromatic molecules specifically, are however more accurate for these structures.

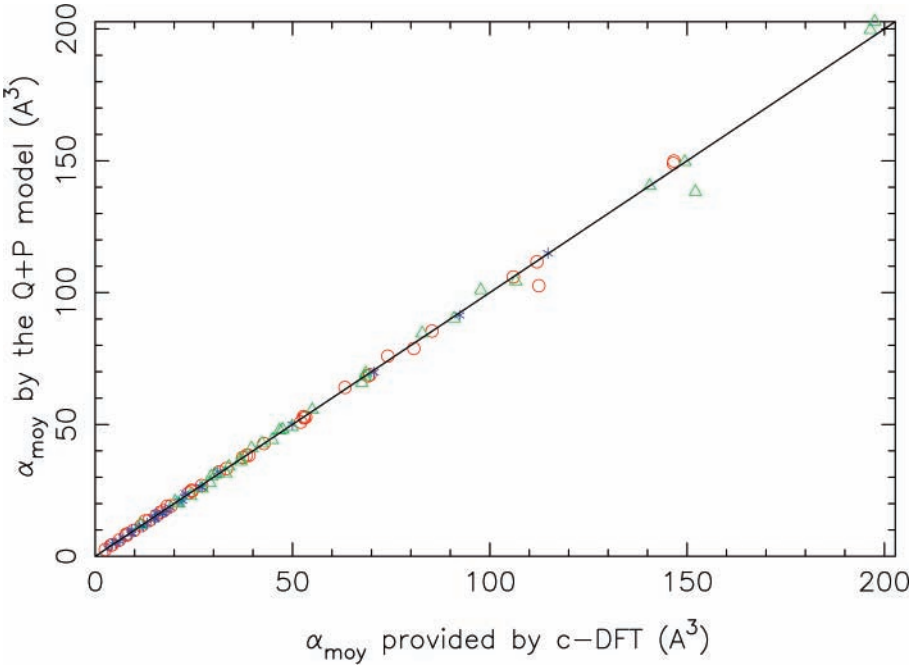

Figure 2. Mean molecular polarizability of alkanes, alkenes, and aromatic molecules, as calculated using c-DFT (horizontal) and using the Q+P aniso [R,α_{par},α_{perp}] model with parameters that are specific to each chemical group (vertical). These parameters are given in Table 1 (anisotropic atomic polarizabilities are used for the carbon atoms). The circles indicate the mean polarizabilities. For planar molecules, the triangles and the asterisks indicate, respectively, the in-plane and the out-of-plane components of the molecular polarizabilities. The molecules represented in this figure are given in section III of the paper.

IV. Molecular Polarizability Of Alkanes, Alkenes, Aromatic Molecules and Alkene-Aromatic Compounds Using Collective Parameters

We seek in this section at reproducing with a common set of parameters the molecular polarizability of alkanes, alkenes, aromatic molecules, and combinations of these three chemical groups. The set of molecules considered includes the alkanes, the alkenes, and the aromatic molecules of the previous section. In addition, we also consider the following structures: biphenyl (two conformations), styrene, *p*-vinyl styrene, 1,2-diphenyl ethene, H−(C_6H_4−CH═CH−)$_2C_6H_5$, and *p*-dibutadienyl benzene. Instead of establishing parameters for a given chemical group, we detect the local environment of each atom and represent it using parameters that are specific to that environment. The objective of this approach is to eventually describe more complex structures.

Hydrogen is described with a single parameter, the isotropic atomic polarizability determined for alkanes. This choice is motivated by the fact that for alkanes, we obtained parameters that fit nearly exactly the c-DFT results (relative error of 0.5% on the mean polarizabilities). Carbon is given parameters that depend on the local bonding environment. We thus distinguish between (i) sp^3 carbon (i.e., the carbon atoms that have four neighbors), (ii) sp^2 carbon in a linear environment (i.e., the carbon atoms that have three neighbors and that are not included in an aromatic ring), and (iii) sp^2 carbon in a cyclic environment (i.e., the carbon atoms that have three neighbors and that belong to an aromatic ring). The classification of the carbon atoms according to these three categories is achieved automatically. We distinguish again between a model in which every atom is described by an isotropic atomic polarizability and a model in which the sp^2 carbon atoms are given an anisotropic atomic polarizability.

When isotropic atomic polarizabilities are used for both the hydrogen and carbon atoms, the relative error on the mean molecular polarizabilities turns out to be 2.7% on average, with a maximal value of 11%, whereas the relative error on the components of the full polarizability tensors is 6.7% on average, with a maximal value of 32%. When applied to alkanes, these parameters provide the relative errors already obtained in section III.A ($\bar{\epsilon}_{rel}$ = 0.5% on the mean polarizabilities and ϵ_{rel} = 2.8% on the full polarizability tensors). When applied to alkenes, the relative errors provided by these parameters are $\bar{\epsilon}_{rel}$ = 2.3% and ϵ_{rel} = 5.5% (instead of 2.4 and 4.5% when using parameters that are specific for alkenes). When applied to the aromatic molecules of section III.C, the relative errors are $\bar{\epsilon}_{rel}$ = 2.6% and ϵ_{rel} = 6.7% (instead of 2.5 and 6.2%). As already observed with alkenes and aromatic molecules when using isotropic atomic polarizabilities for the sp^2 carbon, the out-of-plane component of the molecular polarizabilities turns out to be systematically smaller than the values provided by c-DFT.

The adjustment with the reference data can be substantially improved by using anisotropic atomic polarizabilities for the sp^2 carbon atoms. Compared with the fully isotropic model, the out-of-plane component of the molecular polarizabilities is described as well as the other components. The relative error $\bar{\epsilon}_{rel}$ on the mean molecular polarizabilities is then reduced to 2.5% on average, with a maximal value of 15%, while that on the full polarizability tensors is reduced to 4.7% on average, with a maximal value of 34% (this maximal deviation is again not systematic). Figure 3 illustrates the agreement achieved between the results obtained using c-DFT and those obtained using our model when anisotropic atomic polarizabilities are used. The parameters used for these simulations are given in Table 2. When applied to alkanes specifically, these parameters provide the relative errors already obtained in section III.A ($\bar{\epsilon}_{rel}$ = 0.5% and ϵ_{rel} = 2.8%). When applied to alkenes, the relative errors provided by these parameters are $\bar{\epsilon}_{rel}$ = 2.2% and ϵ_{rel} = 4.2% (instead of 1.4 and 2.6% when using parameters that are specific for alkenes). When applied to the aromatic molecules of section III.C, the relative errors are $\bar{\epsilon}_{rel}$ = 2.1% and ϵ_{rel} = 4.4% (instead of 1.9 and 3.5%).

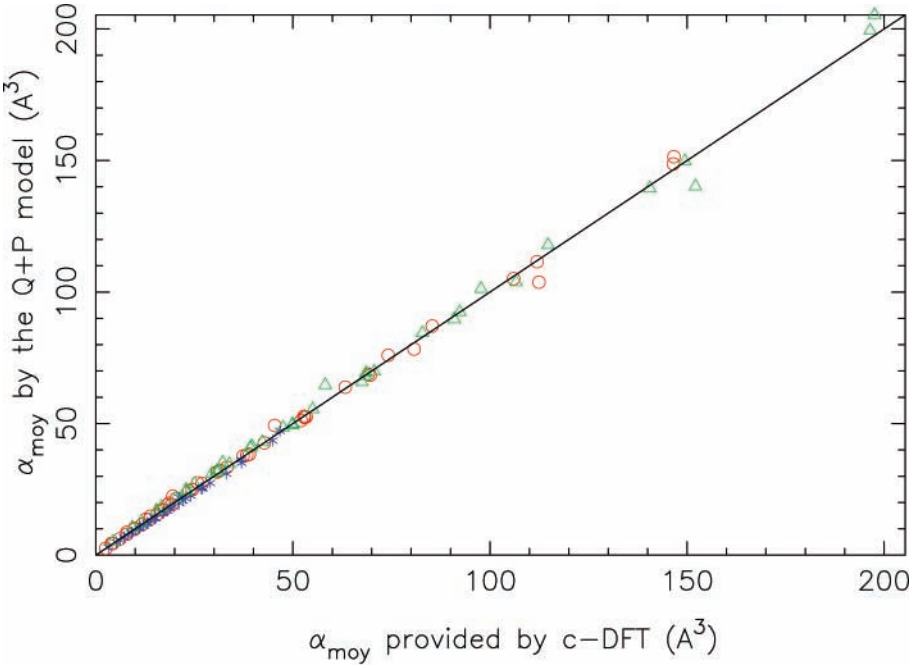

Figure 3. Mean molecular polarizability of alkanes, alkenes, aromatic molecules, and alkene−aromatic compounds, as calculated using c-DFT (horizontal) and using the Q+P aniso [R,α_{par},α_{perp}] model with parameters that are specific to the local environment of each atom (vertical). These parameters are given in Table 2 (anisotropic atomic polarizabilities are used for the carbon atoms). The circles indicate the mean polarizabilities. For planar molecules, the triangles and the asterisks indicate, respectively, the in-plane and the out-of-plane components of the molecular polarizabilities. The molecules represented in this figure are given in sections III and IV of the paper.

TABLE 2: Parameters Used To Compute the Molecular Polarizability of Alkanes, Alkenes, Aromatic Molecules, and Compounds of These Three Chemical Groups Using the Q+P Model with Either Isotropic or Anisotropic Atomic Polarizabilities[a]

	R (Å)	$\alpha_{par}/(4\pi\epsilon_0)$ (Å^3)	$\alpha_{perp}/(4\pi\epsilon_0)$ (Å^3)
hydrogen	0	0.4471	0.4471
carbon, sp^3	0	0.9638	0.9638
carbon, sp^2 linear	0.01758	1.2597	1.2597
carbon, sp^2 cyclic	0.02652	1.2080	1.2080
hydrogen	0	0.4471	0.4471
carbon, sp^3	0	0.9638	0.9638
carbon, sp^2 linear	0.01838	1.5324	2.2360
carbon, sp^2 cyclic	0.03029	1.3632	2.1671

[a] The values in the last two columns provide the isotropic atomic polarizabilities when they are equal and the components of the anisotropic atomic polarizabilities otherwise. The first part of this table corresponds to the fully isotropic model; the second part corresponds to the model in which sp^2 carbon is given anisotropic atomic polarizabilities.

V. Molecular Polarizability of Fullerenes and Carbon Nanotubes

As for alkanes, alkenes, and aromatic molecules, the description of fullerenes and carbon nanotubes requires the use of specific parameters if one seeks at getting the best possible agreement with reference data. One can however apply the parameters determined in the previous section and check whether they provide reasonable values. This extrapolation is justified by the fact fullerenes and carbon nanotubes have a bonding organization that is similar to that of the aromatic molecules considered in this paper. We used for this purpose the parameters given in Table 2 with anisotropic atomic polarizabilities for the sp^2 carbon.

When applied to the C_{60}, C_{72}, and C_{84} fullerenes, we obtain mean polarizabilities of 65.5, 78.0, and 96.2 Å^3. These values are in agreement within 12.6% with the values of 75.1, 89.8, and 109.4 Å^3 determined by Jonsson et al.,[17] which we used as reference in ref 47. When using the parameters that are specific to aromatic molecules (with anisotropic atomic polarizabilities), we obtain mean polarizabilities of 67.8, 80.8, and 99.7 Å^3 (relative error of 9.5% compared to the data by Jonsson). Finally, by using the parameters of ref 47 that are specific to fullerenes and carbon nanotubes, we obtain mean polarizabilities of 74.5, 90.9, and 115.3 Å^3, respectively, for the three fullerenes (relative error of 2.8% compared to the data by Jonsson). These first calculations give some insight into the transferability of our parameters. As the fullerenes have a bonding organization that is similar to that of the aromatic molecules, we obtain a better description of the fullerenes using the parameters determined for these molecules. The best agreement is, of course, obtained using parameters that are specific for fullerenes and carbon nanotubes. This transfer of parameters to the fullerenes turns out to work reasonably well, considering the fact that the aromatic molecules considered in this paper and the fullerenes are different species. It is understood that any chemical family should be described with specific parameters in order to obtain the best possible accuracy. This question of transferability is intrinsic to any model that contains adjustable parameters, and it is known that only a limited accuracy can be expected when transferring parameters from one chemical family to another.

Since the parameters given in Table 2 with anisotropic atomic polarizabilities for the sp^2 carbon atoms turn out to apply to fullerenes with a reasonable accuracy, we also applied our model to hydrogen-terminated (5,5) carbon nanotubes (using the same method as that for geometry optimization). The axial and transverse polarizabilities considering different lengths for the nanotubes are represented in Figure 4. The lengths are expressed in terms of the number of elementary cells in the body of the (5,5) nanotube, where each cell consists of 20 carbon atoms. c-DFT was also used to compute the axial and transverse polarizabilities for the three shortest tubes. The agreement of our results with these reference data is very good. The extrapolation provided by our model shows that the axial

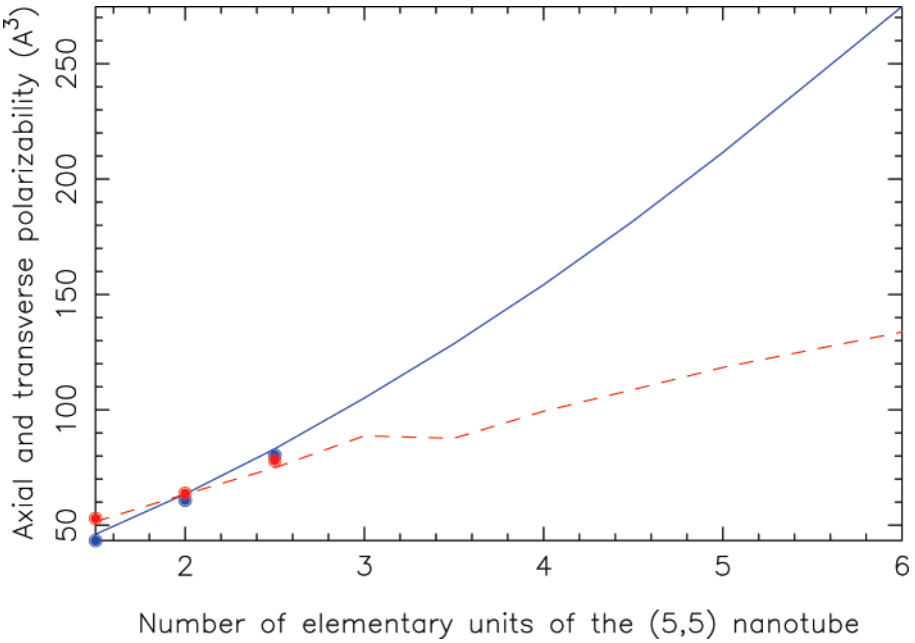

Figure 4. Axial (solid) and transverse (dashed) polarizability of hydrogen-terminated (5,5) carbon nanotubes as a function of the number of elementary cells of the (5,5) nanotube. Each cell consists of 20 carbon atoms. These results are calculated with the Q+P aniso [R,α_{par},α_{perp}] model, using parameters based on the local environment of each atom. The dots indicate results obtained with c-DFT.

polarizability of the (5,5) nanotube dominates the transverse polarizability after only three elementary units. The study of the axial polarizability of longer nanotubes was carried out in ref 47. In DFT calculations, it has been found that infinite (5,5) nanotubes are metallic, which means that a continuum of electronic states exists around the Fermi level. In contrast, the finite-length structures considered in this paper are characterized by a band gap. In this kind of model, this would be reflected by the fact the charge flow increases with the length and dominates entirely for metallic systems. For nanotubes whose length exceeds 10 elementary units, we therefore recommend the use of the parameters given in ref 47. Finally the ability of our technique to deal with much larger systems was demonstrated in ref 45, where we treated a nanotube with 8000 atoms.

VI. Conclusion

The charge−dipole model presented in previous work to compute molecular polarizabilities for carbon systems has been extended to hydrocarbons. The applicability of this technique to realistic structures was demonstrated by considering alkanes, alkenes, and aromatic molecules. In particular, we sought at reproducing the molecular polarizabilities of these structures, the reference data being obtained using c-DFT. In a first approach to this objective, we established parameters for the hydrogen and carbon atoms of each type of molecule separately. For alkanes, a pure dipole representation of the hydrogen and sp^3 carbon atoms provides an excellent agreement with the reference data. Atomic charges and anisotropic atomic polarizabilities are however necessary for the description of the sp^2 carbon in alkenes and aromatic molecules. By using this technique, we could reproduce the molecular polarizability tensors of alkanes, alkenes, and aromatic molecules with relative errors on their components of 2.8, 2.60, and 3.5%, respectively.

In a second approach to our objective, we established parameters based on the local environment of each atom. We hence distinguished between sp^3 carbon, sp^2 carbon in linear chains, and sp^2 carbon in aromatic cycles. Hydrogen and sp^3 carbon were described by isotropic atomic polarizabilities, without net electric charge. The two types of sp^2 carbon were described by a net electric charge and by a dipole. The use of anisotropic polarizabilities for the sp^2 carbon made it possible to reproduce the molecular polarizability of a set of 48 reference structures with relative errors of 2.5% on the mean values and 4.7% on the components of the full tensors. These results compare very well with previous work and with the accuracy that one can expect from the experimental measurement of these quantities.[21−23,35,37,38] Depending on the model and on the reference data, the relative errors quoted in the literature are indeed typically around 3% for the mean polarizabilities and 7% for the main components of the polarizability tensors.[23,27] As a final application, we considered the polarization properties of fullerenes and small hydrogen-terminated (5,5) carbon nanotubes.

In its current form, the formalism presented in this paper makes it possible to study other chemical groups. Future work will address the frequency dependence of the molecular polarizabilities. For structures in which the displacement of free charges is restricted to domains that do not extend on the full set of atoms, an automatic identification of these domains and the enforcement of specific charge neutrality conditions could still improve the range of applicability of the technique. The objective of these developments is to enable the study of structures for which first-principles techniques are currently too demanding from the computational point of view. These developments may also be considered as a mean to accelerate these calculations. The molecular polarizability of the 60 structures considered in this paper is indeed calculated in only 0.5 s on a personal computer with a 1600 MHz clock frequency. This model thus appears as an efficient tool for studying the polarization properties of nanostructures. This may help in understanding the fundamental properties of these systems and developing future technologies.

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