

Determination of Distributed Polarizabilities from a Statistical Analysis of Induction Energies

François Dehez,[†] Jean-Christophe Soetens,[‡] Christophe Chipot,[†] János G. Ángyán,[†] and Claude Millot^{*,†}

Laboratoire de Chimie Théorique, UMR CNRS–Université Henri Poincaré No. 7565, B.P. 239, 54506 Vandœuvre-lès-Nancy, France, and Laboratoire de Physico-Chimie Moléculaire, UMR CNRS–Université de Bordeaux I, No. 5803, 351 Cours de la Libération, 33405 Talence Cedex, France

Received: August 24, 1999; In Final Form: November 2, 1999

A method is proposed to determine models of distributed polarizabilities from induction energies calculated quantum chemically for a molecule polarized by a point charge running over a grid of points. Once a polarizability model is chosen, sets of distributed polarizability components recovering exactly the induction energy for a selection of grid points are obtained by a matrix inversion. Distribution functions of the polarizability components are then built and the set of the most probable values for each polarizability component of the model is determined. The quality of a model is assessed by its ability to reproduce molecular polarizabilities and induction energies as accurately as possible. In addition, the distribution function approach provides valuable help to detect ill-defined components and, thus, select the optimal models. Several models of distributed polarizabilities for the water, methanol, and acetonitrile molecules are presented to illustrate the proposed approach.

1. Introduction

The importance of polarizability effects in various applications of physics and chemistry has motivated many studies devoted to the modeling of molecular and atomic polarizabilities. Over the past twenty years, different schemes for partitioning the molecular polarizability have been published. Several empirical models assign dipolar polarizabilities to atoms, bonds, or functional groups.^{1–14} Applequist has proposed an empirical model utilizing atomic dipolar polarizabilities in which the mutual polarization of the atoms is taken into account.³ Several groups have included the anisotropic character of local polarizabilities in the model.^{5,8,12,14} Recently, Applequist has extended his original model¹¹ by incorporating explicit charge flow polarizabilities.

Another approach consists of deriving atomic polarizabilities from quantum chemical calculations. A number of such partitioning approaches have been proposed. The sum-over-states expression of the polarizability has been formulated by using localized molecular orbitals to define local polarizabilities.^{15–18} Stone¹⁹ has developed a general formalism describing the variation of the charge distribution in response to the potential, the electric field, and its successive derivatives at a selection of polarizable sites. By including local and nonlocal polarizabilities, this model offers a very detailed description of the induction effects. In particular, it includes a charge flow which is absent in most empirical schemes. In the model of Stone, charge flow polarizabilities describe the charge variations on all the sites in response to electrostatic potential at one site of a molecule. This approach is formally distinct from the fluctuating charge model of Rappé and Goddard²⁰ based on the

electronegativity equalization principle. Le Sueur and Stone²¹ have devised practical approaches to calculate distributed polarizabilities. Bader et al.²² have proposed a method to compute local dipolar polarizabilities, based on the topological theory of *Atoms in Molecules*.^{23,24} Ángyán et al.²⁵ have introduced the calculation of distributed polarizabilities, employing the definition of Stone¹⁹ within the topological theory of Bader.²⁴

To model intermolecular interactions accurately, the introduction of distributed polarizabilities of high rank is often necessary, viz. typically up to atomic quadrupolar polarizabilities. To be used in computer simulations of condensed phases, such models are, however, inconvenient and it is necessary to truncate the multipolar expansion of the polarizability at a lower level to reduce the computational effort. This can lead to a nonoptimal representation of molecular polarizabilities and induction energies. For instance, if a Stone distributed polarizability model is truncated at the dipolar rank on each site, the resulting model recovers exactly the molecular dipolar polarizability but the molecular quadrupolar polarizability is underestimated. Thus, such a model will inevitably underestimate the induction energy in situations where molecular quadrupolar polarizability effects are important.

With the goal of generating distributed multipole models aiming at the accurate reproduction of the electrostatic potential near a molecule, Ferenczy et al.^{26–29} have developed a technique in which the multipolar expansion is truncated at a specified relatively low order. From a high rank, local multipole distribution on each site of a molecule, e.g., up to the hexadecapole, these authors compute a local multipole distribution limited to a lower rank that attempts to reproduce the electrostatic potential created by the initial multipole distribution. Fitting of distributed polarizabilities could be performed in a similar way to obtain models which can be utilized in molecular simulations. The

* Corresponding author. Claude.Millot@lctn.u-nancy.fr.

[†] Université Henri Poincaré.

[‡] Université de Bordeaux.

procedure is, however, complicated and requires preliminary quantum chemical computations to be carried out, using a partitioning scheme such as those devised by Stone¹⁹ or Ángyán et al.²⁵

In this article, we propose a simple and general method for constructing models of distributed polarizabilities at a chosen level of complexity from quantum chemical calculations. This method, which will be referred to as statistical analysis of distributed polarizabilities (SADP), optimizes distributed polarizabilities that reproduce the induction energy of a molecule polarized by a charge localized on a grid of points around the molecule. The strategy is identical to that used in the statistical analysis of distributed multipoles (SADM) method,³⁰ a technique designed to obtain distributed multipoles that reproduce the electrostatic potential created by the molecular charge distribution on a grid of points surrounding the molecule of interest. The main feature of the method is that distributed polarizabilities are defined as the most probable values of distribution functions built from sets of parameters reproducing exactly the induction energy on a given number of grid points selected at random.

Related approaches have been used to obtain multicenter local dipolar polarizabilities^{31,32} and hyperpolarizabilities³¹ reproducing in a least-squares sense the polarization energy of a molecule perturbed by a point charge exploring a grid of points. The same philosophy can be used to obtain distributed polarizability models including charge flow, dipolar and quadrupolar polarizabilities.³³

In Section 2, the method is described, using the spherical tensor formalism of Stone.³⁴ Several sets of distributed polarizabilities are presented in Section 3 for the water, methanol and acetonitrile molecules. The quality of the models with respect to their complexity is assessed by comparing the reproduction of induction energies over the grid of points and of the molecular dipolar and quadrupolar polarizabilities.

2. The SADP Approach

2.A. Definitions and Notations. The distributed polarizabilities introduced by Stone¹⁹ are defined by:

$$\alpha_{l_1 m_1, l_2 m_2}(\mathbf{s}_1, \mathbf{s}_2) = \sum_n \frac{\langle 0 | \hat{Q}_{l_1 m_1}^{s_1} | n \rangle \langle n | \hat{Q}_{l_2 m_2}^{s_2} | 0 \rangle + \langle 0 | \hat{Q}_{l_2 m_2}^{s_2} | n \rangle \langle n | \hat{Q}_{l_1 m_1}^{s_1} | 0 \rangle}{E_n - E_0} \quad (1)$$

where $\hat{Q}_{l m}^{s_i}$ is the operator of an electric multipole moment of a region s_i with respect to the position \mathbf{s}_i , $|0\rangle$ the molecular electronic ground state with total energy E_0 , and $|n\rangle \neq |0\rangle$ the excited states with energy E_n . In eq 1, the sum extends over states $|n\rangle$ other than the ground state. If only one site is chosen, these polarizabilities reduce to the usual polarizabilities in spherical tensor notation. If several sites are chosen, one obtains charge–charge ($l_1 = l_2 = 0$), charge–dipole ($l_1 = 0, l_2 = 1$), or dipole–dipole ($l_1 = l_2 = 1$) polarizabilities. These distributed polarizabilities can be either local ($s_1 = s_2$) or nonlocal ($s_1 \neq s_2$).

Rather than using the complex multipole moments \hat{Q}_{lm}^s ($m = -l, \dots, l$) in eq 1, one can transform them to their real counterpart defined with respect to a frame linked to site s :

$$\begin{aligned} \hat{Q}_{lm}^s &= (-1)^m \frac{1}{\sqrt{2}} (\hat{Q}_{lmc}^s + i \hat{Q}_{lms}^s) & m > 0 \\ \hat{Q}_{l-m}^s &= \frac{1}{\sqrt{2}} (\hat{Q}_{lmc}^s - i \hat{Q}_{lms}^s) \end{aligned} \quad (2)$$

Within this convention, one obtains distributed polarizabilities $\alpha_{l_1 \kappa_1, l_2 \kappa_2}(\mathbf{s}_1, \mathbf{s}_2)$ for which κ_i stands for $m_i c$ or $m_i s$, related to the local axes at site s_i .

2.B. Method. The method requires us first to define a grid of points around the molecule. For each point, the energy $\mathcal{E}_i^{\text{QM}}$, where the superscript QM (Quantum Mechanics) denotes a quantum chemical calculation, is computed for the system constituted of the molecule and the charge q located at point i on the grid. If $\mathcal{E}_0^{\text{QM}}$ is the energy of the free molecule and $V_{0,i}^{\text{QM}}$, the molecular electrostatic potential at point i created by the unperturbed molecular charge distribution, the induction energy, $\mathcal{U}_{\text{ind},i}^{\text{QM}}$ of the molecule can be obtained by:

$$\mathcal{U}_{\text{ind},i}^{\text{QM}} = \mathcal{E}_i^{\text{QM}} - \mathcal{E}_0^{\text{QM}} - q V_{0,i}^{\text{QM}} \quad (3)$$

The next step consists of choosing the model of distributed polarizabilities that will be fitted to reproduce the induction energy of the molecule perturbed by the point charge going over the grid of points. The model can accommodate any kind of distributed polarizabilities $\alpha_{l_1 \kappa_1, l_2 \kappa_2}(\mathbf{s}_1, \mathbf{s}_2)$.

Given a polarizability model and provided that penetration and nonlinear effects are negligible—which can be achieved by choosing a polarizing charge sufficiently small and grid points sufficiently far from the atomic centers—the polarizing charge q creates induced moments $\Delta Q_{l_1 \kappa_1}^{s_1}$ at each polarizable site s_1 in the molecule:

$$\Delta Q_{l_1 \kappa_1}^{s_1} = - \sum_{s_2, l_2 \kappa_2} \alpha_{l_1 \kappa_1, l_2 \kappa_2}(\mathbf{s}_1, \mathbf{s}_2) T_{l_2 \kappa_2, 00}^{s_2, i} q \quad (4)$$

where, $T_{l_2 \kappa_2, 00}^{s_2, i}$ are elements of the electrostatic tensor giving the potential and the field created at site s_2 by the charge q located at point i .^{30,34}

The induction energy of the molecule is then obtained by:

$$\mathcal{U}_{\text{ind},i}^{\text{model}} = \frac{1}{2} \sum_{s_1, l_1 \kappa_1} \Delta Q_{l_1 \kappa_1}^{s_1} T_{l_1 \kappa_1, 00}^{s_1, i} q \quad (5)$$

From eq 4 and eq 5 one obtains:

$$\mathcal{U}_{\text{ind},i}^{\text{model}} = - \frac{1}{2} q^2 \sum_{s_1, l_1 \kappa_1} \sum_{s_2, l_2 \kappa_2} \alpha_{l_1 \kappa_1, l_2 \kappa_2}(\mathbf{s}_1, \mathbf{s}_2) T_{l_2 \kappa_2, 00}^{s_2, i} T_{l_1 \kappa_1, 00}^{s_1, i} \quad (6)$$

The double sum in eq 6 has N_c terms, which is the number of nonzero unknown polarizability components. A subset of N_c points i is selected from the complete grid of N_p points, viz. typically $N_p \gg N_c$. Provided that nonlinear effects are negligible, a set of N_c polarizability components, that reproduces exactly the energy induced by each point charge of the subset of grid points, is obtained by solving the following linear system of N_c equations:

$$\mathcal{U}_{\text{ind},i}^{\text{QM}} = - \frac{1}{2} q^2 \sum_{s_2, l_2 \kappa_2} \sum_{s_1, l_1 \kappa_1} \alpha_{l_1 \kappa_1, l_2 \kappa_2}(\mathbf{s}_1, \mathbf{s}_2) T_{l_2 \kappa_2, 00}^{s_2, i} T_{l_1 \kappa_1, 00}^{s_1, i} \quad i = 1, \dots, N_c \quad (7)$$

Determining such a set constitutes one *experiment*. In practice, the components of the polarizability depend on the subset of chosen points, and they are, therefore, different for two different experiments. If a charge flow is allowed in the polarizability model, it is worth noting that as the total charge of the molecule must be conserved, the charge–multipole polarizabilities of each polarizable site s_1 must satisfy the constraint:

$$\sum_{s_2} \alpha_{l_1 k_1, 00}(\mathbf{s}_1, \mathbf{s}_2) = 0 \quad (8)$$

Such constraints are introduced to reduce the number of unknown parameters in the resolution of the linear system of equations eq 7. In practice, the subset of N_c points is chosen at random and if the number of experiments, N_e , is sufficiently large, it is possible to construct, from the N_e values of distributed polarizabilities $\alpha_{l_1 k_1, l_2 k_2}(\mathbf{s}_1, \mathbf{s}_2)$ (λ), $\lambda = 1, \dots, N_e$, a distribution function $s(\alpha_{l_1 k_1, l_2 k_2}(\mathbf{s}_1, \mathbf{s}_2))$, that represents the probability distribution of finding $\alpha_{l_1 k_1, l_2 k_2}(\mathbf{s}_1, \mathbf{s}_2)$ at a given value. For each component of the distributed polarizabilities, the most probable value $\alpha_{l_1 k_1, l_2 k_2}^{\max}(\mathbf{s}_1, \mathbf{s}_2)$, i.e., the value of $\alpha_{l_1 k_1, l_2 k_2}(\mathbf{s}_1, \mathbf{s}_2)$ corresponding to the maximum of the distribution function $s(\alpha_{l_1 k_1, l_2 k_2}(\mathbf{s}_1, \mathbf{s}_2))$, is then determined.

It should be noted that some of the experiments should be rejected, because the $N_c \times N_c$ matrix that is inverted to solve the system of linear equations (eq 7), may be singular for particular sets of selected grid points. This can result, for instance, from symmetry relationships between the chosen points. In the SADP method, no physical meaning should be given to a single experiment. Assuming that N_e is large enough, viz. typically, several thousands, the rejected experiments have no particular influence on the final distributions $s(\alpha_{l_1 k_1, l_2 k_2}(\mathbf{s}_1, \mathbf{s}_2))$.

Just like the distribution functions of the multipolar components obtained in the SADP method,³⁰ the distribution functions of the polarizability components are usually well fitted by Cauchy distributions:

$$s(\alpha_{l_1 k_1, l_2 k_2}(\mathbf{s}_1, \mathbf{s}_2)) = \frac{1}{\pi \sigma_{l_1 k_1, l_2 k_2}(\mathbf{s}_1, \mathbf{s}_2) \left[1 + \left(\frac{\alpha_{l_1 k_1, l_2 k_2}(\mathbf{s}_1, \mathbf{s}_2) - \alpha_{l_1 k_1, l_2 k_2}^{\max}(\mathbf{s}_1, \mathbf{s}_2)}{\sigma_{l_1 k_1, l_2 k_2}(\mathbf{s}_1, \mathbf{s}_2)} \right)^2 \right]} \quad (9)$$

where $\sigma_{l_1 k_1, l_2 k_2}(\mathbf{s}_1, \mathbf{s}_2)$ corresponds to half of the width at mid-height. Sometimes, fitting the probability distribution $s(\alpha_{l_1 k_1, l_2 k_2}(\mathbf{s}_1, \mathbf{s}_2))$ using a single Cauchy function is not satisfactory, and a linear combination of several functions is adapted. To assess the quality of the generated set of distributed polarizabilities, the root-mean-square deviation (RMSD) and the average percentage error (ERR (%)) between the reference induction energy and that obtained from the derived distributed polarizabilities is calculated. The maximum error Δ_{\max} and the maximum percentage error ($\Delta_{\max}(\%)$) of the induction energy over the ensemble of grid points are also provided to estimate the quality of the optimized polarizability sets.

2.C. Determination of the Molecular Polarizabilities. The ability of distributed polarizabilities to reproduce molecular polarizabilities is yet another important criterion to check the quality of the models. The complex molecular polarizability $\alpha_{LM, L'M'}(\mathbf{x})$ at point \mathbf{x} is obtained by translating the local polarizability at each site according to the formula¹⁹:

$$\alpha_{LM, L'M'}(\mathbf{x}) = \sum_{s_1} \sum_{s_2} \sum_{l_1 m_1} \sqrt{C_{l_1+m_1}^{L+M} C_{l_1-m_1}^{L-M} C_{l_2+m_2}^{L'+M'} C_{l_2-m_2}^{L'-M'}} \times R_{L-l_1, M-m_1}(\mathbf{x} - \mathbf{s}_1) \alpha_{l_1 m_1, l_2 m_2}(\mathbf{s}_1, \mathbf{s}_2) R_{L'-l_2, M'-m_2}(\mathbf{x} - \mathbf{s}_2) \quad (10)$$

where \mathbf{x} , \mathbf{s}_1 , and \mathbf{s}_2 are the position vectors of the sites x , s_1 , and s_2 and $R_{jk}(\mathbf{u}) = |\mathbf{u}|^j C_{jk}(\mathbf{u}/|\mathbf{u}|)$ is a regular spherical harmonic.

TABLE 1: Atomic Cartesian Coordinates in Bohr

		x	y	z
H₂O	O	0.000000	0.000000	0.222275
	H ₁	1.429310	0.000000	-0.889101
	H ₂	-1.429310	0.000000	-0.889101
CH₃OH	H ₁	2.050132	0.000000	1.843243
	C	0.087914	0.000000	1.261720
	O	0.087914	0.000000	-1.434450
	H ₂	-1.632739	0.000000	-1.995952
	H ₃	-0.824089	1.676887	2.028986
CH₃CN	H ₄	-0.824089	-1.676887	2.028986
	C ₁	0.000000	0.000000	-0.522413
	N	0.000000	0.000000	-2.731502
	C ₂	0.000000	0.000000	2.23938
	H ₁	1.927343	0.000000	2.939600
	H ₂	-0.963668	1.669110	2.939553
	H ₃	-0.963668	-1.669110	2.939553

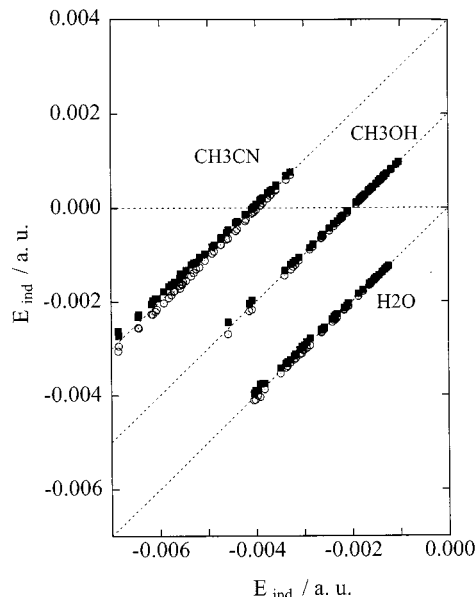


Figure 1. Ab initio induction energies divided by the square of the polarizing charge q versus the same quantity when $q = +1.0e$. ■: $q = +0.7e$. ○: $q = +1.2e$. For each molecule, only the fifty points closest to the atomic positions are considered.

TABLE 2: Models of Distributed Polarizabilities

CF	charge flow (between an atom and its first neighbors)
D	dipolar polarizabilities
CFD	combination of a charge flow and dipolar polarizabilities
1	isotropic dipolar polarizabilities on heavy atoms
2	anisotropic dipolar polarizabilities on heavy atoms
3	isotropic dipolar polarizabilities on all atoms
4	anisotropic dipolar polarizabilities on all atoms
5	isotropic dipolar polarizabilities on the nitrile and methyl carbon
6	anisotropic dipolar polarizabilities on the nitrile and methyl carbon

For all the calculations presented, the real molecular polarizabilities are calculated at the origin of the global frame of reference of the molecules corresponding to the atomic coordinates of Table 1. Formulae to convert complex polarizabilities into real ones can be found in ref 34.

3. Applications

3.A. Technical Details. To probe the method, a few applications for the water, methanol, and acetonitrile molecules are presented in this section. These studies have required the construction of a grid of points for each molecule. The points

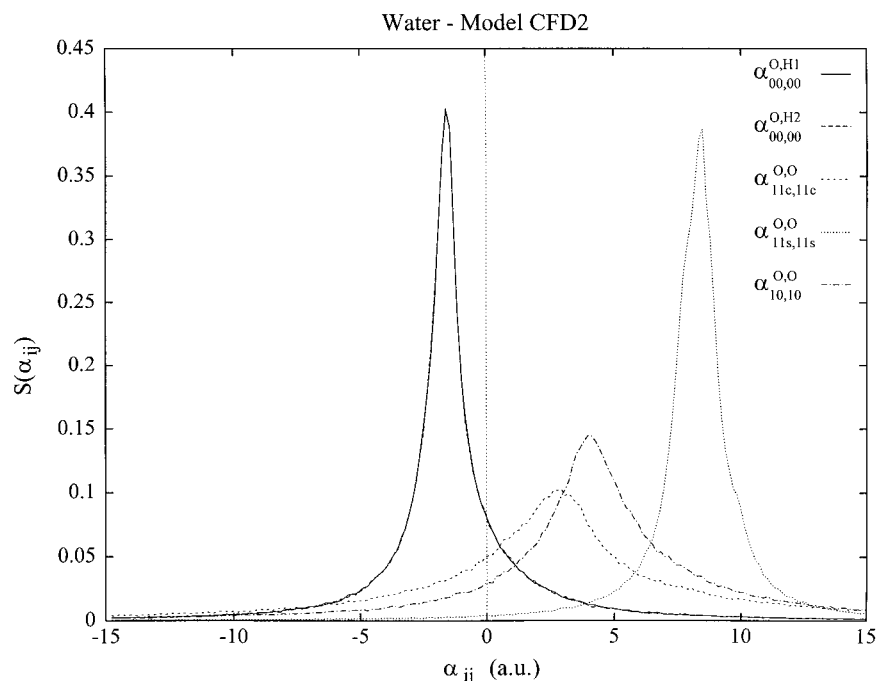


Figure 2. Distribution functions of distributed polarizability components of the water molecule for a model including a charge flow between atoms and an anisotropic dipolar polarizability on the oxygen atom.

TABLE 3: Distributed Polarizabilities of Water, from MP2/6-311++G(2d,2p) Calculations for a Grid of 1236 Points^a

models	CF	D				CFD			
		1	2	3	4	1	2	3	4
O									
$\alpha_{00,00}^{O,O}$	7.998					1.102	3.006	0.434	-2.410
$\alpha_{00,00}^{O,H1}$	-3.399					-0.551	-1.503	-0.217	1.205
$\alpha_{11c,11c}^{O,O}$		7.368	7.624	5.424	4.965	8.495	2.871	5.816	7.948
$\alpha_{11s,11s}^{O,O}$		7.368	8.263	5.424	6.437	8.495	8.413	5.816	6.437
$\alpha_{10,10}^{O,O}$		7.368	7.263	5.424	5.174	8.495	3.970	5.816	7.955
H1									
$\alpha_{00,00}^{H1,H1}$	3.999					0.551	1.503	0.217	-1.205
$\alpha_{11c,11c}^{H1,H1}$				1.586	1.938			1.396	3.216
$\alpha_{11s,11s}^{H1,H1}$				1.586	1.050			1.396	1.003
$\alpha_{10,10}^{H1,H1}$				1.586	1.528			1.396	2.134
$\alpha_{11c,10}^{H1,H1}$					-0.742				-1.239

^a All quantities in atomic units. The polarizabilities involving H2 are equal to those involving H1, except $\alpha_{11c,10}^{H2,H2} = -\alpha_{11c,10}^{H1,H1}$.

are regularly spaced on a parallelepipedic grid with a step equal to 2.0, 2.5, and 1.6 bohr for water, methanol, and acetonitrile, respectively. A study by Colonna et al.³⁵ has shown that artifacts due to penetration effects are negligible at distances larger than 2–3 Å from an atom. Removing the points located at less than twice the van der Waals radius of each atom ensures that spurious effects connected to penetration can be safely ignored.

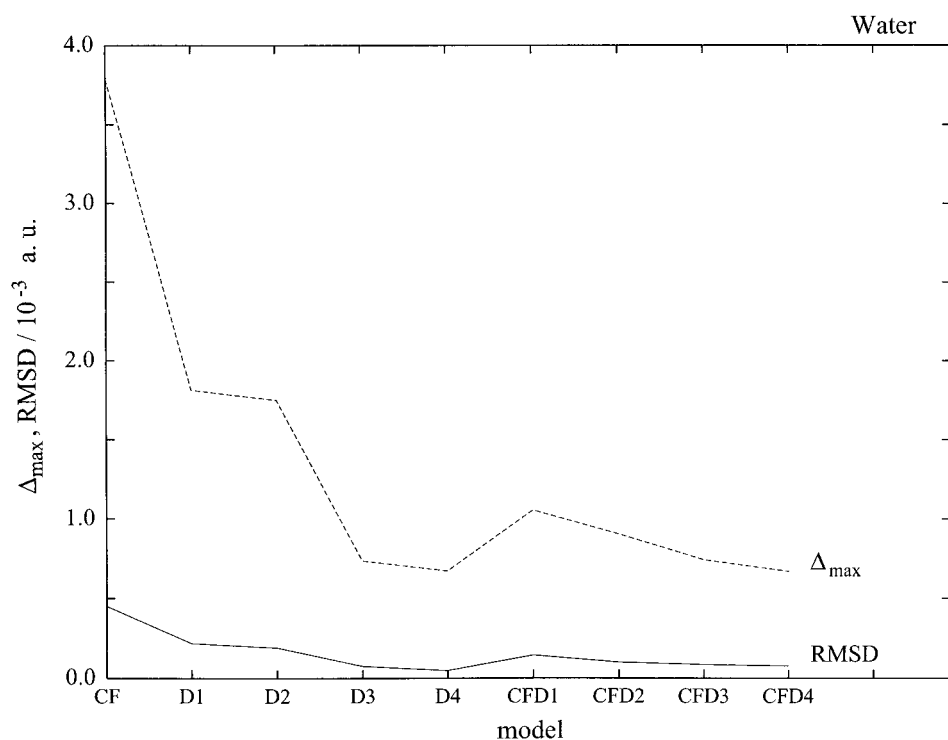
For each molecule, the number of grid points is adjusted to be about 1200. Symmetry considerations have been applied to the grids of points in order to reduce the number of quantum chemical calculations. The polarizing charge is $q = +1.0e$. The induction energies have been evaluated quantum chemically at the MP2/6-311++G(2d,2p) level, using the program package GAUSSIAN94.³⁶ A larger basis set could have been used but the 6-311++G(2d,2p) basis set represents a cost-effective compromise.

To check if the induction energies are contaminated by hyperpolarizability effects, a test has been performed. If

hyperpolarizability effects are negligible, the induction energy of a molecule polarized by a point charge q must scale as q^2 (see eq 7). Deviations from this behavior might be attributed to hyperpolarizability effects. For the three molecules considered, we have selected the fifty closest points from the nuclei and computed the induction energies of the molecule polarized by a charge $+0.7e$ and $+1.2e$. In Figure 1, $\mathcal{L}_{\text{ind}}^{\text{QM}}/q^2$ is plotted for $q = +1.2e$ and $q = +0.7e$ versus the same quantity for $q = +1.0e$ for this set of points. The largest deviations with respect to a linear behavior have been found to be about 3–4 %, for only about 6 points in each grid containing a total of about 1200 points. Assuming that the grid with $q = +0.7e$ is free from hyperpolarizability artifacts, the very small deviations observed for the grid with $q = +1.0e$ suggest that those spurious effects still remain negligible for the latter grid. An additional test has been performed. The molecular first hyperpolarizability (β) has been computed at the MP2/6-311++G(2d,2p) level with GAUSSIAN94 and used to evaluate separate contributions to the induction energy for the molecule polarized by a unit point

TABLE 4: Molecular Polarizabilities of Water, from MP2/6-311++G(2d,2p) Calculations for a Grid of 1236 Points^a

models	CF	D				CFD				TDMP2
		1	2	3	4	1	2	3	4	
$\alpha_{11c,11c}$	13.887	7.368	7.624	8.696	8.840	10.734	9.010	9.495	9.457	8.697
$\alpha_{11s,11s}$	0.000	7.368	8.263	8.696	8.537	8.485	8.413	8.607	8.443	7.877
$\alpha_{10,10}$	8.396	7.368	7.263	8.696	8.230	9.845	7.682	9.144	9.066	7.843
$\alpha_{10,20}$	2.118	3.275	3.229	-3.186	-1.014	4.115	2.701	-2.243	-0.940	-0.462
$\alpha_{10,22c}$	-13.366	0.000	0.000	0.000	0.000	-2.165	-5.909	-0.854	-1.397	-4.550
$\alpha_{11c,21c}$	-21.386	2.837	2.935	-2.760	-7.229	-0.198	-8.349	-3.426	-5.400	-6.955
$\alpha_{11s,21s}$	0.000	2.837	3.181	-2.760	-0.756	3.267	3.239	-2.060	-0.612	-0.823
$\alpha_{20,20}$	0.534	1.456	1.435	17.606	11.063	1.763	1.021	15.714	14.849	23.602
$\alpha_{20,22c}$	-3.372	0.000	0.000	-11.227	-7.184	-0.546	-1.491	-10.093	-10.655	-0.953
$\alpha_{21c,21c}$	32.934	1.092	1.130	27.789	39.967	6.592	14.985	26.696	48.703	34.585
$\alpha_{21s,21s}$	0.000	1.092	1.225	8.343	5.934	1.258	1.247	7.842	5.712	23.062
$\alpha_{22c,22c}$	21.278	0.000	0.000	19.446	23.753	3.447	9.407	18.469	31.879	30.031
$\alpha_{22s,22s}$	0.000	0.000	0.000	19.446	12.870	0.000	0.000	17.409	11.297	25.638
RMSD/ 10^{-3}	0.451	0.218	0.192	0.076	0.048	0.144	0.100	0.085	0.077	
$\Delta_{\max}/10^{-3}$	3.788	1.813	1.750	0.736	0.672	1.054	0.905	0.742	0.670	
ERR (%)	31.065	12.910	9.386	6.108	3.010	15.164	4.044	9.293	8.537	
Δ_{\max} (%)	99.459	45.799	44.794	18.814	17.164	34.461	25.848	19.619	17.911	

^a All quantities in atomic units.**Figure 3.** Absolute maximum error (Δ_{\max}) and root-mean-square deviation (RMSD) between the target induction energy (MP2-6-311++G(2d,2p) level) of a water molecule polarized by a point charge and the induction energy calculated using various distributed polarizability models.

charge. If E is the electric field created at the center of the molecule by the point charge, the part of the induction energy due to the dipolar polarizability α is $-(1/2)\alpha_{\alpha\beta}E_{\alpha}E_{\beta}$ and the part due to the first hyperpolarizability is $-(1/6)\beta_{\alpha\beta\delta}E_{\alpha}E_{\beta}E_{\delta}$. The largest contributions of the hyperpolarizability term are equal to 2 % of the dipolar polarizability term for the closest points in the case of the water molecule.

For all three molecules, the strategy was to compare different distributed polarizability sets in order to isolate some models for which a satisfactory compromise between quality and simplicity is achieved. The molecular polarizabilities (up to the quadrupolar ones) regenerated from the distributed polarizability models are compared to those given by a time dependent MP2 (TDMP2)³⁷ calculation on the isolated molecule done with a program of Hättig.³⁸

With the objective to use distributed polarizabilities in computer simulations of condensed phases, it is necessary to

limit the complexity of the model drastically. It still appears to be too time-consuming to perform molecular dynamics or Monte Carlo simulations with models including atomic quadrupolar or higher order local and nonlocal polarizabilities. For this reason, in this article, we have only considered models including polarizabilities limited to charge flow and dipolar polarizabilities. For each molecule, we have defined nine models CF, D1 to D4 and CFD1 to CFD4. For the acetonitrile molecule, four additional models (D5, D6 and CFD5, CFD6) have been considered. The definitions of the acronyms are gathered in Table 2. CF is a pure charge flow polarizability model taking into account the charge flow between each atom and its first neighbors; the rationale justifying this choice being that, in a molecule, charge can preferentially flow along the chemical bonds.³⁹ D1 to D4 are models including only local isotropic (D1 and D3) or anisotropic (D2 and D4) polarizabilities, on

TABLE 5: Distributed Polarizabilities of Methanol, from MP2/6-311++G(2d,2p) Calculations for a Grid of 1175 Points

models	CF	D				CFD			
		1	2	3	4	1	2	3	4
H1									
$\alpha_{00,00}^{H1,H1}$	1.940					1.181	1.501	0.879	-0.087
$\alpha_{00,00}^{H1,C}$	-1.940					-1.181	-1.501	-0.879	0.087
$\alpha_{11c,11c}^{H1,H1}$				8.549	5.387			4.549	5.257
$\alpha_{11s,11s}^{H1,H1}$				8.549	3.862			4.549	3.927
$\alpha_{10,10}^{H1,H1}$				8.549	2.524			4.549	1.957
$\alpha_{11c,10}^{H1,H1}$					0.598				1.025
C									
$\alpha_{00,00}^{C,C}$	9.624					4.870	4.765	3.930	-0.129
$\alpha_{00,00}^{C,O}$	-2.474					-1.105	0.108	-0.909	0.250
$\alpha_{00,00}^{C,H3}$	-2.605					-1.292	-1.686	-1.071	-0.104
$\alpha_{11c,11c}^{C,C}$		14.749	14.680	-18.345	-4.415	7.948	7.078	-7.792	-3.735
$\alpha_{11s,11s}^{C,C}$		14.749	16.132	-18.345	-6.358	7.948	3.942	-7.792	-6.723
$\alpha_{10,10}^{C,C}$		14.749	12.948	-18.345	2.509	7.948	12.589	-7.792	5.542
$\alpha_{11c,10}^{C,C}$			0.504		1.916		-0.022		1.673
O									
$\alpha_{00,00}^{O,O}$	4.721					2.182	2.229	1.303	-2.458
$\alpha_{00,00}^{O,H2}$	-2.247					-1.077	-2.337	-0.394	2.209
$\alpha_{11c,11c}^{O,O}$		5.916	5.260	9.630	7.029	4.392	-1.141	5.618	11.284
$\alpha_{11s,11s}^{O,O}$		5.916	3.371	9.630	8.426	4.392	6.022	5.618	8.307
$\alpha_{10,10}^{O,O}$		5.916	8.773	9.630	8.204	4.392	8.720	5.618	8.891
$\alpha_{11c,10}^{O,O}$			0.428		-0.580		-0.835		0.498
H2									
$\alpha_{00,00}^{H2,H2}$	2.247					1.077	2.337	0.394	-2.209
$\alpha_{11c,11c}^{H2,H2}$				2.916	1.782			2.126	4.302
$\alpha_{11s,11s}^{H2,H2}$				2.916	1.022			2.126	1.120
$\alpha_{10,10}^{H2,H2}$				2.916	1.093			2.126	1.643
$\alpha_{11c,10}^{H2,H2}$					0.676				1.747
H3									
$\alpha_{00,00}^{H3,H3}$	2.605					1.292	1.686	1.071	0.104
$\alpha_{11c,11c}^{H3,H3}$				8.687	4.523			4.327	4.468
$\alpha_{11s,11s}^{H3,H3}$				8.687	5.759			4.327	5.408
$\alpha_{10,10}^{H3,H3}$				8.687	3.275			4.327	2.981
$\alpha_{11c,11s}^{H3,H3}$					-0.492				-0.442
$\alpha_{11c,10}^{H3,H3}$					-1.016				-0.853
$\alpha_{11s,10}^{H3,H3}$					1.403				1.436

^a All quantities in atomic units. The polarizabilities involving H4 are equal to those involving H3, except $\alpha_{11c,11s}^{H4,H4} = -\alpha_{11c,11s}^{H3,H3}$ and $\alpha_{11s,10}^{H4,H4} = -\alpha_{11s,10}^{H3,H3}$.

atoms except the hydrogen atoms (D1 and D2) or on all atoms (D3 and D4). For an isotropic dipolar site polarizability, the polarizability matrix is diagonal in any frame and the three components are equal, i.e., $\alpha_{10,10} = \alpha_{11c,11c} = \alpha_{11s,11s}$. For an anisotropic dipolar polarizability, this is not the case and the model has six components in general; diagonalizing the polarizability matrix reduces the number of components to three in a local frame. CFD1 to CFD4 adds the charge flow polarizabilities to the four previous models. D5 and D6 models have only two sites with isotropic and anisotropic dipolar polarizabilities respectively, on the methyl carbon and nitrogen atoms. The addition of a charge flow to the previous models leads to CFD5 and CFD6.

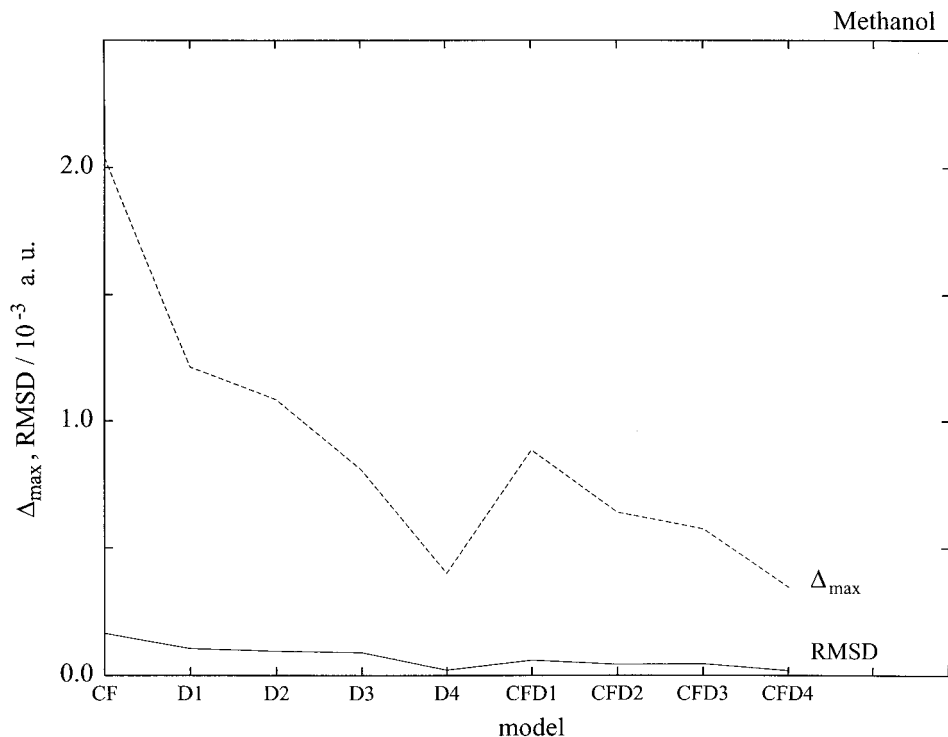
The distributed polarizabilities are defined as the most probable value of the distribution functions $s(\alpha_{l_1 k_1, l_2 k_2}(\mathbf{s}_1, \mathbf{s}_2))$

obtained after 3×10^5 experiments. As an illustration, Figure 2 presents such distribution functions obtained for the water molecule with the model CFD2 (charge flow plus anisotropic dipolar polarizability on oxygen atom).

3.B. Results. The results for the previously mentioned distributed polarizability models are presented in Tables 3–10 for the water, methanol, and acetonitrile molecules. These molecules correspond to three important solvents in chemistry and are representative of polar/polarizable systems studied in computer simulation. The root-mean-square deviation (RMSD) $= (1/N \sum_{i=1}^N (U_{ind,i}^{model} - U_{ind,i}^{QM})^2)^{1/2}$, the average relative error (ERR) (%) $= 100/N \sum_{i=1}^N |U_{ind,i}^{model} - U_{ind,i}^{QM}|/|U_{ind,i}^{QM}|$, the maximum absolute error (Δ_{max}) and the maximum relative error (Δ_{max} (%)) (in percentage) between the exact induction energies and the ones regenerated by each model as well as the regenerated

TABLE 6: Molecular Polarizabilities of Methanol, from MP2/6-311++G(2d,2p) Calculations for a Grid of 1175 Points^a

models	CF	D				CFD				TDMP2
		1	2	3	4	1	2	3	4	
$\alpha_{11c,11c}$	18.455	20.665	19.940	20.123	18.829	22.228	21.442	19.488	19.341	18.856
$\alpha_{10,10}$	22.415	20.665	21.721	20.123	20.881	22.635	23.750	21.443	21.575	21.110
$\alpha_{11s,11s}$	14.651	20.665	19.503	20.123	18.470	19.600	19.445	19.177	18.019	18.375
$\alpha_{11c,10}$	0.738	0.000	0.932	0.000	0.576	0.581	0.754	-0.115	0.858	0.600
$\alpha_{10,20}$	-1.058	20.246	7.422	16.458	7.706	7.061	7.949	7.484	8.339	6.842
$\alpha_{10,21c}$	-9.839	3.147	3.346	-4.015	-3.796	-2.201	-4.988	-4.663	-4.165	-5.471
$\alpha_{10,22c}$	-6.217	0.000	0.142	0.000	-4.843	-2.571	-4.776	-1.698	-4.500	-2.473
$\alpha_{11c,20}$	-7.142	-1.817	-1.708	2.318	-1.508	-4.714	-3.853	-0.969	-0.730	-1.946
$\alpha_{11c,21c}$	16.185	17.534	19.155	14.253	19.020	17.597	22.809	19.614	20.365	19.606
$\alpha_{11c,22c}$	13.736	3.147	3.036	-4.015	4.431	10.404	8.051	5.782	5.944	6.492
$\alpha_{11s,21s}$	51.489	17.534	26.878	14.253	22.592	31.993	26.978	27.763	21.771	26.843
$\alpha_{11s,22s}$	-20.913	3.147	2.970	-4.015	-8.160	-8.491	-12.018	-11.141	-7.791	-8.827
$\alpha_{20,20}$	4.699	142.774	154.801	515.481	241.024	89.165	154.580	291.542	241.899	172.046
$\alpha_{20,21c}$	-8.806	1.541	5.291	16.471	-10.684	-4.313	-9.383	8.379	-6.607	-8.233
$\alpha_{20,22c}$	-6.534	-0.277	-0.260	-11.403	-6.901	-3.689	-2.999	-14.430	-9.711	-7.427
$\alpha_{21c,21c}$	205.646	107.440	103.096	474.706	313.232	174.907	200.958	337.675	315.222	286.724
$\alpha_{21c,22c}$	104.931	2.670	2.917	28.529	59.472	57.589	88.275	62.093	65.097	61.112
$\alpha_{21s,21s}$	180.948	106.961	97.853	454.955	328.020	154.803	173.188	323.509	322.129	289.740
$\alpha_{21s,22s}$	-73.493	2.670	4.093	28.529	-48.124	-35.462	-48.535	-5.988	-42.520	-29.353
$\alpha_{22c,22c}$	55.419	0.479	0.462	312.877	189.076	30.471	43.931	186.001	190.854	120.024
$\alpha_{22s,22s}$	29.850	0.479	0.452	312.877	164.850	15.089	19.551	177.217	164.350	106.043
RMSD/ 10^{-3}	0.165	0.105	0.097	0.104	0.022	0.060	0.044	0.045	0.021	
$\Delta_{\max}/10^{-3}$	2.039	1.213	1.151	0.758	0.415	0.886	0.608	0.576	0.359	
ERR (%)	10.194	6.952	4.675	8.987	0.608	6.443	6.763	4.849	1.746	
Δ_{\max} (%)	46.453	29.348	26.860	26.369	9.067	19.412	13.279	12.595	7.851	

^a All quantities in atomic units.**Figure 4.** Same as Figure 3 for the methanol molecule.

dipolar and quadrupolar molecular polarizabilities are also given in these tables to check the quality of the models.

3.B.1. Water. For this small molecule, one could expect polarizability effects to be described accurately using a simple dipolar polarizability model (D1 or D2). The results in Tables 3–4 and Figure 3, however, show that none of these models nor a pure charge flow polarizability (CF) model constitutes an optimal choice. Adding a charge flow to D1 and D2 (leading to CFD1 and CFD2) increases the quality of the latter models significantly.

Distributing only dipolar polarizabilities on the three atoms

(D3 and D4) improves the model further. In contrast to the previous case, adding a charge flow to these models does not lead to a better reproduction of induction energies.

From the point of view of computational efficiency, it appears, however, that the use of models D3 and D4 in a Molecular Dynamics simulation is roughly three times more expensive than the cost of CFD1 and CFD2. This observation, put in balance with the relatively modest improvement of quality for D3 and D4, can favor the choice of models such as CFD1 or CFD2 to simulate condensed phases.

The results for models D1 and D3 are close to the results of

TABLE 7: Distributed Polarizabilities of Acetonitrile, from MP2/6-311++G(2d,2p) Calculations for a Grid of 1180 Points^a

models	CF	D				CFD			
		1	2	3	4	1	2	3	4
C1									
$\alpha_{00,00}^{C1,C1}$	7.178					2.287	-17.821	2.462	-5.101
$\alpha_{00,00}^{C1,N}$	-4.768					-1.160	11.085	-1.497	3.158
$\alpha_{00,00}^{C1,C2}$	-2.410					-1.127	6.736	-0.965	1.943
$\alpha_{11c,11c}^{C1,C1}$		-20.333	-8.933	-10.278	2.340	-7.751	-8.075	-0.297	1.835
$\alpha_{10,10}^{C1,C1}$		-20.333	4.812	-10.278	12.148	-7.751	82.195	-0.297	14.814
N									
$\alpha_{00,00}^{N,N}$	4.768					1.160	-11.085	1.497	-3.158
$\alpha_{11c,11c}^{N,N}$		20.848	13.518	19.632	11.512	13.423	12.605	11.679	11.429
$\alpha_{10,10}^{N,N}$		20.848	14.285	19.632	13.453	13.423	25.873	11.679	16.387
C2									
$\alpha_{00,00}^{C2,C2}$	8.923					4.784	-3.153	3.205	0.328
$\alpha_{00,00}^{C2,H1}$	-2.171					-1.219	-1.194	-0.713	-0.757
$\alpha_{11c,11c}^{C2,C2}$		24.364	21.421	-3.729	-9.017	12.573	11.093	-5.496	-6.059
$\alpha_{10,10}^{C2,C2}$		24.364	15.528	-3.729	-10.398	12.573	26.402	-5.496	3.824
H1									
$\alpha_{00,00}^{H1,H1}$	2.171					1.219	1.194	0.713	0.757
$\alpha_{11c,11c}^{H1,H1}$				6.711	5.414			4.273	3.105
$\alpha_{11s,11s}^{H1,H1}$				6.711	4.489			4.273	3.105
$\alpha_{10,10}^{H1,H1}$				6.711	4.956			4.273	3.767
$\alpha_{11c,10}^{H1,H1}$					0.755				0.612
H2									
$\alpha_{00,00}^{H2,H2}$	2.171					1.219	1.194	0.713	0.757
$\alpha_{11c,11c}^{H2,H2}$				6.711	4.721			4.273	4.741
$\alpha_{11s,11s}^{H2,H2}$				6.711	5.183			4.273	4.741
$\alpha_{10,10}^{H2,H2}$				6.711	4.956			4.273	3.767
$\alpha_{11c,11s}^{H2,H2}$					-0.400				0.945
$\alpha_{11c,10}^{H2,H2}$					-0.378				-0.306
$\alpha_{11s,10}^{H2,H2}$					0.654				0.530

^a All quantities in atomic units. The polarizabilities involving H3 are equal to those involving H2, except $\alpha_{11c,11s}^{H3,H3} = -\alpha_{11c,11s}^{H2,H2}$ and $\alpha_{11s,10}^{H3,H3} = -\alpha_{11s,10}^{H2,H2}$.

Nakawaga and Kosugi³¹ who give an isotropic one-center polarizability of 7.49 au (model D1) and atomic polarizabilities of 6.44 au for the oxygen atom and 1.53 au for the hydrogen atom (model D3).

3.B.2. Methanol. For this molecule, when going from a pure charge flow polarizability model to the model including charge flow and all-atom anisotropic dipolar polarizabilities, a trend globally similar to what occurs for water is observed. Yet, some models can behave differently (Tables 5–6 and Figure 4).

For example, the D3 model (all-atom isotropic dipolar polarizabilities) is good to reproduce induction energies but presents the unusual property of assigning a negative dipolar polarizability to the carbon atom and too large polarizabilities (8.5–8.7 au) to the hydrogen atoms of the methyl group. Such behavior can arise because the polarizability of the external hydrogens atoms shields the polarizability of the buried carbon, and the role of the hydrogen atoms in the description of the methyl group polarizability is overestimated. Interestingly, the distribution function for the isotropic dipolar polarizability of the carbon atom is found to be extremely flat, denoting a poorly defined parameter.

The models D4, CFD3, and CFD4 also present the same behavior at the carbon atom as the model D3; the distribution functions of the carbon dipolar polarizability are extremely flat

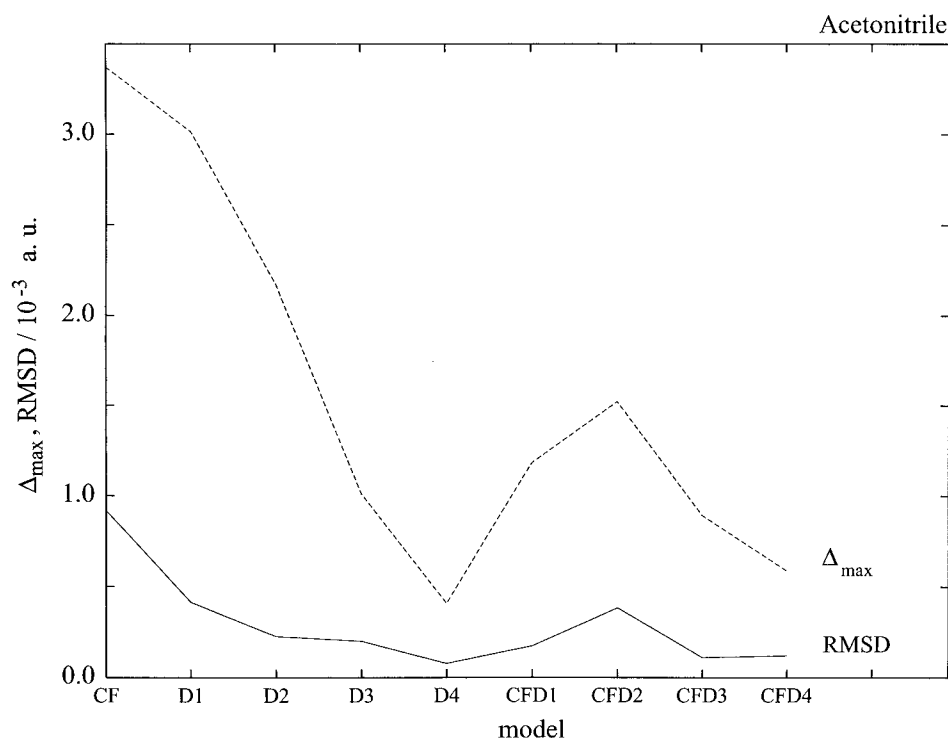
and some polarizability components get a negative value. These models are, however, quite good for reproducing molecular polarizabilities.

3.B.3. Acetonitrile. The results in Tables 7–8 and Figure 5 show that among the nine initially chosen models, the best to reproduce induction energies would be D4, CFD3, and CFD4. For this molecule, all the models with dipolar polarizability exhibit negative values for some components. For computational efficiency reasons, the model CFD1 could be an interesting choice but the negative dipolar polarizability of -7.75 au for the carbon atom of the nitrile group indicates that this site is excessively shielded in this model.

To find a more physically sound description, we have considered some new models, derived from the previous ones by removing the dipolar polarizability of the nitrile carbon atom. It is interesting to note that this site, which often bears a negative polarizability in our scheme, has a very small dipolar polarizability (typically about 1 au) in calculations of distributed polarizabilities based on Bader's topological theory.⁴⁰ The SADP results are presented in Tables 9–10 and Figure 6. The CFD5 model involving charge flow between first neighbor atoms and isotropic dipolar polarizabilities on the methyl carbon and the nitrogen atom seems to realize a good compromise between

TABLE 8: Molecular Polarizabilities of Acetonitrile from MP2/6-311++G(2d,2p) Calculations for a Grid of 1180 Points^a

models	CF	D				CFD				TDMP2
		1	2	3	4	1	2	3	4	
$\alpha_{11c,11c}$	12.095	24.879	26.006	25.758	23.330	25.035	22.277	22.679	23.743	22.013
$\alpha_{10,10}$	44.845	24.879	34.625	25.758	35.169	34.298	30.749	34.424	35.103	37.937
$\alpha_{10,20}$	-36.081	16.472	-13.518	5.154	-22.889	-8.038	-16.719	-21.128	-44.019	-9.933
$\alpha_{11c,21c}$	61.584	14.265	27.214	4.463	6.675	26.847	24.578	9.193	8.885	24.262
$\alpha_{11c,22c}$	20.189	0.000	0.000	0.000	4.631	11.333	11.106	6.633	6.135	7.868
$\alpha_{11s,21s}$	61.582	14.265	27.214	4.463	6.675	26.846	24.577	9.192	8.883	24.262
$\alpha_{11s,22s}$	-20.188	0.000	0.000	0.000	-4.631	-11.333	-11.106	-6.633	-6.135	-7.868
$\alpha_{20,20}$	320.934	1088.723	743.070	1270.541	834.083	741.064	678.452	834.420	860.279	546.266
$\alpha_{21c,21c}$	313.556	816.542	617.533	1008.994	680.311	659.284	614.905	685.235	678.126	582.168
$\alpha_{21c,22c}$	102.791	0.000	0.000	0.000	36.208	57.704	56.548	33.773	41.473	46.235
$\alpha_{21s,21s}$	313.543	816.542	617.533	1008.996	680.308	659.277	614.898	685.230	678.112	582.168
$\alpha_{21s,22s}$	-102.788	0.000	0.000	0.000	-36.204	-53.703	-56.546	-33.769	-41.467	-46.231
$\alpha_{22c,22c}$	33.697	0.000	0.000	224.359	165.548	18.917	18.538	153.918	168.731	112.627
$\text{RMSD}/10^{-3}$	0.917	0.415	0.227	0.201	0.078	0.174	0.385	0.111	0.122	
$\Delta_{\text{max}}/10^{-3}$	3.370	3.014	2.176	1.012	0.408	1.182	1.522	0.892	0.588	
ERR (%)	25.343	9.092	4.684	5.292	2.981	2.479	11.249	3.220	4.554	
Δ_{max} (%)	69.787	36.690	26.496	19.128	7.014	16.717	30.079	15.505	12.014	

^a All quantities in atomic units.**Figure 5.** Same as Figure 3 for the acetonitrile molecule.

accuracy and simplicity and the distributed polarizabilities keep physically reasonable values.

For the models D2 to D4 and CFD1 to CFD4, the distribution functions of polarizability components are usually very flat for the methyl carbon, the nitrile carbon, and to a lesser extent for the nitrogen atom. For example, the component $\alpha_{10,10}^{N,N}$ is extremely ill-defined for the models CFD2 and CFD4 including charge flow and anisotropic dipolar polarizabilities. For the models D5, D6, CFD5, and CFD6, the distribution functions of the polarizability components are systematically better defined than in the previous cases.

3.C. Discussion. From the previous applications of the SADP approach, it is possible to draw some general trends of this methodology. First of all, for a given model, the distribution function of each distributed polarizability component gives useful information about its reliability. The narrower the distribution function, the smaller the uncertainty on the polar-

izability component; whereas broad and flat distribution functions indicate that the overall quality of the fit will not be influenced very much by the value of such a component.

Concerning the computational cost in the context of statistical simulations, the description of polarizability effects by a charge flow is much cheaper than using dipolar polarizable sites, but charge flow only cannot usually describe correctly the molecular dipolar polarizability. The addition of a charge flow to a model including dipolar site polarizabilities usually increases the quality of the description of induction effects significantly. Nevertheless, as soon as a charge flow is included in the polarizability model, the anisotropy of the molecular polarizability is described concurrently by the charge flow and by anisotropic local dipolar polarizabilities. This may lead to unrealistic distributed polarizability components (unexpected sign of the charge flow components, excessive local dipolar anisotropy, etc.). In such cases, a further reduction of the number of parameters in the

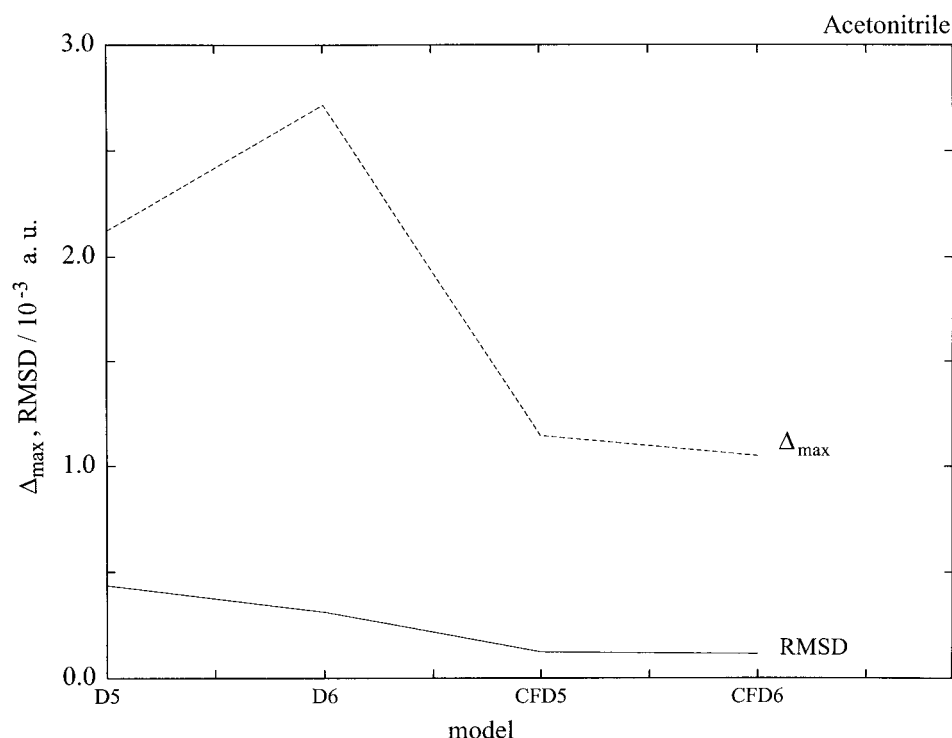


Figure 6. Same as Figure 3 for the acetonitrile molecule using some additional models.

TABLE 9: Distributed Polarizabilities of Acetonitrile, from MP2/6-311++G(2d,2p) Calculations for a Grid of 1180 Points^a

models	D		CFD	
	5	6	5	6
C1				
$\alpha_{00,00}^{C1,C1}$			3.147	2.650
$\alpha_{00,00}^{C1,N}$			-1.747	-1.845
$\alpha_{00,00}^{C1,C2}$			-1.400	-0.805
C2				
$\alpha_{00,00}^{C2,C2}$			4.955	4.597
$\alpha_{00,00}^{C2,H1}$			-1.185	-1.264
$\alpha_{11c,11c}^{C2,C2}$	19.473	17.000	9.512	9.239
$\alpha_{10,10}^{C2,C2}$	19.473	17.727	9.512	11.998
N				
$\alpha_{00,00}^{N,N}$			1.747	1.845
$\alpha_{11c,11c}^{N,N}$	11.846	8.670	8.819	8.942
$\alpha_{10,10}^{N,N}$	11.846	16.475	8.819	10.070
H ₁				
$\alpha_{00,00}^{H1,H1}$			1.185	1.264

^a All quantities in atomic units. The polarizabilities involving H3 and H2 are equal to those involving H1.

model, for example, using isotropic dipolar polarizabilities instead of anisotropic ones, is a possible solution. Using polarizability models of different maximum rank on heavy (carbon, oxygen, nitrogen, etc.) and light (hydrogen) atoms is an alternative solution. For example, models involving charge flow and dipolar polarizabilities on heavy atoms and only charge flow polarizabilities on hydrogen atoms is an attractive choice.

4. Conclusion

A new approach has been presented to obtain distributed polarizabilities from quantum chemical calculations. From the

TABLE 10: Molecular Polarizabilities of Acetonitrile from MP2/6-311++G(2d,2p) Calculations for a Grid of 1180 Points^a

models	D		CFD		TDMP2
	5	6	5	6	
$\alpha_{11c,11c}$	31.319	25.670	24.931	25.224	22.013
$\alpha_{10,10}$	31.319	34.202	39.087	39.069	37.937
$\alpha_{10,20}$	22.449	-10.608	-10.561	-15.345	-9.933
$\alpha_{11c,21c}$	19.485	24.922	28.780	29.390	24.262
$\alpha_{11c,22c}$	0.000	0.000	11.018	11.756	7.868
$\alpha_{11s,21s}$	19.485	24.922	28.779	29.388	24.261
$\alpha_{11s,22s}$	0.000	0.000	-11.019	-11.755	-7.868
$\alpha_{20,20}$	744.147	847.287	586.892	666.498	546.266
$\alpha_{21c,21c}$	558.110	449.822	511.623	521.725	582.168
$\alpha_{21c,22c}$	0.000	0.000	56.098	59.854	46.235
$\alpha_{21s,21s}$	558.110	449.822	511.616	521.718	582.158
$\alpha_{21s,22s}$	0.000	0.000	-56.097	-59.852	-46.231
$\alpha_{22c,22c}$	0.000	0.000	18.390	19.621	112.627
RMSD/10 ⁻³	0.436	0.311	0.123	0.114	
$\Delta_{\max}/10^{-3}$	2.123	2.715	1.144	1.048	
ERR (%)	13.985	7.107	2.848	3.335	
Δ_{\max} (%)	40.828	33.054	13.928	12.762	

^a All quantities in atomic units.

knowledge of the induction energy of a molecule perturbed by a point charge located on a grid of points surrounding the molecule, a set of distributed polarizabilities aimed at reproducing the induction energy is obtained from a statistical analysis. In this article, the grid of induction energies is built by carrying out a few hundred high quality ab initio calculations for a molecule plus a point charge. Such calculations are trivial to perform using standard quantum chemistry packages and for small molecules, the computer time requirement remains reasonable. For large molecules, however, the strategy can become prohibitive. In such cases, alternative schemes should be considered to limit the computational effort. First, semi-empirical methods or Hartree-Fock calculations, perhaps with small basis sets, could be used. The distributed polarizabilities could then be scaled in order to improve the agreement with experimental results. Second, if a full distributed polarizability

model (including, for instance, up to quadrupolar polarizabilities on all atoms) obtained by the methods of Stone¹⁹ or Ángyán et al.²⁵ is available, it can be used to obtain a grid of accurate induction energies. Then, a much simpler polarizability model can be designed using our SADP scheme. Third, the grid of points can be obtained from a single ab initio Hartree–Fock calculation and perturbational formulas.⁴¹

The method is versatile enough to allow us to obtain and compare easily from a single induction energy grid, various polarizability models. Such a comparison is useful for discriminating physically sound models from all the possible ones, which can sometimes contain unrealistic values of some individual distributed polarizability components. For a given distributed polarizability model, each parameter is obtained as the most probable value of its distribution function. The behavior of these distribution functions allows us to easily discriminate between well and poorly defined polarizability components. This feature offers additional help for designing efficient and realistic models.

From test calculations on the water, methanol, and acetonitrile molecules, at the MP2/6-311++G(2d,2p) level, several polarizability models have been obtained. With the objective of using such polarizability models in simulations of condensed phases,⁴² models including charge flow polarizabilities on all atoms and dipolar polarizabilities on heavy atoms appear to provide an acceptable compromise between accuracy and tractability.

Acknowledgment. We acknowledge the Centre Charles Hermite, Vandoeuvre-lès-Nancy, France for an allocation of computer time on the 64-processor Silicon Graphics Origin 2000, Silicon Graphics Power Challenge Array, and Silicon Graphics Origin 200. We thank F.J. Luque and M. Orozco for interesting discussions.

References and Notes

- (1) Lefèvre, J. W. *Adv. Phys. Org. Chem.* **1965**, 3, 1.
- (2) Applequist, J.; Carl, J. R.; Fung, K. K. *J. Am. Chem. Soc.* **1972**, 94, 2952.
- (3) Applequist, J. *Acc. Chem. Res.* **1977**, 10, 79.
- (4) Miller, K. J.; Savchik, J. A. *J. Am. Chem. Soc.* **1979**, 101, 7206.
- (5) Birge, R. R. *J. Chem. Phys.* **1980**, 72, 5312.
- (6) Thole, B. T. *J. Chem. Phys.* **1981**, 59, 3412.
- (7) Liu, S.-Y.; Dykstra, C. E. *J. Phys. Chem.* **1987**, 91, 1749.
- (8) Miller, K. J. *J. Am. Chem. Soc.* **1990**, 112, 8543.
- (9) No, K. T.; Cho, K. H.; Jhon, M. S.; Scheraga, H. A. *J. Am. Chem. Soc.* **1993**, 115, 2005.
- (10) Voisin, C.; Cartier, C. *J. Mol. Struct. (Theochem)* **1993**, 286, 35.
- (11) Applequist, J. *J. Phys. Chem.* **1993**, 97, 6016.
- (12) Stout, J. M.; Dykstra, C. E. *J. Am. Chem. Soc.* **1995**, 117, 5127.
- (13) Bode, K. A.; Applequist, J. *J. Phys. Chem.* **1996**, 100, 17820.
- (14) van Duijnen, P. T.; Swart, M. *J. Phys. Chem. A* **1998**, 102, 2399.
- (15) Karlström, G. *Theor. Chim. Acta* **1982**, 60, 535.
- (16) Garmer, D. R.; Stevens, W. J. *J. Phys. Chem.* **1989**, 93, 8263.
- (17) Wallquist, A.; Ahlström, P.; Karlström, G. *J. Phys. Chem.* **1990**, 94, 1649.
- (18) Åstrand, P.-O.; Karlström, G. *Mol. Phys.* **1992**, 77, 143.
- (19) Stone, A. J. *Mol. Phys.* **1985**, 56, 1065.
- (20) Rappé, A. K.; Goddard, W. A., III. *J. Phys. Chem.* **1991**, 95, 3358.
- (21) Le Sueur, C. R.; Stone, A. J. *Mol. Phys.* **1993**, 78, 1267.
- (22) Bader, R. F. W.; Keith, T. A.; Gough, K. M.; Laidig, K. E. *Mol. Phys.* **1992**, 75, 1167.
- (23) Bader, R. F. W. *J. Chem. Phys.* **1989**, 91, 6989.
- (24) Bader, R. F. W. *Atoms in Molecules—A Quantum Theory*; (Oxford University Press: London, 1990).
- (25) Ángyán, J. G.; Jansen, G.; Loos, M.; Hättig, C.; Hess, B. A. *Chem. Phys. Lett.* **1994**, 219, 267.
- (26) Chipot, C.; Ángyán, J. G.; Ferenczy, G. G.; Scheraga, H. A. *J. Phys. Chem.* **1993**, 97, 6628.
- (27) Ferenczy, G. G. *J. Comput. Chem.* **1991**, 12, 913.
- (28) Ferenczy, G. G.; Winn, P. J.; Reynolds, C. A. *J. Phys. Chem.* **1997**, 101, 5446.
- (29) Winn, P. J.; Ferenczy, G. G.; Reynolds, C. A. *J. Phys. Chem.* **1997**, 101, 5437.
- (30) Chipot, C.; Ángyán, J. G.; Millot, C. *Mol. Phys.* **1998**, 94, 881.
- (31) Nakagawa, S.; Kosugi, N. *Chem. Phys. Lett.* **1993**, 210, 180.
- (32) Alkorta, I.; Bachs, M.; Perez, J. J. *Chem. Phys. Lett.* **1994**, 224, 160.
- (33) Celebi, N.; Ángyán, J.-G.; Dehez, F.; Millot, C.; Chipot, C. *J. Chem. Phys.*, in press.
- (34) Stone, A. J. In *Theoretical Models of Chemical Bonding*; Maksić, H., Ed. Springer-Verlag: Berlin, 1991, Vol. 4, pp 103–131.
- (35) Colonna, F.; Evleth, E.; Ángyán, J. G. *J. Comput. Chem.* **1992**, 13, 1234.
- (36) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. GAUSSIAN94, Gaussian Inc., Pittsburgh, PA, 1995.
- (37) Hättig, C.; Hess, B. A. *Chem. Phys. Lett.* **1995**, 233, 359.
- (38) Hättig, C. FOURIER: calculation of distributed dynamic MP2 polarizabilities, Bonn (1996).
- (39) Ángyán, J. G. *J. Mol. Struct. (Theochem)* in press.
- (40) Ángyán, J. G. unpublished results.
- (41) Cubero, E.; Luque, F. J.; Orozco, M. *Proc. Natl. Acad. Sci. USA* **1998**, 95, 5976.
- (42) Soetens, J.-C.; Millot, C. *Chem. Phys. Lett.* **1995**, 235, 22.