A sequential Monte Carlo/Quantum Mechanics study of the dipole polarizability of liquid benzene

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Abstract. Metropolis Monte Carlo classical simulation and quantum mechanical calculations are performed to obtain the dipole polarizability of liquid benzene. Super-molecular configurations are sampled from NVT Monte Carlo simulation of liquid benzene at room temperature and are used for subsequent quantum mechanical calculations. The auto-correlation function of the energy is used to analyze the statistical correlation between the configurations. Finite-field INDO and DFT calculations are performed in the statistically uncorrelated super-molecular clusters obtained in the simulation. The quantum mechanical results are shown to represent statistically converged values. The final results corroborate the recent contention that the dipole polarizability of liquid benzene suffers only a small change in the condensed phase.

Keywords: Monte Carlo simulation, polarizability, liquid benzene, density-functional theory, intermediate-neglect of differential overlap (INDO)

Mathematics Subject Classification: 31.10.+z, 33.15.-e, 71.10.-w, 71.15.-m

1. Introduction

The theoretical understanding of the electronic structure of gas phase, or isolated, molecules has progressed enormously in the last decades. Since the advent of the Schrödinger equation the progress in methods, techniques and algorithms allied to the computer hardware revolution has permitted theory to achieve a status complementary to laboratory experiments. However, most of the physical and chemical phenomena occur not for isolated molecules but interacting with the environment. This is the case, for instance, of most chemical experiments where solvents are everyday present. This leads to the necessity of treating solvents and much progress has been achieved using continuum models [1–5] where the solvent is described by its macroscopic constants such as the dielectric constant and index of refraction. In fact a liquid is more complex. The proper treatment of liquid systems has to consider its statistical nature [6,7]. Indeed, there are many possible geometrical arrangements of the molecules with with equivalent probability for non-zero temperature. Thus the liquid electronic properties are best described by a statistical distribution [8–12]. The structure of the liquid is represented by the radial distribution function and all properties are obtained from a statistical average [6,7].

Dipole polarizabilities are very important to understand the polarization of an electronic medium [13] and naturally relates to several molecular properties, including the dispersion contribution of the van der

Waals interaction [14]. Understanding the polarizability of a liquid system is thus very important. In this contribution we dedicate ourselves to the theoretical estimate of the dipole polarizability of liquid benzene. The choice of benzene is natural because all permanent odd moments are zero by symmetry. The permanent dipole moment and the first dipole hyper-polarizability, for instance, are zero. Thus the most important contribution to the polarization is the dipole polarizability. Of particular interest is the difference of the average dipole polarizability of the liquid compared to the gas phase. Whereas most continuum theories have obtained that the dipole polarizability is increased in the liquid, recent theoretical studies have challenged this and argued that in the liquid it should not show any appreciable change or be decreased instead [15–17]. The difficulties in obtaining properties of molecular liquid systems are related to the natural uncertainty associated to the complex and disordered liquid phase. In several previous studies it became clear that cluster or even micro-solvation models cannot describe in general the liquid properties [18,19]. The proper description of the liquid state needs a statistical procedure and assuring that the statistical properties are converged is necessary for reliable theoretical estimates. In this paper we use the sequential Monte Carlo quantum mechanics (S-MC/QM) methodology [20,21] where we first generate the structure of the liquid using Metropolis Monte Carlo. Next, statistically relevant configurations are separated and submitted to quantum mechanics calculations. Statistically converged results are obtained. Several QM calculations are necessary to obtain the ensemble average that is necessary to characterize the statistical nature of the liquid. This is an approach that is conceptually sound: the liquid system is explicitly considered and a proper statistical ensemble is used. The drawback is that such an approach is demanding computationally. In this present study the dipole polarizability of liquid benzene is obtained using density-functional theory (DFT) and the semi-empirical INDO models. However, the absolute accuracy is not the major point of interest here. Instead, we want to compare the dipole polarizability in the condensed liquid phase with that for the gas phase. Recent theoretical estimates point to a slight decrease of the polarizability [15–17] in the condensed medium.

2. Theoretical methodology

2.1. Monte Carlo simulation

Monte Carlo (MC) simulations are made using the Metropolis sampling technique and the periodic boundary conditions combined with the minimum image method in a cubic box [7]. The simulations are performed in the NVT ensemble. The total system consists of 343 benzene molecules at room temperature (298 K) and density of 0.8990 g/cm^3. The intermolecular interactions are described by the standard Lennard-Jones potential with 2 parameters for each atom i (ε_i and σ_i)

$$U_{ab} = \sum_i^a \sum_j^b 4\varepsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^6 \right]. \tag{1}$$

The pair-potential parameters are obtained using $\varepsilon_{ij} = (\varepsilon_i \varepsilon_j)^{1/2}$ and $\sigma_{ij} = (\sigma_i \sigma_j)^{1/2}$. We use the six-site OPLS [22] parameters and the experimental geometry. These are shown in Table 1. The intermolecular interactions are spherically truncated within a center of mass separation larger than the cutoff radius, $r_C = 18.4$ Å. Long-range corrections are calculated beyond this cutoff distance. In the simulation the molecules are kept with rigid geometries. The initial configurations are generated randomly, considering the position and orientation of each molecule. A new configuration is generated

Table 1
Geometry (in Å) and parameters of the Lennard-Jones potential of benzene

Site	x	y	z	ε (kcal/mol)	σ (Å)
C	0.0000	1.4000	0.0000	0.110	3.750
C	1.2124	0.7000	0.0000	0.110	3.750
C	1.2124	−0.7000	0.0000	0.110	3.750
C	0.0000	−1.4000	0.0000	0.110	3.750
C	−1.2124	−0.7000	0.0000	0.110	3.750
C	−1.2124	0.7000	0.0000	0.110	3.750
H	0.0000	2.4881	0.0000	0.000	0.000
H	2.1547	1.2440	0.0000	0.000	0.000
H	2.1547	−1.2440	0.0000	0.000	0.000
H	0.0000	−2.4881	0.0000	0.000	0.000
H	−2.1547	−1.2440	0.0000	0.000	0.000
H	−2.1547	1.2440	0.0000	0.000	0.000

after randomly attempting to translate in all Cartesian directions and to rotate around a randomly chosen axis. The simulation consists of a thermalization phase of 1.7×10^6 MC steps, followed by an averaging stage of 17.15×10^6 MC steps. All Monte Carlo simulations and statistical correlation analysis are performed with the DICE [23] Monte Carlo statistical mechanics program. The great advantage of the sequential procedure is that all the important statistical information is available before running into the QM calculations [24–26]. This considerably reduces the number of super-molecular structures that will be submitted to the quantum mechanical calculations, because the configurations are selected according to their statistical correlation, obtained from the auto-correlation function of the energy [11,12,24,25]. Using a correlation step of 2.7×10^5, we separate a total of 62 configurations, with less than 5% of statistical correlation. These 62 structures are used in the quantum mechanical calculations. The solvation shells were defined from the analysis of the radial distribution function. The first solvation shell comprises a total of 14 benzene molecules. The second shell, a total of 63 benzene molecules. This is of course a very large system for most ab initio methodologies and some compromising has to be used. We employ both the semi-empirical INDO and the first principles DFT method.

2.2. Quantum mechanics calculations

The semi-empirical INDO calculations are made using Zerner's program in the original parameterization [27,28]. It has been shown that the INDO model gives reasonably good hyper-polarizabilities within the sum-over-state (SOS) methodology [29]. However, for the dipole polarizability of ground states all terms of the SOS are positive and leads to slow convergence of the sum procedure. The QM calculations of the dipole polarizabilities are then made using the finite-field approximation [30] in the INDO level. Five different electric fields are applied in each of the three cartesian orientations. The field values are ± 0.002, ± 0.001 and 0.0 a.u. The dipole polarizabilities reported are the results of a simple average over the QM INDO results for the 62 statistically uncorrelated super-molecular configurations. Five finite electric fields were used for the small (14 benzene molecules) and large (28 benzene molecules) super-molecular systems in the three cartesian components. A total of 1612 QM calculations are performed. To verify the major assumptions of this study we also employ the DFT gradient corrected Becke's three-parameter hybrid exchange-correlation functional combined with the Lee-Yang-Parr correlation term, the so-called B3LYP model [31,32]. The basis set used is the split-valence 6-31G. For the smaller case (14 benzene molecules) this leads to a total of 924 contracted gaussian-type functions. It should be stressed that the calculations for the super-molecular structures generated in the liquid are made using
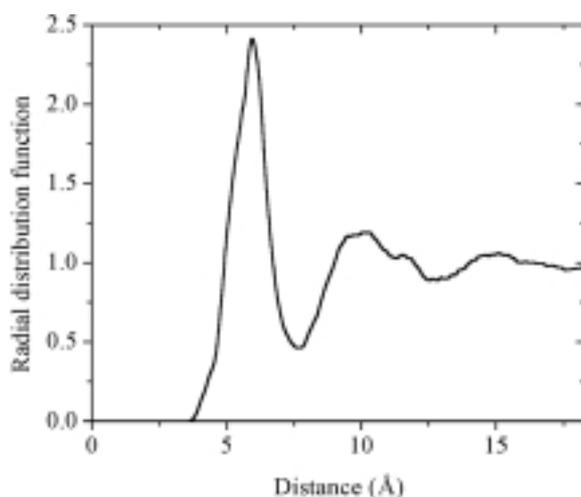
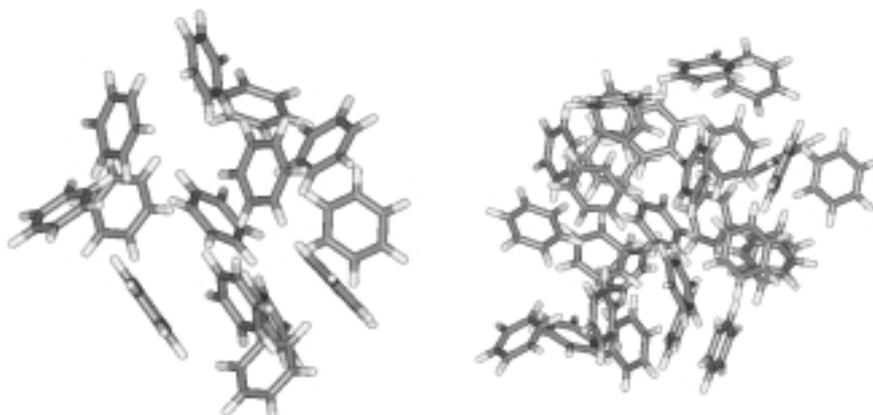Fig. 1. Pair-wise radial distribution function between the center of mass of benzene.

Fig. 2. Illustration of two super-molecular configurations (left with 14 benzene molecules and right with 28 benzene molecules) extracted from the MC simulation.

the antisymmetrization of the entire system. For instance, in the case of the smaller system composed of 14 benzene molecules this corresponds to a total of 420 valence electron in the INDO model and 598 electrons in the B3LYP/6-31G case. The DFT calculations are made using Gaussian 98 [33].

3. Results and discussion

Figure 1 shows the calculated radial distribution function of the center-of-mass of benzene. A clear first solvation shell ending in 7.5 Å is seen. The second solvation shell ends at 12.9 Å. Spherical integration up to these distances give, respectively, 14 and 63 benzene molecules. Between these two minima there is a clear maximum at 10.0 Å and spherical integration of the radial distribution function up to this point gives a number of 28 benzene molecules in this solvation shell. Even at the semi-empirical INDO level we could not perform the finite-field calculations for the 63 benzene molecules. We have thus limited to
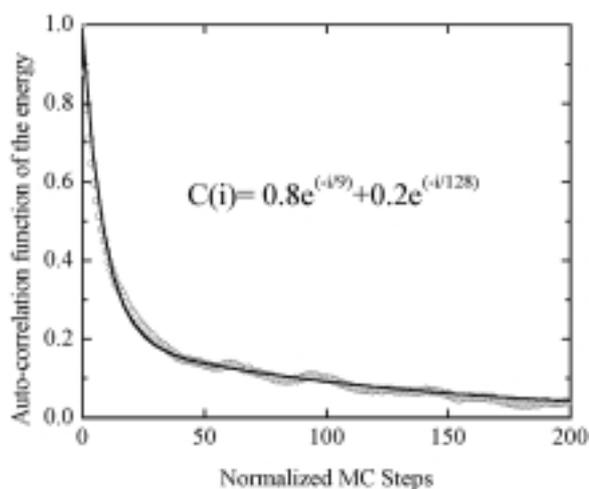
Fig. 3. Calculated auto-correlation function of the energy. MC step is normalized to the total number of molecules.

the first solvation shell (14 molecules) and the in-between shell with 28 molecules. Figure 2 illustrates one of the 62 super-molecular structures composed of 14 and 28 benzene molecules used in the QM calculations. Having defined the size of the super-molecular structures it is now important to establish the number of QM calculations that have to be performed to obtain the statistical convergence. The answer to this question is obtained from the auto-correlation function of the energy [11,12,24,25]. This function, over a chain of size l, is defined as

$$C(i) = \frac{\langle E_j E_{j+i}\rangle_{l-i} - \langle E_j\rangle_{l-i}\langle E_{j+i}\rangle_{l-i}}{\langle^2\rangle_l - \langle E\rangle^2_l} \tag{2}$$

where i, means the interval of MC configurations. For markovian processes this is an exponentially decaying function,

$$C(i) = \sum_{j}^{n} c_j e^{-i/tau_j} \tag{3}$$

The correlation step is

$$\tau \int_{0}^{\infty} C(i)di. \tag{4}$$

Figure 3 shows the calculated auto-correlation function of the energy of liquid benzene. From this and Eq. (4) it can be obtained that the correlation step in normalized MC steps is ~ 40. A normalized step corresponds here to 343 (the number of benzene molecules) MC steps. In calculating the averages we decided to select structures in an interval of 800 normalized steps corresponding to 2.744×105 MC steps. As the total number of configurations generated is 17.15×10^6 (or 50000 normalized steps), the averages are taken over 62 configurations, with a correlation of less than 5%. These 62 configurations will be subjected to quantum mechanical super-molecular calculations. These calculations are made at the INDO and B3LYP/6-31G levels using the finite field model. The wavefunction is antisymmetric
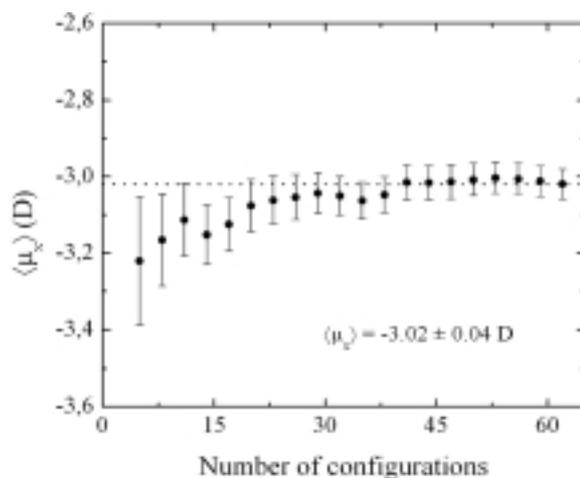
Fig. 4. Statistical convergence of the dipole polarization. Bar represents the statistical error. The example corresponds to the finite-field value of 0.002 a.u. in the small (14 benzene molecules) super-molecular configuration.

over the entire system and the finite field is applied in the entire super-molecular system. The dipole polarization is calculated and therefrom the dipole polarizability is obtained as the linear term of the polarization. Having the dipole polarizability for the entire system composed of N benzene molecules we obtain the condensed phase result of benzene dividing the result by the number N. This gives the polarizability per molecule. An important point is that there are no separate calculations for the solvent. We simply compare the results obtained for the super-molecules with the calculations for the isolated benzene system. The distinction between these two results is the influence of the condensation. The use of a properly antisymmetric wavefunction is important to include the exchange interaction between the different benzene molecules in the liquid and also to obtain the intermolecular interactions. The inclusion of the dispersion contribution to the van der Waals interaction is known to require correlation effects and it is likely to be excluded in the INDO calculations. As the DFT method is correlated it is ideally expected to include the dispersion part of the correlation effect. This is not assured however and the proper and explicit inclusion of van der Waals contribution is a central topic in DFT theoretical methodologies. We only emphasize that the use of the super-molecular approach with a proper antisymmetric wavefunction may include dispersion interaction at a lower level [34]. Indeed, for the benzene molecule the solvatochromic shift upon condensation, that is dictated by the dispersion interaction, is well described using the INDO theoretical methodology used here [11,25].

In the INDO calculations we use both the super-molecules with 14 and 28 benzene molecules. Figure 4 shows the convergence of the calculated dipole moment of the 14 benzene molecules in the external finite-field of 0.002 a.u. As can be seen the calculated dipole moment is statistically well converged after ~ 40 QM calculations. The same procedure is repeated for all the other electric fields and also for the super-molecular configurations with 28 benzene molecules. Statistical convergence is assured in all cases. Using these results for the finite-fields, the dipole polarizability component is obtained as shown in Fig. 5. We report both invariants of the dipole polarizability, the α_{mean}, and the anisotropy. The liquid value is the result of the statistical average $\langle \alpha_{mean} \rangle$ obtained using the calculated dipole polarizabilities of the super-molecules extracted from the MC simulation. The numerical results are finally summarized in Table 2. As expected the calculated dipole polarizability at the INDO semi-empirical level are not competitive with other numerical estimates. Parkinson and Zerner have considered the possibility of

Table 2

Calculated components of the dipole polarizability (in a.u.) of liquid benzene using finite-field approximation in the INDO and DFT models. $\langle \alpha_{mean} \rangle$ is the statistical average of the mean dipole polarizability and $\Delta\alpha$ is the statistical average polarizability anisotropy

Model	$\Delta\alpha$	$\langle\alpha_{mean}\rangle$
INDO		
14 benzene	2.1	42.7
28 benzene	0.9	43.7
B3LYP/6-31G		
14 benzene	12.5	55.6
Ref [17]	36.5	63.7

Conversion factor: 1 Debye is 0.3935 a.u.
Calculated mean dipole polarizability for the gas phase is 43.0 a.u. (INDO) and 53.4 a.u. (B3LYP/6-31G).
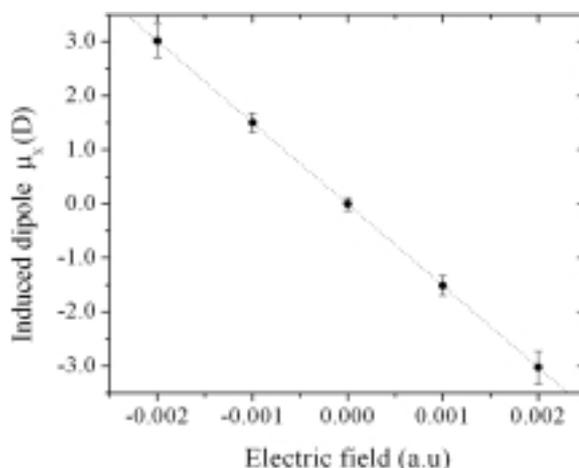Experimental dipole polarizability for the gas phase value is 69.7 a.u. [36].

Fig. 5. Polarization as a function of the applied field for the small (14 benzene molecules) configuration. Each point shown is the result of a converged statistical average of 62 quantum mechanics calculations (See Fig. 4).

extending these calculations to the random-phase approximation (RPA) level [35]. Our theoretical result for the gas phase is 43.0 a.u , which is equivalent to the RPA result but still too small compared to the experimental result [36] of 69.7 a.u. At this point the absence of more diffuse function is responsible for this decreased value. In the condensed phase this lack is less important. However, in comparison with the condensed phase result we can see the trend that the dipole polarizability assumes essentially the same value. Two aspects are worth noting. First, the emphasis in this present study lies in a realistic representation of the liquid. Hence it is worth noticing that the dipole polarizability of the liquid benzene obtained here is nearly isotropic. For the larger super-molecular system of 28 benzene molecules the anisotropic component of the polarizability is only 0.9 a.u. This is indicative that a reasonable representation of the bulk polarizability is obtained here. Second, it should be pointed out that the polarizability is represented by a statistical distribution. Figure 6 illustrates the distribution of
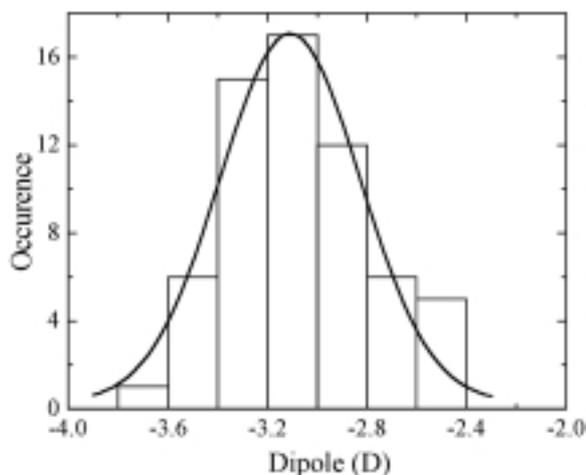
Fig. 6. Statistical distribution of calculated dipole moment for the field of 0.002 a.u in the x-direction.

the polarization in the x-direction for the field of 0.002 a.u. Although the average value is, in this case, $\langle \mu_x \rangle = -3.08$ D, the distribution of polarization values is reasonably broad.

The B3LYP/6-31G calculations for the condensed phase are performed only for the smaller super-molecules composed of 14 benzene molecules. The results for the mean dipole polarizability are shown in Fig. 7 and seems to converge to the average of 55.6 ± 0.5 a.u. As a comparison the gas phase result obtained for the isolated benzene molecule is 53.4 a.u. It is well-known that diffuse functions play an important role in the calculations of dipole polarizabilities. In this present study we are limited to the size of basis function and could only use a relatively small basis without a proper description of the diffuse part of the basis set. Indeed in this study the basis set size for the small cluster of 14 benzene molecules includes nearly one-thousand basis function and could not be extended any further. Note that the result for the dipole polarizability of a single super-molecule requires, in fact, several single-point calculations for the different finite field values. Because the super-molecules including several benzene molecules are extended compared to the single molecule case, it is expected that the lack of diffuse function will be more harmful for the gas phase than the condensed phase. Hence, the difference of 2.2 ± 0.5 a.u between the condensed and gas phases results is likely to be slightly overestimated. Again, the first principle DFT calculations, similar to the semi-empirical INDO results, give an average value for the mean polarizability that is essentially the same result as in the gas phase.

As it was first discussed by Jensen et al. [17] using time-dependent DFT results the dipole polarizability of condensed phase benzene is slightly decreased compared to the gas phase result by 8%. Morita and Kato [15] have earlier considered the medium (water) perturbation on the dipole polarizabilities of small systems like Ne, Ar, CH4 and anions like Cl$^-$. Similarly, they conclude that for the case of neutral systems in water there is a decrease in the dipole polarizability between 13 and 18%. For the anion, Cl$^-$, in water the decrease is as much as 37%. van Duijnen et al. [37] contends that the dipole polarizability of formaldehyde in water shows no appreciable change and that if polarizability is to change due to medium effect it should be decreased. In line with this result we find that the dipole polarizability of liquid benzene shows no appreciable change and, in fact, using statistically converged result we find the results to be equivalent.
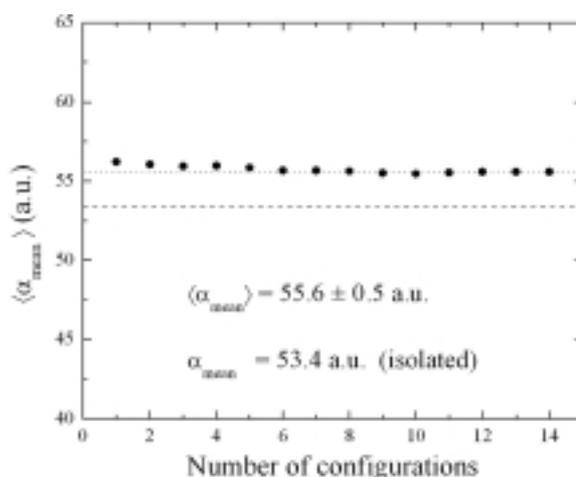
Fig. 7. Calculated results for the mean dipole polarizability per benzene molecule for the super-molecular configurations using the B3LYP/6-31G theoretical model. Dashed line represents the gas phase value.

4. Conclusion

Monte Carlo classical simulation is performed to generate the structure of liquid benzene at room temperature. Configurations are sampled using the auto-correlation function of the energy and the structures used in the subsequent quantum mechanical calculations are less than 5% statistically correlated. INDO finite-field calculations are made in the super-molecular structures including all benzene molecules within 10 Å. For each finite-field value the electronic polarization is verified to be statistically converged. As a complement, the quantum mechanical results are performed also at the density-functional B3LYP/6-31G level. The final results indicate that the dipole polarizability of the liquid is equivalent to the gas phase result. This result corroborates the recent contention that the dipole polarizability of liquid benzene suffers only a small change in condensed phase.

Acknowledgments

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