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Frequency-Dependent Molecular Polarizability Calculated within an Interaction Model

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We have investigated different models for parameterizing the frequency-dependent molecular polarizability. The parameterization is based on an electrostatic model for interacting atoms and includes atomic polarizabilities, atom-type parameters describing the damping of the electric fields and the frequency dependence. One set of parameters has been used for each element. The investigation has been carried out for 115 molecules with the elements H, C, N, O, F, and Cl, for which the frequency-dependent polarizability tensor has been calculated with ab initio methods. We find that the static polarizability of aliphatic and aromatic compounds can be described with the same set of parameters. The conclusion is that a simple electrostatic model to a good degree can model the essential behavior of the frequency-dependent molecular polarizability.

I. Introduction

Photonic materials are becoming a major player in information distribution where data is transferred by electromagnetic waves. Optical methods are the basis for rapid communication systems, a new generation of computers, photonic materials, polymer optical fibers and waveguides, photorefractive materials for optical storage, and materials for frequency conversion and E/O-switching. The statement of P. Ball: "The next revolution in information technology will dispense with the transistor and use light, not electricity, to carry information. This change will rely on the development of photonic materials, which produce, guide, detect, and process light" illustrates clearly the future of photonic materials.[1] Furthermore, as discussed recently, the limit for increasing the density of transistors in traditional silicon-based electronic devices will soon be reached.[2] Therefore, an understanding at the molecular level of not only static (hyper)-polarizabilities but also their frequency-dependent counterparts is of fundamental importance.[3−11] Quantum chemical methods can be used to calculate molecular frequency-dependent (hyper)-polarizabilities but currently, accurate calculations are limited to rather small molecules due to the large requirement of computer resources. Extensions of computational methods to large molecules, and for example molecular crystals as well as effects from the surrounding medium are therefore limitted to less sophisticated models.

For a long time, static molecular polarizabilities have been calculated in quantum chemistry by adopting the finite-field approach, i.e., the molecular dipole moment is calculated for a set of explicit external electric fields and the polarizability obtained from numerical differentiation.[12−14] A conceptually more attractive and computationally more efficient approach is to adopt quantum-chemical response theory.[15] In the Dalton program,[16] self-consistent field (SCF) and multiconfigurational SCF (MCSCF) frequency-dependent polarizabilities are available,[17,18] but applications of these ab initio methods have been restricted to rather small molecules in the gas phase. For example, calculations for *n*-alkanes[19] and other oligomers[20−27] have been restricted to the SCF level and solvent effects have been restricted to modeling the surroundings with a dielectric medium.[28−33]

A long time ago, it was recognized that molecular static polarizabilities to a large extent are additive, i.e., they can be calculated as a sum of transferable atomic, bond, or functional-group contributions.[34−37] Also recently, the concept of additivity has been adopted with success for the static polarizability of organic molecules,[38,39] and it has been demonstrated that both static and frequency-dependent polarizabilities of halogen-derivatives of benzene are transferable and additive.[40]

However, since molecular polarizabilities are tensors, in an additive model also the atomic contributions have to be tensors. By adopting the interaction model introduced by Silberstein,[41] and to a large extent developed by Applequist and co-workers,[42−44] molecular polarizability tensors can be modeled by transferable atomic spherical polarizabilites. The interaction model has been extended to include overlap effects on the

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internal electric fields,[45,46] and the model by Thole[46] has been investigated in more detail recently.[47−49]

Both in the additive and interaction models, the atomic (or bond) polarizabilities are fitted to molecular polarizabilities of a trial set of molecules. If experimental molecular polarizabilities are used, it should be noted that they also include zero-point vibrational and pure vibrational contributions that most probably are not negligible.[50−52] Especially in the interaction model only the electronic polarization is considered, but also for an additive model it should not be expected that vibrational effects are additive. Therefore, it may not be suitable to parameterize *experimental* molecular polarizabilites. Instead it is preferable to use quantum chemical calculations of molecular electronic polarizabilities for the parameterization and then treat the vibrational effects separately.

In quantum chemistry, the frequency dependence of polarizabilities can be calculated for specific frequencies. However, the polarizability often has a smooth dependence on the frequency and the frequency dependence can therefore be described successfully with only a few parameters.[53]

In this work, we investigate several interaction models including both the Applequist and Thole models as well as some modifications of the Thole model. Furthermore, we investigate several models for atomic parameters of the frequency dependence of the molecular polarizability.

II. Theoretical Background

The molecular polarizability $\alpha_{\alpha\beta}^{\mathrm{mol}}$ describes the response to an external electric field, E_β^{ext},

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

where $\mu_\alpha^{\mathrm{ind}}$ is the molecular induced dipole moment. For a set of N interacting atomic polarizabilities, the atomic induced dipole moment on atom p also has a contribution from the other atoms,

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

where $T_{pq,\alpha\beta}^{(2)}$ is the so-called interaction tensor

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

Furthermore, the interacting particles are regarded to have the same symmetry properties as unperturbed atoms,

$$\alpha_{p,\alpha\beta} = \alpha_p \delta_{\alpha\beta} \tag{4}$$

In a supermatrix notation, eq 2 can be rewritten as[42]

$$\mu = (\alpha^{-1} - T^{(2)})^{-1} E^{\mathrm{ext}} \tag{5}$$

If the relay matrix B is defined as

$$B = (\alpha^{-1} - T^{(2)})^{-1} \tag{6}$$

the molecular polarizability is given as[42]

$$\alpha_{\alpha\beta}^{\mathrm{mol}} = \sum_{p,q}^{N} B_{pq,\alpha\beta} \tag{7}$$

However, since the electronic charge distribution is smeared out, the electric field at a nucleus will be damped by the charge distribution. One way to include the damping is to modify the interaction tensor in eq 3, and according to Thole it becomes[46]

$$T_{pq,\alpha\beta}^{(2)} = \frac{3v_{pq}^4 r_{pq,\alpha} r_{pq,\beta}}{r_{pq}^5} - \frac{(4v_{pq}^3 - 3v_{pq}^4)\delta_{\alpha\beta}}{r_{pq}^3} \tag{8}$$

where $v_{pq} = r_{pq}/s_{pq}$ if $r_{pq} < s_{pq}$. Otherwise, $v_{pq} = 1$ and eq 3 is recovered. Thole defined s_{pq} as

$$s_{pq} = c_d(\alpha_p \alpha_q)^{1/6} \tag{9}$$

where $c_{\mathrm{d}} = 1.662$ and thus only one additional fitting parameter is introduced in the model as compared to the Applequist model. We have tested several definitions of s_{pq}: one where c_{d} is chosen as 1.662, another where c_{d} is optimized in line with the work by van Duijnen and Swart,[48] and a third approach where it is assumed that s is related to the atomic second order moment,

$$s_{pq} = (\Phi_p \Phi_q)^{1/4} \tag{10}$$

It may be assumed that Φ_p is proportional to the atomic second order moment of atom p since s_{pq} is a distance. The latter model will here be termed the modified Thole model.

The frequency dependence of the molecular polarizability well below any electronic absorption band is often modeled with an Unsöld-type of expression,

$$\alpha_{\alpha\beta}^{\mathrm{mol}}(-\omega;\omega) = \alpha_{\alpha\beta}^{\mathrm{mol}}(0;0) \times \left[\frac{\bar{\omega}^2}{\bar{\omega}^2 - \omega^2}\right] \tag{11}$$

or with a Taylor expansion around the static polarizability $\omega = 0$

$$\alpha_{\alpha\beta}^{\mathrm{mol}}(-\omega;\omega) = \alpha_{\alpha\beta}^{\mathrm{mol}}(0;0) \times [1 + A\omega^2 + B\omega^4 + ...] \tag{12}$$

as discussed in more detail by Bishop.[53] Here, we assume that the atomic polarizabilities have the same frequency dependence and thus we employ either the Unsöld approximation,

$$\alpha_p(-\omega;\omega) = \alpha_p(0;0) \times \left[\frac{\overline{\omega_p}^2}{\overline{\omega_p}^2 - \omega^2}\right] \tag{13}$$

or a Taylor expansion,

$$\alpha_p(-\omega;\omega) = \alpha_p(0;0) \times [1 + A_p\omega^2 + B_p\omega^4 + ...] \tag{14}$$

where $\overline{\omega_p}$ or A_p and B_p are regarded as atom-type parameters.

III. Quantum Chemical Calculation

The quantum chemical computations of frequency-dependent polarizabilities were invoked at the SCF level using the Dalton program package[16] as described in refs 15, 17, and 18. The basis set by Sadlej[54] was used since it has been shown previously that it gives good results for polarizabilities considering its limited size.[40] The following frequencies have been used: $\omega =$ 0.0, 0.02389, 0.04282, and 0.0774 au (1 au = 27.21 eV), and we carried out calculations for 115 molecules (the frequency dependence has been calculated for 112 molecules)[62] adopting standard bond lengths and bond angles taken from refs 55 and 56. The molecules considered were restricted to aliphatic and aromatic molecules. Olephines have not been included since in this case intramolecular charge-transfer effects are important, and these effects cannot be modeled on the basis of atomic

TABLE 1: Atomic Parameters Fitted to Model the Static Polarizability (in au, 1 au = 0.1482 Å^3)

	Applequist		Thole model				modified Thole model		
atom	α	α^a	α	α	α^b	α^c	α	Φ	c_{d},pp
H	1.61	0.91−1.13	2.84	1.83	3.47	3.50	1.84	2.75	0.965
C	4.20	4.16, 5.92	10.20	12.19	9.46	10.18	11.52	20.99	2.029
N	8.44	3.58	9.03	7.88	7.46	7.60	10.55	26.55	2.349
O	8.78	2.93−3.14	5.18	5.78	5.82	6.39	5.64	12.16	1.959
F	2.44	2.16	2.91	2.54		2.94	2.25	4.78	1.668
Cl	12.65	12.89	14.93	16.21		16.11	16.08	17.64	0.600
c_d			1.662	1.991^d	1.662	1.7278			
rms	139.44		11.30	8.26				6.67	

^{a} See ref 42. ^{b} See ref 46. ^{c} See ref 48. Fitted to experimental polarizabilities. ^{d} Optimized.

polarizabilities only.[57,58] We tried to add a set of 13 small alkenes, but did not obtain any reasonable results. It should, however, be noted that we included for example *p*-nitroaniline which indeed has large charge-transfer effects.

IV. Fitting of Atomic Parameters

The parameters describing the static polarizabilities have been optimized by minimizing the difference between the quantum chemical molecular polarizability tensors, $\alpha^{\mathrm{QC}}_{\alpha\beta,i}$, and the model molecular polarizability tensors, $\alpha^{\mathrm{model}}_{\alpha\beta,i}$, as[63]

$$\mathrm{rms} = \sqrt{\frac{\sum_{i=1}^{N} \sum_{\alpha,\beta=1}^{3} (\alpha^{\mathrm{model}}_{\alpha\beta,i} - \alpha^{\mathrm{QC}}_{\alpha\beta,i})^2}{N-1}} \tag{15}$$

where N is the number of molecules. We have studied four models for the static part of the molecular polarizability: the original Applequist model,[42] the Thole model,[46] an optimization of c_d, and the modified Thole model as described in the previous section.

The parameters describing the frequency dependence of the molecular polarizability have been optimized by minimizing

$$\mathrm{rms} = \sqrt{\frac{\sum_{i=1}^{N} \sum_{\alpha,\beta=1}^{3} [(\alpha^{\mathrm{model}}_{\alpha\beta,i}(\omega) - \alpha^{\mathrm{model}}_{\alpha\beta,i}(0)) - (\alpha^{\mathrm{QC}}_{\alpha\beta,i}(\omega) - \alpha^{\mathrm{QC}}_{\alpha\beta,i}(0))]^2}{N-1}} \tag{16}$$

i.e., we parametrize the frequency dependence only and do not attempt to correct for errors obtained in the parameterization of the static polarizability. For the frequency dependence, we have adopted both the Unsöld model and the Taylor expansion as described previously.

V. Results

The optimized parameters are given in Table 1 and are compared to the parameters given in previous work on the Applequist model[42] and the Thole model,[46,48] respectively. The results are displayed in Figure 1, where the quantum chemically derived polarizabilities have been plotted against the model molecular polarizabilities, including all diagonal components of the polarizability tensors for the 115 molecules using the parameters obtained in this work.

A detailed comparison with the Applequist model is not possible since we have used only one atom-type polarizability for each element whereas normally two or three types have been used for H, C, N, and O, respectively.[42] Such results are included, however, for comparison with the other models. Nonetheless, in comparison with previous work,[42] we find a reasonable agreement for the atomic polarizabilities of most of the elements. Especially, the F and Cl polarizabilities are in good agreement and our C polarizability is close to the carbonyl C parameter of 4.16.[42] Our H polarizability is considerably higher, but especially N and O give different results. The large spread in Figure 1a is probably due to that we included both aliphatic and aromatic molecules since previously, it has been demonstrated that polarizabilites obtained by the Applequist model cannot be adopted for both kinds of molecules.[58]

For the Thole model, we find a good agreement between our results and previous work.[46,48] In line with previous investigations, we find that the Thole model gives a much better description of the molecular polarizability tensor than the Applequist model even though the number of fitting parameters is almost the same. Further, the rms-value is reduced more than an order of magnitude. Recently, van Duijnen and Swart compared Thole polarizabilities fitted to quantum chemical calculations for various basis sets.[48] However, their results show large differences if they are fitted to experimental data or to ab initio calculations. Our parameters compare well to their parameters fitted to experimental data, but not to their ab initio parameters. By comparing the SCF molecular polarizabilities, it is clear that the more flexible Sadlej basis set employed here gives a better description of the molecular polarizabilities than for the series of basis sets adopted by van Duijnen and Swart. Therefore, we restrict the comparison to the parameters they obtained by parameterizing experimental data. Especially for F and C, we find good agreement. The largest relative difference is found for H, where our polarizability is about 20% smaller than the previous values fitted to experimental data.[46,48] This difference for α^{H} is in line with the results by van Duijnen and Swart, who also found substantially smaller polarizabilities for hydrogen when they fitted to quantum chemical calculations, compared to experimental data. This may imply that α^{H} obtained from experimental data contains large contributions from vibrational effects. Our N parameters are slightly larger and the O and Cl parameters slightly lower than the parameters presented previously.[46,48] Since we find the expected relative magnitudes of the parameters (for example $\alpha^{\mathrm{C}} > \alpha^{\mathrm{N}} > \alpha^{\mathrm{O}} > \alpha^{\mathrm{F}}$), and in general a good agreement with previous work, we may conclude that the Thole polarizabilities have a physical significance and are not only fitting parameters. It should be noted that the parameterizations employed here and elsewhere are quite different, especially with respect to the choice of molecules. If we optimize also c_d, we obtain a value of 1.991, a relatively large deviation from the original value of Thole of 1.662,[46] compared to the recent optimized value of 1.7278.[48] The improvement of the fit is about 25% which is good considering that only one extra fitting parameter has been added. The atomic polarizabilities change quite substantially, even though the trends are the same. Since c_d is increasing compared to the original value of 1.662,[46] it is expected either that α_p

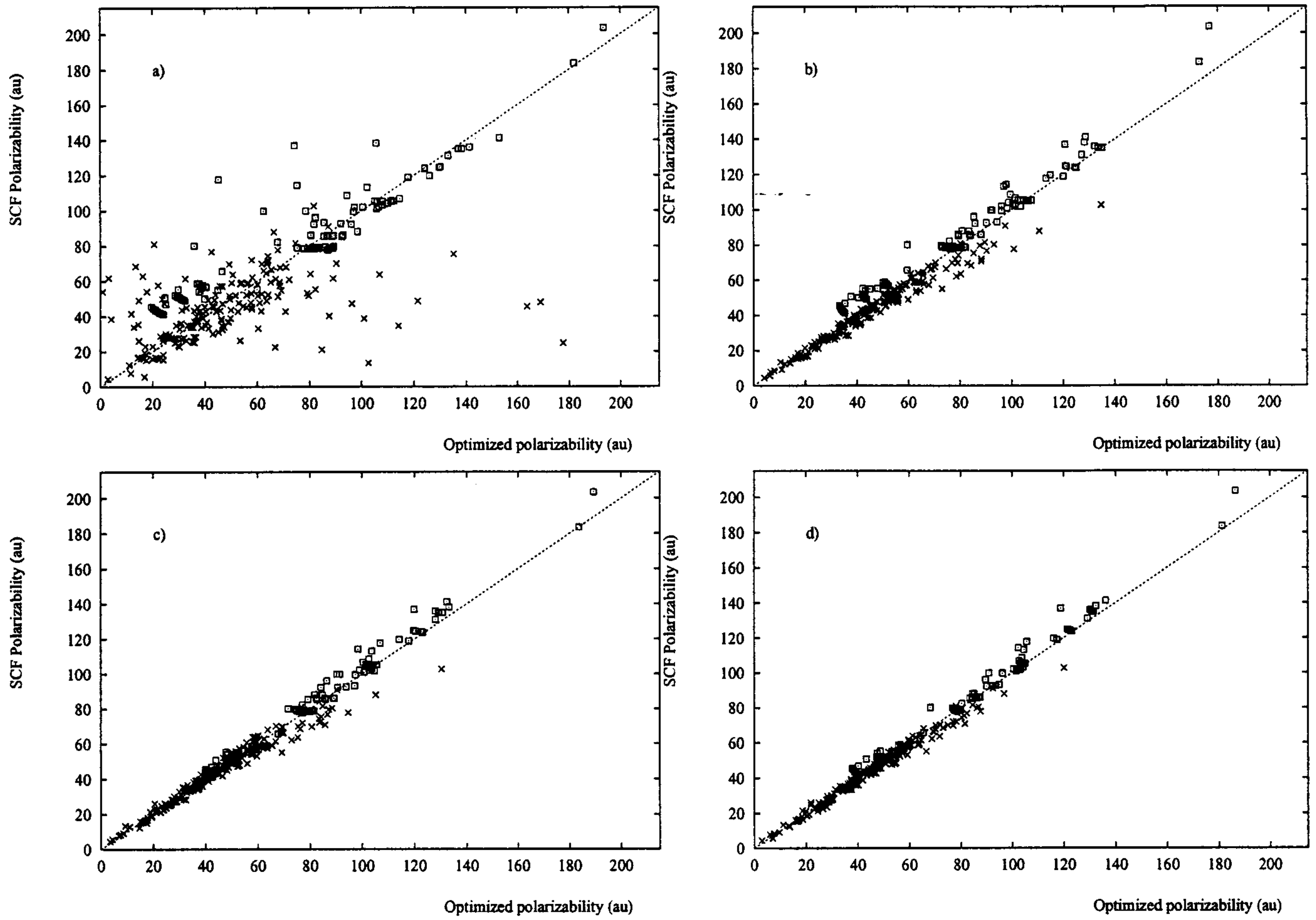

Figure 1. Parameterization of quantum chemically derived polarizabilities with interacting atom models. (a) The Applequist model. (b) The Thole model. (c) The c_d parameter in the Thole model being optimized. (d) Individual damping parameters for each element. (×) indicates aliphatic molecules and (□) aromatic molecules, respectively.

decreases to maintain the same damping in eq 9, or that α_p is increasing to compensate for the increased damping in eq 8. Actually, we find that the polarizabilities of H, N, and F decrease whereas the polarizabilities of C, O, and Cl increase. The largest effect is found for H which decrease from 2.84 to 1.83 au.

The damping of the electric field is a consequence of the charge distributions being smeared out and that they are overlapping. It is then expected that the damping is more due to the extension of the charge distribution rather than the polarization, even though the electronic second moment and the polarizability are related to each other. Nonetheless, a fit with an additional atomic parameter describing the damping gives only a minor improvement (around 20%) considering that two parameters are used for each element (see Table 1). It is also of interest to rewrite Φ_p in terms of α_p and an atomic damping factor, $c_{d,pp}$ to compare with the parameters of the other models. From eqs 9 and 10, we get

$$c_{d,pp} = \frac{\Phi_p^{1/2}}{\alpha_p^{1/3}} \tag{17}$$

which also is presented in Table 1. The $c_{d,pp}$ parameters thus describe the relation between an atomic second order moment and an atomic polarizability. For the second-row elements (C, N, O, and F), $c_{d,pp}$ are in the range 1.6−2.4 which is about the same size as the general c_d values. It is difficult to deduce a trend and the differences may not be significant. The $c_{d,pp}$ parameter of H is, however, a factor of 2 smaller than that for the second-row elements which probably is due to its small second order moment. This result is in line with the distributed multipole moments and polarizabilities calculated in order to obtain intermolecular potentials.[59,60] For the Cl atom, the $c_{d,pp}$ parameter is also much smaller which could be due to its large polarizability. However, further investigations of third-row elements should be carried out before any definitive conclusions can be drawn. Perhaps, a suitable partition scheme for the damping factors c_d is one parameter for each row of elements in the periodic table. Thus, the various values obtained for c_d in the Thole model are probably due to that different sets of molecules have been used with different weight for each element.

In Figure 2, the static polarizability tensor as function of the length of the molecule is presented for the *n*-alkanes. Here, it should be noted that alkanes longer than hexane have not been included in the parameterization and thus they may be regarded as a test of the parameters. In all calculations on *n*-alkanes, we have used completely staggered conformations. SCF calculations are compared to the modified Thole model. For the components perpendicular to the chain, we find a linear dependence with the length of the chain which means that these components can be described with an additive model. For these two components, we also find an excellent agreement between the parameterized model and the SCF calculations. For the component along the chain, we find a super linear dependence with increasing length of the chain. For the parameterized model, this component increases even faster than for the SCF data, but for the largest

TABLE 2: Parameters Describing the Frequency Dependence of Molecular Polarizabilities (in au)

	all molecules				aliphatic				aromatic			
	Unsöld	quadratic	quartic		Unsöld	quadratic	quartic		Unsöld	quadratic	quartic	
atom	$\bar{\omega}_p$	A_p	A_p	B_p	$\bar{\omega}_p$	A_p	A_p	B_p	$\bar{\omega}_p$	A_p	A_p	B_p
H	0.6052	3.0366	2.4521	98.9024	0.4140	6.0475	5.3256	122.6902	0.3509	6.4859	5.8306	126.6553
C	0.4446	5.1418	4.5048	107.9280	0.7141	1.9712	1.3768	100.7323	0.3959	7.1876	6.4144	126.5659
N	0.3423	8.7909	8.0585	124.7032	0.4322	5.5416	4.8219	121.8716	0.2232	17.1930	16.0513	202.0394
O	0.5608	3.8037	3.1573	109.3189	0.4299	5.6044	4.8682	124.5673	1.3390	8.7929	8.0042	139.1782
F	0.4039	6.6054	5.9458	112.1713	0.9725	1.6196	0.9918	103.0175	1.0849	−2.3109	−2.6209	69.1134
Cl	0.4413	5.3456	4.6413	119.3990	0.5299	3.6324	2.9841	109.8527	0.4319	5.2235	4.5482	117.7529
rms	0.809	0.809	0.809		0.424	0.424	0.424		0.712	0.689	0.689	

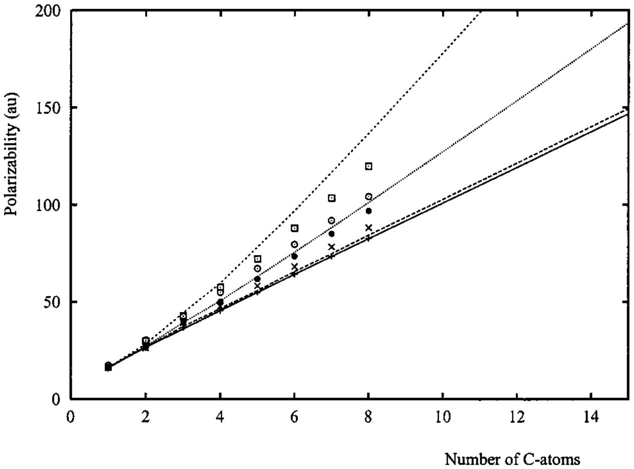

Figure 2. The static polarizability tensors for the *n*-alkanes as a function of the chain length. Quantum chemically calculated and experimental data are presented as dots; the results from the parameterized electrostatic models as lines. (—, +) and (– –, ×) denote components perpendicular to the chain. (– –, □) denotes the component along the chain. (···, ●) denotes the isotropic part of the polarizability. (⊙) denotes the experimental data taken from ref 61.

molecule, C_8H_{18}, the difference is still less than 15%. We also find a good agreement between the model and the quantum chemical calculations for the isotropic part of the polarizability. In this case, we can compare to experiment,[61] and as displayed in Figure 2, the agreement is excellent. Results for the frequency dependent polarizabilities of the *n*-alkanes show a behavior almost identical to that of their the static polarizability.

For the frequency dependence, we have studied three different models: the Unsöld approximation in eq 13, a truncation of eq 14 after the quadratic term (denoted the quadratic model), and a truncation of eq 14 after the quartic term (denoted the quartic model). If all the molecules are included in the parameterization, an rms of 0.809 au is obtained for all three models (see Table 2). In the Unsöld and the quadratic models only one parameter is used per element, whereas two parameters per element have been used in the quartic model. Even if the magnitude of the B_p parameters is significant and the A_p parameters are different in the quadratic and quartic models, the actual contribution from a quartic term of the atomic frequency dependence is negligible for the molecules studied here since the fitting has not improved. Hence, the Unsöld and quadratic models can be regarded as identical since we can carry out a Taylor expansion of eq 13 and keep only the quadratic term since, as just argued, the higher order terms would be negligible.

If the molecules are divided into aliphatic and aromatic molecules, we find a significant improvement of the description within each family (see Table 2 and Figure 3). The rms value is reduced by a factor of 2 if only the aliphatic molecules are included and with about 10% for a parameterization of the aro-

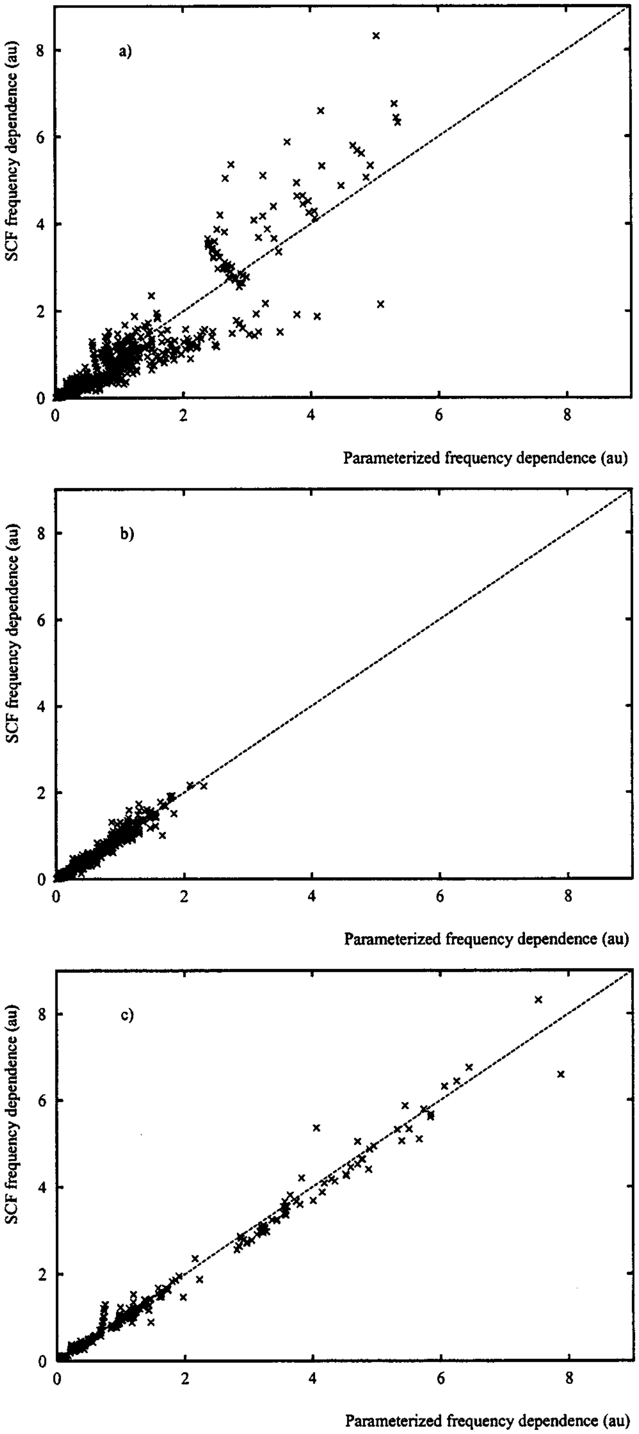

Figure 3. Parameterization of the frequency dependence adopting the Unsöld model. (a) All molecules. (b) Aliphatic molecules. (c) Aromatic molecules.

matic molecules alone. However, the frequency dependence is much larger for the aromatic molecules (see Figure 3) and thus they will still dominate the parameterization when aliphatic molecules are included. Nonetheless, it has been demonstrated that the frequency dependence of molecular polarizabilities can be described with atom-type parameters.

VI. Conclusions

In this work, we have investigated the parameterization of frequency-dependent molecular polarizabilities based on a model for interacting atoms. The study has been carried out for 115 molecules, which is a considerably larger set of molecules than used previously. By adopting one set of parameters for each element, we find that the Thole model is successful in reproducing the static molecular polarizability tensor. The modifications discussed here give significant improvements. Especially the behavior of the damping at the hydrogen atoms is different from that of the other elements and should be treated differently. It is also found that aliphatic and aromatic molecules can be described with the same set of parameters. Furthermore, it is the first investigation where an interacting atom model has been extended also to include the frequency dependence of the molecular polarizability. It has been shown that the frequency dependence of molecular polarizabilities can be described with one parameter for each element.

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(62) The molecules studied are 1-propanol, 2,3-difluorobutane, 2-aminopropane, 2-methylpropane, 2-nitropropane, 2-propanol, 3-pentanone, 4-heptanone, *N*,*N*-dimethylformamide, *N*-methylacetamide, *N*-methylformamide, acetaldehyde, acetone, 1-aminobutane, aminoethane, aminomethane, 1-aminopropane, butane, butanal, butanol, butanoic acid, chloroethane, chlorofluoromethane, trichloromethane, chloroformamide, cyanobutane, cyanoethane, cyanomethane, cyanopropane, cyclohexane, cyclohexanol, cyclopentane, cyclopentanol, 1,2-dichloroethane, 2,3-dichlorobutane, dichloromethane, 1,2-difluoroethane, difluoromethane, difluorochloromethane, ethane, ethylamide, ethanol, acetic acid, fluoroethane, trifluoromethane, fluoroformamide, formaldehyde, water, hexane, hydrogenfluoride, malonic acid, methane, methanol, formic acid, chloromethane, fluoromethane, ammonia, nitrobutane, nitroethane, nitromethane, nitropropane, pentane, pentanal, pentanol, propane, propanal, propionamide, propanic acid, 1,1,2,2-tetrachloroethane, tetrachloromethane, 1,1,2,2-tetrafluoroethane, tetrafluoromethane, 1,1,1-trichloroethane, trichlorofluoromethane, trifluorochloromethane, 1,1,1-trifluoroethane, 1,2,3-trifluorobenzene, 1,2,3,4-tetrafluorobenzene, 1,2,3,5-tetrafluorobenzene, 1,2,4,5-tetrafluorobenzene, 1,3-dichlorotetrafluorobenzene, 1,3,5-trichlorobenzene, 1,3,5-trifluorobenzene, 2,3,5,6-tetrafluoro-1,4-dichlorobenzene, 2,3,5,6-ttrafluorochlorobenzene, 2,4,6-trifluorochlorobenzene, 2,5-difluoro-1,3-dichlorobenzene, 2,6-difluoro-1,4-

dichlorobenzene, 2,6-difluorochlorobenzene, 3,4,5-trifluorochlorobenzene, 3,5-difluorochlorobenzene, 4,5-difluoro-1,2-dichlorobenzene, 4,6-difluoro-1,3-dichlorobenzene, aniline, benzene, planer biphenyl, biphenyl, chlorobenzene, fluorobenzene, hexafluorobenzene, *m*-dichlorobenzene, *m*-difluorobenzene, nitrobenzene, *o*-dichlorobenzene, *o*-difluorobenzene, *p*-aminoaniline, *p*-dichlorobenzene, *p*-difluorobenzene, *p*-fluorochlorobenzene, *p*-dinitrobenzene, *p*-nitroaniline, pentafluorobenzene, pentafluorochlorobenzene, phenol, toluene.

(63) Note that it is *rms* that is presented in Tables 2 and 3 of eq 6 in ref 40.