2270 *J. Phys. Chem. A* **2003,** *107,* 2270−2276

A Dipole Interaction Model for the Molecular Second Hyperpolarizability

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Received: May 30, 2002; In Final Form: November 28, 2002

A dipole interaction model (IM) for calculating the molecular second hyperpolarizability, γ, of aliphatic and aromatic molecules has been investigated. The model has been parametrized from quantum chemical calculations of γ at the self-consistent field (SCF) level of theory for 72 molecules. The model consists of three parameters for each element p: an atomic polarizability, an atomic second hyperpolarizability, and an atomic parameter, Φ_p, describing the width of the atomic charge distribution. The Φ_p parameters are used for modeling the damping of the interatomic interactions. Parameters for elements H, C, N, O, F, and Cl were determined, and typical differences between the molecular γ derived from quantum chemical calculations and from the IM are below 30% and on average around 10%. As a preliminary test, the dipole interaction model was applied to the following molecular systems not included in the training set: the urea molecule, linear chains of urea molecules, and C_{60}. For these molecules deviations of the IM result for the molecular γ from the corresponding SCF value were at most around 30% for the individual components, which in all cases is a better performance than obtained with semiempirical methods.

I. Introduction

The current development of carbon-based functional materials holding a potential for future applications in electronics and photonics has sparked a revolution in materials science.[1,2] An important prospect is the utilization of the intensity dependence of the refractive index in all-optical switching devices, an essential element in future information processing technology.[1] Because the intensity dependence of the refractive index is governed by the third-order nonlinearity, materials with a large third-order optical susceptibility, $\chi^{(3)}$ (where the molecular second hyperpolarizability, γ, is the corresponding microscopic property), are suitable candidates for optical switching components.[1,3,4] These new materials are intended to be designed on a molecular scale and thus a detailed understanding of their electronic structure is indispensable. Therefore, it has been conjectured that applied quantum chemistry will play a central role in the development of such new nonlinear optical (NLO) materials.[5,6] Accordingly, γ has been investigated extensively both theoretically and experimentally for a variety of molecular systems including conjugated polymers,[7−22] near-infrared dyes,[23−25] fullerenes,[26−35] and nanotubes.[36,37]

Sophisticated quantum chemical methods can be applied only on rather small molecules, even though considerable effort has been devoted to calculate NLO properties at the SCF level for relatively large molecules such as fullerenes.[38] In addition, methods based on density-functional theory (DFT) are subject to problems in the calculation of molecular (hyper)polarizabilities, although some recent advances have been presented.[39,40] Hence, to a large extent modeling optical properties for large molecules and molecular clusters is restricted to less sophisticated methods. An example is the empirical Su−Schrieffer−Heeger model,[41,42] which has been applied to describe γ of conjugated polymers,[43] fullerenes,[44] and carbon nanotubes.[45−49]

It is of fundamental importance to seek suitable representations of the molecular electronic structure. A successful representation of a molecular response property, in terms of, for example, atomic parameters, provides an understanding of its behavior in addition to an often computationally attractive scheme for extrapolation to large systems. An example is the derivation of intermolecular potentials from molecular wave functions, which can be used for molecular dynamics simulations of liquids and solutions.[50]

Considering the isotropic part of the molecular polarizability, it has been known for a long time that to a good degree it can be described by an additive scheme, i.e., a summation of transferable atom- or bond-type parameters.[51,52] Also, recently, an additive scheme has been used for modeling the static polarizability tensor of organic molecules[53,54] and for the frequency-dependent polarizability tensor of halogen derivatives of benzene.[55] To model the anisotropy of the polarizability tensor within an additive scheme, however, also the atomic contributions have to be tensors, rendering the model less attractive due to the increased number of parameters thus introduced.

An alternative model, introduced by Silberstein[56] and to a large extent developed by Applequist and co-workers,[57,58] is the so-called dipole interaction model (IM). In this approach, a set of atomic polarizabilities, α, interact with each other according to classical electrostatics in the limit of a vanishing external electrical field. If the molecular α is modeled by a set of isotropic atomic polarizabilities, the anisotropy of the molecular α is introduced by the interatomic interactions. Consequently, the isotropic part of the molecular α to a large degree can be modeled by an additive model for atomic polarizabilities whereas its anisotropy is determined entirely by the geometrical arrangement of the atoms. Similarly, because the atomic first

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10.1021/jp026208j CCC: \$25.00

hyperpolarizability, β, is zero for almost all atoms, also the molecular β is entirely determined by the interatomic interactions.[59] In fact, the leading term in the IM for β arises from atomic dipole−quadrupole hyperpolarizabilities.[60] Considering the molecular γ, the components $\gamma_{\alpha\alpha\alpha\alpha}$ and $\gamma_{\alpha\alpha\beta\beta}$ (α, $\beta = x$, y, or z) are nonzero for atoms,[59] and consequently, these components may to a large degree be modeled by an additive model.[61] To model the molecular β is thus in principle as difficult as calculating the anisotropies of α and γ.

Dipole interaction models have been used extensively, in particular to model the polarizability.[62−66] In addition, we have recently studied the polarizability of carbon nanotubes,[67] boron nitride nanotubes,[68] and fullerene clusters.[69] Examples of other molecular properties studied by the IM include optical rotation,[70,71] Raman scattering,[72,73] absorption,[74,75] circular dichroism,[76,77] and hyperpolarizabilities.[60,78,79] Generalized dipole interaction models for electronic polarization have also been discussed.[58,80]

From a computational point of view the IM is very attractive because computational times are many orders of magnitude smaller than the corresponding quantum chemical methods. The approximations posed by the IM are at the same level as in accurate force field calculations used to derive intermolecular interaction energies, even though interactions within a molecule are considered here.

An important extension of the IM for the molecular polarizability is the inclusion of a damping term for the interatomic interactions.[81,82] In particular, the Thole model has been investigated in detail,[83,84] and recently a new model for the damping was investigated that improved the IM considerably.[69] In the present work, we extend this approach to an IM for the molecular γ and present some initial applications.

II. Theory

The molecular response to an external electric field, E^{ext}_{β}, may be written in terms of an induced molecular dipole moment, $\mu^{\text{ind}}_{\alpha}$, as[59,85]

$$\mu^{\text{ind}}_{\alpha} = \alpha_{\alpha\beta}E^{\text{ext}}_{\beta} + \frac{1}{2}\beta_{\alpha\beta\gamma}E^{\text{ext}}_{\gamma}E^{\text{ext}}_{\beta} + \frac{1}{6}\gamma_{\alpha\beta\gamma\delta}\, E^{\text{ext}}_{\delta}E^{\text{ext}}_{\gamma}E^{\text{ext}}_{\beta} + \ldots \tag{1}$$

where $\alpha_{\alpha\beta}$ is the molecular polarizability, $\beta_{\alpha\beta\gamma}$ is the molecular first hyperpolarizability, and $\gamma_{\alpha\beta\gamma\delta}$ is the molecular second hyperpolarizability with (α, β, γ, δ) designating Cartesian coordinates. In eq 1 and elsewhere in this paper, the Einstein summation convention for repeated indices is employed. For a set of N atom-like interacting particles, we may write the induced atomic dipole moment, $\mu^{\text{ind}}_{i,\alpha}$ as

$$\mu^{\text{ind}}_{i,\alpha} = \alpha_{i,\alpha\beta}E^{\text{tot}}_{i,\beta} + \frac{1}{6}\,\gamma_{i,\alpha\beta\gamma\delta}\, E^{\text{tot}}_{i,\delta}E^{\text{tot}}_{i,\gamma}E^{\text{tot}}_{i,\beta} \tag{2}$$

where $\alpha_{\mathrm{i},\alpha\beta}$ is the polarizability and $\gamma_{\mathrm{i},\alpha\beta\gamma\delta}$ is the second hyperpolarizability of atom i. The total electric field at atom i, $E^{\text{tot}}_{i,\beta}$, is given by the external field and the electric fields from all other atoms as

$$E^{\text{tot}}_{i,\beta} = E^{\text{ext}}_{\beta} + \sum_{j\neq i}^{N} T^{(2)}_{ij,\beta\gamma}\mu^{\text{ind}}_{j,\gamma} \tag{3}$$

where $T^{(2)}_{ij,\beta\gamma}$ is the so-called interaction tensor given as

$$T^{(2)}_{ij,\beta\gamma} = \frac{3R_{ij,\beta}R_{ij,\gamma}}{{R_{ij}}^{5}} - \frac{\delta_{\beta\gamma}}{{R_{ij}}^{3}} \tag{4}$$

$R_{ij,\beta}$ is a component of the distance vector and R_{ij} is the distance between atoms i and j. We have not included an atomic β in eq 2 because β is zero for spherically symmetric particles. Similarly, the same symmetry properties are assumed for the atomic α,

$$\alpha_{i,\alpha\beta} = \alpha_{i}\delta_{\alpha\beta} \tag{5}$$

and the atomic γ,[59]

$$\gamma_{i,\alpha\beta\gamma\delta} = \frac{1}{3}\gamma_{i}(\delta_{\alpha\beta}\delta_{\gamma\delta} + \delta_{\alpha\gamma}\delta_{\beta\delta} + \delta_{\beta\gamma}\delta_{\alpha\delta}) \tag{6}$$

where $\delta_{\alpha\beta}$ is the usual Kroenecker delta function.

Alternatively, if the electric field at each atom is regarded as an independent variable, the atomic induced dipole moment may be expanded in terms of relay tensors in a Taylor expansion as[86]

$$\mu^{\text{ind}}_{i,\alpha} = \sum_{j}^{N}\mathcal{B}^{(2)}_{ij,\alpha\beta}E^{\text{ext}}_{j,\beta} + \frac{1}{2}\sum_{j,k}^{N}\mathcal{B}^{(3)}_{ijk,\alpha\beta\gamma}E^{\text{ext}}_{k,\gamma}E^{\text{ext}}_{j,\beta} + \frac{1}{6}\sum_{j,k,l}^{N}\mathcal{B}^{(4)}_{ijkl,\alpha\beta\gamma\delta}E^{\text{ext}}_{l,\delta}E^{\text{ext}}_{k,\gamma}\,E^{\text{ext}}_{j,\beta} + \ldots \tag{7}$$

where the n-atom relay tensor $\mathcal{B}^{(n)}_{i_1 i_2\ldots i_n,\alpha_1\alpha_2\ldots\alpha_n}$ is defined as

$$\mathcal{B}^{(n)}_{i_1 i_2\ldots i_n,\alpha_1\alpha_2\ldots\alpha_n} = \frac{\partial^{(n-1)}\mu^{\text{ind}}_{i_1,\alpha_1}}{\partial E^{\text{ext}}_{\mathrm{i}_2,\alpha_2}\ldots\partial E^{\text{ext}}_{i_{\mathrm{n}},\alpha_n}} \tag{8}$$

in the limit of vanishing external fields. The molecular induced dipole moment, $\mu^{\text{ind}}_{\alpha}$, is simply the sum of the atomic induced dipole moments in eq 7, and if it is furthermore assumed that the external field is homogeneous, i.e., $E^{\text{ext}}_{j,\beta} = E^{\text{ext}}_{\beta}$ for all j, we have

$$\mu^{\text{ind}}_{\alpha} = \Big(\sum_{i,j}^{N}\mathcal{B}^{(2)}_{ij,\alpha\beta}\Big)E^{\text{ext}}_{\beta} + \frac{1}{2}\Big(\sum_{i,j,k}^{N}\mathcal{B}^{(3)}_{ijk,\alpha\beta\gamma}\Big)E^{\text{ext}}_{\gamma}E^{\text{ext}}_{\beta} + \frac{1}{6}\Big(\sum_{i,j,k,l}^{N}\mathcal{B}^{(4)}_{ijkl,\alpha\beta\gamma\delta}\Big)E^{\text{ext}}_{\delta}E^{\text{ext}}_{\gamma}E^{\text{ext}}_{\beta} + \ldots \tag{9}$$

By comparison of eqs 1 and 9, the molecular (hyper)-polarizabilities may be identified. The two-atom relay tensor, $\mathcal{B}^{(2)}_{ij,\alpha\beta}$, may be obtained from the regular approach for a dipole interaction model for the molecular polarizability as

$$\mathcal{B}^{(2)}_{ij,\alpha\beta} = \alpha_{i,\alpha\gamma}\Big(\delta_{ij}\delta_{\gamma\beta} + \sum_{k\neq i}^{N} T^{(2)}_{ik,\gamma\delta}\,\mathcal{B}^{(2)}_{kj,\delta\beta}\Big) \tag{10}$$

which in supermatrix notation is cast into[57,82]

$$\mathcal{B}^{(2)} = (\boldsymbol{\alpha}^{-1} - \mathbf{T}^{(2)})^{-1} \tag{11}$$

The three- and four-atom relay tensors can be obtained by the scheme devised by Sundberg.[86] The four-atom relay tensor is defined as

$$\mathcal{B}^{(4)}_{ijkl,\alpha\beta\gamma\delta} = \frac{\partial^{3}\mu^{\text{ind}}_{i,\alpha}}{\partial\, E^{\text{ext}}_{j,\beta}\partial E^{\text{ext}}_{k,\gamma}\partial E^{\text{ext}}_{l,\delta}} \tag{12}$$

which is obtained by differentiating eq 2. As demonstrated in Appendix A, the four-atom relay tensor for a system of spherically symmetric particles may be written as

$$\mathcal{B}^{(4)}_{ijkl,\alpha\beta\gamma\delta} = \sum_{m}^{N} \gamma_{m,\lambda\mu\nu\xi} \tilde{\mathcal{B}}^{(2)}_{ml,\xi\delta} \tilde{\mathcal{B}}^{(2)}_{mk,\nu\gamma} \tilde{\mathcal{B}}^{(2)}_{mj,\mu\beta} \tilde{\mathcal{B}}^{(2)}_{mi,\lambda\alpha} \qquad (13)$$

where $\tilde{\mathcal{B}}^{(2)}_{ij,\alpha\beta}$ is defined as

$$\tilde{\mathcal{B}}^{(2)}_{ij,\alpha\beta} = \delta_{ij}\delta_{\alpha\beta} + \sum_{k\neq i}^{N} T^{(2)}_{ik,\alpha\gamma} \mathcal{B}^{(2)}_{kj,\gamma\beta} \qquad (14)$$

Because the electronic charge distribution is smeared out, the electric field at a nucleus will be damped by the charge distribution.[81,82] The damping may be modeled by modifying the distance R_{ij} to obtain a scaled distance S_{ij},[69]

$$S_{ij} = v_{ij} R_{ij} = f(R_{ij}) \qquad (15)$$

where v_{ij} is a scaling factor and $f(R_{ij})$ is an appropriately chosen function of R_{ij}. Furthermore, if each component of R_{ij} also is scaled by v_{ij}, the reduced distance becomes

$$S_{ij} = \sqrt{S_{ij,\alpha} S_{ij,\alpha}} = v_{ij}\sqrt{R_{ij,\alpha} R_{ij,\alpha}} = v_{ij} R_{ij} \qquad (16)$$

consistent with the definition in eq 15. The damped interaction can thus be obtained by modifying the interaction tensors only,

$$T^{(n)}_{ij,\alpha_1\ldots\alpha_n} = \nabla_{\alpha_1}\ldots\nabla_{\alpha_n}\left(\frac{1}{S_{ij}}\right) \qquad (17)$$

which is equivalent to replacing R_{ij} by S_{ij} and $R_{ij,\alpha}$ by $S_{ij,\alpha}$ in the regular formulas for the interaction tensor. The form of the scaling function employed here is[69]

$$f(R_{ij}) = \sqrt{{R_{ij}}^2 + \frac{\pi}{4a_{ij}}} \qquad (18)$$

where a_{ij} is given by $a_{ij} = \Phi_i\Phi_j/(\Phi_i + \Phi_j)$ and Φ_i is the damping parameter for atom i. This particular form of the scaling function was obtained by approximating the interaction between two Gaussian charge distributions on atoms i and j with exponents Φ_i and Φ_j.

III. Quantum Chemical Calculations

To obtain highly accurate values of γ, it is necessary to consider both electron correlation and large basis sets with many diffuse functions.[87−91] Because the aim of this work has been to investigate a dipole interaction model for γ, the quantum chemical computations have been invoked at the SCF level using the Dalton program package,[92] as described in refs 93 and 94. The polarization basis set by Sadlej[95] is used because it has been shown previously that it gives reasonable results for (hyper)polarizabilities considering its limited size[55,91,96−98] and further is consistent with our previous work on the molecular polarizability.[69] Obviously, the choice of method will affect the results and in particular the ratio between tensor components. For example, the out-of-plane component, γ_{zzzz}, for benzene is, unrealistically, larger than the in-plane component, γ_{xxxx}, obtained with the Sadlej basis set at the SCF level. This is due to the fact that the basis set is tailored to describe the dipole moment and polarizability by including the first-order polarized functions, whereas a highly accurate description of γ also requires second-order polarized functions.[91,96]

In the present work, the SCF calculations of the γ tensor have been restricted to the components contributing to the average γ,

$$\bar{\gamma} = \frac{1}{15}\sum_{\alpha,\beta} \gamma_{\alpha\alpha\beta\beta} + \gamma_{\alpha\beta\alpha\beta} + \gamma_{\alpha\beta\beta\alpha} \qquad (19)$$

and we have carried out SCF calculations for 72 molecules[99] adopting standard bond lengths and angles taken from refs 100 and 101. Geometries of molecules not included in the training set, i.e., urea, linear chains of urea molecules, and C_{60} are all taken from ref 69. We will in this work use atomic units (au) for γ but the conversion factor to cgs units is 1 au = 5.03670 × 10^{-40} esu. The molecular geometries are available from ref 69 and the quantum chemical molecular γ are made available as Supporting Informations.

IV. Optimization Procedure

The parameters describing γ have been optimized by minimizing the root-mean-square, rms, of the difference between the components of the SCF tensor, $\gamma^{\mathrm{SCF}}_{\alpha\beta\gamma\delta,n}$, and the IM tensor, $\gamma^{\mathrm{IM}}_{\alpha\beta\gamma\delta,n}$, as

$$\mathrm{rms} = \sqrt{\frac{\sum_{n=1}^{N}\sum_{\alpha,\beta,\gamma,\delta}(\gamma^{\mathrm{IM}}_{\alpha\beta\gamma\delta,n} - \gamma^{\mathrm{SCF}}_{\alpha\beta\gamma\delta,n})^2}{N-1}} \qquad (20)$$

where N is the number of molecules in the training set. It should be noted that in the second sum in eq 20, only components have been included which contribute to $\bar{\gamma}$ in eq 19, implying that the sum includes in total 21 terms per molecule.

V. Results

A. Optimization of the Training Set. We have performed in all two types of optimizations: The parameters in the first optimization (A) have been obtained by optimizing the atomic γ_p, keeping the atomic polarizabilities, α_p, and damping parameters, Φ_p, constant. In the second optimization (B), also the Φ_p parameters were optimized. A third optimization was tried in which all parameters, i.e., α_p, Φ_p, and γ_p, were optimized. This gave only a small improvement in the results compared with the second optimization, although one extra parameter was included for each element. For this reason this optimization was not considered in more detail. The values of α_p used in (A) and (B) and Φ_p used in (A) are taken from a previous study[69] where the parameters were optimized to describe the molecular polarizability for 187 molecules in a similar fashion. The 72 molecules of the present study were among these 187 molecules. The optimized parameters describing the molecular γ are presented in Table 1 and the results from (A) and (B) displayed in Figures 1 and 2, respectively, where the SCF components have been plotted against the corresponding IM tensor components.

A reasonable description of the molecular γ is obtained by procedure (A) by using only one additional parameter per element, γ_p (see Table 1). However, large deviations are found for the aromatic molecules in the γ components perpendicular to the ring. These components have been singled out in Figure 1. The ratios between the diagonal components in the plane ($\gamma_{xxxx} = \gamma_{\mathrm{ip}}$) and perpendicular to the plane ($\gamma_{zzzz} = \gamma_{\perp}$) in the IM are determined by the interactions between the atoms. At small distances the interatomic interactions, and therefore also

TABLE 1: Atomic Parameters Fitted to Model the Static Second Hyperpolarizability (in au)

	(A)			(B)		
atom	α_p[a]	Φ_p[a]	γ_p	α_p[a]	Φ_p	γ_p
H	1.280	0.358	350.309	1.280	0.0909	-211.0525
C	8.465	0.124	233.335	8.465	0.0211	2194.3233
N	6.169	0.269	111.169	6.169	0.0499	888.8899
O	3.754	4.103	-80.050	3.754	14.4795	-233.4550
F	1.907	1.468	-49.390	1.907	2.0271	-1666.8621
Cl	13.081	0.453	732.170	13.081	0.2921	820.2538
rms[b]		8971.54			4434.98	
mean abs dev in $\bar{\gamma}^c$ (%)		18.57			12.70	
mean abs dev in $\gamma_{\alpha\beta\gamma\delta}$ (%)		38.15			21.44	

[a] Parameters taken from ref 69 (not optimized). [b] Optimized error. [c] $\bar{\gamma} = {}^1/_{15}\sum_{\alpha\beta} \gamma_{\alpha\alpha\beta\beta} + \gamma_{\alpha\beta\alpha\beta} + \gamma_{\alpha\beta\beta\alpha}$.

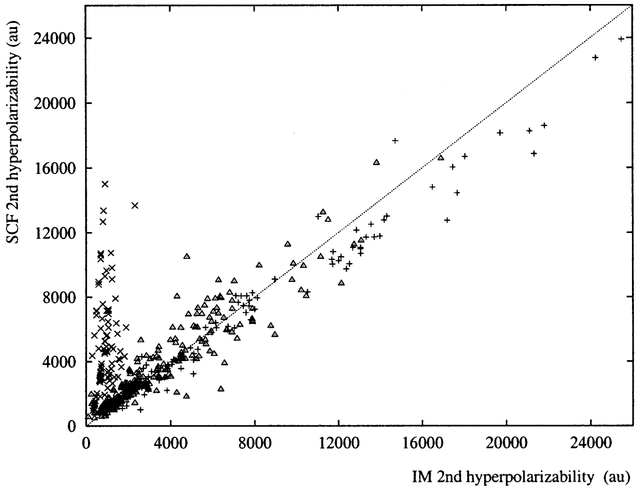

Figure 1. Comparison between the second hyperpolarizability tensor components obtained with the IM and with the SCF/Sadlej method. IM results obtained with parameters from (A) (only γ_p is optimized). (△) indicates aliphatic molecules, and (+, ×), aromatic molecules, respectively. For the aromatic molecules tensor components with an axis perpendicular to the ring are displayed with (×) and other components with (+).

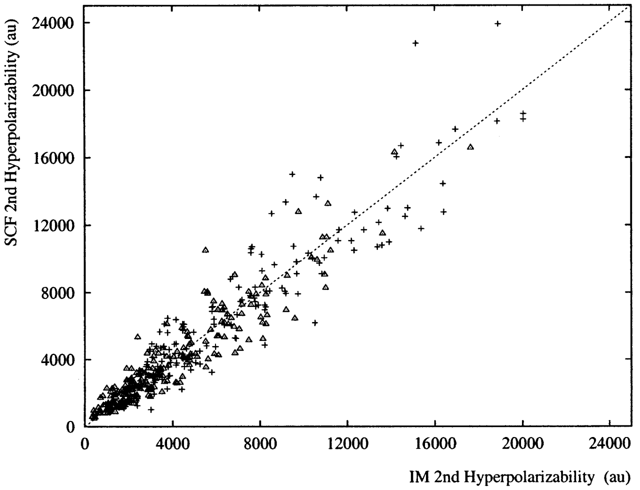

Figure 2. Comparison between the second hyperpolarizability tensor components obtained with the IM and with the SCF/Sadlej method. IM results obtained with parameters from (B) (γ_p and Φ_p are optimized). (△) indicates aliphatic molecules, and (+), aromatic molecules, respectively.

the ratio $\gamma_{ip}/\gamma_\perp$, is determined to a large extent by the damping. In the limit of infinitely large damping, i.e., infinitely small Φ_p parameters, the model becomes additive and the γ_{ip} and $\gamma_\perp$ components are identical. If the SCF/Sadlej results for benzene are considered, the ratio $\gamma_{ip}/\gamma_\perp$ is nearly unity whereas the ratio between the polarizability components, $\alpha_{ip}/\alpha_\perp$, is about 2. Therefore, to predict $\gamma_\perp$ for aromatic compounds, the damping of the interactions has to be modified as compared to a description for polarizability only. The limitations pertinent to the IM for describing the polarizability of π-conjugated systems correctly have been discussed elsewhere[102] as also the importance of damping in predicting the polarizability component perpendicular to the ring.[69,103] On the other hand, in a theoretical study of benzene including electron correlation and a larger basis set, it is found that γ_{ip} is around 40% larger than $\gamma_\perp$.[89]

To improve the description of $\gamma_\perp$ for the aromatic molecules, a second optimization (B) was carried out where also Φ_p was included in the optimization. From the results in Table 1 and Figure 2, it is clear that a substantial improvement in reproducing the SCF/Sadlej results is obtained. The rms is reduced by a factor of 2 and also the mean absolute deviation in the γ components is reduced by nearly a factor of 2. In addition, and foremost, from Figure 2 it is seen that the description of $\gamma_\perp$ for the aromatic molecules is improved considerably. As a consequence, the values of the atomic parameters have also changed considerably. As expected, the damping parameters, except for O and F, are much smaller than the parameters used in (A). The reason that parameters for O and F still are large is that the damping term, $1/a_{ij}$, can be written as $1/a_{ij} = 1/\Phi_i + 1/\Phi_j$, and therefore is dominated by the smallest parameters. The contribution to the damping from Φ_F and Φ_O are thus small and accordingly these parameters are not well determined in the optimization.

Because optimization procedure (A) and (B) utilize identical α_p (previously optimized to reproduce molecular SCF polarizabilities[69]), the stronger damping enforced by procedure (B) implies that the molecular α and γ cannot both be well described using the parameters of optimization (B). Furthermore, for this reason it is not possible to obtain a good description of both the molecular α and γ by, e.g., optimizing all the parameters. The molecular α derived from IM parameters of optimization (B) become almost nearly isotropic due to exaggerated damping (in terms of describing polarizabilities). Using the benzene molecule as an example, the ratio $\alpha_{ip}/\alpha_\perp$ is 1.1 calculated with the IM and 1.8 with the SCF/Sadlej method. However, the mean polarizability predicted with the IM is still within 15% of the SCF/Sadlej results.

Optimization procedure (B) also implies large changes for the γ_p parameters, and in general, they become larger. Because the interatomic interactions are more strongly damped in (B), larger γ_p parameters are necessary to describe the same molecular γ. If the γ_p values from (B) are compared with the results obtained from an additive model for $\bar{\gamma}$,[61] good agreement is found with respect to both the sign and magnitude of the parameters. This again reflects the stronger damping obtained

TABLE 2: Static Second Hyperpolarizability of Urea (in au)[a]

	IM	SCF/Sadlej[a]	MNDO[a]	PM3[a]
γ_{xxxx}	3537.84	4447.95	16956.47	2960.25
γ_{yyyy}	2922.62	4095.59	7317.23	−89.80
γ_{zzzz}	2424.22	3380.39	41.69	11.23
γ_{xxyy}	1096.38	1576.34	5126.71	1335.80
γ_{xxzz}	979.22	1622.84	341.57	4.81
γ_{yyzz}	899.92	1582.75	112.25	205.26
$\bar{\gamma}$	2967.15	4296.04	7095.93	1194.68

[a] *Y* axis parallel to the C−O bond, *X* axis perpendicular to this bond but in the plane, and *Z* axis perpendicular to the molecular plane. For the IM calculation, parameters from (*B*) were used. [a] Taken from ref 104.

for the parameters in (B). In addition, in contrast to (A), the magnitude of γ_H is smaller than γ_C, which is to be expected from the small number of electrons in H.

The IM has previously been used to model the experimental $\bar{\gamma}$ of a set of 16 small haloalkanes,[79] but this work differs in several ways, and a detailed comparison will not be sought. In terms of comparison with experimental data the IM is subject to the same limitations as the ab initio methods from which the parameters are derived; i.e., standard SCF derivations of γ do not include vibrational contributions and various solvent-induced effects. Also, the present study addresses γ in the static limit only, and a proper comparison with experiment will require the dispersion to be evaluated as well. In a previous study of α, the IM was extended to include the frequency dependence,[84] and a similar approach for γ may be adopted.

B. Test on Molecules Not in the Training Set. As a test of the model, we have also performed calculations for some molecules that were not included in the training set, i.e. urea, linear chains of urea molecules, and the fullerene C_{60}. The reason for choosing these molecules is the large body of studies using both semiempirical and first-principle methods thus allowing for comparisons on equal levels of theory. For the urea chains there has only been an ab initio study of the dimer and trimer.[105] The larger chains have been included to illustrate the effects of increasing the chain length.

The results for the urea molecule are presented in Table 2 and compared with ab initio and semiempirical results taken from ref 104. The γ tensor components calculated with the IM are between 20 and 40% lower than the corresponding SCF values yielding a $\bar{\gamma}$ that is 30% too low as compared with the SCF results. However, the general agreement between the IM and SCF methods are better than the agreement between semiempirical and SCF methods. For semiempirical methods, in particular, the components with an axis perpendicular to the plane are underestimated.

In Table 3, γ for linear chains of urea molecules with an increasing number of molecules in the chain, along with its deviation from molecular additivity are presented. We find that γ parallel to the chain increases more than expected from an additive model with increasing chain length, whereas, perpendicular to the chain, γ decreases as expected from an additive model. The largest deviation from additivity is found for the component parallel to the chain, and it is around 35%. For $\bar{\gamma}$, the deviation is only about 3%. The results for the urea chains are in agreement with ab initio results found elsewhere for the urea dimer and trimer;[105] however, a larger deviation from additivity was observed in that study.

Results for C_{60} are presented in Table 4 and are compared with semiempirical and quantum-chemical calculations of γ. A comparison with experiment is difficult due to large differences in the experimental results[106−108] but also because we in this work have neglected vibrational, dispersion, and solvent effects. We find good agreement between the IM results and the quantum chemical results. The IM value of 132 044 au is 16% larger than the SCF result of 113 765 au[107] and 7% larger than the DFT result of 124 000 au,[109] respectively. The semiempirical results[34,110,111] are in good agreement with each other but are about 50% smaller than the SCF result.

VI. Conclusion

In this work, we have investigated and parametrized a model for the molecular γ tensor of aliphatic and aromatic molecules based on a dipole interaction model. The model consists of three parameters for each element: an atomic polarizability, an atomic second hyperpolarizability, and a parameter, Φ_p, describing the damping of the interatomic interactions. By utilizing atomic polarizabilities and damping parameters obtained in a previous study of the molecular polarizability, we demonstrated that γ is modeled reasonably well with only one extra parameter per element. However, for the aromatic molecules the components perpendicular to the ring are underestimated as compared to the SCF calculations. This was corrected by additionally optimizing the damping parameters. Preliminary application of the model to urea, linear chains of urea molecules, and C_{60}, in general shows good agreement with SCF results and clearly illustrates the usefulness of the interaction model to model γ for large molecules and molecular aggregates.

Acknowledgment. L.J. gratefully acknowledges The Danish Research Training Council for financial support. K.O.S. is indebted to Ørsted∗DTU, Electromagnetic Systems, DTU for providing computational resources. K.V.M. thanks Statens Naturvidenskabelige Forskningsråd (SNF), Statens Teknisk-Videnskabelige Forskningsråd (STVF), Danish Center for Scientific Computing and the EU-network: MOLPROP for support.

Supporting Information Available: Tables containing the quantum chemical molecular γ tensor for the 72 molecules studied in this work. This material is available free of charge via the Internet at http://pubs.acs.org.

TABLE 3: Static Second Hyperpolarizability (in au) of Linear Urea Chains Calculated with the IM Using (B) Parameters[a]

N[b]	1	2	4	6	8	10
γ_{xxxx}	3537.84	6631.92 (−6.3)	12642.51 (−10.7)	18602.53 (−12.4)	24548.19 (−13.3)	30487.78 (−13.8)
γ_{yyyy}	2922.62	6618.94 (13.2)	14672.84 (25.5)	22965.15 (31.0)	31324.29 (34.0)	39709.98 (35.9)
γ_{zzzz}	2424.22	4578.63 (−5.6)	8781.06 (−9.4)	12952.30 (−11.0)	17114.64 (−11.8)	21273.21 (−12.2)
γ_{xxyy}	1096.38	2281.60 (4.1)	4712.26 (7.5)	7162.60 (8.9)	9618.31 (9.7)	12076.16 (10.1)
γ_{xxzz}	979.22	1843.23 (−5.9)	3525.13 (−10.0)	5193.71 (−11.6)	6858.48 (−12.4)	8521.66 (−13.0)
γ_{yyzz}	899.92	1880.89 (4.5)	3896.91 (8.3)	5930.62 (9.8)	7969.17 (10.7)	10009.65 (11.2)
$\bar{\gamma}$	2967.15	5968.19 (0.6)	12073.00 (1.7)	18218.76 (2.3)	24375.81 (2.7)	30537.18 (2.9)

[a] Percent deviation from additivity in parentheses. *Y* axis along the chain, *X* axis perpendicular to the chain but in the plane, and *Z* axis perpendicular to the molecular plane. [b] Number of urea molecules in chain.

TABLE 4: Mean Static Second Hyperpolarizability for C_{60} (in au)[a]

Method	$\bar{\gamma}$	ref
IM	132044	This work
LDA	124000	109
SCF	113765	107
PM3	49834	111
SOS−VEH	49040	34
INDO	58967	110

[a] IM results calculated using (B) parameters.

Appendix A. Four-Atom Relay Tensor

The four-atom relay tensor, $\mathscr{B}^{(4)}_{ijkl,\alpha\beta\gamma\delta}$, is obtained from eq 12,

$$\mathscr{B}^{(4)}_{ijkl,\alpha\beta\gamma\delta} = \frac{\partial^3 \mu^{\rm ind}_{i,\alpha}}{\partial E^{\rm ext}_{j,\beta}\partial E^{\rm ext}_{k,\gamma}\partial E^{\rm ext}_{l,\delta}} \qquad \text{(A1)}$$

by differentiating the atomic induced dipole moment, $\mu^{ind}_{i,\alpha}$, in eq 2,

$$\mu^{\rm ind}_{i,\alpha} = \alpha_{i,\alpha\beta}E^{\rm tot}_{i,\beta} + \frac{1}{6}\gamma_{i,\alpha\beta\gamma\delta}E^{\rm tot}_{i,\delta}E^{\rm tot}_{i,\gamma}E^{\rm tot}_{i,\beta} \qquad \text{(A2)}$$

repeatedly with respect to the external field, $E^{\rm ext}_{i,\alpha}$. The straightforward approach is to adopt partial differentiation by noting that the total electric field, $E^{\rm tot}_{i,\alpha}$ in eq 3,

$$E^{\rm tot}_{i,\alpha} = E^{\rm ext}_{i,\alpha} + \sum_{j\neq i}^{N} T^{(2)}_{ij,\alpha\beta}\mu^{\rm ind}_{j,\beta} \qquad \text{(A3)}$$

may be differentiated with respect to the external field as

$$\frac{\partial E^{\rm tot}_{i,\alpha}}{\partial E^{\rm ext}_{k,\gamma}} = \delta_{ik}\delta_{\alpha\gamma} + \sum_{j\neq i}^{N} T^{(2)}_{ij,\alpha\beta}\mathscr{B}^{(2)}_{jk,\beta\gamma} \qquad \text{(A4)}$$

which we in eq 14 denoted as $\tilde{\mathscr{B}}^{(2)}_{ik,\alpha\gamma}$. Furthermore,

$$\frac{\partial^2 E^{\rm tot}_{i,\alpha}}{\partial E^{\rm ext}_{k,\gamma}\partial E^{\rm ext}_{l,\delta}} = \sum_{j\neq i}^{N} T^{(2)}_{ij,\alpha\beta}\mathscr{B}^{(3)}_{jkl,\beta\gamma\delta} \qquad \text{(A5)}$$

which is denoted as $\tilde{\mathscr{B}}^{(3)}_{ikl,\alpha\gamma\delta}$, and

$$\frac{\partial^3 E^{\rm tot}_{i,\alpha}}{\partial E^{\rm ext}_{k,\gamma}\partial E^{\rm ext}_{l,\delta}\partial E^{\rm ext}_{m,\epsilon}} = \sum_{j\neq i}^{N} T^{(2)}_{ij,\alpha\beta}\mathscr{B}^{(4)}_{jklm,\beta\gamma\delta\epsilon} \qquad \text{(A6)}$$

which is denoted as $\tilde{\mathscr{B}}^{(4)}_{iklm,\alpha\gamma\delta\epsilon}$. Repeated differentiation yields

$$\begin{aligned}\mathscr{B}^{(4)}_{ijkl,\alpha\beta\gamma\delta} = {} & \gamma_{i,\alpha\lambda\mu\nu}\tilde{\mathscr{B}}^{(2)}_{ij,\lambda\beta}\tilde{\mathscr{B}}^{(2)}_{ik,\mu\gamma}\tilde{\mathscr{B}}^{(2)}_{il,\nu\delta} + \Big(\alpha_{i,\alpha\lambda} + {}\\ & \frac{1}{2}\gamma_{i,\alpha\lambda\mu\nu}E^{\rm tot}_{i,\nu}E^{\rm tot}_{i,\mu}\Big)\tilde{\mathscr{B}}^{(4)}_{ijkl,\lambda\beta\gamma\delta} + \gamma_{i,\alpha\lambda\mu\nu}E^{\rm tot}_{i,\nu}(\tilde{\mathscr{B}}^{(3)}_{ijk,\mu\beta\gamma}\tilde{\mathscr{B}}^{(2)}_{il,\lambda\delta} + {}\\ & \tilde{\mathscr{B}}^{(3)}_{ijl,\mu\beta\delta}\tilde{\mathscr{B}}^{(2)}_{ik,\lambda\gamma} + \tilde{\mathscr{B}}^{(3)}_{ikl,\mu\gamma\delta}\tilde{\mathscr{B}}^{(2)}_{ij,\lambda\beta}) \qquad \text{(A7)}\end{aligned}$$

Because $\tilde{\mathscr{B}}^{(4)}_{ijkl,\lambda\beta\gamma\delta}$ contains $\mathscr{B}^{(4)}_{mjkl,\epsilon\beta\gamma\delta}$, eq A7 is recast in noniterative form as

$$\begin{aligned}\mathscr{B}^{(4)}_{mjkl,\epsilon\lambda\mu\nu} = {} & \sum_i(\gamma_{i,\alpha\beta\gamma\delta}\tilde{\mathscr{B}}^{(2)}_{il,\delta\nu}\tilde{\mathscr{B}}^{(2)}_{ik,\gamma\mu}\tilde{\mathscr{B}}^{(2)}_{ij,\beta\lambda}\tilde{\mathscr{B}}^{(2)}_{im,\alpha\epsilon} + {}\\ & \gamma_{i,\alpha\beta\gamma\delta}E^{\rm tot}_{i,\delta}\tilde{\mathscr{B}}^{(2)}_{im,\alpha\epsilon}(\tilde{\mathscr{B}}^{(2)}_{ij,\beta\lambda}\tilde{\mathscr{B}}^{(3)}_{ikl,\gamma\mu\nu} + \tilde{\mathscr{B}}^{(2)}_{ik,\beta\mu}\tilde{\mathscr{B}}^{(3)}_{ijl,\gamma\lambda\nu} + {}\\ & \tilde{\mathscr{B}}^{(2)}_{il,\beta\nu}\tilde{\mathscr{B}}^{(3)}_{ijk,\gamma\lambda\mu})) \qquad \text{(A8)}\end{aligned}$$

which apart from notation and definitions is equivalent to the four-atom relay tensor given by Sundberg.[86] For a system of (hyper)polarizabilities the total field, $E^{\rm tot}_{i,\beta}$, vanishes when the external field, $E^{\rm ext}_{i,\beta}$ approaches zero, and thus the second term in eq A8 vanishes and the final result for the four-atom relay tensor becomes

$$\mathscr{B}^{(4)}_{mjkl,\epsilon\lambda\mu\nu} = \sum_i \gamma_{i,\alpha\beta\gamma\delta}\tilde{\mathscr{B}}^{(2)}_{il,\delta\nu}\tilde{\mathscr{B}}^{(2)}_{ik,\gamma\mu}\tilde{\mathscr{B}}^{(2)}_{ij,\beta\lambda}\tilde{\mathscr{B}}^{(2)}_{im,\alpha\epsilon} \qquad \text{(A9)}$$

References and Notes

(1) Prasad, P. N.; Williams, D. J. *Introduction to nonlinear optical effects in molecules and polymers*; Wiley: New York, 1991.

(2) Jortner, J., Ratner, M., Eds. *Molecular Electronics*; Blackwell Science: Oxford, U.K., 1997.

(3) Kanis, D. R.; Ratner, M. A.; Marks, T. J. *Chem. Rev.* **1994**, *94*, 195−242.

(4) Brédas, J. L.; Adant, C.; Tackx, P.; Persoons, A.; Pierce, B. M. *Chem. Rev.* **1994**, *94*, 243−278.

(5) Karna, S. P. *J. Phys. Chem. A* **2000**, *104*, 4671−4673.

(6) Bernholc, J. *Phys. Today* **1999**, 30−35.

(7) Sauteret, C.; Herrmann, J.-P.; Frey, R.; Pradère, F.; Ducuing, J.; Baughman, R. H.; Chance, R. R. *Phys. Rev. Lett.* **1976**, *36*, 956−959.

(8) Agrawal, G. P.; Cojan, C.; Flytzanis, C. *Phys. Rev. B* **1978**, *17*, 776−789.

(9) Wu, W. *Phys. Rev. Lett.* **1988**, *61*, 1119−1122.

(10) Heflin, J. R.; Wong, K. Y.; Zamani-Khamiri, O.; Garito, A. F. *Phys. Rev. B* **1988**, *38*, 1573−1576.

(11) Sinclair, M.; Moses, D.; Akagi, K.; Heeger, A. J. *Phys. Rev. B* **1988**, *38*, 10724−10733.

(12) Fann, W.-S.; Benson, S.; Madey, J. M. J.; Etemad, S.; Baker, G. L.; Kajzar, F. *Phys. Rev. Lett.* **1989**, *62*, 1492−1495.

(13) Thienpont, H.; Rikken, G. L. J. A.; Meijer, E. W.; ten Hoeve, W.; Wynberg, H. *Phys. Rev. Lett.* **1990**, *65*, 2141−2144.

(14) Karna, S. P.; Talapatra, G. B.; Wijekoon, W. M. K. P.; Prasad, P. N. *Phys. Rev. A* **1992**, *45*, 2763−2770.

(15) Wautelet, P.; Moroni, M.; Oswald, L.; Le Moigne, J.; Pham, A.; Bigot, J.-Y.; Luzzati, S. *Macromolecules* **1996**, *29*, 446−455.

(16) Weder, C.; Wrighton, M. S.; Spreiter, R.; Bosshard, C.; Günther, P. *J. Phys. Chem.* **1996**, *100*, 18931−18936.

(17) Lu, D.; Marten, B.; Ringnalda, M.; Friesner, R. A.; Goddard, W. A., III. *Chem. Phys. Lett.* **1996**, *257*, 224−228.

(18) Marder, S. R.; Torruellas, W. E.; Blanchard-Desce, M.; Ricci, V.; Stegeman, G. I.; Gilmour, S.; Brédas, J.-L.; Li, J.; Bublitz, G. U.; Boxer, S. G. *Science* **1997**, *276*, 1233−1236.

(19) Zhan, X.; Liu, Y.; Zhu, D.; Huang, W.; Gong, Q. *Chem. Mater.* **2001**, *13*, 1540−1544.

(20) Zhan, X.; Liu, Y.; Zhu, D.; Liu, X.; Xu, G.; Ye, P. *Chem. Phys. Lett.* **2001**, *343*, 493−498.

(21) Zhan, X.; Yang, M.; Xu, G.; Liu, X.; Ye, P. *Macromol. Rapid Commun.* **2001**, *22*, 358−362.

(22) Gu, F. L.; Bishop, D. M.; Kirtman, B. *J. Chem. Phys.* **2001**, *115*, 10548−10556.

(23) Albert, I. D. L.; Marks, T. J.; Ratner, M. A. *J. Phys. Chem.* **1996**, *100*, 9714−9725.

(24) Dai, Z.; Yue, X.; Peng, B.; Yang, Q.; Liu, X.; Ye, P. *Chem. Phys. Lett.* **2000**, *317*, 9−12.

(25) Yang, M.; Jiang, Y. *Phys. Chem. Chem. Phys.* **2001**, *3*, 4213−4217.

(26) Blau, W. J.; Byrne, H. J.; Cardin, D. J.; Dennis, T. J.; Hare, J. P.; Kroto, H. W.; Taylor, R.; Walton, D. R. M. *Phys. Rev. Lett.* **1991**, *67*, 1423−1425.

(27) Knize, R. J.; Partanen, J. P. *Phys. Rev. Lett.* **1992**, *68*, 2704.

(28) Kafafi, Z. H.; Bartoli, F. J.; Lindle, J. R.; Pong, R. G. S. *Phys. Rev. Lett.* **1992**, *68*, 2705.

(29) Flom, S. R.; Pong, R. G. S.; Bartoli, F. J.; Kafafi, Z. H. *Phys. Rev. B* **1992**, *46*, 15598−15601.

(30) Shuai, Z.; Brédas, J. L. *Phys. Rev. B* **1992**, *46*, 16135−16141.

(31) Kajzar, F.; Taliani, C.; Danieli, R.; Rossini, S.; Zamboni, R. *Phys. Rev. Lett.* **1994**, *73*, 1617−1620.

(32) Liu, H.; Taheri, B.; Jia, W. *Phys. Rev. B* **1994**, *49*, 10166−10167.

(33) Sun, F.; Zhang, S.; Xia, Z.; Zhou, Y. H.; Chen, X.; Qiang, D.; Zhou, X.; Wu, Y. *Phys. Rev. B* **1995**, *51*, 4614−4617.

(34) Moore, C. E.; Cardelino, B. H.; Wang, X.-Q. *J. Phys. Chem.* **1996**, *100*, 4685−4688.

(35) Gu, G.; Huang, H.; Yang, S.; Yu, P.; Fu, J.; Wong, G. K.; Wan, X.; Dong, J.; Du, Y. *Chem. Phys. Lett.* **1998**, *289*, 167−173.

(36) Liu, X.; Si, J.; Chang, B.; Xu, G.; Yang, Q.; Pan, Z.; Xie, S.; Ye, P.; Fan, J.; Wan, M. *Appl. Phys. Lett.* **1999**, *74*, 164−166.

(37) Wang, S.; Huang, W.; Yang, H.; Gong, Q.; Shi, Z.; Zhou, X.; Qiang, D.; Gu, Z. *Chem. Phys. Lett.* **2000**, *320*, 411−414.

(38) Jonsson, D.; Ruud, K.; Taylor, P. R. *Comput. Phys. Commun.* **2000**, *128*, 412−433.

(39) van Gisbergen, S. J. A.; Schipper, P. R. T.; Gritsenko, O. V.; Baerends, E. J.; Snijders, J. G.; Champagne, B.; Kirtman, B. *Phys. Rev. Lett.* **1999**, *83*, 694−697.

(40) van Faassen, M.; de Boeij, P. L.; van Leeuwen, R.; Berger, J. A.; Snijders, J. G. *Phys. Rev. Lett.* **2002**, *88*, 186401.

(41) Su, W. P.; Schrieffer, J. R.; Heeger, A. J. *Phys. Rev. Lett.* **1979**, *42*, 1698−1701.

(42) Heeger, A. J.; Kivelson, S.; Schrieffer, J. R.; Su, W.-P. *Rev. Mod. Phys.* **1988**, *60*, 781−850.

(43) Yu, J.; Su, W. P. *Phys. Rev. B* **1991**, *44*, 13315−13318.

(44) Dong, J.; Jiang, J.; Yu, J.; Wang, Z. D.; Xing, D. Y. *Phys. Rev. B* **1995**, *52*, 9066−9070.

(45) Xie, R.-H.; Jiang, J. *Chem. Phys. Lett.* **1997**, *280*, 66−72.

(46) Xie, R.-H.; Jiang, J. *Appl. Phys. Lett.* **1997**, *71*, 1029−1031.

(47) Xie, R.-H.; Jiang, J. *J. Appl. Phys.* **1998**, *83*, 3001−3007.

(48) Jiang, J.; Dong, J.; Wan, X.; Xing, D. Y. *J. Phys. B: At. Mol. Opt. Phys.* **1998**, *31*, 3079−3086.

(49) Wan, X.; Dong, J.; Xing, D. Y. *Phys. Rev. B* **1998**, *58*, 6756−6759.

(50) Engkvist, O.; Åstrand, P.-O.; Karlström, G. *Chem. Rev.* **2000**, *100*, 4087−4108.

(51) Denbigh, K. G. *Trans. Faraday Soc.* **1940**, *36*, 936.

(52) Vickery, B. C.; Denbigh, K. G. *Trans. Faraday Soc.* **1949**, *45*, 61.

(53) Stout, J. M.; Dykstra, C. E. *J. Am. Chem. Soc.* **1995**, *117*, 5127−5132.

(54) Stout, J. M.; Dykstra, C. E. *J. Phys. Chem. A* **1998**, *102*, 1576−1582.

(55) Sylvester-Hvid, K. O.; Åstrand, P.-O.; Ratner, M. A.; Mikkelsen, K. V. *J. Phys. Chem. A* **1999**, *103*, 1818−1821.

(56) Silberstein, L. *Philos. Mag.* **1917**, *33*, 92−128.

(57) Applequist, J.; Carl, J. R.; Fung, K.-F. *J. Am. Chem. Soc.* **1972**, *94*, 2952−2960.

(58) Applequist, J. *J. Chem. Phys.* **1985**, *83*, 809−826; (erratum) **1993**, *98*, 7664.

(59) Buckingham, A. D.; Orr, B. J. *Q. Rev.* **1967**, *21*, 195−212.

(60) Buckingham, A. D.; Concannon, E. P.; Hands, I. D. *J. Phys. Chem.* **1994**, *98*, 10455−10459.

(61) Zhou, T.; Dykstra, C. E. *J. Phys. Chem. A* **2000**, *104*, 2204−2210.

(62) Bode, K. A.; Applequist, J. *J. Phys. Chem.* **1996**, *100*, 17820−17824.

(63) de Vries, A. H.; P. Th. van Duijnen, Zijlstra, R. W. J.; Swart, M. *J. Electron. Spectrosc. Relat. Phenom.* **1997**, *86*, 49−55.

(64) Burnham, C. J.; Li, J.; Xantheas, S. S.; Leslie, M. *J. Chem. Phys.* **1999**, *110*, 4566−4581.

(65) Torrens, F.; Sánchez-Mar×c1n, J.; Nebot-Gil, I. *J. Mol. Graph.* **1996**, *14*, 245−259.

(66) Soos, Z. G.; Tsiper, E. V.; Pascal, R. A., Jr. *Chem. Phys. Lett.* **2001**, *342*, 652−658.

(67) Jensen, L.; Schmidt, O. H.; Mikkelsen, K. V.; Åstrand, P.-O. *J. Phys. Chem. B* **2000**, *104*, 10462−10466.

(68) Kongsted, J.; Osted, A.; Jensen, L.; Åstrand, P.-O.; Mikkelsen, K. V. *J. Phys. Chem. B* **2001**, *105*, 10243−10248.

(69) Jensen, L.; Åstrand, P.-O.; Osted, A.; Kongsted, J.; Mikkelsen, K. V. *J. Chem. Phys.* **2002**, *116*, 4001−4010.

(70) Applequist, J. *J. Chem. Phys.* **1973**, *58*, 4251−4259.

(71) Applequist, J. *J. Phys. Chem. A* **1998**, *102*, 7723−7724.

(72) Applequist, J.; Quicksall, C. O. *J. Chem. Phys.* **1977**, *66*, 3455−3459.

(73) Bocian, D. F.; Schick, G. A.; Birge, R. R. *J. Chem. Phys.* **1981**, *74*, 3660−3667.

(74) Applequist, J.; Sundberg, K. R.; Olson, M. L.; Weiss, L. C. *J. Chem. Phys.* **1979**, *70*, 1240−1246; (erratum) **1979**, *71*, 2330.

(75) Shanker, B.; Applequist, J. *J. Chem. Phys.* **1996**, *104*, 6109−6116.

(76) Applequist, J.; Bode, K. A. *J. Phys. Chem. A* **2000**, *104*, 7129−7132.

(77) Applequist, J. *J. Phys. Chem. A* **2000**, *104*, 7133−7139; (erratum) **2000**, *104*, 10994.

(78) Levine, B. F.; Bethea, C. G. *J. Chem. Phys.* **1975**, *63*, 2666−2682.

(79) Sundberg, K. R. *J. Chem. Phys.* **1977**, *66*, 1475−1476; (erratum) *J. Chem. Phys.* **1977**, *67*, 4314.

(80) Bancewicz, T. *J. Chem. Phys.* **1999**, *111*, 7440−7445.

(81) Birge, R. R. *J. Chem. Phys.* **1980**, *72*, 5312−5319.

(82) Thole, B. T. *Chem. Phys.* **1981**, *59*, 341−350.

(83) van Duijnen, P. Th.; Swart, M. *J. Phys. Chem. A* **1998**, *102*, 2399−2407.

(84) Jensen, L.; Åstrand, P.-O.; Sylvester-Hvid, K. O.; Mikkelsen, K. V. *J. Phys. Chem. A* **2000**, *104*, 1563−1569.

(85) Buckingham, A. D. *Adv. Chem. Phys.* **1967**, *12*, 107.

(86) Sundberg, K. R. *J. Chem. Phys.* **1977**, *66*, 114−118.

(87) Perrin, E.; Prasad, P. N.; Mougenot, P.; Dupuis, M. *J. Chem. Phys.* **1989**, *91*, 4728−4732.

(88) Sim, F.; Chin, S.; Dupuis, M.; Rice, J. E. *J. Phys. Chem.* **1993**, *97*, 1158−1163.

(89) Adant, C.; Brédas, J. L.; Dupuis, M. *J. Phys. Chem. A* **1997**, *101*, 3025−3031.

(90) Maroulis, G. *J. Phys. Chem. A* **2000**, *104*, 4772−4779.

(91) Pluta, T.; Sadlej, A. J. *J. Chem. Phys.* **2001**, *114*, 136−146.

(92) Helgaker, T.; Jensen, H. J. Aa.; Jørgensen, P.; Olsen, J.; Ruud, K.; Ågren, H.; Andersen, T.; Bak, K. L.; Bakken, V.; Christiansen, O.; Dahle, P.; Dalskov, E. K.; Enevoldsen, T.; Fernandez, B.; Heiberg, H.; Hettema, H.; Jonsson, D.; Kirpekar, S.; Kobayashi, R.; Koch, H.; Mikkelsen, K. V.; Norman, P.; Packer, M. J.; Saue, T.; Taylor, P. R.; Vahtras, O. DALTON, release 1.0, an ab initio electronic structure program, 1997.

(93) Norman, P.; Jonsson, D.; Vahtras, O.; Ågren, H. *Chem. Phys. Lett.* **1995**, *242*, 7−16.

(94) Norman, P.; Jonsson, D.; Ågren, H.; Dahle, P.; Ruud, K.; Helgaker, T.; Koch, H. *Chem. Phys. Lett.* **1996**, *253*, 1−7.

(95) Sadlej, A. J. *Collect. Czech. Chem. Commun.* **1988**, *53*, 1995−2015.

(96) Pluta, T.; Sadlej, A. J. *Chem. Phys. Lett.* **1998**, *297*, 391−401.

(97) Quinet, O.; Champagne, B. *J. Chem. Phys.* **1998**, *109*, 10594−10602.

(98) Zanasi, R. *Chem. Phys. Lett.* **1999**, *315*, 217−223.

(99) The 72 molecules are 1,2,3-trifluorobenzene, 1,2,3,4-tetrafluorobenzene, 1,2,3,5-tetrafluorobenzene, 1,2,4,5-tetrafluorobenzene, 1,3-dichlortetrafluorobenzene, 1,3,5-trichlorobenzene, 1,3,5-trifluorobenzene, 2,3,5,6-tetrafluoro-1,4-dichlorobenzene, 2,3,5,6-tetrafluorochlorobenzene, 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, benzene, fluorobenzene, hexafluorobenzene, *m*-dichlorobenzene, *m*-difluorobenzene, *o*-dichlorobenzene, *o*-difluorobenzene, *p*-dichlorobenzene, *p*-difluorobenzene, *p*-fluorochlorobenzene, pentafluorobenzene, pentafluorochlorobenzene, phenol, toluene, ethylamide, methane, ethane, propane, chloromethane, methanol, pentane, hexane, 1,1,1-trichloroethane, aminomethane, aminoethane, aminopropane, acetone, 3-pentanone, 4-heptanone, *N*,*N*-dimethylformamide, *N*-methylacetamide, *N*-methylformamide, malonic acid, acetaldehyde, aminobutane, formic acid, nitroethane, nitromethane, butanal, nitropropane, butanol, butanoic acid, trichloromethane, chloroformamide, cyanobutane, cyanoethane, cyanomethane, cyanopropane, pentanol, propanol, 2,3-dichlororbutane, propanamide, 1,1,2,2-tetrachloroethane, tetrachloromethane, acetic acid.

(100) Weast, R. C., Ed. *Handbook of Chemistry and Physics*, 62nd ed.; CRC Press: Boca Raton, FL, 1981.

(101) Pople, J. A.; Gordon, M. *J. Am. Chem. Soc.* **1967**, *89*, 4253−4261.

(102) Jensen, L.; Åstrand, P.-O.; Mikkelsen, K. V. *Int. J. Quantum Chem.* **2001**, *84*, 513−522.

(103) Applequist, J. *J. Phys. Chem.* **1993**, *97*, 6016−6023.

(104) Reis, H.; Papadopoulos, M. G.; Munn, R. W. *J. Chem. Phys.* **1998**, *109*, 6828−6838.

(105) Perez, J.; Dupuis, M. *J. Phys. Chem.* **1991**, *95*, 6525−6529.

(106) van Gisbergen, S. J. A.; Snijders, J. G.; Baerends, E. J. *Phys. Rev. Lett.* **1997**, *78*, 3097−3100.

(107) Jonsson, D.; Norman, P.; Ruud, K.; Ågren, H.; Helgaker, T. *J. Chem. Phys.* **1998**, *109*, 572−577.

(108) Norman, P.; Luo, Y.; Jonsson, D.; Ågren, H. *J. Chem. Phys.* **1997**, *106*, 1827−1835.

(109) Iwata, J.-I.; Kabana, Y.; Bertsch, G. F. *J. Chem. Phys.* **2001**, *115*, 8773−8783.

(110) Talapatra, G. B.; Manickam, N.; Samoc, M.; Orczyk, M. E.; Karna, S. P.; Prasad, P. N. *J. Phys. Chem.* **1992**, *96*, 5206−5208.

(111) Matsuzawa, N.; Dixon, D. A. *J. Phys. Chem.* **1992**, *96*, 6241−6247.