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Frequency-Dependent Molecular Polarizability and Refractive Index: Are Substituent Contributions Additive?

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The frequency-dependent polarizabilities of a number of halogen-substituted benzene species are computed using ab-initio methods. The polarizability tensors are analyzed for possible additive properties. Simple group or atom additivity trivially fails (the overall polarizability is not a sum of isotropic atom or group polarizabilities). If, however, the separate polarizability tensor elements are studied, they are additive, to quite substantial accuracy, for benzene with F, Cl, Br, and I substituents. This tensorial additive property has important implications for design of controlled refractive index materials, and we present calculated refractive indices utilizing ab initio calculated polarizability tensors.

I. Introduction

Electronic structure computations are widely used in understanding and design of molecules exhibiting linear or nonlinear optical response.[1−11] Other high-frequency-dependent properties, such as the refractive index, have been less extensively explored.

Any optical medium is characterized by a quantity n, the refractive index, which is the ratio of the speed of light in free space to that in the medium. The effect of the propagation of a high-frequency electromagnetic field in a linear, spatially nondispersive material is represented by the real electric field vector $\boldsymbol{E}(r,t)$ and the induced real polarization vector $\boldsymbol{P}(r,t)$. At each point r in the material the Fourier transforms of the above vectors are connected through the relationship[12−14]

$$\mathbf{P}(\omega) = \chi(\omega)\mathbf{E}(\omega) \tag{1}$$

where $\chi(\omega)$ is a second-rank tensor property termed the dielectric susceptibility. From the Lorentz internal field model it is known that for many materials one can express $\chi(\omega)$ as[15,16]

$$\chi(\omega) = N\alpha(\omega)\left[1 - \frac{4\pi}{3}N\alpha(\omega)\right]^{-1} \tag{2}$$

where N is the average number of molecules per unit volume and $\alpha(\omega)$ is the mean polarizability of the isolated molecule. Rewriting this expression through the relationship[16,17]

$$n^2(\omega) = 1 + 4\pi\chi(\omega) \tag{3}$$

gives the well-known Lorentz−Lorenz relation[16,17]

$$\frac{4\pi}{3}N\alpha(\omega) = \frac{n^2(\omega) - 1}{n^2(\omega) + 2} \tag{4}$$

which involves the refractive index $n(\omega)$ of the medium rather than the dielectric susceptibility $\chi(\omega)$. The Lorentz−Lorenz relation may be approximated with the Lorenz form as[15,16]

$$n^2(\omega) = 1 + 4\pi N\alpha(\omega) \tag{5}$$

where $\chi(\omega)$ in eq 2 is restricted to an additive model as $N\alpha(\omega)$. For designed refractive index materials, the fundamental molecular response property is thus the frequency-dependent polarizability $\alpha(\omega)$. The frequency dependent polarizability tensor may be calculated through ab initio calculations. For example, we have found previously that eq 4, combined with accurate electronic structure calculations for the polarizability, gives a computed value of the refractive index for benzene in quite good agreement with experiment.[18]

The manufacture of optical fibers, optical coatings, optical switching devices, photorefractive materials and acousto-optic devices requires an understanding of the behavior of the refractive index.[19−24] Optical techniques are in many cases well suited to parallel processing of information and data storage.

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TABLE 1: Refractive Indices and Polarizabilities at $\lambda = 589$ nm[a]

compound	$\alpha_{iso}^{HF}(\omega)$	refractive index $n_D(\omega)$			density	$\alpha_{Exp}(\omega)$	
		eq 7	eq 8	exptl	g/ccm	eq 7	eq 8
fluorobenzene	70.301	1.3560	1.4712	1.4684	1.0225	96.902	69.945
o-difluorobenzene	69.624	1.3393	1.4420	1.4451	1.1599	95.449	70.043
m-difluorobenzene	69.552	1.3398	1.4428	1.4390	1.1630	93.666	69.029
p-difluorobenzene	69.398	1.3406	1.4442	1.4422	1.1688	94.004	69.121
1,3,5-trifluorobenzene	68.998	1.3221	1.4130	1.4150	1.2770	92.445	69.295
1,2,3-trifluorobenzene	69.084	1.3231	1.4147	1.4230	1.2800	94.317	70.300
1,2,3,4-tetrafluorobenzene	68.594	1.3106	1.3940	1.4054	1.4000[a]	93.219	70.351
1,2,4,5-tetrafluorobenzene	68.465	1.3150	1.4012	1.4075	1.4255	92.106	69.40
hexafluorobenzene	68.204	1.2905	1.3619	1.3777	1.6184	92.079	70.864
p-fluorochlorobenzene[b]	83.741	1.3718	1.4997	1.4950	1.2260	117.274	83.074
pentafluorochlorobenzene	82.644	1.3106	1.3940	1.4256	1.5680	118.894	88.455
2,4,6-trifluorochlorobenzene[b]	82.945	1.3480	1.4571	1.4560	1.4630	113.679	82.777
2,3,5,6-tetrafluorochlorobenzene	82.953	1.3324	1.4302	1.4420	1.5380	115.476	84.922
tetrafluoro-*m*-dichlorobenzene	97.301	1.3503	1.4610	1.4680	1.6520	136.522	98.572
chlorobenzene	84.821	1.3908	1.5353	1.5241	1.1058	120.079	83.333
o-dichlorobenzene	97.758	1.4047	1.5621	1.5515	1.3048	141.369	96.231
m-dichlorobenzene	98.895	1.4043	1.5614	1.5459	1.2884	141.403	96.635
p-dichlorobenzene	99.397	1.3950	1.5432	1.5285	1.2475	140.418	97.146
bromobenzene	92.599	1.4102	1.5732	1.5597	1.4950	134.174	90.808
o-dibromobenzene	112.316	1.4351	1.6241	1.6155	1.9843	170.671	111.070
m-dibromobenzene	114.741	1.4370	1.6281	1.6083	1.9523	170.967	111.826
iodobenzene	107.498	1.4428	1.6407	1.6200	1.8308	161.414	104.715
o-diodobenzene	140.255	1.4869	1.7408	1.7179	2.5400	225.994	136.934

[a] Experimental densities obtained from ref 31 unless otherwise stated. [b] Beilstein.

We are interested in the achievable change in the index of refraction possible for particular assemblies of molecular compounds and therefore wish to understand how $n(\omega)$ can be manipulated through the assembly of molecular building blocks.

An obvious question then concerns the possible additive properties of α for a molecule with several substituent groups: to what extent is polarizability an additive property (such as molecular mass), and to what extent is polarizability, such as molecular levels, not additive? Polarizability has the dimension of volume, and the good approximate additivity of *molecular* polarizabilities indicates that atomic polarizabilities might well be additive. On the other hand, the polarizability is a response property of the electronic structure, and other such properties, such as the first hyperpolarizability β, are known not to be additive.[8]

We report here ab initio calculations of the polarizability for a series of substituted benzenes, designed to investigate possible additivity. For halogenated benzenes with one, two, three, four, five, or six halogen substituents, we find that the individual tensor elements α_{zz}, $^1/_2(\alpha_{xx} + \alpha_{yy})$, and $^1/_2(\alpha_{xx} - \alpha_{yy})$ are indeed additive (the z-axis is perpendicular to the plane). A description of the total polarizability with isotropic atomic polarizabilities is, however, very far from additive. The reason is trivial. A sum of isotropic atomic polarizabilities gives an isotropic molecular polarizability and the polarizabilities of the aromatic compounds studied here have large anisotropies. We have also calculated the refractive index for the compounds where the experimental densities and refractive indices are available. These results suggest that polarizabilities, and therefore refractive indices, can be predicted using additive principles. The electronic structure calculations on which this conclusion is based are detailed in section II, the polarizability additivity is shown and discussed in section III, the refractive indices are discussed in section IV, and conclusions are given in section V.

II. Computational Details

We have calculated the frequency-dependent molecular polarizabilities at the frequencies: $\omega = 0.0$ au and $\omega = 0.0774$ au (corresponding to 2.106 eV) for 35 halogen-substituted benzenes.[38] (See Table 1.) The polarizabilities have been calculated as described in ref 25 with the Dalton program.[26] Since the aim is more to study fundamental aspects rather than to obtain highly accurate values, we have restricted the calculation to be at the SCF level. Furthermore, we have adopted the Sadlej basis set[27] since it previously has been demonstrated to give accurate polarizabilities[28-30] for the benzene molecule considering its modest size. In all calculations, we have used the following standard bond distances (taken from ref 31): $r_{CC} = 1.40$ Å, $r_{CH} = 1.084$ Å, $r_{CCl} = 1.70$ Å, $r_{CBr} = 1.85$ Å, $r_{CI} = 2.05$ Å.

III. Additivity of Polarizabilities

The description of the molecular polarizability by additive atomic or group polarizabilities is an old concept[32,33] and has also been exploited in some detail recently.[34,35] We have tested three different additivity schemes: scheme 1, isotropic atomic polarizabilities ($\alpha_{xx} = \alpha_{yy} = \alpha_{zz}$); scheme 2, the atoms apart from carbon are treated as if they are part of a diatomic molecule ($\alpha_{xx} = \alpha_{yy} \neq \alpha_{zz}$, where it is assumed that the z-axis is along the C$-$X bond); scheme 3, three independent tensor components for each atom ($\alpha_{xx} \neq \alpha_{yy} \neq \alpha_{zz}$). The fitted atomic polarizabilities have been obtained for each of the three schemes by minimizing the mean-squared deviations of the molecular polarizabilities as

$$\text{msd} = \frac{\sum_{p=1}^{M}\sum_{i,j=1}^{3}(\alpha_{ij,p}^{\text{fitted}} - \alpha_{ij,p}^{\text{HF}})^2}{M-1} \tag{6}$$

where M is the number of molecules. We present the molecular polarizabilities as a rotational-invariant in-plane component $\alpha_{ip} = {}^1/_2(\alpha_{xx} + \alpha_{yy})$, its anisotropic part $\alpha_{ani} = {}^1/_2|\alpha_{xx} - \alpha_{yy}|$, and the out-of-plane component as $\alpha_{oop} = \alpha_{zz}$.

As noted above, the first scheme with only isotropic atomic polarizability tensors fails since the molecular polarizabilities become isotropic (also demonstrated in refs 34 and 35), which is not true for the aromatic compounds considered here. This

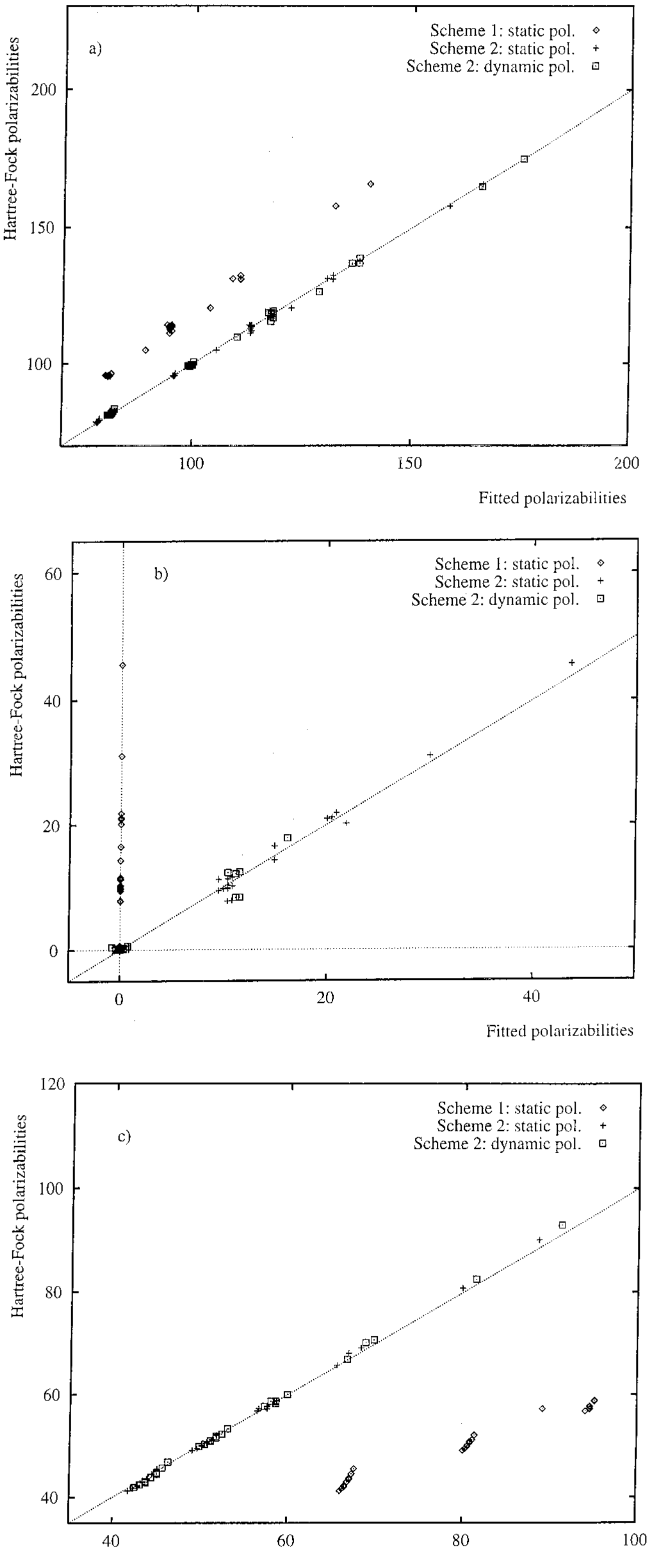

Figure 1. Fitted molecular polarizabilities (in au) assuming additivity of atomic polarizabilites. The static polarizabilities are presented for scheme 1 and scheme 2 and the dynamic polarizabilities for scheme 2: (a) α_{ip} (b) α_{ani}, (c) α_{oop}.

is clearly demonstrated in Figure 1 and Table 2. The second partition scheme with two parameters for each atom gives a much better fit (Figure 1 and Table 2), and an excellent agreement is seen between the additive scheme and the quantum chemically derived polarizabilities. The third partition scheme with three parameters for each atom gives only a minor improvement over the second (Table 2).

TABLE 2: Fitted Static Atomic Polarizabilities (au)

		two components			three components		
atom	isotropic α	α_{xx}	α_{yy}	α_{zz}	α_{xx}	α_{yy}	α_{zz}
C	11.0	12.6		6.4	12.8		6.6
H	0.3	1.1	0.0	1.1	0.7	0.0	0.9
F	0.0	0.6	0.3	0.6	0.6	0.0	0.3
Cl	14.0	7.9	27.7	7.9	7.6	27.5	7.9
Br	21.8	12.7	41.4	12.7	11.5	41.8	12.9
I	36.5	22.9	65.3	22.9	21.5	65.4	23.6
msd	45.3		1.87			1.63	

TABLE 3: Dynamic Atomic Polarizabilities (au) at 589 nm Fitted According to the Two-Component Model

atom	α_{xx}	α_{yy}	α_{zz}
C	13.4		7.1
H	0.7	0.0	0.7
F	0.0	0.1	0.0
Cl	7.4	29.2	7.4
Br	12.3	44.0	12.3
I	23.0	70.5	23.0
msd		2.13	

The atomic polarizabilities change very little between the different partition schemes (Table 2). For example, α_{xx} and α_{zz} are similar even if they are not constrained to be equal. It is also noticed that the isotropic polarizabilities obtained in the first partition scheme are almost equal to $^1/_3(\alpha_{xx} + \alpha_{yy} + \alpha_{zz})$ of the other models. It is also satisfying that we obtain that $\alpha^I > \alpha^{Br} > \alpha^{Cl} > \alpha^F$, which should be expected. Therefore, it seems that the obtained atomic polarizabilities have a physical meaning and are not just fitting parameters. However, it is noted that α^H and α^F are of similarly small magnitudes.

If we interpret our atomic polarizabilities in terms of the Applequist interaction model[36] (where the deviations from isotropic atomic polarizabilities are taken into account by considering couplings between the atomic induced dipole moments), our α_{zz} should be comparable to the Applequist polarizabilities ($\alpha^H = 1$ au, $\alpha^F = 2$ au, $\alpha^C = 4$ au, $\alpha^{Cl} = 13$ au, $\alpha^{Br} = 19$ au, and $\alpha^I = 32$ au), which is in reasonable agreement with our values considering the quite different approaches. Dykstra and co-workers[37,34] have calculated α^C of benzene to $\alpha^C_{xx} = 12.9$ au and $\alpha^C_{zz} = 6.9$ au in close agreement with our values for aromatic carbons.

We have also fitted the molecular polarizabilities at frequency 0.0774 au, and it is found that we obtain a fit with comparable accuracy as that for the static polarizabilities (Figure 1) and the fitted frequency-dependent atomic polarizabilities calculated according to the two-component model listed in Table 3.

We have here restricted the investigation to halogenated benzenes, and the parameters are therefore “benzene” specific. It is demonstrated that aromatic systems may be described with a localized model of atom-type polarizabilities, which is important since delocalized models have been used extensively for describing aromatic systems.

IV. Refractive Indices

Design of molecular or supramolecular photonic devices requires control of how the refractive index changes with the configuration of the molecular constituents. The molecular materials are dispersive and therefore the refractive indices are dependent on the frequency of the applied electromagnetic field. Calculation of frequency-dependent polarizability tensors gives the necessary information about dispersion of the refractive indices.

We have calculated the refractive indices utilizing two different models. Both of them requires the trace of the polarizability tensor and the number of molecules per unit volume. In model 1 we calculated the refractive index using the Lorenz equation[15−18]

$$n(\omega) = \sqrt{1 + 4\pi N\alpha(\omega)} \quad (7)$$

and in model 2 we utilize the Lorentz−Lorenz expression[15−18]

$$n(\omega) = \sqrt{\frac{3 + 8\pi N\alpha(\omega)}{3 - 4\pi N\alpha(\omega)}} \quad (8)$$

As seen in Table 1, refractive indices, calculated through model 2, are in agreement with experimental data to about 2%. On the other hand, model 1 clearly gives a much poorer agreement. This was also observed in ref 18 where we investigated the refractive index of benzene.

We have also investigated the variation of the molecular polarizability of benzene with the molecular geometry. We have employed a very similar standard geometry ($r_{CC} = 1.395$ Å and $r_{CH} = 1.085$ Å), and we found changes in the molecular polarizability of 0.4 au for α_{xx} and 0.2 au for α_{zz}. Consequently, the choice of molecular geometry is expected to have considerable effect on any model for describing polarizabilities of large molecules. The geometrically induced changes in the polarizability tensor lead to changes in the refractive indices. A 30% change in the isotropic polarizability of the molecule leads to a change in the refractive index of 10%. It is important to realize that small changes in the refractive index can lead to modified performance of photonic devices.

V. Conclusions

We have shown that accurate refractive indices of aromatic systems can be calculated from experimental densities and electronic structure calculations of frequency-dependent polarizabilities. Furthermore, we have demonstrated that polarizabilities of aromatic molecules can be described through the additivity of atomic polarizability tensors.

In the future we will investigate the reliability of the model for calculating frequency-dependent refractive indices of larger aromatic systems. The scheme of adding atomic polarizability tensors will be applied to model and design compounds of potential interest within the area of fiber optics based on molecular doped polymers.

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