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Polarizability of phthalocyanine based molecular systems: A first-principles electronic structure study

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A first-principles electronic structure study is performed to determine the optical and static polarizability tensors of various phthalocyanine (Pc) derived molecules, including H_2Pc, CuPc, and MgPc. It is found that the dominant contribution to the polarizability is electronic in origin, and that the metal atoms only marginally enhance the polarizability. An analytical electrostatic model that relates the polarizability of an ellipsoid to its permittivity is then used to estimate the permittivity tensor of these molecular systems. © *2006 American Institute of Physics*.
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Owing to their high chemical stability, various possible synthetic modifications, and their semiconductivity,[1] metal phthalocyanines (Pc) have been considered for several technological applications, including thin film flexible transistors[2] and light emitting diodes.[3] In fact, Pc based materials are part of the discotic liquid crystal class of functional materials, which display an increased charge carrier mobility as compared to conventional conjugated polymers.[4]

Recently, copper phthalocyanine (CuPc) oligomers have been used as a filler to a polymer matrix in developing an all-organic composite actuator material (containing about 40 wt % CuPc) with a high dielectric constant of about 225.[5] However, it is unclear whether the high dielectric constant of CuPc based systems is intrinsic to CuPc.[6] While it has been suggested[6] that extrinsic factors, such as contact metals,[7] oxygen exposure,[8] self-organization of the Pc molecules, and sample treatment,[9] could result in giant values of the dielectric constant (similar to what is observed in inorganic semiconductors[10]), the role played by the individual molecules is unclear.

The present contribution addresses the dielectric properties of Pc based monomer molecules and comes in two steps. Firstly, we present *ab initio* computations of the optical and static polarizability tensors of monomers of CuPc, magnesium phthalocyanine (MgPc), and metal-free phthalocyanine (H_2Pc, in which the metal atom is replaced by two H atoms). Secondly, we estimate the direction dependent dielectric constant of the Pc molecules using a classical electrostatic model that relates analytically the computed molecular polarizability to the dielectric tensor of an ellipsoid.

All calculations reported here were performed using the local density approximation (LDA) within density functional theory (DFT),[11] as implemented in the local orbital SIESTA code.[12] Norm-conserving nonlocal pseudopotentials of the Troullier-Martins type were used to describe all the elements. Atomic configurations of $[\mathrm{He}]2s^2 2p^2$, $[\mathrm{He}]2s^2 2p^3$, $[\mathrm{He}]2s^2 2p^4$, $[\mathrm{Ne}]3s^2$, $[\mathrm{Ar}]3d^{10}4s^1$, and $[\mathrm{Ne}]3s^1$ were used for the C, N, O, Mg, Cu, and Na pseudopotentials, respectively. A double-zeta plus polarization (DZP) basis set was used for all calculations. The equilibrium positions of the atoms were determined by requiring the forces on each atom to be smaller than 0.04 eV/Å.

The polarizability tensor component α_{ij} was determined as d_i/E_j, where d_i is the dipole moment along the i direction induced due to an external electric field E_j along the j direction (with $i,j=x,y$, or z). An electric field of strength 0.01 V/Å was used in the determination of α_{ij}. As a test of our method, we have determined the polarizability of a number of simple atoms and molecules for which prior computational[13] and/or experimental results[14] are available. Comparison of our results with prior work is summarized in Table I. As can be seen, our predictions are in reasonable agreement with experiments and other theory.

Figure 1 shows the structure of the CuPc monomer molecule. The atomic coordinates of this molecule was optimized in the absence of an external electric field. Table II shows the values of selected geometric parameters that characterize the structures of H_2Pc, CuPc, and MgPc as determined here, as well as in prior computational[15] and experimental works.[16] As can be seen, our computed values are in excellent agreement with prior determinations. External electric field was then applied along the x, y, or z directions (for CuPc and MgPc, the x and y directions are identical owing to symmetry). The field induced dipole moment was calculated

TABLE I. Polarizability (in Å^3) of selected molecules. For dimer molecules, $\alpha_\parallel$ and $\alpha_\perp$ represent the polarizability parallel and perpendicular to the bond lengths, respectively.

		This work	Expt.[a]	Other theory[b]
H_2	$\alpha_\parallel$	0.93	1.03	0.93
	$\alpha_\perp$	0.57	0.72	0.66
Na_2	$\alpha_\parallel$	46.1	46.2	47.4
	$\alpha_\perp$	22.9	27.2	27.8
Na_5 (C_{2v})	α_{xx}	110.3	⋯	118.3
	α_{yy}	75.4	⋯	81.9
	α_{zz}	56.1	⋯	60.9
Na_8 (D_{2d})	α_{xx}	93.5	⋯	93.2
	α_{yy}	93.5	⋯	92.6
	α_{zz}	116.4	123.2	105.3
C_{60}		79.8	79.3, 85.2	87.3, 85.0

[a] Reference 14.
[b] Reference 13.

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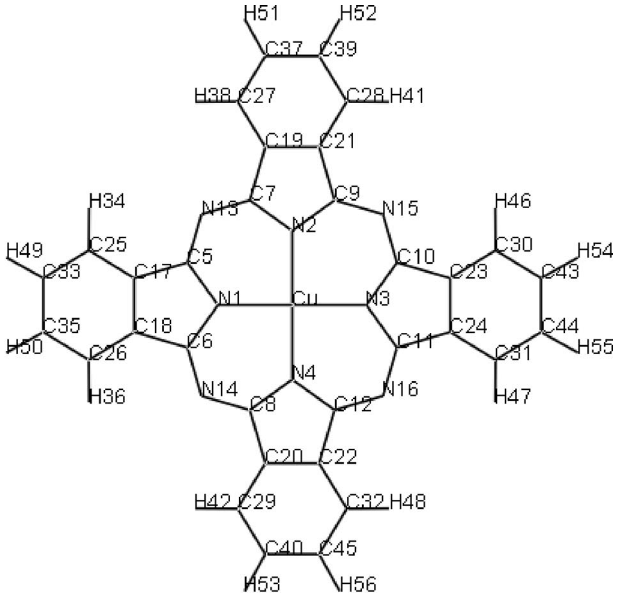

FIG. 1. Atomic structure of the CuPc molecule. In MgPc, the Mg atom sits in the center of the molecule. In H_2Pc, the two H atoms are bound to N^1 and N^3.

both when the atomic coordinates were held fixed at their field-free equilibrium positions (resulting in the *optical* polarizabilities) and when the atomic coordinates were allowed to relax to their field-induced equilibrium positions (resulting in the *static* polarizabilities). The former (optical) case corresponds to the high frequency limit of the polarizability, as at this limit, we expect only the electrons to be able to respond to the external electric field, while the latter (static) case represents the low frequency limit when both the electronic and ionic degrees of freedom contribute to the polarizability.

Table III shows the optical and static polarizability tensors ($\bar{\alpha}^o$ and $\bar{\alpha}^s$, respectively) for H_2Pc, CuPc, and MgPc. Several trends can be observed:

TABLE II. Calculated structural parameters of H_2Pc, MgPc, and CuPc; the atomic numbering scheme of Fig. 1 is used. Experimental values (Ref. 16) of CuPc are shown in parentheses. All bond lengths are in Å and bond angles in degrees.

Parameter	H_2Pc	MgPc	CuPc
$H–N^1$	1.045	⋯	⋯
$Mg–N^1$	⋯	1.992	⋯
$Cu–N^1$	⋯	⋯	1.956(1.935)
$N^1–C^5$	1.376	1.377	1.376(1.366)
$C^5–N^{13}$	1.319	1.334	1.326(1.328)
$C^5–C^{17}$	1.455	1.468	1.462(1.453)
$C^{17}–C^{18}$	1.418	1.417	1.413(1.400)
$C^{17}–C^{25}$	1.405	1.404	1.404(1.388)
$C^{25}–C^{33}$	1.402	1.404	1.404(1.377)
$C^{33}–C^{35}$	1.418	1.416	1.417(1.413)
$C^5–N^1–C^6$	111.77	109.26	108.47(107.3)
$N^1–C^5–N^{13}$	127.95	127.58	128.07(127.6)
$N^1–C^5–C^{17}$	106.90	108.96	109.48(110.4)
$C^5–N^{13}–C^7$	122.36	124.10	122.32(122.2)
$C^5–C^{17}–C^{18}$	107.21	106.41	106.28(106.0)
$C^{18}–C^{17}–C^{25}$	121.38	121.22	121.51(121.1)
$C^{17}–C^{25}–C^{33}$	117.19	117.53	117.06(117.9)
$C^{25}–C^{33}–C^{35}$	121.43	121.25	121.43(121.0)

TABLE III. Optical (high frequency or electronic) and static (low frequency) polarizability tensors (in $Å^3$) of Pc based molecules oriented along the *xy* plane.

Molecule	$\bar{\alpha}^o$	$\bar{\alpha}^s$
H_2Pc	$\begin{pmatrix} 134.2 & 0 & 0 \\ 0 & 134.2 & 0 \\ 0 & 0 & 27.5 \end{pmatrix}$	$\begin{pmatrix} 135.7 & 0 & 0 \\ 0 & 139.9 & 0 \\ 0 & 0 & 27.5 \end{pmatrix}$
MgPc	$\begin{pmatrix} 137.2 & 0 & 0 \\ 0 & 137.2 & 0 \\ 0 & 0 & 28.1 \end{pmatrix}$	$\begin{pmatrix} 139.7 & 0 & 0 \\ 0 & 139.7 & 0 \\ 0 & 0 & 31.3 \end{pmatrix}$
CuPc	$\begin{pmatrix} 135.8 & 0 & 0 \\ 0 & 135.8 & 0 \\ 0 & 0 & 28.1 \end{pmatrix}$	$\begin{pmatrix} 138.0 & 0 & 0 \\ 0 & 138.0 & 0 \\ 0 & 0 & 28.1 \end{pmatrix}$

(1) As one would expect, the polarizability along the direction perpendicular to the plane of the molecules (the *z* direction in our case) is much lower than in other directions.

(2) Regardless of the type of molecule and the tensor component, over 90% of the contribution to the polarizability (in fact, over 99% in most cases) is electronic in origin, characteristic of covalent bonding.

(3) Metal Pc molecules display only a slight enhancement in polarizabilities compared to the metal-free H_2Pc molecule.

The dominant factors that contribute to the polarizability of Pc based molecules thus appear to be unrelated to the presence, absence, or type of the metal cation, and largely determined by the covalent bonding within the molecule.

In order to further understand the significance and the meaning of the calculated polarizabilities, a connection with classical electrostatics was attempted. For an ellipsoidal object made out of an anisotropic, but homogeneous dielectric material, an analytical expression exists that relates the polarizability tensor of the object to its dielectric tensor.[17] If a_x, a_y, and a_z are the semiaxes of a prolate ellipsoid, this expression is given by[17]

$$\alpha_{ii} = \frac{a_x a_y a_z}{3}(\epsilon_{ii} - 1)\frac{1}{1 + N_i(\epsilon_{ii} - 1)}, \tag{1}$$

where ϵ_{ii} is a diagonal component of the dielectric tensor. The depolarization or geometry factor N_i for a prolate ellipsoid is a function of the aspect ratio a_z/a_x, given in terms of elliptical integrals.[17]

Here, we approximate the CuPc molecule by a prolate ellipsoid, with $a_x = a_y = 7.5$ Å, corresponding to the end-to-end distance of about 15 Å for this molecule. Since it is not clear what the exact value of a_z should be within the ellipsoidal model, we treat this as an adjustable parameter. Equation (1) can then be used to determine the CuPc dielectric tensor diagonal components for a range of a_z/a_x values using its polarizabilty tensor given in Table III.

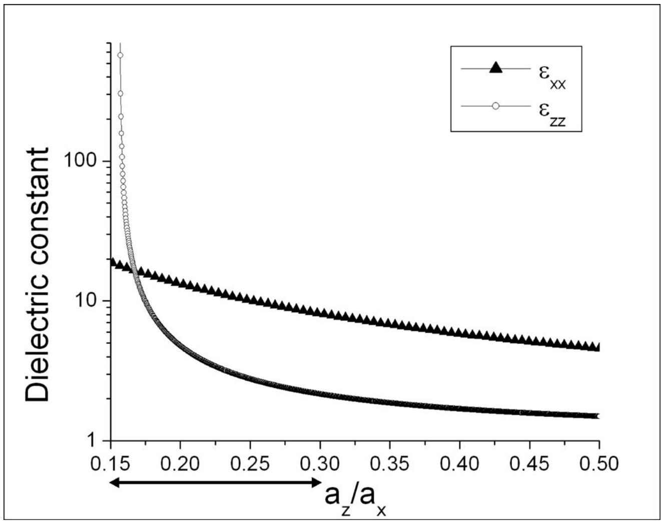

FIG. 2. Estimates of the dielectric constant of CuPc along the plane of the molecule (ϵ_{xx}) and along the perpendicular direction (ϵ_{zz}) as a function of the aspect ratio of a prolate ellipsoid that is intended to represent the molecule. The double-edged arrow represents the expected range of aspect ratios.

Figure 2 displays the ϵ_{xx} and ϵ_{zz} values calculated using the CuPc α^s_{xx} and α^s_{zz} values, respectively. Note that aspect ratios smaller than 0.15 are not considered, as these values correspond to $\alpha^s_{zz} > a_x a_y a_z/(3N_z)$, an unphysical situation. Even in the extreme case when the ellipsoid is made of a metal (the most polarizable material), $\alpha^s_{zz} = a_x a_y a_z/(3N_z)$. Assuming $a_z = 1.15-2.25$ Å implies an aspect ratio in the 0.15–0.3 range (note that the atomic radius of Cu, the largest atom in the CuPc molecule, is 1.44 Å, which falls in this considered range). Figure 2 indicates that for this range of aspect ratios, ϵ_{xx} is 10–20 and ϵ_{zz} is 3-∞. Thus, while this model predicts a modest range of dielectric constant along the plane of the molecule, an extremely wide range is anticipated along the perpendicular direction. Such a wide range is obtained primarily because of the sensitivity of the calculated dielectric constant [given by Eq. (1)] with respect to changes in the aspect ratio, and does not necessarily mean that the dielectric constant along this direction is large. More accurate fully first-principles computation of the dielectric constant for both monomeric and oligomeric Pc molecules, in which the aspect ratio is *not* treated as an unknown adjustable parameter, would aid in a better understanding of the dielectric properties.

In summary, in an initial step towards the understanding of the dielectric properties of Pc based molecules, the optical and static polarizability tensors of metal (Cu, Mg) Pc and metal-free (H_2) Pc monomer molecules have been computed using first-principles DFT based methods. These results suggest that the dominant contribution to the polarizability is electronic in origin, and that the central metal atom plays a minor role in enhancing the polarizability. Estimates of the dielectric tensor for a CuPc monomer using its DFT computed polarizability tensor and a classical electrostatic model indicate that the dielectric constant along the plane of the molecule is modest (10–20) while that along the perpendicular direction is indeterminate at this level of theory.

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