The static dipole polarizability of C70 fullerene

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Abstract

The electronic and vibrational contributions to the static dipole polarizability of C70 fullerene are determined using the finite-field method within the density functional formalism. Large polarized Gaussian basis sets augmented with diffuse functions are used and the exchange-correlation effects are described within the Perdew–Burke–Ernzerhof generalized gradient approximation (PBE-GGA). The calculated polarizability \( \alpha \) of C70 is 103 Å\(^3\), in excellent agreement with the experimental value of 102 Å\(^3\) and is completely determined by the electronic part, the vibrational contribution being negligible. The ratio \( \alpha(C_{70})/\alpha(C_{60}) \) is 1.26. The comparison of polarizability calculated with only local terms (LDA) in the PBE functional to that obtained with PBE-GGA shows that LDA is sufficient to determine the static dipole polarizability of C70.

1. Introduction

C70 is perhaps the most studied carbon fullerene after the C60 fullerene. Several studies have addressed electric response properties of C70 and its more famous cousin C60 [1–17]. The static dipole polarizability \( \alpha_0 \) of C70, which is the subject of the present work, has recently been measured in the gas phase by Compagnon and coworkers [3]. Using the molecular beam deflection technique, they reported the mean static dipole polarizability to be 102 Å\(^3\) with an error bar of ±14 Å\(^3\). Theoretically, polarizability of C70 has been a subject of several investigations [4–6, 9, 15, 16]. Only two of these studies are, however, at the ab initio level of theory. The first study is by Jonsson and coworkers [5], who using the self-consistent field (SCF), and the multi-configuration self-consistent field (MCSCF) theories in combination with the 6-31++G basis set reported polarizability of C70 to be 89.8 Å\(^3\). The second study is due to van Fassen et al [16] who used time-dependent density functional theory (TDDFT) and three different basis sets to calculate \( \alpha_0 \) of C70 [16]. Using the largest basis (triple zeta with an additional field-induced polarization function TZVP+) they found \( \alpha_0 \) to be 104.8 Å\(^3\). These authors also computed \( \alpha_0 \) using the current-dependent Vignale–Kohn functional and concluded that polarizabilities calculated using the current-dependent functional give good agreement with the experimental value.
agreement with experimental values for C60 and C70. The geometric structure of C70 was not
optimized in both these works.

The present communication complements these earlier studies and reports the static dipole
polarizability of C70 calculated within the density functional formalism, using large polarized
Gaussian basis sets augmented by diffuse functions. The calculations are performed within the
generalized gradient approximation using the Perdew–Burke–Ernzerhof parametrization [18].
Unlike in previous works, we first determine the equilibrium structure of the C70 fullerene at
the same level of theory. We then compute the static dipole polarizability. We investigate the
vibrational $\alpha_{\text{vib}}$ contribution to the polarizability $\alpha_0$ as well as the electronic $\alpha_{\text{el}}$ contribution.
The former, which has not yet been computed, is computationally significantly more expensive
than the latter as it requires multiple optimization of C70 geometry in the presence of electric
field or requires the calculation of full vibrational spectrum.

2. Computational details and results

The geometry of C70 was fully optimized using the limited memory Broyden–Fletcher–
Goldfarb–Shanno algorithm [19] using the NRLMOL suit of codes developed by Pederson
and coworkers [20–22]. The code employs an efficient scheme for numerical quadrature for
the exchange-correlation integrals [23]. The $D_{5h}$ symmetry [24] of C70 fullerene was exploited
to reduce the computational expenses during structure optimization. The molecular orbitals in
NRLMOL are expressed as a linear combination of Gaussian orbitals. The Gaussian basis set
for C consists of 5s-, 4p- and 3d-type Gaussians each contracted from 12 primitive functions.
The total number of basis functions used for the structure optimization is 2450 and that used
for polarizability calculations is 2870. The exponents in the basis set are optimized iteratively
by performing a self-consistent calculation on isolated atoms [22]. More details about the
basis set and its construction can be found in [22, 25, 26]. The fully optimized structure of C70
is shown in figure 1. There are five inequivalent atoms in C70. The optimized positions of these
Table 1. The comparison of selected bond distances calculated in this work (PBE/NRLMOL) with those reported in the literature. GED is the gaseous electron diffraction measurements [24]; solid-state electron diffraction (SED) [35]; neutron diffraction (ND) measurements [36]; x-ray diffraction [37]; Hartree–Fock/double zeta basis [38]; BP86/TZP [39]; PBE/NRLMOL (present).

| Bond distance | GED  | SED  | ND   | X-ray | SCF/DZP | BP86/TZP | NRLMOL |
|---------------|------|------|------|-------|---------|----------|--------|
| C1–C2         | 1.461| 1.464| 1.460| 1.458 | 1.451   | 1.454    | 1.439  |
| C1–C6         | 1.388| 1.370| 1.382| 1.380 | 1.375   | 1.401    | 1.389  |
| C6–C7         | 1.453| 1.470| 1.449| 1.459 | 1.446   | 1.450    | 1.436  |
| C10–C12       | 1.386| 1.370| 1.396| 1.370 | 1.361   | 1.395    | 1.383  |
| C7–C8         | 1.468| 1.460| 1.464| 1.460 | 1.457   | 1.449    | 1.433  |
| C8–C9         | 1.425| 1.470| 1.420| 1.430 | 1.415   | 1.441    | 1.426  |
| C9–C31        | 1.405| 1.390| 1.415| 1.407 | 1.407   | 1.424    | 1.410  |
| C31–C32       | 1.538| 1.410| 1.477| 1.476 | 1.475   | 1.471    | 1.452  |

inequivalent atoms in atomic units are a (−2.3127, 0.0000, −7.4352), b (−4.5356, 0.0000, 6.0395), c (5.5080, 1.3063, 4.5799), d (5.9336, 2.6454, 2.2646) and e (6.5245, 1.3720, 0.0000). The C70 fullerene geometry can be generated using the \( xyz \) coordinates of inequivalent atoms and symmetry operations of point group \( D_{5h} \), where the five-fold highest symmetry axis is the \( z \)-axis. In table 1, the calculated bond distances are compared with some experimental and theoretical values reported in the literature. Agreement with experimental bond distances is quite good. The equatorial bond distance of 1.45 Å is smaller than the 1.538 Å measured in the gaseous electron diffraction experiment. However, the smaller value comparable to the prediction of the present calculation has been reported in other experiments. The distance between the polar pentagons is 7.869 Å in good agreement with experimental value of 7.906 Å from the most recent the experimental measurement [24].

The elements of the static dipole polarizability tensor are

\[
\alpha_{ij} = -\frac{\partial^2 E}{\partial F_i \partial F_j}.
\]  

(1)

Here, \( E \) is the total molecular energy and \( F_i \) is the \( i \)th component of the electric field. Equation (1) is the coefficient of the second term in Taylor’s expansion of total energy \( E \) in the presence of field:

\[
E(F) = E_0 + \sum_i \left( \frac{\partial E}{\partial F_i} \right) F_i + \frac{1}{2} \sum_{i,j} \left( \frac{\partial^2 E}{\partial F_i \partial F_j} \right) F_i F_j + \cdots.
\]  

(2)

Alternatively, the polarizability tensor elements could also be obtained from the induced dipole moments. A number of methods have been formulated to obtain \( \alpha_{ij} \) and several review communications describing the details and applications of these methods exist [27, 28]. In this work, we compute \( \alpha_{ij} \) numerically using a finite-difference formula. This requires the calculation of total energy of the molecule for various field values. The electronic contribution to the polarizability \( \alpha_{el} \) is then obtained using a suitable approximation to compute the second derivative in equation (1). Alternatively, the least-squares fitting technique can also be used to extract the polarizability [10, 29, 30]. This way of calculating \( \alpha_{el} \) is known as the finite-field (FF) method. The implementation of the FF method is fairly straightforward. The Hamiltonian of the system is augmented by the term \( -\vec{F} \cdot \vec{r} \) that represents the interaction of an electron with the applied electric field \( \vec{F} \). The self-consistent solution is performed to obtain total energy for a given value of the electric field. The self-consistent process takes into account the field-induced polarization or the so-called screening effects. The drawback is that addition of \( -\vec{F} \cdot \vec{r} \)
Table 2. The comparison of calculated polarizability in (Å³) with the experimental and theoretical values reported in the literature.

| Method                      | \( C_{60} \)     | \( C_{70} \)     | \( C_{70}/C_{60} \) | References |
|-----------------------------|------------------|------------------|----------------------|------------|
| Gas phase                   | 76.5 ± 8         | 102.0 ± 14       | 1.33                 | [3]        |
| Ellipsometry                | 79.0             | 97.0             | 1.23                 | [40]       |
| EELS                        | 83.0             | 103.5            | 1.25                 | [41]       |
| Theory                      |                  |                  |                      |            |
| Coupled Hartree–Fock/STO-3G| 45.6             | 57.0             | 1.25                 | [42]       |
| Pople–Parr–Pariser model    | 49.4             | 63.8             | 1.29                 | [43]       |
| Tight binding               | 77.0             | 91.6             | 1.19                 | [1]        |
| Bond polarizability model   | 89.2             | 109.2            | 1.22                 | [4]        |
| Valence effective Hamiltonian| 154.0           | 214.3            | 1.39                 | [44]       |
| Monopole–dipole             | 60.8             | 73.8             | 1.21                 | [14]       |
| MNDO/PM3                    | 63.9             | 79.0             | 1.24                 | [9]        |
| HF 6-31+G                   | 75.1             | 89.8             | 1.20                 | [32]       |
| TDDFT/SAOP                  | 83               | 101              | 1.22                 | [16]       |
| TDCDFT/VK                   | 76               | 91               | 1.51                 | [16]       |
| PBE/NRLMOL                  | 82.9             | 102.8            | 1.24                 | This work  |

Recent measurements of gas-phase polarizability of \( C_{70} \) indicate \( \alpha_{el} \) to be 102 Å³ with a rather larger error bar of about 14 Å³. The predicted (PBE/NRLMOL) value of 103 Å³ agrees well with the experimental value. As can be seen from table 2, all \textit{ab initio} values fall within the error bar. The PBE/NRLMOL $\alpha_{el}$ agree to the Hamiltonian, in general, breaks the full point-group symmetry. Thus, the computational advantage of the full point group symmetry is lost. In some cases, it may be still possible to use lower symmetry for applied fields along a specific direction. The present calculations of $\alpha_{el}$ of \( C_{70} \) did not use any symmetry. The electric field step was chosen by ensuring that the calculated polarizability is accurate and uncontaminated by higher polarizability. $\alpha_{el}$ obtained from induced dipole moments agrees with that obtained from energy within 1%. The basis set used during structure optimization was augmented by a d-type diffuse function with 0.077 2097 exponent. This methodology has been found to provide a good description of $\alpha_{el}$ of \( C_{60} \) and several molecules and clusters [10, 11, 25, 26, 31]. For more details of methodology and application we refer the reader to a recent review by Pederson and Baruah [26]. As mentioned earlier, the nuclear positions were assumed to be frozen during the calculation of $\alpha_{el}$. The relaxation of nuclear positions in the presence of applied electric field also contributes to the polarizability. This contribution is often called vibrational polarizability $\alpha_{vib}$ and usually is the second largest contribution of the polarizability. In some cases, particularly for the system with ionic or hydrogen bonding it could be even larger than $\alpha_{el}$. Here, we compute $\alpha_{vib}$ within a double-harmonic approximation. A full account of the formulation of calculation of $\alpha_{vib}$ used in this work can be found in [25].

The mean or average polarizability $\alpha_m$ is one-third of the trace of the polarizability matrix:

$$\alpha_m = \frac{1}{3}(\alpha_{xx} + \alpha_{yy} + \alpha_{zz}).$$

(3)

The calculated values of the polarizability components are $\alpha_{xx} = \alpha_{yy} = 99$ Å³ and $\alpha_{zz} = 111$ Å³, where the z-axis is along the five-fold axis. The mean polarizability $\alpha_m$ is 103 Å³. We have also calculated unscreened polarizability using the sum-over-states expression with excitation energies approximated by eigenvalue differences. As in the case of \( C_{60} \) fullerene [10, 11], the unscreened polarizability turns out to be 330 Å³, roughly three times larger than the screened polarizability. In table 2 calculated $\alpha_{el}$ is compared with earlier published theoretical and experimental values. Recent measurements of gas-phase polarizability of \( C_{70} \) indicate $\alpha_{el}$ to be 102 Å³ with a rather larger error bar of about 14 Å³. The predicted (PBE/NRLMOL) value of 103 Å³ agrees well with the experimental value. As can be seen from table 2, all \textit{ab initio} values fall within the error bar. The PBE/NRLMOL $\alpha_{el}$ agree
well with the time-dependent density functional theory calculation with statistically averaged orbital potential (TDDFT/SAOP) polarizability [16]. But it is larger than the predictions by Hartree–Fock (HF) theory (HF/6-31+G) [32] and time-dependent current density functional theory (TDCDFT/VK) [16] models. The differences in the structure of C70 used in those calculations and that optimized in this work are one source of discrepancy. In particular, the higher order polarizabilities are often sensitive to the molecular structure [33]. The other possible cause of differences is in the modeling of many-body effects. In our recent study that compared static dipole polarizabilities of 142 small molecules in the HF and PBE models, the HF polarizabilities were found to be smaller than their PBE counterparts [34]. The larger value of $\alpha_{el}$ in the PBE/NRLMOL than in the HF model is consistent with this observation. $\alpha_{el}$ obtained within the time-dependent current density functional model (TDCDFT/VK) falls intermediate between the HF/6-31+G and PBE/NRLMOL predictions. We repeated calculations with only local terms in the PBE functional to estimate the effect of gradient correction to the exchange-correlation functional. This approximation gives $\alpha_{el}$ to be 100 Å\(^3\), indicating that local approximation is sufficient to determine the dipole polarizability of C\(_{70}\). The vibrational contribution to the polarizability tensor within the double harmonic approximation [25] is given as $\alpha_{\text{vib},i,j} = \sum_\mu Z_{ mass,vib} Z_{i,j,\mu}^T$. Here, $\omega$ is the frequency of the $\mu$th vibrational mode, $Z_{i,j,\mu}$ is the effective charge tensor (see [25] for details). The vibrational contribution along the five-fold axis, $\alpha_{\text{vib},zz}$, is 0.43 Å\(^3\) while that along the transverse axis is 0.74 Å\(^3\). Thus, in comparison with electronic polarizability, the vibrational contribution to the dipole polarizability of C\(_{70}\) is negligible and the static dipole polarizability of C\(_{70}\) is completely determined by the electronic polarizability. This result is consistent with the finding of Pederson and coworkers [25] for C\(_{60}\) and is relevant for the dielectric response of carbon nanotubes.

To conclude, the static dipole polarizability of C\(_{70}\) is calculated within the density functional formalism using large polarized Gaussian basis sets. The calculated values of electronic ($\alpha_{\text{el}} = 102.8$ Å\(^3\)) and vibrational ($\alpha_{\text{vib}} = 4.3$ Å\(^3\)) polarizabilities indicate that the vibrational contribution to the total polarizability of C\(_{70}\) is very small.

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