

# Static and Dynamic Polarizability of C<sub>540</sub> Fullerene

Patrizia Calaminici,\* Javier Carmona-Espindola, Gerald Geudtner, and Andreas M. Köster

State-of-the-art calculations of static and dynamic polarizabilities of the giant fullerene C<sub>540</sub> are presented. These density functional theory calculations have been performed using time-dependent auxiliary density perturbation theory which was recently implemented in deMon2k (Carmona-Espindola et al., JCP 2010, 133, 084102). For the polarizability calculations the local density approximation was used in combination with all-electron double-zeta valence polarization basis sets. To gain insight into the trend of these properties as the fullerene size increases the obtained results for C<sub>540</sub> are discussed with respect to those

obtained for smaller fullerenes such as C<sub>60</sub>, C<sub>70</sub>, C<sub>180</sub>, and C<sub>240</sub>. All fullerene structures were fully optimized without symmetry constraints. As the cluster size increases the dynamic polarizability strongly increases with respect to the static polarizability. Our analysis shows that static and dynamic polarizabilities per atom increase significantly with fullerene size. Moreover, the increase in the dynamic polarizabilities per atom is larger than for the static ones. © 2012 Wiley Periodicals, Inc.

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## Introduction

The study of size-dependent properties of nanoparticles, such as the increasing of electric and magnetic properties, has become a frontier line of research in nanoscience because of the fact that by this investigation different systems can be tailored for possible nanotechnology applications. Fullerenes are carbon clusters which are formed by the closing of a graphitic sheet with the needed curvature supplied by the intersecting, among a given number of graphitic hexagons, of 12 pentagons.<sup>[1,2]</sup> Different from most other nanoparticles, fullerenes present all their atoms on the cluster surface. This characteristic has a big effect in the fast increase of their volume with increasing of the number of carbon atoms. Since the discovery of the C<sub>60</sub> fullerene,<sup>[3]</sup> a myriad of works focused on much larger fullerenes consisting of up to several hundred atoms. These systems, commonly known in these days as giant fullerenes, have been theoretically studied (see, for example, Refs. [4–16] and references therein) with the aim to predict their structural and electronic properties. These theoretical works are very useful because the experimental literature of giant fullerenes is still very scarce. The polarizability ( $\alpha$ ) represents one of the most important observables for the understanding of the electronic properties of clusters, because it is very sensitive to the structure and to the shape of the system under study. As the polarizability is proportional to the volume, fullerenes are prototype systems for theoretical investigation. Because of this reason different studies on the polarizability of giant fullerenes have been performed over the recent years focusing on the understanding of its dependence on increasing system size. So far, carbon clusters up to around 2000 atoms have been studied with different methodologies.<sup>[17–21]</sup> The most reliable methods to determine electronic structures and properties of finite systems are first-principle-based approaches. Over the last two decades density functional theory<sup>[22]</sup> (DFT) has established itself as a very powerful tool for electronic structure calculations.<sup>[23]</sup> Because of the recent developments within this methodology state-of-the-art

calculations of structure and properties of large finite systems are now possible at very modest computational cost.<sup>[16,20,21,24–26]</sup> In particular, static polarizability calculations of giant fullerenes with ab initio DFT-based methods have been pioneered by Zope et al.<sup>[20]</sup> In contrast, only very recently, auxiliary density perturbation theory (ADPT) has been extended to time-dependent perturbation theory allowing dynamical polarizability calculations of fullerenes up to 240 atoms.<sup>[16,21]</sup> In this work, we use time-dependent auxiliary density perturbation theory (TDADPT) to calculate static and dynamic polarizabilities of the C<sub>540</sub> fullerene. The obtained static result is compared with the static polarizability from finite-field calculations available in the literature. The C<sub>540</sub> polarizability results are discussed in terms of the trend of the polarizability calculated for smaller fullerenes using the same methodology. To the best of our knowledge this represents the largest dynamic polarizability calculation at this level of theory ever presented in the literature and shows the potentiality of TDADPT to study molecular properties of large nanometric systems.

## Computational Details

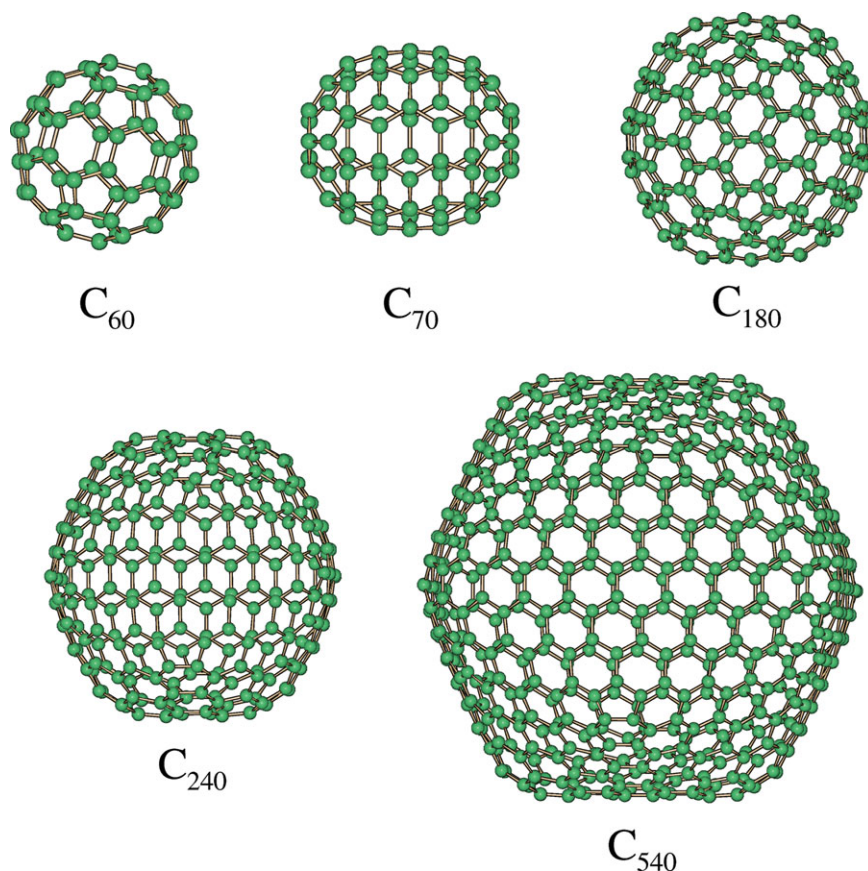
All calculations were performed with the LCGTO-DFT code deMon2k.<sup>[27]</sup> For all calculations the Dirac exchange<sup>[28]</sup> in combination with the VWN<sup>[29]</sup> correlation functional was used in combination with DFT optimized double zeta valence plus polarization (DZVP) basis sets.<sup>[30]</sup> The auxiliary density was expanded in Hermite Gaussian functions.<sup>[31,32]</sup> The GEN-A2

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**Figure 1.**  $C_{60}$ ,  $C_{70}$ ,  $C_{180}$ ,  $C_{240}$ , and  $C_{540}$  fullerenes structures optimized at the VWN/DZVP/GEN-A2 level of theory for which static and dynamic polarizabilities and polarizability anisotropies are calculated. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

auxiliary function set<sup>[33]</sup> was used. The exchange-correlation energies and potentials, calculated from the approximated densities, were numerically integrated on an adaptive grid with  $10^{-5}$  a.u. grid accuracy.<sup>[34,35]</sup> The same grid was used for the exchange-correlation kernel calculation. The molecular structures were fully optimized in delocalized internal coordinates<sup>[36]</sup> with a quasi-Newton method using the above described level of theory. The optimization convergence was based on the analytic gradient and displacement vectors with thresholds of  $10^{-4}$  and  $10^{-3}$  a.u., respectively. This theoretical method provides  $C_{60}$  bond lengths that are within the error bar (1.5 pm) of the experimental gas-phase electron diffraction data.<sup>[37]</sup>

The polarizability tensor elements were calculated from the perturbed density matrix as

$$\alpha_{\lambda\eta}(\omega) = - \sum_{\mu,\nu} P_{\mu\nu}^{(\lambda)}(\omega) \langle \mu | r_{\eta} | \nu \rangle \quad (1)$$

The perturbed density matrix was obtained via TDADPT as described in detail in Ref. [21]. Here, it is also shown that the static and dynamic VWN/DZVP/GEN-A2 ADPT polarizabilities of  $C_{60}$  match well with their experimental counterparts. The reported mean polarizabilities were calculated from the diagonal elements of the polarizability tensor by

$$\bar{\alpha}(\omega) = \frac{1}{3} (\alpha_{xx}(\omega) + \alpha_{yy}(\omega) + \alpha_{zz}(\omega)) \quad (2)$$

The corresponding polarizability anisotropies were calculated in the principal axes system of the polarizability tensor according to

$$|\Delta\alpha(\omega)|^2 = \frac{1}{2} \left[ (\alpha_{xx}(\omega) - \alpha_{yy}(\omega))^2 + (\alpha_{xx}(\omega) - \alpha_{zz}(\omega))^2 + (\alpha_{yy}(\omega) - \alpha_{zz}(\omega))^2 \right] \quad (3)$$

## Results and Discussion

The static and dynamic polarizability and polarizability anisotropy of the  $C_{60}$ ,  $C_{70}$ ,  $C_{180}$ ,  $C_{240}$ , and  $C_{540}$  fullerenes were calculated at the optimized geometries. The geometry optimization was performed without any symmetry constraints starting from icosahedral structures (except for the  $C_{70}$  fullerene) using the VWN functional and using all-electron DZVP basis sets. The same level of theory was used for the electric properties calculations. It was shown recently that this level of theory is the best compromise between performance and accuracy for static and dynamic polarizability calculations of giant fullerenes and that reliable polarizabilities of large systems can be obtained with rather small basis sets as the ones used here.<sup>[21]</sup> The optimized structures are illustrated in Figure 1. The obtained values of the static and dynamic polarizabilities and polarizability anisotropies are given in Table 1 together with available experimental data for the  $C_{60}$  and the  $C_{70}$  fullerenes.

**Table 1.** Static polarizability, static polarizability anisotropy, dynamic polarizability, and dynamic polarizability anisotropy (in atomic units) of  $C_{60}$ ,  $C_{70}$ ,  $C_{180}$ ,  $C_{240}$ , and  $C_{540}$ .

Fullerene	$\bar{\alpha}(0)$	Exp.	$\Delta\bar{\alpha}(0)$	$\bar{\alpha}(1064\text{nm})$	Exp.	$ \Delta\bar{\alpha}(1064\text{nm}) $
$C_{60}$	528.97	$516.77 \pm 54^{[a]}$	0.28	541.62	$533.65 \pm 27^{[b]}$	0.30
$C_{70}$	660.23	$688 \pm 94^{[c]}$	72.91	686.93		71.38
$C_{180}$	2013.97		1.38	2135.23		8.37
$C_{240}$	2902.26		1.48	3143.71		1.52
$C_{540}$	8464.23		5.12	11613.26		13.56

The optimized geometries are used. Available experimental results are also given for comparison.

[a] Static value from molecular beam deflection<sup>[39]</sup>. [b] Dynamic value from light force measurement<sup>[40]</sup>. [c] Static value<sup>[41]</sup>.

**Table 2.** Calculated analytic (ADPT), finite-field (FF) and PBE0/SVPD static polarizabilities (in atomic units) of the  $C_{60}$ ,  $C_{70}$ ,  $C_{180}$ ,  $C_{240}$  and  $C_{540}$  fullerenes

Fullerene	ADPT	FF	PBE0/SVPD
$C_{60}$	528.97	553.9 <sup>[a]</sup>	551.1 <sup>[b]</sup>
$C_{70}$	660.23	695.0 <sup>[c]</sup>	—
$C_{180}$	2013.97	1992.7 <sup>[a]</sup>	—
$C_{240}$	2902.26	2997.0 <sup>[a]</sup>	2017.8 <sup>[b]</sup>
$C_{540}$	8464.23	8050.0 <sup>[a]</sup>	8395.4 <sup>[b]</sup>

The optimized geometries are used.  
 [a] Static value from Ref. [20]. [b] Static value from Ref. [38]. [c] Static value from Ref. [42].

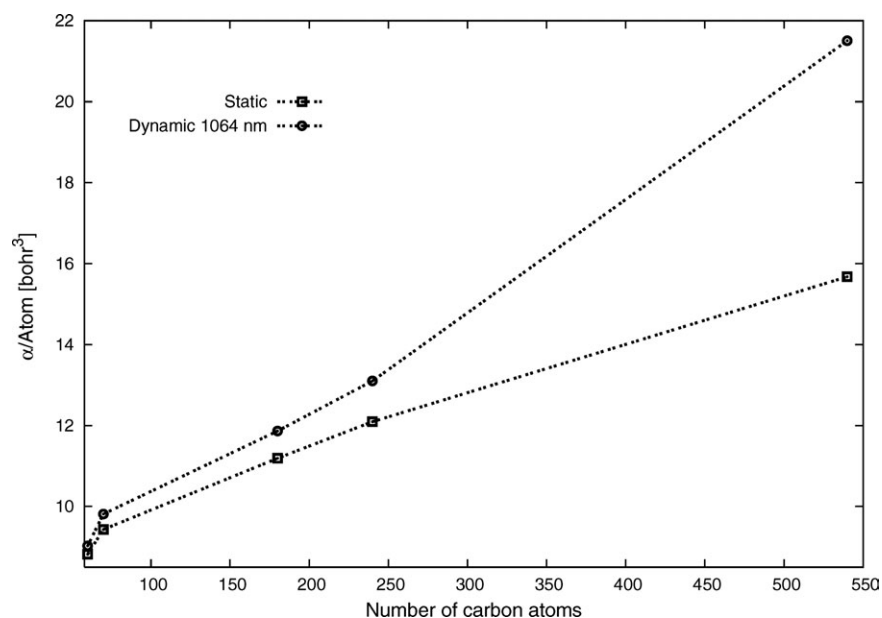
In Table 2, the results of our static polarizabilities for  $C_{60}$ ,  $C_{180}$ ,  $C_{240}$ , and  $C_{540}$  are compared with the corresponding finite-field (FF) values from Zope et al.<sup>[20]</sup> and the PBE0/SVPD results from Rappoport and Furche.<sup>[38]</sup> All values in Tables 1 and 2 are reported in atomic units. As Table 1 shows a good match between the VWN/DZVP/GEN-A2 ADPT polarizabilities and the experimental values can be observed. The calculated polarizabilities increase monotonically with fullerene size. We noticed that this increase is much more pronounced for the dynamic polarizabilities of larger fullerenes (Table 1). Moreover, as it can be seen from Table 2, the comparison between the finite-field values from Zope et al. with our static VWN/DZVP/GEN-A2 ADPT polarizabilities for  $C_{60}$ ,  $C_{70}$ ,  $C_{180}$ ,  $C_{240}$ , and  $C_{540}$  is rather satisfying taking into consideration the different nature of the used basis sets. However, a significant difference is found between the ADPT and PBE0/SVPD  $C_{240}$  polarizability. This is due to a printing error in Table 6 of Ref. [38]. The correct  $C_{240}$  PBE0/SVPD polarizability reads 2914.4 a.u. (Furche, personal communication) and, therefore is in very good agreement with our ADPT result. As a consequence all three ab initio approaches reported in Table 2 predict a monotonically

increasing polarizability per atom for giant fullerenes. In Figure 2 the static and dynamic polarizability per atom (in bohr<sup>3</sup>) as function of the number of carbon atoms is depicted. As Figure 2 shows the calculated static and dynamic polarizabilities per atom increase dramatically with increasing fullerene size. This behavior was already noticed for the  $C_{60}$ ,  $C_{180}$ , and  $C_{240}$  fullerenes.<sup>[21]</sup> However, what is really surprising, is the quite dramatic increase of the dynamic polarizability per atom of the  $C_{540}$  with respect to its static counterpart (Fig. 2). Table 1 also lists the polarizability anisotropies of the studied clusters. Because of the appearance of an inversion center in  $C_{60}$ ,  $C_{180}$ ,  $C_{240}$ , and  $C_{540}$  the polarizability anisotropy of these fullerenes should vanish. As Table 1 shows this is not the case in our calculations. The main reason is the symmetry unconstrained numerical integration of the exchange-correlation potential and kernel (also the finite threshold for the structure optimization leads to a slight distortion of the icosahedral symmetry). Table 1 shows that this numerical noise, given by the static polarizability anisotropy, is in the range of one per thousand or below compared to the corresponding average polarizability. In the case of dynamic polarizability anisotropies larger deviations are found. In any case, the only fullerene of the ones here studied that shows an appreciable polarizability anisotropy is  $C_{70}$ . Here the polarizability anisotropy is roughly 10% of the average polarizability.

## Conclusions

In this article, TDADPT was applied to calculate the static and dynamic polarizabilities and polarizability anisotropies of  $C_{540}$  fullerene. To the best of our knowledge this represents the largest dynamic polarizability calculation ever presented in the literature, so far. The obtained  $C_{540}$  polarizability results were presented along with the values calculated for smaller fullerenes such as  $C_{60}$ ,  $C_{70}$ ,  $C_{180}$ , and  $C_{240}$ .

The electric properties were calculated at the optimized geometry. All fullerenes were fully optimized without any symmetry restriction. For the geometry optimizations and for the property calculations the local density approximation level of theory in combination with an all-electron basis was used. The comparison of the polarizability values obtained in this work with experiment and with previous theoretical data is very satisfying. It was observed that, surprisingly, different from all the smaller studied fullerenes, the  $C_{540}$  fullerene presents a dramatic increase of the dynamic polarizability per atom with respect to its static counterpart. It was noticed that the polarizability anisotropy results are sensitive to the numerical noise associated with the symmetry unconstrained numerical integration of the exchange correlation potential and kernel and that



**Figure 2.** Static and dynamic polarizabilities per atom (in bohr<sup>3</sup>) of the  $C_{60}$ ,  $C_{70}$ ,  $C_{180}$ ,  $C_{240}$ , and  $C_{540}$  fullerenes as a function of the number of carbon atoms.

the dynamical polarizability anisotropies are mostly affected by this numerical noise. In any case, the resulting errors are in the range of one per thousand and, thus, do not effect the reliability of such a study. This work shows the potentiality of TDADPT to calculate molecular properties of very large systems which could be identified for important nanotechnology applications.

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**Keywords:** giant fullerenes · dynamical polarizability · density functional theory · time-dependent auxiliary density functional theory

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