

Electronic and vibrational linear and non-linear polarizabilities
of Li@C_{60} and $[\text{LiC}_{60}]^+$

H. Reis^{a*}, O. Loboda^a, A. Avramopoulos^a, M. G. Papadopoulos^{a*}, B. Kirtman^{b*},
J. M. Luis^{c*}, R. Zaleśny^d

^a *Institute of Organic and Pharmaceutical Chemistry,
The National Hellenic Research Foundation,
48 Vas. Constantinou Avenue, 11635 Athens, Greece*

^b *Department of Chemistry and Biochemistry, University of California,
Santa Barbara, California 93106, USA*

^c *Institute of Computational Chemistry and Department of Chemistry, University of
Girona,
Campus de Montilivi, 17071 Girona, Catalonia, Spain*

^d *Theoretical Chemistry Group, Institute of Physical and Theoretical Chemistry,
Wrocław University of Technology, Wyb. Wyspiańskiego 27,
50-370, Wrocław, Poland*

* e-mail: hreis@eie.gr, mpapad@eie.gr, josepm.luis@udg.edu, kirtman@chem.ucsb.edu

Abstract

Electronic and vibrational nuclear relaxation (NR) contributions to the dipole (hyper)polarizabilities of the endohedral fullerene Li@C_{60} and its monovalent cation $[\text{Li@C}_{60}]^+$ are calculated at the (U)B3LYP level. Many results are new, while others differ significantly from those reported previously using more approximate methods. The properties are compared with those of the corresponding hypothetical non-interacting systems with a valence electron transferred from Li to the cage. Whereas the NR contribution to the static linear polarizabilities is small in comparison with the corresponding electronic property, the opposite is true for the static hyperpolarizabilities. A relatively small, but non-negligible, NR contribution to the dc-Pockels effect is obtained in the infinite frequency approximation.

July 6, 2010

1 Introduction

Since their discovery endohedral fullerenes have been extensively investigated because of their novel structure and properties [1]. Electrical properties have been of major interest owing to a variety of possible applications ranging from qubits for quantum computation [2] to organic photovoltaic devices [3]. Our interest in this connection lies in the theoretical determination of the linear and nonlinear optical properties, i.e. the (hyper)polarizabilities, of these materials. For that purpose we have chosen initially to study the prototypical metal endohedral fullerene, Li@C_{60} , and its cation $[\text{Li@C}_{60}]^+$.

It has been recognized for some time now [4] that large amplitude vibrational motions, due to weak interactions between the dopant Li atom and the fullerene cage, could give rise to large vibrational (hyper)polarizabilities. Thus, both the pure electronic and vibrational

contributions need to be examined. So far both contributions have been treated only at a rudimentary level, to a large extent because of the large size of the fullerene cage and the open shell character of the neutral. Furthermore, only static properties have been considered as far as computations are concerned. The pure electronic first hyperpolarizability [5] and second hyperpolarizability [6] of the neutral have been calculated using an uncoupled Hartree-Fock scheme with molecular orbitals obtained from a restricted open-shell Hartree-Fock calculation. These papers also contain experimental measurements. Very recently Yaghobi, et al. [7] used a modified Su-Schrieffer-Heeger (Huckel-type) Hamiltonian [8], coupled with a sum-over-states procedure, to obtain the Li@C₆₀ electronic linear polarizability and second hyperpolarizability tensors.

Whereas all the theoretical papers mentioned here discuss the vibrational contribution to the (hyper)polarizabilities, only Whitehouse and Buckingham[4] made an attempt to calculate these properties for the type of system in which we are interested. They used a much simplified potential, in conjunction with a classical analysis - estimated to be valid above 20 K - to obtain a (temperature-dependent) expression for the vibrationally averaged dipole moment. Then, from the field-dependence of this expression, formulas for the vibrational linear polarizability and second hyperpolarizability were extracted and the former quantity was evaluated for the [Li@C₆₀]⁺ cation. Their work indicated that the vibrational contribution could be many times larger than the electronic contribution for this system.

As concerns endohedral fullerenes in general, some calculations of their polarizabilities have been reported, usually employing DFT methods [9], but reports on vibrational polarizabilities are rare. We mention here the work of Pederson *et al.* [10], who computed the vibrational polarizability of Kr@C₆₀, as well as of C₆₀ itself, in the lowest order of perturbation theory (double-harmonic approximation). At that level, these contributions were found

to be very small compared with the electronic property.

There have been many important advances in computational capability and theoretical methodology since the articles on Li doped C₆₀ noted above have appeared. While these articles establish a clear interest in the linear and nonlinear optical properties of the prototypical neutral and cation, the time is ripe for a significantly improved treatment. That is the goal of our current paper.

2 Methods

The geometry of Li@C₆₀ and the singly charged cation were optimized at the DFT level using the B3LYP functional in the unrestricted version for the former and the restricted version for the latter. We note here that spin contamination was not an issue in the unrestricted DFT calculations, neither with nor without applied electric fields. In all cases, the expectation value of the total spin squared operator, $\langle S^2 \rangle$ for the converged Li@C₆₀ wavefunctions was found to be between 0.755 and 0.756, which is close to the exact value of 0.75 for a pure doublet. Due to the large size of the molecule, as well as the tight convergence requirement for calculating vibrational (hyper)polarizabilities, the rather small 6-31G basis set was employed in the latter calculations (some 6-31+G values are included for comparison). For the electronic properties, the 6-31G basis was found to be inadequate, thus they were additionally computed with the 6-31+G and 6-31+G* basis sets. In addition, several geometry optimisations were done with 6-31+G and 6-311G*, although no Hessians could be computed with these large basis sets.

The static electronic polarizabilities ($\alpha_{\alpha\beta}^e \equiv \alpha_{\alpha\beta}^e(0;0)$), first hyperpolarizabilities ($\beta_{\alpha\beta\gamma}^e \equiv \beta_{\alpha\beta\gamma}^e(0;0,0)$), and second hyperpolarizabilities ($\gamma_{\alpha\beta\gamma\delta}^e \equiv \gamma_{\alpha\beta\gamma\delta}^e(0;0,0,0)$) are defined by the Taylor series expansions for the dipole moments $\mu_\alpha(F)$ [11] or energies $E(F)$ [11], in terms of

the static field F :

$$E(F) = E(0) - \mu_i^e F_i - \frac{1}{2} \alpha_{ij}^e F_i F_j - \frac{1}{6} \beta_{ijk}^e F_i F_j F_k - \frac{1}{24} \gamma_{ijkl}^e F_i F_j F_k F_l - \dots \quad (1)$$

$$\mu_i(F) = -\frac{\partial E(F)}{\partial F_i} = \mu_i^e + \alpha_{ij}^e F_j + \frac{1}{2} \beta_{ijk}^e F_j F_k + \frac{1}{6} \gamma_{ijkl}^e F_j F_k F_l + \dots \quad (2)$$

From these computed properties, i.e. the dipole moment and energy, the (hyper)polarizabilities were obtained using the Romberg differentiation procedure. Convergence difficulties in the DFT self-consistent orbital calculations severely limit the accuracy of the numerical differentiation as well as the range of fields that can be used. The problem increases for larger fields and thereby impacts the accuracy of the (hyper)polarizabilities. Thus, the second hyperpolarizability could be obtained with sufficient statistical confidence from the dipole moments, but not from the energies. Generally, a third order Romberg differentiation [12] with a minimal applied field strength of 0.001 au was applied. In some cases, only a second order Romberg differentiation was possible due to convergence problems, but in some other cases even a higher order was used to ensure the reliability of the values. In addition to the DFT computations, selected Hartree-Fock (HF) and second order Møller–Plesset (MP2) computations were performed with the 6-31G basis set to provide a comparison with traditional wavefunction theory methods. The computations were done with Gaussian03 [13] and Gaussian09 [14].

Some of the problems mentioned above could have been avoided by using an analytical derivative method, e.g. analytical response theory, as implemented for linear, quadratic and cubic response functions in time-dependent DFT by Jansik *et al.* [15] in the program package Dalton [16]. This method has also been extended using spin-restricted DFT for open-shell systems [17, 18]. However, trials to compute the (hyper)polarizabilities of Li@C₆₀ using the smallest basis set (6-31G) were successful only for linear polarizabilities; convergence prob-

lems in determining the response vectors prevented calculation of the hyperpolarizabilities. Considering that these calculations were quite expensive, and finite fields were needed for the nuclear relaxation treatment of vibrational contributions, we decided to employ finite field techniques throughout. We mention, finally, that the polarizabilities obtained from spin-restricted analytical response theory were nearly identical to those calculated by unrestricted finite field methods, showing again that spin-contamination is not a problem in our case.

Although there has been a lot of progress in the last few years in the field of computing vibrational (hyper)polarizabilities based on vibrational self-consistent field theory and correlated versions thereof (see e.g. Refs. [19, 20]), the corresponding methods are computationally still much too expensive for the large systems of interest here. Thus, the vibrational contributions were mostly computed using the finite field approach pioneered by Bishop, Hasan and Kirtman [21], and later implemented by Luis *et al.* [22]. In this approach, the molecular geometry is first optimized in the presence of a static electric field while strictly maintaining the Eckart conditions [22]. Then the difference in the static electronic properties due to the change in geometry induced by the field is expanded as a power series in the field. Each term in the expansion yields the sum of a static electronic (hyper)polarizability plus a nuclear relaxation (NR) vibrational term. For example, the change of the dipole moment and of the linear polarizability are given by [21]:

$$\Delta\mu_i(F, R_F) = a_{1,ij}F_j + \frac{1}{2}b_{1,ijk}F_jF_k + \frac{1}{6}g_{1,ijkl}F_jF_kF_l + \dots \quad (3)$$

$$\Delta\alpha_{ij}(F, R_F) = b_{2,ijk}F_k + \dots \quad (4)$$

with

$$a_{1,ij} = \alpha_{ij}^e(0; 0) + \alpha_{ij}^{nr}(0; 0) \quad (5)$$

$$b_{1,ijk} = \beta_{ijk}^e(0; 0, 0) + \beta_{ijk}^{nr}(0; 0, 0) \quad (6)$$

$$g_{1,ijkl} = \gamma_{ijkl}^e(0; 0, 0, 0) + \gamma_{ijkl}^{nr}(0; 0, 0, 0) \quad (7)$$

$$b_{2,ijk} = \beta_{ijk}^e(0; 0, 0) + \beta_{ijk}^{nr}(-\omega; \omega, 0)_{\omega \rightarrow \infty} \quad (8)$$

The argument R_F implies structure relaxation in the field, and P^{nr} means the nuclear relaxation part of P , while the subscript $\omega \rightarrow \infty$ invokes the so-called "infinite optical frequency (IOF)" approximation. In principle, this procedure allows one to obtain most of the major dynamic vibrational NR contributions in addition to the purely static ones of Eqs. 5-7. The linear term in the electric field expansion of Eq. (4) gives the dc-Pockels effect; the quadratic term gives the optical Kerr Effect; and the linear term in the expansion of beta yields dc-second harmonic generation (all in the IOF approximation). For laser frequencies in the optical region it has been demonstrated that the latter approximation is normally quite accurate [23, 24, 25]. In fact, this approximation is equivalent to neglecting terms of the order $(\omega_v/\omega)^2$ with respect to unity (ω_v is a vibrational frequency). In terms of Bishop and Kirtman perturbation theory [26, 27, 28] all vibrational contributions through first-order in mechanical and/or electrical anharmonicity, and some of second-order, are included in the NR treatment [29].

The remaining (higher-order) vibrational contributions can, in principle be computed as well using a related formulation [30]. However, that treatment requires computation of the field-dependent zero-point vibrationally averaged properties, which was not feasible for the systems studied here because of their large size and complicated potential energy surface (PES). Indeed, of the dynamic properties mentioned above, we were only able to obtain the dc-Pockels Effect due to instabilities for high fields that will be described later.

Generally, field strengths from 0.0001 au up to 0.0128 au were tried in the Eckart-constrained optimizations and the energies and dipole moments of the successfully optimized

structures were subjected to a numerical Romberg differentiation. As in the case of the electronic properties, the numerical differentiation of the energies was too unstable to yield all the properties of interest. However, the numerical differentiation of field-induced dipole moments allowed us to obtain stable values for most of the components of the NR contribution to the static α , β and γ and to the IOF approximation for the dc-Pockels first hyperpolarizability. Due to the high computational cost of these calculations, the 6-31G basis set had to be used. A few control calculations with the 6-31+G basis set showed that the influence of diffuse basis functions on the vibrational properties is not negligible, but smaller than on the electronic properties.

3 Results and Discussion

3.1 Geometry optimization

Zhang *et. al* [31] have calculated the UB3LYP/6-311G* potential energy surface (PES) for motion of Li along five different rays passing through the center of an undistorted fullerene cage in Li@C₆₀. The two most important rays, as far as the structure is concerned, were along the line from the cage center to the center of a C₆ hexagon (symmetry C_{3v}) and along the line from the cage center to the center of a C₅ pentagon (symmetry C_{5v}). Since localization due to cage distortion can be important, as they found, we carried out geometry optimizations for near C_{3v} and near C_{5v} symmetry at the same level while allowing the cage to fully relax. We also obtained the stationary point at the near icosahedral symmetry under the same conditions. In all cases, it was necessary to lower the actual symmetry to obtain the optimized structure, due to SCF convergence problems in the high symmetry calculations.

Zhang *et al.* [31] report that similar difficulties occurred in their calculations.

In the case of approximate I_h symmetry the cage was slightly distorted yielding a C_s optimized structure with the Li atom slightly (0.015 Å for UB3LYP/6-31G) removed from the cage center. As already well-known this stationary point is not a minimum; in fact, there are four imaginary frequencies. For the two minima (near C_{5v} and near C_{3v}) the Li atom shifts about 0.1 Å off the ray that goes from the center of the cage to the center of the polygon and the symmetry is again reduced to C_s . In both instances, the Li atom was located at about 1.5 Å from the center of the cage in the optimized structure. The eccentric position of Li in Li@C₆₀ has been interpreted in terms of dispersion and repulsion [32] interactions.

All of the above results agree semi-quantitatively with Zhang *et al.* [31] as expected (see further below). The structure with approximate C_{3v} symmetry was found to be 3.4 kJ/mol (1.6 kJ/mol) more stable than the one with C_{5v} symmetry using UB3LYP/6-311G* (UB3LYP/6-31G). Our value is slightly higher than the one found by Zhang *et al.* (2.6 kJ/mol). The reason for this difference may be due to cage relaxation and/or small deviations of the Li atom from the fixed ray they employed. It is also possible that the two minima are not directly related; as shown further below, there seem to be several minima close by. The energy difference between the near- I_h and near C_{3v} symmetry structures was found to be 56.5 kJ/mol at the 6-31G/UB3LYP level. Since we are interested in the ground vibrational state all further investigations were focused on the most stable near- C_{3v} structure. The optimization using the 6-31+G basis was started from the 6-31G optimized structure, and the final optimized structure was very close to the starting one, as expected.

The geometry of the monovalent cation [Li@C₆₀]⁺ was also determined for the near C_{3v} symmetry, using restricted B3LYP and the 6-31G basis set. A control optimization using B3LYP/6-311G* did not show any substantial structural differences. At the minimum, the Li

atom is about 1.4 Å off the center of mass of the cage. The average C-C bond-length (1.4406 Å) is nearly the same as that of the neutral (1.4412 Å). However, the cation is somewhat more spherical. As a measure of the sphericity we use $\Delta I = [(I_a - I_b)^2 + (I_a - I_c)^2 + (I_b - I_c)^2]^{1/2}$, where I_x is the principal component of the cage inertia tensor, with respect to the center of mass, in the x -direction. Our values are $\Delta I = 1.4 \text{ g \AA}^2/\text{mol}$ for the cation and $\Delta I = 31.5 \text{ g \AA}^2/\text{mol}$ for the neutral. For comparison, the average moment of inertia $I = 1/3(I_a + I_b + I_c)$ is about 3050 g Å²/mol for both species. Finally, the coordinates of both near C_{3v} optimized structures can be obtained from the authors.

3.2 Electronic properties

In order to assess the reliability of the level of theory chosen, we show in Table I the computed static electronic properties of Li@C₆₀ and [Li@C₆₀]⁺, along the dipole moment direction (defined as z), at different levels of theory and with different basis sets. Due to the convergence problems mentioned above, it was not possible to determine the second hyperpolarizability, γ , at the (U)MP2 level for either species. Because of the horizontal shift of the Li atom in the optimization process (*vide supra*), the z -axis does not coincide with the axis containing the cage center of mass and the Li atom, but is tilted away by about 10°. For [Li@C₆₀]⁺ the dipole moment is determined by placing the (arbitrary) origin at the cage center of mass.

The rather small dipole moment of the neutral depends strongly on the basis set and correlation treatment. Fortunately our interest lies in the (hyper)polarizabilities. Nonetheless, we can say that our dipole moment results are in qualitative agreement with the value computed by Campbell et al. [5], but much smaller than reported by Li and Tomanek [33]. The comparison of our calculated (hyper)polarizabilities with those of Campbell, et al. will be made later. We note that the addition of diffuse functions to the 6-31G basis is always

crucial. But whereas the further addition of polarization functions has a minor effect on α and γ , for β they partially (or totally) offset the effect of the diffuse functions. Comparison of HF and (U)MP2 shows that correlation has a very large effect on β , but not α . The fact that (U)B3LYP yields values similar to (U)MP2 suggests that both account fairly well for correlation (even though the calculations are only at the 6-31G level). Due to the unavailability of γ at the (U)MP2 level, no conclusions can be drawn in this respect for the second hyperpolarizability. The cation properties are somewhat less sensitive to correlation than those of the neutral. Overall, we conclude that (U)B3LYP/6-31+G* is the minimal level required to obtain reliable electronic properties. Finally, the large change in hyperpolarizabilities upon going from the cation to the neutral is not unexpected in view of the additional electron in a (formerly) unoccupied orbital localized on the C_{60} moiety. For γ the effect is more evident for the other two diagonal components shown in Table II (see below).

In Table II we show the computed static (U)B3LYP/6-31+G* electronic properties of $Li@C_{60}$, $[Li@C_{60}]^+$, C_{60}^- , C_{60} and Li. The several additional species were included for comparison of $Li@C_{60}$ with both non-interacting $Li + C_{60}$ and $Li^+ + C_{60}^-$, as well as for comparison of $[Li@C_{60}]^+$ with non-interacting $Li^+ + C_{60}$. For α and γ only selected components useful for this purpose are displayed whereas, for β , all symmetry allowed components are given (see later). The 6-31+G* basis is inadequate for the Li atom. Although it is not important here, we have added results for Li atom obtained with two larger basis sets (aug-cc-pVQZ and aug-cc-pV5Z) showing that the negative 6-31+G* value of γ becomes positive for the larger Dunning basis sets. The properties of Li^+ are negligible [34] in the current context and are not taken into account in the discussion below. For our comparisons the geometry of the endohedral fullerenes was optimized at the (U)B3LYP/6-31G level and the same geometry was retained for the non-interacting species. In principle, a BSSE correction should be applied to

the Li-doped fullerenes, but is omitted since it would have no effect on our conclusions.

As compared to the hypothetical non-interacting species the interaction between the Li^+ cation and either the C_{60}^- or C_{60} cage leads to a moderate reduction of the diagonal polarizabilities and, in the case of $[\text{LiC}_{60}]^+$ also of the second hyperpolarizabilities. The reduction for α may be due to a contraction of the electron density caused by the attraction of the cation. Such an explanation will not suffice for γ since the effect of the interaction on the diagonal components is quite different for Li@C_{60} , and the second hyperpolarizability is not simply related to the size of the electron distribution. The first hyperpolarizabilities arise from asymmetry of the charge distribution and are, consequently, strongly enhanced in the endohedral species.

Campbell et al. [6] used an uncoupled approximation to coupled-perturbed HF theory - or, as they prefer to call it, a "computationally expensive tight-binding approach" to compute the hyperpolarizabilities of Li@C_{60} , using the 6-31G* basis set, and obtained for γ the values $\sim(320, 540, -320)\times 10^3$ au, for the x, y, and z diagonal components respectively. While the x value is quite close to ours, the other two values do not agree even in sign. In Ref. [5], Campbell *et al.* also computed the first hyperpolarizability using the same methodology. The values they obtained ($\beta_{zzz} \sim 15000$ au, $\beta_{yyy} \sim -7000$ au) are at least one order of magnitude larger than ours in the most similar geometry they considered (Li displaced about 1.5 Å from the center towards an hexagon). Campbells' values are based on orbitals obtained from a ROHF calculation, while ours are computed at the UB3LYP level. The large differences between the two results confirm the unreliability of the HF method for the hyperpolarizabilities of Li@C_{60} , as found here for the UHF values (cf. Table I). In the same approximation, but now using RHF, they obtain ~ 50.000 au for the diagonal component in C_{60} [6]. This value is about 2.5 times smaller than ours, which may be mostly due to the different basis sets, but

also due to different approximations in both approaches, as well as differences in geometry etc. Finally, we note that Jansik *et al.* [15] computed values for the (hyper)polarizabilities of C_{60} in I_h symmetry with analytic response theory using larger basis sets, specifically tailored for the purpose of computing hyperpolarizabilities, and obtained $\alpha_{av} = 547.0$ au and $\gamma_{av} = 118 \cdot 10^3$ au with B3LYP using the cc-pVDZ+*spd* (their notation) basis set. These values are quite comparable to ours, taking into account the differences in symmetry (I_h versus C_s), geometry, and basis set (it was assumed in our case that the geometry of C_{60} is sufficiently spherical so that the nondiagonal terms of γ do not deviate appreciably from the relation $\gamma_{iijj} = 1/3\gamma_{iiii}$).

We also investigated the influence of the position of the Li atom along the dipole axis on the electric properties of $Li@C_{60}$. The UB3LYP/6-31+G* values for different distances r_{Li-O} , where O denotes the center of mass of the cage, are shown in Table III. For reference purposes the surface of the cage is at a distance of ~ 3.4 Å. Interestingly, the diagonal z -component of the polarizability, first hyperpolarizability, and dipole moment change little (μ , α) or moderately (β) (for μ we are assuming that the value of the change is reliable even though the value of the dipole moment itself is not) between $r = 0.729$ Å and $r = 2.0$ Å, but γ_{zzzz} is altered much more drastically, even undergoing a sign change at small distances from the cage center. This is consistent with γ being due to electron density that is distant from the surface of the cage.

The large gradient in γ_{zzzz} for $Li@C_{60}$ could possibly be used in a potential nonlinear "flip-flop" device. This would require a mechanism such as an STM electric field to shift the equilibrium position of the Li atom between different regions. The magnitude of such a shift has been investigated by Delaney and Greer [2] who found that it is difficult to move the Li atom very far because of the large screening effect of the fullerene cage. In the calculations

reported below we find that a shift from the field-free position of about $\Delta z \sim 0.03$ au will result when a 0.0128 au field is applied. According to Table III, this shift is much too small to change γ_{zzzz} appreciably.

3.3 Nuclear relaxation contribution to vibrational nlo properties

In this sub-section we present the nuclear relaxation (NR) contributions to the vibrational (hyper)polarizabilities of Li@C₆₀ and [Li@C₆₀]⁺. As mentioned in Sec.II our treatment requires a geometry optimization in the presence of a finite field. A problem can arise when there are multiple minima on the PES separated by low energy barriers. The finite field method works satisfactorily in that event as long as the field-dependent optimized structure corresponds to the same minimum as the field-free optimized structure. This was the case in previous work on ammonia [35], which has a double minimum potential. However, it is sometimes not the case for the endohedral fullerenes considered here, especially Li@C₆₀. In fact, we were unable to determine the NR contribution in the x direction, i. e. perpendicular to the symmetry plane, for that molecule. It was possible to obtain α_{xx}^{nr} , based on the alternative analytical formulation [26, 27, 28], utilizing field-free dipole (first) derivatives and the Hessian. The analytical polarizability components in the other two directions were, then, used to confirm the values of the corresponding finite field method for those properties.

In addition to the situation just discussed, it was also found that the electric field can sometimes lead to a change of electronic state, as detected by a sudden jump in the computed polarizability. This further limited the range of applicable field strengths and, thus, the range of properties that could be computed with sufficient statistical confidence.

Our results for the static NR contributions to the diagonal (hyper)polarizability components are shown in Table IV. Most of the values were obtained at the (U)B3LYP/6-31G level.

For comparison, a few calculations were also done for Li@C_{60} at the UB3LYP/6-31+G level. As seen from the Table, diffuse basis functions have a non-negligible effect on the computed values, although the effect is smaller than on the electronic properties (cf. Table I). Note in particular that there is no *qualitative* change of any vibrational property upon going from 6-31G to 6-31+G, in contrast to the electronic properties where 6-31G gives a negative value for γ_{zzzz} , while it is positive for 6-31+G. Thus, we expect that the values of vibrational properties obtained with the 6-31G basis are qualitatively correct, although the accuracy becomes worse for γ^{nr} than it is for α^{nr} or β^{nr} .

For α the vibrational contributions are quite small in comparison with their electronic counterparts (cf. Table II). In the case of $[\text{Li@C}_{60}]^+$ this appears, at first glance, to contrast with what Whitehouse and Buckingham (WB) [4] have previously found. However, their values were obtained by classical averaging in the high temperature limit - in this case above 20 K - while ours are for 0 K. Another difference is that WB obtain the complete vibrational polarizability and second hyperpolarizability, albeit very approximately, whereas we have not included the so-called curvature contribution [30]. For the polarizability one would "normally" expect the latter to be substantially smaller than the NR term, but endohedral fullerenes are not "normal" molecules and that may not be the case here. Of the several approximations in the WB treatment, one of the most questionable is the spherical approximation for the field-free potential, which Zhang, et al. have shown does not qualitatively reproduce the low energy vibrational spectrum of the neutral. This is not to mention that WB considered a rigid cage and motion along the C_{5v} symmetry axis, rather than the lower energy C_{3v} symmetry axis.

In contrast to α , the NR contributions to β and γ , are quite large. For the cation, in particular, two diagonal components of γ^{nr} are larger than the corresponding electronic

components. Such an increase in the relative magnitude of the NR (hyper)polarizabilities, as compared to the electronic values, as the order of nonlinearity increases is often observed in conjugated systems [25, 36]. However, it is usually not to as large an extent as found here. The relationship with degree of nonlinearity may be connected with the fact that only dipole derivatives enter into the linear NR polarizabilities, whereas β^{nr} and γ^{nr} depend additionally on polarizability derivatives, as the perturbation expressions for these quantities show [28]. Because of the conjugation the polarizability derivatives tend to be large (small changes in bond length alternation cause large changes in α). Furthermore, the higher-order vibrational polarizabilities (as opposed to the linear vibrational polarizability) depend upon electrical and mechanical anharmonicity which, undoubtedly, is especially large for the systems we are considering. WB give an expression for γ , but no numerical values. In addition, they considered only linear terms in their field-dependent vibrational Hamiltonian. This omits contributions to the vibrational hyperpolarizability that are generally important as suggested above.

In Table V we show the computed NR contribution to several components of the dc-Pockels effect for Li@C₆₀, i.e. $\beta_{ijy}^{nr}(-\omega; \omega, 0)$ and $\beta_{ijz}^{nr}(-\omega; \omega, 0)$ where $ij = xx, yy, yz$, and zz . (see eq. 8). Comparison with the corresponding electronic values of Table II shows that the vibrational contribution is relatively small, compared to the corresponding static electronic component, but not negligible. The values obtained here may be compared with those of a typical donor-acceptor molecule, H₂N-(CH=CH)₃-NO₂, for which the ratio $\beta_{iii}^{nr}(-\omega; \omega, 0)_{\omega \rightarrow \infty} / \beta_{iii}^e(0; 0, 0)$ along the dipole direction was found to be about 0.7 at the RHF level and about 0.2 at the MP2 level [36]. For LiC₆₀ this ratio is 0.13 at the UB3LYP level.

4 Conclusions

We have computed both electronic and NR vibrational contributions to the (hyper)polarizabilities of the prototype endohedral fullerene Li@C_{60} and its cation. A number of these properties were obtained for the first time. In other cases our results differ quite significantly from those previously determined using more approximate approaches. The latter include the static electronic properties calculated by Campbell et al. [5, 6]. Although, for the cation, there is a large difference between our values of the static vibrational contribution to α and those reported by Whitehouse and Buckingham [4], these results are not really comparable because their calculations include the effect of temperature. In addition, they applied several strong approximations, such as assuming a spherical field-free potential inside the cage. On the other hand, our calculations do not include higher-order vibrational contributions omitted in the NR treatment. It would be worthwhile to add temperature-dependence to the NR approach as we plan to do in the future. Whereas the NR contribution to the static α is quite small for both endohedral fullerenes, it becomes quite large for the static hyperpolarizabilities. This contribution is reduced for the dynamic Pockels effect, computed in the infinite optical frequency approximation, but is still not negligible.

For $[\text{Li@C}_{60}]^+$ the calculated (hyper)polarizabilities are roughly comparable to those of the hypothetical non-interacting system obtained by charge transfer of the Li valence electron to the cage giving $\text{Li}^+ + \text{C}_{60}$. The same is true for the linear polarizability of the neutral but the non-interacting charge transfer model completely breaks down for the hyperpolarizabilities.

We consider our work as a substantial step towards the final goal of a full computational characterization of the linear and nonlinear electric dipole properties of endohedral fullerenes. As far as vibrational contributions are concerned, in addition to the NR treatment

of low-order perturbation terms, there is an established method for obtaining all remaining contributions through calculation of zero-point vibrationally averaged properties at the relaxed field-dependent geometry [30]. What is needed is a robust procedure for carrying out the geometry optimizations when the PES has multiple minima and/or other strongly anharmonic features. Work is in progress on a reduced dimensionality scheme that may be combined with quasidegenerate perturbation theory to treat such circumstances [35].

5 Acknowledgments

We gratefully acknowledge support from the European Union (MTKD-CT-2006-042488), and the use of computing resources of the Barcelona Supercomputing Centre (BSC), the HPC resources of CINECA and the Pittsburgh Supercomputing Centre (PSC). One of the authors (RZ) is the recipient of a fellowship co-financed by the European Union within the European Social Fund.

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Table I: Electronic contribution to dipole moment (μ), first- (α^e), second- (β^e) and third-order polarizability (γ^e) for Li@C₆₀ and [Li@C₆₀]⁺ using different levels of theory and different basis sets, for the (U)B3LYP/6-31G optimized geometry. All values in a.u.

Method	Basis set	Li@C ₆₀				[Li@C ₆₀] ⁺		
		μ_z^e	α_{zz}^e	β_{zzz}^e	$\gamma_{zzzz}^e \times 10^3$	α_{zz}^e	β_{zzz}^e	$\gamma_{zzzz}^e \times 10^3$
(U/R)B3LYP	6-31G	0.049	508.0	1540.8	-39	468.9	-237	28
(U/R)B3LYP	6-31+G	0.328	578.56	1839	64	520.2	-53	99
(U/R)B3LYP	6-31+G*	0.390	589.03	1532.6	66	533.9	-118	99
(U/R)HF	6-31G	-0.18	479.0	5540	900	445.8	-83	54
(U/R)MP2	6-31G	1.39	527.1	1362.6	-	463.6	-192	-

Table II: Electronic (e) contribution to diagonal components of α , β and γ for Li@C₆₀, [Li@C₆₀]⁺, C₆₀, C₆₀⁻ and Li calculated at the UB3LYP/6-31+G* level of theory. A couple of larger basis set calculations are reported for Li.

$i =$	Li@C ₆₀ ^a			[Li@C ₆₀] ^{+b}				
	x	y	z	x	y	z		
α_{ii}^e	560.03	590.29	589.03	533.86	533.86	533.89		
β_{iii}^e	0.0	-290.0	1532.6	0	0	-118.1		
$\gamma_{iiii}^e \times 10^3$	293	-20	66	102	102	99		
$i, j =$	x, y	x, z	y, z	z, y	x, y	x, z	y, z	
β_{ij}^e	98	-1104	514	-58	0	-52	-52	
$i =$	C ₆₀ ^{-a}			C ₆₀ ^b			Li	
	x	y	z	x	y	z	$x = y = z$	
α_{ii}^e	575.9	617.7	620.5	550.5	550.5	551.3	138.6, 143. ^c , 142.9 ^d	
β_{iii}^e	0	-88	441	0	0	-11	0	
$\gamma_{iiii}^e \times 10^3$	211	-46	-86	136	135	136	-250,568 ^b , 631 ^c	

^a At the geometry of Li@C₆₀/UB3LYP/6-31G
aug-cc-pVQZ basis

^b At the geometry of [Li@C₆₀]⁺/B3LYP/6-31G

^c

^d aug-cc-pV5Z basis

Table III: Electronic dipole moment and (hyper)polarizabilities for Li@ C_{60} along the dipole (z) axis as a function of the distance between the center of the cage and the Li atom ($r_{\text{Li-O}}/\text{au}$), computed at the UB3LYP/6-31+G* level.

$r_{\text{Li-O}}$	μ_z^e	α_{zz}^e	β_{zzz}^e	$\gamma_{zzzz}^e (\times 10^3)$
0	-0.117	597.6	416	-86
0.729	0.159	594.4	1112	-19
0.958	0.243	592.8	1278	8
1.058	0.278	592.1	1340	20
1.158	0.310	591.4	1396	32
1.358	0.367	589.9	1492	55
1.458	0.390	589.0	1533	66
1.558	0.409	588.2	1569	76
1.658	0.424	587.3	1601	87
2.0	0.440	584.5	1676	123

Table IV: Nuclear relaxation (NR) contribution to the diagonal components of the static α , β and γ of Li@C_{60} and $[\text{Li@C}_{60}]^+$ calculated at the (U)B3LYP/6-31G level and the UB3LYP/6-31+G level (in square brackets).

$i =$	Li@C_{60}			$[\text{Li@C}_{60}]^+$		
	x	y	z	x	y	z
α_{ii}^{nr}	14.7 ^a	10.3	10.2 [11.9]	10.4	9.4	4.5
β_{iii}^{nr}	- ^b	-125.9	794.6 [(912-915)]	0	95	18
$\gamma_{iii}^{nr} \times 10^3$	- ^b	-90	(25 - 40) [(52 - 81)]	560	190	37

^a Computed analytically; see text. ^b Not determined; see text

Table V: Components of the NR contribution to the dc-Pockels effect ($\beta_{ijk}^{nr}(-\omega; \omega, 0)_{\omega \rightarrow \infty}$) computed for Li@C₆₀ in the infinite optical frequency approximation from eq. 8, at the (U)B3LYP/6-31G level.

$ij =$	xx	yy	yz	zz
β_{ijy}^{nr}	-23	-33	51	-9
β_{ijz}^{nr}	-199	119	15	200