Z. Phys. D 37, 277–280 (1996)

ZEITSCHRIFT FÜR PHYSIK D

Monolayer metal coverage of fullerenes: the optical response

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Received: 4 December 1995/Final version: 29 January 1996

Abstract. A first-principles investigation of the photoabsorption cross section of the specially stable cluster $Li_{12}C_{60}$ is carried out, including the icosahedral symmetry of the cluster and treating the ions via ab initio pseudopotentials. The role of the coating metal is assessed by computing the same quantity for the fullerene "seed". It is found that the main absorption features are determined by the carbon molecule, both at low and high excitation energies, in spite of a reduction of 60% for the ionization threshold of $Li_{12}C_{60}$ as compared to C_{60}. Nonetheless the lithium coating is responsible for small yet clearly observable effects throughout the spectrum, in particular for a more structured and broad strength distribution at excitation energies below the ionization threshold of C_{60}, and a double peak structure in the Mie resonance at ≈ 20 eV.

PACS: 36.40.+d; 31.50.+w; 33.20.Kf

Inspired by electrochemical evidence of a stable $Li_{12}C_{60}$ phase [1], the cluster $Li_{12}C_{60}$ has been predicted to be particularly stable, due to the favourable combination of a closed-shell electronic structure, realized in a highly-symmetric icosahedral geometry [2]. This structural property is a somewhat surprising result, because with other alkali elements saturation occurs at $x = 6$ for the intercalated compounds M_xC_{60}. Prompted by these results, T. P. Martin and his group co-evaporated C_{60} and different alkali metals in a gas aggregation cell, registering the mass spectrum for several types of C_{60} clusters coated with metal atoms [3]. The lithium coating experiments confirmed the special stability of the $Li_{12}C_{60}$ cluster, which develops also a well defined peak in the mass spectra of singly and doubly ionized lithium-coated C_{60} clusters.

Theoretically, a good deal is known about the structural properties of $Li_{12}C_{60}$ [2], as well as other lithium-coated fullerenes [4]. This is not the case concerning their optical properties, which are expected to display a size-dependent behaviour. In fact, by increasing the number of alkali coating atoms, it is likely that the cluster undergoes a non-metal to metal transition, in which the C_{60} cage becomes the seed for a metallic nanostructure. Qualitatively, and taking as a reference the optical spectrum of the isolated C_{60} cage, one may expect that alkali coverage will induce important effects in the low-energy region ($0 < E < 6$ eV) of the absorption spectrum, where the collective charge density oscillations of alkali clusters take place, whereas at higher excitation energies ($E \approx 20$ eV) the spectrum will be characterized by a (strongly screened) bump which originates in the so-called Mie plasmon [5] of C_{60}.

Several physical phenomena may lead to such effects. On one hand, the layers of alkali-coating atoms will induce, in general, new geometrical equilibrium shapes for these clusters, as compared to the icosahedral shape of the C_{60} fullerene. The deviations from the icosahedral shape correspond to symmetry breakings which may induce important modifications in the energy sequence and degeneracies of the one-electron levels, thereby affecting the optical properties. On the other hand, metallic screening is also expected to become increasingly important, due to the mobile valence electrons of the metal coating atoms, which will fill the weakly bound states of the cluster.

The symmetry breaking effect has been conjectured [3] in order to interpret the abundance spectra of alkali-coated fullerenes, and corroborated by the results of the simulations carried out by Martin's group [4]. In this context, $Li_{12}C_{60}$ is a very special cluster, since it is the only cluster predicted so far to maintain the symmetry of the fullerene seed. Therefore, it constitutes an ideal "laboratory" to investigate the role of electronic effects, since for $Li_{12}C_{60}$ the ionic symmetry-breaking effect is absent. In particular, one can investigate to which extent the additional electrons occupying the weakly bound orbitals of the cluster can influence the optical spectrum of $Li_{12}C_{60}$. This is the purpose of the present work.

In what follows we carry out a first-principles investigation of the electronic response of $Li_{12}C_{60}$ to an external electromagnetic field, assessing the role of the lithium coating in the features of the photo-response by comparing the results for this cluster with those obtained for the fullerene cage alone. This is done in the framework of the Time-Dependent Local Density Approximation (TDLDA) [6], which has proved to constitute a very successful method to describe the optical properties of atoms [6], small molecules [7], metallic clusters [8], fullerenes [9] as well as bulk metals [10]. It will be concluded that the optical response of $Li_{12}C_{60}$ is strongly influenced by the fullerene cage, which determines the main features of the spectra of one-electron transitions upon which the screened response is built. However, the lithium coating is found to change both the unscreened one-electron transition strength distribution as well as the screening of the external field, leading to an overall broader optical spectrum and a double peak resonance in the region of the fullerene Mie-plasmon (see below).

The calculations of [2] have been carried out in the Local Density Approximation (LDA) to Density Functional Theory (DFT), the structural minimization being performed using the Car-Parrinello method, with associated supercell plane-wave basis expansion. Instead of extending the plane-wave-basis method to the computation of the dynamical response [10], we adopt a molecular-physics strategy [7] of solving the Kohn-Sham LDA equations as well as the TDLDA response equations, using a one-center expansion, together with a spherical basis-set, resulting in a set of angular-momentum coupled equations. The equations to be solved are well-known, so we will not elaborate them here, referring the reader to [9] for details.

The optimized structure obtained in [2], displayed in Fig. 1, is based on a C_{60} cage which is deformed with respect to the isolated molecule, the single and double bonds being now nearly equal, with the values of 1.445 Å and 1.435 Å, respectively. In what follows, this structure will be called deformed C_{60}. The deformation of the C_{60} cage, induced by the lithium coating, follows similar trends found already for solid compounds M_xC_{60} ($M = K, Rb$), and results in a reduction of bond alternation which is associated with a charge transfer taking place for metal-coated fullerenes [2]. It is worth mentioning that this charge transfer induces a deformation of the fullerene cage comparable to its maximum zero-point amplitude deformation [11, 12]. However, the icosahedral structure with associated pentagonal and hexagonal rings is maintained, with the difference between the lengths of hexagonal and pentagonal bonds considerably reduced. This feature alone, as will be shown below, has already an effect in the optical response, which is further complemented by the lithium coating.

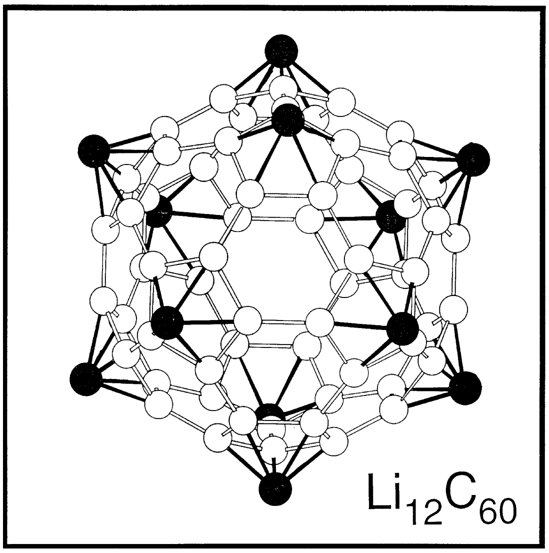

Fig. 1. Geometric structure of the cluster $Li_{12}C_{60}$, corresponding to the minimum energy configuration obtained in [2]. The 12 lithium atoms, as well as the Li – C bonds, are drawn in *black*

The twelve lithium atoms – shown in black in Fig. 1, as well as all Li – C bonds – stand on top of the 12 pentagons of the deformed C_{60} cage, at a distance of 1.54 Å from each pentagonal plane. In this way, the icosahedral structure of the carbon 'seed' is maintained in the coated cluster. From Fig. 1 of [2] one can see that the deformation of the C_{60} cage induces a small shift of the one-electron LDA eigenvalues, which are further perturbed by the lithium coating. Therefore, the optical response of $Li_{12}C_{60}$ will depend on the combined effect associated with the deformation of the fullerene cage and with the lithium coating. We shall explore the possibility of introducing these effects step by step and will disentangle the effects associated with these two contributions by computing and comparing the optical response of three clusters: the isolated C_{60} cage, deformed C_{60} and, finally, the metal coated fullerene, the optical response of which will be computed for the equilibrium geometry found in [2] – see Fig. 1.

The pseudopotential for C adopted in this work is slightly different from the one used in [2] (we used for C and Li the parametrization of [13] for the Bachelet, Hamman and Schlüter norm-conserving pseudopotentials [14]). Yet, our LDA levels show a very good agreement [15] with the findings of [2]. Subsequently, we computed the photo-response of all clusters in TDLDA. The results exhaust in all cases 92% of the energy weighted sum rule. As is well known [17], the use of non-local pseudopotentials to describe the single-particle motion, leads to a violation of the Thomas-Reiche-Kuhn (TRK) sum-rule. In this sense, and since the non-local pseudopotential effects in lithium are known to play a sizeable role [18, 19], we expect them to add to the non-local effects associated with the carbon atoms. For the static polarizabilities we obtained 89 $Å^3$ for C_{60}, 92 $Å^3$ for deformed C_{60} and 116 $Å^3$ for $Li_{12}C_{60}$. A detailed comparison of the optical response of C_{60} (upper panels), deformed C_{60} (mid-panels) and $Li_{12}C_{60}$ (lower panels) is shown in Figs. 2 and 3. The low energy spectrum is shown in Fig. 2, whereas the high-energy spectrum up to 30 eV is shown in Fig. 3. In this way, we distinguish two different scales for one-electron transitions: Between 0 and 6 eV, one has rather isolated transitions; therefore, we computed the spectra using an intrinsic width [9] of 10^{-2} eV. Such a value, while allowing some saving of computer time in the calculation of the absorption spectra, is still small enough to allow for the identification of all one-electron transitions occurring below 6 eV. Above 6 eV, the energy at which the threshold for unbound one-electron transitions takes place, one has a continuum of one-

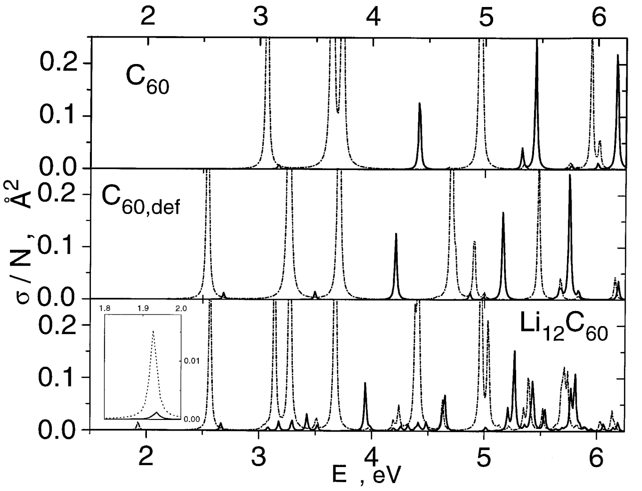

Fig. 2. Electromagnetic response of C_{60} (*upper panel*), deformed C_{60} (*middle panel*) and $Li_{12}C_{60}$ (*lower panel*) computed at two different levels of approximation. The low-energy spectrum is displayed, in which the curves shown were computed with a numerical damping [9], $\eta = 10^{-2}$ eV. In the *inset*, the lowest optical transitions of $Li_{12}C_{60}$ are detailed, in order to put in evidence the role of screening due to the lithium coverage

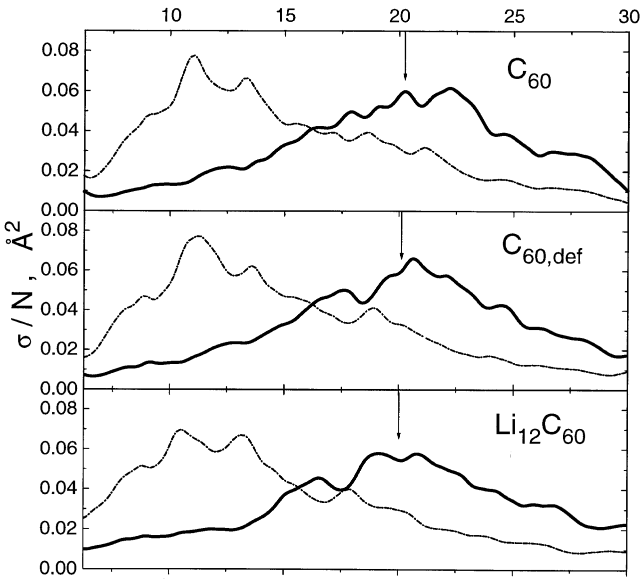

Fig. 3. Electromagnetic response of C_{60}, deformed C_{60} and $Li_{12}C_{60}$, in the continuum part of their optical spectra. Same notation as in Fig. 2. The curves have been smoothed by folding the calculated strength distribution with Lorentzian functions with an intrinsic width of 1 eV. In this way we simulate the coupling of the collective excitation to the normal modes of vibration of the cluster [11]. The *arrows in each panel* indicate the position of the centroid energy of each spectra, computed between 15 and 25 eV

electron excitations which, due to the finite basis-set adopted here, maps into a large, yet finite, number of one-electron transitions. Indeed, the number of transitions becomes so large that a smoothing of the data is more elucidative.

In order to smooth the data above 6 eV, we shall make use of the results of [11]. There it has been found that the adiabatic coupling of the charge oscillations in C_{60} to the ionic motion of the cluster would contribute with ≈ 1 eV to the linewidth of the photoabsoption cross-section. This effect was found to be present even at $T = 0$, due exclusively to the zero-point motion of the carbon-ions, and can be taken as a lower bound [20] to the linewidth associated with the photoabsoption cross-section of $Li_{12}C_{60}$. Therefore, we smooth the data by folding the computed lineshapes above 6 eV excitation with Lorentzian curves with an intrinsic width of 1 eV.

In Figs. 2 and 3, dot-dashed curves show the independent particle – unscreened – response, whereas solid curves show the screened TDLDA response. We first concentrate on Fig. 2, where the optical absorption is plotted for excitation energies below 6 eV.

In going from C_{60} to deformed C_{60}, there is an overall red-shift of both the screened and unscreened lineshapes, with small redistributions of strength. The spectra are dominated by sharp peaks which are associated, to a large extent, to bound-to-bound one-electron transitions. Note however, the significant reduction of the optical gap [21], which, in deformed C_{60} takes place ≈ 0.5 eV below that of C_{60} (cf. Fig. 2), both for the screened and unscreened responses. The optical gap can be easily identified in Fig. 2, being associated with the energy of the lowest optical transition.

The red-shift obtained in going from deformed C_{60} to $Li_{12}C_{60}$ is less pronounced – see Fig. 2. However, two major effects take place as a result of lithium coverage: On one hand, and concentrating first on the unscreened response, the valence electrons of lithium, which fill the weakly bound valence states of the cluster, contribute to the significant reduction of the optical gap in going from deformed C_{60} to $Li_{12}C_{60}$. This, in turn, is related to the values we obtain for the thresholds for excitations into continuum states: ≈ 5 eV for deformed C_{60} and ≈ 2 eV for $Li_{12}C_{60}$. On the other hand, this sizeable reduction of the threshold leads to a spreading of the oscillator strength, which is no longer concentrated into a small number of well-defined sharp transitions. Yet, this spreading is centered at transition energies around those of deformed C_{60}, reflecting the major role played by carbon seed in determining the spectrum of one-electron transitions. Note finally that $\approx 70\%$ of the unscreened one-electron transitions in $Li_{12}C_{60}$ in the energy region $0 \leq E \leq 6$ eV, correspond to bound-to-bound one-electron excitations, accounting for nearly half of the corresponding optical strength.

When screening is incorporated, this scenario is maintained to a large extent, although the spreading of oscillator strength increases. However, it is worth examining in detail the behaviour of the optical gap in screened-$Li_{12}C_{60}$: The lowest sizeable optical transition takes place at essentially (0.02 eV below) the same energy as the corresponding transition in deformed C_{60}. This feature is rather remarkable, in view of the strong reduction of the optical gap observed for the unscreened response, and may be attributed to the screening due to the lithium coverage. Indeed (cf. inset in Fig. 2), it should be pointed out that there exists a tiny peak at ≈ 1.93 eV, the energy associated with the lowest unscreend transition in $Li_{12}C_{60}$. However, the strength associated with this transition is ≈ 20 times smaller than the one associated with its unscreened partner. Therefore, we believe this is a fingerprint of the screening effect of the lithium coverage at low energy. This effect is most remarkable if we notice that it is due to 12 out of a total of 252 active electrons.

In the region of the Mie-type plasmon (Fig. 3), the situation is rather different, since this energy domain falls well into the continuum of one-electron excitations and therefore, the carbon to lithium ratio plays an important role. One observes a small overall red-shift of the strength distribution when going from C_{60} (upper panel) to deformed C_{60} (mid-panel), which is further increased in $Li_{12}C_{60}$ (lower panel). These features are common in both responses, the overall effect being illustrated in Fig. 3, in which the centroid positions of the screened responses are indicated with arrows. Furthermore, the detailed lineshape of the Mie-type plasmon undergoes a subtle evolution, which cannot be explained solely by the increase of volume of the cluster. If one would naively compare the lineshapes of C_{60} and of $Li_{12}C_{60}$, one might conclude that the volume increase of the cluster would simply shift strength from the high energy side of the Mie-peak to its low-energy side. In this context, the lineshape of deformed C_{60} is elucidative. Indeed, one can see that the shoulder at ≈ 16 eV in the lineshape of $Li_{12}C_{60}$ originates from a red-shift of the corresponding shoulder at ≈ 17.5 eV in deformed C_{60}, whereas the detailed shape of the Mie-peak results from a rearrangement of strength induced by the lithium coating, and not from a rigid red-shift of the Mie-type plasmon of C_{60}.

The Mie-type plasmon peak is broad due to the high density of independent one-electron transitions which take place in the same energy interval (compare, e.g., screened and unscreened curves in each panel of Fig. 3). This, in turn, leads to the well-known phenomenon of Landau damping, thoroughly discussed in [9, 11] in connection with the excitation of the plasmon resonance in C_{60} [9, 11] and C_{70} [11].

In summary, the optical response of $Li_{12}C_{60}$ is dominated by a strong, Landau damped, plasmon excitation at ≈ 20 eV, displaying a double peak structure. This plasmon is closely related to the "σ-plasmon", also observed in C_{60} and C_{70}. In this sense, the carbon atoms play a major role in the production of such a plasmon peak. Yet, the lithium atoms can account for fine features of the spectra, even in this energy region. Indeed, by direct comparison of the lineshapes of $Li_{12}C_{60}$ and of deformed C_{60} (Fig. 3), one can conclude that the double peak structure present in $Li_{12}C_{60}$ results from the lithium coating. The ionization threshold of $Li_{12}C_{60}$ is strongly reduced with respect to the corresponding quantity for the fullerene cage. As a result, the lineshape of the electromagnectic response in the region between 0 and 6 eV is richer, broader and more structured for $Li_{12}C_{60}$, as compared to the corresponding response of C_{60}. However, the lithium coverage is responsible for a redistribution of optical strength and for an effective screening of the external field, which maintains the optical gap at ≈ 2.7 eV.

Financial support from FEDER and PRAXIS XXI program under contract PRAXIS/2/2.1/FIS/26/94 and by NATO under grant CRG 940231 is gratefully acknowledged. F.A. gratefully acknowledges financial support from Consorzio Milano Ricerche as well as the warm hospitality provided to him at the Center for Theoretical Physics, Coimbra, where this work has been carried out.

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21. We would like to point out that it remains an open problem to which extent TDLDA is able to provide an adequate prediction for the optical gap. As shown recently [22], one needs a full many-body calculation of the non-local response function in order to answer this question. Work along these lines is in progress [23]
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