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Structural and Vibrational Study of PCBM

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Abstract: The 1-(3-methoxycarbonyl) propyl-1-phenyl-(6,6)C_{61} (also called PCBM) is a C_{60} derivative widely used as an electron-acceptor in organic solar cells. To date, all the infrared spectra reported are experimental, mainly because of the calculations needed to study these structures are highly time-consuming. In this report we address for the first time the infrared spectrum calculation of PCBM with C_s symmetry by using the PW91/dnp level as implemented in the Dmol^3 code. In this calculation we have found two intense peaks in the IR spectrum, that agree fairly with the 1187 and 1787 cm^{-1} measured experimentally.

Key words: PCBM, DFT, IR, solar cells, C_s symmetry.

1. Introduction

With the implementation of new quantum codes and the enhancement of performance in computers there has been an increasing activity in the study of a variety of molecular systems which have big technological importance due to their novel and astonishing properties. At the present time, there are researching groups around the world working to get deep into the understanding of the properties of these new materials; specifically in the nanosciences and nanotechnology fields, there is a new interest in the design and prediction of better materials for applications in environment, health, and fuels; as the experimental and theoretical techniques get continuously improved, the next years appear to be very promising in these fields [1].

It is well known that fullerenes and their derivatives are systems with striking properties [2]. While the potential uses of these materials have extended to cover areas that include, for example, organic solar cells [3], their study by computational means is still somewhat incomplete. Up to now, the theoretical study of fullerenes involves large time-consuming calculations and requires a large amount of memory, and these needs increase greatly when more accuracy is required. However, these difficulties may be at least partially overcome when the symmetry of the molecule is explicitly exploited into the calculations, because this consideration can save a considerable amount of computational time [4].

In the case of PCBM, the first report of its synthesis [5] and its characterization by IR techniques [6] show that the PCBM bands are located in the 527-1737 cm^{-1} range, which include the observed four IR bands to the C_{60} [7]. In this work, we have studied the PCBM spectra in an IR range wide enough to include wavelengths of about 3200 cm^{-1}, in order to take into account the vibrations due to C-H bonds. The paper is organized as follows: In next section the structures and calculation methods are described, and in the results section we compare the spectra and structure of the two PCBM isomers considered in this work. In the final section we make some concluding remarks and set the conditions for future work in the same direction.

2. Methodology

Model

Among the ab-initio methods, Density Functional

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Theory (DFT) [8-9] is among the most reliable tools for the determination of the vibrational modes and characteristic frequencies of molecular systems. Indeed, DFT accuracy is considerably better than semiempirical methods [10], for example, in the determination of the frequencies of the normal modes of vibration. In regard of DFT performance, there exist previous reports about successful prediction in the assignment of actives modes in infrared (IR), when compared with experimental studies of several fullerenes [11-13].

In order to study the PCBM structure and IR spectrum, we have carried out a series of calculations using DFT. The generalized gradient approximation (GGA) into the PW91 [14] functional scheme was used to define the exchange-correlation term, and all electrons were considered in the core treatment. We imposed a SCF convergence criterion of 10^{-6} a.u, both on the total energy and electron density. Throughout the geometry optimization, the Broyden-Fletcher-Goldfarb-Shanno (BFGS) algorithm was used. All the calculations were done using the Dmol^3 code, as implemented in the Materials Studio 4.0 suite [15].

3. Initial Structures

PCBM is a molecule which has an alkyl and a phenyl side chains attached to the C_{60} framework in two possible ways: the chains may be attached to a single (5,6) bond, or linked to a double (6,6) bond; in both cases, the resulting structure has a C_s symmetry. The isomer with the lowest known energy, corresponds to the one with the side chains attached to the C_{60} into a (6,6) bond. Since this isomer has C_s symmetry, there is just one symmetry plane, which cuts the carbon backbone by the middle of the (6,6) bond attached to the side chains. In addition, the phenyl chain can be attached to C_{60} cage in two possible ways: either parallel to the symmetry plane, or perpendicular to it (see Fig. 1). Both configurations differ a right angle.

The structures were built starting from a C_{60} cage structure with I_h symmetry, where all the bonds have a 1.42 Å length [4]. Two kinds of chain were attached to the C_{60} cage: an alkyl chain and a phenyl group. The alkyl chain was placed along the symmetry plane, and the phenyl group was placed either at the plane of symmetry (which we call isomer 1), or perpendicular to it (isomer 2). Both isomer 1 and 2 have a total of 120 bonds: 90 into the C_{60} cage, 28 into the alkyl chain, and two formed by the union between chain and C_{60} cage (forming a cyclopropane-like ring).

4. Results and Discussion

4.1 Isomer 1

The optimized isomer 1 of PCBM has the attached phenyl and alkyl chains forming an angle of 122.4 degrees. This value was measured between the carbon atom in phenyl chain, the carbon atom in the cyclopropane-like ring and the carbon atom in the ending methyl chain. This implies that the alkyl chain forms a 57.6 degree angle with respect to the horizontal plane, getting away the C=O group from the C_{60} framework. The cyclopropane-like ring in the optimized structure had two angles of 59.01 degree and one of 61.97 degree. The measured bond lengths were two of 1.55 Å and one of 1.60 Å, the latter corresponding to the distance in the (6,6) bond.

In Fig. 2 we show the calculated bond lengths for isomer 1 of PCBM, and from this is evident that the C_{60} cage has mainly two types of bonds with values around those obtained for the C_{60} fullerene. We optimized the C_{60} (I_h symmetry) in an independent run, finding 1.4502 and 1.3970 Å for single and double bond lengths respectively, which are in agreement with the experimental values reported elsewhere [16].

Near to the area where cage and chains join, the distortion is large. In total there are 12 bonds distorted around the cage-chains union: five for cage, four for alkyl chain, one for phenyl chain, and two in the union itself. The larger distance found is around 1.55 Å and it represents the distance between the atoms originally forming the double bond (C=C bond or (6,6) bond) in the cage. The others bond lengths are those owing to an

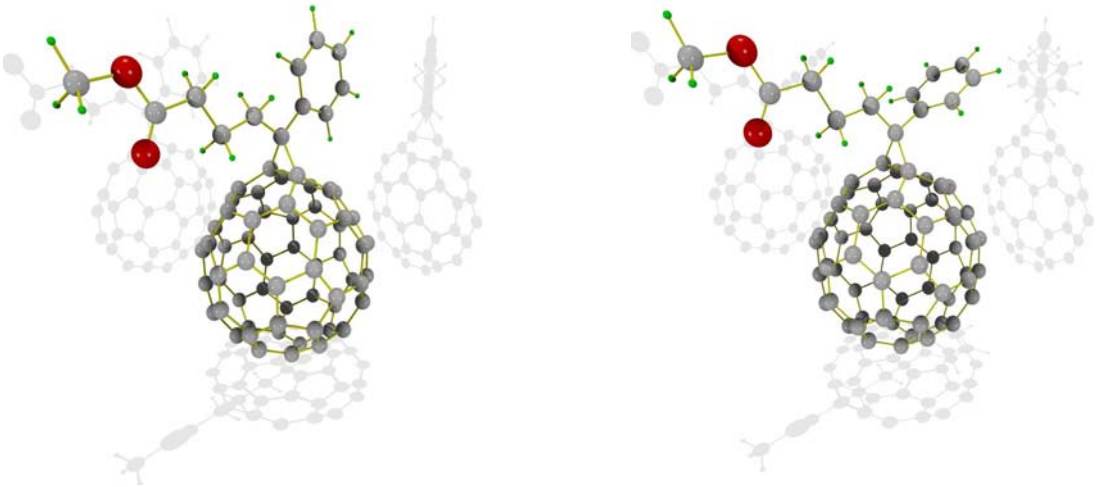

Fig. 1 Ball and stick models of the structures of PCBM isomers, along with their projection on the cartesian planes. The atoms sizes are represented proportional with respect to their atomic radios. The C_s symmetry can be observed by looking at the projections shown. The difference between both structures is the phenyl ring taking two positions; the left isomer has the phenyl ring on the symmetry plane (isomer 1), and the right one has this ring perpendicular to the symmetry plane (isomer 2).

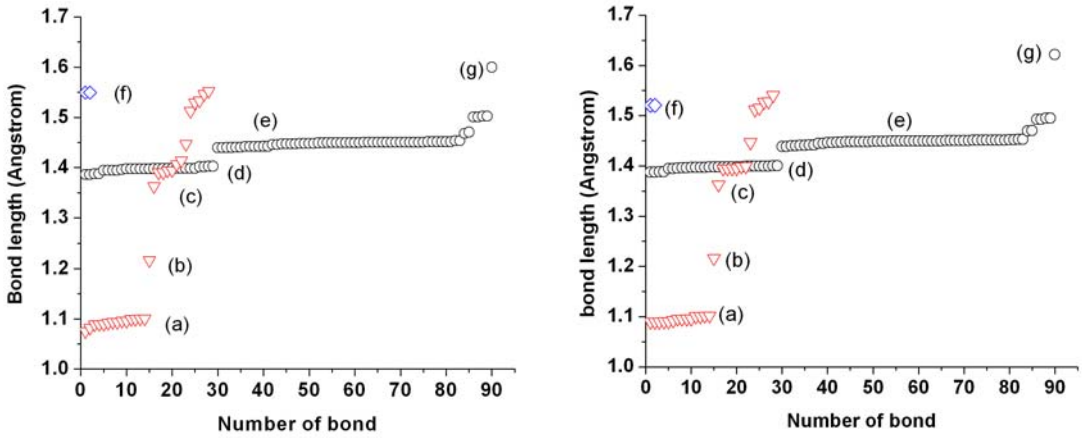

Fig. 2 Bond lengths of PCBM isomers. The graph to the left is for the PCBM isomer with the phenyl group on the symmetry plane (isomer 1). Right graph is for the PCBM isomer with phenyl group perpendicular to the symmetry plane (isomer 2). The same labels are used in both graphics. The open circles represent the distances in the C_{60} framework; inverted triangles correspond to the distances into the attached chains, and diamonds represent the distances found in the union region of C_{60} cage and attached chains. The bond lengths are: (a) C-H bonds, were one bond into phenyl ring and near to C_{60}, and another one pointing to the alkyl chain are the shortest for the PCBM isomer 1, (b) C=O bond length, (c) C-O bond length, (d) C=C bonds in C_{60} and C=C bonds in phenyl ring, (e) C-C bonds in C_{60} cage, (f) Two C-C bonds in the union cage-chains, and (g) One C-C bond being part of the cyclopropane-like ring.

O atom bonding to its two neighbors; the bond length for an O linked to C atom of the methyl group is 1.45 Å, and for an O atom linked to the C carbon of C=O bond is 1.36 Å (C-O bond). On the other hand, C=O bond is 1.22 Å long. Moreover, bond lengths of C and H atoms (C-H bond) in general are approximately 1.09 Å, but we also observed two more type of distances of 1.082 and 1.075 Å, which correspond to C-H bonds of the phenyl group pointing to the C_{60} cage, and a distance of 1.075 Å, corresponding to a C-H bond pointing to the alkyl chain. The C to C atom bonding, into the phenyl ring is around 1.41 Å. As mentioned above, the more affected bonds are those near to the union chains-C_{60} cage, which get longer than normal, and two C-H bonds into the phenyl group, which get shorter.

4.2 Isomer 2

Basically the trend in the bond lengths is the same that all those discussed to the isomer 1. However, this isomer has less affected bonds into the C_{60} cage and into the linked chains; for example, all the C-H distances are around 1.09 Å and there is not "short bonds", as in isomer 1. The triangle (cyclopropane-like ring) formed between the (6,6) bond and the C atom of the chains has two angles of 57.87 degree, and one of 64.29 degree, while their oppose bonds were of 1.52 Å and 1.62 Å, respectively. This last bond length indicates that the isomer 2 has a more open structure, compared to isomer 1 (see Fig. 2).

The angle formed between the phenyl, the bridge C atom, and the C atom in the methyl ending group is of 127.07 degree. In this isomer, the closest distance between H atoms into the phenyl ring and H atoms into alkyl chain is of 2.82 Å, different from the 1.94 Å measured in isomer 1.

Because of phenyl ring is sufficed away from the C_{60} cage, there is more uniformity in the bond lengths, which means less affected bonds in PCBM isomer 2, due to C_{60} proximity.

5. Normal Modes

After calculating the corresponding vibrational modes to both isomers, we found an imaginary frequency at -66.04 cm^{-1} for the isomer 2, which must be interpreted as the isomer 2 being a metastable structure. This is the main reason of focus the remaining discussion only to isomer 1.

In order to discuss vibrational modes of PCBM, as a first step is necessary to obtain the C_{60} vibrational modes, which can then be used as reference modes. For C_{60}, with I_h symmetry, we obtained 4 peaks at 520.83, 577.47, 1195.90, and 1437.82 cm^{-1}, having all of them a three-fold degeneracy (see Fig. 3). Since PCBM is a non-lineal molecule, it has 3*N*-6 normal modes, where *N* is the number of atoms that constitute the structure. There are 88 atoms in PCBM, and consequently 258 normal modes must be present in its IR spectrum. This not necessarily means that there will be 258 peaks in the IR spectrum, since this number may be reduced due to symmetry considerations. Highly symmetric molecules in general present degeneracy in the vibrational frequencies, which produce the reduction in the number of the peaks present in their IR spectra. As shown in Fig. 3, PCBM isomer 1 has two main peaks in its IR calculated spectrum; the most intense peak is localized at 1151.8 cm^{-1} (see Fig. 4(d)), associated with the coupled C-O stretching and C-H bending modes into the alkyl chain. The peak at 1737.2 cm^{-1} corresponds mainly to the C=O stretching mode in the alkyl chain (see Fig. 4(i)); this vibrational mode had been measured experimentally at 1740 cm^{-1} by Barbour and co-workers in 2006 using 2D infrared vibrational spectroscopy [17]. C-O and C=O peaks were reported for Hummelen et al. [5] for the first time at 1737 and 1187 cm^{-1}, respectively. Although our results have a fair agreement in the position of the peaks with the experimental measurements, there are differences between our calculated intensities and those of the experiments. We have obtained the most intense peak in the IR spectrum being due to a C-O stretching coupled with C-H bending modes into the alkyl chain, rather than the C=O stretching mode (see Fig. 4(d)).

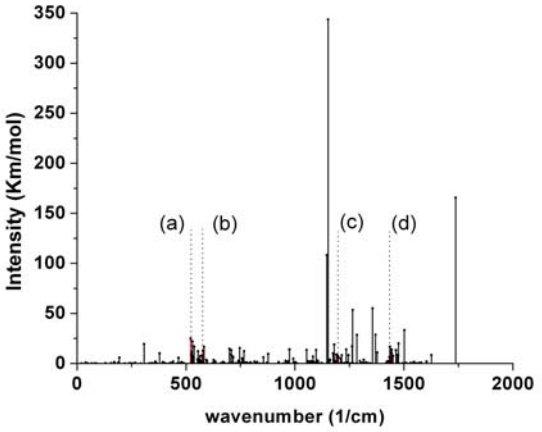

Fig. 3 IR stick spectrum for isomer 1 of PCBM and C_{60} of I_h symmetry in the range from 0 to 2000 cm^{-1}. For C_{60} (I_h symmetry) only the positions of the peaks are shown as dotted lines of height not related with the signal intensity. (a) Vibrational mode at 520.83 cm^{-1} for C_{60}, (b) C_{60} mode at 577.47 cm^{-1}, (c) C_{60} mode at 1195.90 cm^{-1}, and (d) Mode at 1437.82 cm^{-1} for C_{60}.

These differences may be partially attributed to the experimental setup, and partially to our calculation considerations. For instance, the solvent effects, always present in the experiments, were not included in this study.

We have found also differences in the C-H stretching modes present in the alkyl and phenyl chains. The C-H stretching mode in the alkyl chain, near to the phenyl group, was localized at 2983.1 cm^{-1}, while for the phenyl group is at 3166.7 cm^{-1}, and the C-H symmetric stretching for the ending methyl group was found at 3046.4 cm^{-1} (see Fig. 4(j)).

Another difference between our calculated spectrum and the existent experimental study is the peak at 527 cm^{-1}. In our study, this peak is weak and localized at 526.4 cm^{-1} (Fig. 4(a)), whereas in the experimental spectrum this peak appears as a higher, strong signal.

In this study we have found the correspondence with the experiments for the kind of vibrational motions of the two most intense peaks reported for the PCBM. Finding a correspondence with the other reported peaks is a more difficult task, mainly because for these frequencies the peaks are less intense. For purposes of qualitative comparison, the experimental reported results and the calculated values in this study are shown in Table 1.

6. Effect of the Attached Chains

In the IR spectrum of PCBM (Fig. 3), the peaks related to the C_{60} cage vibrations are not clearly seen,

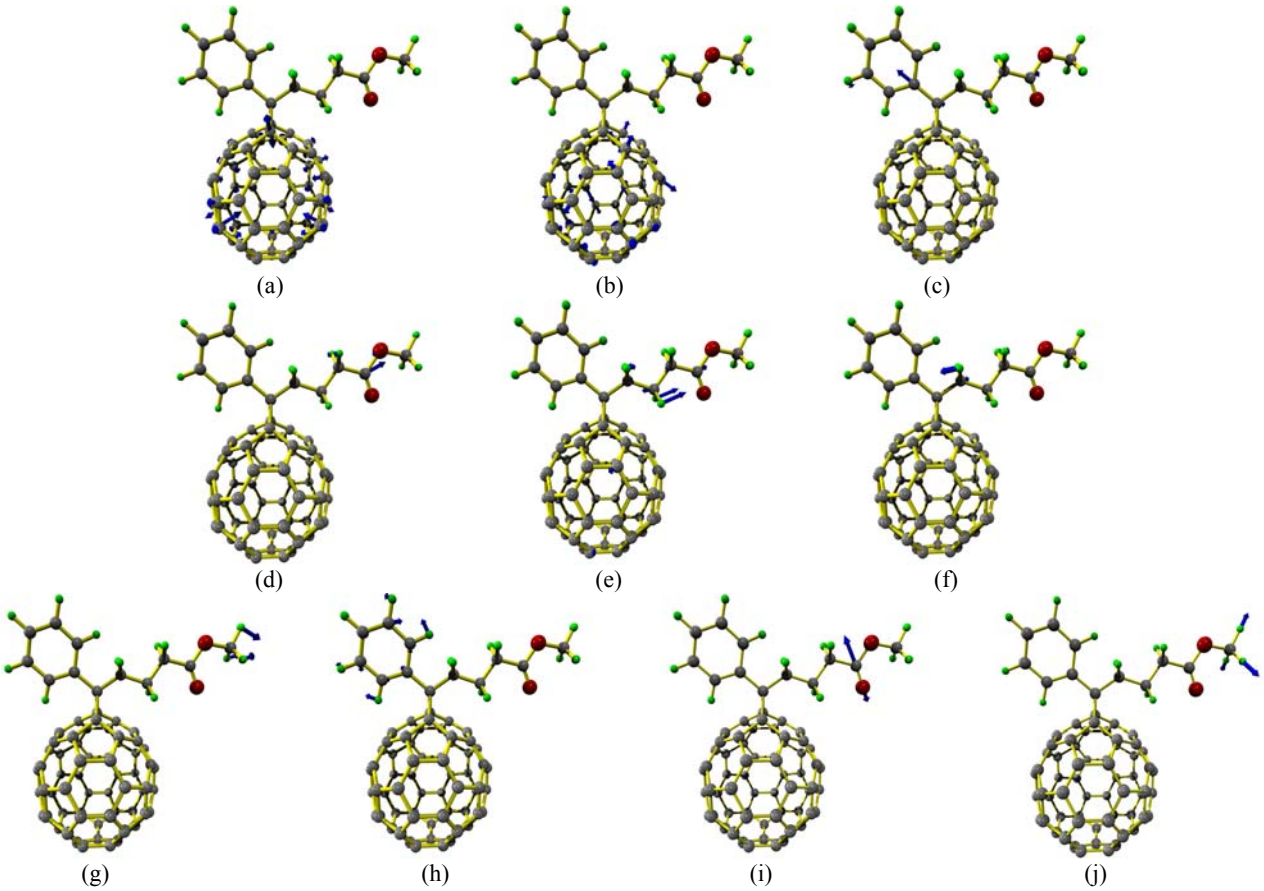

Fig. 4 Illustration of several normal modes of PCBM isomer 1. The atomic displacements and their magnitudes are shown with arrows. (a) C_{60} core vibration at 526.4 cm^{-1}, (b) C_{60} core vibration at 576.40 cm^{-1}, (c) C-C stretching mode at 1145.3 cm^{-1}, (d) C-O stretching mode at 1151.8 cm^{-1} (being the most intense peak calculated); (e) C-H bending mode into alkyl chain at 1264.6 cm^{-1}, (f) C-H wagging mode into alkyl chain at 1356.1 cm^{-1}, (g) Bending mode of C-H bonds of ending methyl chain at 1435.6 cm^{-1} near to the vibrations in C_{60} I_h cage at 1437.82 cm^{-1}, (h) Bending mode in plane of C-H bond in phenyl ring at 1502.2 cm^{-1}, (i) Stretching C=O mode in alkyl chain at 1737.2 cm^{-1}, (j) Stretching C-H mode of ending methyl chain at 3046.4 cm^{-1}.

Table 1 Calculated frequencies (v) and their intensities for PCBM versus experimental ones.

$\nu_{Experimental}$[(a)], cm^{-1}	$\nu_{Calculated}$, cm^{-1}
527(s)	526.4 (11.22)
550(m)	555.1 (12.26)
559(w)	559.8 (4.02)
564(w)	564.3 (7.29)
572(m)	572.6 (1.18)
585(m)	582.4 (16.70)
689(m)	698.9 (14.76)
1187(m)	1189.6 (9.02)
	1145.3 (108.12)
	1151.8 (343.97)
1428(m)	1435.6 (16.79)
1445(m)	1443.9 (10.40)
1737(s)	1737.2 (165.66)

(a) In the first column, experimental intensities are reported in Ref. 6. The label s stands for strong signal, m for medium, and w for weak signal. In the second column the theoretical intensities for the PCBM isomer 1 (in Kmol/mol) calculated are indicated between parentheses.

because the two most intense peaks due to vibrations of the alkyl chain are up to ten times stronger, which forces the C_{60} cage peaks to appear at a diminished scale. When the isomers of PCBM are formed, both the C_{60} cage and the attached chains conserve their C_s symmetry separately. In order to investigate how large are the changes in the intensity of the vibrations due to the C_{60} framework in PCBM isomer 1, compared to those of an isolated hypothetical C_{60} molecule with C_s symmetry, we carried out a calculation subjected to the condition of keeping the original symmetry of the structure. We also performed this kind of calculation for a neutral C_{60} with I_h symmetry, and we compared the spectra for these two structures with the PCBM spectrum. The IR spectrum of the neutral C_{60} with C_s symmetry calculated has 3 peaks at: 535.1, 536, and 537.2 cm^{-1}, with intensities of 23.89, 23.19, and 26.78 km/mol, respectively, while for neutral C_{60} with a I_h symmetry there has a peak at 520.8 cm^{-1}, with an intensity of 24.95 km/mol. In comparison, the PCBM isomer 1 spectrum has a peak at 537.4 cm^{-1}, with an intensity of 12.44 Km/mol.

In general, the chains attached to the C_{60} have a marked effect in the number and intensities of the possible modes of vibration. Before the chain is attached to C_{60} with C_s symmetry, there is one peak at 537.2 cm^{-1} and, after the chain is attached, this intensity decreases in around 53%. This peak, located in the range from 520 to 530 cm^{-1}, is related to vibrations in the fullerene cage (Figs. 4(a) and 4(b)).

In order to compare the stability, we also calculated the HOMO-LUMO gaps for C_{60} with C_s and I_h symmetries, and for the PCBM isomers (see Table 2). We found that C_{60} with I_h symmetry is more energetically stable than C_{60} with C_s symmetry, for about 23.08 eV.

A last remark is in order. As mentioned before, we found that the isomer 2 presents a negative frequency in its spectrum, which means this structure is not a minimum in the energy landscape, but a transition state. Without the vibrational calculation of the isomer 2 and just taking into account the energy difference, we would conclude that the more stable isomer between isomer 1 and 2 is the latter. However this is not the case, because a necessary condition to compare stability of two structures is that both of them are in a minimum of energy. The recommendation is that a vibrational calculation must always be done to characterize the structures as minima in a trustful manner.

Table 2 Summarized results for the studied structures.

Structure	E_{total}, Ha	$E_{binding}$, eV/atom	Gap, eV	Dipole moment, Debye
C_{60} I_h	-2287.9972632	7.5648	1.672	0.0000
C_{60} C_s	-2288.8452740	5.42	1.509	0.0017
PCBM isomer 1[(a)]	-2904.7859490	6.73176	1.482	4.8811
PCBM isomer 2[(b)]	-2904.8142065	6.7404965	1.487	5.4626

(a) PCBM isomer with the phenyl ring parallel to the symmetry plane.

(b) PCBM isomer where phenyl ring is perpendicular to the symmetric planes, which has a negative frequency.

7. Conclusions

We have calculated the energetic and vibrational properties for the PCBM, a fullerene derivative important for the development of organic photovoltaic components. The calculations were performed using Density Functional Theory, the most powerful tool at the day for the in-depth study of molecular systems in general, and for the study of fullerene-based structures in particular. Our results were obtained exploiting the fact that DFT calculations are considerably less time-consuming if the condition of conservation of symmetry is imposed, fact that becomes critical for molecular systems of this size.

We have found that the reported experimental IR spectrum and spectrum calculated by DFT coincide in the position of the strongest peaks. However, there are important differences between the calculated heights of the calculated peaks and those measured in the experiments. These results encourage us to keep exploiting in the future the symmetries present in the structures, which will allow us to take full advantage of the existent power and accuracy of modern methods in quantum chemistry available up to now. The source of the differences between our results and those of experimental measurements is still not fully understood, and we believe that future theoretical work that includes solvent effects, for example, will answer some of the unanswered questions, and enhance our knowledge of these fullerene derivatives.

Acknowledgments

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