

# A DFT study of addition reaction between fragment ion (CH<sub>2</sub>) units and fullerene (C<sub>60</sub>) molecule

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**Abstract** The theoretical study of the interaction between CH<sub>2</sub> and fullerene (C<sub>60</sub>) suggests the existence of an addition reaction mechanism; this feature is studied by applying an analysis of electronic properties. Several different effects are evident in this interaction as a consequence of the particular electronic transfer which occurs during the procedure. The addition or insertion of the methylene group results in a process, where the inclusion of CH<sub>2</sub> into a fullerene bond produces the formation of several geometric deformations. A simulation of these procedures was carried out, taking advantage of the dynamic semi-classical Born-Oppenheimer approximation. Dynamic aspects were analyzed at different speeds, for the interaction between the CH<sub>2</sub> group and the two bonds: CC (6, 6) and CC (6, 5) respectively on the fullerene (C<sub>60</sub>) rings. All calculations which involved electrons employed DFT as well as exchange and functional correlation. The results indicate a tendency for the CH<sub>2</sub> fragment to attack the CC (6, 5) bond.

**Keywords** Addition reaction · Density functional theory · Fullerene · Molecular dynamic

## Introduction

An efficient procedure was devised for the functionalization of fullerene [1–3], which involved observing the C<sub>60</sub><sup>2-</sup> ion in a reaction which occurs with the addition of benzylideneacetal [4]. Another reaction between azides and C<sub>60</sub> [5] was also explored because of the electrochemically attractive properties exhibited by its products. The formation of methanofullerenes or methanoannulene isomers is predicted [6] when the C<sub>60</sub> core is joined to the fragment unit (CR<sub>2</sub>), as well as when the CH<sub>2</sub> is specifically linked to the C<sub>60</sub> bond. This kind of functionalization occurs when fullerene C<sub>60</sub> reacts with diazomethane to form an unstable molecule which converts to H<sub>2</sub>C<sub>61</sub> [7]. Spectroscopy is also used for the structural characterization, in order to identify the different electronic properties in a particular case study, where the addition of CH<sub>2</sub> to the molecular structure of fullerene produces conformational isomers of methanofullerene [8]. A number of studies exist which have attempted [9, 10] to show that this kind of addition manifests a certain energetic preference. These have focused on the nature of the C-C bond of a particular aromatic ring. Two different bonds are possible contenders: the CC(6,6) and CC(6,5) bonds, both within the structural conformation of fullerene [11]. Besides this, theoretical and experimental features of magnetic susceptibility in the cycloaddition reaction between C<sub>60</sub> and diazo compounds [12] provide evidence of paramagnetic and diamagnetic currents. All of these studies aid in the description of the chemical characteristics of these new compounds [13]. Therefore, this study will explain the reactivity between C<sub>60</sub> and CH<sub>2</sub>, where an interaction promoted by radicals is expected to constitute an exothermic addition reaction and where carbon atoms with pyramidalization in their bond sp<sup>2</sup> are obtained as a result. In this process, the fullerene's carbon atoms change their

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hybridization from a trigonal  $sp^2$  to a tetrahedral  $sp^3$  [14]. Fullerene adducts have been extensively studied [15]. Theoretically, four possible isomers can exist: CC(6,5) open, CC(6,5) closed, CC(6,6) open, CC(6,6) closed, depending on the addition of the fragment to either the (6,5) or (6,6) bond, and furthermore, taking into account whether the distance between the carbon atoms is sufficient to generate a bond or not. The isomers: CC(6,5) closed, and CC(6,6) open have not yet been observed in experiments. Theoretical results have indicated that these two isomers are not propitious because they have two (6,5 closed) and three (6,5 open) double bonds in endocyclic position on the pentagonal ring. Thus a controversy exists concerning the addition of  $CH_2$  as a basic molecule to  $C_{60}$  in these isomers. Moreover, they are included in the present study in order to validate this assumption.

The aim of the present work is to establish the most favorable interaction between fullerene and  $CH_2$ , the simplest species that can generate stable  $\eta^2$  derivatives with fullerene, considering different cycle addition channel reactions in order to achieve an energetically stable  $C_{60}$ - $CH_2$  compound. The different channel reactions are provoked by changing the initial conditions in terms of their dynamics; namely the departure speeds of  $CH_2$ , but with an initial preferential orientation imposed on this molecule in relation to the CC-bonds of  $C_{60}$ . The results indicate not only a possible reaction mechanism, but also the nature of the final product.

## Methodology

The electronic structure of  $C_{60}$  is commonly studied by first principle methods that include electronic correlation and spin-orbital corrections. Density functional theory [16] (DFT), included in the NWChem software [17] has been used in this instance. This is a pure DFT method; containing Becke's gradient correction for exchange [18] and Perdew-Wang's for correlation [19]. B88-LYP methods were also employed for the geometry optimization. In the case of the B88-LYP functional, the non-local correlation was provided by the LYP expression [20] and the correction was carried out by means of the VWN functional. The DZVP basis set was used in all calculations for hydrogen and carbon atoms. This level of computation has provided good results in terms of the molecular geometry optimization and the energies of the bond orders for fullerene [21]. The optimized geometry of fullerene was taken as the starting point in the molecular dynamics study, bearing in mind that the geometry was obtained with a minimum of energy in order to identify the different paths for the reaction. The algorithm of quasi-Newton algorithm which seeks Hessian approximations is implemented as a part of the NWChem package.

The molecular dynamics simulation technique is important, because it reveals the dynamic nature of the nuclear particles. It helps to provide a deeper understanding of the reaction mechanism which takes place on the addition of  $CH_2$  to fullerene. These reactions are simulated by applying Born-Oppenheimer's semiclassical dynamics method. The electronic wave function is revealed, taking into account that electrons are immersed in a field of instantaneously fixed nuclei, whereas the nuclear particle is immersed in an average electronic field. The heavy masses and very short spatial extension of the nuclear particles compared to those of electrons permit us to simplify the problem by considering the nuclei as classical particles. In order that this should occur, each nucleus follows a newtonian trajectory due to quantum forces derived from the electron potential plus the electrostatic force exerted by the other nuclear particles. This computational level has provided good results for molecular dynamic calculations [22–25]. In all molecular dynamic calculations, the representation is described in terms of a displacement with multiplicity of triplet without charge (double free radical) or a charge of  $(-2)$ , as the starting point. This feature implies a rearrangement of the electronic configuration of  $C_{60}$ . This has a tendency to change its configuration due to the pyramidalization phenomenon, and it is also expected that the reaction will follow a mechanism where one of the double bonds on the fullerene surface [CC(6,5) or CC(6,6)] provides the electrons for the new bond, which may also cause strain on the bucky ball.

## Model

The fullerene is composed of aromatic rings. This feature is fundamental to the suggestion that the reaction with  $CH_2$  takes a single preferential direction which could involve either the CC(6,6) or the CC(6,5) bonds. Correspondingly, the chosen model consists of a buckyball  $C_{60}$  identified by geometrical optimization which is composed of aromatic rings in a regular pattern. The buckyball  $C_{60}$  has 20 six-member rings and 12 five-member rings. The  $C_{60}$  molecule belongs to the  $I_h$  point group of symmetry; therefore it is possible to separate a symmetrical fragment for study purposes, while conserving the symmetry and permitting the selection of portions from the fullerene molecule. The buckyball  $C_{60}$  was identified by geometry optimization calculations, where the atoms that compose the portions selected from the fullerene molecule were unfrozen in the movement, permitting the analysis of the structural and electronic changes that take place during this interaction. The atoms of the first and second neighbours with respect to CC(6,5) and CC(6,6) bonds were also unfrozen, whereas in the case of the rest of the fullerene atoms, they were

frozen when the dynamic calculation was made. The first and second portion atoms of fullerene were considered as active for the interaction between  $\text{CH}_2$  and  $\text{CC}(6,5)$ , as shown in Fig. 1. In order to obtain the structural and electronic properties in this interaction, the  $\text{CH}_2$  manifest a displacement with an initial speed throughout the preferential direction, sufficient to impact over aromatic rings of fullerene. A number of calculations were carried out at the level of first principles for the interaction between fullerene and the  $\text{CH}_2$  ion.

Although, potential repulsive interaction is present at the surface of the fullerene molecule, the most important factor is the participation of  $\text{CH}_2$  which is an electron donor in this case, and one of the hydrogen atoms joined to the  $\text{CH}_2$  fragment, because these particles present a different conformation when this fragment is considered as a receptor of an ion or a double free radical. The determination of the electronic participation of  $\text{CH}_2$  initiates in all cases with the  $\text{CC}(6,5)$  and  $\text{CC}(6,6)$  closed conformations and the dynamic process is monitored searching for the possibility to open the bond (yielding the open variations) or the remains of the single bond (in all these cases it is considered that fullerene is a weak electron acceptor and  $\text{CH}_2$  with a double negative charge donates the electrons for the whole process). Total energy and charge analysis are the main sources of information relating to the reaction mechanism.

The study involve two cases:

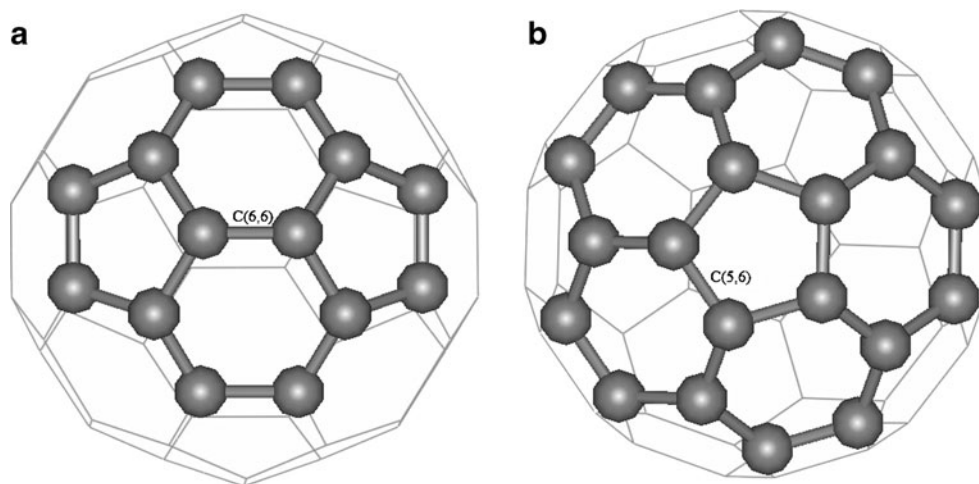
- Total charge: 0 for the interaction  $\text{C}_{60}$  (singlet, charge 0) +  $\text{CH}_2$  (triplet, charge 0) which implies a  $\text{C}_{60}\text{—CH}_2$  triplet system under study. In this case  $\text{CH}_2$  presents two lone electrons (bi-radical)
- Total charge: -2 for the interaction  $\text{C}_{60}$  (singlet, charge 0) +  $\text{CH}_2$  (singlet, charge -2) which implies a  $\text{C}_{60}\text{—CH}_2$  singlet system under study. In this case  $\text{CH}_2$  presents two lone pairs.

## Results and discussion

The interaction between two molecules provides sufficient information relating to changes in electronic properties (in particular the charge transference and structural atomic bond modifications). These results were analysed according to the respective reaction profiles. These structural changes are schematic and presented as a function of total energy. The values are obtained from dynamic simulation which shows the entire range of changes associated with the different stages in the reactions. Therefore, in the addition reaction, the  $\text{CH}_2$  fragment was positioned at a constant distance of  $10 \text{ \AA}$  from the  $\text{C}_{60}$ , then an impetus was applied to the fragment in order that it should collide with the  $\text{C}_{60}$  molecule, a process which varies in terms of the time elapsed, ranging between 120 to 500 femtoseconds, depending on the speed of the fragment.

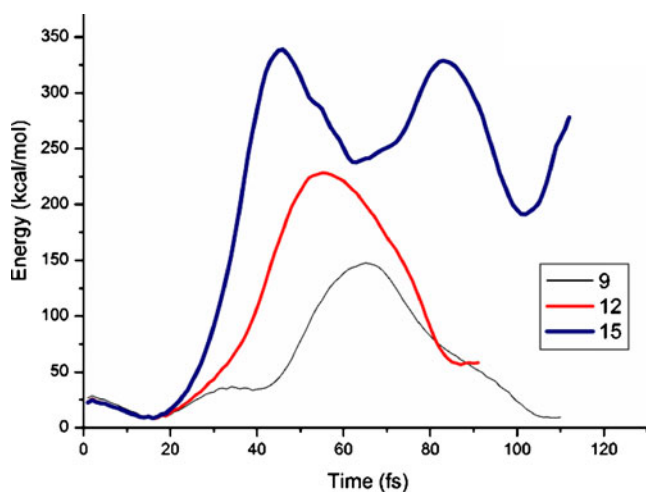
The dynamic Born-Openheimer calculations were applied in order to reveal the total energy values for the interaction between  $\text{C}_{60}$  and  $\text{CH}_2$  molecules. The different energy values correspond to different simulations associated with different charges or multiplicity, as well as depending on the initial speed acquired by the  $\text{CH}_2$  fragment. This specific speed permits the production of kinetic energy sufficient for surmounting the potential barrier of the transition state. At this point, the electronic properties of both species were identified, indicating two possibilities. The first one consists of when  $\text{CH}_2$  interacts with the  $\text{CC}(6,5)$  bond on fullerene, whereas the second one concerns the interaction with the  $\text{CC}(6,6)$  bond. There are different structural changes and charge distributions in each instance and the result even varies when different initial speeds are tested for each simulation, for the purpose of defining the optimal speed for collision and observing the reaction mechanism.

**Fig. 1** Atom assets comprising the first and second neighbours of the molecular structure of fullerene, used for calculating the energy values in the molecular dynamic in the case of an interaction between the  $\text{CH}_2$  fragment and; **a)**  $\text{CC}(6,6)$ , **b)**  $\text{CC}(6,5)$  fullerene bonds

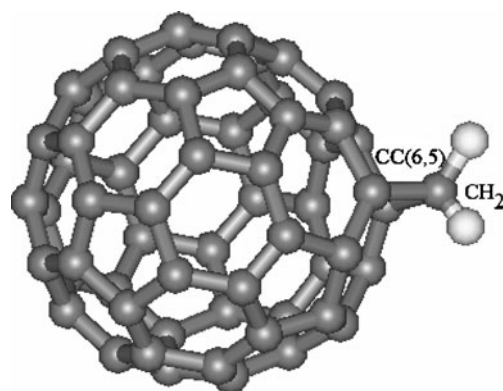


A systematic method is to draw a graph of the electronic energy data as a function of time, taking into account a specific speed for CH<sub>2</sub> during its interaction with the fullerene C<sub>60</sub> CC(6,5) bond, as shown in Fig. 2. The energy calculations indicated the electronic activation energy for three different speeds and it also became apparent that the addition process occurred when the speed reached 15 angstroms/femtosecond (Å/fs), it is important to note that the first part of the figure shows an almost null interaction and a potential barrier due to repulsive effects, besides the first maximum is about 40 fs whereas the second one is given between 80 and 90 fs and corresponds to the activated complex. Conditions were similar for all these speeds and the behaviour manifested in the first collisions for the other two speeds indicated the repulsion effect during the interaction. The multiplicity was 3 or the entire system bore a charge of -2. The energy values plotted on the graph are associated with the interaction which takes place when the CH<sub>2</sub> fragment moves at velocities of 9, 12 and 15 Å/fs.

The results for energy values of the interaction when the speed reached 9 Å/fs indicated that the CH<sub>2</sub> fragment interacted slowly with the fullerene surface. The energy values presented an increase when the CH<sub>2</sub> covered a short distance to the fullerene and showed a maximum value that corresponded to the potential barrier of repulsion. Under the same conditions, the energy values that correspond to the speed of 12 Å/fs when compared to the last case indicated that on this occasion no addition took place between CH<sub>2</sub> and the fullerene surface. These behaviours indicated a number of small bonding changes due to the effects of repulsion, but there was no addition of the CH<sub>2</sub> fragment, indicating that under these conditions the potential barrier is



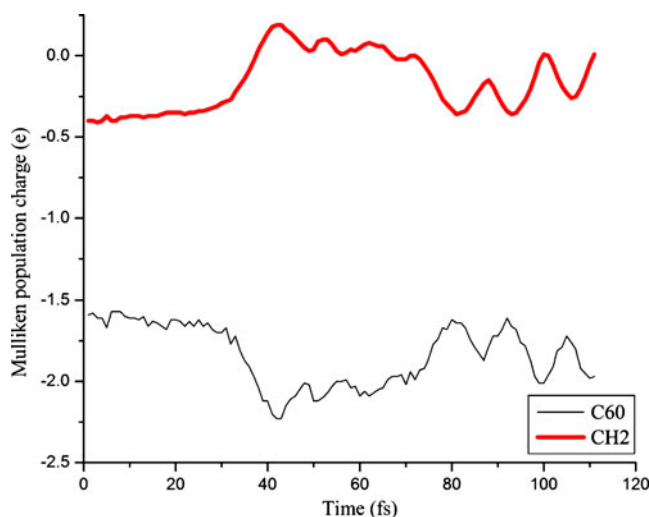
**Fig. 2** Interaction between CH<sub>2</sub> and CC(6,5) bond fullerene molecule C<sub>60</sub> at 15 units of speed. The phenomenon shows different behaviour in this instance; the potential barrier is surmounted the second after first minimum when velocity is 15



**Fig. 3** The interaction between fullerene and the CH<sub>2</sub> fragment produced a reaction mechanism of addition, pyramidation in the CH<sub>2</sub> fragment was observed, shown as a CC(6,5) bond open addition

greater than the kinetic energy associated with the movement of CH<sub>2</sub>. This effect of repulsion on the part of CH<sub>2</sub> is represented by an almost symmetrical curve in the right zone of the plot. The effect of repulsion at speeds of 9 and 12 Å/fs was an indicator that partial charge is not an essential factor for the reaction mechanism and indicated that the speed needed to be increased.

Applying the same reaction condition, speed was increased to 15 Å/fs. The results of the interaction for both species were obtained by applying molecular dynamics. In this instance, there are changes in energy associated with bond length changes; a situation which sketches a typical addition reaction mechanism, resulting in structural changes and charge transference (see below). In the three cases with three different speeds, the CH<sub>2</sub> fragment takes a preferential direction to collide with the CC(6,5) bond, forming a straight line between the carbon atom of the CH<sub>2</sub> fragment and the



**Fig. 4** Charge transfer for the interaction between CH<sub>2</sub> and the CC(6,5) bond fullerene molecule C<sub>60</sub> at the moment when CH<sub>2</sub> was added

bond between both rings in the fullerene molecule. In the case of 15 Å/fs, it was revealed that the main part of the reaction refers to the addition of the CH<sub>2</sub> fragment to the surface of the fullerene. This stage should be considered as an important stage in the reaction mechanism and here the electronic donation of the double bond to the CH<sub>2</sub> fragment on the surface of fullerene is apparent, as shown in Fig. 3.

Energy values are also associated with significant changes in the atomic bond lengths where both fragments are united at the maximal energy point. This characteristic indicates similar behaviour to that occurring in the case of charge transfer. Under these conditions, the graph plotted in Fig. 2 displays three important sections. The first one is associated with an almost null interaction and a potential barrier due to the effect of repulsion, in the second section the reaction occurs showing an elongation around the CC(6,5) ring bond; at this point the curved section corresponds to a maximum peak at 350 kcal mol<sup>-1</sup> and a minimum in the range of 20–60 fs and a third section which corresponds to the relaxed bond, taking into account the activated complex at ≈330 kcal mol<sup>-1</sup>, which represents the addition of CH<sub>2</sub> to the aromatic ring.

The Mulliken population analysis was applied to the interaction between CH<sub>2</sub> and CC(6,5) of the fullerene C<sub>60</sub> because this is the best option for attack. The dynamic charge transference is presented in Fig. 4, plotted as the calculated Mulliken charge versus various time intervals. This is considered to be the addition mechanism which takes place during this interaction. The system was divided into fragments; one fragment corresponded to the fullerene and the other to the CH<sub>2</sub>, both before and after the reaction. During the first stage (before the CH<sub>2</sub> had made impact on the fullerene), the system exhibited a total charge of -2, made up of the CH<sub>2</sub> with a charge of -0.25 and the fullerene with a net charge of -1.75. The graph plot showed little variation because the fragments retained their charge, even when they were far apart. However, there was a short time period when greater variation was apparent, this corresponded to the modification in bond lengths and an increase in the energy correlated with Fig. 3. It is interesting to note that the major change occurred in the period between 40 and 60 fs where the whole charge of -2 (or bigger) is totally concentrated in the fullerene fragment, whereas the methylene fragment reduced its charge to zero (or possibly a small positive charge) allowing the system to remain as it was at the beginning, but with the new bond having been formed. The likely interpretation is that the double bond on the CC(6,5) was retained on the fullerene until the bond was formed, suggesting that the reaction speed depends mainly on the concentration of C<sub>60</sub>.

On the other hand, we carried out calculations at different speeds for the interaction between CH<sub>2</sub> and the

CC(6,6) bond, with results indicating that no reaction takes place if the same conditions are applied. Only an effect of repulsion was evident in the system comprising CH<sub>2</sub> and CC(6,6). This result confirms the proposition derived from experimental evidence [6] that the preferred mechanism was that which comprised the CH<sub>2</sub> fragment and the CC(6,5) bond.

During the process of the revision of this work, the authors found out about a similar study [26] in which other kind of methods carried out on similar systems leads to the same conclusions that in the present case, this is an excellent situation that validates both studies.

## Conclusions

The energy analysis carried out by applying molecular dynamics brings us to the conclusion that the main condition necessary for ensuring that the addition of CH<sub>2</sub> to C<sub>60</sub> depends on certain energy being present, exceeding that of the potential barrier presented by the CH<sub>2</sub> ion fragment with a charge of -2 or a biradical with multiplicity of 3. This pathway is more likely to occur with the bond CC(6,5), taking specific speed into consideration. These results agree with experiments which suggest that there is a certain conformation which favours this reaction, as shown in the case of the electronic configuration of the bonding interaction.

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