

## Neutral and charged boron-doped fullerenes for CO<sub>2</sub> adsorption

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### Full Research Paper

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### Abstract

Recently, the capture and storage of CO<sub>2</sub> have attracted research interest as a strategy to reduce the global emissions of greenhouse gases. It is crucial to find suitable materials to achieve an efficient CO<sub>2</sub> capture. Here we report our study of CO<sub>2</sub> adsorption on boron-doped C<sub>60</sub> fullerene in the neutral state and in the 1e<sup>-</sup>-charged state. We use first principle density functional calculations to simulate the CO<sub>2</sub> adsorption. The results show that CO<sub>2</sub> can form weak interactions with the BC<sub>59</sub> cage in its neutral state and the interactions can be enhanced significantly by introducing an extra electron to the system.

### Introduction

The continuous dependence on fossil fuel combustion for the generation of energy has dramatically increased the atmospheric CO<sub>2</sub> concentrations over the last century. Despite concerns for global climatic changes and many attempts to sustainably generate energy, fossil fuel combustion continues to be the main source of electricity while releasing 13 Gt of CO<sub>2</sub> [1] to the atmosphere each year. Therefore CO<sub>2</sub> capture and storage (CCS) technology is a promising solution to reduce atmospheric CO<sub>2</sub> emissions [2]. Solvent absorption that is based on amines is the most common technology for the capture of CO<sub>2</sub>. However this method is criticized for its very high energy consumption and operational limitations such as corrosion, slow

uptake rates, foaming and large equipment. Hence there is a huge interest in solid adsorbent materials for CCS [3-6]. In past few years metal organic frameworks (MOFs) have emerged as solid CO<sub>2</sub> adsorbent materials due to their tuneable chemical and physical properties.

Particularly, there is growing interest for metal free carbon-based nanomaterials for gas adsorption. Carbon-based nanomaterials such as fullerene, carbon nanotubes and graphene offer excellent thermal and chemical stability as CO<sub>2</sub> adsorbents [7,8]. Heterofullerenes are fullerene structures in which one or more cage carbon atoms are substituted by heteroatoms [9]. In

addition to the properties mentioned above, which are inherent to carbon-based nanomaterials, heterofullerenes also offer excellent tuneable chemical and physical properties [10]. Gas adsorption on heterofullerenes is an appealing subject. B. Gao et al. [11] studied CO<sub>2</sub> adsorption on calcium decorated C<sub>60</sub> fullerene and F. Gao et al. [12] studied O<sub>2</sub> adsorption on nitrogen-doped fullerene.

Boron-doped C<sub>60</sub> fullerenes are one of the most structurally stable heterofullerenes [9]. Guo et al. synthesized B-doped C<sub>60</sub> fullerenes for the first time, in microscopic amounts by laser vaporisation [13]. Zou et al. [14] demonstrated the synthesis of B-doped C<sub>60</sub> fullerene by using radio frequency plasma-assisted vapour deposition. Recently Dunk et al. [15] introduced a method to produce BC<sub>59</sub> directly from exposing C<sub>60</sub> fullerene to boron vapour. Wang et al. [16] stated that substituting a single C atom of the C<sub>60</sub> fullerene with a B atom does not cause a significant distortion in the cage structure. The net change in the dihedral angle due to the doping is only 1.6% and Kurita et al. [17] predicted that due to the similarity between the C–B bond and the C–C bond, the changes in the bond lengths are less than 5%. Therefore the BC<sub>59</sub> fullerene has a similar structural and thermal stability as C<sub>60</sub> fullerene. Despite the numerous study results, which confirm the structural stability of B-doped C<sub>60</sub> fullerene, very little studies have been done on applications of B-doped fullerene. Here, for the first time we report a study about the CO<sub>2</sub> adsorption on B-doped C<sub>60</sub> fullerene, in which a single C atom is replaced with a B atom.

Sun et al. [8] predicted an enhanced CO<sub>2</sub> adsorption on 1e<sup>-</sup>- and 2e<sup>-</sup>-charged boron nitride sheets and nanotubes, which show very little chemical affinity towards CO<sub>2</sub> in their neutral state. Also Sun et al. [18] showed that chemical interactions between boron–carbon nanotubes (B<sub>2</sub>CNT) and CO<sub>2</sub> can be enhanced by introducing extra electrons to the system. The enhanced interaction of CO<sub>2</sub> with adsorbent materials by electron injection has been further proved by Jiao et al. [19]. Therefore, we will investigate the CO<sub>2</sub> adsorption on BC<sub>59</sub> fullerene in both the neutral and the 1e<sup>-</sup>-charged states.

## Computational Details

First-principles density functional theory (DFT) calculations were carried out to study CO<sub>2</sub> adsorption on the BC<sub>59</sub> cage. The BC<sub>59</sub> structure was fully optimized in the given symmetry. The calculations were carried out at B3LYP [20–22] level of theory while using the split valence polarized basis set 6-31G(d). B97d [23,24] with the same basis set was used for calculations when non-covalent interactions are predominant. The CO<sub>2</sub> adsorption on BC<sub>59</sub> was studied in the neutral state and in the 1e<sup>-</sup>-charged state. The electron distribution and transfer were analysed with Mulliken population analysis method [25].

The adsorption energies were calculated using the following equation.

$$E_{\text{ads}} = E_{\text{CO}_2/\text{BC}_{59}} - (E_{\text{BC}_{59}} + E_{\text{CO}_2}), \quad (1)$$

where  $E_{\text{ads}}$  is the adsorption energy,  $E_{\text{CO}_2/\text{BC}_{59}}$  is the total energy of the BC<sub>59</sub> cage with a CO<sub>2</sub> molecule adsorbed and  $E_{\text{BC}_{59}}$  and  $E_{\text{CO}_2}$  are the energies of the isolated BC<sub>59</sub> cage and CO<sub>2</sub> molecule, respectively. For a favourable adsorption the calculated adsorption energy should have a negative value. To provide more accurate results for the chemisorption energy the counterpoise corrected energy [26,27] was also calculated.

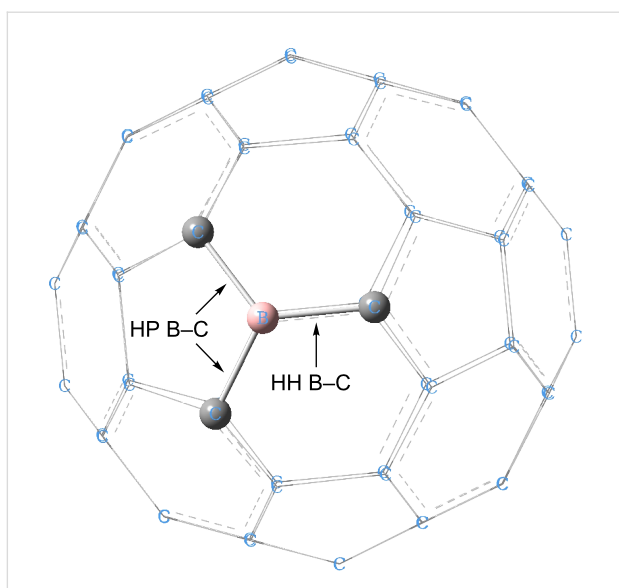
The transition state was located by using the synchronous transit-guided quasi-Newton (STQN) method [28,29], which was then fully optimized by using the Berny algorithm at the B3LYP/6-31G(d) level. The optimized transition structure was used for IRC calculations at the same level of theory [30,31]. All calculations were carried out by using the Gaussian 09 package [32]. The GaussView 5 package [33] was used to visualize the optimized molecular structures, molecular orbitals and charge distributions.

## Results and Discussion

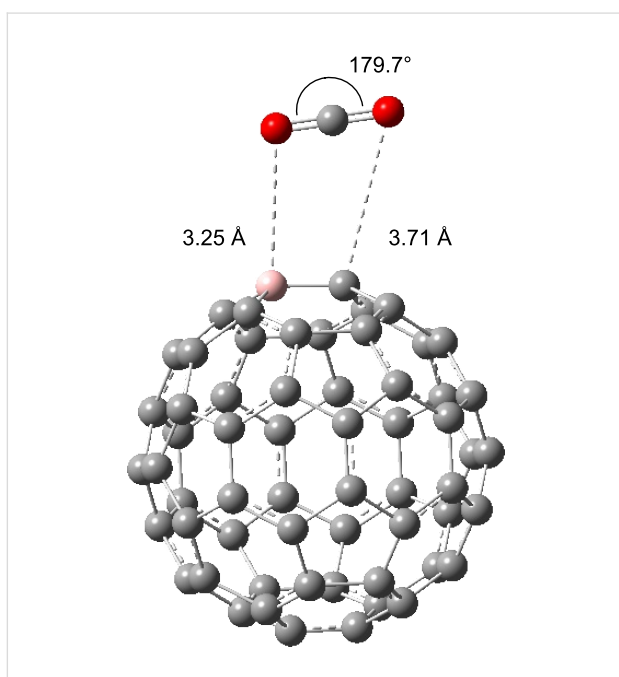
The substitution of a C atom in the C<sub>60</sub> fullerene by a B atom causes a charge transfer between C and B atoms, which results in an unbalanced charge distribution in the fullerene cage. The unbalanced charge distribution forms B–C complex sites for the adsorption of CO<sub>2</sub> (Figure 1). Here we considered two possible sites for the CO<sub>2</sub> adsorption: the B–C atomic site between two hexagonal rings (HH B–C site) and two identical B–C sites between a hexagonal ring and pentagonal ring (HP B–C site).

### Adsorption of CO<sub>2</sub> on uncharged BC<sub>59</sub> fullerenes

According to our simulation results, the CO<sub>2</sub> molecules can only form weak interactions with BC<sub>59</sub> cage in its neutral state. The physisorption energy is a weak –2.04 kcal/mol (–4.1 kcal/mol for B97D/6-31G(d) calculations) and the weak interactions are mainly van der Waals interactions between the CO<sub>2</sub> molecule and the adsorbent. The CO<sub>2</sub> physisorbed configuration is shown in Figure 2. The CO<sub>2</sub> molecule sits parallel to the boron–carbon plane of the BC<sub>59</sub> fullerene cage. The B···O and C···O bond distances are 3.25 Å and 3.71 Å, respectively. The CO<sub>2</sub> molecule undergoes very slight structural changes upon physisorption on the uncharged BC<sub>59</sub> fullerene cage. The O–C–O angle is slightly bent to 179.7° and the changes to the C=O bond lengths are negligibly small. The doped fullerene cage hardly undergoes any structural change. The charge transfer between CO<sub>2</sub> and BC<sub>59</sub> is only 0.008e.



**Figure 1:** Sites for CO<sub>2</sub> adsorption on BC<sub>59</sub>. The B and C atoms of HH B–C and HP B–C sites are represented as 'ball and bond'-type and the rest of the atoms are represented as 'wireframes'. Atom colour code: grey, carbon; pink, boron.

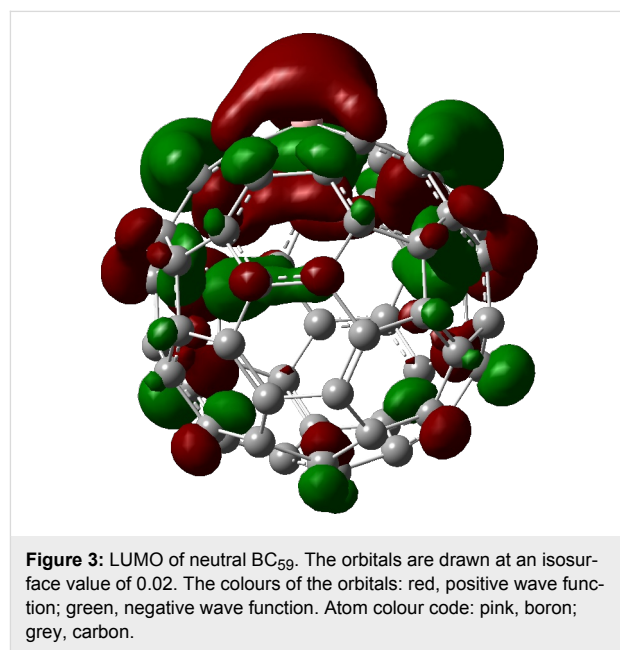


**Figure 2:** Configuration of physisorbed CO<sub>2</sub> on neutral BC<sub>59</sub>. Atom colour code: grey, carbon; pink, boron; red, oxygen.

### Effects of charges on the structure

Kim et al. [34] predicted that C<sub>59</sub>B<sup>−</sup> should be a stable entity because of the isoelectronic configuration with C<sub>60</sub>. This claim is further validated by experimental observations by Dunk et al. [15]. The Mulliken charge analysis and the electron density distributions of the lowest unoccupied molecular orbitals

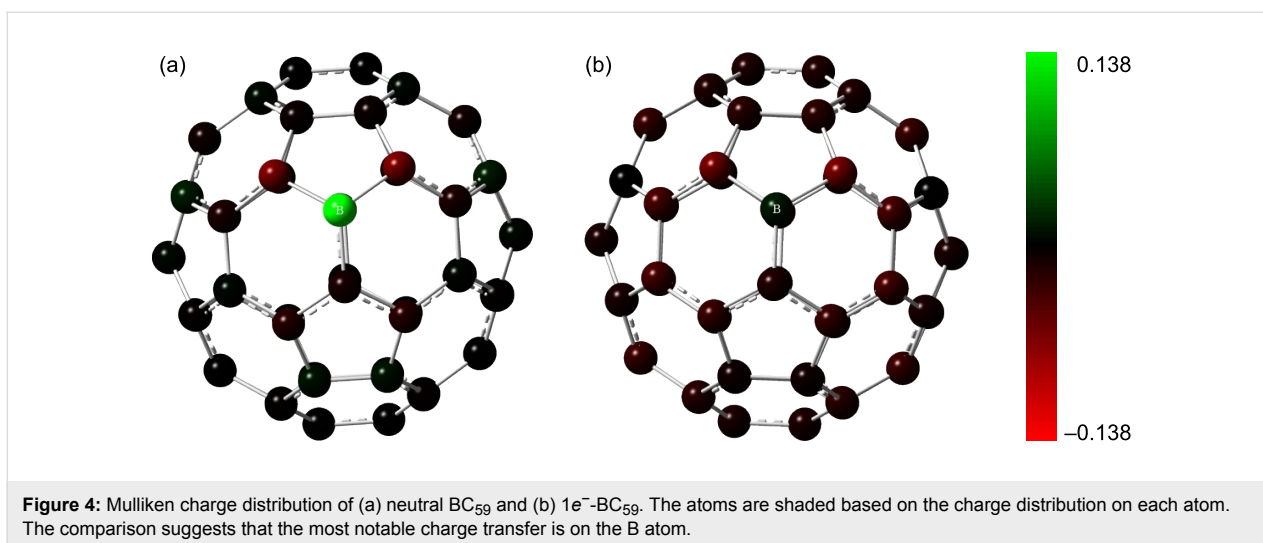
(LUMO) are adopted to assess the influence of changing the charge state of BC<sub>59</sub>. Figure 3 shows that the LUMO of the neutral BC<sub>59</sub> is noticeably concentrated on the B atom and the neighbouring C atoms. Furthermore experimental results of Guo et al. [13] showed that boron doping creates an electron deficient site at the B atom. This suggests that an additional electron added to the system will be accepted by the B atom. This hypothesis is consistent with theoretical predictions of Kurita et al. [17] and Xie et al. [35], who stated that the doped B atom in C<sub>60</sub> fullerene acts as an electron acceptor. The comparison of the Mulliken population analysis of the neutral and the 1e<sup>−</sup>-state of BC<sub>59</sub> proves that the negative charge introduced to the system is essentially accepted by the B atom. The Mulliken atomic charge of the B atom in the BC<sub>59</sub> structure in the neutral state has changed from 0.138 to 0.012 upon the introduction of the negative charge, while as shown in Figure 4 the charges on the C atoms are not changed significantly.



**Figure 3:** LUMO of neutral BC<sub>59</sub>. The orbitals are drawn at an isosurface value of 0.02. The colours of the orbitals: red, positive wave function; green, negative wave function. Atom colour code: pink, boron; grey, carbon.

### CO<sub>2</sub> adsorption on BC<sub>59</sub> fullerene in the 1e<sup>−</sup>-state

Next we studied the CO<sub>2</sub> adsorption on a 1e<sup>−</sup>-charged BC<sub>59</sub> cage. The results confirm that the negatively charged BC<sub>59</sub> fullerene exhibits a stronger interaction with CO<sub>2</sub>. Unlike the neutral BC<sub>59</sub>, for which the interaction with CO<sub>2</sub> molecule was only physical, here the charged BC<sub>59</sub> forms a substantial chemical interaction with CO<sub>2</sub> causing the molecule to undergo significant structural deformations. A stable CO<sub>2</sub> adsorption is observed at the HH B–C site. The chemisorption energy of −15.41 kcal/mol (−64.48 kJ/mol) (−13.48 kcal/mol with BSSE correction) agrees well with the ideal range of chemisorption energy (40–80 kJ/mol) for a good CO<sub>2</sub> adsorbent [36].

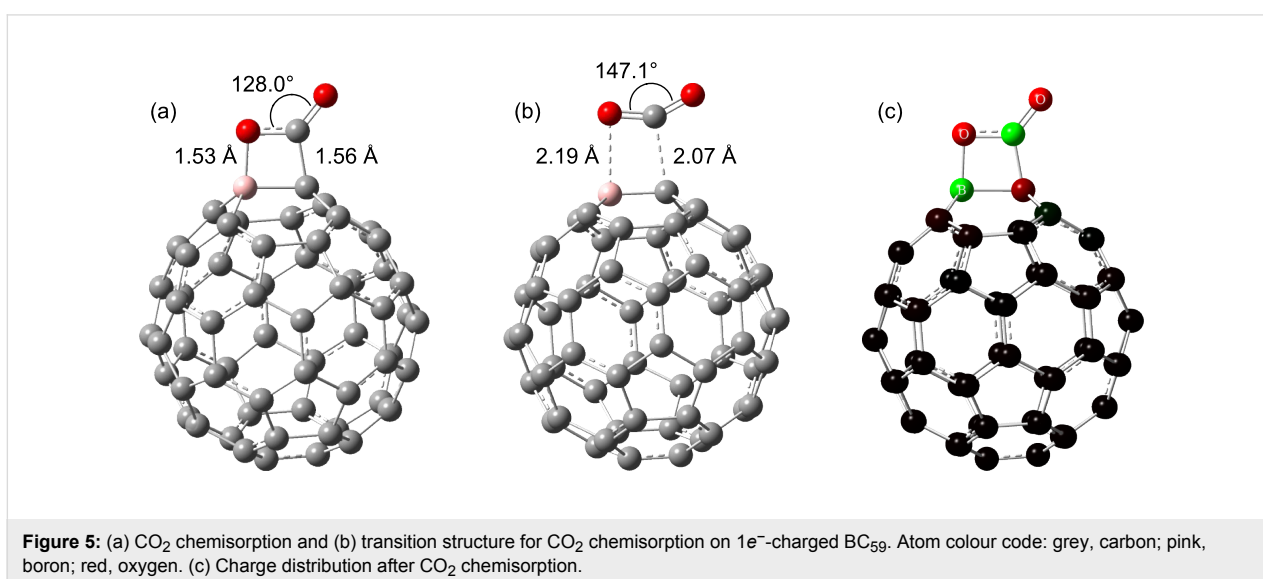


The  $CO_2$  molecule undergoes considerable distortion upon chemically adsorbing on the  $1e^-$ -charged  $BC_{59}$  fullerene. A C=O bond of the  $CO_2$  molecule is broken when one oxygen atom forms a bond with the boron atom (which will be referred as  $O_a$  in the following discussion and the other oxygen atom as  $O_b$ ) and the C atom of the  $CO_2$  molecule forms a bond with the C atom on the HH B–C site of the cage structure. The linear O–C–O bond of  $CO_2$  is bent to  $128.0^\circ$  in the adsorbed form. The C=O<sub>b</sub> bond which is originally 1.169 Å (experimentally 1.162 Å [37]) is elongated to 1.208 Å, while the length of the C–O<sub>a</sub> bond is expanded to 1.336 Å. The adsorption site of the  $BC_{59}$  fullerene also undergoes considerable stretching. The HH B–C site is protruded outwards by about 0.05 Å. The B–C bond of the HH B–C site has stretched from 1.496 to 1.672 Å. The Mulliken population analysis shows that a charge transfer of 0.42 has occurred from the  $BC_{59}$  fullerene to the  $CO_2$  molecule.

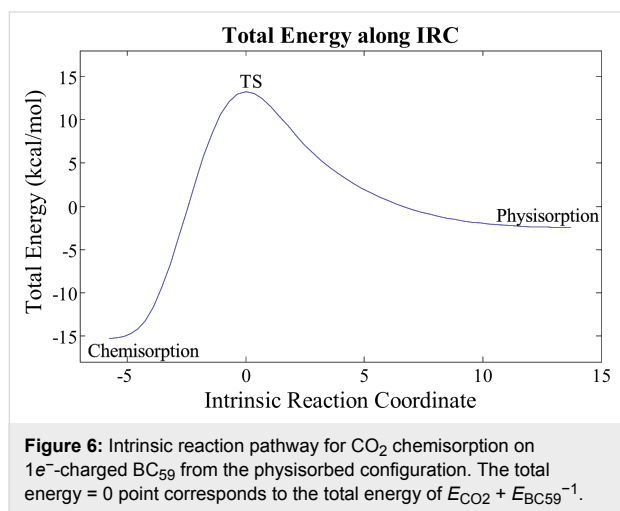
Comparison of the charge distribution on  $BC_{59}^-$  before (Figure 4b) and after (Figure 5c)  $CO_2$  adsorption, confirms that the injected electron is occupied by the  $CO_2$  molecule.

The higher adsorption energy and the significant distortions in the structure confirm a stronger interaction between  $CO_2$  molecule and negatively charged  $BC_{59}$  than its neutral state. These interactions can be explained due to the Lewis acidity of  $CO_2$ , which prefers to accept electrons [18]. On the other hand the B atom of the  $BC_{59}$  becomes less positively charged upon the addition of an extra electron. Therefore it becomes more likely to donate electrons to the  $CO_2$  molecule leading to stronger interactions between the two molecules.

Figure 6 shows the minimum energy pathway for the adsorption from the physisorbed state to the chemisorbed configuration.



ation. We performed frequency calculations on the optimized transition structure, which confirms that it is a first order saddle point and hence an actual transition structure. From this figure, the activation barrier for the chemisorption is estimated to be 13.25 kcal/mol (55.43 kJ/mol). The low barrier of the reaction indicates that the reaction is energetically favourable.



For the desorption step, the removal of the added charge will decrease the stability of the bond between CO<sub>2</sub> and the doped fullerene. The thermodynamic analysis of the reaction shows that the CO<sub>2</sub> chemisorption is spontaneous only for temperatures less than 350 K. Therefore we suggest a method of manipulating the charge state and the temperature of the system for adsorbent recycling. Charging the system can be achieved by electrochemical methods, electrospray, and electron beam or gate voltage control methods [8].

## Conclusion

By using DFT calculations we have studied the adsorption mechanisms of CO<sub>2</sub> on a C<sub>60</sub> fullerene cage, in which a single C atom is substituted by a B atom. Our calculation results show that the BC<sub>59</sub> cage, in its neutral state, shows a low chemical interaction with CO<sub>2</sub> molecule, which only physisorbs with  $E_{\text{ads}} = -2.04$  kcal/mol. However CO<sub>2</sub> adsorption on the BC<sub>59</sub> can be significantly enhanced by injecting negative charges into the structure. The CO<sub>2</sub> molecule chemisorbs on the 1e<sup>-</sup>-charged BC<sub>59</sub> with  $E_{\text{ads}} = -15.41$  kcal/mol. This study suggests that we can conclude 1e<sup>-</sup>-charged BC<sub>59</sub> cage structure is a promising CO<sub>2</sub> adsorbent.

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