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Adsorption of C_{60} and $N@C_{60}$ on Si (100)

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Abstract

The interactions between C_{60} molecules and the Si(100) surface, as well as the interactions between the endohedrally doped $N@C_{60}$ molecules and the Si(100) surface have been explored via ab initio total energy calculations. Configurations which have the cage located upon the dimer row bonded to two dimers (r2) and within the dimer trench bonded to four dimers (t4) have been investigated, as these have previously been found to be the most stable for the C_{60} molecule. We show that our results for the adsorption of the C_{60} molecule upon the Si(100) surface are comparable with previous studies. We have investigated the differences between the adsorption of the C_{60} and $N@C_{60}$ molecules upon the Si(100) surface and found that there are only minimal differences. Two interesting cases are the r2g and t4d configurations, as they both exhibit differences that are not present in the other configurations. These subtle differences have been explored in-depth. It is shown that the effects on the endohedral nitrogen atom, due to its placement within the fullerene cage, are small. Bader analysis has been used to explore differences between the C_{60} and $N@C_{60}$ molecules.

Key words: Computer simulations, Density functional calculations, Chemisorption, Silicon, Fullerenes

PACS: 61.46+w, 61.48+c, 71.15Mb

1 Introduction

It has been over twenty years since the allotrope of carbon commonly known as the fullerene was first discovered. This quite remarkable molecule possesses a cage structure constructed of pentagonal and hexagonal faces. The number of constituent carbon atoms can vary greatly, however the most common

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structure size consists of sixty atoms. This particular variation is named buckminsterfullerene, and has a high degree of symmetry.

It has been shown that if an endohedral species is placed within the confines of the fullerene cage, then the endohedral species behaves as if it were in isolation, with little or no interaction with the fullerene cage itself [1]. Of course this depends on the size of the atom or molecule that is placed within the cage, as the cage needs to be large enough to adequately house the endohedral species. The C_{60} fullerene has been successfully manipulated across a surface with a scanning tunneling microscope (STM) tip [2,3]. Only a small amount of the cage actually interacts with the surface itself, because of the curvature of the cage (which is due to the pentagonal regions of the cage's surface). These properties, as well as others, make the study of endohedrally doped fullerenes an exciting area of research, that may have a far-reaching impact in the burgeoning field of nanotechnology.

A number of differing solid-state quantum computing architectures have been proposed that rely on the unique properties of endohedral fullerenes (some of which are mentioned above), in order to represent the quantum bits (qubits), within the system. Some of these schemes suggest the usage of chains of endohedral fullerenes, with alternating endohedral species (nitrogen and phosphorus are discussed as candidates) [4,5]. The use of both the electronic and nuclear spin as qubits has also been discussed [5]. There are still some fundamental issues that need to be addressed with an architecture of this type, for example the qubit readout, however various solutions have been suggested [5].

Many studies [6–12] have been carried out experimentally which show that the C_{60} molecule adsorbs in the dimer trench at room temperature, and is only observed above the dimer row when the system is heated. A study of the larger endohedral $La@C_{82}$ molecules suggested that the adsorption of an endohedral molecule is similar to that of a fullerene without the presence of an endohedral atom [13].

The adsorption of the C_{60} molecule onto the Si(100) surface has been extensively studied with density functional theory (DFT) [1,14–16]. As the computing power available to these studies has increased, so has the completeness of the descriptions used for the atoms within the systems. These studies have found four groups of configurations for the C_{60} molecule upon the silicon surface. These are above the dimer trench, bonded to either two or four dimers (denoted as t2 and t4 respectively), and above the dimer row, bonded to either one or two dimers (denoted as r1 and r2 respectively). The most stable of the groups has been shown to be the r2 and t4 configurations, which are the focus of the work presented here.

Here we re-examine the r2 and t4 configurations, with a view to determining

the effect on the endohedral nitrogen atom due to its placement within the C_{60} molecule on the Si(100) surface, and the effect on the C_{60} and the molecules bonding to the Si(100) surface due to the inclusion of the endohedral nitrogen atom. We compare our results for the adsorption of the C_{60} molecule onto the Si(100) surface, and then proceed to confirm that the effects on both the endohedral nitrogen atom and the C_{60} molecule are minimal.

2 Methodology

We have employed the density functional theory [18,19] code PLATO [17], which utilises a localised orbital basis set, for all our calculations. Within our calculations we have used the Perdew-Burke-Ernzerhof GGA [20] for the exchange-correlation potential, as the LDA has been shown to overbind for systems such as the one studied. The electron-ion interactions were modelled using pseudopotentials of the type described in [21].

In order to describe the system of an isolated fullerene (or endohedral fullerene) on the Si (100) surface, we first had to create a silicon surface. The surface we have used consists of six layers of silicon atoms, with the surface layer being represented by two rows of four dimers. We have chosen a 2×2 tilted dimer reconstruction, as this has been shown to be energetically most favourable within our approach [15]. The bottom two layers of silicon are pinned in their respective bulk positions, and the bottom layer's dangling bonds are saturated with hydrogen atoms (which in turn, have been pinned in their own relaxed positions).

Periodic boundary conditions have been imposed in all directions, with a large vacuum gap included above the silicon surface, to ensure a sufficient gap between the top of the fullerene cage and the bottom of the surface for the periodic repeat, so as to minimise the interaction between the two. Due to the size of the system, all the calculations have been carried out using just the Γ -point for k -point sampling.

In order to describe the differing atom species present in our simulation cell, we have created a series of basis sets that vary greatly in complexity. The simplest is our description of the hydrogen atoms, which we describe with a single s function. This is because the only purpose of the hydrogen atoms in our simulation cell is to saturate the dangling bonds from the final silicon layer, so a more complete description is not necessary. The silicon and carbon basis sets consist of three sets of s , three sets of p and two sets of d functions, which accounts for 22 basis functions per carbon and silicon atom. We denote these basis sets as triple numeric with double polarisation (TNDP). Using basis sets of the TNDP level of completeness has been shown [22] to reduce the basis

set superposition error (BSSE), without the need to correct the results via the the Boys and Bernardi counterpoise method [23].

The endohedral nitrogen atoms contained within the fullerene cages, are described with three sets of s , three sets of p , two sets of d and one set of f functions, accounting for 29 basis functions per atom. We have denoted this basis set as TNDP+F. With the increasing number of basis functions there is of course an increased computational cost associated with the calculations. In order to accommodate the use of f orbital functions within PLATO, we have implemented the generic Slater-Koster routines detailed in [24,25]. This recursive approach allows us to employ basis sets containing basis functions with any angular component.

The commonly used measure of assessing the favourability of a specific orientation of the fullerene cage on the silicon surface, is the binding energy between the fullerene cage and the silicon surface. This is calculated as the difference between the sum of the energies of the relaxed components and the energy of the relaxed combined system (see Equation 1).

$$E_{\text{binding}} = E_{\text{fullerene on surface}} - E_{\text{isolated fullerene}} - E_{\text{isolated surface}} \quad (1)$$

The binding energies from our calculations not only allow comparison between our work and previous studies, but provide a measure of difference between the fullerene and the endohedral fullerene configurations.

To analyse the bonding and the charge transfer in the systems, we have used the algorithm devised by Sanville *et al.* [26], that implements Bader’s principles from his atoms in molecules work [27]. The method works by examining a pair of atoms, first finding the midpoint between the atoms and then calculating the Hessian of the electron density and the gradient at this point. Atoms that are chemically bonded are characterised by a saddle point in the electron density, so they possess one positive and two negative eigenvalues. The method then iteratively searches to find the minimum along the positive eigenvector, and the maxima along the two negative eigenvectors, until the gradient is zero. The two negative eigenvalues describe the curvature of the bond perpendicular to the direction of the bond.

The ratio of the two negative eigenvalues provide a measure of the bond’s characteristic, in particular it indicates how much p characteristic the bond possesses (which corresponds to an elongation of the circular shape of the perfect single bond). As a reference we use the single and double bonds found in ethane and ethene, which have bond ratios of 1.00 and 1.27 respectively. Bonds which have ratios between the two values are considered as having some interaction between the p orbitals of the constituent atoms. For the isolated

C_{60} we see two distinct bond types that fall between these perfect bond ratios. The weaker type of bonds are found around the pentagons, and have ratios ~ 1.13 and the stronger type of bonds, which are the bonds shared by hexagons, have a ratio of 1.19.

Since atomic charge is not a quantum mechanical observable, we will use Bader charge analysis to determine the amount of charge on each atom in the system. This is achieved by splitting the cell into a group of subsystems, and calculating the charge contained within each subsystem. The volumes are defined by mapping out the surface of zero charge density flux between atoms. Bader’s method allows the charge on atoms to be calculated, relatively independently of the basis set, for a given charge density, which is not the case with the often used Mulliken population analysis.

3 Results

Previous studies [1,14–16] involving the adsorption of fullerene molecules onto silicon substrates have identified four groups of configurations that the fullerene cage can take upon the surface. In this study we have focused on the two of these groups that produced the most stable structures. These are those with the cage above the dimer row, centred between two dimers (r2), and with the cage above the dimer trench, bonded to four dimers (t4). These configurations are shown in Figs. 1 and 2, respectively. We have replicated all of the structures identified in [14] and the more stable structures identified in [16].

The results of this work for the adsorption of the C_{60} on the Si(100) surface, are given in Table 1; they show a good level of agreement with previous studies. There are some subtle differences, for example our r2 configurations are in general more favourable than previously shown. We attribute this to two factors; the first relates to the differences between the surface reconstructions used, and the second being the ease at which the fullerene forms stable bonds with the silicon surface. In general the binding energy is more favourable when the two dimers directly underneath the fullerene molecule (the dimers that the fullerene bonds to) are flat (i.e. as the angle of the tilted dimer reconstruction tends to zero). For the r2d configuration we produced a range of relaxed systems, all using the 2×2 surface reconstruction, that differed only in the measure of flatness of the dimers with which the cage bonds. In this case a difference of $\sim 0.03\text{\AA}$ in the amount of dimer flatness, accounted for a difference of ~ 0.3 eV. Considerable efforts have been taken to ensure that the dimers are as flat as possible in the r2 configurations. The 2×2 surface reconstruction appears to be much more likely to naturally relax into this type of dimer configuration, than the 2×1 surface reconstruction. This leads to the second factor, which is the existence of many metastable states for the C_{60}

molecule on the Si(100) within any one configuration. Thus, it is very difficult to determine with any degree of certainty the global minimum.

The final relaxed configurations for the adsorption of the C_{60} molecule on the Si(100) surface were used for the initial atom positions in the $N@C_{60}$ calculations. The nitrogen atom was added into the fullerene cage at the centre of mass for the fullerene. The endohedral systems were then relaxed in the same manner, and the binding energies calculated are also presented in Table 1. The total energy of the isolated $N@C_{60}$ is substituted in Equation 1 instead of the energy for the isolated C_{60} . As Table 1 demonstrates there is very little change in the binding energies between the C_{60} and $N@C_{60}$ systems for all of the configurations investigated. In general, the $N@C_{60}$ configurations are marginally more favourable than their C_{60} counterparts. There are two outlier results, those for the r2g and t4d configurations, which we shall directly address in the subsequent discussion, explaining these results in the context of subtle differences within other system properties. As a whole we believe our results are consistent with the consensus that the endohedral nitrogen is almost perfectly isolated within the fullerene cage.

If we compare the hierarchies of the most favourable configurations from this work with that of previous studies, there is a good level of agreement, see Table 2. The less stable configurations are the most closely in agreement between the studies. Our results show a slight skew in favourability towards the r2 configurations, as explained previously, however, in general these differences are minor. The subtle differences between the hierarchies of our C_{60} and $N@C_{60}$ work, illustrates the small, but varying differences, between the systems as discussed below.

A good measure to determine how well the endohedral nitrogen atom is isolated, is to observe the change in spin on the nitrogen atom. This is achieved by comparison of the spin on the nitrogen atom in each of the endohedral configurations with the spin on the nitrogen atom in the isolated $N@C_{60}$. We have calculated the spin using two different schemes, the Mulliken spin and the Bader spin. The Mulliken spin analysis for the nitrogen atom in an isolated $N@C_{60}$ gives a spin value of 1.48. With the exception of the r2g configuration, which gives a spin value of 1.38, all the spin values for the adsorbed configurations range from 1.44 to 1.47, which represents a very small change in the level of electron spin.

With the Bader analysis the picture is a little different, as we see greater variation in the spin values. The spin on the nitrogen atom in the isolated $N@C_{60}$, using Bader analysis, has a value of 1.43, and the spin values for the adsorbed fullerene systems range from 1.33 to 1.43. In the context of only the r2 configurations, the r2g configuration remains an outlier. There is, however, much greater variation within the t4 configurations than was present

in the Mulliken analysis. There appears to be no direct correlation between change in spin and the change in binding energy between the C_{60} and $N@C_{60}$ configurations. In both the Mulliken spin and the Bader spin the maximum difference between the isolated case and any of the endohedral configurations is ~ 0.1 .

When studying the charge on the nitrogen atom in the $N@C_{60}$ configurations, it is clear that there is very little charge transfer between the nitrogen atom and the fullerene cage. In the main the charge transfer to the nitrogen atom is less than 0.1 of an electron, with only a couple of outlier cases, the largest being ~ 0.25 of an electron. There does not appear to be a direct relationship between charge transfer and system favourability, however again we find the r2g configuration amongst the outliers. We believe that the larger shift in the r2g binding energy for the $N@C_{60}$ from the C_{60} , when compared to the other configurations, is the result of the greater charge transfer to the C_{60} cage containing the endohedral nitrogen atom.

A previous study [1] of endohedral fullerenes that used nitrogen as the endohedral species, found the nitrogen atom in its final relaxed position to be a little below the centre of the fullerene cage. This calculation was performed for the t4c configuration. A further difference between their calculation and our own is that we differ on the initial placement of the nitrogen atom. In their calculations it was placed off-centre, whereas as previously stated, in our calculations we have initially placed the nitrogen atom at the centre of mass for the fullerene cage. This minor difference aside, for the t4c configuration we also found that the largest displacement for the nitrogen atom would be in the negative z axis (i.e. the nitrogen atom moves towards the surface).

There appears to be little in the way of correlation between the magnitude and direction of the displacement of the nitrogen atom, and the binding energy of the $N@C_{60}$ or the spin lost on the nitrogen atom. The magnitude of all the displacements are small, with all being $\leq 0.1\text{\AA}$, the only exception being the t4b configuration with a displacement $\sim 0.3\text{\AA}$. In fact, by visually analysing the configurations, it is only the t4b configuration (which has not only the largest displacement magnitude, but the displacement is almost all in the negative z axis), in which the nitrogen displacement is noticeable.

When comparing the lengths of the carbon-silicon bonds that are formed between the fullerene cage and the silicon surface, there is good agreement to be found between not only the C_{60} and $N@C_{60}$ results, but those results found by Godwin *et al.* [14]. There appears to be no pattern concerning differences in bond length between the C_{60} and $N@C_{60}$ systems of the same configuration. It is when examining the carbon-silicon bonds that we are able to explain the increase in binding energies found between the $N@C_{60}$ t4d, and the C_{60} t4d configurations. The $N@C_{60}$ t4d configuration is a metastable minimum, with

shorter carbon-silicon bond lengths than those found in the C_{60} t4d configuration. It is only the presence of the endohedral nitrogen atom that provides this stability, as the removal of the nitrogen atom leads to the fullerene and surface relaxing into the form found for the C_{60} t4d configuration. This is the only case where the presence of an endohedral nitrogen has affected bonding, and is a direct product of the unfavourability of the 2×2 surface reconstruction for the t4d configuration, especially for this small cell size. For the remainder of the configurations the range of bond lengths is greater in our results (1.93-2.19Å) compared to those presented elsewhere (1.96-2.19Å), however, this difference is minimal. The more favourable binding energy (compared to other results), as shown in Table 1, for the r2a configuration may be explained by the fact that it has a much lower average carbon-silicon bond length. In general, however, the carbon-silicon bond length does not seem to have a direct relationship with binding energy.

When analysing the bonding within the lower part of the fullerene cage (the region which bonds to the silicon surface), our results compare favourably with those by Frangou *et al.* [22]. The carbon-carbon bonds for the carbon atoms that form the carbon-silicon bonds have all decreased bond ratios (see Figure 3), which results from the formation of the carbon-silicon bonds. While the majority of the rebonding is localised within the immediate vicinity of these carbon atoms, there are areas of delocalised rebonding taking place, as the fullerene has to internally readjust to the changes in its shape and curvature. As expected the bonding within the adsorbed fullerenes no longer resembles that found in the isolated fullerene cage (i.e. single bonds around pentagons and double bonds shared by hexagons). Comparing the C_{60} and $N@C_{60}$ Bader bond ratios of the cage around the bonding region (see Figure 3), it is clear that the presence of the endohedral nitrogen atom has little or no effect on the internal rebonding of the fullerene cage due to adsorption on the silicon surface.

4 Conclusions

Adding an endohedral nitrogen atom to the buckminsterfullerene cage has little effect on how the cage bonds to the silicon surface, in terms of the rebonding within the fullerene and the carbon-silicon bond lengths. The binding energies are slightly different, and in general this change makes the $N@C_{60}$ configurations more favourable than their C_{60} counterparts. The spin on the endohedral nitrogen atom is almost unchanged, the displacement of the endohedral nitrogen atom is relatively small, and the charge transfer between the endohedral nitrogen atom and the fullerene cage is minimal. The effect of these factors on the binding energies is minimal in the vast majority of cases. We feel that the results presented here indicates that the endohedral nitrogen atom is almost

perfectly isolated from the fullerene cage, and that the fullerene cage is largely unaffected by the endohedral atom's presence. As such, we believe that there is a very strong and valid case for using nitrogen doped C_{60} molecules as part of a quantum computing qubit.

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Fig. 1. Pictured above are all the r2 configurations that have been investigated in this study. The pale orange strips represent the dimer rows. The silicon dimers with which the cage bonds are represented by the yellow and orange bars. The yellow part represents one silicon atom of the pair, and orange part represents the other silicon atom. The white region between the dimer rows represents the trench. Carbon atoms are depicted as white circles, with the exception of those which bond with the silicon surface which are depicted as grey circles.

Fig. 2. Pictured above are all the t4 configurations that have been investigated in this study. The colour scheme is the same as used in Fig. 1.

Fig. 3. The r2a configuration for the C60 on the left, and the N@C60 on the right, with the accompanying ratios of the negative eigenvalues. For the C60, the bond ratios for the isolated cage are bracketed underneath, and are shown in black. The differences between the ratios for the r2a configuration and the isolated cage are shown in red for a decrease in the C60 bond ratio from the isolated cage, and are shown in green for an increase in the C60 bond ratio from the isolated cage. Those bond ratios that remain unchanged, are shown in black. For the N@C60, the differences between the C60 and N@C60 bond ratios are shown in blue, with an arrow indicating the direction of change. For both diagrams the carbon atoms that bond with the silicon surface are shown in grey, and those carbon atoms that do not bond with the silicon surface are shown in white.

Config.	SIESTA[16]	VASP[16]	Frangou[22]	C ₆₀	N@C ₆₀
r2a	-2.58	-2.78	-3.02	-3.23	-3.19
r2b	-2.49	N/A	-2.72	-3.01	-3.08
r2c	-2.00	N/A	-2.85	-2.82	-2.92
r2d	-0.87	N/A	-1.29	-1.52	-1.56
r2e	-1.68	N/A	-2.16	-2.21	-2.28
r2f	-2.19	N/A	-2.32	-2.60	-2.66
r2g	-1.10	N/A	-1.42	-1.89	-2.11
t4a	-2.16	-2.45	-2.77	-2.84	-2.90
t4b	-2.53	N/A	-3.15	-3.14	-3.18
t4c	-2.63	-2.75	-3.02	-3.14	-3.19
t4d	-1.96	N/A	-2.32	-2.40	-2.64
t4g	-2.53	-2.74	-2.78	-2.77	-2.82
t4h	-1.94	N/A	-1.87	-2.52	-2.55
t4i	-1.83	N/A	-2.45	-2.41	-2.49

Table 1

Binding energies of the C₆₀ molecule on the Si(100) surface in eV. For comparison, the results of previous calculations [16,22] are given. The results using SIESTA include the Boys-Bernardi correction [23].

Rank	SIESTA[16]	Frangou[22]	C60	N@C60
1	t4c	t4b	r2a	r2a / t4c
2	r2a	t4c / r2a	t4b / t4c	r2a / t4c
3	t4b / t4g	t4c / r2a	t4b / t4c	t4b
4	t4b / t4g	r2c	r2b	r2b
5	r2b	t4g	t4a	r2c
6	r2f	t4a	r2c	t4a
7	t4a	r2b	t4g	t4g
8	r2c	t4i	r2f	r2f
9	t4d	t4d / r2f	t4h	t4d
10	t4h	t4d / r2f	t4i	t4h
11	t4i	r2e	t4d	t4i
12	r2e	t4h	r2e	r2e
13	r2g	r2g	r2g	r2g
14	r2d	r2d	r2d	r2d

Table 2

The fourteen configurations investigated here are placed in the table above in descending order of stability.