

# Binding of Carbon Rings to a Graphite Plane

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We expand a previous model developed for the study of the interaction of fullerenes with graphite planes to consider carbon rings. The model assumes that the ring is rigid and the interaction energy arises from the cumulative effect of adding the pairwise interaction energies for all the pairs of the atoms in the ring and in the plane, respectively. We have seen that the preferred orientation of the ring with respect to the surface is parallel. This relative orientation has a binding energy five times larger than that of its corresponding perpendicular orientation. The calculated potential energy functions have been used to estimate the force constant and harmonic frequency of the rings on the graphite surface. Subsequently we have calculated and discussed the results of a feasible temperature-programmed desorption experiment.

## Introduction

The identification of  $C_N^+$  carbon cluster cations<sup>1</sup> up to  $N = 190$  and, the elucidation<sup>2</sup> of the fullerene structure for  $C_{60}$  caused an explosion of interest in the properties of these materials. Advances in carbon nanotubes<sup>3</sup> have recently raised interest in carbon cluster research.

Carbon clusters show different relative stability trends among the various possible isomers, with changing the number of atoms of the cluster. In fact, it has recently been determined that the most stable structure for carbon clusters with 10, 12, 14, and 16 carbon atoms is a monocyclic ring.<sup>4</sup>

However, experimental identification, in situ, of the most stable isomers of  $C_N$  clusters is difficult due to the high temperatures often used to prepare them. One way to avoid this problem would be to deposit the generated clusters on a graphite surface and then desorb them selectively. Naturally, to understand this process one has to elucidate first the binding of various carbon clusters to a graphite surface. This is crucial for the successful extraction and separation of the carbon clusters deposited on graphite matrices, such as soot produced by the Kraetschmer–Huffmann process.<sup>5</sup> This idea, posed by Ruoff and Hickman<sup>6</sup> for fullerenes, can be extended to other carbon clusters as well, once the binding of these clusters to the graphite surface has been understood.

In this paper we present a study of the binding of carbon rings to a graphite surface.

## Methods

The interaction energy between the carbon ring and the graphite plane will be approximated as the sum of the interaction energies between every pair of atoms of the ring and the plane, respectively. This method has been earlier applied for the prediction of the binding energies of various systems including two graphite planes,<sup>7</sup> two  $C_{60}$  molecules and the fcc crystal structure of the  $C_{60}$  fullerite,<sup>8,9</sup> and spherical fullerenes and a graphite plane.<sup>6</sup> More recently, the same procedure has also been applied to the calculation of the interaction energy between shells of spherical carbon onions.<sup>10,11</sup> At this point it is worth noting that the interaction of fullerenes with a graphite plane can also be computed by using a discrete dipole formalism, in

which  $C_N$  is viewed as a rigid cluster of  $N$  polarizable C atoms and the graphite surface as a continuous dielectric medium.<sup>12</sup>

The interaction within individual atom pairs of all these systems is dominated by dispersion forces.<sup>13</sup> Therefore, a pairwise potential of the van der Waals type appears to be appropriate for most of these systems, as suggested by the recent study of Qian et al.<sup>14</sup> where they compare, with the available experimental data, the equation of state for the graphite system evaluated from a Lennard-Jones potential and from a Morse-type potential derived from first principles local density approximation (LDA) calculations. The result is that neither of the potentials is entirely satisfactory. The LDA model is better for short interlayer distances, while the Lennard-Jones potential fits better experimental data for distances larger than  $\sim 3.0$  Å. It will be seen later that our distances of interest are larger than 3.0 Å, hence, the above result is very supportive of the appropriateness of the Lennard-Jones potential for the purposes aimed at this work.

In this paper we shall assume that the interaction energy of every carbon atom in the ring and every carbon atom in the graphite plane is given by the Lennard-Jones potential

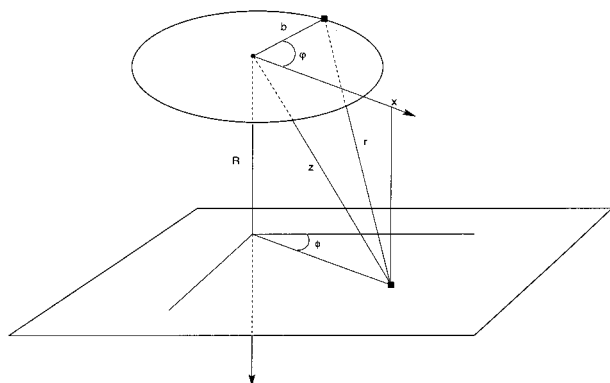
$$V(r) = \frac{C_{12}}{r^{12}} - \frac{C_6}{r^6} \quad (1)$$

with  $C_{12} = 34808.34 \text{ eV} \cdot \text{\AA}^{12}$  and  $C_6 = 19.97 \text{ eV} \cdot \text{\AA}^6$  as recommended by Girifalco.<sup>9</sup>

We model the  $C_N$  carbon ring as a circle of radius  $b$  with the  $N$  carbon atoms uniformly distributed with linear density  $\gamma$  on its periphery. Then  $N = 2\pi\gamma b$ . The graphite plane will be modeled by an infinite surface with a constant carbon atom surface density  $\sigma = 0.38 \text{ atom/\AA}^2$ .

Recall that, due to the decreased symmetry of the carbon ring as compared to a spherical fullerene,<sup>6</sup> we have to take into account the actual relative orientation of the ring with respect to the plane. In particular, we will consider explicitly the two relative orientations of high symmetry, i.e., first, when the carbon ring lies parallel with respect to the graphite plane and second, when the carbon ring lies perpendicular with respect to the graphite plane.

**A. The Ring Lies Parallel with Respect to the Plane.** Following Ruoff and Hickman,<sup>6</sup> we will evaluate the interaction



**Figure 1.** Schematic diagram of a carbon ring of radius  $b$  and a test atom of the graphite surface. The distance between the differential curve element,  $bd\phi$ , of the ring and the test atom is denoted as  $r$ .

energy of our system in two steps. The former step will consist of the calculation of the interaction of the ring whose center is at a distance  $R$  ( $R \geq b$ ) from the plane, with a single atom of the plane located at the coordinates  $(x, 0, R)$ , see Figure 1, namely:

$$Q_n(z, \phi) = C_n \gamma b \int_0^{2\pi} \frac{d\phi}{r^n} \quad (2)$$

for  $n = 6, 12$ . The analytic integration is straightforward and yields the following results:

$$Q_6(z, \phi) = C_6 N \frac{(b^2 + z^2)^2 + 2b^2(z^2 - R^2)\cos^2\phi}{[(b^2 + z^2)^2 - 4b^2(z^2 - R^2)\cos^2\phi]^{5/2}} \quad (3)$$

and

$$Q_{12}(z, \phi) = C_{12} N \times \left[ (b^2 + z^2)[30(z^2 - R^2)^2 b^4 \cos^4\phi + 20(b^2 + z^2)(z^2 - R^2)b^2 \cos^2\phi + (b^2 + z^2)^4] / [(b^2 + z^2)^2 - 4b^2(z^2 - R^2)\cos^2\phi]^{11/2} \right] \quad (4)$$

for the two pieces of the interaction potential (1). Then, the total interaction energy is achieved by integrating over all the atoms in the plane, namely:

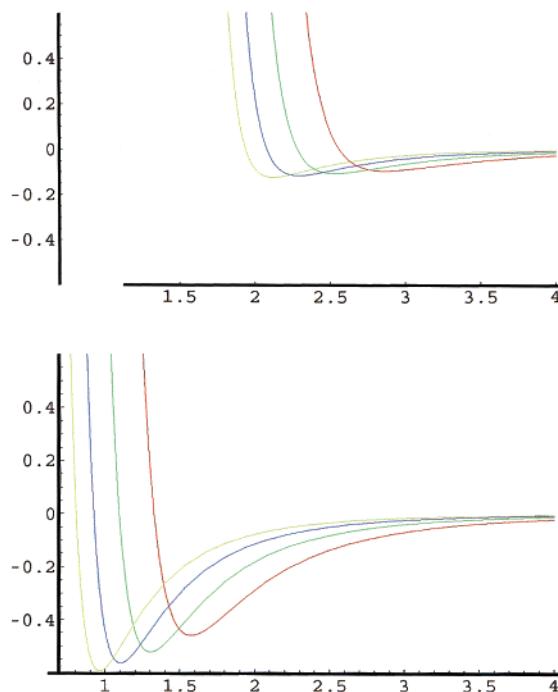
$$W^{\parallel}(R) = \sigma \int_0^{2\pi} d\phi \int_R^{\infty} z dz [Q_{12}(z, \phi) - Q_6(z, \phi)] \quad (5)$$

The final result is

$$W^{\parallel}\left(\frac{R}{b}\right) = \frac{2\pi N \sigma}{4b^4} \left[ \frac{C_{12} \left( 128 \left(\frac{R}{b}\right)^8 + 256 \left(\frac{R}{b}\right)^6 + 288 \left(\frac{R}{b}\right)^4 + 160 \left(\frac{R}{b}\right)^2 + 35 \right)}{160b^6 \left(\frac{R}{b}\right)^9 \left[ \left(\frac{R}{b}\right)^2 + 1 \right]^{9/2}} - \frac{C_6 \left( 1 + 2 \left(\frac{R}{b}\right)^2 \right)}{\left(\frac{R}{b}\right)^3 \left[ \left(\frac{R}{b}\right)^2 + 1 \right]^{3/2}} \right] \quad (6)$$

### B. The Ring Lies Perpendicular with Respect to the Plane.

The evaluation of the total interaction energy for this relative orientation is also straightforward. For the sake of brevity we shall only present the final result,



**Figure 2.** Interaction potential in eV, on the y-axis, of carbon rings with a graphite plane as a function of  $(R/b)$ , on the x-axis, for  $N = 10$  (red), 12 (green), 14 (blue), and 16 (yellow). The top plot corresponds to rings oriented perpendicularly with respect to the graphite plane and the bottom plot corresponds to rings oriented parallel to the graphite plane.

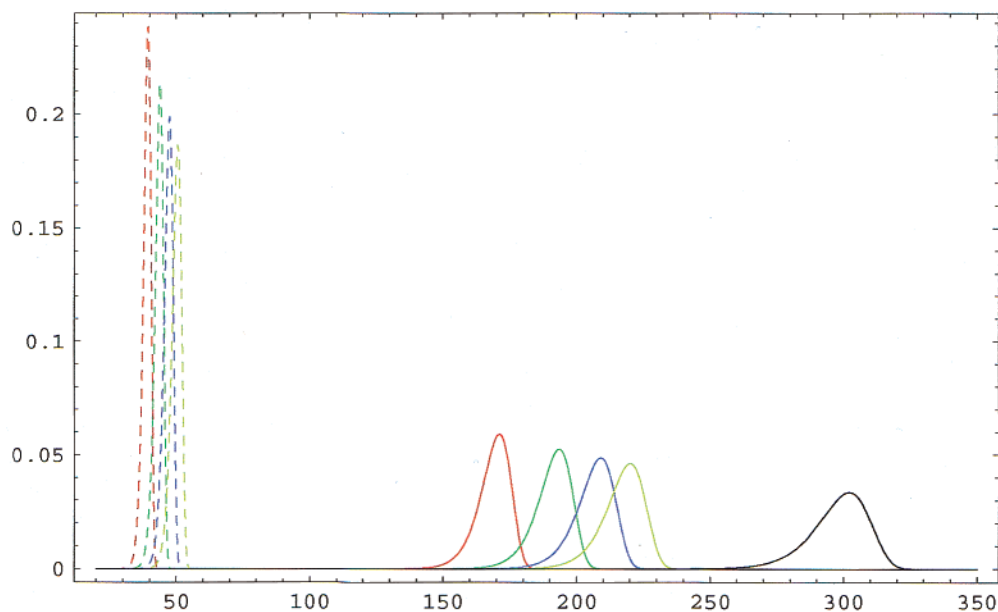
$$W^{\perp}\left(\frac{R}{b}\right) = \frac{2\pi N \sigma}{b^4} \left[ \frac{C_{12} \left( 36 \left(\frac{R}{b}\right)^8 + 126 \left(\frac{R}{b}\right)^6 + 271 \left(\frac{R}{b}\right)^4 + 126 \left(\frac{R}{b}\right)^2 + 36 \right)}{45b^6 \left[ \left(\frac{R}{b}\right)^2 - 1 \right]^9} - \frac{C_6 \left( \left(\frac{R}{b}\right)^2 + 1 \right)}{4 \left[ \left(\frac{R}{b}\right)^2 - 1 \right]^3} \right] \quad (7)$$

## Results

We have considered  $C_N$  rings for  $N = 10, 12, 14$ , and  $16$ , which, according to Jones,<sup>4</sup> constitute the most stable isomeric forms of these species. Their radii are 2.08, 2.49, 2.92, and 3.33 Å for  $N = 10, 12, 14$ , and  $16$ , respectively. Since one of the assumptions of the model is the rigidity of the carbon ring, those clusters having the ring as the most stable isomer will likely possess the largest possible cohesive energy and consequently will be the most likely candidates for this assumption to be satisfied.

The calculated potential energy functions  $W^{\perp}$  and  $W^{\parallel}$ , as a function of  $(R/b)$ , are shown in Figure 2. The predicted optimum  $R_e$  distances and the binding energies, corrected for the zero point vibrational energy, are shown in Table 1 and Table 2 for the two high-symmetry orientations considered in this paper: parallel and perpendicular, respectively.

It is immediately observed that the binding energies for the rings lying parallel with respect to the graphite plane are approximately five times large than for the rings oriented perpendicularly with respect to the graphite plane. Observe also that in both cases the binding energy increases as the number carbon atoms of the ring increases, as expected, since the total binding energy comes from the cumulative effect of adding up



**Figure 3.** Predicted TPD signals in arbitrary units on the y-axis for submonolayer coverage of  $C_N$ ,  $N = 10$  (red), 12 (green), 14 (blue), and 16 (yellow) carbon rings on a graphite plane, as a function of the temperature in Kelvin on the x-axis. The temperature ramp rate was taken  $\beta = 50$  °/min. The dashed curves correspond to rings oriented perpendicularly with respect to the graphite plane and the full curves correspond to rings oriented parallel to the graphite plane. For comparison purposes the TPD signal corresponding to the  $C_{60}$  fullerene is shown in black.

**TABLE 1: Optimum Distance  $R_e$ , in Å, Binding Energy  $D_o$ , in eV, and Harmonic Vibrational Frequencies  $\nu$ , in  $10^{12}$  Hz, for  $C_N$  Carbon Rings on a Graphite Plane<sup>a</sup>**

N	$R_e$	$D_o$	$\nu$
10	3.27	0.449	5.15
12	3.24	0.511	5.02
14	3.22	0.554	4.78
16	3.21	0.584	4.54

<sup>a</sup> The rings lie parallel with respect to the graphite plane.

**TABLE 2: Optimum Distance,  $R_e$ , (in Å), Binding Energy,  $D_o$ , (in eV), and Harmonic Vibrational Frequencies,  $\nu$ , (in  $10^{12}$  Hz) for  $C_N$  Carbon Rings on a Graphite Plane<sup>a</sup>**

N	$R_e$	$D_o$	$\nu$
10	5.95	0.094	1.94
12	6.30	0.105	1.90
14	6.68	0.115	1.85
16	7.06	0.122	1.80

<sup>a</sup> The rings lie perpendicular with respect to the graphite plane.

the interaction energies of all the individual atom pairs formed with atoms of the ring and the plane, respectively. However, still the largest binding energy calculated, 0.584 eV for parallel  $C_{16}$ , is smaller than binding energy of 0.812 eV for the smallest fullerene,  $C_{60}$ , as reported by Ruoff and Hickman.<sup>6</sup>

Additionally, inspection of Tables 1 and 2 reveals that the optimum  $R_e$  equilibrium distance between the center of ring and the plane for the perpendicularly oriented rings is approximately two times the corresponding equilibrium distance found for that ring lying parallel with respect to the plane. Interestingly, the optimum distance for the parallel rings decreases as the number of carbons in the ring increases. Notice that our calculated  $R_e$  values approach smoothly to 3 Å, which corresponds to the closest distance between fullerenes and a graphite plane.<sup>6</sup>

For the perpendicular rings, the optimum value of  $R$  increases as  $N$  increases, as shown in Table 2. However, the minimum distance between an atom of the ring and the plane decreases from 3.87 Å for  $N = 10$  to 3.73 Å for  $N = 16$ . Recall that this

closest distance is still far away as compared with the closest distance of 3 Å between fullerenes and a graphite plane.

The binding energies of carbon clusters and surfaces can be probed experimentally by temperature-programmed desorption experiments, as wisely suggested by Ruoff and Hickman.<sup>6</sup> The expected signal  $S$  as a function of the temperature  $T$  for surface coverage of much less than one monolayer is

$$S(T) = A\gamma_o \exp \left[ -\frac{D_o}{kT} - \frac{AT}{\beta} E_2 \left( \frac{D_o}{kT} \right) + \frac{AT_o}{\beta} E_2 \left( \frac{D_o}{kT_o} \right) \right] \quad (8)$$

where it has been assumed a linear temperature ramp rate  $T = T_o + \beta t$ ,  $D_o$  is the binding energy of the cluster and  $A$  can be approximated by  $\nu/2\pi$ , where  $\nu$  is the vibrational frequency of the cluster in the interaction potential. These frequencies are listed in Tables 1 and 2.  $E_2$  is the exponential integral function.<sup>15</sup>

The calculated TED signals for  $C_N$ ,  $N = 10, 12, 14$ , and 16 on graphite are shown in Figure 3 for two the relative orientations of the ring with respect to the plane considered in this paper. Also, for comparison purposes the corresponding signal for the  $C_{60}$  fullerene is shown on the same plot.

We clearly observe from Figure 3, three realms of maximum desorption temperatures which correspond, respectively, (i) to the rings oriented perpendicular with respect to the plane, (ii) to the rings oriented parallel with respect to the plane and, (iii) to the fullerenes. These three regions do not overlap with each other. Hence, it is predicted that each class of adsorbate could be separated cleanly. This suggests that TPD experiments could be useful to ascertain the relative population between rings absorbed parallel and rings absorbed perpendicular to the graphite plane, under monolayer coverage conditions.

## Summary

We have presented a simplified model to account for the interaction of carbon rings with a graphite surface. This model is an extension of Ruoff and Hickman's model to study the absorption/desorption phenomena of fullerenes on graphite. One important prediction is that the binding energy of the carbon

ring to graphite surfaces depends on their relative orientation. We have seen that the preferred orientation of the ring is parallel to the surface. The binding energy is approximately five times larger than the perpendicular orientation of the ring.

The calculated temperature-programmed desorption signals of submonolayer coverages of carbon rings of different sizes from a graphite surface can be directly compared with the experimental observations and, hence, probe the validity of the underlying assumptions of the model. We have predicted that for a temperature ramp rate of 50 °/min, the perpendicularly oriented rings will desorb at around 50°, in a narrow temperature range of 40°. However, rings oriented parallel to the surface will commence to desorb at 150° and will continue until approximately 230°. This wider temperature range provides greater change for an efficient separation of the various carbon rings considered in this work. Recall that fullerenes will begin to desorb at temperatures larger than 250° for these experimental conditions. Hence, this information, which complements the earlier data reported by Ruoff and Hickman, could be useful for those who wish to extract and purify carbon clusters.

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