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Carbon clusters near the crossover to fullerene stability

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The energetic stability of structural isomers of C_{24}, C_{26}, C_{28}, and C_{32} clusters, including fullerenes, is studied using diffusion quantum Monte Carlo methods. We predict that a C_{24} isomer is the smallest stable graphitic fragment and that the smallest stable fullerenes are the C_{26} and C_{28} clusters with C_{2v} and T_d symmetry, respectively. Given suitable experimental conditions these small fullerenes should therefore be producible in abundance, facilitating production of fullerene-based solids.

Since the discovery of the C_{60} fullerene in 1985,[1] the study of carbon clusters has revealed a surprisingly rich variety of physical and chemical properties. Fullerene clusters can now be synthesized in macroscopic quantities, which may lead to the development of new and useful materials. However, despite many experimental and theoretical advances in our knowledge of the detailed energetics of these systems, our understanding of their relative stabilities and the mechanisms of their self-assembly remains incomplete.

Carbon clusters are typically formed by laser vaporization of graphite followed by an annealing process, which yields a broad spectrum of cluster sizes. The mass spectra of C_n clusters presented in Refs. 2 and 3 show a high intensity for $10 \leqslant n \leqslant 18$ and $32 \leqslant n \leqslant 60$. The lower mass range consists of clusters with n both odd and even and is believed to correspond mostly to monocyclic rings, while the higher mass range is mainly composed of clusters with n even and is believed to correspond mostly to fullerene molecules. These molecules are believed to be the lowest-energy isomers for these values of n, although small abundances of other isomers such as chains and polycyclic rings are also observed.[4]. It is now widely believed that fullerenes are formed by a ''fullerene road'' mechanism,[5,6] in which small fullerenes grow by the addition of carbon atoms. The details of this mechanism and the origin of the small fullerenes are not entirely clear, but the fullerene road mechanism is consistent with many experimental observations.[7] If the fullerene road mechanism is to explain the observed high abundances of fullerenes it must start with $n \leqslant 32$. The smallest possible fullerene, defined as a closed cage containing only pentagonal and hexagonal faces,[6] consists of 20 atoms, although this is not thought to be the most stable isomer of C_{20}.[8,9] On the other hand the smallest fullerene most commonly identified in high abundance in laser vaporization and annealing experiments is the C_{32} fullerene, although there is also evidence for the C_{30} fullerene.[2,4]. It therefore seems probable that the crossover to fullerene stability occurs in the range $20 < n \leqslant 30$.

The energetic ordering of clusters in the range $18 < n < 32$ is far from understood. Our main aim is to establish sufficient understanding of the ordering of the even numbered clusters in this range to allow us to answer the question ''which is the smallest stable fullerene?'' This question is both interesting and contentious due to the sensitivity of cluster formation to experimental conditions and the challenges posed to theoretical methods. Understanding the energetics of clusters near the crossover to fullerene stability could shed light on the start of the fullerene road and indicate limitations on which fullerene materials can be produced. For example, whether or not one could in practice form the C_{28} solid which has been proposed and investigated theoretically[10–12] depends critically on the stability of individual clusters of this size. Furthermore, a recent theoretical investigation[12] suggested that C_{28}-based solids are potentially superconducting at room temperatures.

To investigate these issues of stability we have studied the energetics of C_{24}, C_{26}, C_{28}, and C_{32} clusters using highly accurate quantum Monte Carlo methods. For each cluster size we have calculated the energetic ordering of the isomers and identified the most stable isomer. For clusters containing between 24 and 32 atoms, three classes of isomer are energetically competitive: fullerenes, planar or near-planar sheets and bowls, and monocyclic rings. Even for quite small clusters the number of low-energy candidate structures can be large, which precludes exhaustive theoretical searches with highly accurate methods. In practice, a hierarchy of methods of increasing accuracy and computational cost must be used. The initial step is to select candidate structural isomers via empirical methods based on bond counting and geometric ''rules'' such as minimizing the number of adjacent pentagons.[13] Quantum mechanical calculations based on tight-binding[14] and density functional theory (DFT) methods[15–18] can then be used to refine the selection. To finally establish the energetic ordering of different isomers, highly accurate calculations must be performed. For this purpose we have used the diffusion quantum Monte Carlo (DMC) method.[19,20]

Carbon clusters are very challenging to model accurately due to the wide range of geometries and the occurrence of single, double, and triple bonds. The need for highly accurate calculations with a sophisticated treatment of electron correlation has been clearly illustrated by several previous studies. The DMC study of C_{20} by Grossman *et al.*[8] showed that the fullerene is not energetically stable with respect to other C_{20} isomers, contradicting the predictions of earlier DFT calculations. Subsequently, high-order quantum chemical calculations of the C_{20} isomers[9] confirmed the DMC results. The DMC method gives an accurate treatment of electron correlation which, combined with an absence of basis set error, a favorable scaling with system size, and suitability for parallel computation, renders it ideal for these studies. DMC calculations have reproduced experimental binding energies of small hydrocarbons to within 1%.[8] As a further demonstration of the accuracy of the DMC technique for carbon sys-

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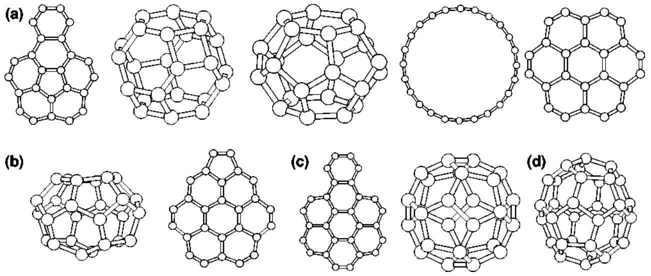

FIG. 1. The structures of the C_n clusters. (a) C_{24} one-pentagon bowl, O_h cage, D_6 fullerene, ring, and sheet, (b) C_{26} fullerene and one-pentagon sheet, (c) C_{28} sheet and fullerene, (d) C_{32} fullerene. The $n=26$, 28, and 32 rings are not shown.

tems we have calculated the cohesive energy of bulk diamond, obtaining 7.46(1) eV per atom, which is in very good agreement with the experimental value of 7.37 eV.

In the DMC method,[19,20] the imaginary time Schrödinger equation is used to evolve an ensemble of electronic configurations toward the ground state. The ''fixed node approximation'' is central to this method; the nodal surface of the exact fermionic wave function is approximated by that of a guiding wave function. We used Slater-Jastrow guiding wave functions consisting of the product of a sum of Slater determinants of single-particle orbitals obtained from CRYSTAL95 (Ref. 21) or GAUSSIAN94 (Ref. 22) with a Jastrow correlation factor.[23] Core electrons were modeled by an accurate norm-conserving pseudopotential,[24] and the nonlocal energy was evaluated stochastically within the locality approximation.[25] Optimized uncontracted valence Gaussian basis sets of four *s*, four *p*, and one *d* function were used to represent the single-particle orbitals, although we should emphasise that the DMC results are not limited by this basis set. Jastrow factors containing up to 80 parameters were optimized using efficient variance minimization techniques.[26,27]

The initial selection of candidate structures was made after studying the results of a number of DFT calculations in the literature.[28,15,16,29,18] Fully relaxed geometries were obtained by performing all-electron calculations[22] using the B3LYP hybrid density functional[30] and Dunning's cc-pVDZ basis set,[31] which has been found to be an accurate and affordable combination.[29,15,16] The final structures obtained are illustrated in Fig. 1. Although it would be desirable to optimize the geometries self-consistently using the DMC method, interatomic force calculations within DMC are not currently practicable for systems with many inequivalent atoms. Instead, we assess the sensitivity of the total energies to the geometries using the fully relaxed ring and D_6 fullerene isomers of C_{24} (see Fig. 1) obtained with the B3LYP hybrid density functional[30] and the BLYP generalized gradient approximation density functional.[32] These functionals give significantly different energetic orderings, but the differences between the geometries are small—less than 0.03 Å in bond lengths and 0.4° in bond angles. The maximum change in the energy of the ring and fullerene isomers calculated with either functional due to using the two different relaxed geometries was 0.14 eV. Moreover, the maximum change in the energy difference between the ring and fullerene isomers with geometries obtained from one functional but calculating the energy with the other was only 0.03 eV. These changes are small and do not affect the conclusions we draw.

We considered the following isomers of C_{24}, as depicted in Fig. 1: a polyacetylenic monocyclic ring, a flat graphitic sheet, a bowl-shaped structure with one pentagon, a caged structure with a mixture of square, pentagonal, and hexagonal faces having O_h symmetry, and a fullerene of D_6 symmetry. Other candidate structures, such as bicyclic rings and a three-pentagon bowl, were excluded on the grounds that DFT calculations using several different functionals have shown them to be significantly higher in energy.[28,29,18] Our DMC calculations predict the graphitic sheet to be lowest in energy, being 1.3(2) eV more stable than the D_6 fullerene, which was almost isoenergetic with the ring structure. The O_h cage was 0.7(2) eV higher in energy than the fullerene and the bowl was higher still by 0.5(2) eV. The low energy of the C_{24} graphitic sheet is expected because the structure is compact and accommodates a large number (seven) of hexagonal rings without significant strain. Smaller graphitic sheets are high in energy[18] and therefore we predict that the C_{24} sheet is the smallest stable graphitic fragment.

Three isomers of C_{26} were considered: a cumulenic monocyclic ring, a graphitic sheet with one pentagon, and a fullerene of C_{2v} symmetry (see Fig. 1). Few studies of the C_{26} fullerene have been made, in part due to the large strains evident in its structure.[6] Recently Torelli and Mitáš have demonstrated the importance of using multideterminant guiding wave functions to describe the aromatic nature of $n=4N+2$ carbon rings[33] with $N=1-4$. This effect is substantial for small rings, but decreases for larger *N*. We have tested this for the C_{26} ring ($N=6$), using a 43-determinant guiding wave function obtained from a configuration-interaction (CI) singles-doubles calculation. The multideterminant wave function gave a slightly lower DMC energy than the single-determinant wave function, by 0.5(5) eV per cluster, confirming that the CI wave function has a better nodal surface than the Hartree-Fock (HF) wave function. The ring and sheetlike isomers are close in energy, but the fullerene is 2.2(4) eV below these isomers and is therefore predicted to be the most stable C_{26} isomer and the smallest stable fullerene.

Three C_{28} isomers were investigated: a monocyclic ring, a graphitic sheet, and a fullerene of T_d symmetry (see Fig. 1). Other bowl and sheetlike structures were excluded on energetic grounds.[16,18] Spin-polarized DFT and HF calculations show the ground state of the T_d symmetry fullerene to be a spin-polarized $^5A_2$ state.[16,17] We have performed both spin-polarized and non-spin-polarized DMC calculations for this fullerene and have found that in either case it is more stable than the sheet and ring isomers. The spin-polarized fullerene is the more stable, and we find it to be 4.2(3) eV lower in energy than the ring and 3.2(3) eV lower than the sheet. The spin-polarized fullerene has four unpaired electrons and is therefore highly reactive. This property has already been exploited in atom trapping experiments in which fullerenes containing single four-valent atoms, $C_{28}M$, have been prepared by laser vaporization of a graphite-MO_2 ($M=$Ti, Zr, Hf, or U) composite rod.[10] Our prediction that the fullerene is the most stable isomer of C_{28} indicates that isolated fullerenes might be produced, facilitating the production of C_{28} fullerene solids.[10–12] (A C_{36} fullerene solid has been reported.[34])

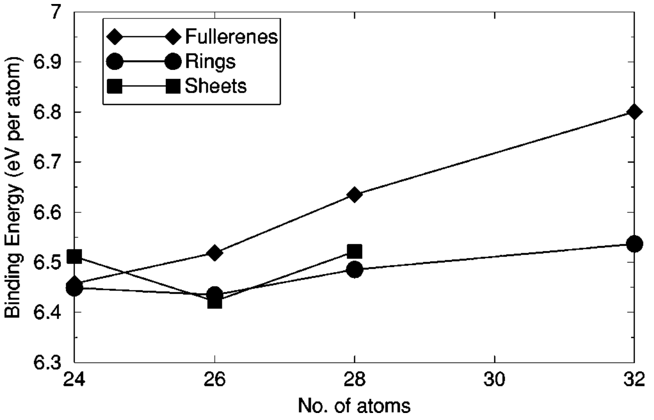

FIG. 2. The DMC binding energies per atom of the lowest-energy ring, sheet/bowl, and fullerene C_n structures. The lines drawn are for guidance only. The statistical error bars are smaller than the symbols.

Our DMC calculations for the C_{32} monocyclic ring and fullerene show that the fullerene is 8.4(4) eV per molecule lower in energy, which is consistent with the observation of a large abundance of C_{32} fullerenes in a recent cluster experiment.[2]

In Fig. 2 we plot the DMC binding energies per atom of the lowest-energy ring, sheet/bowl, and fullerene structures. The binding energies per atom of the rings and fullerenes gradually increase with cluster size due to the reduction in strain energy. However, the binding energy per atom rises much more steeply with cluster size for fullerenes than for rings for these cluster sizes due to the large amount of strain present in the smaller fullerenes. The DMC binding energy per atom of the C_{32} fullerene is approximately 1 eV per atom less than the experimental binding energy of C_{60}, so for larger cluster sizes the fullerene binding energy curve flattens off considerably. The fullerene and ring curves in Fig. 2 cross at C_{24}; below this critical value rings are predicted to be more stable than fullerenes and above it fullerenes are predicted to be more stable. This is consistent with the DMC calculations of Grossman *et al.*,[8] who found the C_{20} ring to be more stable than the fullerene.

The binding energies per atom of the sheet/bowl structures do not vary so smoothly with cluster size because of the strong dependence of the energy on the compactness of the structure and the number of high-energy pentagonal rings. For example, the sheet structure of C_{24} is particularly stable because it is a compact arrangement of hexagonal rings, whereas the C_{26} sheet is less compact and contains a pentagon. Interestingly, our results show that a sheet structure is most stable for clusters with 24 atoms and the DMC calculations of Grossman *et al.*[8] showed that a bowl structure was most stable for 20 atoms. Our prediction of a small window of stability for sheet/bowl structures is most intriguing, especially as neither of these sheet/bowl structures has been identified in experimental studies.

The final test of our predictions must lie with experiment. It is clear that the actual abundances of different clusters depend sensitively on experimental conditions. Analysis of the stability of clusters against fragmentation, growth, and other chemical reactions is complicated. One issue is that the clusters are formed at temperatures of order 1000 K and therefore the vibrational contributions to the free energy can be significant. Fortunately, a simple picture emerges from computations of vibrational properties.[28,29,16] Fullerenes are relatively rigid and have higher vibrational free energies than rings, which have many low-lying vibrational modes. Vibrational effects therefore tend to favor the ring isomers at high temperatures. These effects and energetic barriers to formation might explain the absence in experimental observations of the sheet/bowl structures that have been predicted to be stable at zero temperature. For larger clusters, however, according to our DMC calculations the C_{26} and C_{28} fullerenes are several eV per cluster lower in energy than the other isomers, so that significant amounts of fullerene could exist at the temperatures of formation.

Were thermodynamic stability alone to determine which cluster sizes were observed then only the largest fullerenes would ever be observed. There is overwhelming evidence that thermodynamic stability to rearrangements of clusters of a particular size is important in determining which isomers are observed. This is the only conclusion consistent with the observation of rings in the range $10\leqslant n\leqslant 18$ and fullerenes for $n\geqslant 32$. For the intermediate range $18<n<32$, in which little material was found in the mass spectra of Refs. 2 and 3, we find that the energy differences between the competing structures are significantly smaller. To develop a full understanding of the behavior in the intermediate range it is therefore even more important to calculate the relative energies of the isomers using accurate methods such as DMC.

In conclusion, we have clarified the energetic ordering of C_n (n even) isomers near the crossover to fullerene stability. Our DMC calculations show the lowest-energy isomer of C_{24} to be a graphitic sheet, which is expected to be the smallest stable graphitic fragment. We predict that the smallest energetically stable fullerenes are the C_{2v} symmetry C_{26} cluster and the reactive spin-polarized $^5A_2$ state of the T_d symmetry C_{28} cluster. These predictions lend weight to proposals that a superconducting C_{28}-based solid[10–12] could be synthesized by surface deposition of C_{28} fullerenes. We call for experimental investigation of these materials, and their potential superconducting properties.

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