Precursors to C_{60} fullerene formation

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It is shown that the free energy of C_{20} clusters favors a transformation from a closed cage (fullerene) structure at low temperatures to a more open corrannulene structure and then to a ring structure as the temperature is increased. The corrannulene structure can be thought of as a fragment of C_{60} and is an efficient precursor to its formation. These results are applicable to other carbon clusters of similar sizes and are consistent with the experimental findings that high temperatures are necessary for the formation of substantial quantities of C_{60}.

Since the C_{60} fullerene was first discovered[1] and made in quantity,[2] its structure and many of its properties have been studied intensively. In spite of the great effort devoted to this system, the precise mechanism of C_{60} formation is not yet understood. In this paper, we present the first calculation of the free energy of likely precursors to the C_{60} structure at different temperatures, using state of the art techniques. The results demonstrate that for small clusters undergoing fusion at high temperatures, the gain in entropy is likely to stabilize more open structures with respect to the energetically favored closed cage isomers.

We focus our investigation on C_{20} isomers, specifically the C_{20} corrannulene structure,[3] which is a perfect precursor to fullerenes, and on ring and chain structures, which are the preferred structures of small carbon clusters. A comparison of these structures to the other C_{20} isomers, based on intuitive arguments[4] and calculations,[5(a),6] shows that the case or fullerene structure of C_{20}, a dodecahedron, is energetically most stable. Although the yield of the C_{60} fullerene can be very high, no substantial quantities of C_{20} have yet been detected. Our quantum molecular dynamics and semiemperical calculations show that a substantial fraction of the cages transforms to more open structures at high temperatures, which facilitates a high-yield production of C_{60}.

Quantum molecular-dynamics simulations use the well-established Car-Parrinello (CP) method.[7] This method couples the motion of atomic nuclei to the electron system which is described within the density-functional formalism. The electronic wave functions are expanded in a plane-wave basis, and the carbon atom cores are represented by the same soft-core pseudopotential as in our previous work.[8] Tests have shown that this method reproduces the structural properties of diamond and graphite, as well as the results of a previous calculation for C_4. The clusters corresponding to each of the configurations are placed in a periodically repeated supercell. In order to minimize errors in the relative energies, a single simple cubic cell with cube side of 26 a.u. was used in all the calculations except those involving the linear chain. A minimum distance of 5.0 Å is maintained be-

tween neighboring clusters to prevent interactions. Plane waves with kinetic energies of up to 35 Ry are included in the structure optimizations of the various clusters. The semiempirical calculations use tight-binding parameters of Refs. 5(a) and 5(b), which were fitted to reproduce the electronic and bulk properties of graphite, diamond, the C_2 molecule, and the well-known AM1 parameters,[5(c)] which were fitted to molecules.

The images of the relaxed configurations of the basic structures of the C_{20} cluster are shown in Fig. 1. The C_{20}
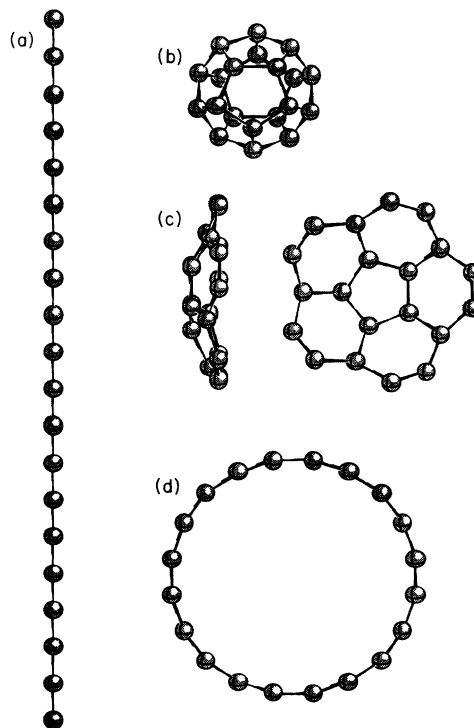

FIG. 1. The four C_{20} structures in their minimum energy configurations: structure (a) the chain; (b) the cage; (c) the cap (side and front view); and (d) the ring.

fullerene (cage) consists of twelve fivefold rings forming a dodecahedron. The corrannulene (cap) consists of a five-fold ring surrounded by five sixfold rings. It is curved, resembling a fragment of C_{60}, and has been hypothesized to be the initial building block for the growth of spiral carbon cluster cages.[3] Other possible structures of C_{20} are linear chains and monocyclic rings, which are the preferred configurations for small carbon clusters.[9] The relaxed cage has bond lengths between 1.42 and 1.49 Å. The relaxed cap has bond lengths between 1.40 and 1.45 Å, and the outermost bonds have the length of 1.25 Å. The relaxed ring is planar and has bond lengths alternating between 1.33 and 1.25 Å. The relaxed chain is linear and has bond lengths ranging from 1.26 Å in the middle to 1.31 Å at the ends.

The cage structure is found to be the minimum energy configuration, but the cap and the ring are only 0.75 and 2.65 eV higher in energy. The chain is substantially higher in energy: Our somewhat more approximate calculations find it to be 10 eV higher.[10] Since the difference between the cage and the cap structure is only 0.04 eV per atom and entropic effects favor more open structures, the ordering between these structures will change at sufficiently high temperatures. However, for an evaluation of the temperature effects on the preferred structure of C_{20} and thereby on the formation of C_{60}, a quantitative estimate of the free-energy differences is needed.

The free energy of an ensemble of identical clusters in equilibrium with a surrounding carrier gas of temperature T can be written as

$$F = -kT \ln Z = -kT(\ln Z_s + \ln Z_r + \ln Z_e + \ln Z_t + \ln Z_v).$$

(1)

Here, the total partition function Z has been decomposed into structural, rotational, electronic, translational, and vibrational components, assuming that coupling between these degrees of freedom is small. The structural partition function is obtained from the QMD calculations and Z_r is computed from the QMD-optimized geometries. Since the gaps above the highest occupied orbital in all the clusters are large, the electronic entropies are small and can be neglected. The translational contributions are independent of the C_{20} isomer structures and can also be neglected. The only challenging aspect of the calculation of the free-energy differences is thus the evaluation of the vibrational partition function. We treat the vibrational degrees of freedom in the harmonic approximation, which is justified in the temperature range of interest, i.e., well below the melting point. Since the evaluation of all the vibrational frequencies of the isomers by QMD methods would be prohibitively expensive, we use the substantially more economical semiempirical methods to compute them.[11]

Figure 2 shows the free-energy differences between the four structures relatively to the cage structure as a function of temperature, computed using the AM1 Hamiltonian. At $T = 0$ K, the closed cage is the preferred geometry, followed by the cap, the ring, and the chain. As the temperature is increased, however, the free energy of the cap structure becomes lower than that of the cage. This is
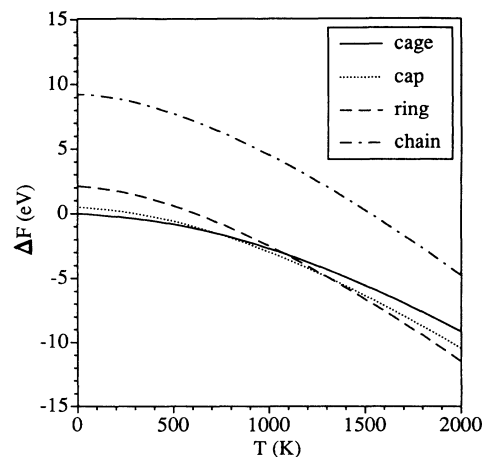

FIG. 2. Free-energy difference ΔF, with respect to the cage at 0 K, for the four structures as a function of temperature T. See text.

caused by the larger entropy of the more "floppy" structure. Thus the likelihood for the formation of the cap structure increases with temperature. Since the cap arrangement of twenty atoms is contained in the C_{60} structure, it could be the seed upon which the other fragments attach to form the complete closed C_{60} shell. Indeed, a recent "hot shrinking sphere" simulation of C_{60} formation showed that fivefold rings are the first to form out of the carbon vapor.[6] If C_{20} or a larger carbon cluster cap structure is a precursor to C_{60} formation, then ligands attached to the concave side of the cap might survive the formation of a fullerene. The introduction of a suitable ligand during the formation process might then lead to trapping of atoms or small molecules inside large fullerenes.

Further increase in temperature lowers the free energy of the ring below that of the cage and the cap. This is expected, since the ring structure allows for a number of very-low-frequency "flexing" modes, which have large entropies. These low-frequency modes are sensitive functions of the semiempirical parameters and the precise temperatures at which the crossings in Fig. 2 occur depend on the choice of the semiempirical Hamiltonian. The presence of low-frequency modes indicates also that anharmonic effects will be important in determining the lowest free-energy structues even at moderate temperatures. Kinetic routes to the various structures will also have an effect on the relative abundance of the isomers. Nevertheless, the general trend of progressing towards more open structures with increasing temperature is very likely.

A model of the formation of C_{60} and other cage structures postulates that the stability of intermediate-size carbon clusters is determined by maximizing the number of nonadjacent pentagons in curved graphitic flakes.[12] A "no adjacent pentagons" rule would then naturally explain the formation of C_{60} as the first flake which can close upon itself without violating the rule. The calculations presented here, however, show that the structure of C_{20} with the lowest internal energy is a closed cage, even though it consists entirely of adjacent pentagonal rings.

Therefore, if this cluster is able to assume its closed cage structure, the formation of C_{60} would be inhibited, since a closed cage presents steric hindrances for insertion of atoms into its skeleton. Clearly, considerations based on the internal energy alone cannot explain the lack of significant amounts of C_{20} fullerenes in graphite arc or laser vaporization sources, or the high yield of C_{60}.

Another model of C_{60} formation[13] assumes that C_{60} and other high abundance fullerenes form primarily by repeated fusion of clusters of the same size. Further, purely geometrical analysis led the authors to conclude that this dominant cluster is C_{10} and that it consists of two fused sixfold rings.[13] However, several calculations, both semiempirical[9] and *ab initio*,[14] have established that the lowest-energy structure of C_{10} is a monocyclic ring. The experimental results[15] show magic number peaks of the type C_{4n+3}, exactly as expected for monocyclic rings.[9,16] If the structure of C_{10} is different from the one proposed in Ref. 13, the growth sequences suggested in that reference would no longer lead to C_{60}.

Our proposed mechanism is applicable to other clusters of similar sizes. Such clusters should prefer closed cages at $T = 0$ K, but convert to open flakes at higher temperatures. For C_{60}, C_{70}, and other "perfect" fullerenes, the energetic preference for the closed cage structure is so large that high temperatures alone are not enough to crack them open. Since the closed cages should be less reactive than the open structures, in particular towards larger clusters, they have a greater survival rate and therefore a higher abundance, as observed experimentally. Smoluchowski's aggregation equations for clusters show that the peak in cluster distribution depends on the residence time and annealing conditions.[9] Consequently, further increases in the yield of specific clusters can be achieved by optimizing the residence time and/or cluster density. This explains the ability of optimizing the experimental conditions for an increased yield of C_{60}, C_{70}, or C_{84}, although the yield of C_{60} is always substantial.

In summary, we have shown that at $T = 0$ K C_{20} prefers a cage structure. At higher temperatures, however, a substantial fraction of C_{20} prefers open structures, such as a cap; the latter lends itself more easily to the C_{60} formation process. This temperature dependence has been observed in previous experimental studies. The above mechanism should also be applicable to other clusters of similar sizes. If fullerene formation proceeds via the cap precursor, ligands attached to the concave side of the cap structure may survive fullerene formation and thus become trapped inside.

Note added in proof. The interesting work of von Helden *et al.*[17] shows that carbon clusters form in several structures following laser vaporization. In their experiment, supersonic expansion directly follows laser vaporization and only clusters which remain charged during the entire formation process are detected. Under these conditions, the abundance of C_{60} is not significantly larger than that of other clusters of similar sizes. For C_{20}, the results indicate the presence of rings, which may be due to the formation temperature, kinetic conditions or charge state and charge transfer between the clusters. Preliminary QMD calculations indicate that the removal of one electron significantly affects the relative energetics of the competing cluster structures.

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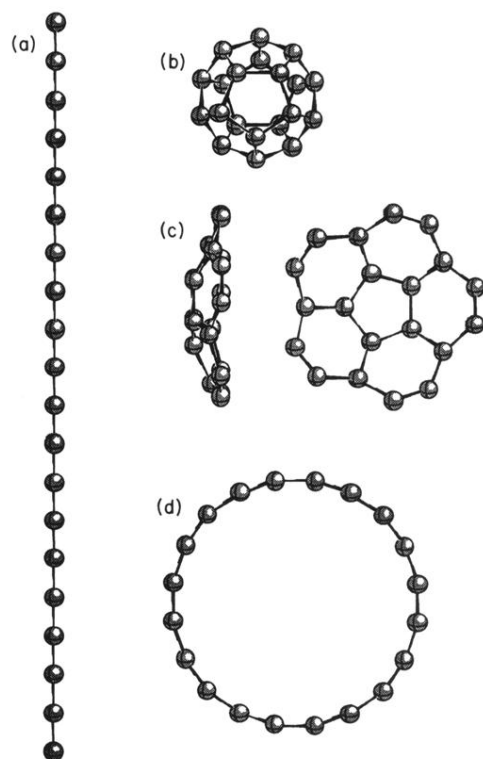
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