Microscopic mechanism of fullerene fusion

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Combining total energy calculations with a search of phase space, we investigate the microscopic fusion mechanism of C_{60} fullerenes. We find that the $(2+2)$ cycloaddition reaction, a necessary precursor for fullerene fusion, may be accelerated inside a nanotube. Fusion occurs along the minimum energy path as a finite sequence of Stone-Wales transformations, determined by a graphical search program. Search of the phase space using the "string method" indicates that Stone-Wales transformations are multistep processes, and provides detailed information about the transition states and activation barriers associated with fusion.

The discovery of fullerenes[1] and nanotubes[2] has ignited strong interest in these and related carbon nanostructures. Due to the unusual stability of the graphitic sp^2 bond, large-scale structural changes in bulk fullerene crystals occur only under extremely high pressures and temperatures.[3,4] On the other hand, fullerenes in nanotube peapods[5] have been observed to fuse[6,7] at relatively low temperatures near 1100 °C, significantly below the decomposition temperature of fullerenes[8] or graphite[9] near 4000 °C. No information is available about the detailed fusion process except the obvious conclusion that strong sp^2 bonds should not be broken during structural rearrangements leading to fusion. In view of the fact that even minor structural changes in carbon nanostructures may modify significantly their physical properties, including magnetism,[10,11] there is additional interest in understanding fusion as a way to control large-scale structural transformations.

Here we study the microscopic fusion mechanism of fullerenes. We show that large-scale structural changes, including fusion, can be achieved by a finite sequence of generalized Stone-Wales transformations, which involve only bond rotations and avoid bond breaking. Using a graphical search program,[12] we determine the optimum reaction pathway for thermal fusion of fullerenes. Search of the phase space by the "string method" provides detailed information about the optimum pathway, including the identification of activation barriers and transition-state geometries. We find the fusion process to be exothermic. The fusion dynamics is fast in spite of the formidable total activation barrier close to 5 eV, associated with each Stone-Wales transformation. These bond rotations turn out to be multistep processes with lower individual activation barriers.

We calculate the total energy of the fullerene system using an electronic Hamiltonian that had been applied successfully to describe the formation of peapods,[13] multiwall nanotubes,[14] the dynamics of the "bucky shuttle,"[15] and the melting of fullerenes.[8] Our numerical results are compared to those of *ab initio* density functional calculations, which use a numerical basis to represent localized atomic orbitals,[16] and which have been applied successfully to nanotubes and

fullerenes.[17] Structural optimization is performed using the conjugate gradient technique. Our total energy formalism describes accurately not only the covalent bonding within the sp^2 bonded fullerenes, but also the weak interaction between fullerenes. We find it crucial to use an electronic Hamiltonian in this study, since analytical bond-order potentials do not describe the rehybridization during the fusion process with a sufficient precision.

The fusion of two C_{60} molecules to a C_{120} capsule, which has been observed in peapods,[6,7] is driven by the energy gain associated with reducing the local curvature in the system. Still, this reaction involves a large-scale morphological change and will only occur, if the required activation barrier is small.

A previous study,[18] based on minimizing the classical action, suggests that the fusion reaction should be a multistep process. Due to the computational limitations associated with the formidable task to find a contiguous minimum-energy path in the 360-dimensional configurational space of the system, and to anticipate the optimum one-to-one atomic mapping between the initial and the final structure, we expect the "true" activation barrier for this reaction to lie below the relatively high postulated value of ≈ 8 eV. Combining a very similar total energy functional with a method to identify all intermediate steps, we identify in the following an alternate reaction path with lower activation barriers.

It appears that the most likely fusion path may involve a sequence of bond rotations, called generalized Stone-Wales (GSW) transformations. GSW transformations are known to require much lower activation energies than processes involving bond breaking, and have been studied extensively in sp^2 bonded carbon structures.[12,19,20] A possible GSW pathway for fusion has been suggested based on a "qualitative reasoning assisted search" for structures along the minimum-energy path.[21] The initial step in that study, however, is a reaction between two pentagons facing each other, which is energetically unaccessible.

In order to obtain microscopic insight into the fusion reaction, avoiding the above shortcomings, we investigated the optimum reaction path for the the $2C_{60} \rightarrow C_{120}$ fusion. It is
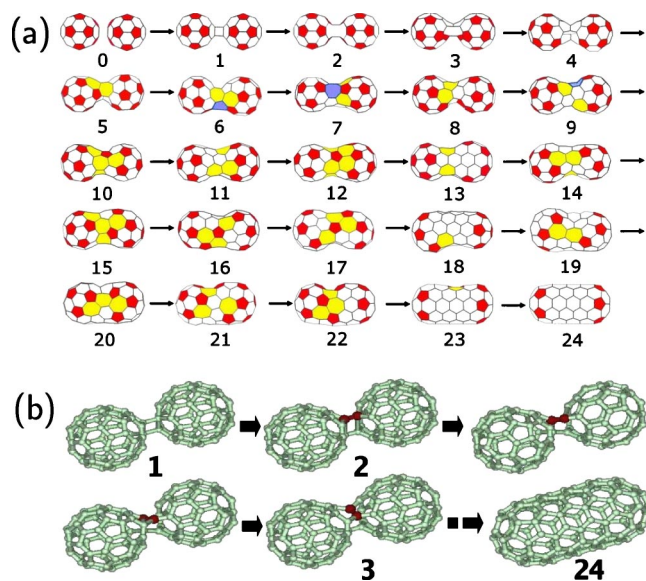
FIG. 1. (Color online) Microscopic mechanism of fullerene fusion in peapods. (a) Optimum pathway for the $2C_{60} \rightarrow C_{120}$ fusion reaction, involving the smallest number of generalized Stone-Wales bond rotations, determined by a graphical search of all possible bond rotation sequences (Ref. 24). Polygons other than hexagons are emphasized by color and shading. (b) Snapshots of the optimized initial and final structures, and the metastable structures "2" and "3," depicted in (a). Also shown are two intermediate structures along the optimum fusion pathway between "2" and "3," resulting from the phase space search by the "string method." The bond involved in the $2 \rightarrow 3$ Stone-Wales transformation is emphasized by dark color.
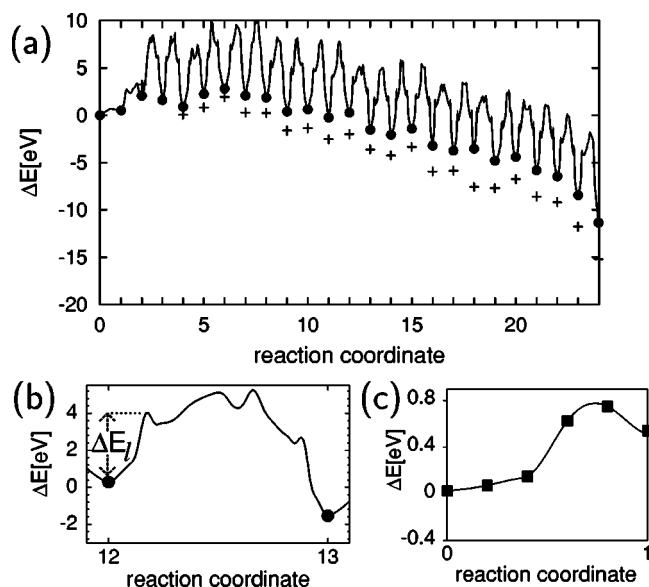

FIG. 2. Energetics of the fullerene fusion in peapods. (a) Energy change along the optimum reaction path, given by the solid line (Ref. 38). Energy results for the 25 intermediate structures, shown in Fig. 1, based on our total energy functional (●), are compared to *ab initio* density functional results (+). The contiguous minimum energy path in configurational space was identified using a "string" technique. (b) Details of the energy change along the optimum path between structures "12" and "13" of Fig. 1, showing several local minima and implying a multistep nature of this Stone-Wales transformation. The activation barrier limiting the reaction rate is denoted by ΔE_l. (c) Energetics of the $(2+2)$ cycloaddition reaction, corresponding to the $0 \rightarrow 1$ transition in Fig. 1(a), which is a necessary prerequisite for the fusion process.

well established that polymerization[22] and subsequent fusion[23–25] of fullerenes starts by the $(2+2)$ cycloaddition reaction. This reaction, depicted as the $0 \rightarrow 1$ transition in Fig. 1(a), requires two "double bonds," which connect adjacent hexagons in the C_{60} molecule, to face each other at the contact point of adjacent fullerenes.

With the $(2+2)$ cycloaddition reaction completed, we investigated the possibility to complete the $2C_{60} \rightarrow C_{120}$ fusion by generalized Stone-Wales transformations only. We searched all topologically possible pathways for the reaction with the aid of a graphical search program.[12,24] Among these, we identified the shortest pathway, which is likely associated with the fastest fusion mechanism. This pathway involves only 23 GSW transformations and is depicted in Fig. 1(a). Tracing the atomic positions during this structural rearrangement, we found that the diffusion range of individual carbon atoms is limited to about three atomic bond lengths in the structure. Snapshots of intermediate state geometries along the optimum fusion pathway are shown in Fig. 1(b).

The energetics of the $2C_{60} \rightarrow C_{120}$ fusion process along the optimum path is depicted in Fig. 2(a). The energy results for the optimized metastable states of Fig. 1(a) are given by the data points. We conclude that the *ab initio* density functional and our parametrized total energy functional give consistent results for the relative energies of the intermediate states,[26] and also for the large net energy gain of ≈ 13 eV associated with the fusion.

We employed the recently developed "string" method[27,28] to efficiently determine the detailed minimum energy path, including identifying the reaction barriers of individual GSW transformations between the 24 intermediate states. This method represents the reaction pathway connecting the initial and final 120-atom geometry in the 360-dimensional atomic configuration space by a string line. The string is initially subdivided into finite segments of equal length, connecting structural replicas. For an optimum path, we require that the atomic force acting on each replica has a vanishing component normal to the string. We employ 60–100 replicas for each GSW step and relax the atomic positions, until the normal component of the atomic force becomes less than 0.05 eV/Å in magnitude.

Close inspection of the reaction energy along the contiguous optimum fusion path in Fig. 2(a) indicates a sequence of 23 activated processes connecting the 24 metastable states. We find the activation energy barriers $\Delta E_{GSW} \approx 5$ eV of these GSW transformations to be significantly lower than in graphite,[26] as expected for Stone-Wales processes in nonplanar structures due to the deviation from sp^2 bonding. In presence of extra carbon atoms, the activation barriers for GSW transformations may be lowered further to below 4 eV by autocatalytic reactions.[29,30] Also, under electron irradiation, this process can proceed relatively fast in view of the high rate of subthreshold energy transfer to the structure.[31] In

extended fullerene systems, moreover, the energy release during the fusion process should heat up the structure locally, thus further promoting activated processes in the local vicinity.

Maybe the most significant finding of our study is the occurrence of multiple shallow local energy minima in the course of each GSW transformation. Details for the energy landscape, associated with the $12 \rightarrow 13$ reaction, are shown in Fig. 2(b). This implies that GSW transformations are multistep rather than single-step[32] or two-step[33] processes, as postulated earlier. The local minima originate from global stress release during the bond rotation, which can be viewed as breaking two C-C bonds at the same time as new bonds are being formed. Performing unconstrained conjugate gradient structure optimization at the local extrema, we confirmed the presence of local energy minima and were able to identify the geometry of the transition states in-between. We notice that GSW transformations are multistep processes only in nonplanar structures, as no such local minima occur during Stone-Wales transformations in a graphene layer due to the absence of tensile stress in that system.

To estimate the overall reaction time at the temperature of 1100 °C, where the onset of fusion has been observed,[6,7] we considered the fusion process as a sequence of 23 GSW transformations. Assuming the attempt frequency of 3×10^{13} Hz for the GSW transfomations[30] and a limiting activation barrier $\Delta E_l = 4.5$ eV in the Arrhenius formula,[34] we find that the fusion reaction should be completed in 7 h. Reduction of the activation barrier by 0.5 eV should reduce the total fusion time to 6 min. In view of the fact that fusion is generally more complex than an optimum sequence of GSW transformations, these values agree well with the observed fusion time of several hours.[6,7]

In spite of its relatively low activation barrier depicted in Fig. 2(c), the initial $(2+2)$ cycloaddition reaction between the structures "0" and "1" may play an important, possibly even the rate-limiting role in the fusion process. Fusion can only be initiated in the optimum geometry, where two double bonds in adjacent fullerenes face each other at the contact point. The probability of this configuration appears as a factor in the attempt frequency ν of the $0 \rightarrow 1$ reaction in the Arrhenius formula[34] and thus reduce the reaction rate, since the low activation barrier of ≈ 0.7 eV only applies to attempts with the optimum fullerene orientation.

At low temperatures, polygons rather than double bonds should preferentially face each other in adjacent fullerenes, effectively preventing the fusion. Only at high enough temperatures, when unhindered fullerene rotation is activated,[35] will the probability of double bonds facing each other increase, while each fullerene probes the configurational space. At that moment, the $(2+2)$ cycloaddition reaction should stop the rotation,[36] and may initiate fusion.

To estimate the probability of the configuration required for the $(2+2)$ cycloaddition to occur, we first consider the phase space describing the motion of two rigid fullerenes at constant equilibrium distance (structure "0" in Fig. 1), which are freely rotating in space. The eight-dimensional configurational space, spanned by the three Euler angles defining the orientation of each fullerene and the two-dimensional vector defining the orientation of the interfullerene connection, is

explored uniformly by the rotating fullerenes. Next, we assume that the difference between a "correct" and an "incorrect" fullerene alignment corresponds to a misorientation exceeding $\Delta\varphi \gtrsim 1°$ in any dimension, which naturally introduces a grain size for the discretized configurational space.

In view of the fact that each fullerene has thirty double bonds, each of which can have two orientations, 3600 out of 3×10^{19} cells in this space represent favorable configurations. Assuming that the configurational space exploration by the freely rotating fullerenes occurs at random in-between two cycloaddition attempts, separated by the period of the inter-fullerene vibration, the probability of finding an optimum configuration is $\approx 10^{-14}$. Using $\nu = 7 \times 10^{12}$ Hz for the interfullerene vibration frequency,[37] the $(2+2)$ cycloaddition step with an activation barrier $\Delta E = 0.725$ eV should occur on the time scale of one week at 1100 °C, significantly longer than the time frame of a GSW transformation. Thus, this step should be rate limiting in a close-packed three-dimensional C_{60} system, which—while molten at this temperature—could be prevented from evaporation by external pressure.

Restricting the configurational space to one dimension, which occurs when chains of fullerenes are packed in peapods, increases the fusion probability substantially. The crucial role played by the enclosing nanotube is to keep adjacent fullerenes in place long enough for them to probe the configurational space at close range. Since the vector connecting adjacent fullerenes coincides with the nanotube axis, the possibility of noncentral collisions is eliminated, the dimensionality of the configurational space is reduced to six, and the number of discrete cells to only 5×10^{14}. This increases the probability of the optimum fullerene orientation by five orders of magnitude, and reduces the reaction time of the $(2+2)$ cycloaddition step to only 7 s at 1100 °C. We conclude that fusion should occur more easily, when fullerenes are packed in peapods, than in three-dimensional bulk C_{60}.

In a three-dimensional C_{60} system, the fusion rate should further be reduced due to the fact, that more than one GSW transformation involving the same fullerene may occur simultaneously. Each C_{60} molecule has initially the ability to form at least four initial connections with neighboring fullerenes by the $(2+2)$ cycloaddition reaction.[4] Considering the finite size of the C_{60} molecule, GSW transformations associated with one fusion reaction are likely to interfere with transformation necessary for a separate fusion reaction, occurring concurrently. Due to resulting frustration, the activation barriers of individual GSW transformations could increase significantly, possibly even stopping the fusion. Since this effect is less severe in lower dimensions, the reduction of the overall fusion rate associated with concurring binary fusion reactions should be much less important in one-dimensional peapods than in bulk C_{60}.

In summary, we combined total energy calculations with a search of phase space to investigate the microscopic fusion mechanism of C_{60} fullerenes. We found that the $(2+2)$ cycloaddition reaction, a necessary precursor for fullerene fusion, may be accelerated inside a nanotube due to the

reduced freedom of the system. Fusion should occur along the minimum energy path as a sequence of 23 generalized Stone-Wales transformations, determined by a graphical search program. These reactions can be viewed as bond rotations, involving relatively low activation barriers. Our search of the phase space using the "string method" indicates that Stone-Wales transformations are multi-step processes, and provides detailed information about the transition states and activation barriers associated with fusion.

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