Relaxation dynamics of C\textsubscript{60}

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The relaxation dynamics of C\textsubscript{60} from high-energy isomers to Buckminsterfullerene is examined using a master equation approach. An exhaustive catalog of the C\textsubscript{60} fullerene isomers containing only five- and six-membered rings is combined with knowledge of the Stone-Wales rearrangements that connect all such isomers. Full geometry optimizations have been performed for all the minima and the transition states which connect them up to six Stone-Wales steps away from the global minimum. A density-functional tight-binding potential was employed to provide a quantum mechanical description of the bonding. The resulting picture of the potential energy landscape reveals a “weeping willow” structure which offers a clear explanation for the relatively long relaxation times observed experimentally. We also predict the most important transient local minima on the annealing pathway. © 1998 American Institute of Physics. [S0021-9606(98)50940-3]

I. INTRODUCTION

Due to the time scale involved, of around 0.001 s, the formation mechanism of Buckminsterfullerene\textsuperscript{1,2} (BF) presents difficulties for theoretical modeling. Isotopic substitution experiments have proved that fullerene formation occurs from the condensation of atomic carbon vapor.\textsuperscript{3} Speculation on the possible formation mechanisms of Buckminsterfullerene was first advanced by Kroto.\textsuperscript{4} The icospiral particle nucleation scheme (or “pentagon road” scheme, as it is now known) involves the growth of a nautiluslike shell. As the shell curves around itself, Kroto suggested that closure may occasionally occur, therefore stopping any further growth, while species that do not close will “snowball” into “Buckyonions.”\textsuperscript{5} A study of the energetics of various pentagon road intermediates from C\textsubscript{20} to C\textsubscript{60}, using both model and \textit{ab initio} potentials, has been presented recently by Bates and Scuseria.\textsuperscript{6}

In the “fullerene road” model, due to Heath,\textsuperscript{7} carbon radicals in the vapor condense to form graphitelike sheets, but the cage closes when it contains around 30 atoms. Since cages containing pentagons and hexagons at this nuclearity must necessarily contain adjacent pentagons, insertion of C\textsubscript{2} fragments (followed by annealing) continues until a deep minimum is reached at C\textsubscript{60} or C\textsubscript{70}. The mechanism of dimer insertion was first proposed by Endo and Kroto.\textsuperscript{8} In a theoretical study, Murry \textit{et al.}\textsuperscript{9} identified a connection between the C\textsubscript{2} extrusion (or evaporation) process and the annealing process, which they suggest can proceed via the same transition state.

Strout and Scuseria have recently proposed the cycloadition model,\textsuperscript{10} where various cycloaducts form from monocyclic rings, which in turn form hoops, and through successive 1,2-carbon shifts create new faces which can eventually cap the top and bottom of the hoop. This model is supported by data from ion-chromatography experiments.\textsuperscript{11,12} The authors also make connections between the nucleation and annealing mechanisms. Their calculations indicate an energy lowering from monocyclic rings to fullerenes of the order of 20 eV, which they suggest will be converted into vibrational energy, and therefore assist the annealing process.

Manolopoulos and Fowler\textsuperscript{13} presented a model to explore the viability of the fullerene road mechanism. They proposed a building game\textsuperscript{14} for fullerene growth based on energetics and the number of adjacent pentagons at each nuclearity. They showed that the fullerene road can explain the experimental abundance of C\textsubscript{60} and C\textsubscript{70} if the driving force is solely due to minimization of the energy of the system.

Regardless of how the cage actually grows and closes, it seems unlikely that under the harsh experimental conditions a perfect icosahedral C\textsubscript{60} isomer will be formed spontaneously once the cage has closed. If the cage closes at another nuclearity, then extrusion or insertion of carbon radicals must occur. This process evidently stops at the magic-numbered C\textsubscript{60} or C\textsubscript{70} clusters, indicating that the fullerene undergoes a search for the lowest energy structure of each nuclearity before insertion/extrusion can occur again. Annealing provides the means for a fullerene to explore configuration space. In contrast to the many nucleation mechanisms posited so far, there exists only one real candidate for the annealing mechanism, namely the Stone-Wales (SW) rearrangement.\textsuperscript{15} Other pathways advanced so far differ from the original SW rearrangement only in detail.

The SW mechanism enables a pair of hexagons and a pair of pentagons to interchange positions, and therefore provides a means for pentagons to migrate. The original proposal considered the symmetrical arrangement of hexagons and pentagons which is found in C\textsubscript{60}, now known as a pyracylene patch, or “Stone-Wales” patch. Specific to this patch is a central bond, sometimes called a “Stone-Wales bond.” The mechanism proceeds through a rotation of the SW bond by 90°, as shown in Fig. 1. The SW rearrangement is not specific to C\textsubscript{60}, and can be applied to any fullerene which contains a Stone-Wales patch. A generalized SW process has been proposed which can act on any edge of a carbon polyhedron.\textsuperscript{16}
A symmetric transition state for the concerted SW process is thermally forbidden under the Woodward-Hoffmann rules. However, Murry et al. have located true transition states for the SW process, one of which contains an $sp^3$ coordinated carbon atom and is asymmetric. They reported a two-step mechanism for the SW rearrangement via a single $sp^3$ transition state, and their best estimate of the corresponding barrier lies 0.5 eV lower than that of the symmetrical concerted rearrangement. These barriers are the results from single point density functional theory (DFT) calculations with the BLYP functional at modified neglect of differential overlap.

A study of the effect of nearby carbon atoms on the SW rearrangement has been recently reported. The barrier for the SW process in the presence of an additional carbon atom was found to be substantially lower than the conventional SW barrier. The authors suggest that the presence of a carbon atom near the SW site has an autocatalyzing effect, and may offer an explanation for the apparently efficient annealing process of high-energy C$_{60}$ down to the global minimum.

The SW rearrangement has proved useful in the generation of fullerene isomers, and in determining the connectivity of these isomers through SW rearrangements (“Stone-Wales” maps). It appears to represent the most likely route for interconversion of fullerene isomers. As a vital part of C$_{60}$ formation, the process by which a high-energy C$_{60}$ isomer anneals to the global minimum is still not understood. Several molecular dynamics (MD) studies of C$_{60}$ formation and annealing using a variety of potentials failed to find a route from high-energy minima to BF within the simulation times employed.

The first attempt at simulated annealing was made by Ballone and Milani, using an interatomic bond-order potential due to Tersoff. After several simulated annealing cycles and further annealing of product structures, defects were still present. Chelikowsky and Jing and Chelikowsky have published a number of MD simulations of fullerene nucleation. Their initial studies were restricted to systems containing 60 atoms confined to a cubic box, using Langevin MD and a tight-binding potential. None of the annealing runs managed to produce a C$_{60}$ structure free from pentagon–pentagon defects, despite the long simulation times employed. Chelikowsky ascribed the lack of defect free final structures to cooling the system too quickly. He also suggested that confining the system to 60 atoms was a limitation, since it does not allow for growth of the cluster. A further study by Jing and Chelikowsky attempted to simulate gradual nucleation through an accretion model. Their longest annealing time of around 1 nsec for C$_{60}$ yielded only structures with pentagon–pentagon defects. The time scale of the simulation (in comparison with the 0.001 s time scale of experiment) was again a problem.

Wang et al. published results from an MD simulation using 60 atoms confined to a sphere, interacting through another tight-binding potential for carbon. Their conclusions echoed those of Chelikowsky. The first fully ab initio MD study of fullerene formation was reported by Yi and Bernholc, who employed the Carr-Parrinello method. They examined carbon fragment insertion into a fullerene cage. This insertion process is reported to have virtually no activation barrier (although the insertion must occur at specific orientations), and is highly exothermic.

Murry et al. have previously drawn attention to a transition state for the SW rearrangement which also connects the global minimum to a C$_2$ fragmentation process. Xu and Scuseria further explored this scenario in their MD simulation, using a tight-binding potential. While some of the other simulations discussed here employed constant temperature trajectories, the latter authors used constant energy, suggesting that this approach is more suitable to the study of fragmentation. They found that only dimers were lost. They successfully annealed the lowest energy defect structure into BF.

A thermally activated mechanism for the SW rearrangement has been proposed by Marcos et al. The authors report results of constant energy MD simulations, using the Tersoff potential, and simulated the transition from BF to the lowest energy pentagon defect structure on a time scale of around 0.1 $\mu$s. They identified an SW rearrangement to the lowest defect structure, and analyzed the trajectory for this rearrangement using thermal quenching. The SW process in their simulation is reported as a multistep, multiminimun path, in contrast to previous MD and ab initio pathway calculations for a variety of other potentials. However, Marcos et al. did not locate true transition states, but instead generated a continuous low energy pathway, along a predetermined reaction coordinate.

Very recently, Maruyama and Yamaguchi have reported the first MD simulation in which high-energy C$_{60}$ minima are annealed to BF. They used a novel temperature control method in their simulations and employed the Brenner potential, which is very similar to the Tersoff potential. Taking a semiclosed C$_{60}$ pseudocage as the starting point, the authors found relaxation to BF after around

![Diagram of fullerene isomer rearrangement](image_url)
250 ns. This relaxation appears to proceed through a series of both ordinary and general (involving other polygons) Stone-Wales rearrangements, mediated by what appear to be asymmetric transition states. From an Arrhenius plot they extrapolate an activation energy for the Stone-Wales rearrangement of 241 kJ mol\(^{-1}\), which is very low compared with other current estimates.

As the time scale for fullerene formation is of the order of 0.001 s, it seems that MD studies are not appropriate, since current simulation times are orders of magnitude lower. The successful relaxation to BF observed by Maruyama and Yamaguchi\(^{33}\) is probably due to the low barriers obtained with their chosen potential, which will clearly accelerate the dynamics. In any case, energetics alone is not sufficient to explain the abundance of C\(_{60}\) in experiment, since many calculations have shown that C\(_{70}\) (\(D_{5h}\)) has far greater thermal stability.\(^{35-37}\) The formation mechanism must be, in part, kinetically driven. Furthermore, many theoretical studies of the nucleation mechanism suggest that BF is formed through a series of exothermic reactions, which may assist in surmounting the large barriers encountered upon a Stone-Wales rearrangement, and drive the annealing process.

In the present contribution, the topography of the global potential energy surface (PES) is surveyed, and the relaxation dynamics problem for C\(_{60}\) is cast in terms of energy landscape theory. We find that the form of the PES explains why MD simulations have usually failed to provide a satisfying description of fullerene annealing.

II. METHODS

To simplify the present investigation we consider only stationary points corresponding to ‘‘classical’’ fullerenes and transition states corresponding to Stone-Wales rearrangements.

A. Isomer enumeration for fullerenes

Two independent studies have outlined systematic methods for enumerating fullerenes,\(^{38,39}\) and agree on a total of 1812 unique C\(_{60}\) isomers (not counting enantiomers). The spiral algorithm\(^{39}\) has recently been made available\(^{40}\) for generating catalogs of fullerene isomers of a given nuclearity. The adjacency matrix for the fullerene vertices may be deduced from this algorithm, and can be used to prepare a set of Cartesian coordinates to provide a starting point for subsequent geometry optimizations. Assuming that all admissible fullerene isomers are pseudospherical in form, it is possible to take advantage of Stone’s tensor surface harmonic theory.\(^{41,42}\) This theory demonstrates that the eigenvectors of an adjacency matrix for any pseudospherical cluster span the same irreducible representations in the point group as those of the scalar spherical harmonics. These spherical harmonics are of the \(S^m, P^m, D^m\) type, and the energy increases roughly with the orbital angular momentum. A correspondence between the \(x, y, z\) components of the first three \(P^m\) eigenvectors and the \(X, Y, Z\) Cartesian coordinates of the fullerene was noted by Manolopoulos and Fowler.\(^{43}\) With a trial geometry comes a guess for the point group symmetry, which can be deduced from the connectivity graph of the molecule. However, these symmetry assignments should be regarded as tentative, as they do not accommodate such effects as Jahn-Teller distortion.

B. The Stone-Wales map for C\(_{60}\)

Once an exhaustive catalog of all possible fullerene isomers of a given nuclearity has been obtained, the next step in a study of the dynamics is to locate the transition states connecting them. The topology of the SW map for C\(_{60}\) has been generated and examined in some detail by Austin et al.\(^{21}\) Their results are cast in the framework of graph theory,\(^{44}\) and indicate that the graph for the SW map for C\(_{60}\) comprises 44 disjoint sets: the main component of 1710 connected isomers contains the global minimum BF, while the other disconnected graphs contain no more than 27 isomers. Therefore, the global minimum is contained in a giant ‘‘basin’’ in the SW map, and it is here that the focus of the present study will concentrate.

Austin and co-workers used their graph theoretical representation to determine the smallest number of Stone-Wales isomerizations (or ‘‘SW steps’’) required to reach BF from each local minimum. Each SW step away from the global minimum defines a set of structures, referred to collectively as a ‘‘Stone-Wales stack.’’ BF itself is connected to only one other isomer with \(C_{2v}\) symmetry and two sets of fused pentagons. Hence any relaxation process leading to BF must involve this \(C_{2v}\) isomer. Austin et al. also found that no more than 30 successive SW rearrangements are required to convert any local minimum in the SW map to BF. The authors deduced the number of isomers in each SW stack, and the connectivities, both between successive stacks and within each stack.

In the present work, the connectivities of the isomers were independently confirmed through modifications of the basic SPIRAL code.\(^{39,40}\) For each isomer (starting with BF), we locate all the SW patches and note which atoms are involved. The local adjacencies in each patch are then reset so that the SW bond is effectively rotated by 90\(^\circ\). The new adjacency matrix is then diagonalized. The adjacency matrix for each fullerene isomer yields a unique eigenvalue spectrum which provides a convenient means of identification. Rotations are performed for every SW patch in each isomer, and for every isomer in each SW stack. With the exception of BF, this approach yields both forward and backward connections. Backward connections were deleted using knowledge of the isomer indices of the previous stack. In this way it is possible to work outward from the global minimum, determining connectivities for each successive stack.

The resulting distribution of isomers connected to a given minimum also reveals the number of symmetry equivalent SW patches in that structure. For example, application of the above procedure to BF yields a total of 30 SW patches, all of which lead to the lone \(C_{2v}\) isomer. Therefore, every one of these SW patches is symmetry equivalent. These multiple pathways were correctly accounted for in the dynamical calculations described below. However, since most isomers in the SW map have \(C_1\) symmetry, they do not support any symmetry equivalent SW patches. In the present
work, the SW map was deduced using the above method up to and including the seventh stack. This includes a total of 197 minima and 547 transition states.

C. Geometry optimization for Buckminsterfullerene

Many theoretical studies have reported results of geometry optimizations of BF, using a variety of potentials. Some results for BF from Carr-Parrinello molecular dynamics using the local density approximation (LDA) functional are available and are shown in Table I, but the Hessian index was not generally checked. In the present work, BF has been optimized using a density-functional tight-binding (DF-TB) potential for carbon based on the work of Frauenheim et al., using conjugate-gradient minimization techniques and subsequent eigenvector-following to confirm that all eigenvalues of the Hessian are positive. Our implementation of the latter approach has been described elsewhere. The two unique C–C bond lengths for BF were found to be 1.481 and 1.424 Å. A comparison of bond lengths found with other potentials is presented in Table I.

Vibrational frequencies have also been calculated using many potentials. Only a small set of frequencies can be observed experimentally, two of $A_g$ symmetry, which are Raman active, four of $T_{1u}$ symmetry, which are infrared active, and eight of $H_g$ symmetry, which are also Raman active. The experimental frequencies are not harmonic, in contrast to the calculated vibrational frequencies, and so one cannot make a direct comparison. However, the frequencies calculated using the present DF-TB potential may be compared with those for other potentials. As Table II shows, agreement among the various calculated frequencies is not particularly good. The average % deviations from experiment indicate that the vibrational frequencies calculated from the DF-TB potential are reasonable, although they are systematically low. Hence the isomerization rates calculated in this work, which are based on the DF-TB frequencies, will only be qualitatively correct.

The energy of the C$_{60}$ isomer in stack 2 has also been reported previously in the literature. In the present work, this isomer has a relative energy of 114.1 kJ mol$^{-1}$. Other relative energies are shown in Table III. The present DF-TB energy is the lowest reported. In a study of the energetics of the isolated pentagon C$_{60}$ map, Fowler et al. found that the QCFF/PF potential showed a much larger spread of energies than DF-TB. As shown in Table IV, the energy of the tran-

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$^a$Reference 9.
$^b$At the MNDO geometry.
$^c$Reference 27.
$^d$Constrained calculation.
$^e$Reference 20.
sition state between this first defect isomer and the global minimum is also lowest for the DF-TB potential. Therefore, it seems quite likely that an improvement in the description of the potential would lead to a modest upward revision of both the barrier heights and the relative energies of the local minima. If the energies of the remaining local minima follow the same trend as the first local minimum, then it is likely that the gradient of the potential energy funnel discussed below would also increase. Given that an increase in barrier height and an increase in the funnel slope are factors that work against each other, it is difficult to predict what effect this will have on the rate of relaxation.

D. Energetics of the Stone-Wales map

Once the connectivities have been deduced, the next task is to optimize the geometries and calculate the energies of the minima in each SW stack. As pointed out earlier, no \textit{ab initio} geometry optimizations of isomers aside from BF and the next lowest $C_{2v}$ local minimum have been reported. Austin \textit{et al.}\cite{austin2000} optimized all 1812 geometries in the SW map using the semiempirical QCFF/PI method. We performed analogous calculations using the DF-TB potential and a conjugate-gradient\cite{conjugate-gradient} search with analytic first derivatives. In agreement with Austin \textit{et al.}\cite{austin2000}, all 1812 candidate structures were found to be local minima, as verified through reoptimization of each structure using eigenvector-following.\cite{eigenvector-following, conjugate-gradient}

In examining the dynamics it is possible to use the connectivity information to obtain true transition states for each SW rearrangement. For each isomer a list of all unique SW patches and the isomers they connect was compiled following modification of the SPIRAL code. This information was then used along with a projection operator which effectively rotated the SW bond of each SW patch by 22.5°. The starting geometries were then optimized using the DF-TB potential and a hybrid eigenvector-following/conjugate-gradient technique.\cite{hybrid} Each of these structures was then reoptimized using eigenvector-following, as the Hessian eigenvalues are needed for the following rate calculations. All transition states located were asymmetric, with an $sp^3$ carbon atom. Table IV shows a selection of barriers for the transition between BF and the next highest isomer, for a variety of methods. In the present work all possible minimum-transition state-minimum sequences have been identified and then connected head-to-tail, as far as possible, to give "monotonic sequences."\cite{monotonic}

Austin \textit{et al.}\cite{austin2000} note that of the 1710 isomers contained in the main basin of the SW map, 898 isomers are connected by downhill paths to the global minimum. However, Austin \textit{et al.} did not construct any monotonic sequences or pathways, or report any explicit connectivity information aside from the number of isomers in each stack and the number of outward connections between adjacent stacks. Instead, they focused on the spread of total energies of isomers within each SW stack, and estimated the energetic penalty for introducing pentagon–pentagon adjacencies. They report a scatter plot of total energies as a function of SW steps, which shows a roughly linear correlation, and from this they deduced that the average energetic penalty for introducing such defects is $33 \text{ kJ mol}^{-1}$. Using the DF-TB potential, it is possible to construct an analogous plot, and this is shown for the first seven SW stacks (or steps) in Fig. 2. Agreement between the scatter plots calculated here and that of Austin \textit{et al.} is very good. The main difference is that the DF-TB energy range appears to be narrower than for the QCFF/PI potential. This feature has been noted previously for other fullerences.\cite{wide-energy-range}

E. The potential energy surface and funnels

The development of energy landscape theory has recently emerged as a consequence of the efforts directed toward understanding relaxation processes in proteins and clusters.\cite{energy-landscape-proteins, energy-landscape-clusters} In particular, a funnel topography\cite{funnel} enables the PES to "guide" relaxation to the global minimum, and we have recently described a number of different archetypal energy landscapes.\cite{archetypal-energy-landscapes} The efficiency with which the global minimum is located depends upon the gradient, ruggedness and the extent of the funnel.\cite{funnel-efficiency} The gradient is defined as the slope of the funnel, or more specifically as the difference in energy between successive minima. We describe a funnel as rugged if it has high barriers between adjacent minima. A rugged surface may be associated with systems which readily form "trapped" states, where the global minimum will only be reached over very long time scales. The extent of the funnel indicates the size of the configurational space within it.

A fast folding system has also been identified with an energy surface which supports a single folding funnel.\cite{fast-folding-systems} Glassy systems which support a manifold of trapped, misfolded states have been associated with energy landscapes which contain several funnels, each supporting minima of differing morphology. In practical terms, it is useful to have additional parameters with which to identify the various configurations within the funnel, and to group them accordingly. Previous theoretical studies on protein folding have used criteria such as the number of favorable contacts, the distance from the global minimum in configuration space and the energy of configurations relative to the global minimum. Such order parameters\cite{order-parameters} serve to stratify the funnel and cast the
folding kinetics into a manageable (if somewhat coarse grained) framework. For example, the properties of a funnel may be averaged over each level to give the average energy of the minima in each stack, or the average barrier height between stacks.

In the present work the number of SW steps from the global minimum emerges as a natural order parameter. We have checked the connectivity of the C\textsubscript{60} PES against the results of Austin et al.\textsuperscript{21} up to six SW steps away from BF. In Table V we provide a list of the number of minima in each stack, the number of true transition states connecting minima in this stack to the next, and the number of transition states which mediate rearrangements within each SW stack. For internal connections our values are half those reported by Austin et al., because the latter authors counted both forward and reverse pathways.

Using this information, the average energy per SW stack and the average outward barrier height between SW stacks can be calculated. As shown in Fig. 2, the average energy of minima within each stack rises monotonically. In contrast, the average outward barrier height between SW stacks decreases somewhat with increasing SW step (Fig. 3). These data indicate that although the gradient of the funnel in the outermost SW stacks is quite small, it increases sharply in the neighborhood of BF. The change in average barrier height is small compared to the change in average isomer energy per SW stack. A model study on relaxation dynamics has shown that the ‘‘folding time’’ depends on both barrier height and funnel gradient.\textsuperscript{83} In particular, it is the optimal combination of these two parameters which governs the relaxation time, since the slope affects the ratio of the barrier height for the forward process to that of the backward process. Therefore, a reasonable slope is a necessary but not a sufficient condition to guarantee relaxation on a feasible time scale. If the funnel had no gradient at all, there would be no thermodynamic driving force to find the global minimum, regardless of barrier height. If the slope is steep but the barrier heights (relative to the slope) are large, then relaxation will also be slow. An optimal combination of these parameters probably satisfies gradient\textsuperscript{3}+barrier height.

The monotonic sequences for C\textsubscript{60} are sawtoothed in character, as shown in Fig. 4. An alternative representation of the landscape is provided by a disconnectivity graph.\textsuperscript{70} For any given total energy we can work out which of the local minima in our sample are connected by pathways that lie below the energy threshold. At finite energy the minima are divided into disconnected sets of mutually accessible structures, separated by insurmountable barriers. As the total energy increases the disconnected sets merge. The total energy increases along the vertical axis and we draw a line corresponding to every local minimum starting from a height determined by the potential energy at the bottom of the corresponding well. A node joins lines at the lowest energy for which the minima become mutually accessible. We choose the horizontal displacements to give the clearest possible representation of the resulting graph. Graphs such as these, which are connected but contain no cycles, are known as ‘‘trees,’’ and the result for C\textsubscript{60}, shown in Fig. 5, is classified as a ‘‘weeping willow’’ in our recently proposed scheme.\textsuperscript{67}

It is clear from both the monotonic sequences and the disconnectivity graph that it will be difficult for high-energy isomers of C\textsubscript{60} to reach BF, unless the energy of the system is high enough to scale the relatively large barriers. In addi-

<table>
<thead>
<tr>
<th>SW stack</th>
<th>Number of minima</th>
<th>Outward connections</th>
<th>Internal connections</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>6</td>
<td>0</td>
</tr>
<tr>
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<tr>
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<td>19</td>
<td>111</td>
<td>0</td>
</tr>
<tr>
<td>5</td>
<td>39</td>
<td>172</td>
<td>8</td>
</tr>
<tr>
<td>6</td>
<td>60</td>
<td>184</td>
<td>23</td>
</tr>
<tr>
<td>7</td>
<td>71</td>
<td>190</td>
<td>32</td>
</tr>
</tbody>
</table>

FIG. 3. Range of energies (in kJ mol\textsuperscript{-1}) of barriers encountered along all possible outward pathways in the first seven Stone-Wales stacks, relative to the global minimum. Stack 1 refers to the global minimum. The horizontal line connects the average outward barrier height between each stack.

FIG. 4. A representative monotonic sequence for the C\textsubscript{60} PES, showing the energies of minima and the transition states which connect them as a function of the SW stack.
tion, the slope of the funnel for C_{60} is quite small, so while the funnel can guide the system into BF, the effect is not dramatic. In contrast to the optimum conditions for efficient relaxation, the funnel for C_{60} exhibits barrier heights funnel gradient. These results are in good agreement with the experimental time scale on which BF is formed. Starting from Stack 7, there are 3699 possible pathways which lead down to the global minimum. Just under half ~1789! of these pathways form monotonic sequences. The remaining pathways contain sequences with at least two consecutive minima which do not exhibit the energy decrease required for a monotonic sequence.

III. RELAXATION DYNAMICS

A. Reaction rates

The thermodynamics of this system were investigated within the microcanonical (constant energy) ensemble. All the results can easily be transformed to the canonical ensemble and our conclusions are unaffected. The total energy density of states, Ω(E), is calculated using the harmonic superposition method,\textsuperscript{71} summing the vibrational density of states, Ω_i(E), for each minimum accessible on the PES at the energy E. The harmonic vibrational density of states for a minimum, i, is given by

\[ \Omega_i(E) = \frac{2N! (E-E_i)^{\kappa-1}}{\hbar_i^{\text{PE}} \Gamma(\kappa) \Pi_{j=1}^{\kappa-1} \nu_j}, \]

where N=60 is the number of atoms, \( \hbar_i^{\text{PE}} \) is the order of the point group of minimum i, \( \kappa=174 \) is the number of vibrational degrees of freedom, \( E_i \) is the potential energy of minimum i, and the \( \nu_j \) are the harmonic vibrational frequencies (j = 1...174) of minimum i. The master equation approach indicates how the probability of occupation of each configuration, \( P_i(t) \), in the sample will change with time, t.

Starting in a region far from equilibrium at \( t=0 \), the system will tend to equilibrium as \( t \to \infty \). At equilibrium, the probability of occupation of each minimum in the harmonic superposition approximation, \( P_i^{\text{eq}} \), is

\[ P_i^{\text{eq}} = \frac{2N! (E-E_i)^{\kappa-1}}{\hbar_i^{\text{PE}} \Omega(E) \Gamma(\kappa) \Pi_{j=1}^{\kappa-1} \nu_j}. \]

The equilibrium probability for each of the 197 minima of C_{60} up to SW stack 7 was calculated over a range of energies, and the probabilities were then summed over each Stone-Wales stack. These equilibrium probabilities for a range of energies are shown in Fig. 6. The population is concentrated in stacks 1 and 6 and the only other stack to show significant population at equilibrium in this energy range is stack 2.

The master equation approach requires the transition rates between all minima that are connected in the sample, and we have calculated them using Rice-Ramsperger-Kassel (RRKM) theory\textsuperscript{72–74} within the harmonic approximation. The transition rate from minimum j to i is then

\[ W_{ij}(E) = \frac{\hbar_i^{\text{PE}} (E-E_j)^{\kappa} \Pi_{a=1}^{\kappa} \nu_a}{\hbar_j^{\text{PE}} (E-E_i)^{\kappa} \Pi_{a=1}^{\kappa} \nu_a}. \]

B. The master equation approach

The master equation approach can describe the irreversible behavior of a system with respect to time,\textsuperscript{75} and is therefore ideally suited to the investigation of relaxation processes.
in large clusters. In the present work, solutions to the master equation were obtained numerically using Bulirsh-Stoer integration. The initial population distribution consisted of the minima in the seventh Stone-Wales stack with equal weights, and the system was relaxed from this point. Figure 7 shows the probability of the global minimum being populated for a range of energies and for times ranging from 3 msec to 0.1 msec. Figure 7 shows that for longer times, the maximum probability is large and is attained quite rapidly with increasing energy. Once the maximum has been reached, the probability tails off less steeply as a function of energy. For shorter times it takes more energy to reach the maximum population of the global minimum. The population maximum also increases as time increases. By 0.1 msec, there is a broad relatively symmetrical probability which peaks at a value of around 0.24.

The evolution with time of the total probability for each Stone-Wales stack, \( P_s(t) \), may be calculated by summing the probabilities of finding the system in any of the states for each stack. By construction, at \( t = 0 \), \( P_s(0) = 1 \) and all other probabilities are zero. Results for relaxation at a total energy of 3360 kJ mol\(^{-1} \) are shown in Fig. 8 for times up to 1.75 msec. This figure shows the rapid decay of population in stack 7 and transient populations in stacks 5 and 6 which decay relatively slowly. The population of the global minimum grows steadily until it is the dominant state after about 1.5 msec. The growth in the probability of occupying the global minimum is accompanied by a small increase in the population of the single state in stack 2, which also grows steadily.

The experimental time scale of formation for Buckminsterfullerene is in the range of 0.1–0.3 msec. In order to see the global minimum obtain a majority population on this time scale in our calculations, the energy of the system needs to be greater than 3360 kJ mol\(^{-1} \). The evolution of the probability distribution at a higher total energy is shown in Fig. 9. The population in stack 7 rapidly decays, stacks 5 and 6 show transient populations and the population of the global minimum grows steadily, dominating after about 0.1 msec. The final probability is smaller than for Fig. 8, and the increase in energy leads to a larger population in stack 2.

**IV. CONCLUSIONS**

Inspection of Figs. 2–5 reveals that the potential energy funnel consisting of the first seven Stone-Wales stacks has a modest slope punctuated by large barriers. However, the landscape has the requisite focusing properties to ensure relaxation to BF if there is sufficient energy to surmount the barriers. The large barriers, relative to the slope of the funnel, mean that relaxation will be very slow at a total energy of 1000 kJ mol\(^{-1} \), which corresponds to a vibrational temperature of around 700 K assuming equipartition. The minima span a range of 500 kJ mol\(^{-1} \), which is about the same as the average barrier height. Figure 7 indicates that once a threshold of around 2800 kJ mol\(^{-1} \) has been reached (corresponding to an equipartition temperature of about 1900 K), relaxation to the global minimum can proceed on a millisecond time scale.

Chelikowsky and co-workers suggested that their failure to find even the first defect structure (in stack 2) is due to the rapid rate of cooling in their simulations. Given
the high barriers for Stone-Wales rearrangements and the small funnel gradient, it is not surprising that cooling from around 6000 to 300 K over a few picoseconds left the system trapped in a high-energy minimum. It seems that conventional MD simulations are not suitable for studying the relaxation dynamics of \( C_{60} \), simply because the feasible simulation time is several orders of magnitude smaller than the experimental time scale. The master equation approach does not suffer from any such limitations on time scale, but rather requires a large and representative sample of minima and transition states on the PES.

Inclusion of anharmonicities in RRKM theory can change predicted rates by orders of magnitude. Hence, the harmonic approximation represents perhaps the weakest point of these calculations, but is unfortunately the most difficult to remedy. It should also be noted that consideration of Stone-Wales rearrangements alone represents an idealized version of relaxation compared to what probably occurs in experiment. Within the manifold of energies spanned by hexagon and pentagon containing cages, there is a body of evidence which supports the idea that cages containing heptagons and squares will have energies which also span this manifold.\(^6\),\(^7\),\(^8\) In addition, calculations show that \( C_2 \) insertion has almost no barrier, and it is possible that the dynamics of \( C_{60} \) relaxation may involve insertion reactions to \( C_2 \) which could undergo a SW rearrangement and then release a \( C_2 \) to yield a different \( C_{60} \) isomer.

**ACKNOWLEDGMENTS**

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