

Atomistic Simulation Study of the Pressure Induced Incorporation of Helium into C₆₀

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We present a mixed quantum/classical molecular dynamics study of the pressure driven incorporation of helium into C₆₀. As a simulation system a C₆₀ molecule in a helium gas bath is chosen. From our path sampling molecular dynamics simulations, we clearly identify the preferred insertion mechanism. It involves the opening of 3 C–C bonds of a 6-ring, forming a “window” in the C₆₀ molecule, which facilitates the incorporation of a helium atom. From a manifold of trajectories, each describing a reaction event, the role of the nonreacting heat bath is elaborated. The approach appears widely applicable to the investigation of reactions in complex systems in general.

Introduction

The investigation of reactions in complex systems is of great interest to the understanding of a large variety of processes. A frequently encountered situation is that only a few atoms or molecules undergo bond formation or breaking, whereas the majority of particles solely act as a heat bath or solvent. For such systems, mixed quantum/classical approaches have proven to be very useful. Therein, the electronic degrees of freedom of a small number of atoms are described by quantum approaches. Nonreacting atoms are modeled classically, which helps saving computational resources.

The time scales accessible to molecular dynamics simulations of such models typically do not exceed nanoseconds. Most reactions take place on a much longer time scale. Quite often this discrepancy is in the range of 10 orders of magnitude. A widely spread approach to overcome this limitation is the use of the blue moon ensemble method.¹ This implies the predefinition of a reaction coordinate. For small systems it is often quite clear how the reaction coordinate looks. However, many particle systems typically involve much more complicated reaction coordinates and their definition is far from straightforward. Even worse, an inappropriate choice of the reaction coordinate may bias the mechanistic analysis.

In this paper, we present the combination of a mixed quantum/classical molecular dynamics simulation with the path-sampling algorithm developed by Chandler et al.^{2,3} This method does not involve the predefinition of a reaction coordinate. Though it is based on a pregiven initial trajectory of the reaction event, memory effects are diminished in sufficiently large numbers of path sampling iterations. It may be interpreted in terms of a Monte Carlo sampling of trajectories of a desired process. Accordingly, the relevance of a mechanism may be related to the probability of finding corresponding dynamical pathways.

The simulation scheme is applied to the pressure driven incorporation of helium into C₆₀. In principle, two classes of mechanisms for the insertion of noble gas atoms in fullerenes

are possible. Given a sufficiently high velocity, a noble gas atom may cross the energy barrier for passing through one of the 5- or 6-rings of the fullerene. Such high energy bombardment of C₆₀ was investigated from both experiment^{4,5} and theory.^{6,7} On the other hand, Saunders et al. proposed that some bonds of the C₆₀ molecule could temporarily break and thus open a “window” that would facilitate the diffusion of a gas atom into the fullerene.^{8,9} From high-pressure experiments of fullerenes in a helium atmosphere, these authors could observe the formation of He@C₆₀. The related reaction barrier was found as 3.5 eV.⁸ Because the activation barrier estimated for the permeation of He through an intact C₆₀ is around 10 eV,^{10,11,12} only the window mechanism can account for the yield of endohedral helium from these experiments.^{8,9}

The question of how such a window actually looks could not be answered to date. For example, Patchkovskii et al. investigated as many as 21 different insertion pathways on the basis of minimum energy path calculations.¹³ However, none of the investigated pathways turned out to be realistic. The related activation barriers were estimated as 9 eV or higher. The manifold of possible windows of C₆₀ is quite large, if not even infinite. In the present work, we thus do not choose further specific routes and investigate their likeliness. Instead, we rely on the path-sampling algorithm to explore the ensemble of helium insertion trajectories. In the course of sampling iterations, the obtained pathways evolve toward routes of low barriers and hence lead to the favored mechanism.

Simulation Methods

As a simulation system a cubic simulation box including a C₆₀ molecule and 1000 He atoms was prepared. To model an infinite gaseous system, periodic boundary conditions were applied. The simulation pressure and temperature was chosen as 50 atm and 1000 K, respectively. A density functional tight-binding method¹⁴ is used for describing the carbon–carbon interactions. Though computationally much less demanding, this approach was shown to be of similar accuracy as full density functional calculations.¹⁵ Classical force fields for the He–He¹⁶ and for the He–C interactions¹⁷ were taken from the literature. The potentials and their respective parameters are listed in Table 1. Molecular dynamics simulations were run using the DLPOLY

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TABLE 1: He–He and He–C Interaction Parameters

interaction	parameters
$V_{\text{He-He}} = 4\epsilon[(\sigma/r)^{12} - (\sigma/r)^6]$	$\epsilon = 0.083682 \text{ kJ mol}^{-1}$ $\sigma = 2.556 \text{ \AA}$
$V_{\text{He-C}} = A \exp(-r/\rho)$	$A = 48.0 \text{ kJ mol}^{-1}$ $\rho = 0.1226 \text{ \AA}$

package.¹⁸ Therein the density functional tight-binding method of Seifert et al.¹⁴ was implemented for treating the quantum degrees of freedom. To ensure good time reversibility, a relatively small time step of 0.25 fs was chosen.

For generating an initial trajectory of the He incorporation process, we prepared a helium atom in proximity of the fullerene. A velocity of

$$v = \sqrt{\frac{k_B T}{m_{\text{He}}}}$$

directed to the center of the C₆₀ molecule was assigned, and the system is propagated in both directions of time. By placing the He atom sufficiently close (4 Å from the C₆₀ center of mass) to the fullerene before changing its momentum, a trajectory was found in which the desired process takes place.

The mechanistic analysis is based on a manifold of trajectories, each corresponding to a He incorporation event. Starting from an initial trajectory of the process of interest, new trajectories are obtained in an iterative way using the path sampling method developed by Chandler et al.^{2,3} This is accomplished by selecting a configuration from the preceding trajectory and slightly modifying the atomic momenta of all atoms. Velocity changes are incorporated in a manner conserving the total energy and momentum, respectively. The modified configuration is propagated in both directions of time. The resulting trajectory is then checked for the process of interest. In case the desired event takes place, the trajectory is used for generating a new trajectory, repeating the above procedure.

Results

The modeling of the initial trajectory for the path sampling study of helium incorporation into C₆₀ did not involve the preparation of a window in the fullerene. However, after only 5 path sampling iterations, trajectories were obtained, in which some carbon–carbon bonds were observed to temporarily split and re-form after the helium atom passed into the C₆₀ molecule. Thus, path sampling quickly converged toward trajectories corresponding to the window mechanism, exclusively. This indicates a strong preference over the helium permeation through intact buckyball molecules. The mechanistic analysis described in the following is based on 100 reactive events, obtained from path sampling after convergence to the favored class of insertion routes. As a consequence of the iterative nature of path sampling, subsequent trajectories are not independent from each other. An upper estimate of how many iterations are required to ensure decorrelation may be given by the number of sampling runs needed for convergence from the initial to the preferred type of pathways. As these routes are related to different mechanisms their decorrelation is evident. On the basis of this estimate, our mechanistic analysis is based on $100/5 = 20$ independent reactive events.

A characteristic insertion trajectory is illustrated in Figure 1a–c. Figure 1a shows the distances of the carbon atoms of the 6-ring, which is penetrated by the He atom, as functions of time. In the course of thermal motion and the bombardment by helium atoms at high pressure, the C–C bonds of the fullerene

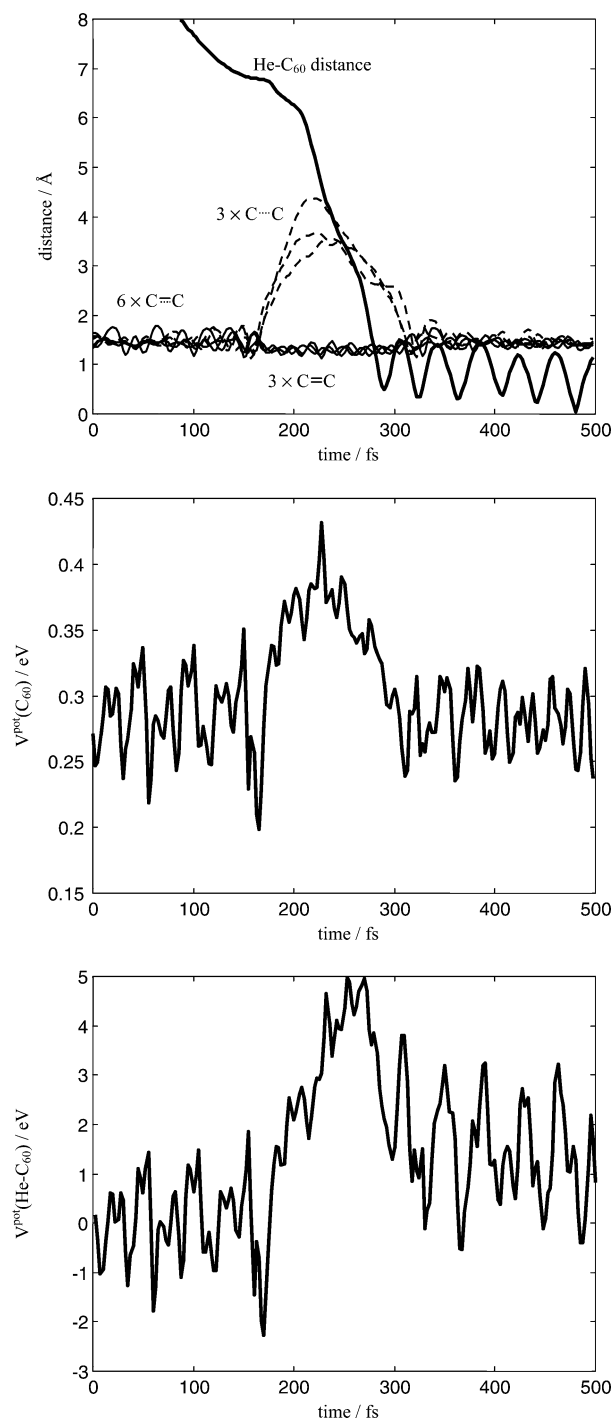


Figure 1. (a) Opening of a C₆₀ buckyball and diffusion of a He atom into the fullerene. During the window formation, the C–C distances of the 6-ring change significantly. While 3 C–C bonds are broken (dashed curves) the remaining 3 C–C bonds (solid curves) become more stiff, i.e., change from single to double bond character. (b) Potential energy of the C₆₀ buckyball during the window opening and diffusion of a He atom into the fullerene. The origin is set to the 0 K energy of C₆₀ in a vacuum. During the window formation, the breaking of the 6-ring leads to an increase in potential energy of about 0.1 eV. The energy profile corresponds to the trajectory shown in (a). (c) Potential energy related to the interaction of the helium atom being inserted and the C₆₀ for the trajectory illustrated in (a). The origin is set to the average energy value corresponding to the situation in which the helium atom is outside of the C₆₀. During the insertion process, a barrier of roughly 5 eV is crossed. The barrier for the reverse process is about 4 eV.

exhibit strong fluctuations. The opening of the window is initiated by the dissociation of one of these bonds. Though the

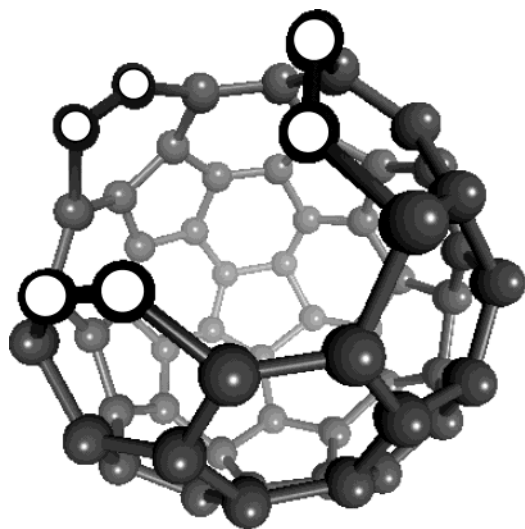


Figure 2. Snapshot of a C₆₀ fullerene during the opening of a window. The carbon atoms of the 6-ring, which is broken are highlighted.

remaining C–C bonds of the two carbon atoms, which were separated become stiffer, the next but one bonds of the 6-ring are destabilized. The dissociation of these two bonds was observed to start only 5–25 fs later. As a consequence of the breaking of 3 C–C bonds of a 6-ring, the remaining 3 bonds exhibit a double bond character. The related bond lengths are typically reduced by about 0.1 Å. The resulting metastable formation is illustrated in Figure 2.

The energy required for the opening of a 6-ring of the C₆₀ buckyball may be monitored from the potential energy related to the C–C interactions only. For this purpose, snapshots from the trajectory illustrated in Figure 1a were taken. While the positions of the carbon atoms were kept constant, the He atoms were cut. The resulting potential energy curve is shown as a function of time in Figure 1b. During the opening of the window the potential energy related to the C–C interactions of the C₆₀ was found to increase by around 0.1 eV. At the simulation temperature of 1000 K this corresponds to only 1.2 $k_B T$.

The lifetime of the opening of a window varied from 50 to 150 fs. Within this period there is a chance of He atom diffusion into the C₆₀ molecule. This is indeed the most critical part of the incorporation process. During path sampling a large number of trajectories were obtained, in which the opening of the 6-ring occurs, but the He atom fails to enter the C₆₀ molecule.

The insertion of He in C₆₀ was addressed in theoretical studies prior to the present work.^{13,19} Therein, a single helium atom and a C₆₀ molecule was used as the simulation system. The investigations were based on minimum energy path calculations assuming the He–C₆₀ distance as the reaction coordinate. On the basis of this approach the spontaneous opening of a window cannot be assessed. Patchkowski et al. constructed a series of model transition states for helium insertion. Therein the opening of zero, one, and two C–C bonds was considered.¹³ The energy barriers derived from these models are more than 5 eV over those obtained from experiment, indicating that the right transition state and thus the correct mechanism could not be found. The path sampling simulations presented in the present work start from a modeled transition state as well. However, in the course of sampling iterations, the generated trajectories converge toward regions in trajectory space that correspond to favorable insertion routes. As a consequence, the presented pathways may be considered as optimized with respect to their likelihood to occur in nature. In Figure 1c the potential energy profile related to the interaction of the C₆₀ and the helium atom

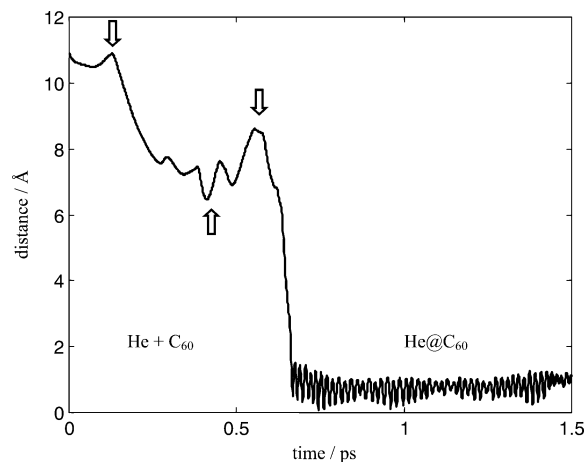


Figure 3. Distance of the center of the fullerene molecule and the He atom, which is being incorporated taken from a representative trajectory. The arrows indicate collisions with other He atoms of the gas atmosphere.

being incorporated is shown. The barrier observed for this pathway is around 5 eV, the average taken of all sampled trajectories is 5 ± 1 eV. We interpret the closeness to the experimental value of 3.5 eV⁸ as an indicator that the helium incorporation routes obtained from our simulations are realistic.

We wish to point out that the mechanisms of incorporation by bombardment of C₆₀ with single helium atoms does not necessarily reflect the pathway observed in a bath of helium atoms at high pressure. In the first case, the energy required for the possible opening of a window in C₆₀ needs to be taken from the kinetic energy of the approaching helium atom. In a heat bath, the opening of the window may happen spontaneously and can thus occur before the helium atom is inserted.

From the collection of trajectories of successful incorporation events we found the helium insertion to be initiated by a series of collisions of He atoms (Figure 3). Collisions of atoms in the gas happen quite frequently. What makes the incorporation a rare event is the need for the impact to occur in such a way that one He atom is pushed through the window of the C₆₀. In more general terms, the kinetic energy required to pass the reaction barrier is taken from the heat bath. After crossing the barrier, the reactants drop into the product state and hence (re-)gain kinetic energy. To remain in this state, the reactants must dissipate their kinetic energy to degrees of freedom other than the reaction coordinate. In our simulations, the inserted He atom was found to enter the fullerene, pass through the center and get reflected from the opposite side of the buckyball molecule. In a few cases this collision failed to absorb enough kinetic energy and the He atom was expelled from the C₆₀. More often, we observed the He atom to be trapped. Its kinetic energy is too low to exit the C₆₀ and the He oscillates in the fullerene cage (Figure 3).

Conclusions

A mixed quantum/classical molecular dynamics study of the pressure-induced helium incorporation into C₆₀ was presented. Therein the limitation of the process being rare was overcome by applying the path sampling method. The analysis is based on a large number of trajectories, each exhibiting the desired event. The trajectory sampling was initiated from preparing a dynamical pathway of helium incorporation into C₆₀. This did not involve the preparation of dissociated C–C bonds, which could act as a window facilitating helium permeation. However, after only a few tens of iterations, path sampling quickly

converged toward trajectories in which 3 C—C bonds of a 6-ring were temporarily broken and re-formed after the helium atom passed into the C₆₀ molecule (Figures 1a and 2). From this the strong preference of the window mechanism may be concluded. Because helium is the smallest noble gas atom, the opening of a window is expected to be even more favored for the heavier noble gas atoms.

The combination of mixed quantum/classical models with path sampling molecular dynamics simulation appears perfectly suited for the study of reactions in complex systems. The mechanistic analysis benefits from not being biased by predefinition of a reaction coordinate. Instead, the reaction coordinate may be obtained as a result from the simulations.

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