# Mechanism of fullerene hydrogenation by polyamines: *Ab initio* density functional calculations

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We use *ab initio* density functional calculations to study the microscopic mechanism underlying the recently demonstrated hydrogenation of the $C_{60}$ fullerene by diethylenetriamine reagent. Our results indicate that the optimal monoaddition reaction is exothermic, involving an $\approx 0.5$ eV high activation barrier associated with the simultaneous docking of the polyamine functional group and H transfer to $C_{60}$. Our calculated vibrational frequencies can be used to experimentally confirm the presence of hydroamination adducts as a necessary prerequisite for successful hydrogenation of $C_{60}$.

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Chemical functionalization of well defined carbon nanostructures such as $C_{60}$ is an important direction to obtain a new class of molecules with intriguing properties. Among the many ways to chemisorb atomic hydrogen on $C_{60}$ and other $sp^2$ bonded nanocarbons, the recently introduced chemical reaction using high boiling polyamines appears as most promising.[1–3] Alternative ways of hydrogenation using surfactants leave undesirable residue behind, and physical treatments such as ultrasonication[4,5] often cause structural damage. In spite of the demonstrated efficiency of the polyamine-based hydrogenation, the microscopic mechanism underlying this reaction remains obscure.

In this Brief Report, we investigate the microscopic hydrogenation mechanism of $C_{60}$ by diethylenetriamine (DETA) reagent using *ab initio* density functional calculations. By exploring the DETA-$C_{60}$ potential-energy surface, we identify the structural changes and energetics along the optimal monoaddition reaction pathway. We find the hydrogenation to be exothermic, involving an $\approx 0.5$ eV high activation barrier associated with the simultaneous docking of the functional group and H transfer to $C_{60}$. We also provide the vibrational spectrum of the hydroamination adduct to assist in the experimental confirmation of a successful hydrogen transfer to $C_{60}$.

Our total-energy calculations, as well as global and constrained structure optimization studies, have been performed using the density functional theory (DFT) within the local density approximation (LDA), utilizing first-principles pseudopotentials, as implemented in the DMOL3 (Refs. 6 and 7) and SIESTA (Ref. 8) software. In our DMOL3 (Ref. 6) calculations, we used the parametrization of Perdew and Wang[9] for the exchange-correlation energy and a double numerical basis set, including polarization functions on all atoms (DNP). The DNP basis set corresponds to a double-$\zeta$ quality basis set with a *p*-type polarization function added to hydrogen and *d*-type polarization functions added to heavier atoms, and is comparable to 6–31G** Gaussian basis sets,[10] providing a better accuracy at a similar basis set size.[6] In the generation of the numerical basis sets, we used a global orbital cutoff of 3.7 Å. The energy tolerance in the self-consistent field calculations was set to $10^{-6}$ hartree. Optimized geometries were obtained without symmetry constraints, using an energy convergence tolerance of $10^{-5}$ hartree and a gradient convergence of $2\times10^{-3}$ hartree/Å. In our SIESTA (Ref. 8) calculations, we used an optimized double-$\zeta$ basis set with polarization orbitals,[11] the Perdew-Zunger[12] parametrization of the exchange-correlation functional, and norm-conserving *ab initio* pseudopotentials[13] in their fully separable form.[14] We used 0.01 eV/Å as a strict gradient convergence criterion during structure optimization.

The optimized geometries of DETA and $C_{60}$ reagents are shown in Fig. 1(a). In order to better understand the mechanism of hydrogen transfer from DETA to the $C_{60}$ molecule, we found it convenient to separate the DETA docking process from the hydrogen transfer between the docked polyamine and $C_{60}$. We considered different docking approaches, with the DETA axis normal or tangential to the $C_{60}$ surface. We found the latter, corresponding to DETA approaching with its end rather than its center, to provide the most favorable conditions for hydrogen transfer.

Our SIESTA results for the DETA docking process are shown in Fig. 1. To understand the energetics of the reaction, we performed a structure optimization of the DETA-$C_{60}$

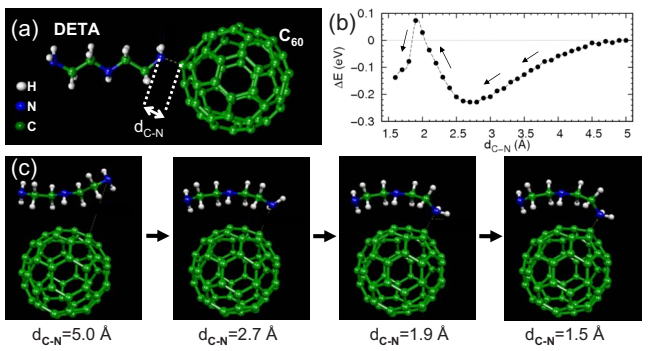


FIG. 1. (Color online) (a) Schematic of DETA docking to the $C_{60}$ molecule with the distance $d_{C\text{-}N}$ between the terminal nitrogen of DETA and the closest C atom of the fullerene defining the reaction coordinate. (b) Total-energy change $\Delta E$ of the system as a function of $d_{C\text{-}N}$, taking the separated system as a reference. (c) Snapshots of the docking process, including the initial, transition, and final states.

 

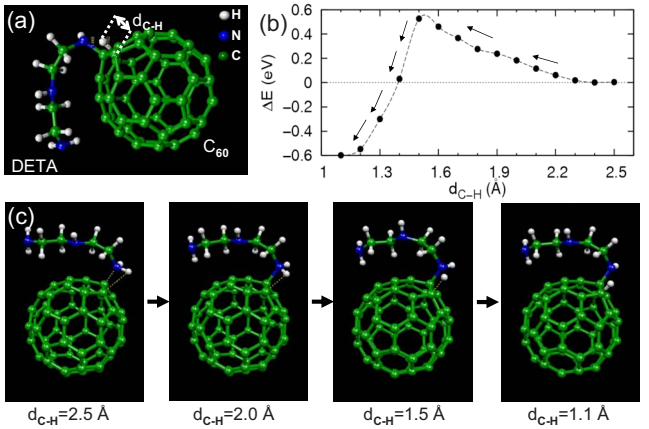


FIG. 2. (Color online) (a) Schematic of the hydrogen transfer from the docked DETA to the $C_{60}$ molecule, with the distance $d_{C\text{-}H}$ between the terminal hydrogen of DETA and the closest C atom of the fullerene defining the reaction coordinate. (b) Total-energy change $\Delta E$ of the system as a function of $d_{C\text{-}H}$, taking the initial-state system as a reference. (c) Snapshots of the hydrogen transfer process, including the initial, transition, and final state.

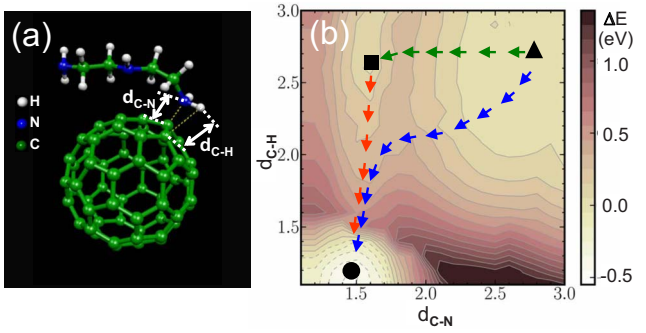


FIG. 3. (Color online) (a) Schematic of the DETA-$C_{60}$ geometry associated with the simultaneous docking and H transfer process, characterized by the key variables $d_{C\text{-}N}$ and $d_{C\text{-}H}$. (b) Potential-energy surface of the DETA-$C_{60}$ complex as a function of $d_{C\text{-}N}$ and $d_{C\text{-}H}$. ▲ labels the physisorbed state, ■ the docked state, and ● labels the final state, with a H atom transferred from DETA to $C_{60}$.

complex, constraining the distance between a terminal nitrogen atom in DETA and an atom of the $C_{60}$ cage, as seen in Fig. 1(a). The total energy of the system as a function of the carbon-nitrogen distance $d_{C\text{-}N}$ is depicted in Fig. 1(b). Our results indicate that DETA gains about 0.2 eV as it approaches from infinity and physisorbs near the fullerene. We note that physisorption with the DETA axis tangential to the surface, as seen in Fig. 1(c), is comparable in energy to a geometry with a radial orientation of the DETA molecule. Since in the latter case the overlap of DETA and $C_{60}$ orbitals is less favorable for hydrogen transfer, we concentrate on the tangential adsorption geometry in the following. From the physisorbed state, DETA has to cross an activation barrier to chemisorb on the $C_{60}$ cage at $d_{C\text{-}N} \approx 1.6$ Å, characteristic of a covalent bond. We found no ionic interactions between DETA and the $C_{60}$ cage during the entire docking process since results of our Mulliken population analysis indicate absence of substantial charge transfer. Snapshots of the intermediate structures occurring during the docking process are shown in Fig. 1(c). The most striking change is the conformational change in the DETA molecule from its equilibrium linear geometry to a structure that adopts the curvature of the $C_{60}$ cage upon adsorption.

To understand the transfer of a hydrogen atom from the chemisorbed DETA to the $C_{60}$ cage, we performed a set of global optimizations starting with the docked structure, constraining the distance between a terminal hydrogen atom and a C atom in the cage, $d_{C\text{-}H}$, as seen in Fig. 2(a). The energetics of this hydrogen transfer reaction is depicted in Fig. 2(b). In view of the stability of the H-N bond, the initial energy investment of ≈0.5 eV to detach the H atom from DETA is rather small. The main reason for the reduced activation energy is the fact that bond breaking occurs simultaneously with the formation of a new bond in this concerted mechanism. The net energy gain during this exothermic reaction amounts to 0.6 eV. Following a simple Redhead's analysis of the migration temperature on solid surfaces,[15] we estimate the temperature necessary to overcome the energy barrier to be $T \approx 200$ K [$E=0.06$ T kcal/(mol K)], consistent with the experimental observation that polyamines aminate $C_{60}$ at room temperature.[2]

To better characterize the transition state seen in Fig. 2, we have explored the saddle-point region using the linear synchronous transit (LST) and quadratic synchronous transit (QST) methods as implemented in DMOL3, combined with a standard conjugate gradient optimization of the transition state structure. The transition state has one negative eigenvalue in the Hessian matrix corresponding to an imaginary vibrational frequency of $-1581.7$ $cm^{-1}$. Animation of this frequency shows that this mode corresponds to the vibration of the H atom transiting between the terminal N atom of DETA and the closest C atom of the $C_{60}$ cage leading to the energetically favored 1,2-hydroamination adduct.[16] The atomic structure corresponding to the transition state was confirmed by an independent intrinsic reaction coordinate calculation.

To explore the possibility of different reaction paths and to decide if the optimum reaction path is a one-step or a multistep process, we investigated the energetics of the system by varying the values of $d_{C\text{-}N}$ and $d_{C\text{-}H}$ from 1 to 3 Å by performing 400 independent calculations. The potential-energy surface shown in Fig. 3 represents total energies of the DETA-$C_{60}$ complex that have been optimized with the only constraints being fixed values of $d_{C\text{-}N}$ and $d_{C\text{-}H}$. Our results indicate that the transition from the physisorbed state of DETA to the final state of the reaction, where a hydrogen atom has been transferred to the $C_{60}$ cage, may occur either as a single-step process with a slightly higher activation barrier or a two-step process with a lower activation barrier. In particular, the shallow potential well of docked DETA in the $d_{C\text{-}H}$ direction suggests an efficient H transfer. Preferred reaction paths are indicated by arrows in Fig. 3.

Careful analysis of our computational results helped us to elucidate the chemical bonding changes associated with hydrogen transfer from DETA to the $C_{60}$ cage. The recently proposed hydrogenation mechanism of $C_{60}$ by polyamines[3] suggests the hydrogen transfer to be initiated by an electron transfer from the polyamine to the fullerene followed by a

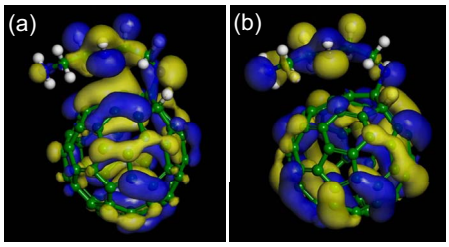


FIG. 4. (Color online) Optimal docking geometry of DETA on $C_{60}$ superimposed with the wave-function isosurface for (a) the HOMO and (b) the HOMO-1. The wave-function phase is distinguished by color.

proton transfer from the N-H group to $C_{60}$. Close inspection of our results suggests an alternative mechanism, involving neutral hydrogen transfer from DETA to $C_{60}$ during a concerted motion reaction. Both in the previously proposed and the present theoretical scenario, the transfer of hydrogen is promoted by the charge-density lobe near the N atom in the nonbonding highest occupied molecular orbital (HOMO) and second highest occupied molecular orbital (HOMO-1) orbitals of the DETA molecule, depicted in Fig. 4. In either case, the final product is a neutral $C_{60}H$ radical and a neutral N-centered polyamine radical that is missing one hydrogen.

To allow for an independent confirmation of our findings

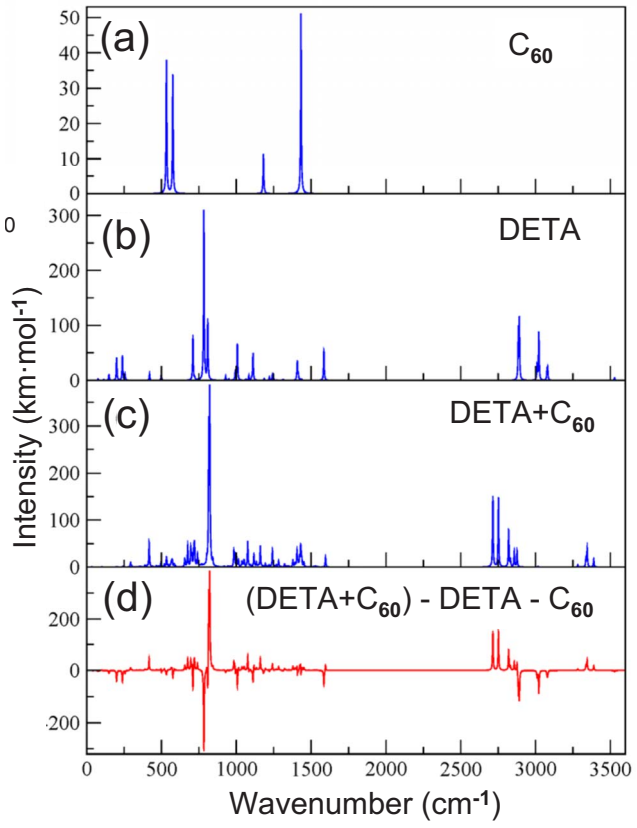


FIG. 5. (Color online) Vibrational frequency spectra of (a) pristine $C_{60}$, (b) DETA, and (c) DETA docked on $C_{60}$. (d) The difference spectrum of DETA docked on $C_{60}$ and pristine DETA and $C_{60}$. The spectra have been convoluted with a Lorentzian function with the full width at half maximum (FWHM) of 5.0 $cm^{-1}$.

TABLE I. Frequencies of the vibrational normal modes of pristine $C_{60}$ and DETA (in $cm^{-1}$).

| Structure | This work | Expt.[a] | Vibrational mode |
|---|---|---|---|
| $C_{60}$ | 531.7 | 521.0 | C-C-C bending |
| | 575.0 | 571.8 | Radial breathing mode |
| | 1180.3 | 1178.0 | Sym. C-C stretching |
| | 1431.4 | 1424.8 | Asym. C-C stretching |
| DETA | 199.9, 238.6 | | Twisting of terminal $NH_2$ groups |
| | 419.8 | | Scissoring of central C-N-C group |
| | 498.8 | | Scissoring of central N-C-C group |
| | 710.0 | | Wagging of central H atom |
| | 783.2, 809.0 | | Wagging of terminal $NH_2$ groups |
| | 1006.5 | | Asym. C-C stretching |
| | 1111.5 | | Asym. stretching of central C-N |
| | 1407.7 | | Rocking of central H atom |
| | 1585.0 | | Scissoring of terminal $NH_2$ |
| | 2885.3, 2891.4 | | Sym. stretching $\alpha$C-H |
| | 3010.0, 3021.8 | | Sym. stretching of terminal C-H |
| | 3076.9, 3081.1 | | Sym. stretching of $\alpha$C-H |
| | 3528.1 | | Asym. stretching of terminal N-H |

[a]Reference 18.

regarding the formation of a DETA-$C_{60}$ complex as a necessary prerequisite of the hydrogenation reaction, we performed a vibrational analysis of this adduct, as well as isolated $C_{60}$ and DETA. Calculated frequencies should allow a quantitative comparison with infrared spectra, thus confirming or disproving the presence of the complex. We constructed the Hessian matrix for the final state of the hydrogenation reaction, labeled as ● in Fig. 3(b), using finite differences of the analytical forces with respect to the atomic positions. The normal modes and their frequencies were obtained by diagonalizing the Hessian matrix in mass-weighted Cartesian coordinates. Calculated vibrational frequency spectra of isolated $C_{60}$ and DETA, along with the DETA-$C_{60}$ complex, are shown in Fig. 5. The numerical frequency values along with the normal-mode assignments are listed in Table I. Comparison of our calculated vibrational frequencies with observed spectra for $C_{60}$ in Table I indicates that the theoretical values can be trusted with an uncertainty $\Delta\nu \lesssim 10$ $cm^{-1}$.

In presence of DETA, successful hydrogen transfer to the $C_{60}$ cage cannot be identified by the occurrence of H-related vibrations since both H-$C_{60}$ and DETA exhibit similar H-C stretch modes at frequencies near $\approx 3000$ $cm^{-1}$. Comparison of vibrational modes of the complex in this frequency range, shown in Fig. 5(c), with that of the individual reactants, shown in Figs. 5(a) and 5(b), indicates a frequency shift associated with the coupling between DETA and the $C_{60}$ cage.

The frequency shift can be best judged by considering the difference vibrational spectrum between the complex and isolated DETA and $C_{60}$ adducts. In the complex, we find the band of H-C modes strongly redshifted by $\lesssim 500$ $cm^{-1}$. The coupling between DETA and the $C_{60}$ cage is also reflected in the wagging mode of terminal $NH_2$ groups of the DETA, which are blueshifted by 20–30 $cm^{-1}$ due to the stronger coupling between the terminal N and $C_{60}$ in the complex.

So far, we have considered the energetically favorable 1,2-hydroamination adduct as the final state of the reaction. Experimentally, the hydroamination reaction has been reported to lead to $C_{60}H_{18}$, suggesting the docking and subsequent desorption of many DETA radicals on a single $C_{60}$ cage.[2] If $C_{60}H_{18}$ is the final product, there must be a way to desorb DETA without significantly detaching the chemisorbed hydrogen or modifying the $C_{60}$ cage. In view of the strong bond between the terminal N atom of DETA and the $C_{60}$ cage, we see no simple way to desorb an isolated amine radical. Indirect experimental evidence that this step is not easy may be seen in the fact that DETA chemistry is not gentle, as it requires high temperatures of 205–380 °C for successful hydrogenation of $C_{60}$ by polyamines.[17] A possible way to detach polyamines while keeping hydrogen chemisorbed may involve simultaneous adsorption and docking of more than one polyamine at adjacent sites. Following successful hydrogen transfer to the $C_{60}$ cage, the two terminal nitrogens of adjacent DETA radicals could form a covalent bond while simultaneously desorbing from $C_{60}$. During this concerted reaction the energy gain associated with the N-N bond formation may be able to offset the energy cost of DETA desorption. In this case, DETA dimers should be observed following a successful hydrogenation.

In conclusion, we used *ab initio* density functional calculations to study the microscopic mechanism underlying the recently demonstrated hydrogenation of $C_{60}$ by diethylenetriamine reagent. Our results indicate that the optimal monoaddition reaction is exothermic, involving an $\approx 0.5$ eV high activation barrier associated with the simultaneous docking of the functional group and H transfer to the $C_{60}$ fullerene. We propose to compare our calculated vibrational frequencies with IR spectra to identify the presence of hydroamination adducts, which we propose as a necessary prerequisite for successful hydrogen transfer to $C_{60}$.

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