



Low-energy hydrogen uptake by small-cage C_n and $C_{n-1}B$ fullerenes

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ABSTRACT

We present a theoretical study of the hydrogen uptake capability of carbon fullerene cages C_n and their boron-doped heterofullerene equivalents $C_{n-1}B$, with $n = 20, 40,$ and 60 , irradiated by hydrogen atoms in an impact energy range of $0.1–100$ eV. In order to predict exohedral and endohedral hydrogen captures as well as the scattering probability of hydrogen for various cage types and sizes, we perform quantum-classical molecular dynamics (QCMD) calculations using the self-consistent-charge density-functional tight-binding (SCC-DFTB) method. Maximum endohedral hydrogen capture probabilities of 20% for $n = 60$ and 14% for $n = 40$ are found at impact energies close to 15 eV for both C_n and $C_{n-1}B$ systems. For $n = 20$, however, endohedral capture is observed at a maximum of 2%, while the exohedral capture reaches a maximum of 5% both at 15 eV. Similar results for the hydrogen capture are obtained by classical molecular dynamics based on the ReaxFF potential. Finally, the stopping cross section per carbon atom from the QCMD simulations for all cage sizes displays a linear dependence on the projectile velocity with a threshold at 0.8 eV, and extrapolates well to the available theoretical data.

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1. Introduction

A better understanding of hydrogen capture processes in C_n fullerenes and $C_{n-1}B$ heterofullerenes by hydrogen irradiation is of scientific interest and of importance for hydrogen storage applications. Carbon-based fullerene cages which store hydrogen atoms endohedrally ($H@C_n$) have promising applications in nano-electronics and hydrogen storage devices [1–5] due to their thermal and electronic properties [6–8]. The I_h-C_{60} buckminsterfullerene molecule is the most studied cage isomer because of its high synthetic yield [6,9], low production cost [10], and high symmetry. For example, solid C_{60} was exposed in an experiment [11] to 50 bar of hydrogen pressure in a temperature range of 350–440 K and the reaction products were analyzed by *in-situ* and *ex-situ* techniques to investigate the interactions of hydrogen with the carbon cages, obtaining the $C_{60}H_{18}$ and $C_{60}H_{52}$ fullerenes. Hydrogenated C_{60}

isomers have been studied theoretically in terms of energetics and molecular structure [12] and a meta-genetic algorithm was developed for predicting exohedrally hydrogenated fullerene isomers [13]. The endohedral encapsulation mechanism was also studied by bombardment of C_{60} with heavier filling ions, e.g. He^+ , Li^+ , Ne^+ , and Ar^+ [14–18], where charge transfer was identified as the leading process for ion impact energies below 100 eV, while the endohedral complex formation was only dependent on the relative translational energy of the projectile rather than on the internal energy of the cage. We note that the usual metal-containing endohedral metallofullerenes are normally produced in carbon plasma, where metal oxide is added to the carbon laser target or electrode [19].

An accurate study of the hydrogen uptake kinetics in fullerene requires computationally expensive *ab initio* approaches, since the accuracy of reaction rates depends critically on the magnitude of reaction barriers and adsorption energies. Furthermore, one needs to perform the analysis using a statistically significant number of dynamical trajectories, making such studies computationally formidable when the Density Functional Theory (DFT) method is used in quantum-classical molecular dynamics (QCMD). In this work we therefore use a QCMD methodology based on the

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computationally more economical density-functional tight-binding (DFTB) method [20], which is an approximate DFT approach. It is roughly two to three orders of magnitude faster than conventional DFT. It has been applied successfully in many dynamic studies, for example for the investigation of the self-assembly of endohedral metallofullerenes for cooling gas and metal-carbon bonding [21], for the synthesis of boron-nitride nanostructures in arc plasma [22], for the deuterium retention in boronized and oxidized carbon surface [23], for the detection of hydrogen by graphene [24] and borophene [25] sheets, and for C_{20} isomer and fullerene cage isomer energetics and molecular geometries [26]. Classical molecular dynamics simulations of fullerene formation in carbon plasma based on the reactive force field (ReaxFF) potentials [27] were found to be in qualitative agreement with DFTB-based QCMD simulations [28].

In addition to fullerene hydrogenation and hydrogen uptake, an interesting subject of investigation is the boronization of the carbon fullerene cage, $C_{n-m}B_m$. The first step for this process is the $C_{n-1}B$ isomer, which was synthesized experimentally by evaporation of boron-doped graphite rods in a modified fullerene reactor [5,29]. We investigate quantitatively the effect of a single-atom substitution in C_n by boron as a first step towards more extensive application of boronization in C_n . We are interested in defects in the fullerene π -conjugation, which directly affect hydrogen uptake capabilities of the cage. Hydrogen endohedral carbon fullerenes with a B impurity (e.g. $H@C_{59}B$) have been studied previously, experimentally [29,31] and theoretically [30], due to its promising electronic properties in semiconducting and photoelectric devices [29]. One or two C atoms in C_{60} can be substituted by B using laser vaporization of a graphite pellet containing hexagonal boron nitride (h-BN) [29]. The exposure of C_{60} fullerenes to boron vapor results in the formation of gas-phase $C_{59}B$, becoming most efficient when a pulsed laser vaporization cluster source is used [32]. The molecular and electronic structure of $H@C_{59}B$ has been previously studied theoretically and analyzed in terms of regioselectivity [33]. The electronic structure of the $C_{59}B$ and $H@C_{59}N$ molecules were reported [30], emphasizing that a single B substitution induces a radical electronic state between the fully occupied HOMO and the unoccupied LUMO, resulting in an increased chemical reactivity relative to a pure carbon fullerene cage. The radial distribution function of hydrogen on C_{20} and $C_{19}B$ molecules at different temperatures was investigated by Monte Carlo simulations [34], where the maximum of the gravimetric storage capacity of H for $C_{19}B$ was 7.6% at 273 K, similar to the result for C_{20} (7.2%). Furthermore, the fully functionalized $C_{40}H_{40}$ cage was predicted to be thermodynamically and kinetically more stable than the fully hydrogenated $C_{60}H_{60}$ cage [35], which was related to the fact that the thermodynamic stability of their pure carbon “parent” molecules was increasing with decreasing cage size.

Our primary motivation for the present study is to obtain a quantitative understanding of the dynamics of hydrogen atom capture on either the fullerene wall (exohedral capture) or inside of the cage (endohedral capture) for both C_n and $C_{n-1}B$. The scattering dynamics of H by fullerenes allows one to extract information about properties like the hydrogen energy loss and the electronic stopping power, which we also report in this work. Ehlich et al. [36] studied collisions of C_{60} with Ne and He atoms at low impact energies (1–200 eV in the center-of-mass frame) by Classical Molecular Dynamics (CMD) and their analysis of inelastic scattering and fragmentation of the fullerene showed a bimodal distribution. Schlathölter et al. [37] studied experimentally the electronic stopping cross section for He^+ colliding with C_{60} in the 2.50–25 keV ion energy range, showing a considerable loss of projectile kinetic energy transferred to the target through electronic excitations.

Opitz et al. [38] carried out a proton impact study on fullerenes at high collision energies (above 20 keV) using the TRIM code [39], concluding that there was a velocity dependence of the ionization cross-section which matched up the electronic stopping power caused by electronic excitations of C_{60} . Kunert and Schmidt [17] investigated the kinetic energy loss of protons colliding with fullerenes in the 2.50–12.50 keV energy range, reporting a constant energy loss for impact energies in the 6.25–12.50 keV range. This behavior was in contrast to the results of Moretto-Capelle et al. [40] for the same system, where the free electron gas model of Lindhard and Scharff [41] was used. They found that the C_{60} molecule behaved similar to a carbon foil, since both had similar absolute stopping cross sections per atom. All these theoretical studies used classical force fields or simplified models, and to the best of our knowledge, no QCMD simulations on the subject have been reported thus far.

In the present work, we study low-energy hydrogen impacts (capture and scattering) at C_n and $C_{n-1}B$ fullerenes with cage size $n = 20, 40,$ and 60 atoms, employing a DFTB-based QCMD approach. The QCMD simulations are performed in an impact energy range between 0.1 and 100 eV to estimate the amount of hydrogen atoms captured by the cages, the energy loss distributions of the scattered H atoms, and its stopping cross section. The interesting and important problem of a H_2 capture and release by fullerenes is beyond the scope of this paper, and is the purpose of a future work.

The paper is organized as follows. We briefly describe the computational method in Section 2. The QCMD results obtained for hydrogen irradiation simulations of C_n and $C_{n-1}B$ targets, as well as a discussion of the results, are reported in Section 3. Finally, in Section 4, we present concluding remarks. Additional details of our calculations and a comparison of the QCMD with Classical Molecular Dynamics (CMD) results (using the ReaxFF potentials) are given in the Supplementary Material.

2. Computational approach

The SCC-DFTB method is an approximation to the conventional density functional theory (DFT), where only valence electron interactions are explicitly considered [20,42]. The Kohn-Sham (KS) equations are solved for the total valence electronic densities and energies using a predetermined Hamiltonian, which is constructed on the basis of a two-center approximation with optimized pseudo-atomic orbitals as basis functions. Tabulated Hamiltonian matrix elements, overlap integrals, and repulsive splines fitted to DFT dissociation curves of reference molecular systems are contained in the Slater-Koster parameter files (SKF) [20,43] and are read into computer memory only once during the QCMD simulation runs. In this study, we utilize the SKF pair potentials set for materials science simulations (MATSCI-03) [42]. The electronic energies are calculated as a sum over the occupied KS single-particle energies and the sum over diatomic repulsive energy contributions. SCC corrections, as implemented in the DFTB + code [44], are included in the total energy via an iteration procedure that converges to a new electron density at every time step during a QCMD simulation, where the convergence is improved by using an electronic temperature of 1000 K. This approach was used in our previous work on the study of electronic properties of the 2D nanomaterial borophene, proposed for a boron based hydrogen detector [25], showing excellent agreement with first principles DFT calculations. SCC-DFTB as implemented in the publicly available DFTB+ code [44] version 1.2 is used throughout this work for all geometry optimizations and QCMD simulations.

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