

Dehydrogenation of graphane by external driving

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Abstract. The dehydrogenation of graphane due to external harmonic driving is studied by molecular dynamics simulation. It is found that the dehydrogenation can be initiated by harmonic driving of carbon atoms with as small amplitude as 0.02 Å, if the driving frequency is somewhat above the small-amplitude vibration frequency of the C-H bond. Thus, a novel mechanism for the dehydrogenation of graphane is reported.

1. Introduction

Graphene, a zero band gap two dimensional material where carbon atoms are arranged in a honeycomb lattice, presents outstanding properties by itself and when combined with other organic molecules. Its chemical [1], electrical [2], mechanical [3, 4, 5] and optical [6] characteristics have attracted a tremendous attention of researchers over the last decade. Graphene can be effectively modified via the surface functionalization, in which the carbon atoms are converted from sp^2 to sp^3 hybridization to bond with the adatoms. Hydrogenation has been widely accepted as an efficient way to manipulate the electronic [7], magnetic [8], and mechanical [9] properties of graphene. Moreover, hydrogenated graphene is a very promising structure for hydrogen storage. Previously, it was shown that a gravimetric density of 8% could be achieved for corrugated graphene with satisfactory reversibility [10]. In the case of carbon nanofibers and carbon nanotubes, hydrogen uptake of 1.5 wt.% per 1000 m² g⁻¹ was observed under ambient temperature and pressure conditions [11].

About a decade ago, hydrogenation of a graphene sheet has been successfully achieved, and a hydrocarbon often referred to as “graphane” was experimentally fabricated [12]. In this structure, each hydrogen (H) atom is bonded to a carbon atom (C) alternately on each side of the graphene sheet. Each C atom in this conformation is pulled out of the plane by an H atom at a small distance, forming a not perfectly flat structure in contrast to graphene. Previously, in [13, 14, 15, 16, 17, 18], the role of nonlinear localized modes or discrete breathers (DBs) in the dehydrogenation process was discussed. DBs can affect various properties of crystals, and they were found in different carbon structures [19, 20]: in graphene [21, 22, 23], diamond [24] and carbon nanotubes [25, 26]. The existence of DBs in graphane was shown for the first time by molecular dynamics (MD) simulation [15] and was proved



later by ab-initio simulation [18]. It was shown that spontaneously exited at elevated temperatures DBs can lead to a detachment of a hydrogen atom from a graphene sheet.

Recently the effect of external harmonic driving on the nonlinear dynamics of graphene has been analyzed, and it has been observed that DBs can assist energy transfer from driven atoms to a graphene nanoribbon [27]. In the present work, MD simulation of harmonically driven graphene is studied to analyze the possibility of dehydrogenation under such conditions.

2. Model description and simulation procedure

In figure 1a the structure of graphane is presented with black and white circles, showing carbon and hydrogen atoms, respectively. The computational cell used in the present simulation included 12×12 primitive translational cells and was subjected to periodic boundary conditions. According to the considered stoichiometry, each primitive cell includes two C and two H atoms. The mass of hydrogen atom is equal to 1 g/mole or $1.66 \cdot 10^{-27}$ kg.

The simulations are performed using the LAMMPS package with the adaptive intermolecular reactive empirical bond order (AIREBO) potential [28] to describe the interatomic interaction in graphane. The AIREBO potential was successfully used to study various properties of hydrocarbon systems, e.g., in [13, 14, 15]. The equations of motion for atoms were integrated numerically using the fourth-order Verlet method with a time step of 0.1 fs.

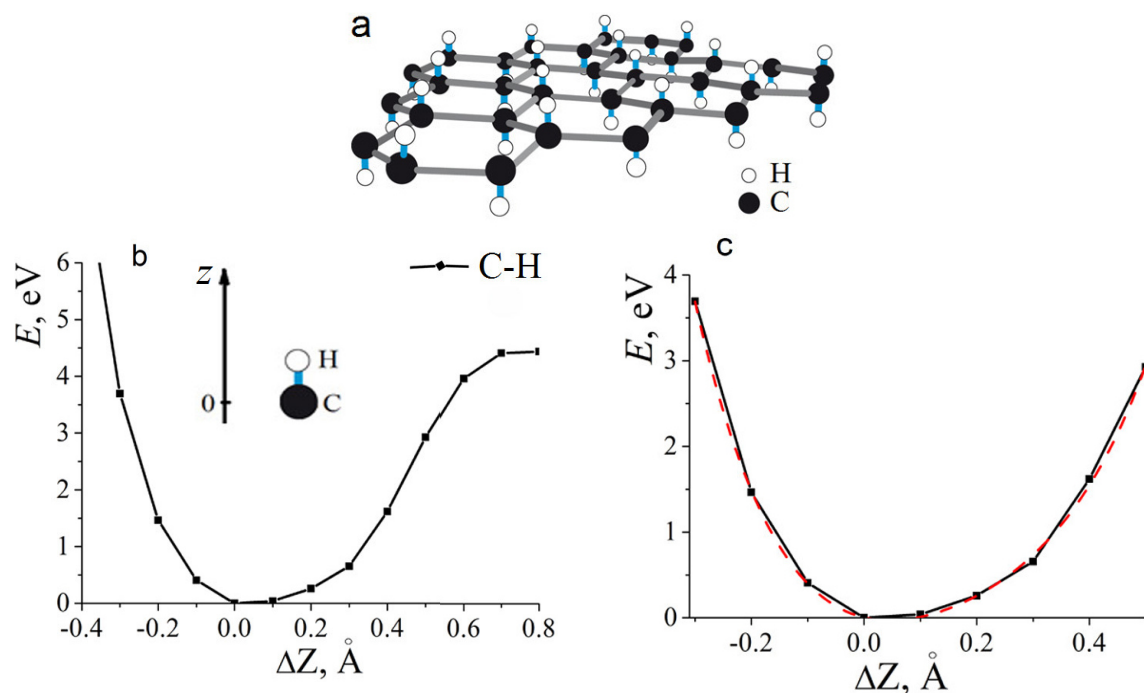


Figure 1. (a) Structure of graphane crystal and (b,c) potential energy of C-H bond as a function of the displacement from the equilibrium distance between C and H atoms. Inset in (b) shows the single degree of freedom model. In (c) polynomial fit (2) of C-H bond energy is shown by the red dashed line.

All carbon atoms are forced to move in accordance with the harmonic law

$$\Delta Z_C(t) = A \sin(\omega t), \quad (1)$$

where ΔZ_C is the displacement of C atoms from their initial positions in the direction normal to the graphane sheet, A and ω are the driving amplitude and frequency, respectively. At $t = 0$ all H atoms have zero initial displacements from equilibrium positions and zero initial velocities.

Since all C atoms move synchronously, assuming that the hydrogen atoms also move synchronously, the problem under consideration can be reduced to analyzing a single degree of freedom model, schematically shown in the inset of figure 1b. The model includes single C atom moving according to the law (1) and H atom attached to it by the C-H bond. It is instructive to calculate the interaction energy E between H and C atoms. This was done by a quasistatic change of the distance ΔZ between C and H atoms and calculating the potential energy of their interaction. The result is shown in figure 1b. Close to the energy minimum, a potential function can be approximated by the polynomial function

$$E = a_0 + a_1\Delta Z + a_2(\Delta Z)^2 + a_3(\Delta Z)^3 + a_4(\Delta Z)^4, \quad (2)$$

with the coefficients $a_0=0$, $a_1=-1.586278$, $a_2=19.52419$, $a_3=-37.08165$, $a_4=55.90332$. This function is plotted in figure 1c by a red dashed line together with numerical data (black symbols and a black line). We have also found that the frequency of the small amplitude oscillations of the C-H bond is about $\omega^* = 80$ THz.

3. Simulation results and discussion

Figure 2 shows the energy of the C-H bond as a function of time for the driving amplitude $A=0.04$ Å and three driving frequencies: 80, 86, and 90 THz in panels a to c, respectively. As it can be seen, for 80 THz the bond is quasiperiodically pumped with energy up to a value of 2.2 eV, and then its energy decreases to zero. This regime is always observed at sufficiently small driving amplitudes and frequencies not close to the resonance value ω^* . At high driving amplitudes or driving frequency close to ω^* , the H atom separates from the C atom. From figures 2 b, c it is seen that the disorption energy is approximately equal to 5.3 eV.

Figure 3 shows the maximal energy of the C-H bond as a function of the driving frequency for four driving amplitudes. For the driving amplitude $A=0.01$ Å the C-H bond does not break. For higher driving amplitudes, bond breaking takes place for driving frequencies around 90 THz. The higher the driving amplitude, the wider is the driving frequency range where bond breaking occurs.

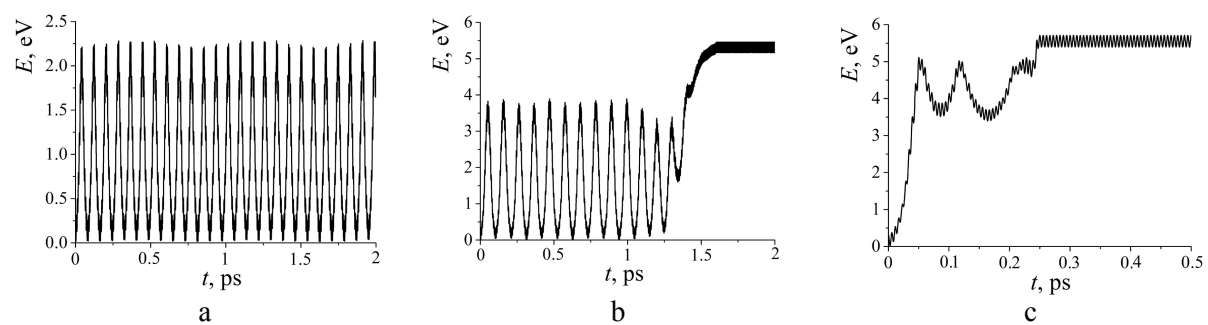


Figure 2. Energy of the C-H bond as a function of time for driving amplitude $A=0.04$ Å and for driving frequencies (a) 80 THz, (b) 86 THz, and (c) 90 THz.

4. Conclusions

Molecular dynamics simulations confirmed that dehydrogenation of graphene can be initiated by external driving at frequencies slightly above the frequency of small-amplitude vibration of the C-H bond. The presented work describes a new mechanism for the dehydrogenation of graphene which may be important for solving the problem of transportation and storage of hydrogen.

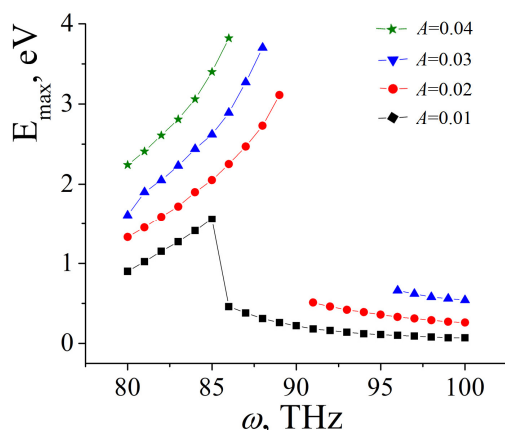


Figure 3. Maximal energy of C-H bond as the function of driving frequency for four driving amplitudes.

Acknowledgments

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