Accelerating Dynamics of H on Graphene by Coadsorbates

Manh-Thuong Nguyen[†] and Pham Nam Phong*,[‡]

[†]Center for Computational Physics, Institute of Physics, Vietnam Academy of Science and Technology, 10 Dao Tan Street, Hanoi 100000, Vietnam

[‡]School of Engineering Physics, Hanoi University of Science and Technology, Hanoi 100000, Vietnam

ABSTRACT: There are several factors that affect the dynamics of adsorbed hydrogen atoms on a carbon surface. Using density functional calculations we show that coadsorption can be a highly influential factor. The diffusion of hydrogen adsorbed on graphene is explored in the presence of H-containing molecules. Without coadsorbates the diffusion barrier of H on graphene is 0.94 eV, while with water/ammonia it is 0.85/0.12 eV. The low barrier in the case of ammonia is attributed to the formation of a stable intermediate state NH_4, while such a stable state is not found in the case of water. In addition, hydrogen fluoride, hydrogen sulfide, arsine, and phosphine were also considered. We found that stronger hydrogen−hydride bonds lead to lower diffusion barriers of H on graphene.
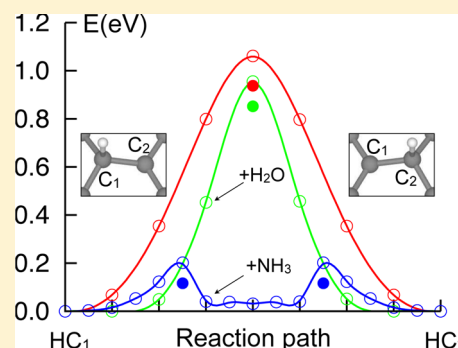
INTRODUCTION

The adsorption of hydrogen on carbon surfaces is a problem related to numerous practical uses, and understanding the formation of H-adsorbed structures is of central importance toward those applications such as hydrogen storage,[1,2] electronics,[3,4] or catalysis.[5,6] Hydrogen structures on a carbon surface, like many other on-surface nanostructures, are determined by a subtle competition between the stability and mobility of the adsorbates,[7,8] and these two factors have been addressed in studies. Various factors controlling the diffusion barrier of hydrogen atoms have been identified, for example, surface curvature,[9] doping,[10] strain,[11] and coadsorption.[12,13] The coadsorption effect here is referred to systems of graphene-bound hydrogen atoms and other atomic or molecular species in the vicinity of each other, where they form a very stable structure compared with structures in which they are apart.

We shall look at the coadsorption of chemically adsorbed hydrogen and physical adsorbates at graphene, a widely studied carbon surface. Small hydrides, namely, water, ammonia, arsine, hydrogen sulfide, phosphine, and hydrogen fluoride are chosen as model coadsorbates of H on graphene. Of these coadsorbates, ammonia shows a remarkable strength of assisting H diffusion by not only reducing its activation barrier from 0.94 to 0.12 eV but also guiding H to perform long jumps. In most cases, significantly reduced barriers are in the cases of XH_3 hydrides and connected to the formation of XH_4 intermediates. We shall interpret the correlation between the diffusion barrier and hydrogen−hydride binding energy.

METHODOLOGY AND MODELS

We have carried out spin-polarized plane-wave density functional calculations using Quantum ESPRESSO code.[14] We employed the exchange-correlation density functional developed by Perdew, Burke, and Ernzerhof (PBE)[15] and the ultrasoft pseudopotentials developed by Vanderbilt.[16] A kinetic energy cutoff of 50 Ry was applied. We used the charge analysis method of Bader[17] as encoded by Tang and coworkers.[18] The climbing image nudged elastic band (CI-NEB) approach was adopted to estimate diffusion barriers.[19] Force convergence thresholds of 10^{-3} and 10^{-4} au are used for structural and elastic band optimizations, respectively. Zero point energies (ZPEs) were determined from normal modes. A graphene unit cell of 4×4 periodicity was employed. This unit cell was shown to be large enough to minimize the interaction between H an its periodic images.[20] We used a k-point grid of $3 \times 3 \times 1$ for Brillouin zone sampling in self-consistent and of $6 \times 6 \times 1$ in postprocessing calculations.

RESULTS AND DISCUSSION

We first study energetic properties of H and water/ammonia coadsorption on graphene by determining the interaction energy between two coadsorbates (Table 1). Here we found the interaction energy of H and water/ammonia on graphene,

Table 1. Interaction Energy ΔE_{int} between Adsorbed H and Water/Ammonia on Graphene Adsorption Energy ΔE_{ads} of Water/Ammonia on Graphene[a]

	water	ammonia
ΔE_{int} (eV)	−0.08	−0.14
ΔE_{ads} (eV)	−0.02	−0.03
E_a (eV)	0.85	0.12

[a]Diffusion energy barrier of H on graphene with the water/ammonia coadsorbate, corrected with ZPE.

$\Delta E_{int} = E(GHM) + E(G) - E(GH) - E(GM)$, where E is the total energy and GHM, G, GH, and GM are systems of graphene with H and water/ammonia, of graphene, of graphene with H, and of graphene with a water/ammonia molecule, respectively. A negative energy means H and water/ammonia will be coadsorbed. Theoretical understanding of H adsorbed on graphene is very well documented;[2,21] H is chemisorbed and most stabilized on top of the carbon atoms. Water or ammonia is, on the other hand, physisorbed on graphene, and the adsorption site selectivity is not obvious, as reported in independent studies. Here we found the adsorption energy of water/ammonia on graphene, $\Delta E_{ads} = E(GM) - E(G) - E(M)$, with $E(X)$ being the energy of system X, is $-0.02/-0.03$ eV, in agreement with previously reported PBE values of $-0.03/-0.04$ eV.[22] By geometric property and bonding charge analyses shown below, the interaction between the adsorbed H and water/ammonia is mainly attributed to the hydrogen bond CH⋯X (X = O, N in water and ammonia), and interaction energy was found to be $-0.08/-0.14$ eV. This shows that ammonia binds more strongly to the adsorbed H atom. It has also been shown that CH⋯O (O in H_2O) is weaker than CH⋯N (N in NH_3) using semiempirical[23] or ab initio[24] calculations.

For the diffusion of H from one carbon C_1 site to an adjacent C_2 site, we considered two possibilities: First, from C_1 site H can get close enough to water/ammonia, forming $[H_3O]^+$/$[NH_4]^+$-like intermediates; then, from these intermediates a H jumps to C_2, and second, H directly jumps from C_1 to C_2 positions without forming such intermediates. Our calculations predict that with ammonia the first possibility is more likely, while the second possibility is more likely with water. Figure 1
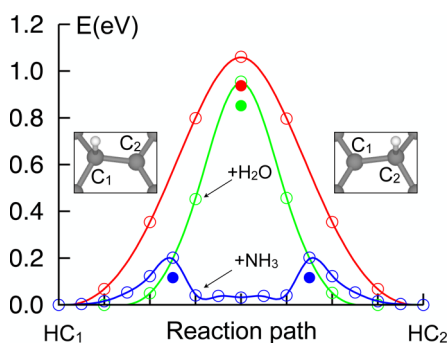

Figure 1. Potential energy profile of a H (in white, inset) atom on graphene diffusing from a C_1 adsorption site to an adjacent C_2 one, without (red) and with water (green) or ammonia (blue). The filled circles show energies corrected with ZPE.

shows the potential energy profile along the diffusion path of H without and with water/ammonia. One can see that both water and ammonia reduce the reaction barrier of H; however, the latter appears to be much more influential. Quantitatively, without coadsorbates, ZPE-corrected diffusion barrier of H is 0.94, which is reduced to 0.85 and 0.12 eV with water and ammonia, respectively. This leads to a significant difference in the diffusion coefficient D. The diffusion coefficient is given by $D = \frac{1}{3}d^2\nu_0 \exp(-E_a/k_BT)$, where prefactor 1/3 accounts for the fact that H can jump from one C site to one of the three adjacent sites; $d = C_1C_2$ bond length; ν_0 is computed from normal modes of the transition state (TS) and the initial state (IS).[25] In the case of NH_3 coadsorption, D will further be divided by 2 because from the intermediate state (IM) H can

jump back to the initial C site. At room temperature, we found D of 1.5×10^{-19}, 1.05×10^{-18}, and 3.53×10^{-7} cm^2/s in the case of without coadsorbates, with H_2O, and with NH_3, respectively. This shows that NH_3 can increase the diffusivity of H by 12 orders of magnitude.

To relate geometric and electronic properties to the stability and then the diffusion barrier of H, we now look at the three systems in their IS. As listed in Table 2, the CH bond length is

Table 2. Structural Properties of H without and with Water/Ammonia on Graphene[a]

			water			ammonia		
	C_1H	C_1C_2	C_1H	C_1C_2	H⋯O	C_1H	C_1C_2	H⋯N
IS	1.13	1.50	1.13	1.50	2.49	1.14	1.49	2.14
TS	1.34	1.47	1.34	1.48	2.24	1.39	1.46	1.37

[a]C_1/C_2 is the bonding partner of H in the IS/FS. The bond lengths are in angstroms.

not changed by water but slightly elongated by ammonia, consistent with the previous finding that the H−water interaction is weaker than the H−ammonia one. Moreover, the C_1C_2 bond in the case of H adsorption or H−water coadsorption is longer than in the H−ammonia adsorption case, and the strength of the C_1C_2 bond is directly influenced by the CH bond; this implies that the CH bond is stronger in the former case. Significantly, the lengths of two hydrogen bonds CH⋯O and CH⋯N are 2.49 and 2.14 Å, respectively. In Figure 2a,b we show the induced charge density, $\Delta\rho =$
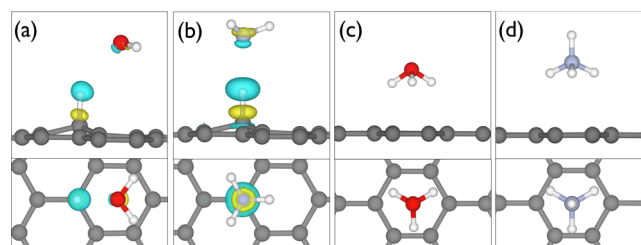

Figure 2. Induced electron density of H−graphene systems with water (a) and ammonia (b). Isosurface value set at 0.002 au, depletion in light blue, and accumulation in yellow. Intermediate structures are (c) $[H_3O]^+$- and (d) $[NH_4]^+$-like. Side view: top panels; top view: bottom panels.

$\rho(GHM) - \rho(GH) - \rho(M)$, where $\rho(X)$ is the electron density of the system X. Obviously, the hydrogen-bonding characteristic is more pronounced in the CH⋯N bond. In addition, Bader analyses predict an amount of 0.15/0.07 electrons transferred from ammonia/water to the H−graphene. As pointed out in previous studies,[20,26] electron doping leads to the weakening of H adsorption graphene. For these reasons, intermolecular interactions weaken the CH bond more strongly in the case of ammonia coadsorption. Indeed, the CH bond length is 1.13 and 1.14 Å with water and ammonia, respectively. In the TS, the C_1C_2 bond is shorter (and closer to the C−C bond length of pristine graphene) in the case of ammonia than that in the case of water coadsorption. Importantly, the CH⋯N distance of 1.37 Å, which is much shorter than the CH⋯O distance of 2.24 Å, indicates that a chemically strong bond is already formed between the two coadsorbates H and NH_3.

A clear difference between the diffusion pathways of H with water and ammonia is the involvement of an intermediate state.

Obviously, a $[NH_4]^+$-like intermediate (Figure 2d), which is almost as stable as the IS structure (Figure 2b), is crucial for the diffusion of H. This is not held in the case of water coadsorption because the intermediate H_3O (Figure 2c) is much less stable than the IS (Figure 2a), by ~3.0 eV.

To this end, the bonding strength of H and ammonia or H and water on graphene is an important factor that affects the diffusion barrier of H on graphene. We have carried out further calculations for other coadsorbates. Figure 3 shows the H-
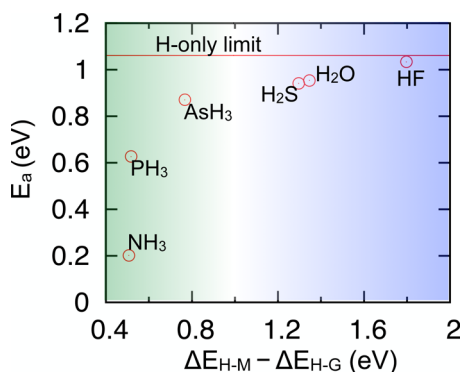

Figure 3. Diffusion barrier of H on graphene, E_a, against the difference between ΔE_{H-M} and ΔE_{H-G}.

diffusion barrier, E_a, against $\Delta E_{H-M} - \Delta E_{H-G}$, where ΔE_{H-M} is the binding energy between the molecule M (M = NH_3, PH_3, AsH_3, H_2S, H_2O, and HF) and a H atom in the gas phase and ΔE_{H-G} is the adsorption energy of the H atom on graphene. Needless to say, $\Delta E_{H-M} - \Delta E_{H-G}$ implies the relative strength of H−M and H−graphene bonds; a positive/negative value of $\Delta E_{H-M} - \Delta E_{H-G}$ means H binds more/less strongly to graphene than to M molecule. Data in Figure 3 reveal that stronger H−M binding leads to lower diffusion barrier of H. With XH_3 coadsorbates, we found stable $[XH_4]^+$-like intermediates. "Stable" here means the total energy of the intermediate state, which is larger than that of the $XH_3\cdots$H-graphene structure by an amount ΔE_{IM-IS}, lower than the diffusion barrier of H on graphene without any coadsorbate. ΔE_{IM-IS} is 0.05, 0.35, and 0.59 eV in the case of X = N, P, and As, respectively. These intermediates lead to much lower barriers. More details regarding the $[XH_4]^+$-like intermediates are provided below. The XH_2 or XH coadsorbates do not form stable $[XH_3]^+$- or $[XH_2]^+$-like intermediates, which are not involved in H diffusion. These coadsorbates just slightly reduce the diffusion barrier of H.

Given the significance of stable $[XH_4]^+$-like intermediates, we now look closer to their properties by comparing them to gas-phase $[XH_4]^+$ ions. Table 3 shows that the XH_4 complexes are positively charges. In specific, the NH_4, PH_4, and AsH_4 complexes are charged by 0.86, 0.25, and 0.22|e|, respectively. They can thus be denoted as $[XH_4]^{+\delta}$. The charges $+\delta$ here are

Table 3. Bader Charges and Average Bond Lengths of $[NH_4]^+$-like Intermediates on Graphene (Denoted as $[XH_4]^{+\delta}$) Compared with That of Gas-Phase $[NH_4]^+$ Ions

	q(|e|)	XH (Å)
$[NH_4]^{+\delta}/[NH_4]^+$	+0.86/+1	1.04/1.03
$[PH_4]^{+\delta}/[PH_4]^+$	+0.25/+1	1.49/1.41
$[AsH_4]^{+\delta}/[AsH_4]^+$	+0.22/+1	1.59/1.50

correlated well with the XH bond length change from $[XH_4]^{+\delta}$ to gas-phase $[XH_4]^+$. As listed in Table 3, the NH bond length is changed by 0.01 Å, while the PH and AsH bond lengths are changed by 0.08 and 0.09 Å, respectively. This also implies that the likeness of $[XH_4]^{+\delta}$ and $[XH_4]^+$ can act as an indicator for the stability of $[XH_4]^{+\delta}$ and for the reduction of H diffusion.

■ SUMMARY

We have studied effects of coadsorbed molecules on the diffusion of H adsorbed on graphene. Significantly, ammonia can reduce the diffusion barrier by ~0.82 eV, while water shows a slight influence. This is related to the formation of a stable intermediate state NH_4. We found a trend for the hydride-assisted diffusion barrier of H against the binding strength between H and hydrides relative to the H-graphene binding energy. This work provides an example of how to manipulate the dynamics of adsorbed H atoms on carbon surfaces by means of coadsorption.

■ AUTHOR INFORMATION

Corresponding Author
*E-mail: phong.phamnam@hust.edu.vn. Phone: (84) 438692801. Fax: (84) 438693498.

ORCID ⓘ
Pham Nam Phong: 0000-0003-3367-5920

Notes
The authors declare no competing financial interest.

■ REFERENCES

(1) Ströbel, R.; Garche, J.; Moseley, P.; Jörissen, L.; Wolf, G. Hydrogen storage by carbon materials. *J. Power Sources* **2006**, *159*, 781−801.
(2) Tozzini, V.; Pellegrini, V. Prospects for hydrogen storage in graphene. *Phys. Chem. Chem. Phys.* **2013**, *15*, 80−89.
(3) Balog, R.; et al. Bandgap opening in graphene induced by patterned hydrogen adsorption. *Nat. Mater.* **2010**, *9*, 315−319.
(4) Kim, K.; Bae, D.; Kim, J.; Park, K.; Lim, S.; Kim, J.-J.; Choi, W.; Park, C.; Lee, Y. Modification of Electronic Structures of a Carbon Nanotube by Hydrogen Functionalization. *Adv. Mater.* **2002**, *14*, 1818−1821.
(5) Wang, J.; Zhong, H.-X.; Wang, Z.-L.; Meng, F.-L.; Zhang, X.-B. Integrated Three-Dimensional Carbon Paper/Carbon Tubes/Cobalt-Sulfide Sheets as an Efficient Electrode for Overall Water Splitting. *ACS Nano* **2016**, *10*, 2342−2348.
(6) Yeh, T.-F.; Cihlář, J.; Chang, C.-Y.; Cheng, C.; Teng, H. Roles of graphene oxide in photocatalytic water splitting. *Mater. Today* **2013**, *16*, 78−84.
(7) Wang, Y.; He, J.; Liu, C.; Chong, W. H.; Chen, H. Thermodynamics versus Kinetics in Nanosynthesis. *Angew. Chem., Int. Ed.* **2015**, *54*, 2022−2051.
(8) Bieri, M.; Nguyen, M.-T.; Gröning, O.; Cai, J.; Treier, M.; Aït-Mansour, K.; Ruffieux, P.; Pignedoli, C. A.; Passerone, D.; Kastler, M.; Müllen, K.; Fasel, R. Two-Dimensional Polymer Formation on Surfaces: Insight into the Roles of Precursor Mobility and Reactivity. *J. Am. Chem. Soc.* **2010**, *132*, 16669−16676.
(9) Kayanuma, M.; Nagashima, U.; Nishihara, H.; Kyotani, T.; Ogawa, H. Adsorption and diffusion of atomic hydrogen on a curved surface of microporous carbon: A theoretical study. *Chem. Phys. Lett.* **2010**, *495*, 251−255.
(10) Lueking, A. D.; Psofogiannakis, G.; Froudakis, G. E. Atomic Hydrogen Diffusion on Doped and Chemically Modified Graphene. *J. Phys. Chem. C* **2013**, *117*, 6312−6319.
(11) McKay, H.; Wales, D. J.; Jenkins, S. J.; Verges, J. A.; de Andres, P. L. Hydrogen on graphene under stress: Molecular dissociation and

gap opening. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2010**, *81*, 075425.

(12) Nguyen, M.-T.; Phong, P. N.; Tuyen, N. D. Hydrogenated Graphene and Hydrogenated Silicene: Computational Insights. *ChemPhysChem* **2015**, *16*, 1733−1738.

(13) Erni, R.; Rossell, M. D.; Nguyen, M.-T.; Blankenburg, S.; Passerone, D.; Hartel, P.; Alem, N.; Erickson, K.; Gannett, W.; Zettl, A. Stability and dynamics of small molecules trapped on graphene. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2010**, *82*, 165443.

(14) Giannozzi, P.; et al. QUANTUM ESPRESSO: a modular and open-source software project for quantum simulations of materials. *J. Phys.: Condens. Matter* **2009**, *21*, 395502.

(15) Perdew, J. P.; Burke, K.; Ernzerhof, M. Generalized Gradient Approximation Made Simple. *Phys. Rev. Lett.* **1996**, *77*, 3865−3868.

(16) Vanderbilt, D. Soft self-consistent pseudopotentials in a generalized eigenvalue formalism. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1990**, *41*, 7892−7895.

(17) Bader, R. F. *Atoms in Molecules: A Quantum Theory*; Oxford University Press: Oxford, 1990.

(18) (a) Tang, W.; Sanville, E.; Henkelman, G. A grid-based Bader analysis algorithm without lattice bias. *J. Phys.: Condens. Matter* **2009**, *21*, 084204. (b) Code: Bader Charge Analysis. http://theory.cm.utexas.edu/bader/.

(19) Henkelman, G.; Uberuaga, B. P.; Jónsson, H. A climbing image nudged elastic band method for finding saddle points and minimum energy paths. *J. Chem. Phys.* **2000**, *113*, 9901−9904.

(20) Nguyen, M.-T.; Phong, P. N. Atomic Transport at Charged Graphene: Why Hydrogen and Oxygen Are So Different. *ChemistrySelect* **2017**, *2*, 2797−2802.

(21) Casolo, S.; Løvvik, O. M.; Martinazzo, R.; Tantardini, G. F. Understanding adsorption of hydrogen atoms on graphene. *J. Chem. Phys.* **2009**, *130*, 054704.

(22) Hamada, I. Adsorption of water on graphene: A van der Waals density functional study. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2012**, *86*, 195436.

(23) Bonchev, D.; Cremaschi, P. C-H Group as proton donor by formation of a weak hydrogen bond. *Theor. Chim. Acta* **1974**, *35*, 69−80.

(24) Mondal, S.; Chandra Singh, P. Noble gas induced surprisingly higher stability of π hydrogen bonded complex: comparative study of hydrogen bonded complexes of HKrCCH and HCCH with H_2O, NH_3, CH_3OH and CH_3NH_2. *RSC Adv.* **2014**, *4*, 20752−20760.

(25) Vineyard, G. H. Frequency factors and isotope effects in solid state rate processes. *J. Phys. Chem. Solids* **1957**, *3*, 121−127.

(26) Huang, L. F.; Ni, M. Y.; Zhang, G. R.; Zhou, W. H.; Li, Y. G.; Zheng, X. H.; Zeng, Z. Modulation of the thermodynamic, kinetic, and magnetic properties of the hydrogen monomer on graphene by charge doping. *J. Chem. Phys.* **2011**, *135*, 064705.