Structure and stability of hydrogenated carbon atom vacancies in graphene

Marina Casartelli\textsuperscript{a}, Simone Casolo\textsuperscript{a}, Gian Franco Tantardini\textsuperscript{a,b} and Rocco Martinazzo\textsuperscript{a}\textsuperscript{b}\textsuperscript{*}

\textsuperscript{a} Dipartimento di Chimica, Università degli Studi di Milano, via Golgi 19, 20133 Milan, Italy.
\textsuperscript{b} Istituto di Scienza e Tecnologia Molecolari, Consiglio Nazionale delle Ricerche, via Golgi 19, 20133 Milan, Italy.

Adsorption of hydrogen atoms to a carbon atom vacancy in graphene is investigated by means of periodic first principles calculations, up to the fully hydrogenated state where six H atoms chemically bind to the vacancy. Addition of a single H atom is highly exothermic and barrierless, and binding energies remain substantial for further hydrogenation, with a preference towards structures with the least number of geminal pairs. Thermodynamic analysis shows that defective graphene is extremely sensitive to hydrogenation, with the triply hydrogenated anti-structure prevailing at room temperature and for a wide range of H\textsubscript{2} partial pressures, from $\sim 1$ bar down to $< 10^{-20}$ bar. This structure has one unpaired electron and provides a spin-half local magnetic moment contribution to graphene paramagnetism. Comparison of our results with recent TEM, STM and $\mu$-SR experiments suggest that carbon atom vacancies may actually be hydrogenated to various degrees under varying conditions.

I. INTRODUCTION

Defects in graphene such as ad-species or missing carbon atoms (commonly referred to as “$\pi$ vacancies”) play important roles in charge transport, magnetism and chemistry of graphene. Most often they are unavoidable byproducts of the fabrication process (for instance, when reducing graphene oxide) but they can also be deliberately introduced by cold plasma treatment, heavy-ion bombardment or high-energy electrons, in the latter case employing the same transmission-electron-microscopy (TEM) setup used to image the surface\cite{1}. Vacancies and other under-coordinated sites are known to be starting sites for metal-induced etching\cite{2-4}, to Vacancies and other under-coordinated sites are known to be starting sites for metal-induced etching\cite{2-4}, to show an enhanced chemical reactivity\cite{5, 6} and to incorporate dopant species\cite{7}.

All the above defects introduce semi-localized $\pi$ “midgap” states which decay slowly (as $\sim 1/r$) from the defect position\cite{8-10} and host itinerant electrons which are free to move on one of the two sublattices of which graphene is made (the one opposite to the sublattice containing the closest defect). As such, they act as resonant scatterers and determine graphene conductivity at zero and finite carrier densities\cite{11-15}, provide spin-half semi-local magnetic moments detectable by magnetometry experiments\cite{16, 17} and bias graphene chemical reactivity towards specific lattice positions\cite{18, 19}.

Carbon atom vacancies occupy a special position in this context since, in addition to the above $\pi$ “midgap” state, they have $\sigma$ dangling bonds arising upon atom removal from the breaking of the C-C bonds which held the lattice atom in place. In the bare vacancy a structural (Jahn-Teller) distortion occurs that removes two of these bonds, as predicted by theory\cite{20, 26} and confirmed by scanning tunneling microscopy (STM)\cite{10, 27, 31} and TEM\cite{32} experiments. Even though is not clear whether such distortion is static or dynamic\cite{20}, thereby breaking or preserving the threefold symmetry of the ideal vacancy, it leaves one single $\sigma$ electron which is free to couple with the above $\pi$ one. As a result, the ground state of a bare vacancy is a triplet, but the singlet with one spin flipped (which is only $\sim 0.2$ eV higher in energy) can be easily accessed if ripples in the graphene sheet or interaction with a substrate are taken into account\cite{20}. However, the newly formed C-C bond is rather weak, as expected from its length ($\sim 2.0$ Å) which is much larger than a typical single C-C bond, and can in principle be broken by addition of $\text{e.g.}$ H atoms. Thus, under typical laboratory conditions, the question arises to what extent hydrogenation occurs, and which structures result. This question is of interest in many respects: the degree of hydrogenation (and their relative arrangement) determines the residual magnetic moment of the defect, influences the structure of the carbon atom vacancy (which might be locked in a distorted geometry\cite{32} or be statically symmetric), and possibly explain recent muon spin-resonance ($\mu$-SR) experiments suggesting formation of geminal adducts of muonium species on singly hydrogenated vacancies.

In this paper we study the structure, the stability, the magnetic properties and the mechanism of the carbon mono-vacancy hydrogenation, from one to six hydrogen atoms, and discuss the relevance of our results to a number of experimental investigations. The paper is organized as follows: Section II outlines the method used and the adopted computational set-up, Section III discusses the results and Section IV summarizes and concludes.

II. THEORY

The structure and the energetics of single and multiple hydrogenated vacancies in graphene was investigated in periodic models with plane-wave density functional theory (DFT) as implemented in the Vienna \textit{ab initio} simulation package (VASP)\cite{33, 34}. The size of the supercell, as well as the relevant computational parameters (k-mesh, plane wave cutoff for expanding the wavefunc-
tion and the charge density, etc.) were selected by preliminary tests similarly to our recent work\cite{26} and chosen to be a good compromise between the need of minimizing interactions between periodic images and computational cost. The exchange-correlation effects were included via the Perdew-Burke-Ernzerhof\cite{35, 36} functional within the generalized gradient approximation, in its spin-polarized form. Kohn-Sham orbitals were expanded in a plane-wave basis set limited to a 500 eV energy cutoff and core electrons described by the projector augmented-wave\cite{37, 38} method. A 6 × 6 supercell with 20 Å vacuum between periodic replica normal to the surface was used, and the Brillouin zone was sampled with a 6 × 6 × 1, Γ-centered k-point mesh; geometry relaxation was performed till the Hellman-Feyman forces on each atom decreased below 0.01 eV/Å.

Reaction energies for adsorbing \( n \) hydrogen atoms were computed as

\[
\Delta E_n = E_{VH_{n}} - E_V - E_{nH}
\]

(1)

where \( E_{VH_{n}} \) is the total energy of the \( n \)-times hydrogenated vacancy (denoted as \( VH_{n} \)), \( E_V \) that of the bare vacancy (in its ground-state) and \( E_{nH} \) is the reference state of \( n \) hydrogen atoms, \( E_{nH} = n E_H \). The latter, along with the molecular energy \( E_{H_{2}} \) to be introduced below, was obtained with a setup similar to that described above, using a Γ point calculation on a cubic cell with a 20 Å long side. Reaction energies for sequential adsorption, \( \Delta \Delta E_n \), were defined similarly as

\[
\Delta \Delta E_n = \Delta E_n - \Delta E_{n-1} = E_{VH_{n}} - E_{VH_{n-1}} - E_H
\]

(2)

(where, unless otherwise stated, \( \Delta E_{n-1} \) refers to the most stable \( n-1 \)-times hydrogenated state) and used to compare the relative strength of the different CH bonds which may form during the adsorption process. We also computed a few selected activation energies (barriers) following the nudged elastic bands method\cite{39} as implemented in VASP.

III. RESULTS

A. Structure and energetics

As mentioned in the introduction, a vacancy in graphene forms upon the extraction of a carbon atom which leaves three \( \sigma \) dangling bonds and one unpaired \( \pi \) electron on the lattice. The \( \sigma \) electrons are tightly localized on the sites which are nearest neighbors of the vacant one, while the \( \pi \) electron delocalizes on one of the two sublattices (similarly to the case of several monovalent chemisorbed species such as H and F) as a consequence of the aromatic character of the sublattice\cite{19}.

As a result, the bare vacancy is three-fold symmetric in a doubly-degenerate electronic state and undergoes a Jahn-Teller (JT) distortion, where two of the three carbon atoms above close a pentagon by forming a weak CC bond\cite{20, 26}, which may be referred to as JT-induced C-C bond. There are three such possibilities which differ in the identity of the carbon atom opposing the pentagon, the so-called apical atom. The remaining unpaired electrons give rise to singlet and triplet manifolds whose relative stability mainly depends on the height of such apical carbon atom above the surface\cite{26}, the planar triplet being most stable. Within the present theoretical approach the electronic ground state has ‘dirty’ magnetization \( M = 1.56 \mu_B \) because of both the allowance of fractional occupation and the spin-polarized framework (see discussion on this point on Ref. 26), but has an energy which is only few meV below that of the correct \( M = 2 \mu_B \) state. Thus, in the following we use this state as a reference state for the bare vacancy.

Adsorption of a first H atom is strongly exothermic, \( \Delta E_1 = -4.24 \) eV, and barrierless, as shown in Fig.\ref{fig1} where we plot the adsorption profile obtained when optimizing all the atom coordinates but the height of the hydrogen atom above the surface. The H atom binds to the apical C atom where much of the unpaired electron density resides, and a strongly covalent bond forms between the two (notice for comparison that a typical value for the CH binding energy is \( \sim 4 \) eV). The carbon atom moves slightly out of the plane (and correspondingly the CH bond gets tilted), suggesting that full \( sp^3 - sp^3 \) rehybridization of its valence orbitals occurs. This structure has one unpaired electron left, even though the computed magnetization \( (M = 0.56 \mu_B) \) is lower than one, for the same reasons mentioned above for the bare vacancy; indeed, the energy obtained upon constraining the magnetization to \( M = 1 \mu_B \) is only few meV higher.

When adsorbing a second H atom at the vacancy site a more complex scenario arises since the two adsorbates may bind to either the same C atom (geminal configuration) or two distinct C sites (dimeral configuration).
In the latter case, the two atoms may share the same (syn-) or the opposite (anti-) graphene face. All these processes are exothermic when referenced to H atoms [much more than H atom adsorption on the basal plane of graphene/graphite, $\Delta E = -0.97$ eV according to the most recent works[40]] but with a clear preference towards formation of an anti-dimer: $\Delta \Delta E_2 = -2.42, -3.09$ and $-3.34$ eV for the geminal, the syn- and anti-dimer respectively. Activation barriers are small and probably beyond the accuracy limits of the adopted computational approach, but suggestive of a fast adsorption kinetics: they are 22 meV for the geminal product and 21 meV for both dimers.

The above doubly-hydrogenated structures have different magnetic properties, with a net magnetization $M = 2.00 \mu_B$ for the anti-dimer and $M = 0.00 \mu_B$ for the geminal one (the syn- structure turns out to have $M = 0.00 \mu_B$ with two unpaired electrons, and is thus similar in many respects to the anti-isomer). This follows from the different binding processes involved. The first case corresponds overall to the addition of two H atoms on the weak JT C-C bond of the reconstructed vacancy, a process which breaks such C-C bond but leaves the two unpaired electrons of the bare vacancy unaltered. On the other hand, the geminal product may be thought as obtained by double addition to the apical C atom and corresponding saturation of its unpaired electron density. This is confirmed by the geometrical parameters of the optimized structures: the shortest C-C bond of the bare vacancy ($d_{CC} = 1.98$ Å; for comparison the remaining two bonds are 2.72 Å long) is almost unaffected in the geminal adduct ($d_{CC} = 2.06, 2.58, 2.58$ Å) while is largely increased (above the value of the longer bonds) in the dimer structures, $d_{CC} = 2.82, 2.72, 2.72$ Å and $d_{CC} = 2.80, 2.65, 2.65$ Å for the anti- and syn- structures respectively. Notice also that, among the latter, the syn-structure experiences an unfavorable H-H steric interaction which forces the system to additional relaxation and reduces its stability compared to the anti-one by $\sim 23$ meV.

Next, we consider adsorption of further hydrogen atoms to the three carbon atoms surrounding the vacancy, and their relative arrangements, see the schematics reported in Fig. 2 as a reference. Similarly to the sticking of the second H atom, three hydrogen atoms may have a geminal pair or sit on different sites. In the latter case they are considered as syn- when they all sit on the same face of the graphene sheet, and anti- otherwise. With four H atoms formation of a geminal pair is unavoidable, yet the arrangement of the remaining two atoms may be geminal or syn- / anti- dimer. The five and six atom cases parallel in a complementary way the single H and bare vacancy cases with just one possible arrangement.

The main results of this study can be summarized as follows. Among the three-atom adducts the anti-
structure is \( \sim 1.4 \) eV most stable than the geminal one \((\Delta \Delta E_3 = -3.82 \) eV vs. \( \Delta \Delta E_3 = -2.43 \) eV\) and the syn-structure is not binding at all. The two structures have one unpaired electron (we obtained \( M = 1.00 \mu_B \) in both cases) either because the additional H atom breaks the JT C-C bond and leaves one unpaired electrons (if we start from the doubly hydrogenated geminal structure and form the VH\(_3\) geminal one) or because it couples (at low spin) with one of the two unpaired electrons of the anti- dimer structure and form either the geminal or the anti- VH\(_3\) structure. In any case, the JT C-C bond no longer exists and the C-C distances are considerably increased \((d_{CC} = 2.75, 2.72, 2.62 \) Å in the geminal and \( d_{CC} = 2.86, 2.85, 2.81 \) Å in the anti- structure\). The energetics follows consistently: starting from the most stable anti- dimer structure addition of a third H atom is easier (and more exothermic) when a \( \sigma \) bond is formed on the apical atom than when \( H \) binds to an already hydrogenated site to form a geminal product, since in the latter case a bond is formed with the \( \pi \)-like electron left unpaired on that site.

Among the possible four-fold hydrogenated structures the syn- is slightly more stable than the anti- \((\Delta \Delta E_4 = -2.39 \) eV vs. \( \Delta \Delta E_4 = -2.38 \) eV\) and definitely more stable than the geminal one \((\Delta \Delta E_4 = -1.57 \) eV starting from the geminal VH\(_3\) structure\). At this stage all the four unpaired electrons initially available upon vacancy formation get saturated with hydrogen, and both the syn- and the anti- structures are non-magnetic, different from the geminal one which has two unpaired electrons (we obtained \( M = 0.00 \mu_B \) in the first two cases and \( M = 2.00 \mu_B \) in the latter). Further hydrogenation is remarkably less exothermic \((\Delta \Delta E_5 = -1.69 \) eV and \( \Delta \Delta E_6 = -1.21 \) eV\) since it necessarily requires further breaking of the aromaticity, and produces magnetic structures with one and two unpaired electrons, respectively. Indeed, compared to the bare vacancy, full hydrogenation requires (i) saturation of the three \( \sigma \) dangling bonds, (ii) saturation of the \( \pi \) (midgap) state and (iii) breaking of two C-C double bonds (a first C-C double bond needs to be broken when hydrogenating the VH\(_4\) anti- or syn- structure).

Fig. 3 gives an overview of the energetics of the hydrogenated carbon atom vacancy in graphene. There, the H-atom binding energies (or affinities) \( D_n = -\Delta \Delta E_n \) to form the most stable \( n \)-times hydrogenated structure from the most stable \( n-1 \) isomer are plotted as a function of \( n \). Such structures are the anti- structures, the \( n = 4 \) case being an exception which shows a slight \((\sim 0.01 \) eV\) preference towards the syn- structure. For comparison, the values of the H binding energy in several different situations are given as horizontal lines; such values comprise the adsorption energy to the basal graphene plane\(^{[30]}\), the binding energy of the secondary H atom to form a para- dimer\(^{[19]}\) (a similar result holds for the orto- dimer\(^{[19]}\)) and the binding energy for adsorption on an armchair edge and a zig-zag edge which are \( H \) terminated\(^{[11]}\). The latter represents the largest energy gain when adsorbing \( H \) on pristine graphene and compare rather well with the binding energies of the fourth and fifth hydrogen atoms; larger energies are obtained for the first three H atoms where bonding involves \( \sigma \) orbitals and/or unpaired electrons.

Of interest are also some general structural changes accompanying hydrogenation. We find that structures with \( n \geq 4 \) are more open than the less hydrogenated ones, with \( d_{CC} \gtrsim 2.7 \) Å. This value has to be compared with the corresponding value in graphene \((i.e. \text{the next-to-nearest neighbors C-C distance in the bare, unrelaxed vacancy})\) which is \( d_{CC} = 2.46 \) Å. This `expansion' is accompanied by a substantial movement of the C atoms out of the plane, up to \(0.7 - 0.8 \) Å. For instance, in the VH\(_3\) anti- structure we obtained \( \delta z = 0.68, 0.49 \) and \(-0.34 \) Å and in the VH\(_2\) structure \( \delta z = 0.79, 0.66 \) and \( 0.18 \) Å. C-H bond lengths fall in the range \(1.07 - 1.12 \) Å, bonds in geminal pairs being the longest and almost similar to CH in perfect graphene \((1.13 \) Å\). With the same token, H-H distances in geminal pairs all fall in the range \( d_{HH} = 1.73 - 1.79 \) Å and distances in syn- and anti- pairs are generally larger than these values, but smaller values are possible for syn- pairs. For instance we found \( d_{HH} = 1.51 \) Å for the VH\(_2\) syn- structure and \( d_{HH} = 1.42 \) Å for the syn- pair in the VH\(_3\) anti- structure.

**B. Thermodynamic analysis**

With the whole energetics of the hydrogenated vacancy at hand we performed a thermodynamic analysis to investigate the relative stability of the various hydrogenated
species under reasonable hydrogen partial-pressure and temperature conditions. We considered the lowest molar Gibbs free energy of formation \( \Delta G_n^f(p, T) \) at a H\(_2\) partial pressure \( p \) and temperature \( T \), which -analogously to Eq. (1) - is given by

\[
\Delta G_n^f(p, T) = G_{VH_n}(p, T) - G_V(p, T) - \frac{n}{2} G_{H_2}(p, T)
\]

where \( G_{VH_n} \), \( G_V \) and \( G_{H_2} \) are Gibbs free energies for the \( n \)-times hydrogenated vacancy, the bare vacancy and molecular hydrogen, respectively. For the first two terms we neglected any temperature and pressure dependence and thus relied on the DFT energies above (\( G_{VH_n} \approx E_{VH_n} \) for \( n = 0, 1 \), etc.). For hydrogen, some thermodynamic data are available from standard tables \([42]\) and ideal-gas dependence on its partial pressure \( p \) can be assumed to write

\[
G_{H_2}(p, T) = H_{H_2}(p^\odot, T) - TS_{H_2}(p^\odot, T) + RT \ln \left( \frac{p}{p^\odot} \right) = E_{H_2} + \Delta G_{H_2}(p, T)
\]

where \( R \), as usual, is the perfect gas constant, \( S_{H_2}(p^\odot, T) \) is the hydrogen molar entropy at temperature \( T \) and standard pressure \( p^\odot = 1 \) bar, and the enthalpy is written as \( H_{H_2} = E_{H_2} + \frac{5}{2} RT \) for \( T < T^\odot \) and \( H_{H_2} = E_{H_2} + \frac{5}{2} RT^\odot + \Delta H_{H_2}(p^\odot, T) \) otherwise. Here \( E_{H_2} \) is the DFT energy of H\(_2\) in its equilibrium configuration and \( \Delta H_{H_2}(p^\odot, T) \) is the H\(_2\) molar enthalpy change from \( T = T^\odot = 298.15 \) K to \( T \) at the standard pressure \( p^\odot \) (Ref. \([42]\)). \( \Delta G_{H_2}(p, T) \) is defined by the above equation and is the appropriate free-energy change from \( T = 0 \) to \( T, p \). Accordingly,

\[
\Delta \Delta G_n = \Delta G_n^f - \Delta G_{n-1}^f = \Delta \Delta E_n^m - \frac{1}{2} \Delta G_{H_2}(p, T)
\]

where \( \Delta \Delta E_n^m \) differs from the energy for sequential adsorption defined above by half the dissociation energy \( D_m \) of the H\(_2\) molecule,

\[
\Delta \Delta E_n^m = E_{VH_n} - E_{VH_{n-1}} - \frac{1}{2} E_{H_2} = \Delta \Delta E_n + \frac{1}{2} D_m
\]

where \( D_m = 4.5 \) eV with our setup.

The results of such an analysis are reported in Fig. 4 in the temperature range \( T = 250 - 1800 \) K and for a wide hydrogen partial pressure range \( p = 10^{-20} - 10^5 \) bar, comprising standard atmospheric conditions \( (T \sim 300 \) K and \( p = 5.55 \times 10^{-7} \) bar in dry atmosphere) and ultra-high vacuum conditions (UHV) where the pressure is \( \sim 10^{-12} \) times smaller than the standard value; \( p = 1 \) bar and higher, on the other hand, can be achieved upon hydrogen exposure. Fig. 4 shows that the bare vacancy is thermodynamically stable only at high temperature and low hydrogen pressure; for instance, thermal annealing at \( T > 1200 \) K would be required in atmospheric conditions to free vacancy defects from hydrogen atoms, whereas annealing at \( T = 600 \) K, while sufficient for desorbing H atoms and dimers from the basal plane, is not enough to desorb H atoms form the vacancy. Even under UHV conditions annealing at \( T \geq 800 \) K is required to have bare vacancies, thereby suggesting that, at least for naturally occurring vacancies, hydrogen passivation is ubiquitous and extensive, with the triply hydrogenated species most abundant up to \( T \sim 600 \) K. Different results may be expected when vacancies are intentionally introduced into the substrate by e.g. electron or ion bombardment, since the hydrogenation kinetics and ensuing equilibration may be considerably slowed down by the low operating partial pressures and temperatures. For instance, STM experiments are often performed at low temperatures \( (T \sim 10 \) K) where a VH\(_3\) isomer is the most stable species under a wide range of pressures, but where the hydrogenation kinetics is extremely slow unless high hydrogen partial pressures are used. Similarly for TEM experiments, despite the larger temperature typically used (ambient conditions).

Noteworthy is the absence in Fig. 4 of any doubly hydrogenated species, neither the geminal nor the \( \text{syn}-/\text{anti}- \) dimer: upon increasing the temperature at constant pressure the most stable isomers change from the triply hydrogenated form to the singly hydrogenated one, without passing from a \( (p, T) \) region where dimers are stable against hydrogenation/dehydrogenation; see also Fig. 5 which reports the molar free-energies of the most stable isomers for different temperatures, at ambient hydrogen partial pressure.

Finally, it is worth noticing that, as a consequence of the energetics discussed in the previous subsection, no geminal species prevails at equilibrium. Geminal adducts have been recently invoked to explain long-time oscillations in the zero-field \( \mu \)-SR decay asymmetry \([43, 44]\), which were attributed to dipolar interactions between a muon (Mu, a H isotope \( \sim 10 \) times lighter than H) and a H atom in a -CHMu geminal structure. Though not stable at the experimental conditions \( (T = 300 \) K) these structures might easily form from the stable singly-
and triply- hydrogenated species prevailing under a wide range of conditions, and dominate the \( \mu \)-SR signal over alternative arrangements because of structural reasons. Among these, as observed above, the H-H distance in geminals has a well defined value \( (d_{HH} \approx 1.75 \text{ Å}) \), in good agreement with the dipolar distance extracted by the \( \mu \)-SR signal, \( d = 1.70 \pm 0.02 \text{ Å} \), irrespective of the specific structure and unaffected by low-frequency vibrations of the lattice (the lowest-frequency motion altering such distance is a H-C-H bending). However, further investigation is required to establish whether such a product can indeed form in a collision between a muonium and a hydrogenated vacancy.

### C. Magnetic properties

The magnetic properties of carbon atom vacancies in graphene have been recently subjected to experimental investigations with conflicting results. Early reports of paramagnetism due to spin-1 species\[^{[16]}\], in accordance with a triplet ground-state configuration of the bare vacancy\[^{[26]}\], have been questioned on the light of magnetometry measurements on carefully prepared samples, which showed the presence of spin-1/2 species for both fluorine ad-species and vacancies\[^{[16]}\], at odds with the different numbers of unpaired electrons left upon defect formation. Later measurements from the same group showed that in the presence of carbon atom vacancies two different spin-1/2 local magnetic moments contribute to the observed paramagnetic signal, one arising from the \( \sigma \) network and one from the \( \pi \) band system\[^{[17]}\]. This finding would agree with the above mentioned electronic structure of the Jahn-Teller distorted vacancy if the singlet-triplet separation (Hund’s coupling) were vanishing small to allow a decoupled response of the two unpaired electrons left upon reconstruction, a possibility which has been recently ruled out by accurate \( \text{ab initio} \) results\[^{[26]}\]. In the same work it has been shown that the energetics is sensitive to the out-of-plane motion of the apical carbon atom, thereby suggesting that ripples and/or interactions with a substrate could explain why the above mentioned unpaired electrons of the vacancy are uncoupled. Here we consider a different scenario, \( i.e. \) the possibility that the vacancy is hydrogenated to some extent and thus presents a net magnetic moment which depends on the degree of hydrogenation.

Table I summarizes the computed magnetic moment for each structure investigated, along with the number \( m \) of unpaired electrons left on the C-vacancy after the hydrogenation process, along with their character.

| \( M/\mu_B \) \( n \) | Character |
|------------------------|-----------|
| 1.00                   | \( \pi \)  |
| 2.00                   | \( \sigma, \pi \) |
| 1.00                   | \( \sigma \) |
| 1.92                   | \( \sigma, \pi \) |
| 0.00                   | -          |
| 1.00                   | \( \pi \)  |
| 2.00                   | \( \pi, \pi \) |

Figure 5: Molar free-energy of formation for the most stable isomers \( V_{H_3} \) at atmospheric conditions \( p = 0.55 \times 10^{-6} \text{ bar} \), for different temperatures. Circles, squares, rhombus, triangles up and triangles down for \( T = 0, 300, 600, 1000 \) and \( 1500 \text{ K} \), respectively.

Table I: Computed total magnetization \( M \) in \( \mu_B \) and predicted number \( m \) of unpaired electrons left on the C-vacancy.
A quick look at Table I reveals that hydrogenated vacancies have magnetic moments in the range 0.0–2.0 $\mu_B$, even though the corresponding singly occupied states may have very different character. For instance, despite the presence of one unpaired electron in both the VH$_{3}$-geminal and the VH$_{3}$-anti structure, the corresponding singly occupied state has either a $\sigma$ or a $\pi$ origin. More interestingly, taking into account the results of the previous section, we observe that in a wide range of temperature and hydrogen partial pressure of interest in many practical situations, the magnetic moment of the most stable hydrogenated species (VH$_{3}$, VH$_{3}$ and VH$_{4}$ structures) has one and the same value, namely $M = 1.00 \mu_B$. Thus, with the exception of the bare vacancies, thermodynamically stable vacant species on a wide range of ambient conditions are expected to behave as spin-1/2 magnetic moments as a consequence of hydrogenation.

D. STM imaging

Finally, in order to help identifying and distinguishing the various hydrogenated species investigated we performed, on a few relevant optimized structures, simulations of the STM images within the standard Tersoff-Hamann approximation. The sample bias was fixed at $-0.5 \text{V}$ and constant-current images obtained by integrating the local density of states in the range $[-0.5, 0] \text{eV}$ from the Fermi level, as the (largest) height $z$ of an isosurface of the resulting function.

Several situations were envisaged. First we considered the bare vacancy which, in its stable structure, should present a distorted configuration, with a C-C distance sensibly shorter than the other two. However, since three equivalent minima are possible, each differing by the orientation of the JT bond, we also considered the possibility that orientational averaging occurs on the time-scale of imaging (few seconds). This could happen either because of thermal hopping between the minima, or because a dynamic Jahn-Teller effect is operative whereby the ground-state structure is a superposition of the three possible distorted one and robust against environmental dephasing. Fig. 6 shows these two possibilities, panel (a) for the averaged structure and panel (b) for the distorted one, the latter with a superimposed molecular model to help identifying the lattice positions. As is evident from Figs. 6(a,b), despite the structural differences, the distorted and the symmetrical configurations of the bare vacancy are hardly distinguishable from each other. Both structures present a bright signal with exact or approximate three-fold symmetry which extends far from the vacant site and which corresponds to the above mentioned $\pi$-midgap state, in agreement with STM/STS experiments [10], but no further distinguishing feature.

A distorted structure similar to that of the bare vacancy but with a locked configuration appears upon single hydrogenation. In this case, the attached H atom is not free to move on neighboring C atoms of the vacancy (even though we did not compute it, the barrier for hopping likely matches the desorption barrier, as happens for hydrogen atoms adsorbed on the basal plane of graphene[18, 19]) and the simulated STM image, reported in Fig. 6(c), shows a clearer breaking of symmetry than in the case of the bare vacancy. It further shows an increase of brightness in the vacancy at the expense of the a reduced intensity of the signal due to the $\pi$-midgap state, probably related to the admixture of $\sigma$ and $\pi$ character (remember that the H atom is accommodated out-of-plane with a CH bond originating from a $sp^3$ C orbital, and an unpaired electron is left on the remaining $sp^3$ orbital, free to hybridize with the $\pi$-band states. Fig. 6 is the simulated image for the structure with the H atom above the plane).

Finally, we considered one further thermodynamically stable structure, the triply hydrogenated anti-structure which prevails under standard conditions. Here, too, a number of equivalent configurations is possible (three possible orientations of the dimers in sym-relationships times two possible positions, above or below the surface plane) and we decided to average over them since their interconversion does not involve any H atom transfer and should thus be possible under ordinary temperature conditions. Fig. 7 reports the simulated image of the structure which shows a clear increase of the intensity in the vacant site, as well as the expansion of the lattice accompanying hydrogenation which was mentioned above. Note that this structure still bears one unpaired $\pi$-moment of the kind similar to the one in Figs. 6(a-c) and thus, far from the vacant site, displays the same ‘typical’ three-fold symmetric signal, though with a reduced intensity.

A symmetric structure has been recently observed by Robertson and co-workers[22] with TEM, under conditions where the vacancy would be triply hydrogenated if equilibrium conditions prevailed. However, our computed C-C distances in the VH$_{3}$-anti structure ($d_{CC} \sim 2.8 \text{Å}$) are sensibly larger than those found in the experiment ($d_{CC} = 2.5 \pm 0.1 \text{Å}$) that the observed structure is likely to be a bare vacancy which dynamically switches between its equivalent configurations (or an excited state of the vacancy with electronic different configuration).

IV. CONCLUSIONS

We reported on a thorough investigation of the structure and energetics of several hydrogenated states of a carbon atom vacancy in graphene. We found large H-atom adsorption energies for the first few hydrogen atoms (related to saturation of $\sigma$-dangling bonds) which progressively decrease towards values similar to those found for adsorption at graphene edges. As a consequence, under equilibrium conditions, triply- and singly-hydrogenated species prevail over a wide range of hydrogen partial pressure and temperatures relevant in many experimental situations. The computed energetics shows
Figure 6: Simulated STM images of the vacancy of the bare vacancy (a,b) and of the singly hydrogenated vacancy (c) with molecular models showing the lattice arrangement. Image on panel (a) has been obtained by averaging over the three equivalent orientations of the structure.

Figure 7: Simulated STM images of the most stable triply hydrogenated isomer of the vacancy, averaged over its equivalent configurations.

that geminal pairs are invariably less stable than different hydrogen arrangements with adsorbed H atom on different sites (if possible), preferably in an anti-configuration. Thus, whether geminal products are formed (as suggested by recent $\mu$-SR experiments\(^{[44, 45]}\)) requires further investigation of the dynamical aspect of the process.

Most of the investigated structures have a net non-zero magnetic moment capable of a paramagnetic signal. In particular, one spin-$1/2$ moment related to an unpaired electron in a semilocalized $\pi$-midgap state appears both in the singly- and triply-hydrogenated species which dominate the $(p,T)$ phase-diagram describing hydrogenation.

Comparison with existing STM investigations of defective graphene\(^{[10]}\) showed agreement for the presence of the signal due to the $\pi$-midgap state, but further studies are needed to establish whether the observed vacancies are Jahn-Teller distorted, dynamically averaged or hydrogenated to some extent. Simulated STM images hardly distinguish a locked from an averaged bare vacancy but present a few marked features accompanying hydrogenation which may help identifying hydrogenated species.

V. ACKNOWLEDGMENTS

The authors acknowledge Quentin Ramasse for useful discussions. This work has been supported by Regione Lombardia and CILEA consortium through an ISCRA and LISA (Laboratory for Interdisciplinary Advanced Simulation) 2012 initiative grants.

[1] A. V. Krasheninnikov and K. Nordlund, J. Appl. Phys. 107, 071301 (2010).
[2] Q. M. Ramasse, R. Zan, U. Bangert, D. W. Boukhvalov, Y. W. Son, and K. S. Novoselov, ACS Nano 6, 4063 (2012).
[3] T. J. Booth, F. Pizzocchero, H. Andersen, T. W. Hansen, J. B. Wagner, J. R. Jinschek, R. E. Dunin-Borkowski, O. Hansen, and P. Bøggild, Nano. Lett. 11, 2689 (2011).
[4] N. Severin, S. Kirstein, I. M. Sokolov, and J. P. Rabe, Nano. Lett. 9, 457 (2009).
[5] M. Bonfanti, S. Casolo, G. Tantardini, A. Ponti, and R. Martinazzio, J. Chem. Phys. 135, 164701 (2011).
[6] H. Terrones, R. Lv, M. Terrones, and M. S. Dresselhaus, Rep. Prog. Phys. 75, 062501 (2012).
[7] Q. M. Ramasse, C. R. Seabourne, D. M. Kepaptsoglou, R. Zan, U. Bangert, and A. J. Scott, Nano. Lett. 13, 4989 (2013).
[8] V. M. Pereira, J. M. B. Lopes dos Santos, and A. H. Castro Neto, Phys. Rev. B 77, 115109 (2008).
[9] V. M. Pereira, F. Guinea, J. Lopes dos Santos, N. Peres, and A. Castro Neto, Phys. Rev. Lett. 96, 036801 (2006).
[10] F. G. M. Ugeda, I. Brühne and J. M. Gomez-Rodriguez, Phys. Rev. Lett. 104, 096804 (2010).
[11] N. M. R. Peres, F. Guinea, and A. H. Castro Neto, Phys. Rev. B 73, 125411 (2006).
[12] J. P. Robinson, H. Schomerus, L. Oroszlány, and V. I.
[13] T. O. Wehling, S. Yuan, A. I. Lichtenstein, A. K. Geim, and M. I. Katsnelson, Phys. Rev. Lett. 105, 056802 (2010).

[14] N. M. R. Peres, Rev. Mod. Phys. 82, 2673 (2010).

[15] A. Ferreira, J. Viana-Gomes, J. Nilsson, E. R. Mucciolo, N. Peres, and A. C. Neto, Phys. Rev. B 75, 165402 (2011).

[16] R. R. Nair, M. Sepioni, I.-L. Tsai, O. Lehtinen, J. Keinonen, A. V. Krasheninnikov, T. Thomson, A. K. Geim, and I. V. Grigorieva, Nature Phys. 8, 199 (2012).

[17] R. R. Nair, I.-L. Tsai, M. Sepioni, O. Lehtinen, J. Keinonen, A. V. Krasheninnikov, A. H. C. Neto, M. I. Katsnelson, A. K. Geim, and I. V. Grigorieva, arXiv:1301.7611 (2013).

[18] L. Hornekær, E. Rauls, W. Xu, Ž. Šljivančanin, R. Otero, I. Stensgaard, E. Lægsgaard, B. Hammer, and F. Besenbacher, Phys. Rev. Lett. 97, 186102 (2006).

[19] S. Casolo, O. M. Løvvik, R. Martinazzo, and G. F. Tantardini, J. Chem. Phys. 130, 054704 (2009).

[20] A. A. El-Barbary, R. H. Telling, C. P. Ewels, M. I. Heggie, and P. R. Bridgdon, Phys. Rev. B 68, 144107 (2003).

[21] P. O. Lehtinen, A. S. Foster, Y. Ma, A. V. Krasheninnikov, and R. M. Nieminen, Phys. Rev. Lett. 93, 187202 (2004).

[22] O. V. Yazyev and L. Helm, Phys. Rev. B 75, 125408 (2007).

[23] M. W. C. Dharma-Wardana and M. Z. Zgierski, Physica E 41, 80 (2008).

[24] X. Q. Dai, J. H. Zhao, M. H. Xie, Y. N. Tang, Y. Li, and B. Zhao, Eur. Phys. J. B 80, 343 (2011).

[25] J. J. Palacios and F. Yndurain, Phys. Rev. B 85, 245443 (2012).

[26] M. Casartelli, S. Casolo, G. F. Tantardini, and R. Martinazzo, Phys. Rev. B 88, 195424 (2013).

[27] H. A. Mizes and J. S. Foster, Science 244, 559 (1989).

[28] J. G. Kushnerick, K. F. Kelly, H.-P. Rust, N. J. Halas, and P. S. Weiss, J. Phys. Chem. B 103, 1619 (1999).

[29] T. Kondo, Y. Honma, J. Oh, T. Machida, and J. Nakamura, Phys. Rev. B 82, 153414 (2010).

[30] K. F. Kelly, D. Sarkar, G. D. Hale, S. J. Oldenburg, and N. J. Halas, Science 273, 1371 (1996).

[31] Y. Niimi, H. Kambara, T. Matsui, D. Yoshioka, and H. Fukuyama, Phys. Rev. Lett. 97, 236804 (2006).

[32] A. W. Robertson, B. Montanari, K. He, C. S. Allen, Y. A. Wu, N. E. Harrison, A. I. Kirkland, and J. H. Warner, ACS Nano 7, 4495 (2013).

[33] G. Kresse and J. Hafner, Phys. Rev. B 49, 14251 (1994).

[34] G. Kresse and J. Furthmüller, Phys. Rev. B 54, 11169 (1996).

[35] J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. 77, 3865 (1996).

[36] J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. 78, 1396 (1997).

[37] P. E. Blöchl, Phys. Rev. B 50, 17953 (1994).

[38] G. Kresse and D. Joubert, Phys. Rev. B 59, 1758 (1999).

[39] H. Jonsson, G. Mills, and K. W. Jacobsen, 'Nudged Elastic Band Method for Finding Minimum Energy Paths of Transitions', in 'Classical and Quantum Dynamics in Condensed Phase Simulations' (World Scientific, 1998).

[40] V. V. Ivanovskaya, A. Zobelli, D. Teillet-Billy, N. Rogeau, V. Sidis, and P. R. Bridgdon, Eur. Phys. J. B 76, 481 (2010).

[41] K. May, B. V. Unterreiner, S. Dapprich, and R. Ahlrichs, Phys. Chem. Chem. Phys. 2, 5089 (2000).

[42] http://webbook.nist.gov, NIST Chemistry Webbook.

[43] L. Hornekær, Ž. Šljivančanin, W. Xu, R. Otero, E. Rauls, I. Stensgaard, E. Lægsgaard, B. Hammer, and F. Besenbacher, Phys. Rev. Lett. 96, 156104 (2006).

[44] M. Riccó, D. Pontiroli, M. Mazzani, M. Choucair, J. A. Stride, and O. V. Yazyev, Nano. Lett. 11, 4919 (2011).

[45] M. Riccó, M. Aramini, M. Mazzani, D. Pontiroli, M. Gaboardi, and O. V. Yazyev, Phys. Scr 88, 068508 (2013).

[46] A. Ney, P. Papakonstantinou, A. Kumar, N.-G. Shang, and N. Peng, Appl. Phys. Lett. 99, 102504 (2011).