# Scanning tunneling microscopy fingerprints of point defects in graphene: A theoretical prediction

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Scanning tunneling microscopy (STM) is one of the most appropriate techniques to investigate the atomic structure of carbon nanomaterials. However, the experimental identification of topological and nontopological modifications of the hexagonal network of  $sp^2$  carbon nanostructures remains a great challenge. The goal of the present theoretical work is to predict the typical electronic features of a few defects that are likely to occur in  $sp^2$  carbon nanostructures, such as atomic vacancy, divacancy, adatom, and Stone-Wales defect. The modifications induced by those defects in the electronic properties of the graphene sheet are investigated using first-principles calculations. In addition, computed constant-current STM images of these defects are calculated within a tight-binding approach in order to facilitate the interpretation of STM images of defected carbon nanostructures.

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# I. INTRODUCTION

Their unusual electronic and structural physical properties promote carbon nanomaterials as promising candidates for a wide range of nanoscience and nanotechnology applications. Carbon is unique in possessing allotropes of each possible dimensionality and, thus, has the potential versatility of materials exhibiting different physical and chemical properties. Diamond (three-dimensional), fullerenes (zero-dimensional), nanotubes (one-dimensional), and two-dimensional (2D) graphite platelets are selected examples. Because of their remarkable electronic properties, carbon nanotubes (CNTs) are expected to play an important role in the future of nanoscale electronics.<sup>1</sup> Although they have been considered as ideal objects in the vast majority of studies, they may have various atomic-scale defects. Examples of those are heptagonpentagon topological defects, adatoms, and atomic vacancies. Those defects can appear at the stage of CNT growth and purification or be deliberately created by irradiation<sup>2</sup> and chemical treatment<sup>3</sup> or induced by unidirectional strains<sup>4</sup> in order to achieve a desired functionality. Due to similarities in the atomic structures, the properties of defects in nanotubes can be considered to be qualitatively the same as those in graphite and related materials.<sup>5–7</sup> In these materials, defect studies were first motivated by the understanding of the radiation damages occurring in graphite-moderated nuclear reactors. Recently, graphene, which is a monolayer of carbon atoms packed into a dense honeycomb crystal structure, has been the subject of intense experimental scrutiny,<sup>8,9</sup> especially because this kind of structure was previously presumed not to exist in the free state. By rubbing graphite layers against an oxidized silicon surface, graphene samples can be obtained, with the likely formation of defects. The presence of defects has become an essential part of diverse processes in carbon materials synthesis. A true realization of different devices requires a good understanding of both geometrical and electronic properties of not only the carbon nanostructures themselves but also of their defects. For instance, structural and electronic properties of carbon nanomaterials could be tuned by such a presence in their structures. It was reported that vacancy defects created by electron irradiations could induce structural changes within carbon nanotubes.<sup>10,11</sup> Moreover, vacancies induced the occurrence of magnetism which could be useful in some applications.<sup>12</sup> Thus, structure and diffusion of vacancy defects in graphene layers have been studied by a number of theoretical calculations, in the case of CNTs,<sup>13–17</sup> graphite,<sup>12,18,19</sup> and graphene.<sup>6,20–27</sup>

In this paper, the properties of the most frequent defects occurring in graphene are investigated, with a primary focus on their electronic properties as well as their corresponding STM images. Defects are difficult to observe directly. Of course, pentagon-heptagon pairs are believed to induce observable structural changes such as a tapering of the nanotube<sup>28,29</sup> or its sharp bending.<sup>30</sup> Even with highresolution transmission electron microscopy, it is difficult to image a point defect in a CNT because the resolution is generally not good enough to separate the  $sp^2$ -bound C atoms. Recently, through a sequence of high-resolution transmission electron microscopy images recorded in situ on one single-wall carbon nanotube (SWNT). Hashimoto et al. reported that vacancy in graphene layers such as single-wall carbon nanotubes is very stable in the in situ experimental condition.<sup>31</sup> A possible route to the observation of defects is through the local variation of the electronic or vibrational density of states. Probing the local vibrational density of states is presently accessible through inelastic electron tunneling spectroscopy (IETS) using a STM.<sup>32</sup> With this method, the changes in the local phonon spectrum related to topological defects have been put forward. Recently, the possibility of characterizing defects in a carbon nanotube from its local vibrational densities of states that could be probed by IETS-STM have been explored theoretically using a simple dynamical model.<sup>33</sup>

Since its discovery, scanning tunneling microscopy has proven to be a powerful technique for scrutinizing the surface structure of various systems with atomic resolution, including nonperiodic atomic arrangements. Despite its



FIG. 1. Fully optimized structures of five different defects. (a) Top view of a nonreconstructed vacancy, keeping the  $D_{3h}$  symmetry of graphene. (b) Top and side views of the reconstructed vacancy with  $C_s$  symmetry. (c) Top view of the divacancy. (d) Top and side views of the adatom equilibrium bridgelike position. (e) Top view of a Stone-Wales defect. Some carbon atoms are numbered; see text.

success, the interpretation of a STM image is by far not trivial since it typically results from a convolution of both the atomic and electronic structures of the sample. The tip structure may be convoluted with the sample, making the image confusing. In particular, the determination of defectinduced features in experimental STM images is not straightforward due to various electronic effects, as observed, for example, in graphite.<sup>34–36</sup> The purpose of this paper is to explain the state of the art in the identification of atomic defects in graphene. Our main goal is to facilitate the interpretation of experimental STM images and more precisely to determine how such defects can affect the STM images.



FIG. 2. Electronic properties of the  $D_{3h}$  vacancy. (a) Comparison between the electronic band structure calculated with DFT-LDA (left) and our modified TB model (right). For both calculations, the Fermi level is set to zero. (b) Isodenstity surfaces of specific defect states at  $\Gamma$ point, calculated with DFT-LDA. The shaded spots label the two  $\sigma$  states (degenerated in  $\Gamma$ ) and the white spot represents the  $\pi$  band.



FIG. 3. Electronic properties of the  $C_s$  vacancy. (a) Comparison between the electronic band structure calculated with DFT-LDA (left) and our modified TB model (right). For both calculations, the Fermi level is set to zero. (b) Isodensity surfaces of specific defect states at  $\Gamma$ point calculated with DFT-LDA. Degeneracy of the former  $\sigma$  states is broken, according to the bonding and antibonding character of the state between the two atoms that move closer.

The paper is organized as follows. In Sec. II, we briefly review the methodology used to simulate the STM images within a tight-binding framework. Section III presents the electronic properties of the different defects studied using first-principles calculations. In Sec. IV, we introduce the tight-binding model and the fitting procedure used to determine the parameters in our model. Computed STM images are presented and discussed in Sec. V.

### II. TIGHT-BINDING THEORY OF SCANNING TUNNELING MICROSCOPY

In this section, a brief description of a tight-binding theory of STM is presented, which is suitable for application to carbon materials whose band structure is dominated by  $\pi$  electrons around the Fermi level.<sup>37</sup> Generalization of the theory to other structures is possible.

Let us consider an occupied state  $\alpha$  on the tip and an unoccupied state  $\beta$  on the sample and let us introduce at time t=0 a small coupling v between the tip and the sample. A general, first-order perturbation expression of the tunneling current between the tip and the sample is then possible. In tight-binding theory, assuming one orbital per atom (an *s* orbital on the tip, like with the Tersoff-Hamann theory,<sup>38</sup> and one  $\pi$  orbital on the carbon-based sample), the electronic states of the isolated tip and sample are linear combinations of atomic orbitals (LCAOs),

$$|\alpha\rangle = \sum_{i \in t} \chi_i^{\alpha} |\eta_i\rangle, \quad |\beta\rangle = \sum_{j \in s} \psi_j^{\beta} |\theta_j\rangle.$$
 (1)



FIG. 4. Isodensities of different vacancies: (a)  $D_{3h}$ , (b)  $C_s$ , and (c) divacancy.







All that is needed is to insert the LCAO expansions in the matrix element  $\langle \alpha | v | \beta \rangle$  to end up with the following expression of the STM current valid at zero temperature:

$$I = (2\pi)^{2} \frac{e}{h} \int_{E_{F}-eV}^{E_{F}} dE$$

$$\times \sum_{i,i' \in t} \sum_{j,j' \in s} v_{ij} v_{i'j'}^{*} n_{ii'}^{t} (E - \delta E_{F} - eV) n_{jj'}^{s} (E), \quad (2)$$

where V is the tip-sample bias potential (e > 0), the  $E_F$ 's are the Fermi levels of the separated systems, and  $\partial E_F = E_F^t - E_{f^*}^s$ . The current is a sum over sites of the tip and sample of tight-binding representations of the coupling interaction,  $v_{ij} = \langle \chi_i | v | \theta_j \rangle$ , and the imaginary part of energy-dependent Green's function elements *G* of the separated tip and sample.<sup>39</sup> The diagonal elements of the Green's function are easily evaluated by the recursion method.<sup>40</sup> Nondiagonal elements can also be computed, as long as they can be expressed in terms of diagonal ones.<sup>41</sup>

The application of the above formalism to the case of graphitic structures has further been simplified by considering just one  $\pi$  orbital per C atom. The assumed pointlike tip is modeled by a single *s* orbital, with a local density of states  $n_{ii}^t(E)$  represented by a Gaussian function having its maximum 1 eV below the Fermi level. The Slater-Koster coupling  $s-\pi$  elements are assumed to decrease exponentially with the separation distance  $d_{ij}$  between the coupled atoms (tunneling regime),





FIG. 6. Electronic properties of the adatom. (a) Comparison between the electronic band structure calculated with DFT-LDA (left) and our modified TB model (right). For both calculations, the Fermi level is set to zero. (b) Isodenstity surfaces of specific defect states at  $\Gamma$  point, labeled in the band structure and calculated with DFT-LDA.

$$v_{ij} = V_0 w_{ij} \cos \theta_{ij} e^{-d_{ij}\lambda}, \qquad (3)$$

$$w_{ij} = e^{-ad_{ij}^2} / \sum_{j'} e^{-ad_{ij'}^2}.$$
 (4)

In these expressions,  $\theta_{ij}$  is the angle between the  $\pi$  orbital axis and the C atom–tip apex direction,  $\lambda = 0.085$  nm, and a = 60 nm<sup>-2</sup>. The  $w_{ij}$  are convergence factors aimed at simulating the narrow channel through which the tunneling current flows.<sup>42</sup>

The present theory is simple enough to be used routinely for the computation of STM images, making it possible to investigate specific effects due to the presence of defects in graphene.

#### **III. ELECTRONIC PROPERTIES OF DEFECTS**

The electronic structure of graphene, a single planar sheet of  $sp^2$  bonded carbon atoms, is well known.<sup>43</sup> Starting with

the graphene sheet, the electronic properties of nontopological and topological modifications of the hexagonal lattice are studied. Mainly three kinds of defects may occur in such an  $sp^2$  structure: vacancies, adatom, or Stone-Wales defect (see Fig. 1). More complex defects can be obtained by a combination of these three basic defects.

Using first-principles calculations, we studied the modification of the electronic structure of graphene induced by these defects. The electronic properties were investigated using the ABINIT code,44 based on density functional theory (DFT) within the local density approximation (LDA). A norm-conserving pseudopotential was used for the carbon atom,<sup>45</sup> and the plane wave basis set was given a cutoff energy  $E_{cut}$ =30 hartree. The system consists of a central defect site within a supercell sufficiently large to minimize boundary effects on the energies of interest. We adopted a  $(5 \times 5)$ grid of 50 atoms for the monovacancies and the adatom, whereas a  $(6 \times 6)$  grid of 72 atoms was necessary for the Stone-Wales defect and the divacancy to avoid interaction between the periodically repeated defects. The size of the supercell in the c direction was set to  $\sim 10$  Å to avoid the interaction between neighboring defects. Integrations over the Brillouin zone are based on a 3×3 Monkhorst-Pack 2D grid,<sup>46</sup> which is sufficiently fine to ensure the numerical convergence of all the calculated properties. All the structures were fully relaxed using the Broyden-Fletcher-Goldfarb-Shanno minimization scheme, keeping the supercell geometry fixed. The atomic positions are relaxed until the forces on the atoms are reduced to  $10^{-6}$  hartree/bohr. The cold smearing method of Marzari47 was used for the Brillouin zone integration with a smearing parameter of 2  $\times 10^{-3}$  hartree, leading to formation energies converged to 0.01 eV.

In order to study the properties of the vacancies, we first consider a graphene sheet with a single carbon atom removed. For this monovacancy, two structures have been reported:<sup>6</sup> the bare, nonreconstructed vacancy, keeping the  $D_{3h}$  symmetry of the honeycomb network [Fig. 1(a)], and the reconstructed vacancy with  $C_s$  symmetry [Fig. 1(b)]. In this last case, the vacancy undergoes a Jahn-Teller distortion upon relaxation, where two of the atoms near the vacancy move closer, forming a pentagonlike structure while the third atom is displaced by 0.43 Å out of the plane, as illustrated in Fig. 1(b). Our results agree well with previous values of 0.47 Å also calculated with DFT.<sup>6</sup> The vertical displacement is larger than the 0.18 Å value found with spin-polarized calculations.<sup>12,21</sup> However, by restricting their system to an equal spin-up and spin-down density solution, Lehtinen et al. recover a nonmagnetic ground state with an atom displacement of 0.46 Å. The energy of the  $C_s$  configuration is 0.23 eV lower than the nonreconstructed one, in good agreement with the 0.20 eV found with other first-principles calculations.6

The vacancies have a significant influence on the electronic structure of honeycomb lattices. Indeed, due to the presence of a vacancy in the supercell, bands arise near the Fermi level [Figs. 2(a) and 3(a)] that were not present in the previous band structure for pristine graphene. These bands are flat (low electronic group velocity) and predominantly result from the atoms located around the corresponding va-

cancies, as shown for the  $D_{3h}$  structure [Fig. 2(b)] and the  $C_s$ structure [Fig. 3(b)]. In the first case, the planar symmetry allows one to separate the bands: there are two symmetric ( $\sigma$ ) and one antisymmetric ( $\pi$ ) bands. The planar symmetry is lost for the second case; however, the transformation of eigenstates is sufficiently weak to still recognize their shape. However, the main issue of the  $D_{3h} \rightarrow C_s$  recombination is that one of the previous  $\sigma$  bands is moving far above  $E_F$ . All these electronic states of the single vacancies in graphene are strongly localized and yield typical defect states with sharp peaks located around  $E_F$  and are responsible for conductance damping in the case of nanotubes, as shown by Choi *et al.*<sup>49</sup>

The divacancy is also a defect of great interest [Fig. 5(c)], which has been proven to play an important role on the conducting properties of irratiated SWNTs, as discussed recently.<sup>48</sup> It has been shown that even a low concentration of vacancies in CNTs can produce a large damping of their electrical conductance. A divacancy is formed when two neighboring vacancies coalesce, upon relaxation, leading to the displacement of atoms closest to the defect, thus forming pentagonallike structures [Fig. 1(d)]. The energy gain with respect to two isolated monovacancies is around 6 eV. This can become smaller than that of one single monovacancy in the case of a SWNT with a small diameter.<sup>50</sup> The energy gain can be understood by analyzing the isodensity plots around the different vacancies (Fig. 4). On the one hand, the electronic density between two of the atoms closest to the vacancy in the case of the nonreconstructed structure is very weak with C-C bonds close to 2.45 Å, which means the presence of dangling bonds. One the other hand, we observe an increase of the electronic density in the case of the reconstructed structures. This suggests the creation of a weak covalent bond for the  $C_s$  structure with the formation of an extended C-C bond of 2.02 Å in comparison with the standard length of 1.42 Å for graphene. Moreover, this bond is further reduced to 1.71 Å for the divacancy, thereby further stabilizing the structure through the formation of covalent bonds and the disappearance of the dangling bonds. This defect has also an important influence on the electronic properties (see Fig. 5). Around the Fermi level, only the  $\pi$  bands are present, whereas the  $\sigma$  bands are moving far away.

Since a carbon adatom is a common defect in graphitic lattices, it is important to study its influence on the electronic structure of graphene. The equilibrium position [see Fig. 1(d)] of the adatom was found to be in a bridgelike structure. This geometry is similar to previous LDA calculations on a similar surface.<sup>7,22,51,52</sup> The distance of the adatom perpendicular to the graphene plane is 1.76 Å with C–C bonds equal to 1.49 Å and bond angles close to 60°. The presence of the adatom, incorporated into the graphene sheet, strongly modifies the electronic properties of the system. Again, a flat band arises that corresponds to localized states in the vicinity of the defect, in analogy with the monovacancies (Fig. 6).

The last structure considered in this paper is a Stone-Wales defect which is a 90° rotation of two carbon atoms in the hexagonal network with respect to the midpoint of the bond. This leads to the formation of two pentagons and two heptagons [see Fig. 1(e)], substituting four hexagons.<sup>53</sup> This defect, studied extensively,<sup>54</sup> is believed to play an important role in the structure transformation of different carbon nano-



FIG. 7. (Color online) Band structure of a graphene sheet, calculated using both *ab initio* (full lines) and tight-binding (dashed lines) techniques, with the Fermi level set to zero.

structures, such as the coalescence of fullerenes<sup>55</sup> or the fusion of carbon nanotubes.<sup>56</sup> This transformation has been shown to give rise to extremely high-energy barriers of 6-7 eV, which can be reduced within the range 0.7-2.3 eVin the presence of an adatom.<sup>57</sup>

### **IV. TIGHT-BINDING PARAMETERS**

In a second step, the *ab initio* results, presented previously, are reproduced at best by a tight-binding (TB) Hamiltonian where both 2s and 2p electrons of the carbon atoms are taken into account. To calculate the band structures of  $sp^2$ carbon systems, we assume the same atomic energy levels for carbon and the same hopping integrals as given by Lambin et al.58 This approach has been successfully used to study the electronic band structure of multilayered carbon tubules.<sup>59</sup> In Fig. 7, this tight-binding model is found to reproduce correctly the band structure of the graphene sheet calculated using the *ab initio* method. The model accounts for four orbitals per carbon atom, the 2s level is located  $\epsilon_s$ =-5.49 eV below the triply degenerated 2p levels that is taken as the energy of reference ( $\epsilon_p = 0$  eV). In the present work, a distance dependence of the hopping integrals has been added in order to take into account different distances due to the relaxation of the structures. The Slater-Koster parameters related to the hopping integrals are assumed to decay with respect to the bond length  $r_{ij}$  as

$$\boldsymbol{\beta}_{\lambda}(r_{ij}) = \boldsymbol{\beta}_{\lambda}^{0} \left(\frac{r_{0}}{r_{ij}}\right)^{2}.$$
(5)

|                  | Atomic site 1  |                 |                 |                 | Atomic site 2  |                 |                 |                 | Atomic site 3  |                 |                 |                 |
|------------------|----------------|-----------------|-----------------|-----------------|----------------|-----------------|-----------------|-----------------|----------------|-----------------|-----------------|-----------------|
|                  | $\epsilon_{s}$ | $\epsilon_{px}$ | $\epsilon_{py}$ | $\epsilon_{pz}$ | $\epsilon_{s}$ | $\epsilon_{px}$ | $\epsilon_{py}$ | $\epsilon_{pz}$ | $\epsilon_{s}$ | $\epsilon_{px}$ | $\epsilon_{py}$ | $\epsilon_{pz}$ |
| $D_{3h}$ vacancy | -7.13          | -0.655          | -0.655          | 1.12            |                |                 |                 |                 |                |                 |                 |                 |
| $C_s$ vacancy    | -2.082         | -0.927          | -0.927          | 0.1             | -2.418         | -0.93           | -0.93           | 2.154           |                |                 |                 |                 |
| Divacancy adatom | -8.49          | 0.2             | 0.6             | 0.0             |                |                 |                 |                 |                |                 |                 |                 |
| Stone-Wales      | -5.49          | 0.0             | 0.0             | -1.62           | -5.49          | 0.0             | 0.0             | -1.67           | -5.49          | 0.2             | 0.6             | 3.21            |

TABLE I. Tight-binding parameters (in eV) related to specific atomic sites, as labeled in Fig. 1.

The values of  $\beta_{\lambda}^{0}$  corresponding to the different interactions<sup>58</sup> at the graphene interatomic distance  $r_{0} = 1.41$  Å are  $\beta_{ss\sigma}^{0} = -4.80$  eV,  $\beta_{sp\sigma}^{0} = +4.75$  eV,  $\beta_{pp\sigma}^{0} = +4.39$  eV, and  $\beta_{pp\pi}^{0} = -2.56$  eV. The atomic energy levels ( $\epsilon_{s}, \epsilon_{p}$ ) of the C atoms located around the defect are adjusted to reproduce correctly the band structure, especially around the Fermi level. Moreover, the second-neighbor interactions between two-coordinated atoms is necessary to saturate the dangling bonds of the different vacancies. These optimal parameters are summarized in Table I.

These parameters are used to compute the STM image as depicted below. These adjustments were performed using a least squares energy minimization scheme between LDA and TB band structures. For all the structures considered, the band structures obtained with our TB model are in very good agreement with ab initio calculations, especially around the Fermi level [Figs. 2(a), 3(a), 5(a), and 6(a)]. In the STM technique, a small voltage is applied between the sample and a metal tip, which yields a tunneling current at typical tip surface separations of several angstroms. At small bias voltages, the tunneling current is sensitive to the specific electronic character of the states of the sample near the Fermi energy. In many systems, the charge distribution of these states is characteristic of the total charge density and the corresponding STM images give a direct view of the atomic arrangement at the surface. Consequently, a good description of the band structure near the Fermi level, within our tightbinding approach, is necessary to image defects with a virtual STM. Only  $\pi$  electrons, which dominate the electronic structure near the Fermi level, were taken into account for the STM calculations.

### V. SCANNING TUNNELING MICROSCOPY IMAGES

Highly oriented pyrolytic graphite is a real benchmark in STM microscopy: atomic resolution can easily be obtained in air. The surprising result, although quite well known, is that the STM image does not usually reproduce the honeycomb structure of the topmost atomic sheet, but it does reveal the triangular Bravais lattice instead.<sup>60</sup> Everything takes place as if every other atom were missing in the image. In fact, the two atoms per surface unit cell are not equivalent. One atom has a neighbor in the layer underneath, whereas the other atom has none. It is precisely the latter atom that protrudes in the STM picture at low bias because the local density of states on this atom has a peak at the Fermi level, while the former atom, being more coupled to the bulk, does not.<sup>61</sup> The situation is of course different in graphene: both

atoms in the unit cell are equivalent. All atoms appear the same in the STM image and the honeycomb structure is now clearly reproduced. In addition, calculations reveal that the STM current is small when the tip apex is located above the center of a honeycomb hexagon. This is due to destructive interferences of the coupling terms between the tip and the six C atoms. As a result, the hexagon centers in graphene look like corrugation holes in the STM image.

As illustrated in Fig. 8 (top), the computed STM image of the nonreconstructed vacancy has a large protrusion in the form of a hillock with trigonal symmetry at the center of the defect, which is due to localized electronic states induced by the three dangling bonds. The image also reveals electrondensity oscillations resulting from interferences of Fermi waves elastically backscattered by the defect, as frequently observed by STM in irradiated graphite. Experimental STM images of graphite indeed show defects in the form of protrusions with trigonal symmetry and, often, a  $\sqrt{3} \times \sqrt{3}$  periodic superstructure away from them.<sup>62</sup> Recent experiments, however, have demonstrated that this superstructure, when present, is induced by an interstitial atom (in between two layers in graphite) but it is absent when there is a vacancy.<sup>5</sup> This result agrees with the present calculation for graphene, where there is clearly no periodic superstructure in the computed images. However, the horizontal extension and the height of the hillock in the calculated STM image are by far much smaller than what is observed experimentally. The reason for this discrepancy is unknown. The reconstructed vacancy is even worse in that respect. The STM image of the reconstructed vacancy shown in Fig. 8(b) no longer has a threefold symmetry. The largest protrusion is located on the sole two-coordinated atom located in front of the pentagon with a long C-C bond produced by the reconstruction. The trigonal symmetry of the image can be restored by invoking a dynamical Jahn-Teller effect, where the pentagon rotates by  $\pm 2\pi/3$ . This dynamic switching between degenerate structures is activated by a barrier of 0.13 eV, as shown by El-Barbary *et al.* using first-principles calculations.<sup>6</sup> The image would then be an average of three structures equivalent to that of the nonreconstructed one rotated by  $\pm 2\pi/3$ , as represented in Fig. 8(c).

Figure 9(a) shows the STM images of a divacancy in graphene for a positive tip potential. There is no dangling bond in the structure. A dumbbell-like feature decorates the two pentagons. Interestingly, the maximum of protrusion is located right at the center of the defect, where there is no atom. In defect-free graphene, the centers of the hexagons correspond to depressions. Again, contrast oscillations are present around the defect.



FIG. 8. (Color online) Computed constant-current STM images of defects in graphene calculated with a positive tip potential of 0.2 V: (a) nonreconstructed  $D_{3h}$  and (b) reconstructed  $C_s$ . (c) Average of the three equivalent  $C_s$  structures rotated by  $\pm 2\pi/3$ . All atomic coordinates are expressed in Å.

The last structural defect we consider is a Stone-Wales  $\pi/2$  rotation of a C–C bond, which produces two pentagons and two heptagons at the location of four hexagons. Figure 9(b) shows the optimized, planar geometry of graphene with such a defect. The STM images, calculated with a positive potential of the tip, are characterized by an elongated ring of protrusion having its major axis parallel to the Stone-Wales



FIG. 9. (Color online) Computed constant-current STM images of defects in graphene calculated with a positive tip potential of 0.2 V: (a) divacancy and (b) Stone-Wales defect. All atomic coordinates are expressed in Å.

bond and extending from 0.3 to 0.5 nm around the center of the defect. It is clear from the examples above that the defects destroy the atomic resolution of the STM images, although the images were calculated with a pointlike tip. Since there is no, or possibly small, buckling of the defected atomic structure in the direction perpendicular to the graphene sheet, all these effects revealed by the STM have an electronic origin. The electron states probed by the tip have a wavelength close to the Fermi wavelength (0.75 nm), different from the lattice parameter. Since, in addition, there are six equivalent Fermi points, strong interference effects take place, washing out at least locally the apparent periodicity of the atomic structure. For the adatom, disregarding the sigma states and ignoring any variation of the  $\epsilon_{pz}$  certainly affect the STM image in the vicinity of the defect. The calculation of the STM image of the adatom can be done but some important effects related to the presence of the adatom will be missing. Actually, in this present case, the atomic energy level  $\epsilon_{pz}$  was not adjusted to reproduce the *ab initio* band structure (see Table I).

All the computed STM images presented here have been obtained with a positive tip potential. We have also calculated STM images with opposite tip potentials, but no significant differences have been observed.

## **VI. CONCLUSION**

Despite the already large amount of experimental STM data obtained so far on carbon nanomaterials, the identification of topological and nontopological modifications of the hexagonal lattice of a graphene sheet remains an experimental challenge. STM is the perfect tool to study defects, allowing one to probe the electronic structure of solids with atomic resolution. However, defects, which can occur in graphene, are complex, so their experimental identification remains a nontrivial matter, thus needing some theoretical predictions. Consequently, we have simulated STM images of different models of defects. In addition, thanks to a simple but accurate theoretical approach, we simulate the signatures of these defects in graphene in order to contribute thereby to their identification. Moreover, the effects of these defects on the first-principles electronic structure of graphene are also discussed.

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