**Single and Double Carbon Vacancies in Pyrene as First Models for Graphene
Defects: A Survey of the Chemical Reactivity toward Hydrogen**

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Abstract

Graphene is regarded as one of the most promising materials for nanoelectronics applications. Defects play an important role in modulating its electronic properties and also enhance its chemical reactivity. In this work the reactivity of single vacancies (SV) and double vacancies (DV) in reaction with a hydrogen atom H_r is studied. Because of the complicated open shell electronic structures of these defects due to dangling bonds, multireference configuration interaction (MRCI) methods are being used in combination with a previously developed defect model based on pyrene. Comparison of the stability of products derived from C- H_r bond formation with different carbon atoms of the different polyaromatic hydrocarbons is made. In the single vacancy case the most stable structure is the one where the incoming hydrogen is bound to the carbon atom carrying the dangling bond. However, stable C- H_r bonded structures are also observed in the five-membered ring of the single vacancy. In the double vacancy, most stable bonding of the reactant H_r atom is found in the five-membered rings. In total, C- H_r bonds, corresponding to local energy minimum structures, are formed with all carbon atoms in the different defect systems and the pyrene itself. Reaction profiles for the four lowest electronic states show in the case of a single vacancy a complex picture of curve crossings and avoided crossings which will give rise to a complex nonadiabatic reaction dynamics involving several electronic states.

Keywords: graphene; single and double vacancies; hydrogenation; C-H bond formation; multireference configuration interaction

1. Introduction

Graphene has many extremely appealing electrical, physical, and thermal properties which have made it an exciting material that is the subject of intensive research ever since it was first isolated [1]. Graphene is a particular allotrope of carbon in which a two-dimensional hexagonal lattice is composed of benzene rings. Though it has been suggested that graphene's ability to conduct electricity could allow it to replace silicon in next-generation organic semiconductors, two problems remain, however, which detract from this potential. The first issue is that there are no effective methods for obtaining amounts of pristine graphene sheets of one atom thickness necessary for industrial applications. The second problem is that graphene's electronic properties come with a down side, though it conducts electricity well, it is a semi-metal with a zero-energy band gap.

The chemical functionalization of graphene sheets for the purpose of tuning its band gap has shown great promise [2, 3]. The hydrogen atom is a natural starting point when beginning the investigation of the ability of graphene sheets to form sp^3 bonds between an incoming atom or molecule and the bonding carbon atom. Hydrogen chemisorption on a graphene surface has been studied in detail by Casolo et al. [4] using density functional theory (DFT) and periodic boundary conditions. In fact, hydrogenation has been shown to be an efficient tool for band gap tuning of graphene [5, 6, 7, 8]. Formation of the sp^3 bond disrupts the existing sp^2 bond network by breaking the local π system. This has the effect of not only increasing the reactivity of the carbon atoms neighboring the new C-H bond, but it also creates a potential barrier to the conducting electrons opening a band gap, which is tunable depending on the concentration of the chemisorbed species and properties of the sp^3 network that has been formed. By reacting graphene sheets with atomic hydrogen, hydrogenated regions of graphene are formed which are referred to as graphane islands. The presence and extent of hydrogenation has been previously confirmed through the use of scanning tunneling microscopy (STM) and angle-resolved transmission electron microscopy (TEM) [5]. These images also show details pertaining to the arrangement of graphane islands with respect to each other. Polyaromatic hydrocarbons (PAH) and their reaction with hydrogen are not only of interest as molecular models for graphene but also as possible catalysts for H_2 formation in interstellar space [9]. Hydrogenation studies of pyrene have been performed [10] to investigate energetic stabilities of hydrogen attached to different carbon atoms and the existence of energy barriers.

The arrangement of bonded hydrogen atoms in graphane islands and the proximity of islands to one another are also contributing factors to the overall electronic character of the hydrogenated graphene sheet due the dependence of the created band gap on such. A small group of low hydrogen-concentration graphane islands have shown clearly the beginning of the formation of a band gap [5]. On a larger scale, graphane islands created in strips parallel to each other, called graphene roads, have been shown to create environments similar to graphene nanoribbons [11]. Hydrogen atoms adsorbed on graphene have also been reported to induce magnetic moments [12]. The spin-polarized state is shown to be essentially located on the carbon sublattice opposite to the one belonging to the adsorbed hydrogen atom. This finding goes very well along with previous success in experimentally engineering band gaps and has been shown by the Haddon group using substituted benzene radicals, nitrophenylene, interacting with graphene sheets [3]. As a consequence of this functionalization, residual spins are available to couple and allow the possibility of ferromagnetism at room temperatures.

Vacancies defects, absences of carbon atoms in the hexagonal structure, have shown to be an interesting area with regards to the investigation of the chemical reactivity of graphene. When one or multiple carbons are removed, the created dangling bonds represent areas of greater chemical reactivity. The presence of these dangling bonds then implies high polyradical character with many closely spaced locally excited electronic states which are difficult to describe computationally. This situation then strongly advises the use of flexible multireference theory [13] in which quasi-degenerate orbitals are treated at equal footing and the correct construction of wavefunctions of well-defined symmetry and spin properties is possible.

The electronic structures of both single vacancy (SV) and double vacancy (DV) pyrene (Scheme 1) which has been used as a prototype for a graphene defect structure, have recently been described using multireference configuration interaction (MRCI) [14, 15] and DFT [16]. The single vacancy investigation of pyrene using MRCI calculations [14] showed several closely spaced electronic states of triplet and singlet multiplicity (Scheme 1, Pyrene-1C) with the weight of the main configurations not exceeding a value of ~70%. The electronic ground state of the double vacancy defect [15] (Scheme 1, pyrene-2C) possesses 50% closed shell character which indicates a significantly different character as compared to the SV case. Nevertheless, the just-mentioned percentages of the contributions of the dominating configuration to the total wavefunction for both types of defects demonstrate the importance of other configurations and

the consequent need for a multireference approach, especially because of the goal of describing all closely spaced states simultaneously. The pristine pyrene is depicted in Scheme 1, top, and as is, of course, to be expected the chemically most stable structure of the three candidates discussed.

Pyrene

Pyrene-1C

Pyrene-2C

Scheme 1. Atomic numbering scheme for pristine pyrene, pyrene-1C (single vacancy) and pyrene-2C (double vacancy), respectively. H_r is the hydrogen atom moving across the different pyrene structures as shown by arrows.

The purpose of this work is to explore the chemical reactivity of pyrene and the two defect structures by studying their interaction with hydrogen radical (H_r). The role of H_r is two-fold. It is used in the spirit of a test particle by moving it in a grid search across the different pyrene structures as the arrows in Scheme 1 indicate. In this way a stability surface with respect to C- H_r bond formation is constructed. In the second step optimizations of C- H_r structures are performed and C- H_r dissociation curves are constructed to the lowest dissociation products. The previous MRCI calculations on the SV and DV pyrene defect structures had shown the existence of several low-lying excited states. We wanted to reproduce this asymptotic limit at complete C-H dissociation and, thus, computed in all respective cases potential energy scans and C-H dissociation curves for the four lowest electronic states. In addition to the determination of local energy minima for different C-H bonding situations, these data should provide an overview of the most important aspects for the approach and bonding of a hydrogen atom to a pristine or defect graphene sheet surface.

2. Computational Details

The geometries of each pyrene structure (Scheme 1) were optimized using complete active space (CAS) self-consistent field (CASSCF) theory [17, 18]. Based on the experience with previous pyrene defect calculations [14, 15] a CAS(5,5) was used comprised of five electrons in five orbitals where, in C_s symmetry, three orbitals belonged to the A' irreducible representation and two orbitals belonged to the A'' irreducible representation. The CAS(4,4) is chosen for the description of the isolated pyrene defect and one active orbital and electron is added to account for the hydrogen atom. The active orbitals used in the CAS for pyrene+ H_r were 31a', 32a', 33a', 22a'', 23a'' (Figure S1 of the Supporting Information (SI)). For pyrene-1C+ H_r active orbitals were 29a', 30a', 31a', 21a'', 22a'' (Figure S2) and for pyrene-2C+ H_r active orbitals were 27a', 28a', 29a', 20a'', 21a'' (Figure S3). The 6-31G* basis set [19] was used. The state-averaging included four states (SA4). In case of C_s symmetry the two lowest $^2A'$ and two lowest $^2A''$ states were chosen. Single point calculations were carried out using SA4-CASSCF(5,5)/6-31G* and MRCI with all singles and doubles (MR-CISD) again using the 6-31G* basis set. As reference space, the same CAS(5,5) as used in the CASSCF(5,5) calculations was selected. Single and double excitations were constructed from the doubly-occupied and active orbitals applying the interactive space restriction [20]. The 1s orbitals of all carbon atoms were kept frozen. Size-extensivity corrections were included by means of the extended Davidson correction [13, 21, 22]

$$E_Q = \frac{(1 - C_0^2)(E_{CI} - E_{REF})}{(2C_0^2 - 1)} \quad (1)$$

denoted as +Q (MR-CISD+Q). C_0^2 is the sum of square coefficients of the reference configurations in the MR-CISD expansion and E_{REF} denotes the reference energy.

The potential energy surface (PES) scan was carried out using the SA4-CASSCF(5,5)/6-31G* approach for pyrene-1C+H_r and pyrene-2C+H_r and the CASSCF(5,5)/6-31G* approach for pyrene+H_r. For that purpose, the previously relaxed pyrene defect (pyrene-1C and -2C) structures computed earlier [14, 15] and an optimized pyrene structure using the density functional theory (DFT) and the hybrid Becke, 3-parameter, Lee-Yang-Parr (B3LYP) functional [23] together with the 6-31G** [19] basis set were used to move H_r around in a grid with an increment of 0.3 Å and at a distance of 1.0 Å from the plane structures. Single-point calculations were performed for each point on the grid.

Using the local minima in the PES's scans as starting structures, geometry optimizations were carried out. To simulate the constraints present in a larger graphene system, the coordinates of the carbons connected to hydrogen atoms at the periphery of the pyrene and pyrene defect systems were always frozen in all geometry optimizations since they would be connected to neighboring carbon atoms in a graphene sheet. All other atoms were allowed to relax. Geometry optimizations using SA4-CASSCF(5,5)/6-31G* for the defect cases plus H_r and CASSCF(5,5) calculations for the pristine pyrene+H_r were performed by placing H_r at an initial distance of 1.1 Å over each unique carbon in each of the pyrene system.

The CASSCF, MR-CISD and MR-CISD+Q calculations were carried out using COLUMBUS [24, 25, 26, 27, 28]; the geometry optimizations used the program system DL-FIND [29] interfaced to COLUMBUS. The DFT calculations were performed with the Turbomole suite of programs [30].

3. Results and Discussion

3.1. Potential Energy Scans

The two-dimensional PES scans of the single vacancy pyrene-1C+H_r for the ground state and the first three excited states are shown in Figure 1. For that purpose, the H_r atom has been moved systematically in a grid 1.0 Å above the fixed, planar structure of pyrene-1C. These scans

detail the ability of the test particle, H_r , to bond in a particular region of pyrene-1C. For the ground state, deep local minima can be seen at the carbons in the five-membered ring, C1, C2, C3, C13 and C14 (see Scheme 1 for numbering of atoms). The lowest minimum at C15 persists through all four states; for the excited states the local minimum at the five-membered ring is considerably higher in energy. Shallower minima are present for C5, C7, C9, and C11. Generally, the minima for carbons in the six-membered ring, aside from C15, give minima much shallower than for the remaining carbon atoms.

Figure 1. PES scans in terms of the location of H_r for the four lowest states of pyrene-1C+ H_r using the SA4-CASSCF(5,5)/6-31G* approach. The atom H_r is located in a plane parallel and 1 Å above the plane defined by the frozen carbon atoms. Lowest energies: ^a -574.222889 Hartree, ^b -574.198174 Hartree, ^c -574.149530 Hartree, ^d -574.117820 Hartree. The energy (color scale) is given in eV, relative to the ground state lowest minimum.

3-D pictures of the PES scan of the double vacancy defect pyrene-2C+ H_r for the electronic ground- and first excited states are displayed in Figure 2 and Figure 3, respectively. The plots for the second and third excited state are shown in Figure S4. For the ground state deep potential wells are seen at C1, C2, C14 and C7, C8, C9, these being the carbons at the outer sections of the five-membered rings, with the strongest minima present at C1 and C8. Additional shallower minima are seen at each of the remaining carbons. The ground and first excitation are seen to be on average energetically closer as compared to the single vacancy defect just discussed above. On the other hand, the scans for the second and third vertical excitations (Figure S4) are closely spaced and quite higher, by ~ 2-2.5 eV, than the lowest minimum.

Figure 2: PES scan in terms of the location of H_r for the lowest state of pyrene-2C+ H_r using the SA4-CASSCF(5,5)/6-31G* approach. The atom H_r is located in a plane parallel and 1

Å above the plane defined by the frozen carbon atoms. Lowest energy = -536.385046 Hartree. The energy (color scale) is given in eV, relative to the ground state lowest minimum.

Figure 3: PES scan in terms of the location of H_r for the 2^2A state of pyrene-2C+ H_r using the SA4-CASSCF(5,5)/6-31G* approach. The atom H_r is located in a plane parallel and 1 Å above the plane defined by the frozen carbon atoms. Lowest energy = -536.347629 Hartree. The energy (color scale) is given in eV, relative to the ground state lowest minimum at -536.385046 Hartree.

The ground state PES for pyrene+ H_r is shown in Figure 4. Pronounced minima can be seen at C4, C5, C11, and C12. While for each of the remaining carbon atoms in the pyrene system local minima can be found, C2, C7, C9, and C14 show to be especially stabilized among them.

Figure 4: PES scan of the lowest state of pyrene+H_r using the CASSCF(5,5)/6-31G* approach. The atom H_r is located in a plane parallel and 1 Å above the plane defined by the frozen carbon atoms. Lowest energy = -612.270253 Hartree. The energy (color scale) is given in eV, relative to the ground state lowest minimum.

3.2. Geometry optimizations

The PES scans discussed in the previous section give a good global overview of the chemical reactivity of the different pyrene defects (including the pristine case) concerning the strength of different C-H_r bonds as well as to the location of the centers of most stable bond formation. In the following sections more detailed information on the properties of individual structures will be discussed.

In the search for local minima structures containing C-H_r bonds, geometry optimizations were performed as described in the Computational Details by placing H_r on top of each carbon atom and performing a geometry optimization in each case only freezing selected carbon atoms as discussed above to simulate geometrical restrictions due to neighboring carbon atoms in a graphene sheet. Each carbon tested was found to give rise to a local minimum for all structures investigated.

Starting with the single vacancy pyrene-1C+H_r case, the nine ground state structures found are described in Figure 5. The global minimum is given by bonding H_r to C15 with a C-H_r bond distance of 1.060 Å. This is the smallest C-H bond distance determined for the nine structures and is much smaller than the C-H_r bond distance of the other minima whose bond

distance is around 1.095 Å. When H_r is bonded to C1, C2, C4, and C5, planarity of the ring system is mostly maintained. However, the existing hydrogen is moved out-of-plane away from the incoming H_r due to the formation of a tetrahedral sp^3 hybrid at this carbon atom. This behavior repeated in all analogous cases. When H_r is bonded to C3 and C6, the carbon atoms reacted by rising out of plane. When H_r was bonded to C7 and C8, the bonding carbon could not move since it was frozen, but C6, C10, and C15 moved out of plane. Finally, when H_r bonded to C15 in the global minimum structure, again C6, C10, and C15 moved out of plane.

Figure 5. Plots of the different minimum structures (labeled according to the bonding carbon atom) on the ground state energy surface of pyrene-1C+H_r using the SA4-CASSCF(5,5)/6-31G* approach. Bond distances are given in Å.

In the double vacancy pyrene-2C+H_r case, the four ground state structures are characterized in Figure 6. The global minimum was found when H_r is bonded to C2 in the five-membered ring with a C-H_r distance of 1.093 Å and gave the smallest C-H_r distance of all the minimum structures. The largest C-H_r bond distance of 1.121 Å to C1 is notable here as it is the largest one of all three pyrene structures. For C3, as before, since it was not frozen and only bonded to other carbons, the carbon atom rose out of the plane of the frozen carbon atoms when rehybridizing from sp² to sp³.

Figure 6. Plots of the different minimum structures (labeled according to the bonding carbon atom) of the ground state energy surface of pyrene-2C+H_r using the SA4-CASSCF(5,5)/6-31G* approach. Bond distances are given in Å.

Finally, for pyrene+H_r, the characterization of the five ground states is presented in Figure 7. The global minimum was found when H_r was bonded to C4 with a C-H_r bond distance of 1.097 Å. This C-H_r distance was the smallest one of the four minima found, though it can be noted that the C-H_r bond distances for this structure do not vary greatly as the largest C-H_r bond distance is only slightly larger with 1.103 Å given for C1-H_r. In cases where the bonding carbon

was already bonded to hydrogen (carbons 1, 2, 11), H_r formed a C-H bond by pushing the other hydrogen away, as reported also in previous cases. When H_r bonded to a hydrogen-free carbon (carbons 3 and 16), the bonding carbon responded by rising out of the plane of the frozen carbon atoms by about 0.5 Å. A similar observation was made by Rasmussen et al. [10] by means of DFT calculations where binding of a hydrogen atom on the interior positions (C3 and C16) of the pyrene led to a significant puckering of these carbon atoms (~ 0.4 Å) out of the molecular plane. This behavior on hydrogenation of graphene is generally feasible in the free graphene sheet [4] but is also true for the pyrene defect plus H_r cases as explained above.

Figure 7: Plots of the different minimum structures (labeled according to the bonding carbon atom) on the ground state energy surface of pyrene+ H_r using the CASSCF(5,5)/6-31G* approach. Bond distances are given in Å.

3.3 Energetic Stabilities

Table 1 shows the vertical excitation energies for pyrene-1C+H_r the lowest two A' and A'' states for structures having C_s symmetry, i.e. H_r bonded to C15 (global minimum), C1 and C8 using the SA4-CASSCF, MR-CISD and MR-CISD+Q approaches. The 1²A' state is the ground state. At MR-CISD+Q level, in the C15 structure the first excited state is only ~0.8 eV above the ground state, followed by states about 2.4 eV and 3.6 eV above the ground state. The ground state C1 structure is about 1.4 eV higher at MR-CISD+Q level than the respective one for C15; the C8 structure is located significantly higher (4.2 eV) above the C15 ground state. The order of the states computed at MR-CISD and MR-CISD+Q levels is reproduced well by the SA4-CASSCF(5,5) calculations even though there are non-negligible numerical differences up to 0.8 eV.

Table 1. Vertical energy differences (eV) of the lowest two A' and A'' states relative to the C15 ground state computed for the C1, C8 and C15 pyrene-1C+H_r structures using the SA4-CASSCF(5,5), MR-CISD and MR-CISD+Q approaches and the 6-31G* basis set.

	CASSCF	MR-CISD	MR-CISD+Q
State	ΔE_{rel}	ΔE_{rel}	ΔE_{rel}
C15			
1 ² A'	0.000 ^{a,d}	0.000 ^{b,d}	0.000 ^{c,d}
1 ² A''	1.154	1.023	0.834
2 ² A'	2.571	2.504	2.375
2 ² A''	4.100	3.904	3.594
C1			
1 ² A'	0.636 ^d	0.960 ^d	1.393 ^d
2 ² A'	3.775	4.073	4.444
1 ² A''	4.828	4.973	5.074
2 ² A''	5.854	6.069	6.186
C8			
1 ² A'	3.542 ^d	3.930 ^d	4.246 ^d

$2^2A'$	3.900	4.214	4.456
$1^2A''$	4.216	4.604	4.947
$2^2A''$	4.643	4.994	5.187

^a Total energy= -574.277274 Hartree, ^b Total energy= -575.610208 Hartree, ^c Total Energy= -576.244081 Hartree, ^d The SA4-CASSCF(5,5) optimized geometry was used.

Figure 8: Location and relative stability (eV) of the minima on the ground state energy surface of pyrene-1C+H_r using the MR-CISD+Q/6-31G* method. Blue: 2A ground state, red: lowest vertical excitation. Note: the rigid pyrene-1C structure shown does not reflect the actual structure of the optimized minima.

In Figure 8 (see also Table S1) are the relative energies of each carbon minimum in pyrene-1C+H_r given with respect to the global minimum structure at C15 computed at MR-CISD+Q level. The first vertical excitations are given in the figure as well. C15 marks the global minimum followed by C2, C3, and C1, respectively, in the five-membered ring. Except for the structure C15, all first excited states are located in energy higher by ~3.5 eV or more. This shows that in case of the reaction of H_r with a single vacancy graphene defect at thermalized kinetic energies nonadiabatic interactions between different electronic states will be relevant mostly for the C15 approach, which, is however, energetically the most relevant one.

The energy profiles for the reaction of H_r with the pyrene-1C defect are shown in Figure 9 for the case of bond formation with C15. The reaction curves have been created by fixing the C15-H_r distance and optimizing the remaining part of the pyrene defect structure for the ground state at SA4-CASSCF(5,5)/6-31G* level. Selected carbon atoms as discussed above were frozen to simulate also in this case geometrical restrictions due to neighboring carbon atoms in a

graphene sheet. Using these geometries, MR-CISD calculations were performed for the four lowest states. These calculations have been performed in C_1 symmetry. Nevertheless, the C_s symmetry analysis of Table 1 for the ground state minimum, as indicated in Figure 9, can be used for the analysis of states. For the $1^2A'$ ground state the figure shows a smooth dissociation without change of the character of the wavefunction. The second state is $1^2A''$ at the energy minimum. A crossing between this state and the $2^2A'$ state is observed at a C15- H_r distance of about 2 Å. For large distances the two $^2A'$ states become practically degenerate. The $2^2A'$ and $2^2A''$ states show a spike at 1.5 Å indicating the crossing with higher states of different character. These states are repulsive and are responsible for the correct asymptotic behavior of the dissociation. The energy minima of the first three states are located below the lowest dissociation limit so that on reaction with an incoming hydrogen atom several electronic states could be involved in the relaxation process to the ground state.

Figure 9: Dissociation curve of the lowest four 2A states of pyrene-1C+ H_r when H_r is bonded to C15 using the MR-CISD/6-31G* approach. Minimum energy = -574.277274 Hartree

Figure 10 shows the dissociation/bonding process of H_r from/to C1. Evident is the lack of a potential barrier in the ground state curve, though potential energy barriers and avoided crossings exist in the excited state curves. However, differently to the case of the C15- H_r bond dissociation, the excited states are not expected to play a major role for the relaxation process to the energy minimum on formation of the C1- H_r bond due to their high energies around the ground state minimum.

Figure 10: Dissociation curve of the lowest four 2A states of pyrene-1C+H_r when H_r is bonded to C1 using the MR-CISD/6-31G* approach. Minimum energy = -574.277274 Hartree

The H_r dissociation curves computed at SA4-CASSCF(5,5) level for bonding to C2 to C8, respectively, are collected in the SI. For C2 and C3, Figures S5 and S6, there is no potential barrier for the incoming H_r ground state. In the remaining cases (Figures S7 – S11), however, there are potential barriers present for the bond formation to C4, C5, C6, C7 and C8. Estimated barrier heights with respect to the dissociation limit are collected in Table 2. They show a variation between 0.4 eV to 1.4 eV indicating that the approach from that side of pyrene-1C is not so favorable.

The dissociation energy of the C15 global minimum pyrene-1C + H_r structure into the lowest state of pyrene-1C + H_r is given in Table 2. At MR-CISD+Q level a value of 4.61 eV is found. Comparison with the MR-CISD (4.13 eV) and SA4-CASSCF(5,5) (3.66 eV) values shows the importance of including size-extensivity and dynamic electron correlation contributions to the dissociation energy. Dissociation of H_r for the other structures can be obtained from Figure 8 by subtracting the relative stabilities from the just-mentioned dissociation limit of the C15 structure. The strongest C-H_r bonds following the one to C15 can be found for C-H bonding to carbons in the five-membered ring. Some of the other structures, though being local minima, are close in energy to the C-H_r bond dissociation limit.

Table 2: Dissociation energies ΔE_{diss} (eV) for the C15 global minimum pyrene-1C+H_r structure and estimated energy barriers $\Delta E_{\text{barr}}(\text{est.})$ (eV) for the approach of H_r on the ground state surface toward the different carbon atoms of pyrene-1C using different theoretical methods and the 6-31G* basis set.

ΔE_{diss}		
SA4-CASSCF(5,5)	MR-CISD	MR-CISD+Q
3.660	4.128	4.605
$\Delta E_{\text{barr}}(\text{est.})^{\text{a}}$ (SA4-CASSCF(5,5))		
C1, C2, C3, C15: no barrier		
C4	C5	C6
0.914	0.426	1.403
C7	C8	
1.138	1.051	

^a Estimated barriers were computed as the energy difference between the asymptotic energy and the maximum energy point computed for each of the potential curves.

The relative stabilities in the electronic ground state and the lowest vertical excitations of pyrene-2C+H_r are presented in Figure 11 for the MR-CISD+Q/6-31G* approach. SA4-CASSCF(5,5) and MR-CISD results are collected in Table S2. Numerical agreement between the different methods is within 0.1 – 0.2 eV. The global minimum was found to be for H_r bonded to C2 in the five-membered ring. The minima are ordered from most stable to least stable as C2<C1<C3<C4. The variation in the relative energies is much smaller than observed for the pyrene-1C+H_r case (Figure 9).

Figure 11. Location and relative stability (eV) of the minima on the ground state energy surface of pyrene-2C+H_r defect using the MR-CISD+Q/6-31G* method. Blue: ²A ground state, red: lowest vertical excitation. Note: the rigid pyrene-2C structure shown does not reflect the actual structure of the optimized minima.

The dissociation energy for the process pyrene-2C+H_r is given in Table 3 for the global minimum structure with H_r bound to C2 for the CASSCF, MR-CISD and MR-CISD+Q methods. Compared to the pyrene-1C+H_r case (Table 2), the C-H_r bond strength is significantly reduced. However, it should be noted that all local ground state minima (Figure 11) are below the dissociation limit of 2.269 eV.

Table 3: Dissociation energies ΔE_{diss} (eV) for the double vacancy pyrene-2C+H_r and pristine pyrene + H_r cases using different methods and the 6-31G* basis set.

	SA4-CASSCF(5,5)	MR-CISD	MR-CISD+Q
<hr/>			
pyrene-2C+H _r			
$\Delta E_{\text{diss}}(\text{C2})$	2.224	2.257	2.269
pyrene+H _r ^a			
$\Delta E_{\text{diss}}(\text{C2})$	0.833	0.902	0.943

^a For pyrene+H_r CASSCF(5,5) was used instead of SA4-CASSCF(5,5).

For the reaction of pyrene with H_r, pyrene+H_r, only the electronic ground state has been investigated. Relative stabilities of the different C-H_r bonded local minima are shown in Figure 12. CASSCF(5,5), MR-CISD and MR-CISD+Q results are collected in Table S3. A similar good agreement between different methods is obtained as for the pyrene-2C+H_r case discussed above in Table S2. The minima are ordered energetically as C2<C4<C3<C1<C16. Though the structure where H_r bound to C2 is most stable than C4, the difference is negligibly small, which is in good agreement with Ref. [10]. The stabilization energy of the various minima was found to be quite close to each other, with all five minima being found within 0.7 eV of the global minimum. With the dissociation energy of 0.943 eV computed at MR-CISD+Q/6-31G* level (Table 3) all of the minima are located below the dissociation limit, even though several cases are very close to it. A similar value has been found by Casolo et al. [4] in their hydrogenation studies of graphene performed at DFT level.

Figure 12: Location and relative stability (eV) of the minima on the ground state energy surface of pyrene+H_r using the MR-CISD+Q/6-31G* method. Note: the rigid pyrene structure shown does not reflect the actual structure of the optimized minima.

4. Conclusions

The chemical reactivity of a single and double vacancy in graphene and of a pristine surface toward C-H bond formation with a reactive hydrogen atom H_r has been investigated using a pyrene model with peripheral carbon atoms connected to H atoms frozen. Multireference methods (MR-CISD and MR-CISD+Q) have been used to describe (i) the dissociation processes properly and (ii) the manifold of quasi-degenerate states of the isolated defect [14, 15]. In a first step energy grids have been computed by moving an atom H_r across the rigid surface of the pyrene defects structures in order to obtain an overview of the stabilization energies in the different regions in space. The results show for the single vacancy a preference for bonding to C15 which possessing a dangling bond. The relative stabilization in this position is also observed in the lowest excited states. However, the carbon atoms in the five-membered ring show also strongly attractive positions in the ground state. The double vacancy displays similar stability preferences in the five membered rings; also the pristine pyrene model indicates attractive interactions primarily around the peripheral carbon atoms.

Geometry optimizations performed for the ground state at CASSCF level followed by single-point MR-CISD and MR-CISD+Q calculations refine this picture. Importantly, separate local energy minima for C-H_r bond formation have been determined for each of the carbon atoms in all defect structures and in pyrene itself. In the single vacancy case, C15 remains the position with greatest stability followed by C2 towards the top of the five-membered ring. In case of the double vacancy position C2 in the five-membered ring gives rise to the strongest C-H_r bond and in pyrene itself these are positions C2 and C4.

C-H_r dissociation curves have been computed for the four lowest electronic states for the single vacancy model starting from all minima found. Barrierless ground state processes have been found for C15 and the C-H_r bonds involving the five-membered ring. An incoming hydrogen atom though approaching the pyrene-C defect toward the other carbon atoms would encounter barriers of about 0.5 – 1 eV, depending on the incoming approach angle. Curve crossings and avoided crossings are found especially for H_r approaches to the most stable carbon positions which lead to the expectation of a complex nonadiabatic reaction dynamics. In summary, a remarkably complex picture of the bonding options of a hydrogen atom reacting with a graphene vacancy structures is observed both in terms of different bonding positions within the defect but also in terms of the reaction dynamics involving several excited states. It is expected that these properties found for the pyrene model are fairly representative for a localized graphene defect. Preliminary density functional studies confirm this view. More detailed investigations are in preparation.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at (link to be inserted).

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