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Emulating porphyrins with a rippled multivacancy graphene system

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ABSTRACT

The interaction between a complex porphyrin-like system formed by an iron atom and multivacant graphene layer and O₂, CO and CO₂ molecules is studied, using Density Functional Theory (DFT) calculations. The multivacancy graphene system used for this study, consists in the removal of a 1,4-dimethylbenzene-like moiety, in a 6 × 6 supercell. This removal and the structural optimization subsequently performed, yield to a biaxial vacancy, where the location of an iron atom embedded in it, lead to a system with resemblance to iron-porphyrin systems. This similar structure could be used to form complexes where gas molecules are allowed to interact with these iron-octavacant graphene systems. The study focuses on the structure of the system and the net magnetic moment for different gas molecules: O₂, CO₂ and CO. Rippling in the vacant graphene is enhanced through this interaction.

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1. Introduction

Since the obtaining of graphene by Geim and Novoselov, extensive research has been performed on this material due to the extraordinary properties that it shows [1,2]. The interest for opening up the gap in graphene in order to make it useful for application in electronics, has led to the study of defected graphene and particularly there has been great interest in the opening up of gaps driven by the creation of vacancies [3–8]. While single- and di-vacancies have been theoretically studied and experimentally created [9–11], multivacancies have also been studied due to their possible formation under more controlled and low-cost conditions which make these systems potentially more frequent and easier to produce [12–16]. Research has been performed studying the interaction between metal atoms or clusters and single- and di- [17] and multivacancy systems [18,19].

In particular, the stability of the presence of an iron atom in an already magnetic heptavacant graphene has been demonstrated [18], being the complementary figure extracted from the pristine carbon structure, an equivalent to a methylbenzene -the definition of complementary figure in this reference is the geometric figure of the atomic arrangement that is extracted from graphene when the multivacancy is created-.

This kind of structures gives the opportunity to study the interaction between graphene systems and iron atoms and furthermore,

the binding of gases molecules, resembling the behavior of porphyrin molecules. The presence of iron atoms in the vacancy, either accidentally under the form of impurity or located there in purpose, taking advantage of the stability of the multivacancy graphene systems [18], could be helpful to get a closer insight about this resemblance. In the same way that these systems give rise to extremely important species such as the heme group, the study of multivacant graphene with iron could be of interest due to their potential to design sensors, taking advantage on the properties of oxidation and reduction when interacting with oxygen and when replacing this molecule with another. Approaches to similar systems have been undertaken in order to simulate iron-porphyrin complexes and then to study their properties in the pursuit of potential applications.

As an example, the study of single wall carbon nanotubes with iron atoms embedded in a vacancy has been reported, as well as their interaction with oxygen [20]. Other approaches with vacancies in graphene, require the precise replacement of carbon by nitrogen in very specific locations in the vacancy, which seems to demand very restrictive conditions to occur [21]. The location of an iron atom at the center of an already formed multivacancy graphene -i.e. allowed to relax before the iron atom is placed-, could be a more feasible scenario.

In this report, we present the interaction between O₂, CO and CO₂, and an octavacancy graphene system, with an iron atom in its centroid, with the aim to study the interaction between iron and these molecules in a different system and taking into account the potential for its use as sensors. The octavacancy graphene system used in this report is obtained through the periodic extraction of a

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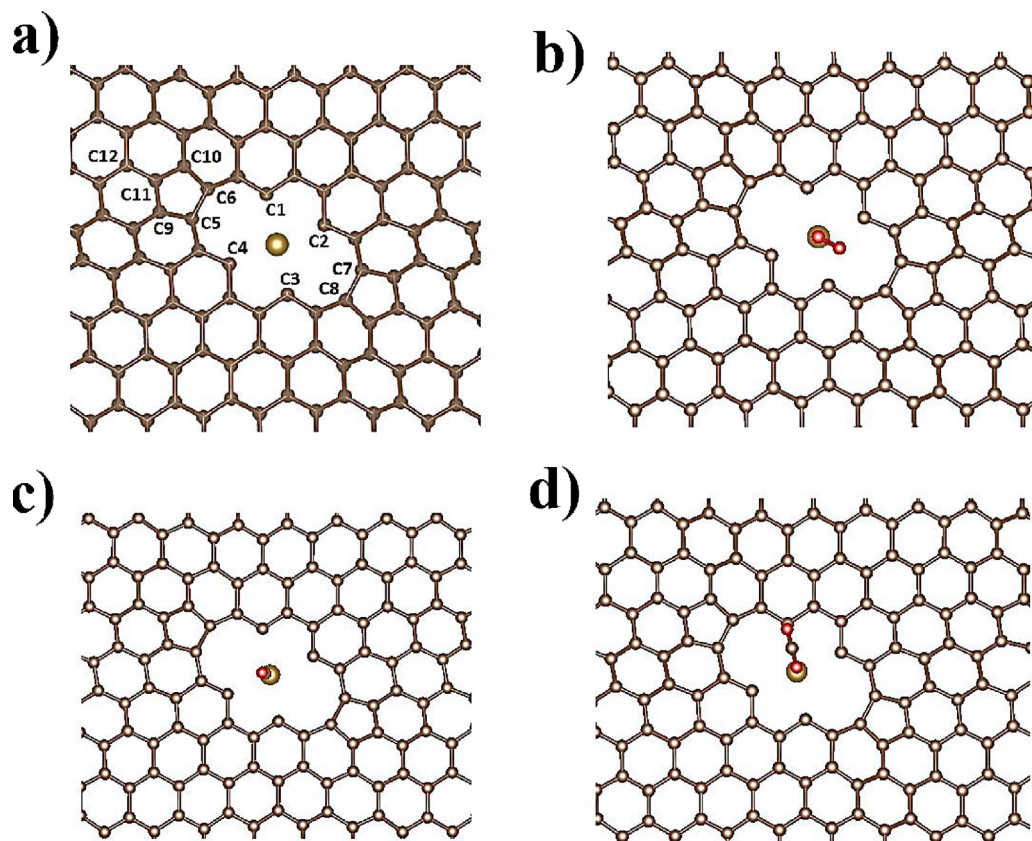


Fig. 1. Top view for structure a) g66v8Fe, b) g66v8FeO₂, c) g66v8FeCO, d) g66v8FeCO₂. In a), the scheme of carbon atoms labels can be seen [43].

1,4-dimethybenzene-like moiety from a pristine graphene, yielding to a C_{2v} symmetry and has been previously studied in a pure carbon system, with no metal atom present [22].

2. Computational methods

Electronic structure calculations were performed on iron - multivacancy graphene system interacting with O₂, CO and CO₂ with the use of the Density Functional Theory (DFT) [23,24] as implemented in the VASP code [25–28] (Vienna ab initio simulation package). Pseudopotentials were applied with a plane-wave basis set utilizing projector augmented wave (PAW) method [29], using generalized gradient approximation (GGA) as the exchange-

correlation functional according to Perdew-Burke-Ernzerhof (PBE) [30,31]. An energy cutoff of 300 eV was used to expand the Kohn-Sham orbitals into plane wave basis sets. Atomic charges were estimated from the atomic projections inside the Wigner-Seitz spheres as determined from the utilized pseudopotential file. In all of the calculations reported here the k-point mesh was taken equivalent to $4 \times 4 \times 1$ for the full (reducible) Brillouin Zone, allowing the convergence of stress components, total energy and ionic forces down to 1 kbar, 0.01 eV and 0.02 eV/Å, respectively.

We constructed a 6×6 graphene supercell with an 8-order vacancy system and we included the iron atom in the center. This iron-multivacancy graphene system was allowed to interact with the following molecules: O₂, CO and CO₂. A vacuum distance was

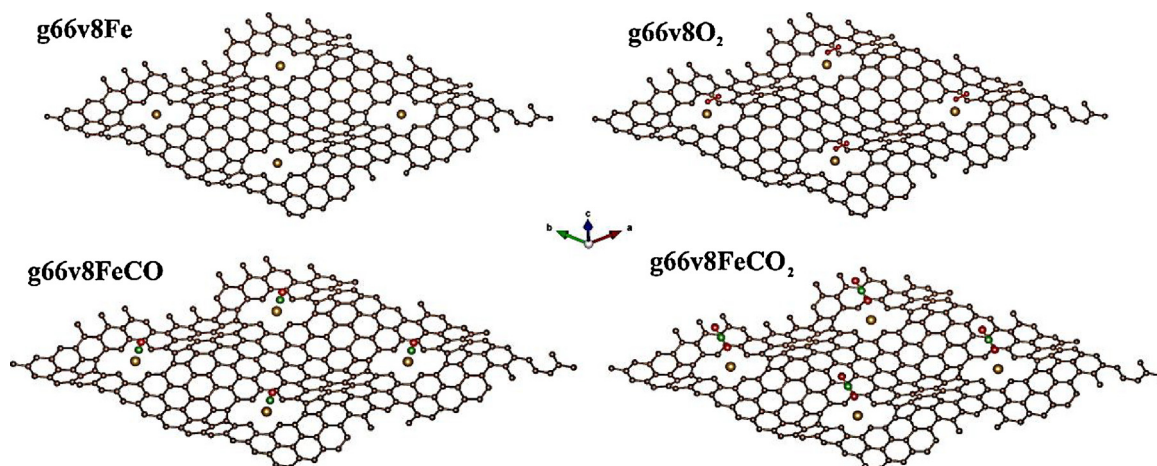


Fig. 2. Structures in perspective for g66v8Fe and g66v8FeO₂ in the top, g66v8FeCO and g66v8FeCO₂ in the bottom.

Table 1
Selected distances and angles.

	g66v8Fe	g66v8FeO ₂	g66v8FeO ₂ Fe(2+)	g66v8FeCO	g66v8FeCO ₂
Fe-X ₁ (Å)	Unlinked Fe	O ₂ /exp [32].	O ₂ (2+)	CO/exp [33].	CO ₂
X ₁ -X ₂ (Å)	–	1.85/1.75(2)	1.85	1.70/1.77(2)	2.70
X ₂ -O _b (Å)	–	1.30/1.15(4)	1.26	1.17/1.12(2)	1.18
Fe-C ₁ (Å)	2.21	2.21	2.27	2.22	2.20
Fe-C ₂ (Å)	2.21	2.17	2.17	2.18	2.20
Fe-C ₃ (Å)	2.21	2.17	2.17	2.18	2.19
Fe-C ₄ (Å)	2.21	2.21	2.27	2.22	2.20
C ₁ -Fe-C ₂ (°)	79.1	79.5	79.0	79.0	79.3
C ₂ -Fe-C ₃ (°)	100.9	101.0	103.0	102.6	100.7
C ₃ -Fe-C ₄ (°)	79.1	79.5	78.9	79.0	79.5
C ₄ -Fe-C ₁ (°)	100.8	98.2	96.8	99.1	100.4
Fe-X ₁ -X ₂ (°)	–	125.9/131(2)	127.7	179.2/180	125.3
O-C-O _b (°)	–	–	–	–	179.4
Dihedral ₁ (°) C5-C6-C7-C8	0.1	0.9	0.6	0.0	0.0
Dihedral ₂ (°) C9-C10-C11-C12	153.5	151.7	152.9	152.8	152.7

With X₁ = C for CO, X₁ = O for O₂ and CO₂, and X₂ = C for CO₂, X₂ = O for O₂ and CO.

The experimental data in this Table correspond to an iron porphyrin complex.

(+2) indicates an octavacancy graphene system with attached Fe, where a nominal 2+ charge is present.

kept at $c \sim 30$ Å in order to avoid interferences between periodical images. Dipole corrections were included in order to minimize the effect of polarization in the electronic structure.

3. Discussion and results

3.1. Geometry and charge density

Structures of an octavacancy graphene system with an iron atom in the centroid of the vacancy, with the different situations studied in this report -i.e. with unlinked iron (without any molecule at apical positions), with O₂, CO and CO₂ named as g66v8Fe, g66v8FeO₂,

g66v8FeCO and g66v8FeCO₂, respectively-, are represented in different spatial orientations as shown in Figs. 1 and 2. Selected distances and angles for these structures are summarized in Table 1, with a labeling scheme shown in Fig. 1a). The symmetrical location of the Fe atom inside the vacancy was confirmed by selective phonons, in which we confirm the local structure of the reported structure, where the iron is placed at the centroid of the vacancy.

It is clear that the main distances and angles that appear in the literature between the iron atom and the interacting gaseous molecules in porphyrin systems are in agreement with the ones that we report in this manuscript [32,33]. Due to the potential role of the five-membered ring in the distortions and the flatness, in order

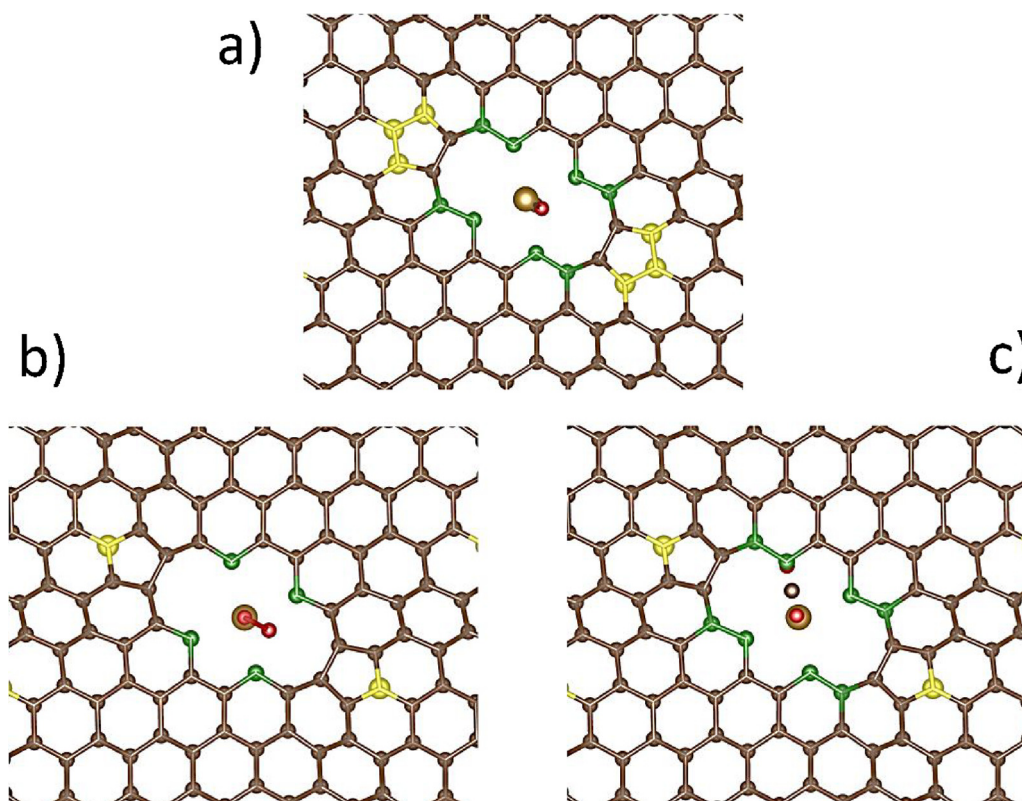


Fig. 3. Top view for structure a) g66v8FeCO, b) g66v8FeO₂ and c) g66v8FeCO₂. The reason why some carbon atoms are colored in green and yellow is explained in text. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

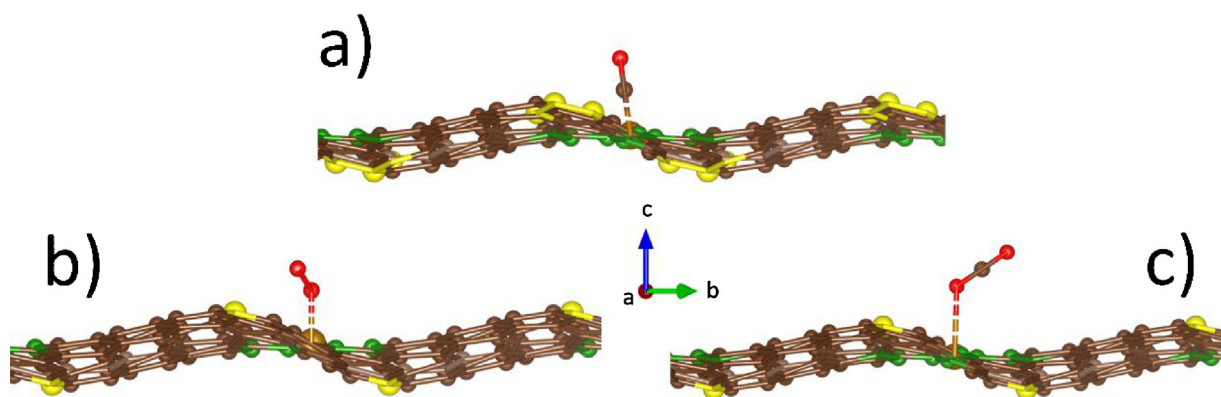


Fig. 4. Side view for structure of a) g66v8FeCO, b) g66v8FeO₂ and c) g66v8FeCO₂. The reason why some carbon atoms are colored in green and yellow is explained in text. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

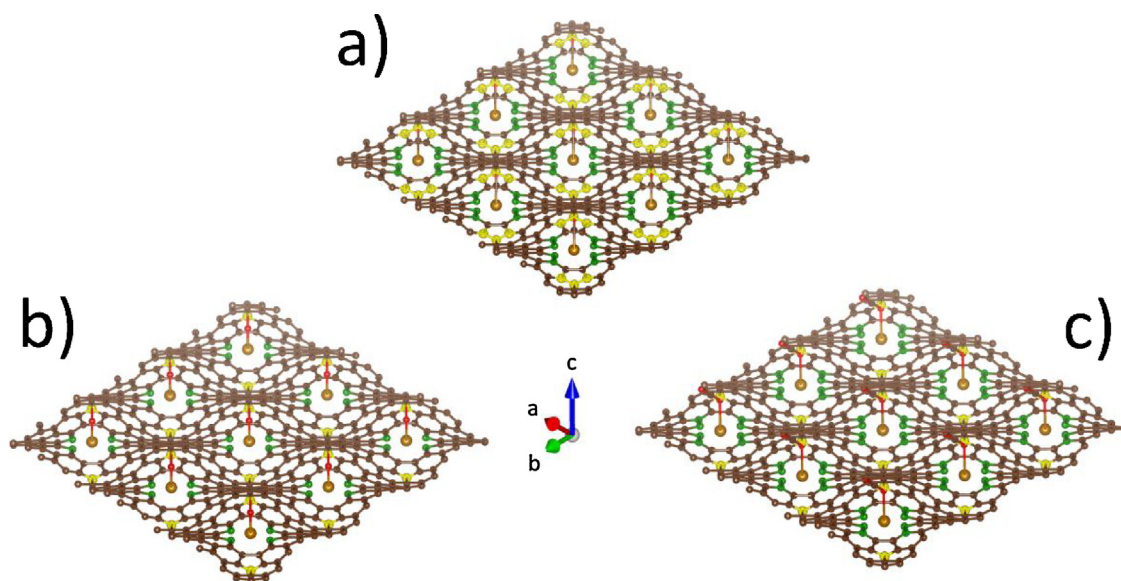


Fig. 5. Structures in a perspective that allows seeing the rippling of the graphene layers. a) g66v8FeCO, b) g66v8FeO₂, and c) g66v8FeCO₂. The reason why some carbon atoms are colored in green and yellow is explained in text. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

to compare the four structures, two dihedral angles are considered, in both cases, in regions of their influence.

As in other graphene systems where the occurrence of rippling has been observed through simulations [34,35] and experiments [36–39], we observed non-planar structures for the three compositions with a molecular aggregate and for the unlinked graphene system, g66v8Fe [19], as well. The presence of ripples or roughness is a well-known experimental fact [36–39],[36–39],40], but in spite of some exceptions, mainly considering oxidation of graphene [41,42], these features are not easily obtained in conventional DFT calculations. The non-flatness of the defected graphene moiety for the octavacancy system that is the focus of the present manuscript has been studied [22], as well as the ripples that appear for the iron embedded to the same octavacancy graphene system [19]. The rippling parameters, defined as the maximum difference in z-coordinates for each case, are 1.97 and 2.23 Å, for g66v8 [22] and g66v8Fe [19], respectively. The same kind of rippling –i.e. following a shape resembling a sinusoidal function– is observed for the cases where O₂, CO or CO₂ molecules are linked to the iron atom, and the rippling parameters are 2.53, 2.40 and 2.40 Å, respectively. The enhancement of the distortion of the graphene lamellar structure towards layers with more pronounced periodic rippling is the con-

sequence of the charge redistribution due to the molecules linked to the iron atom. Figs. 3–5 show this effect. In spite of the fact that almost all the charges in the vacancy graphene layer exhibit changes in their charges, the ones shown in green and yellow colors show differences beyond certain limits: $q < 0.975Q$ and $1.025Q < q$, for green and yellow color, respectively –being Q the average charge for the carbon atoms in each case–. Thus, the atoms that are shown in brown color are considered to show non-significant variations. Selected values of charge difference and average distances in the depletion charge, the unchanged and the excess charge regions are shown in Table 2. As it can be deduced from Fig. 4, the green and the yellow regions –i.e. the regions with charge depletion or charge excess– are the ones where the bending occurs in order to form the ripples and flatness is seen in the brown zone, where no significant charge variation is seen. The carbon atoms in the vacancy show charge depletion for the three studied cases –CO, O₂ and CO₂– and the pentagonal figures act as charge reservoirs for the imbalance along the defective graphene layer.

Thus, the vacancies and particularly the four carbon atoms available for the coordination complex formation –named C1, C2, C3 and C4–, have charge imbalance, and the positions of the dangling

Table 2

Main charge variation and average distances in different charge regions for g66v8Fe, g66v8FeO₂, g66v8FeCO and g66v8FeCO₂.

gas molecule attached to the iron atom	CO	CO ₂	O ₂
lowest Δq	−0.179	−0.171	−0.172
highest Δq	0.094	0.093	0.083
highest Δq - lowest Δq	0.273	0.264	0.255
average distance in the depletion charge region (Å)	1.443	1.444	1.438
average distance in the unchanged charge region (Å)	1.429	1.429	1.427
average distance in the excess charge region (Å)	1.405	1.405	1.407

Δq is in reference to the q mean value.

bonds become prone to interact with the iron atom in the centroid, as previously reported [18,19].

At this point it is important to compare this system with porphyrins where heteroatoms (nitrogen atoms) coordinate with a transition metal atom. The 8-order multivacancy system in this manuscript has no heteroatom but instead the four carbon atoms, C1, C2, C3 and C4 are the ones that coordinate with the iron atoms. There is charge transference between these carbon atoms and the iron atom, which help the resemblance with the porphyrin sys-

tems where the presence of nitrogen plays a key role, coordinating with the transition metal atom. In fact, the iron atom increases its charge by 0.40 e^- , 0.65 e^- and 0.11 e^- , for the O₂, CO and CO₂ systems, respectively, in reference to the unlinked Fe system. This charge is extracted from the whole graphene vacant system, with special emphasis on the carbon atoms at the vacancy, which helps them to work similarly as heteroatoms. In this way, it is possible to study a realistic and feasible system since the iron atoms could be located in multivacancies in graphene, where the presence of nitrogen atoms in particular places is not needed and then, the whole system could react with gas molecules.

The rippling is oriented in a similar way for all cases. In spite of the fact that it exhibits the higher rippling parameter, the O₂ case shows the lower charge differences and also the milder differences in C-C average distances in the charge depletion and the charge excess region.

We also performed simulations with a +2 charged system, thus emulating the biological system where iron has +2 oxidation state. As it can be seen in Table 1, there are no significant variations with or without the application of this charge, since it is diluted in the extended graphene layer. This result allows us to think of the conclusions extracted from the present report as valid ones, regardless of the oxidation state of the metal atom.

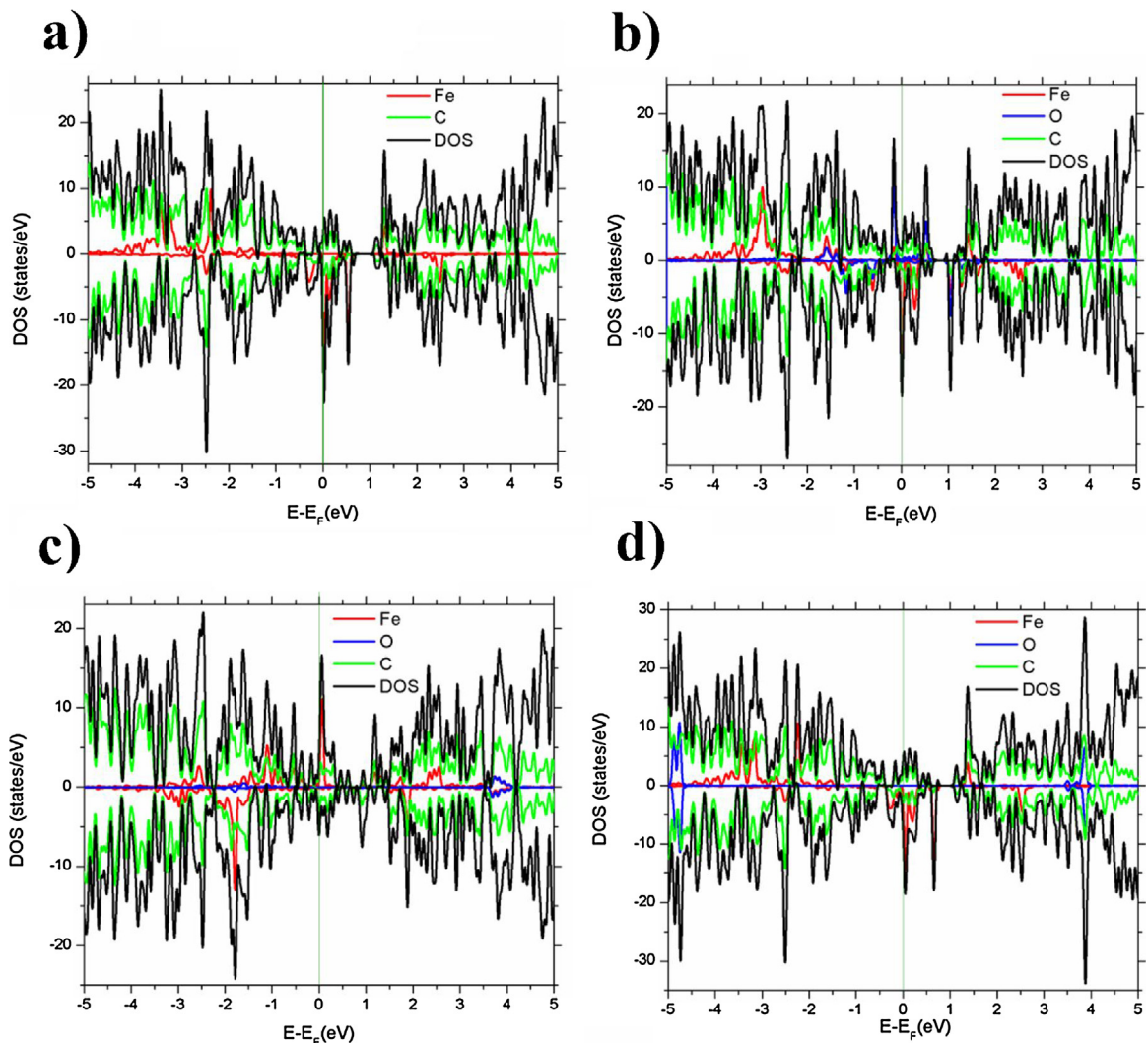


Fig. 6. Density of states (DOS) for a) g66v8Fe, b) g66v8FeO₂, c) g66v8FeCO and d) g66v8FeCO₂ are represented in black. Different contributions are represented the different contributions, red for Fe, green for C and blue for O. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

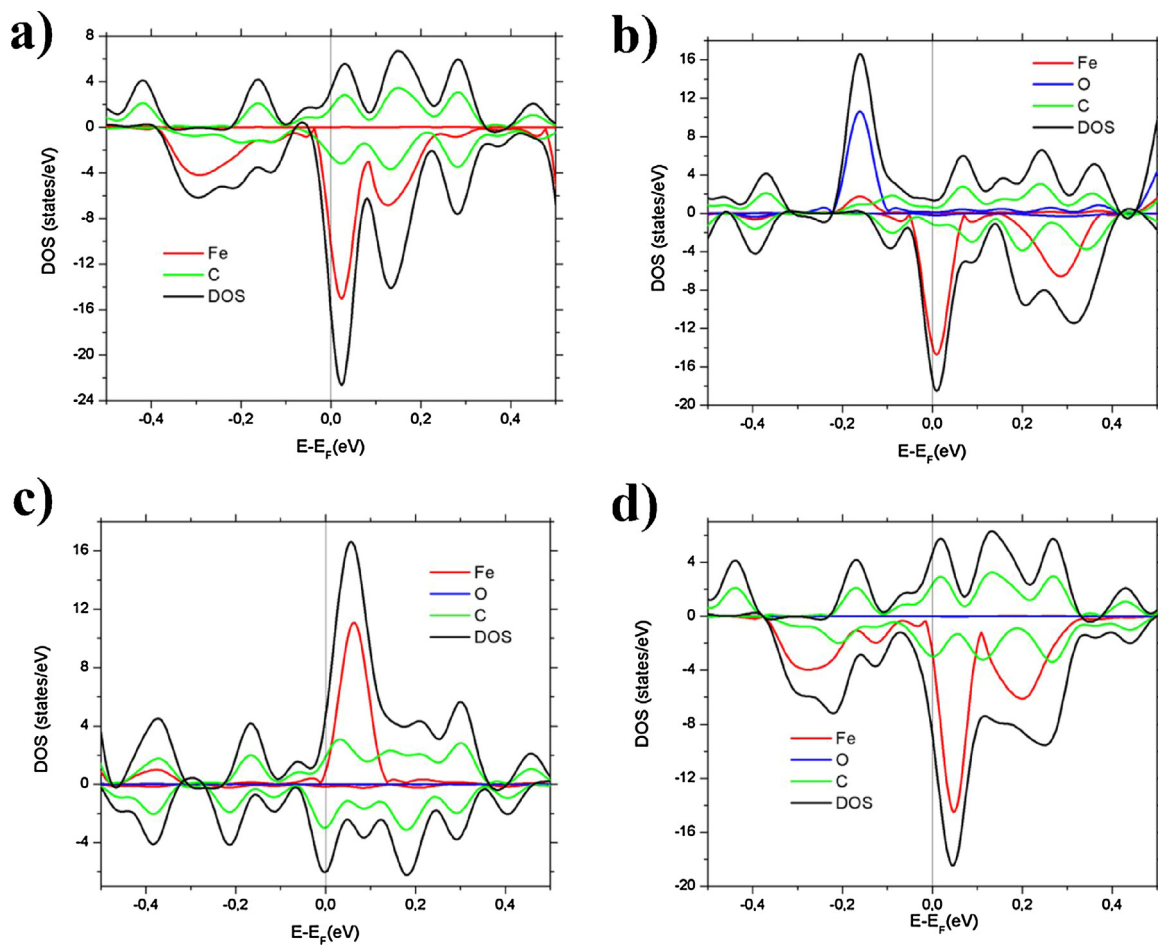


Fig. 7. Density of states (DOS) for a) g66v8Fe, b) g66v8FeO₂, c) g66v8FeCO and d) g66v8FeCO₂ are represented in black. Different contributions are represented the different contributions, red for Fe, green for C and blue for O. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

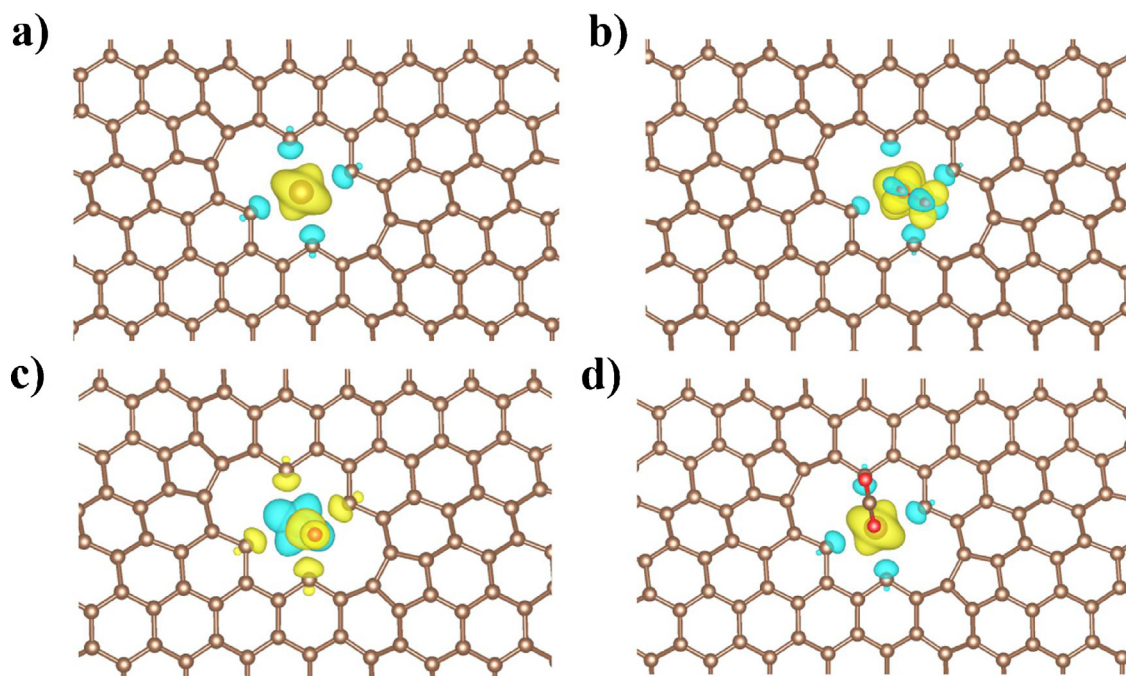


Fig. 8. Spin-up and spin-down isosurfaces at 50% of maximum value are presented in yellow and cyan, respectively. For a) g66v8Fe, b) g66v8FeO₂, c) g66v8FeCO and d) g66v8FeCO₂.

Table 3Magnetic moment and absorption energies for g66v8Fe, g66v8FeO₂, g66v8FeCO and g66v8FeCO₂.

	Unlinked Fe	O ₂	CO	CO ₂
Magnetic moment (μ_B)	3.01	3.05	1.17	2.92
Absorption energy (eV)	–	–7.53	–1.44	–0.15

As it is the case for the unlinked Fe structure, all the systems show metal character, with an important role of the iron atom with a semimetal contribution at the Fermi level, complementing with the carbon layer to the other spin channel. This can be seen in Fig. 6. All the systems are stable, as deduced from the favorable formation energies and they all exhibit important magnetic moments, mainly due to the iron presence (see Table 3). Fig. 8 shows the interaction between the spin density in the dangling bonds of the four carbon atoms in the vacancy that coordinates with the iron atom and the opposite spin density of this last one. In the cases of the gas molecules, while CO₂ does not play any role, O₂ and CO counterbalance the spin contribution of iron, slightly enhancing it for the first one and clearly depleting the total spin density for the last one.

3.2. Magnetism

In reference to the magnetism, all the studied structures present spin-polarization. The situation involving iron is evident, but the interesting fact is how the spin-polarization is extended to the carbon backbone. This situation can be evident from the projected density of states, particularly in the region close to the Fermi energy, in which the difference between up- and down- states is present for all the atoms, see Fig. 7. This picture is accompanied by the spin-density maps, presented in Fig. 8, where the ferrimagnetic coupling between Fe and the porphyrin-like C atoms is evidenced. In the case of O₂ and CO both molecules becomes magnetized, while CO₂ remains diamagnetic, as would be expected from their particular electronic structure. Due to this fact, the system with CO₂ is very similar to the unlinked Fe one.

The estimated critical temperature, T_c , extracted from density of states graphics, for g66v8Fe, g66v8FeO₂, g66v8FeCO, g66v8FeCO₂ were ~220, 302, 93 and 226 K, respectively –using $k_B T_c = \Delta E$, being $\Delta E = E_u - E_d$, where E_u and E_d are the energy values at maxima in pDOS for carbon, for spin -up and -down, and k_B is Boltzmann constant-. These values could give us an approximation regarding which system is the harder magnet when the different molecules are linked. We could observe that g66v8FeO₂ and g66v8Fe are harder magnets than g66v8FeCO and g66v8FeCO₂.

From DOS graphs, the differences in the contributions to the number of states at the Fermi level are evident, when considering different molecules, comparing among them and with the situation without molecule too.

4. Conclusions

We have studied a porphyrin-like system consistent of a periodic octavacant graphene with an iron atom embedded and its interaction with O₂, CO and CO₂. The linkage between iron and the gas molecules is energetically favorable, yielding to complexes with the same geometric characteristics than the porphyrin ones. Although this resemblance can be seen, no heteroatoms are necessary to be present due to the difference of charge that occurs in the four coordinating carbon atoms when the vacancy is created and the iron atom is linking those atoms. The rippling in the graphene structures that is enhanced when the complexes form, is originated by the pentagonal figures concentration [22] but with the key role of charge redistribution along the atoms of this layer, due to the interaction between the iron atom and the coordinated molecule.

The regions in graphene with charge depletion are important for the bending, yielding to the enhanced rippled structures that the doped materials show. The interaction with gas molecules modifies the properties of the systems. We here conclude that the search for new materials with enhanced rippling occurrence in graphene structures, could be oriented to interacting molecules that could affect the distribution of charge along the carbon layer. This system could be considered as a platform for the design of new materials with advanced properties that could be potentially used for sensor devices purposes.

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