



3.15 A Proposal based on quantum phenomena for the ORR mechanism on Nitrogen-doped Carbon-based electrocatalysts. A DFT study

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ABSTRACT

Several theories attempt to explain how nitrogen-doped carbon-based electrocatalysts work during the oxygen reduction reaction (ORR). However, no consensus has been reached on which of the proposed mechanisms is the most accurate. The present work aims to establish a hypothesis of this mechanism, based on the hybridization change of graphene lattice carbons, from sp^2 to sp^3 . As shown in several studies, carbons with sp^3 hybridization are able to store electrons (i.e. work as capacitors), this phenomenon, along with nitrogen inversion, due to lattice defects, presumably allows nitrogen to work as a switch, by letting pass or stopping the flow of electrons, thus generating active sites to enhance the ORR. Computational chemistry has been proposed to prove this hypothesis. Ninety-two doped and undoped graphene atoms were constructed using the Gaussian View 5.0® program and geometries optimized by applying the DFT in Gaussian 09® program, to compare lattice changes in bond angles and lengths. The obtained results did not present significant changes to help demonstrating the hypothesis. The understanding of this phenomenon will allow to evaluate the feasibility of continuing the study and development of these type of materials or if they have reached their limit as low-cost electrocatalysts.

Keywords: ORR, Carbon-based electrocatalysts, nitrogen inversion, DFT.

1. Introduction



One of the main processes during the operation of fuel cells is the oxygen reduction reaction (ORR). The rate at which this reaction takes place is slow in comparison to hydrogen oxidation, which limits the performance of fuel cells. For this reason, the development of electrocatalysts has been studied in the last decades. According to diverse investigations, metal-free carbon compounds present adequate electrocatalytic activity, making them one of the most promising options as low-cost electrocatalytic materials.

Among carbon compounds recently studied are those doped using heteroatoms^{i,iii,iii}, mainly nitrogen^{iv}(N), which significantly improves the reaction rate.

There is no clear understanding of the effect of these atoms within the carbon lattice, so the scientific community has the task of explaining this phenomenon, since these materials prove to be more economical and chemically stable.

The inclusion of heteroatoms (N, S, P) and the generation of defects in carbon compounds such as graphite, graphene and carbon nanotubes, from pyrolytic processes, modify their atomic and electronic structure, resulting in a wide range of new materials with outstanding properties, thus providing a broad outlook for research into the development of electrocatalysts, supercapacitors and batteries.

Remarkable researches related to the mechanism of heteroatom-doped carbon-based electrocatalysts in ORR are Zahoor *et al.* who explain the effect in carbon-based materials with sp^2 electron configuration (graphite, graphene and carbon nanotube), which have abundant π (π) electrons. These electrons are transferred without resistance due to the type of their hybridization. This electron flow makes these materials potential catalysts for reactions in need of electrons like the ORR. However, these electrons are not enough reactive to be used directly for this purpose. It is then considered that π electrons can be activated by bonding with the solitary electron pairs of N, so that O_2 molecules are reduced in the positively charged carbons by the effect of neighboring nitrogen atoms^v.

Li Ting *et al.* explain that the factors contributing to the electrocatalytic activity of heteroatom-doped graphene in the ORR are the microstructure and high spin density or charge density on adjacent carbon atoms. Edge plane sites or defects in graphene are the primary source of their electrochemical activity, the addition of impurities alter the basal surface and create defects or sites in the edge of the plane, which are responsible for controlling the catalytic activity^{vi}.

Some simulation aided researches: Wang *et al.* examined three BCN graphene models using DFT models. In these models, B and N atoms were distributed either randomly or without any BN bonds. The spin density, charge density and energy gap models were



calculated and compared. The authors observed that highly doped graphene has no spin density and possesses higher energy gap than pure graphene and the other models^{vii}. Yu *et al.* using a DFT study revealed that the possibility of doping two or more nitrogen atoms into two neighboring defect sites is quite low by examining the interaction energy between the two nitrogen atoms^{viii}. Okamoto *et al.* using the Atom TEchnology (STATE) simulation tool calculated the atomic geometry and electronic structure according with their DFT results to investigate oxygen reduction reactions (ORRs) on N-doped carbon. Graphene sheets having one to four N impurities in the substitutional site of C around a C=C bond were examined as a model structure. They found that the binding interaction between graphene and O₂ becomes stronger as the number of N bonding atoms with the C=C increases^{ix}.

These studies provide a preliminary understanding of the ORR, but until today, a thorough explanation of why different compounds derived from carbon doped with heteroatoms achieve good performance as electrocatalysts is missing.

This work is the first part of several calculations that will be performed in an attempt to explain the nitrogen-doping graphene lattice mechanism in ORR electrocatalysts. It differs from other mechanisms based on platinum, as it presents the possible interaction of nitrogen atoms in the graphene lattice and the electron flow necessary for ORR at a stage prior to oxygen adsorption on the electrocatalyst. The theoretical studies are based on phenomena of quantum nature, the tunnel effect and nitrogen inversion. Computational chemistry has been proposed to prove the theory by working with Gaussian 09 ® and Gaussian View 5.0 ®.

Quantum tunnel effect.

The quantum tunnel effect occurs when a particle is able to penetrate a potential or impedance barrier greater than the kinetic energy of the particle. According to theory, even though the particle does not have sufficient energy to penetrate this barrier, it passes through it energetically, because at the quantum level it exhibits a wave behavior that is possible to describe as a wave function, where there is a possibility that this particle is displaced through the structure^x.

Nitrogen inversion

A type of quantum tunnel is the phenomenon called nitrogen inversion, which is the translation of the pair of lone nitrogen electrons through the nitrogen nucleus and their

reappearance on the opposite side. This effect has an intermediate state with the appearance of orbitals with a trigonal structure. The structure goes from hybrid sp^3 orbitals to sp^2 to later stabilize in the sp^3 form of its optical isomer. Nitrogen must have three different groups and a pair of lone electrons. Theoretically many molecules are capable of this inversion, but laboratory measurements show that only in nitrogen the inversion barrier is low enough for this phenomenon to occur constantly^{xi}.

Nitrogen inversion in the graphitic lattice

As mentioned previously in a graphene lattice, carbon is present in sp^2 hybridization, causing resonance with adjacent carbon atoms, producing an electron flow throughout the graphene lattice. It would behave as an excellent electrical conductor with a gap close to 0 with a metallic character, like other graphene compounds such as carbon nanotubes (NTC).

The ORR is favored in a graphene lattice environment with multiple defects, as evidenced by various studies that relate electrocatalytic activity to Raman spectrometry analysis. These topological defects can be produced by heteroatom (nitrogen) insertions, by various chemical processes or by mechanical ball-milling, producing sp^3 hybridizations with tetrahedral structures, different from sp^2 bonds that have a flat trigonal structure. Additionally, this distortion of the graphene lattice produces a variation in the measurement of angles of carbons attached to the nitrogen atom. This could cause those adjacent carbons to function with the nitrogen atom as if they were different radicals (even though they are the same carbon) achieving nitrogen inversion, causing the electron pair to travel across the nitrogen nucleus causing hybrid states $sp^2 - sp^3$ and vice versa continuously at a very high speed. This phenomenon may result in nitrogen to behave mainly as an on-off switch. As it switches back, nitrogen inversion produces its change to sp^3 hybridization interrupting resonance and electron flow, thus causing nitrogen to take the function of a diode where current follows a single direction. Then, these electrons are able to interact with the oxygen and achieve the overpotential required for the ORR.

Another factor that could favor this reaction is that carbon structure in sp^3 hybridization may retain electrostatic charges, since its behavior is that of an electrical insulator as several studies claim^{xii,xiii} that this would work as a capacitor with charge-discharge interactions, during the nitrogen inversion, helping with the concentration of electrons that can be used in ORR.

2. Computational details

2.1 Molecular construction

Using a graphene lattice model comprised by 25 hexagonal carbon rings with resonance, with 92 atoms. Two different lattices were constructed using Gaussian View 5.0®, one graphene lattice with 70 carbons sp^2 hybridization and 22 hydrogen atoms, with the second one using the first one as a base, with the difference of just a central sp^2 carbon being replaced by a nitrogen atom.

2.2 Geometry optimization and frequency

The lattices were optimized and frequencies were calculated to verify the geometry in the minimum energy state, using density functional theory (DFT). All calculation were developed with Gaussian 09 ® program. The employed calculation methodology has been widely used by NANOCOSMOS group at CIMAV and is the combination of the hybrid functional Lee, Yang and Parr (B3LYP) and 6-31G basis set^{xiv,xv,xvi}. All calculations were performed in gas phase.

3. Results and Discussion

The graphene lattice structure is planar, with an average length bond of 1.42Å and the measure of its angles is 120° ^{xvii}. A variation in bond length and/or opening of angles between atoms where carbon was replaced by a nitrogen atom were expected. The graphene lattice before and after the optimization presented a planar structure without deformations (*Figure 1*). *Table 1* shows bond length and angle measurements for the optimized lattice. The values are according with experimental measurements¹⁷. The nitrogen-doped graphene lattice before the optimization show a small deformation (*Figure 2 (A)*), after optimization the lattices present a planar structure (*Figure 2 (B)*). *Table 2* shows bond lengths and angles being present in the doped lattice after optimization.

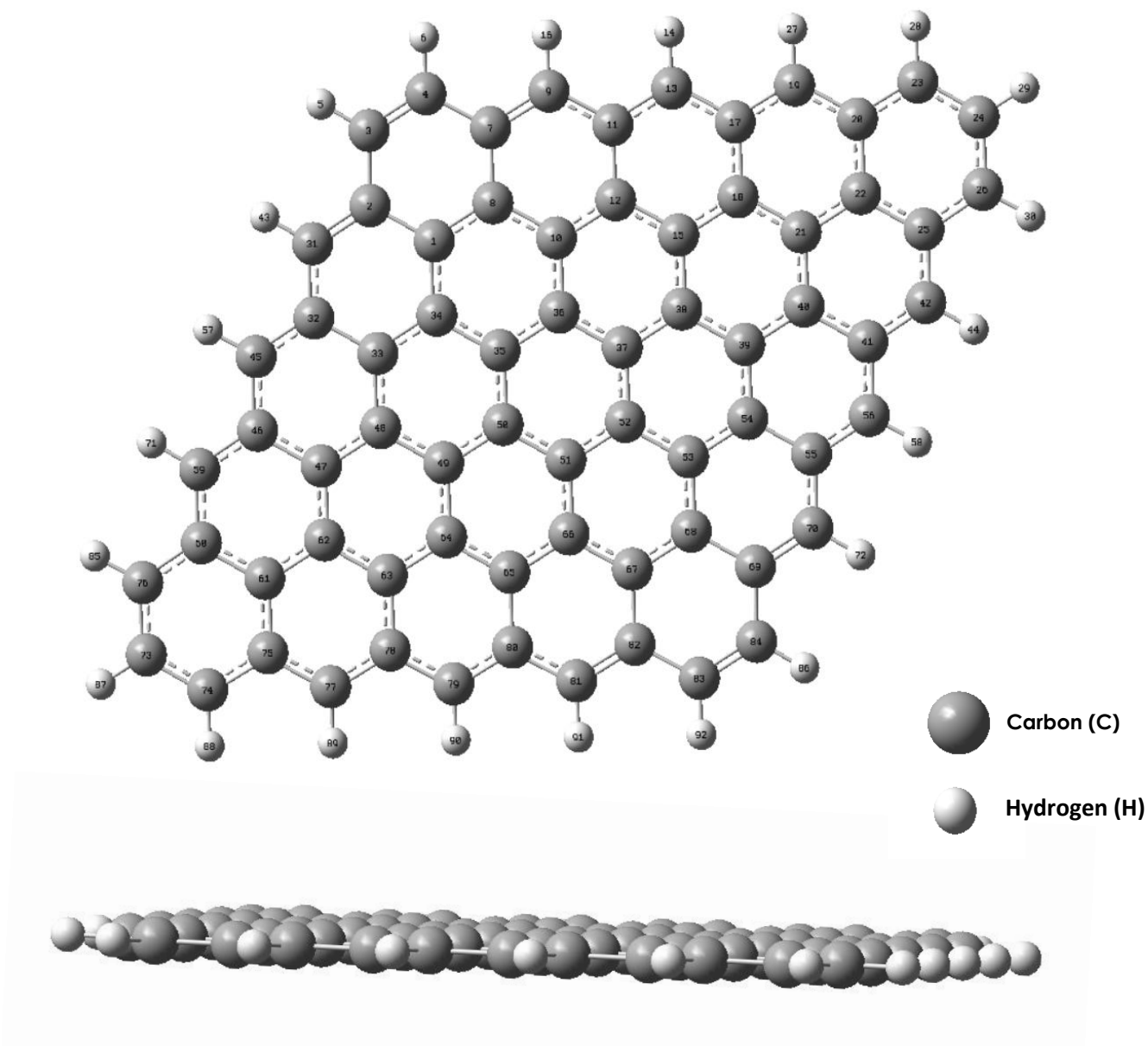


Fig 1. Graphitic lattice optimized by DFT.

Table 1. Bond lengths and angle measurements in the graphene lattice.

OPTIMIZED GRAPHENE B3LYP	
Bond	Length (Å)
C ₃ -H ₅	1.08611
C ₂₄ -H ₂₉	1.08539



$C_{84}-H_{86}$	1.0811
$C_{73}-H_{87}$	1.08539
C_3-C_4	1.35913
C_4-C_7	1.4491
C_7-C_9	1.38072
C_3-C_2	1.4491
$C_{24}-C_{26}$	1.3959
$C_{24}-C_{23}$	1.3959
$C_{70}-C_{69}$	1.38072
$C_{69}-C_{84}$	1.4491
$C_{84}-C_{83}$	1.35913
$C_{73}-C_{74}$	1.3959
$C_{73}-C_{76}$	1.3959
$C_{18}-C_{21}$	1.42863
$C_{54}-C_{55}$	1.44776
$C_{65}-C_{66}$	1.41178
$C_{47}-C_{62}$	1.42863
Atoms	Angle (°)
$C_3-C_4-C_7$	121.608
$C_4-C_7-C_8$	117.872
$C_{20}-C_{23}-C_{24}$	120.907
$C_{23}-C_{24}-C_{26}$	120.907
$C_{82}-C_{83}-C_{84}$	121.608
$C_{83}-C_{84}-C_{69}$	121.608
$C_{76}-C_{73}-C_{74}$	120.907
$C_{73}-C_{74}-C_{75}$	120.827

OPTIMIZED GRAPHENE B3LYP	
Bond	Length (Å)
C ₃₅ -C ₃₆	1.41601
C ₃₅ -C ₃₄	1.43262
C ₃₅ -C ₅₀	1.42971
C ₃₆ -C ₃₇	1.42971
C ₃₄ -C ₃₃	1.41177
C ₃₆ -C ₁₀	1.43262
C ₅₀ -C ₅₁	1.42972
C ₃₄ -C ₁	1.43949
C ₁₀ -C ₁₂	1.41177
Atoms	Angle (°)
C ₃₄ -C ₃₅ -C ₃₆	120.111
C ₃₄ -C ₃₅ -C ₅₀	119.842
C ₅₀ -C ₃₅ -C ₃₆	120.047
C ₃₅ -C ₅₀ -C ₅₁	119.905
C ₃₅ -C ₅₀ -C ₄₉	120.047
C ₃₅ -C ₃₄ -C ₁	119.555
C ₃₅ -C ₃₄ -C ₃₃	120.034
C ₃₅ -C ₃₆ -C ₁₀	120.111

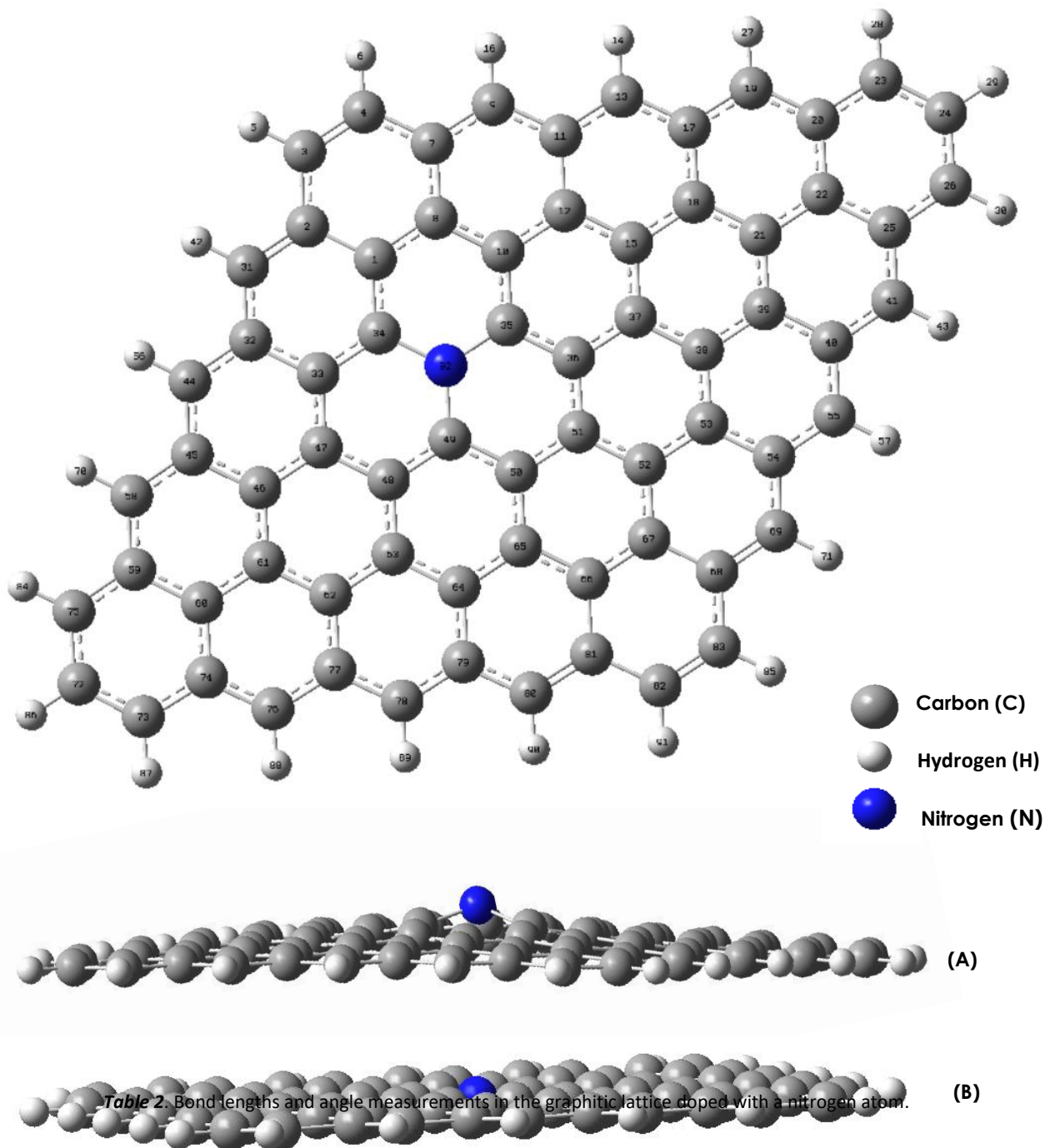


Fig 2. Graphene lattice with one nitrogen optimized by DFT, using the B3LYP functional. (A) Graphene lattice before the optimization shows deformation. (B) Graphene lattice after optimization, with a planar structure.

OPTIMIZED GRAPHENE WITH NITROGEN B3LYP	
Bond	Length (Å)
C ₃ -H ₅	1.08561
C ₂₄ -H ₂₉	1.08572
C ₈₄ -H ₈₆	1.08597
C ₇₃ -H ₈₇	1.08573
C ₃ -C ₄	1.35993
C ₄ -C ₇	1.44411
C ₇ -C ₉	1.38877
C ₃ -C ₂	1.44429
C ₂₄ -C ₂₆	1.39821
C ₂₄ -C ₂₃	1.39294
C ₇₀ -C ₆₉	1.38244
C ₆₉ -C ₈₄	1.44747
C ₈₄ -C ₈₃	1.3593
C ₇₃ -C ₇₄	1.38936
C ₇₃ -C ₇₆	1.40234
C ₁₈ -C ₂₁	1.42414
C ₅₄ -C ₅₅	1.43819
C ₆₅ -C ₆₆	1.41381
C ₄₇ -C ₆₂	1.43322
Atoms	Angle (°)
C ₃ -C ₄ -C ₇	121.326
C ₄ -C ₇ -C ₈	118.047
C ₂₀ -C ₂₃ -C ₂₄	120.802
C ₂₃ -C ₂₄ -C ₂₆	121.082
C ₈₂ -C ₈₃ -C ₈₄	121.677



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$C_{83}-C_{84}-C_{69}$	121.507
$C_{76}-C_{73}-C_{74}$	121.098
$C_{73}-C_{74}-C_{75}$	120.88

OPTIMIZED GRAPHENE WITH NITROGEN B3LYP	
Bond	Length (Å)
N ₉₂ -C ₃₅	1.4107
N ₉₂ -C ₃₄	1.4227
N ₉₂ -C ₄₉	1.41979
C ₃₅ -C ₃₆	1.41968
C ₃₄ -C ₃₃	1.40679
C ₃₅ -C ₁₀	1.42263
C ₄₉ -C ₅₀	1.42415
C ₃₄ -C ₁	1.42583
C ₁₀ -C ₁₂	1.41806
Atoms	Angle (°)
C ₃₄ -N ₉₂ -C ₃₅	120.165
C ₃₄ -N ₉₂ -C ₄₉	119.547
C ₄₉ -N ₉₂ -C ₃₅	120.289
N ₉₂ -C ₄₉ -C ₅₀	119.637
N ₉₂ -C ₄₈ -C ₄₉	120.263
N ₉₂ -C ₃₄ -C ₁	119.47
N ₉₂ -C ₃₅ -C ₁₀	120.112
N ₉₂ -C ₃₄ -C ₃₃	120.122

4. Conclusion

Comparison of measurements obtained from bond lengths and angles between the nitrogen-doped and undoped graphene lattice, do not show a significant difference. It is necessary to continue this work by including more parameters (e.g. electron density) to see if it is possible to observe an effect that will provide enough information to prove or disapprove our hypothesis, which is based on the nitrogen inversion and sp³ carbon



influence on the activity enhancement of nitrogen-doped carbon electrocatalysts towards the ORR.

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