Electronic States Generated by Single and Double Carbon Defects in Pyrene, Extended Pyrene and 7a,7z-Periacene as a Model for Graphene Sheet

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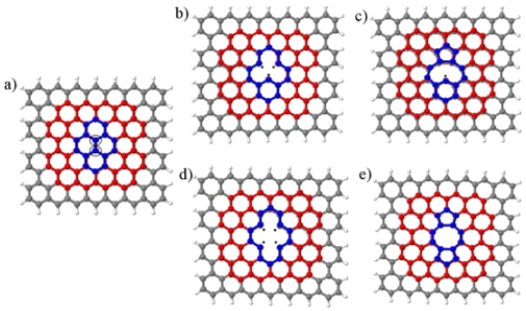
INTRODUCTION

Graphene consists of a single atomic layer of graphite and possesses exceptional electronic, thermal, and mechanical properties. A variety of defects can occur in graphene, often times through single or multiple vacancies of carbon atoms, yielding dangling bonds, which arise during defective growth or after irradiation of the material. The dangling bonds can associate with a multitude of closely spaced excited electronic states with different spin multiplicities, which leads to a very challenging theoretical description. This work focuses on prototypes of single and double vacancies in a graphene sheet using pyrene (blue), extended pyrene (red) and 7a,7z-periacene (gray) as model structures, as shown in Scheme 1.



Scheme 1. b,c) unrelaxed; d,e) relaxed.

METHODS

The pyrene, extended pyrene, and 7a,7z-periacene structures were optimized using the B3LYP density functional with the 6-31G* basis set. Next, the one and two innermost carbon atoms were removed from the structures. (U)DFT/B3LYP single point and geometry optimizations were performed for some low-lying electronic states with singlet and triplet multiplicities. Linear interpolation curves between the unrelaxed and relaxed structures were also performed. All calculations were carried out using the TURBOMOLE program.

RESULTS AND DISCUSSION

Recently, using pyrene as a model, we have shown[1,2] by means of MRCI calculations, that single and double vacancy defects induce a complex set of several closely spaced electronic states leading to geometry relaxation effects with carbon-carbon bond formation. The B3LYP/6-31G* excitation energies for low-lying states in the relaxed structure are presented in Table 1.

Table 1. B3LYP/6-31G* excitation energies (eV).

State	Pyr-1C	Ext. Pyr-1C	Periac-1C
$^3B_2$	0.000	0.000	0.017
$^1B_2$	0.114	0.111	0.017
$^3A_2$	0.231	0.079	0.002
$^1A_2$	0.258	0.061	0.000
State	Pyr-2C	Ext. Pyr-2C	Periac-2C
^1A_g	0.000	0.000	0.596
$^3B_{2u}$	0.441	1.218	1.523
$^1B_{2u}$	0.479	1.435	1.595
$^3B_{3u}$	1.430	1.530	0.000

CONCLUSIONS

We have obtained a detailed picture of the manifold of electronic states occurring due to the removal of one and two carbon atoms from a graphene sheet based on the local environment of the defect. We found good agreement between the MRCI[1,2] and DFT results using pyrene as a model, which give us confidence in the DFT accuracy for the investigation of larger graphene models. This will provide better insight into the embedding effects and their consequences on the electronic and geometrical structure of single and double vacancy defects.

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[1] F.B.C. Machado, A.J.A. Aquino and H. Lischka, ChemPhysChem., 15, 3334 (2014).

[2] F.B.C. Machado, A.J.A. Aquino and H. Lischka, Phys.Chem.Chem.Phys., 17, 12778 (2015).