

Influence of 5-atom rings on the optical properties of amorphous carbon nitride

R. M. Valladares^a, Alipio G. Calles^a and Ariel A. Valladares^b

^a Departamento de Física, Facultad de Ciencias, UNAM, Ciudad Universitaria, México, D. F., 04510, MEXICO

^b Instituto de Investigaciones en Materiales, UNAM, Ciudad Universitaria, México, D. F., 04510, MEXICO

Abstract

The optical properties of three amorphous tetrahedral carbon-based clusters of the type $a-C_{17-i}N_iH_{24}$ with 5-atom rings have been calculated. The hydrogens are used to passivate the outermost dangling bonds and i is 0, 1 or 4. The theoretical DFT-LDA based method used minimizes the energy of the clusters and provides the energy spectrum and the optical transitions for the minimum energy structures. The optical absorption spectrum of each cluster is analyzed and a comparison is made with previously reported spectra for clusters with 6-atom boat-type rings in order to see the influence of the present atomic topology.

Keywords: Amorphous semiconductors, Clusters, Tetrahedral carbon, Ab initio density functional calculations

1. Introduction

Amorphous carbon has a variety of bondings, atom topologies and coordination numbers. In general both sp^3 and sp^2 hybridizations coexist leading to 3d- and 2d-like structures and the presence of 5-atom and 7-atom rings, in addition to 6-atom boat-type rings, is not uncommon. This has made experimental results difficult to interpret unambiguously and theoretical studies hard to carry out since they both are strongly sample dependent [1]. The theoretical treatment of an amorphous material in bulk becomes rather difficult when the structure is quite bond-type dependent. In order to circumvent this problem we have undertaken a systematic study of amorphous clusters with characteristics that appear in an amorphous bulk sample [2-4]; in particular, in this work we report results for the optical properties of carbon clusters with 5-atom ring topologies, both pure and contaminated with nitrogen to better comprehend the electronic processes that take place when an electromagnetic field is applied to the bulk. To simulate the bulk we force the outermost atoms to be fixed to account for the inertia of the bulk, fit gaussian functions to the energy levels and maintain the four-fold coordinated environment with tetrahedral symmetry.

2. The Clusters

Four-fold coordinated clusters of the type $a-C_{17-i}N_iH_{24}$, where $i=0, 1$ or 4 , with 5-atom planar rings were studied, Fig. 1. Recent results for carbon clusters contaminated with nitrogen [2] indicate that this approach is promising since it allows the analysis of particular characteristics, specific restrictions or geometries that may contribute to understanding the role of different factors that are relevant to the electronic structure of these materials. The clusters were constructed using the Builder Module within the *InsightII* graphical user interface of MSI [5]. There is a central atom

that is a common vertex for 6 pentagons tetrahedrally arranged. The interior angles of the pentagons are: one of 109.47° at the common vertex, two of 106.84° closest to the previous angle and the remaining two of 108.425° . The interatomic distances are all 0.154 nm before energy optimization. The clusters were hydrogenated and the H atoms placed at a distance of 0.107 nm, without altering the tetrahedral symmetry; the central atom has 4 nearest neighbors, nn , and 12 second neighbors, $2n$. The 21 hydrogens are the outermost circles. They all have T_d point group symmetry with 6 degrees of freedom and were geometry-optimized maintaining tetrahedral symmetry. In order to simulate the inertia of the bulk and to avoid spurious changes introduced by possible motion of the hydrogens, the positions of C in the outermost layer were kept fixed, as were those of the H atoms. Nitrogen was incorporated substitutionally in the center of the cluster for $i=1$ and in the nn positions for $i=4$.

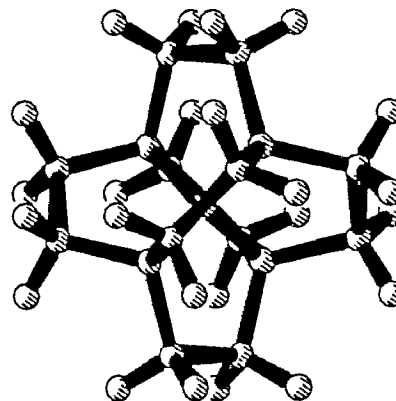


Fig. 1. $a-C_{17}H_{24}$ cluster used in the present work.

3. The Method

The theoretical *ab initio* DFT-LDA self-consistent method

used allows the minimization of the energy of each cluster and provides the energy spectrum and the optical transitions for the minimum energy structures implemented in *DMol* [6]. All minimizations were carried out for unrestricted spin using the local density approximation (LDA) of Vosko, Wilk and Nusair [7]. The solutions to the DFT equations were calculated variationally and self-consistently and these solutions provide the molecular wave function, the electron energy levels and the intensity of the dipole transitions that allow the evaluation of the optical properties of the system *without* relaxing the cluster when electrons are in excited states.

4. The Optical Absorption

The pure cluster has an absorption spectrum with an optical gap of 6.12 eV, as can be seen in Fig. 2. There are six transitions at this energy value and each one has an intensity of 0.12. For $i = 1$ the single nitrogen impurity induces three very intense transitions at low energies, 1.29 eV, with an intensity of 2.36, Fig. 3. For an optical gap of 2.25 eV three transitions appear with an intensity of 1.11. In Fig. 4 the spectrum for $i = 4$ is depicted. There are six transitions at almost the same low energy, 1.27 eV, with intensities of 2.64, 1.98, 1.98, 0.66, 0.66 and 0.00, within an overall more complicated structure. Also, there are six transitions with intensity 2.21 and energy 2.04, three with 3.46 and 2.62 eV and three with 3.29 and 2.63 eV.

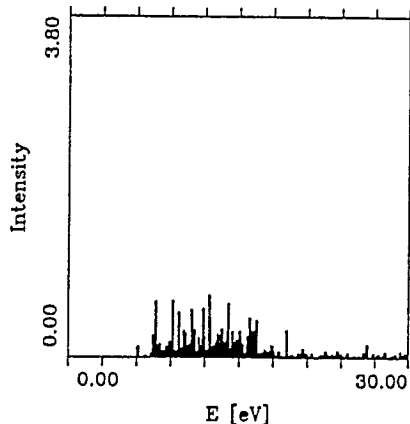


Fig. 2. Optical absorption spectrum of $a - C_{17}H_{24}$.

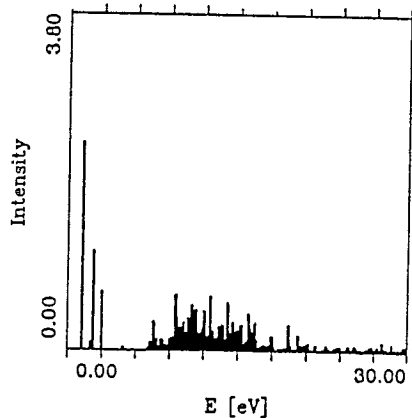


Fig. 3. Optical absorption spectrum of $a - C_{16}N_1H_{24}$.

5. Conclusions

The effect of the presence of 5-atom rings makes the impurity transitions for the $i=1$ cluster appear at lower energies than for the 49-atom clusters: 1.29 eV below the conduction band (LUMO) with an intensity of 2.36, in contrast to 1.66 eV. This indicates that the pentagonal structure affects the location of the impurity energy levels and moves them closer to the LUMO. The fact that these clusters are smaller than those of 49 atoms [2] manifests itself in that their energy gap is larger than the gap for the bigger ones (6.12 vs 5.42), but nevertheless the impurity levels here appear closer to the LUMO. For 4 nitrogens there are six transitions at 1.27 eV with intensities of 2.64, 1.98, 1.98, 0.66, 0.66 and 0.00, in comparison to 1.24 eV for the 49-atom cluster. In that case the energy levels for the larger cluster are closer to the LUMO band than are the levels for the 41-atom cluster. We have assumed that the energy levels for the excited states are obtained from the minimization supposing that the structure does not change when electrons are excited. We should bear in mind that although DFT calculations tend to underestimate the gap values no "cut and shift" operator has been applied to our results.

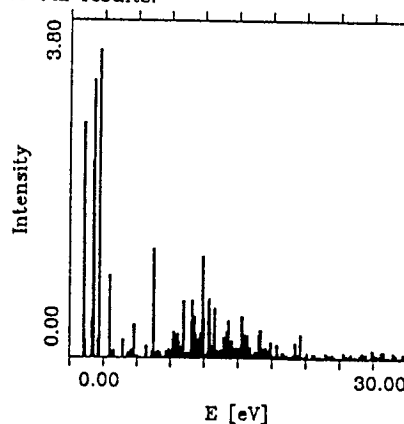


Fig. 4. Optical absorption spectrum of $a - C_{13}N_4H_{24}$.

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