Density Functional Calculations of N-14 and B-11 NQR Parameters in the H-capped (5, 5) Single-Wall BN Nanotube

Ahmad Seif, Karim Zare, Asadallah Boshra, and Mehran Aghaie

Abstract—Density functional theory (DFT) calculations were performed to compute nitrogen-14 and boron-11 nuclear quadrupole resonance (NQR) spectroscopy parameters in the representative model of armchair boron nitride nanotube (BNNT) for the first time. The considered model consisting of 1 nm length of H-capped (5, 5) single-wall BNNT were first allowed to fully relax and then the NQR calculations were carried out on the geometrically optimized model. The evaluated nuclear quadrupole coupling constants and asymmetry parameters for the mentioned nuclei reveal that the model can be divided into seven layers of nuclei with an equivalent electrostatic environment where those nuclei at the ends of tubes have a very strong electrostatic environment compared to the other nuclei along the length of tubes. The calculations were performed via Gaussian 98 package of program.

Keywords—Armchair Nanotube, Density Functional Theory, Nuclear Quadrupole Resonance.

I. INTRODUCTION

THE discovery of carbon nanotubes by Iijma has raised great interest in these quasi-one-dimensional structures [1]. The CNTs have a wide range of application from nano-electrones to nano-biotechnology e.g., they are used as either electron field emitters or artificial muscles [2-3]. Chemical and physical properties of the novel materials, being dependent also on the size and shape of the nanostructures, differ from fullerenes and carbon nanotubes [4]. The stable one-dimensional structure of BNNT was firstly recognized by heoretical calculations and after, was also successfully synthesized by experiments [5-6]. Nuclear quadrupole resonance (NQR) spectroscopy is an insightful technique to study the Physical properties of matters in solid– phase [7]. The NQR measurable parameters are Quadrupole Coupling Constant (CQ) and asymmetry parameter (η_Q) which both are also reproduced by quantum chemical calculations of the electric field gradient (EFG) tensors. Nuclei with spin angular momentum, I, greater than one-half (I >1/2), have the nuclear

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electric quadrupole moment, eQ, which interacts with the electric field gradient, EFG, tensor originated at the site of quadrupole nuclei [8]. For B-11 and N-14 spin angular momentum in order of are 1.5 and 1[9], therefore B-11and N-14 are very sensitive to the electronic density at the sites of their nuclei and feel changes by any perturbation.

The present computational work studies the electrostatic properties of BNNT systematically. To this purpose, the EFG tensors are calculated to evaluated the B-11 and N-14 NQR parameters (CQ and η_Q) (Table I) as a first predication for BNNT in the representative model of a 1-nm of length (5, 5) single-wall BNNT.

II. COMPUTATIONAL PROCEDURE

All quantum chemical calculations were performed at the level of the density functional theory (DFT) by the Gaussian 98 package of the program (10). In this study, one representative model of the single-wall armchair BNNT with tube length of 1 nm is considered in the quantum chemical calculations. This model consisting of 35 B and 35 N atoms where the two end of the tube are capped by 20 H atoms (see Fig. 1). Firstly, the considered model system was allowed to fully relax during the geometrical optimization by the BLYP method [11] and the 6-31G* standard basis set. Secondly, the EFG tensors are calculated at the level of BLYP method and the 3-21G * standard basis set in the optimized structures.

Since the EFG tensors are quantum chemically calculated in the principal axes system (PAS), to relate directly with the experiments, they are converted to measurable NQR parameters, Quadrupole Coupling Constant (CQ) and asymmetry parameter (η_Q) using Eqs. 1-2: CQ refers to the interaction energy of the nuclear electric quadrupole moment, (eQ), and the EFG tensors at the site of quadrupole nucleus while η_Q is a measure of the EFG tensors deviation from cylindrical system at the site of quadrupole nucleus. Quantum chemical calculations yield principal components of the EFG tensor, q_{ii}, in atom unit (1 au = 9.717365 × 1021 V m−2). Equations (1) and (2) are used to directly relate the calculation EFG tensors with the measurable parameters CQ and η_Q. The standard Q values reported by pyykkö [12], are employed in (1), and Q (B-11) =$0.4059×10^{-29}m^2$ And Q (N-14) = $0.2044× 10^{-29}$ m^2. Table II exhibits the calculation NQR parameters for B-11and N-14 respectively.

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$$QCC \ (MHz) = e^2 Q q_{zz}/h$$
$$\eta_Q = |(q_{yy} - q_{xx})/q_{zz}|, \quad 0 \leqslant \eta_Q \leqslant 1$$

TABLE I
THE OPTIMIZED GEOMETRIES OF THE (5, 5) BNNT

Bonding nuclei	Bond lengths (A°)	Bonding nuclei	Bond angles(deg)
B-N		N-B-N	
2-1	1.45	2-3-4	120
2-3	1.46	2-1-6	119
6-1	1.43	4-5-6	120
6-5	1.46	4-7-8	120
4-3	1.46	8-9-10	120
4-5	1.46	8-9-14	120
4-7	1.46	B-N-B	
8-7	1.45	1-2-3	117
8-9	1.46	1-6-5	120
10-9	1.46	3-4-5	118
10-11	1.46	3-4-7	117
12-11	1.43	7-8-9	116
12-13	1.46	9-14-15	118
14-9	1.46		
14-13	1.46		
14-15	1.46		
16-3	1.46		

See Fig. 1 for details

TABLE II
THE N-14 AND B-11 C_Q PARAMETER IN THE (5, 5) BNNT

Layers	B-11		N-14	
	CQ(MHz)	ηQ	CQ(MHz)	ηQ
Layer 1	2.38	0.32	1.68	0.88
Layer 2	1.90	0.04	0.73	0.60
Layer 3	1.88	0.05	0.72	0.43
Layer 4	1.42	0.06	0.72	0.2

See Fig. 1 for details
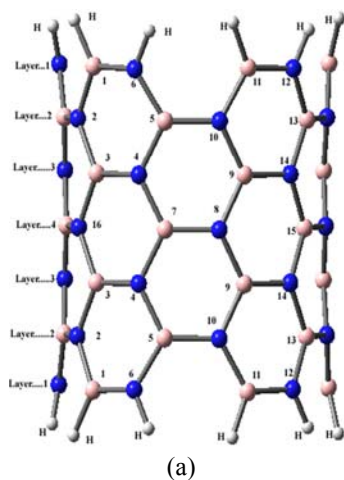
(a)
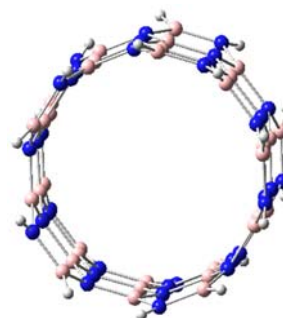
(b)

Fig. 1 (a) 2D and (b) 3D views of the considered H-capped (5, 5) SW- BNNT

III. RESULTS AND DISCUSSION

A. Geometrical Properties of BNNTs

At the first step of this study, the considered armchair representative model of BNNT was permitted to fully relax during the geometrical optimization at the level of the BLYP DFT method and the 6-31G* standard basis set. The results of Table I indicate that B-N bond lengths have almost negligible fluctuations with average values of 1.46 Å in the length of armchair tube; however, this is considerable for the bond angles. Comparison of the zigzag and armchair models optimized geometries reveals that the changes of these parameters are in parallel with each other in the length of the tube. However, in contrast with zigzag BNNTs which have two different ends, the ends of armchair BNNTs are similar to each other having both N and B nuclei. Hence, the diameter of the tube at both ends are alike but in the armchair model the ends of the tube are elliptically oriented, meaning that at each end, the N-N diameter is 6.96 Å and that of B-B is 6.85 Å.

B. NQR Parameter

The 11B and 14N NQR parameters in the geometrically optimized BNNT model was evaluated by calculations of the EFG tensors at the level of the BLYP DFT method and the 3-21G* standard basis set. The results are exhibited in Table II. A quick look at the results reveals that the calculated C_Q parameter is not similar for diverse nuclei; therefore, the electrostatic environment of BNNT is not equivalent in length in BNNT model. Since, in contrast with CNTs, the ends of BNNTs are different, the C_Q values decrease from each end to the center of the tube in the armchair model.

There are 35 N atoms in the considered armchair model of BNNT where they can be divided into four layers according to their calculated C_Q parameter, meaning that the parameter in each layer are equivalent (see Table II and Fig. 1). In this model, since each layer includes both N and B atoms, the layers are thus named and also because the C_Q parameter is symmetrically changed from both ends to the central layer (layer 4), these layers are similarly numbered. In the armchair model, CQ(14N1) has the largest value among other values, meaning that the N nuclei located at the end of the armchair tube are very important. The N (2)-layer is placed at the

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second layer in the considered model of BNNT. From Table I, there are small differences between the geometrical properties of this layer and the N (3)-layer, the third layer. However, the results of Table II reveal that the CQ parameter for these two layers are not completely similar, indicating the sensitivity of the EFG tensors to the changes of the geometrical properties in the considered BNNT model: CQ(14N2)= 0.73MHz; CQ(14N3)= 0.72 MHz. The last layer of N nuclei in the length of the considered model is the N (4)-layer which placed in the center of the armchair tube comparison with the N (3)-layer doesn't show change. Table II exhibits the calculated CQ parameter for B-11 nuclei in the representative model of BNNT consisting of 35 B, which are the same as the numbers of N atoms. A quick look at the results reveals that the electrostatic environment of BNNT is not equivalent at the locations of various B nuclei in the length of tube which can be divided into four equivalent layers in the considered model of BNNT; B(1)-, B(2)-, B(3)-, and B(4)-layer. It is noted that since each layer includes both N and B atoms in this model, the layers are thus numbered in this model. Table I the discussion of Section 3.A reveals different geometrical properties for one layer rather than other B-layers. furthermore the calculated CQ parameter of the B(1)-layer are significant rather than the other ones, CQ(11B1) =2.38 MHz. The next B-layer in the length of armchair tube belongs to the B(2)-layer which has geometrical properties similar to the B(3)-layer (see Tables II Section 3. A). In this BNNT model, the B nuclei placed at layers 2 and 3 show some differences in the CQ values, CQ(11B2) =1.90 MHz, CQ(11B3)=1.88 MHz. In this model (B-4) layer location is in the center of the tube which has a CQ value different of layer 3, CQ(11B4)=1.42 MHz. It is remarkable that since N has a lone pair of electrons in the valence shell, the CQ parameter at the sites of N nuclei differs more significantly in the length of the tube from those of B nuclei which lack electrons in their valence shell. Almost Parallel results are observed for changes of ηQ in the length of considered BNNT as well.

IV. CONCLUDING REMARKS

The work was performed to calculate the CQ parameter at the sites of 14N and 11B nuclei in the representative armchair model of SW-BNNT for the first time. To this end, the geometry optimization and CQ calculation were carried out on one proper model of H-capped (5, 5) SW-BNNT. From the results, some trends were received.

First, the N nuclei were relaxed outward and the B nuclei were relaxed inward of the nanotube after geometry optimization. Second, the diameters at both ends were the same; however, the N–N and B-B diameters at each end were different, yielding an elliptical mouth. Third, the calculated NQR parameters revealed that four equivalent layers were present in the considered models. Fourth, the nuclei at the ends had the largest value of CQ which is in agreement with the previous trends about the growing importance and field emission of end nucleiand eventually, the CQ value of nucleus decreased from its end to central layer in the model.

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