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## A DFT study of NMR parameters for MgO nanotubes

### ABSTRACT

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Magnesium oxide nanotubes of finite length are investigated by the Density Functional Theory (DFT) at the B3LYP/6-31G (d) level. The (6, 0) zigzag and (4, 4) armchair of MgO nanotubes were considered and nuclear magnetic resonance properties including isotropic and anisotropic chemical shielding parameters (CSI and CSA) were calculated for <sup>25</sup>Mg and <sup>17</sup>O atoms of the optimized structures for the first time. The calculated CS parameters indicated that the Mg atoms cause slight changes of electronic environment in the MgONT structures, but the changes for the O atoms are more significant. Results indicated that the zigzag MgONTs could be considered a more reactive material than the armchair model for interactions with other atoms or molecules.

**Keywords:** *Density Functional Theory (DFT); Magnesium Oxide nanotubes; Chemical shielding; Nuclear Magnetic Resonance(NMR).*

### INTRODUCTION

Ever since the discovery of single-walled carbon nanotubes (SWCNTs) by Iijima in 1991 [1], a number of different composite nanoscale tubular structures such as boron nitride (BN), silicon carbide (SiC) [2,3], MoS<sub>2</sub>, WS<sub>2</sub>, [4,5] has been fabricated and existence of some others such as BeB<sub>2</sub> B<sub>2</sub>O,<sup>[6]</sup> BeO,<sup>[7]</sup> and MgO [8,9] have been suggested based on their calculated crystal structures. The electronic characteristics in non-carbon solids depend strongly on the type of intra-particle chemical bonding. This is in contrast to CNTs where nanotubes are either metallic or semiconducting, depending on their tubular diameter and chirality [10, 11]. In 2004, Bilalbegovic [12] reported structural and electronic properties of MgO nanotube calculated by the pseudo potential density functional theory within the local-density approximation and found that a mixed ionocovalent bonding exists in investigated MgO nanotubes. Nuclear magnetic resonance (NMR) properties including isotropic and anisotropic chemical shielding parameters (CSI and CSA), which are among the important elements in the study of the properties of matter, could be well reproduced by quantum calculations [13, 14].

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Earlier studies indicated the usefulness of calculations of CS parameters for the investigation of properties of nanotubes [15,16]. Indeed, due to the electronic complexity of nanotubes, performing experimental NMR measurements on these materials is a formidable task; therefore, calculations of these parameters are advantageous [16].

To the best of our knowledge, no NMR data are available for MgONTs in the literature; therefore, the present work evaluates the  $^{17}\text{O}$  and  $^{25}\text{Mg}$  NMR parameters as a first prediction for MgONTs. Two representative models of zigzag and armchair

MgONTs are considered in the calculations. The first model includes 36 pairs of O and Mg atoms in a (6, 0) single-walled (SW) zigzag MgONT where the two ends of tubes are capped by H atoms (see Figure 1). The second model includes 48 pair of O and Mg atoms in a (4, 4) SW armchair MgONT where the two ends of tubes are capped by H atoms (See Figure 2). NMR calculations were performed on the optimized models. The calculations were performed at the B3LYP/6-31G (d) level of Density Functional Theory (DFT) and the results are shown in Figures 3 and 4.

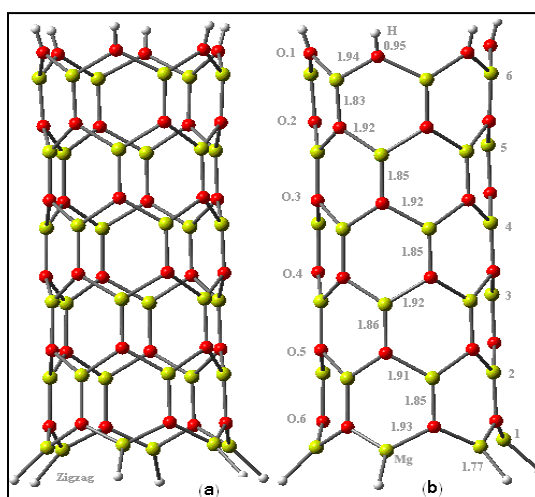


Fig. 1. (a) The 3D view and (b) the 2D view of (6,0) zigzag MgO nanotube. Average bond length values ( $\text{\AA}$ ) are shown

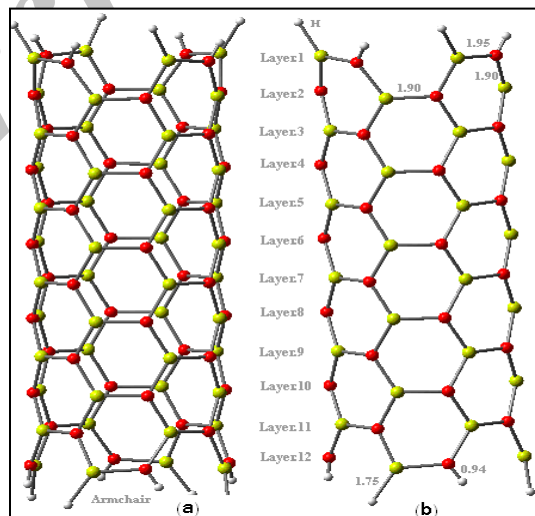


Fig. 2. (a) The 3D view and (b) the 2D view of (4, 4) armchair nanotube. Average bond length values ( $\text{\AA}$ ) are shown

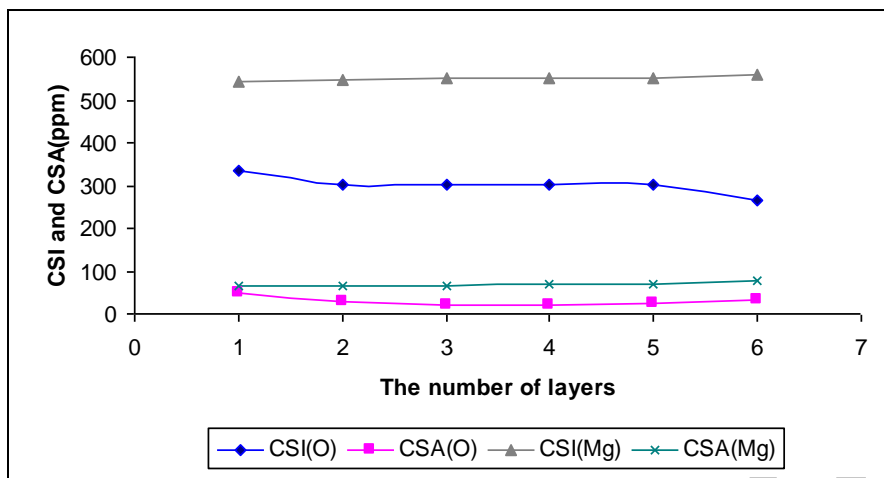


Fig. 3. The NMR parameters for zigzag (6, 0) MgONT.

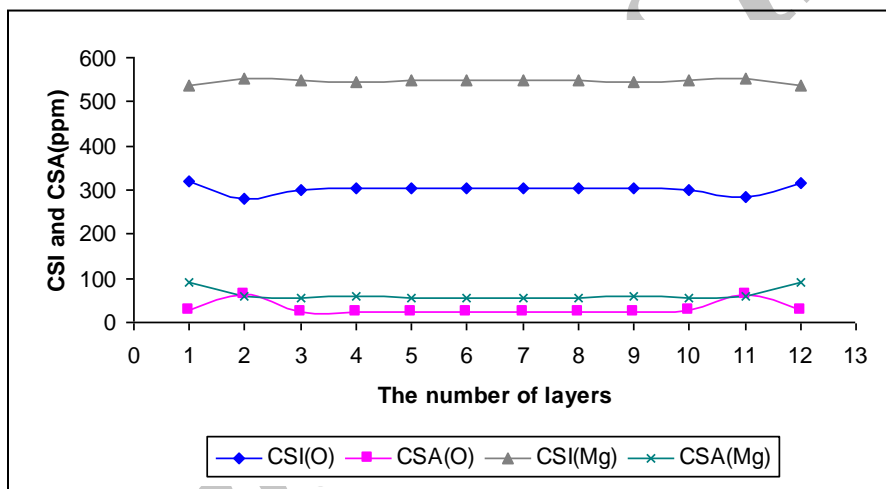


Fig. 4. The NMR parameters for armchair (4, 4) MgONT.

## EXPERIMENTAL

We chose two finite-length MgO nanotubes consisting of zigzag (6, 0) and armchair (4, 4) models. The formula for zigzag model is  $Mg_{36}O_{36}$  and for other model is  $Mg_{48}O_{48}$ , in which the tips are saturated by hydrogen atoms to avoid dangling effects. We investigated those structures by Density Functional Theory (DFT) calculations employing the B3LYP exchange functional and the 6-31G\* standard basis set [17].

All geometrical coordinates were allowed to relax during the optimization process, and the chemical shielding (CS) parameters were subsequently calculated for the optimized

structures. To compute the CS parameters for the  $^{25}Mg$  and  $^{17}O$  atoms, the gauge-included atomic orbital (GIAO) approach was employed. The calculated CS tensors in the principal axes system (PAS) were converted to the isotropic CS (CSI) and anisotropic CS (CSA) parameters using equations 1 and 2 [13].

$$ICS \text{ (ppm)} = (\sigma_{11} + \sigma_{22} + \sigma_{33})/3 \quad (1)$$

$$ACS \text{ (ppm)} = \sigma_{33} - (\sigma_{11} + \sigma_{22})/2 \quad (2)$$

It is important to note that the CS parameters could be experimentally measured by NMR spectroscopy; however, the complexity of the

electronic environment of nanotubes makes NMR experiments on these materials very difficult. Figures 3 and 4 show the evaluated NMR properties, consisting of the absolute values of the CSI and CSA parameters for  $^{25}\text{Mg}$  and  $^{17}\text{O}$  atoms of (6,0) zigzag and the (4,4) armchair models of MgONT (Figures 1 and 2). The Gaussian 09 package was used to perform the DFT calculations of this study.

## RESULTS AND DISCUSSION

Figure 1, 2 shows the (6, 0) zigzag and (4, 4) armchair structures of the investigated MgONTs - the optimized bond lengths are shown for selected representative bonds. Comparing the Mg-O bond lengths with those of the Be-O bonds from earlier studies indicates that the average Mg-O bond length ( $1.89 \text{ \AA}$ ) is notably longer than that for Be-O bonds ( $1.54 \text{ \AA}$ ) [18]. Previous studies have proposed that longer bond lengths of nanotubes could yield better surfaces for interactions with other atoms or molecules [18], so the longer bond lengths of MgO nanotubes make them better than BeO nanotubes as components of interacting systems. Calculated NMR properties, consisting of CSI and CSA parameters for  $^{25}\text{Mg}$  and  $^{17}\text{O}$  atoms of the optimized (6, 0) MgONTs, are presented in Figure 3. In agreement with earlier studies [14, 15], the calculated CS parameters for atoms of the zigzag MgONT could be divided into layers based on similarities of their values for the atoms of each layer. Since the CS parameters originate from the electronic sites of the atoms, they could be related to the electronic environments that each atom detects in the nanotube structure. Based on this trend, different electronic environments are observed for the  $^{25}\text{Mg}$  and  $^{17}\text{O}$  atoms of the zigzag MgONT. The results reveal that the values of CSI ( $^{17}\text{O}$ ) decrease from the O-end to the opposite end of the zigzag tube where the O-end layer has the largest value. CSI (O.1=334ppm) and CSI (O.6=267ppm) values show that the average electronic density at the O.1 layer is stronger rather than the other layers in the length of the tube. The middle layers of  $^{17}\text{O}$  atoms have similar values of the CSI parameter, which means that the average electronic densities at the sites of these atoms are similar. However, different

values of the CSA parameter indicate that the orientations of the CS tensors are not similar for the O atoms of the mentioned layers. However, different values of the CSA parameter indicate that the orientations of the CS tensors are not similar for the O atoms of the mentioned layers. Among the layers of O atoms, the properties of atoms of the O.2, O.3, O.4 and O.5 layers are similar, whereas those of other layers are different. The values of the CSA parameter for atoms of the O.1 layer, which makes the O tip, and the O.6 layer which is close to the Mg tip of zigzag nanotubes, are the largest among the O atom layers. This trend may show that atoms of the O.1 and O.6 layers are more appropriate for interactions with other atoms or molecules. The results reveal that the values of CSI (Mg) and CSA (Mg) increase from the Mg-end to the opposite end of the zigzag tube where the Mg-end layer has the smallest CSI and CSA values, namely 541 and 65 ppm, respectively.

It is noted that the magnitude of the changes of the CS parameters is smaller for the Mg-layers than for the O-layers and the values of the CSA parameter indicate that atoms of the O.1 and O.6 layers could be considered as the best O atoms for interactions with other atoms or molecules among the available layers of O atoms of the zigzag MgONTs. Figure 4 shows the calculated NMR properties (CSI and CSA parameters) for the optimized structure of the (4, 4) armchair MgONT (Figure 2). As for the zigzag model, the results indicate that the CS parameters of the armchair model also could be divided into layers due to similarities of their values for atoms of each layer. The values of the CSI parameter indicate that O atoms of the O.3, O.4, O.5, O.6, O.7, O.8, O.9 and O.10 layers have similar electronic densities, but different densities are observed for O atoms of other layers. The O.2 and O.11 layers have smallest CSI value and largest CSA value (281, 65 ppm, respectively) among all O atoms of other layers. The observed largest values of the CSA parameter for atoms of the O.2 layer, which makes second layer of the armchair nanotube, indicate that it is the best layer for interactions with other atoms or molecules among the O atoms.

Slight changes of the CS parameters are observed for the Mg atoms of different layers in the structure of armchair MgONT. This trend implies that the Mg atoms of armchair MgONT detect slightly different environments in which the atoms

of the Mg.1 and Mg.12 layers could be considered as the best layer of Mg atoms for interactions with other atoms or molecules. In comparison with armchair MgONTs, the values of the CS parameters for O and Mg atoms of the zigzag model are larger, which means that the zigzag model could be more reactive than the armchair model of MgONT.

## CONCLUSIONS

DFT-calculated CS parameters for (6, 0) and (4, 4) models of MgONT indicate that the structure of nanotubes could be divided into layers based on similarities of the CS parameter values for atoms of each layer. The CS parameters for the layers of Mg atoms exhibit only slight changes, but notable changes are observed for the layers of O atoms. Moreover, comparison of the results for the zigzag and armchair models indicates that the zigzag model could be considered as a more reactive material for interactions with other atoms and molecules due to the larger values of the CS parameters than for armchair MgONT.

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