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Density functional theory on 13C NMR chemical shifts of fullerene

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ABSTRACT

13C NMR chemical shifts of pristine fullerene have been studied computationally using gauge–independent atomic orbital (GAIO) and density functional theory (DFT). The molecular structure of C_{60} were optimized by DFT/B3LYP method with 6-31G basis set using Gaussian 09 program. The shielding constants for 13C atom have been calculated by GIAO/B3LYP/6-31G(d,p) approach and analyzed both in gas and solvent phases. The solvent effect is mimicked by PCM polarizable continuum model. A single sharp line in the nuclear magnetic resonance spectrum is observed. The NMR spectra of the investigated compound are in good agreement with the structures optimized by DFT calculations. With the shielding magnetic tensor (GIAO), the magnetic shielding density and magnetically induced current density with the mapped surface for the nucleus of the molecule were simulated and analyzed. The results indicate that the complete information may be obtained from 13C NMR of pristine fullerene. The high symmetrical nature of the sample paves way for designing the bioactive materials which will be useful in the field of carbon nano medicine and targeted drug delivery applications.

1. Introduction

Since the discovery of Buckminster fullerene, C_{60}, by Kroto et al. [1] in 1985 and the discovery of large quantity synthesized by Kratschmer et al. [2] in 1990, this molecular allotrope of carbon has attracted intense interests because of its unique physical and chemical properties. The interest in fullerenes spreads in many scientific and technological fields and has several potential applications in various research fields, including pharmaceutical and biological science with therapeutic devices [3,4]. C_{60} is a beautiful spherical hollow molecule with a diameter of ~1 nm (0.7–0.8 nm) possessing high degree of symmetry of all known molecules [5].

In chemistry, one of the most versatile experimental tools to study the geometry and electronic structure of molecules and solids is nuclear magnetic resonance (NMR). So far, NMR has not been among the main tools for the characterization of carbon nanostructures. However, recently the field has started to bloom and an increasing amount of experimental and theoretical researches has been devoted [6]. 60 carbon atoms in C_{60} fullerene are known to be located at the vertices of a truncated icosahedron where all carbon sites are equivalent. This is consistent with the observation of a single sharp line in the nuclear magnetic resonance (NMR) spectrum [7]. Since 1960s, high-resolution nuclear magnetic resonance (NMR) spectroscopy has enabled the rapid determination and investigation of molecular structure in organic chemistry. This revolutionary technique depends on the sensitivity of the resonance frequency of an atomic nucleus (shielding) to its chemical environment when the magnetic field is applied. Currently, the shieldings and other NMR properties can be predicted using density functional theory and gauge-including atomic orbital methods with enough accuracy to identify chemical shift and shielding constant [8].

13C NMR measurements on pristine fullerene have identified as isotropic shifts of 140.38–150.05 ppm [8,9]. Nuclear magnetic resonance has provided a powerful tool for the studies of C_{60}. Most of the nuclear resonance studies have been made on the 13C nucleus which are abundant nuceli [10–12]. It has 12 pentagons and 20 hexagons sites which follow the building principles of Euler's theorem predicting that exactly 12 pentagons and an arbitrary number n of hexagons are required for the closure of a carbon closed cage. Otherwise, C_{60} is the most stable fullerene, because it is the smallest possible to obey the isolated pentagon rule (IPR) [9]. Thus, C_{60} molecule has the highest degree of symmetry of any known molecule. So, due to the lack of NMR data, to the best of our knowledge, we are interested in utilizing computational techniques to explore the nuclear properties of the C_{60} by computing GAIO tensors.

The paper is organized as follows. In section 2, the computational details on a relatively simple and effective quantum chemical

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calculation by theoretical approach, the detailed description on the assessment of exchange and correlational functional, basis set for the calculation of the equilibrium geometry and the NMR of C_{60} are reported. The results are discussed in section 3. The brief conclusion is described in the last section.

2. Computational method

All quantum chemical calculations are carried out using density functional theory namely Gaussian 09 package of program [13–15]. Geometries of all systems were fully optimized by means of the hybrid, non-local exchange and correlation functional of Becke-Lee, Parr and Yang (B3LYP) [16,17]. The standard 6-311G(d,p) basis set is employed with affordable and accurate enough for geometry optimization of even large molecules [18,19]. These optimized structures have been subjected to calculation of 13C chemical shielding tensors using the B3LYP/6-311G(d,p) level of theory. NMR shielding tensors were computed using the GIAO method, to calculate chemical shift [20]. All chemical shifts were determined with respect to TMS (Tetramethysilane) as computational reference, however for the 13C data, benzene was used as the internal (computational reference). It has been demonstrated that this strategy results in systematic error cancellation, yielding shifts which should be closer to those measured experimentally. Therefore, using C_{60} instead of benzene as the internal reference will not have a substantial impact on the results [21]. With the shielding tensor, the magnetic shielding density and magnetically induced current density with mapped surface for the nucleus of the molecule are simulated and analyzed [21,22]. NMR calculations were performed on all optimized structures to ensure stable minima were obtained.

3. Results and discussion

3.1. Molecular geometry and symmetry

The optimized molecular energy of C_{60} molecule was calculated by the DFT/B3LYP method with 6-31G (d,p) basis set and 6-31G basis set. Fig. 1 shows the photo shot of the above optimized molecule. The lowest optimized molecular energy of the C_{60} molecule was obtained by using the 6-31G (d,p) basis set for the stable structure. Hence, 6-31G(d,p) basis set was used for all DFT calculations in the present investigation.

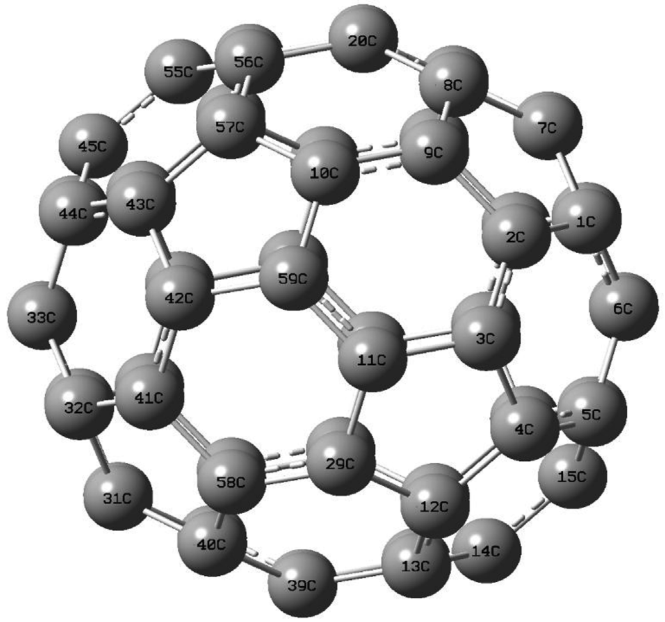

Fig. 1. The optimized molecular structure of C_{60}.

C_{60} carbon atoms are approximately sp^2 hybridization with sp^3 contribution due to the curvature of cage. Although all sixty carbon atoms are chemically equivalent, the structure contains two distinct bond types inter-pentagonal, double bonds being short ~1.3954 Å, intra-pentagonal, single bonds are long typically 1.4535 Å. The intermolecular vibrations of an isolated C_{60} molecule involve changes of the bond distances or bond angles of the carbon atoms on the C_{60} molecule [23].

3.2. 13C nuclear magnetic resonance spectroscopy

Fig. 2 shows the simulated NMR spectra of C_{60} (a) gas phase and (b) liquid phase respectively. The icosahedral symmetry (I_h) of fullerene C_{60} renders all the 60 carbon atoms equivalent, giving one signal in the NMR spectrum. The observed chemical shift for C_{60} ranges from 140.68 to 150.2 ppm. The chemical shift predicted at the B3LYP/6-31G(d,p) level is 133.38 ppm–150.03 ppm [7,8]. This is in very good agreement with experimental data [21]. In the spectrum, there is only one peak, showing extremely simple character, at a chemical shift of 133.38 ppm in gas phase and 150.03 ppm for solvent phase relative to tetramethylsilane (the standard computational reference molecule for 13C NMR spectroscopy). This only-one-peak character confirms that each carbon atom in the C_{60} molecule is equivalent in the gas as well as solution environment [21]. The shifting of chemical shift (δ ppm) between gas and solvent phase is due to the interaction of atoms in solvent phase. The high frequency signal at 133–150 ppm can be attributed unambiguously to unreacted, pristine, olefinic carbons atoms (C=C) [24]. For solid C_{60}, this signal (situated at 133–150 ppm) is very sharp because of the symmetrical characteristics of the molecule. This high frequency sharp peak around 130 ppm is ascribed to the graphitic sp^2 carbon hybridization and unreacted carbon atoms [25].

3.3. NMR chemical shifts

Fig. 3 shows the simulated NMR chemical shift (δ ppm) spectra summary in view of C_{60} (a) gas phase and (b) liquid phase respectively. The tabulated chemical shift (δ ppm) parameters are presented in Table 1. In NMR spectroscopy, a standard system is chosen as a reference, thus the chemical shift is taken as the shielding difference between the atom of interest and the corresponding atom in the reference system. In the theoretical calculations, the magnetic shielding must then be subtracted from the shielding in the reference system. The calculated chemical shielding for the carbon atoms in C_{60} is fund to be 49.16–49.07 ppm. This reference value will be used to calculate the chemical shifts [8].

The NMR chemical shifts (δ ppm) calculated using the following formula [9,20]

$$\delta(i) = \delta(C_{60}) + \sigma(C_{60}) - \sigma(i) \quad (1)$$

where $\delta(C_{60})$ is taken as 143.15 ppm. The calculated chemical shielding of C_{60} was found to be 50.59 ppm [9,20] whereas our predicated chemical shift of C_{60} is found to be 49.16 ppm and (i) is the carbon atom under consideration. Since the calculated 13C chemical shielding of TMS is around 189.31 ppm at the B3LYP/6-31G(d,p) level, our predicated chemical shift of C_{60} is 130.30 ppm and 150.03 ppm for gas and solvent phases respectively. The benzene is taken as solvent which is the standard solvent for C_{60} [21]. The experimentally observed chemical shift for C_{60} has been reported by several groups and the values range from 142.68 to 143.2 ppm [9,21–23]. The difference between our calculated chemical shift and experimental values ranges from 4.48 to 7.35 ppm which signifies the accuracy of the computational effect and efficacy of GIAO basis set. In the differences given by the Eq. (1), the reference values cancel out and therefore, the chemical shifts are referred simply as the difference between the shielding of the reference