Magnetic properties of endohedral metallofullerenes based on asymmetric nitride yttrium cluster within azafullerenes

Hitoshi Nakagawa, Atsushi Suzuki and Takeo Oku

Department of Material Science, The University of Shiga Prefecture
2500 Hassaka, Hikone, Shiga 522-8533 Japan.

E-mail: suzuki@mat.usp.ac.jp

Abstract. Magnetic properties of endohedral metallofullerene based on asymmetric triyttrium cluster of Y_3N within azafullerene cage of C_{79}N were studied to control spin-flop of nuclear magnetic resonance quantum computer. Difference of nuclear magnetic resonance peaks were exerted by symmetry of structure, electron density distribution and magnetic interaction. In the present calculation, magnetic properties of Y_3N@C_{80}, (Y_3N@C_{80})^1, Y_3N@C_{80} (CF_3)_2, Y_3N@C_{79}N and (C_{79}N)^+ were compared for spin controlling in nuclear magnetic resonance quantum computers. The chemical shift of Y_3N@C_{79}N appeared the highest magnetic field side. Difference of electron density and magnetic parameters are cause of this result. The chemical shift of Y_3N@C_{80} (CF_3)_2 had the widest peak in all of samples. Substituent groups of (CF_3)_2 caused the wide peaks by breaking symmetry of the an fullerene cages. The effect of difference of fullerene cage was shown in NMR chemical shift.

1. Introduction

Endohedral metallofullerenes have various magnetic properties [1-3]. Those are used for monomolecular transistor, spin electronics, nuclear magnetic resonance (NMR) quantum computer [4-6], molecular spintronics, organic field-effect transistor (FET) and organic electroluminescence (EL) displays. Recently, the endohedral magnetic fullerene within single walled carbon nanotube (SWCNT) called carbonpeapods has been studied by spectroscopic analysis measures like electron spin resonance (ESR), NMR, Raman and ultraviolet (UV)-visible-near-infrared (NIR) to make a valuation of those electron structure and magnetic properties. Moreover, experimental results of magnetic properties and theoretical analysis by density functional theory (DFT) calculation evinced that endohedral metallofullerenes has a great potential to do spin controlling of NMR quantum computer. The magnetic interaction based on spin-orbit interaction and dipole-dipole interaction and nuclear quadroouple interaction of ^{14}N@C_{60}-SWCNT has been reported by experimental result in late years [7, 8].

In the present work, electronic structures and magnetic properties of encapsulated nitride yttrium cluster of Y_3N within azafullerene [9] cage were studied for spin controlling of NMR quantum computer. Magnetic interactions of spin-orbit interaction, spin-spin interaction and dipole-dipole interaction are discussed on the basis of magnetic parameters and excitation energies. A yttrium belongs to the rare earth. Both electron spin and nuclear spin is 1/2. Electronic configuration is 4d^{1/2}5s^{1/2}. The yttrium has strange behavior in their orbital [10].
2. Quantum chemical calculation

Isolated molecular structures were optimized by calculation using Hartree-Fock and DFT of UB3LYP with STO, 3-21G* and 6-31G* as basic set because of computational limitations (Gaussian 03 and 09). Highest occupied molecular orbital (HOMO), lowest unoccupied molecular orbital (LUMO) and the HOMO-LUMO energy gap ($E_g$) were obtained by calculation. Mulliken charge and spin density distribution were estimated by Mulliken population analysis. DFT calculation of NMR/GIAO with hybrid function UB3LYP and 3-21G* was performed to calculate isotropic chemical shift ($\delta$), principle g-tensor ($g_{xx}$, $g_{yy}$, $g_{zz}$), A-tensor ($A_{xx}$, $A_{yy}$, $A_{zz}$) in hyperfine coupling constant (hfc) and Q-tensor ($Q_{xx}$, $Q_{yy}$, $Q_{zz}$) of $^{13}$C, $^{14}$N and $^{38}$Y atoms. Nuclear quadruple interactions were estimated on basis of multiplication of nuclear quadruple moment $Q$ and the electro field gradient (EFG) tensor that is generated by charge distribution around nucleus. Excited energy and wavelength in UV-vis-NIR spectra of Y$_3$N@C$_{79}$N, (Y$_3$N@C$_{80}$)$^{-1}$ and Y$_3$N were calculated by TD-DFT with B3LYP using 3-21G* as basis set.

3. Results and Discussion

Electronic structures of molecular orbital at HOMO, LUMO and energy levels of Y$_3$N@C$_{79}$N were calculated by DFT with UB3LYP using 3-21G*. Figure 1 shows (a) molecular structure, (b) HOMO and LUMO, (c) energy levels of Y$_3$N@C$_{79}$N and (d) HOMO of Y$_3$N@C$_{80}$, (Y$_3$N@C$_{80}$)$^{-1}$, Y$_3$N@C$_{80}$ (CF$_3$)$_2$, Y$_3$N@C$_{79}$N and (C$_{79}$N)$^{+1}$. Electron spin density distribution of Y$_3$N@C$_{79}$N was localized on surface of azafullerene cage. The spd-hybrid orbital was identified around $^{89}$Y in nitride yttrium cluster as shown in Fig 1 (b). Energy gap of Y$_3$N@C$_{79}$N is 1.0 eV as shown in Fig 1 (c). As shown in Fig 1 (d), electron spin density distribution of (Y$_3$N@C$_{80}$)$^{-1}$, Y$_3$N@C$_{79}$N and Y$_3$N@C$_{80}$ (CF$_3$)$_2$ were localized on carbon surface of azafullerene cage. Existence of radical in substance and substituent of trifluoromethyl group of CF$_3$ as drawn in Y$_3$N@C$_{80}$ and (C$_{79}$N)$^{+1}$, electron spin density distribution were delocalized on surface of fullerene cage. The effects of fullerene cage and nitride yttrium cluster within fullerene cage were suggested.

The calculated energy levels and band gaps of endohedral metallofullerenes were listed in Table 1. The energy gaps of Y$_3$N@C$_{79}$N and (Y$_3$N@C$_{80}$)$^{-1}$ were both 1.00 eV. Those $E_g$ were smaller than Y$_3$N@C$_{80}$ (2.61 eV). The asymmetrical structure of modified metallofullerene with trifluoromethyl group and azafullerene has a tendency to arise energy level at HOMO, with a narrow energy gap.

| Sample     | HOMO  | LUMO  | $E_g$(eV) |
|------------|-------|-------|-----------|
| Y$_3$N@C$_{79}$N | -4.23 | -3.23 | 1.00      |
| Y$_3$N@C$_{80}$(CF$_3$)$_2$ | -5.76 | -3.51 | 2.25      |
| (Y$_3$N@C$_{80}$)$^{-1}$ | -1.33 | -0.33 | 1.00      |
| Y$_3$N@C$_{80}$ | -6.13 | -3.5  | 2.61      |
| C$_{80}$     | -5.76 | -4.98 | 0.78      |
| Y$_3$N      | -3.73 | -1.82 | 1.91      |

The Irago Conference 2012
Journal of Physics: Conference Series 433 (2013) 012005
doi:10.1088/1742-6596/433/1/012005
Table 2 shows magnetic parameters of principle g-tensor, A-tensor in hfs, Q-tensor in Y₃N@C₇₉N. Atomic charge of Y and N atom, which were 2.1 e and -0.9 e, confirmed charge transfer. Approximately 6 electrons moved from yttrium atom to nitrogen atom on azafullerene cage. A slight charge of Milliken atomic spin density of Y and N was caused by inductive effect. The chemical shift of NMR was represented by Karplus-Pople equation as written by following equation (1).
Karpulus-Pople equation was divided diamagnetic term ($\sigma_d$) and paramagnetic term ($\sigma_p$). The paramagnetic term was under the control of spin-local interaction and mixed hybrid orbital between excited and ground states. In the Karpulus-Pople equation, the $e$, $m$, $c$ and $L$ represent charge of electron, mass of electron, the speed of light and the operator of orbital angular momentum, respectively.

Spin Hamiltonian was written by following equations from (2) to (5).

$$H = g_S \beta SH - g_N \beta IH + SAI + IQI$$  \hspace{1cm} (2)

$$g_{ii} = g_e \left(1 + \sum_{m} \frac{\psi_m |L| \psi_p}{\varepsilon_p - \varepsilon_m}\right)$$  \hspace{1cm} (3)

$$A_{iso} = \frac{8 \Pi}{3 g_N \mu_N \rho(0)}$$  \hspace{1cm} (4)

$$A'_{ii} = g_N \mu_N \int \frac{\cos^2 \theta - 1}{e^3} \rho(r) \, dv$$  \hspace{1cm} (5)

Spin Hamiltonian is shown in eq. (2). In the spin Hamiltonian, the $g_e$, $\psi$, $L$, $\varepsilon_m$, $\varepsilon_p$, $g_n$, $\mu$ and $\rho$ represent $g$ factor of free electron spin, the wave function, the operator of orbital angular momentum, energy of each orbital, energy of ground state, $g$ factor of nuclear, magnetism moment of nuclear and density of electrons, respectively. Formulas are configured by a sum of free radical Zieman interaction, dipole-dipole interaction and nuclear quadrupole interaction. Norm of $g$-tensor is approximately 2.0023. $A_{iso}$ means Isotropic Fermi constant. $A'_{ii}$ is same with $A_{aniso}$ and it means anisotropic spin coupling constant in hyperfine structure (hfs). Both $A_{iso}$ and $A_{aniso}$ contain electron density ($\rho$). $A_{iso}$ pertains to s orbital. $A_{aniso}$ has angle dependence of p and d orbital. Magnetic parameters of $g$-tensor and $A$-tensor (both $A_{iso}$ and $A_{aniso}$) in hfs and nuclear quadrupole constant ($Q_{XX}$, $Q_{YY}$, $Q_{ZZ}$) were listed in Table 2. The $g$-tensor, ($g_{xx}$, $g_{yy}$, $g_{zz}$) were $g_{xx} = 1.859$, $g_{yy} = 1.959$ and $g_{zz} = 1.971$, respectively. Anisotropic $A$-tensors of yttrium have prominent value around 10 MHz. In the case of central nitrogen atom, anisotropic $A$-tensor in hfs had angle dependence of p spin distribution. The nuclear quadrupole interaction depends on the nuclear quadrupole moment and electron field graduate (EFG) with a bias of charge around nuclei. The anisotropic $A$-tensor ($A'_{XX}$, $A'_{YY}$, $A'_{ZZ}$) of $^{14}$N atom in the fullerene cage were $A'_{XX} = -0.514$, $A'_{YY} = -0.479$ and $A'_{ZZ} = 0.993$, respectively. This result indicates a large extent of density distribution of p-orbital in N atom in fullerene cage.
Table 2  Magnetic parameters of principle g-tensor, A-tensor in hfc, Q-tensor in Y3N@C79N.

| Atomic charge (e) | Mulliken atomic spin density | Aiso (MHz) | A'xx (MHz) | A'yy (MHz) | A'zz (MHz) | Qxx (MHz) | Qyy (MHz) | Qzz (MHz) |
|-------------------|-----------------------------|------------|------------|------------|------------|-----------|-----------|-----------|
| N                 | -0.937                      | -0.011     | -0.919     | -0.273     | 0.016      | 0.257     | -0.719    | -0.216    | 0.935      |
| Y_1               | 2.119                       | 0.011      | 1.027      | 0.498      | -0.062     | 0.257     | 0         | 0         | 0          |
| Y_2               | 2.092                       | 0.132      | -11.857    | 1.452      | 1.098      | -0.436    | 0         | 0         | 0          |
| Y_3               | 2.055                       | 0.128      | -13.771    | 1.703      | 0.935      | -2.55     | 0         | 0         | 0          |
| N_{out}           | -0.851                      | 0.007      | 0.862      | -0.514     | -0.479     | 0.993     | 1.518     | 1.206     | -2.724     |

A_{iso}: Isotropic Fermi constant, A_{aniso}: Anisotropic spin coupling constant in hfc, Q: Nuclear quadrupole constant.

The calculated chemical shifts of (a) Y3N@C79N, (b) 13C-NMR in Y3N@C79N and (c) Y3N@C80 (CF3)2 are shown in Fig 2. The chemical shift of 14N, 89Y and 13C in Y3N@C79N were appeared separately in Fig 2 (a). Especially, yttrium could be around 2500 pmm. And chemical shifts of 13C atom in 13C-NMR had wide peak between around 70 ppm and 95 ppm in Fig 2 (b). As shown in Fig 2 (c), the chemical shift of 14N, 89Y, 19F and 13C in Y3N@C80 (CF3)2 also appeared separately. But the chemical shifts of 89Y in Y3N@C80(CF3)2 appeared around 30 ppm, which was completely different position as compared to those of 89Y in Y3N@C79N. The reason of this difference was thought that a different extent of electron density of spd-hybrid orbital. Substituent group of (CF3)2 played a role of falling spin density distribution on the fullerene cage.

Figure 2  Calculated chemical shifts of (a) Y3N@C79N, (b) 13C-NMR in Y3N@C79N, (c) Y3N@C80 (CF3)2.
Figure 3 shows Calculated chemical shifts of $^{13}$C-NMR in Y$_3$N@C$_{80}$, (Y$_3$N@C$_{80}$)$^{-1}$, Y$_3$N@C$_{80}$ (CF$_3$)$_2$ and Y$_3$N@C$_{79}$N. Those samples had different chemical shifts. The chemical shift of Y$_3$N@C$_{79}$N appeared the highest magnetic field side. Difference of electron density as shown in Fig 1 and Magnetic parameters in table 2 are cause of this results. The chemical shift of Y$_3$N@C$_{80}$ (CF$_3$)$_2$ had the widest peak in all of samples. The range of chemical shift of Y$_3$N@C$_{80}$ (CF$_3$)$_2$ was between 90 ppm and 150 ppm. The substituent group of (CF$_3$)$_2$ cause this wide peak by breaking symmetry of fullerene cage. The effect of difference of fullerene cage was shown obviously in NMR chemical shift.

![Figure 3](image)

**Figure 3** Calculated chemical shifts of $^{13}$C-NMR in Y$_3$N@C$_{80}$, (Y$_3$N@C$_{80}$)$^{-1}$, Y$_3$N@C$_{80}$ (CF$_3$)$_2$ and Y$_3$N@C$_{79}$N.

Details of chemical shifts of $^{13}$C on fullerene cage in Y$_3$N@C$_{79}$N, Y$_3$N@C$_{80}$ and (Y$_3$N@C$_{80}$)$^{-1}$ are shown in Fig 4. In the $^{13}$C-NMR chemical shift of Y$_3$N@C$_{79}$N, $^{14}$N on fullerene cage was pointed. The numerical vales of $^{13}$C-NMR around $^{14}$N on the fullerene cage were displayed. The $^{13}$C-NMR chemical shift of Y$_3$N@C$_{80}$ and (Y$_3$N@C$_{80}$)$^{-1}$ were displayed exactly same point on the fullerene cage compared with the $^{13}$C-NMR chemical shift of Y$_3$N@C$_{79}$N. The numerical value of $^{13}$C-NMR of Y$_3$N@C$_{79}$N was marked low values compared with Y$_3$N@C$_{80}$ and (Y$_3$N@C$_{80}$)$^{-1}$. The $^{14}$N on fullerene cage could be localized factor in Y$_3$N@C$_{79}$N. Therefore the $^{13}$C-NMR chemical shift of Y$_3$N@C$_{79}$N appeared higher side of magnetic field than others.

![Figure 4](image)

**Figure 4** Calculated chemical shifts of $^{13}$C on fullerene cage in Y$_3$N@C$_{79}$N, Y$_3$N@C$_{80}$ and (Y$_3$N@C$_{80}$)$^{-1}$.
4. Conclusion

Electronic structures and magnetic properties of endohedral metallofullerenes based on asymmetric nitride yttrium cluster within fullerene cage are studied to control the spin flopping of NMR quantum computer. The effects of fullerene cage and inside nitride yttrium cluster were investigated by quantum chemical calculation. Characterization of NMR chemical shifts, $g$-tensor, $A$-tensor, $Q$-tensor of $^{89}$Y and $^{14}$N atoms with magnetic interaction between electronic spin and nuclear spin were calculated. The significance of sorts of fullerene cages to control the NMR chemical shift were explained by Spin Hamiltonian. The Karplus-Pople equation exhibited the effect of radical in metallofullerenes. Substituent group of (CF$_3$)$_2$ and inside metal cluster within fullerene cage could control a variable position of chemical shift. The endohedral metallofullerenes based on asymmetric nitride yttrium cluster within azafullerenes should have a great potential for NMR quantum computer to quantum-calculate at multiple-state.

References
[1] Jing L, Xinwei Z, Xiangeng Z, 2000 J. Phys. Chem., 332 51
[2] Shustova N B, Peryshkov D V, 2011 J. Am. Chem. Soc. 133 2672
[3] Schiemenz S, Avdoshenko S M, Yangv S, Cuniberti G, Dunsch L, 2011 J. Phys. Chem. C 115 15257.
[4] Chen N, Fan L Z, Tan K, Wu Y Q, Shu C H, Lu X, and Wang C R, 2007 J. Phys. Chem. C 111 11823
[5] Tiaming Z, Liasa X, Christine M B, Marilyn M O, 2008 J. Am. Chem. Soc 130 12992
[6] Lieven M K, Matthias S, Gregory B, Costantino S, 2001 Nature 414 883
[7] Suzuki A, Oku T, 2011 Physica B 406 3274
[8] Suzuki A, Oku T, 2012 J. Phys. Conf. Series 352 012012
[9] Van D S T, Wang Z H, Blok M S, Bernien H, Taminial T H, 2012 Nature 485 82
[10] Popov A A, Zhang L, Dunsch L, 2010 ASC Nano 4 795