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Jing Lu

University of Nebraska-Lincoln

Wai-Ning Mei

University of Nebraska-Lincoln, physmei@unomaha.edu

Yi Gao

University of Nebraska-Lincoln, ygao3@unl.edu

Xiao Cheng Zeng

University of Nebraska-Lincoln, xzeng1@unl.edu

Mingwei Jing

Peking University

See next page for additional authors

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Authors

Jing Lu, Wai-Ning Mei, Yi Gao, Xiao Cheng Zeng, Mingwei Jing, Guangping Li, Renat F. Sabirianov, Zhengxiang Gao, Liping You, Jun Xu, Dapeng Yu, and Hengqiang Ye

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Structural and electronic properties of Gd@C_{60} : All-electron relativistic total-energy study

Jing Lu,^{1,2} W. N. Mei,¹ Yi Gao,³ Xiaocheng Zeng,³ Mingwei Jing,² Guangping Li,¹
Renat Sabirianov,¹ Zhengxiang Gao,² Liping You,² Jun Xu,² Dapeng Yu,² and Hengqiang Ye²

1. Department of Physics, University of Nebraska—Omaha, Omaha, NE 68182-0266, USA

2. Mesoscopic Physics Laboratory, Department of Physics, Peking University, Number 209, Chengfu Road, Beijing 100871, China

3. Department of Chemistry, University of Nebraska—Lincoln, Lincoln, NE 68588, USA

Corresponding authors — Jing Lu, W. N. Mei, & Xiaocheng Zeng.

Address: Mesoscopic Physics Laboratory, Department of Physics, Peking University,
Number 209, Chengfu Road, Beijing 100871, China. Fax: 86 10 6275 1615 (Jing Lu).

Email: jinglu@pku.edu.cn (Jing Lu), wmei@mail.unomaha.edu (W. N. Mei), xczeng@phase1.unl.edu (Xiaocheng Zeng)

Abstract

Water soluble Gd-based metallofullerenes have potential application as magnetic resonance imaging contrast agent due to its higher proton relaxivities and lower toxicity. In this letter, we have investigated the structural and electronic properties of Gd@C_{60} , which is the most abundantly produced Gd-based metallofullerene in carbon arc process, by using all-electron relativistic density functional theory. It is found that the Gd^{3+} ion is bonded to a hexagonal ring of C_{60} by electrostatic interaction. The total spin multiplicity of Gd@C_{60} is $S = 7$. The Gd atomic orbitals are hybridized with the C_{60} molecular orbitals.

Water soluble Gd-based metallofullerenes ($\text{Gd@C}_{82}(\text{OH})_x$, $\text{Gd@C}_{60}[\text{C}(\text{COOH})_{10}]$, $\text{Gd@C}_{60}(\text{OH})_x$) have attracted recent interest [1–3] as a possible new generation of magnetic resonance imaging (MRI) contrast agent because they not only can produce proton relaxivities greater than commercially available MRI contrast agent but also are safer than the latter because the toxic Gd ions are completely encaged inside the fullerenes and do not dissociate under physiological condition. Gd@C_{60} is the most abundantly produced species of Gd-based metallofullerenes in carbon arc process. Unlike soluble Gd@C_{82} , which has been studied by extensive experiments and two theoretical works [4, 5], the structural and electronic properties of insoluble Gd@C_{60} are overlooked largely. Only Lu et al. [6] have calculated the electronic structure of Gd@C_{60} assuming that Gd is located on the center of C_{60} and found that only two 6s electrons of Gd are ionized, leaving the 5d electron behind. Nevertheless, the electronic properties

of metallofullerenes may change dramatically with different arrangements of the metal atom inside the fullerene cage.

In this Letter, we have presented for the first time the optimized structure of Gd@C_{60} and the resulting electronic properties by using all-electron relativistic density functional theory. Double numerical atomic orbital basis set plus polarization function (DNP) [7] is used for C and Gd atoms. Generalized gradient corrected exchange-correlation functional proposed by Perdew and Wang (PW91) [8] is used. The electronic configuration of Gd is $4s^2 4p^6 4d^{10} 4f^7 5s^2 5p^6 5d^1 6s^2$. The calculated ground-state spin multiplicity of Gd_2 dimer is $S = 19$, which is in accordance with the previous all-electron relativistic density functional theory calculation [9]. The calculated bond length (3.00 Å) and bond energy (2.03 eV) of Gd_2 dimer are comparable with the previously calculated bond length (2.90 Å) [9] and experimental bond energy (1.784 ± 0.35 eV) [10].

Our computational procedures start from five initial positions for Gd inside C₆₀: (1) on the center of C₆₀, (2) on the top of the six-membered ring, (3) on the top of the five-membered ring, (4) on the top of the single bond and (5) on the top of the double bond. Full geometry optimization is performed without any symmetry constraint. The most stable structure of Gd@C₆₀ has the Gd ion situated on the center of the six-membered ring (Figure 1), whereas the previously assumed configuration with Gd on the cage center is 1.82 eV higher in energy. Addition of Gd slightly lengthens the proximal C-C double and single bonds by 0.04 and 0.02 Å, respectively. In Gd@C₈₂ [5] and La@C₆₀ [11], the Gd and La ions are positioned slightly away from the C-C double bond based on the density functional theory calculations with the effective core potential approximation. The calculated distances between the Gd ion and the proximal C atoms are 2.47 and 2.38–2.41 Å [5] in Gd@C₆₀ and Gd@C₈₂, respectively. The calculated distances between the La ion and the proximal C atoms are slightly larger with values of 2.55–2.64 Å [11] in La@C₆₀. The calculated binding energy of Gd inside C₆₀ (3.77 eV) is significantly smaller than that of Gd inside C₈₂ (5.64 eV [5]), but larger than that of La inside C₆₀ (2.65 eV [11]).

The total spin multiplicity of the ground state is $S = 7$. The spin densities on the Gd ion and C₆₀ are 6.74 and -1.26, respectively; therefore the seven spins on the Gd

ion and one spin on C₆₀ are antiferromagnetically coupled, similar to the case of Gd@C₈₂ [5]. The spin multiplicities of $S = 5, 7$, and 9 are 0.08, 0.10 and 0.67 eV higher in energy, respectively, than that of $S = 7$. In the $S = 5$ spin multiplicity, the seven spins on the Gd ion and three spins on C₆₀ are antiferromagnetically coupled. In the $S = 9$ and 11 spin multiplicities, the seven spins on the Gd ion are ferromagnetically coupled with one and three spins on C₆₀, respectively. The molecular level diagram of the three lowest energy spin multiplicities is depicted in Figure 2. This energy difference between $S = 7$ and $S = 9$ spin multiplicity is greater by two orders of magnitude than the experimental value of 0.0023 eV [12] and the theoretical value of 0.0026 eV [5] in Gd@C₈₂, reflecting prompt enhancement in the spin coupling between Gd ion and fullerene with decreasing fullerene size.

From Figure 2, the Gd 6s and 5d-derived orbitals are empty and the C₆₀ t_{1u} -derived are half occupied, suggesting that the three valence electrons of Gd are completely transferred to C₆₀. The charge transfer from Gd to C₆₀ according to a commonly used Mulliken population analysis, however, is only 1.09 electrons. It was shown recently [13] that the natural population analysis is more suitable for determining charge transfer of a donor-acceptor system than Mulliken population analysis. The charge transfer from Gd to C₆₀ is 2.23 electrons according to the natural population analysis by using CEP-121G basis set for C and Gd atoms implemented in Gaussian 03 package [14]. The natural populations on the Gd 6s and 5d orbitals are 0.21 and 0.52 electrons, respectively. The charge transfer from Gd to C₈₂ according to the natural population analysis was 2.43 electrons with a population of 0.48 electrons on the Gd 5d orbitals. The population of about half electrons on the Gd 5d was ascribed to a back-donation of the occupied orbitals of the fullerene cage. The charge state of the encapsulated Gd ion therefore is approximately described as +3. The

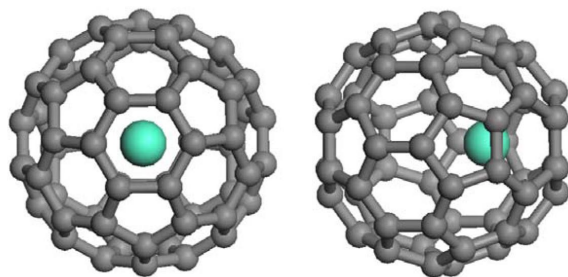


Figure 1. Optimized structure of Gd@C₆₀.

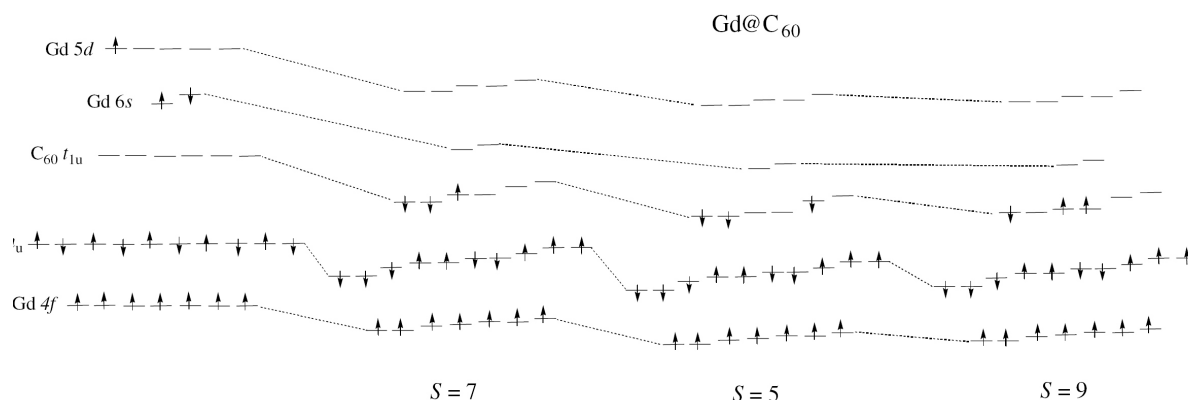


Figure 2. Electronic level diagram of Gd, C₆₀ and Gd@C₆₀ ($S = 5, 7$ and 9) near the Fermi level. The Gd two 6s and one 5d electrons are transferred to the C₆₀ t_{1u} -derived orbitals. The level degeneracy of Gd and C₆₀ is partially lifted upon complexation. In the $S = 7$ and 5 spin multiplicities of Gd@C₆₀, the net spins on the C₆₀ t_{1u} -derived orbitals are antiferromagnetically coupled with the seven spins on the Gd 4f orbitals. In the $S = 9$ spin multiplicity of Gd@C₆₀, the net spins on the C₆₀ t_{1u} -derived orbitals are ferromagnetically coupled with the seven spins on the Gd 4f orbitals.

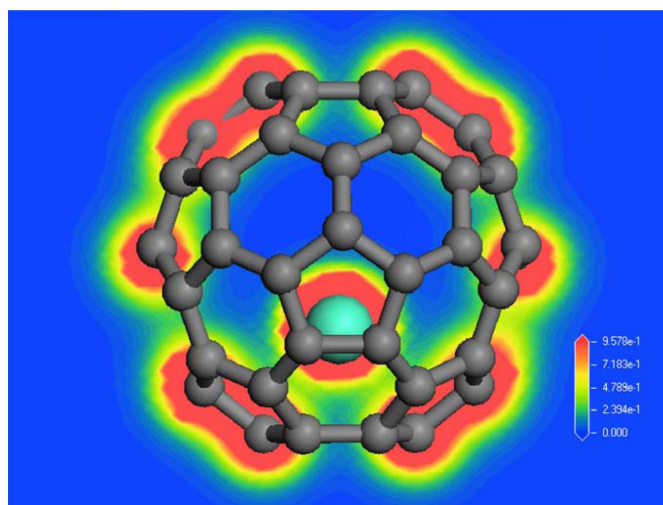


Figure 3. Electronic density in the plane passing through the Gd ion in Gd@C₆₀.

calculated dipole moment of Gd@C₆₀ is about 1.83 Debyes as a result of off center arrangement of Gd inside C₆₀. Fig. 3 displays the electron density in a plane containing the Gd ion. There is no significant electron accumulation between Gd and proximal C atoms. Therefore the interaction between Gd and C₆₀ is primarily ionic in character.

The highest occupied molecular orbital (HOMO) of Gd@C₆₀ and the lowest unoccupied Gd 5d derived molecular orbital in Gd@C₆₀ are showed in Fig. 4a,b, respectively. The HOMO of Gd@C₆₀ is derived from one of the C₆₀ *t*_{1u} orbitals but has some component on the Gd atom. On the other hand, the lowest unoccupied Gd 5d derived molecular orbital has some component on C₆₀. The orbital hybridization between the guest transition metal (and lanthanide) atoms and fullerene is another common character in metallofullerenes [15–18] in addition to the charge transfer, and accounts for the nonzero population on the Gd 6s-dominated orbital.

In conclusion, our all-electron relativistic density functional theory calculations show that the ground state of Gd@C₆₀ has the Gd ion on the top of the hexagonal ring of C₆₀. The electronic structure of Gd@C₆₀ is characterized by a nearly complete transfer of the three outmost valence electrons of Gd to C₆₀ and the orbital hybridization between the Gd atomic orbitals and C₆₀ molecular orbitals. The Gd 4f spins are nearly intact and antiferromagnetically coupled with that on C₆₀.

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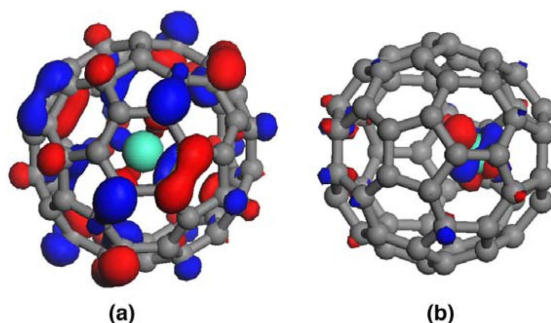


Figure 4. Isosurfaces (the isovalue is 0.03 a.u.) of: (a) the highest occupied molecular orbital Gd@C₆₀ and (b) the lowest unoccupied Gd 5d derived molecular orbital in Gd@C₆₀. Red and blue are used to indicate the positive and negative sign of the wavefunction, respectively.

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