

The structural determination of endohedral metallofullerene Gd@C₈₂ by XANES†

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Although the Gd ion in Gd@C₈₂ has been shown to lie above the C–C bond on the C₂ axis as an anomalous structure from the MEM/Rietveld analysis, the present XANES study reveals that it lies above the hexagon on the C₂ axis as a normal structure, and Gd oscillates around its equilibrium position with an amplitude increasing with temperature increase.

The structures and electronic properties of endohedral metallofullerenes have been extensively investigated both experimentally and theoretically.^{1,2} The maximum entropy method with Rietveld analysis (MEM/Rietveld) of synchrotron X-ray powder diffraction data has been used for structural determination of endohedral metallofullerenes³ such as Y@C₈₂,⁴ La@C₈₂,⁵ Sc@C₈₂,⁶ La₂@C₈₀,⁷ Sc₂@C₆₆,⁸ Sc₂C₂@C₈₄,⁹ Sc₃@C₈₂,¹⁰ Sc₂@C₈₄,¹¹ Gd@C₈₂,¹² and Eu@C₈₂.¹³ From the MEM/Rietveld analysis of synchrotron X-ray powder diffraction data of Y@C₈₂, La@C₈₂, and Sc@C₈₂, Takata *et al.* suggested that the metal atom was located at an off-centered position on the C₂ axis adjacent to a hexagonal ring of the C₈₂ cage in agreement with a theoretical suggestion.¹⁴ However, from the MEM/Rietveld analysis for both Eu@C₈₂ and Gd@C₈₂ an anomalous structure in which the metal atom is located on the C₂ axis but adjacent to the C–C double bond on the opposite side of the C_{2v}-C₈₂ cage has also been reported.^{12,13} These data are not in agreement with earlier experimental studies¹⁵ and theoretical calculations.^{14,16,17} However, the third generation synchrotron radiation X-ray sources significantly improved earlier powder diffraction experiments and the structure previously recognized as Sc₃@C₈₂ has now been revised to Sc₃C₂@C₈₀,¹⁸ a structure originally determined by means of NMR spectral analysis and single crystal X-ray structural determination of its derivative.¹⁹ In addition, a recent NMR study of Sc₂C₈₄ and a single crystal X-ray analysis of its derivative reveal that the fullerene structure is Sc₂C₂@C₈₂²⁰ rather than the widely accepted Sc₂@C₈₄.¹¹ Here, we present an investigation of the metal atom's position in both Gd@C₈₂ and

La@C₈₂ by X-ray absorption near-edge structure (XANES) combined with density functional theory (DFT) calculations, confirming the normal structure of Gd@C₈₂ suggested by recent theoretical calculations¹⁶ and the dynamic behavior of the Gd ion in the cage.

For the Gd@C₈₂ system, four different structures were previously addressed by experimental and theoretical studies.^{12,15–17} In Fig. 1, we outline the four proposed Gd configurations inside the cage for the sake of comparison. The MEM/Rietveld method assigned the Gd ion above the C–C bond on the C₂ axis (see the C₂-bond structure in Fig. 1a). An extended X-ray absorption fine structure (EXAFS) study recognized for the Gd ion the same position labeled as the C₂-hexagon structure (Fig. 1b) selected by the other metal ions. A recent density functional theory at the B3LYP level calculation proposed a structure,¹⁷ labeled as the CC-hexagon (Fig. 1c), in which the Gd ion is above the hexagon of the C₂-hexagon structure, but off the C₂ axis and adjacent to a C–C bond of the hexagon. Schrier²¹ suggested another structure optimized by his group: the C-pentagon structure (see Fig. 1d) in which the Gd ion is further apart from the C₂ axis and above a nearby pentagon. However, DFT calculations indicated that it is energetically much more favorable for the Gd ion to be in an off-centered position adjacent to a hexagonal ring rather than a C–C double bond.^{16,22}

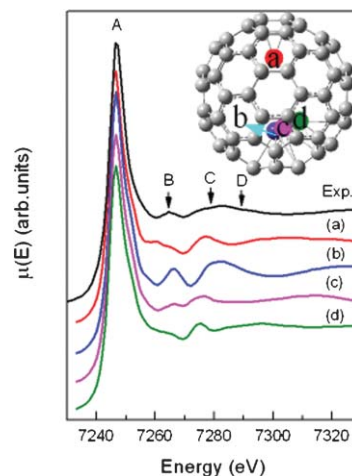


Fig. 1 Simulated spectra of the four structures available in the literature (a) to (d) compared with the Gd L_{III}-edge experimental spectrum recorded at 25 K. At the top are the four configurations of the Gd ion inside the cage: (a) the C₂-bond structure, (b) the C₂-hexagon structure, (c) the CC-hexagon structure and (d) the C-pentagon structure.

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The XANES technique as an atomic selective and short range sensitive method²³ has been used to collect the Gd L_{III} -edge XANES spectrum of Gd@C₈₂ from 25 K to 300 K in the transmission mode at the XAFS station of the Beijing Synchrotron Radiation Facility.

All XANES calculations for Gd@C₈₂ were carried out by the one-electron full multiple-scattering (MS) theory²⁴ with the FEFF8.2 code.²⁵ Geometry optimizations as well as frequency calculations were performed using the above mentioned structures as an initial guess. All calculations were performed with the GAUSSIAN 03 package²⁶ at the B3LYP level. The relativistic effective core potential CEP-121G basis set and the 6-31G basis were employed for the gadolinium and carbon atoms, respectively. The spin multiplicity was set to 7, according to the experimental results.^{27,28}

The Gd L_{III} -edge XANES spectrum of Gd@C₈₂ at 25 K (Fig. 1) is in good agreement with data of ref. 15 and exhibits four main features labeled as A, B, C and D. Among the calculated XANES spectra for the four proposed local structures (Fig. 1), the four spectral features are present in the spectrum of the C_2 -hexagon structure (curve b) while the spectra of the other three structures show large differences, suggesting that the C_2 -hexagon structure is the most reliable one. We also performed the geometry optimization for all structures, and all the optimizations were complete when the maximum remaining force on an atom, the average force on all atoms, the maximum structural change of one coordinate as well as the average change over all structural parameters fall below 0.00045, 0.0003, 0.0018, and 0.0012, respectively. However, additional frequency calculations showed that only for the C_2 -hexagon structure do all vibrational modes correspond to real frequencies, which means that only the C_2 -hexagon structure is a true minimum and the most stable structure among the four configurations. This conclusion is consistent with total energy calculations which showed that the C_2 -hexagon structure is characterized by the lowest energy while the CC -hexagon, C -pentagon and the C_2 -bond structures have energy 1.0, 6.9 and 54.5 kcal mol⁻¹ higher, respectively.

In Fig. 2, 100 positions in the vicinity of the C_2 -hexagon structure were calculated and optimized with the same constraints. (The position of the gadolinium and the angle between Gd and C located near the C–C bond on the C_2 axis are fixed to prevent C₈₂ from rotating around the C_2 axis. See ESI† for more details). The potential energy surface around the C_2 -hexagon structure is quite flat (Fig. 2). Among these various positions, we chose two

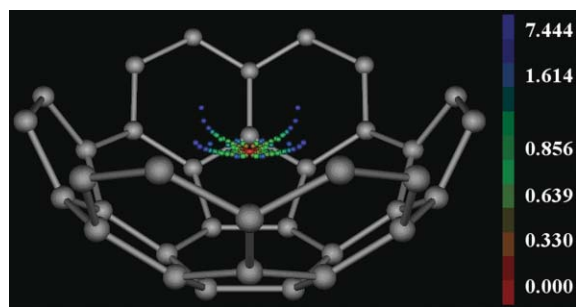


Fig. 2 The potential energy surface in the vicinity of the C_2 -hexagon structure in a section of the fullerene cage (the energy unit in the figure is kcal mol⁻¹).

representatives to investigate the influence of the spin multiplicity and basis set on the relative energies: one is the true minimum C_2 -hexagon, and the other is the second most far from C_2 -hexagon (the distance is about 1.15 Å). The calculated energies are available in the ESI.† The energies with multiplicities of 5 and 11 are much higher than those of 7 and 9 for both configurations, while the energy difference between multiplicities of 7 and 9 is very small taking into account all the error sources and inaccuracies in the calculation. Hence setting the spin multiplicity to 7 is a reasonable choice consistent with other experimental data.^{27,28} The influence of polarization functions on the relative energies is quite small, and then the results obtained with the 6-31G basis set are reliable and probably the only reasonable option for such a large number of calculations.

The zero point energy (ZPE) corrections have also been taken into account for the four proposed local structures as shown in the ESI.† We need to underline here that the differences between the corresponding structures with and without ZPE corrections are quite small, so that the ZPE corrections do not significantly affect the potential energy surface, which is rather smooth and flat. The Gd ion is thus expected to oscillate within the flat region of the potential energy surface with an amplitude increasing with temperature increase. The measured spectrum does not correspond to a single configuration, but to the average of all spatial configurations of Gd along the potential energy surface. If we consider that the oscillations of the Gd ion are mainly due to thermal energy, the resulting spectrum can be obtained using the Boltzmann statistical average. The calculated spectra at 25 K and 300 K (Fig. 3 left) are in good agreement with the experimentally observed temperature dependence. Features B and C (inset of Fig. 3 left) decrease and widen at high temperature, indicating that the oscillation amplitude of the Gd ion on the potential energy surface increases with temperature increase. A better agreement with experimental data could be obtained by increasing the number of configurations on the potential energy surface, which requires a huge number of calculations that are beyond our current computational capacities.

To confirm our model, we also performed XANES experiments at the La L_{III} -edge of La@C₈₂ (Fig. 3 right) where a large

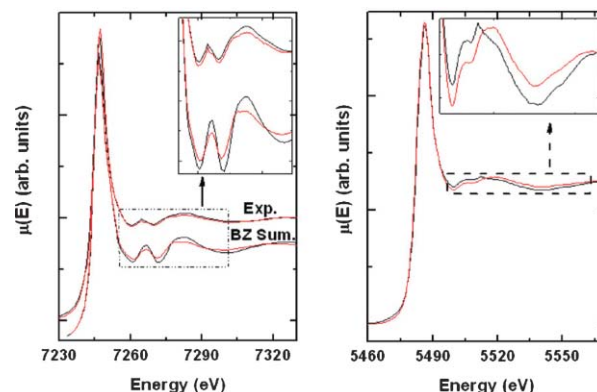


Fig. 3 Left: Gd@C₈₂: Comparison of the Gd L_{III} -edge experimental (Exp.) spectra and that representing the Boltzmann statistical averaged spectra (BZ Sum.) at 25 K (black line) and 300 K (red line). Right: La@C₈₂: The La L_{III} -edge experimental spectra recorded at 35 K (black line) and 300 K (red line).

difference is evident between the two spectra recorded at low and room temperature. Because of the different metal hybridization of La with respect to Gd, the observed behavior can be interpreted in terms of wider La oscillations with temperature increase. Additional analysis of the dynamics of the La inside the C₈₂ cage is in progress.

In conclusion, the location of the Gd ion in Gd@C₈₂ has been a matter of debate with several possible models, but by XANES data we found the local structure for the Gd ion inside the C₈₂ fullerene cage to be only the C₂-hexagon position characterized by a true minimum. Therefore, the Gd ion is situated at the same position as other metal ions in conventional endohedral metallofullerenes. Moreover, we observed a temperature dependent dynamic behavior that suggests an oscillation of the Gd ion on the flat potential energy surface with an amplitude increasing with temperature increase. Similar dynamic behavior has also been observed for the La ion in La@C₈₂, although a large difference between the XANES spectra is observed between low and room temperature in this case, supporting the occurrence of a wider La oscillation with temperature increase.

This structural study on the Gd@C₈₂ metallofullerene demonstrates the unique capabilities of the XANES technique for structural determinations of endohedral metallofullerenes and the relevance of frequency calculations in order to determine the true energy minimum in different metal ion configurations. The existing controversy on the Gd@C₈₂ structure has been resolved and we showed how the method may be used for local structural determinations of other endohedral metallofullerenes. Nowadays, the dynamic behavior of metal atoms inside fullerenes is mostly studied by an NMR technique,²⁹ while the combination of XANES and DFT calculations as illustrated in this study may be a real alternative to investigate such dynamic behavior.

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