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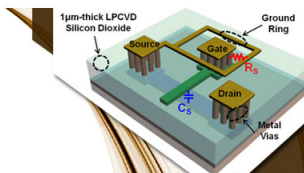
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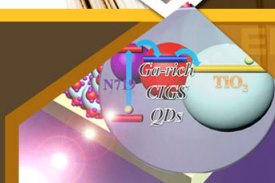
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# Identification of metal-cage coupling in a single metallofullerene by inelastic electron tunneling spectroscopy

J. Jiang,<sup>1,a)</sup> B. Gao,<sup>2</sup> Z. P. Hu,<sup>3</sup> Wei Lu,<sup>4</sup> Z. Y. Wu,<sup>2</sup> J. L. Yang,<sup>3</sup> and Y. Luo<sup>1,3,a)</sup>

<sup>1</sup>Department of Theoretical Chemistry, School of Biotechnology, Royal Institute of Technology, S-106 91 Stockholm, Sweden

<sup>2</sup>Institute of High Energy Physics, Chinese Academy of Sciences, Beijing 100049, People's Republic of China

<sup>3</sup>Hefei National Laboratory for Physical Science at the Microscale, University of Science and Technology of China, Hefei, Anhui 230026, People's Republic of China

<sup>4</sup>National Lab for Infrared Physics, Shanghai Institute of Technical Physics, Chinese Academy of Sciences, Shanghai 200083, People's Republic of China

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We report hybrid density functional theory calculations for inelastic electron tunneling spectroscopy (IETS) of a single metallofullerene Gd@C<sub>82</sub>. It is found that the metal atom inside the carbon cage can have significant impact on the IETS spectral profiles of the system, by modulating both the vibration and electron density. It is demonstrated that the IETS signals are very sensitive to the changes in the metal position and charge states, so that provide a unique tool for identifying the metal-cage coupling in metallofullerenes. © 2010 American Institute of Physics.

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Endohedral fullerene molecules have received significant attention both experimentally<sup>1,2</sup> and theoretically,<sup>3,4</sup> owing to their remarkable electrical and magnetic properties, and possible applications in future molecular electronics.<sup>5,6</sup> It is expected that the coupling between metal atom and the carbon cage could play an important role in determining their unique properties.<sup>7-9</sup> However, very few analytical techniques are capable of providing such information. The most relevant one is probably the inelastic electron tunneling spectroscopy (IETS), which is directly related to electron density and molecular electron-phonon coupling. Starting with an important experiment by Stipe *et al.*,<sup>10</sup> IETS with scanning tunneling microscope (STM), IETS-STM, has become an established technique to probe the local vibration density.<sup>2,11,12</sup> In a recently joint experimental and theoretical study on IETS-STM of isolated Gd@C<sub>82</sub> molecules residing on Ag(001), Grobis *et al.*<sup>2</sup> have found that dominant inelastic signal is spatially localized and detectable only on certain parts of Gd@C<sub>82</sub> molecule. Such a dominant spectral feature seems to be reproducible by the density functional theory calculations for a C<sub>82</sub><sup>4-</sup> model system. It was then concluded that coupling between the inner Gd atom and carbon cage appears to be unimportant in the experimental regime.<sup>2</sup> This finding is quite surprising since the metal atom is known to be coupled with the carbon cage electronically and geometrically.<sup>8,9</sup>

In this paper, we report a first principle study on IETS of Gd@C<sub>82</sub>, which is the largest system that has ever been calculated in this context. Metallofullerenes are complex nanomaterials, and there are still many ambiguities concerning the location of Gd atom inside the C<sub>82</sub> cage. Until now, different geometries have been proposed and investigated in many studies.<sup>8,13,14</sup> Starting from these suggested models, we have performed both conductance-STM and IETS-STM im-

age simulations to solve these ambiguities concerning Gd position. With the program DMOL3 (Ref. 15) package at local density approximation (LDA) level, we are able to compute out the electron density over the shell of Gd@C<sub>82</sub> molecules with different geometries, to compare with the experimentally measured conductance-STM image over the carbon cage surface. Our theoretical approach has described IETS of several molecular junctions with great accuracy,<sup>16,17</sup> in which simulations have not only reproduced the experimental IETS spectra but also provided many detailed structure information that were not accessible in the experiments. We have adopted Born–Oppenheimer and harmonic approximations as done by Grobis *et al.*,<sup>2</sup> i.e., only the first derivative like  $\partial\Psi(Q)/\partial Q_a$  is considered, where  $Q_a$  is the vibrational normal mode  $a$  of the system under investigation. Our working formula for IETS can be found in Refs. 16 and 17. The geometry optimization and vibrational analysis are performed using GAUSSIAN03 program<sup>18</sup> at hybrid density function theory (DFT) and Becke three-parameter, Lee–Yang–Parr exchange–correlation functional (B3LYP) level with a 6–31G basis for carbon atom and a CEP-121G basis for Gd atom. IETS spectra are generated using the QCME program.<sup>19</sup> We have shown that IETS is very sensitive to the location of metal atom and the charge state, indicating that it is a very useful tool to identify the structure of metallofullerenes, as well as the metal-cage coupling status.

First, we have performed theoretical simulations of conductance-STM image, to check the possible locations of Gd atom inside the carbon cage. We have tested several possible structures of Gd@C<sub>82</sub> following the suggestions of previous experimental and theoretical studies.<sup>8,13,14</sup> For instance, an extended x-ray absorption fine structure study of Gd@C<sub>82</sub> suggested that Gd atom was located above the carbon hexagon ring on the opposite side of the C<sub>2</sub> axis,<sup>13</sup> namely, as R1-Gd@C<sub>82</sub>. While a DFT study suggested that Gd atom should lie above the hexagon as in R1-Gd@C<sub>82</sub> structure, but off the C<sub>2</sub> axis and in adjacent to a C–C bond of the hexagon.<sup>8</sup> This structure is named as G1-Gd@C<sub>82</sub>.

<sup>a)</sup>Authors to whom correspondence should be addressed. Electronic addresses: junjiang@theochem.kth.se and luo@kth.se.

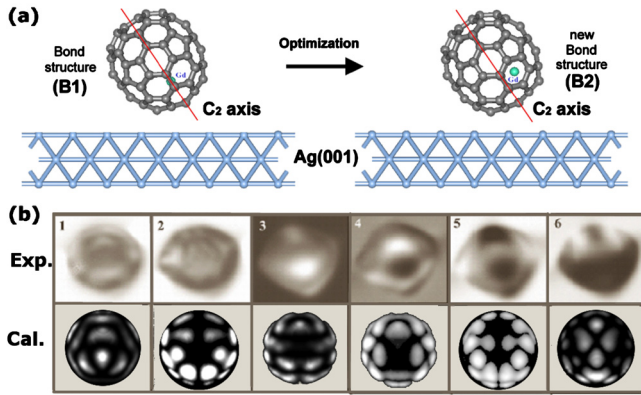


FIG. 1. (Color online) (a) Geometry optimization of B1-Gd@C<sub>82</sub> over Ag surface lead to a more stable structure B2-Gd@C<sub>82</sub>. (b) Experimentally measured (Ref. 2) conductance-STM map and theoretically computed electric density for B2-Gd@C<sub>82</sub> over Ag surface system at external voltage (1) -0.75, (2) 0.10, (3) 0.70, (4) 1.05, (5) 1.30, and (6) 1.60 V.

Another kind of structure being studied is the one obtained from a recent experimental study by means of the maximum-entropy method (MEM) and Rietveld refinement method,<sup>14</sup> in which Gd atom is determined to be located above the C-C bond on the C<sub>2</sub> axis of Gd@C<sub>82</sub>,<sup>14</sup> as shown in Fig. 1(a). We name this structure as B1-Gd@C<sub>82</sub>. To be able to compare with the experimental work done by Grobis *et al.*,<sup>2</sup> geometry optimizations with the Ag atoms fixed had been carried out at LDA level implemented with the DMOL3 package.<sup>15</sup> Geometry optimization and vibrational analysis are always done for state with spin multiplicity of 7.<sup>8</sup> The Vosko-Wilk-Nusair local correlation functional and all-electron calculations with double numerical with polarization basis were used in calculation. The electric density has been computed out by using Tersoff-Hamann approach,<sup>20</sup> which could be corresponding to the conductance-STM map. However, none of the R1-Gd@C<sub>82</sub>, G1-Gd@C<sub>82</sub>, and B1-Gd@C<sub>82</sub> structures was able to provide the simulated conductance-STM map matching the experimental one.<sup>2</sup> On the other hand, after optimizing the structure of B1-Gd@C<sub>82</sub> molecule, we reached a new structure being more stable in the energy representations. In this new structure, the Gd atom still locates above the C-C bond, but no longer stays on the C<sub>2</sub> axis, which can be seen in Fig. 1(a). Here we name this new structure as B2-Gd@C<sub>82</sub>. We have done frequency analysis at B3LYP level with the same basis set described in Ref. 2 for free Gd@C<sub>82</sub> molecule with B1 structure and B2 structure by GAUSSIAN03 package. The frequency analysis showed that molecule with B1 structure had two negative frequencies which indicated this structure was not a stable one, and molecule with B2 structure did not have a negative frequency but 0.922 eV lower in energy than the molecule with old structure. The conductance-STM image for B2-Gd@C<sub>82</sub> have then been computed out, as shown in Fig. 1(b), which exhibits distributions agreeing well with the experiments.<sup>2</sup>

As the B2-Gd@C<sub>82</sub> system provides electron density agreeing with the experimental conductance-STM image,<sup>2</sup> we started our IETS simulations with it. The topographic structure of B2-Gd@C<sub>82</sub> (from the view point of the above STM tip) is plotted in the inset of Fig. 2(a), which is consistent with experimental structure reported in Ref. 2. Employing the GAUSSIAN03 program, the theoretical vibrational modes for an isolated B2-Gd@C<sub>82</sub> have been computed out,

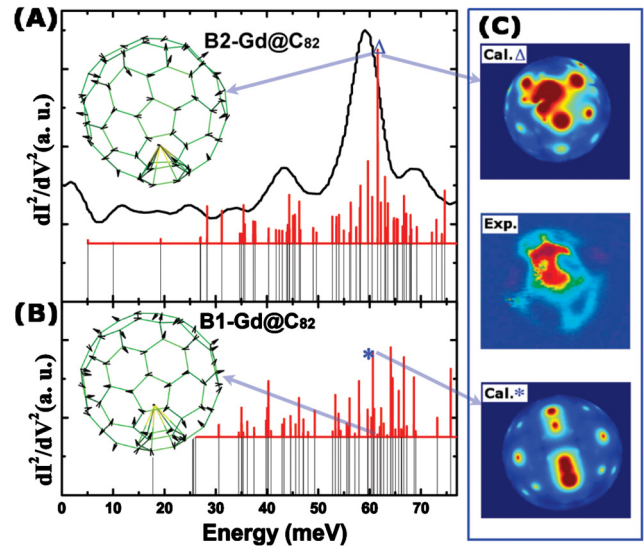


FIG. 2. (Color online) (a) Calculated density of vibrational modes (bottom black bars), and IETS spectra (middle gray/red bars) at the position marked of the optimized B2-Gd@C<sub>82</sub>, together with the experimental IETS (top black curve). The left inset graph lists the atomic motions of the vibration mode at 61.6 meV. (b) Theoretically computed IETS spectra in B2-Gd@C<sub>82</sub> (61.6 mV) and B1-Gd@C<sub>82</sub> (60.6 mV) system, respectively. The measured map for the dominated IETS peak at 60 mV in experiments was illustrated together. (c) Calculated density of vibrational modes (bottom black bars), and IETS spectra (top gray/red bars) of the optimized B1-Gd@C<sub>82</sub>. The left inset graph exhibits the atomic motions of the vibration mode at 61.6 meV. All the experimental results are extracted from Ref. 2.

with black bars shown at the bottom of Fig. 2(a). The distribution of vibration modes obtained from our calculations alone cannot fit with the top black curve in Fig. 2(a) for the experimentally measured IETS. The vibration information has then been used to compute the IETS, with results shown as the red bars in the middle of Fig. 2(a). Obviously, only some of the vibrational modes contribute to the inelastic electron tunneling process. Comparing to experiments, one can see the computed IETS of B2-Gd@C<sub>82</sub> fits with the experimental one very well. In particular, a strong spectral feature is found at 61.6 meV, which agrees with the maximum of the experimental spectrum. The vibration motions of the mode at 61.6 meV have been illustrated by arrows in the left inset graph of Fig. 2(a), which seems to be unrelated to the metal atom. Actually, most Gd related vibration modes locate in the low frequency region with energy less than 30 meV, so that most of IETS signals are induced by the vibration of the carbon cage. We have also made the spatial map for the strongest inelastic peak at 61.6 mV, and plotted it in Fig. 2(b) to compare with the measured dominated inelastic peak at 60 mV. The localization behavior of this mode is clearly reproduced by the calculation. The overall pattern of B2-Gd@C<sub>82</sub> is in better agreement with the experiment than the computation of C<sub>82</sub>,<sup>2</sup> implying that the metal atom can influence the IETS signals of the cage.

To confirm the location of Gd atom inside the cage, it is very necessary to do IETS simulations of other possible Gd@C<sub>82</sub> structures. Being as one of the local minimal of system energy in the optimization process of Gd@C<sub>82</sub>, B1-Gd@C<sub>82</sub> system is also appropriate for the theoretical IETS studies. The theoretical vibration modes for B1-Gd@C<sub>82</sub> were plotted as black bars at the bottom of Fig. 2(c). One can see that the vibration density of B1-Gd@C<sub>82</sub>



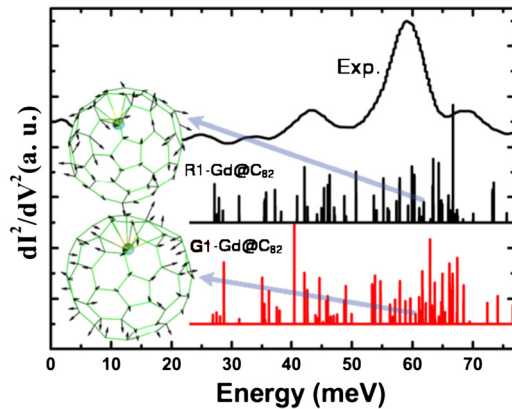


FIG. 3. (Color online) Calculated IETS spectra for R1-Gd@C<sub>82</sub> (middle black bars) and G1-Gd@C<sub>82</sub> (bottom gray/red bars) structures. Experimental IETS (top black curve) (Ref. 2) is included for comparison. The atomic motions of the vibration mode at 61.6 meV are shown in the inset.

is different to that of B2-Gd@C<sub>82</sub>. For instance, the vibration motions of B1-Gd@C<sub>82</sub> at mode 61.6 meV are illustrated by arrows in the left inset graph of Fig. 2(c), which is now different to those of B1-Gd@C<sub>82</sub> at 61.6 meV in the inset of Fig. 2(c). Moreover, as we have found in the conductance-STM image simulations, there are strong overlaps of the electron distribution between Gd and carbon cage.<sup>8,9</sup> Therefore, both of the electron density and vibrations are strongly affected by the metal-cage coupling. As the inelastic electron tunneling process is directly induced by the electron-vibration coupling, IETS has to be very sensitive to the change in metal-cage coupling. Thus we can see very different IETS from Figs. 2(a) and 2(c) for B2- and B1-Gd@C<sub>82</sub> system, respectively. The vibration at mode 61.6 meV leads to the strongest IETS peak in B2-Gd@C<sub>82</sub> system but merely has few contributions to the IETS of B1-Gd@C<sub>82</sub>. At around 60 meV, the dominated IETS peak of B1-Gd@C<sub>82</sub> comes from the mode at 60.6 meV, whose IETS spatial map in Fig. 2(b) is very different to that of B2-Gd@C<sub>82</sub>. As we introduced above, the Gd position in B1-Gd@C<sub>82</sub> has only small difference to that of B2-Gd@C<sub>82</sub>, which however leads to completely different IETS and spatial distributions. The involvement of Gd atom in inelastic electron tunneling process is quite evident. In stark contrast to previous prediction,<sup>2</sup> we have found that the metal atom has significant effect on the spectral profile of IETS spectra and shown that neglecting of metal atom in simulation is not justified.

Due to the large complexity concerning the Gd@C<sub>82</sub> structure, some other geometries also need to be investigated in IETS simulations. For instance, the optimized structures of R1-Gd@C<sub>82</sub> and G1-Gd@C<sub>82</sub> are shown in Fig. 3 together with calculated IETS spectra. It can be seen that none of these two structures can give spectrum that slightly resembles the experimental one. These results clearly illustrate the sensitivity of IETS on the position of metal atom, and demonstrate the existence of B2-Gd@C<sub>82</sub> structure in Grobis' experiment.<sup>2</sup>

It is noted that experimental measurements were done for Gd@C<sub>82</sub> on Ag surface. The use of  $-4$  charge state for C<sub>82</sub> cage was based on the reasoning that Gd atom can donate three electrons to the cage and Ag substrates are ex-

pected to donate charge to fullerenes.<sup>2</sup> We have examined the possible charging effect on IETS by calculating Gd@C<sub>82</sub><sup>-1</sup>, i.e., it is assumed that Ag substrates can donate one electron to the molecule. The calculated vibration density and IETS for B2-Gd@C<sub>82</sub><sup>-1</sup> are very different to the neutral ones in Fig. 2(a). Moreover, we have found that the inclusion of  $-1$  charge in B1-, G1-, R1-Gd@C<sub>82</sub> structures lead to IETS inconsistent with experiments. Our calculations thus show that the Ag substrates is unlikely to donate one electron to Gd@C<sub>82</sub>, although a charge transfer process should still take place between them.

In conclusion, we have carried out hybrid density functional theory calculations for IETS of Gd@C<sub>82</sub> molecule. Our calculations have been able to reproduce previous experimental IETS spectrum and spatial map of Gd@C<sub>82</sub> molecule. It is found that IETS spectrum of Gd@C<sub>82</sub> is drastically affected by not only the inclusion of Gd atom but also the exact location of Gd atom inside the cage. Calculations have also shown that Ag substrates can exchange charges with Gd@C<sub>82</sub> but it is unlikely to transfer one electron to the carbon cage. The theoretical study gives an important implication that metals should not be neglected in the computational modeling of IETS for molecular devices, as some previous works did. Most importantly, our study suggests that IETS can be used as a unique tool to identify the situation of metal-cage coupling in metallofullerenes.

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