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Photoabsorption spectra of the Ce atom encapsulated inside a C_{82} fullerene

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The differential oscillator strengths for the photoabsorption spectra of the Ce atom encapsulated inside C_{82} fullerene have been investigated using the time-dependent density-functional theory. The geometry optimization was performed for the C_{82} and Ce@C_{82} molecules. The final position of the Ce atom was found at 1.85 Å off the center of the C_{82} molecule along the C_2 axis. The photoabsorption spectra demonstrate a great suppression of the $4f$ autoionization process for the encaged Ce atom. This calculation confirms the experimental result which showed no confinement resonance in the photoionization measurement of the Ce@C_{82} endohedral fullerene.

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I. INTRODUCTION

In recent years much attention has been devoted to the endohedral fullerenes with rare earth elements encapsulated inside the carbon cage, such as Dy@C_{82} [1,2], La@C_{82} [3,4], Ce@C_{82} [5–14], Pr@C_{82} [15], etc. These endohedral metallofullerenes have unique properties that are not seen in empty fullerenes. For example, the field effect transistor (FET) with a thin film of Dy@C_{82} [2] exhibited a normally "on" type property, which is different from those of C_{60} and C_{70} FETs, which show normally "off" characters. This suggests the possibility of the development of electronic devices and materials based on the intrinsic nature of metallofullerenes. These materials and devices are interesting and important in many fields such as nanomaterials, quantum computing, and superconductors.

Scientists are interested in the encapsulation of lanthanide atoms having f electrons. A system having $4f$ electrons on the Ce atom and π electrons on the C_{82} cage may provide new information on bifunctional molecular systems. Two types of isomer structures are possible for the Ce@C_{82} molecule and have been observed by x-ray diffraction patterns [5]: isomer I (C_{2v}) and isomer II (C_s). It is well known that there are nine isolated pentagon isomers of the empty C_{82} [6]. Three have C_2, three have C_s, two have C_{3v}, and one has C_{2v} symmetries. The most commonly observed structure of the empty C_{82} is C_2. However, the ^{13}C NMR experimental spectrum [6] has confirmed that the most stable symmetry for the metallofullerene Ce@C_{82} is C_{2v}.

Theoretical calculation [10] has also demonstrated the same result. The NMR spectra measured by Yamada *et al.* [7] suggested that the Ce atom is located at an off-centered position adjacent to the hexagonal ring along the C_2 axis of the C_{2v}-C_{82} cage, unlike the Eu and Gd atoms in the Eu@C_{82} and Gd@C_{82} molecules, where they are located near the C-C double bond on the opposite end. The uv-vis-near-ir spectrum and x-ray photoelectron spectroscopy (XPS) of the Ce@C_{82} molecule performed by Ding *et al.* [8] suggests that the La@C_{82} and Ce@C_{82} molecules in the common C_{82} cage have an open-shell electronic structure. Shibata *et al.* [9] demonstrated, based on the Raman spectra, that the oxidation number of the Ce ions in the Ce@C_{82} molecule was +3. A density-functional theory (DFT) calculation of the Ce@C_{82} molecule has been performed by Muthukumar and Larsson [10] to explain the preferential bonding site for the Ce atom. Their result reveals that only a part of an electron has been transferred from the Ce to the cage. This charge is not delocalized but remains local in the chemical bonds between the Ce and the carbon cage and on the neighboring carbon atoms. The band gaps of the Ce@C_{82} molecule have been measured by Rikiishi *et al.* [5]. Their results show that the Ce@C_{82} molecule is a normal semiconductor with a small gap of 0.33 eV for isomer I and 0.55 eV for isomer II. The absorption spectra and the photoionization cross section of the Ce@C_{82} molecule have been studied recently by Wakahara *et al.* [6], Takeshi *et al.* [4], Shibata *et al.* [9], Mitsuke *et al.* [11], and Müller *et al.* [12,13]. A dramatic reduction and redistribution of the ionization contribution to the $4d$ photoabsorption spectrum has been observed [12,13].

In this paper we have employed our recently developed TDDFT to evaluate the differential oscillator strengths (DOSs) of the encapsulated Ce atom and compared our results with the experimental data. Our calculated data show a great suppression of the $4f$ decay channel and confirm the experimental observation of no confinement resonance in the photoionization measurement of the Ce@C_{82} endohedral fullerene.

II. METHOD AND RESULTS

Results presented in this paper are based on the following approach. First, a C_{82}-C_{2v} fullerene was optimized using the DMol$_3$ software, a package of DFT. Then a Ce atom, ground-state configuration [Xe]$4f5d6s^2$ ^1G was added inside the C_{82} along the C_2 axis near the six-member ring of the cage. The chemical bonds were built between the Ce and C atoms. The geometry optimization was performed again for all 550 electrons. The atomic coordinates were obtained by minimizing the total energy using the generalized gradient approximation (GGA) with the Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional [16] along with all-electron double numerical plus polarization (DNP) basis sets as implemented in the DMol$_3$ package. The optimization of atomic positions proceeded until the change in energy was less than 5×10^{-4} eV and the forces were less than 0.01 eV/Å.

Figure 1 shows the optimized configuration of the Ce@C_{82} endohedral fullerene. It demonstrates that the Ce@C_{82} fullerene preserves the C_{2v} symmetry. The Ce atom is located at the 1.85 Å off-center position of the C_{82}, which agrees well with the 2 Å obtained by the x-ray measurement [5]. A

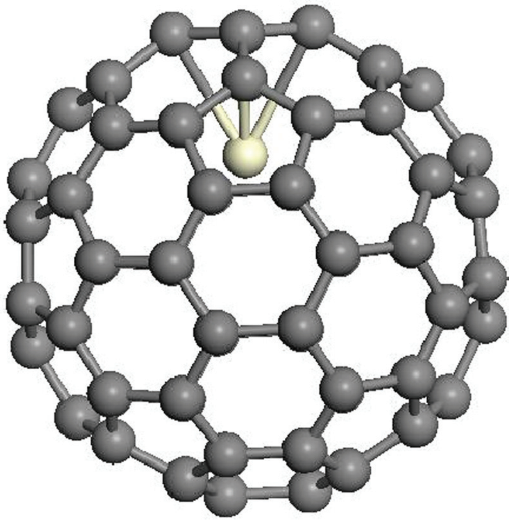

FIG. 1. (Color online) Structure of the Ce@C_{82} endohedral fullerene. The Ce atom is located at 1.85 Å off the center of the C_{82} molecule along the C_2 axis.

charge distribution has been calculated using the Mulliken's equation [17]. Our calculation shows that 1.11 electrons have been transferred from the Ce atom to the carbon cage, which should correspond to the oxidation state of +3 [8–10]. The result of Muthukumar and Larsson [10] indicated that 0.42 electrons have been transferred. Therefore our results support the suggestion of Ref. [10] that it is a faulty hypothesis that the endohedral metal atom donates a number of electrons equal to their oxidation number to the fullerene. Actually the charge is shared through chemical bonds with the cage. In the following calculation we do not account for the localized transferred electrons. For simplicity we consider the structure of the Ce atom encapsulated inside the C_{82} fullerene along the C_2 axis at the location of 1.85 Å off the center.

The resultant structure was subsequently validated using a plane wave approach as implemented in the QUANTUM ESPRESSO package [18]. The Kohn-Sham equation was solved with a cutoff kinetic energy of 952 eV and a supercell of edge 23.8 Å to eliminate the interactions among cells. The core electrons are taken into account using the ultrasoft separable pseudopotential proposed by Vanderbilt [19]. We note that the original software package, uspp-736, allowed only five valence shells in the pseudopotential creation. To include the Ce 4*d* shell in the valence electron we have recompiled the software with a maximum of six valence shells. The pseudopotential has been generated using 2*s*, 1*p*, 2*d*, and 1*f* nonlocal projectors and the PBE exchange-correlation functional [16] and including the nonlinear core corrections and the scalar relativistic effect.

The Kohn-Sham eigenvalues and eigenvectors were obtained through a standard ground-state DFT calculation. The linear response of the ground state to an external perturbation by an electric field was evaluated using the TDDFT method [20–22].

Figure 2 demonstrates the calculated photoabsorption spectra of the C_{82} and Ce@C_{82} molecules. Similar to the C_{60} fullerene the C_{82} molecule has a giant resonance, which corresponds to a collective oscillation of delocalized electrons relative to the ionic cage. The peak around 5.3 eV is the π plasmon resonance. The largest peak around 21.4 eV is related to the σ surface plasmon resonance. While those peaks around 110–150 eV are caused by the Ce 4*d* giant resonance. The photoabsorption cross section of a molecule can be evaluated approximately from $\sigma = \sum n_i \sigma_i$, where n_i is the number of atoms of element i and σ_i is the photoabsorption cross section for an individual atom of type i. Using this relationship we can find the photoabsorption peak of the C_{82} fullerene from the peak of C_{60} fullerene. The C_{60} fullerene has a maximum of 1200 (10^{-2} eV^{-1}) around 22 eV [23]. The C_{82} fullerene should have a maximum equal to $82/60 \times 1200 = 1640$ (10^{-2} eV^{-1}). Figure 2 indicates that the maximum is about 1612 (10^{-2} eV^{-1}), which agrees very well with the 1640 (10^{-2} eV^{-1}) value.

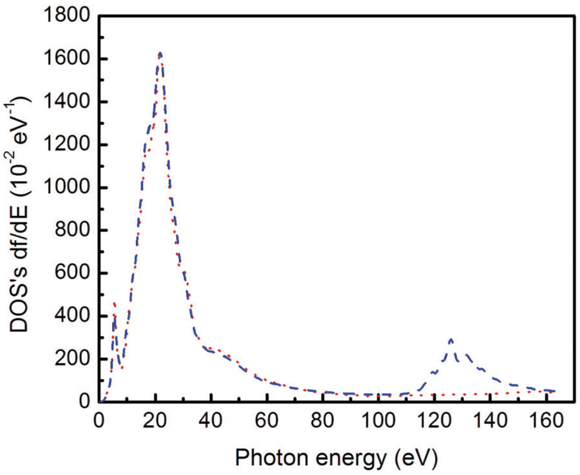

FIG. 2. (Color online) Dotted and dashed curves represent, respectively, the DOSs for the photoabsorption of the C_{82} and Ce@C_{82} molecules.

Figure 3 compares the DOSs of our TDDFT calculation with the experimental data [13]. Note that the calculated result

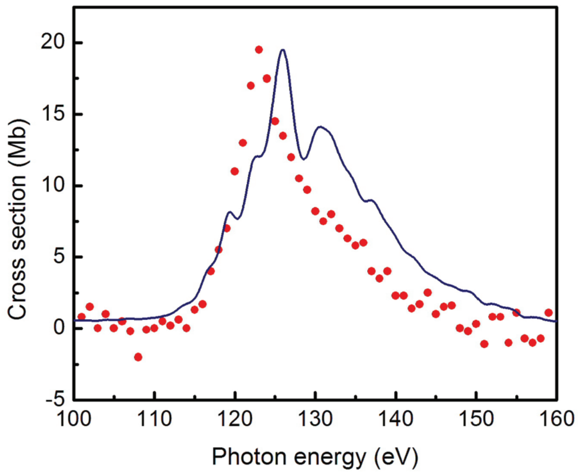

FIG. 3. (Color online) The solid curve and dots are, respectively, the photoionization cross section of the Ce atom encapsulated inside the C_{82} molecule obtained by TDDFT calculation and the measurement. The theoretical result has been reduced by a factor of 14.

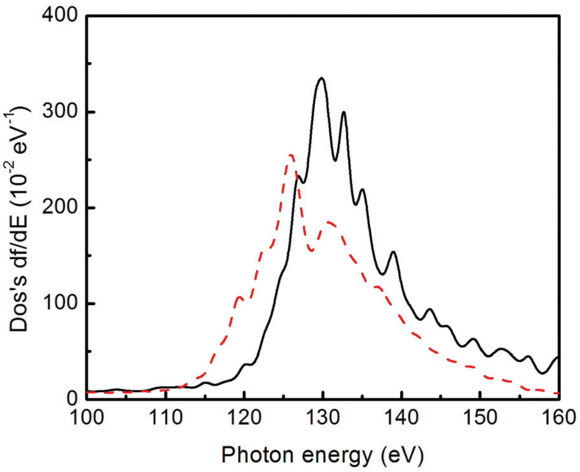

FIG. 4. (Color online) The solid and dashed curves are, respectively, the DOSs of the photoabsorption for the Ce atom and the Ce atom encapsulated inside the C_{82} molecule.

has been reduced by a factor of 14. The situation is similar to the Xe@C_{60} endohedral fullerene [23], where the main peaks have been reduced by a factor of 8. The giant resonance of the Xe $4d$-ϵf is caused mainly by the dipole interaction between the $4d$ and ϵf electrons. The overlap of the bound f orbital with the $4d$ orbital is very small. Most of the $4d \rightarrow f$ oscillator strength is associated with the continuum state. The resonance takes a one-step process: continuum enhancement due to the centrifugal-barrier shape resonance [24].

However, the Ce $4d$ giant resonance belongs to the second type of giant resonance, which corresponds to a decaying discrete resonance [24]. From previous published studies this kind of resonance takes a two-step process: photoexcitation of a $4d$ electron into the $4f$ subshell, followed by the autoionization of the $4d^9 4f^2 5d 6s^2$ state. The reduced factor of 14 in the comparison with the experimental data is probably related to the great suppression of this $4f$ autoionization process for the encaged Ce atom. A similar situation has also been discussed in Ref. [25]. The decaying discrete resonance has a collapsed f wave function. In this situation the inner well is deep enough to support a bound state and the $4f$ orbital "collapses" into the inner well. The mean radius of the $4f$ electrons is therefore small, only 0.99 a.u. It is much smaller than those of the $5s$ electrons (1.60 a.u.), the $5p$ electrons (1.79 a.u.), the $5d$ electrons (2.68 a.u.), and the $6s$ electrons (4.87 a.u.) and is comparable to those of the $4s$ electrons (0.67 a.u.), the $4p$ electrons (0.69 a.u.), and the $4d$ electrons (0.74 a.u.). Most of the $4d \rightarrow f$ oscillator strength is associated with the $4f$ state.

The solid and dashed curves in Fig. 4 are, respectively, the DOSs of the photoabsorption for the Ce atom and the Ce atom encaged inside the C_{82} molecule. These curves confirm the experimental result which showed no confinement resonances in the photoionization of the encaged Ce atom.

III. CONCLUSION

In conclusion the DOSs for the photoabsorption of the Ce atom encapsulated inside a C_{82} molecule have been evaluated using the TDDFT method. The optimization of the Ce@C_{82} molecule was performed and the position of the Ce atom was found at 1.85 Å off the center of the C_{82} molecule along the C_2 axis. The results show that the Ce $4f$ autoionization process for the encaged Ce atom has been greatly suppressed. This calculation confirms the experimental result which showed no confinement resonances in the photoionization of the encaged Ce atom.

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