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Off-center effect on the photoabsorption spectra of encapsulated Xe atoms

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The photoabsorption spectra of the Xe atoms encapsulated at different locations of the C_{60} have been evaluated using the time-dependent density-functional theory. The calculations are performed in the energy region of the Xe 4d giant resonance. The results demonstrate that the main confinement resonances can result only when the Xe atom is located within a very small sphere of radius 0.3 Å around the center of the fullerene. The small resonance peak around 100 eV has now been identified as a shape resonance of the free Xe $4d$-ϵf transition; it is not a confinement resonance.

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I. INTRODUCTION

Recently, a method has been developed to calculate the spectra of the photoabsorption of atoms encapsulated inside a fullerene cage [1–3]. This method has been successfully used to study the photoabsorption spectra of the Xe [1], Ar [2], and Ne [2] atoms encaged inside the C_{60} fullerene, and the Sc_3N cluster encapsulated in the C_{80} fullerene [3]. The obtained results demonstrate that the method can be used to study the photoabsorption spectra of atoms located at the center of the fullerene [1,2] and the off-center positions as well [3].

In the photoionization studies of endohedral fullerenes the most attractive problem is the Xe 4d giant resonance of the Xe@C_{60} molecule [4–9]. The advantage of studying the Xe@C_{60} photoionization is that the Xe atom can be assumed to be located at the center of the C_{60}. The energy region of the Xe 4d giant resonance is far away from the C_{60} plasmon resonance, and the most important factor is the availability of the measured photoionization cross section for the encapsulated Xe atom [9]. In a recent investigation using the time-dependent density-functional theory (TDDFT) the three main resonance peaks observed in the experiment [9] were confirmed [1]. This excellent agreement with the measurement has motivated Chen and Msezane [1] to extend the exploration to the interesting problem, when the Xe atom is located at the off-center positions.

The off-center effect has been studied by several groups [10–13]. Baltenkov *et al.* [13] studied the off-center effect within the framework of the Dirac-bubble potential model. They found that the confinement resonances decreased with increasing the displacement of the atom from the center of the fullerene. However, their method ignored the fact that the photoelectron momentum vector is not normal to the fullerene sphere surface for the off-center position of an atom. This omission becomes significant for a large shift off center. Korol and Solov'yov [10] utilized a δ-like potential to study the confinement resonance due to the interference of the direct and the scattered waves. They ignored the multiple scattering from the cage. Their results demonstrate that the confinement resonance is very sensitive to the mean displacement $\langle a\rangle$ of the atom from the cage center. They found that the resonances are strongly suppressed if $2\langle a\rangle$ exceeds the photoelectron half-wavelength. In [11] they reported that the Auger decay rate is very sensitive to the atom's location in the fullerene cage. In an endohedral system, two additional decay channels appear. These additional channels can dominate the direct Auger decay resulting in pronounced broadening of the atomic emission line. The dynamical screening of an endohedral atom located off the center has also been investigated by Lo *et al.* [12] in a semiclassical approach. Their results show that the dynamical screening factor can depend strongly on factors such as the distance between the endohedral atom and the fullerene cage. All these investigations contribute toward the understanding of the off-center problem. However, a calculation, which can directly demonstrate the off-center effect for the system of the Xe@C_{60} endohedral fullerene, is still needed.

II. METHOD AND RESULTS

The method used to evaluate the photoabsorption spectra of an encapsulated atom has been discussed in Refs. [1–3]. Here we simply give a brief description of the calculational procedures. We first calculate the photoabsorption spectra of the C_{60} fullerene. The C_{60} geometric optimization was performed using the $DMol_3$ software package [14] with the generalized gradient approximation and the Perdew-Burke-Ernzerhof (PBE) [15] exchange-correlation functional along with all electron double numerical plus polarization basis sets as implemented in the software package. The optimization of atomic positions proceeded until the change in energy was less than 5×10^{-4} eV. The optimized structure was then introduced into a supercell of 18 Å. The Kohn-Sham equation was solved using a plane-wave approach and an ultrasoft pseudopotential [16]. 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 [17–19]. Following the C_{60} calculation a Xe atom was then introduced into the C_{60} fullerene. The locations of the Xe atom are chosen to be at the center, or 0.2 Å, 0.3 Å, 0.4 Å off the center. For each location of the Xe atom the photoabsorption cross sections of the Xe@C_{60} were calculated using the same procedure as stated above for the C_{60}. Finally, the cross sections of the encaged Xe atom were obtained by subtracting the cross sections of the C_{60} from the corresponding cross sections of the Xe@C_{60} at the same photon energy.

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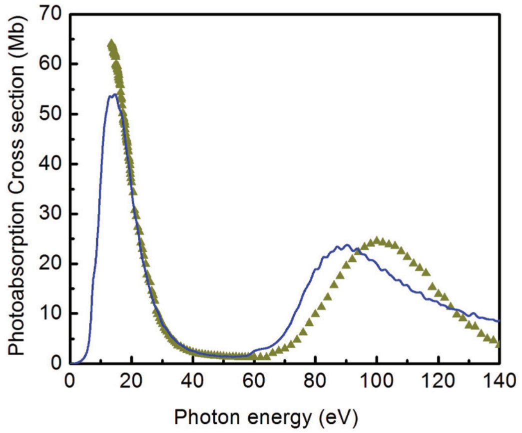

FIG. 1. (Color online) Photoabsorption spectrum of free Xe atom. Solid curve is our TDDFT results. Triangles are from measurements [20].

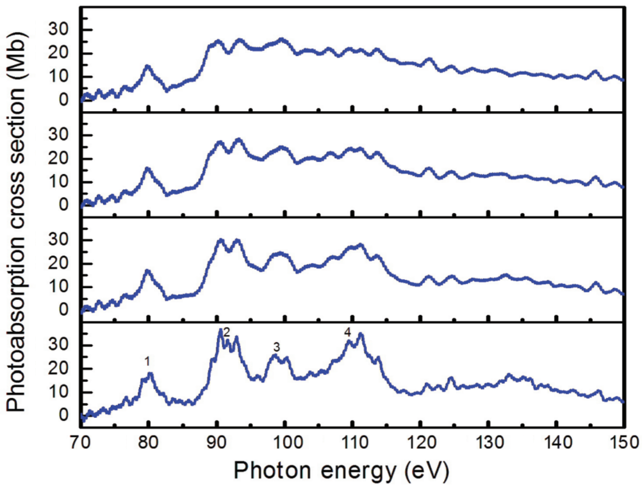

FIG. 2. (Color online) Photoabsorption spectra, from bottom up, of Xe atom encapsulated at the center, 0.2 Å, 0.3 Å, and 0.4 Å away from the center, respectively.

The TDDFT method has been used to evaluate the photoabsorption spectra for a free Xe atom. The pseudopotential uses the PBE exchange-correlation functional and the relativistic effect.

It is noted that in the calculation of the photoabsorption spectra of a free Xe atom the spectra are greatly affected by the size of the supercell. The interferences among the cells cause unwanted oscillations in the spectra. Therefore, the calculation should use a supercell which is sufficiently large, such as 31 Å in order to reduce or eliminate the interaction among the cells.

Figure 1 shows the calculated photoabsorption spectra of a free Xe atom and the experimental data. Triangles are the experimental data of Chan *et al.* [20] using a low-resolution spectrometer. The solid curve is our TDDFT results. The agreement is very good in the energy range less than 60 eV. In the energy region larger than 60 eV our peak of the Xe 4*d* giant resonance is about 10 eV lower than the measurement. Because of this, to compare with the experimental data in this energy range our curve needs to be shifted to the right by 10 eV. This has been done for the curves in Figs. 2 and 3.

Figure 2 shows the photoabsorption spectra of a Xe atom encapsulated inside the C_{60} in the energy region of the Xe 4*d* giant resonance.

We also calculated the photoabsorption spectra of the Xe@C_{60} when the Xe was at the center of the C_{60} using a bigger supercell of 23.8 Å. We found no significant change in the spectral features except some small wiggles. This may be caused by the C_{60}, which reflects the photoelectron back to the Xe atom. This kind of reflection reduces the interference among the cells. The original calculation with a supercell of 18.5 Å used 96 processes and lasted 24 h on the Kraken system of the NICS (National Institute for Computational Science, The University of Tennessee). However, the same job takes 72 h if the supercell was enlarged to about 23.8 Å. Because of this, in the off-center calculation of the Xe@C_{60} we used a supercell of 18.5 Å. We believe that the calculation using this size of a supercell yields a good spectra as well as consumes reasonable computing resources.

The four figures beginning from bottom to the top in Fig. 2 represent, respectively, the spectra of the encaged Xe atom located at the center, and at 0.2 Å, 0.3 Å, and 0.4 Å off the center. We number the peaks in the bottom panel of Fig. 2 from left to right as peaks 1, 2, 3, and 4. Figure 2 shows that the peaks are located at the photon energies of 80.42, 90.60, 98.43, and 111.20 eV. The panels of Fig. 2 show that the amplitudes of the peaks 2 and 4 decrease when the Xe atom moves away from the center. However, peak 3 is almost fixed; it does not change. As will be discussed later, peak 3 belongs to the original Xe 4*d* giant resonance. It is not caused by the confinement effect. Peaks 2 and 4 are the main features of the confinement resonances and are very sensitive to the positions of the Xe atom. Figure 2 demonstrates that the main confinement resonances result only if the Xe atom is located within a very small sphere around the center of the fullerene, with a radius of 0.3 Å.

Figure 3 contrasts the spectra of the free Xe atom and the Xe atom encapsulated at the center of C_{60}. This figure confirms that the peak 3 in Fig. 2 belongs to the Xe 4*d* giant resonance because the value of the peak 3 is almost equal to that of

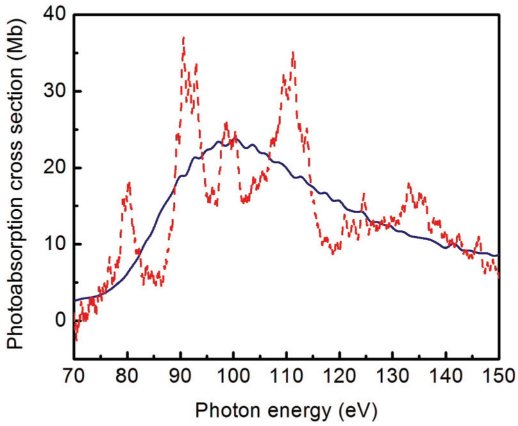

FIG. 3. (Color online) Solid and dashed curves represent, respectively, the photoabsorption cross sections of the free Xe atom, and Xe atoms encapsulated at the center of C_{60}.

the free Xe giant resonance at about 100 eV. Incidentally, in Fig. 2 we can find this (peak 3) in the curves when the Xe atom is located at 0.2 Å, 0.3 Å, and 0.4 Å away from the center. From these figures we conclude that the peak 3 is an original shape resonance of the Xe $4d$-ϵf transition. It is not a confinement resonance. Of course, peak 3 is also affected by the locations of the Xe atom. Therefore, it suffers a little perturbation and reveals differences when the Xe atoms are at different locations.

It is well known that the confinement resonance is the result of the interference between the wave of the photoelectron emitted by the Xe atom and the wave reflected by the C_{60} cage. When the amplitudes of the direct wave and the reflected wave are enhanced by each other we will observe the confinement resonances and the resonance peaks. This may likely occur if the atom and the carbon cage are both the wave node. If we know the radius of the fullerene and the ionization threshold of the encaged atom, we can estimate the photon energy at which the atom and the cage are the wave nodes. For example, the radius of the C_{60} fullerene is about 3.5 Å and the ionization threshold for the Xe $4d_{\frac{5}{2}}$ is about 67.55 eV [21]. If the photon energy equals 79.80 eV, 95.11 eV, and 116.55 eV, the wavelength of the photoelectron will be 3.5 Å, 2.33 Å, and 1.75 Å, respectively; these are equal to the C_{60} radius divided by 1, 1.5, and 2. Our TDDFT results in Fig. 2 show the confinement peaks located at the energies of 80.42 eV, 90.60 eV, and 111.20 eV, which are close to 79.80 eV, 95.11 eV, and 116.55 eV.

III. CONCLUSION

In conclusion, the photoabsorption cross sections of the Xe atoms encapsulated at different locations of the C_{60} have been calculated using the TDDFT method. The results demonstrate that the confinement resonances result only when the Xe atom is confined within about 0.3 Å around the center of the C_{60}. The results also indicate that the peak 3 in our Fig. 2 belongs to the Xe $4d$ giant resonance; it is not a confinement resonance.

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[1] Zhifan Chen and A. Z. Msezane, Eur. Phys. J. D **66**, 184 (2012).
[2] Zhifan Chen and A. Z. Msezane, Phys. Rev. A **86**, 063405 (2012).
[3] Zhifan Chen and A. Z. Msezane, J. Phys. B **45**, 235205 (2012).
[4] M. J. Puska and R. M. Nieminen, Phys. Rev. A **47**, 1181 (1993).
[5] M. Ya. Amusia, A. S. Baltenkov, L. V. Chernysheva, Z. Felfli, and A. Z. Msezane, J. Phys. B **38**, L169 (2005).
[6] M. E. Madjet *et al.*, Phys. Rev. A **81**, 013202 (2010).
[7] Zhifan Chen and A. Z. Msezane, Eur. Phys. J. D **65**, 353 (2011).
[8] T. W. Gorczyca, M. F. Hasoglu, and S. T. Manson, Phys. Rev. A **86**, 033204 (2012).
[9] A. L. D. Kilcoyne *et al.*, Phys. Rev. Lett. **105**, 213001 (2010).
[10] A. V. Korol and A. V. Solov'yov, J. Phys. B **43**, 201004 (2010).
[11] A. V. Korol and A. V. Solov'yov, J. Phys. B **44**, 085001 (2011).
[12] S. Lo, A. V. Korol, and A. V. Solov'yov, Phys. Rev. A **79**, 063201 (2009).
[13] A. V. Baltenkov, U. Becker, S. T. Manson, and A. Z. Msezane, J. Phys. B **43**, 115102 (2010).
[14] DMol$_3$, Accelrys Software, Inc., 2010.
[15] J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. **78**, 1396 (1997).
[16] P. Giannozzi *et al.*, J. Phys.: Condens. Matter **21**, 395502 (2009).
[17] B. Walker, A. M. Saitta, R. Gebauer, and S. Baroni, Phys. Rev. Lett. **96**, 113001 (2006).
[18] D. Rocca, R. Gebauer, Y. Saad, and S. Baroni, J. Chem. Phys. **128**, 154105 (2008).
[19] B. Walker and R. Gebauer, J. Chem. Phys. **127**, 164106 (2007).
[20] W. F. Chan, G. Cooper, X. Guo, G. R. Burton, and C. E. Brion, Phys. Rev. A **46**, 149 (1992).
[21] D. Čubrić *et al.*, J. Phys. B **26**, 4425 (1993).