Effect of C$_{60}$ giant resonance on the photoabsorption of encaged atoms

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(Dated: May 2, 2014)

The absolute differential oscillator strengths (DOS’s) for the photoabsorption of the Ne, Ar, and Xe atoms encapsulated in the C$_{60}$ have been evaluated using the time-dependent-density-functional-theory, which solves the quantum Liouvillian equation with the Lanczos chain method. The calculations are performed in the energy regions both inside and outside the C$_{60}$ giant resonance. The photoabsorption spectra of the atoms encaged in the C$_{60}$ demonstrate strong oscillations inside the energy range of the C$_{60}$ giant resonance. This type of oscillation cannot be explained by the confinement resonance, but is due to the energy transfer from the C$_{60}$ valence electrons to the photoelectron through the intershell coupling.

PACS numbers: 33.80.-b, 33.80.Eh

I. INTRODUCTION

Recently a method to evaluate the absolute differential oscillator strengths (DOS’s) for the photoabsorption of atoms encapsulated inside a fullerene has been developed [1, 2]. This method takes three steps to calculate the photoabsorption spectra of the fullerene and the endohedral fullerene separately. Firstly, the structures of the fullerene and endohedral fullerene are optimized [3]. Secondly, the ground state eigenvalues and eigenvectors are created by solving the Kohn-Sham equation self-consistently using superscell [1] and a plane wave approach [4]. Thirdly, the linear response of the system to the perturbation by an external electric field is described by the quantum Liouvillian equation [5]. The photoabsorption spectra are evaluated using the time-dependent-density-functional-theory (TDDFT) with the Liouville-Lanczos approach [6, 8]. Finally, the absolute DOS’s for the photoabsorption of an atom encapsulated inside a fullerene can be calculated by subtracting the DOS’s of the fullerene from the correspondent DOS’s of the endohedral fullerene at the same photon energy.

This method has been successfully used to study the photoabsorption spectra of the Xe@C$_{60}$ [1] and Sc$_3$N@C$_{60}$ [2] molecules. These examples demonstrate the great advantage of the method. The method can be used to study the atoms located at the center of the fullerene [1] and the off-center positions as well [2]. It also allows us to evaluate the spectrum in a broad energy region.

In the photoionization studies of endohedral fullerenes the most interesting problem is probably the Xe 4d giant resonance of the Xe@C$_{60}$ molecule [9–14]. The theoretical calculations that used model potentials [10, 12] and the TDDFT with jellium approximation [12] ignored the effect of the C$_{60}$ giant resonance because, fortunately the Xe 4d giant resonance is found at the energy region far from the C$_{60}$ resonance. Amusia and Balenkov [15] and Madjet et al [16] have studied the C$_{60}$ resonance effects on the photoionization cross sections of the Xe 5s and Ar 3p electrons encaged in the C$_{60}$. However, the photoabsorption spectra of the Ar and Xe atoms encapsulated in the C$_{60}$ is still unknown. In this paper we have evaluated the absolute DOS’s for the photoabsorption of the Ne, Ar, and Xe atoms encapsulated in the C$_{60}$ in the regions both inside and outside the C$_{60}$ giant resonance. The results demonstrate a strong oscillation and a significant increase of the DOS’s in the C$_{60}$ resonance region for all these atoms.

II. METHOD

As stated in the Introduction the method of calculation used here takes three steps to evaluate the photoabsorption spectra of the fullerene and endohedral fullerene. In the first step we utilize the DMol$_3$ software package [3] to determine the optimized structure of the fullerene. Geometry optimization of the C$_{60}$ was performed using the generalized gradient approximation (GGA) to the density-functional-theory (DFT) [4], with Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional [17] along with all electrons double numerical plus polarization (DNP) basis sets and dispersion correction as implemented in the DMol$_3$ package [3]. The optimization of atomic positions proceeded until the change in energy was less than $5 \times 10^{-4}$ eV and the forces were less than 0.01 eV/Å. The optimized structure was then introduced into a supercell of 18Å. The Kohn-Sham equation was solved self-consistently to create the ground state eigenstates and eigenvalues for the total of 240 electrons and 120 states using the plane wave approach [3].

An ultrasoft pseudopotential using Rappe-Rabe-Kaxiras-Joannopoulos (RRKJ) pseudization algorithms [18], which replace atomic orbitals in the core region with smooth nodeless pseudo-orbitals, has been employed in the calculation. The kinetic energy cutoff of 408 eV for the wave function and 2448 eV for the densities and potentials were employed in a standard ground state DFT calculation [3]. The linear response of the ground state to an external perturbation by an electric field was described by the quantum Liouvillian equation [6, 7] (atomic units are used throughout, unless stated otherwise):
\[ \frac{d\rho}{dt} = [H_{KS}(t), \rho(t)], \]

where \( H_{KS}(t) \) is time dependent Kohn-Sham (KS) Hamiltonian and \( \rho(t) \) is one-electron KS density matrix. The KS Hamiltonian can be written as

\[ H_{KS}(t) = -\frac{1}{2} \nabla^2 + v_{ext}(r, t) + v_{Hxc}(r, t) \]

where \( v_{ext}(r, t) \) is the external potential and \( v_{Hxc}(r, t) \) is the time dependent Hartree potential plus exchange-correlation potential.

Linearization of Eq. (1) with respect to the external perturbation leads to:

\[ i \frac{d\rho'(t)}{dt} = [H_{KS}^{GS}, \rho'(t)] + [v'_{Hxc}(t), \rho_0] + [v'_{ext}(t), \rho_0] \]

where \( H_{KS}^{GS} \) is time independent ground-state Hamiltonian, \( v'_{ext}(t) \) is the perturbing external potential, \( v'_{Hxc}(t) \) is a linear variation of the Hartree plus exchange-correlation potential induced by \( \rho'(t) \). \( \rho'(t) = \rho(t) - \rho_0 \).

The linearized Liouvillian equation is given by

\[ i \frac{d\rho'(t)}{dt} = L \cdot \rho' + [v'_{ext}(t), \rho_0], \]

The action of the Liouvillian super-operator \( L \) on \( \rho' \) is given by

\[ L \cdot \rho' = [H_{KS}^{GS}, \rho'] + [v'_{Hxc}, \rho'](t), \rho_0 \]

Fourier analyzing Eq. (5) we have:

\[ (w - L) \cdot \rho'(w) = [v'_{ext}(w), \rho_0] \]

if \( v'_{ext}(w) = -E(w) \cdot r \), the response of the dipole to an external electric field \( E(w) \) is given by

\[ d_i(w) = \sum \alpha_{ij}E_j(w) \]

The dynamical polarizability, \( \alpha_{ij}(\omega) \) is defined by

\[ \alpha_{ij}(\omega) = -< r_i | \frac{[r_j, \rho_0]}{(w - L)} > \]

Eq. (9) indicates that the dynamical polarizability can be expressed as an appropriate off-diagonal matrix element of the resolvent of the non-Hermitian Liouvillian superoperator between two orthogonal vectors [6]. These matrix elements are calculated using the Lanczos algorithm [7,8]. Finally the absolute DOS’s of the C\(_{60}\) are obtained from

\[ S(\omega) = \frac{4\omega}{3\pi} \sum I_m \alpha_{jj} \]

After the C\(_{60}\) calculation a Xe atom was introduced into the center of the C\(_{60}\). The DOS’s of the Xe@C\(_{60}\) was evaluated using the same procedure as described above. Finally the DOS’s of Xe atom encapsulated in the C\(_{60}\) were obtained by subtracting the DOS’s of the C\(_{60}\) from the corresponding DOS’s of the Xe@C\(_{60}\) molecule.

III. RESULTS

Fig. 1 presents the spectra of a Xe atom encapsulated inside the C\(_{60}\) in the energy range of Xe 4d giant resonance. Solid curve and dashed curve represent respectively the results of the TDDFT [1] and using our C\(_{60}\) model potential [13]. Both the TDDFT and model potential results confirm the three main peaks observed in the experiment [14] if the spectra are reduced by a factor of 8 or 10 as discussed in Refs. [1,13].

The photoabsorption spectrum of the Xe atom encapsulated in the C\(_{60}\) in the energy region of C\(_{60}\) giant resonance can be evaluated using the same method as mentioned above. It is well known that there are two giant resonances in the C\(_{60}\) photoionization spectrum [19,21], which correspond to a collective oscillation of the 240 delocalized valence electrons relative to the ionic cage of the C\(_{60}\) fullerene. These delocalized electrons are distributed over the surface but confined in a thickness of a single carbon atom in the radial direction. The valence electrons may move coherently in photoexcitation. The strong peak around 6.3 eV [19] is interpreted as collective excitations of the \( \pi \) electrons, the giant resonance between 15 – 25 eV, peaked at 22 eV belongs to the \( \sigma \) electrons [20,21]. In addition to these there are two broad structures around respectively 29 eV and 32 eV which are caused by shape resonance [21]. The whole C\(_{60}\) spectrum can be found in Ref. [1].

Solid and dashed curves in Fig. 2 are, respectively the absolute DOS’s for the photoabsorption of the encapsulated and free Xe atom calculated by TDDFT method. In the energy range of 65 - 140 eV, the solid curve is same as that in Fig. 1. Within the C\(_{60}\) giant resonance region the spectrum of the Xe atom encapsulated in the C\(_{60}\) shows strong oscillation. It is noted that the ab-
FIG. 2. Absolute DOS’s for the photoabsorption of the Xe atom. Solid and dashed curves represent, respectively the TDDFT results of the encapsulated and free Xe atoms.

absolute DOS’s for the atom encapsulated in the C$_{60}$ was obtained by subtracting the DOS’s of the C$_{60}$ from the corresponding results of the Xe@C$_{60}$ molecule. Therefore if the DOS’s of the C$_{60}$ fullerene is larger than the DOS’s of the Xe@C$_{60}$ molecule the curve has negative values. This means that the Xe atom disturbed the C$_{60}$ resonance and reduced the DOS’s of the C$_{60}$. Fig. 2 indicates that the negative value usually happens in the low energy range. If the photon energy cannot ionize the Xe 5p electron the C$_{60}$ valence electrons hardly transfer their resonance energy to the Xe electrons through inter-shell coupling. Otherwise the energy transfer from C$_{60}$ valence electrons to the photoelectron is strong. Because of this, the peak at 25 eV may be related to the Xe 5s ionization (see Fig. 2). The ionization threshold for the 5s of a free Xe is 25.4 eV.

Strong oscillations as in Fig. 2 can also be found in the spectra of the Ne and Ar atoms encapsulated in the C$_{60}$. In the following, we first evaluate the DOS’s for the photoabsorption of the free Ne and Ar atoms. The ultrasoft pseudopotentials for these atoms have been created using the PBE exchange-correlation functional and including the relativistic effect and nonlinear core corrections. The valence electrons for Ne and Ar are respectively, 2s, 2p and 3s, 3p. Solid curves in Figs. 3 and 4 are, respectively the calculated absolute DOS’s for the free Ne and Ar atoms. The open circles in Figs. 3 and 4 represent the correspondent experimental data. The measurements used the low-resolution dipole spectrometer. The data started from the first ionization potentials, 21.6 eV of the Ne 2p state and 16.0 eV of the Ar 3p state. The present TDDFT calculations are in good agreement with the experimental results reported by Ref. 22.

The solid curves in both Figs. 3 and 4 rise rapidly initially. The experimental spectra of Ne and Ar, reach their maxima, respectively at the 31.5 and 21.6 eV. After reaching its maximum the Ar curve drops quickly to approach the Cooper minimum around 47 eV. The 3s ionization threshold of a free Ar atom is about 34.7 eV. At this energy a small peak is found in the theoretical curve.

The curves in Figs. 3 and 4 demonstrate that our ultrasoft pseudopotentials describe the photoabsorption processes of the Ne and Ar atoms very well. The photoabsorption spectra of the endohedral fullerenes, Ne@C$_{60}$ and Ar@C$_{60}$ have also been calculated using the same TDDFT method. The DOS’s of the Ne and Ar atoms encapsulated in the C$_{60}$ are obtained by subtracting the DOS’s of the C$_{60}$ from the correspondent DOS’s of the endohedral fullerenes.

Dashed and solid curves in Figs. 5 and 6 represent, respectively the DOS’s for the photoabsorption of the free and encaged Ne and Ar atoms. The solid curves in Figs. 5 and 6 demonstrate the strong oscillations in the region
FIG. 5. (Color online) Solid and dashed curves are respectively, the calculated absolute DOS's for the photoabsorption of the encapsulated and free Ne atoms.

FIG. 6. (Color online) The symbols have the same meaning as in figure 5, except that the curves represent the data for the Ar atom.

of the C$_{60}$ giant resonance. The solid curve in Fig. 5 can be divided roughly into two parts, a positive part and a negative part. When the photon energy is larger than the first ionization potential of the Ne atom the DOS’s show positive values. This implies that the C$_{60}$ valence electrons transfer resonance energy to the photoelectron through intershell coupling. Otherwise the resonance of the C$_{60}$ is perturbed and the DOS’s are reduced by the Ne atom.

Figure 6 shows that when the photon energy is large the DOS’s are positive; otherwise the DOS’s of the C$_{60}$ are reduced by the Ar atom. This causes negative DOS’s of the Ar atom encaged in the C$_{60}$.

The solid curves in figures 2, 5 and 6 demonstrate that the DOS’s of the atoms encaged in the C$_{60}$ are positive only when the photon energies are large. This indicates that strong energy transfer can occur only between the C$_{60}$ valence electrons and the photoelectron.

IV. CONCLUSION

In conclusion, the absolute DOS’s for the photoabsorption of the Ne, Ar, and Xe atoms encapsulated in the C$_{60}$ have been calculated in the energy regions both inside and outside the C$_{60}$ giant resonance. Within the C$_{60}$ giant resonance the spectra of the Ne, Ar, and Xe atoms engaged in the C$_{60}$ demonstrate strong oscillation with significant increase of the DOS’s. This large enhancement of the DOS’s cannot be explained by confinement resonance but is due to the energy transfer from the C$_{60}$ valence electrons to the photoelectron through the intershell coupling. The energy transfer occurs only when the photon energy is large enough to ionize the atom encapsulated in the C$_{60}$. To study the confinement resonance it is recommended to avoid the C$_{60}$ resonance region by selecting the photon energy larger than 40 eV.

ACKNOWLEDGMENTS

This work was supported by the U.S. DOE, Division of Chemical Sciences, Geosciences and Biosciences, Office of Basic Energy Sciences, Office of Energy Research, AFOSR and Army Research Office (Grant W911NF-11-1-0194). Calculations used Kraken System (account number TG-DMR110034) of the National Institute for Computational Science, The University of Tennessee.

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