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Strong oscillations in the photoionization of 5*s* electrons in Xe@C_{60} endohedral atoms

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The photoionization cross sections of $5s$ electrons in Xe atom in the Xe@C_{60} endohedral complex have been calculated. It is shown that within the wide frequency region, from the threshold to the giant resonance, the cross section is qualitatively modified, acquiring additional resonances due to inner reflection of the photoelectron from the surrounding carbon atoms. The strong dependence of this effect upon the radius of the fullerene shell has been predicted.

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At present there are many papers devoted to the study of the properties of endohedral atoms [1], i.e., atoms located inside the C_{60} fullerene cage. The number of different atoms which may be introduced into C_{60} continuously increases and has already reached about one-third of the Periodic Table including the rare gases [2,3]. The unusual geometrical structure of endohedrals makes them extremely attractive objects to study. The analysis of elementary processes of these particles will provide information on their very specific structure, which is affected to a large extent by the mutual influence of the C_{60} cage and the inner atom. To understand this influence, and for the development of experimental photoelectron spectroscopy of these giant molecules, the comparison between photoionization spectra of an isolated M atom and the same atom, but inside the endohedral M@C_{60}, is of great interest. Such studies would make it possible to analyze the influence of a fullerene shell on optical characteristics of an atom located inside the endohedral. From the other side, the analysis of the carbon electron spectra from M@C_{60} would permit us to investigate the opposite action—that from the atom M upon C_{60}. This is a very complicated theoretical problem, more complex by orders of magnitude than that of an isolated atom. Therefore, considerable simplifications are inevitable. They are suggested, for example, in papers [4–6], where the photoabsorption spectrum of atoms inside the C_{60} molecule was calculated using a jelliumlike model for the fullerene shell.

The aim of the present paper is to study of the photoionization of the Xe $5s^2$ electrons when the Xe atom is located inside the C_{60} fullerene. Recently we have suggested a simple model [7], which in spite of its simplicity predicted an important qualitative feature of the electron scattering in the field of the C_{60} shell—the cross-section oscillation due to electron wave reflection from the fullerene carbon atoms. This model was applied in [8,9] to consider the photoionization of M atoms inside the M@C_{60} endohedral complexes. It was demonstrated that the reflection of an electron from a fullerene shell leads to resonances in the M-atom photoionization cross sections, which without the C_{60} shell would be more or less structureless and smooth. Therefore, it is particularly interesting to see how the frequency dependence of the $5s^2$-subshell photoionization cross section of the Xe atom is modified in the Xe@C_{60} endohedral. For an isolated Xe atom it is strongly affected by the outer $5p^6$ electrons and particularly by the giant resonance in the $4d^{10}$ subshell [10,11]. In this paper we want to demonstrate a prominent effect which comes from the C_{60} action—a kind of a resonator which surrounds Xe in Xe@C_{60}.

The analysis of the influence of the surrounding atoms on the endohedral photoionization may be simplified considerably by replacing the real potential of C_{60}, formed as a superposition of the constituent atomic fields, by a model potential $V(r)$ of the fullerene shell. It is quite natural to assume, as it is usually done, that this potential is equal to zero in all space except for the spherical shell formed by the partially delocalized valence electron of the carbon atoms. Inside this shell the function $V(r)$ is nonzero and can be approximated by different functions [12–14]. The parameters of this potential can be found, for example, using the experimental data for the negative $C_{60}{}^{-}$ ion [7]. It is known that the electron affinity in this ion is $I \approx 2.65\,\mathrm{eV}$, while the radius of the fullerene shell is $R \approx 6.64a_0$ [15], a_0 being the Bohr radius. The thickness of the carbon atom shell is approximately $2a_0$. Using these data, we may estimate the depth of the fullerene shell potential well using the following simple model [12,13]:

$$V(r)=\begin{cases} -V_0 & \text{for} \quad r_i \leqslant r \leqslant r_o \\ 0 & \text{elswhere} \end{cases} \tag{1}$$

where r_i and r_o are the inner and outer radii of the shell, and $\Delta r = r_o - r_i$ is its thickness. The wave function of the additional electron of a negative ion in this spherically symmetric well has the form $\psi(\vec{r}) = [\chi_l(r)/r] Y_{lm}(\vartheta,\varphi)$. Its radial part in the case of the s ground state is given by the expression [5]

$$\chi_0(r) \propto \begin{cases} \exp(\kappa r) - \exp(-\kappa r), & r \leqslant r_i \\ \exp(-\kappa r), & r \geqslant r_o, \end{cases} \tag{2}$$

where κ is the wave vector $\kappa = \sqrt{2I}$. Note that throughout this paper we use atomic units: $\hbar = m = e = 1$.

Inside the fullerene shell the wave function $\chi_0(r)$ has the form

$$\chi_0(r) \propto \sin qr + C\cos qr. \tag{3}$$

The constant C and the wave vector $q=\sqrt{2(V_0-I)}$ are determined by the equality of the logarithmic derivatives of the wave functions on the inner $L_i=\kappa\coth\kappa r_i$ and outer $L_o=-\kappa$ surfaces of the fullerene shell:

$$\kappa\coth\kappa r_i = q\,\frac{1-C\tan qr_i}{C+\tan qr_i}, \quad -\kappa = q\,\frac{1-C\tan qr_o}{C+\tan qr_o}. \tag{4}$$

The system of equations (4) is transformed into the following transcendental equation:

$$q(L_o-L_i)+(q^2+L_oL_i)\tan q\Delta r=0, \tag{5}$$

with a constraint: $\tan qr_i \tan qr_o + 1 \neq 0$. The solution of Eq. (5) for $r_i \approx 5.75$ and $r_o \approx 7.64$ [12,13] and $\kappa \approx 0.441$ [7] leads to the following results: $q \approx 0.641$ and $C \approx 0.443$. This gives for the depth of the potential well V_0 the following value: $V_0 \approx 8.24\,\text{eV}$. This is small compared to the ionization potential of the inner subshells of the M atom, and the potential $V(r)$ is located well outside the localized inner shells. Hence, we can neglect the influence of the fullerene shell on the wave function of the ground state, and should only take into account the action of the potential $V(r)$ upon the electron continuum states.

For the considered parameters of the potential $V(r)$, the logarithmic derivatives are almost independent of the particular choice of r_i and r_o: $L_i \approx \kappa$ and $L_o=-\kappa$. Therefore, they can be considered as localized at the point R and the potential well, which in fact has the nonzero thickness Δr, and can be replaced by a δ potential: $V(\vec{r})=-A\delta(r-R)$, as it was suggested earlier [7,16]. The strength of the δ potential A is connected to the jump of the logarithmic derivative $\Delta L = L_o - L_i$ by the relation $A=-\Delta L$ [7,8]. In this paper we will use the model potential $V(\vec{r})=-A\delta(r-R)$ to describe the photoionization of the atoms located inside the fullerene shell.

Suppose that we know the regular $u_{kl}(r)$ and irregular $v_{kl}(r)$ solutions of the radial Schrödinger equation for the optical electron of the free M atom

$$\frac{1}{2}\left(u''_{kl}-\frac{l(l+1)}{r^2}u_{kl}\right)+[E-U(r)]u_{kl}=0. \tag{6}$$

The functions $v_{kl}(r)$ obey the same equation in all space except for $r=0$. Here $U(r)$ is the self-consistent field created by the atomic nucleus together with all atomic electrons, acting upon the optical electron. The functions $u_{kl}(r)$ and $v_{kl}(r)$ at $kr \gg 1$ are of the following form:

$$\begin{aligned} u_{kl}(r) &\propto \sin\left(kr+\frac{1}{k}\ln 2kr-\frac{\pi l}{2}+\Delta_l(k)\right), \\ v_{kl}(r) &\propto -\cos\left(kr+\frac{1}{k}\ln 2kr-\frac{\pi l}{2}+\Delta_l(k)\right), \end{aligned} \tag{7}$$

where $\Delta_l(k)$ are the phase shifts of the wave functions in the potential field of the M^+ ion.

Let us represent the Xe@C$_{60}$ endohedral as a Xe atom located in the center of the fullerene shell. The radial parts of the electron wave functions of the endohedral atom are determined by the equation

$$\frac{1}{2}\left(\chi''_{kl}-\frac{l(l+1)}{r^2}\chi_{kl}\right)+[A\delta(r-R)-U(r)+E]\chi_{kl}=0. \tag{8}$$

The wave function of the Xe $5s^2$ electrons is located relatively close to the coordinates origin, within a region of approximate size which can be estimated as $\sim(I_{5s}/\text{Ry})^{-1/2} < R$, where $I_{5s} \approx 1.712$ Ry is the ionization potential of the Xe $5s^2$ subshell. The binding energy of the $5s$ level is nearly three times greater than the depth of the potential well V_0. Therefore, we will consider the wave function of the $5s$ electron of the endohedral Xe atom as coinciding with that of the isolated Xe atom $\chi_{5s}(r) \approx u_{5s}(r)$.

The situation is quite different for the wave functions of the continuous spectrum. For $r<R$ they are proportional to the atomic wave functions, with the proportionality coefficient $D_l(k)$ being only k-dependent: $\chi_{kl}(r)=D_l(k)u_{kl}(r)$. Outside the shell, i.e., for $r \geqslant R$, they become linear combinations of the regular and irregular solutions of the Schrödinger equation (6). By matching the logarithmic derivatives of the function $\chi_{kl}(r)$ at $r=R$, we obtain, for the wave-function amplitudes $D_l(k)$ inside the fullerene shell and the photoelectron phase shifts $\delta_l(k)$ on the $V(r)$ potential, the following formulas:

$$D_l(k)=\cos\delta_l(k)\left(1-\tan\delta_l(k)\frac{v_{kl}(R)}{u_{kl}(R)}\right), \tag{9}$$

$$\tan\delta_l(k)=\frac{u_{kl}^2(R)}{u_{kl}(R)v_{kl}(R)+k/2A}. \tag{10}$$

The photoionization amplitude of the Xe atom $5s^2$ subshell is defined by the matrix element $\langle kp|r|5s\rangle$, calculated using the wave function $\chi_{5s}(r)$ of the ground state of the Xe atom and the continuum wave function $\chi_{kl}(r)$ of the electron with momentum k. The main contribution to this matrix comes from the inner region of the fullerene sphere. Therefore, we represent it as

$$\langle kp|r|5s\rangle \approx D_1(k)\int_0^R u_{kp}(r)\,r\,u_{5s}(r)\,dr = D_1(k)R_1. \tag{11}$$

The integral in Eq. (11), R_1, is the photoionization amplitude of the $5s^2$ subshell of the isolated Xe atom. Hence, the partial cross sections $\sigma_{l\pm1}(\omega)$ of the endohedral atom photoionization, up to a k-dependent factor $D_1^2(k)$, coincide with the partial cross sections $\sigma_{l\pm1}^a(\omega)$ of the isolated Xe atom

$$\sigma_{5s}(\omega)=D_1^2(k)\sigma_{5s}^a(\omega), \tag{12}$$

where $\omega=I_{5s}+k^2/2$ is the photon energy.

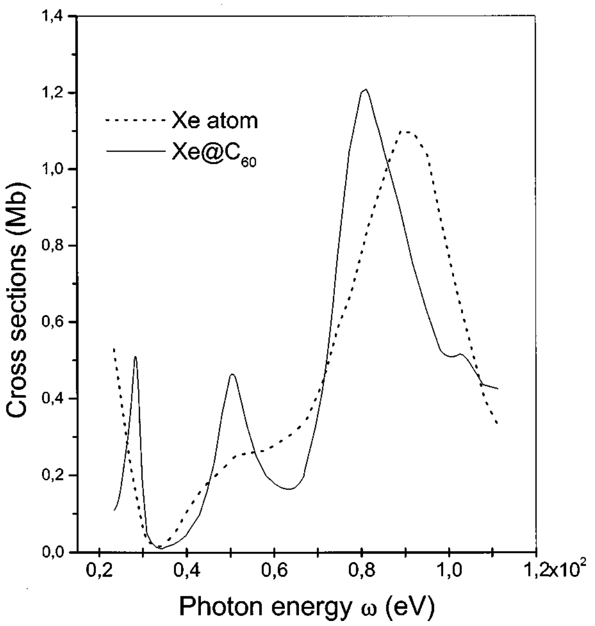

FIG. 1. Photoionization cross section of Xe $5s^2$ electrons. Solid line, endohedral Xe@C$_{60}$ complex; dashed line, free Xe atom.

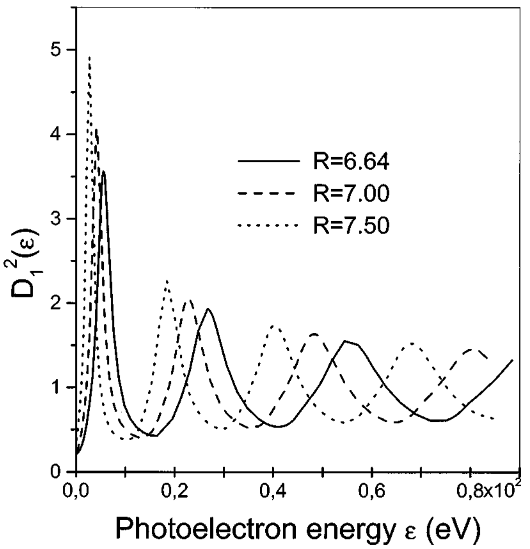

FIG. 2. The dependencies of $D_1^2(\epsilon)$ upon fullerenes radius R.

Equation (12) connects the partial photoionization cross section of the Xe@C$_{60}$ endohedral and the free Xe atom with the parameters of the fullerene shell, namely the radius R and the electron affinity I, of the $C_{60}{}^{-}$. Due to the connection between oscillations of the wave functions inside and outside the fullerene shell, the amplitudes $D_l(k)$ have a resonance character. This is why in the photoionization cross sections of endohedrals the resonance behavior appears, resulting from the inner reflections of photoelectrons from the fullerene shell [4,5,8,13].

Taking into account Eqs. (9) and (10), the squares of the amplitudes $D_l(k)$ can be written in the form

$$D_l^2(k)=\frac{(k/2A)^2}{[u_{kl}(R)v_{kl}(R)+k/2A]^2+u_{kl}^4(R)}. \tag{13}$$

According to Eq. (13), for low strength of the δ potential $(A\rightarrow 0)$, the amplitude $D_l(k)$ behaves as $D_l^2(k)\rightarrow 1$. For high strength $(A\rightarrow\infty)$ the amplitudes $D_l^2(k)$ are different from zero only for k, which obeys the condition $u_{kl}(R)=0$. Thus, the stronger the δ-sphere potential is, the more pronounced the resonance effects are.

The calculation results for the $5s^2$ subshell of the free Xe atom and endohedral atom in the Xe@C$_{60}$ complex are presented in Fig. 1. The wave functions of the isolated atoms in the ground state $u_{nl}(r)$ and in the continuum $u_{kl}(r)$ were calculated in the one-electron Hartree-Fock approximation using the package of computing codes [17]. The irregular solutions $v_{kl}(r)$ were determined by a known formula

$$v_{kl}(r)=u_{kl}(r)k\int\frac{dr}{u_{kl}^2(r)}. \tag{14}$$

Using these functions, the coefficients $D_1^2(k)$ determined by Eq. (13) were calculated. The following parameters of the fullerene shell corresponding to the empty C$_{60}$ were used: $R=6.64a_0$ and $\kappa=\sqrt{2.65/13.6}\approx 0.441$.

As it is well known, the subvalent $5s^2$ subshell of the Xe atom is under extremely strong influence from the neighboring $5p^6$ and $4d^{10}$ electrons (see [10] and references therein). Indeed, it has been known since long ago that the calculation of $\sigma_{5s}^a(\omega)$ in the one-electron approximation leads to incorrect results. To determine the cross section precisely enough, one must take into account the intershell correlations in the framework of random-phase approximation with exchange (RPAE); it is the virtual excitations of $5p^6$ and $4d^{10}$ electrons as it was described in [10]. The multielectron correlations qualitatively alter the frequency dependence of the photoionization cross section of the $5s^2$ subshell, thus leading to the appearance of a new minimum at about $\omega\approx 2.5$ Ry and a maximum at $\omega\approx 6.5$ Ry, the latter being tightly bound to the giant resonance in photoabsorption by $4d^{10}$ electrons. The photoionization cross section $\sigma_{5s}^a(\omega)$ of a free Xe atom [10] is presented in Fig. 1 by a dashed line. The solid line is the photoionization cross section $\sigma_{5s}(\omega)$ of the endohedral Xe atom calculated with Eq. (12). As seen from this figure, the photoelectron reflection from the fullerene shell drastically modifies the frequency dependence of the $5s^2$-photoabsorption cross section in a very broad frequency region, up to the giant resonance domain. Additional resonances in the cross section appear, namely at least one new minimum and maximum. At the resonance energies, the cross section of the endohedral atom is up to two to three times greater than that of the free Xe atom.

The calculations of the coefficients $D_1^2(\epsilon)$ show that the locations of resonance peaks on the photoelectron energy ϵ scale are very sensitive to the magnitude of the fullerene shell radius R. The results of $D_1^2(\epsilon)$ calculations for three values of R, which are different from the radius of the empty C$_{60}$ by less than one Bohr radius, are presented in Fig. 2. The differences between these curves in the amplitude values and in the peak locations become more pronounced with increasing photon energy. This result is very important and interesting for the photoelectron spectroscopy of the fullerenes with heavy atoms inside the carbon cage. It can be expected that the insertion of these atoms into C_{60} results in an increase of the geometrical size of the fullerene shell. Experimental studies investigating the location of the resonance peak can indicate that the fullerene shell radius increased after the insertion of an atom inside.

In summary, we have demonstrated that the photoionization cross sections of $5s^2$ electrons of the Xe atom inside C_{60} have prominent resonance structure in a broad frequency region. The experimental study of this structure by photoelectron spectroscopy methods can be currently performed, and very useful valuable information on the endohedral system, in particular on their radii, can be obtained.

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