

Photoionization of Onion-type atoms

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The photoionization of a two-shell (“onion”) endohedral $A@C_{N_1}@C_{N_2}$ is considered. The effect of the fullerenes shells upon photoelectron from atom A is taken into account substituting the action of the fullerene by two zero-thickness “bubble potentials”. The fullerenes shells polarization is included assuming that the radius of the outer shell R_2 is much bigger than the inner R_1 and both much exceed the atomic radius r . The interaction between shells C_{N_1} and C_{N_2} is taken into account in the Random Phase Approximation (RPA). The effect of photoelectron scattering by both “bubble potentials” is included in the RPA frame. As concrete examples, two endohedrals $Ar@C_{60}@C_{240}$ and $Xe@C_{60}@C_{240}$ are considered. We investigate $3p4$ Ar and $5p$ Xe subshells.

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1. In this Letter we present results for photoionization of atoms caged by a two-shell fullerene that is called “onion” endohedral. A lot of attention is given in recent years to photoionization of ordinary endohedrals [1–4]. These are objects consisting of a fullerene C_N and an atom A , caged inside it, $A@C_N$. The attention is concentrated on the modification of these atom photoionization characteristics. Indeed, the difference of them as compared to that of isolated atoms A gives information on the fullerenes structure. In a sense, the inner atom A in $A@C_N$ serves as a “lamp” that shines “light” in the form of photoelectron waves that “illuminates” the fullerene C_N from the inside.

Specific features were predicted in photoionization of $A@C_N$ that makes it different from photoionization of an isolated atom A itself. Most prominent features are the so – called confinement [5] and Giant endohedral [6] resonances that are consequences of two most important effects – the reflection of the photoelectrons by the fullerenes shell and modification of the incoming photon beam due to C_N polarization [7, 8].

It appeared that fullerenes could be not only one-shell but also two-shell structures [9, 10]. It seems, therefore, timely to consider an endohedral of such type that we denote as $A@C_{N_1}@C_{N_2}$. To study the reflection, we apply a rather simple approach that substitutes both shells by infinitely thin potential layers – the two-bubble potential. Since the radius of the outer bubble is considerably bigger than the inner one, they are weakly affecting each other. Therefore for experimentally known radiuses R_1 , R_2 and corresponding number of carbon atoms in it, N_1 , N_2 , we obtain the potential strength of both of them V_1 , V_2 , using experimentally known

electron affinities I_1 , I_2 of fullerenes C_{N_1} and C_{N_2} , respectively just as it was done for an ordinary bubble potential [11]. We will also take into account the polarization effect from both fullerenes shells. As a concrete example, we will consider two fullerenes, with $N_1 = 60$ and $N_2 = 240$.

Assuming that R_1 and R_2 are much bigger than the atomic radius, the effect of fullerenes polarization upon the incoming photon beam can be expressed via fullerenes polarizability [7]. The latter via dispersion relation is connected to the experimentally measurable fullerenes photoionization cross-section [12]. We will assume for simplicity that the outer fullerenes radius is much bigger than the inner one. In this approximation we will take into account not only the fullerenes action upon the atom’s photoionization, but mutual influence of both fullerenes shells as well. Since the photoionization cross-section of C_{240} is unknown, we will use rather approximate scaling to estimate the polarizability of this object.

2. The two-bubble potential is of the form

$$V(r) = -V_1\delta(r - R_1) - V_2\delta(r - R_2). \quad (1)$$

At $r < R_1$ the solution $\chi_{kl}(r)$ of the Schrodinger equation for a photoelectron with linear $k = \sqrt{2E}$ and angular momentum l , moving under the action of atomic potential and $V(r)$ can be presented as¹⁾:

$$\chi_{kl}(r) = F_l(k)u_{kl}(r), \quad (2)$$

¹⁾Atomic system of units is used in this paper, with electron charge e , mass m , and Planck constant \hbar equal to one, $e = m = \hbar = 1$.

where $u_{kl}(r)$ is the regular at $r = 0$ solution of the same equation, but without $V(r)$.

After some algebra we obtain the following expression for the reflection factor $F_l(k)$ and additional photoelectron's phase shift $\Delta\delta_l^R$:

$$\begin{aligned} F_{l'} &\equiv F_{l'}(k) = \\ &= \frac{k \sin \Delta\delta_{l'}^R}{2[V_1 u_1^2 + V_2 u_2^2 - 2V_1 V_2 u_1 u_2 (u_1 v_2 - u_2 v_1)/k]}, \quad (3) \\ \tan \Delta\delta_{l'}^R(k) &= \\ &= \frac{u_1^2 + u_2 V_2 [u_2/V_1 + 2u_1 V_1 (u_2 v_1 - u_1 v_2)/k]}{u_1 v_1 + k/2V_1 + u_2 v_2 V_2/V_1 - 2u_1 v_2 V_2 (u_2 v_1 - u_1 v_2)/k}, \end{aligned}$$

where the following notation are employed

$$\begin{aligned} u_1 &\equiv u_{kl}(R_1), \quad u_2 \equiv u_{kl}(R_2), \\ v_1 &\equiv v_{kl}(R_1), \quad v_2 \equiv v_{kl}(R_2). \end{aligned} \quad (4)$$

It is seen from (3) that $F_l(k)$ and $\Delta\delta_l^R$ acquires terms $\sim 1/k$. As a result at $k \rightarrow 0$ $F_{l'}(k) \rightarrow 0$ and $\Delta\delta_{l'}^R(k) \rightarrow -u_2 V_1/v_2$. The presence of a second fullerene leads in principle to the possibility that two shells with compensate the action of each other thus leading for some k to a "reflection window", where $F_{l'}(k) = 1$.

3. As it was already demonstrated quite a while ago, the following relation can account for the polarization of the fullerene under the action of the incoming photon beam [7]:

$$D_{AC}(\omega) \cong D_A(\omega) \left[1 - \frac{\alpha(\omega)}{R^3} \right], \quad (5)$$

where $D_{AC}(\omega)$ is the endohedral atom $A@C_n$ photoionization dipole amplitude, $D_A(\omega)$ is the same for an isolated atom, $\alpha(\omega)$ is the fullerenes dipole polarizability, R is its radius. This relation is derived under valid assumption that $R \gg r_A$.

For two-shell fullerene the corresponding expression is much more complex, since in principal the interaction between two groups of electrons, belonging to fullerenes 1 and 2 must be taken into account. Under a reasonable qualitatively correct assumption, that holds at least for considered in this Letter C_{60} and C_{240} , the following relation is used $r \ll R_1 \ll R_2$. In this case the amplitude $D_{AC}(\omega)$ is presented as

$$\begin{aligned} D_{AC}(\omega) &\cong D_A(\omega) \times \\ &\times \left[1 - \left(\frac{\alpha_1}{R_1^3} + \frac{\alpha_2}{R_2^3} \right) \frac{1 - \frac{\alpha_1 \alpha_2}{\alpha_1 R_2^3 + \alpha_2 R_1^3} \left(+ \frac{R_1^3}{R_2^3} \right)}{1 - \frac{\alpha_1 \alpha_2}{R_2^6}} \right] \equiv \end{aligned}$$

$$\equiv G_{12}(\omega) D_A(\omega), \quad (6)$$

where $G_{12}(\omega)$ is the polarization amplitude factor for two-shell fullerene.

It is seen that the correction due to simultaneous polarization of both fullerenes shells proportional to $\alpha_1 \alpha_2$ considerably modifies a simple formula that would account only for the sum of both shells action.

It is essential to have in mind that (6) can in principle take into account electron correlations beyond the RPAE frame. Namely, each of the polarizabilities, α_1 or α_2 , can include all correlations inside each fullerene, 1 or 2, respectively. It means that as polarizabilities, accurately calculated or experimentally measured values can be used. In principle, depending upon ω the dipole excitation of shells may be "in phase", enhancing induced by photon beam polarization of the fullerenes shell, or in "anti-phase", suppressing the common polarization.

4. Directly determinable in experiment are only static polarizabilities, namely their values at $\omega \approx 0$. To obtain dynamic polarizability, calculations are needed. However, if photoionization cross-section $\sigma_N(\omega)$ of a considered object is measured, the dynamic polarizability can be derived using the following relations:

$$\begin{aligned} \text{Im } \alpha_N(\omega) &= c \frac{\sigma_N(\omega)}{4\pi\omega}, \\ \text{Re } \alpha_N(\omega) &= \frac{c}{2\pi^2} \int_{I_N}^{\infty} \frac{\sigma_N(\omega') d\omega'}{\omega'^2 - \omega^2}, \end{aligned} \quad (7)$$

where c is the speed of light and I_N is the fullerene ionization potential. Note that in the second relation in (7), so-called dispersion relation, it is assumed that the contribution of discrete excitations can be neglected. That is indeed confirmed by existing experimental data on fullerenes photoionization [13].

5. To perform photoionization calculations we need to know the fullerenes potentials V_1 and V_2 . They can be determined using for each of the shells the same formula that is usually employed for a single-shell fullerene [11], so that

$$V_{1,2} = \frac{1}{2} \sqrt{2I_{1,2}} (1 + \coth \sqrt{2I_{1,2}} R_{1,2}), \quad (8)$$

where $I_{1,2}$ are the electron affinities of the fullerenes C_{N_1} and C_{N_2} . By doing this we make a reasonable assumption that well separated shells are inessential affecting each other so that a two-shell "onion" C_{N_1, N_2} really consists of two fullerenes C_{N_1} and C_{N_2} . We will take the electron affinities I_1 and I_2 for C_{60} and C_{240} from [14]. The values are $I_{60} = 0.0974$ and $I_{240} = 0.140$. For completeness let us add the value $I_{540} = 0.386$.

The radiuses of these fullerenes are also known, being equal to $R_{60} \cong 6.75$, $R_{240} \cong 13.5$ and $R_{60} \cong 19.8$. It is remarkable that for at least considered objects the ratio $\eta_N \equiv N_N/R_N^2$ are almost the same $\eta_{60} = 1.317$, $\eta_{240} = 1.317$, $\eta_{540} = 1.38$.

Analysis of the C_{60} polarizability permitted to conclude that at least for static value $\alpha_{C_{60}} \approx 60\alpha_C$. Since the electron density of all big enough fullerenes is the same, it seems natural to assume that $\alpha_{C_N} \approx N\alpha_C$. It is reasonable to suggest that $\sigma_N(\omega)$ of C_{240} is characterized by a Giant resonance with the same frequency as in C_{60} , since the surface electron density $n_N = N/4\pi R_N^2$ determines it. Assuming that $\sigma_N(\omega)$ for all considered fullerenes as functions of ω are similar, it follows from the sum-rule for $\sigma_N(\omega)$ that $\sigma_{N_2}(\omega)/\sigma_{N_1}(\omega) \approx N_2/N_1$. It means that the relation $\alpha_{N_2}(\omega)/\alpha_{N_1}(\omega) \approx N_2/N_1$ is valid.

For our system $A@C_{60}@C_{240}$ one has $N_{240}/N_{60} = 4$, $R_{240}/R_{60} \approx 2$ and $\alpha_{240}(\omega)/\alpha_{60}(\omega) \approx 4$, leading from (9) to the following expression

$$D_{AC}(\omega) \approx D_A(\omega) \times \left[1 - 1.5 \frac{\alpha_{C_{60}}(\omega)}{R_{C_{60}}^3} \frac{1 - 0.375\alpha_{C_{60}}(\omega)/R_{C_{60}}^3}{1 - 0.0625[\alpha_{C_{60}}(\omega)/R_{C_{60}}^3]^2} \right] \equiv \bar{G}_{12}(\omega)D_A(\omega), \quad (9)$$

where $\bar{G}_{12}(\omega)$ is the approximate value of the polarization amplitude factor. The data for $\alpha_1(\omega)$ as well as for $S_1(\omega) = |(1 - \alpha_1(\omega)/R_1^3)|^2$ are taken from [12].

6. In this section we will present the formulas required to calculate the photoionization cross-sections and dipole angular anisotropy parameters for two-shell endohedral atom $A@C_{N_1}@C_{N_2}$.

Usually the action of the fullerene shell is strong enough, so it is not sufficient to take the reflection as a factor to the atomic cross-section only, but is necessary to modify also the intermediate electron states. It is natural to do it within the RPAE frame that proved to be very effective in describing photoionization of multi-electron atomic shells [15]. That is achieved by solving the following equation for the dipole amplitude that generalizes atomic RPAE to include potential (1)

$$\langle v_1 | D(\omega) | v_2 \rangle = \langle v_1 | \hat{d} | v_2 \rangle + \sum_{v_3, v_4} \frac{\langle v_3 | D(\omega) | v_4 \rangle [F_{v_3}^2 n_{v_4} (1 - n_{v_3}) - F_{v_4}^2 n_{v_3} (1 - n_{v_4})]}{\varepsilon_{v_4} - \varepsilon_{v_3} + \omega + i\eta(1 - 2n_{v_3})} \langle v_4 v_1 | U | v_3 v_2 \rangle. \quad (10)$$

The following relation gives the partial endohedral atomic cross-section $\sigma_{nl,kl'}^{AC}(\omega)$ for transition $nl \rightarrow kl', l' = l \pm 1$

$$\sigma_{nl,kl'}^{AC}(\omega) = |F_{l'}(k)|^2 S_{12}(\omega) \bar{\sigma}_{nl,kl'}^A(\omega), \quad (11)$$

where $\bar{\sigma}_{nl,kl'}^A(\omega) = 16\pi^2 \omega l' |D_{l'}^A(\omega)|^2 / 3c$, c is the speed of light and $S_{12}(\omega) = |G_{12}(\omega)|^2$ is the polarization factor. In (11) $\bar{\sigma}_{nl,kl'}^A(\omega)$ is in general different from the corresponding pure atomic value $\sigma_{nl,kl'}^A(\omega)$.

The total photoionization cross-section of nl electrons is obtained from (11) by summing over l' :

$$\sigma_{nl}^{AC_{12}}(\omega) = \sum_{l'=l\pm 1} \sigma_{nl,kl'}^{AC_{12}}(\omega). \quad (12)$$

The differential in angle $d\Omega$ cross-section of the photoelectron's emission under the action of non-polarized light is given for spherically symmetric fullerenes shells, having the same center, by the following expression

$$\frac{d\sigma^{AC_{12}}(\omega)}{d\Omega} = \frac{\sigma_{nl}^{AC_{12}}(\omega)}{4\pi} \left[1 - \frac{1}{2} \beta_{nl}(\omega) P_2(\cos\theta) \right]. \quad (13)$$

Here $P_2(\cos\theta)$ is the Legendre polynomial.

The dipole angular anisotropy parameter $\beta_{nl}(\omega)$ is not affected by the fullerenes shell polarization amplitude and is given by relation similar to presented in [15] for isolated atoms

$$\beta_{nl}(\omega) = \frac{1}{(2l+1)[(l+1)F_{l+1}^2 \bar{D}_{l+1}^2 + lF_{l-1}^2 \bar{D}_{l-1}^2]} \times \times [(l+1)(l+2)F_{l+1}^2 \bar{D}_{l+1}^2 + l(l-1)F_{l-1}^2 \bar{D}_{l-1}^2 - -6l(l+1)F_{l+1}F_{l-1}D_{l+1}D_{l-1} \cos(\bar{\delta}_{l+1} - \bar{\delta}_{l-1})]. \quad (14)$$

Here the dipole photoionization amplitudes $\bar{D}_{l\pm 1}(\omega)$ are complex numbers with module $\bar{D}_{l\pm 1}(\omega)$, with phases $\Delta_{l\pm 1}$ given by relation $D_{l\pm 1}(\omega) \equiv \bar{D}_{l\pm 1}(\omega) \exp[i\Delta_{l\pm 1}(k)]$. The relation $\bar{\delta}_{l'} = \delta_{l'} + \Delta_{l'}^R + \Delta_{l'}$, with $\delta_{l'}$ being the photoelectron's scattering phase in Hartree-Fock approximation for the isolated atom A, determines the phases $\bar{\delta}_{l'}$ in (14).

7. Consider here $3p^6$ Ar@ $C_{60}@C_{240}$ and $5p^6$ Xe@ $C_{60}@C_{240}$ subshells with the fullerenes parameters, presented in Section 5. The data are presented in Fig.1–5. They are obtained with the help of (11), (12) and (14). The results for reflection by a single fullerenes shell we denote on the figures as FRPAE, while that with two shells taken into account are marked as FRPAE2. Specially mentioned is the effect of polarization factor $\bar{C}_{12}(\omega)$.

Since the reflection amplitudes $F_l(k)$ are different for different atoms, we are not presenting their values separately.

Fig.1 depicts polarization factors $S_1(\omega)$ for C_{60} , $S_2(\omega)$ for C_{240} and $S_{12}(\omega)$ for $C_{60}@C_{240}$. The S factor for the big fullerene is small but its combination with the inner shell enhances the common S -factor impressively.

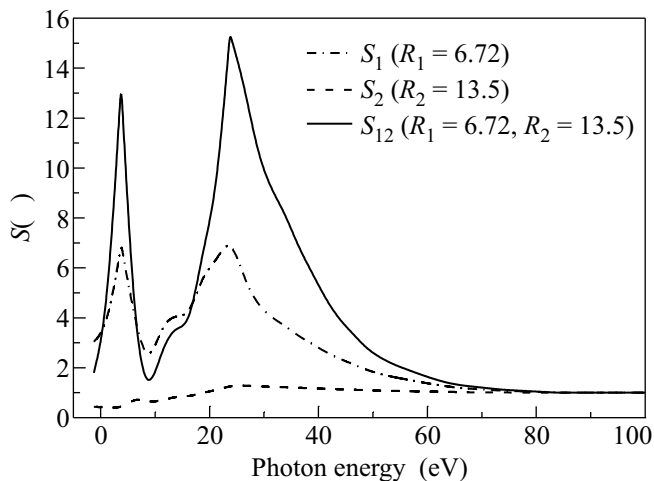


Fig.1. Polarization factors $S_1(\omega)$ for C_{60} , $S_2(\omega)$ for C_{240} and S_{12} for $C_{60}@C_{240}$

As it should be, effects of polarization are rapidly decreasing with ω growth, so that it approaches almost 1 at $\omega > 60$ eV.

Fig.2 presents the photoionization cross-section for $3p$ in Ar, Ar@ C_{60} , Ar@ C_{240} and Ar@ $C_{60}@C_{240}$, demonstrating profound action of the polarization factor

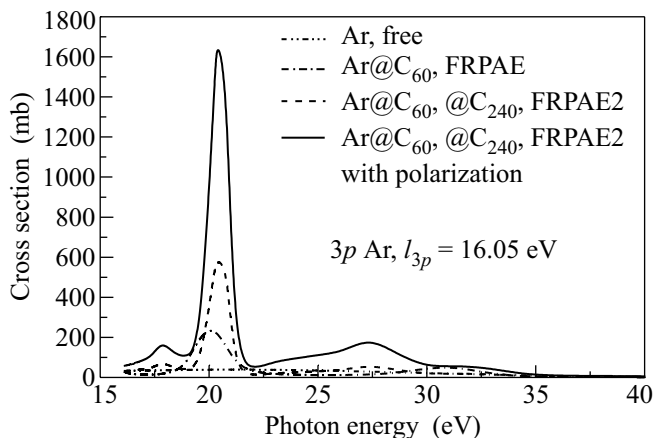


Fig.2. Photoionization cross-section of $3p$ electrons in Ar, Ar@ C_{60} and Ar@ $C_{60}@C_{240}$ with account of reflection factors F and the latter with account of polarization factor $S_{12}(\omega)$

S_{12} upon the Ar photoionization cross-section. Note that two-shell reflection concentrates almost all cross section into a single maximum the two-shell endohedral Giant resonance. The increase of the cross-section is up to 80 times as compared to the atomic case and up to 3 as compared to one-shell endohedral.

Fig.3 demonstrates the angular anisotropy parameter $\beta_{3p}(\omega)$ of $3p$ electrons in Ar, Ar@ C_{60} and Ar@ $C_{60}@C_{240}$ with account of reflection factors F . The effect of re-

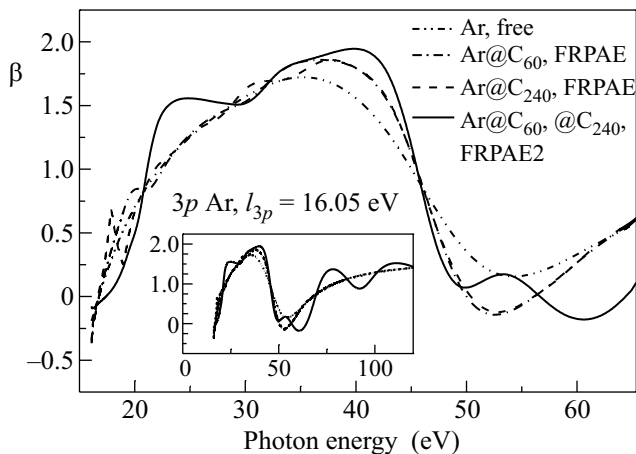


Fig.3. Dipole angular anisotropy parameter $\beta_{3p}(\omega)$ of $3p$ electrons in Ar, Ar@ C_{60} and Ar@ $C_{60}@C_{240}$ with account of reflection factors F

flexion is noticeable, leading to prominent oscillations around the photon energy region $\omega \approx 20$ eV.

Fig.4 depicts photoionization cross-section for $5p$ in Xe, Xe@ C_{60} , Xe@ $C_{60}@C_{240}$ and demonstrates profound

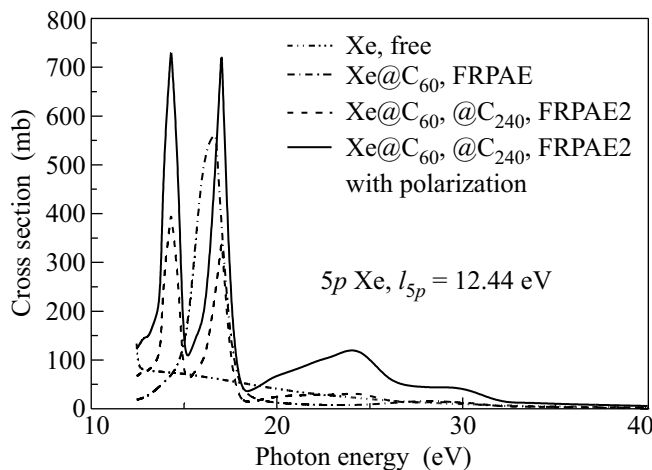


Fig.4. Photoionization cross-section of $5p$ electrons in Xe, Xe@ C_{60} and Xe@ $C_{60}@C_{240}$ with account of reflection factors F and the latter with account of polarization factor $S_{12}(\omega)$

action of the polarization factor S_{12} upon the Xe $5p$ photoionization cross-section. The effect of scattering by the second fullerenes shell is strong enough, presenting a distinctive second maximum and decreasing the maximum that appear due to one-shell scattering. Polarization of fullerenes increases quite noticeable the cross section giving a prominent two-maximum Giant resonance.

Fig.5 demonstrates the dipole angular anisotropy parameter $\beta_{5p}(\omega)$ of $5p$ electrons in Xe, Xe@ C_{60} and

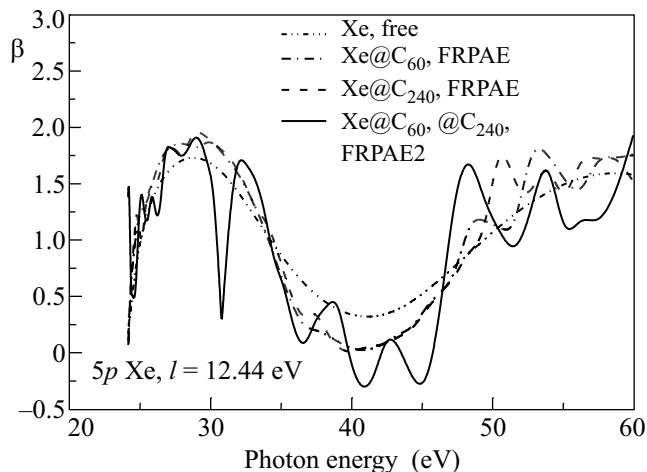


Fig.5. Dipole angular anisotropy parameter $\beta_{5p}(\omega)$ of $5p$ electrons in Xe, Xe@C₆₀ and Xe@C₆₀@C₂₄₀ with account of reflection factors F

Xe@C₆₀@C₂₄₀ with account of reflection factors F . The effect is similar in size to that in Fig.3, but there are two regions of oscillations in $5p$ Xe instead of one in $3p$ Ar.

8. We present results for photoionization of outer Ar and Xe subshells for atoms caged inside “onion” fullerenes Ar@C₆₀@C₂₄₀ and Xe@C₆₀@C₂₄₀. We have investigated effects of photoelectron scattering by two zero-thickness potential wells and modification of the incoming photon beam due to dipole polarization of both fullerenes shell. No doubt that similar profound effects of “onion” fullerene will appear for other caged atoms as well.

Other fullerenes can create “onions” with quite different characteristics from that of C₆₀@C₂₄₀. A whole variety of resonances are found that obviously deviate

far from being a simple sum of effects, given by single fullerenes shell. We admit that the moment when investigation of photoionization of such objects is not literally tomorrow. However, we hope see them being performed in not too distant future, thus believing that possible findings justify the current efforts.

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