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Explanation of the recent results on photoionization of endohedral atoms

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We suggest an explanation of the recently observed discrepancy between the experimental and theoretical results on ionization of atoms, encapsulated into the fullerenes, by photons with the energies of about 80–190 eV. On the ground of previous theoretical considerations we conclude that for endohedrals the photoionization without emission of additional electrons or fullerenes shell atoms has a low probability even at such relatively low photon energies.

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1. In recent publications on ionization of atoms caged inside the fullerene shell by photons with energies $\omega \leq 190$ eV [1–3] the observed cross sections were compared with those, calculated for the isolated atoms. Calculations of photoionization of various atomic endohedrals were presented in a number of works [4–9].

The RPAE calculations for the endohedral atom Xe@C_{60} [4] were succeeded by calculations with more accurate treatment of the fullerene shell (FS) [6–8] and those with inclusion of the hybridization effects [9]. This improved the understanding of the processes in FS at small values of the photoelectron energies. In this paper we focus on the region of the photoelectron energies exceeding 40 eV, where the difference between the results of [4] and [6–9] is small, and demonstrate that here to calculate the photoionization cross-section we need very little information on the structure of the FS.

The results of calculations strongly exceed all the experimental data. We show that this is a direct manifestation of a very low probability of photoionization without an accompanying inelastic process in the FS. This was predicted recently for relatively high photon energies [10, 11]. In the present paper we compare the data obtained in [1–3] with our calculations. We demonstrate that in fact the inelastic processes become decisively important starting already from comparatively low energies, less than 100 eV.

2. The results on photoionization of the $4d$ subshell of xenon placed inside the fullerenes Xe@C_{60}^+ were reported initially in [1]. Much more detailed and accurate data on the same subject are presented in [2]. The paper [3] reports similar results for Ce@C_{82}^+. The experimental total photoionization cross-sections from [2] are presented in Fig. 1 along with the results of the RPAE calculations [4] multiplied by reduction factor ρ, chosen to fit the sum rule (atomic system of units with $e = m = \hbar = 1$ is used in this Letter):

$$\frac{c}{2\pi^2}\int_I^\infty \sigma(\omega)d\omega = N. \tag{1}$$

Here $\sigma(\omega)$ is the total photoionization cross section, I is the ionization potential, N is the number of electrons in the ionized object.

Expression (1) can be applied also to ionization of a single subshell. Using the experimental data on the total photoionization cross-section the authors of [1] found the value $N_{4d@C_{60}} = 6.2 \pm 1.4$ for the $4d$ state of Xe@C_{60}^+. Note that for isolated Xe atom $N_{4d} = 10$. So, the corresponding reduction factor is given by the relation $\rho = N_{4d@C_{60}}/N_{4d} = 0.62$.

Multiplying the calculated results by this factor we find the experimental results for Xe@C_{60}^+ to become quite close to that of calculations for isolated Xe atom in the region $\omega \leq 150$ eV. However, we are confident and see some indications of it in Fig. 1 that even after this fitting the calculations carried out in various approaches (see [4, 5] and references therein) still overestimate experimental data at the upper end of the interval, i.e. at 140 eV $\leq \omega \leq$ 150 eV.

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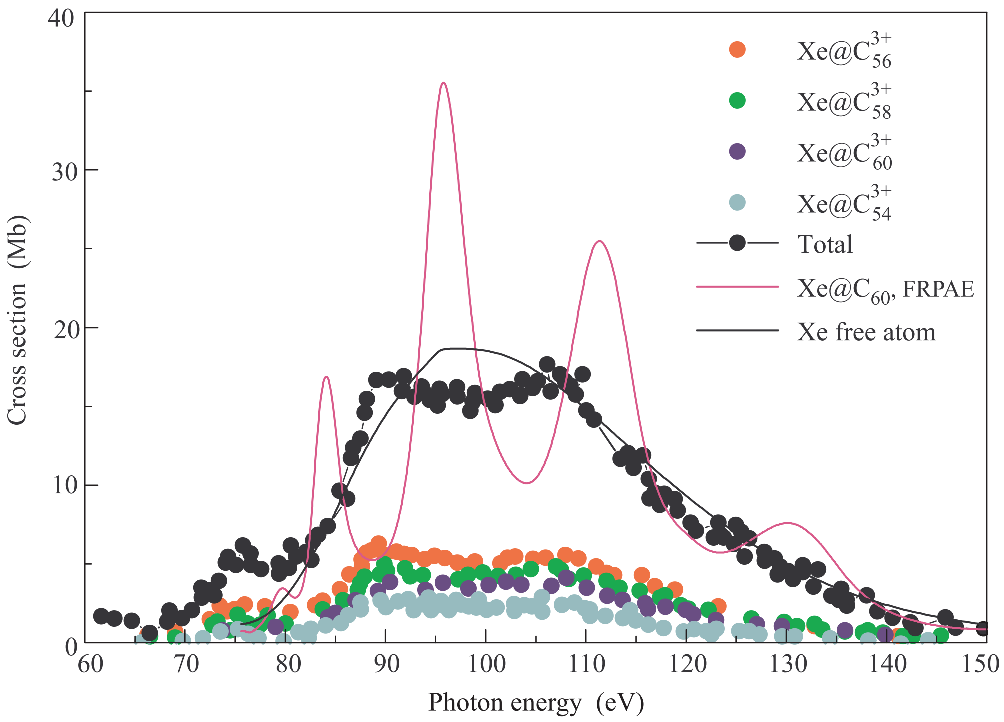

Fig. 1. Total and partial photoionization cross-sections of Xe@C$_{60}^{+}$ compared to total cross-section for Xe. Experiment for Xe@C$_{60}^{+}$ – from [2], calculations – from [4]

The most essential result of [1] is the measurement of photoionization cross section of the caged atom in Xe@C$_{60}^{+}$ that is accompanied by emission of carbon atoms. It is seen from Fig. 1 that in the cross-sections of ionization considered in [1], final states Xe@C$_{56}^{3+}$, Xe@C$_{58}^{3+}$, Xe@C$_{60}^{3+}$, and Xe@C$_{54}^{3+}$ all are almost equally important. We see also that the channel Xe@C$_{60}^{3+}$ that at the first glance seemed to be the most important contributes in fact only 1.71 ± 0.38 to the left hand side of Eq. (1). This means that the integrated probability $P = \int_{l}^{\omega_{\max}} P(\omega)d\omega$, where $\omega_{\max} = 150$ eV, of the "elastic" photoionization of Xe@C$_{60}^{3+}$ (i.e. that, in which the fullerenes shell remains in the ground state) is $P \leq 20\,\%$. Note that processes with emission of several electrons were not traced in [1].

3. Photoionization of the $4d$ subshell of Ce@C$_{82}^{+}$ was studied experimentally in [3] and theoretically in [5]. Only processes with emission of several (up to three) electrons from the FS were investigated in the experiment. The authors of [3] stated that the absorption by the encapsulated Ce atom is much smaller than that of the isolated one. Here the theoretical investigation becomes more complicated, since, contrary to the case of C_{60}, C_{82} is non-spherical. To simplify the calculations we have replaced the non-spherical FS by a spherical one with the same volume. As in the case of Xe@C$_{60}^{+}$, we carried out the RPAE calculations. The endohedral potential was of the square-well type with the finite thickness Δ and inner and outer radii r_1 and $r_1 + \Delta$, contrary to the δ-type potential for C_{60}.

The corresponding cross-section is depicted in Fig. 2. To normalize results of calculations to those of the experiments [3], we used the reduction factor 0.15. Note that in the considered energy region $100\,\text{eV} \leq \omega \leq$ $\leq 180\,\text{eV}$ the photoionization cross sections of Ce^{2+} and Ce^{2+}@C_{82} almost coincide. The small reduction factor means that about 85 % of photoionization acts are accompanied by emission of extra electrons or carbon atoms from the fullerenes shell. As well as in the case of C_{60}, the calculations for photoionization of the caged atom overestimate the experimental data at the photoelectron energies of about 60–80 eV even after the fitting of the data at 20–30 eV. Thus, some other inelastic channels should be taken into account to obtain the agreement.

4. In the mentioned above measurements of the photoionization cross sections [1–3] the possible energy loss due to excitations of the fullerene shell or due to the loss of several C atoms from the fullerene was not taken into account. However, as we have shown recently [10, 11], the excitation of the fullerene follows the photoionization of the caged atom with the probability close to unity, if the energy of the photoelectron is large enough, but does not reach the values of several keV for the tar-

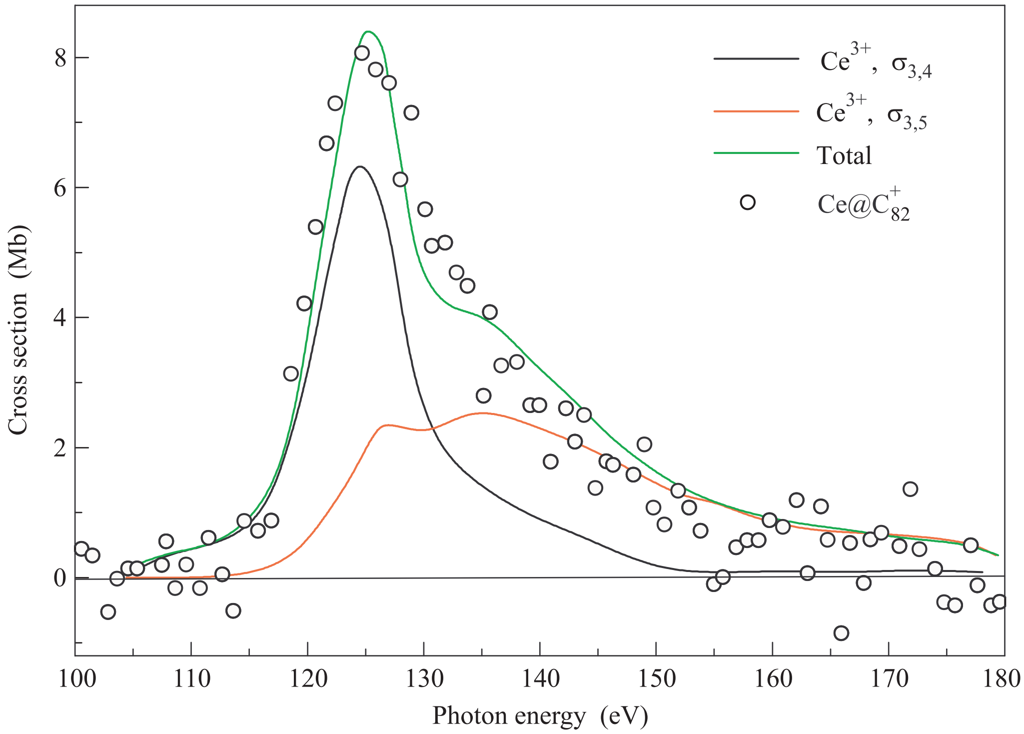

Fig. 2. Total and partial photoionization cross-sections of Ce@C_{82}^+ compared to total cross-section for Ce. Experiment for Ce@C_{82}^+ – from [3], calculations – from [5]

gets considered in this Letter. We shall clarify below, what the words "large enough" mean.

At the first glance the conclusion of [10, 11] looks surprising, since due to large radii R of the FS $R \gg r_a$ (r_a is the size of the caged atom), the shake-off effects in the FS are small. The same refers to the interaction of the photoelectron with *each* electron of the FS, which is determined by the Somerfield parameter

$$\xi^2 = \frac{1}{v} \approx \frac{13.6}{E}, \tag{2}$$

with v being the velocity of the photoelectron in atomic units, and E being the energy of the photoelectron in eV.

The large size and the small width Δ ($\Delta \ll R$) of the FS enabled to sum the probabilities of the FS excitations. We find that the ratio of the sum of cross sections of inelastic processes in the FS during photoionization of the caged atom to that of photoionization of the isolated atom is

$$R(E) = 1 - h\exp[-N_F \ln(1+\xi^2)]; \quad H = |\langle\Phi_0|\Psi_0\rangle|^2. \tag{3}$$

Here $h < 1$ is the square of the overlap of the FS wave functions in the ground state with neutral and ionized caged atom; N_F is the number of the FS electrons that can participate in inelastic processes in the FS. Note that the derivation of (3) [10, 11] employs only the closure condition and does not depend on the structure of the FS spectrum. Applying Eq. (3) to the cases considered in [1–3], we find $r(E) \approx 1$. Thus, the photoelectron almost inevitably loses some part of its energy due to interactions with the FS and almost no electrons with the energy $E = \omega - I$ will be detected in the measurement process.

However, Eq. (3) was obtained in [10, 11] by employing the closure condition for the final state FS wave functions. Hence, the energy of the photoelectron should be so large that the most important FS excitations could be included. In other words, E should be much larger than the average energy loss $\bar{\varepsilon}$ in the fullerene. The photon energies $\omega \approx (100-150)$ eV correspond to $E \approx 80$ eV for the case of Xe considered in [1, 2] and to $E \approx 50$ eV for the case of Ce studied in [3]. For the energies ε of the excitation of the fullerene, which exceed strongly the FS binding energies I_{FS} (e.g. $I_{\mathrm{FS}} \approx 7$ eV for C_{60}) the energy distributions drop as $1/\varepsilon^2$. Thus, the values of $\bar{\varepsilon}$ for the valence FS electrons are determined by $I_{\mathrm{FS}} \ll \varepsilon \ll E$. The energy distribution at these energies is proportional to $1/\varepsilon^2$ and the energy loss can be estimated as [12]

$$\bar{\varepsilon} \approx \frac{\xi^2 N_v}{4R^2} \ln \frac{E}{I_{\mathrm{FS}}}. \tag{4}$$

This gives $\bar{\varepsilon} \approx 15$ eV for C_{60} and $\bar{\varepsilon} \approx 25$ eV for C_{82}. In both cases $\bar{\varepsilon}/E \approx 1/5$, and Eq. (3) can be employed to estimate the probability of inelastic processes in the fullerene with the accuracy of about 20 %.

5. Since the presented above estimations did not require any knowledge on the spectrum of the FS, they are strictly valid for high enough ω. Thus, we demonstrate that the elastic-to-inelastic cross section ratio $\sigma_0(E)/\sigma_1(E)$ is much smaller than unity also for smaller energies up to $E \geq 40$ eV, i.e. at $\xi^2 < 1/3$. Let us denote the cross section of photoionization of the caged atom itself as $\sigma_c(E)$. The cross section of this process, followed by transitions in the FS is $\sigma_1(E) = \sigma_c(E)w_1(E)$. The cross section of the process, in which the state of the FS remains unaltered is $\sigma_0(E) = \sigma_c(E)w_0(E)$.

In the high energy limit we can employ the closure condition, finding $w_0 + w_1 = 1$ for $E \gg \varepsilon$ defined by Eq. (4). If the photoelectron energy does not satisfy this inequality, but still $\xi^2 \ll 1$, one obtains $w_0 = \exp[-N(1+\xi^2)]h \ll 1$. Since some of the excited states are not taken into account by the closure condition, we have now $w_0 + w_1 < 1$.

Note, that the configuration, in which a large number n of the FS electron does not change their states, is also quenched. Indeed, this contribution to $w_0(E)$ is equal to $\exp[-n\ln(1+\xi^2)]h$, and does not exceed 0.1 for $n > 8$. Analysis of the spectrum of C_{60} carried out in [13] demonstrates that the most important collective excited states (plasmons) have the excitation energy of about 20 eV. In the case of C_{82} the important excitations are concentrated at $E < 30$ eV [14]. Thus, even at $E \approx 40$ eV we miss only some of the single-particle excited states, in which a large number of electrons is moved to the continuum. Such contribution is quenched by the phase volumes of the ejected electrons. Thus, one has $1 - w_1(E) \approx 1$. Hence, already at $E \sim 40$ eV the inelastic processes in the FS during photoionization of the caged atom dominate over the elastic one. It explains why even at relatively low ω the measured cross section of photoionization of the caged atom is much smaller than the theoretical value for the isolated atom.

6. A very important consequence of the results, presented above is that the description of interaction between the photoelectron and the FS by a simple effective potential is not justified even at relatively small photoelectron energies of several dozens of eV. The large role of the inelastic processes demonstrates that it should be rather an optical potential, similar to that employed in nuclear physics.

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