LETTER TO THE EDITOR

Photoionization of the fullerene ion $C_{60}^+$. 

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Abstract.

Photoionization cross section of the fullerene ion $C_{60}^+$ has been calculated within a single-electron approximation and also by using a consistent many-body theory accounting for many-electron correlations. Electronic wave functions of the ground and excited states have been determined within the jellium model based on the local density approximation. It is predicted a giant resonance in the photoionization cross section at the photon energy $\sim 25$ eV. It is demonstrated that the resonance profile is much higher and narrower than in the case of the neutral fullerene $C_{60}$.

Since the discovery till nowadays the fullerene $C_{60}$ attracts a permanent rapt attention of investigators. From the physical point of view an interest to this object is associated with its exotic hollow, but highly stable structure caused by a significant delocalization of a large number of valence electrons in this molecule. These features manifest themselves in a number of interesting physical phenomena occurring in collision processes involving fullerenes. For example, surface plasmon oscillations in the fullerene $C_{60}$ can be excited. The plasmon excitations have a profound collective nature and they influence significantly the formation of the cross sections in collisions of various kind involving fullerenes [1]. The plasmon excitations in the fullerene $C_{60}$ have been well investigated both experimentally and theoretically [2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12]. Usually, they manifest themselves as giant resonances in the excitation spectrum of $C_{60}$. In this connection, there arises a question on the possibility of excitation of the plasmon oscillations in fullerene $C_{60}$ ions of different multiplicity. Recently, the photoionization cross section of singly charged fullerene ion $C_{60}^+$ has been measured [13]. However, theoretical calculation of this cross section has not been performed so far.

In this work, for the first time, we have calculated the photoionization cross section of the fullerene ion $C_{60}^+$ within the photon energy range from the $C_{60}^+$ ionization threshold up to 40 eV. This energy range has been chosen, because the photoionization cross section...
section for the neutral fullerene $C_{60}$ possesses a very strong giant resonance centered at the photon energy about 20 eV [9, 10]. Using the theoretical framework developed earlier by us and applied for the description of photoionization of the neutral fullerene $C_{60}$ [11, 12], we have determined the location of the giant resonance in the photoionization spectrum of $C_{60}^+$ (to be equal $\sim 25$ eV) and described it’s shape.

The atomic system of units is used throughout the paper, $m_e = |e| = \hbar = 1$.

The total photoionization cross section is equal to a sum of partial photoionization cross sections for each of the fullerene ion orbitals. The amplitude of ionization of each orbital is calculated both within the single-electron approximation and also by taking into account many-electron correlations. At the first stage, we use the frozen core model and the local density approximation assuming that there is a single electron transition only during the photoionization process. Then, the correlations between the transitions from different electron states are taken into account within the random phase approximation (RPA). The RPA amplitudes of photoionization $D_{\nu_2 \nu_1}(\omega)$ are found from the matrix form of the RPA equations [14]

$$D_{\nu_2 \nu_1}(\omega) = d_{\nu_2 \nu_1} + \sum_{\nu_3 \nu_4} D_{\nu_2 \nu_1}(\omega) \chi_{\nu_4 \nu_3}(\omega) V_{\nu_2 \nu_1 \nu_4 \nu_3}. \quad (1)$$

Here, the matrix elements $D_{\nu_2 \nu_1}$ are expressed via the single-electron photoionization amplitudes $d_{\nu_2 \nu_1}$, the matrix elements of virtual electron-hole excitation $\chi(\omega)$, and the matrix elements of interelectron interaction $V_{\nu_2 \nu_1 \nu_4 \nu_3}$ [14]. Note that the excitation spectrum has the Rydberg series of discrete excited states because the self-consistent potential of the fullerene ion has the Coulomb asymptotic. Therefore, the virtual electron transitions to the discrete excited states of the fullerene ion play more important role than in the neutral fullerene $C_{60}$ case.

The photoionization cross section and the oscillator strengths calculated both within single-electron approximation and also by taking into account many-electron corellations have been checked on the consistancy with the sum rule.

The inter-electron interaction within the local density approximation reads as follows [12]

$$V^{LDA}(\vec{r}, \vec{r}') = \frac{1}{|\vec{r} - \vec{r}'|} + \frac{\partial^2 \epsilon_{xc}^{\text{hom}}[n]}{\partial n^2} \bigg|_{n=n_0(\vec{r})} \delta(\vec{r} - \vec{r}'), \quad (2)$$

where $\epsilon_{xc}^{\text{hom}}[n]$ is the exchange–correlations energy of homogeneous electron gas with density $n$ within the Gunnarson-Lundqvist approximation [15]

$$\epsilon_{xc} = -\frac{3}{4} \left(\frac{9}{\pi^2}\right)^{1/3} \frac{1}{r_s(r)} - 0.0333 G \left(\frac{r_s}{11.4}\right), \quad (3)$$

$$G(x) = (1 + x^3) \ln(1 + \frac{1}{x}) - x^2 + \frac{x}{2} - \frac{1}{3}, \quad (4)$$

where $r_s(r) = \left(\frac{3}{4\pi n_0(r)}\right)^{1/3}$ is the Wigner-Zeith radius, $n_0$ is the equilibrium density.

Single-electron states of the fullerene ion have been calculated within the spherical jellium model with the self-consistent potential [11, 12] determined within the local
density approximation. Analogously to an atom, the single-electron wave functions of $C_{60}^{+}$ within this model, are given by

$$\phi_i \equiv \phi_{n_i, l_i, m_i}(r) = \frac{1}{r} P_{n_i l_i}(r) Y_{l_i m_i}(\theta, \phi),$$  \tag{5}$$

where $n_i, l_i, m_i$ is the usual set of quantum numbers for the $i$-th spherical shell; $Y_{l i m}(\theta, \phi)$ is the spherical harmonic; $P_{n_i l_i}(r)$ is the radial part of the wave function determined in the self-consistent potential of the fullerene ion. The number of nodes of the radial wave function $P_{n_i l_i}(r)$ is equal to $(n_i - l_i - 1)$. The main limitation of this method arises from the electrons self-interaction. Note that the self-interaction correction does not change the order of the electronic energy levels and the value of the total electronic energy, but it alters the value of the ionization potential very significantly.

As in the case of neutral fullerene, we assumed that four 2s2p electrons of each carbon atom are delocalized in the fullerene ion $C_{60}^{+}$. The ionic core of the fullerene is formed by fourfold-charged positive carbon ions $C^{4+}$ with the electronic configuration $1s^2$. The charges of the carbon ions are averaged over the sphere of radius $R$, being a hypothetic radius of the fullerene ion. In this paper we neglect the variation of the fullerene’s radius caused by its ionization and put the radius of the fullerene ion equal to the radius of the neutral fullerene, i.e. $R = 6.69$ a.u. \[16\].

For better understanding of the electronic properties and interatomic bonding in the fullerene molecules, it is useful to establish the correspondence of the electronic eigenstates introduced in our model to the $\sigma$ and $\pi$ orbitals widely used for modeling the planar graphite surface \[11\]. The ground state configuration for the ion $C_{60}^{+}$ has been chosen in a similar way as for the neutral fullerene $C_{60}^{0}$. Removing one electron from the highest occupied molecular orbital of $C_{60}$, one derives

$$1s^2 2p^6 3d^{10} 4f^{14} 5g^{18} 6h^{22} 7i^{26} 8k^{30} 9l^{34} 10m^{18} 2s^2 3p^6 4d^{10} 5f^{14} 6g^{18} 7h^9$$

without nodes, 180e$^-$

$$2s^2 3p^6 4d^{10} 5f^{14} 6g^{18} 7h^9$$

one node, 59e$^-$

Here an atomic notation of electronic configuration $n l^N_e$ is used \[17\].

The calculated energy level spectrum is shown in figure 1. The ionization potential 5.5 eV obtained within the LDA differs from the experimental value 11.5 eV \[18\]. The origin for this difference is discussed above.

The maximum number of electrons in a shell characterized by the orbital momentum $l$ is equal to $N_l = 2(2l + 1)$. The most outer $\sigma$- ($l=9$) and $\pi$- shells ($l=5$) in $C_{60}$ are open and have $N_\sigma = 18$ and $N_\pi = 9$ electrons respectively, whereas $N_\pi = 38$ ($\sigma$- shell) and $N_\pi = 22$ ($\pi$- shell). This means that the total orbital moment $L$ and the total spin $S$ of such a system are non-zero.

It is well known that an accurate calculation of the photoionization cross section of an atomic system with open electronic shells is much more complicated than that for a closed shell atomic system, because for an open shell system the calculation involves a huge number of additional terms which vanish in the case of a closed shell system \[19\]. In order to avoid this technical problem we have used the averaged term approximation.
Figure 1. Calculated energy levels spectrum of the fullerene ion $C_{60}^+$. The outer none-nodes and one-nodes orbitals are partially filled.

We have assumed that the electrons from the most outer open shells behave in the photoionization process as if the shells would be closed. This implies that one can put $L = 0$, $S = 0$ when calculating the partial contribution to the photoionization cross section from these shells and take into account their filling ratios $g_l = N_e/(2l + 1) < 1$.

It is natural to expect that the averaged term approximation affects the photoionization cross section behavior. The numerical analysis shows that the cross section calculated within the single-electron averaged term approximation does not obey the sum rule. Therefore, one should introduce appropriate correction when calculating the photoionization cross section in the random phase approximation. Thus, we have input extra coefficients decreasing the amplitude of electron-hole excitations from the open shells. These coefficients have been determined from the sum rule analysis of the partial photoionization cross sections of the open fullerene shells performed within the single-electron approximation. The coefficients enter as numerical factors in the matrix elements of operator $\hat{\chi}(\omega)$ in equation (1). Although this procedure improves the consistence with the sum rule of the photoionization cross sections calculated within
the RPA, it leaves the deviation of the RPA photoionization cross sections from the sum rule on the level of 30%.

Figure 2 shows the $C_{60}^+$ photoionization cross sections calculated by different methods: RPA and the averaged term approximation, RPA with extra coefficients, RPA with extra coefficients normalized on the sum rule. The last curve is the most accurate result of our calculations of the $C_{60}^+$ photoionization cross section. These calculations demonstrate that the giant resonance pattern is not affected much by the choice of the coefficient in equation (1), but the maximum value of the cross section depends strongly on their choice.

The calculated cross section is compared with theoretical [12] and experimental cross sections [9] for the neutral $C_{60}$ in figure 3. In order to elucidate the difference between the photoionization cross sections for $C_{60}$ and $C_{60}^+$, the $C_{60}^+$ photoionization cross section is shifted in figure 3 towards the ionization threshold of $C_{60}$. Under the

**Figure 2.** Photoionization cross section of the fullerene ion $C_{60}^+$ calculated within different approximations. Dotted line is the result of RPA and the averaged term approximation, dashed line is the same as dotted line but obtained with the optimal values of additional coefficients in the averaged term approximation, solid line is the same as dashed line but normalized according to the sum rule.
Figure 3. Comparison of the photoionization cross sections for the neutral fullerene $C_{60}$ and the ion $C_{60}^+$. Solid line is the most accurate result of calculation of the photoionization cross section for the fullerene ion $C_{60}^+$. This curve is shifted on $\Delta = I_{p}^{C_{60}} - I_{p}^{C_{60}^+}$, where $I_p$'s are the ionization potentials. Dashed line shows the experimental photoionization cross section for $C_{60}$ [9], dotted line is the photoionization cross section for the neutral $C_{60}$ calculated within our model [12].

condition of coincidence of the ionization thresholds of $C_{60}$ and $C_{60}^+$, the giant resonance in the $C_{60}^+$ photoionization spectrum is placed at the photon energy 21 eV. It is well known that the resonance energy of the plasmon oscillation can be easily evaluated for a spherical fullerene with the use of the classical Mie formula

$$\omega_l = \sqrt{\frac{l(l+1)N_e}{(2l+1)R^3}},$$

(6)

where $\omega_l$ is the frequency of a surface plasmon oscillation with angular momentum $l$ and $N_e$ is the number of delocalized electrons. For the dipole plasmon mode, $l = 1$, in the fullerene $C_{60}$ with $R = 6.69$ a.u. [16] and $N_e = 240$, one derives $\omega_1 = 20$ eV.

Since we have assumed the same radius for the fullerene ion as for the neutral fullerene and there is only a small difference in the number of delocalized electrons, it is natural to expect that the plasmon resonance energies in the ion and in the neutral fullerene are close. Figure 3 illustrates this fact. It shows that nevertheless there is a
slight shift of the position of the giant resonance in the \( C_{60}^+ \) photoionization spectrum, which might be a result of a slight variation of the radius of the fullerene ion neglected in our calculations.

Our analysis demonstrates that the giant resonance in the photoionization cross section for the fullerene ion arises due to the correlation between transitions from \( \sigma - \) orbitals. This fact proves the similarity of the nature of the giant resonances in the cases of the neutral fullerene and the ion. Qualitatively, one can explain the origin of the giant plasmon resonance by oscillations of the \( \sigma - \) electrons density against the ionic core.

It is also necessary to point out that the giant plasmon resonance in the photoionization spectrum of \( C_{60}^+ \) is much stronger as compared with that for \( C_{60} \). The similar behaviour is well known from the investigation of giant resonances in many-electron atoms and their ions. It can be explained by enhanced influence of the Coulomb core potential on the ground and excited states of valence electrons in the case of ionic target [10].

In conclusion we stress that the method developed in our work allowed us to predict the plasmon resonance pattern in the photoionization cross section of the fullerene ion \( C_{60}^+ \). This method can be straightforwardly utilized for the calculation of the photoionization cross sections of positive and negative ions of \( C_{60} \) of larger multiplicity, which are of great interest for experimental investigations.

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References


