FAST TRACK COMMUNICATION

Interplay of the volume and surface plasmons in the electron energy loss spectra of C₆₀

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Abstract

The results of a joint experimental and theoretical investigation of the C₆₀ collective excitations in the process of inelastic scattering of electrons are presented. The shape of the electron energy loss spectrum is observed to vary when the scattering angle increases. This variation arising due to the electron diffraction of the fullerene shell is described by a new theoretical model which treats the fullerene as a spherical shell of a finite width and accounts for the two modes of the surface plasmon and for the volume plasmon as well. It is shown that at small angles the inelastic scattering cross section is determined mostly by the symmetric mode of the surface plasmon, while at larger angles the contributions of the antisymmetric surface plasmon and the volume plasmon become prominent.

The interaction of a charged particle or an electromagnetic field with a many-particle system may lead either to the excitation of a single particle state of the system or to the excitation of collective states involving many particles. The latter case is described by the formation of the so-called giant resonances which are characterized by the collective motion of charged particles against that of the particles of opposite charge. Being a general physical phenomenon, this effect has been considered in nuclei [1], many-electron atoms [2], atomic clusters [3, 4] and condensed media [5, 6].

Like condensed media, metal clusters and fullerenes have delocalized electrons which oscillate against the positively charged ions forming collective plasmon excitations. A significant fundamental interest has been aroused in studying the plasmon formation in these systems [4, 7, 8]. Investigation of potential applications [9, 10] of plasmons formed a new field of physics, named nanoplasmonics.

It is known [11] that collective electron excitations in metal clusters can be of two different types, namely the surface and the volume plasmons. The dipole surface plasmons are responsible for the formation of giant resonances in photoabsorption spectra of metal clusters, while the volume plasmon modes, which have higher resonance frequencies, provide an essential contribution to the formation of the electron impact ionization cross section.

Existence of a giant resonance in the excitation spectra of fullerenes at about 20 eV was predicted theoretically [12] and then observed experimentally in the case of C₆₀.
in photoionization [13] and inelastic scattering of electrons [14]. Recent experiments on photoionization of neutral [15] and charged [16] C60 molecules revealed the existence of the second collective resonance at about 40 eV, which firstly was assigned to the volume plasmon [16]. Then its assignment to the second surface plasmon has been proposed [17] and discussed [18].

Theoretical investigations of the scattering of fast electrons on fullerenes [19, 20] within the single-plasmon model predicted the existence of diffraction phenomena, which were then experimentally observed in C60 in [21].

In this paper, we reveal for the first time the contribution and the interplay of the three plasmons to the inelastic scattering cross section of electrons on the C60 fullerene. As opposed to the photoionization, the electron impact ionization causes the formation not only of two surface plasmons but the volume plasmon as well. We show, both experimentally and theoretically, that the volume plasmon manifests itself as the scattering angle increases.

We use a simple but physically reasonable model [22–26] which treats the fullerene as a spherical shell of a finite width, $\Delta R = R_2 - R_1$ (where $R_{1,2}$ are the inner and the outer radii of the molecule, respectively). Interaction with an incident electron leads to the variation of the volume electron density, occurring inside the shell, and of the surface electron densities at the inner and the outer surfaces of the shell. These variations lead to the formation of the volume plasmon [11] and two coupled modes of the surface plasmon, a symmetric and an antisymmetric one [23, 25, 26]. Within the plasmon resonance approximation [19, 20, 27], the differential inelastic scattering cross section of fast electrons in collision with fullerenes can be defined as a sum of three contributions (we use the atomic system of units, $\hbar = \epsilon = 1$):

$$
\frac{d^3\sigma}{d\Omega_2 d\Omega_1 p} = \frac{d^3\sigma^{(v)}}{d\Omega_2 d\Omega_1 p} + \frac{d^3\sigma^{(s)}}{d\Omega_2 d\Omega_1 p} + \frac{d^3\sigma^{(o)}}{d\Omega_2 d\Omega_1 p},
$$

where

$$
\frac{d^3\sigma^{(v)}}{d\Omega_2 d\Omega_1 p} = \frac{2R_2 p_2}{\rho_1^2 \rho_1^2} \sum_{l} \omega_2^2 \Gamma_{l l}^{(v)} V_l(q)
$$

$$
\frac{d^3\sigma^{(s)}}{d\Omega_2 d\Omega_1 p} = \frac{2R_2 p_2}{\rho_1^2 \rho_1^2} \sum_{l} \omega_2^2 \Gamma_{l l}^{(s)} S_l(q)
$$

$$
\frac{d^3\sigma^{(o)}}{d\Omega_2 d\Omega_1 p} = \frac{2R_2 p_2}{\rho_1^2 \rho_1^2} \sum_{l} \omega_2^2 \Gamma_{l l}^{(o)} S_2(q)
$$

are obtained within the plane-wave first Born approximation. Here $E_0 = p_2^2/2$ is the kinetic energy of the scattered electron, $\Omega_1$, its solid angle, $\rho_1$ and $\rho_2$ the initial and the final momenta of the projectile electron, $q = \rho_1 - \rho_2$ the transferred momentum, $\omega = \epsilon_1 - \epsilon_2$ the energy loss and $\epsilon_1$ the kinetic energy of the incident electron. $\omega_2 = \sqrt{3N/R_2^2 - R_1^2}$ is the volume plasmon frequency ($N$ stands for a number of delocalized electrons in the fullerene), $\omega_1^{(s)}$ and $\omega_2^{(s)}$ are the frequencies of the symmetric and antisymmetric surface plasmons of multipolarity $l$ [23]:

$$
\frac{\omega_2^{(s)}}{\omega_1^{(s)}} = \frac{1}{2} \pm \frac{1}{2(2l + 1)} \sqrt{1 + 4l(l + 1)(R_1/R_2)^{2l+1}},
$$

where the signs ‘−’ and ‘+’ correspond to the symmetric ($\omega_1^{(s)}$) and the antisymmetric ($\omega_2^{(s)}$) modes, respectively. $\Gamma^{(v)}_l$ and $\Gamma^{(o)}_l$ ($j = 1, 2$) are the widths of the plasmon excitations. Functions $V_l(q)$, $S_l(q)$ and $S_2(q)$ are the diffraction factors depending on the transferred momentum $q$. They determine the relative contribution of the multipole plasmon modes in various ranges of electron scattering angles and, thus, the resulting shape of the differential energy loss spectrum. Explicit expressions for these functions are presented in [28].

The introduced model is applicable within the long wavelength limit, when the characteristic scattering length, $1/q$, is large. Under the condition of the small transferred momentum $q$, the volume plasmon is characterized by the constant frequency $\omega_p$, which does not depend on the transferred momentum [29]. In this paper, we do not consider the dependence of the plasmon widths on the transferred momentum which was studied in [11]. The widths are treated as external parameters which are not calculated within the present model.

Assuming $R_1 \rightarrow R_2 \equiv R$, we come to the model which treats a fullerene as an infinitely thin sphere. In this limit, the cross section, $d^3\sigma \equiv d^3\sigma^{(v)}$, is defined only by the single surface plasmon, and (1) and (2) transform into the following expression [19–21]:

$$
\frac{d^3\sigma}{d\Omega_2 d\Omega_1 p} = \frac{4R p_2}{\pi q^2 \rho_1} \sum_{l} (2l + 1) \omega_2^2 \Gamma_{l l}^{(v)} J_l(qR).
$$

where $\omega_2 = \sqrt{l(l + 1)N/(2l + 1)R^3}$ is the surface plasmon frequency and $\Gamma_{l l}^{(v)} J_l^{(v)}$ is its width.

According to [19], we can estimate the angular momentum range which should be considered within the model. In the case of the C60 fullerene, multipole excitations with $l > 3$ are formed by single electron transitions rather than collective electron excitations, so only terms corresponding to the dipole ($l = 1$), quadrupole ($l = 2$) and octupole ($l = 3$) plasmon excitations should be included to the sum over $l$ in (2) and (4). The diffraction phenomena observed in [21] manifest themselves in the dominating contribution of different multipolar excitations at different electron scattering angles [30].

The theory presented in the paper is based on the model assumptions governed by two parameters: the number of multipole terms to be accounted for ($l_{\max} = 3$) and the widths of plasmon resonances, $\Gamma^{(v)}_l$ and $\Gamma^{(o)}_l$. The choice of these parameters is limited by their physical meaning, and thus, allows one to vary the overall behavior of the inelastic scattering cross section only a little. These parameters can be chosen on the basis of data available in the literature according to their actual physical limitations. The concrete calculation of the values of these parameters can be done, but it is beyond the topic of this paper, and will be a subject for further investigations.

The main advantage of the method developed is that it provides a clear explanation of the main resonance-like structure of the inelastic scattering cross section on the basis of the major physical phenomena at play, namely by the excitation of multipole plasmon resonances by electron impact. More accurate calculations based on the explicit use
of quantum-mechanical methods should reveal a further, more detailed structure of the cross section. Therefore, the plasmon resonance approximation utilized and further advanced in the present work turns out to also be a very useful tool for the interpretation of the results of such quantum simulations. The validity of the plasmon resonance approximation was proved by the comparison of its results with those following from ab initio quantum calculations for the case of metal clusters [11, 27], and also by the comparison with available experimental data [19, 21].

A crossed-beam apparatus [31] has been used to measure the energy loss spectrum of C\(_{60}\). The vacuum chamber contains an electron gun, two twin 180\(^\circ\) hemispherical electrostatic analysers, rotatable independently in the scattering plane and a resistively heated, anti-inductively wounded oven to produce the C\(_{60}\) beam [32]. The typical operational temperature of the oven was about 500 \(^\circ\)C. The compensation of the earth’s magnetic field has been performed by three pairs of orthogonal square coils [31] external to the vacuum chamber and by an internal 0.4 mm thick Skudotech layer [32].

The scattered electrons have been analysed in energy by one of the two electron spectrometers. A three-element electrostatic lens focuses the electrons from the target region onto the entrance slit of the hemispherical analyser (60 mm mean radius). After the angle and energy selection, the electrons have been detected by a channeltron electron multiplier. In these experiments the 1000 eV scattered electrons have been slowed down to a pass energy of 50 eV. The energy resolution was 1.2 eV full width at half maximum, as measured by detecting the elastic scattered electrons, and the angular resolution about \(\pm 2^\circ\). The output signals of the detector have been sent to a PCI-6024E National Instruments card through a preamplifier and a constant fraction discriminator. The typical incident current, monitored by a Faraday cup, has been in the range of a few \(\mu\)A. A personal computer via Labview software scans the energy of the incident beam, changing the energy loss of the scattered electron, controls the movement of the turntables, sets the dwell time of the measurements, monitors the current of the beam during the acquisition and stores the results. The scattered angle scale has been calibrated by checking the symmetry of the measured yield at a fixed energy loss with respect to the direction of the primary beam, while the zero of the energy loss scale has been defined by elastically scattered electrons. In the present measurements, the energy of the scattered electrons and the scattering angle have been fixed, while the incident energy has been varied to cover the energy loss region of interest.

A series of energy loss spectra, EELS, measured in the scattering angle range 3\(^\circ\)...13\(^\circ\) are presented in figure 1. For the sake of convenience, all spectra are normalized to 1. The spectra show a series of structures, starting at about \(\omega = 5\) eV, overimposed to a broad feature peaking above 20 eV. The peaks below 20 eV corresponding to the electronic excitations are marked by dashed lines in figure 1. A prominent peak at about 6 eV is consistent with those measured in solids by Lukas et al. [33] and observed in the gas phase C\(_{60}\) by Keller and Coplan [14]. According to Barton and Eberlein [34] and Bertsch et al. [12], this feature is assigned to the plasmon arising from the collective motion of \(\pi\) electrons. The sequence of the peaks in the range 10...17 eV has been assigned [33] to electronic excited states converging to different ionization bands observed in photoemission [35] and \((\sigma, 2\epsilon)\) experiments [36]. Above 20 eV the differential cross section, \(d^3\sigma / d\Omega d\omega\), displays a broad feature which may be assigned to the \((\sigma + \pi)\)-plasmon formed by the collective excitation of the delocalized electrons [23, 37]. With increasing the scattering angle, the shape of the energy loss spectra varies significantly and the existence of two different peaks between 20 and 30 eV is clearly seen for the angles \(\theta = 6^\circ \ldots 8^\circ\).

In this paper we focus on the study of the behavior of the main peak above 20 eV. To understand the reason of the EELS shape variation we calculated the differential cross section within the three-plasmon model (see (1) and (2)). Radius of the C\(_{60}\) molecule is equal to 3.54 Å, and the width of the spherical shell is set to 1.5 Å, which was obtained by Rüdel et al. [24]. The ratio \(\gamma_{ij}^{(1)} = \Gamma_{ij}^{(1)} / \omega_{1ij}\) for the symmetric mode is equal to 0.6 which is close to the experimental values obtained from the photoionization and energy loss experiments on neutral C\(_{60}\) [13, 21]. The value \(\gamma_{ij}^{(1)} = 0.6\) is chosen according to the previous theoretical investigations of the electron energy loss based on the plasmon resonance approximation [19, 20]. The widths of the antisymmetric mode as well as of the volume plasmon were varied to obtain a better agreement with the experimental data. In the present calculations, the ratios \(\gamma_{ij}^{(2)} = \Gamma_{ij}^{(2)} / \omega_{2ij}\) and \(\gamma_{ij}^{(3)} = \Gamma_{ij}^{(3)} / \omega_{3ij}\) are equal to 1. The value \(\gamma_{ij}^{(2)} = 1.0\) corresponds to the widths of the second plasmon resonance obtained by Scully et al. [16] studying photoionization of C\(_{60}^{+}\) (\(q = 1\ldots3\)) ions. In the case of the infinitely thin fullerene, we used the ratio \(\gamma_i = \gamma_{ij}^{(1)} = 0.6\) according to [19, 20].
Figure 2. Comparison of the experimental EELS with theoretical results obtained within the three-plasmon model and the single-plasmon model for the scattering angles $\theta = 3^\circ \ldots 9^\circ$. Black squares represent the experimental data, cross section obtained for the case of the infinitely thin fullerene is presented by the dashed (red) line, the solid (blue) line denotes the cross section for a fullerene with the finite width.

The comparison of the experimental data with the model calculations for the scattering angles $\theta = 3^\circ \ldots 9^\circ$ is presented in figure 2. Both the experimental and the theoretical curves are normalized to 1. Black squares represent the experimental data, differential cross section obtained for the case of the infinitely thin fullerene is presented by the dashed (red) line while the solid (blue) line denotes the cross section for a fullerene with the finite width. At the small scattering angle, $\theta = 3^\circ$, both models show quite good agreement with the experimental curve. It means that in this case the symmetric mode of the surface plasmon dominates the cross section, while the influence of the two other plasmons is rather weak. Increasing the scattering angle, the cross section formed by the single surface plasmon (dashed red line) becomes much narrower than the experimental spectrum. On the other hand, the three-plasmon model (solid blue line) leads to a good quantitative agreement with the experiment. It means that for the scattering angle larger than $\theta = 5^\circ$, the second surface plasmon and the volume plasmon begin to play a significant role in the formation of the energy loss spectrum. They may also contribute to the formation of the two resonances between 20 and 30 eV at the scattering angles $\theta = 6^\circ \ldots 8^\circ$ (see figure 1). As seen from figure 2, at $\theta = 7^\circ$ the width of the plasmon resonance calculated within the three-plasmon model (solid blue line) corresponds to the total width of the experimental broad structure but does not reproduce the two more narrow individual peaks. Refining further the theory presented in this paper, one should be able to reproduce also the details of the two-resonant structure appearing between 20 and 30 eV at the angles $\theta = 6^\circ \ldots 8^\circ$. This is one of the questions for a further investigation.

A few words should be said about possible thermal effects on the energy loss spectra. Ab initio calculations of atomic clusters based on the dynamical jellium model [38] revealed the broadening of the linewidths of single-electron excitations in the vicinity of the plasmon resonance due to the electron coupling with the surface and volume vibrational modes of the ionic background. For the case of the Na$_{40}$ cluster it was shown that the broadening width increases slightly with the temperature and is about 0.15 eV for $T = 400$ K [38]. For the C$_{60}$ fullerene, the additional broadening of the spectra should be of the similar order of magnitude, therefore possible thermal effects due to the operational temperature of 500 °C should not influence significantly the energy loss spectra. The multifragmentation process does not play a role at this temperature, since the multifragmentation of C$_{60}$ in C$_2$ dimers or other small carbon fragments occurs at significantly higher temperatures, being above 3000 K [39].

To illustrate a relative role of each of the three plasmons in the formation of the energy loss spectrum, in figure 3 we present the calculated partial contribution of each plasmon (2) as well as their sum for the scattering angles in the range $\theta = 3^\circ \ldots 9^\circ$. At the small scattering angle, $\theta = 3^\circ$, the symmetric mode of the surface plasmon (thin solid black line) dominates the cross section. A similar behavior was revealed by Scully et al [16] in the photoionization. In fact, in the case of the uniform external field ($q \to 0$), there is no volume plasmon excitation in the system and the symmetric plasmon mode exceeds significantly the antisymmetric mode. Non-uniformity of the external field causes the formation of the volume plasmon whose contribution to the cross section
The symmetric (s) and the antisymmetric (a/s) modes of the surface plasmon are shown by the thin solid black line and the dashed red line, respectively; the volume plasmon contribution is shown by the dash–dotted blue line. The total cross section is shown by the thick green line.

is insignificant when the scattering angle is small. With increasing the scattering angle ($\theta = 5^\circ$ and $7^\circ$), the symmetric mode of the surface plasmon becomes less relevant and the antisymmetric mode (dashed red line) more prominent. At the larger angle ($\theta = 9^\circ$), the symmetric surface plasmon almost does not contribute to the cross section while the volume plasmon (dash–dotted blue line) becomes dominant. Thereby, the origin of the two peaks in the energy loss range from 20 to 30 eV at the angles $\theta = 6^\circ$ ... $8^\circ$ can be explained by the contribution of the antisymmetric surface and the volume plasmons.

The peak position of each plasmon resonance (2) as well as of the resulting cross section $d^2\sigma/d\omega d\Omega_p$, is influenced by the manifestation of the diffraction effects. It was shown [21] that plasmon modes with different angular momenta provide dominating contributions to the differential cross section at different scattering angles, which leads to the significant angular dependence of the energy loss spectrum. This phenomenon was described in terms of the electron diffraction at the fullerene edge [21]. As seen from (2), the resonance peak of each plasmon is defined not only by the plasmon frequencies $\omega_p$, $\omega_{11}$ and $\omega_{22}$ but also by the multipolar diffraction factors $V_1(q)$, $S_{11}(q)$ and $S_{22}(q)$ which depend on the transferred momentum $q$. In the limiting case of an infinitely thin layer, this dependence is described by the spherical Bessel functions $j_q^2(qR)$ (see (4)) which oscillate with $q$ and, thus, give suppression and enhancement of the partial plasmon modes at certain angles [21]. The incident energy of the projectile does not influence this behavior and defines only the absolute value of the cross section.

To conclude, we performed a joint experimental and theoretical investigation of collective excitations in C$_{60}$ in the process of inelastic scattering of electrons in collision with fullerenes. An extensive set of measurements of the energy loss spectrum of the C$_{60}$ molecule has been performed for the scattering angle range from $3^\circ$ to $13^\circ$. We have introduced a new theoretical model which accounts for the two modes of the surface plasmon as well as the volume plasmon, when the fullerene is modelled as a spherical shell of a finite width. Theoretical results obtained within this model are in good agreement with the experimental data. The present results show that collective excitations provide the main contribution to the inelastic scattering cross section of electrons over a broad energy range and, as opposed to the photoionization, both the surface plasmons as well as the volume one contribute to the cross section. It has been shown that the symmetric mode of the surface plasmon dominates at smaller scattering angles, while at larger angles the antisymmetric and the volume plasmons make the most prominent contribution.

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