(e,2e) experiments on C\textsubscript{60}

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Abstract. The ionization of C\textsubscript{60} in gas phase has been studied by (e,2e) experiments at about 1000 eV in asymmetric kinematics and 0.6 a.u. momentum transfer. The binding energy spectrum has been compared with previous photoemission data and theoretical calculations, while the measured coincidence angular distributions corresponding to the ionization of the HOMO and HOMO-1 have been compared with calculations that account for the ionic symmetry and electronic structure of C\textsubscript{60}.

1. Introduction

Electron impact ionization of atoms and molecules is one of the basic processes in nature. Ionizing collisions induced by electrons are relevant to different scientific and technological areas like gas discharges, cold plasmas used in chemical vapour deposition of materials, lasers and the chemistry of the upper atmosphere. Moreover their theoretical understanding involves the modeling of the few-body Coulomb interaction. As such electron impact ionization has attracted a lot of experimental and theoretical interest. The most complete characterization of the dynamics of an ionization process by electron impact is achieved by detecting the scattered and ejected electrons in coincidence after energy and angular selection \cite{1}. The quantity measured in these experiments, known as (e,2e) experiments, is the triple differential cross section (TDCS) $\frac{d^3\sigma}{d\Omega_a d\Omega_b dE_a}$, i.e. a cross section that is differential in the solid angles of the scattered and ejected electrons, labelled as ‘a’ and ‘b’ respectively, and in the energy of one of them. The energy of the second electron is determined by the energy conservation, $E_a+E_b=E_0-\text{IP}$, where IP is the ionization potential of the target and $E_0$ the incoming electron energy. The (e,2e) technique has scored several successes in describing both the ionization mechanisms in one

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and two electron targets [2] and the structure of molecular orbitals via electron momentum spectroscopy [3].

In this work we present results of the first application of the (e,2e) technique to the study of C\(_{60}\) in gas phase. Carbon is the fourth most abundant element in the Universe and forms more compounds than any other element, with almost ten million pure organic compounds described to date. One of carbon allotrope forms, the fullerene discovered in 1985 by Kroto and Smalley [4] is attracting a lot of interest for its amazing properties [5]. Fullerene can be considered as an intermediate form between a molecule and a cluster. This makes it a very special target for the investigation of the electron-electron interactions. Its highly symmetric and stable structure shows, already at the single molecule level, both atomic and collective behaviors. Valence electron properties of C\(_{60}\) have been investigated via (e,2e) experiments on thin films [6]. The experimental data have been interpreted by comparison with the calculated orbitals of a C\(_{60}\) molecule. To our best knowledge no gas phase (e,2e) data on C\(_{60}\) have been reported in the literature, while an extensive series of photoionisation studies have been performed [7-10].

2. Experiments

A crossed-beam apparatus has been used to measure the ionization cross-section of C\(_{60}\). The apparatus has been described in detail elsewhere [11], here only information relevant to the present measurements will be reported. The vacuum chamber contains an electron gun, two twin 180° hemispherical electrostatic analysers, rotatable independently in the scattering plane and a resistively heated, anti-inductively wounded oven to produce the beam of C\(_{60}\) [12]. The compensation of the earth magnetic field is performed by three pairs of orthogonal square coils [11] external to the vacuum chamber and by an internal 0.4 mm thick Skudotech layer [12].

The scattered/ejected electrons are analysed in energy by one of the two electron spectrometers, with an energy resolution of about 1eV. A three element zoom electrostatic lens focuses the electrons from the target region onto the entrance slit of the hemispherical analyser, with an angular acceptance of ±2 and ±4° for the scattered and ejected electrons respectively. The electrons, after angle and energy selection, are then detected by a channeltron electron multiplier. The output signals of the detectors are sent to the TAC (Time to Amplitude Converter) through preamplifiers and constant fraction discriminators. Finally, the TAC output is analysed by a triggered ADC PCI card displaying the time spectrum. The typical incident current, monitored by a Faraday Cup, was about 5 μA. A personal computer via a Labview software scans the energy of the incident beam, changes the energy loss of the scattered electron, controls the movement of the turntables, sets the dwell time of the measurements, stores the non-coincidence and coincidence data and monitors the current of the beam during the acquisition.

Even though the role of ‘scattered’ and ‘ejected’ electron cannot be uniquely related to the energy of the two electrons, in this paper the convention of labeling the fast electron, ‘a’, as the scattered electron and the slow electron, ‘b’, as the ejected one has been adopted. In the measurements the scattered electrons (E\(_a\)=1000 eV) were detected at a fixed angle θ\(_a\)=4°, while the ejected electrons (E\(_b\)=20 eV) were measured in the angular range θ\(_b\) varying from 40 to 130°. The θ\(_b\) scale was calibrated by determining the symmetry of the scattered electron yield around the incident beam direction. The energy resolution measured as full-width-half-maximum (FWHM) of the coincidence binding energy spectrum of He was about 1.4 eV. A check of any anisotropic response of the set-up was done by measuring the TDICS of He in the same kinematic conditions of the C\(_{60}\).

For the present experiments the crucible was filled by about 300 mg of C\(_{60}\) powder from Sigma-Aldrich, with purity >97%, used without further purification. In the typical operating conditions, the oven was kept at about 515 and 475°C on the top and bottom of the furnace respectively, running
continuously for at least a month before some recharging of the sample was required. The stability of the oven was checked at the beginning and at the end of each coincidence run by a measurement of the energy loss spectrum in the valence region. A series of these energy loss measurements taken over few weeks is shown in figure 1. The spectrum shows a well resolved excitation peak at 6 eV, and some other structures at about 10, 13 and 17 eV superimposed to a broad feature with its maximum at about 28 eV. All these features are in agreement with the observation by Keller and Coplan [13], who also provided some assignment for the different features and a comparison with a solid state experiment by Lucas et al. [14].

![Figure 1. C₆₀ energy loss spectra taken over a period of 45 days measured to check the performance of the set-up during the (e,2e) experiments. The arrows indicate the main structures identified in previous works [13, 14].](image)

3. Theory

The (e,2e) process from C₆₀ is a challenge for theory and one has to resort to appropriate approximations. For an adequate description of the experiments two aspects should be accounted for: 1) the scattering dynamics in the initial and the final channels; and 2) the electronic and ionic structure of the target. As for the first point the appropriate choice depends on the experimental parameters. For example, for strongly asymmetric energy sharing of the final state electrons (Eₐ>>Eₜ), large impact energy, and small momentum transfer, the first Born or even the plane wave approximation may provide a good description. In fact the application of both of these approximations to fullerenes is more justified than for atoms because of the effective screening [15, 19] that makes the interaction of the continuum electrons with the target short ranged. The price to be paid for this is the calculation of the screening which is a challenging task in itself [18]. As shown in [18] however the screening effects are easily described in the high impact energy regime. In the present experiment the arrangements are such that the continuum electrons may be described with decoupled plane waves. We put more effort in the ab-initio description of the target: C₆₀ is nearly, but not exactly spherically symmetric. Its lower symmetry (Iₜₜ) leads to additional splitting of the energy levels. Also the final results for the TDCS must be averaged over the possible orientations of the molecule. An important ingredient of the theory...
is the knowledge of the target electronic wave-functions. We computed the single particle wave-functions in the basis of Gaussian functions centered at the ionic positions using the Hartree-Fock method (all technical details can be found in [16]). We note that the density functional theory (DFT) can also be used to obtain the single-particle states. However, we find that both methods provide very consistent results for the space-dependent wave-functions; the difference is mostly in the energy of the states.

As was demonstrated in [16], the angular momentum quantum number \( \ell \) governs the energy spectrum of \( \text{C}_{60} \). All valence electrons (240) of the molecule can be grouped into two parabolas (principal quantum numbers \( n=1,2 \)) with 60 (180) electrons in the upper (lower) branch as a function of \( \ell \). The highest occupied molecular orbital (HOMO) has \( h_u \) symmetry and can be assigned \( \ell=5 \) value. However, this state is only 5-fold degenerate. Six other states with \( \ell=5 \) can be grouped into 2 groups above the Fermi level. The HOMO-1 state with \( \ell=4 \) is split in \( \text{I}_h \) environment into 5-fold and 4-fold substates with symmetries \( h_g \) and \( g_g \), respectively. The energy separation is rather small to be resolved in the present experiments (table 1). On the basis of this electron counting one can already expect that the ratio of signal from HOMO-1 and HOMO states should be 9:5. However, further important differences come from the exact shape of the electron momentum distribution, \( |\psi(q)|^2 \), of the electronic states. Here \( q \) denotes the norm of the bound-state electron momentum in radial direction from the center of molecule.

In the first approximation the electrons in \( \text{C}_{60} \) can be considered as free particles confined to the surface of the sphere with radius of approximately \( r=6.75a_B \), where \( a_B \) is the Bohr radius. For the HOMO state from a simple relation \( \ell=|q\times r| \) we obtain an estimate for the maximum of the momentum distribution to be at \( q\approx0.74 \text{ a.u.} \). For HOMO-1 we likewise obtain \( q\approx0.60 \text{ a.u.} \). These numbers reflect the trend that decreasing the state energy the position of the maximum of the electron momentum distribution is shifted towards lower \( q \) values. However, such a simple consideration misses the quantum mechanical nature of the states. Two parabolic branches in the energy dispersion can be distinguished by the principal quantum number, \( n \), which characterizes electronic states in the confining potential [17]. In accordance with the oscillation theorem of quantum mechanics the states in the lowest branch are nodeless, while the states in the upper branch have one node. The nodal surface lies approximately at the potential minimum, i.e. at the radius of the molecule (\( r \)). Accordingly, the states from the upper branch have two maxima and one nodal surface in the momentum space.

The maxima in the momentum distribution translate into the positions of the lobes in the angular resolved \((\text{e,2e})\) spectra. Within the first Bohr approximation the spectrum is symmetric with respect to the direction of the momentum transfer \( \mathbf{K}=\mathbf{k}_0-\mathbf{k}_a \), where \( \mathbf{k}_0 \) and \( \mathbf{k}_a \) are the momenta of the incident and scattered electrons respectively. We will see below that for \( \text{C}_{60} \) this condition does not strictly hold. From general considerations, three sources can be identified for this behavior: i) interactions among the continuum state electrons; ii) effects of dynamical screening, and iii) many-body initial state correlations that go beyond the mean-field correlation incorporated in the calculations below or effective exchange and correlation, as described within the local density approximation to the exchange and correlation functional that enters the DFT calculations. A detailed analysis of these aspects and a comparison with the atomic case is scope of the present work.

4. Results

We have performed two types of \((\text{e,2e})\) experiments on \( \text{C}_{60} \). In a first experiment the analyser of the ejected electron was set at fixed \( \theta_b \) and a binding energy spectrum was measured. In the kinematic conditions of the present experiment (\( E_a=1000 \text{ eV}, \ E_b=20 \text{ eV and } \theta_a=4^\circ \)) the momentum transfer \( \mathbf{K}=\mathbf{k}_0-\mathbf{k}_a \) in the collision is about 0.6 a.u.. In the second type of experiments the TDCS of the two lowest in energy ionic states have been measured. The binding energy spectrum provides both the energetic of the ionic states and allows to establish the relative intensity of their measured TDCS.
In figure 2.a the binding energy spectrum measured at $\theta_b=80^\circ$ is shown. The present gas phase (e,2e) data are compared to the results of photoemission experiment [18] of condensed-phase pure $C_{60}$ and to the calculations by Colavita et al. [8] employing a convergent one-centre expansion and an LDA Hamiltonian.

![Figure 2](image_url)

**Figure 2.** (a) Binding energy spectrum of $C_{60}$ measured at $E_a=1000$ eV, $E_b=20$ eV, $\theta_a=4^\circ$ and $\theta_b=80^\circ$. The bars below the spectrum are the positions of the electronic bands measured in [18] and calculated in [8]; (b) comparison between the binding energy spectra of $C_{60}$ thin film integrated over the momenta between 0 and 2.5 a.u. [6] and the sum of four binding energy spectra of gas phase $C_{60}$ measured at $\theta_b=60$, 80, 100 and 120$^\circ$. The dashed line is the best fit to the sum of the spectra with Gaussian functions. The four energy spectra measured in the present work scan a momentum region between 0.4 and 0.9 a.u.
The spectrum has been fitted with a series of Gaussian functions where the intensity, energy position and FWHM were used as fitting parameters. The use of the FWHM as a free parameter is justified by the fact that in certain regions a condensation of several states (see table 1) is expected to produce broader spectral features. Nine Gaussian functions have been used in the fit. The number has been chosen according to the previous experimental observation in photoelectron spectroscopy [18]. Increasing or decreasing the number of Gaussian functions may result in an acceptable “visual” representation of the experimental data, but in unphysical values of the fitting parameters (FWHM smaller than the experimental resolution or uncertainties in the peak positions larger that their relative spacing). An absolute calibration of the binding energy scale has not been done, thus we assign the main feature of the spectrum to the HOMO-1 orbital observed in the photoemission experiment. The comparison of the relative position of the different features in the spectrum is reported in table 1.

Table 1. Experimental and calculated ionization energies of the valence and inner valence states of C60. Peak positions, in eV, are referred to the HOMO-1 state at 9 eV [8, 18]. The labeling of the band is done according to ref [8].

| Band     | Present work (+0.1 eV) | Experiment (ref.18) | Theory (ref. 8) | Symmetry (ref. 8) |
|----------|------------------------|---------------------|-----------------|-------------------|
| HOMO     | -1.2                   | -1.4                | -1.13           | π                 |
| Band 1   |                        |                     |                 |                   |
| HOMO-1   | 0                      | 0                   | 0.00            | π                 |
| Band 2   |                        |                     | 0.09            | π                 |
| Band 3   | 2.0                    | 1.8-2.6             | 1.67            | π                 |
|          |                        |                     | 1.97            | σ                 |
|          |                        |                     | 2.17            | π                 |
|          |                        |                     | 2.26            | σ                 |
| Band 4   | 4.2                    | 3.4-4.8             | 3.29            | σ                 |
|          |                        |                     | 3.45            | π                 |
|          |                        |                     | 3.76            | σ                 |
|          |                        |                     | 4.03            | σ                 |
|          |                        |                     | 4.40            | σ                 |
|          |                        |                     | 4.52            | π                 |
|          |                        |                     | 4.88            | σ                 |
|          |                        |                     | 5.07            | π                 |
| Band 5   | 5.6                    | 5.8                 | 5.55            | σ                 |
| Band 6   | 6.6                    | ~6.4-7.6            | 6.17            | σ                 |
|          |                        |                     | 6.43            | σ                 |
|          |                        |                     | 7.17            | σ                 |
| Band 7&7’| 8.9                    | ~9.6                | 8.36            | σ                 |
|          |                        |                     | 8.68            | σ                 |
|          |                        |                     | 8.83            | σ                 |
|          |                        |                     | 9.86            | σ                 |
| Band 8   | 10.0                   | 10.6                | 10.9            | σ                 |
|          |                        |                     | 11.06           | σ                 |
| Band 9   | 11.8                   | 12.6                | 12.55           | σ                 |
|          |                        |                     | 13.03           | σ                 |
| Band 10  | 14.6                   |                     | 14.29           | σ                 |
|          |                        |                     | 15.15           | σ                 |
|          |                        |                     | 16.14           | σ                 |
|          |                        |                     | 17.10           | σ                 |
|          |                        |                     | 17.6            | σ                 |
The relative positions measured in the present work are in reasonable agreement with the ones determined by the photoemission experiment in condensed phase [18]. This result is consistent with the findings of the comparison of the energy loss spectra [13] and is due to the fact that C_{60} molecules weakly interact in the solid. Vos et al. [6] have reported a binding energy spectrum of a C_{60} thin film measured in a high energy transmission (e,2e) experiment integrated over all the momenta \( q = k_0 + (k_0 + k_b) \) of the target electron before the collision between 0 and 2.5 a.u.. In the present experiment we have measured the binding energy spectra of C_{60} at four different \( \theta_b \)'s, namely 60, 80, 100 and 120°. The sum of our spectra, which are normalized to each other, is compared with the spectrum measured by Vos et al. in figure 2.b. There is a good agreement between the two spectra as for the position of the bands, with the present data characterized by a slightly better energy resolution, but the relative intensity of the bands is quite different. This can be explained considering that the present measurements map a smaller region of the momentum \( q \), extending from about 0.4 to 0.9 a.u., compared to the one on the thin film [6] experiment. According to the calculation of the spherical averaged momentum densities reported in figure 2 of Vos et al. [6] the first two \( \pi \) bands have a quite large intensity in the \( q \) region measured in this work, while the bands at IP > 10 eV display a large fraction of their intensity outside this region. This explains the agreement between the two spectra of figure 2.b in the low binding energy region and the quite different intensities in the higher energy region.

The TDCS of the HOMO and HOMO-1 states are shown in figure 3, where they are compared with the calculations. The two TDCS are reported on the same relative scale of counts, via the binding energy spectrum of figure 2. The TDCSs under asymmetric conditions are characterized by the presence of two lobes [1]. The first one, oriented nearly in the direction of \( \mathbf{K} \), is associated with a binary collision of the incident electron, and it is indeed named as ‘binary peak’. The second peak, near the opposite direction, -\( \mathbf{K} \), is known as the recoil peak and it is commonly associated with a backscattering mechanism. The relative intensity of these lobes, their widths and positions with respect to \( \pm \mathbf{K} \) are the observables which provide the information on the dynamics of the ionizing process. The measurements have been concentrated on the binary region because the measured recoil/binary ratio in the \( \pm \mathbf{K} \) direction gave 0.1±0.1, consistent with the expected vanishing recoil peak intensity predicted by the theory. The measured angular distributions of both the HOMO and HOMO-1 bands have a maximum at around \( \theta_b = 87° \), that is about +10° away from the \( \mathbf{K} \) direction. The ratio between the two TDCS is about 3 and the TDCS of the HOMO is broader than the one of the HOMO-1. The intensity ratio can be traced back to the number of electrons occupying the HOMO-1 (8+10) and HOMO (10) states. Different shapes of angular distributions can be explained by considering their momentum distribution \( |\psi(q)|^2 \). The electronic states also have an angular dependence. However, the final results must be averaged over all possible orientations of the molecule. Therefore in \( |\psi(q)|^2 \) the angular averaging is already performed. As we noted above from very general consideration, the HOMO state is characterized by the presence of two maxima. Our numerical calculations yield their position at q=0.66 a.u. and q=1.28 a.u.. The HOMO-1 state is characterized by the smaller value of the orbital angular momentum (\( \ell = 4 \)). Correspondingly, the maxima are shifted to lower values (q=0.51 a.u. and q=1.11 a.u.). These numbers are also consistent with momentum distributions obtained for the C_{60} film [6]. In order to qualitatively understand the angular dependence of the (e,2e) signal the kinematics of the experiment should also be taken into account. Only peaks at smaller values of momentum q are relevant in the present measurements, since other peaks lie outside the experimentally observed window of 0.4<q<0.9 a.u., where the smallest value of momentum is in the direction of \( \mathbf{K} \). The HOMO-1 state is peaked at the smaller values of q, thus electrons emitted from this state will be predominantly observed in a smaller angular interval around \( \mathbf{K} \). Reversely, for the HOMO state the peak is shifted towards higher values of q, attained for larger angular deviations (\( \theta_b \)) from the \( \mathbf{K} \) direction. Correspondingly, the angular distribution is
broader. As for the deviation of the binary peak position from the direction of the momentum transfer and even for the interpretation of the origin of the peak one should note here some differences between the atomic case and the case of a polarizable many-electron system: due to the dynamical screening effects caused by the valence-band electrons of the target, the interaction potential becomes frequency dependent and nonlocal [15]. In fact, as discussed in [15] within the jellium model the potential in an (e,2e) experiment is even geometry dependent.

5. Conclusions
This work reports some pioneering results on the investigation of the ionization of gas phase C_{60} with the (e,2e) technique. It is shown that (e,2e) measurements well reproduce the electronic structure which was established by previous measurements and calculations, mainly in condensed phase, confirming the weak interaction of C_{60} molecules in the solid [13, 6].

Figure 3. Angular distribution of the HOMO and HOMO-1 states compared with the calculations.
The TDCS of the HOMO and HOMO-1 orbitals have been described by calculations that account for ionic symmetry and electronic structure of C_{60}. The discussion of the differences observed in the comparison between calculations and experiment hints to the role of the screening and its consequences for the interactions between the continuum state electrons. This is the subject of ongoing work.

These first gas phase studies show that a detailed investigation of the dynamics of the electron impact ionization of this prototype molecule of fullerene compounds, which has shown intriguing relationship between dynamic and structure [19] can be undertaken. The comparison of gas phase and solid state studies is expected to help disentangle single molecule and condensed phase properties.

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