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Influence of many-electron effects in the C_{60} carbon K-shell absorption spectrum

P. Joyes
Laboratoire de Physique des Solides, Bâtiment 510, Université Paris–Sud, 91405 Orsay, France

R. J. Tarento
Laboratoire de Physique des Matériaux, 1 place Aristide Briand, 92195 Meudon, France

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In the first part of this work we develop a model describing the influence of many-electron effects in C_{60} K-shell photoemission (only the π valence electrons are taken into account). Then we extend this model to the calculation of the C_{60} K-shell absorption spectrum. We first determine a one-electron spectrum obtained by considering only direct transitions from the 1s to the unoccupied valence levels. This spectrum exhibits three main peaks. Then, following a previous Friedel's analysis, we add two kinds of many-electron effects. In the first step, we include the transitions with shake-off excitations. The obtained spectrum is similar to the one-electron spectrum for the positions and the relative intensities of the three peaks, however, a high-energy tail appears. In a second step we also include replacement transitions. Then the relative intensities of the three peaks vary and are in better agreement with experiment than in the one-electron spectrum. The differences with experiment which still remain are discussed.

I. INTRODUCTION

The discovery of a way to extract sufficient amounts of pure C_{60} and of other fullerenes (C_{70}, C_{84}, etc.) (Ref. 1) has stimulated a variety of experimental and theoretical studies of the crystalline carbon phases obtained by condensing these molecules. The field of spectroscopic studies has been particularly active. Experiments using a primary photon beam have been performed both in the x-ray range (XANES: x-ray-absorption near-edge structure)[2–4] or 1s (or K) photoemission[5] and in the UV or optical range.[1,6,7] Simultaneously, other works employing primary electron beams were achieved in the high-energy range (EELS: electron-energy-loss spectrometry) (Refs. 8–12) or in the low-energy range.[13] Recently, experimental works using different techniques have been published. A high-resolution Auger spectrum, corresponding to the K-valence, valence transition, has been obtained by Lof *et al.*[14] (primary excitation ~1.5-keV photons) and x-ray K-emission spectra[15,16] (primary excitation ~4-keV electrons) have also been measured. Since the growth of high-quality C_{60} epitaxial layers (on GeS) was successful, it becomes feasible[17] to apply the KRIPES technique ($k_{\parallel}$-resolved photoelectron spectroscopy) to investigate the dispersion curves in solid C_{60} for the bands near the Fermi level corresponding to the highest occupied and lowest unoccupied molecular orbitals (HOMO and LUMO).

From a theoretical point of view, one may say that a one-electron description often allows us to understand the mean features of the experimental data. This has been applied in the interpretation of some spectra related to the isolated molecule,[2,18] or to various C_{60} solid phase studies.[19] We will come back to these works later in the discussion of our parameters. In this paper we also use a one-electron approach as the first step of our calculation. Then we go beyond this approximation by analyzing the dynamical screening effects (also called many-electron effects) which may lead to important deviations with respect to the one-electron models. We will concentrate on transitions where a 1s level is involved, and therefore we will not consider the UV or visible range. Our results will be compared to various experimental data. In Sec. II we introduce our model and recall the main results obtained in the 1s photoemission case.[20] In Sec. III we extend our model to the more complex case of 1s absorption, where a comparison to XANES or EELS spectra is possible. Physically, the main difference between the processes described in Secs. II and III is that, in photoemission, the transiting electron leaving the 1s level goes onto a free external level, while in absorption it goes onto a C_{60} valence level where it participates in the dynamical screening.

Dynamical screening effects and their influence on the various kinds of spectra were first studied for the bulk about 20 years ago.[21–26] In the literature these works were named MND theories (from Mahan[21] and Nozières and de Dominicis[22]). Other important papers on this subject are also due to Friedel.[27,28] It was shown that many-electron effects were responsible for the asymmetry of both discrete x-ray line and photoemission deep-level line spectra.[29] They also explained edge singularities in deep-level absorption or emission spectra.[30,31] We will come back to some of these bulk results below. It can be mentioned that in some systems a pure MND-like description has been criticized and, for example, in the interpretation of alkali-metal spectra it seems that the influence of charge-density waves must be added to the model.[32] Nevertheless, the MND-like models are still often used for explaining various features of the experimental spectra.[33,34]

More recently theoretical studies have been extended to systems with a finite number of electrons.[35,36] The importance of such works is obvious now that experiments have begun on these systems, particularly Au_{55} (Ref. 37)

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and, as we saw above, C_{60}. However, there is also a more fundamental interest. When studying finite systems the asymptotic approximation, which is necessary for simplifying the bulk problem can be abandoned. Then our spectra are no longer limited to an energy range close to the edge. Among works concerning finite systems we will often refer to the extensive paper of Von Barth and Grossman,[36] who studied aggregates with 80, 100, and 120 electrons in the photoemission and emission cases. We have also published a study on linear molecules with up to 30 electrons.[37]

Let us also mention that, for sake of simplicity, we will limit ourselves to π electrons; consequently, only a part of the experimental spectra will be discussed.

II. THE MODEL: APPLICATION TO PHOTOEMISSION

In a photoemission experiment, where a photon with energy ε_{ph} ejects a $1s$ electron with energy ε_{1s}, if we suppose that the valence electrons are in the ground state before and after the transition, the photoemitted electron energy will be

$$\varepsilon_m = \varepsilon_{\text{ph}} + \varepsilon_{1s} + \varepsilon_i^0 - \varepsilon_f^0 \ , \tag{1}$$

where $\varepsilon_i^0(\varepsilon_f^0)$ is the energy of the 60 π electrons in the initial (final) ground state (ε_{1s}, ε_i^0, and ε_f^0 are negative energies with $\varepsilon_f^0 < \varepsilon_i^0$). When many-electron effects are included, the spectrum is no longer limited to one peak at energy ε_m, but on the low-energy side of this peak satellite structures appear. It can be shown that, in a good approximation,[28] the spectrum intensity at energy $\varepsilon_m - E$ is given by

$$\sigma_{\text{ph}}(\varepsilon_m - E) \propto \omega^2 \sum_f |\langle \Psi_i^0 | \Psi_f \rangle|^2 \delta(\varepsilon_f - \varepsilon_f^0 + E) \ , \tag{2}$$

where $\omega = \langle \phi_{1s} | \mathbf{e} \cdot \nabla | \phi_{\text{free}} \rangle$ is a matrix element between the initial and final states of the transiting electron, $\mathbf{e}$ is the direction of the electric field, $|\Psi_i^0\rangle$ and $|\Psi_f\rangle$ are the 60-electron wave function of the initial ground state and of one of the final states. From formula (2), we see that an excitation of the 60-electron system to a final state with energy ε_f contributes to the satellite spectrum at energy $\varepsilon_m - E = \varepsilon_m - (\varepsilon_f - \varepsilon_f^0)$.

In this kind of calculation the difficulty comes from the huge number of possible final states: $(C_{60}^{30})^2 \sim 10^{34}$. Thus we have to remove some of them under the control of the completeness criterion, i.e., by calculating for a particular choice of "f" states:

$$\sum_f |\langle \Psi_i^0 | \Psi_f \rangle|^2 \tag{3}$$

and by verifying that the sum (3) is close to 1. In all the calculations that are presented here, the completeness criterion was fulfilled with a precision better than 10^{-4}.

Let us now shortly describe how each overlap term appearing in formula (2) is obtained. By separating the two spin directions, we write

$$\langle \Psi_i^0 | \Psi_f \rangle = \langle \Psi_i^0 | \Psi_f \rangle_\uparrow \langle \Psi_i^0 | \Psi_f \rangle_\downarrow \ . \tag{4}$$

Let us call $\{if\uparrow\} = 1f\uparrow, 2f\uparrow, \ldots, 30f\uparrow$ the set of 30 numbers (with $if\uparrow \le 60$) which labels the one-electron wave functions occupied in $|\Psi_f\rangle_\uparrow$; then we get

$$\langle \Psi_i^0 | \Psi_f \rangle_\uparrow = \begin{vmatrix} \langle \phi_1 | \phi'_{1f\uparrow} \rangle & \langle \phi_1 | \phi'_{2f\uparrow} \rangle & \cdots & \langle \phi_1 | \phi'_{30f\uparrow} \rangle \\ \langle \phi_2 | \phi'_{1f\uparrow} \rangle & \langle \phi_2 | \phi'_{2f\uparrow} \rangle & \cdots & \langle \phi_2 | \phi'_{30f\uparrow} \rangle \\ \vdots & \vdots & & \vdots \\ \langle \phi_{30} | \phi'_{1f\uparrow} \rangle & \langle \phi_{30} | \phi'_{2f\uparrow} \rangle & \cdots & \langle \phi_{30} | \phi'_{30f\uparrow} \rangle \end{vmatrix} , \tag{5}$$

where $|\phi_i\rangle$ ($|\phi'_i\rangle$) are the one-electron molecular levels, with $i = 1, \ldots, 60$, in the initial (final) state. They are obtained by diagonalizing the Hückel Hamiltonian (transfer integral β between nearest neighbors). In the initial state all the sites of the polyhedral C_{60} shape (truncated icosahedron) are equivalent; in the final state, the Hückel matrix is the same except for one site, say site 1, where a negative diagonal term Δ is added. We will see later how β and Δ have been determined.

It is interesting to make a brief discussion of the overlap term between ground states, $\langle \Psi_i^0 | \Psi_f^0 \rangle$, by comparing it to the bulk result. In this last case and if we only include s scattering, Anderson[23] shows that

$$|\langle \Psi_i^0 | \Psi_f^0 \rangle_\sigma|^2 \sim N^{-\alpha(\delta/\pi)^2} \ , \tag{6}$$

where N is the number of sites which tends to infinity for the bulk, δ the phase shift at the Fermi energy, and α a coefficient which depends on the dimensionality of the problem. Is it possible to propose a similar formula for our 60-electron case? We already answered this question positively in a previous study on linear chains ($\alpha = 1$),[38] where it was relatively easy to define δ since it clearly appeared in the final-state molecular wave functions:

$$|\phi'_i\rangle_{\text{ring}} \propto \sum_n \cos[k_i(n-1) + \delta_i] |n\rangle \ . \tag{7}$$

In the C_{60} structure it is no longer possible to write simple expressions such as (7), and δ must be defined otherwise. We can introduce it by using the populations $n_{i\sigma}^1$ and $n_{f\sigma}^1$ of spin-σ electrons on site 1 in the final and initial ground states, and by extending to our case the Friedel sum rule

$$\frac{\delta}{\pi} = n_{f\sigma}^1 - n_{i\sigma}^1$$

strictly valid for infinite media. For $\Delta = 2\beta$ we then obtain $\delta/\pi = 0.30$ (from $n_{f\sigma}^1 = 0.798$, $n_{i\sigma}^1 = 0.5$). Our direct calculation for the overlap gives

$$|\langle \Psi_i^0 | \Psi_f^0 \rangle_\sigma|^2 \sim 0.88 \ .$$

Then, by using (6) we obtain $\alpha \sim 0.34$, which is close to the expected value ($\alpha = \frac{1}{3}$) (Ref. 23) for a three-dimensional problem. Hence there is a good agreement which shows that formula (6) can be applied even for finite systems.

The photoemission spectrum obtained from formula (2) and its comparison to experiment is given in Ref. 20. Two experimental features were used for fixing our parameters. We found $\beta \sim -1.05 - 1.15$ eV, and $\Delta/\beta = 2$.

Then other features concerning the positions, widths, or intensities of the experimental peaks[5] were well reproduced.[20]

A theoretical analysis of the three π photoemission peaks[20] shows that they are due mainly to one-electron-hole pair excitations. This result agrees with the Von Barth and Grossman conclusions (Table 1 of Ref. 36). A rather surprising result is that the largest satellite peak is mainly due to a high-energy "$1 \rightarrow 31$" electron-hole pair (1: bottom of the band; 31: LUMO). Physically, this excitation is preferred because all of the final occupied one-electron states are delocalized, and therefore present a better overlap with the delocalized corresponding initial states.

III. APPLICATION TO 1*s* ABSORPTION

Let us now consider the transition from a 1*s* level to a π level of the valence band. The absorption probability will occur for energies larger than $\varepsilon_{\min}$ with

$$\varepsilon_{\min} = \varepsilon_{\mathrm{LUMO}} - \varepsilon_{1s} - \tilde{\varepsilon}_1^0 + \tilde{\varepsilon}_f^0 , \tag{8}$$

where $\tilde{\varepsilon}_i^0$ and $\tilde{\varepsilon}_f^0$ are the energies of 61 electrons in the initial and final ground states. An important element of the discussion is the "static spectrum" given by the one-electron free levels of the final state. This spectrum, smoothed by Gaussian (of 0.2 $|\beta|$ width, a value commonly used in this type of study[2,39]), is given in Fig. 1.

Now let us consider how many-electron effects can be introduced. We will describe direct transitions as transitions contributing to the static spectrum; they can be labeled by k ($k=31,\ldots,60$) for a $1s \rightarrow k$ transition. Following Friedel,[28] we will associate two kinds of many-body effects to each k direct transition. First, each of these transitions can be accompanied by shake-off electron-hole pairs. For describing this phenomenon, which is reminescent of the photoemission case in Sec. II, we will write [as in formula (2)] a $\sigma_{k,1}(E)$ contribution to the absorption spectrum given by

$$\sigma_{k,1}(E) \propto \omega_a^2 \sum_f |\langle \tilde{\Psi}_{i,k}^0 | \tilde{\Psi}_f \rangle|^2 \delta(\tilde{\varepsilon}_f - \tilde{\varepsilon}_f^0 + E) , \tag{9}$$

where $E > 0$ is the energy distance to $\varepsilon_{\min}$; $|\tilde{\Psi}_{i,k}^0\rangle$ is a 61-electron initial state, where 60 electrons are in the ground state and one in state k; $|\tilde{\Psi}_f\rangle$ is any one of the 61-electron final states with energy $\tilde{\varepsilon}_f$; and ω_a is a matrix element of $\mathbf{e}\cdot\nabla$ between the 1*s* and valence levels that we will suppose is k independent. The k direct transition is one of the terms included in sum (9); we will call the corresponding final state ket $|\tilde{\Psi}_{f,k}^0\rangle$ (60 electron in the final ground state plus one in state k). The total spectrum is obtained by summing over all the k values:

$$\sum_{k=31,\ldots,60} \sigma_{k,1}(E) , \tag{10}$$

and it is given in Fig. 2.

For energies $E \lesssim 2\beta$, it looks like the one-electron spectrum, since peaks 1, 2, and 3 of Fig. 1 have almost the same position and relative intensities. For $E > 2\beta$ we note the presence of a high-energy tail which is a many-electron effect.

The second kind of terms to be introduced are due to replacement transitions. Friedel[28] showed that these terms were important in the bulk case. Let us briefly recall that, for an *s* hole, the bulk absorption spectrum can be written

$$\sigma(E) \propto \left[\frac{E}{\xi_0}\right]^{-(\delta/\pi)^2} \left[\frac{E}{\xi_0}\right]^{-(2\delta/\pi)} , \tag{11}$$

where E has the same meaning as before, ξ_0 is an energy of the order of the Fermi energy, and δ is the phase shift. The first factor corresponds to the results of the previous paragraph, i.e., to direct transitions with shake-off excitations, while the second factor is due to replacement transitions. We note that, as δ can be of any sign, the re-

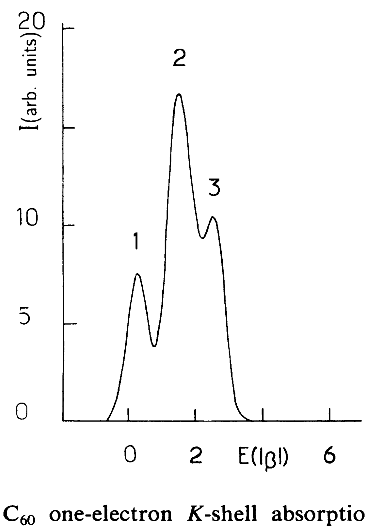

FIG. 1. C_{60} one-electron K-shell absorption spectrum (π valence levels). The energy E is the distance to the edge [given by formula (9)] in $|\beta|$ units.

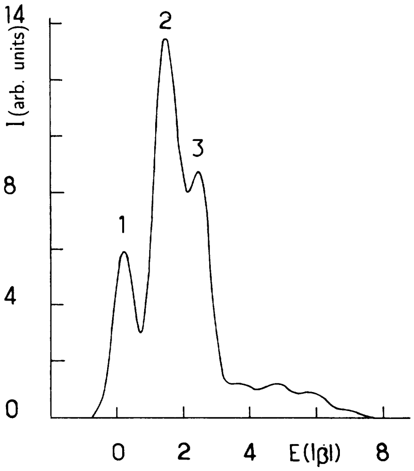

FIG. 2. C_{60} K-shell absorption spectrum (π valence levels) when shake-off excitations are included (same definition as in Fig. 1 for E). We note the presence of a high-energy tail while the relative intensities of the three peaks are almost the same as in Fig. 1. The integrated absorption intensity is the same as in Fig. 1.

placement transitions can lead to an absorption spectrum with a peaked ($\delta > 0$) or rounded edge ($\delta < 0$).[21–28] In a simple scheme, a replacement transition can be (imperfectly) viewed as the creation of one or various electron-hole pairs in the valence band and the occupation of one of the holes by the transiting electron. In what follows we will limit ourselves to replacement transitions with only one $k' \rightarrow k$ electron-hole pair, which are the most probable.[36,20] If we remember that the k' hole of the $k' \rightarrow k$ pair is finally filled by the transiting electron, we observe that a $k' \rightarrow k$ replacement transition simply leads to the $|\tilde{\Psi}^0_{f,k}\rangle$ state already encountered. Hence there are various ways to arrive to this state: by a direct transition, or by $k' \rightarrow k$ replacement transitions. For estimating the overlap terms due to replacement transitions, we will suppose that we can disregard the transiting electron and simply write that the terms $\langle \tilde{\Psi}^0_{i,k} | \tilde{\Psi}^0_{f,k} \rangle$ (direct transition) and $\langle \tilde{\Psi}^0_{i,k} | \tilde{\Psi}^0_{f,k} \rangle_{k'k}$ ($k' \rightarrow k$ replacement transition) are proportional to their 60-valence electron counterparts:

$$\langle \tilde{\Psi}^0_{i,k} | \tilde{\Psi}^0_{f,k} \rangle \sim a \langle \Psi^0_i | \Psi^0_f \rangle \ , \tag{12}$$

$$\langle \tilde{\Psi}^0_{i,k} | \tilde{\Psi}^0_{f,k} \rangle_{k'k} \sim a \langle \Psi_i | \Psi_{f(k' \rightarrow k)} \rangle \ , \tag{13}$$

where $|\Psi_{f(k' \rightarrow k)}\rangle$ is a 60-electron final state with one $k' \rightarrow k$ electron-hole pair. The two members of Eq. (12) are known, so it is easy to obtain the a proportionality factor and to verify that it is almost k independent. Then, taking into account replacement transitions will lead us to replace $\langle \tilde{\Psi}^0_{i,k} | \tilde{\Psi}^0_{f,k} \rangle$ in sum (9) with

$$a \langle \Psi^0_i | \left\{ | \Psi^0_f \rangle + \sum_{k'} | \Psi_{f(k' \rightarrow k)} \rangle \right\} \ . \tag{14}$$

We obtain the spectrum $\sigma(E)$ given in Fig. 3.

It is worth noting that the use of formula (14) results in an increase of some peaks and a decrease of others, with a global compensation for the integrated intensity. Here we observe that the differences from Figs. 2 to 3 are a decrease of peak 1, an increase of peak 2, and the intensities of peak 3 and the high-energy tail being almost conserved.

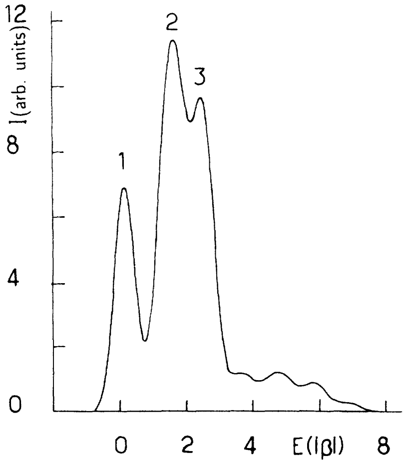

FIG. 3. C_{60} K-shell absorption spectrum (π valence levels) when shake-off excitations and replacement transitions are taken into account (same definition as in Fig. 1 for E). We note that the relative intensities of the three peaks are different from those of Fig. 2. The integrated absorption intensity is the same as in Figs. 1 and 2.

IV. DISCUSSION AND COMPARISON TO EXPERIMENT

When reporting their EELS results,[11] Sohmen, Fink, and Krätshmer noticed that the various experimental C_{60} K-shell absorption spectra were in good agreement, even when different excitation beams were used (EELS or XANES).[10,2]

Most of the authors attribute the first low-energy three peaks to π transitions, while the σ contribution begins for higher energies. Let us focus on some features of the various π spectra. The energy distances between peaks 3 and 1 and between peak 3 and 2 are, respectively, $\Delta_{21} \sim 1.6$ eV and $\Delta_{32} \sim 2$ eV. The relative intensities in Refs. 11, 2, or 10 are, respectively, $I_{12} \sim 1.75$, 1.48, and 1.08, and $I_{23} = 1.5$, 1.2, and 1.3 (peak 1 is larger than 2, which is larger than 3). Only in the work of Shinohara (XANES) (Refs. 3 and 4) are the relative intensities inverted: I_{12} and $I_{23} \lesssim 1$.

As we can see in Figs. 1–3, the global aspect of our spectra roughly agree with experiment, since we obtain three peaks due to the grouping of one-electron molecular levels, respectively: ($5t_{1u}, 2t_{1g}$), ($8h_g, 5t_{2u}, 5h_u, 5g_g$), and ($5g_u, 2t_{2g}$) levels.[40,41] When we consider the final results of Fig. 3 (with $\beta = -1.1$ eV, $\Delta/\beta = 2$), various characteristics agree with experiments: $\Delta_{21} \sim 1.65$ eV and $I_{23} \sim 1.2$; however, two other features, $I_{12} \sim 0.6$ and $\Delta_{32} \sim 1$ eV, are different. We note that by introducing many-electron effects we obtain a better agreement than with the one-electron model (since, in Fig. 1, $I_{12} \sim 0.45$), but we do not reach the experimental ratio. It is also worth mentioning that the high-energy tail found in this work (Figs. 2 and 3) cannot be observed since it falls in the range of σ transitions and then is hindered by them.

Let us discuss our parameters. The $\Delta/\beta = 2$ value is obtained from the photoemission experimental spectrum, and more precisely from the ratio between the intensities of the main peak and the π satellite structure. This Δ/β value leads (as we saw above) to a phase shift $\delta = 0.3\pi$ which is close to the values introduced by Von Barth and Grossman[36] for photoemission in alkali metals. Our β parameter is comparable to the one used by Terminello *et al.*[2] (~ -1.3 eV) in their comparison of the one-electron spectrum to the experimental K-absorption spectrum. Such values (~ -1 eV) also appear in the description of the cohesive energy of various aromatic molecules.[42] In a recent theoretical study of the band structure of C_{60} and alkali-metal-doped C_{60},[19] Salpathy *et al.* employed $\beta \sim -2.59$–2.78 eV (β is different for a pentagonal or hexagonal bond). These authors also determine β values for the hopping between neighboring C_{60} in solid structures, and they give tight-binding descriptions of unidirectional, bidirectional, and quadridirectional structures. In the case of unidirectional fcc structure they compare their results to the *ab initio* LDA LMTO (local-density approximation linear-muffin-tin orbitals). Various characteristics such as the dispersion curve in the conduction (LUMO) band, the density of states in this band, and the various bandwidths are similar in the two descriptions. The quasiparticle approach developed by Shirley and Louie[43] shows that, in agreement with Salpathy *et al.*,[19] the important banding effects are restricted to neighboring C_{60}. Moreover the LUMO bandwidth used by Lof *et al.*[14] in an analytical calculation of Frenkel-type molecular excitons are of the same order of magnitude as in Ref. 19. Then, following this work, we are led to discuss how our results would be changed by a $|\beta|$ increase of about a factor of 2. We observe that the situation is globally equivalent, since the agreement with experiment is better for Δ_{23} but worse for Δ_{12}. This means that this simple homothetic correction of the energy scale is not sufficient. We have to add new elements in our oversimplified one-electron step. For example, we have supposed that the one-electron atomic basis was orthonormalized. This point can be improved by taking into account an overlap between next-nearest neighbors. Then it is well known[42] that for the free levels the energy scale is dilated toward high energies in a nonuniform way, which would result, as expected, in an increase larger for Δ_{32} than for Δ_{12}.

Let us examine the peak intensities. An improvement of our results can be brought about by considering the variation with k of the ω_a matrix element between the 1s and k valence levels. This might be the key to understanding the surprisingly high intensity of peak 1. Including this factor is beyond the scope of this paper, and we will examine it in a future work.

We also note that our technique can be extended without any formal difficulty to any transition where a 1s C level is involved. This is the case of the *KVV* Auger and *K*-emission processes, where experimental data are available.[14–16]

To conclude one may say, as we do in Sec. II, that the introduction of many-electron effects allows a complete understanding of the C_{60} photoemission satellite structure.[5] In the case of the *K*-shell absorption spectrum it provides some improvements with respect to a one-electron description; however, some features of the experimental spectra are still unexplained.

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