PHYSICAL REVIEW B VOLUME 48, NUMBER 19 15 NOVEMBER 1993-I

C_{1s} shakeup spectrum of C_{60}: Global charge-transfer satellites and their relation to the x-ray threshold singularities in macroscopic systems

Christer Enkvist and Sten Lunell
Department of Quantum Chemistry, Uppsala University, Box 518, S-751 20 Uppsala, Sweden

Bo Sjögren
Department of Physics, Linköping University, S-581 83 Linköping, Sweden

Svante Svensson, Paul A. Brühwiler, Anders Nilsson, Andrew J. Maxwell, and Nils Mårtensson
Department of Physics, Uppsala University, Box 530, S-751 21 Uppsala, Sweden

(Received 12 July 1993)

The C_{1s} core photoelectron shakeup spectrum of C_{60} has been studied experimentally and theoretically. It is found that the lowest shakeup satellites correspond to global charge-transfer excitations which move charge from the opposite side of the fullerene cage to the core-hole region, while more localized excitations give rise to higher-energy satellites. This finding is in accord with a generalized version of the Mahan-Nozières–de Dominicis model of core excitation, in which a local dielectric response is included with the original adiabatic contribution.

I. INTRODUCTION

Core photoelectron shakeup spectra of free molecules provide unique and detailed information on the screening of the core hole that is created in the photoionization process. In particular, the use of high-resolution x-ray photoelectron spectroscopy (XPS), incorporating a monochromatization of the exciting x rays, has opened up the possibilities of core photoelectron shakeup spectra in great detail.

The shakeup spectrum gives information on the excited state of the C_{1s} ionized molecule. It is therefore interesting to compare such a spectrum with the optical-absorption spectrum or the inelastic electron energy-loss spectrum (IES), where information is obtained on the excited states of the neutral molecule. However, it is important to point out a fundamental difference between these experiments. The C_{60} molecule is highly symmetric, all carbon atoms being equivalent. The optical transitions are governed by dipole selection rules in this high symmetry. The intensities in a shakeup spectrum, on the other hand, obey a monopole selection rule. In a localized core-hole description, calculations for the core ionized species are performed in a lower symmetry than in the neutral ground state. This implies that the monopole selection rule, when applied to a molecular system, has to be implemented using the reduced symmetry of the localized core-hole ionized system.

The first assignments of core photoelectron shakeup spectra of free molecules were obtained using *ab initio* quantum-mechanical calculations[1–3] and were limited to molecules with only a few atoms. For unsaturated organic molecules it has, however, been shown that it is possible to assign shakeup spectra of quite large molecular systems using semiempirical quantum-mechanical methods such as the Pariser-Parr-Pople configuration interaction,[4] complete neglect of differential overlap including configuration interaction, and intermediate neglect of differential overlap including configuration interaction (INDO/CI) (Refs. 5–12) calculation schemes. Notably, the $\pi \rightarrow \pi^*$ valence region of the spectra has been shown to be well described using semiempirical methods.

The C_{60} molecule has been the object of a large number of photoelectron spectroscopic studies in the last two years,[13–19] spurred by the recent availability of macroscopic quantities of purified material.[20] The similarity of the overall C_{1s} shakeup structure of C_{60} to that of smaller aromatic molecules like benzene has drawn attention recently.[21]

In this paper, we will show that a combined experimental and theoretical study of the shakeup processes in core ionized C_{60} can give further understanding of general charge transfers in large aromatic systems. We find that the charge rearrangements accompanying the low-lying shakeup excitations induced by the core ionization possess, to a considerable extent, a global character, i.e., charge is moved over large distances. Excitations of primarily localized character, i.e., charge transfers mainly within the rings containing the core hole, appear only at higher shakeup energies. We will also discuss shakeups at a much higher energy, corresponding to the correlation (or plasmon) satellite region around 25 eV, and compare them with the benzene shakeup spectrum.

The appearance of global shakeup excitations suggests that C_{60} could be used as a model molecule for larger systems such as graphite. We consider this extension to the case of graphite, and show that there is a direct link between the present results and the well-known Mahan-Nozières–de Dominicis theory of x-ray singularities.

II. EXPERIMENT

The experimental solid C_{60} spectra were taken from condensed films using monochromatized Al $K\alpha$ x rays from a rotating anode, in a high-resolution photoelectron

0163-1829/93/48(19)/14629(9)/$06.00

spectrometer in Uppsala.[22] Pure C_{60} was obtained from UCLA (Ref. 23) and a commercial source. A thick film was deposited on a Mo(110) surface by evaporation from a Ta crucible, which was heated radiatively to a temperature of approximately 300±50 °C. Evaporation temperatures were monitored using a thermocouple in contact with the crucible. The film thicknesses were estimated by studying the carbon and substrate core lines. Evaporations were made at a pressure of 3×10^{-9} Torr, while the base pressure when the spectra were taken was 5×10^{-10} Torr. Subsequent measurements taken at lower pressures show no differences. All spectra shown here have been normalized to the main line intensity.

Electron energy-loss spectra were acquired on the same instrument using a monochromatized electron gun in the specular geometry at an incident angle of 45°. The initial electron energy was chosen to be 1200 eV, the kinetic energy of an electron ejected from the C_{60} C_{1s} level. In this way it was possible to obtain information on extrinsic effects in the shakeup satellite spectrum. The IES spectrum is similar to a recent gas phase measurement with an incident energy of 1 keV.[24]

Finally, a good approximation of the molecular spectrum was obtained using a dilute concentration of C_{60} isolated in Xe. To obtain such films, the substrate was cooled to 30±10 K and the preparation chamber was held at 3.5×10^{-7} Torr of Xe during C_{60} evaporation at a rate of ~0.14 saturated layers/min. Xe was chosen for its high melting point, lack of interfering core lines, and large band gap,[25] which encompasses most of the π-like manifold[26] including the highest occupied molecular orbital (HOMO) and the next two occupied bands, the lowest unoccupied molecular orbital (LUMO), and all of the bound states at higher energy. Thus the shakeup spectrum should be minimally influenced by hybridization effects, and inelastic scattering induced by the matrix has a threshold of 8 eV. The latter effect is important to consider, as shown by a study of a similar energy range for benzene[27] in the gas phase.

III. COMPUTATIONAL DETAILS

The calculations were performed using the INDO/CI approximation, using the equivalent core description for the core ionized species. The wave functions were computed with the ZINDO program[28–30] and by a program package by Freund and Bigelow.[4] Calculations were performed on two levels: (i) an uncorrelated initial state coupled with a final-state CI including only single excitations; and (ii) a correlated initial state (including singly and doubly excited configurations) and singly and doubly excited states in the final-state CI.

The first option allows for an almost exhaustive account of the singly excited space, whereas the second includes the effects of the initial-state correlation, while the available space for the singly excited states is reduced. In the first case the shakeup intensities were calculated using the SHAKEINT program[31] with wave functions generated by the ZINDO program. In the second case we used a modified version of Freund's program, allowing also for the use of a correlated initial state.[12] The shakeup spectra calculated by the two options were in all cases very similar, indicating that initial-state correlation is unimportant in the studied shakeup energy range for these systems. The results reported in this paper will mainly be from calculations using single excitations in the final-state CI and an uncorrelated initial state.

IV. RESULTS AND DISCUSSION

As noted in the Introduction, the C_{60} molecule is highly symmetric (I_h symmetry), which has the consequence that most of the energy levels are degenerate. The HOMO is fivefold degenerate, and the LUMO is threefold degenerate. Upon core ionization, the symmetry is enormously reduced, since the core hole can be considered to be localized. The only symmetry element that persists in the core ionized molecule is one plane of reflection yielding C_s symmetry, and consequently the energy levels are no longer degenerate (see Fig. 1). The MO's are in this case classified as symmetric (a') or antisymmetric (a'') with respect to reflection in the mirror plane which contains the core ionized atom and bisects the molecule. In the following discussions of the shakeup spectra we will use both the symmetry of the neutral molecule and the symmetry of the ionized species in the labeling of the molecular orbitals in order to derive a more detailed picture of the excitations involved in the shakeup process.

A. Experimental results

In this section we will discuss the low-energy shakeup ($\Delta E \leq 10$ eV) which we treat theoretically in Sec. IV B.

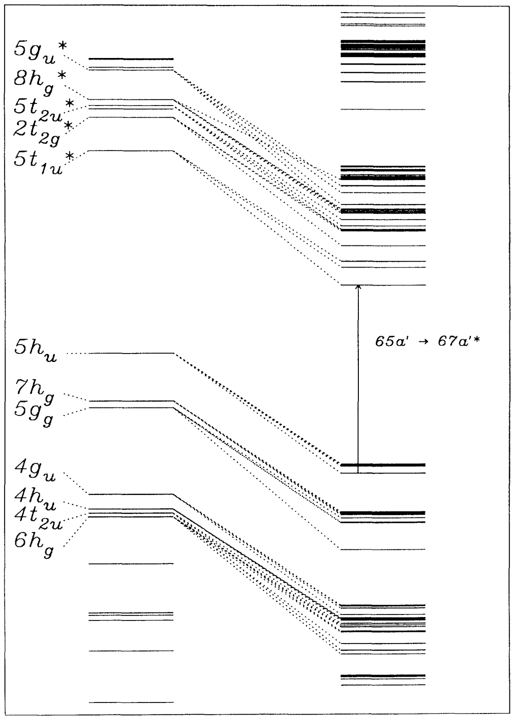


FIG. 1. Molecular energy levels of C_{60}, before (left-hand side) and after (right-hand side) core ionization.

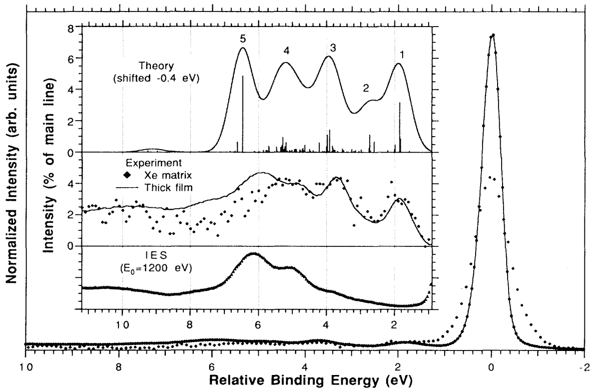


FIG. 2. Experimental and theoretical shakeup spectra of C_{60}.

In Sec. IV C we discuss the higher-energy excitations.

The results from the high-resolution XPS study of C_{60} can be found in Fig. 2 and in Table I. The spectrum has been recorded with the C_{60} condensed into a thick film and with C_{60} in a Xe matrix. The two samples give rise to similar spectra, although the Xe matrix isolated C_{60} spectrum has lower intensity in the shakeup energy range of 5–10 eV from the main line.

In Fig. 2 four structures are immediately noticeable (at 1.8, 3.7, 4.8, and 5.9 eV). We also note a shoulder at 2.9 eV. Two broad structures can also be found at higher energies, one at 7.4 eV and the other at 9.7 eV. Structure 8 in Ref. 13, at approximately at 15 eV from the main line, is not reproduced in our data as a strong feature (see Fig. 5), nor is it apparent in Fig. 2 of Ref. 21; otherwise, there is a good correspondence between our high-resolution data and those in Ref. 13.

In Fig. 2, an IES spectrum is also inserted, from which it can be deduced that the first structure in the shakeup spectrum should be completely free from contributions due to inelastic scattering, and that the next two peaks will have relatively minor inelastic components. At 4.5–6.5 eV there is, however, a large contribution to the spectrum from the inelastic scattering, which, together with the results from the matrix isolation measurement, implies that the true shakeup intensity of the peaks at 4.8 and 5.9 eV of the thick film should be substantially less than what is found in the thick-film measurement. This is reminiscent of the case for benzene.[27]

B. Theoretical results

The theoretical shakeup spectrum of C_{60} is inserted in Fig. 2 and the results of the calculations are also displayed in Tables II–VI. From Fig. 2 one may conclude that the theoretical spectrum represents the shakeup satellites found in the experiment quite well. However, the calculated peak energies are somewhat too high; this shift, which increases with the energy, is a consequence of the limited CI space used and is unavoidable in calculations of this type.

The first peak in the theoretical spectrum of C_{60} is located at 2.2 eV and obviously corresponds to the lowest experimental peak at 1.8 eV. It derives most of its intensity from the $65a' \rightarrow 67a'^{*}$ excitation (see Table II). This excitation corresponds in the neutral molecule to the HOMO-LUMO excitation $5h_u \rightarrow 5t^{*}_{1u}$ (see Fig. 1).

The character of the $65a' \rightarrow 67a'^{*}$ excitation in C_{60} is illustrated in Fig. 3. From the figure it is seen that the $65a' \rightarrow 67a'^{*}$ excitation moves charge from one side of the molecule to the other. The charge is moved from the side furthest away from the core hole to the core-hole region. In particular, the neighbor atom of the core-hole site, bonded along the mirror-symmetry axis, gains charge. The core ionized atom itself, together with the two sites furthest away from the core hole in the two six rings, also gains significant charge by this excitation. This is typical of the alternation found in the charge distribution for aromatic systems after core excitation, for which every other atom characteristically gains and every other atom loses net charge.[32]

The intensity of the first peak in the experimental spectrum can thus be assigned to excitations originating from the HOMO and LUMO of the neutral molecule ($5h_u$ and $5t^{*}_{1u}$ in the symmetry of the neutral molecule). It can be noted that the $65a' \rightarrow 67a'^{*}$ excitation of the ionized species, which gives the main contribution to the intensity of the first peak, involves those orbitals in the originally degenerate $5h_u$ and $5t^{*}_{1u}$ sets which have the lowest energy, i.e., are most strongly perturbed by the core hole.

The assignments of the second, third, and fourth peak in the theoretical spectrum are much more complex than for the first peak since both the number of CI states giving intensity to the peaks and the number of excitations with large coefficients in the CI states have increased (see Tables III–V). In the scheme of the neutral molecule the excitations giving intensity to the second peak originate in the excitation between the $5h_u \rightarrow 5t^{*}_{2u}$ molecular

TABLE I. Intensities and energies in the experimental spectrum of C_{60} and the assignments made from the theoretical calculations.

Experimental			Theoretical	
Peak No. (in Fig. 2)	Energy (eV)	Excitation	I_h labeling	Energy (eV)
I	1.8	$65a' \rightarrow 67'^{*}_{a}$	$5h_u \rightarrow 5t^{*}_{1u}$	2.2
II	2.9	see Table II	$5h_u \rightarrow 3t^{*}_{2g}$	3.1
III	3.7	see Table III	see Table III	4.3
IV	4.8	see Table IV	see Table IV	5.7
V	5.9	$51a' \rightarrow 67a'^{*}$	$6h_g \rightarrow 5t^{*}_{1u}$	6.9

TABLE II. Analysis of the excitations in the most intense states contributing to peak 1 in the theoretical shakeup spectrum of C_{60}. Only CI coeff. ≥ 0.3 are included in the table.

State	Excitation	I_h labeling	CI coeff.	Energy (eV)	Intensity (%)
1	$53a'' \to 55a''^*$	$5h_u \to 5t_{1u}^*$	−0.81	2.22	0.87
	$65a' \to 67a'^*$	$5h_u \to 5t_{1u}^*$	0.35		
2	$65a' \to 67a'^*$	$5h_u \to 5t_{1u}^*$	0.74	2.25	3.19
	$53a'' \to 55a''^*$	$5h_u \to 5t_{1u}^*$	0.33		
	$54a'' \to 55a''^*$	$5h_u \to 5t_{1u}^*$	0.30		
3	$66a' \to 68a'^*$	$5h_u \to 5t_{1u}^*$	0.68	2.38	0.49
	$52a'' \to 55a''^*$	$5h_u \to 5t_{1u}^*$	0.52		
	$65a' \to 67a'^*$	$5h_u \to 5t_{1u}^*$	−0.31		

orbitals, whereas the excitations responsible for the intensity of the third and fourth peak belong to the $(5h_u, 7h_g, \text{and } 4g_g) \to (5t_{1u}^*, 5t_{2u}^*, 8h_g^*, \text{and } 5g_u^*)$ set of excitations. The general behavior of these peaks is that the charge, as in the case of the first peak, is moved over quite large distances, mainly from the back to the front but also in other patterns (e.g., from/to the core-hole region to/from the sides of the molecule). In the case of the fourth peak a nonnegligible contribution to the intensity comes from charge transfers within the two six-membered rings connected to the core hole. The main feature of the peak is, however, charge transfers over rather long distances.

The last major peak in the spectrum, at 6.9 eV is, as the first peak, possible to assign to a single excitation, the $51a' \to 67a'^*$ ($6h_g \to 5t_{1u}^*$ in the neutral molecule; see Table VI). In contrast to the first peak, this excitation not only moves the charge over large distances but redistributes the charge within the two six-membered rings connected to the core hole. The charge is mainly donated from the core hole towards the neighboring site along the symmetry axis and to the sites farthest away in the local ring system. The molecular orbitals involved in this, the $51a' \to 67a'^*$ excitation, are plotted in Fig. 4.

As seen above, it is possible to roughly divide the shakeup excitations into two groups: interring excitations, where the charge is moved over large distances, and intraring excitations, in which the charge is redistributed only within isolated subregions of the molecule. A typical such subregion of C_{60} is the three rings containing the core hole. Thus, the first states in the calculation, see Fig. 3 and Table II, are global interring transitions. As a contrast the peak at 6.9 eV in the experimental spectrum is seen to be connected to a typical local, intraring, almost benzenelike transition,[12] involving mainly the two six-membered rings which share the core hole (see Table VI and Fig. 4).

C. Higher-energy satellites

We now turn to the energy region beyond 10 eV from the main line, shown for C_{60} and benzene in Fig. 5. In the case of benzene, the region out to 30-eV relative binding energy has been presented previously, but not discussed.[27] For C_{60} this region has been measured in both the condensed[13] and gas[33] phases, and the structure near 28 eV attributed to plasmon excitations.

Aside from a small structure about 15 eV from the main line, the shakeup of C_{60} is dominated by a broad humplike structure centered at about 28 eV. This is quite similar in appearance on the low-energy side to a structure in the same energy region in the IES data, but has relatively greater intensity to higher binding energy. For gas phase benzene, also shown, the same energy region shows instead a very broad structure roughly centered at 30 eV. However, it is noteworthy that solid benzene[34] has a structure similar to that of solid C_{60} in this region.

In the rest of this section we briefly discuss the merits of the following two perspectives on this and nearby regions of the spectrum: (i) The condensed-matter, or "plasmon satellite" picture, and (ii) the aromatic molecule picture.

There have been a number of studies of plasma excitations in C_{60}, both theoretical[35–38] and experimental.[13,33,39,19,24,40] Starting from the theoretical[38] or experimental[19,24] plasma mode energies of the isolated molecule, it is possible to account well for the shifts of those

TABLE III. Major contributions to peak 2 in the theoretical shakeup spectrum of C_{60}. Only CI coeff. ≥ 0.3 are included in the table.

State	Excitation	I_h labeling	CI coeff.	Energy (eV)	Intensity (%)
1	$66a' \to 69a'^*$	$5h_u \to 2t_{2g}^*$	0.43	3.00	0.69
	$53a'' \to 56a''^*$	$5h_u \to 2t_{2g}^*$	0.39		
2	$65a' \to 69a'^*$	$5h_u \to 2t_{2g}^*$	−0.44	3.12	1.14
	$66a' \to 69a'^*$	$5h_u \to 2t_{2g}^*$	0.36		
	$66a' \to 70a'^*$	$5h_u \to 5t_{2u}^*$	−0.31		

TABLE IV. Major contributions to peak 3 in the theoretical shakeup spectrum of C_{60}. Only CI coeff. ≥ 0.3 are included in the table.

State	Excitation	I_h labeling	CI coeff.	Energy (eV)	Intensity (%)
1	$48a''\rightarrow 55a''^*$	$4g_g\rightarrow 5t_{1u}^*$	−0.47	4.22	0.43
	$62a'\rightarrow 68a'^*$	$4g_g\rightarrow 5t_{1u}^*$	0.42		
	$52a''\rightarrow 60a''^*$	$5h_u\rightarrow 8h_g^*$	0.36		
2	$60a'\rightarrow 67a'^*$	$4g_g\rightarrow 5t_{1u}^*$	0.48	4.30	1.46
	$65a'\rightarrow 74a'^*$	$5h_u\rightarrow 8h_g^*$	−0.35		
	$52a''\rightarrow 61a''^*$	$5h_u\rightarrow 5g_u^*$	−0.34		
3	$52a''\rightarrow 61a''^*$	$5h_u\rightarrow 5g_u^*$	−0.51	4.37	1.11
	$53a''\rightarrow 61a''^*$	$5h_u\rightarrow 5g_u^*$	0.34		
	$60a'\rightarrow 67a'^*$	$4g_g\rightarrow 5t_{1u}^*$	−0.31		
4	$53a''\rightarrow 62a''^*$	$5h_u\rightarrow 5g_u^*$	0.45	4.40	0.36
	$65a'\rightarrow 75a'^*$	$5h_u\rightarrow 5g_u^*$	−0.40		
5	$62a'\rightarrow 69a'^*$	$7h_g\rightarrow 2t_{2g}^*$	−0.53	4.61	0.64
	$66a'\rightarrow 76a'^*$	$5h_u\rightarrow 5g_u^*$	−0.46		
	$52a''\rightarrow 62''^*$	$5h_u\rightarrow 5g_u^*$	0.32		

energies observed in condensed C_{60} via a dielectric formalism.[39,19,40] The dispersion of the high-energy plasmon considered here is also attributed to solid-state effects.[40] However, there is a residual uncertainty in this assignment due to the approximations made. It is interesting to note that it is possible to calculate the excitation spectra of C_{60} using widely varying approaches,[36,38] though quantitative and qualitative agreement with experimental data varies; this suggests that there is much left to elucidate regarding these modes.

Returning to the question of the origin of the 28-eV feature in the shakeup of solid C_{60}, Krummacher *et al.*[33] attribute the shift of the shakeup maximum observed in their gas phase data to the lack of excitation of multipole modes, which they indicate are induced by the lower symmetry of the solid. Another possibility is that the plasmon mode, if considered as a true normal mode of the molecular electron "sea," may be altered in energy by the presence of the core hole. This is readily apparent if one takes the perspective of a Lindhard dielectric ap-

TABLE V. Major contributions to peak 4 in the theoretical shakeup spectrum of C_{60}. Only CI coeff. ≥ 0.3 are included in the table.

State	Excitation	I_h labeling	CI coeff.	Energy (eV)	Intensity (%)
1	$62a'\rightarrow 75a'^*$	$7h_g\rightarrow 5g_u$	0.52	5.58	0.65
2	$49a''\rightarrow 59a''^*$	$4g_g\rightarrow 8h_g$	0.41	5.62	0.38
	$60a'\rightarrow 70a'^*$	$4g_g\rightarrow 8h_g$	−0.35		
	$63a'\rightarrow 75a'^*$	$7h_g\rightarrow 5g_u$	−0.35		
3	$48a''\rightarrow 60a''^*$	$4g_g\rightarrow 8h_g$	0.45	5.68	0.97
	$49a''\rightarrow 58a''^*$	$4g_g\rightarrow 5t_{2u}$	0.32		
4	$48a''\rightarrow 60a''_*$	$4g_g\rightarrow 8h_g$	−0.67	5.71	0.45
	$61a'\rightarrow 72a'^*$	$4g_g\rightarrow 8h_g$	−0.37		
5	$61a'\rightarrow 75a'^*$	$4g_g\rightarrow 5g_u$	0.57	5.74	0.34
	$49a''\rightarrow 58a''^*$	$4g_g\rightarrow 5T_{2u}$	0.31		
6	$61a'\rightarrow 73a'^*$	$4g_g\rightarrow 8h_g$	−0.50	5.87	0.36
	$60a'\rightarrow 71a'^*$	$4g_g\rightarrow 5t_{2u}$	−0.38		
	$50a''\rightarrow 61a''^*$	$7h_g\rightarrow 5g_u$	0.34		
7	$63a'\rightarrow 76a'^*$	$7h_g\rightarrow 5g_u$	0.61	6.08	0.33
	$48a''\rightarrow 61a''^*$	$4g_g\rightarrow 5g_u$	−0.31		
8	$48a''\rightarrow 61a''^*$	$4g_g\rightarrow 5g_u$	−0.66	6.10	0.42
	$49a''\rightarrow 61a''^*$	$4g_g\rightarrow 5g_u$	−0.32		

TABLE VI. Major contributions to peak 5 in the theoretical shakeup spectrum of C_{60}. Only CI coeff. ≥ 0.3 are included in the table.

State	Excitation	I_h labeling	CI coeff.	Energy (eV)	Intensity (%)
1	$51a' \rightarrow 67a'^*$	$6h_g \rightarrow 5t_{1u}$	0.90	6.87	4.88
2	$60a' \rightarrow 76a'^*$	$4g_g \rightarrow 5g_u$	−0.92	7.02	0.67

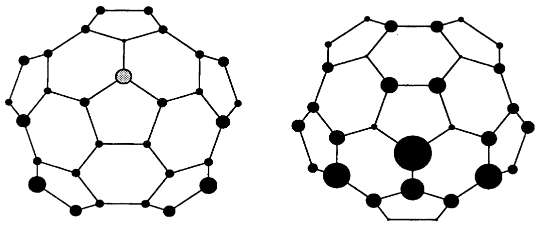
proach,[41] which is employed in two calculations,[36,37] such that we consider the collective modes to be built up out of coherent sums of single-particle excitations. As we have shown above, the core hole strongly perturbs the energies and symmetries of all of the orbitals. This is seen to be true for the deeply bound σ-like states as well in our calculations. Hence the 28-eV plasmonlike shakeup, which has both σ and π character, as well as any other collective mode, will be built up from a different set of single-particle excitations than in the ground state.

The C_{1s} XPS spectrum for solid C_{60} produces a plasmonlike shakeup satellite at the same location as the IES spectrum of the same film, also shown in Fig. 5. This suggests that the feature obtains the major part of its intensity from inelastic scattering of the outgoing photoelectron. This has been shown to occur, e.g., in the case of benzene, for which the solid phase C_{1s} XPS spectrum[34] shows greatly enhanced intensity for shakeup excitations beyond 6 eV; note also that the effects of inelastic scattering can be pronounced even for gas phase data.[27] This suggests that care should be taken in interpreting the intensities of the recent gas phase C_{60} core spectra of Krummacher *et al.*[33] Thus a satisfactory understanding of the plasmonlike region of the shakeup spectrum is clearly impossible at this point.

The other perspective which we would like to discuss concerning the plasmonlike energy region is that of small molecules. It has, e.g., been shown that features of similar intensity and energy as the 28-eV plasmon (20-eV gas phase) of C_{60} occur in C_{1s} spectra of molecules such as CO (Ref. 42) and benzene.[27] The existence of strong structure in this energy range for small molecules such as CO implies a mechanism which is very local for the generation of this type of structure. The correspondence between spatial localization and shakeup energy will be discussed further in the next section.

Finally, another mechanism for producing the plasmonlike structure which one must consider is shape resonances.[43] It should be noticed that the "plasmon"-like structures in benzene lie above the shakeoff threshold.[44] A Rydberg series is also found in the gas phase shakeup spectrum just below 17-eV shake energy.[27] Therefore, the structure in this region is resonant and the large width of the "plasmon"-like structures in the free molecular case indicates that a rapid decay takes place into the double-ionization continuum. It is noteworthy

C60 MO 65a'



C60 MO 67a'*

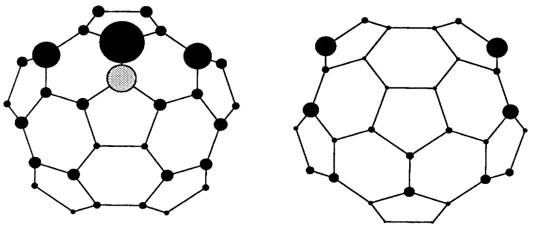
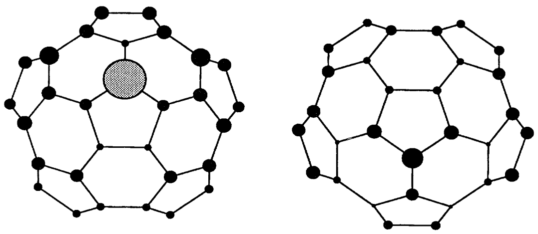


FIG. 3. MO's $65a'$ and $67a'^*$ of C_{60}. The left-hand side of the picture shows the sites on the front of the molecule whereas the right-hand side shows the back of the molecule. The core ionized site is marked in grey and the size of the circles is proportional to the charge density on the site. The excitation $65a' \rightarrow 67a'^*$ moves the charge from the back of the molecule to the front and the immediate surroundings of the core hole.

C60 MO 51a'



C60 MO 67a'*

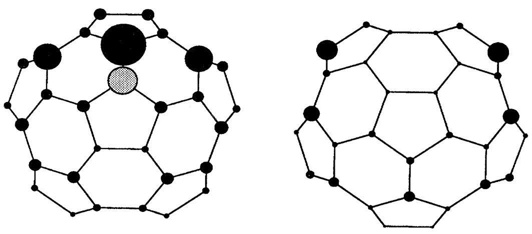


FIG. 4. MO's $51a'$ and $67a'^*$ of C_{60}. The $65a' \rightarrow 67a'^*$ excitation moves the charge mainly from the core hole to the two six-rings connected to the core hole.

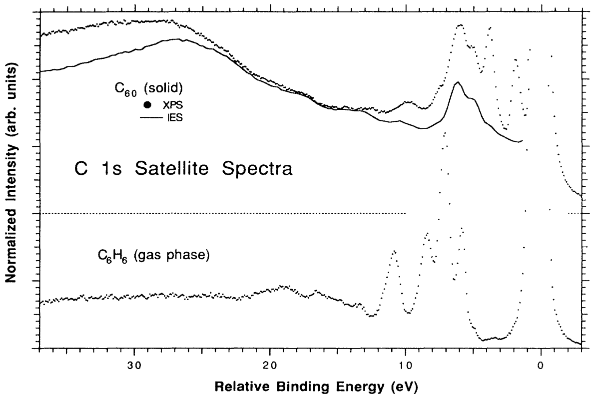


FIG. 5. Experimental spectra of the high-energy satellites of benzene and C_{60}.

that, for C_{60}, the shape resonances in the photoabsorption spectrum are quite strong.[45] However, the difference between the solid and gas phase benzene shakeup spectra suggests that it is premature to discuss the relative importance of plasmonlike excitations and resonant shakeup processes for C_{60}.

D. C_{60} as a model for a graphite layer: Dynamics of core excitation

In a previous study of the development of the shakeup excitations as a function of system size for some aromatic molecules, all of which may be considered as subunits of C_{60}, we have found that the rearrangement of charge involved in the lowest-energy shakeup occurs over larger and larger distances as the system size is increased, both for this sequence and for other extended π-electron systems.[46]

This trend, extrapolated to the macroscopic length scale, suggests that the electron-hole pair tail well known for core spectra in metallic systems will manifest itself in charge transfer from infinity to the core-ionized site for zero-energy transitions just at threshold. Indeed, this is one of the early results of a different approach to the spectra of x-ray excitations based on solid-state techniques, known as MND, which was initially developed by Mahan,[47] Anderson,[48], and Nozières and de Dominicis[49] for the problem of x-ray absorption and emission.[50] This approach was applied to XPS by Doniach and Šunjić.[51] A fundamental assumption of MND is that the screening of a suddenly created core hole can be described by a comparison of the ground state and fully relaxed excited-state potentials. Differences in the phase shifts for electrons scattering off these two potentials correspond to a screening charge. This is strictly valid only near threshold, which in a response function framework corresponds to letting electrons infinitely far away scatter off the core-hole potential, but it has been applied away from threshold with empirical justification in several cases.[52] The MND methodology has been applied to graphite as well,[53] and it was found that final-state effects on the unoccupied states[54] coupled with unperturbed occupied levels could account completely for the fact that the C_{1s} line has an asymmetry similar to that of a metal core level.

However, other workers have suggested within the MND picture that dynamic effects requiring more complex descriptions of the excited states are required for an accurate picture of the screening response away from threshold.[55,56] Experimental evidence for this in the sudden limit has been lacking, and indeed the opposite point of view has been advocated,[57,58] though there have been studies of such effects at lower energies.[59] Our results, extrapolated to the "infinite fullerene" graphite, make clear the importance of dynamic effects on XPS line shapes of metals in the sudden limit, and the role of perturbations on the occupied levels. As the system size grows and the band gap becomes negligible, excitation just at threshold corresponds to transfer of screening charge from infinity to the core-hole site, via the simultaneous relaxation of particular unoccupied levels to that site,[54] and particular occupied levels to infinity, in full agreement with the MND model. Expressed in another way, for an infinite metallic system the Anderson orthogonality[48] brings the shakeup onset right to threshold, such that the entire spectrum consists of shakeup. This effect has also been seen in model calculations of shakeup in x-ray emission in simple metals,[60,61] for which the relative shakeup intensity increases with the system size. An interesting perspective from which to see this is to view C_{60} as a graphite plane projected onto a sphere. In that case, the $65a'$ orbital localized on the side of the cage opposite the core hole represents points at infinity.

Another aspect of the core excitation which we have already touched on is the role of bonding interactions in the final state, as they are perturbed by the core hole. Thus, $C_{59}N^+$ is an excellent model of the final-state valence electronic structure. This $Z+1$ approximation has been used in core spectroscopy of small molecules for many years, but its role in the core excitations of macroscopic systems has not been fully elucidated. Much work on this area has been carried out by the group of Flynn.[62] Other groups have applied these concepts to chemisorbates, and found that the $Z+1$ model accounts very well for both XPS and photoabsorption measurements.[63-65] Thus we support the conclusions of Flynn *et al.* that the MND model needs to be modified to take, effectively, the configuration of the induced screening charge into account.

We have concentrated thus far in this section on the lowest-energy shakeup structure of C_{60}, but as we show elsewhere[46] all of the single-particle-like shakeup structure within 10 eV of the main line for the model molecules and C_{60} involve significantly relaxed initial and final orbitals. A generalization of our results is that a proper dielectric-response formalism for core excitations is required to understand XPS away from threshold in systems with extended states, much the same as recently shown for soft-x-ray absorption and emission of metals.[66] We have seen that excitations closer to the main line are more global in character. Conversely, as one moves away from threshold in an extended system, more and more localized and strongly perturbed energy levels will be important in the shakeup. One implication of this is that the plasmon tail in XPS of extended systems can be considered, aside from so-called extrinsic effects, to be the result of coupling of an excitation confined almost entirely to a single atomic site with delocalized plasma modes. Thus, one can aim in the future for an understanding of the relationship between the energy of the shakeup, and the spatial extent of the perturbation associated with it.

V. CONCLUSION

A study of the structure of the excitations giving intensity to the shakeup spectrum of C_{60} shows that charge is, in general, moved over large distances, more so for the lower than for the higher satellites.

The main contribution to the first peak in the C_{60} shakeup spectrum comes from the $65a' \rightarrow 67a'^*$ excitation which moves the charge from the opposite side of the molecule, as viewed from the core hole, towards the core-hole region. An extrapolation of C_{60} onto a plane, as an approximation of one layer of graphite, yields then that the first shakeup structures would be charge transfers from infinity towards the core hole and that the energy of those excitations should be zero. This result is in agreement with other theories, as for example, the MND model.

ACKNOWLEDGMENTS

We would like to acknowledge Bo Wästberg for sharing his program to generate the C_{60} geometry, R. L. Whetten for C_{60} provided in the early stages of this study, and J.-O. Forsell for assistance in the experiments. This work has been supported by the Swedish Natural Science Research Council (NFR) and the Swedish National Board for Industrial and Technical Development (NUTEK). Part of the calculations were performed on the Cray X-MP/416 of the Swedish Supercomputer Center (NSC).

---

[1] H. Basch, J. Electron Spectrosc. Relat. Phenom. **5**, 463 (1974).

[2] I. Hillier and J. Kendrick, J. Electron Spectrosc. Relat. Phenom. **6**, 325 (1975).

[3] S. Svensson, U. Wahlgren, and H. Ågren, Chem. Phys. Lett. **38**, 1 (1976).

[4] H.-J. Freund and R. Bigelow, Phys. Scr., **T17**, 50 (1987).

[5] S. Lunell, S. Svensson, P.-Å. Malmquist, U. Gelius, E. Basilier, and K. Siegbahn, Chem. Phys. Lett. **54**, 420 (1978).

[6] S. Lunell, M. P. Keane, and S. Svensson, J. Chem. Phys. **90**, 4341 (1989).

[7] M. P. Keane, A. Naves de Brito, S. Lunell, N. Correia, and S. Svensson, J. Chem. Phys. **155**, 379 (1991).

[8] M. P. Keane, S. Svensson, A. Naves de Brito, N. Correia, S. Lunell, and W. R. Salaneck, Synth. Met. **40-43**, 1373 (1991).

[9] M. P. Keane, S. Svensson, A. Naves de Brito, N. Correia, S. Lunell, B. Sjögren, O. Inganäs, and W. R. Salaneck, J. Chem. Phys. **93**, 6357 (1990).

[10] M. P. Keane, A. Naves de Brito, N. Correia, S. Svensson, L. Karlsson, B. Wannberg, U. Gelius, S. Lunell, W. R. Salaneck, M. Lögdlund, D. B. Swanson, and A. G. MacDiarmid, Phys. Rev. B **45**, 6390 (1992).

[11] B. Sjögren, S. Svensson, A. Naves de Brito, N. Correia, M. P. Keane, C. Enkvist, and S. Lunell, J. Electron Spectrosc. Relat. Phenom. **96**, 6389 (1992).

[12] B. Sjögren, J. Chem. Phys. **96**, 8338 (1992).

[13] J. H. Weaver, J. L. Martins, T. Komeda, Y. Chen, T. R. Ohno, G. H. Kroll, N. Troullier, R. E. Haufler, and R. E. Smalley, Phys. Rev. Lett. **66**, 1741 (1991).

[14] D. L. Lichtenberger, M. E. Jatcko, K. W. Nebesny, C. D. Ray, D. R. Huffman, and L. D. Lamb, in *Clusters and Cluster-Assembled Materials,* edited by R. S. Averback, J. Bernholc, and D. L. Nelson, MRS Symposia Proceedings No. 206 (Materials Research Society, Pittsburgh, 1991), p. 673.

[15] P. A. Brühwiler, A. J. Maxwell, A. Nilsson, R. L. Whetten, and N. Mårtensson, Chem. Phys. Lett. **193**, 311 (1992).

[16] C. T. Chen, L. H. Tjeng, P. Rudolf, G. Meigs, J. E. Rowe, J. Chen, A. B. Smith III, J. P. McCauley, Jr., A. R. McGhie, W. J. Romanow, and E. W. Plummer, Nature **352**, 603 (1991).

[17] R. W. Lof, M. A. van Veenendaal, B. Koopmans, H. T. Jonkman, and G. A. Sawatzky. Phys. Rev. Lett. **68**, 3924 (1992).

[18] M. Merkel, M. Knupfer, M. S. Golden, J. Fink, R. Seemann, and R. L. Johnson, Phys. Rev. B **47**, 11 470 (1993).

[19] I. V. Hertel, H. Steger, J. de Vries, B. Weisser, C. Menzel, B. Kamke, and W. Kamke, Phys. Rev. Lett. **68**, 784 (1992).

[20] W. Krätschmer, L. D. Lamb, K. Fostiropoulos, and D. R. Huffman, Nature **347**, 354 (1990).

[21] P. J. Benning, D. M. Poirier, T. R. Ohno, Y. Chen, M. B. Jost, F. Stepniak, G. H. Kroll, J. H. Weaver, J. Fure, and R. E. Smalley, Phys. Rev. B **45**, 6899 (1992).

[22] A. Nilsson and N. Mårtensson. Phys. Rev. B **40**, 10 249 (1989).

[23] H. Ajie, M. M. Alvarez, S. J. Anz, R. D. Beck, F. Diederich, K. Fostiropoulos, D, R. Huffman, W. Krätschmer, Y. Rubin, K. E. Schriver, D. Sensharma, and R. L. Whetten, J. Phys. Chem. **94**, 8630 (1990).

[24] J. W. Keller and M. A. Coplan, Chem. Phys. Lett. **193**, 89 (1992).

[25] B. Sonntag, in *Rare Gas Solids,* edited by M. L. Klein and J. A. Venables (Academic, London, 1977), Vol. II, p. 1022.

[26] J. L. Martins, N. Troullier, and J. H. Weaver, Chem. Phys. Lett. **180**, 457 (1991), discuss this terminology for the case of solid C_{60}.

[27] D. Nordfors, A. Nilsson, N. Mårtensson, S. Svensson, U. Gelius, and S. Lunell, J. Chem. Phys. **88**, 2630 (1988).

[28] J. E. Ridley and M. C. Zerner, Theor. Chim. Acta **32**, 111 (1973).

[29] J. E. Ridley and M. C. Zerner, Theor. Chim. Acta **42**, 223 (1976).

[30] A. D. Bacon and M. C. Zerner, Theor. Chim. Acta **53**, 21 (1979).

[31] S. Lunell (unpublished).

[32] S. Canuto, J. L. Calais, and O. Goscinski, J. Phys. B **14**, 1409 (1981).

[33] S. Krummacher, M. Biermann, N. Neeb, A. Liebsch, and W. Eberhardt (unpublished).

[34] J. Riga, J. J. Pireaux, and J. Verbist, Mol. Phys. **34**, 131 (1977).

[35] G. F. Bertsch, A. Bulgac, D. Tománek, and Y. Wang, Phys. Rev. Lett. **67**, 2690 (1991).

[36] A. Bulgac and N. Ju, Phys. Rev. B **46**, 4297 (1992).

[37] P. Lambin, A. A. Lucas, and J.-P. Vigneron, Phys. Rev. B **46**, 1794 (1992).

[38] D. Östling, P. Apell, and A. Rosén, Europhys. Lett. **21**, 539 (1993).
[39] E. Sohmen, J. Fink, and W. Krätschmer, Z. Phys. B **86**, 87 (1992).
[40] E. D. Isaacs, P. M. Platzman, P. Zschack, K. Hämäläinen, and A. R. Kortan, Phys. Rev. B **46**, 12 910 (1992).
[41] J. M. Ziman, *Principles of the Theory of Solids* (Cambridge University Press, Cambridge, 1972).
[42] J. Schirmer, G. Angonoa, S. Svensson, D. Nordfors, and U. Gelius, J. Phys. B **20**, 6031 (1987).
[43] S. Svensson and H. Ågren, Chem. Phys. Lett. **205**, 387 (1993).
[44] Estimated from the difference between the double- and single-ionization energy to be in the range 16–20 eV from threshold.
[45] L. J. Terminello, D. K. Shuh, F. J. Himpsel, D. A. Lapiano-Smith, J. Stöhr, D. S. Bethune, and G. Meijer, Chem. Phys. Lett. **182**, 491 (1991).
[46] S. Lunell, C. Enkvist, E. M. W. Agback, P. A. Brühwiler, and S. Svensson, Int. J. Quantum Chem. (to be published).
[47] G. D. Mahan, Phys. Rev. **163**, 612 (1967).
[48] P. W. Anderson, Phys. Rev. Lett. **18**, 1049 (1967).
[49] P. Nozières and C. T. de Dominicis, Phys. Rev. **178**, B 1097 (1969).
[50] K. Ohtaka and Y. Tanabe, Rev. Mod. Phys. **62**, 929 (1990), review MND theory.
[51] S. Doniach and M. Šunjić, J. Phys. C **3**, 285 (1970).
[52] P. A. Brühwiler and S. E. Schnatterly, Phys. Rev. B **41**, 8013 (1990); **42**, 9713(E) (1990).
[53] P. M. T. M. van Attekum and G. K. Wertheim, Phys. Rev. Lett. **43**, 1869 (1979).
[54] E. J. Mele and J. J. Ritsko, Phys. Rev. Lett. **43**, 68 (1979).
[55] P. Minnhagen, J. Phys. F **7**, 2441 (1977).
[56] K. Shung and D. C. Langreth, Phys. Rev. B **23**, 1480 (1981).
[57] P. H. Citrin, G. K. Wertheim, and Y. Baer, Phys. Rev. B **16**, 2256 (1977).
[58] P. H. Citrin, G. K. Wertheim, T. Hashizume, F. Sette, A. A. MacDowell, and F. Comin, Phys. Rev. Lett. **61**, 1021 (1988).
[59] F. J. Himpsel, D. E. Eastman, and E. E. Koch, Phys. Rev. Lett. **44**, 214 (1980).
[60] U. von Barth and G. Grossmann, Phys. Rev. B **25**, 5480 (1982).
[61] P. A. Brühwiler, P. Livins, and S. E. Schnatterly, Phys. Rev. B **39**, 5480 (1989).
[62] C. P. Flynn, Surf. Sci. **158**, 84 (1985).
[63] N. Mårtensson and A. Nilsson, J. Electron Spectrosc. Relat. Phenom. **52**, 1 (1990).
[64] P. A. Brühwiler, G. M. Watson, and E. W. Plummer, Surf. Sci. **269/270**, 643 (1992).
[65] A. Nilsson, O. Björneholm, E. O. F. Zdansky, H. Tillborg, N. Mårtensson, J. N. Andersen, and R. Nyholm, Chem. Phys. Lett. **197**, 12 (1992).
[66] E. Zaremba and K. Sturm, Phys. Rev. Lett. **66**, 2144 (1991).