

C 1s core photoemission of C₆₀ and C₄₈N₁₂

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Abstract. We make a theoretical study of the shake-up of the 1s photoemission of C₆₀. The method takes into account the N-body reactions of the π and σ electrons which appear during the formation of the photoemission hole on one carbon atom. We analyze the origin of the satellite in the spectra due to transitions between N-body states. Our calculation shows that the satellite spectra is essentially given by N-body transitions which involve the creation of one or two electron-hole pairs. The method has been applied also to C₄₈N₁₂. The situation is more complex. The spectra of the two most stable species have been investigated. Moreover the influence on the spectra of the position of the hole created on the carbon atom in C₄₈N₁₂ has been examined (all the carbon positions are not equivalent for some isomers).

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1 Introduction

Heterofullerenes, which have one or more of the carbon atoms substituted by other elements such as boron and nitrogen have stimulated a great interest of researchers in physics and chemistry to investigate its structural [1], electronic, optical [2] and other properties [3, 4]. In particular, such material display rather strong non linear optical behavior [3]. The fact that the band gaps is easily modified with different substitute doping could be convenient in potential application in nanometer electronics [5]. Nitrogen heterofullerenes experiments have achieved great progress since the report on C_xN_y production by Rao [6]. Firstly C₅₉N⁺, formed by fragmentation of iminofullerene has been detected by Hirsch et al. [7]. Theoretical studies on the C₅₉N electronic structure have intensively been carried out [8–10]. In particular, quantum molecular dynamics has been used to study stable structure of C₅₉N [11]. The deformation of the fullerene cage is limited to the environment impurity. The gap is small (0.3 eV) and the molecule would act rather as a electron donor.

Hultman et al. [12] report a new fullerene-like material consisting of cross-linked nano-onions of C and N. Electron microscopy and energy loss spectroscopy show that the core shell correspond to C₄₈N₁₂ aza-fullerene composition and suggest the existence of a novel C₄₈N₁₂ molecule. The existence of two stable C₄₈N₁₂ isomers has been suggested. The most stable which has symmetry of the S₆ group is 0.56 eV lower than the second stable [13, 14] with gap of 1.6 eV for the former and 0.9 eV for the latter.

Synchrotron-radiation and X-ray photoemission of the valence states bring some insight on the electronic structure. This technique has been applied firstly by Weaver et al. to C₆₀ [15]. They perform evaporation of C₆₀ molecules on GaAs or InP substrates. They report seventeen distinct molecular features extending ≈ 23 eV below the highest occupied molecular states (mention that their spectra analysis in terms of transition of molecular levels neglect the N-body electron shake up). Moreover the interaction between the substrate and the fullerene layers is important and has been investigated during the growth mode of chemisorption of C₆₀ on a InP(100) [16] or GeS [17] surfaces and also for C₇₀ on MoS₂ [18]. The C 1s core photoemission spectra shape depends strongly on the fullerene coverage of the substrate and the annealing treatments. For large number of fullerene monolayer we could expect that the interaction with the substrate could be neglected. Such experiments on heterofullerene could be achieved in the next future. Let us give some remarks on the photoemission theory. It is generally admitted that the many-electron effects govern the discrete X-ray line and the $|E|^{\alpha_H-1}$ photoemission spectra (Mahan-Nozières-de Dominicis theory) [19, 20]. This phenomenon has been studied in bulk metals where it is characterized by two effects: the Anderson orthogonality between the initial and final ground states and the spectrum behavior, where E is the emitted particle energy defect (with respect to the one-electron energy) and α^H (with $0 < \alpha^H < 1$) an exponent related to the phase shift at the Fermi level due to the localized hole potential. A study on a finite media (close loop with N atoms) has shown that the overlap between the groundstates overlap tends to zero as N

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increases like the Anderson behavior [21]. Previous studies of the C 1s core photoemission has been performed for C₆₀, C₁₁₀ and C₂₀ [22,23] in an emitted particle energy range of 0–5 eV; a Hückel Hamiltonian neglecting the σ electrons has been used in the calculation. Section 2 describes the model which takes account of the shake up of the electron gas during the photoemission process. Sections 3 and 4 deal with the results for the C 1s core photoemission for C₆₀ and C₄₈N₁₂.

2 The model

The excitation probability of a system into a state of energy ϵ_f by a photo of energy ϵ_{ph} is given by:

$$\sigma(\epsilon_f) \propto \sum_f \langle \tilde{\Phi}_i^o | \sum_n \nabla_n e | \tilde{\Phi}_f \rangle^2 \delta(\epsilon_f - \epsilon_{ph} - \epsilon_i^o) \quad (1)$$

where e is an unitary vector along the polarization direction, n labels the electrons $\tilde{\Phi}_i^o$, ϵ_i^o and $\tilde{\Phi}_f$, ϵ_f are the wavefunctions and energies of the system before and after the transition. The label o in $\tilde{\Phi}$ and ϵ refers to the initial state and f is a label which runs over all the possible states of the final states after the transitions.

Let us introduce $|\phi_a\rangle$ and $|\phi_b\rangle$ the one-electron levels of the transition respectively for the initial deep level and the final free state. Let us be $|\phi_j\rangle$ and $|\phi_j'\rangle$ the π and σ valence levels of the C₆₀ or C₄₈N₁₂ molecule before and after the transition ($j = 1, \dots, 240$). In equation (1) the sum over n can be limited only to the main contribution (i.e.: the dipolar moment is calculated between the states $|\phi_a\rangle$ and $|\phi_b\rangle$ and the others electrons are projected from $|\phi_j\rangle$ onto $|\phi_j'\rangle$). Hence

$$\langle \tilde{\Phi}_i^o | \sum_n \nabla_n e | \tilde{\Phi}_f \rangle \approx \omega_{ab} \langle \tilde{\Phi}_i^o | \tilde{\Phi}_f \rangle \quad (2)$$

with $\omega_{ab} = \langle \phi_a | \nabla e | \phi_b \rangle$. $|\tilde{\Phi}_i^o\rangle$ and $|\tilde{\Phi}_f\rangle$ are Slater determinants built up with the one-electron wavefunctions $|\phi_j\rangle$ and $|\phi_j'\rangle$.

The energy of the photoelectron is fixed but it varies in an energy range which is small and we assume that ω_{ab} is a constant ($\omega_{ab} \approx \omega$). Let $\tilde{\epsilon}_f$ ($\epsilon_f = \tilde{\epsilon}_f - \epsilon_b$) be the energy associated to the state $|\tilde{\Phi}_f\rangle$. Equation (1) is recasted into:

$$\sigma(E) \propto \omega^2 \sum_f |\langle \tilde{\Phi}_i^o | \tilde{\Phi}_f \rangle|^2 \delta(\tilde{\epsilon}_f - \epsilon_{ph} + E) \quad (3)$$

where the negative energy E ($E = \epsilon_b - \epsilon_{b,max}$) is the difference between the photoemission energy and its maximal value $\epsilon_{b,max}$ ($\epsilon_{b,max} = \epsilon_i^o + \epsilon_{ph} - \tilde{\epsilon}_f$) which happens when the final state $|\tilde{\Phi}_f\rangle$ is the fundamental state $|\tilde{\Phi}_f^o\rangle$ what is not forbidden in finite system.

3 The C 1s core photoemission of C₆₀

Let us model the C₆₀ molecule in the tight binding framework. The Hamiltonian H^o taking into account the σ and

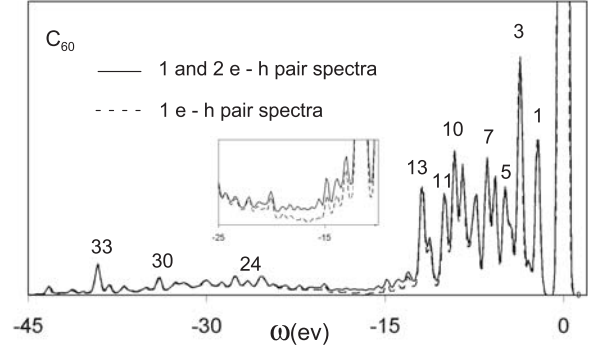


Fig. 1. Shake-up structure of carbon 1s photoemission spectrum in C₆₀ I^{ph} (a.u): in dashed (solid) line is the spectra including the one (the one and two electron-hole) pairs contributions). In Table 1, we report the nature of transition giving the labelled peaks. The peak at $\omega = 0$ eV is the transition between the two fundamental states. In insert the spectra is reported for ω between -25 and -10 eV.

π electrons of the molecule is written as:

$$H^o = \sum_{i \neq j, \gamma, \mu, \sigma} \beta_{\gamma\mu}^{ij} C_{\gamma i \sigma}^+ C_{\mu j \sigma} + \sum_{i, \gamma, \sigma} E_{\gamma} C_{\gamma i \sigma}^+ C_{\gamma i \sigma} \quad (4)$$

where γ, μ label the orbital components of $2s, 2p_x, 2p_y, 2p_z$. The $\beta_{\gamma\mu}^{ij}$ are the hopping term between site i and j and worth $-6.79, 7.25, 9.53, -3.05$ eV respectively for $\beta_{ss\sigma}, \beta_{sp\sigma}, \beta_{pp\sigma}, \beta_{pp\pi}$. The energy $E_s(E_p)$ worth $-16(-9)$ eV. C₆₀ has 240 electrons ($120\uparrow, 120\downarrow$). Thus each C₆₀ state is described with a Slater determinant which is the product of two determinants of size (120×120) .

In Figure 1 the C₆₀ one-electron levels obtained with H^o in the vicinity of the LUMO level are reported. The gap is 2.15 eV similar to the experimental value of 1.73 eV. The difference is due because we neglect the electronic correlation in H^o and as it has been shown that the electronic correlation effects reduce the gap value.

The photoemission process can be described by the Hamiltonian H

$$H = H^o + \sum_{\gamma, \sigma} \Delta_{\gamma} C_{\gamma 1 \sigma}^+ C_{\gamma 1 \sigma} a a^+ \quad (5)$$

The second contribution in H is the apparition of attractive term ($\Delta_{\gamma} < 0$) due to the deep hole creation on site 1, a^+ is the creation operator of an electron on the 1s level of site 1 (site 1 has been chosen arbitrary as all the sites are equivalent). Δ_{γ} is an effective term we derive it by comparing our calculated photoemission spectra with experiments to get the same ratio between the integrated surface under the main line and the surface under the satellite contributions in the photoemission spectra ($\Delta_{\pi} = -4.16$ eV, $\Delta_{\sigma} = -6.8$ eV).

The determination of the photoemission spectra need the calculation of $\langle \tilde{\Phi}_i^o | \tilde{\Phi}_f \rangle$. The initial state is no degenerate: it is the ground state we put the electrons on the 120 lowest energy states for each spin direction. For the final state the number of possibility is tremendously huge. In fact for each spin direction we have to consider all the

Table 1. Analysis of the N-body transition between C₆₀ state and C₆₀ with a deep hole which give the satellite peaks of carbon 1s photoemission in C₆₀ (see Fig. 1). Only the one electron-hole pair excitation are reported. L and H stand for Lumo and Homo. The contribution in percent is given for transitions involved in peaks 1 to 7 (in parenthesis).

Peak	Transition $\pi \rightarrow \pi^*$	Transition $\pi \rightarrow \sigma^*$	Transition $\sigma \rightarrow \pi^*$
1	H-1 \rightarrow L (1.34)		
2	H \rightarrow L+3 (0.24)		
3	H-3 \rightarrow L (2.01)		
4	H-2 \rightarrow L+3 (0.563)		
5	H-4 \rightarrow L (0.548), H \rightarrow L+5 (0.362)		
6	H-5 \rightarrow L (0.178), H-3 \rightarrow L+3 (0.868), H \rightarrow L+10 (0.138)		
7	H-4 \rightarrow L+3 (0.256), H-2 \rightarrow L+5 (0.922), H \rightarrow L+3 (0.510)		
8	H-6 \rightarrow L, H-3 \rightarrow L+5, H-2 \rightarrow L+10, H \rightarrow L+17		
9	H-7 \rightarrow L, H-5 \rightarrow L+3, H-4 \rightarrow L+5, H-3 \rightarrow L+10		
10	H-6 \rightarrow L+3, H-4 \rightarrow L+10, H-3 \rightarrow L+13		H-8 \rightarrow L
11	H-7 \rightarrow L+5, H-6 \rightarrow L+10, H-5 \rightarrow L+17		
12	H-6 \rightarrow L+5, H-5 \rightarrow L+10		
13	H-7 \rightarrow L+5; H-6 \rightarrow L+10; H-5 \rightarrow L+17; H-4 \rightarrow L+21		
14	H-7 \rightarrow L+13, H-6 \rightarrow L+17, H-1 \rightarrow L+21		
15	H-7 \rightarrow L+17	H-2 \rightarrow L+34	
16	H-7 \rightarrow L+21		

Peak	Transition $\pi \rightarrow \sigma^*$	Transition $\sigma \rightarrow \pi^*$	Transition $\sigma \rightarrow \sigma^*$
17	H-7 \rightarrow L+34		
18		H-9 \rightarrow L+28	
19			H-9 \rightarrow L+35
20			H-12 \rightarrow L+29, H-9 \rightarrow L+39
21		H-14 \rightarrow L+28	H-12 \rightarrow L+5
22			H-16 \rightarrow L+29
23		H-26 \rightarrow L+5, H-17 \rightarrow L+28	
24		H-27 \rightarrow L+15, H-20 \rightarrow L+28	H-20 \rightarrow L+29, H-18 \rightarrow L+35 H-16 \rightarrow L+40
25		H-21 \rightarrow L+28	H-20 \rightarrow L+36, H-18 \rightarrow L+39 H-14 \rightarrow L+40
26		H-23 \rightarrow L+28	H-21 \rightarrow L+35
27		H-29 \rightarrow L+5, H-27 \rightarrow L+21 H-25 \rightarrow L+28	H-24 \rightarrow L+29, H-23 \rightarrow L+34 H-16 \rightarrow L+71
28		H-31 \rightarrow L+5	H-24 \rightarrow L+34, H-20 \rightarrow L+71
29			H-26 \rightarrow L+34
30		H-31 \rightarrow L+17	H-27 \rightarrow L+34
31			H-29 \rightarrow L+34
32			H-31 \rightarrow L+29, H-30 \rightarrow L+34
33			H-31 \rightarrow L+34

ways of distributing 120 electrons among 240 levels and the number is C_{240}^{120} , hence the number of final states is $(C_{240}^{120})^2$. The contribution to the sum rule of the transition with final state equal to the fundamental state is 0.81077, the contribution of the one electron-hole pair states is 0.17609, the contribution with two electron-hole pair states is respectively 0.0077 for pairs with different spins and 0.0045 for pairs with the same spin. The contribution of these states to the sum rule is 0.999 what suggest to limit our calculation to these states. As we do not work in a space of determinants built from molecular wavefunctions (but in a space of atomic determinants) we are not impeded by the numerous degeneracies occurring in the molecular wavefunctions.

In Figure 1 we report the 33 photoemission satellites in C₆₀. Note, the first satellite is at an energy of 2.10 eV which is the gap value obtained in our calculation. Weaver et al. [15] associate the satellite peaks to 1-electron molecular transitions. In our calculation they are N-body transitions between one C₆₀ and one state of C₆₀ with a deep hole. In Table 1 the analysis of the satellite transitions is reported. For each satellite several transitions are generally involved which could be ($\pi \rightarrow \pi^*$, $\pi \rightarrow \sigma^*$, $\sigma \rightarrow \pi^*$, $\sigma \rightarrow \sigma^*$) transitions. The contribution in percent of each transition is reported for the satellites 1 to 7. Note that for the first satellite the N-body transition is a $\pi \rightarrow \pi^*$ type between the (Homo-1) state of C₆₀ and with the Lumo

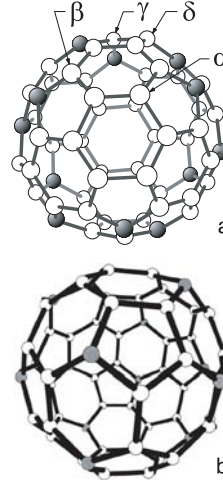


Fig. 2. C₄₈N₁₂ isomers: isomer 1 (a) has an energy lower than the isomer 2 (b). Nitrogen atoms are in grey. For isomer 1 α , β , γ and δ label the four different carbon sites of deep hole creation.

state of C₆₀ with an deep hole and not as expected in a 1-electron picture a transition between Homo \rightarrow Lumo levels. The contribution of the two electron-hole state (insert Fig. 1) is significant in the range of energy (-20 eV, -11 eV) what gives a smoother spectra. The agreement with the Weaver et al. results is not perfect, in particular the relative heights of the first satellites. In fact the experiments are not done on free clusters and the discrepancy could be due to the interaction between the C₆₀ layers and the substrate.

4 C 1s core photoemission of C₄₈N₁₂

We have applied our formalism to the case of C₄₈N₁₂. We limit our study to the case where the hole 1s is always created on the carbon. As mentioned previously two C₄₈N₁₂ isomers seem stable. The geometrical structures are given in Figure 2. For the isomer 1, they are 4 different kinds of carbon site where a deep hole could be created. They are labelled α , β , γ and δ in Figure 2. For the isomer 2 all carbon sites are equivalent to create a hole. Respectively for the α , β , γ and δ case of isomer 1, the contributions to the sum rule of the transition with final state equal to the fundamental state perturbed by the hole are 0.8223, 0.7850, 0.7181 and 0.8325 the contribution of the one electron-hole pair states is 0.16513, 0.1982, 0.2537 and 0.15703, the contribution with two electron-hole pair states is respectively 0.00906, 0.0098, 0.0204 and 0.0061 for pairs with different spins and 0.0028, 0.0045, 0.0054 and 0.0036 for pairs with the same spin. The position of the deep hole on the carbon affect significantly the diverse contributions and also the structure of the spectra (Fig. 3). Nevertheless the spectra is essentially given by the one and two hole-electron pair excitations. The spectra of the isomer 1 obtained by averaging over the hole position has more intense satellite peaks than the isomer 2 spectra (Fig. 4). The two spectra are quite different and could be perhaps used for the knowledge of the structure of C₄₈N₁₂. For the isomer 2, the contributions to the sum rule of the transition with final state equal to the fundamental state is 0.8127 the contribution of the one electron-hole pair states is 0.1749,

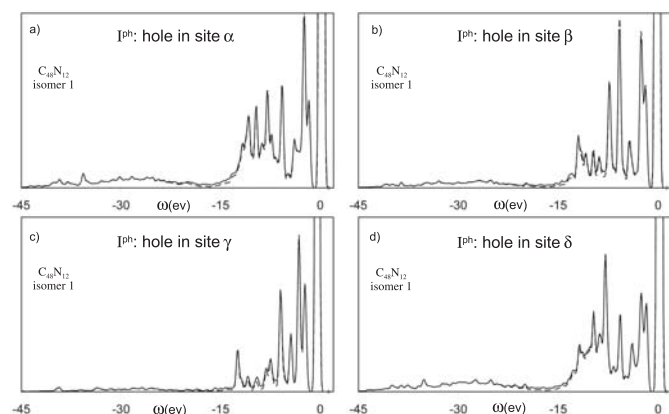


Fig. 3. Shake-up structure of the carbon $1s$ core photoemission spectrum I^{ph} (a.u) given by the isomer 1 of $C_{48}N_{12}$. The deep hole is created on carbon site α (a), β (b), γ (c) and δ (d). The one (one and two) electron-hole pair contribution to the photoemission are in dashed (solid) line. The peak at $\omega = 0$ eV is the transition between two fundamental states.

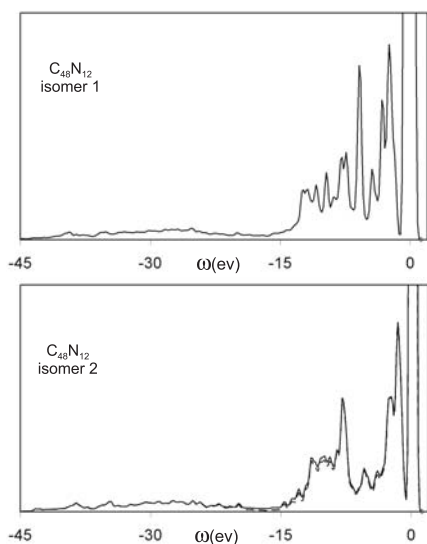


Fig. 4. Shake-up structure of the carbon $1s$ core photoemission spectrum I^{ph} (a.u) given by the isomers 1 and 2 of $C_{48}N_{12}$. For isomer 1 the spectra is averaged over the position of the deep hole and is given by the one and two electron-hole pair excitation contribution. As for the isomer 2, the one (one and two) electron-hole pair contribution to the photoemission are in dashed (solid) line: the peak at $\omega = 0$ eV is the transition between the two fundamental states.

the contribution with two electron-hole pair states is respectively 0.0092 for pairs with different spins and 0.0029 for pairs with the same spin.

5 Conclusion

The electron shake-up produced during the formation has been investigated for C_{60} and $C_{48}N_{12}$. The satellite peaks have been analyzed as N-body transitions. The calculations show that we can limit our study to excitations with only one and two electron-hole pair excitations. The effect of the two electron-hole pair contribution is to smooth the spectra i.e.: it fills the spectra with state energies which was not produced with the one electron-hole excitation. It will be interesting to compare our results with experiments for $C_{48}N_{12}$ and to investigate for C_{60} the spectra dependence on the number of C_{60} layers.

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