Determination of some C_{60} electronic properties. Application to the cohesive energy in C_{60} ionic compounds

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Résumé. — Les affinités électroniques EA^n des agrégats libres C_{60}, définies comme l'énergie gagnée dans la réaction $C_{60} + ne \rightarrow C_{60}^{n-}$, sont déterminées par la méthode de Gutzwiller. Nous les utilisons dans l'étude de l'énergie de cohésion de composés $C_{60}M_x$, avec M = K, Rb et x = 3 ou 6. Nous considérons 4 termes : les énergies de Madelung, d'ionisation, de répulsion de coeur et de champ cristallin. Les paramètres décrivant la répulsion de coeur sont tirés de la littérature pour $C_{60}K_3$ et sont déterminés pour les autres composés. Nous montrons que l'énergie de cohésion des composés considérés n'est positive que si l'on tient compte du terme de champ cristallin. La stabilité d'autres composés ioniques du C_{60} est aussi discutée.

Abstract. — The electron affinities EA^n, defined as the gained energy in $C_{60} + ne \rightarrow C_{60}^{n-}$ reactions, are determined by the Gutzwiller method for free C_{60}. We use them in the study of the cohesive energy of $C_{60}M_x$ compounds, where M = K, Rb and x = 3 or 6. We consider 4 terms: the Madelung, ionization, core-repulsion and crystal field energies. The core-repulsion parameters are taken from the literature for $C_{60}K_3$ and determined for the other compounds. We show that the cohesive energy of the considered compounds is positive only if we take into account the crystal field term. The stability of other C_{60} ionic compounds is discussed.

1. Introduction.

In 1984, Rohflin, Cox and Kaldor [1] observed for the first time the specific behaviour of the C_{60} aggregates. In their experiment, C_n aggregates were produced by the seeded supersonic beam technique and were mass-analyzed after postionization. A very large peak appeared for C_{60}^{+}, much larger than for any other cluster. In fact, carbon aggregates had already attracted the attention of physicists.

As soon as in the early 1960s, Slodzian and Castaing designed and built the Castaing-Slodzian Microanalyzer [2, 3]. Simultaneously theoretical models were developed in the same laboratory for understanding the secondary emission mechanism [4]. One of the great advantage of the Castaing-Slodzian Microanalyzer was that it delivered mass-spectra where peaks corresponding

to various polyatomic species were present [3]. Thus, by bombarding a graphite sample interesting odd-even alternations were observed in the C_n^+ and C_n^- spectra, $n \leq 15$ [5]. These effects were interpreted as due to larger stabilities of the corresponding aggregates and various theoretical descriptions confirmed these conclusions [6]. In particular, it was possible to show that, in this range of sizes, the shape was linear.

The large intensity of C_{60}^+ was also attributed to the C_{60} stability and different authors [7,8] made the hypothesis that C_{60} might take the shape of a regular truncated icosahedron which is one of the 13 Archimedean polyhedra. This shape appeared as very likely since each carbon atom is in an almost sp^2 hybridization state, as in benzene or graphite. Moreover, a simple Hückel calculation shows that the π electronic level structure is complete and the total π energy close to the graphite π energy.

The interest of the subject has been recently reactivated by Krätschmer *et al.* [9] who were able to produce large amounts of C_{60} aggregates. Then, many interesting results were obtained as the discovery of a new phase of solid carbon where C_{60} aggregates are at the vertices of a close-packed fcc lattice with a nearest neighbour distance of 10.04 Å. Moreover, various confirmations of the assumed C_{60} truncated icosahedral shape were found [10]. Another important result has been obtained on $C_{60}M_x$ compounds (M: alkali metal; $x = 1$ to 6) which are superconductors for $x = 3$ with transition temperatures at $T_c = 18$ and 28 K for K and Rb respectively [11-13].

For understanding the properties of these new compounds a good knowledge of C_{60} electronic parameters are first required. In particular, we need to know the various electron affinities, EA^n, i.e. the energy gained in negative ionization reactions:

$$C_{60} + ne \rightarrow C_{60}^{n-}$$
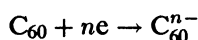
In the next chapter we present our EA^n calculations and in chapter 3 we use them for estimating the cohesive energy of some $C_{60}M_x$ compounds. A discussion of the existence of other compounds is also made.

2. C_{60} electron affinities.

In this part we will limit ourselves to the study of π electrons (one π electron per C atom) and will suppose that C_{60} has the shape of a regular truncated icosahedron. Following numerous authors, as for instance Lee [14, 15] we will use the Hubbard Hamiltonian:

$$H_{\text{Hub}} = \beta \sum_{\substack{i,j \text{ neighbours} \\ \sigma}} c_{i\sigma}^+ c_{j\sigma} + U \sum_i n_{i\uparrow} n_{i\downarrow}$$

where the first term is the one-electron Hückel part and the second the correlation term, where U is the intraatomic correlation energy. As in previous studies about aromatic polyenes [16], we adopt the values $\beta = -2.35$ eV and $U = 5.5$ eV. These parameters describe a system which is intermediate between the two limits: $U \sim 0$ (Hückel theory) and $U \sim \infty$ (Heisenberg Hamiltonian). In this range of $U/|\beta|$ values, the Gutzwiller approximation [17] gives a good approximate solution of H_{Hub}. It is also worth-noticing that the Gutzwiller theory has a better accuracy for equivalent atom systems, a condition which is strictly fulfilled here.

Let us give a brief description of the Gutzwiller technique [17]. The determinant Ψ_0 which represents the solution of the Hückel Hamiltonian is projected on the basis of the atomic determinants Φ_k:

$$\Psi_0 = \sum_k c_k \Phi_k$$

Then, a new wave function is built by multiplying the weights c_k by a factor η^{ν_k} $(\eta \leq 1)$:

$$\Psi = \sum_k c_k \, \eta^{\nu_k} \Phi_k$$

where ν_k is the number of doubly occupied sites in Φ_k and η is a variational parameter. This last parameter is fixed by minimizing:

$$\epsilon(\eta) = \frac{<\Psi|H_{\text{Hub}}|\Psi>}{<\Psi|\Psi>}$$

and the electronic energy E_{el} is the minimum of $\epsilon(\eta)$.

The details of the calculation are given in the original Gutzwiller work [17] and the adaptation of the original Gutzwiller technique to aggregates is presented in [18]. As we intend to study charged aggregates we must add to the Gutzwiller model a capacitive $C(n)$ term [19]. The origin of this last term is in the long range repulsion between the added negative charges. The total energy of C_{60}^{n-} can be written:

$$E = E_{\text{el}} + C(n)$$

with

$$C(n) = \frac{5(ne)^2}{8 \times 4\pi\epsilon_0 R}$$

In these calculations we take for R, the external radius of the π electronic distribution, $R \sim 4.5$ Å which is larger than the σ skeleton radius, $R \sim 3.5$ Å. For any n value the same R is used, which is justified by the fact that from C_{60}^{-} to C_{60}^{6-} all the added electrons occupy the same LUMO level. The EA^n values are given in table I.

Table I. — *Electron affinities EA^n (in eV) for the $C_{60} + ne \rightarrow C_{60}^{n-}$ reactions.*

n	1	2	3	4	6
EA^n	2.23	0.37	−5.5	−15.48	−47.58

Our result for EA^1, $EA^1 = 2.23$ eV, is in reasonable agreement with the experimental result $EA^1 \sim 2.6$ eV [20]. For $n \geq 2$, the EA^n values are negative (or small for $n = 2$) which agrees with the fact that free C_{60}^{n-} have not been observed. However, an indirect comparison of our values to experiment can be made if we consider C_{60} aggregates in solution. The redox potentials, RP^n, have been measured by Cox *et al.* [21] for the reactions:

$$C_{60}^{(n-1)-} + e \rightarrow C_{60}^{n-}$$
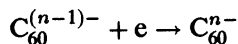
These authors obtain: $RP^n = -0.51, -0.9, -1.38$ V for $n = 1$, 2 and 3. A recent study of the redox potentials of silver aggregates [22] has shown that this quantity can be related to the electron affinity in the free state by the relation:

$$|e|RP^n = EA^n - EA^{n-1} + \Delta G_{\text{sol}}^n - \Delta G_{\text{sol}}^{n-1} + E_{\text{shift}} \tag{1}$$

where ΔG_{sol}^{n} is the solvation energy of C_{60}^{n-} in the solvant and E_{shift} an energy shift which depends on the type of electrode. Since we know three RP^n values, we can write the same number of equations of type (1) in which ΔG_{sol}^{n} and E_{shift} are unknowns. According to the electrostatic origin of ΔG_{sol}^{n} we will write:

$$\Delta G_{sol}^{n} \sim n^2 \, \Delta G_{sol}^{1} \qquad (2)$$

which reduces the number of unknowns to two, ΔG_{sol}^{1} and E_{shift}. In reference [23] we present our calculations where the values of ΔG_{sol}^{1} and E_{shift} are fixed by using two of the three equations of type (1) and where the last equation serves as a control of the method. There is a good agreement with experiment.

At the end of this section let us briefly mention the estimate of EA^n made by some authors by simply calculating the repulsive energy of n point charges on a sphere [24, 25]. The main defect of these models is the neglect of the delocalized character of the π electrons which is taken into account here by using H_{Hub}.

3. Cohesive energy in some C_{60} ionic compounds.

For calculating the cohesive energy in $C_{60}M_x$ ionic compounds we will first suppose that each M and each C_{60} is in M^+ and C_{60}^{x-} state respectively. The crystalline structures of these compounds are known and depend on the number, x, of alkali elements. For $x = 3$, it is the same as in the pure C_{60} crystal, i.e.: fcc, with alkali atoms intercalated at the center of tetrahedral and octahedral interstices of the fcc lattice [26]. The length of the cubic cell, a, varies with M, it is given in table II. For $x = 6$, the C_{60} aggregates are at the nodes of a cc lattice and K atoms are on the surface of the cubic cell [25, 27].

Table II. — *Madelung energy* E_M, *ionization energy* E_P, *core-repulsion energy* E_C *and crystal field energy* E_{CF}. *All the energies are in* eV. *The cohesive energy is given per* $C_{60}M_x$ *group of atoms.* a *is the length of the cubic cell (in* Å).

Compound	Lattice a	E_M	E_P	E_C	Partial total	E_{CF}	Cohesive energy
$C_{60}K_3$	fcc 14.24	22.44	−18.52	−3.11	0.81	∼ 6	∼ 6.81
$C_{60}Rb_3$	fcc 14.44	22.13	−18.04	−3.08	1.01	∼ 6	∼ 7.01
$C_{60}K_6$	cc 11.39	71.44	−73.62	−9.43	−11.61	∼ 18	∼ 6.39
$C_{60}Rb_6$	cc 11.55	70.44	−72.66	−8.95	−11.23	∼ 18	∼ 6.77

We define the cohesive energy as the gained energy in the formation of the compound when the initial state is made of free and neutral C_{60} and alkali atoms. This corresponds to the experimental situation where the compounds are formed by direct reaction of C_{60} with alkali vapours in evacuated sealed tubes [27].

The cohesive energy is the algebraic sum of four contributions:
– the attractive (or gained) Madelung energy, E_M;
– the positive and negative ionization energies, E_P (to be furnished);
– the core repulsive energy E_C;

  – the crystal field energy, E_{CF}.

Let us discuss our results given table II. The Madelung energy has been calculated with a numerical program which also gives the map of the potential inside the crystal. The ionization energy is the sum of the atomic ionization potentials of the x alkali atoms and of the corresponding electron affinity of C_{60} aggregates given in table I. For the core-repulsion energy of $C_{60}K_3$ we have used the values determined by Zhang *et al.* [28] who describe the core repulsive interactions by:

$$V_{ij}(r) = A_{ij} \, e^{-r/\rho}$$

where ρ is supposed to be the same for all the kinds of interactions. By writing the equilibrium conditions of local potential on the three different lattice sites, these authors obtain:

$$A_{C_{60}-K} = 53.9 \text{ eV}, \quad A_{C_{60}-C_{60}} = 2204.9 \text{ eV}, \quad \rho = 0.076 \, a$$

(the repulsion between K cores is neglected). By using the same method we have determined the corresponding values for $C_{60}Rb_3$ where $A_{C_{60}-Rb} = 62.4$ eV (the two other parameters are supposed to be the same as in $C_{60}Rb_3$). For $C_{60}K_6$ and $C_{60}Rb_6$ we obtain $A_{C_{60}-C_{60}} = 13175$ eV and use for the other parameters the same as in $C_{60}K_3$ and $C_{60}Rb_3$ respectively-.

If we limit the study to the E_M, E_P and E_C contributions, we obtain the cohesive energy writen in column "partial total" of table II. The obtained cohesive energy is small or negative for $C_{60}M_6$ which does not correspond to experiment. This leads us to include the crystal field effects. Indeed, the surface zone of C_{60} aggregates in ionic compounds is immerged in a relatively strong positive potential whose effect is to stabilize the π electronic levels. The stabilization of the LUMO levels by the crystal field can be observed in photoemission experiments on $C_{60}K_x$ [29] where, as x increases, the LUMO level gets deeper. A very crude estimate of the energy shift from the experimental curve gives -2 eV between pure C_{60} and $C_{60}K_3$ and -1 eV between $C_{60}K_3$ and $C_{60}K_6$. The order of magnitude is confirmed by the analysis of the electric potential inside the compounds. For example, the average potential value at a distance of 4 Å from the center of a C_{60} aggregate in $C_{60}K_6$ is 2.7 V which would lead to a shift of $-e \times 2.7 = -2.7$ eV, a value coherent with the observed shift from C_{60} to $C_{60}K_6$ ($-2 - 1 \sim -3$ eV). A more precise calculation of the energy shifts could be made. In a first order perturbative treatment, these shifts would be given by the diagonalization of a matrix with elements given by:

$$-e \int \varphi_i(\mathbf{r}) \, V_{CF}(\mathbf{r}) \, \varphi_j(\mathbf{r}) \, d^3r$$

where $\varphi_i(\mathbf{r})$ ($i = 1, 2, 3$) are the degenerate LUMO wave functions. We will not undertake this calculation here and will use the "experimental" estimations of -2 eV and -3 eV per LUMO electron in $C_{60}M_3$ and $C_{60}M_6$, respectively. Let us notice that the resulting cohesive energy given table II if of the same order of magnitude as the estimation of Benning *et al.* [29] who give 1 eV per K atom, and therefore 3 eV for $C_{60}K_3$ and 6 eV for $C_{60}K_6$.

We see that our final conclusion is only qualitative, due to the lack of precision in the crystal field effect study. However this simple model can also be used for understanding some experimental behaviours.

As we already saw, the experimental method for producing $C_{60}M_x$ compounds (M = K, Rb) is the direct reaction of C_{60} with the alkali metal vapour, it is no longer the case for Na. In reference [30] the authors give an explanation to this observation based on higher vapour pressures and higher diffusivity for alkali atoms with larger sizes. If we apply the present model we see that the ionization energy E_P increases from K to Na (0.78 eV). Therefore, if all the other parameters are supposed to be the same as in $C_{60}K_3$ (in fact, there is a little a change, $a = 14.18$ Å) the

cohesive energy of $C_{60}Na_3$ per C_{60} would be $6.81 - 3 \times 0.78 = 4.47$ eV which means that there is a significant reduction of the cohesive energy in $C_{60}Na_3$ compounds with respect to $C_{60}K_3$. This is a complementary argument for explaining the difficulty for producing $C_{60}Na_3$ compounds by direct reaction.

Let us now consider the hypothetical $C_{60}Be_3$ compound in which Be and C_{60} would be in Be^{2+} and C_{60}^{6-} states. By assuming a fcc structure and the same a length as in $C_{60}K_3$ we obtain $E_M = 89.76$ eV which is much smaller (in absolute value) than $E_P = -129.78$ eV. In such a system the energy deficit given by $E_M + E_P$ is so large that, even by including crystal field effects, the cohesive energy will never be positive and one may conclude that $C_{60}Be_3$ cannot be produced by direct reaction.

In these two last examples, $C_{60}Na_3$ and $C_{60}Be_3$, alternative preparative routes have to be explored [30] where the metallic element is preformed in an ionic state.

It is also worth-noting that the EA^n values given table I could also be used in the study of the stability of endohedral complexes of C_{60}, i.e., when a positive ion singly-, doubly- or triply-charged is inside the C_{60} cage [31]. This study is in progress.

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