Common Electronic Structure and Pentagon Pairing in Extractable Fullerenes

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We have found the bunching of the lowest three unoccupied states and the pentagon pairing in extractable fullerenes. These should be related to each other since lower unoccupied states are found to be spatially distributed on pentagons. In addition, the presence of both prevalent and rare structural units constituting extractable fullerenes has been revealed. A series of these findings sheds new light on the fullerene growth mechanism and on the design of larger-fullerene conductors.

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After the proposal of a spherical cage-structure C_{60} cluster [1], the electronic structure of C_{60} and metal-encapuslated C_{60} was studied theoretically from the viewpoint of using them as atomlike units for new materials [2,3]. Actually, the occupied π states of C_{60} were pointed out to correspond to the spherical harmonics states (Y_{lm}) as in the case of ordinary atoms, not only by the empirical quantum-chemical calculation on π states [4] but also by the *ab initio* density-functional (DF) calculation on σ and π states [3,5]. Solids consisting of C_{60} are then found to have hierarchical electronic structure [5], which are considered to be of essential importance in their interesting physical properties such as superconductivity [6]. In addition to C_{60}, larger fullerenes such as C_{70}, C_{76}, and C_{84} have been successfully extracted from carbon soot [7,8], and are also found to have pseudospherical electronic structure [9,10]. Hence, there have been many attempts to build new solids out of these various atomlike spheres [11]. On the other hand, it is now becoming clear that only a limited number of larger fullerenes among many possible fullerene isomers can be extracted from soot. In the case of C_{84}, for example, only three among 24 possible isomers have been extracted [12]. The origin(s) of this selection rule has not been revealed yet. It must be related also to an important unsolved problem, the selective high-yield production mechanism of C_{60}.

In this Letter, we report the presence of the universal electronic structure in the lower unoccupied states of *extractable* fullerenes. Their lowest three unoccupied states are found to bunch together. In addition, the next three states also tend to bunch up. Remarkably, this level bunching is found to be related to the details of their network geometry characteristic of extractable fullerenes, i.e., the dimerized arrangement of 12 pentagons. This pentagon pairing, considered to be one of the major origins of the selective extractability of fullerenes, is found to place a very strong restriction on the possible network geometry of larger fullerenes. Accordingly, we can select a couple of candidates for C_{86} and C_{88} fullerenes extracted recently as well as for C_{82}. Furthermore, we also report the presence of prevalent and rare structural units. These common geometrical features are pointed out to have mostly an electronic origin at the fullerene-production process and partly a solvability origin at the extraction process. Finally, we discuss the possible high-yield production mechanism of C_{60}.

Figure 1(a) shows the electronic structure of all the fullerenes which have been extracted from soot *and* whose network geometries have been determined [12]: C_{60}, C_{70}, $C_{76}(D_2)$, $C_{78}(C_{2v})$, $C_{78}(C_{2v}')$, $C_{78}(D_3)$, $C_{84}(D_2)$, and C_{84} (D_{2d}). In the present calculation, C_{60} and C_{70} geometries used are the same as those in our previous work [9], while other fullerene geometries have been optimized using the empirical model potential for C atoms by Tersoff [13] with an appropriate scaling for fullerenes [10]. Then, their electronic structure has been obtained by using the generalized tight-binding model for C $2s$ and $2p$ states, which includes not only the transfer matrix elements but also the overlap matrix elements with adequate atomic-distance dependences [14,15]. For discussing the overall distribution of the electronic states and the relative level bunchings in various fullerenes, the present procedure provides sufficient accuracy as can be seen in the electronic structure of C_{60} and C_{70}. In both cases, there is a considerable energy gap and the lowest three unoccupied states above the gap are found to bunch together perfectly (i.e., degenerate) in C_{60} and nearly perfectly in C_{70}, in accord with the DF-calculation results, which have been found to show excellent agreement with experimental inverse photoemission spectra [9]. In addition to the lowest three unoccupied states, the next three states also show the perfect and nearly perfect bunching in C_{60} and C_{70}, respectively.

These similarities in the lower unoccupied electronic structure in C_{60} and C_{70} are in sharp contrast to their differences in the occupied states just below the gap. Although the higher occupied states also show the bunching, the number of bunched states (5 and 10 states in C_{60} and C_{70}, respectively) depends on the size, because it originates from the above-mentioned correspondence to the

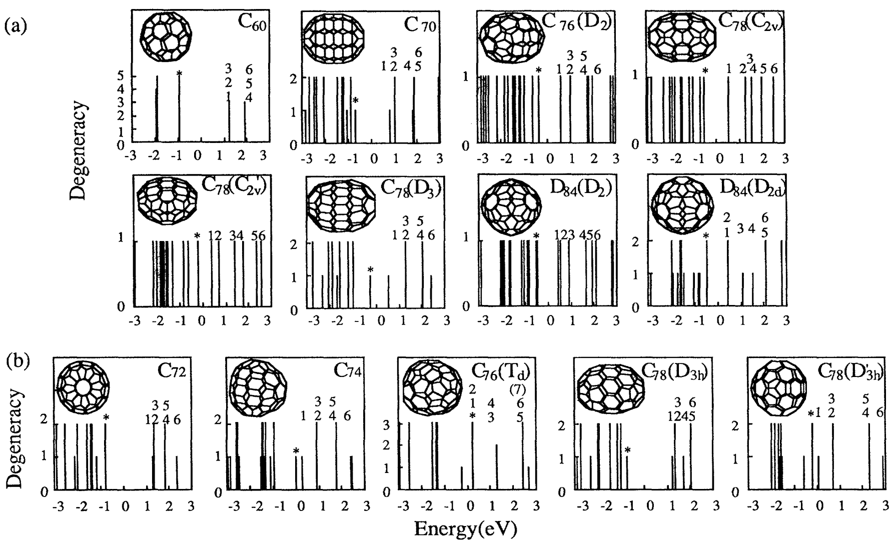

FIG. 1. Electronic-state distributions of (a) fullerenes experimentally extracted and identified so far and (b) those unextracted yet. In each case, the highest-occupied state is denoted by an asterisk. Numbers 1 to 6 (=*n*) indicate the *n*th lowest unoccupied states.

spherical harmonics states. Surprisingly, the same three- and three-state bunchings above the considerable energy gap are found to take place in the next extractable fullerene D_2 C_{76}. Also all the other extractable fullerenes show similar level bunchings above the well-developed energy gap.

This level bunching characteristic of extractable fullerenes is not always common to unextracted ones as will be shown below. In considering the candidates for extractable fullerenes, we can adopt the so-called isolated-pentagon rule (IPR), which requires that each pentagon should be surrounded only by hexagons. The origin of the IPR can be considered in the following way [16]. If there are fused pentagons on the fullerene network, C atoms shared by two (or three) pentagons should have not sp^2-like but sp^3-like hybridization character due to the similarities between the pentagon angle (180°) and the sp^3 angle (109.5°), and, consequently, possess not the π state but the dangling-bond state. This dangling-bond state can easily form a chemical bond with C atoms outside. Then, the fullerene would hardly be dissolved by solvents. In Fig. 1(b), the electronic structure of the IPR-satisfying, but unextracted fullerenes smaller than C_{80}, is shown. In contrast to the extractable-fullerene group, some fullerenes such as C_{74}, $C_{76}(T_d)$, and $C_{78}(D_{3h}^{\prime})$ do not show the three-state bunching. Their energy difference between the lowest-unoccupied state and the next state is even larger than the energy gap just below. On the other hand, some of the remaining unextracted fullerenes [e.g., $C_{78}(D_{3h})$] have a well-developed energy gap and the level bunchings as in the case of extractable fullerenes. Such fullerenes may be extracted in the future with different experimental conditions. Actually, the presence of several additional fullerenes not previously observed has been pointed out recently [17].

In order to examine the origin of the common level bunching in the electronic structure of extractable fullerenes, spatial distributions of the three lowest-unoccupied states in C_{70} and C_{76} obtained using a constant-transfer tight-binding model for π states are shown in Fig. 2. Interestingly, all three states are distributed at C sites on pentagons. This is consistent with the classical electrostatic consideration that the charge added to a conducting material should mainly reside at certain surface regions with large positive curvature.

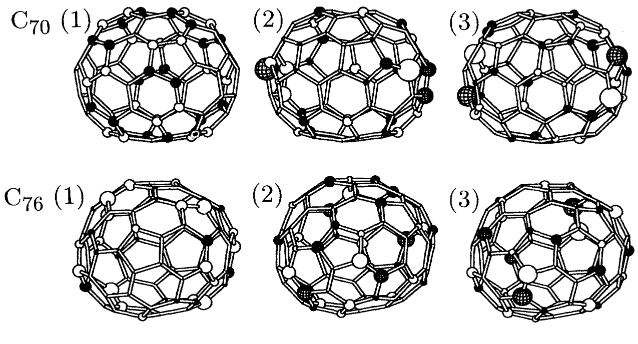

FIG. 2. Spatial distributions of the three lowest-unoccupied states of C_{70} and $C_{76}(D_2)$ ["(*n*)" denotes the *n*th lowest-unoccupied state]. The radius and the kind (open or hatched) of each sphere, respectively represent the magnitude and the sign of the amplitude at each C site. All states avoid nonpentagon sites (5 C_2 units in C_{70} and 2 C_6 chains and 2 C_2 units in C_{76}). The electron distribution is proportional to the square of the amplitude and even more strongly localized at pentagonal sites.

Since the lower unoccupied states of fullerenes accomodate the additional electrons when negatively charged, their spatial distribution does indicate the location of the electrons added. On the other hand, it is well known that the curvature of a fullerene is concentrated on 12 pentagons since a hexagon is essentially a flat unit.

These spatial distributions and the universal electronic structure around lower unoccupied states in extractable fullerenes imply the presence of common geometrical pentagon arrangements. Actually, in all the extractable-fullerene geometries, we can find the "pentagon pairing" shown in Fig. 3(a). There, 12 pentagons dimerize to form six pairs. However, pentagons on some of the unextracted fullerenes [e.g., $C_{76}(T_d)$ and $C_{78}(D'_{3h})$] cannot be grouped into six pairs. It is well known that π states on a hexagon (benzene) form a closed-shell electronic structure with a considerable gap. On the other hand, π states on a single pentagon form an open-shell electronic structure, while the pentagon dimer has a closed-shell electronic structure [Fig. 3(b)] and should be more stable than two separated pentagons. Therefore, pentagons should tend to dimerize during the growth process with an appropriate quenching condition [18].

The larger the fullerene considered, the stronger the restriction placed on its network by the pentagon-pairing rule. For example, we can select two and three candidates for experimentally extracted C_{86} and C_{88} fullerenes of which only the symmetries are known to be C_2 [12]. Also, we can choose two candidates for C_2 C_{82} [8]. These selected candidates are shown in Fig. 4.

By analyzing the network geometries further, i.e., considering the fullerenes to consist of 12 pentagons *and* other units, we can find both prevalent and rare units [20]. Prevalent units are even-atom chains including a dimer (C_2), while a typical rare unit is a C monomer. For example, C_{70} consists of 12 pentagons and 5 C_2 units. In this sense, *C_{60} is a perfect fullerene consisting only of pentagon units.* Unextracted fullerenes C_{74} and T_d C_{76}, on the other hand, both have several C monomers as a structural unit. These selectivities may also be related to the open- and closed-shell electronic structures of a C monomer and an even-atom chain, respectively. C monomers are expected to dimerize to form C_2 units during the fullerene growth process.

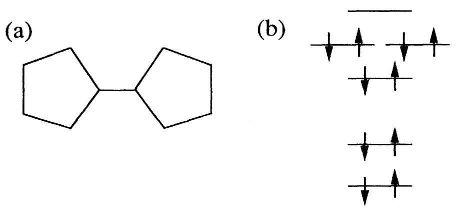

FIG. 3. (a) Pentagon pair, the universal geometry of all the pentagons on extractable fullerenes, and (b) its schematic electronic structure up to the lowest-unoccupied state.

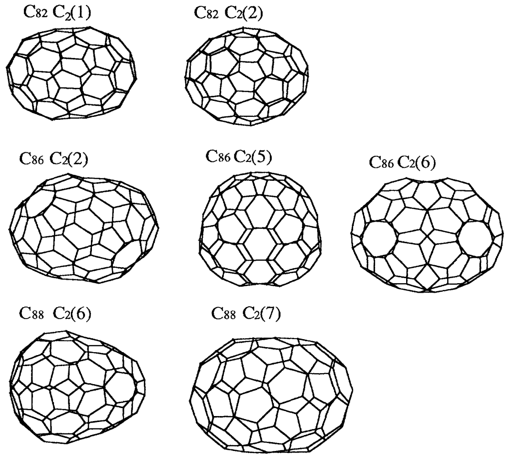

FIG. 4. Structural candidates for C_{82}, C_{86}, and C_{88} fullerenes extracted from soot but not yet identified. (There are two C_2 C_{86} isomers extracted.) These are the only possible candidates having the pentagon-paired geometry. Identification numbers are from Ref. [8] for C_{82} and Ref. [19] for others.

Another rare unit is, surprisingly enough, a hexagonal C_6 ring. Although C_{60} and larger fullerenes have many more hexagons than pentagons, a C_6-ring unit scarcely remains as a structural unit in the case of extractable fullerenes if we remove 12 pentagons from their network. On the other hand, structural units of the smallest unextractable IPR-satisfying fullerene C_{72} other than 12 pentagons are two C_6 rings. Also three large-energy gap candidates proposed for C_{84} with T_d, D_{6h}, and D_2 symmetries [21], all having two or more C_6-ring units, have not been extracted yet. This rarity of a C_6 ring may be related to the degree of solvability at the extraction process. A C_6-ring unit in the above brings about six more surrounding hexagons on a network, and forces the nearby wide area to be flat, where van der Waals interaction with outer graphitic material in soot should be rather strong. Hence, such fullerenes might hardly be dissolved.

One of the most surprising results by Krätschmer *et al.* [22] is the selective high-yield production of C_{60}, which is energetically less stable than C_{70} and larger fullerenes [9,10,23]. Although the growth mechanism of C_{60} and other fullerenes has been discussed before [24], the origin of this C_{60} selectivity has not been clarified in detail. A series of present findings can shed new light on this important problem. As has been mentioned, C_{60} can be considered to consist of 12 pentagons. Although the number of hexagons on C_{60} (20) is much larger than that of pentagons, it is impossible to construct I_h C_{60} out of 10 C_6 rings. Hence, not hexagons but pentagons should be considered to be the fundamental units of C_{60}. The preference for pentagons rather than hexagons in group-IV clusters was pointed out in our previous work where the dodecahedral (pentagon-faced) 20-atom cluster, now known as the smallest possible fullerene, was proposed

[25]. This preference is due to the fact that a pentagonal cluster can have more bonds than a hexagonal cluster. However, C atoms in the dodecahedral (IPR breaking) C_{20} must take not sp^2 but sp^3 hybridization. Hence, if C atoms would insist on the sp^2 hybridization during the fullerene growth process, the best solution under the preference for pentagons is C_{60}. Avoiding the sp^3 hybridization is also consistent with the IPR. The presence of such local rules can be supported also by the local geometrical rules found in the present work. Additional units other than pentagons occasionally incorporated in the network would lead to larger fullerenes which are less abundant than C_{60}. This strong preference for pentagons may be another reason for the rarity of a C_6 ring discussed above.

In addition to the growth issue, one of the present findings, i.e., the spatial distribution of lower unoccupied states on pentagon sites, reveals an important point to be considered in designing larger-fullerene conductors by electron doping. In order to enhance the conductivity, the overlap between pentagon-site π states on the nearest-fullerene pair should be preferable.

In summary, we have found a common level bunching of the three lowest-unoccupied states and pentagon pairing in extractable fullerenes. These two findings are considered to be related to each other since we have also observed that the lower unoccupied states are spatially distributed at pentagonal C sites in accord with the electrostatic consideration. From these findings, we propose structural candidates for C_{82}, C_{86}, and C_{88} fullerenes already extracted but not yet identified. In addition, by considering fullerenes to consist of 12 pentagons and other units, we have found prevalent units such as C_2 and even-atom chains and rare units such as a C monomer and a C_6 ring. These selectivities can be attributed mainly to their open- or closed-shell electronic structure affecting the growth process, and partly to the solvability at the extraction process. The presence of these rather "local" rules combined with the decomposition of fullerenes into pentagons and others then supports also the local rule naturally leading to the selective production of C_{60}: keep the sp^2 hybridization and form as many pentagons as possible. Now larger and larger fullerenes are being extracted from soot. The present findings will play an important role in considering their geometries and designing new materials from them.

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