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Electronic and geometric structures of C₇₀

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We have calculated the electronic structure of the C_{70} cluster of the D_{5h} geometry by the localdensity approximation. The electronic levels obtained show excellent agreement with photoemission experiments, which provides a further strong support for this geometry. The bunching of levels is observed at several energies, including the regions around the highest-occupied state and the lowest-unoccupied state, showing the possibility of superconductivity in doped solid C_{70} . The totalenergy calculation suggests that the bond-length alternation found in C_{60} is also present in C_{70} . The calculated binding energy per atom of the C_{70} cluster is found to be slightly larger than that of the C_{60} cluster. This implies the importance of dynamical effects on the relative abundance of fullerenes.

In the last decade, atomic clusters have attracted much interest and mass spectra of various kinds of clusters have been reported.¹ In the case of carbon clusters, C_N , only even-N clusters have been found for medium-size clusters (N > 30) in early work on the mass spectrum.² A later experiment with an additional space for cluster growth at the supersonic nozzle has revealed the extraordinary stability of C₆₀.³ The reported mass spectrum has only two clear peaks at C_{60} and $\mathrm{C}_{70},$ although the peak at C_{60} is much stronger than that at C_{70} . To account for these unusual mass spectra, cage structures are proposed for C_N (fullerenes).³ The proposed structures for C_{60} (Ref. 3) and C_{70} (Ref. 4) are shown in Fig. 1. These cagestructure C_N are expected to trap atoms and molecules inside $(C_N X)$, and C_N and $C_N X$ are believed to have a great potential of application in various fields.

Recently, carbon soot produced by the contact arc in inert gas was found to contain considerable amounts of C_{60} and C_{70} clusters. The $\mathrm{C}_{70}\text{-to-}\mathrm{C}_{60}$ ratio is about 0.1 to 0.3. Moreover, both C_{60} and C_{70} are found to form crystalline solids.⁵ Since then, many kinds of studies on C₆₀ have already been done. In NMR experiments, sixty atomic sites in C_{60} are found to be equivalent,^{6,7} and the proposed truncated icosahedron structure [Fig. 1(a)] has been confirmed. In the truncated icosahedron, there are two kinds of bonds. One is on the pentagon and believed to have a single-bond character. The other is shared by hexagons, having double-bond character. The NMR experiments on C_{60} have also provided the estimated values of bond lengths of 1.45 ± 0.015 and 1.40 ± 0.015 Å for these single and double bonds.⁸ Electronic structures of C_{60} cluster and solid C_{60} have also been reported.⁹⁻¹¹ In the case of C_{70} , on the other hand, NMR experiment⁶ has revealed that there are five different atomic sites, supporting a structure with D_{5h} symmetry [Fig. 1(b)]. Hückel,¹² complete neglect of differential overlap,¹³ and Hartree-Fock¹⁴ calculations on the electronic structure of the $D_{5h} C_{70}$ cluster have been reported. The one-electron energy levels of C₇₀, however, have not been discussed quantitatively so far. In the present work, we have calculated the electronic structure of the C_{70} cluster of the D_{5h} geometry by using the local-density approximation (LDA) in the density-functional theory.¹⁵ The energylevel distribution obtained shows interesting differences as well as similarities compared to that of C_{60} , suggesting the possibility of superconductivity of doped solid C_{70} . The electronic structure is also found to show excellent agreement with recent photoemission and inverse photoemission spectra,¹⁶ providing another strong support for this geometry. The binding energy per atom of C_{70} is found to be comparable to or slightly larger than that of C_{60} , also showing the high stability of the D_{5h} C_{70} .

In the electronic-structure calculation, we have used norm-conserving pseudopotentials for the C atom.¹⁷ The basis functions used are the Gaussian orbitals.¹⁸ Successful results on diamond $(sp^3 \text{ C atoms})$ and graphite $(sp^2$ C atoms) by the present method have been reported elsewhere,¹¹ showing the applicability of the present method to fullerenes where C atoms have not only an sp^2 component but also a small amount of sp^3 component. In order to obtain the electronic structure of an isolated C_{60} cluster, we have studied the face-centered-cubic C₆₀ crystal with large unit cell (lattice constant of 17.0 Å), where clusters do not interact with each other.¹¹ In the present calculation, a large hexagonal-primitive cell (a = 12.5Å and c = 20.6 Å) is used for C₇₀. Energy eigenvalues at the Γ point in reciprocal space are considered to be the discrete one-electron energies of the isolated cluster. The C_{70} cluster studied has the C_{60} bond lengths for r_1 to r_6 and the graphite bond length for r_7 and r_8 in Fig. 1(b) $(r_1 = r_3 = r_5 = r_6 = 1.46 \text{ Å}, r_2 = r_4 = 1.40 \text{ Å}, \text{ and}$ $r_7 = r_8 = 1.42$ Å). This C₇₀ is obtained by dividing the C_{60} cluster into halves and adding C_{10} [type *e* atoms in Fig. 1(b)] with graphite bond length around them.

In Table I, the calculated binding energy per atom for the C_{70} cluster is listed together with those of C_{60} and graphite. The LDA is known to overestimate the binding

11 532

TABLE	Ι.	Calcul	ated	bindin	ig e	energies	per	atom	of
graphite, 1	the C	C ₆₀ clus	ter, a	nd the	C_{70}	cluster	(eV).		

	Binding energy per atom
graphite	8.11
C_{60}	7.40
C70	7.42

energy of the system. (The experimental binding energy per atom for graphite is about 7.4 eV.) Therefore, only relative values in Table I are important. C_{60} and C_{70} are found to have similar binding energies per atom, about 91% of that of graphite. It is interesting to note that the calculated binding energy per atom of the C_{70} cluster is larger than that of the C_{60} cluster, although the abundance of C_{60} is much higher than C_{70} in the C_N cluster







FIG. 1. Geometry of (a) $I_h C_{60}$ and (b) $D_{5h} C_{70}$. In the C_{70} cluster, there are five inequivalent atomic sites (a - e) and eight kinds of bonds $(r_1 - r_8)$.

beam as well as in carbon soot. This implies the importance of dynamical effects on the relative abundance of carbon clusters. If C_{60} clusters are less reactive than C_{70} clusters, more C_{60} will survive in the cluster formation process, yielding a high abundance of C_{60} . We have also studied another geometry of the C_{70} cluster in which all bond lengths are equal to that of graphite. We have found that this C_{70} has smaller binding energy by about 2 eV per cluster than the C_{70} discussed above (i.e., C_{70} with C_{60} and graphite bond lengths). Hence, the bondlength alternation of single and double bonds found in C_{60} is also expected to be present in the C_{70} cluster.¹⁹

In Fig. 2, the calculated energy levels of the C_{70} cluster are shown. The energy width between the deepest valence state and the highest-occupied state is about 19 eV, which is similar to that of the C_{60} cluster,¹¹ and to the valence-band widths of graphite and diamond. Since the assumed symmetry is D_{5h} , there are only up to twofold degenerate states in C₇₀. Still the bunching of the levels at several energies is observed. This bunching probably comes from the spheroidal shape of the C_{70} . In the case of C_{60} , the bunching of levels has been attributed to its nearly spherical symmetry since levels can be characterized by spherical harmonics. One-electron levels in a spheroid are expected to show a similar shell structure to the spherical shell with minor splittings to spheroidal subshells²⁰ if the spheroidal deformation from the sphere is not so large. The D_{5h} symmetry may introduce further small splittings to these spheroidal subshells. Ten occupied and three unoccupied orbital states are bunched together around the highest-occupied state and the lowestunoccupied state, respectively. The rather large energy gap (1.65 eV) between the highest-occupied state and the lowest-unoccupied state is found. This is in good agreement with the experimental value of 1.6 eV obtained by the photoelectron spectroscopy.²¹ Since the energy gap found here is of similar magnitude to that of the C_{60} cluster,¹¹ we can expect that solid C₇₀ is a semiconductor as in the case of solid C_{60} . The lower thirty-five states above the energy gap (at +1.65 to +7.14 eV) are considered to have mainly π characters. There is a small gap



FIG. 2. Calculated energy levels of the C_{70} cluster. Energy is measured from the highest-occupied state.

above it. To compare the energy level distribution of C_{70} to that of C_{60} , we have shown the Gaussian-broadened "density of states (DOS)" for C_{60} and C_{70} in Fig. 3. The overall similarity between them is clearly seen. At the same time, there are some differences between them. For example, the first peak of the occupied states in order of decreasing energy in C_{70} is higher than the second peak. In the case of C_{60} , the first peak is lower than the second. These calculations are in good accord with experimental spectra.¹⁶ In Fig. 3 we have also shown the photoemission and inverse photoemission spectra for solid C_{60} (Refs. 9 and 22) and solid C_{70} .¹⁶ Although the experimental spectra contain a cross-section effect,²³ good agreement



FIG. 3. Calculated density of states per cluster of (a) C_{60} and (b) C_{70} obtained by the Gaussian broadening of the discrete energy levels (solid lines). The full width at half maximum of the Gaussians used is 2 eV for the levels which are lower than -10 eV, and 0.5 eV is used for higher levels. The experimental photoemission and inverse photoemission spectra (Refs. 9, 16, and 22) are also shown by the broken lines. (The used photon and electron energies are 65 and 27.25 eV, respectively.)

between the DOS and the experimental spectra for both C_{60} and C_{70} is obtained. This shows that intercluster interaction in solid C_{60} and solid C_{70} is rather small. Hence, solid C_{70} is also expected to be a van der Waals solid as in the case of solid C_{60} .¹¹ The overall feature of the unoccupied-state DOS of C_{70} is also found to show good agreement with the x-ray absorption spectrum.²⁴ These correspondences strongly support the D_{5h} geometry for C_{70} . In the case of C_{60} , the occupied-state DOS has been found to show the excellent agreement also with the electron-beam x-ray emission spectrum.²⁵ In a recent theoretical work, photoemission spectra of C_{60} and C_{70} have been reported,²⁶ and the results are found to be in accord with the experimental spectra, and therefore, with the present results.

Recently, alkali-atom-doped solid C_{60} and solid C_{70} are found to become conductive.²⁷ Moreover, superconductivities of $K_x C_{60}$ (Ref. 28) and $Rb_x C_{60}$ (Ref. 29) have been discovered. In the case of $K_x C_{60}$, the composition of the superconducting phase is found to be very close to K_3C_{60} . In our recent work,³⁰ it has been found that K_xC_{60} is an exotic ionic metal and K_3C_{60} has high density of states at the Fermi energy, which seems essential to its relatively high superconductivity transition temperature. Since the present calculation suggests that solid C_{70} also has rather high density of states around the energy gap, electron-doped as well as hole-doped solid C_{70} are also potential candidates for the superconductor. The peak in the C_{70} DOS including the highest-occupied state is higher than the peak including the lowest-unoccupied state. Hence, the hole-doped solid C_{70} may have higher transition temperature. The mixed solid of C_{60} and C_{70} at arbitrary composition is also an interesting candidate. Moreover, since the C_{70} cluster has larger space inside than the C_{60} cluster, there will be more flexibility in doping atoms and molecules inside the C_{70} cluster. The present work has revealed the great possibilities of application of the second most abundant fullerene C_{70} .

In summary, the electronic structure of the C_{70} cluster of the D_{5h} geometry has been obtained by the LDA pseudopotential method. Both the occupied and unoccupied states show excellent agreement with experimental photoemission and inverse photoemission results, supporting the assumed geometry of the C_{70} cluster. Moreover, the bunching of levels is found at several energies including the regions around the highest-occupied state and the lowest-unoccupied state, showing the possibility of superconductivity of doped solid C₇₀. Bond-length alternation of single and double bonds observed in C_{60} is also expected to be present in C_{70} from the calculated total energies. The binding energy per atom of the C_{70} cluster is found to be comparable to or slightly larger than that of the C_{60} cluster. This implies the importance of the dynamical effect on the relative abundance of carbon clusters.

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