

Electronic Structure of Solid C₆₀: Experiment and Theory

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Synchrotron-radiation and x-ray photoemission studies of the valence states of condensed phase-pure C₆₀ showed seventeen distinct molecular features extending ~23 eV below the highest occupied molecular states with intensity variations due to matrix-element effects involving both cluster and free-electron-like final states. Pseudopotential calculations established the origin of these features, and comparison with experiment was excellent. The sharp C 1s main line indicated a single species, and the nine satellite structures were due to shakeup and plasmon features. The 1.9-eV feature reflected transitions to the lowest unoccupied molecular level of the excited state.

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The structure of C₆₀ has been proposed to be a truncated icosahedron with twenty six-membered rings and twelve five-membered rings.¹ In this allotrope, the atoms are equivalent, giving a closed-shell electronic structure and a molecule that is unique in nature. While the existence of C₆₀ has been known for several years, moderately large-scale production and phase separation of C₆₀ and other fullerenes were not possible before the work of Krätschmer *et al.*² That breakthrough virtually assured rapid development in understanding the properties of these novel forms of matter.

This paper focuses on the electronic states of C₆₀. The experimental results, obtained with photoemission, show seventeen resolvable features within ~23 eV of the highest occupied electronic state. Many of these structures are remarkably sharp, rising from near-zero backgrounds. Indeed, the spectra resemble those of simple molecules rather than other forms of pure carbon, while exhibiting an overall bandwidth and a distribution of σ and π character that is the same as for graphite and diamond.^{3,4} These results provide a long awaited test for calculations of the electronic configuration of C₆₀ and related fundamental properties. The theoretical results presented here were obtained with a pseudopotential-based local-density-approximation calculation of the truncated icosahedral structure. Comparison with experiment shows agreement for all of the features, with a maximum error of 0.5–0.7 eV in the p_{σ} levels ~10 eV below the highest occupied states. These results demonstrate that the properties of this symmetric stable structure of carbon can be described quantitatively to a high level of accuracy, in contrast to what has been found for clusters with substantial numbers of atoms but less definite structure.

The fullerenes were formed by the contact arc method,⁵ with subsequent separation by solution with toluene. Phase-pure C₆₀ was obtained by a liquid chroma-

tography process on alumina diluted with mixtures of hexanes. The resulting C₆₀ was then rinsed in methanol, dried, and placed in Ta boats that were ~10 cm from the substrate onto which C₆₀ was to be condensed. Degassing to ~475 °C desorbed the toluene, as well as H₂O and CO. Evaporations were performed at ~550 °C. The uppermost experimental features were very sharp, and the emission intensity between them was essentially “base line,” indicating the phase-pure character of films grown in this manner. Substrates were prepared by cleaving GaAs(110) and InP(110) *in situ* at $< 10^{-10}$ Torr, and C₆₀ was condensed onto these mirror-like surfaces at 300 K. The synchrotron-radiation studies exploited the tunability of the source to obtain high-resolution valence-band spectra for $40 \leq h\nu \leq 200$ eV, as well as C 1s spectra at higher energy. The x-ray photoemission measurements used a monochromatized Al K α source ($h\nu = 1486.6$ eV) to examine C 1s-derived structure and the valence bands. The results presented here are for relatively thick films that attenuated the substrate emission completely. For thinner films, the persistence of the substrate core-level features provided an independent energy reference.

To our knowledge, these results are the first to reveal the full valence-band region and structure associated with the C 1s level. However, Lichtenberger *et al.*⁶ have obtained photoemission results with $h\nu = 21.2$ and 40.8 eV, and comparison shows good agreement in the region of overlap, although our results show additional structure. They did not detect shakeup or plasmon features associated with the C 1s emission, but we show that there are nine such structures above the main line. The only previous studies⁷ used ultraviolet photoemission to investigate the gap between the highest occupied and lowest empty molecular orbitals for gas-phase C₆₀⁻.

The calculations were performed using the pseudopotential plane-wave formalism and the local-density ap-

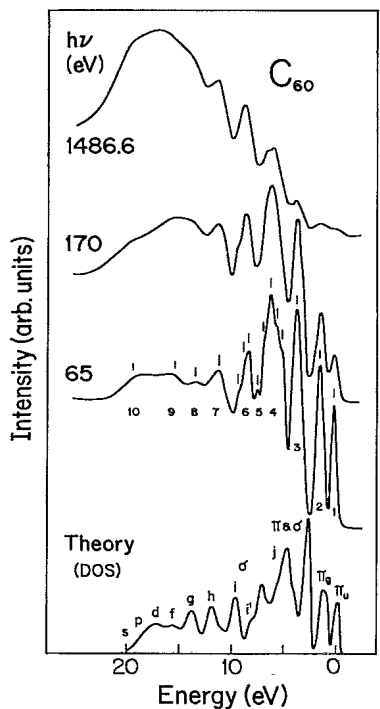


FIG. 1. Representative photoemission EDCs for condensed C_{60} showing the full valence band and modulation with $h\nu$ of the cluster features. Those within ~ 5 eV of the highest occupied level are p_x derived, those between ~ 5 and ~ 12 eV are hybrids of s - p_σ character, and features below ~ 12 eV are primarily s derived. The full bandwidth is the same as graphite and diamond, but only C_{60} has the richness in structure. The bottom curve is the density of states (DOS) calculated with the pseudopotential local-density method. The numbers and vertical lines associate experimental and theoretical features.

proximation.⁸ The atomic positions for C_{60} were determined from the minimization of the total energy, yielding C-C bond lengths of 1.382 and 1.444 Å. We assumed that the solid has a fcc lattice with a tetrahedral space group. Plane waves with an energy up to a cutoff of 49 Ry were included in the basis set (~ 28000 plane waves). With this energy cutoff and using new "soft" pseudopotentials,⁹ the total energy was converged to within 50 meV per atom. The one-electron Schrödinger equation was solved with an iterative method.¹⁰ The self-consistent potential was calculated using the single Γ point for the Brillouin-zone integration. Two special \bar{k} points¹¹ were used to calculate the density of states.

Figure 1 shows representative energy distribution curves (EDCs) for C_{60} taken at $h\nu = 65, 170,$ and 1486.6 eV; additional spectra acquired from 20 to 200 eV in 2-eV increments will be discussed elsewhere.¹² Figure 2 shows an EDC acquired at 50 eV with an experimental resolution of 0.2 eV. The zero of energy is the emission maximum of the highest occupied feature. Calculations for neutral C_{60} , C_{60}^- , and C_{60}^+ indicate that the removal or addition of one electron would displace these levels rigidly.¹³ With account of the position the Fermi level

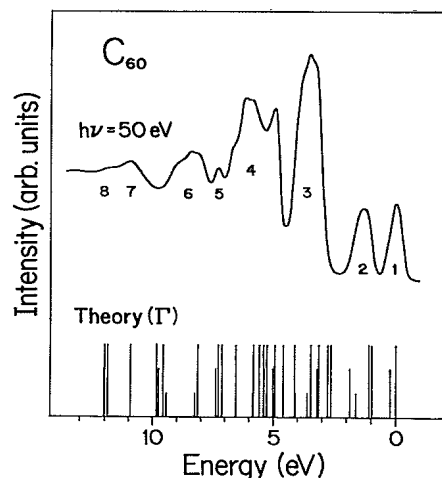


FIG. 2. High-resolution EDC showing seventeen resolvable experimental features in the photoemission spectrum of C_{60} . The theoretical lines show the electron levels at the point Γ of the Brillouin zone. Their height is proportional to the degeneracy.

E_F and the electron affinity of the GaAs(110) substrate, the highest occupied feature of photoexcited solid C_{60} would be 7.3 eV below the vacuum level, assuming alignment of the vacuum level of C_{60} with the substrate. An independent check of this energy was obtained by x-ray-photoemission-spectroscopy studies of C_{60} on InP(110) where a value of 7.4 eV was obtained. Lichtenberger *et al.*⁶ reported a value of 7.6 ± 0.2 eV.

The results of Figs. 1 and 2 show dramatic variations in the line shapes as a function of photon energy. The lower-photon-energy results show dominant emission from the upper half of the valence bands, especially those features labeled 1-4. With increasing $h\nu$, the intensity of features 1-4 diminished relative to the deeper structures, notably 9-10. Features 6 and 7 were well defined at all energies. These changes reflect the photoionization cross sections of the s - and p -derived states. In particular, the cross section of C $2p$ -derived states is large at low energy, is comparable to that of the s states at $h\nu = 125$ eV, and is about 13 times smaller than the s states for energies of about 1486 eV.¹⁴ The $2s$ enhancement relative to the $2p$ character reflects the nodal structure of the former and the larger matrix elements for coupling to plane-wave states at ~ 1475 eV. McFeely *et al.*³ and Bianconi, Hagström, and Bachrach⁴ used this property to identify the character of the states in graphite and diamond. Both groups concluded that $2p_\pi$ levels fell within ~ 5 eV of E_F , that $2p_\sigma$ levels were concentrated between ~ 5 and ~ 10 eV of E_F , and that deeper states were derived from s -like σ bands. From Figs. 1 and 2, we see that C_{60} exhibits an analogous behavior, despite differences in bond angles and structure, with π character in the leading structures and s character at the bottom. Significantly, the overall bandwidths of C_{60} , graphite, and diamond are essentially the same, namely,

~ 23 eV. Such similarities notwithstanding, C_{60} exhibits much more detailed structure, and these features give insight into the electronic structure.¹²

Analysis of the variations in relative intensities of the peaks identified in Figs. 1 and 2 for the cluster levels shows that the high-lying final states of the cluster play an important role in the photoexcitation probability. From Figs. 1 and 2, and especially from more closely spaced EDCs,¹² it is clear that the intensities of features 1–3 oscillate until about $h\nu=140$ eV. For example, the peak-height intensity ratio I_1/I_2 was 0.88 at $h\nu=40$ eV, 1.48 at 45 eV, 1.06 at 50 eV, and 0.78 at 65 eV. Such changes reflect excitations to states in the continuum which are not free-electron-like, with differences due to the fact that feature 1 has odd symmetry while feature 2 has even symmetry. The importance of direct transitions and selection rules to ~ 140 eV stands in contrast to results for crystalline graphite where the free-electron-like final-state regime was reached by ~ 90 eV.⁴ For C_{60} , the spectra replicate the state density by $h\nu \cong 170$ eV, with fivefold degeneracy of feature 1 and ninefold degeneracy of feature 2.

Our results also show interesting matrix-element effects for features 4 and 5. In particular, the shallowest component of peak 4 at 6 eV is almost resolution limited at $h\nu=50$ eV (Fig. 2) but is only a weak shoulder at $h\nu=65$ eV (Fig. 1). Feature 5 is clear from $h\nu=50$ to 80 eV but was not discernible at other energies, despite the fact that the experimental resolution was not varied. Again, these effects demonstrate the importance of dipole selection rules for these highly symmetric molecules. In contrast, solids rarely exhibit modulation in structure at such high photon energies except for transitions related to critical points, i.e., primary Mahan cone emission.¹⁵

Examination of the high-resolution EDC of Fig. 2 shows seventeen distinct molecular levels associated with ten spectral features. The width of feature 2 almost certainly indicates that it is derived from at least two lines or a broadened band, but we have not yet been able to resolve them at 300 K. We know of no cluster containing sixty atoms that retains levels so well resolved as those in Figs. 1 and 2. While studies of small molecules have shown very detailed structure with vibrational splittings,¹⁶ such effects are lost for clusters with such large numbers of metal or semiconductor atoms and the accompanying thermal broadening. C_{60} , with its high symmetry and high molecular level degeneracy, is a beautiful counterexample. One can only speculate that such detail will be found in larger fullerenes.

In Fig. 2 we show the predicted energy levels at Γ for the ground state of C_{60} , aligned to the highest occupied level. The degeneracy is indicated by the height of the lines. The first feature (derived from the fivefold-degenerate h_u state of the isolated molecule) appears as a pair of levels split by the tetrahedral crystal field with threefold and twofold degeneracy, while feature 2 has

four distinct eigenvalues derived from h_g and g_g states. The density of states of solid C_{60} calculated using two special \bar{k} points is shown in the bottom of Fig. 1. The theoretical spectrum was convoluted with a Gaussian of width $0.23 \text{ eV} + 0.2|\Delta E|$ to simulate experimental resolution and lifetime effects. ΔE is the binding energy with respect to the highest occupied level. The agreement between theory and experiment is very good, with discrepancies of ~ 0.5 and ~ 0.7 eV in the positions of features 6 and 7.

The quasispherical shape of the C_{60} molecule suggested that we should analyze the wave functions in terms of their expansion in spherical harmonics. We found that they were dominated by a single l component and we used it to label the lowest peaks of the density of states in Fig. 1 (s, p, d, \dots). The highest peaks also have well-defined angular character, but they have significant splittings and overlaps that will be described in detail elsewhere. Features 1 and 2 in the spectrum, for example, correspond to π states with $l=5$ and 4 angular character, respectively.

Several authors¹⁶ have reported calculations of the electronic states of isolated C_{60} , and their analyses show p_z -derived eigenstates within ~ 4 eV of the highest molecular level arising from orbitals directed radially from the cluster center with $h_u, g_g, h_g,$ and g_u symmetry. Our experimental and theoretical results are in qualitative agreement with them, supporting their predictions that the levels were narrow with little orbital mixing. Comparison of the predictions of Saito¹³ and Bernholc¹⁷ to the experimental results shows good agreement. Note that all of the calculations were done without knowledge of the experimental spectra, and peak associations may change as refinements are added.

Figure 3 shows the C $1s$ spectrum measured with $h\nu=1486.6$ eV. Of the ten structures that can be readily resolved, the first corresponds to the main line itself, centered at 282.9 eV relative to the center of the leading valence-band feature. Its FWHM, 0.65 eV, is probably resolution limited by the spectrometer. The main line is symmetric and offers no indication of more than a single C species. Features 2–9 probably represent π to π^* or σ^* transitions, with linewidths comparable to those observed in small molecules such as benzene. Following the discussion of Bigelow and Freund,¹⁸ we can assume that the energy levels of the π^* configuration that result from the sudden creation of the core hole are displaced rigidly from those of the ground state. In this simple approximation, the first feature at 1.9 eV could be attributed to a shakeup process involving direct excitation across the gap. Such transitions involve states of the same symmetry and are dictated by monopole selection rules.

The satellite features of Fig. 3 for C_{60} resemble those of small molecules at low energy but also mimic the behavior of graphite, glassy carbon, and diamond in the region of the plasmon losses, ~ 30 eV.³ Here we see a broad feature centered ~ 28 eV below the main line.

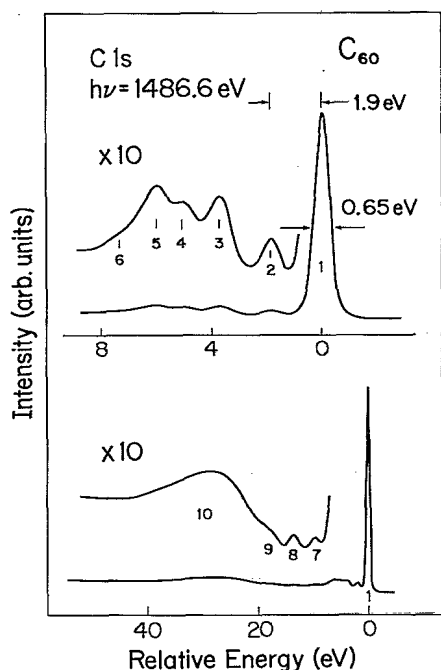


FIG. 3. C 1s features for C_{60} referenced to the main line 282.9 eV below the center of the highest-occupied-state feature. Features 2-9 reflect shakeup structures of the form π^* or σ^* akin to those in small C-based molecules. Feature 2 probably reflects excitation across the gap of the excited state. Feature 10 reflects a plasmon loss due to excitation of a collective mode of the cluster or the condensed solid.

The origin of this feature is particularly intriguing because equivalent structures are not observed in small molecules. We can speculate that it is due to collective excitations of the electrons of the cluster itself, representing the normal modes of a spherical shell of charge of average radius ~ 3.5 Å with a charge-free central region. At the same time, the loss structure might be due to a bulk plasmon associated with solid C_{60} . Inverse-photoemission studies and investigations of C_{60} condensed in a dispersed form should make it possible to choose one or the other possibility, and such studies are presently underway.¹⁹

This study has shown that seventeen experimental features can be identified in the high-resolution photoemission spectrum of C_{60} and that their origins can be determined from *ab initio* calculations of the eigenstate spectrum. The sharpness and number of such levels is reminiscent of the molecular orbits of smaller molecules. There appears to be no fundamental limitation in our ability to fully explore these levels and their implication on the physical and chemical properties of C_{60} . At the same time, it is remarkable that a structure containing so many electrons can have such a sharp distribution, a fact that no doubt reflects the high symmetry of the molecule. In the near future, it can be anticipated that the preparation of phase-pure C_{70} and other fullerenes will allow detailed comparisons of their orbital structures. In the meantime, we regard the agreement of theory based on a

truncated icosahedron with the experiment as strong evidence that the structure is correct.

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