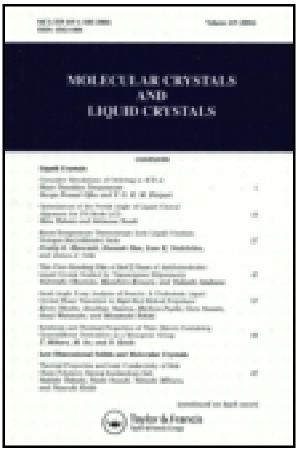

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Occupied and Unoccupied Orbitals of C_{60} and C_{70}

J. A. Carlisle [a], L. J. Terminello [a], A. V. Hamza [a], E. A. Hudson [a], E. L. Shirley [a], F. J. Himpsel [b], D. A. Lapiano-smith [b], J. J. Jia [c], T. A. Callcott [c], R. C. C. Perera [d], D. K. Shuh [d], S. G. Louie [e], J. Stöhr [f], M. G. Samant [f] & D. L. Ederer [g]

[a] Lawrence Livermore National Laboratory, Livermore, CA, 94550

[b] IBM Research Division, Thomas J. Watson Research Center, Yorktown Heights, NY, 10598

[c] University of Tennessee, Knoxville, TN, 37996

[d] Lawrence Berkeley Laboratory, Berkeley, CA, 94720

[e] Department of Physics, U.C. Berkeley, CA, 94720

[f] IBM Research Division, Almaden Research Center, 650 Harry Road, San Jose, CA, 95120-6099

[g] Tulane University, New Orleans, LA, 70118

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OCCUPIED AND UNOCCUPIED ORBITALS OF C_{60} and C_{70}

J. A. CARLISLE, L. J. TERMINELLO, A. V. HAMZA, E. A. HUDSON, E.L. SHIRLEY
Lawrence Livermore National Laboratory, Livermore, CA 94550

F. J. HIMPSEL, D. A. LAPIANO-SMITH
IBM Research Division, Thomas J. Watson Research Center, Yorktown Heights, NY 10598

J. J. JIA, T. A. CALLCOTT
University of Tennessee, Knoxville, TN 37996

R. C. C. PERERA, D. K. SHUH
Lawrence Berkeley Laboratory, Berkeley, CA 94720

S. G. LOUIE
Department of Physics, U.C. Berkeley, CA 94720

J. STÖHR, M. G. SAMANT
IBM Research Division, Almaden Research Center,650 Harry Road, San Jose, CA 95120-6099

D. L. EDERER
Tulane University, New Orleans, LA, 70118

Abstract The full spectrum of occupied and unoccupied σ and π orbitals is presented for solid C_{60}, C_{70}, and graphite, using C1s emission and absorption spectroscopy. There are significant differences between C_{60} and C_{70}, and even larger changes relative to their infinite analog graphite (C_{∞}). A comparison is made with photoemission and inverse photoemission results, along with first principles quasiparticle calculations.

INTRODUCTION

The aim of our work is to characterize the orbital structure of the fullerenes, and to pursue its evolution from a cluster to the infinite solid. For obtaining a complete picture of the electronic structure we compare a variety of experimental techniques, i.e. photoemission and core level emission for occupied orbitals and inverse photoemission and core level absorption for unoccupied orbitals.[1-6] Our experimental results focus on optical probes involving the C1s core level, i.e. absorption via transitions from the C1s level into unoccupied π^* and σ^* orbitals and emission involving transitions from occupied orbitals into a C1s hole. Due to the simplicity of the C1s level there exist clear selection rules. For example, only transitions to and from orbitals with p-character are dipole-allowed. These results on the p-projected density of states are compared with inverse photoemission and photoemission results, where the selection rules are less definitive. In addition, a first-principles quasiparticle calculation of the density of states is used to assign the orbital features. The spectra from C_{60} and C_{70} are still far from their infinite analog, i.e., graphite, which is also measured with the same techniques. In order to determine the effect of electron transfer onto C_{60}, as in superconducting alkali fullerides, we are studying resonant emission of C_{60}. An electron is placed in the lowest unoccupied molecular orbital (LUMO) by optical absorption from the C1s level and the C 1s emission detected in the presence of this spectator electron.

ORBITAL STRUCTURE OF C_{60}

Figure 1 compares the spectra of occupied (left) and unoccupied orbitals (right) of condensed C_{60} obtained with different techniques, i.e. C1s emission and photoemission for occupied orbitals and C1s absorption and inverse photoemission (from Ref. 3) for unoccupied orbitals. In addition, the density of states (DOS) is given, using state-of-the-art quasiparticle theory[7]. In general one can distinguish π and σ manifolds, with a larger bonding-antibonding splitting for the more strongly interacting σ bands. The assignments to π- and σ-states can be made either by detailed comparison with calculations (Fig. 1), or by analogy with graphite, where well-defined onsets are observed for the of π^* and σ^* states in the absorption spectrum (Fig. 2 right). Similar onsets are seen in the fullerene absorption spectra, except for a downwards shift of about 1 eV. In the C 1s emission spectra (Fig. 2 left) the distinction between π and σ states is not so clear. The graphite spectrum shows only σ states, due to the experimental geometry, where emission along the c-axis of graphite is detected. In this case dipole selection rules do not allow transitions from π orbitals to the C 1s (see Ref. 6). For the fullerenes with curved carbon sheets, on the other hand, emission from both σ and π orbitals is allowed. Extra π emission peaks show up at the top of the spectrum. For a detailed analysis we use a comparison with the calculated density of states in Fig. 1.

Various calculations,[7-9] both in the solid state and for the free C_{60} molecule, have been published, which allow an identification of the observed peaks in terms of molecular orbitals. We use a state-of-the-art quasiparticle calculation for the density of states of condensed C_{60} in the Fm3 structure[7] It is bases on local density theory, and adds the self-energy that is induced by creating a hole in an occupied band or adding an electron to an unoccupied band. Condensing C_{60} molecules into a thin film broadens molecular orbitals into bands, giving rise to multiple density-of-states peaks per orbital (Fig. 1 bottom). Nevertheless, the interamolecular interaction is weak enough to prevent overlap of neighboring

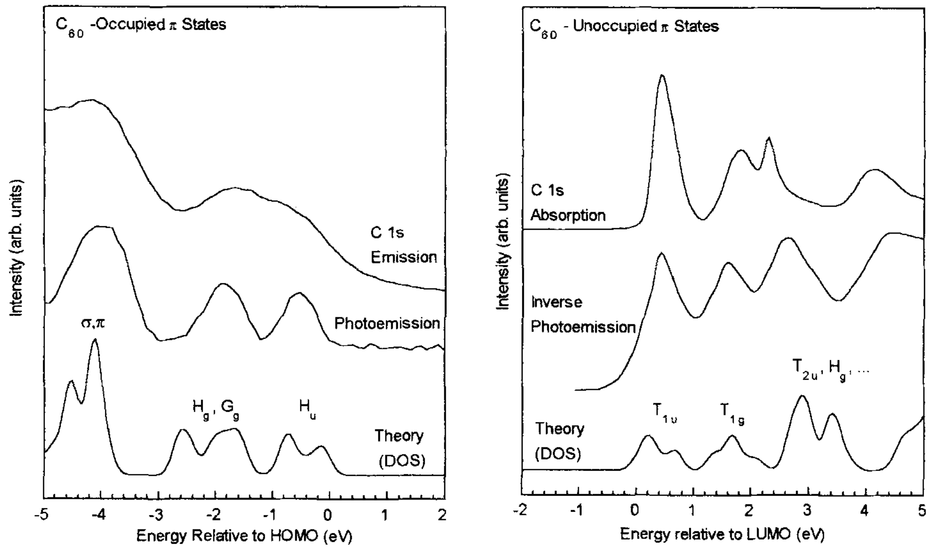

Figure 1: Comparison of various spectroscopies for obtaining the spectrum of occupied (left) and unoccupied (right) π orbitals of condensed C_{60}. The energies are referenced to the HOMO and LUMO, respectively. These data are compared with the density of states (DOS) from first principles quasiparticle calculations (shown at the bottom of each figure), which allows an assignment of the orbitals.

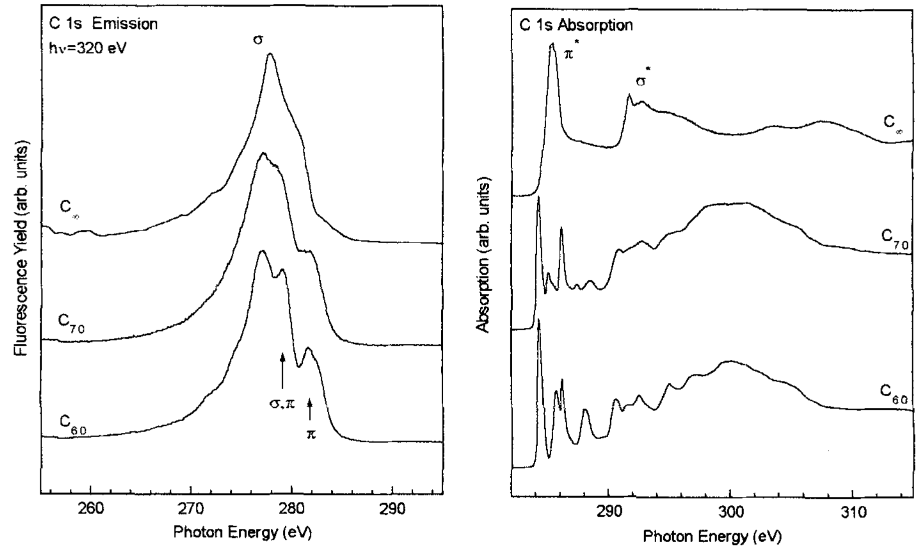

Figure 2: Fluorescence and absorption spectra from the C 1s core level for C_{60}, C_{70}, and their infinite analog graphite. Significant differences are seen between all three materials, showing that the orbital structure varies with cluster size, even for large clusters, and that C_{70} is still far from the limit C_{∞}.

bands near the fundamental gap. Therefore, we can assign the observed peaks in terms of the icosahedral orbital symmetry of the C_{60} molecule, in particular the H_u HOMO, the T_{1u} LUMO, and the next higher T_{1g} orbital. Farther away from the fundamental gap the bands from different orbitals start overlapping. All structures shown in Fig. 1 are π orbitals, except for one near -4 eV, which is a combination of σ and π orbitals.

For the comparison between calculated density of states and the various spectra in Fig. 1 we have aligned the centroids of the highest occupied and the lowest unoccupied bands. The actual band edges, which serve as the equivalent of the HOMO and LUMO in the solid state, are somewhat shifted from the centroids due to band dispersion. First, we notice that the calculated multiple features in the density of states for each orbital are not resolved in the experiments, possibly due to disorder in the film. An extra broadening of the DOS produces single peaks very similar to the data (see Ref. 7). One finds a clear correlation between calculated orbital centroids and peaks in the spectra, which allows the assignment indicated in Fig. 1. Comparing different types of experiments we find the number of peaks to be identical, but their positions not always in coincidence. These differences in orbital spacing are particularly apparent in the comparison between the inverse photoemission and C 1s absorption spectra (Fig. 1 right). They could be due to different selection rules for the two spectroscopies, selecting out different portions of the bands. A more likely reason is an orbital-dependent electron-hole interaction in C 1s absorption. It is not included in the calculated density of states. The electron hole interaction can be obtained by comparing the optical transition energy with the photoemission and inverse photoemission values of the initial and final state, respectively. It comes out to about 2 eV for the C 1s - to - LUMO transition, an amount large enough to rationalize the observed orbital-dependent variations.

EFFECT OF CLUSTER SIZE

An interesting aspect of carbon clusters is the possibility to follow the transition from an isolated atom to the solid over a wide range of well-defined cluster sizes. As demonstrated in Fig. 2 for C_{60}, C_{70}, and C_{∞} (graphite), there are significant differences between the two cluster sizes, e.g. in the structure of the lower π orbitals see with C 1s absorption (compare Ref. 4). Both clusters are far from reaching the continuous spectrum of the infinite solid. The sharpness of the molecular orbitals suggests an extension of these experiments to larger fullerenes, and even carbon tubules. In addition to the discrete - to - continuous transition one also expects a chemical transition from non-aromatic to aromatic. The resonant bonding structure normally exhibited by hexagon rings is disrupted by the presence of single-bonded pentagons in the fullerenes[9,10], and it would be interesting to know how much the five-fold rings have to be diluted in order to recover a resonant bonding structure.

RESONANT EMISSION WITH A SPECTATOR ELECTRON

The transfer of electrons onto fullerenes[10] by doping with alkali atoms has attracted substantial interest due to the discovery of superconductivity in these systems. We have made an attempt to simulate this charge transfer with pure C_{60}, placing an extra "spectator" electron onto the molecule by populating the LUMO from the C 1s. This is achieved by tuning the photon excitation to the lowest absorption peak at 284.3 eV with an undulator at the Advanced Light Source (Fig. 3). To extract the change in the electronic structure induced by the spectator electron we compare the C 1s emission at this resonance with an off-resonant spectrum obtained at a higher photon energy (compare Ref. 5 for a similar experiment). Ignoring any fine structure for a course analysis, we find that spectral weight is missing at the top of the occupied states, and extra weight appears at the bottom. Effectively, the center of gravity of the emission spectrum has shifted down in energy by 0.5 eV. Such a downwards shift has been seen in resonant emission from other systems. A simple explanation starts from the observation that the spectator electron shifts all states upwards in its Coulomb field. The C 1s core state is shifted more than the valence state since its wave function lies completely within that of the spectator electron, while the valence state extends in part beyond the spectator charge. As a consequence, the energy difference between the core and the valence state is reduced, and the

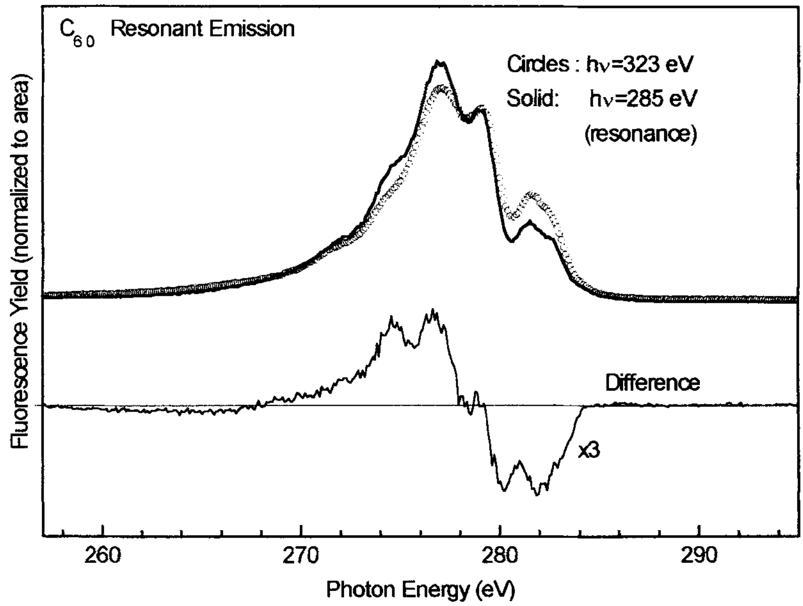

Figure 3: Resonant Fluorescence from C_{60}. By exciting a C 1s core electron into the first π^* orbital, the recombination fluorescence is observed in the presence of a π^* spectator electron (solid curve). Compared to the non-resonant fluorescence excited far above threshold (circles), one observes a shift of spectral weight towards lower valence orbitals (see the difference spectrum at the bottom).

emitted photon has less energy. If we know the shift of the C 1s we can determine the shift of the valence state, and from that the reduction of the electron affinity in the presence of an extra spectator electron. This number is important for determining the capability of fullerides to accomodate extra electrons[10]. As a measure of the C 1s shift induced by a spectator electron we may take the electron-hole interaction of the C 1s - to - LUMO transition. Using a value of 2.2 eV (see Ref. 2) we obtain an upwards shift of the HOMO of 2.2-0.5 = 1.7 eV in the presence of a LUMO spectator, and from there a reduction of the electron affinity from 2.7 eV [10] in neutral C_{60} to 1.0 eV in negatively-charged C_{60}. This compares to an estimate[10] of 0.1-0.4 eV for the affinity of the negative C_{60} ion in the gas phase. An increase of the affinity in the solid is expected due to partial screening of the negative charge of the ion.

An explanation of the changes in the fine structure at resonance has been given in Ref. 5 in terms of resonant inelastic photon scattering (i.e. the X-ray Raman effect). In this interpretation the selection rules at resonance differ from the normal dipole selection rules, enhancing certain valence orbitals and suppressing others.

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