Unfilled orbitals of C_{60} and C_{70} from carbon K-shell X-ray absorption fine structure

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The K-shell near-edge X-ray absorption fine structure spectra of solid C_{60} and C_{70} have been recorded with high spectral resolution. The spectra exhibit sharp resonances associated with transitions to unfilled π^* molecular orbitals and, at higher energy, broader resonances associated with σ^*-like orbitals. The observed energy splitting of the π^* resonances can be accounted for by published extended Hückel calculations. Our data clearly reveal that the fullerene films resemble molecular solids with considerably stronger intra-molecular than inter-molecular interactions.

Following the early predictions of the existence of all-carbon spherical or pseudo-spherical cage-like structures, so-called fullerenes [1–3], it has recently become possible to produce purified solid films composed of such molecules [4–7]. Buckminsterfullerene, C_{60}, and an as yet unnamed C_{70} species are the most easily produced fullerenes. Both molecules are composed of pentagons and hexagons of carbon atoms, with the best structural data coming from solution [8–10] and solid state [11–13] NMR. C_{60} has an icosahedral soccer ball structure with all carbon atoms being equivalent but with two different C–C bond lengths of 1.40 and 1.45 Å [12]. C_{70} resembles a rugby ball with D_{5h} symmetry [14] and five different chemically distinct carbon atoms. The high number density of the molecules in the films allows

their investigation with nearly every spectroscopic technique available. Since the molecules interact only weakly (van der Waals interaction) with one another the spectroscopic data are expected to predominantly reflect the electronic and geometric structure of the individual molecules. The abundance of electronic structure calculations for free C_{60} and C_{70} [15–21] thus offers the opportunity for a comparison of experimental and theoretical results.

Here we present the results of a near-edge X-ray absorption fine structure (NEXAFS) study of C_{60} and C_{70} purified films and compare them to a calculation of the electronic structure of the π-systems of the two molecules [18]. NEXAFS spectroscopy utilizes soft X-ray radiation to probe excitations of K-shell electrons to unoccupied molecular orbitals (MOs) [22], and is thus complementary to ultra-violet photoemission spectroscopy or X-ray emission spectroscopy which probe the filled MOs. NEXAFS spectra of C_{60} and C_{70} are found to exhibit

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distinctly different, pronounced resonances which can be associated with the lowest unfilled MOs of the molecules. The narrowest and most pronounced resonances are observed near the K-shell excitation threshold and can be associated with unfilled π^* orbitals directed perpendicular to the molecular sphere. The energies of these resonances are compared with published orbitals energies obtained by means of extended Hückel calculations for the two molecules [18]. Our comparison reveals a remarkable agreement between experiment and theory, indicating that for appropriate structural models of the free molecules, simple theoretical results can account for the energetics of the π electron systems.

C_{60} and C_{70} were produced by arc heating graphite in helium (100–150 Torr pressure) [4,5,7], and removing the fullerenes from the raw soot by toluene extraction. Purification and separation of C_{60} and C_{70} was accomplished by chromatography using a column of activated alumina eluted with hexane and hexane/benzene mixtures [23,24]. Mass spectrometry indicated that the separated C_{60} contained $\leqslant 1\%$ C_{70}, while the C_{70} fractions had $\leqslant 5\%$ C_{60}. Thin films of the fullerenes were prepared by loading a few hundred µg of purified material (dissolved in toluene) into a resistively heated stainless steel tube oven, and heating it to 200–300°C in vacuum to drive off the solvent. The molecules were then sublimed onto tantalum foil substrates placed about 5 mm above the 1 mm opening in the tube oven by heating the oven to ≈ 550°C for several minutes.

Samples of highly oriented pyrolytic graphite and thin films of C_{60} and C_{70} were transferred from atmosphere into a UHV sample-preparation/electron-analyzer system [25,26] where C 1s and O 1s NEXAFS and C 1s photoelectron spectra were measured. All near-edge and photoemission measurements were made at the National Synchrotron Light Source on beamline U8b using a 10 m toroidal grating monochromator to produce the variable-energy monochromatic X-rays employed in our experiment. The instrumental (monochromator) resolution was about 0.2 eV. Carbon 1s NEXAFS spectra were measured in the "partial-yield" mode [27] by collecting 0–9 eV electrons emitted from the samples while the photon energy was incremented from 275 to 324 eV. An ellipsoidal-mirror electron-energy analyzer [25,26] detected the electron yield from the samples

in a configuration that had the synchrotron radiation polarization vector 45° with respect to the surface normal. This geometry had the sample normal pointing directly into the center of the electron analyzer which has an angular acceptance of 0.76 sr. Carbon 1s photoemission was measured at a photon energy of 323 eV which produced surface-sensitive photoelectron spectra for all samples. Such measurements were useful in assessing the quality of our materials.

Adsorbed water on the graphite was removed by outgassing the sample by heating in vacuum immediately prior to measurement of the C 1s photoemission and near-edge absorption. Absorption features in the graphite NEXAFS served as a reference for monochromator calibration and for comparison to the π-conjugated systems of C_{60} and C_{70}. Because methods of handling solid films of C_{60} and C_{70} are not well established, and atmospheric contamination surely must have occurred, we chose to heat the samples to a temperature high enough to allow desorption of contaminants (outgassing to 2×10^{-9} Torr), but ensured retention of the fullerene thin films. However, as a precaution against thermal destruction of the films, the NEXAFS and C 1s photoemission were measured from C_{60} and C_{70} samples prior to and after heating the substrates. Carbon 1s photoemission for these samples narrowed after heating, but there was little change discernable in the near-edge measurements made before and after heating. This indicates that contaminants driven off by heating were localized at the surface because the surface-sensitive C 1s photoemission sharpened after outgassing whereas the bulk-sensitive NEXAFS remained unchanged. the presence of oxygen contamination in the bulk (most likely in the form of water) was probed by O 1s NEXAFS which showed no oxygen to be present. In order to remove artifacts in the electron yield spectra of the samples arising from structure in the monochromator transmission function [28], the C 1s spectra were divided by the electron yield from a resistively cleaned, carbon-free Si(111) sample. The so-normalized NEXAFS spectra from annealed graphite, and C_{60} and C_{70} films are shown in fig. 1.

There are significant differences in the NEXAFS spectra of C_{60} and C_{70}. An even larger change is seen for graphite. For highly ordered pyrolytic graphite, polarization-dependent NEXAFS spectra can distin-
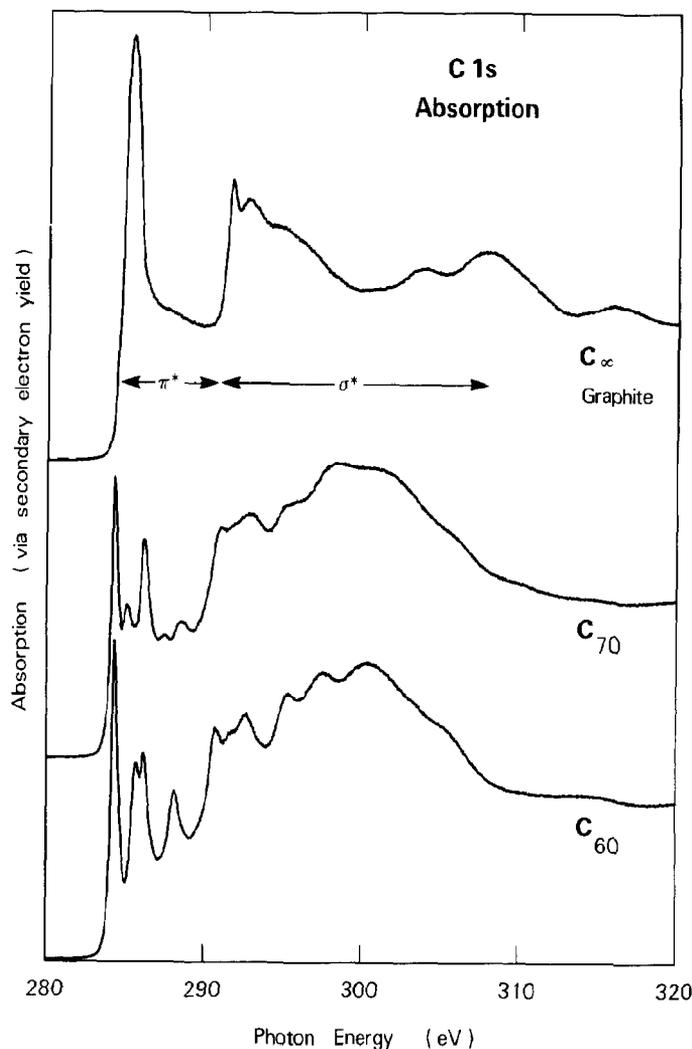
Fig. 1. NEXAFS spectra of highly ordered pyrolytic graphite, and C_{60} and C_{70} films, recorded by means of electron yield detection. In all cases the X-rays were incident at a 45° angle with respect to sample surface. The labeling identifies transitions to molecular orbitals of π and σ symmetry.

guish between transitions to final states of π versus σ symmetry [22,29]. The onset of transitions to σ-like bands occur around 291 eV and is evident in fig. 1 by a rise in the absorption. In C_{60} and C_{70} we can expect transitions to the π^* and σ^* orbitals to occur over a similar energy range and this is again borne out by their NEXAFS spectra in fig. 1, where a step-like increase in absorption is observed near 290 eV. The lowest energy π^* resonances and the threshold steps of the σ^* regions in C_{60} and C_{70} are lower by about 1 eV relative to graphite, with the lowest π^*

peak moving from 284.3 to 285.35 eV. We note that the trend in the C 1s binding energy is opposite, but is ill-defined due to a possible change of the Fermi level pinning in the gap of C_{60} and C_{70}. The NEX-AFS line-shapes also differ substantially; the width of the π^* resonance observed in graphite is greater than those measured for C_{60} and C_{70}. In solids with infinite periodicity such as graphite the π orbitals interact to form bands. In such cases the observed NEXAFS resonances correspond to transitions to flat bands which have a high density when averaged over

the Brillouin zone. In contrast, the spectra for C_{60} and C_{70} exhibit sharp resonances characteristic of MO-like final states [22,30]. This observation indicates that C_{60} and C_{70} condensed films contain discrete, chemically non-interactive molecules, as has been indicated by other measurements, for example, by ultraviolet photoemission [31]. Below we shall focus our discussion on the substantial changes in the energy and intensity of the π^* resonances for C_{60} and C_{70} in the 284–290 eV region.

Resonances in NEXAFS spectra of C_{60} and C_{70} arise from transitions of a K-shell electron to unfilled MOs. For systems with unsaturated C–C bonds the lowest-energy excitations always occur to MOs of π symmetry and at excitation energies less than the 1s ionization potential (IP) [22]. this is also the case for C_{60} and C_{70}. For solid films of C_{60} and C_{70} we can guess the 1s IP relative to the vacuum level to occur around 289 eV, using the 290.3 eV IP of benzene gas [32] [#1], lowered by an extra-molecular relaxation correction of about 1.5 eV. Hence the lowest-energy π^* resonances correspond to bound-state transitions, a fact that explains their narrow width. A rigorous calculation of the energies and intensities of the π^* resonances requires treatment of the effect of the 1s hole created in the excitation process. Such calculations do not exist at present. What is available in the literature are mostly semi-empirical MO calculations, most notably Hückel calculations of the filled π and empty π^* system [16–21,23]. To a good approximation the measured splitting of the π^* resonances can, nevertheless, be directly compared to the splitting of the π^* system calculated for the molecular ground state as previously demonstrated for naphthalene by Robin et al. [34]. This is possible because the K-shell excitation energies can be obtained from a one-electron approximation by assuming that there is a rigid shift of the π^* orbitals in the presence of the core hole 322].

We have chosen the Hückel calculation of Fowler and Woodrich [18] to compare with the data in fig. 2. This work gives results for both C_{60} and C_{70}. In addition, the HOMO–LUMO gap is given (1.1 eV for C_{60}), which provides an energy scale and allows one to fix the Hückel parameter β. In order to compare experimental π^* resonance positions and cal-

culated π^* orbital energies, we have chosen identical β values for C_{60} and C_{70}. The results are shown in fig. 2, where for better comparison with experiment, the π^* levels are represented by Gaussians of 0.35 eV full width half maximum at the calculated energies and the intensities of the peaks are representative of the degeneracy of the MOs. It should be noted that this scheme is not expected to reproduce the NEXAFS intensities because the dipole matrix elements are not property accounted for. These matrix elements would take account of both the symmetry and the radial part of the initial and final states, and by inclusion of the core hole, of excitonic effects as well. All such effects are ignored in the curves labeled "calculation" in fig. 2.

Nevertheless, the observed resonances exhibit a remarkable correlation with the calculated peaks, as indicated by tickmarks in fig. 2. In each case only a small calculated feature located near 1.5 eV for C_{70} and 2.5 eV for C_{60} has no experimental counterpart in the spectra. The energy positions do not agree exactly, indicating the need for more theoretical work. The overall width of the π^* manifold is reproduced correctly, however. One can also observe characteristic trends in the level splittings from C_{60} to C_{70}, for example between the lowest two π^* levels. While clearly separated in C_{70}, the levels merge in C_{60} and give rise to a single peak containing the sum of the two intensities. In C_{70} the lower of the two peaks appears larger, while the degeneracy of the calculated π^* orbitals indicates equal intensities. This is probably due to an excitonic enhancement of the lowest energy peak, similar to that observed for the lowest π^* resonance in conjugated hydrocarbons [22,34,35].

In summary, the splittings of the π^* manifolds of C_{60} and C_{70} have been determined by high-resolution soft X-ray absorption measurements. The data show characteristic trends between C_{60} and C_{70} that can be reproduced qualitatively by existing Hückel calculations. This fact and the narrow width of the individual π^* resonances clearly shows that the fullerene films resemble a molecular solid with considerably stronger intra-molecular than inter-molecular interactions. The NEXAFS spectra are therefore characteristic of the intra-molecular electronic structure of the C_{60} and C_{70} molecules. A quantitative understanding of the observed splitting of the π^* resonances in the NEXAFS spectra and of their

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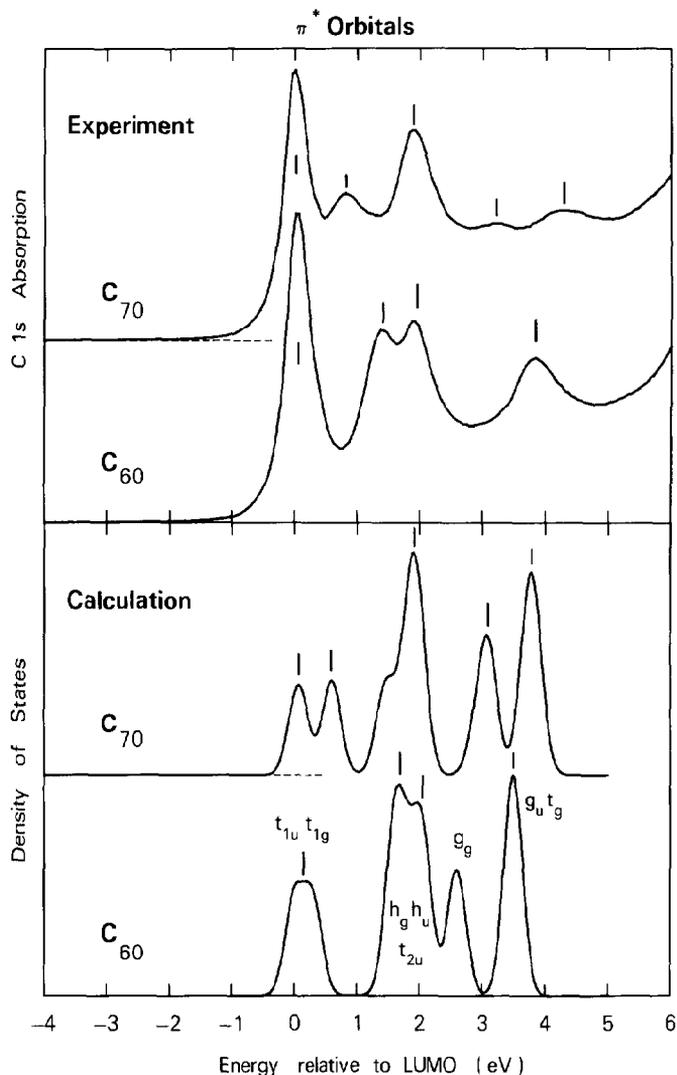[#1] An update is available from W.L. Jolly on request.

Fig. 2. Lowest energy π^* NEXAFS resonances for C_{60} and C_{70} and π^* energy levels obtained by an extended Hückel calculation [18]. The theoretical "spectra" were obtained by assigning Gaussians of 0.35 eV fwhm to all calculated orbitals. For C_{60} the peaks are labeled by the irreducible representations of the corresponding MOs [16,18].

intensities requires further theoretical work. In addition, it would be desirable to understand the observed splitting of the σ^* manifolds in the spectra in fig. 1 through first-principle electronic structure calculations.

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