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Resonant Photoemission Study at the C-1*s* Threshold of Solid C_{60}.

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Abstract. – We report on a resonant photoemission (PE) study of solid films of C_{60} in the region of the C-1*s* absorption threshold. The results show that the occupied p_π and the unoccupied p_π^* electronic states have mostly bandlike character, while the lower-lying occupied p_σ states are fairly localized at the C_{60} molecular clusters. A recently reported narrow PE feature close to the Fermi level in resonant PE spectra of C_{60} is identified as a C-1*s* core line due to second-order light from the grating monochromator.

Since the discovery of high-symmetry carbon-clusters of the fullerene family in 1985, the electronic structure of solid C_{60} has already been thoroughly investigated. Previous core-level and valence-band photoemission (PE) [1-3] as well as inverse photoemission (IPE) [4] studies performed in the angle-integrated mode provided a wealth of information on occupied and unoccupied electronic density of states as well as their symmetries. The experimental spectra exhibit generally quite good agreement with the results of electronic-structure calculations performed by different groups [1, 5, 6].

These experimental studies, however, did not yet provide information on the question whether the electronic structure in the valence-band region originates from molecularlike electronic states of the C_{60} cluster or from band states due to interactions between the clusters. The theoretical studies have shown that at least the lowest unoccupied molecular orbitals (LUMO) as well as the highest occupied molecular orbitals (HOMO) are bandlike in character giving rise to a dispersion of these states in $\boldsymbol{k}$-space. On the other hand, a recent X-ray absorption near-edge structure (XANES) study of solid C_{60} and C_{70} films [7] reveals that these films resemble molecular solids with considerably stronger intramolecular as compared to intermolecular interactions.

In the present letter we report on an investigation of the interplay between molecular and solid-state character of the electronic structure of polycrystalline thin solid films of C_{60}

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employing the technique of resonant PE at the C-1*s* threshold at photon energies of $\simeq 280$ eV. In comparison to normal PE, where electrons from occupied valence-band or core states are directly photoexcited to unoccupied states far above the vacuum level, an additional channel leading to the same final state as direct PE is opened in resonant PE. In the latter process, with photon energies in the region of a core threshold, a core electron is excited into empty states above the Fermi level. If these states are localized and the core hole is not fully screened by itinerant electrons, the excited electron can refill the core hole. The energy released can be transferred to a valence electron, which is then excited into a final state far above the vacuum level identical to the one reached by direct PE. The interference of these two processes will lead to an enhancement of the valence-band PE cross-section. In case of nonlocalized intermediate unoccupied states, the primary excited core electron will leave its location immediately after photoexcitation, so that the described resonant PE process cannot occur and the core hole will decay by Auger-electron emission. In this way, the degree of localization of the unoccupied state above the Fermi level can be inferred from the relative strengths of resonant PE and Auger-decay processes following a primary core excitation.

The resonant PE measurements as well as XANES studies were performed at the SX700/II beamline of the Freie Universität Berlin at the Berliner Elektronenspeicherring für Synchrotronstrahlung (BESSY) [8] employing an experimental chamber equipped with a VG-CLAM electron energy analyser. C_{60} films with a thickness of $\simeq 100$ Å were prepared by the standard procedure of sublimation from a degassed C_{60}/C_{70} mixture, containing less than 10% of C_{70}, onto a previously cleaned Ta metal substrate. The pressure in the experimental chamber was $< 10^{-10}$ Torr rising to $\simeq 10^{-9}$ Torr during evaporation.

To characterize the quality of the C_{60} films, a high-resolution PE study with HeI and HeII excitation was performed using a Leybold-Heraeus hemispherical electron analyser (model EA-11). The spectra presented in fig. 1 have the same shape and contain all features of the

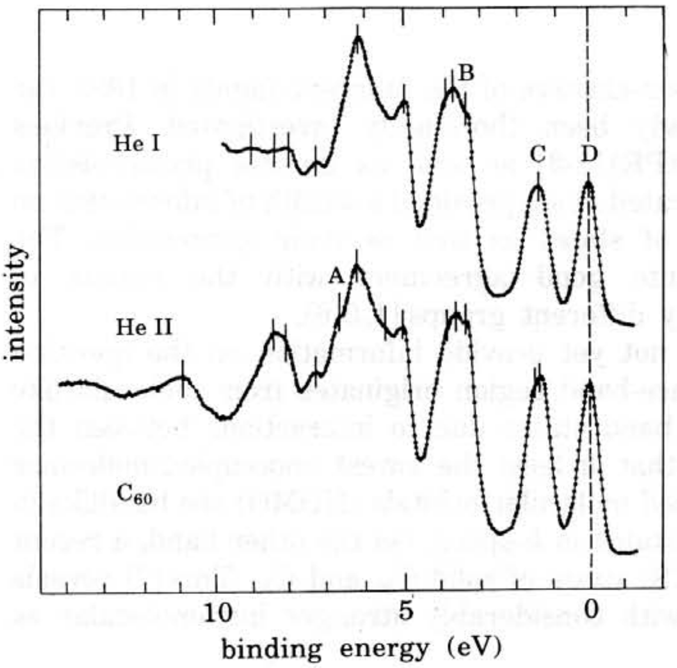

Fig. 1.

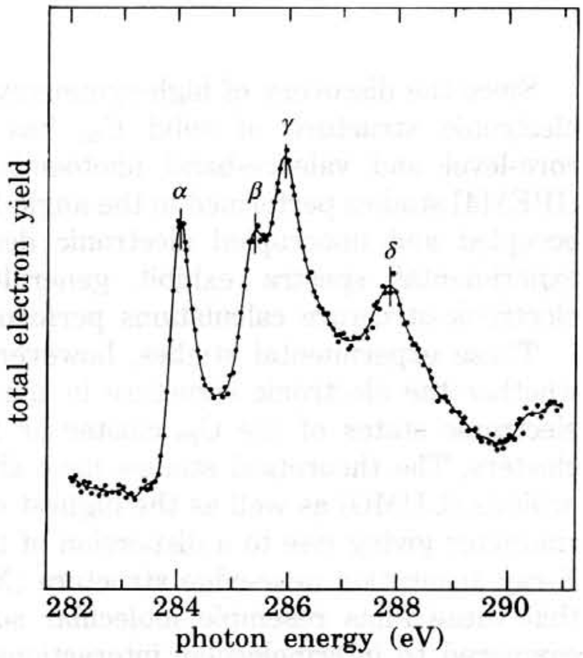

Fig. 2.

Fig. 1. – HeI-and HeII-excited PE spectra of a solid C_{60} film. Binding energies are relative to the highest occupied states (PE line D). All resolved spectral features are marked by vertical bars.

Fig. 2. – XANES spectrum of a solid C_{60} film taken at the C-1*s* threshold. The various C-1*s* core-excited final states are labelled by Greek letters.

spectra reported previously. The energy scale is referenced to the position of the HOMO (marked D in fig. 1), which is known to be 7.3 eV below the vacuum level [1]. With the present solid C_{60} films and a total system resolution of 25 meV (FWHM), however, we were able to resolve features A and B, which were weakly noticed in previous PE studies [1-3]. No traces of C_{70} were detected, which would result in a splitting of the PE lines C and D [9].

A typical XANES spectrum of an *in situ* prepared solid C_{60} film, recorded in total-electron-yield mode in the region of the C-1*s* threshold, is displayed in fig. 2. This spectrum is not influenced by carbon contaminations of the beamline optics, since the total-yield signal has been normalized to the photoyield of a gold reference. The shape of this spectrum, which was recorded here in order to obtain exact core-excitation energies, agrees well with previously reported data [7, 10]. Resonant PE spectra were recorded upon excitation of a C-1*s* electron into the various core-excited states α, β, γ, and δ.

Krummacher *et al.* [11], using the same type of grating monochromator in form of the lower resolution SX700/I beamline of BESSY, have recently reported PE spectra upon excitation into the core-excited states α and β/γ (without resolving states β and γ). For resonance α, they observed a prominent and relatively narrow feature in the region of the leading edge of the valence-band PE spectrum. This feature was assigned by these authors to a PE signal from the HOMO state. We are forced to give a different interpretation of this feature, since it can be observed for various photon energies using the SX700 monochromator, shifting by twice the variation in photon energy. This clearly identifies the reported peak as due to a C-1*s* core-level PE line excited by second-order light, which is normally quite intense in plane-grating monochromators.

The valence-band resonant PE spectrum taken at $h\nu = 285.9$ eV is shown in fig. 3*a*) (photoexcitation into state γ, see fig. 2). The feature from second-order light at a kinetic energy of $\simeq 285$ eV (dashed curve) was least-squares fitted on the basis of a C-1*s* core-level PE spectrum measured in the second-order mode at a higher photon energy, when core-level and valence-band PE signals are not overlapping. In agreement with previous observations by Weaver *et al.* [1], shake-up (sh) and plasmon-loss (pl) peaks were observed, which were taken into account in the procedure of subtracting the PE signal from second-order light. The resulting PE spectrum (fig. 3*b*)) is almost structureless with exception of the high-kinetic-energy region, where peak E and shoulders F and G can be distinguished. A broad shoulder H in the low-kinetic-energy region cannot be assigned to valence-band PE, since the valence band of solid C_{60} is not wider than 25 eV; instead, feature H is related to Auger-electron emission. In order to extract the pure PE signal from spectrum *b*), an Auger-electron spectrum excited with 380 eV photons was also recorded (spectrum *c*)). The high photon energy guarantees zero overlap between PE and Auger signals. Possible post-collision interaction effects on the Auger spectra excited with photon energies near threshold are expected to be negligible in the present case due to the poor localization of the p_π^* orbitals of the C_{60} solid [5, 6, 12]. This is also in agreement with the observations in the spectra of fig. 3, where shoulder H, *e.g.*, does not shift with photon energy. Spectrum *d*) in fig. 3 gives the difference between spectra *b*) and *c*) representing the pure resonant PE signal. Note that spectrum *d*) is plotted with the vertical scale expanded by a factor 4.

An analogous procedure of extracting pure resonant PE signals was applied to the other three PE spectra that were recorded upon excitation of C-1*s* electrons into the states α, β, and δ (see fig. 2). In each case, qualitatively similar results were obtained. Representative spectra taken with $h\nu = 245$ eV (nonresonant, top spectrum), as well as in resonance with $h\nu = 284$ eV (excitation into state α, middle spectrum) and $h\nu = 285.9$ eV (excitation into state γ, bottom spectrum) are displayed in fig. 4. In comparison to spectrum *a*), the lower two spectra show extra features due to resonance excitation. More specifically, an enhancement of intensity is observed for the middle part of the spectra excited with 284 eV and 285.9 eV

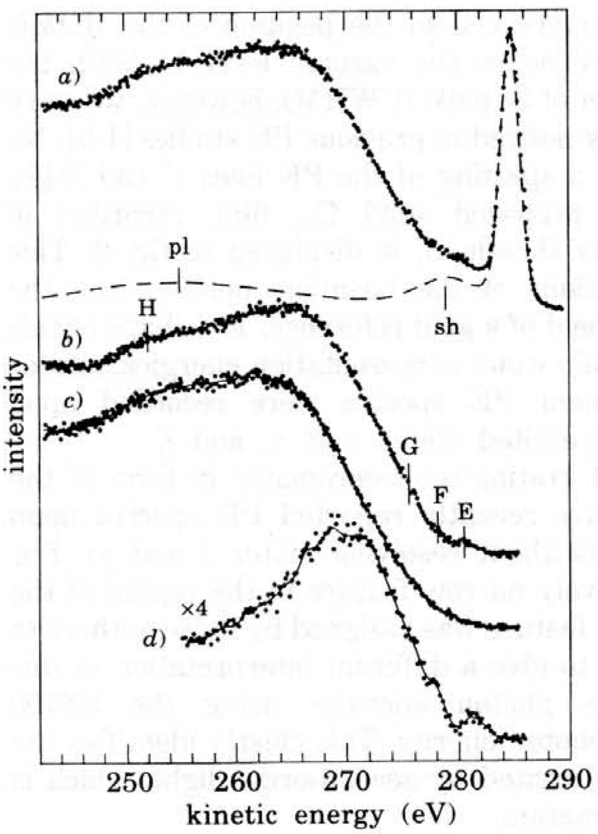

Fig. 3.

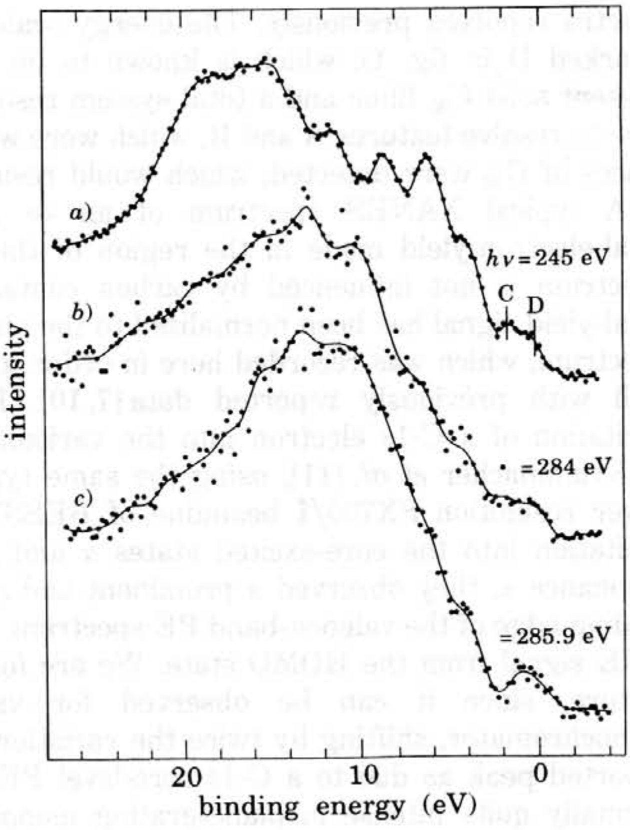

Fig. 4.

Fig. 3. – *a*) Resonant PE spectrum upon excitation into state γ at $h\nu = 285.9$ eV. The dashed subspectrum represents the C-1*s* PE signal due to excitation by 2nd-order light ($h\nu = 571.8$ eV). *b*) Corrected spectrum *a*) after subtraction of 2nd-order-light PE signal. *c*) Auger-electron spectrum excited with 380 eV photons. The bottom spectrum *d*) is the difference curve *b*) − *c*) representing the resonant PE signal (see text).

Fig. 4. – PE spectra of a solid C_{60} film recorded *a*) off-resonance ($h\nu = 245$ eV), *b*) on-resonance with excitation into state α ($h\nu = 284$ eV), and *c*) on-resonance, into state γ ($h\nu = 285.9$ eV).

photons. On the other hand, the PE features at lower and higher binding energies do not show resonance behaviour. This is particularly true for features D and C that exhibit no changes in intensity on and off resonance, respectively. A higher spectral weight of the resonating part of the PE spectrum for core excitation into state γ at a photon energy of 285.9 eV can be explained by the higher excitation cross-section at the photon energy of state γ as compared to state α (see fig. 2).

According to a recent electronic-structure calculation for solid C_{60}, the resonating part of the valence-band PE spectrum correlates mainly with p_σ-derived occupied states that are hybridized with *s* states at the surface of C_{60} clusters [1]. These states are located on the C_{60} clusters and are of molecular origin. They are much more localized than the higher-lying occupied p_π-states (C and D features in fig. 1 and 4), which are mainly responsible for the interaction between neighbouring C_{60} clusters. Since resonant PE processes are generally localized on a single atom (or molecule), the resonance behaviour of PE from p_σ states can be qualitatively understood.

In summary, an investigation of resonant PE at the C-1*s* threshold reveals a considerable bandlike character of the unoccupied molecular orbitals with p_π^* symmetry of solid C_{60} (α, β, γ and δ features in fig. 2) on the basis of much higher Auger-electron decay rates as compared to resonant PE decay. This is in agreement with theoretical results [5, 6]. On the other hand, the p_π^* states carry also nonnegligible localized character, since substantial resonance effects were observed for the PE signal from occupied p_σ states. This resonance behaviour confirms theoretical conclusions on the localized nature of occupied p_σ states, which are located at the surface of the C_{60} clusters. On the other hand, essentially no resonance effects were observed for PE from occupied p_π states, which is in agreement with their predominantly itinerant character as predicted by theory.

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REFERENCES

[1] WEAVER J. H., MARTINS J. L., KOMEDA T., CHEN Y., OHNO T. R., KROLL G. H., TROULLIER N., HAUFLER R. E. and SMALLEY R. E., *Phys. Rev. Lett.*, **66** (1991) 1741.

[2] BENNING P. J., POIRIER D. M., TROULLIER N., MARTINS J. L., WEAVER J. H., HAUFLER R. E., CHIBANTE L. P. F. and SMALLEY R. E., *Phys. Rev. B*, **44** (1991) 1962.

[3] LICHTENBERGER D. L., NEBESNY K. W., RAY C. D., HUFFMAN D. R. and LAMB L. D., *Chem. Phys. Lett.*, **176** (1991) 203.

[4] MARTINS J. L., TROULLIER N. and WEAVER J. H., *Chem. Phys. Lett.*, **180** (1991) 457.

[5] SATPATHY S., ANTROPOV V. P., ANDERSEN O. K., JEPSEN O., GUNNARSSON O. and LICHTENSTEIN A. I., *Phys. Rev. B*, in print.

[6] XU Y.-N., HUANG M.-Z. and CHING W. Y., *Phys. Rev. B*, **44** (1991) 13171.

[7] TERMINELLO L. J., SHUH D. K., HIMPSEL F. J., LAPIANO-SMITH D. A., STÖHR H., BETHUNE D. S. and MEIJER G., *Chem. Phys. Lett.*, **182** (1991) 491.

[8] DOMKE M., MANDEL T., PUSCHMANN A., XUE C., SHIRLEY D. A., KAINDL G., PETERSEN H. and KUSKE P., *Rev. Sci. Instrum.*, **63** (1992) 80.

[9] JOST M. B., BENNING P. J., POIRIER D. M., WEAVER J. H., CHIBANTE L. P. F. and SMALLEY R. E., *Chem. Phys. Lett.*, **184** (1991) 423.

[10] CHEN C. T., TJENG L. H., RUDOLF P., MEIGS G., ROWE J. E., CHEN J., MCCAULEY jr. J. P., SMITH III A. B., MCGHIE A. R., ROMANOW W. J. and PLUMMER E. W., *Nature*, **352** (1991) 603.

[11] KRUMMACHER S., CRAMM S., SZOT K., EBERHARDT W. and KRÄTSCHMER W., *Europhys. Lett.*, **16** (1991) 437.

[12] CHIANG T.-C., EASTMAN D. E., HIMPSEL F. J., KAINDL G. and AONO M., *Phys. Rev. Lett.*, **45** (1980) 1846.