Experimental band gap and core-hole electron interaction in epitaxial C_{60} films

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This work employs a common experimental energy scale for photoemission, inverse photoemission, and x-ray absorption data, which is essential for a reliable experimental determination of energy separations (gaps) between occupied and empty states of solids. For epitaxial layers of C_{60} prepared on layered VSe_2 single crystals we demonstrate a good agreement between experiment and previous quasiparticle calculations of the HOMO-LUMO distance and the band gap. Comparison of inverse photoemission and x-ray absorption data from the same sample on a common energy scale shows that conduction-band states cannot be derived from absorption data and enables us to determine the direct experimental value of the core-hole electron interaction U in solid C_{60}. [S0163-1829(98)08743-8]

I. INTRODUCTION

In recent years many investigations on the electronic structure of pristine and doped C_{60} have been performed.[1–11] But as far as the region around the Fermi level is concerned there are still several open questions. For instance, the experimental energy distance between the center of the HOMO (highest occupied molecular orbital) bands and the LUMO (lowest unoccupied molecular orbital) bands varies from 3.5 to 3.8 eV,[1–3] while theoretical calculations predict only 3.0 eV.[4] What is the correct value and how can it be determined? How do sample preparation, its structure, and the underlying substrate affect the measurements? What is the adequate reference level when photoemission and inverse photoemission spectra are measured separately? How will charging influence the results? How does the C $1s$ absorption spectrum, which is often believed to mirror empty states,[6,7] fit the results obtained on the empty conduction-band states by inverse photoemission? Can we give an experimental value for the core-hole electron interaction?

With regard to the above questions it is the aim of this work to perform a thorough study of the electronic structure of C_{60} around the gap by means of combined angle-resolved photoemission and inverse photoemission (CARPIP),[12] C $1s$ core photoemission and x-ray absorption near-edge spectroscopy (XANES). Applying these techniques in a combined way to the same sample provides a well-defined unique energy scale and allows a detailed comparison of valence and conduction band states and a determination of C $1s$ core-hole electron interaction.

We will first focus on the reliable determination of the HOMO-LUMO distance and the band gap of epitaxial $C_{60}(111)$ films by means of combined angle-resolved photoemission and inverse photoemission. In our investigations of several monolayers of C_{60} grown on single-crystalline VSe_2 we demonstrate that the HOMO-LUMO distance appears to be significantly lower than the values achieved previously on different samples.[1–3] We have obtained good agreement between recent quasiparticle calculations[4,5] and our experimental data. Combination of photoemission and XANES yields conduction-band states relative to the HOMO in the presence of a core hole. By comparison with combined photoemission and inverse photoemission results we determine an experimental value for the core-hole electron interaction of solid C_{60}.

II. EXPERIMENT

All results described in this paper were obtained on $C_{60}(111)$ films[13] grown epitaxially on the layered material VSe_2, which serves as an ideal substrate in view of a suitable lattice constant $a = 3.35$ Å matching to a third of the nearest neighbor distance in fcc C_{60}. Together with the weak van der Waals forces at the surface the substrate supports epitaxial growth of C_{60} even for the first monolayer. Before evaporation of C_{60} the substrate material was cleaved along the hexagonal (0001) face *in vacuo*. Thickness of the grown C_{60} layers was determined by scanning tunneling microscopy. The metallic character of VSe_2 was expected to prevent charging effects in inverse photoemission. After the CARPIP measurements the chemical purity of the C_{60} crystals has been studied applying Auger spectroscopy. No contamination by other elements has been observed.

Angle-resolved photoemission (ARPES) spectra were taken at room temperature with He I radiation of a gas discharge lamp and synchrotron radiation from the undulator beamline BW3 and W3.2 of the positron storage ring DORIS III at Hamburg Synchrotron Radiation Laboratory (HASYLAB) for photon energies 15 eV $\leq h\nu \leq$ 350 eV. For an accurate photon energy calibration of the SX 700 monochromator the binding energies of suitable core levels were determined in first and second order before and after each measurement. The remaining uncertainty was estimated to be lower than 20 meV. The electrons were detected with an angle resolution better than 0.5° by use of a 180° spherical analyzer mounted on a two axes goniometer. Total energy resolutions of 90 meV and 175 meV were chosen for He I and synchrotron radiation, respectively. XANES investigations were performed in the constant final energy mode of photoemission for low kinetic energies (8.6 eV).

The angle-resolved inverse photoemission (ARIPES) spectra were taken by using a compact grating spectrometer with parallel detection of photons in the energy range of 10 eV $\leq h\nu \leq$ 30 eV.[12,14] Electrons were focused on the

sample with ~ 1 mm^2 spot size and angle divergence $<2°$. Energy and momentum resolution are typically 400 meV and 0.05 Å^{-1}. For combined angle-resolved photoemission and inverse photoemission data a common energy scale is established directly by detecting the electron energy from the inverse photoemission electron gun with the photoemission electron energy analyzer. Therefore it is possible to measure very accurate values (± 20 meV) for the energy separation (gaps) between occupied and empty states and, in addition, to obtain independently the position of the Fermi level on the same scale without using the latter as energy reference level.[12,15]

III. RESULTS AND DISCUSSION

For a detailed discussion of the electronic structure around the gap of any semiconducting material it is essential to achieve a reliable common energy scale for all spectroscopic techniques applied. Furthermore, uncertainties in the spectroscopic results due to the preparation of different samples for either valence or conduction-band studies have to be ruled out. Therefore, we have applied all different experimental techniques (photoemission, inverse photoemission, and XANES) *in situ* to the same sample. In addition, it has been carefully checked for charging and band bending, which may lead to shifts of inverse photoemission relative to photoemission spectra. For the metallic substrates like VSe$_2$ and Au we did not observe any charging induced shifts. Combined photoemission and inverse photoemission spectra of epitaxial layers of C$_{60}$ on VSe$_2$ with increasing thickness from one to seven monolayers (ML) are shown in Fig. 1. The spectrum of the pure VSe$_2$ substrate is depicted at the bottom. From the VSe$_2$ spectra the position of the Fermi level due to the metallic character of the substrate is discernible. All spectra were recorded at the same excitation energy in photoemission (21.22 eV) and inverse photoemission (18.78 eV). Already for one monolayer the complete structure of bulk fcc C$_{60}$ is apparent. But there are also weak underlying substrate signals that are most prominent in the energy gap. The signals of VSe$_2$ decrease substantially with increasing C$_{60}$ coverage. There are no differences in the spectra for three to seven monolayers and the substrate features vanish completely.

From the 7-ML spectrum representing bulk C$_{60}$ we determine a center to center distance between the HOMO and the LUMO bands of 3.34 eV. This value is also obtained for C$_{60}$ on a polycrystalline gold substrate. It should be noted here that for the semiconducting substrate GeS we observe a significantly larger energy separation of 3.74 eV that is in line with previous studies on semiconducting substrates.[3] In this case charging as large as 0.1 eV/μA occurs leading to the observed shift in the inverse photoemission spectra (see Fig. 2). With the use of metallic substrates, however, no charging effects were observable.

For a comparison of the experimental data with the theoretical gap (derived from band structure calculations)[4] one has to consider the uncertainty in determining $k_\perp$ in the (inverse) photoemission process. In general, the value of $k_\perp$ changes with varying photon energy of the electronic transition. Thus, we measured (inverse) photoemission normal incidence spectra with initial energies of the incoming elec-
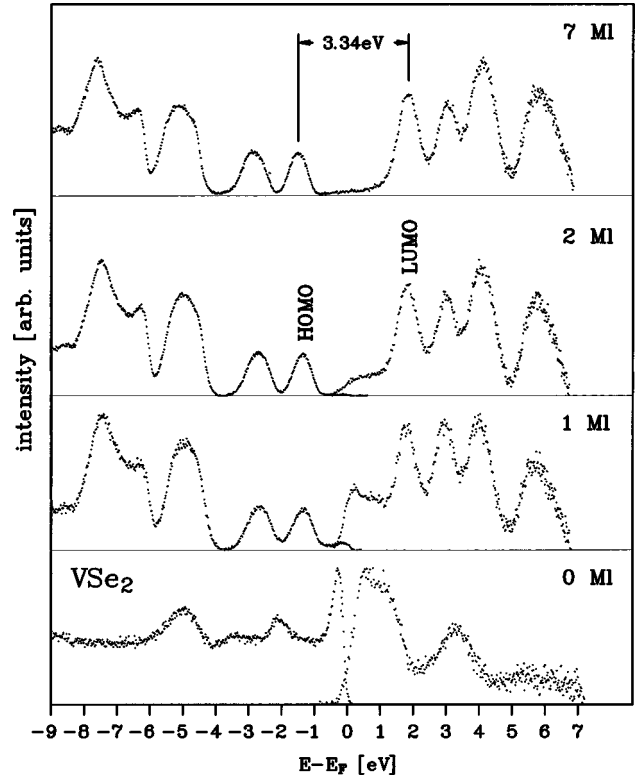

FIG. 1. CARPIP spectra for different C$_{60}$ coverages on single crystalline VSe$_2$ (1 ML = 1 monolayer). The photoemission measurements were performed with an excitation energy $h\nu = 21.22$ eV, while the inverse photoemission data were recorded for an initial kinetic energy of 18.78 eV.

trons (photons) from 15 to 25 eV corresponding to the ΓL direction of the Brillouin zone. Each spectrum was normalized to the (charge and to the spectral sensitivity of the grating spectrometer) beam current.

The sum over all spectra is shown in Fig. 3(a), which can be compared to the partial density of states along ΓL. The energy separation between the HOMO and the LUMO amounts to 3.36 eV, which is slightly larger (~ 20 meV) than the value obtained from the spectra shown in Fig. 1 because of $k_\perp$ dispersion effects. To compare these experimental results with theory one can extract a partial density of
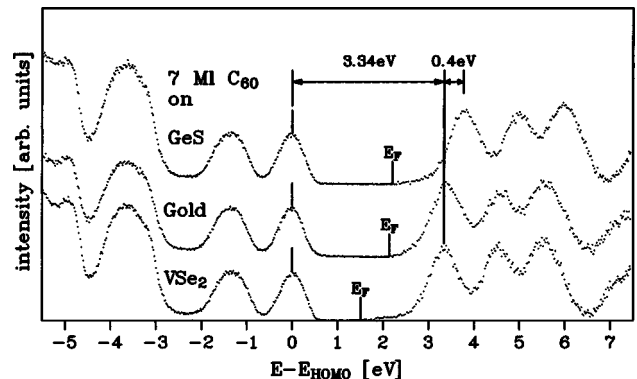

FIG. 2. CARPIP spectra of seven monolayers C$_{60}$ on different substrates. The photoemission spectra were taken with 21.22-eV photon energy. An initial kinetic energy of 20.90 eV was used for inverse photoemission.
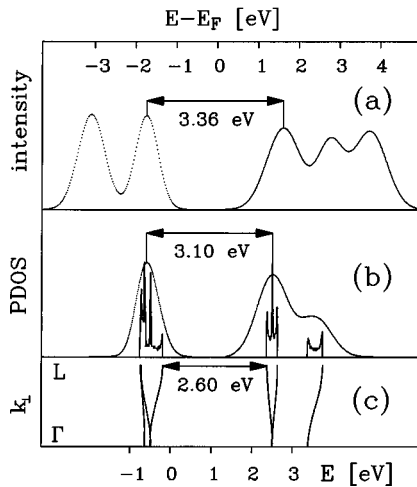
FIG. 3. (a) CARPIP spectrum for 7 ML C_{60} on VSe_2 integrated along ΓL. (b) Partial density of states (PDOS) along ΓL resulting from the quasiparticle calculation of Ref. 4 [shown in part (c)] convoluted with the experimental resolution.

states along ΓL from the quasiparticle calculation of Ref. 4. The result is shown in Fig. 3(b) together with the Gaussian convolution to account for the experimental resolution. The resulting theoretical HOMO-LUMO separation is found to be 3.10 eV, which is about 260 meV smaller than the experimental one.

To derive the experimental energy gap the deviation of 260 meV is to be added on the theoretical gap of 2.60 eV at the L point. We obtain an experimental energy gap at the L point of the Brillouin zone of 2.86 eV. It is noteworthy that this value is unaffected by dispersion effects. Calculations within the GW approximation predict a fundamental gap of 2.15 eV at the X point.[4] This value cannot be derived from angle-resolved CARPIP data along ΓL alone. In particular, determining gap values from onsets of spectra (see, e.g., Refs. 1,2) can generally not be applied since the results depend on the experimental resolution. It should be noted here that calculations including solid state screening effects give evidence for a larger HOMO-LUMO splitting by about 0.25 eV for the topmost and 0.14 eV for the second layer of $C_{60}(111)$ because of a lower coordination number at the surface.[16] This should result in a broadening and small shift of the HOMO and/or LUMO, which, however, has not been observed in the spectra for 1 and 2 ML of Fig. 1.

In order to investigate the core-hole electron interaction of solid C_{60} we have taken C $1s$ XANES spectra. Theoretically it is well established that XANES results are dramatically affected by including core-hole electron interactions (see, e.g., Ref. 17 and references therein). In particular, oscillator strength is transferred to lower photon energies. Although there is a reasonable agreement between experimental and theoretical XANES results for a variety of materials thorough calculations for solid C_{60} as well as experimental data elucidating core-hole electron interactions are still lacking. For the experimental study of core-hole effects it is essential to be able to compare XANES results with inverse photoemission data on a common energy scale. Therefore, XANES was applied to the same sample used for the combined photoemission and inverse photoemission investigations by transferring it to BW3/SX700 at HASYLAB em-
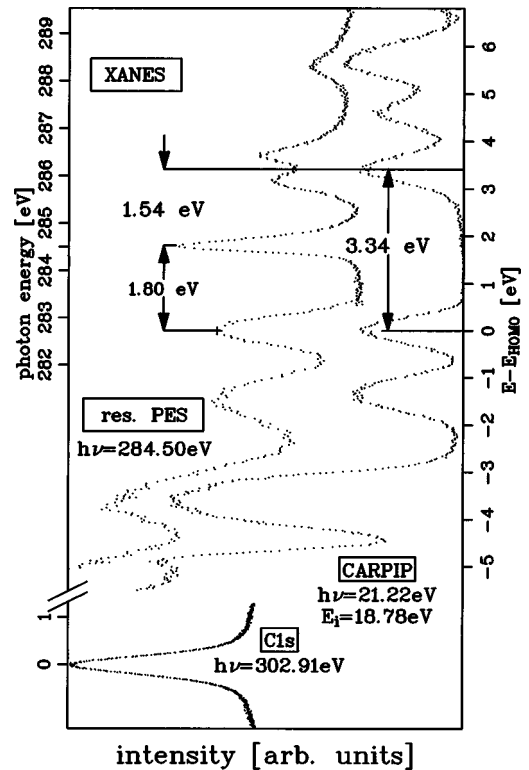

FIG. 4. Comparison of a XANES spectrum (the kinetic energy of the analyzer was set to 8.60 eV) and core photoemission with the results of combined angle resolved photoemission and inverse photoemission.

ploying a transportable UHV chamber. The combination of photoemission and inverse photoemission data is described above. For an additional combination of these results with XANES data we first took photoemission spectra of the valence bands and the C $1s$ core level of C_{60}. This gives an energetic distance between the HOMO and the C $1s$ core level of 282.70 eV. Applying XANES to the same sample we take the C $1s$ level as zero of the photon energy scale and consequently can plot XANES data relative to the energy of the HOMO. The result of the compilation of the CARPIP, C $1s$ core photoemission and XANES results on a common energy scale is presented in Fig. 4.

The prominent XANES maximum at the lowest photon energy represents the first possible transition from the C $1s$ level into a state 284.50 eV above the C $1s$ level. The comparison of the XANES data with the inverse photoemission spectrum reveals that there are almost no similarities regarding absolute energy positions, energy differences between maxima, or intensities. Note that the first strong peak in the XANES spectrum is located within the fundamental band gap of the CARPIP spectrum 1.54 eV below the LUMO. This clearly demonstrates that the information about the unoccupied states one might infer from XANES is extremely modified by the presence of the core hole. In particular, the shift between the LUMO and the first XANES peak is a direct measure of the Coulomb attraction U of the core hole and electron on the same site in solid C_{60}. More generally, U is defined as $U = E_I - E_A - \Delta$ with E_I the ionization energy, E_A the electron affinity, and Δ the energy of the first excited
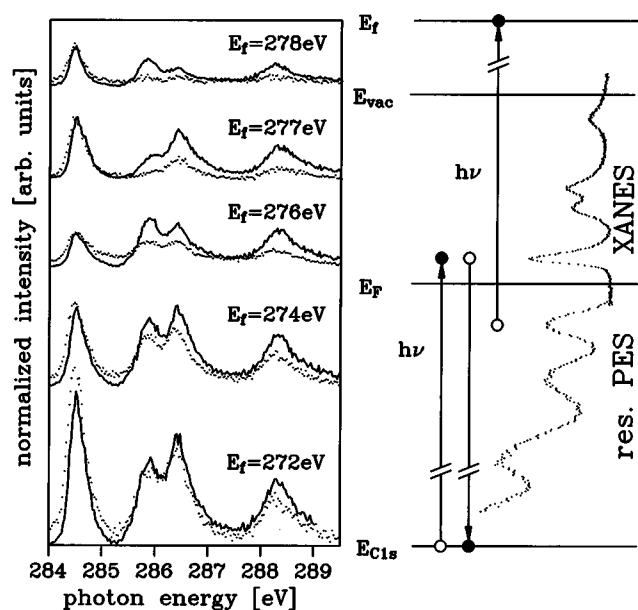
FIG. 5. On the left hand a series of CFS data recorded for varying kinetic energies E_f of the electrons in the range from 272-278 eV is shown. The solid lines are the results from simulating the spectra according to equation (1) using the resonant photoemission spectrum and the XANES data depicted in figure 4. The right part of this figure illustrates the participator process.

state. By means of CARPIP we have experimentally determined $E_I = 6.83$ eV and $E_A = 3.49$ eV. Combination of photoemission and XANES gives the first excited state 1.80 eV above the HOMO. Thus the Coulomb attraction adds up to $U = 6.83$ eV $- 3.49$ eV $- 1.80$ eV $= 1.54$ eV. To the best of our knowledge this is the first experimental result giving a value for the core-hole electron interaction of solid C_{60}.

For a valence hole, however, one can give an estimate based on screened gas phase values. Taking experimental data for the C_{60} molecule [$E_I = 7.6$ eV,[18] $E_A = 2.65$ eV,[19] and $\Delta = 1.7$ eV (Ref. 20)] one gets $U = 7.6$ eV $- 2.65$ eV $- 1.7$ eV $= 3.25$ eV. Putting C_{60} in a solid and including screening would reduce the ionization energy and increase the electron affinity by the same amount.[21] The screening model described by Shirley *et al.*[16] suggests that solid state screening effects should reduce U by about 1.6 eV from what it would be in the gas phase. This changes the ionization energy and electron affinity for the molecule to $E_I = 6.8$ eV and $E_A = 3.45$ eV. These estimated values are very close to the values we have measured on solid C_{60}. Since the valence-hole and the electron are not always on the same C_{60} molecule the full strength of the screening potential is not felt. This may reduce U by another 10%.[22] Thus, for the valence-hole electron interaction the estimate is $U = 1.5$ eV, which, in fact, is very similar to our experimental result for the core-hole electron interaction (1.54 eV).

In order to investigate the decay channel of the excitations observed in the XANES spectrum we took resonant photoemission spectra in the constant final energy mode (CFS) for high energies. They are shown in Fig. 5 (dots) for final kinetic energies between 272 eV and 278 eV. Intensities are normalized with respect to the incident photon flux. A close similarity of the 272-eV and the 274-eV CFS data with the
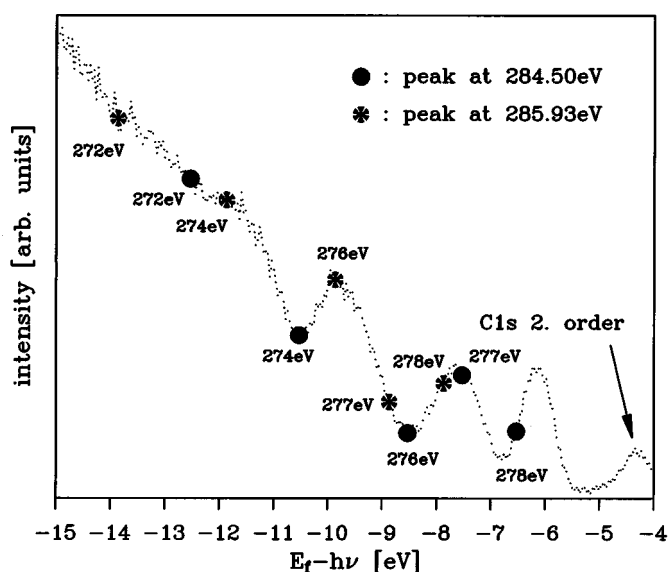

FIG. 6. The resonant photoemission spectrum recorded for $h\nu = 284.50$ eV explains the origin of the intensity modulations in figure 5. The binding energy labelled with the symbols denote the corresponding binding energy of the participator valence electrons.

XANES spectrum in Fig. 4 with respect to the shape and the energy positions of the peaks can be ascertained. But there are remarkable intensity modulations of the features with increasing E_f. For instance, the highest intensity of the 284.50-eV transition is found for $E_f = 272$ eV. It reaches a minimum if E_f is increased to 276 eV and with $E_f = 277$ eV the intensity increases again. The intensity of the 285.93-eV peak falls drastically with increasing E_f. To demonstrate that valence band information is inherent in CFS spectra at these energies we simulated CFS spectra under the assumption that the participator process is the main decay channel. The energy level diagram of the participator process is shown in Fig. 5 (right side). A core electron is excited to an unoccupied state. Then it annihilates the core hole in a direct recombination process and the released energy is used to eject a valence electron leading to the same final state as in photoemission (resonant photoemission). A simple approximation for the photoemission intensities measured by CFS yields

$$I^{\mathrm{CFS}}(h\nu, E_f) \sim f(h\nu) N(E_f - h\nu) N(E_f) \qquad (1)$$

with $f(h\nu)$ describing the absorption as given by XANES and $N(E_f - h\nu)$, $N(E_f)$ giving the initial and final density of states. The resonant photoemission spectrum of Fig. 4 serves as $N(E_f - h\nu)$ while $N(E_f)$ is assumed to be constant at these relative high kinetic energies. The results of the simulation are shown as solid lines in Fig. 5. The agreement between the measurement (dotted spectra) and the simulation (solid lines) is very good. Another more illustrative explanation for the intensity variations of the CFS spectra is given in Fig. 6. Obviously the density of states in the valence band is scanned by the series of CFS data. Therefore a CFS spectrum in the used energy range can be explained to be a XANES spectrum, whose intensities are modulated with the valence-band structure. A resonant photoemission spectrum of the valence bands is shown in Fig. 6. The symbols denote the initial energies of the participator electrons emitted from the

valence bands for the CFS peaks observed at 284.50-eV and 285.93-eV photon energy, respectively. The intensity modulations of the first two CFS peaks can be traced easily.

The results of the CFS spectra at high kinetic energies together with the simulation demonstrate that the electron– C $1s$ core hole pair directly recombines with the emission of a valence electron (participator). This direct recombination supports the strong localization of the C $1s$ core electron excitation. XANES spectra, in contrast, only probe the absorption due to excitation of the core electron and cannot give direct information about the decay channel.

IV. CONCLUSIONS

In summary, employing a common energy scale for photoemission, inverse photoemission and x-ray absorption data of epitaxial C_{60} films on the metallic layered material VSe_2 enabled us to determine reliable experimental values for the HOMO-LUMO distance, the band gap, and the core-hole electron interaction of solid C_{60}. Combined photoemission and inverse photoemission yields a HOMO-LUMO distance of 3.36 eV, which is only about 260 meV larger than GW calculations.[4] Combination of photoemission and x-ray absorption on the same sample in comparison to inverse photoemission data demonstrates experimentally that the XANES spectra associated with empty states are significantly affected by core-hole effects. Thus, conduction bands may not be simply derived from absorption data. We determine the C $1s$ core-hole electron interaction of solid C_{60} to 1.54 eV, which is comparable to the gas phase estimate for the valence hole when screening is included. Constant final-energy spectra at high kinetic energies can be well described by simulating a participator process which supports a strong localization of the C $1s$ excitation.

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