PHYSICAL REVIEW B **76**, 193311 (2007)

Investigation of polarization effects in organic thin films by surface core-level shifts

M. B. Casu,* Y. Zou, S. Kera, D. Batchelor, Th. Schmidt, and E. Umbach
Universität Würzburg, Experimentelle Physik II, Am Hubland, D-97074 Würzburg, Germany

(Received 21 September 2007; published 26 November 2007)

We study charge delocalization and polarization effects in organic thin films by comparing surface- and bulk-sensitive, high-resolution C 1s photoemission data using tunable synchrotron radiation. In three cases, perylene-tetracarboxylicacid-dianhydride, coronene, and metal-free phthalocyanine, no surface core level shifts are observed (upper limit 100 meV). This unexpected finding shows that polarization effects, and hence polarization differences between surface and bulk, are rather small, and implies that the effective charge is not localized on the core-ionized molecule but delocalized over several neighboring molecules.

DOI: 10.1103/PhysRevB.76.193311 PACS number(s): 79.60.−i, 71.20.Rv, 73.20.Jc, 73.61.−r

Semiconducting organic solids are commonly considered to be governed by van der Waals interactions. Their main characteristics are strong intramolecular bonds but weak intermolecular forces. The electric charges are believed to be localized on individual molecules, and charge transport occurs via hopping, at least at room temperature. A localized charge is accompanied by a polarization of the neighboring molecules with consequences for the energetic situation of electrons and holes in different environments, e.g., in the bulk or at a surface or interface due to the different number and types of neighbors that are polarized by the charge. Thus the question of charge localization and polarization in organic materials is of eminent importance for the understanding of issues like charge transport, energetic position of bands, or the interpretation of electron spectroscopic results.

In order to investigate this question we have performed surface- and bulk-sensitive photoemission measurements. The measured binding energy (BE) depends on the electronic level or band structure, on the chemical state, and on dynamic screening effects. The latter lead to a polarization of the solid ranging from a complete delocalization of the positive charge in the solid, e.g., in the s-band of a metal at the Fermi level, to a localized point charge in an ionized atom that is surrounded by a weakly interacting, polarizable medium as, e.g., in a condensed rare gas solid. If the picture of a localized charge is correct this should be observable in, e.g., a surface core level shift (SCLS) experiment. SCLS is defined as the photoemission binding energy difference of a core level of a surface with respect to a bulk atom and/or molecule. For a localized hole the polarization and hence the measured BE must be different for surface and bulk as long as the effective charge remains localized within the atom and/or molecule. Indeed this effect has often been observed, e.g., in photoemission or Auger experiments of condensed rare gases,[1] and its explanation as difference of polarization screening is well-accepted. In previous experiments on various rare gases a binding energy reduction of 10–40 meV per surrounding atom has been found leading to a BE increase of the surface with respect to the bulk atoms of about 0.3 eV.[2]

For organic materials such an effect would play an important role. For instance, it would have a considerable influence on the interpretation of photoemission data, e.g., for distinguishing surface and bulk species or for determining the transport gap.[3] Also the charge transport is influenced; transport should not occur along a surface of an organic material or along the interface to a less polarizable medium [e.g., in an organic field effect transistor (OFET)], for energetic reasons. In this sense, Duke *et al.*[4] suggested in 1977 that in polymers and molecular solids the molecules on top of an organic layer could feel a different dielectric environment with respect to bulk molecules, with differences up to 0.5 eV. In 1978 Salaneck[5] concluded from angle-dependent UV photoemission (UPS) measurements for anthracene on gold that the observed splitting of the highest occupied molecular orbital (0.3 eV) is due to the difference between surface and bulk molecules. Recently, Tsiper *et al.*[6] reported that the polarization energy in perylene-tetracarboxylicacid-dianhydride (PTCDA) is reduced at the surface by 0.41 eV compared to the bulk. This value was obtained by using a self-consistent calculation in the zero-overlap limit, using the picture of localized carriers. To our knowledge, a dedicated measurement of the difference in the electronic polarization energies between surface and bulk has not been carried out so far.

SCL shifts have been found in various materials and are related to different origins. In metals, they have been attributed to a narrowing of the valence band at the surface introducing a downward or upward shift for a less or more than half-filled d band.[7] In semiconductors, surface reconstruction and a redistribution of the charge on the surface atoms in the ground state,[8] differences between surface and bulk Madelung potential,[9] changes in the screening of the core hole in photoemission,[10] or a combination of these effects[11] have been proposed. In insulators such shifts have been related to different polarization energies, as mentioned above for condensed rare gases. Recently, the study of SCLS has provided valuable information about the chemical and physical properties of surfaces for many inorganic systems.[12–14] From the experimental point of view, the improved resolution of analyzers and synchrotron radiation has increased the possibility to determine also very small shifts, e.g., far below 0.1 eV. Despite the success with metals and inorganic semiconductors, SCLS investigations have not been used much to get information on organics.[15]

In this Brief Report, we present high resolution x-ray photoemission (XPS) measurements taken at different photon energies and take off angles in order to investigate SCLS on three different organic systems. Thin films of PTCDA, coronene, and metal-free phthalocyanine (H_2Pc) were deposited on a Ag(111) single crystal substrate. The organic molecules were chosen to represent systems with different degrees of interaction ranging from stronger interaction like in PTCDA

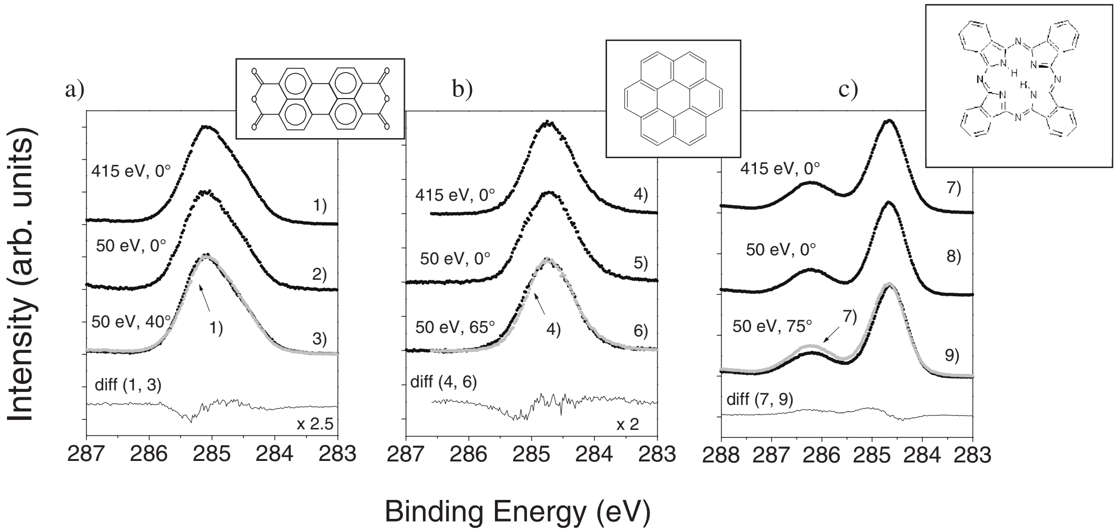

FIG. 1. C 1s XPS spectra of multilayers of (a) PTCDA, (b) coronene, and (c) H_2Pc. The kinetic energies and emission angles for each spectrum are indicated. Magnified difference spectra are shown at the bottom. The most bulk sensitive curves (in gray) are also superimposed to the most surface sensitive curves. Molecular structures are shown as insets.

or H_2Pc and to a certainly weaker interacting system like coronene, all as highly ordered thin films on Ag(111).

The measurements were performed at beamline UE52-PGM at BESSY (Berlin, Germany) (energy resolving power of $E/\Delta E = 10\,500$ at 401 eV). For all XPS data a pass energy of 40 eV was used corresponding to an analyzer resolution of 50 meV (Scienta SES200 spectrometer).

The Ag(111) single crystal was cleaned in UHV by means of repeated cycles of Ar-sputtering and subsequent annealing. The organic materials were purified by using thermal gradient sublimation and deposited on the sample under UHV conditions by using *in situ* strictly controlled organic molecular beam deposition (OMBD). The nominal thickness (ten layers for PTCDA and coronene, and 20 layers for H_2Pc) was determined by using the attenuation of the XPS substrate signal (Ag 3d). The homogeneity of the samples was checked on micro and large scale by using XPS. The spectra were recorded at room temperature in normal emission (0°) for photon energies of 335 and 700 eV and of 335 eV for emission angles θ of 40°, 65°, and 75° for PTCDA, coronene, and H_2Pc. The different electron kinetic energies and emission angles were used for varying the inelastic mean free path, λ, and therefore the surface sensitivity of the photoelectrons. The binding energies were calibrated according to Ref. 16. All organic thin films were carefully checked for radiation damage during beam exposure. In addition, special attention was dedicated to avoid nonlinearity effects of the detection system. An exponential background was subtracted, and the spectra were normalized to equal peak heights for comparison.

Figure 1(a) shows the photoemission spectra of the C 1s core levels of PTCDA films. The spectra were taken under bulk-sensitive ($h\nu=700$ eV, $E_{kin}=415$ eV, $\theta=0°$) (curve 1), surface-sensitive ($h\nu=335$ eV, $E_{kin}=50$ eV, $\theta=0°$) (curve 2), and more surface-sensitive conditions ($h\nu=335$ eV, $E_{kin}=50$ eV, $\theta=40°$) (curve 3). At first glance, no changes are visible in peak position or shape even if the spectra are superimposed [cf. Fig. 1(a), curves 3, gray and black curves]. The peak maxima are identical within the detection limit (~50 meV). The (enlarged) difference curve at the bottom of Fig. 1(a) shows a minor structure which is probably due to some inelastic scattering contributions that are enhanced at low E_{kin} and increased emission angles. However, since it cannot be completely ruled out that a small surface peak shift also contributes this has to be taken into account for an estimate of the upper limit of a SCLS (see below).

In previous works[17,18] we had analyzed the C 1s line shape in detail and had thus established that the peak asymmetry observed in Fig. 1(a) stems from the superposition of signals from the distinct carbon atoms within the PTCDA molecule. Moreover, we note that the film was thick enough to completely attenuate the signal from the first PTCDA layer forming the interface to the metal which has a very different spectral signature due to chemisorption. Thus the only difference that might be observable could be the expected surface core level shift which—if any—must be very small (see below).

In order to check the SCLS for other molecular layers we also studied coronene and H_2Pc thin films on Ag(111), the former because it has a weaker intermolecular interaction and the latter because the planar molecules are inclined with respect to the surface. The results are displayed in Figs. 1(b) and 1(c), curves 4–9. Again the spectra from the most bulk- and most surface-sensitive measurements look identical with no shift of the observed peak within the detection limit (~50 meV). Also the difference curves appear very similar to those of PTCDA [Fig. 1(a)]. We note two minor differences: first, in the case of coronene the origin of the negative peak of the difference at 285.3 eV most probably includes a contribution from some radiation damage which occurs for coronene on a much shorter time scale than for PTCDA. We took particular care to minimize the beam exposure by scanning the photon beam across the sample but cannot completely exclude a minor contribution from radiation damage,

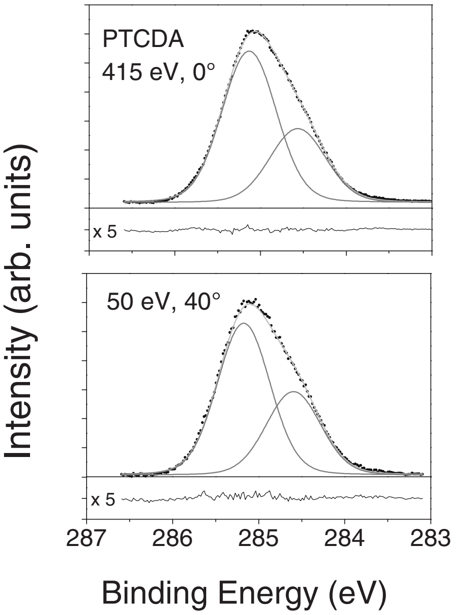

FIG. 2. Experimental C 1s spectra (dotted curves) of PTCDA are compared with fit results (light gray curves) using two components (gray curves) for the two extreme sensitivity cases. The difference curves underneath are magnified by a factor of 5.

especially in the surface-sensitive spectrum, where a peak grows at this energy for higher radiation doses. Second, for H_2Pc we note an enhancement of the peak at 286.2 eV and a very small shift (~100 meV) of the main peak of the bulk-sensitive spectrum towards *higher BE* which seems to contradict the expectation of improved screening of the bulk molecules. The reason for both effects is most probably the morphology of the Pc film as detected by x-ray absorption experiments[19] which show strongly inclined molecules with respect to the surface (in contrast to PTCDA and coronene with parallel molecules). The inclination leads to a different attenuation of the pyrrolic (at 286.2 eV) and aromatic (at 284.6. eV) signals, respectively, and to different forward scattering effects for the two different kinetic energies used. This effect explains the enhanced intensity of the pyrrolic signal at high photon energy which in turn also influences the shape of the main peak.

Next, we address the question whether the different components contributing to the (asymmetric) line shapes change as a function of surface sensitivity. For this purpose we performed fits of the measured spectra assuming the presence of at least two components representing different carbon atoms within the molecules. The number of fit parameters was kept as small as possible to yield stable and reliable fit results. The fit was performed by using a Voigt profile; the Gaussian (0.70 eV) and Lorentzian (0.08 eV) contributions were from previous near edge x-ray absorption fine structure investigations[18] and assumed to be identical for surface and bulk. We focus our attention on the PTCDA XPS C 1s edge (Fig. 2). If we compare the fit results for the most bulk sensitive (top) with that of the most surface sensitive spectrum (bottom), we find an energy shift of 30–40 meV (from 285.13 and 284.57 eV to 285.17 and 284.60 eV, respectively) and differences in the intensities of about 2% which is less than the accuracy limit of such analyses. Analogous results were obtained for coronene and H_2Pc yielding no energy shifts for the former and −10 to −30 meV for the latter.

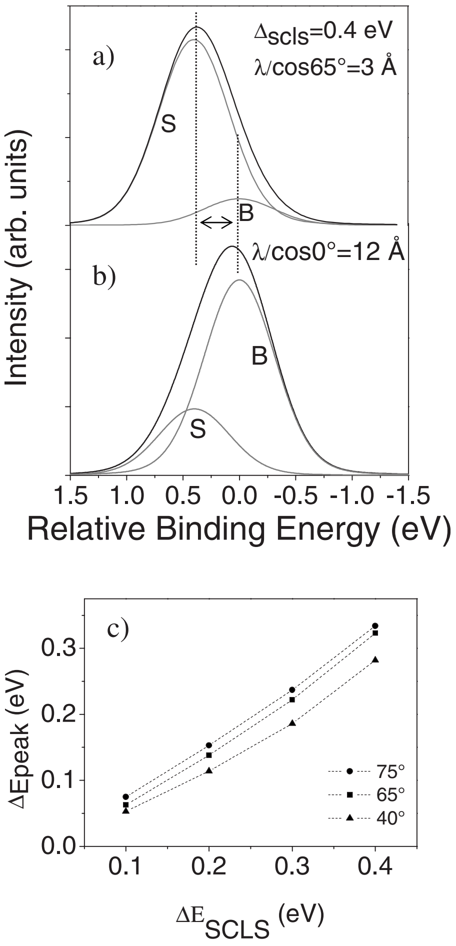

FIG. 3. Simulated spectra for (a) $\lambda=4$ Å, $\theta=65°$, surface sensitive, and (b) $\lambda=14$ Å, $\theta=0°$, bulk sensitive, for an SCLS, ΔE_{SCLS}, of 0.4 eV. In the lower part (c) the simulated apparent peak shifts, ΔE_{peak}, are plotted versus SCLS values for three different emission angles.

Finally, we should provide an idea about the surface or bulk sensitivity of the present experiments and the expected influence. In this way we can also give an estimate for the upper limit of the SCLS. For this purpose we need suitable inelastic mean free paths λ in organic materials. For PTCDA films we have previously performed two detailed studies which used laboratory Mg $K\alpha$ sources and a detailed knowledge about the homogeneity of the organic film.[20,21] Both arrived at rather similar values, 15 and 18 Å, for $E_{kin}=885$ eV which is in rough agreement with other data.[22] If we assume an energy dependence of λ as found for the so-called universal curve[22] we obtain λ values of about 4 and 12 Å for $E_{kin}=50$ and 415 eV, respectively. By applying the common exponential attenuation behavior and inserting the emission angles given above, we can calculate changes of the measured peak shape if a bulk and a different surface component exist. For the simulation of spectra we took an SCLS, ΔE_{SCLS}, between 0.4 and 0.1 eV and the linewidths parameters given above, and then integrated the contributions from the various layers. For clarity, we took only one component instead of the two components suggested by Fig. 2. The simulated spectra are shown in Figs. 3(a) and 3(b) for the two extreme sensitivity cases and for an SCL shift of 0.4 eV yielding an apparent peak shift, ΔE_{peak}, of 0.3 eV which is not observed. For smaller SCLS the apparent peak shift is reduced as indicated by the curves in Fig. 3(c). Thus we find that an SCLS of 100 meV would still yield a clearly distinguishable peak shift of 40 ($\theta = 40°$) and 60 meV (65°), respectively, which is not found here (see Fig. 1). Thus in all three cases we conservatively give an upper limit of the SCLS of 100 meV.

The experimental finding leads to the conclusion that the difference of surface vs bulk polarization is much smaller than previously expected. It is indeed much smaller than the polarization difference (apparent SCLS) found for rare gas layers,[1,2] which is in the order of a few tenths of eV as mentioned above. A negligible or very small polarization difference can only be explained if one assumes that the charge is delocalized over at least a few molecules. Of course, the core hole remains in the ionized molecule on the time scale of the photoemission process but its screening by charge rearrangement of the valence orbitals is apparently not limited to the ionized molecule, causing some charge transfer between adjacent molecules and leading to a distribution of the positive charge over a few neighboring molecules. The common picture with a positively charged (ionized) molecule and polarized neighboring molecules which are electronically decoupled from the ionized molecule would not suffice to describe the here observed negligible or very small SCLS as shown by theoretical calculations.[6]

What are the implications of the present finding? First of all, electron spectroscopists do not have to worry about distinguishing surface and bulk contributions and/or about making corrections for surface effects. Second, the surface layer, and hence also an interface layer to another organic or inorganic material, is energetically not very different from bulk layers. This has implications for optical spectroscopy (e.g., access of interface traps) as well as for transport phenomena. For instance, if a positive charge in the surface layer has a significantly higher binding energy than in the bulk it would prefer to flow along the second or deeper layers, in contrast to experimental observations in OFETs implying that the first (interface) layer carries most of the current.[23] Third, if charges are delocalized over a few molecules other properties like exciton binding energies could be influenced and are perhaps smaller than commonly believed. Finally we note that the present finding should stimulate theoretical work to better understand the effects of polarization and charge delocalization in organic materials which is a key issue for both basic understanding and applications. Also, further experimental studies are needed to investigate the influence of disorder (the present films were polycrystalline), intermolecular interaction, and molecular structure.

In conclusion, we have presented high resolved XPS data, taken at a "state-of-the-art" experimental end station at a third generation synchrotron. The data sets for each sample were taken *in situ* and compared under the same preparation and experimental conditions making the data highly reproducible. In addition, XPS, unlike UPS, measurements are not influenced by band dispersion or band/orbital splitting due to interaction, e.g., for two or more molecules per unit cell, which is a great advantage for an unambiguous assignment of bulk and surface species. Our results, revealing no or very small SCLS in organic thin films provide evidence for a rather small polarization difference between the bulk and surface which can be understood as a charge delocalization over at least a few molecules which significantly reduces the difference between bulk and surface.

The authors would like to thank the BESSY staff, in particular Ch. Jung, S. Pohl, and H. Marchetto (Fritz-Haber-Institut), A. Schöll, and P. Imperia. Financial support by the DFG (Projects No. Um 6/8-2 and Um 6/8-3) and by the BMBF under Contracts No. 05KS1WWA/5 and No. 05KS4WWC/2 is gratefully acknowledged.

---

*Present address: Institut für Physikalische und Theoretische Chemie, Universität Tübingen, Auf der Morgenstelle 8, 72076 Tübingen, Germany. FAX: +7071 29 5490.

[1] T. C. Chiang, G. Kaindl, and T. Mandel, Phys. Rev. B **33**, 695 (1986).

[2] C. Buchberger, Ph.D. thesis, Universität Würzburg, 2001.

[3] I. G. Hill *et al.*, Chem. Phys. Lett. **327**, 181 (2000).

[4] C. B. Duke, T. J. Fabish, and A. Paton, Chem. Phys. Lett. **49**, 133 (1977).

[5] W. R. Salaneck, Phys. Rev. Lett. **40**, 60 (1978).

[6] E. V. Tsiper *et al.*, Chem. Phys. Lett. **360**, 47 (2002).

[7] S. F. Alvarado, M. Campagna, and W. Gudat, J. Electron Spectrosc. Relat. Phenom. **18**, 43 (1980).

[8] D. E. Eastman, T. C. Chiang, P. Heimann, and F. J. Himpsel, Phys. Rev. Lett. **45**, 656 (1980).

[9] R. E. Watson, J. W. Davenport, M. L. Perlman, and T. K. Sham, Phys. Rev. B **24**, 1791 (1981).

[10] W. F. Egelhoff, Jr., Surf. Sci. Rep. **6**, 253 (1987).

[11] R. E. Watson and J. W. Davenport, Phys. Rev. B **27**, 6418 (1983).

[12] G. Paolucci and K. C. Prince, Phys. Rev. B **41**, 3851 (1990).

[13] C. Heske, U. Winkler, G. Held, R. Fink, E. Umbach, C. Jung, P. R. Bressler, and C. Hellwig, Phys. Rev. B **56**, 2070 (1997).

[14] A. Baraldi, S. Lizzit, G. Comelli, A. Goldoni, P. Hofmann, and G. Paolucci, Phys. Rev. B **61**, 4534 (2000).

[15] G. Beamson, J. Electron Spectrosc. Relat. Phenom. **121**, 163 (2001).

[16] A. Schöll *et al.*, J. Electron Spectrosc. Relat. Phenom., **129**, 1 (2003).

[17] Y. Zou, Ph.D. thesis, Universität Würzburg, 2003; Y. Zou *et al.*, Surf. Sci. **600**, 1240 (2006).

[18] A. Schöll *et al.*, J. Chem. Phys. **121**, 10260 (2004).

[19] S. Kera *et al.*, Surf. Sci. **600**, 1077 (2006).

[20] L. Knoth, Ph.D. thesis, Universität Würzburg, 2002.

[21] V. Shklover, Ph.D. thesis, Universität Würzburg, 2002.

[22] http://xdb.lbl.gov/ and references therein

[23] G. Horowitz, J. Mater. Res. **19**, 1946 (2004), and references therein.