Determination of transport levels of organic semiconductors by UPS and IPS

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Abstract. In this paper, we present a comprehensive discussion on the determination of transport levels of organic semiconductors using a combination of UV and inverse photoemission spectroscopies (UPS and IPS, respectively). We discuss the key question of how the spectra should be evaluated to obtain the correct values for the transport levels. Our evaluation results in much smaller exciton binding energies than generally assumed, ranging from 0.1 to 0.4 eV for CuPc, PTCDA and Alq\(_3\). Moreover, we find that polarization effects, vibrations, experimental resolution and inhomogeneous broadening contribute very little to the position and width of the broad photoelectron spectroscopy (PES) and IPS signals. Thus, we suggest a model that explains much of the broadening as a result of dynamic charge delocalization. We discuss our data in analogy to those obtained for inorganic semiconductors (IOSCs), which are presented in a separate paper.
1. Introduction

Organic semiconductors consisting of small organic molecules or polymers are presently a field of intensive research due to their potential in complementing, or even surpassing, the properties of their inorganic counterparts in opto-electronic applications. However, fundamental properties of organic materials, such as the geometric structure and the electronic properties as well as their interplay with charge injection and charge transport, are lacking a comprehensive understanding.

For example, for a detailed understanding of the properties of organic materials and for tailoring the molecules and device structures it is of utmost importance to know the position of the transport levels and the size of the optical gap (OG), and hence the exciton binding energy. And it is, of course, desirable to know the dependence of these properties on the molecular structure and on the geometric arrangement of the molecules. However, the findings of e.g. the exciton binding energy range from \( \sim 0 \) to 1.5 eV even for the same molecular species \([1, 2]\). A reason for this discrepancy is the approach to how the levels are defined, how the spectroscopic data are analysed, and how the results are interpreted. This is the topic of the present paper.

1.1. Definition of the transport level for organic semiconductors

When organic semiconductors were first investigated their electronic structure was treated in analogy to inorganic materials and, as consequence, the determination of e.g. the energy gap relevant for charge carrier transport was measured with optical absorption spectroscopy, as is common for inorganic semiconductors (IOSCs) \([3]–[5]\). Later, Kahn and co-workers \([6]\)
and Seki and co-workers [7] pioneered the approach of using photoelectron spectroscopy (PES) with UV- and x-ray excitation (UPS and XPS, respectively) and inverse photoelectron spectroscopy (IPS). They interpreted their findings using the concept that in an organic solid the electronic structure of the single molecule is essentially preserved; therefore they associated the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) with the levels relevant for charge transport. As a result of the assumed weak van der Waals interaction the (transport) charge was generally expected to be strongly localized. Thus a response of the ionized molecule and its surroundings, such as a relaxation of the intramolecular electronic system and a polarization of the neighbours, has to be taken into account for correctly describing the transport levels.

For organic materials it is not straightforward to determine what exactly the transport levels are since this depends on the mechanism of charge transport. In the case of hopping transport the charge is localized on a single molecule for about $10^{-14}$ s (see [8]) before it ‘hops’ to the next molecule. Thus, the relevant transport levels are those of the relaxed ionic states (RIS) in which all fast ($<10^{-14}$ s) screening processes, such as polarization and relaxation, have already occurred. In the case of coherent band-like transport, the relevant levels are (HOMO- and LUMO-derived) delocalized wave functions. A completely delocalized wave function would correspond to a fully screened charge state in which polarization and relaxation effects are zero because the charge is spread over the whole sample. The most important question in the present context is how the spectroscopic findings correlate with localized or delocalized charge states.

1.2. Techniques to determine the transport levels

In order to probe the energetic position of electronic levels in general and the transport levels in particular a variety of experimental techniques can be applied. However, each method has a specific influence on the investigated system, which leads to differences in the experimental findings according to the respective technique. A straightforward approach to quantify these differences and to identify the accurate values of the transport levels is to apply and compare the results of different techniques. In the following, we will briefly introduce important methods and sketch the influence of the measuring process on the result.

UPS and IPS probe the energy position of the occupied and unoccupied levels directly by using ultraviolet radiation (for occupied valence levels, UPS) or electrons (for unoccupied levels, IPS). UPS is based on the photoelectric effect; the kinetic energy of the emitted electron is equal to the photon energy minus the binding energy of the emitted electron in the solid (minus the surface work function if the energies are referred to the Fermi level). In IPS, electrons that are emitted by an electron gun with a preset kinetic energy ‘fall’ into unoccupied levels while emitting a photon with an energy equal to the difference between the initial kinetic energy and the energy of the unoccupied level. Thus, in principle, the final state of the system is obviously not the electronic ground state but an (excited, negatively charged) ionized state.

The most common technique for the determination of energy gaps is optical absorption. In this case, an electron–hole pair is created by the absorption of a photon, and the gap energy is derived from the onset of the optical absorption. However, this e–h pair may still be bound due to Coulomb interaction, a state usually referred to as an exciton. Therefore the optically measured gap is smaller than the transport gap (TG) by the amount of the exciton binding energy and hence is called OG. If the exciton is strongly localized, e.g. on a single atom, its binding energy may be large (≈1 eV; Frenkel exciton). The potential difference between OG and TG in fact strongly
influences the properties, since, e.g. in photovoltaics, the created exciton has to be separated in a subsequent process to create free charge carriers that can diffuse to the corresponding electrodes. Thus, for charge separation a built-in electric field is needed which reduces the resulting open circuit voltage, and the finite probability for charge separation reduces the short circuit current. In the case of IOSCs so-called Mott–Wannier excitons occur which have large radii and hence small binding energies (a few microelectronvolt). Thus, they can be neglected when comparing OG and TG.

Another direct method to measure the transport levels is the photoconductivity technique (see [8, 9]). Light with an appropriate wavelength excites electrons from the valence band into the conduction band; if the energy is sufficient, the exciton is separated thus increasing the number of free carriers. If the photon energy is scanned, the current rapidly increases as soon as the energy of the photon matches the TG, thus allowing the determination of the gap, but not the absolute energy positions of the transport levels.

Another useful method is the combination of near edge x-ray absorption fine structure (NEXAFS) and resonant inelastic x-ray scattering (RIXS). In NEXAFS, the incident x-rays with an energy close to the absorption edge of one of the elements in the investigated material excite a core electron into an unoccupied state. Thus, information about unoccupied states can be derived. However, the interpretation may be complicated by the influence of the core hole. RIXS uses x-rays to excite core electrons into the conduction band. The core hole can then be filled by an electron from the valence band, which consequently emits x-rays of less energy than needed for the excitation. The energy difference is essentially equal to the energy difference of conduction and valence band. If both processes occur resonantly, the k-vector is conserved, and if the signals from the edges are taken, then the k-dependent band gap can be derived. However, the influence of the core hole and the distinction of core and valence excitons complicate the interpretation.

1.3. The choice of proper energy values

UPS/IPS spectra of organic and IOSCs usually yield broad peaks (FWHM 0.5–1 eV) even if high experimental energy and k-vector resolution is applied and highly ordered systems are investigated. Thus, the question arises which energy value should be taken to determine the band edges. Some authors take the peak maxima which have successfully been utilized to extract band structures and orbital positions. For IOSCs early authors also took maxima, but many recent authors take peak onsets because otherwise the band gaps come out much too large (∼1 eV). Recent investigators of organic systems again used peak maxima and—after some corrections—stated band gaps that were significantly larger than those obtained by optical absorption [2]. The energy difference was then attributed to the exciton binding energy which could be as high as 1.5 eV. As a consequence, many researchers accepted the concept of strongly bound (Frenkel) rather than weakly bound (Mott–Wannier [8]) excitons for organic semiconductors, but the discrepancy between the methods applied and the results obtained for organic and IOSCs was not addressed.

In this paper, we present UPS and IPS measurements on various organic semiconductors and discuss the data against the background of well-understood inorganic systems [10]. We suggest a consistent interpretation that will help to understand the dichotomy between TG and OG and may allow a correct determination of the exciton binding energies in organic semiconductors.
2. Experimental

All measurements were performed in a VG ESCALAB UHV system equipped with an Mk II electron spectrometer at a base pressure of better than $2 \times 10^{-10}$ mbar. A gas discharge lamp was used for UPS, which can be operated with either helium for photon energies of 21.22 or 40.80 eV or with argon (11.62 eV). The IPS system consists of a Ciccacci-type low-energy electron gun with a BaO cathode [11] and a Geiger–Müller detector with SrF$_2$ window filled with Ar and I$_2$ [12]. It was used in the isochromatic mode with fixed photon energy of about 9.5 eV. The energy resolution was determined as 50 meV for UPS and 400 meV for IPS from the width of the Fermi edge of a sputter-cleaned gold foil.

The growth rate of the film was controlled with a quadrupole mass spectrometer during deposition; its thickness was derived from the deposition time and a calibrated rate using XPS and a calibration point. The final film thickness was checked by measuring the attenuation of the substrate signal with XPS.

In each case, a homogeneous film of 10–20 molecular layers onto a well-cleaned Ag(111) surface was prepared before the spectra were taken. Accompanying experiments using XPS ensured the homogeneity of the organic film; no signal from the substrate or the interface layer was detected in our experiments. To achieve this, the substrate had to be LN$_2$ cooled below 220 K.

3. Results and discussion

3.1. Experimental results

Figure 1 presents combined UPS and IPS spectra for three different organic semiconductors, Alq$_3$ (tris(8-hydroxy-quinoline)aluminum), PTCDA (3,4,9,10-perylenetetracarboxylicacid dianhydride) and CuPc (copper phthalocyanine). The spectra were recorded with great care; since radiation damage is an issue particularly with respect to IPS, the measurement times were minimized and the spectra from various identically prepared layers were summarized until a sufficiently good signal-to-noise ratio was achieved. If signs of radiation damage were detected, which was a particular problem for IPS of Alq$_3$, significantly shorter recording intervals were chosen. The influence of radiation damage or instabilities in the detecting system as well as differences in the sample preparation may lead to a significant peak broadening or to the appearance of spurious shoulders in the spectra. It is important to note in this respect that our data show very sharp signals in both, IPS and UPS, if compared to analogous experiments in the literature. This demonstrates the high quality of the sample preparation, the negligible effect of radiation damage in the present case, and the reliability of our results.

The spectra show a variety of peaks which have been interpreted and discussed in several previous publications [13]–[16]. We concentrate on the peaks close to zero energy which represent the frontier orbitals, HOMO and LUMO, and which are marked by bars in figure 1. The important question now is how to determine the TG from the present data. There are at least two possible ways. One is the intuitive idea to take the peak maxima as energy positions of the HOMO and the LUMO and to use the energy difference between the peak maxima ($\Delta E_{\text{PM}}$) as the TG. The alternative way is to utilize the corresponding peak onsets as indicated in figure 1 as valence band maximum and conduction band minimum, respectively, and their energy difference ($\Delta E_{\text{PO}}$) as TG. The thus derived TG values from the two methods differ...
enormously by 1.3–1.9 eV; they are summarized in Table 1 together with equivalent values obtained by Hill et al [2] and the values of the OG derived from optical spectroscopy [2, 17].

3.2. Discussion of the different evaluation methods

At a glance, the TG values of the peak maxima method yield too large exciton binding energies\(^4\) ranging from 1.4 to 2.3 eV, whereas those derived from the onset method result in seemingly rather small exciton binding energies (0.1–0.4 eV). Previously, it had been argued that peak maxima have to be used [10] because they represent the average value of a disordered

\(^{4}\text{The exciton binding energies were calculated from the difference between the } \Delta E_{\text{PM}}/\Delta E_{\text{PO}} \text{ of our data and the optical gaps from [2].}\)
Table 1. Energy gaps determined from the combined UPS–IPS data of figure 1 in comparison to analogue values determined\(^a\) by Hill et al [2] and the respective OG. \(\Delta E_{PM}\) refers to the distance of the HOMO and LUMO peak maxima, \(\Delta E_{PO}\) is the distance between the peak onsets.

| Material | \(\Delta E_{PM}\) (eV) | \(\Delta E_{PM}\) (eV) | \(\Delta E_{PO}\) (eV) | \(\Delta E_{PO}\) (eV) | \(E_{g,\text{opt}}\) (eV) |
|----------|-----------------------|-----------------------|-----------------------|-----------------------|-----------------------|
| Alq\(_3\) | 5.4                   | 5.5                   | 4.1                   | 3.6                   | 3.2                   |
| PTCDA    | 4.0                   | 3.8                   | 2.3                   | 2.5                   | 2.2                   |
| CuPc     | 3.1                   | 3.1                   | 1.7                   | 1.8                   | 1.7                   |

\(^a\)The \(\Delta E_{PO}\) values were determined graphically from the spectra in [2].

(inhomogeneous) molecular layer with a distribution of energy positions due to varying interactions with neighbouring molecules resulting in an inhomogeneous peak broadening. It was furthermore argued that the energy difference was too large due to polarization and polaronic effects and hence had to be reduced by \(2 \times 0.3\) eV = 0.6 eV resulting in exciton binding energies of 0.8–1.6 eV (the factor of 2 results from UPS and IPS) [2]. The energy difference was derived from calculations showing that a photo-ionized molecule of the topmost layer is less well screened (difference 0.3 eV) by polarization of neighbouring molecules than a bulk molecule because for the top layer polarization screening of the molecular ion is only provided by the layers underneath, while bulk molecular ions are screened from all sides. Note that a binding energy of more than 1 eV is still rather large for an exciton in a molecular layer since excitons in Xe layers have binding energies of only about 0.8–1.0 eV [18]–[20] and are essentially localized on a single atom, whereas in our molecules they are at least delocalized over a significant part of the molecule.

3.3. Comparison to IOSCs

The use of the onsets is strongly corroborated by our findings for IOSCs. Previously, we have shown [21] that for a single crystal of HgTe(100), which is a semimetal (= zero energy gap), indeed a band gap of 0 eV is found by using the present experimental methods and by evaluating the onsets, whereas a gap of 1.2 eV is found when using the peak maxima. For CdTe(100), the known band gap is 1.65 eV which is exactly reproduced if the present methods and the onset evaluation are applied, while peak-to-peak evaluation leads to a gap of 3.2 eV. The idea that UPS and IPS only measure the topmost layer and hence the surface band gaps which might be significantly larger than the bulk gaps [22] can easily be falsified by angle-resolved measurements, by a variation of the photon energy and hence the sampling depth, by calculations, by band structure measurements, and by cases where a surface state is observed in addition to the clearly seen bulk states [23].

3.4. Polarization effects

If we take the onsets the question arises whether we should consider polarization differences at the surface and bulk, respectively, as done before [2] and as mentioned above. If a reduction of our TG values obtained with the onset method by 0.6 eV would be applied we would obtain...
TG values smaller than the OG values which would not make sense. On the basis of recent experiments, we are certain that the polarization differences between ionized surface and bulk molecules are zero or at least very small (detection limit: 50–100 meV, depending on molecule). Polarization screening and in particular the difference between surface and bulk signals have been investigated by Casu et al \cite{24,25} by directly measuring the surface shift of core states with high-resolution XPS. By tuning the probing depth (by variation of the photon energy and the electron emission angle) the difference between bulk and surface contributions to the measured signal could be shown to be smaller than 50 meV for PTCDA and 100 meV for CuPc. Note that these values are upper limits given by the limit of the experimental resolution; the actual surface core-level shift may be smaller or zero. Since core levels are archetypes for strongly localized charge, since their evaluation is not obscured by band dispersion effects or level splitting due to mutual interaction like valence levels, and since they are very sensitive to screening and relaxation effects, 100 meV can also be taken as an upper limit for the surface shift of valence levels. This is corroborated by recent data on \textit{C}_{60} which reduce the surface shift to less than 10 meV \cite{26}.

It should be noted that a surface polarization effect was concluded from an earlier UPS measurement of Salanek \cite{27} who observed a splitting of the HOMO level into two components separated by 0.3 eV, which were interpreted as surface and bulk components. We disagree on this interpretation since we also found a splitting of HOMO levels in several cases but arrived at different interpretations after careful experiments and analyses. For instance, a similar HOMO splitting was observed in angle-dependent ARUPS experiments of PTCDA on Ag(111) by Kilian \cite{28} and in energy-dependent UPS experiments of the same system by Zou \cite{29}. The authors tried to fit and evaluate the two HOMO components under the assumption of surface and bulk origin but failed in both cases. They independently concluded that either the mutual interaction of the two different molecules per unit cell in the highly ordered molecular layer lead to a level splitting or that band dispersion effects or multiple scattering effects caused the appearance of two peaks. A similar explanation was given by Yamane \textit{et al} \cite{30} for PTCDA on MoS$_2$ and by Gavrila \textit{et al} \cite{31} for DiMe–PTCDI on n-GaAs (100) who investigated band dispersion effects. The derived dispersion of 0.2 eV is in the order of the above mentioned splitting. Unpublished results of band dispersion in ordered NTCDA layers on Ag(111) yielded an even larger band width of 0.35 eV \cite{29}.

3.5. Discussion of the smaller exciton binding energies

Based on the comparison with the results from IOSCs, plausible arguments for the size of the expected exciton binding energy, and on the finding of a negligible influence of polarization differences between surface and bulk species, we come to the following conclusion: the onset method gives by far the better approximation to the actual transport level and exciton binding energy values as compared to the peak-to-peak method. If this interpretation is correct and generally true, we need an explanation for the here measured, rather small exciton binding energies.

Firstly, one could ask which exciton binding energies one would expect in a molecular system. Considering the relatively small Frenkel exciton binding energies (~1 eV) of rare gases and strongly ionic species (e.g. alkali halides) with their small exciton radii one can easily understand that excitons in a molecular species with an extended \pi -electron system like PTCDA or CuPc may have a considerably larger exciton radius (comparable to the distribution of the
LUMO and HOMO, respectively). Due to the resulting strong reduction of the correlation, a considerably smaller exciton binding energy results in molecular solids compared to rare gases or ions. Thus the present exciton binding energies, 0.1 eV (CuPc), 0.3 eV (PTCDA) and 0.4 eV (Alq$_3$), look fairly convincing and consistent with this simple picture.

Next, we should discuss the influence of polarization screening and other effects that may influence the evaluation of the TG values. As mentioned in the introduction, the peak maxima were often used in organic materials to determine the energy of the HOMO and LUMO. The assumption that molecules in organic semiconductors are not interacting by covalent bonds as the atoms in IOSCs gives a reason for speculations why the gaps determined by the peak-to-peak method deviate strongly from the values obtained by optical absorption. In an organic material with only van der Waals and electrostatic intermolecular forces the orbitals of neighbouring molecules hardly overlap thus essentially keeping the electronic structure of a free molecule. As a consequence, charge produced on a particular molecule, e.g. by photoemission, should remain localized on this molecule until it ‘hops’ or ‘tunnels’ to the neighbouring molecule. In addition, the polarizability in molecular materials is relatively large, particularly for compounds with large (delocalized) $\pi$-electron systems. Therefore, the electronic relaxation effects essentially occur within the ionized molecule (intra-molecular screening) while additional screening is provided by polarization of neighbouring molecules (inter-molecular screening). The latter leads to substantial peak shifts towards lower binding energies. Salaneck [27], Sato et al [32], Crispin et al [33] and Dori et al [15] compared gas phase and solid-state photoemission results and attributed the shift of the ionization energy to (additional) polarization screening in the condensed phase (shifts range from 0.9 to 3 eV).

Based on this finding it is often assumed that molecules in organic semiconductors in different relative positions with respect to each other experience different screening; thus, different sites lead to an inhomogeneous distribution of peak energies. Of course, this effect should lead to inhomogeneous peak broadening and to different binding energies for surface and bulk molecules, as mentioned above (0.3 eV for Anthracene [27]). Theoretical considerations of this effect assuming the charge to remain completely localized in the ionized molecule also lead to a shift of 0.4 eV between surface and bulk PTCDA molecules [34]. Indeed, in XPS and UPS experiments of rare gas films such differences between surface and bulk atoms of 0.12–0.25 eV have been detected [35]–[38]. The effect is large enough to be observable even with poor experimental resolution. However, this effect is not observed for PTCDA and CuPc in a high-resolution photoemission experiment, as mentioned above.

In addition, a shift due to vibrational excited final states, which is negligible for IOSCs, has to be considered for organic molecules; a value of 0.2 eV has been estimated [8, 39]. Salaneck et al [40] investigated the HOMO broadening of isopropyl benzene by fitting a Gaussian at different temperatures. The temperature-dependent increase of the Gaussian width is $2.6 \times 10^{-2} T^{1/2}$ eV (= 450 meV at 300 K), which corresponds to a shift of the onset of about 50–100 meV. According to [2], these two contributions, surface polarization and vibrational broadening, have to be subtracted from the measured peak-to-peak distance to obtain the correct TG.

In this context, we should also comment on inhomogeneous broadening effects as often suggested for molecular layers. In fact, we do not observe a significant inhomogeneous broadening in our highly ordered layers of PTCDA and CuPc, as derived from the line shapes of high-resolution XPS measurements of very differently prepared organic thin films. This finding is corroborated by a careful line shape analysis of high-resolution NEXAFS data of highly
ordered PTCDA and NTCDA films, which yielded an overall Gaussian broadening of about 100 meV setting an upper limit for the contribution of inhomogeneous broadening [41]. This finding also sets an upper limit for the temperature effect mentioned before since this should contribute to a Gaussian line shape.

3.6. The influence of polarons

In the context of polarization, the influence of polarons to the photoemission spectrum also has to be considered. In the case of molecular solids, the term is often used for electron–vibron coupling, i.e. in a different way as compared to the original definition, which refers to an electron–phonon coupling (so called lattice polaron, see [42]). In a molecular crystal lattice phonons usually have very small energies due to the weak intermolecular forces and large molecular masses, and thus play a minor role. The review by Zhu [43] distinguishes two additional types of polarons for molecular solids depending on the strength of interaction. An electron can very effectively couple to a dipole-active molecular vibration which is then called a small molecular polaron. Moreover, the so-called electronic polaron can appear if the next neighbours of a molecule have high polarizability. Unlike the others, this polaron involves no nuclear but only electronic motion and is usually meant if polaronic excitations are referred to in organic molecular condensates. In this context, it is important to note that the different polarons occur on different timescales. Electronic polarons are fast (0.1–1 fs) whereas small molecular (2–20 fs) and lattice phonons (>100 fs) need more time due to the inertia of the involved nuclei. The timescale of the PES process, however, is shorter than a few femtoseconds, which is too fast for most dipole-active molecular vibrational modes, and PES might thus not be sensitive to the excitation of small molecular polarons. Electronic polarons, in contrast, occur on the same timescale as the PES process and the respective binding energies are estimated to be in the order of 1 eV. These excitations could thus generally contribute to PES spectra and should be clearly identified due to their energy separation. This, however, was not observed in the experiments by Casu et al [24, 25].

3.7. The effect of inhomogeneous broadening

The influence of inhomogeneous broadening can best be investigated for Alq\textsubscript{3} since it condenses in amorphous films due to its complex 3D structure, and thus generally grows in films with no long-range structural order. As a consequence, charge produced by the photoemission process can be expected to be particularly strongly localized in this case which in turn should result in relatively high exciton binding energies. Moreover, inhomogeneous broadening, caused by the variation of the relative molecular orientation and its effect on the electronic screening, should be comparably strong in the case of an amorphous system. The binding energies of the frontier orbitals are therefore expected to exhibit a distribution as illustrated by figure 2 (exaggerated).

If this effect is large, one would expect a significant difference of the widths of the Alq\textsubscript{3} HOMO and LUMO levels as compared to systems with high structural order, as, e.g. PTCDA. Table 2 shows the fit results for the LUMO levels of the IPS spectra (figure 1). The difference is in the order of 500 meV (Gaussian widths add quadratic). This can be considered as an upper limit for the inhomogeneous contribution due to the amorphous structure of Alq\textsubscript{3}. It is an upper limit since we also have to consider several electronic states underneath each peak, and any additional peak in the fit function would decrease the width of the other components.
Figure 2. Sketch of the variation of the molecular energy levels due to inhomogeneities of the local molecular environment. This effect results in a probability distribution $P(E)$ of the energy levels (displayed on the right).

Table 2. Parameters (peak positions and FWHM) derived from the fit of the IPS spectra (after subtraction of a quadratic background). $\Delta E$ is the shift of the LUMO peak onset after deconvolution.

|       | LUMO (meV) | FWHM (meV) | LUMO+1 (meV) | FWHM (meV) | LUMO+2 (meV) | FWHM (meV) | LUMO+3 (meV) | FWHM (meV) | $\Delta E$ (meV) |
|-------|------------|------------|--------------|------------|--------------|------------|--------------|------------|----------------|
| Alq$_3$ | 2.44       | 1026       | 3.49         | 1058       | 4.62         | 1096       | –            | –          | 41             |
| PTCDA  | 1.26       | 853        | 2.74         | 930        | 3.92         | 1113       | –            | –          | 50             |
| CuPc   | 1.51       | 918        | 2.30         | 989        | 3.43         | 1073       | 4.92         | 1209       | 46             |

3.8. Deconvolution of IPS spectra

It has previously been argued that the TG values experience a significant increase if the instrumental broadening is taken into account by a proper deconvolution [44, 45]. Figure 3 presents the result of our deconvolution efforts (displayed as red solid lines) and show the influence on the position of the onsets. We applied the deconvolution to the experimental IPS spectra of figure 1, which are of course influenced by the relatively poor ($\sim$400 meV) experimental resolution of the IPS set-up. After subtraction of a quadratic background the spectra were fitted with a series of Gaussian peaks. The thus obtained Gaussian line widths were subsequently corrected by the detector broadening; the resulting peaks yielded the ‘deconvoluted’ spectrum shown in figure 3. In the case of PTCDA, the width of the LUMO peak in the experimental spectrum was 853 meV. The width of the deconvoluted LUMO peak can thus be calculated to 753 meV. This leads to only a relatively small shift of the onset of $\Delta E = 50$ meV. The results for Alq$_3$ and CuPc are very similar and are summarized in table 2. The broadening due to the limited experimental resolution is thus a relatively small effect, which has to be taken into account, however, for an accurate evaluation. The discrepancy to [44] of the shift of the onset due to deconvolution probably arises since linear rather than quadratic addition of Gaussian line width contributions has been applied.
Figure 3. IPS spectra of (a) Alq$_3$, (b) PTCDA and (c) CuPc after background subtraction. The light grey lines correspond to curve fits with Gaussian peaks utilizing the parameters of table 2. The black lines are based on the same peaks but the Gaussian widths for the detector broadening of 400 meV FWHM have been included.

3.9. UPS and IPS peak shape

Obviously, neither inhomogeneous broadening nor the influence of vibrations nor the influence of the detection system can account for the majority of the peak width in the UPS and IPS data. However, the peak shape can be explained by the dynamic charge delocalization which occurs upon photo ionization. We have already introduced this interpretation in our previous paper on IOSCs [11]. This interpretation attributes the low binding energy onsets of the bands (the band extrema) to the case in which the photo-generated hole (or electron, respectively) is completely delocalized. In this case, no more intermolecular screening is required or, in other words, the screening is perfect. However, since the delocalization process is statistical (and not binary) it leads to a distribution of well and less well-screened states and hence to a broadening of the PES signals. This is sketched in figure 4. The resulting PES signal, as illustrated by the Gaussian curve on the right-hand side, consists of a superposition of signals, each of which corresponds to a particular ‘snap shot’ recorded during the charge redistribution. As consequence, the UPS and IPS peak onsets correspond to well-screened ionic states, which are analogous to the situation of a charge during transport. We would hence conclude that a charge in an organic semiconductor is generally delocalized over at least a few molecules. This is consistent with the absence of

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surface core level shifts in organic materials which also lead Casu et al [24, 25] to the conclusion of delocalized charge.

3.10. Reason for small exciton binding energies

How do we explain the relatively small exciton binding energies? The most likely explanation is that the charges are more delocalized than commonly assumed. If the exciton charges are distributed over, say, three molecules rather than localized on just the ionized molecule, the observed effects would be completely explained. This interpretation is also fully consistent with the above onset/peak shape discussion and the observation of missing surface core level shifts in high-resolution XPS measurements. Although in the latter case the core hole remains localized, the valence electrons needed for optimal screening of the core hole are redistributed such that the charge is delocalized on several molecules. This could be called charge transfer screening and has been discussed in surface science more than 20 years ago [46]–[49]. As a consequence, this delocalization process needs fast intermolecular charge transfer and puts the picture of pure van der Waals and electrostatic interaction up for reconsideration. This finding is corroborated by recent results of Holch et al [50] who used NEXAFS to compare the electronic structure of PTCDA and similar organic compounds in the gas and condensed phase. The spectra show marked differences which can only be explained by a substantial intermolecular interaction of the aromatic \( \pi \)-system of adjacent molecules. A strongly interacting \( \pi \)-system is an ideal prerequisite for the delocalization of screening electrons.

4. Conclusions

The determination of the transport band gap from UPS/IPS measurements is of essential interest for various applications. Thus, the question whether the TG has to be evaluated from the separation of the peak maxima or from that of the peak onsets must be clarified. In this respect, the presented experimental data and the corresponding discussion are of fundamental relevance.
Table 3. Comparison of the TG $\Delta E_{\text{PO}}$ (derived from the peak onsets) to the optical data $E_{\text{g,opt}}$. $\Delta E$ is the correction that has to be taken into account due to the detector broadening. The residual deviation between the corrected $\Delta E_{\text{PO}}$ and $E_{\text{g,opt}}$ from table 1 can be attributed to the exciton binding energy $E_{\text{B,exciton}}$.

| Material | $\Delta E_{\text{PO}}$ (eV) | $\Delta E$ (eV) | $E_{\text{g,opt}}$ (eV) | $E_{\text{B,exciton}}$ (eV) |
|----------|-----------------|----------------|-----------------|-----------------|
| Alq$_3$  | 3.6             | 0.04           | 3.2             | 0.4             |
| PTCDA    | 2.5             | 0.05           | 2.2             | 0.3             |
| CuPc     | 1.8             | 0.04           | 1.7             | 0.1             |

Up to now, there is no established and commonly accepted approach. In the case of IOSCs, both methods are applied depending on what fits best for a particular question and system, but usually an explanation or justification for the used method is missing. In an associated paper [10], which deals with the gap determination in IOSCs, we show that the use of the peak onsets is the correct approach to determine the band extrema in these cases.

However, in the past spectra of organic semiconductors have been evaluated by referring to the peak maxima (although very recently peak onsets have been used [44]) and various conclusions were based on the resulting relatively large discrepancy between TG and OG. This discrepancy has been attributed to a large extent to surface polarization effects, which have very recently been shown to be much smaller if existing at all [24, 25]. Moreover, if adequate-photon energies are employed for photoemission the respective methods have substantial bulk sensitivity and thus allow probing bulk properties. Thus, the UPS/IPS spectra should at least contain a very significant bulk contribution which can be much larger than 50% such that the spectra are at least representative for surface plus bulk species.

Another important question is whether the nature of excitons in organic semiconductors can be described in the commonly applied Frenkel picture. This assumption is usually based on the relatively large difference between OG and TG if the peak-to-peak evaluation method is used. This leads (even after subtraction of other contributions; see above) to very large values for the exciton binding energies, which can only be assigned to strongly bound Frenkel excitons. These have a small radius which requires their localization within a molecule. Such behaviour would be expected if the intermolecular forces and the intermolecular orbital overlap are small. However, even in the case of prototype van der Waals solids such as noble gas crystals already the excitonic ground state can only be described as mixed Frenkel and Mott–Wannier exciton [51]. A strictly Frenkel-like nature of the excitons in condensed organic semiconductors is hence questionable.

In the present paper, we have given good reasons to use the onsets of the frontier orbitals for the determination of the band extrema. Together with the previous finding of negligible surface polarization, we find values for the exciton binding energy between 0.1 and 0.4 eV, which can be directly determined from the difference between $\Delta E_{\text{PO}}$ and $E_{\text{g,opt}}$ (see table 3). The exciton binding energies thus depend on the respective material but are in general substantially smaller than assumed so far. This is good news for the efficiency of photovoltaic devices for which an as small as possible exciton binding energy is preferred for effective charge separation.

The nature of the excitonic state and the intermolecular interaction are very important for the delocalization of charge and the transport mechanism. The stronger the interaction...
the easier the charge can delocalize and the less important local relaxation effects become. Moreover, the charge transport may change from coherent band-like transport to incoherent hopping depending on the strength of interaction. Recent experimental [52] and theoretical [53] results point towards the existence of both transport channels in organic solids including a broad transition region which depends on temperature. At low temperatures (i.e. below 50 K for naphthalene), the molecules have only few excited vibrational modes, and hence band formation occurs. With increasing temperature, though, vibrations disturb the band formation and the predominant transport mechanism changes to hopping. The charge transport channel also influences the delocalization probability, which will affect the peak shape depending on temperature. We therefore did not subtract vibrational broadening from our exciton binding energies.

In summary, we presented a comprehensive discussion on the determination of transport levels by the combination of UPS and IPS for organic semiconductors. We particularly focused on the question whether the peak maxima or onsets provide the correct values for the HOMO and LUMO levels and propose the use of peak onsets. As a result exciton binding energies in organic materials are smaller than generally assumed as we have shown for the examples PTCDA, CuPc and Alq3. Our interpretation is corroborated by the finding, that surface polarization, experimental resolution, vibrations and inhomogeneous broadening, which have previously been used to explain the large discrepancy between optical gap and TG when evaluating peak maxima, play only a minor role. In contrast, we propose that the broadening of the valence levels arises from the dynamic hole or electron delocalization, respectively, which occurs in response to photoexcitation.

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