Valence Electronic Structure of π-Conjugated Materials: Simulation of the Ultraviolet Photoelectron Spectra with Semiempirical Hartree−Fock Approaches

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A detailed understanding of the electronic structure of π-conjugated materials can be reached by means of two widely available semiempirical quantum-chemical methods: Austin model 1 (AM1) and intermediate neglect of differential overlap (INDO). This is illustrated by calculating the ultraviolet photoelectron spectra (UPS) of π-conjugated oligomers and polymers and comparing the theoretical data to experimental spectra. The approach is applied here to a series of compounds with varying molecular topology and chemical constitution: oligomers of *p*-phenylenevinylene and various derivatives, fluorinated derivatives of polyisothianaphthene, and 4,4′-bis(*m*-tolyphenylamino)biphenyl (TPD). The AM1- and INDO-calculated UPS spectra are also compared to data obtained with the valence effective Hamiltonian method, which is known to provide reliable results for the simulation of UPS spectra of these types of molecules. An easily applicable procedure is proposed to obtain the best fit to the experimental spectra from the AM1 and INDO molecular orbital energies. Both techniques accurately reproduce the lower energy part of the spectrum, which contains the most important part of the π electronic structure; INDO is also found to perform well for the inner part of the UPS spectrum, which mainly corresponds to the σ electronic states.

I. Introduction

Over the past two decades, π-conjugated materials have attracted a growing interest in view of potential technological applications in fields such as electronics, photonics, sensors, or corrosion protection.[1] These prospects have spurred intensive research aimed in particular at the design of polymers and oligomers tailored for specific tasks. This requires a detailed understanding of the relationship between chemical structure and electronic structure since the latter governs the following: (i) the capacity of conjugated systems of being doped, for applications in which they are used as electrical conductors; (ii) their linear and nonlinear optical properties and the nature of the excited states, of importance for optoelectronic devices such as light-emitting diodes or photovoltaic cells and photonic devices; and (iii) their interactions with other materials, such as metals.

Ultraviolet photoelectron spectroscopy (UPS) constitutes the method of choice for investigating the valence electronic structure of π-conjugated systems.[2,3] The use of synchrotron radiation and the fabrication of high-resolution spectrometers now allows for a detailed determination of the density of valence electronic states, with special emphasis on the upper π levels which are responsible for the electronic properties of the conjugated materials.

The wealth of information contained in the UPS spectra provides the most direct experimental comparison with the nature and energies of the one-electron molecular orbitals obtained from theoretical calculations.[2−4] In principle, ab initio Hartree−Fock and post-

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Hartree−Fock approaches are well adapted to this task, provided large enough basis sets are used.[5] However, even today, performing ab initio calculations on long conjugated oligomers and polymers can be in many instances a rather complex enterprise best left to quantum chemistry experts. This is why simpler alternatives have been proposed over the years. One approach that has been widely used in conjunction with conjugated materials has consisted in designing a nonempirical valence effective Hamiltonian (VEH), to reproduce the valence one-electron energies obtained at the ab initio double-ζ level.[6] The VEH method has been very successful for the description of the electronic structure of conjugated polymers and oligomers and its evolution upon doping (formation of solitons, polarons, or bipolarons)[7] and for the interpretation of the corresponding UPS spectra.[8] Recently, the method has been used to predict the electronic properties of conjugated (random or block) copolymers and to rationalize the influence of π-electron donor or acceptor groups on the energies of the frontier orbitals in polymers for light-emitting devices.[9,10] However, the effective Hamiltonian has been developed only for a limited set of atoms (H, C, N, S, O, Si); this prevents its use for a wide range of systems, such as halogen derivatives and organometallic molecules. In the 1970s, a semiempirical Hartree−Fock Hamiltonian, based on the complete neglect of differential overlap approximation with special parametrization for spectroscopic data (CNDO/S), was also developed and successfully used by Duke and co-workers to interpret the UPS spectra of organic molecules and conjugated oligomers.[11]

In this work, we investigate the ability of two widely available semiempirical Hartree−Fock techniques, the Austin model 1 (AM1) and the intermediate neglect of differential overlap (INDO), to reproduce the UPS spectra of conjugated materials. These two techniques are now included in numerous quantum-chemistry packages (such as Hyperchem, Spartan, Chem3D Pro, Mopac, Ampac, Gaussian, Cerius[12]) running not only on large workstations but also on personal computers. If it can be shown that the theoretical spectra calculated with these methods are in good agreement with the experimental data, AM1 and INDO would represent interesting, wide-ranging, and facile alternatives to the methods used so far for the interpretation of UPS data on conjugated materials and the understanding of their electronic structure. This is the reason why the present paper is addressed primarily to the materials chemistry community.

Compared to VEH, the advantage of the AM1 and INDO methods is that they are parametrized for a large set of atoms, including transition metals; when compared with CNDO/S, the treatment of the differential overlap is more sophisticated, which is expected to provide reliable results for a broader range of molecules. The AM1 or INDO approach can also be combined to a configuration interaction (CI) scheme in order to characterize the excited states and investigate the optical properties of conjugated systems;[13] this possibility does not exist for VEH, and it is less useful with the CNDO Hamiltonian, since the latter does not allow the singlet and triplet excited states to be distinguished. The INDO method has been used previously to interpret the UPS spectra of organometallic compounds.[14] We also note that the applicability of the semiempirical Hartree−Fock modified neglect of differential overlap (MNDO) approach to simulate UPS spectra has also been studied.[15]

Our work thus focuses on the use of AM1 and INDO to calculate the UPS spectra of a selected set of conjugated systems, shown in Figure 1. These compounds are particularly interesting for the following reasons: poly(p-phenylenevinylene) (PPV), its oligomers (Figure 1a), and their derivatives (Figure 1b−d) constitute the active elements in a novel generation of electrooptic devices, such as light-emitting devices,[16−18] photovoltaic cells,[19,20] and solid-state lasers;[21,22] 4,4′-bis(m-tolyphenylamino)biphenyl, TPD (Figure 1e), is used

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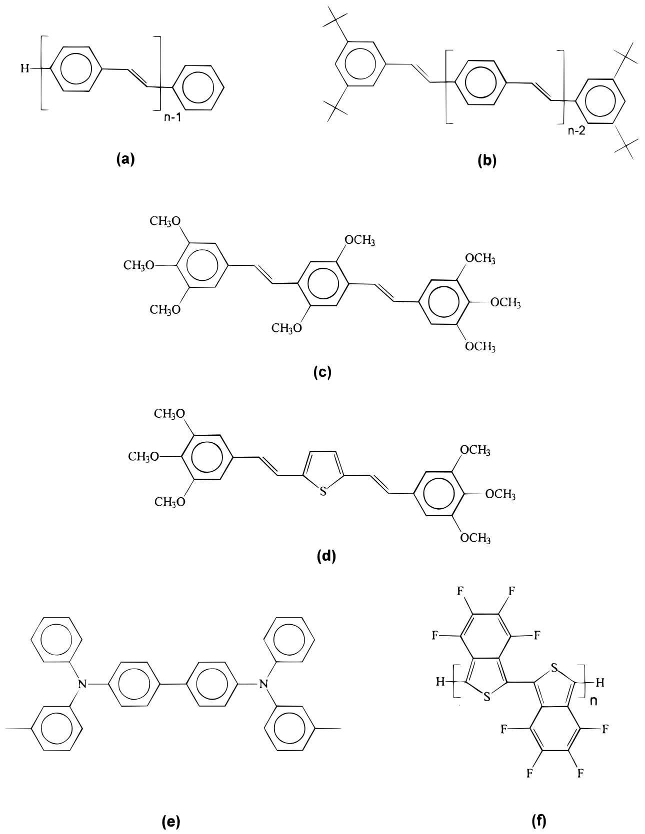

Figure 1. Chemical structure of the investigated compounds: (**a**) oligomers of poly(*p*-phenylenevinylene) (PPV); (**b**) PPV oligomers substituted by *tert*-butyl groups; (**c**) 2,5-dimethoxy-1,4-bis[(3,4,5-trimethoxyphenyl)-2-ethenyl]benzene; (**d**) 2,5-bis[2-(3,4,5-trimethoxyphenyl)ethenyl]thiophene; (**e**) 4,4′-bis(*m*-tolyphenylamino)biphenyl, TPD; and (**f**) oligomers of fluorinated polyisothianaphthene.

as hole-transporting material in emitting devices.[23] Thus, a tremendous number of theoretical and experimental studies have been undertaken in order to gain a good understanding of their electronic and optical properties. In this context, it is noteworthy that in recent years the study of conjugated oligomers has emerged as a powerful tool to shed light into the complex properties of the corresponding polymers.[24] Since the effective conjugation length is generally reduced in actual polymer samples due to the presence of chemical or physical defects along the backbone, the properties calculated for relatively long conjugated oligomers parallel those measured for the polymers.[13] Polyisothianaphthene (PITN) is a low-band-gap polymer; its main interest stems from the fact that in the oxidized state it becomes both electrically conducting and transparent in the visible region of the optical spectrum.[25,26] Replacing all the hydrogen atoms on the six-membered rings by fluorine atoms (Figure 1f) results in a polymer soluble in common organic solvents with enhanced stability in solution, even though the substitution slightly increases the band gap.[27]

Where possible, we have tested the AM1 and INDO UPS spectra versus the VEH data; in all cases, we have compared the results of the calculations to the experimental UPS spectra. One major criterion to assess the quality of the AM1 and INDO data has been the simulation of the low-energy part of the spectra, which is mostly made of π electronic states. Nevertheless, we have also examined the agreement at higher energy since the understanding of the σ electronic structure, which is responsible for the stability of the backbone, is also of importance. The origin of the spectral features appearing in the experimental data has been interpreted on the basis of the linear combination of atomic orbitals (LCAO) description of the molecular levels.

II. Theoretical Methodology

The geometries of the various compounds investigated in this study (see Figure 1) are optimized by means of the AM1 Hamiltonian;[28] the parametrization of this technique has been developed to best reproduce the geometry, heat of formation, and ionization potential of organic molecules in their ground state. When compared to experimental data and/or ab initio studies, the AM1 results have been shown to provide reliable geometries for PPV and derivatives[29] while slight discrepancies can be found for molecules with thiophene units.[30] Nevertheless, it is found that the simulations of UPS spectra are not markedly sensitive to small changes in geometric parameters; AM1 thus suffices for obtaining a reasonable optimized geometry. During the geometry optimization, we have assumed a planar conformation for the conjugated backbone when the experimental data relate to solid-state measurements; we have however given a full degree of freedom to the methoxy groups in compounds **c** and **d** in Figure 1, to limit the steric hindrance between adjacent substituents.

A rigorous simulation of UPS spectra would require assignment of each UPS feature to a molecular level at an energy corresponding to the difference between the total energy of the system in the neutral state and that of the system with an electron removed from the considered level, taking into account the possibility of shake-up phenomena (i.e., the possibility of electron−hole pair excitations simultaneous to the ionization process); however, such a many-body approach is time-consuming and certainly requires major expertise.[5] More simple simulations are thus carried out within Koopmans' theorem, thus neglecting correlation effects: peaks in the simulated spectra are then associated with the energies calculated for the one-electron

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levels in the neutral molecule. Here, the one-electron levels are calculated via the AM1 method and the INDO Hamiltonian as developed by Zerner[31] (with the electron interaction terms expressed via the Mataga−Nishimoto potential[32]), as well as the valence effective Hamiltonian (VEH) technique. No photoionization cross sections are included in the calculations; this results in the relative intensities of the calculated peaks being somewhat different from those observed in the experimental spectra.

Several systematic corrections have to be applied to the raw results provided by the three techniques:

First, it is customary to compress the energy scale of the calculated spectrum (starting from the HOMO level) to compensate for the relaxation and electron correlation effects neglected in Koopmans' approximation. Over the years, a compression factor of 1.3 has been found to best adapt for VEH data;[8] the same value is found to be applicable for the INDO data while no compression appears to be required when using the AM1 Hamiltonian: this illustrates the difference in the amount of correlation effects implicitly included in the parametrization of the two techniques. The compression ensures in many cases a remarkable description of the number and relative positions of the UPS peaks at low energies. Note, however, that the analysis of the high-energy part of the spectrum must be addressed with great caution in view of the drastic approximations used in our approach.

Second, when the measurements are taken on solid films, the calculated spectrum is shifted rigidly to lower energies to account for the shift from the gas phase, to which the calculations performed on single isolated molecules relate, to the solid state. The shift is made up of two contributions: (i) the difference in the energy reference (vacuum level in the gas phase versus Fermi energy in the solid state); and (ii) the stabilization of the photohole by the surrounding molecules or chains (solid-state polarization). The latter is on the order of 1.5−2.0 eV for organic molecular solids.[33] Note that the amplitude of the shift to be applied for a given compound depends on the nature of the semiempirical approach used: the ionization potential is found to be typically increased by ∼1 eV when going from INDO to AM1.

Finally, all the spectra are convoluted with Gaussian functions with a full width at half-maximum (fwhm) chosen to match the experimental width; the fwhm values vary between 0.3 and 1.4 eV.

III. Experimental Aspects

The phenylenevinylene oligomers (Figure 1, **a** ($n = 3$), **c**, and **d**) were synthesized in Antwerpen following a previously described procedure.[34] Thin films of those compounds were prepared in situ in ultrahigh vacuum by sublimation onto clean stainless steel substrates. The thin-film UPS spectra of these samples were recorded on the FLIPPER II beamline at the DESY synchrotron facility in Hamburg, with a photon energy of 32.0 eV. The fluorinated PITN polymer was synthesized in Durham.[27] The samples were prepared by spin-coating, onto optically flat silicon substrates, from solutions in chloroform. The valence band spectra of these samples were recorded at the synchrotron radiation laboratory, MAX-lab, in Lund, with a photon energy of 80 eV.

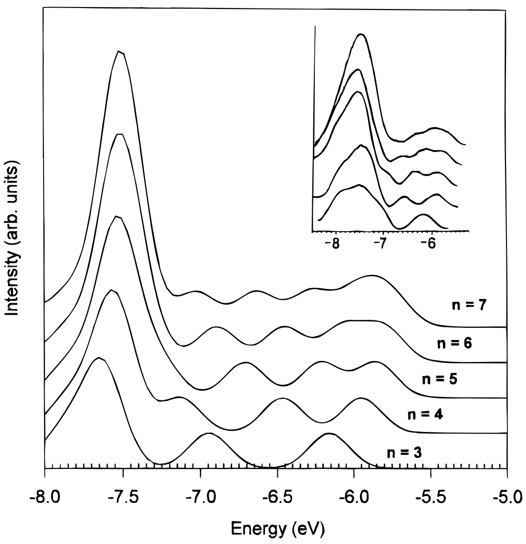

Figure 2. INDO-calculated UPS spectra of unsubstituted PPV oligomers containing from 3 to 7 phenylene rings (fwhm = 0.4 eV in all cases). The inset displays the experimental solid-state UPS spectra obtained for the same oligomers substituted by two *tert*-butyl groups on the terminal units, as extracted from ref 36. The energy scale is referenced to the vacuum level.

The He I gas-phase UPS of TPD was recorded using an instrument that features a 36 cm radius, 8 cm gap hemispherical analyzer (McPherson) and custom-designed excitation source, sample cells, and detection and control electronics that have been described in more detail previously.[35] TPD sublimed at 230−245 °C (10^{-4} Torr), which was monitored using a "K" type thermocouple, passed through a vacuum feedthrough and attached directly to the sample cell. The argon $^2P_{3/2}$ ionization at 15.759 eV was used as an internal calibration lock of the absolute ionization energy. The difference between the argon $^2P_{3/2}$ ionization and the methyl iodide $^2E_{1/2}$ ionization at 9.538 eV was used to calibrate the ionization energy scale. During data collection the instrument resolution (measured using fwhm of the argon $^2P_{3/2}$ peak) was 0.030−0.040 eV. All data are intensity corrected with an experimentally determined instrument analyzer sensitivity function. The He I spectrum was also corrected for He Iβ resonance line emission from the source, which is about 3% the intensity of the He Iα line emission and at 1.869 eV higher photon energy. Ionization peak positions are reproducible to ±0.02 eV.

IV. Results and Discussion

IV.a. Phenylenevinylene Oligomers. To validate the use of the INDO Hamiltonian, we report in Figure 2 the INDO-simulated UPS spectra of unsubstituted PPV oligomers containing from 3 to 7 phenylene rings, together with corresponding experimental measurements extracted from ref 36. Note that the solid-state experimental data refer to PPV oligomers substituted by two *tert*-butyl groups on each terminal ring.[36] A detailed analysis of the spectra reveals the close cor-

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respondence between the theoretical and experimental line shapes.

First, there is an intense peak at ca. −7.5 eV that grows in intensity as the chain length is increased and consistently appears around the same energy. This peak is the signature of the occupied localized π-molecular orbitals of PPV chains. The wave functions corresponding to such levels are characterized by the presence of nodes on the para carbon atoms of the phenylene rings;[37] this pattern prevents any significant electronic interaction from taking place between the rings. The levels localized on the individual rings are thus quasi-degenerate, which explains the absence of any significant energy shift for this peak as the chain grows. These localized levels contribute to the description of the optical transitions observed at high energy in the absorption spectra of PPV and derivatives;[37−39] recent calculations have also shown that they play a key role in determining the line shape of the photocurrent action spectra.[40]

The theoretical and experimental spectra also display a few peaks at lower binding energies, whose number and position vary as a function of chain length. This indicates that these peaks are affected by the extent of conjugation and thus originate from delocalized π-levels that have significant contributions from all carbon atoms of the phenylene rings. At the scale of an infinite chain, these levels give rise to the formation of a wide valence band extending over the narrow band arising from the localized molecular orbitals.[8b] The peak with the lowest binding energy corresponds to the HOMO (highest occupied molecular orbital) level and is progressively shifted to lower binding energies as the chain length is increased. This evolution is consistent with experimental data showing a linear relationship between ionization potential and inverse chain length, as reported for instance for PPV,[36] polythiophene,[41] and polythienylenevinylene[42] oligomers.

The global shape of the experimental UPS spectra at low energies is nicely reproduced by the calculations; note, however, that the calculations deal with unsubstituted PPV oligomers while the spectra have been obtained on derivatives carrying two *tert*-butyl groups on the external rings (see Figure 1b). Accordingly, we have investigated the possible influence of such substituents on the relative positions of the highest occupied π-levels; the results are displayed in Figure 3 in the case of the three-ring PPV oligomer. The modifications induced in the UPS spectrum upon substitution mostly result from the loss of degeneracy of the three localized levels of the unsubstituted oligomer: the two localized levels having significant weight on the external substituted rings (HOMO minus 2 and HOMO minus 3, denoted H-2 and H-3 in Figure 3) are indeed shifted to lower binding energies while the third level localized on the central ring (H-4) is only weakly affected. This explains the increase in intensity calculated around −7.0 eV when going from the unsubstituted to the substituted trimer in Figure 3. The calculated line shape for the *tert*-butyl derivative is in remarkable agreement with the corresponding experimental spectrum (lower curve in the inset of Figure 2). We stress that energy shifts are also observed for delocalized levels presenting a high electronic density on the substituted carbon atoms of the phenylene rings, such as the H-5 level contributing to the UPS peak around −7.5 eV in the substituted oligomer. This emphasizes that an explicit account of the full chemical structure is required to provide the best match between the experimental and theoretical line shape of the UPS spectra.

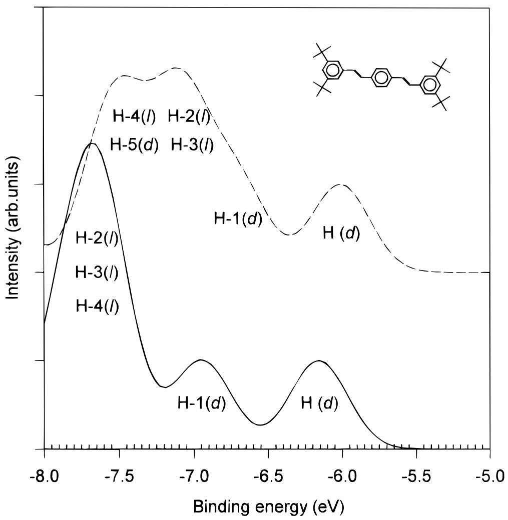

Figure 3. INDO-simulated UPS spectrum of the unsubstituted three-ring PPV oligomer (solid line), compared to that of the same oligomer substituted by two *tert*-butyl groups on the terminal rings (dashed line), whose chemical structure is shown in the upper right corner (fwhm = 0.6 eV in both cases). We also indicate the localized (l) versus delocalized (d) character of the highest occupied levels giving rise to the UPS peaks at the lowest binding energies (H refers to the HOMO level). The energy scale is referenced to the vacuum level.

To compare the reliability of the INDO and AM1 methods, we display in Figure 4 the calculated UPS spectra of the three-ring unsubstituted PPV oligomer together with the VEH-calculated spectrum and the solid-state experimental UPS spectrum. The results illustrate that the two semiempirical techniques (as well as VEH) reproduce very well the intensity and relative positions of the UPS peaks in the low binding energy part of the experimental spectrum, i.e., above −9.0 eV; a suitable description of the delocalized versus localized π-levels is thus provided by the three different levels of theory we have considered. In contrast, significant changes in the shape of the calculated spectra are observed at higher binding energies, where the σ levels start contributing to the spectra. The broad band extending from −10.0 to −12.0 eV in the experimental spectrum is reproduced in VEH by a pair of peaks located at −10.0 and −11.2 eV while AM1 and INDO give a single broader peak around −10.5 eV. We also note that only VEH shows an intense peak in close correspondence with the experimental band around −13.0 eV. In terms of comparison with the high binding

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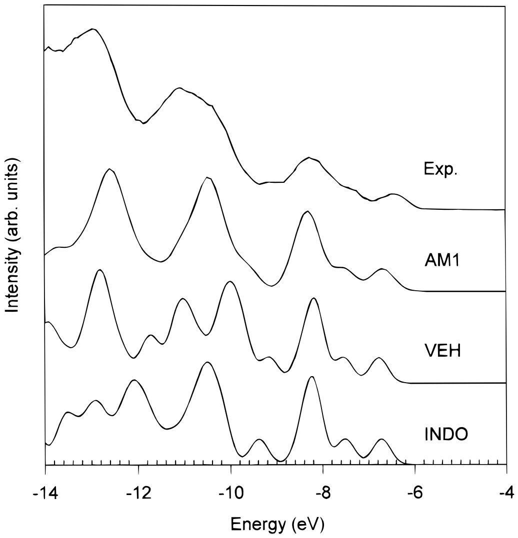

Figure 4. Simulated UPS spectra of the three-ring unsubstituted PPV oligomer simulated with the AM1, INDO, and VEH approaches (fwhm = 0.6 eV in all cases), compared to the solid-state experimental spectrum. The energy scale is referenced to the vacuum level.

energy region of the experimental UPS spectrum, VEH appears to perform best; the agreement of the other two techniques is nevertheless quite reasonable.

IV.b. Methoxy-Substituted Compounds. The study of PPV chains substituted by π-donor and/or π-acceptor groups has also attracted considerable attention in recent years. This is motivated by the fact that the positions of the threshold of the valence and conduction bands can be significantly modulated by the grafting of electroactive π-moieties along the backbone.[10,43] Such substitutions can help in balancing the efficiency of charge injection at the electrodes and lead to changes in the color of the luminescence of the conjugated chains. The use of PPV derivatives has allowed for the fabrication of highly efficient double-layer LEDs optimizing the injection processes at the metal/polymer interfaces and the quantum yield of luminescence.[44] In this context, we have extended the validation of the INDO and AM1 techniques by comparing the UPS spectra calculated for two PPV derivatives to the corresponding experimental data. The first one is a three-ring PPV oligomer substituted by methoxy groups, 2,5-dimethoxy-1,4-bis[(3,4,5-trimethoxyphenyl)-2-ethenyl]benzene (Figure 1c); alkoxy substitution is widely used to increase the solubility and modulate the electronic and optical properties of conjugated chains. Further tuning can be achieved by building mixed systems[45] containing for instance thiophene, vinylene, and phenylene units, such as in the second test compound, 2,5-bis[2-(3,4,5-trimethoxyphenyl)]thiophene (Figure 1d); this molecule is a good candidate for the fabrication of blue LEDs[46] and for use in sensors.[47]

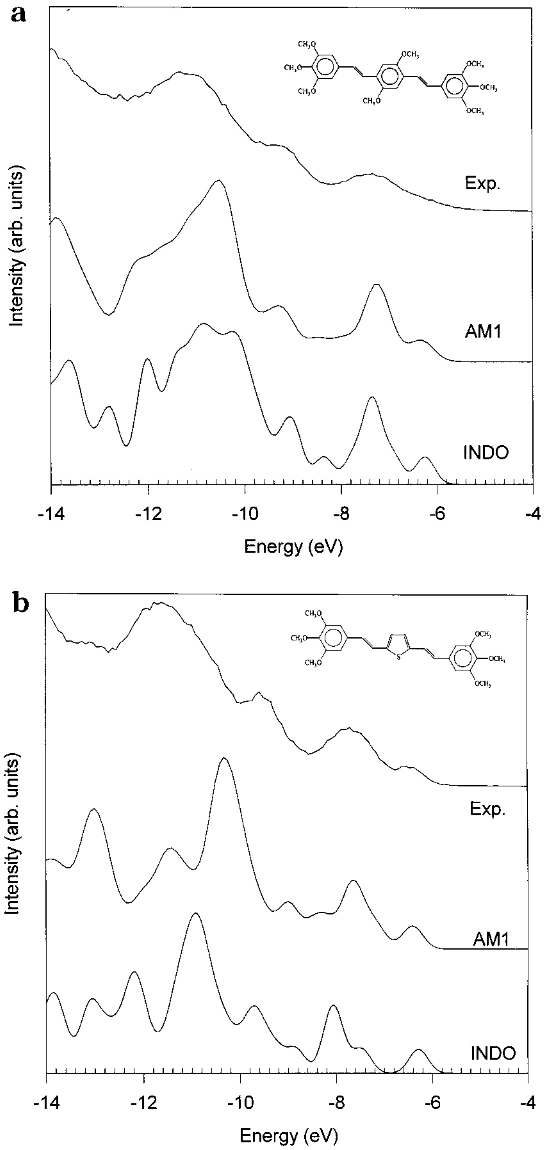

Figure 5. UPS spectra of compounds **1c** (a) and **1d** (b) simulated with the AM1 and INDO Hamiltonians (fwhm = 0.6 eV in both cases), compared to the experimental spectra. The energy scale is referenced to the vacuum level.

Both the AM1 and INDO calculations indicate that the HOMO level is destabilized by 0.16 eV in going from the three-ring unsubstituted PPV oligomer to the methoxy-substituted derivative shown in Figure 1c. AM1 shows no change in the energy of the HOMO when going from PPV3 to the thiophene-based derivative whereas a stabilization of 0.34 eV is obtained with INDO. As found previously, we observe for both compounds that the low binding energy part of the spectrum is described in a very similar way by the two approaches while significant deviations occur for the peaks at higher binding energy. The agreement of the two theoretical curves with the experimental spectrum appears similar for the methoxy-substituted derivative (Figure 5a); for the thiophene-containing compound, the INDO calculation better reproduces the shape of the broad band around −11 eV (Figure 5b).

When going from the unsubstituted three-ring PPV oligomer to the methoxy-substituted derivative (Figure 1c), we observe a lift of degeneracy of the three localized π-levels upon substitution due to mesomeric effects

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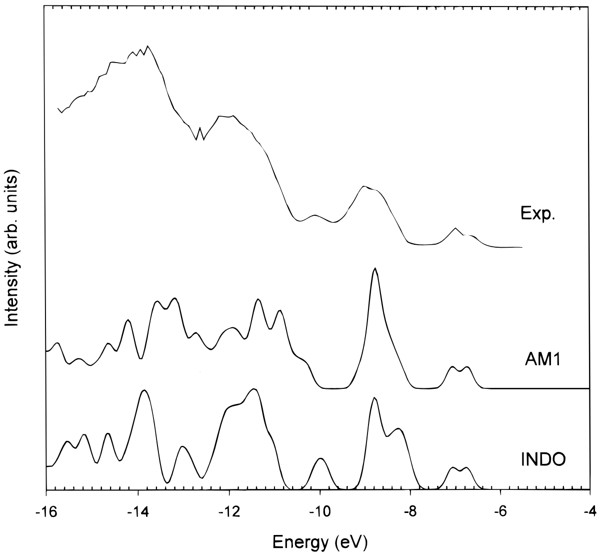

Figure 6. UPS spectra of TPD simulated with the AM1 and INDO approaches (fwhm = 0.3 eV in both cases) together with the corresponding gas-phase experimental spectrum. The energy scale is referenced to the vacuum level.

induced by the oxygen atoms:[37] two of them are shifted by 0.6 eV to lower binding energy with respect to the unsubstituted chain while the third level is stabilized by 3.6 eV. This explains the apparent shift of the localized π-band observed in the experimental spectra. The significant changes observed in the high binding energy part of the spectrum result from the interaction of the atomic orbitals of the oxygen atoms with the π-levels of the unsubstituted chain. In the thiophene-based compound, the UPS feature around −8.0 eV is associated with the HOMO-2 and HOMO-3 levels that possess significant LCAO weight only on the phenylene moieties; this explains why this peak is at the same energy as that of the localized levels in the unsubstituted oligomer. Note that the HOMO-4 level, which is delocalized over the whole molecule, also contributes to the peak at −8.0 eV.

IV.c. 4,4′-Bis(*m*-tolyphenylamino)biphenyl, TPD. The reliability of the INDO and AM1 approaches for compounds containing nitrogen atoms is illustrated in Figure 6 where we have collected the experimental *gas-phase* UPS spectrum of TPD together with the corresponding theoretical simulations. We observe again a remarkable agreement between the experimental and theoretical line shapes in the low binding energy part of the spectra. This allows us to assign the doublet feature around −7.0 eV to the signature of the HOMO and HOMO-1 levels. Interestingly, the INDO-calculated ionization potential of TPD (6.74 eV) matches remarkably well the experimental value (6.69 eV) while the AM1 value (7.73 eV) is overestimated by ~1 eV. As noticed previously, significant deviations between the shapes of the theoretical and experimental curves emerge in the high binding energy part of the spectra (below −10 eV); here, INDO clearly provides the best fit, in particular for the weak feature detected at −10 eV and the shape of the band centered at −11.5 eV. A detailed characterization of the electronic structure of TPD and derivatives will be provided in a forthcoming paper.

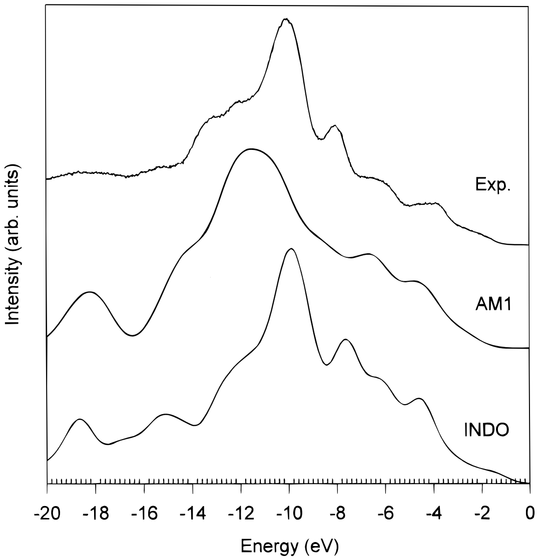

Figure 7. UPS spectra of the hexamer of fluorinated isothianaphthene simulated with the AM1 and INDO approaches (fwhm = 1.4 eV in both cases). We present on top the solid-state experimental spectrum obtained for the corresponding polymer. The energy scale is referenced to the Fermi level.

IV.d. Fluorinated Polyisothianaphthene. The above results have established that, when compared to experimental data, the semiempirical Hartree−Fock INDO and AM1 techniques behave very well. It is now of interest to determine whether this reliability holds true for compounds containing chemical elements not parametrized in the VEH technique, such as fluorine atoms. Figure 7 displays the UPS spectra calculated for the hexamer of fluorinated isothianaphthene ($n = 3$ in Figure 1f) together with the experimental data obtained for the corresponding polymer. We observe that the intensity and energy of the numerous features observed in the highly resolved experimental spectrum are remarkably well-reproduced by the INDO calculation; this excellent agreement further demonstrates the suitability of the oligomer approach. As noted before, the AM1 approach yields a less good though reasonable agreement with the experimental line shape.

On the basis of the INDO results, we can interpret the full experimental spectrum as follows: starting from the low binding energy end of the spectrum, the broad, low-intensity feature extending from −3.0 to −1.0 eV corresponds to the upper five π molecular orbitals of the hexamer. These levels are made only of carbon contributions; they are fully delocalized along the conjugated backbone and extend both on the phenylene and thiophene rings of all monomer units. This first feature is the signature of the delocalized π levels mostly responsible for the electronic properties.

The band located around −4.0 eV is also of π character, with both carbon and sulfur contributions; the corresponding levels tend to be more localized than the states closer to the Fermi level, i.e., their wave functions do not possess coefficients on all atoms of the backbone, and/or they have nodes on the carbons connecting the rings. The nature of the lowest two UPS bands in polyisothianaphthene is thus reminiscent of that observed in aromatic-based conjugated chains, such as polythiophene, PPV, and poly-*p*-phenylene.[37−39]

The upper σ states appear at −5.8 eV, with strong S 3p coefficients and minor C 2p and F 2p contributions. The broad band centered around −6.0 eV is built from localized π states with marked sulfur character. On its high binding energy side, it also contains σ states with mostly sulfur contributions; this band can thus be considered as the signature of the sulfur lone pairs. A group of σ molecular orbitals of mixed origin (C 2p, S 3p, F 2p) is responsible for the peak located at −8.0 eV; a few π states delocalized on carbon, sulfur, and fluorine atoms are found around −8.5 eV. They do not produce a clear feature in the spectrum but contribute to filling the valley between the surrounding peaks.

The peak dominating the UPS spectrum at −10.0 eV corresponds to a large group of levels (about 30 molecular orbitals in the hexamer) of almost pure F 2p character; these are the fluorine lone pairs. Because the corresponding wave functions do not possess contributions on the carbon atoms, the fluorine atoms are essentially isolated from each other. As a result, there is no dispersion of these levels; they all appear close in energy, giving rise to a very intense peak. The broad shoulder on the high binding energy side of the peak is built from two types of contributions: (i) around −11.0 eV, a group of π states localized on the fluorine atoms and the adjacent carbon atoms; (ii) from −11.0 to −12.5 eV, σ states with significant S 3s, C 2p, and F 2p coefficients.

The first molecular orbitals containing C 2s contributions appear at −13.5 eV. The weak feature located near −15 eV in the experimental spectrum, which is represented by a small band in the INDO-calculated curve, corresponds to σ levels of mixed character while the states involving the terminal hydrogen atoms are located in the energy range between −15.5 and −16.5 eV. Accordingly, the experimental spectrum taken on the polymer shows very little intensity there. Finally, below −17.0 eV, the molecular orbitals are dominated by C 2s contributions, along with minor F 2s coefficients. The deepest observable spectral band, extending from −17 to −19 eV, contains both localized and delocalized, skeleton-like C 2s states, below and above −18 eV, respectively.

V. Synopsis

We have found that simulated UPS spectra of conjugated systems, obtained with the AM1 and INDO semiempirical Hartree−Fock methods, are in good agreement with the corresponding experimental data. These two techniques perform as reliably as the well-established VEH method for the simulation of the low-energy part of the spectrum, which contains most of the π electronic levels. This allows for a detailed interpretation of the one-electron structure in the low binding energy range for unsubstituted and substituted conjugated compounds. INDO is also found to reproduce accurately the major features of the inner part of the UPS spectra, which contains information on the σ backbone.

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