Valence effective Hamiltonian study of the electronic structure of poly(p phenylene) and poly(pphenylene sulfide)

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Valence effective Hamiltonian study of the electronic structure of poly(*p*-phenylene) and poly(*p*-phenylene sulfide)

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The parametrization of atomic potentials for sulfur is presented in the framework of the valence effective Hamiltonian (VEH) technique for polymers. The VEH method is applied to band structure and density of states calculations on poly(*p*-phenylene) and poly(*p*-phenylene sulfide), compounds of interest with regard to the conducting polymers area. The quality of the electronic structure description afforded by the VEH technique is demonstrated via a comparison of experimental XPS spectra for these polymers with spectra predicted theoretically. The ionization potential of poly(*p*-phenylene sulfide) is predicted to be 0.7 eV higher than poly(*p*-phenylene) in good agreement with experimental estimates.

I. INTRODUCTION

The discovery that polyacetylene can be doped with electron donors or electron acceptors to yield highly conducting derivatives[1] has resulted in a great deal of interest in doped polymer systems and their potential for commercial application as replacements for semiconductors or metals. This interest has been heightened by the subsequent discovery of additional conducting polymer systems, based on polypyrole,[2] poly(*p*-phenylene),[3] and poly(*p*-phenylene sulfide).[4]

Many fundamental aspects of the electronic and structural properties of conducting polymers are still not well established. A reason for this is that doped conjugated polymers represent rather complicated systems whose properties are expected to be affected by factors such as disorder, low dimensionality of electronic motion, and strong electron–phonon coupling.[5,6] Recently, however, a rather inexpensive quantum chemical method for polymeric systems has been developed based on the use of valence effective Hamiltonians (VEH).[7] We have demonstrated through calculations on a number of hydrocarbon polymers[7,8] that the VEH technique can help in explaining experimental results gathered through efforts to dope these polymers with electron accepting agents. The polymer VEH technique not only affords *ab initio* double zeta quality results for band structures and densities of states[7], but perhaps more important with regard to the conducting polymers area, provides reliable relative ionization potentials and bandwidths. These parameters are of prime importance for the acceptor doping process. The ionization potential determines whether a particular acceptor is capable of ionizing or partly ionizing the polymer. The bandwidth of the highest occupied band provides a measure of the extent of delocalization in the system and can be roughly correlated with the mobilities of the charge carriers in that band. We have found a qualitative correlation in hydrocarbon polymers between the widths of the highest occupied bands and the conductivities achieved upon doping.[8]

Hence, in this paper, we would like to extend the applicability of the VEH technique to sulfur containing compounds, a process which requires the parametrization of sulfur atomic potentials. A number of sulfur containing polymers are now known that can be successfully doped to conductivity levels of the order of 0.1 S/cm. These systems include polythiophene[9] and poly(phenylene chalcogenides) compounds[10] such as poly(*p*-phenylene sulfide), poly(*m*-phenylene sulfide), poly(dibenzothiophene sulfide), and poly(benzothiophene). Polymers such as poly(*p*-phenylene sulfide) PPS are especially interesting because of their processibility (at least in the virgin state), an important consideration for many potential commercial applications.

This paper is structured as follows. In Sec. II, we briefly describe the general principles of the valence effective Hamiltonian technique and the determination of atomic potentials for sulfur, as obtained from calculations on model molecules including dimethylsulfide and thiophene. In Sec. III, we present detailed calculations on two systems of prime interest in the conducting polymers area, poly (*p*-phenylene sulfide), a sulfur containing polymer, and poly (*p*-phenylene) PPP, a hydrocarbon system. As well resolved XPS data are available on both systems,[11,12] this enables us to (i) test the applicability of the VEH technique to sulfur compounds, (ii) compare the quality of the theoretical

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descriptions for hydrocarbon and for sulfur containing systems, and (iii) discuss in detail the comparison of the electronic properties of PPS and PPP.

II. ATOMIC POTENTIALS FOR SULFUR CONTAINING SYSTEMS

The complete methodology for obtaining molecular one-electron effective Hamiltonians from first principles has been developed in Ref. 13. The effective Fock Hamiltonian of a molecule is taken to be the sum of the kinetic energy and of the various atomic potentials in the molecule

$$F_{eff} = - \frac{\Delta}{2} + \sum_A V_A , \qquad (1)$$

where V_A is the effective potential of atom A. For computational reasons, simple nonlocal atomic potentials are chosen,

$$V_A = \sum_l \sum_m \sum_{i,j} C^A_{ij,lm} |\chi^A_{ilm}\rangle \langle \chi^A_{jlm}| , \qquad (2)$$

where the summations over l and m define the angular dependence of V_A. The numerical coefficients $C_{ij,lm}$ are independent of m in the case of spherical symmetry, which we consider throughout this paper. The χ_{ilm} terms are normalized Gaussian functions of the form

$$\chi_{ilm} = N_i r^l \exp[- \alpha_i r^2] Y_{lm} (\theta, \phi) , \qquad (3)$$

where N_i is the normalization factor and $Y_{lm} (\theta, \phi)$ indicates the usual spherical harmonics. Only $1s$ and $2p$ Gaussian Cartesian functions are used.

For hydrogen and carbon, universal atomic potentials for the whole series of the hydrocarbon compounds have been previously determined[7] according to the technique described in Ref. 13. These potentials are used in the present work when the hydrogen and carbon atoms are bonded to a carbon atom. New parametrizations have been carried out for the sulfur atoms and the carbon atoms bonded to sulfur atoms. In the polymers of interest, sulfur atoms are bonded either to sp^2 or sp^3 carbon atoms. Consequently, dimethyl sulfide and thiophene have been chosen as the simplest model molecules.

In a first step, valence SCF calculations are performed for the model molecules by a theoretical pseudopotential method[14] with first a STO-3G minimal basis set of Slater orbitals[15] and then a double zeta basis set.[16] The experimental geometries are taken from Ref. 17. For each molecule, the Fock operator is

$$F = \sum_v \epsilon_v |\phi_v\rangle \langle \phi_v| , \qquad (4)$$

where the summation is over all occupied levels. F is constructed with the valence orbitals ϕ_v determined from the STO-3G minimal basis set, whereas the corresponding energies ϵ_v are those obtained from the double zeta basis set. The choice of the above theoretical Fock operator leads to valence effective Hamiltonians [Eq. (1)], which provide monoelectronic energies of double zeta accuracy when solved within a STO-3G basis set. Some information is lost for the wave func-

TABLE I. Parameters of atomic effective potentials for S atoms and C atoms bonded to S.

Atom	l	m	i	j	α_i	$C_{ij,lm}$
S	0	0	1	1	1.00	3.683
			2	2	0.30	1.521
			1	2		-3.454
	1	-1,0,+1	1	1	0.90	-1.899
			2	2	0.20	-0.047
			1	2		-0.017
C(bonded to S)	0	0	1	1	3.63	-6.506
			2	2	0.33	-0.514
			1	2		0.354
	1	-1,0,+1	1	1	6.50	-12.380
			2	2	0.52	-0.474
			1	2		-0.069

tions, but this is of little consequence for, e.g., the comparison of calculated one-electron energies with the corresponding data from XPS experiments.

In a second step, parametrization of atomic potentials for sulfur and carbon bonded to sulfur is determined by minimizing the quantity

$$(F - F_{eff}|F - F_{eff})_{dimethyl\ sulfide}$$
$$+ (F - F_{eff}|F - F_{eff})_{thiophene} . \qquad (5)$$

In Eq. (5), $(F - F_{eff}|F - F_{eff})$ denotes the scalar product of $F - F_{eff}$ with itself in the subspace of the occupied valence orbitals. The linear coefficients $C_{ij,lm}$ of V_A in Eq. (2) are obtained by solving a linear system of equations with the Fourier techniques developed in Ref. 13; the determination of the nonlinear α_i exponents of the Gaussian functions of Eq. (3) requires the direct minimization of the quantity defined by Eq. (5). Parameters of potentials V_S and V_{C-S}, respectively, for sulfur atoms and carbon atoms bonded to sulfur are given in Table I. It must be stressed again that these potentials do not contain any experimental data and that they have been completely determined from first principles. Table II compares the VEH and the double zeta SCF orbital energies on the two model molecules. The agreement is quite good, the standard deviation being on the order of 0.02 a.u. The highest occupied levels are especially well reproduced for the two model molecules—a result which suggests the accurate determination of relative ionization potentials in a series of similar polymers.

Note that no information pertaining to the excited states is included in the atomic potentials. This could in principle be done, as has been demonstrated in Ref. 13, but would not be very useful in the framework of the Hartree–Fock Hamiltonian, since Hartree–Fock excited states are known to bear little meaning. As a result, no special attention is, in principle, to be given to the unoccupied levels. However, for the planar hydrocarbon systems considered previously, surprisingly good agreement between experiment and theory was obtained for the lowest energy optical transition (band gap).[8]

The above atomic potentials allow band structure cal-

TABLE II. Valence molecular one-electron energies (a.u.). Comparison of VEH and double zeta SCF calculations.

| | Dimethylsulfide | | Thiophene | |
	Effective Hamiltonian	SCF	Effective Hamiltonian	SCF
	−0.346	−0.348	−0.341 π	−0.334 π
	−0.455	−0.440	−0.345 π	−0.353 π
	−0.489	−0.461	−0.461	−0.469
	−0.570	−0.557	−0.527	−0.527
	−0.600	−0.580	−0.496 π	−0.530 π
	−0.616	−0.617	−0.523	−0.559
	−0.617	−0.623	−0.567	−0.588
	−0.825	−0.821	−0.695	−0.706
	−0.971	−0.946	−0.746	−0.757
	−1.103	−1.101	−0.792	−0.773
			−0.958	−0.998
			−0.996	−1.003
			−1.235	−1.199
$\bar{x}^a$	−0.010		+0.009	
σ_x^b	0.011		0.021	

[a]Mean error in the valence molecular orbital energies (a.u.).
[b]Standard deviation of the error (a.u.).

culations on a large series of hydrocarbon polymers and sulfur derivatives. It must be noted that more accurate potentials can be determined within our methodology. For example, we have derived effective potentials for sulfur and all the carbon atoms in thiophene and dimethyl sulfide model molecules. These potentials lead to improved agreement with the SCF calculations presented in Table II, especially for thiophene. However, with a such parametrization, we lose the usefulness of an unique potential for a carbon atom bonded to any other type of carbon atom.[7] Therefore, we prefer to keep more transferable potentials as presented in this work.

Since a complete description of the VEH technique for polymers has been previously given,[7,18] we do not repeat it here. However, it should be stressed that the VEH method, while providing ab initio double zeta quality results, remains quite inexpensive due to the evaluation of only one-electron integrals and the complete avoiding of SCF iterative cycles.

III. APPLICATION TO POLY (p-PHENYLENE) AND POLY (p-PHENYLENE) SULFIDE

Poly(p-phenylene) PPP and poly (p-phenylene sulfide) PPS are of prime interest in the conducting polymers area. PPP can be doped with strong electron acceptors such as AsF_5 and SbF_5 to yield complexes with conductivities as high as 500 S/cm.[3] Only doped polyacetylene provides a higher conductivity (~1000 S/cm). Though doped PPS has lower conductivity (~1 S/cm) it is especially significant, since it represents the first conducting system containing a polymer which is processible by conventional polymer techniques.[4,10]

Only semiempirical calculations have so far been reported on PPP and PPS. Extended Huckel calculations

on PPP[19,20] and CNDO/S3 calculations on large PPP and PPS oligomers.[21] We report here the first band structure calculations on both polymeric chains of ab initio quality. The ionization potential and valence bandwidth results have been reported previously for PPP along with a large collection of other hydrocarbon polymers.[8] The structures of PPP and PPS are displayed in Fig. 1.

A. Poly (p-phenylene)

Poly(p-phenylene) is usually prepared by oxidative cationic polymerization of benzene,[22] a process which yields a brown powder of very high stability. X-ray diffraction data on p-phenylene oligomers strongly suggest that adjacent phenyl rings in PPP are rotated by some 23° with respect to one another.[23] This corresponds to a compromise between the effects of conjugation and crystal packing energy, which favor a planar structure, and the steric repulsion between ortho hydrogen atoms, which favors a nonplanar structure.

The bond lengths and bond angles we have used have been taken from averaged x-ray data on p-quaterphenyl.[23] Bond lengths within the rings are averaged to 1.406 Å, bond lengths between the rings to 1.502 Å and bond angles to 120°. The torsion angle is set at 22.7°. The translational unit cell, considered in the band structure calculations, corresponds to $(C_6H_4)_2$.

The VEH band structure is presented in Fig. 2, along with the density of states computed from the band structure by the method due to Delhalle.[24] Because of the glide plane running along the chain axis in the translational unit cell, the bands are degenerate two by two at the end of the Brillouin zone. The VEH band structure is in general agreement with the published semiempirical band structures.[19,20] Table III collects the absolute positions and widths of the upper bands.

Because the band structure for the 22.7° rotated polymer is very similar to the band structure for the coplanar system, we will use, by extension, σ and π band terminology. Taking into account the glide plane symmetry, we can identify three π bands. The lowest occupied π band, (band 11–11′) 1.6 eV wide, corresponds as usual to the π wave function with no nodes. The next π band (band 14–14′) is very flat because by
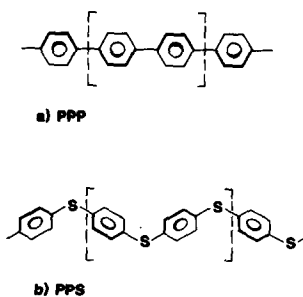

a) PPP

b) PPS

FIG. 1. Structure of a polymeric chain of: (a) poly(p-phenylene), PPP; unit cell: $(C_6H_4)_2$: (b) poly(p-phenylene sulfide), PPS; unit-cell: $[C_6H_4-S]_2$. The torsional angle for PPP is ~23°; for PPS it is almost 90°.
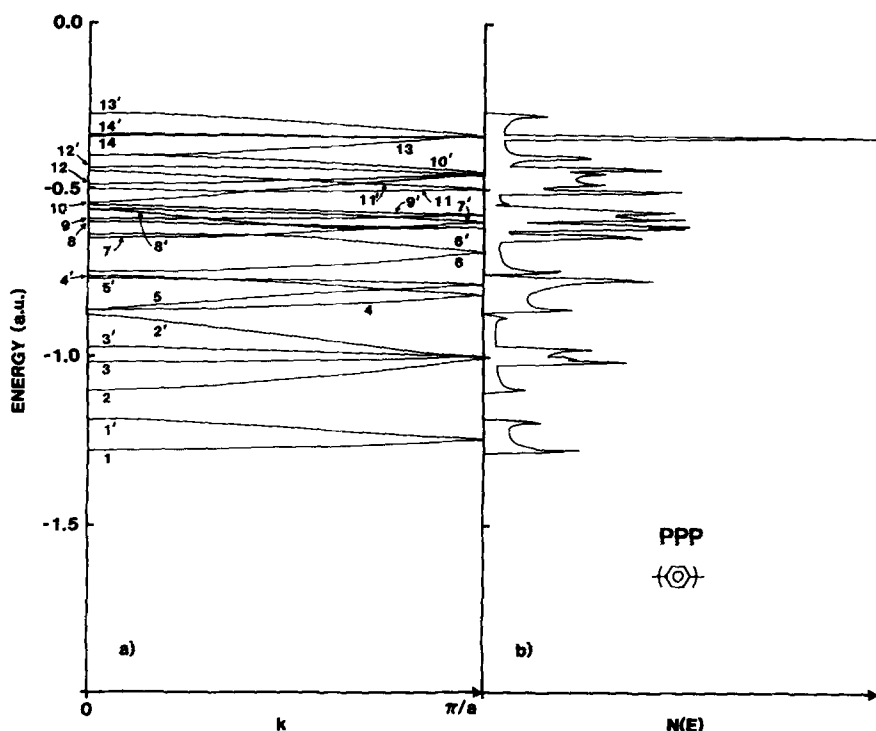
FIG. 2. Poly(p-phenylene) VEH calculations: (a) band structure (with band labels) for a $[C_6H_4]_2$ unit cell; (b) density of states.

symmetry it has almost no contribution from the $2p_z$ orbitals on the carbon atoms connecting the rings. The highest occupied π band (band 13–13'), likely the most important with respect to the conduction mechanism, has a large width of the order of 3.5 eV. This suggests an important delocalization along the backbone and is qualitatively consistent with the high conductivities achieved upon doping of PPP.

Applying Koopmans' theorem, the calculated ionization potential (I.P.) is 7.5 eV. As we have shown on previous VEH calculations,[8] by scaling the theoretical I.P. value downward by 1.9 eV (to correct approximately for polarization energy and possible shortcomings of the model), we obtain a very good fit with experimental I.P. data on hydrocarbon polymers. (Note that experimentally determined polarization energies for a wide range of hydrocarbon materials have recently been reported as 1.7 ± 0.4 eV[25].) The same is true for PPP as the corrected I.P. value is 5.6 eV, close to the 5.5 eV experimental estimate.[26] This I.P. value, 0.8 eV larger than polyacetylene, is consistent with the fact that only strong acceptors, such as AsF_5, effectively dope PPP.

Although no specific information pertaining to the excited states has been included in the VEH model, we previously observed on a number of hydrocarbon polymers that the $\pi \rightarrow \pi^*$ transition is quite accurately computed.[8] The bandgap ($\pi \rightarrow \pi^*$) value we obtain for 22.7° twisted PPP is 3.5 eV, in very good agreement with the experimental estimate of 3.4 eV.[26] This wide bandgap explains the low intrinsic conductivity of PPP, smaller than 10^{-15} S/cm at room temperature.[3]

The XPS theoretical spectrum of PPP is displayed in Fig. 3 along with the experimental spectrum due to

Riga et al.[11] The theoretical spectrum is computed from the density of states (DOS) following the method due to Delhalle.[27] In this method, the DOS curves are corrected for the photoionization cross-section factors according to Gelius' model[28] and convoluted by a Gaussian function whose halfwidth is chosen in order to take into account the resolution of the spectrometer. For solid state spectra, the halfwidth is usually taken as 0.7 eV. This method has given excellent results in previous instances and provides an elegant way of interpreting the experimental XPS data.[29–31] The experimental peak positions presented in Fig. 3 have been rescaled (multiplied by a factor of 1.3, the same as the factor we used previously

TABLE III. VEH absolute positions (in a.u.) and widths (in eV) of the five upper bands of poly(p-phenylene). Bandwidths are given for the smallest possible unit cell taking all symmetry elements into account, i.e., (C_6H_4).

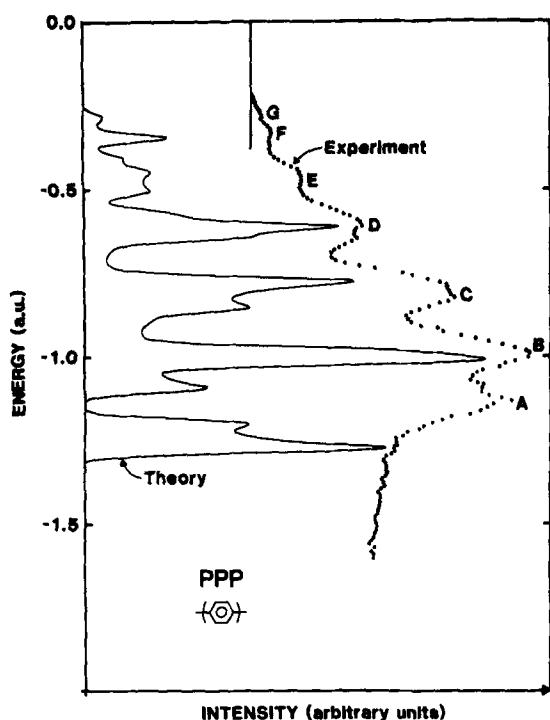| Band	Absolute Positions		Widths
	$k = 0$	$k = \pi/a$	
10	−0.546	−0.450	>3.92
10'	−0.402	−0.450	
11 (π)	−0.506	−0.497	>1.63
11' (π)	−0.449	−0.497	
12	−0.488	−0.453	>1.41
12'	−0.438	−0.453	
13 (π)	−0.404	−0.336	>3.45
13' (π)	−0.277	−0.336	
14 (π)	−0.344	−0.342	>0.11
14' (π)	−0.340	−0.342	

FIG. 3. Comparison of XPS spectra for poly(p-phenylene). Solid line: VEH theoretical spectrum; Data points: experimental spectrum from Ref. 11, rescaled (multiplied by a factor 1.3) on the energy axis.

for all-*trans* polyacetylene[7]) in order to get a better fit on the energy axis. Note that the cross section of a carbon $2p$ electron is ~13 times smaller than for a carbon $2s$ electron.[28] As a result, the bottom of the valence band is enhanced and the π bands are almost completely smeared out in the XPS spectrum.

The agreement of the theoretical spectrum with the experimental data is very good. Relative peak positions and intensities for the experimental data are reproduced quite well in the theoretical spectrum. The only exception comes in regard to the position of the peak corresponding to the bottom of the valence band. The latter is usually located at too low an energy in a VEH calculation.[7]

The assignment of the XPS peaks is straightforward (and can be easily visualized by superimposing the band structure and the density of states on the XPS spectrum). Peak A comes from band 1–1', a σ band of mainly C-$2s$ character. Peak B is due to σ (C-$2s$) band 3–3' and to a lesser extent to σ band 2–2'. The high intensity of peak B stems from the flatness of band 3–3' which is due to the very small contributions to that band from the $2s$ orbitals on the carbon atoms connecting the rings. Peaks C and D originate respectively from σ bands 4–4' and 5–5', and σ bands 7–7', 8–8' and 9–9'. The plateau corresponding to peak E arises not only from the lowest π band 11–11', but also from the σ bands 10–10' and 12–12'. Peak F comes from the flat π band 14–14' and peak G from the top of the highest occupied π band 13–13'. Hence, the narrowness of peak G is not inconsistent with a ~3 eV wide highest occupied

band, because it does not correspond to the full bandwidth.

From the good agreement between the theoretical and experimental XPS, IP, and bandgap data for PPP, we conclude that the VEH method provides a good description of the one-electron energy levels of this hydrocarbon polymer.

B. Poly (p-phenylene sulfide)

PPS is commercially available from Phillips Petroleum Company and can be obtained as a highly crystalline material with a number average molecular weight of 11 000.[32] Heavy doping of PPS with AsF_5 yields a conductivity of about 3 S/cm.[10] However, chemical modifications of PPS are evident and correspond primarily to an intramolecular bridging process leading to polybenzothiophene linkages.[10] Conductivities measured on more lightly doped samples, for which no chemical modification is detected, are about 0.01 S/cm.[10]

X-ray diffraction data on PPS indicate that adjacent phenyl rings are nearly perpendicular.[33] Note that VEH calculations on a hypothetical perpendicular conformation of PPP results in a highest occupied bandwidth of only 0.2 eV.[8] It is then highly interesting to perform a detailed study of the electronic structure of PPS in order to understand the influence of the presence of sulfur atoms along the chain.

The bond lengths, bond angles, and torsion angle for PPS are taken from Ref. 33. Bond lengths and bond angles within the rings are averaged to, respectively, 1.400 Å and 120°. The C–S bond lengths correspond to 1.744 Å and C–S–C angle to 110°. The torsion angle is set at 90°. The VEH band structure (for a $[C_6H_4-S]_2$ translational unit cell) and density of states of PPS are displayed in Fig. 4. As in the case of PPP, bands stick two by two at the end of the Brillouin zone because of a glide plane symmetry. The physically most interesting bands are the three upper bands whose absolute positions and widths are presented in Table IV. They lead to a density of states scheme similar to the one found by Duke and Paton on oligomers.[21] The lowest of these three bands, band 15–15', is 1.6 eV wide and has mainly contributions from $3p_z$ sulfur and $2p_z$ carbon orbitals (where z is the direction perpendicular to the

TABLE IV. VEH absolute positions (in a.u.) and widths (in eV) of the three upper bands of poly(p-phenylene sulfide). Bandwidths are given for the smallest possible unit cell taking all symmetry elements into account, i.e., (C_6H_4-S).

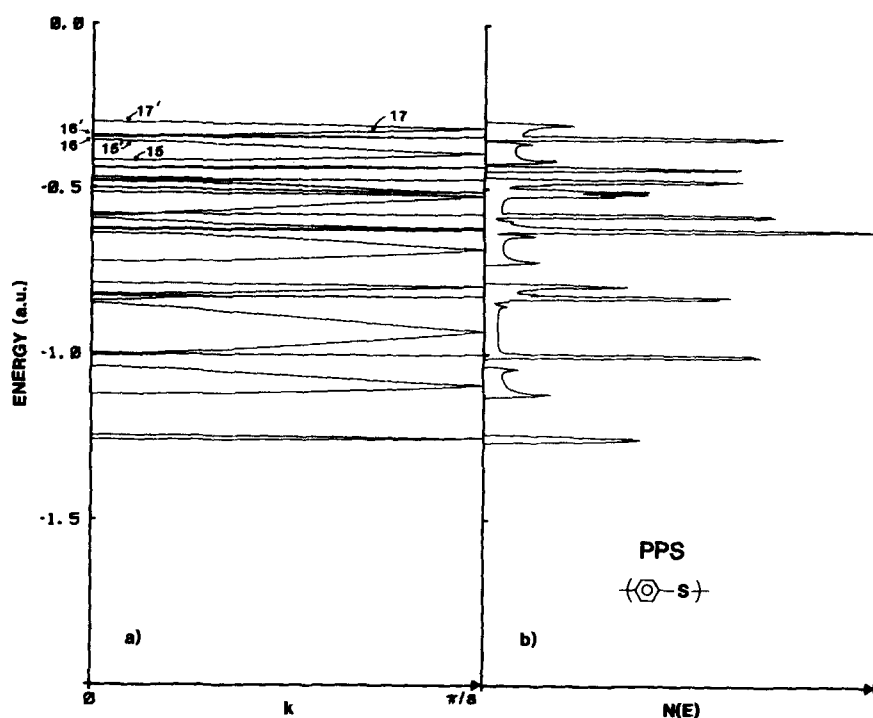| Band	Absolute positions		Widths
	$k = 0$	$k = \pi/a$	
15	−0.417	−0.393	>1.63
15'	−0.357	−0.393	
16	−0.347	−0.343	>0.14
16'	−0.342	−0.343	
17	−0.344	−0.317	>1.17
17'	−0.301	−0.317	

FIG. 4. Poly(p-phenylene sulfide) VEH calculations: (a) band structure (with band labels for the upper bands), for a [C₆H₄—S]₂ unit cell; (b) density of states.

plane containing the sulfur atoms). This band has a bonding character between the p_z orbitals on sulfur atoms and sulfur connected carbon atoms. The flatness of band 16–16' which gives rise to a very high peak in the density of states is due to the very small contributions coming from the sulfur atoms, as well as the carbon atoms bonded to sulfur. This band is similar in

origin to band 14–14' in the PPP case, which is also very flat. The highest occupied band 17–17' is very similar to band 15–15', but with antibonding interactions between sulfur atoms and their neighbors. As this band is 1.2 eV wide, i.e., 1.0 eV wider than for perpendicular PPP,[8] we conclude that sulfur atoms play an important role in connecting the conjugated systems of adjacent phenyl rings and account for some delocalization. The narrower highest occupied band in PPS compared to PPP is qualitatively consistent with the smaller conductivities achieved upon doping PPS.
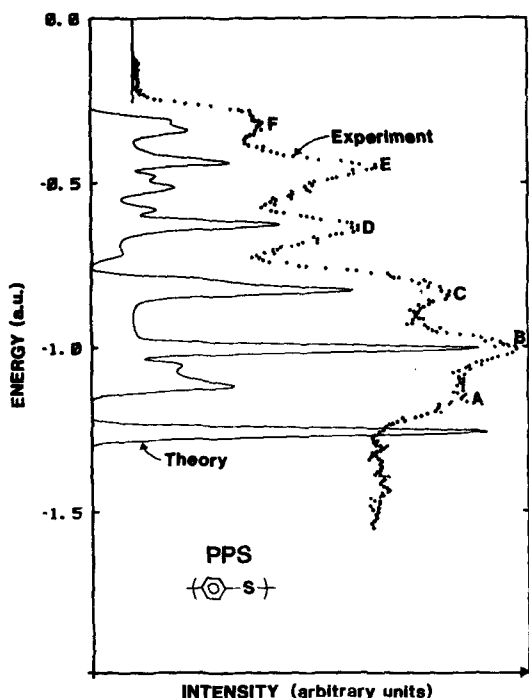
The theoretical XPS spectrum is displayed in Fig. 5 along with the experimental data recorded by Riga et al.[12] The experimental peak positions on the energy axis have been rescaled (multiplied by 1.3), as done previously for PPP and polyacetylene.[7] Such a scaling process is quite commonly performed. However, it is generally achieved with a different scaling factor for every spectrum—a procedure that has been criticized by Leupin et al.[34] It should be stressed that for all the XPS spectra we have simulated by VEH calculations (polyacetylene,[7] PPP, and PPS), we obtain a very good fit using the same scaling factor (1.3).

The general agreement between theoretical and experimental data for PPS is of the same quality as in the case of PPP with the bottom of the valence band less well reproduced than the top. As mentioned before, we chose to use the universal atomic potentials obtained in the framework of pure hydrocarbon systems for the carbon atoms which are not bonded to sulfur atoms. Although a complete optimization of the potential parameters of all carbon atoms is possible and could lead to an even better fit, the description afforded with the more transferable universal C atomic potentials (for carbon atoms not connected to sulfur) is very

FIG. 5. Comparison of XPS spectra for poly(p-phenylene sulfide). Solid line: VEH theoretical spectrum; Data points: experimental spectrum from Ref. 12, rescaled (multiplied by a factor 1.3) on the energy axis.

satisfactory and justifies our choice.

The VEH ionization potential for PPS including the polarization correction is 6.3 eV, i.e., 0.7 eV larger than the value calculated for PPP. This difference is in excellent agreement with experiment as the lowest binding energy XPS peak in PPP is located at 2.0 eV,[11] and in PPS at 2.7 eV.[12] The 6.3 eV IP value for PPS limits possible p-type dopants to very strong acceptors such as AsF_5.

In the case of PPS, the top of the valence band is not smeared out in the XPS spectrum as for PPP. This is because S-3s and S-3p cross-section factors are roughly equal and similar to C-2s cross-section factors.[26] With regard to the assignment of the peaks, we just mention that the three upper bands contribute only to peak F, with the exception of the bottom of band 15-15′ which also contributes to peak E.

From these calculations, we conclude that the description of the electronic structure of PPS obtained with the VEH method is of comparable quality to that found for hydrocarbon compounds. We expect the same quality results for other sulfur containing systems and are especially confident in the reliability of the VEH computation of relative ionization potentials.

IV. SUMMARY

In this paper, we have extended the range of applications of the valence effective Hamiltonian polymer technique by presenting the parametrization of atomic potentials for sulfur and carbon connected to sulfur. The VEH technique has then been applied to the study of the electronic structure of poly(p-phenylene) and poly(p-phenylene sulfide), systems of interest with regard to the conducting polymers area. Theoretical data have been compared to experimental XPS data and found to be in very good agreement for both polymers. These results demonstrate that the VEH technique provides an equally satisfactory description of the one-electron energy levels of hydrocarbon and sulfur containing systems and suggest that the VEH parametrization warrants extension to other atomic potentials such as nitrogen or oxygen. Although both PPP and PPS are not coplanar, the widths of the highest occupied band are rather large (3.5 eV in PPP, 1.2 eV in PPS)—a result which is qualitatively consistent with the high conductivities achieved via acceptor doping. The quite high values of the ionization potentials (5.6 eV in PPP, 6.3 eV in PPS) restrict the p-type dopants to strong acceptors.

ACKNOWLEDGMENTS

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