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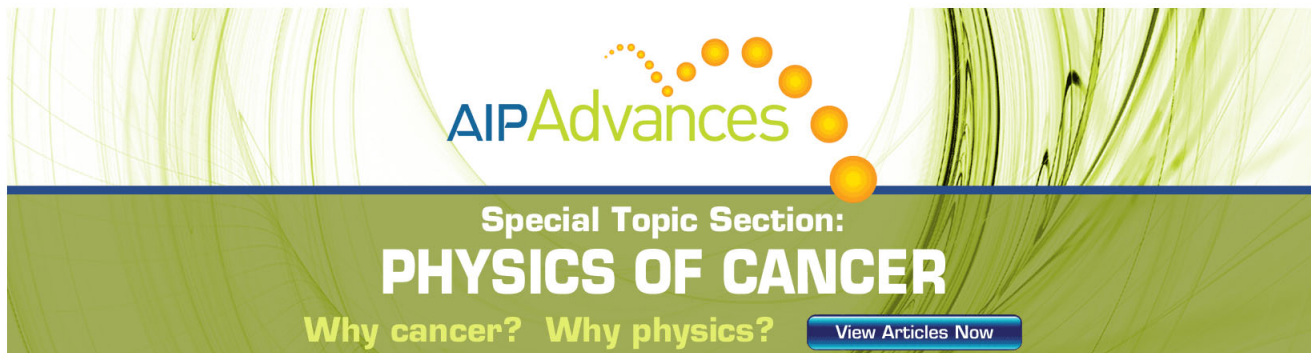
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Electronic properties of sulfur containing conjugated polymers

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Valence effective Hamiltonian (VEH) calculations are performed on a number of sulfur containing organic conjugated polymers of interest to the conducting polymers area. Theoretical results for parameters related to conductivity such as ionization potentials, bandwidths, and bandgaps are presented. Systems considered include various derivatives of poly (*p*-phenylene sulfide), polybenzothiophene, and polythiophene, as well as potentially interesting compounds such as polythieno [3,2-*b*] thiophene and polyvinylene sulfide. The electronic structure description afforded by the VEH method for sulfur containing polymers is demonstrated to be of the same quality as that presented previously for hydrocarbon polymers. In particular, for ionization potentials, good agreement with available experimental data on poly (*p*-phenylene sulfide) and polybenzothiophene is obtained, after scaling downward the VEH values by a 1.9 eV polarization correction. The comparison between the theoretical and experimental XPS spectra for polybenzothiophene is excellent with use of the same energy scaling factor previously employed for polyacetylene, poly(*p*-phenylene), and poly(*p*-phenylene sulfide). These results, in conjunction with previous results obtained on hydrocarbon polymers, lend confidence in the predictive capabilities of this purely theoretical technique. Calculations show that polyvinylene sulfide, as yet unsynthesized, should display very promising characteristics as a conducting polymer.

I. INTRODUCTION

Conducting polymers are the subject of major research activity worldwide. This interest initiates from the discovery that a relatively large number of organic polymers can be doped with either electron acceptors or donors to yield highly conducting complexes.¹⁻⁷ The electronic properties of conducting polymer systems are not well understood theoretically and, in fact, many of these systems are not well characterized. The level of understanding is much higher for the ground state properties of undoped polymers, since in that case accurate calculations are feasible.⁸ Such calculations are useful in explaining experimental results obtained through efforts to dope numerous organic polymers, as well as in predicting new conducting polymer candidates. In this framework, we have recently established the *ab initio* Valence Effective Hamiltonian (VEH) technique as being a very useful tool to explore the electronic properties of organic conjugated polymers.^{9,10,11} In particular, on hydrocarbon systems we have been able to provide an excellent qualitative correlation between those parameters obtained theoretically on neutral polymers, such as ionization potentials and bandwidths, with the conductivities achieved by doping the polymer with electron acceptors such as I₂ and AsF₅.¹⁰ More recently we have extended the range of applicability of the VEH method by deriving the parameterization of atomic potentials for sulfur.¹¹

In this paper, we consider a variety of sulfur containing polymers and obtain the same kind of information as previously presented for the hydrocarbon polymers.¹⁰ A number of sulfur containing polymers are now known that can be successfully doped to conductivity levels of the order of, or larger than, 0.1 S/cm, such as polythiophene¹² [poly(2,5-thienylene)] and polyphenylene chalcogenide compounds.¹³ Other potentially interesting derivatives that are also studied in this paper include polythiophene vinylene, polydimethylphenylene sulfide, polythieno[3,2-*b*]thiophene, and polyvinylene sulfide.

The VEH method is structured so as to reproduce double zeta quality *ab initio* calculations. This is accomplished via a parameterization of atomic potentials so that self-consistent field iterative cycles are completely avoided—a fact that renders VEH calculations very economical. The VEH method yields gas phase ionization potentials and contains no provision for the polarization energy corrections which are necessary in comparisons to condensed phase ionization potentials. This correction is made *ex post facto*. We demonstrate here that the same polarization correction factor (1.9 eV) applies to hydrocarbon and sulfur-containing polymers. We also compare VEH computed XPS spectra with experiment. As is commonly done with the *ab initio* calculations which VEH is designed to reproduce, energies must be rescaled to obtain best agreement with experiment.⁹⁻¹¹ We confirm here that the same scaling factor applies to hydrocarbon and sulfur-containing polymers.

The paper is structured as follows. In Sec II, we

^aChargé de Recherches du Fonds National Belge de la Recherche Scientifique (FNRS).

TABLE I. VEH results for ionization potential (I. P.)^a, bandwidth of highest occupied band (BW)^b and $\pi \rightarrow \pi^*$ bandgap (E_g) of sulfur containing conjugated polymers. All energies in eV; conductivities (σ) in S/cm.

Polymer	I. P.	BW	E_g	σ_{\max}	Dopant
Poly(<i>p</i> -phenylene sulfide)	6.3 [6.3]	1.2		0.1	AsF ₅ (Ref. 13)
Poly(dimethyl- <i>p</i> -phenylene sulfide)	6.1	0.9		< 0.01	AsF ₅ (Ref. 23)
Polybenzothiophene	5.5 [5.6]	1.3	3.1	3	AsF ₅ (Ref. 13)
Polythiophene	5.0	2.6	1.6	0.1	I ₂ (Ref. 12)
				10–100	ClO ₄ (Ref. 30)
Polythiophene vinylene	4.9	2.5	1.6		
Polythieno[3,2- <i>b</i>] thiophene	5.1	1.7	1.7		
Polyvinylene sulfide	5.6	3.3	3.3		

^aTheoretical ionization potential after subtracting 1.9 eV to correct approximately for polarization energy of lattice. Experimental I. P. estimates from junction measurements are given in brackets.

^bThe BW values refer to the smallest possible unit cell taking into account screw axis symmetry.

briefly describe the general principles of the valence effective Hamiltonian technique for polymers. Our computational results obtained on the sulfur compounds cited above are presented and discussed in Sec. III. Conclusions of this work are given in Sec. IV.

II. GENERAL PRINCIPLES OF THE VALENCE EFFECTIVE HAMILTONIAN TECHNIQUE FOR POLYMERS

The complete methodology for obtaining molecular one-electron valence effective Hamiltonians from first principles has been developed by Nicolas and Durand¹⁴ and extended to polymers systems by André *et al.*¹⁵ and Brédas *et al.*⁹ For the sake of completeness in this paper, we briefly describe the main concepts of the method.

In the Hartree–Fock LCAO theory for polymers,¹⁶ the crystalline one-electron orbitals are expressed as linear combinations of Bloch functions. The band structure $E(k)$, where k is a point in the first Brillouin zone of the polymer, is obtained as eigenvalues of the set of secular equations:

$$F(k)C(k) = S(k)C(k)E(k), \quad (1)$$

where $F(k)$ and $S(k)$ are the Fock and overlap matrices between Bloch functions and $C(k)$ collects the coefficients of the linear combinations.

In the VEH model, the usual one-electron Fock operator is simulated by a valence effective Fock operator F_{eff} assumed to be the sum of the kinetic term and the various atomic potentials in the system:

$$F_{\text{eff}} = -\frac{\Delta}{2} + \sum_g \sum_A V_A(g), \quad (2)$$

where the summations over g and A extend, respectively, over the polymer unit cells and the atoms present in one cell. V_A represents the atomic potential of atom A .

The atomic potentials are constructed on model molecules to yield valence effective Hamiltonians that provide one-electron energies of *ab initio* Hartree–Fock

double zeta quality when solved within a minimal basis set. Such potentials are now available for carbon,⁹ hydrogen,⁹ sulfur,¹¹ and nitrogen.¹⁷ The main advantages of the VEH technique are that it is completely theoretical and gives *ab initio* double zeta quality results with negligible computer time, since only one-electron integrals need to be evaluated and SCF iterative cycles are completely avoided.

III. RESULTS AND DISCUSSION

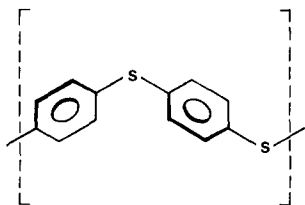
The VEH results for ionization potentials (I. P.), bandwidths (BW) of the highest occupied band, and electron band gaps (E_g) are listed in Table I. The I. P. value determines whether a particular acceptor will be capable of ionizing the polymer. The BW of the highest occupied band provides a measure of the extent of the delocalization in the system and can be roughly correlated with the mobilities of the charge carriers in that band. Also included in Table I are the I. P. experimental estimates, where available, and the maximum conductivities achieved upon doping with acceptors. As previously reported,^{9–11} the theoretical I. P. values are scaled downward by 1.9 eV in order to correct for polarization energy and possible shortcomings of the model and can be viewed as having been scaled to the experimental estimate for transpolyacetylene (4.7 eV).¹⁸ This 1.9 eV factor is quite reasonable, since experimentally determined polarization energies for planar polycyclic aromatic hydrocarbon molecules as well as for *p*-terphenyl have been reported to be around 1.7 eV.¹⁹ It is interesting to note that the polarization energy of tetrathiatetracene also equals 1.7 eV and is only 0.1 eV smaller than that of tetracene.¹⁹ Polarization energy results for tetrathiafulvalene (TTF) derivatives are however more scattered, ranging between 0.9 and 2.3 eV and mainly depending on the polarizability of the molecule.^{19,20}

A. Poly (*p*-phenylene sulfide) and derivatives

The electronic structure (band structure, density of states, XPS theoretical spectrum) of poly(*p*-phenylene

sulfide) (PPS) has been presented in detail in a previous paper.¹¹

We now summarize the main results obtained there on PPS for the sake of easy comparison with the electronic structure of the PPS derivatives. PPS is commercially available from Phillips Petroleum Company and can be obtained as a highly crystalline material with a number

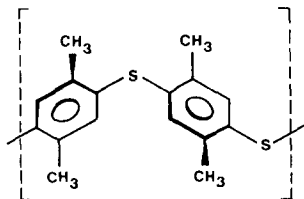


poly(*p*-phenylene sulfide)

average molecular weight of 11 000.²¹ X-ray diffraction data indicate that adjacent phenyl rings are nearly perpendicular.²² Despite this conformation, the bandwidth of the highest occupied band is relatively large, 1.2 eV. This bandwidth implies that the sulfur atoms play an important role in connecting the conjugated systems of consecutive phenyl rings and accounts for the substantial conductivity achieved on doped and unmodified PPS.^{13,23} These findings are consistent with the calculations of Duke and Paton on PPS oligomers.²⁴ To contrast, BW for the highest occupied band of an hypothetical perpendicular conformation of poly(*p*-phenylene) is only 0.2 eV. The large I. P. value in PPS limits the *p*-type dopants to strong acceptors such as AsF₅.

Poly(2,5-dimethylphenylene sulfide) (PDMPs) prepared from 2,5-dichloro-*p*-xylene and sodium sulfide according to Edmonds and Hill,²¹ is a melt and solution processable polymer. Upon doping at room temperature with AsF₅, this polymer shows conductivities as high as 0.5 S/cm. Subsequent analyses have shown, however, that that material underwent substantial chemical modification via intramolecular bridging of adjacent phenyl rings. Low temperature doping with AsF₅ gave material with a conductivity of only 10⁻² S/cm. Analysis of this material has shown it too has undergone the bridging process upon doping but only to a moderate extent.²³ One would estimate the conductivity for the unbridged material to be somewhat less than 10⁻² S/cm.

Calculations on PDMPs provide an insight into the

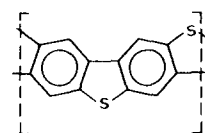


poly(2,5-dimethylphenylene sulfide)

influence of methyl substitution on the aromatic rings. With respect to PPS, the I. P. value is slightly lowered but the bandwidth is significantly reduced. Similar results were obtained on polymethylacetylene with respect

to polyacetylene.¹⁰ Again, qualitatively, the calculations are consistent with the estimates on the conductivities obtained on doped PDMPs in the absence of chemical modifications.

Recently, it has been demonstrated that exposure of PPS to AsF₅ at room temperature causes substantial changes in the backbone structure of the polymer.¹³ The dopant appears to predominantly induce the formation of carbon-carbon bonds bridging the sulfur linkages to form thiophene rings which leads to a polybenzothiophene structure. This chemical modification enhances the conductivity of the complex from about 0.01 S/cm up to 3 S/cm. Calculations on polybenzothiophene PBT are performed assuming a coplanar geometrical structure combining the features of PPS²² and dibenzothiophene.²⁵ The band structure for a (C₆H₂S)₂ translational unit cell, and the density of states are presented in Fig. 1. Bands stick together two by two at the end of the Brillouin zone



Polybenzothiophene

as a result of the presence of a screw axis of order 2 along the chain. The highest occupied band, the most important with respect to the conducting properties, is a π band that by symmetry has no contributions coming from the sulfur atoms.

The XPS theoretical spectrum of PBT is displayed in Fig. 2, along with the experimental spectrum recorded by Boutique *et al.*²⁶ The PBT sample was obtained by heavily doping PPS with AsF₅ at room temperature, followed by neutralization of the conductive complex with ammonia and extraction of the inorganics with water. Infrared and elemental analyses have shown the material to be extensively bridged¹³ and free of nitrogen and arsenic containing species. The theoretical spectrum is calculated from the density of states by a method due to Delhalle²⁷ in which the density of states is corrected for the photoionization cross-section factors according to the Gelius model²⁸ and convoluted by a Gaussian function whose half-width (0.7 eV) is chosen in order to take account of the resolution of the spectrometer. The experimental peak positions in Fig. 2 have been rescaled (multiplied by a factor of 1.3) in order to get a better fit on the energy axis. The fact that this 1.3 factor is the same as the one used previously for all-*trans* polyacetylene,⁹ poly(*p*-phenylene),¹¹ and PPS¹¹ suggests that the bandwidths computed by the VEH method are consistently 1.3 times wider than the experimental bandwidths. This correction is not taken into account in Table I. Note that the peak of highest binding energy (i. e., of energy larger than 1.25 a. u.) in the experimental spectrum actually corresponds to oxygen impurities and has to be disregarded when comparing with the theoretical spectrum.

The agreement between the theoretical spectrum and

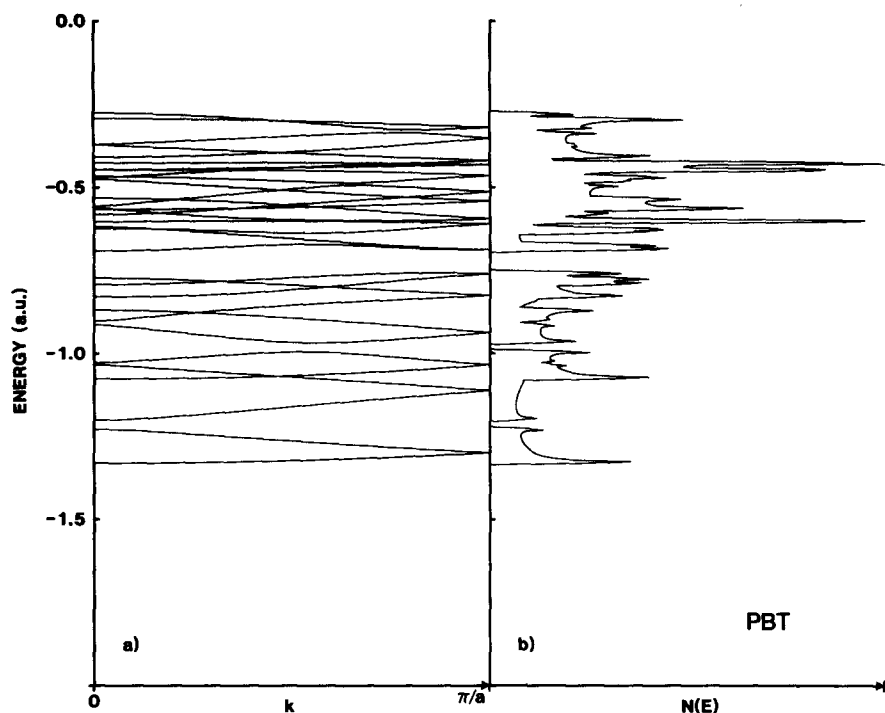


FIG. 1. Polybenzothiophene VEH calculations: (a) band structure for a $[C_6H_2S]_2$ unit cell; (b) density of states.

experimental data is very good, though with the usual exception of the bottom of the valence band which is consistently located at too low an energy in a VEH calculation.^{9,11} These results confirm the quality of the VEH method in providing accurate one-electron energies of organic polymers.

The XPS experimental difference between the positions of the peak of lowest binding energy between PBT and PPS is 0.6 eV,²⁴ to be compared with a theoretical I. P.

difference estimate of 0.8 eV. The experimental difference could, however, correspond to a lower limit since, as noted earlier, the highest occupied band of PBT has only contributions from $2p_z$ carbon atomic orbitals. As the cross-section factor for a C_{2p} orbital is more than one order of magnitude smaller than that for C_{2s} , S_{3s} , and S_{3p} orbitals,²⁸ that band is almost completely smeared out in the XPS spectrum. From junction measurements, the I. P. difference is of the order of 0.7 eV.²⁹

The increase in the BW value for the highest occupied band in PBT vs PPS, though small (~ 0.15 eV), is qualitatively consistent with the increase of conductivity in going from PPS to PBT.

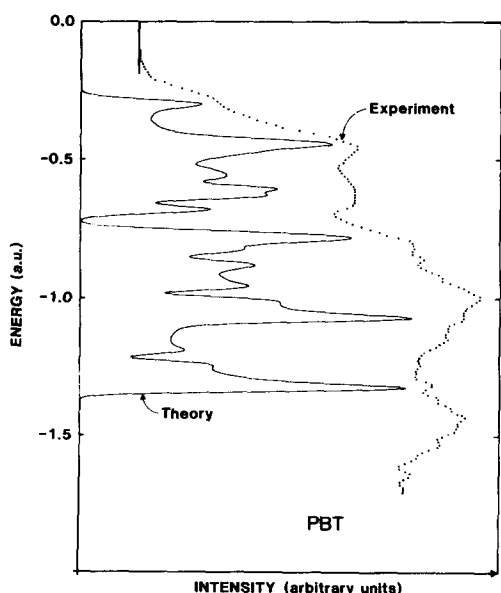
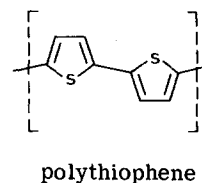
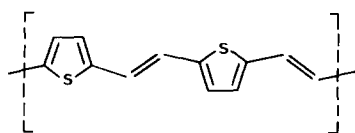


FIG. 2. Comparison of XPS spectra for polybenzothiophene. Solid line: VEH theoretical spectrum. Data points: experimental spectrum (Ref. 25) rescaled (multiplied by a 1.3 factor) on the energy axis.

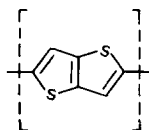
B. Polythiophene and derivatives

Polythiophene [poly(2,5-thienylene)] (PT) is usually synthesized from dihalogenated thiophene by utilizing a transition metal catalyzed dehalogenation polymerization.¹² This process leads, however, to a polymer of quite low molecular weight (500–1300),³⁰ implying a chain length of only 6 to 15 monomer units. Polythiophene vinylene [poly(2,5-thiophendiylylene)] (PTV) can be prepared with only *trans* vinylene units via a variation of the Wittig reaction due to Kossmehl.³¹ To our knowledge, polythieno[3,2-*b*]thiophene (PTT) has not been synthesized.





Poly(thiophene vinylene)

polythieno[3, 2-*b*]thiophene

Geometries used in the VEH calculations are taken from the x-ray structure of 1,4 bis(2-thienylvinyl)benzene.³² Within the thiophene rings, bond lengths and bond angles are averaged as follows: $R_{C-S} = 1.71 \text{ \AA}$, $R_{C=C} = 1.38 \text{ \AA}$, $R_{C-C} = 1.426 \text{ \AA}$; $\langle C-S-C \rangle = 92^\circ$; other angles = 112° . Between the rings, the carbon-carbon single bond is averaged to 1.45 \AA (a value which is also suggested by MNDO geometry optimizations on thiophene oligomers³³); the double bond in the case of PTV is set at 1.335 \AA .

The band structure and XPS theoretical spectrum of PT are displayed in Fig. 3. As in the case of PBT, the highest occupied band is one having no contribution from the sulfur atoms. As a result, this band is very similar to the highest occupied band in *cis*-polyacetylene. This result is in agreement with CNDO/S3 calculations carried out by Duke *et al.*³⁴ It is also consistent with the small ionization potential difference between the two polymers (0.3 eV smaller in *cis*-polyacetylene)¹⁰ and consequently predicts the possibility of doping PT with relatively weak electron acceptors such as I_2 .^{12,30} The electronic properties of PTV are almost identical to

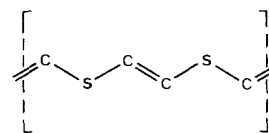
those of PT. The experimental estimate for the band gap in PTV from the absorption maximum is 2.2 eV .³¹ This is 0.6 eV larger than our calculated value which, however, corresponds to the band edge.

The large BW value of the highest occupied band in PT suggests the possibility of obtaining upon doping conductivities higher than in the polyphenylene chalcogenides compounds. This is in contradiction with the low conductivity level ($\leq 0.1 \text{ S/cm}$) reported by Yamamoto *et al.*^{12,30} It has, however, recently been claimed that electrochemically prepared ClO_4^- doped polythiophene shows conductivities as high as 10 to 100 S/cm.³⁵ Doping of PTV has not yet been reported.

From a molecular viewpoint, thieno[3, 2-*b*]thiophene appears very interesting because its ionization potential is 0.80 eV smaller than that of thiophene.³⁶ (VEH calculations on both monomer molecules lead to a 0.89 eV difference.) The possible polymer is however less attractive, having I.P. and E_g values comparable to PT and a narrower highest occupied band.

C. Polyvinylene sulfide

Polyvinylene sulfide (PVS) $\langle CH=CH-S \rangle$ is the simplest conjugated polymer based on sulfur, carbon, and hydrogen. However, it has not yet been prepared, contrary to its saturated counterpart, polymethylene sulfide $\langle CH_2-S \rangle$.³⁷ As expected, polymethylene sulfide leads to an I.P. value larger than 7 eV and a highest occupied BW of the order of a few tenths of eV.



polyvinylene sulfide

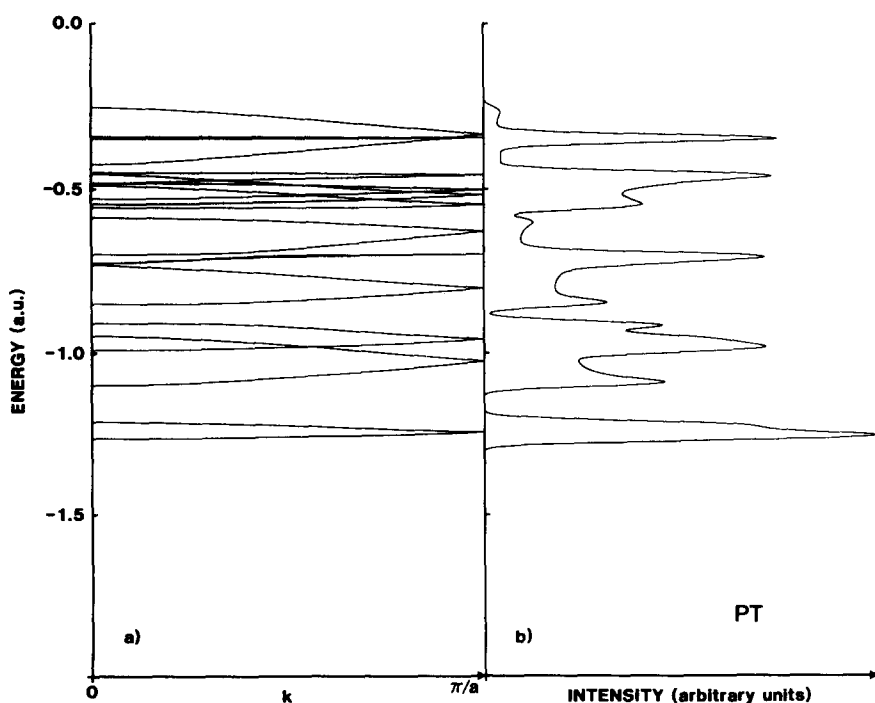


FIG. 3. Polythiophene VEH calculations: (a) band structure for a $[C_4H_2S]_2$ unit cell; (b) XPS theoretical spectrum.

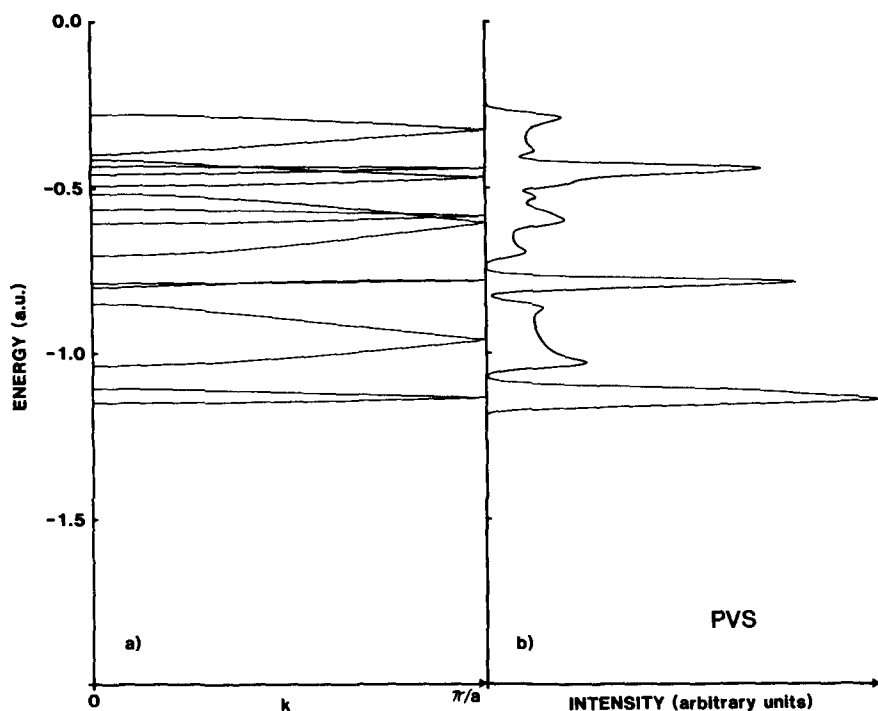


FIG. 4. Polyvinylene sulfide VEH calculations: (a) band structure for a $[C_2H_2S]_2$ unit cell; (b) XPS theoretical spectrum.

The VEH calculation performed on PVS is based on an all-*trans* conformation with C-S bond lengths (1.744 Å) and C-S-C bond angles (110°) chosen from what is known in PPS²¹ and a carbon-carbon double bond 1.35 Å long. Interestingly, all-*trans* PVS shows characteristics very similar to poly(*p*-phenylene) for which conductivities as high as 500 S/cm upon doping have been reported.² The ionization potential is identical and the highest occupied BW and E_g are only slightly smaller.

The band structure and XPS theoretical spectrum of PVS are presented in Fig. 4. The highest occupied band is a π band which has important contributions from each atom in the unit cell, the C-S interaction being antibonding. On the other hand, the first unoccupied π band has no contributions from the sulfur atoms. The predicted properties of PVS would appear to be promising.

IV. SUMMARY

As in the case of hydrocarbon polymers, the valence effective Hamiltonian technique offers a reliable and inexpensive way of calculating the valence electronic properties of sulfur containing polymers. The ionization potentials, after correction for polarization effects (1.9 eV) are in good agreement with the experimental estimates and consistent with the acceptor strength needed to dope the polymer; the bandwidth values correlate satisfactorily with the maximum conductivities achieved upon doping. It is interesting to note that the results obtained on polythiophene suggest that the polymeric material behaves as a substituted polyacetylene.^{34,38} This idea is consistent with the high conductivity obtained on polypyrrole³⁹ which can be also thought of as being a substituted polyacetylene.^{17,40} The

quality of these results lends confidence in the predictive capabilities of the method when applied to materials yet to be synthesized such as polythieno[3,2-*b*]thiophene and poly(vinylene sulfide). The large highest occupied bandwidth of poly(vinylene sulfide) together with its reasonable ionization potential suggest the possibility that it would form highly conducting complexes comparable to those of poly(*p*-phenylene) when doped with strong electron acceptors.

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