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Conformational Origin of Peak Structure Arising in the XPS Spectrum of an Isotactic Polypropylene

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Extended Hückel crystal orbital (EHCO) calculations on zig-zag planar and helical conformations of regular infinite (model) isotactic polypropylene are reported. Significant changes in the theoretical XPS spectra and comparison with experimental data support the idea of possible detection of conformations in the case of good stereoregular polymers.

Key words: Crystal orbital calculation – Stereoregular polymers

1. Introduction

Applications of X-ray photoelectron spectroscopy (XPS or ESCA) to polymers has become increasingly important over the last decade. It is a versatile and powerful technique to obtain an experimentally based description of the electrons levels distribution, it is also well designed for the investigation of structure, bonding and reactivity of polymeric materials. Most of the studies have been primarily directed towards measurements of core level binding energies and chemical shifts associated with changes in the chemical environment. Further applications and new developments in this area have been recently reviewed [1]. Though XPS energy resolution is usually not better than 0.5 eV and despite the low intensity of valence bands it is now recognized that this portion of the spectra provides a valuable and complementary source of information [2]. However, the nature, position and intensity of peaks arising in the valence bands are difficult to interpret without any theoretical basis. Preliminary comparisons between measured valence bands and theoretically simulated spectra of polymers have demonstrated the potential of quantum mechanical calculations as an interpretative and predictive tool for chemical substitution [3–5].

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All the calculations so far performed for sake of comparison with XPS spectra have assumed a zig-zag planar conformation in the case of polyvinyl compounds (polyethylene [6] and its substituted derivatives [5]: linear fluorosubstituted polyethylene, polypropylene and polyglycine). Crystalline polyethylene exhibits this type of geometrical disposition [7] and indeed a good agreement between theory and experiment is observed. For polypropylene [5] however, when a zig-zag planar conformation is assumed, the agreement limits to band widths and it is impossible to establish a sound correlation between observed peaks and the theoretical spectrum. Since atoms and bonds are so closely similar in nature for both polymers the EHCO method should not be incriminated for such a discrepancy.

A preliminary computer experiment [8] on various conformations of polyethylene (*T*, *G*, *TG*, *TGTG'*) has predicted definite and actually observable influences of the conformation on the electronic density of states distributions. Unfortunately it is impossible, at least to our knowledge, to trap and isolate individual conformations of polyethylene thus making unachievable any confrontation with experiment.

It is the purpose of this note to report on the conformational influence on the electronic density of states of an isotactic polypropylene and compare these new results with previously reported measurements [5].

2. Theory and Methodology

Theoretical results discussed in this paper have been obtained with the parametric extended Hückel method (EHCO) generalized for infinite chain-like systems (model polymers); the description of its formation can be found in the literature (e.g. see Ref. [4], and papers cited). Original Hoffmann's parameters [9], calibrated on ethane, have been used, simulated XPS spectra computed according to the technique described in Ref. [10] and relative photoionization cross-sections taken from the work of Gelius [11]. Those initial data are collected in Table 1 where I_r, ζ_r and σ_r denote respectively ionization potential, exponent and relative photoionization cross-section of valence Slater atomic functions χ_r.

Table 1. Valence ionization potential, I_R, exponent, ζ_r, and relative photoionization cross-section σ_r of the Slater functions used in the theoretical calculations (I_r in eV), $K=1.75$

	H			C		
r	I_r	ζ_r	σ_r	I_r	ζ_r	σ_r
1s	13.6	1.2	0.0	—	—	—
2s	—	—	—	21.936	1.625	1.000
2p	—	—	—	11.400	1.625	0.077

A far-reaching similarity between Hartree-Fock and extended Hückel results has been observed as to the order of energy levels, molecular shapes, and changes in hybridization and ionization potentials with angles [12]. This consistency holds also for trends in series of similar compounds. However attention must be paid when relying on such elementary methods. Preliminary studies on prototype compounds with firmly based methods are helpful in testing and comparing data produced by the approximate techniques. For this purpose we have calculated one-electron energy levels of propane in the C_{2v} symmetry with both Gaussian 70 series of programs [13] using the minimal STO-3G basis set [14] and with the molecular extended Hückel program [15] (same parameters as for the forthcoming polymer calculations). Table 2 contains the results for the lowest occupied valence energy levels we are specifically interested in. It comes out a good correlation between *ab initio* STO-3G and extended Hückel values. Therefore isotactic polypropylene, $-[CH_2-CH(CH_3)]-$, a saturated hydrocarbon polymer, appears to be a suitable candidate for a reliable EHCO investigation on conformational effects.

Table 2. Values of the three lowest valence one-electron energy levels of propane obtained with an *ab initio* (STO-3G) and with an extended Hückel method (EH) (in eV)

C_{2v}	$\varepsilon_{\text{STO-3G}}$	ε_{EH}
$1a_1$	−27.646793	−27.474759
$1b_2$	−24.226244	−23.881523
$2a_1$	−20.936014	−20.528950

$\varepsilon_{\text{EH}} = a_0 + a_1 \cdot \varepsilon_{\text{STO-2G}}$, $a_0 = 1.16032$, $a_1 = 1.03513$ and $r^2 = 0.9999$

The C–C and C–H bond lengths are 1.54 and 1.08 Å, Fig. 1 illustrates the geometrical disposition [16] of atoms in the unit cell of a regular isotactic polypropylene; a) in a zig-zag planar conformation, b) in an isoclined isomorphous 2 × 3/1 helix [17]. Unit cell lengths are 2.5151 Å for the zig-zag conformation and 6.1608 Å for the helix. As it is required by the crystal orbital theory a strict head-to-tail sequence of monomeric units is considered in this model.

3. Results and Discussion

From top to bottom of Fig. 2 we successively have the theoretical (EHCO) valence spectrum for an isotactic polypropylene of assumed zig-zag planar conformation (2a), the experimental valence spectrum [5] (2b) and the theoretical valence spectrum (EHCO) for the helix form (2c). Simulated XPS spectra, (2a) and (2c), have been obtained on the basis of electronic density of states histograms computed from energy bands known at 21 k-points and modulated according to the intensity model of Gelius [10, 11]. The width of the histogram boxes was 0.01 a.u. (0.2721 eV) and the final form of the spectra is the result of convoluting the modulated density of electronic states distributions with an experimental resolution function approximated by a Gaussian of full width at half maximum of 0.026 a.u. (0.7 eV). More about these technical details can be found in Ref. [10]. Original experimental data [5] of Fig. 2b have been scaled in intensity and abscissas (energies) have been shifted so as to bring the C peak of Fig. 2b into coincidence with the corresponding one of Fig. 2c. The portion of the experimental photoelectron

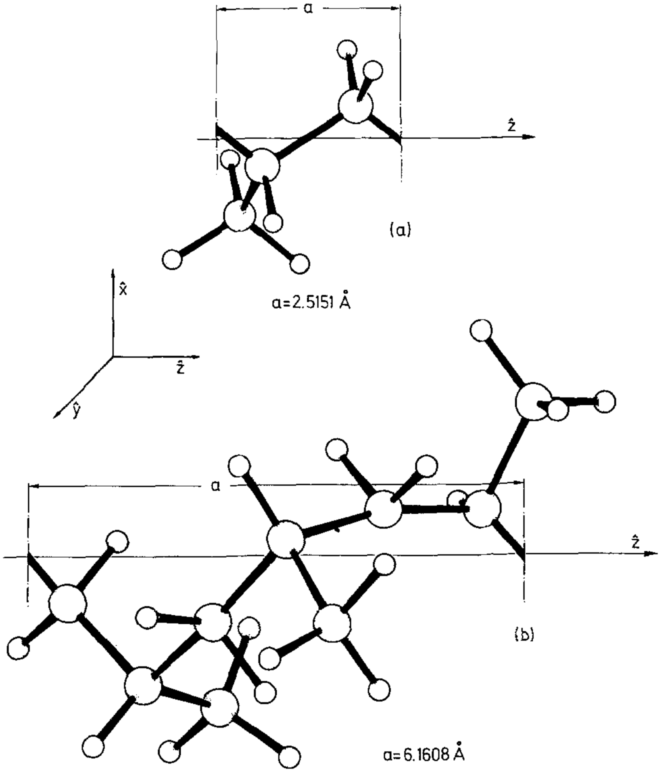

Fig. 1. Geometrical disposition of atoms in the unit cell of isotactic polypropylene for:
(a) the zig-zag planar conformation
(b) the helix 2 × 3/1 conformation

spectrum [5] (ranging from 12 to 22 eV) which is presently of interest to us is characterized by a well defined structure consisting of three peaks (*A*, *B* and *C* in Fig. 2b). Each of the outermost sub-bands in this part appears to be split into two components, at 12.8 and 13.9 eV and at 18.6 and 19.9 eV respectively for *A* and *B*.

A tentative interpretation of this experimental spectrum with the first EHCO calculation (Fig. 2a) where a zig-zag planar conformation is assumed has been reported in a previous paper [5]. No satisfactory agreement as to the peak structure was obtained, for instance the intense and sharp peak (*C*) emerging in the middle of the experimental C–C clump does not appear in this theoretical calculation. Moreover only four distinct peaks are observed in this calculated spectrum instead of five in the experiment. At that time we suspected a possible conformational effect but we could not handle such a large calculation to verify our conjecture. Indeed a previous and inspiring computer experiment [8] had shown definite and specific effects of the conformation on the resulting density of electronic levels of polymers.

Following these indications we decided to reinvestigate the problem by computing the electronic energy bands and the simulated valence spectrum of an isotactic

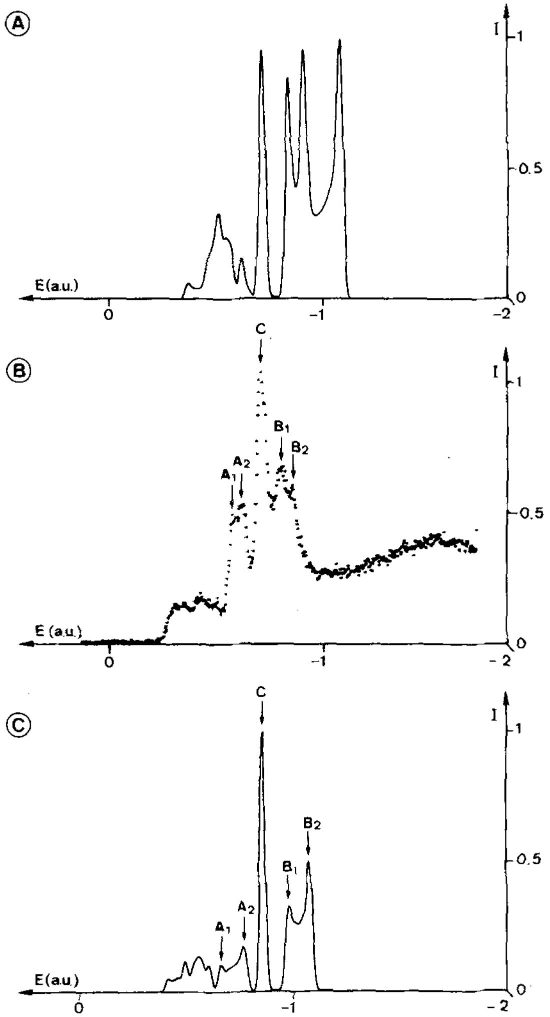

Fig. 2. XPS spectra of isotactic polypropylene:

(a) theoretical (EHCO) for the zig-zag planar conformation

(b) experimental [5]

(c) theoretical (EHCO) for the helical 2 × 3/1 conformation. Intensities and energies are respectively given in arbitrary and atomic units

polypropylene in the helix form. It is important to stress again the fact that the model polymer is an infinite regular (head-to-tail) and isolated chain free of structural defects and impurities. However we estimate this idealized system close enough to the reality for our quest. As a matter of fact, crystal environment has been shown to play negligible effects on the shape of recorded valence bands of large normal paraffins [18, 19] and the high tacticity degree of the experimental sample (98 %) kindly provided by Montedison S.p.A. and checked at the G. Donegani research center supports this assumption. The influence of the tertiary structure still remains to appreciate, and other investigations on appropriate compounds will certainly be required in the future. The theoretical results for the helix form show significant changes in the expected direction. As a consequence of the sole conformation inclusion the right structure now appears in the C–C clump: the missing intense and sharp peak (*C*) is now present and the outermost sub-bands split into two components. Though in less agreement with experiment, peak intensities also follow the right order. Our hybrid approach to intensity evaluations (we have used the σ_r's estimated for a particular atomic basis set in an *ab initio* calculation [11]) and the lack of electron density readjustment (or SCF process) in the EHCO method are among the possible explanations. No doubt that more firmly based methods would provide closer agreement. Table 3 sums up energy characteristics of the theoretical and experimental spectra.

Table 3. Positions of the five peaks belonging to the C–C region as they appear in the theoretical and experimental spectra (units in eV)

Peak	Theory (helix)	Experiment [5]
A_1	17.574	12.8
A_2	21.000	13.9
C	23.086	16.3
B_1	26.163	18.6
B_2	29.320	19.9

$\varepsilon_{EH} = a_0 + a_1\ \varepsilon_{exp}$; $a_0 = 1.4842$, $a_1 = -0.8640$ and $r^2 = 0.9685$

Several conclusions can be drawn from this exploratory and qualitative study:

1. XPS valence bands, dealing with bonding electrons can give a wealth of information on structural aspects (substitution [4, 5], conformation, . . .) of stereoregular polymers provided appropriate resolution is available.
2. Theoretical calculations prove to be the only way out in elucidating those cases where no basis exists for interpreting puzzling experimental results of this type.
3. Geometry is often at the origin of fine but significant features in the electronic structure and it can be dangerous to ignore or oversimplify it when coming to the point of comparing theory and experiment. It is of particular significance at this time when numerous and important studies on quasi one-dimensional systems are being undertaken.
4. More firmly based type of calculation would certainly be useful for quantitative comparison, however, when enough care has been taken, parametric methods such as extended Hückel can provide at low cost the essential of the underlying physics and chemistry.

It is our hope to return on this and similar cases to get a better insight and additional information on structural characteristics of stereoregular polymers as they are displayed by XPS.

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