X-ray Photoelectron Spectroscopic Study of Kevlar Fiber and the Valence Band Interpretation by Xα Calculations

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Both core level and valence band X-ray photoelectron spectroscopy (XPS) was used to analyze the surfaces of Kevlar-29 and Kevlar-49 fibers, solid benzene, terephthalamide, isophthalamide, and phthalamide. Valence band XPS, unlike core XPS, is more sensitive to the subtle chemical differences between the latter three isomers. The chemical shifts in the C 1s and other core regions can be used to identify functionalized carbon, but sometimes the results are ambiguous, especially when hydrocarbon and graphite carbon or isomeric structures are involved. Valence band XPS spectra, interpreted by Xα calculations, can provide information allowing these compounds to be identified and distinguished.

Introduction

X-ray photoelectron spectroscopy (XPS) has been widely used in material surface studies, and it is normally a chemically sensitive technique. Core levels XPS spectra can provide elemental information about material surfaces. Although atomic core level orbitals are not directly involved in chemical bonding, the chemical shifts in the core region XPS spectra can be related to the chemical environments on material surfaces. Valence band XPS spectra provide information about the electrons that contribute to chemical bonding and are often more sensitive to chemical environments than core level spectra, allowing subtle chemical structure changes to be identified.

Our research group has been using surface science techniques, especially XPS, to study carbon, functionalized carbon and hydrocarbons in graphite, carbon fibers, polymers and other organic compounds for many years.[1-9] In particular, a series of systematic studies of carbon fiber surfaces has been performed (see refs 1-7 and the references therein). Core level (e.g., C 1s and O 1s etc.) XPS chemical shifts can be used to identify differently functionalized carbon species. However, unfunctionalized carbons or hydrocarbons usually give identical core level XPS spectra in the C 1s region. Sometimes, even the core level XPS chemical shifts of functionalized carbon and hydrocarbons are not unambiguous. Furthermore, in the case of nonconducting samples, such as polymer and organic compounds, surface charging (especially uneven surface charging) may cause problems, leading to uncertainty in the binding energy calibration, and possible peak broadening.

Valence band XPS can be a very promising method to distinguish unfunctionalized carbons or hydrocarbons with different chemical structures, as well as for the investigation of functionalized carbon species.[22] In the valence band XPS spectra, relative peak positions or separations between peaks are more interesting than the absolute peak positions. Although valence band photoemission using X-ray, UV, and synchrotron radiation has been extensively examined over the years, the analytical applications of these spectra have been limited.

Our group has used XPS valence band photoemission for analytical purposes in both metal[8] and carbon systems.[6] Since the XPS valence band can be well understood in terms of the ground state, we have used Xα and other calculations to interpret such spectra. The calculations are important since the spectra of model compounds alone cannot exclusively explain the valence band region, because we can never be sure that the bulk of a model compound is always representative of its surface.

Our previously reported work in carbon systems[1-7] showed that considerable use can be made of valence band XPS spectra in analyzing the surface structure of various carbon fibers and compounds with subtle chemical differences, especially when these subtle differences cannot be distinguished in core level XPS spectra. Pireaux and co-workers[10] discussed the use of valence band photoemission to polymer systems and pointed out the potential for the analytical application of valence band photoemission to polymers. Calculations that allow the valence band spectra to be understood have been carried out by us for carbon systems by performing multiple-scattered wave Xα and traditional *ab initio* calculations. We have found that the valence band XPS spectra were more sensitive to the carbon fiber surface chemical changes, and the combination of the valence band experiment data and the results of the Xα calculations can be used to predict the valence band features of other similar or related compounds. However it should be noted that effective use of valence band XPS requires the recording of the spectra of model compounds, and the calculation of expected spectra from appropriately accurate calculation methods.

In this work, both core level and valence band XPS were used to analyze the surfaces of Kevlar-29 and Kevlar-

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Table I. Parameters Used and Features of Xα Calculations

	hydrogen	carbon	nitrogen	oxygen	outersphere[a]	intersphere[a]
α values	0.77654	0.75928	0.75197	0.74447	0.76397	0.76397
max l values	0	1	1	1	4	

model compound	benzene	phthalamide	isophthalamide	terephthalamide
symmetry	D_{6h}	C_2	C_{2v}	C_{2h}
C–C bond length in benzene ring (Å)	1.3700	1.3700	1.3700	1.3700
C–H bond length in benzene ring (Å)	1.0900	1.0900	1.0900	1.0900
C–C bond length in C–C=O (Å)		1.4700	1.4700	1.4700
C–O bond length in C–C=O (Å)		1.200	1.200	1.200
C–N bond length in O=C–N (Å)		1.3200	1.3200	1.3200
N–H bond length in C–N–H (Å)		1.0100	1.0100	1.0100
hydrogen sphere radius (Å):	0.42333	0.42333	0.42333	0.42333
carbon sphere radius (Å):	0.82021			
α-carbon[b]		0.78980	0.75556	0.76617
β-carbon		0.82021	0.80882	0.82021
γ-carbon		0.84616	0.82103	0.83253
δ-carbon		0.84781	0.82252	
nitrogen sphere radius (Å):		0.83729	0.80273	0.81400
oxygen sphere radius (Å):		0.87227	0.82730	0.83892
outer-sphere radius (Å):	2.88333	5.07596	5.07596	5.26857
virial ratio (−2T/V):	1.01828	1.01921	1.02372	1.02308
convergence:	when the difference in potentials at the beginning and the end of the iteration were less than 10^{-5} of the potential at the start of the iteration. This gives energy levels that differed by less than 10^{-6} Ry between the last two iterations.			
core electrons:	"thawed" so that they retained atomic character while being fully included in the iterative process. C(1s), O(1s), and N(1s) electrons were treated as core electrons.			

[a] For benzene, the α value of outersphere and intersphere was 0.767 91. [b] See Chart I for atom labeling.

49 fibers, frozen benzene, terephthalamide, isophthalamide, and phthalamide. Xα calculations were carried out to interpret the valence band features of the model compounds of benzene, phthalamide, terephthalamide, and isophthalamide. The results of the Xα calculations were converted to valance band spectra and compared with the experimental XPS data. Furthermore, both the experimental data and the Xα calculation results of benzene and terephthalamide were used to synthesize new photoemission spectra. Then these synthesized photoemission spectra were compared with the Kevlar fiber valence band experimental data.

Experimental Section

Kevlar fiber samples were provided by the Fibers Department of the du Pont Co. Both the Kevlar-29 fiber sample (Lot No. 1500-1000-R80-962) and the Kevlar-49 fiber sample (Lot No. 1986261) were free of surface finish. The Kevlar fibers were not pretreated in our laboratory before XPS analysis. The fiber bundle (either Kevlar-29 or Kevlar-49 fiber) was cut into a 3-cm length, with both ends tied with aluminum foil. Then this fiber sample was mounted in a metal sample holder and transferred into the XPS spectrometer chamber. The metal sample holder was grounded by connecting to the system ground, and the sample position was adjusted so that neither the aluminum foil at the sample ends nor the metal sample holder was seen by the analyzer.

The terephthalamide (CAS 3010-82-0) sample was purchased from Pfaltz and Bauer (Catalog No. T00950), and the phthalamide (CAS 88-96-0, Lot No. 99812-00-302, Catalog No. 8600) and the isophthalamide (CAS 1740-57-4, Lot No. 96349-00-304, Catalog No. 5137) samples were purchased from Lancaster Synthesis. All these samples were powders. The powder samples were mounted to a copper sheet with double sided tape, and the copper sheet mounted in the metal sample holder. Then the sample was transferred into the XPS spectrometer for analysis.

Benzene (CAS 71-43-2) was purchased from Aldrich (ACS reagent grade, Catalog No. 31,995-3). A piece of clean copper sheet was mounted in the metal sample holder and transferred into the XPS sample chamber, and then the copper sheet was cooled with liquid nitrogen through a special sample probe. The liquid benzene was stored in a small stainless steel container which was connected to a leak-valve on the XPS sample chamber. After the copper sheet was cooled down inside the sample chamber, the leak-valve was very carefully opened and the benzene vapor was very slowly leaked into the chamber. Observation through the view port of the chamber showed that the benzene vapor was condensed onto the copper sheet and finally completely covered the copper sheet. Then the leak-valve was closed and the sample was cooled continuously by liquid nitrogen. When the vacuum in the chamber reached about 1×10^{-8} Torr, XPS analysis was started. The base pressure of the XPS chamber was usually about 1×10^{-9} Torr when the fiber sample was analyzed, and about 5×10^{-9} Torr when powder sample mounted with double sided tape was analyzed.

The XPS spectra were collected on an AEI (Kratos) ES200B X-ray photoelectron spectrometer. The XPS spectrometer was operated in the constant retarding ratio (FRR) mode (retarding ratio 1:23) using Mg K$\alpha_{1,2}$ X-ray radiation (240 W). Analyzer resolution was of the same order as the X-ray line width (0.7 eV). The curve fitting of the C 1s spectra was carried out using a nonlinear least-squares curve-fitting program with a Gaussian/Lorentzian product function.[7,8] The binding energy of the main aromatic C 1s peak of each sample was taken as 284.6 eV for calibration purposes.

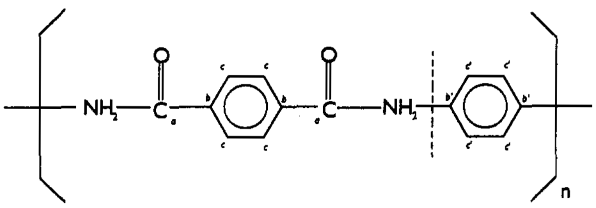
Multiple-scattered wave Xα calculations were performed on an IBM RISC/6000 system using highly optimized double-precision Fortran code. Table I shows the input parameters and calculation features for the four compounds studied. The calculated spectra was obtained by weighing the atomic contributions to the molecular orbitals with the Scofield cross sections[13] in the manner described previously.[6,7] The component energy levels were made up of equal-width (2.35 eV) Gaussian/Lorentzian product functions with a 50% mixture including X-ray satellite features for the Mg X-radiation used in the experimental spectra.

Results and Discussion

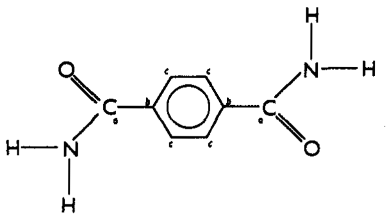
XPS Survey Spectra. The survey spectra of the Kevlar-29 and Kevlar-49 fibers, and terephthalamide, isophthalamide and phthalamide are shown in the left column of Figure 1. All the survey spectra have a very intense C 1s peak at 284.6 eV, an intense O 1s peak at 530.3 eV, an intense N 1s peak at 399.7 eV, and some weak C(KVV), N(KVV), and O(KVV) Auger features at about 990, 873, and 745 eV, respectively. The relative peak intensity ratios of O1s/C1s and N1s/C1s in (a) and (b) are

Chart I. Molecular Structures

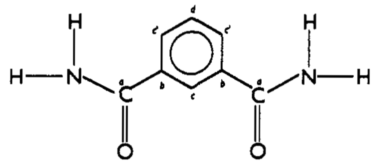
(a) Kevlar fiber structure



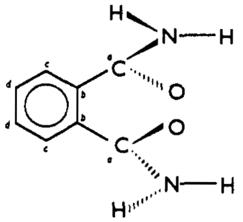
(b) Terephthalamide



(c) Isophthalamide



(d) Phthalamide



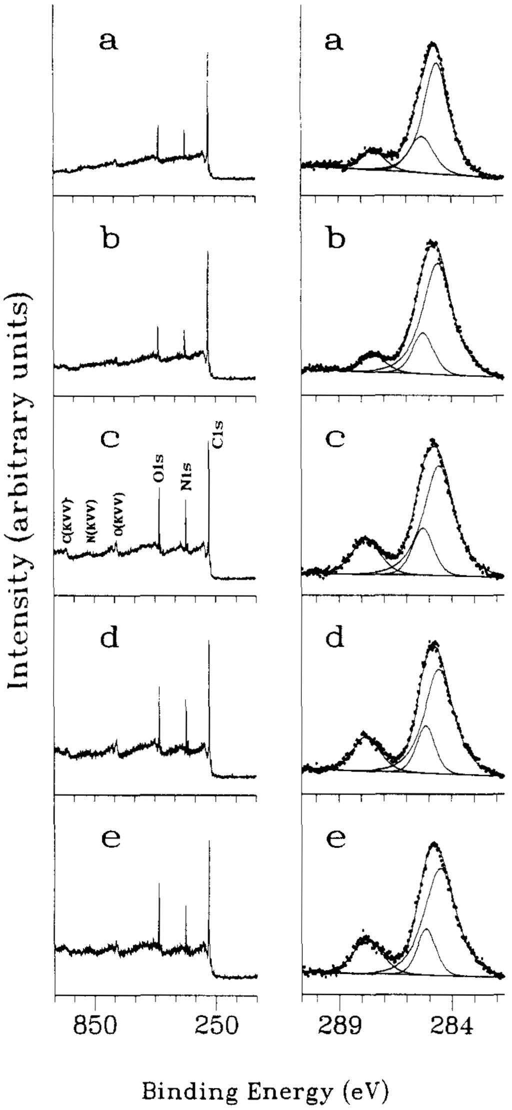


Figure 1. XPS overall survey and curve fitted C 1s core region spectra. Left column: overall survey. Right column: C 1s core region. (a) Kevlar-29 fiber; (b) Kevlar-49 fiber; (c) terephthalamide; (d) isophthalamide; (e) phthalamide.

about the same, but they are about half of those ratios in (c), (d) and (e). This is consistent with the structural formulas shown in Chart I.

XPS C 1s Core Region Spectra. Figure 1 shows the C 1s core region spectra of Kevlar-29 and Kevlar-49 fibers, and terephthalamide, isophthalamide, and phthalamide in the right column. The C 1s spectra of (a) and (b) look the same, and those of (c), (d), and (e) are very similar, too, All these C 1s spectra were curve fitted with three peaks. From the lower binding energy, the first peak is the main aromatic C 1s signals from the γ and δ C atoms (labeled as *c*, *c'*, and *d* in Chart I), which was taken as 284.6 eV for calibration purposes. The second peak has a chemical shift of about 0.7 eV from the first main peak. This arises from the C 1s signals from those carbon atoms at the β position of the C═O groups (>*C*—C═O, labeled as *b* in Chart I) and those bonded to nitrogen atom (*C*–N, labeled as *b'* in Chart I). The third peak is the C 1s peak of the α C atoms which was double-bonded to oxygen and single-bonded to nitrogen (O═*C*—N, labeled as *a* in Chart I). This peak is shifted about 3.2 eV from the first peak in (a) and (b), while it is about 3.6 eV shifted in (c), (d), and (e). These three peaks have area ratios of about 4:2:1 in (a) and (b) but 2:1:1 in (c), (d), and (e). This is also consistent with the structure in Chart I.

XPS O 1s and N 1s Core Region Spectra. Figure 2 shows the O 1s spectra in the left column and the N 1s spectra in the right column. All the O 1s and N 1s spectra are very similar, having an intense peak wiht a rather symmetric peak shape. The O 1s peak appeared at about 530.3 eV, while the N 1s peak at 399.7 eV.

XPS Valence Band Spectra. The left column in Figure 3 shows the experimental valence band data. The middle column is the smoothed spectra from the left column. The smoothing was carried out by using a quadratic/cubic central smooth of 1.4-eV width and repeated 100 times. The right hand column is the second derivative spectra from the smoothed spectra in the middle column. The valence band spectra of the Kevlar fibers (a and b) have some different features than those of the organic compounds (c, d, and e). The range of features labeled from 1 to 3 are less distinct than those labeled from 4 to 7 in (a) and (b). The same range in (c), (d), and (e) are more distinct, and in particular they do not show the shoulder labeled 3 that appears in (a) and (b).

Peak 1 is the O 2s signal from the oxygen double-bonded to carbon atom, and it appears at about 26 eV in all the valence band spectra. Peak 2 is due to the N 2s signal, and it appears at about 22 eV. Peak 3 and peak 4 are the contributions from the C 2s signals. In (c), (d), and (e),

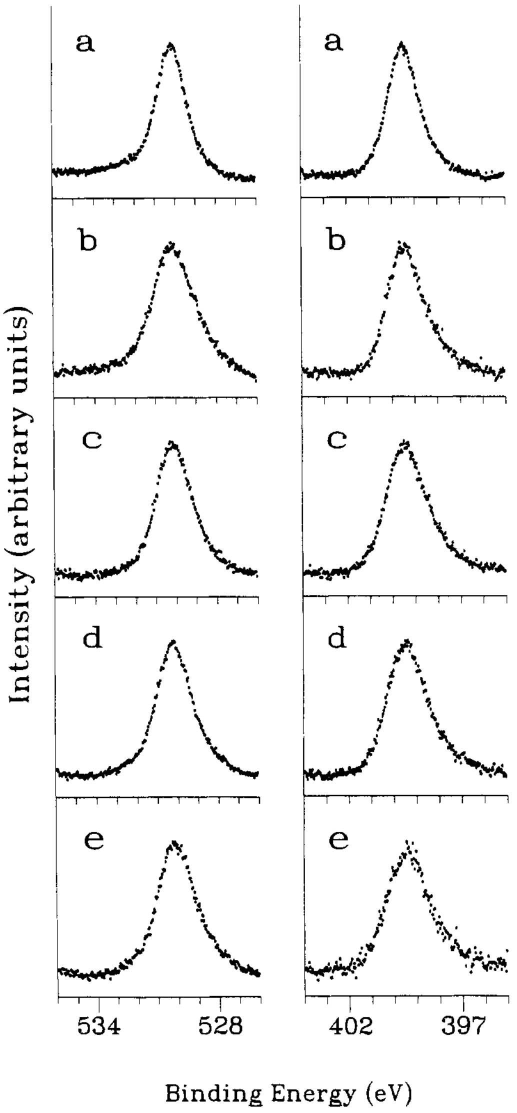


Figure 2. XPS O 1s and N 1s core region spectra. Left column: O 1s core region. Right column: N 1s core region. (a) Kevlar-29 fiber; (b) Kevlar-49 fiber; (c) terephthalamide; (d) isophthalamide; (e) phthalamide.

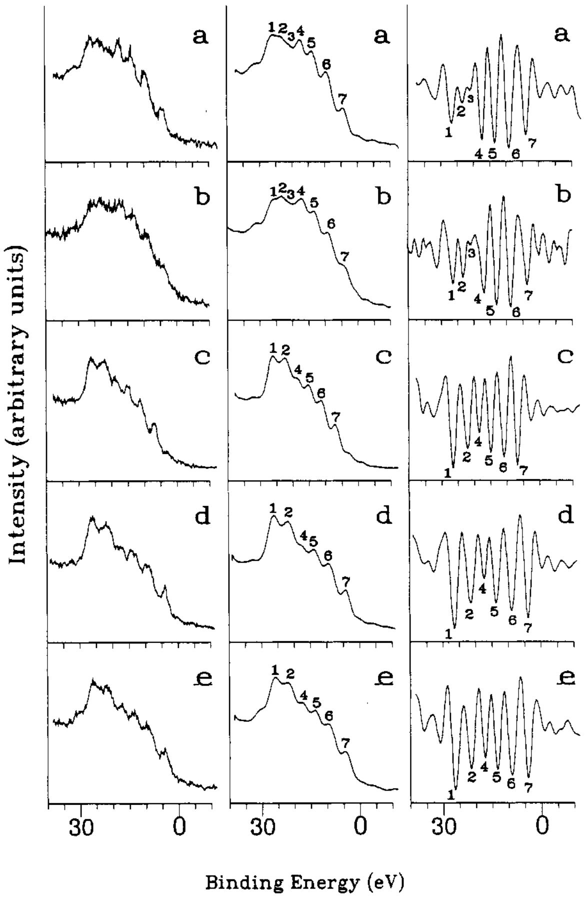


Figure 3. XPS valence band spectra. Left column: original valence band spectra. Middle column: smoothed valence band spectra. Right column: second derivative spectra. (a) Kevlar-29 fiber; (b) Kevlar-49 fiber; (c) terephthalamide; (d) isophthalamide; (e) phthalamide.

Table II. Peak Positions in the Experimental and Calculated Valence Band Spectra

	peak separations in Figures 3–5					
spectrum label[a]	1–2	1–3	1–4	1–5	1–6	1–7
3-a (5-a)	3.3	5.7	9.3	13.0	17.4	22.5
3-b (5-b)	3.1	5.5	9.6	13.4	17.6	22.6
(5-c)	*3.5*	*4.4*	*8.0*	*10.7*	*14.3*	*18.9*
(5-d)	*3.2*	*6.7*	*9.4*	*12.8*	*17.4*	*21.5*
3-c (4-a)	4.4		8.0	11.5	15.6	19.6
3-d (4-c)	5.0		9.1	12.9	17.4	22.5
3-e (4-e)	4.9		9.1	12.9	17.3	22.2
4-b	*3.5*		*6.0*	*12.8*	*17.0*	*21.2*
4-d	*3.8*		*6.4*	*13.4*	*18.1*	*21.8*
4-f	*3.6*		*9.2*	*13.2*	*18.4*	*21.6*
4-g	5.0	6.4	11.0	13.3		
4-h	*5.0*	*6.7*	*12.8*	*14.7*		

[a] Calculated results are shown in italics.

the intensity of peak 4 is lower than that in (a) and (b), and feature 3 did not appear. This is because the aromatic carbon atom concentration is much lower in terephthalamide, and its isomers than in Kevlar fiber (see the structures in chart I) and feature 3 could be covered by the much more intense peak 2 in (c), (d) and (e). Peaks 5, 6, and 7 are the features involving C 2p, N 2p, and O 2p contributions. In the valence band XPS spectra, relative peak positions or separations between peeks are more interesting than the absolute peak positions. Table II lists the separation (in eV) of peak 1 from all the other peaks (2–7). The separations are similar for (a) and (b), and for (d) and (e), but they are significantly different between (a and b) and (c, d, and e), with (c) having different peak separations from (d) and (e). Our previous work[1–9] showed that valence band XPS spectra are capable of revealing more subtle chemical differences on the surface than core level XPS spectra. However, valence band XPS probes more deeply into the surface due to the higher electron kinetic energy involved and so is less surface sensitive than the core region. In this work, the core level spectra of C 1s, O 1s, and N 1s regions again do not show as much of a difference as those found in the valence band spectra of these samples, even though curve-fitting the core regions can increase the chemical information content of the core level spectra. This difference is particularly true when the isomers are concerned.

Valence Band Xα Calculations. Our previous work[1,6–9] also showed that Xα calculations could be used to interpret the experimental valence band XPS data and to predict the valence band spectrum of new materials. In this work, multiple-scattered wave Xα calculations were first performed on benzene, and the isomers terephthalamide, phthalamide, and isophthalamide. These compounds were selected because the structural unit of Kevlar can be split into terephthalamide and benzene as shown

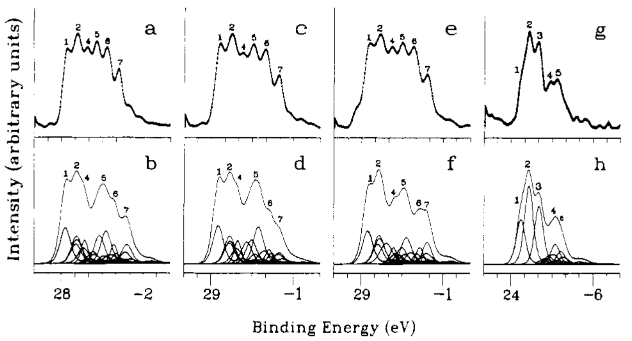


Figure 4. XPS valence band spectra and Xα calculation results for model compounds. Top row: experiment spectra with nonlinear background removed. Bottom row: X-alpha calculation results of model compounds. (a and b) terephthalamide; (c and d) isophthalamide; (e and f) phthalamide; (g and h) benzene.

in Chart I, and that these compounds are easily available and can be readily analyzed by XPS. The Kevlar spectrum can thus be constructed by adding together spectra calculated for these units, and the spectra of the individual units can be compared with the experimental data for these units. This avoids a complex calculation of a very large molecule unit. We have found this approach to be effective in other polymer systems.[6,7]

The calculation results were converted to valence band spectra by the method described in the Experimental Section and were compared with the experimental XPS valence band spectra. Figure 4 shows the experimental data on the top row (a, c, e, and g), and the calculated spectra at the bottom row (b, d, f, and h). The experimental data for terephthalamide (a), isophthalamide (c), phthalamide (e), and benzene (g) were smoothed and had a nonlinear background[11] removed for comparison with the calculated spectra of terephthalamide (b), isophthalamide (d), phthalamide (f), and benzene (h), respectively. Although the spectral envelope shapes showed some difference, all the peak features in the experimental data (a, c, e, and g) have their matching peak features in the corresponding calculated spectra (b, d, f, and h), with the best agreement in benzene spectra (g and h). Table II also lists the peak separations of the benzene experimental spectrum and all the Xα calculated spectra. In the experimental data of terephthalamide and its isomer (a, c, and e), peak 1 at about 26 eV largely corresponds to O 2s character. Peak 2 at about 22 eV corresponds to mainly N 2s character. Peak 4 is due to largely C 2s character and the other peaks (5 to 7) arise from contributions of C 2p, N 2p and O 2p character. In the benzene experimental data (g), peaks 1, 2, and 3 (at 20, 17 and 14 eV, respectively) are the three characteristic mainly C 2s features of the benzene ring,[6] while peaks 4 and 5 (at 9 and 7 eV, respectively) are mainly due to C 2p character. All these assignments were confirmed by the Xα calculation results.

In the Xα calculated spectra of terephthalamide, isophthalamide and phthalamide (Figure 4 (b), (d) and (f)), peak 1 mainly contains O 2s contributions (61.1%, 64.1%, and 61.5%, respectively). Peak 2 is mainly due to the N 2s contributions (71.8%, 71.8%, and 68.8%, respectively). Peak 4 mainly arises from the C 2s features (91.0%, 90.7%, and 47.1%, respectively). Peaks 5 to 7 have more contributions from C 2p, O 2p, and N 2p character. The Xα calculated spectrum of benzene (Figure 4h) also agreed well with the experimental data in terms of the peak assignments.

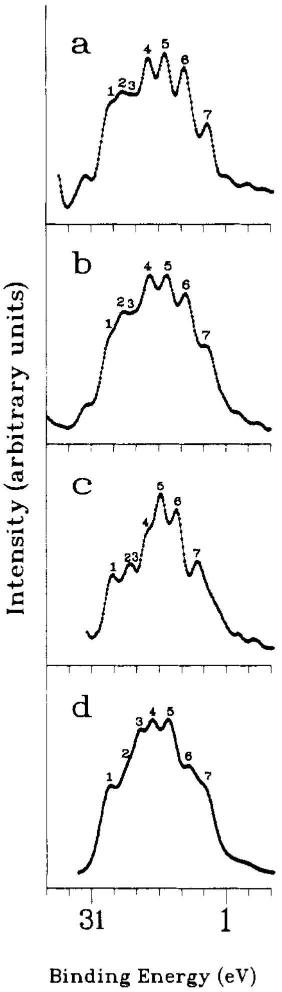


Figure 5. XPS valence band experiment spectra of Kevlar fibers and synthesized spectra from model compounds. (a) Experiment data of Kevlar-29 fiber (nonlinear background removed). (b) Experiment data of Kevlar-49 fiber (nonlinear background removed). (c) Synthesized from experiment data of model compounds (Figure 4a,g). (d) Synthesized from calculated data of model compounds (Figure 4b,h).

An important result that comes from the experimental data in Figures 3 and 4 and Table II is that the separations between peak 1 and the other peaks (2–7) are greater for isophthalamide and phthalamide than for terephthalamide, suggesting that valence band XPS can be used to distinguish between these isomers. The Xα calculations confirm that the separations between peak 5 and 6 should follow this trend, though the agreement between the experimental data and the calculated spectra was not perfect.

The experimental valence band data of terephthalamide and benzene (Figure 4a, g) were added together to generate a new spectrum as shown in Figure 5c. This spectrum was used to compare with the experimental valence band data of the Kevlar-29 fiber (Figure 5a) and Kevlar-49 fiber (Figure 5b). The experimental spectra of the Kevlar fibers in Figure 5a,b were also smoothed and had a nonlinear background removed.

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The Xα calculated spectra of terephthalamide and benzene (Figure 4b,h) were added together to generate another new spectrum as shown in Figure 5. In terms of the spectral shape, one may say that Figure 5c is not as close to 5a and 5b as 5d. However, both 5c and 5d clearly have all the peak features found in 5a and 5b. The peak positions in 5c and 5d are also quite close to those in 5a and 5b, with 5d better than 5c. Table II also lists all the peak separations of all the spectra in Figure 5. The peak assignment is about the same as for the compounds presented in Figures 3 and 4.

The approach of generating a polymer spectrum from the spectrum of the components of the repeat unit can be effective. This is illustrated by the agreement between the polymer spectrum generated from the experimental spectrum of the repeat unit components (Figure 5c). The synthesized spectrum in Figure 5d generated in the same way but using the spectra calculated from the Xα calculations does not give such good agreement to the experimental data of the actual Kevlar fiber samples, but the method can be effectively used to interpret the valence band structure and to predict the valence band spectrum of Kevlar and other polymer materials.[6-9] It is particularly useful when the polymer structure is complicated and the valence band experiment data are too complex to be easily understood, because the method may be used to predict the possible valence band spectrum.

Conclusions

The Kevlar fiber and other organic samples (e.g., isomers of terephthalamide, isophthalamide and phthalamide) can be well analyzed by XPS valence band spectra. The differences in the valence band spectra of the isomers indicate that the valence band XPS can be used to distinguish those compounds, which usually have identical core level XPS spectra.

The Kevlar fiber valence band can be modeled from either the experimental spectra of the repeat unit components or the calculated spectra of those components. The agreement between the experimental XPS valence band spectra and the Xα calculated spectra of the compounds may indicate that the surface of those compounds is representative of their bulk.

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