

Surface Molecular Structure of Self-Assembled Alkanethiols Evidenced by UPS and Photoemission with Synchrotron Radiation

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Received: September 25, 1996; In Final Form: December 5, 1996[®]

With the aim of investigating the configurational and conformational characteristics of monolayers of alkanethiols on gold by means of a photoemission experiment, we compare the valence data obtained from these layers using synchrotron radiation and ultraviolet photoemission spectroscopy (UPS). The incident energy used for synchrotron radiation has been chosen very close to the Cooper minimum of the 5d levels of gold, in order to limit as much as possible interference from the substrate. The recorded spectra differ markedly from one sample to another, notwithstanding their closely related chemical nature. These variations are compared consistently with semiquantitative simulations on model clusters and found thereby to reflect specifically the influence of the connectivity and of specific interactions on the electronic structure of long hydrocarbon chains.

1. Introduction

Characterization of the molecular structure of organic surfaces and interfaces is a scientific challenge of continuing importance for understanding properties of technologically useful organic materials. Electron spectroscopies have an important role to play in this context, since they can be used to collect highly specific information on the molecular structure of the investigated samples. Combined experimental and theoretical studies^{1–6} have indeed built over the years evidence of direct relationships between the electronic structure and the molecular architecture. Owing to their very small sampling depth, photoelectron spectroscopies offer a direct and highly specific insight into the chemical bonding, configurational, or conformational characteristics at the extreme surface of polymer materials and within organic thin films. This potential is worth being explored, since the more usual techniques for structural analysis (X-ray diffraction, infrared, Raman) are in general less convenient in surface characterization and because the reliability of techniques such as STM or AFM is most often impeded by a necessary preconditioning of organic samples.

Previous works on thick films (thicker than 1 μm) and gas phase samples of saturated hydrocarbon chains have shown that XPS valence spectra contain useful information on their primary and secondary structure.^{7–10} High-resolution valence XPS measurements were used to study the changes induced in the electronic structure by different molecular conformations and configurations. In particular, several theoretical investigations on large saturated hydrocarbon chains^{11–13} or cycloalkane compounds¹⁴ have assessed evidence for striking conformational signatures at the top of the inner valence region of their ionization spectra. These signatures have been shown^{12–15} to relate to a mixing of the C_{2s} and $\text{C}_{2p} + \text{H}_{1s}$ states at the border of the inner and outer valence bands, as a result of long-range methylenic hyperconjugation interactions developing over zigzag planar segments or related structures. XPS measurements on

thin films and microcrystalline lamellae of polyethylene have confirmed¹⁶ these findings and impelled further investigations on polypropylene,¹⁷ or gaseous samples⁹ of *n*-pentane, *n*-hexane, cyclopentane and cyclohexane.

Along the lines of these studies,^{8–17} this work aims at an evaluation of the potential of photoelectron spectroscopies in the elucidation of the molecular structure of organic surfaces. For this purpose, we consider here self-assembled monolayers of alkanethiols, which from their well-defined composition, thickness, and molecular structure,^{18,19} provide particularly well-suited reference samples. In this study, specifically, we consider the monolayers obtained by grafting on gold the following compounds: octadecanethiol ($\text{CH}_3(\text{CH}_2)_{17}\text{SH}$), 1,9-nonanedithiol ($\text{HS}(\text{CH}_2)_9\text{SH}$), 1-cyclohexyl-12-dodecanethiol ($\text{C}_6\text{H}_{11}(\text{CH}_2)_{12}\text{SH}$), 1-cyclopentyl-12-dodecanethiol ($\text{C}_5\text{H}_9(\text{CH}_2)_{12}\text{SH}$), and 1-cyclobutyl-13-tridecanethiol ($\text{C}_4\text{H}_7(\text{CH}_2)_{13}\text{SH}$). These molecules are chemically very similar, but differ in their primary and secondary structure. By comparing the synchrotron and UPS spectra of the self-assembled monolayers derived from these compounds, we intend to make a preliminary assessment of the extent to which variations in the connectivity and conformation of chains manifest themselves through the interplay of their electronic structure.

In the case of self-assembled thiols, however, one of the problems that has to be dealt with is the presence of a very intense Au 5d signal superimposed to the valence band of the organic material. The film thickness is indeed fixed by the length of the molecules, i.e. 1–2.5 nm, and XPS measurements probe the gold substrate to such an extent that the information on the organic film itself is completely hidden. Moreover, the photoionization cross section of the gold 5d levels, much larger than those of C 2s and C 2p, further reduces the hope of using XPS for valence spectra recorded in the case of ultrathin films. Therefore, it is interesting to work with a photon energy chosen in such a way that the ionization cross section of the 5d levels of gold is minimum, i.e. 200 eV. With a photoionization cross section of the gold 5d levels proportionally much lower than

[®] Abstract published in *Advance ACS Abstracts*, January 15, 1997.

for XPS, UPS (He I) also overcomes to a certain extent the problem of interference from the substrate.

In section 2, we briefly describe some experimental details of relevance for the present purpose, such as the purity and quality of the monolayers, as well as the conditions in which the UPS and synchrotron measurements have been obtained. In section 3, after comparing the experimental results among themselves, we undertake a systematic structural investigation of the monolayers by comparison with theoretical simulations dealing at a semiquantitative level with the leading electronic correlation effects.

2. Experimental Details

Materials. Gold substrates were prepared by evaporation of gold (~ 100 nm) onto silicon wafers (111). The non-commercially available α -cycloalkyl- ω -alkanethiols ($C_nH_{2n-1}-(CH_2)_mSH$) are prepared from the coupling of the Grignard reagents $C_nH_{2n-1}MgBr$ with 1,12-dibromododecane. The Grignard reagent used for the synthesis of the 1-cyclobutyl-13-tridecanethiol is $C_4H_7(CH_2)MgBr$. Combining the product of this reaction with thiourea leads to the α -cycloalkyl- ω -alkanethiol. Octadecanethiol (Aldrich 98%) and 1,9-nonanedithiol (Aldrich 95%) have been used as received, and absolute ethanol was obtained by distillation of denatured ethanol (Aldrich 95%).

Preparation of Monolayers. Monolayers are formed by the spontaneous adsorption of the alkanethiols onto the gold substrates. Prior to their use, the gold substrates are cleaned to ensure a good adsorption of the thiols. The surfaces are freed from contaminants by oxygen plasma treatment. Adsorption is then carried out from 10^{-3} M solutions of alkanethiols using absolute ethanol as a solvent, by immersing the gold substrates for 2 h in these solutions. After removal from the solution, the samples are rinsed twice with n-hexane and absolute ethanol and dried in an argon stream.

Quality of the Monolayers. The atomic ratios C/S, obtained by comparison of the area of the photoemission peaks corresponding to the C 1s and S 2p levels, are very close to the expected theoretical value: C/S ≈ 18 for the octadecanethiol and 1-cyclohexyl-12-dodecanethiol monolayers, C/S ≈ 4.5 for the 1,9-nonanedithiol monolayer, and C/S ≈ 17 for the 1-cyclopentyl-12-dodecanethiol and 1-cyclobutyl-13-tridecanethiol monolayers. These ratios have been obtained from X-ray photoemission spectra (XPS) recorded using the (Al K $\alpha_{1,2}$) monochromatized radiation (1486.6 eV). No oxygen contamination could be found in these spectra.

UPS Measurements. Photoelectron spectra were obtained on an ESCA-Scienta-300 spectrometer using the He I light (21.21 eV). The takeoff angle is modified by rotation of the sample. The angle between the detector and the incident direction of the photons and the angle between the axis of rotation of the sample and the incident beam have both been fixed at 45°. The binding energies of the valence band lines in the UPS spectra are referenced to the vacuum level. The Fermi level of gold is measured at 4.65 eV.

Synchrotron Radiation Measurements. The spectra have been recorded at Desy (HASYLAB), Hamburg, Germany, using a photoemission spectrometer with a cylindrical mirror analyzer (Flipper II). The incident angle of the photons has been fixed at 45°. The photon energy ranges from 15 to 160 eV. The equipment used is described elsewhere.²⁰

3. Results and Discussion

3.1. Valence Photoemission Measurements. (a) *Synchrotron Radiation Measurements.* Figure 1 presents the valence

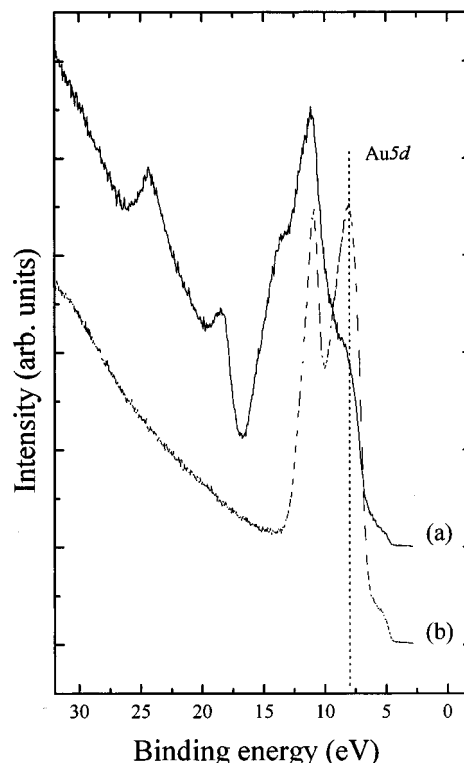


Figure 1. Valence spectra of the octadecanethiol monolayer (a) and the gold substrate (b), for an incident energy of 70 eV.

region of the octadecanethiol monolayer and of the clean gold substrate, for an incident energy of 70 eV. By comparing the spectra displayed in this figure, it is easily noted that the structure around 8.5 eV in the spectrum of the monolayer belongs to gold (5d levels). This structure manifests itself as a shoulder in the valence region recorded on the octadecanethiol monolayer (Figures 1a and 2d). When the incident energy increases from 70 to 150 eV (Figure 2), the intensity of this shoulder at 8.5 eV decreases and becomes barely visible at 150 eV. This will justify the use of a photon energy of 150 eV for further synchrotron measurements. At this energy the contribution of the 5d orbitals of gold is insignificant, since we are rather close to the Cooper minimum, at about 200 eV.²¹

At an incident energy of 150 eV (energy beyond which we cannot work under favorable conditions with the equipment used), the photoionization cross section of the gold 5d levels is about 1.3 times larger than that of C 2s and 5 times larger than that of the C 2p levels.²¹ The C 2s levels are not distorted by the gold contribution. To fully assess the origin of the structure at 8.5 eV, we subtracted the gold spectrum from that of the monolayer, with a variable weight since the electron mean free path in the monolayer is unknown (Figure 3). From that figure, it can be seen that the structure at 8.5 eV disappears when the contribution of gold in the monolayer spectrum is reduced, justifying its assignment to the 5d orbitals of gold. Despite the uncertainty on the intensity of the gold contribution, the results of the subtraction are quite clear as for the region around 8.5 eV.

Figure 4 reports the valence spectra of the five alkanethiol monolayers considered here, at an incident energy of 150 eV. In this section, we mostly focus on the inner valence band (C 2s), leaving the interpretation of the outer valence region (C 2p) to the better resolved UPS measurements.

The C 2s band of the octadecanethiol compound (Figure 4a) consists of two peaks that are located 5.5 eV apart, the one at a lower energy (19.3 eV) being more intense. For the

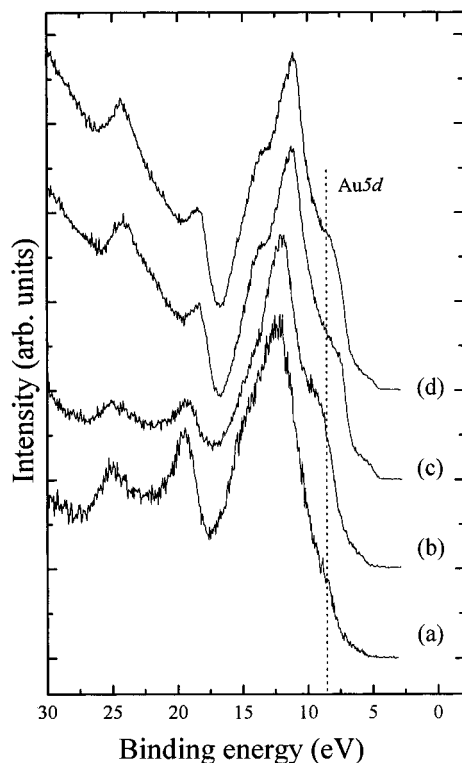


Figure 2. Valence spectra of the octadecanethiol monolayer for an incident energy of 150 eV (a), 130 eV (b), 80 eV (c) and 70 eV (d).

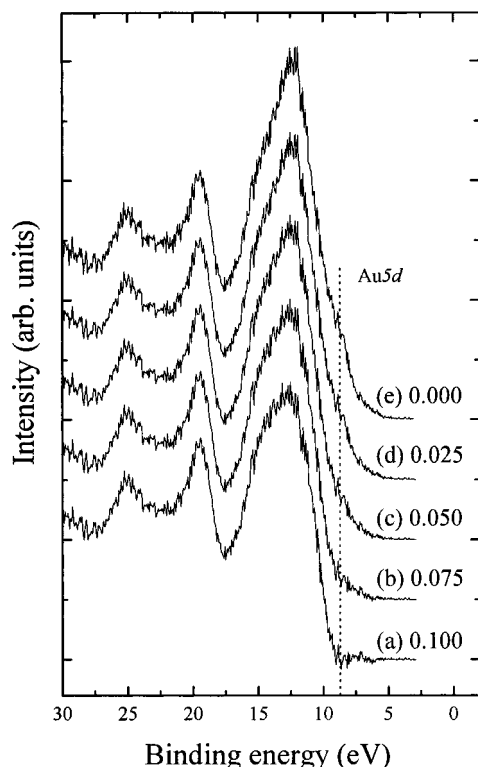


Figure 3. Valence spectra of the octadecanethiol monolayer for an incident energy of 150 eV, after removal of the contribution of the substrate. The different curves are characterized according to the variable weight assigned to the gold signal.

1,9-nonanedithiol film, the C 2s region consists also essentially of two peaks situated at 18.5 and 22.3 eV (Figure 4b). The peak at the top of the inner valence band (18.5 eV) has a much weaker intensity than the peak bordering the inner valence region of octadecanethiol. It is further found to fall 0.8 eV below. As

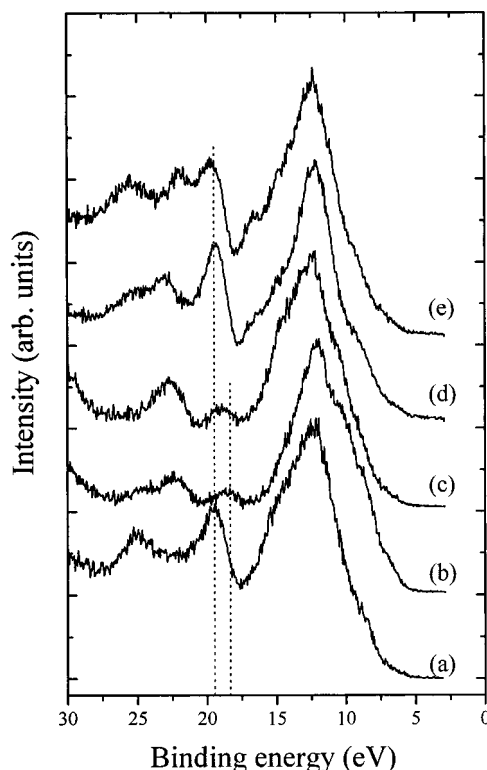


Figure 4. Valence spectra of the octadecanethiol (a), 1,9-nonanedithiol (b), 1-cyclohexyl-12-dodecanethiol (c), 1-cyclopentyl-12-dodecanethiol (d), and 1-cyclobutyl-13-tridecanethiol monolayers (e) for an incident energy of 150 eV.

we shall see below, these differences are consistent with a departure of the chain structure from the zigzag planar conformation.

The inner valence region of the 1-cyclohexyl-12-dodecanethiol monolayer (Figure 4c) contains a weak peak at 18.8 eV and a more intense one at 22.6 eV. In this case, one can notice a shift of 0.5 eV between the peak at the top of the inner band and the one recorded for the octadecanethiol monolayer. At this stage, it is important to relate this observation to the fact that the above mentioned monolayer has been prepared on a several weeks old substrate, which, as we shall see further, induces possibly some significant changes in the conformation of the *n*-alkyl segments.

The outer valence band recorded for the 1-cyclopentyl-12-dodecanethiol monolayer (Figure 4d) is dominated by an intense and rather narrow structure at 12 eV. The C 2s region is bordered on its low-binding-energy edge by a sharp and intense peak at 19.4 eV. This region displays also a much more broadened structure at 23 eV and a shoulder at 25 eV. Three peaks are contained in the C 2s band in the case of 1-cyclobutyl-13-tridecanethiol (Figure 4e): 19.6, 22.0, and 25.3 eV.

(b) UPS (He I) Measurements. Figure 5 presents the He I spectra of the octadecanethiol, 1-cyclohexyl-12-dodecanethiol, 1-cyclopentyl-12-dodecanethiol, and 1-cyclobutyl-13-tridecanethiol monolayers. As can be seen from that figure, the contribution of the gold substrate in the monolayer spectrum is negligible, with a takeoff angle (TOA) of 20°. An exception to this observation arises with the 1,9-nonanedithiol monolayer of very small thickness (~ 5 Å), for which the valence spectrum is totally dominated by the gold features. With UPS, it is thus in this case impossible to extract information about the C 2p band. We therefore do not present UPS results for the 1,9-nonanedithiol monolayer.

Figure 5 presents the He I spectra of the octadecanethiol, 1-cyclohexyl-12-dodecanethiol, 1-cyclopentyl-12-dodecanethiol,

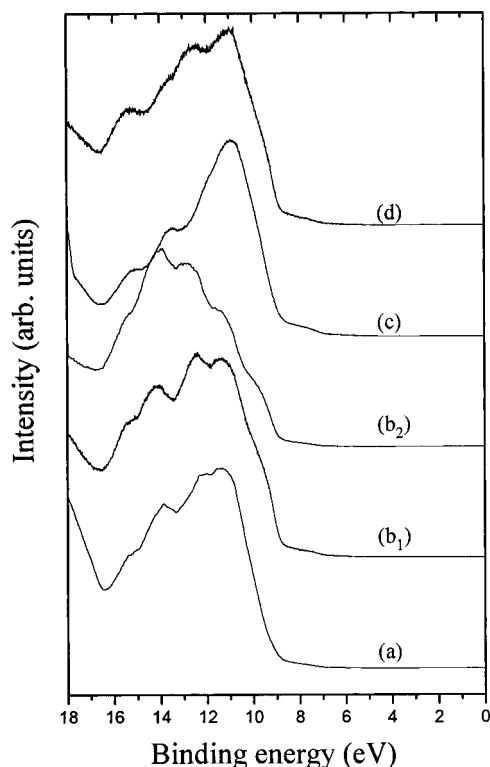


Figure 5. UPS spectra (He I) of the octadecanethiol (a), 1-cyclohexyl-12-dodecanethiol (b), 1-cyclopentyl-12-dodecanethiol (c), and 1-cyclobutyl-13-tridecanethiol (d) monolayers recorded at a TOA of 20°. b_1 corresponds to the monolayer prepared on a freshly evaporated gold substrate and b_2 to that prepared on an old substrate.

and 1-cyclobutyl-13-tridecanethiol monolayers. Two spectra are displayed for the 1-cyclohexyl-12-dodecanethiol film: one of these (b_1) has been recorded on a monolayer prepared on a freshly evaporated gold substrate, and the other one (b_2) on a monolayer prepared on a several weeks old substrate. The outer valence spectrum of the octadecanethiol sample is composed of four peaks (11.3, 12.1, 13.8, and 15.3 eV) of decreasing intensity with higher binding energies. The 1-cyclohexyl-12-dodecanethiol outer valence spectrum (b_1) contains a shoulder around 9.6 eV and four rather well-resolved peaks at 11.3, 12.4, 14.1, and 15.5 eV. The other spectrum (b_2) contains also five peaks but with very dissimilar relative intensities. For the 1-cyclopentyl-12-dodecanethiol monolayer (Figure 5c), an intense and dominating structure is found at 10.9 eV, together with two smaller peaks at 13.5 and 15.2 eV. Finally, four peaks are found in the outer valence region of the 1-cyclobutyl-13-tridecanethiol monolayer (Figure 5d): at 10.9, 12.5, 13.6, and 15.1 eV.

3.2. Theoretical Simulations. Recent theoretical simulations^{11–13,15} of the X-ray photoionization spectra of large saturated hydrocarbon chains indicate that the normally prevailing zigzag planar conformation is specifically fingerprinted by a high and narrow peak at the top of the inner valence band, in excellent agreement with the XPS signal recorded from an amorphous sample of polyethylene (Figure 6).¹⁶ This signature reflects a much denser accumulation of one-electron energy levels around 18 eV. It ultimately relates to the development of constructive through-space interactions in a long-range hyperconjugation pattern,^{12–15} in the form of binding overlaps between the H_{1s} and C_{2py} atomic orbitals located on adjacent and all-staggered methylenic groups (CH_2).

As contrasted with a zigzag planar chain, methylenic hyperconjugation in a folded structure is prevented because of the relative disposition of a few CH_2 groups in left conformation.

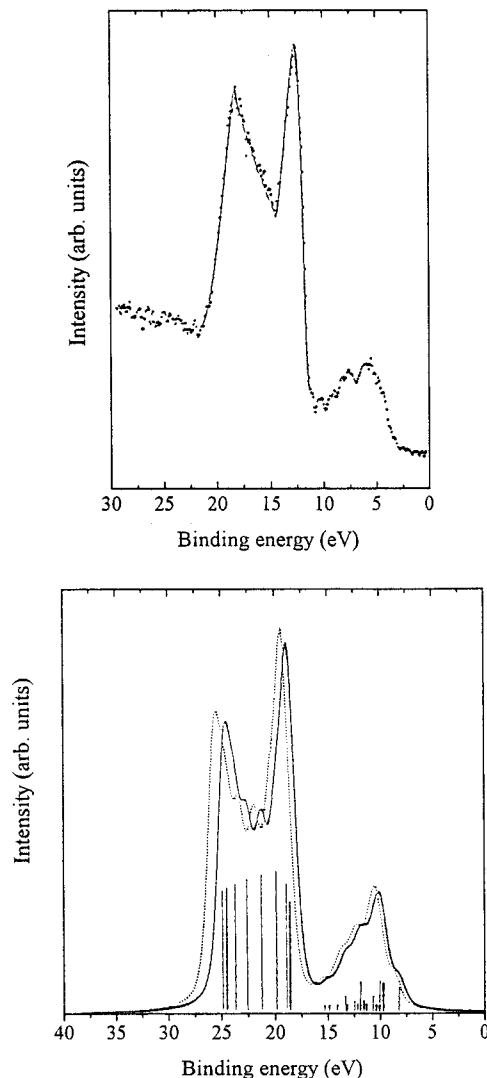


Figure 6. XPS valence spectrum of amorphous polyethylene (a) and theoretical XPS spectra of zigzag planar n -nonane (b).

Any disruption of the long-range hyperconjugation pattern tends to result in a more homogeneous distribution of energy levels at the top of the inner valence band. Accordingly, as the extra stabilization due to hyperconjugation is ruled out in this case, the highest levels in the inner valence band shift by about 1 eV^{12,15} toward lower binding energies. As compared with zigzag planar structures, the final outcome of a fold of the hydrocarbon chain is therefore a net broadening of the peak at the top of the inner valence band.

To reliably elucidate questions concerning the relative disposition of lines, one has to rely on quantitative theoretical grounds, coping with the leading electronic correlation and relaxation effects on binding energies, together with the dispersion of photoionization intensity into satellite (shake-up) structures. For this purpose we use the so-called diagonal two-particle-hole Tamm–Dancoff approximation scheme (ref 13 and references therein), an approach that already has proved to yield fairly good agreement with inner valence records obtained on saturated hydrocarbons,^{9,13} despite the neglect of hole-mixing (i.e. configuration interaction) effects in the cation. Another drawback in the simulations considered here lies in the neglect of cross section effects, which are known to be highly sensitive to the composition of orbitals.

As shown recently by a series of calculations fully coping with these effects, which are described in the most thorough investigation²³ available to date on the correlation states of large

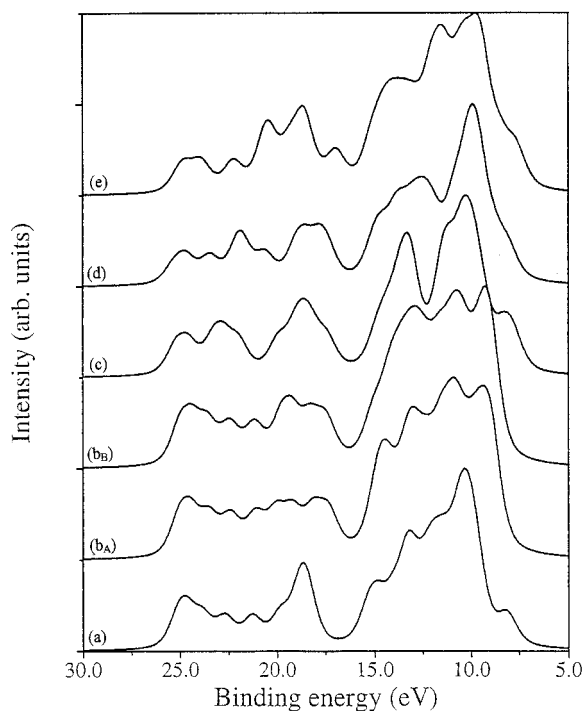


Figure 7. Density of states calculations for the zigzag planar *n*-nonane (a), fold A (*b_A*) and fold B (*b_B*) of *n*-nonane, 1-cyclohexylbutane (c), 1-cyclopentylpentane (d), and 1-cyclobutylhexane (e).

alkane compounds, one can reasonably retain the idea of the one-particle picture of ionization for saturated hydrocarbons, up to a binding energy threshold of about 23 eV. The main spectral features characterizing the molecular conformation of saturated hydrocarbons remain therefore free from shake-up satellites,²³ justifying therefore the neglect of configuration-mixing effects in the cation.

Figure 7 presents ionization spectra calculated for model oligomers (Figure 8) of the compounds considered in this work: the *n*-nonane in its zigzag planar and folded conformations, the 1-cyclohexylbutane, the 1-cyclopentylpentane, and the 1-cyclobutylhexane. The spread function used to convolute these spectra has been taken as a linear combination of one Gaussian and one Lorentzian with equal weight and width (fwhm = 1.5 eV).

These simulated spectra exhibit significant differences from one compound to the other, in relationship with disturbances of the methylenic hyperconjugation pattern and the enforcement of near energy degeneracies with cyclization of the terminal alkyl segment. This confirms the proposition that photoionization spectra can be successfully used to assess the structural characteristics of the investigated layers, an observation that we shall now exploit in a detailed comparison between theory and experiment.

3.3. Detailed Characterization of the Monolayers. (a) *Octadecanethiol and 1,9-Nonanedithiol.* The zigzag planar *n*-nonane theoretical C 2p spectrum (Figure 7a) is similar to the UPS spectrum of octadecanethiol (Figure 5a). It contains indeed four peaks situated around the same binding energies and with gradually decreasing intensity. The C 2s theoretical band (Figure 7a) is formed by two main peaks separated by 5.8 eV, which reproduce rather accurately the inner band recorded at 150 eV (Figure 4a). The high and narrow peak at the top of the inner valence band (19.3 eV) of octadecanethiol is typical of a zigzag planar conformation. This confirms that linear alkanethiols adopt a conformation typical of the crystalline paraffines,¹⁸ as it has already been shown by infrared reflection

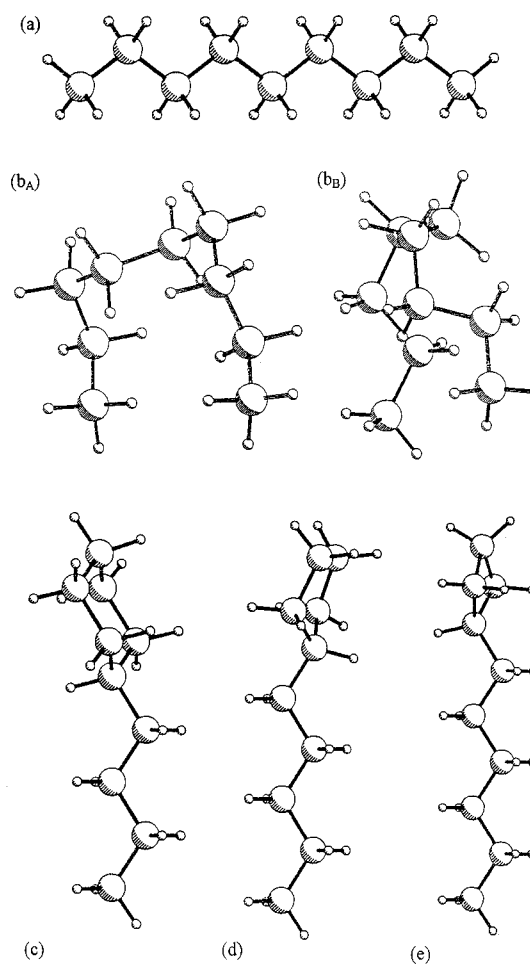


Figure 8. Model systems corresponding to the alkanethiols studied: zigzag planar *n*-nonane (a), fold A and fold B of *n*-nonane (b), 1-cyclohexylbutane (c), 1-cyclopentylpentane (d), and 1-cyclobutylhexane (e).

spectroscopy.^{24–27} The inner valence spectrum of the 1,9-nonanedithiol compound (Figure 4b) consists also essentially of two peaks, but the one at the top of the inner band has a much weaker intensity and lies at a lower binding energy compared to the corresponding one in zigzag chains, in fair agreement with the simulations drawn (Figure 7 *b_A,b_B*) for folded *n*-nonane clusters (Figure 8 *b_A,b_B*). This confirms the folded structure of the molecules in the self-assembled layer of 1,9-nonanedithiol on gold. At this stage, however, it is yet impossible to determine whether this layer consists dominantly of folds of the (*b_B*) type (Figure 8), as found in the [110] growth sector of crystalline polyethylene.^{9,15}

(b) *1-Cyclohexyl-12-dodecanethiol. Monolayer Prepared on a Freshly Evaporated Gold Substrate.* The shoulder around 9.5 eV in the UPS spectrum (Figure 5b₁) is clearly visible on the calculated spectrum (Figure 7c). Two pairs of peaks separated with a small gap are observed in the UPS spectrum as well as in the theoretical spectrum. The well-marked peak found around 14 eV in the simulation also fits fairly well with a shoulder in the synchrotron spectrum (Figure 4c). This feature is typical of the cyclohexane ring in the chair conformation,^{14,15,23} enabling stabilizing interactions along a transannular methylenic hyperconjugation pattern. An overall satisfactory agreement with the simulation drawn (Figure 7c) for the 1-cyclohexylbutane cluster (Figure 8c) is therefore obtained with the spectra recorded on this sample.

Monolayer Prepared on an Old Substrate. In this case, the shape of the UPS spectrum (Figure 5b₂) is rather dissimilar to

the theoretical simulation (Figure 7c). A major difference lies in the intensity and position of the peak at the top of the inner valence band (Figure 4c). As compared with experiment, this peak in the theoretical simulation is slightly too intense and appears shifted by about 0.6 eV toward higher binding energies. As these differences are consistent with the variations found in the theoretical spectra from the zigzag planar form of *n*-nonane to folded conformations, one may conclude a bad organization of the 1-cyclohexyl-12-dodecanethiol monolayer, which should then mostly contain folded structures. Spectrum b_2 is therefore most likely the outcome of a mixing between the signal of the cyclohexyl and that of the alkane chains in folded conformations. The old substrate used for this film has probably impeded the formation of a well-ordered monolayer.

(c) *1-Cyclopentyl-12-dodecanethiol*. The shape of the outer valence band (C 2p) on the UPS (Figure 5c) as well as on the synchrotron spectrum (Figure 4d) is typical of the cyclopentyl moiety: for an ideal structure of D_{5h} symmetry, the six outermost ionization lines fall in three degenerate pairs within a short energy interval, yielding a high and narrow peak at the top of the C 2p region. The C 2s region recorded by synchrotron radiation is similar to the theoretical band (Figure 7d) where three main peaks can be observed (19.0, 22.7, and 25.0 eV). The intense and narrow structure at 19.4 eV on the experimental spectrum indicates a zigzag planar conformation for the linear segments of the molecules.

Interestingly, the shape of the signal recorded at the top of the outer valence band differs remarkably from that presented elsewhere⁹ for gas phase samples of cyclopentane, an observation that calls for a more detailed analysis. As explained in ref 9, a striking broadening of the peak at 11.0 eV gives evidence for strong vibronic coupling effects in the cation, a result of the high degree of degeneracy of the outermost energy levels of cyclopentane, yielding possibly fast rotating vibrations in the molecular cation. The emergence of an intense peak at the top of the outer valence region of the 1-cyclopentyl-12-dodecanethiol (Figures 4d and 5c), in fairly good agreement with theoretical simulations (Figure 7d) that do not address a relaxation of the molecular structure in the ionized system, indicates that strong vibronic coupling effects are ruled out in this case, owing to the removal of energy degeneracies and the locking of rotons in the ring by the external alkyl segment.

(d) *1-Cyclobutyl-13-tridecanethiol*. The features of the C 2p theoretical (Figure 7e) and UPS spectra (Figure 5d) are similar: two peaks separated by about 1.5 eV and a well-marked peak around 15 eV. The C 2s region, in the experimental (Figure 4e) as well as in the calculated spectra, is made of two sharp peaks separated by about 2 eV and a much broader one around 25 eV. As with the 1-cyclopentyl-12-dodecanethiol monolayer, the intense and narrow peak at 19.6 eV indicates that the linear part of the chain is dominantly in its zigzag planar conformation. The cyclobutyl ring is also nicely fingerprinted from the overall shape of the outer valence region.

Besides solid states effects, the most likely explanation for the striking broadening of the innermost peak lies in strong interactions between excited states of the cation. As this peak falls much below the average energy threshold of 23 eV for shake-up transitions in saturated hydrocarbons,²³ it must undergo a severe breakdown of the molecular orbital picture of ionization,²⁵ and consists thereby of many satellites of weak intensity. Although this breakdown complicates seriously the interpretation of the innermost part of the spectrum, its apparent importance is also consistent with the presence of the cyclobutyl moiety. From a direct transposition of the results displayed in ref 23 for the cyclobutane compound, the shake-up lines derived from

the C 2s region must indeed spread over a large energy interval, as a result of strong cyclic strains in the investigated structure.

4. Conclusions and Outlook for the Future

UPS and photoemission with synchrotron radiation enable access to very specific information on the primary and secondary structures of ultrathin organic films. Although these monolayers are made of chemically related molecules, one can find typical signatures for each type of self-assembled layer. The differences between the spectra reflect directly the structural changes induced by the folding and by the cyclic structure at the end of the grafted hydrocarbon chains. The C 2s region recorded by synchrotron radiation reflects the development of methylenic hyperconjugation effects in the structures with dominating zigzag planar conformations, through the interplay of the line position and intensities. Structural assignment is further justified by the good agreement obtained between semiquantitative calculations on model clusters and the recorded signals. The nature of the process at the origin of structural signature implies that theory is a necessary companion to experiment for a sound interpretation of the valence spectra of organic monolayers.

In the case of the 1-cyclohexyl-12-dodecanethiol monolayer assembled on an old substrate, evidence has been found for a folded conformation of the *n*-alkyl segment. It has not been possible to record the valence spectrum with synchrotron radiation in the case of a freshly evaporated substrate. This bad organization of the film does not seem to concern the other monolayers, for which the valence spectra are similar for a new and an old substrate. This observation at least suggests that photoionization spectroscopy can be used to evaluate consistently the degree of organization in grafted ultrathin films. Besides the search for photoemission fingerprints of the primary and secondary molecular structure, this problem of bad ordering leads us therefore to new interesting prospects.

A very challenging problem, yet to be addressed, is to determine whether the disordering of the 1-cyclohexyl-12-dodecanethiol monolayer finds its origin in cluttering effects, which may not be so important when the cyclohexyl group is replaced by a cyclopentyl or a cyclobutyl. Thorough investigations on the grafting process itself should be conducted, using, for example, molecular dynamics simulations.

Acknowledgment. The support of R. L. Johnson (II Institut für Experimentalphysik, Universität Hamburg, Germany) during the synchrotron radiation part of this work was greatly appreciated. A.-S.D. is supported by FRIA (Fonds pour la Formation à la Recherche dans l'Industrie et l'Agriculture). M.D. and J.G. thank the NSFR (Belgian National Fund for Scientific Research) for their senior research assistant and research associate positions, respectively. This work was partly financed by the Région Wallonne (Project No. 3119) and by the Large Installation Programme of the European Commission and by the Bundesminister für Bildung, Wissenschaft, Forschung und Technologie (BMBF).

References and Notes

- (1) Delhalle, J.; André, J.-M.; Delhalle, S.; Pireaux, J.-J.; Caudano, R.; Verbist, J. J. *Chem. Phys.* **1974**, *60*, 595.
- (2) Salaneck, W. R. In *CRC Critical Reviews in Solid State and Materials Science*; CRC Press: Cleveland, 1985; Vol. 12, pp 267–296, and references therein.
- (3) Seki, K. In *Optical Techniques to Characterise Polymer Systems*; Bässler, H., Ed.; Elsevier: Amsterdam, 1989; p 115.
- (4) Boulanger, P.; Magermans, C.; Verbist, J. J.; Delhalle, J.; Urch, D. S. *Macromolecules* **1991**, *24*, 2757.
- (5) Boulanger, P.; Pireaux, J.-J.; Verbist, J. J.; Delhalle, J. J. *Electron Spectrosc. Relat. Phenom.* **1993**, *63*, 53.

- (6) Salaneck, W. R.; Brédas, J.-L. In *Organic Materials for Electronics*; Brédas, J.-L., Salaneck, W. R., Wegner, G., Eds.; North-Holland: Amsterdam, 1994; p 15.
- (7) Pireaux, J.-J.; Riga, J.; Caudano, R.; Verbist, J. J. In *Photon, Electron and Ion Probes of Polymer Structure and Properties*; Dwight, D. W., Fabish, T. J., Thomas, H. R., Eds.; ACS Symp. Series 162; American Chemical Society: Washington, DC, 1981; p 169.
- (8) Delhalle, J.; Deleuze, M. *J. Mol. Struct. (THEOCHEM)* **1992**, 261, 187.
- (9) Deleuze, M.; Delhalle, J.; Pickup, B. T.; Svensson, S. *J. Am. Chem. Soc.* **1994**, 116, 10715.
- (10) Riga, J.; Delhalle, J.; Deleuze, M.; Pireaux, J.-J.; Verbist, J. *J. Surf. Interface Anal.* **1994**, 22, 507.
- (11) Delhalle, J.; Delhalle, S.; Riga, J. *J. Chem. Soc., Faraday Trans. 2* **1987**, 83, 503.
- (12) Deleuze, M.; Denis, J.-P.; Delhalle, J.; Pickup, B. T. *J. Phys. Chem.* **1993**, 97, 5115.
- (13) Deleuze, M.; Delhalle, J.; Pickup, B. T. *Chem. Phys.* **1993**, 175, 427.
- (14) Deleuze, M.; Delhalle, J.; Pickup, B. T. *J. Phys. Chem.* **1994**, 98, 2382.
- (15) Deleuze, M. Etude de la Structure Electronique de Chaînes Modèles par l'Approche en Propagateurs à une Particule. Ph.D. Thesis, FUNDP-Namur, Belgium, 1993.
- (16) Delhalle, J.; Riga, J.; Denis, J.-P.; Deleuze, M.; Dosière, M. *Chem. Phys. Lett.* **1994**, 210, 507.
- (17) Famant, I.; Mosley, D. H.; Deleuze, M.; André, J.-M.; Delhalle, J. *Int. J. Quantum Chem.* **1994**, S28, 469.
- (18) Bain, C. D.; Troughton, E. B.; Tao, Y.-T.; Evall, J.; Whitesides, G. M.; Nuzzo, R. G. *J. Am. Chem. Soc.* **1989**, 111, 321.
- (19) Ulman, A. *An Introduction to Ultrathin Organic Films*; Academic Press: New York, 1991.
- (20) Johnson, R. L.; Reichardt, J. *Nucl. Instrum. Methods* **1983**, 208, 791.
- (21) Yeh, J. J.; Lindau, I. *Atomic Data Nucl. Data Tables* **1985**, 32, 1.
- (22) Duwez, A.-S.; Riga, J.; Han, B.-Y.; Delhalle, J. *J. Electron Spectrosc. Relat. Phenom.* **1996**, 81, 55.
- (23) Deleuze, M.; Cederbaum, L. S. *J. Chem. Phys.*, accepted for publication.
- (24) Laibinis, P. E.; Whitesides, G. M.; Allara, D. L.; Tao, Y.-T.; Parikh, A. N.; Nuzzo, R. G. *J. Am. Chem. Soc.* **1991**, 113, 7152.
- (25) Laibinis, P. E.; Nuzzo, R. G.; Whitesides, G. M. *J. Phys. Chem.* **1992**, 96, 5097.
- (26) Atre, S. V.; Liedberg, B.; Allara, D. L. *Langmuir* **1995**, 11, 3882.
- (27) Parikh, A. N.; Liedberg, B.; Atre, S. V.; Ho, M.; Allara, D. L. *J. Phys. Chem.* **1995**, 99, 9996.