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Valence and core-shakeup photoelectron spectra of solid polyacetylene and related free model molecules

M. P. Keane, A. Naves de Brito, N. Correia,* S. Svensson, L. Karlsson, B. Wannberg, and U. Gelius
Department of Physics, Uppsala University, Box 530, S-751 21 Uppsala, Sweden

Sten Lunell
Department of Quantum Chemistry, Uppsala University, Box 518, S-751 20 Uppsala, Sweden

W. R. Salaneck and M. Lögdlund
Department of Physics IFM, Linköping University, S-581 83 Linköping, Sweden

D. B. Swanson and A. G. MacDiarmid
Department of Chemistry, University of Pennsylvania, Philadelphia, Pennsylvania 19104
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The x-ray photoelectron spectrum of polyacetylene and the related model molecules ethene, 1,3-butadiene, and 1,3,5-hexatriene are studied with respect to the valence and C 1*s* shakeup regions. The interpretation of the polyacetylene spectra is accomplished by a detailed assignment of the gas-phase results. It is shown that the development of the band structure of solid polyacetylene can be followed step by step for the molecules. The electron correlation is shown to play a dominant role for the description of the inner-valence structures. The outermost band centered at 3 eV below the Fermi level is unambiguously assigned to the band structure arising from the out-of-plane π-type molecular orbitals. The polyacetylene shakeup spectrum exhibits several structures that have been assigned by comparison to experimental results and incomplete-neglect-of-differential-overlap–configuration-interaction calculations on the model molecules.

INTRODUCTION

Polyacetylene has been the subject of much attention during the past decade due to its unusual properties as a semiconductor as well as its conducting ability upon doping with a suitable element. The relatively simple geometrical structure of this material has made it the prototype for theoretical models dealing with conjugated polymers. A recent review of such studies is given in Ref. 1. Ultraviolet photoemission spectroscopy (UPS) and x-ray photoemission spectroscopy (XPS) spectra of polyacetylene have been recorded earlier by Salaneck *et al.*[2] and by Brundle *et al.*, as referenced,[3] although a detailed analysis of the spectra was not made. In earlier studies[4,5] we have used model molecules in the analysis of the electronic structure of larger polymer systems. In particular, these studies have been related to both core lines and shakeup states. In the case of polythiophene[6,7] it was possible to confirm an earlier model suggested for the thermochromism exhibited by this polymer. In the present paper we report a further study of a series of model molecules for the interpretation of both the core- and valence-photoelectron spectra of polyacetylene. High-resolution gas-phase XPS spectra of both the core-shakeup region and valence region of 1,3-butadiene (C_4H_6) and 1,3,5-hexatriene (C_6H_8) are presented along with recently recorded high-resolution spectra of polyacetylene. The XPS valence spectrum of ethene (C_2H_4) is also included for the sake of comparison. The model molecules represent the smallest oligomers of the infinite polymer chain.

EXPERIMENT

The gas-phase XPS spectra were recorded on a high-resolution electron spectrometer at the Department of Physics, Uppsala University. This spectrometer incorporates a monochromatized Al $K\alpha$ x-ray ($h\nu = 1487$ eV) excitation source.[8] The samples were commercially obtained and of spectroscopical purity ($>99.9\%$). The pressure in the gas cell was maintained below the threshold for inelastic scattering events, i.e., below about 0.2 mbar. The calibration of the gas-phase XPS valence spectra was performed from a comparison with the outermost line in earlier recorded UPS spectra.[9–12] The core lines were calibrated against the Ar $2p_{3/2}$, at 248.63 eV,[8] by simultaneously recording a spectrum from the gas mixture. In all recordings the temperature of the gas was room temperature (≈ 295 K).

The polyacetylene spectra were recorded on a high-resolution Scienta 300 series spectrometer at the Department of Physics, Uppsala University. The excitation was again performed by monochromatized Al $K\alpha$ x-rays.[13] The samples were essentially pure *trans*-polyacetylene [*trans*-$(CH)_x$], of the Shirakawa type produced at the Department of Chemistry, University of Pennsylvania. Although the samples had been stretched by about a factor of 2 ($l/l_0 \approx 2$), separate UPS studies using polarized light failed to show any orientation effects. No form of charge compensation was required in the recording of the spectra. The energies of the valence lines were calibrated to the Fermi level, which was taken as zero energy. The Fermi level was determined from Ag metal.

COMPUTATIONAL METHODS

The shakeup spectra from the gas-phase molecules have been analyzed with the aid of semiempirical calculations. The wave functions and energies were calculated from the equivalent core, $Z+1$ approximation, using the incomplete-neglect-of-differential-overlap–configuration-interaction (INDOCI) package of Zerner and coworkers.[14,15] The bond distances and angles for the molecules were taken from Ref. 16. Calculations were carried out for each symmetry-unique carbon atom in each molecule, i.e., in the case of 1,3-butadiene two independent calculations and for 1,3,5-hexatriene three independent calculations. The configuration-interaction calculations were performed so that all single $\pi \rightarrow \pi^*$ and $\sigma \rightarrow \sigma^*$ excitations were considered. In addition, a large selection of double excitations was included up to the program limit of approximately 200 final-state configurations; however, in all cases all double $\pi \rightarrow \pi^*$ transitions were present. The intensities were calculated using the SHAKEINT package of Lunell.[17] This program package incorporates the sudden approximation where the intensity of a given shakeup line is proportional to the factor $P_n = |\langle \Phi_n | \Psi_0 \rangle|^2$ where Ψ_0 is the wave function of the $N-1$ remaining electrons in the neutral molecule and Φ_n is the wave function corresponding to the nth state of the $(N-1)$ electrons in the singly ionized molecule.

RESULTS AND DISCUSSION

XPS valence spectra of the model molecules

The valence XPS spectra of ethene, 1,3-butadiene, and 1,3,5-hexatriene recorded in the present study are shown in Fig. 1. The first recording, using monochromatized x rays for excitation, of the valence-photoelectron spectrum of ethene was reported in Ref. 18. The present spectrum is taken at better resolution and with better statistics; in particular, the number of data points per eV is sufficient to reveal the detailed features of the photoelectron bands. No earlier monochromatized XPS recordings of the 1,3-butadiene and 1,3,5-hexatriene molecules could be found in the literature. Several structures in the spectra can be observed and are numbered in order of increasing binding energy. He I-excited UPS results for the outer valence region of these molecules are reported in Refs. 9–12. Also He II-excited spectra of the two former molecules, involving the energy region up to about 25 eV, have been presented in Ref. 9.

In all the spectra of Fig. 1 three more-or-less separate regions can be distinguished. The first region has a very low intensity in the XPS experiments presented here, whereas they tend to dominate the UPS. This region is associated with ionization from the molecular orbitals derived primarily from the C 2p and H 1s atomic orbitals, which have a very low atomic photoionization cross section in the high-energy limit.[19] In the XPS the spectra are dominated by the lines in the inner-valence region from approximately 18–25 eV. This region corresponds to ionization from the inner-valence orbitals which are mainly constructed from the C 2s atomic orbitals, as indicated in the figure. The third region at still higher energies shows several intense and broad structures that cannot be explained in terms of a one-electron model, since there is no one-to-one correspondence between molecular orbitals and structures in the spectra. This region is labeled the correlation region in the figure. It should

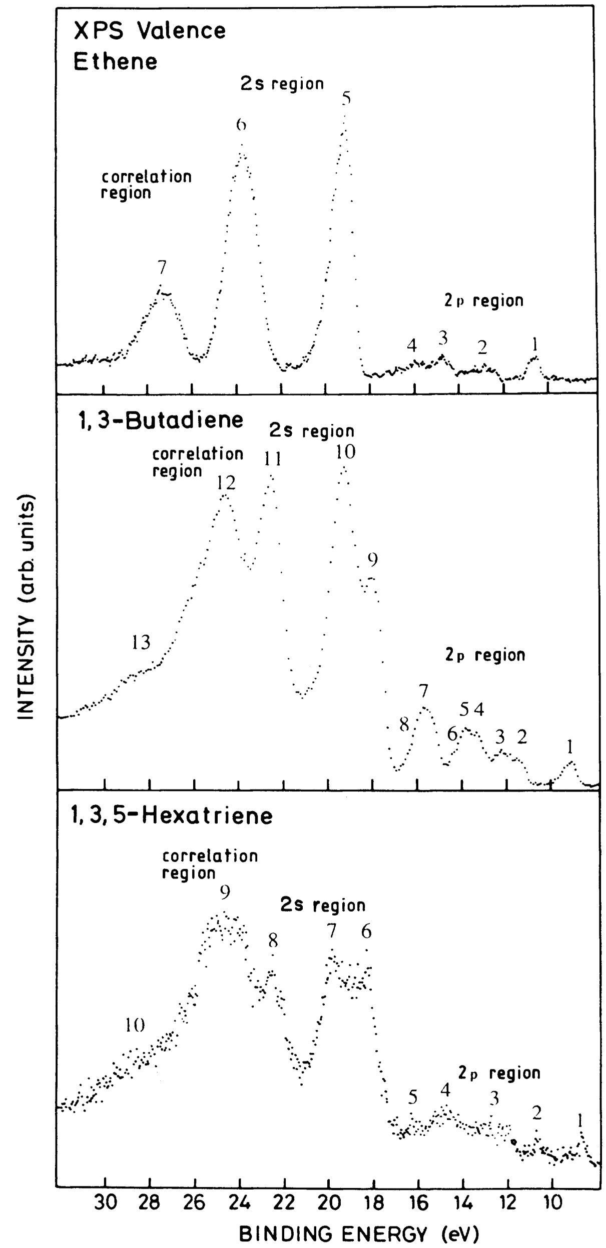

FIG. 1. The XPS valence spectra of ethene, 1,3-butadiene, and 1,3,5-hexatriene.

perhaps be noticed that the very weak structure in the ethene spectrum, inferred in Ref. 18 as "line 8," has not been confirmed in the present study.

There is a general agreement on the assignment of the ethene XPS and UPS of the valence region up to 25 eV. The binding energies of the lines observed in the present spectrum are given in Table I. Line 1 originates from ionization out of the out-of-plane $1b_{3u}$ π orbital. Lines 2–4 are explained by the in-plane σ-type orbitals, mostly of C 2*p* and H 1*s* origin, but with a small and varying C 2*s* component, that explains the different intensities in the XPS. Lines 5 and 6 are associated with the $2b_{1u}$ and $2a_g$ σ-type orbitals. As can be seen from Green's-function calculations, ionization from the latter orbital leads to a great number of final states that acquire an appreciable intensity. Notably, two correlation states have been calculated with approximately the same intensity and a splitting of about 0.7 eV. This could be one explanation for the increased width of line 6 when compared to line 5. However, vibrational effects also can give rise to such differences in the line shape.

Line 7 was assigned as a correlation satellite already in Ref. 18. Extensive theoretical calculations have confirmed this assignment using both CI (Ref. 20) and Green's-function[21] methods. Both calculations put states of ${}^2A_g$ symmetry in the energy region of this line and it therefore acquires intensity by mixing with the state associated with line 6. Correlation satellites, i.e., peaks arising from ionization to states not describable within a one-electron model, were shown to exist already in the π region.[20]

The He II-excited spectrum of 1,3-butadiene[9] shows the region up to 25 eV. In the outer-valence region the first two bands are associated with ionization from the $1b_g$ and $1a_u$ π-type out-of-plane orbitals. The corresponding lines 1 and 2 in the XPS of Fig. 1 are accordingly very weak. The remaining part of the 2*p* region consists of σ-type orbitals, constructed mainly from C 2*p* and H 1*s* atomic orbitals. A gradual increase in the intensity of the bands in the XPS is observed towards higher-binding energies and this is, as in the case of ethene, explained by a successively increased mixing with the C 2*s* atomic orbitals. At least four structures, labeled 9–12, can be inferred in the 2*s* region of 1,3-butadiene. These structures also seem to be present with low intensities in the He II-excited spectrum.[9] According to Green's-function calculations[21] they correspond to ionization from the $4b_u$, $4a_g$, $3b_u$, and $3a_g$ orbitals in order of increasing binding energy. However, the pole strengths for the single-hole states are only 0.66 and 0.40 for the two first states, respectively, while for the two latter states a complete breakdown of the one-particle model seems to persist. This is clearly observed for the extremely broad structure 12, which hardly resembles a photoelectron band associated with ionization leading to a single-hole state. It should also be noticed that the double-ionization energy, as determined from an Auger-electron study that will be presented elsewhere,[22] lies below 25 eV and consequently, line 12 falls in the double-ionization continuum. The structure 12 has not been observed in previous studies and must be interpreted as a correlation satellite. The binding energies of the lines observed in the present spectrum are given in Table II.

At this point it is interesting to compare the valence-photoelectron spectra of ethene and 1,3-butadiene with previously published valence XPS of ethane and *n*-butane.[4] The latter spectra are much less complicated in the inner-valence region, which even in the high-binding-energy part can be described in a very simple orbital model. The 2*s* region of the alkane's XPS represents a textbook example of the development of a (tight-binding) band structure. In the limit of a very long alkane chain the bottom and the top of the band achieves a high density of states, with corresponding high intensities in the XPS. No strong correlation effects can be inferred from the photoelectron spectra of the alkanes due to the very low intensity of the satellite structures. From Fig. 1 it is seen that the present molecules, representing the first steps in the buildup of an unsaturated carbon chain, exhibit photoelectron spectra of a much more complicated character. The strong correlation associated with structure 7 in the case of the ethene molecule is found to extend over a large part of the 2*s* region already in the case of 1,3-butadiene. Moreover, the double-ionization continuum starts already in this region and, therefore, shake-off resonances between this continuum and the singly ionized states should also be considered in a full

TABLE I. Valence-binding energies of ethene.

Valence region	Peak No.	Binding energy (eV)
2*p*-orbital region	1	10.63
	2	13.15
	3	14.90
	4	15.90
2*s*-orbital region	5	19.20
	6	23.85
Correlation region	7	27.45

TABLE II. Valence-binding energies of 1,3-butadiene.

Valence region	Peak no.	Binding energy (eV)
2*p*-orbital region	1	9.09
	2	11.49
	3	12.19
	4	13.29
	5	13.76
	6	14.29
	7	15.59
	8	16.29
2*s*-orbital region	9	18.00
	10	19.19
	11	22.44
Correlation region	12	24.53
	13	28.29

theoretical treatment. The correlation region is even broader and more complex for 1,3-butadiene and 1,3,5-hexatriene and, in fact, seems to fill out the gap in the 2*s* region in these cases. Furthermore, the double-ionization continuum should be at even lower energy for these molecules than for ethene and is expected to strongly influence most of the structures, at least in the high-energy part of the inner valence region. In addition, the 2*p* region in the present spectra from the alkenes differs considerably from that of the earlier recorded spectra of the alkanes.[4] In the latter case a normal (tight-binding) band structure starts to develop already in the *n*-butane spectrum, whereas the orbital structure is still present in the spectra of the alkenes.

The 1,3,5-hexatriene valence-photoelectron spectrum is shown in the lowest part of Fig. 1. The binding energies of the lines observed in the present spectrum are given in Table III. A He I UV-excited photoelectron spectrum of 1,3,5-hexatriene has earlier been reported in Ref. 12. A calculation has also been published.[23] The three outermost photoelectron bands at 8.2, 10.4, and 11.6 eV are due to ionization from the three out of plane π-type orbitals. The first two can be clearly seen in the XPS as lines 1 and 2, while the third state at 11.6 eV contributes to the low binding energy edge of line 3. The main part of line 3 and structures 4 and 5 contain all the in-plane, σ-type orbitals that are mainly constructed from the C 2*p* and H 1*s* atomic orbitals. As in the case of 1,3-butadiene we notice an increased intensity in this region compared to lines 1 and 2, which reflects an increasing mixing with the C 2*s* atomic orbitals. The C 2*s* region, extending from about 17 eV up to about 26 eV, is clearly divided into two separate parts. This behavior of the band was already inferred in the case of 1,3-butadiene. We are thus observing the development of the complex inner valence-band structure of an infinitely long quasi-one-dimensional crystal. The outermost part of the C 2*s* region between 17 and 21 eV seems to exhibit a shape of a (tight-binding) band structure where line 6 corresponds to the increased density of states at the top of the band and line 7 corresponds to the bottom of a band. It should be noticed that in the 1,3,5-hexatriene case only three one-particle states are expected in this energy region. However, the development of the band structure is evident in Fig. 1.

TABLE III. Valence-binding energies of 1,3,5-hexatriene.

Valence region	Peak no.	Binding energy (eV)
2*p*-orbital region	1	8.78
	2	11.73
	3	12.68
	4	14.68
	5	16.28
2*s*-orbital region	6	18.18
	7	19.73
	8	22.48
Correlation region	9	24.63
	10	25.3

The high-binding-energy part of the C 2*s* region shows a line 8 at about 22.7 eV and a very broad and complex structure labeled 9. At even higher energies a broad continuum structure labeled 10, which is due to correlation, is seen. The effect of strong correlation that was seen as line 7 in the ethene spectrum, and was seen to influence lines 12 and 13 in the 1,3-butadiene spectrum, persists in the whole energy region of lines 8–10 in the 1,3,5-hexatriene spectrum. It is clear, therefore, that the development of one single (tight-binding) C 2*s* band, that was found in the case of the *n*-alkanes,[4] is not present in the case of an unsaturated chain. For the present molecules, two bands are formed, an outer band formed from molecular valence orbitals, and an inner band involving strongly correlated states. Furthermore, at about 28 eV a third band with weaker intensity, seen as line 10 in the 1,3,5-hexatriene spectrum, also builds up due to correlation effects. In addition, the states in the inner part with binding energies above about 22 eV are probably strongly influenced by the double-ionization continuum which, by comparison to the 1,3-butadiene Auger spectrum, is expected to be opened in the 22–24-eV energy range.

Figure 2 shows the spectrum of *trans*-$(CH)_x$ in the region between 0 and 32 eV. The binding energies, referred to the Fermi level, of the lines observed in the present spectrum are given in Table IV. Similar spectra, both UV (Ref. 2) and x-ray excited,[3] have been obtained in earlier studies, although in the latter case with lower resolution. Both spectra show four bands between 0 and 20 eV, which agree well in energy with the present result. Also, band-structure calculations have been carried out.[3,24–30] In particular, in Ref. 26 a comparison is made between an experimental and a theoretical valence-XPS spectrum. The theoretical spectrum was obtained by scaling the energies with a factor of 1.3 and the intensities with the photoionization cross sections.

The interpretation of the *trans*-$(CH)_x$ spectrum in Fig.

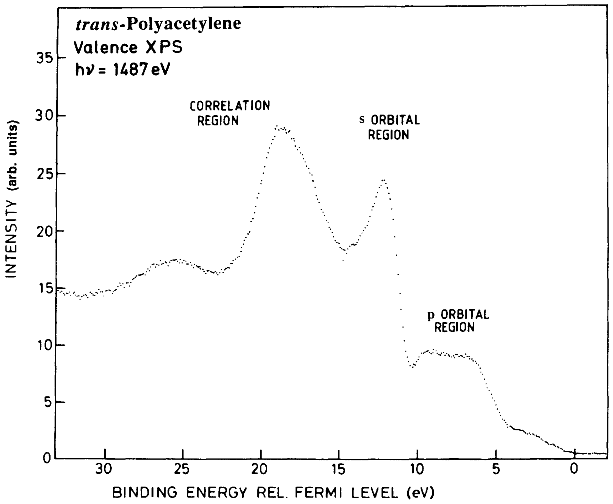

FIG. 2. The valence XPS of *trans*-$(CH)_x$. The spectrum has been calibrated to the Fermi level as determined from a calibration against Ag metal.

TABLE IV. Valence-binding energies of *trans*-polyacetylene. Binding energies relative to the Fermi level.

Valence region	Peak no.	Binding energy (eV)
2*p*-orbital region	1	3.0
	2	6.8
	3	9.3
2*s*-orbital region	4	11.9
Correlation region	5	18.7
	6	26.0

2 can be achieved from a comparison with the spectra of the model molecules shown in Fig. 1. All the separate regions, as discussed above, are present in the *trans*-$(CH)_x$ spectrum. It should be noted that the energy scale of the spectrum from the solid sample is referred to the Fermi level, whereas the gas-phase spectra are referred to the vacuum level. Around 3 eV a weak structure is seen. It corresponds to a band formed from the out-of-plane π-type molecular orbitals. This band can probably be well described within a single particle model. Between 5 and 10 eV a second band is observed which corresponds to the second region associated with in-plane C 2*p* σ-type orbitals. This band shows a regular and simple tight-binding shape and weak maxima can be inferred at the top and bottom of the band at about 6.8 and 9.3 eV, respectively. Thus, it seems possible to describe theoretically this band in a single-particle model. The weak band around 3 eV seems to have been misinterpreted in some of the earlier theoretical studies.[3] However, in Ref. 31 it was stated that "...the π band should contribute to a shoulder at low binding energies. This feature is not observed." We do observe this structure and thereby confirm this conjecture.

The regular tight-binding behavior of the next band (lines 6 and 7 in the 1,3,5-hexatriene spectrum) seems to be disturbed for the infinite chain. The simple tight-binding structure is not seen in Fig. 2 for the third structure observed around 12 eV. Instead, a single-peak maximum is observed at 12.1 eV and the structure is broadened on the high-binding-energy side. We propose that the correlation region which, in the case of 1,3,5-hexatriene extends over the energy range of the lines 8 and 9 in Fig. 1, now extends to lower binding energy and influences the high-binding-energy side of this band.

As already discussed above, the innermost and most intense structure at about 18.7 eV, basically associated with C 2*s* atomic orbitals, in the *trans*-$(CH)_x$ spectrum is strongly dominated by the electron correlation, and theoretical calculations that do not include electron correlation in an explicit way are not expected to give any reasonable description of this part of the spectrum. Compare, for instance, this structure with the sharp intense line associated with the bottom of the 2*s* band in Fig. 4 of Ref. 26. This also applies to the broad feature centered at around 25.9 eV. It should also be noted that, in comparison with the model molecules, we expect the double-ionization continuum to start in the C 2*s* region and therefore the shape of the bands may also be strongly influenced from interaction of singly ionized states with the double-ionization continuum.

XPS shakeup spectra of the model molecules

We discuss below the shakeup spectrum of 1,3-butadiene and 1,3,5-hexatriene in terms of transitions between molecular orbitals in the core-ionized species. It should be pointed out, however, that the extent of configuration mixing in the shakeup states is large and the proposed assignment is referred to as the dominant configuration, as displayed in Tables V and VI. The shakeup spectrum of *trans*-$(CH)_x$ is analyzed by comparing it with the corresponding spectra from the model molecules.

1,3-butadiene C 1s shakeup spectrum

The shakeup spectrum of 1,3-butadiene is presented in Fig. 3 along with the convoluted theoretical spectra. Although it is known that at room temperature the *trans* configuration dominates,[32] whereas at lower temperatures (198 K) the *cis*-isomer dominates, calculations were performed for each of the symmetry-unique carbon atoms for both the *cis*- and *trans*-configurations. The theoretical spectrum reproduced in Fig. 3 is then a sum of the results obtained for C(1) and C(2) core ionization in both *cis* and *trans* conformations. Figure 4 shows the structures of the molecules and the labeling of the different carbon atoms. The results of these calculations, energies and intensities,

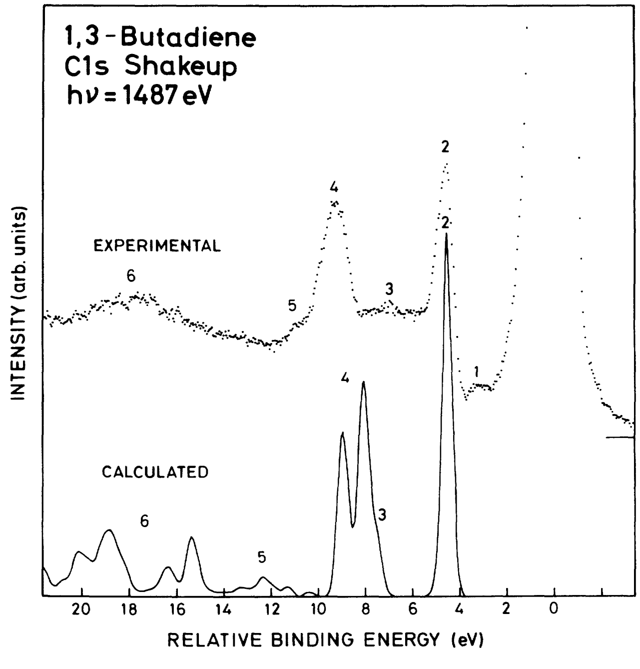

FIG. 3. The C 1*s* shakeup spectrum of 1,3-butadiene along with the INDOCI energies and intensities convoluted with Gaussians of full width at half maximum of 0.5 eV. The convolution has been performed merely as an illustration and no attempt to simulate the complex line shape has been performed.

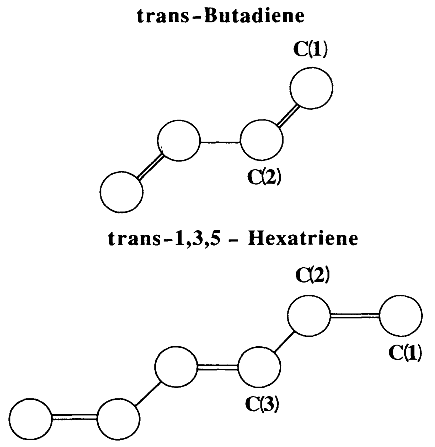

FIG. 4. Schematic figure of the *trans*-configuration of the model molecules used in this study, indicating the nomenclature used in the text.

are presented in Table V, where the chemical shifts obtained from a deconvolution of the main line[33] have been added.

The first structure in the experimental spectrum, labeled 1, is of very low intensity and is not accounted for in these calculations. The low energy and intensity of this structure would suggest the assignment of a triplet-coupled-valence excitation, which is neglected at the level of these calculations.[34] The first strong peak at 4.5 eV, labeled 2, is calculated to arise from a transition from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO), the $2\pi \rightarrow 3\pi^*$ transition, upon C(1) ionization. The differences between the *cis*- and *trans*-configurations of 1,3-butadiene are seen from the table to be small. The second intense peak, labeled 4, picks up intensity from the $1\pi \rightarrow 3\pi^*$ transition upon both C(1) and C(2) ionization, and its width and intensity in the experimental spectrum clearly indicates the presence of more than one transition. Between these two peaks, a broad continuum is observed in the experimental

TABLE V. Experimental and calculated INDOCI energies and intensities for the shakeup satellites in 1,3-butadiene.

Geometry parameter	Before CI		After CI			Experimental		
Atom position	Energy[a] (eV)	Intensity (%)	Energy[a] (eV)	Intensity (%)	Peak no.	Energy (eV)	Intensity (%)	Dominant configuration
trans								
C(1)	4.76	16.3	4.54	13.4	2	4.5	5.0	$2\pi\rightarrow3\pi^*$
	7.62	<0.1	7.43	1.0	3	7.15	2.6	$2\pi\rightarrow4\pi^*$
	8.18	9.95	7.98	9.8	4	9.25	4.3	$1\pi\rightarrow3\pi^*$
	18.08	<0.1	18.25	0.8	6	17.70	2.7	$9\sigma\rightarrow14\sigma^*$
	22.52	1.7	22.72	1.4				$10\sigma\rightarrow18\sigma^*$
	23.66	0.2	23.80	1.3				$9\sigma\rightarrow20\sigma^*$
C(2)	4.70	0.8	4.62	0.7				$2\pi\rightarrow3\pi^*$
	7.80	2.0	7.51	0.7	3			$2\pi\rightarrow4\pi^*$
	9.16	10.5	8.98	10.0	4			$1\pi\rightarrow3\pi^*$
	12.50	0.2	12.31	0.8	5	10.55	2.1	$13\sigma\rightarrow14\sigma^*$
	19.83	0.9	20.19	2.0	6			$9\sigma\rightarrow15\sigma^*$
cis								
C(1)	4.62	15.2	4.47	13.7	2			$2\pi\rightarrow3\pi^*$
	7.70	<0.1	7.47	2.6	3			$2\pi\rightarrow4\pi^*$
	8.15	10.6	8.12	8.0				$1\pi\rightarrow3\pi^*$
	16.41	0.3	16.30	0.9	6			$10\sigma\rightarrow14\sigma^*$
	19.46	2.1	19.63	1.6	6			$11\sigma\rightarrow18\sigma^*$
	21.00	0.6	20.74	1.1	6			$9\sigma\rightarrow15\sigma^*$
	22.02	0.6	21.51	1.8	6			$9\sigma\rightarrow16\sigma^*$
C(2)	4.52	0.8	4.95	0.5				$2\pi\rightarrow3\pi^*$
	7.85	1.7	8.75	3.3	3			$2\pi\rightarrow4\pi^*$
	11.29	1.5	11.83	0.7	5			$1\pi\rightarrow4\pi^*$
	11.93	0.1	12.24	0.6				$13\sigma\rightarrow14\sigma^*$
	13.55	0.04	15.04	1.0	6			$(1\pi\rightarrow3\pi^*;\ 2\pi\rightarrow3\pi^*)^2$
	16.06		15.37	2.7	6			$9\sigma\rightarrow15\sigma^*$
	16.79	0.3	18.76	2.3	6			$(1\pi\rightarrow3\pi^*)^2$

[a] A chemical shift of −0.54 eV for C(1) and +0.06 eV for C(2) has been added to the shakeup energies.

spectrum with a discernable peak at approximately the center of the structure at 7.15 eV. In the calculations, the $2\pi\rightarrow4\pi^*$ transitions accompanying C(1) as well as C(2) ionization are found to fall in or slightly above this energy range. Since the orbital basis describing the π space is very limited (four orbitals in all), the highest π level will be poorly described. The calculated values of the $2\pi\rightarrow4\pi^*$ are, therefore, expected to fall at excessively high energies. A lowering of all $2\pi\rightarrow4\pi^*$ transitions by, e.g., 1 eV, which is approximately the energy shift found in our earlier calculations,[34] would make these transitions fall in the energy range 4.9–7.9 eV, which fits well with the continuum observed on the experimental spectrum. The shoulder at approximately 10.6 eV, labeled 5 in the experimental spectrum, could be assigned to a $13\sigma\rightarrow14\sigma^*$ transition (cf. Table V).

Above this energy no well-resolved line is observed. A broad structure, labeled 6, is observed in the experimen-

TABLE VI. Experimental and calculated INDOCI energies and intensities for the shakeup satellites in 1,3,5-hexatriene.

Geometry parameter	Before CI		After CI			Experimental		
Atom position	Energy[a] (eV)	Intensity (%)	Energy[a] (eV)	Intensity (%)	Peak no.	Energy (eV)	Intensity (%)	Dominant configuration
trans								
C(1)	3.51	21.0	3.46	18.5	1	3.2	6.4	$3\pi\rightarrow4\pi^*$
	5.91	<0.1	5.82	1.0	3	7.4	4.1	$3\pi\rightarrow5\pi^*$
	6.14	7.9	6.21	4.3	4	9.4	2.1	$2\pi\rightarrow4\pi^*$
	8.15	8.0	7.90	5.4	4			$1\pi\rightarrow4\pi^*$
	15.88	0.2	15.75	5.3	6	17.7	2.3	$(1\pi\rightarrow4\pi^*)^2$
C(2)	3.70	0.28	3.99	0.05				$3\pi\rightarrow4\pi^*$
	5.88	3.1	6.12	2.4	3			$3\pi\rightarrow5\pi^*$
	9.36	9.2	8.82	1.2	4			$1\pi\rightarrow4\pi^*$
	12.29	<0.1	14.00	1.4	6			$(1\pi\rightarrow4\pi^*)^2$
	15.49	<0.1	17.27	3.9	6			$(1\pi\rightarrow4\pi^*;\ 2\pi\rightarrow4\pi^*)^2$
	17.41	0.2	19.12	2.6				$(1\pi\rightarrow4\pi^*)^2$
C(3)	4.01	8.5	4.03	5.9	2	4.7	3.3	$3\pi\rightarrow4\pi^*$
	7.07	0.8	7.37	2.5	4			$3\pi\rightarrow5\pi^*$
	7.19	1.7	7.88	1.0				$(1\pi\rightarrow4\pi^*;\ 3\pi\rightarrow6\pi^*)^2$
	13.83	0.4	13.99	1.0				$17\sigma\rightarrow21\sigma^*$
	13.45	0.3	14.77	3.2	6			$(1\pi\rightarrow4\pi^*;\ 3\pi\rightarrow4\pi^*)^2$
	15.85	<0.1	17.34	1.0	6			$(1\pi\rightarrow5\pi^*;\ 3\pi\rightarrow5\pi^*)^2$
			18.99	3.8				
cis								
C(1)	3.42	20.0	3.41	17.1	1			$3\pi\rightarrow4\pi^*$
	5.88	<0.1	5.88	0.8	3			$3\pi\rightarrow5\pi^*$
	6.08	7.8	6.12	5.2	4			$2\pi\rightarrow4\pi^*$
	8.16	8.2	7.88	5.4	4			$1\pi\rightarrow4\pi^*$
	15.46	<0.1	15.67	3.1	6			$16\sigma\rightarrow22\sigma^*$
	15.74	0.2	15.79	3.1	6			$(1\pi\rightarrow4\pi^*)^2$
C(2)	3.67	0.19	3.98	0.04				$3\pi\rightarrow4\pi^*$
	5.95	3.1	6.22	2.3	3			$3\pi\rightarrow5\pi^*$
	9.36	9.2	8.81	1.4	4			$1\pi\rightarrow4\pi^*$
	11.49	<0.1	11.72	0.8	5			$19\sigma\rightarrow20\sigma^*$
	12.43	<0.1	14.07	1.0				$(1\pi\rightarrow4\pi^*;\ 3\pi\rightarrow4\pi^*)^2$
	15.57	<0.1	17.36	3.2	6			$(1\pi\rightarrow4\pi^*;\ 2\pi\rightarrow4\pi^*)^2$
	16.85	0.2	17.80	1.4				$19\sigma\rightarrow20\sigma^*$
	17.42	0.2	19.22	2.7				$(1\pi\rightarrow4\pi^*)^2$
C(3)	4.06	8.3	4.06	6.0	2			$3\pi\rightarrow4\pi^*$
	7.03	1.0	7.33	2.3	4			$3\pi\rightarrow5\pi^*$
	8.90	8.1	7.89	1.1				$1\pi\rightarrow4\pi^*$
	13.55	0.3	14.69	3.7	6			$16\sigma\rightarrow21\sigma^*$
	15.64	<0.1	18.91	3.3	6			$(1\pi\rightarrow4\pi^*;\ 2\pi\rightarrow5\pi^*)^2$

[a] A chemical shift of −0.56 eV for C(1), 0.18 eV for C(2) and −0.15 eV for C(3) has been added to the shakeup energies.

tal spectrum at 17.7 eV, which would appear to be made up from a number of peaks. The calculations place a number of $\sigma \rightarrow \sigma^*$ and $(\pi \rightarrow \pi^*)^2$ double-type excitations over the energy range 16–21.5 eV, which probably contribute in this energy range.

1,3,5-hexatriene C 1s shakeup spectrum

The shakeup spectrum of 1,3,5-hexatriene is presented in Fig. 5 along with the convoluted theoretical spectrum. The calculations were performed in the same manner as outlined above, for both the *cis* and *trans* configurations. Table VI gives the shakeup energy and intensity for those transitions gaining 1% or greater intensity, where the chemical shift has been taken into consideration. The lowest-energy shakeup structure, labeled 1, is assigned to arise from the HOMO-LUMO transition from ionization of the C(1) carbon, the $3\pi \rightarrow 4\pi^*$ transition, as in the case of 1,3-butadiene. The calculated energy of this peak, 3.46 eV for the *trans*- and 3.41 eV for the *cis*-isomer, is in very good agreement with the experimentally observed value of 3.22 eV. On the high-binding-energy side of this structure there is an observable shoulder, labeled 2. The $3\pi \rightarrow 4\pi^*$ transition from ionization of the C(3) carbons is calculated to fall at 4.03 eV which is again in very good agreement with the energy of this peak. In the case of C(2) ionization the $3\pi \rightarrow 4\pi^*$ transition is calculated to have a negligible intensity.

In the experimental spectrum a broad band is observed over an energy range starting at 6 eV and reaching a maximum at 9.6 eV. At least two structures can be identified in this region and are labeled 3 and 4. Structure 3 is associated with the $3\pi \rightarrow 5\pi^*$ transition upon C(1) and C(2) ionization while structure 4 would correspond mostly to $2\pi \rightarrow 4\pi^*$ and $1\pi \rightarrow 4\pi^*$ transitions. In this energy range, we also find transitions of the type $3\pi \rightarrow 6\pi^*$ and $1\pi \rightarrow 5\pi^*$. It should, however, be pointed out that configuration interaction is very strong for all transitions in this range so that orbital assignments become less meaningful. This is related to the existence of a number of closely spaced energy levels, which gives rise to a number of different excitations of approximately the same energy. It also points toward the development of a band structure which, of course, is fully developed in the case of an infinitely long chain. The limited basis used here, however, makes the description of the higher π orbitals approximate, if possible at all, which can be seen from the relatively poor agreement between calculated and observed shakeup spectra in this energy range (6–10 eV). There are also two broad structures seen at the energies of 13.0 and 17.5 eV in the experimental spectra. The calculations predict a large number of intense heavily mixed double- $(\pi \rightarrow \pi^*)^2$ type transitions over this energy range, as was also the case in the 1,3-butadiene spectrum. Also in this energy range, any attempts at definite orbital assignments would be very tentative.

From a comparison of the results of 1,3-butadiene and 1,3,5-hexatriene a number of conclusions can be drawn. The structure in the low-energy part of the shakeup spectrum, up to 9 eV, arises predominantly from $\pi \rightarrow \pi^*$ transitions. In both molecules the intense transition at lowest energy is calculated to arise from the HOMO-LUMO transition upon ionization of the end carbon, C(1). It could be said, in general, that the C(1) carbon donates far more intensity to the shakeup structure than either the C(2) carbon in 1,3-butadiene or the C(2) and C(3) carbons in 1,3,5-hexatriene. This can be physically understood in terms of stronger polarization upon C(1) ionization as compared to C(2) or C(3) and to a larger charge concentration around C(1) already in the neutral ground state. The oscillatory intensity for the HOMO-LUMO transition in going from C(1) to C(2) and to C(3) in 1,3,5-hexatriene (cf. Table VI) can be associated with a corre-

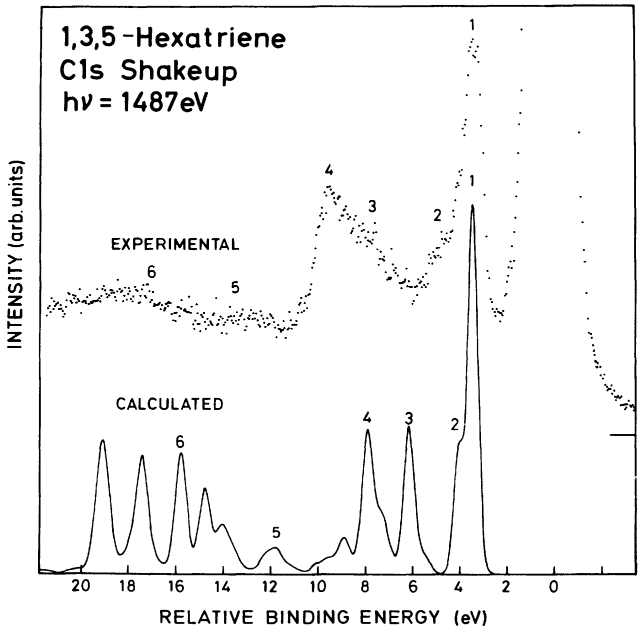

FIG. 5. The C 1*s* shakeup spectrum of 1,3,5-hexatriene along with the convoluted INDOCI energies and intensities obtained from the calculations.

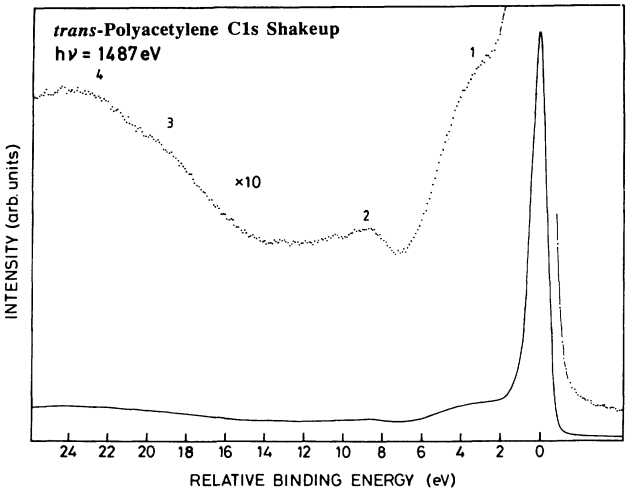

FIG. 6. The experimental C 1*s* shakeup spectrum of *trans*-$(CH)_x$.

TABLE VII. Experimental shakeup satellites in *trans*-polyacetylene.

Peak no.	Energy (eV)	Intensity (%)
1	3.1	9.0
2	8.5	5.3
3	19.5	7.1
4	23.0	8.6

sponding oscillation in the HOMO population associated with those atomic centers, as stems from a Muliken population analysis. The trend toward an overall decrease in the shakeup probability, relative to the main line, previously experimentally observed in a series of fused-ring aromatic molecules,[35] is followed also in the spectra presented here. However, the calculations would tend to suggest that the intensity borrowed from the C(1) carbon is not greatly reduced, and may in fact be increased, at least in the case of the $\pi \rightarrow \pi^*$-type transitions. However, the level of calculations used in this study, as well as the neglect of transitions to higher states, makes this observation somewhat tentative since there may be a buildup of intensity on certain transitions which should be assigned to the neglected transitions. The shift in the center-of-mass of the shakeup spectra on increasing size of the system is also observed for these alkenes and is very well reproduced, at least for the lower-lying transitions, in the calculations.

Shakeup spectrum from trans-$(CH)_x$

The shakeup spectrum from *trans*-$(CH)_x$ is presented in Fig. 6. The shakeup energies of the lines observed in the present spectrum are summarized in Table VII. The analysis of the spectrum from the solid is more complicated than for the two model systems. In the spectrum three structures can be clearly seen. The first of these, labeled 1, lies very close to the main C 1*s* line and displays a structureless broad band centered at 3.1 eV. In our earlier studies of conjugated unsaturated systems, benzene[34] and polythiophene,[6] it was observed that a structure due to inelastic scattering was found at this low energy. The width of structure 1 in *trans*-$(CH)_x$ could not be explained by such events alone, although there may be a contribution. The shakeup energy of this peak also lies at approximately the experimentally determined band gap of about 2 eV,[36] although in this case we are dealing with an ionized system as opposed to the neutral system.

The origin of this first peak should be assigned to the HOMO-LUMO transition. However, in the case of the model molecules the first strong peak originated from ionization of the end carbon in the chain whereas, in the case of the long polymer chain, the contribution from such atoms in negligible. Therefore, it is not possible to find this structure in the polymer spectra. The second intense structure in the model molecules follows the same systematic decrease in energy on increasing size and in going from 1,3-butadiene to 1,3,5-hexatriene where this structure becomes much broader. In the case of the molecules it is made up of a large number of transitions among the lower lying π-type orbitals. In the case of *trans*- $(CH)_x$, it is not unlikely that these orbitals form the higher-energy part of the band structure. The structure labeled 2 in the polymer spectrum may be due to transitions involving σ-type orbitals as well as multiple excitations, since a number of these transitions are calculated to gain quite large intensity in the 1,3,5-hexatriene molecule, however this assignment is more tentative. The last broad structure, labeled 3, at high shakeup energy is more than likely due to other secondary events, since its appearance can not be explained within the systematics observed for shakeup spectra.

CONCLUSIONS

By the study of a series of model molecules in the gas phase it has been possible to interpret the *trans*-$(CH)_x$ valence XPS. It is shown that the outermost two bands, centered at 3 and 8 eV, correspond to ionization from the out-of-plane π-type orbitals and the in-plane σ-type orbitals constructed from C 2*p* atomic orbitals, respectively. The C 2*s* region is shown to be strongly influenced by electron correlation and also to an interaction mechanism between singly ionized states and doubly ionized continuum states. This interpretation of the spectrum confirms the earlier theoretical results that place the out of plane π-type band around 3 eV from the Fermi level. Although the present solid sample corresponds to a disordered system, this disorder does not seem to seriously influence the spectrum. This is strongly supported by the XPS of the model molecules, where the band structure gradually starts to develop.

The C 1*s* shakeup spectrum of *trans*-$(CH)_x$ has been assigned using results from the C 1*s* shakeup spectra from the model molecules that were interpreted using INDOCI calculations. The shakeup probability is shown to vary strongly for the different carbon atoms in the model molecules, giving insight into the relaxation mechanisms associated with core photoionization. The 1,3,5-hexatriene C 1*s* shakeup spectrum has been shown to be useful in the interpretation of the corresponding *trans*-$(CH)_x$ spectrum. It must, however, be noticed that influences from the band formation is seen already in the case of 1,3,5-hexatriene which makes the assignments somewhat more complex than in the case of ethene and 1,3-butadiene.

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[*] On leave from Department of Physics, University of Brasilia, 70910 Brasilia DF, Brazil.

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