

Interaction of Na with sexithiophene thin films

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The effects of Na on the electronic structure and electrical properties of α -sexithiophene ($\alpha 6T$) are investigated with electron spectroscopic methods under UHV conditions. A shift of the valence-band edge away from the Fermi level, and the evolution of states in the gap, can be determined. In a classical band-structure picture this could be explained as an n -type doping process. However, all results point at a high localization of the negative charge at the sulfur atom which is reflected in a very low specific conductivity. [S0163-1829(98)05412-5]

I. INTRODUCTION

Organic semiconductors are interesting candidates for an electronics with molecular materials with its advantages of lower weight, high mechanical flexibility, and sometimes lower costs as compared to conventional electronics. Such organic materials are often conjugated polymers with a quasi-one-dimensional structure. An important representative of this substance class is polythiophen.

In general, polymers possess decisive disadvantages, as their uncontrolled structure (length, defects such as sp^3 carbons, etc.), making a systematic study of their physicochemical properties difficult or impossible. Furthermore, the preparation of ultrapure and geometrically homogeneous thin films is hindered due to impurities and a distribution of different chain lengths in the polymeric systems.

In this context oligomers may have advantages. This is, in particular, the case for α -sexithiophene ($\alpha 6T$), an oligomer of six thiophene units, which can be viewed as a "model system" for polythiophene with respect to its electronic structure.¹ Furthermore, ultrapure thin films can be prepared by UHV sublimation, which form highly ordered thin films under suitable conditions.^{2,3} With the construction of a field-effect transistor based on $\alpha 6T$, Garnier *et al.* showed also that $\alpha 6T$ is suitable for an application in organic semiconductor devices.⁴ For this purpose, "doping" is required because of the low intrinsic conductivity of $\alpha 6T$.

"Doping" of organic molecular materials follows a different process if compared to inorganic covalent solids, but the phenomenological changes upon "doping" are quite similar, i.e., an increase in the p - or n -type conductivity can be observed, and often also the Fermi level shifts into the right direction. However, whereas in covalent semiconductors only ppm amounts of the dopant are required due to the delocalized electronic band structure, organic semiconductors are doped in nearly equal amounts of "dopant" per organic molecule. These "dopants" oxidize or reduce the organic material. This process can be discussed from two different ideal viewpoints: In the first, a bandlike character of the electronic structure is assumed. These bands are usually rather narrow. In the course of doping states from the band edges move into the bandgap and give rise to the higher conductivity. These states are called polarons, or, for higher dopant concentration and hence interacting polarons, bipo-

larons. (For a detailed review see, e.g., Refs. 5 and 6). The other view is that of completely localized molecular orbitals. In this model a chemical reaction between the "dopant" and the organic molecule leads to a compound which is often regarded as saltlike. Resulting electronic states in this model are due to a completely changed electronic structure, as expected for this compound. In most cases it is not easy to decide which model is more appropriate, and at first an evaluation along the band picture is followed which is more familiar to most solid-state physicists. However, often corrections to such interpretations are necessary.

" p doping" in sexithiophene is often established by (also unintentional) "air doping" due to oxygen or by "doping" with $FeCl_3$ in water,^{7,8} or under UHV conditions.⁹ This leads to an increase of the (room temperature) conductivity from $<10^{-9} (\Omega \text{ cm})^{-1}$ (pure $\alpha 6T$) to $10^1 (\Omega \text{ cm})^{-1}$ (maximally "doped" $\alpha 6T$). This p -doping process has been studied by many groups (see Ref. 1, and references therein).

In view of other semiconductor devices like bipolar transistors or pn diodes, it is also necessary to obtain a detailed understanding of the n -type "doping" process. There are only a few results on " n doping" of oligothiophene thin films. The essential results of ultraviolet photoelectron spectroscopy (UPS) studies on Na interaction with $\alpha 6T$ are the evolution of states in the band gap and the shift of the Fermi level toward the conduction-band edge.¹⁰ This was explained by the creation of polarons and bipolarons.

Here the evolution of these gap states was investigated for different doping levels not only by UPS but also with high-resolution electron-energy-loss spectroscopy (HREELS). X-ray photoelectron spectroscopy (XPS) allowed the determination of the dopant concentration, the purity and the stoichiometry of the film, and changes in the chemical states of the C and S core levels. Finally, first conductivity measurements were performed. The results will be evaluated in the delocalized as well as in the localized model. Both models will finally be compared with respect to their suitability in the characterization of the " n doping" of sexithiophene by the reaction with Na.

II. EXPERIMENT

The preparation of $\alpha 6T$ films was carried out in UHV by evaporation from a Knudsen cell. Gold foils (Heraeus,

99.99% purity) were used as substrates. Sputtering with Ar^+ ions led to clean surfaces with impurities such as oxygen below the XPS detection limit of 1%. The sublimation was performed at a pressure of 8×10^{-9} mbar, and with a deposition rate of 0.8 nm/min. Layer thicknesses of around 70 nm were adjusted by monitoring deposited masses with a quartz-crystal balance (LH Inficon) by assuming a bulk density of 1.5 g cm^{-3} for $\alpha 6T$. The *in situ* n doping was performed by subsequent sodium evaporation from a SAES getter source on the as-prepared $\alpha 6T$ films. The doping levels were derived from XPS measurements by using the intensity ratio between the C 1s and the Na 1s peaks. The cross section was taken into account, but neither the transmission of the spectrometer nor the mean free path of the electrons. The former is difficult to calibrate for small kinetic energies (Na 1s), so that no better values would be obtained. Another error arises from the fact that a homogeneous distribution of Na with depth has to be assumed. This may lead to an error larger than the usual 10% for the absolute value of the dopant concentration. However, relative amounts can be determined with higher accuracy.

X-ray photoelectron spectroscopy measurements were performed with a LH hemispherical analyzer (RQ 10) and a Mg $K\alpha$ source (1253.6 eV). A pass energy of 50 eV leads to a resolution of 1.2 eV as determined from the full width at half maximum (FWHM) of the Ag 3d peaks. For ultraviolet photoelectron spectroscopy measurements He I (21.22 eV) and He II (40.81 eV) radiation was used. They were performed at 2.5 eV pass energy and an overall resolution of 50 meV as deduced from the FWHM of the Fermi edge of clean gold.

HREELS investigations were carried out with a LH ELS22 system, in specular reflection geometry. The incident angle was set to $\Theta = 60^\circ$ normal to the surface of the specimen. At a primary energy of 15 eV, the FWHM of the elastic peak on the sample was 45 meV.

Conductivity measurements were performed with *in situ* prepared calcium electrodes on Suprasil glass in a four point Valdes configuration. The strip electrodes were 0.7 mm wide, 1.5 cm long and 150 nm thick. The distance between the inner two electrodes was 7 mm and between the inner and outer electrodes 4 mm. The current-voltage characteristics were registered with a Keithley 237 source measure unit.

III. RESULTS AND DISCUSSION

A. XPS

Figure 1 shows the C 1s and S 2p emissions as a function of the doping level. The C/S atomic ratio ranges between 4.4:1 and 4.1:1, and therefore resembles the expected stoichiometric composition within the experimental error of 10%.

A shift ΔE_b of the C 1s, S 2s, and S 2p emissions to higher binding energies can be noticed with increasing dopant concentration. At 0.3 Na/ $\alpha 6T$, the shift amounts to 0.3 eV. From Table I it can be determined that the shift is not parallel to the increase in the dopant concentration, but shows a plateaulike behavior at $\Delta E_b = 0.55$ eV between 1 Na/ $\alpha 6T$ and 5.5 Na/ $\alpha 6T$, and saturates at a concentration of 8.6 Na/ $\alpha 6T$ ($\Delta E_b = 1.03$ eV). Lögdlund *et al.*¹⁰ found a

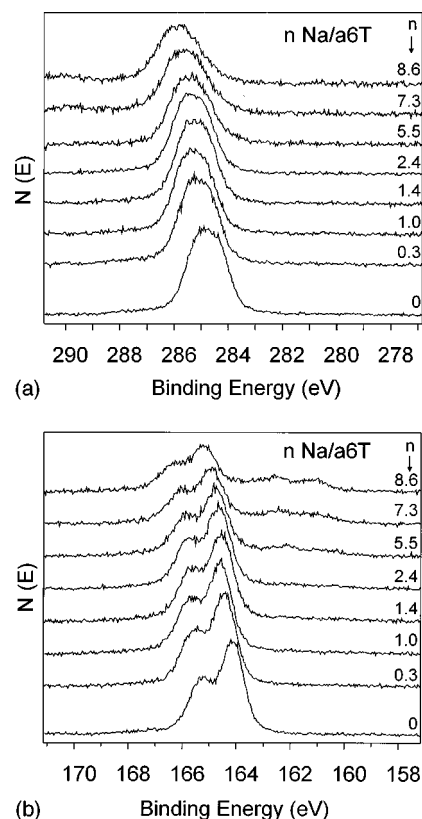


FIG. 1. XPS spectra of a 70-nm-thick $\alpha 6T$ film with increasing Na concentration. (a) C 1s peak, (b) S 2p region.

saturation at 6 Na/ $\alpha 6T$. However, this deviation lies within the large experimental error of the concentration determination (see Sec. II). Another explanation will be given below in Sec. III C1.

This shift can only partly be explained by the shift of the Fermi level as determined by UPS (see Sec. III B 1 below). In the UP spectra a greater shift appeared if compared to XPS, e.g., the maximum shift of the Fermi level at 5.5 Na/ $\alpha 6T$ is 1.06 eV, and thus 0.45 eV higher than the shift in XPS binding energy. Therefore a chemical shift of 0.45 eV down to lower binding energy has to be considered due to the negative charge.

In the sulfur emissions new peaks at 3.7 eV lower binding energies arise above doping levels of 2.4 Na/ $\alpha 6T$. The intensity of these peaks remains always below 10% of the “normal” sulfur emissions. There are two possible explanations for this shift.

On the one hand, the difference in the binding energies between oligothiophene and alkali sulfide sulfur is exactly 3.7 eV.¹¹ Alkali sulfide could be generated by destroying $\alpha 6T$ during Na deposition. However, this is unlikely because the stoichiometry between C and S as calculated from the XPS-peak ratio remains constant during the “doping” process. Furthermore the shoulder disappears upon exposure to air and “dedoping” of the thiophene. Alkali sulfides should be more stable in air and should not be decomposed to thiophene.

On the other hand, a highly localized negative charge at the sulfur atom could also cause such a shift. This is in line with EPR investigations, where the g factor of dodecylsexithiophene in solution is derived as 2.0046, which is sub-

TABLE I. Shift of the C 1s binding energy, of Na-doped $\alpha 6T$, the low-energy cutoff ΔE_E , the valence-band edge ΔE_V (determined by a linear extrapolation of the high-energy side of the valence band), the surface dipole χ as the difference $\Delta\Delta = \Delta E_V - \Delta E_E = \chi$ of the two values, and the work function Φ of Na-doped $\alpha 6T$. All energies are given in eV.

Na/ $\alpha 6T$	0.0	0.3	1.0	1.4	2.4	5.5	7.3	8.6
$\Delta E_b(\text{C } 1s)$	0.00	0.30	0.46	0.44	0.53	0.61	0.78	1.03
ΔE_E	0.00	-0.67	-0.80	-0.90	-1.15	-1.25	-1.11	-1.08
ΔE_V	0.00	-0.58	-0.61	-0.78	-0.96	-1.06	-0.96	-0.92
$\Delta\Delta$	0.00	0.09	0.19	0.12	0.19	0.19	0.15	0.16
ϕ	3.62	2.95	2.82	2.71	2.47	2.37	2.51	2.54

stantially higher than the value of 2.0023 for the free electron,¹² and the results presented in the next sections.

In contrast to p doping of sexithiophene⁹ and n doping of bithiophene,¹³ no shoulder at the high-binding-energy side of the C 1s, S 2s, and S 2p levels could be determined upon Na interaction. This shoulder is usually explained by additional shake-up events due to the new states in the band gap. This, however, should only be the case if the band-structure model is appropriate.

B. UPS

In Fig. 2(a) the UP spectra over the entire energy range are shown for various degrees of Na doping. Table I summarizes the important data. The spectrum for neutral $\alpha 6T$ is in good agreement with earlier measurements.^{9,14}

1. Band-structure interpretation

In the band-structure model the energetic difference between valence-band edge (determined by a linear extrapolation of the high-energy side of the valence band) and Fermi level is about 1.1 eV [Fig. 2(b)]. From HREELS measurements (Fig. 3), an optical band gap of 2.2 eV can be deduced (determined by a linear extrapolation of the low-energy side of the conduction band) which shows that the Fermi level is situated in the middle of this optical band gap.

As expected for n -type doping (in the band model), in the course of doping a significant shift of all emissions away from the Fermi level can be noted [Fig. 2(b)]. The maximum shift of the valence-band edge amounts to 1.06 eV, and is seen for 5.5 Na/ $\alpha 6T$. For higher doping levels a small shift results back to lower binding energies. The low-energy cut-off does not shift completely parallel to the valence-band edge, which may be caused by changes of the surface dipole χ .

The shift to lower binding energies at very high doping levels is also found by other authors. In Ref. 15 it is discussed as a relaxation shift due to a higher screening of charges, i.e., the complex $\alpha 6T$ -Na is more polarizable than the pristine molecule. Lögdlund *et al.*¹⁰ showed in theoretically calculated spectra that these results may also be explained by initial-state effects: The highest occupied molecular orbital (HOMO) is destabilized by transfer of one or two electrons per $\alpha 6T$, while it is stabilized by the transfer of three or more electrons. These authors find that at the saturation level of 6 charges per $\alpha 6T$ the binding energy of the initial HOMO is shifted back to the value of the undoped molecule. However, in the measurements presented here,

such a complete shift of the binding energy back to the initial data could not be determined.

The most important result is the appearance of a new peak in the band gap. In the UP-He I-spectrum [see Fig. 2(b)] this state shows up at a distance of 0.55 eV above the valence-band edge at doping levels of 2.4 Na/ $\alpha 6T$ and above. The intensity of this peak increases with dose at the expense of the two highest occupied MOs at 1.5- and 2.2-eV binding energies.

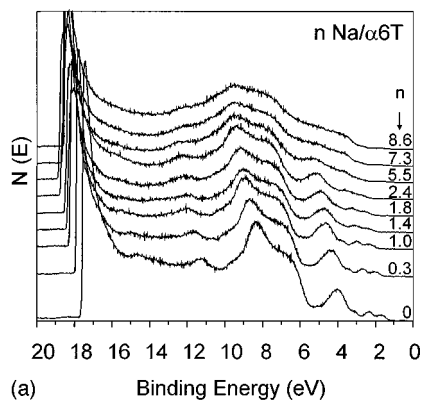
This behavior is in line with the consideration that the new peak is created by the movement of the HOMO and the lowest unoccupied molecular orbital (LUMO) into the gap, i.e., by the formation of a polaron ($\alpha 6T^-$). Alternatively one could assign this peak to a sodium state. However, in this case a constant energetic difference to the Fermi level would be expected rather than to the valence band edge.

Therefore, this peak corresponds to the lower doubly occupied state. However, there is no indication for a density of states at the Fermi edge where the occupied upper polaron state would be expected. Furthermore a shift of the new peak as expected for the transition from polaron to bipolaron gap states and subsequently for interacting polarons/bipolarons could not be found within the sensitivity of our experimental set up.

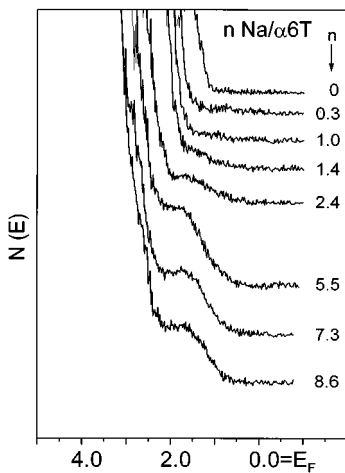
At higher doping levels it may, however, be deduced from the He II data that the lower doubly occupied state is split into two peaks at 0.4 and 0.75 eV above the valence-band edge for doping levels of 7.3 Na/ $\alpha 6T$ and above. However, this splitting could not be reproduced in all experiments. Such a splitting was observed by Ramsey *et al.*¹⁶ for cesium-doped sexiphenyl, which was interpreted as interacting bipolarons, forming bonding and antibonding peaks.

2. Molecular-orbital interpretation

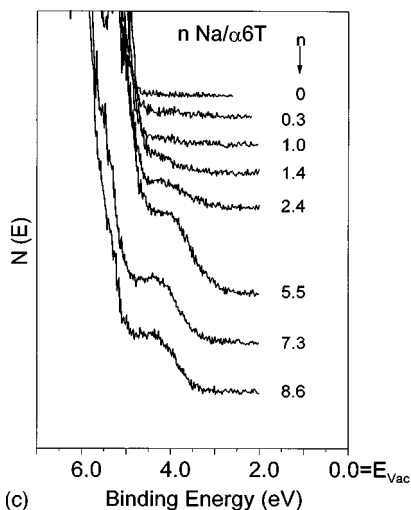
The same data will now be discussed in terms of a reaction of Na with sexithiophene, resulting in a new compound. The energetic difference between the HOMO peak maximum and E_F is 1.5 eV. From theoretical calculations¹⁷ the energetic difference between HOMO and LUMO is 4.29 eV (for comparison with optical transitions, compare Sec. III C 2), i.e., E_F is situated nearer to the HOMO level in this model. However, molecular orbitals are usually discussed with reference to the vacuum level and not the Fermi level, as will be discussed below. A detailed discussion of the Fermi-level definition in molecular systems is beyond the scope of this paper, see, e.g., Refs. 18–20.



(a)



(b)



(c)

FIG. 2. UPS spectra of a 70-nm-thick $\alpha 6T$ film with increasing Na concentration. (a) He I spectra. A binding energy of zero corresponds to the Fermi level. (b) He I spectra referenced to the Fermi level [$E_b(E_F) = 0$ eV]. (c) He I spectra referenced to the vacuum level [$E_b(E_{vac}) = 0$ eV].

Upon reaction one would expect that a different HOMO of the freshly generated compound appears. To the same extent the HOMO emission of the bare sexithiophene should vanish. There could be several cases for Na concentrations below the saturation concentration: Either there is only $Na_6^{6+} \alpha 6T^{6-}$ a stable compound, then just one (changed) HOMO is expected. Or there are several or all compounds

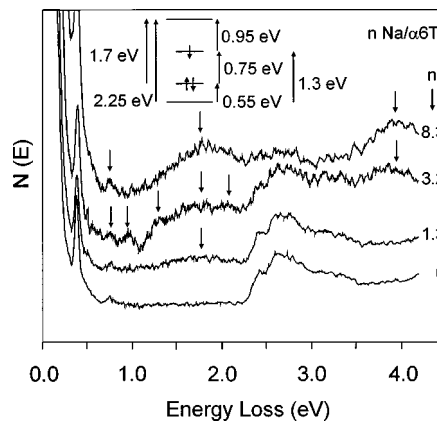


FIG. 3. HREELS spectrum of a 70-nm-thick $\alpha 6T$ film with increasing Na concentration. The inset shows a possible energy scheme with polaron levels.

stable beginning with $Na^+ \alpha 6T^{6-}$ up to $Na_6^{6+} \alpha 6T^{6-}$. Then the HOMOs of all the stable compounds could appear, either subsequently or simultaneously, depending on the relative stabilities and the formation kinetics.

Figure 2(c) shows the same spectra as in Fig. 2(b) but with reference to the vacuum level. As can be seen, in fact, a peak at a constant binding energy of 4 eV with respect to the vacuum level appears up to 5.5 $Na/\alpha 6T$. For higher Na concentrations this peak shifts to $E_b = 4.3$ eV. This can be explained by two stable compounds which are subsequently formed.

C. HREELS

In the HREELS spectra of doped and undoped $\alpha 6T$ (Fig. 3), the first two loss peaks are found at 0.37 and 0.75 eV. They can be attributed to the C-H stretch vibration and its overtone. There are no other loss peaks for energies below 2.2 eV.

At a concentration of 1.3 $Na/\alpha 6T$ a very broad loss structure appears at 1.7 eV. With further Na deposition the intensity of this loss peak increases very strongly, and dominates the spectrum at the highest concentration of 8.3 $Na/\alpha 6T$. Simultaneously a loss peak at 3.9 eV arises. Both effects lead to a less clear peak structure at energies between 1.0 and 4.5 eV due to the broadness of the peaks. Depending on the Na concentration maxima may also be detected at 1.3 and 2.1 eV which arise within the 1.7-eV peak structure as shoulders. There may also be a peak at 0.95 eV for 3.2 $Na/\alpha 6T$ accompanied by a slight increase of the peak intensity at 0.75 eV. This intensity increase can only be explained by an additional electronic energy loss at 0.75 eV because the intensity of the overtone of the C-H stretch vibration is constant.

1. Band-structure interpretation

At the position of the threshold of higher loss emissions of pure $\alpha 6T$ an optical band-gap energy of 2.2 eV can be determined. The latter is usually not identical with the real electronic band gap due to electron-electron interactions. As for p doping, where levels at 0.5 and 1.1 eV were found,⁹ these results can also convincingly be explained within the polaron model. The energetic positions of possible polaron levels are shown in the inset of Fig. 3. The position of the

lower level was taken from the UP spectra. Again these results are not totally in line with Lögdlund *et al.*¹⁰ because at these high dopant concentrations completely occupied bipolaron levels should be present according to their calculations. This contradiction cannot be explained as long as a complete reaction of Na with sexithiophene is assumed. In our experiments a metallic density of states at the Fermi level could definitively be excluded. This excludes the formation of large metallic islands or a continuous Na film. This also excludes the interpretation of the 1.7- and 3.9-eV losses as a plasmon peak and its overtone, which should be accompanied by a density of states at the Fermi level. On the other hand an incomplete charge transfer could also lead to very small Na clusters like Na_2^+ or with even more Na atoms per cluster [theoretical calculations predict a charge transfer of $0.93e$ per Na (Ref. 21)]. Na has only a medium oxidation potential ($E_H^0 = -2.7109$ V), at least in aqueous solution. It will be shown in a subsequent paper that the reaction of $\alpha 6T$ with Cs ($E_H^0 = -2.923$ V) leads to changes in the electronic structure at lower Cs concentrations if compared to Na.²² However, it remains unclear why an incomplete reaction should occur in our experiments but not in those presented in Ref. 10.

2. Molecular-orbital interpretation

Next to the threshold of 2.2 eV in pristine $\alpha 6T$, the loss peaks by π - π^* transitions follow, whereby the pronounced part of the peak at 2.35 eV can be attributed to the lowest transition of the C=C vibration progression of the ${}^1A_g \rightarrow {}^1B_u$ transition. In the further course of the spectrum there is a broad peak at 2.7 eV (${}^1A_g \rightarrow {}^1B_u$) and two less pronounced peaks at 3.2 and 3.4 eV. The reason for the quite large peak width is a vibrational coupling.^{23,24}

All results of Na interaction can also be explained by the levels caused by radical anions of the resulting compound. The loss peak at 1.7 eV would then be due to a transition in which the HOMO and a higher unoccupied level of the resulting compound are involved. Because nothing is known about this compound(s), all loss peaks can be explained in this model. In comparison with the UP spectra, which favor the subsequent formation of two different species, the loss peaks at 1.3 and 2.1 eV would be assigned to the first compound, and the 1.7- and 3.9-eV transitions to both compounds.

D. Conductivity

In Fig. 4 the four-point current-voltage curve of a “doped” film of $\alpha 6T$ ($2.3 \text{ Na}/\alpha 6T$) with a nominal thickness of 100 nm is presented. Influence from light during the measurement was excluded. The resulting conductivity is $\sigma = 2.5 \times 10^{-6} \Omega^{-1} \text{ cm}^{-1}$. Furthermore, two-point measurements were performed. In both cases a linear I - V characteristic between +5 and -5 V (+15 and -15 V for the four-point measurement) and identical conductivities can be deduced, indicating that the resistance of the contacts between the electrode and the sample is Ohmic. These low conductivities also point to the fact that the negative charge is highly localized at the sulfur.

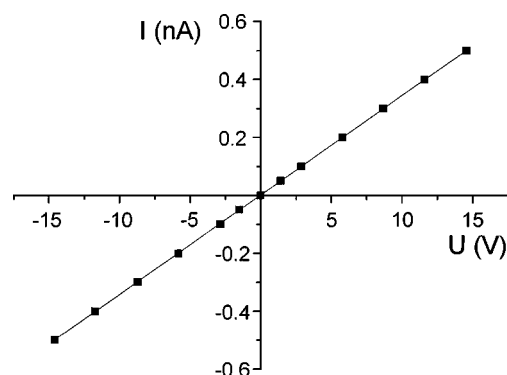


FIG. 4. I - V curve, measured in a four-point Valdes configuration, of a 100-nm-thick $\alpha 6T$ film with a Na concentration of $2.3 \text{ Na}/\alpha 6T$.

E. Comparison of the band-structure and molecular-orbital interpretation

As shown in the previous paragraphs, most of the results on the interaction of Na with sexithiophene can convincingly be explained by both models. However, negative charges seem to be highly localized as derived from XPS (additional sulfur core levels at lower binding energy), EPR spectra¹² (substantial deviations from the free electron g factor), the fact that at least six charges can be transferred to $\alpha 6T$, photoionization cross sections of Cs-doped bithiophene,¹⁵ and the low conductivity. All this favors the molecular orbital interpretation. Furthermore, the interaction with Cs leads to qualitatively similar changes in the electronic structure, but at completely different energetic positions.²² This would not be expected for a perfect bandlike behavior and negligible influence of the counterions. However, if the interaction with the counterions Na^+ or Cs^+ would be very different, these results can also be in line with the band-model interpretation. Theoretical calculations, on the other hand, show that the interaction energies seem to be relatively similar, although different locations of the different alkali ions with respect to a bithiophene ring system were deduced.²⁵ Last but not least, there are two experimental findings which do not fit into the band model: In the polaron model there should be two additional states in the band gap. The second, half-occupied state (compare the inset of Fig. 3) should also be seen in the UP spectra unless it has a negligible transition moment. The second contradiction is the lack of a shoulder on the high-binding-energy side of the C $1s$ and S $2p$ spectra which are found for p doping and also for “ n doping” of bithiophene with Cs but not for Na interaction with sexithiophene.

All these results favor interpretation through the localized molecular-orbital model. However, it should be kept in mind that due to the complete lack of information on the electronic structure of the newly formed compound(s), nearly all findings would fit into the molecular orbital picture. Therefore care has to be taken because the counter arguments against the band model are not too strong so that it cannot be completely ruled out.

IV. CONCLUSIONS

The effects of n doping with Na on the electronic structure and the electrical properties of $\alpha 6T$ were investigated

with electron spectroscopic methods under UHV conditions. The formation of a changed electronic structure can be observed by UPS and HREELS. Four point measurements show linear I - V characteristics with a conductivity of $\sigma = 2.5 \times 10^{-6} \Omega^{-1} \text{ cm}^{-1}$ for $2.3 \text{ Na}/\alpha 6T$. All results point at a high localization of the negative charge at the sulfur atom. Alternatively to the polaron/bipolaron model, therefore, a model of the formation of compounds with localized molecular orbitals was discussed in detail which may be more realistic. In the latter model two different compounds with

lower and higher Na contents are formed. These compounds have an electronic structure which gives rise to the observed changes in the electronic structure.

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