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π ELECTRON DELOCALIZATION IN POLY-(p-PHENYLENE) (PPP), POLYPHENYLENE SULFIDE (PPS) AND POLYPHENYLENE OXIDE (PPO) AND AsF_5 DOPING OF PPP

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Résumé - Les largeurs des bandes π dans le poly-(p-phénylène), le sulfure de polyphénylène et l'oxyde de polyphénylène sont déterminées par les expériences de pertes d'énergie d'électrons. Une estimation de la charge sur les atomes de carbone dans des environnements différents est déduite des mesures du déplacement du seuil d'absorption K du carbone. Deux niveaux à l'intérieur du gap ont été détectés dans le polyparaphénylène dopé par AsF_5. Ce résultat est en accord avec un modèle bipolaron pour la conductibilité.

Abstract - The relative widths of π bands in poly-(p-phenylene), polyphenylene sulfide and polyphenylene oxide are deduced from electron energy loss experiments. From measurements of the chemical shift of the carbon K absorption edge, the charge on carbon atoms in different coordination is estimated. In AsF_5 doped poly-(p-phenylene) two states inside the gap have been seen, consistent with a bipolaron model for the conductivity.

Upon doping with AsF_5, PPP and PPS can be transformed into a metallic state having conductivities σ of 500 S/cm , and 1 S/cm /2,3/, respectively. In PPO conductivities of only 10^{-3} S/cm are reached upon doping with AsF_5 /4/. In a simple rigid band model, the mobilities of the charge carriers and thus the conductivity of doped samples should be roughly correlated with the width of the highest occupied band. Electron energy loss spectroscopy provides the unique possibility to estimate the extent of delocalization of electrons which is connected to the width of the bands by determining the momentum dependence of excitations between these bands. In addition the charge on carbon atoms in different coordination can be deduced from measuring the chemical shift of the carbon K absorption threshold. With high resolution electron energy loss spectroscopy it is also possible to investigate the buildup of states in the band gap with increasing dopant concentration. Data were recorded with a 170 KeV electron energy loss spectrometer operated at an energy resolution of 0.1 eV and at variable momentum resolution between 0.03 and 0.16 $Å^{-1}$ with beam currents between 1 and 5 nA. PPP samples were prepared by the Kovacic and the Yamamoto method /5,6/, Ter-(p-phenylene) (TPP), PPS and PPO samples were obtained from commercial material. PPP samples were heat treated at 420°C for 24 hrs, both PPS and PPO samples at 240°C for 2 hrs.

I From benzene to PPP

To understand the development of π-π*-bands upon polymerization of benzene rings, we compare the valence spectra of PPP with those of TPP. The oscillator strength of these two compounds as deduced from a Kramers Kronig analysis is shown in Fig. 1. The oscillator strength derived by a LCAO-SCF-CNDO calculation /7/ for $(C_6H_4)_x$ for x=1-4 broadened by a Lorentian of 1 eV FWHM is shown as a broken line in Fig. 1. For x = 3 (TPP) the agreement between theory and experiments is excellent. The calculations show that the lower excitations near 4 eV are associated with π electrons which are spread over several benzene rings. The excitations near 6 eV are due to transitions between π electrons confined to individual benzene rings. The results of our calculations for x = 1-4 suggest, that the localized and delocalized nature of the two groups of excitations is preserved in PPP. This should be reflected in the momentum dependence of the excitation energies in PPP.

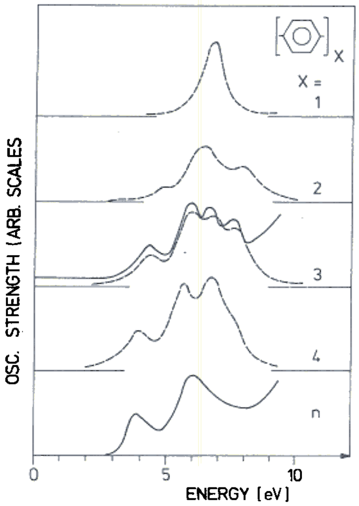

Fig. 1 Oscillator strength of $(C_6H_4)_x$. Broken line: LCAO-SCF-CNDO calculations broadened by 1 eV. Full line: derived from ELS experiments.

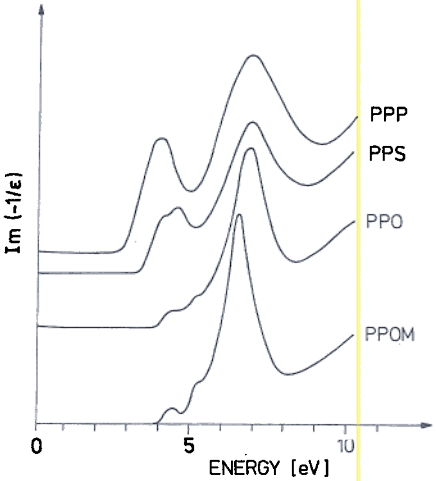

Fig. 2 Energy loss spectra in the region of valence excitations for PPP,PPS,PPO and PPOM

II Momentum dependence of valence excitations in PPP, PPS and PPO

In Fig. 2 we show typical electron energy loss spectra of the valence excitations of PPP, PPS, PPO and PPOM (PPO with methyl side groups) for small momentum transfer ($q=0.08$ Å^{-1}). For all compounds there is a pronounced structure near 7 eV,showing no momentum dependence. The excitation near 4 eV in PPP on the other hand shows strong dispersion with a dispersion coefficient $\alpha = 1.15$ eV/Å^2 defined by $E=E_0+\alpha q^2$, where E_0 is the excitation energy for momentum transfer $q=0$. This dispersion coefficient is comparable to that found in graphite.This indicates that in PPP the highest occupied π band shows a large band width whereas the next lower occupied π band is rather narrow. These results are in accordance with band structure calculations/8,9/. In PPS the dispersion coefficient for the lowest observed excitation $\alpha = 0.2$ eV/Å^{-2} is much smaller than in PPP. We conclude that the width of the highest occupied π band in PPS is much smaller compared to that of PPP in good agreement with theoretical results /9/. In PPO and PPOM only small intensity is observed below 5 eV showing no dispersion. Thus in PPO and PPOM π bands are rather narrow, that means π electrons are confined to the benzene rings and there is no delocalization. Thus, for PPP, PPS and PPO a strong correlation between the width of the highest occupied π band and the conductivity of doped samples has been confirmed experimentally.

III The charge on the carbon atoms

In Fig. 3 we show the loss spectra in the region of carbon K-shell excitations for PPP, PPS, PPO and PPOM. The spectra do not reflect the density of unoccupied states. They are interpreted by an interaction of the conduction band with the core hole leading to strong resonance-like absorption at the bottom of the conduction band /10/. Then, the different peaks are explained by carbon atoms in different coordination, having different charge and thus different chemical shifts.

Our LCAO-SCF-CNDO calculations show that in PPP those carbon atoms located at junctions of benzene rings have about 0.1 electrons less than the other carbon atoms. In PPS, the charge difference calculated for carbon atoms in different (

has about the same value. However, in PPO and in PPOM the charge on carbon atoms adjacent to oxygen atoms is about 0.3 electrons less compared to that of the other carbon atoms in the benzene ring. Comparison between MO-calculations and chemical shifts as determined by ESCA /11/ yield a relation between chemical shifts and the change of charge on carbon atoms of about 6 eV per electron. From this we expect in PPP and PPS chemical shifts for the carbon atoms in the two different coordination of about 0.5 eV. This is in line with the observed features near 285 eV for PPP and PPS, which is composed of two peaks separated by about 0.5 eV. In PPO and PPOM, chemical shifts of about 2 eV are expected in accordance with the finding of two peaks in the spectra separated by about 2 eV. The origin of the shoulders at the first peaks in PPO and PPOM is not yet clear.

IV AsF_5 doped poly-(p-phenylene)

In Fig. 3 we show electron energy loss spectra of PPP as a function of AsF_5 content. The lowest curve shows data for pristine PPP, the upper curves are measured on PPP samples with increasing amounts of AsF_5. The relative AsF_5 doping level was estimated from structural changes measured by elastic electron scattering. At low dopant content we see in addition to the spectrum of pristine PPP a peak near 0.7 eV . At higher doping-levels, there are peaks at 1.1 eV and 2.7 eV in the low energy range. At the highest doping concentration, the lower structure is very high in intensity compared to the rest of the spectrum and cannot be separated from the elastic peak at zero energy. The second peak is now near 2 eV. Structures at higher energies also change at this doping level. A peak near 2 eV has also been observed in optical absorption spectra on SbF_5 doped PPP samples /14/.

In summary, we find peaks near about 1 eV and near about 2 eV, corresponding to transitions from the valence band to two states in the gap. Brédas et al. /12,13/ have proposed two states at 0.6 - 0.9 eV above the valence band and 0.6 - 0.9 eV below the conduction band in their bipolaron model for the conductivity of doped PPP. These predictions are consistent with our measurements. Also the broadening

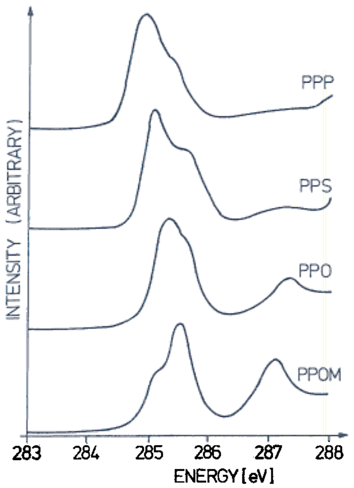

Fig. 3 Energy loss spectra in the region of carbon K-shell excitation for PPP, PPS, PPO and PPOM.

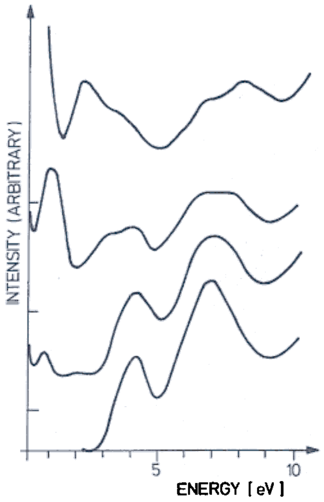

Fig. 4 Energy loss spectra in the region of valence excitations for PPP (lowest curve) and PPP doped with increasing amounts of AsF_5 (upper curves).

of the bipolaron states at higher dopant concentrations is in line with our spectra For a quantitative comparison of theory and experiment, more measurements are needed and a calculation of the oscillator strength for the transitions from the valence states to the bipolaron states would be highly desirable.

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