Sociedade Brasileira de Química (SBQ) Electronic relaxation effects in condensed polyacenes: a high-resolution photoemission study

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Keywords: High-resolution photoelectron spectroscopy, polyacenes, shake-up satellites, electronic relaxation, synchrotron radiation

Introdução

Ultrathin films of polyacenes show very interesting chemical, optical, and electrical properties and are thus used for novel technological approaches in organic electronic and electro-optic devices such as organic LEDs, solar cells, FETs, or lasers [1-3]. The understanding of the electronic structure of the molecular films employed is therefore crucial for the development of such devices. This information can be obtained directly by electron spectroscopic techniques like, e. g., photoelectron spectroscopy (PES) and x-ray absorption spectroscopy (NEXAFS - near-edge X-ray absorption fine structure) as demonstrated extensively in the past. Nowadays, the availability of high-brilliance and high-resolution soft x-ray beamlines at 3rd generation synchrotron radiation sources has opened up the possibility to organic molecules data on with acquire unprecedented spectroscopic quality. It is thus possible to explore in greater detail the complex fine structure obtained by high-resolution x-ray absorption as well as valence and core level PES spectra. In this work, we present a comparative study with emphasis on the fine structure in the highresolution PES data of condensed benzene and polyacenes, namely naphthalene, anthracene, tetracene, and pentacene measured at the UE52-PGM undulator beamline at BESSY II. The molecules were chosen in order to provide a systematic variation of the size of the molecular aromatic system.

Resultados e Discussão

The PES spectra appear very similar, a dominant peak accompanied by less intense rather small satellites at higher binding energies The shake-up satellite spectra reveal trends, which give insight into the charge redistribution within the molecule upon photoexcitation. In particular, the HOMO-LUMO shake-up increases in intensity and moves closer towards the C1s main line, if the size of the aromatic system is increased. A comparison of the HOMO-LUMO shake-up position to the optical band gap gives additional insight into the reorganization of the electronic system upon photoexcitation. The energy difference between optical gaps and shake-up energy apparently stabilizes for larger molecules at

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a value of approx. 0.85 eV [4]. The valence data demonstrate the increasing complexity of the molecular valence levels. If the molecular size increases, the HOMO level moves closer to E_{Fermi} due to the decreasing band gap.

Conclusões

We have measured core and valence level PES of benzene, naphthalene, anthracene, data tetracene, and pentacene in the condensed phase. The data were acquired with very high spectral quality and thus allow a detailed analysis of the fine structure with particular respect to the systematic variation of the molecular size. The line shapes of the C1s main lines were analyzed with respect to different contributions of inhomogeneous the broadening, vibronic coupling, and chemical shifts. A comparison of the shake-up spectra for the different molecules implies interesting trends regarding the intensity and energy positions of the shake-up transitions, which gives insight into the charge redistribution within the molecule upon photoexcitation. A preliminary explanation is given on the basis of the delocalization of the aromatic system and its capability in screening the photogenerated core hole. A comparison of the HOMO-LUMO shake-up position to the optical band gap shows that while the HOMO-LUMO separation is not affected for benzene, it is strongly decreased for the larger polyacenes.

Agradecimentos

Financial support by the CAPES/DAAD/PROBRAL n. 267/07, the BMBF (contract 05KS4WWC/2), and the DFG (GRK1221) is gratefully acknowledged. One of us (M.L.M.R.) would like to thank the DAAD and FAPERJ for a fellowship grant.

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