Understanding photoemission of organic molecular films

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Ultra-thin films made of organic molecules form the basis of future semiconductor technologies. Because organic molecules are extremely flexible, they can be used in a whole new range of applications, making it equally possible to create pliable screens and cost-effective photo-voltaic cells. A successful application of organic semiconductors in such devices, however, asks for a better understanding of the fundamental interactions between the organic material and the inorganic carrier substances. These interactions are largely determined by the molecule's frontier orbitals, i.e., the highest occupied and the lowest unoccupied molecular orbital. Methods to determine their spatial distribution will allow for to better understanding of how organic semiconductor components work and thus help to improve their efficiency. This proposal investigates the photoemission process from organic molecular films from an ab-initio perspective. Commonly, angle-resolved photoemission spectroscopy (ARPES) is applied to study the band structure of solids by measuring the kinetic energy versus angular distribution of the photoemitted electrons. In recent publications however, it was shown that this experimental technique can also be used to characterize discrete orbitals of large pi-conjugated molecules. In particular, a simple relation between the observed angular intensity distribution and the Fourier transform of the initial state orbital could be established enabling a reconstruction of the real space electron distribution of individual molecular orbitals [1,2]. While these results demonstrated the proof of principle, several simplifying assumptions have been made. Thus, the proposed research plan will improve the theoretical description of the photoemission from organic molecular layers in several aspects, thereby allowing for a quantitative interpretation of ARPES intensity maps. The outcome of this proposal will not only be interesting from a fundamental point of view but will also serve as a valuable tool for the investigation of organic molecular films and monolayers given recent advances in ARPES instrumentation. Moreover, we anticipate that reciprocal space maps from ARPES experiments together with their theoretical interpretation could nicely complement scanning probe techniques in continued attempts to image individual molecular orbitals. This will facilitate the tailoring of organic semiconductor interfaces with desired properties.

[1] P. Puschnig et al. "Reconstruction of Molecular Orbital Densities from Photoemission Data", Science 326, 702-706 (2009).
[2] J. Ziroff et al.,"Hybridization of Organic Molecular Orbitals with Substrate States at Interfaces: PTCDA on Silver", Phys. Rev. Lett. 104, 233004 (2010).