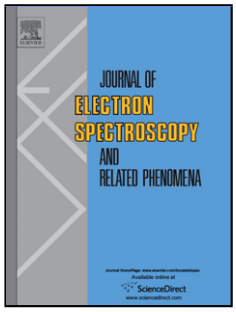

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PII: S0368-2048(15)00039-0
DOI: http://dx.doi.org/doi:10.1016/j.elspec.2015.02.007
Reference: ELSPEC 46393

To appear in: *Journal of Electron Spectroscopy and Related Phenomena*

Received date: 2-1-2015
Revised date: 6-2-2015
Accepted date: 11-2-2015

Please cite this article as: X.-Y. Zhu, Photoemission from Excitons in Organic Semiconductors, *Journal of Electron Spectroscopy and Related Phenomena* (2015), http://dx.doi.org/10.1016/j.elspec.2015.02.007

Photoemission from Excitons in Organic Semiconductors

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An exciton is an atomic hydrogen-like quasi-particle, consisting of a Coulombically bound pair of an electron and a hole in conduction and valence bands, respectively. While excitons are traditionally investigated by optical spectroscopies, photoelectron spectroscopy can be a powerful tool in providing a unique view on the energetics and dynamics of excitons in semiconductor materials. The experiment typically relies on time-resolved two-photon photoemission (TR-2PPE) spectroscopy in which the first laser pulse creates excitons in a material and the second laser pulse ionizes the excitons for detection. In this short note, I discuss unique insights provided by TR-2PPE on exciton dynamics in organic semiconductors and challenges in the application of this technique.

Ultraviolet photo-emission spectroscopy (UPS), also known as angle-resolved photoemission spectroscopy, has been the workhorse in experimental determination of electronic structures, namely valence bands, of solid materials. A complementary, albeit less capable, technique is inverse photoemission spectroscopy for the conduction bands. Both techniques probe transport levels, i.e., a system with an excess hole in the valence band or an excess electron in the conduction band. However, in many physical processes involving light-matter interaction, particularly in optoelectronic devices, we are interested in not only single particle electronic states but also quasi-particles, namely, excitons. Here I briefly describe the application of time-resolved two-photon photoemission (TR-2PPE) spectroscopy [1 - 5] to probe excitons in semiconductors, with an emphasis on organic semiconductors.[6,7]

Across band-gap optical excitation in a semiconductor does not lead to a free electron and a free hole when the Coulomb attraction energy is higher than thermal energy. Instead, a bound electron-hole pair called an exciton is formed. In the limit of weak Coulomb interaction, the Mott-Wannier picture is appropriate in describing an exciton in a semiconductor.[8,9] A Mott-Wannier exciton consists of a nearly free electron in the conduction interacting with a nearly free