Photoemission Orbital Tomography: a renaissance of UV photoemission.

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"If we could experimentally obtain any knowledge of HOMO and LUMO patterns, chemistry would be profoundly affected. In that event the orbital pattern concept, which is at present of a somewhat unreal nature, will be provided with a certain empirical foundation"
(Kenichi Fukui 1977)

The frontier orbitals of molecules are the prime determinants of their chemical, optical, and electronic properties. Arguably, the most direct method of addressing the (filled) frontier orbitals is ultra-violet photoemission spectroscopy (UPS). Although UPS is a mature technique from the early 1970s on, the angular distribution of the photoemitted electrons was thought to be too complex to be analyzed *quantitatively*. Recently angle-resolved UPS work on conjugated molecules, both in ordered thick films and chemisorbed monolayers, has shown that the angular (momentum) distribution of the photocurrent from orbital emissions can be simply understood when a plane wave final state is assumed. This approach, becoming known as photoemission orbital tomography (POT), relates the emission distribution to the Fourier transform of the ground state orbitals - essentially the momentum maps of POT are images of the molecular orbitals envisaged by the 1981 Nobel laureate Kenichi Fukui. Examples will be shown for using POT to reconstruct real space orbitals, determine molecular orientation and conformation, quantify the charge transfer to molecules on surfaces and yield insight into the surface chemical bond. These will introduce photoemission tomography and demonstrate its potential as a technique to determine both electronic and geometric structure, not just complementary but also competitive to methods as diverse as scanning tunneling microscopy and near-edge X-ray absorption spectroscopy