Photoemission Orbital Tomography for Chemical Analysis of Surface Species

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Photoemission orbital tomography (POT) is a combined experimental / theoretical approach which reveals information about the spatial distribution of individual molecular orbitals [1]. Experimentally, it uses angle-resolved photoemission spectroscopy (ARPES) to obtain constant binding energy photoemission angular distribution maps, so-called tomograms, to reveal information about the electron probability distribution in molecular orbitals. Theoretically, one rationalizes these tomograms as hemispherical cuts through the molecular orbital in momentum space.

In this contribution, I will show how POT is utilized to trace the modifications of molecules in surface chemical reactions. On the example of the disc-shaped aromatic molecule bisanthene ($C_{28}H_{14}$), which is synthesized on a Cu(110) surface via a thermally induced dehalogenation and cyclodehydrogenation reaction from a pre-cursor molecule, it is demonstrated how a series of molecular orbitals over a remarkably broad energy range can be imaged by POT. While the frontier molecular π orbitals are used to detect a possible hydrogen abstraction at the molecular periphery [2], the deeper lying σ orbitals serve as fingerprints to reveal reactions of the molecule with metal ad-atoms [3]. This illustrates the potential of POT as a unique tool for the detailed analysis of surface chemical reactions.

[1] Puschnig, P.; Berkebile, S.; Fleming, A. J.; Koller, G.; Emtsev, K.; Seyller, T.; Riley, J. D.; Ambrosch-Draxl, C.; Netzer, F. P.; Ramsey, M. G. "Reconstruction of Molecular Orbital Densities from Photoemission Data". *Science* **326**, 702–706 (2009).

[2] Yang, X.; Egger, L.; Hurdax, P.; Kaser, H.; Lüftner, D.; Bocquet, F. C.; Koller, G.; Gottwald, A.; Tegeder, P.; Richter, M.; Ramsey, M. G.; Puschnig, P.; Soubatch, S. & Tautz, F. S. “Identifying surface reaction intermediates with photoemission tomography”, *Nature Communications* **10**, 3189 (2019).

[3] Haags, A.; Yang, X.; Egger, L.; Brandstetter, D.; Kirschner, H.; Bocquet, F. C.; Koller, G.; Gottwald, A.; Richter, M.; Gottfried, J. M.; Ramsey, M. G.; Puschnig, P.; Soubatch, S. & Tautz, F. S. “Momentum-space imaging of σ-orbitals for chemical analysis” arXiv:2111.00250 (2021).