

Identifying on-surface site-selective chemical conversions by theory-aided NEXAFS spectroscopy: The case of free-base corroles on Ag(111)

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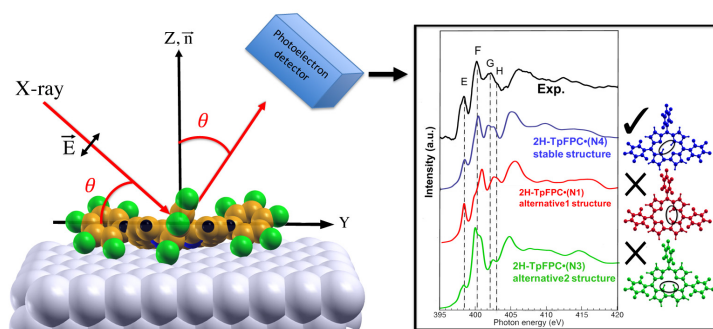
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The identification of unknown molecular species and in particular their covalent conversions is a highly interesting topic for various fields ranging from traditional ones such as heterogeneous catalysis to more timely ones such as the pulsating topic of on-surface synthesis.

It is well known that the unambiguous insights of such conversions are notoriously complicated to achieve in these research areas. X-ray photoemission spectroscopy (XPS) is often employed to unravel the on-surface chemistry of smaller molecules. However, for challenging tasks, e.g., the distinction of highly similar species such as tautomeric or isomeric structures of larger compounds, the obtained spectral information remains ambiguous.

We introduce a novel combined approach extending the existing tools for analyzing on-surface chemical conversions. We demonstrate that by analyzing angle-dependent near-edge X-ray absorption fingerprints on the bases of a high-quality theoretical description it is possible to trace on-surface reactions in a complex system reaching site-selectivity [1-4].

On the prototype example of free-base corrole adsorbed on a silver surface, we show that our approach features the resolving power to distinguish between the possible tautomers of the intact species, discriminate between three potential dehydrogenation places, and identify at which out of six sites a defluorinative ring-closure reaction actually occurs (see Figure 1).



Calculated angle-dependent N K edge spectra points out the power of the theoretical approach to discriminate between the different tautomeric structures of 2H-TpFPC•.

References:

- [1] H. Aldahhak, et al., Chem. Euro. J., submitted (2017).
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