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Quantification of finite-temperature effects on adsorption geometries of π-conjugated molecules

Experimentally determined adsorption geometries of molecular switches are essential both for understanding their functionalities and for benchmarking ab initio calculations. The prototypical molecular switch azobenzene is investigated on the Ag(111) surface by means of the normal incidence x-ray standing wave (NIXSW) technique and dispersion-corrected density functional theory (DFT) calculations.

We show that, besides the average positions of each chemical species, the molecular geometry can be retrieved from the coherence of the NIXSW signal using a new analysis method generally applicable to all molecular adsorbate. In this way azobenzene is found to exhibit a substantial torsion in a dense monolayer. The inclusion of non-local collective substrate response (screening) in the dispersion correction scheme improves the description of azobenzene adsorption geometry. Nevertheless, we show that for a quantitative agreement with experiment explicit consideration of the (hitherto generally neglected) effect of vibrational mode anharmonicity due to finite temperature on the molecular geometry is crucial.

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