Towards a mechanistic understanding of photoinduced (non-)switching of metal surface adsorbed Azobenzenes.

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Adsorption of functional molecules on metal surfaces is of specific interest to nanotechnology as it could lead to novel functionality not present in gas phase. Unfortunately, overly strong coupling with the substrate electronic degrees of freedom often quenches photo-induced reactions, such as in the case of the molecular switch azobenzene on coinage metal surfaces. Nevertheless, recent experiments revealed such a photo-induced mechanism for tetr.-*tert*-butyl functionalized azobenzene (TBA) at Au(111). It is believed that isomerization is triggered by excitation from the metal *d*-bands rather than from the adsorbate states followed by subsequent charge-transfer to the adsorbate[1]. Employing dispersion-corrected Density-Functional-Theory calculations we were able to rationalise the non-switching of azobenzene and derivatives on Ag(111) already in terms of modified groundstate energetics, which lead to an effectively destabilized metastable state[2]. In order to further investigate the detailed photo-isomerization dynamics we have established an efficient approach to low lying excited states of large adsorbate systems based on the recently proposed linear expansion Δ-Self-Consistent-Field method[3]. The method yields a topologically correct description of excited state potential energy surfaces and a qualitative account of hybridization and image charge effects. We present here excited states of adsorbed azobenzene relevant for gasphase isomerization as well as for a possible STM- or light-induced charge-resonant isomerization. Systematic mappings along important degrees of freedom for azobenzene on Ag(111) and Au(111) allow a detailed comparison with the well known gasphase case. We will also present current limitations of this approach, namely the effective treatment of hybridization and the remaining self-interaction error due to semi-local xc-treatment. The fact that some conclusions can already be drawn from the static picture encourages us to seek for a complete non-adiabatic dynamic treatment of the corresponding mechanisms.

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