

Finite-Temperature Effects on Structure and Energetics: Organic Adsorbates from a First-Principles Perspective

Reinhard J. Maurer¹

¹*Department of Chemistry, Yale University, New Haven CT 06520, USA*

email: reinhard.maurer@yale.edu

An often imposed assumption in vacuum surface science is that equilibrium properties of molecular adsorbates on metal surfaces are largely unaltered by finite temperature effects. This talk revisits this assumption for large organic adsorbates in the context of surface functionalization and hybrid organic--inorganic interfaces. Employing Density-Functional Theory including the account of many-body dispersion effects we assess the accuracy of geometries and adsorption energies for a variety of systems in comparison to X-ray standing wave and Temperature Programmed Desorption (TPD) measurements, both experiments usually performed at medium to high temperatures. Specifically for functional and flexible adsorbates the above assumptions break down as here shown for the molecular switch azobenzene adsorbed on an Ag(111) surface. Only by explicit account of anharmonic effects and vibrational mode coupling using *ab-initio* molecular dynamics are we able to correctly recover the experimental adsorption geometry and temperature. This not only raises questions concerning the reliability of typical approximations in simulation, but also has consequences for the typical TPD analysis in the framework of the Polanyi-Wigner equation.