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Mind the Entropy: Electronic and Thermal Fluctuations of Large Molecules on Metals REINHARD MAURER, Yale University, WEI LIU, IGOR POLTAVSKYI, Fritz-Haber Institute of the Max-Planck Society , HARALD OBERHOFER, THOMAS STECHER, Technische Universitaet Muenchen, ALEXANDRE TKATCHENKO, Fritz-Haber Institute of the Max-Planck Society, KARSTEN REUTER, Technische Universitaet Muenchen — The prevailing working hypothesis in vacuum surface science is that equilibrium properties of adsorbed molecules are largely unaltered by finite temperature effects. In this work we illustrate that this is not the case for the adsorption geometry, energetics, and desorption temperature of the molecular switch Azobenzene adsorbed to Ag(111). Comparing with X-ray standing wave measurements and temperature programmed desorption experiments we find strong discrepancies to static Density-Functional Theory calculations. Anharmonic corrections and ab-initio molecular dynamics simulation of the free energy of desorption account for the thermal fluctuations and inclusion of many-body dispersion effects accounts for the electronic fluctuations that govern the interaction strength. In both cases more modest, typically employed approaches fail to capture the sizable entropy of desorption and the correct desorption temperature. This implies that an accurate description of adsorbate interactions and entropies of adsorption in most realistic functional hybrid metallic organic systems necessitates a full account of the inherent anharmonicity of adsorbate and substrate in addition to an accurate description of dispersion interactions.

Reinhard J. Maurer
Yale University

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