Quantitative Comparative Force Spectroscopy on Molecules

Xinzhe Wang,[1] Percy Zahl,[2] Jara Trujillo Mulero,[3] Hailiang Wang,[4] Rubén Pérez,[3] Eric Altman,[5] and Udo D. Schwarz[1,5,6*]

[1] *Department of Mechanical Engineering, Yale University, New Haven, CT 06511, USA.*
[2] *Brookhaven National Lab, Upton, NY 11973, USA.*
[3] *Departamento de Fisica Teorica de la Materia Condensada, Universidad Autonoma de Madrid, Spain.*
[4] *Department of Chemistry, Yale University, New Haven, CT 06511, USA.*
[5] *Department of Chemical and Environmental Engineering, Yale University, New Haven, CT 06511, USA.*
[6] *Department of Materials Science, Yale University, New Haven, CT 06511, USA.*

* Corresponding author. E-mail: udo.schwarz@yale.edu

Understanding molecular-scale interactions at surfaces is essential for advancing catalyst design and developing efficient energy conversion processes. Here, we report ongoing efforts to improve the spatial accuracy and quantitative reliability of three-dimensional atomic force microscopy (3D-AFM) by refining data correction techniques for CO-functionalized tips. These developments allow us to minimize tip- and substrate-induced artifacts and isolate the intrinsic molecular interaction at atomic resolution.

As a testbed for this approach, we investigate cobalt phthalocyanine (CoPc) and its amino-functionalized counterpart ($(NH_2)_4CoPc$) adsorbed on Ag(111), both of which are of interest in CO_2 electroreduction catalysis. By identifying and removing asymmetric force contributions caused by the metallic structure of the tip, we obtain corrected force spectroscopy data that reveal equilibrium interaction distances and energies across individual molecules. Our analysis shows that NH_2 substitution alters the spatial distribution of interaction strength, decreasing equilibrium distances near ligand attachment points while broadly reducing interaction energy with the tip.

These experimental observations agree well with DFT-based simulations and suggest that side-group functionalization directly modulates the molecule's chemical landscape. The methodology provides a direct route toward correlating molecular structure with catalytic behavior at the single-molecule level, thereby enabling a deeper understanding of functional molecular systems on surfaces.

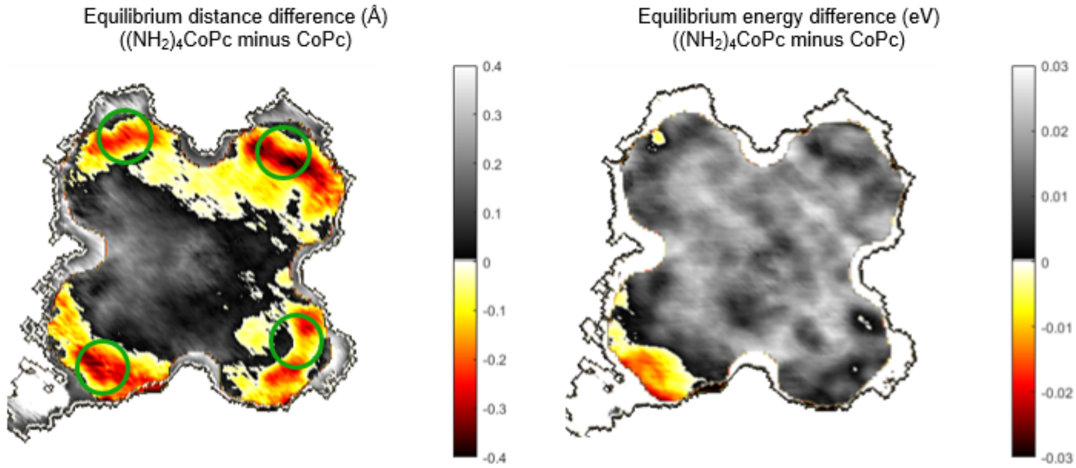

Figure 1. Difference maps for the equilibrium distance (left) and energy (right) between CoPc and its amino-functionalized counterpart ($(NH_2)_4CoPc$) when it is adsorbed on Ag(111). Note that the presence of a water molecule at the lower-left lobe (visible as a "white blur") is influencing the results near that lobe.