

Abstract Submitted  
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**Single Molecule Electrochemistry: Impact of Surface Site Heterogeneity.**<sup>1</sup> BO FU, COLIN VAN DYCK, STEPHANIE ZALESKI, RICHARD VAN DUYNE, MARK RATNER, Northwestern University — The efforts on coupling the electrochemistry with single molecule spectroscopy increased significantly during the past decade in observing the redox processes at the nanoscale level. Zaleski et al recently studied the reduction reaction of the rhodamine 6G (R6G) molecule by electrochemical single molecule surface-enhanced Raman spectroscopy (EC-SMERS) and showed a broader reduction potential distribution than that observed in the ensemble electrochemistry experiment. In order to understand and explain this experiment theoretically, we related the adsorption energy of R6G cation on AgNP with its reduction potential and computed this binding energy at various local surface sites using periodic density functional theory. Eight local surface sites and five molecular configurations at each site were explored. A semi-quantitative agreement was obtained between the reduction potential distribution of the Faradaic events and the adsorption energy distribution of the strongest binding states at each explored surface site. We further inferred that the underpotential reduction events corresponds to the less stable binding states compared to those matched with Faradaic events.

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