MAR08-2007-007245

Abstract for an Invited Paper
for the MAR08 Meeting of
the American Physical Society

Imaging hot-electron transport using chemical reactions on metal surfaces

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We have investigated a new regime of single-molecule excitation in the scanning tunneling microscope, where hot electrons locally injected from the STM tip spread out via surface resonances over length scales of up to 100 nm and electronically excite surrounding molecules causing chemical reactions. Such non-local reactions were observed for several different molecules on the (111), (110) and (100) terminated surfaces of gold and copper. The hot-electron origin of these reactions was differentiated from the possible electric field effect in the tip-surface junction on the basis of the statistical analysis of the dissociation yield as well as the non-local excitation in the presence of artificially fabricated nanoclusters. One of the new opportunities provided by the non-local excitation is a direct measurement of hot-electron transport on a metal surface. Using a phenomenological kinetic model for the statistical analysis of the non-local reactions, it is shown that the reaction rate increases linearly with tunneling current and decays exponentially with the distance from the excitation pulse. Since the attenuation length of the non-local reaction has little dependence on the STM-tip and the parameters of the excitation, we argue that it is proportional to the inelastic mean-free path of hot-electrons in the surface resonance. The angular distribution of the reaction events is isotropic on Au(111), which is consistent with the symmetry of its surface resonances in the energy range of the non-local reaction. It is also shown that the total yield of the non-local reaction provides a measure of hot-electron transport across single-atom steps. Although the reflectance of the hot-electrons by single atom steps on Au(111) is less than 20% at energies above 1.5 V, the yield of the reaction becomes surprisingly asymmetric if hot-electrons are injected in the immediate vicinity of the step.