Direct observation of the Linear Combination of Molecular Orbitals model in real space by combined scanning tunneling microscopy and atomic force microscopy

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Scanning probe microscopy, most notably scanning tunneling microscopy (STM) and atomic force microscopy (AFM) have been used to study chemical reactions, such as bond formation, and dissociation on the level of single molecules [1-3]. Whereas single-molecule chemistry is not useful for mass-production, it offers the possibility to study model systems in a well-defined environment in a controlled manner. Progress in STM and AFM now allows the electronic and geometric structure of electronically decoupled molecules and their complexes to be investigated with atomic scale spatial resolution, as well as atomic scale manipulation of the species of interest. The combination of these techniques offers the prospect of unraveling chemical reaction mechanisms on surfaces.

Here, we present a combined STM/AFM study of a chemical reaction between individual metal atoms (gold) and organic molecules (phenazine) deposited on an ultrathin insulating film. Metal-ligand complexes where synthesized by means of inelastic excitations. Using atomically resolved AFM images [4], we directly identify between which atoms chemical bonding has occurred. Finally, the electronic structure is studied by scanning tunneling spectroscopy. By exploiting the symmetry of the complex, it will be shown that the electronic structure of the complex can be rationalized from the linear combination of molecular orbitals model. Our results provide a direct experimental observation of this basic quantum chemical principle.

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