

Surveying Molecular Vibrations in Single Molecule Nanojunctions

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Charge transport through metal-molecule junctions is a major subject of study in a rapidly growing interdisciplinary research field. It deals with fundamental and applied aspects of science at the nanoscale aiming to control the electron conductance at the molecular level and the uprising of nanotechnology. One of the major results of this research is that the atomistic arrangement at the junction and the coupling between the molecule and the metal electrodes can significantly alter the electronic and structural properties of the molecule. It is therefore relevant to characterize the influence of the metal contact formation in the electron transport process through a single molecule.

With this aim, we have combined spectroscopic techniques based on scanning tunneling microscopy (STM) with first-principles calculations to achieve a precise characterization of the metal-molecule interaction during the formation of a nanocontact.[1] We use the inelastic tunneling spectroscopy (IETS) signal measured at various molecule-metal distances by approaching the tip of an STM to the CO molecule adsorbed on a Cu(111) metal surface. The vibration modes and inelastic transport have been modeled using density functional theory (DFT) combined with nonequilibrium Green's function methods (NEGF). Both the measured data and the calculations show characteristic shifts of the vibration modes. In particular, we observe a continuous but nonlinear blue shift of the frustrated rotation mode in tunneling with decreasing distance followed by an abrupt softening upon contact formation. This indicates that the presence of the metal electrode sensibly alters the structural and conductive properties of the junction even without the formation of a strong chemical bond.

We have shown that by combining high resolution IETS data and first-principles calculations it is possible to monitor the structural and electronic properties of a molecular nanocontact during its formation. As the tip of the STM can be more widely understood as the presence of any metallic electrode, we believe that these results have a general validity to the measurements of conductance through molecular junctions.

Finally, we report simulated vibrational spectra for CO using chemically functionalized STM tips. Our results indicate that functionalized tips can increase the resolving power of IETS and can yield inelastic signals not observed with a Cu-adatom tip. Such effects are originated by changes in the symmetry of the orbitals involved in the inelastic scattering, and reveal that single-molecule IETS can be optimized by selecting the appropriate tip orbital symmetry.[2]

[1] L. Vitali, R. Ohmann, K. Kern, A. Garcia-Lekue, T. Frederiksen, D. Sánchez-Portal, A. Arnau, *NanoLetters* **10**, 657 (2010).

[2] A. Garcia-Lekue, D. Sanchez-Portal, A. Arnau, and T. Frederiksen, manuscript in preparation.