

Single Molecules Junctions: Conductance, Formation and Evolution Statistics

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Proposal Title:

Physical Properties of Metal-Molecule Link Motifs in Single Molecule Electronic Circuits

Research Achievement:

Background: The size of electronic devices in commercially integrated circuits has been dropping exponentially over the past few decades, following a trend originally identified by Gordon Moore. This miniaturization of the building blocks of traditional Silicon devices, and the idea that single molecules could function as active electronic components have motivated the field of molecular electronics. The primary challenge in molecular electronics has been the ability to fabricate single molecule devices, a molecule attached to two metal electrodes to form a circuit reliably.

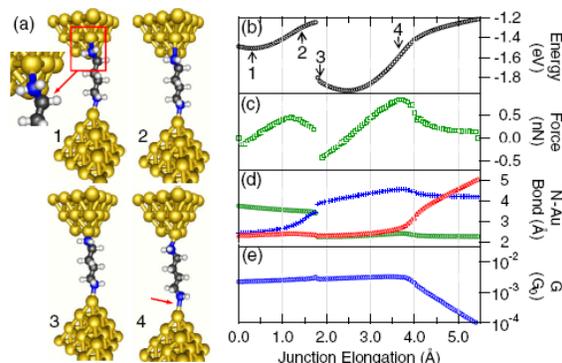
Prior Accomplishments: Over the past two years, we have very successfully implemented a point-contact technique to study electron transport through single molecule junctions in a modified scanning tunneling microscope (STM), a method which overcomes the major difficulties in single molecule transport measurements as it allows the measurements of molecules as small as 5 Å, and can be used to study thousands of junctions easily. We have implemented this method using amine chemical link groups rather than thiols to attach the molecules to gold metal electrodes [1,2]. The discovery of amine-gold link chemistry is a major breakthrough in the study of conductance through single molecule junctions, allowing reliable and reproducible measurements. This innovation has enabled the conductance measurements of over 50 different molecules in a short period of time, allowing the systematic studies of the impact of molecular structure on conductance [4]. We have shown, for example, that the conductance for alkanes and polyphenyls decreases exponentially with increasing length, decaying faster for the saturated molecules when compared to the conjugated molecules [1,2]. This has provided direct evidence that the transport mechanism through these junctions is through non-resonant tunneling. We have also shown, by measuring transport through a series of biphenyl derivatives that the conductance decreases as the twist angle between the two rings is increased. Our measurements are consistent with the cosine squared relationship expected from consideration of the conjugation in the pi-system [2]. For substituted benzenes, we have found that the conductance varies inversely with the calculated ionization potential of the molecules, providing evidence that the occupied states are closest to the gold Fermi energy [3].

Scientific Questions: In this work, we focused our experimental and theoretical research on answering fundamental questions regarding single molecule junction formation, link bond stability and junction evolution under stress. These were addressed both experimentally and theoretically, for single-molecule junctions bonded to gold electrodes using amine, methyl sulfide, and dimethyl phosphine link groups by measuring conductance as a function of junction elongation. Key questions addressed were: (1) How do single molecule junctions sustain elongation lengths comparable to the molecular length? (2) How does the conductance of a single molecule junction vary under stress? (3) How do the different binding strengths of the Amine and Phosphine link groups affect single molecule junction evolution.

Results: Our measurements showed that for each link, the maximum elongation and formation probability increase with molecular length, strongly suggesting that processes other than just metal-molecule bond breakage play a key role in junction evolution under stress. Density

functional theory (DFT) based calculations, performed by Dr. Koentopp in my group at Columbia using CFN computing facilities and in collaboration with Dr. Mark Hybertsen through the CFN User Program, simulated the junction elongation process for the NH_2 and PMe_2 links. They show clearly that the long steps result from multiple processes including changes in the molecular binding site, changes in the gold electrode structure, and molecular rearrangements, as well as bond breakage.

Bond breakage contributes only a small fraction of the total junction elongation distance. Furthermore, the zero-bias transmission does not change significantly upon changes in the molecular binding site or gold electrode structure, consistent with experiment [5].



Future Work

We have recently developed and applied an approach to measure simultaneously, the conductance as well as the force applied across the molecular junction and we can now measure forces required to break gold point-contacts in the presence of different molecules, as well as the forces required to break gold-molecule bonds. Our preliminary results show that the gold-gold bond strength depends on the environment around the point contact. Specifically, we find that when amine terminated molecules are present around the gold point contact, the gold-gold bond strength decreases. We find a similar result when Methyl sulfide terminated molecules. Dr. Koentopp has done preliminary calculations modeling the influence of a nearby adsorbate on the physical evolution of gold point contacts. Under the new User proposal (Title: *Understanding the correlation between bond breaking forces and chemistry at the single molecule scale*), we plan to fully develop these calculations, closely tied to the developing experimental results.

Acknowledgements

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References:

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Publications:

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