

# Determination of energetically preferable Au-S contact atomic structure in stretched single-molecule junctions

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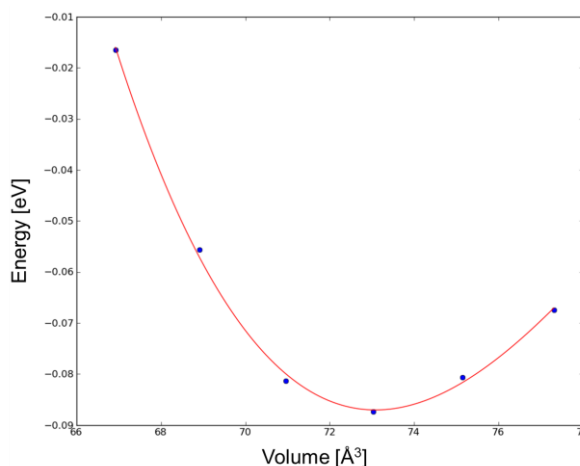
Based on the first-principles computations, the nature of the microscopic geometry of the molecule-electrode contacts was addressed. The single-molecule junction was prepared by connecting hexanedithiolate (HDT) to Au(111) electrodes via one, two, and three Au adatoms having coordination number of one (CN1), two (CN2), and, three (CN3), respectively. The contact atomic structure and energy of the stretched Au-HDT-Au junction was observed. The analysis revealed that the contact geometry with lowest coordination number (CN1) is energetically more stable than CN2 and CN3.

## INTRODUCTION

A major breakthrough in the molecular electronics research in the past decade was the introduction of the scanning probe microscopy (STM) or the mechanically controlled break junction (MCBJ) approach to establish single-molecule junctions in a systematic and robust fashion [1]. The molecule-electrode contacts have as much impact as the molecules themselves on the conductance of the molecular junctions [2]. Multiple energetically favorable contact atomic structures were claimed to produce different conductance peaks [3-7], signifying a potential route to realize a binary switch [8]. In spite of these achievements, the correlation between the contact atomic structures and conductance curves for Au-S contacts has not been well established [9]. The fundamental understanding of Au-S contacts is very essential as it represents the most well-established venue in molecular self-assembly and nanofabrication for the electronic, energy, and biological applications. Wide usage of Au-S contacts is the result of its desirable physical properties; Au-S contacts provide much better conductivity and thermodynamic stability in establishing molecular junctions than that of Au-NH<sub>2</sub> contacts [10]. Applying computational methods, Au-S contact geometry and energy of stretched Au-HDT-Au junction was examined to determine the most preferable contact atomic structure.

## SIMULATION DETAILS

Using the LCAODFTLab of EDISON Nanophysics, density functional theory (DFT) calculations were performed. The Perdew-Burke-Ernzerhof (PBE) [11] parameterization of the



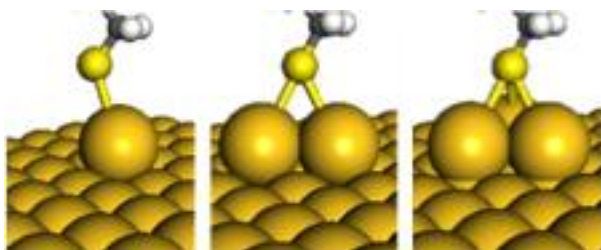
**Fig. 1.** Total energy as a function of volume with Birch-Murnaghan fitting

generalized gradient approximation (GGA) exchange-correlation functional was employed. The atomic cores were replaced by norm-conserving pseudopotentials [12]. The pseudopotential was controlled to produce cutoff radius with an error of 2%. Equation of state calculation was performed in order to obtain the correct lattice constant for this pseudopotential as shown in Figure 1. Numerical atomic basis sets of

the double- $\zeta$ -plus-polarization (DZP) quality optimized for the corresponding GGA pseudopotentials were adopted. In constructing the junction models, vacuum gap of 20Å was placed along the surface-normal z-direction to make the interactions of slab models with their periodic images negligible. A single-point shifted off from the gamma point was sampled along the two electrode-surface directions.

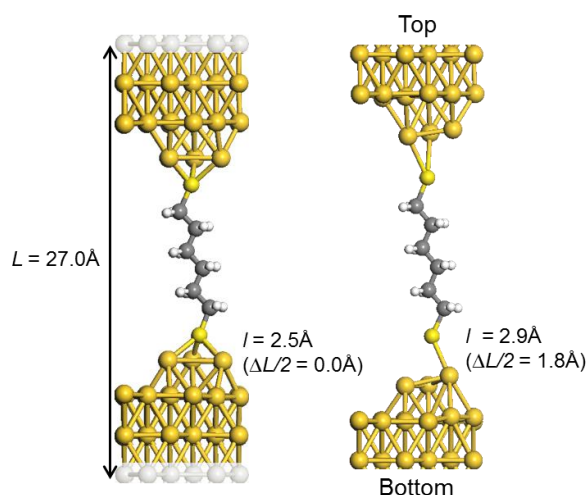
## RESULTS AND DISCUSSION

To model the tip of STM or MCBJ electrodes with well-defined Au-S coordination numbers, one, two, and three Au adatoms on top of the five-layer ( $2\sqrt{3} \times 2\sqrt{3}$ ) $R30^\circ$  Au(111) slabs were introduced as illustrated in Figure 2. After preparing the symmetric contact models—CN1-1, CN2-2, and CN3-3—each model was stretched along the surface normal direction by pulling the fixed electrode layers at the step of  $\Delta L = 0.6\text{\AA}$  and its geometry was successively optimized.

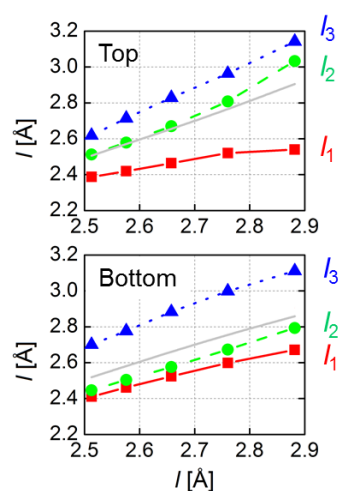


**Fig. 2.** Atomic structures of HDT junction based on CN1, CN2, and CN3.

The continuous pulling of the junction causes the model with a higher coordination number to undergo modification of its contact geometry into a model with a lower coordination number. As seen in Figure 3, the coordination numbers for top and bottom electrodes decreased from CN3 to CN2 and from CN3 to CN1, respectively. This can be clearly observed by the individual Au-S distances of the top and bot contacts in Figure 4. It depicts that one of the Au adatoms is closer to the S linker than others on the top electrodes as the junction is being pulled and vice versa for the bottom electrode. This CN transformation corresponds well with general knowledge on the response of metal atoms by pulling process.



**Fig. 3.** Optimized atomic structures of CN3-3 junction models at the low and high strain.  $L$  and  $l$  represent the distance between the top and bottom fixed Au layers during the optimization and the averaged Au-S distance, respectively.

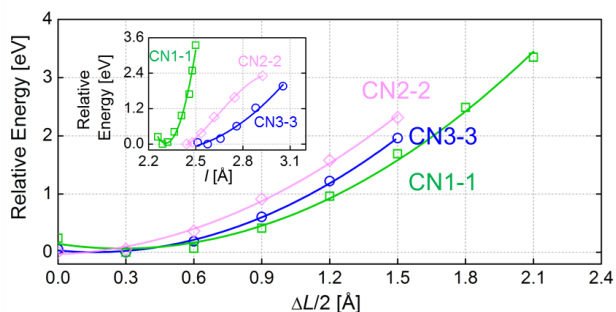


**Fig. 4.** Individual Au-S distances of the bottom and top contacts as a function of the averaged Au-S distance at the bottom and top contacts.

The total energy variation curves, in Figure 5, obtained as a function of  $\Delta L/2$ , illustrate that CN2 is energetically less stable than CN3 and CN1. Note that Au has very strong bond strength in low-coordinated structures that lead to surface reconstructions and monoatomic chain formation [13]. Experimental results have shown there is a correlation between contact geometry, coordination number of the Au-S contact, and the conductance of the single-molecule junction [14]. Therefore, the multiple conductance peaks could perhaps be related to the contact geometries with each coordination number. This can be further

examined by analyzing the electronic properties of the molecular junctions with these different geometries.

- [12] M. Fuchs et al., *Comput. Phys. Commun.* **119**, 67 (1999).  
 [13] S. R. Bahn et al., *Phys. Rev. Lett.* **87**, 266101 (2001).  
 [14] F. Chen et al., *Annu. Rev. Phys. Chem.* **58**, 535 (2007).  
 [15] Li et al., *J. Am. Chem. Soc.* **97**, 2135 (2006).



**Fig. 5.** Stretching-induced relative energy variation of CN1-1, CN2-2, and CN3-3 models. Inset shows the same relative energy variation according to  $l$ .

## CONCLUSION

In this paper, the nature of the microscopic geometry of the molecule-electrode contacts was addressed. By pulling the junction in the surface normal direction, it was observed that the coordination number of Au-S lowered. This is because contact atomic structure of CN1 is energetically preferable over CN2 and CN3. This study will serve as a stepping-stone to identify the correlations between the Au-S coordination numbers and the conductance variations of pulled molecular junctions.

## ACKNOWLEDGEMENT

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## REFERENCES

- [1] H. B. Akkerman et al., *J. Phys. Condens. Matter* **20**, 013001 (2008).  
 [2] E. Lortscher, *Nature Nanotech.* **8**, 381 (2013).  
 [3] X. Li et al., *J. Am. Chem. Soc.* **128**, 2135 (2006).  
 [4] F. Chen et al., *J. Am. Chem. Soc.* **128**, 15874 (2006).  
 [5] C. H. Ko et al., *J. Am. Chem. Soc.* **132**, 756 (2010).  
 [6] M. Taniguchi et al., *Chem. Sci.* **1**, 247 (2010).  
 [7] Y. Kim et al., *Phys. Rev. Lett.* **106**, 196804 (2011).  
 [8] S. Y. Quek et al., *Nature Nanotech.* **4**, 230 (2009).  
 [9] H. Hakkinen, *Nature Chemistry* **4**, 443 (2012).  
 [10] M. Tsutsui et al., *J. Am. Chem. Soc.* **131**, 10552 (2009).  
 [11] J. P. Perdew et al., *Phys. Rev. Lett.* **77**, 3865 (1996).