



An Electromechanical Spectroscopy for Determining the Atomic-Configuration of Single-Molecule Devices

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Introduction

The development of molecular-scale electronic devices has made considerable progress over the last decade, and single-molecule transistors, diodes, and wires have all been demonstrated. Despite this remarkable progress, the agreement between theoretically predicted conductance values and those measured experimentally remains limited. One of the primary reasons for these discrepancies lies in the difficulty of experimentally determining the contact geometry and configuration of a molecule when bound between two electrodes. In this poster, we describe the development of a novel electromechanical spectroscopic ("alpha" spectroscopy) tool that is capable of determining the most probable binding and contact configurations for a molecular junction. In this technique a small-amplitude, high-frequency, sinusoidal, mechanical signal is applied to a series of single-molecule devices during junction formation and breakdown. By measuring the current response at this frequency, it is possible to obtain information about the mechanical properties of the system. From these results it is possible to determine the most probable binding and contact configurations for the molecular junction, and to obtain information about how an applied strain is distributed within the molecular junction. These results provide insight into the complex configuration of single-molecule devices that can be used to further improve the agreement between theory and experiment.

Defining and Measuring "Alpha"

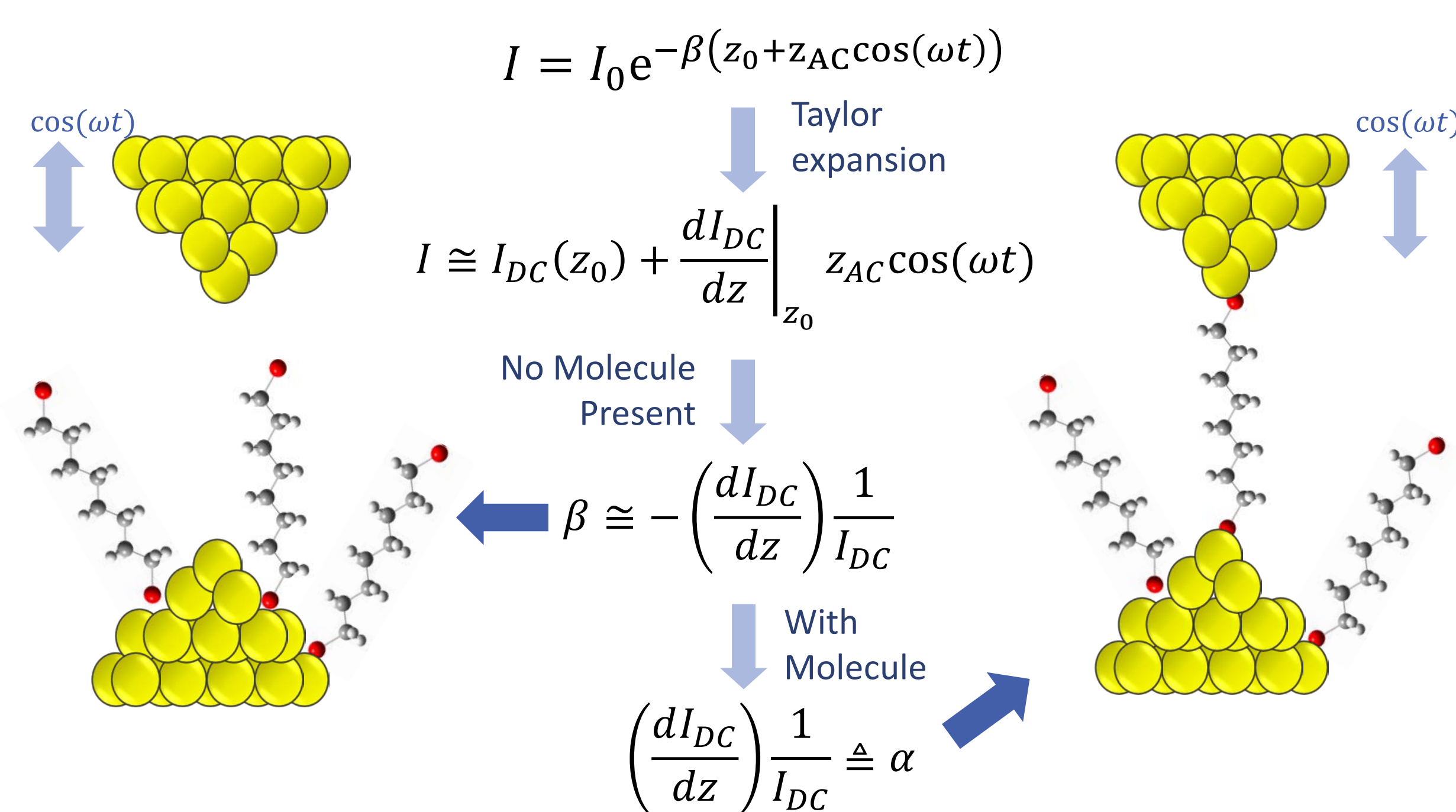


Figure 1. Definition of Alpha. By applying a high frequency sinusoidal mechanical modulation to a tunneling gap, it is expected that the tunneling decay constant, β , can be extracted by normalizing the AC response at that frequency by the DC component of the current (left). However, if a molecule is bound between the two electrodes (right), the mechanical stiffness of the molecule modifies the modulation amplitude (z_{AC}), and results is a modified tunneling decay constant, which we call "alpha" (α). α represents the electromechanical response of the molecular tunneling junction, and can therefore provide information about the relative stiffness of the molecule, electrodes, and molecule-electrode contact.

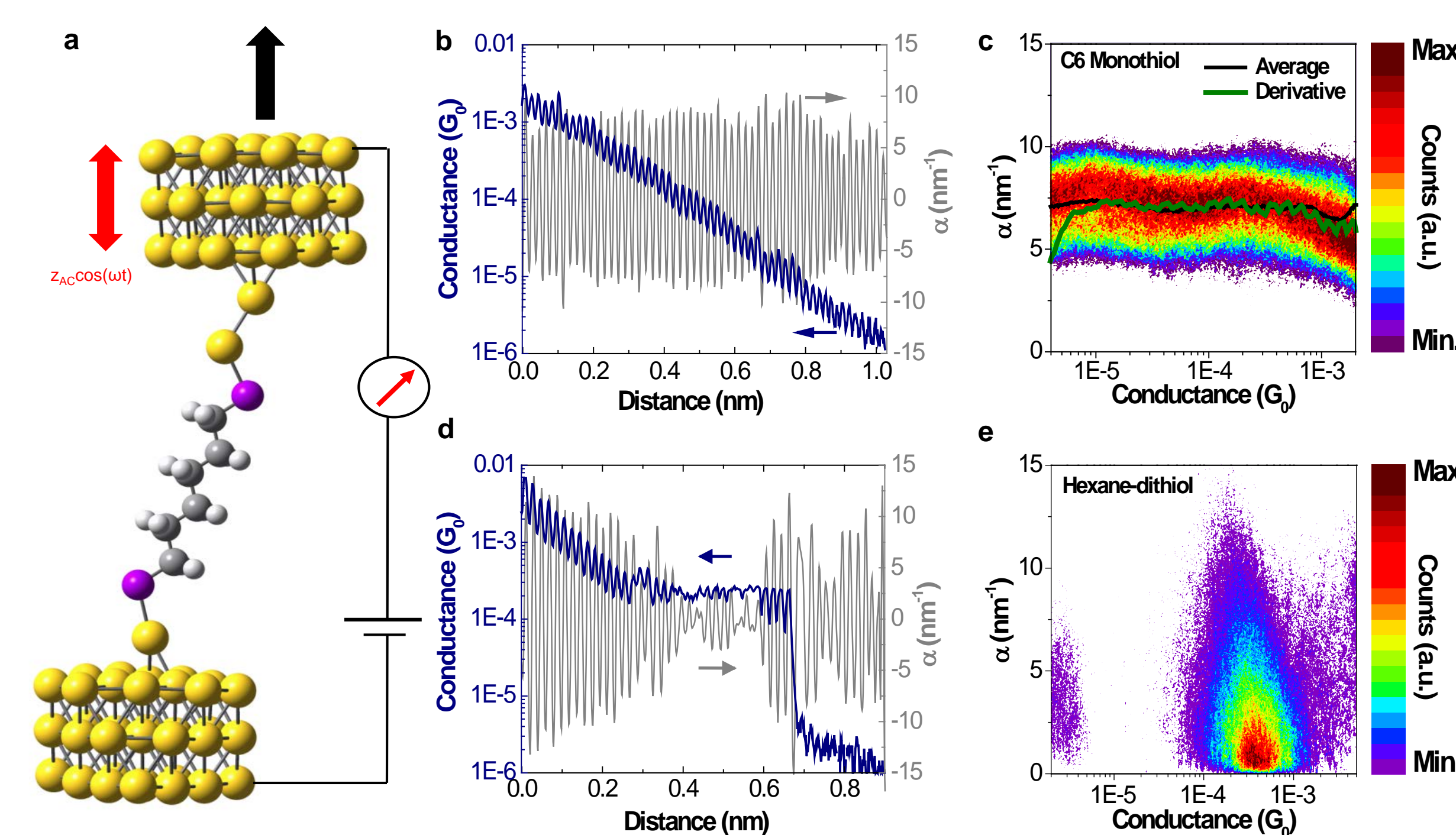


Figure 2. Measuring α in a single-molecule junction. a) Schematic of the experimental setup. b) An example of a current vs. distance trace obtained during tip withdraw (blue trace) showing no steps in the current. The normalized current (a) at the modulation frequency (2 kHz) is extracted from this trace (grey curve). c) Histogram from thousands of hexane-monothiol traces similar to those shown in (b). The black trace shows the most probable α -value at each conductance. The green trace shows the β -value obtained by averaging thousands of current vs. distance traces and taking the derivative. d) Representative conductance vs. distance (blue) and α vs. distance (gray) curves measured during electrode separation for a hexane-dithiol junction. e) 2-Dimensional histogram for hexane-dithiol showing a maximum population at the conductance of $\sim 3 \times 10^{-4} G_0$ and corresponding α -value of $\sim 0.8 \text{ nm}^{-1}$.

Comparing α and β

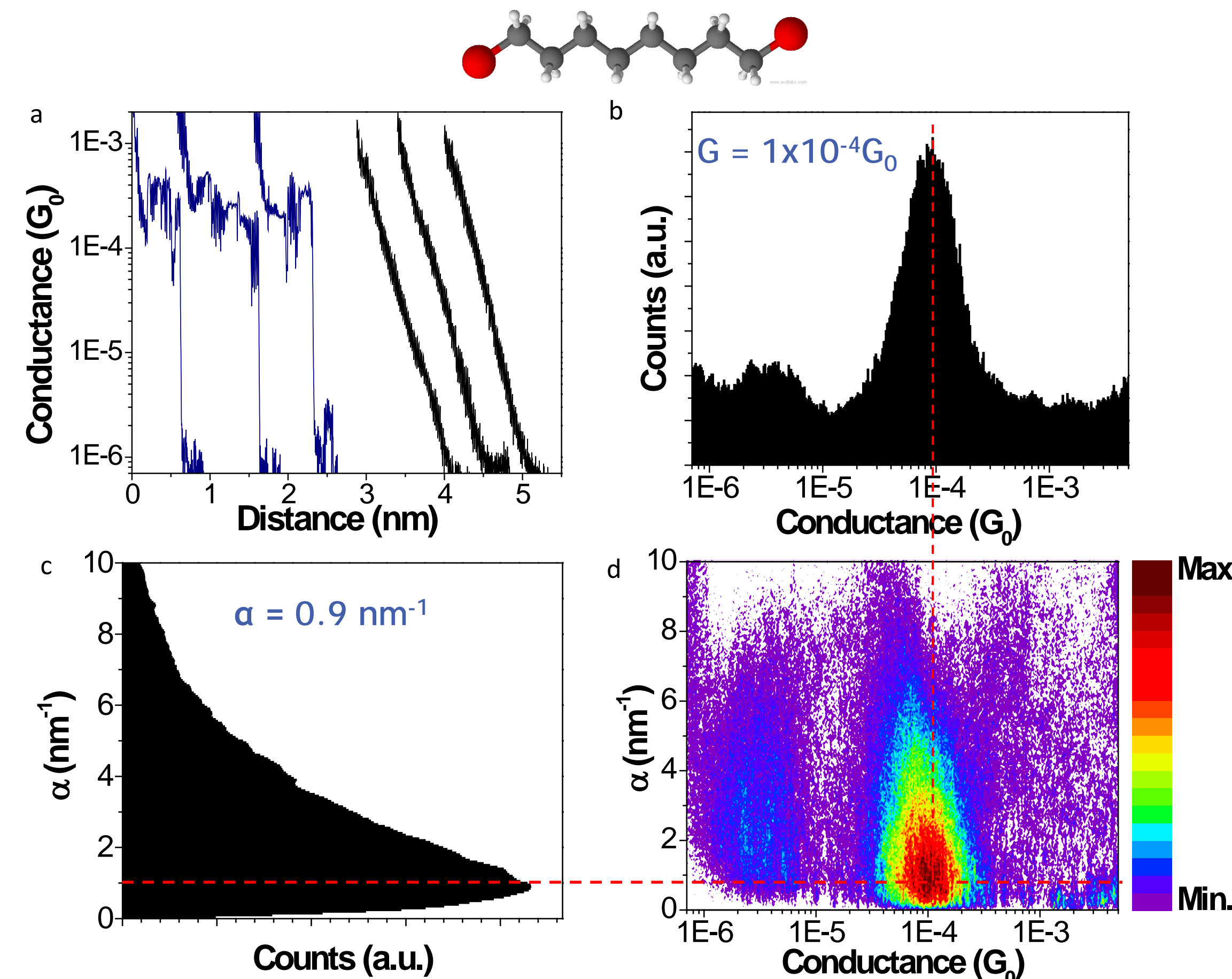


Figure 3. Statistical Measurement of Conductance and Alpha from Single-Molecule Junctions. a) Individual measurements from an octane-dithiol sample (shown top), from 1000's of these traces a 2-dimensional histogram showing conductance vs. alpha value can be obtained as shown in (d). From the 2-dimensional histogram, the most probable conductance (b) and α -value (c) can be determined.

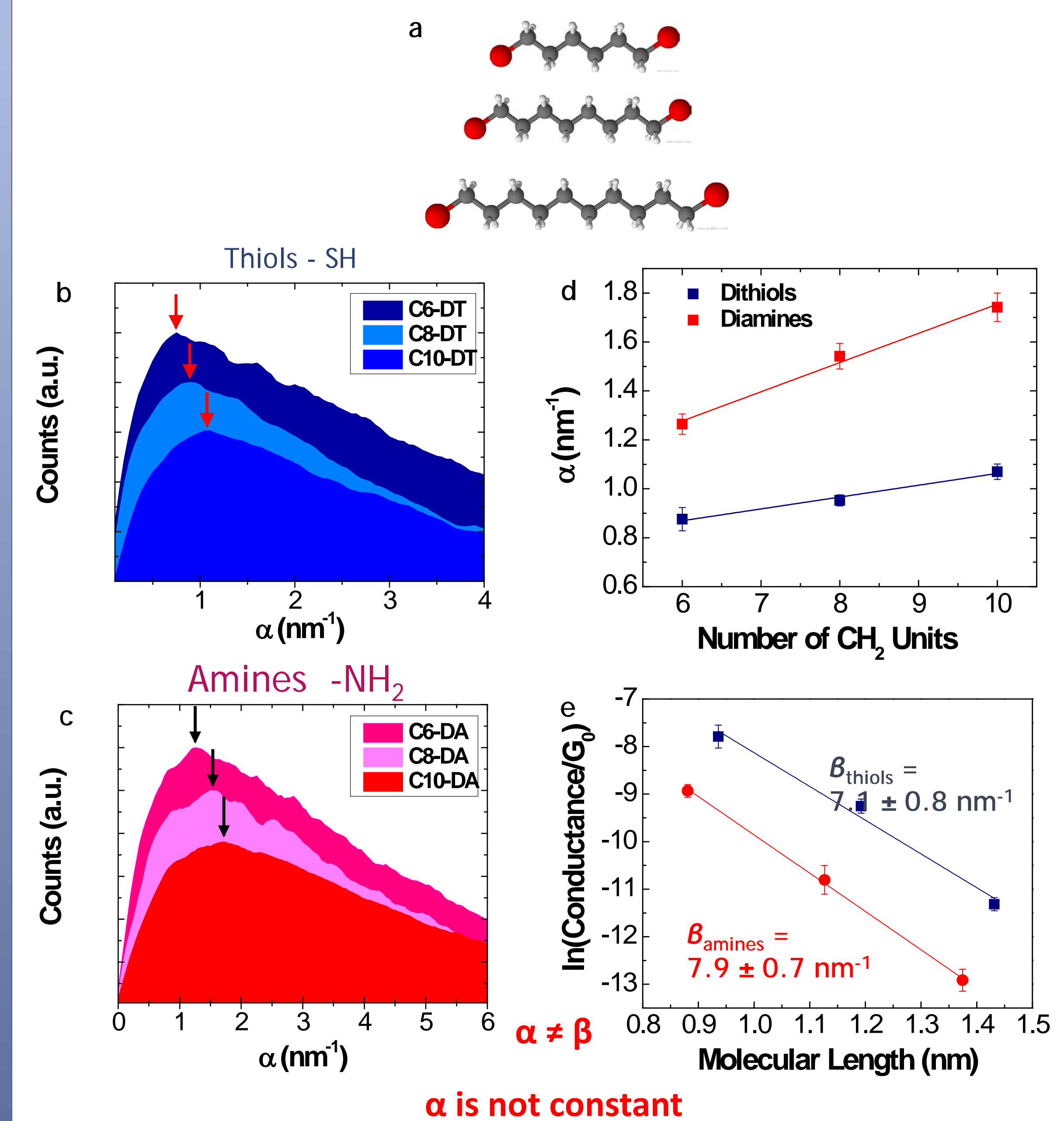


Figure 4. Systematic Studies of α and β . a) Series of alkane molecules that can be terminated with either thiols (sulfur) or amines (nitrogen). By systematically studying this series of molecules and extracting the conductance and α -values it is possible to examine systematic changes in α , and to compare with β . b) α -histograms for three alkane-dithiols with either 6, 8, or 10 atoms in the molecular backbone. c) α -histograms for the diamine version of the same three molecules. d) Plot of α -values vs. molecular length for both the alkane-dithiols and -diamines. Note that in all cases the α -value changes with molecular length, and is on the order of unity (nm^{-1}). This is significantly different from the β -value as is shown in (e). The β -value is extracted from the length dependence of the conductance and is constant for each molecular family. Also the β -values are $\sim 7 \text{ nm}^{-1}$, which is significantly larger than the values obtained for α .

References:

Rascón-Ramos, H.; Artés, J. M.; Li, Y.; Hihath, J., "Binding configurations and intramolecular strain in single-molecule devices." *Nature Materials* 2015, 14 (5), pp. 517-522.

Mechanical Model for Single-Molecule Junctions

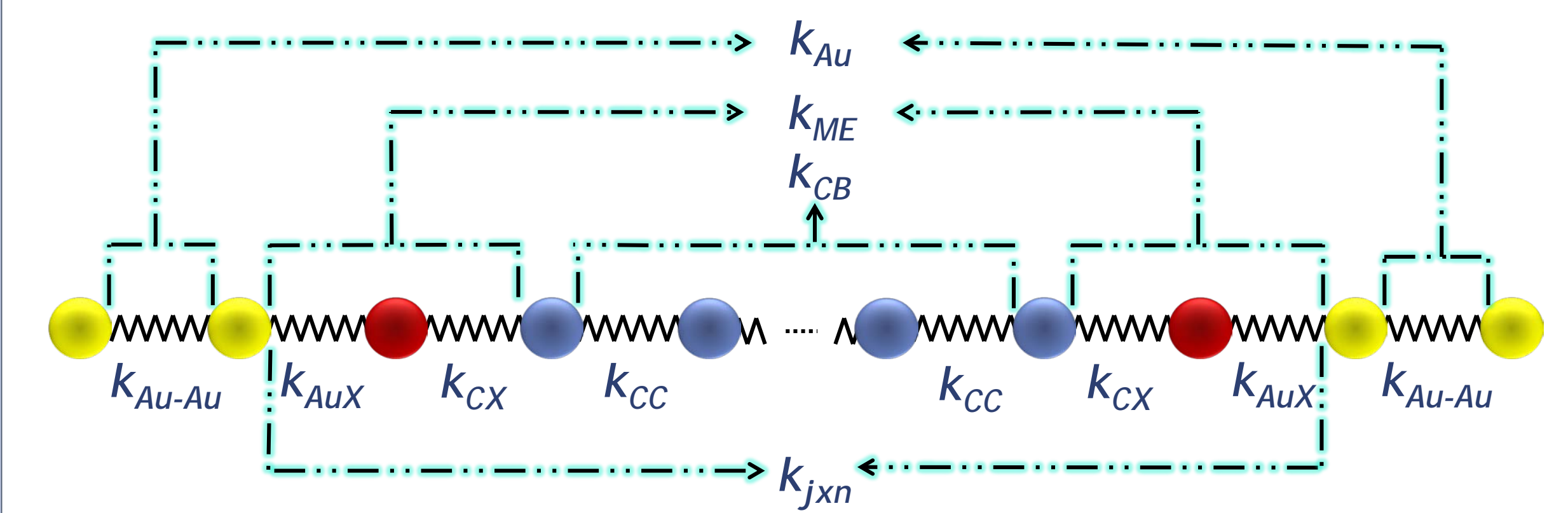


Figure 5. Mechanical Model of a Single-Molecule Junction. The primary reason for the difference between α and β is due to the fact that the mechanical modulation will be applied across both the electrodes and molecule, while the electrical potential will be applied to the molecular junction (denoted by k_{jxn}). Therefore, we constructed a mechanical model for the molecular-junction where the bonds between atoms were treated as springs as shown above. The spring constants were obtained from Density Functional Theory (DFT).

Determining The Binding Configuration

$$\frac{\alpha}{\beta} = \frac{A_{jxn}}{A_{applied}}$$

$$A_{applied} = A_{jxn} + A_{Au}$$

$$F = k_{jxn} A_{jxn} = k_{Au} A_{Au}$$

$$\frac{A_{jxn}}{A_{Au}} = \frac{M(k_{Au})}{k_{CC}} + \frac{k_{Au}}{k_{AuX}}$$

$$\text{Thiols: } \frac{k_{Au}}{k_{CC}} = 0.009 \pm 0.001$$

$$\text{Amines: } \frac{k_{Au}}{k_{CC}} = 0.023 \pm 0.002$$

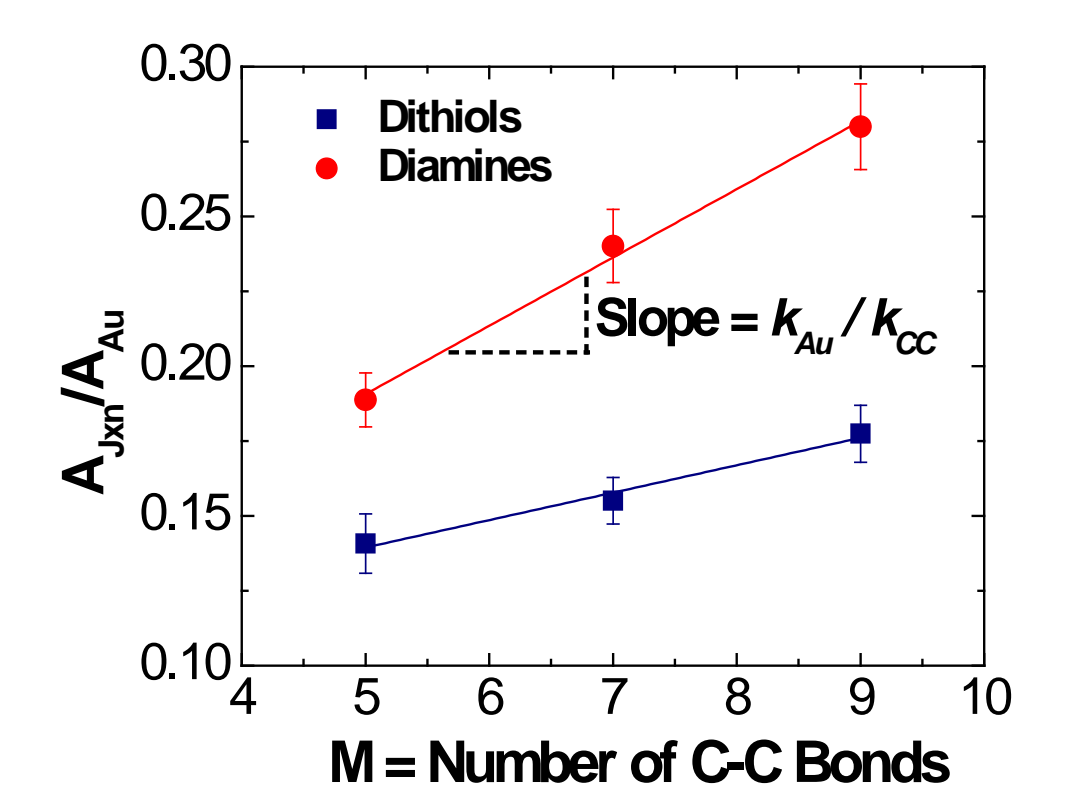


Figure 6. Extracting the Electromechanical Response. The ratio of α to β can be approximated by the ratio of the modulation amplitude applied to the junction over the total applied modulation. By invoking Hooke's Law, it is possible to demonstrate that plotting the ratio of the junction modulation amplitude over the Au electrode modulation amplitude as a function of the number of carbon-carbon bonds for each molecular family will yield the ratio of the Au electrode spring constant over the spring constant of a single carbon-carbon bond.

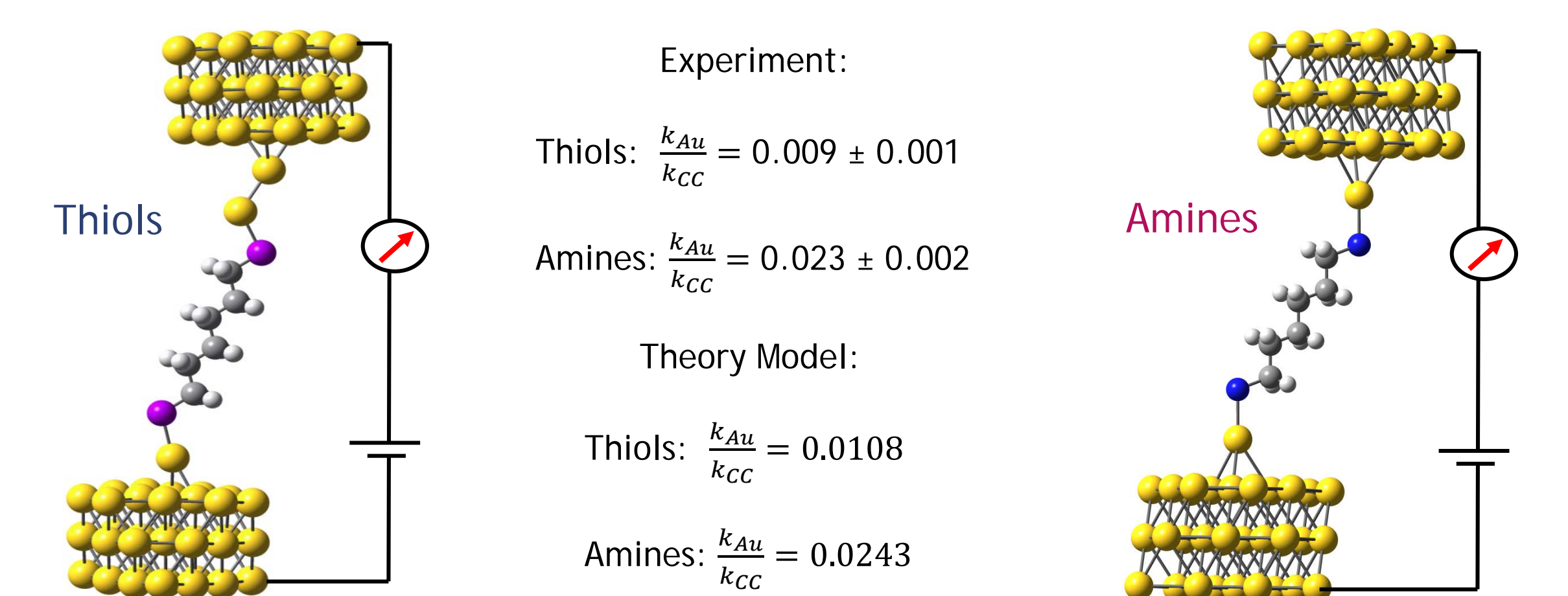


Figure 7. Determining the binding configuration. By using the slopes extracted from Figure 6 and the mechanical model in Figure 5. It is possible to explore the spring constants of various Au electrode atomic configurations to determine the most likely binding configuration for each molecular family. As shown in the left, in the case of the thiols each sulfur binds in a top configuration with the apex atom in a top configuration on side and a bridge site on the other (left). In the case of the amines, each nitrogen binds in a top site to an apex Au atom in a hollow-site (right).

Conclusions

We have shown that applying a small mechanical modulation to a single-molecule junction and measuring the effect of this modulation on the current allows new insights into the contact configuration and binding geometry of a single-molecule device. We have used this methodology to determine the contact and binding configuration of both alkanedithiols and alkanediamines. The method outlined here will allow provide new information about the origin of the different conductance values found in single-molecule devices. Thus, these results pave the way for the complete understanding and control of the binding configurations in single molecule devices at room temperature, a prerequisite for the design of functional molecular electronic devices.

Acknowledgements

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