

## Supplementary Materials

### **Mechanics and Chemistry: Single Molecule Bond Rupture Forces Correlate with Molecular Backbone Structure**

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#### **Experimental Details:**

Experimental Setup and Procedures: The conductive AFM consists of a modified AFM head (Multimode Veeco), external adder and filter circuits (SRS), as well as a homebuilt cantilever holder. A bias was applied between a gold coated, conductive cantilever (TAP300 BudgetSensors) and an Au substrate placed on top of a single-axis piezoelectric positioner with built-in position sensor (Mad City Labs). The resulting current was converted to a voltage with a current amplifier (Keithley 428). Data collection and control of the piezoelectric positioner were done by means of a data acquisition board (National Instruments, PXI-4461) driven by a customized program using Igor software (Wavemetrics Inc.).

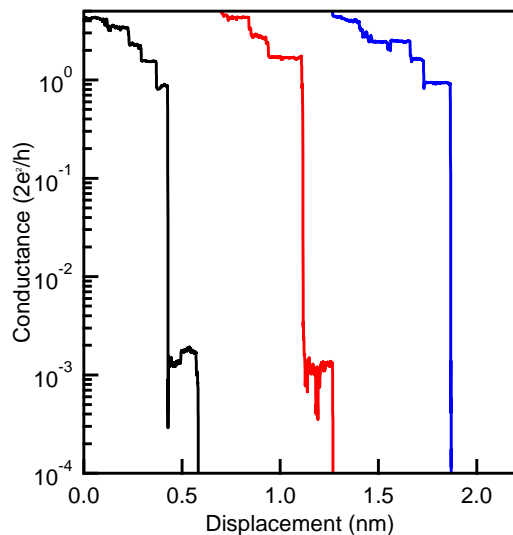
An AFM micro cantilever used was coated with a 5 nm Chromium adhesion layer and 100 nm of gold (99.999% purity, Alfa Aesar) served as one electrode. A gold substrate (mica with 100 nm gold, 99.999% purity, Alfa Aesar) served as the second electrode. The cantilever and substrate were UV/ozone cleaned prior to use. Force was determined by

measuring the deflections of a laser spot focused on the back of the cantilever which was calibrated using the thermal power spectrum method<sup>12</sup>.

For the simultaneous conductance and force trace measurements, the substrate approached the cantilever tip until a set conductance larger than  $5G_0$  was measured to ensure that the Au/molecule/Au junction from the previous measurement was completely destroyed. For standard conductance and force measurements, the sample was withdrawn at a rate of 18 nm/s and the current and force versus position data was recorded at a sampling frequency of 100 kHz. All position determinations were based on measurements with a built-in position sensor within our custom piezoelectric positioner. This position sensor was calibrated both by the manufacturer and by us using laser interference measurements. We found the absolute values of the measured displacements to be accurate to within 5%.

Cantilever Calibration details: Force resolution along the pulling direction is achieved by measuring the deflection of a focused laser that is reflected off the back of a cantilever using a quadrant detector. The voltage signal corresponding to the deflection of the laser is converted to force in two steps. First the quadrant detector signal is converted to a deflection in nm by forcing a solid contact between the sample substrate and the cantilever and subsequently moving the substrate by a known distance using the piezo. Second, the spring constant of the cantilever is determined using the power spectrum method<sup>1</sup>. The voltage signal in nm is converted to a force by multiplying by the cantilever spring constant. The determined Au-Au breaking force which is consistent with accepted values from literature<sup>2</sup>, validates our calibration method.

Conductance Step Detection: The molecular junction conductance step detection was carried out as follows. First, 1D conductance histograms were computed from all measured traces for each molecule to determine the conductance peak and width of the conductance signature. This determines a minimum and maximal conductance value for each of the molecules studied. For each measured trace, the number of data points within this conductance range was determined. If its value was larger than the number required for a 0.02 nm plateau, the plateau length and slope, normalized to the average conductance value of the plateau, was obtained. Traces with a conductance plateau longer than 0.02 nm, with a normalized slope larger than -5, were selected for further analysis. Finally, the end of the conductance plateau was determined, and the conductance trace was analyzed to ensure that there was a sharp conductance drop following this plateau by requiring that the conductance after the plateau was less than 0.2 times that of the plateau.



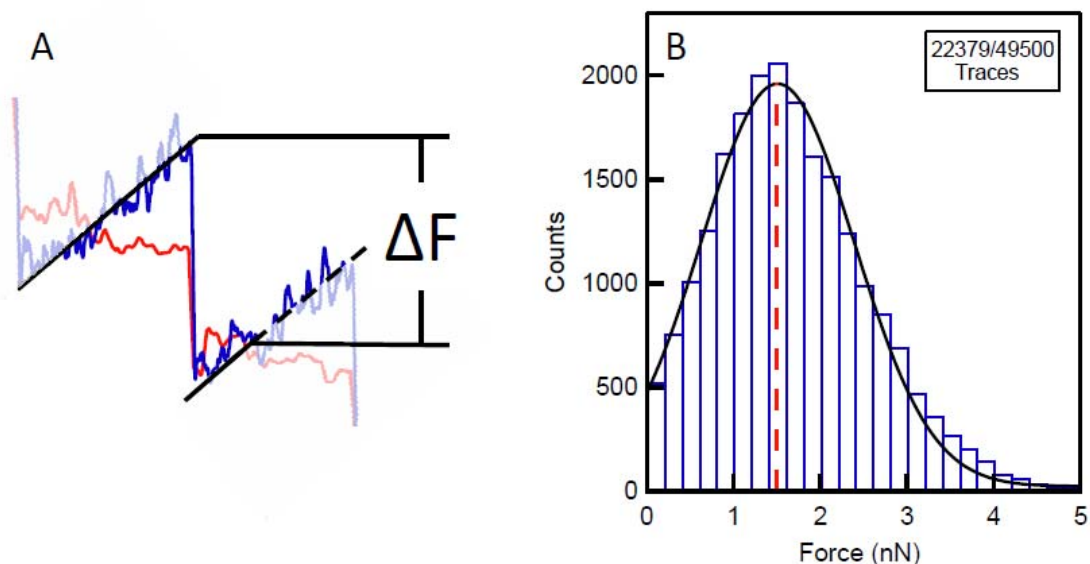
*Figure S1: Black- sample accepted conductance trace showing both a  $G_0$  and molecular plateau. Red- sample rejected conductance trace lacking the  $G_0$  plateau. Blue- rejected conductance trace lacking a molecular plateau.*

These selection criteria were molecule independent. 2D conductance and force histograms were then generated from all traces that showed a conductance plateau

satisfying these criteria. A sample selected and two sample rejected traces are shown in SI Figure S1.

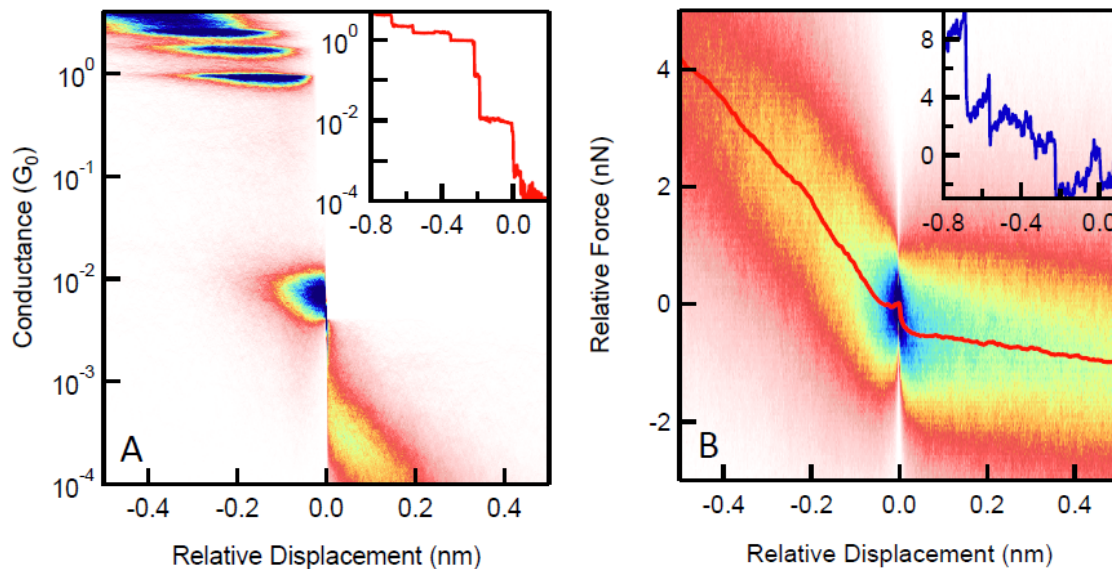
Traditional Force Analysis Results: The force data do not show plateaus, but rather saw-tooth patterns. Unlike in the case of conductance data, calculation of a force drop on a trace by trace basis, without using the 2D analysis method, cannot be achieved by simply creating a histogram. Analysis of the force data relies on the simultaneously acquired conductance data. The force associated with a given breaking event (which is determined from the conductance data) is the difference between the cantilever deflection prior to the break and that right after the break. This can be determined on a trace by trace basis using an automated algorithm by fitting a line to the force data in the region before and after the break, and extrapolating these fits to the breaking point to get the breaking force. Figure S2A shows, for a single force trace, how this is carried out. Figure S2B shows a cumulative histogram of over 22000 breaking forces determined using this technique for the  $G_0$  Au-Au bond breaking event selected out of 46500 collected traces. The data has been collected over nineteen separate experiments, each involving separate calibration of the cantilever force constant (as detailed above). Our algorithm fails to determine the breaking force for a significant fraction of the measured traces resulting in this high selectivity, primarily because of the signal to noise limitations on the force measurements. Nonetheless, this procedure shows that the most probable breaking force measured over a statistically large data set is 1.5 nN, in excellent agreement with the theoretical value of 1.4-1.6 nN<sup>3, 4</sup> and experimental value of 1.5 nN from literature<sup>2</sup> and supports the validity of our measurements, cantilever calibration, and analysis methods. Although this force analysis method works well for larger breaking forces such as the

Au-Au breaking force, it is biased towards larger forces which are easier to determine on a trace by trace basis. Since two line sections have to be fit for each force trace, this method introduces larger uncertainty for junctions with smaller signal to noise ratio, as observed for junctions that exhibit smaller breaking forces. The single molecule junctions, e.g. for 1,4 benzenediamine exhibited this issue. In order to eliminate this problem, we rely on statistical force analysis based on a two-dimensional force histogram method as discussed in the paper.

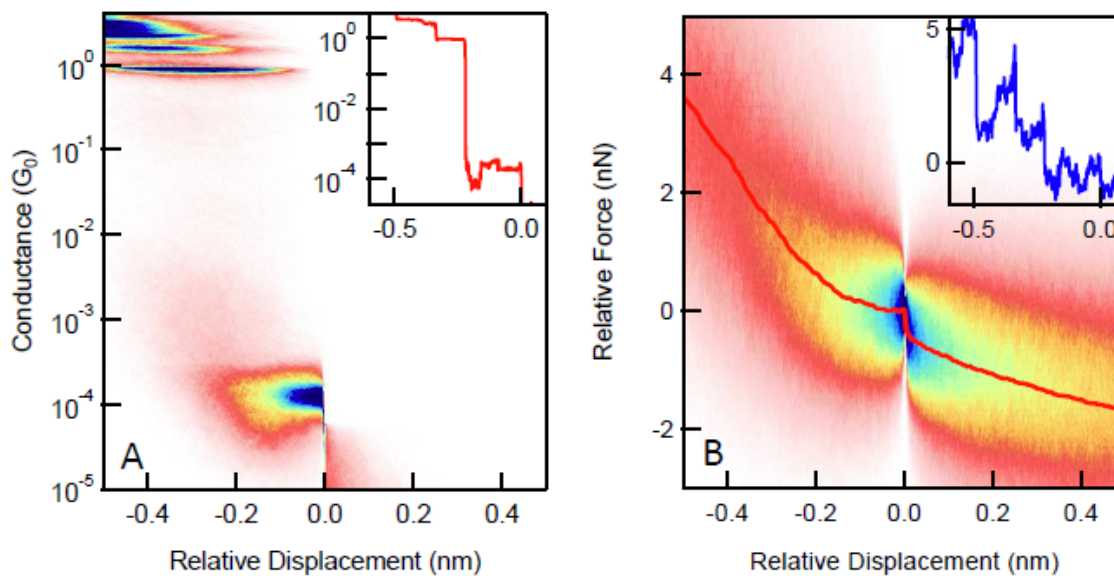


*Figure S2: (A) Schematic illustrating how bond rupture force is determined on a trace-by-trace basis for the traditional force analysis method. (B) Histogram of  $G_0$  bond-rupture force determined for 22000 traces selected from 49500 traces. A Gaussian fit is shown, and force peak is at 1.5nN.*

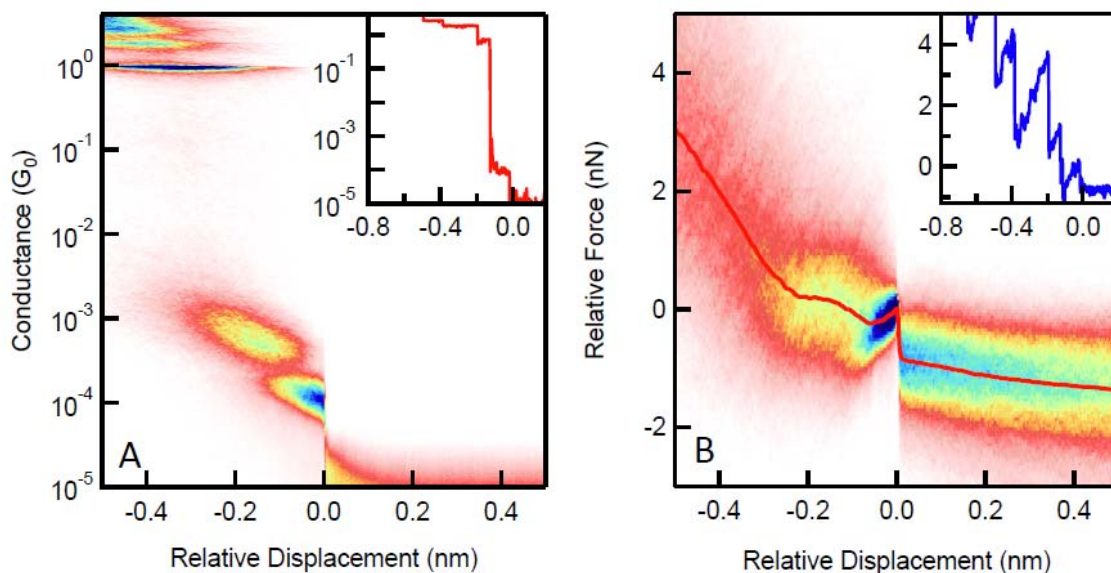
Conductance and Force Histograms for Molecular Junctions:



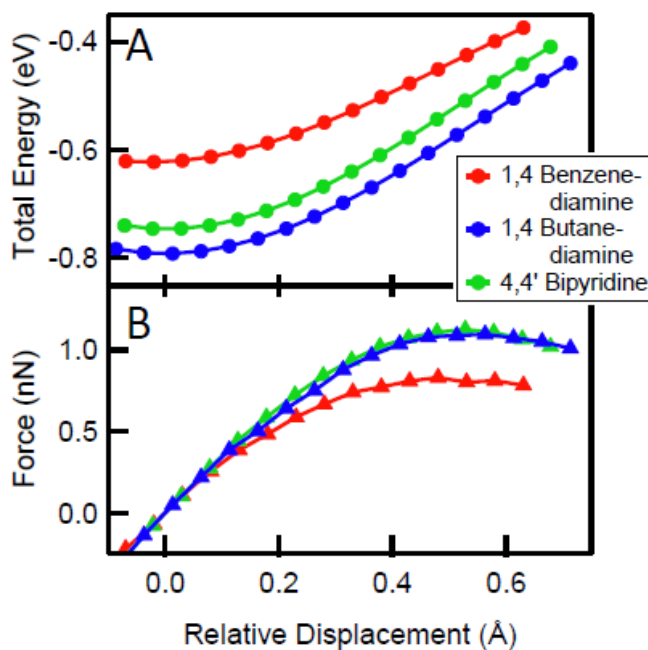
*Figure S3: (A) Two-dimensional conductance and (B) force histograms for 1,4 benzenediamine. Histograms are for 7345 traces selected from 58000 traces.*



*Figure S4: (A) Two-dimensional conductance and (B) force histograms for 1,6 hexanediamine. Histograms are for 6431 traces selected from 34000 traces.*



*Figure S5: (A) Two-dimensional conductance and (B) force histograms for 4,4' bipyridine for one tip/sample pair. Histograms are for 3423 traces selected from 11000 traces. Calculated Single N-Au Bond Rupture Trajectories:*



*Figure S6: (A) Calculated total energy and (B) force curves from adiabatic trajectories for a well-aligned model structure for 1,4-benzenediamine (red), 1,4-butanediamine (blue), and 4,4' bipyridine (green) shown as a function of displacement. Initial geometry as illustrated in Figure 4E in the text, with the N-Au bond aligned to vertical. Displacement controlled by fixing the position of the back plane of Au atoms in the cluster modeling the electrode and the N atom bonded to the Au tip atom.*

## References:

1. Hutter, J. L. & Bechhoefer, J. Calibration of atomic-force microscope tips. *Review of Scientific Instruments* 64, 1868-1873 (1993).
2. Rubio, G., Agrait, N. & Vieira, S. Atomic-sized metallic contacts: Mechanical properties and electronic transport. *Physical Review Letters* 76, 2302-2305 (1996).
3. Tavazza, F., Levine, L. E. & Chaka, A. M. Elongation and breaking mechanisms of gold nanowires under a wide range of tensile conditions. *Journal of Applied Physics* 106, 043522 (2009).
4. Rubio-Bollinger, G., Bahn, S. R., Agrait, N., Jacobsen, K. W. & Vieira, S. Mechanical properties and formation mechanisms of a wire of single gold atoms. *Physical Review Letters* 8702, 026101 (2001).