Supplementary Materials

Quantitative Bond Energetics in Atomic-Scale Junctions

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1. Experimental setup and materials studied

We use a home-built conducting atomic force microscope (AFM) to perform simultaneous conductance and force measurements on Au and Ag single atomic contacts as well as Au-molecule-Au single molecule junctions. See table S1. The experiments are performed at room temperature and in ambient. The Aucontacted junctions are formed between a gold-on-mica substrate and a commercial Si cantilever tip (NanoAndMore, Inc.), both coated with an ~100 nm evaporated layer of Au. For the cantilever an initial Cr adhesive layer of ~35 nm was applied prior to Au deposition. A laser reflected from the back of the cantilever reports the displacement of the cantilever, which is directly related to the force applied on the junction through the cantilever spring constant; the nominal stiffness of the Au-coated cantilevers is 50 N/m. The substrate is repeatedly brought into contact with the cantilever tip to form Au point contacts with a conductance above 5 G₀ (G₀= $2e^2/h$ is the quantum of conductance) and then pulled apart at the rate of 18 nm/s using a piezo stage. Using the break-junction procedure, single atomic contacts and singlemolecule junctions are formed such that the Au coated mica substrate and the tip of the Au-coated AFM cantilever represent the two metallic electrodes. The Ag point-contacts are studied using freshly polished Ag pucks as substrates and AFM tips that are analogously prepared¹. The AFM cantilever is calibrated using its thermal spectrum² at the end of each experiment. The experimental setup has been described in detail previously $^{3, 4}$ and has been optimized for an high cantilever displacement resolution of ~ 2 pm between DC and 10 kHz, translating into a force noise of ~0.1 nN.

| Junction | Molecule | Structure | Comment |
|----------------------------|---------------------------|----------------------------------|--------------------------------------|
| Au-Au | - | - | Rupture of G ₀ junctions |
| Ag-Ag | - | - | Rupture of G_0 junctions |
| Au- C4SMe | 1,4-bis(methylthio)butane | s s | - |
| Au-C4A | 1,4-diaminobutane | H ₂ N NH ₂ | - |
| Au-BDA | 1,4-diaminobenzene | H ₂ N NH ₂ | - |
| Au- BP L | 4,4'-bipyridine | | Rupture from low G configuration |
| Au- BP _H | 4,4'-bipyridine | - | Rupture from high G configuration |

TABLE S1. Summary of junctions studied.

| Junction | Molecule | Structure | Comment |
|-------------------------|----------------------------|-----------|--------------------------------------|
| Au- BPE _L | 1,2-bis(4-pyridyl)ethylene | | Rupture from low G configuration |
| Au- BPE _H | 1,2-bis(4-pyridyl)ethylene | - | Rupture from high G configuration |

2. Analysis techniques

We use an automated algorithm to analyze force events on a trace-by-trace basis ⁵. This algorithm consists of four steps illustrated for a **C4SMe** single-molecule junction in Fig. S1.

- 1) The location of the start and the end of the conductance plateau is determined (arrows in Fig. S1a).
- 2) The force trace is analyzed between these two locations and all force fluctuations larger than the instrument noise are determined (arrows in Fig. S1b).
- 3) The last load and rupture event in the force data is fit to a straight line to extract the junction stiffness (correcting for the cantilever stiffness). The rupture force is calculated as the drop in force at the end of this event. Histograms of these quantities are shown in the manuscript (Fig. 1d, 1e) and in the additional data section of this document in Fig. S8 and S9.
- 4) The same load and rupture event is fit with the hybrid model with three fitting parameters: E_{bind} , L_{bind} , and x_{Fmax} (the location of maximum force in the experimental data). The fitting involves three steps because of the highly non-linear nature of the model as well as the fact that E_{bind} and L_{bind} enter the model through a linear and an exponential term, respectively. At least one constraint is required to provide reliable fitting of the model to the experimental data on a trace-by-trace basis. The three steps are:
 - a) A fit is performed by constraining E_{bind} to the value obtained from Eq. 1 from the manuscript using the most frequent rupture force as F_{max} and the most frequently measured stiffness as K_{harm} . Then the value x_{Fmax} from this fit is determined $(x_{Fmax,l})$.
 - b) A fit is performed by constraining L_{bind} to the value obtained from Eq. 2 from the manuscript and the value of x_{Fmax} from this fit is also determined ($x_{Fmax,2}$).
 - c) A final fit is performed by constraining x_{Fmax} to the average of $x_{Fmax,1}$ and $x_{Fmax,2}$. Note that in this final fit, neither E_{bind} nor L_{bind} is constrained. The trace is kept in the dataset if the root mean square deviation of the data from the fit is less than 0.15 nN (~1.5× instrumental force noise).

This gives the E_{bind} and L_{bind} for each experimental trace. Histograms of these quantities are shown in the manuscript (Fig. 3c, 3d) and in the additional data below (SI Fig. S10 and S11).



Fig. S1. Four-step analysis process of a sample simultaneous conductance (red, left axis) and force (blue, right axis) measurement of a C4SMe single-molecule junction. (a) location of the junction through the conductance data, (b) identification of structural rearrangement events (black arrows) in force, (c) determination of junction stiffness (dashed black line) and rupture force (denoted by the double-headed black arrow) in the force data, (d) and fitting this force event to the hybrid model force profile.

3. Model Derivation

The harmonic segment of the potential is:

$$U_{harm}(x) = \frac{1}{2}K_{harm}(x - x_0)^2 + U_0$$
(1)

The logistic segment of the potential is:

$$U_{log}(x) = \frac{D}{1 + e^{-(x - x_{Fmax})/r}}$$
 (2)

The two are connected requiring:

(A) The logistic segment pass through the harmonic potential minimum. This requires $U_{harm}(x_0) = U_{log}(x_0)$.

- (B) The logistic and harmonic segments must coincide at a connection point x_1 chosen such that $U_{harm}(x_1) = U_{log}(x_1) = \frac{D}{4}$. Note that changing this connection point does not change the results presented here.
- (C) The derivative of the logistic and harmonic segments must coincide at this same connection point, $x_{1.}$

Using (A) above, we get:

$$\frac{D}{1 + e^{-(x_0 - x_{Fmax})/r}} = U_0$$
(3)

Using (B) above, we get:

$$\frac{D}{1+e^{-(x_1-x_{Fmax})/r}} = \frac{1}{2}K_{harm}(x_1-x_0)^2 + U_0 = \frac{D}{4}$$
(4)

Using (C) above, we get:

$$\frac{dU_{harm}}{dx}\Big|_{x_1} = K_{harm}(x_1 - x_0) = \left.\frac{dU_{log}}{dx}\right|_{x_1} = \frac{D}{r} \left.\frac{e^{-(x_1 - x_{Fmax})/r}}{\left(1 + e^{-(x_1 - x_{Fmax})/r}\right)^2}\right.$$
(5)

We can get two relations from Eq. 4 above:

$$\frac{D}{4} = \frac{D}{1 + e^{-(x_1 - x_{Fmax})/r}} \rightarrow e^{-(x_1 - x_{Fmax})/r} = 3 \rightarrow x_1 - x_{Fmax} = -rln(3)$$
(6)
$$\frac{D}{4} = \frac{1}{2} K_{harm} (x_1 - x_0)^2 + U_0$$
(7)

Combining Eqs. 6 and 7:

$$\frac{D}{4} = \frac{1}{2} K_{harm} (x_{Fmax} - x_0 - r \ln 3)^2 + \frac{D}{1 + e^{-(x_0 - x_{Fmax})/r}}$$
(8)

From Eq. 5:

$$K_{harm}(x_1 - x_0) = K_{harm}(x_{Fmax} - x_0 - r\ln 3) = \frac{D}{r} \frac{e^{\ln 3}}{(1 + e^{\ln 3})^2} = \frac{3D}{16r}$$
(9)

From Eqs. 8 and 9, eliminating *K*_{harm}:

$$\frac{D}{4} = \frac{3D}{32r}(x_{Fmax} - x_0 - r\ln 3) + \frac{D}{1 + e^{-(x_0 - x_{Fmax})/r}}$$
(10)

Let $x_{Fmax} - x_0 = L_{bind}$

$$\frac{1}{4} = \frac{3}{32} (L_{bind}/r - ln3) + \frac{1}{1 + e^{L_{bind}/r}}$$
(11)

Solving the above equation numerically gives $L_{bind} = 3.43097r$. Plugging into Eq. 3, we get:

$$U_0 = \frac{D}{1 + e^{L_{bind}/r}} = .03134D$$

and

$$K_{harm} = \frac{3D}{16r(L_{bind} - r\ln 3)} = \frac{3D}{16r^2(L_{bind}/r - \ln 3)} = .08039 \frac{D}{r^2}$$

4. Hybrid model fits to DFT Energy Profiles for Exemplary Junction Structures

We use results from calculations described previously for C4SMe, C4A, BDA and BP ³⁻⁵.



Fig. S2. Calculated junction binding energy and force for an Au-C4SMe-Au single molecule junctions (open circles) as a function of junction elongation based on DFT in comparison to fits to the Leonard-Jones model potential (a) and the universal binding curve model (b). The blue and red curves show the model potential fit to this data in harmonic and the entire region respectively. The hybrid fit to the entire DFT energies curve is shown for comparison (black curves).

The DFT-based results for C4SMe together with fits to the Morse potential form are shown in the manuscript (Fig. 3a and 3b). The same data is shown with fits to the L-J form and the universal binding curve in Fig. S2a and S2b respectively. None of these three empirical forms provides a good fit to the entire force extension curve. The fit to our proposed hybrid model shown in the manuscript (Fig. 2a and 2b) is excellent. As shown in Fig. S3, the same high quality fit extends to the DFT-based results for C4A,

BDA, and **BP**_L. As described previously⁵, the van der Waals interaction plays an important role in the **BP**_H rupture force. In the case of **BP**_H single-molecule junctions, only one side of the junction is considered and the role of Van der Waals interactions with nearby rough Au is included through DFT-D2. The overall fit is adequate, but the shape of the calculated force is rather sharply peaked near the maximum. The hybrid model fits poorly near and beyond F_{max} . This likely reflects approximations made in the treatment of the van der Waals contribution ⁵. For other junctions considered here, the role of van der Waals interactively relatively small, as illustrated in Fig. S4 for the C4SMe case. The binding energy is increased by 0.2 eV and the maximum sustainable force is about 0.15 nN larger. Also, the distance from the potential minimum to the maximum sustained force increases from 1.3Å to 1.6Å. Finally, the binding curve approaches the asymptote somewhat more slowly. As for BP_H, the fit to



the hybrid model is less good near F_{max} .

Fig. S3. (a) DFT-based calculations of junction energy in an adiabatic trajectory simulations (open symbols), and fits to the hybrid model potential (solid lines). (b) DFT calculated forces (open symbols) and derivative of the hybrid model potential (solid lines). The DFT calculation for BP_H included van der Waals corrections.



Fig. S4. Illustration of the role of van der Waals interactions, as estimated using the DFT-D2 method, in the C4SMe calculated junction energy (a) and force (b). Also shown in (b) are contributions from long range van der Waals interactions between the extended body of the AFM tip and the substrate based on the model illustrated in Fig. S5 (green lines corresponding to two tip-substrate absolute separations, z_0). These are much smaller than the short-range forces and comparable to the instrumental noise level of ~0.1 nN.

5. Role of long-range van der Waals interactions

Modeling both tip and substrate by finite clusters neglects two contributions from van der Waals interactions. First, the proximal asperity represented by the cluster interacts with the larger surface on the opposite side through the long-range dispersion interaction. Direct estimates of this effect with extended atomic scale models suggest that this effect is essentially negligible (less than 30 meV over the full range of the curves shown in Fig. S4). Second, there is a long-range interaction between the substrate and the extended body of the AFM tip. This component of the tip-substrate interaction and measured force varies with distance and presents a roughly constant profile that is superposed on all the short to intermediate range contributions discussed above. Here we assume that the local, roughly nm scale asperities on both substrate and tip have already been captured by the cluster models. This leaves the relatively flat substrate below and the body of the AFM tip. The latter is modeled as a hemisphere with the typical radius of curvature of the AFM tip. To see the impact on the portion of the force-extension curve that is being modeled here, we focus on a scenario that represents either Au-Au atomic contact or a molecular junction in the final segment of the elongation prior to complete rupture, where it is fully extended, but near a potential minimum. Accounting for typical dimensions for the local asperities (up to 1 nm), the molecule backbone length (from a minimum of 0.5 nm and up), and the typical length of the force-extension

segment being analyzed (up to 0.2 nm), the separation between this hemisphere and the nominal flat part of the substrate that covers the relevant experimental range should roughly span 2-4 nm. A given force-extension segment is a small slice of this that depends on the details of asperity size, backbone length and segment length.

The specific estimate starts with the known form for van der Waals interaction of an atom with a semi-infinite slab⁶. Integration over the hemispherical tip model can be carried out analytically. The model and the result are summarized in Fig. S5. Numerical estimates use the recently recommended value for C₆ that includes metal screening ⁶, 80 eV-Å⁶. Note that this is different from the value we previously used in conjunction with the Grimme DFT-D2 model, but likely most representative of the long-range component pertinent to this estimate. Results for two different scenarios for the value of d (corresponding in this model to separation where the short-range chemical interaction has its potential minimum) are superposed on the force extension curves in Fig. S4b. Over the range typically sampled in the experimental force extension curves being fitted here, this background contribution has a very weak dependence on elongation and a value that is a small fraction of the typical maximum force (0.03 nN and 0.1 nN for initial d values of 2.5 nm and 1.5 nm respectively). In view of the distribution of measured F_{max} values, this background contribution is unimportant. Furthermore, we note that vdW forces at typical tip-substrate distances are smaller than our noise resolution (~0.1 nN). Moreover, vdW forces and other long-range interactions such as hydrostatic force due to ambient measurement conditions have a weak distance-dependence over the length scales accessed in our experiments. Therefore, since we define the force datum on a trace-by-trace basis as the value immediately after junction rupture, we are effectively subtracting these long-range contributions from the short-range contributions of interest in our study.



Fig. S5. Model for van der Waals interaction between the body of the AFM tip and the extended substrate.

6. Additional data:



Fig. S6. Additional sample conductance (red, left axis) and force (blue, right axis) traces for Au point contacts. The last force event within the $1G_0$ conductance plateau is fit with the hybrid model (green trace) as detailed above. The arrow indicates x_{Fmax} for each fit.



Fig. S7. Additional sample conductance (red, left axis) and force (blue, right axis) traces for **C4SMe** single-molecule junctions. The last force event within the molecular conductance plateau is fit with the hybrid model (green trace) as detailed above. The arrow indicates x_{Fmax} for each fit.



Fig. S8. Histograms of rupture forces for Au and Ag point contacts and Au-molecule-Au single-molecule junctions with C4SMe, C4A, BDA, BP (BP_L and BP_H) and BPE (BPE_L and BPE_H). Gaussian fits are overlaid.



Fig. S9. Histograms of junction stiffness for Au and Ag point contacts and Au-molecule-Au singlemolecule junctions with C4SMe, C4A, BDA, BP (BP_L and BP_H) and BPE (BPE_L and BPE_H). Gaussian fits are overlaid.



Fig. S10. Histograms (solid lines) of E_{bind} obtained from trace-by-trace analysis for Au and Ag point contacts and Au-molecule-Au single-molecule junctions with C4SMe, C4A, BDA, BP (BP_L and BP_H) and BPE (BPE_L and BPE_H). Dotted lines are log-normal fits to the histograms from which the peak positions corresponding to the most frequently observed E_{bind} tabulated in Table 1 of the manuscript are obtained.



Fig. S11. Histograms (solid lines) of L_{bind} obtained from trace-by-trace analysis for Au and Ag point contacts and Au-molecule-Au single-molecule junctions with C4SMe, C4A, BDA, BP (BP_L and BP_H) and BPE (BPE_L and BPE_H). Dotted lines are Gaussian fits to the histograms from which the peak positions corresponding to the most frequently observed L_{bind} tabulated in Table 1 of the manuscript are obtained.



Fig. S12. Two-dimensional universal force curves obtained by scaling the individual experimental force traces of Au and Ag point contacts and Au-molecule-Au single-molecule junctions with C4SMe, C4A, BDA, BP (BP_L and BP_H) and BPE (BPE_L and BPE_H).

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