Feeling the Invisible: Probing Quantum Interference at the Single-molecule Level

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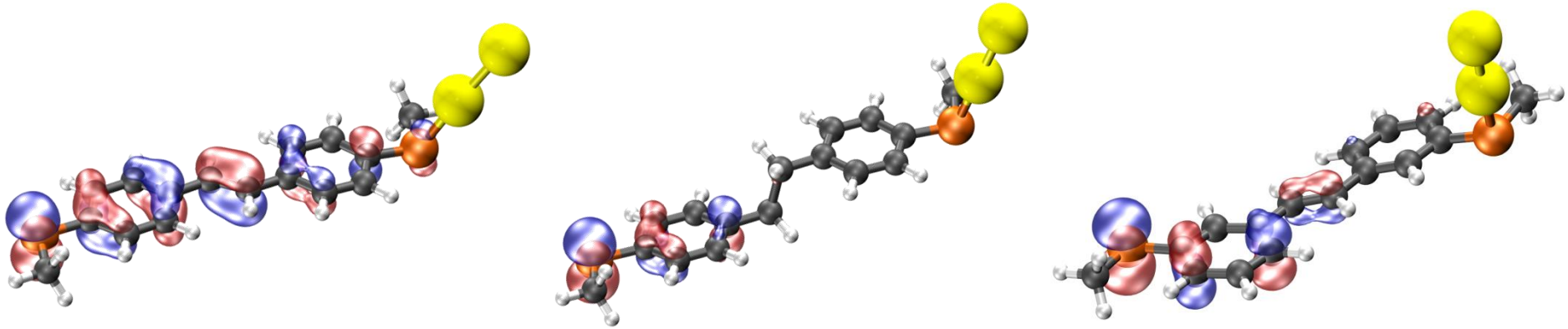

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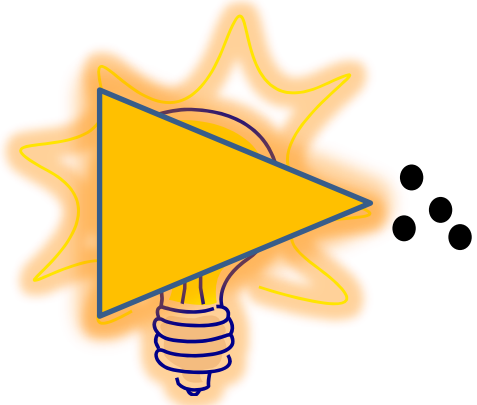
APAM Research Conference – Spring 2012

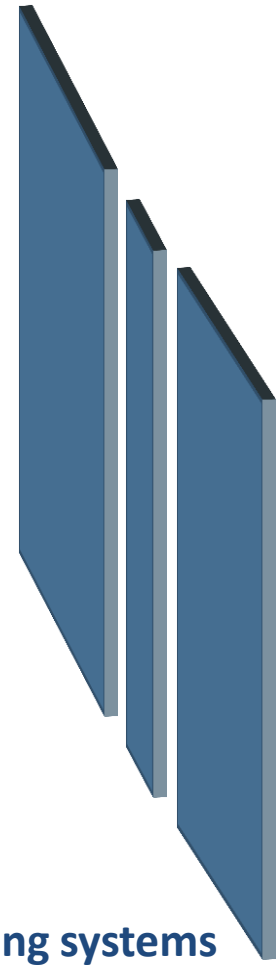
Introduction

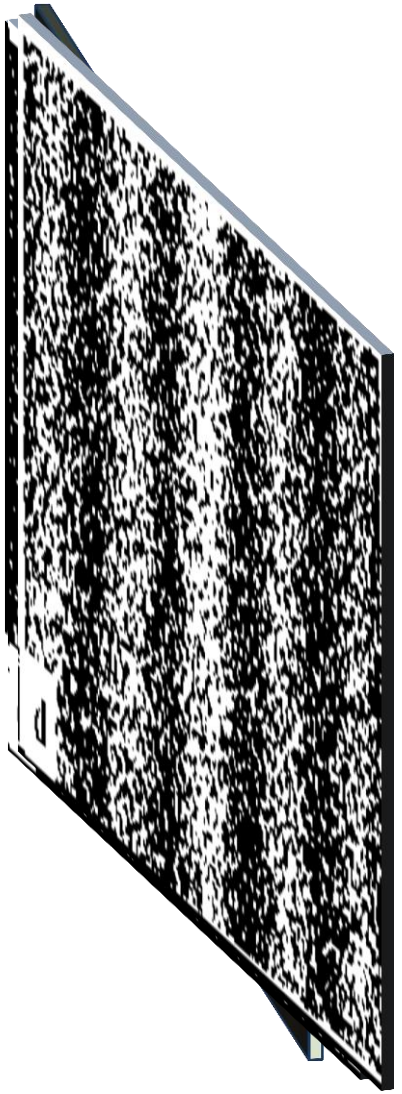
Source **Paths** **Interference**



Photon source

Single electron source

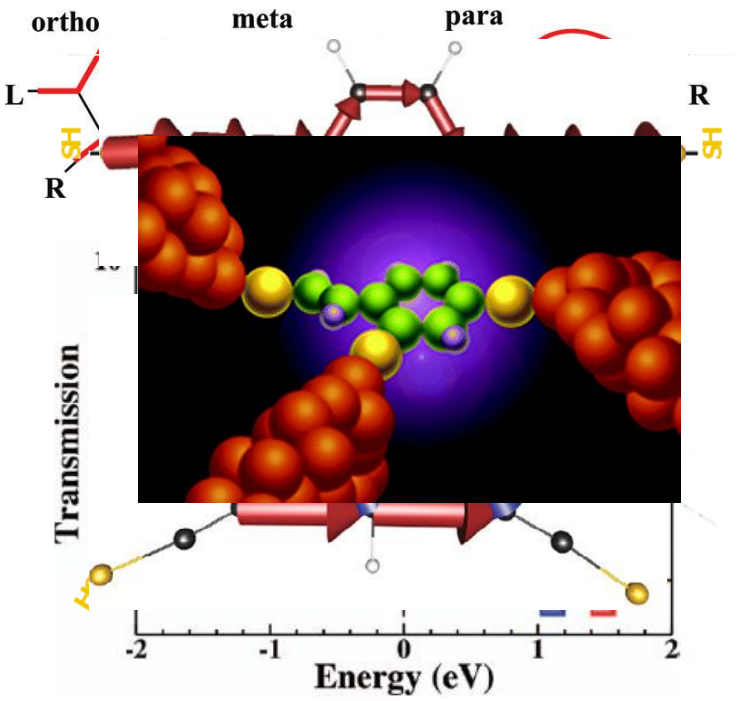




Single molecules provide interesting systems where interference can dominate electronic transport

Tonomura et al., Am. J. Phys., 1989

Background – Theory



- Several prediction schemes motivated by tight binding models
- More sophisticated DFT treatments exhibit interesting microscopic phenomena
- New types of molecular devices
- **How to test these predictions?**

Markussen et al., Nano Lett, 2010
Solomon et al., J Chem Phys, 2008
Solomon et al., Nat Chem, 2010
Cardamone et al., Nano Lett, 2006

EXPERIMENTS

Background – Experiment

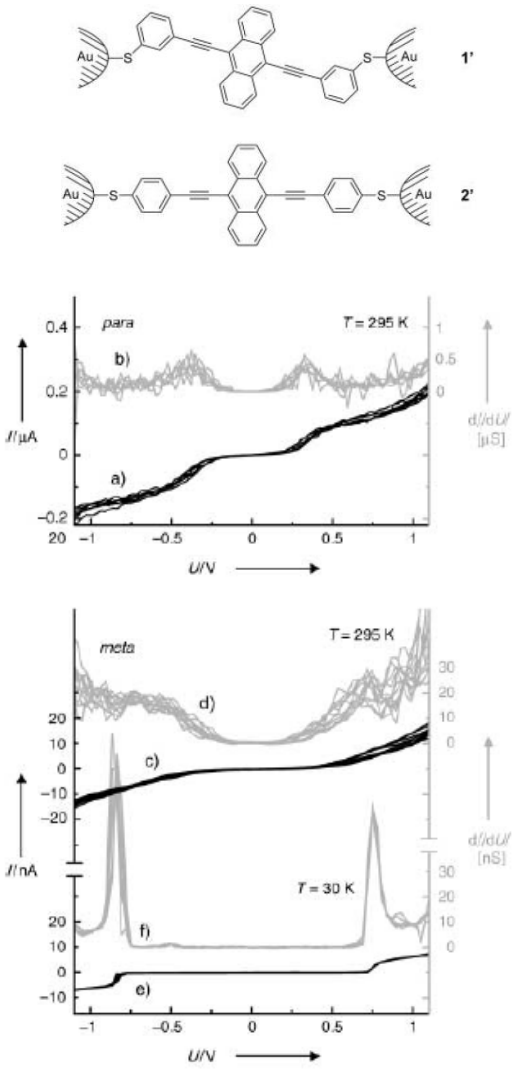


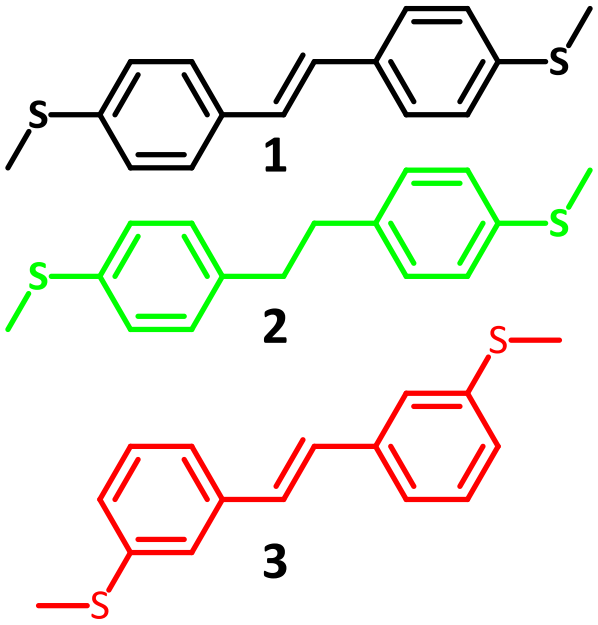
Figure 2. I/U characteristics reproducibly recorded for a stable junction in a MCB and their numerical derivative dI/dU. a) I/U and b) dI/dU for Au-**2'**-Au at room temperature. c) I/U and d) dI/dU for Au-**1'**-Au at room temperature and e) I/U and f) dI/dU at $T \approx 30$ K.

- I-V study of meta and para substituted anthracene
- Current levels are very different

- High voltage range applied, low-bias conductance unknown
- Other contributions to current?
- What about binding probabilities?
- What about binding geometries?

Mayor et al., Angew. Chem. , 2003

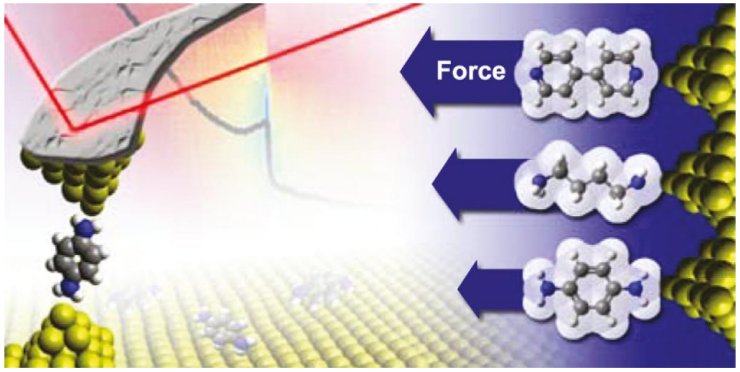
Need for a rigorous experiment

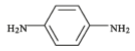
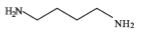
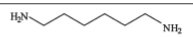
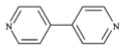


1. Design molecules such that only a **few** things are **reliably** changed (benzene derivatives are not the best)
2. Measuring only low-bias conductance gives null result for interference, so measure additional property
3. Verify that binding isn't altered by the changes

How do we dissect interference effects from extraneous factors?

Force and conductance



Molecule	Structure	Conductance (G_0)	Bond Rupture Force (nN)	
			Experiment	Theory
1,4 Benzene-diamine		6.2×10^{-3}	0.53±0.09	0.46
1,4 Butane-diamine		9.0×10^{-4}	0.69±0.06	0.84
1,6 Hexane-diamine		1.1×10^{-4}	0.62±0.09	N/A
4,4' Bipyridine		1.0×10^{-4}	0.80±0.08	1.00

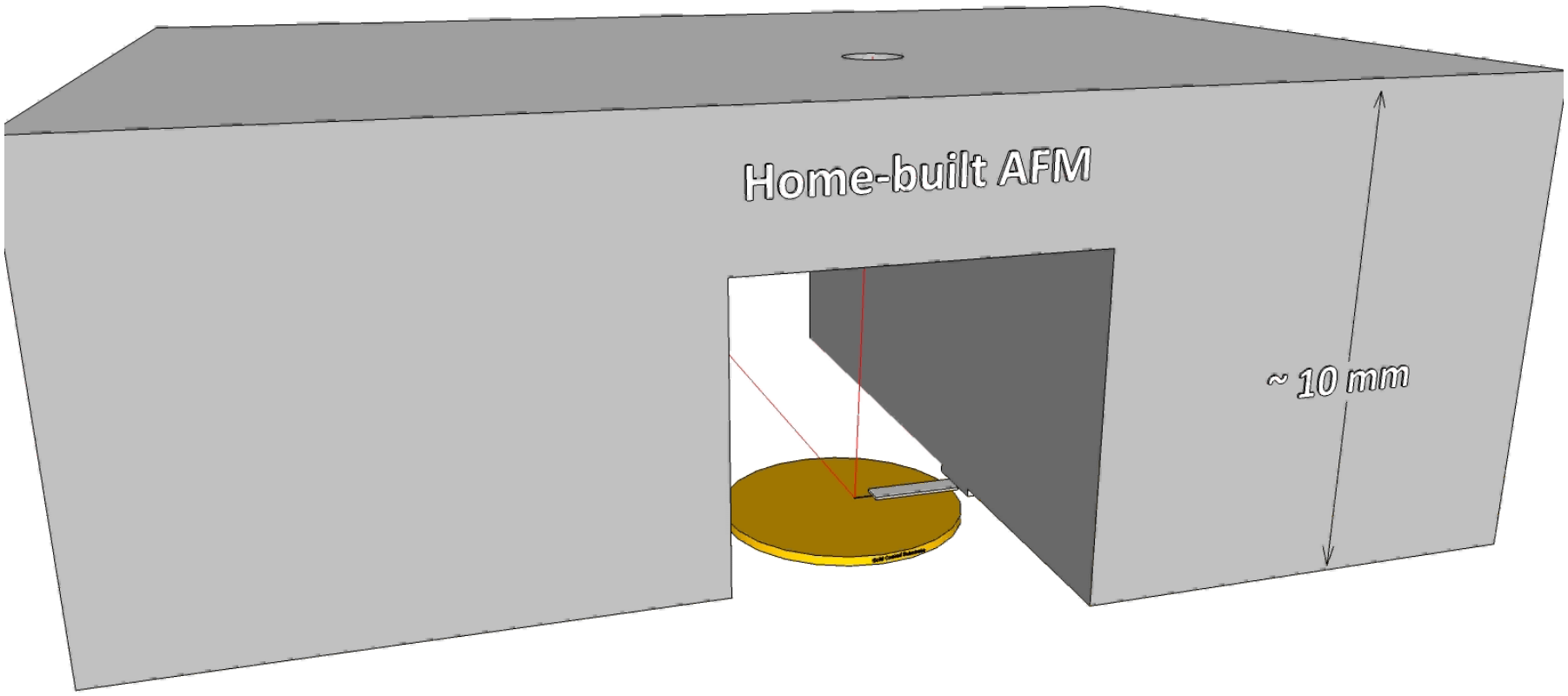
1. Simultaneous measurement of force and conductance
2. Sensitive to both linker group, as well as molecular backbone
3. Information about junction mechanics, even in the absence of conductance features*
4. An independent analysis of force holds is an attractive way to study destructive interference at the single molecule level

"Feeling the invisible"

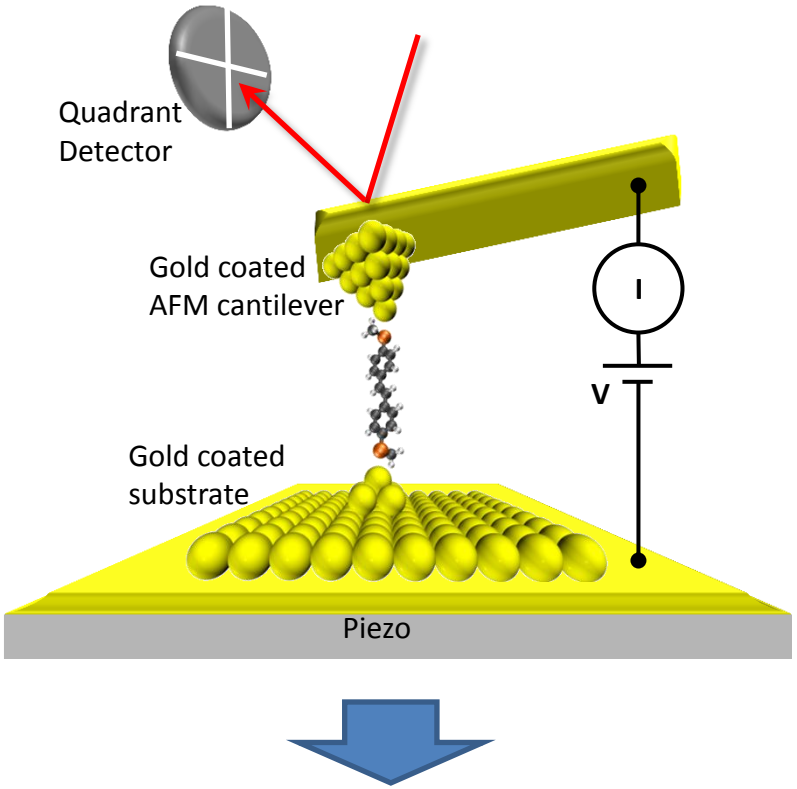
Frei et al., Nano Lett , 2011

TECHNIQUE

Experimental Setup

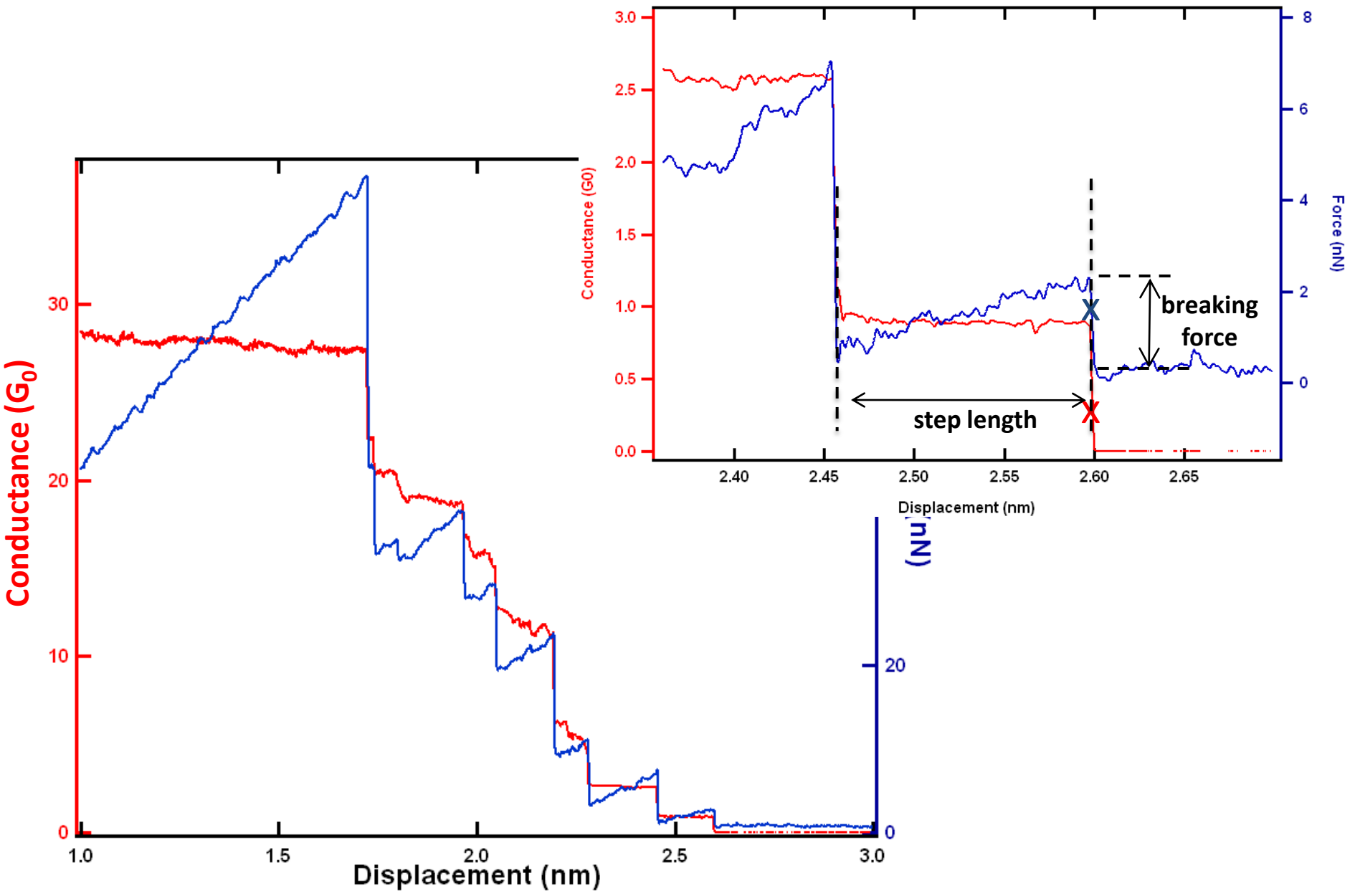


Experimental details

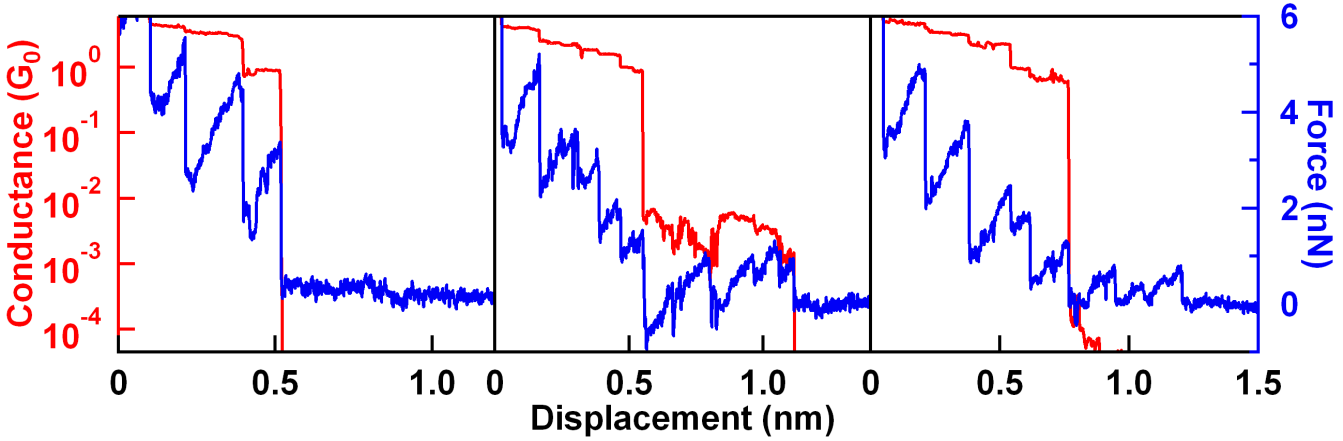


- Au coated cantilever and Au coated mica substrate
- Piezo moved to elongate the junction
- Force is reported by the reflected laser beam
- Molecules deposited as a solution

Analysis

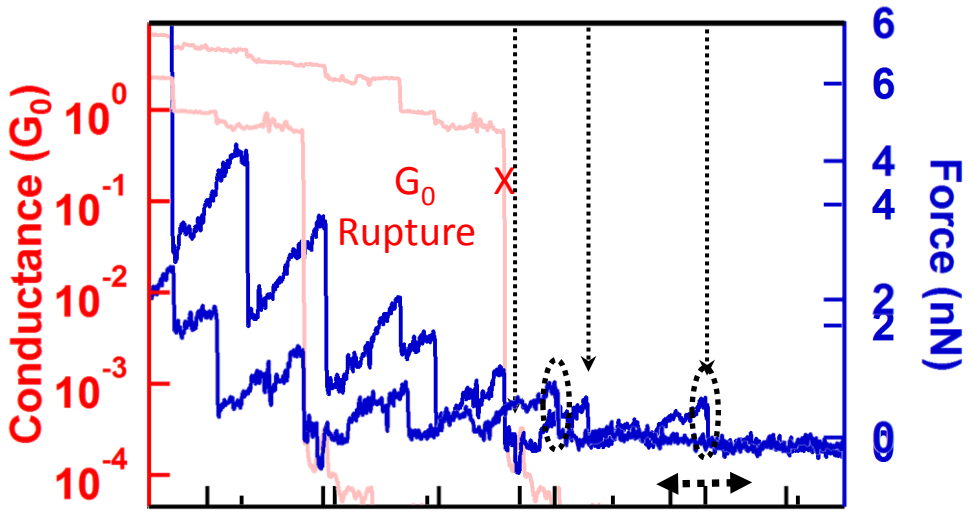

Conductance (G0)
Force (nN)
Displacement (nm)
breaking force
step length
Conductance (G0)
Displacement (nm)
(nN)

Sample traces



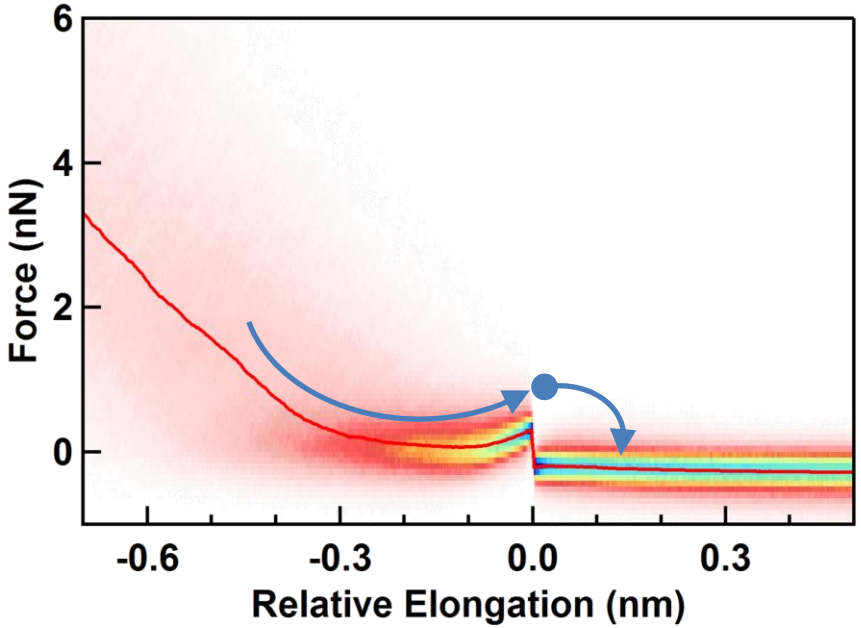
- In the absence of molecules, Au junctions are formed and ruptured
- In the presence of conducting para linked molecule, there is a clear molecular conductance plateau, along with a complex structural evolution signature in force
- In the case of the meta linked molecule, there is no clear conductance plateau but there are still force signatures, ending with a rupture event

Analysis technique



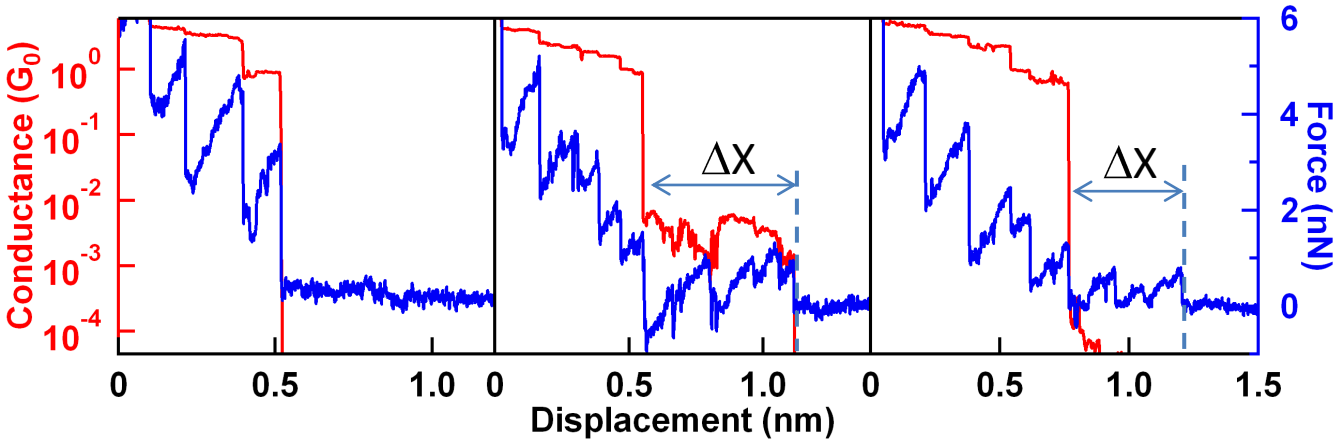
1. Locate G_0 rupture
2. Identify all subsequent force events with **sustained**, **significant** events
3. Pick last force event
4. Center traces at the last force event

Analysis technique



- Characteristic shape in individual force traces – load and rupture
- Shape preserved when thousands of traces are statistically averaged – 2D force histogram
- 2D conductance histogram conductance is also aligned

Analysis technique

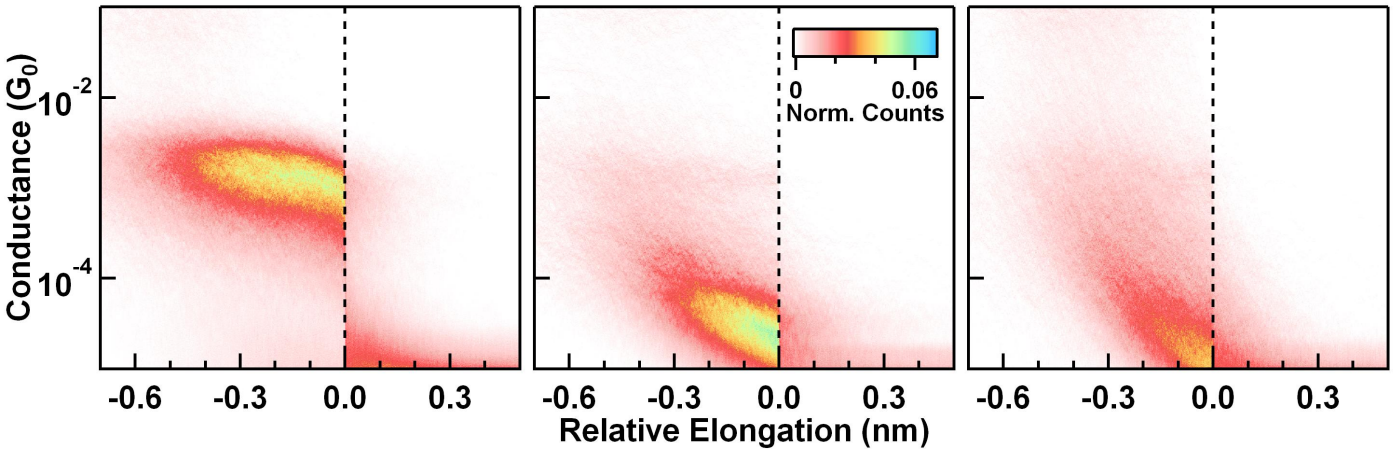


- Define elongation length as the distance from G_0 rupture to molecular junction rupture – irrespective of conductance signature
- Elongation length is a measure of the junction mechanics, and for other series of molecules it has scaled with molecule length

Kamenetska et al., PRL, 2009

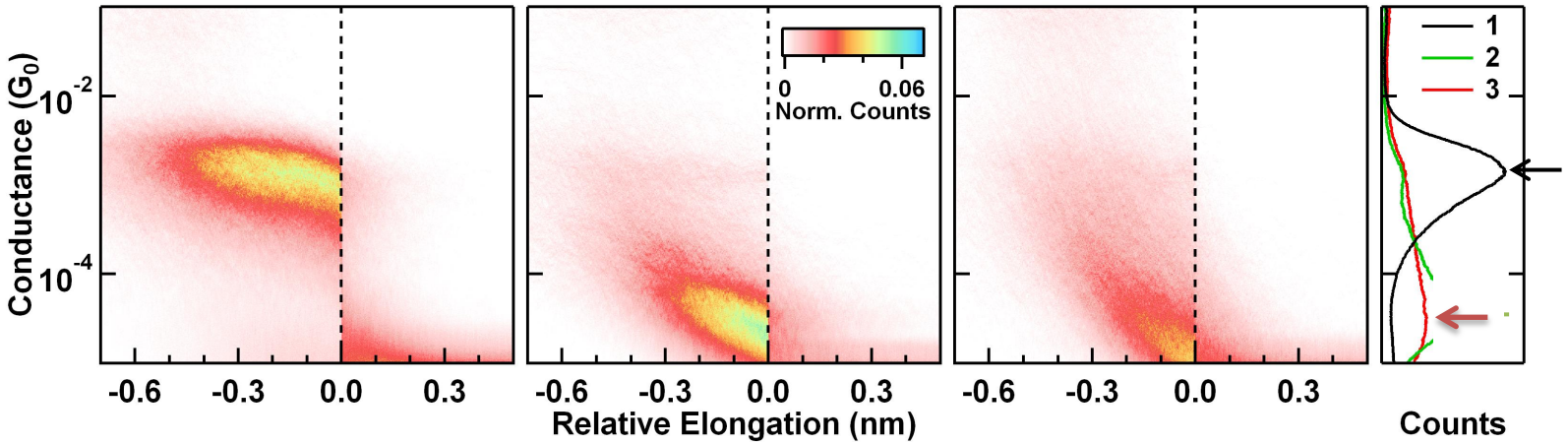
RESULTS: CONDUCTANCE, FORCE & ELONGATION LENGTH

Conductance – 2D and profile



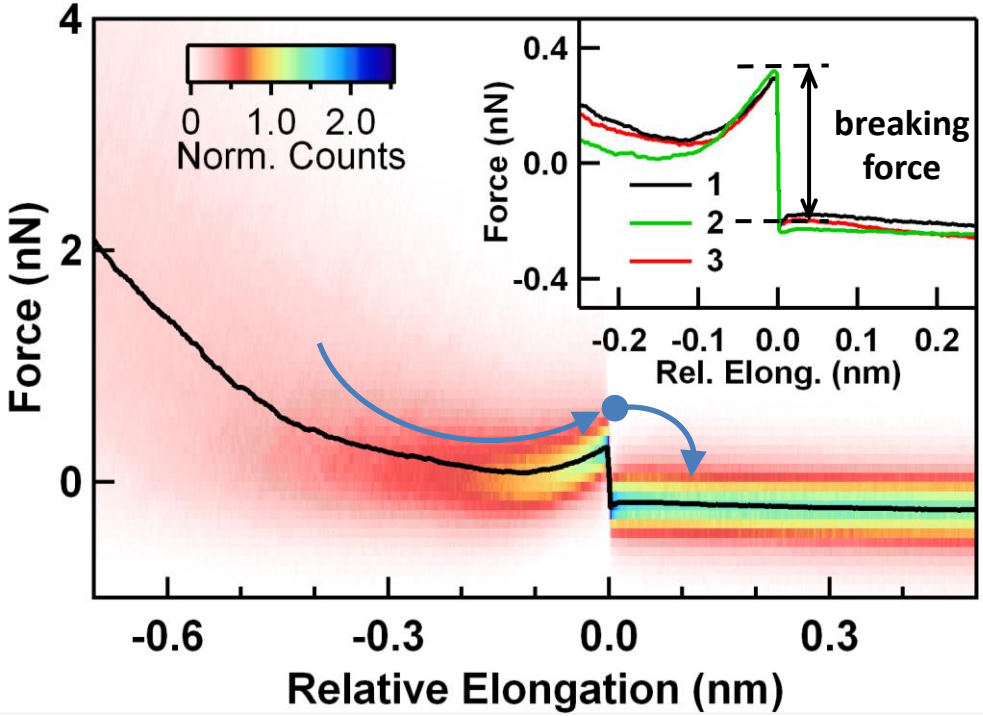
- Zero displacement (dashed line) is the rupture location
- Conductance rupture is automatically aligned, even though it wasn't imposed
- Result # 1 – meta molecule <u>does not</u> show a clear conductance signature in the 2D histogram

Conductance – 2D and profile



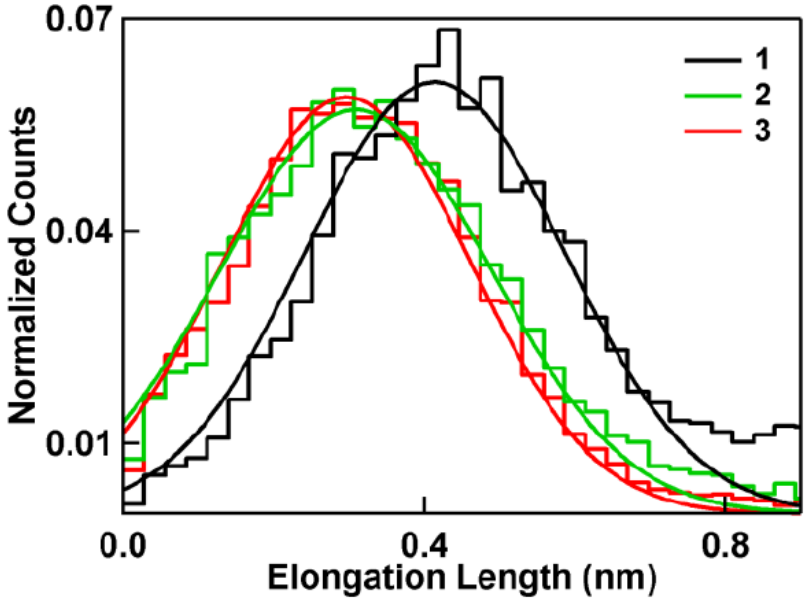
- Line profiles of the conductance **before** rupture ("1D histograms") show well defined peaks for **1** and **2**
- There is a slight shoulder for the molecule **3**
- Result # 2 – This is due to non-zero contribution of σ channel, through-space tunneling and possibly dispersive interactions

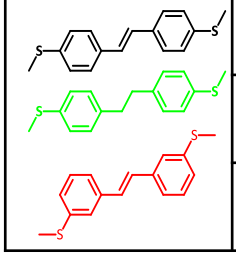
Force – 2D and profile



- Force profiles shows a loading followed by rupture – mirrors individual traces
- In fact, all three molecules show very similar force profiles, and rupture force is 0.5 nN in each case
- Result # 3 – Since changes to the molecule are happening farther from the S-Au bond, the donor-acceptor interaction is not altered significantly

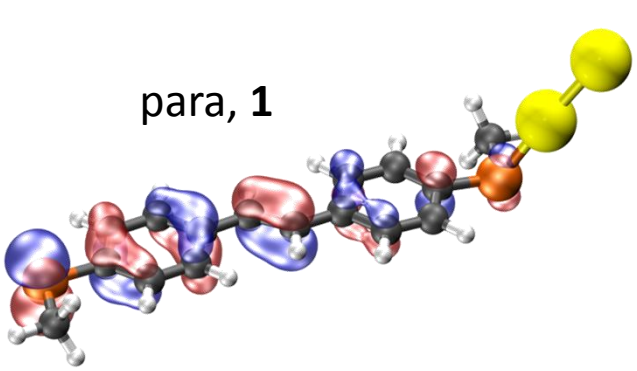
Elongation lengths

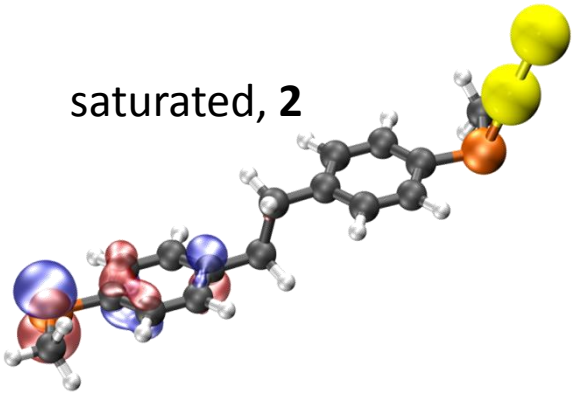


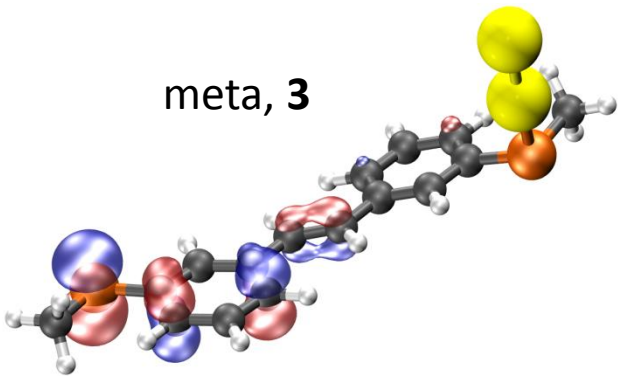
Molecule	Experiment	DFT
	Elongation Length (nm)	S-S distance[a] (nm)
	0.42	1.31
	0.32	1.29
	0.31	1.17

- Elongation length distributions can be fitted with a Gaussian curve with a well-defined mean
- Elongation lengths scale with S – S distance
- Result # 4 – binding geometry is not significantly different

DFT MO calculation

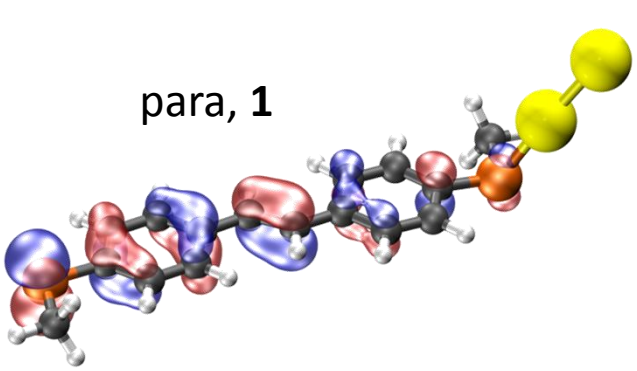


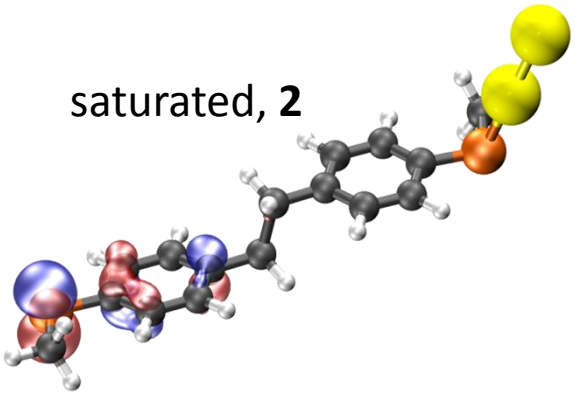


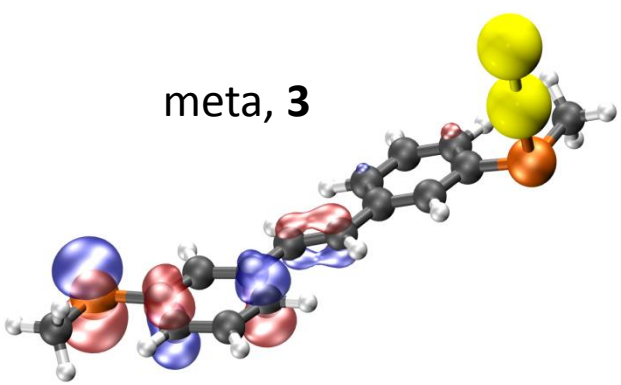


- A simple DFT structure + Molecular Orbital calculation is performed to visualize the origin of these observations (using Jaguar, Dr Steigerwald)
- Result # 5 – The HOMO clearly allows us to visualize the presence or absence of communication between the two S atoms

DFT MO calculation







- In the para molecule, both S atoms have significant amplitude of HOMO
- In the meta molecule, the HOMO spreads out on the conjugated bridge, but there is no amplitude on the S atom at the other end
- In the saturated molecule, the HOMO becomes localized to one ring
- Result # 5 – The HOMO clearly allows us to visualize the presence or absence of communication between the two S atoms

Conclusion

- Successfully able to analyze force, independent of the molecular conductance signature
- Studied a reliable set of molecules to test the interference hypothesis
- The S-Au bond is not significantly altered – junctions are indeed formed, and have the same rupture force for each
- Direct proof of destructive interference at the single-molecule level

Quantum interference due to elegantly designed molecules may open the possibility of unique new functions in single molecule devices

Acknowledgements

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