Carbon fiber tips for scanning probe microscopes and molecular electronics experiments

LOW TEMPERATURE LAB

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DFT CALCULATIONS

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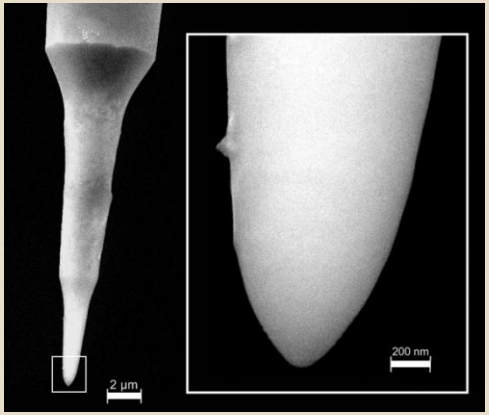
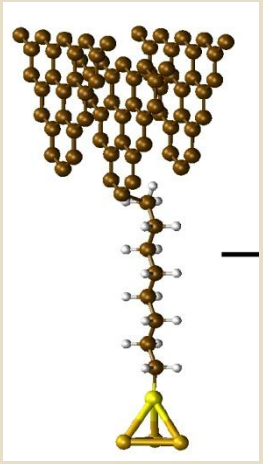




Carbon fiber tips

- **PART 1:**
  - Fabrication.
  - Combined STM/AFM. Tuning fork (TF) based force sensor
  - Suitability for STM, AFM.

- A. Castellanos-Gomez, N. Agrait, and G. Rubio-Bollinger, Nanotechnology 21, (2010), 145702.
- A. Castellanos-Gomez et al., Ultramicroscopy, (2011) 111 (3): p. 186-190.

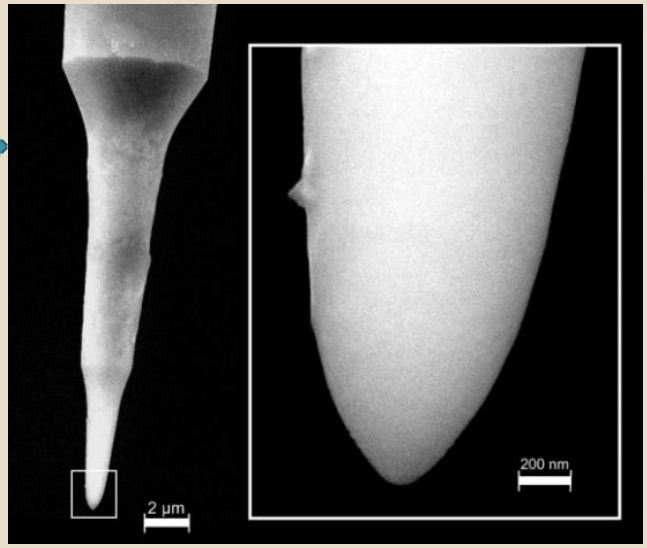
- **PART 2:**
  - Single molecule electronics: the importance of anchoring groups AND electrodes; carbon electrodes.

- A. Castellanos-Gomez et al., Appl. Phys. Lett. 99, 123105 (2011)

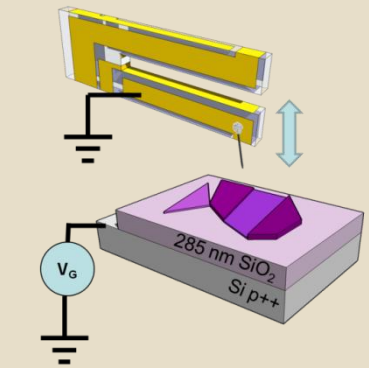
Carbon tips for STM and AFM

- Industrial carbon fiber. Each *carbon* filament thread is a *bundle* of many thousand *carbon* single GRAPHITIC fibers, diameter 7 microns in our case

- *"carbon fiber* is stronger than steel, lighter than aluminum and as stiff as titanium"

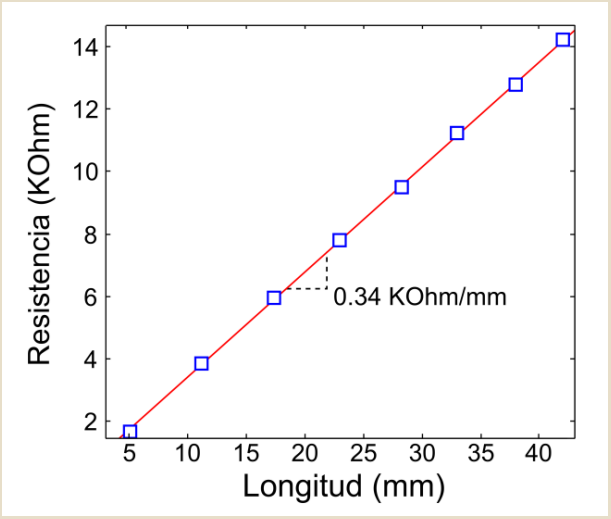


AFM/STM

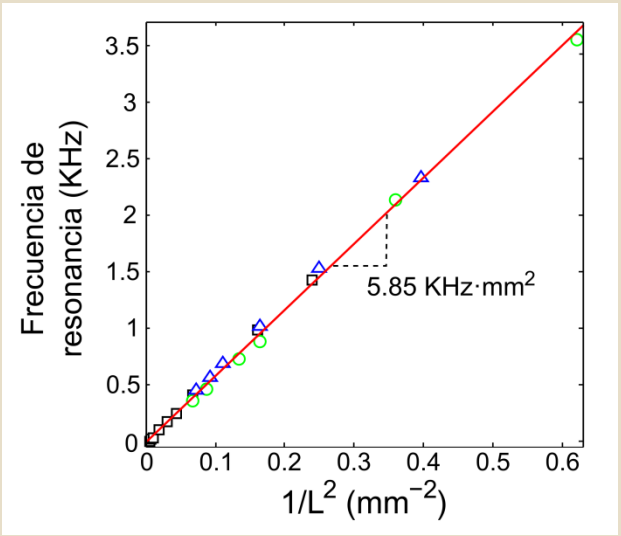


Carbon fiber based tips: electrical and mechanical properties

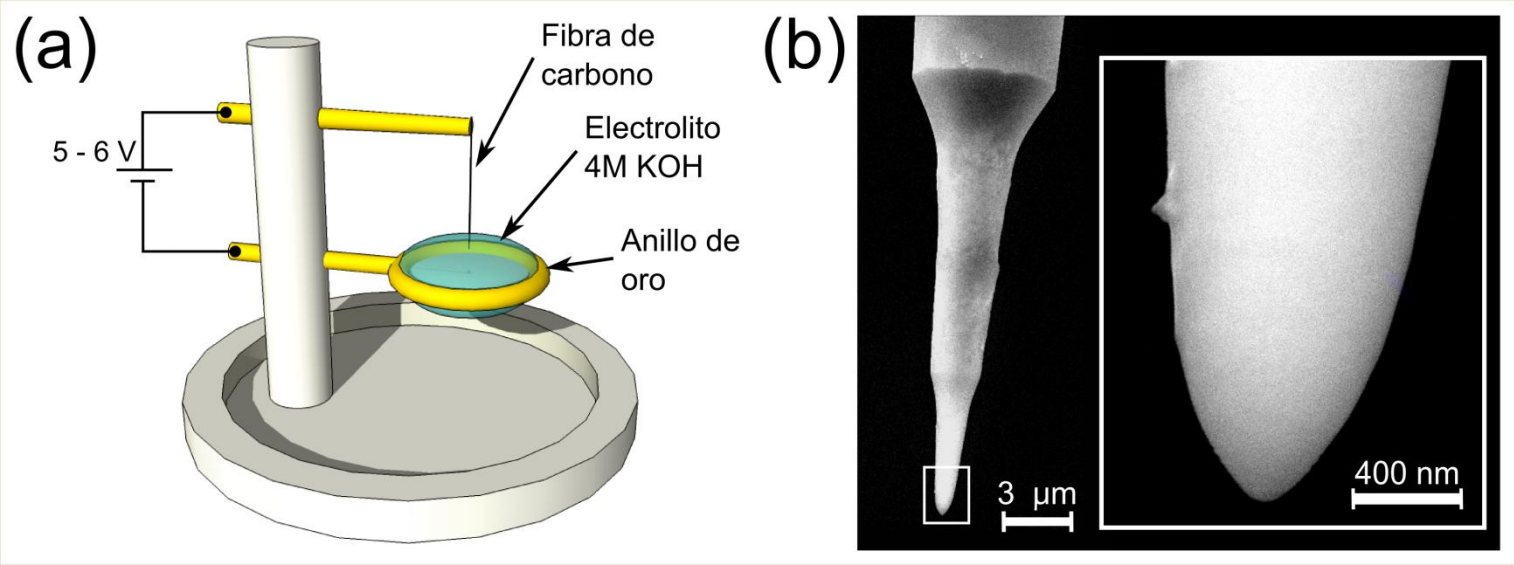
- **Electrical properties**
  - *Resistivity* ρ (fiber)= 1.3×10^{-5} Ωm
  - $\rho(Pt)=1\times10^{-7}$ Ωm
  - $\rho(graphite\ T)=5\times10^{-6}$ Ωm
  - $\rho(graphite\ ==)=3\times10^{-3}$ Ωm
  - Typical fiber tip length is < 0.2 mm -> R<80 Ohm.



- **Mechanical properties**, obtained from length dependent resonant frequency
  - Young Modulus *E*=265 GPa
  - Elastic Limit 4 GPa (vs 0.5 GPa for PtIr)
  - Elastic limit is close to yield.



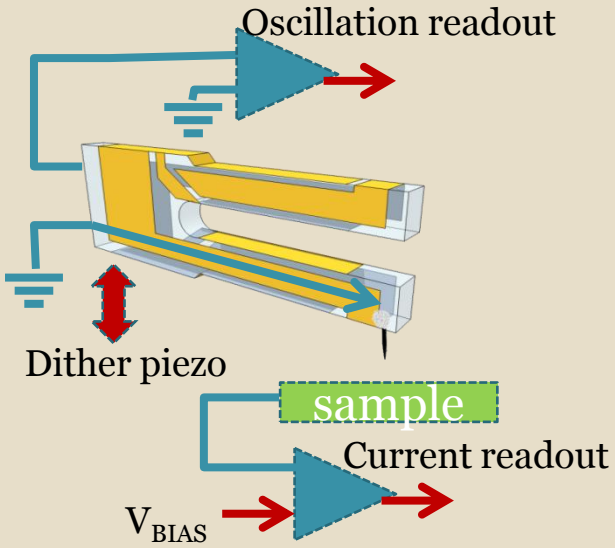
Carbon fiber tips: electrochemical etching

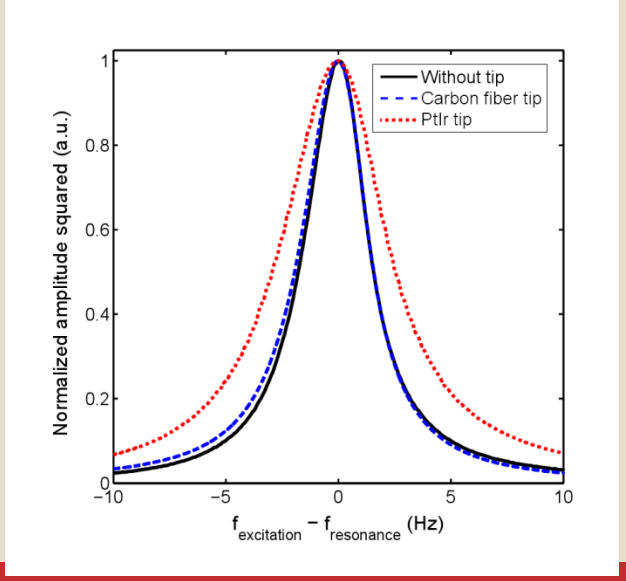


- Insert the fiber in a suspended drop of 4M KOH in a gold ring.
- Apply 5 to 6 volts between the fiber and the electrolyte.
- Wait for 30 seconds, and the fiber finally ‘breaks’ and etching is stopped.
- Apex radius of curvature < 50 nm, and high aspect ratio

Attachment of the carbon fiber tip to a tuning fork force sensor

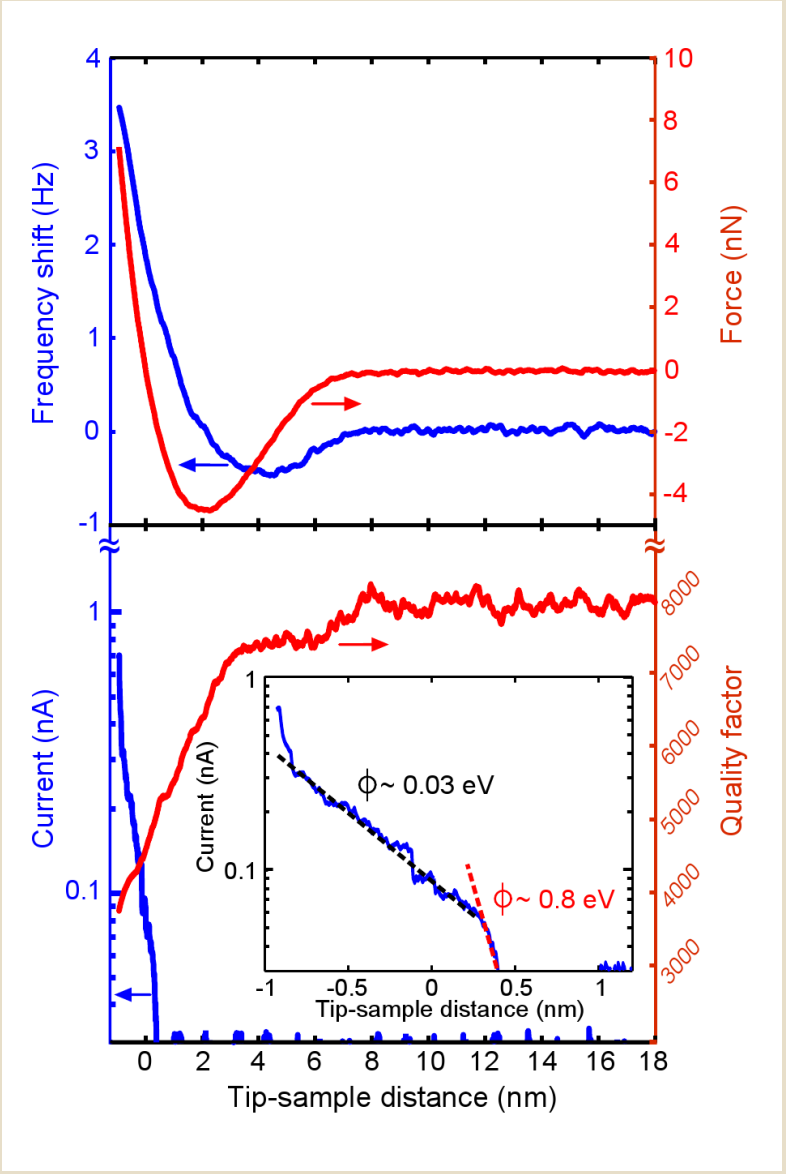
- The carbon fiber tip is attached to the end of one of the prongs of a TF resonator.
- A force gradient acting on the tip shifts the resonant frequency of the tuning fork.
- For STM operation, the tip is electrically connected to one of the electrodes of the TF.
- Voltage bias and current are monitored from the electrical connection to the sample.
- Because the fiber tip is very light, the resonant frequency of the TF does not change significantly and its quality factor Q remains high.





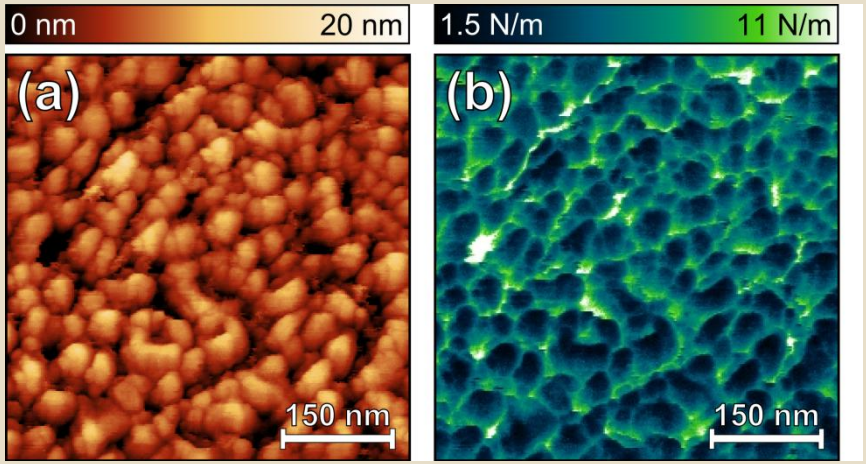
Combined AFM/STM behavior

- Tip-sample distance dependence of force and tunneling current (simultaneous)
- Tunneling current of up to 0.1 nA is observed while in the attractive force regime.
- The apparent tunneling barrier height is high, even under ambient conditions.
- This behavior lasts for days, suggesting a low oxidation/degradation rate

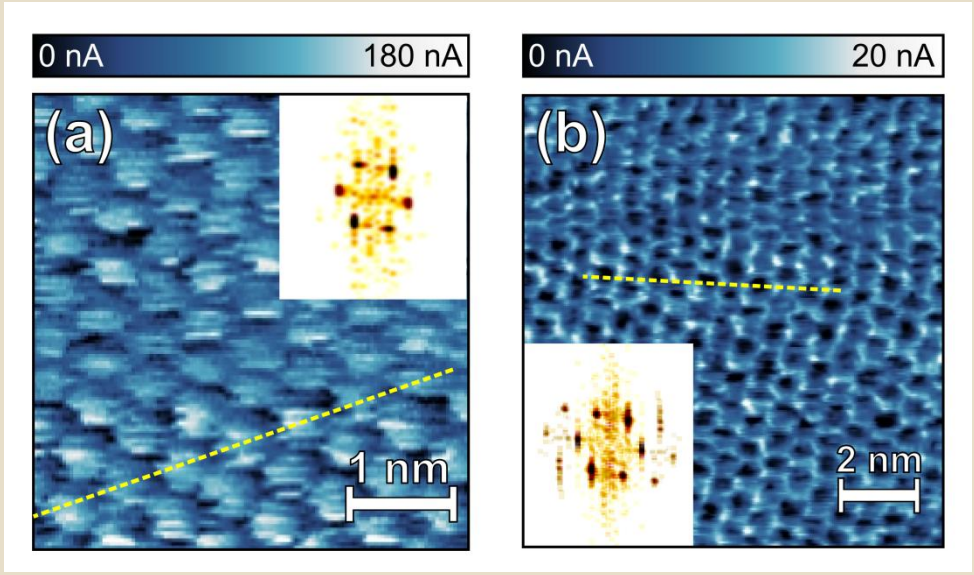


Resolution under ambient conditions

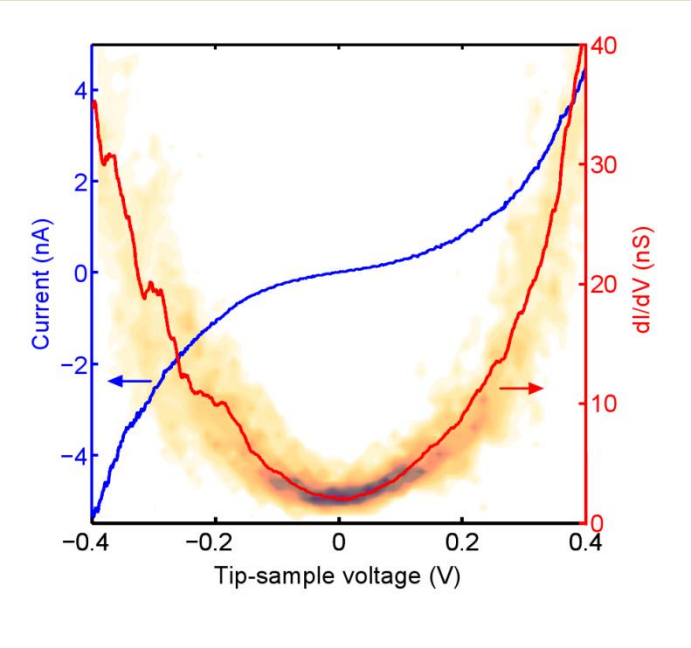
- <10 nm on polycrystalline gold, both in STM and simultaneous force image (blue-green)

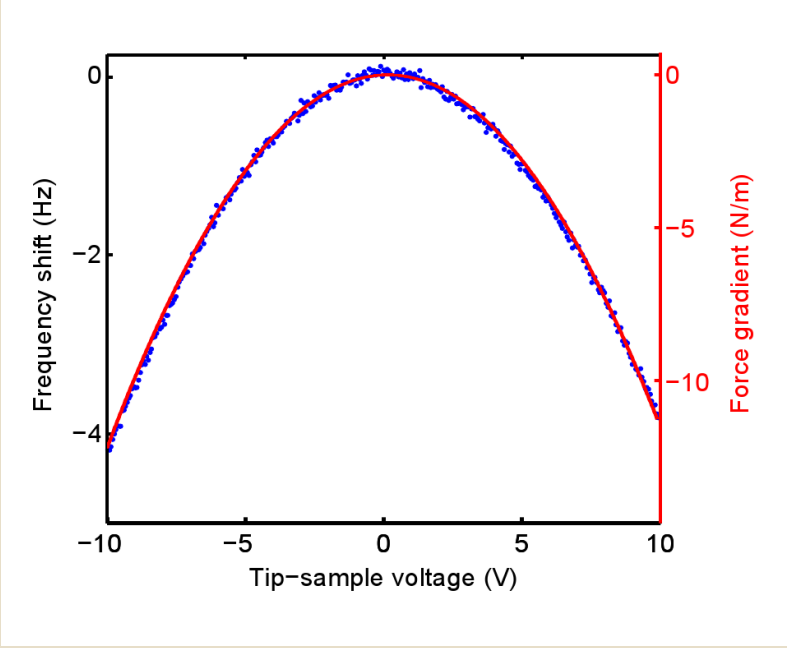


- Atomic resolution on Graphite (HOPG)



Tunneling spectroscopy and electrostatic force microscopy



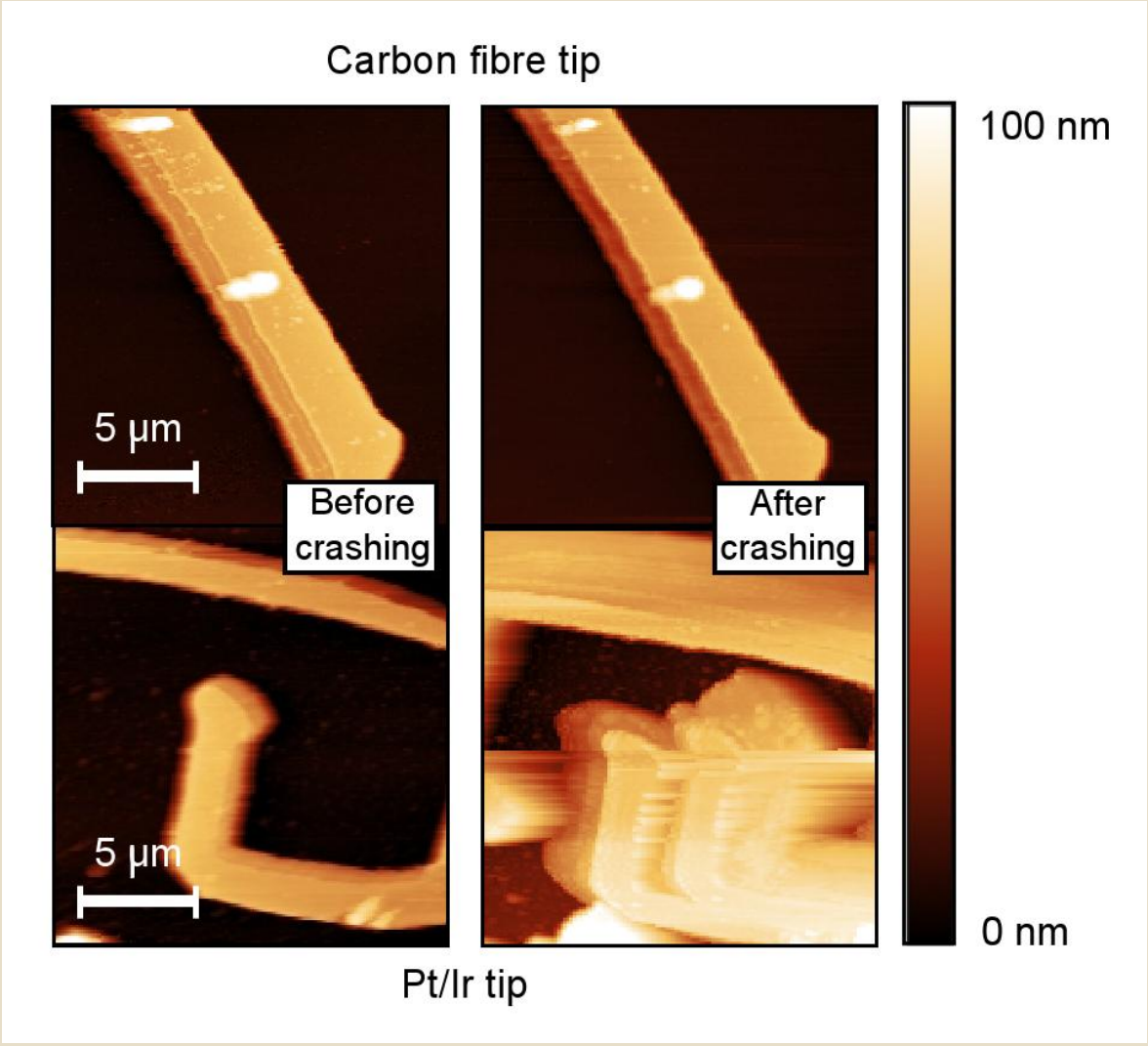


- Tunneling spectroscopy on a Au(111) surface. Result is typical for a gold-graphite junction.
- Electrostatic force vs tip-sample bias: tip is suitable for kelvin probe force microscopy (KPFM).

Robust against accidental tip crashes

- The carbon (/metallic) fiber tip is intentionally slightly crashed against a sample (here an e-beam fabricated track of Au on silicon oxide)

- The carbon fiber tip survives after the intentional crash due to its high flexibility, being the elastic limit close to the yield limit.



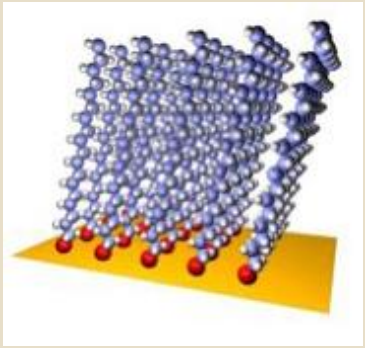
Carbon fiber tips for scanning probe microscopes

- SUMMARY. Carbon fiber based tips
  - Suitable for STM:
    - Not oxidizing under ambient conditions
    - High electrical conductivity
    - Significant tunneling current while in the attractive force regime
  - Suitable for AFM
    - Sharp, suitable for electrostatic force microscopy
    - Robust against tip crashes
  - Combined STM/AFM; tuning fork (TF) based
    - lightweight

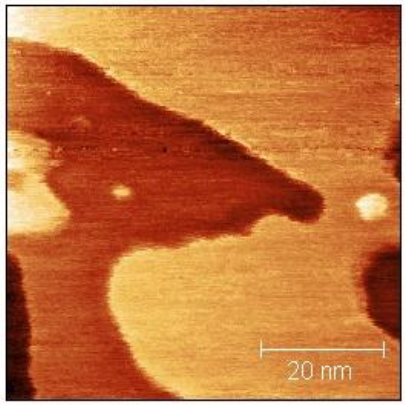
PART 2: Carbon fiber tips for molecular electronics

- Fabricate single molecule junctions based on the break-junction technique using carbon fiber tips as electrodes: the tip is approached to the surface until contact with a single molecule is detected.

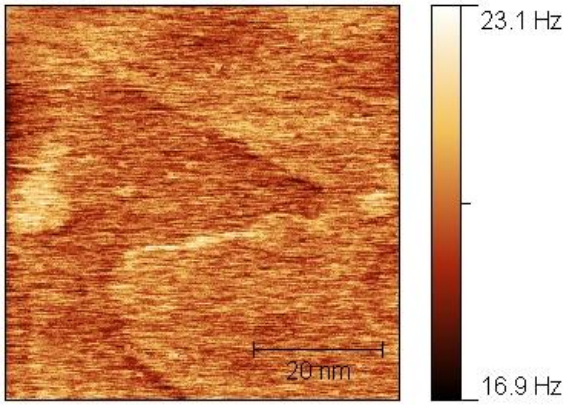
- Model system: octanehiol Self Assembled Monolayer (SAM) on gold (111).



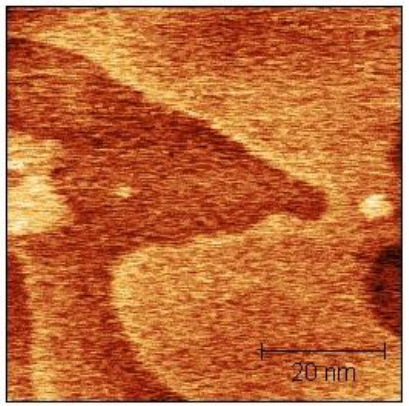
- DynSTM topography



df (freq. shift)



damping



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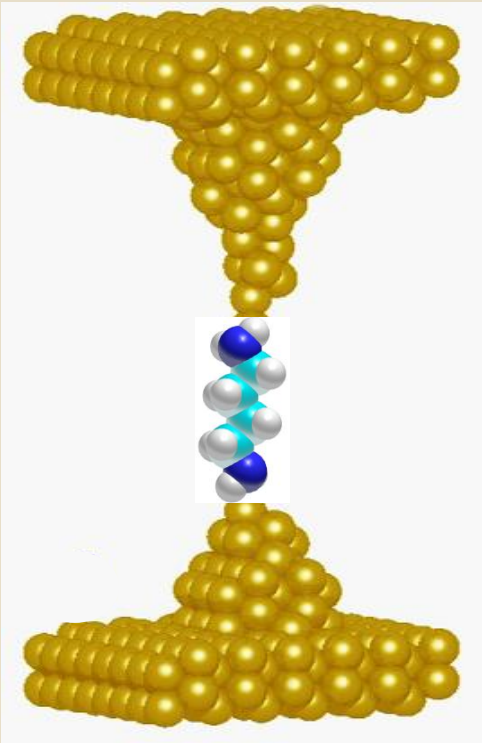
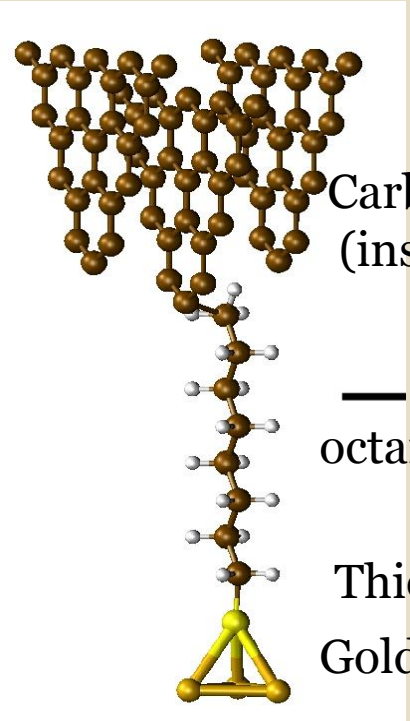
Single molecule electronics

Break-junction
thechnique

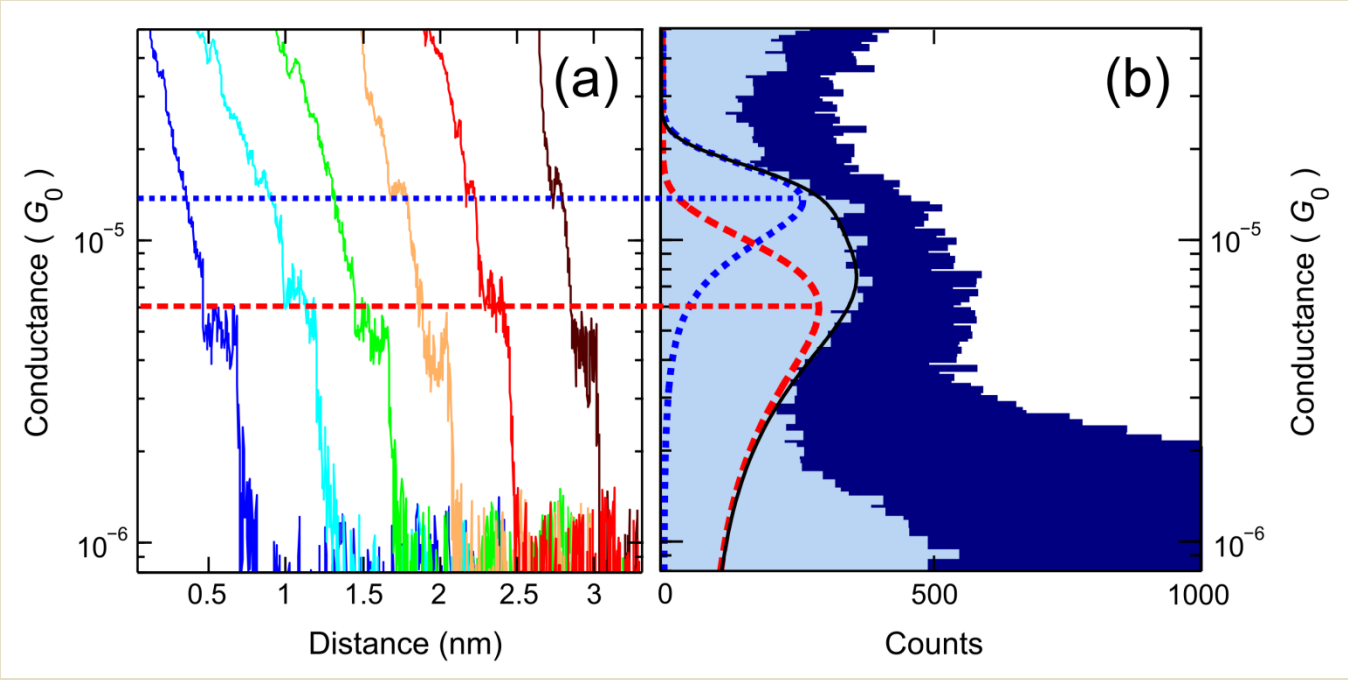


CARBON electrode



Conductance histograms

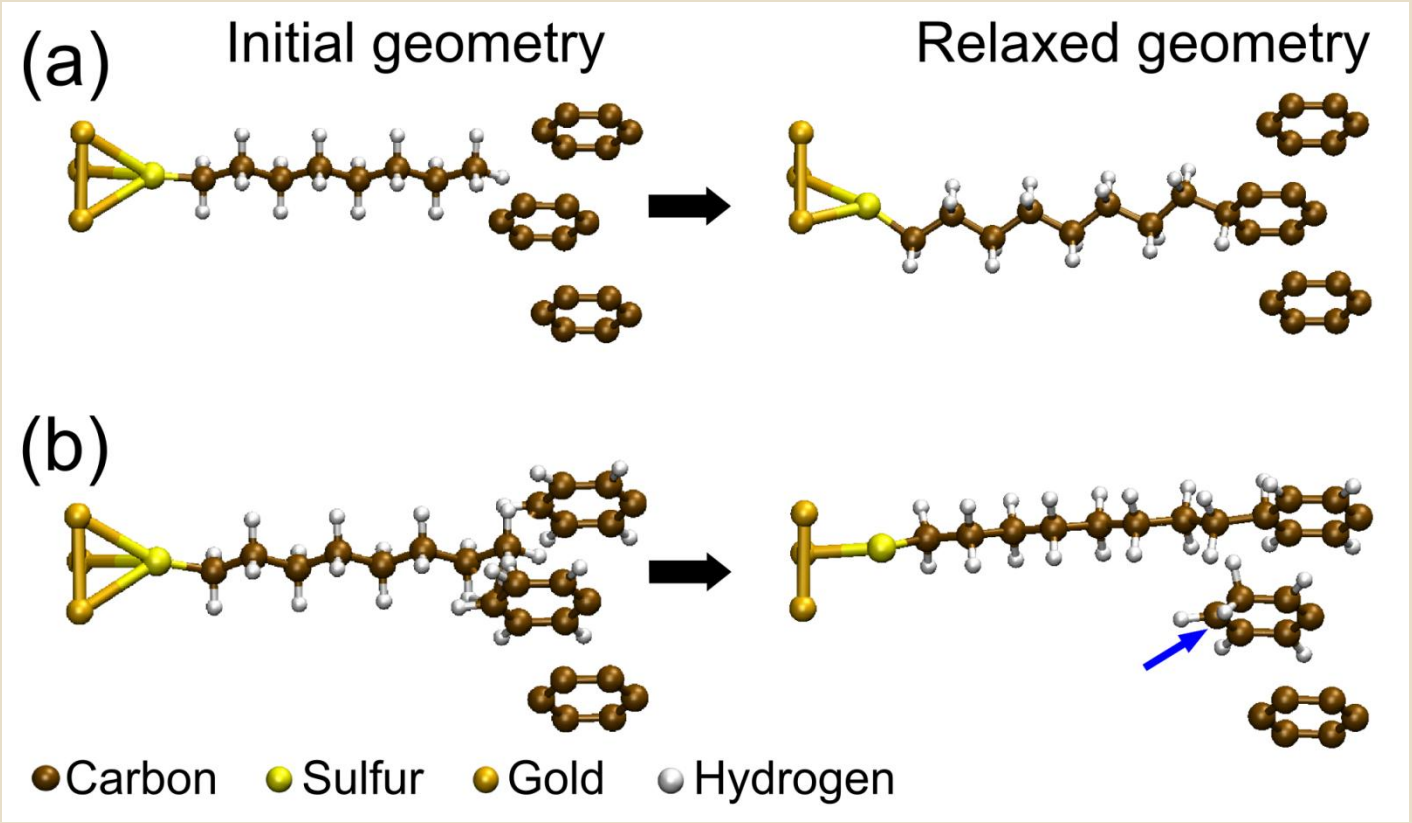
- Record electrical conductance during repeated indentation-retraction cycles.
- Each junction realization shows a slightly different behavior due to the subtle dependence of conductance on exact molecular configuration and strain.
- Conductance plateaus are associated to the presence of a molecule in the junction, due to a well known (discrete) mechanical behavior of metallic nanocontacts, early predicted by MD simulations (U. Landman).
- Build a conductance histogram. Peaks will appear at more frequent conductance plateaus, and therefore the conductance of a molecule (6 x 10^{-6} Go).



DFT calculations

- DFT calculations (J.C. Cuevas, UAM)

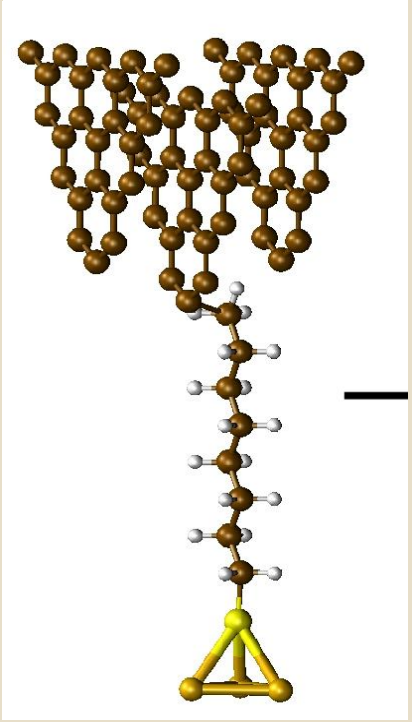
- Upon sufficient strain a H atom is transferred from the methil termination of the octanethiol molecule to one of the carbon ‘rings’ of the tip.
- The conductance of the molecule is due to tunneling through its backbone.



SUMMARY. Carbon tips for single molecule electronics

- Graphitic carbon tips provide a suitable electrode to form single molecule octanethiol junctions.

- They provide a proper mechanical linking to the methil group and conductance traces show well defined plateaus at 6 x 10^{-6} Go.



SUMMARY. Carbon fiber tips for AFM/STM

- Valid for STM and Tuning Fork sensor based AFM.
- Robust against tip crashes.
- Stable under ambient conditions.
- Valid for electrostatic force microscopy.
- Valid for tunneling spectroscopy.
- Valid for single molecule electronics.