Nanoscale Contact Formation Dynamics

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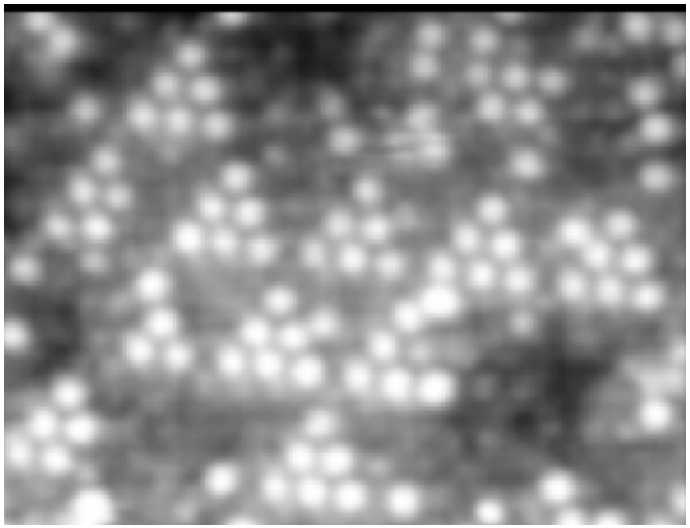
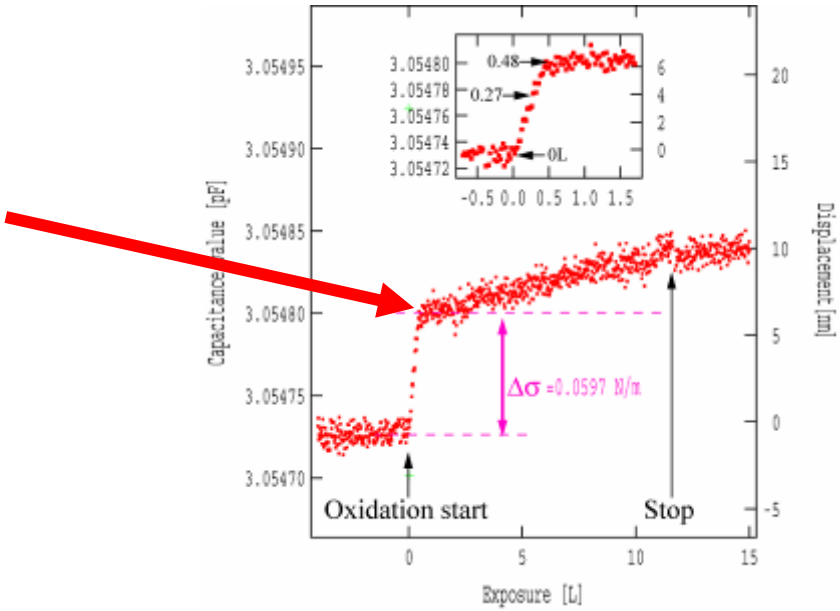
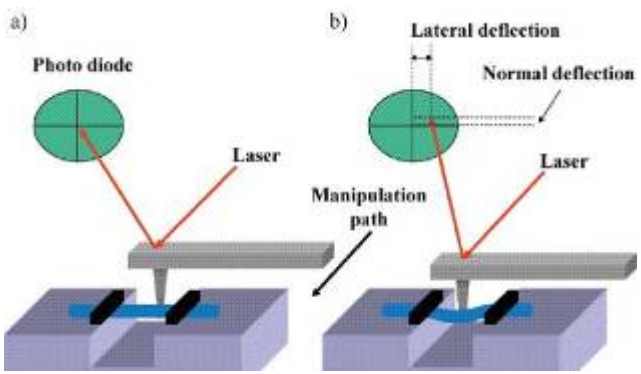
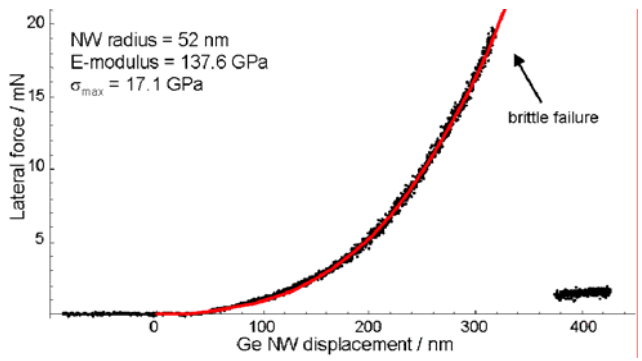
Other Research Activities









NanoMechanical and electromechanical measurements

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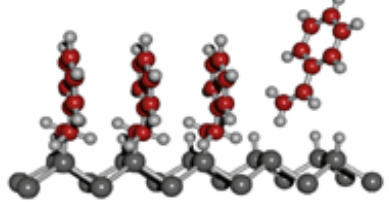
Why Contacts?



- **The success of future nanoscale devices is critically dependent on gaining an atom-level understanding of contact formation**
  - How are electronic properties of the molecule/nanomaterial affected by contact?
  - How does the molecule/material respond when contact is established?
  - What role is played by the contact metal?
  - Can we predict the conductance of nanoscale systems?
- **How can one go about answering these types of questions?**
  - Approach: develop new methodologies based on cryogenic STM

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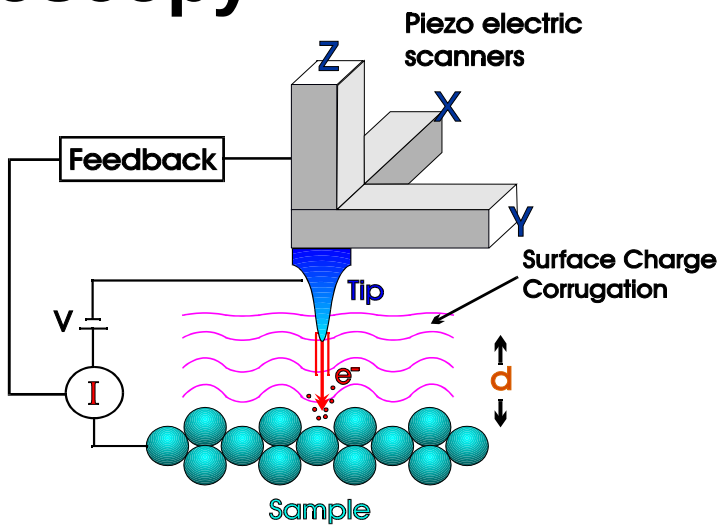
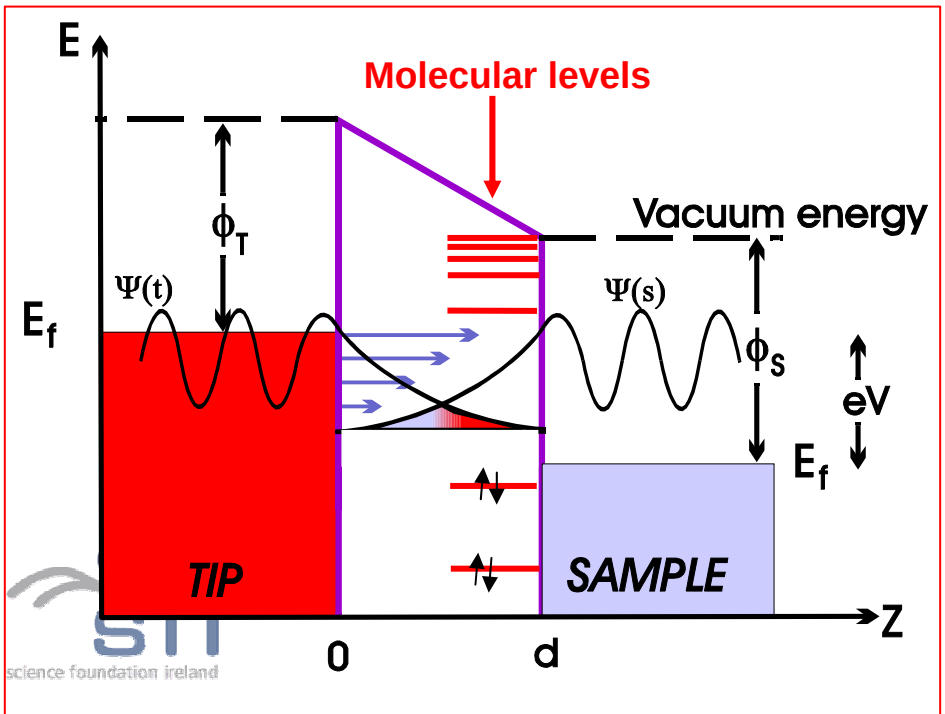
Scanning Tunneling Microscopy

- Overlap of tip and sample wavefunctions
- Applied bias defines the energy window sampled
- Study HOMO and LUMO levels





$$I_t \propto \rho_s(0, E_F)\, e^{-\phi^{1/2} Z}$$

LDOS at location z and energy E

$$\rho(z, E) = \frac{1}{\epsilon} \sum_{E_n = E - \epsilon}^{E} |\psi_n(z)|^2$$

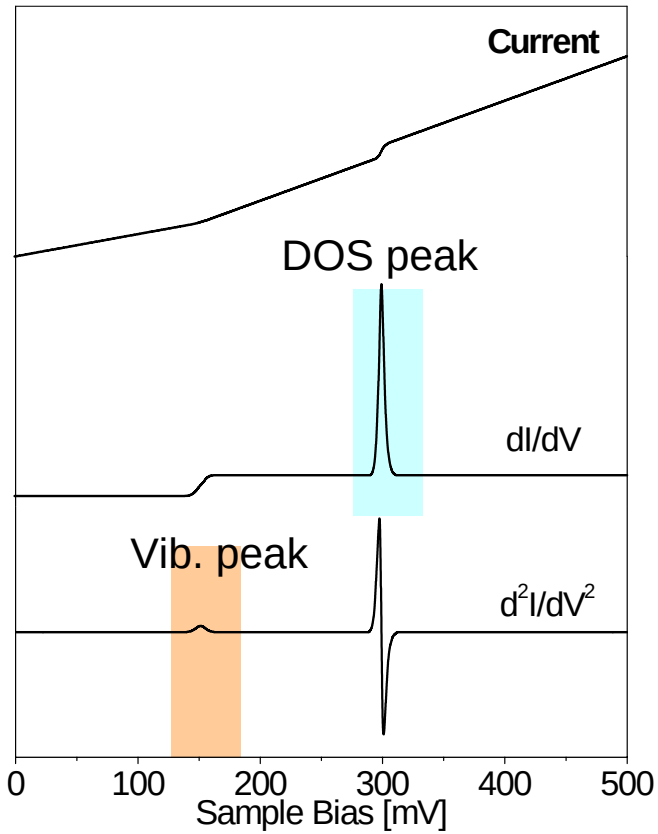
DOS, Molecular Vibrations, and Barrier-height

$$I(V) \propto \int_{E_F}^{E_F+eV} DOS(E)\,T(E,V)\,dE$$

$$\frac{dI}{dV} \Rightarrow peaks^{DOS}$$

$$\frac{d^2I}{dV^2} \Rightarrow \frac{d}{dV}(DOS) + peaks^{IETS}$$

$$I \propto \exp(-A\sqrt{\phi}Z) \Rightarrow \quad \phi \propto \left(-\frac{dI/dZ}{IA}\right)^2$$



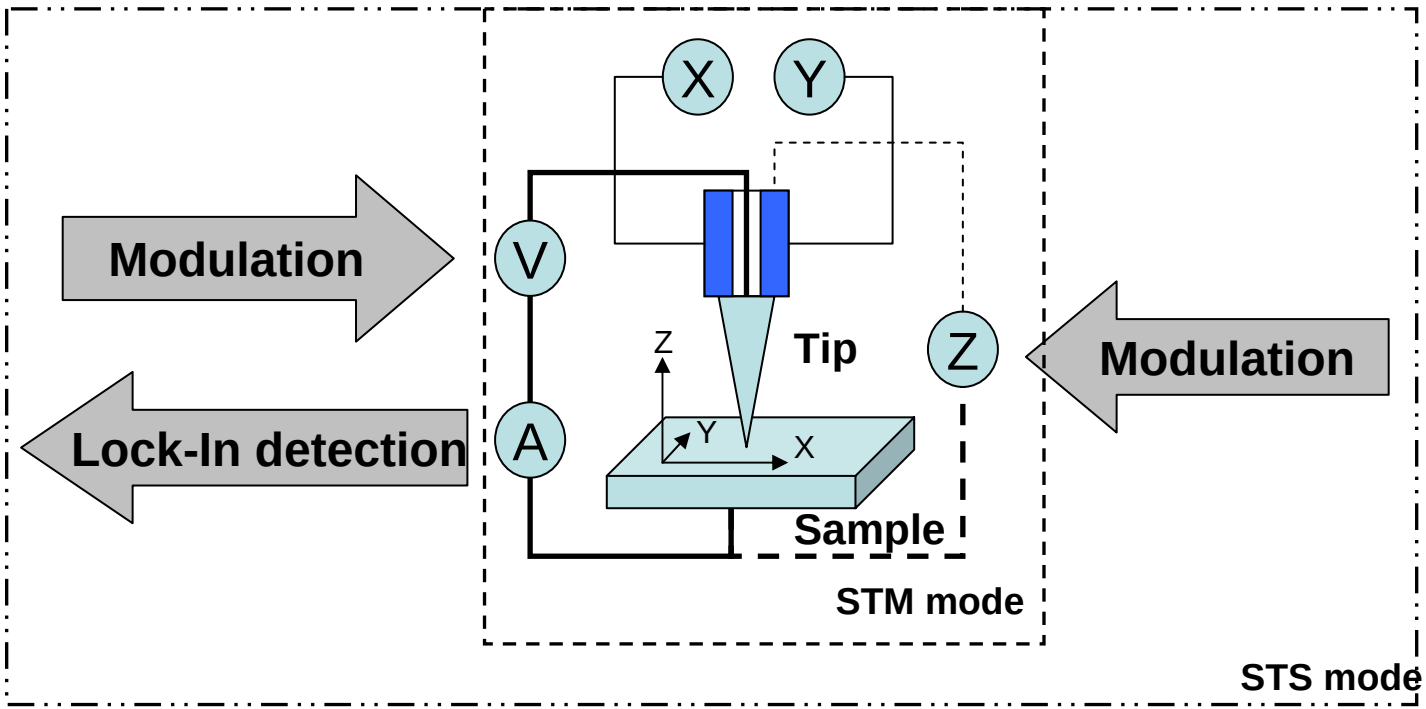
In principle STM can provide significant insights

Not delivered in practice, poor correlation of properties with contact formation, no ability to account for forces involved

Strategy

- Separate the electronic and mechanical effects:
  - Record detailed changes in the electronic and vibrational properties of molecule as probe approaches to contact
  - Measure forces experienced during contact
    (new technique, refer to as relaxation spectroscopy)
  - Study contacts with molecules and nanomaterials

Scanning Tunnelling Spectroscopy (STS)



Conventional STS measurements

$I(V)\,\vert_{Z\ constant}$	$I(Z)\,\vert_{V\ constant}$
$dI/dV\,\vert_{Z\ constant}$	$dI/dZ\,\vert_{V\ constant}$
$d^2I/dV^2\,\vert_{Z\ constant}$	$d^2I/dZ^2\,\vert_{V\ constant}$

Basis for force measurements

Only for specific energy window defined by the applied bias

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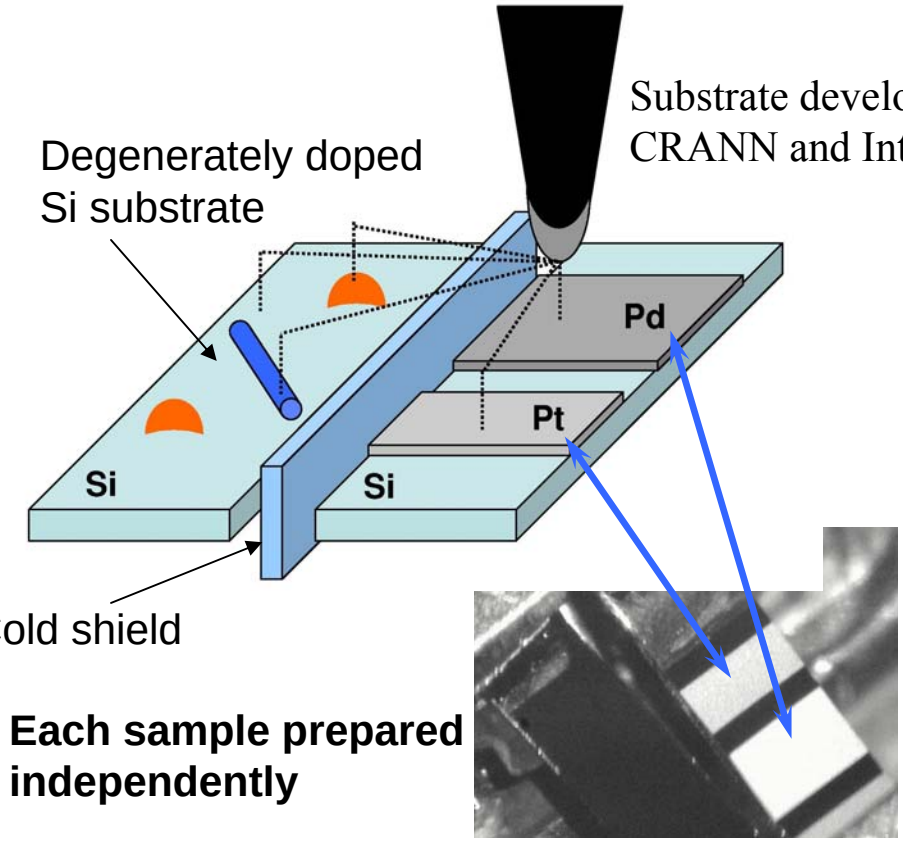
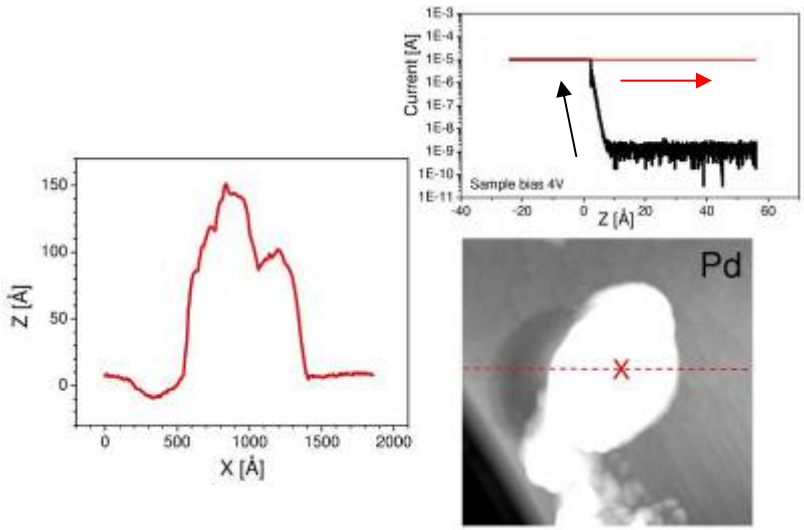
Integrated Substrate* for probe preparation



Each sample prepared independently

Metal-inking: drawing material from the surface onto the probe apex



Metal-inking essential to control composition and electrical properties of probe
Guarantees that bias maps onto the energy scale in STS measurements

*co-developed with Intel, processing at Tyndall National Institute

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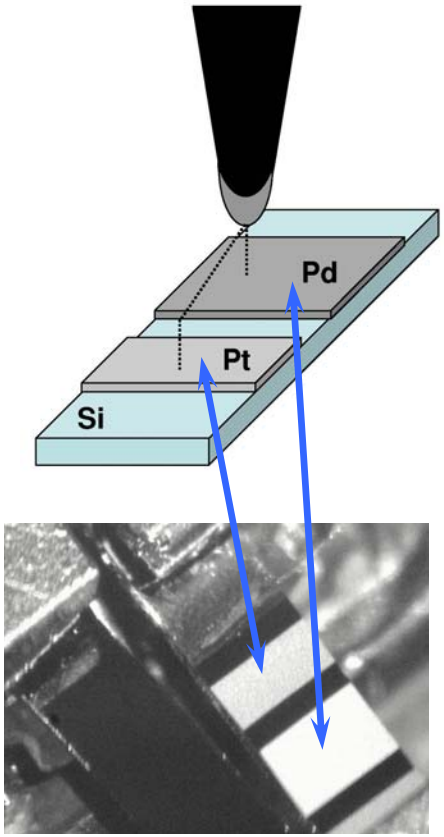
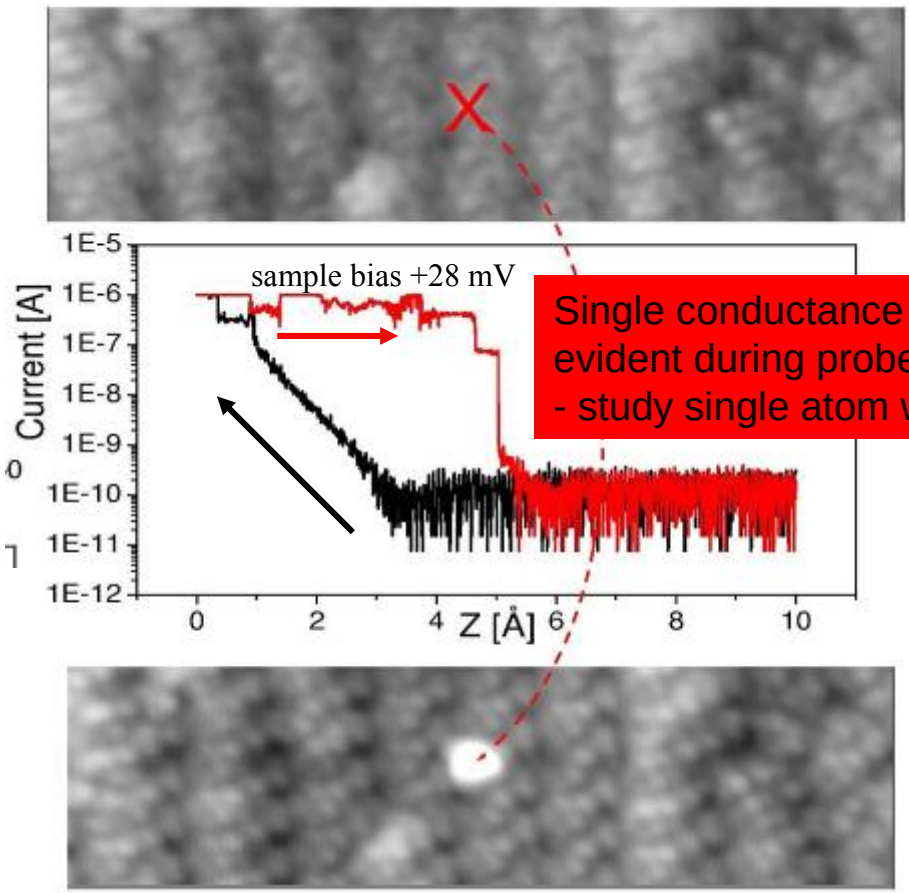
Integrated Substrate for probe preparation



Top view

Probe sharpening on Pd surface



Single conductance channels evident during probe retraction - study single atom wires

Characterize sharpened probe by STS and barrier height measurements on known samples

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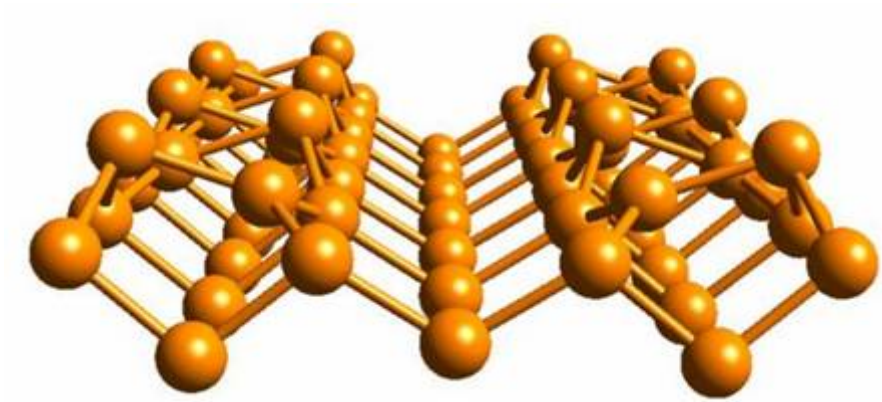
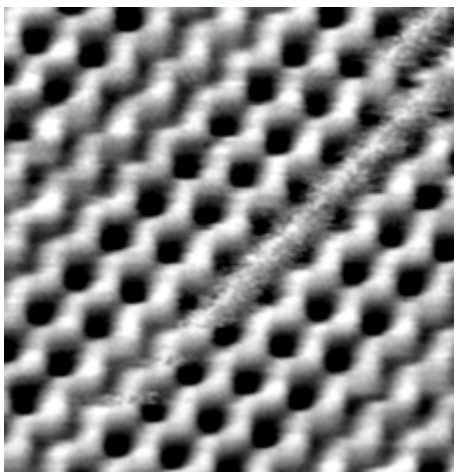
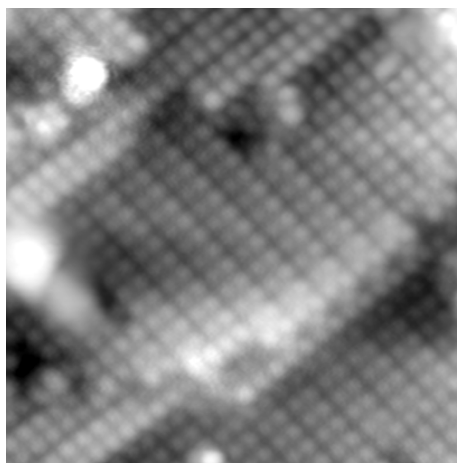
Example A: Si(100) Substrate and Molecule

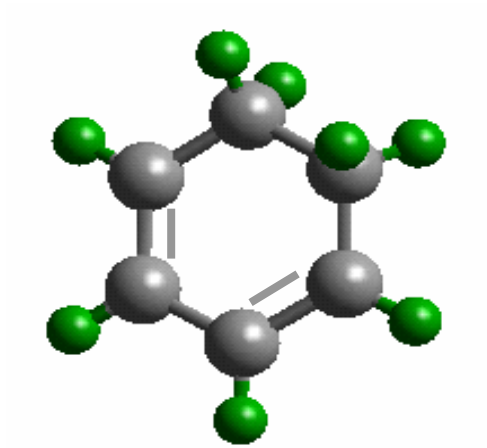






Bare surface **H passivated**

5 K STM image of Si(100)



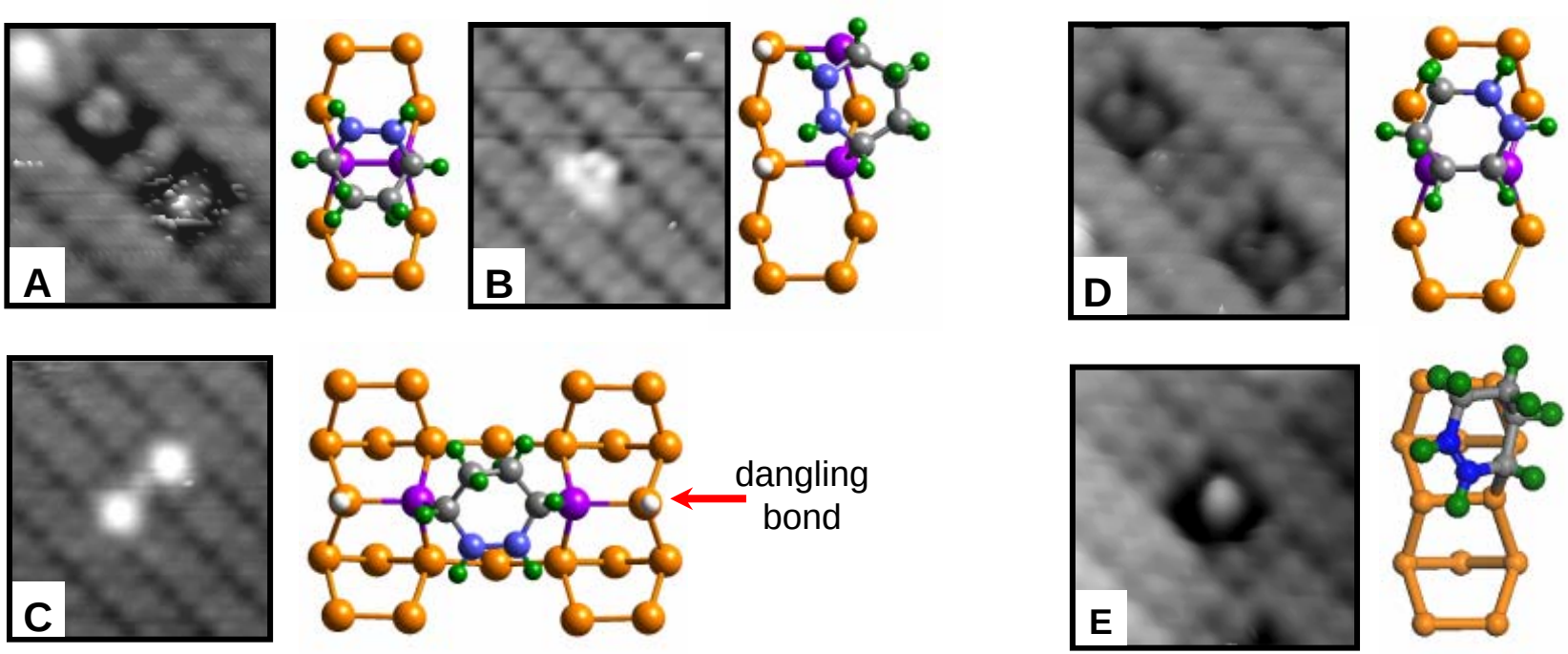
1,3-cyclohexadiene (1,3-CHD)

After reaction one C=C double bond remains and corresponds to the topographic maximum visible in STM (5 different possible configurations)

1,3-CHD on bare Si(100) surface

[4+2] Products

[2+2] Products



Color Key: Si C C=C H Si-C

Product identification based on location of single remaining C=C

Always some noisy sites on surface

Empty state images: tunnelling into π^* level of C=C?

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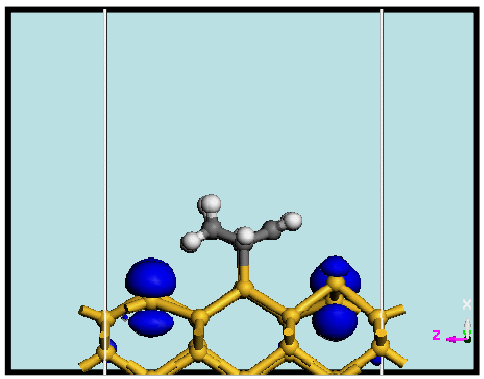
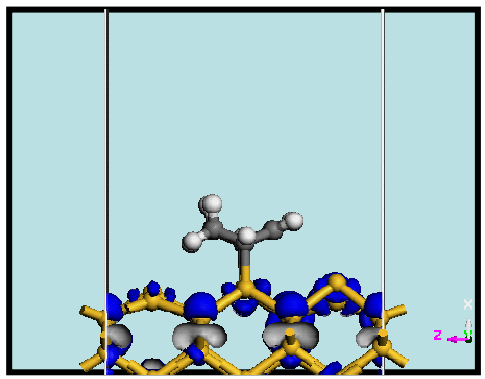
Can't explain origin of STM contrast

- DFT reveals broadened π^* state at +3.5eV
- Broadened π^* does not extend appreciably below +2 eV

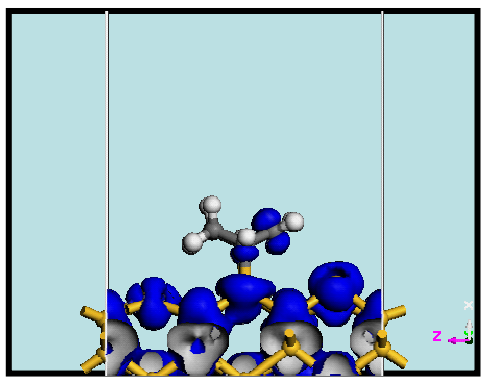
Bias +1.0eV



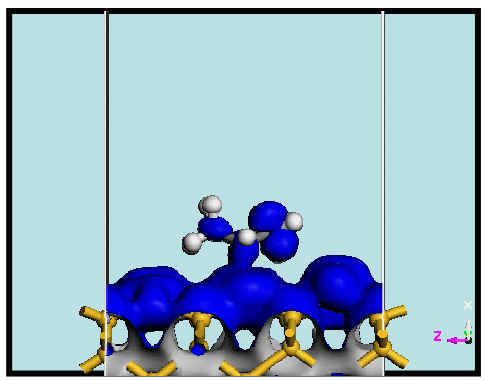
Energy window 0-1eV



Energy window 1-2eV

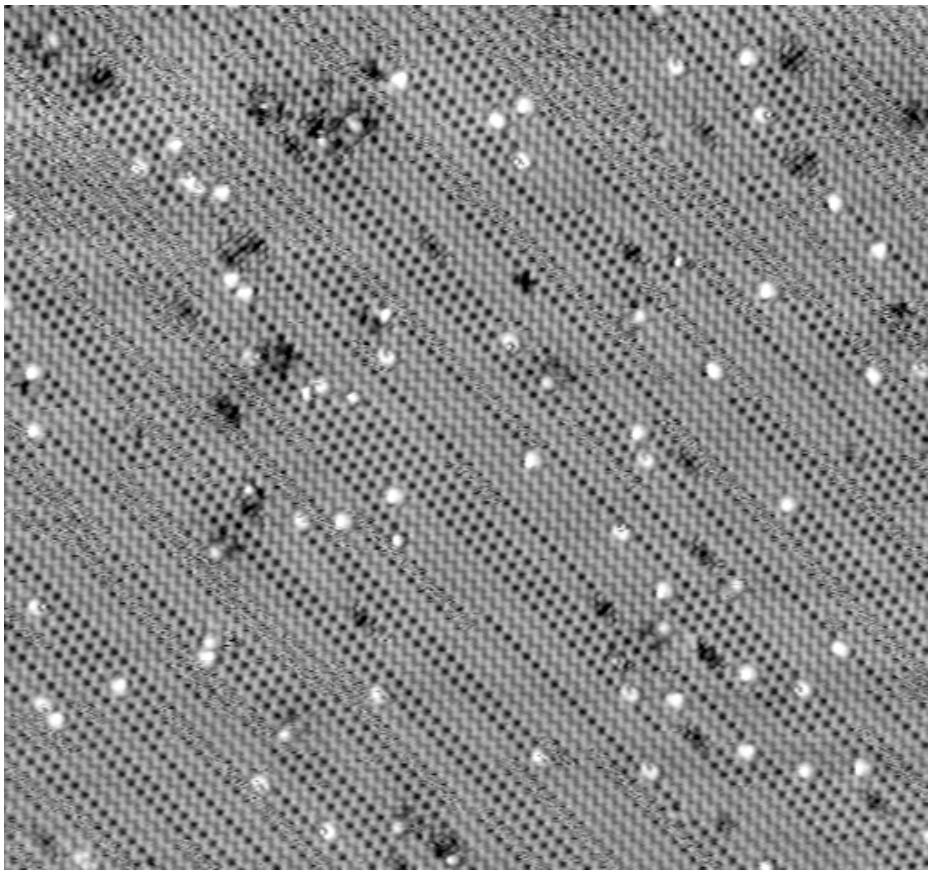


Energy window 2-3eV

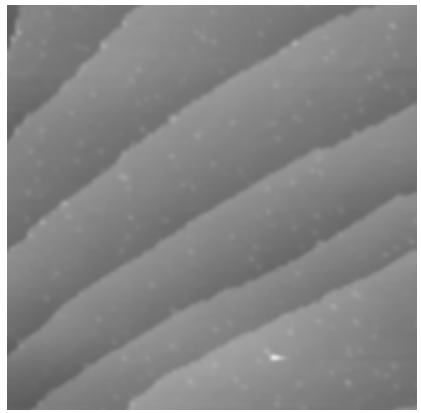


Energy window 3-4.5eV

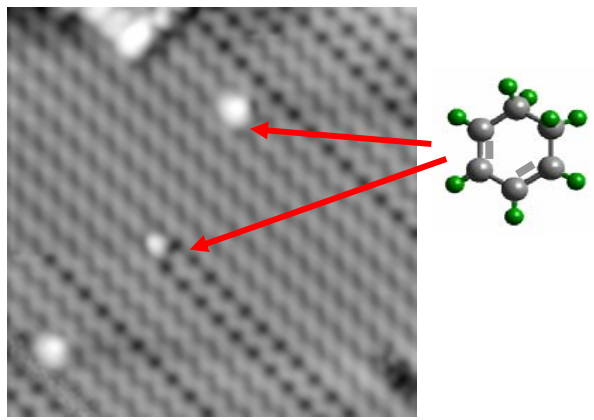
1,3-CHD reacted Si(100) surface at 5 K



50x50 nm 100pA 700mV 5K



Pt(111) 63.5x63.5nm 0.1nA 450mV

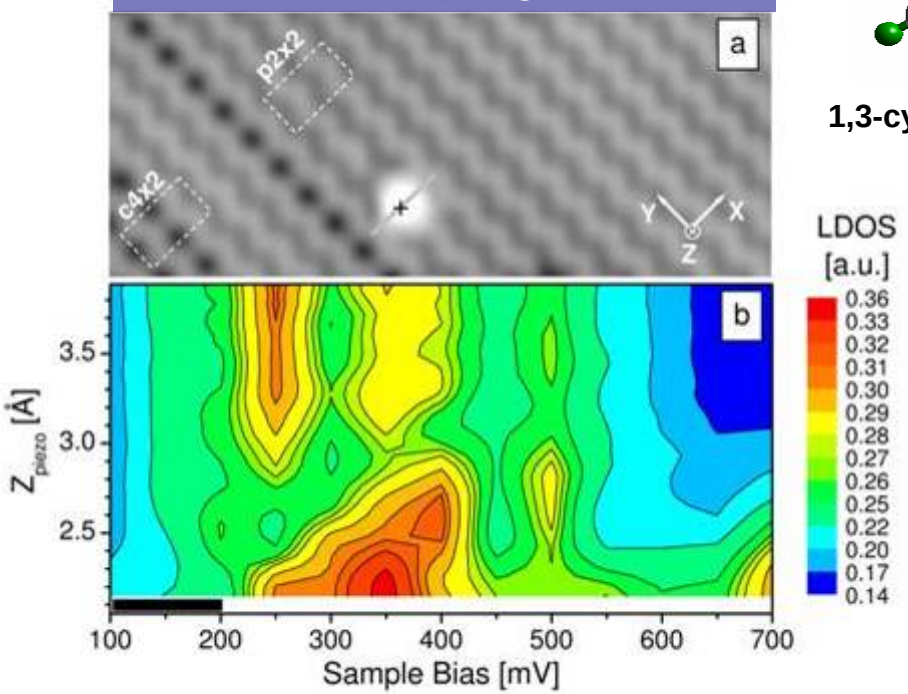


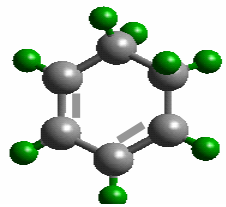
Si(100) 13x12.6nm 0.1nA 700mV

Dimer flipping at 5 K, especially under high bias/current conditions

Contacts: Single Molecule on Si(100)

Electronic density of states



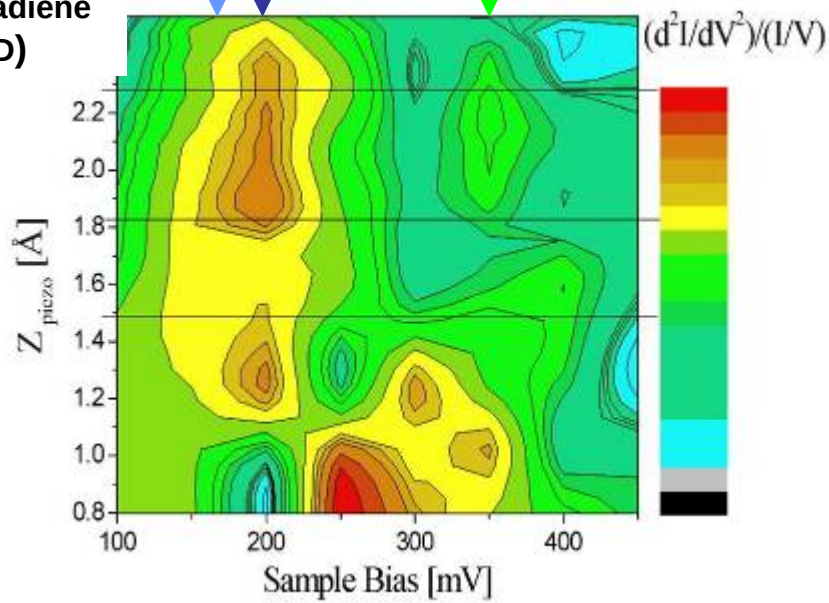


1,3-cyclohexadiene
(1,3-CHD)

C-H bending mode

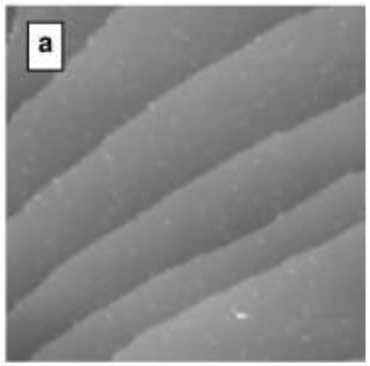
C=C stretch

C-H stretch

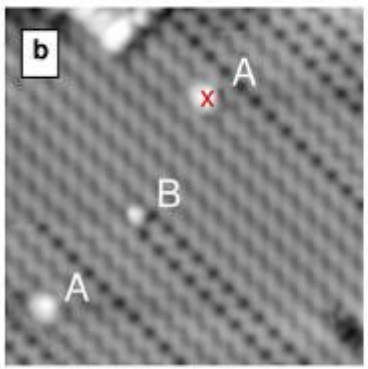


- Large LDOS feature grows in at 350meV (completely reversible) and anticorrelated with disappearance of C=C vibrations
- Bias window 0 – 200meV LDOS independent of separation (basis for subsequent relaxation and force measurements)

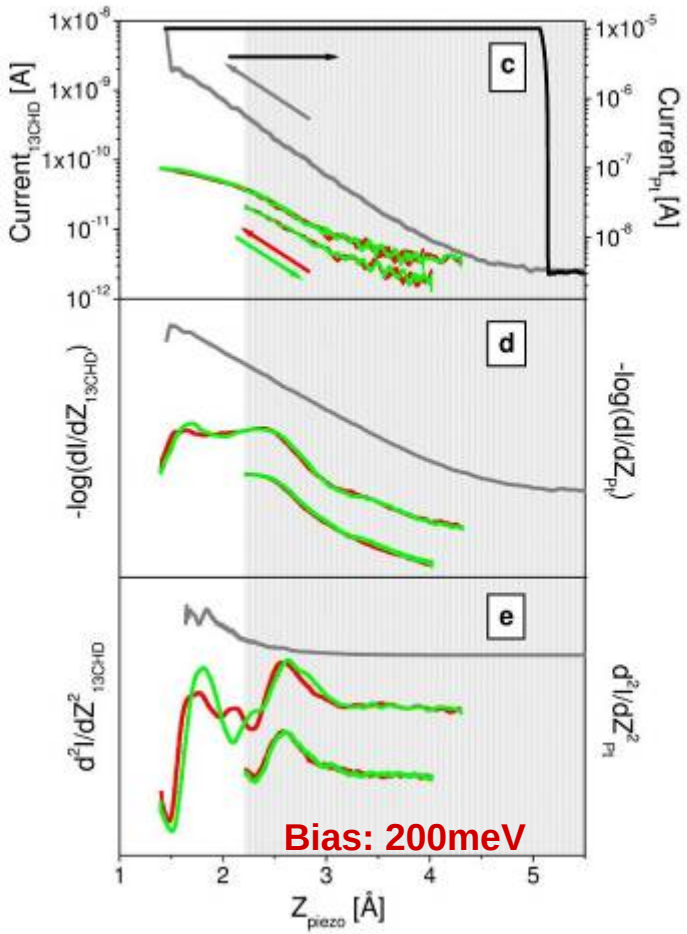
Current during approach to contact



Pt(111) 63.5x63.5nm
0.1nA 450mV



13CHD/Si(100) 13x12.6nm
0.1nA 700mV



Contact with Pt surface

Current well described by:

$$I \propto \exp(-A\sqrt{\phi_A}\, z) \qquad (1)$$

Jump to contact & neck formation

Contact with 1,3-CHD molecule

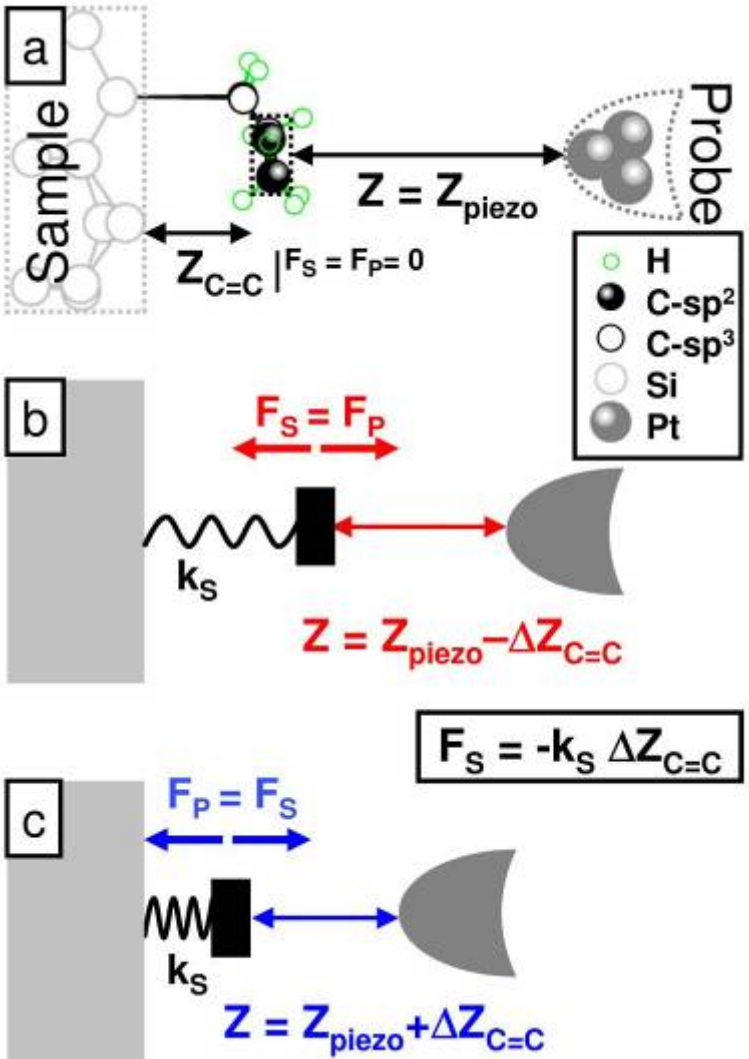
Current not globally described by Eq. (1)

Deviations seen in harmonics

Shaded region: no hystersis

What is the origin of these deviations from Eq. (1) ?

Origin of Relaxation Interaction



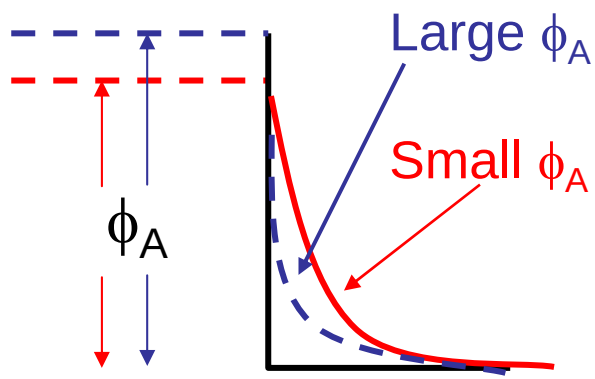
$$\Delta Z_{gap} = -(\Delta Z_{piezo} + \Delta Z_{C=C})$$

$$= -\Delta Z_{piezo} + F_P / k_S$$

$$= -\Delta Z_{piezo} + \alpha F_P$$

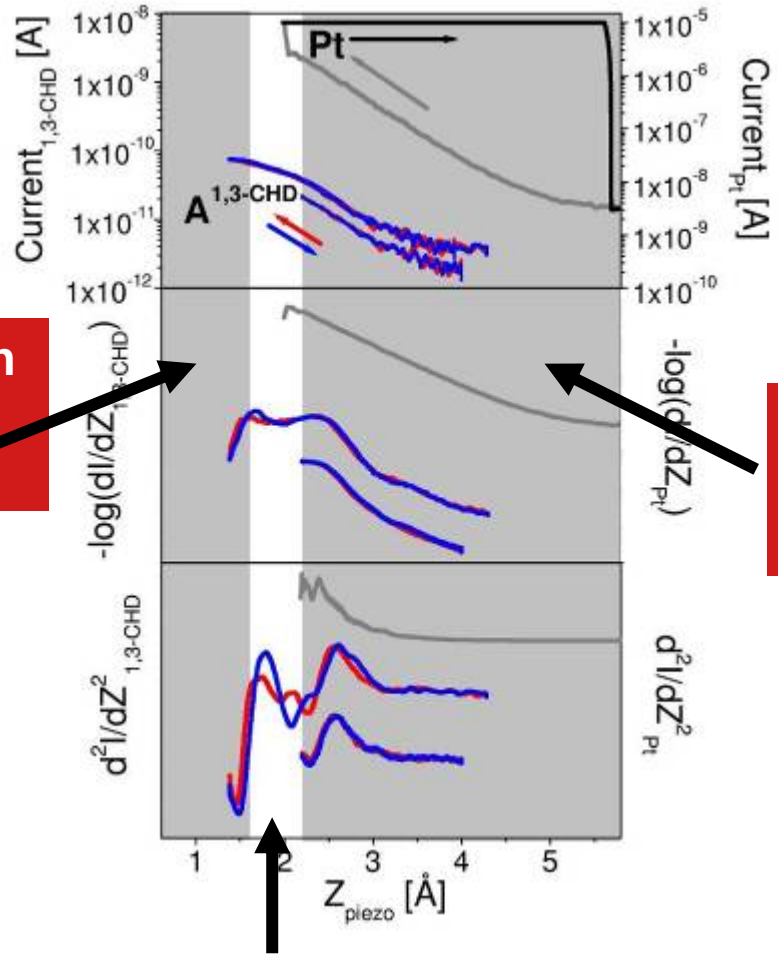
Current increase during approach deviates from $I \propto \exp(-A\sqrt{\phi_A}\, z_{piezo})$

Interpreted locally as a change in the apparent barrier height ϕ_A



Qualitative Analysis of Current Hysteresis

Shaded hysteresis-free regions



Bond compression and relaxation (reversible)

Approach to bond formation (reversible)

Bond-making and breaking region (dissipative)

Quantitative Analysis

$F = 0$

$$I \propto \exp\left(-A\sqrt{\phi}\,Z\right)$$

$$I' = \frac{dI}{dZ} \propto -A\sqrt{\phi}\,I$$

$$I'' = \frac{d^2I}{dZ^2} \propto A^2\phi\,I$$

$$\left(-\frac{I'}{IA}\right)^2 \propto \phi_{A1}$$

$$\frac{I''}{IA^2} \propto \phi_{A2}$$

$$\left(-\frac{I''}{I'A}\right)^2 \propto \phi_{A3}$$

Nominally identical

$F \neq 0$

$$I \propto \exp\left[-A\sqrt{\phi}\left(Z_{piezo} + Z_0 + \alpha F\right)\right]$$

$$I' \propto -A\sqrt{\phi}\left(1+\alpha F'\right)I$$

$$I'' \propto \left[A^2\phi\left(1+\alpha F'\right) - A\sqrt{\phi}\,\alpha F''\right]I$$

$$\left(-\frac{I'}{IA}\right)^2 \propto \phi\left(1+\alpha F'\right)^2$$

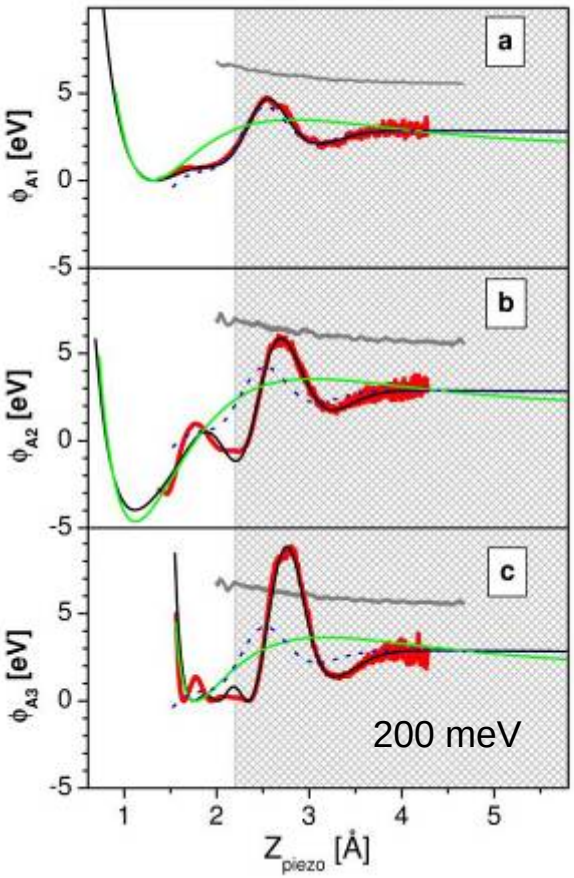
$$\frac{I''}{IA^2} \propto \phi\left(1+\alpha F'\right)^2 - \frac{\sqrt{\phi}}{A}\alpha F''$$

$$\left(-\frac{I''}{I'A}\right)^2 \propto \left[\sqrt{\phi}\left(1+\alpha F'\right) - \frac{\alpha F''}{A\left(1+\alpha F'\right)}\right]^2$$

Forces present: harmonics dI/dZ and d^2I/dZ^2 are related to the local force gradient

Quantitative Analysis: Interaction Potentials

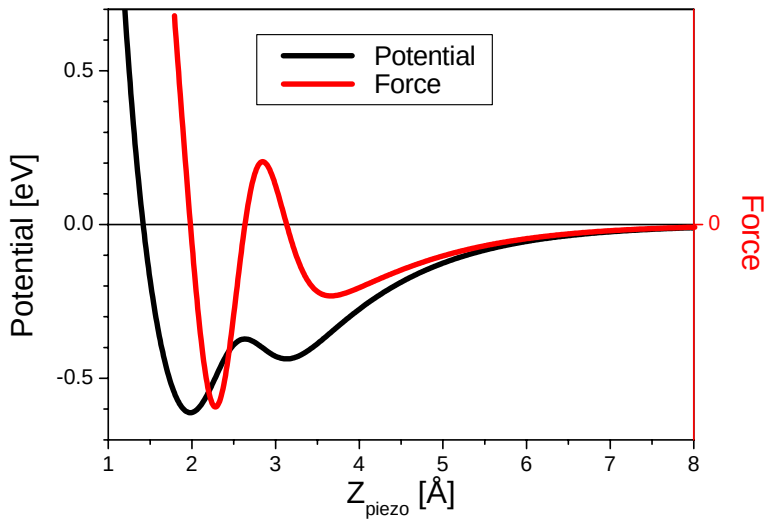
Invert current and barrier height data to determine forces & potentials



Morse potential

Morse + Gaussian barrier

Force gradient



Description of the ϕ data requires a barrier term

Questions:

1. Is the well depth meaningful?
2. What is the origin of this barrier?

} **Use DFT**

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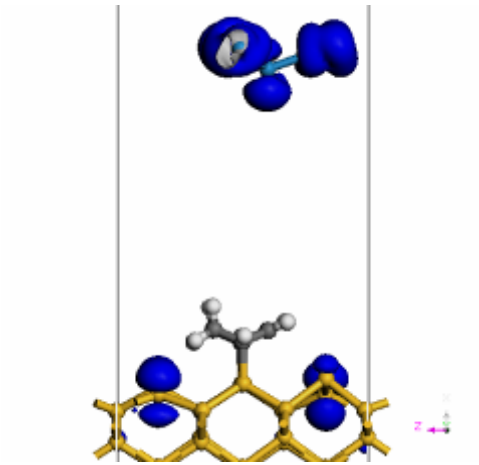
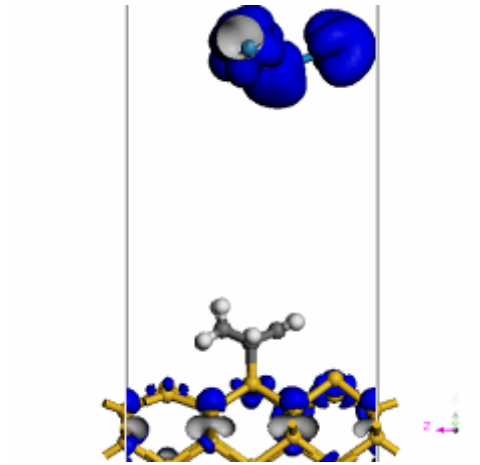
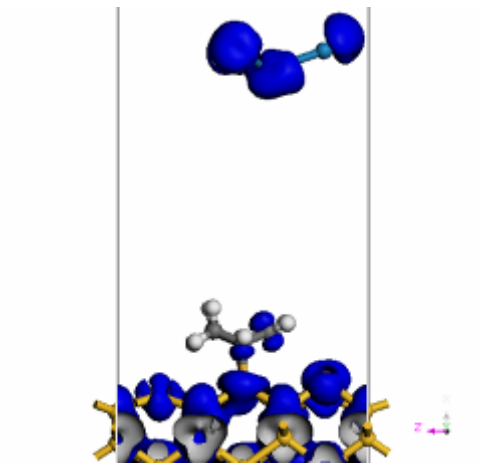
Emergence of LDOS feature



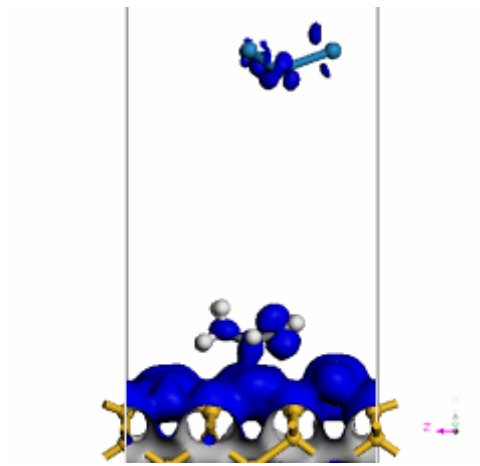
Energy window 0-1ev



Energy window 1-2ev

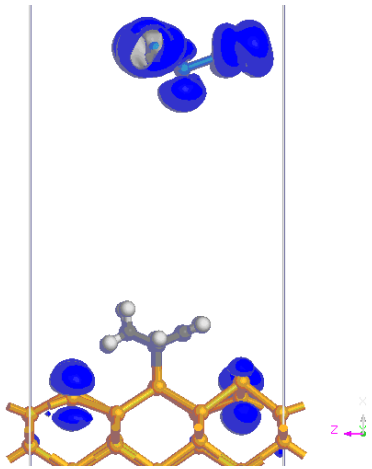


Energy window 2-3ev

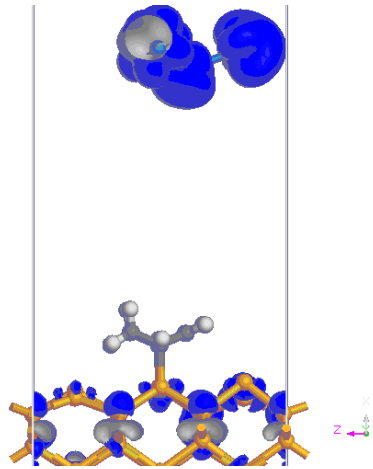


Energy window 3-4ev

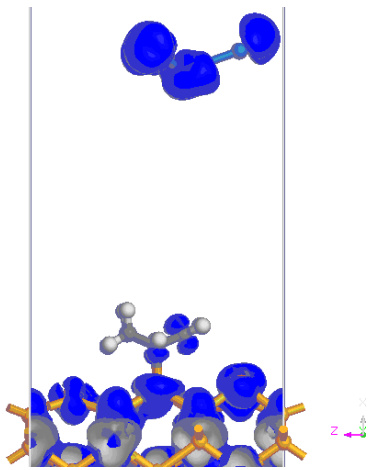
DOS in the presence of the probe tip



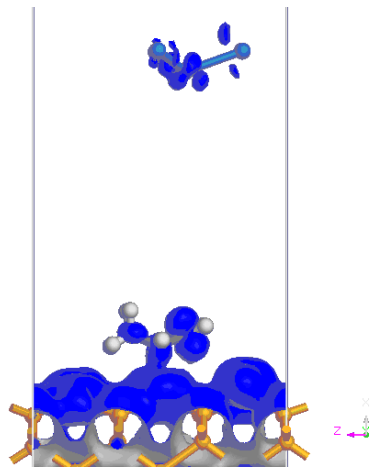
Energy window 0-1ev



Energy window 1-2ev



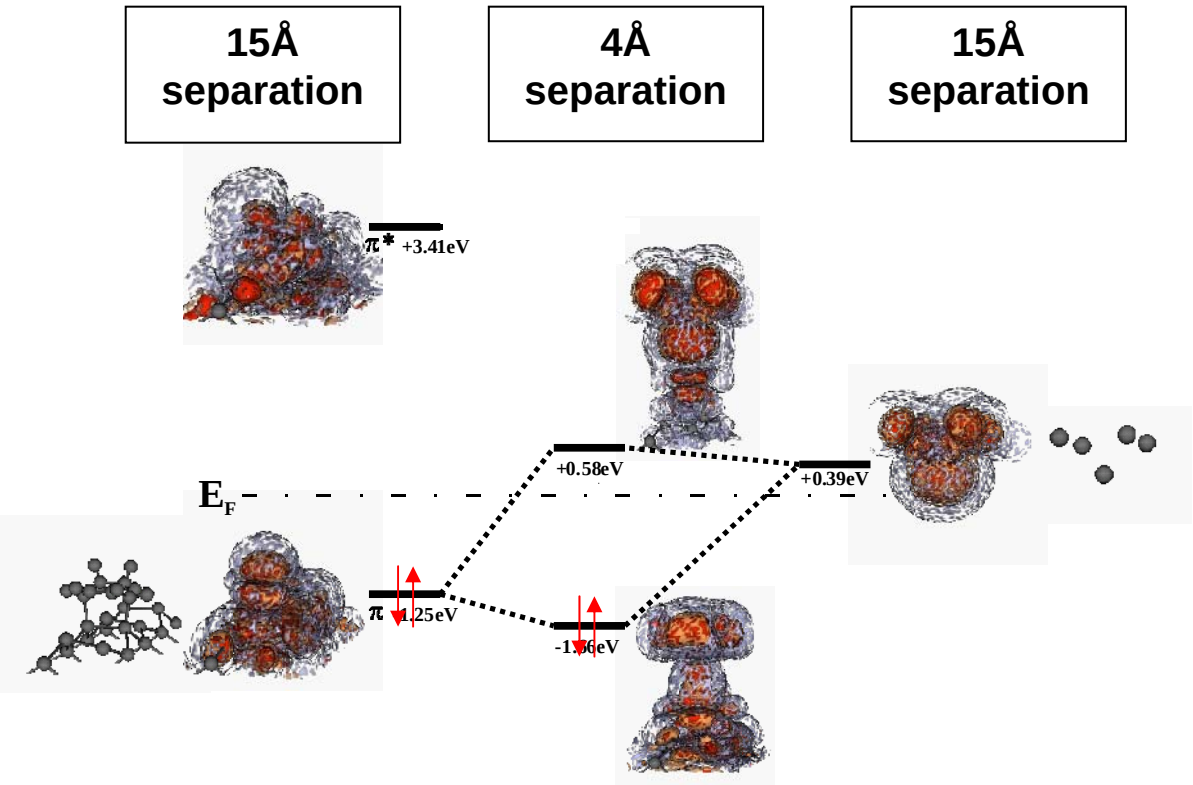
Energy window 2-3ev

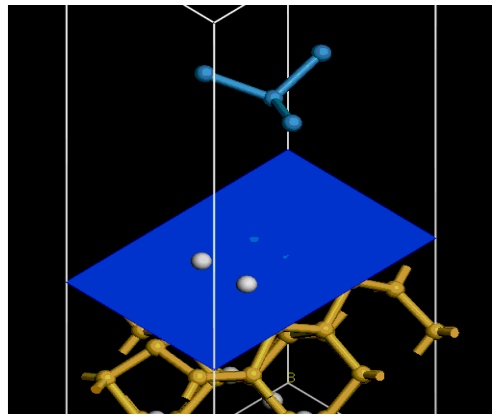


Energy window 3-4ev

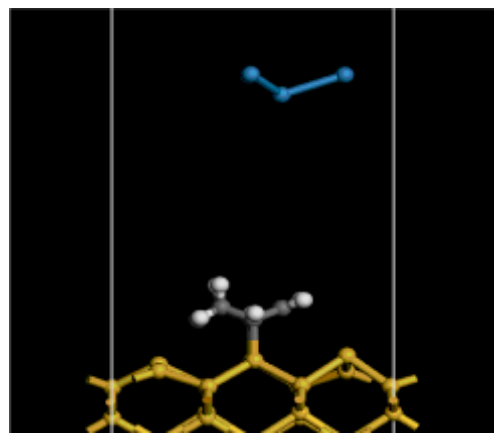
Interaction of probe with C=C bond upon contact yields interface state in 0 – 1eV

Origin of Interface State





∫ LDOS (0-1.5 eV) ~ STM image



Tip above C=C

Bonding interaction associated with pπ→dπ charge transfer from C=C to Pt apex atom

Molecule conductance dominated by interface state which is responsible for STM image

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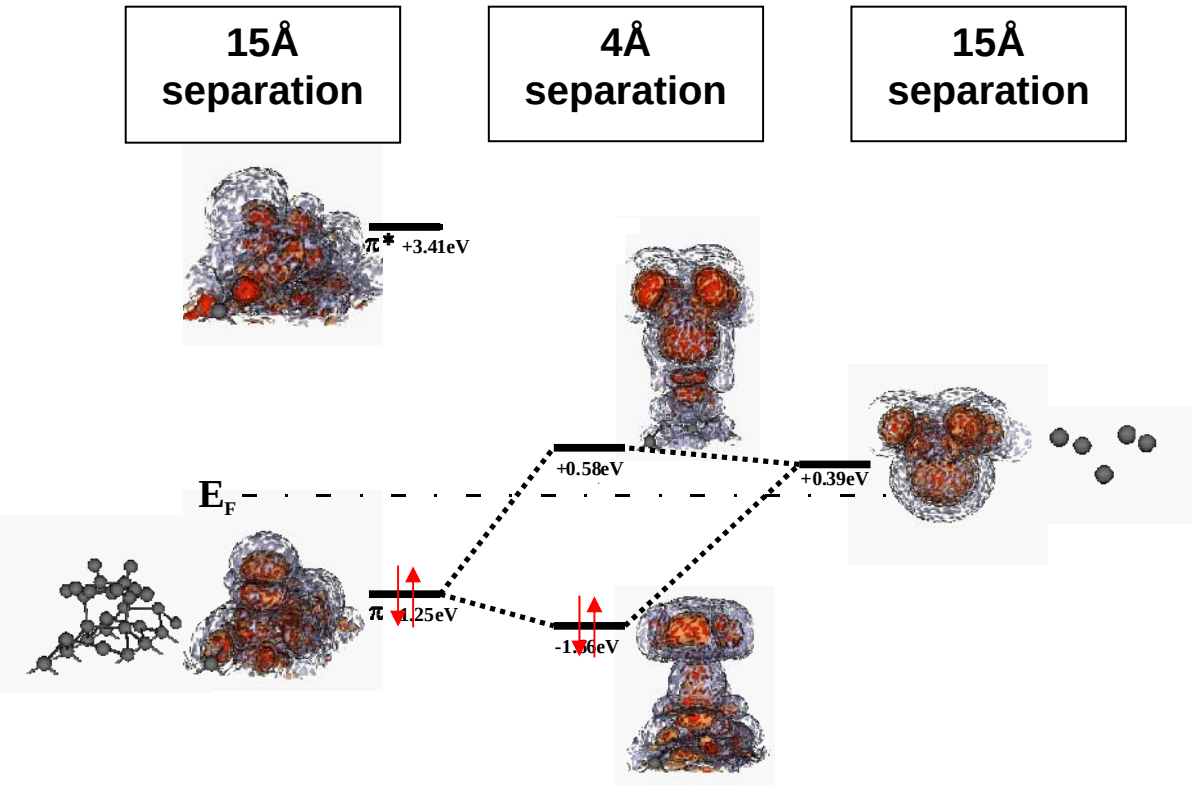
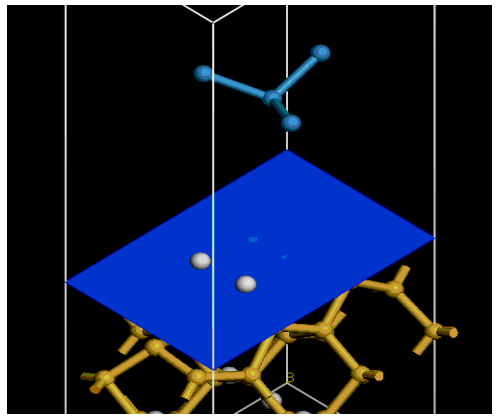
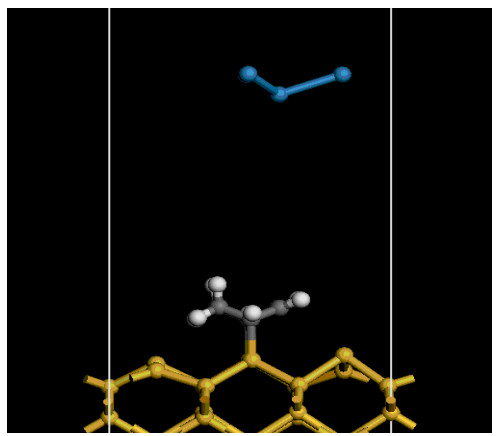
Origin of Interface State





Tip approach: Interface state



Deformation of molecule

DFT also observes barrier - due to deformation and rehybridisation of the molecule C=C bond

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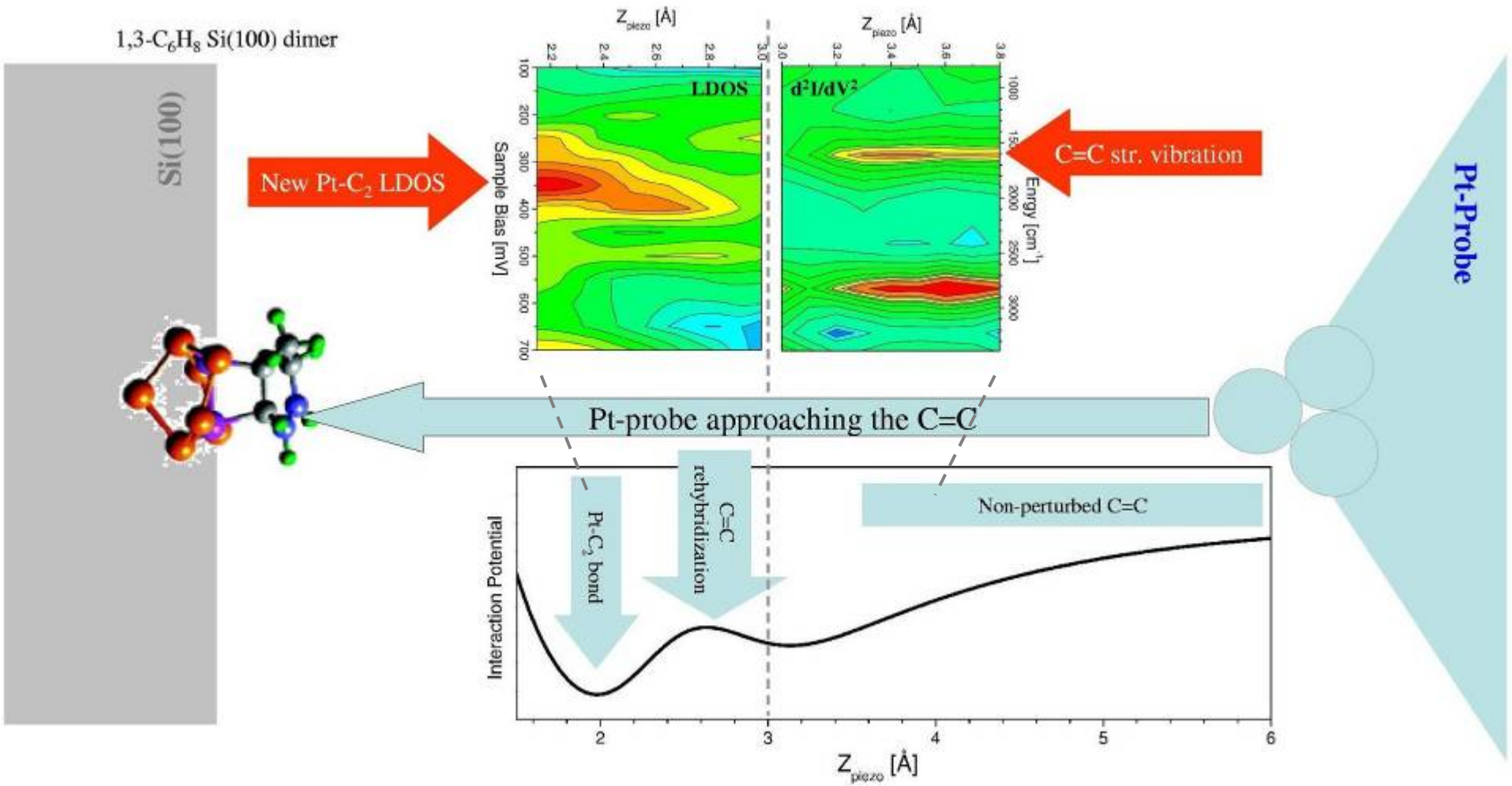
Comprehensive picture of contact bond formation



Track dynamics of contact formation Precise overlay of potential, electronic and vibrational properties

***NANO LETTERS* 6(9) 2006**; ***PRL* 97, 098304, 2006.**

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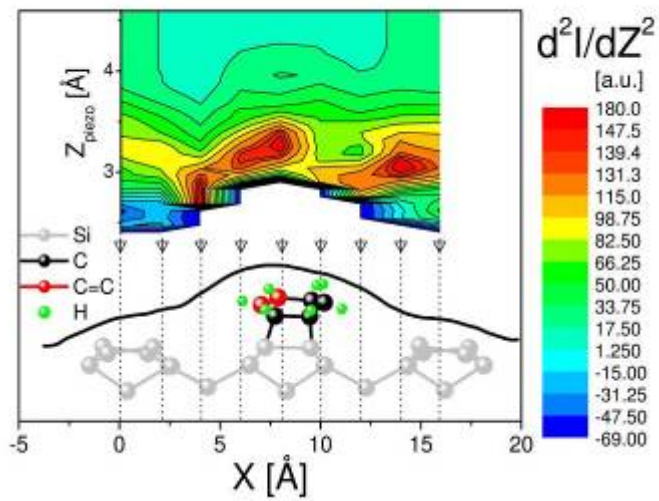
Conclusions: Molecular Contacts

- Three types of current-approach curves
  - Smooth exponential increase (tunnelling)
  - Sharps jumps (local atomic motion)
  - Slow, reproducible change in slope (relaxation forces)



Relaxation map of single 1,3 CHD

- Interface states may provide route to tailor molecule transport properties
- Track actual formation of contacts (chemical bond formation, evolution of vibrations, actual measure of potential)
- Widely applicable; catalysts and studies of general reaction dynamics

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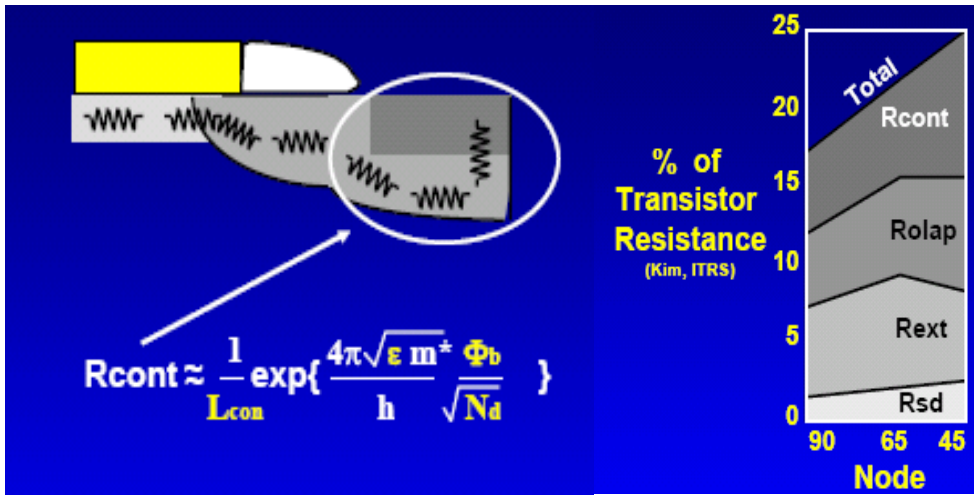
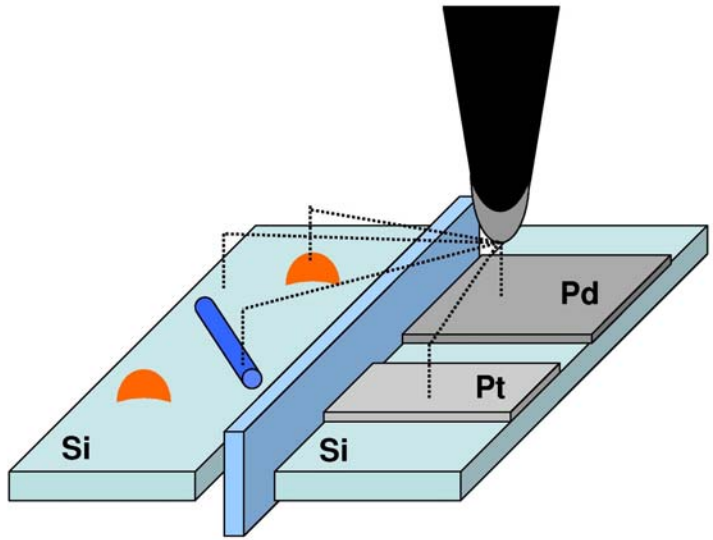
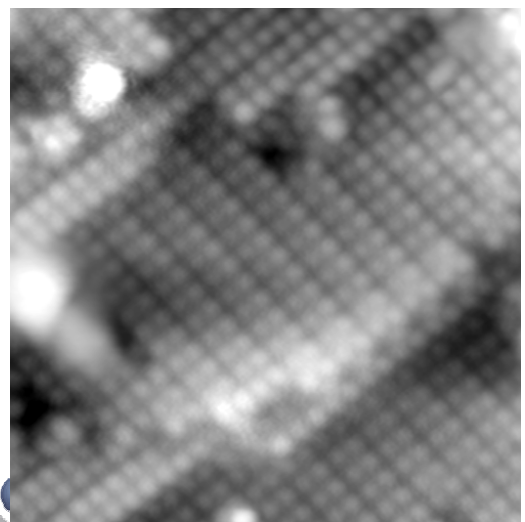
Example B: Nanoscale contact with Si(100):H





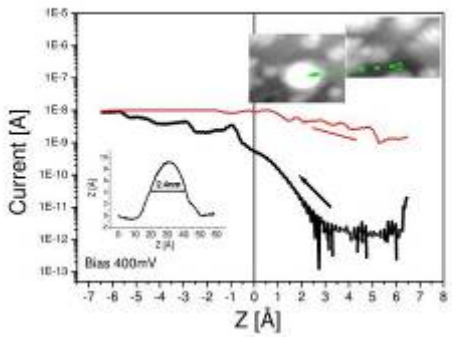


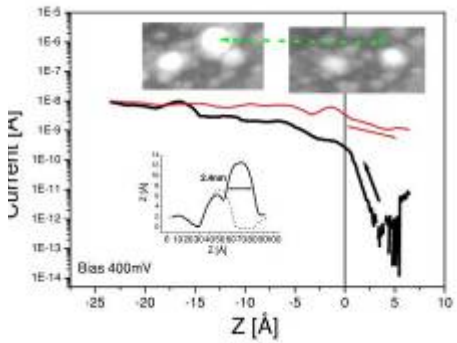
Si(100):H passivated

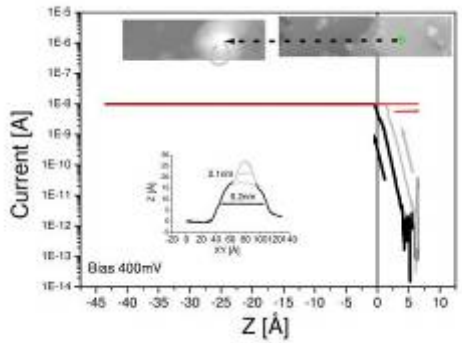
Specific Problem: contact resistance between contact metal and n+ region at source and drain limiting device performance

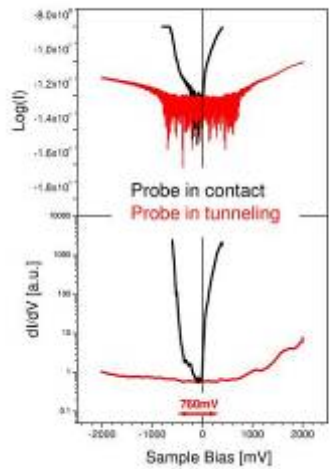
Approach: study of controlled contact formation at 5K. Measure local forces, electronic density of states and vibrations simultaneously

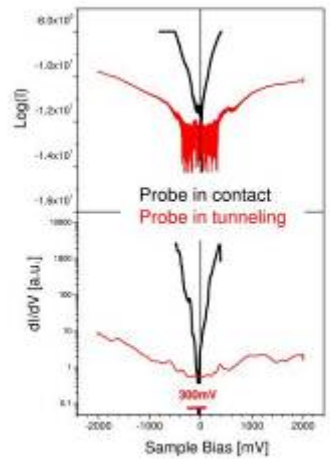
Pd Nanocontacts on n+ Si(100):H

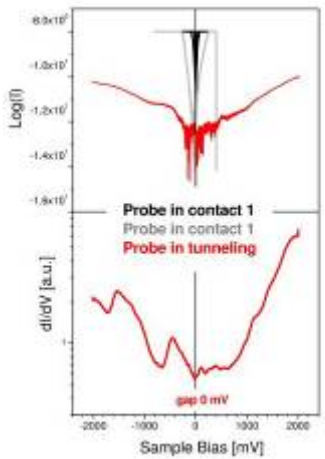




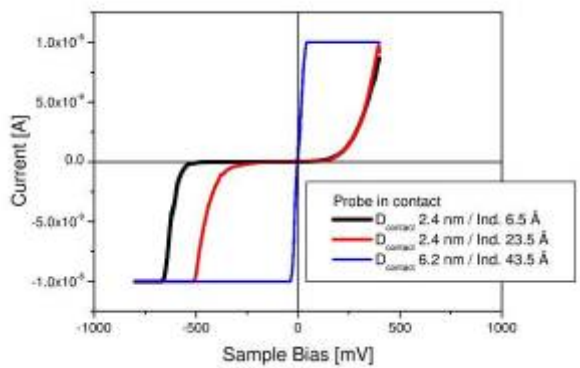








Ohmic behaviour observed even with tunnelling contact – not an E-field point contact effect



Control of the electrical contact

$D_{contact}$ from 2 to 7 nm shift from non-ohmic to ohmic behaviour

No evidence for Schottky barrier

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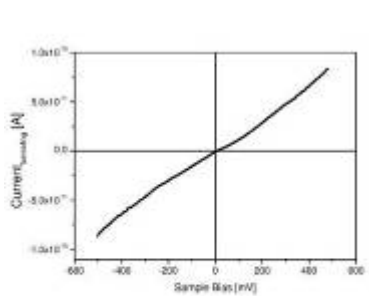
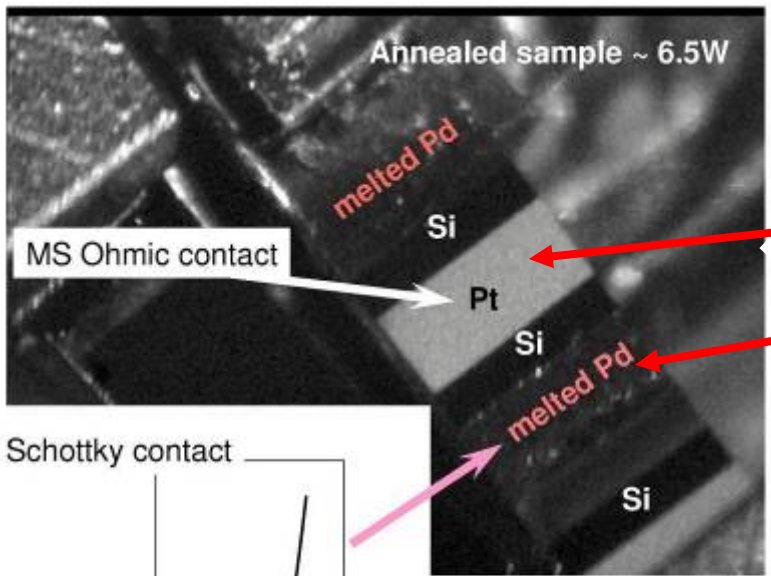
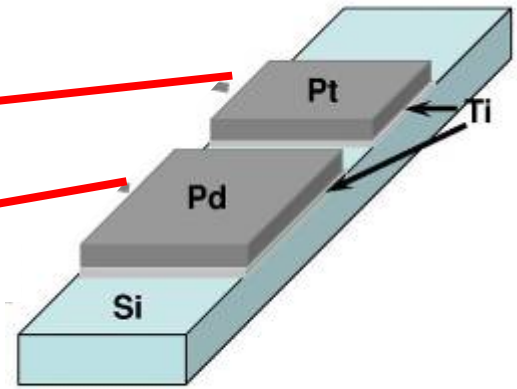
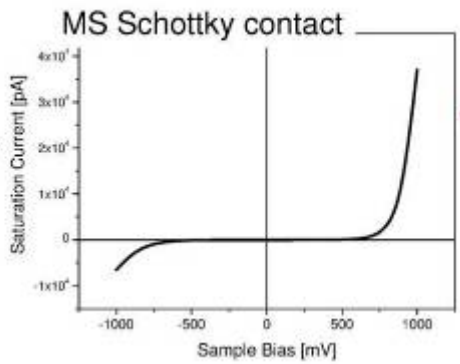
Macroscopic Pd:Si(100) Contacts



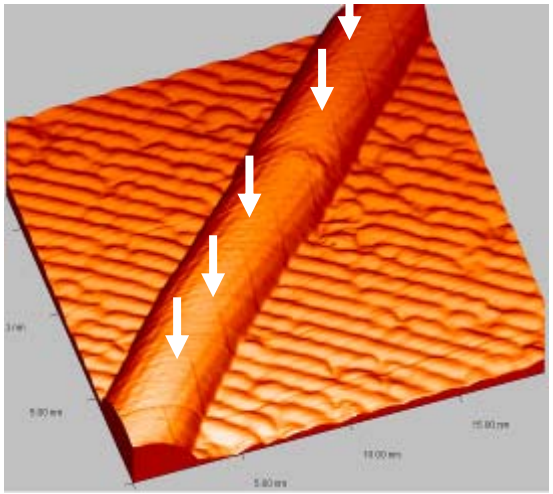


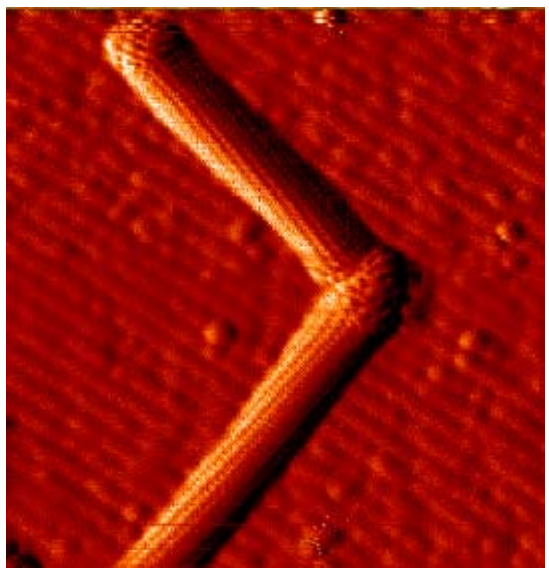


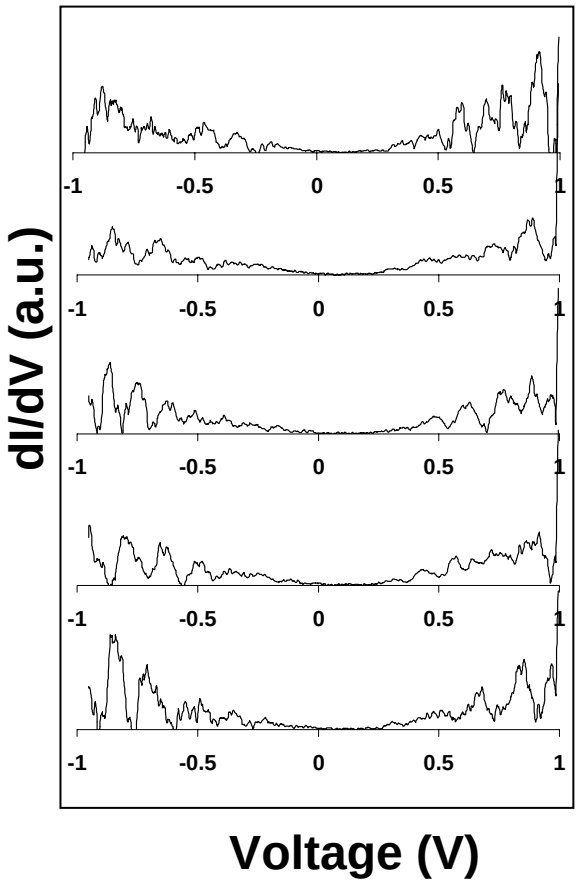
Pd melting



Measurements on Carbon Nanotubes







Well defined van Hove singularities
RT study – peak broadening
No contact studies at 5 K yet

Address issue of Pd vs Pt contacts etc

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