Electron Transport in Strongly Coupled Molecular Electronic Junctions

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NRC·CNRC
ALBERTA INGENUITY FUND
UNIVERSITY OF ALBERTA
NSERC CRSNG
Canada Foundation for Innovation

National Institute for Nanotechnology
University of Alberta, Edmonton, Alberta, Canada

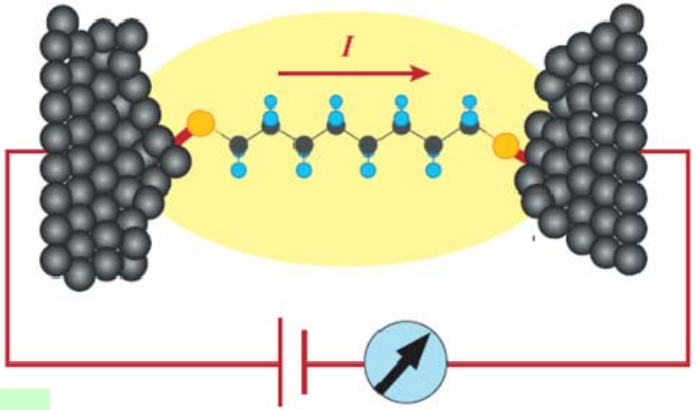
Founded 2002
Building dedicated 2006

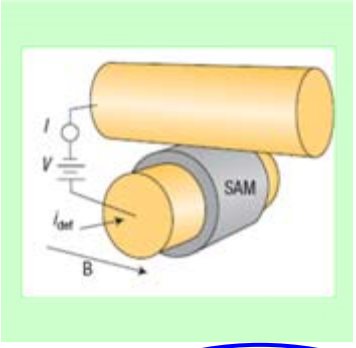
$$$:

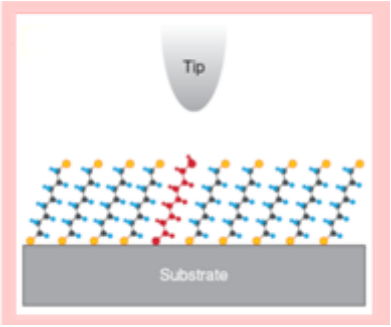
National Research Council
NSERC (Canada)
Alberta Ingenuity Fund
Canada Fund for Innovation

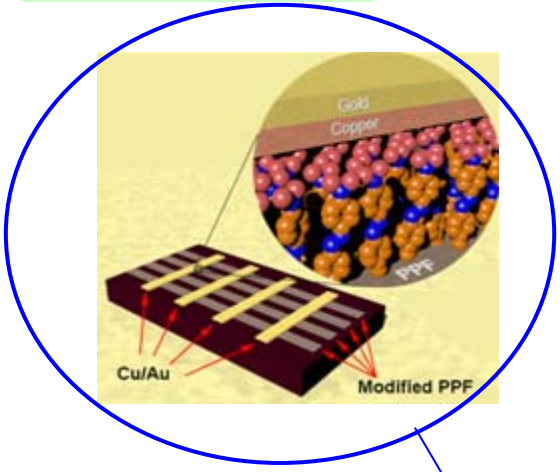
“Molecular electronics”

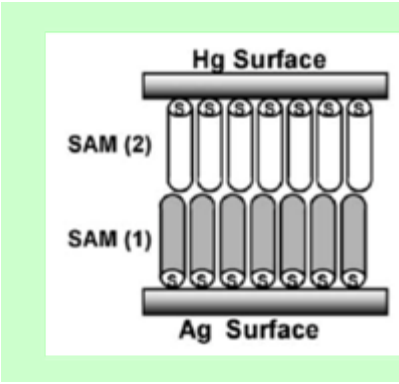
“molecular junctions:”









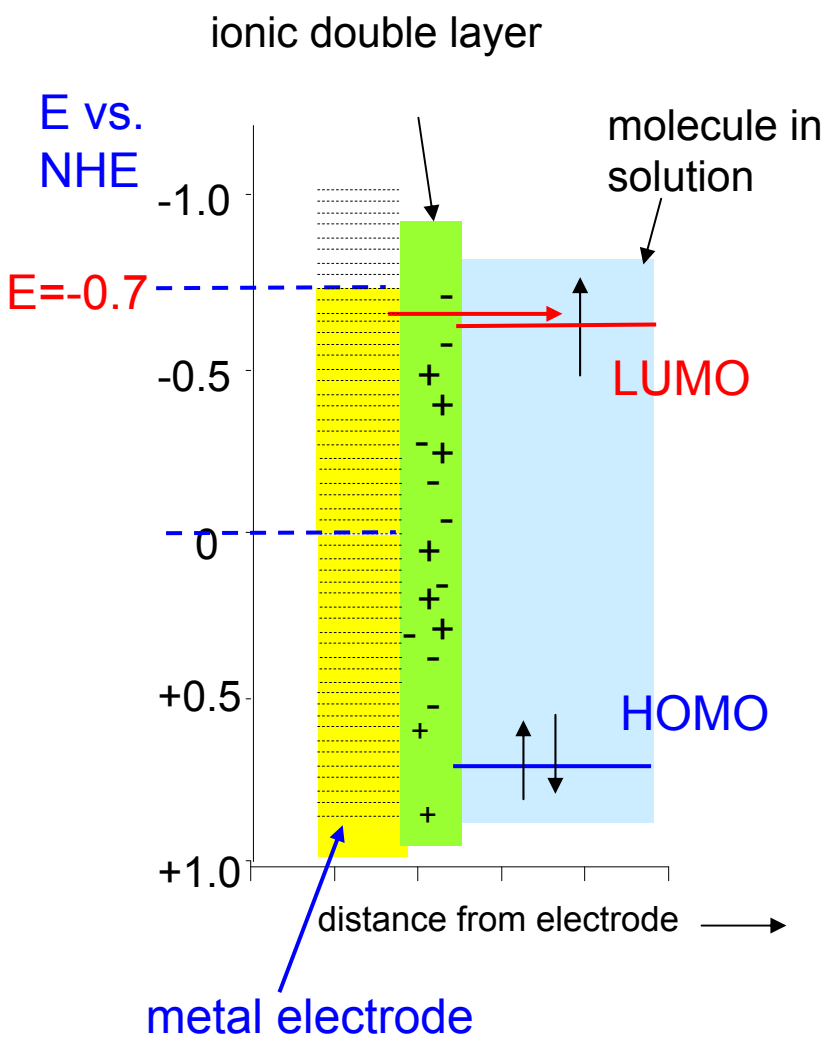


Note:

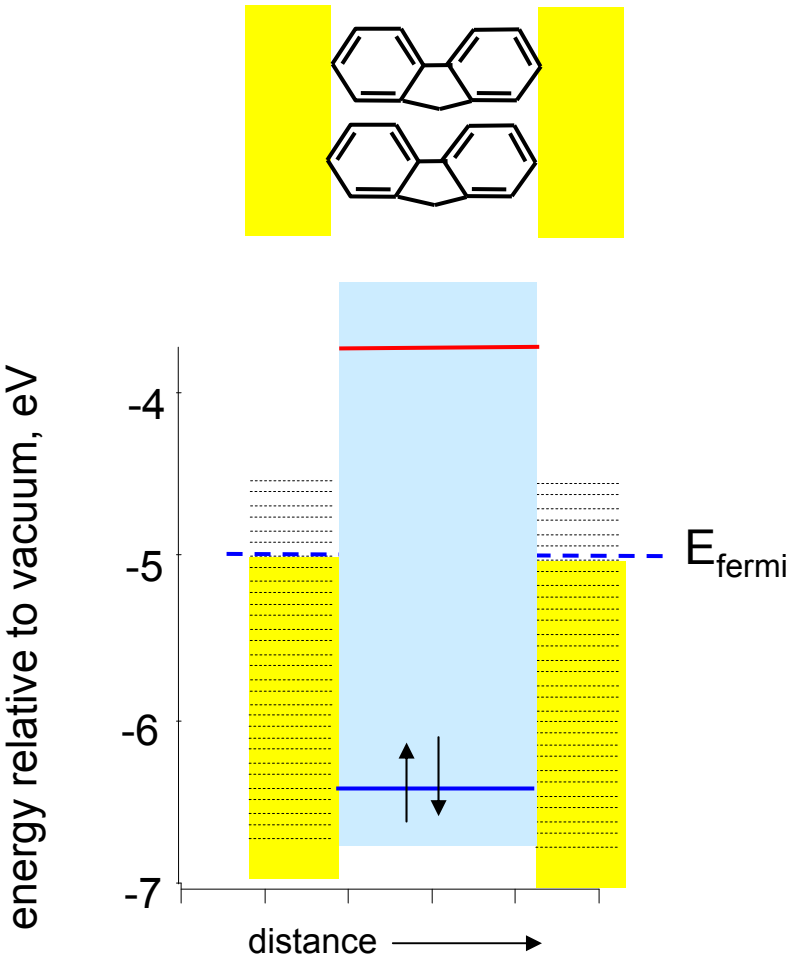
- molecules become circuit elements
- critical dimension is 1-10 nm

Today’s question: How are electrons transported through molecules ??

Electrochemical reduction:



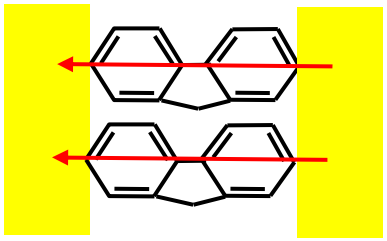
Molecular junction:

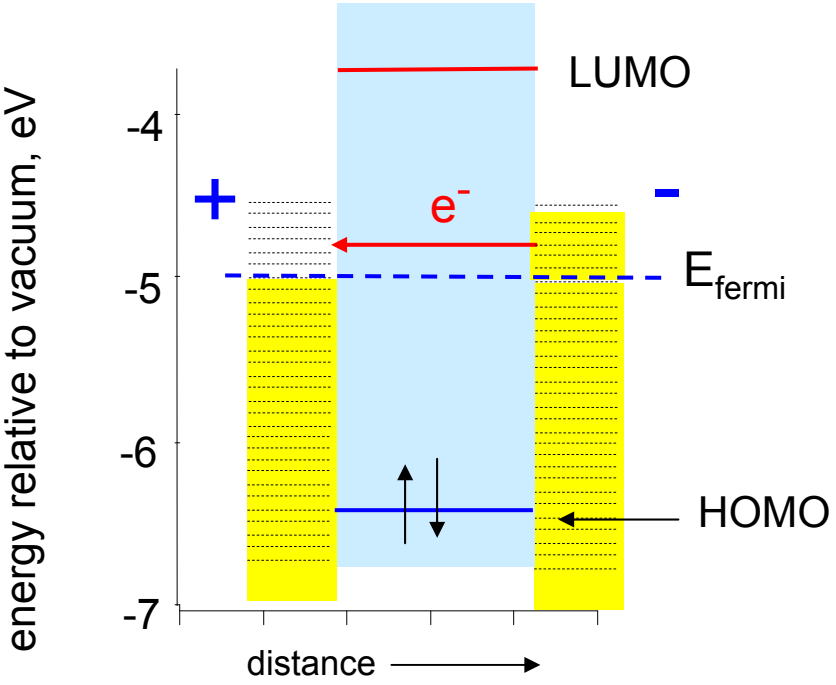


two electrodes, no double layer, no solution

Two common electron transport models:

"off-resonant"

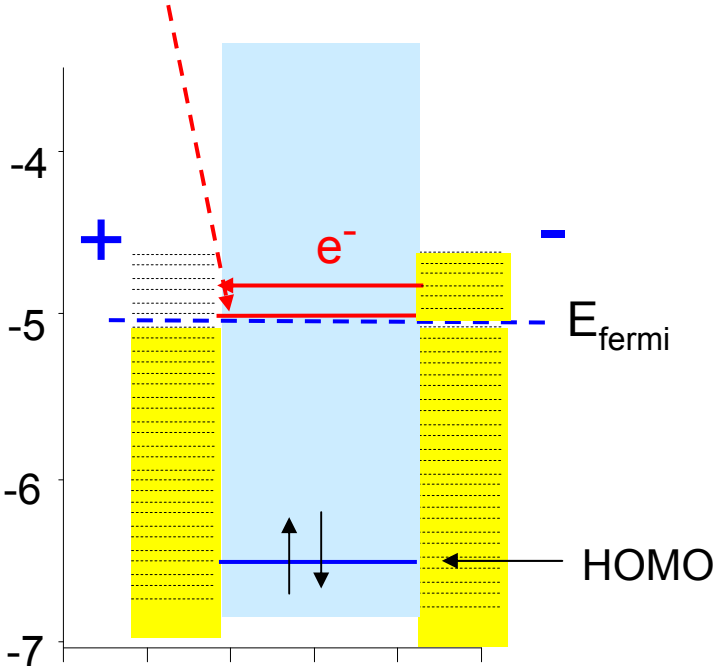




e.g. tunneling, Schottky, field emission

"resonant"

LUMO is close (~within kT) to Fermi level



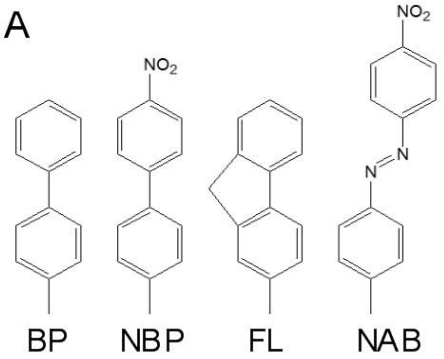
e.g. "resonant tunneling", "orbital mediated tunneling"

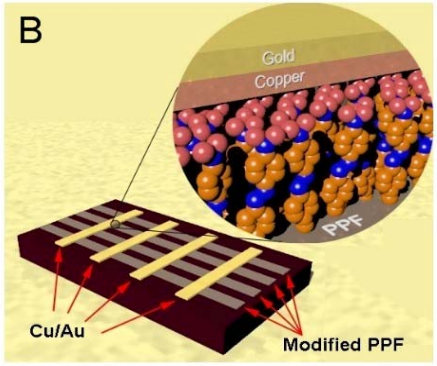
The scientific question:

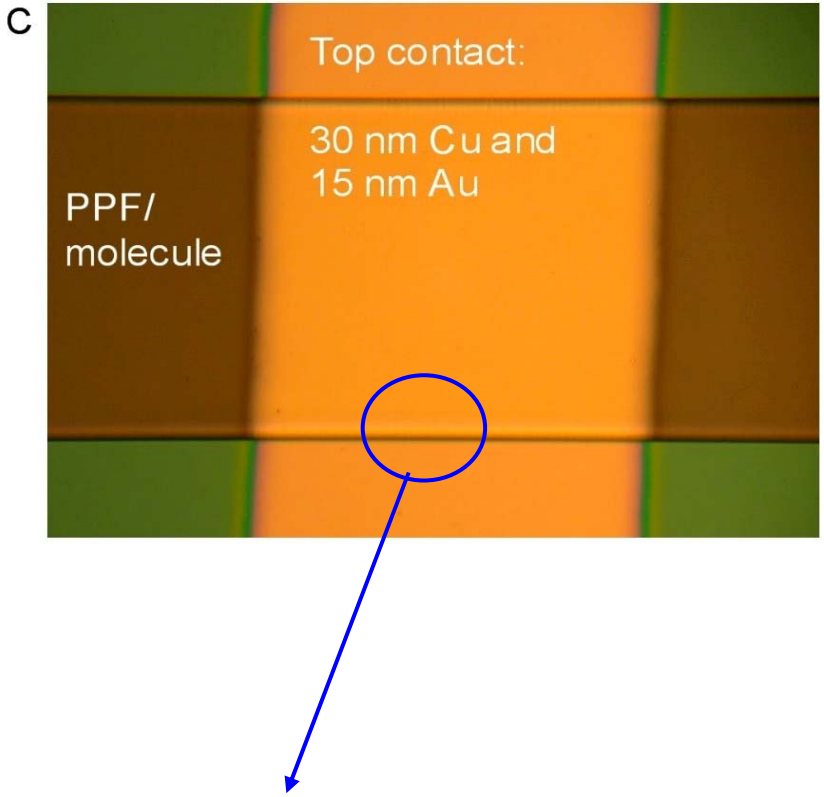
How are electrons transported through 1-5 nm thick molecular layers?

Outline:

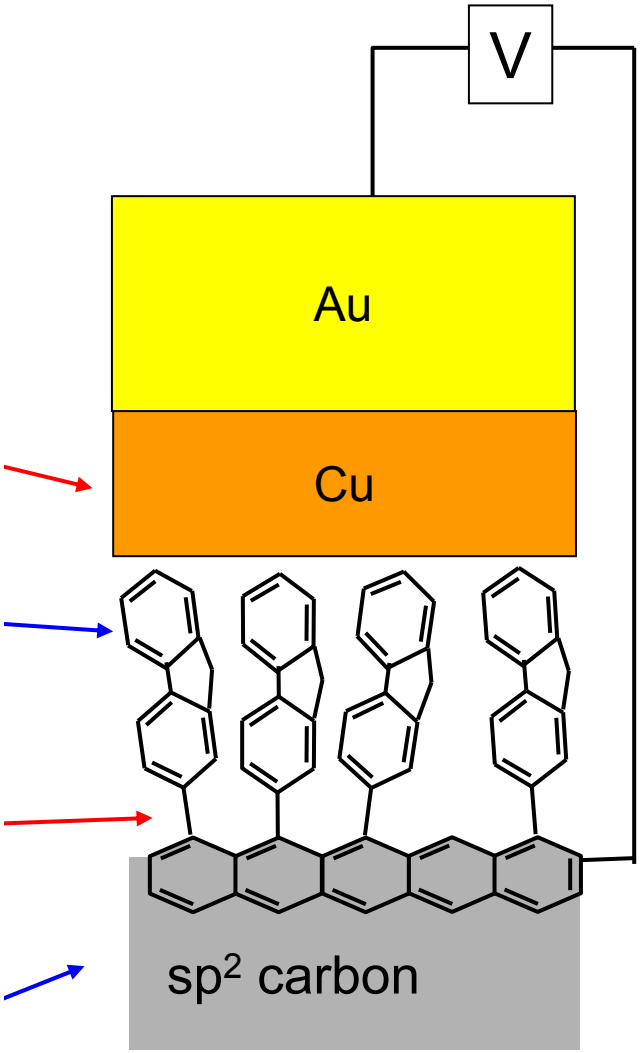
- fabrication of molecular junctions
- characterization
- electronic properties
- transport mechanism







next slide

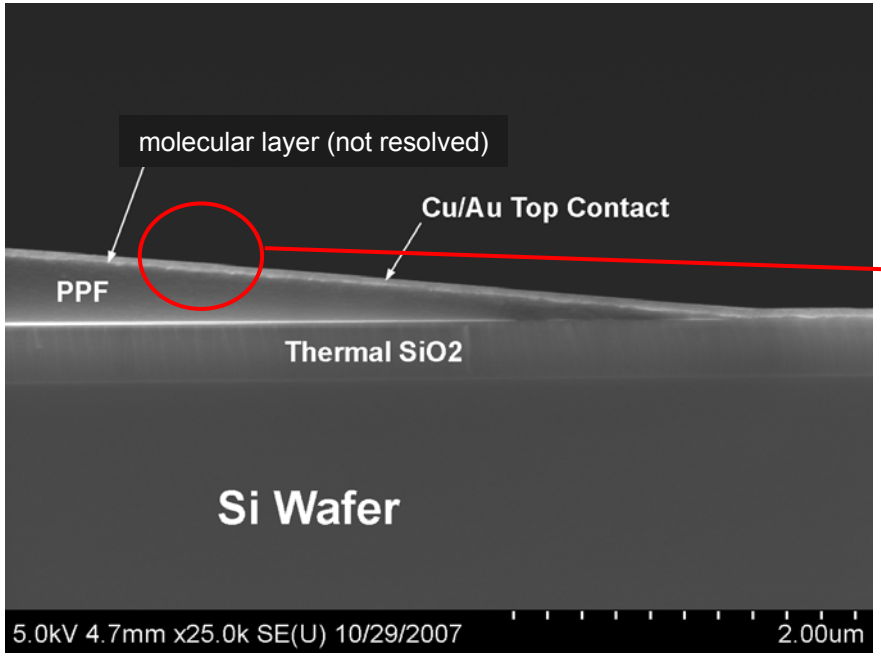


Phys. Chem. Chem. Phys, ***2006***, *8*, 2572
J. Chem. Phys. ***2007***, 126, 024704

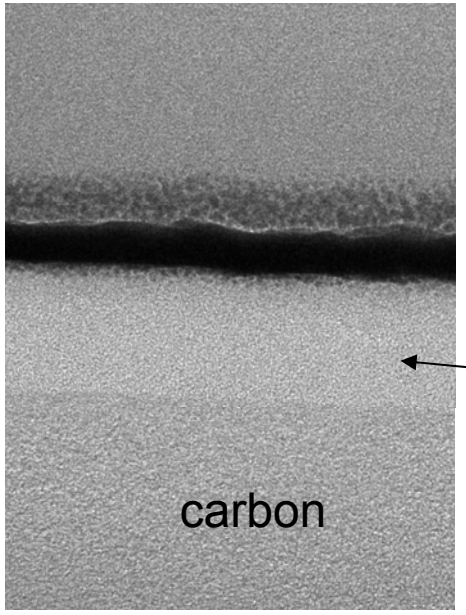
J. Phys. Cond. Matter, 20, 374117 (2008)

SEM

TEM



1 µm



EM mount

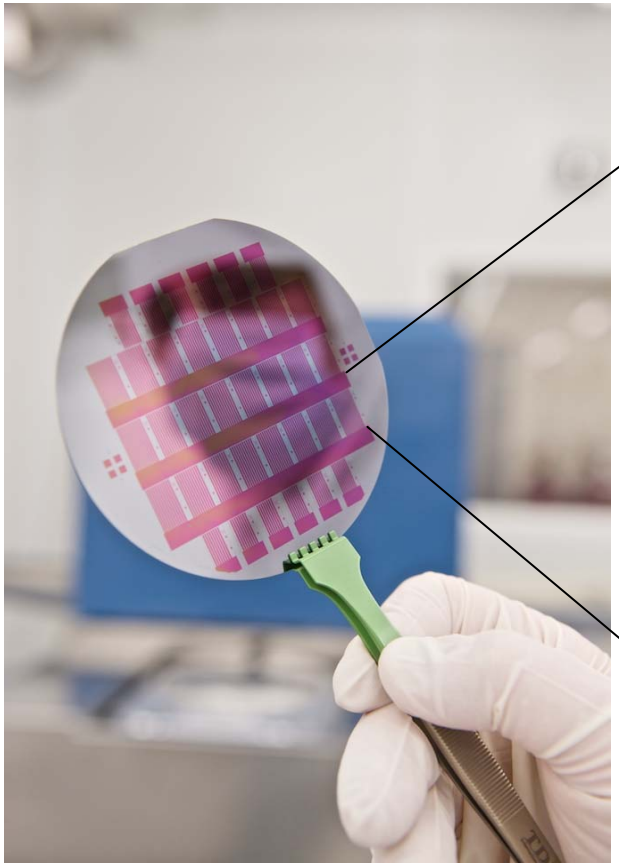
metal

polypyrrole

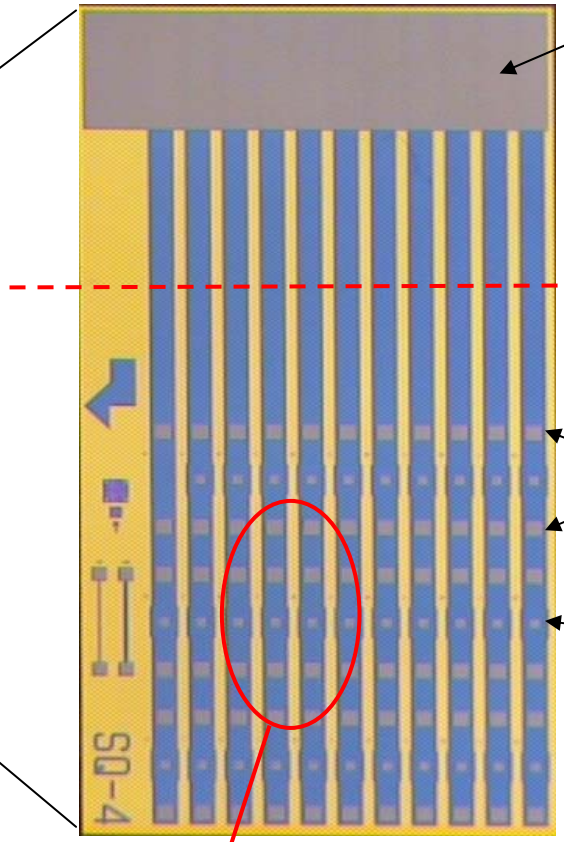
20 nm

Microfabricated “E-chips”

PPF Echip 4’’ wafer



PPF Echip



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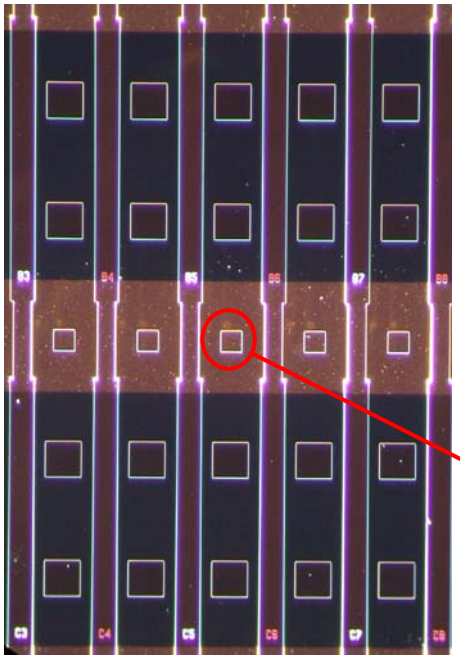
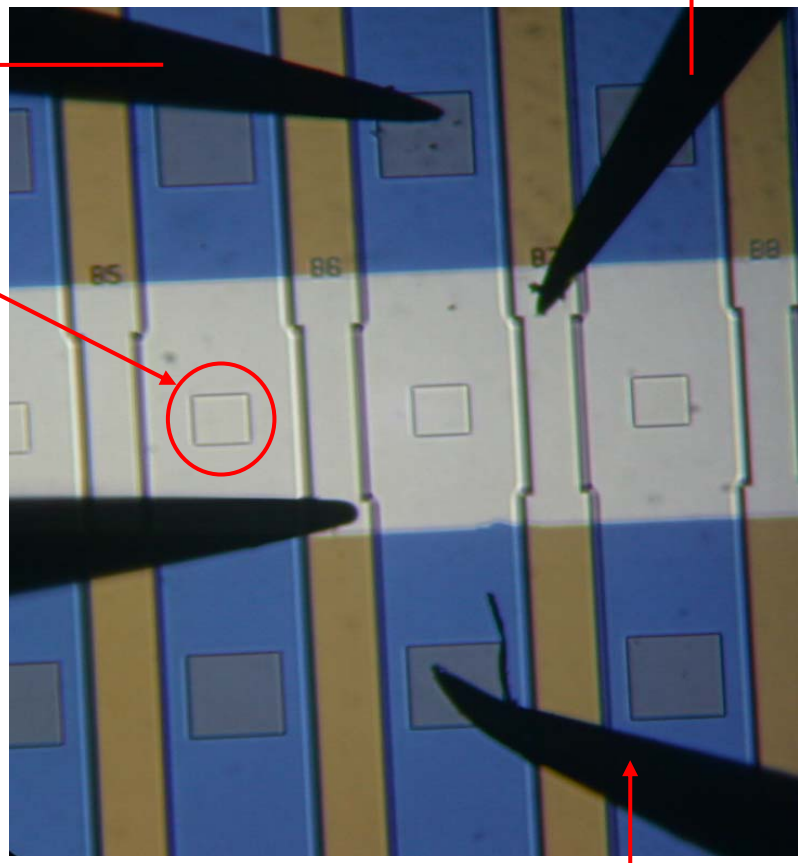
Jie Ru



500 µm

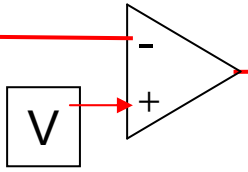
current amplifier



Junction area:

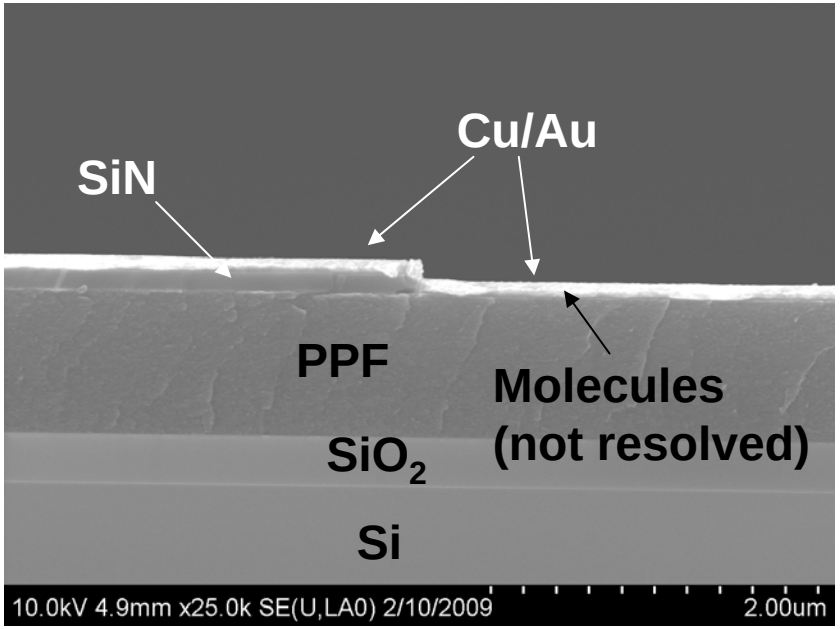
2.5 x 2.5 µm to
400 x 400 µm

V_{sense}

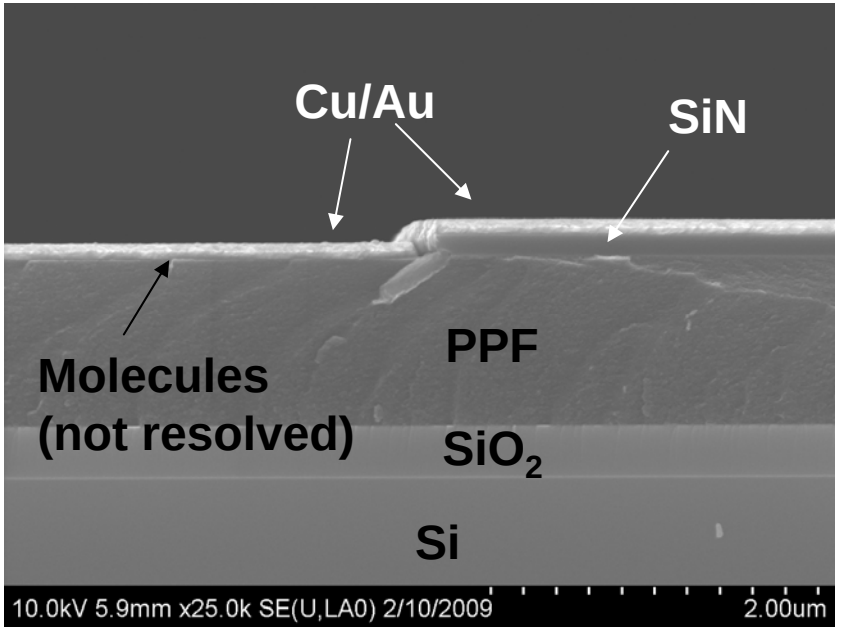


Cross section of a PPF/NAB/Cu/Au junction (SEM)

Left side

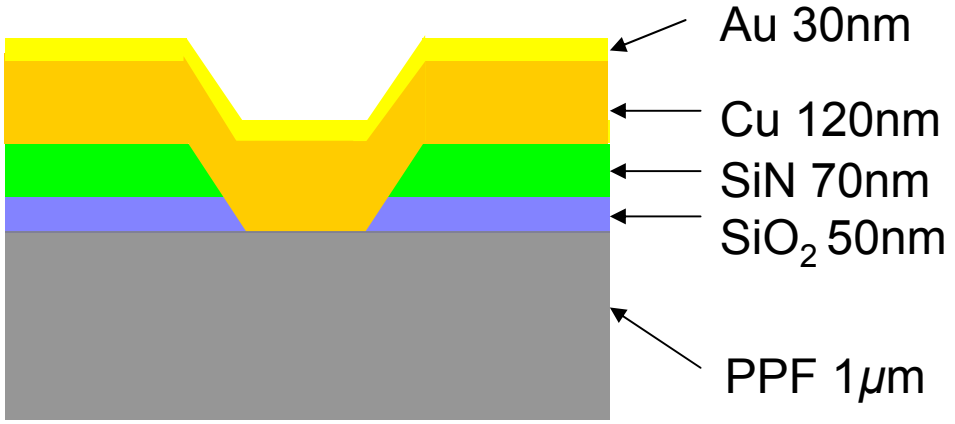


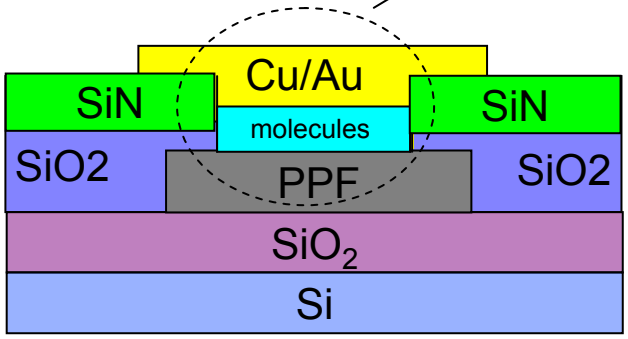
Right side



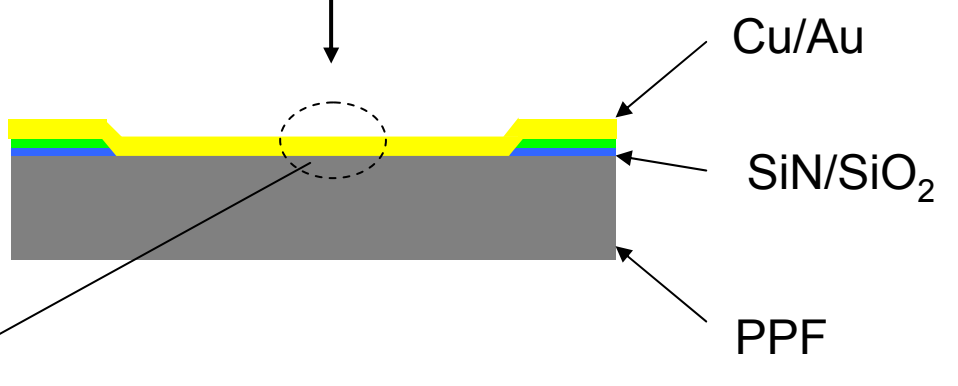
Schematic of junction structure:

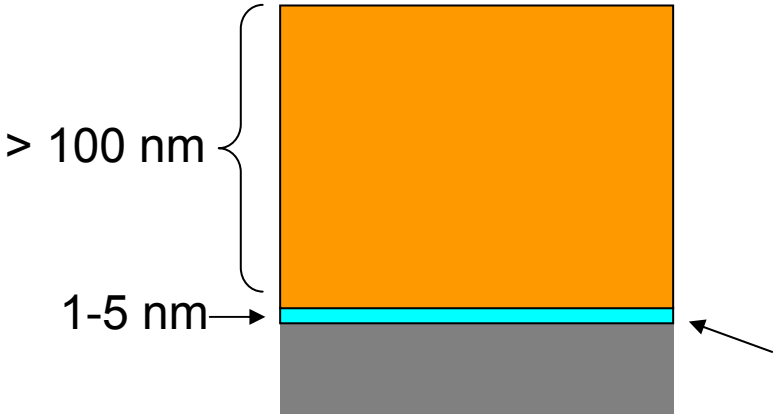
(not to scale)





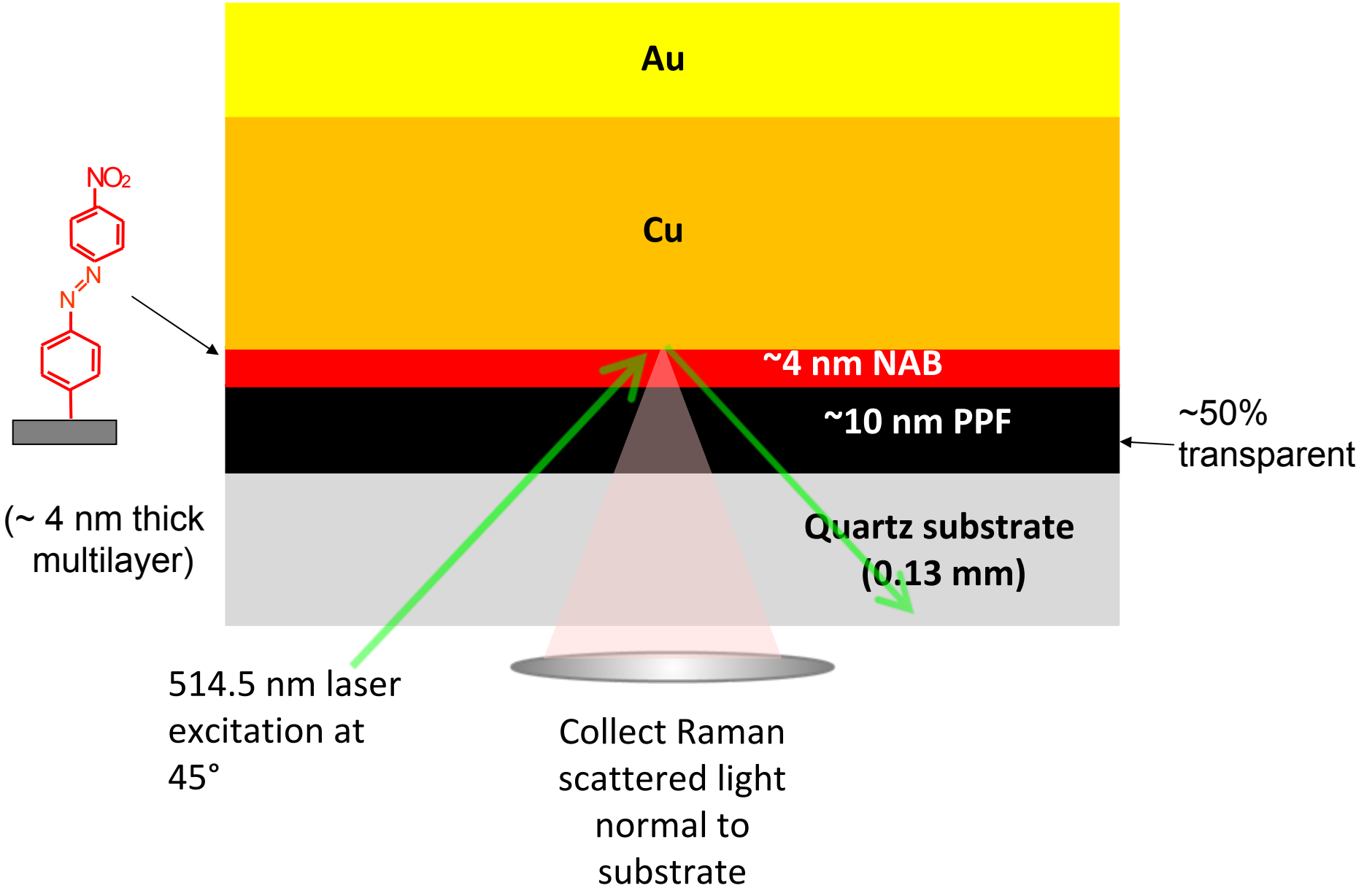
to scale:

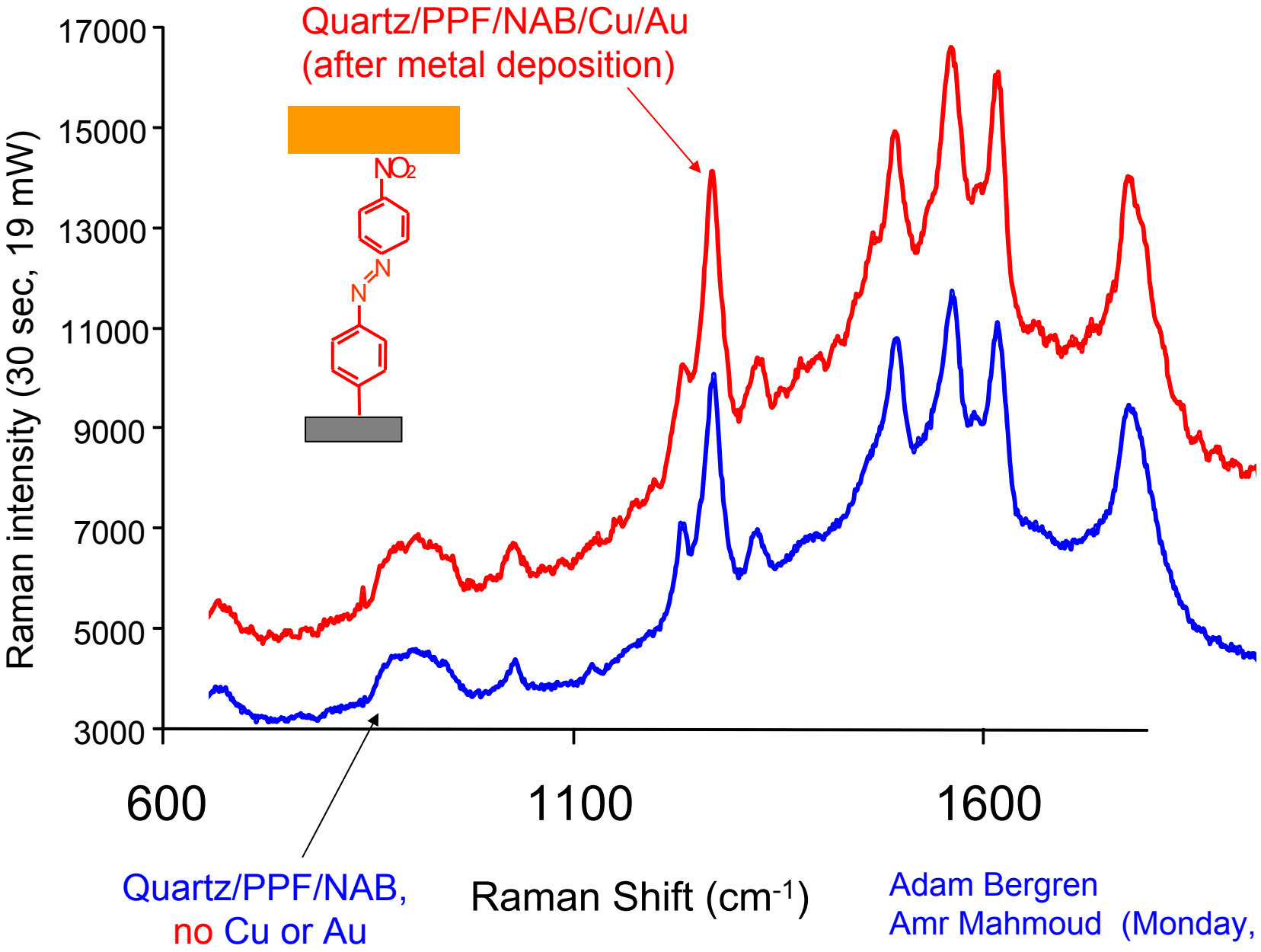




molecular layer is really thin compared to metals, does it survive metal deposition??

"backside" Raman of buried interface:





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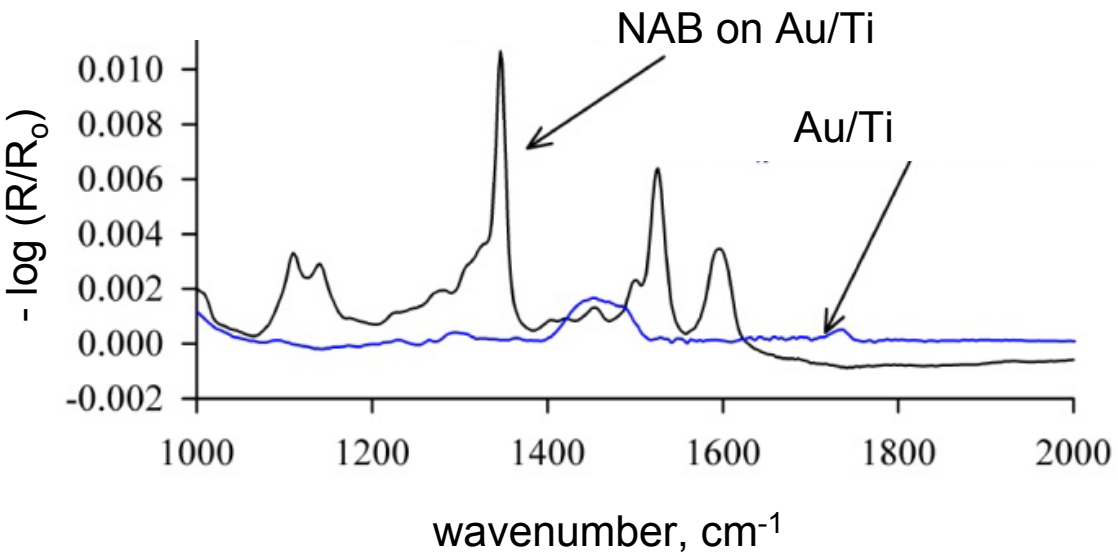
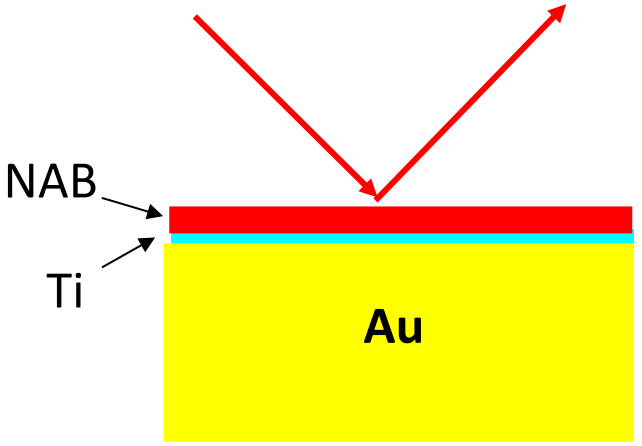
Amr Mahmoud (Monday, 4:20 PM)

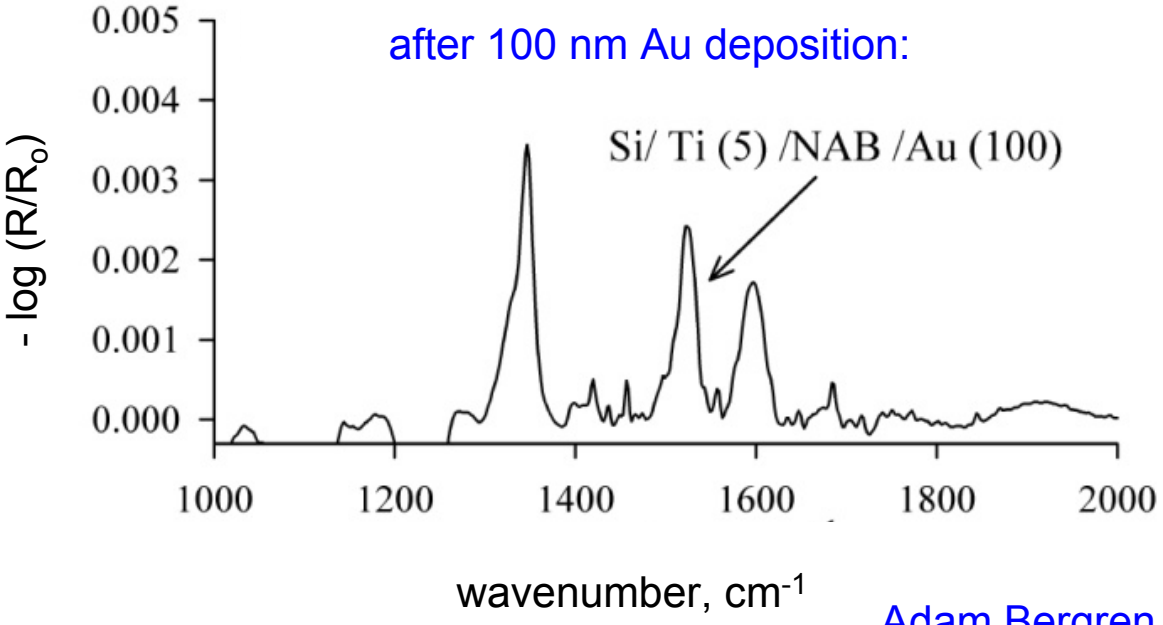
FTIR of buried interface:

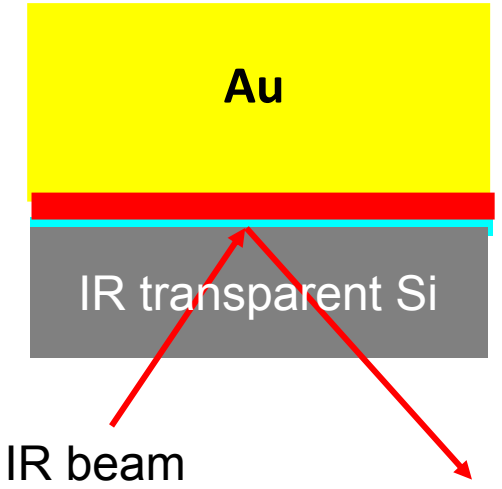




Ti is “primer layer” for NAB bonding to Au

after 100 nm Au deposition:





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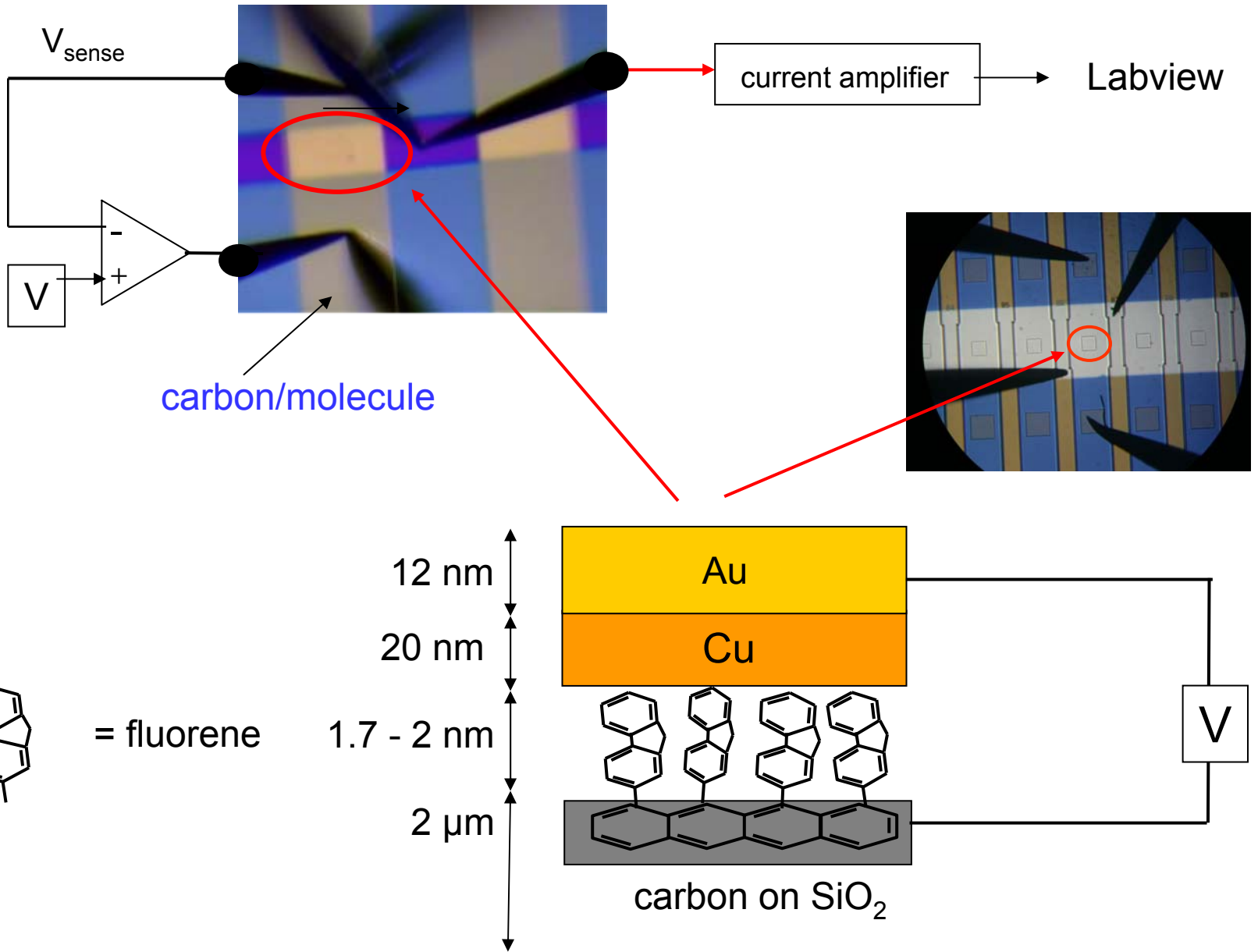
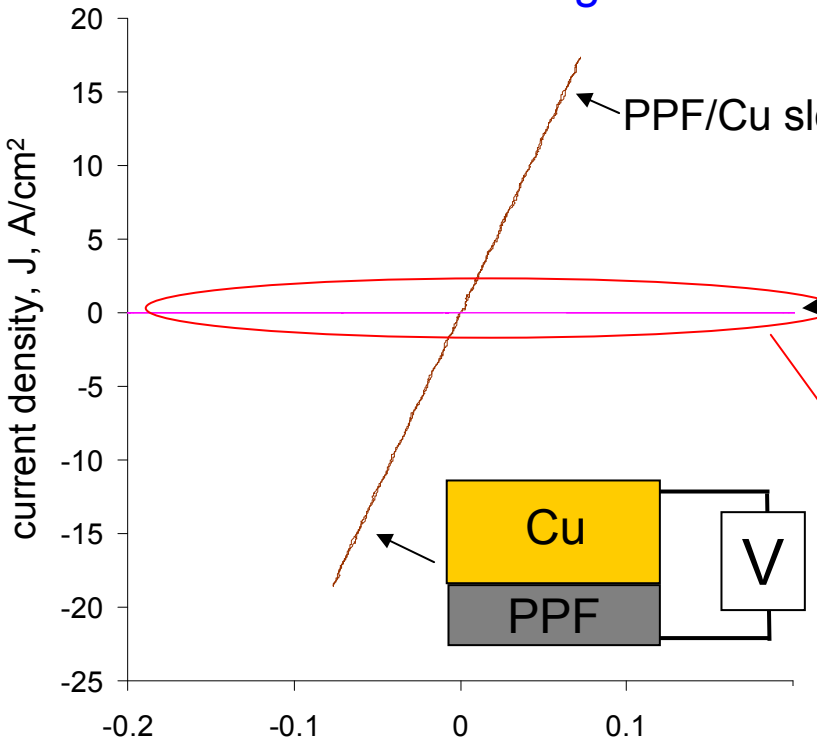
Electronic behavior:

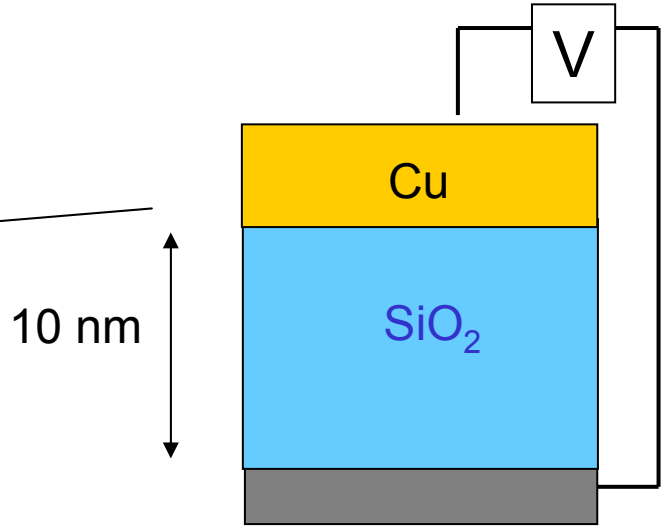


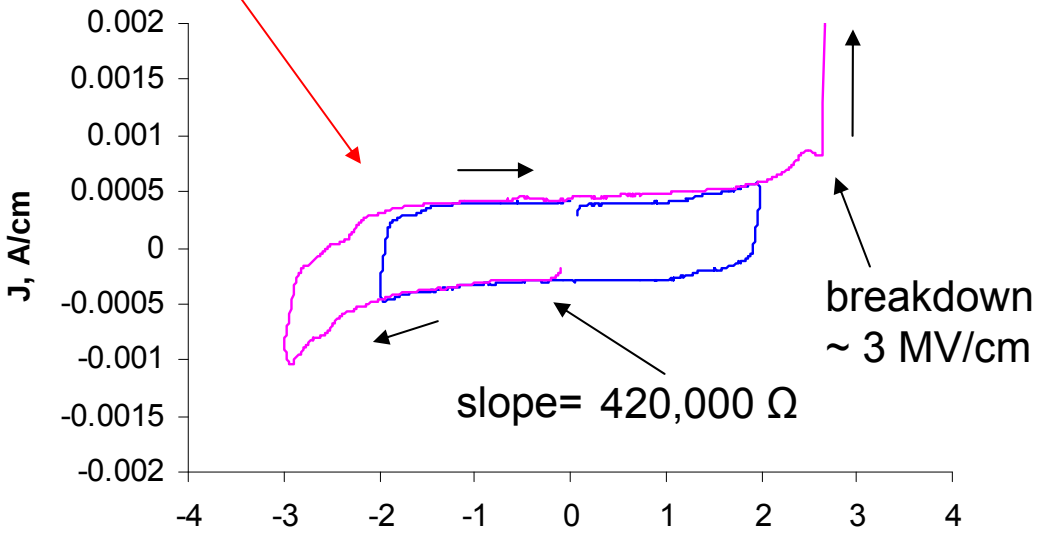
Start with something familiar:



V, carbon relative to Au

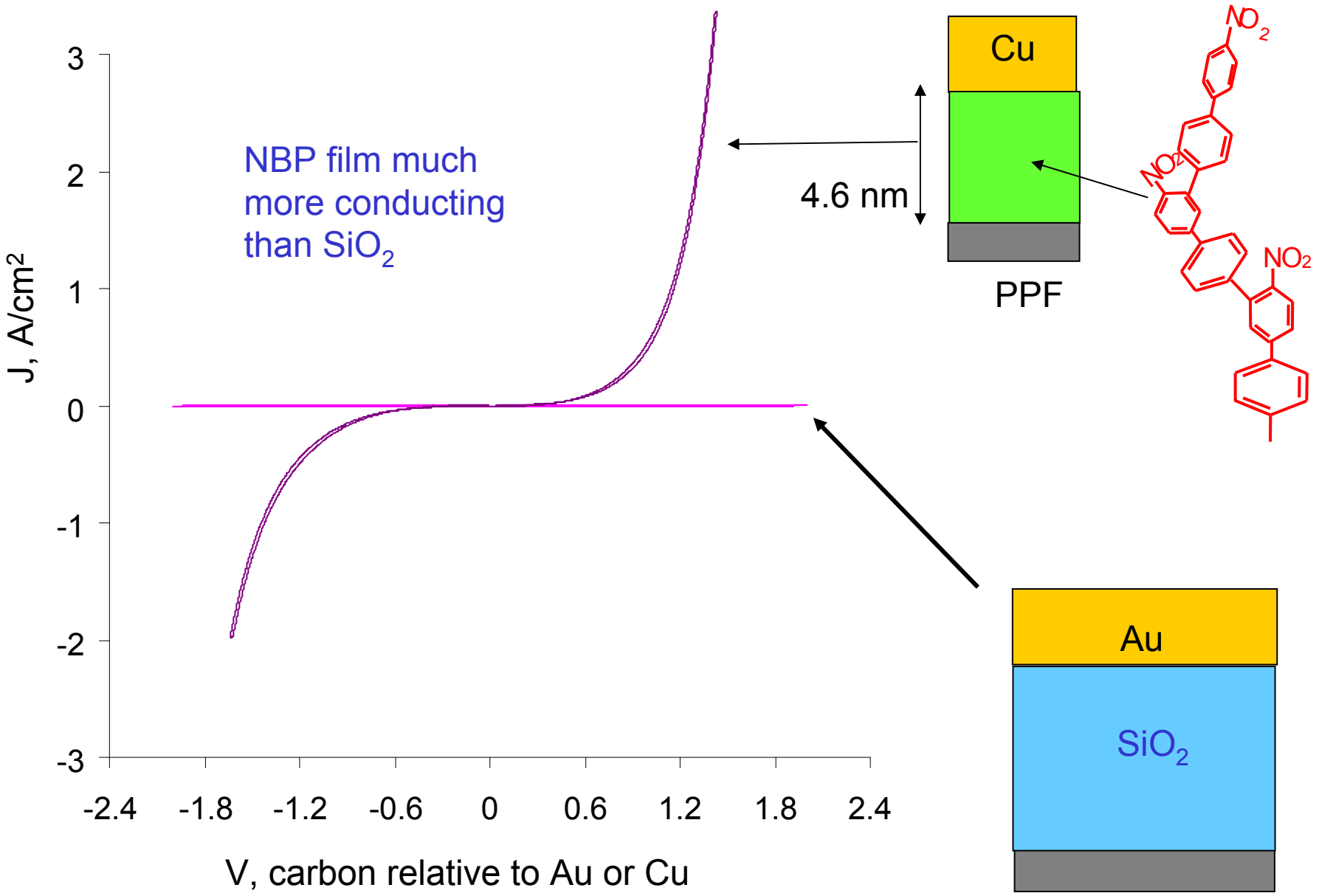
PPF/SiO_2/Cu



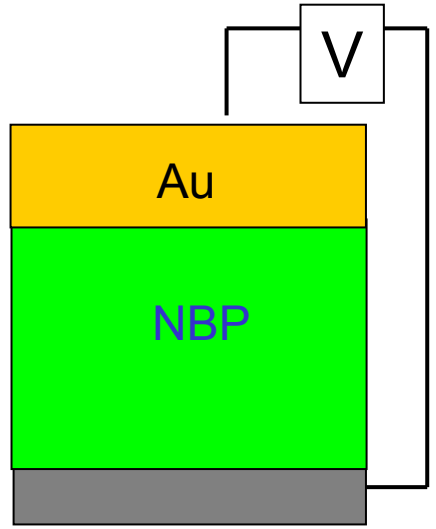


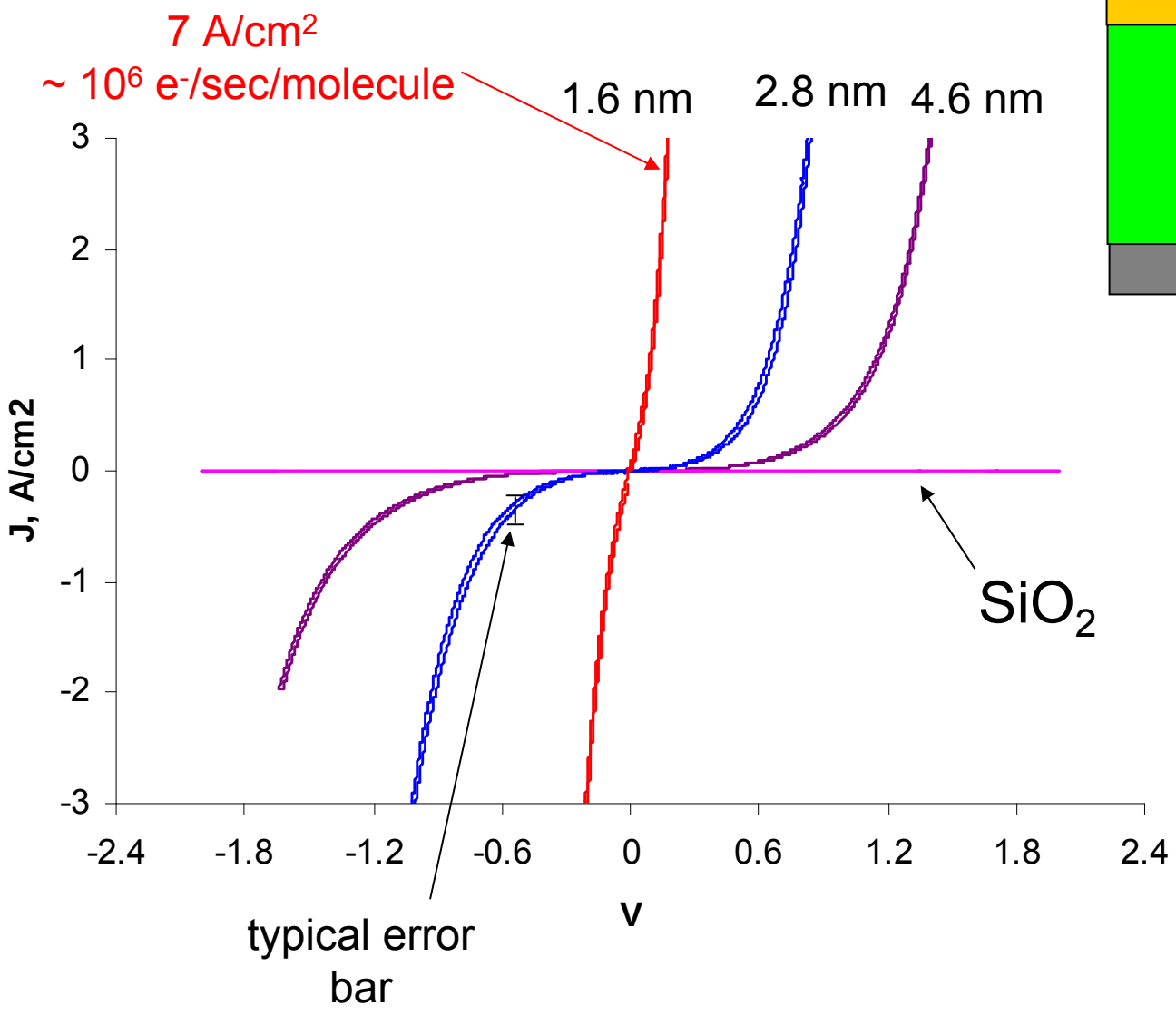
How about a molecule instead of SiO_2 ?

nitrobiphenyl multilayer
4.6 nm thick:



Nitrobiphenyl junctions of differing thickness:

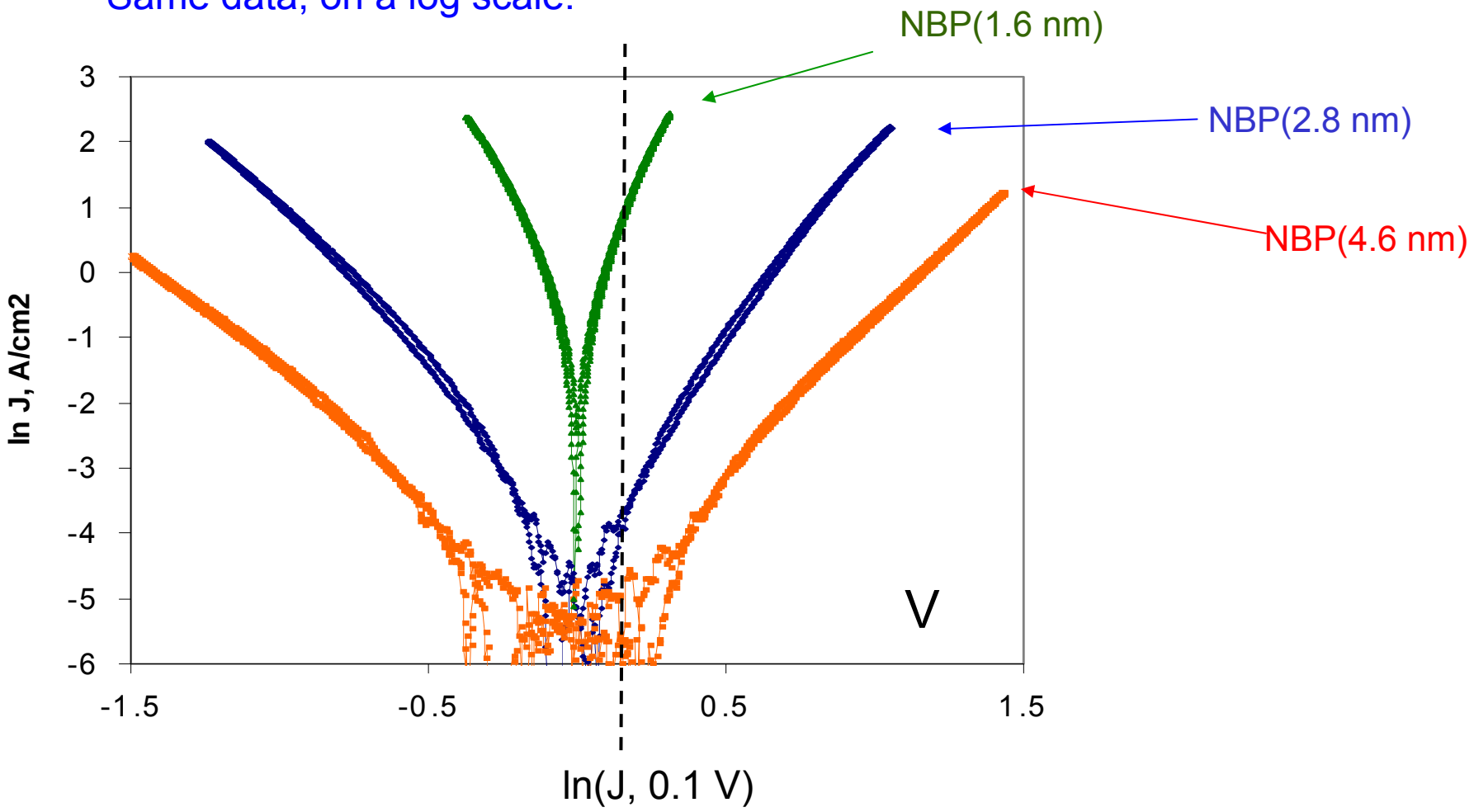




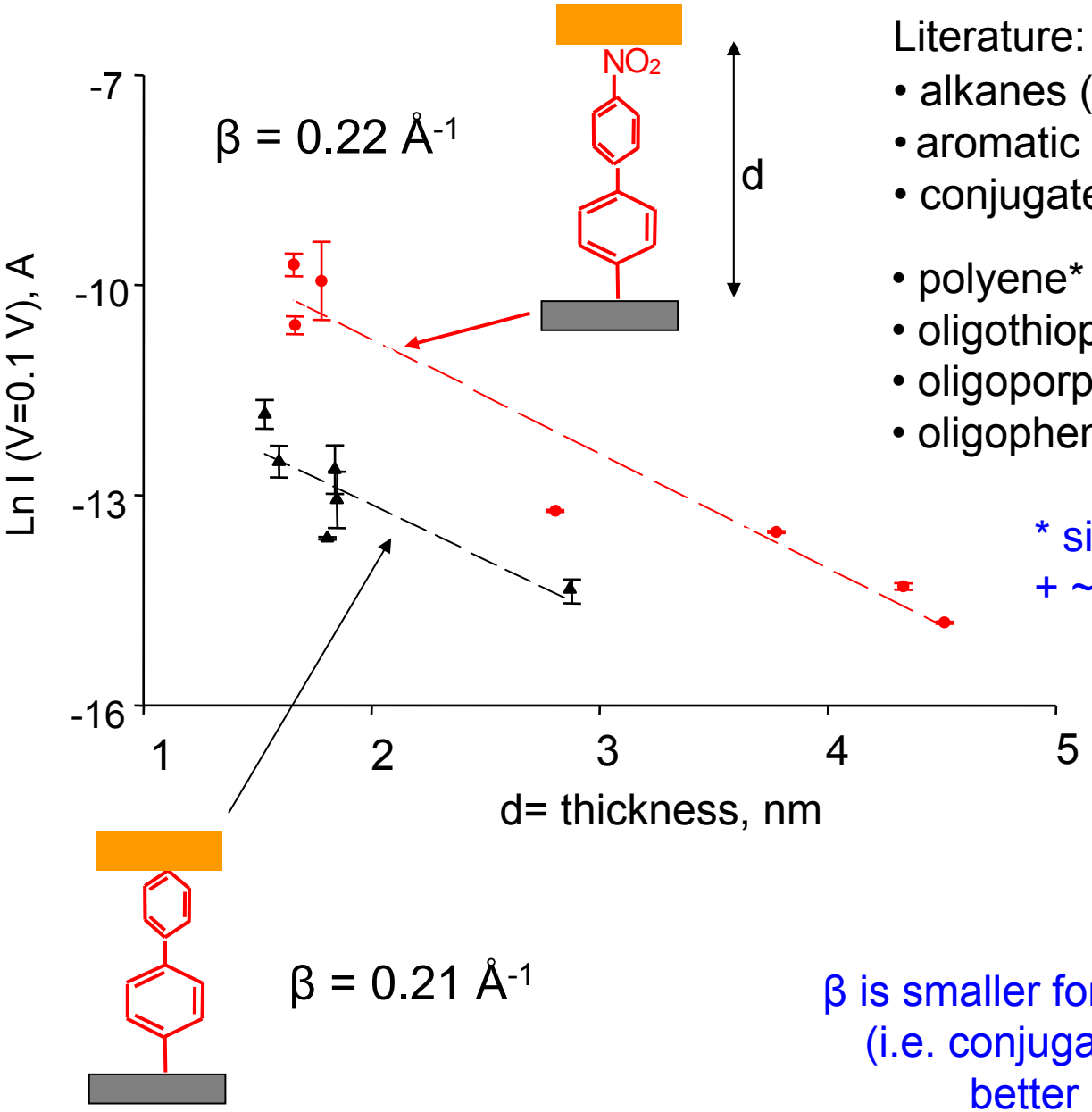
rsd 5-15%
yield > 90%

J. Phys. Chem. B, 2005, **109**, 11163

Same data, on a log scale:



- No obvious shape change from 1.6 to 4.6 nm thickness
- Symmetric with minimal hysteresis
- Repeatable > 10^8 cycles



Literature: β

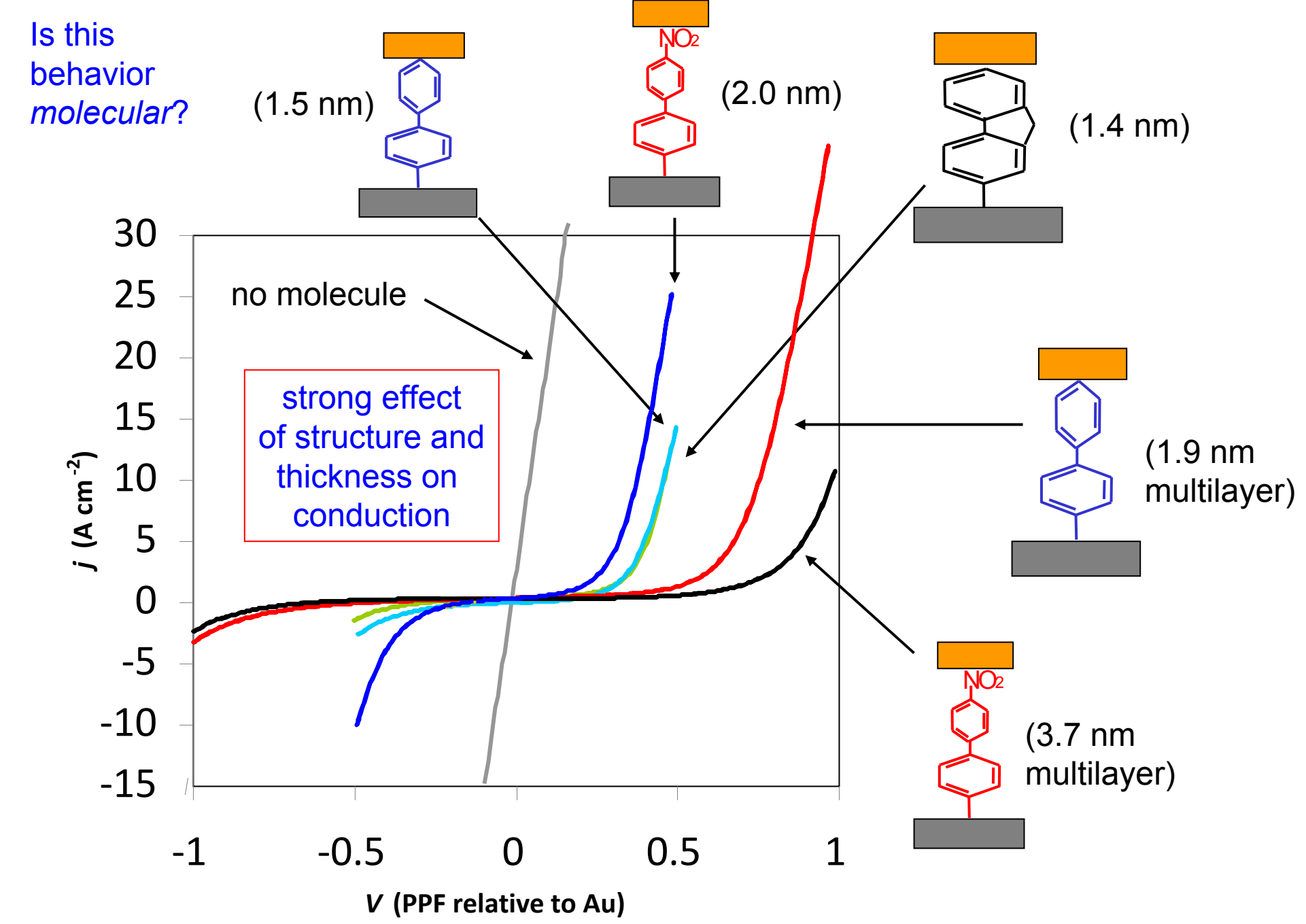
- alkanes (echem or junctions) 0.8 Å^{-1}
- aromatic (echem, 1999) 0.22
- conjugated (echem, SAM) 0.3 to 0.6

- polyene* (2005) 0.22
- oligothiophene* (2008) 0.1
- oligoporphyrin* (2008) 0.04
- oligophenyleneimine^{+} (2008) 0.3

* single molecule junction
\+ ~100 molecule junction

β is smaller for aromatic structures (i.e. conjugated molecules are better "conductors")

Is this behavior *molecular*?



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Various transport mechanisms:

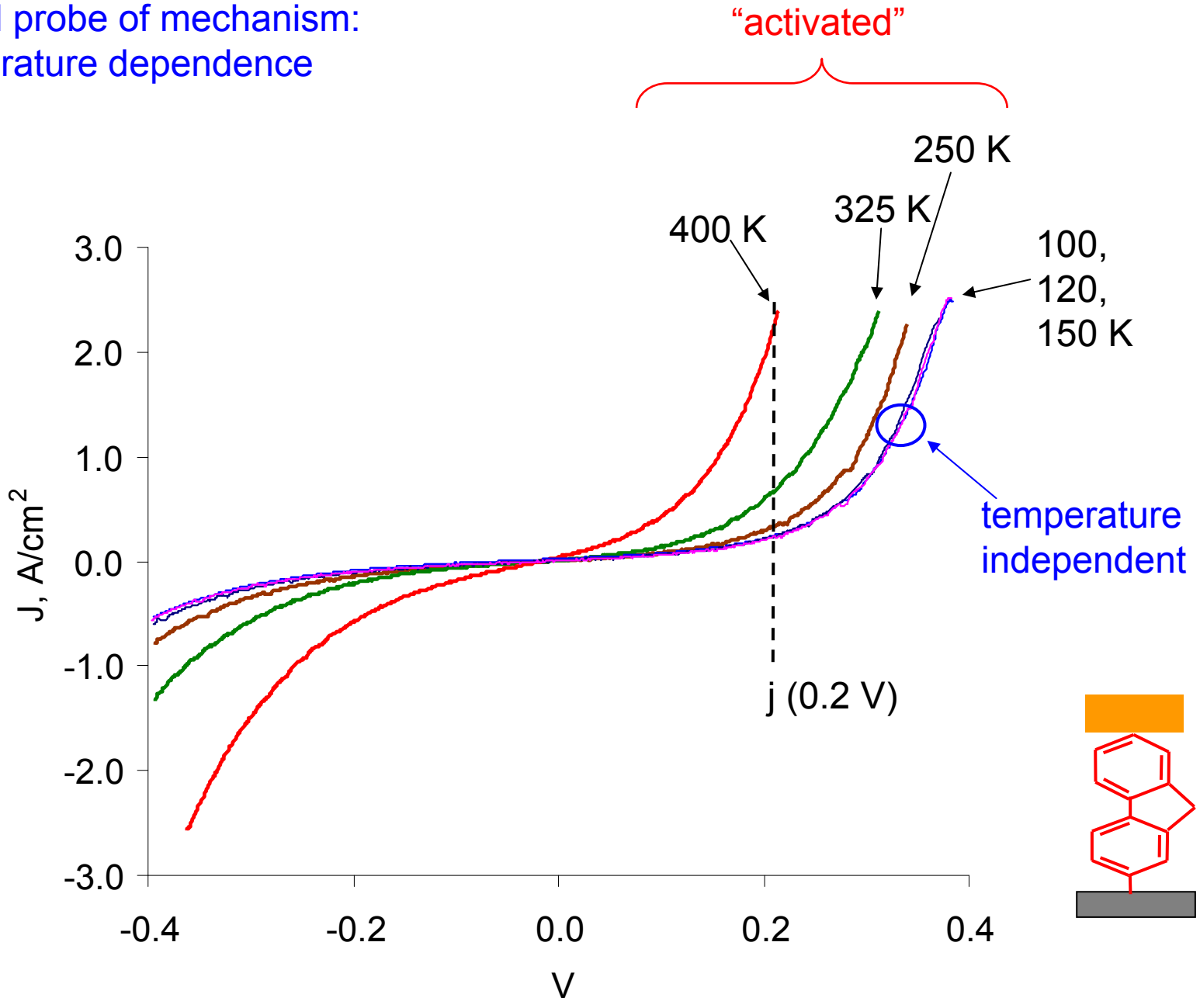
Weakly Temperature dependent:

	distance dependence:
Coherent tunneling, "superexchange"	$\exp(-\beta d)$
Incoherent, diffusive tunneling	$\exp(-\beta' d)$
Field emission (Fowler Nordheim)	$(V/d) \exp(-a d)$

Strongly Temperature dependent ("activated"):

Thermionic (Schottky) emission	$\exp(-c d^{1/2})$
Poole-Frenkel effect ("coulombic traps")	$\exp(-c' d^{1/2})$
"hopping", including redox exchange (Marcus-Levich)	d^{-1}

A good probe of mechanism:
Temperature dependence



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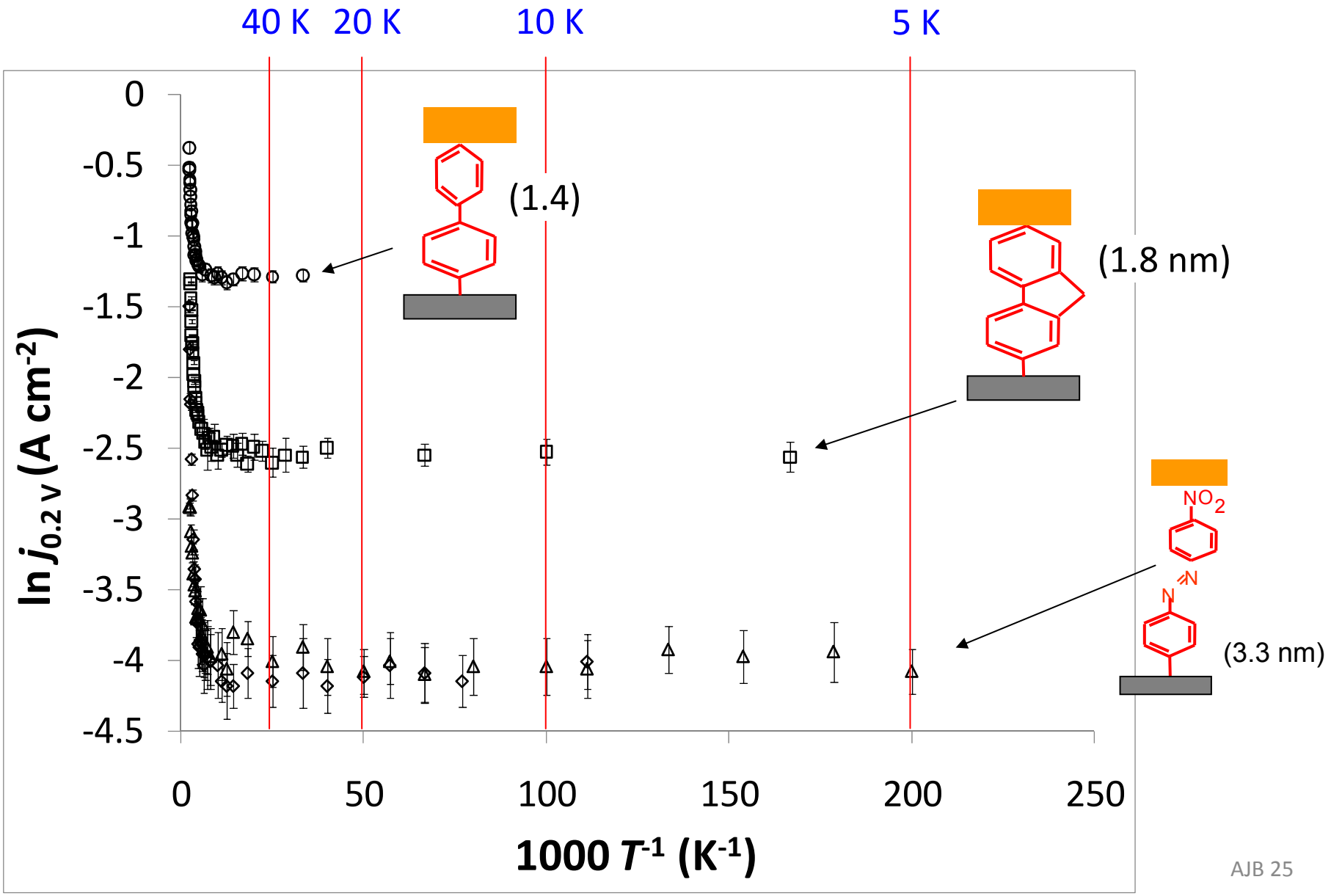
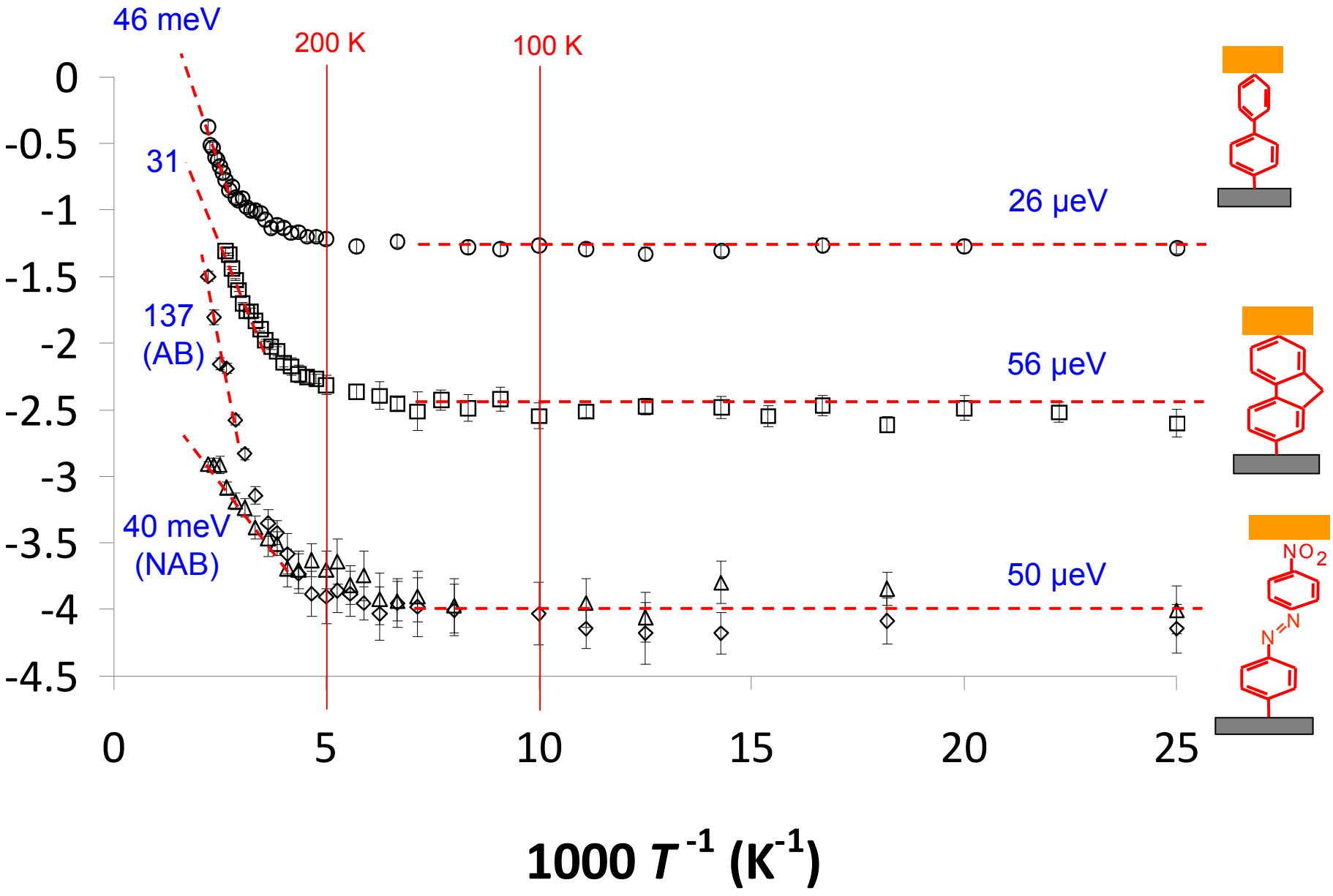
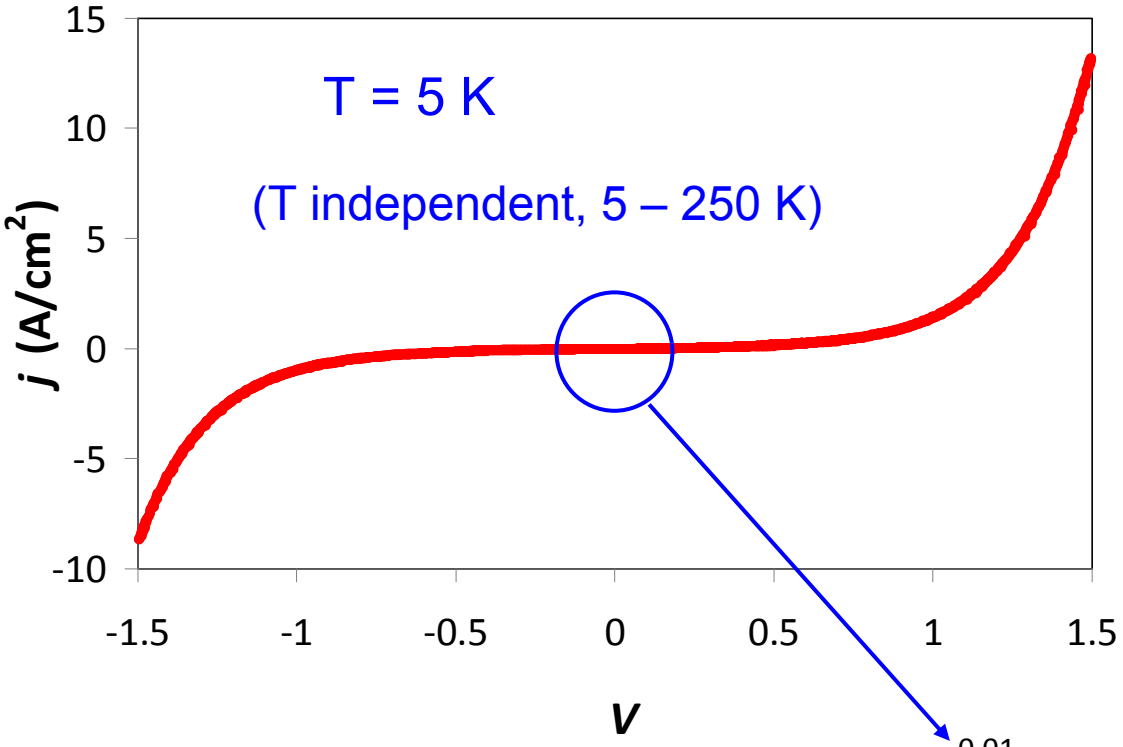
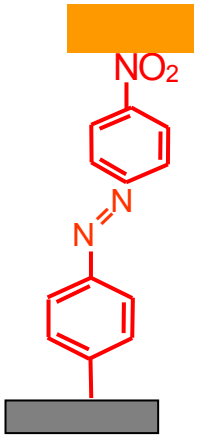
Arrhenius plots




46 meV
200 K
100 K
0
-0.5
-1
-1.5
-2
-2.5
-3
-3.5
-4
-4.5
31
137
(AB)
40 meV
(NAB)
26 μeV
56 μeV
50 μeV
NO2
N
N
0
5
10
15
20
25
1000 T -1 (K-1)

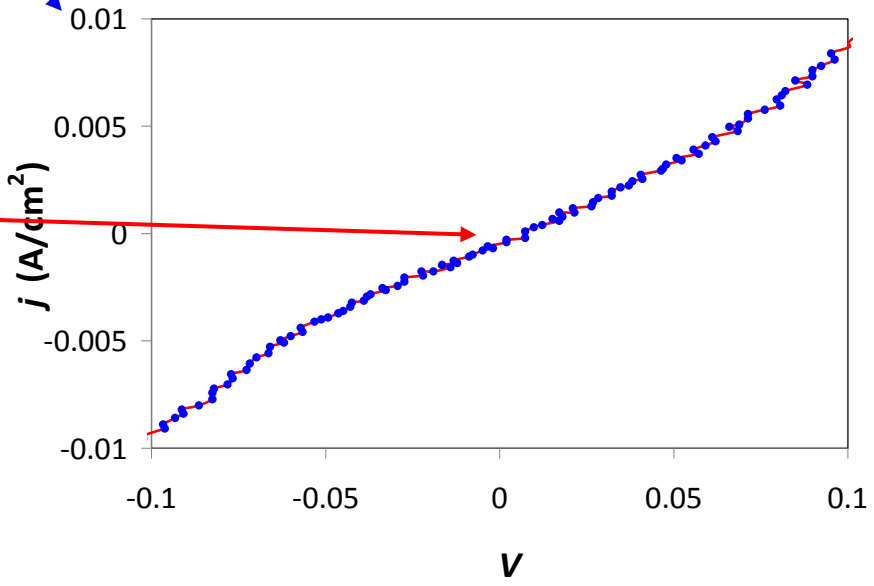




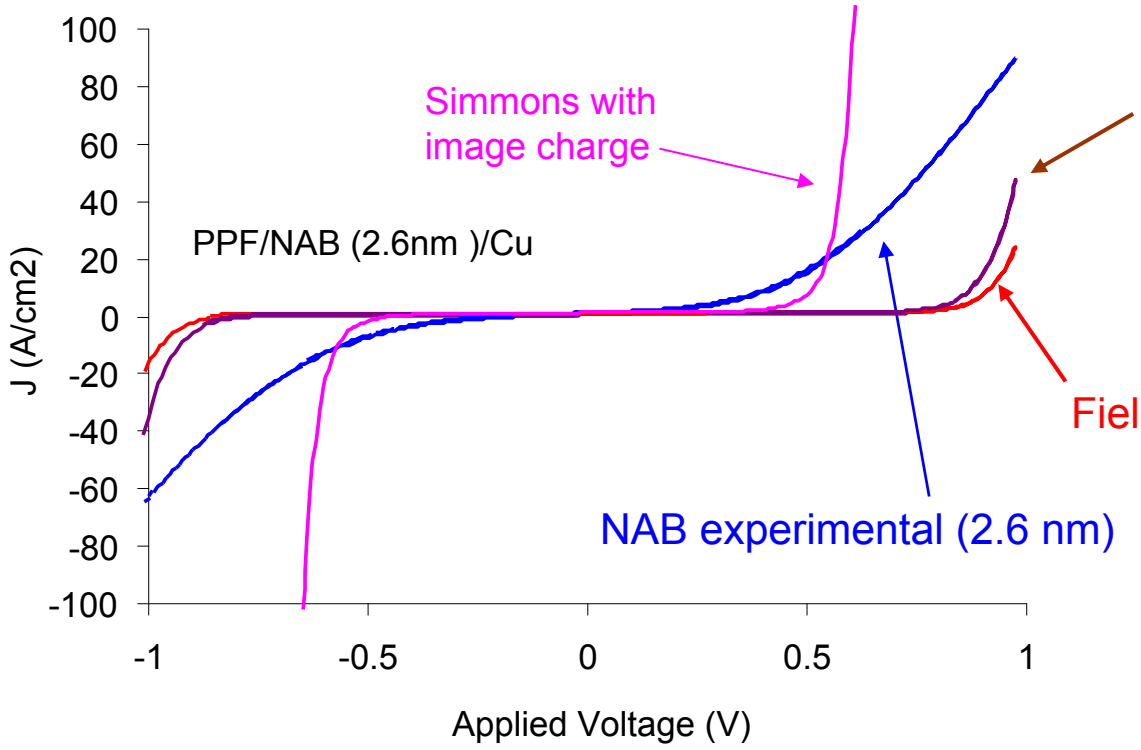
(4.5 nm multilayer)

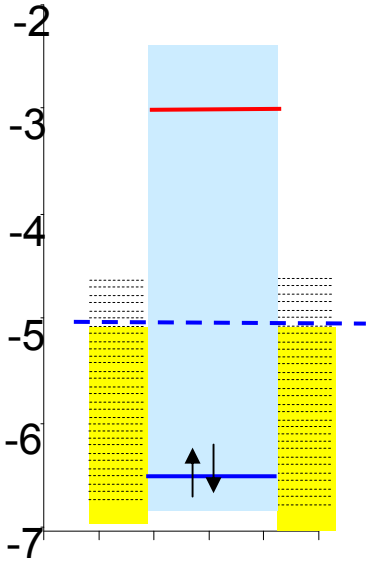
need to explain:

- apparent ohmic contact
- T-independent, despite:
- 4.5 nm thick (too thick for tunneling)



All common off-resonance tunneling mechanisms fail:

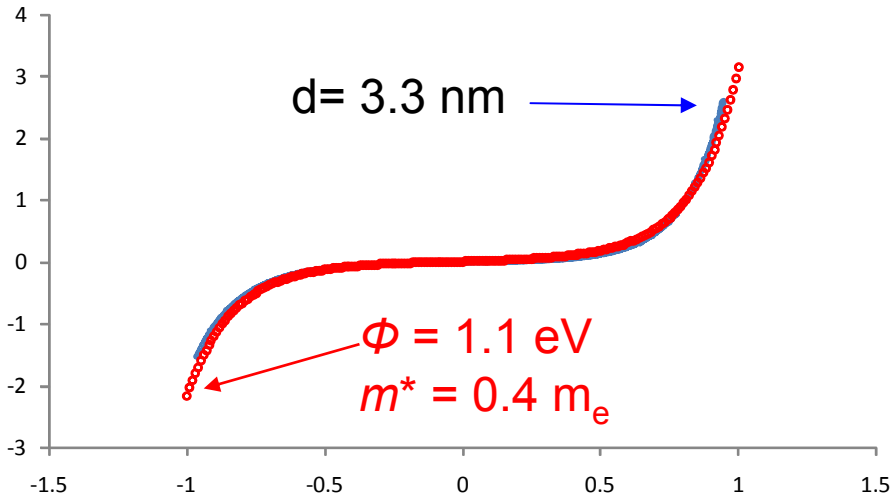


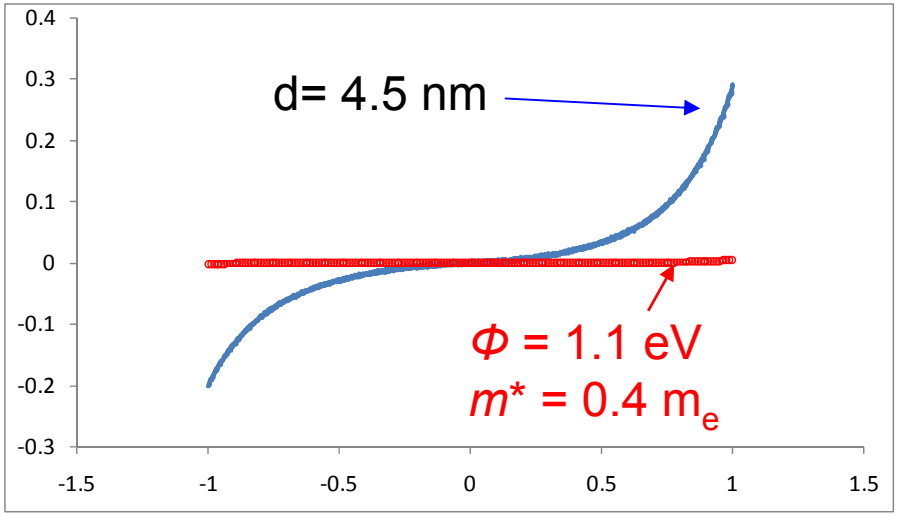


Tunneling with reduced electron mass (modified Simmons equation):

$$J = \frac{q}{4\pi^2 \eta d^2}\left\{\left(\phi - \frac{qV}{2}\right)\times\exp\left[-\frac{2\sqrt{2m^*}}{\eta}\sqrt{\left(\phi - \frac{qV}{2}\right)}d\right] - \left(\phi + \frac{qV}{2}\right)\times\exp\left(-\frac{2\sqrt{(2m^*)}}{\eta}\sqrt{\left(\phi + \frac{qV}{2}\right)}d\right)\right\}$$

m^* = effective electron mass, where mass of charge carrier = m^* x 9.1 x 10^{-31} kg





Experimental data collected at 5 or 6 K

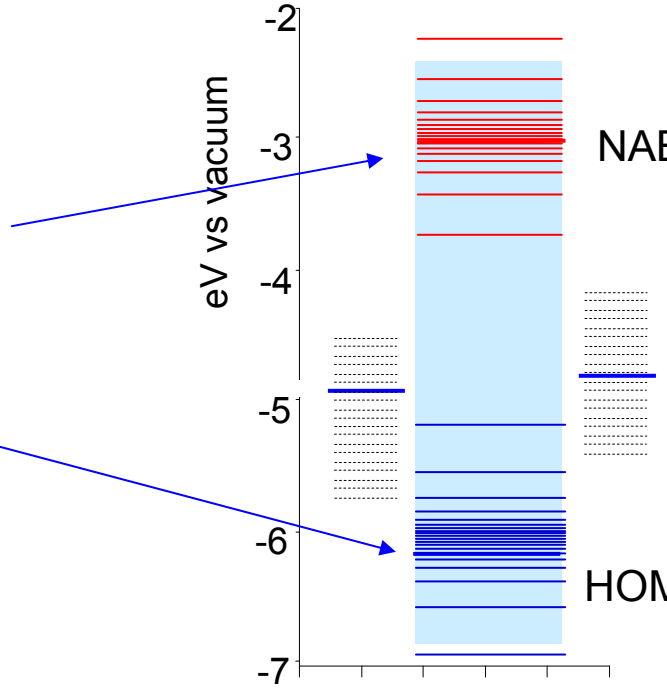
"off resonant" tunneling just doesn't work

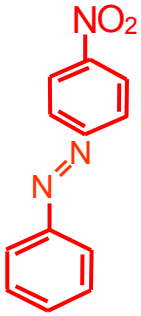
Simmons, J. G. *Journal of Applied Physics* (**1963**), *34*, 1793-1803

An alternative approach:

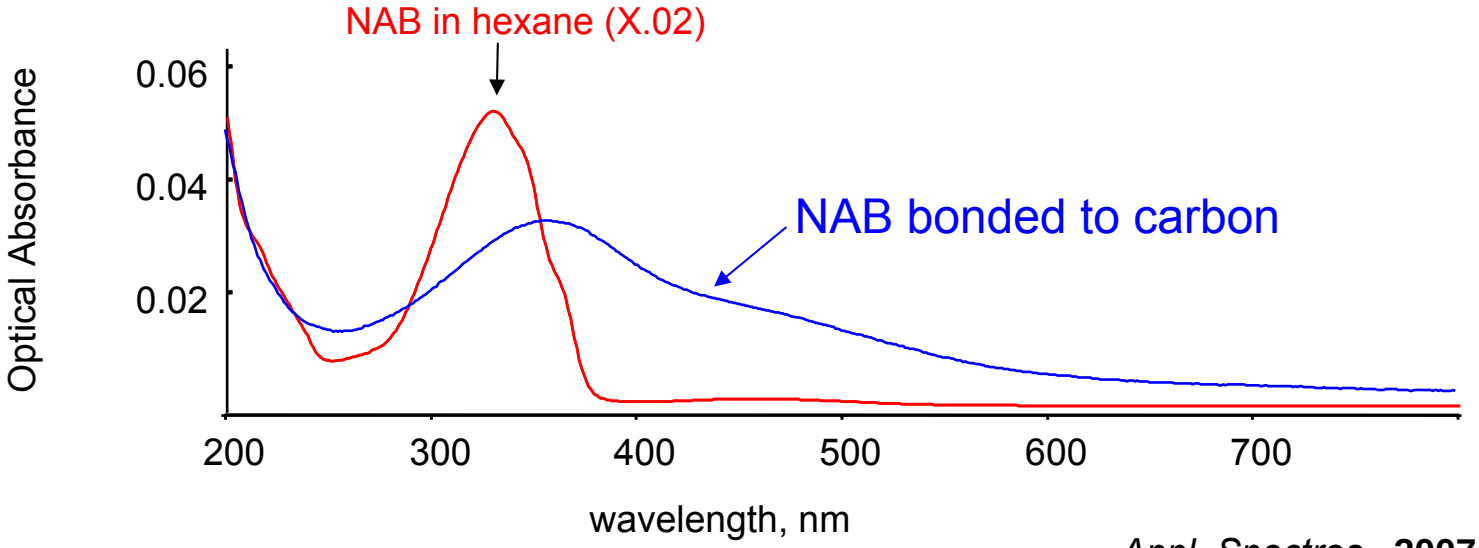
we expect these levels to be broadened, by:

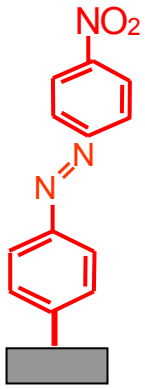
- electronic coupling to substrate
- intermolecular interactions
- variable bonding geometry
- uncertainty (i.e. lifetime) broadening





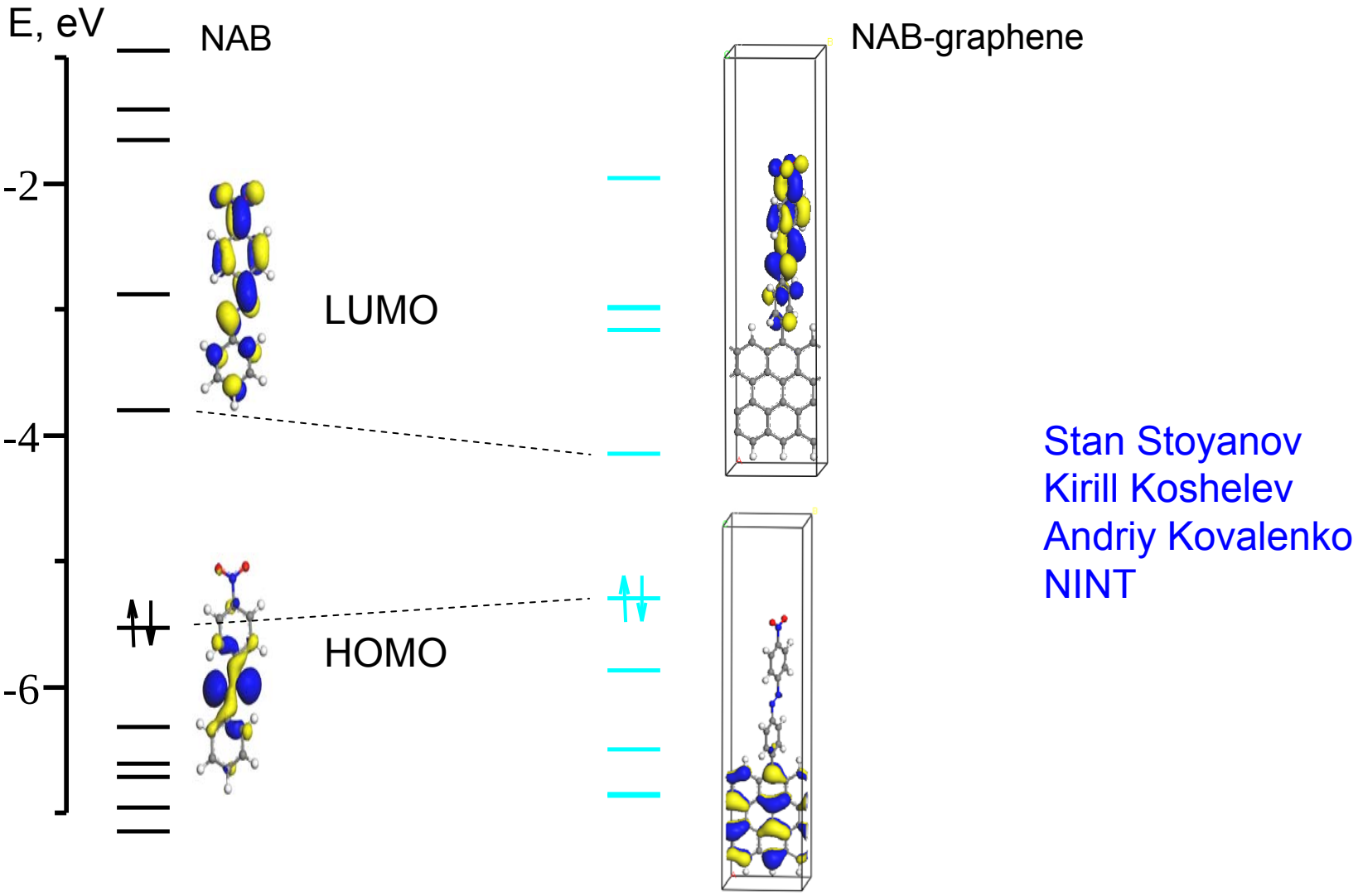
Some evidence for broadening:





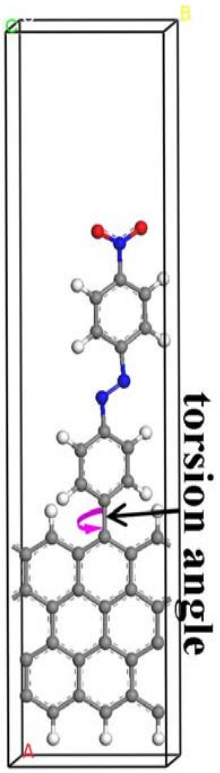
Appl. Spectros. **2007**, 61, 1246-1253

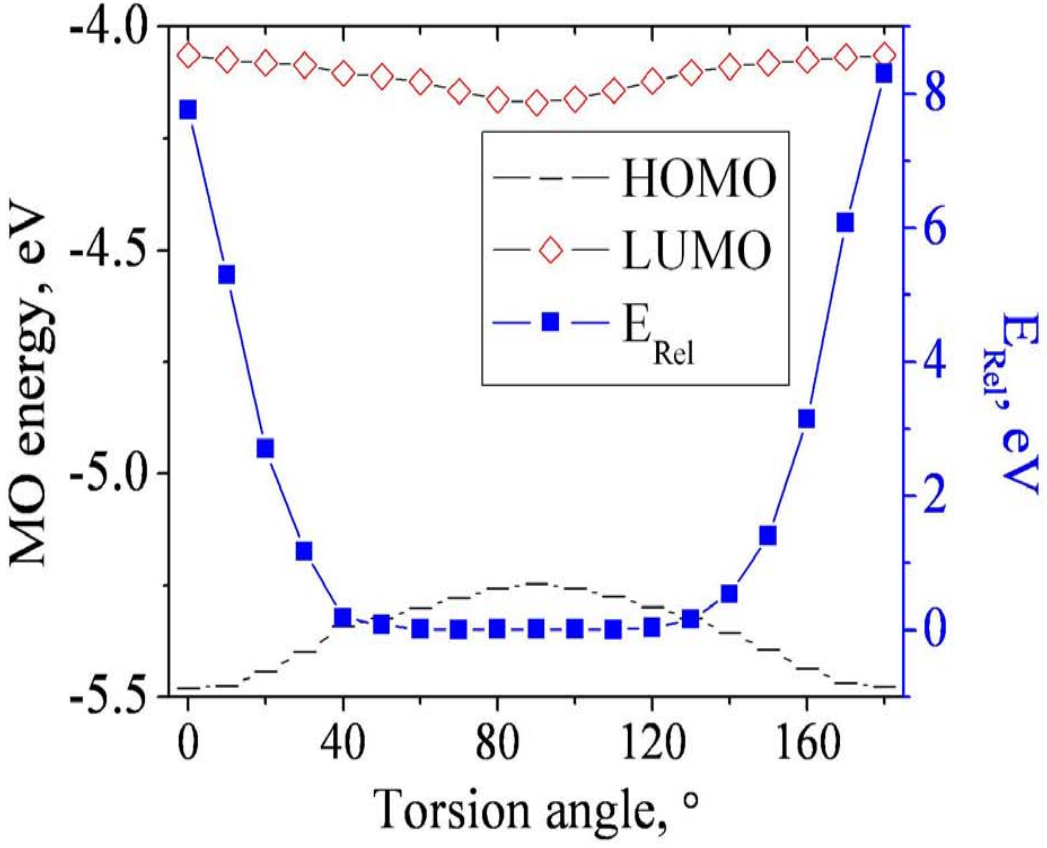
DFT with periodic boundary conditions for graphene

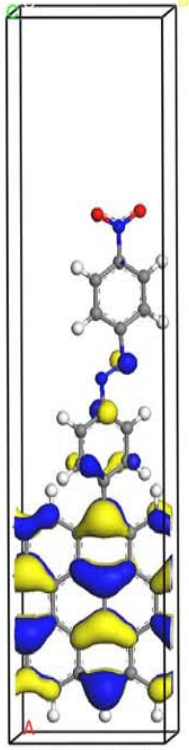


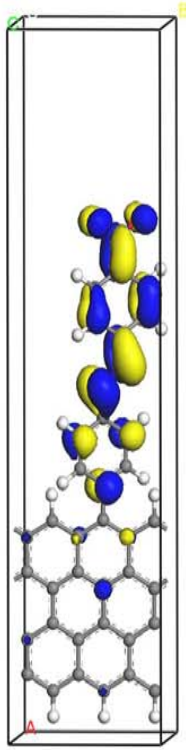
Stan Stoyanov
Kirill Koshelev
Andriy Kovalenko
NINT

HOMO and LUMO energies vary with torsion angle

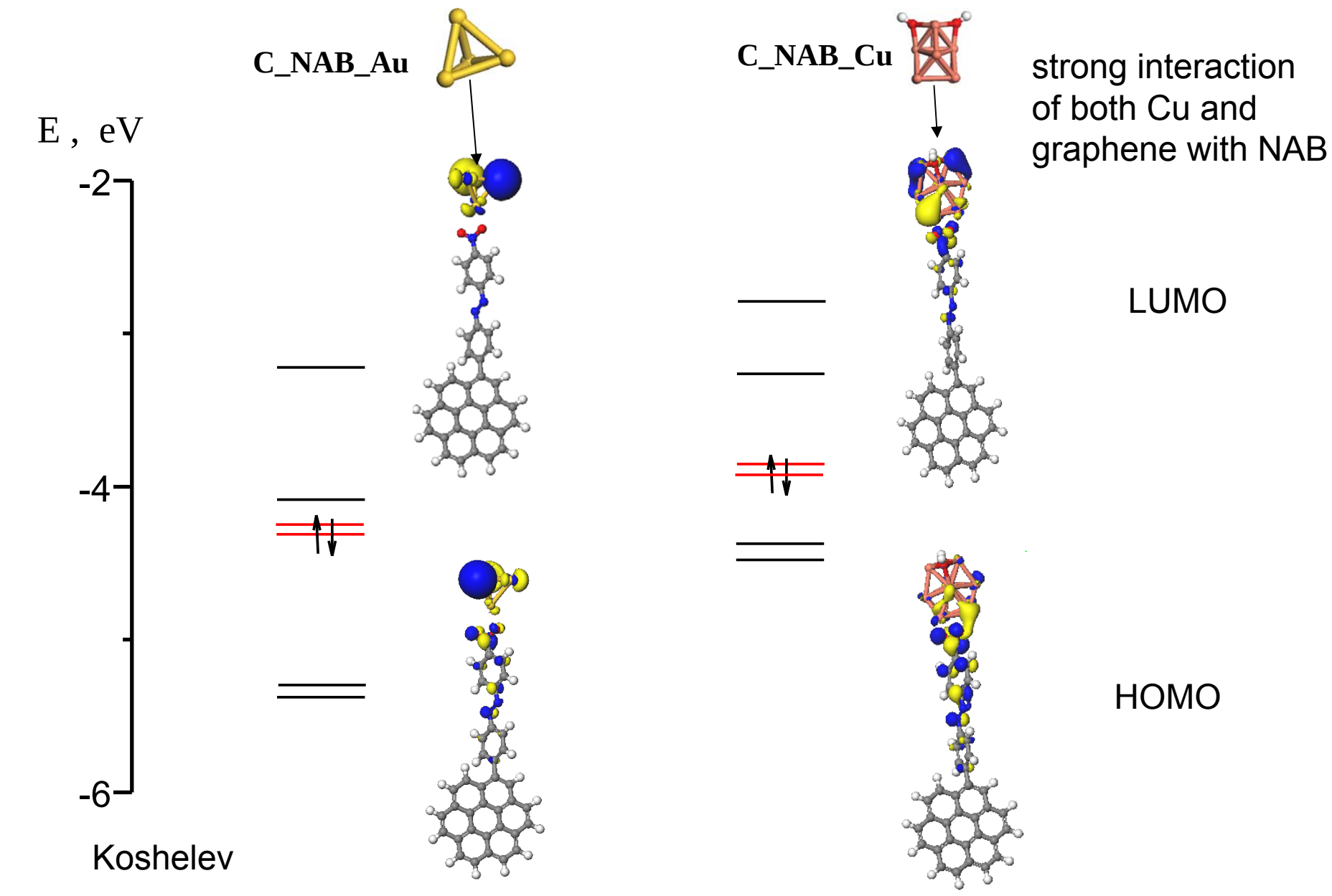


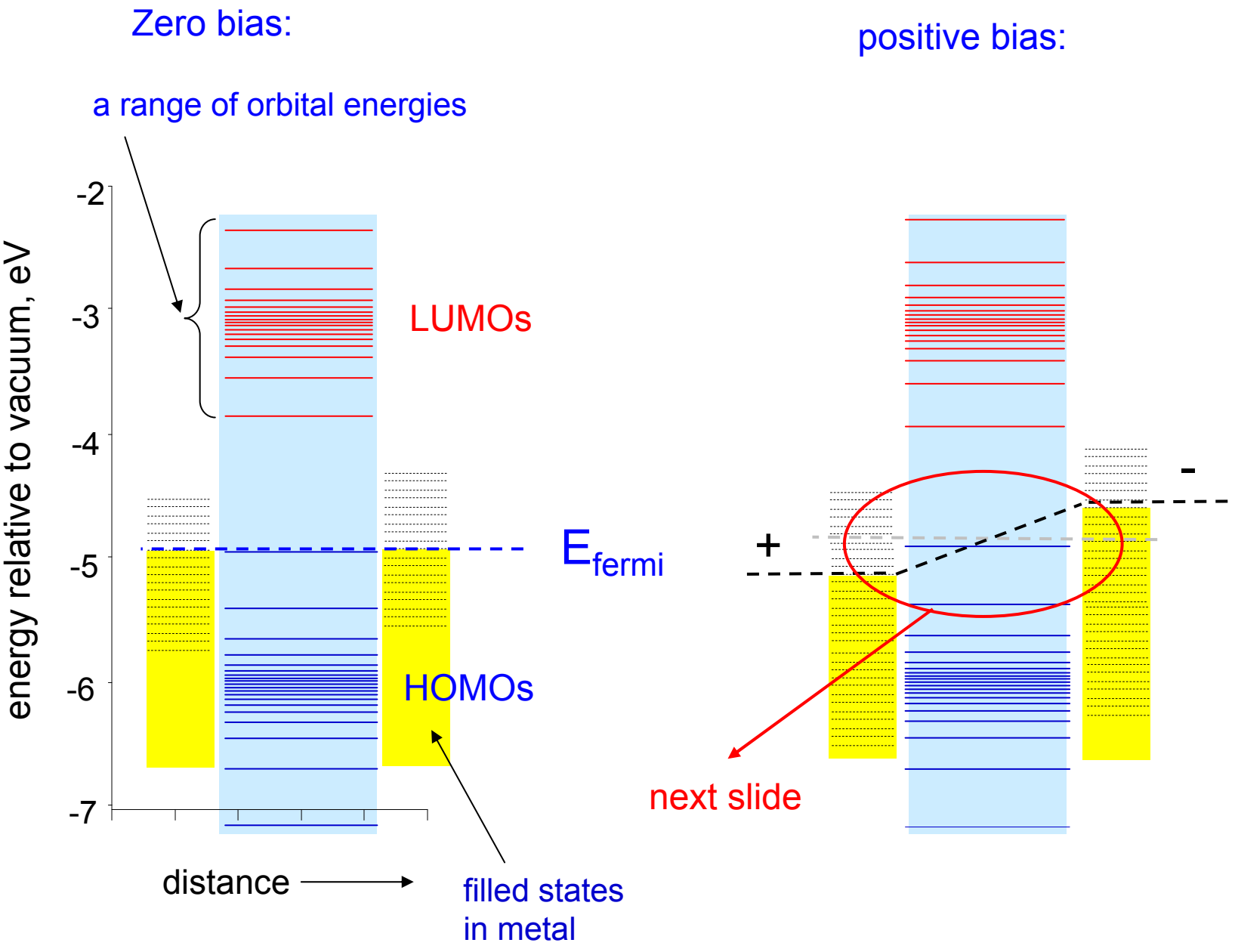






Modeling of both contacts and molecule




Zero bias:
positive bias:
a range of orbital energies
energy relative to vacuum, eV
-2
-3
-4
-5
-6
-7
LUMOs
HOMOs
E fermi
+
-
next slide
distance
filled states
in metal

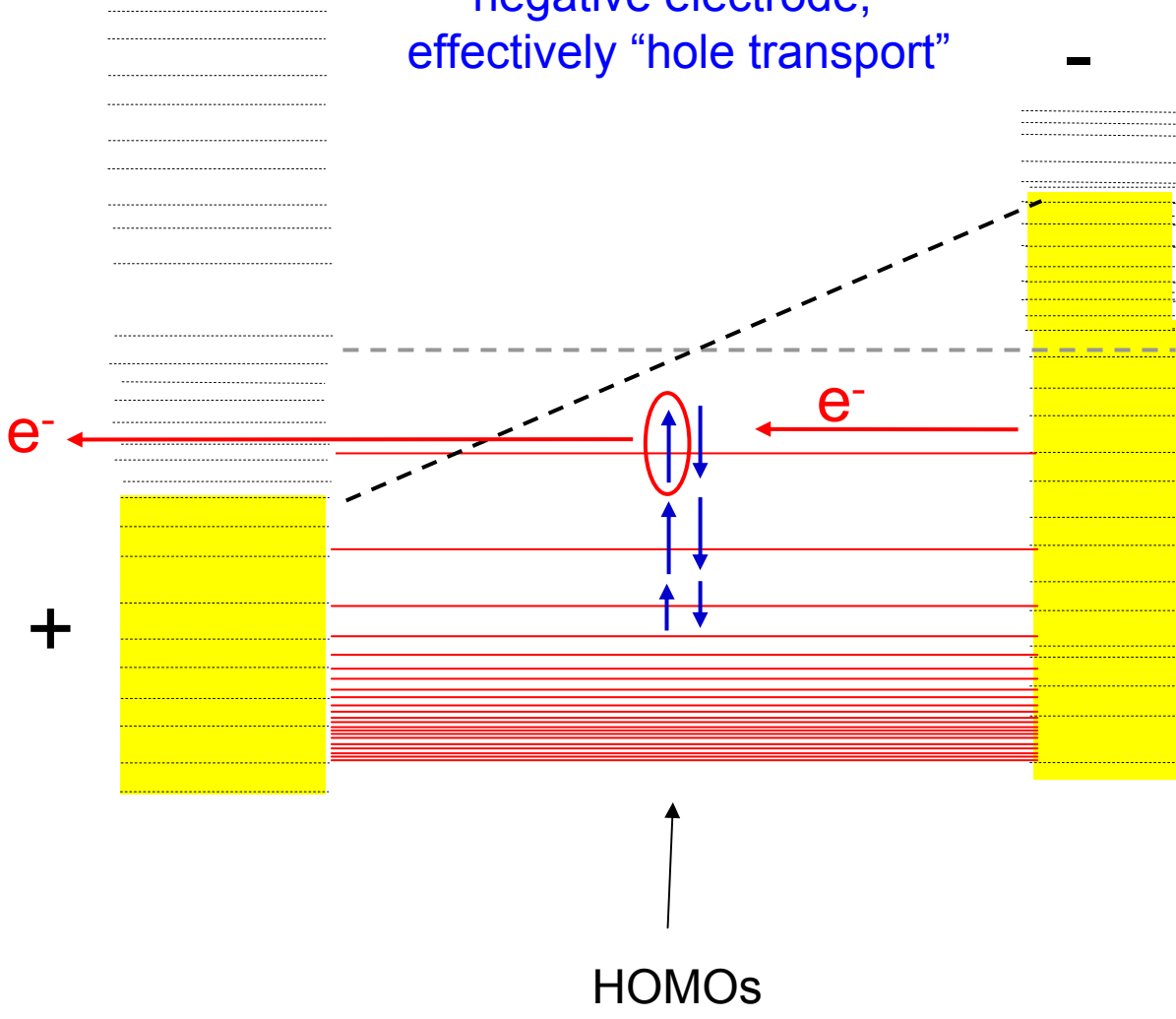
once + bias creates empty metal orbitals, electrons can leave HOMO

+ bias

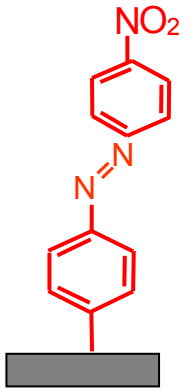
+

HOMO fills again from negative electrode, effectively “hole transport”

-



Note that more HOMOs become accessible for higher bias, causing upward curvature



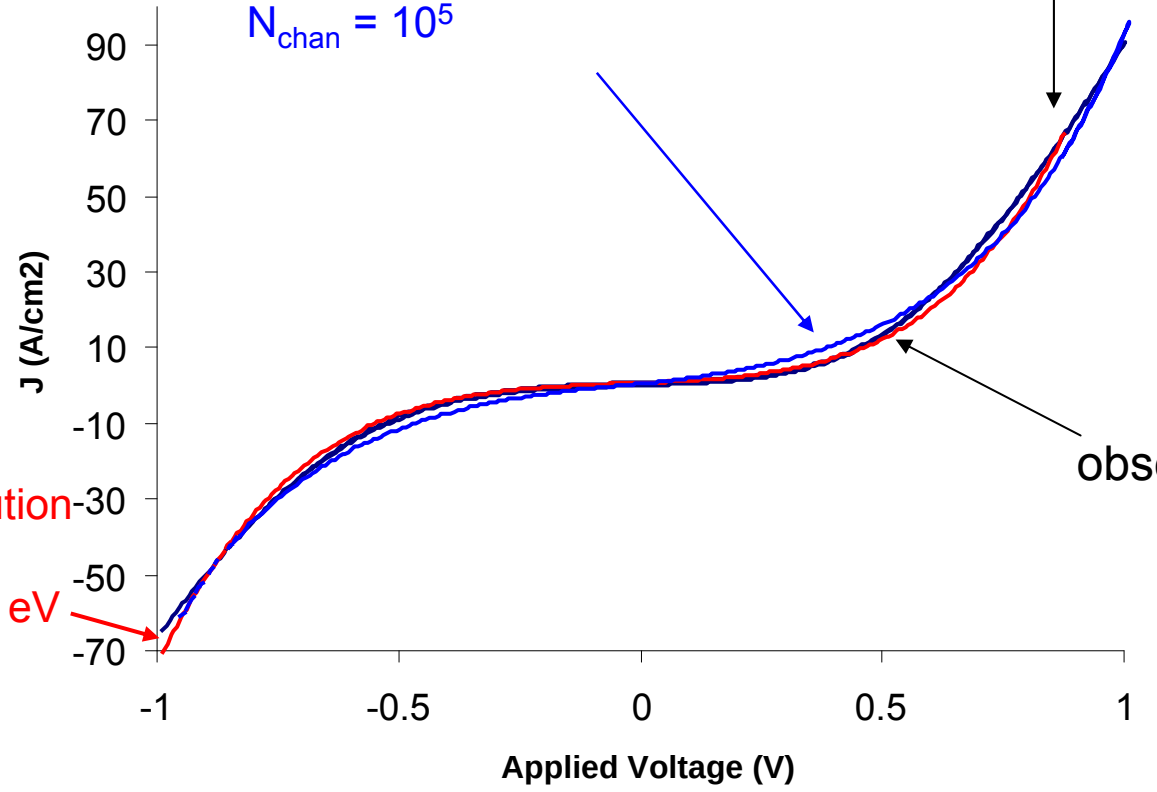
2.6 nm

sech distribution
σ = 0.31 eV
$E_f - E_{HOMO}$ = 1.7 eV
$N_{chan} = 10^5$

more HOMOs becoming accessible with increased bias

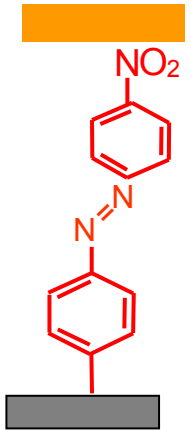
observed

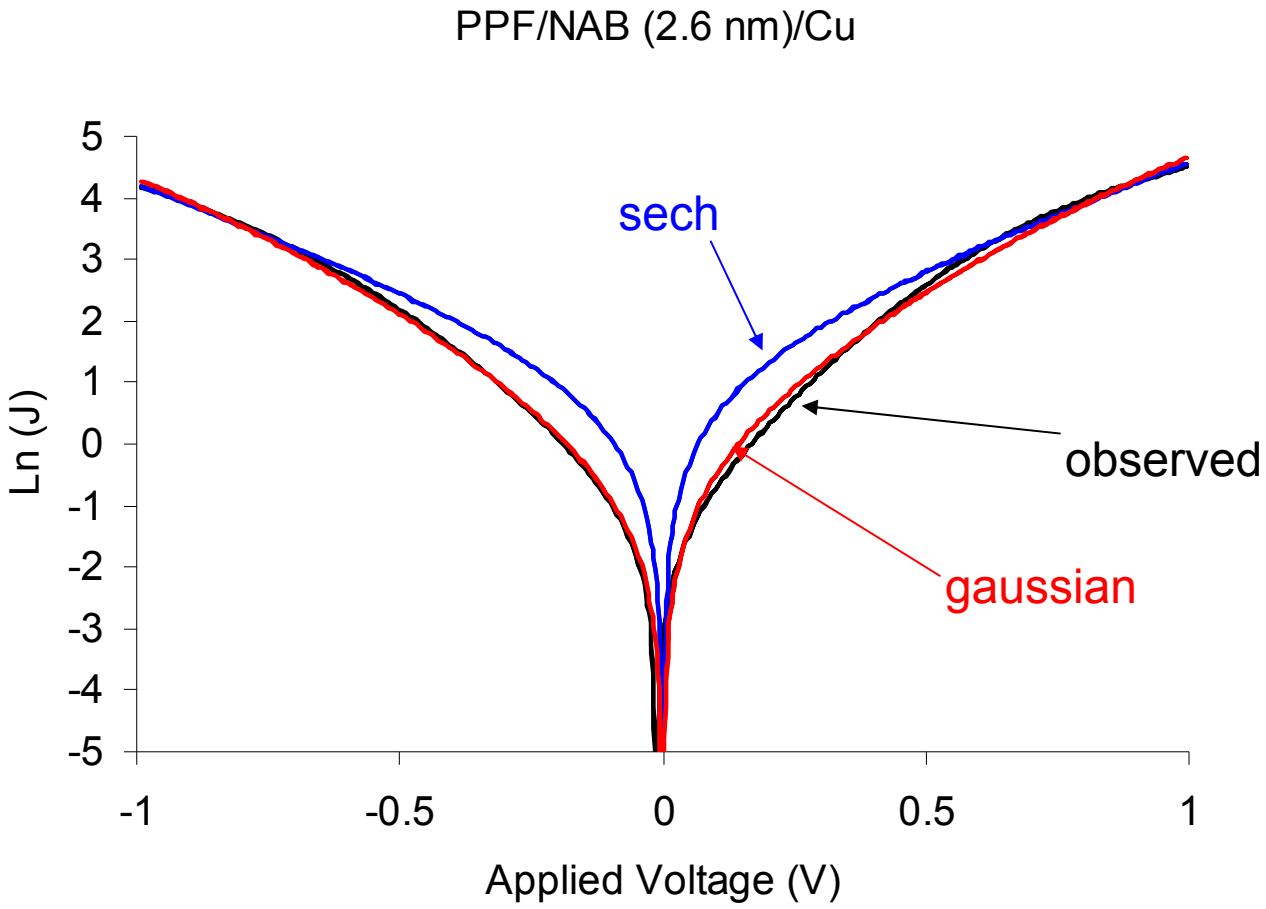
gaussian distribution
σ = 0.52 eV
$E_f - E_{HOMO}$ = 1.7 eV
$N_{chan} = 10^5$



σ = half width of orbital energy distribution
$E_f - E_{HOMO}$ = Fermi level to orbital offset
N_{chan} = total number of active channels

Sergio Jimenez
Adam Bergren





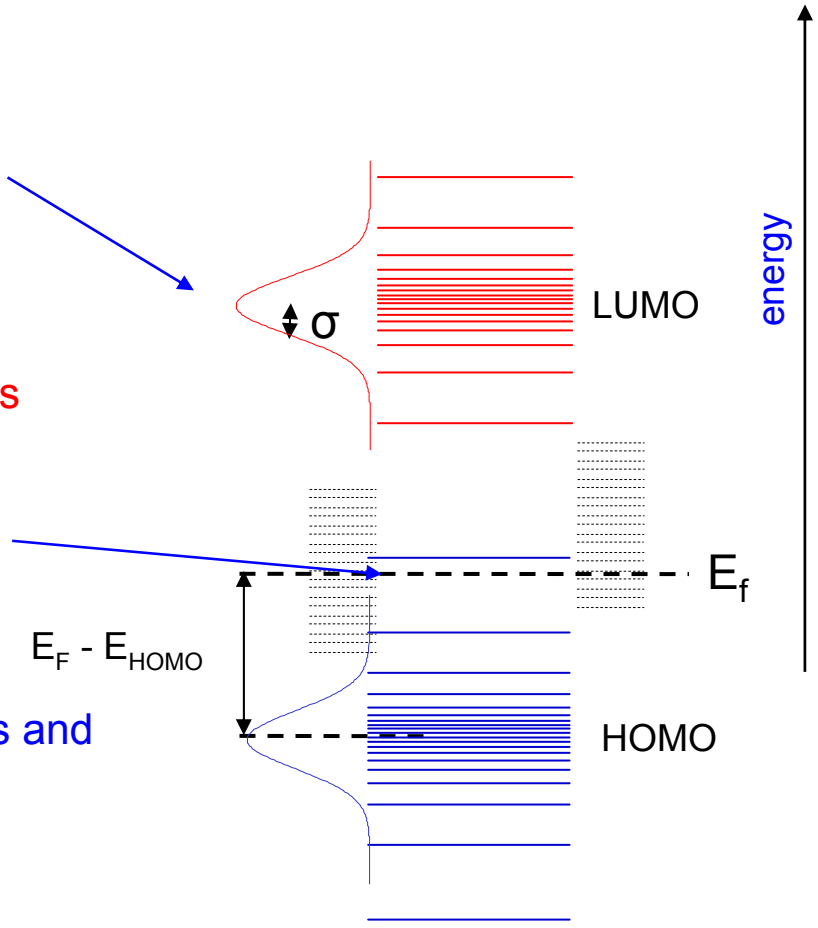
Main parameters of the model:

- $E_f - E_{HOMO}$
- HOMO "linewidth" (σ)
- and number of channels (N)
- molecular layer thickness (d)

for the electrochemists:
NOT Marcus/Butler-Volmer;
similarity due to distribution of orbital energies rather than thermal fluctuations

Important notes:

- broadening caused by coupling and local environment, not thermal fluctuations
- main parameters are distribution width (σ), energy offset ($E_F - E_{HOMO}$), and thickness
- overlap of metal and molecule orbitals may (and probably does) occur at zero bias
- depending on offset between molecular orbitals and Fermi level, we can greatly vary conductance



The punch line: strong interactions between molecule and contacts result in *resonant* electron transport rather than classical tunneling

Adam Bergren (NRC)
Sergio Jimenez (visit. prof.)
Andriy Kovalenko
Stan Stoyanov
Kirill Koshelev
Jie Ru (Uof Alberta)
Bryan Szeto

NINT

Also :

Rory Chisholm (2:00 PM Monday)
Mark McDermott