National Institute For Nanotechnology

Molecules in Circuits, a New Type of Microelectronics?

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ALBERTA INGENUITY FUND

UNIVERSITY OF ALBERTA

NSERC CRSNG

Canada Foundation for Innovation

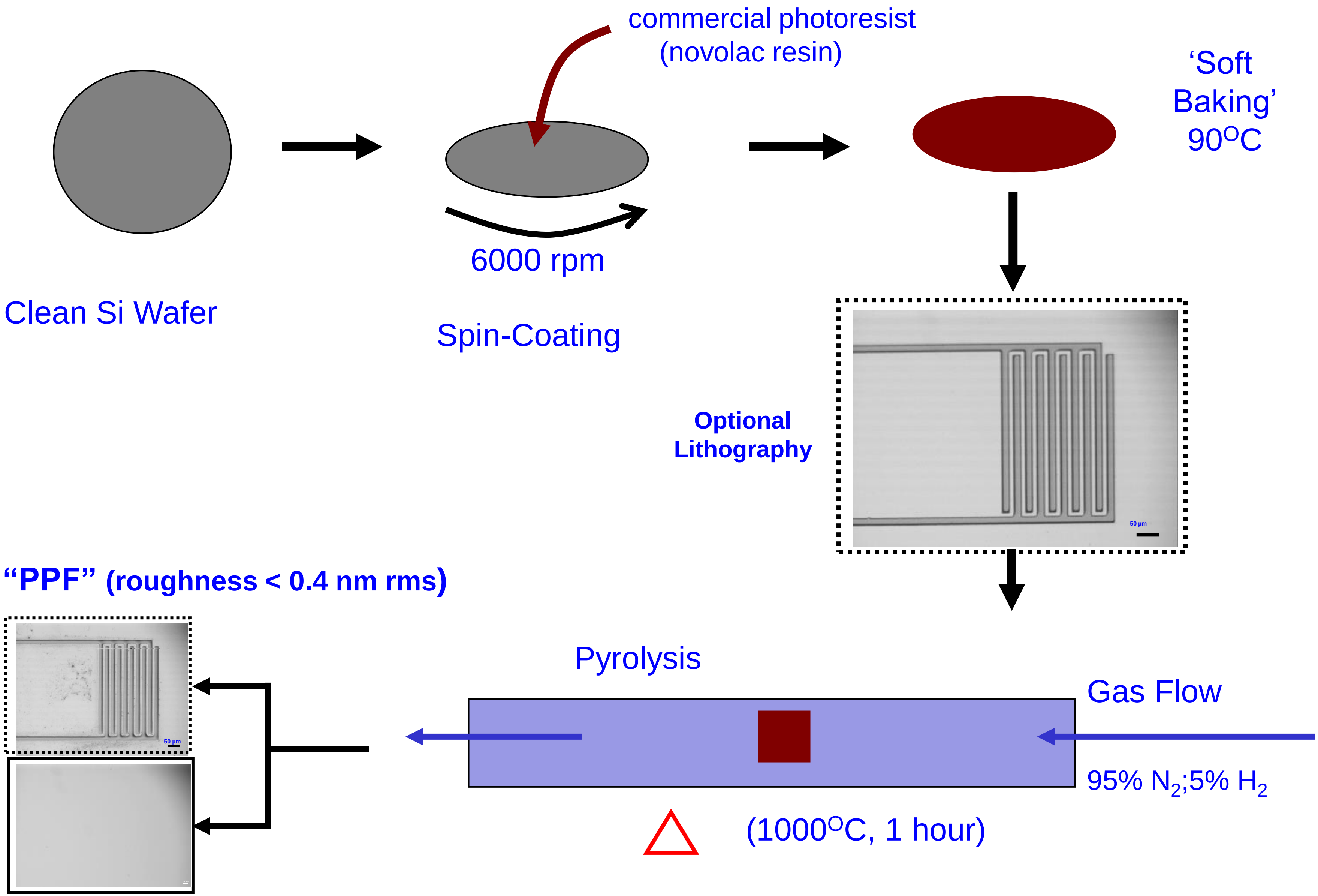
"Organic Electronics":

Sony organic LED display

- charge transport by "hopping" across 100 nm – 10 μm distances
- carriers are radical ions and/or "polarons", often low stability

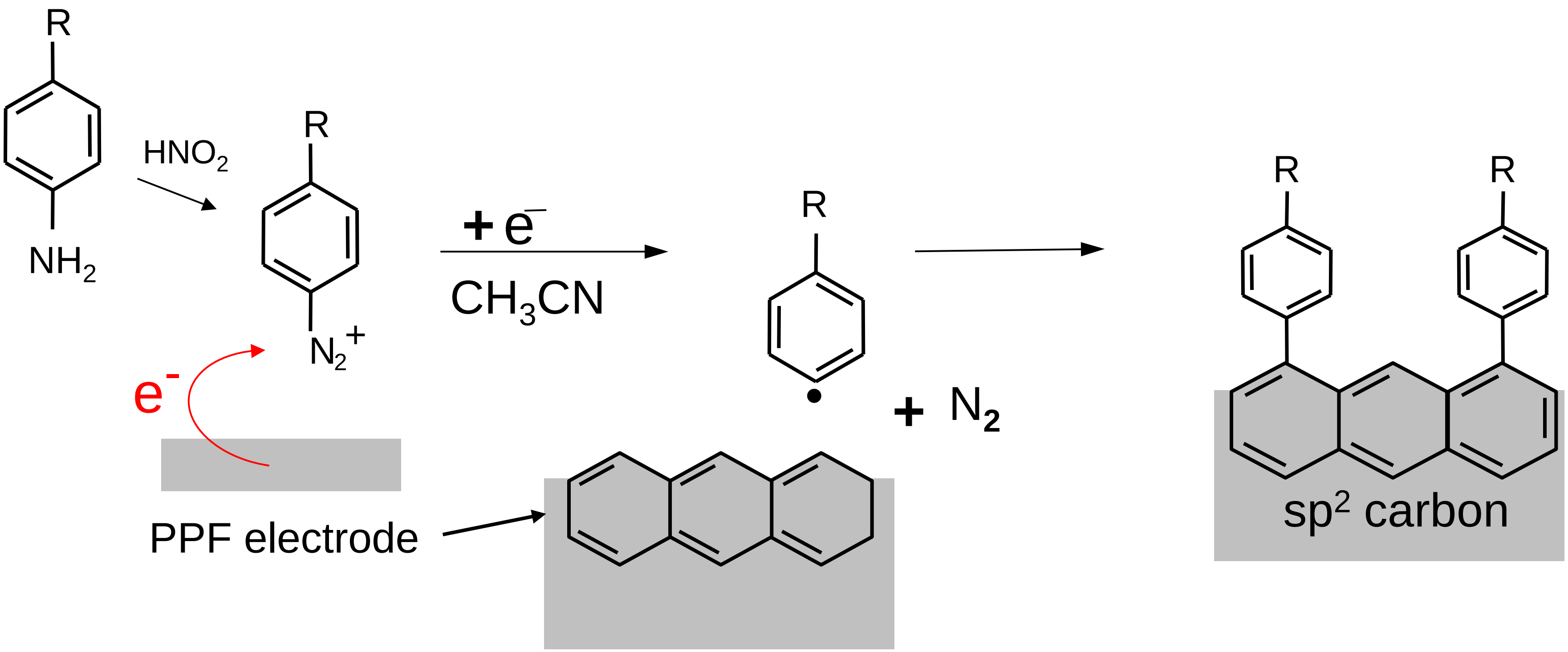
What happens when charge transfer distance is decreased to 1-25 nm, and electric fields may exceed 10^6 V/cm ?

Our substrate: Pyrolyzed Photoresist Films (PPF)



Kim, Song, Kinoshita, Madou, and White, *J. Electrochem. Soc.*, **1998**, 145, 2315
Ranganathan, McCreery, Majji, and Madou, *J. Electrochem. Soc.*, **2000**. 147, 277–282
Ranganathan, McCreery, *Anal. Chem***, 2001**, *73*, 893-900.

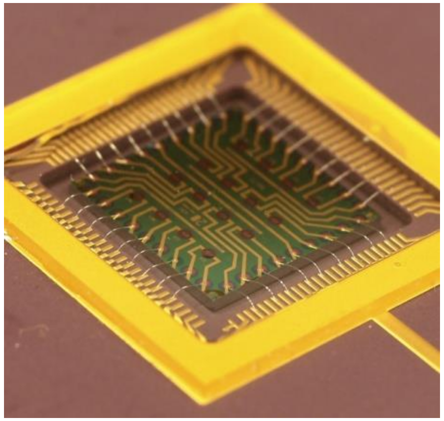
Surface modification via diazonium reduction:

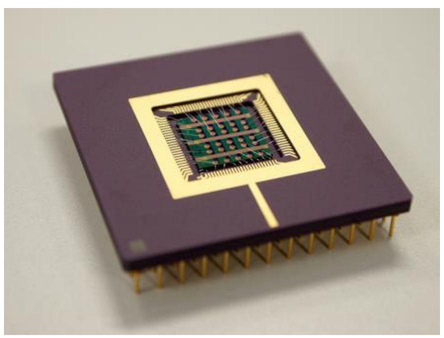


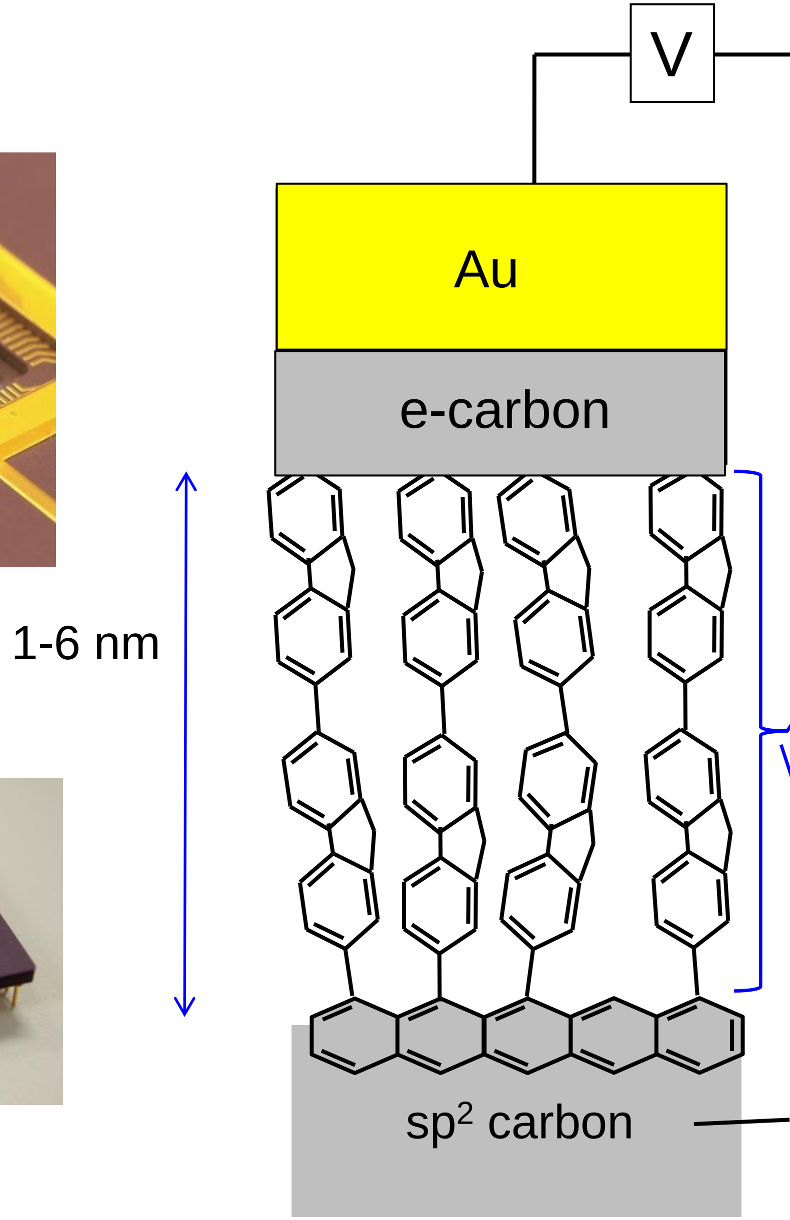
- surface bond stable to > 500 ^{o}C
- high coverage
- very low in pinholes
- prone to multilayer formation.

Delamar, M.; Hitmi, R.; Pinson, J.; Saveant, J. M.; *J. Am. Chem. Soc.* **1992**, *114*, 5883.
Liu, McCreery, *J. Am. Chem. Soc.*, **1995**, 117, 11254.
Belanger, Pinson, *Chem. Soc. Reviews* **2011**, 40, 3995

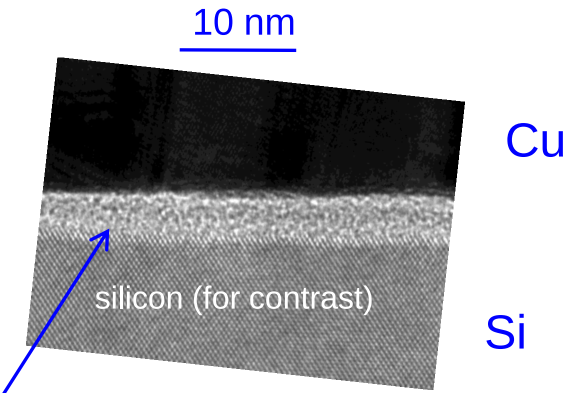
Packaged:

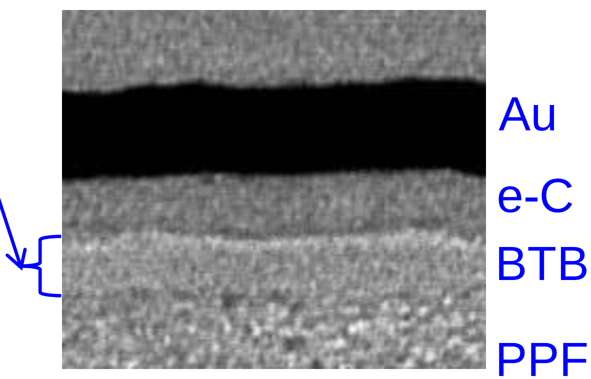






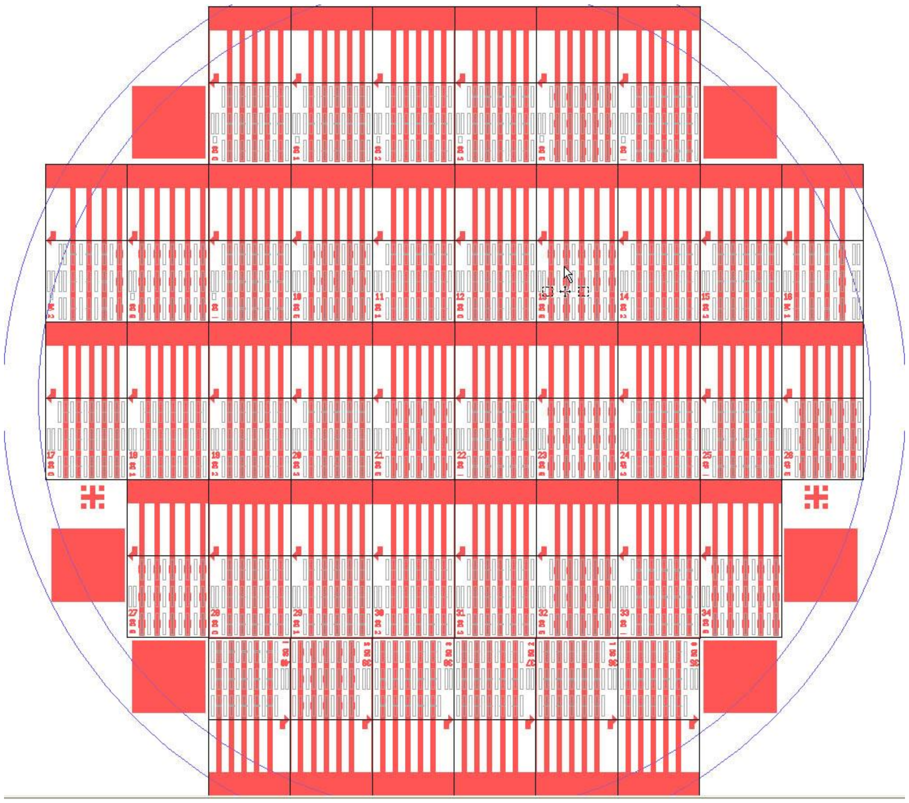
FIB/TEM:





Adv. Mater. ***2009***, 21, 4304
J. Phys. Chem. C ***2010,*** 114, 15806
J. Am. Chem. Soc. ***2011***, 133, 19168

Pyrolyzed Photoresist Film (PPF) microfabrication:



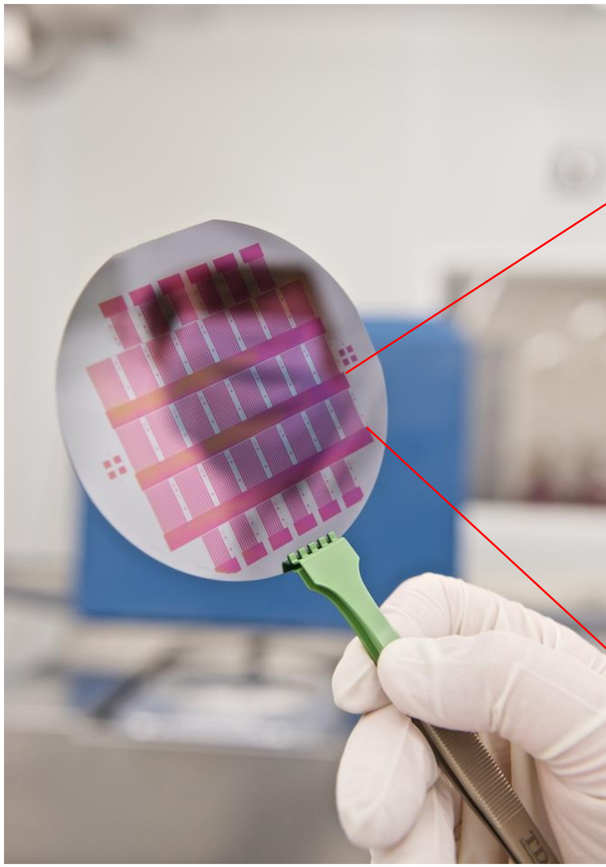
1. lithography

2. pyrolysis

100 mm

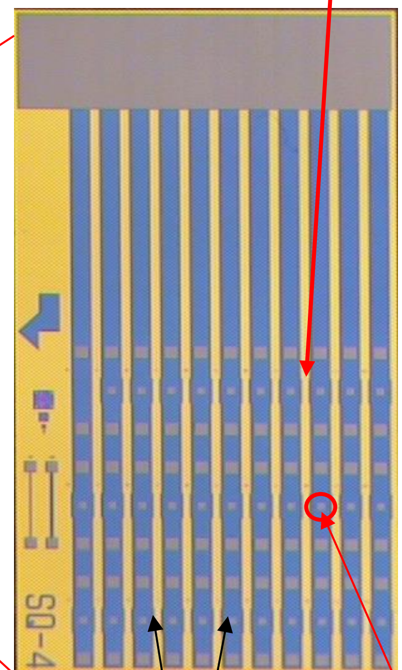
PPF structure and conductivity similar to glassy carbon
roughness < 0.5 nm rms by AFM

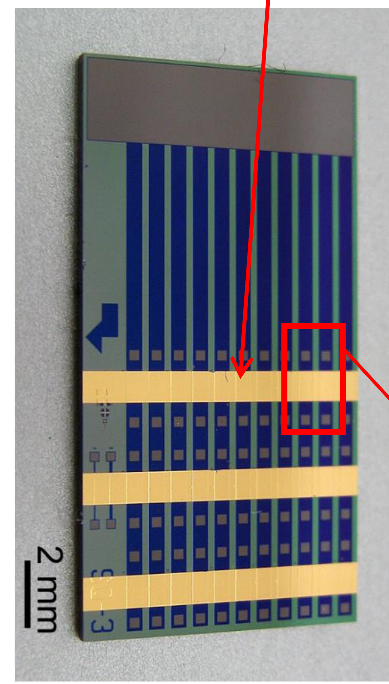
PPF Echip 4” wafer



molecules attached to PPF by electrochemical reduction of diazonium ions

Cu/Au deposited through shadow mask





next slide

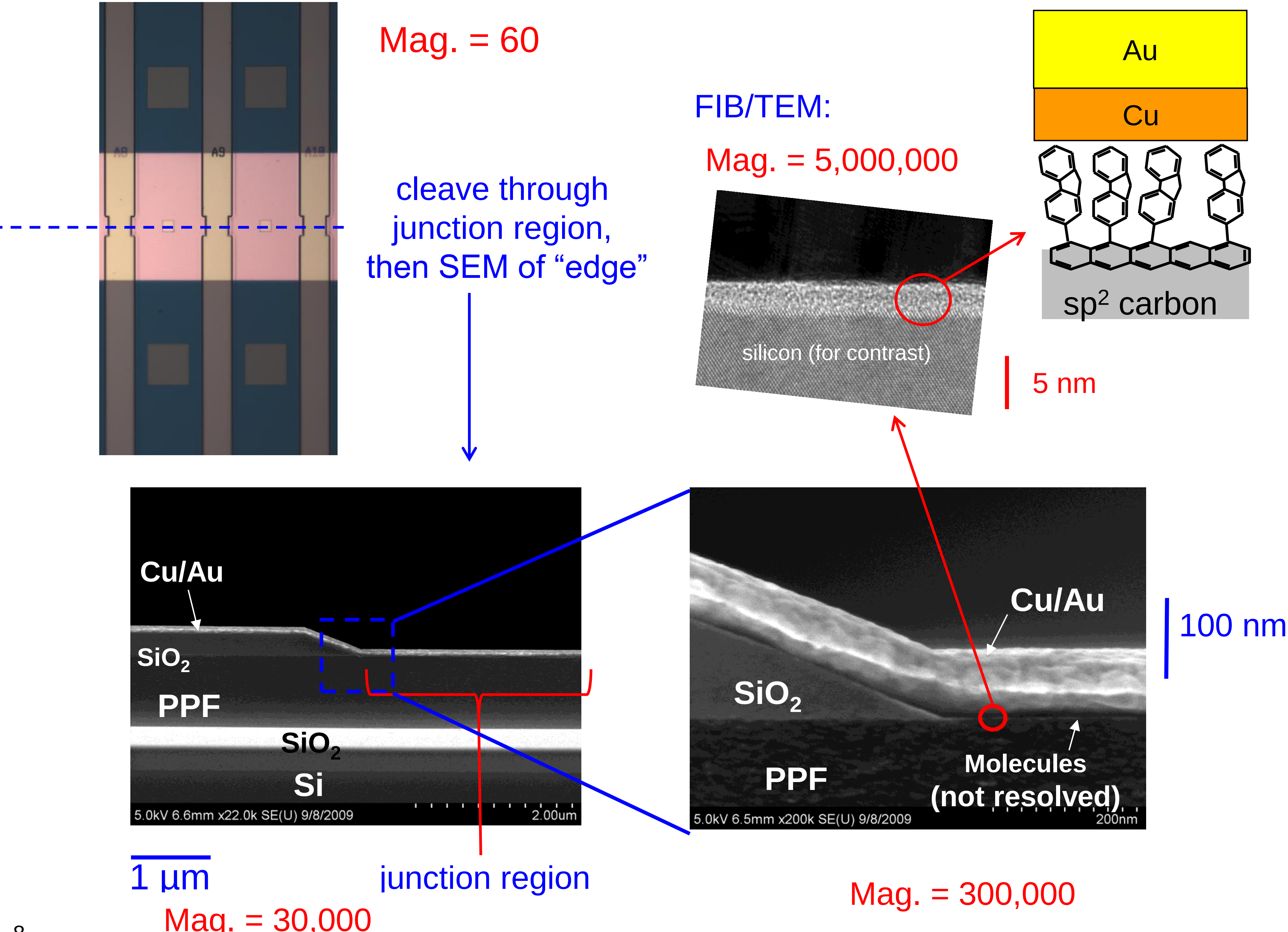
PPF leads

Junction

Magnification = 1

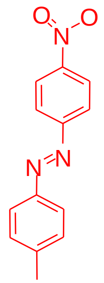
Mag. = 10

Mag. = 10

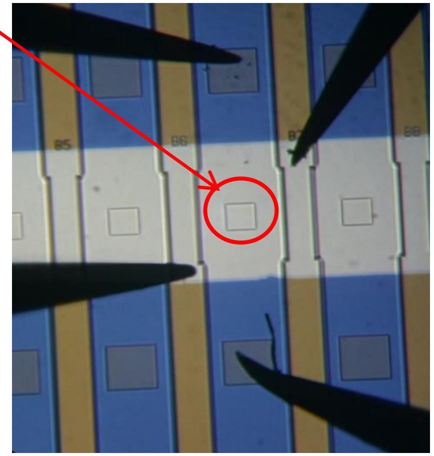


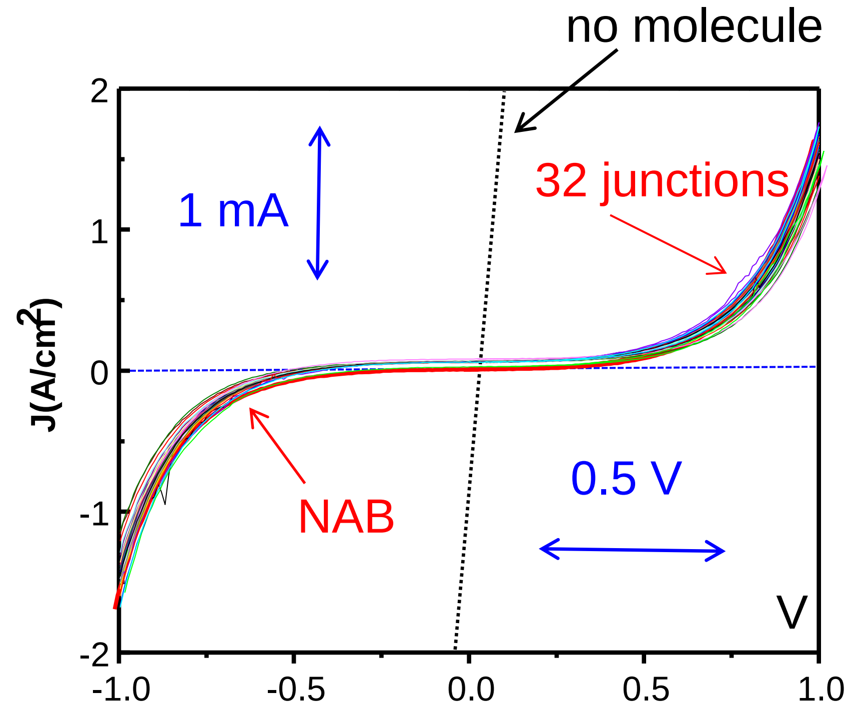
Mag. = 60
A8
A9
A10
cleave through
junction region,
then SEM of "edge"
FIB/TEM:
Mag. = 5,000,000
silicon (for contrast)
5 nm
Au
Cu
sp^2 carbon
Cu/Au
SiO_2
PPF
SiO_2
Si
5.0kV 6.6mm x22.0k SE(U) 9/8/2009
2.00um
1 µm
Mag. = 30,000
junction region
Cu/Au
SiO_2
PPF
Molecules
(not resolved)
5.0kV 6.5mm x200k SE(U) 9/8/2009
200nm
100 nm
Mag. = 300,000

near Jasper, Alberta

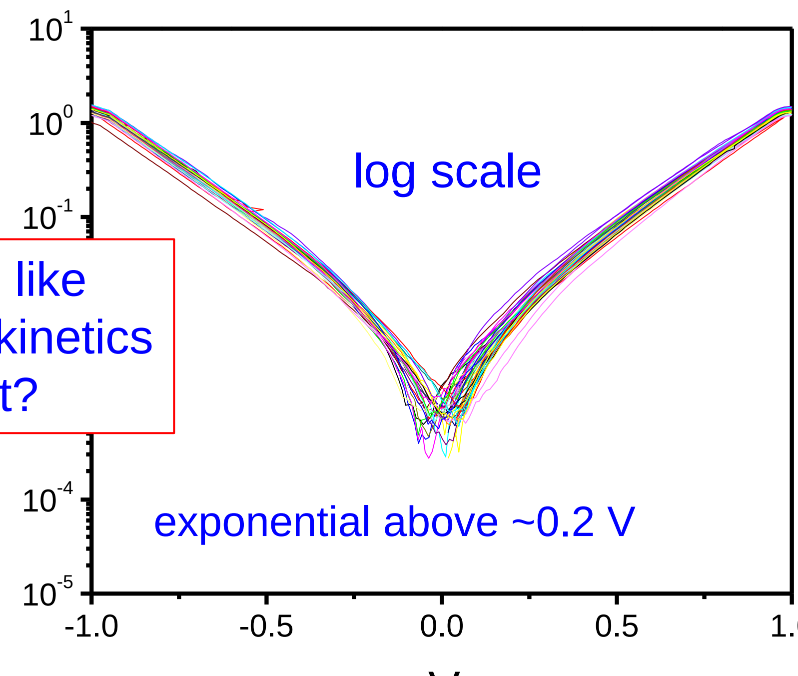


NAB
(nitroazobenzene)



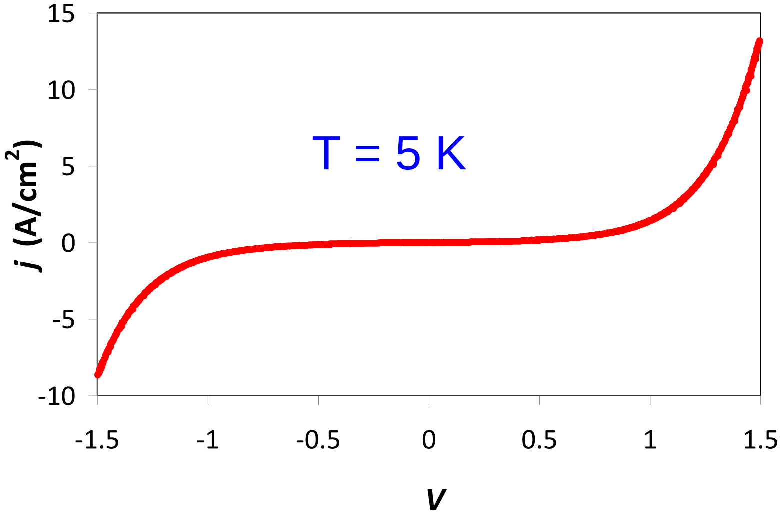


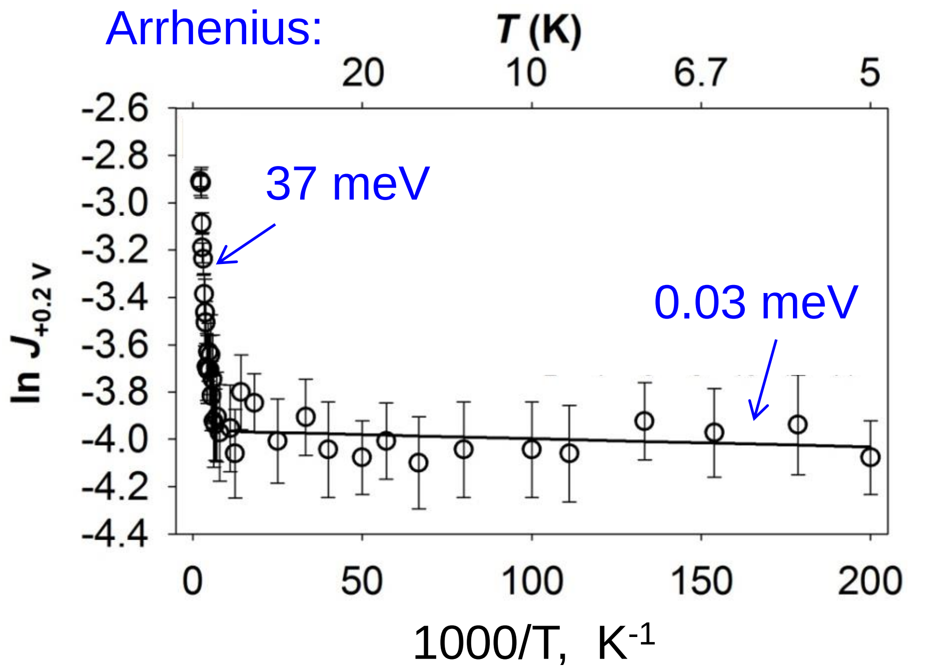
- frequency independent,
  0.01 to 10^5 Hz
- symmetric
- can scan > 10^9 cycles without change
- survived 150 °C for > 40 hrs

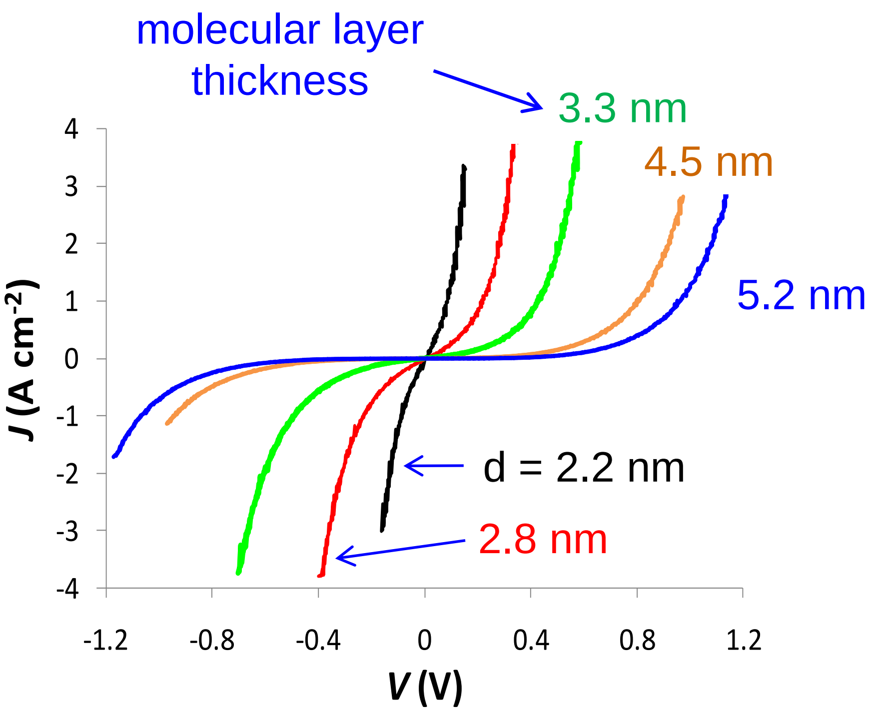


looks like
Marcus kinetics
Is it?

ACS Applied Materials & Interfaces ***2010,*** 2, 3693



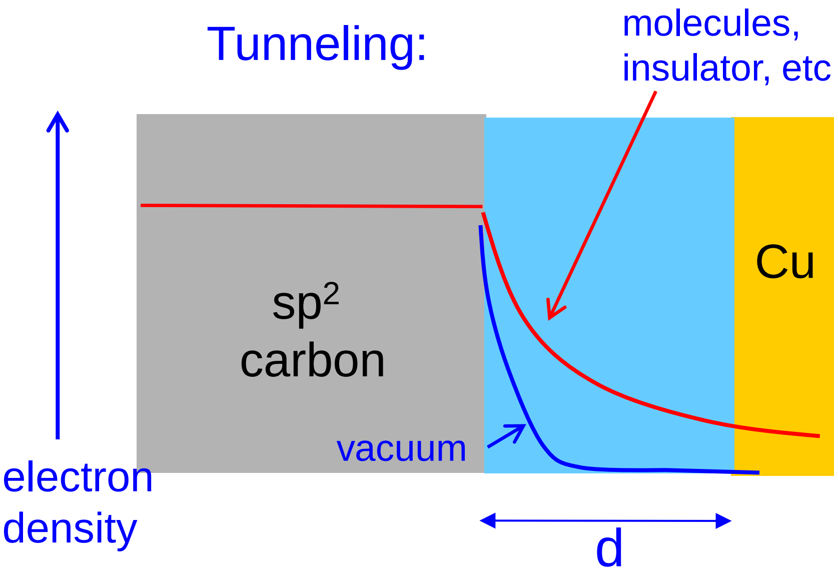




- not activated for T<200 K
- strong thickness dependence
- NOT activated electron transfer, so what is it?

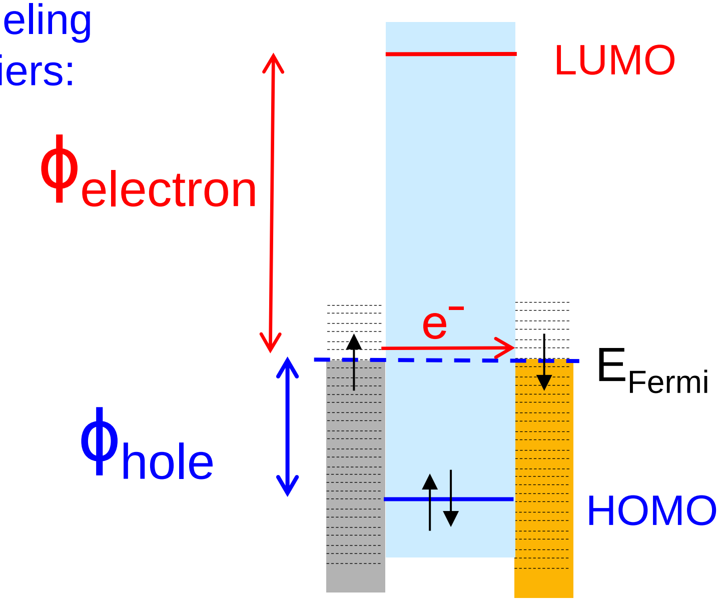
J. Phys. Chem C, **2010**, 114, 15806

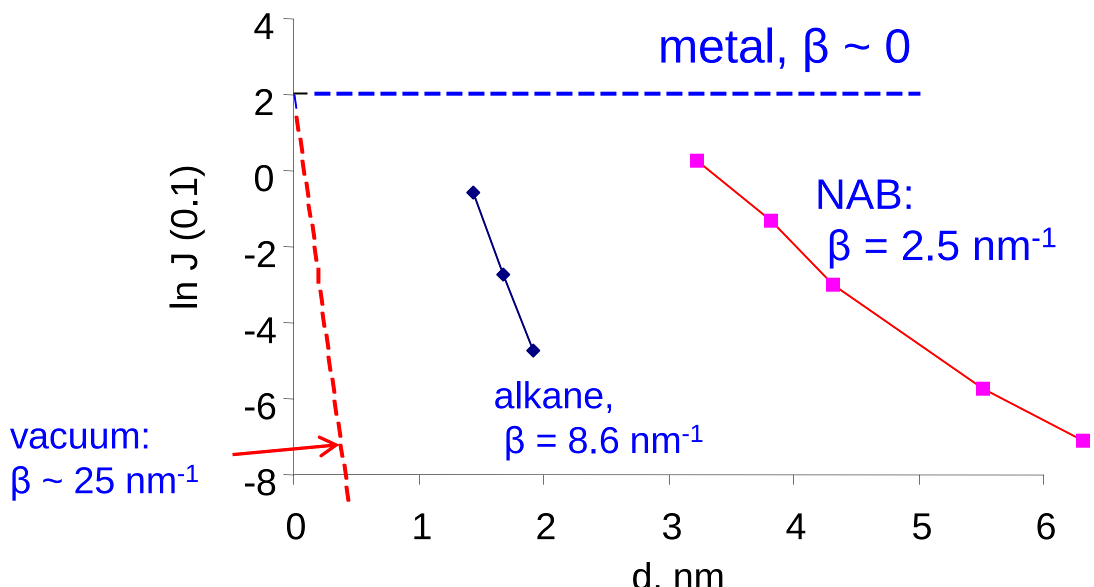
Tunneling:



$$J\ (A/cm^2) = K \exp(-\beta d)$$

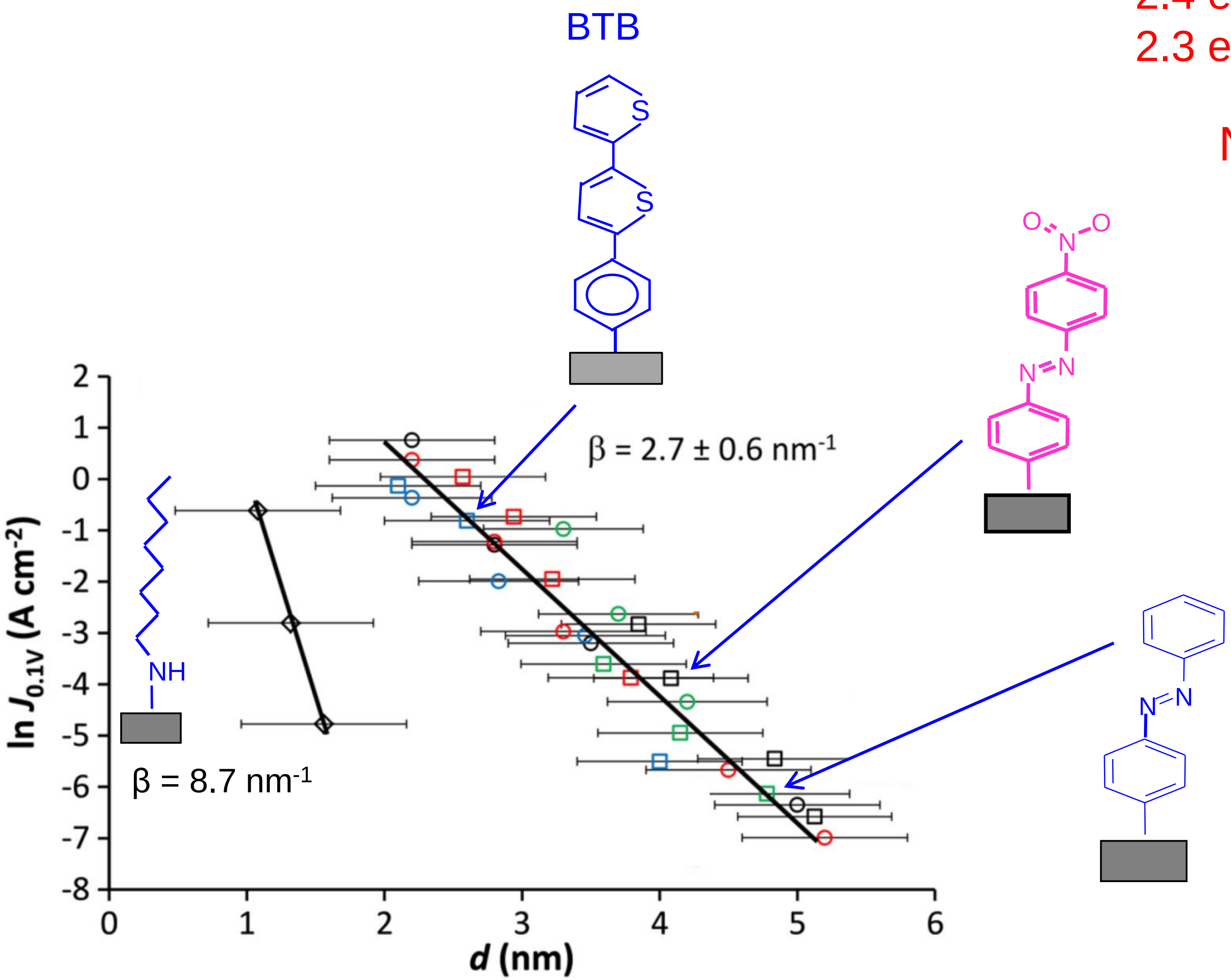
tunneling
barriers:





now, vary HOMO
and LUMO energies

More molecules:



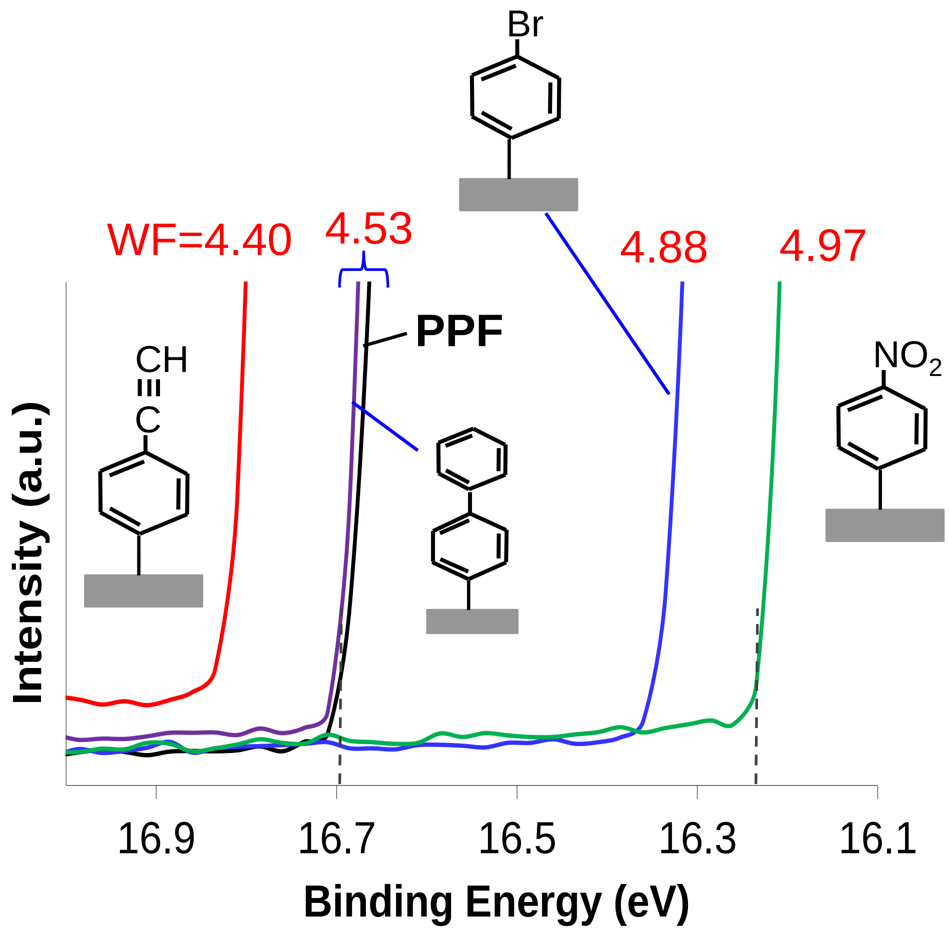
2.4 eV range of HOMOs,
2.3 eV range of LUMOs

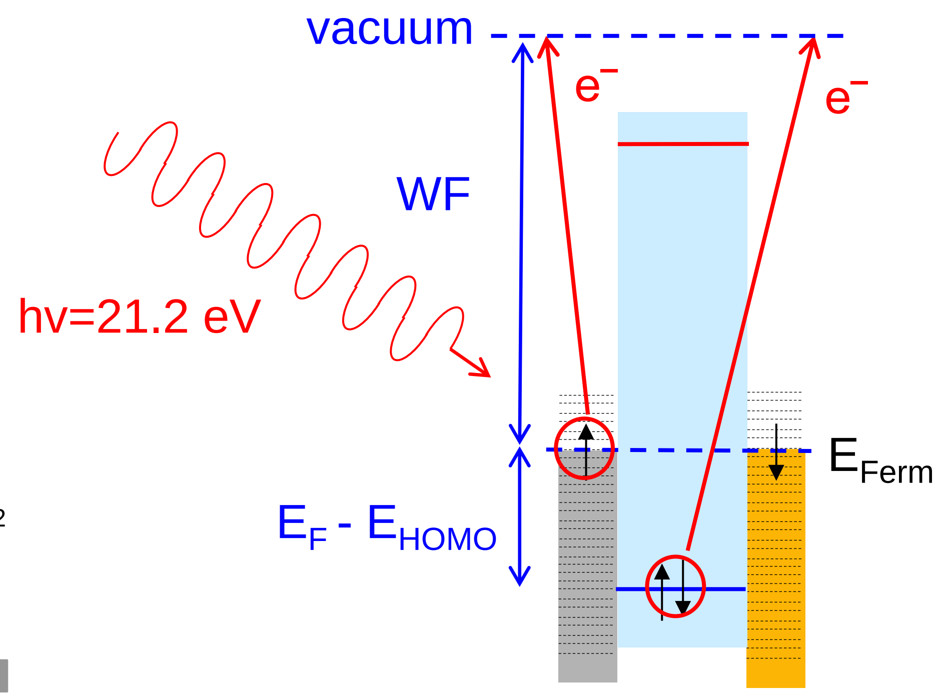
NO EFFECT!

also: biphenyl, nitrophenyl, ethynyl benzene, anthraquinone (9 molecules, >400 junctions)

Sayed, Fereiro, Yan, McCreery, Bergren; *PNAS* ***(2012)*** *109, 11498.*

Energy levels of PPF/molecule from Ultraviolet Photoelectron Spectroscopy:



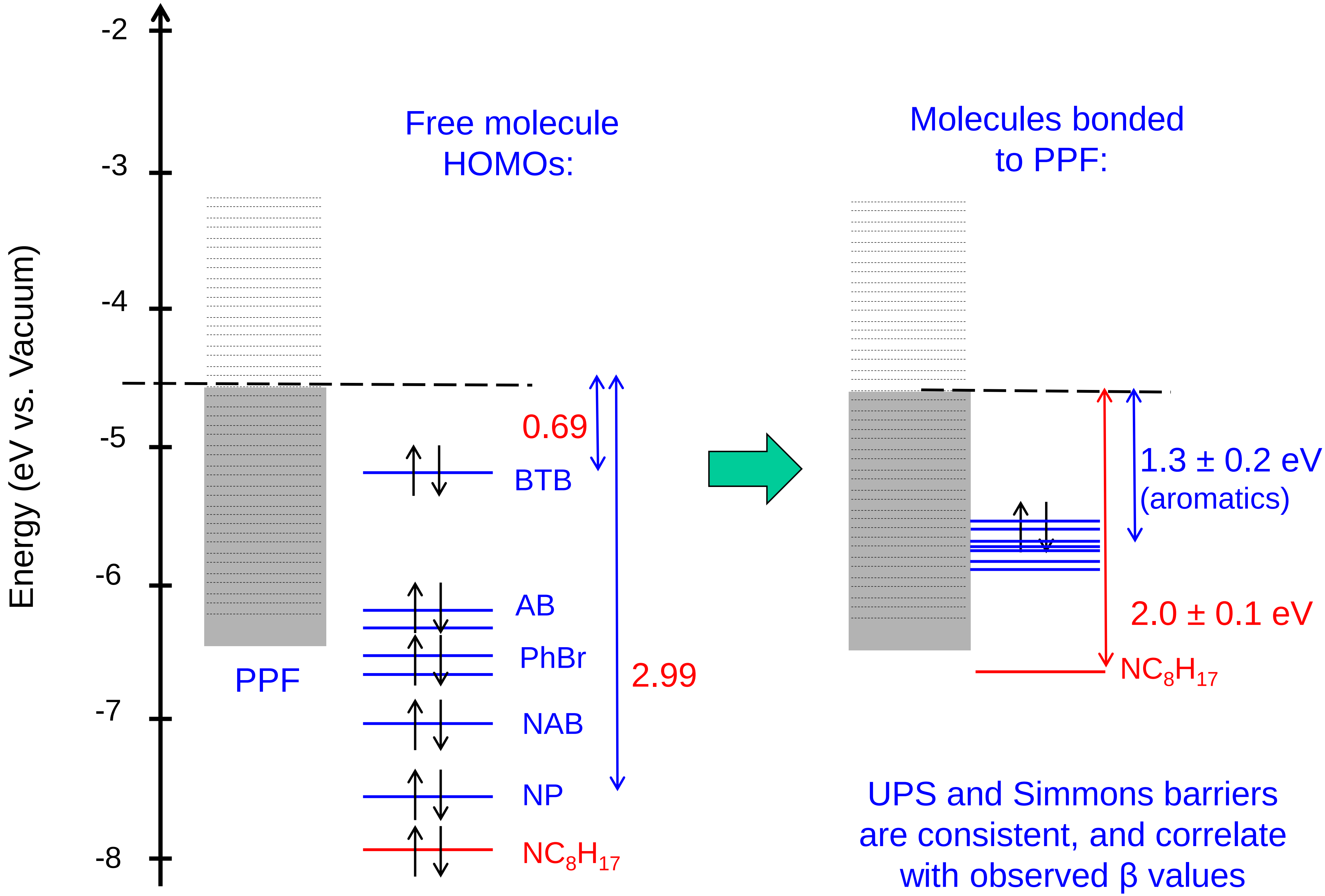


	WF, eV	E_F - E_{HOMO}*
PPF (bare)	4.53	
biphenyl	4.53	1.7
PhCCH	4.40	1.4
PhBr	4.88	1.5
PhNO2	4.97	1.4
NAB	5.07	1.2
C8	4.93	2

mean for 8 aromatics= 1.3 ± 0.2 eV

aliphatic= 2.0 ± 0.1 eV

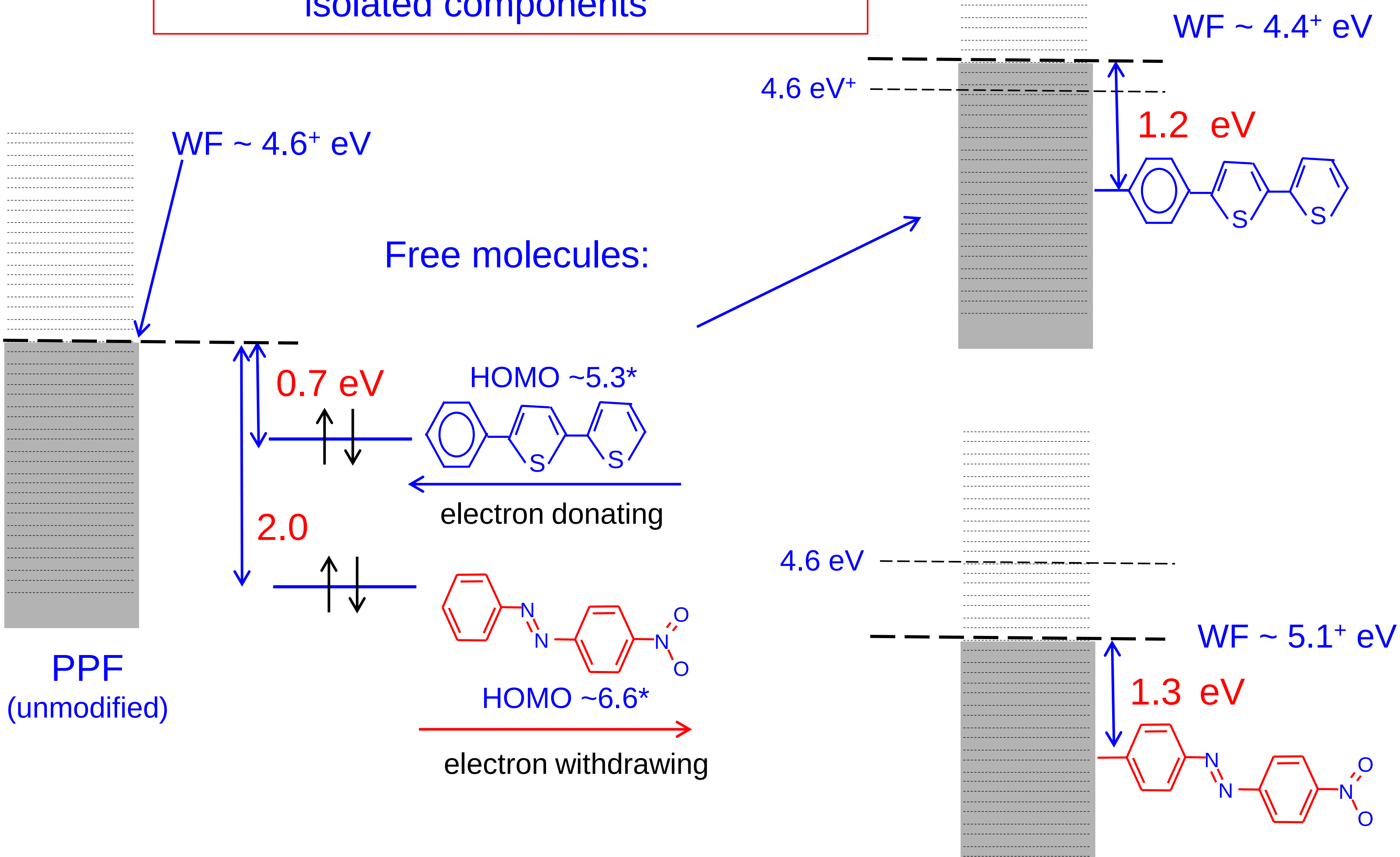
* method of Kim, Choi, Zhu, Frisbie, *JACS* 2011, 133, 19864



Sayed, Fereiro, Yan, RLM, Bergren, PNAS, 109, 11498 (2012)

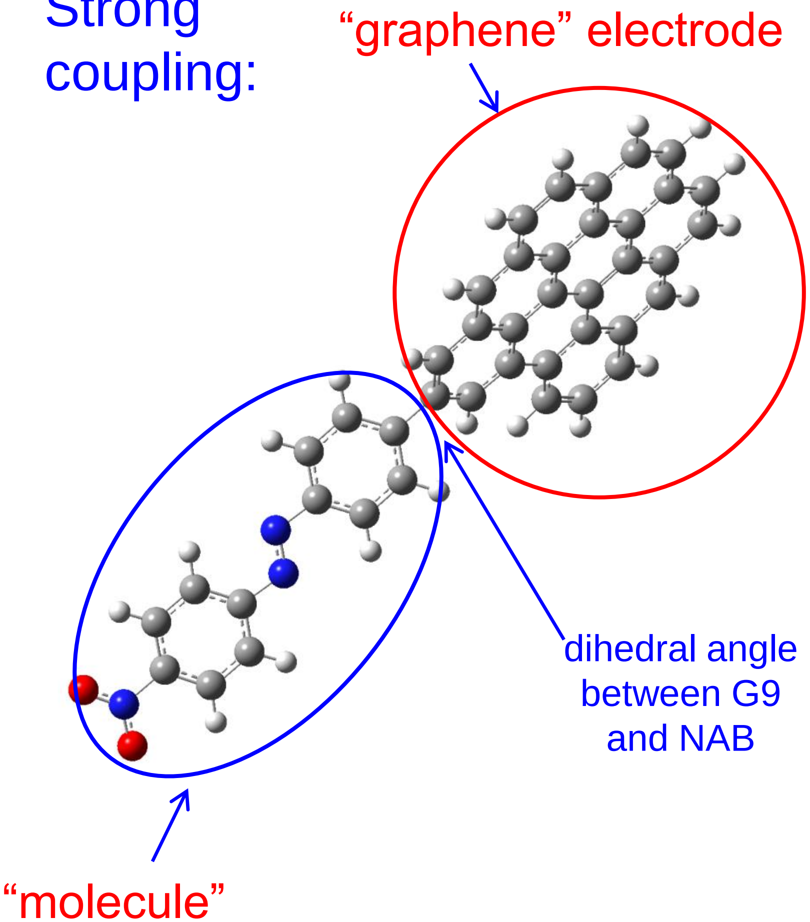
Why?

- “leveling” effect of strong coupling
- need to consider the system, not just isolated components



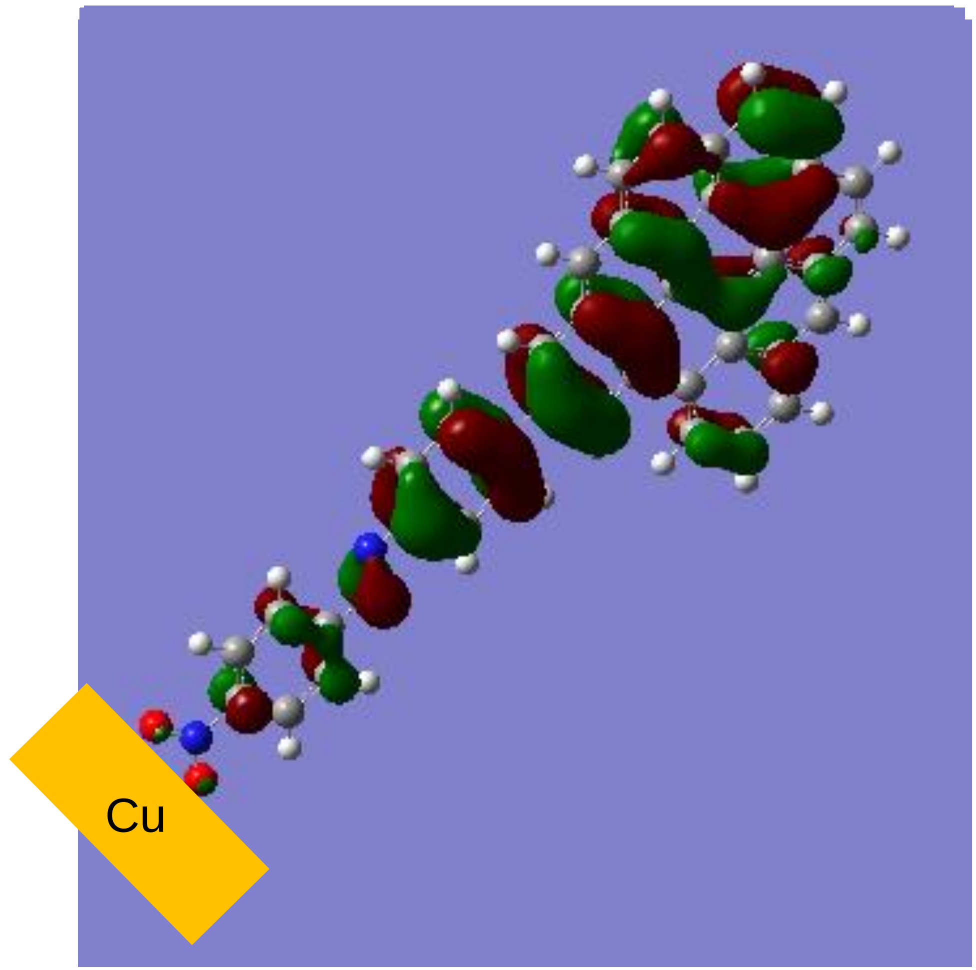
* B3LYP 6-31G(d)
\+ experimental

Strong coupling:



HOMO-1 orbital*

0^o dihedral

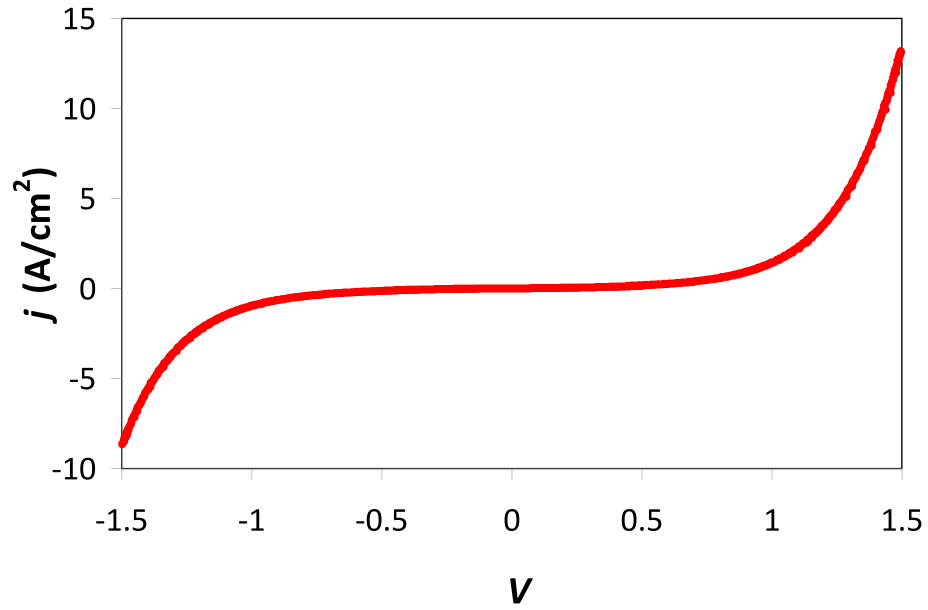


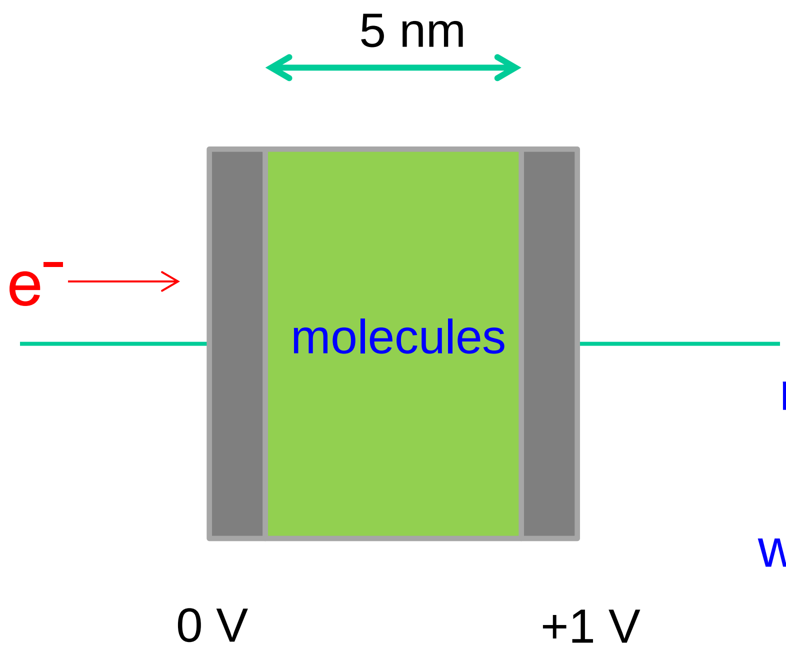
Substituents on molecule affect *both* HOMO and Fermi levels in “strong coupling” limit

Where does the electrode stop and the molecule begin?

*Gaussian ‘03, B3LYP/6-31G(d)

Something special about molecular tunnel junctions:



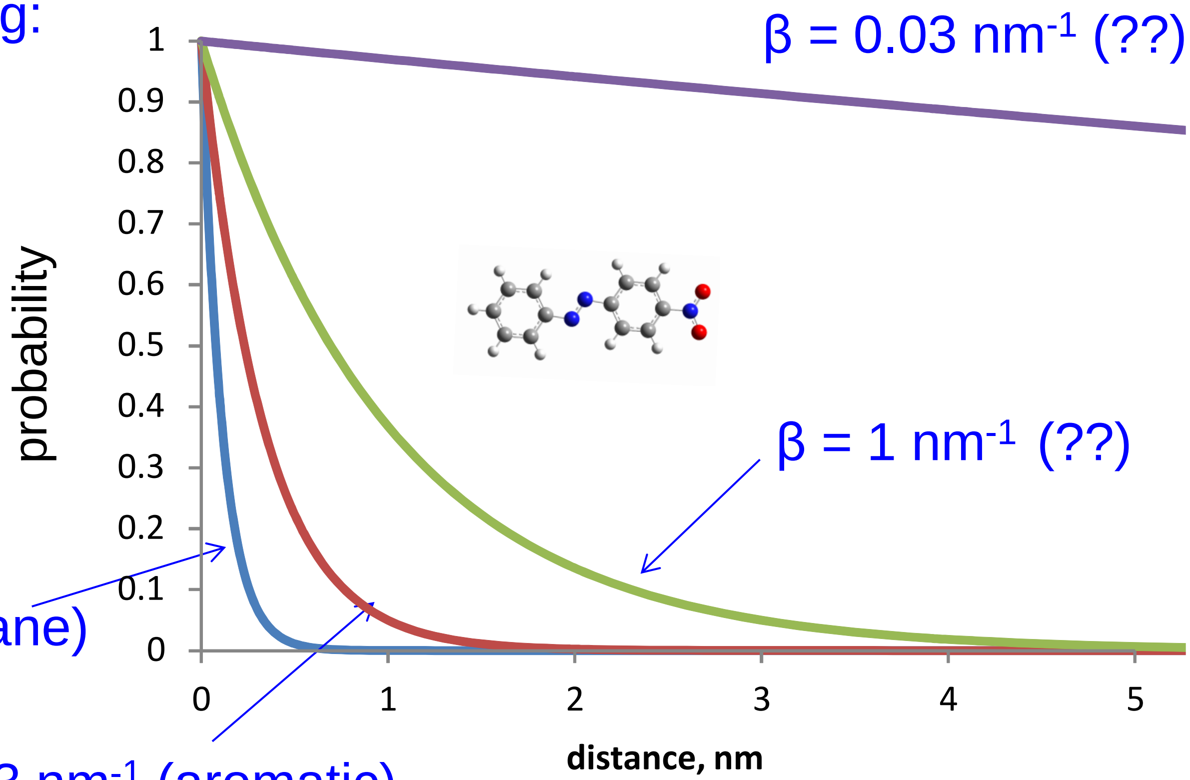


electron transit time ≈ 15 fsec
(15×10^{-15} seconds)

maximum frequency > 10,000 GHz

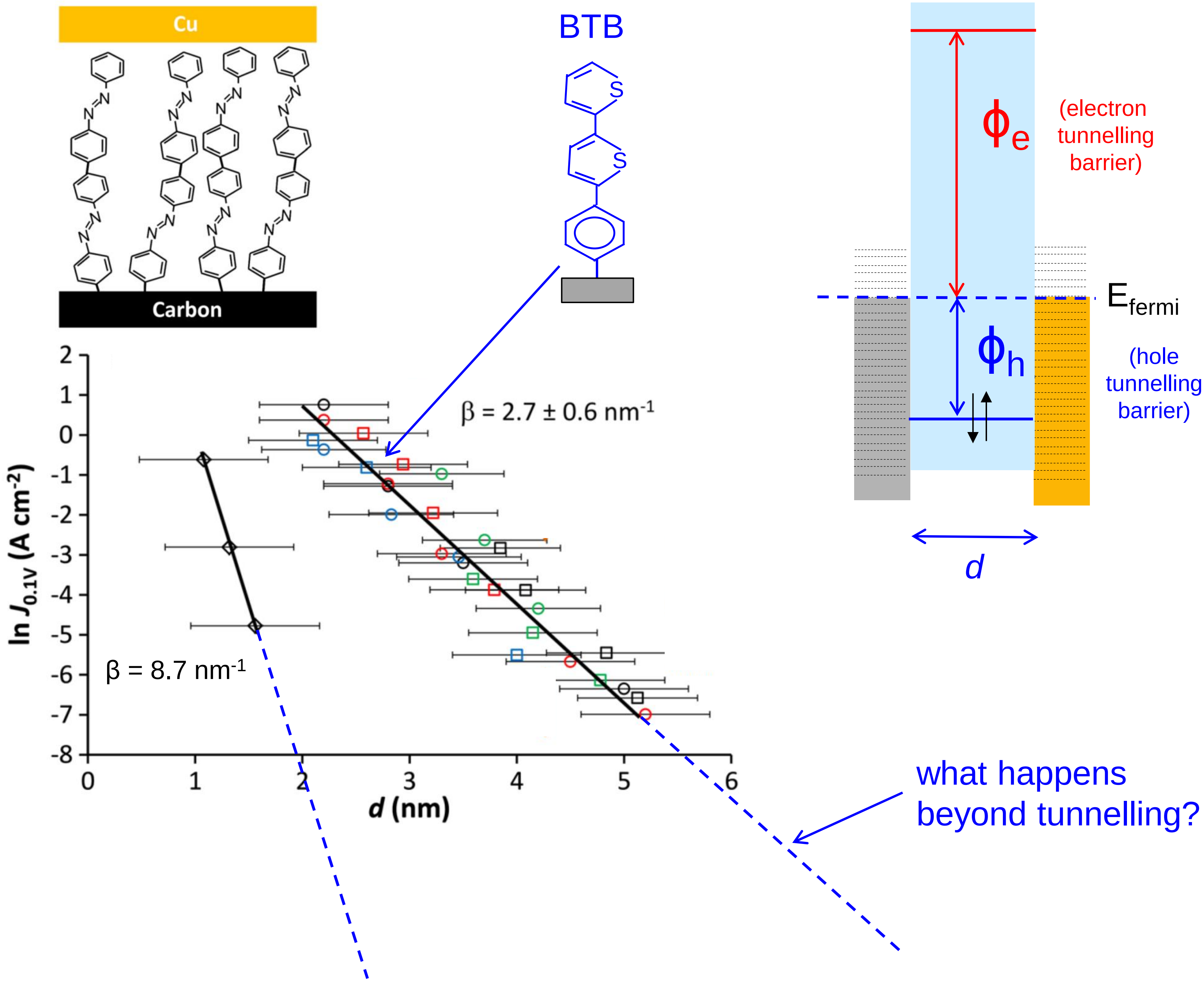
whatever we can do with tunnel junctions should be VERY fast a problem with tunneling:

$$J\ (A/cm^2) = K \exp(-\beta d)$$



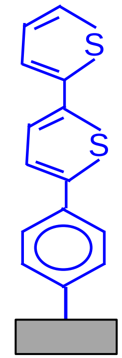
we need to seriously reduce β if molecular electronics is to be broadly practical

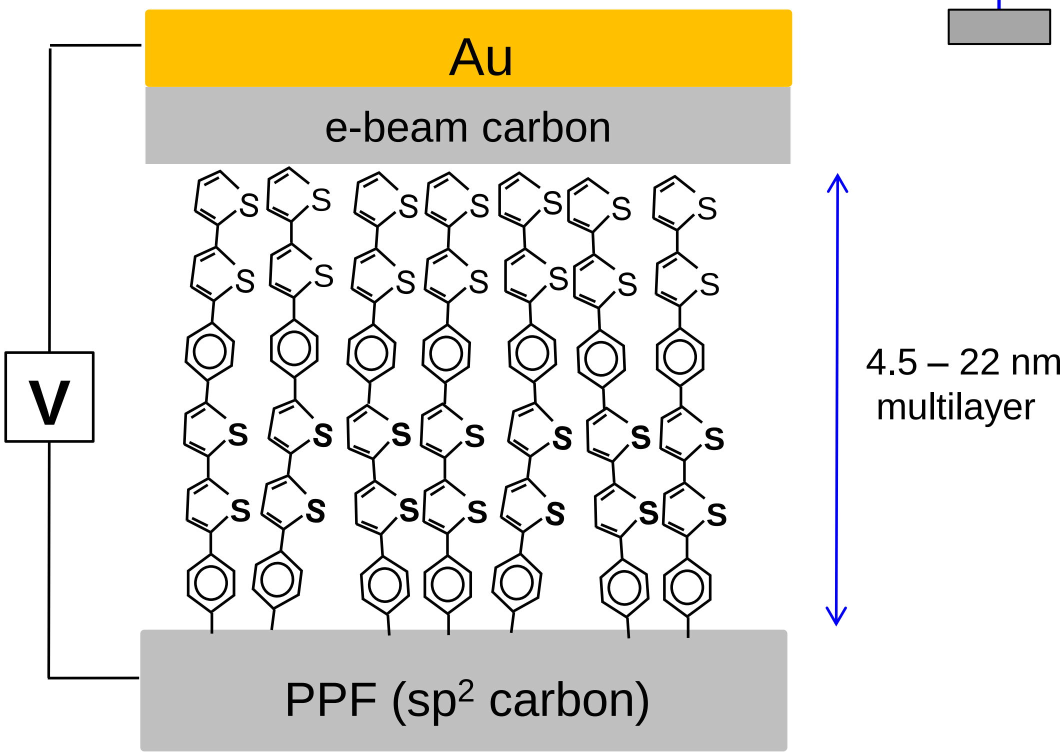
so far, we are really doing “barrier” electronics

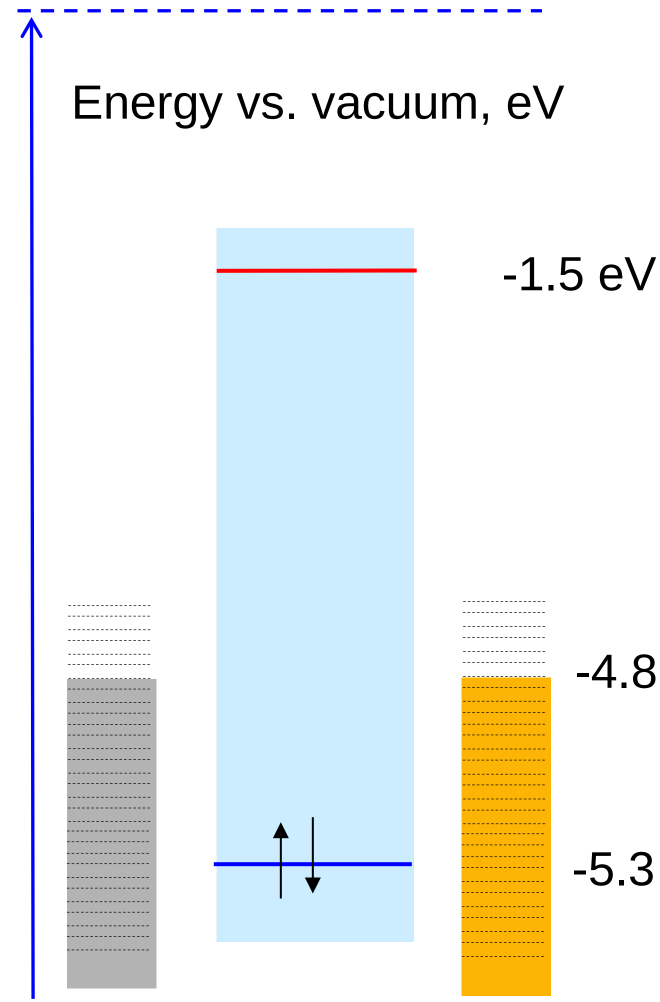


Cu
Carbon
BTB
S
S
β = 2.7 ± 0.6 nm-1
β = 8.7 nm-1
ln J0.1V (A cm-2)
d (nm)
ϕe
(electron tunnelling barrier)
Efermi
ϕh
(hole tunnelling barrier)
d
what happens beyond tunnelling?

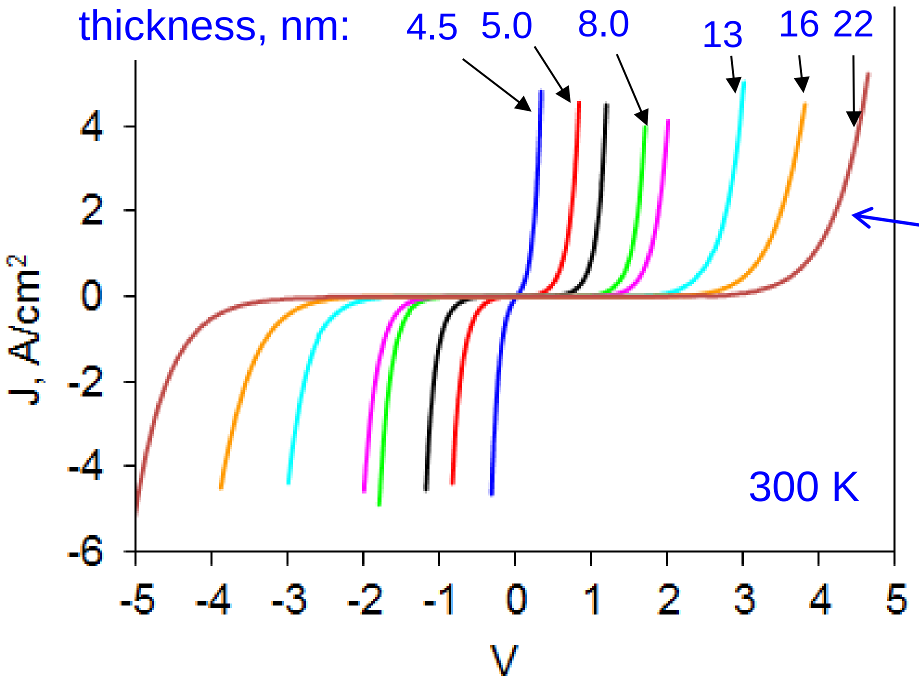
BTB (bis-thienyl benzene) in “all-carbon” junction





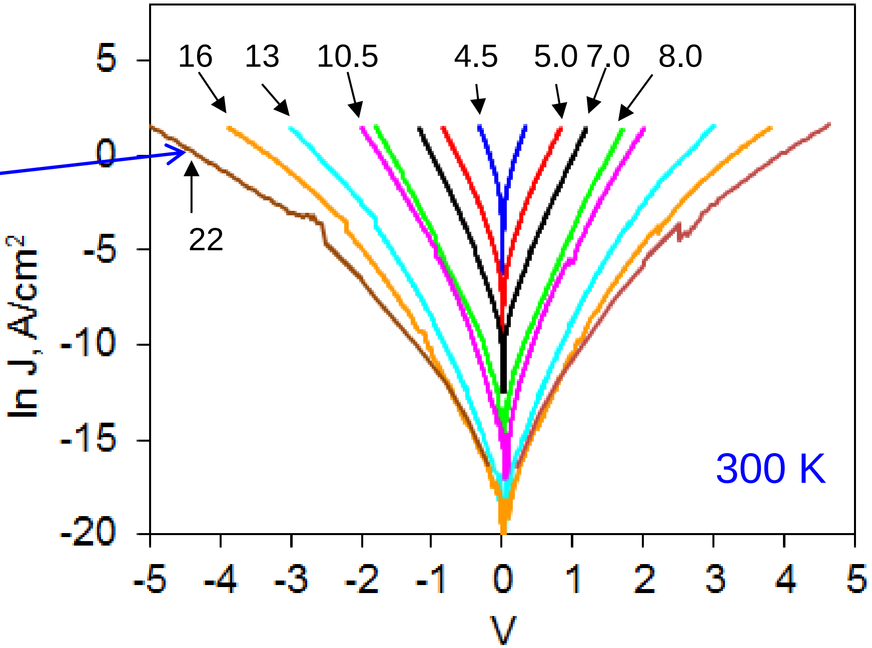


collaboration with: Maria Luisa Della Rocca, Pascal Martin, Philippe Lafarge, Jean-Christophe Lacroix, University of Paris

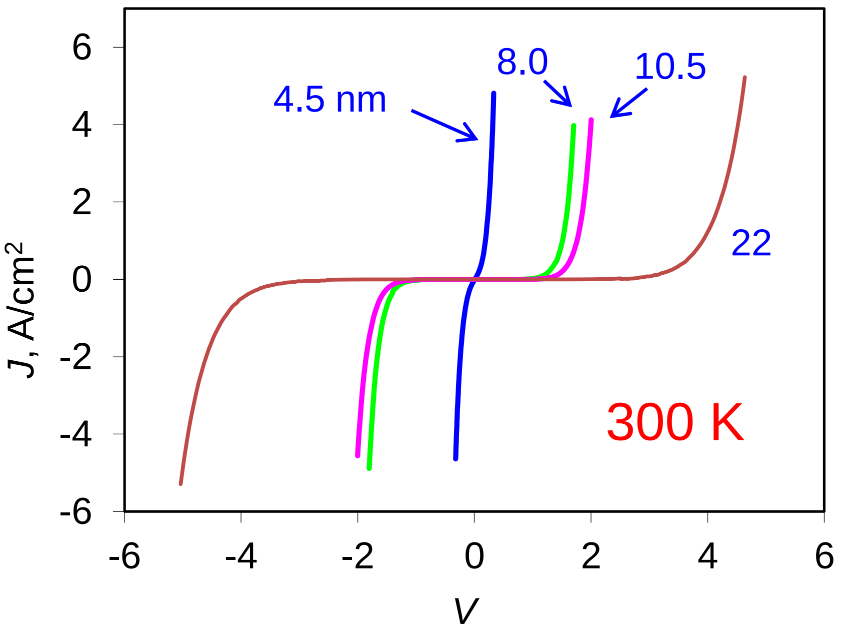


tunnelling? unlikely across 22 nm

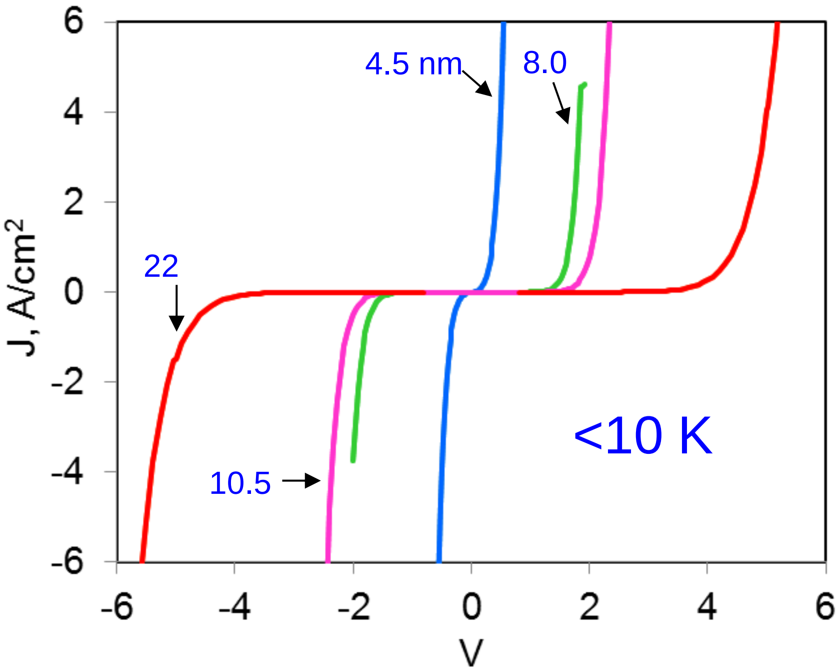
note curvature, not simple exponential



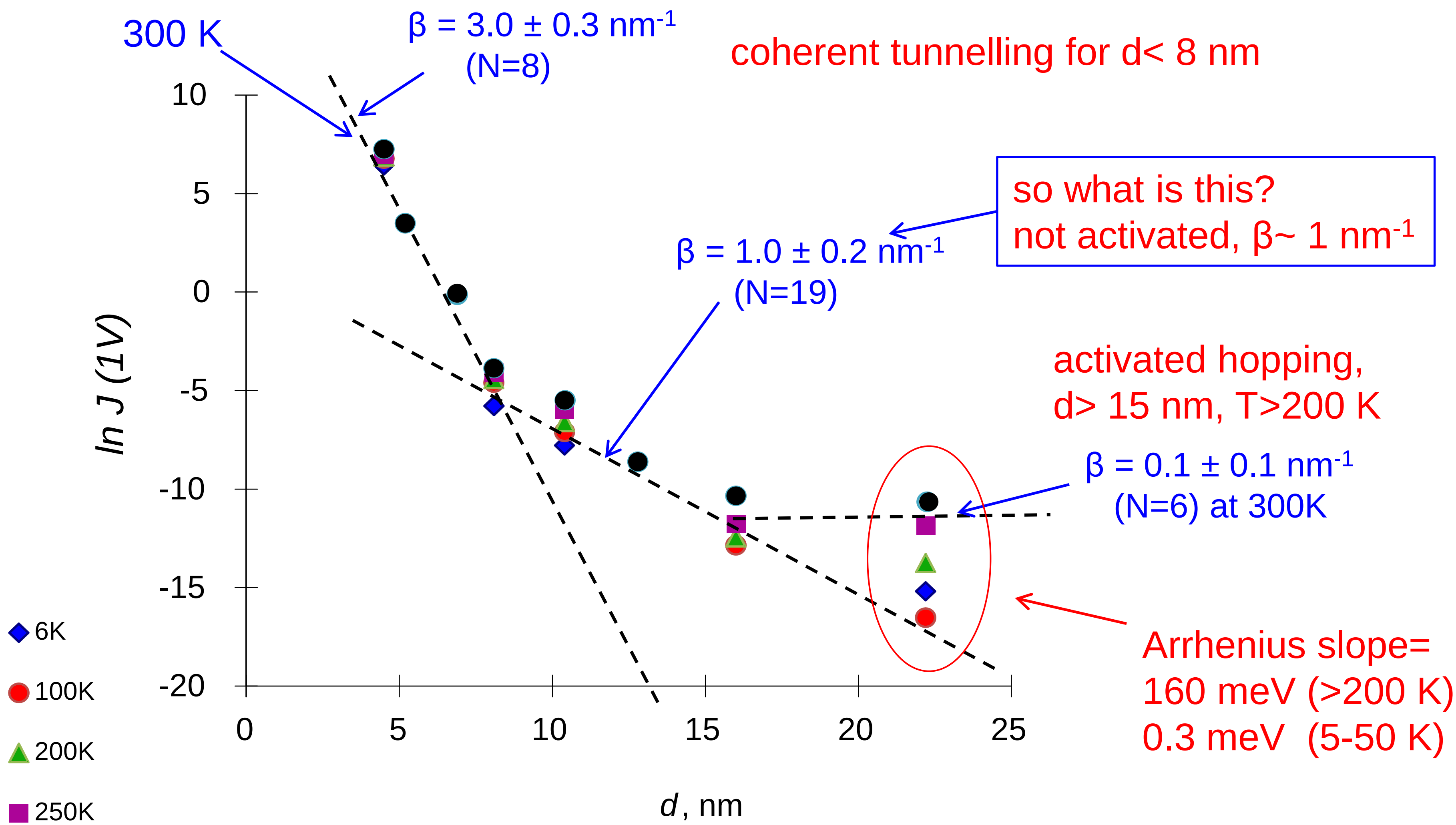
conventional wisdom:
activated "hopping" by redox exchange for d > 5-10 nm



weakly activated, if at all,
not consistent with redox exchange



What about β, the attenuation coefficient ?



(bulk polythiophene:
130 – 280 meV)

Haijun Yan, et al. *PNAS*, 110, 5326 (2013) the usual suspects:

Fowler Nordheim (field emission)
variable range hopping
Schottky emission (i.e. thermionic)
redox hopping
space charge limited conduction

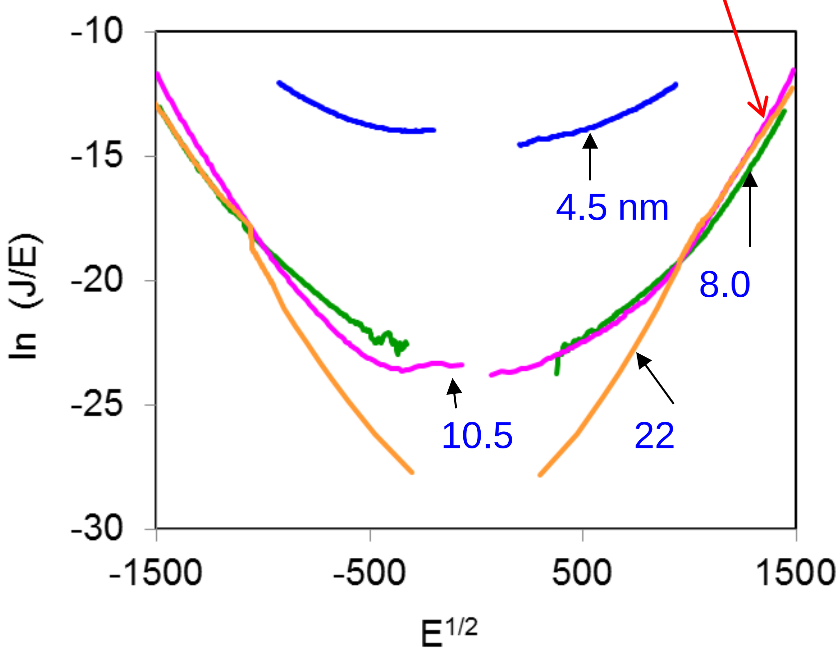
characteristic plot:

linear lnJ vs 1/E (E= electric field)
linear lnJ vs $T^{-1/2}$ or $T^{-1/4}$
linear lnJ vs 1/T
linear ln J vs 1/T
linear J vs V^2

Poole-Frenkel transport between "traps"   linear ln (J/E) vs $E^{1/2}$

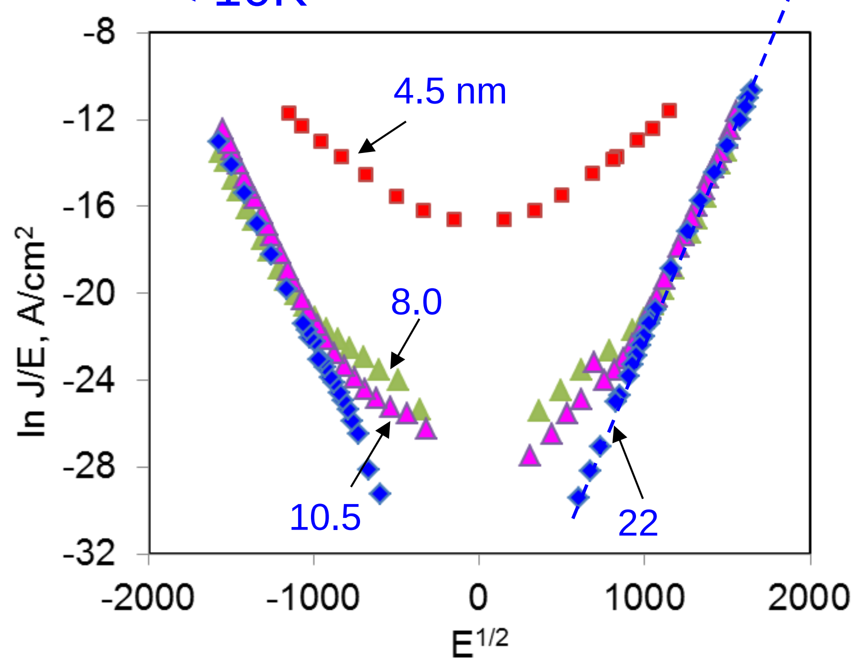
(note: controlled by electric field, not thickness. certainly NOT tunneling)

300 K

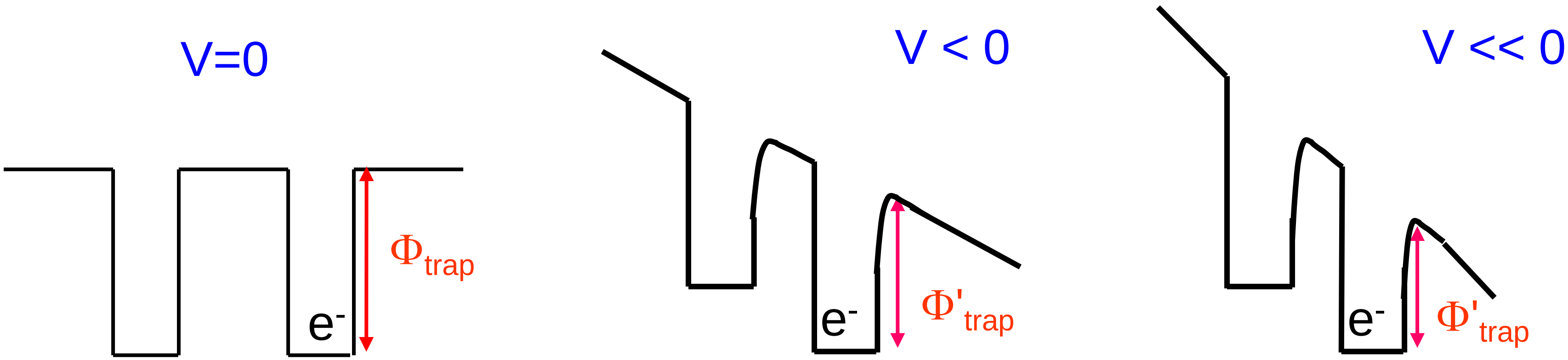


R^2 = 0.9989

< 10K



Poole-Frenkel transport between "coulombic traps":



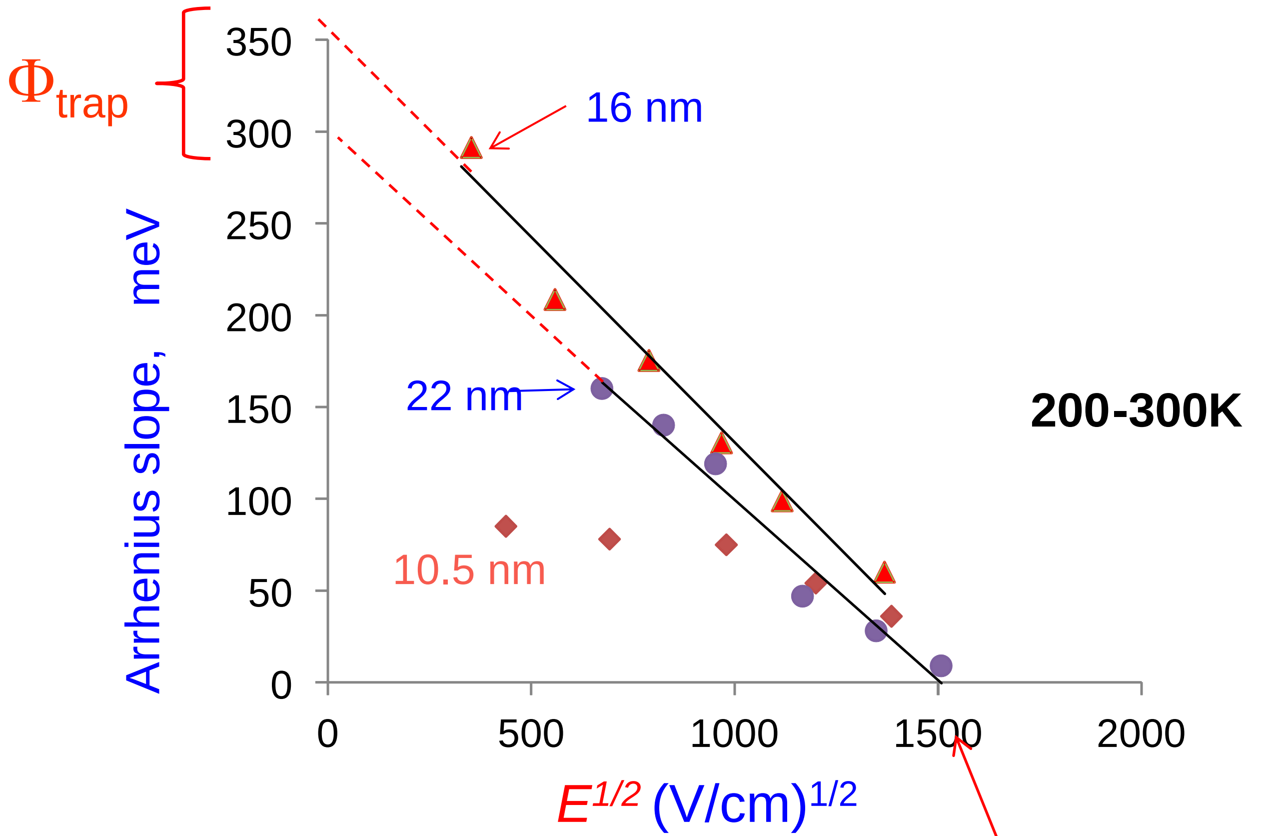
trap depth decreases
with increasing electric field

$$J_{PF} = q n_0 \mu E \exp\left[-\frac{q}{kT}\left(\phi_{trap} - \sqrt{\frac{qE}{\pi\varepsilon}}\right)\right]$$

$$\text{Arrhenius slope (ln J vs 1/T)} = \left[\phi_{trap} - \left(\frac{q}{\pi\varepsilon}\right)^{1/2} E^{1/2}\right]$$

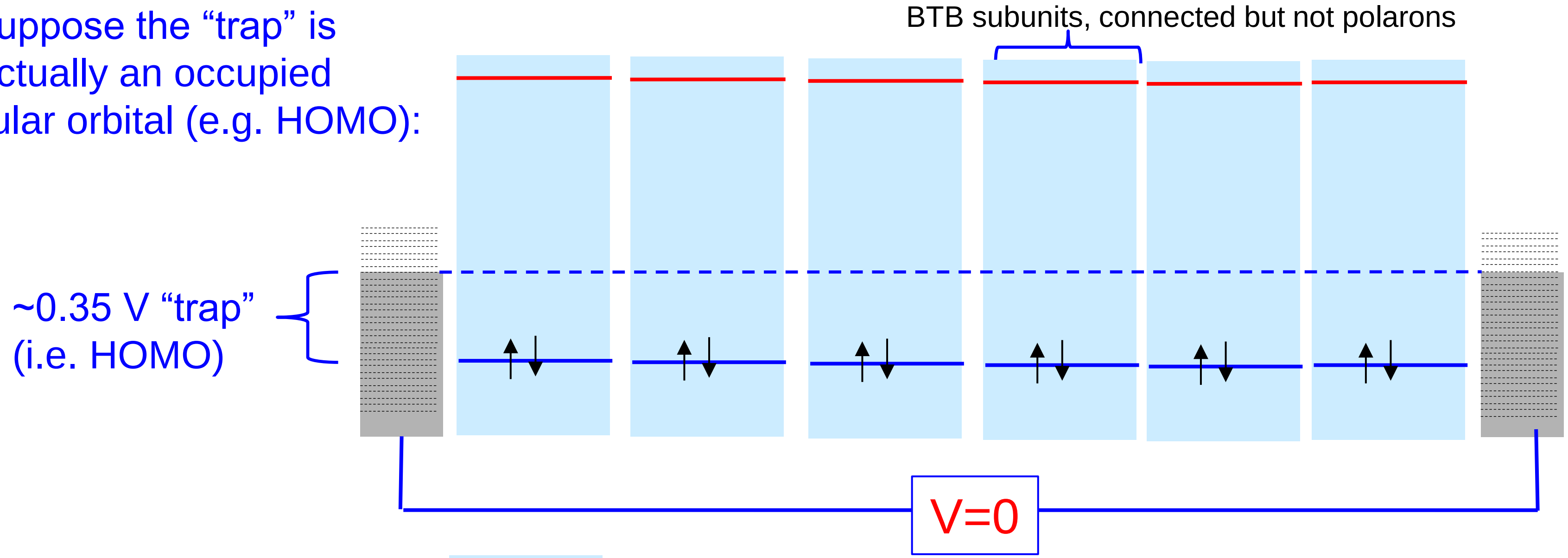
note: a field-dependent "activation" barrier

Arrhenius slope (ln J vs 1/T) = $\phi_{trap} - \left(\frac{q}{\pi\varepsilon}\right)^{1/2} E^{1/2}$



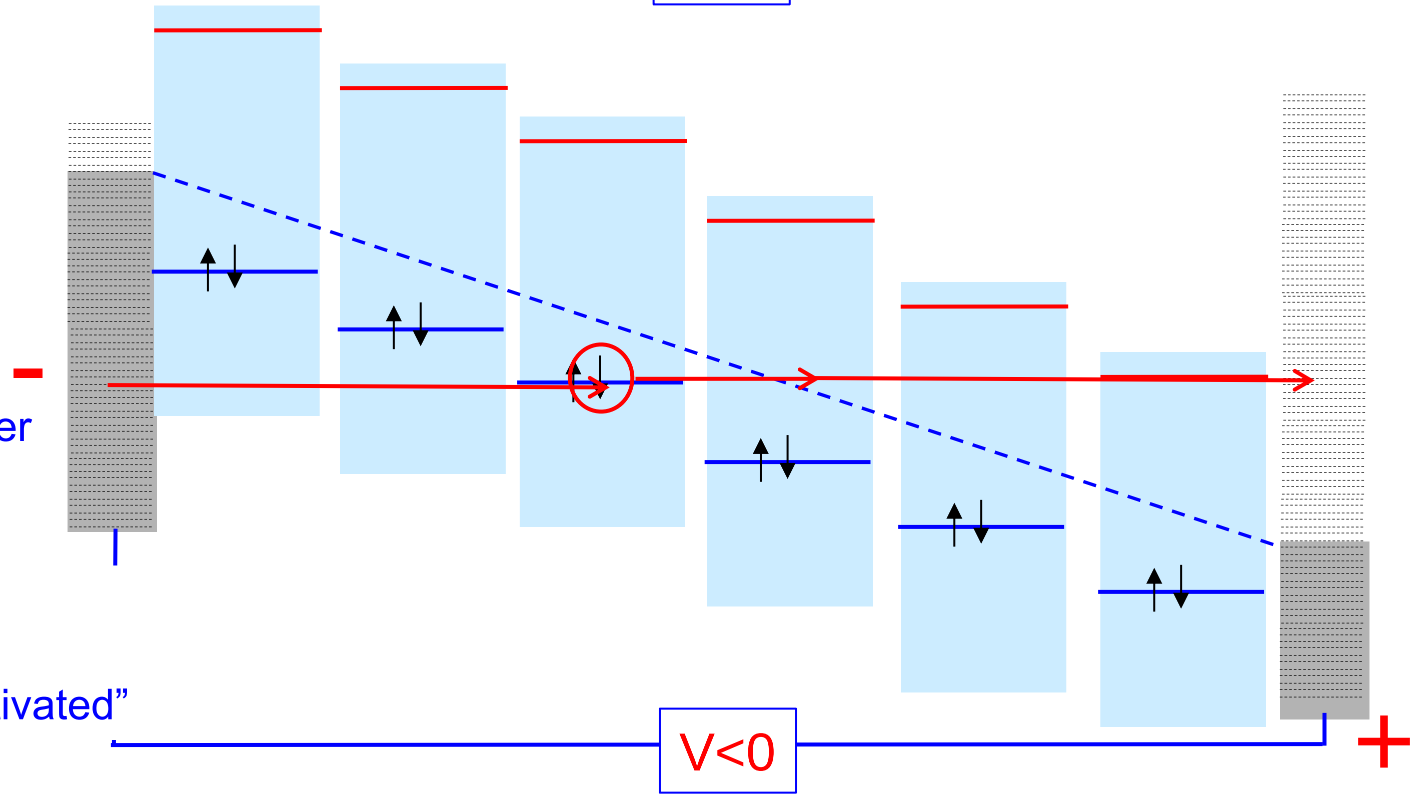
activation barrier → 0 at high field

Suppose the "trap" is actually an occupied molecular orbital (e.g. HOMO):



"Molecular field ionization"

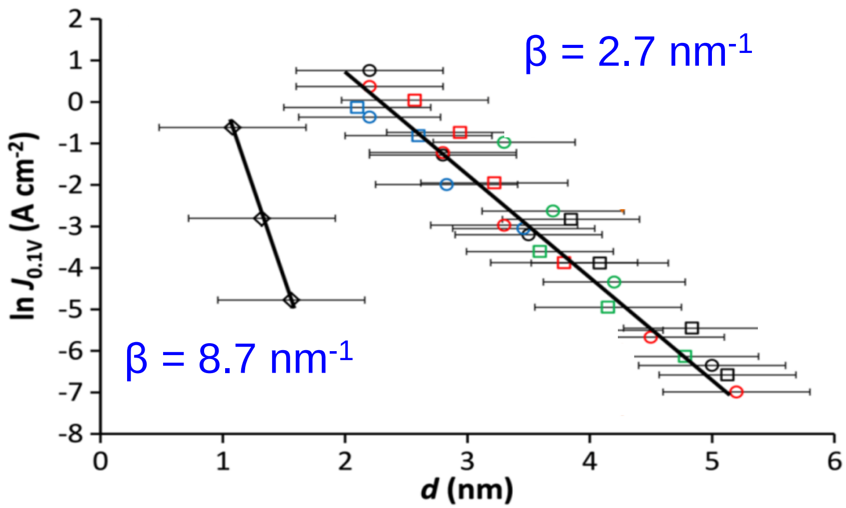
Note: field ionization in gas phase occurs at ~10^7 V/cm; our field is ~10^6 V/cm, but "trap" is much shallower



A bit like "dry electro-chemistry", but without a double layer and not "activated"

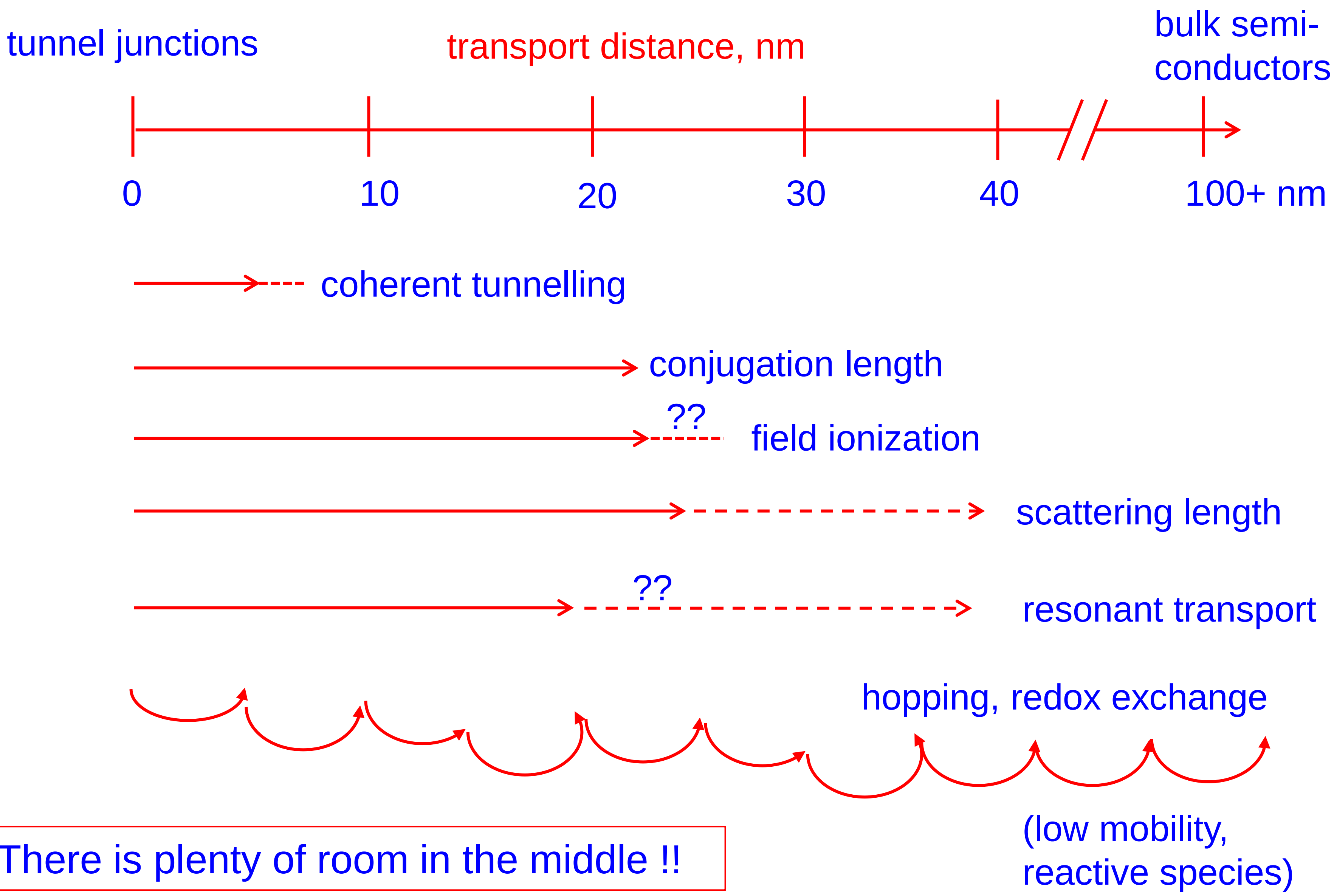
Richard Feynman, 1959

"There's Plenty of Room at the Bottom"



"the bottom" for aromatic molecular junctions ?

"barrier electronics" and not much control over barrier height



There is plenty of room in the middle !!

Phys. Chem. Chem. Phys., 2013,**15**, 1065

A preview of some new molecules: