Toward a Molecular-Scale Nanoelectronics

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SAMFET (Schön & Bao, Lucent Bell Labs)

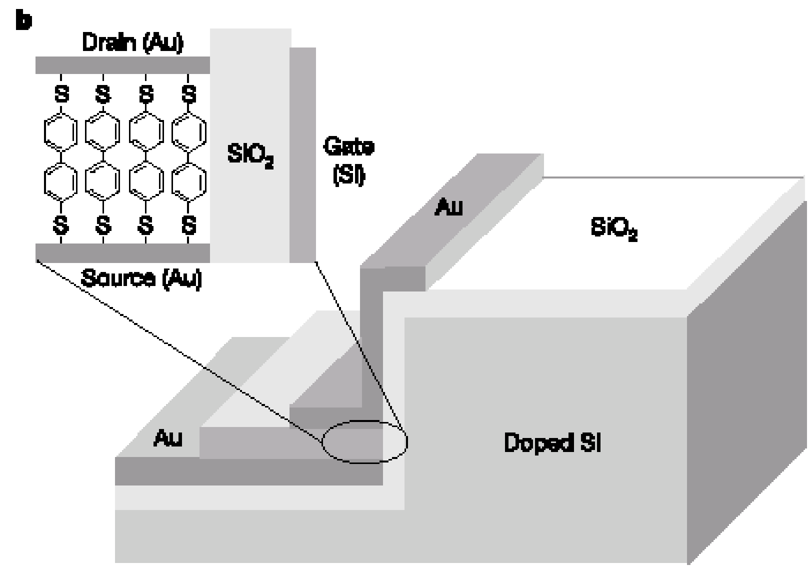


Figure 1 Structure of the investigated molecules and transistors. **a**, Molecular structure of the investigated materials; **b**, SAMFET structure: a highly doped Si-substrate is used as the gate electrode, a thermally grown SiO_2 layer acts as gate insulator, the gold source electrode is deposited by thermal evaporation, the active semiconducting material is a self-assembled monolayer (SAM) of one of the six molecules (**1–6**), and the drain contact is defined by shallow-angle shadow evaporation of gold. The active region of the device is magnified.

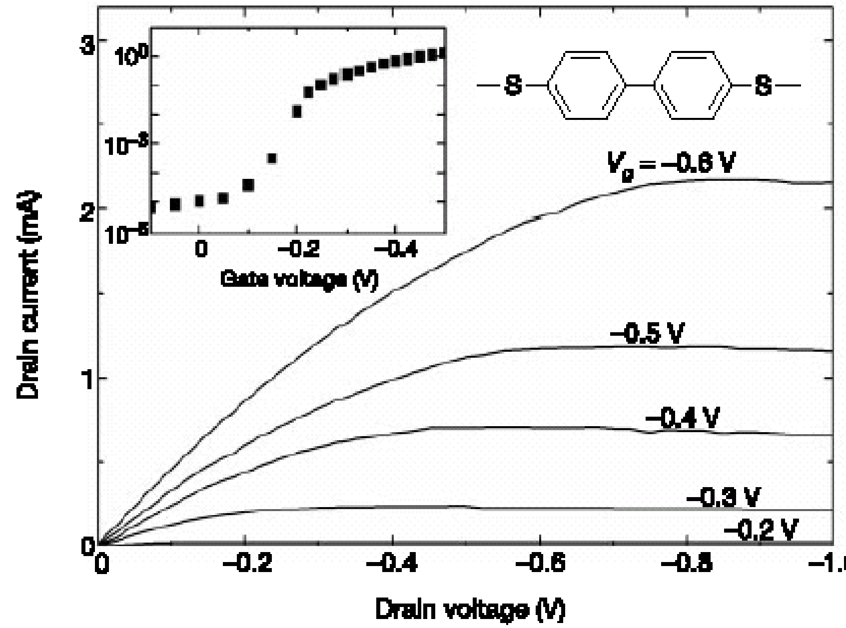
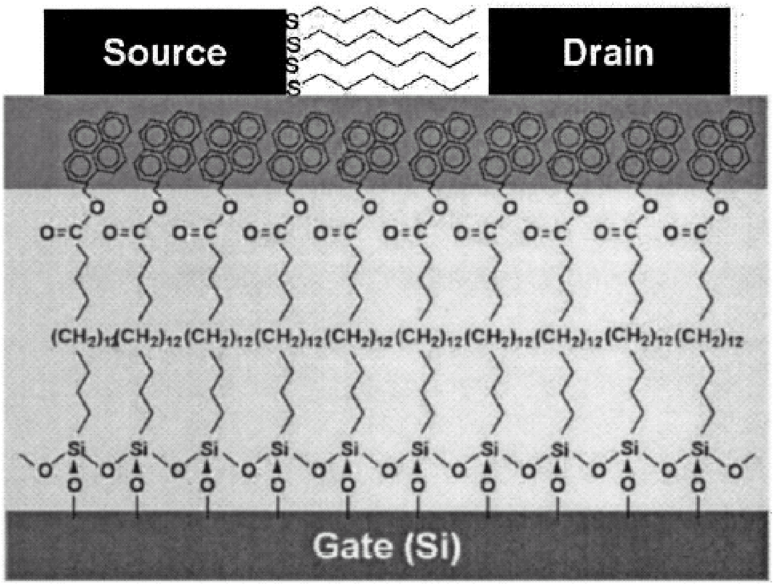


Figure 2 Transistor characteristics of a 4,4′-biphenyldithiol (molecule **2**) SAMFET at room temperature. The inset shows the transfer characteristics, that is, drain current at $V_d = -1$ V as a function of V_g.

Jan Hendrik Schon, Hong Meng & Zhenan Bao, *Nature 413*, 713 (2001).

And More!



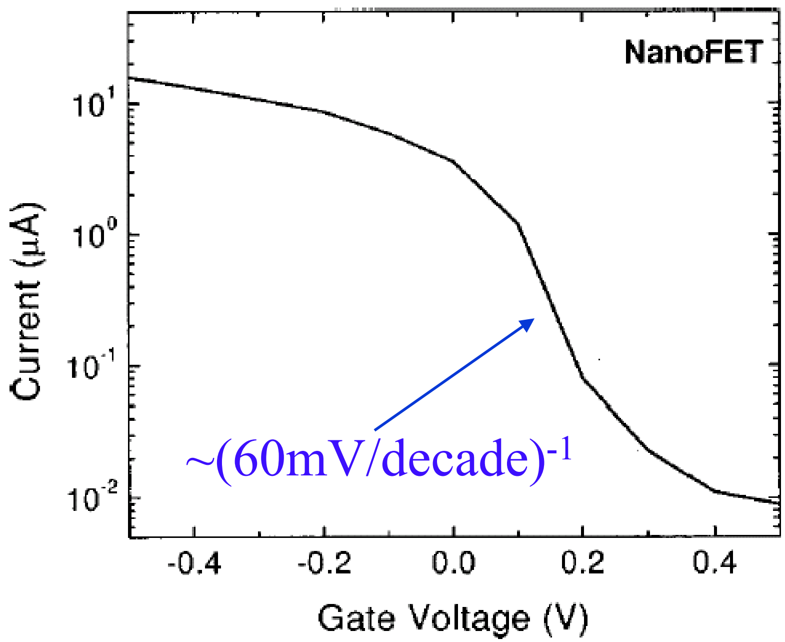


FIG. 4. Transfer characteristics of an ultrashort channel $\sigma-\pi$ SAM FET (nano-FET) at room temperature. Channel length is defined by an alkanethiol layer (~2 nm).

J. H. Schon & Z. Bao, *Appl. Phys. Lett. 80,* 332-333 (Jan 14, 2002).

Outline

- Future of electronics
- Molecular Acceptors & Marcus theory
- Study tunneling with self-assembled monolayers
- Recent data on oligophenylenevinylene bridges
- Bridge conformers and electron tunneling

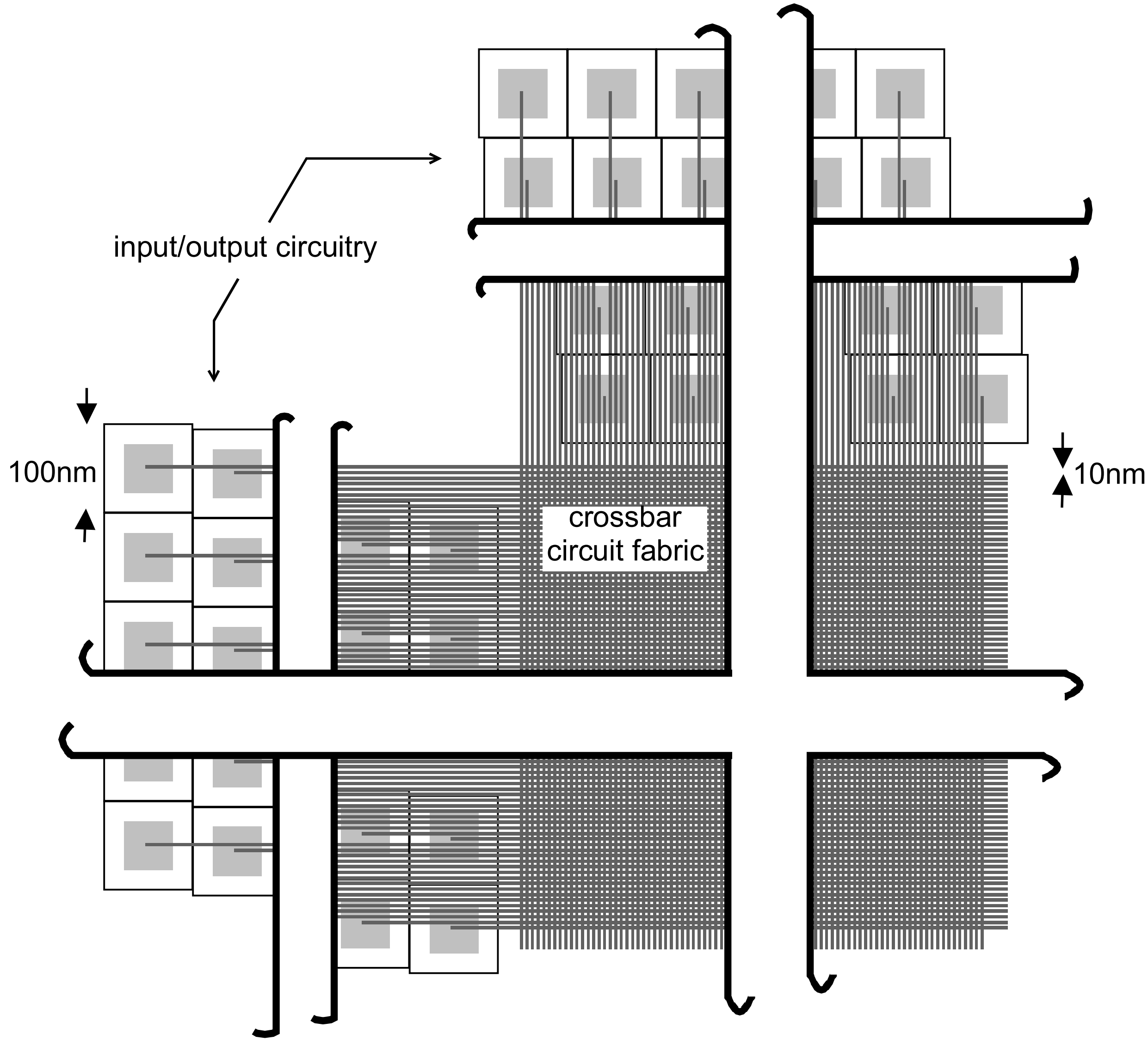
Tunneling Limit to Electronics

•Bohr radius of an "electron" is 0.1 to 1 *nanometers* in insulating media.

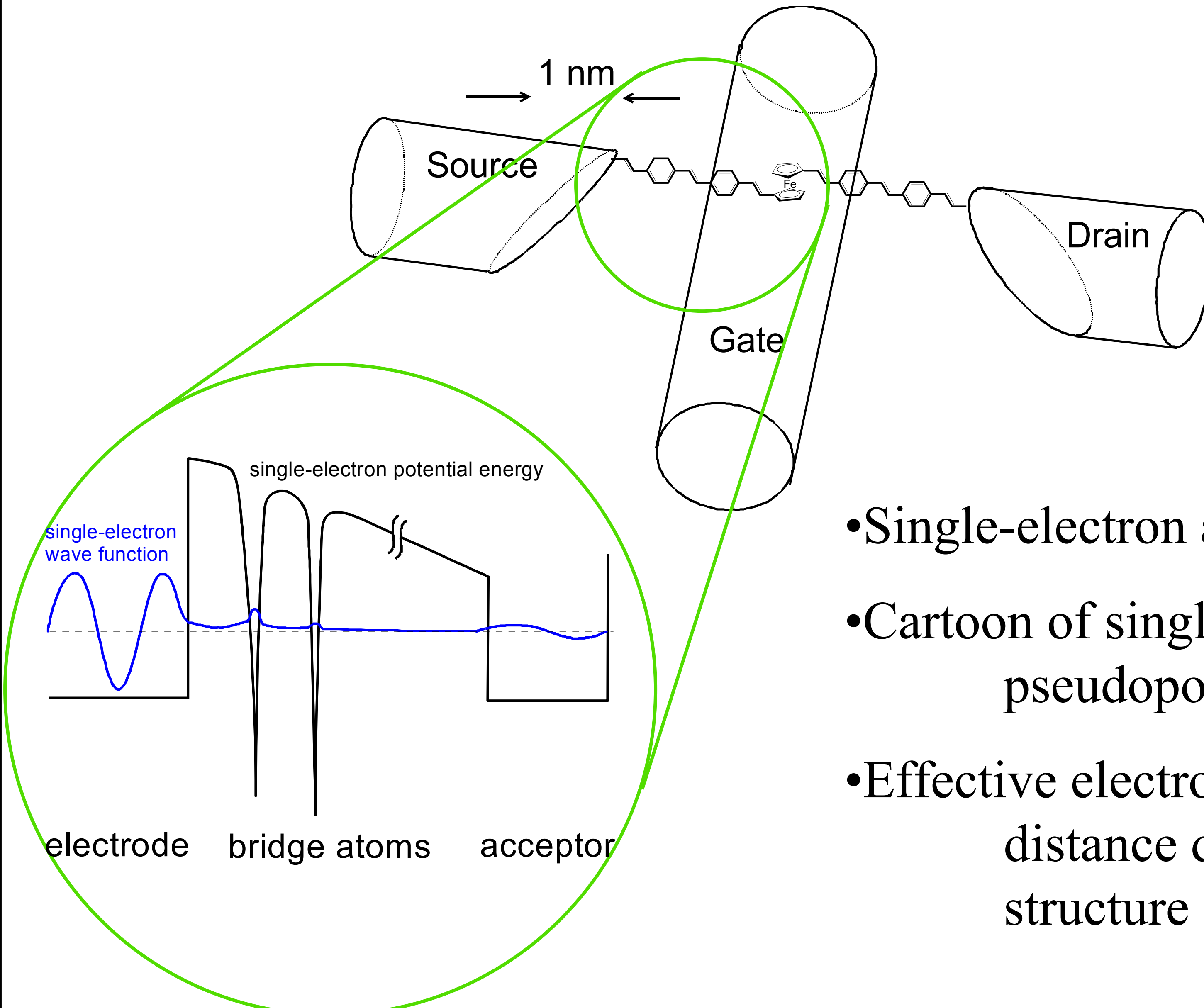
•*Nano*electronics is the limit for circuits with electrons as information carriers because electrons will *tunnel* between wires spaced less than a few nm apart.

•Since we are stuck with electron tunneling, we should exploit *differential* electron tunneling in nanoelectronics.

10nm-Pitch Circuits?

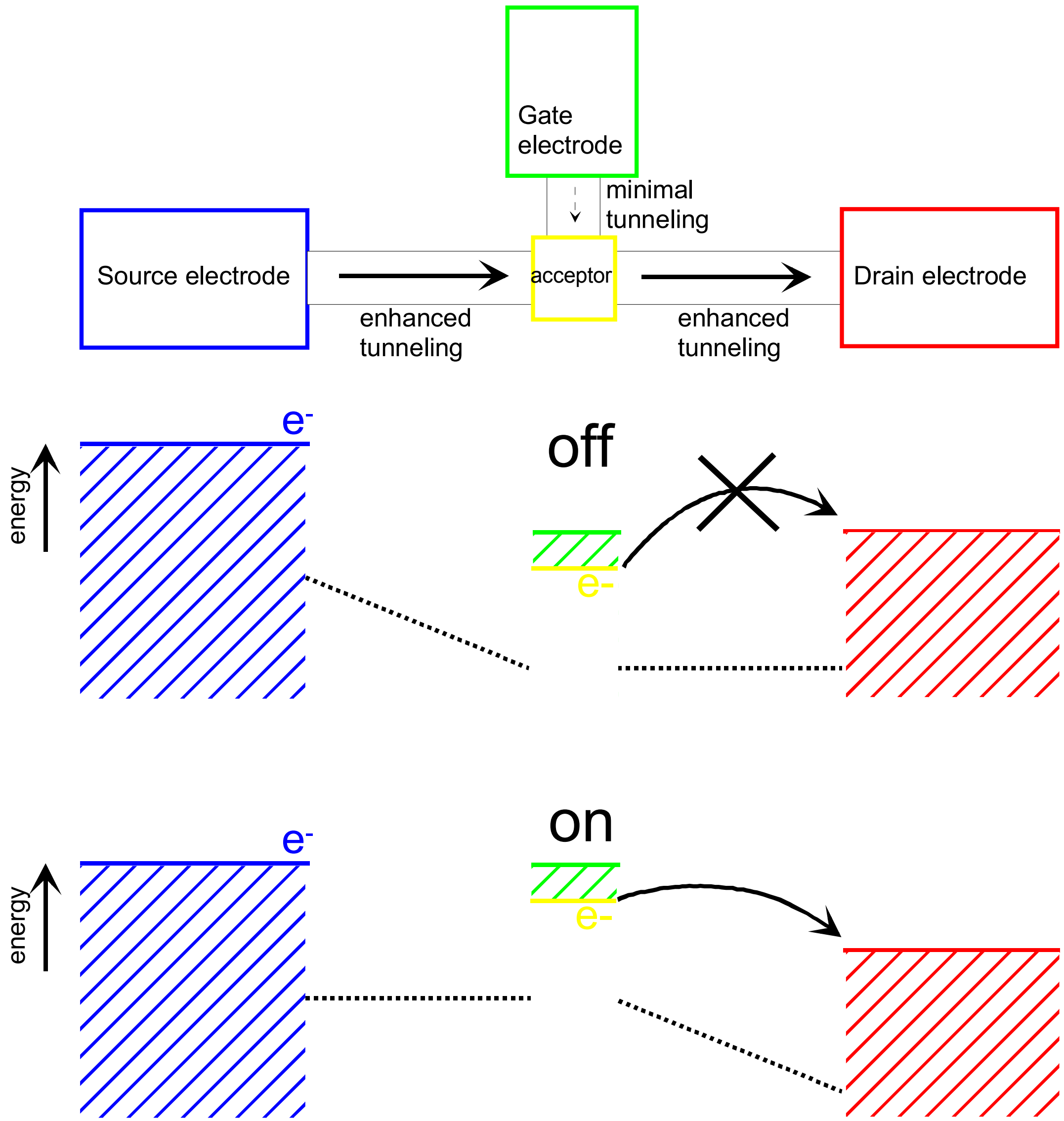


A Possible Molecule-Based Nanotransistor



- Single-electron approximation
- Cartoon of single-electron pseudopotential
- Effective electron tunneling distance depends on structure of bridge

Single Electron Transistor



Exploit differential tunneling to:

1. **Maximize electrostatic effect of gate**
2. **Minimize gate current**

This is a familiar problem:

•**Need *high κ dielectric* or *ferroelectric* on gate!**

How fast could it switch?

Limit electronic coupling, and thus level broadening,

to of order $k_B T$:

Tunneling therefore will have a rate of order:

$2\pi k_B(300K)/h = (25fs)^{-1}$

This should easily allow of order 1THz gates

Some Challenges in Nanoelectronics

Problem	Possible Solution
nanometer control	molecular devices (molecular chemistry)
two electrodes	crossed nanowires (solid-state chemistry)
nanometer circuits	directed assembly of nanowires (colloidal and solid-state chem)
three electrodes	broken crossed nanowires (electrochemistry)
more than 2N wires	breaks and vias (electrochemistry)

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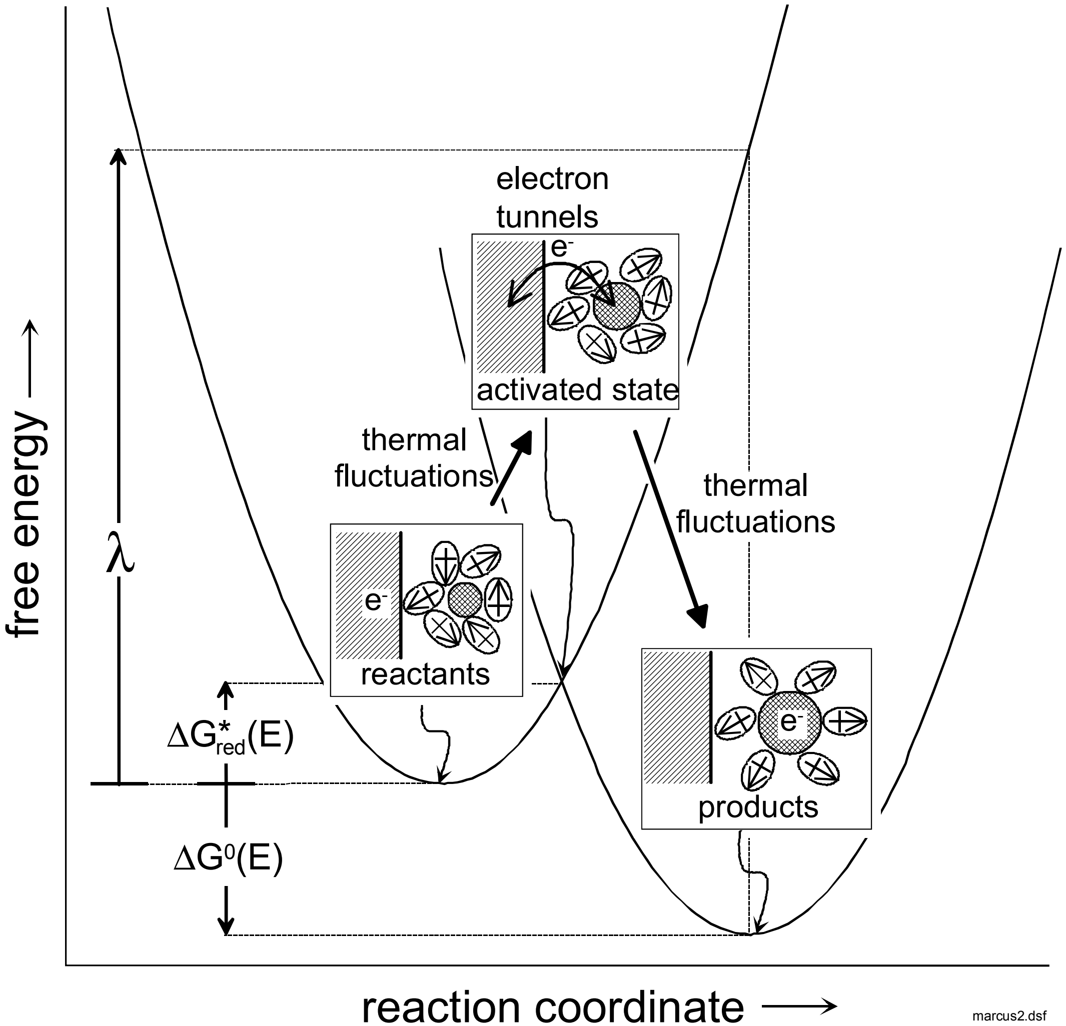
Molecular Acceptors & Marcus Theory

- molecular acceptors $\rightarrow$ localized electronic charge
- localized charge $\rightarrow$ structural reorganization (polaron formation)
- reorganization $\rightarrow$ activation barrier + limitation on barrier crossing rate

Marcus Structural Reorganization Barrier



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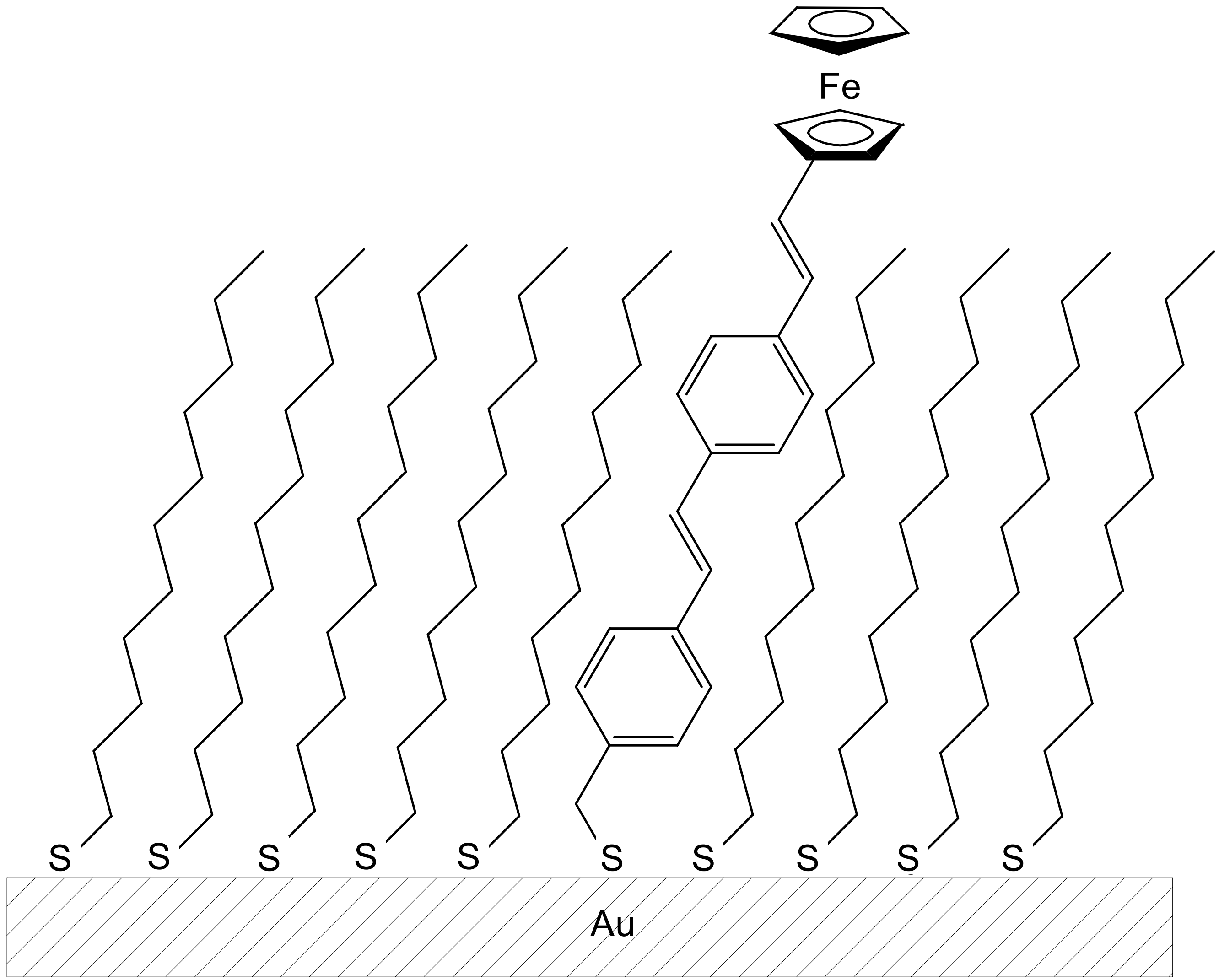
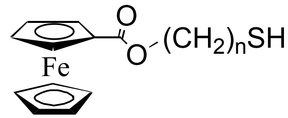
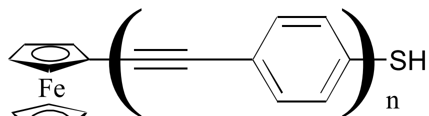
Self-assembled monolayer



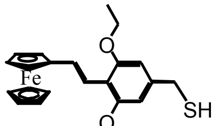
Some molecules to study electron tunneling



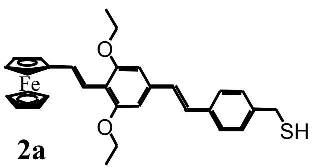
Oligomethylenes (n=5-18)



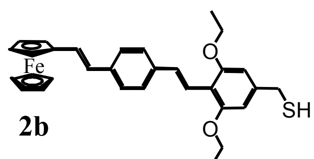
Oligophenyleneethynylenes (n=1-4)



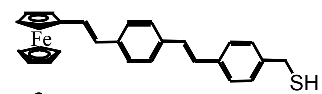
1



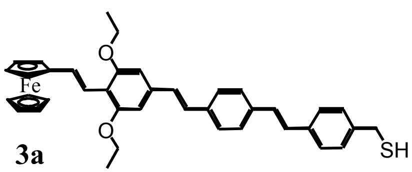
2a



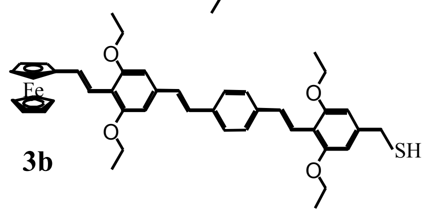
2b



2c



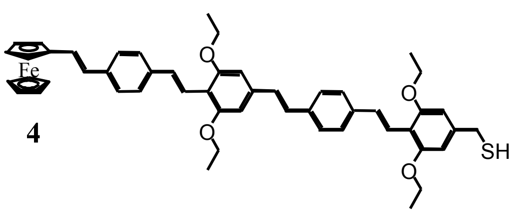
3a



3b

Oligophenylenevinylenes

Steve Dudek



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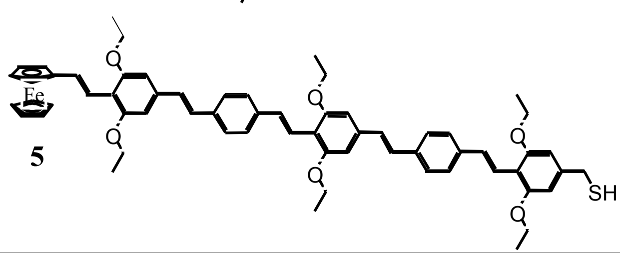
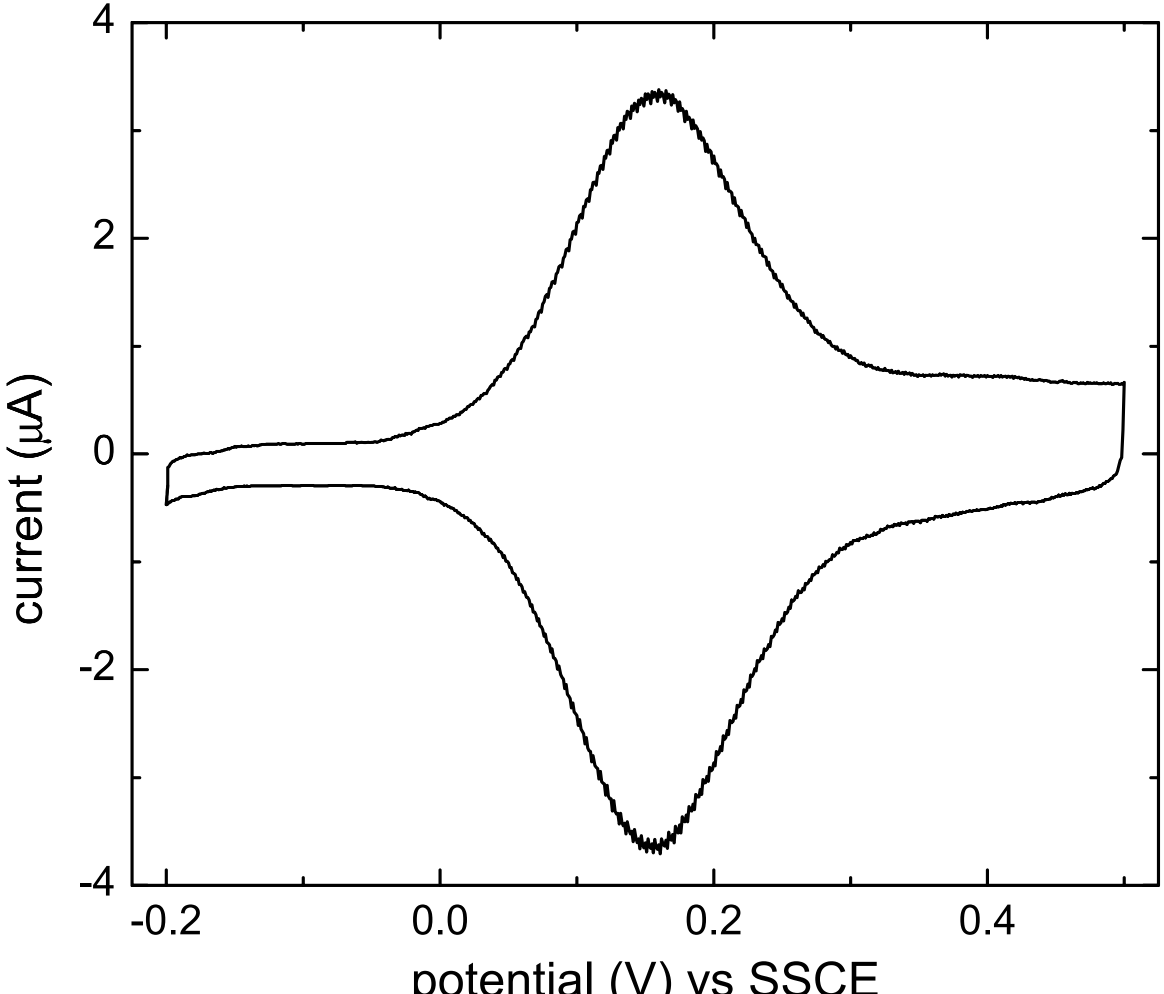


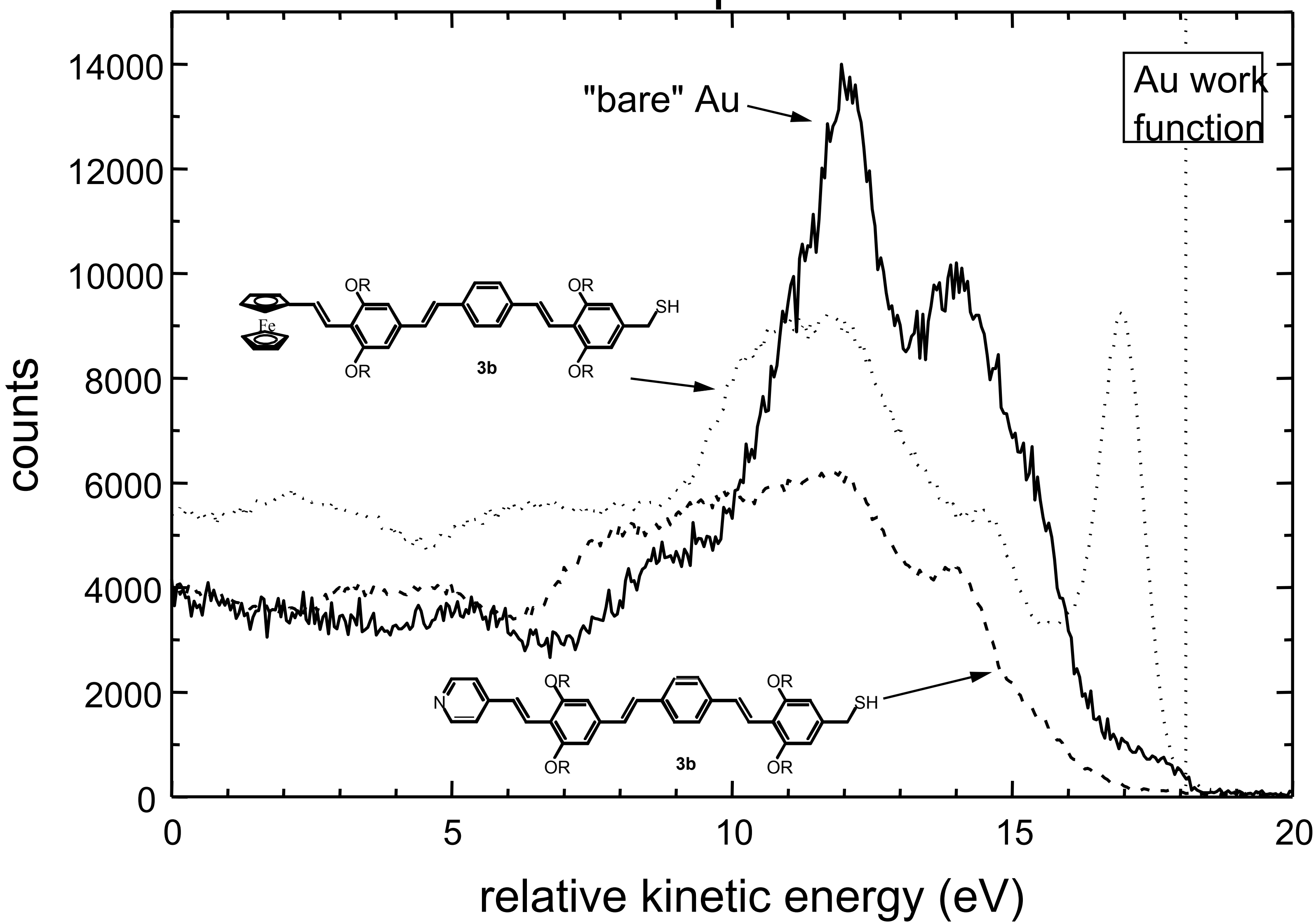
5

Cyclic Voltammetry of Fc



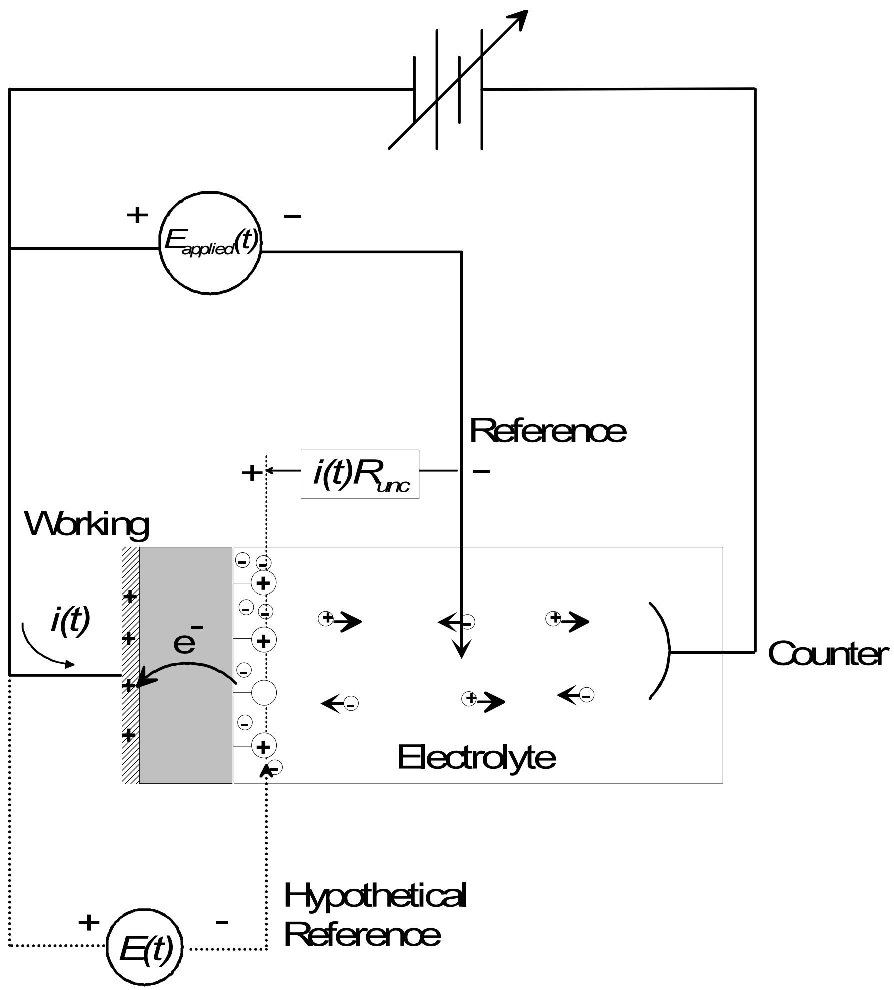
- Nearly ideal peak shape (90mV fwhm) indicates isolated, independent acceptors
- 0.8eV above OPV HOMO
- 1.6eV below OPV LUMO

Photoemission Spectra



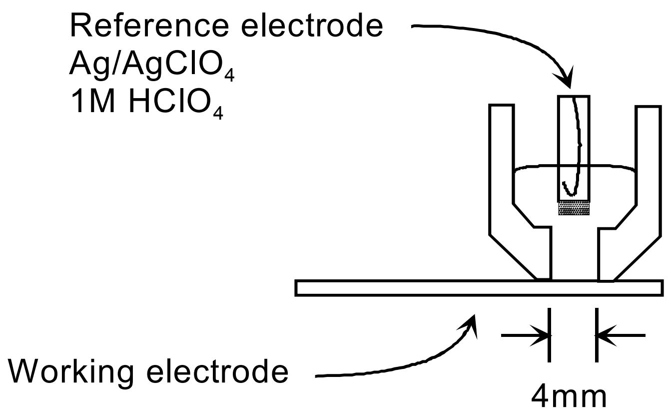
(measured by Hadley Sikes and Steven Sun)

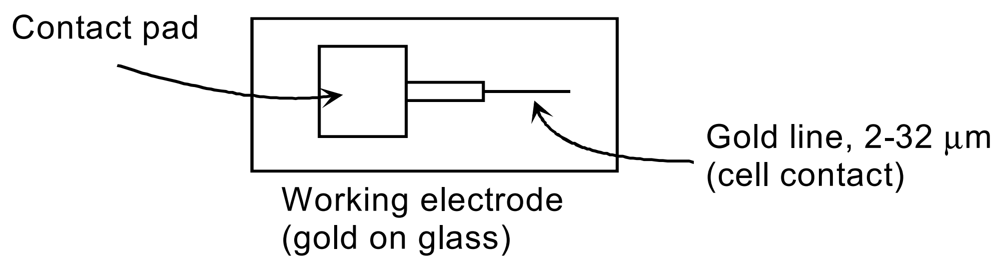
Chronoamperometric method: (usually limited to ~10^4 s^{-1})



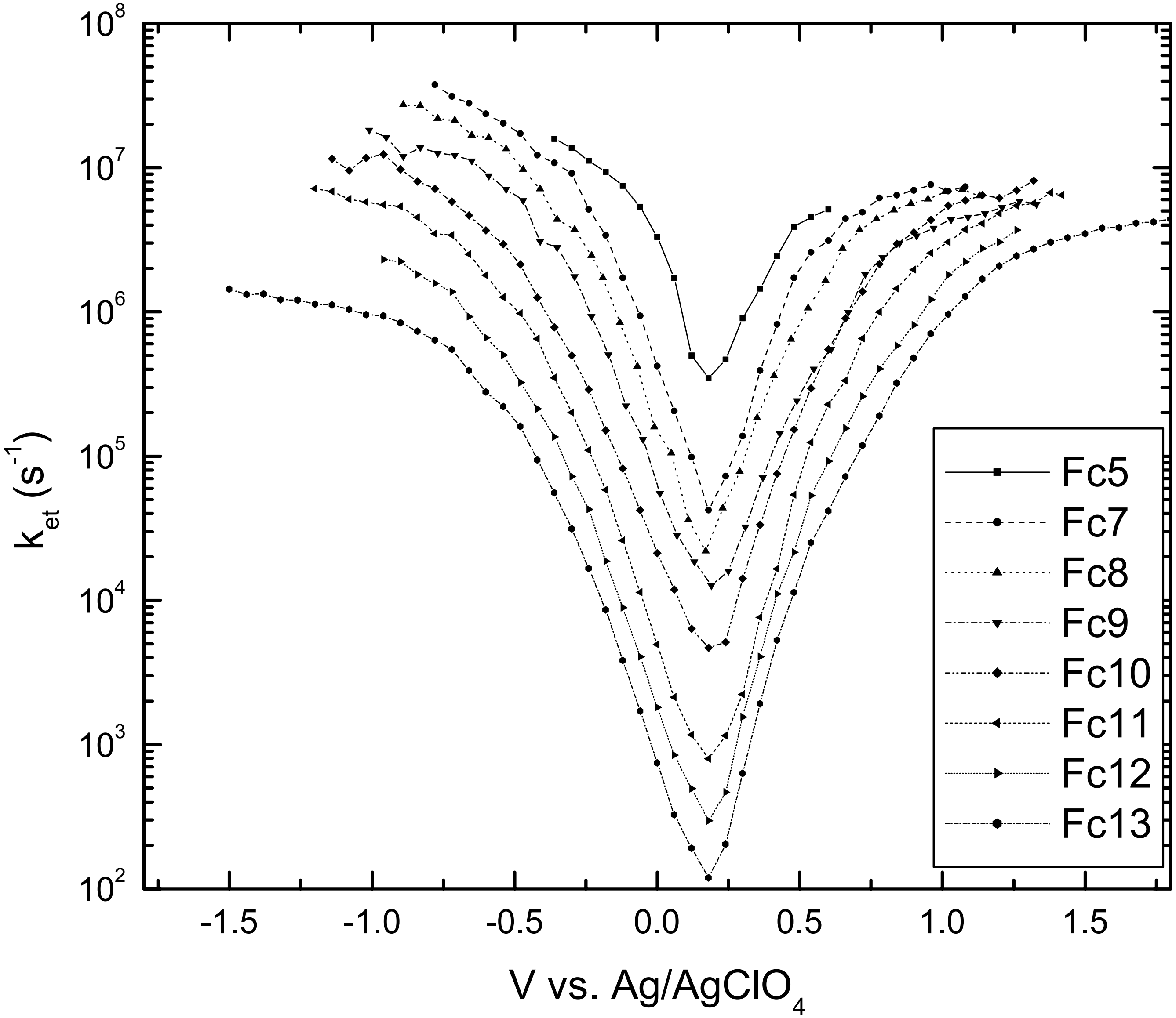
Use microelectrode to speed up (Dave Robinson PhD thesis)

Planar microelectrode geometry

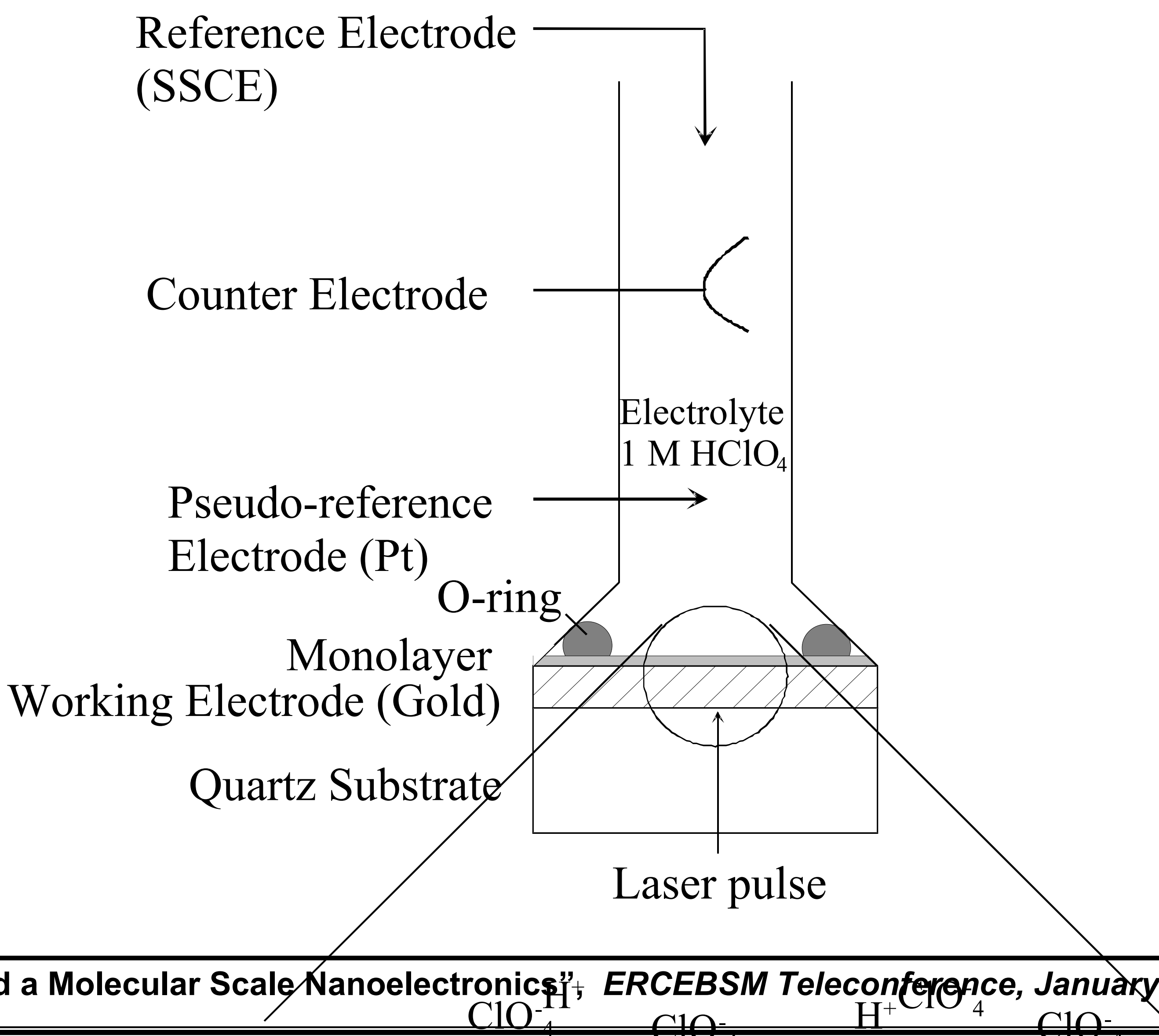




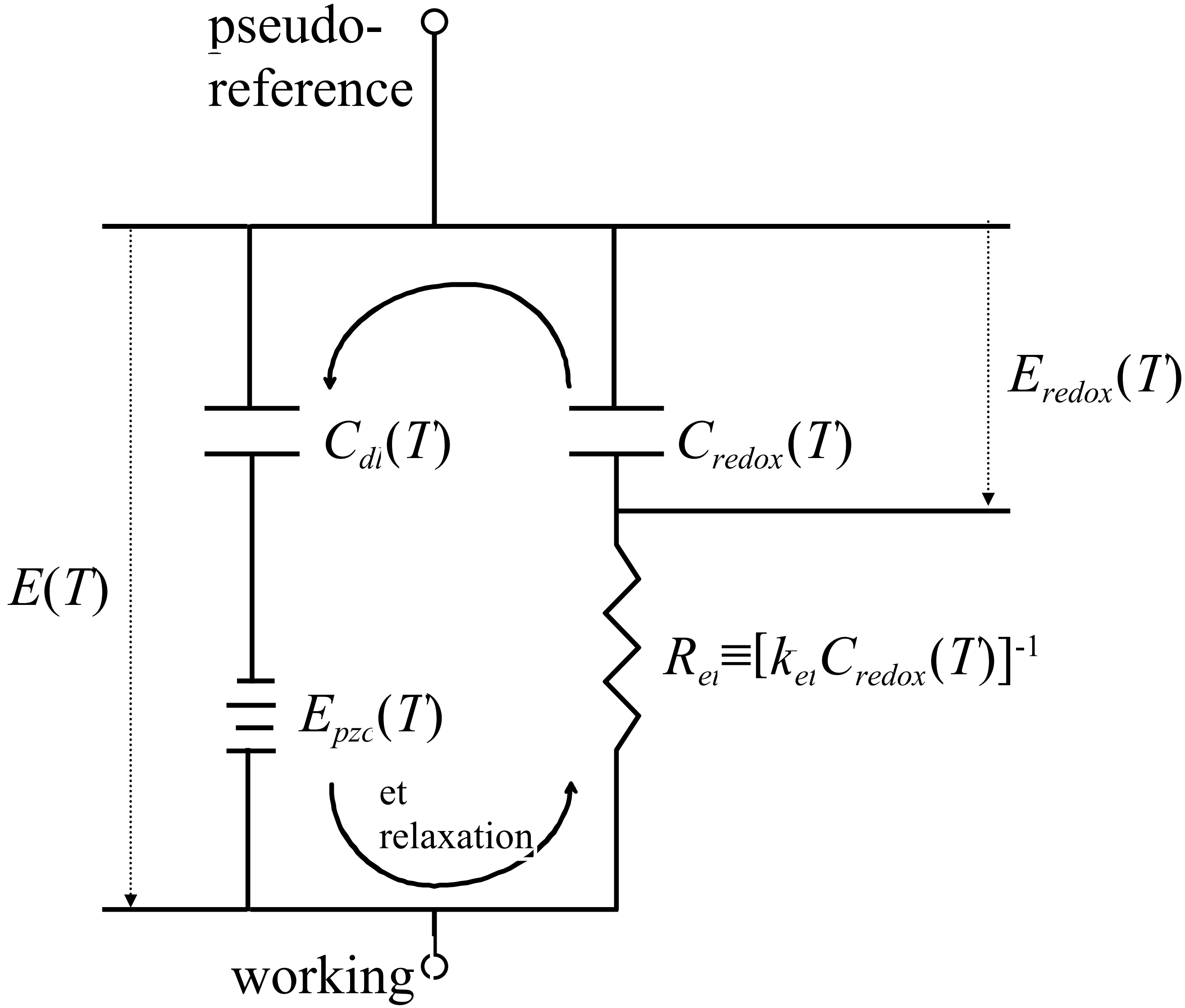
Electron-Transfer Rate vs. Energy and Alkyl-Chain Length



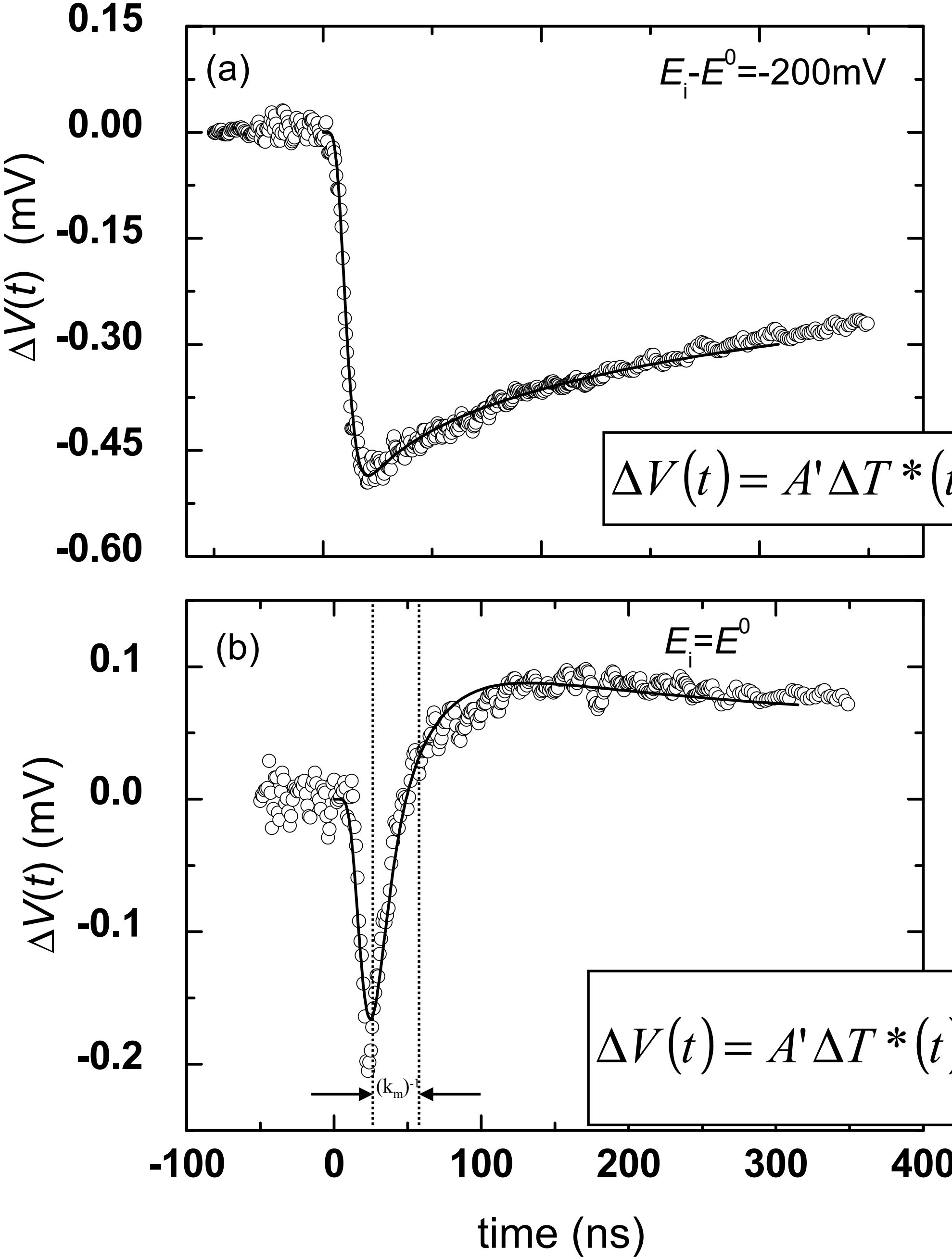
A Potentiometric Method: Indirect Laser Induce Temperature Jump



Equivalent circuit



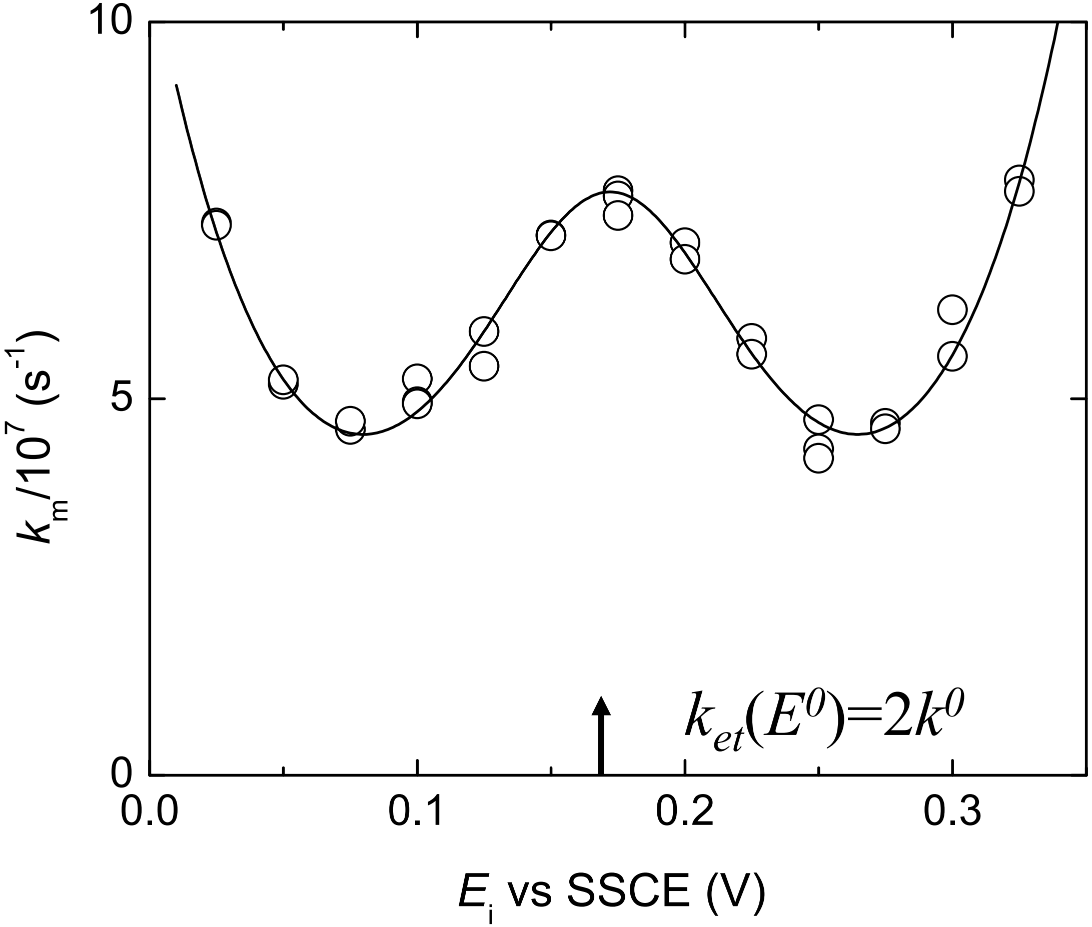
ILIT Data



$$\Delta V(t) = A'\Delta T^*(t).$$

- Pure double-layer ILIT response
- Sets time scale for measuring electron-transfer kinetics
- Electron transfer due to T-dependence of double-layer and redox potential
- Fit to convolution of (a) and exponential decay

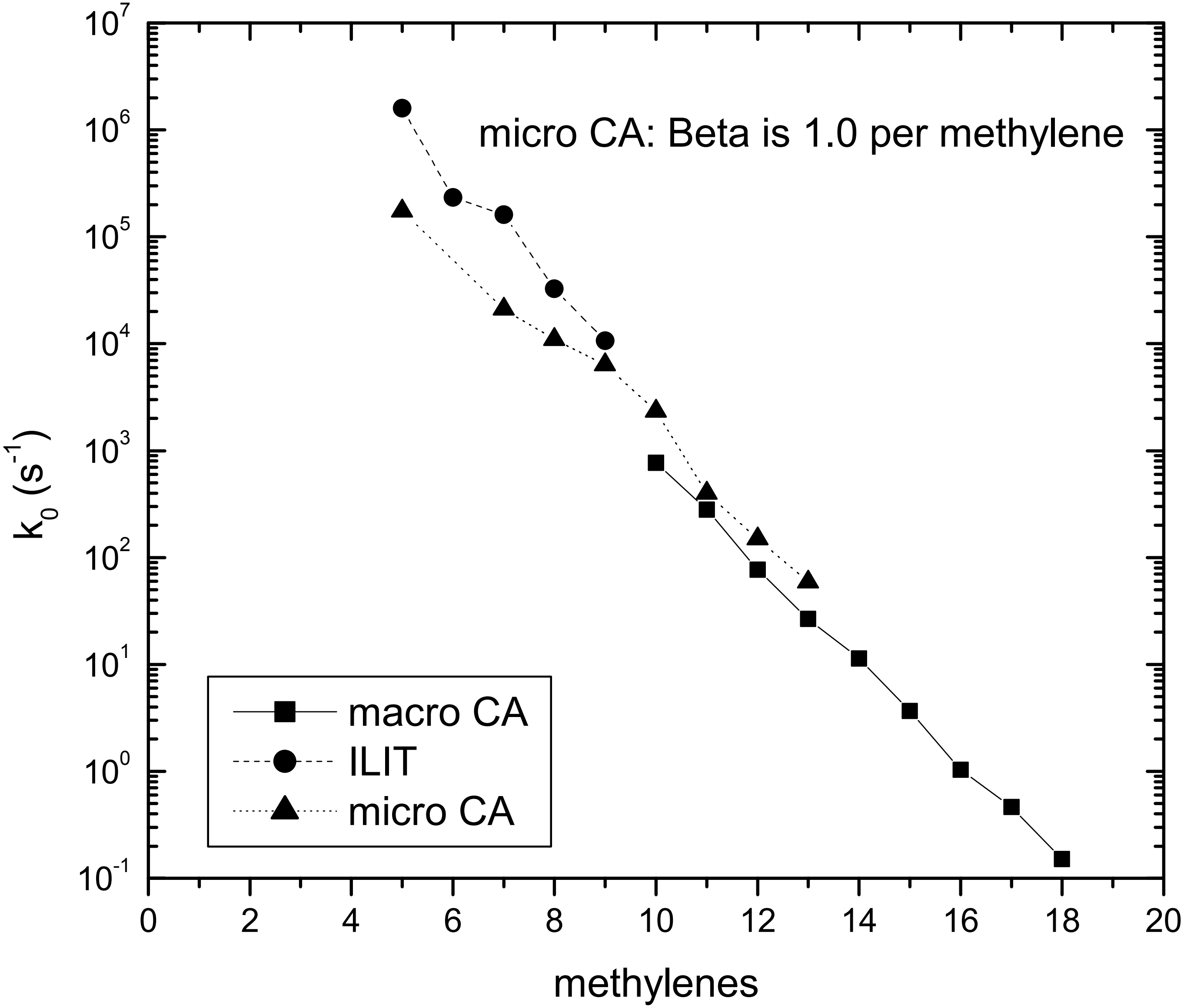
$$\Delta V(t) = A'\Delta T^*(t) + k_{\mathrm{m}}(E_{\mathrm{i}})B'\int_0^t e^{-k_m(t-\tau)}\Delta T^*(\tau)\,d\tau$$



$$k_m(E_i) \equiv k_{et}(E_i)\frac{C_{redox}(E_i)+C_{dl}}{C_{dl}}$$

$$k_{et}(E_i) = k^0\left\{\exp\left[-\frac{e\left(E_i - E^{0'}\right)}{2k_BT}\right] + \exp\left[+\frac{e\left(E_i - E^{0'}\right)}{2k_BT}\right]\right\}$$

Distance dependence of k_o



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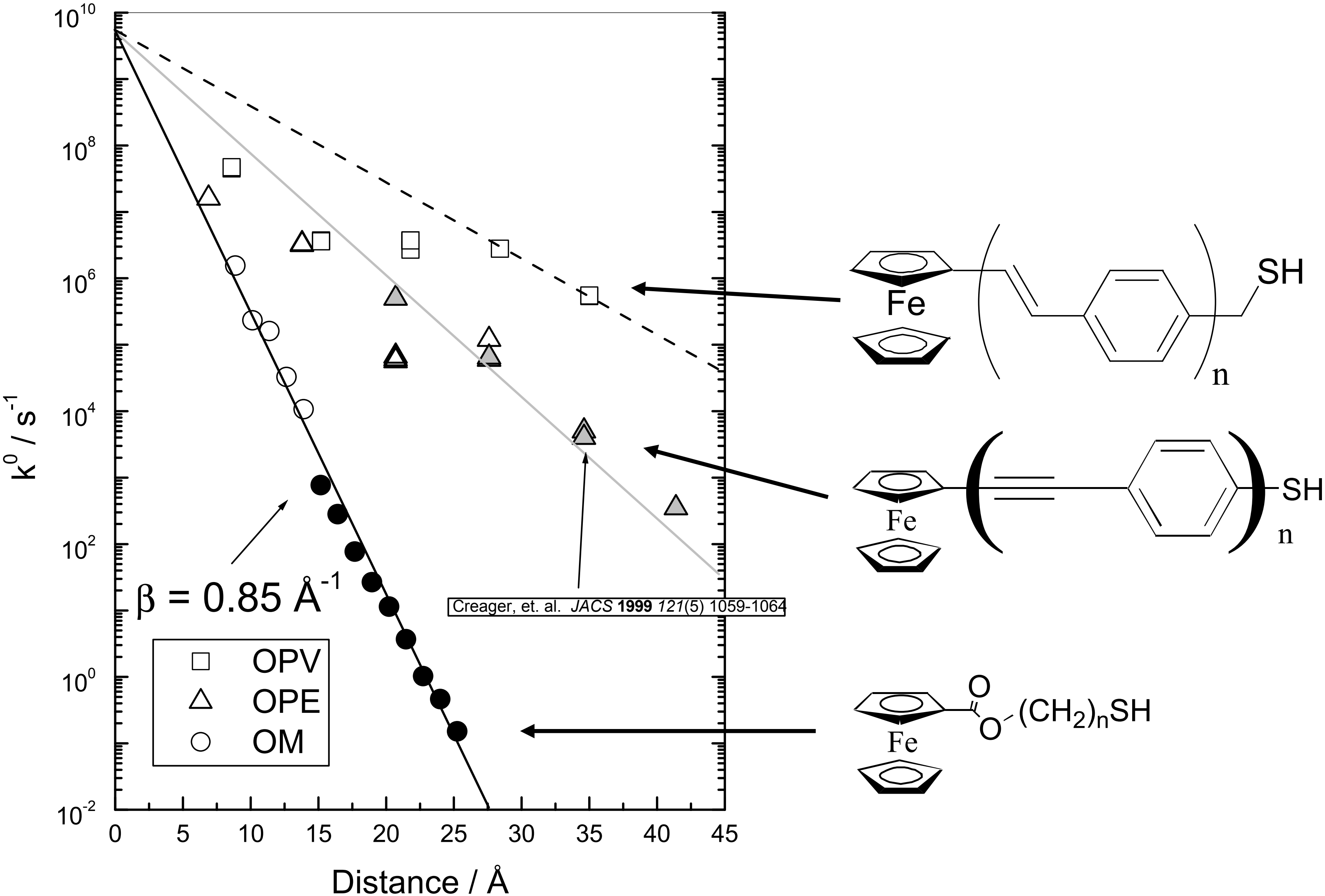
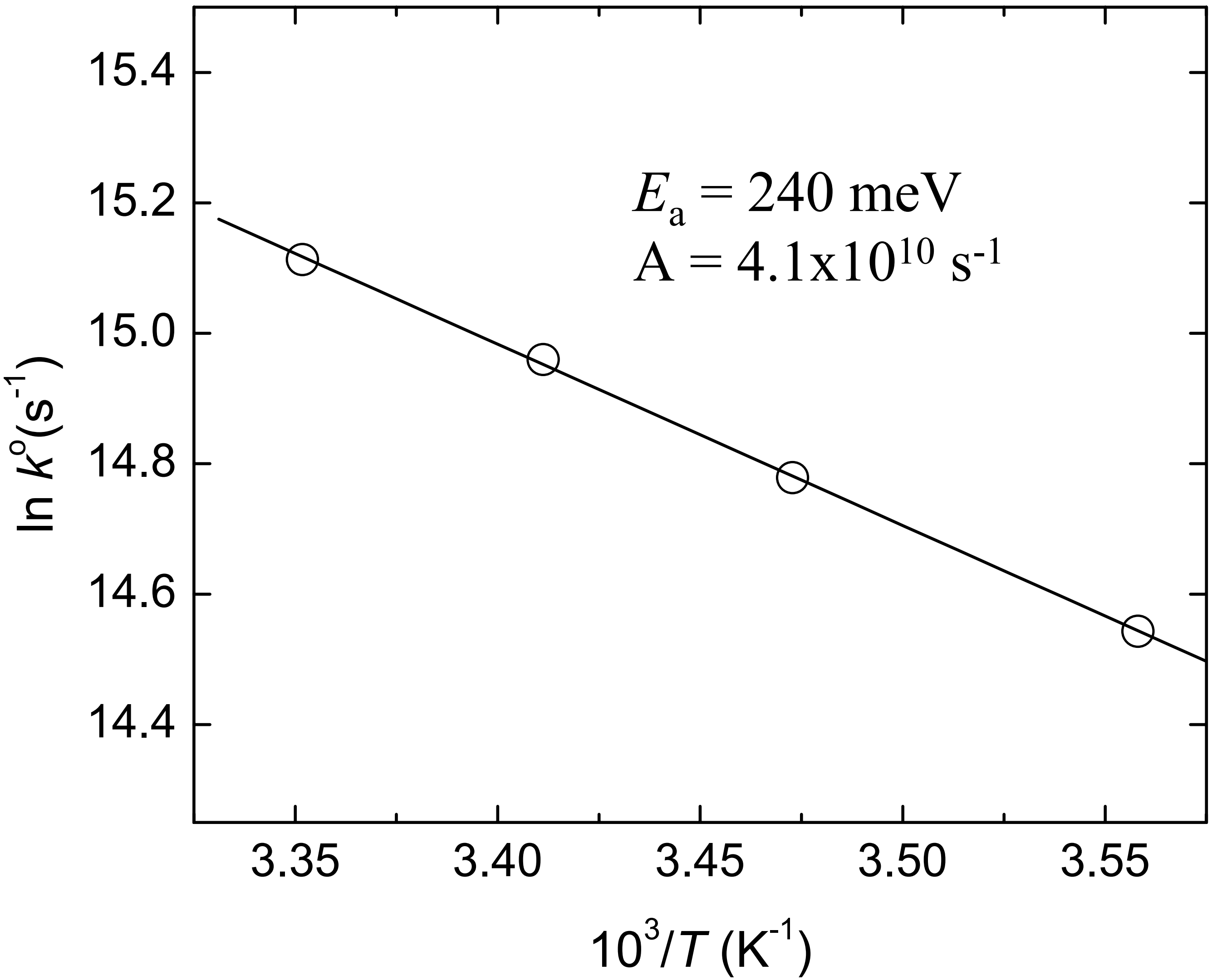
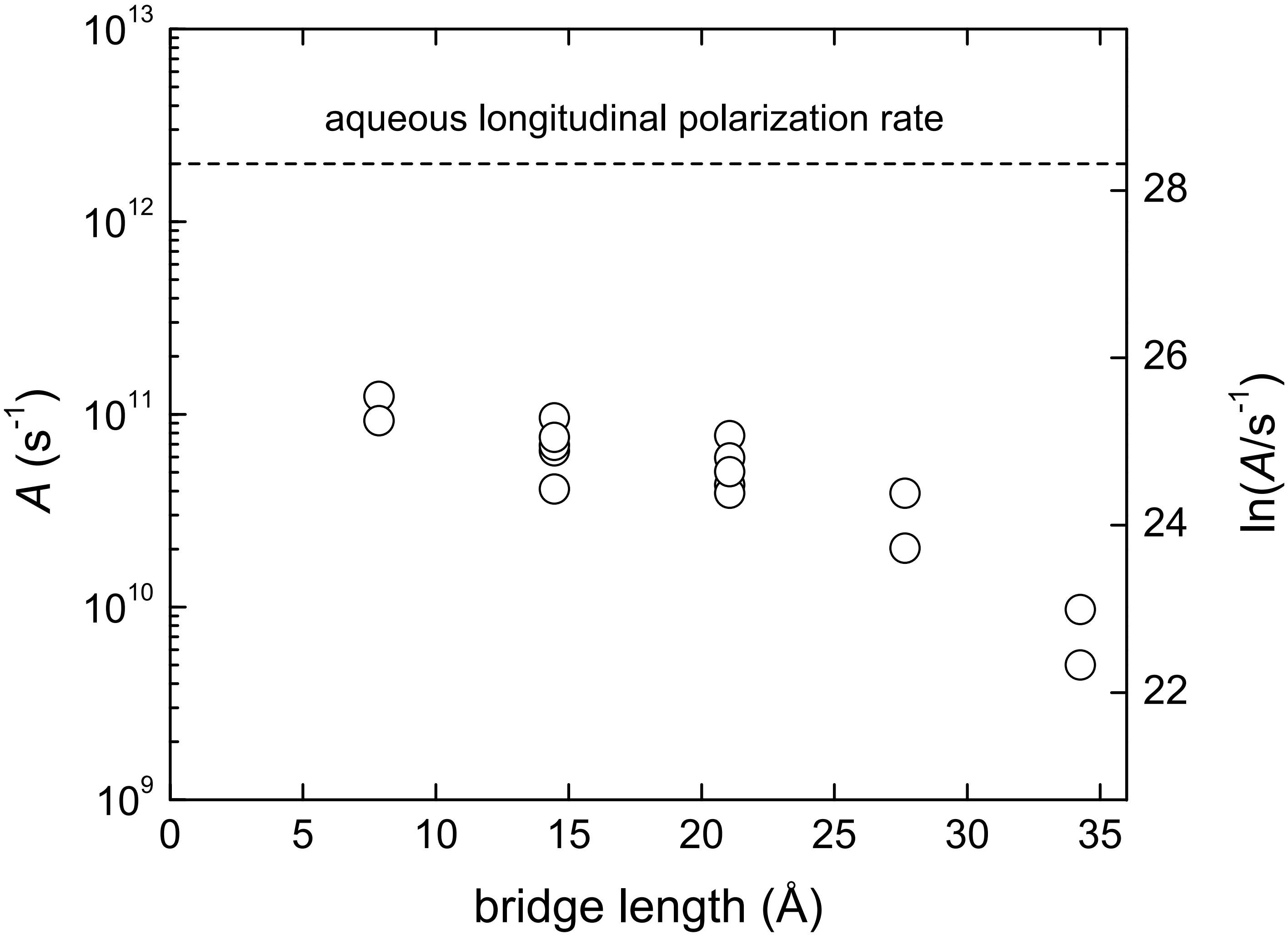
Data for various bridges



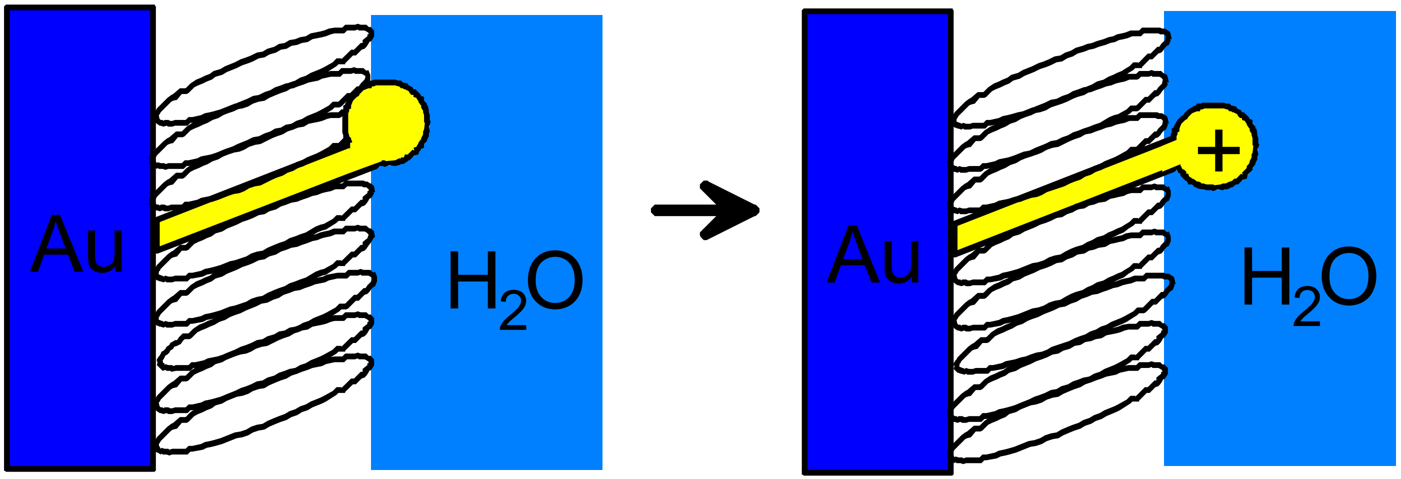
Example of Arrenhius Plot of k^0



Arrhenius Prefactors of OPVs



Suggestion for Slow Reorganization Dynamics



Expect translational diffusion time of ~10 ps

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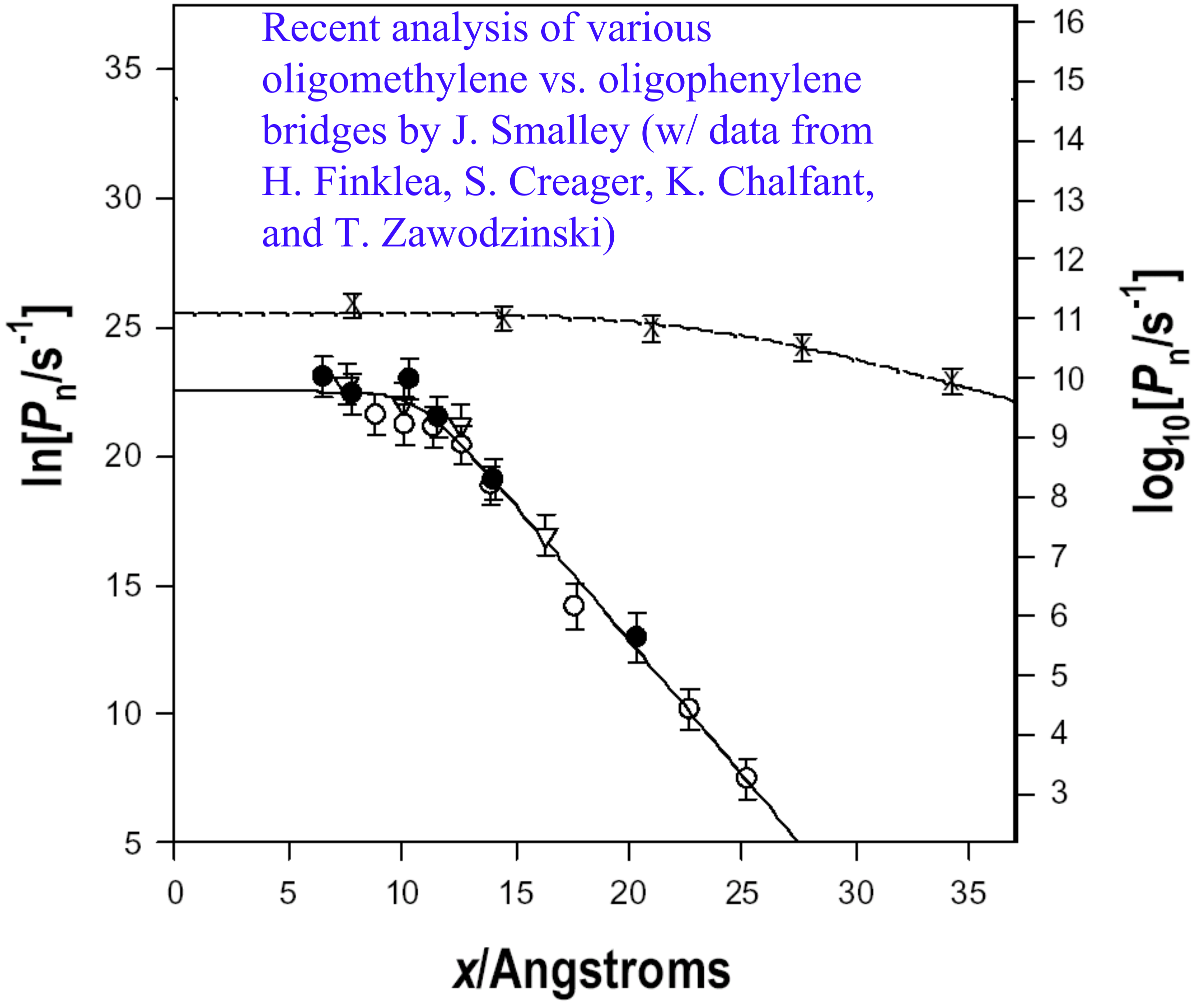
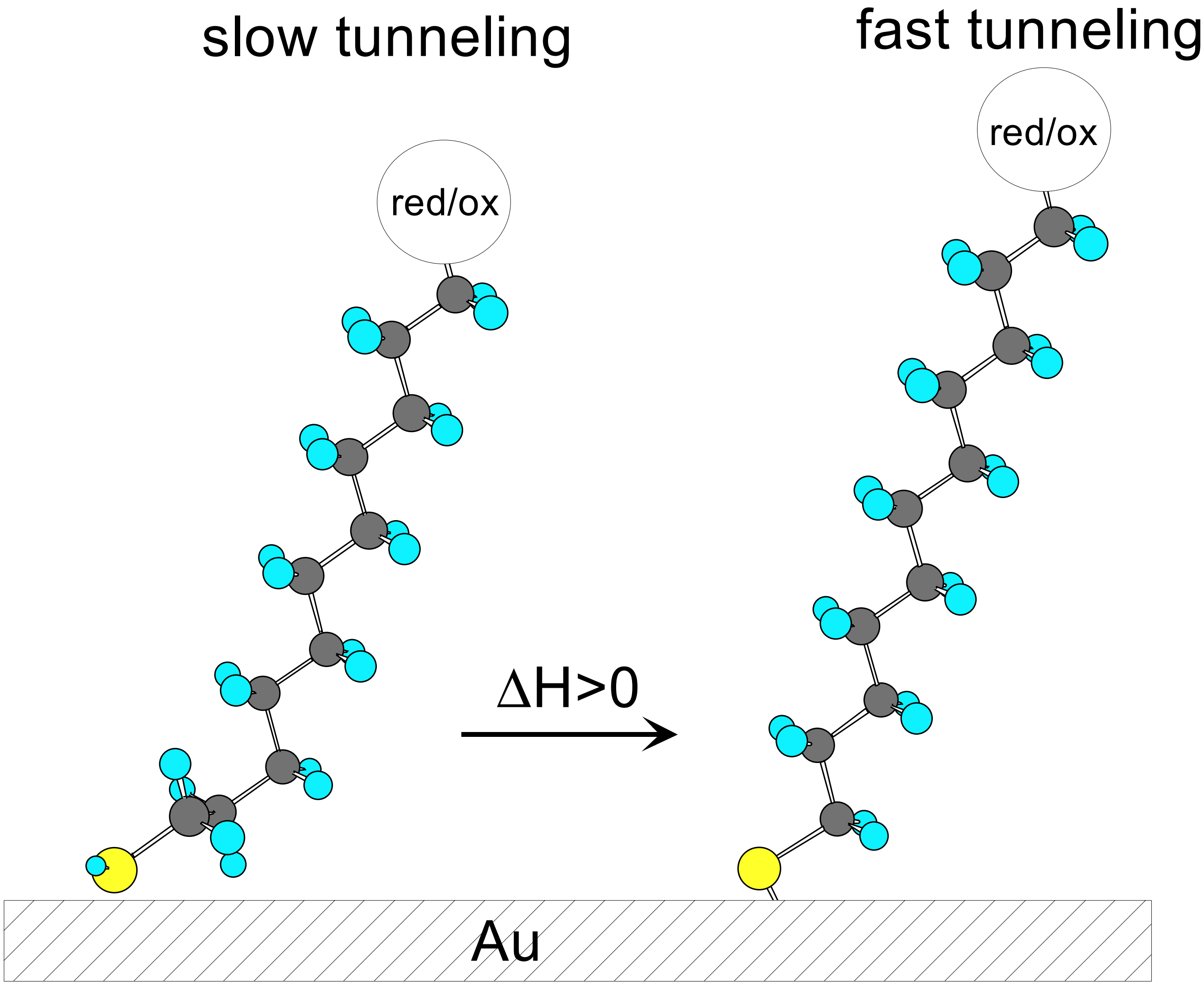
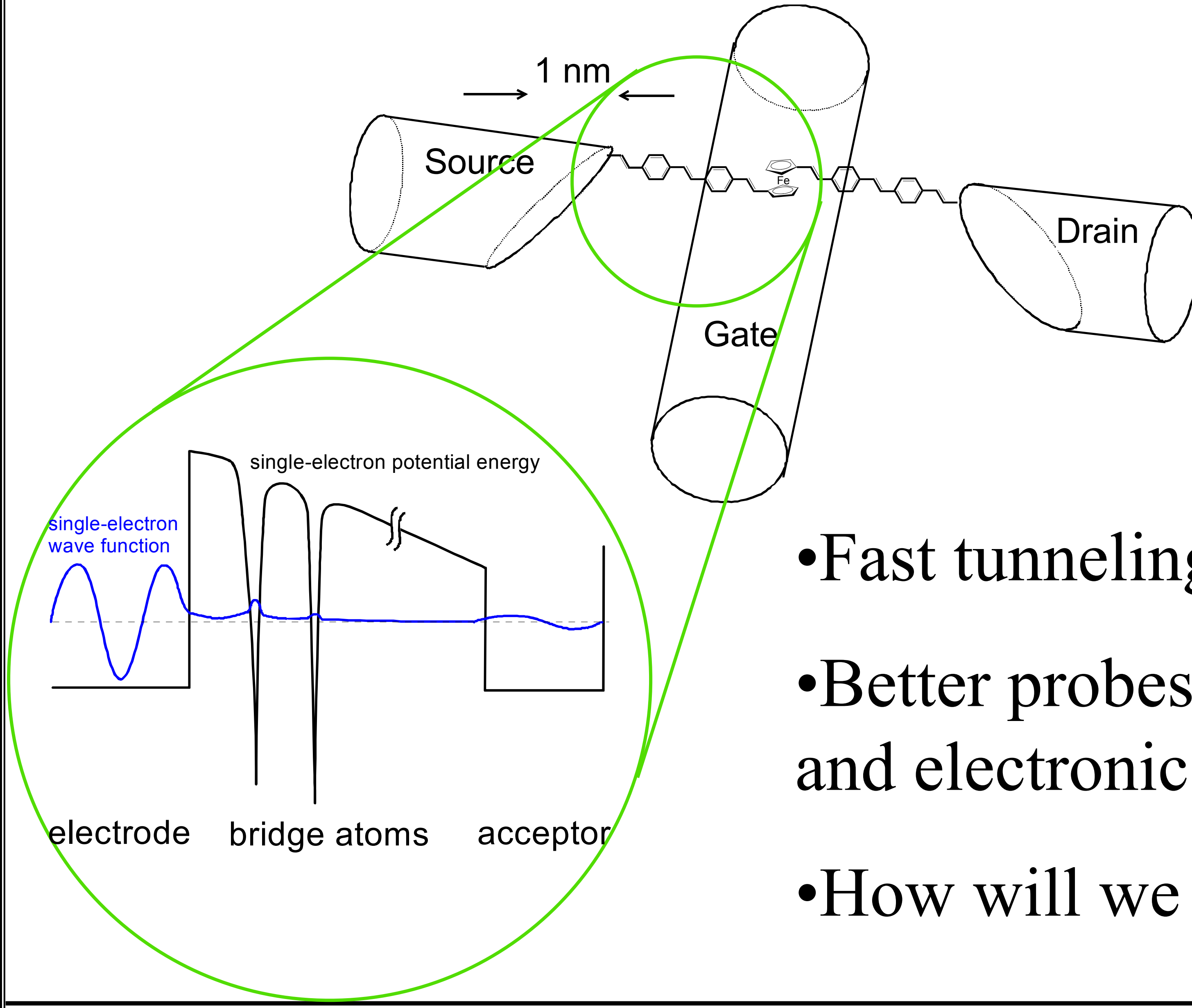
Curious dependence of limiting prefactors on bridge type



Possible origin of limits



Outlook: Molecule-Based Nanotransistors?



- Fast tunneling limits?
- Better probes of atomic and electronic structure?
- How will we build them?