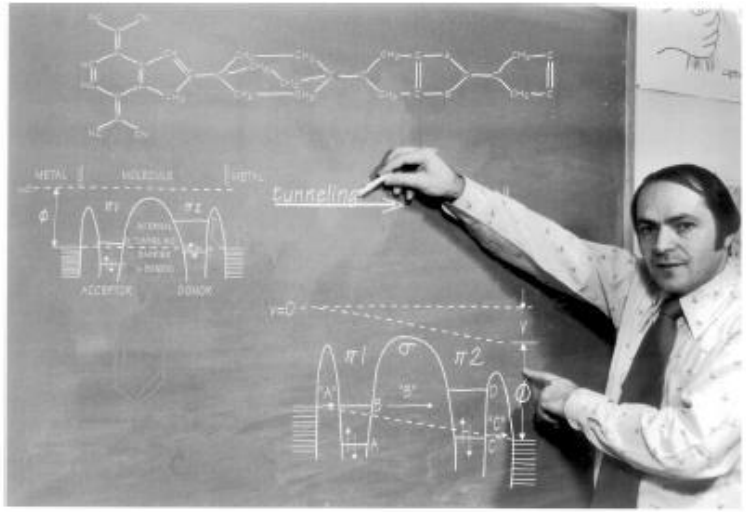
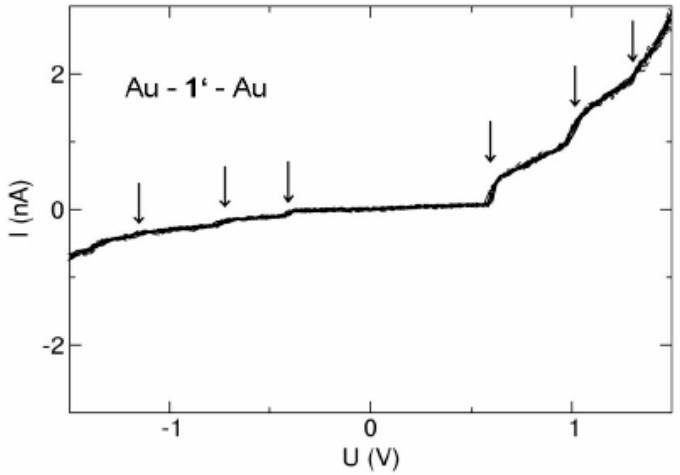
A Single-Molecule Diode

the Aviram-Ratner concept **&** ***recent exp. realization (Elbing et al.)***

Chem. Phys. Lett. **29**, 277 (1974) PNAS, to appear (2005)



A. Aviram (IBM Thomas J. Watson , 1979)



PNAS preprint to appear (2005)

Florian Pump, *J-Club*, Regensburg, 27.04.2005

Outline

Aviram-Ratner Concept

- Idea of rectifying molecules
- Principle of rectification
- Expected IV-curve

Recent Experiments

- Design & Characterization of the molecules
- Experimental Technique: Mechanically Controllable Break junctions (MCB)
- Conductance measurements
- Theory

Summary

Aviram-Ratner Concept

Aviram, A., Ratner, M.A., *Chem. Phys. Lett.*, **29**, 277-283 (1974).

Idea: Construction of a rectifying electronic device based on the use of a single organic molecule consisting of a donor π-system and an acceptor π-system separated by a sigma-bonded tunneling bridge.

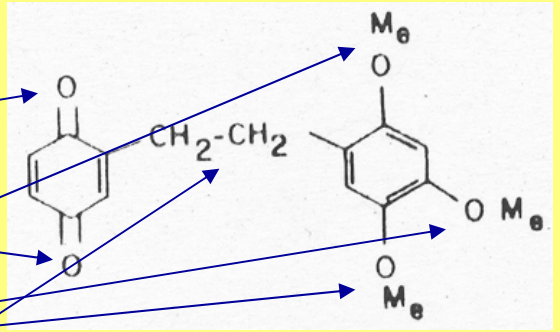
Common solid-state rectifiers: p-n-junctions

Rectifying Organic molecules

- Substituent groups on aromatic systems
- Increase/Decrease π-electron density
- Electron-rich (n-type) and electron-poor (p-type) subunits

Aviram-Ratner Concept

Example: **Hemiquinone molecule**



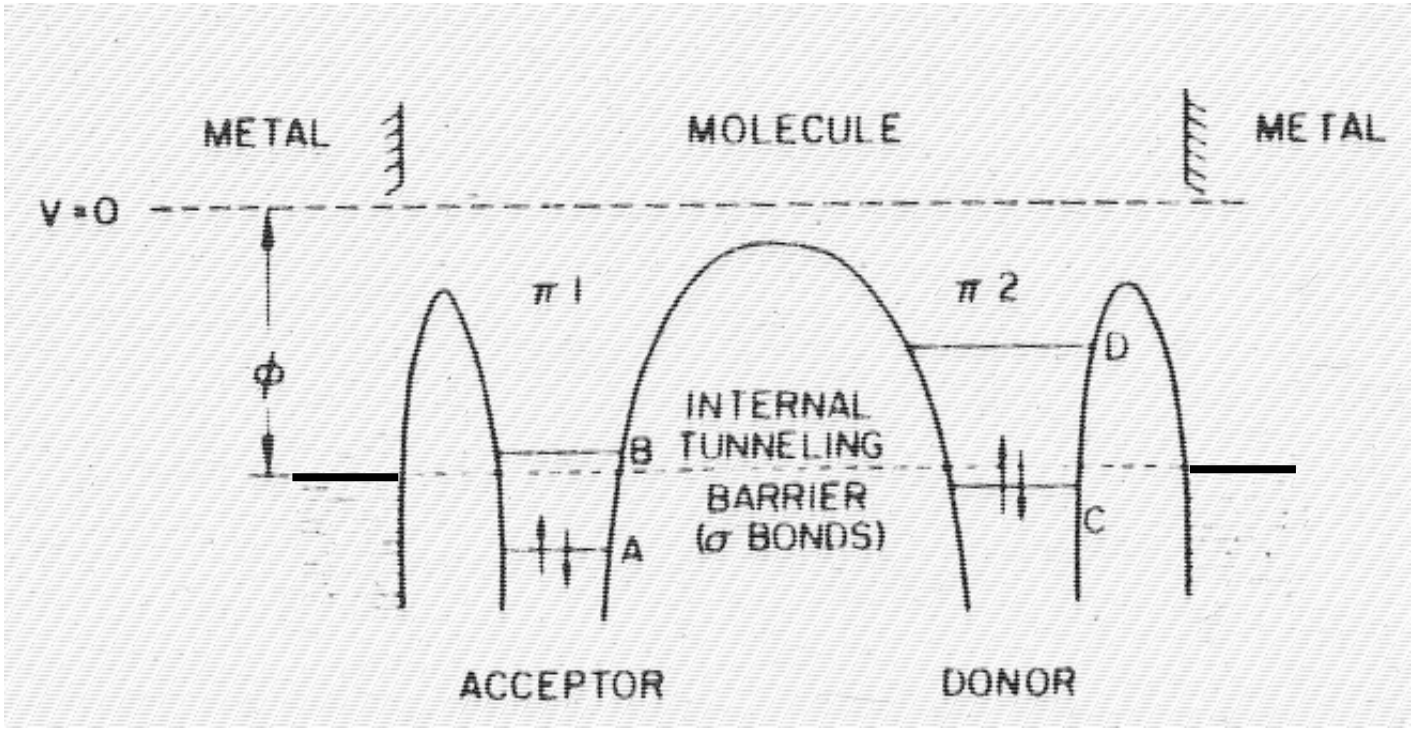
- Quino(=0)-Group:
  decrease π-density, raise electron affinity
  ⇒ **(Acceptor)**
- Methoxy(-OCH_3)-Group:
  increase π-density, lower ionization potential
  ⇒ **(Donor)**
- Methylene(-CHH_2-)-Bridge:
  separation of the two π-systems but σ-coupling

Electron transfer: Left → Right preferred

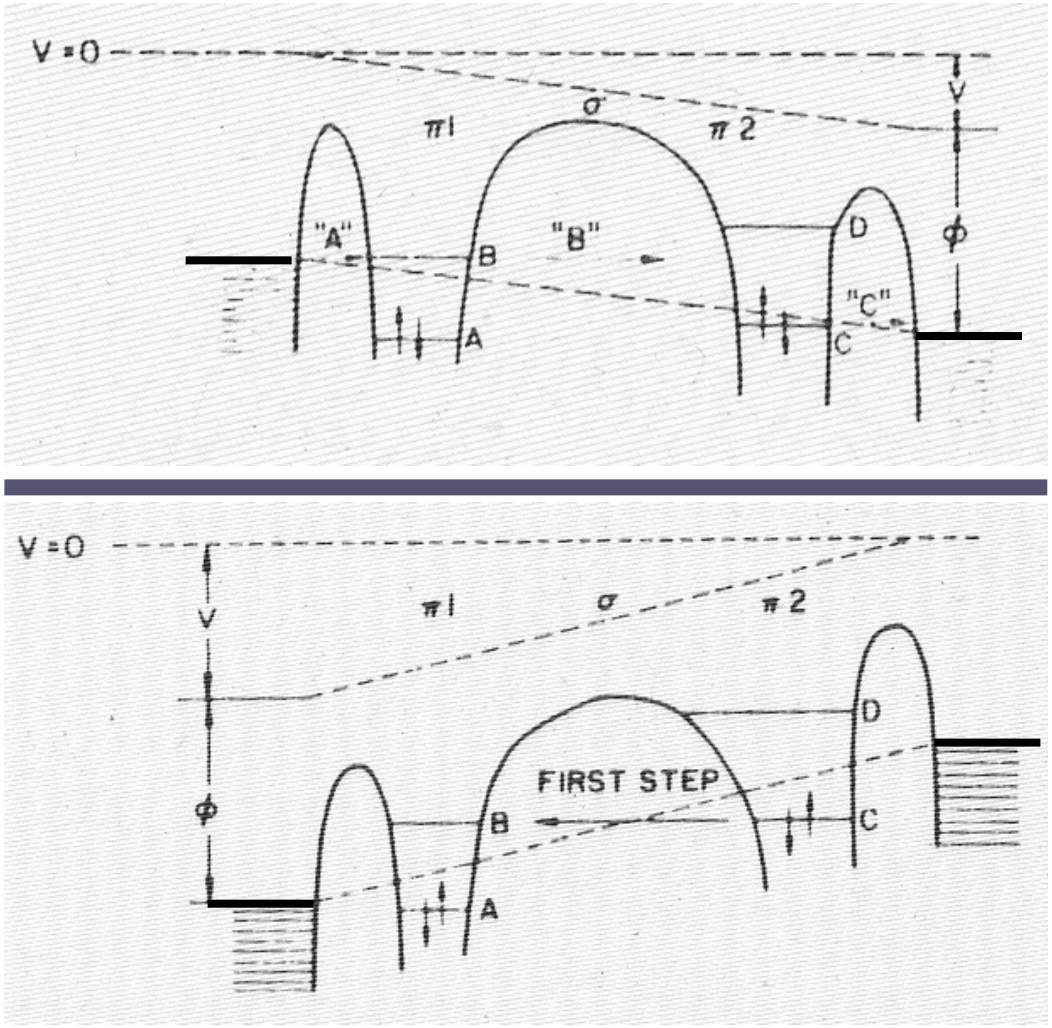
(cathode → acceptor → donor → anode)

Aviram-Ratner Concept

Energy vs. Distance of the device:



Aviram-Ratner Concept



Different thresholds for conductance

⇒ RECTIFICATION

Aviram-Ratner Concept

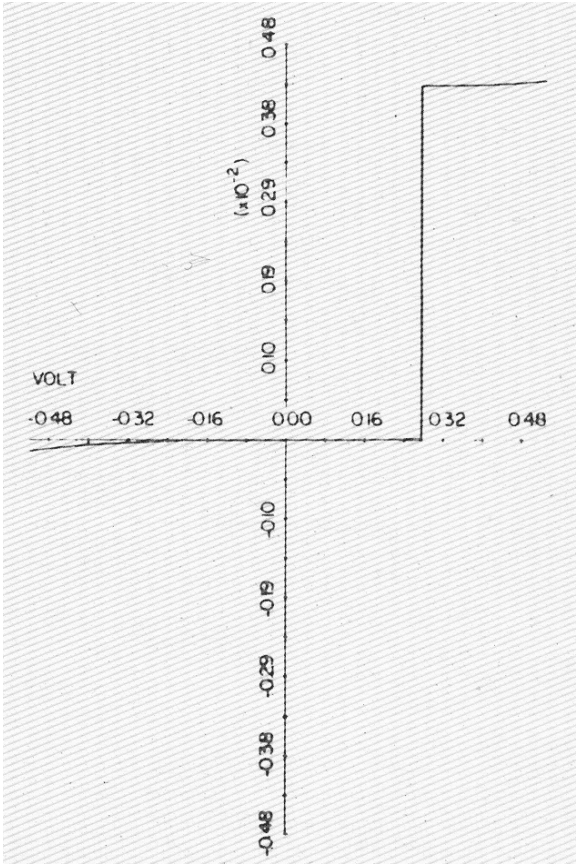
Calculations (Aviram-Ratner)

Three steps:

- Left Lead → Acceptor
- Acceptor → Donor (via σ-bridge)
- Donor → Right Lead

Asymmetric IV-curve

⇒ Designed and explained a molecule with rectifying properties



I-V characteristics of a molecular rectifier
Arbitrary choice of parameters

Recent Experiment (2005)

A Single-Molecule Diode

Mark Elbing, Rolf Ochs, Max Köntopp, Matthias Fischer, Carsten von Hänisch,
Florian Weigend, *Ferdinand Evers, Heiko B. Weber, Marcel Mayor*

Forschungszentrum Karlsruhe

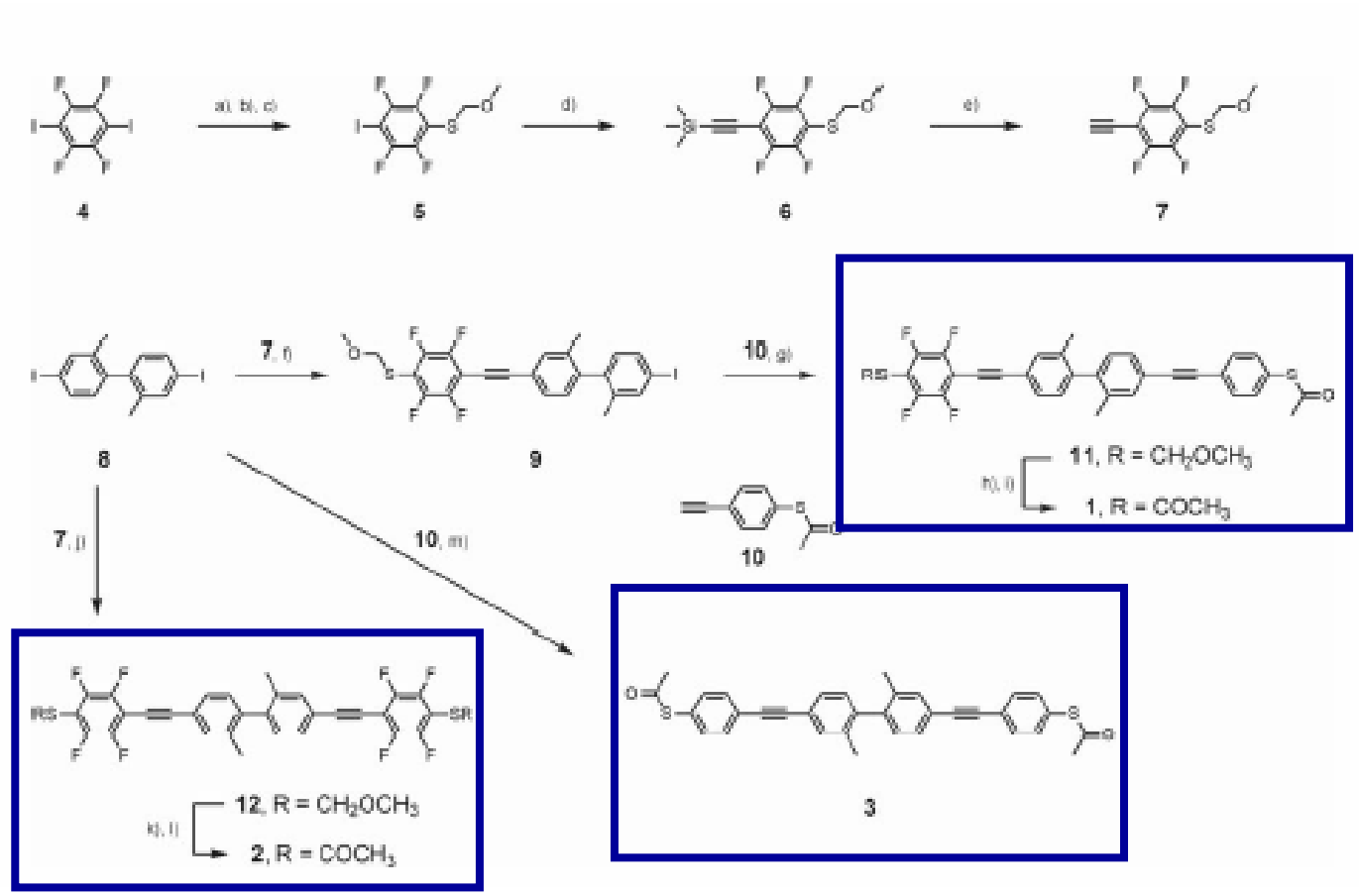
Design of the Molecules

Idea: Design a molecule separated in two segments of comparable structure but different electronic properties

- Two phenyl-ethynyl-phenyl π-systems
- Donor vs. acceptor part: substitute H by F (at one phenyl group)
- Fused by a biphenylic carbon-carbon bond
- Methyl groups in *ortho* position: torsion angle between the two (almost planar) π-systems:

  Reduced overlap between the π-systems

Design of the Molecules



Used molecules

1: asymmetric (F,H)

2: symmetric (F)

3: symmetric (H)

distance

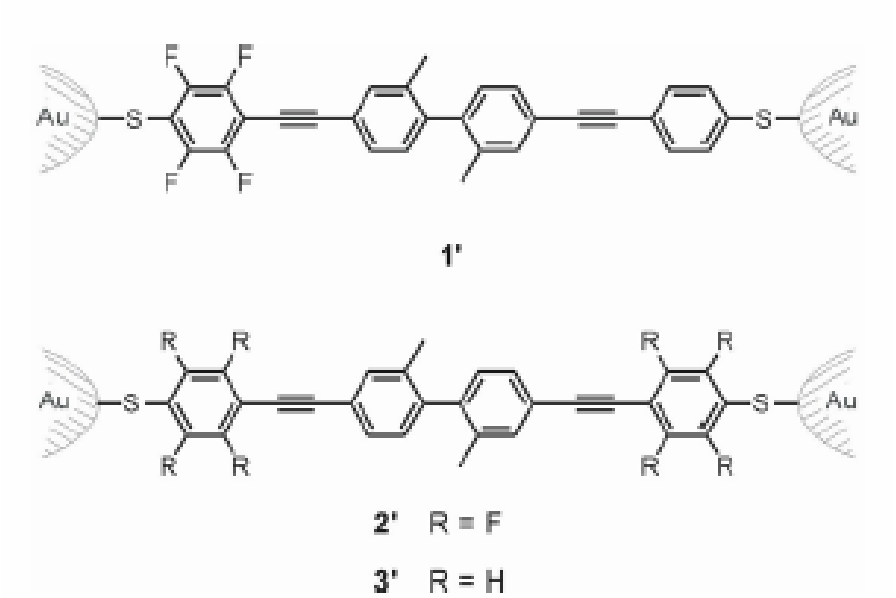
Sulfur-Sulfur:

2.43 nm

Acetyl groups:

Disappear when connected to the leads

Conductance Experiments



- Au-1`-Au junction: Asymmetric IV-curve expected
- Au-2`-Au / Au-3`-Au: Control experiments

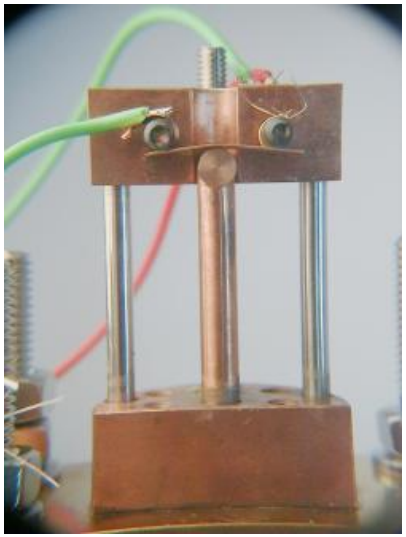
Problem: Connecting the single molecules to the Au-leads

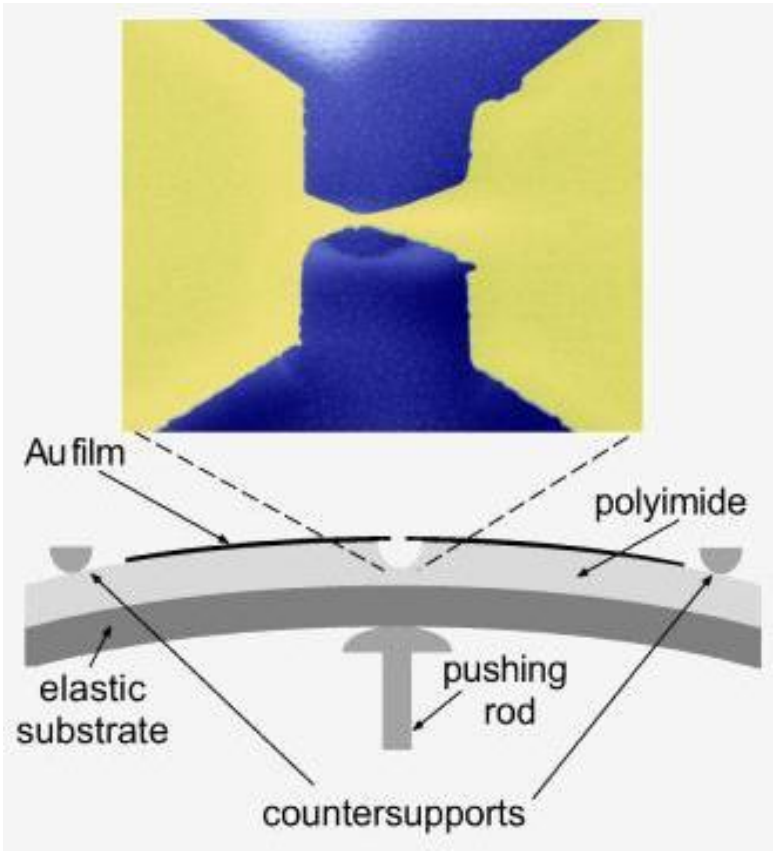
Conductance Experiments

Contact the **single** molecules to metallic electrodes

Experimental technique:

Mechanically controllable break junction





MCB Technique

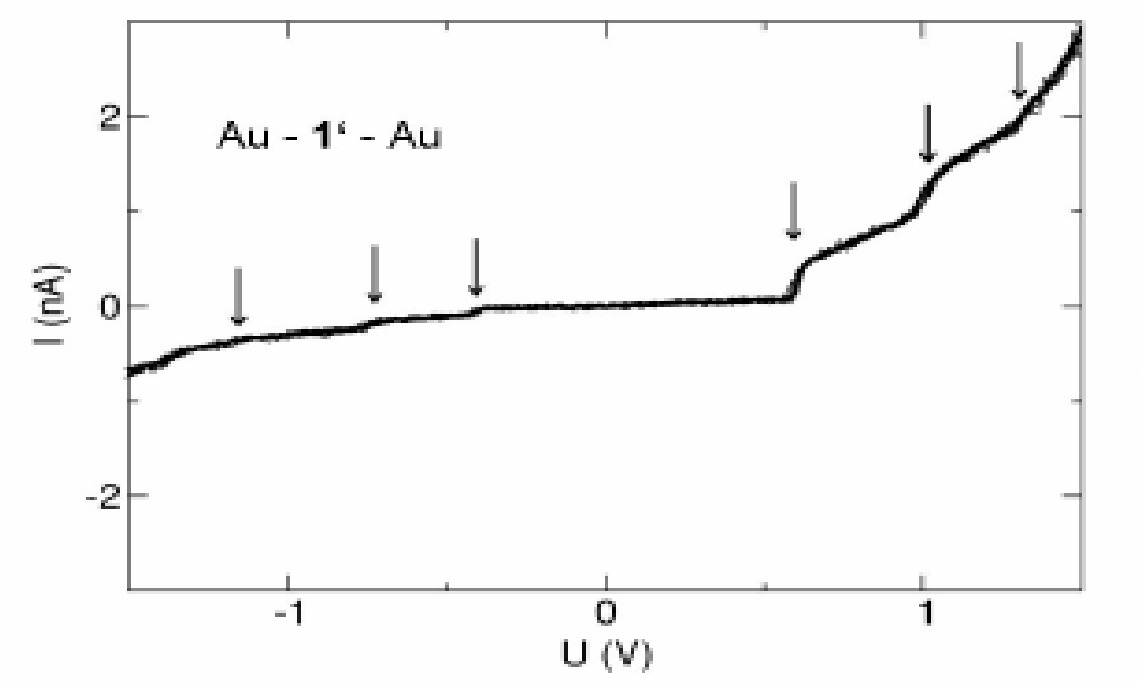
- Establish an electrode pair by breaking a lithographically fabricated gold wire
- Contact is opened and closed mechanically
- Atomically sharp gold tips with distance comparable to length of single molecules can be shaped
- **Single (or at most very few) molecules can be contacted**

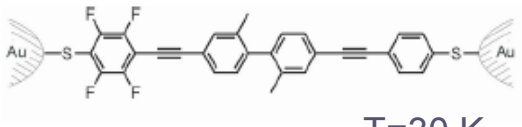
Immobilize single molecules:

- Molecules with acetyl protected sulfur groups are exposed for a short time from solution
- Reduced density of molecules on the Au-surface
- Repeatedly opening and closing the junction

Stable conditions under which the IV-characteristics of single molecules can be recorded repeatedly

Results for the asymmetric molecule 1´





T=30 K

Step-like features, less pronounced at negative voltages

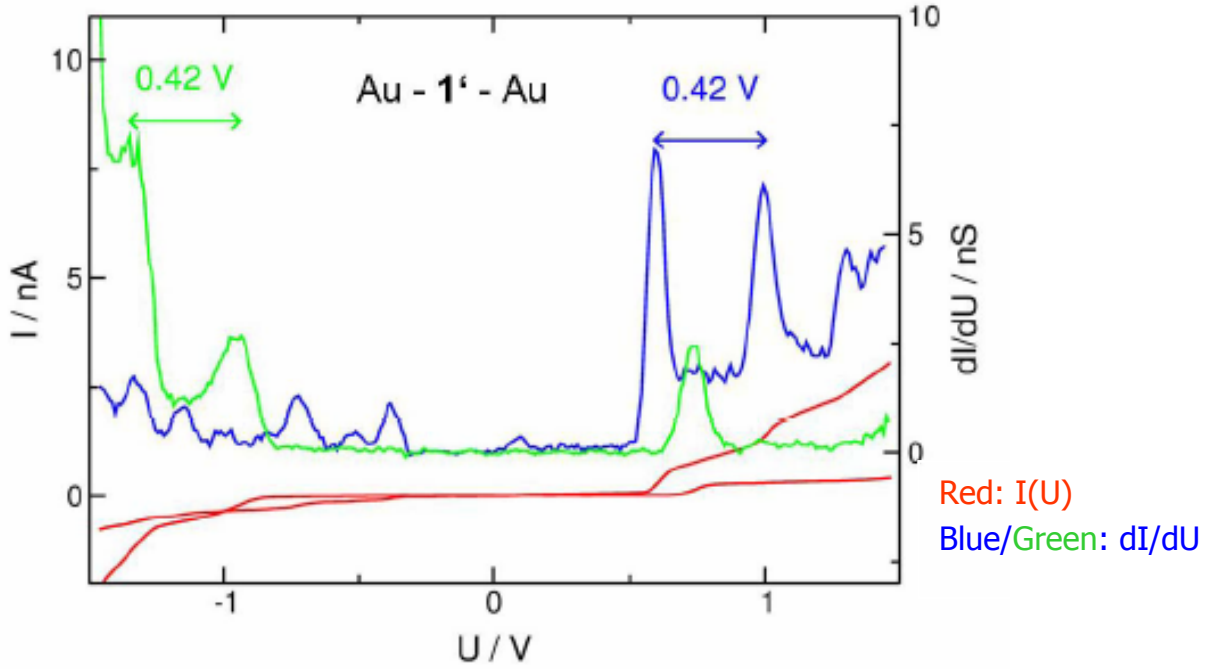
General shape **ASYMMETRIC,** rectification ratio 1:4.5 (at ±1.5V).

Results for the asymmetric molecule

Comparison of the IV-curves for two samples

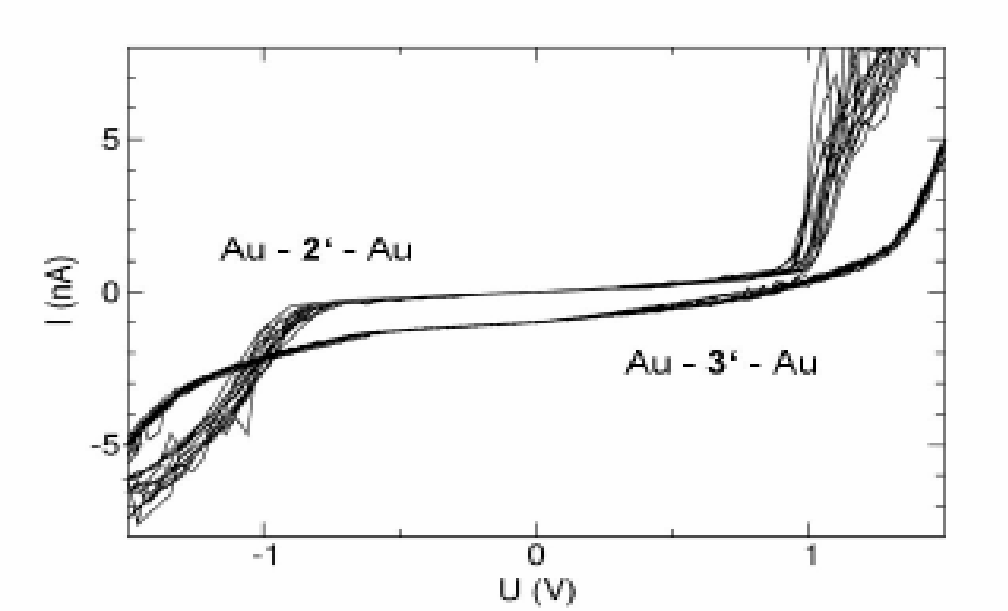
Curves inverted:

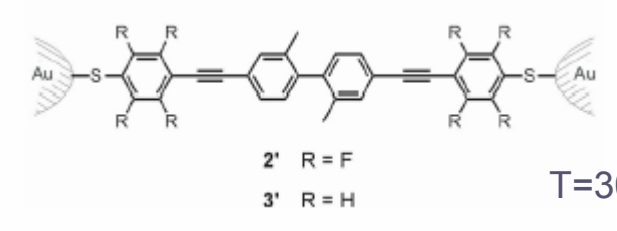
Molecules oriented oppositely



- Energy shifts: Different bonding types and influence of the environment
- **Peak distance unaffected (determined by the molecule)**

Results for the symmetric molecules 2´& 3´





T=30 K

(Au-3`-Au curves shifted by –1 nA)

Au-2´-Au (F-doped):
Symmetric shape, current blockade up to U ~ 0.8 V, strong increase for U > 0.8 V

Au-3´-Au:
Generally symmetric shape, similar current at U = ± 1.5 V

Qualitative Results

Comparing the results for symmetric/asymmetric molecules:

- Sample molecules are contacted
- Molecules are contacted as expected, no polymer-like chains or bulk-like assemblies
- A single molecule (or at most very few) forms the contact

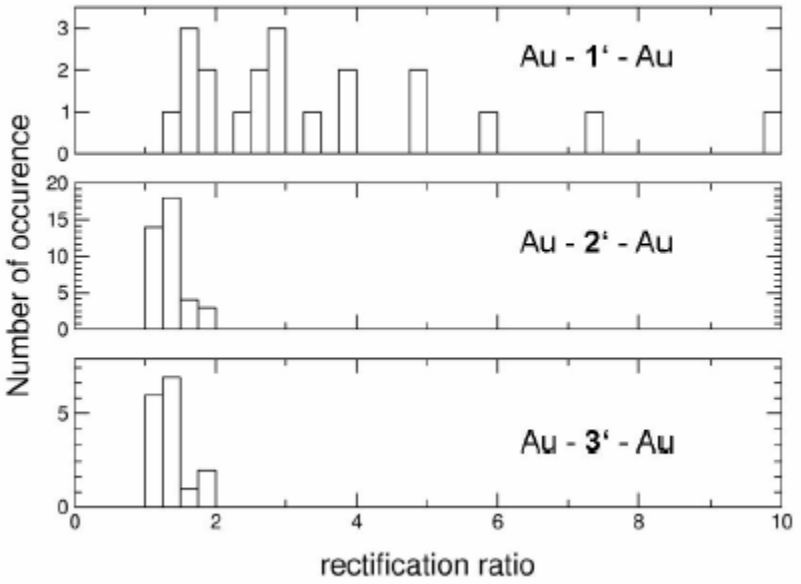
Statistical Comparison

… sample-to-sample fluctuations

Comparing current ratio at ±1.5 V for several samples:

Au-1´-Au:
Rectification 1.4 to 10
Average 4.5

Au-2`-Au / Au-3`-Au:
Rectification close to 1
(between 1 and 1.8)



Symmetric/Asymmetric behavior depends on the choice of the molecule

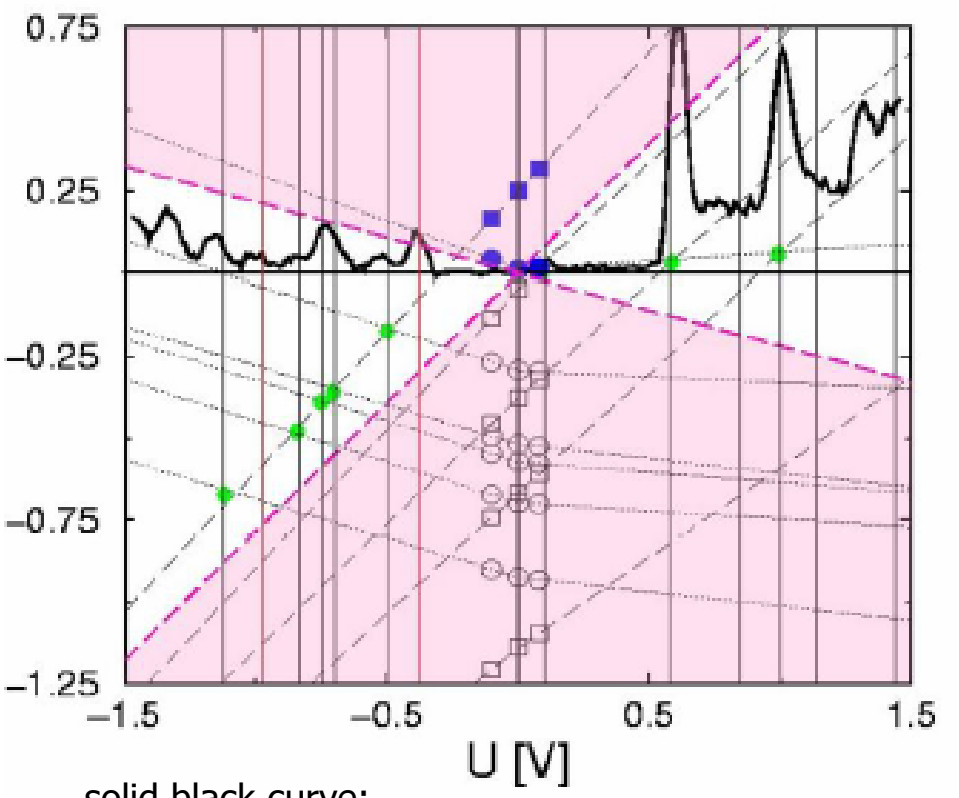
Sample-to-sample fluctuations:
electronic properties affected by uncontrolled presence of other molecules or irregular environment (rectification ratio >1 for symmetric molecules)

Theoretical Analysis

- Asymmetric Molecule in Au-1´-Au junction:
  Two different quantum dots in series: F-dot and H-dot
- Sweeping the bias voltage: electronic levels of both dots are shifted
- Certain Voltages: two levels cross (e.g. HOMO of the upwards moving H-dot with LUMO of downwards moving F-dot)
- Unoccupied level passes by an occupied: new channel is opened for transmission (subsequently into leads)
  $\Rightarrow$ Steps in IV-curve (Peaks in dI/dU)

Agreement with experiment ???

Theoretical Analysis



solid black curve:
dI/dU for an Au-1`-Au-sample

TURBOMOLE calculations:

- Energy levels for
  U=-0.1 V, U=0 V, U=0.08 V
  (circles: F-dot, squares: H-dot)
- Linear extrapolation for lager U
  (dotted: F-dot, dashed: H-dot)
- LUMO: blue filled symbols

Green dots, black vertical lines:
theoretical peak positions
(crossing of two extrapolated lines)

(Red vertical lines:
peaks not confirmed theoretically)

Position of steps in IV-curve can be explained

Theoretical Analysis

Explain the asymmetric IV for Au-1´-Au with level flow

- Slope of level flow: Indicator for polarizability of the electron system
  Small slope: "metallic character" (F-dot)
  larger slope: "insulating character" (H-dot)

- Levels of F-dot: larger slope at negative bias voltage

- $\Rightarrow$ asymmetric polarizability of the F-dot
  Current larger for pos. bias (F-dot shows a larger polarizability)

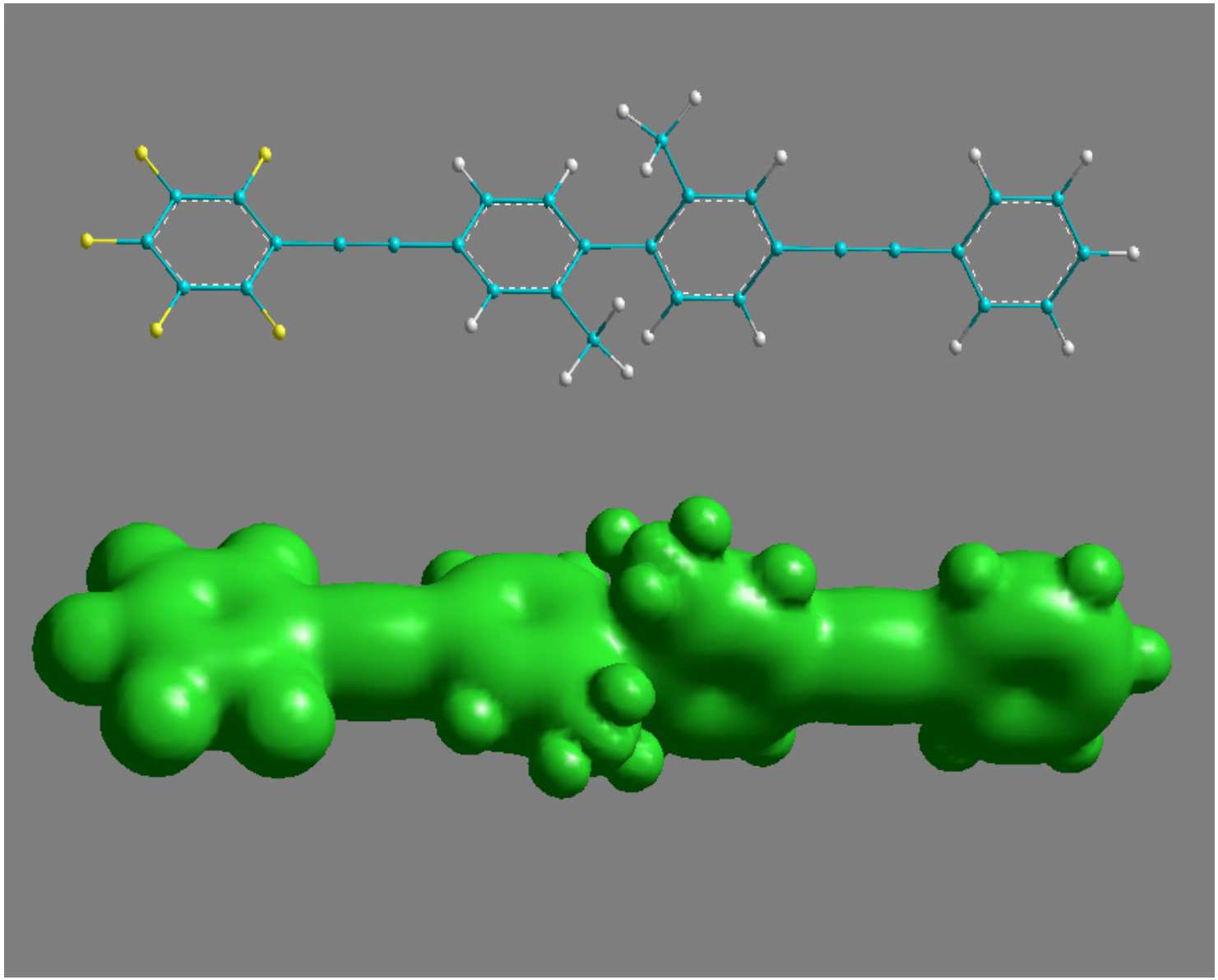
Differently polarized electron systems result in different transmissions and different current steps (when levels are crossing) for the two bias directions

Summary

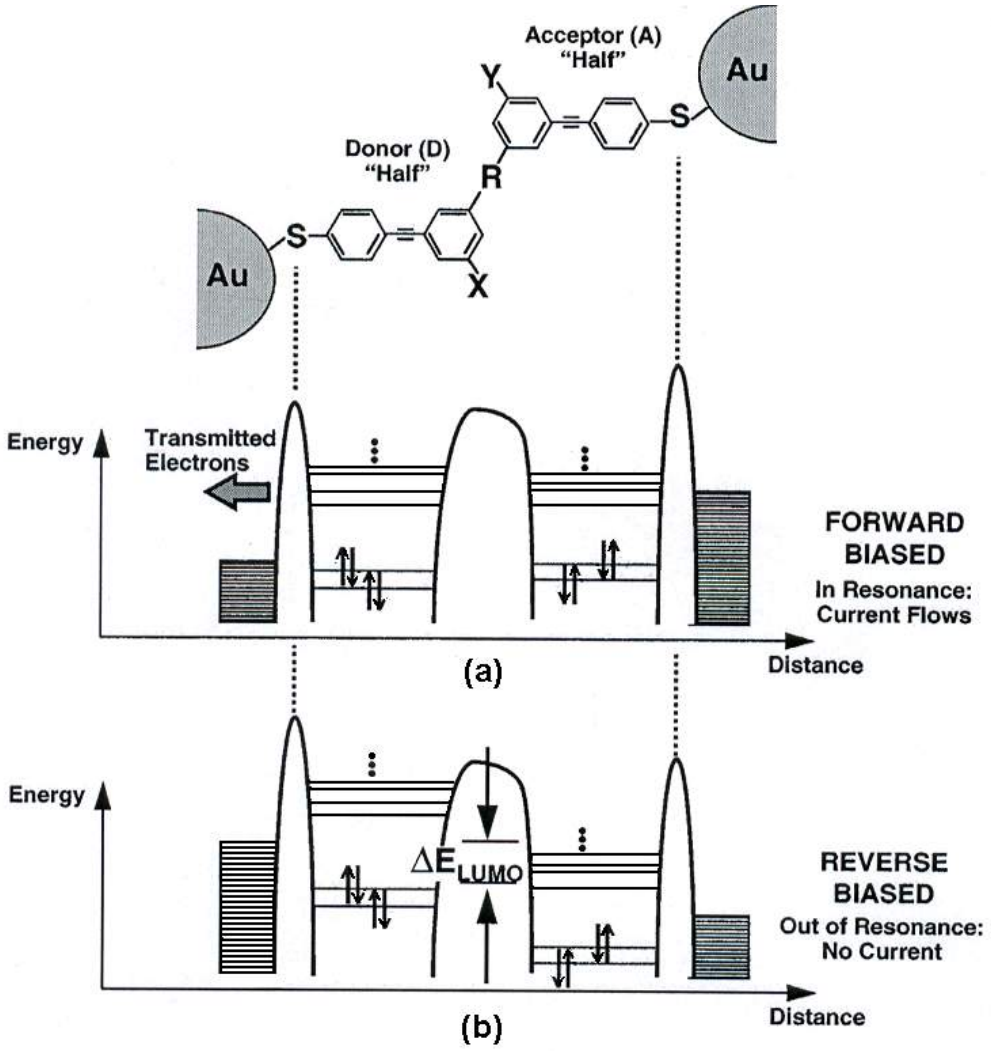
- Designed and synthesized a molecule with donor and acceptor unit
- Single-molecule conductance measurements: diode-like IV-curve
- Control experiments & Statistical evaluation:
  single-molecule contacts
- DFT analysis shows good agreement with experimental data and provides an explanation for the diode-like behavior
- Different mechanism compared to the original Aviram-Ratner Concept

preliminary e-structure calculations

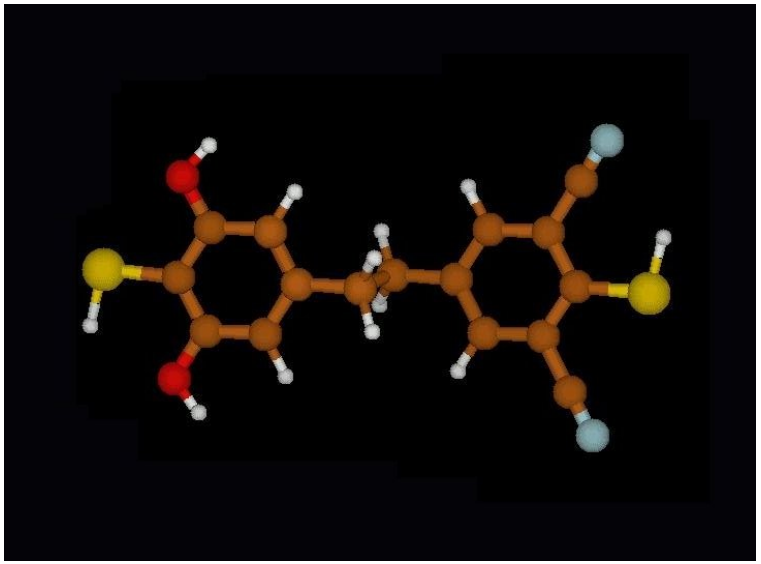
the molecule

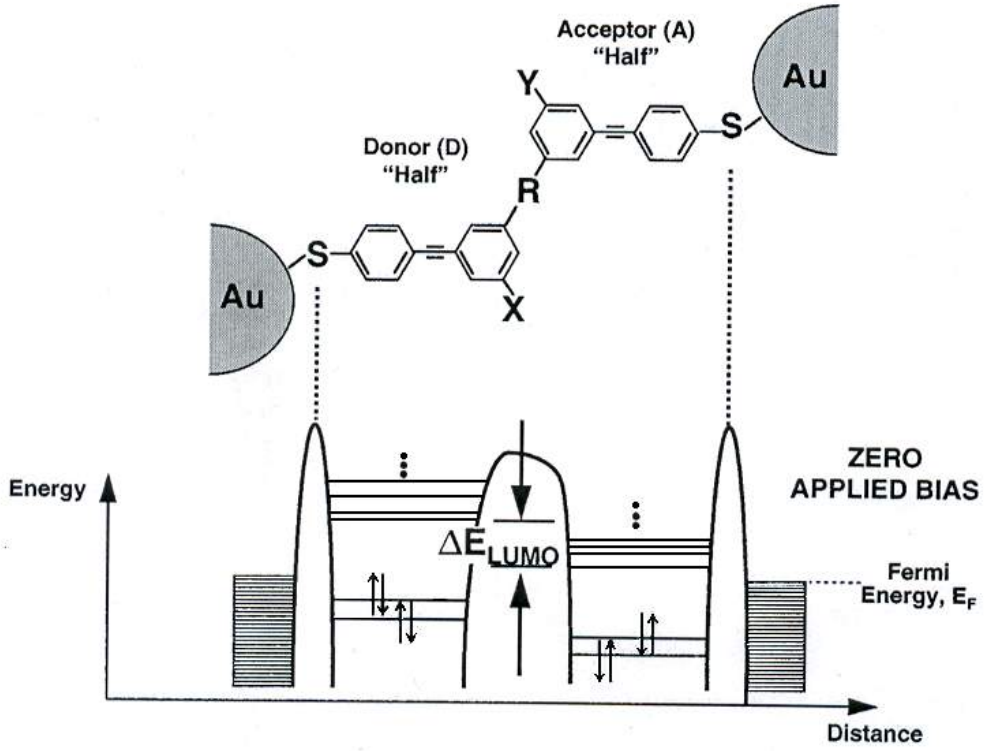


Mechanism


Acceptor (A)
"Half"
Au
Y
S
Donor (D)
"Half"
R
S
Au
X
Energy
Transmitted
Electrons
FORWARD
BIASED
In Resonance:
Current Flows
Distance
(a)
Energy
ΔE LUMO
REVERSE
BIASED
Out of Resonance:
No Current
Distance
(b)

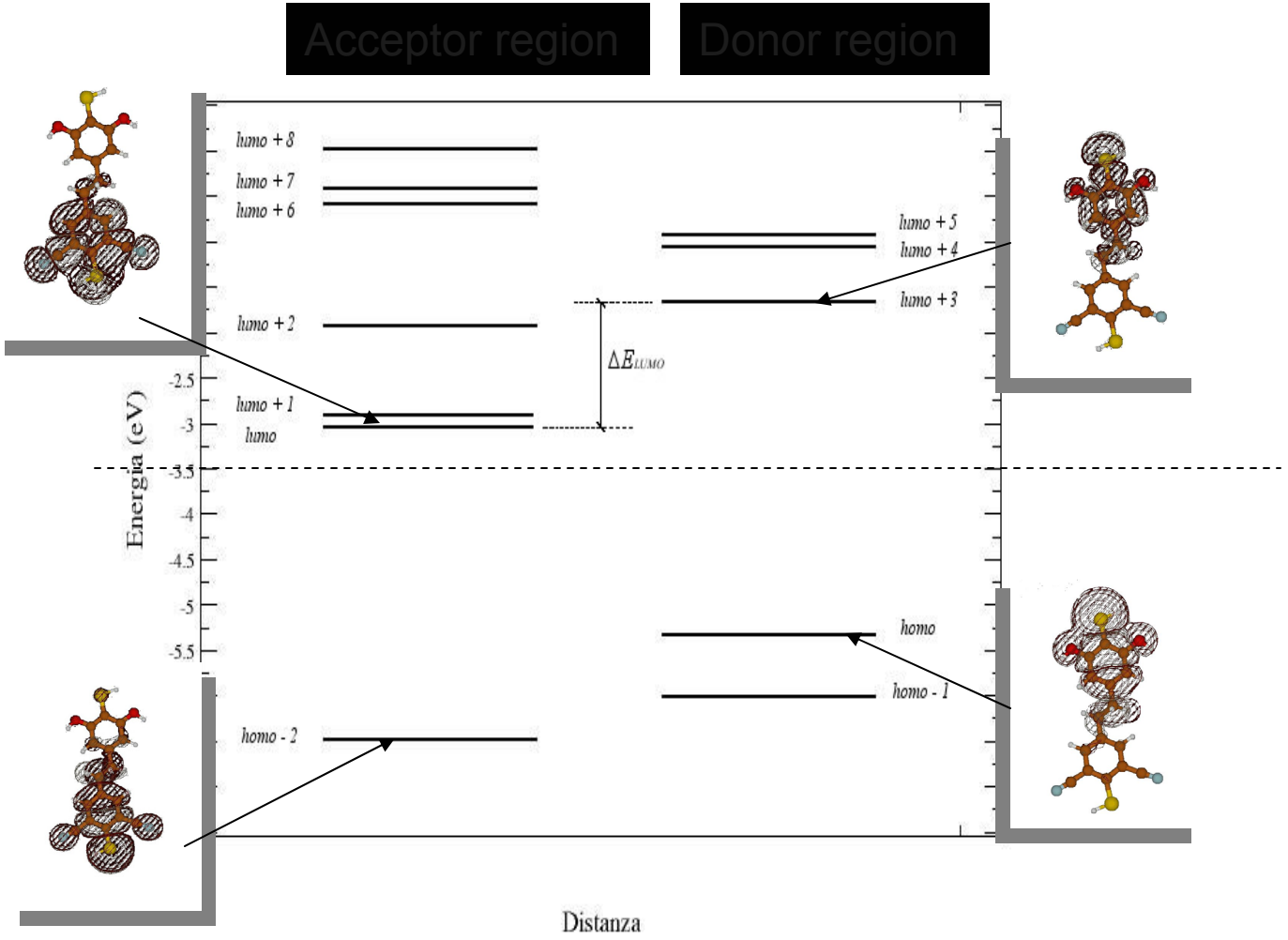
An example



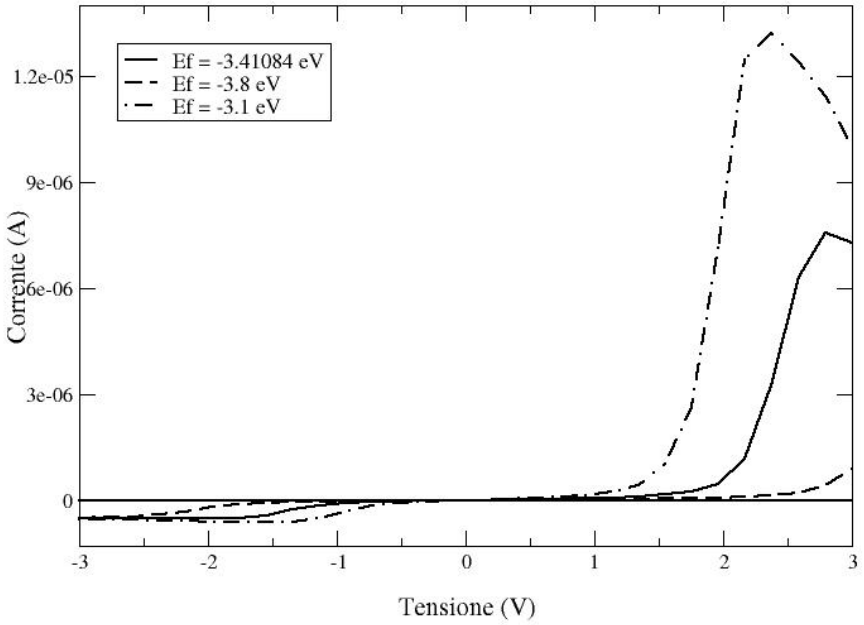


J.C.Ellenbogen, Proc. IEEE 88, 386 (2000)

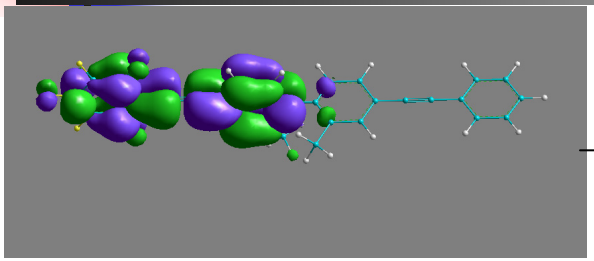
Molecular orbitals



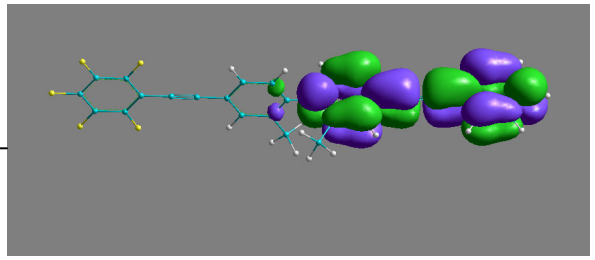
Computation of IV



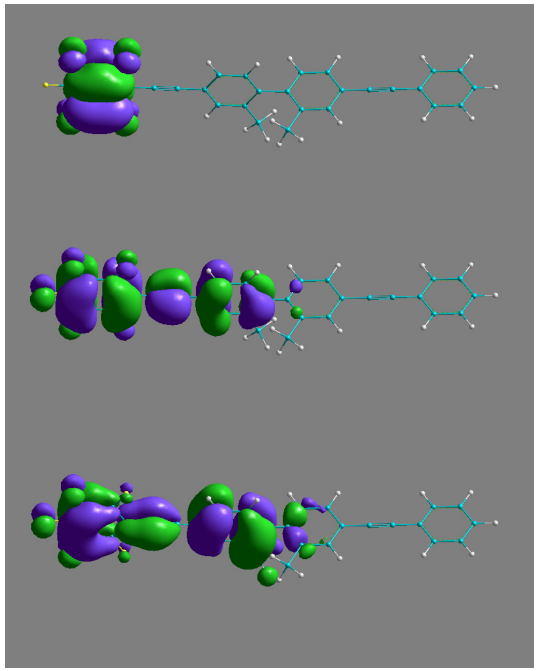
Energy levels (Non SCC)



-2.351



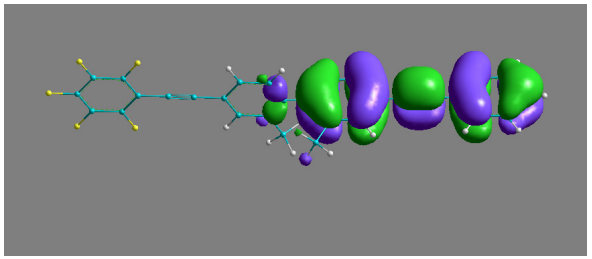
-2.659



-5.787

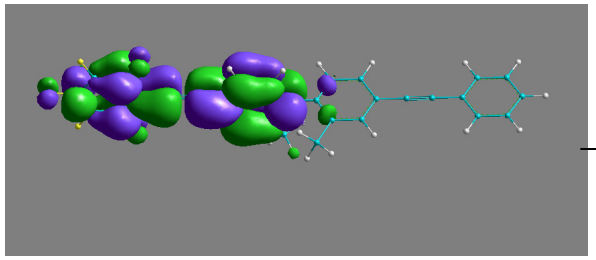
-5.946

-6.982



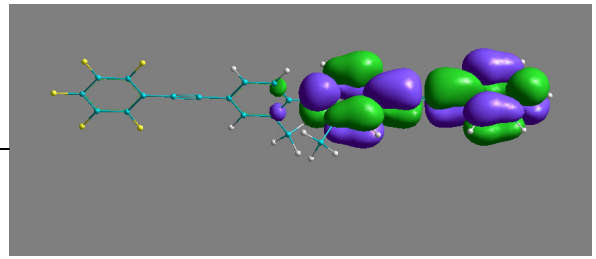
-6.516

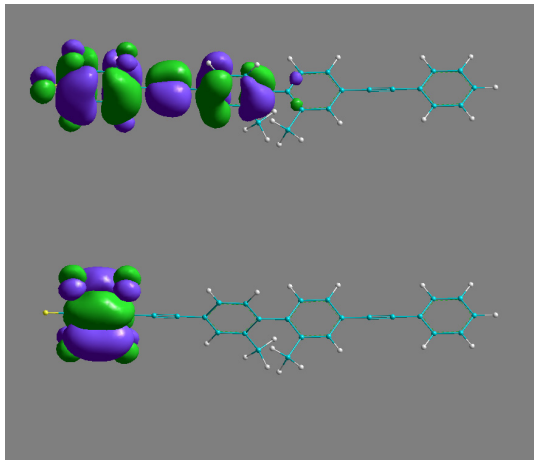
Energy levels (SCC)



-2.694

-2.374

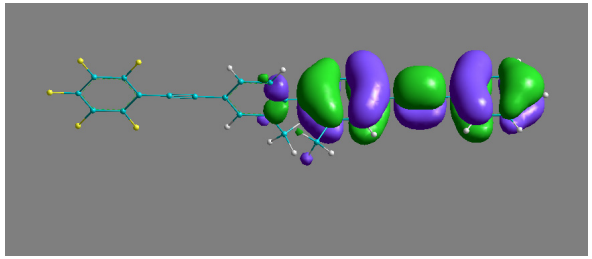




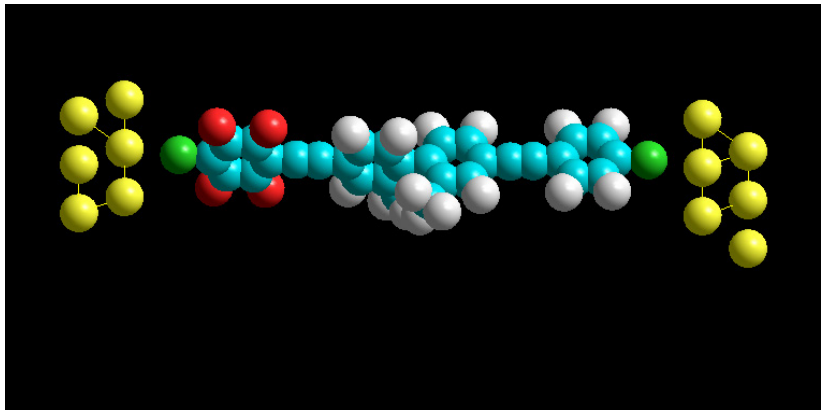
-6.350

-6.629

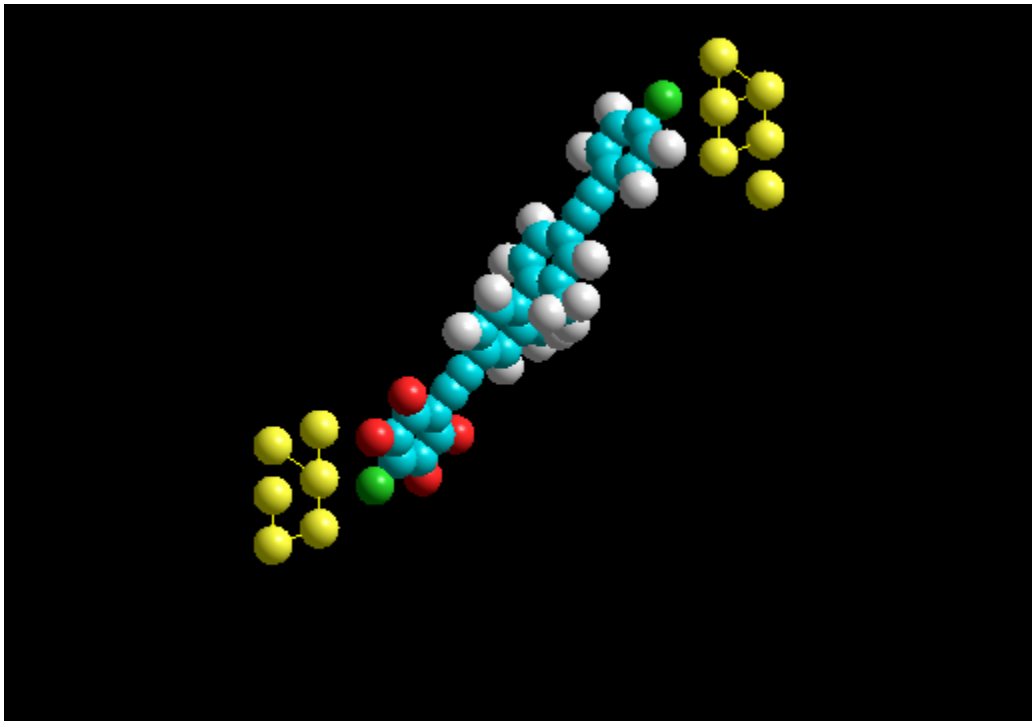
-6.231



the molecule between contacts

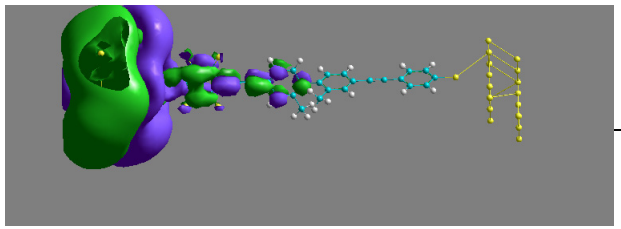


A

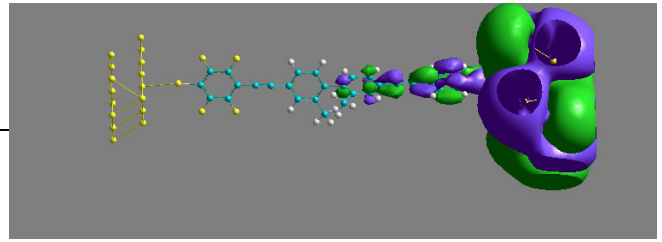


B

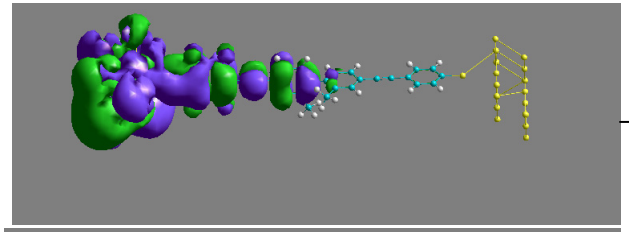
Orbitals with leads



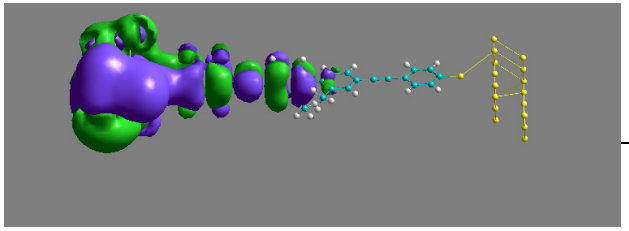
-3.01



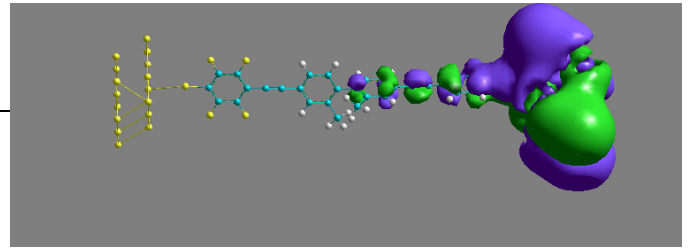
-3.26



-5.867

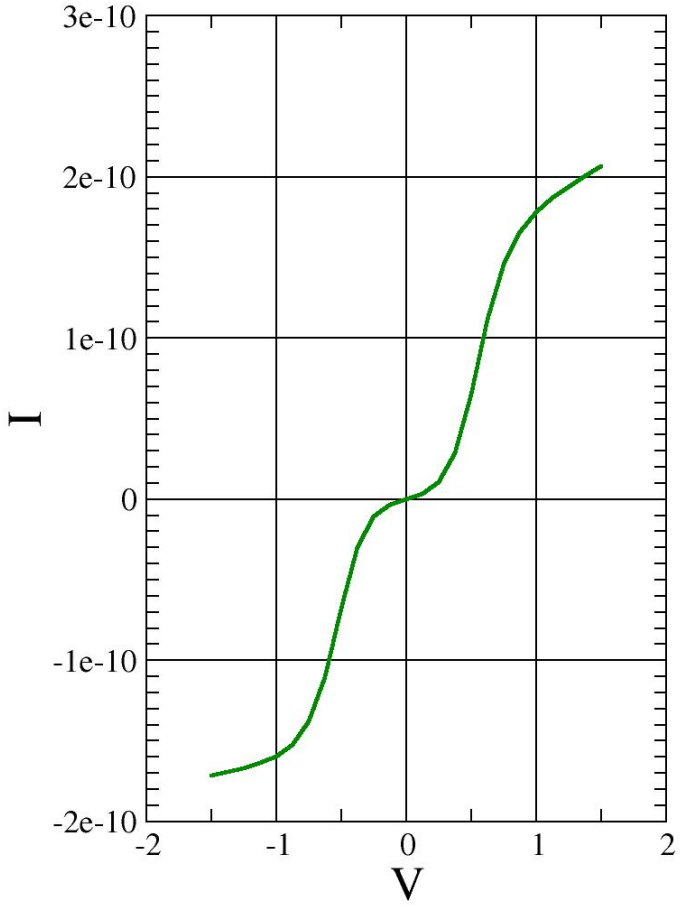


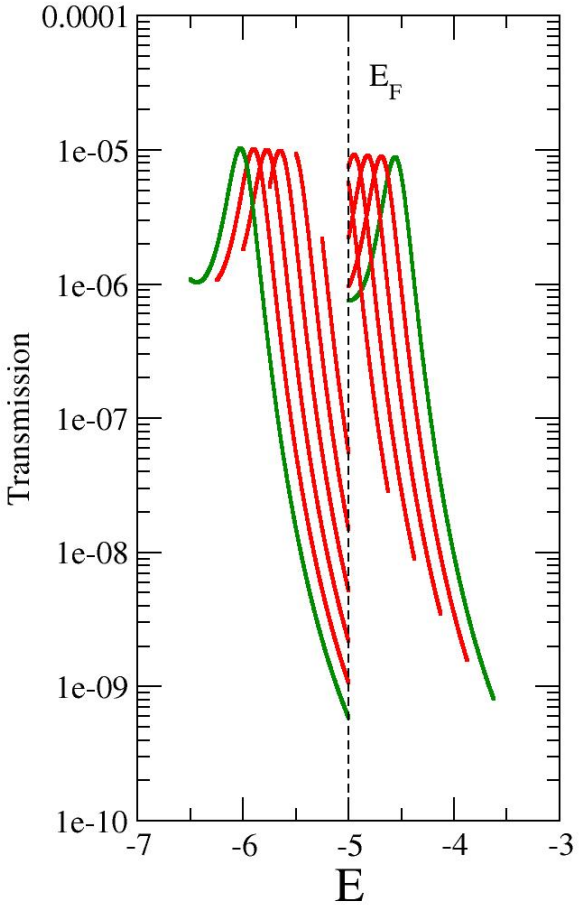
-5.95



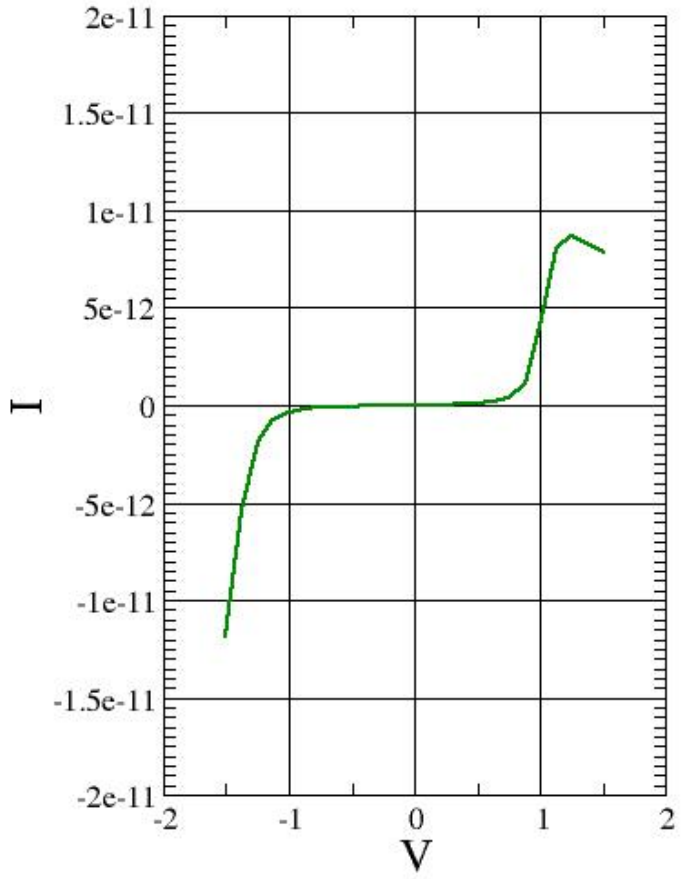
-5.90

IV … Self-consistent





IV … Non - SCC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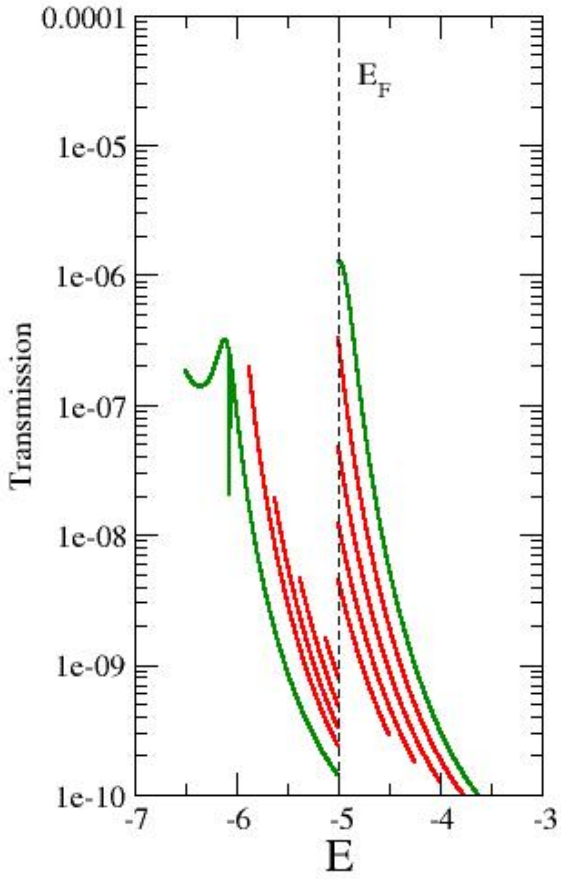
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Transmission
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