Graphene as a Promising Electrode for Low-Current Attenuation in Nonsymmetric Molecular Junctions

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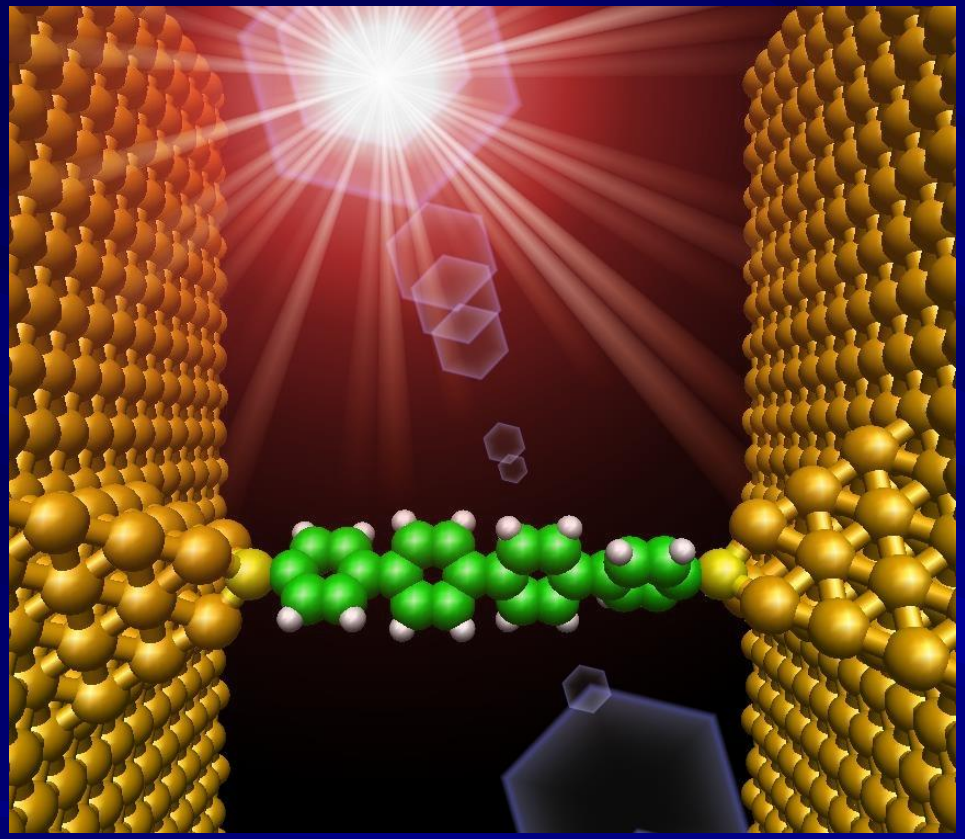
Introduction to Molecular Electronics



J. C. Cuevas, E. Scheer, Molecular Electronics: An Introduction to Theory and Experiment; World Scientific: Singapore, 2010.

Molecular Electronics :
a field of science which studies the electronic transport through molecular systems and its applications

Some questions :

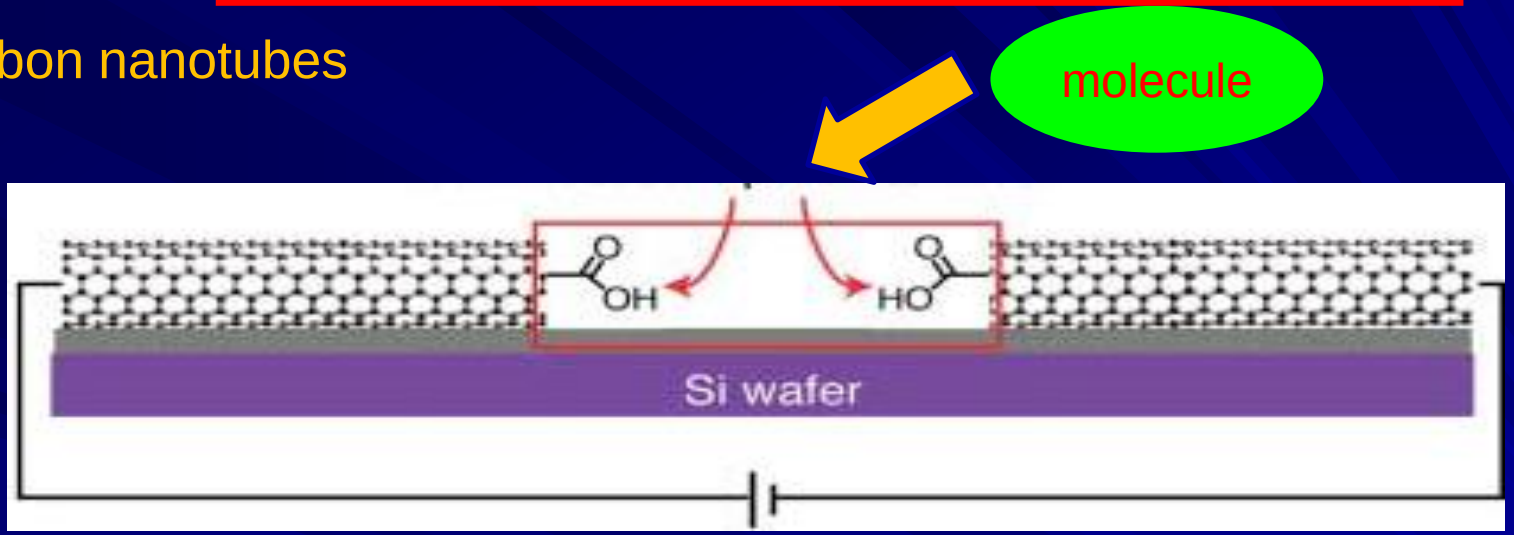
- how do the electrons flow through a single molecule?

- can a molecule mimic the behavior of an ordinary silicon device or even bring new functionalities?

- influence of the anchoring groups / electrodes in the electronic transport ?

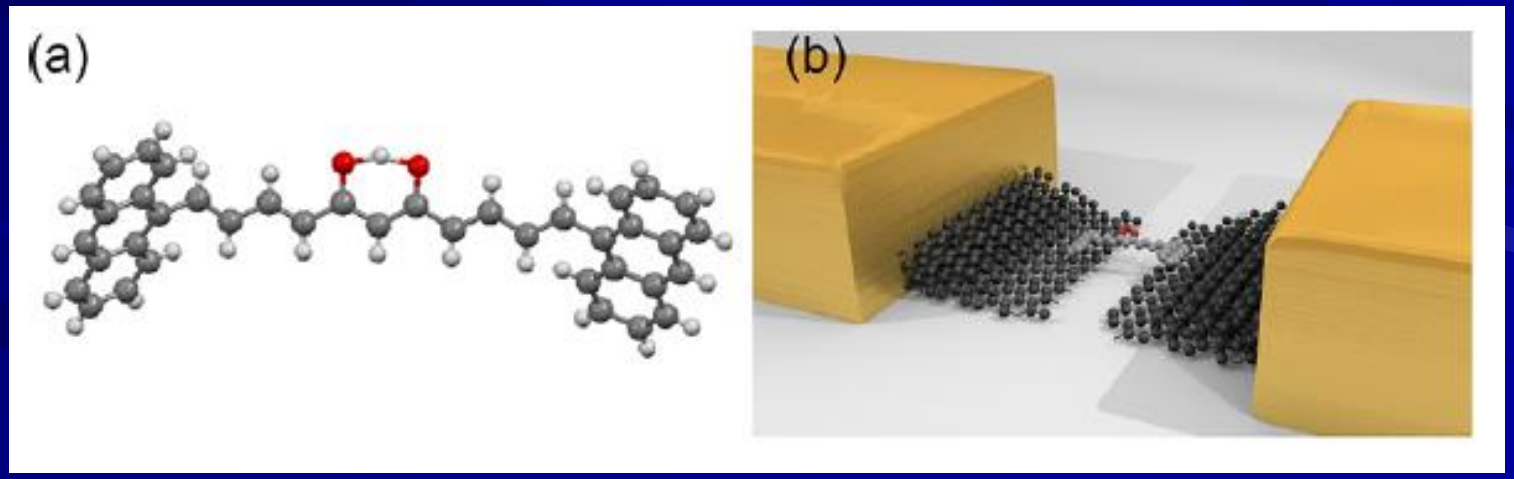
Some example of graphitic electrodes

- carbon nanotubes

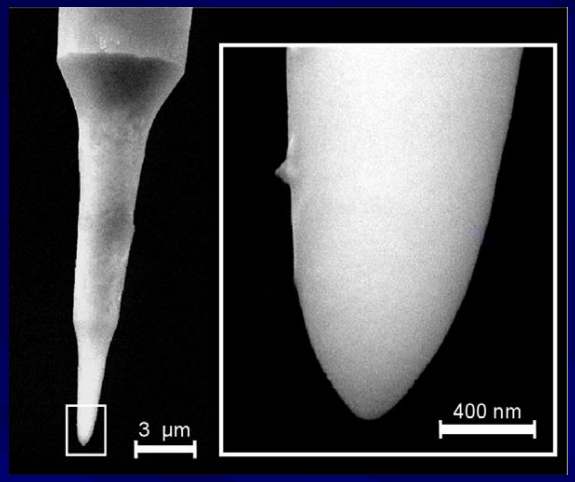


*X. Guo et al., Science **311**, 356 (2006)*

- graphene electrodes

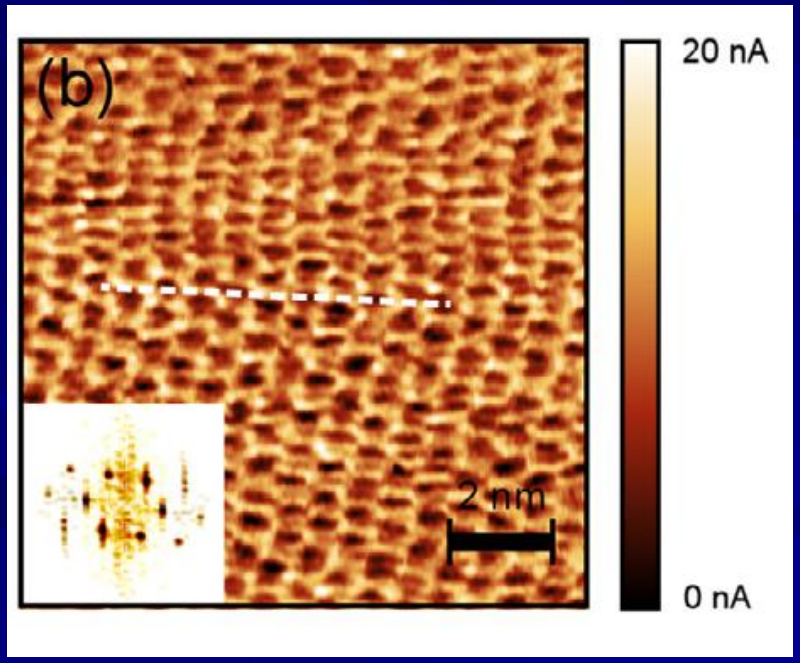


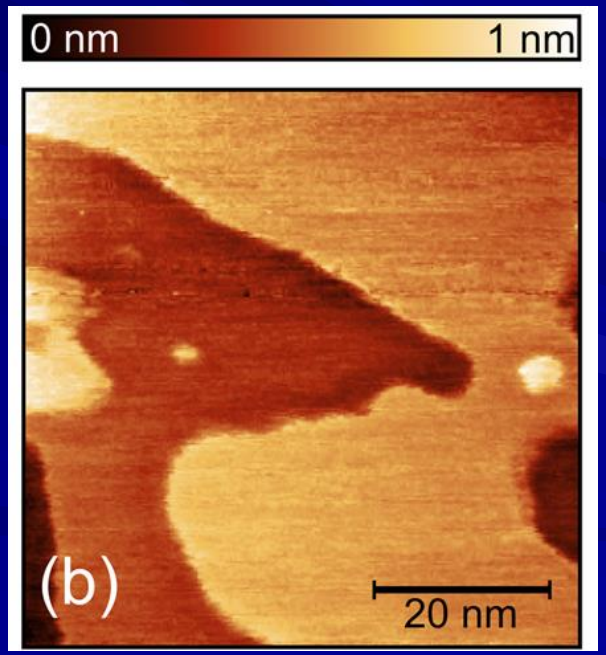
*H.S.J. van der Zant et al., ACS Nano **10**, 2521 (2016)*



- carbon tip fiber for STM/AFM imaging : application to gold surfaces and graphite, and to octanethiols SAM on gold.

A. Castellanos-Gomez et al., Nanotechnology ***21****, 145702 (2010)*

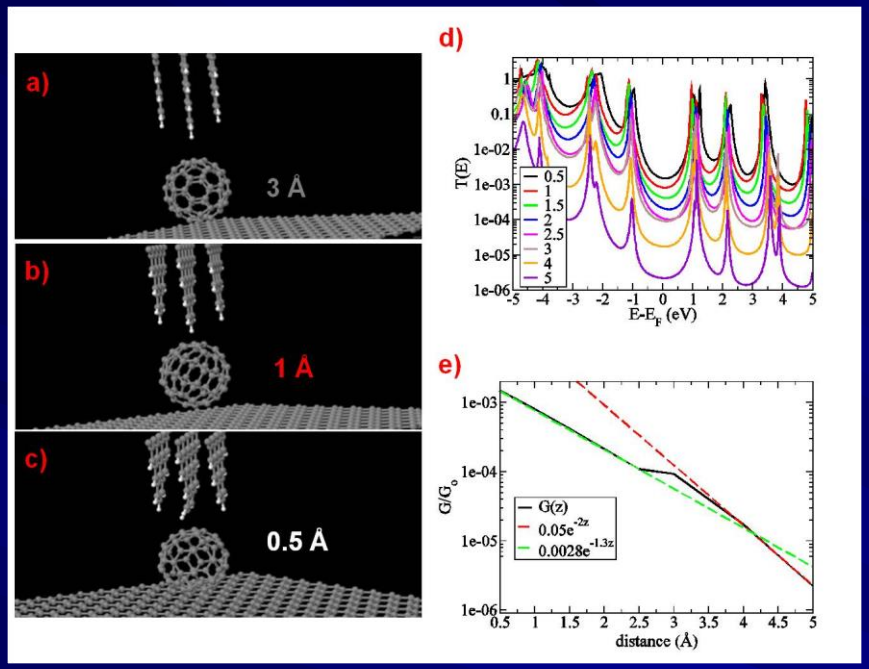


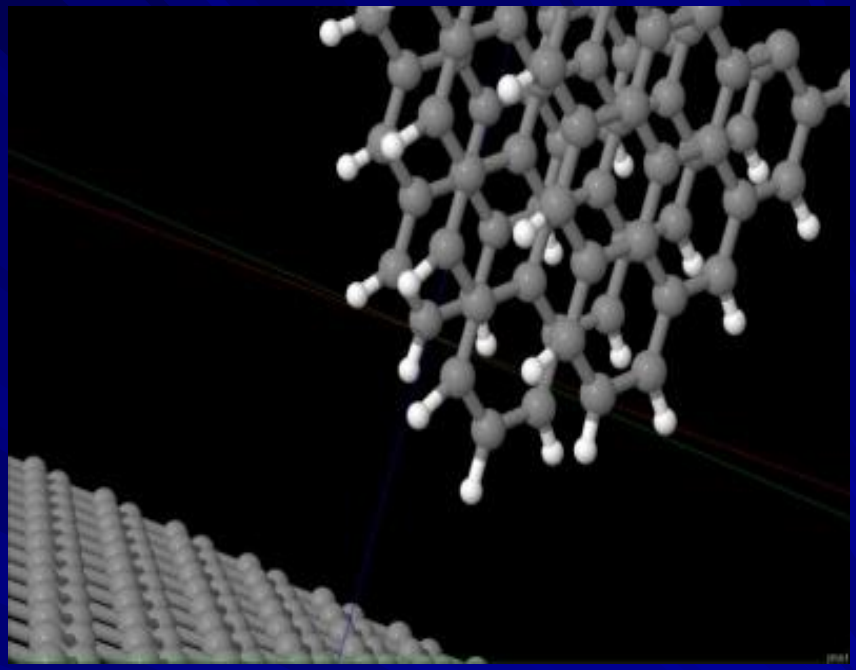


- carbon tip for STM/AFM imaging on graphene/SiC

J. Moran Meza et al., Nanotechnology, ***26****, 255704 (2015)*

- conception of a model graphene tip : “all carbon” molecular junction

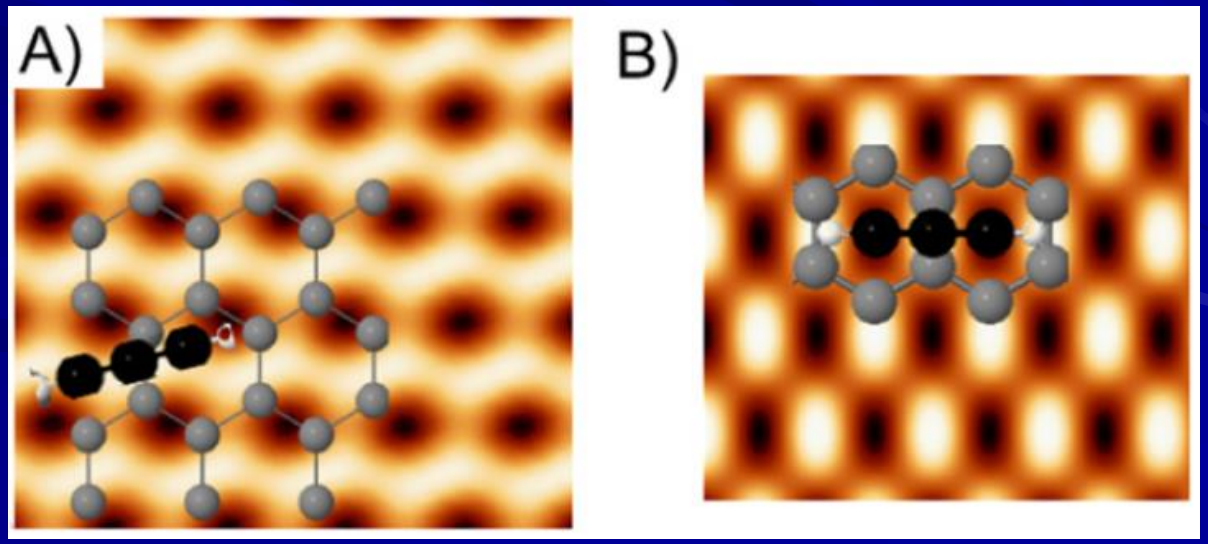




*Nanoscale **6**, 6953 (2014)*

- STM images calculations

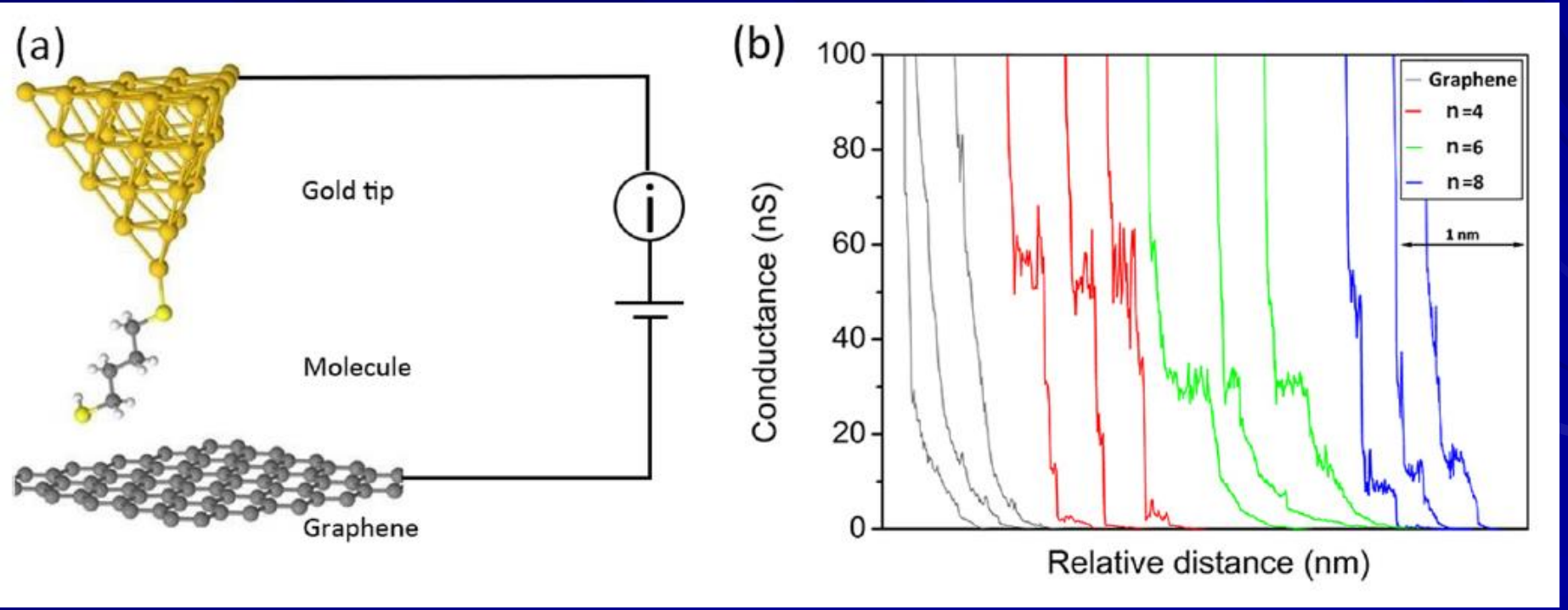
*Nanotechnology **27**, 105201 (2016).*



Hybrid metal/molecule/graphene junctions for Molecular Electronics

- I(s) measurements of alkanedithiol conductances with Au STM tip and graphene/Ni(111) substrate

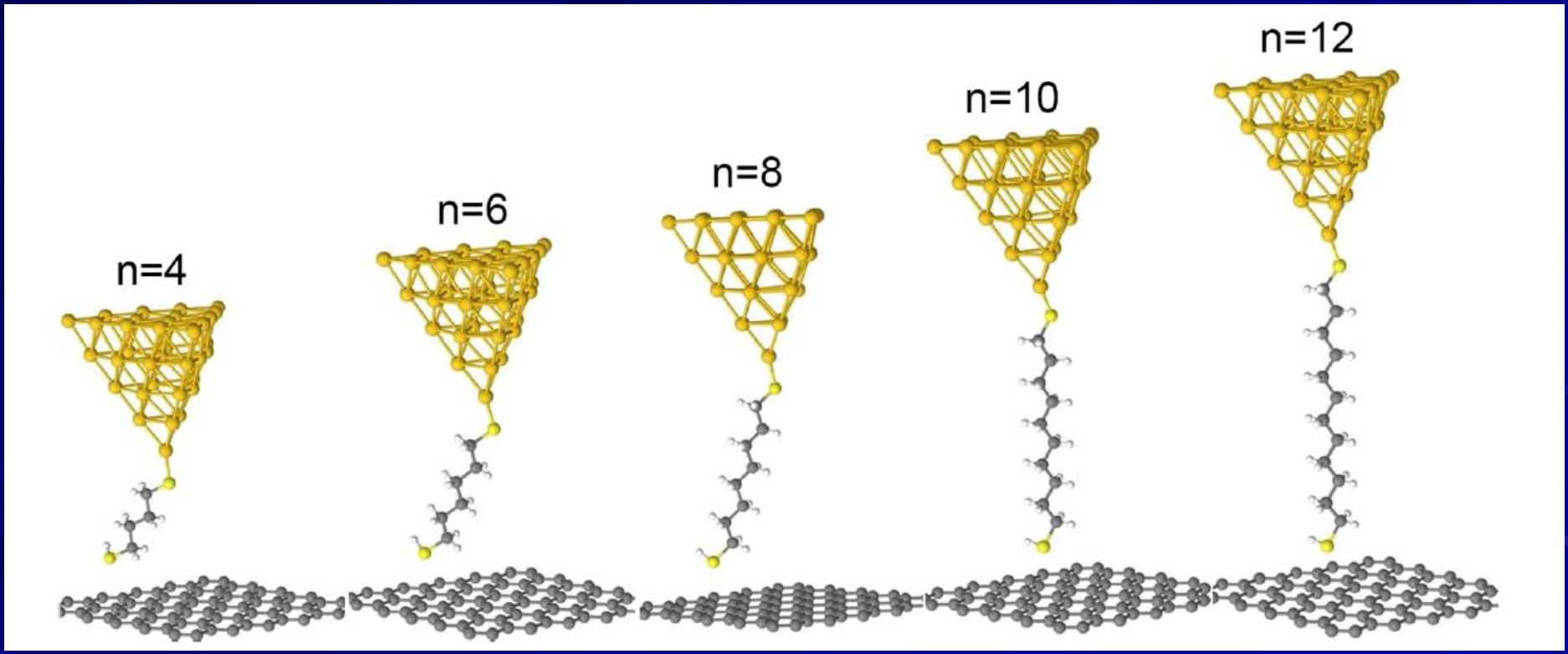
- DFT + Keldysh-Green formalism for configuration and electronic structure and transport calculations



*Q. Zhang et al, Nano Letters **16**, 6534 (2016).*

- evolution of the conductance with the molecular length (non-resonant tunneling regime) : $G = A \exp(-\beta L)$

- determination of the attenuation factor β, comparison with standard metallic junctions



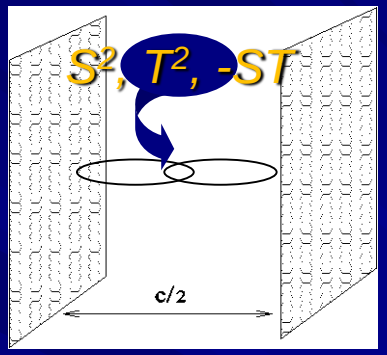
Density Functional Theory (DFT) in localized orbital basis set Fireball

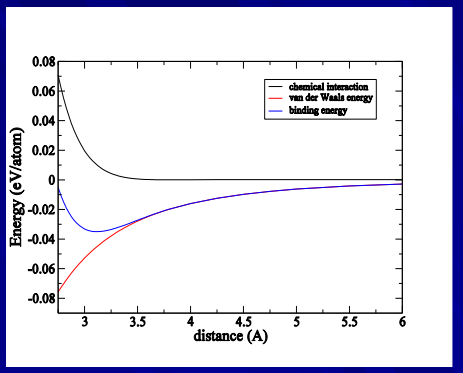
+

vdW Interaction

- intermolecular perturbation theory
- dipolar approximation
- sum rule

Phys. Rev. ***B 79*** *(2009), Phys. Rev.* ***B 74*** *(2006), Europhys. Lett.* ***70*** *(2005)*





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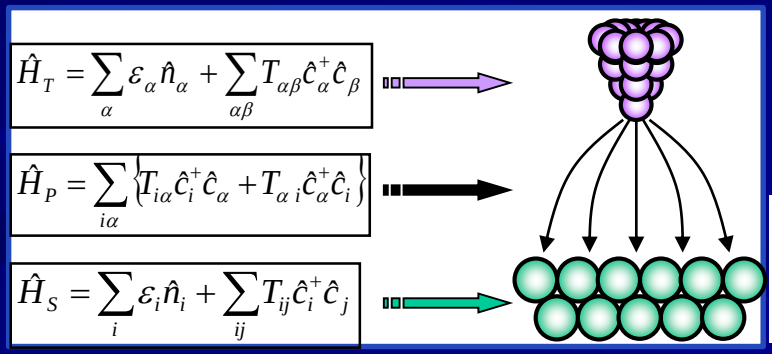
STM model for electronic tranport calculations



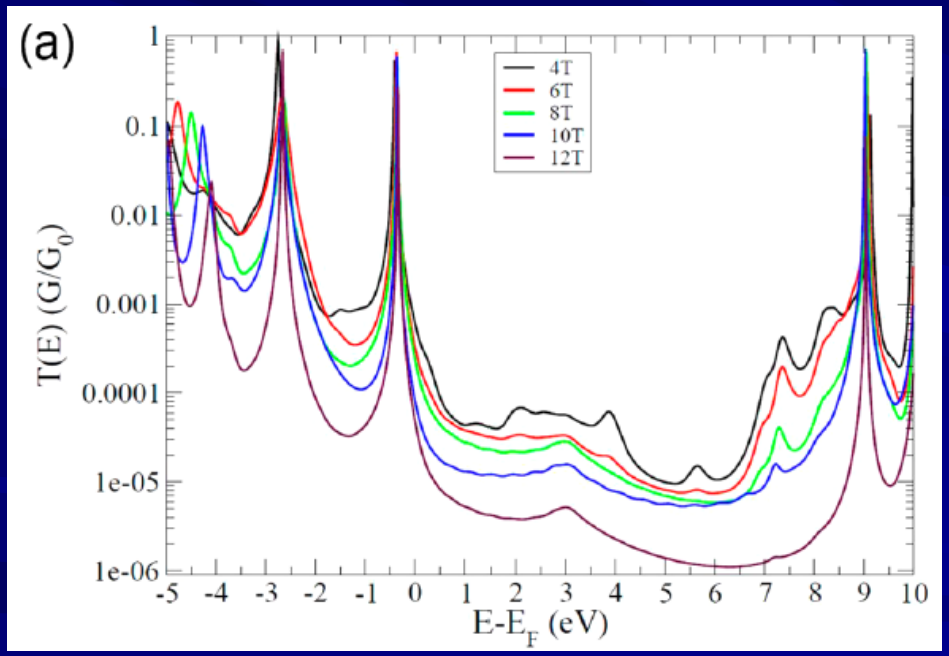
Current calculation : Keldysh-Green formalism for out of equilibrium systems

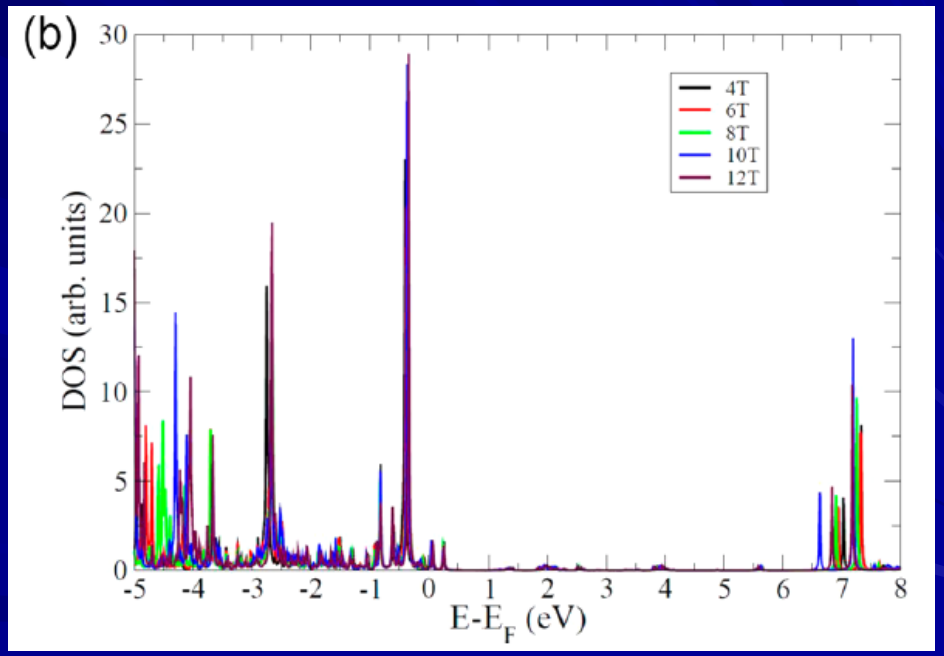
$$I = \frac{4\pi e^2}{h} \int_{E_F}^{E_F+eV} \mathrm{Tr}[T_{TS}\rho_{SS}(E) D^r_{SS}(E) T_{ST}\rho_{TT}(E-eV) D^a_{TT}(E-eV)]dE.$$

C. González et al., Nanotechnology ***27****, 105201 (2016).*

- theoretical results : transmission of the molecular junctions and projected Density of States (PDOS) on the molecular chains

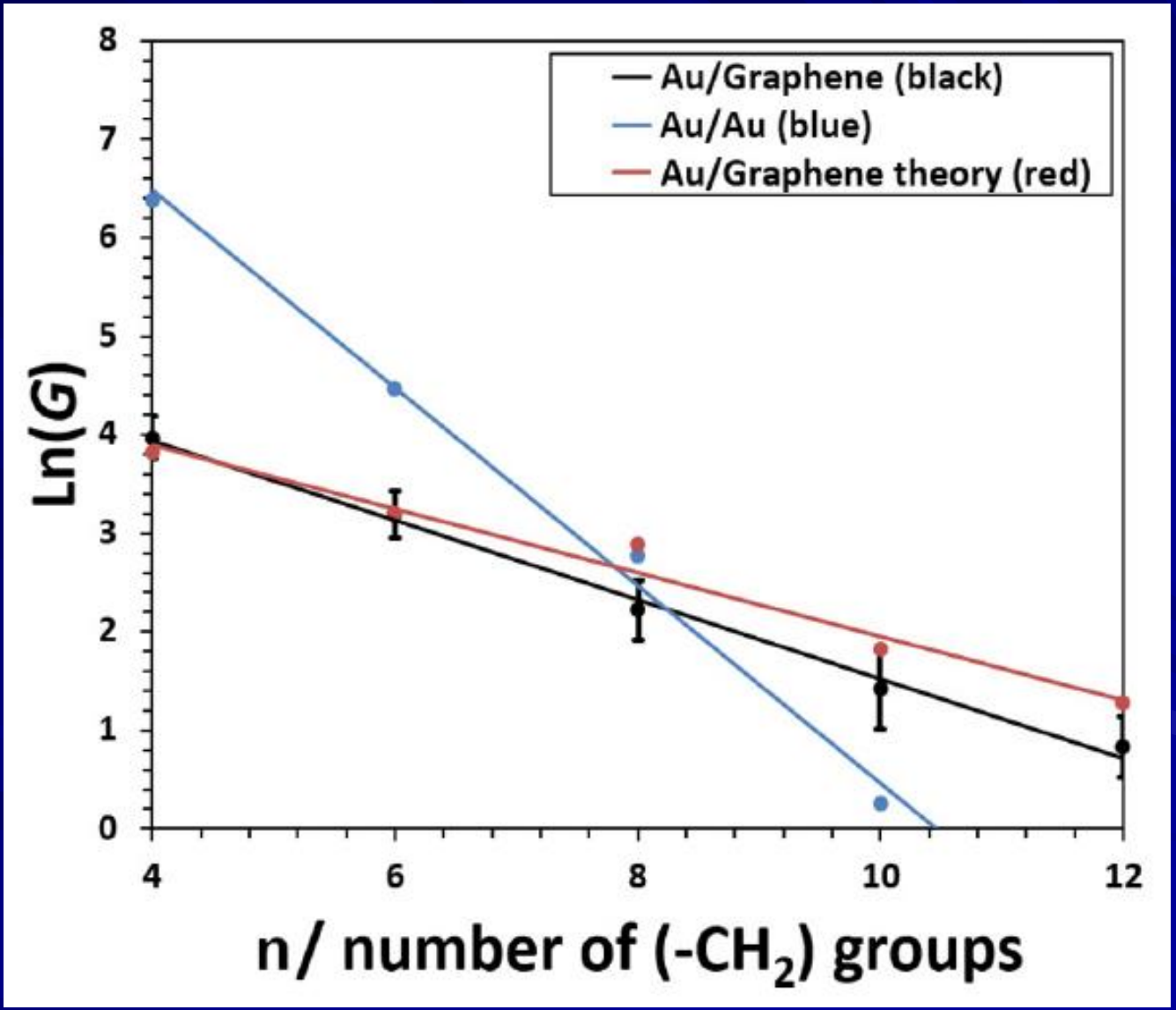
- conduction through the HOMO level





- comparison with experiments and standard metallic junctions

- for length > 1nm, better conduction of the hybrid junction

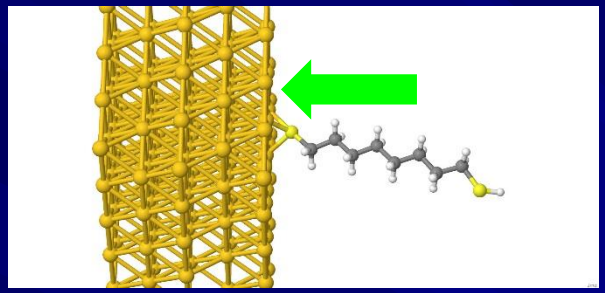


Interpretation

- $\beta \sim \sqrt{(2m\varphi/\hbar)}$ where φ is the electronic potential barrier

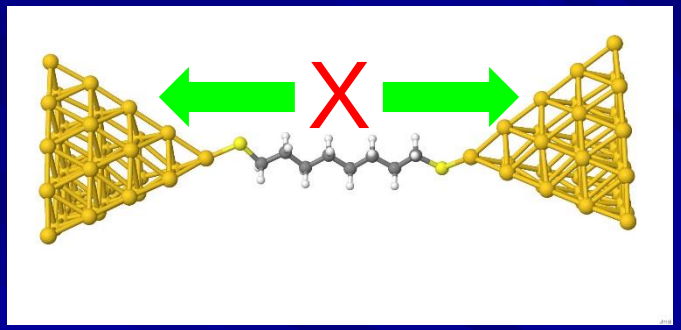
- $\varphi = E_F - E_{HOMO}$

- thiol adsorption on gold :

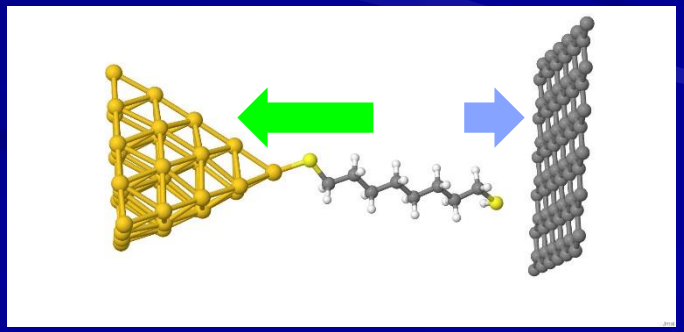


strong interface dipole, $E_F - E_{HOMO}$ very small

- thiol molecular junction with gold electrodes :
zero resulting dipole, $E_F - E_{HOMO} \sim 2$ eV
$\Rightarrow \beta \sim 0.9$



- thiol molecular junction with gold and graphene electrodes :
resulting dipole at the gold/molecule interface,
$E_F - E_{HOMO} \sim 0.4$ eV
$\Rightarrow \beta \sim 0.3$



- much lower attenuation, better conductance for longer junctions

Conclusions and perspectives

- introduction to Molecular Electronics with graphitic electrodes

- I(s) method for conductance measurements on hybrid metal/molecule/graphene junctions for Molecular Electronics

- different results from standard metallic molecular junctions

- key parameter : molecule/surface interaction, Physics at the interface

- different interface dipoles due to different couplings : different molecular levels alignments leading to different attenuation factors

- importance of the HOMO position with respect to the Fermi level

- interest of graphene for low consumption molecular electronics devices

Perspectives : 2D materials electrodes like MoS_2, WS_2 or small vdW heterostructures, or different anchoring groups, for new electrical behaviors in molecular junctions