The current-voltage characteristic of a metal-molecule-metal junction studied by an integrated and piecewise thermal equilibrium

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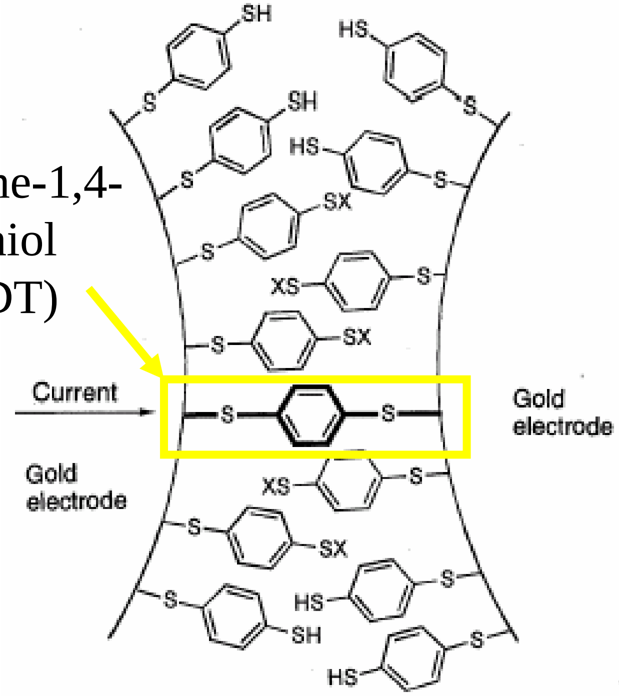
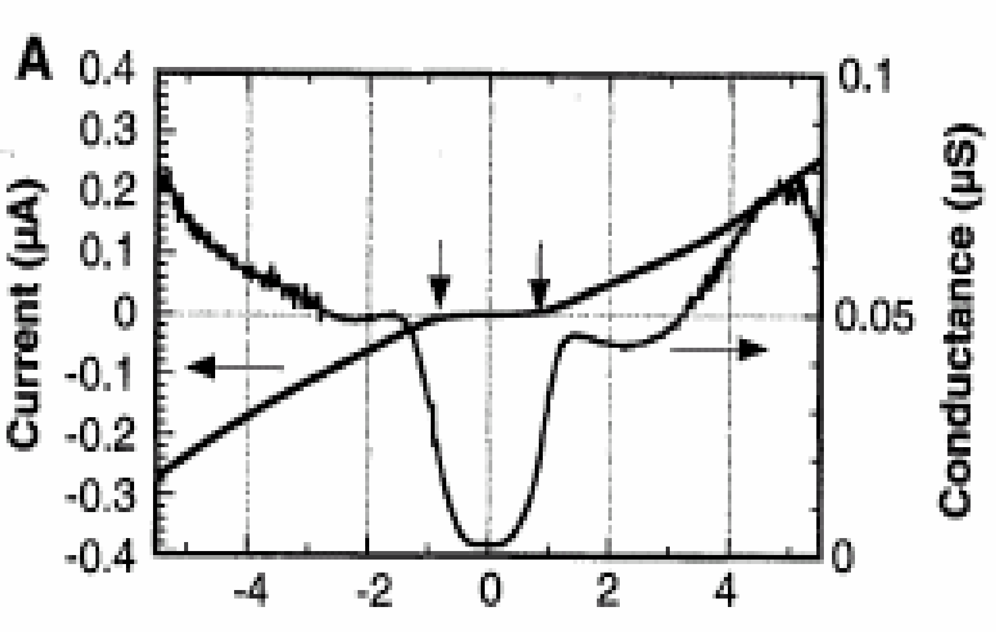
Motivation

- Fabrication and measurements of current-voltage (I-V) and conductance-voltage (C-V) characteristics of metal-molecule-metal systems using various organic molecules have been achieved by many groups.

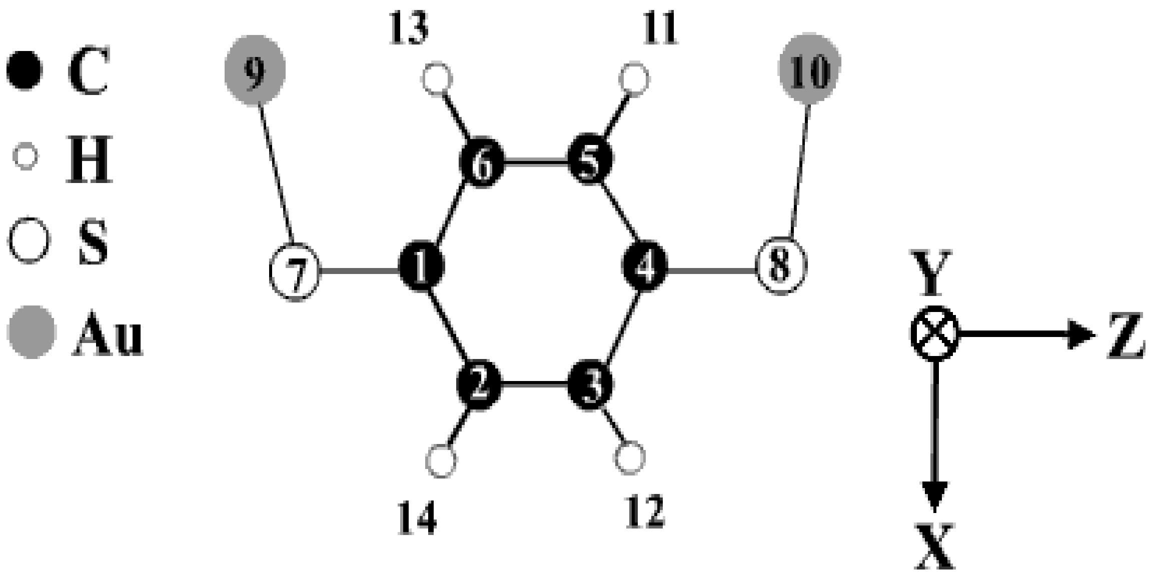


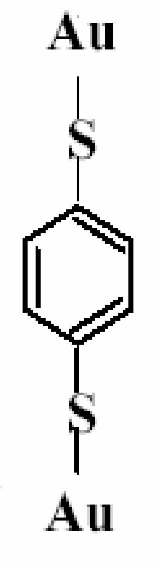
Benzene-1,4-dithiol (BDT)



M. A. Reed et al., Science 278, p.252 (1997)

Au-benzene-1,4-dithiol(BDT)-Au molecule





Experimental –S– bond angle is **~100**^{o}

(CRC Handbook of Chemistry and Physics)

- Conventional calculation methods for the current, I, have been commonly based on

$$I = \frac{2e}{\hbar}\int_{-\infty}^{\infty} T(E)\left[f(E-\mu_1) - f(E-\mu_2)\right]dE$$

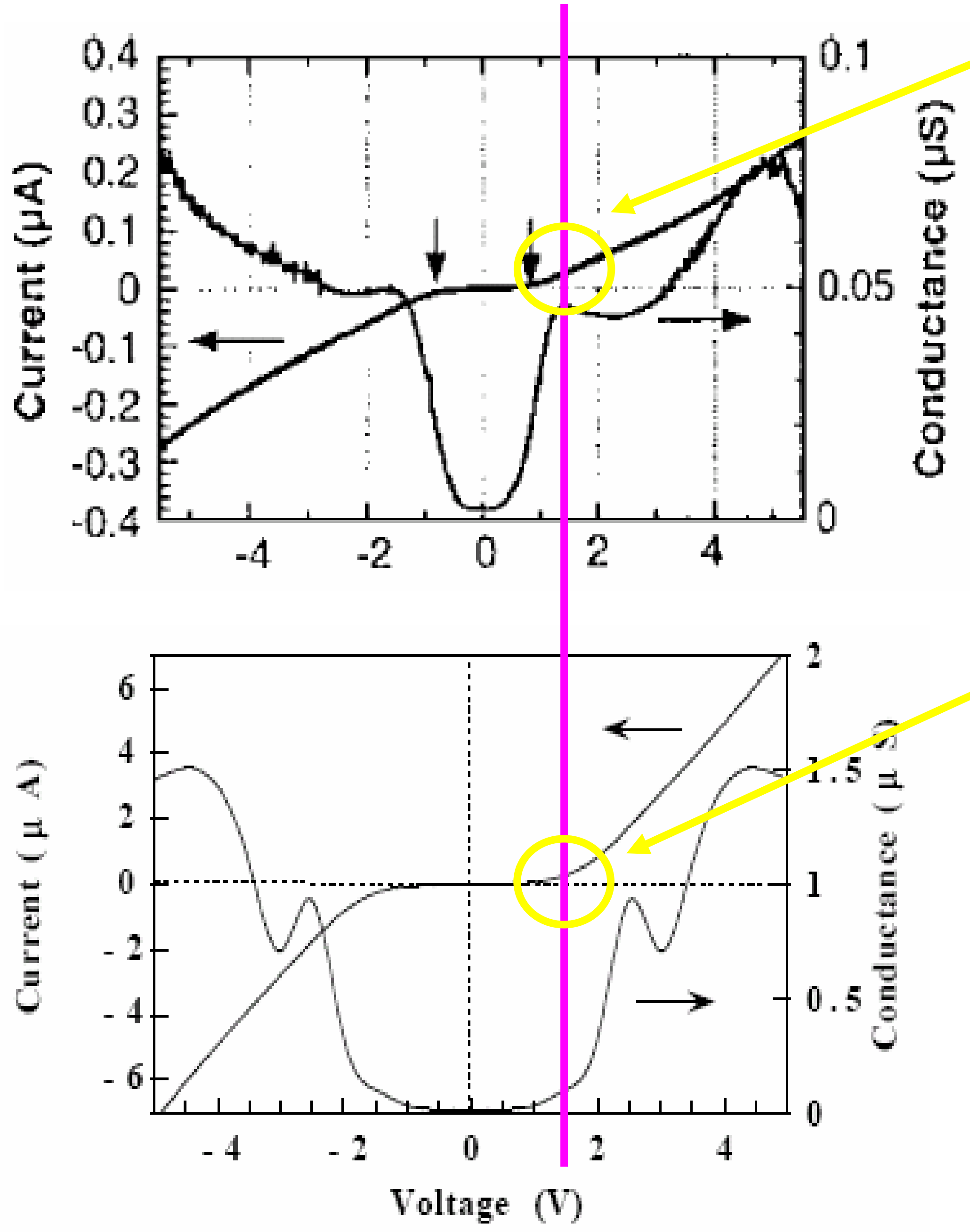
$f(E-\mu_{1,2})$———Fermi-Dirac distribution function

μ_1--------chemical potential in the **1st electrode**

μ_2--------chemical potential in the **2nd electrode**

$T(E)$-------**Transmission probability**---obtained by the

Green function method (conventional or non-equilibrium)



~**0.03** μA

Experimental I-V curve

M. A. Reed et al.,

Science 278, p.252 (1997)

~**0.5** μA

Calculated I-V curve

M. Di. Ventra

Phys Rev Lett 84, p.979 (2000)

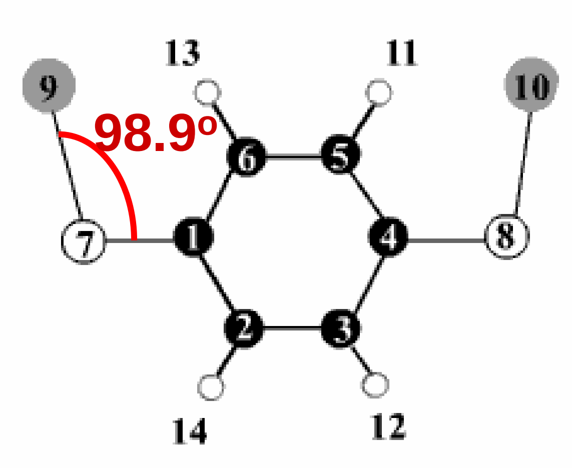
One order larger than
experimental ones!!

Problems with previous calculations

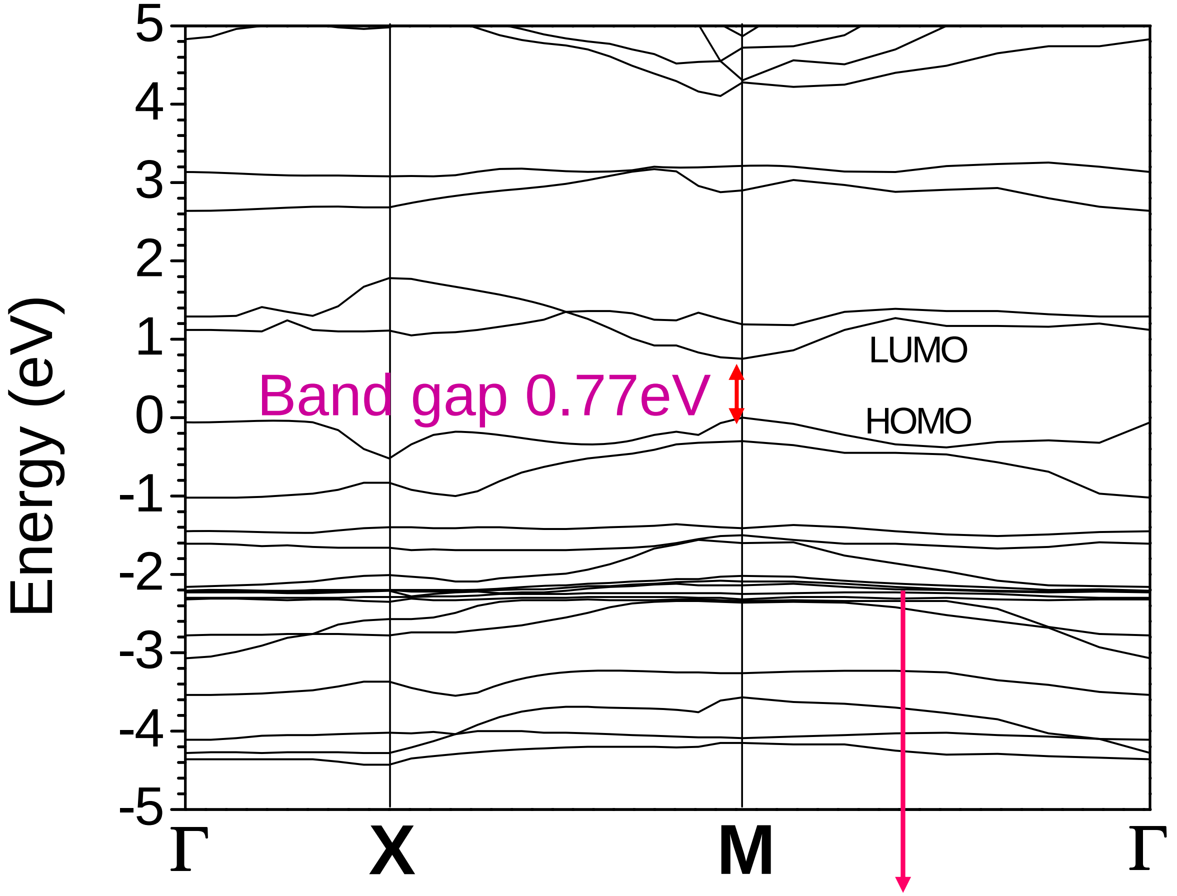
1. **The T(E) formalism is based on the first-order time-dependent perturbation theory.**
2. The electrode-molecule contact potential **can not be accurately treated.**
3. **Ambiguity** in dividing the electrode-molecule-electrode system into $\mathbf{H_0}$ and the perturbing potential, **V**.
4. **Au 5d orbitals were ignored** for Au electrode-molecule contact. (Au 5d is only **0.4eV** below Au 6s).
5. **Unreasonable** Au-S-C **bond angle**:~180^{o}.

- The calculated **Au-S-C** bond angle, **98.9^o is** in good agreement with observed –S– bond angles of ~100^o).

compounds	Bond angle of –S– (from CRC)
SF_2	∠ F-S-F=98.2^o
SCl_2	∠ Cl-S-Cl =103^o
CH_3CH_5-SH	∠ C-S-H =96.4^0



The band structure of the SAM of Au-BDT-Au molecules



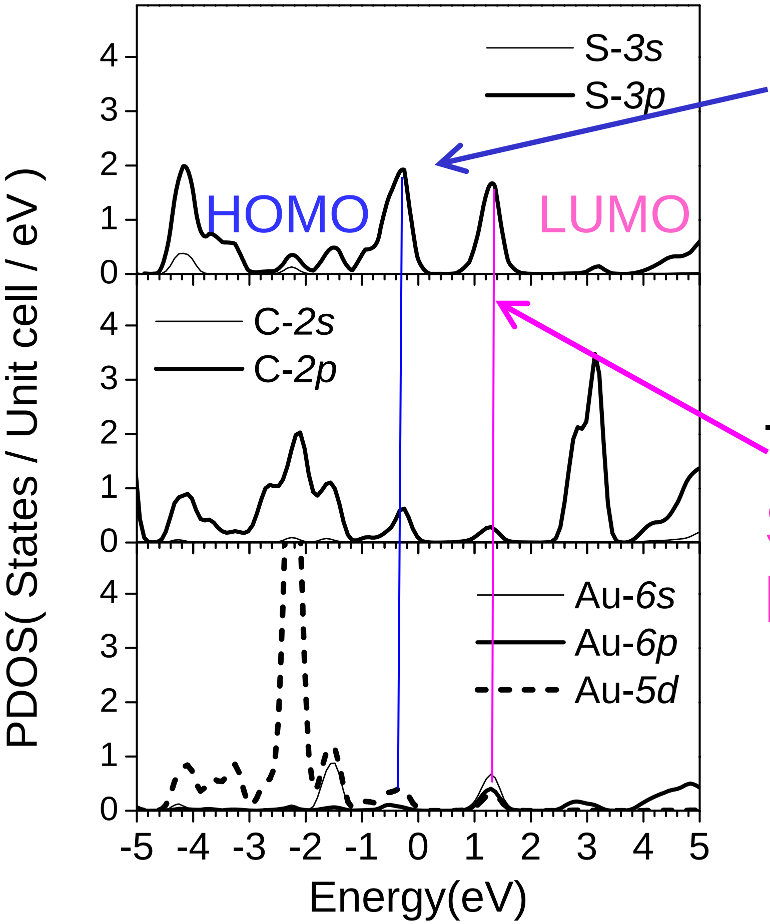
Γ : Brillouin zone center

X : $\frac{2\pi}{a}\left(\frac{1}{2},0\right)$

M: $\frac{2\pi}{a}\left(\frac{1}{2},\frac{\sqrt{3}}{2}\right)$

a=8.655Å

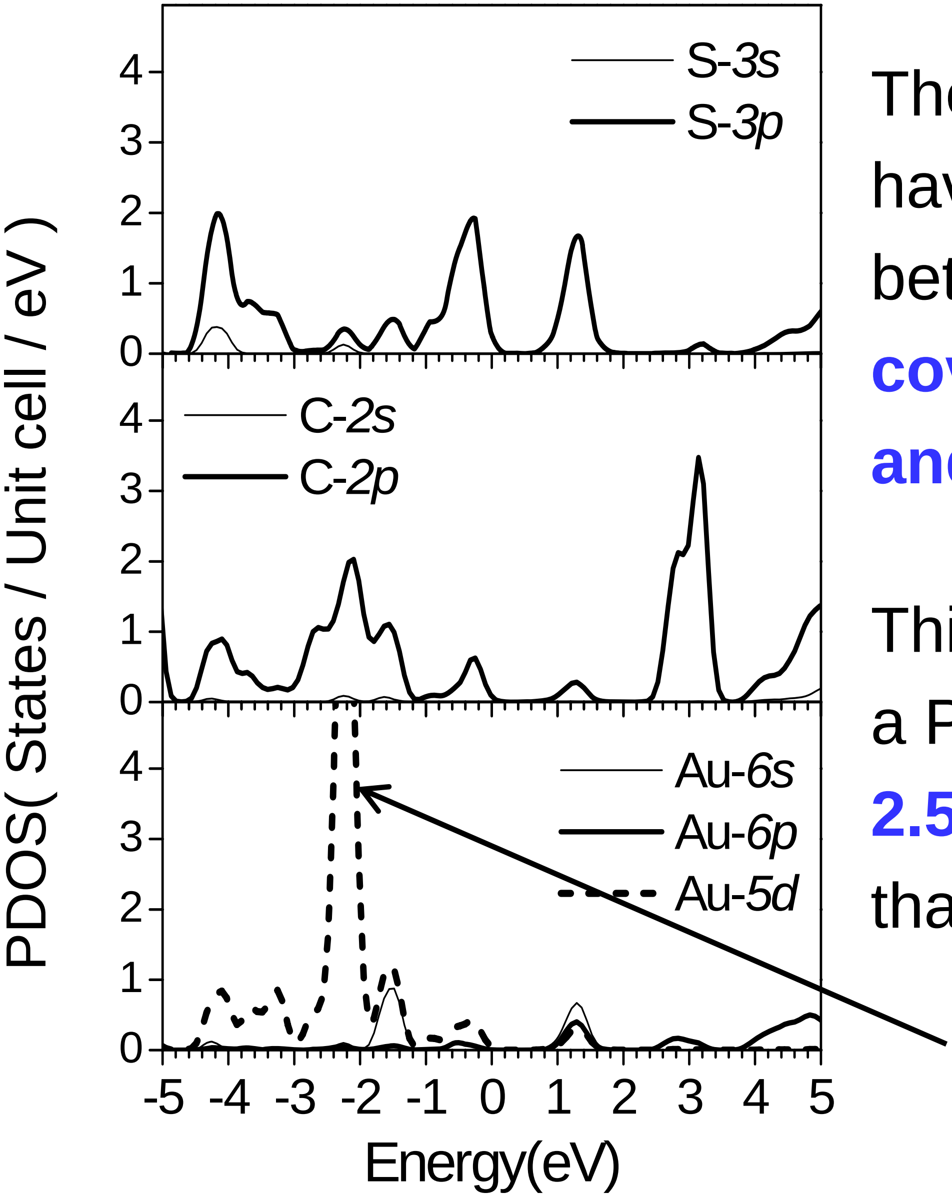
The flat and dense bands located at about -2.3eV are localized Au 5d states.



The HOMO energy band is composed of S 3p, C 2p and **Au 5d** hybridized states

The LUMO energy band contains S 3p, C 2p, Au 6s and **Au 5d** hybridized states.

It indicates that **Au 5d** states have more significant contribution to the transport property of the molecule than that of Au 6s state.



The PDOS's of Au 5d and S 3p have significant overlapping between -4.6eV and 1.5eV-------- **covalent bonding between Au and S via Au 5d orbitals.**

This is reasonable because Au has a Pauline **electronegativity** of **2.54**, which is only slightly less than thatof S of **2.58**

Localized Au 5d states

Spreading of Au 5d band--delocalized

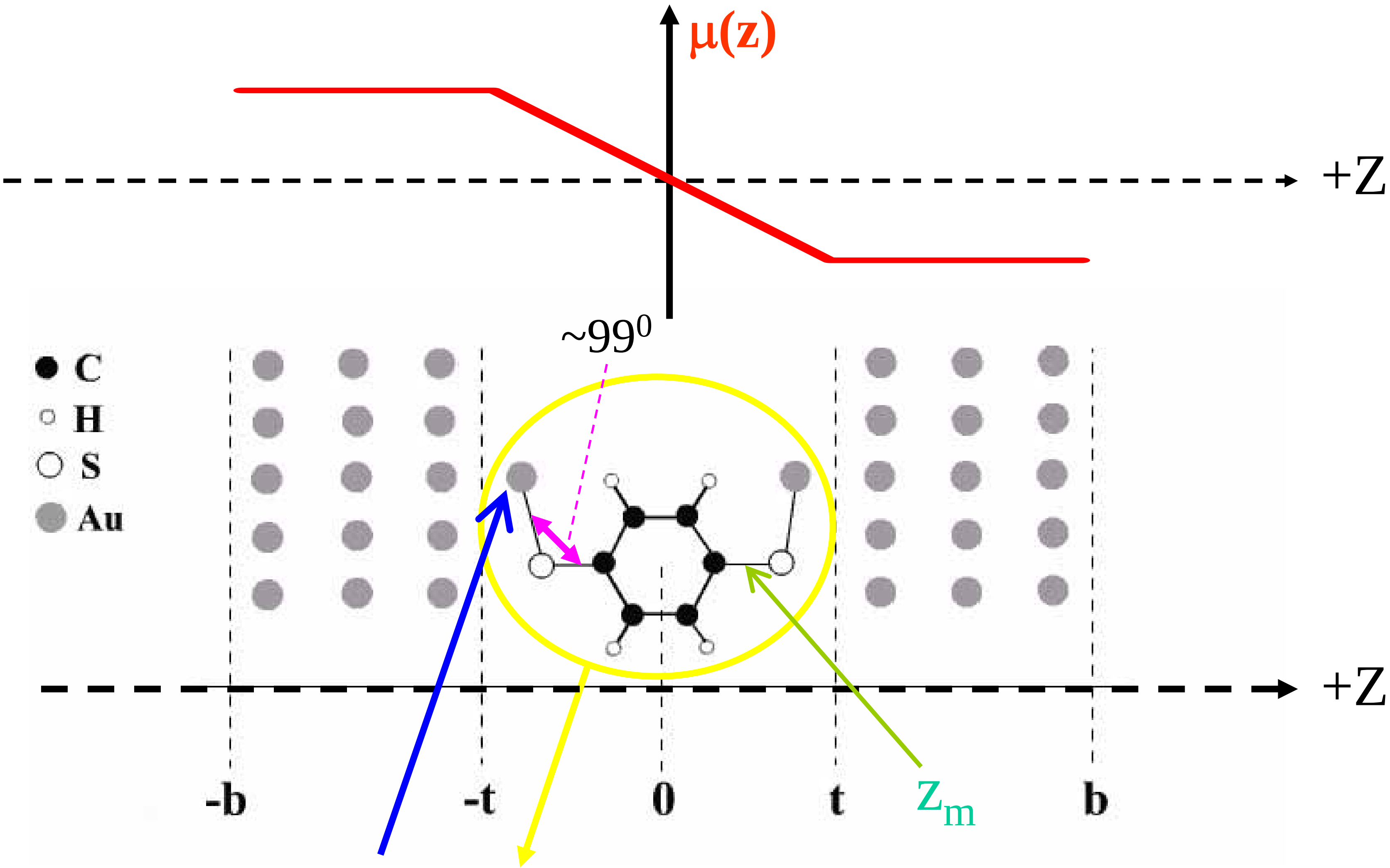
The integrated piecewise thermal equilibrium approach

- The electronic states of the **whole** Au-film-SAM-Au-film system under a bias are calculated by the first-principles method.
- The **non-equilibrium distribution function** of electrons with a bias applied between two metal electrode is approximated by a **piecewise thermal equilibrium distribution function,**

$$f(E,T,z)=\frac{1}{1+\exp\left[\left(E-\mu(z)\right)/\left(k_B T\right)\right]}$$

where **μ (z)** is a **z-dependent chemical potential.**

Approximation of the z-dependent chemical potential



Attached at the fourfold site of the Au(111) film

The physical picture of this approach

- The Au-molecule-Au junction structural model is **not a closed circuit**, so that there is **no net current**. ($I_{net}=0$)

- The **electronic states** of the Au-molecule-Au model are regarded as **standing waves**, which can be decomposed into **+z-** and **–z-direction traveling waves**, Ψ_+ and Ψ_- , respectively.

- The +z- and –z-direction current densities, $j_+(z)$ and $j_-(z)$, respectively, are calculated by the **standard quantum mechanics flux or probability current equation**.

$$j_+(z) = \frac{\hbar}{2m_e i}\left[\Psi_+^* \frac{\partial \Psi_+}{\partial z} - \Psi_+ \frac{\partial \Psi_+^*}{\partial z}\right]$$

$$j_-(z) = \frac{\hbar}{2m_e i}\left[\Psi_-^* \frac{\partial \Psi_-}{\partial z} - \Psi_- \frac{\partial \Psi_-^*}{\partial z}\right]$$

Calculation of the current per molecule

- At one end of the molecule, z_m, there are probability currents $\mathbf{j^+(z_m)}$ and $\mathbf{j^-(z_m)}$ and at another end of the molecule, $-z_m$, there are probability currents $\mathbf{j^+(-z_m)}$ and $\mathbf{j^-(-z_m)}$.

- In this approach, the **electric current per molecule** is calculated as

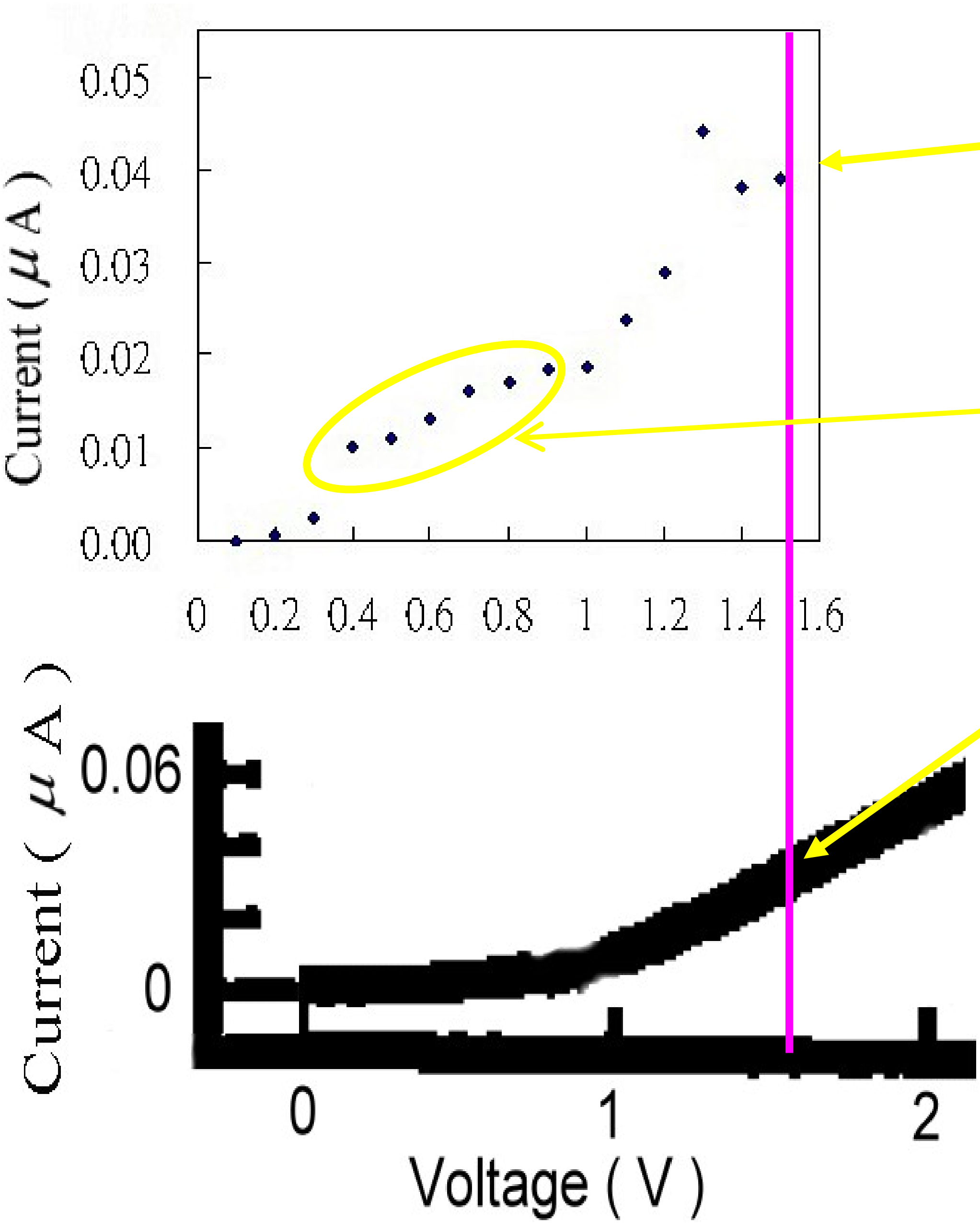
$$\mathbf{I\ /\ molecule = (-e)[\ j^+(z_m) - j^-(-z_m)]}$$

(**-e** is the electronic charge)

The currents $\mathbf{(-e)j^-(z_m)}$ and $\mathbf{(-e)j^+(-z_m)}$ are considered to be **drained into** the electrodes of the voltage source, e.g. **a battery or power supply**, when a **closed circuit** is connected.

Advantages of this approach

- No artificial division of the system into two electrodes and the molecule parts.
- Do not need to guess a contact potential between the electrode and the molecule.
- The molecule is not treated in a perturbed way.
- The 5*d*-orbital contributions of Au atoms to the current are taken into account properly.



~0.04 μ A

Not well converged

~0.03μA

Calc. & Expt. comparable

M. A. Reed et al., Science 278, p.252 (1997)

Conclusion

Au 5d orbitals should be considered for Au-S bonding.

Au-S-C bond angle is about 89^o not ~180^o used in previous calculations

The present approach avoids the inherent approximation and the difficulty of accurately determine the metal-molecule contact potential

The calculated I-V characteristic is in reasonably good agreement with the experimental data.