Are molecules calm enough in molecular electronics junctions?

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Collaborators

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First principle calculations of transport properties

Prof. Nongjian Tao
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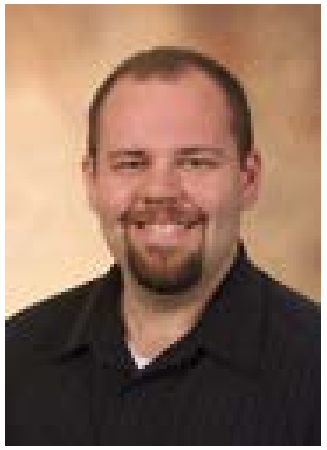


Prof. Joshua Hihath
(Arizona State Univ.)

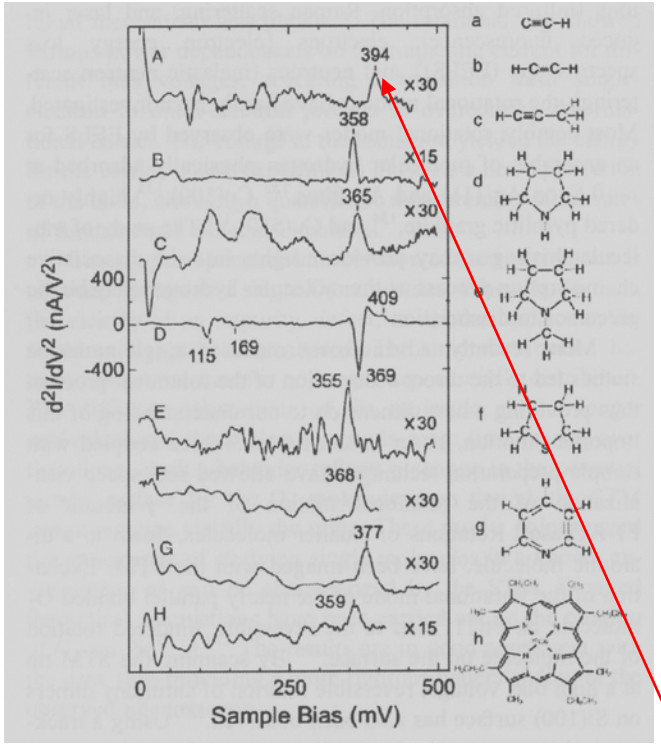
Experimental studies of diode molecule

Experimental studies of small β of organometallic Ru complexes

Dr. Takao Ishida (AIST) and Prof. M. Haga (Chuo Univ)

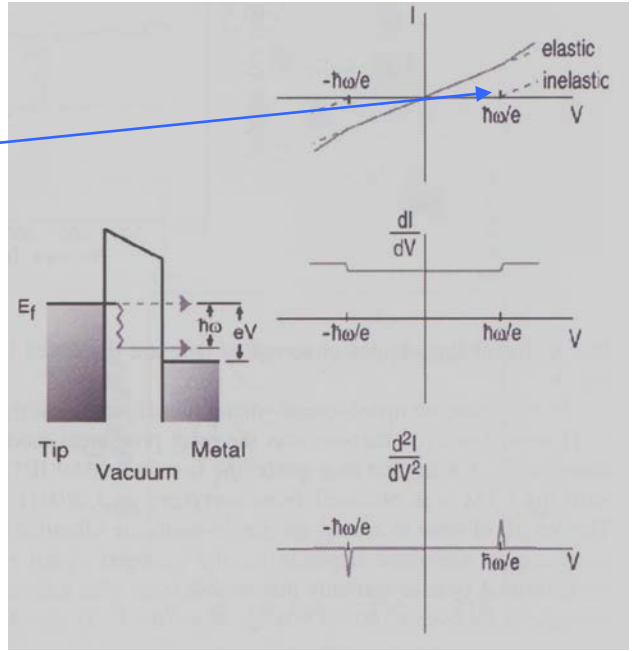
Local heating and inelastic scatterings

InElastic Tunneling Spectroscopy (IETS) in the tunneling region



Stipe,(1999)

New channel open when $V>h\omega/e$



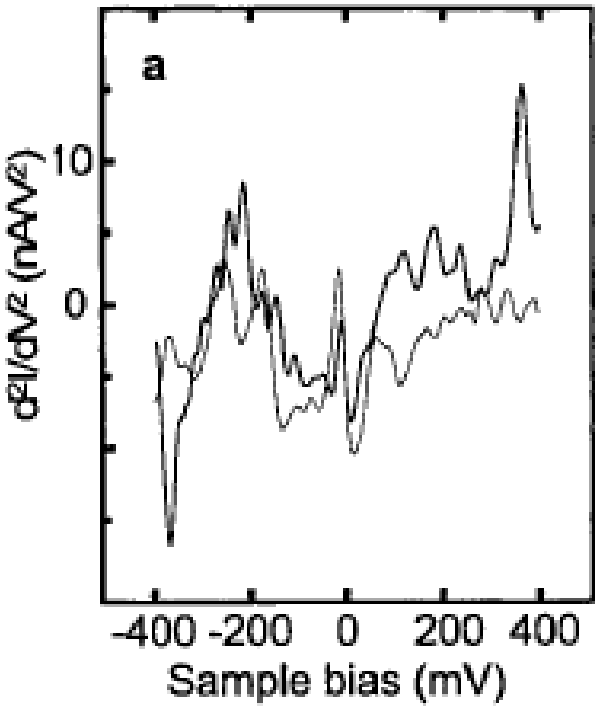
Ho(2002)

The peak position = vibrational energy
Electric current couples with molecular vibration inelastically

The Line shape of IETS

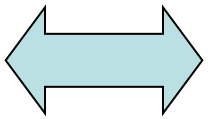
Importance of the energy gap to determine the line shape?

molecule



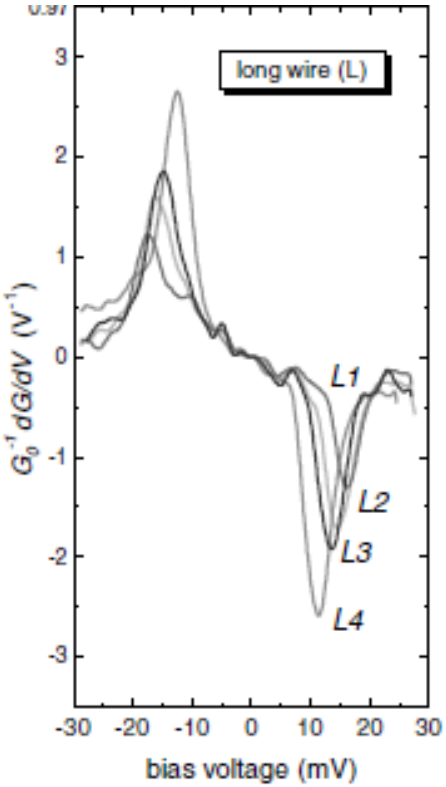
K.Kim, T. Komeda, and M. Kawai,
Phys. Rev. Lett. 89, 126104 (2002)

experiments



different!

atomic wire

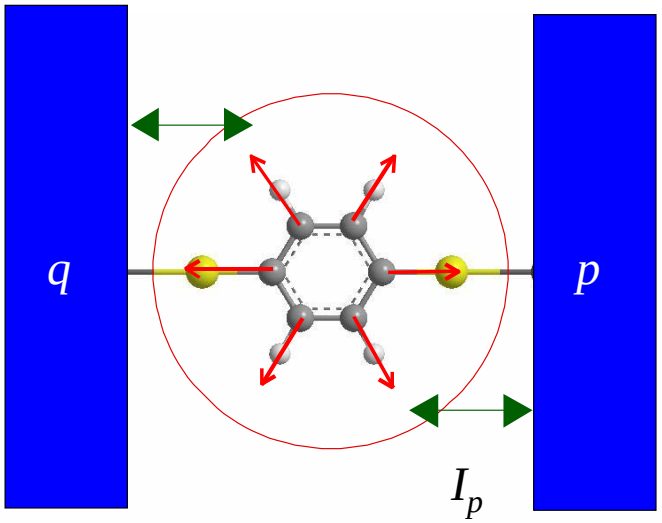


N. Agraït, C. Untiedt, G. Rubio-Bollinger, and S. Vieira,
Phys. Rev. Lett. 88, 216803 (2002)

Keldysh GF theory of electric current

Electron-phonon coupling effects

$$\mathbf{G}_q^{<(>)}(E) = \mathbf{G}_C^R(E)\boldsymbol{\Sigma}_q^{<(>)}(E)\mathbf{G}_C^A(E)$$



Elastic component

$$I_p = I_{elastic,p} + I_{inelastic,p}$$

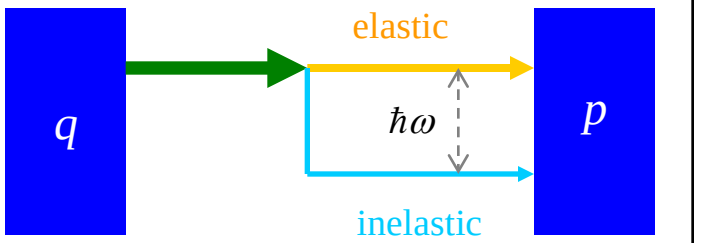
$$I_{elastic,p} = \frac{2e}{h}\sum_q \int_{-\infty}^{\infty} Tr\left[\boldsymbol{\Sigma}_p^{>}(E)\mathbf{G}_q^{<}(E) - \boldsymbol{\Sigma}_p^{<}(E)\mathbf{G}_q^{>}(E)\right]dE$$

$$= \frac{2e}{h}\sum_q \int_{-\infty}^{\infty} Tr\left[\boldsymbol{\Gamma}_p(E)\mathbf{G}_C^R(E)\boldsymbol{\Gamma}_q(E)\mathbf{G}_C^A(E)\right]\left\{f_q(E) - f_p(E)\right\}dE$$

Inelastic component

$$I_{inelastic,p} = \frac{2e}{h}\int_{-\infty}^{\infty} Tr\left[\boldsymbol{\Sigma}_p^{>}(E)\mathbf{G}_{e-ph}^{<}(E) - \boldsymbol{\Sigma}_p^{<}(E)\mathbf{G}_{e-ph}^{>}(E)\right]dE$$

$$\mathbf{G}_{e-ph}^{<(>)}(E) = \mathbf{G}_C^R(E)\boldsymbol{\Sigma}_{e-ph}^{<(>)}(E)\mathbf{G}_C^A(E)$$



Standard theory of IETS

Thermal equilibrium phonon supposed!

Does it work well ?

Inelastic current calculation

Self-consistent Born approximation

$$i_p = i_{elastic} + i_{inelastic}$$

$$i_{elastic} = \frac{ie}{h}\sum_q Tr\left[\Sigma_p^< G^R \Gamma_q G^A - \Gamma_p G^R \Sigma_q^< G^A\right]$$

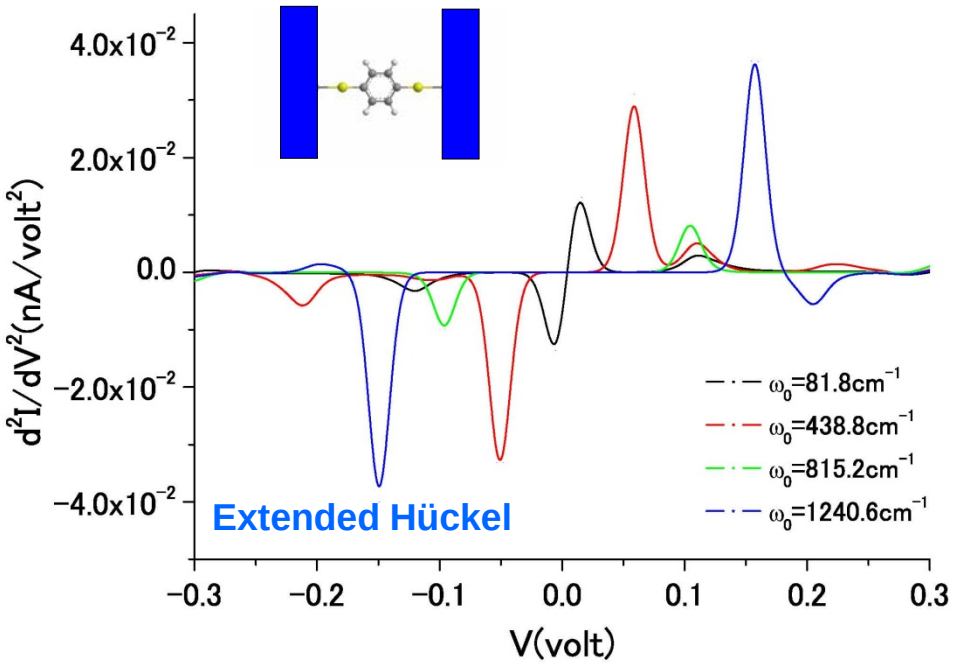
$$i_{inelastic} = \frac{ie}{h} Tr\left[\Sigma_p^< G^R \Gamma_\varphi G^A - \Gamma_p G^R \Sigma_\varphi^< G^A\right]$$

$$\Sigma_{rs}^{<\varphi}(E) = \sum_{ab} \lambda_{rs}^{ab} \int d\omega D(\omega) G_{ab}^<(E-\omega)$$

$$\Sigma_{rs}^{>\varphi}(E) = \sum_{ab} \lambda_{rs}^{ab} \int d\omega D(\omega) G_{ab}^>(E+\omega)$$

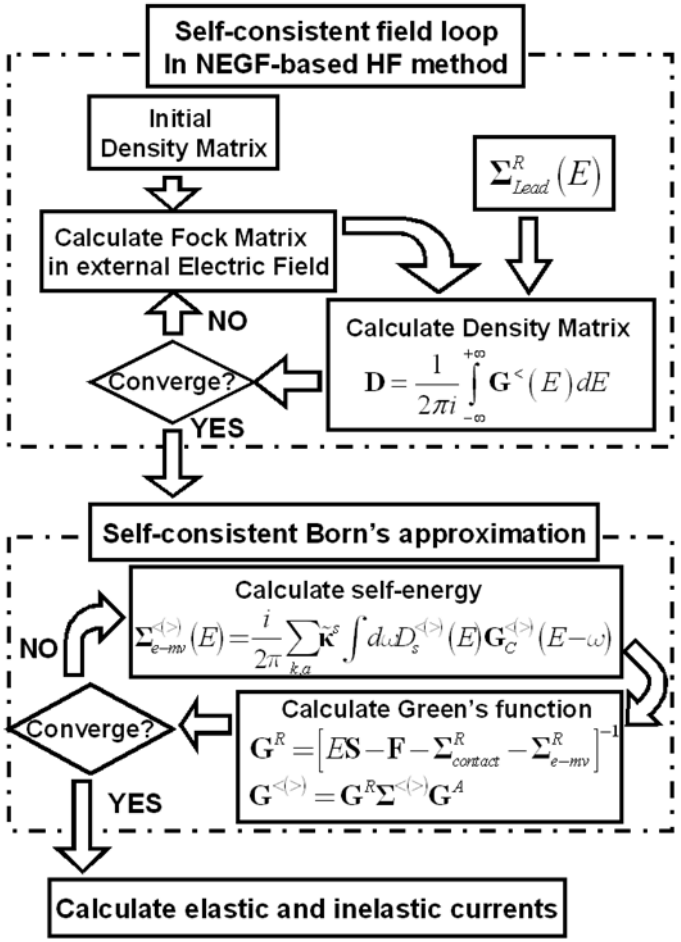
$$\lambda_{rs}^{ab} = \frac{1}{2\omega_0}\sum_k \langle \chi_r | \psi_k \rangle \left(\frac{\partial \varepsilon_k}{\partial Q}\right)^2 \langle \psi_k | \chi_s \rangle u_{ka}^* u_{kb}$$

$$\varepsilon_\gamma(Q) = \varepsilon_\gamma(0) + \sum_n \left(\frac{\partial \varepsilon_\gamma}{\partial Q}\right)_0 Q_n + \sum_{nm} \left(\frac{\partial^2 \varepsilon_\gamma}{\partial Q_n \partial Q_m}\right)_0 \frac{Q_n Q_m}{2} + \cdots$$

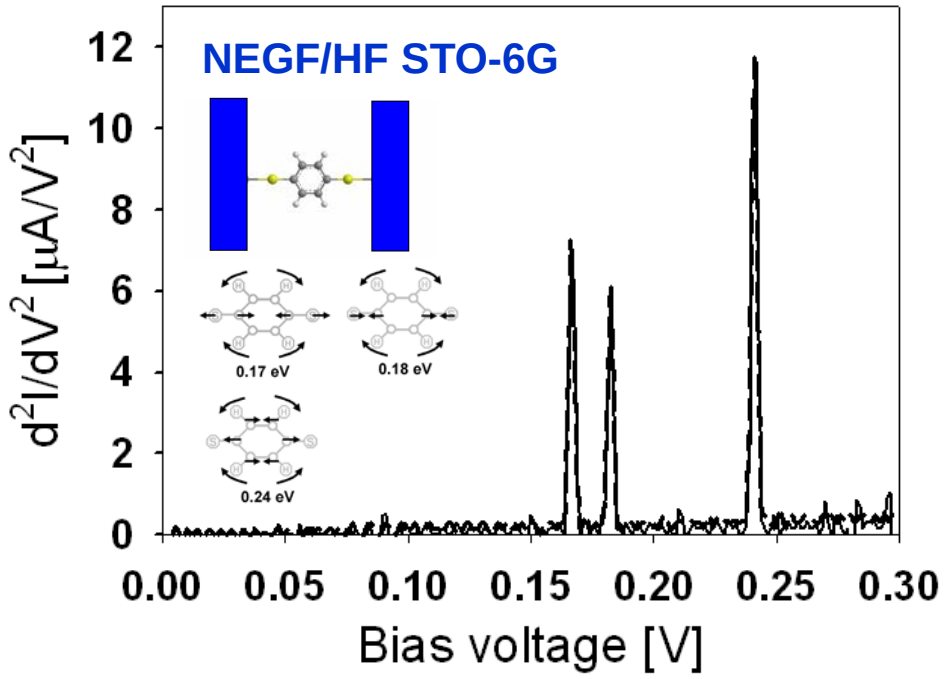


Y. Asai, Phys. Rev. Lett. 93, 246102 (2004); 94, 099901(E) (2005).

ab intio calculation of inelastic current



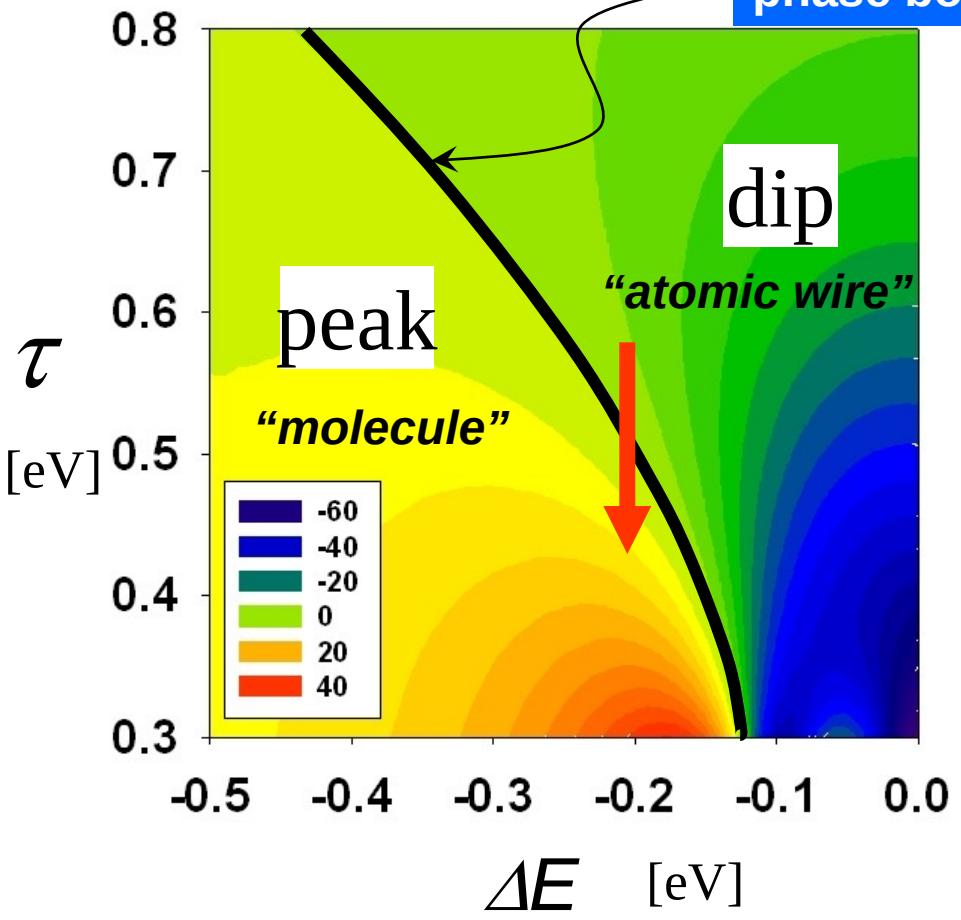
***ab initio* quantum chemistry**

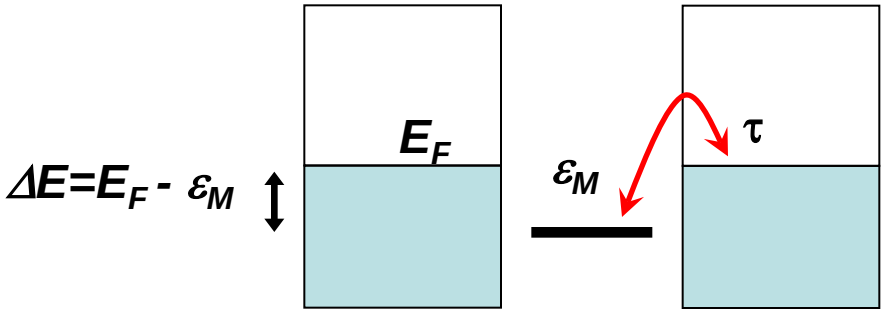


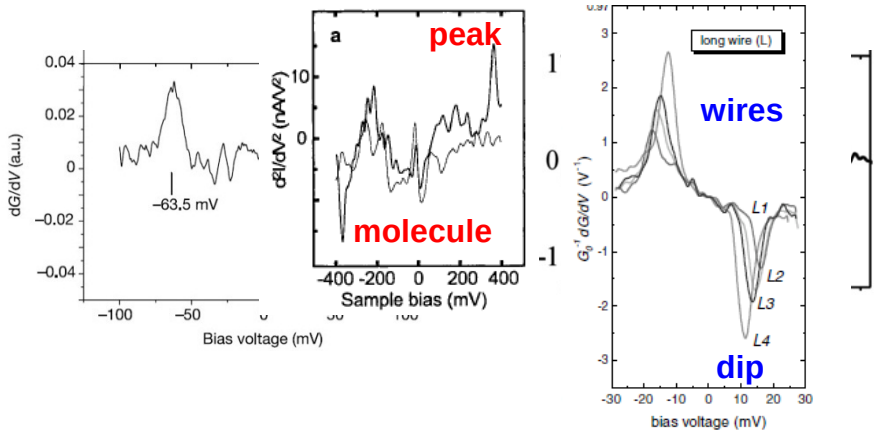
T. Shimazaki and Y. Asai, Phys. Rev. B77, 075110 (2008).

Line shape of d^2I/dV^2 resonant and tunneling regimes

phase boundary line: no “peak” and “dip”







cf) M. Galperin et al, H.Ueba et al
T. Shimazaki and Y. Asai, Phys. Rev. B77, 115428(2008)

Ex) opposite line shapes both in $Pt/H_2/Pt$

cf) van Ruitenbeek et al
M. Kiguchi et al

Standard theory of IETS

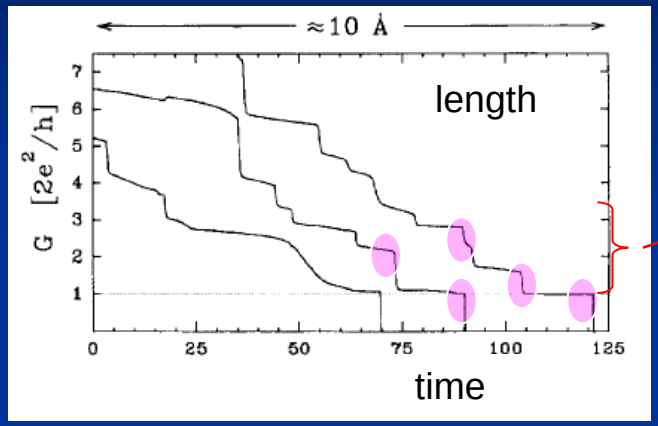
Thermal equilibrium phonon supposed!

It describes overall features of line shape and mode dependencies

It may not be useful to describe energy conversion processes because phonon is always supposed to be damped because of thermal bath, i.e., phonon heat transport cannot be described.

What is the local heating ?

Conductance measurements by MCBJ

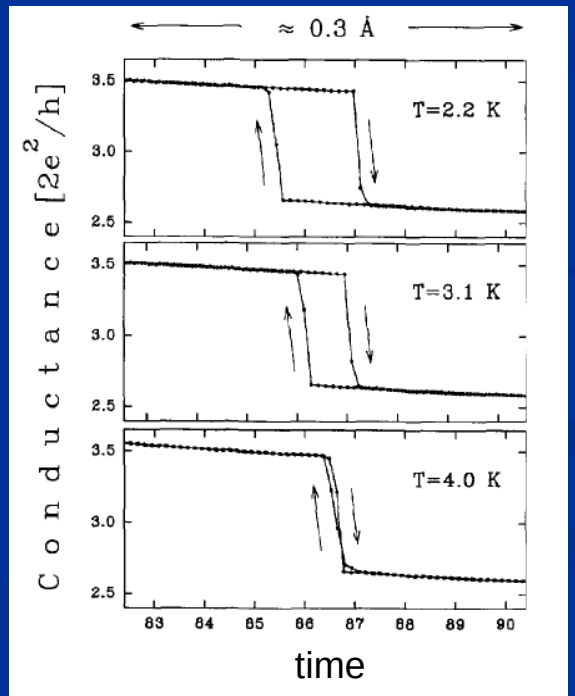


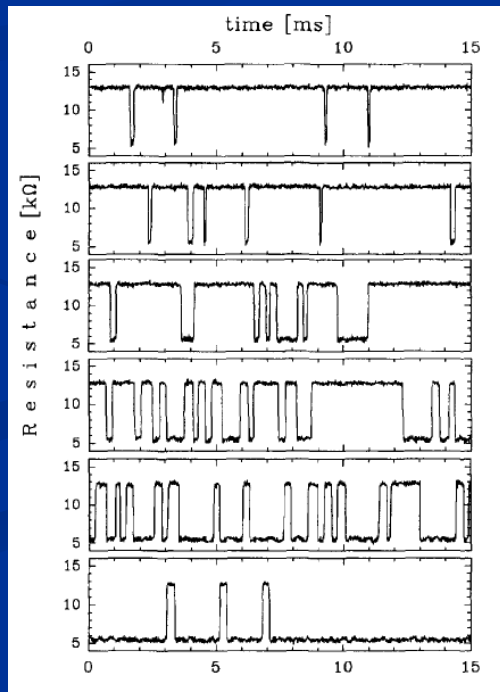
J.M. Krans, J.M. van Ruitenbeek, L.J. de Jongh, Physica B218, 228 (1996).

transient regions

hysteresis

two level fluctuation





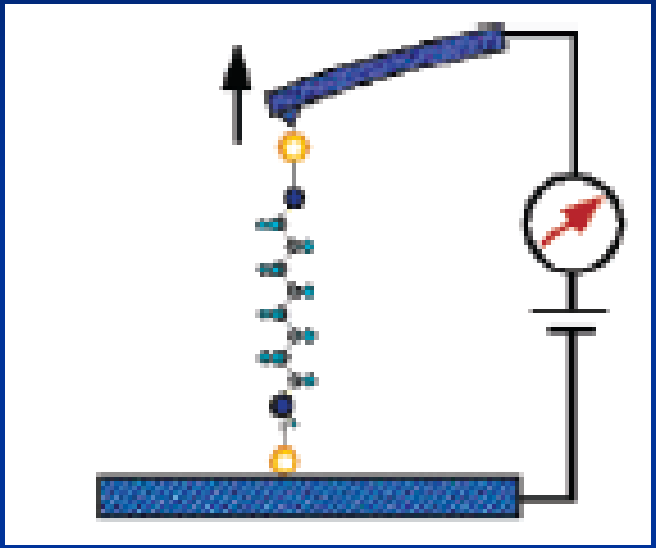
thermally activated structure change

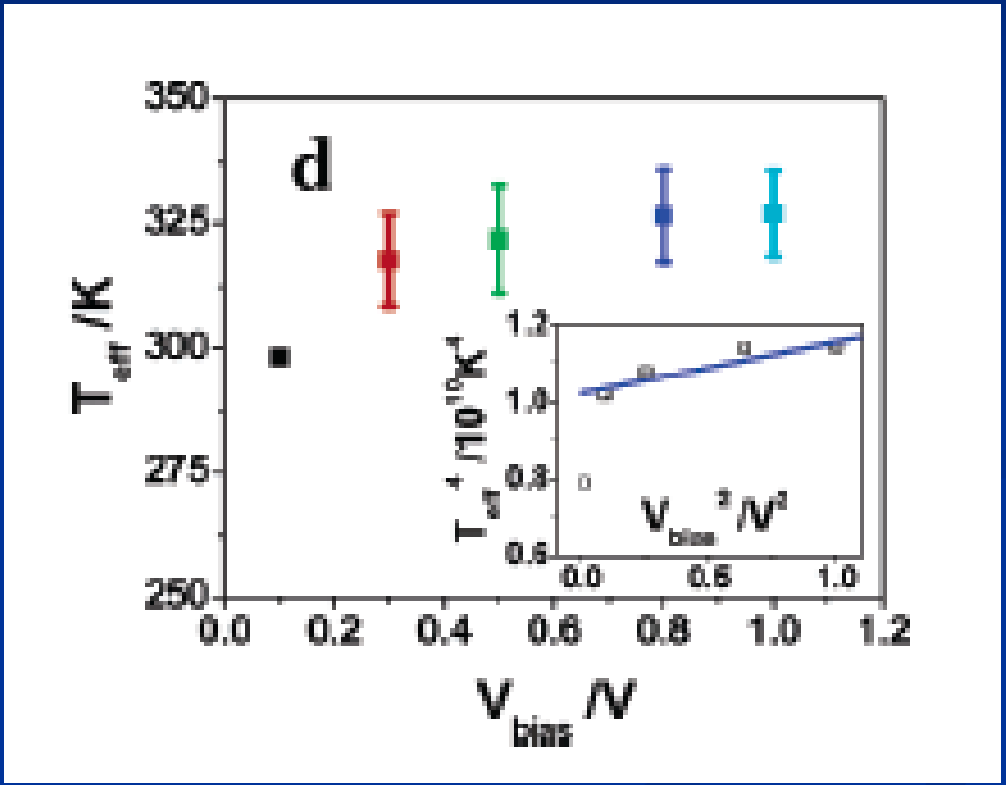
Why at low temperature T=2K?

local heating due to current ,T_{eff}?

inelastic scatterings

Experimental measurements of the local heating in alkanedithiol





T_{eff} is estimated from lifetime of the junction fracture due to current flow: It is not a thermodynamic "temperature".

Z. Huang, B. Xu, Y. Chen, M. Di Ventra and N.J. Tao, *Nano Letter*, 6, 12403 (2006)

New theory of inelastic scatterings
... to describe local heating

Non-equilibrium phonon effect
(phonon heat transport / phonon diffusion effect) is included!

How does it work?

Theoretical scheme to treat the local heating

1. Keldysh GF theory for electrons and phonons

$$I = \sum_q \int_{-\infty}^{\infty} j_q(E)\,dE$$

$$j_q(E) = \frac{2e}{h} Tr \begin{bmatrix} \boldsymbol{\Sigma}_p^{>}(E)\mathbf{G}^R(E)\left(\boldsymbol{\Sigma}_q^{<}(E) + \boldsymbol{\Sigma}_{e-ph}^{<}(E)\right)\mathbf{G}^A(E) \\ -\boldsymbol{\Sigma}_p^{<}(E)\mathbf{G}^R(E)\left(\boldsymbol{\Sigma}_q^{>}(E) + \boldsymbol{\Sigma}_{e-ph}^{>}(E)\right)\mathbf{G}^A(E) \end{bmatrix}$$

$$Q = -\sum_q \int_{-\infty}^{\infty} \frac{E}{e} \cdot j_q(E)\,dE + \int_{-\infty}^{\infty} 2\pi q(E)\,dE$$

$$q(E) = \frac{2\pi E}{h} Tr \begin{bmatrix} \boldsymbol{\Pi}_p^{>}(E)\mathbf{D}^R(E)\left(\boldsymbol{\Pi}_q^{<}(E) + \boldsymbol{\Pi}_{e-ph}^{<}(E)\right)\mathbf{D}^A(E) \\ -\boldsymbol{\Pi}_p^{<}(E)\mathbf{D}^R(E)\left(\boldsymbol{\Pi}_q^{>}(E) + \boldsymbol{\Pi}_{e-ph}^{>}(E)\right)\mathbf{D}^A(E) \end{bmatrix}$$

2. Self-consistent Born approx. to treat the SSH e-ph coupling both for electrons and phonons

$$\boldsymbol{\Sigma}_{e-ph}^{<(>)}(E) = i\frac{\kappa^2}{M}\int \mathbf{G}^{<(>)}(E-E')\mathbf{D}^{<(>)}(E')\,dE'$$

$$\mathbf{G}^{<(>)}(E) = \mathbf{G}^R(E)\left(\sum_q \boldsymbol{\Sigma}_q^{<(>)}(E) + \boldsymbol{\Sigma}_{e-ph}^{<(>)}(E)\right)\mathbf{G}^R(E)$$

$$\boldsymbol{\Pi}_{e-ph}^{<(>)}(E) = i\frac{\kappa^2}{\pi M}\int \mathbf{G}^{<(>)}(E+E')\mathbf{G}^{>(<)}(E')\,dE'$$

$$\mathbf{D}^{<(>)}(E) = \mathbf{D}^R(E)\left(\sum_q \boldsymbol{\Pi}_q^{<(>)}(E) + \boldsymbol{\Pi}_{e-ph}^{<(>)}(E)\right)\mathbf{D}^R(E)$$

3. Thermal boundary conditions both for electrons and phonons

$$-i\boldsymbol{\Sigma}_q^{<}(E) = if_q(E)\left[\boldsymbol{\Sigma}_q^R(E) - \boldsymbol{\Sigma}_q^A(E)\right]$$

$$i\boldsymbol{\Sigma}_q^{>}(E) = i\left[1 - f_q(E)\right]\left[\boldsymbol{\Sigma}_q^R(E) - \boldsymbol{\Sigma}_q^A(E)\right]$$

$$-i\boldsymbol{\Pi}_q^{<}(E) = -ib_q(E)\left[\boldsymbol{\Pi}_q^R(E) - \boldsymbol{\Pi}_q^A(E)\right]$$

$$i\boldsymbol{\Pi}_q^{>}(E) = i\left[1 + b_q(E)\right]\left[\boldsymbol{\Pi}_q^R(E) - \boldsymbol{\Pi}_q^A(E)\right]$$

(electrons and phonons are thermalized only in electrodes)

4. Quantum phonon across the bridge junction

$$\bar{\mathbf{D}}_{CC}^R(\omega) = \frac{\hbar}{2\pi}\left\{\omega^2\mathbf{I}_{3N_C\times 3N_C} - \mathbf{K}_C - \frac{1}{2\pi\hbar}\sum_{L_x,L_y}^{L+L'}\mathbf{K}_{L_y}\left[\int_{-\pi}^{\pi}\int_{-\pi}^{\pi}\mathbf{D}_{0,0}^R(\vec{Q}_\parallel,\omega)\,dQ_x dQ_y\right]\mathbf{K}_{L_y}\right\}^{-1}$$

displacement correlation function

$$D_{\alpha\beta}^<(i,j,t) = -i\theta(t)\left\langle\left[\xi_{i\alpha}(t),\xi_{j\beta}(0)\right]\right\rangle$$

equation of motion

$$i\partial_t D_{\alpha\beta}^<(i,j,t) = \delta(t)\left\langle\left[\xi_{i\alpha},\xi_{j\beta}\right]\right\rangle + \theta(t)\left\langle\left[\partial_t\xi_{i\alpha}(t),\xi_{j\beta}(0)\right]\right\rangle$$

$$\sum_{k\alpha}\left\{\omega^2\delta_{ik}\delta_{\alpha\alpha} - K_{i\alpha}(i,k)\right\}D_{k\alpha,j\beta}^A(k,j,\omega) = \frac{\hbar}{2\pi}\delta_{ij}\delta_{\alpha\beta}$$

surface Green's function

$$\mathbf{D}_{0,0}^A(\vec{Q}_\parallel,\omega) = \frac{\hbar}{2\pi}\left\{\omega^2\mathbf{I} - \mathbf{K}_0(\vec{Q}_\parallel) - \mathbf{K}_+(\vec{Q}_\parallel)\mathbf{T}_{p0}(\vec{Q}_\parallel,\omega)\right\}^{-1}$$

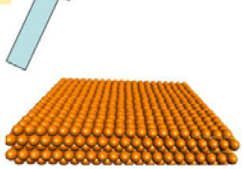
partitioning into semi-infinite electrodes and molecule

$$\begin{pmatrix} \omega^2\mathbf{I}_{3N_0\times 3N_0} - \mathbf{K}_M & -\mathbf{K}_{L_0} & 0 \\ -\mathbf{K}_{L_0} & \omega^2\mathbf{I}_{3N_C\times 3N_C} - \mathbf{K}_C & -\mathbf{K}_{L_0} \\ 0 & -\mathbf{K}_{L_0} & \omega^2\mathbf{I}_{3N_0\times 3N_0} - \mathbf{K}_M \end{pmatrix}\begin{pmatrix} \mathbf{D}_{MM}^A & \mathbf{D}_{MC}^A & \mathbf{D}_{M0'}^A \\ \mathbf{D}_{CM}^A & \mathbf{D}_{CC}^A & \mathbf{D}_{C0'}^A \\ \mathbf{D}_{0'M}^A & \mathbf{D}_{0'C}^A & \mathbf{D}_{0'0'}^A \end{pmatrix} = \frac{\hbar}{2\pi}\mathbf{I}_{3N\times 3N}$$

dividing electrodes into layers

$$\sum_{i'\alpha'}\left\{\omega^2\delta_{ii'}\delta_{\alpha\alpha'} - K_{i\alpha}(i,i',\vec{Q}_\parallel)\right\}D_{i'\alpha',j\beta}^A(i',j',\vec{Q}_\parallel,\omega) = \frac{\hbar}{2\pi}\delta_{ij}\delta_{\alpha\beta}$$

$$\begin{pmatrix} \omega^2\mathbf{I} - \mathbf{K}_0(\vec{Q}_\parallel) & -\mathbf{K}_+(\vec{Q}_\parallel) & 0 & \cdots \\ -\mathbf{K}_-(\vec{Q}_\parallel) & \omega^2\mathbf{I} - \mathbf{K}_0(\vec{Q}_\parallel) & -\mathbf{K}_+(\vec{Q}_\parallel) & \cdots \\ 0 & & & \end{pmatrix}\begin{pmatrix} \mathbf{D}_{00}^A(\vec{Q}_\parallel,\omega) & \mathbf{D}_{01}^A(\vec{Q}_\parallel,\omega) & \cdots \\ \mathbf{D}_{10}^A(\vec{Q}_\parallel,\omega) & \mathbf{D}_{11}^A(\vec{Q}_\parallel,\omega) & \cdots \\ \vdots & & \end{pmatrix} = \frac{\hbar}{2\pi}\mathbf{I}_{3N\times 3N}$$



recursion equation to solve the semi-infinite GF equation

Real space approach: normal coordinate unavailable

alkanedithiol: parameters (π)

τ of π orbitals … small and sensitive to conformations

Au 6s band

$$\varepsilon_{C_1}, \varepsilon_{C2}, \varepsilon_S, t_{SC_1}, t_{C_1C_2}, t_{C_2C_3}$$

… determined by fitting with the 4 π orbitals

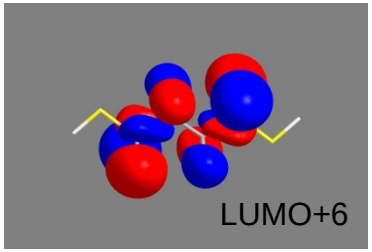
$$\Phi_{\alpha\beta}$$

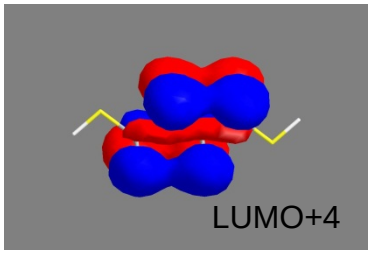
… from literatures, cf) Shimanouchi (1967)

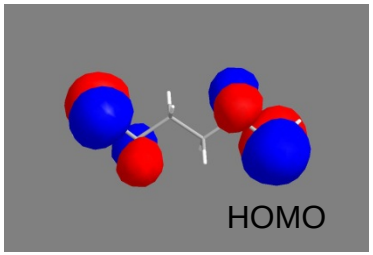
$$\lambda_{ij}^{\beta}$$

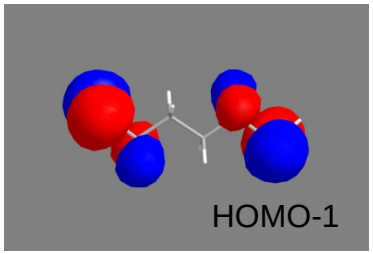
… from the equilibrium condition of the stable structure of the molecule

$$d\langle H\rangle/dr = 0$$









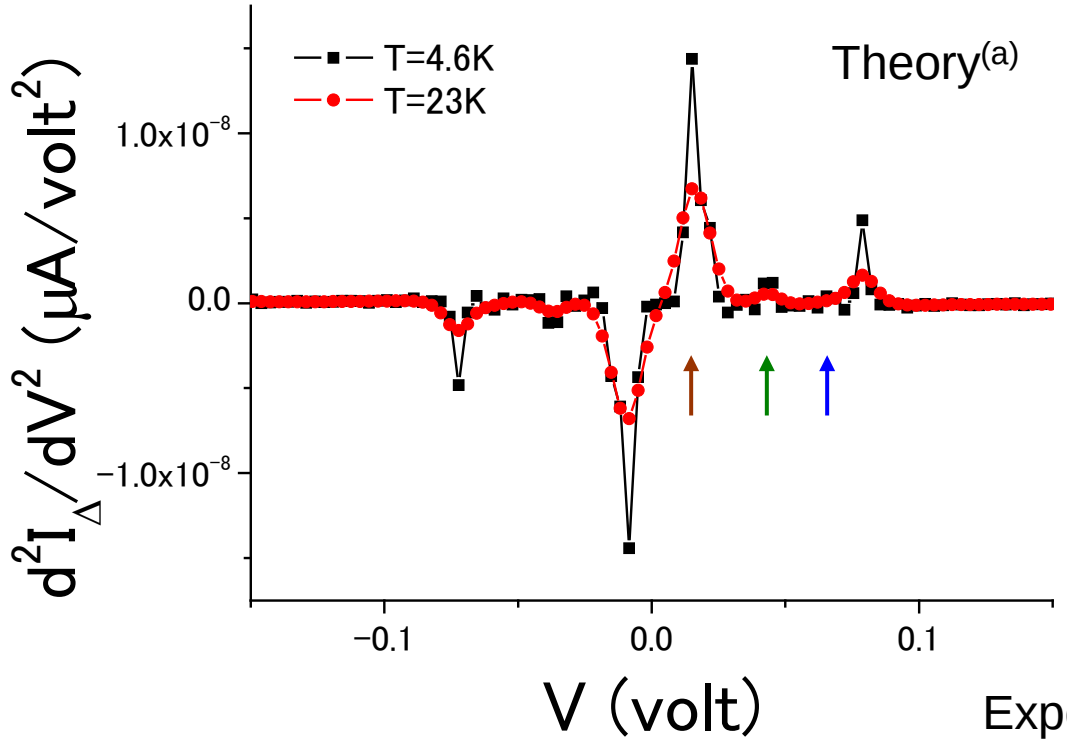
π orbital contact

SSH model augmented by LJ potential

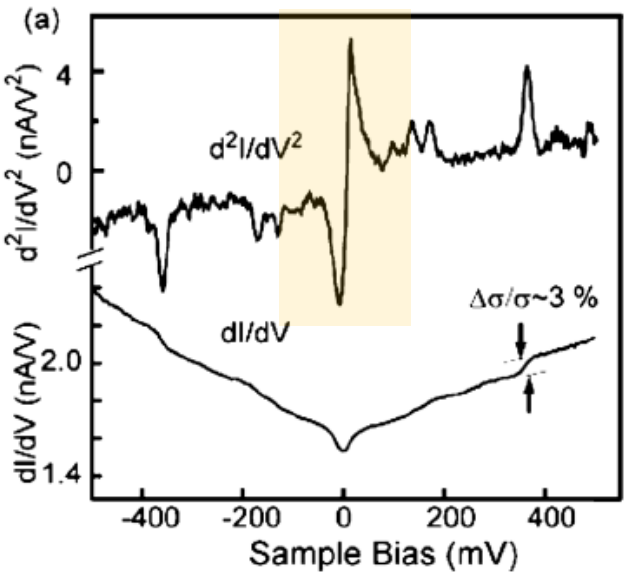
$$H_{SSH+LJ} = -\sum_{\langle ij\rangle,\beta,\sigma} t_{ij}\left[1-\lambda_{ij}^{\beta}\left(u_{i\beta}-u_{j\beta}\right)\right]\left(c_{i\sigma}^{\dagger}c_{j\sigma}+H.c.\right)+\sum_{i,\sigma}\varepsilon_i n_{i\sigma}$$
$$+1/2\sum_{j=1}^{N}\sum_{\alpha=1}^{3}M_j\left(du_{j\alpha}/dt\right)^2+1/2\sum_{ij}^{N}\sum_{\alpha\beta}^{3}u_{i\alpha}\Phi_{\alpha\beta}\left(\vec{R}_i-\vec{R}_j\right)u_{j\beta}$$

IETS of alkanedithiol
- comparison with experiments -

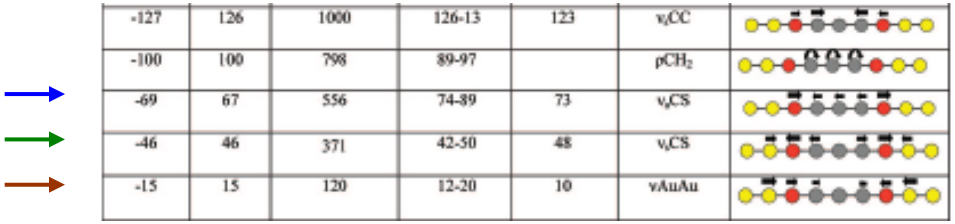
Theory(a)



Experiment (c)

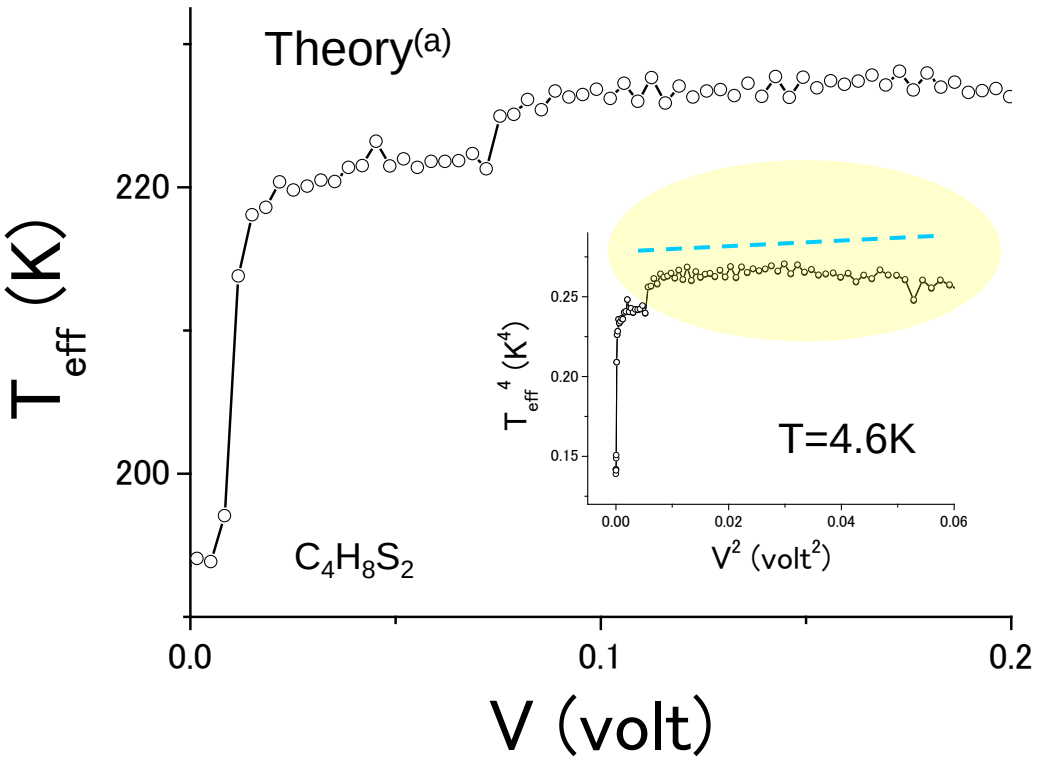


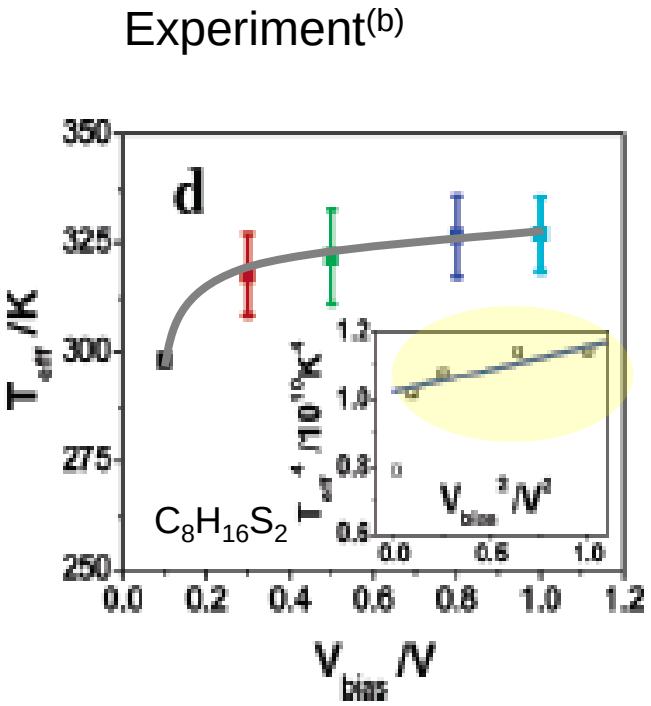
Experiment (b)



(a) Y. Asai, Phys. Rev.B78,045434 (2008), and in preparation.
(b) J. Hihath, C. R. Arroyo, G. Rubio-Bollinger, N.J. Tao, and N. Agraït, *Nano Letter*, 8, 1673 (2008).
(c) N. Okabayashi, Y. Konda and T. Komeda, Phys. Rev. Lett. 100, 21708 (2008)

local heating





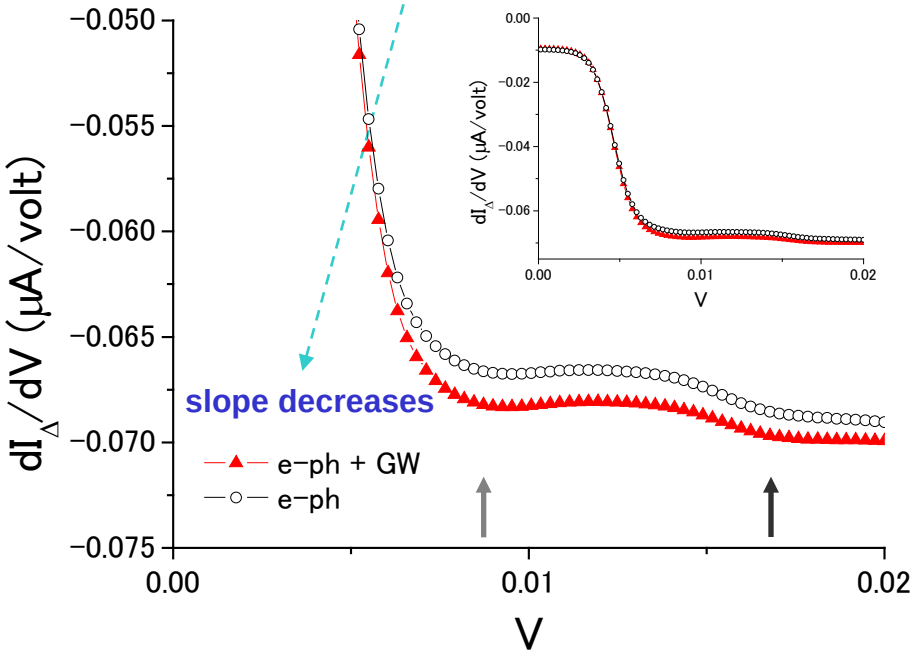
(a) Y. Asai, Phys. Rev.B78,045434 (2008), and in preparation.
(b) Z. Huang, B. Xu, Y. Chen, M. Di Ventra and N.J. Tao, *Nano Letter*, 6, 12403 (2006).

dumping life time of phonon is very important to describe the local heating precisely

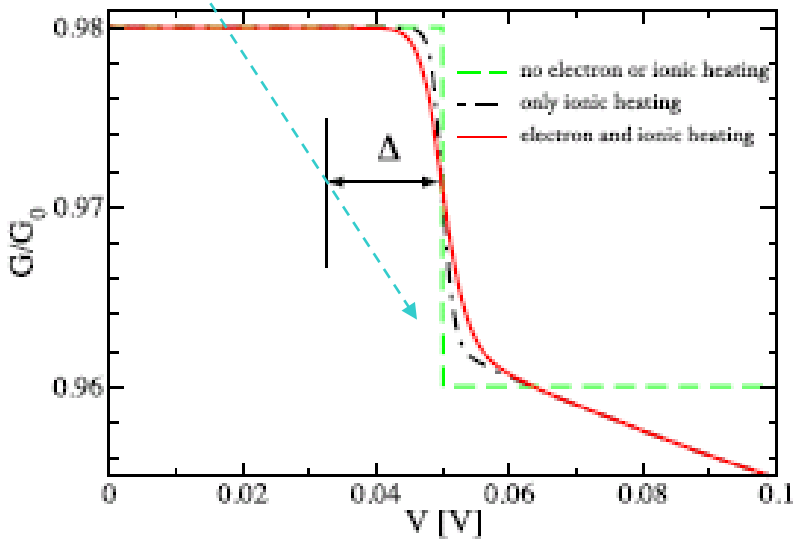
Electron correlation effect on IETS

both e-e and e-ph scattering effects included !

it means a decrease of the offset in IETS



it brings a broadening of the main peak in IETS



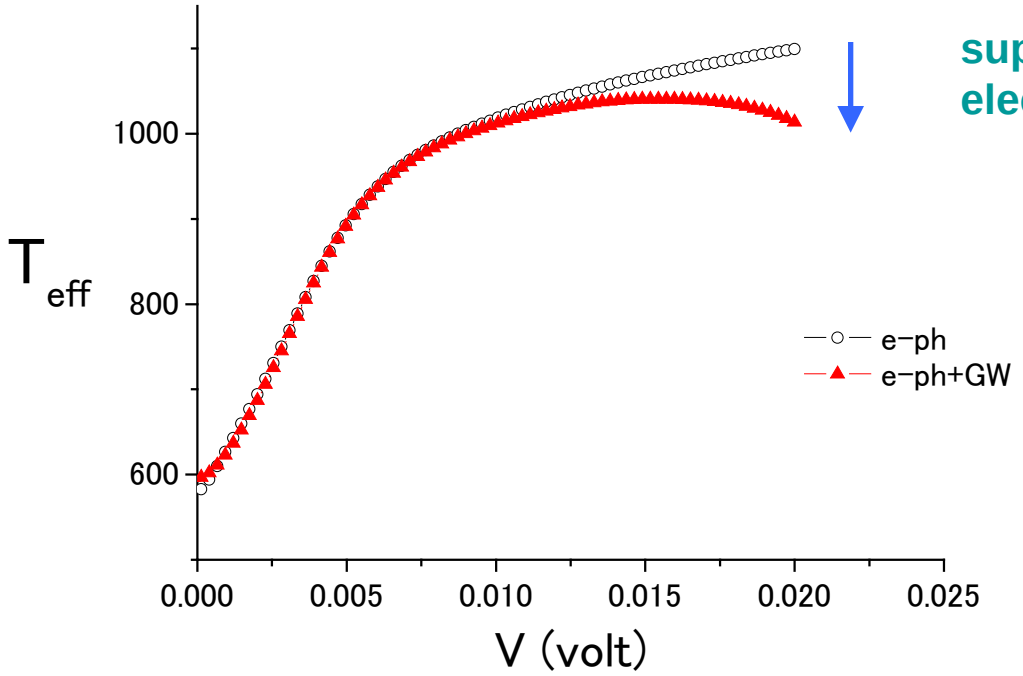
R.D Agosta and M. Di Ventra (2008)
"Hydrodynamical approach"

diagram calculation:
SCB for e-ph + SCGW for e-e

Y.Asai, in preparation

Electron correlation effect on the local heating

both e-e and e-ph scatterings included !



suppression of e-ph coupling due to electron correlation ?

- suppression of the dimerization due to electron correlation (conducting polymer theory)
  - Subbaswamy, Grabowski (1981)
  - Horsch (1981)
  - Hirsch (1983)
  - Campbell (1984)
  - Kilvelson (1986)

Y.Asai, in preparation

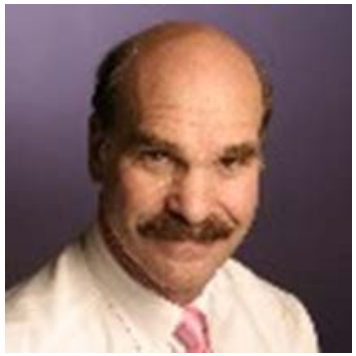
summary (local heating)

- Non-equilibrium phonon effect (phonon heat transport / phonon diffusion effect) is very important to describe voltage dependence of the local heating and its “effective temperature”.

- $T_{eff}{}^4 \simeq cV^2$ almost holds but there is a deviation at higher voltage region which should be ascribed to the quasi-ballistic phonon transport, which may become possible either with larger energy gap with E_F or electron correlation

Diode property

Molecular rectifier



MOLECULAR RECTIFIERS

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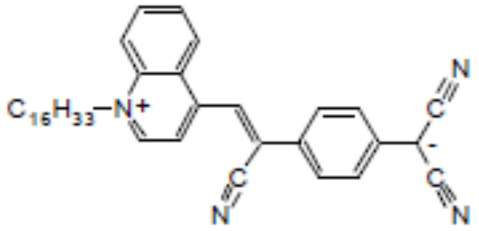
Received 10 June 1974



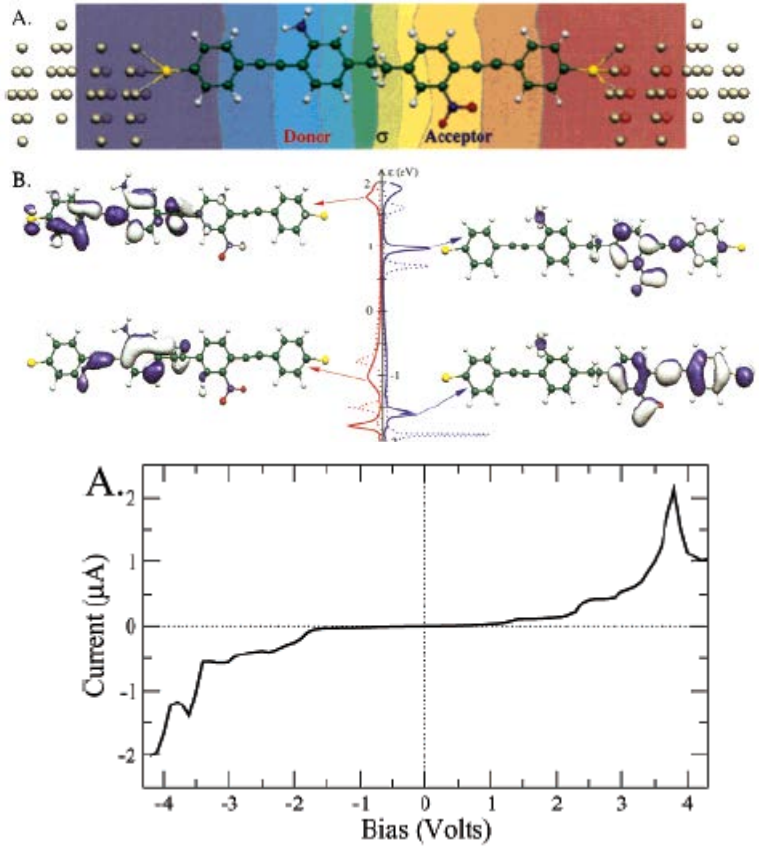
1, $C_{16}H_{33}$Q-3CNQ

eleven unimolecular rectifiers

A-R mechanism?

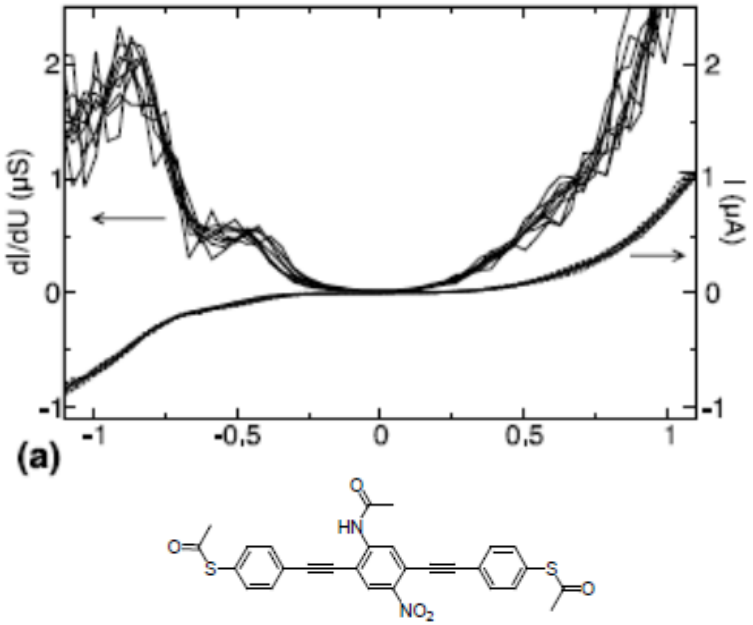
Need to know the mechanism at work!!

Only small asymmetry, if any, in first principle MF theories



K. Stokbro et al, JACS (2003)

Very small asymmetry limited to high bias voltage (LDA calculation)

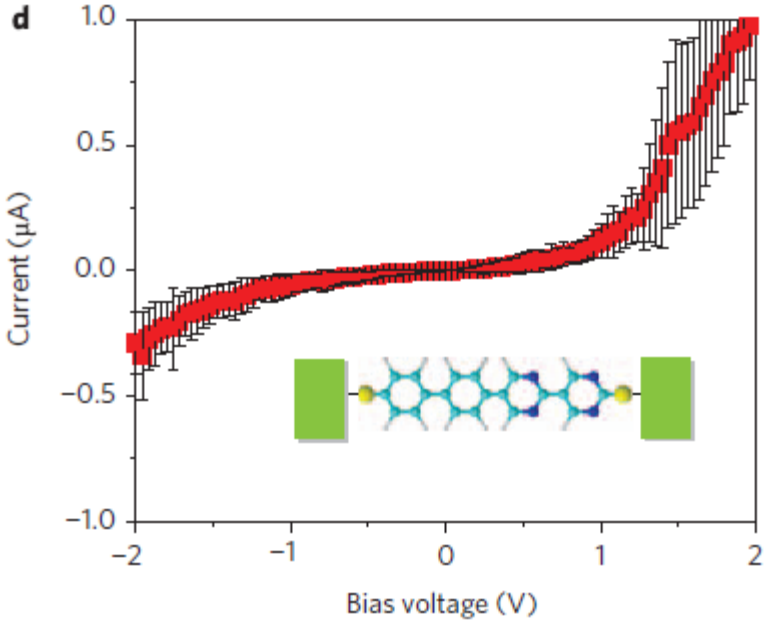


experiments

H.B. Weber et al, Chem. Phys. (2002).

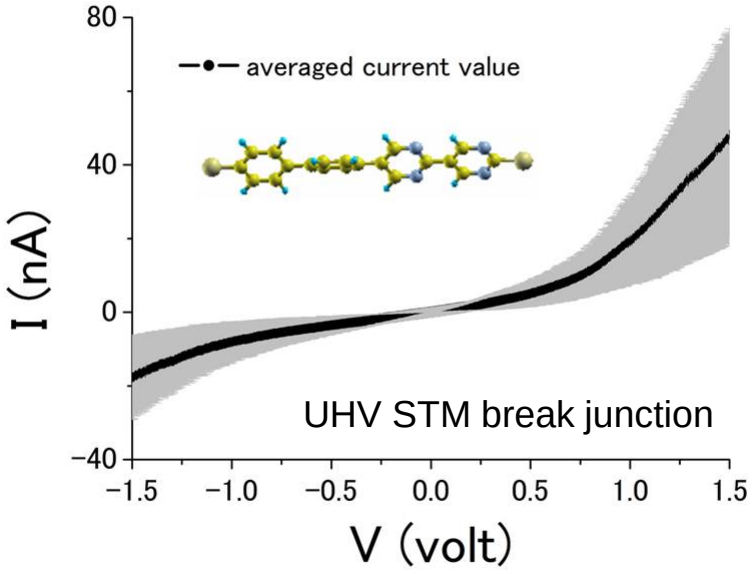
Large asymmetry

found in tetraphenlydithiol derivative (dipyrimidinil-diphenly diblock)



STM break junction in wet environment

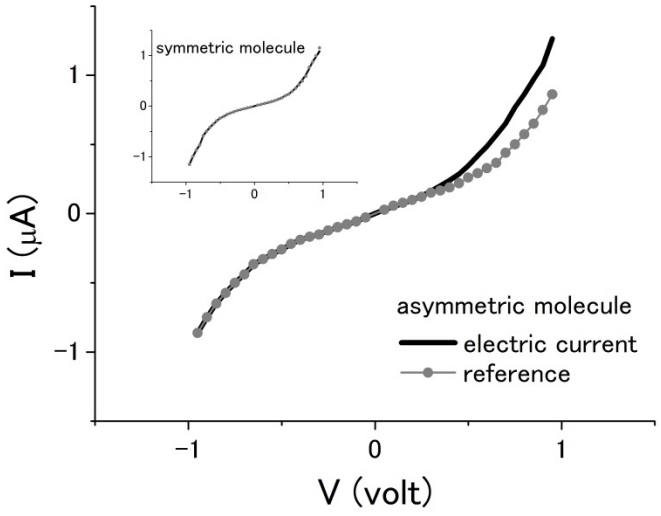
I.Díez-Pérez et al, Nature Chemistry (2009)



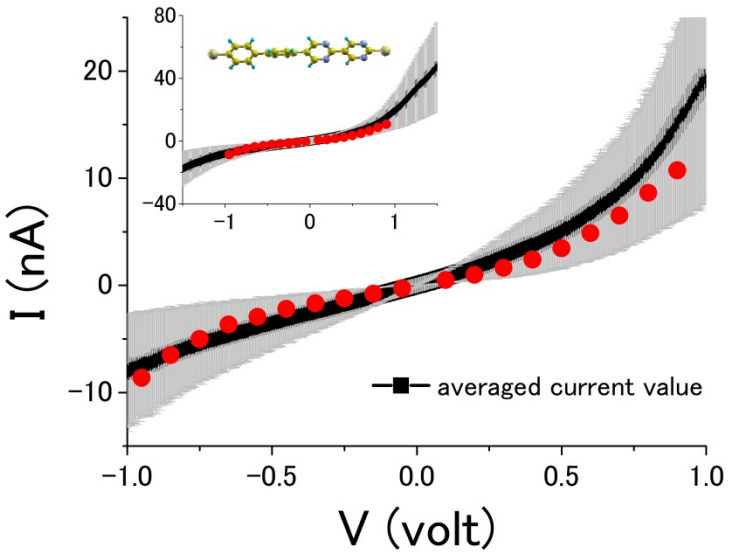
Y. Asai, H. Nakamura, J. Hihath, C. Bruot, and NJ Tao, submitted.

Larger asymmetry in UHV!

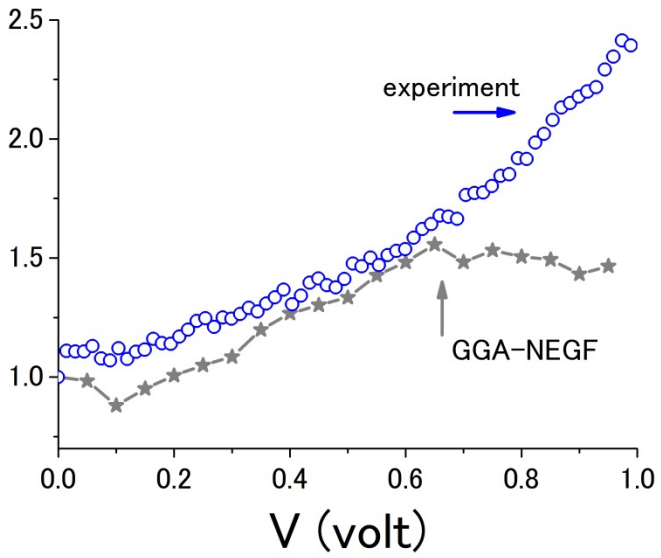
Pro & cons of first principles MF



I X 10^{-2}



η



asymmetry parameter: $\eta(V)=I(V)/I(-V)$

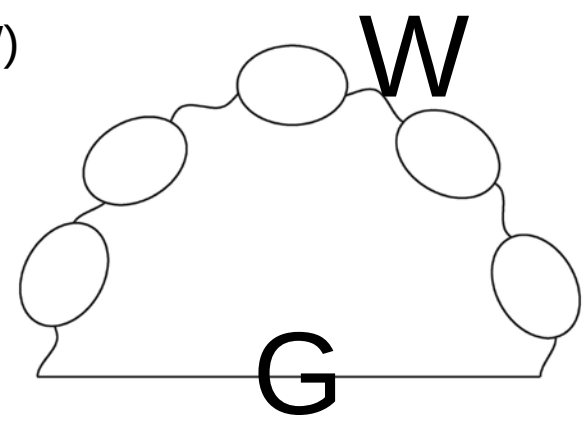
MF theory works when V<0.5, but it fails when V>0.5 where the asymmetry grows

H. Nakamura et al, in preparation

Electron correlation effects on non-equilibrium transport properties

RPA (GW)

$\Sigma =$



SSH＋LJ+U+V model

$$H_{SSH+LJ+U+V} = H_{SSH+LJ} + \sum_i U n_{i\uparrow} n_{i\downarrow} + V \sum_{\langle i,j \rangle} n_i n_j$$

Negligible in tunneling region:
Calculations on resonant systems

Kadanoff-Baym (1962)

$$\Sigma^{<(>)}(\omega) = \int \frac{d\lambda}{2\pi} W^{<(>)}(\omega - \lambda) G^{<(>)}(\lambda)$$

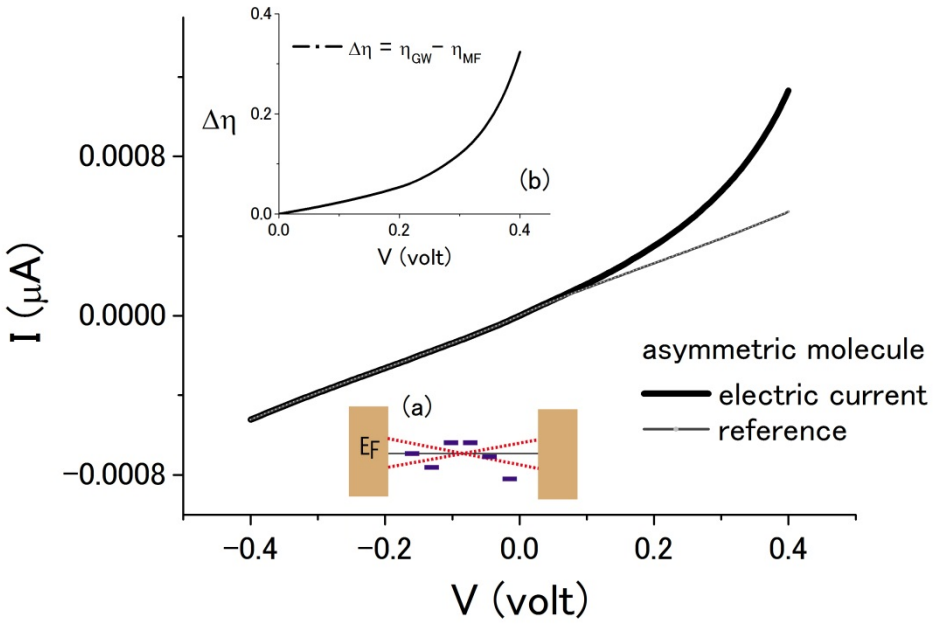
$$W^{<(>)}(\omega) = W^R(\omega)\Pi^{<(>)}(\omega)W^A(\omega)$$

$$\Pi^{<(>)}(\omega) = \int \frac{d\omega'}{2\pi i} G^{>(<)}(\omega' - \omega/2) G^{<(>)}(\omega' + \omega/2)$$

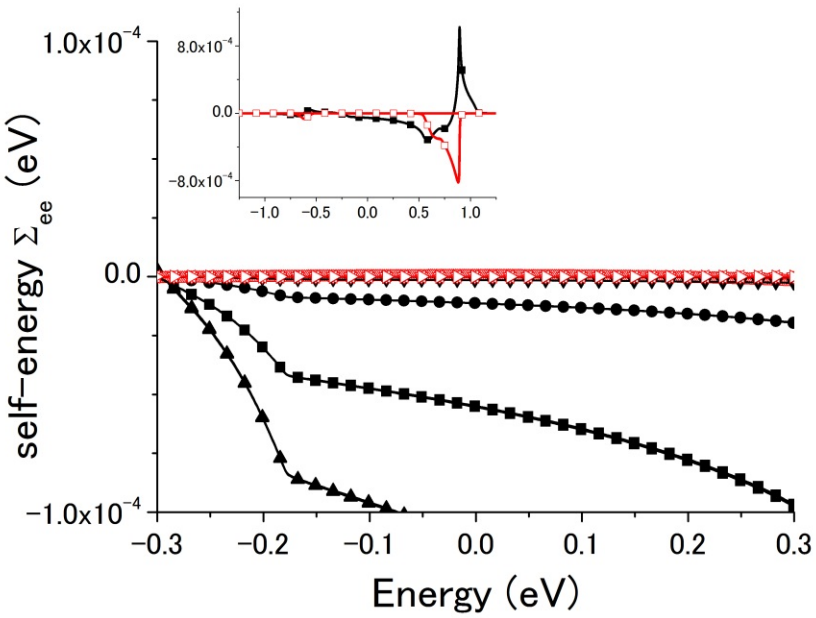
$$W^R(\omega) = v + vR^R(\omega)v$$

$$R^R(\omega) = \left(1 - \Pi^R(\omega)v\right)^{-1} \cdot \Pi^R(\omega)$$

Electron correlation effect within GW approximation



Electron self-energy Σ_{GW} at V=0:



Large asymmetry in *I* due to electron correlation in asymmetric molecule (SSH+U+V model)

Y. Asai, H. Nakamura, J. Hihath, C. Bruot, and NJ Tao, submitted.

Near E_F: Im $\Sigma_{GW} \simeq 0$
energy dependent Re Σ_{GW} → **Correlation effect beyond LDA is important**

summary (diode molecule)

- The giant diode property found experimentally in tetraphenlydithiol derivative (dipyrimidinil-diphenly diblock) cannot be described within LDA/GGA.

- The diode property is largely determined by electronic correlation effect and is mostly explained by screened Coulomb Random Phase Approximation (GW).

Summary

- Lots of non-equilibrium physical processes accompanying electric current have now become possible to be discussed with atomistic theory. Some can be done with *ab initio*. The number of the latter case being increased!
- Detail comparison between theory and experiments has become possible in many problems.
- These advances let me conclude that;

COMPARED WITH EXPERIMENTS
... MOLECULES ARE NOT "CALM" ENOUGH BUT IS IN NOISY ENV.