Chapter 10:
Beyond Electrical Conductance: Shot Noise and Thermopower

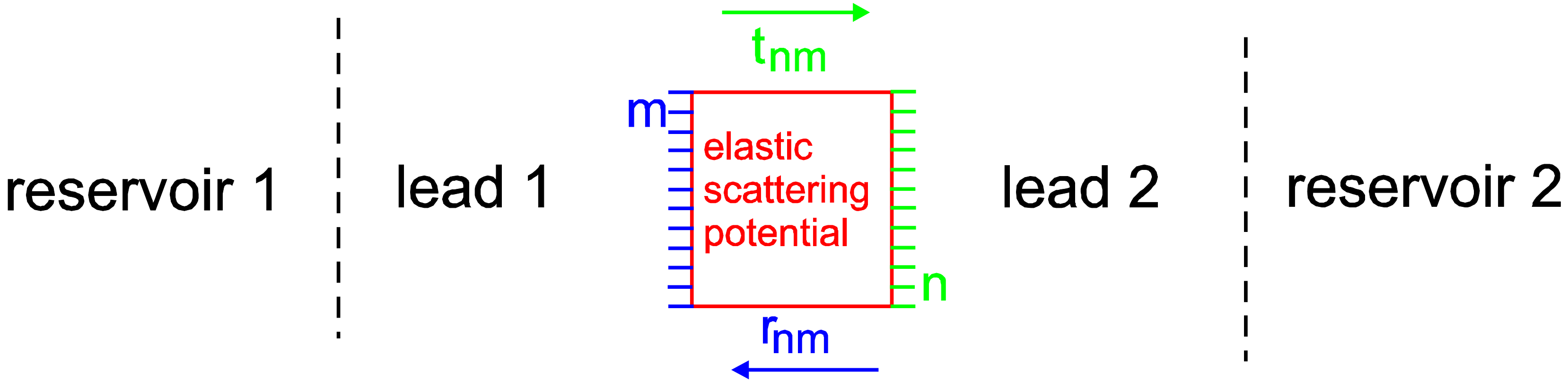
REFERENCES

1) Chapters 4 & 19 of Cuevas & Scheer.

2) M. J. M. de Jong and C. W. J. Beenakker, *Shot noise in mesoscopic systems*, in L. L. Sohn, L. P. Kouwenhoven, G. Schön (Eds.), *Mesoscopic Electron Transport*, NATO-ASI Series E, Vol. 345, p. 225, (Kluwer Academic Publishers, Dordrecht, NL, 1997).

3) Y. M. Blanter and M. Büttiker, *Shot noise in mesoscopic conductors*, Phys. Rep. 336, 2 (2000).

10.0 Reminder: Landauer Formula and Transmission Coefficients



reservoir 1

lead 1

t_{nm}

m

elastic scattering potential

n

r_{nm}

lead 2

reservoir 2

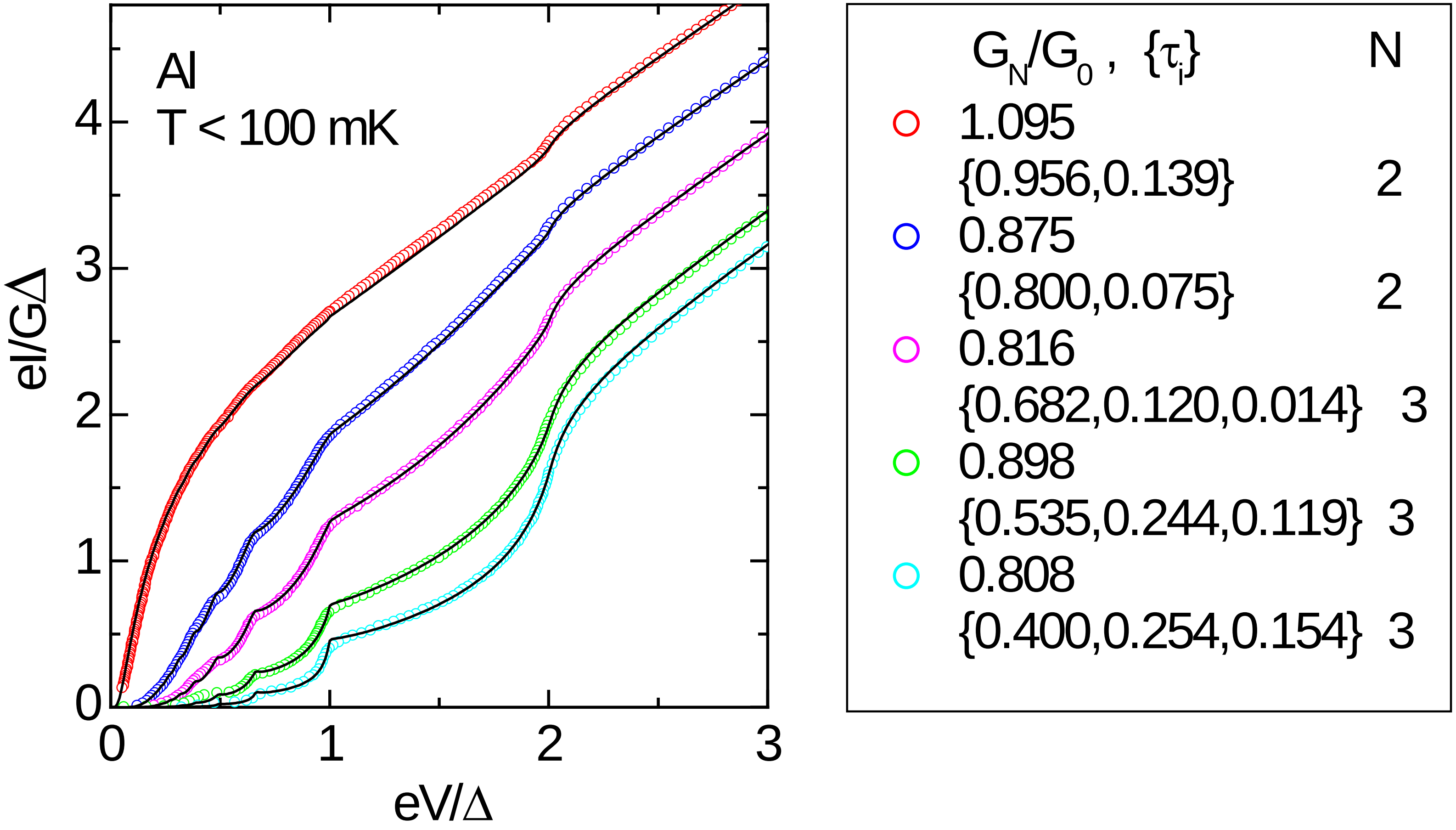
Channels are scattering eigenstates, τ_i are eigenvalues

Landauer formula: $G=\frac{2e^2}{h}\tau=G_0\tau$ with $\tau=\sum_{n=1}^{N}\sum_{m=1}^{M}|t_{nm}|^2=\mathrm{Tr}[tt^\dagger]=\sum_{i=1}^{N}\tau_i$

Problem: G measures sum of τ_i.
No information about individual τ_i available from measuring G!

Note: In this chapter we use τ instead of T for labeling the transmission coefficients.

10.0 Reminder to Chapter 7: Experimental Determination of Transmission Coefficients of Metallic Contacts



Superconducting IVs: Nonlinearities due to MAR

10.1 Nonlinear Functions of Transport Channels

Shot noise: v. d. Brom & v. Ruitenbeek, PRL 82 (1999) 1526, R. Cron et al., PRL 86 (2001) 4104

$$S \propto \sum_i \tau_i (1-\tau_i)$$

Conductance fluctuations: Ludoph et al., PRL 82 (1999) 1530

$$\Delta G \propto \sum_i \tau_i^{\,2} (1-\tau_i)$$

Thermopower fluctuations:
Ludoph et al., PRB 59 (1999) 12290

$$\sigma \propto \sum_i \tau_i^{\,2} (1-\tau_i)$$

Supercurrent: Goffman et al., PRL 85 (2000) 170

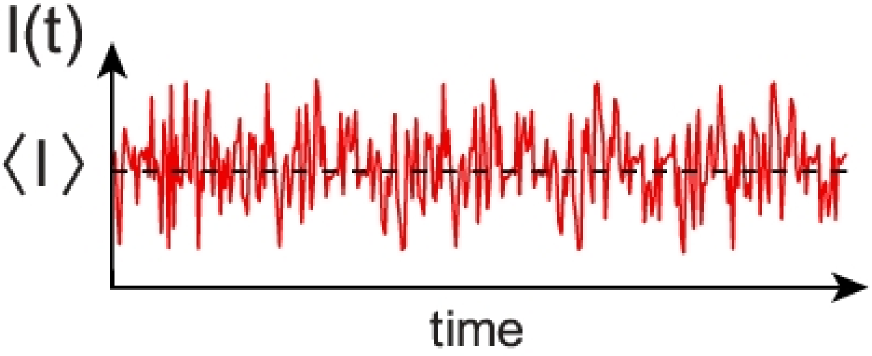
$$I_J \propto \sum_i \tau_i (1-\tau_i \sin^2(\delta/2))^{-1/2} \cos(\delta/2)$$

Superconducting IVs/MAR: Scheer et al., PRL 78 (1997) 3535

→ can be used for measuring channels

10.1 Shot noise

Intrinsic current fluctuations of an electrical resistor:



Noise: Definition

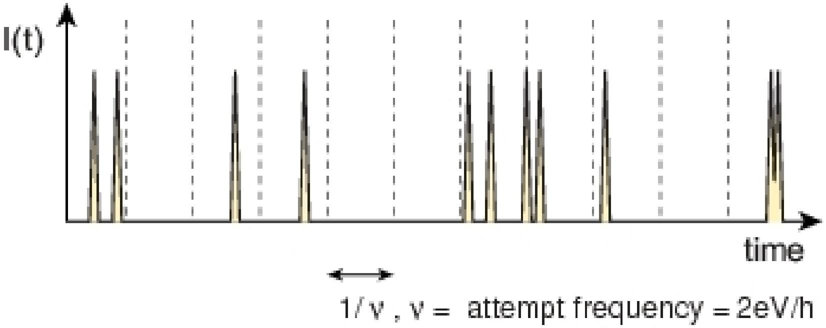
$$S_I(\omega) = 2\int dt e^{i\omega t}\left\langle \Delta\hat{I}(t+t_0)\Delta\hat{I}(t_0)\right\rangle$$

$$\Delta\hat{I}(t) \equiv \hat{I}(t) - \left\langle \hat{I}(t)\right\rangle$$

- Thermal fluctuations:

  Johnson /Nyquist noise $S_I = 4k_BTG$

- Non-equilibrium fluctuations (shot noise): randomly distributed tunneling of *q* discrete charges.



$$S_{Poisson} = 2q\,|\,I\,|$$

(W. Schottky 1918)

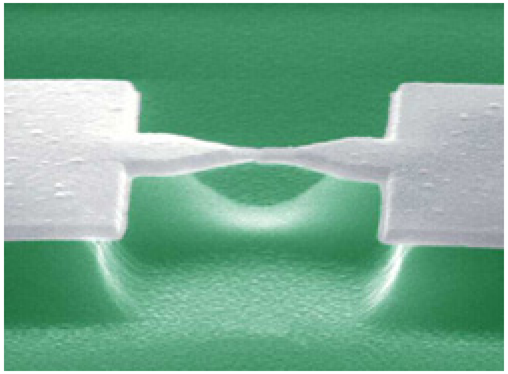
10.1 Shot noise in atomic contacts

R. Cron, M. Goffman, D. Esteve and C. Urbina, Phys. Rev. Lett. ***86,*** *4104 (2001)*

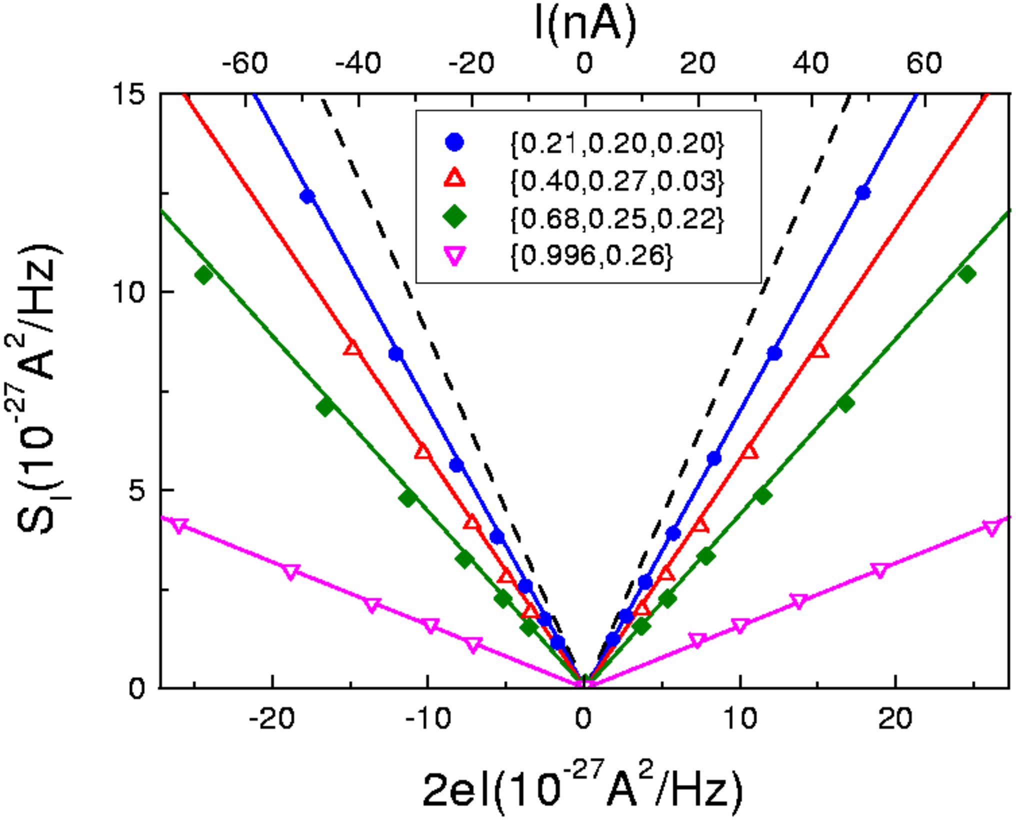
Physical Review Focus

Focus Archive PNU Index Image Index Focus Search

30 April 2001

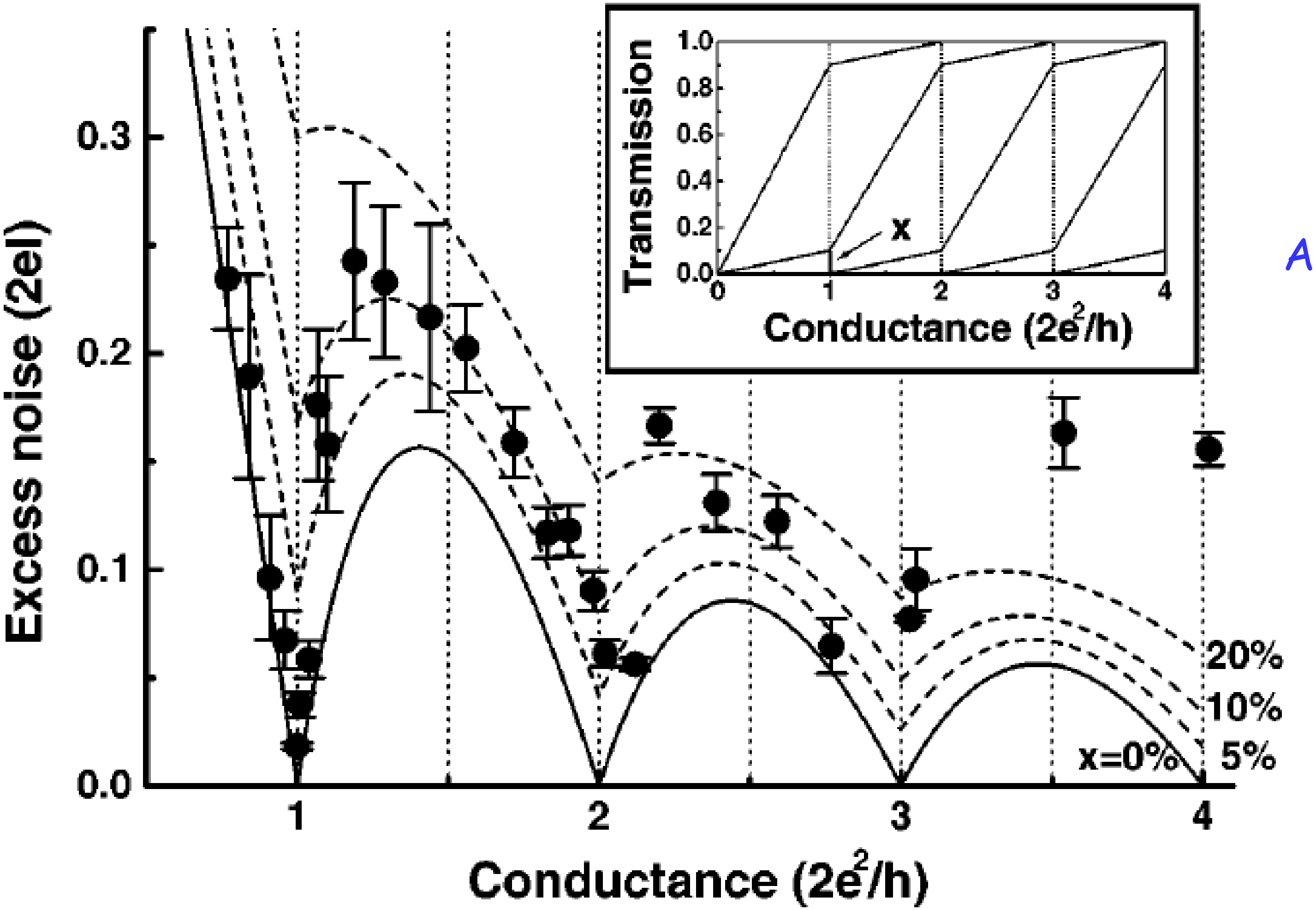


$$S_I(V)=\int\left(\left\langle I(t)I(0)\right\rangle-\left\langle I\right\rangle^2\right)dt=2eV\frac{2e^2}{h}\sum_n\tau_n(1-\tau_n)$$



10.1 Shot noise in atomic contacts

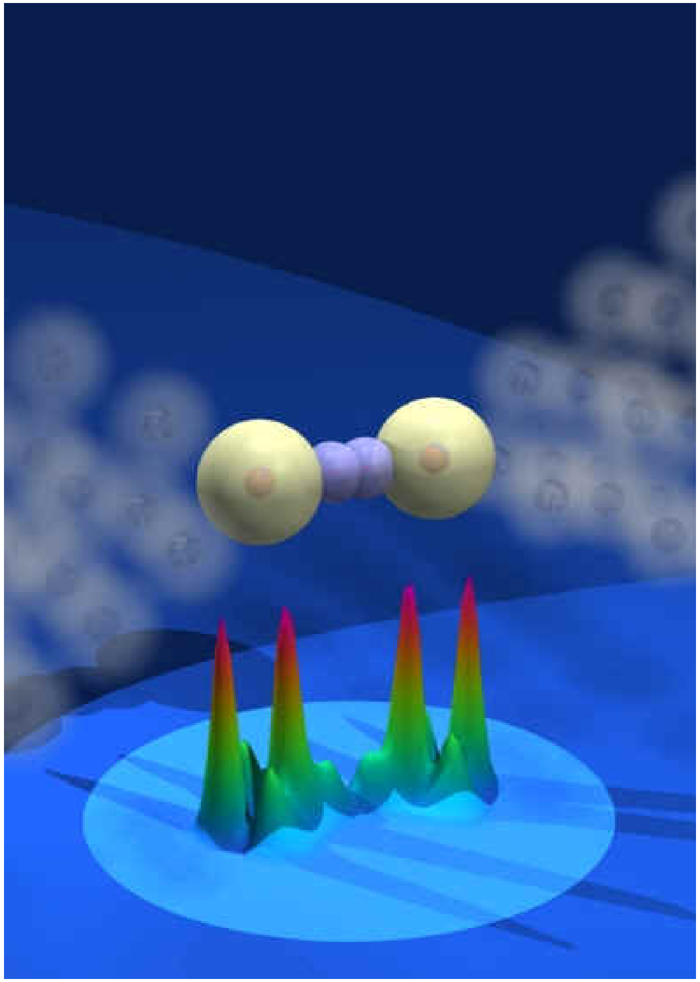
H.E. van den Brom et al, Phys. Rev. Lett. ***82*** *, 1526 (1999)*

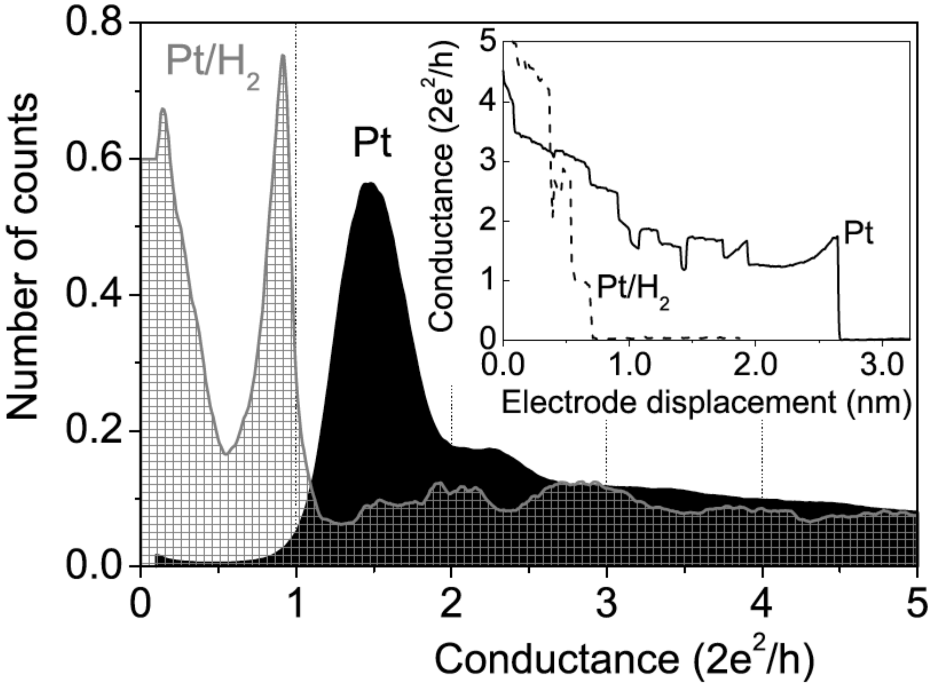


Au @ 4.2K

10.1 Pt-hydrogen-Pt junctions: Conductance histograms

R.H.M. Smit, Y. Noat, C. Untiedt, N.D. Lang, M.C. van Hemert, J.M. van Ruitenbeek, Nature ***419****, 906 (2002)*





- The hydrogen molecule forms a stable bridge between Pt electrodes.
- The conductance is $G \approx G_0$ and is largely dominated by a single conduction channel.

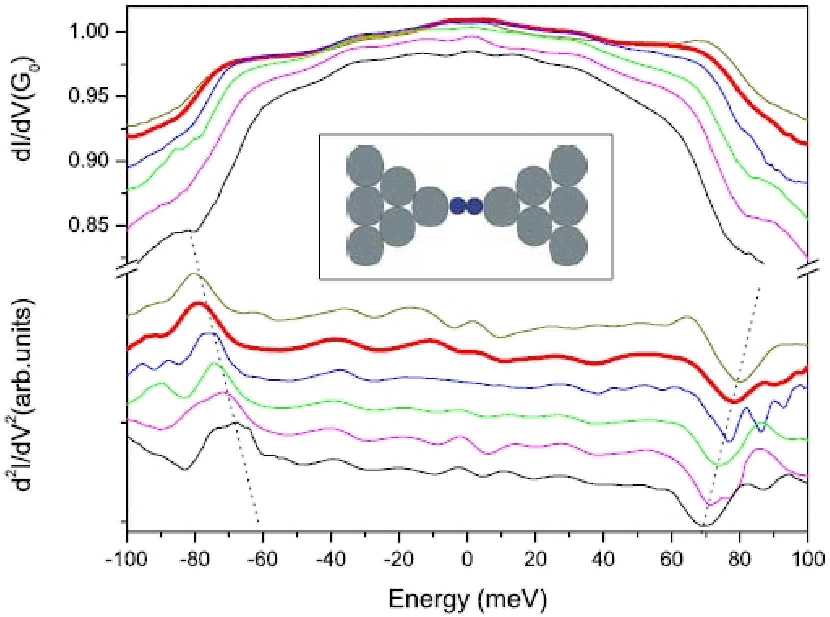
10.1 Pt-hydrogen-Pt junctions:
Shot noise measurements

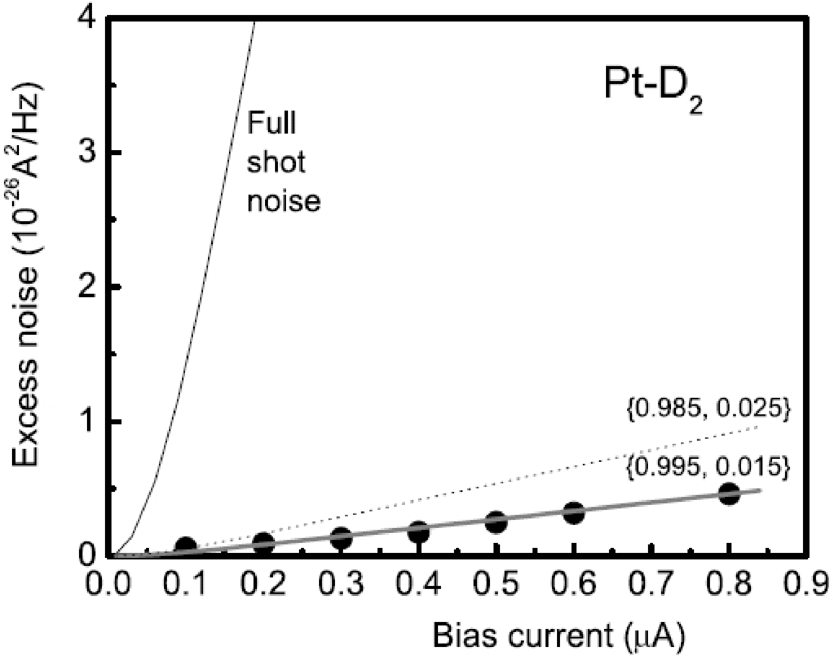
D. Djukic and J.M. van Ruitenbeek, Nano Lett. ***6****, 789 (2006).*

$$S_I = 2eV \coth\left(\frac{eV}{2k_BT}\right)\frac{2e^2}{h}\sum_i \tau_i(1-\tau_i) + 4k_BT\frac{2e^2}{h}\sum_i \tau_i^2$$

$$\text{If } k_BT \ll eV: \quad S_I = 2eI\left(1-\frac{\sum_i \tau_i^2}{\sum_i \tau_i}\right) = 2eIF(\{\tau_i\})$$

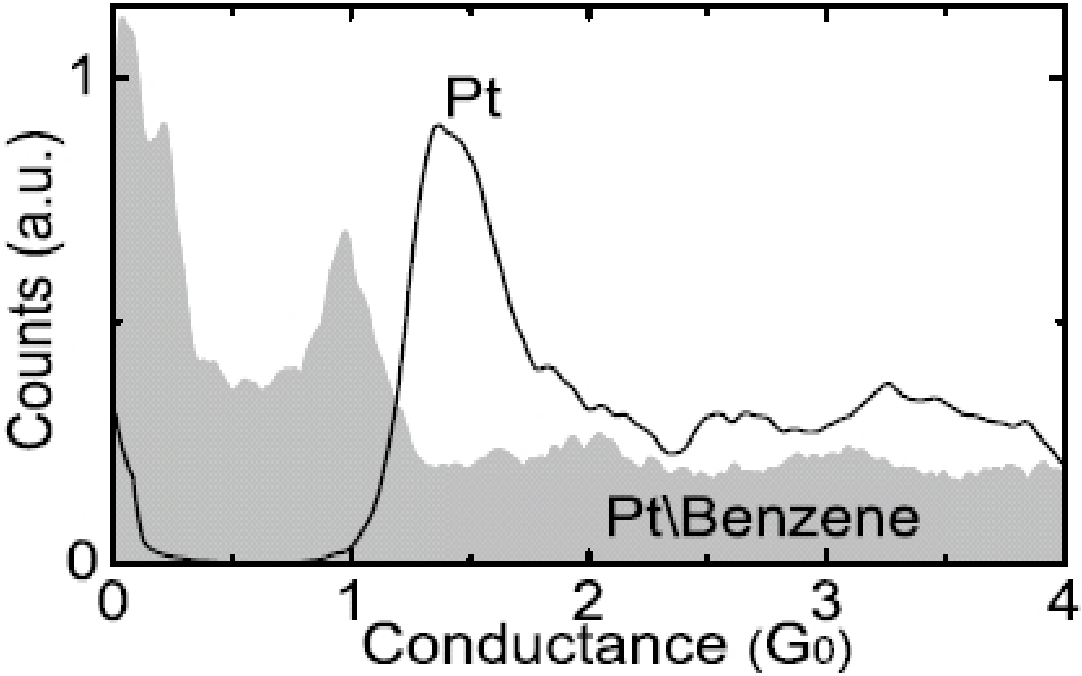
F = Fano factor





10.1 Pt-benzene-Pt junctions: Conductance histogram

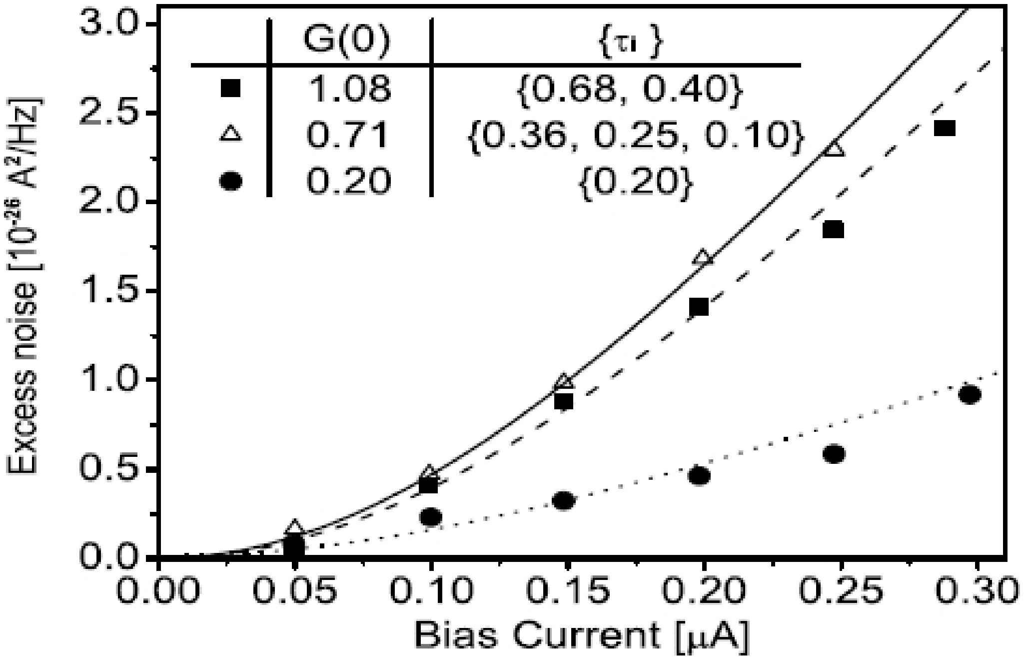
M. Kiguchi et al. Phys. Rev. Lett. ***101****, 046801 (2008)*



- The introduction of benzene supresses the formation of pure Pt contacts.
- New junctions with preferred conductance of $1G_0$ and sometimes $0.2G_0$ are formed while stretching the contact.

10.1 Pt-benzene-Pt junctions: Shot noise measurements

$$S_I = 2eV\coth\left(\frac{eV}{2k_BT}\right)G_0\sum_i \tau_i(1-\tau_i) + 4k_BTG_0\sum_i \tau_i^2$$



- Several channels contribute to transport for high conductances (ca. 1G_0).
- The number of channels is reduced to one when the conductance is reduced to around 0.2G_0.

10.2 Thermopower

- **Thermopower (or Seebeck coefficient):**

$$\boxed{S = -\frac{\Delta V}{\Delta T}}$$

$$\left\{\begin{array}{lcl} \Delta V & = & \text{thermoelectrical voltage} \\ \Delta T & = & \text{temperature difference} \end{array}\right.$$

- **Thermopower in the coherent transport regime:**

$$S = \frac{1}{eT}\frac{\int_{-\infty}^{\infty}(E-\mu)\tau(E)\left[\partial f(T,E)/\partial E\right]dE}{\int_{-\infty}^{\infty}\tau(E)\left[\partial f(T,E)/\partial E\right]dE};$$

$$\left\{\begin{array}{l} \tau(E) = \text{transmission} \\ f(E) = \text{Fermi function} \end{array}\right.$$

Low-temperature expansion:

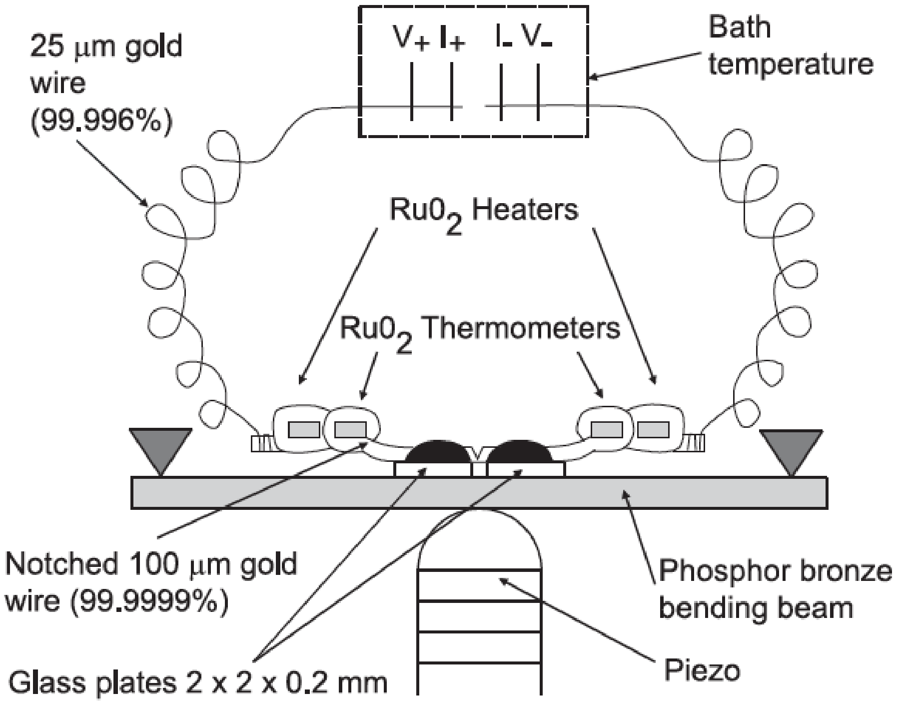
$$\boxed{S = -\frac{\pi^2 k_B^2 T}{3e}\frac{\tau'(E_F)}{\tau(E_F)}}$$

$$\left[\tau'(E_F) = \left.\frac{d\tau}{dE}\right|_{E=E_F}\right]$$

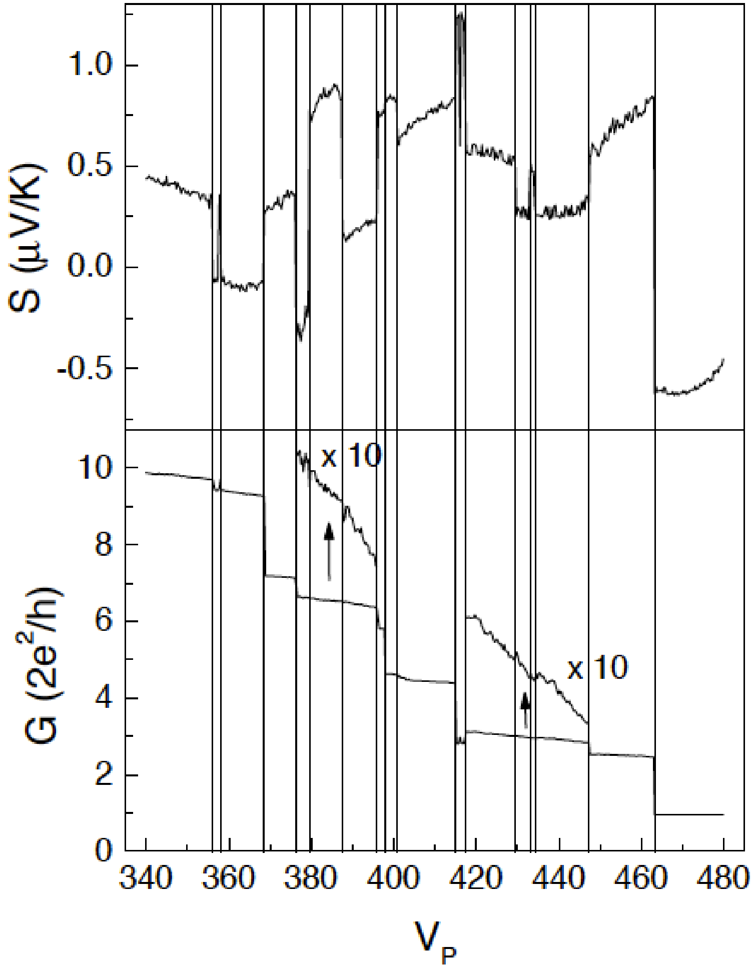
10.2 Thermopower measurements of Au atomic contacts

*B. Ludoph and J.M. Van Ruitenbeek, Phys. Rev. B **59**, 12290 (1999)*

Break-junction setup



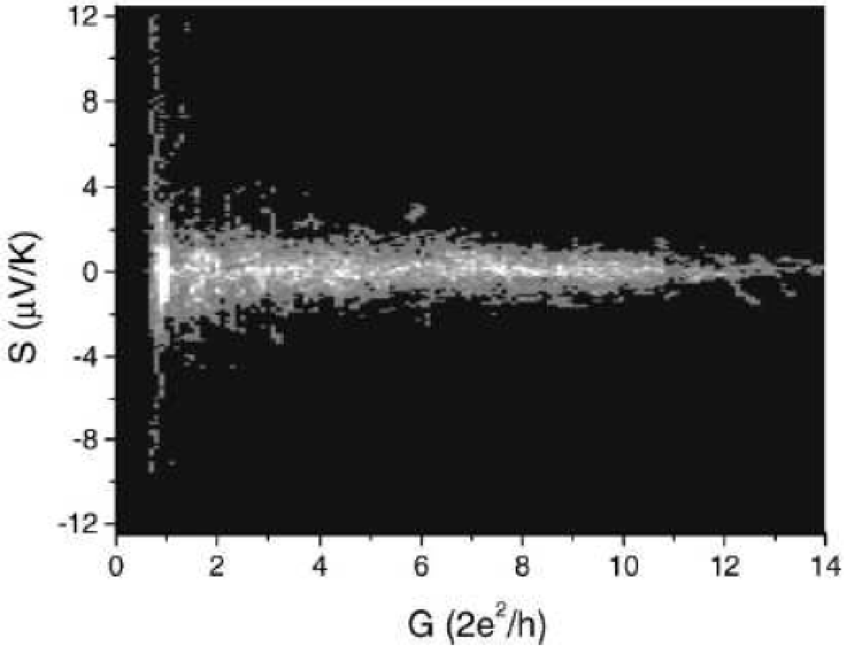
Thermopower vs. piezo voltage

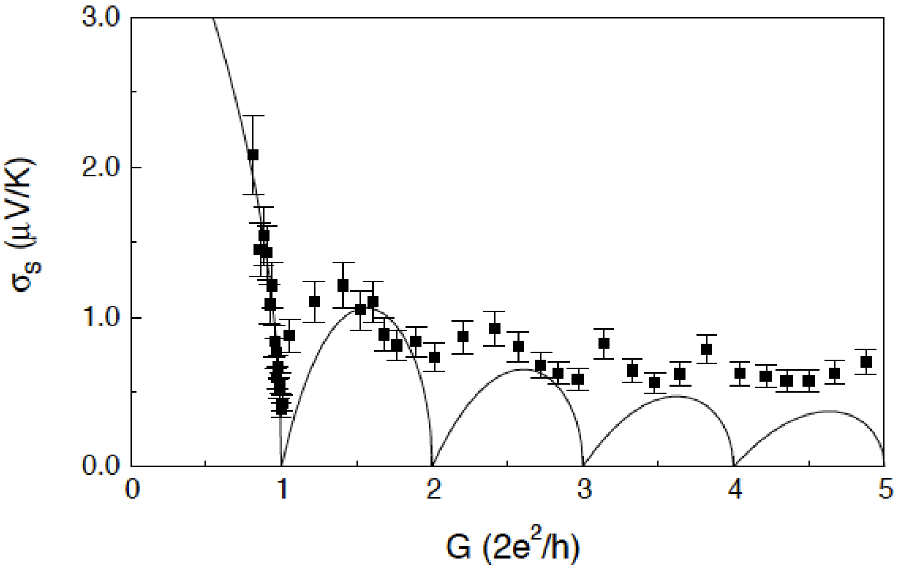


10.2 Thermopower measurements of Au atomic contacts

*B. Ludoph and J.M. Van Ruitenbeek, Phys. Rev. B **59**, 12290 (1999)*

Thermopower vs. conductance **Standard deviation vs. conductance**





- **The thermopower can be both positive and negative, but it vanishes on average.**
- **The thermopower fluctuations of Au reach a minimum close to $1G_0$.**
- **Interpretation: the thermopower is due to interference effects induced by the presence of impurities nearby the contact region.**

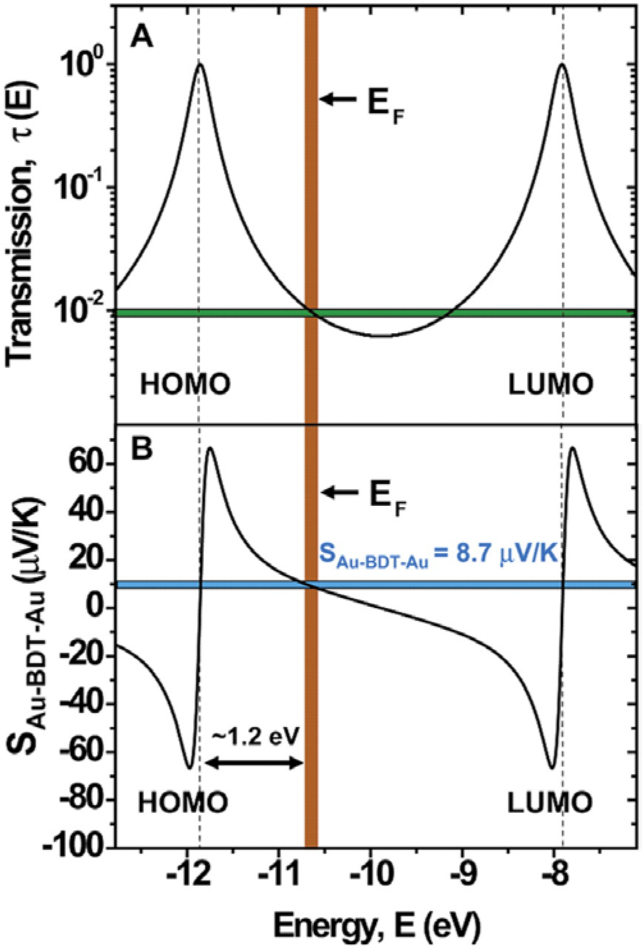
10.2 Why thermopower of molecular junctions?

M. Paulsson and S. Datta, Phys. Rev. B ***67****, 241403 (2003).*

- It is measurable.
- It gives valuable information about the location of the Fermi level.
- It is rather insensitive to the details of the coupling to the contacts.

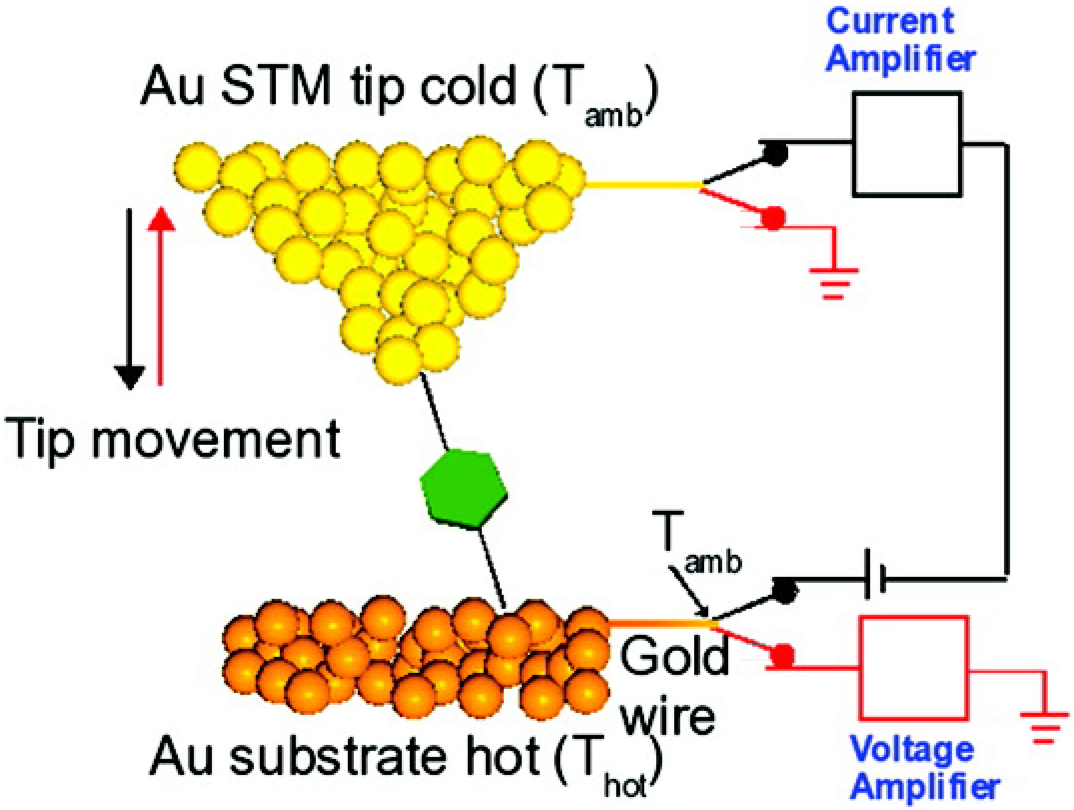
Thermopower or Seebeck coefficient

$$S = \frac{1}{eT}\frac{\int_{-\infty}^{\infty}(E-\mu)\tau(E)\left[\partial f(T,E)/\partial E\right]dE}{\int_{-\infty}^{\infty}\tau(E)\left[\partial f(T,E)/\partial E\right]dE}$$



10.2 Thermopower measurements in molecular junctions

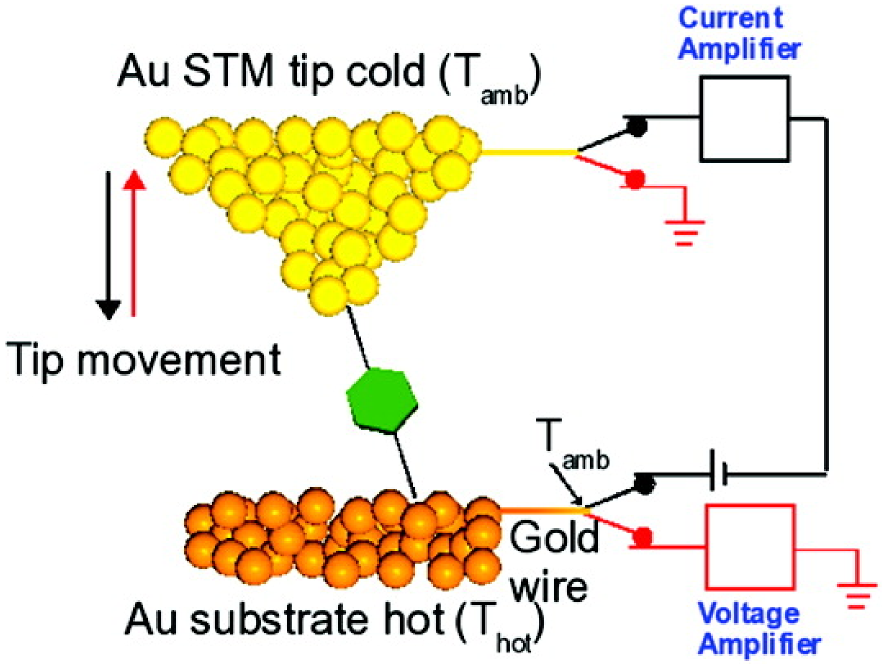
K. Baheti, J.A. Malen, P. Doak, P. Reddy, S.-Y. Jang, T. Don Tilley, Arun Majumdar, and R. A. Segalman, Nano Lett. ***8****, 715 (2008).*

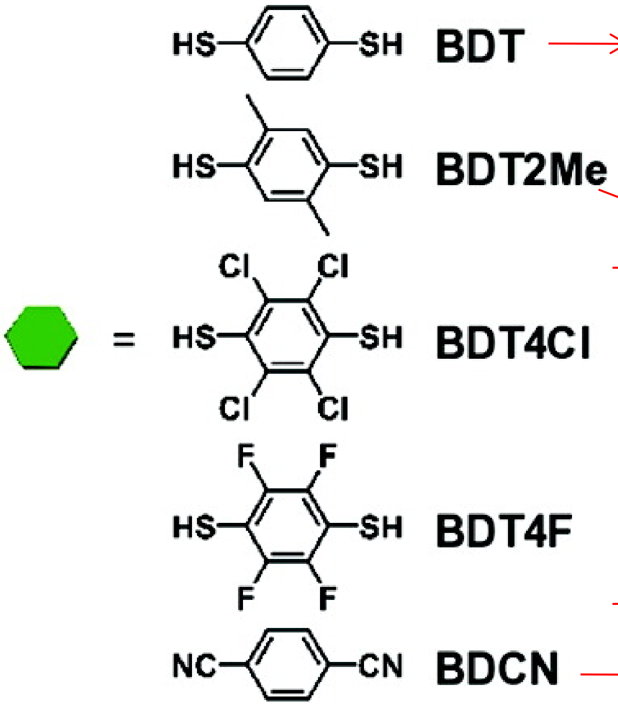


10.2 Probing the chemistry of molecular heterojunctions using thermoelectricity

K. Baheti, J.A. Malen, P. Doak, P. Reddy, S.-Y. Jang, T. Don Tilley, Arun Majumdar, and R. A. Segalman, Nano Lett. ***8****, 715 (2008).*

Study of the effect of different substituents and end groups





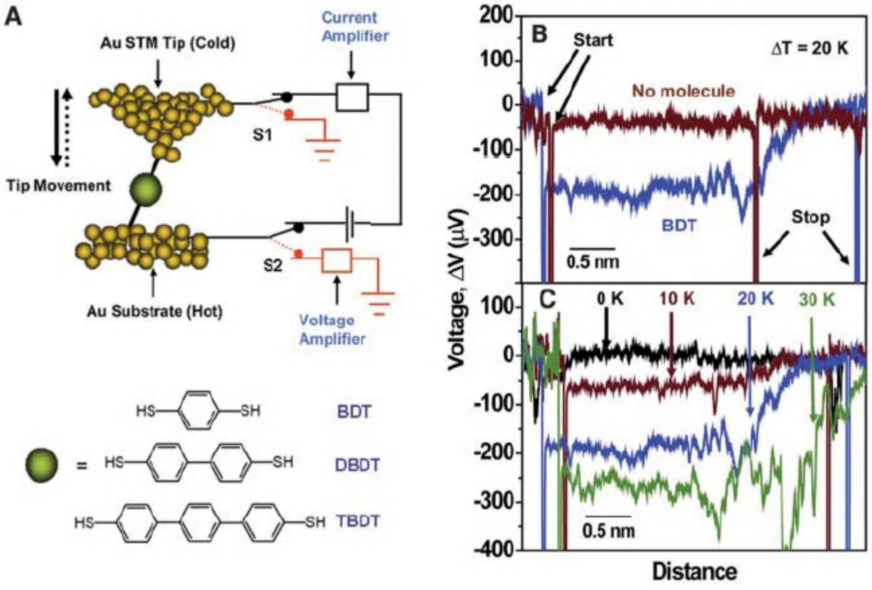
BDT → Reference molecule

BDT2Me → Electron-donating group

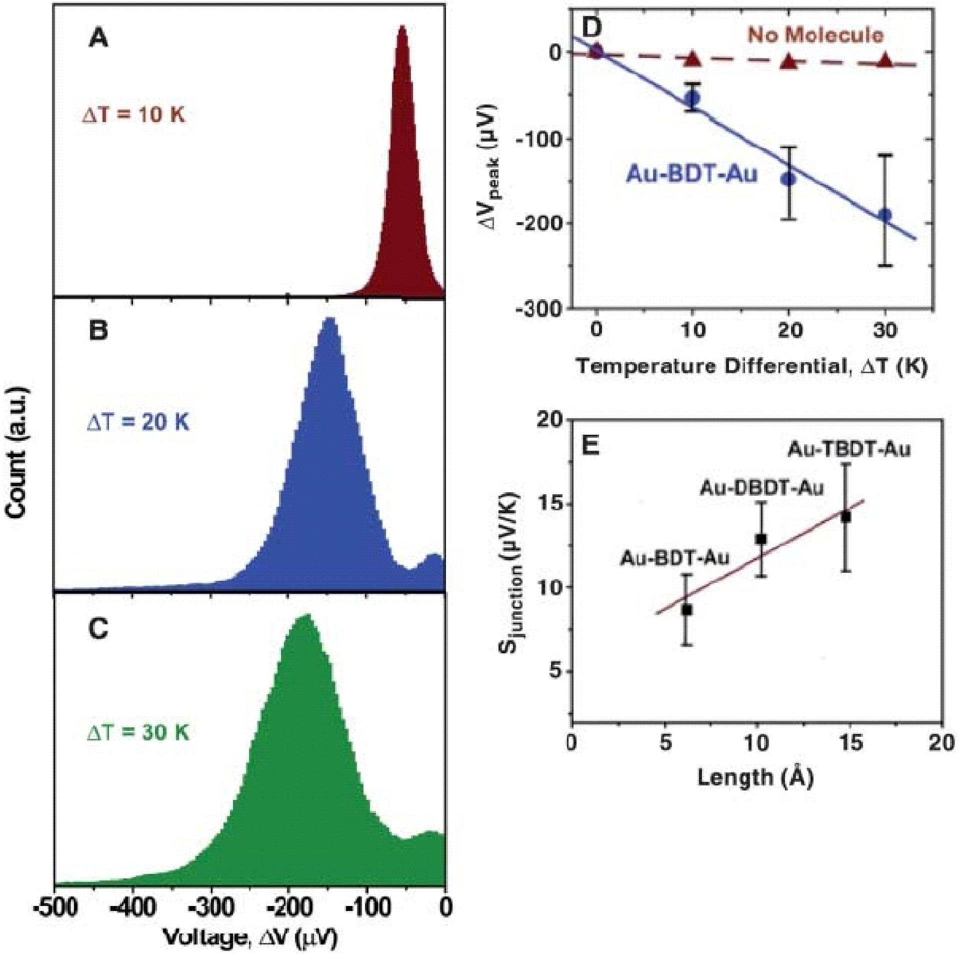
BDT4Cl, BDT4F: Electron-withdrawing groups

BDCN → Different end group

10.2 Thermopower measurements in molecular junctions



P. Reddy, S.-Y. Jang, R.A. Segalman and A. Majumdar, Science ***315****, 1568 (2007).*

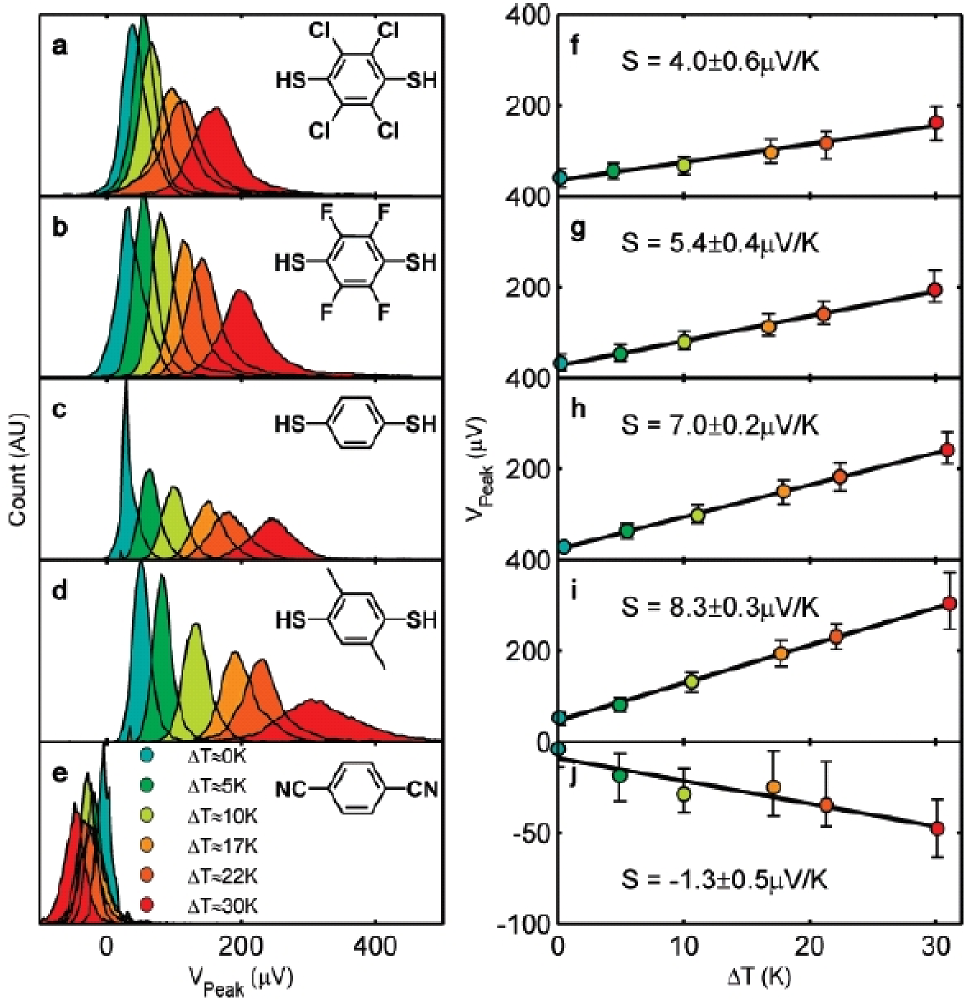


Thermopower or Seebeck coefficient

$$S = \frac{1}{eT}\frac{\int_{-\infty}^{\infty}(E-\mu)\tau(E)\left[\partial f(T,E)/\partial E\right]dE}{\int_{-\infty}^{\infty}\tau(E)\left[\partial f(T,E)/\partial E\right]dE}$$

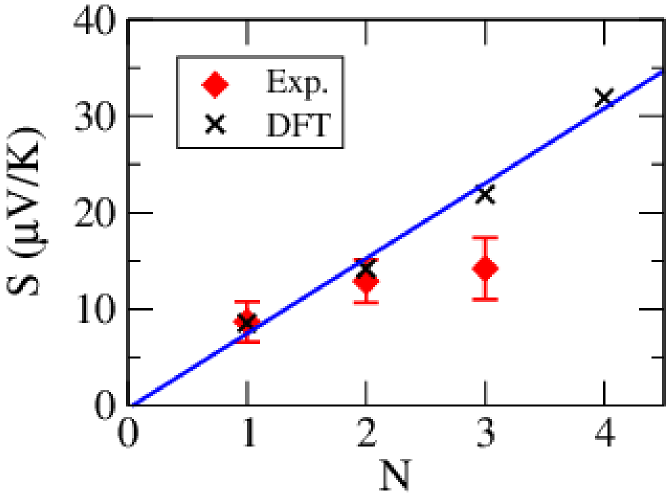
10.2 Probing the chemistry of molecular heterojunctions using thermoelectricity

K. Baheti, J.A. Malen, P. Doak, P. Reddy, S.-Y. Jang, T. Don Tilley, Arun Majumdar, and R. A. Segalman, Nano Lett. ***8****, 715, (2008).*



- The electron-withdrawing groups reduce the thermopower: HOMO lies further away from Fermi level.
- The electron-donating groups increase the thermopower by moving the HOMO closer to the Fermi level.
- BDCN has a negative thermopower: Transport is dominated by the LUMO.

10.2 Ab-initio studies of the thermopower



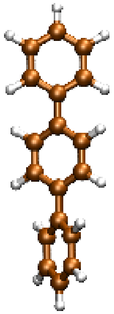
Length dependence

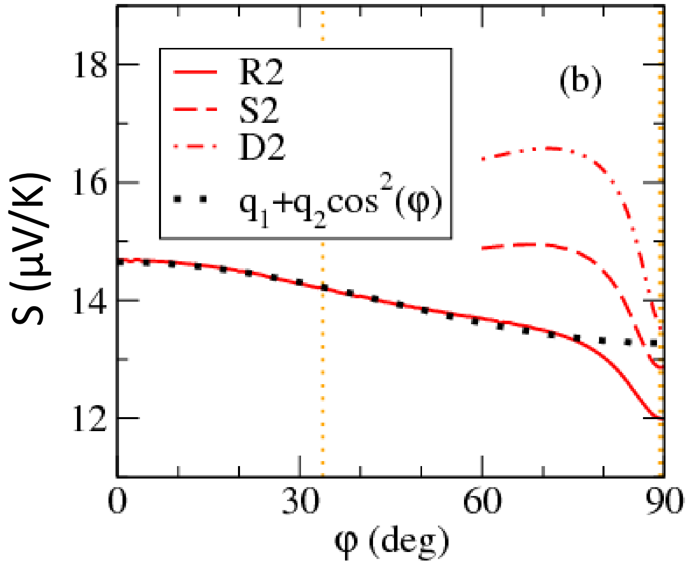
$$\tau(E) \approx \alpha(E)\exp(-\beta(E)N)$$

$$S = S^{(0)} + S^{(1)}N$$

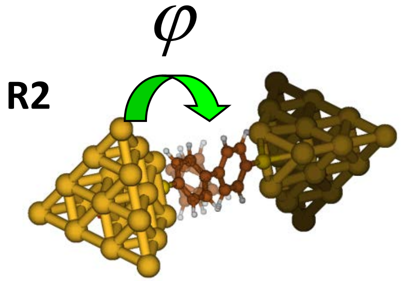
Exp.: P. Reddy *et al.*, Science 2007
Theory: F. Pauly *et al.*, PRB 2008

N=3





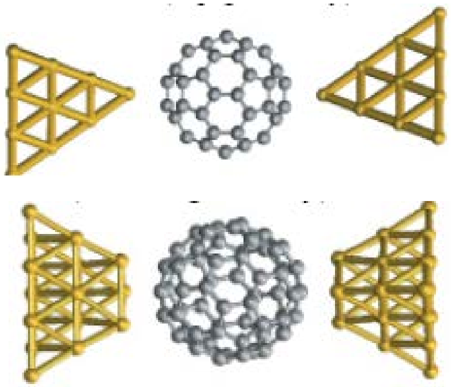
Influence of conjugation



F. Pauly *et al.*, PRB 2008
M. Bürkle *et al.*, PRB 2012

C_{60} junctions

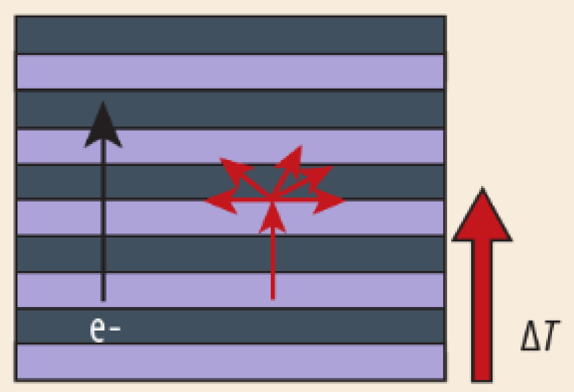
S. Bilan et al., PRB 2012



10.2 Towards efficient thermoelectrics

Thermoelectric elements

- Conversion of waste heat into electrical energy
- Nanorefrigerators

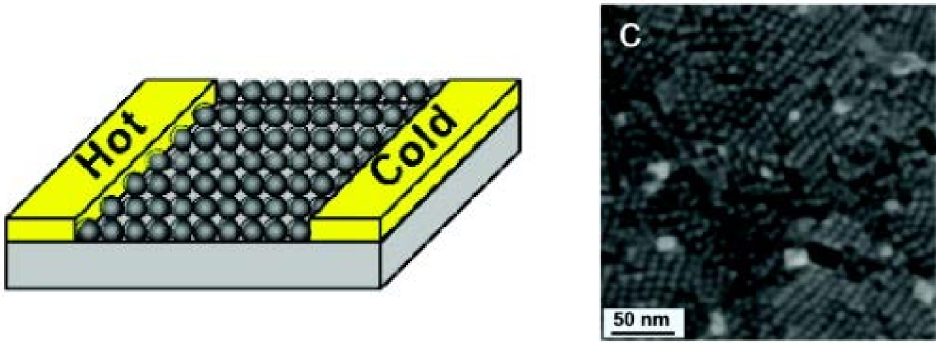


Phonon transport

Figure of merit: $ZT=S^2GT/\kappa$

Thermopower S
Temperature T
Electric conductance G
Thermal conductance κ

$$\kappa = \kappa_{el} + \kappa_{ph}$$



R. A. Segalman (UC Berkeley):
R.Y. Wang *et al.*, Nano Lett. 2008

Ultimate Goal: Enhancement of *ZT* through appropriate nanostructuring