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10TH CONFERENCE ON HOPPING AND RELATED PHENOMENA

(1 - 4 September 2003)

"Charge Carrier Properties below and above the Metal-Insulator Transition in Conjugated Polymers - Recent Results"

presented by:

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Charge carrier properties below and above the MIT in conjugated polymers.

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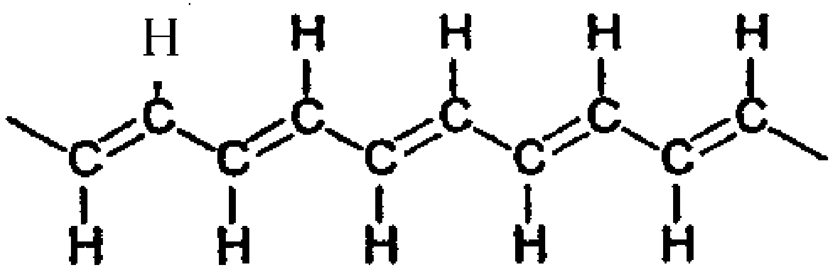
A.K. Mukerhjee (Bangalore), Reghu Menon(Bangalore)

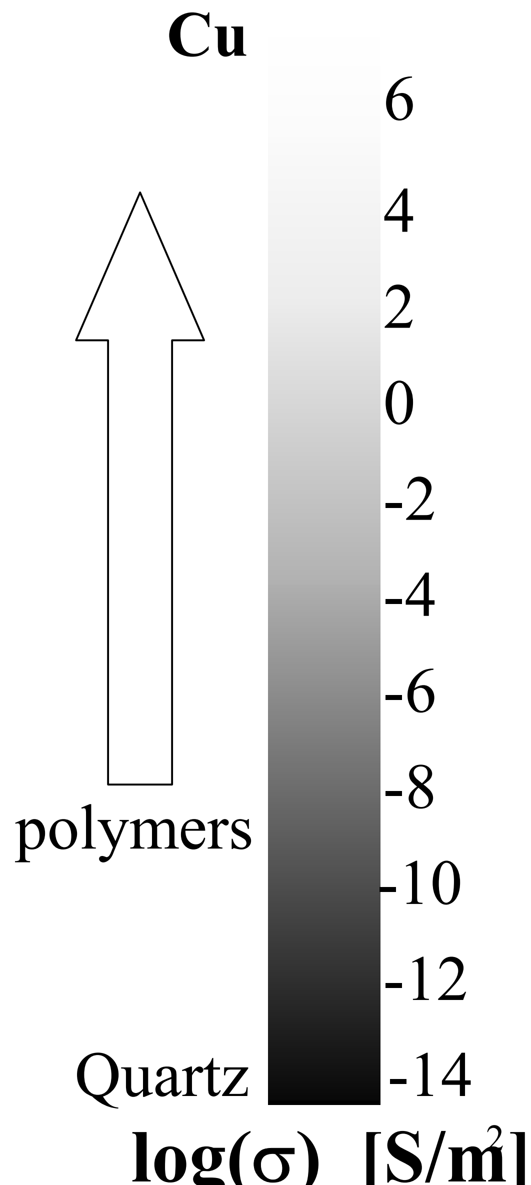
References:
Martens et al., Phys. Rev. B. 67, 121203(R) (2003)
Romijn et al., Phys. Rev. Lett. 90, 176602 (2003)

HRP10, Trieste, September 4 2003

Conducting polymers



polyacetylene
doped with iodine

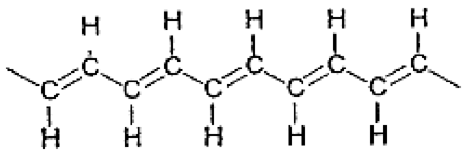


1977 : Discovery of highly conducting polymers

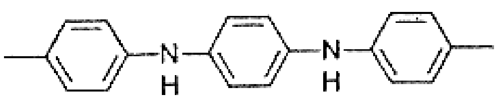
2000 : Nobel prize in Chemistry
A.Heeger, A.MacDiarmid and H. Shirakawa

What causes the conductivity?

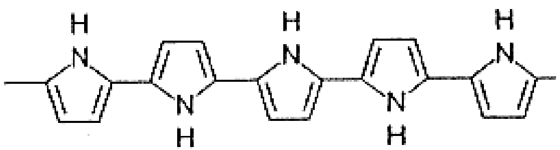
conjugated polymers



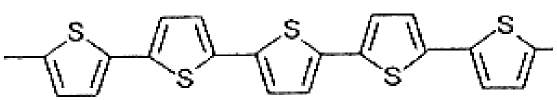
polyacetylene



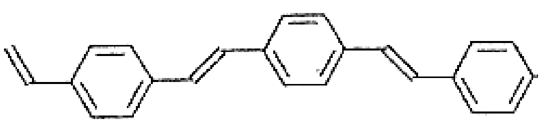
polyaniline



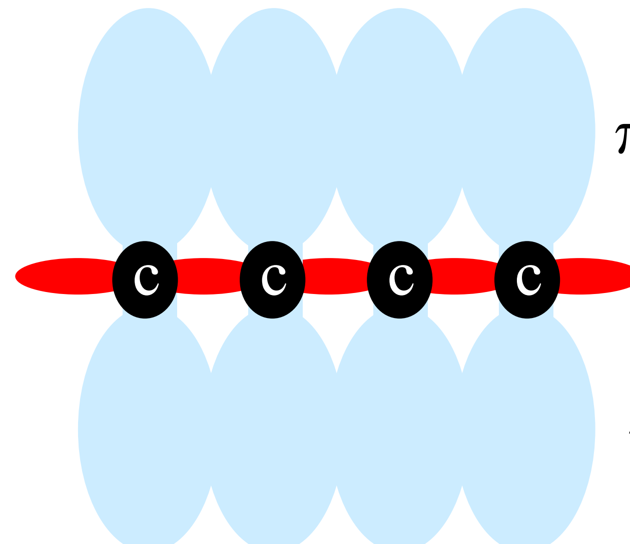
polypyrrole



polythiophene



poly(phenylene-vinylene



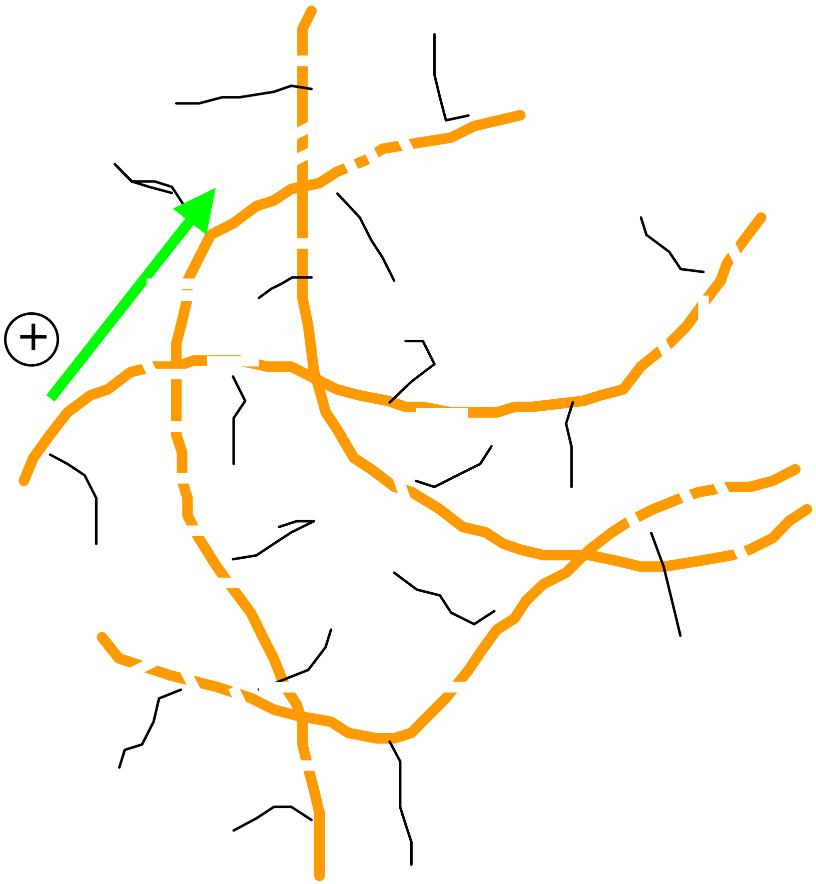
delocalized electrons

Chemically doping: introducing charges

Charged carriers can move via π-bonds through the polymer

Reality conjugated polymers

Conjugation broken by kinks, defects

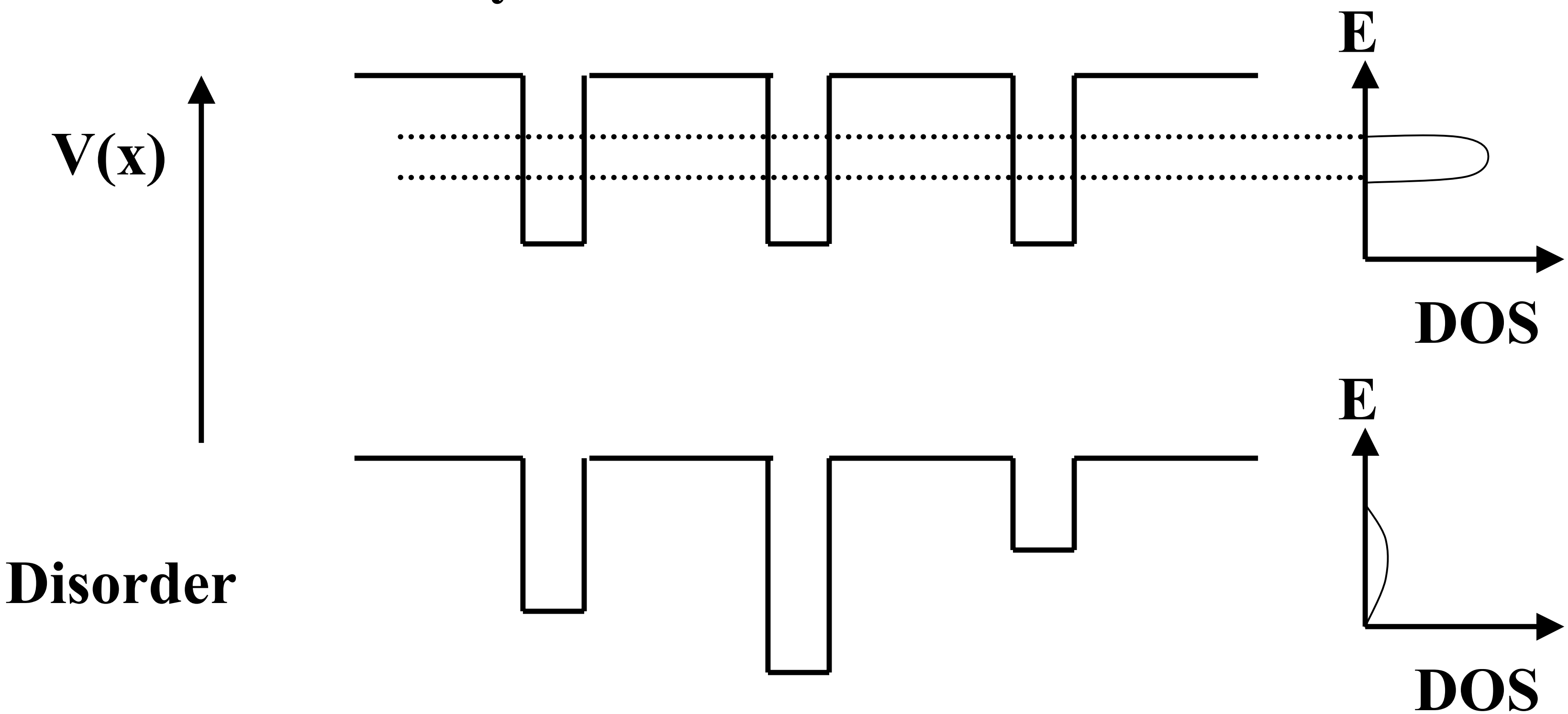


Hopping between conjugated parts – disorder dominant

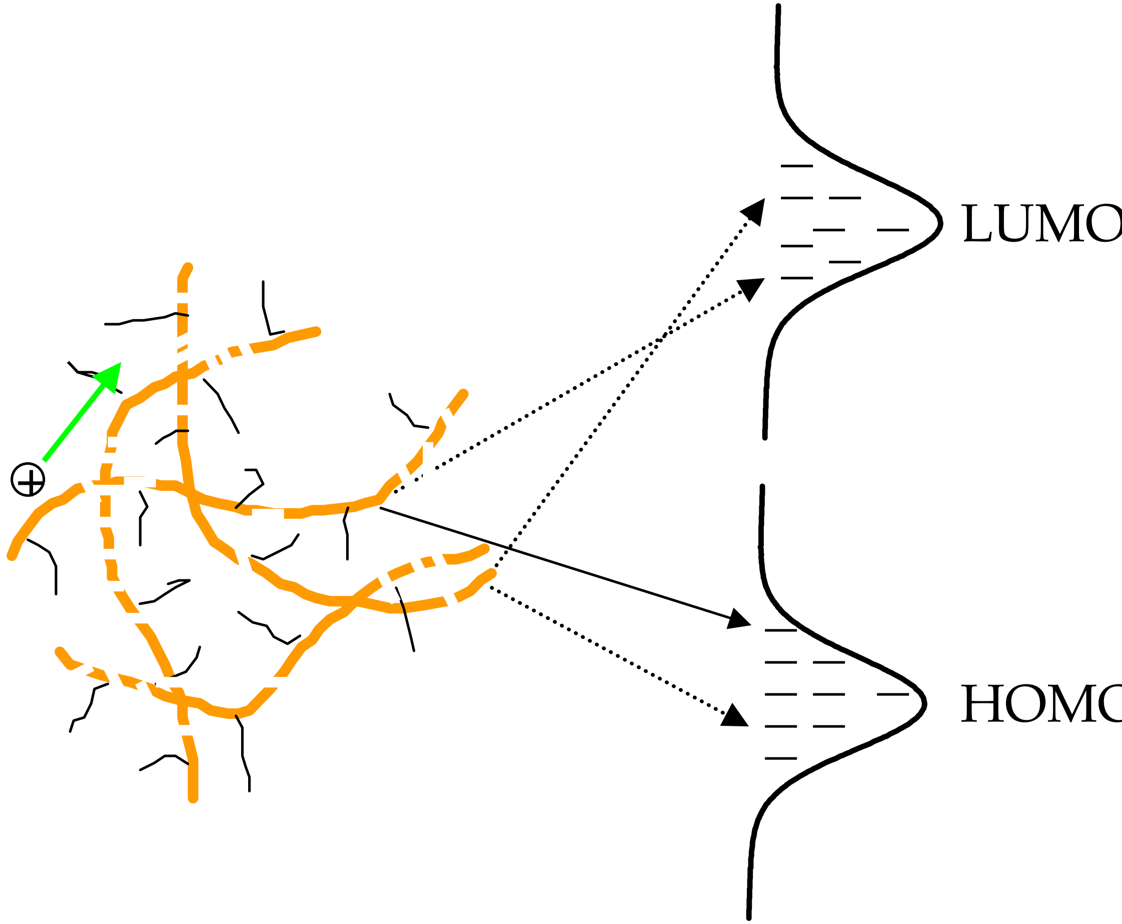
Disorder – localized states

Sufficient disorder produces localized states (Anderson)

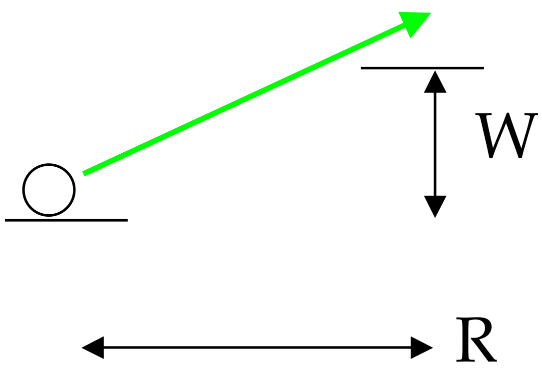
Potential Wells for Crystalline Lattice



Energetic and spatial disorder

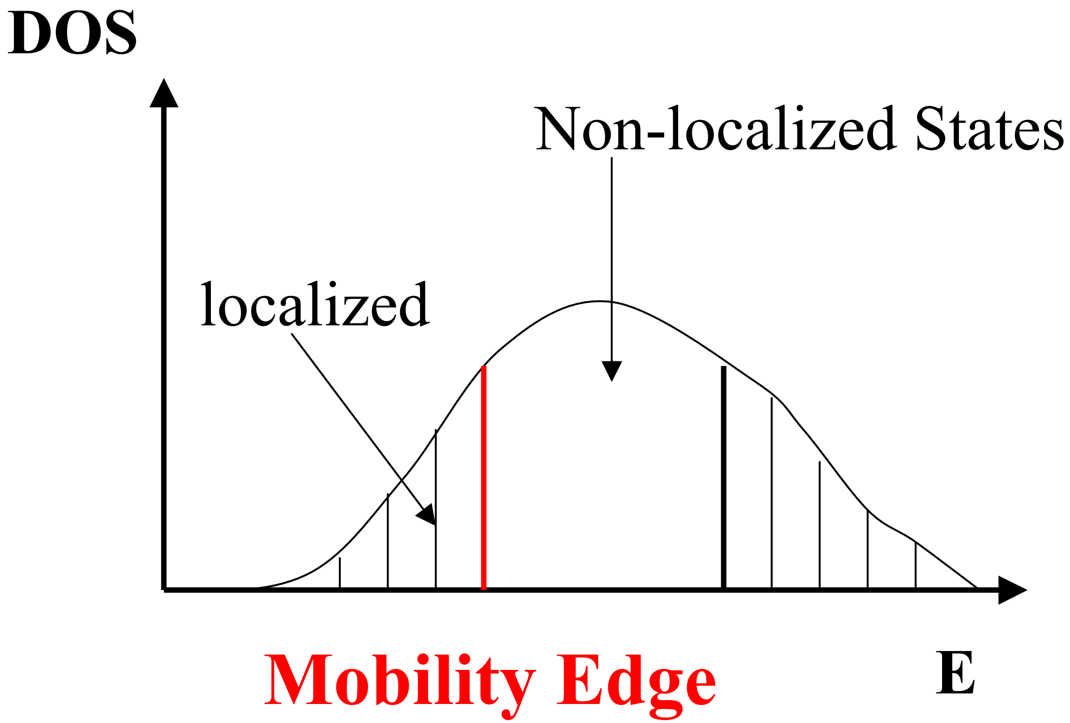


Hopping Process: VRH



$$p_{hop} \approx \exp(-2\gamma R)\exp(-W / kT)$$

Transport in Disordered Conductors 1

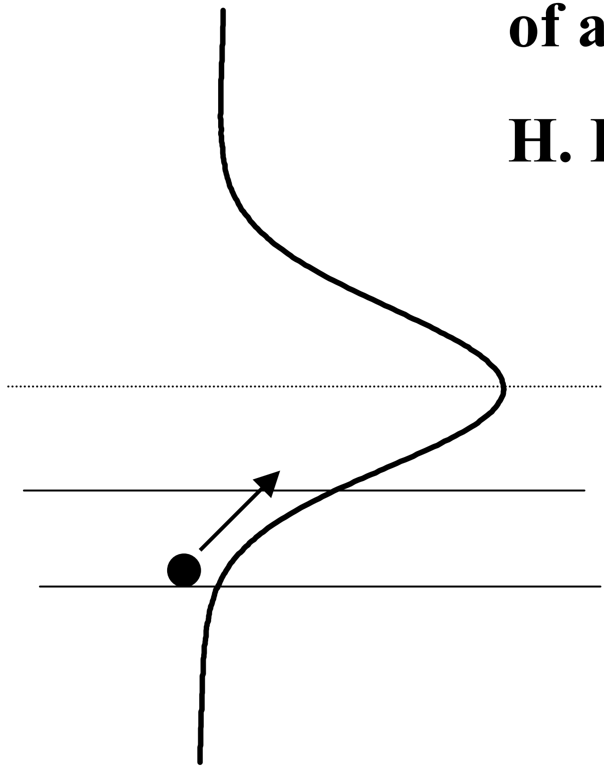


Fermi-level in localized region gives rise to hopping conduction (Fermi glass) – hopping between localized states or activated

Transport in Disordered Conductors 2

Refinement: Gaussian DOS and the presence of a transport level

H. Bässler, Phys. Stat. Sol. (b) 175, 15 (1993)



0

$-\frac{5\sigma^2}{9kT}$ Transport level

$-\frac{\sigma^2}{kT}$ Equilibrium level

Questions

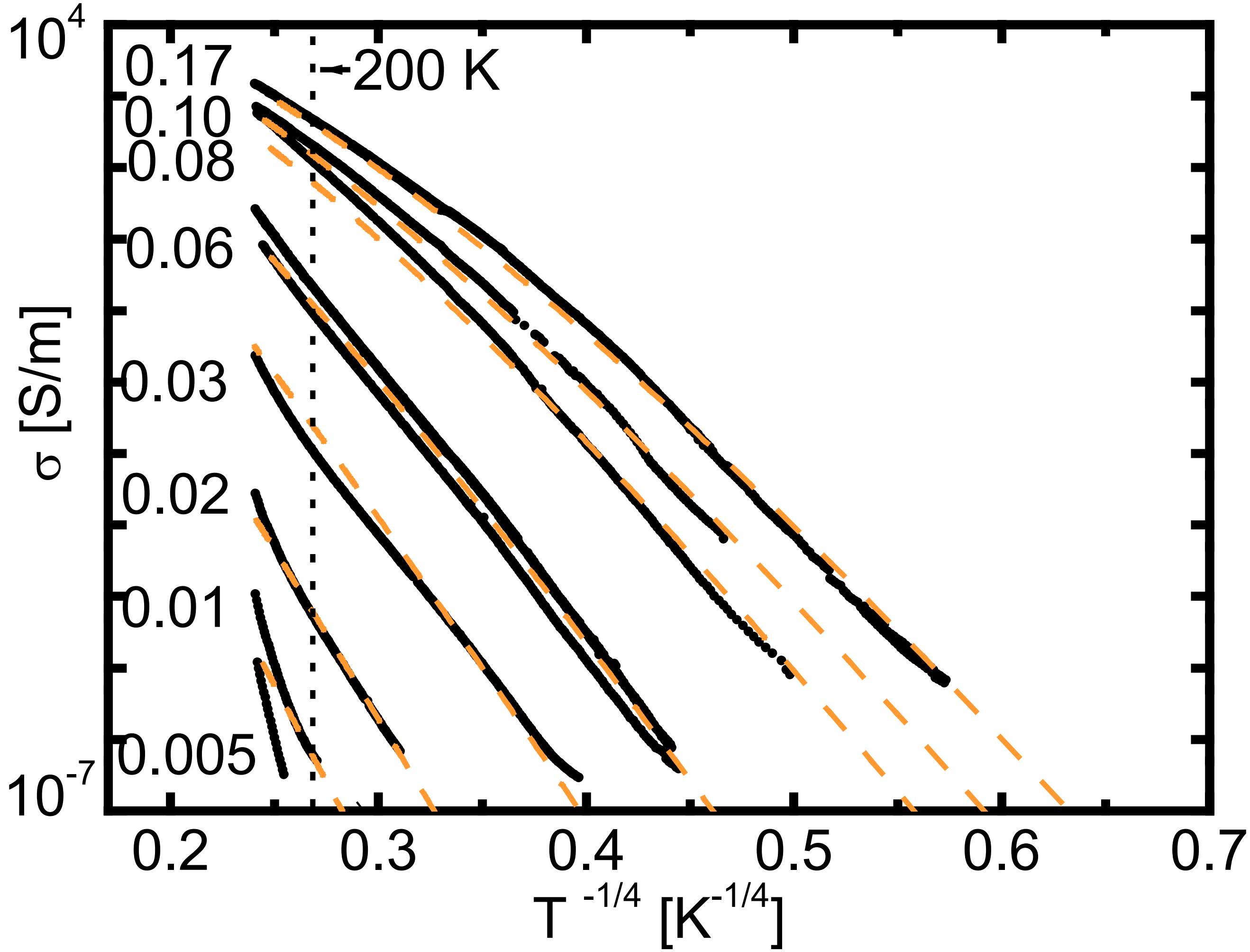
How well can the insulating state be described within the framework of variable range hopping (VRH)?

How strong are the changes when we cross the MIT – which and how many carriers do contribute to metallic transport?

Can we deduce the density of states vs E; is it Gaussian?

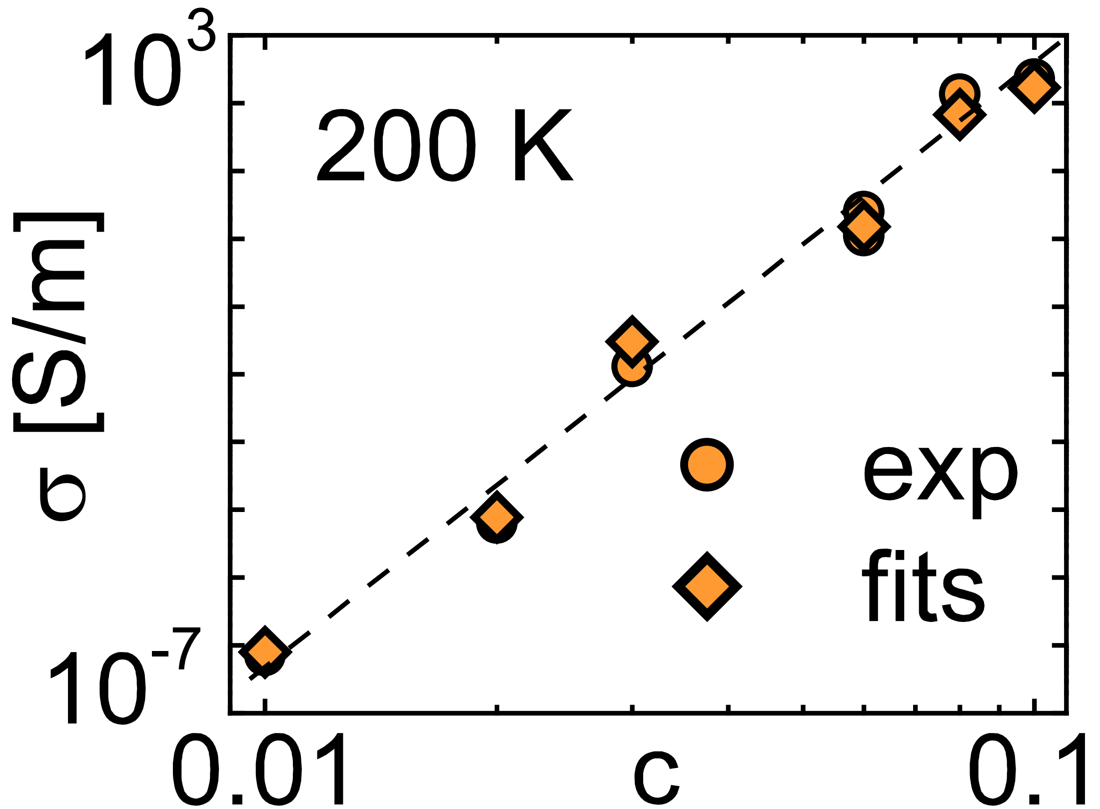
Two experiments:
DC – transport in $FeCl_3$ doped PPV (below MIT)
Dielectric measurements in PF_6 doped polypyrrole (above MIT)

Data $FeCl_3$ doped PPV vs. T and c



concentration in numbers of carriers per monomer

Data $FeCl_3$ doped PPV vs. c at fixed T



At fixed T, 8 orders of magnitude increase in σ with one order increase in c (more than expected from any previous model).

Summary experimental observations

What happens if the doping level is increased:

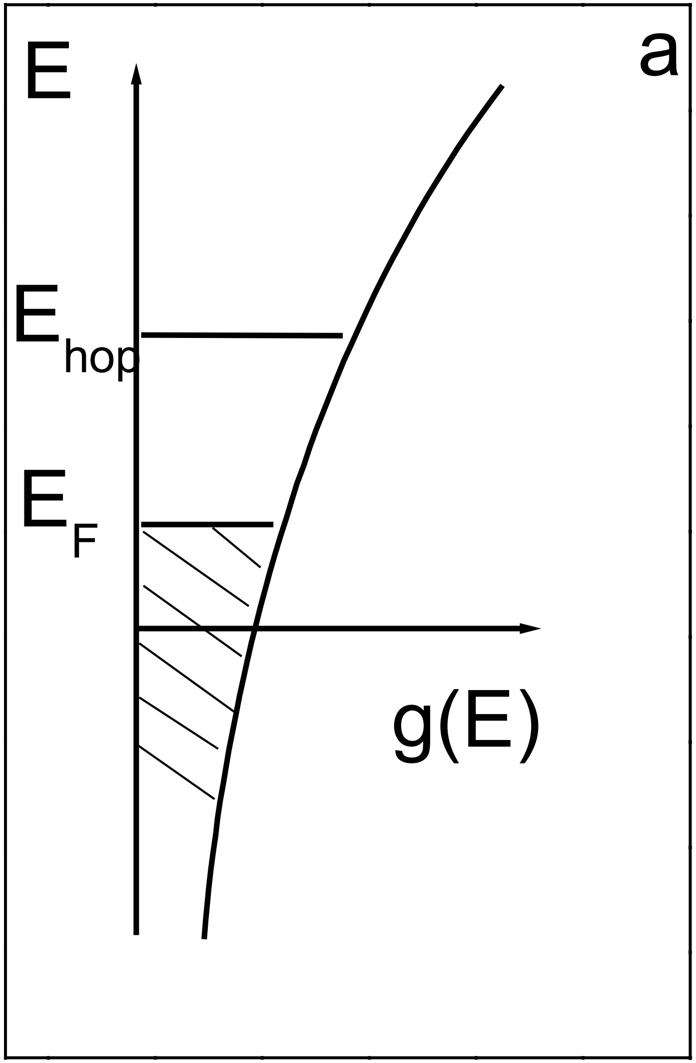
Experimentally

1. **enormous increase in σ at fixed T (8 orders of magnitude with one order in concentration)**
2. **Change in slope of σ vs T. At low T $\sigma \propto \exp\,(T/T_0)^{1/4}$**
3. **Flattening of the curves at high c and T**

How can we model these results?
Take into account the variation of the DOS (g) and the size of the delocalized volume (radius A)

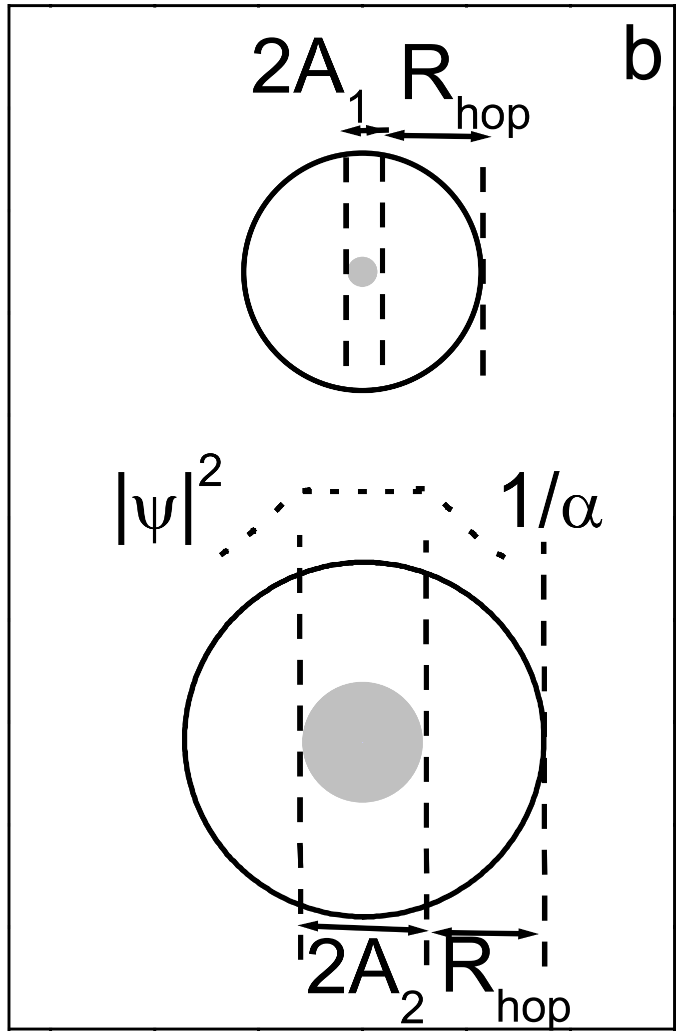
Ref.: Martens, Hulea, Romijn, Brom, Pasveer and Michels, Phys. Rev. B 67, 121203(R) (2003)

Density of states



new carriers will fill up higher energy states given by g(E) (if doping does not create new states).

Extension of states



Because by doping states with higher energy are filled, the extension of the localized state might grow

Results of the model

Take into account the variation of A and g with c by combined analytic and numerical approach

A is a measure for the size of the localized volume.
g represents the increasing density of states.
(dopant supposed to fill only existing states)

Starting relations:

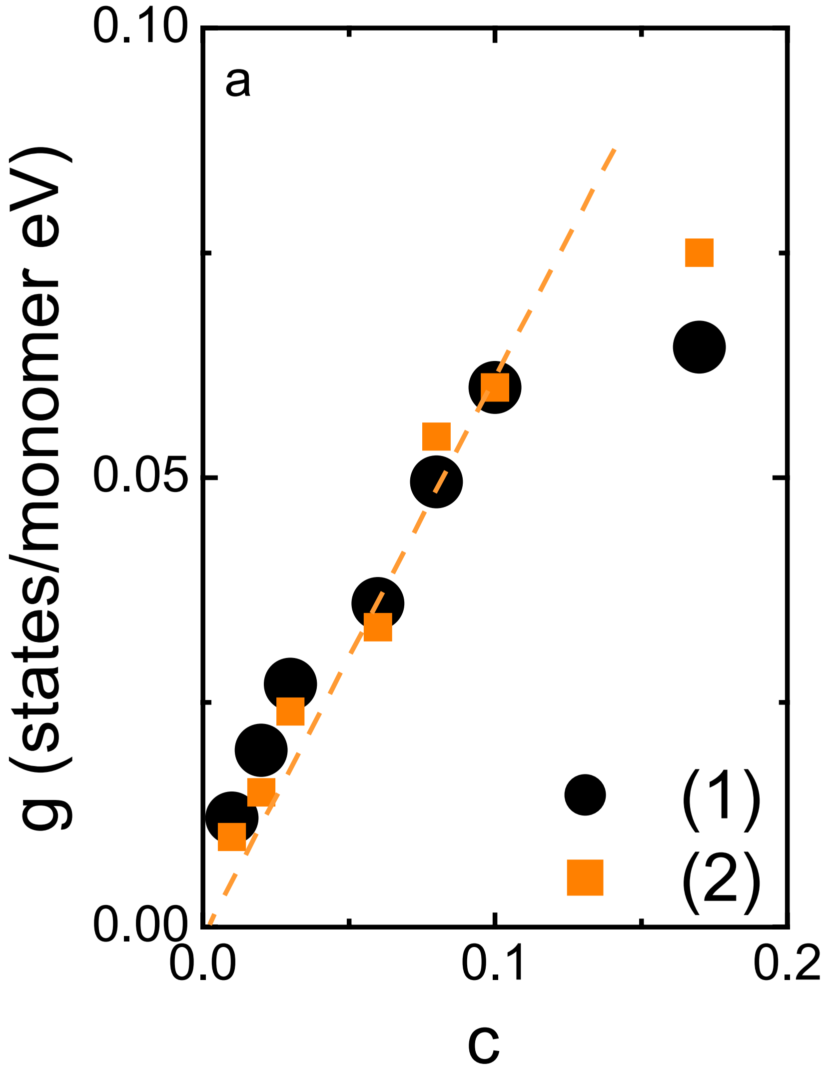
$$\sigma(T,c) = \sigma_0(c) \exp(-\alpha R - \beta(E - E_F)) \text{ and } VN \sim 1$$

Include the c-dependence on A (new) and g explicitly.

One of the results is that 3D Mott's law is recovered for low c (full eq. is much stronger):

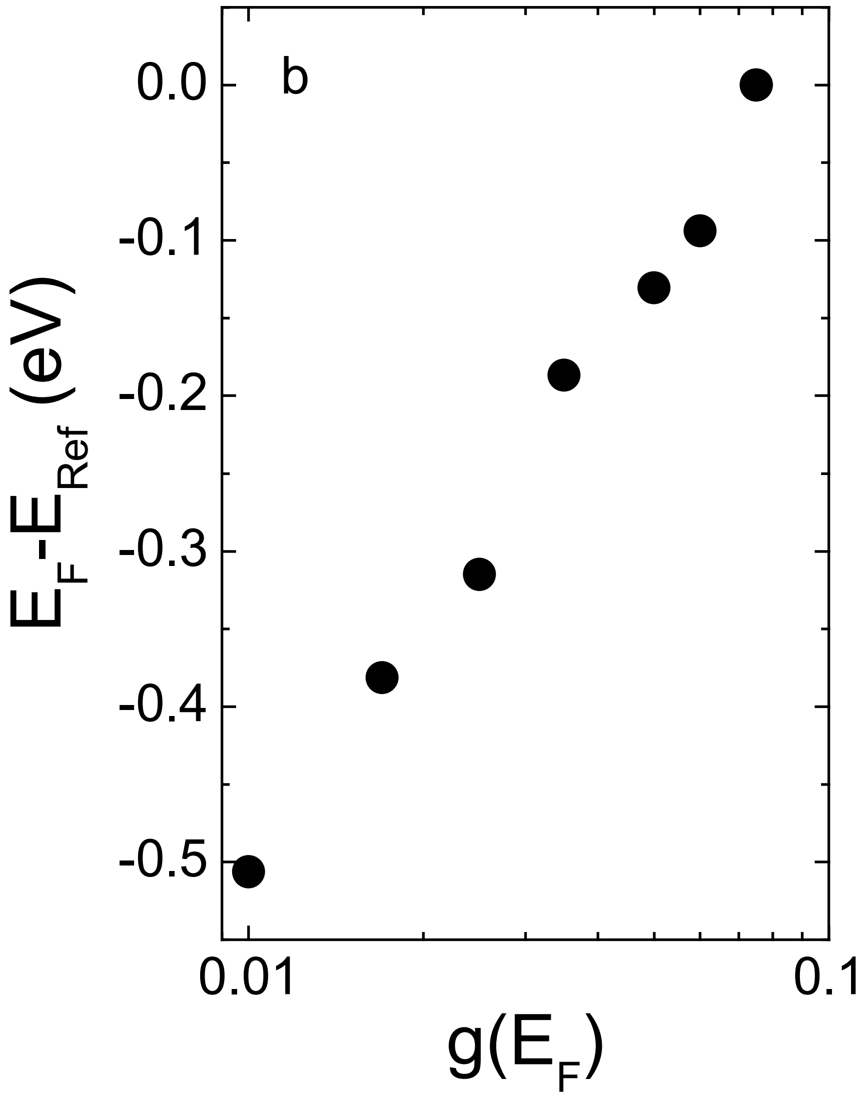
$$\sigma = \sigma_0(c) \exp(\alpha A(c)) \exp(-T_0(c)/T)^{1/4}$$

Results for g(c)



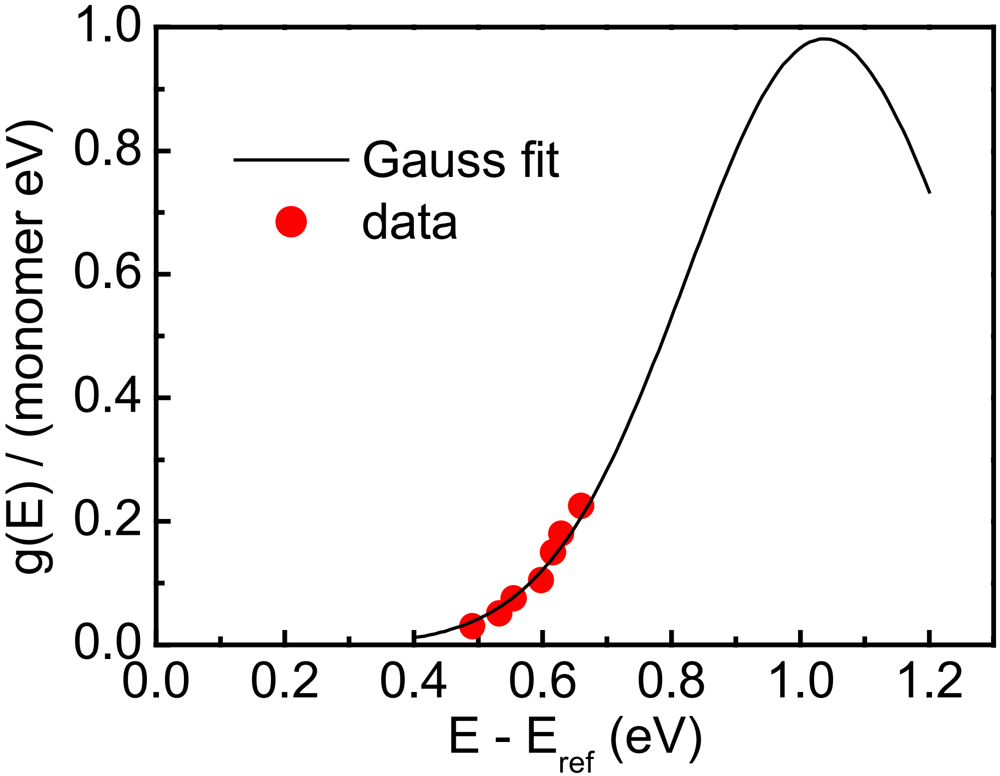
g can be determined in two ways:
(1) low T : $k_B T_0 \sim 1/g$
(2) fitting based on the numerical approach

Results for E_F–E vs g



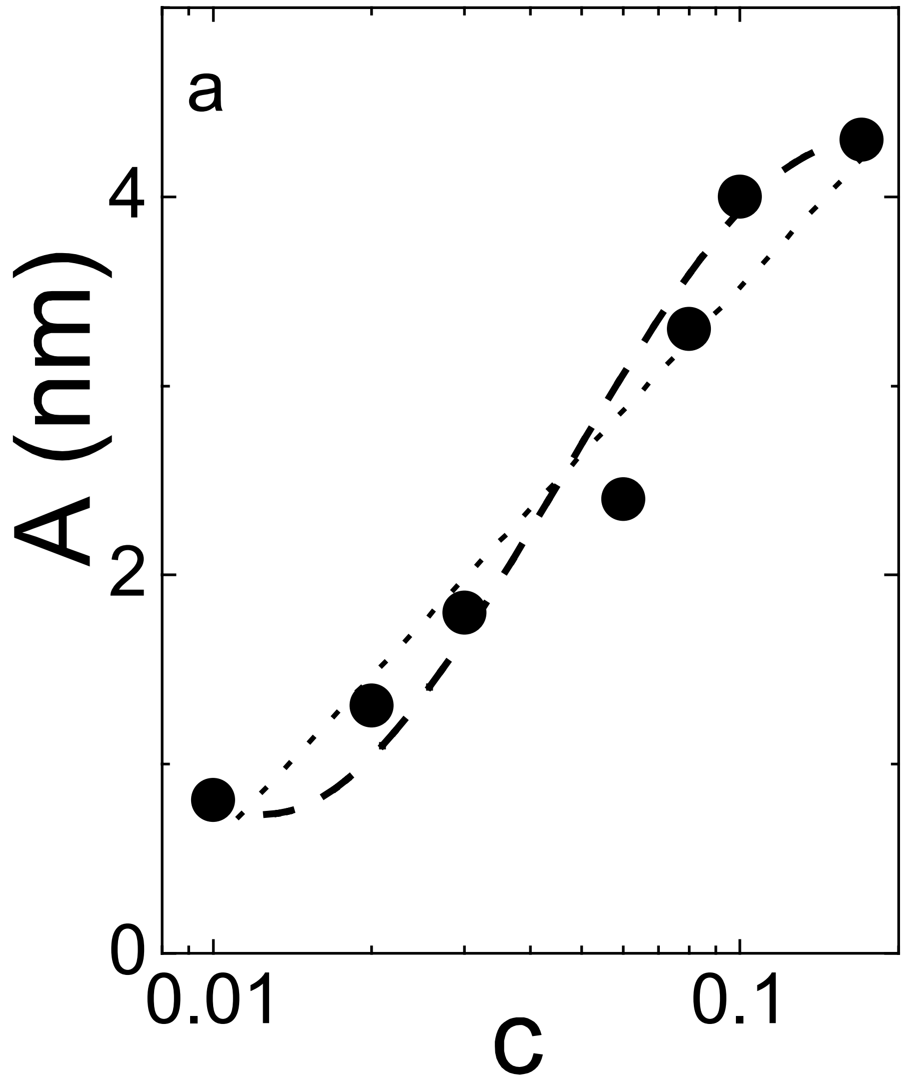
Scaled to the activation energy obtained at high T for c=0.01.

g(E) gaussian?



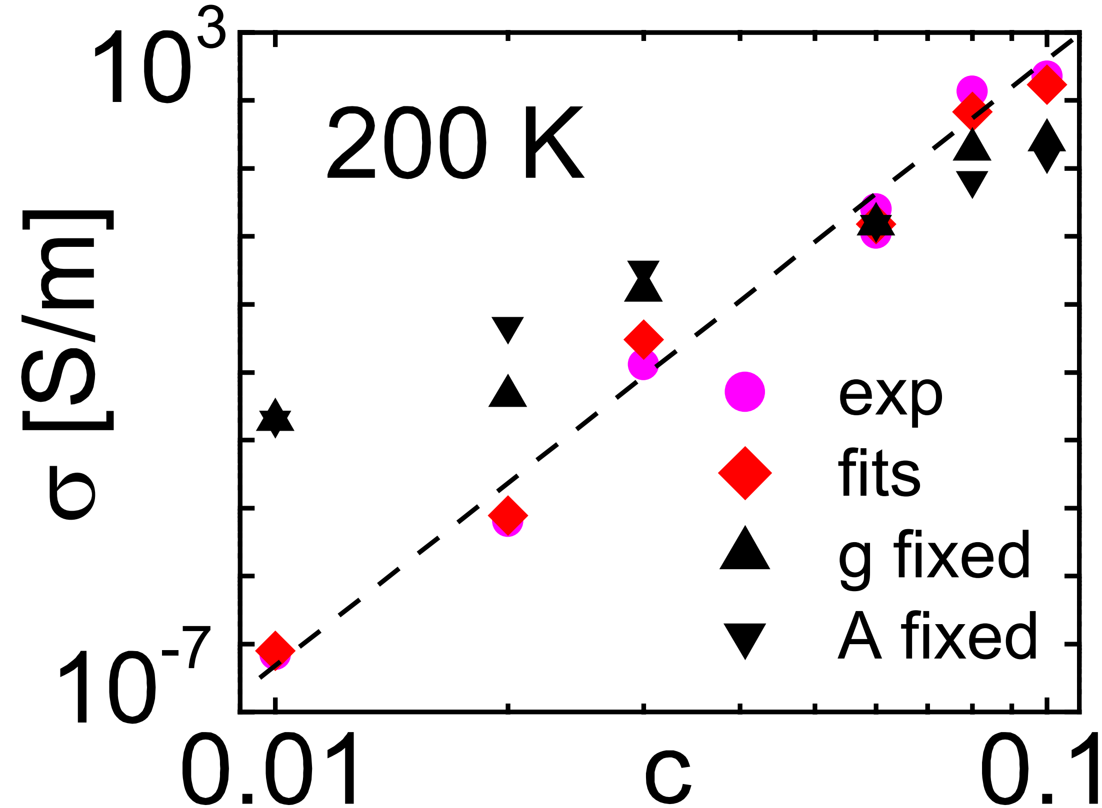
Comparison with prelimary data from el. chem. gated transistor confirm gaussian profile
(Hulea, Brom, Meulenkamp, Vanmaekelbergh et al. , not published)

A vs c



A is a measure for the size of the localized volume.
Dotted line accounts for the logarithmic dependence expected from $\sigma \sim c^8$.
Dashed line accounts for the saturation at low and high doping. A grows with factor 4

A(c) vs g(c)



Approximate: $\sigma = \sigma_0(c)\exp(\alpha A(c))\exp(-T_0(c)/T)^{1/4}$

Fixed T: $\sigma \propto \sigma_0(c)\exp(\alpha A(c))$ **with** $A(c) \sim \log c$

Transport below MIT

- **the T and c dependence of**
  $\sigma = \sigma_0(c) \exp(\alpha\, A(c)) \exp(-T_0(c)/T)^{1/4}$
  is a good starting point for the analysis.

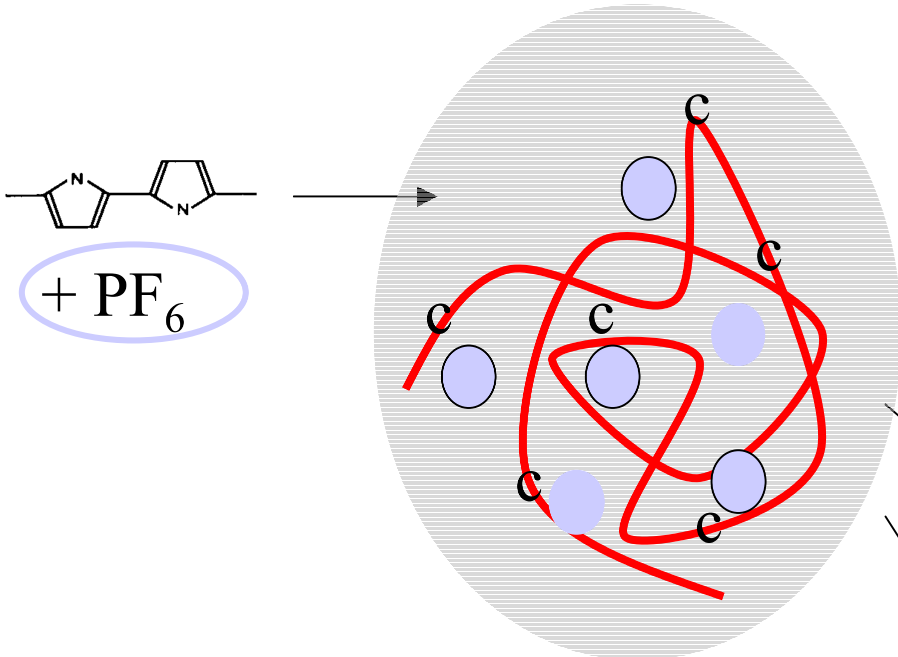
- **the contributions of both g(c) and A(c) are essential to explain the c and T dependence of σ.**

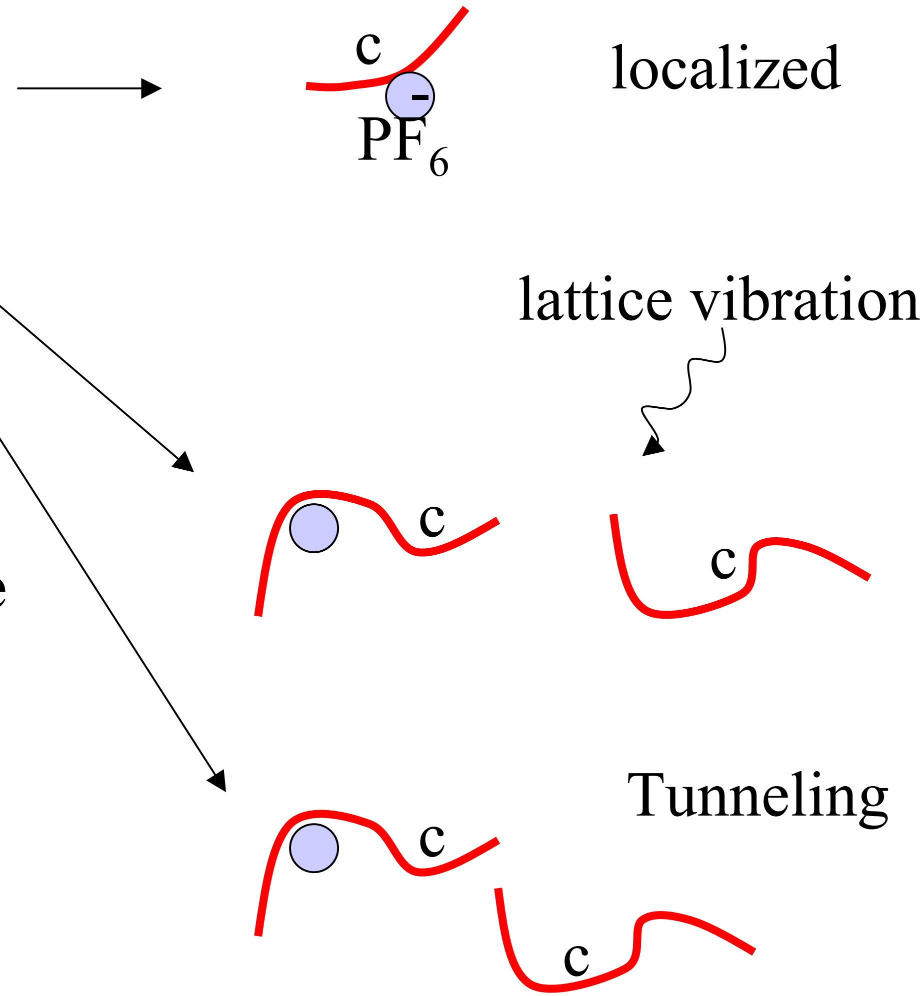
- **reconstructed dos complies with Gaussian shape**

More references

N.F. Mott, Phil. Mag 19, 835 (1969).
H. Bässler, Phys. Stat. Sol. (b) 175, 15 (1993).
S.D. Baranovskii *et al.*, PRB 62, 7934 (2000).
M.C.J.M. Vissenberg and M. Matters, PRB 57, 12964 (1998)

Transport in polymers above MIT

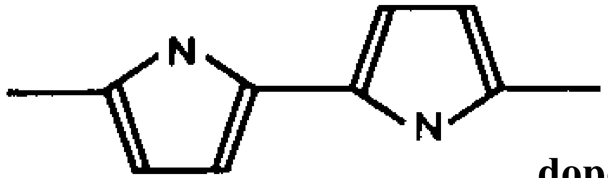




Example of PF_6 doped polypyrrole

- **PF_6^- introduces charges (c) on chain-segments**
- **Part of charges might remain localized**
- **Transport possible by thermally activated hopping or QM tunneling**

Test case: PF_6 doped polypyrrole



polypyrrole

doped with hexafluorophosphate

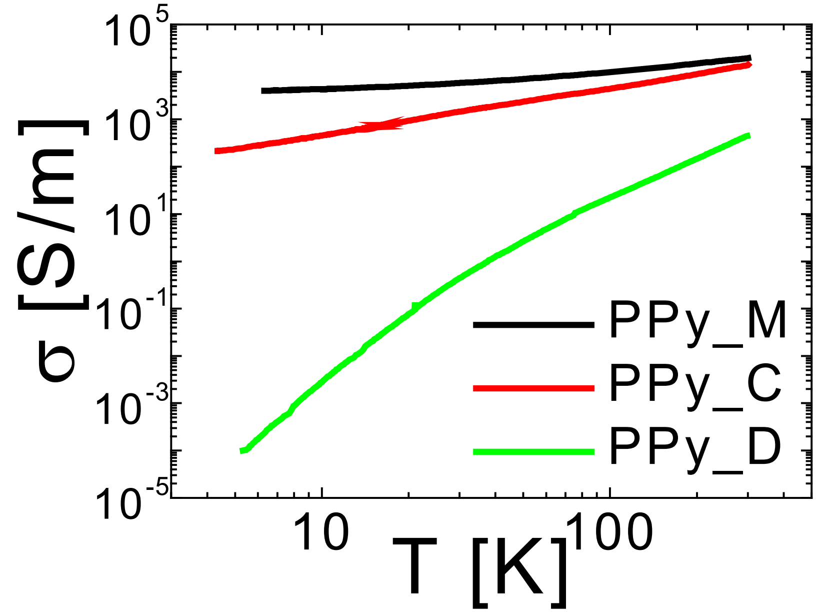
Why PPy?

PPy is very stable – survives in air for a long time

PPy can be made from deep in the insulating (PPy_D) to well into the metallic state (PPy_M)

For PPy_M: ≈ 1 dopant/PPy unit

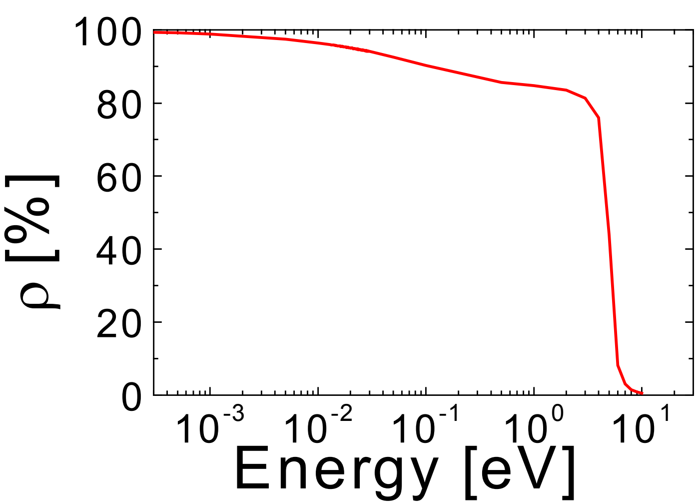
Metallic? Go to low T

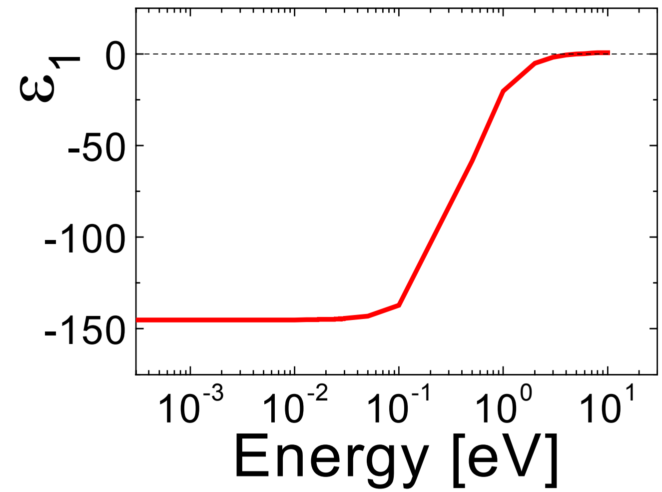


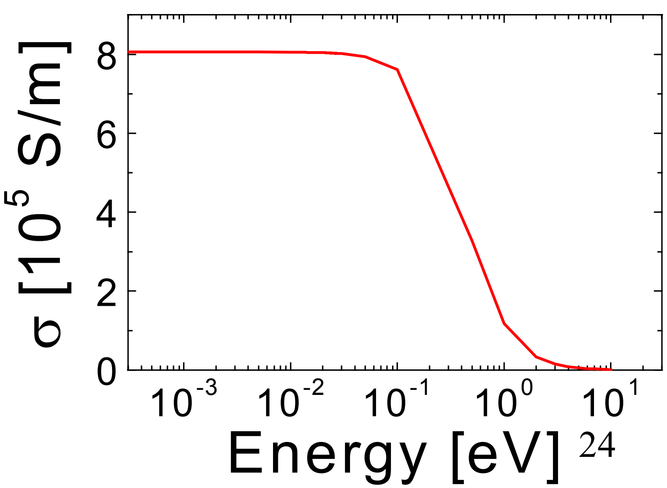
DC conductivity

Metallic charge transport: high frequency dielectric spectroscopy

Case of metal





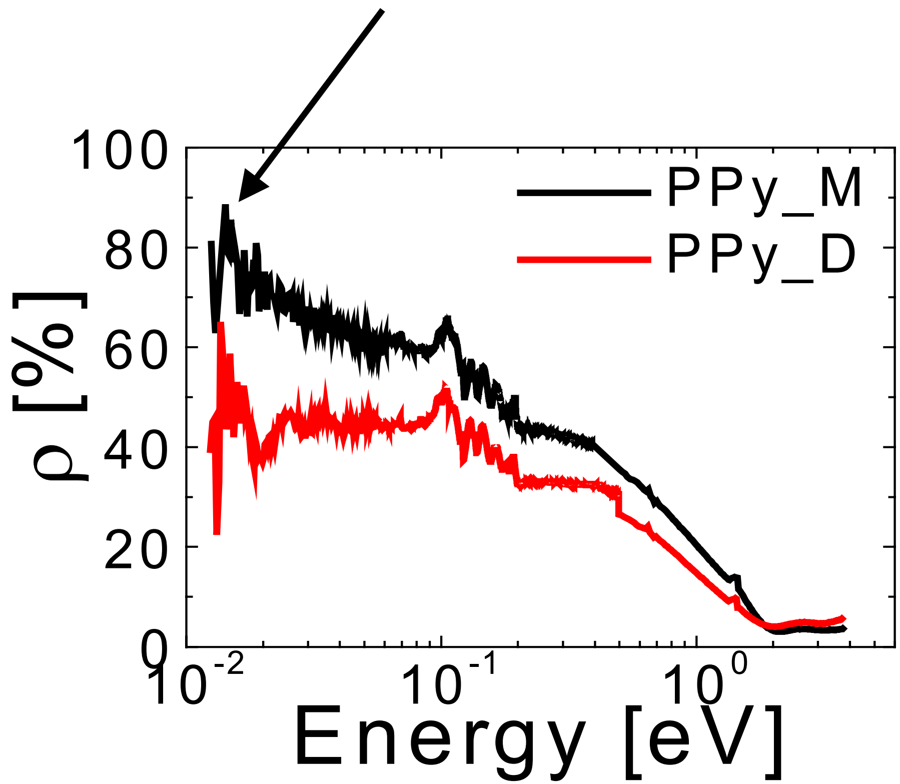


$$R(\omega) = \rho(\omega)e^{i\theta(\omega)}$$

$$\sigma(\omega) = \sigma_1(\omega) + i\sigma_2(\omega)$$

$$\varepsilon_1 = i\sigma_2/\varepsilon_0\omega$$

Reflection PPy



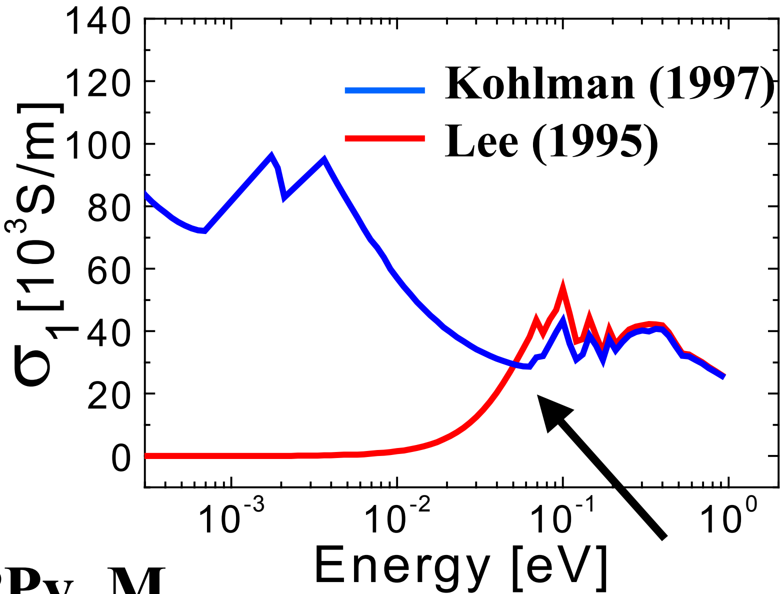
Bruker FTIR (5 meV – 0.5 eV)
Perklin Elmer UV/VIS (0.5 – 3.5 eV)

$\rho(\omega)$ and $\theta(\omega)$: $\sigma_1(\omega)$ and $\varepsilon_1(\omega)$
Only real part $\rho(\omega)$ measurable
Calculate imaginary part $\theta(\omega)$
from $\rho(\omega)$ by application of
Kramers-Kronig

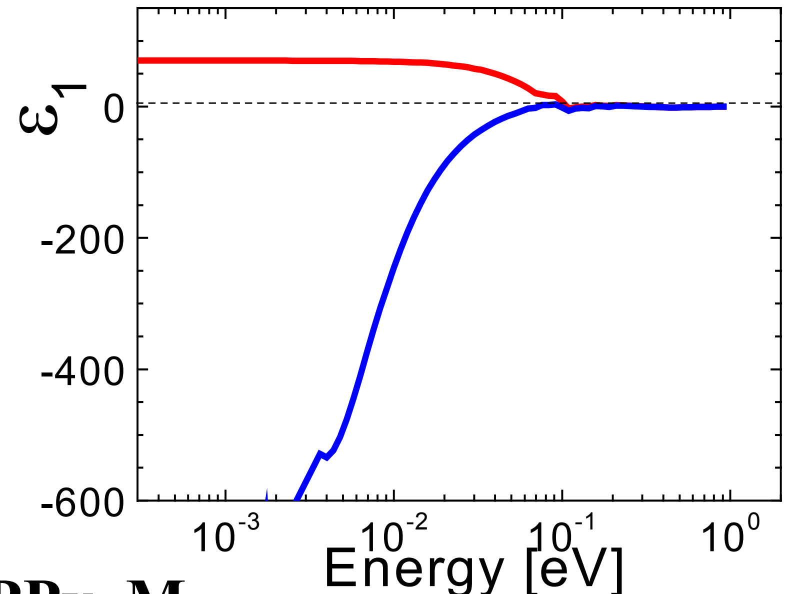
$$\theta(\omega) = -\frac{2\omega}{\pi}\int_0^\infty \ln\frac{[\rho(\omega')/\rho(\omega)]}{[(\omega')^2 - \omega^2]}d\omega'$$

Extrapolate data $\rho(\omega)$

Old data controversal



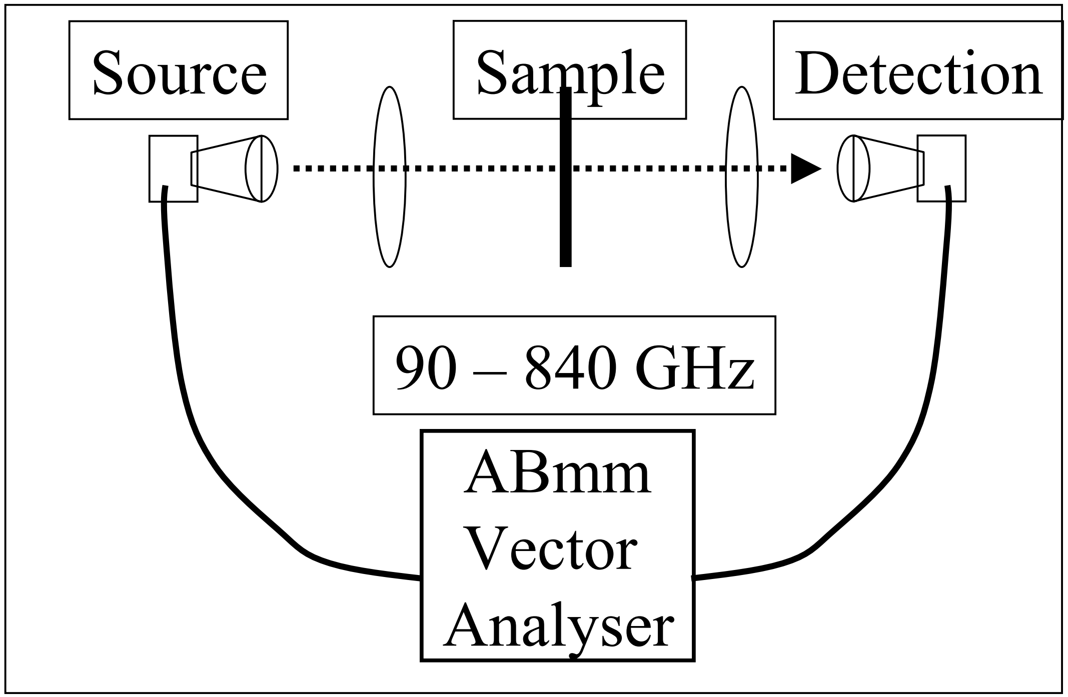
PPy_M

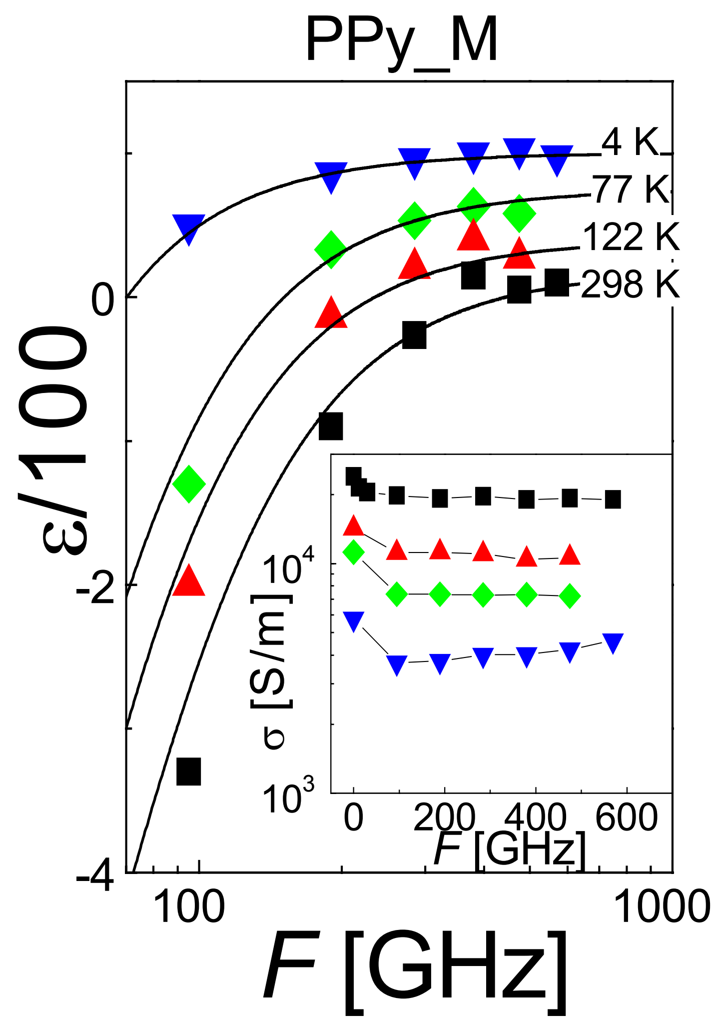


PPy_M

Depending on extrapolation at low energies several groups found completely different conductivity σ_1 and dielectric constant ε_1 ($\varepsilon_1 = i\sigma_2/\varepsilon_0\omega$)

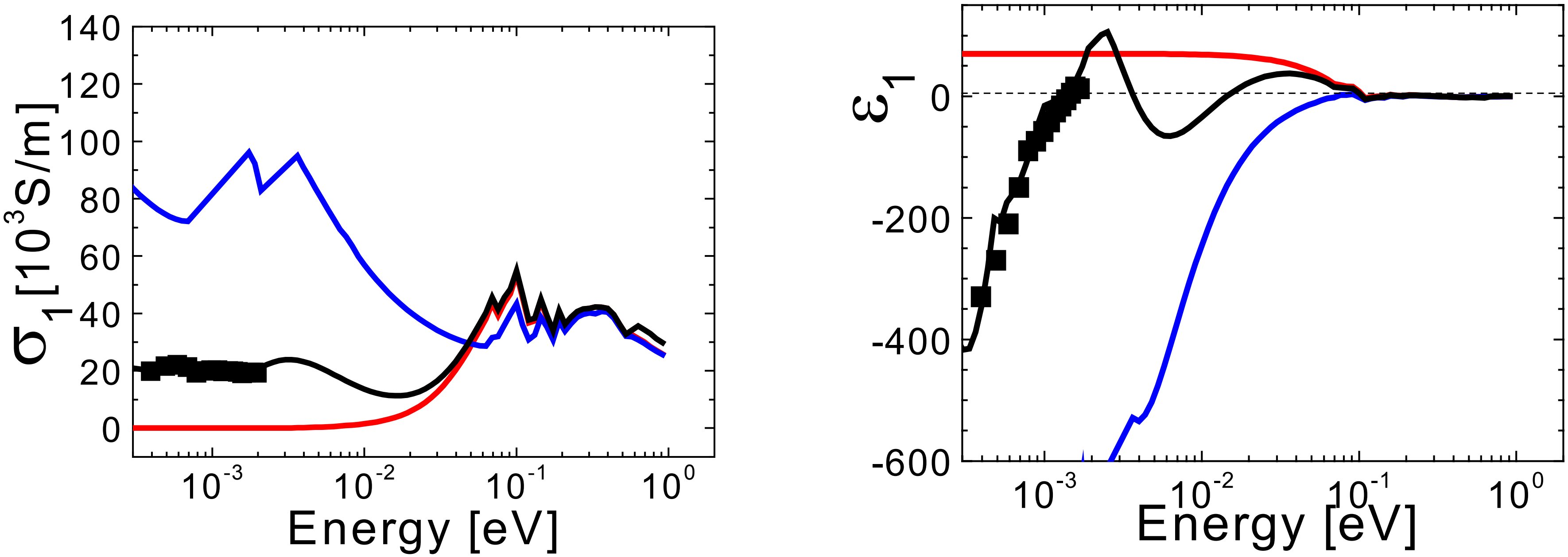
Additional data below 1 THz





Complex transmission - ε_1 and σ_1 can be determined simultaneously down to 4 K

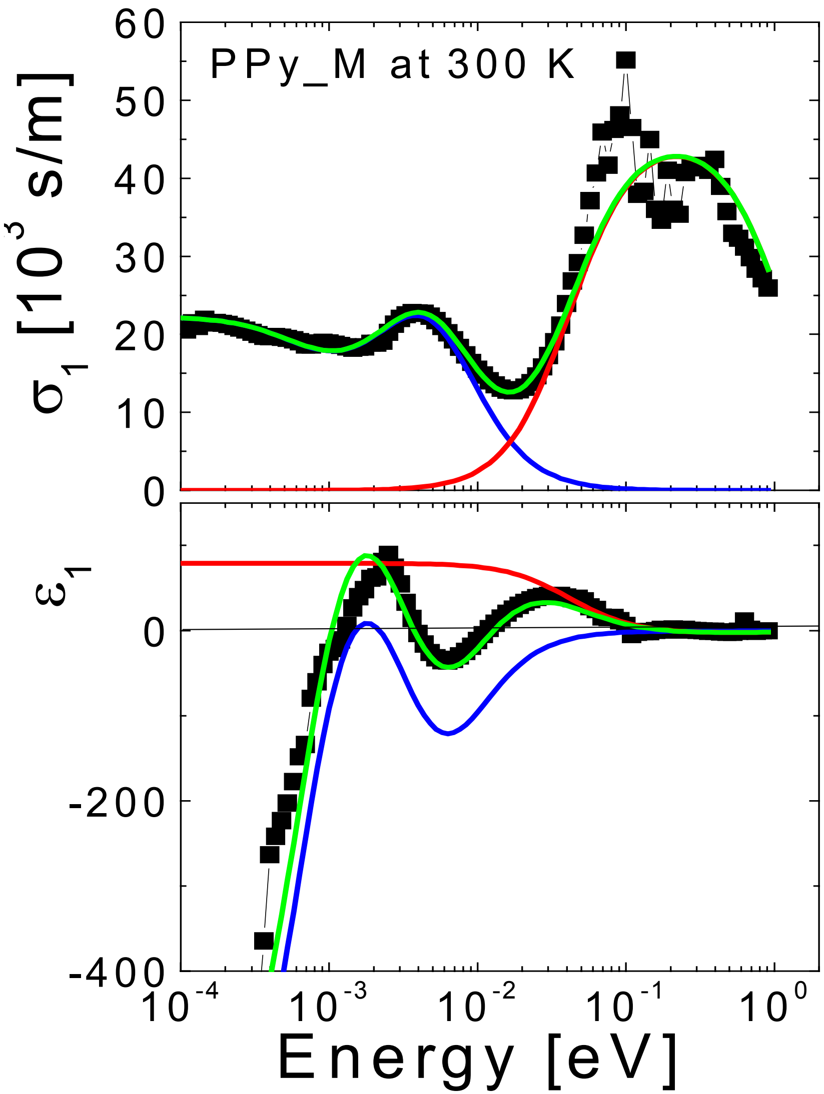
KK analysis



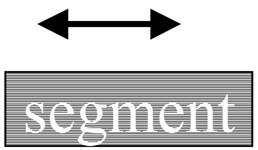
Kohlman et. al., Lee et. al., GHz data, our K.K. fit

The low frequency data give nice boundary conditions for the Kramers-Kronig analysis

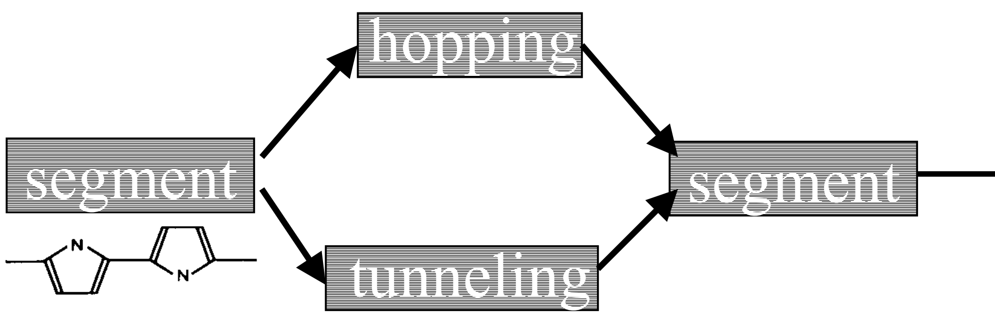
Model applied to data



99 %: Localized charges:



1%: charges are delocalized: transport possible



Conclusions (conjugated polymers)

- **By doping the number of levels increases as does the delocalization radius (factor of 4)**
- **Map of density of states supports Gaussian model**
- **At the MIT 99% of the introduced charges are localized and do not contribute to the dc-conductivity**
- **The movement of delocalized charges (1%) is governed by thermally activated hopping and QM tunneling between chain segments**

More references

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V.N. Prigodin and A.J. Epstein, Synth. Met. 125, 43 (2002)