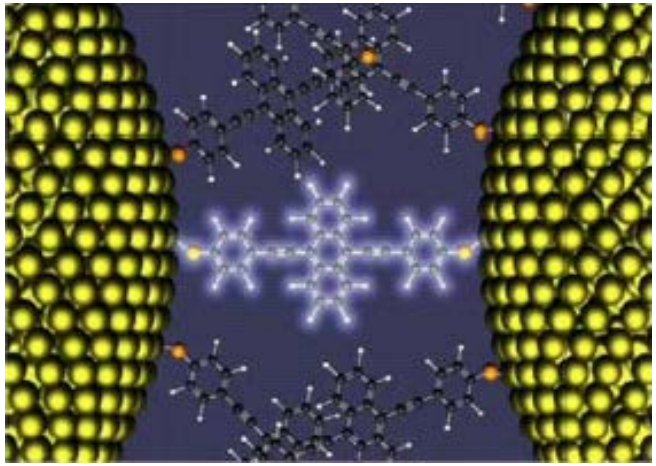
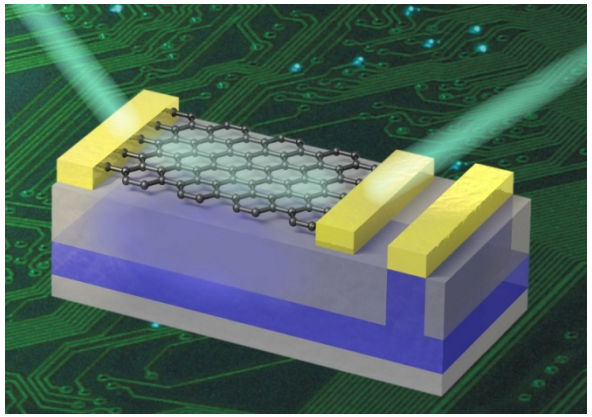
Single-Molecule Junctions: Vibrational and Magnetic Degrees of Freedom, and Novel Experimental Techniques

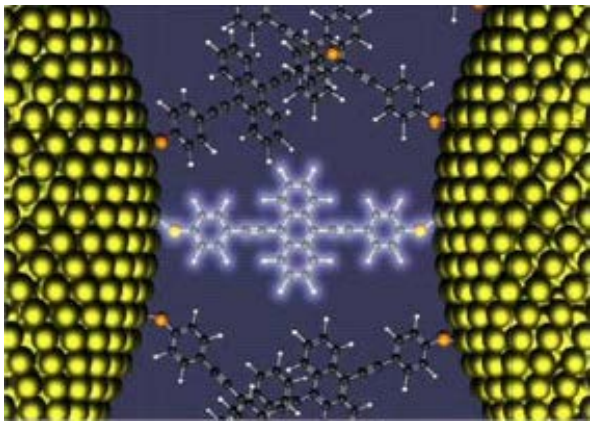


Heiko B. Weber
Lehrstuhl für Angewandte Physik

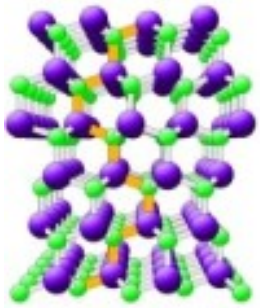
Friedrich-Alexander-Universität Erlangen-Nürnberg



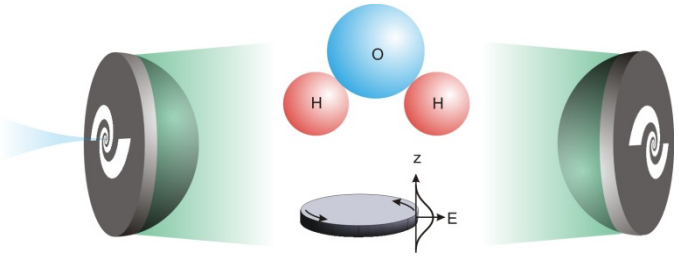
Electronic Properties of epitaxial graphene



Electron transport on the molecular scale



Semiconductors and their doping
(Dr. Michael Krieger)



THz generation and detection
(Dr. Sascha Preu)

People

Daniel Secker

Stefan Wagner

Stefan Ballmann

Ferdinand Kisslinger
Benjamin Gmeiner

Konrad Ullmann

How does charge flow through single molecules ?

- Introduction: our technique

- vibrational degrees of freedom

- magnetic degrees of freedom

- novel experimental tools

How does charge flow through single molecules ?

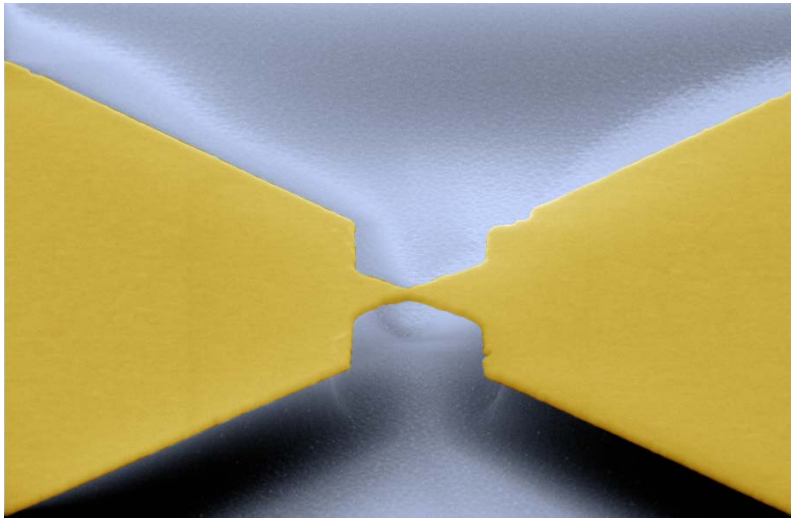
FRIEDRICH-ALEXANDER UNIVERSITÄT ERLANGEN-NÜRNBERG

- **Introduction: our technique**

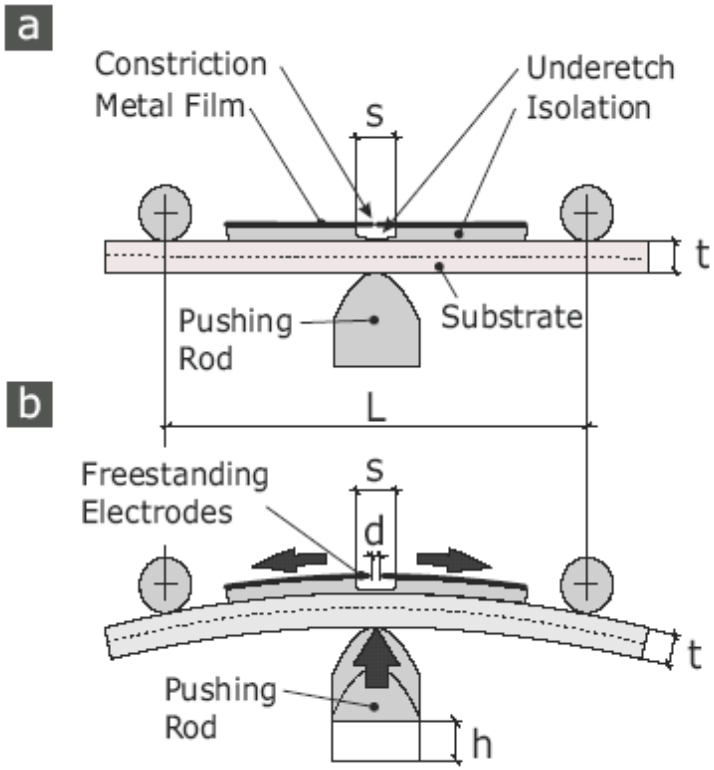
- vibrational degrees of freedom

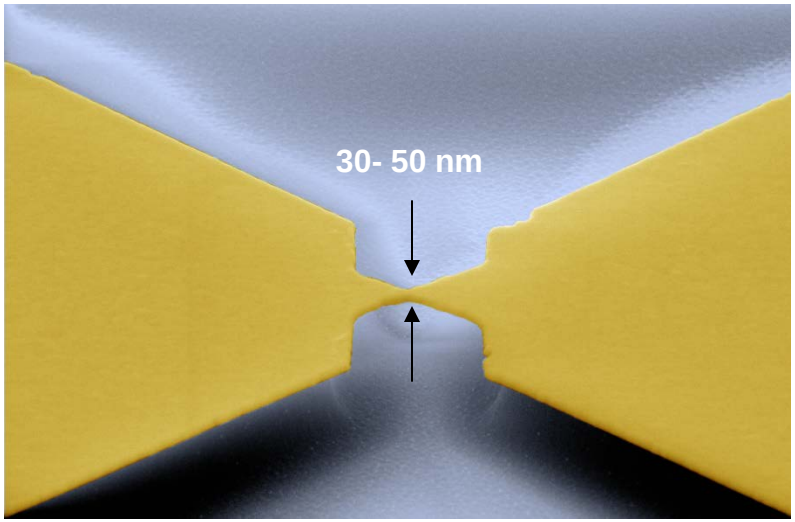
- magnetic degrees of freedom

- novel experimental tools



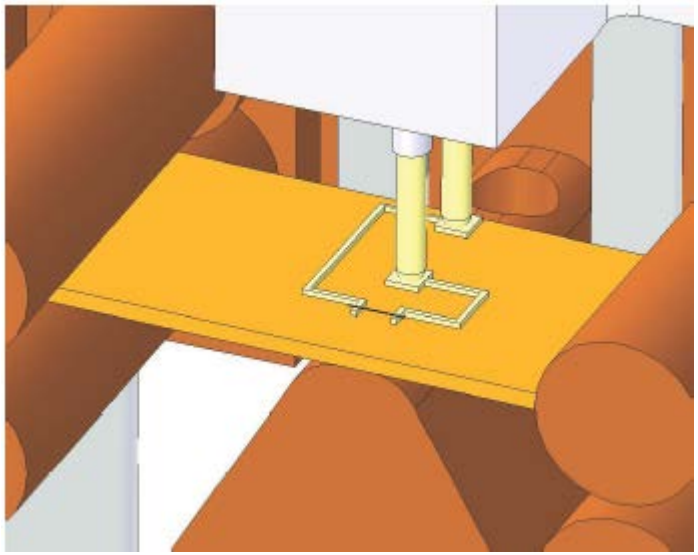
Single - molecule contacts

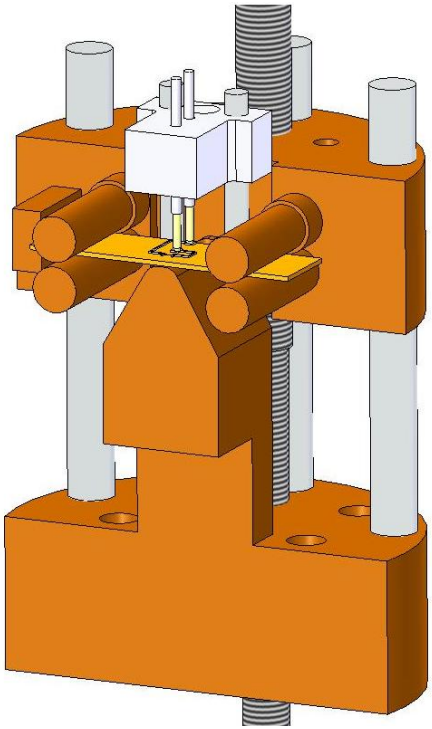


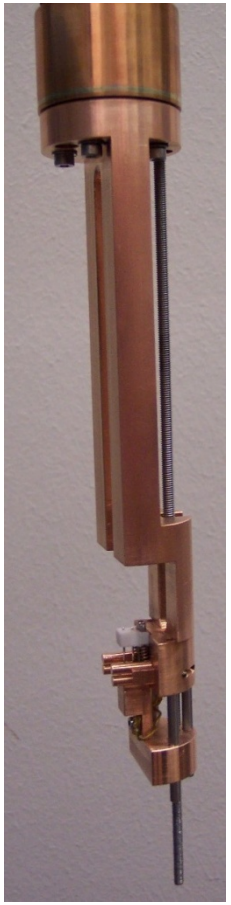


Mechanically controlled break junction technique

Experimental



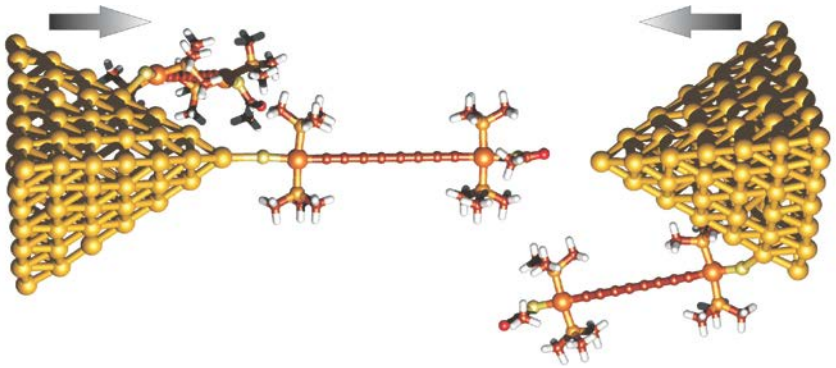


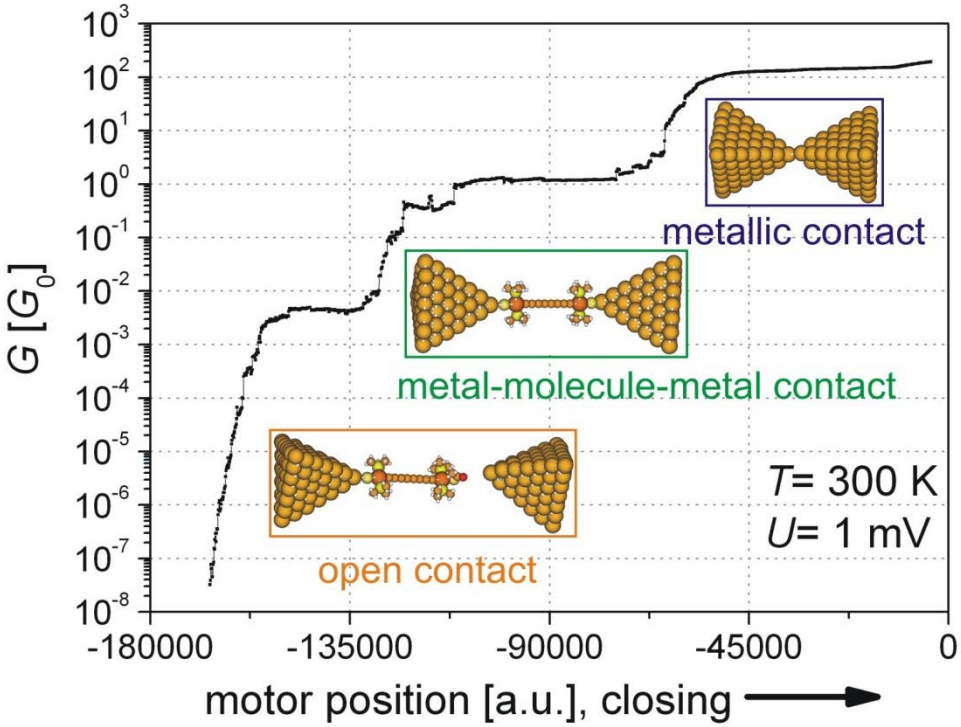


Mounted either in a ^{3}He or ^{4}He cryostat,

in vacuum, at temperatures down to 300mK

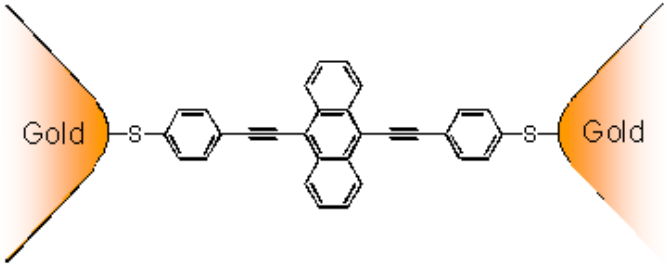
Conductance traces



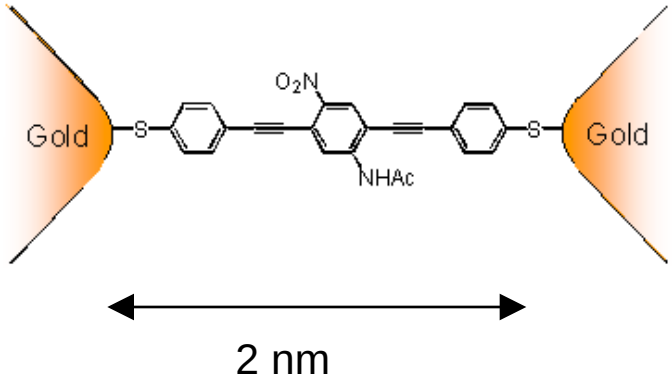


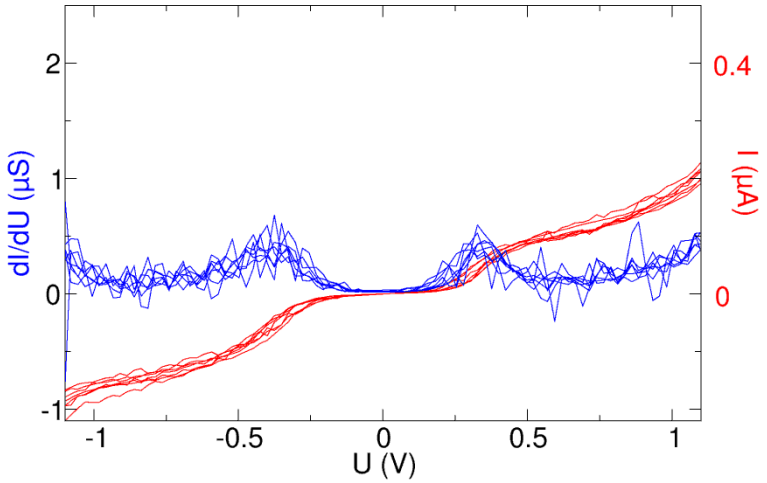
First experiments

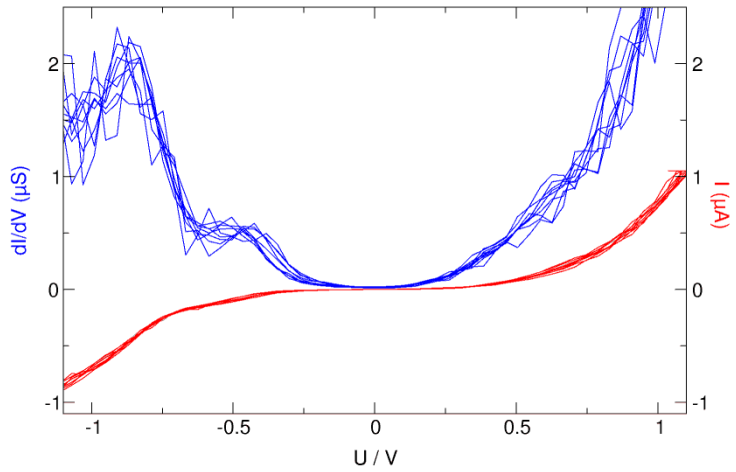
Symmetric molecule



Asymmetric molecule



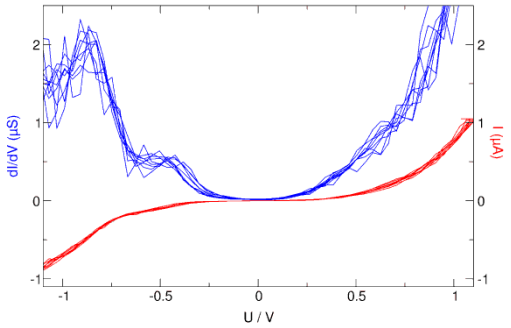


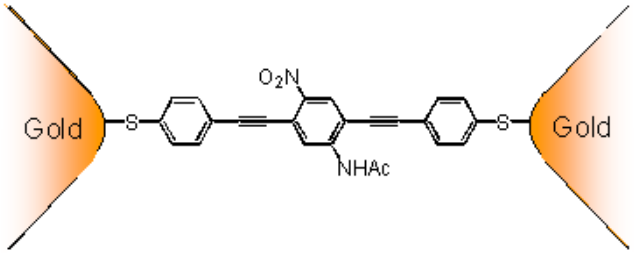


with Marcel Mayor, Phys. Rev. Lett. 88, 176804 (2002)

Room temperature vs. low temperature

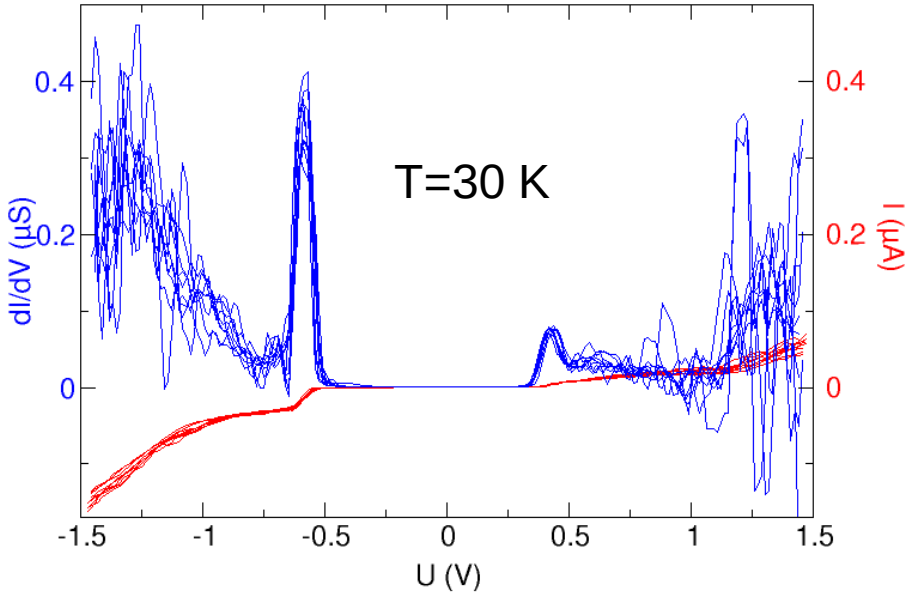
T=300 K

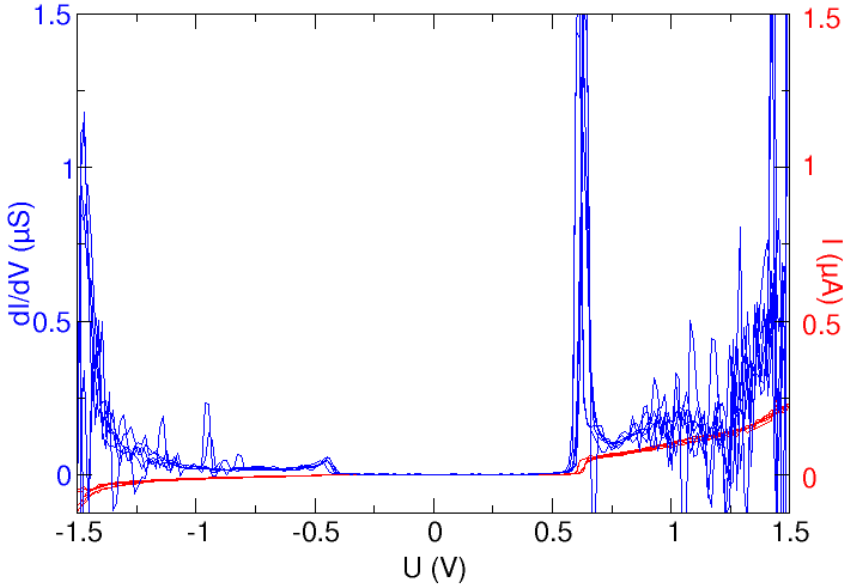




Phys. Rev. Lett. 88, 176804 (2002)

Appl. Phys. Lett. 82, 4137 (2003)





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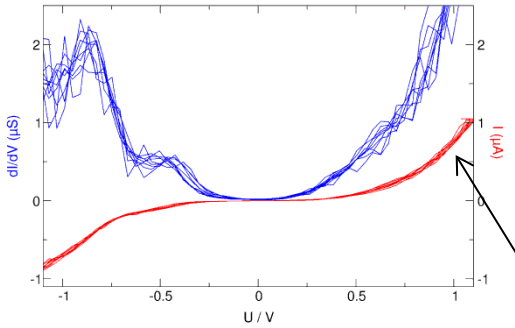
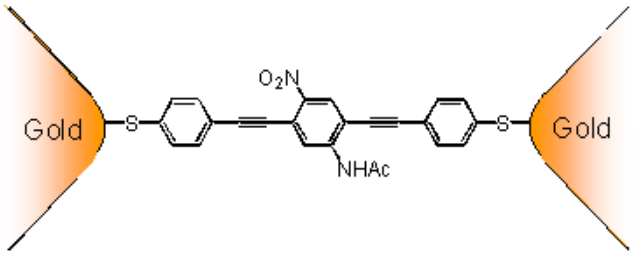
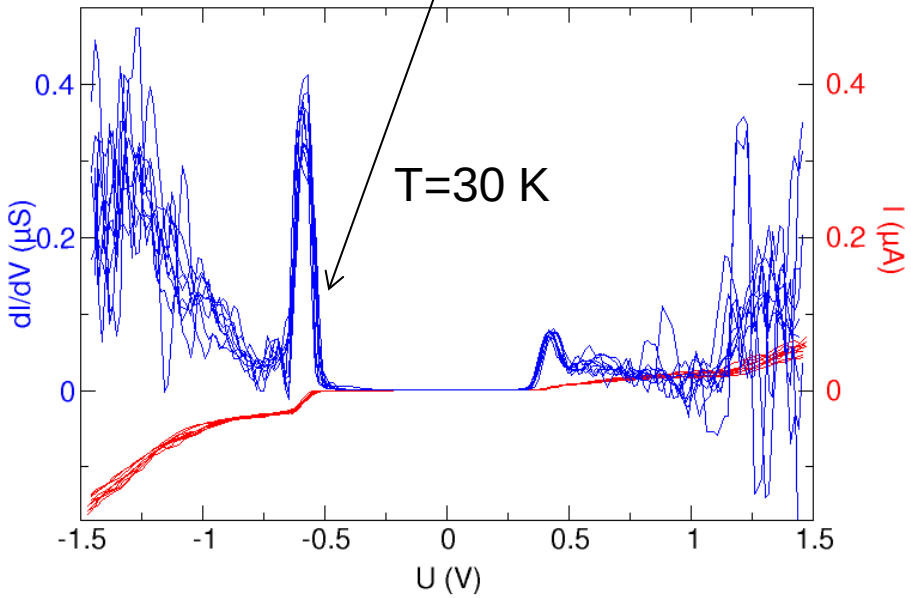
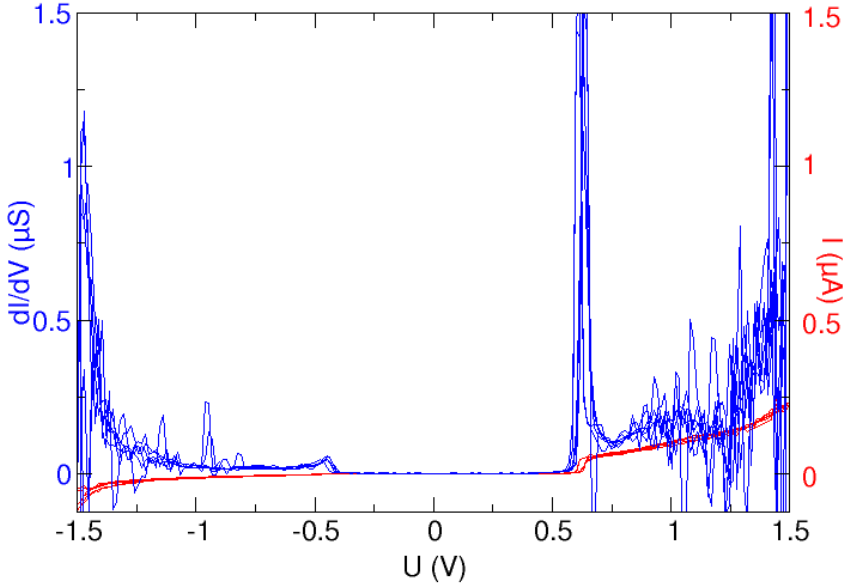




What determines the current level?

What is the nature of the first peak?





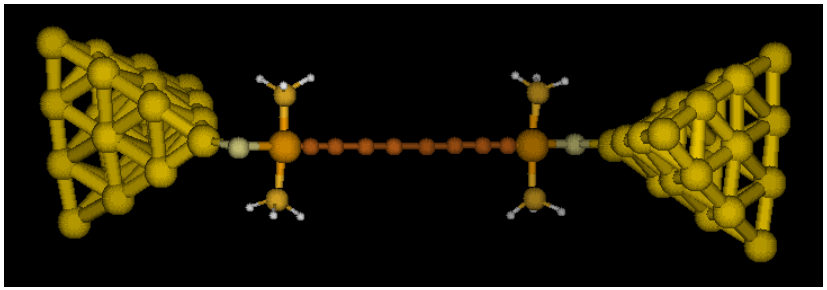
How does charge flow through single molecules ?

- Introduction: our technique

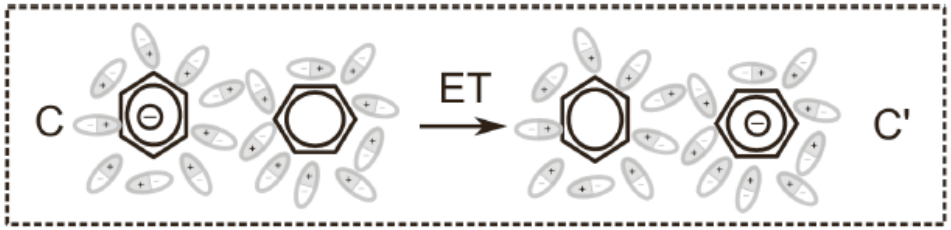
- vibrational degrees of freedom

- magnetic degrees of freedom

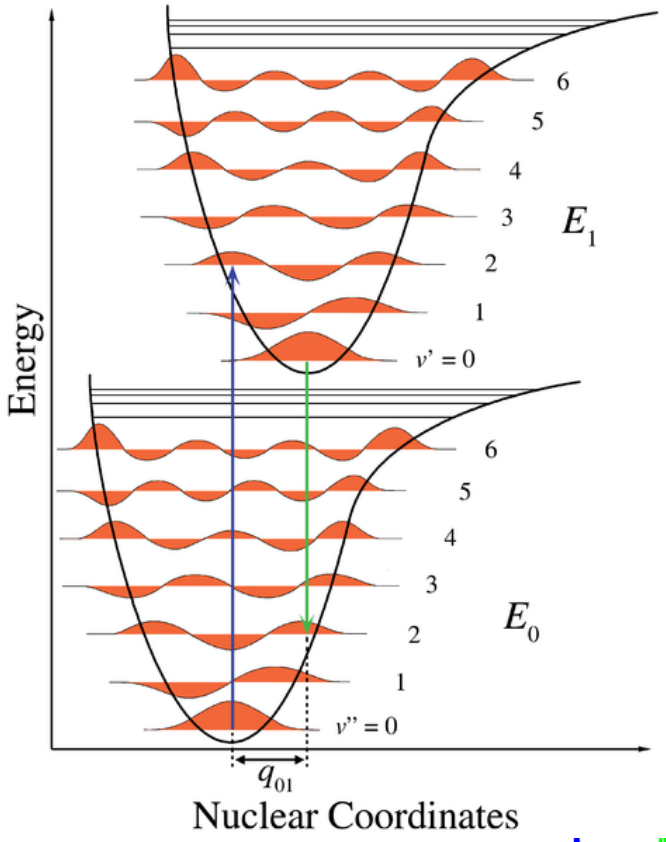
- novel experimental tools



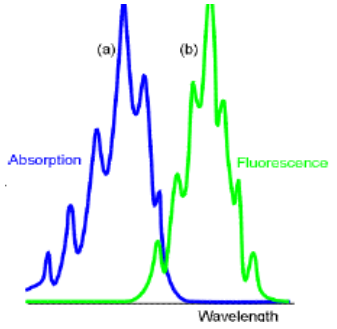
Electronic processes in molecules are related to vibrations!



Electron transfer

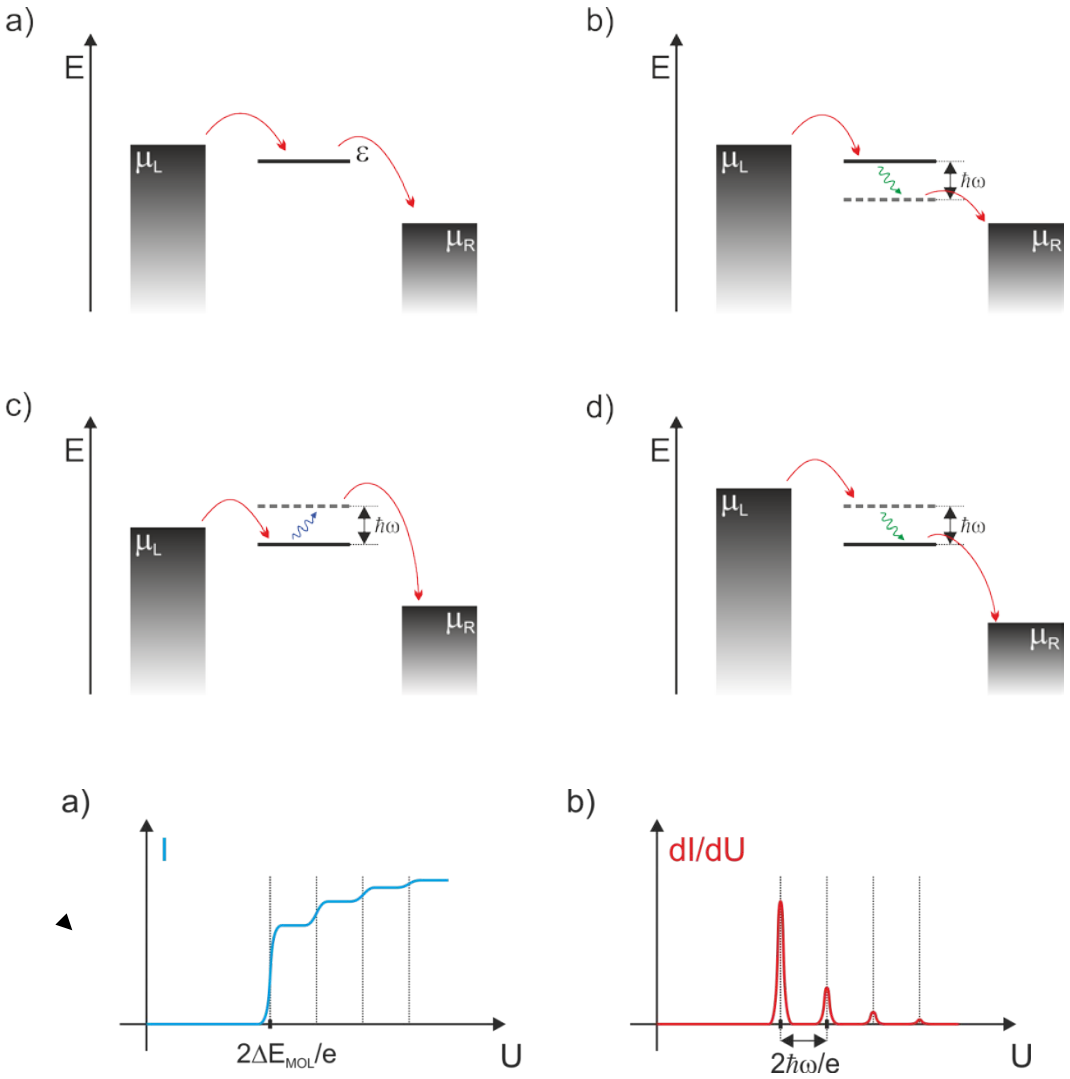


Optical absorption



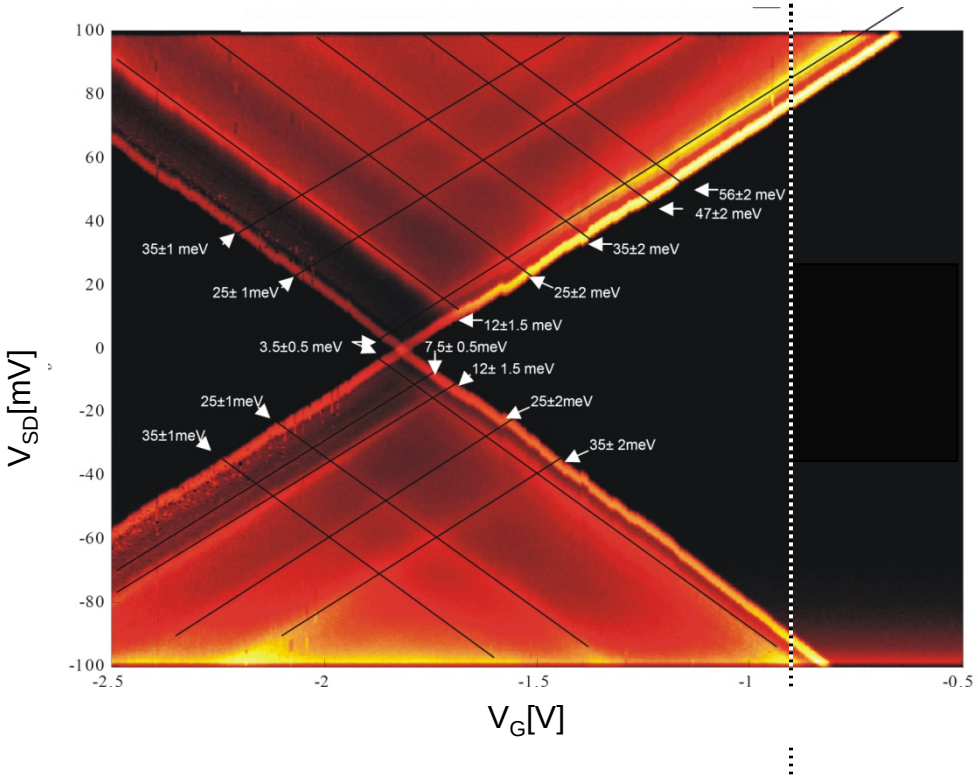
Simplest model

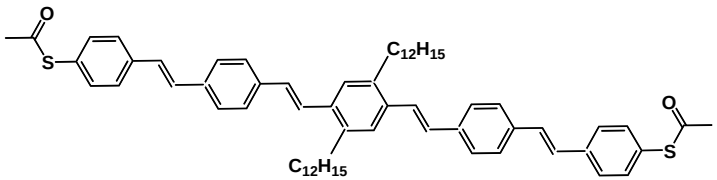
One electronic level ε and one vibrational mode ω:

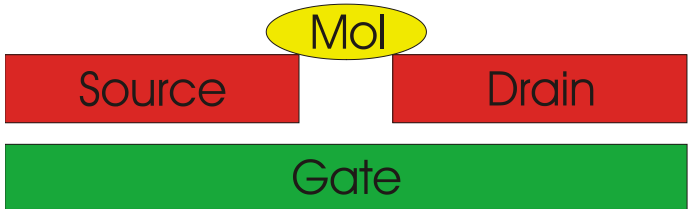


Comparison with quantum dots

We have fixed gate potential,
provided by the local environment

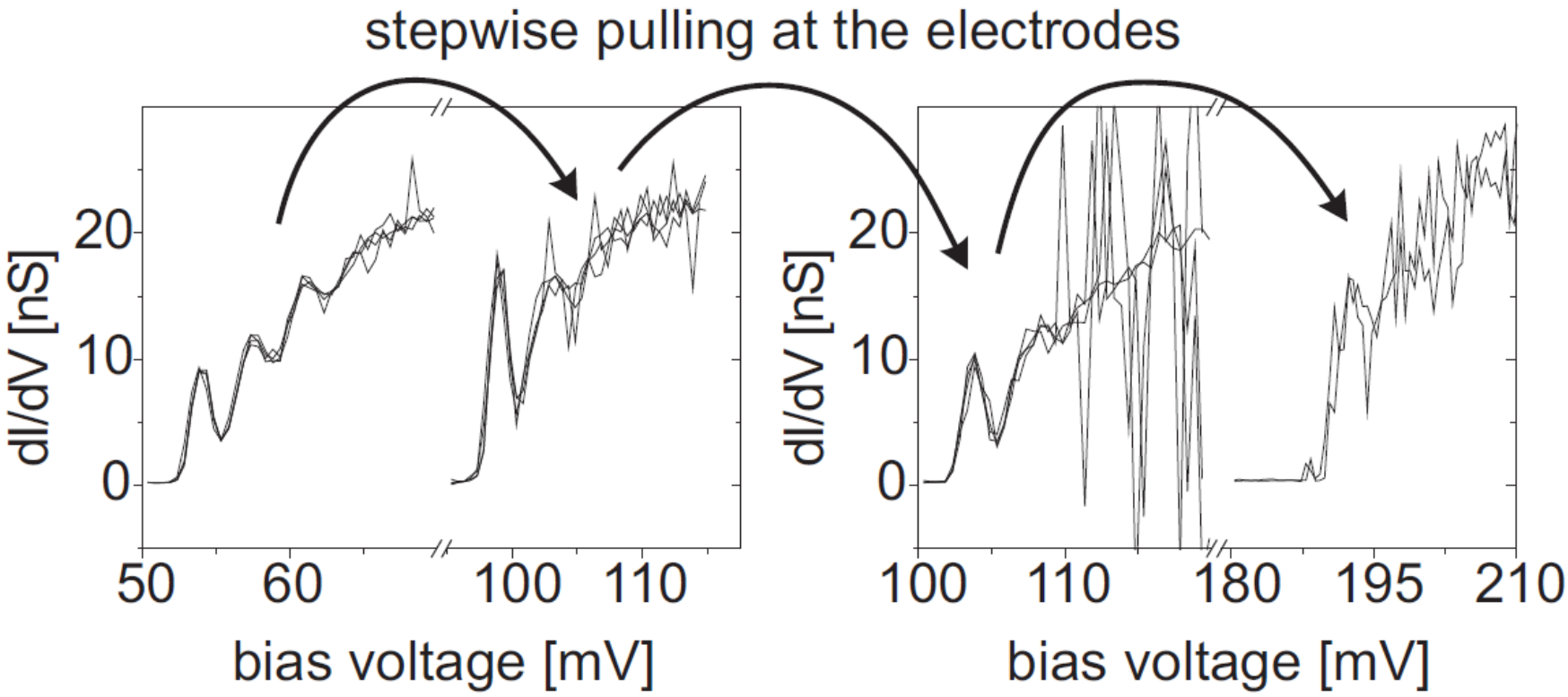






H. Van der Zant et al.

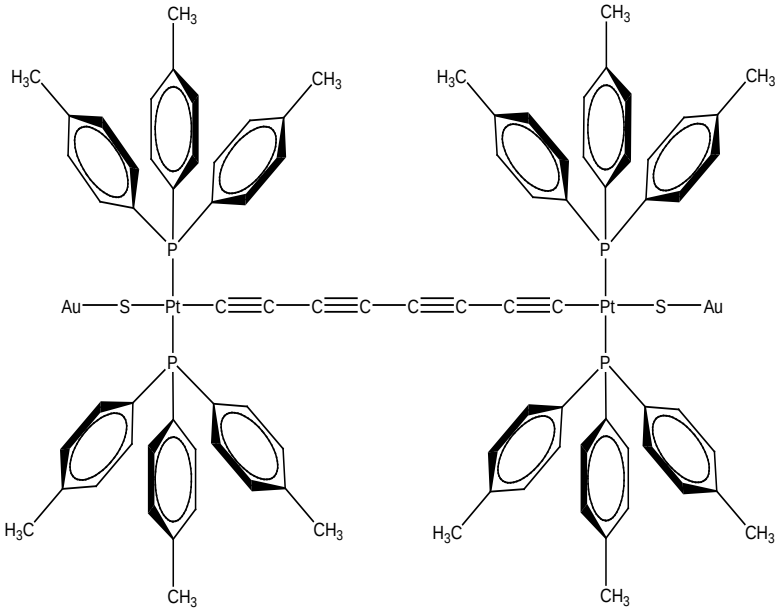
Peaks appear too broad

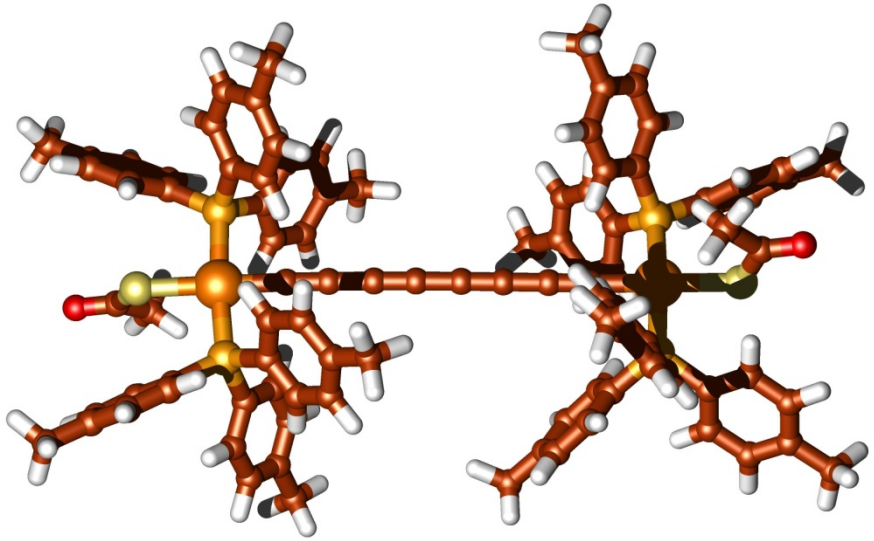


For nearly all molecules:
At low voltages vibrations may be resolved, at higher V peaks appear smeared

→ Seeking for a model system for vibrations

Single-molecule string

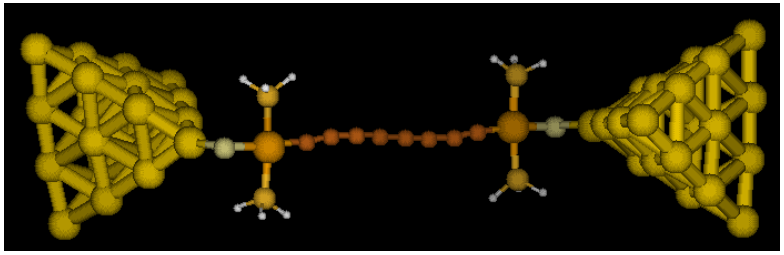




John Gladysz, Erlangen / Texas A&M

Oligoyne: ideal linear sp bond
- no aryl rings, no rotational degree of freedom
- heavy Pt ions provide fixed ends

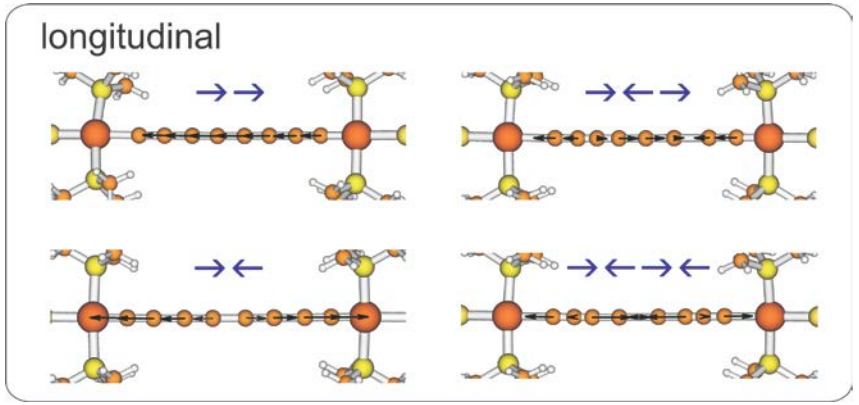
ChemPhysChem 11, 2256 (2010)

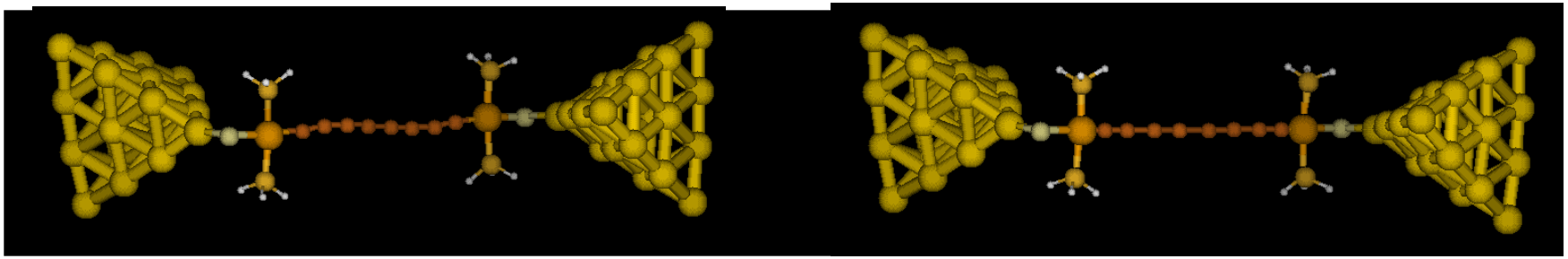


Density functional theory

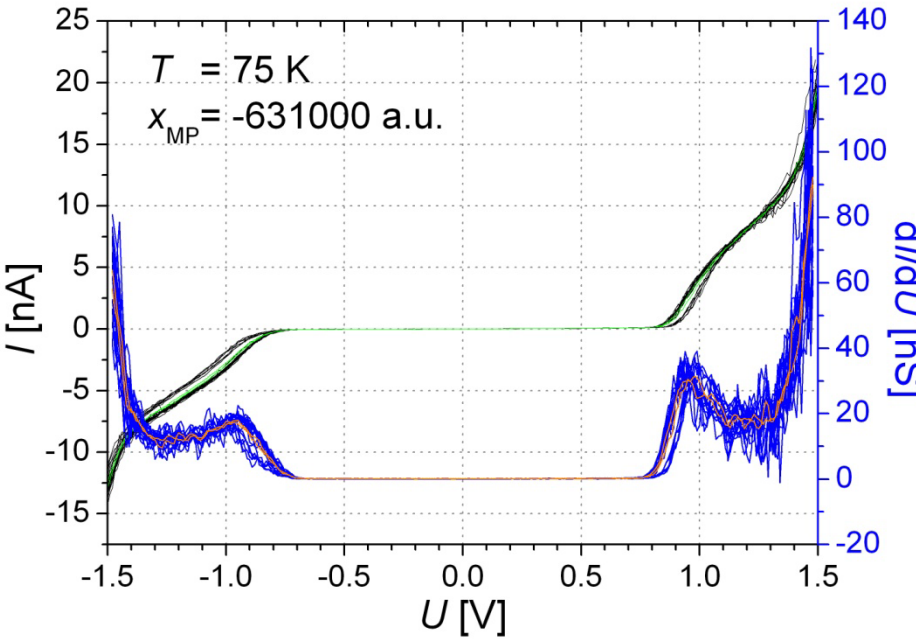
- DFT (calculations using TM 5.7: BP86/SVP,TZVP, B3LYP/TZVP
- Electronic structure + vibrational frequencies (3N-6 normal modes)

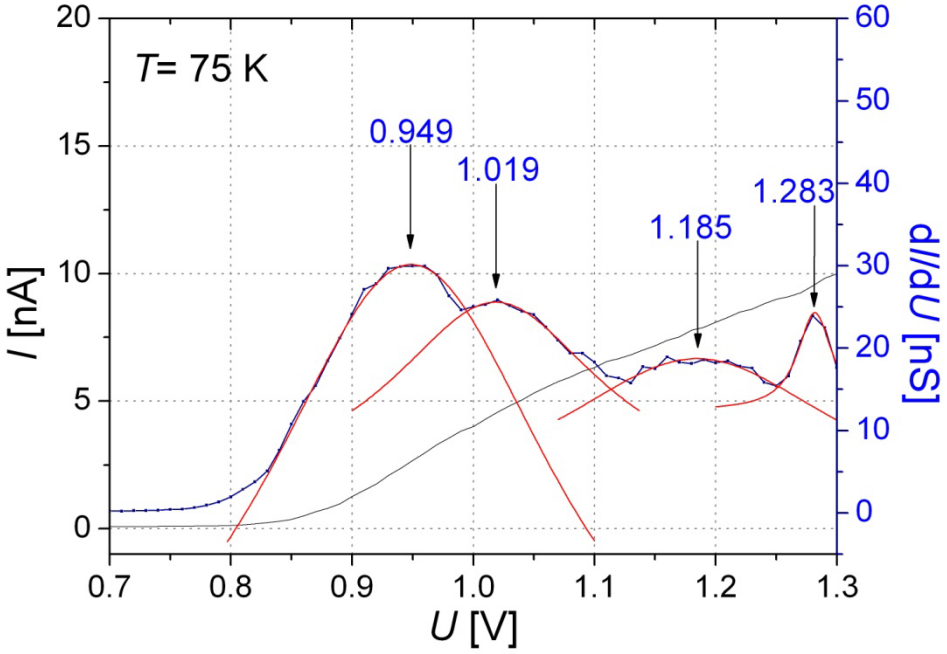
DFT in collaboration with:
Wolfgang Hieringer, Andreas Görling, Erlangen





Vibrational features



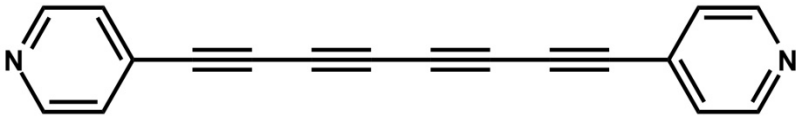


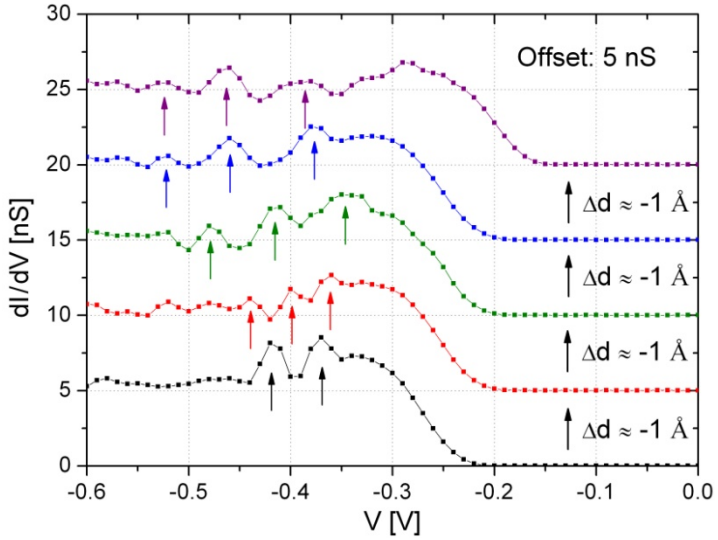
DFT (longitudinal string-like excitations)	Experiment
37.9 mV	37 ± 1.5mV
79.4 mV	89 ± 0.9mV
126.6 mV	130 ±1.5 mV

Vibrations are detected as sidepeaks, but the peaks are still too broad!

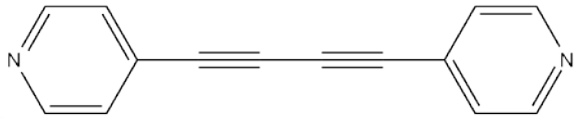
Further oligoines

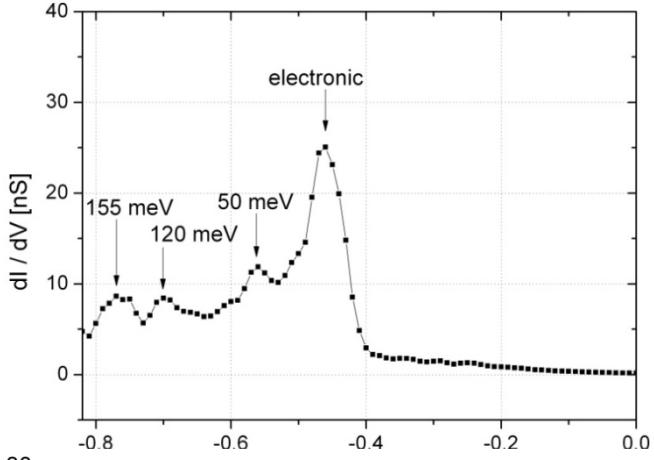
Martin Bryce, Durham

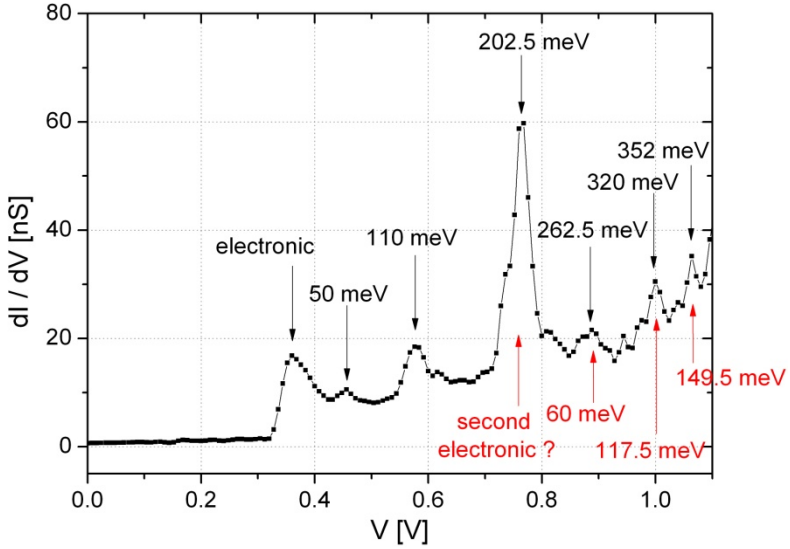




vibrational energies [meV]		
15	40	
15	35	55
20	55	87.5
30	70	100
52.5	87.5	120







Theory: vibrations and decoherence

PRL 107, 046802 (2011) PHYSICAL REVIEW LETTERS week ending 22 JULY 2011

Quantum Interference and Decoherence in Single-Molecule Junctions: How Vibrations Induce Electrical Current

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[1]*Institut für Theoretische Physik und Interdisziplinäres Zentrum für Molekulare Materialien, Friedrich-Alexander-Universität Erlangen-Nürnberg, Staudtstr. 7/B2, D-91058 Erlangen, Germany*

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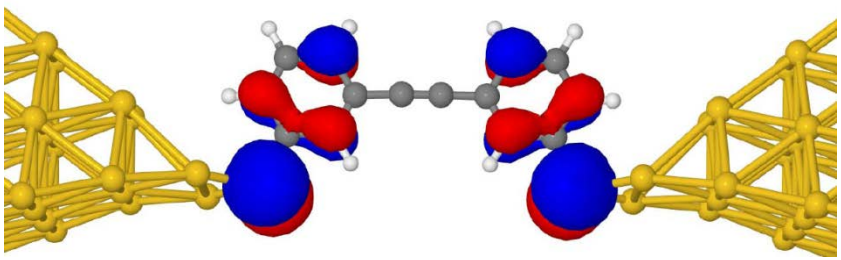
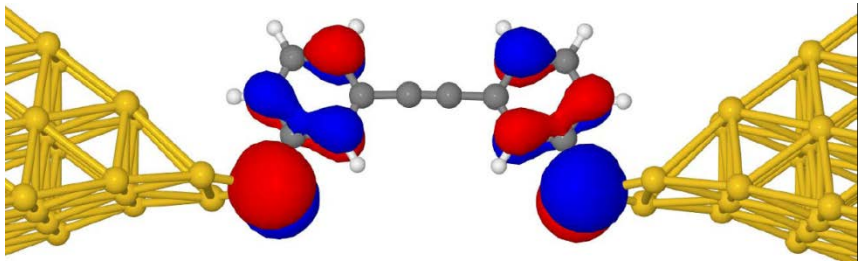
(Received 21 February 2011; revised manuscript received 16 June 2011; published 21 July 2011)

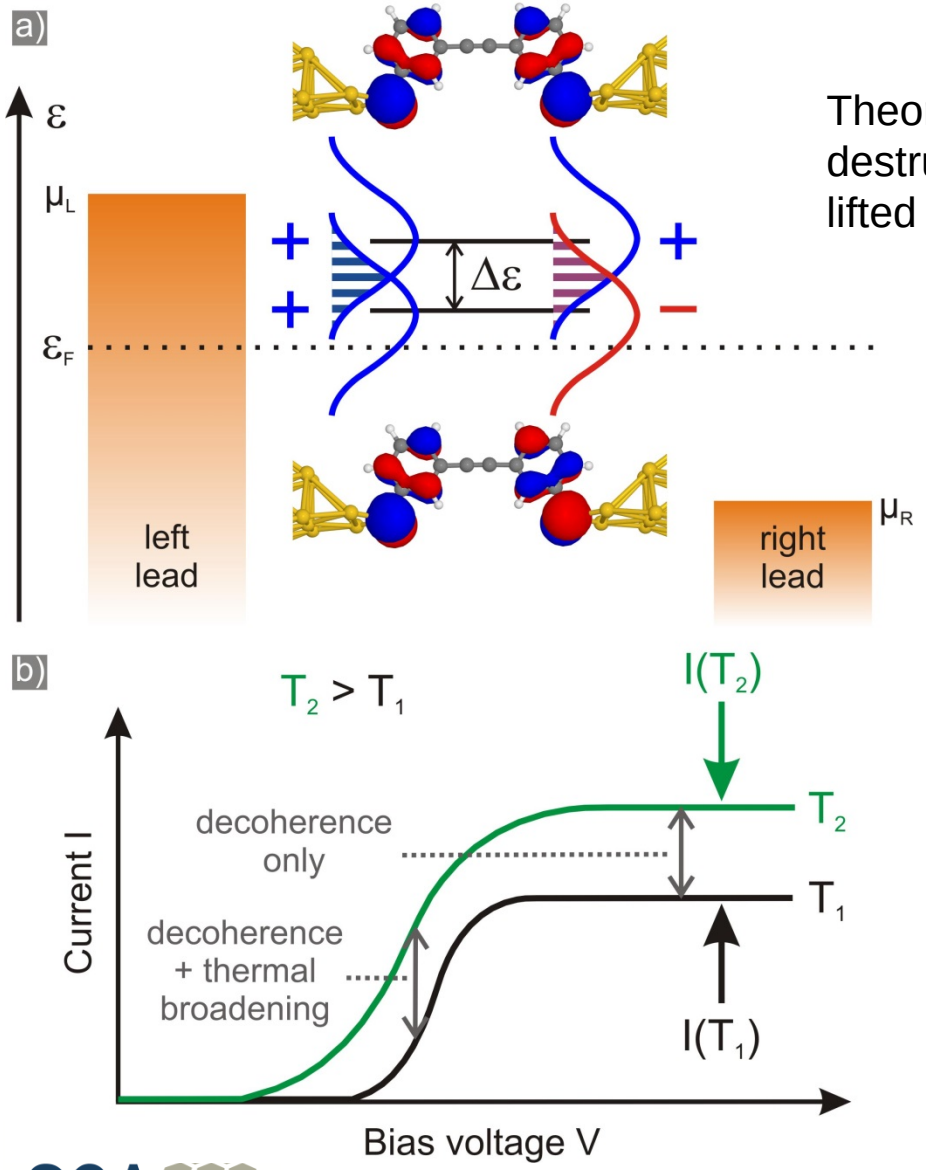
Quantum interference and decoherence in single-molecule junctions is analyzed employing a non-equilibrium Green's function approach. Electrons tunneling through quasidegenerate states of a molecular junction exhibit interference effects. We show that electronic-vibrational coupling, inherent to any molecular junction, strongly quenches such interference effects. This decoherence mechanism may cause significantly larger electrical currents and is particularly pronounced if the junction is vibrationally highly excited, e.g., due to inelastic processes in the resonant transport regime.



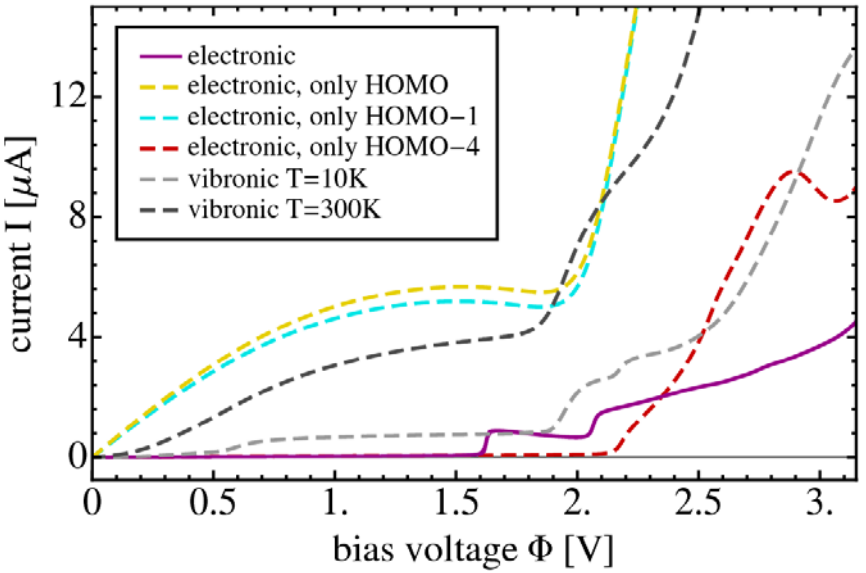


In dithiols: nearly degenerate orbitals, which differ in symmetry

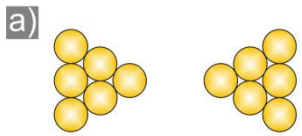
Vibrations

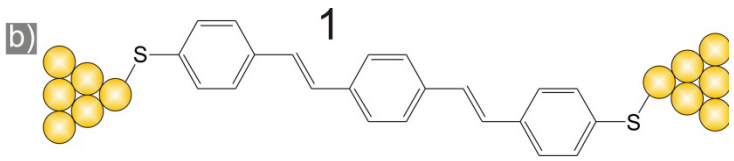


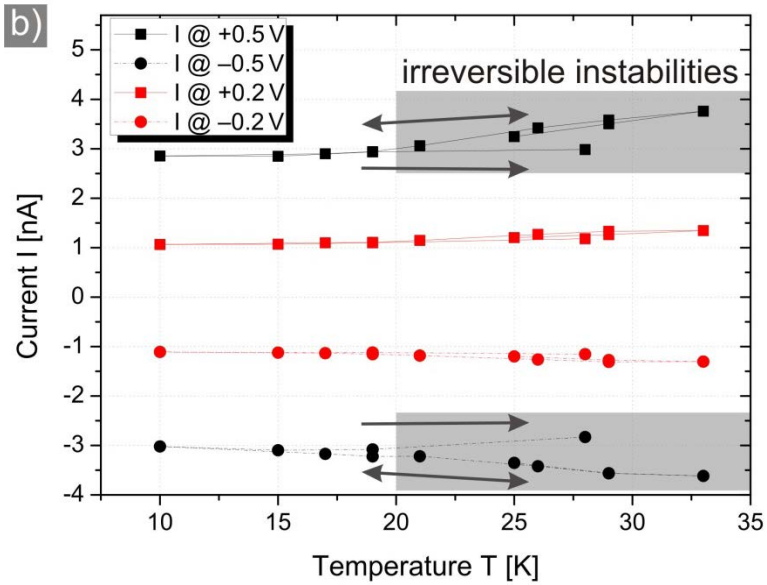
Theory:
destructive interference, suppression of conductance, lifted by vibrations

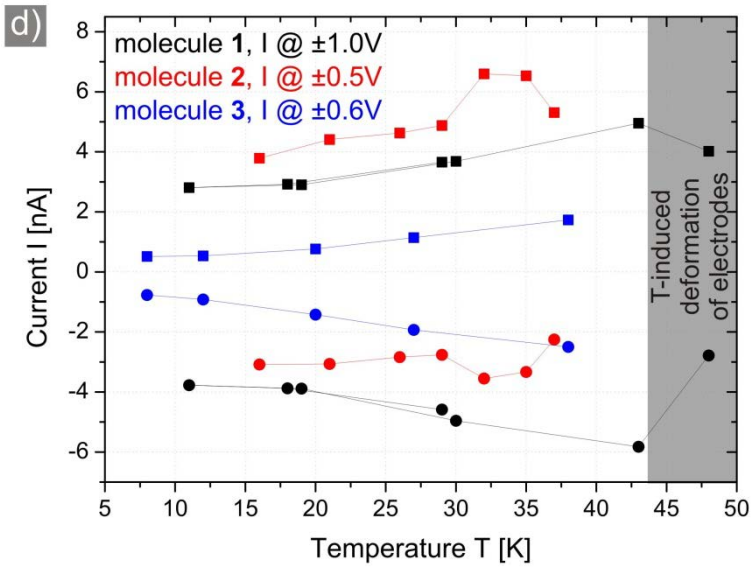


Experiment: stability check

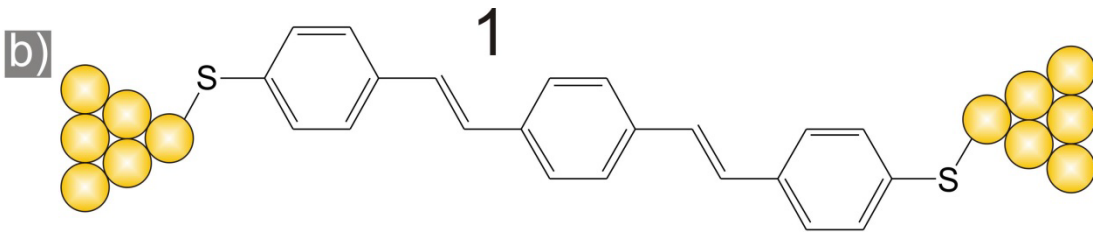


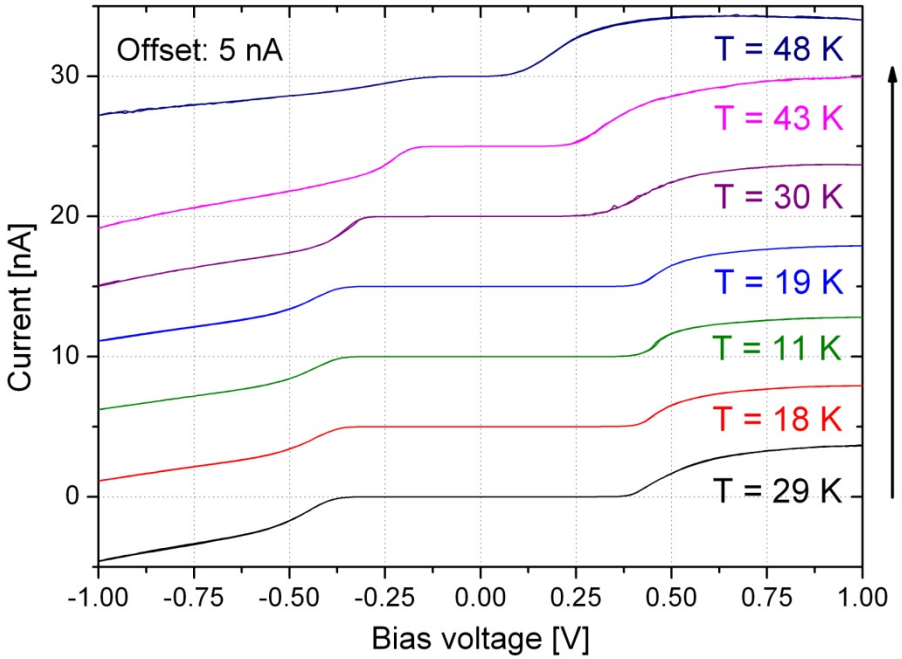


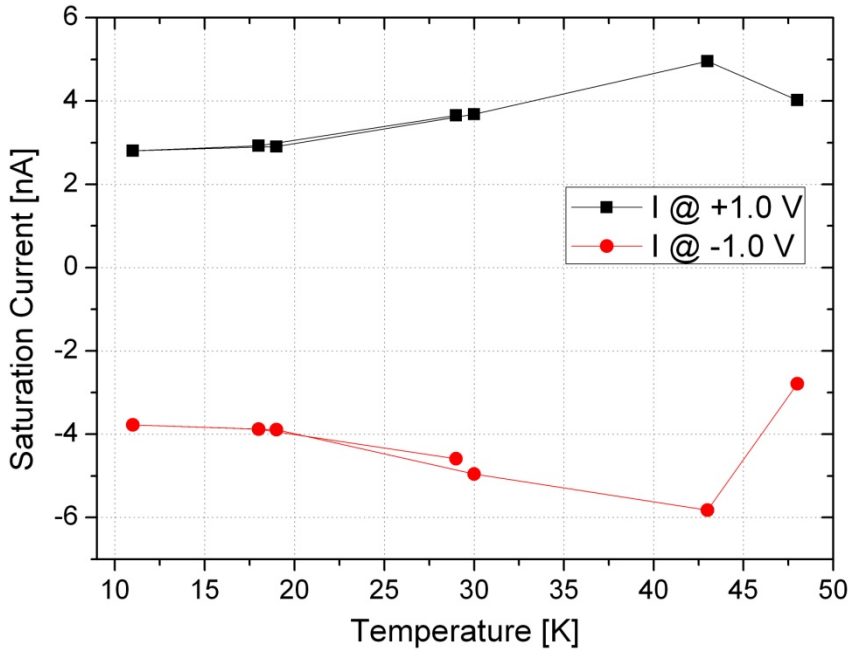




Data extraction

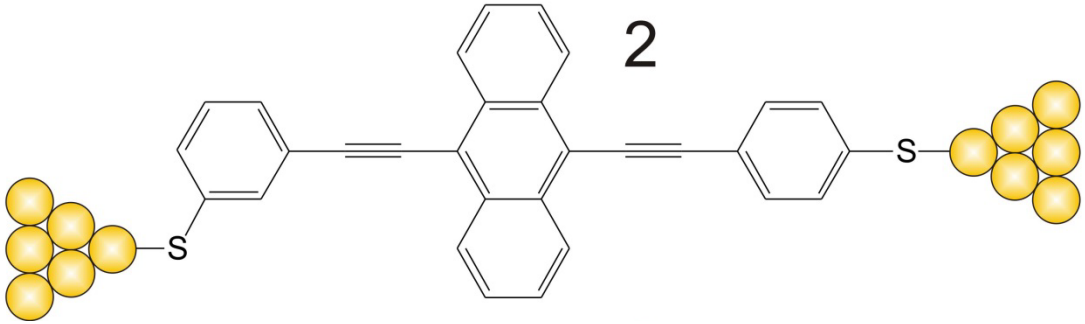


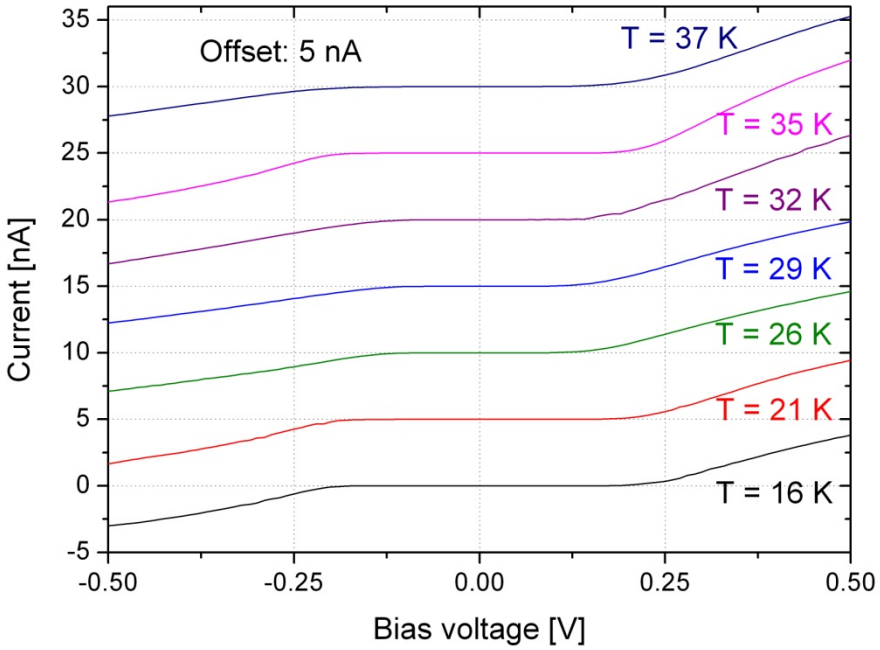


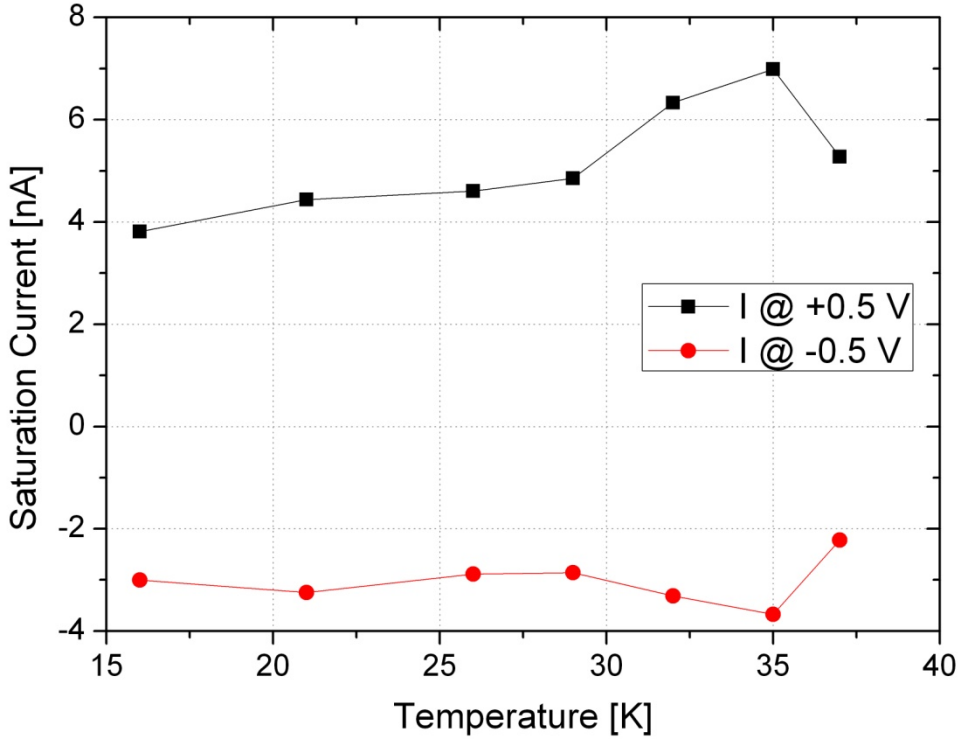


Broken symmetry

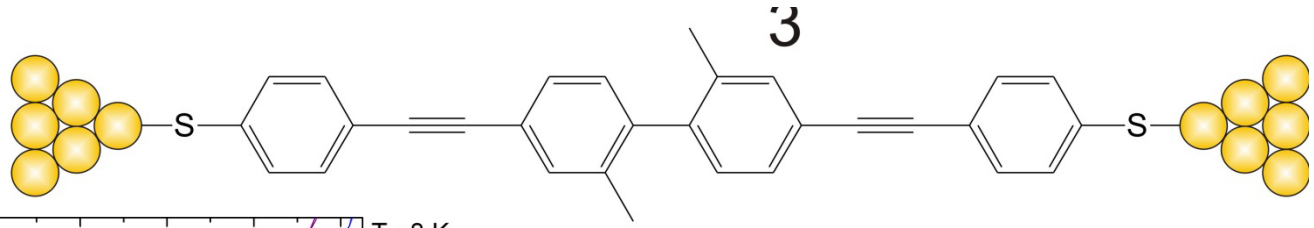
Experiment

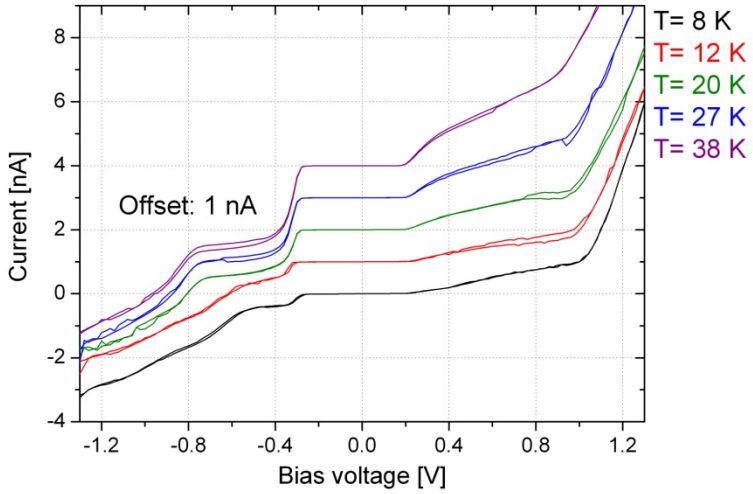


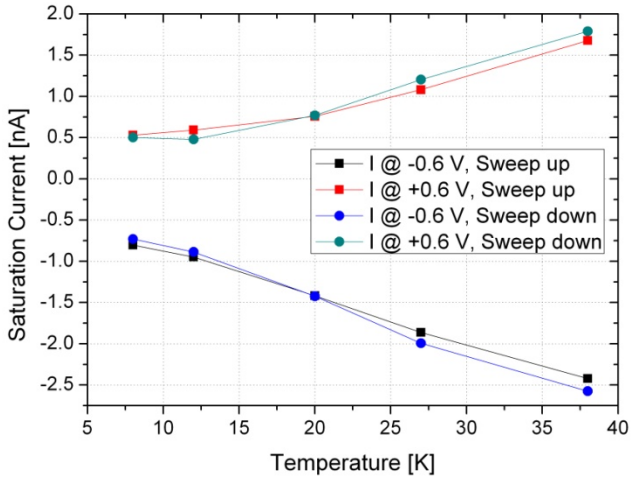


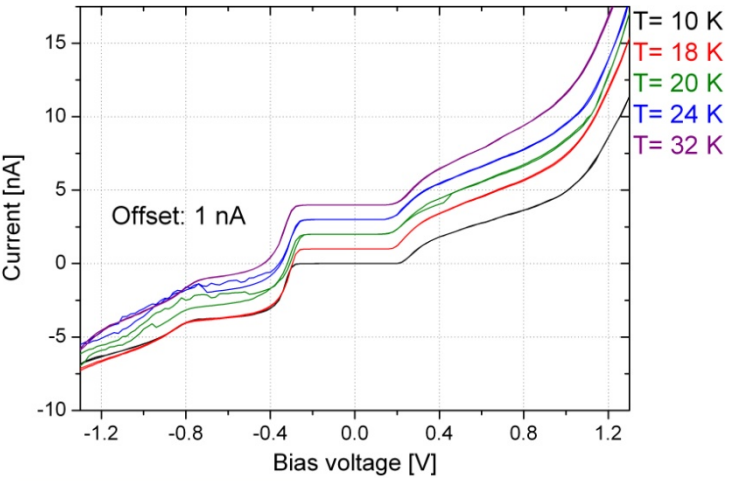


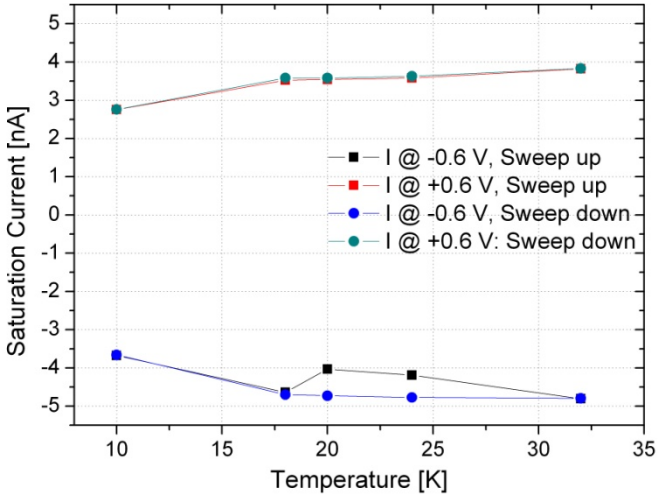
Split conjugation





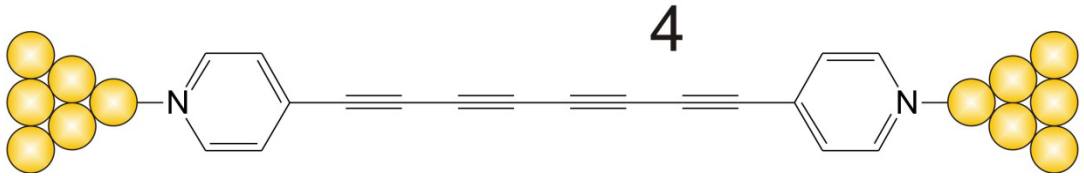




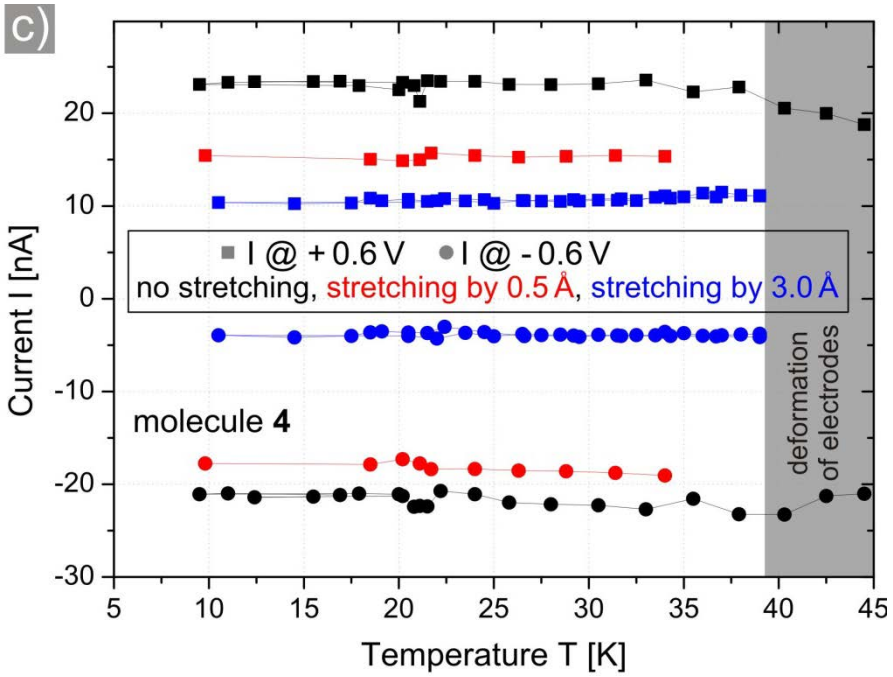


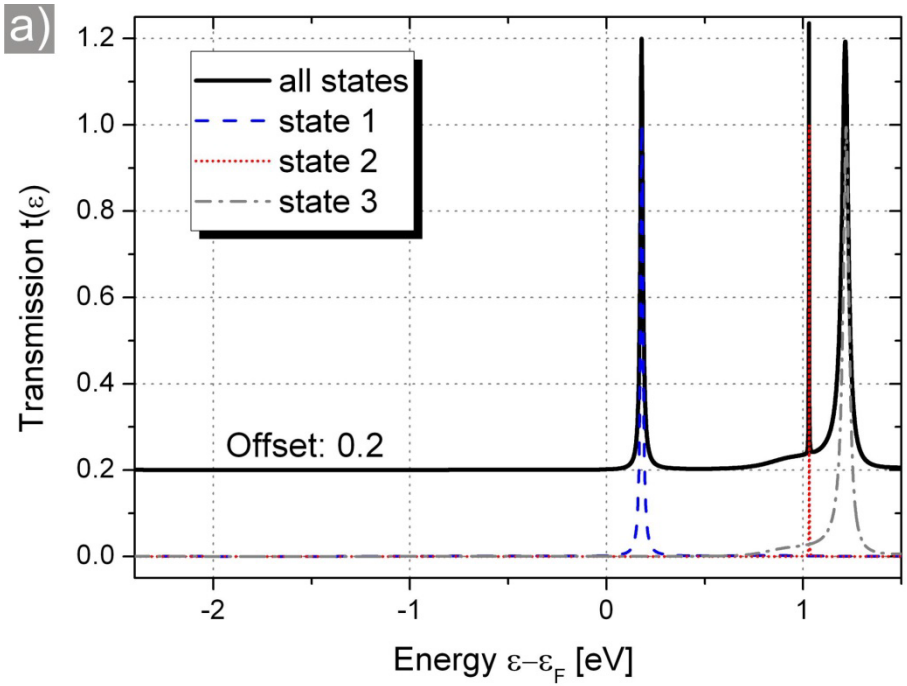
A counter example

Experiment



Martin Bryce, Durham





When even/odd state pairs are remote, no T dependence is observed.

Vibrations and Interference

Intermediate conclusion:

Oligoines show vibrational substructure in the first peak

Destructive interference provided by degenerate levels suppresses conductance

Vibrations contribute to enhance the current level

D. Secker, S. Wagner, S. Ballmann, R. Härtle, M. Thoss, H.B. Weber,
PRL **106**, 136807 (2011)

S. Ballmann, R. Härtle, P.B. Coto, M. Elbing, M. Mayor, M.R. Bryce, M. Thoss, H.B. Weber,
PRL **109**, 056801 (2012)

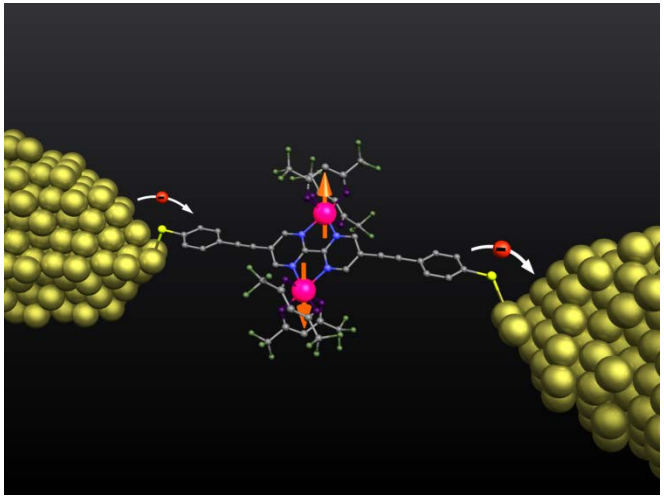
How does charge flow through single molecules ?

- Introduction: our technique

- vibrational degrees of freedom

- magnetic degrees of freedom

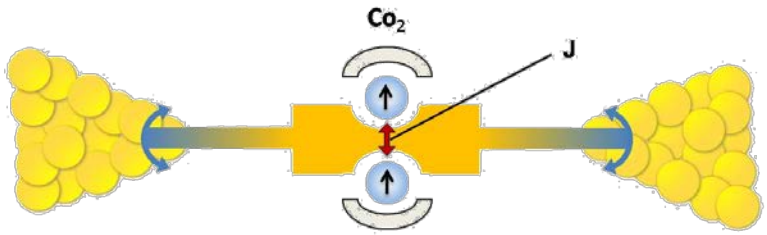
- novel experimental tools

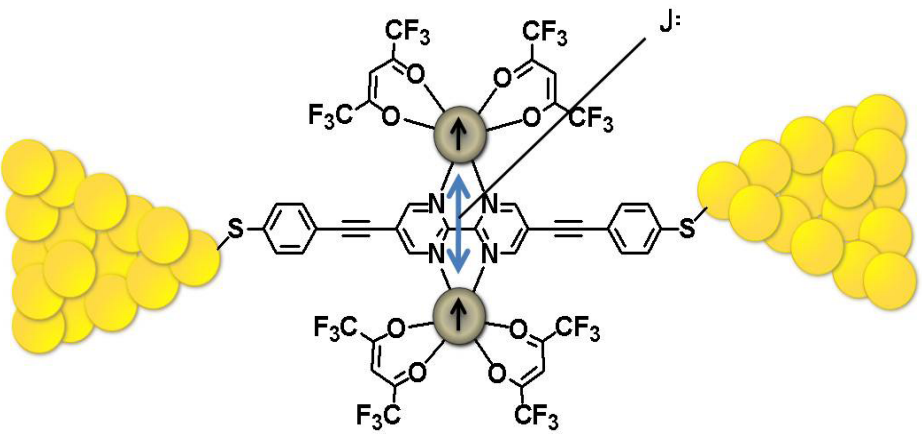


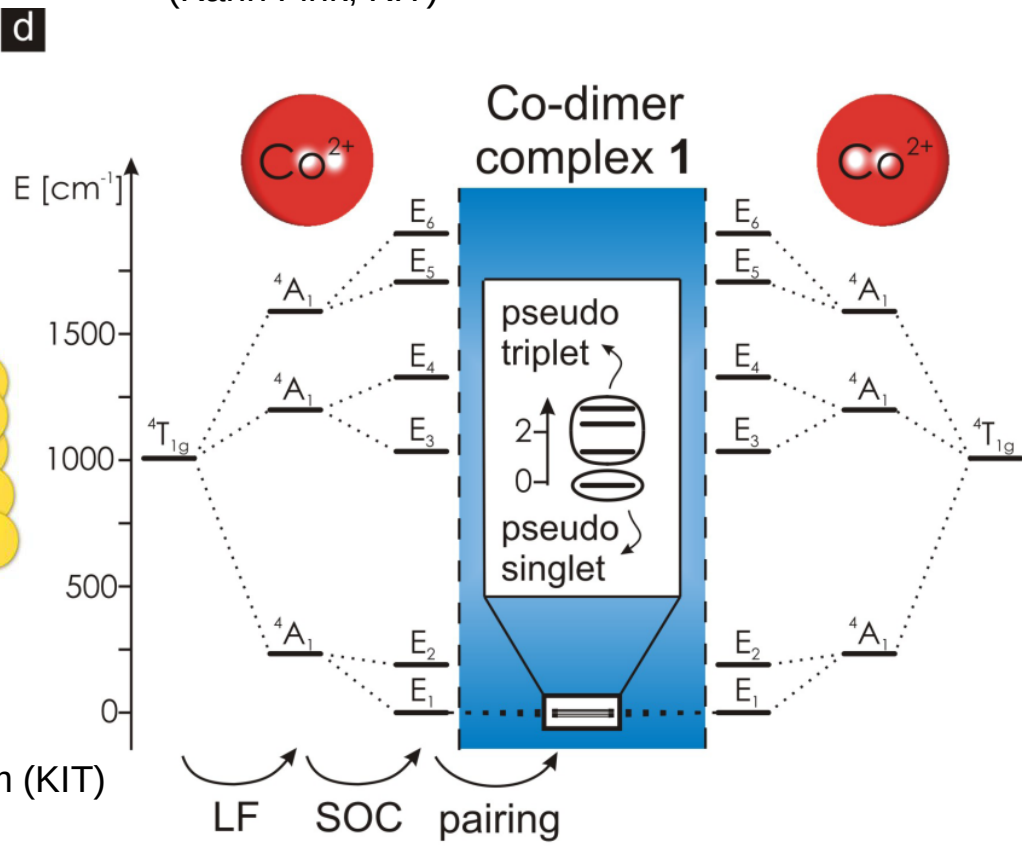
Even electron number:
Can we detect the spin state of a coupled spin pair ?

A spin pair occurs either as singlet or triplet

Here: pseudo singlet, pseudo triplet
(Karin Fink, KIT)

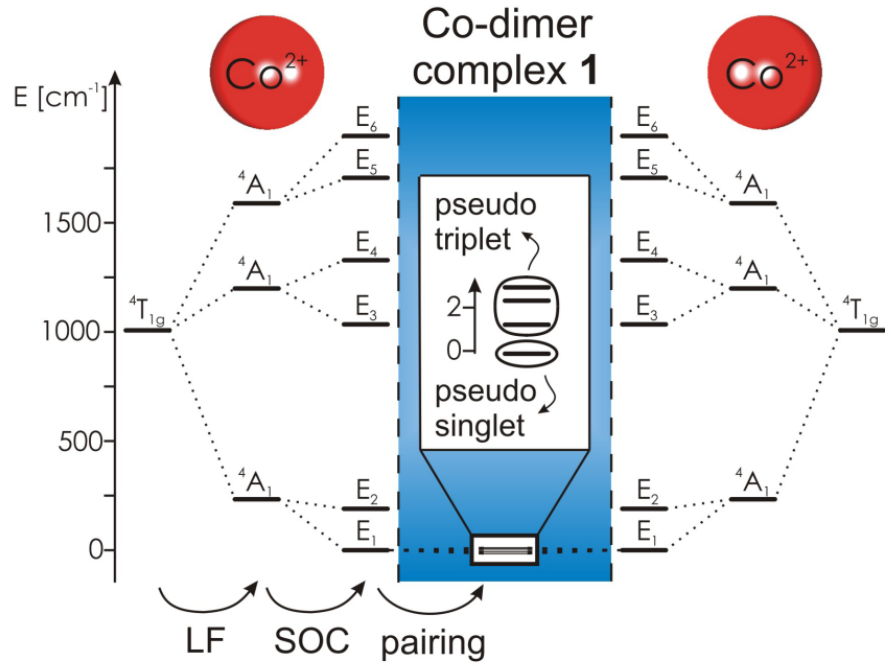


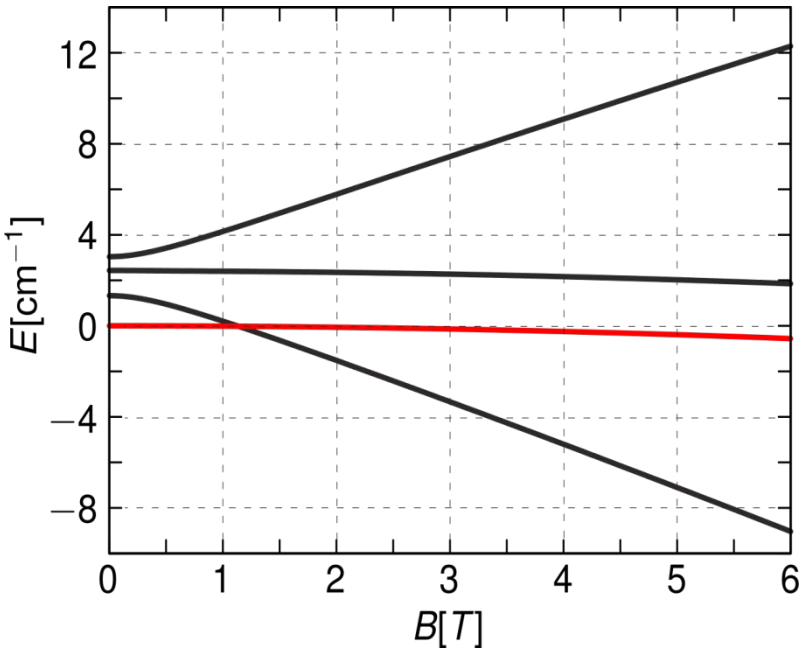




Mario Ruben, Frank Schramm (KIT)

d

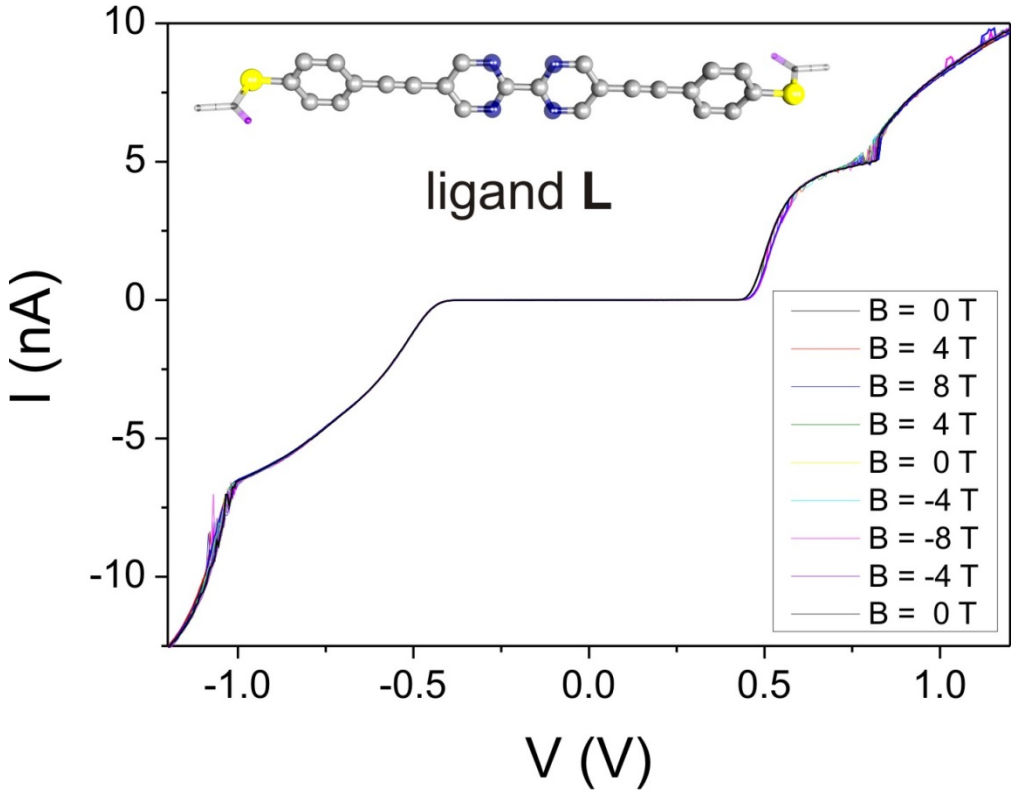




Black: pseudo triplet
Red: pseudo singlet

Karin Fink (KIT)

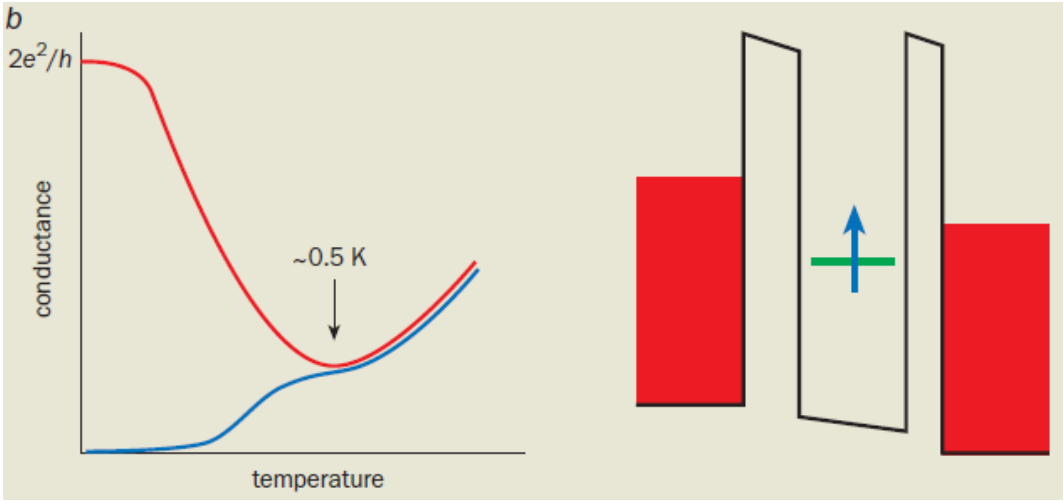
Blind experiments



Kondo effect

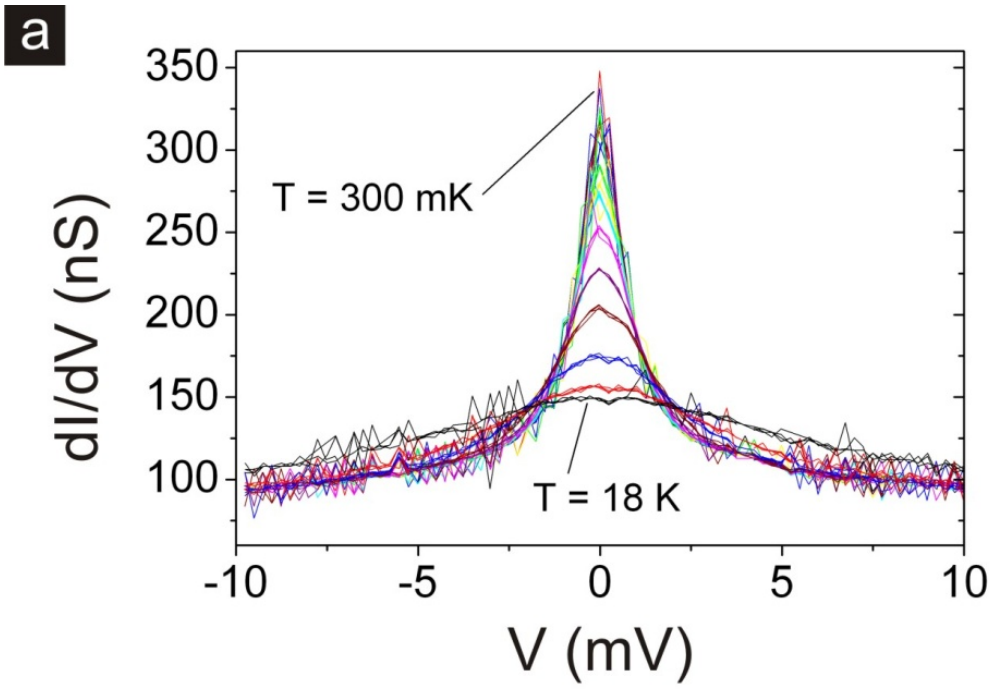
Jun Kondo

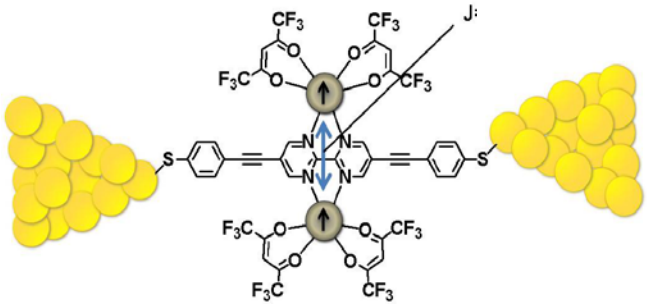
Kondo effect in quantum dots:

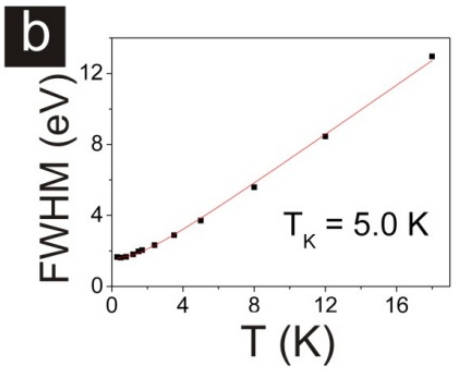


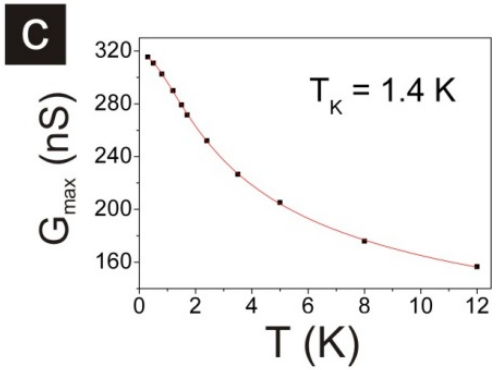
Zero bias conductance enhancement due to a new correlated ground state
in which an unpaired spin is screened by the surrounding electrons

Kondo-like anomaly

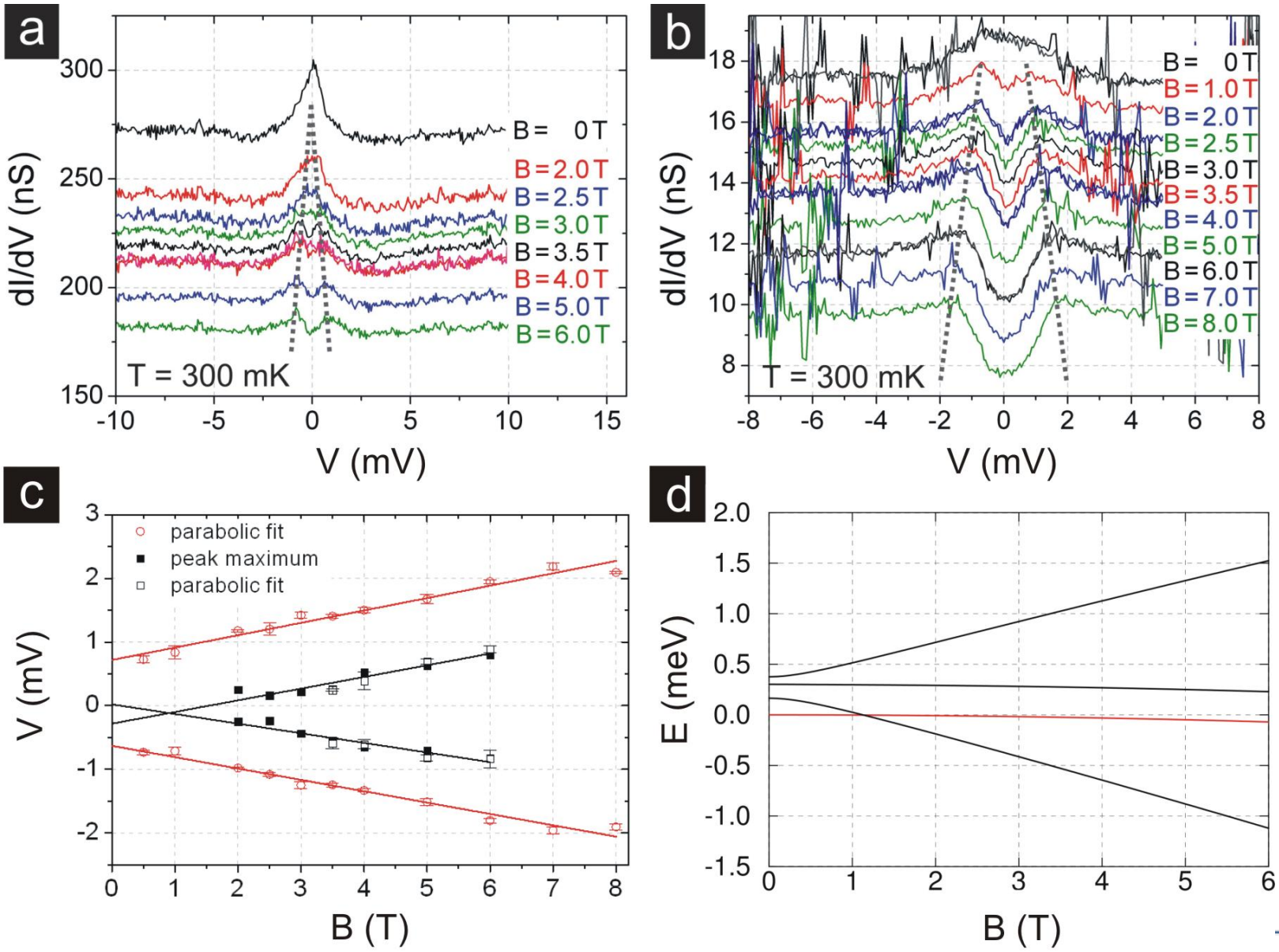






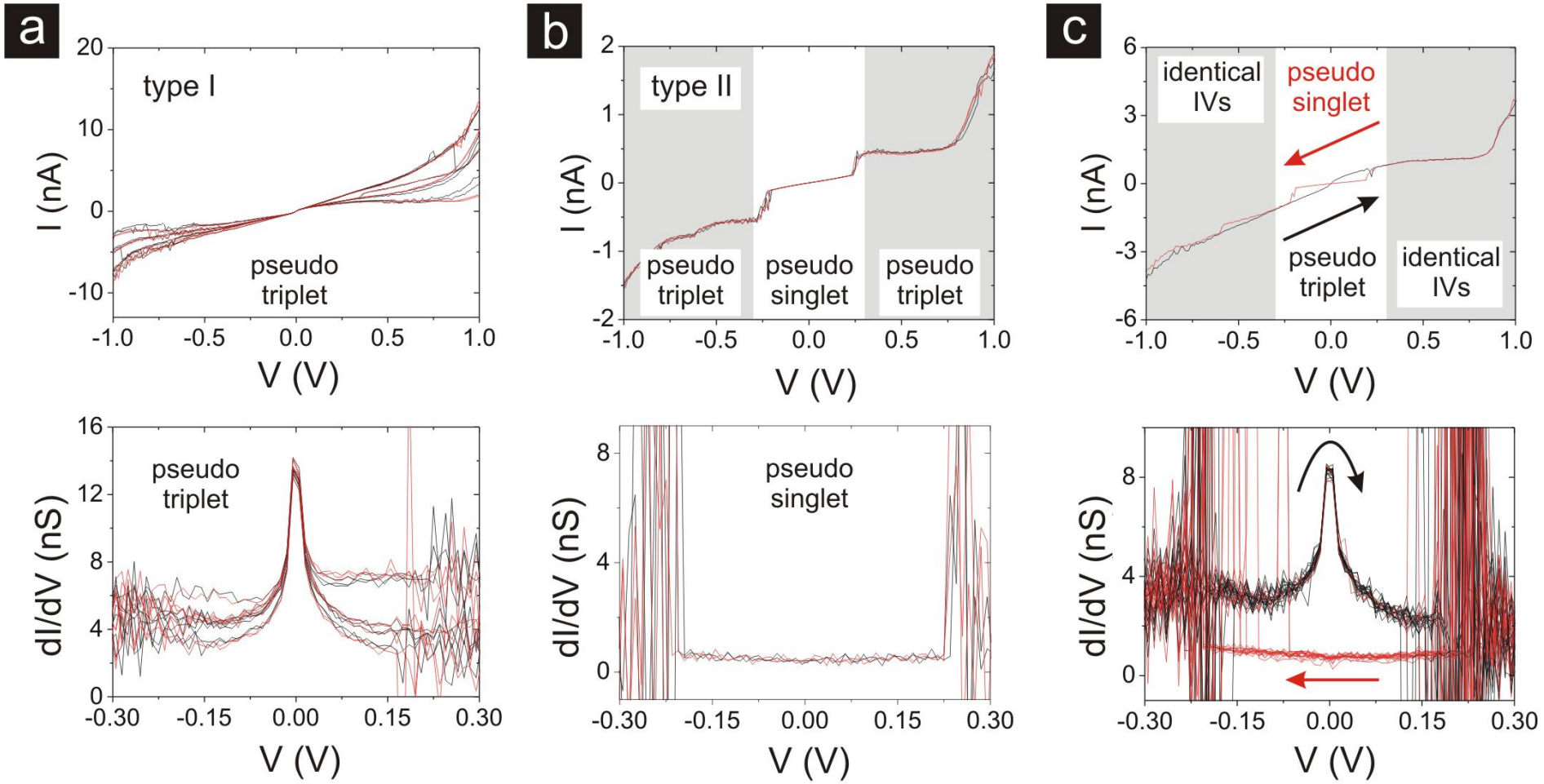


Magnetic degree of freedom

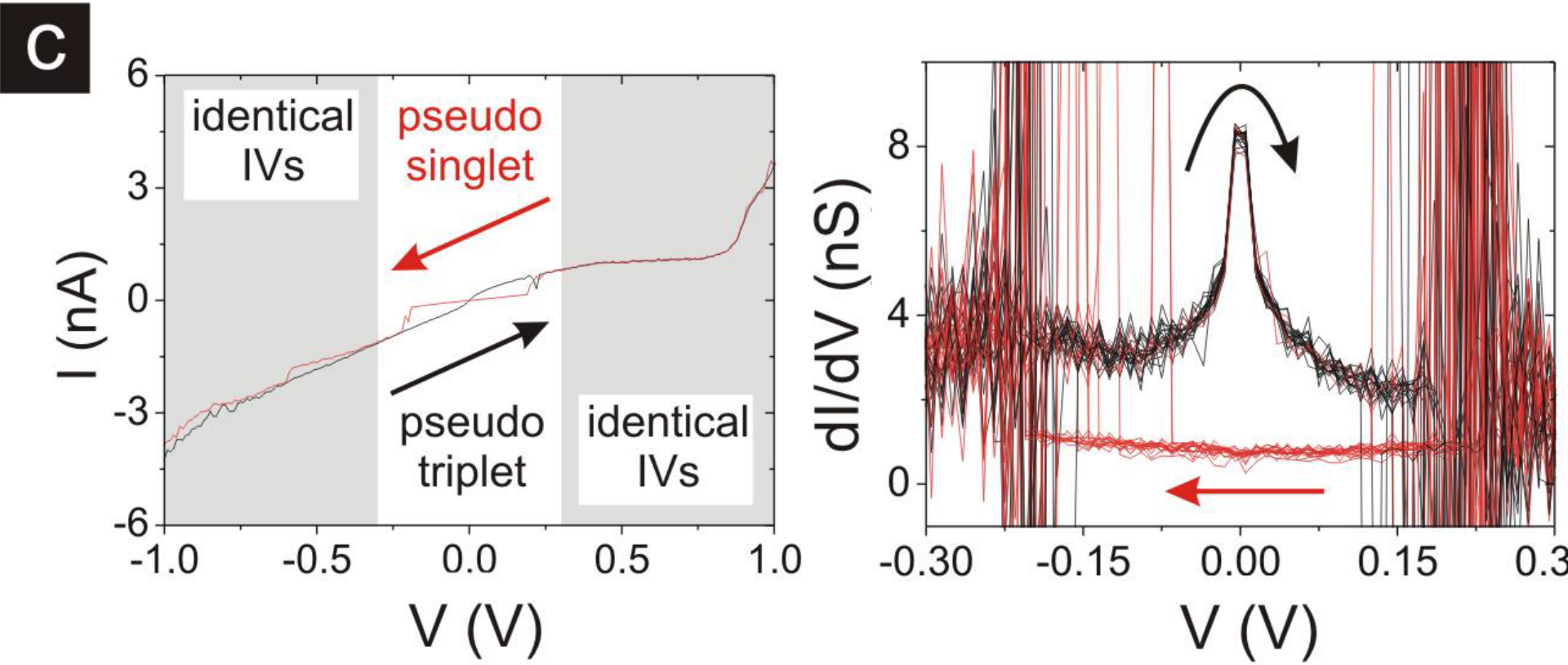


SCA
Synthetic Carbon Allot

Switching the spin states



Switching the spin states



Magnetic degrees of freedom

Intermediate conclusion:

The results suggests that one observes the spin state of a pair of a coupled spin system by a Kondo-like anomaly

We observe a bias-driven transition from the pseudo-singlet to the pseudo-triplet state

S. Wagner, F. Kißlinger, S. Ballmann, F. Schramm, R. Chandrasekar, T. Bodenstein, O. Fuhr, D. Secker, K. Fink, M. Ruben, H. B. Weber:
Nature Nanotechnology (2013)

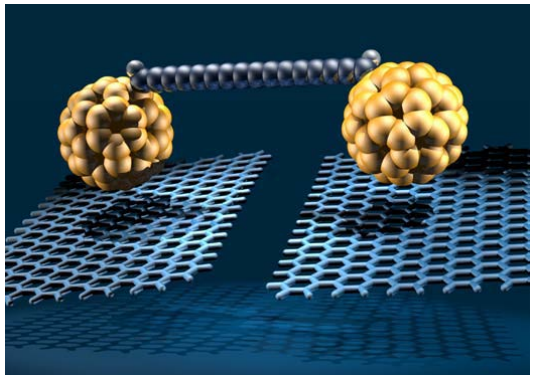
How does charge flow through single molecules ?

- Introduction: our technique

- vibrational degrees of freedom

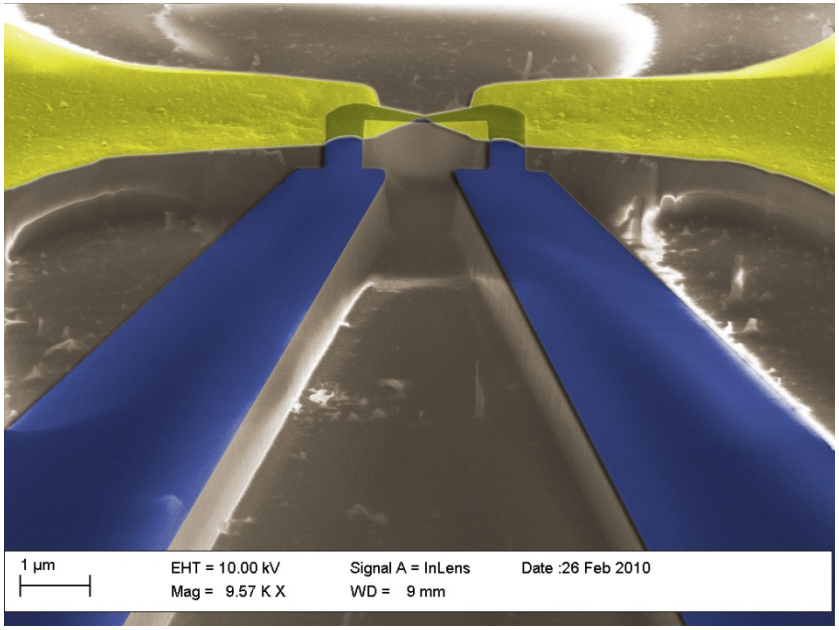
- magnetic degrees of freedom

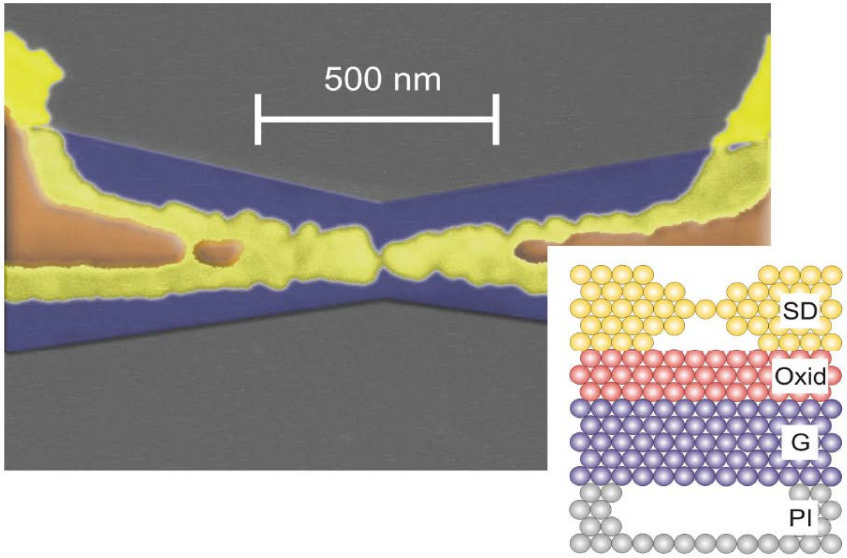
- novel experimental tools

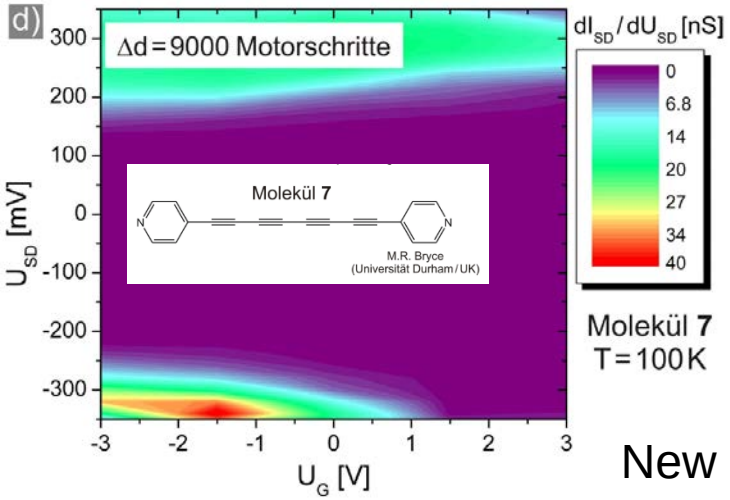


SFB 953: Synthetic carbon allotropes

Experimental improvements







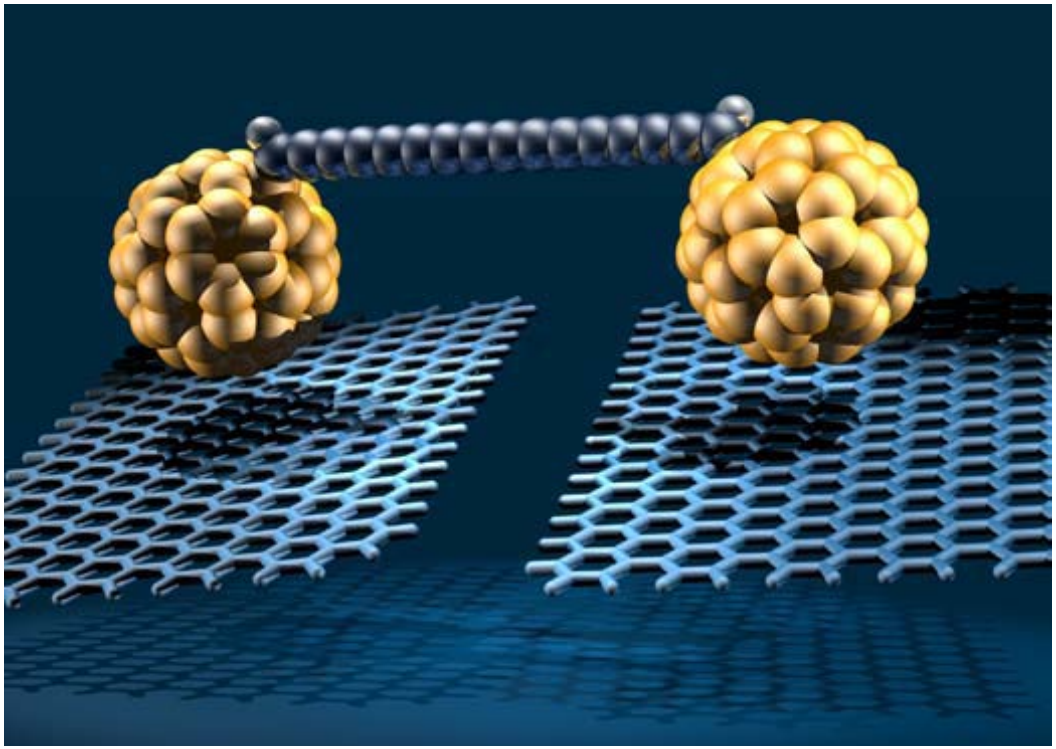
Nearly ideal device achieved

- 9 nm low-κ dielectric (Ta_2O_5, ε = 27)
- <10 pA leakage currents at 7V
- single-molecule contacts

-Gate action is still poor and inhomogeneous

New Journal of Physics 14, 123028 (2012)

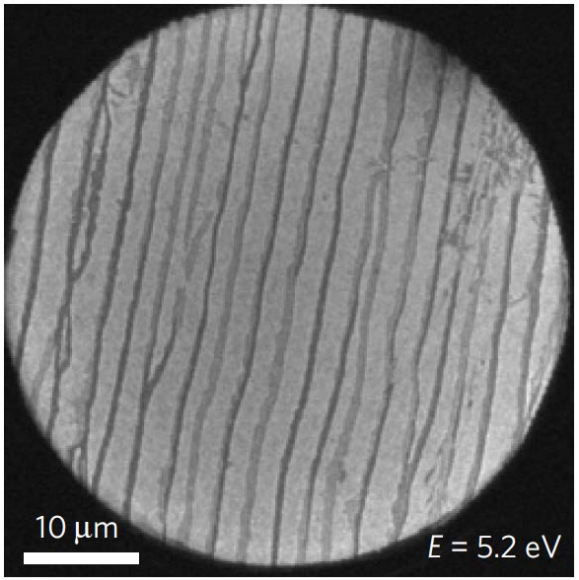
SFB 953: Synthetic carbon allotropes

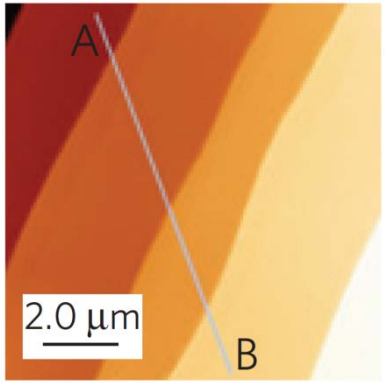


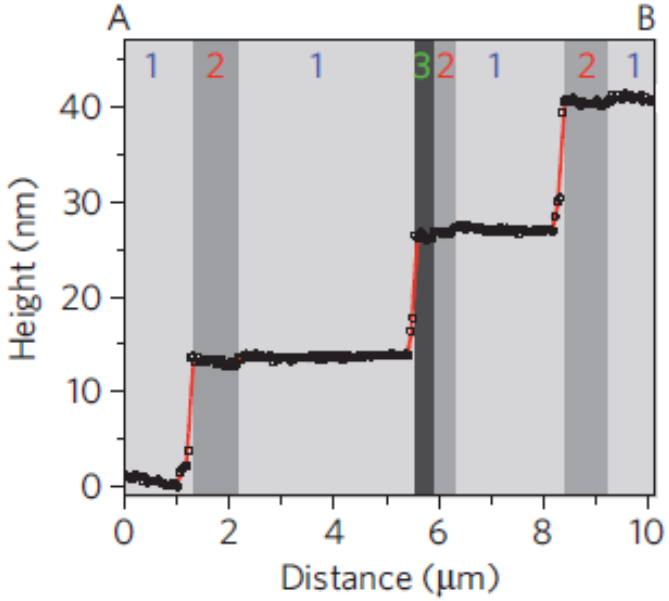
Epitaxial graphene

We produce epitaxial monolayer graphene on wafer scale on silicon carbide

K. Emtsev…H.B.Weber, T. Seyller: Nature materials **8,** 203 (2009)

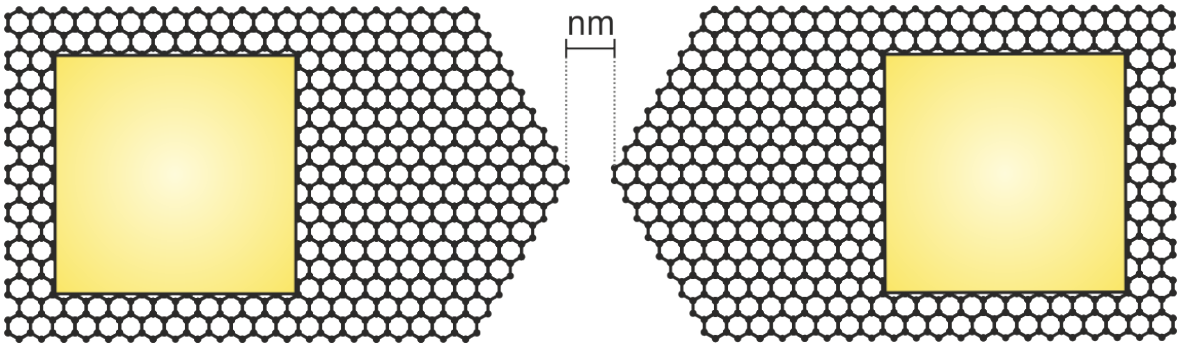






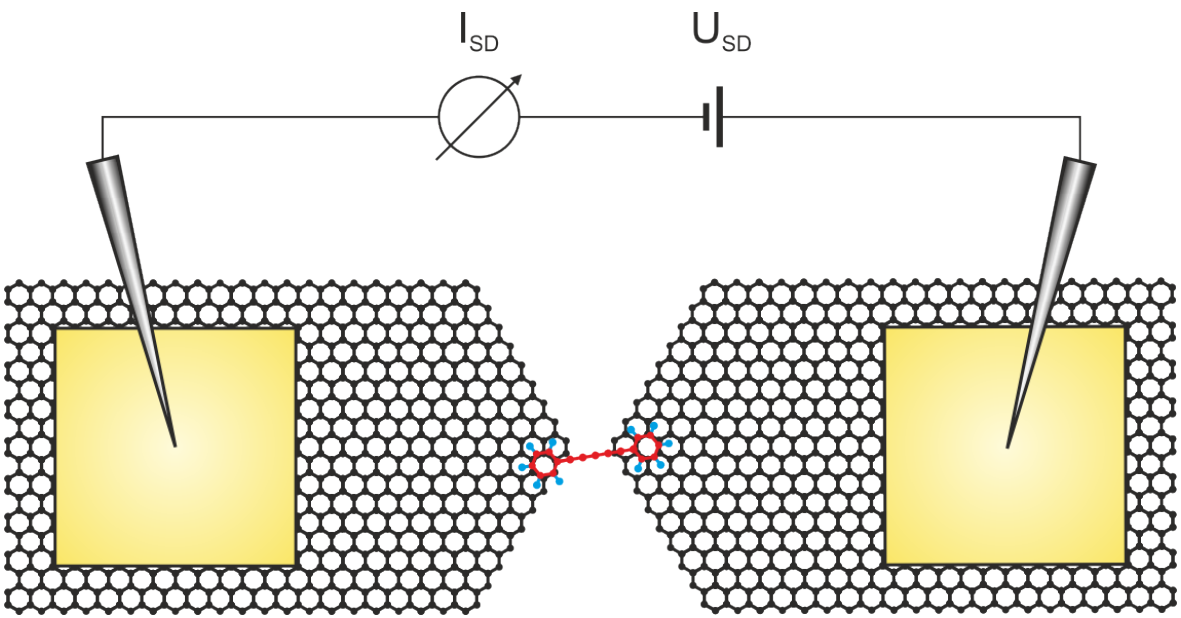
Scheme

Creation of graphene-electrodes with nanometer separation



Scheme

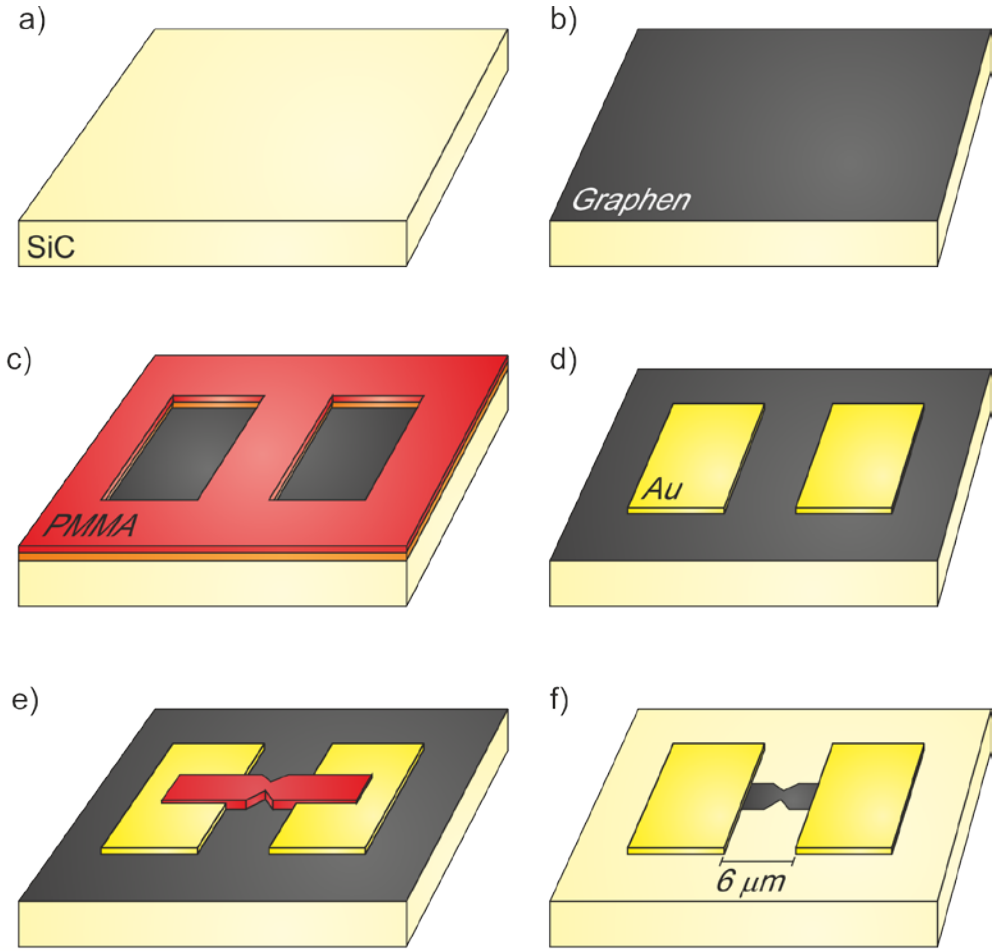
Goal: creation of graphene-electrodes with nanometer separation

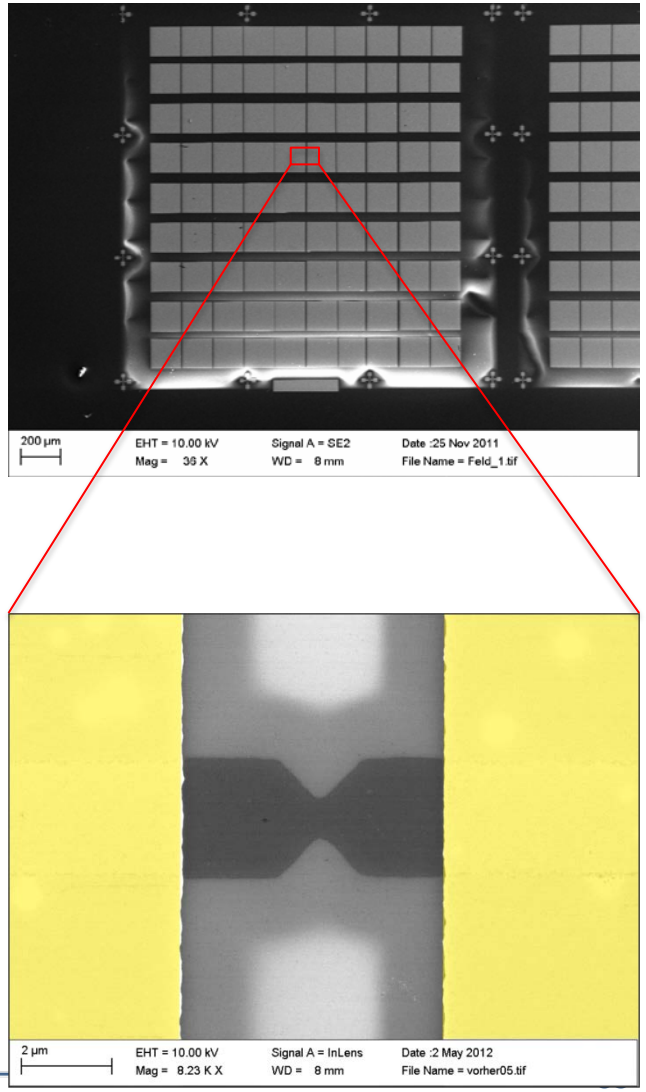


→ Contacting single molecules

Fabrication of nanogaps

Sample preparation:





Siliziumkarbid
Graphen
PMMA 950K
PMMA 200K
Gold

data

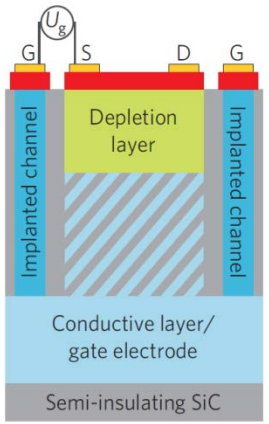
(unpublished data are removed in this public version)

Why graphene junctions ?

Molecular Nanojunctions become accessible with/to

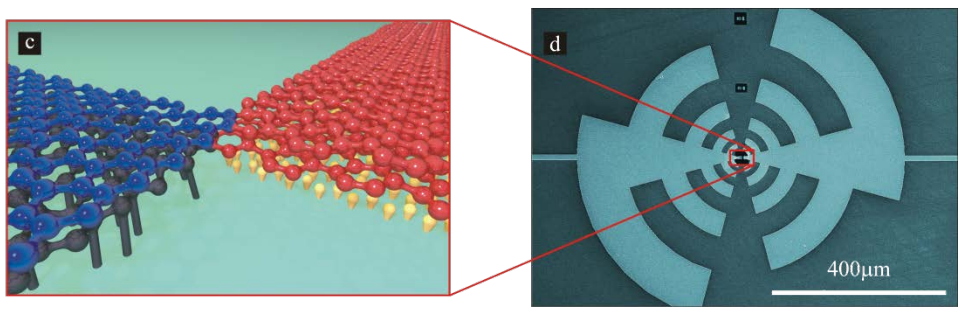
- electrostatic gates
- STM, AFM,
- light pulses
- Raman spectroscopy
- High-frequency exitations
- chemistry
- superconductivity

…



D. Waldmann …H.B.W.

Nature materials. 10, 357(2011)



THz antenna

Conclusions

Charge transport in single molecules is affected by vibrations

- the first peak

- vibrations lift interferences

Magnetic moments are detectable as Kondo anomalies,

- the combined spin of two magnetic cores can be detected

New tools are available:

- gated break junctions

- graphene electrodes

People

In my group:

Daniel Secker
Stefan Ballmann
Stefan Wagner
Konrad Ullmann
Ferdinand Kisslinger

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John Gladysz, Texas A & M
Mario Ruben, Karlsruhe
Nazario Martin, Madrid
Martin Bryce, Durham
Rik Tykwinski, Erlangen

Theory:

Andreas Görling, Erlangen
Felix von Oppen, Berlin
Michael Thoss, Erlangen
Karin Fink, Karlsruhe