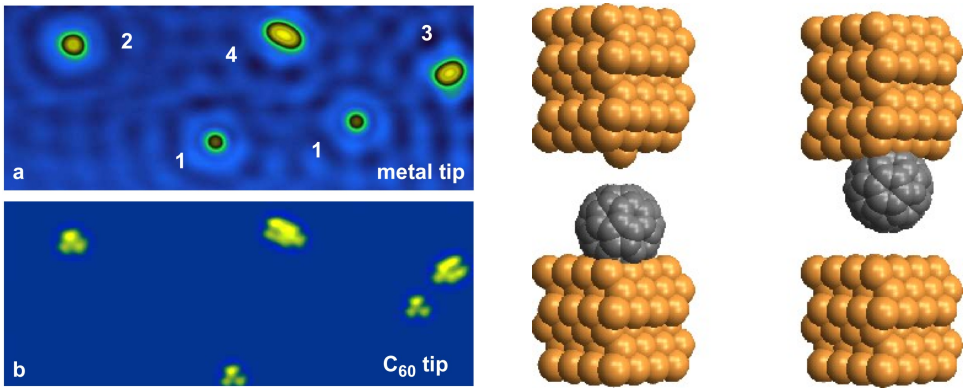
Atomic-scale engineering of electrodes for single-molecule contacts



Thomas Frederiksen
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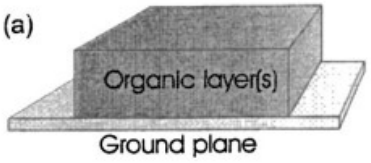
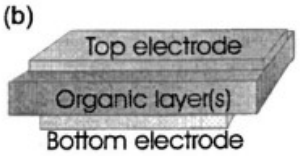
Guillaume Schull (Strasbourg), Andres Arnau (San Sebastián),
Daniel Sánchez-Portal (San Sebastián), Richard Berndt (Kiel)

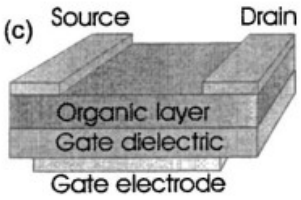
The problem of electronic contacts

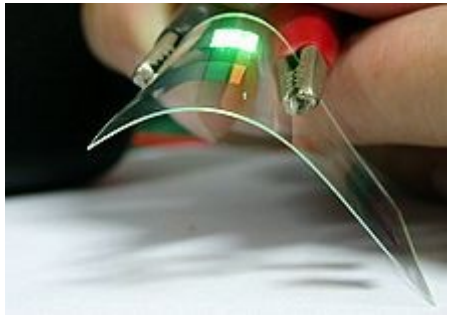
Transport of charge through a conducting material
- intrinsic ability of the material to conduct current
- charge injection efficiency at the contacts

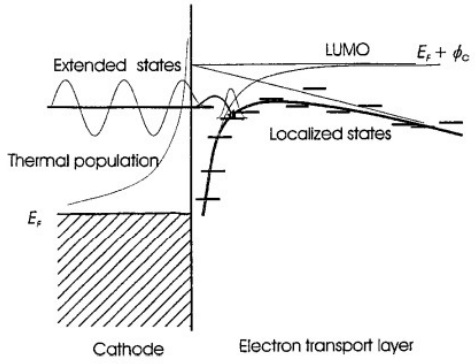
Organic materials (OPC, OLED, OFET)





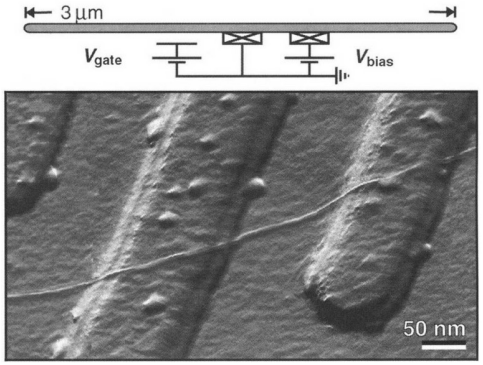


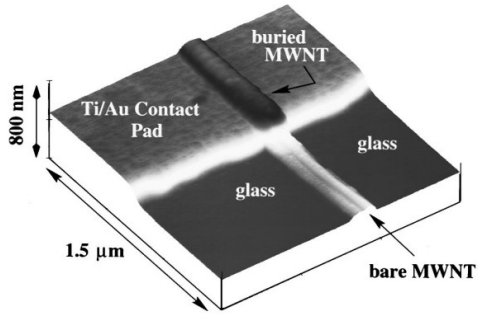




J. C. Scott, J. Vac. Sci. Technol. A 21, 521–531 (2003)

Carbon nanotubes

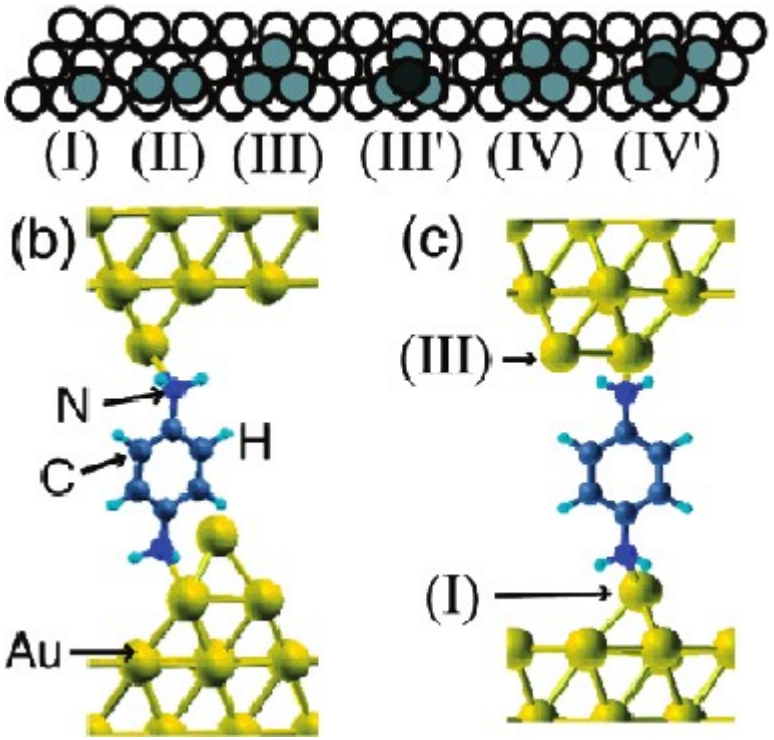




S. J. Tans et al., Nature 386, 474 (1997)
P. J. de Pablo et al., APL 74, 323 (1999)

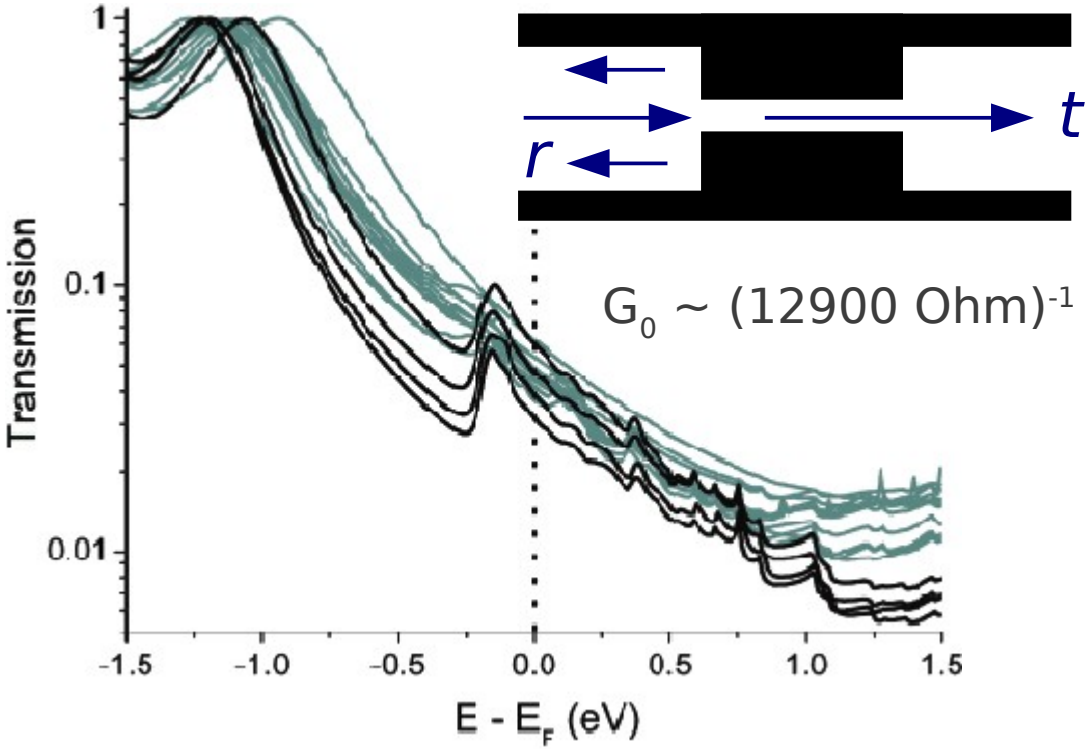
Valid down to a single molecule?

Atomistic theories suggest “yes”



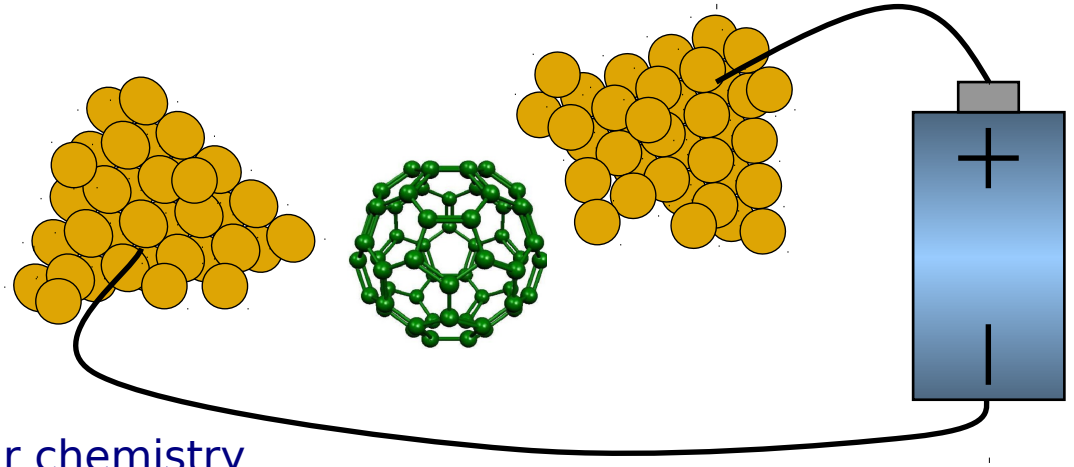
Zero-temperature Landauer formula

$$G = G_0 \mathrm{Tr}[\mathbf{t}^\dagger \mathbf{t}] = G_0 \sum_i T_i$$



Y. Xue and M. A. Ratner, PRB 68, 115407 (2003)
K. H. Müller, PRB 73, 045403 (2006)
S. Quek et al., Nano Lett. 7, 3477 (2007)
M. Paulsson et al., Nano Lett. 9, 117 (2009)

First-principles methods: DFT+NEGF



Big and complex systems:
- Coupling to electrodes
- Chemical bonding
- Interface geometry

Density Functional Theory (DFT):
- Handles 100-1000 atoms and their chemistry
- No fitting parameters
- Vibrational frequencies and modes from ground state

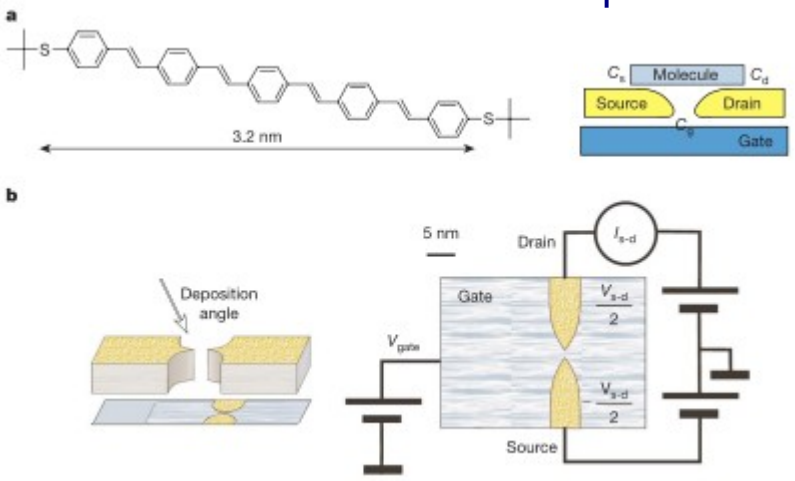
Nonequilibrium Green's functions (NEGF):
- Open systems
- Finite currents
- Particle interactions in the scattering region

SIESTA: Soler, Artacho, Gale, García, Junquera, Ordejón, Sánchez-Portal, J. Phys.: Condens. Matter 14, 2745 (2002)

TranSIESTA: Brandbyge, Mozos, Ordejón, Taylor, Stokbro, PRB 65, 165401 (2002)

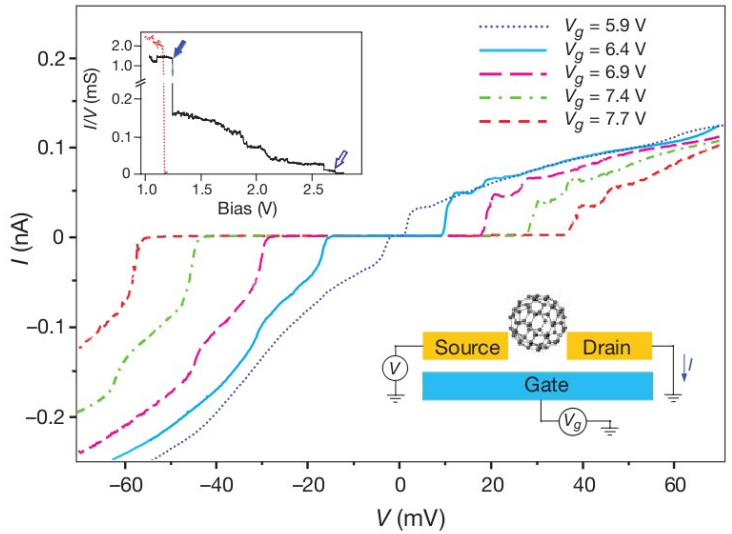
Contacting single molecules

Shadow-mask technique



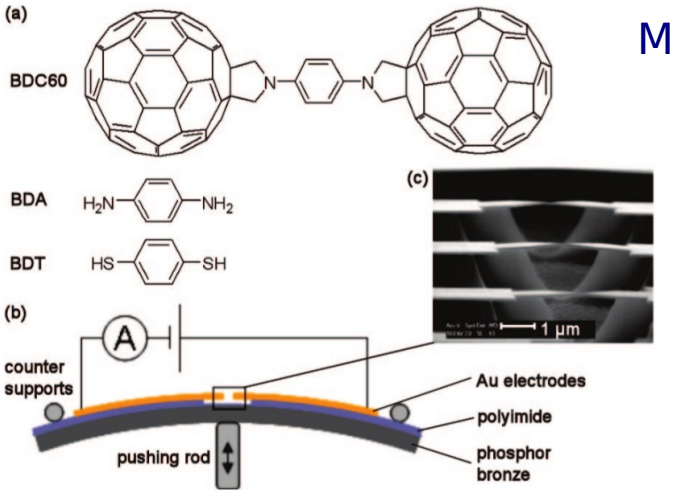
S. Kubatkin et al., Nature 425, 698 (2003)

E-beam lithography

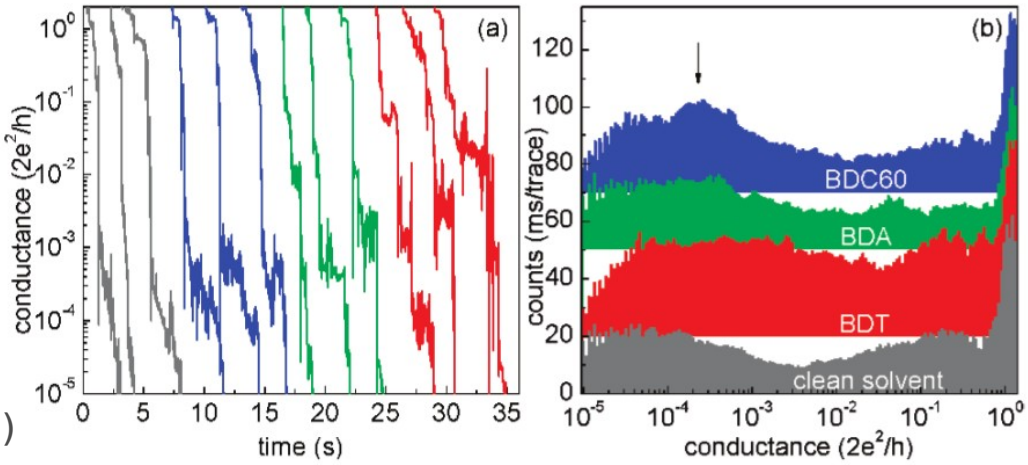


H. Park et al., Nature 407, 57 (2000)

Mechanically controllable break Junctions (MCBJ)



C. Martin et al., JACS 130, 13198 (2008)



Using STM to contact fullerene molecules

VOLUME 74, NUMBER 11 PHYSICAL REVIEW LETTERS 13 MARCH 1995

Electronic Transparence of a Single C_{60} Molecule

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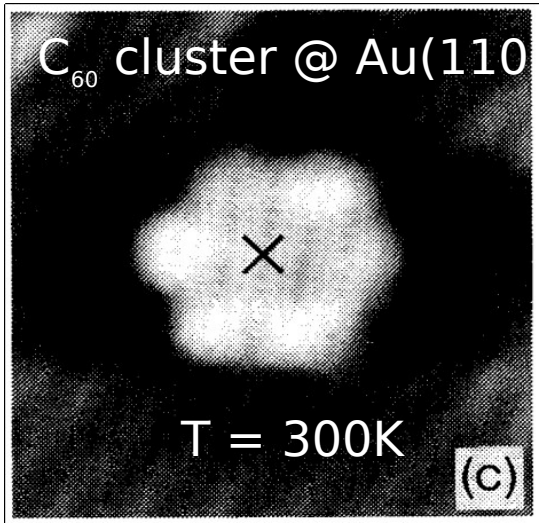
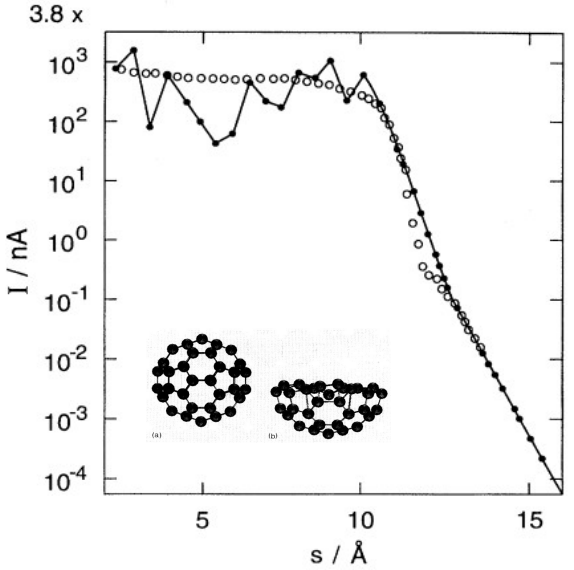
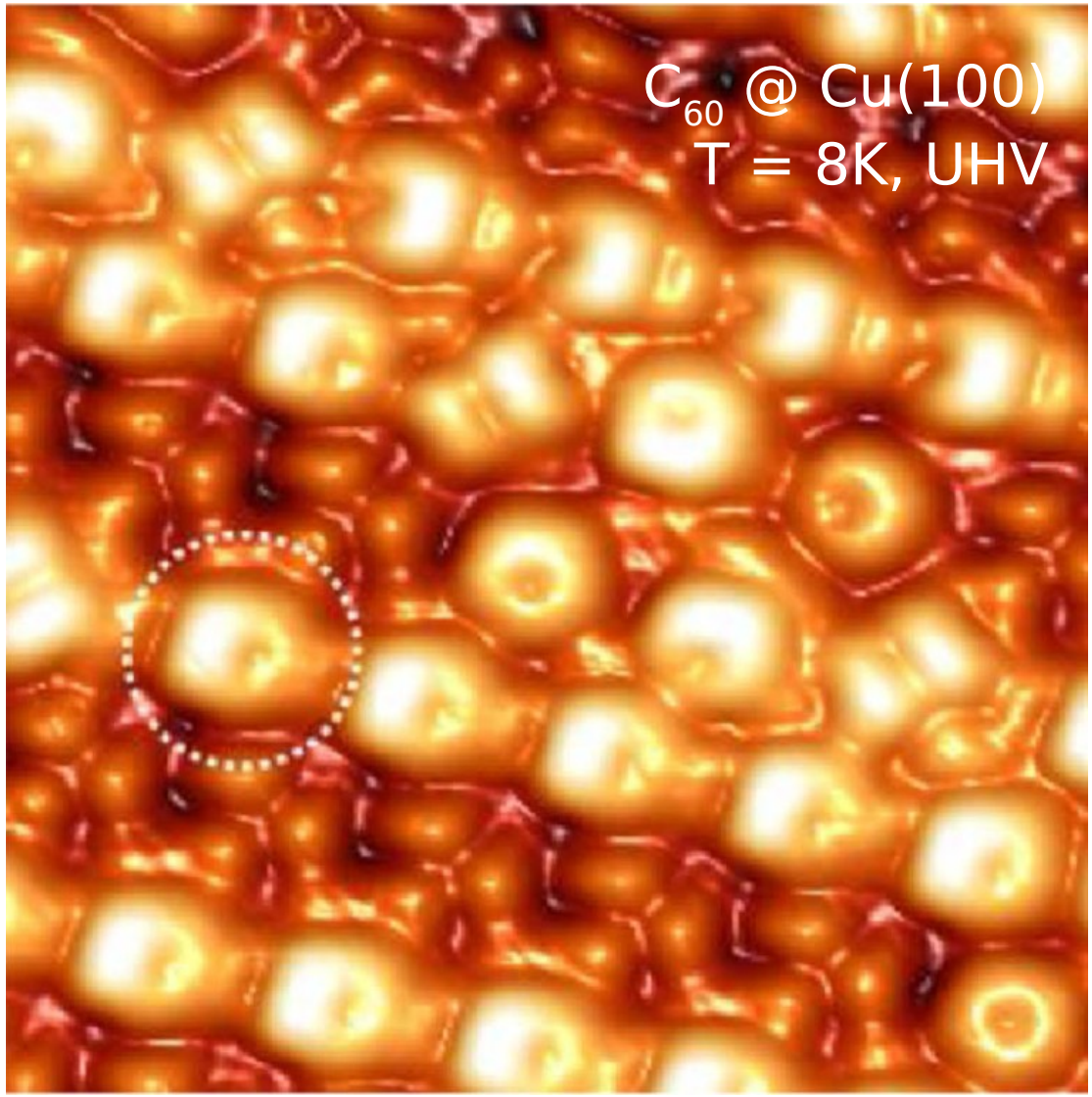
(Received 5 July 1994)

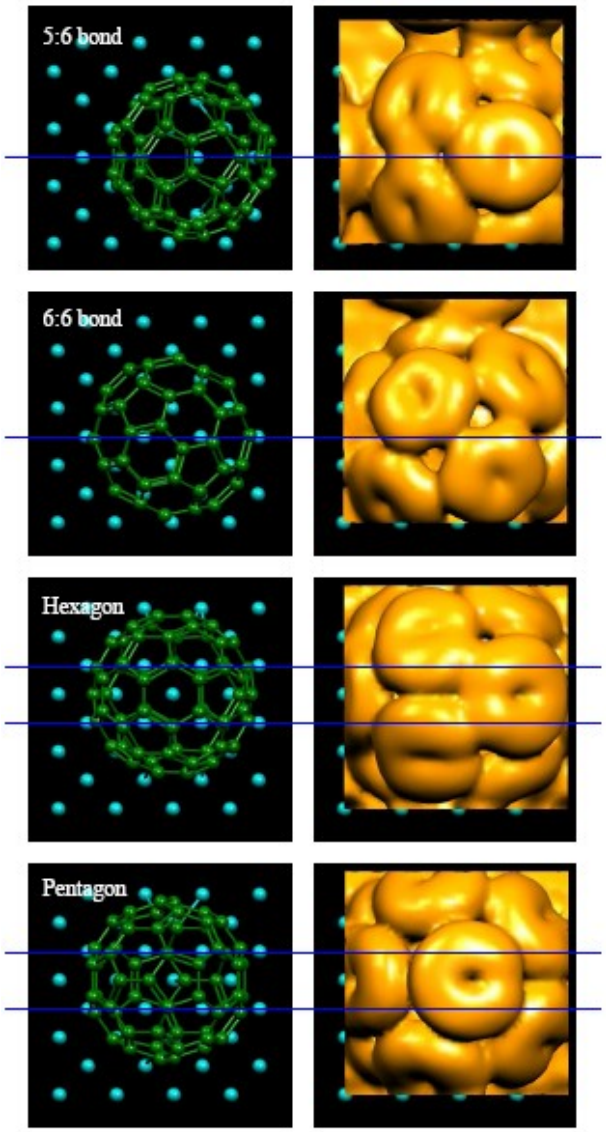
We report the first study of electrical contact with an individual molecule (C_{60}). Using a scanning tunneling microscope tip, the electrical current I flowing as a function of tip displacement s towards the molecule is investigated [$I(s)$ characteristics]. The tunneling current increases approximately exponentially with tip displacement in the tunnel regime, but this behavior changes significantly as contact is established. From the $I(s)$ data and calculations for C_{60} we determine an apparent electrical resistance of 54.80 MΩ for the junction at "tip contact." In the Landauer formalism, this value is a measurement of the electronic transparence 2.35×10^{-4} of the molecule under the tip.





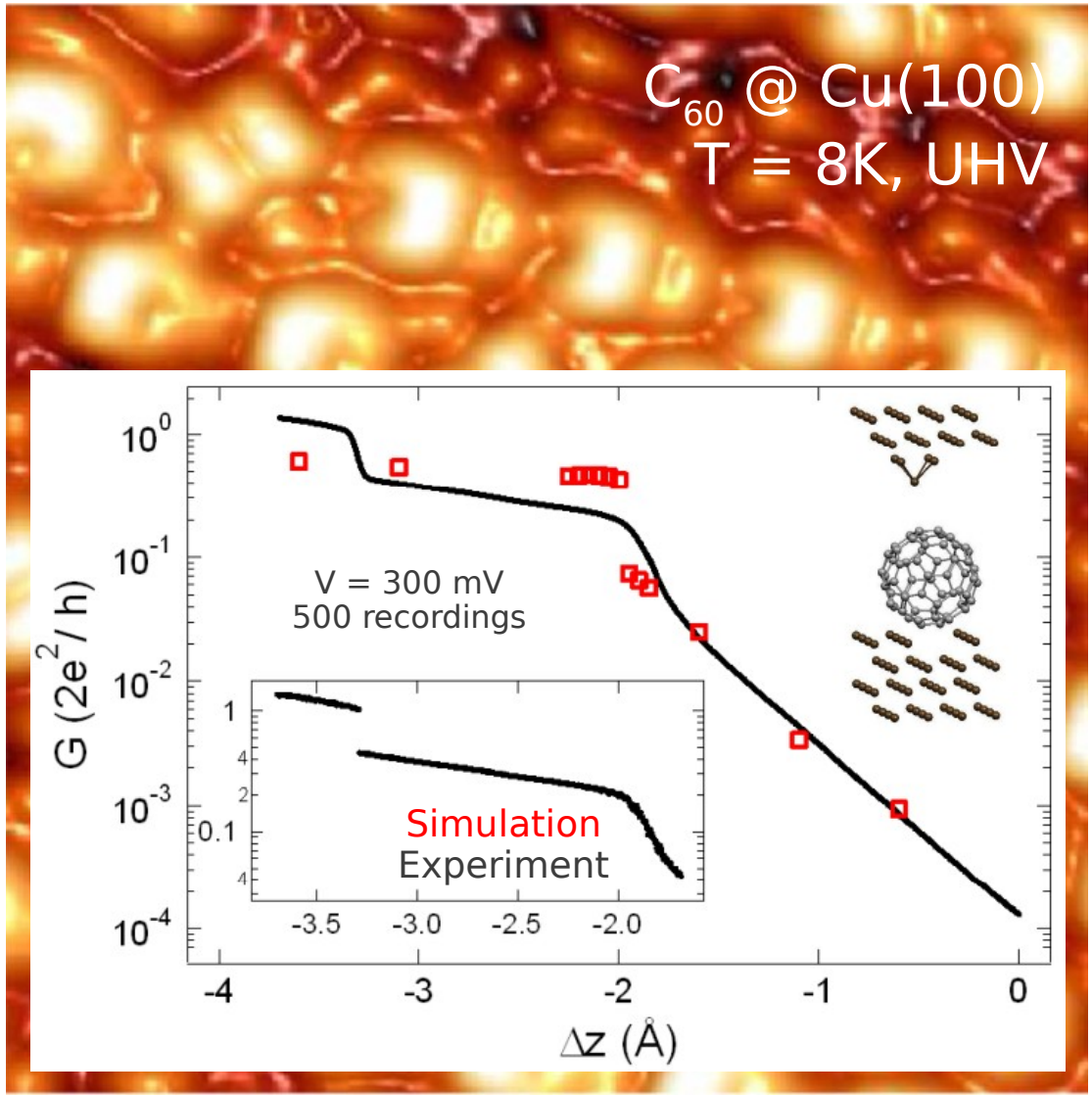
Controlled contact with the STM

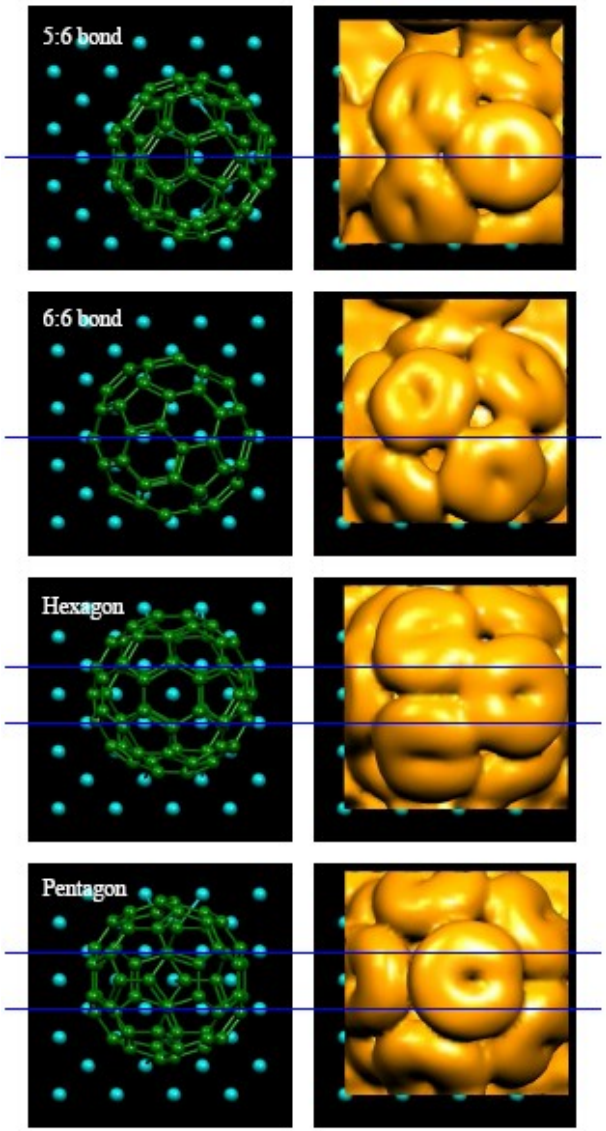




N. Néel, J. Kröger, L. Limot, TF, M. Brandbyge, R. Berndt, PRL 98, 065502 (2007)

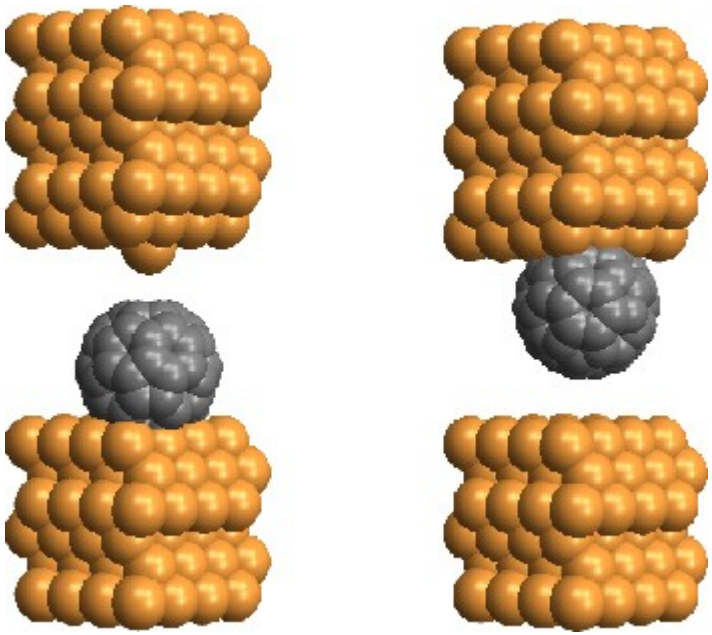
Controlled contact with the STM





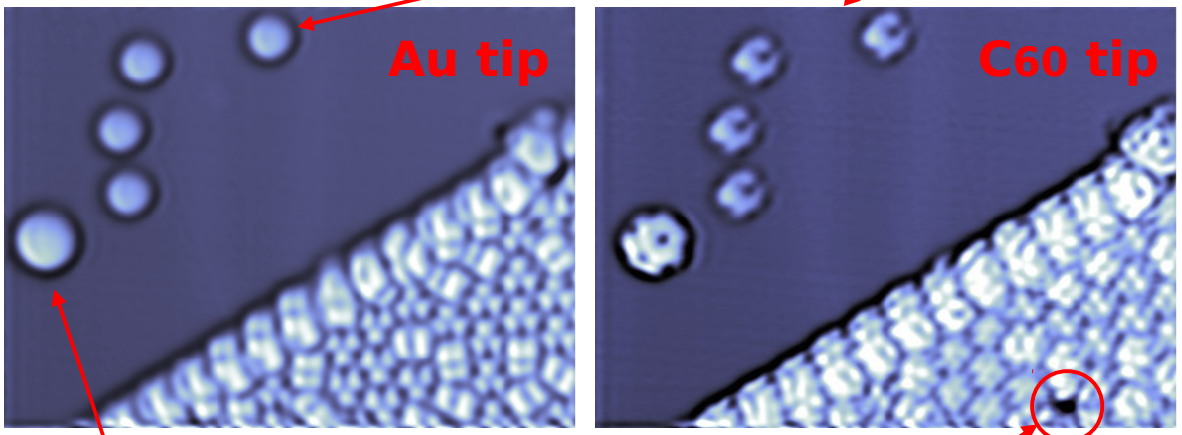
N. Néel, J. Kröger, L. Limot, TF, M. Brandbyge, R. Berndt, PRL 98, 065502 (2007)

Attaching a C_{60} molecule to the STM tip



Experimental procedure:
1. Position metallic tip over target C_{60} molecule
2. Set constant current (100nA)
3. Ramp voltage from 2V to 0.01V and back
4. C_{60} tips characterized by “reverse” imaging

Au adatoms on Au(111)



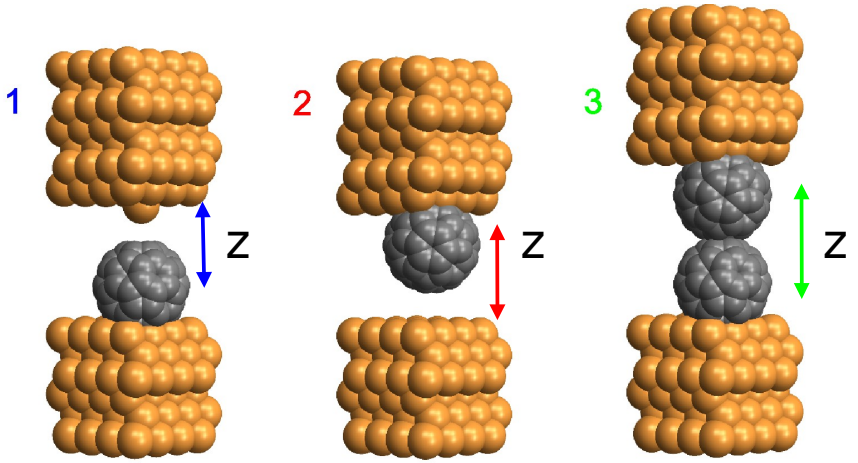
Cluster of Au adatoms

Hole after target C_{60} molecule was transferred to the tip

G. Schull, TF, M. Brandbyge, R. Berndt, PRL 103, 206803 (2009)

Contact experiments with C_{60} tips

Model structures for the three experiments:



Three experiments:

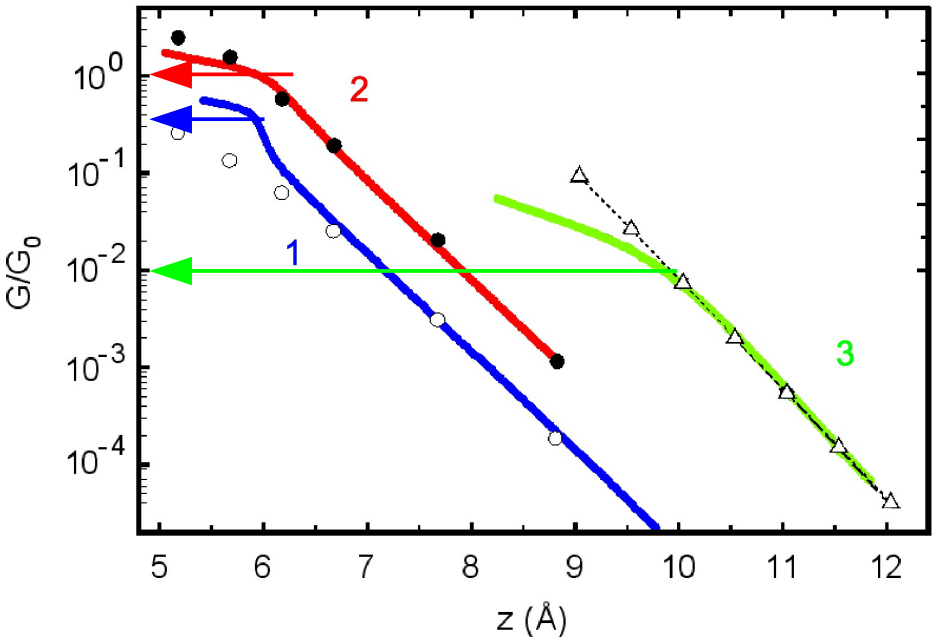
1. Metal tip to C60 molecule
2. C60 tip to flat Cu(111) surface
3. C60 tip to C60 molecule

What is the (maximum) conductance of these junctions?

$$G^{(2)} > G^{(1)} > G^{(3)}$$

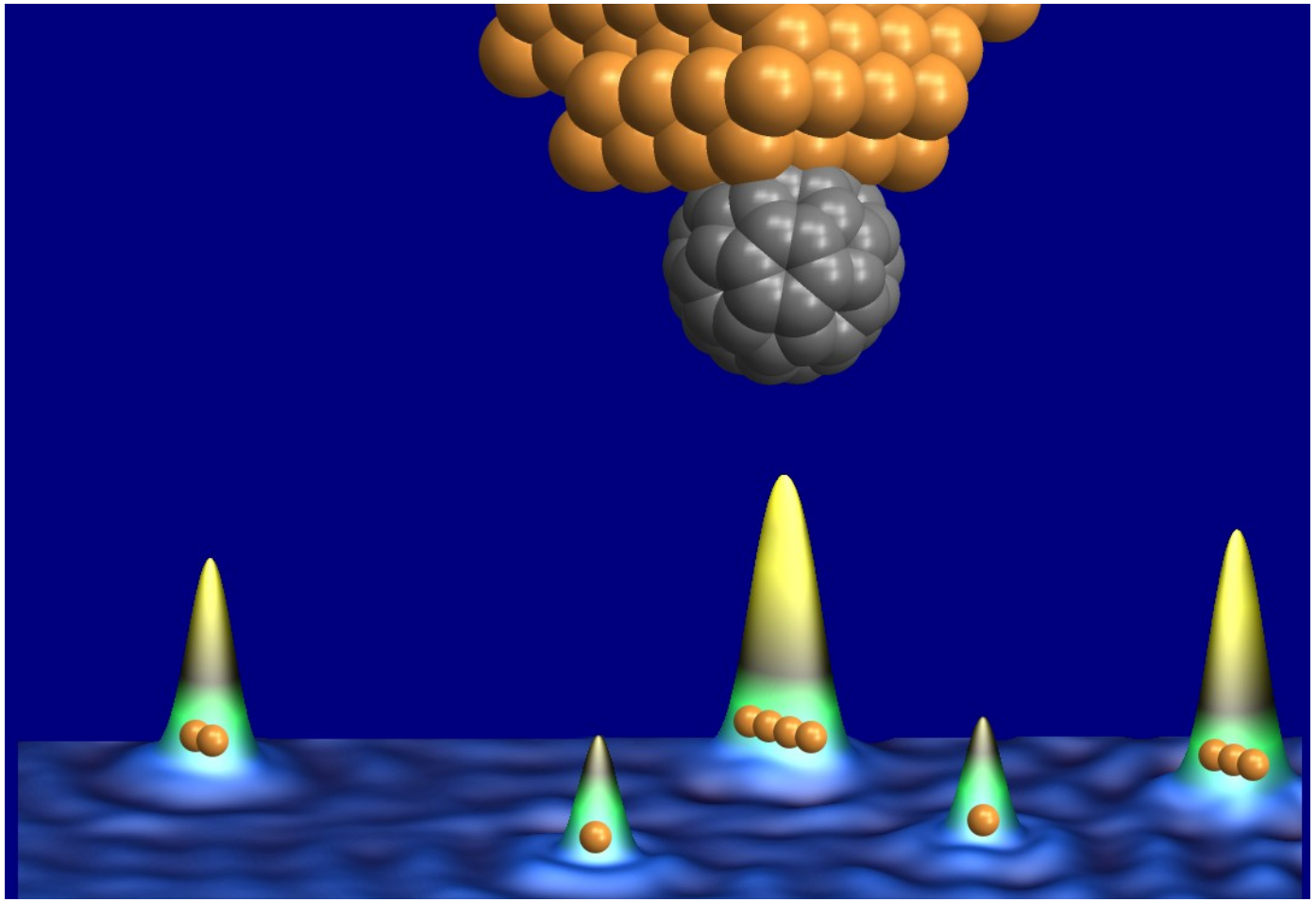
This tells us that:

- The conductance through a single C_{60} molecule is affected by the number of atomic contacts
- The conductance of a pair of C_{60} molecules is much lower than for for single molecules



Theory (symbols) allows to calibrate absolute distances of the experimental data (full lines)

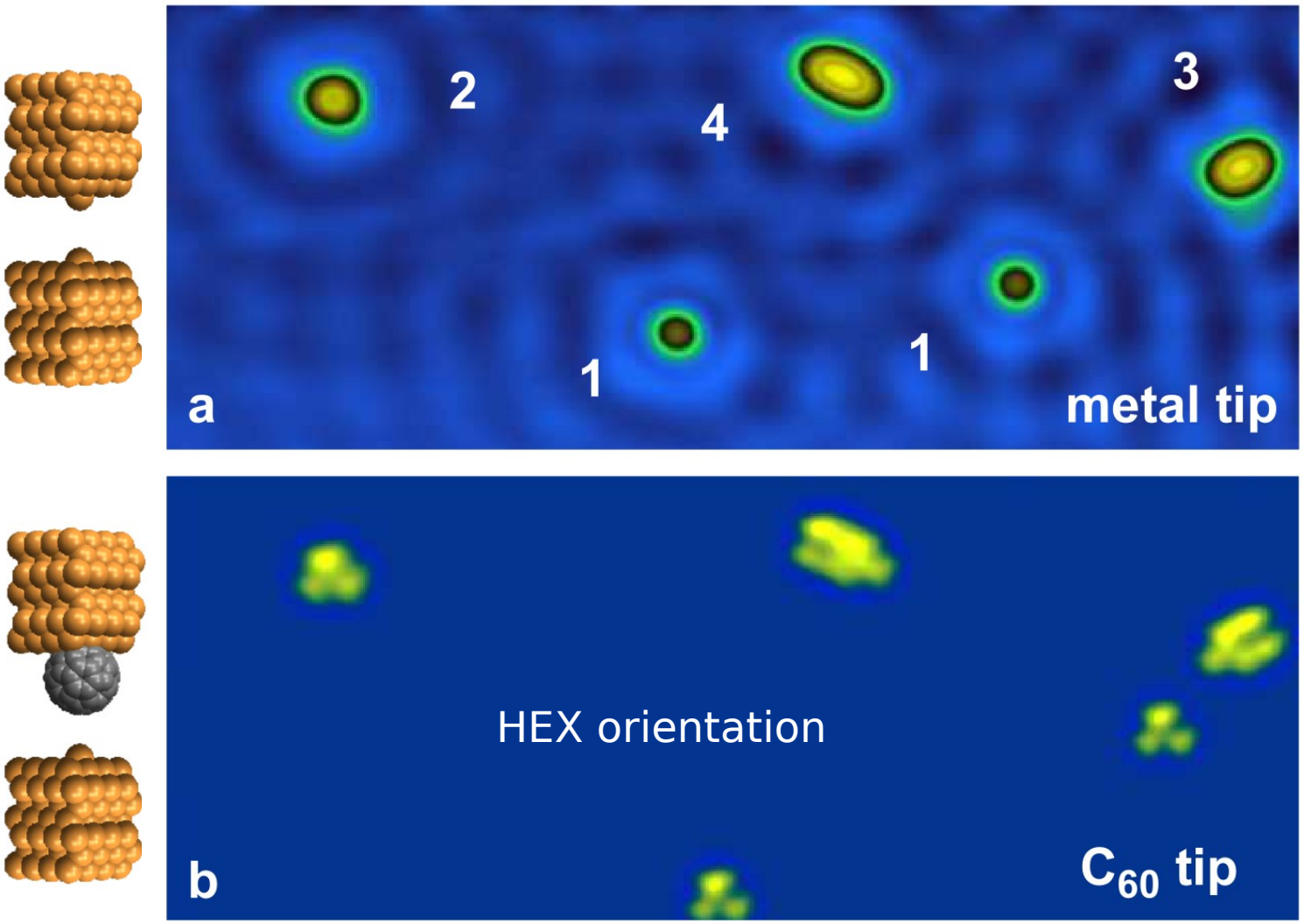
Atomic-scale engineering of the contacts



How does the conductance of a single C_{60} molecule depend on the number of contacting atoms?

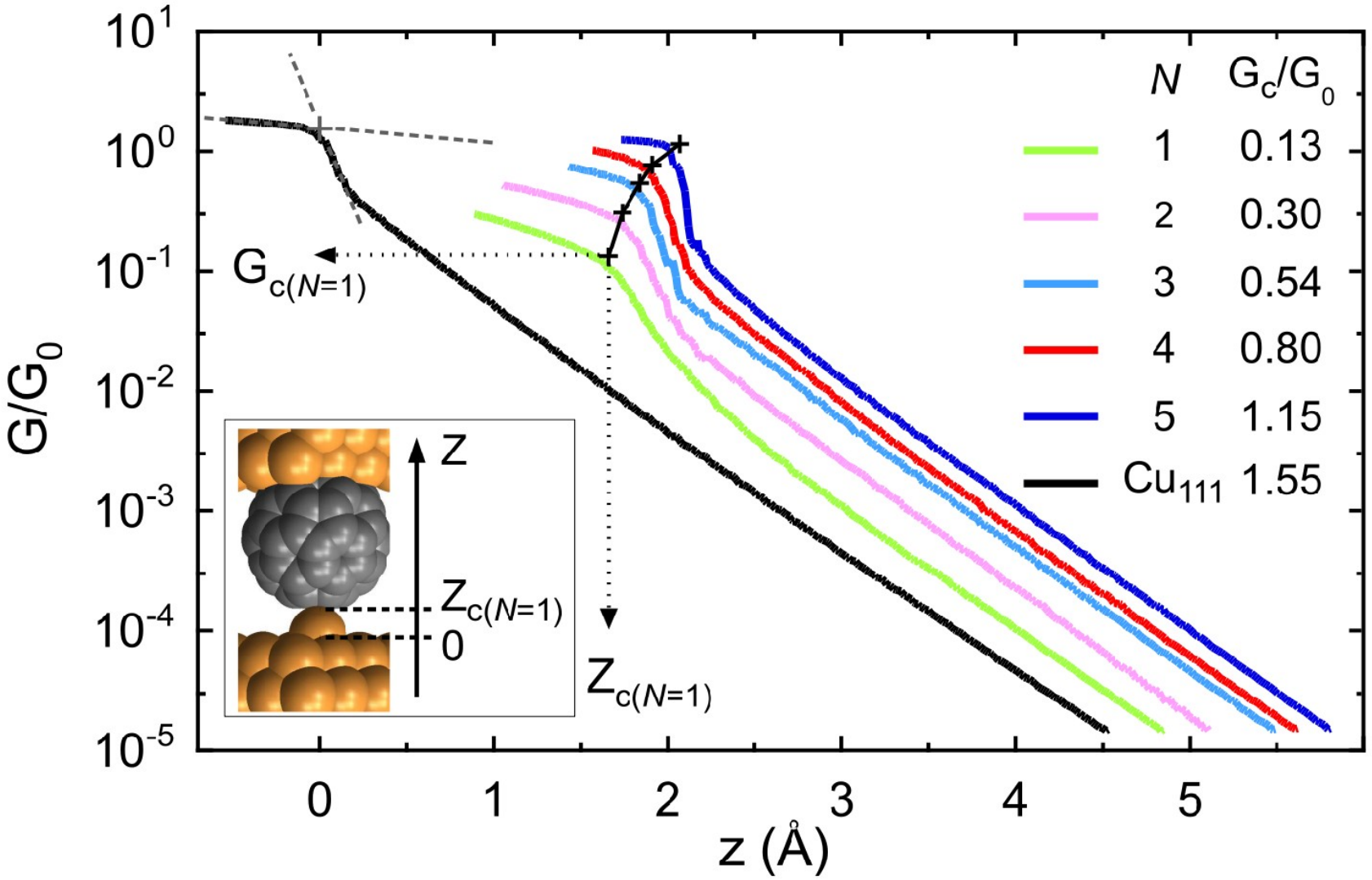
Atomic-scale engineering of the contacts

Preparing Cu adatoms on Cu(111)



How does the conductance of a single C_{60} molecule depend on the number of contacting atoms?

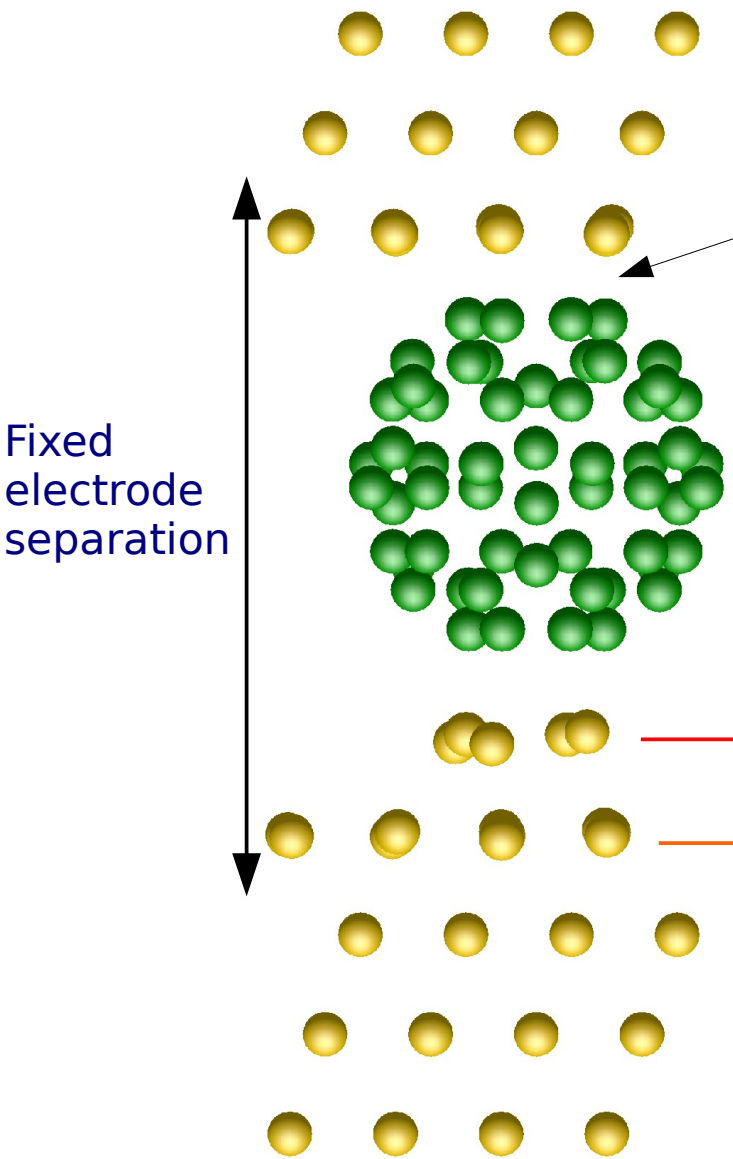
Experimental conductance traces



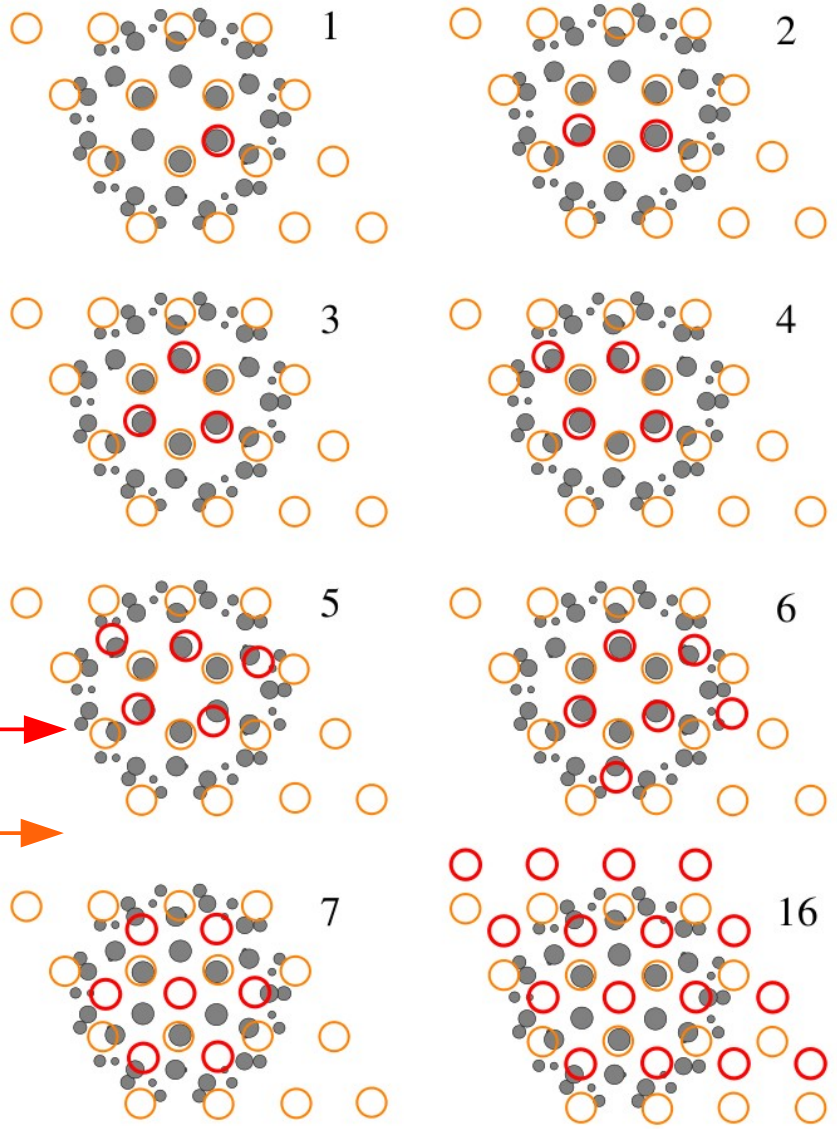
Contact conductance varies by more than an order of magnitude

Simulating contact geometries

Setup for DFT+NEGF calculations:

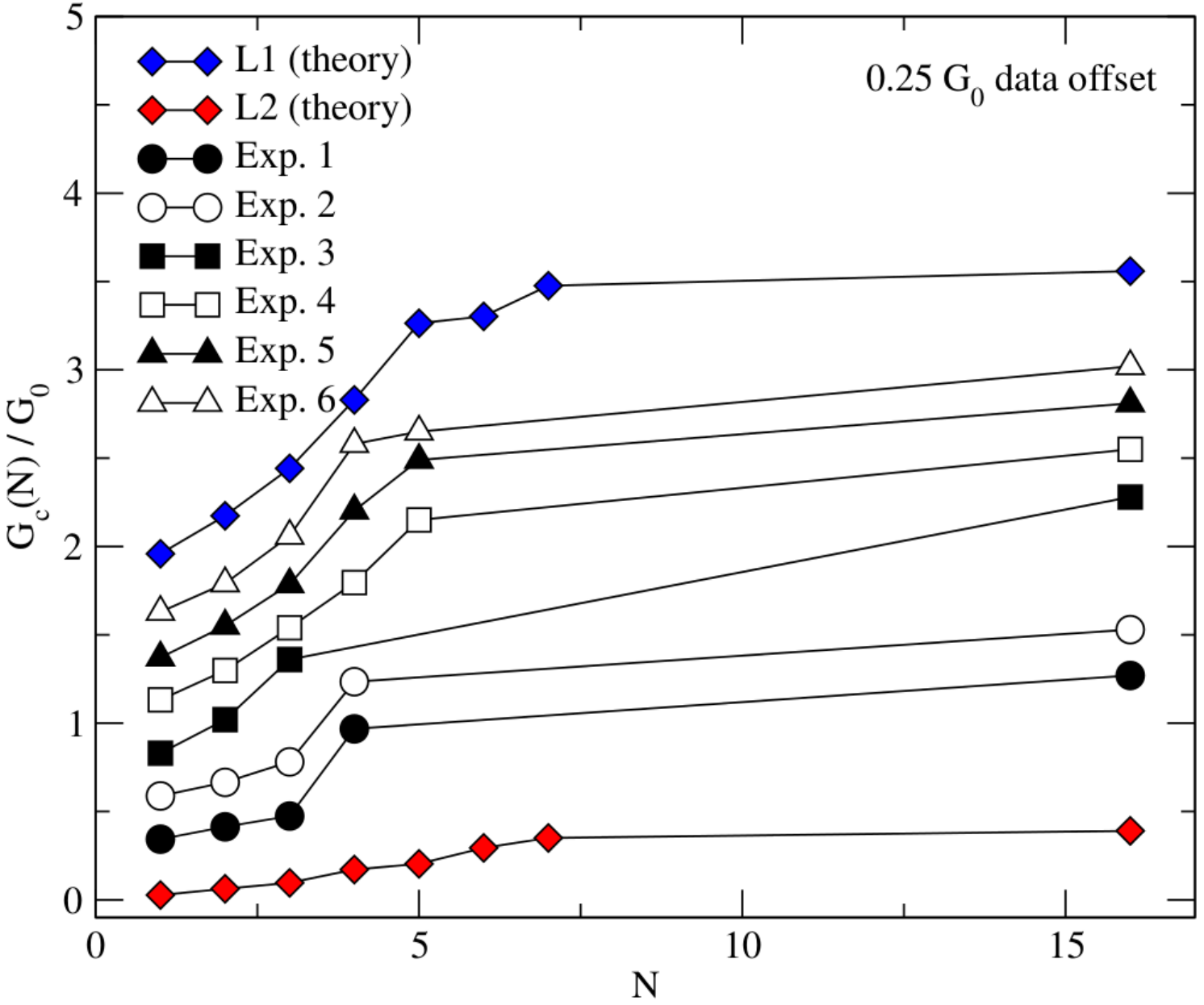


Relaxed cluster configurations:

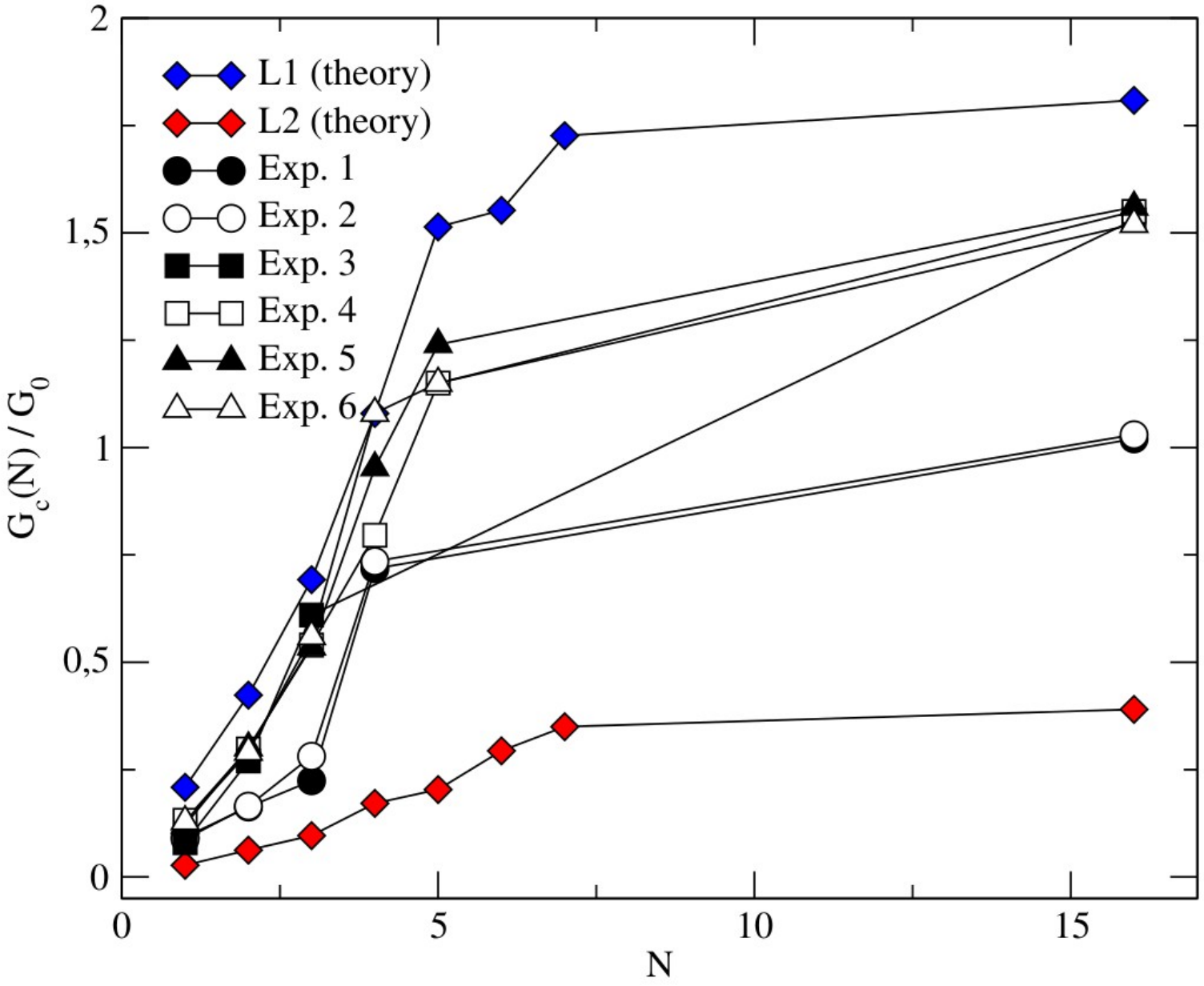


Projection of geometries onto plane parallel to substrate

Comparison: Experiment vs Theory



Comparison: Experiment vs Theory

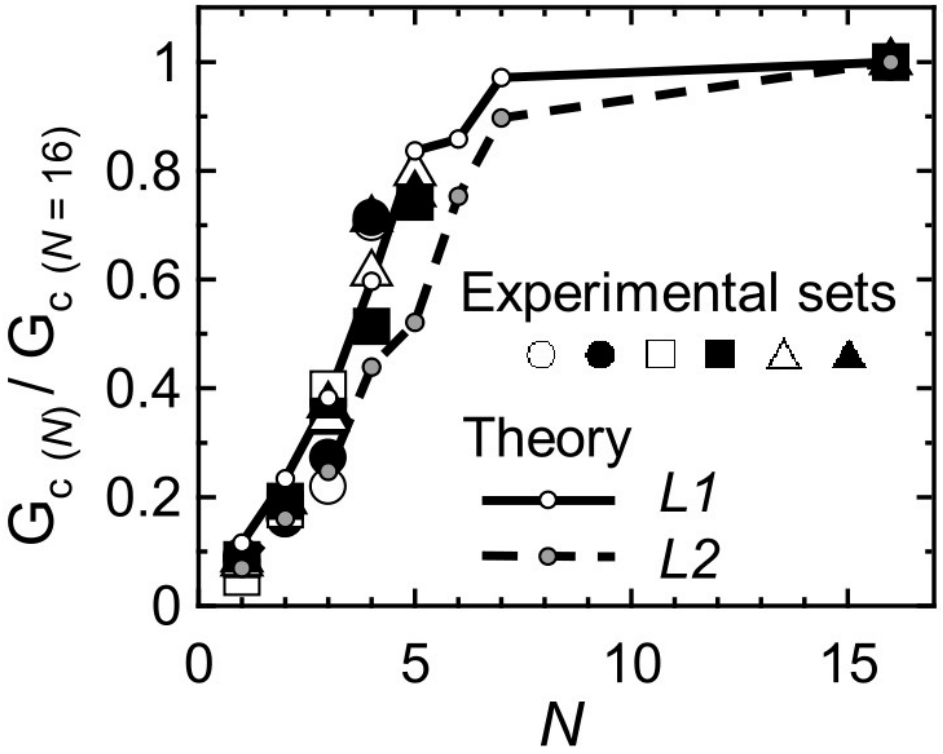


Theory part: Electrode separation

Exp. part: Variations in tip-molecule interface?

Comparison: Experiment vs Theory

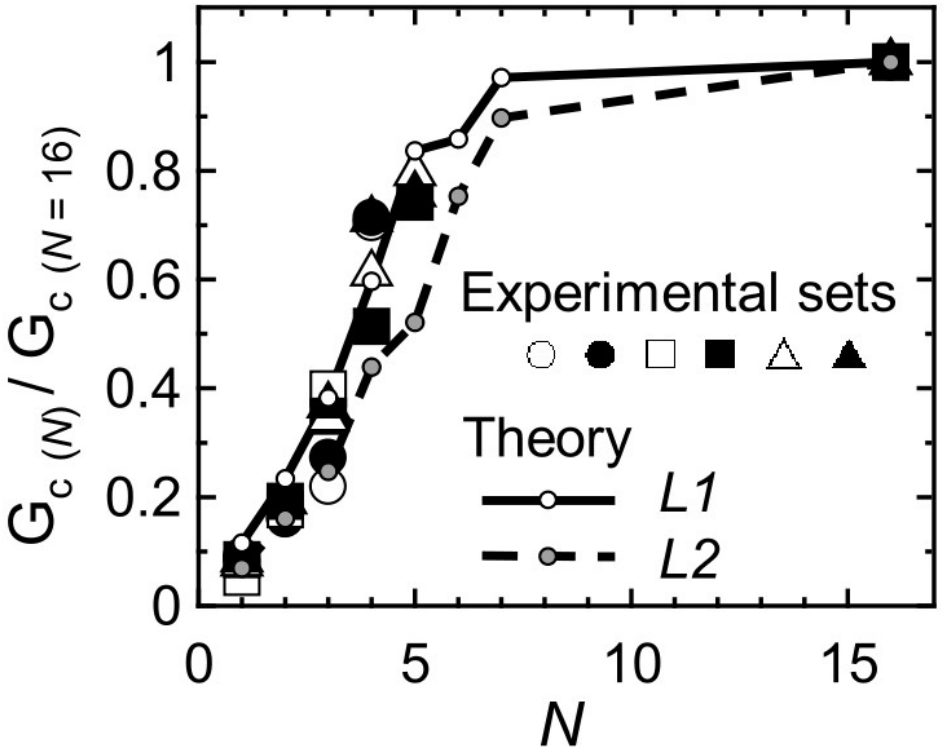
Theory: Two different electrode separations
Experiment: Clusters approached with 6 different tips

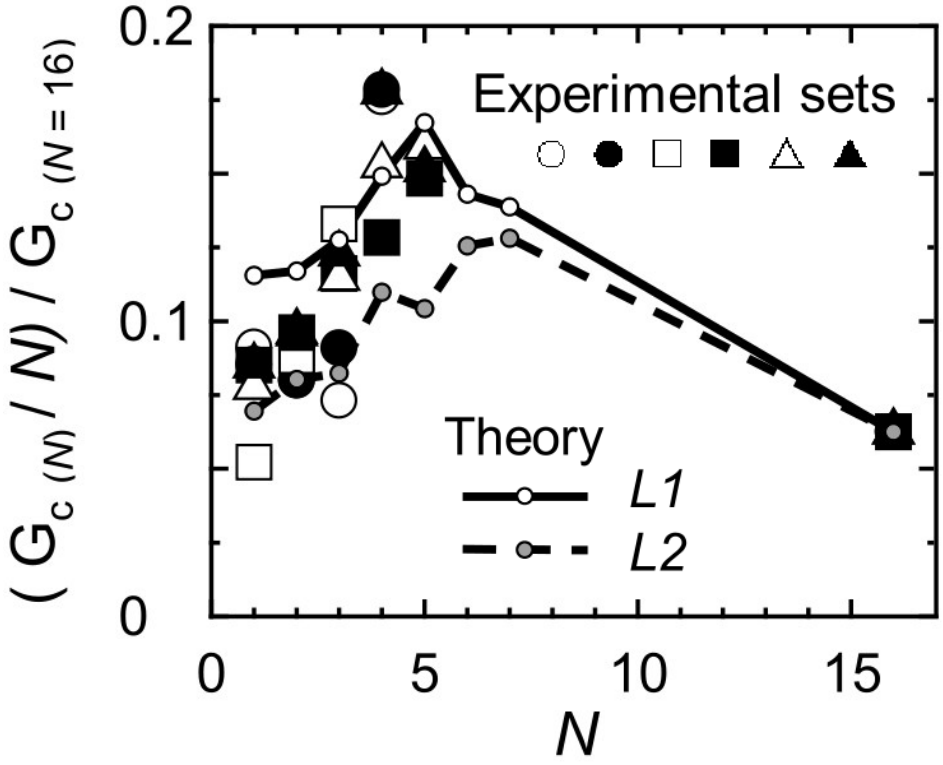


- Flat surface defined as $N = 16$
- Good agreement between theory and experiment
- $G(N)$ scales approximately linearly with N

Comparison: Experiment vs Theory

Theory: Two different electrode separations
Experiment: Clusters approached with 6 different tips

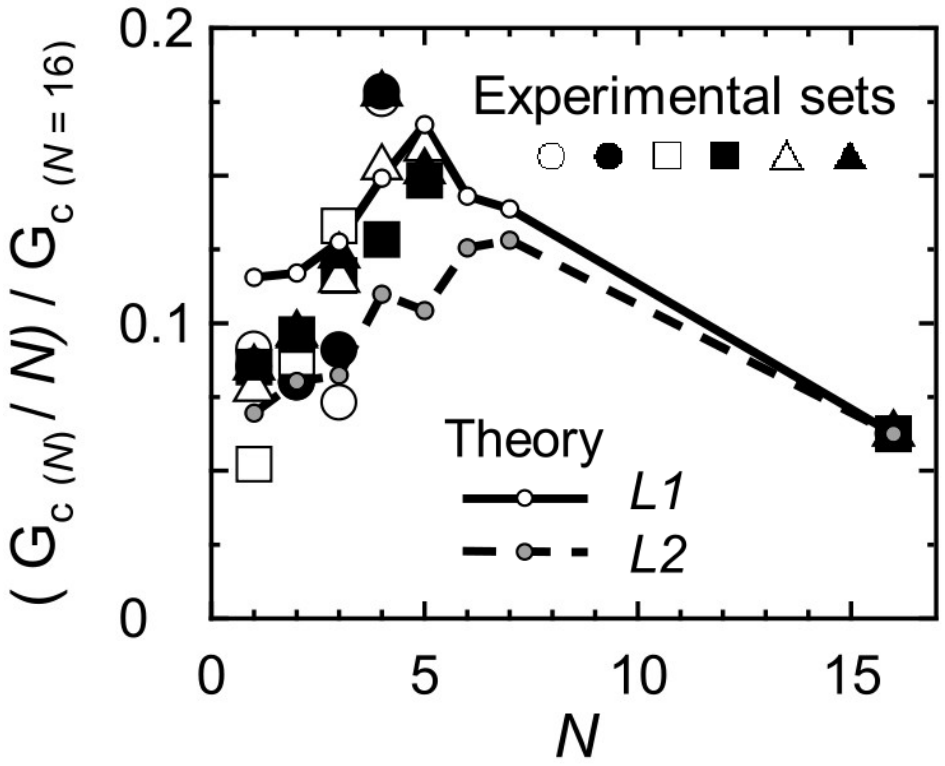




Comparison: Experiment vs Theory

Theory: Two different electrode separations
Experiment: Clusters approached with 6 different tips

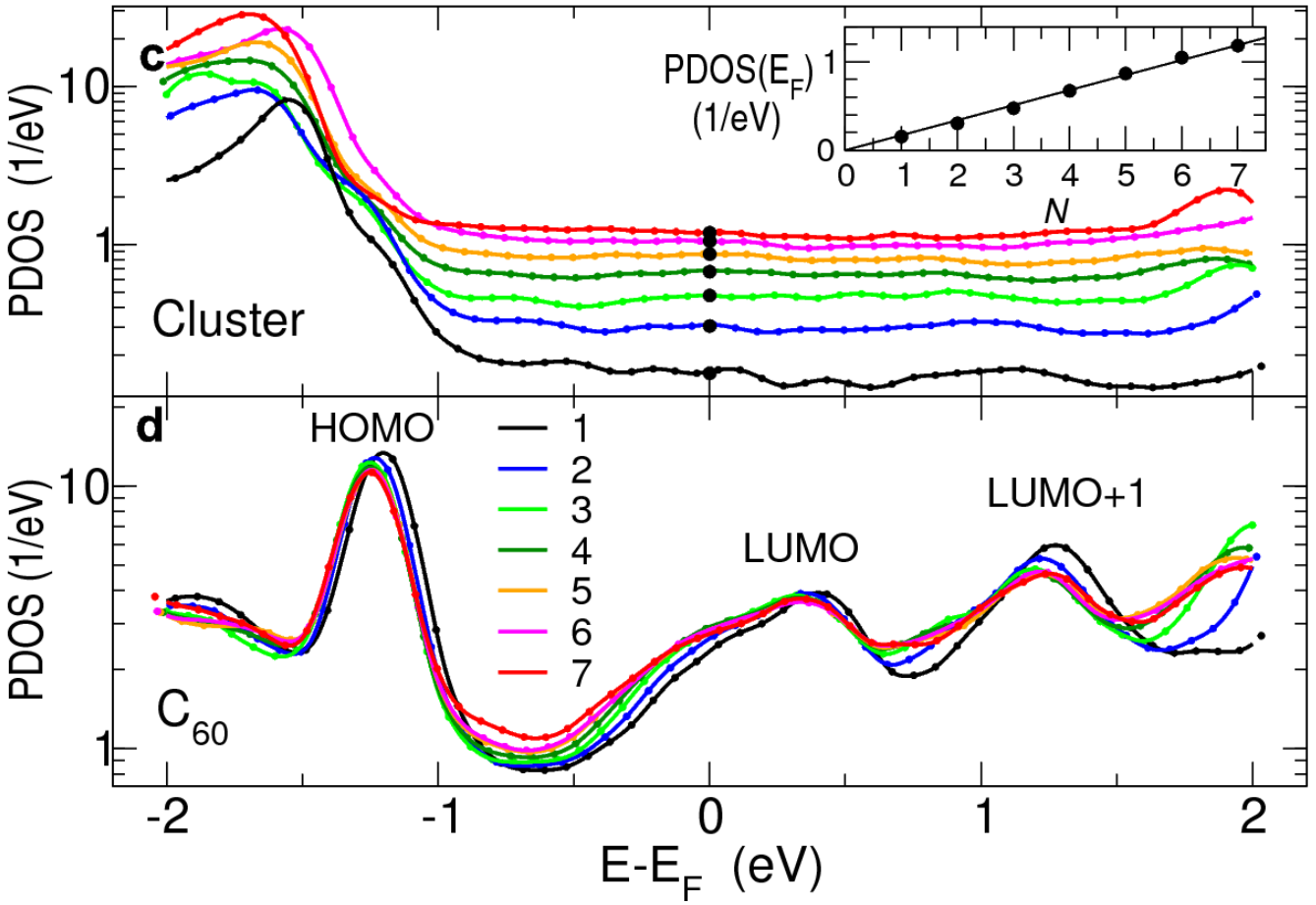
- Good agreement between theory and experiment
- *G(N)/N* grows with *N* for small *N*
- Maximum at *N = 5* marks crossover between cluster-size limited (“bad contact”) and molecule-limited (“good contact”) transport regimes

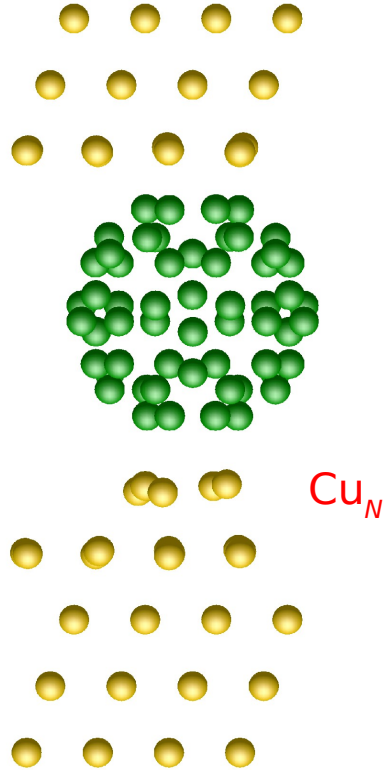


Origin of the super-linear increase?

$$T(E) = Tr[\ \Gamma_{tip}(E)\ G(E)\ \Gamma_{CuN}(E)\ G^{\dagger}(E)\ ]$$

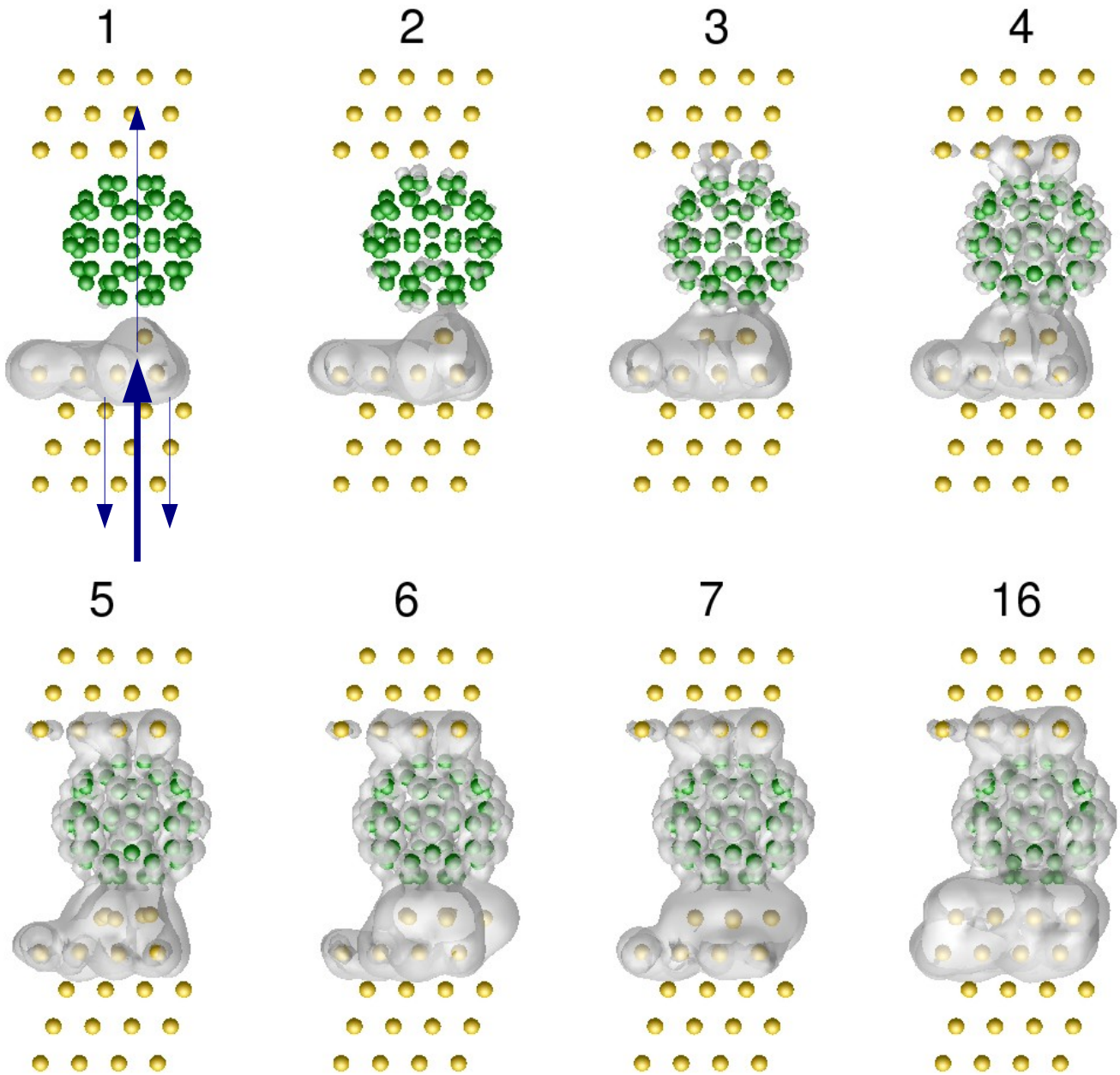
$\Gamma_{CuN}(E) \sim V^2\ DOS(E)$; $G(E) = [E - H + i\Gamma_{tip}/2 + i\Gamma_{CuN}/2]^{-1}$





G. Schull, TF, A. Arnau, D. Sanchez-Portal, R. Berndt, Nature Nanotechnol. 6, 23 (2011)

Visualization of transmission eigenchannels



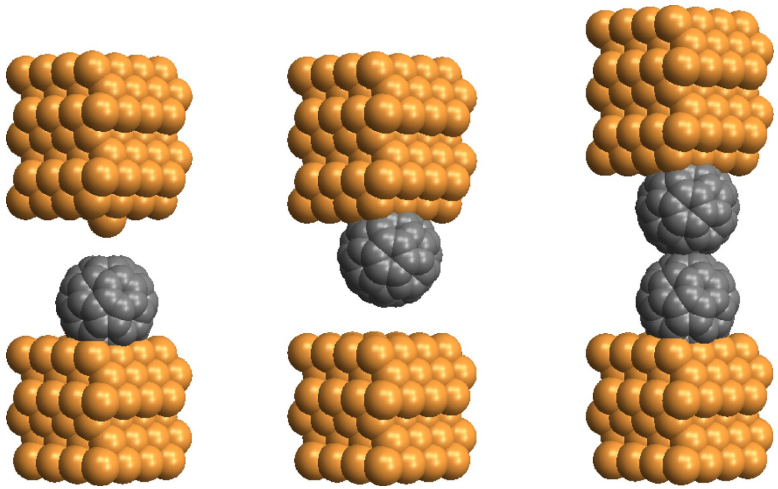
M. Paulsson and M. Brandbyge, PRB 76, 115117 (2007)

- Incoming electron waves from below
- Flux density at $E=E_F$
- Sum over three most transmitting channels
- Scattering states only calculated in region defined by topmost Cu layers
- Around $N = 5$ no specific part singled out as “bottleneck”

G. Schull, TF, A. Arnau, D. Sanchez-Portal, R. Berndt, Nature Nanotechnol. 6, 23 (2011)

Conclusions and outlook

- Demonstration of atomic-scale engineering of contact interfaces
- Contact geometry strongly influences on electronic conduction
- Conductance of a single C_{60} junction varies up to a factor 20
- “Good” and “bad” contact regimes identified for C_{60} (crossover $N \sim 5$)
- DFT+NEGF simulations reproduces quantitatively exp. results
- Theory provides insight into mechanisms controlling transport
- Molecular orientation? Contact position?



Acknowledgments

Experiment:

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Depto. Física de Materiales UPV/EHU