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Perspectives of Molecular Manipulation and Fabrication

September 28, 2016 | F. S. Tautz
Peter Grünberg Institut, Forschungszentrum Jülich

Workshop I, Machnine Learning Meets Many-Particle Problems,
Long Program „Understanding Many-Particle Systems with Machine Learning“,
Institute for Pure and Applied Mathematics, UCLA

Feynman‘s Vision

„There is plenty of room at the bottom“
(R. Feynman, APS meeting, Pasadena, December 1959)

→ inspired the nanoscience revolution

Nanoscience in broad sense: Every activity involving structures smaller than 100 nm

But: Feynman had a more specific vision:

miniaturized **manufacturing** and **fabrication technology** in analogy with macroscopic world, but ultimately **at the atomic scale.**

The Grand Challenge

A universal **molecular assembly machine**

„3D printing“ of molecular structures
at the single molecule level.

The Prize

Making and harnessing artificial molecular nanostructures

There is a lot of activity in this direction...

- Study biological examples
- Develop concepts of artificial functional nanostrucures:

  Inspiration by nature + physical and chemical intuition + simulations
- Design and synthesis of appropriate molecules

- But: How to assemble the molecular building blocks?

Self-assembly ?

Directed manufacture !

Where Do We Stand?

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Scanning Tunneling Microscopy

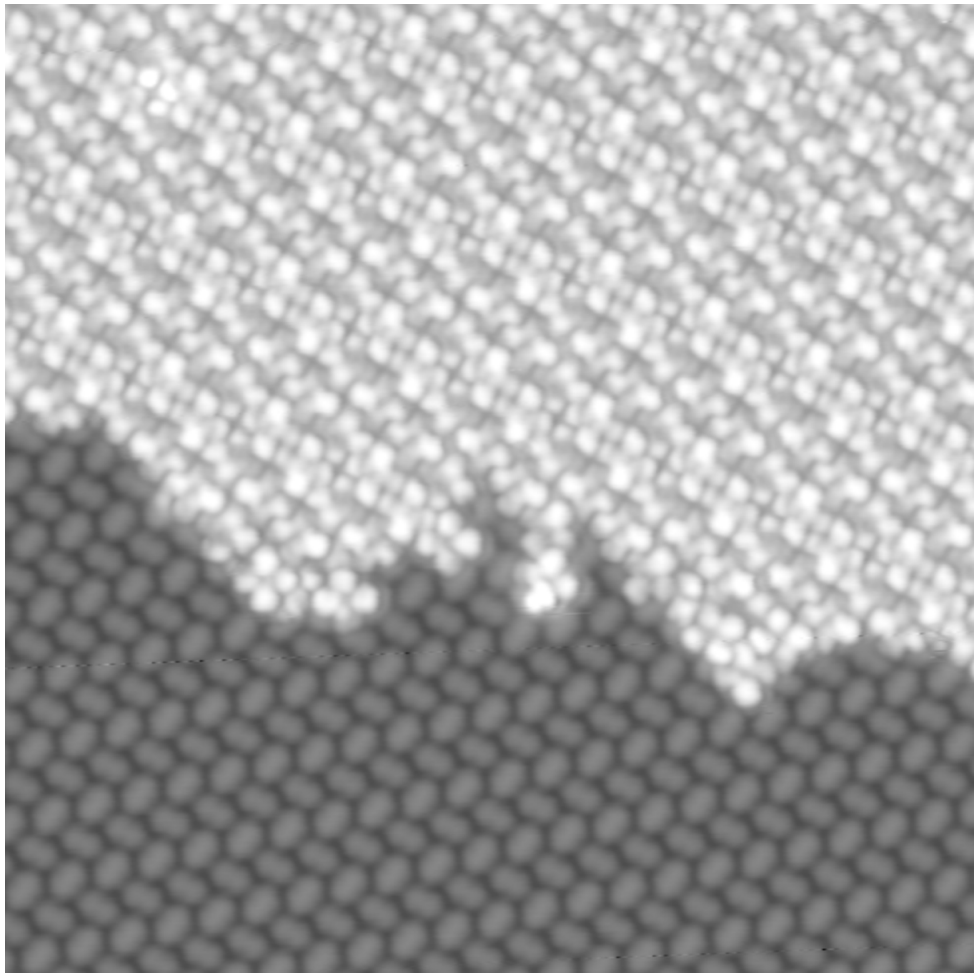
Binnig and Rohrer, Nobel Prize in Physics in 1984

B. Voigtländer, Forschungszentrum Jülich

Where Do We Stand?

Scanning Tunneling Microscopy

Binnig and Rohrer, Nobel Prize in Physics in 1984



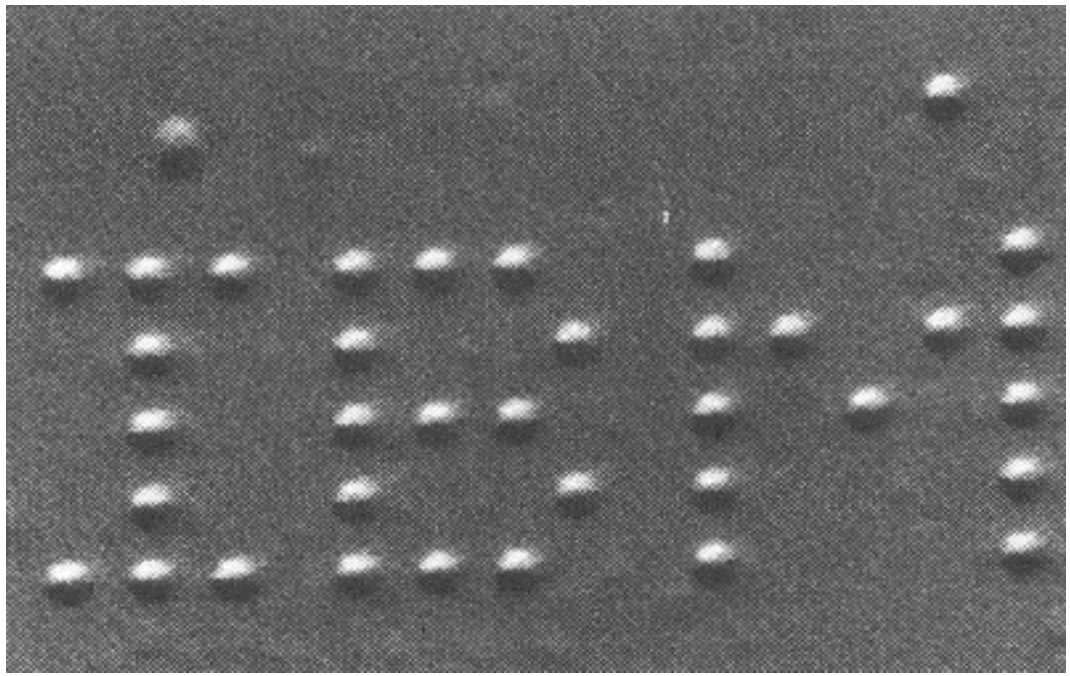
Where Do We Stand?

Scanning Tunneling Microscopy

Binnig and Rohrer, Nobel Prize in Physics in 1984

STM @ Low temperature: Immobilize single atoms and molecules (Xe on Nickel)

Eigler and Schweizer 1990



SPM and Molecular Fabrication

- Cannot work atom-by-atom: Energy released when covalent bonds form is disruptive in weakly bonded structures

  → work with molecules

- Cannot use **push, pull, pick-up – transfer – drop approaches**, because molecules are anisotropic and floppy (many internal degrees of freedom).

  → need a more controlled approach

- **„Complexity Gap“** (information gap, control gap)

  Many degrees of freedom to be measured / controlled

  vs.

  Two quantities (force, conductance) that can be measured and three degrees of freedom that can be controlled (tip)

Perspectives of Molecular Manipulation & Fabrication

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- Two-Contact Manipulation
- Determining van der Waals Coefficients
- Molecular Manipulation Lab (MomaLab)
- The Connection to Machine Learning

Two-Contact Manipulation

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Atomic Manipulation

Since Eigler, manipulation techniques have not changed

push, pull, pick-up – transfer – drop

(Logic gates, movie, ...)

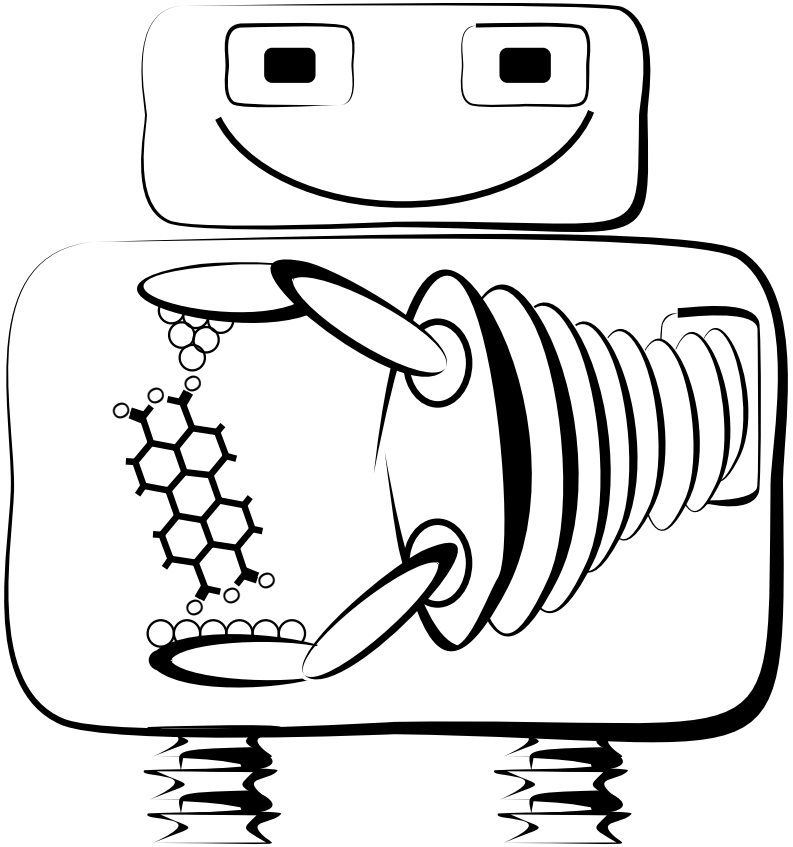
Drawbacks:

- Essentially, these are **stochastic** techniques: During key steps of manipulation, the **control is lost**
- This presents a **serious limitation for molecular** (as opposed to atomic) **manipulation**

Two-Contact Manipulation

At any time, **two contacts** to the entity to be manipulated are maintained.

- Fully **deterministic** (at least in principle)
- **Internal degrees of freedom** become addressable



Two-Contact Manipulation

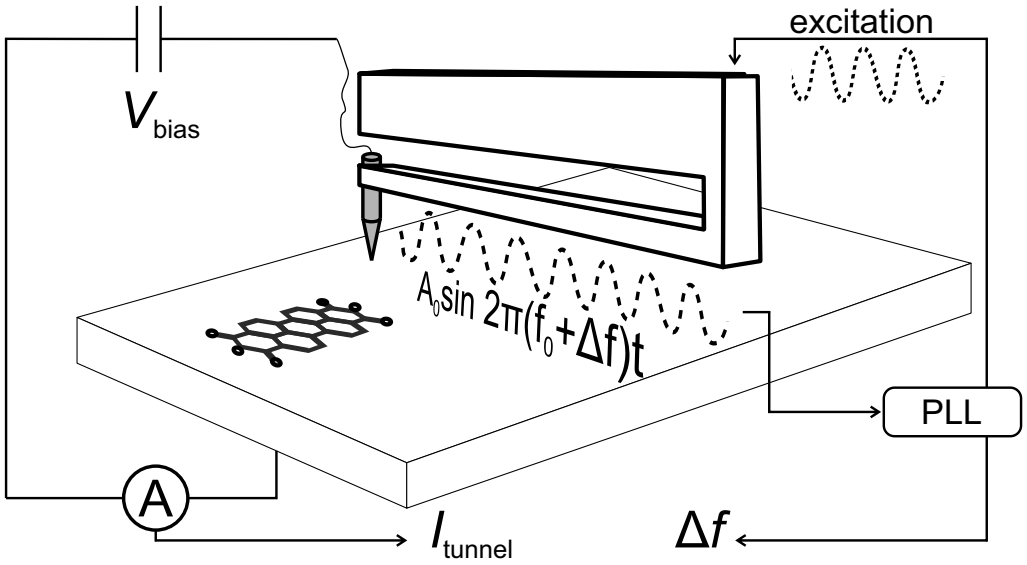
Desirables:

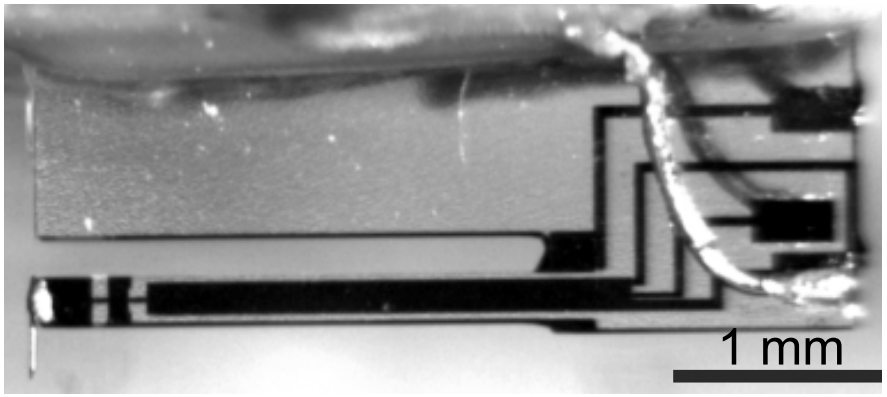
- As many information channels about the state of the junction
  → simultaneous STM and AFM (current and force)

Pre-requisites:

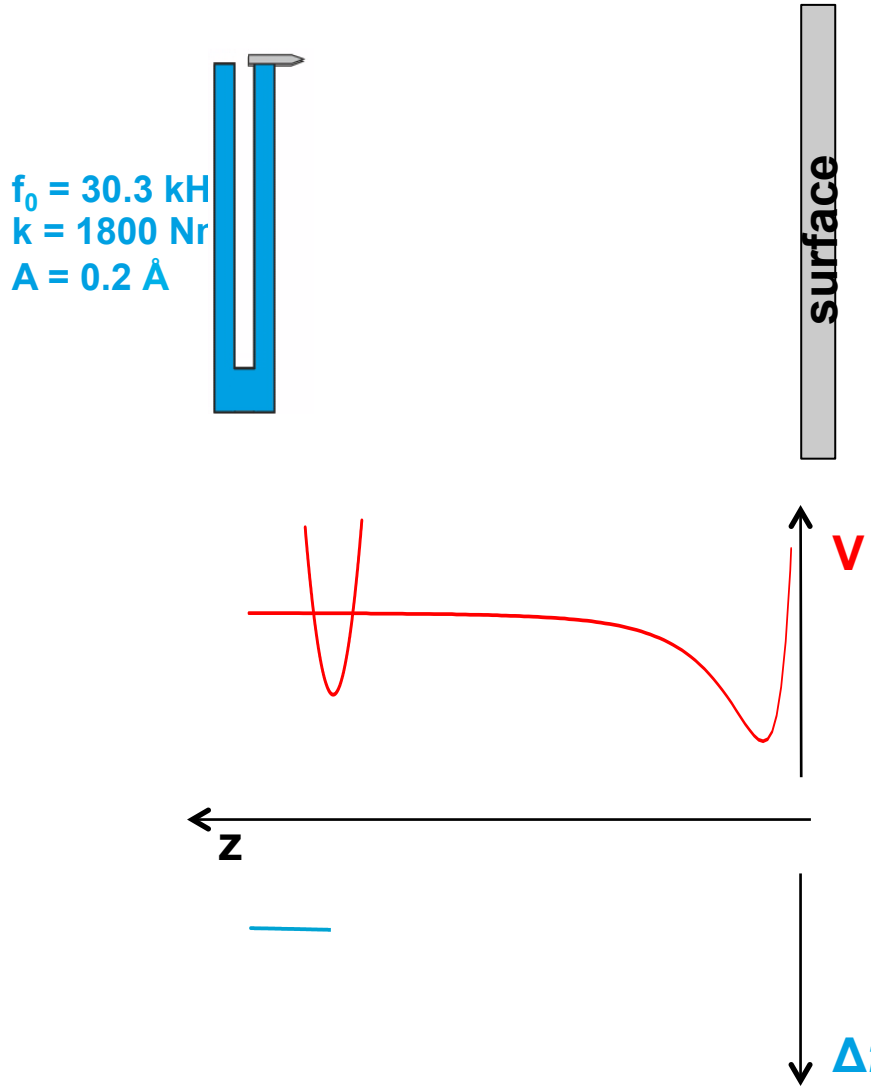
- Ultra-high vacuum
- Low temperature
- **Stiff cantilevers:** The force measuring unit must be able to counter all force gradients that arise during the experiment. (otherwise: temporary loss of control)

Dynamic Non-Contact Atomic Force Microscope





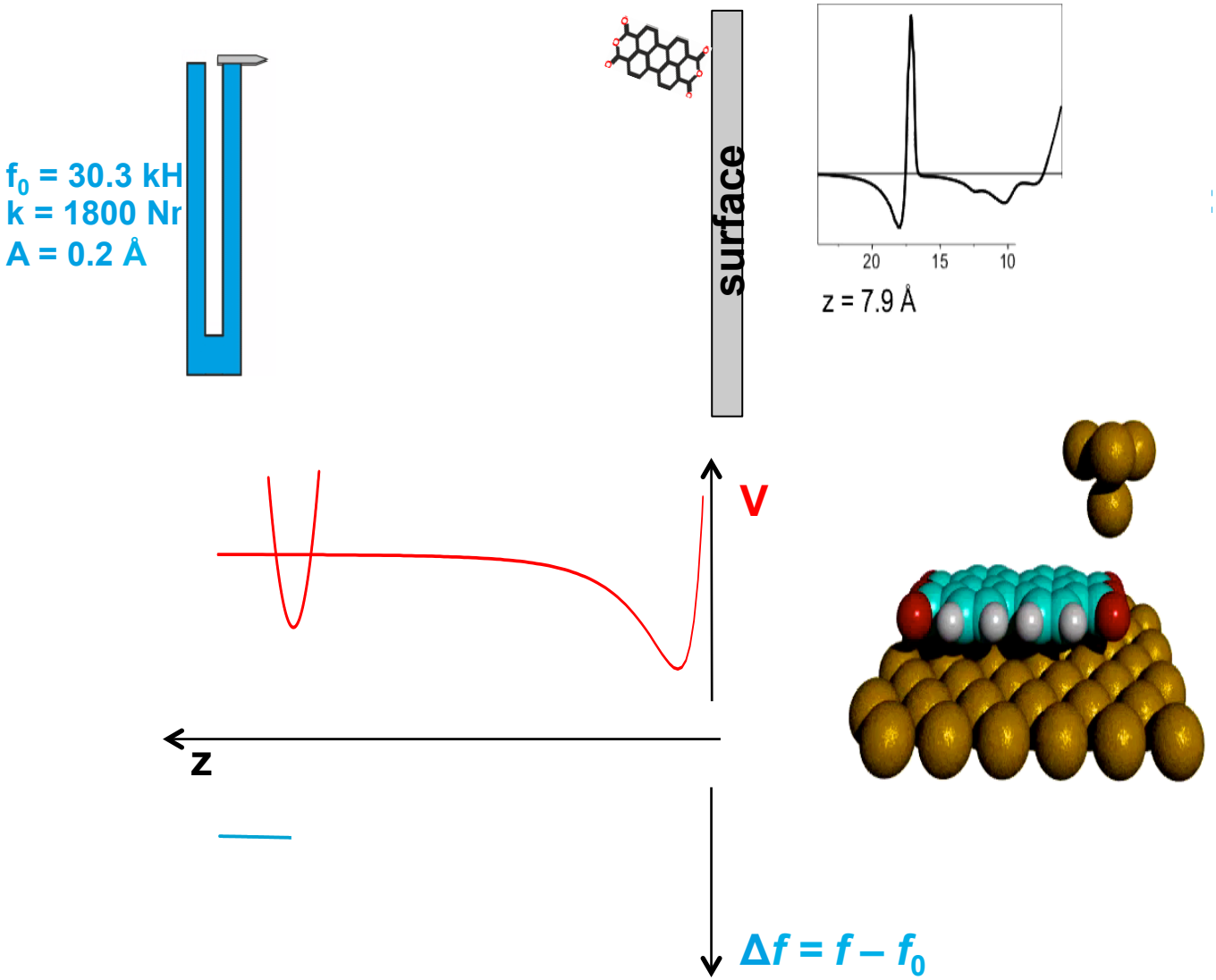
Dynamic Non-Contact Atomic Force Microscope



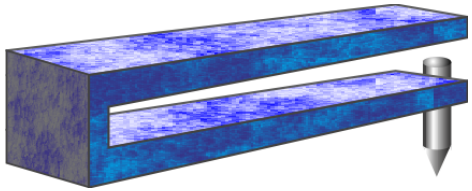
Tuning fork sensor:

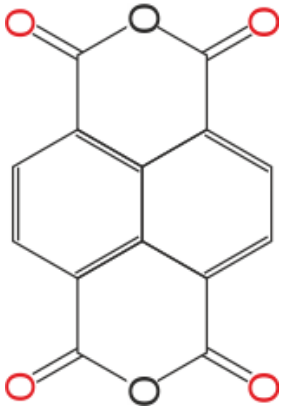
- **Current and force gradient measurement.**
- $dF_z/dz \approx 2k\Delta f / f_0$

Dynamic Non-Contact Atomic Force Microscope

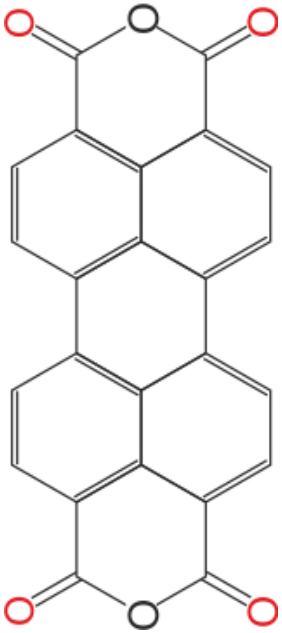


Two-Contact Manipulation

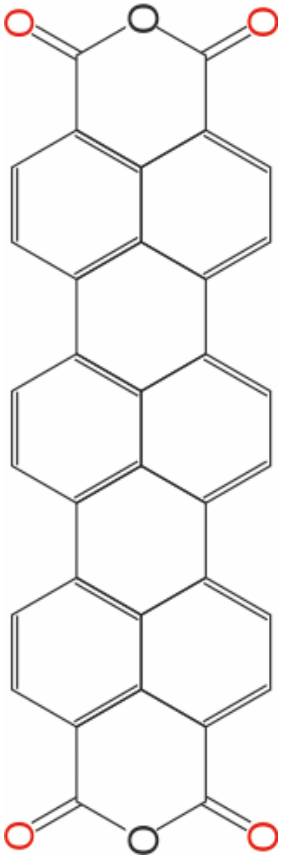




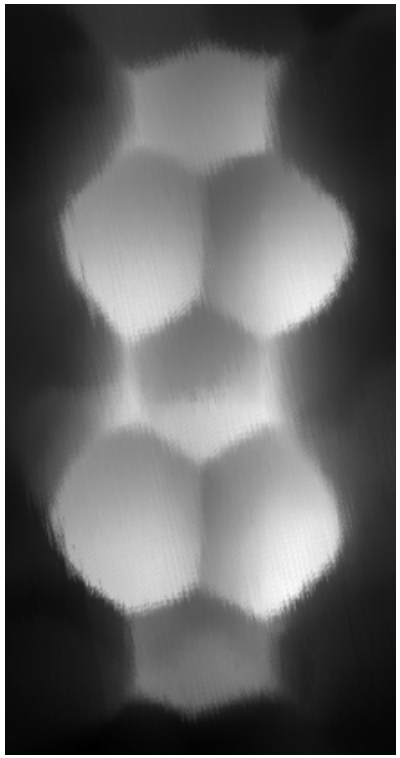
NTCDA



PTCDA

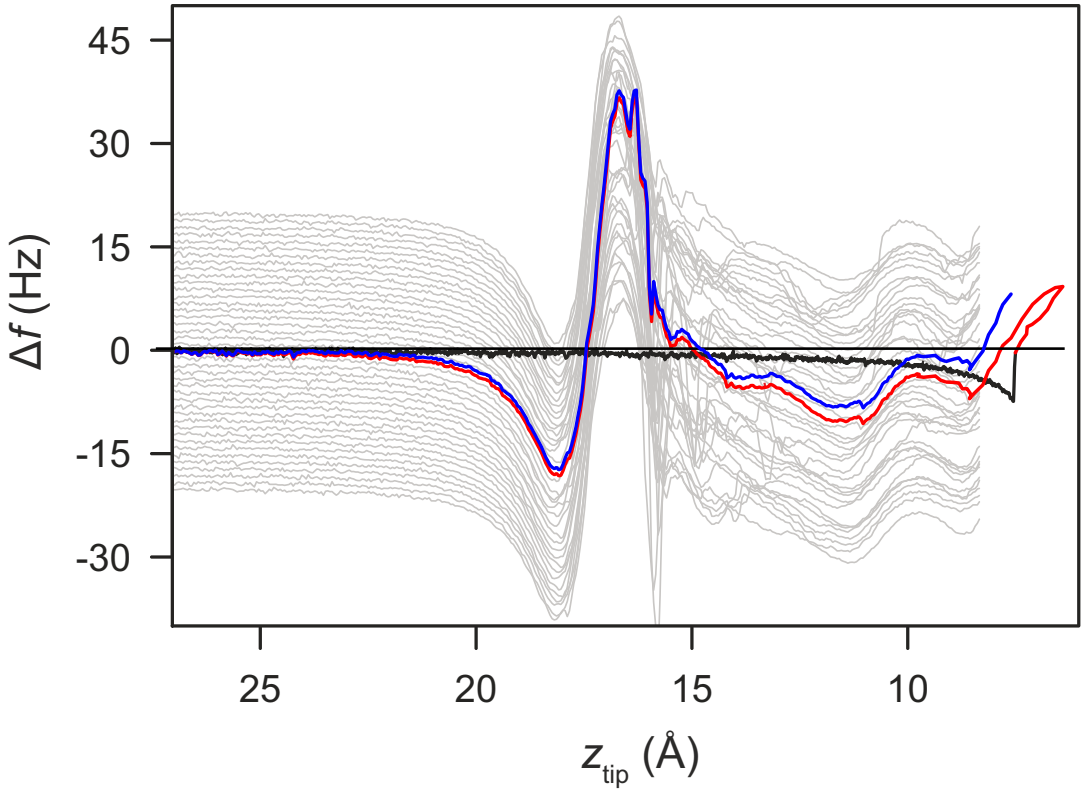


TTCDA



Two-Contact Manipulation

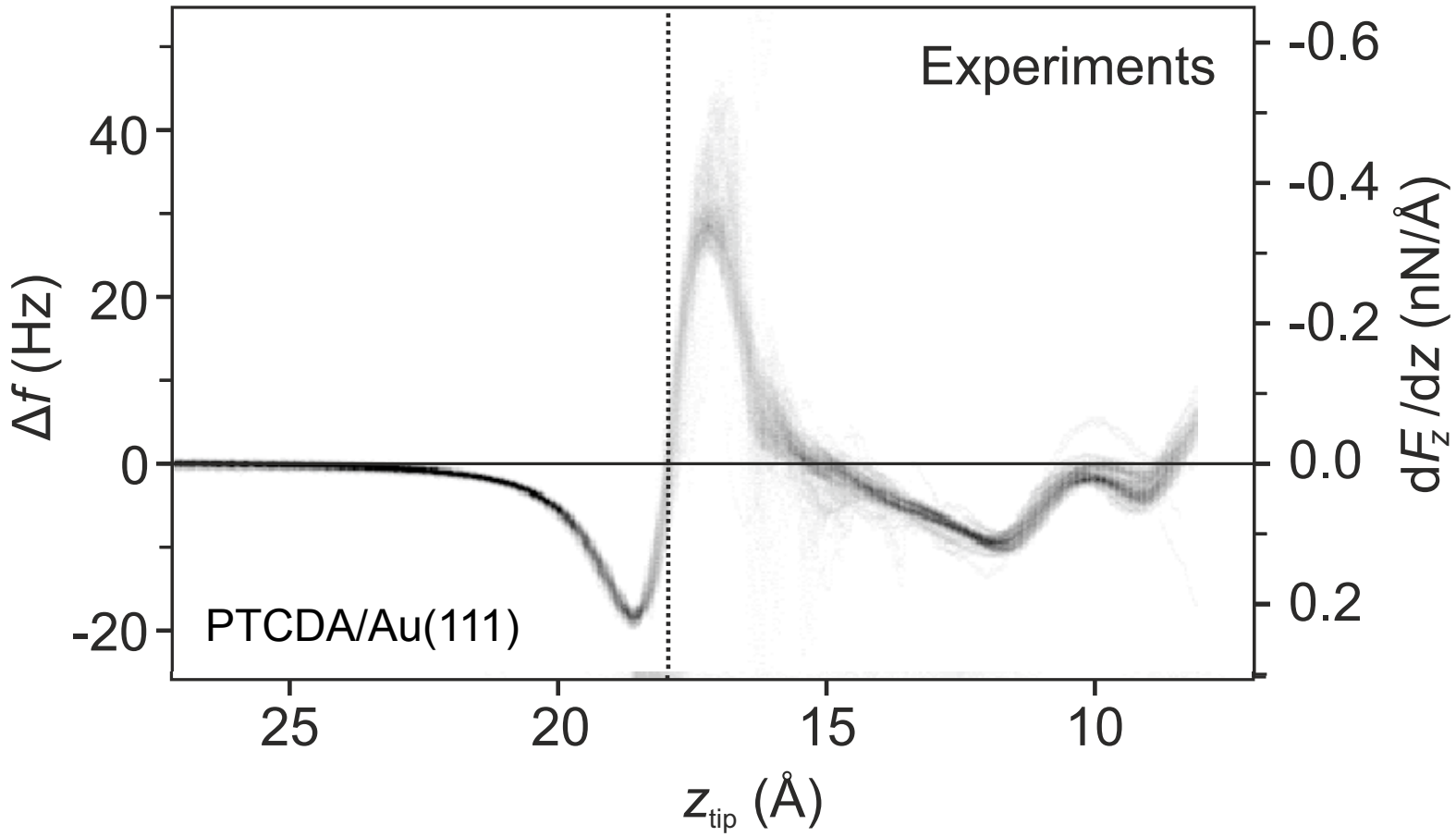
Individual Δf(z) „spectra“



Continuous – Reproducible – Reversible

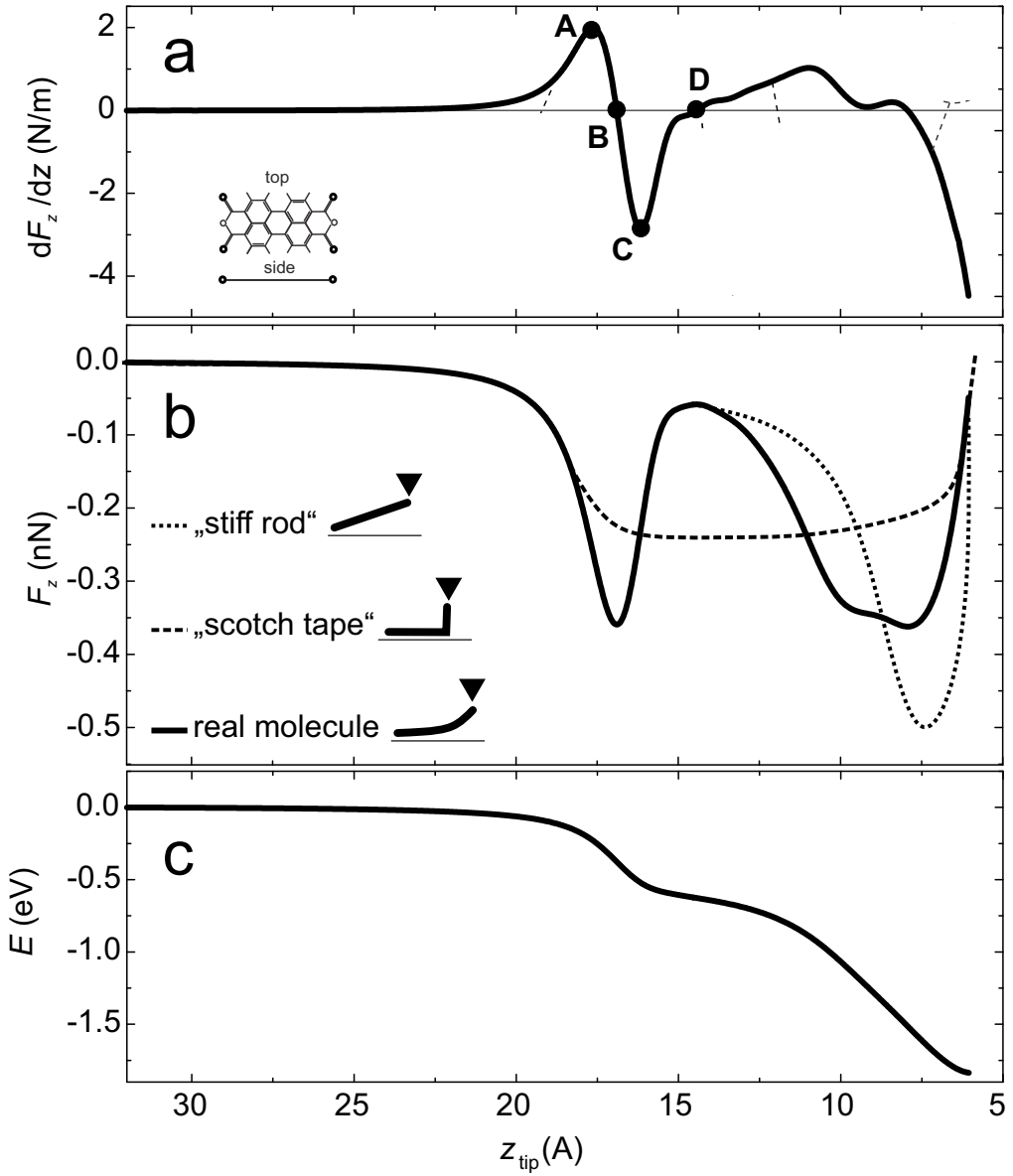
Two-Contact Manipulation

Histograms



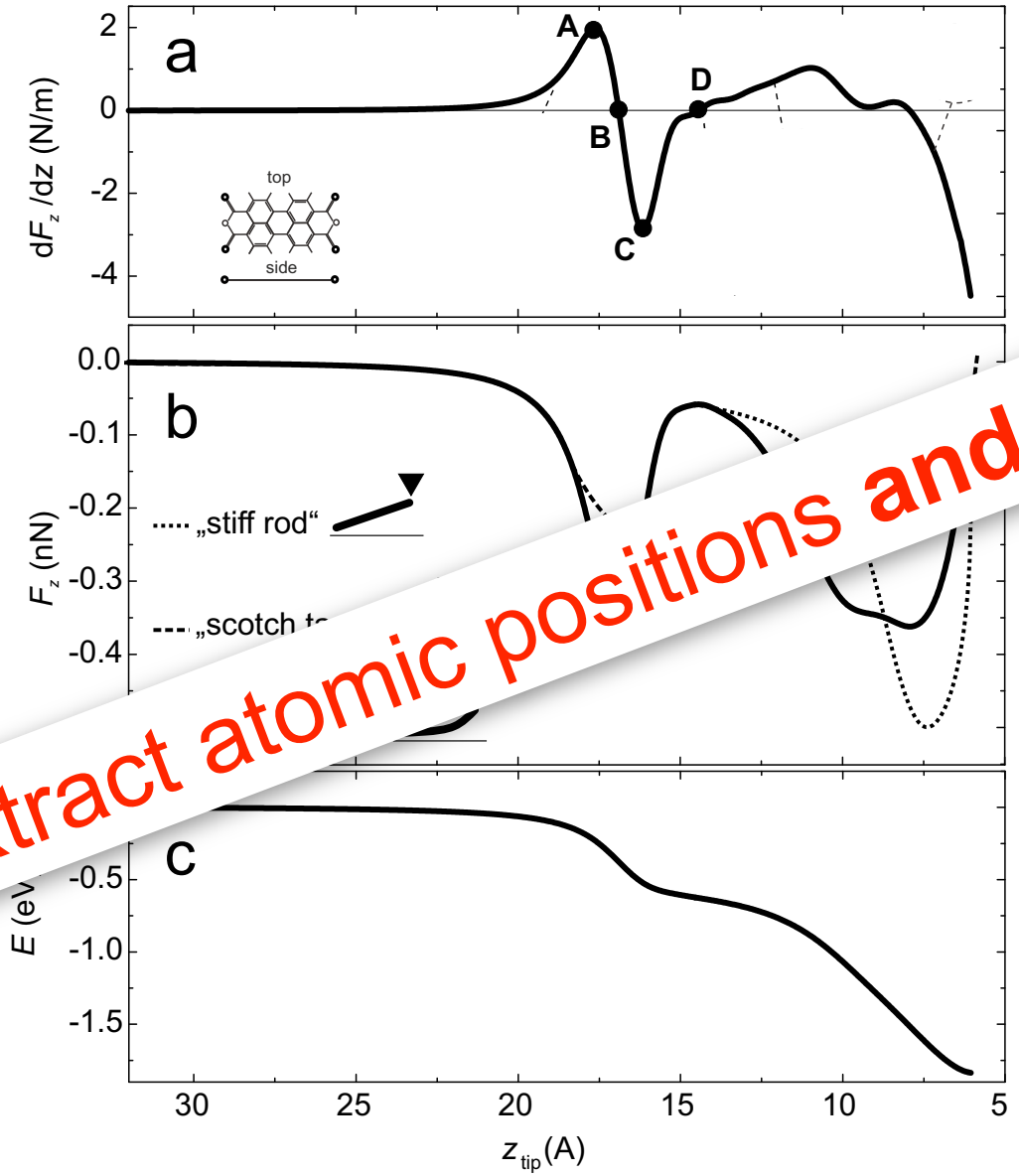
Phys. Rev. Lett. 109, 076102 (2012)

Two-Contact Mamipulation



Qualitative Understanding

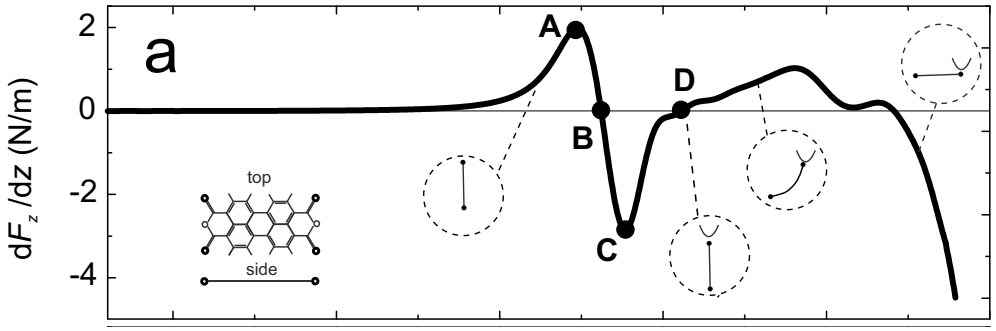
Two-Contact Mamipulation



Qualitative Understanding

Goal: Extract atomic positions **and** potentials

Two-Contact Manipulation



Inverse Problem

$$\begin{pmatrix} \mathbf{R}_1^*(\boldsymbol{\mathcal{R}}_1 \ldots \boldsymbol{\mathcal{R}}_\mathbf{P}) \\ \mathbf{R}_2^*(\boldsymbol{\mathcal{R}}_1 \ldots \boldsymbol{\mathcal{R}}_\mathbf{P}) \\ \vdots \\ \mathbf{R}_M^*(\boldsymbol{\mathcal{R}}_1 \ldots \boldsymbol{\mathcal{R}}_\mathbf{P}) \end{pmatrix} = \underset{\forall\, \mathbf{R}'_i \in \mathbb{R}^3}{\arg\min} V(\mathbf{R}'_1, \mathbf{R}'_2, \ldots, \mathbf{R}'_M, \boldsymbol{\mathcal{R}}_1 \ldots \boldsymbol{\mathcal{R}}_\mathbf{P})$$

$$\mathbf{R}_1 \ldots \mathbf{R}_M$$

Configuration of the molecule in the junction

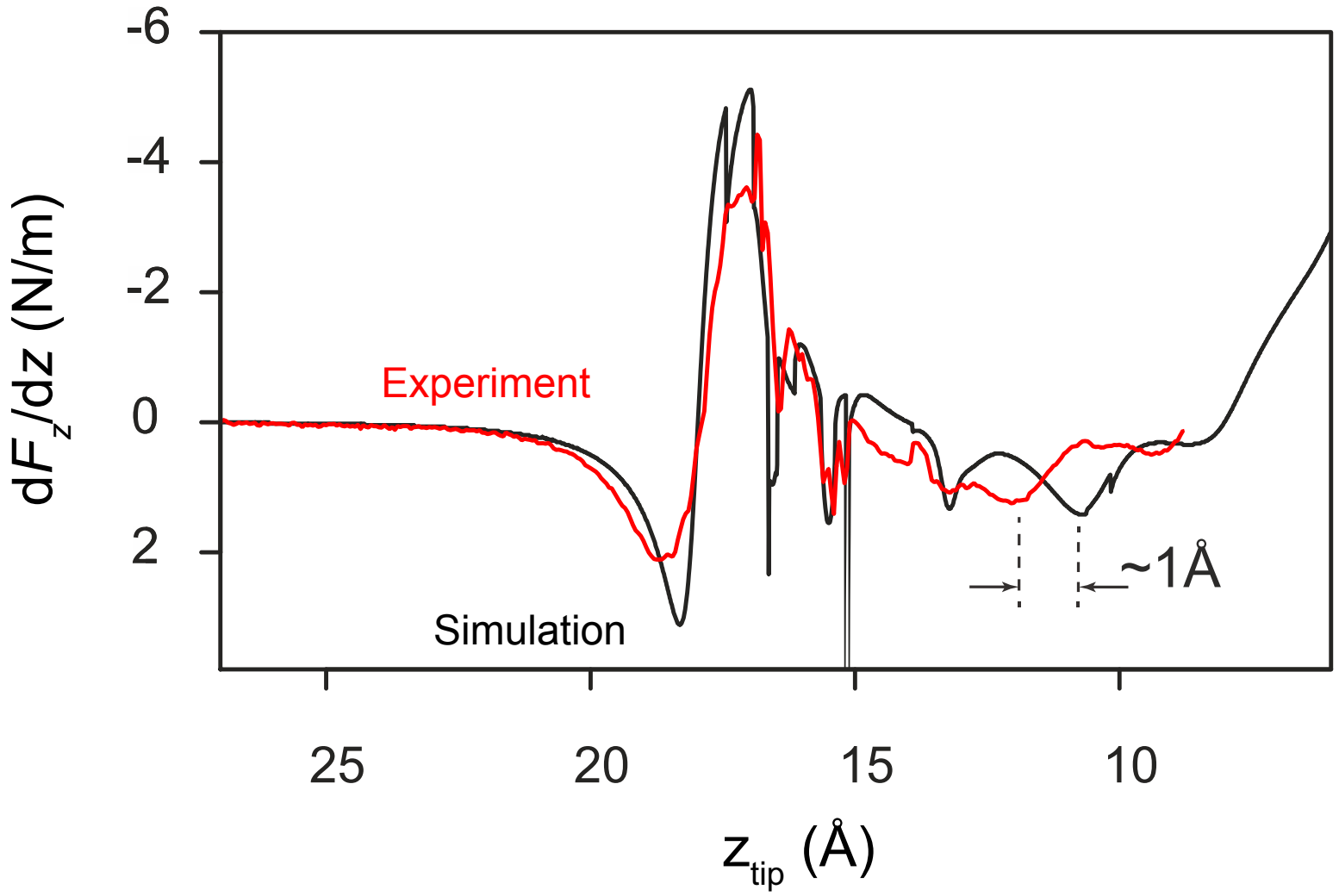
Classical, Quasistatic Simulation

$$V = V_{\mathrm{intra}} + V_{\mathrm{mol-surf}} + V_{\mathrm{mol-tip}}$$

$$V(\vec{R}_1 \ldots \vec{R}_M; \vec{\mathcal{R}}_1 \ldots \vec{\mathcal{R}}_P) = \sum_{i,j} V_{i,j}^{\mathrm{bond}} + \sum_{i,j,k} V_{i,j,k}^{\mathrm{angle}} + \sum_{i,j,k,l} V_{i,j,k,l}^{\mathrm{dihedral}}$$
$$+ \sum_{i,j} V_{i,j}^{\mathrm{nb}} + \sum_{i} V_{i}^{\mathrm{a-s}} + \sum_{i} V_{i}^{\mathrm{corr}} + V_{\mathrm{mol-tip}},$$

Molecular mechanics (“force field”)

Classical, Quasistatic Simulation



Van der Waals Potential

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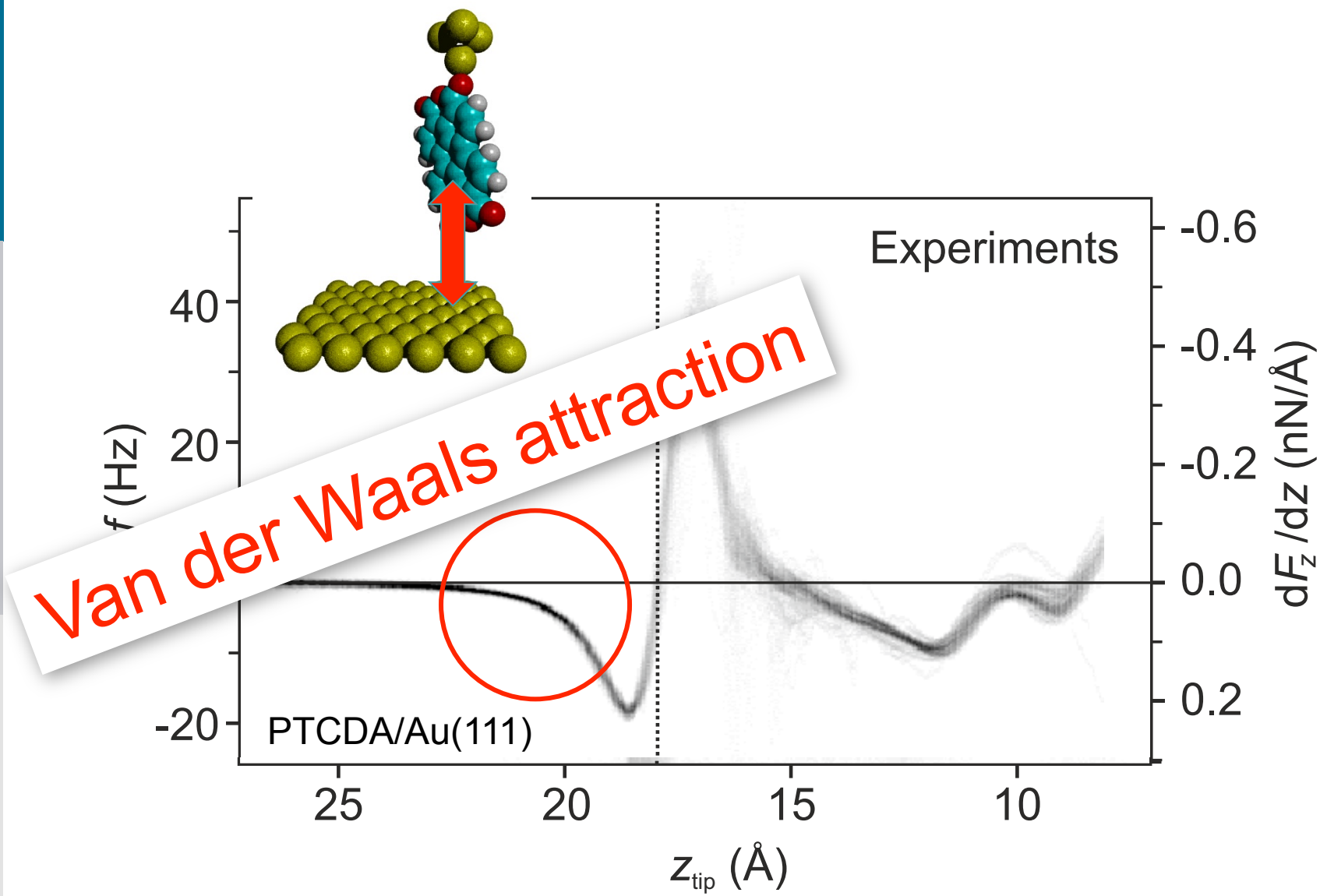
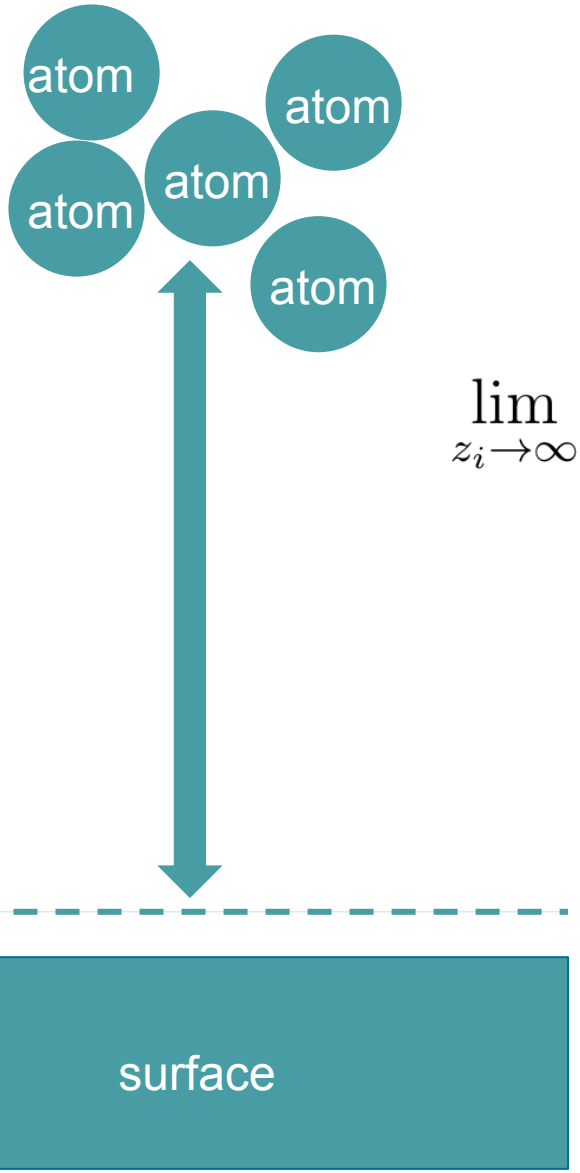
Asymptotic Potential



Phys. Rev. Lett. 109, 076102 (2012)

Lifshitz-Zaremba-Kohn

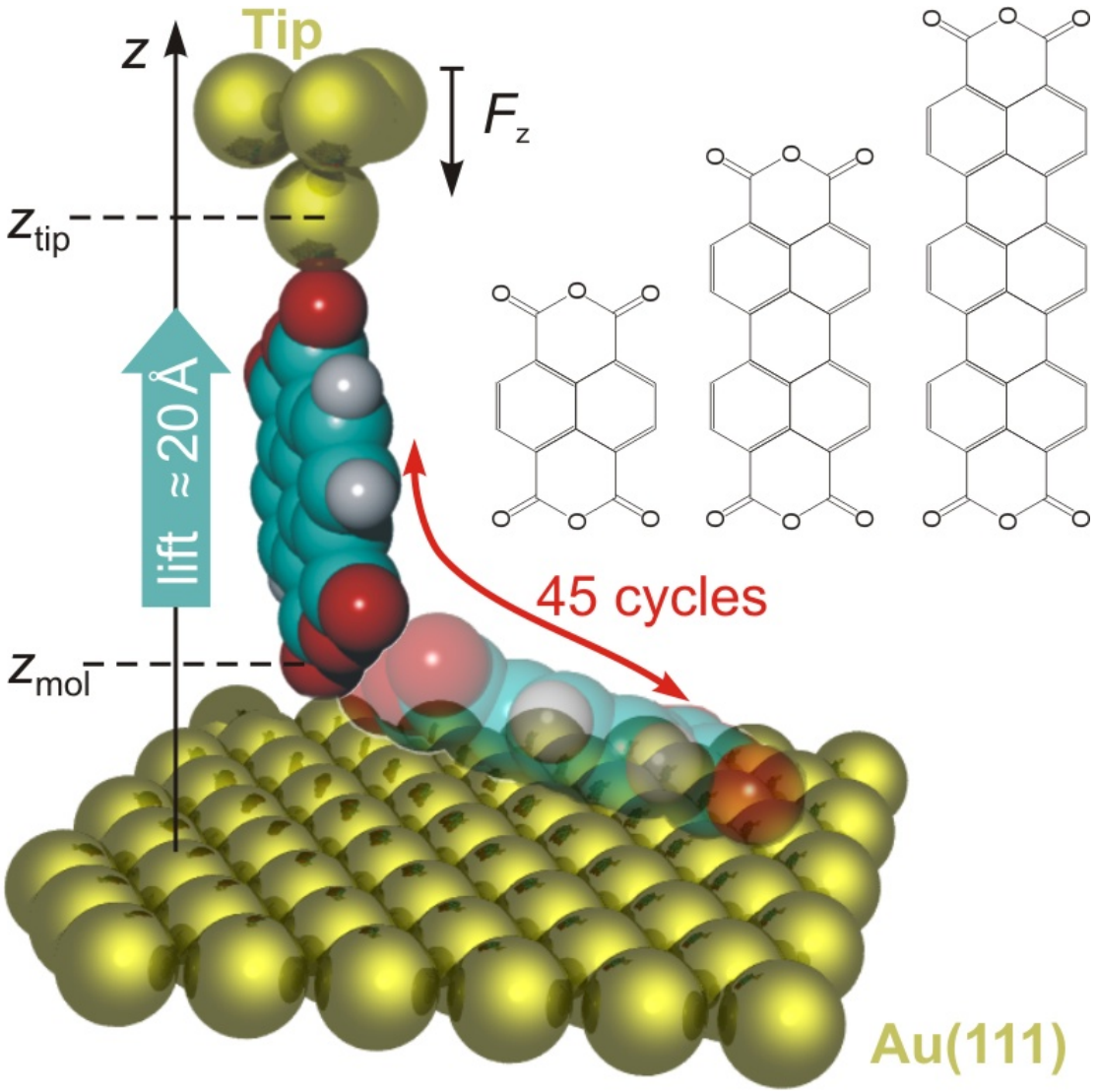


$$\lim_{z_i \to \infty} V_{\mathrm{mol-surf}}(z_1 \ldots z_M) = \sum_{i=1}^{M} V_i^{\mathrm{a-s}}(z_i)$$

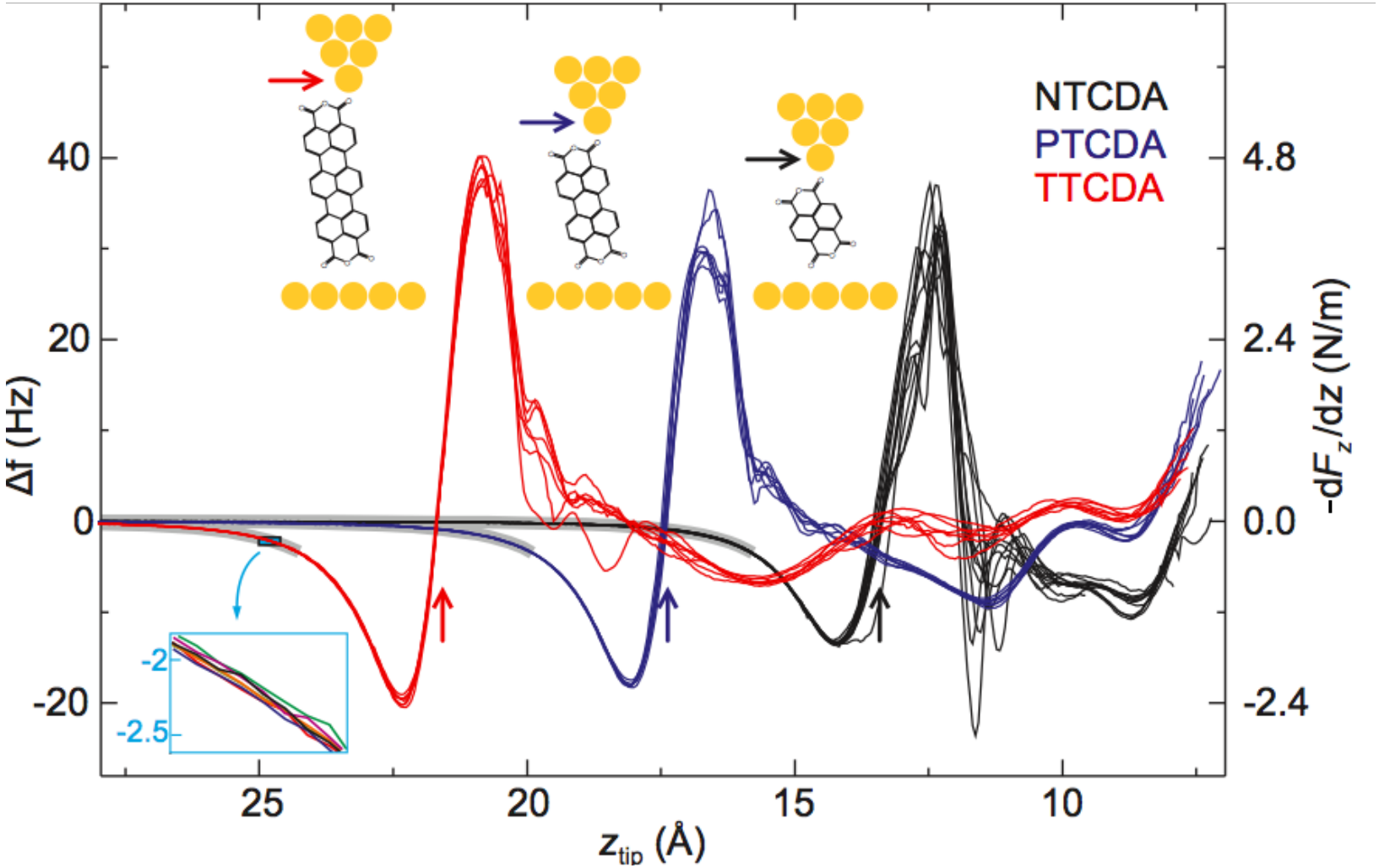
$$= \sum_{i=1}^{M} -\frac{\gamma_i C_3}{(z_i - z_0)^3}$$

z_0: van der Waals plane (related to dynamic image plane)

Experiment

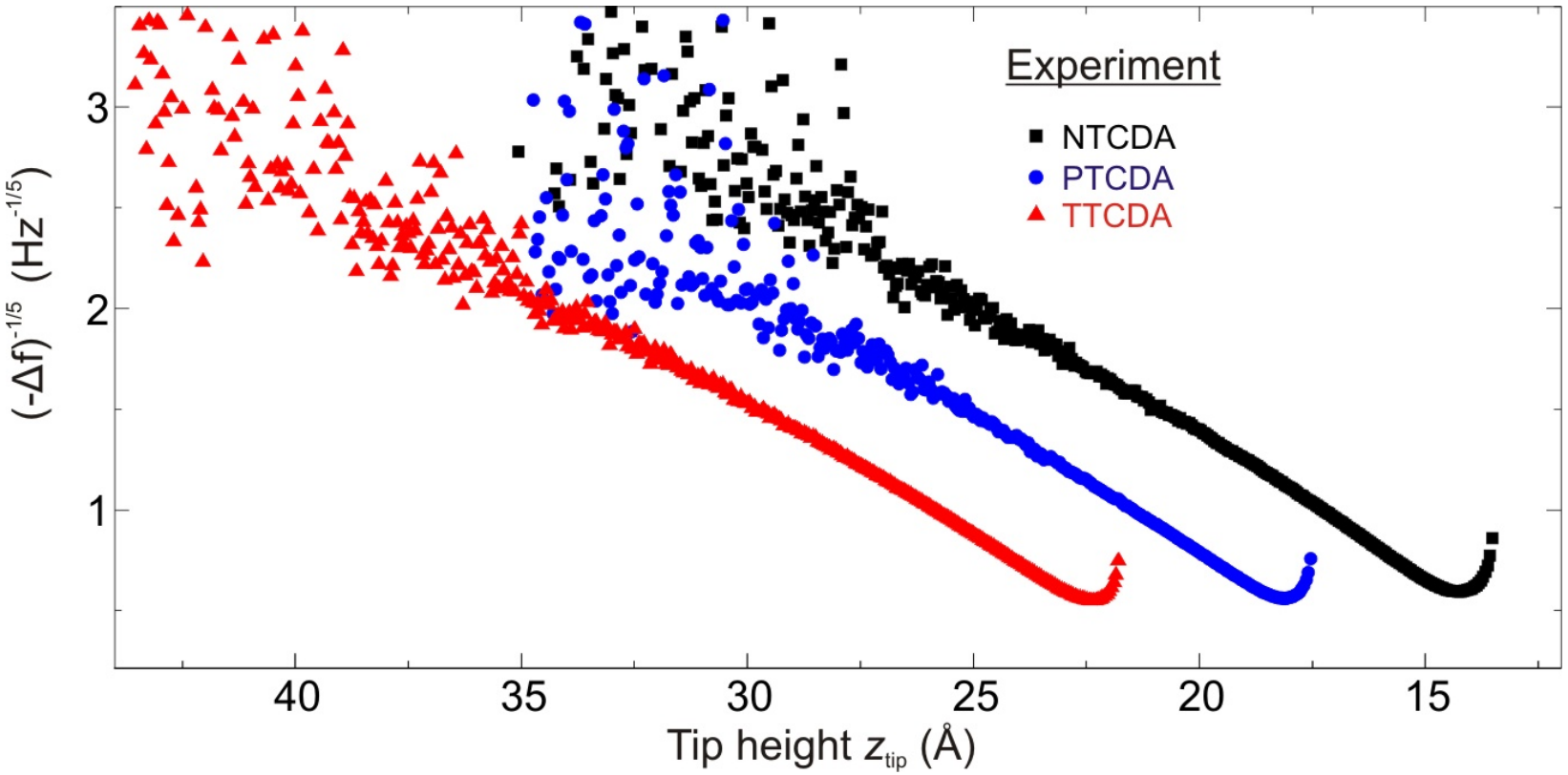


Experimental Results: NTCDA, PTCDA, TTCDA



Nature Communications 5, 5568 (2014)

Experimental Results: NTCDA, PTCDA, TTCDA



$$\Delta f \propto z^{-5}$$

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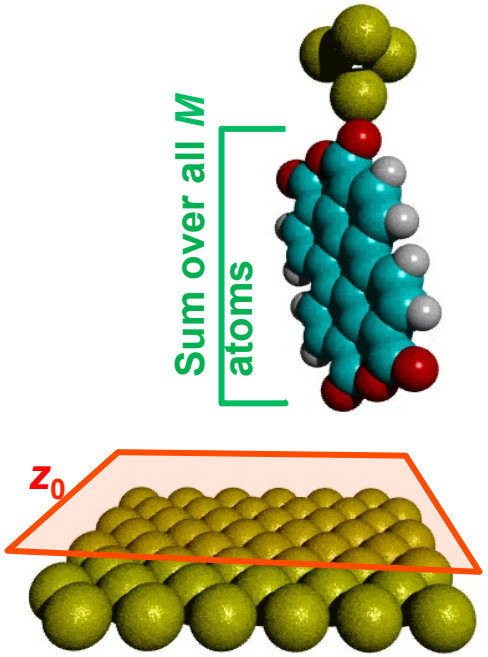
Fitting the Experimental Data



$$\Delta f_{[\mathrm{N,P,T}]}(z_{\mathrm{tip}}) = \frac{d^2V}{dz_{\mathrm{tip}}^2}$$

$$V = -\sum_{i=1}^{M} \frac{\gamma_{\mathrm{i}} C_{\alpha,[\mathrm{N,P,T}]}}{((z_{\mathrm{tip}} - d_{\mathrm{i}}) - z_0)^{\alpha}}$$

Fit parameters α, $C_{\alpha,N}$, $C_{\alpha,P}$, $C_{\alpha,T}$, z_0

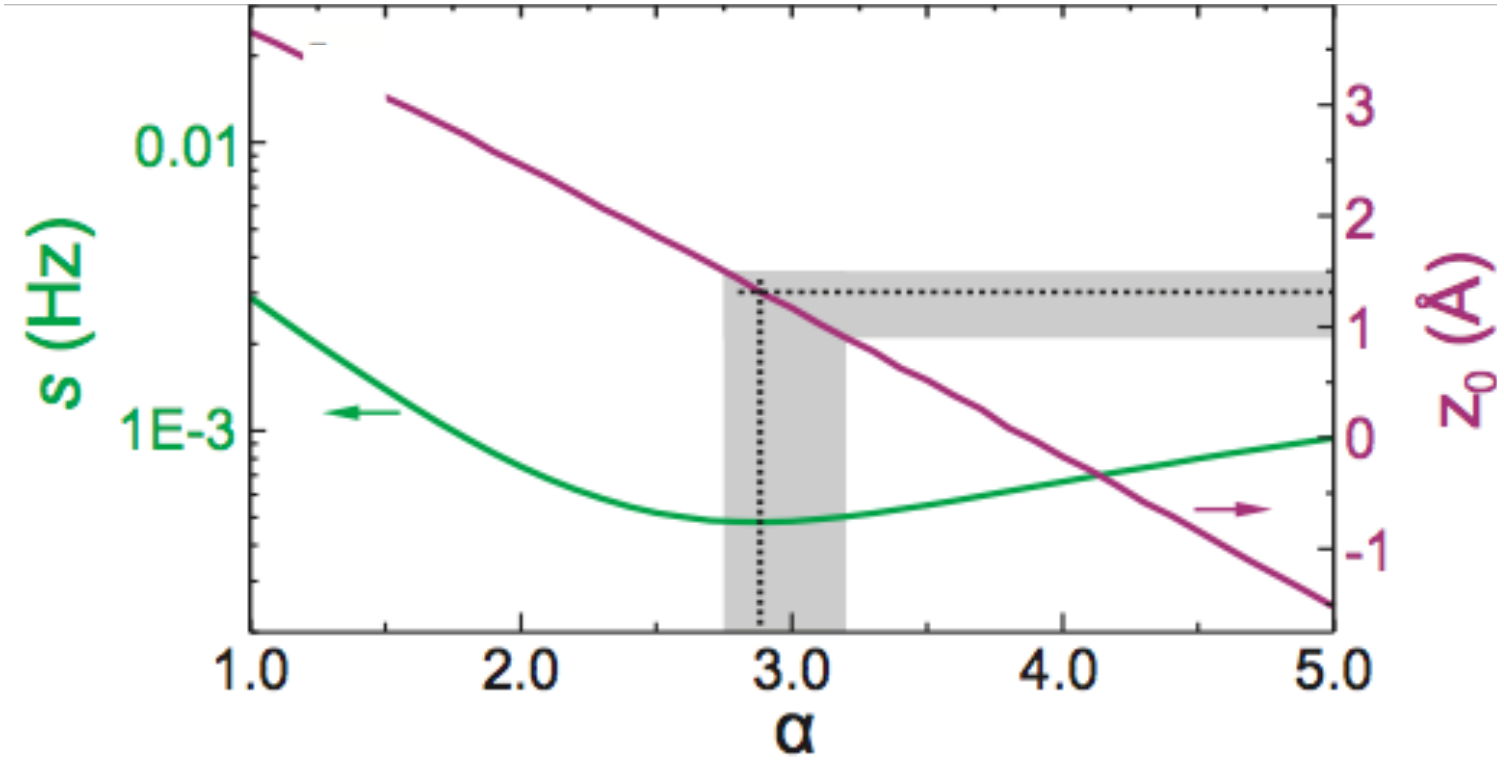
NTCDA, PTCDA, TTCDA are fitted **simultaneously**

Individual C-coefficients for each molecule (beyond additivity)

Atomic weighting factors from V. G. Ruiz et al., PRL 2012:

$\gamma_H = 0.29$ $\gamma_O = 0.67$ $\gamma_C = 1.00$

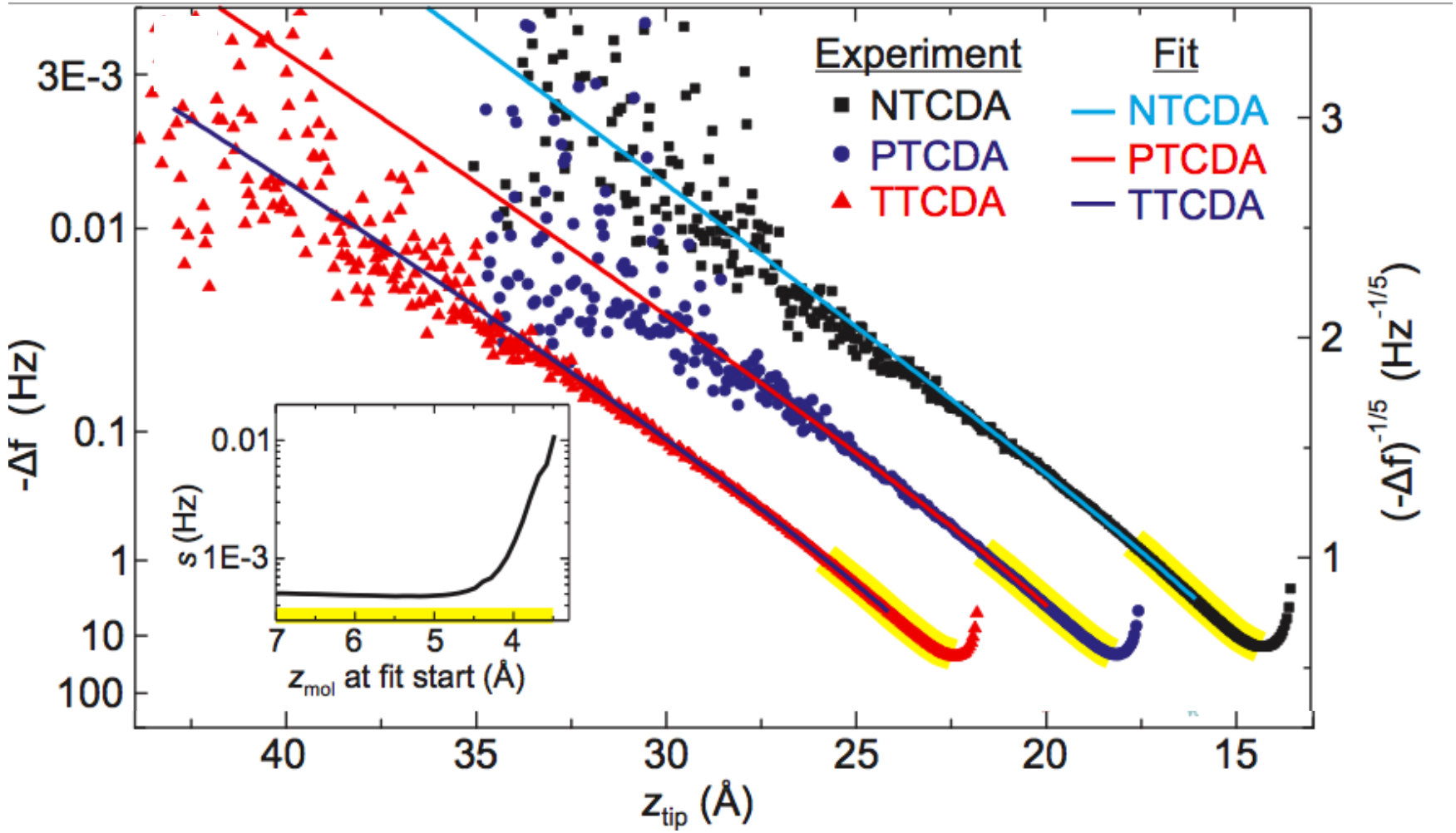
Step 1: Fitting the Asymptotic Force Law



$\alpha \approx 3$ (vdW interaction dominates the molecule-surface potential)

$z_0 \approx d_{Au(111)}/2$ (correct distance calibration)

Step 2: Fitting C_3 Coefficients and z_0 (with $\alpha \equiv 3$)



Asymptotic α=3 behaviour for z_{mol}**> 5 Å**

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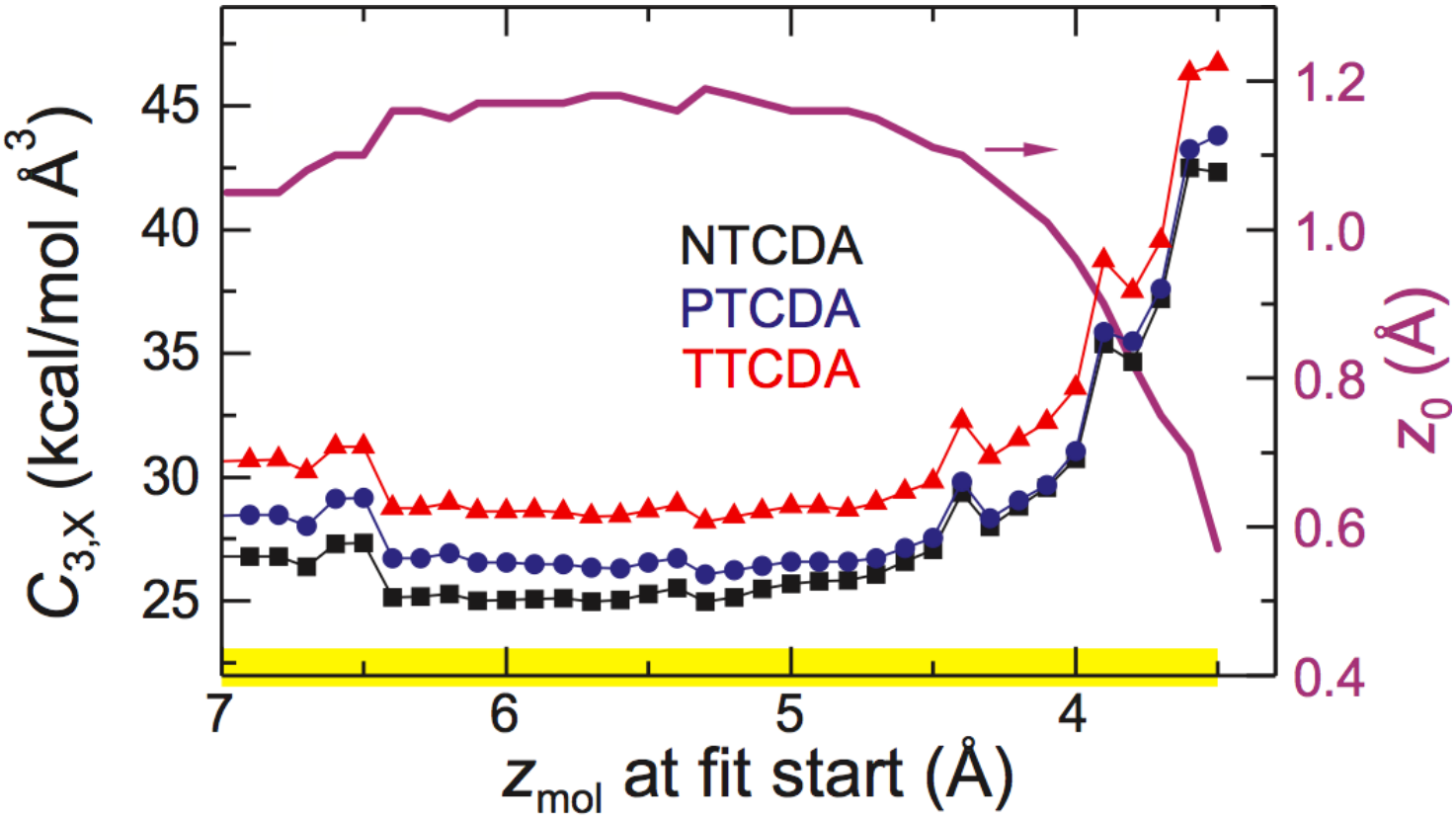
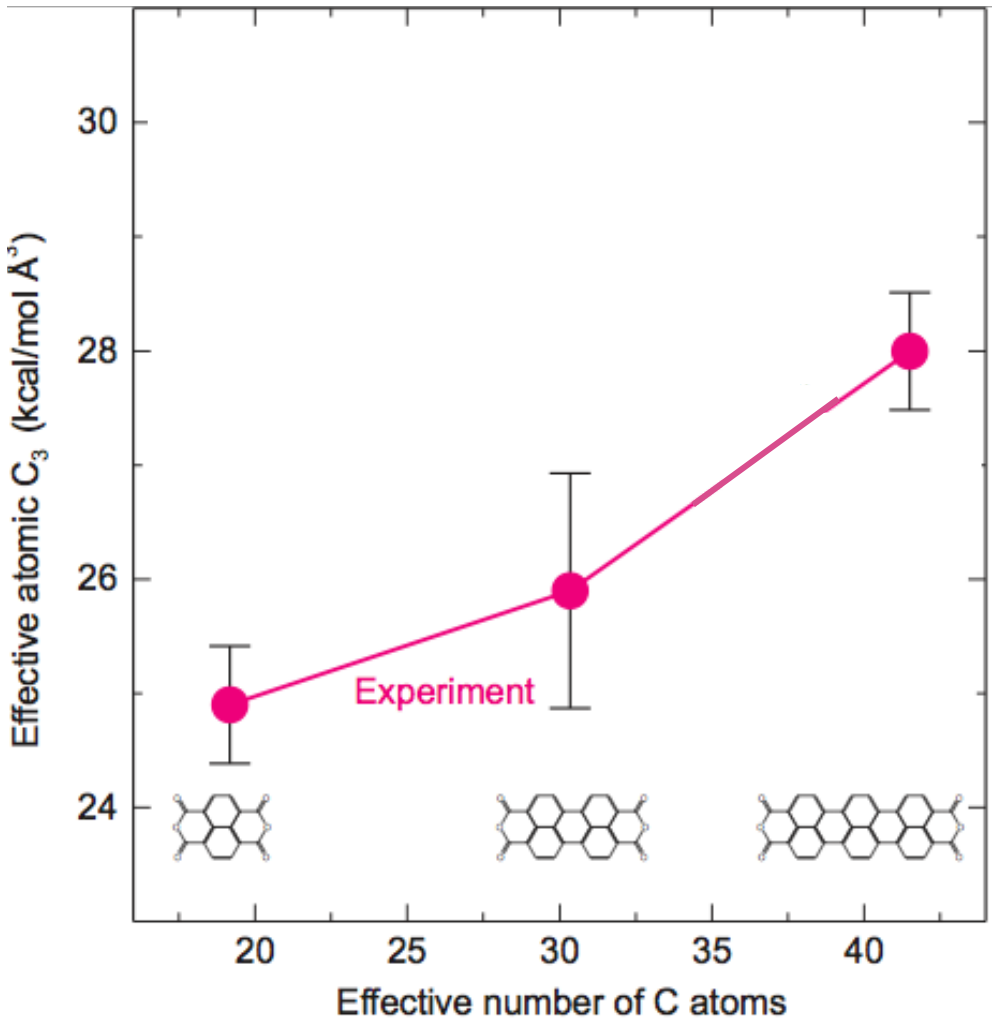
Step 2: Fitting C_3 Coefficients and z_0 (with $\alpha \equiv 3$)



C_3-coefficients converge for $\mathbf{z_{mol} > 5}$ **Å,** to **different** values for the three molecules

Superlinear Rise of the Molecular C_3 Coefficients



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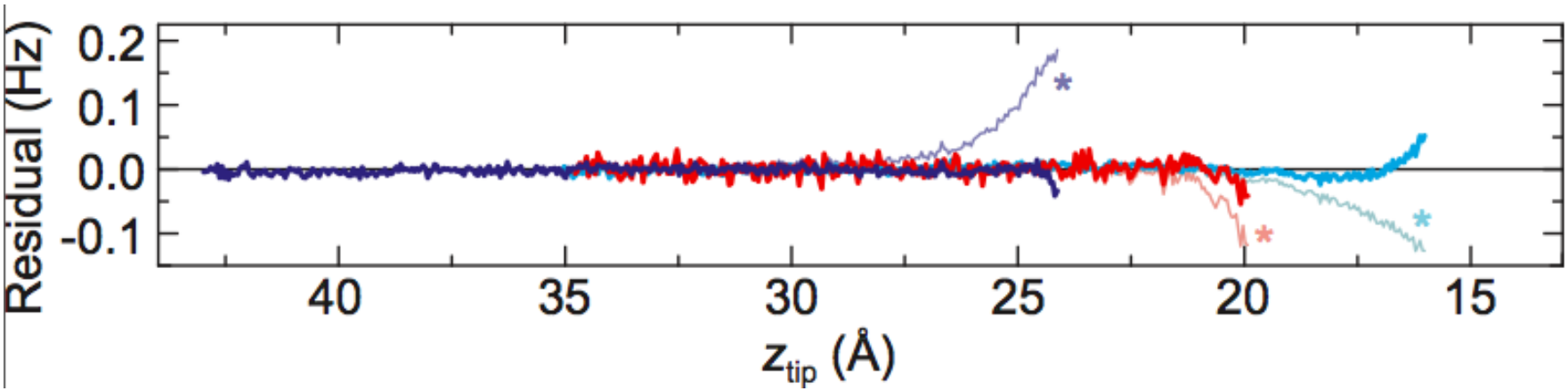
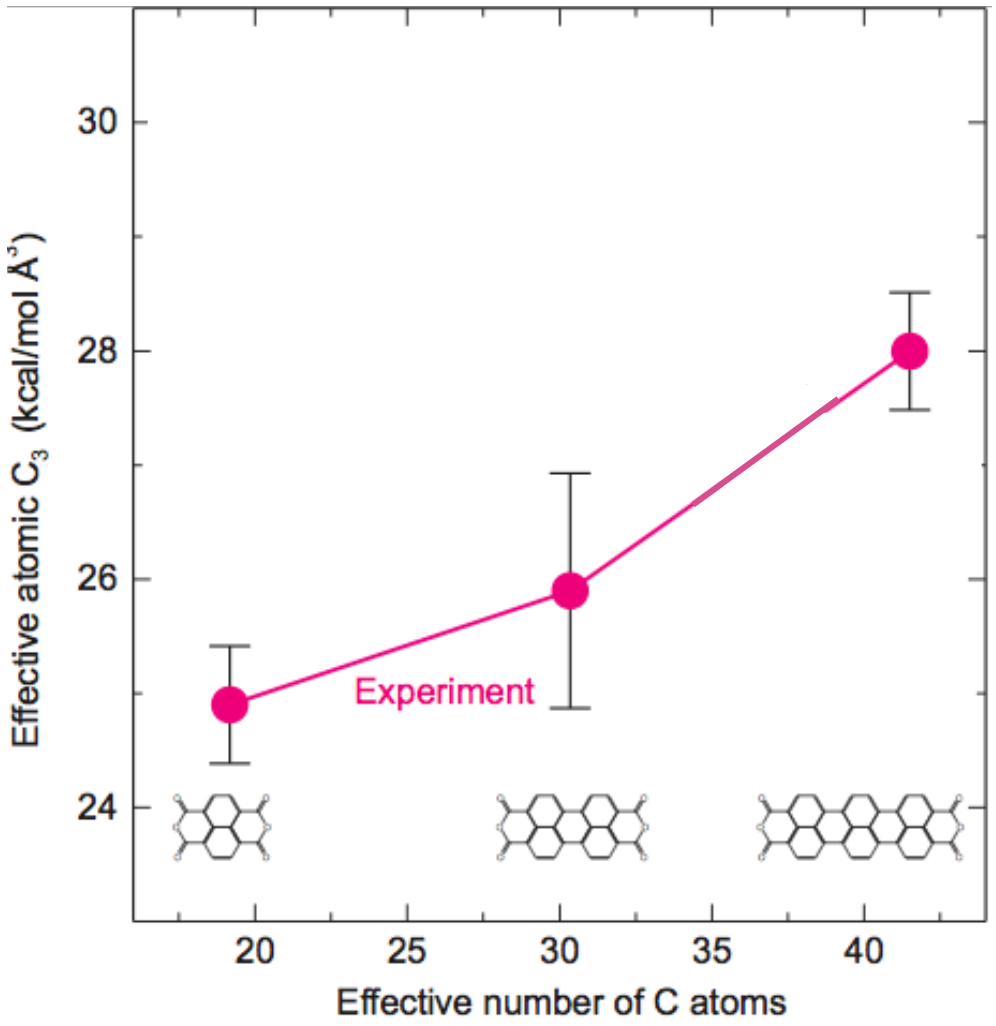
Superlinear Rise of the Molecular C_3 Coefficients



* Residuals of a fit in which C_3 coefficients are forced to be identical

Superlinear Rise of the Molecular C_3 Coefficients



Carbon atoms in TTCDA are **more polarizable** than in NTCDA,

i.e. the van der Waals interaction is **not additive** over the carbon atoms.

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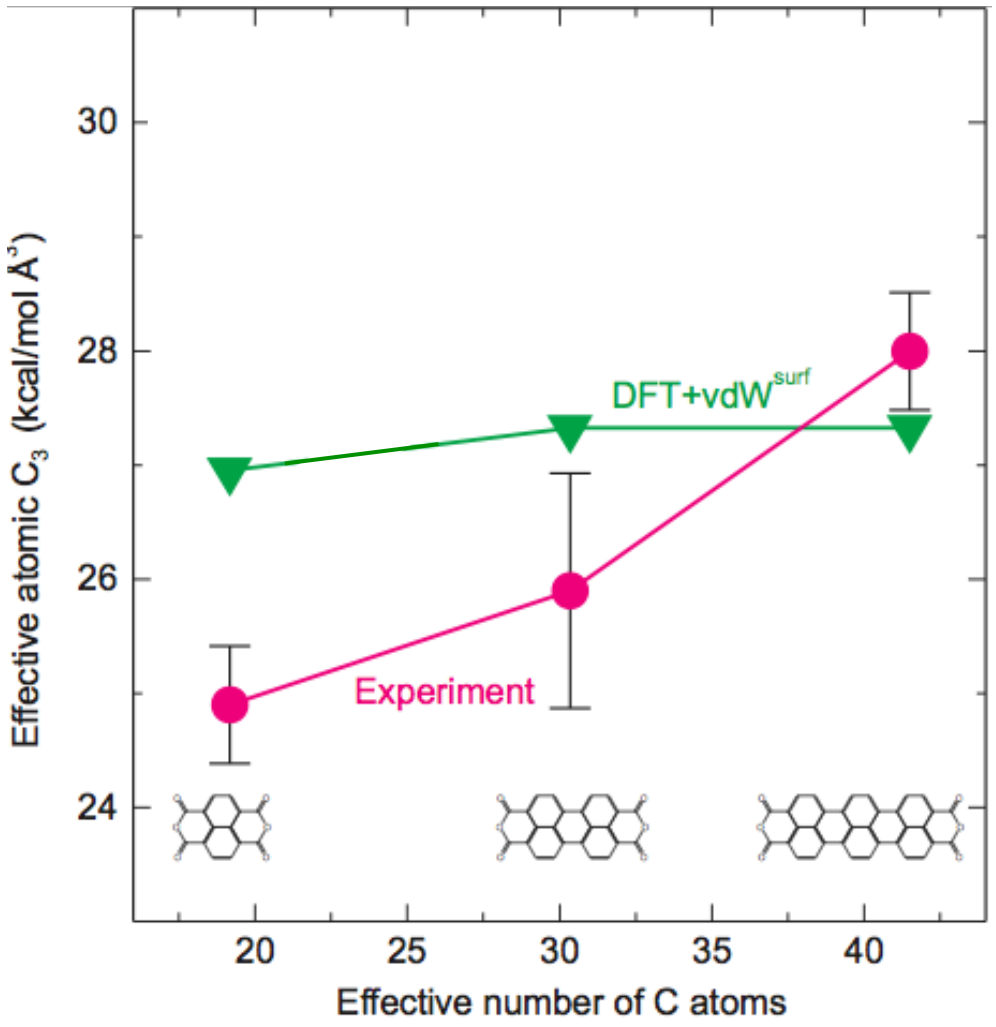
Superlinear Rise of the Molecular C_3 Coefficients

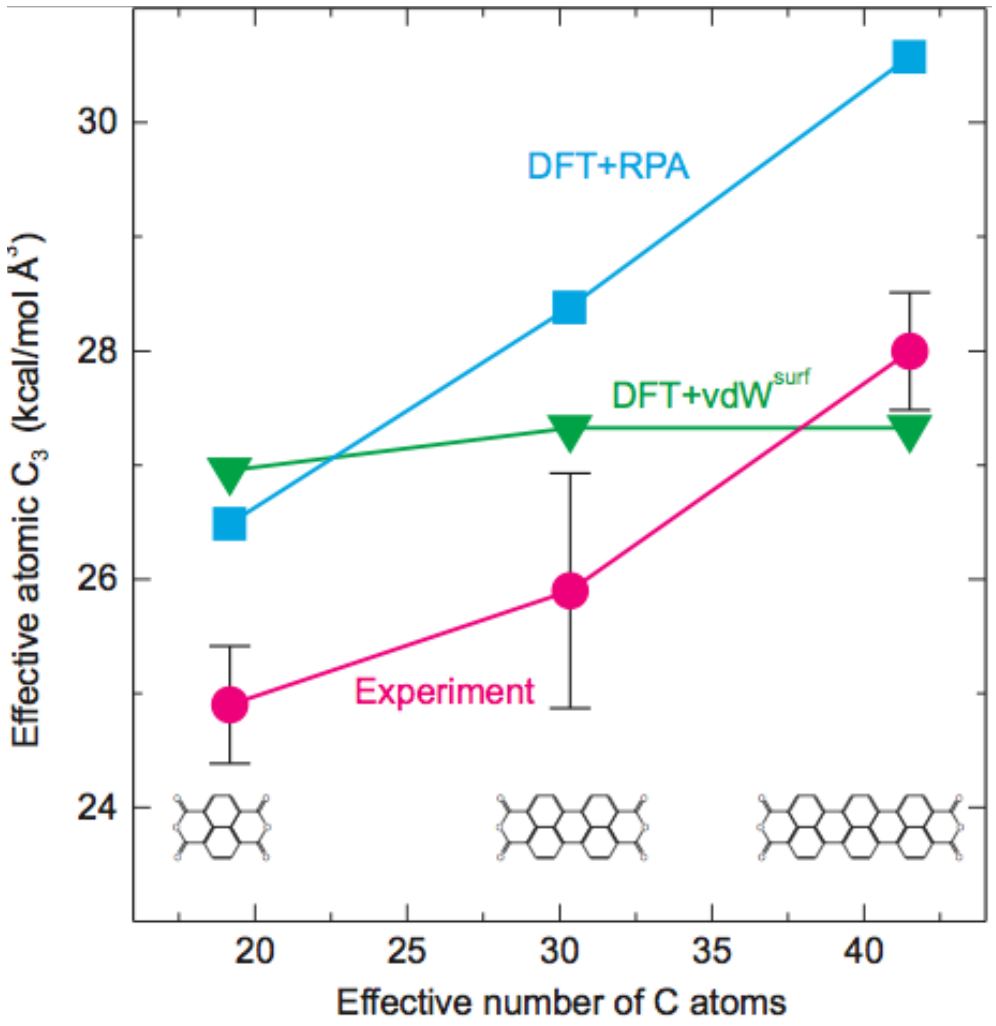


DFT + **semi-empirical vdW^{surf}**:
(=isotropic free-atom static polarizability, volume-scaled for immediate chemical environment).

by construction all carbon atoms are the same

(vdW^{surf}: Ruiz et al PRL 2012)

Superlinear Rise of the Molecular C_3 Coefficients



DFT + **random phase approximation**:
(=dynamic linear response theory, self-consistent but linearized Hartree calculation of electron density in the molecule in presence of external perturbation and its screening in molecule).

The same superlinearity as in experiment is observed.

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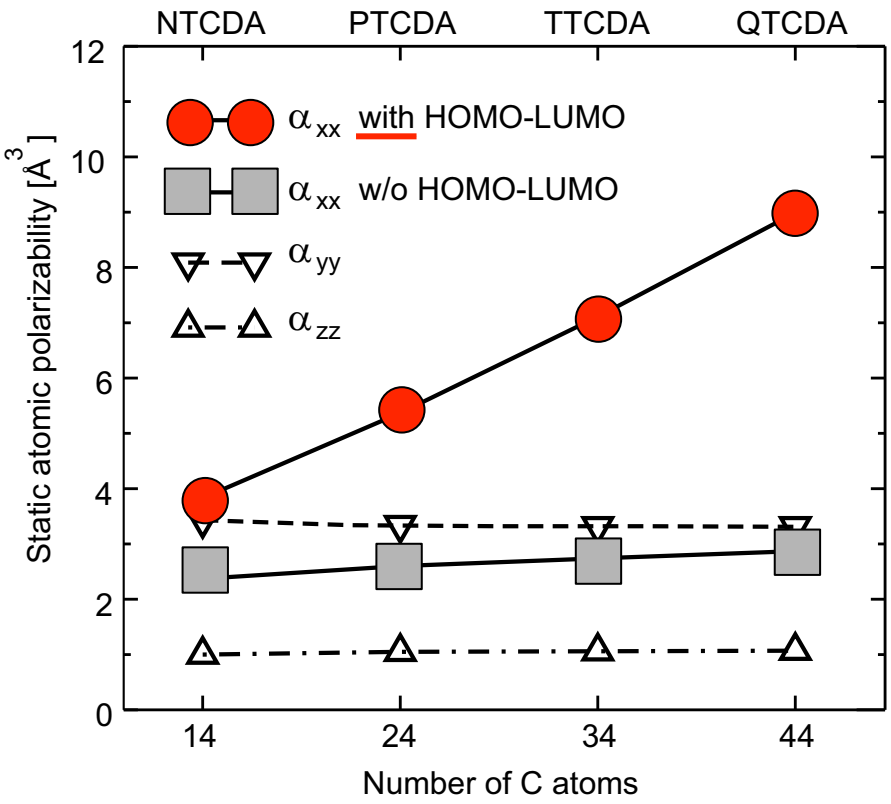
Origin of Superlinearity

Microscopic response function of the molecule: 1st order perturbation of wave functions

$$\chi(\mathbf{r},\mathbf{r}',\omega) = -4\frac{1}{V}\sum_{m}^{occ}\sum_{n}^{empty}\psi_m(\mathbf{r})\psi_m^*(\mathbf{r}')\psi_n^*(\mathbf{r})\psi_n(\mathbf{r}')\frac{E_n - E_m}{(E_n - E_m)^2 - \omega^2}$$



HOMO-LUMO gap enters here, decreases with length of the molecule due to **electron deconfinement** along the long axis of the molecule

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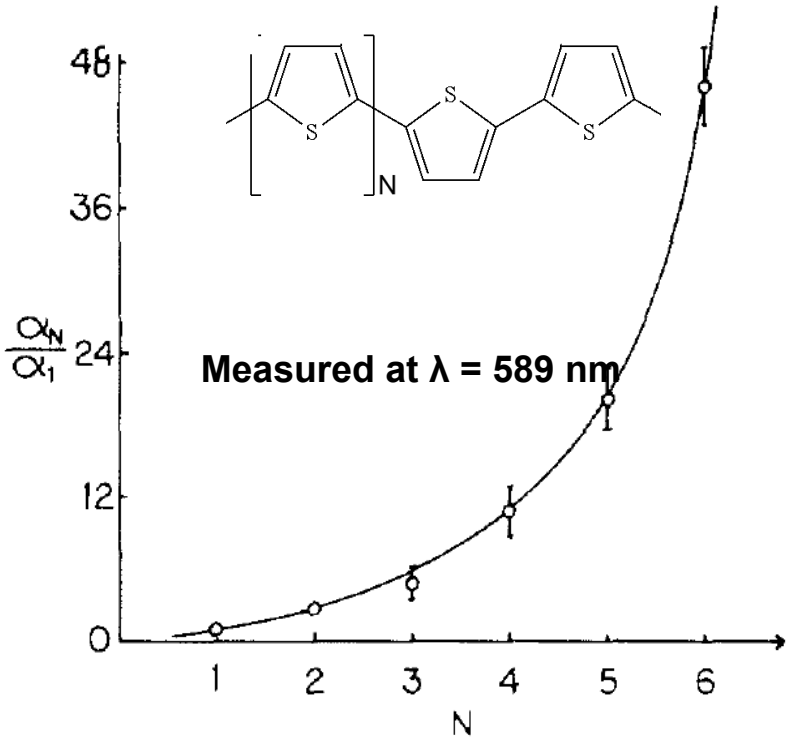
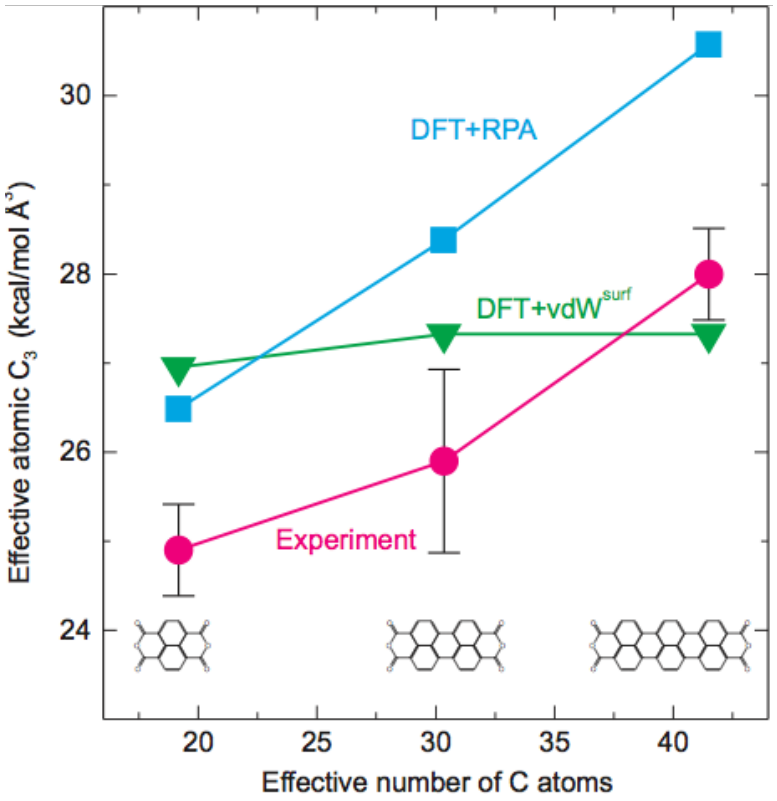
Optical Polarizability vs. van der Waals Force

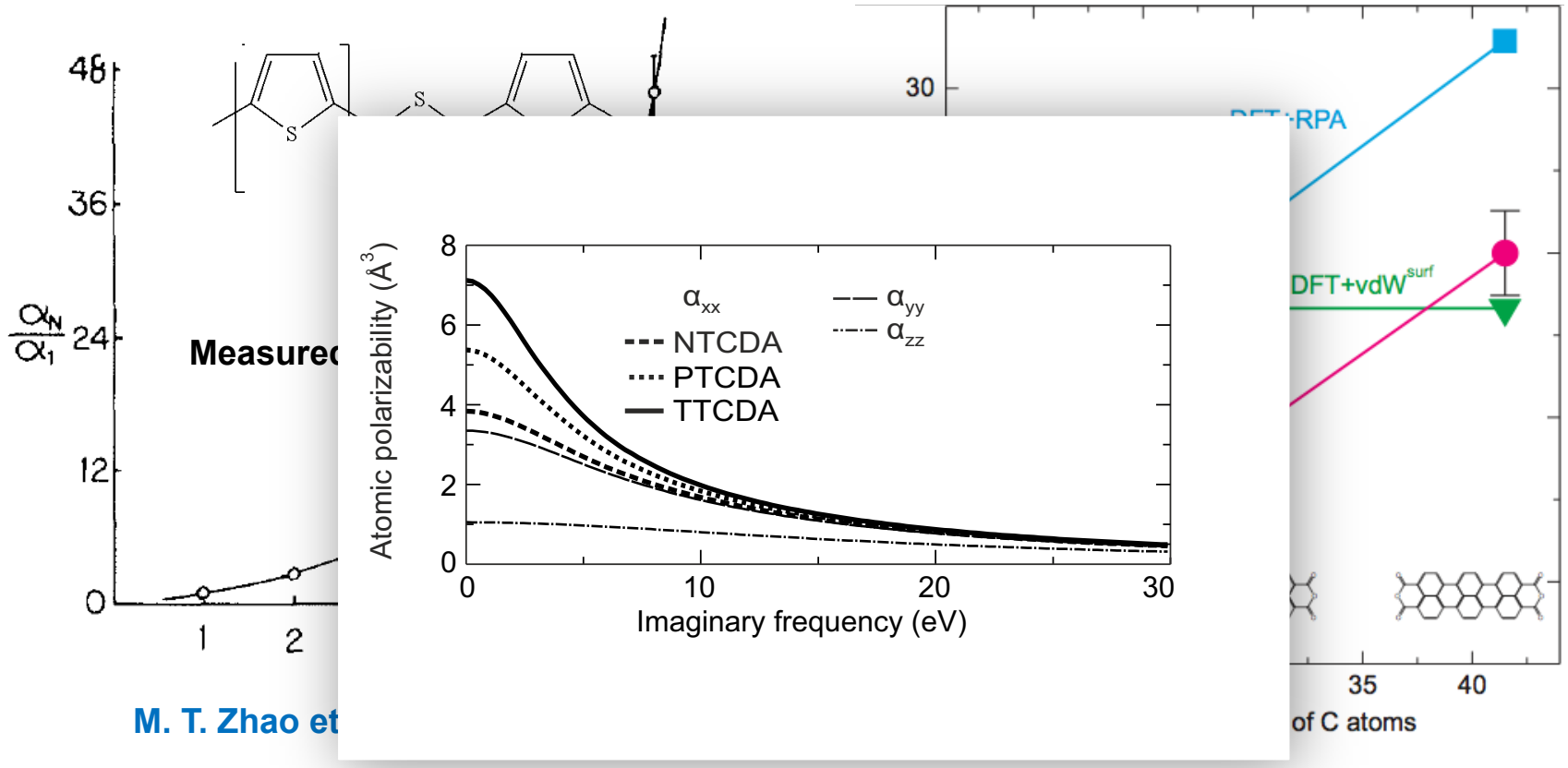


M. T. Zhao et al., *J. Chem. Phys.* 1988



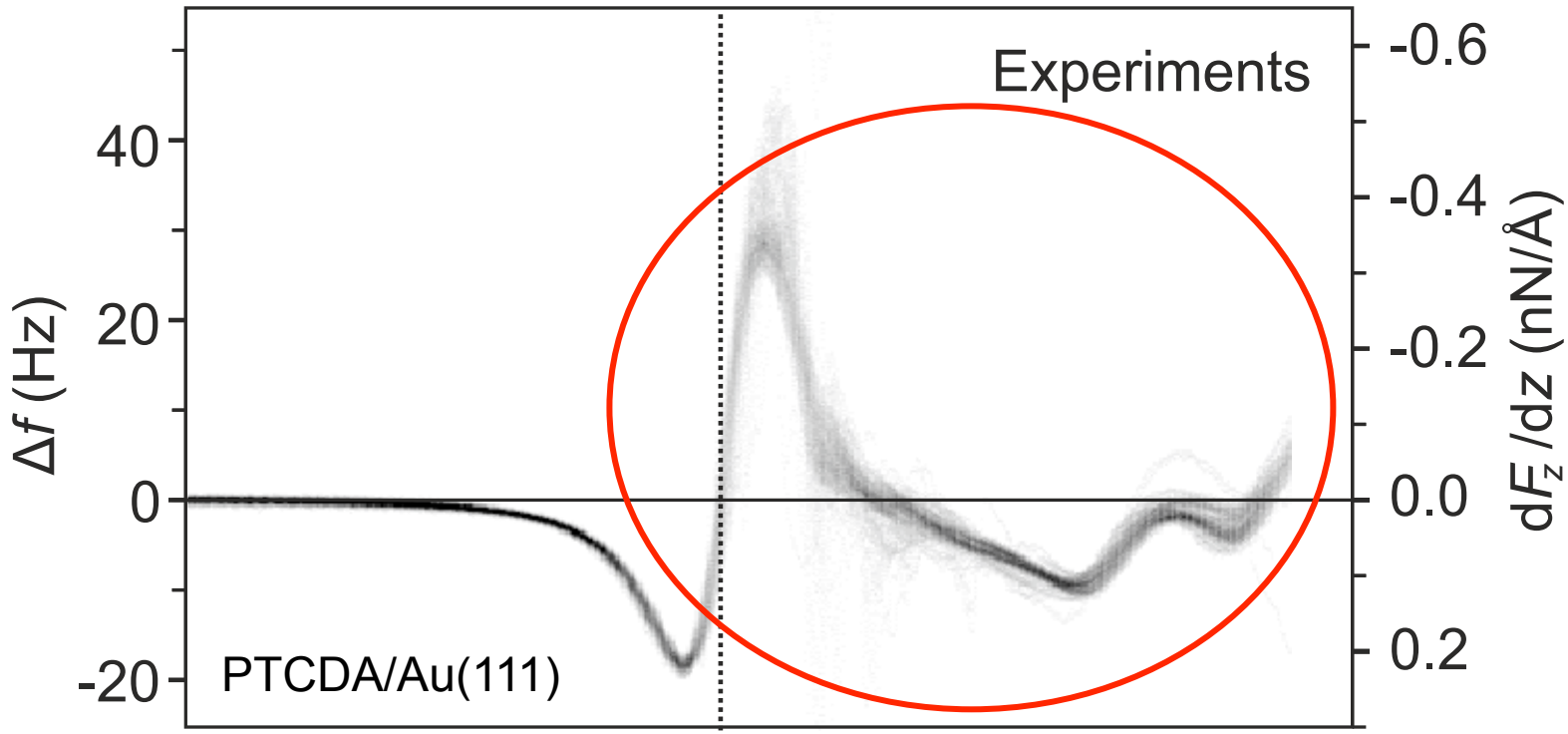
Why is the superlinear effect in the van der Waals interaction so small?

Optical Polarizability vs. van der Waals Force



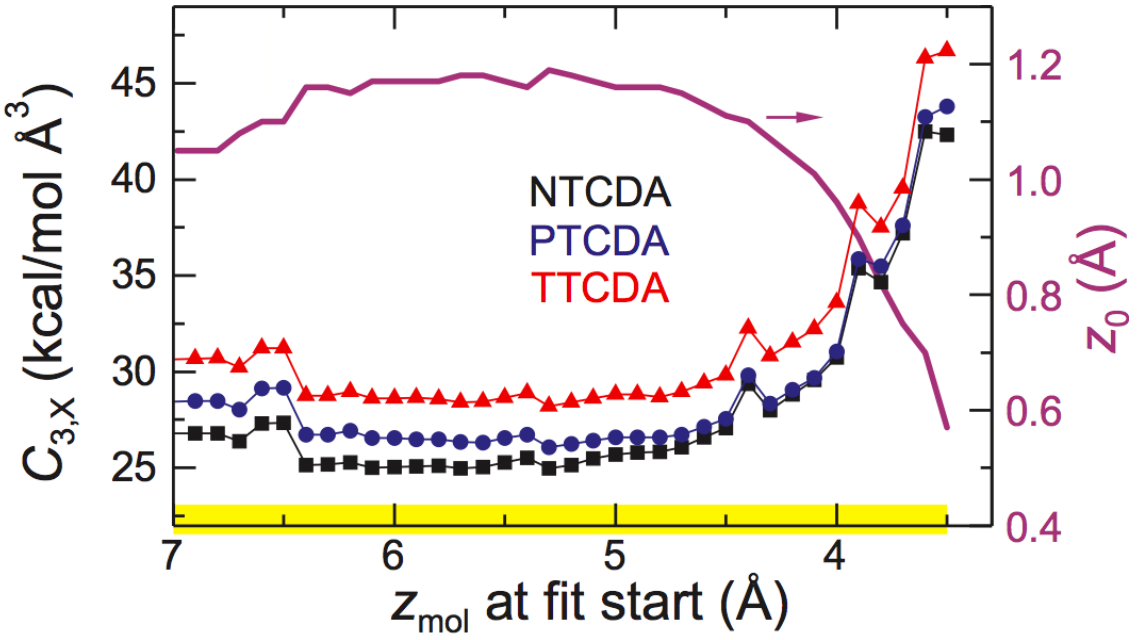
Why is the superlinear effect in the van der Waals interaction so small?

Short Range Potential



Phys. Rev. Lett. 109, 076102 (2012)

Short Range Potential



$$V_{\mathrm{mol-surf}}(z_1 \ldots z_M) = \sum_{i=1}^{M} V_i^{\mathrm{a-s}}(z_i)$$

$$= \sum_{i=1}^{M} D_i^{\mathrm{P}} e^{-A_i^{\mathrm{P}} z_i} - D_i^{\mathrm{C}} e^{-A_i^{\mathrm{C}} z_i} - \frac{\gamma_i C_3^{\mathrm{eff}}}{z_i^3}$$

Chemical bonding

Pauli repulsion

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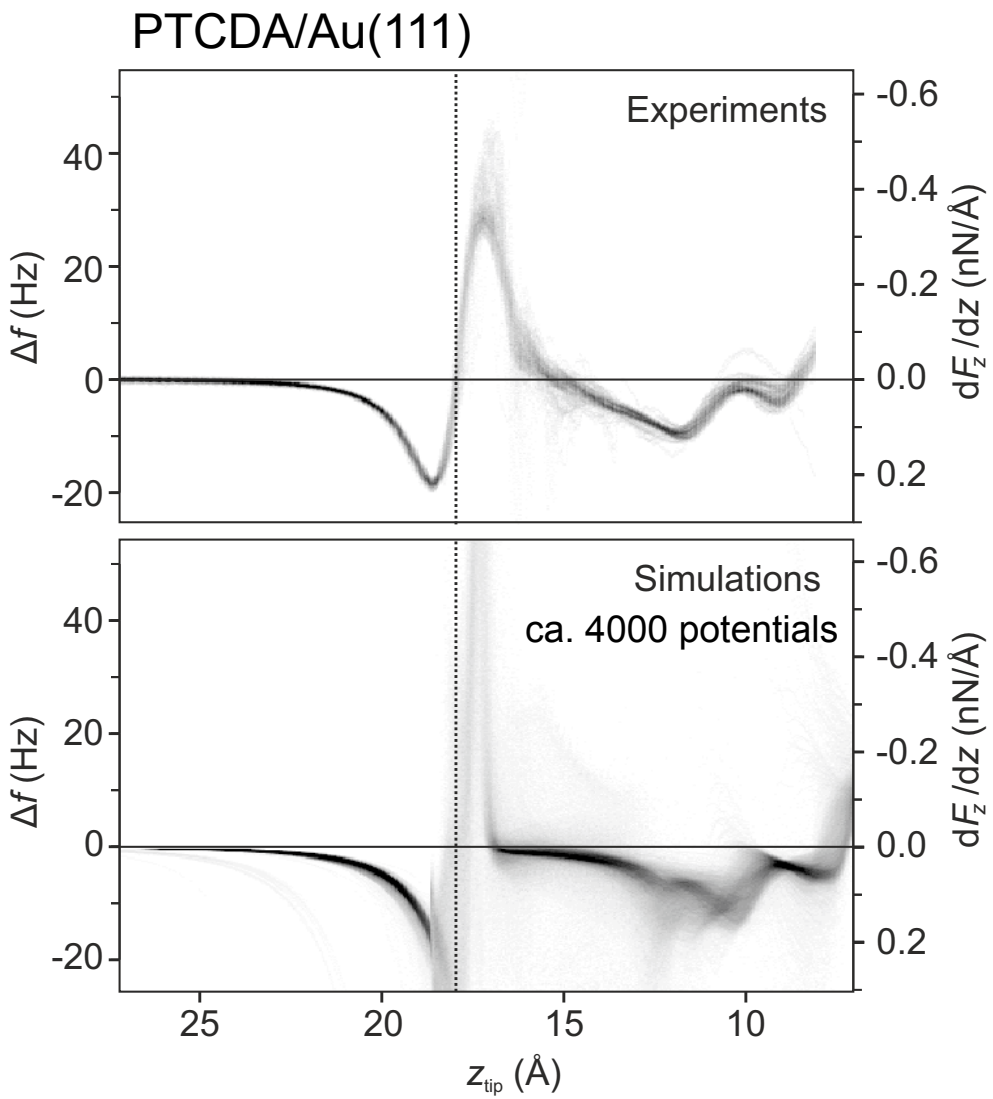
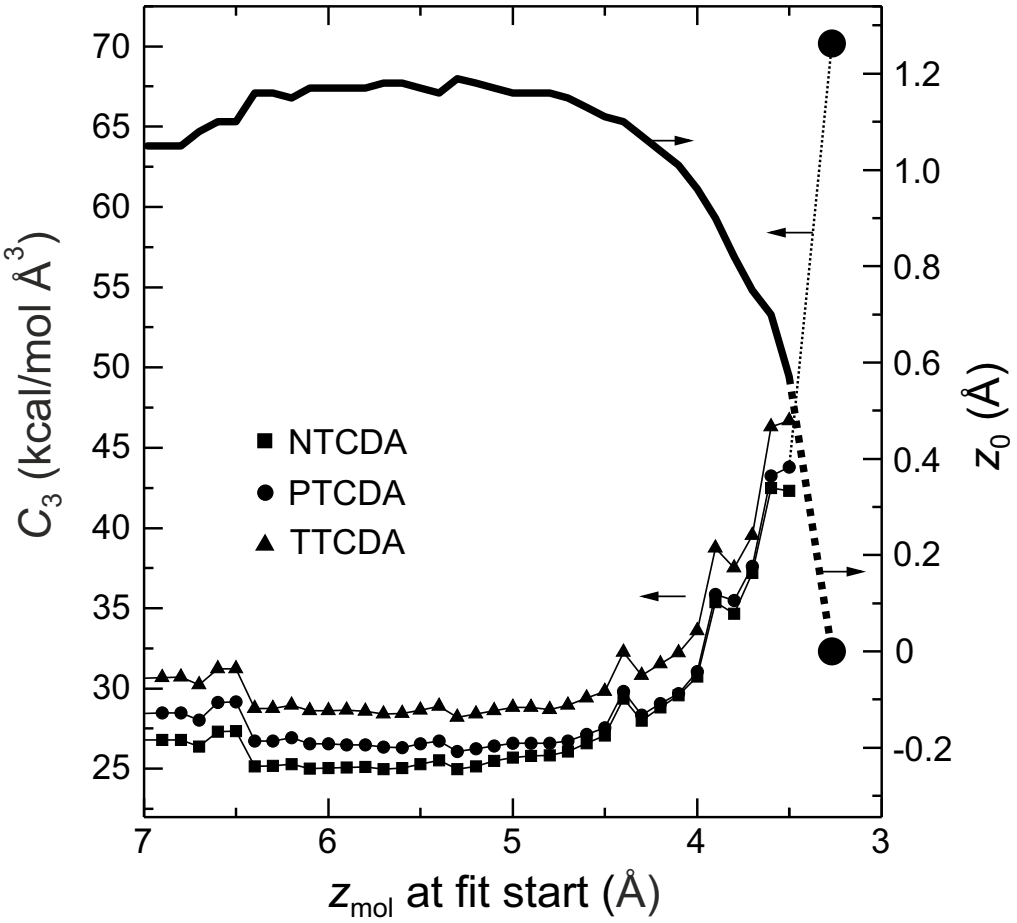
Fit Result



$C_3^{\text{eff}} \approx 70$ kcal / mol Å^3

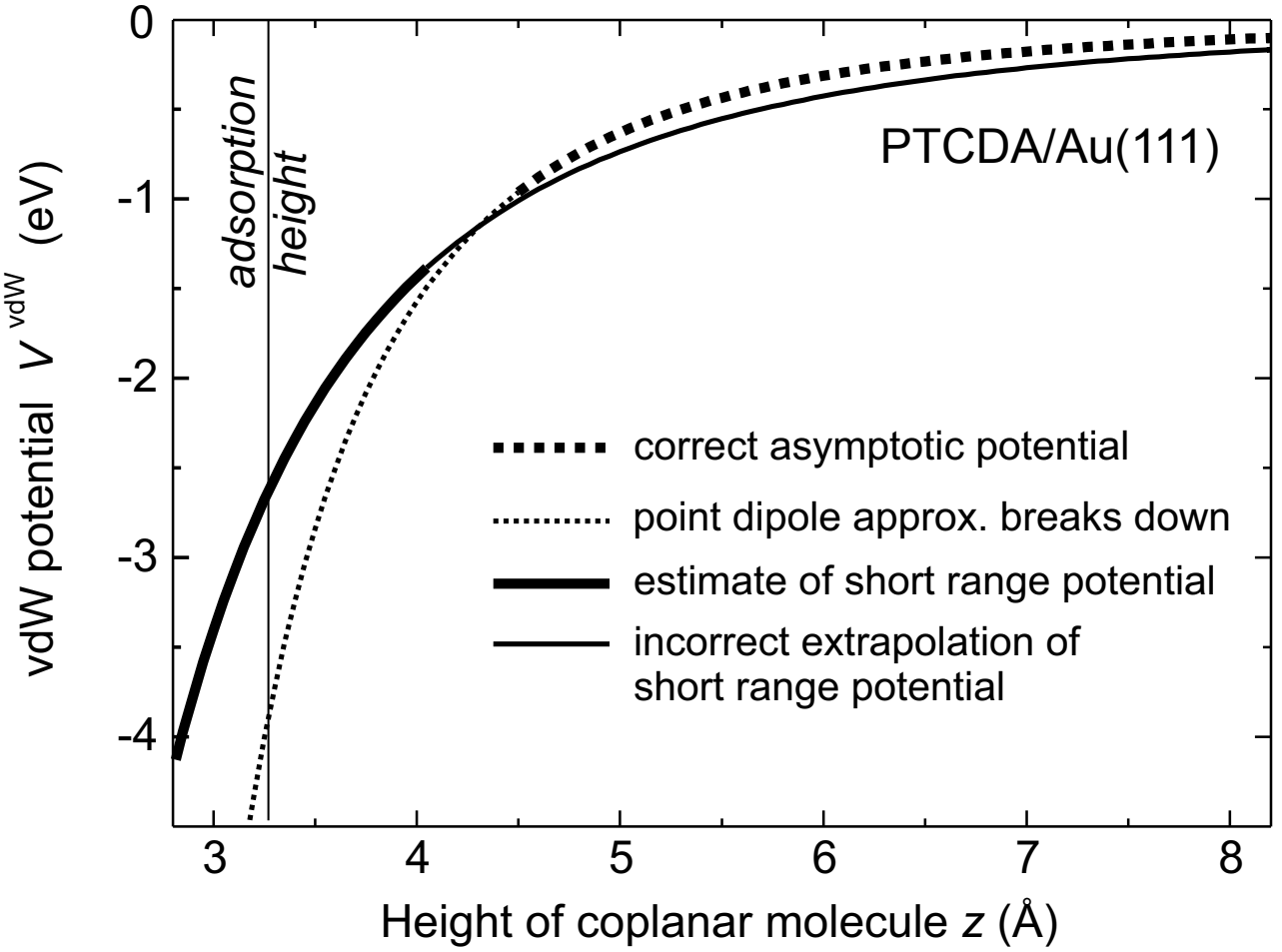
Phys. Rev. Lett. 109, 076102 (2012)

Consistency btw. Asymptotic and Short Range

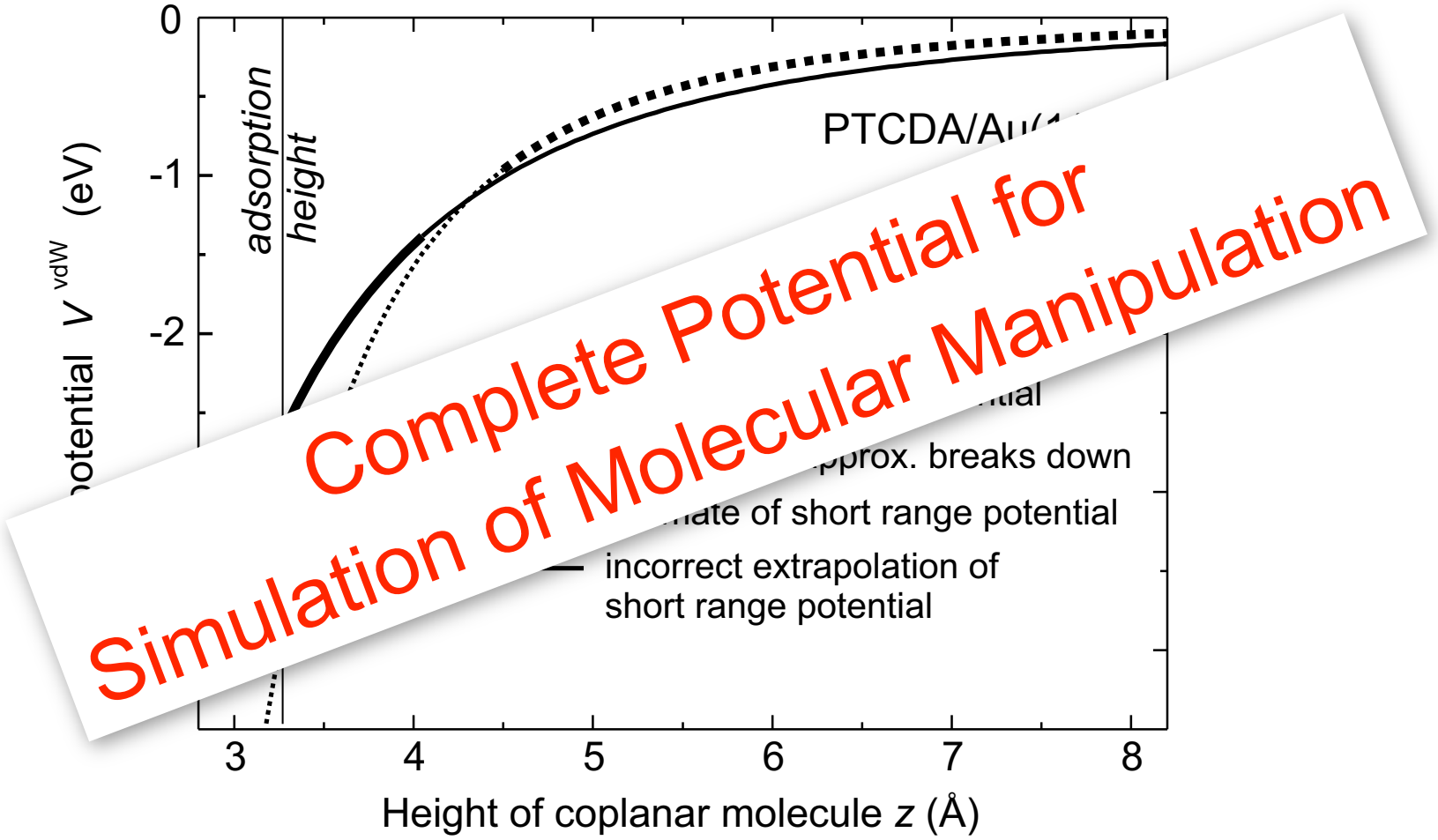


$C_3^{eff} \approx 70$ kcal / mol Å^3

Seamless Matching

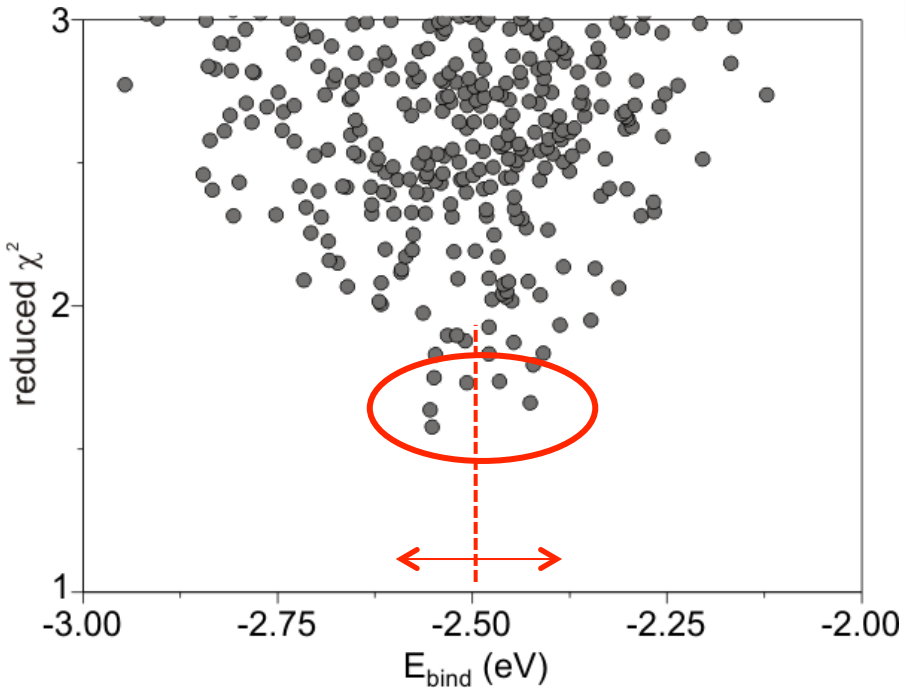


Seamless Matching



Complete Potential for Simulation of Molecular Manipulation

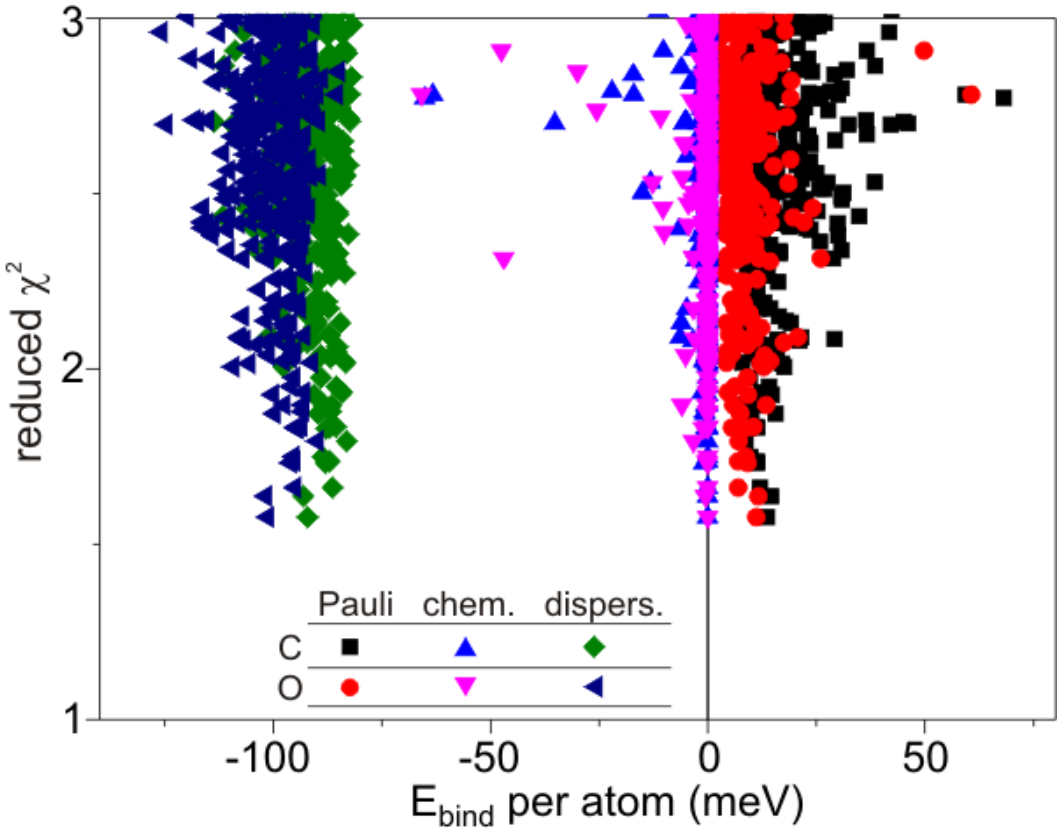
Adsorption Energy



PTCDA/Au(111)

Single molecule adsorption energy of **2.5 eV**

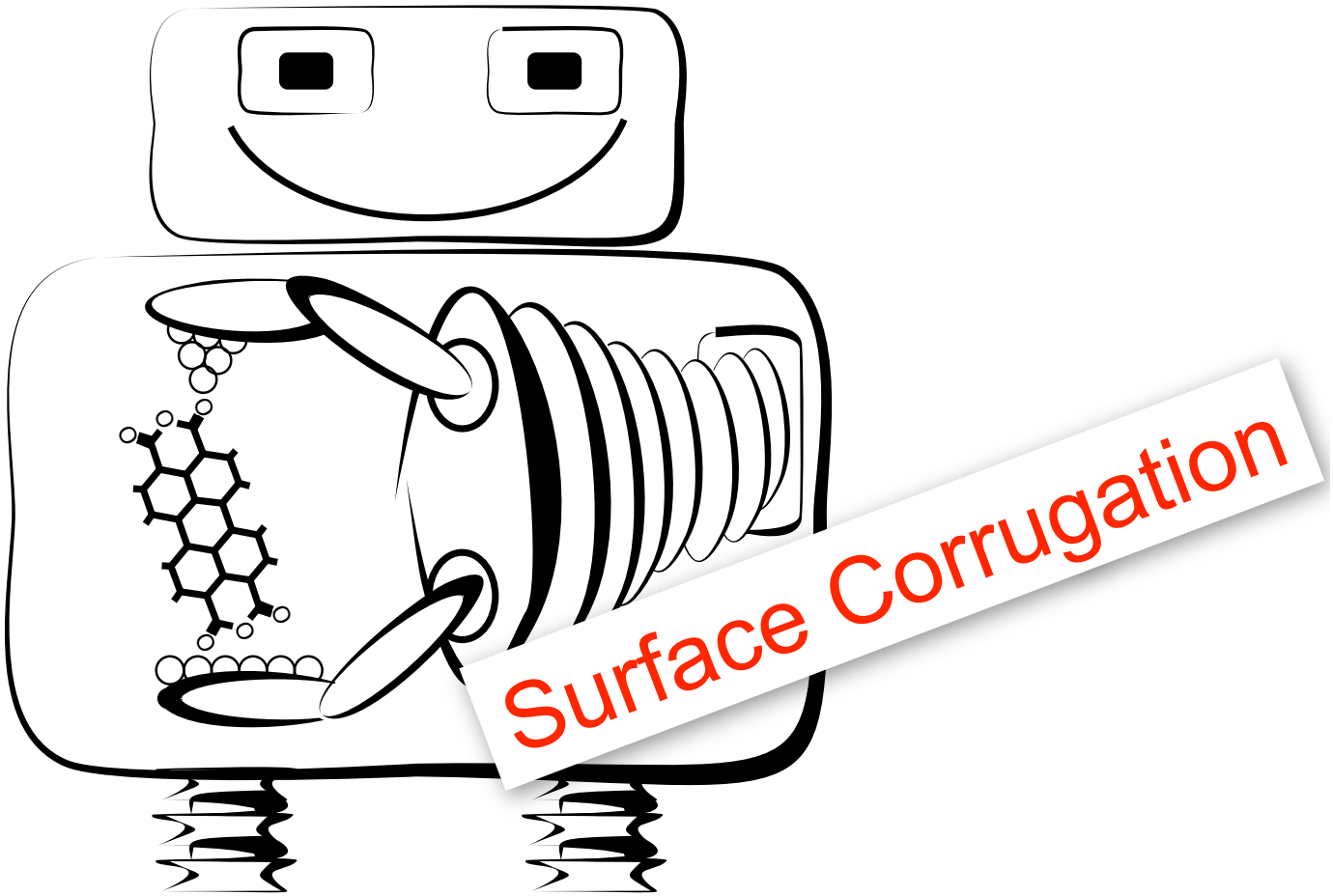
Dissecting the Bonding Type



Pure van der Waals bond, no chemical interaction

Dispersion interaction V_{disp} ≈ 90 meV / atom

Phys. Rev. Lett. 109, 076102 (2012)



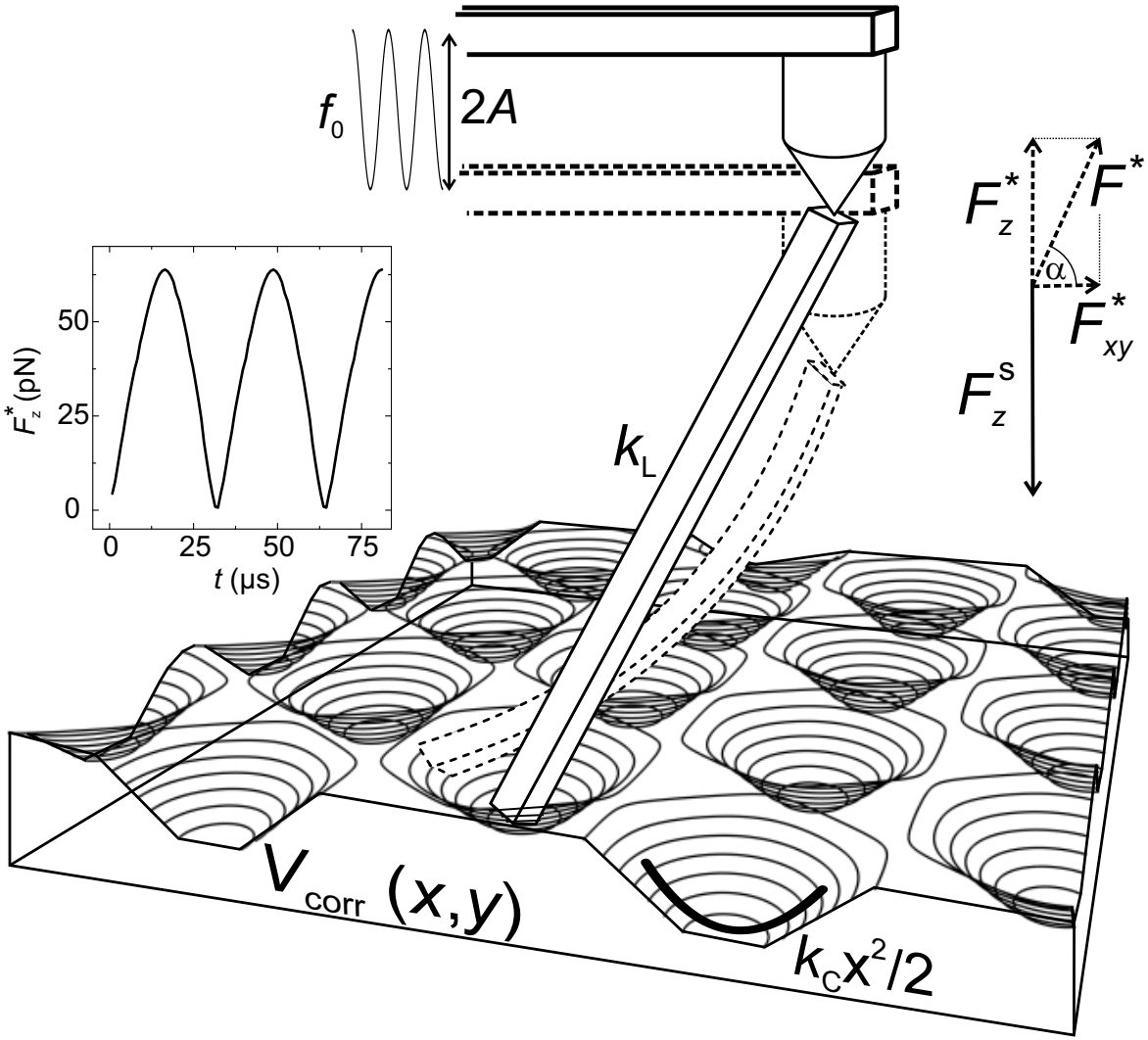
$$V(\vec{R}_1 \dots \vec{R}_M; \vec{\mathcal{R}}_1 \dots \vec{\mathcal{R}}_P) = \sum_{i,j} V_{i,j}^{\text{bond}} + \sum_{i,j,k} V_{i,j,k}^{\text{angle}} + \sum_{i,j,k,l} V_{i,j,k,l}^{\text{dihedral}}$$
$$+ \sum_{i,j} V_{i,j}^{\text{nb}} + \sum_{i} V_i^{\text{a-s}} + \sum_{i} V_i^{\text{corr}} + V_{\text{mol-tip}},$$

Molecular mechanics (“force field”)

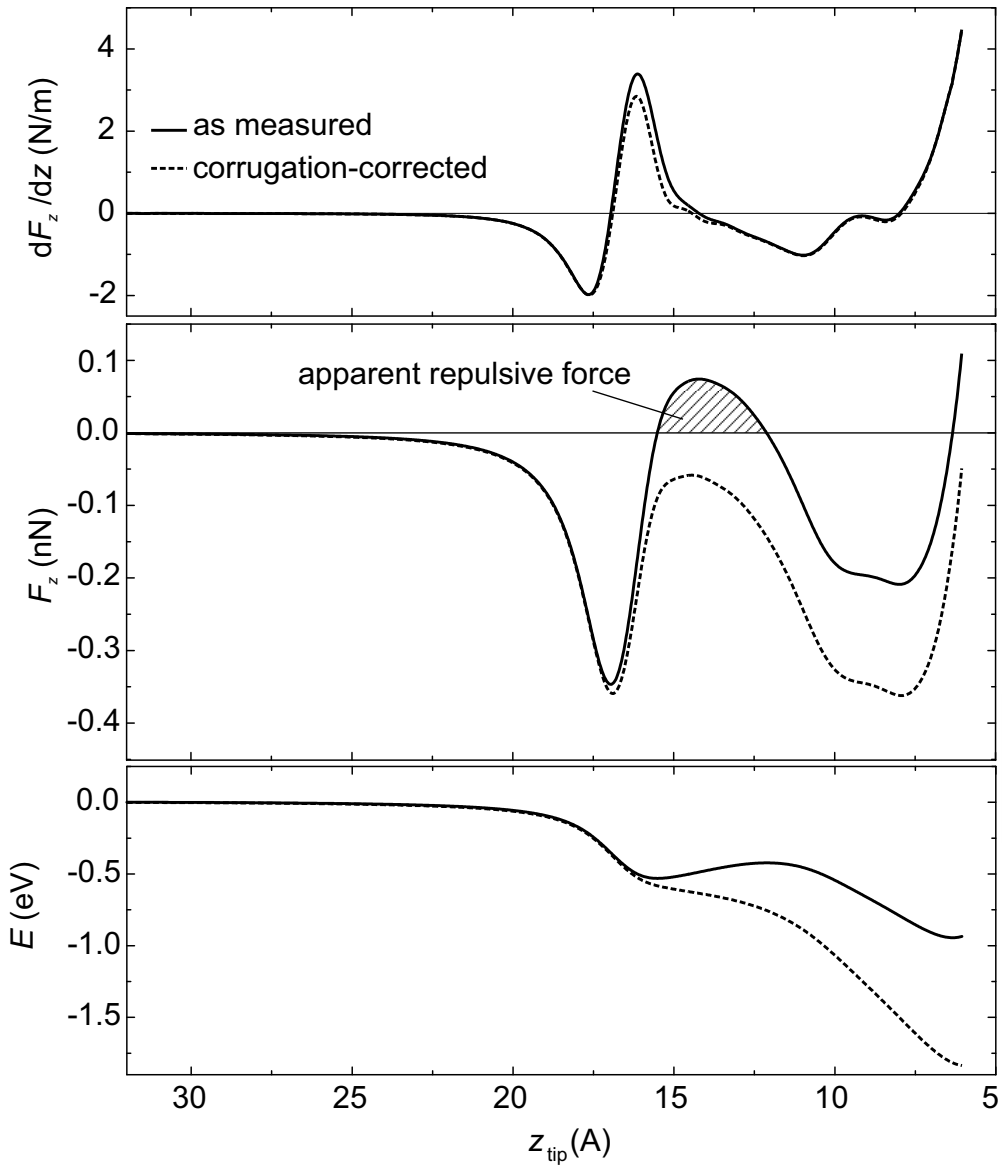
$$V(\vec{R}_1 \dots \vec{R}_M; \vec{\mathcal{R}}_1 \dots \vec{\mathcal{R}}_P) = \sum_{i,j} V_{i,j}^{\text{bond}} + \sum_{i,j,k} V_{i,j,k}^{\text{angle}} + \sum_{i,j,k,l} V_{i,j,k,l}^{\text{dihedral}}$$
$$+ \sum_{i,j} V_{i,j}^{\text{nb}} + \sum_{i} V_i^{\text{a-s}} + \sum_{i} V_i^{\text{corr}} + V_{\text{mol-tip}},$$

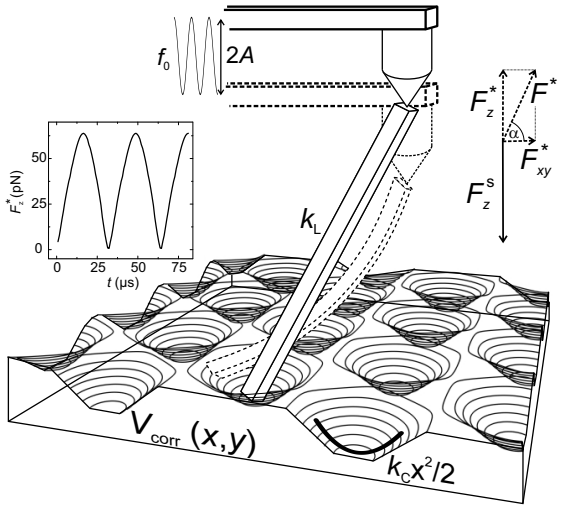
Molecular mechanics (“force field”)

Surface Corrugation: Model



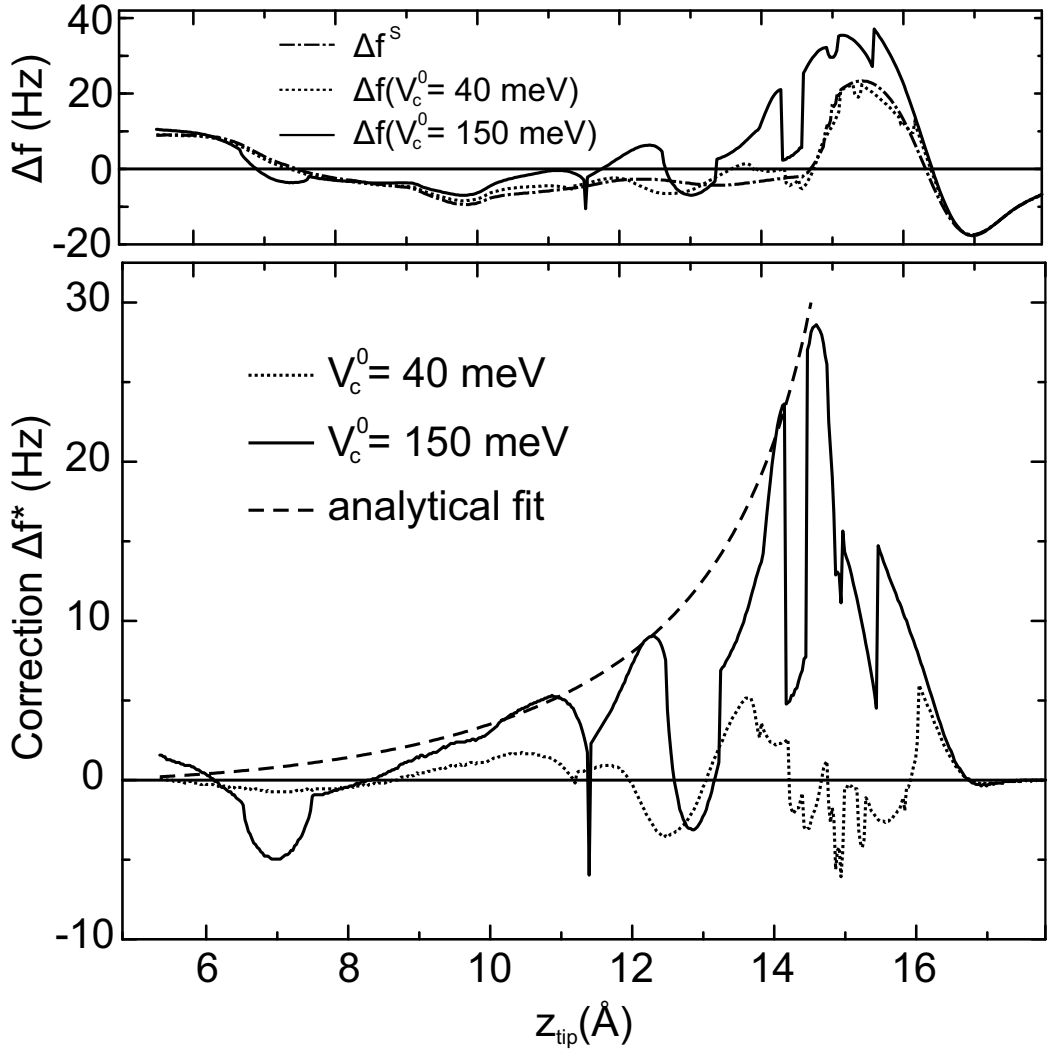
Surface Corrugation: Apparent Repulsive Force



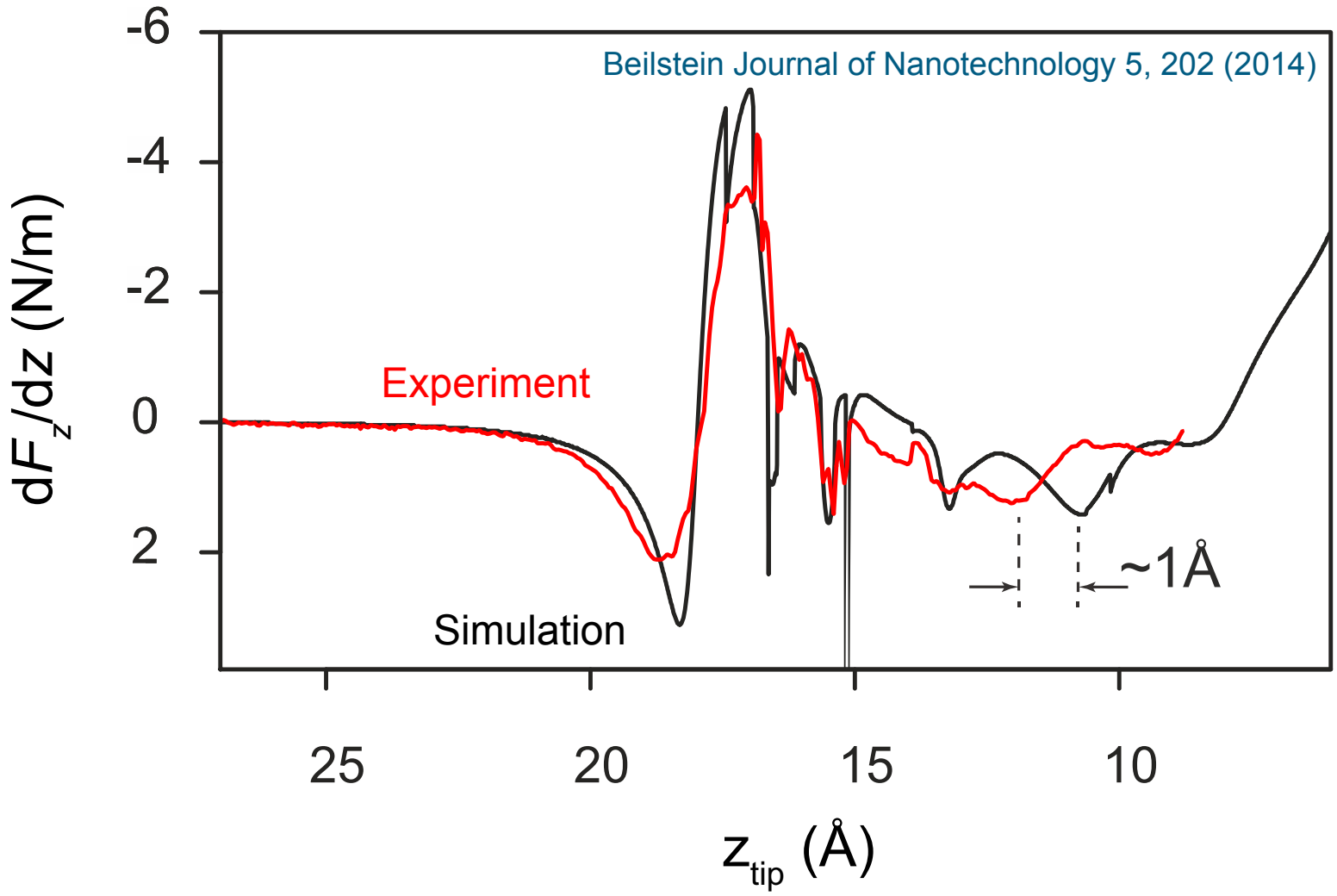


$$\frac{dF_z^*}{dz}(\alpha) = -\frac{k_\mathrm{L} \sin^2\alpha \cdot k_\mathrm{C} \tan^2\alpha}{k_\mathrm{L} \sin^2\alpha + k_\mathrm{C} \tan^2\alpha}$$

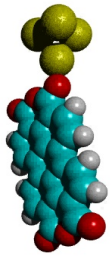
Surface Corrugation: Simulation

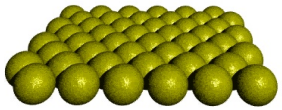


Comprehensive Simulation



Summary





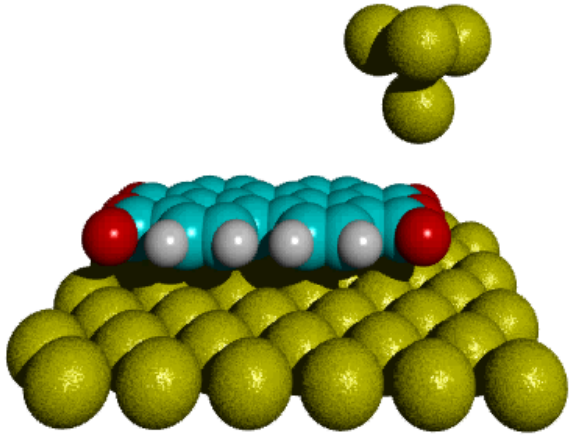
- ✓ “Molecules with handle” + STM/AFM:
  Highly reproducible manipulation experiments
- ✓ van der Waals energy of a single molecule on a metal can be measured

  asymptotic exponent α=3, reference plane position z_0≈1.1Å , validity range z>5 Å,
  absolute size of C_3 coefficients ≈25-28 kcal/mol Å^3, ≈10% superlinearity (i.e. non-additivity)
- ✓ Full surface holding potential can be reconstructed (z_0≈0, C_3≈70 kcal/mol Å^3)
- ✓ Adsorption energy can be determined (≈2.5 eV)
- ✓ Bonding energy can be partitioned (≈90 meV/atom)
- ✓ Lateral corrugation introduces apparent repulsive force and jerky sliding
- ✓ Force-field simulations describe the manipulation process reasonably accurate

Molecular Manipulation Lab

F. S. Tautz

How to develop two-contact manipulation into a fabrication technique?



- drop the restriction to vertical (and rectilinear) tip motion: **curvilinear tip motion**
- enable **playful, intuitive handling of molecules**, by introducing hand-controlled manipulation
- obtain complementary information about the state of the junction from **simulations**
- link experiments and simulations **in real time**

Wagner, Temirrov Tautz, in „Molecular Architectonics“
Ed. T Ogawa, Springer 2017

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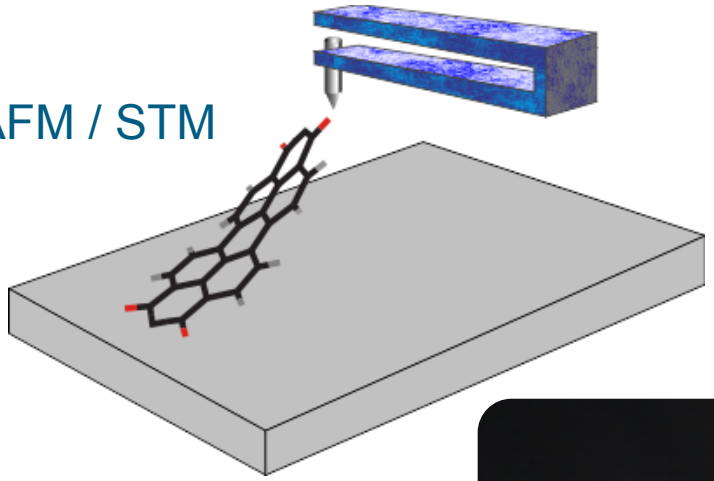
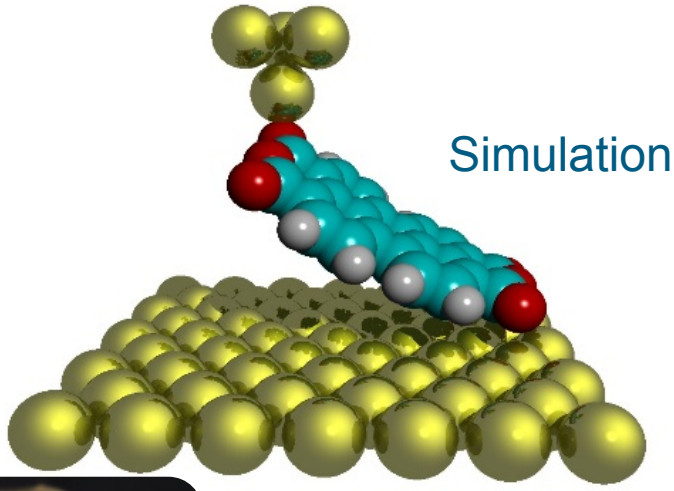
nc-AFM / STM

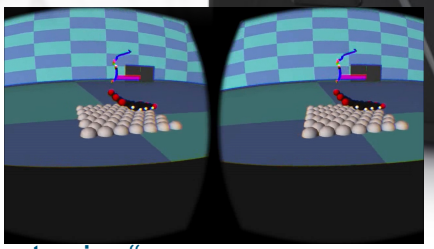


Simulation



Motion control

3D visualization



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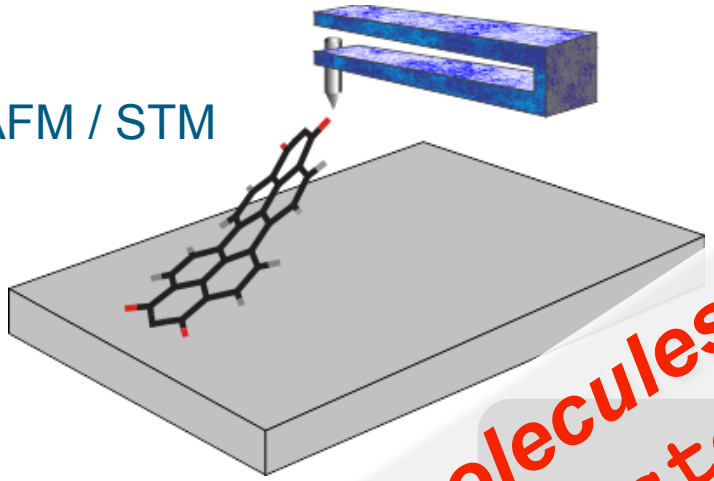
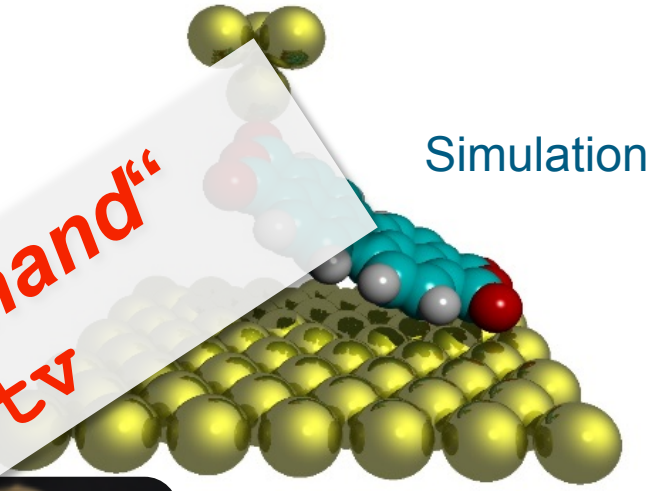
nc-AFM / STM



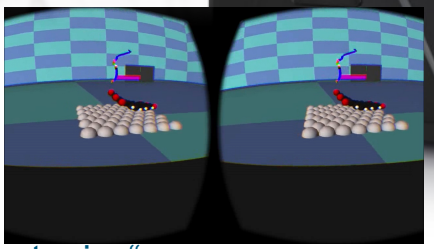
Simulation



„Moving molecules by hand“
www.beilstein.tv

Motion control

3D visualization



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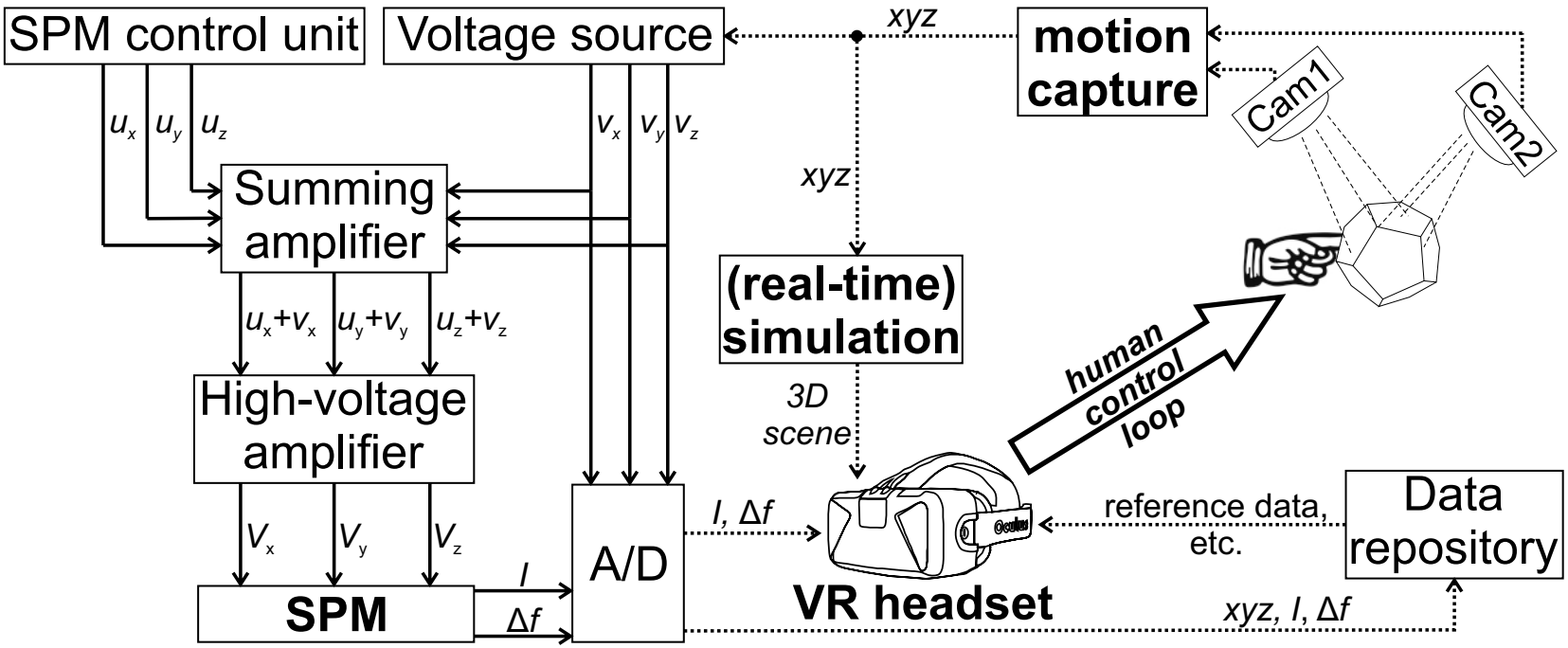

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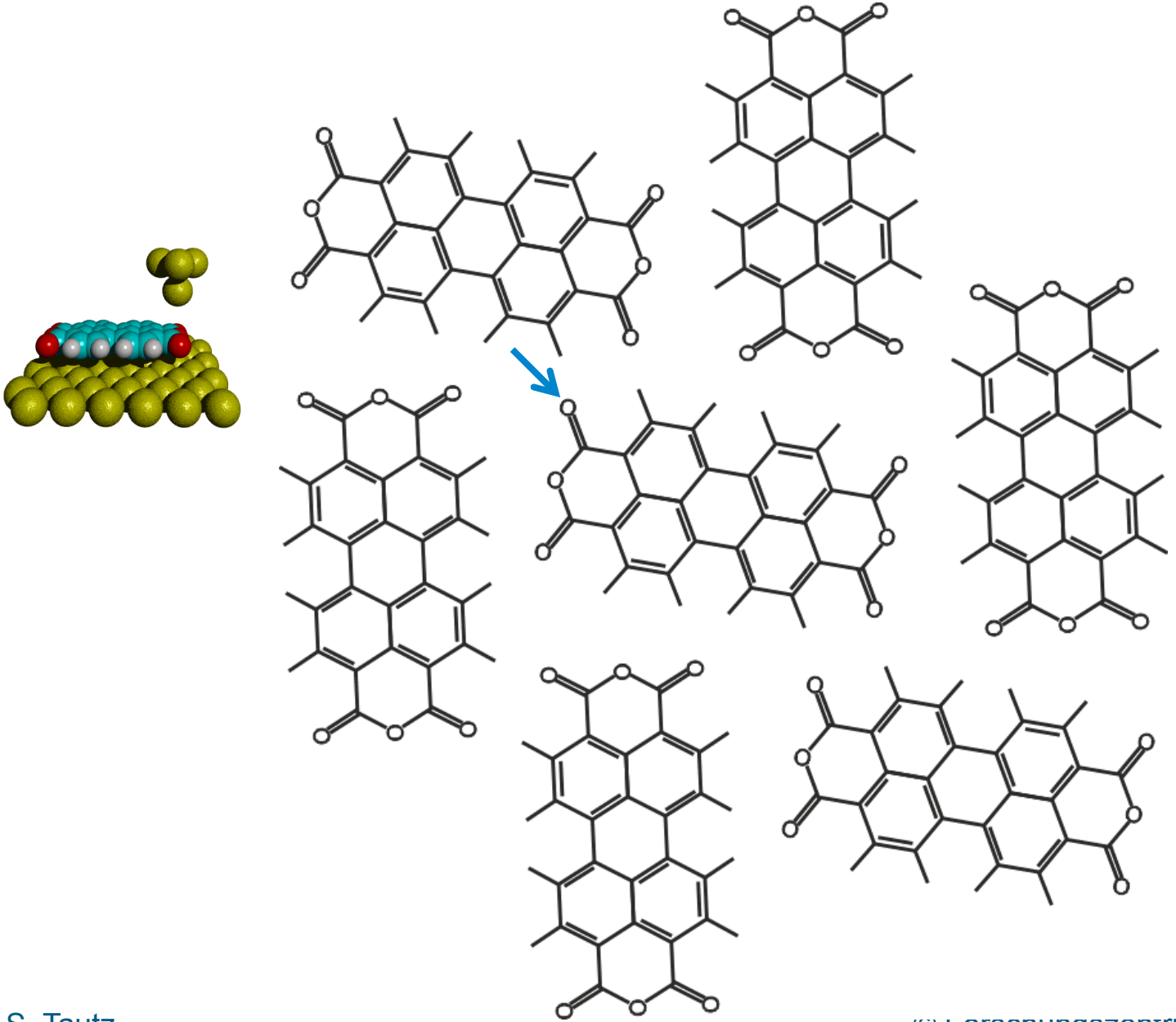
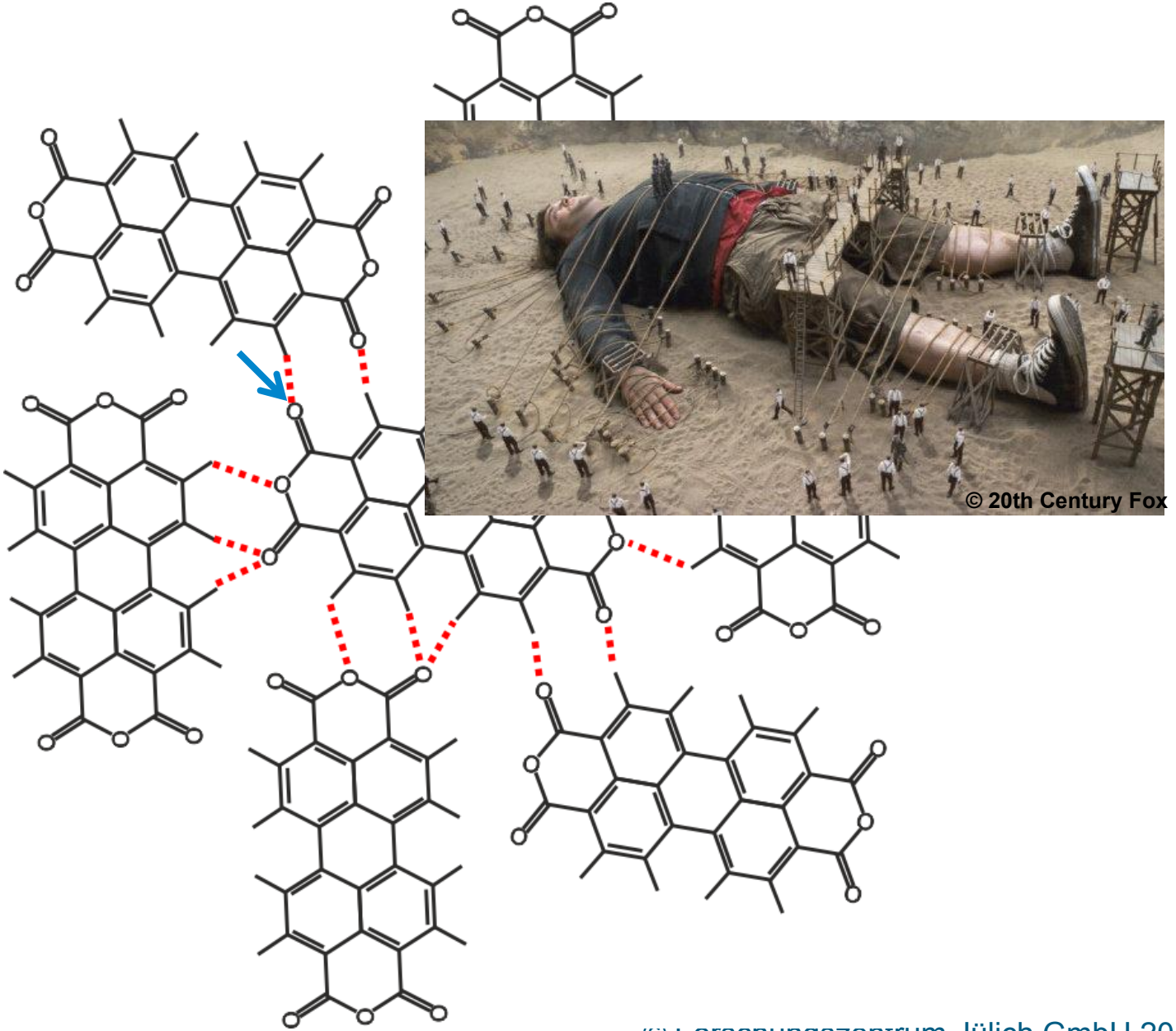
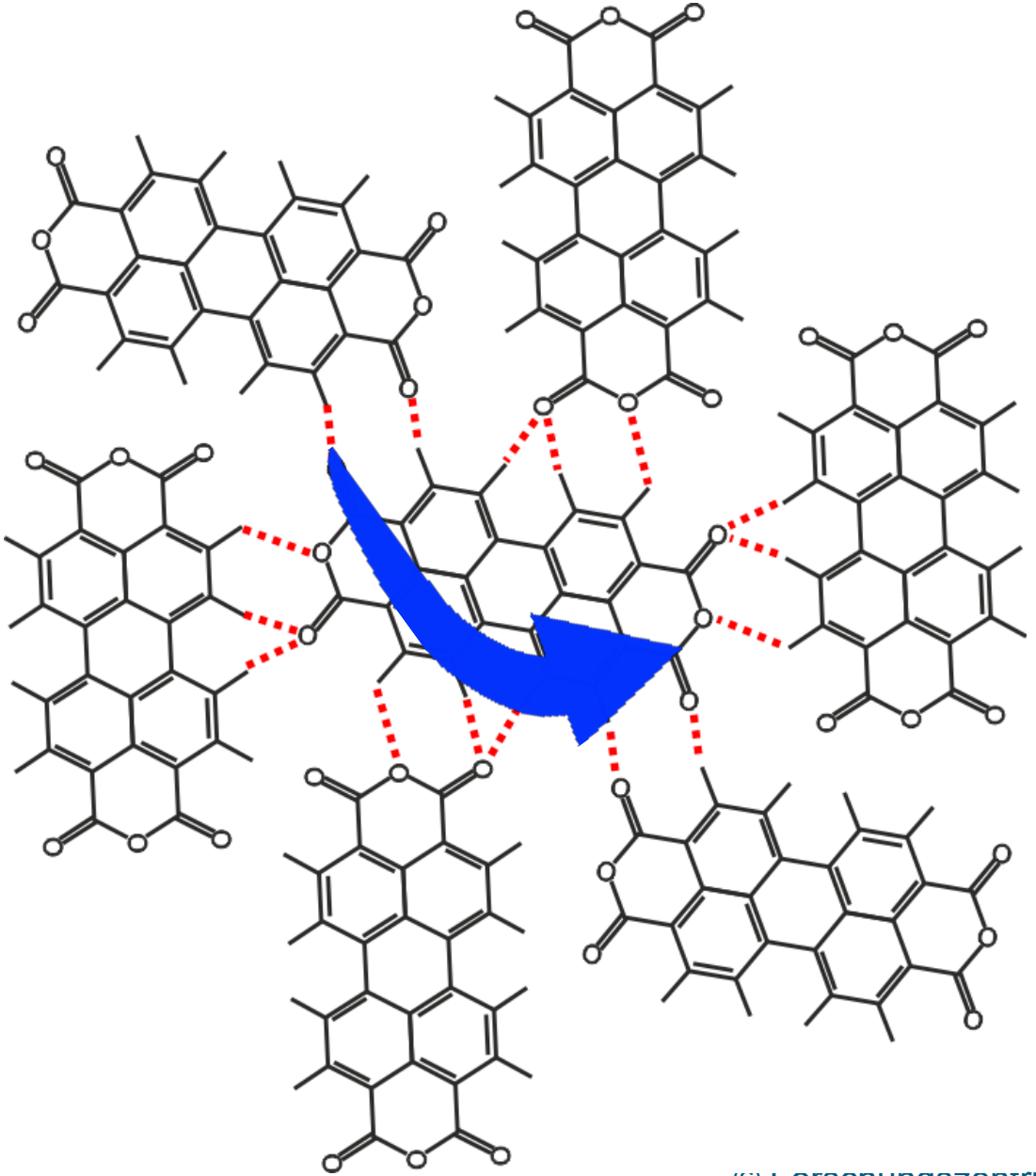
Curvilinear Tip Motion, Hand Control, Intuition



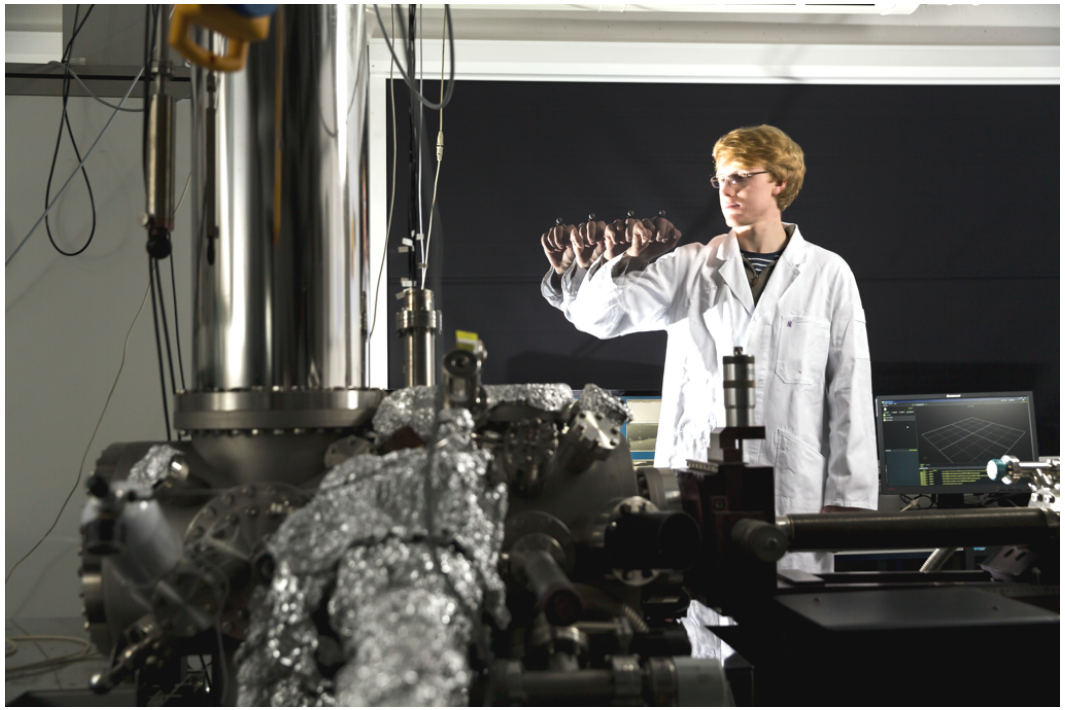
Curvilinear Tip Motion, Hand Control, Intuition



Curvilinear Tip Motion, Hand Control, Intuition



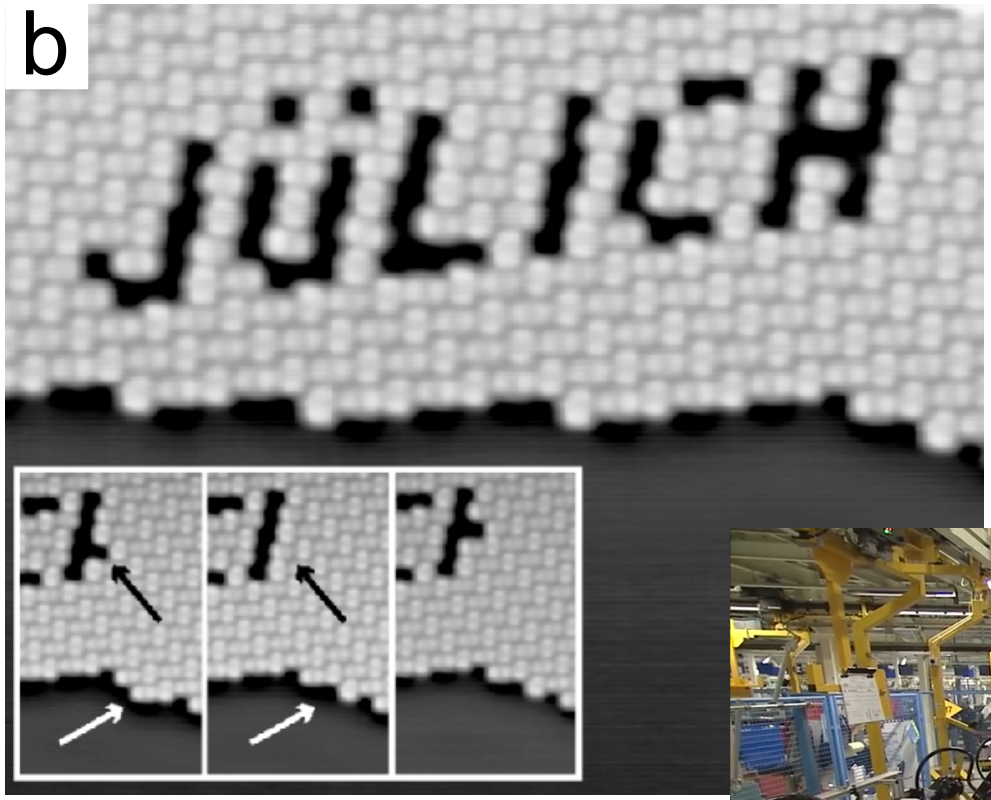
Curvilinear Tip Motion, Hand Control, Intuition



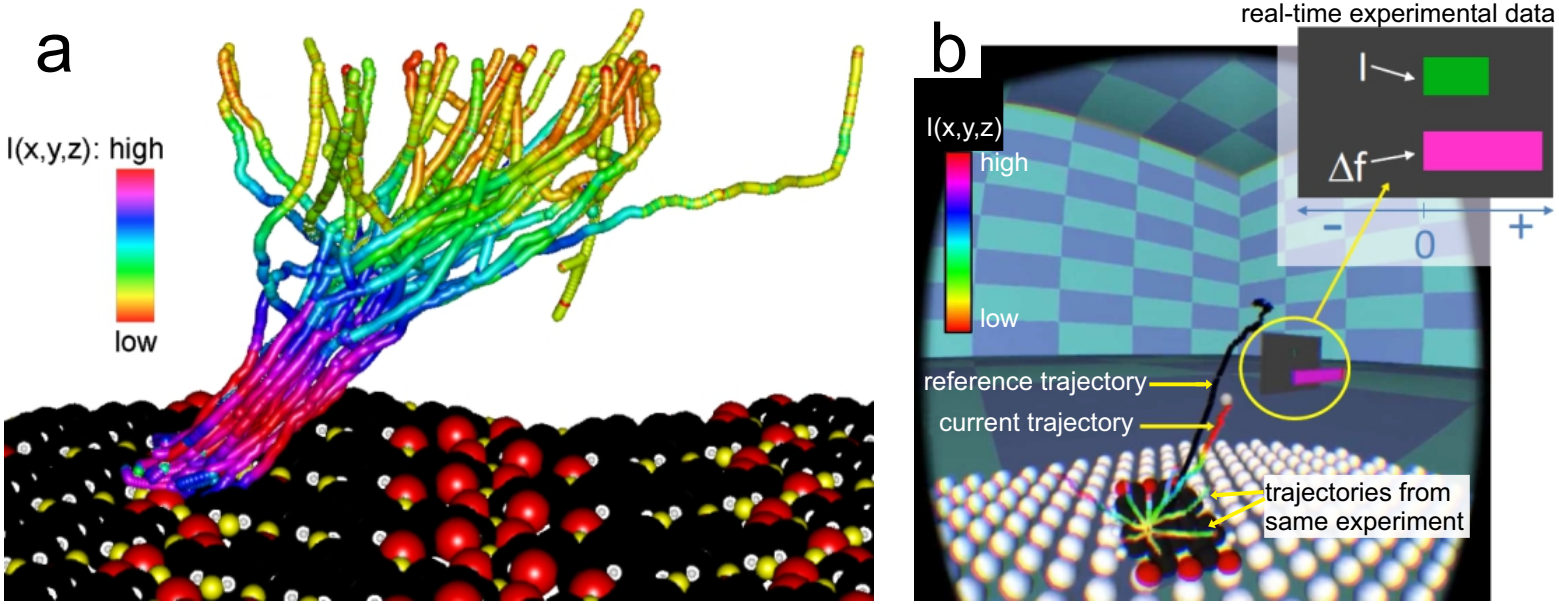
Hand controlled manipulation

Curvilinear Tip Motion, Hand Control, Intuition

Curvilinear Tip Motion, Hand Control, Intuition



Virtual Reality

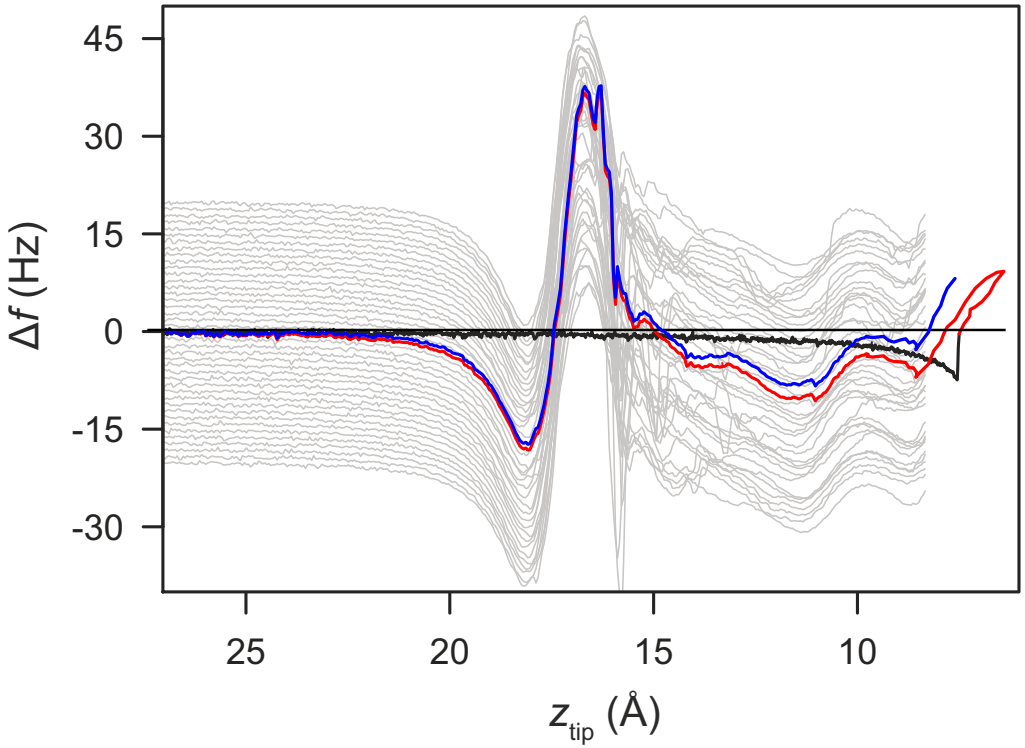


- Offline data visualization
- Guiding and transfering hand-controlled manipulation protocols
- In conjunction with real-time simulation:
  The operator sees at the atomic scale what he is doing while doing it

Outlook

Lack of Robustness

(residual stochasticity, not every tip works etc.)



thermal, quantum mechanical ?

Is there a **quantum mechanical limit** to controlling the position of the molecule during manipulation?

(i) The molecule might **tunnel out of a potential minimum**:

$$\exp(-d\sqrt{2m(V_0 - E)}/\hbar$$

→ negligible because of the molecule‘s large mass.

(ii) Because of **zero point motion**, the position of the molecule is indeterminate.

We have $\hbar\omega > k_{\mathrm{B}}T \quad (T \simeq 10\,\mathrm{K})\,(k \simeq 25\,\mathrm{N/m})$

→ the molecule behaves as a quantum oscillator.

But: $\Delta x = \sqrt{\hbar/(2m\omega)} \simeq 0.04\,\text{Å}$

Wagner, Temirrov Tautz, in „Molecular Architectonics“
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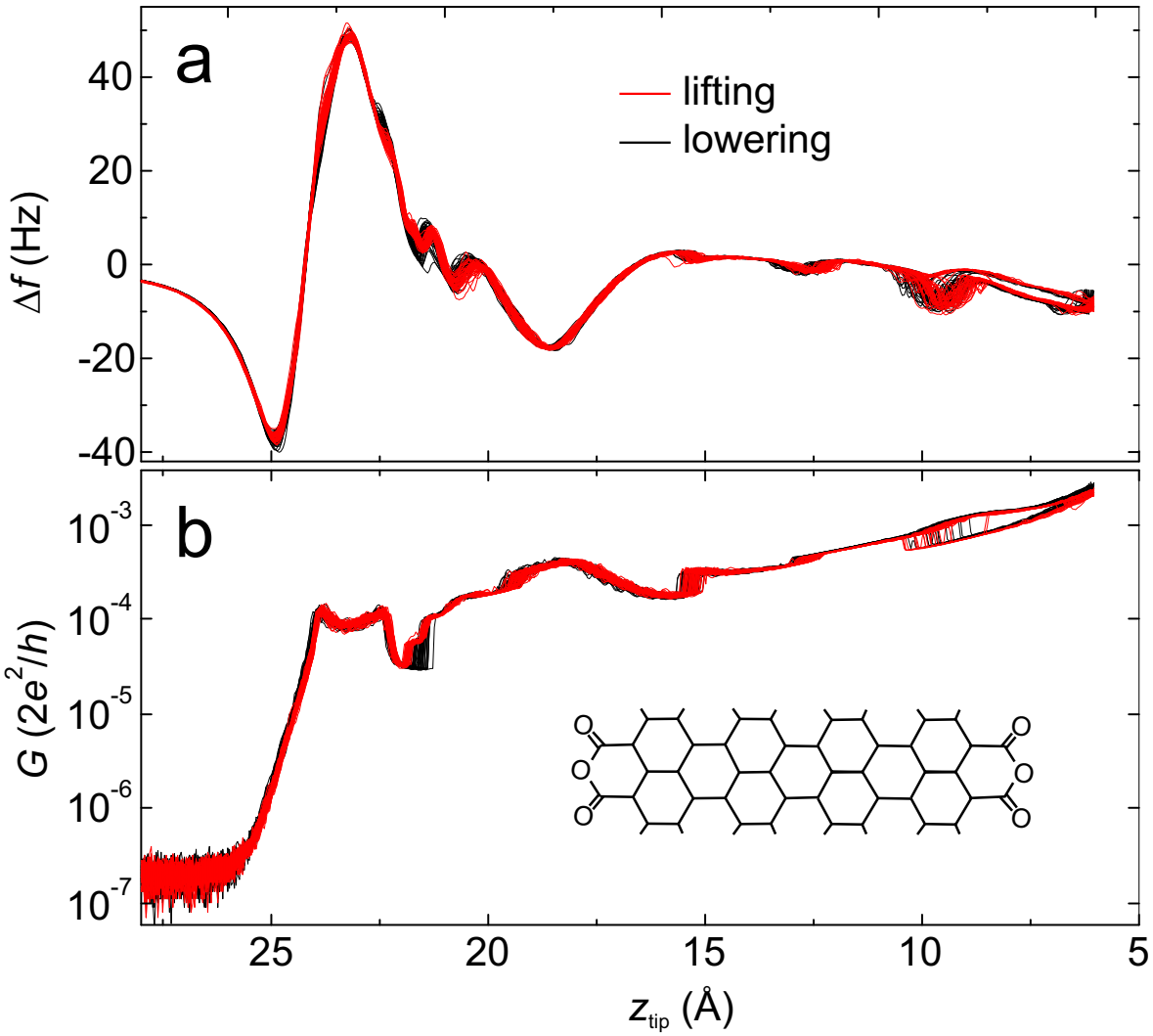

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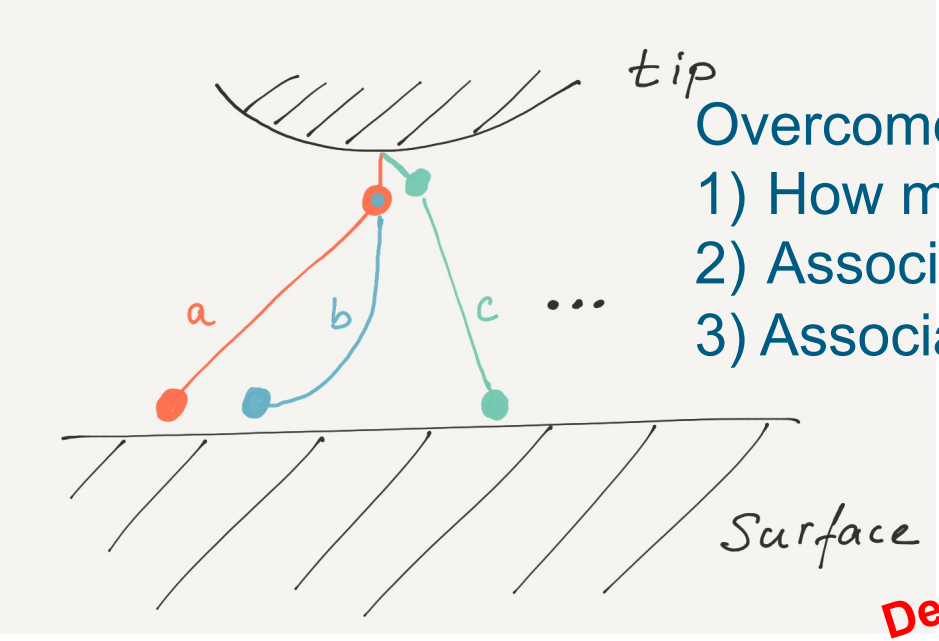
Information Gap

Lack of information about the state of the junction



Overcome the information gap:

1) How many configurations are there?
2) Associate each to a Δf observable?
3) Associate each to a $\{R_1, \ldots R_M\}$?

Details in Talk by Christian Wagner

- configurations a,b,c, are specified by $\{R_1, \ldots R_M\}$,
- each corresponds to a local minimum in the PES over 3M-dimensional configuration space $E(\{R_1, \ldots R_M\})$

Coming Back to Feynman‘s Vision...

...of being able to make everything which can possibly be made, molecule by molecule:

Even if this will never replace self-assembly as bread-and-butter approach to nanotechnology,

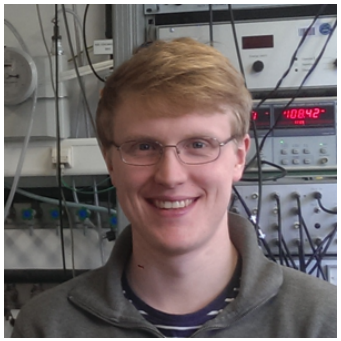
being able to make a **prototype of every conceivable molecular nanostructure** gives us **unlimited freedom** to study **emergent phenomena at the quantum scale**

„...might tell us much of great interest about the phenomena that occur in complex situations“

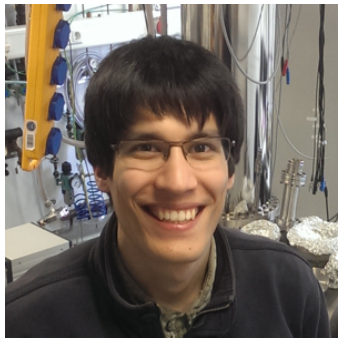
Christian Wagner

Ruslan Temirov

Serguei Soubatch



Matthew Green



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